Visible Light Induced Reduction and Pinacol Coupling of Aldehydes and Ketones Catalyzed by Core-Shell Quantum Dots

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Supplementary Informations

1. Absorption and photoluminescence spectra of CdSe and CdSe/3CdS QDs

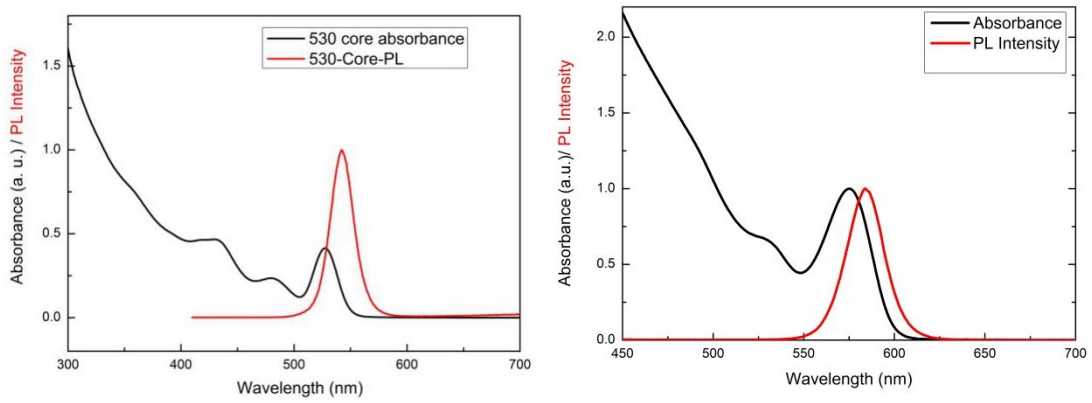

Figure S1 Absorption and photoluminescence spectra of CdSe (left) and CdSe with 3 monolayer CdS shells (right).

2. Transient photoluminescence spectra of CdSe/3CdS QDs

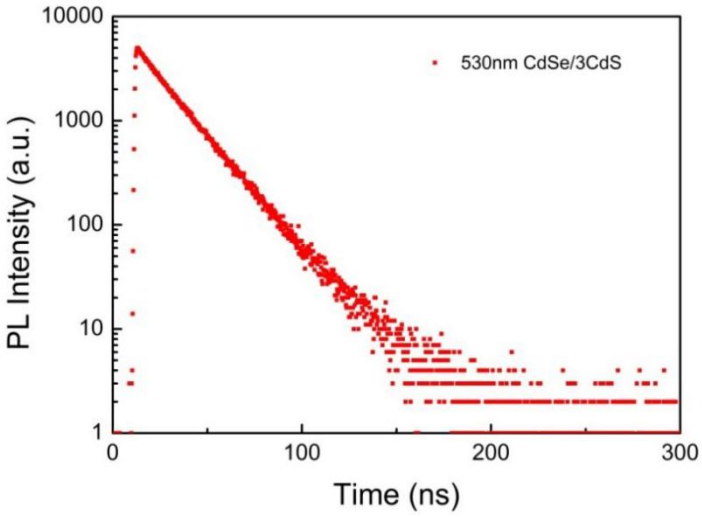

Figure S2 Transient Photoluminescence spectra of CdSe/ 3CdS QDs

3. Comparison of TON values of different catalysts

(1) Reduction of benzaldehyde

Table S1

Entry	Catalyst	Conditions	Solvent	Time	Yield(%)	TON
1	CdSe/CdS	p-Toluenethiol, CH_3COOCs, Ar	toluene	8 h	90 (GC)	40000
2[1]	Ru(II) complexes	KOH, 80 ℃	2-propanol	0.5 h	100 (GC)	1000
3[2]	Ru/AlO(OH)	HCOOK, water, N_2, 100 ℃	DMF	2 h	100	202
4[3]	Ru(II)(η^6-*p*-cymene) complexes	KOH, 82 ℃	2-propanol	12 h	95	956
5[4]	Iridium catalysts	HCOOH, 80 ℃	water	2 min	99	4950
6[5]	MOA-Rh-2	$PhSiH_3$, 25 ℃	DCM	5-7 h	>99	250
7[6]	[Fe(PNP^{Me}-*i*Pr)(CO)(H)(Br)]	DBU, H_2 (30 bar),	EtOH	16 h	96 (H-	20000

	complex	40 ℃			NMR)	
8[7]	Pd-NPs	H_2 (1 atm), rt	H_2O	2 h	>99 (HPLC)	5688
9[8]	Pd/TiO_2	H_2 (1atm), 25 ℃	ethanol	1 h	99	2797
10[9]	$LaCu_{0.67}Si_{1.33}$ catalyst	H_2 (3 MPa), 120 ℃	methanol	3 h	99 (GC)	54750

(2) Coupling of benzophenone to pinacol

Table S2

Entry	Catalyst	Conditions	Solvent	Time	Yield(%)	TON
1	CdSe/CdS	p-Toluenethiol, CH_3COOCs, Ar	toluene	8 h	92	400000
2[10]	$Ir[FCF_3ppy]_2(dtbbpy)]PF_6$	NBu_3, rt, Ar	degassed DMF	15 h	87	87
3[11]	RuDmb	100 mM Asc^{2-}, pH12.7	aqueous media	3 h	65	65
4[12]	coumarins	Et_3N, rt	DMF	36 h	50	10
5[13]	Perylene	*i*-Pr_2NEt, rt, Ar	CH_3CN	16 h	38	3

Reference

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4. Absorption and photoluminescence spectra of CdS QDs

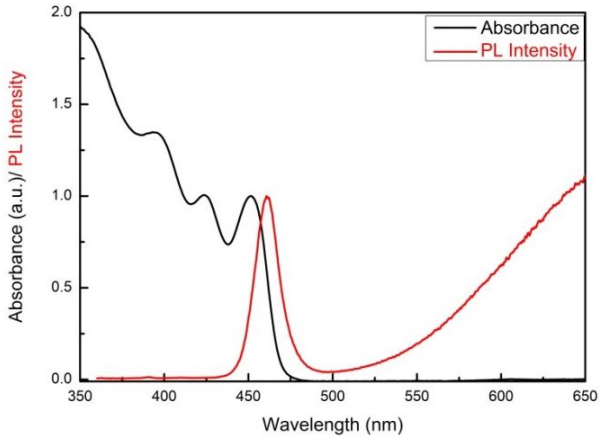


Figure S3 Absorption and photoluminescence spectra of CdS.

5. NMR monitoring

Reactions performed with methyl 4-formylbenzoate (0.1 mmol), QDs with 3 monolayers of CdS (2.0×10^{-9} mol, 2×10^{-3} mol %), p-toluenethiol (0.15 mmol, 1.5 equiv.) in deuterated toluene (2 mL) illuminated with 2×3 W green LED.

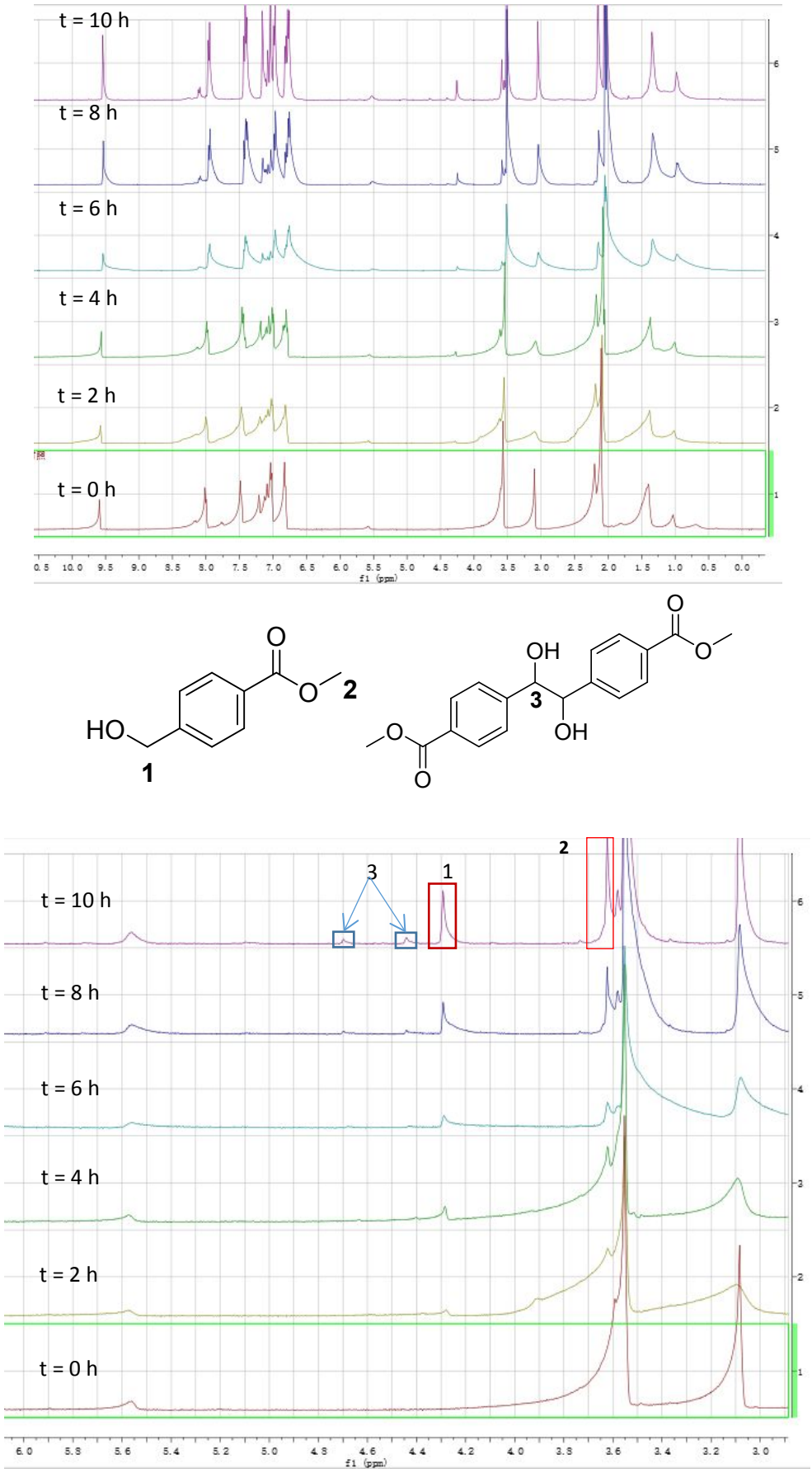


Figure S4 ^{1}H NMR spectra (400 MHz, $CDCl_3$)

6. Recycling of quantum dots

(1) 4,4-Dimethylbenzophenone (0.1 mmol, 21.8 mg), p-toluenethiol (0.15 mmol, 21.4 mg, 1.5eq), CdSe/3CdS (2.0 $\times 10^{-9}$ mol, 2×10^{-5} mol/L, 2×10^{-3} mol %) in hexane(2 ml), purging with argon gas for 15 minutes before illumination by 2×3 W green LED. After 22 hours, the product was removed by centrifugation. The raw material and p-tolylthiophenol were added to the reaction in which the product had been removed, and the reaction was continued after argon gas purge. After 10 cycles, the total yield reached 90 %. The turnover number reached 4.117×10^{5}.

Table S3 Catalyst recycling reactions

entry	4,4'-Dimethylbenzophenone(mg)	p-Thiocresol(mg)	Time(h)	Yield(mg)	Yield(%)
1	21.8	21.4	22	17.4	79
2	21.7	21.4	22	26.0	119
3	22.0	26.2	22	17.9	81
4	20.2	16.7	23	19.7	89
5	20.5	24.3	23	16.5	80
6	19.8	21.4	23	16.9	85
7	19.8	25.0	27	13.7	69
8	18.0	11.1	26	15.8	87
9	18.2	16.6	28	11.8	64
10	9.7	8.5	38	18.6[b]	191
sum	191.7			174.3	90 %

[a]4,4-Dimethylbenzophenone, p-toluenethiol, QDs with 3 monolayers of CdS (2.0 $\times 10^{-9}$ mol, 2×10^{-5} mol/L, 2×10^{-3} mol %) in hexane(2 ml), purging with argon gas for 15 minutes before illumination by 2×3 W green LED. [b]11.5 mg of it was obtained by silica gel column chromatography.

The solvent lost during the first reaction was not replenished during the second cycle, so that there was very little solvent remaining after the second cycle. After the second cycle, the product remaining in the solvent in the first reaction and the product generated in the second cycle are precipitated together in a very small amount of solvent, which results in a yield of over 100 %. In the following cycle, the solvent is added. Due to the continuous loss of quantum dots during the cycle, the reaction time is prolonged. The continuous accumulation of disulfides affects the precipitation of products from the solution. Finally, we decided to stop the experiment after 10 cycles. In the last cycle, the products accumulated in the reaction solution were separated by column chromatography, resulting in a yield of more than 100 %. Due to the continuous addition of excessive thiophenol during the cycle, the content of thiophenol in the later reaction system is greater than 1.5 equivalents, which leads to an increase in the proportion of alcohol products, so that the final yield is only 90 % but not 99 %.

(2) 4,4-Dimethylbenzophenone (0.1 mmol, 21.8 mg), p-toluenethiol (0.15 mmol, 21.4 mg, 1.5eq), CdSe/3CdS (2.0 $\times 10^{-9}$ mol, 2×10^{-5} mol/L, 2×10^{-3} mol %) in hexane (2 ml), purging with argon gas for 15 minutes before illumination by 2×3 W green LED. After 22 hours, the product

was removed by centrifugation. The methanol (2 mL) was added to recover the QDs, the rest of the product was recovered by silica gel column chromatography and then the QDs reused for three times. The first run yield is 83%, the second run yield is 96%,the third run yield is 55%, and the total yield is 78%.

7. TEM images of CdSe/3CdS before and after the reaction

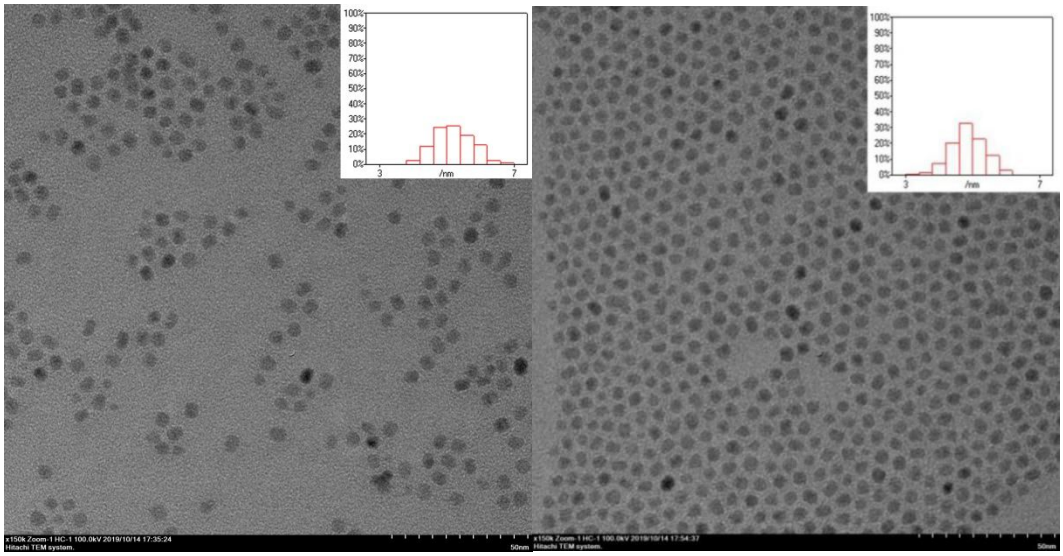


Figure S5 TEM images of CdSe/3CdS before (a) and after (b) the reaction.

8. UV image of CdSe/3CdS before and after the reaction

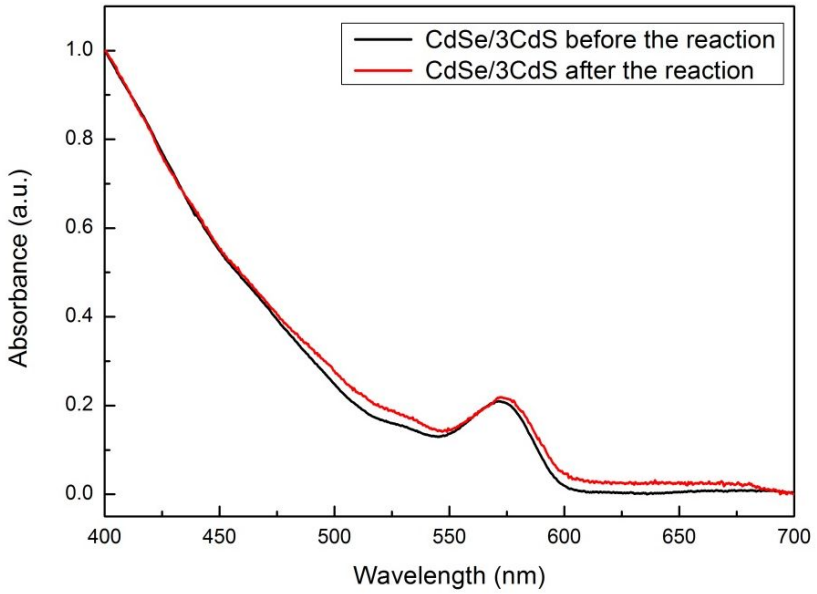


Figure S6 UV image of CdSe/3CdS before and after the reaction.

9. XPS image of CdSe/3CdS before and after the reaction

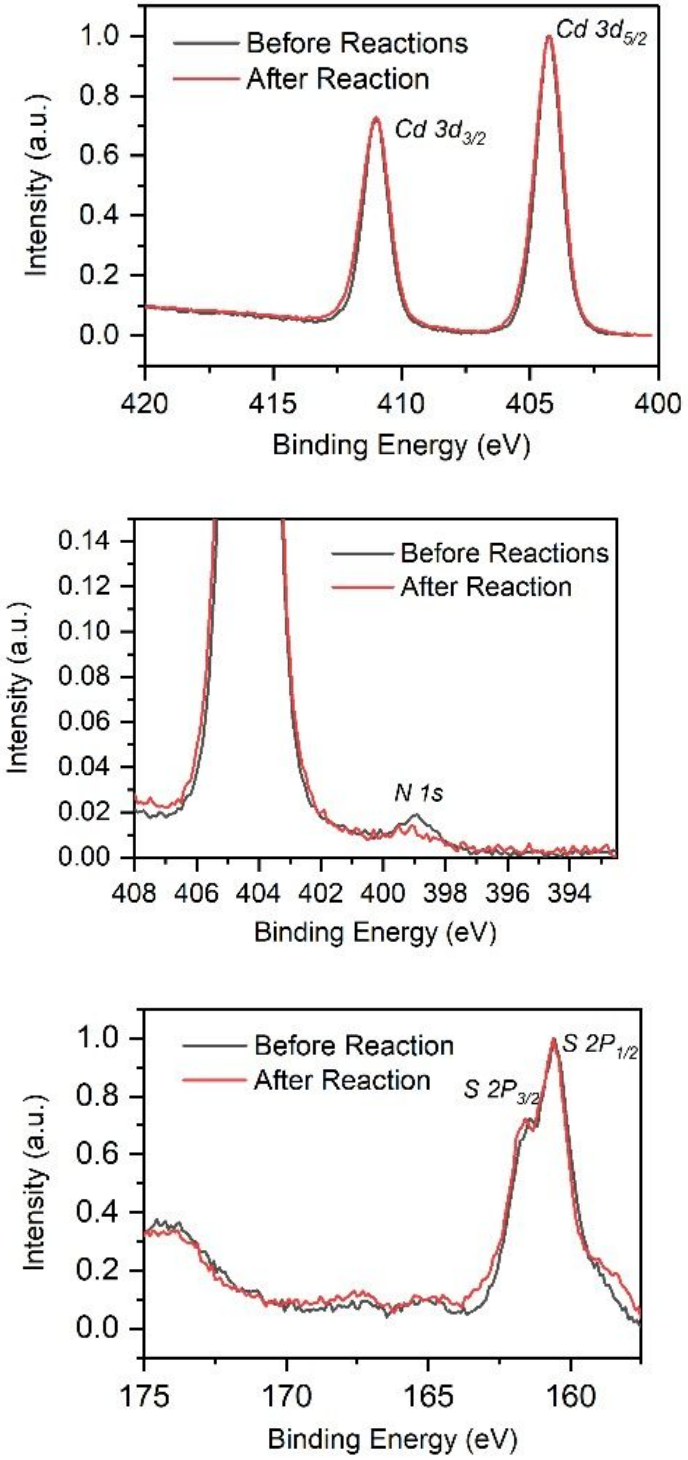


Figure S7 XPS image of CdSe/3CdS before and after the reaction.

10. Photoreaction setup for scale-up reaction

(1) Aldehyde reduction

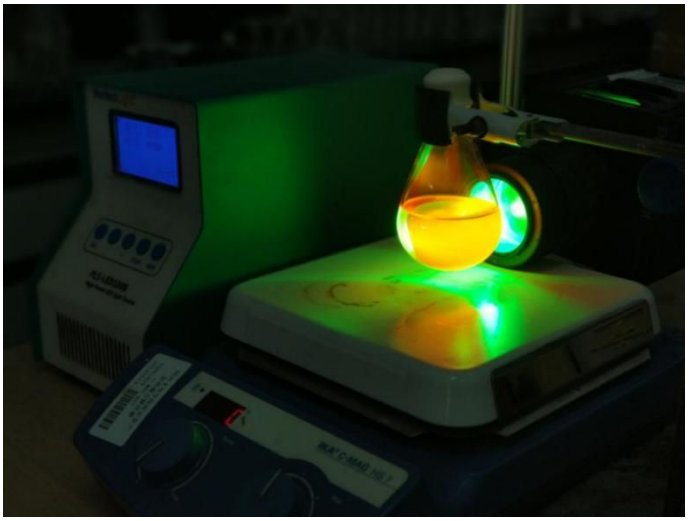
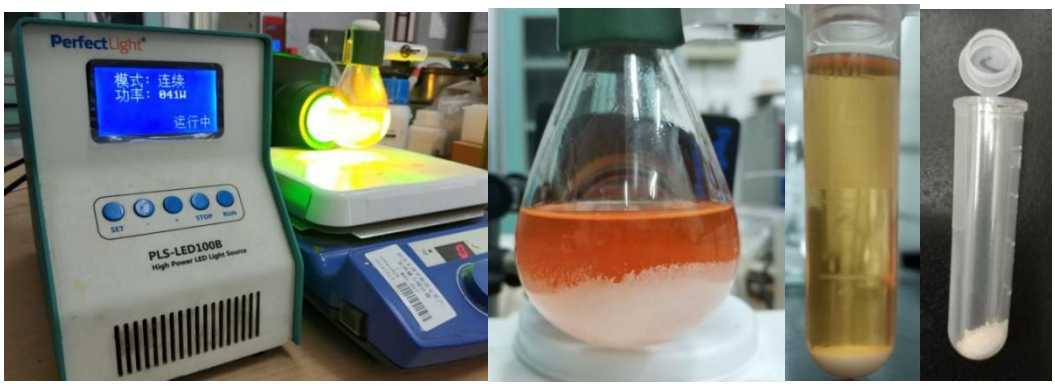


Figure S8

(2) Reductive coupling reaction



Figurre S9

11. Photoredox transfer hydrogenation under solar irradiation

This experiment was carried out on a clear day (Nov. 1-2, 2019) on a balcony at Zhejiang Sci-tech University (30°27' north latitude and 120°20' east longitude, 10 meters above the sea level). It took 11.5 hours to reach a completion to give the product **3l** in 87% yield.

12. Fluorescence quenching Studies

Fluorescence quenching experiments were performed on an Edinburgh instruments FLS920 spectrofluorometer with an excitation wavelength of 450 nm.

A solution of purified CdSe/3CdS core/shell QDs (120 μL) was added to an appropriate amount of substrates and toluene. The total volume of each solution was 2 mL, the final concentration of QDs in each solution was 1.2×10^{-6} M. All the photoluminescence spectra are collected 10 minutes after the mixing. When testing the quenching effect of thiophenol in the exist of cesium acetate, the concentration of cesium acetate is fixed to 5×10^{-3} M, which can barely quench the QDs. Therefore, the PL quenching is almost own to the products of thiophenol and cesium acetate.

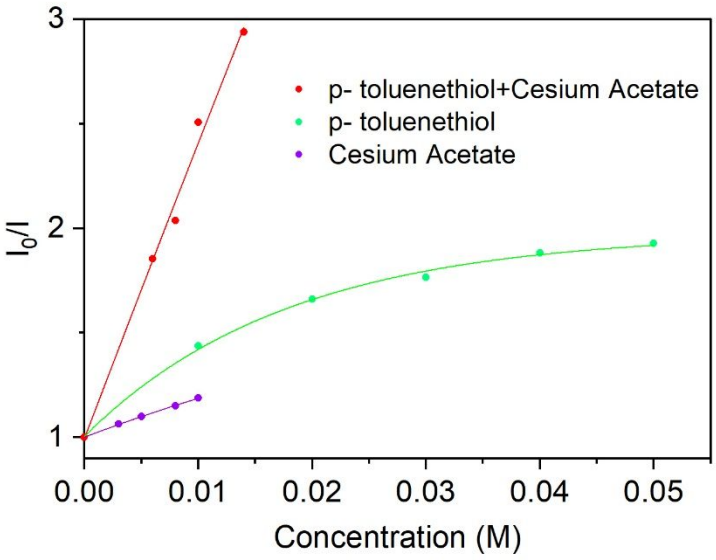


Figure S10 Fluorescence quenching data

13. The radical trapping experiments

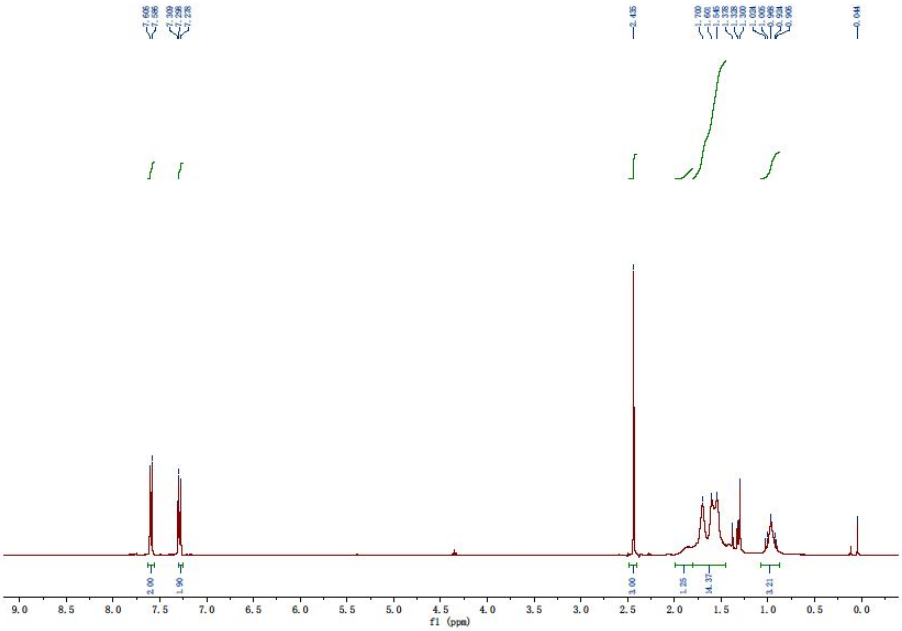


Figure S11 ^{1}HNMR of the radical trapping product (400 MHz, $CDCl_3$)

14. Micro-injector setup

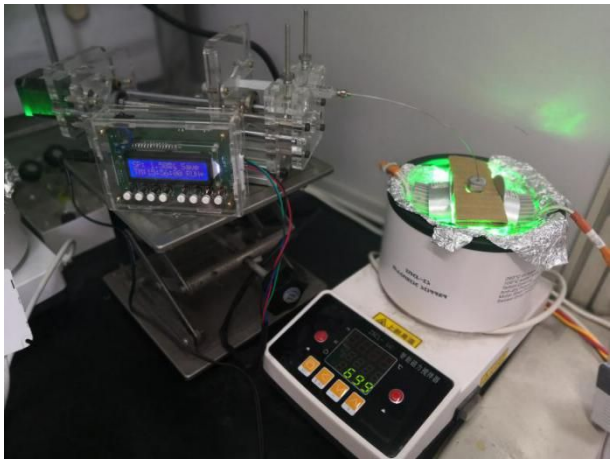
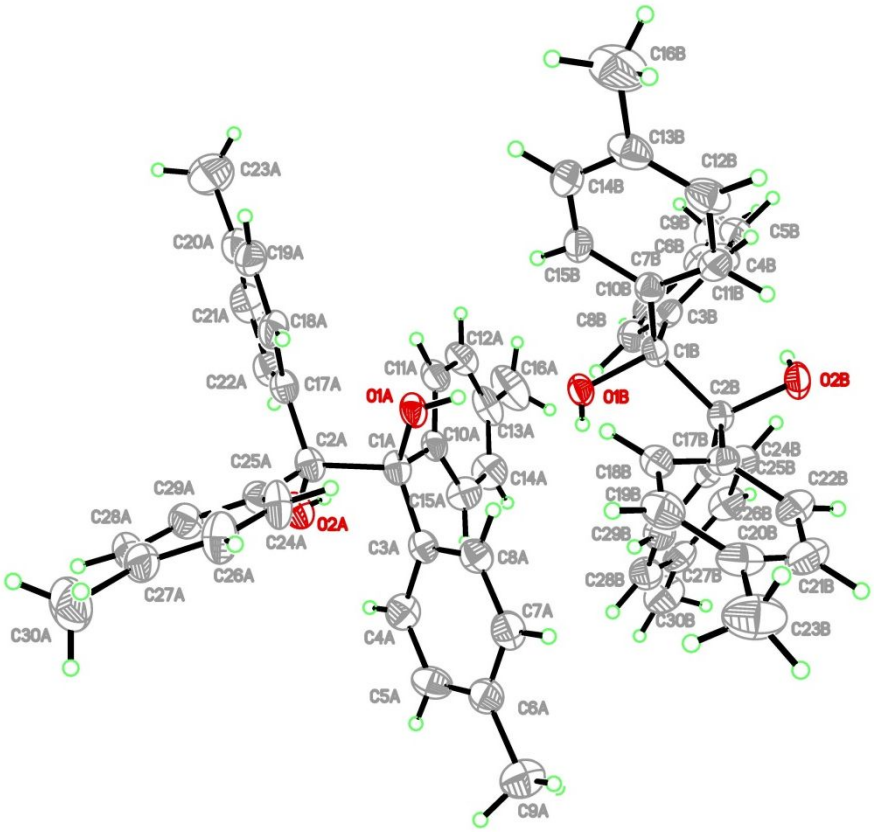


Figure S12

Methyl 4-formylbenzoate **1n** (0.1 mmol, 16.4 mg), p-toluenethiol (0.03 mmol, 4.3 mg, 0.3 eq), CdSe/3CdS (2.0×10^{-9} mol, 2×10^{-5} mol/L, 2×10^{-3} mol %) in hexane(1.6 ml), purging with argon gas for 15 minutes before illumination by 2×3 W green LED, then a solution of p-toluenethiol (0.12 mmol, 17.1 mg, 1.2eq) and 0.4 mL hexane was added using an injection pump within 15 hours.

15. X-ray crystallographic of 7b

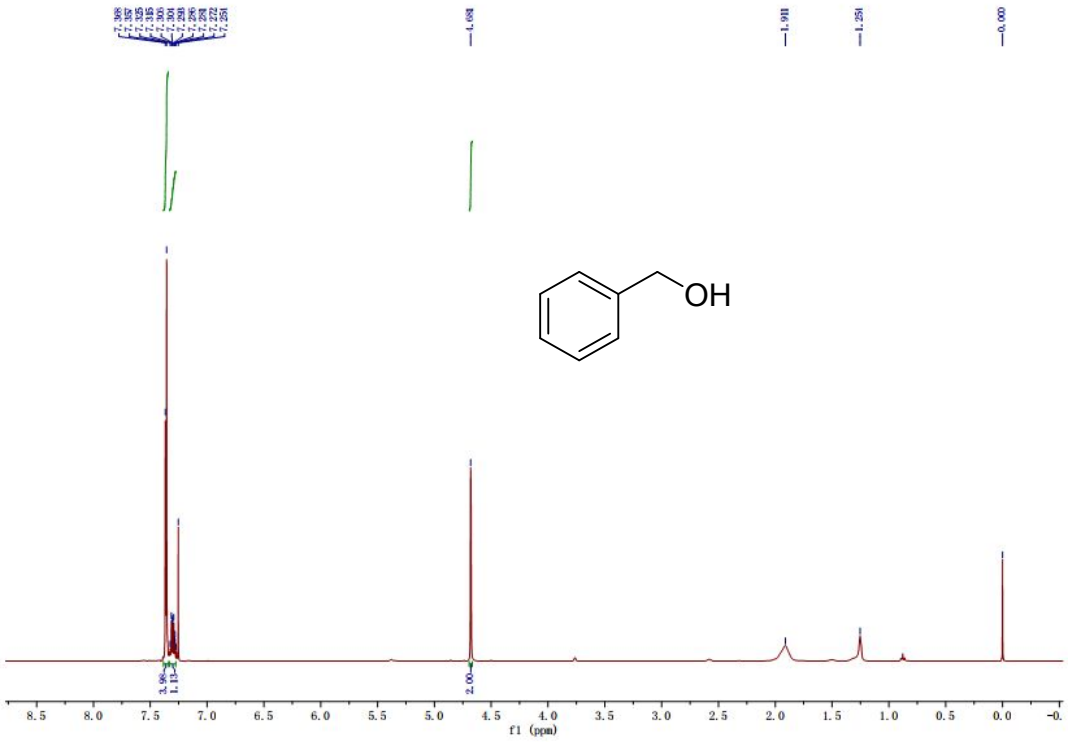


ORTEP drawing of product **7b** in thermal ellipsoidal representation at 30% probability level.

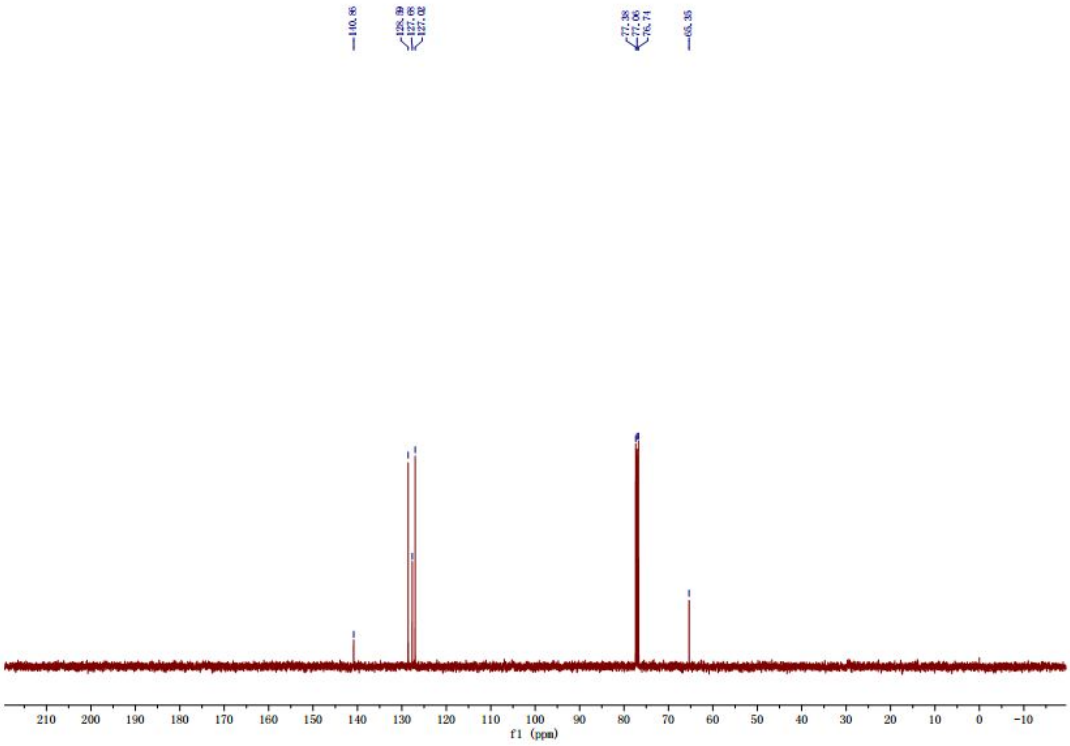
16. ^{1}H NMR and ^{13}C NMR

FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for all these synthesized compounds.

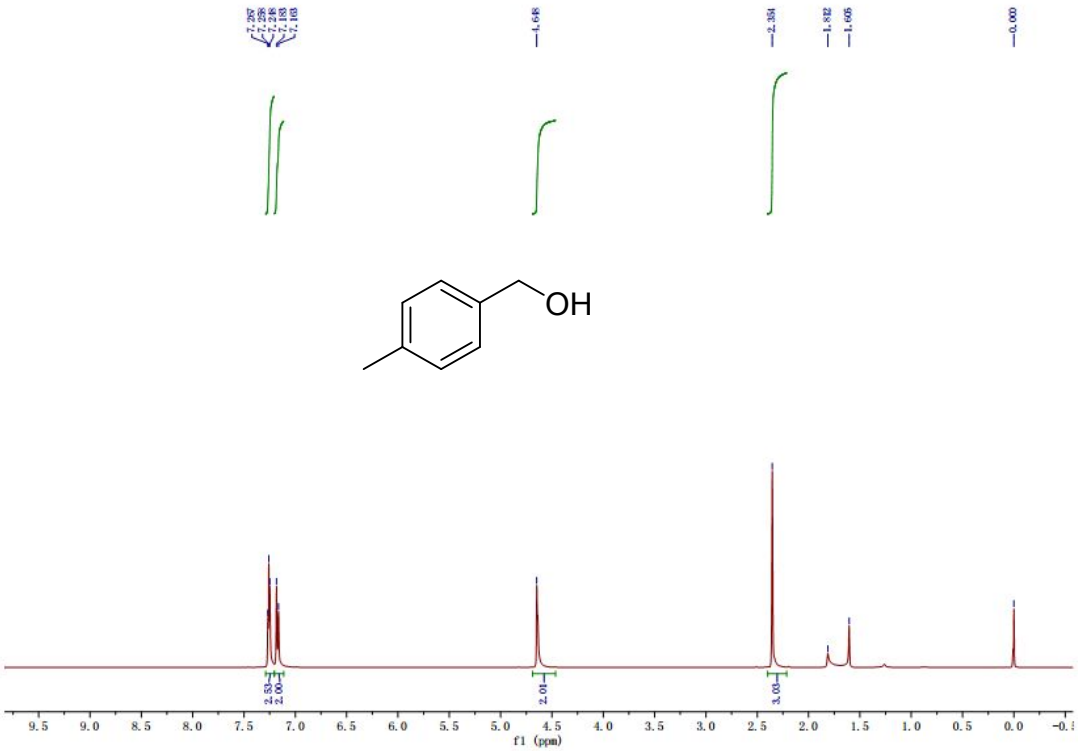
^{1}H NMR spectra of **3a** (400 MHz, $CDCl_3$):



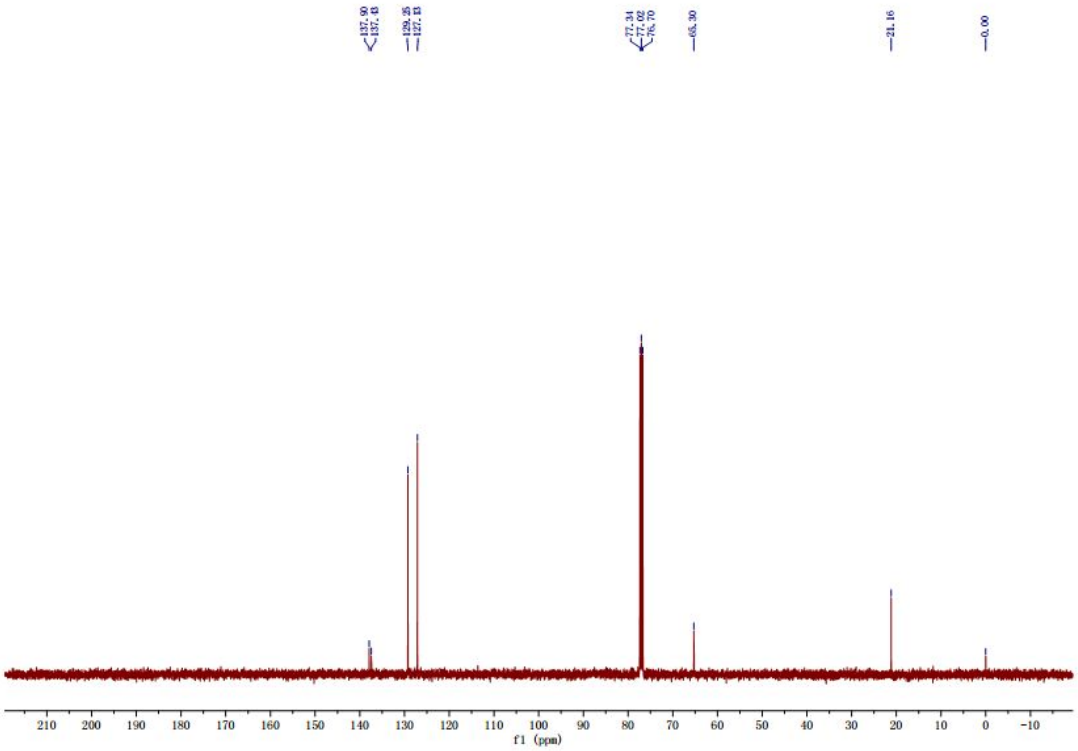
^{13}C{1H} NMR spectra of **3a** (100 MHz, $CDCl_3$) :



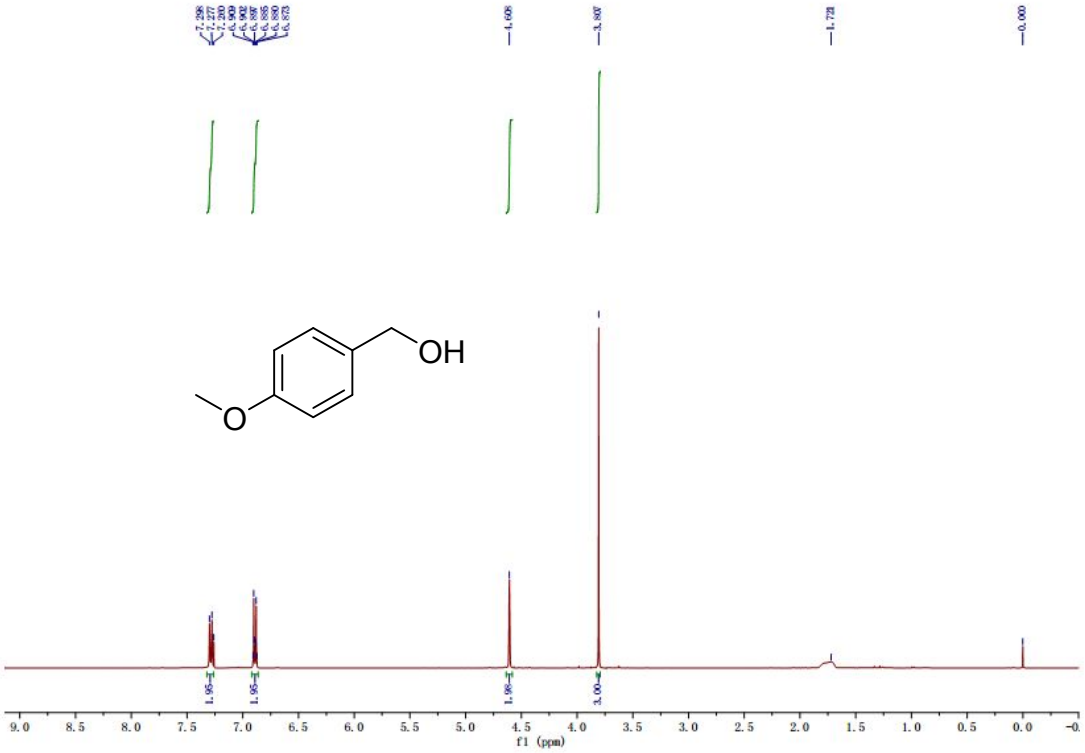
^{1}H NMR spectra of **3b** (400 MHz, $CDCl_3$):



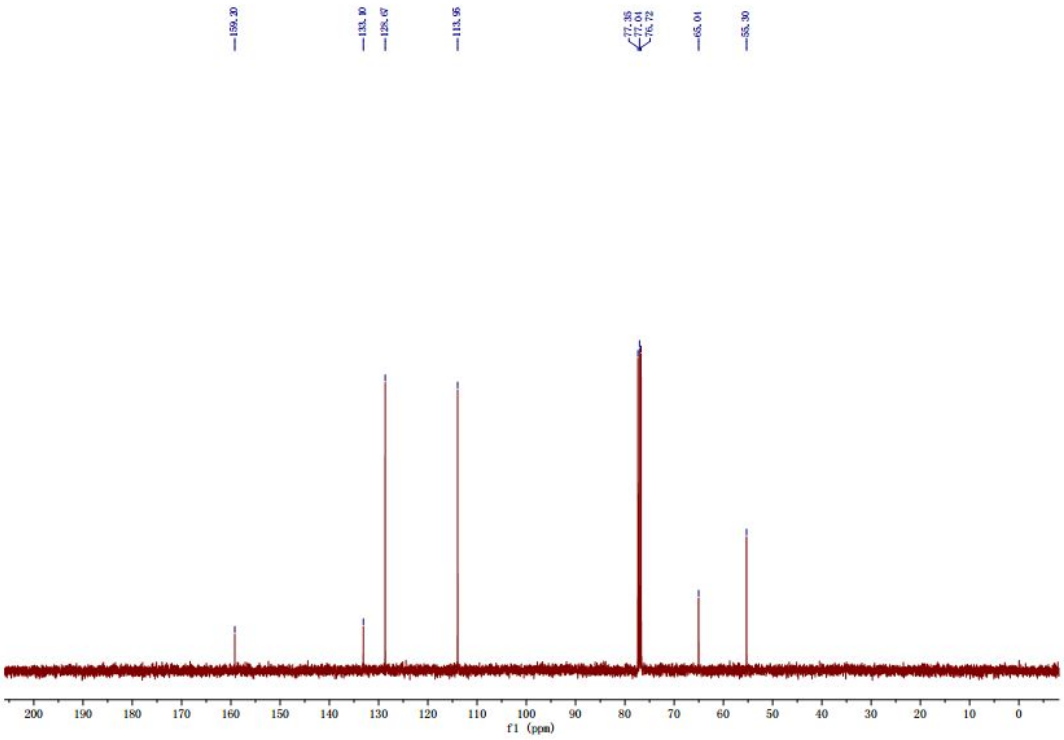
^{13}C{1H} NMR spectra of **3b** (100 MHz, $CDCl_3$):



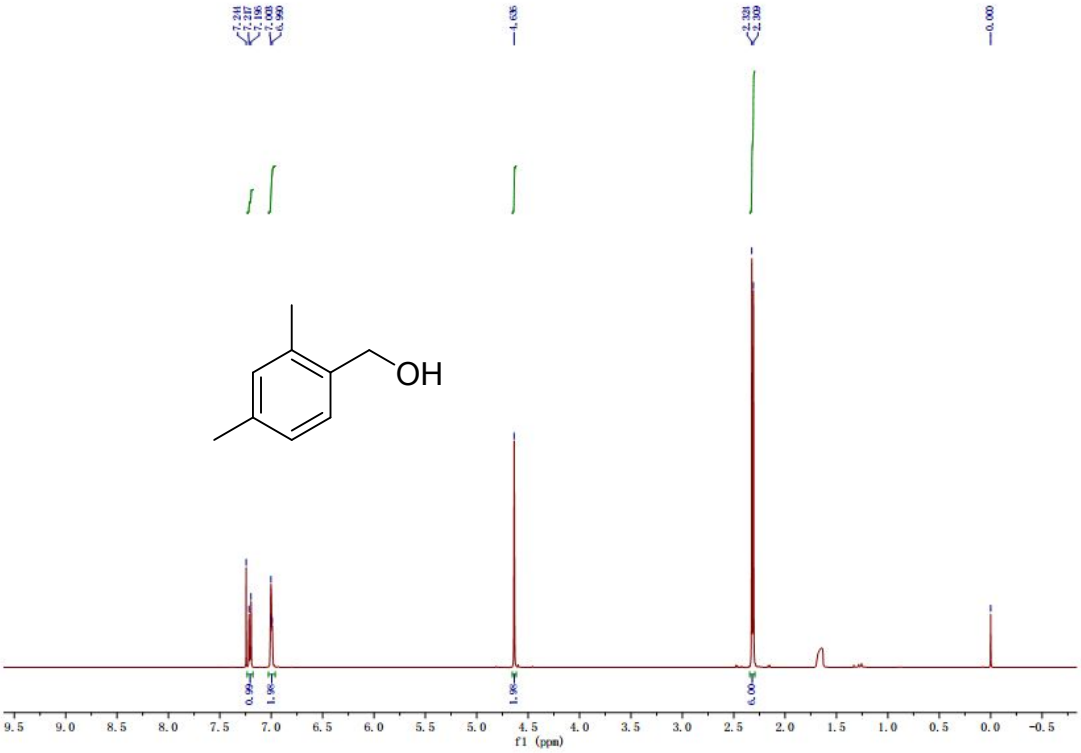
^{1}H NMR spectra of **3c** (400 MHz, $CDCl_3$):



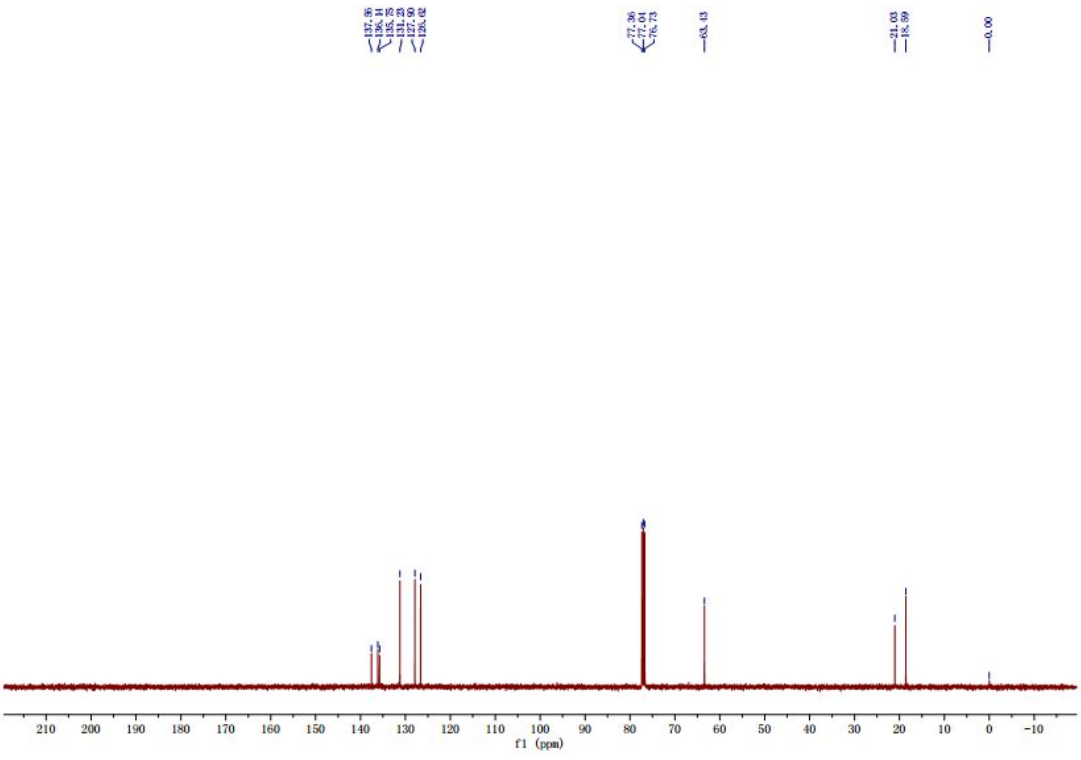
^{13}C{1H} NMR spectra of **3c** (100 MHz, $CDCl_3$):



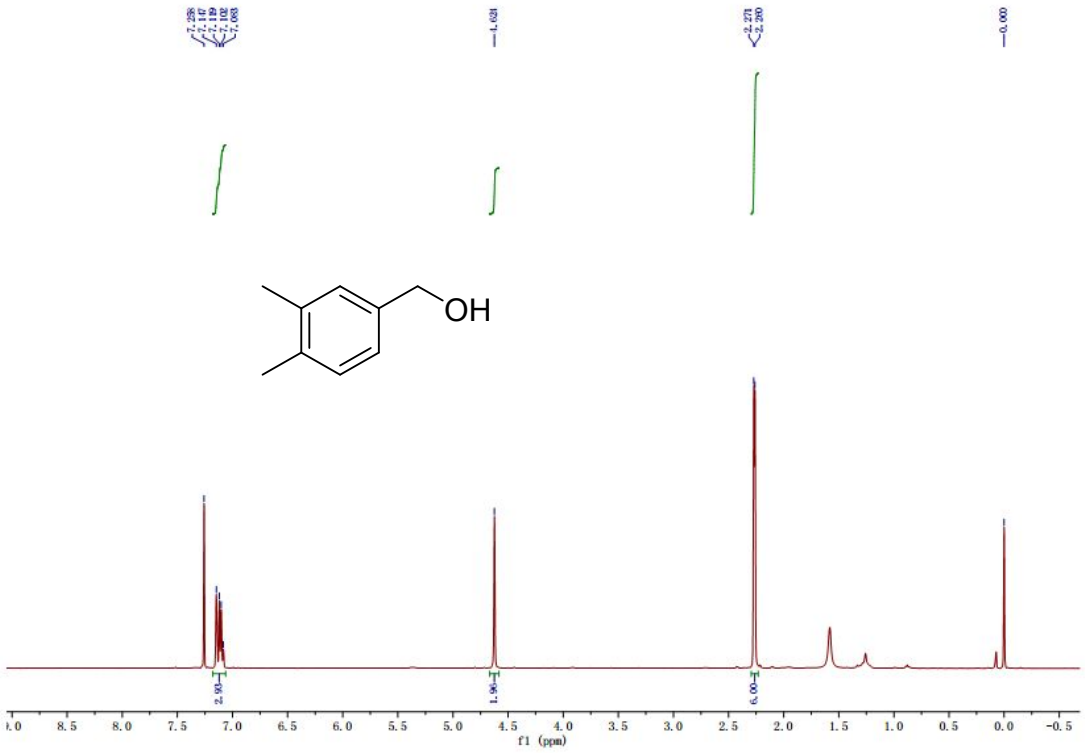
^{1}H NMR spectra of **3d** (400 MHz, $CDCl_3$):



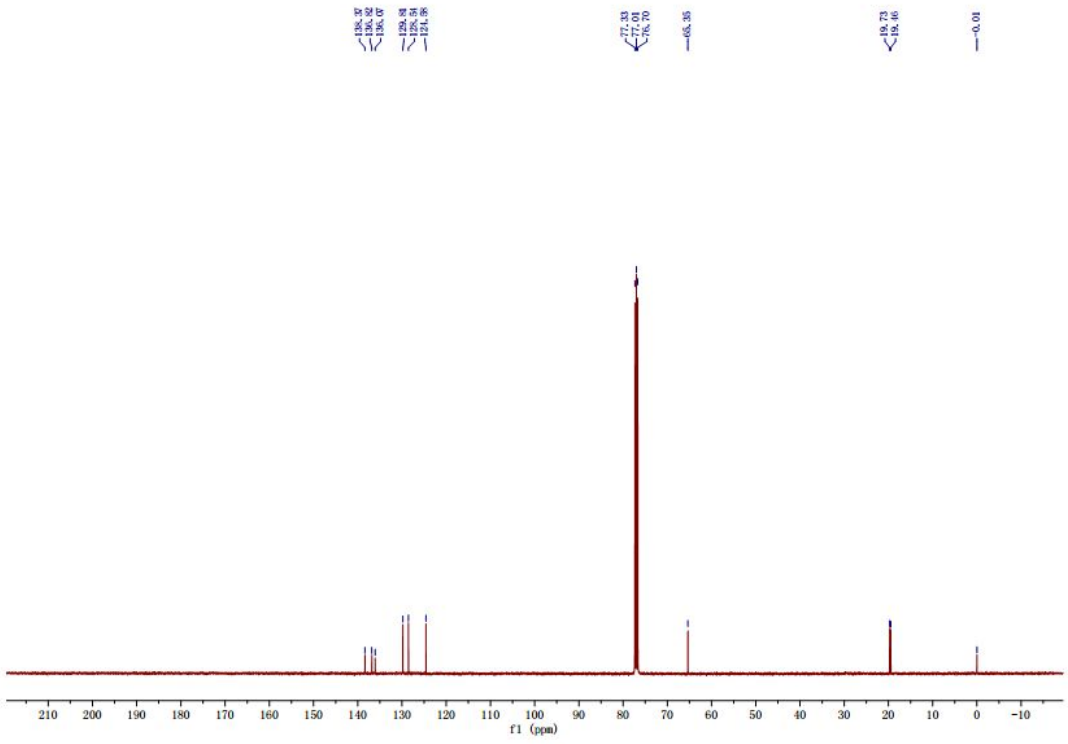
^{13}C{1H} NMR spectra of **3d** (100 MHz, $CDCl_3$):



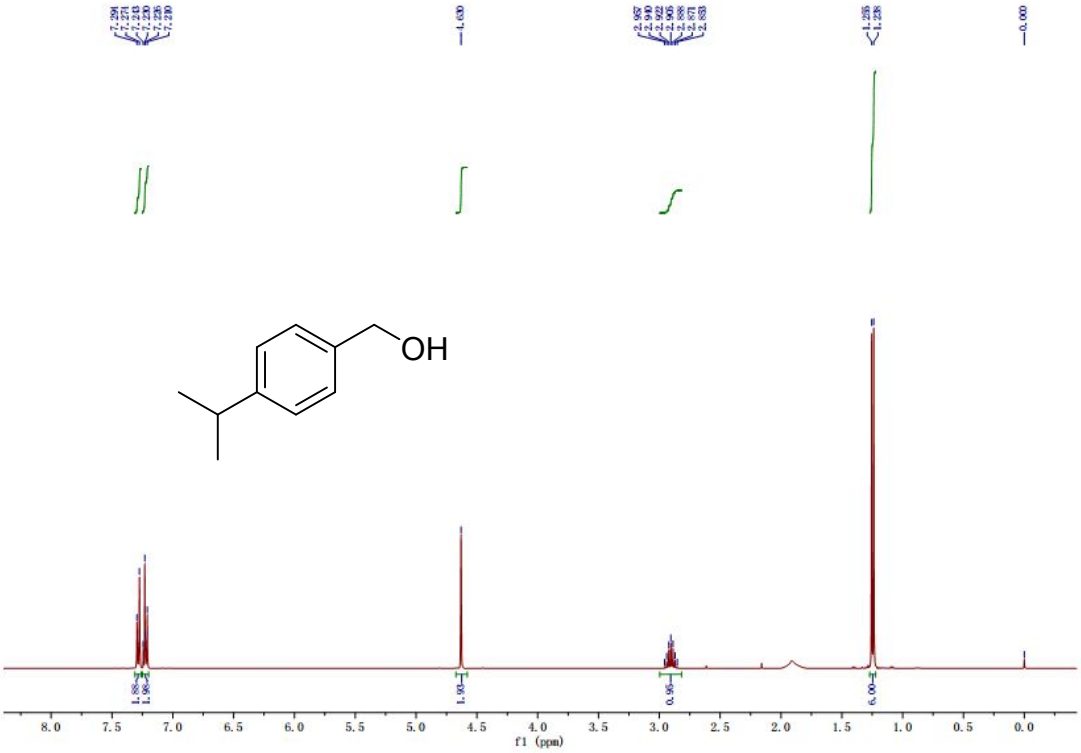
^{1}H NMR spectra of **3e** (400 MHz, $CDCl_3$):



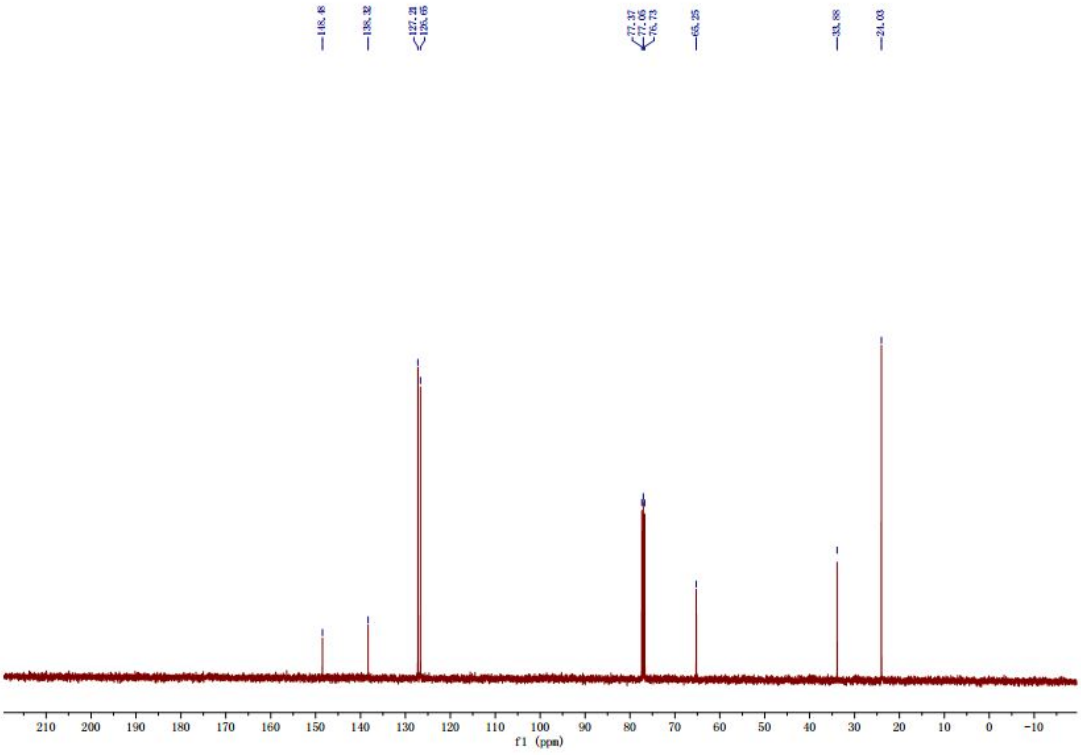
^{13}C{1H} NMR spectra of **3e** (100 MHz, $CDCl_3$):



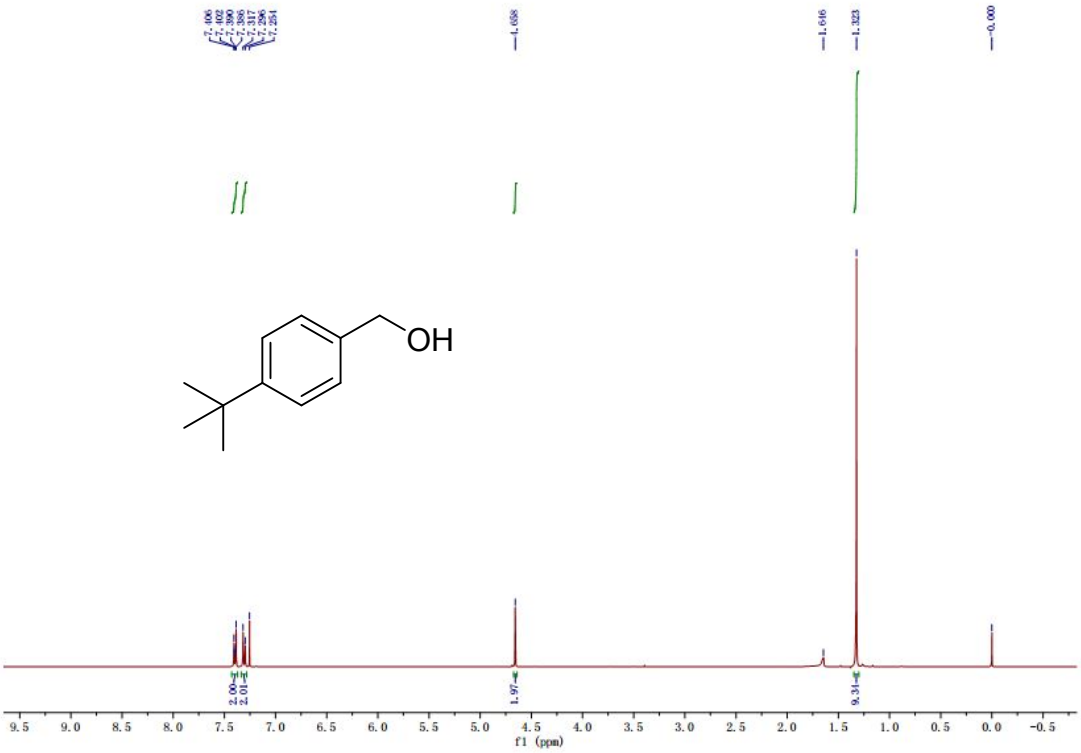
^{1}H NMR spectra of **3f** (400 MHz, $CDCl_3$):



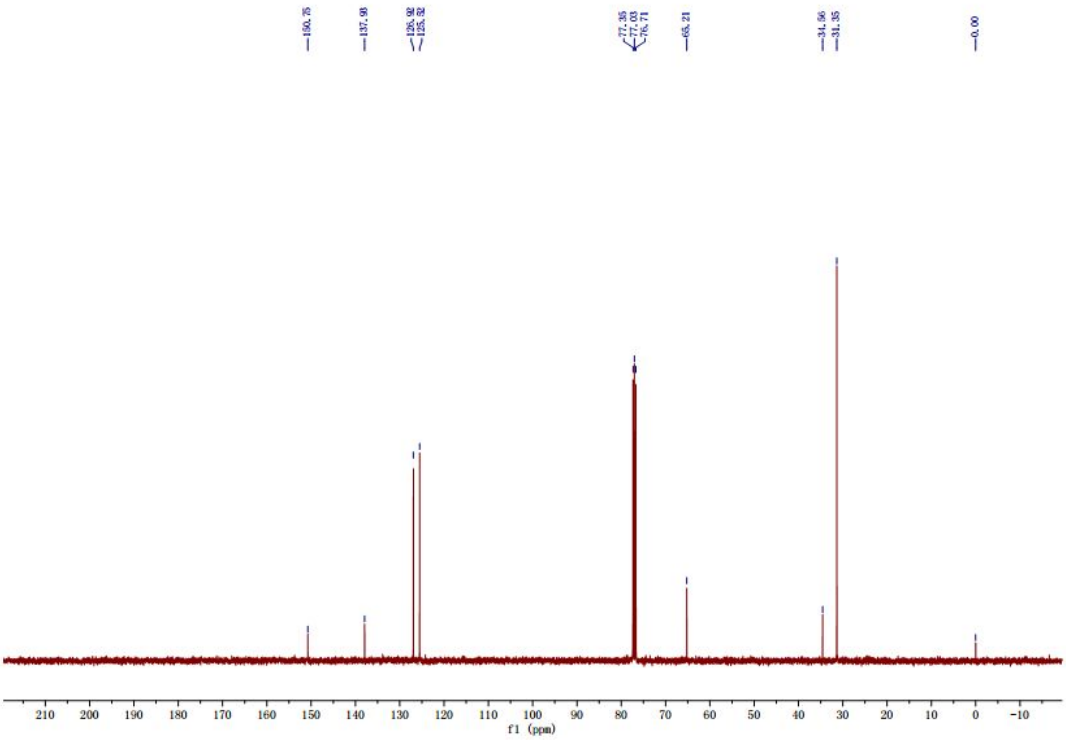
^{13}C{1H} NMR spectra of **3f** (100 MHz, $CDCl_3$):



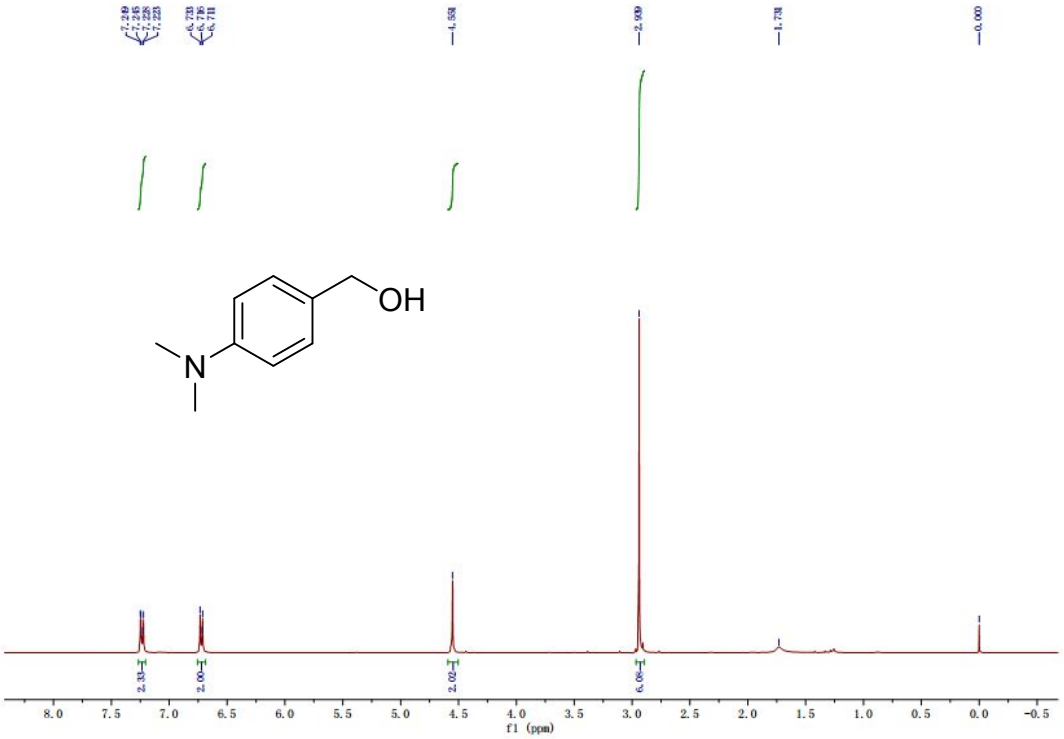
^{1}H NMR spectra of **3g** (400 MHz, $CDCl_3$):



^{13}C{1H} NMR spectra of **3g** (100 MHz, $CDCl_3$):



^{1}H NMR spectra of **3h** (400 MHz, $CDCl_3$):



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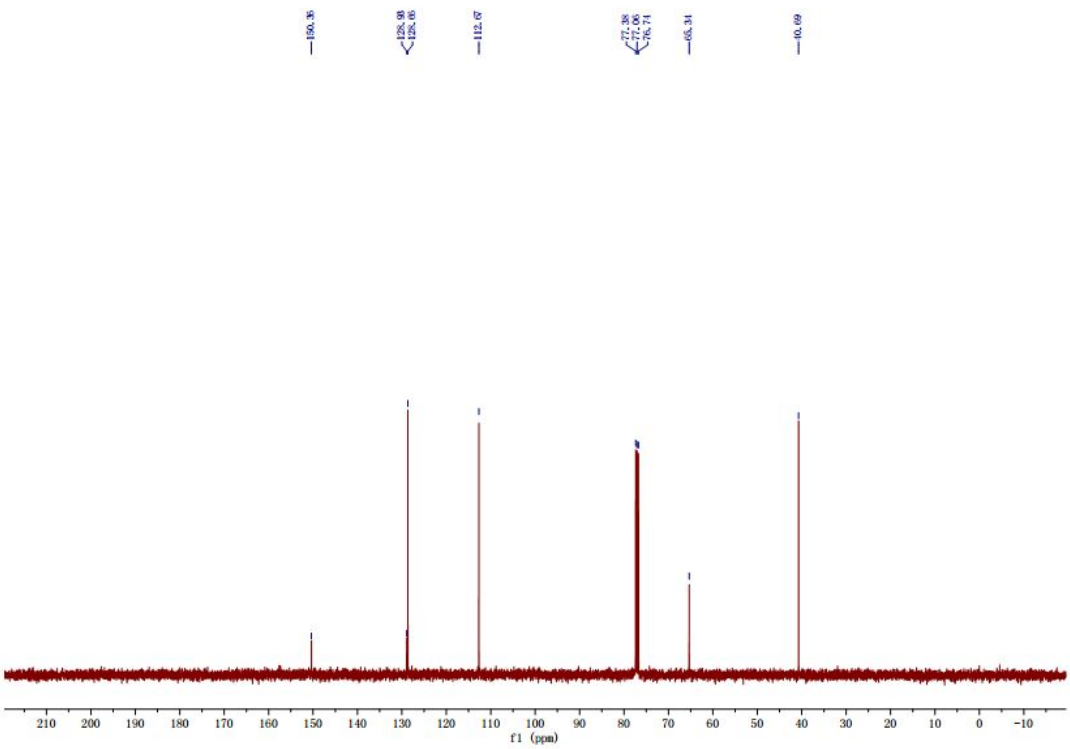
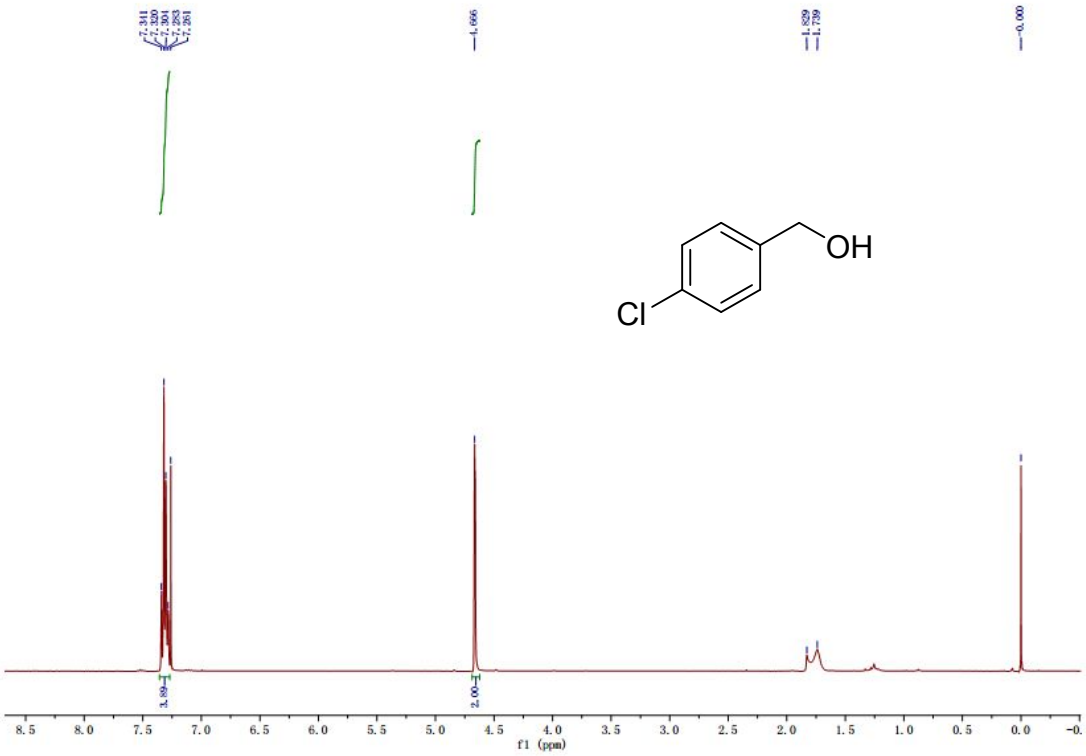
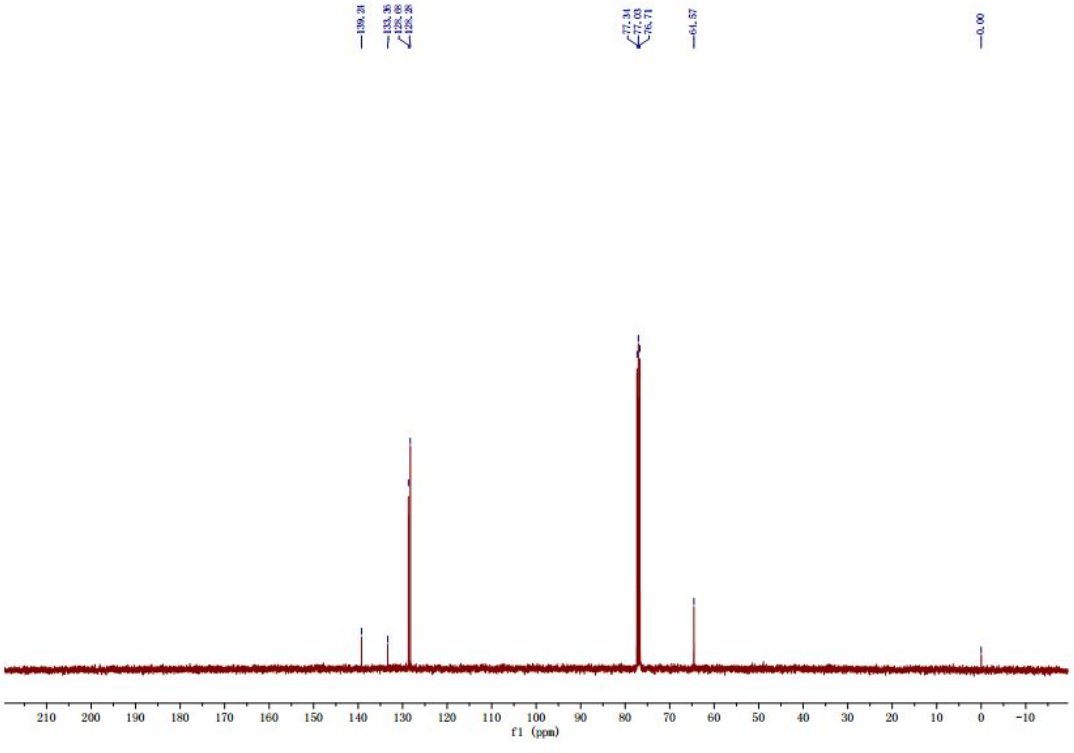


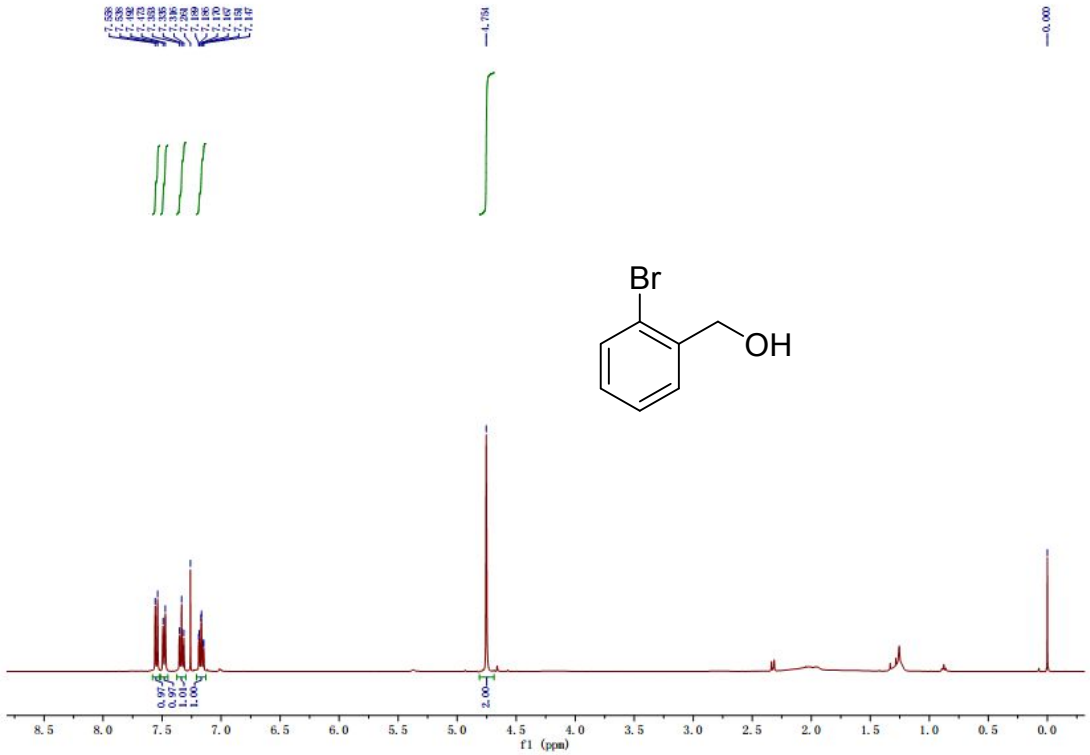
^{1}H NMR spectra of **3i** (400 MHz, $CDCl_3$):



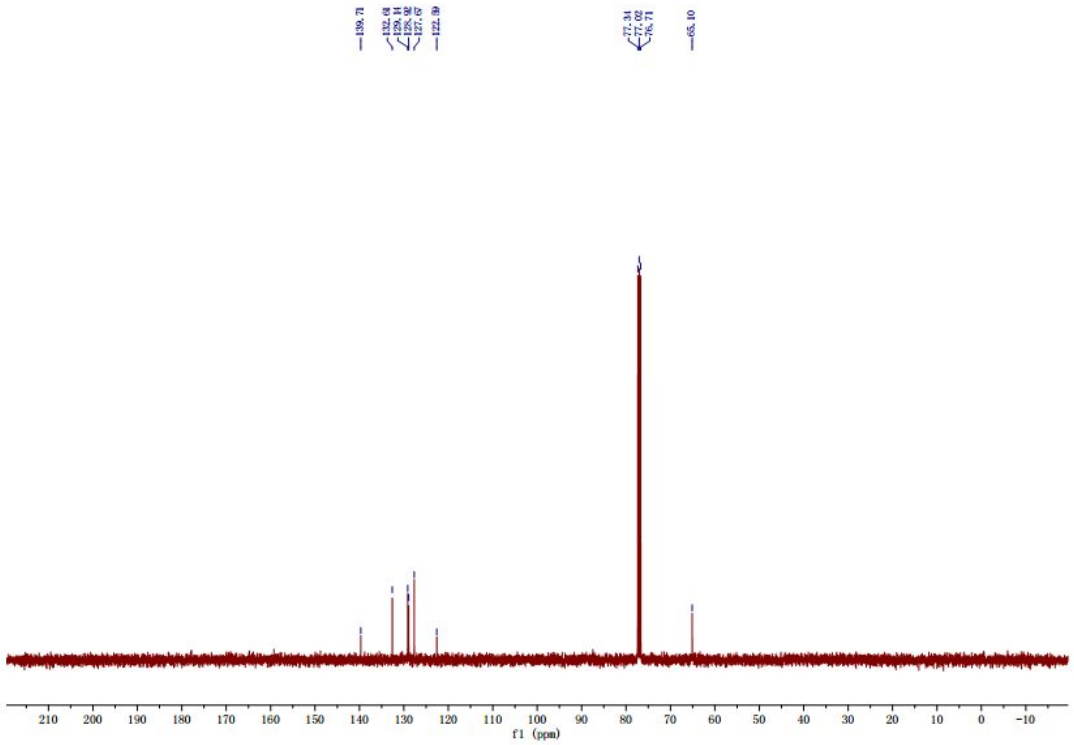
^{13}C{1H} NMR spectra of **3i** (100 MHz, $CDCl_3$):



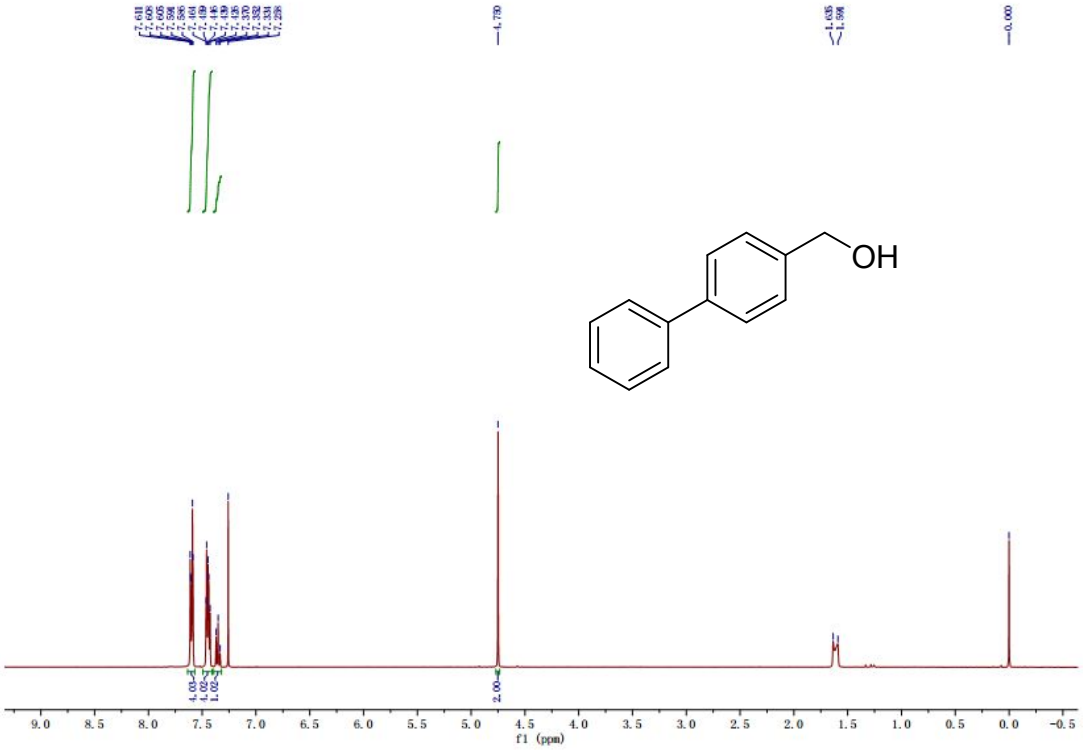
^{1}H NMR spectra of **3j** (400 MHz, $CDCl_3$):



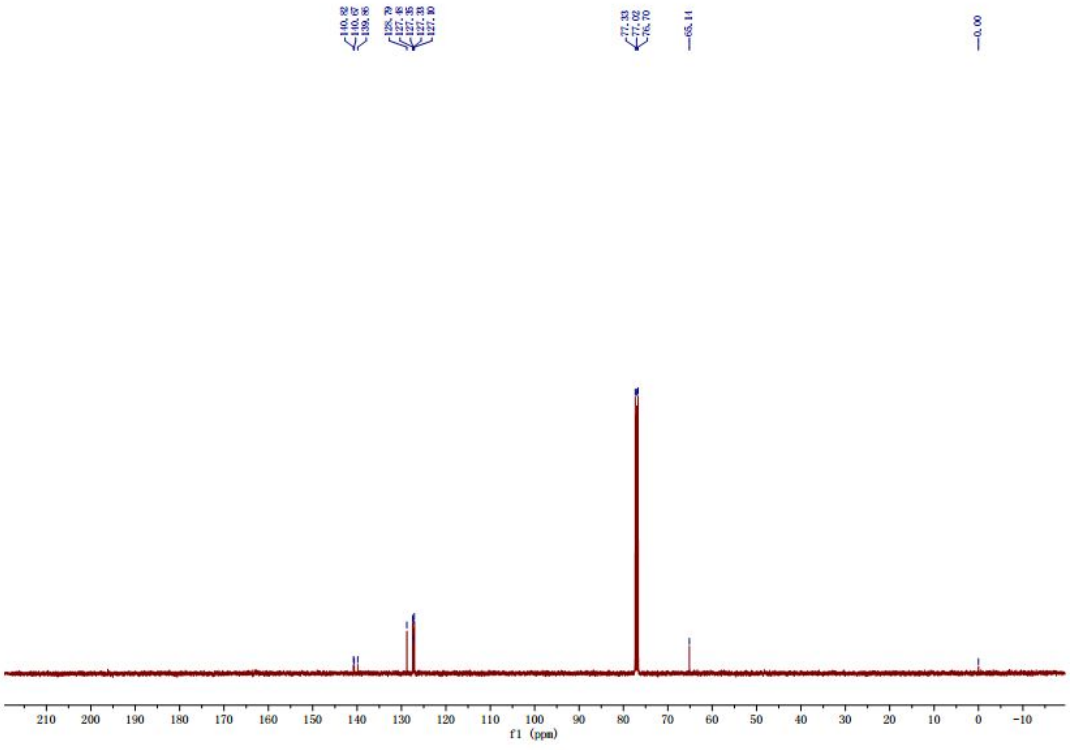
^{13}C{1H} NMR spectra of **3j** (100 MHz, $CDCl_3$):



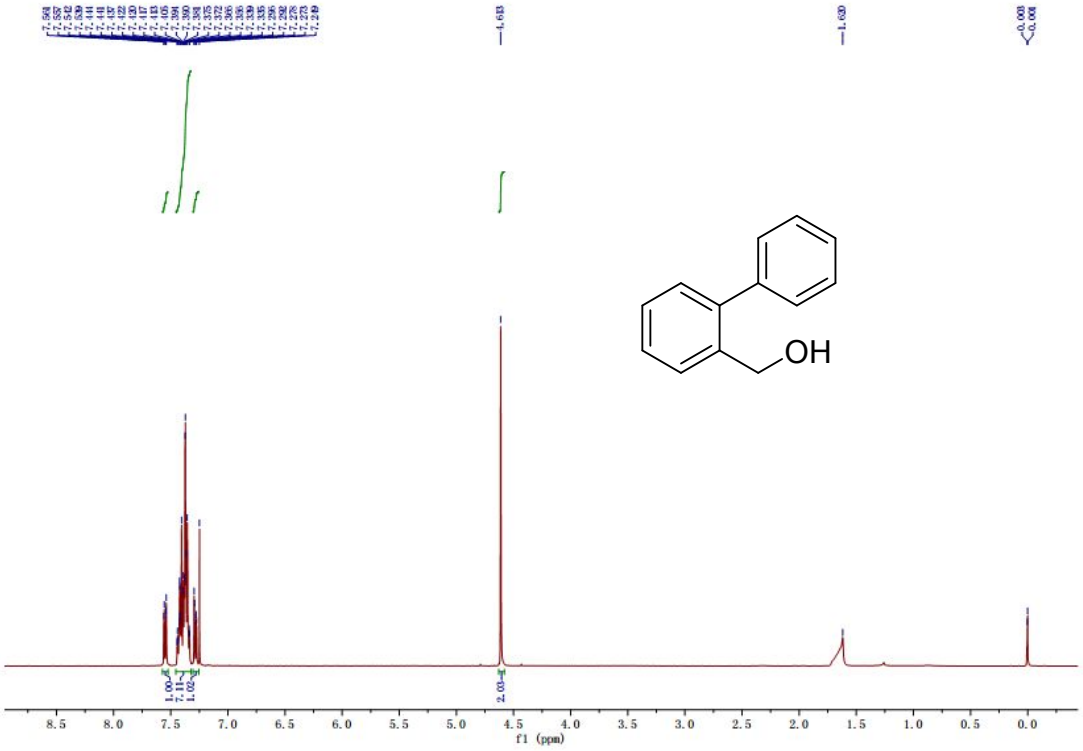
^{1}H NMR spectra of **3k** (400 MHz, $CDCl_3$):



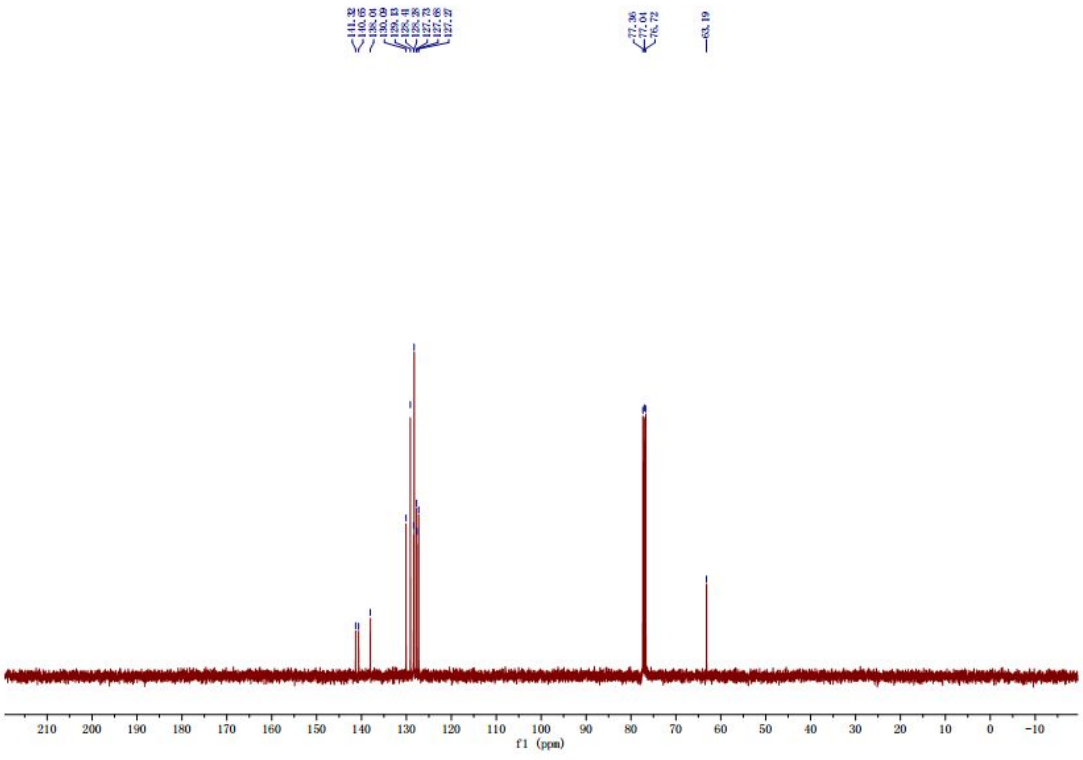
^{13}C{1H} NMR spectra of **3k** (100 MHz, $CDCl_3$):



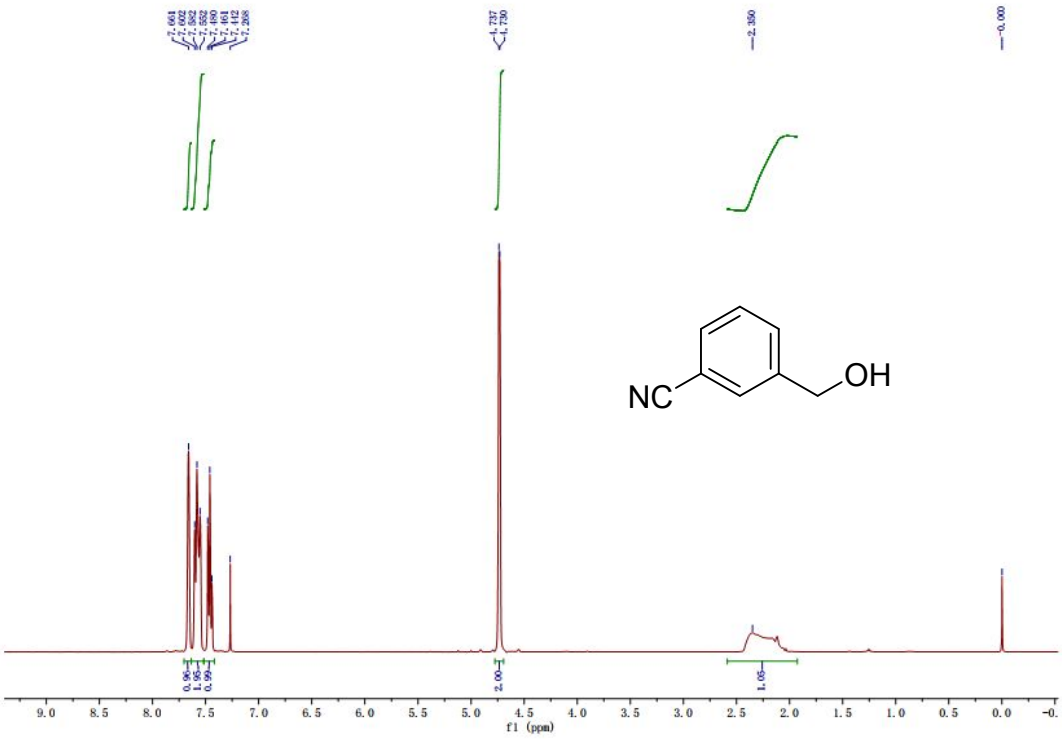
^{1}H NMR spectra of **3l** (400 MHz, $CDCl_3$):



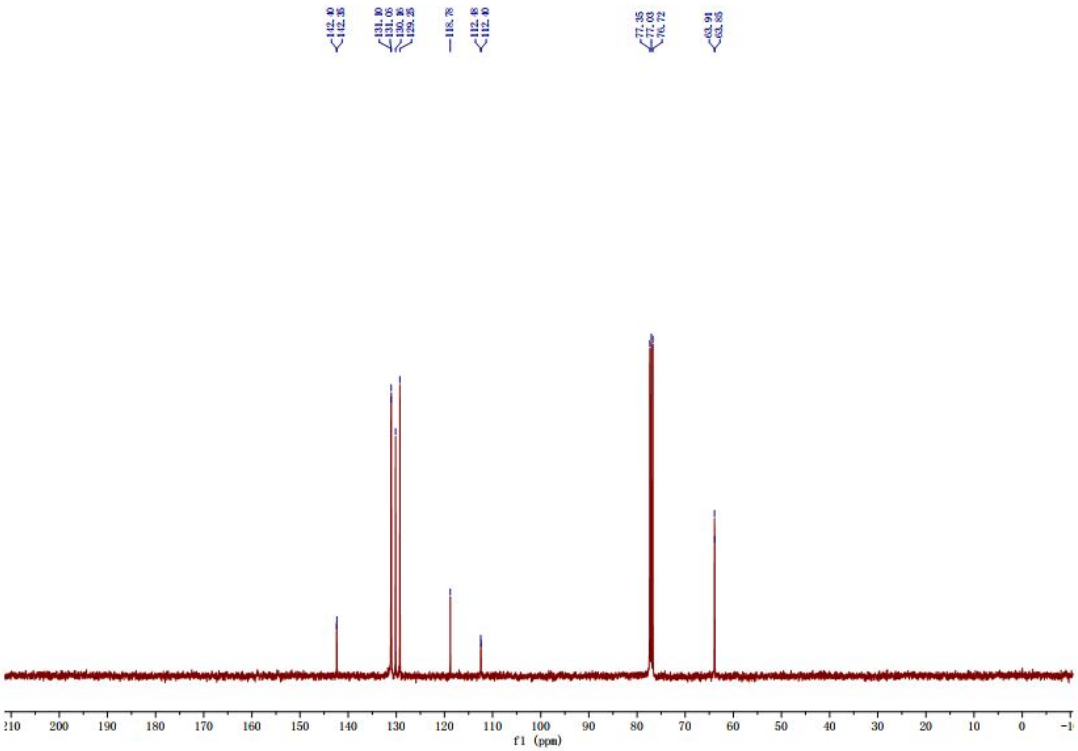
^{13}C{1H} NMR spectra of **3l** (100 MHz, $CDCl_3$):



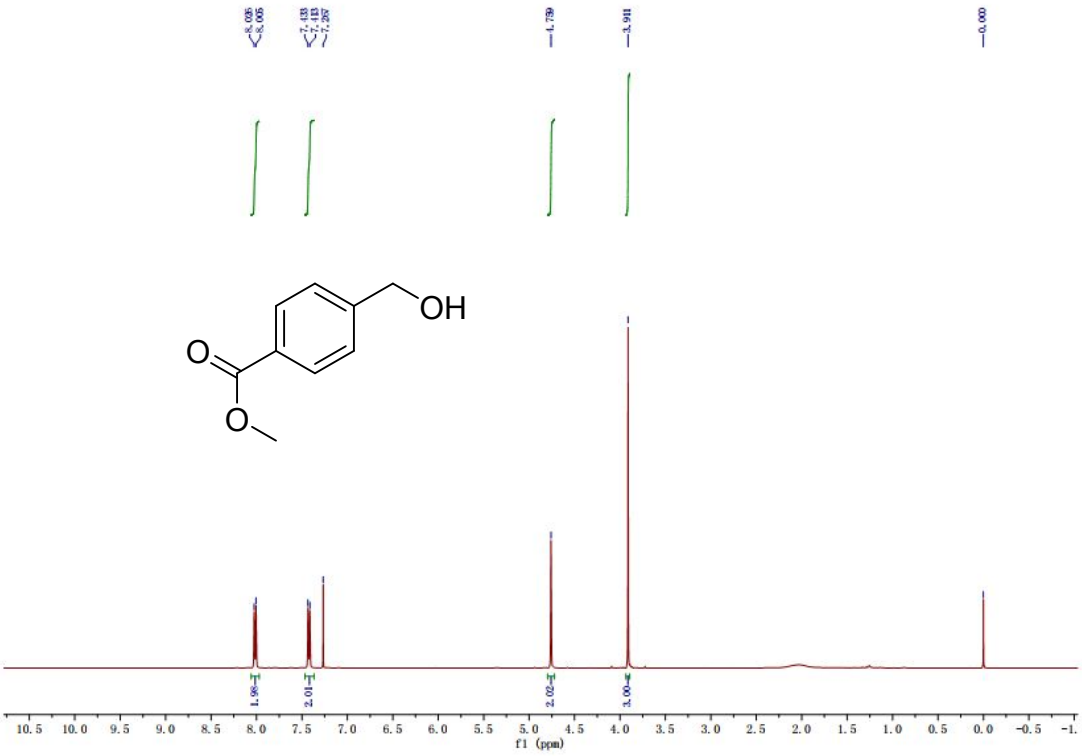
^{1}H NMR spectra of **3m** (400 MHz, $CDCl_3$):



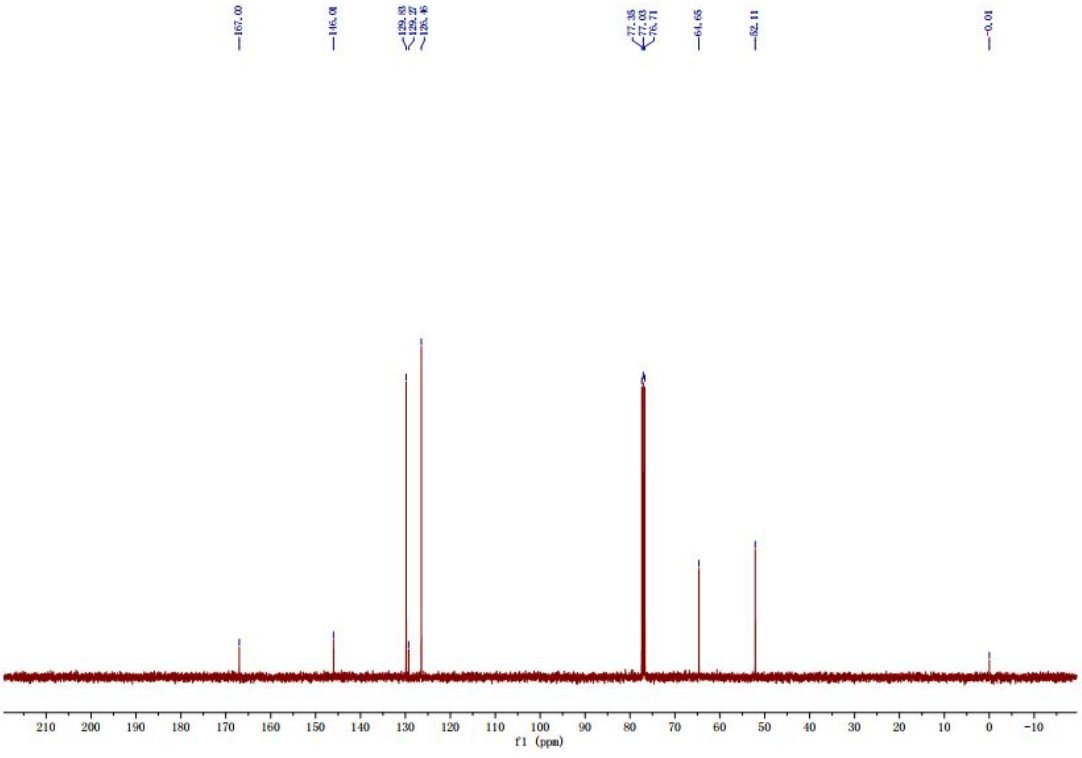
^{13}C{1H} NMR spectra of **3m** (100 MHz, $CDCl_3$):



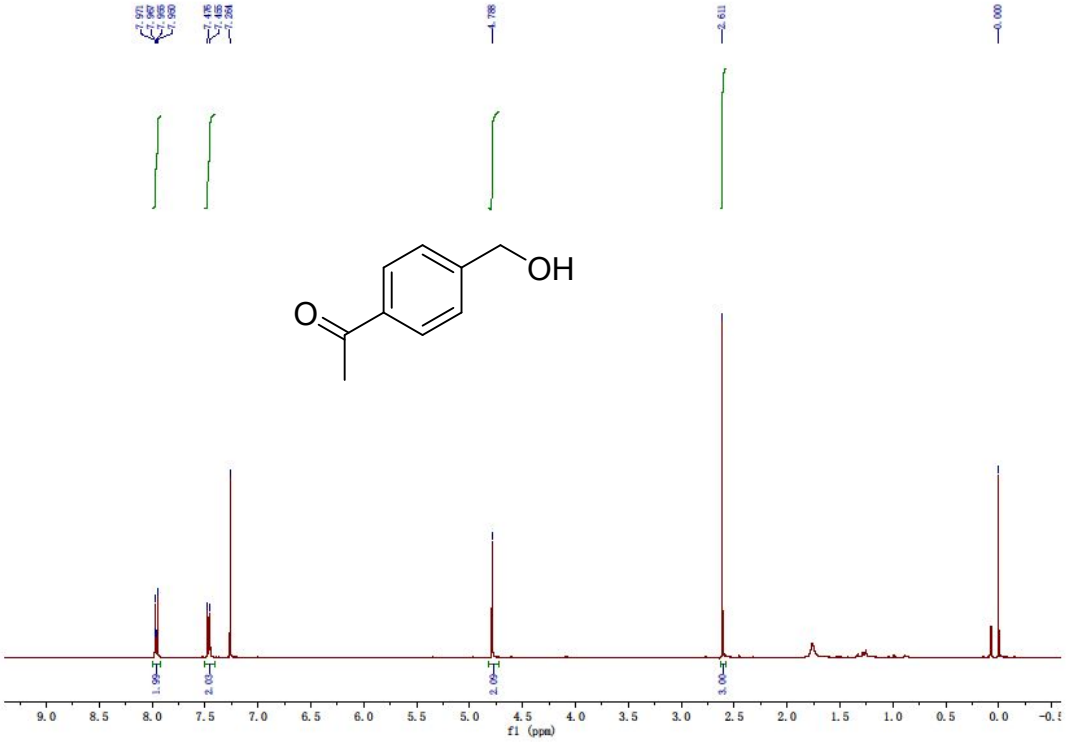
^{1}H NMR spectra of **3n** (400 MHz, $CDCl_3$):



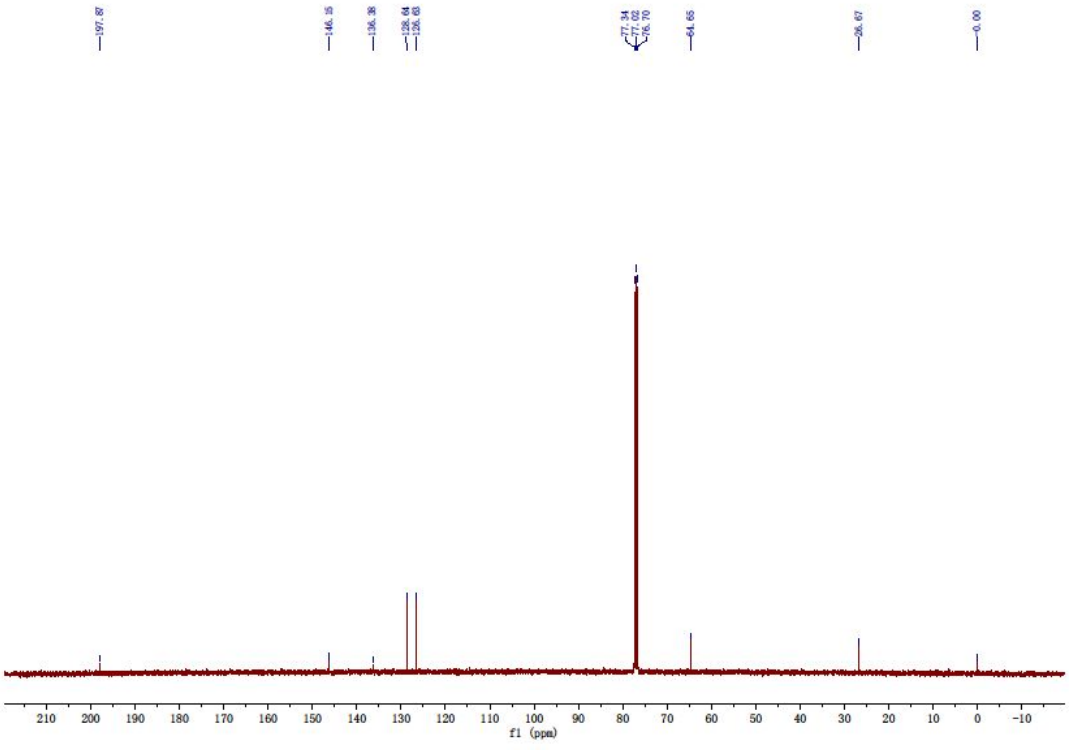
^{13}C{1H} NMR spectra of **3n** (100 MHz, $CDCl_3$):



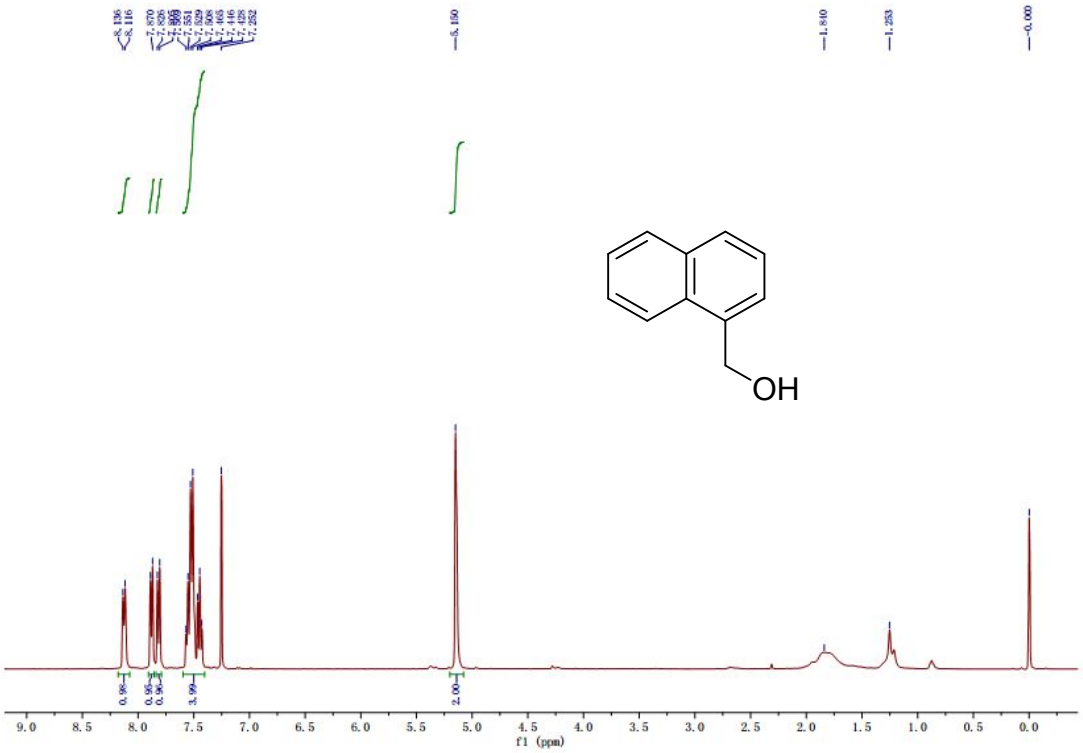
^{1}H NMR spectra of **3o** (400 MHz, $CDCl_3$):



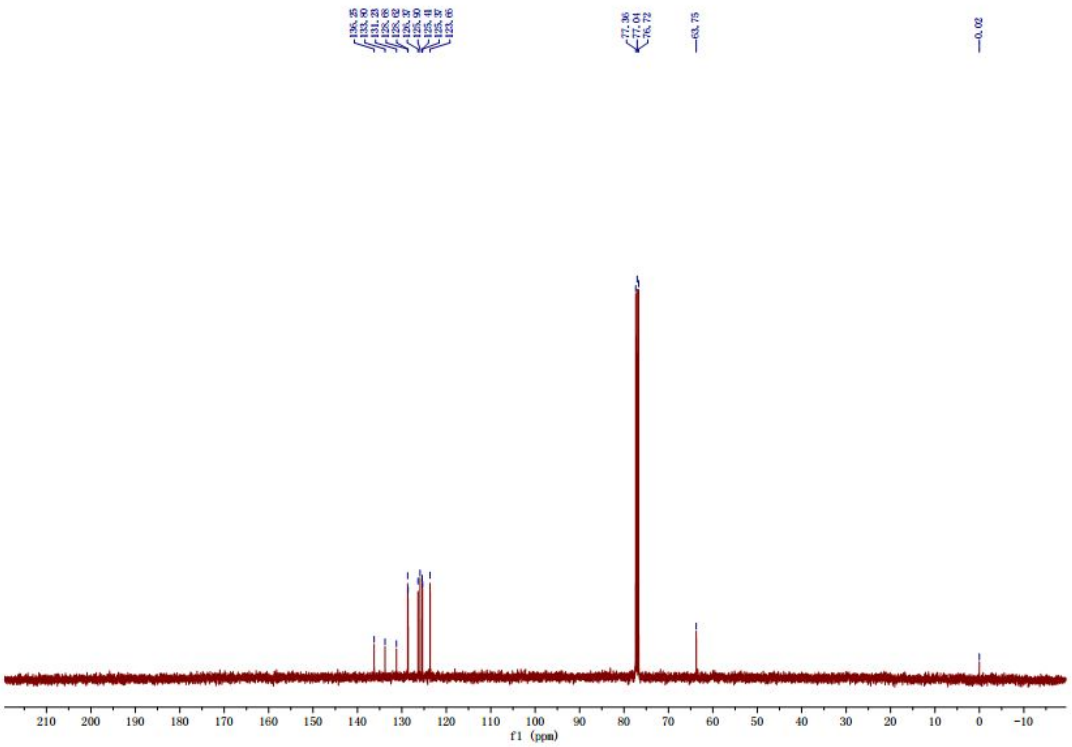
^{13}C{1H} NMR spectra of **3o** (100 MHz, $CDCl_3$):



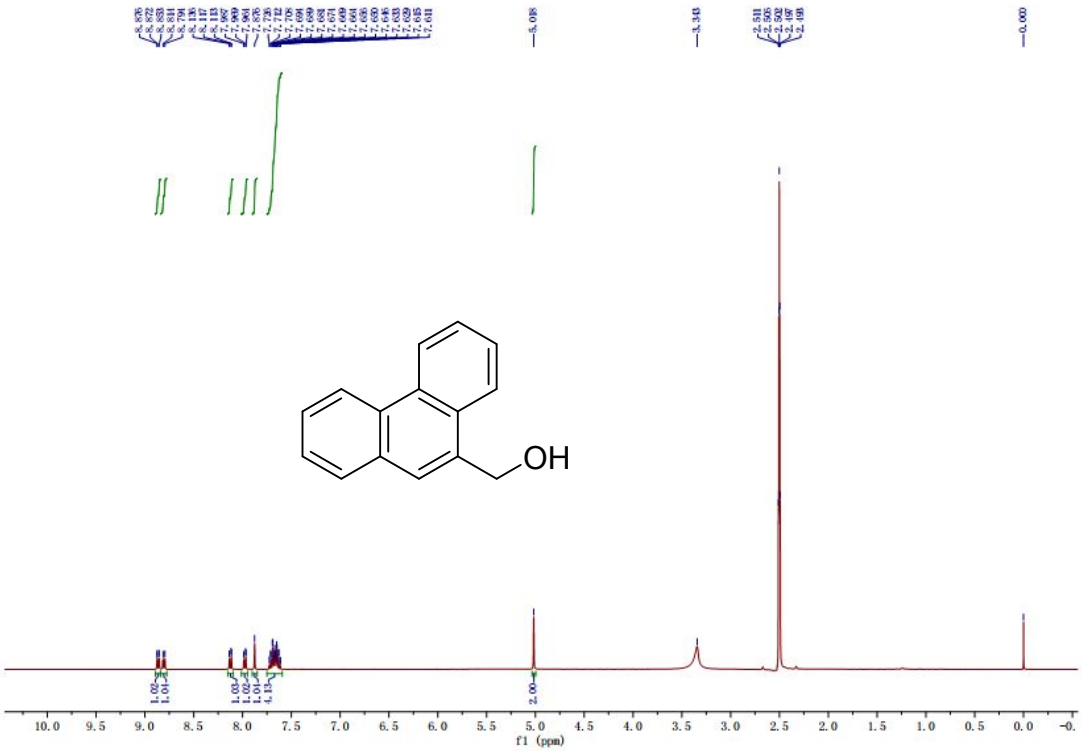
^{1}H NMR spectra of **3p** (400 MHz, $CDCl_3$):



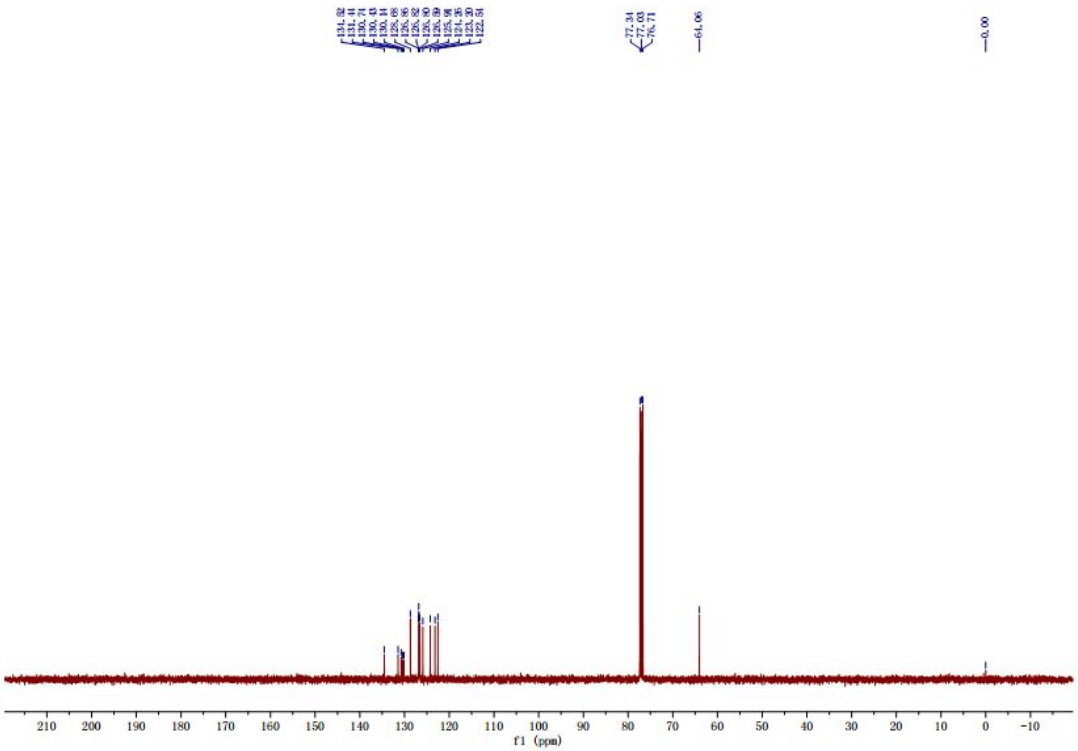
^{13}C{1H} NMR spectra of **3p** (100 MHz, $CDCl_3$):



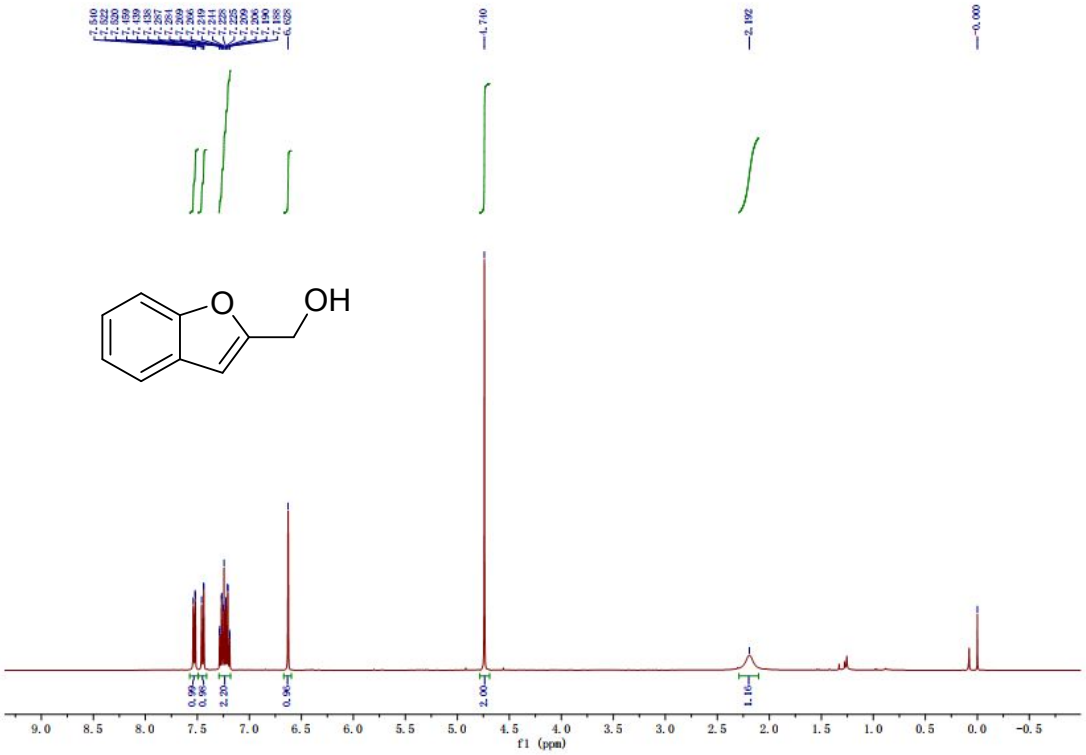
^{1}H NMR spectra of **3q** (400 MHz, $CDCl_3$):



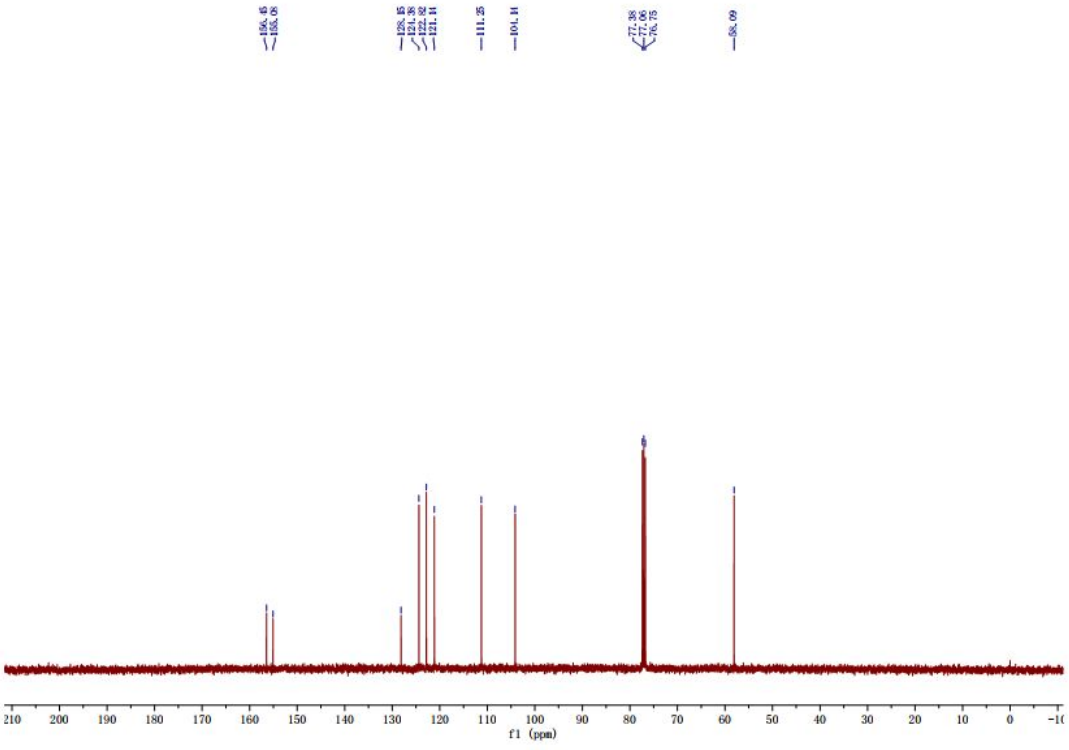
^{13}C{1H} NMR spectra of **3q** (100 MHz, $CDCl_3$):



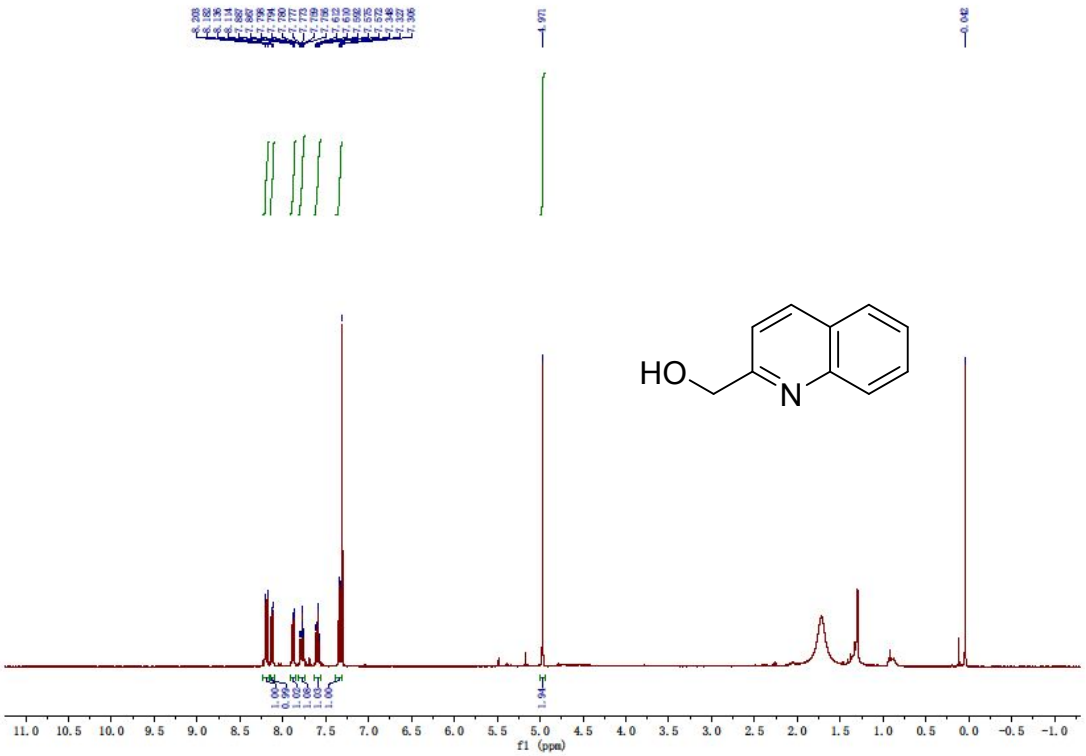
^{1}H NMR spectra of **3r** (400 MHz, $CDCl_3$):



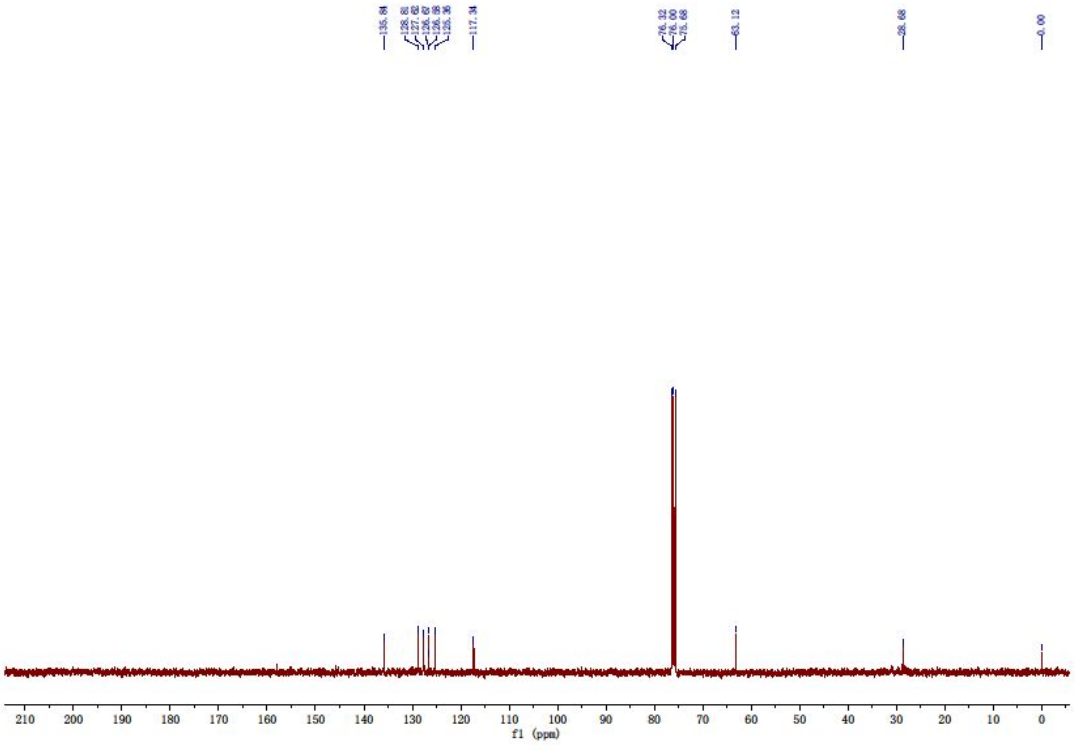
^{13}C{1H} NMR spectra of **3r** (100 MHz, $CDCl_3$):



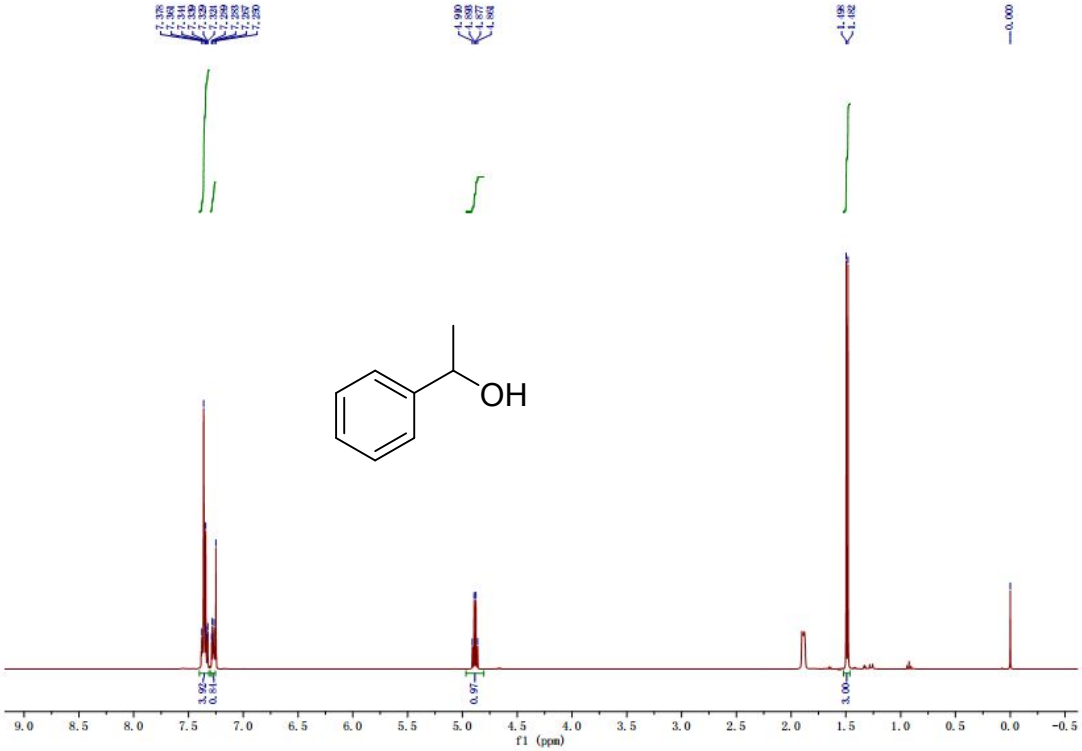
^{1}H NMR spectra of **3s** (400 MHz, $CDCl_3$):



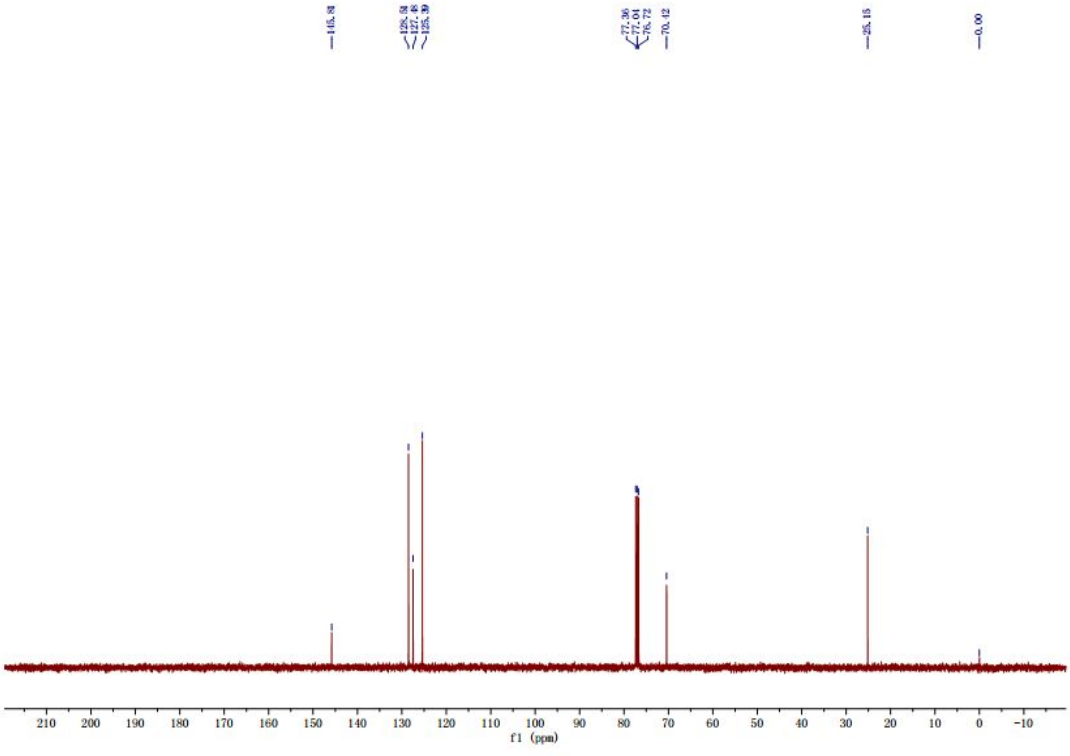
^{13}C{1H} NMR spectra of **3s** (100 MHz, $CDCl_3$):



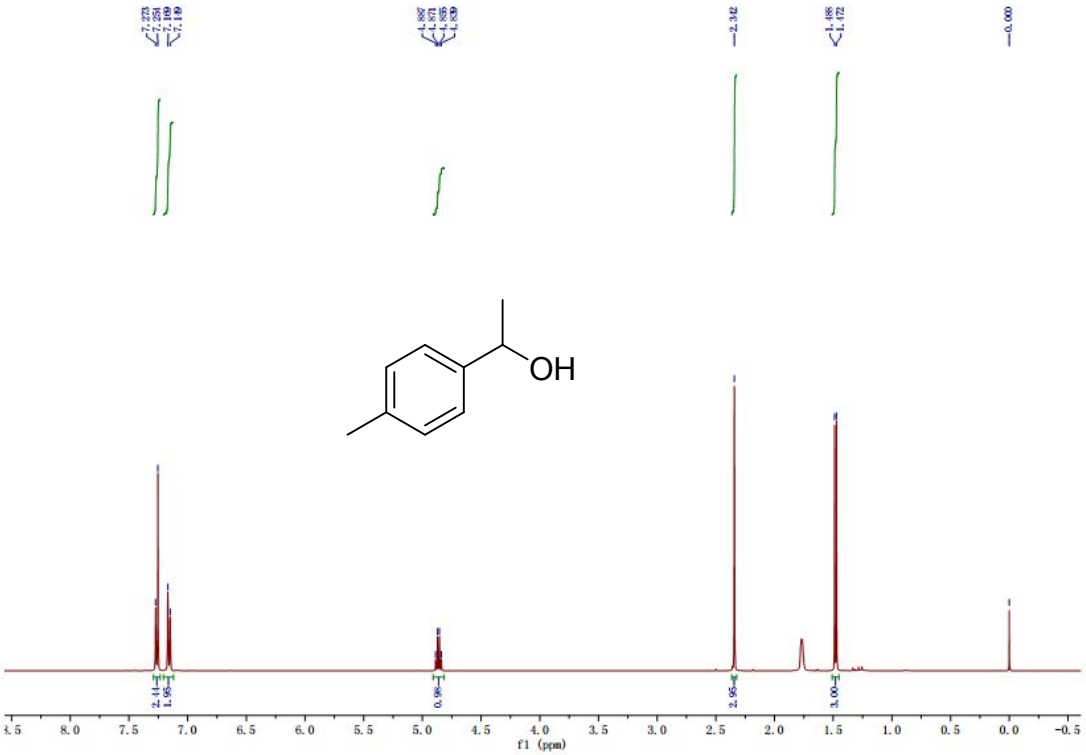
^{1}H NMR spectra of **5a** (400 MHz, $CDCl_3$):



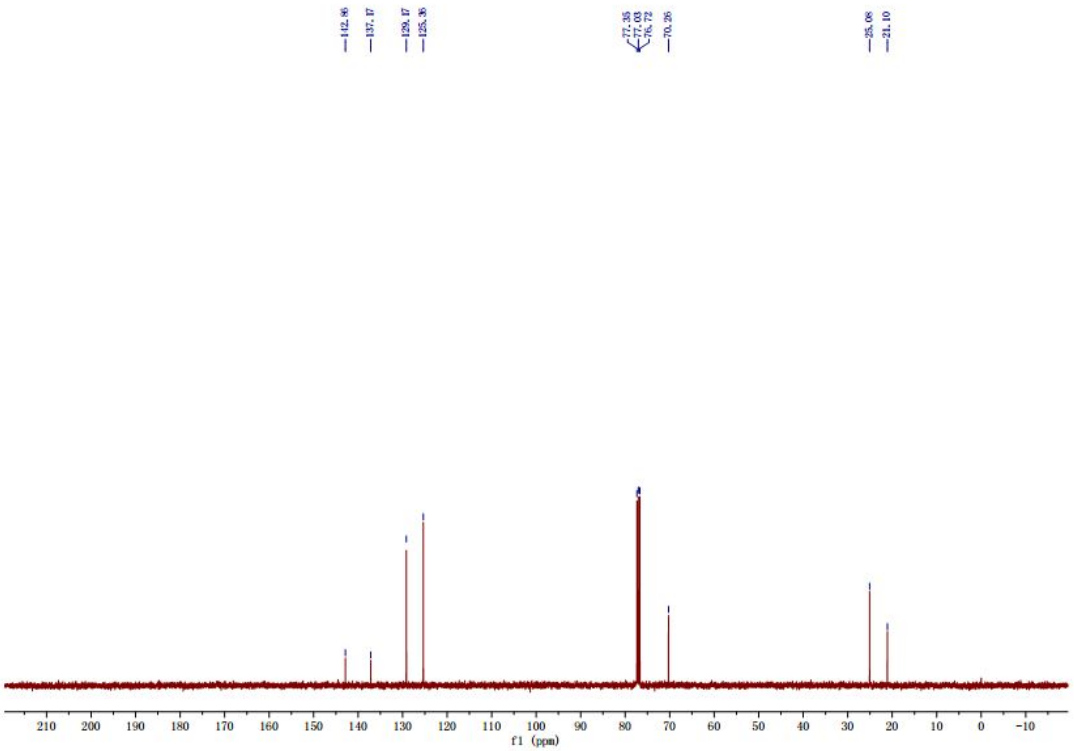
^{13}C{1H} NMR spectra of **5a** (100 MHz, $CDCl_3$):



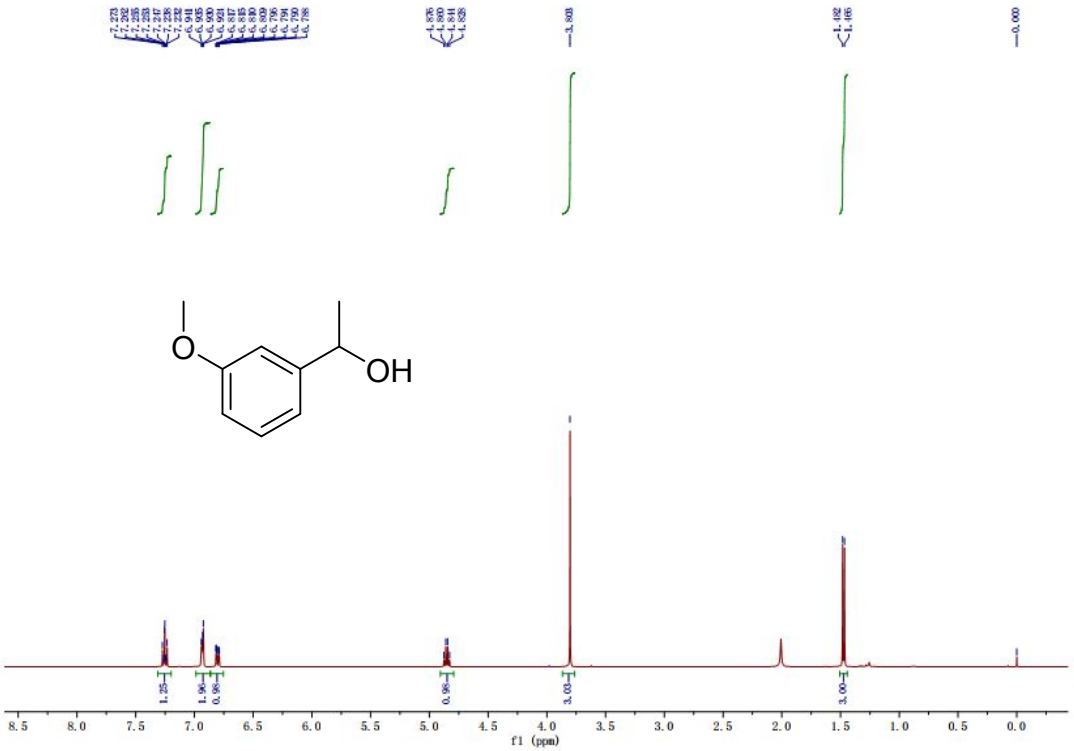
^{1}H NMR spectra of **5b** (400 MHz, $CDCl_3$):



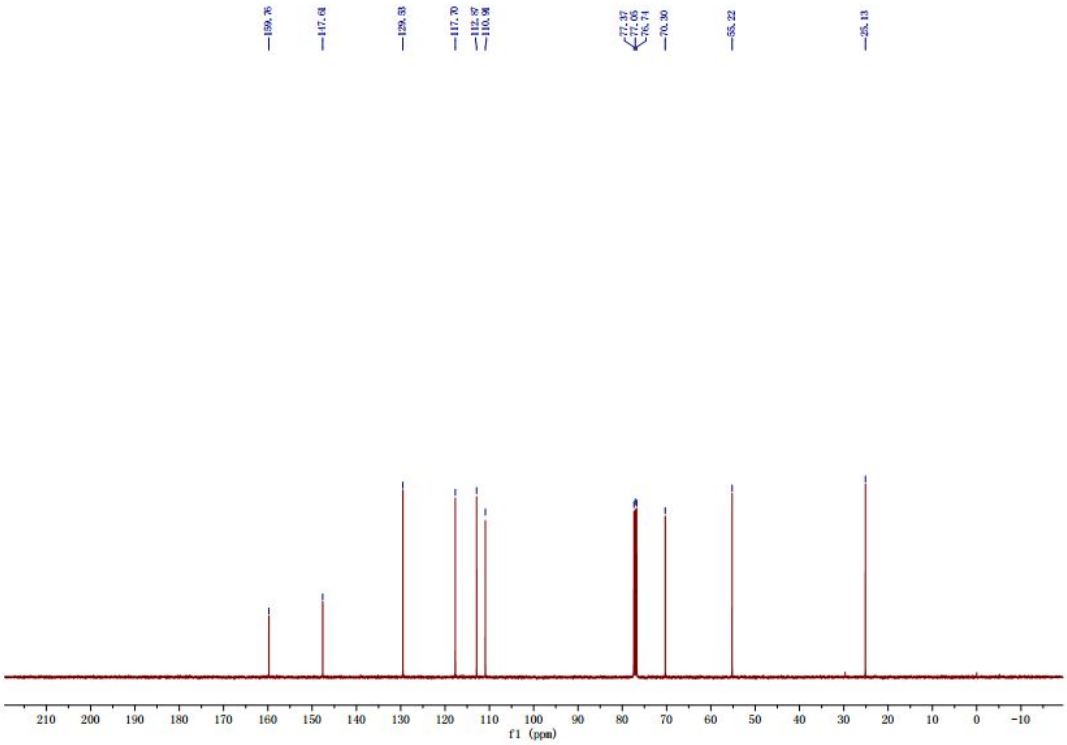
^{13}C{1H} NMR spectra of **5b** (100 MHz, $CDCl_3$):



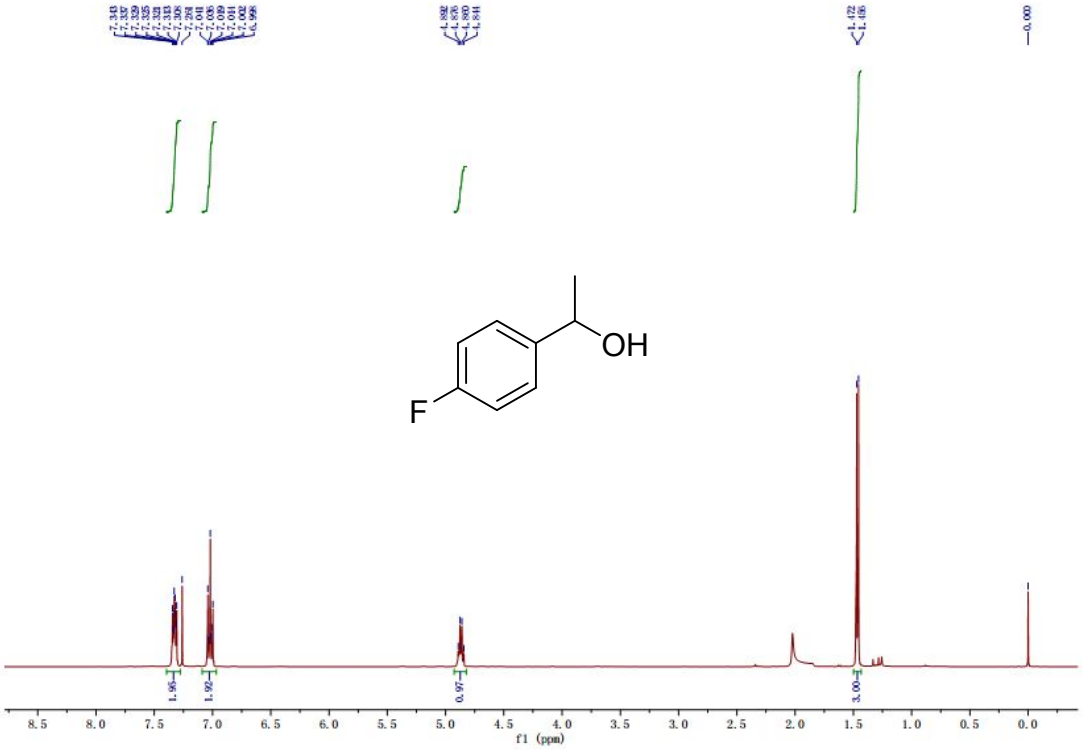
^{1}H NMR spectra of **5c** (400 MHz, $CDCl_3$):



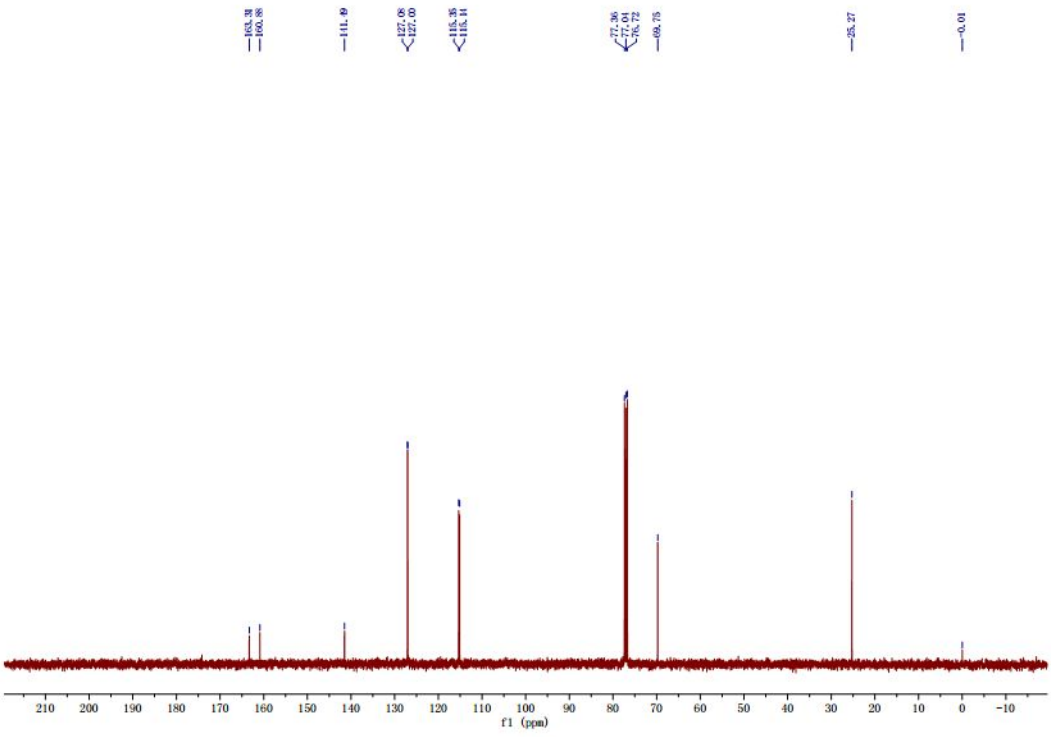
^{13}C{1H} NMR spectra of **5c** (100 MHz, $CDCl_3$):



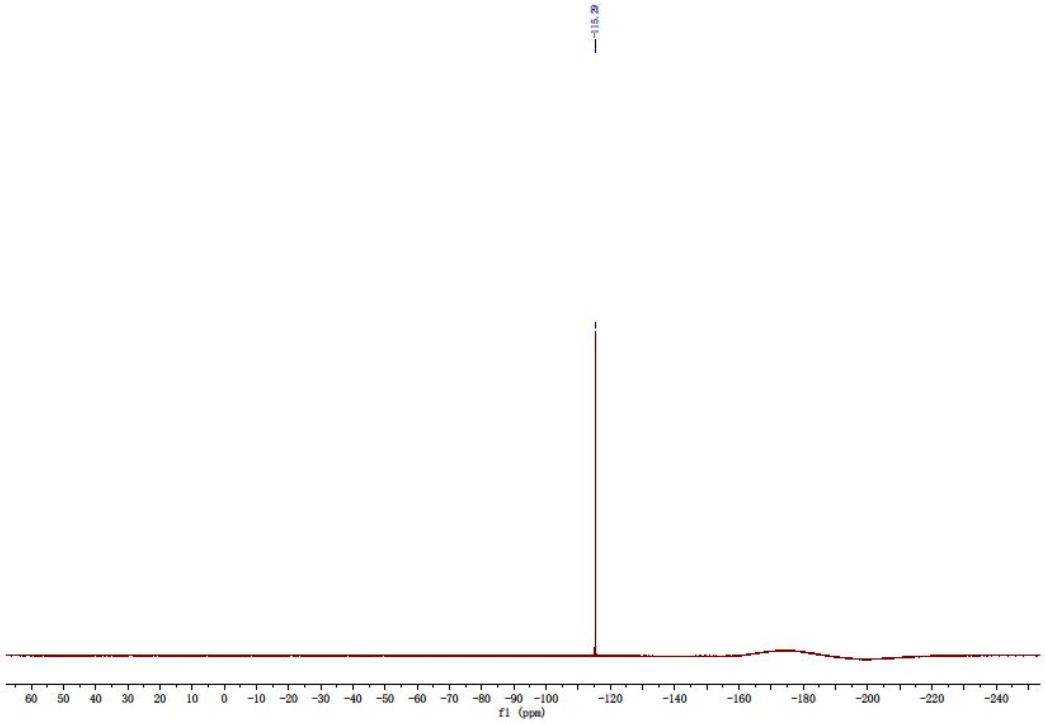
^{1}H NMR spectra of **5d** (400 MHz, $CDCl_3$):



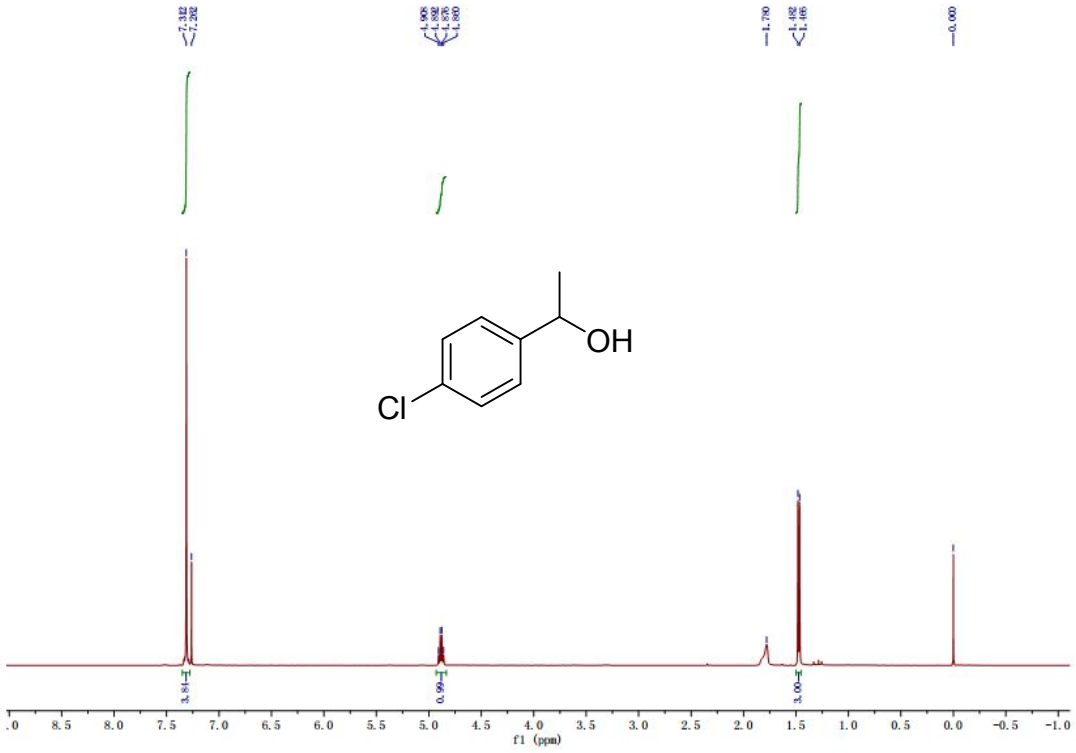
^{13}C{1H} NMR spectra of **5d** (100 MHz, $CDCl_3$):



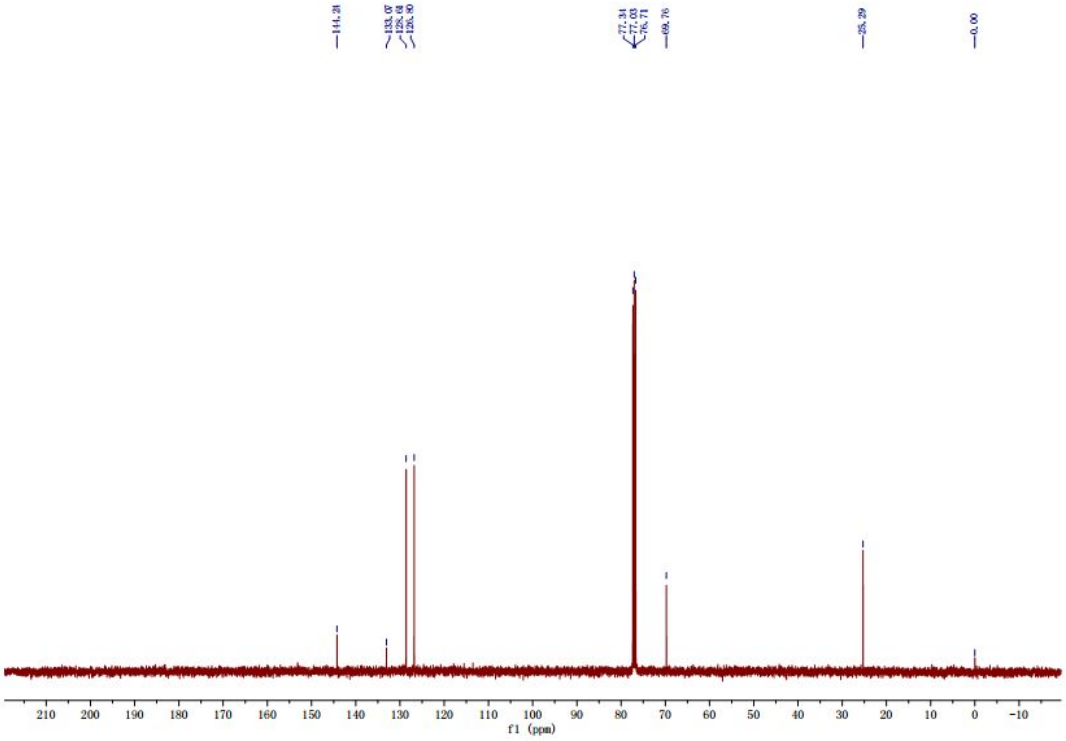
^{19}F NMR spectra of **5d** (377 MHz, $CDCl_3$):



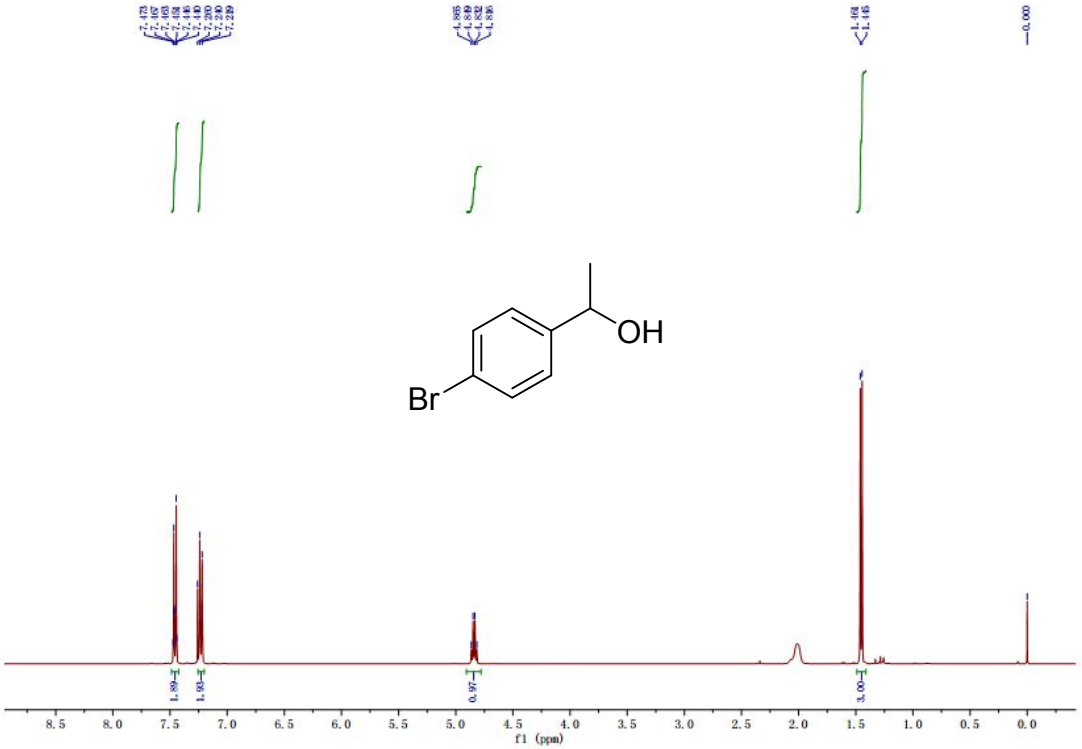
^{1}H NMR spectra of **5e** (400 MHz, $CDCl_3$):



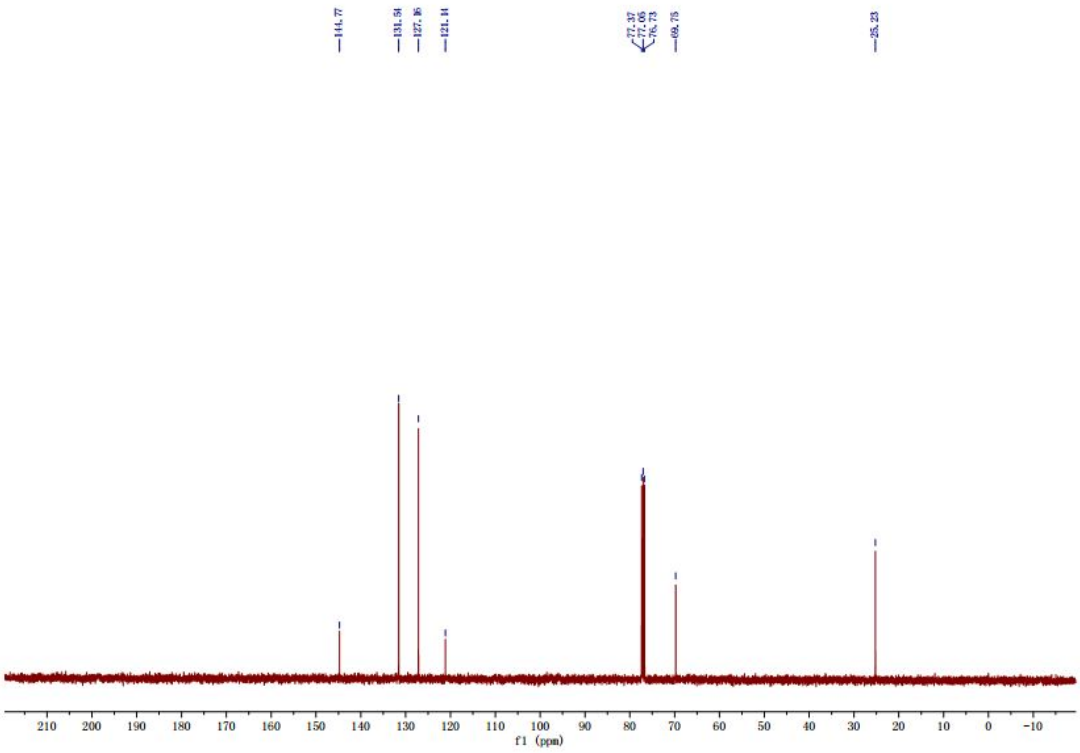
$^{13}C\{1H\}$ NMR spectra of **5e** (100 MHz, $CDCl_3$):



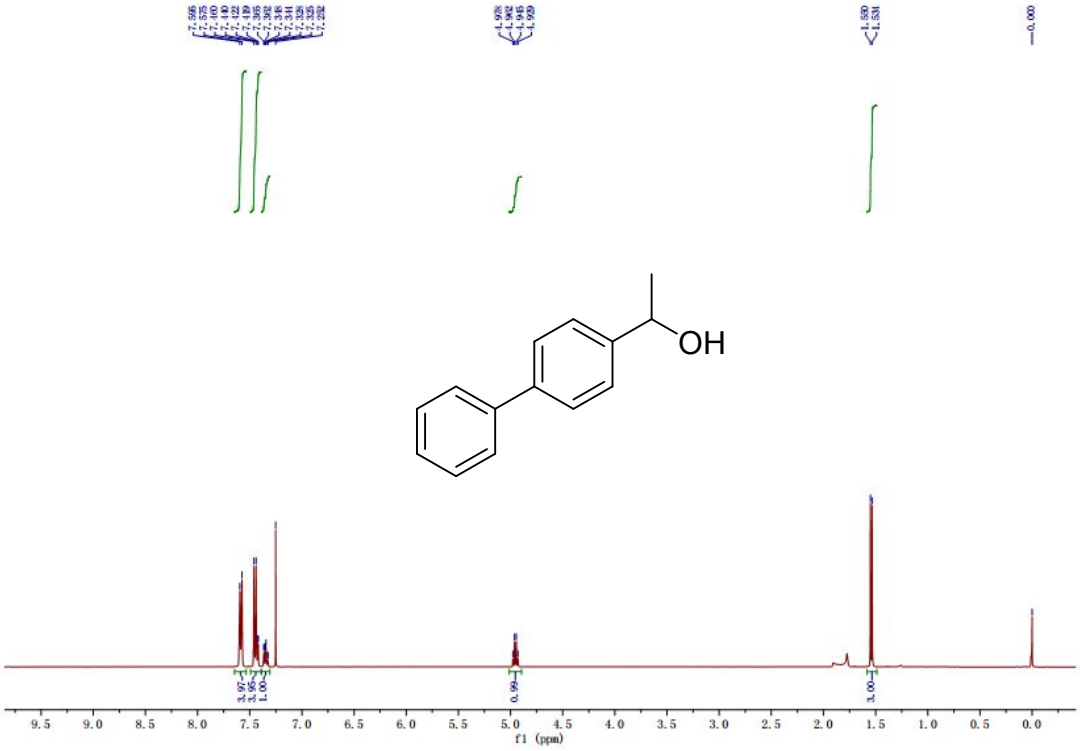
^{1}H NMR spectra of **5f** (400 MHz, $CDCl_3$):



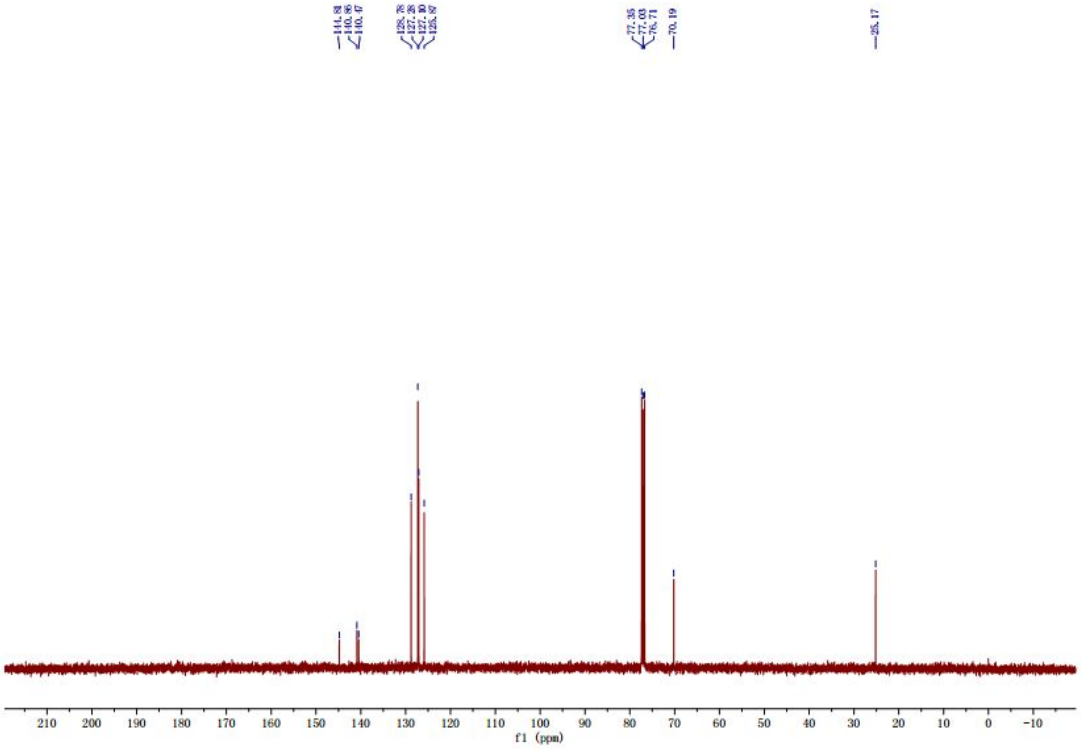
$^{13}C\{1H\}$ NMR spectra of **5f** (100 MHz, $CDCl_3$):



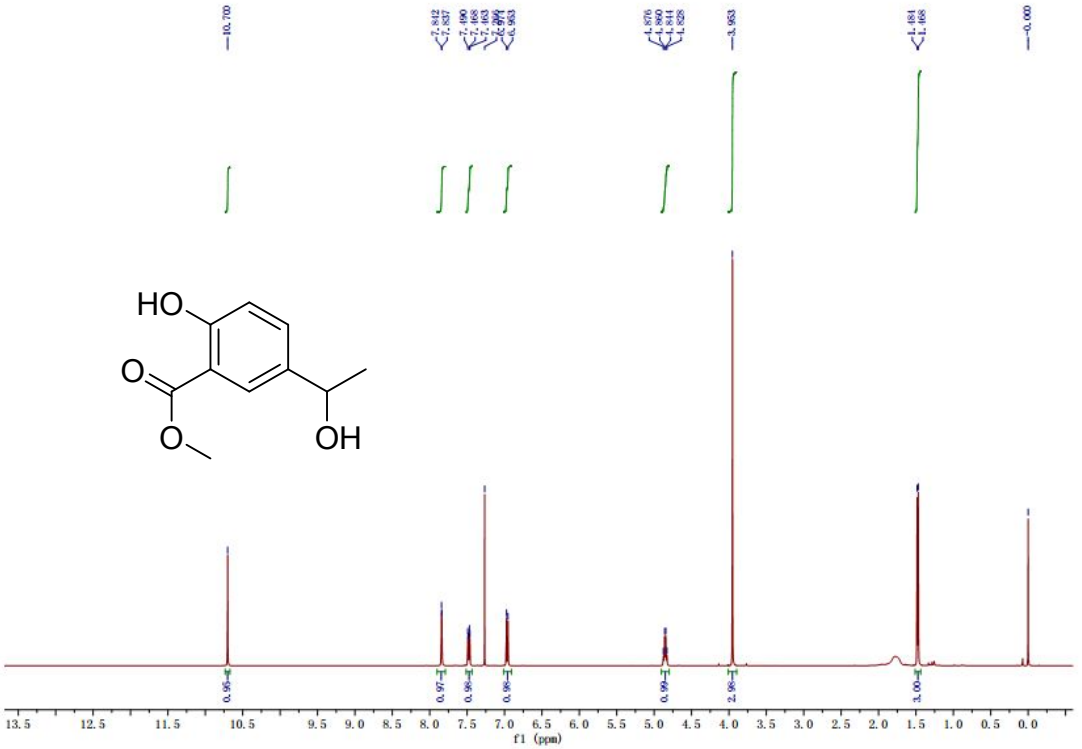
^{1}H NMR spectra of **5g** (400 MHz, $CDCl_3$):



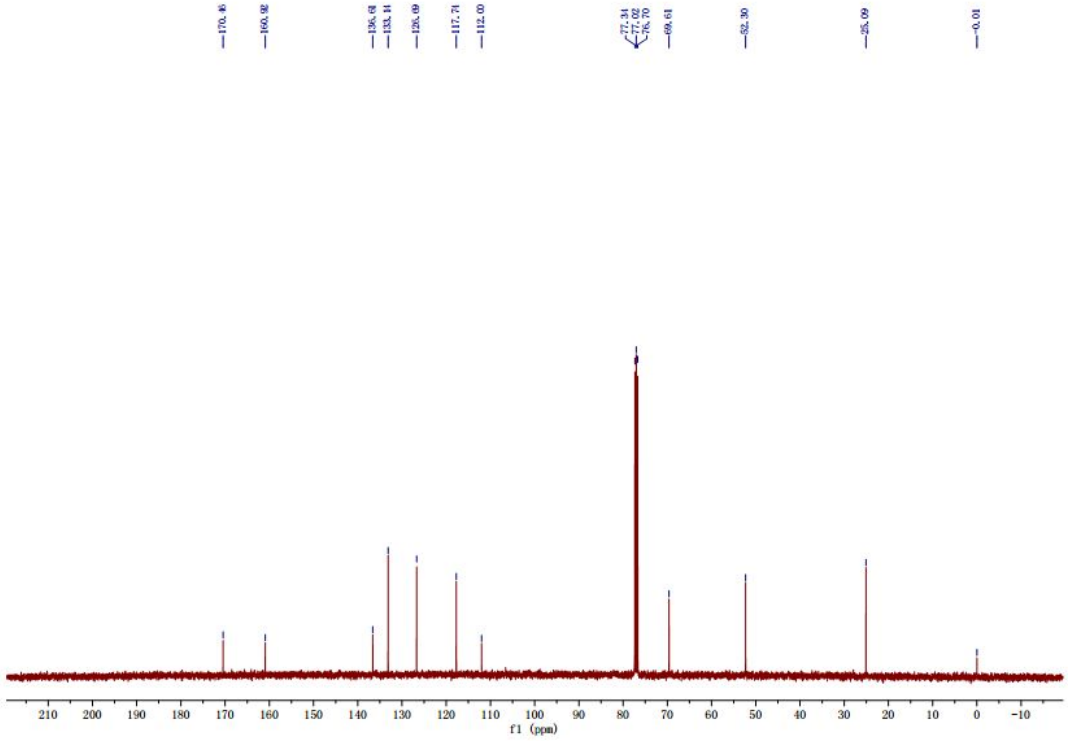
$^{13}C\{1H\}$ NMR spectra of **5g** (100 MHz, $CDCl_3$):



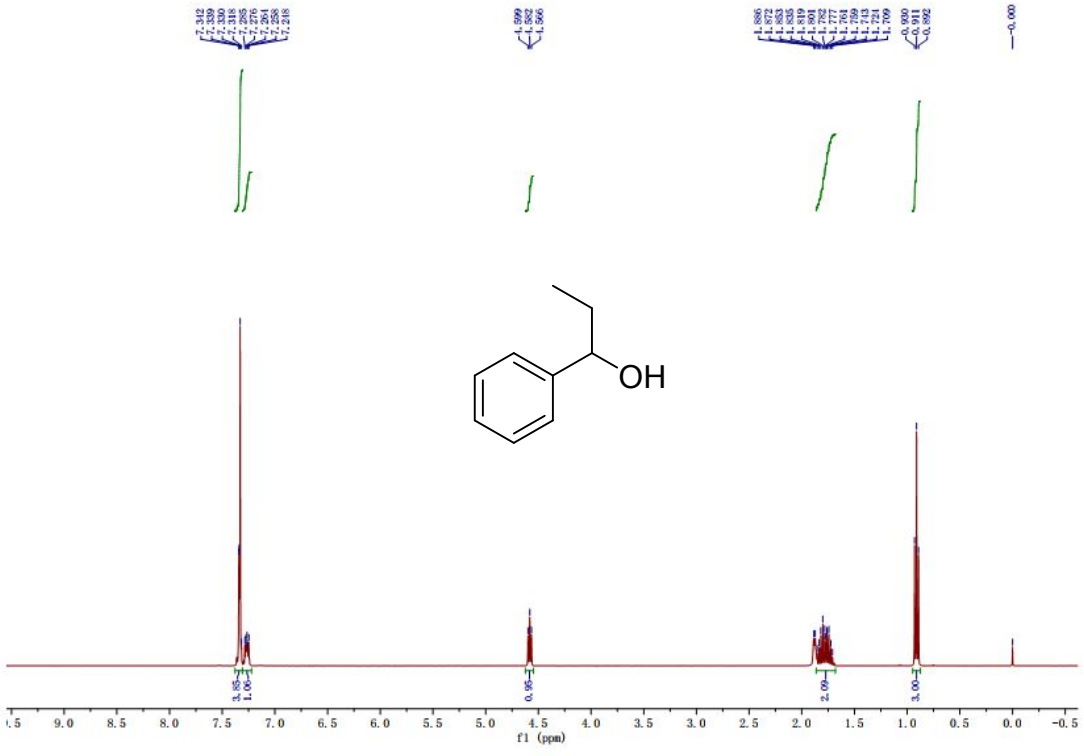
^{1}H NMR spectra of **5h** (400 MHz, $CDCl_3$):



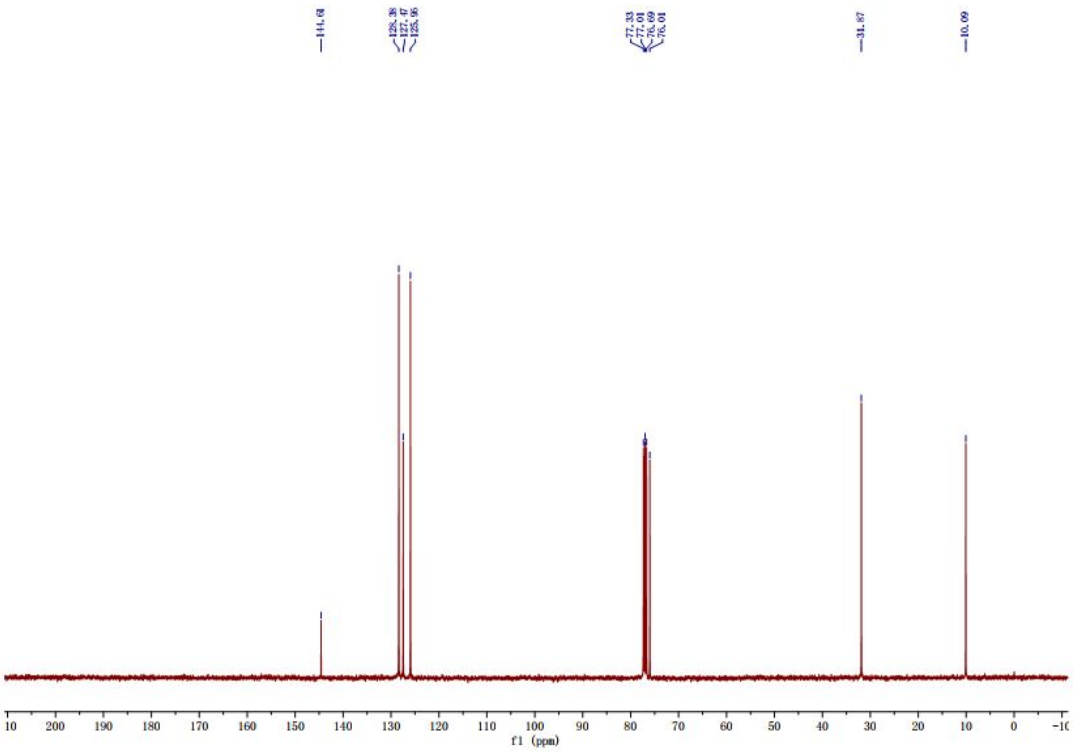
$^{13}C\{1H\}$ NMR spectra of **5h** (100 MHz, $CDCl_3$):



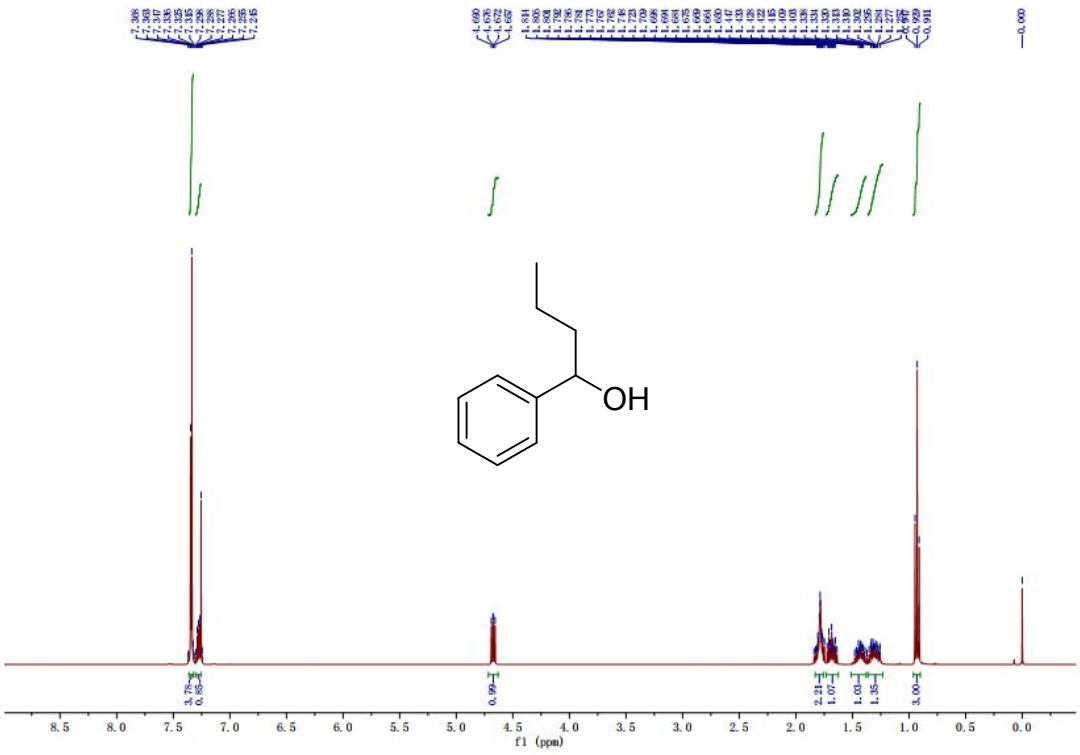
^{1}H NMR spectra of **5i** (400 MHz, $CDCl_3$):



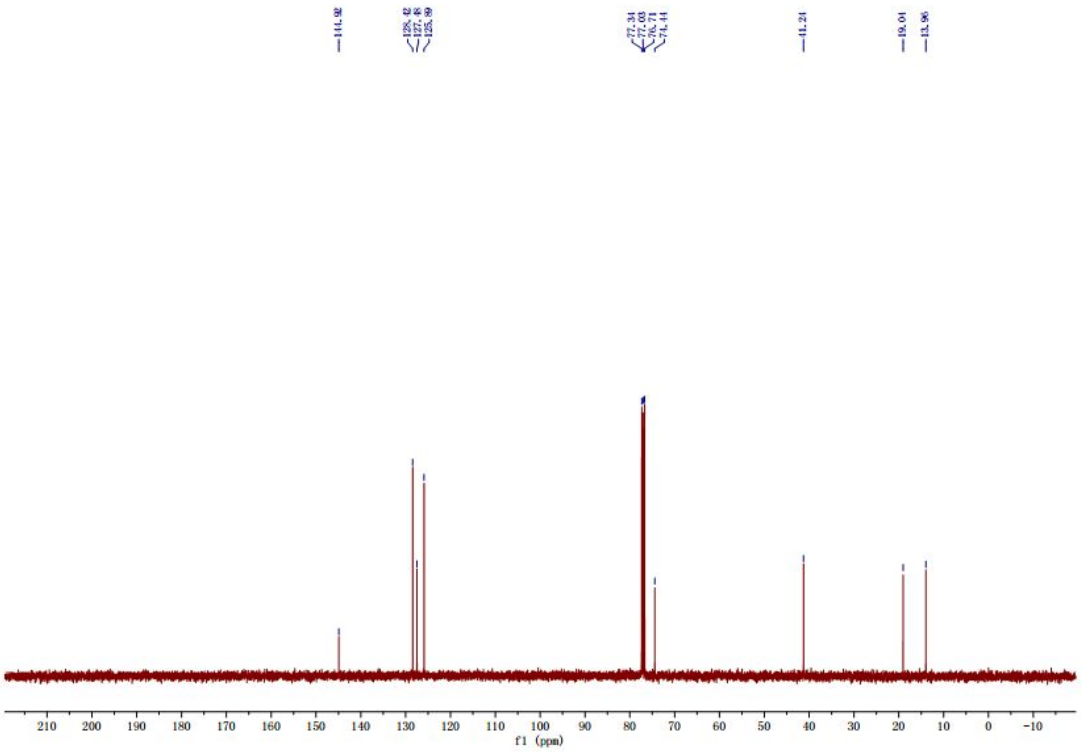
$^{13}C\{1H\}$ NMR spectra of **5i** (100 MHz, $CDCl_3$):



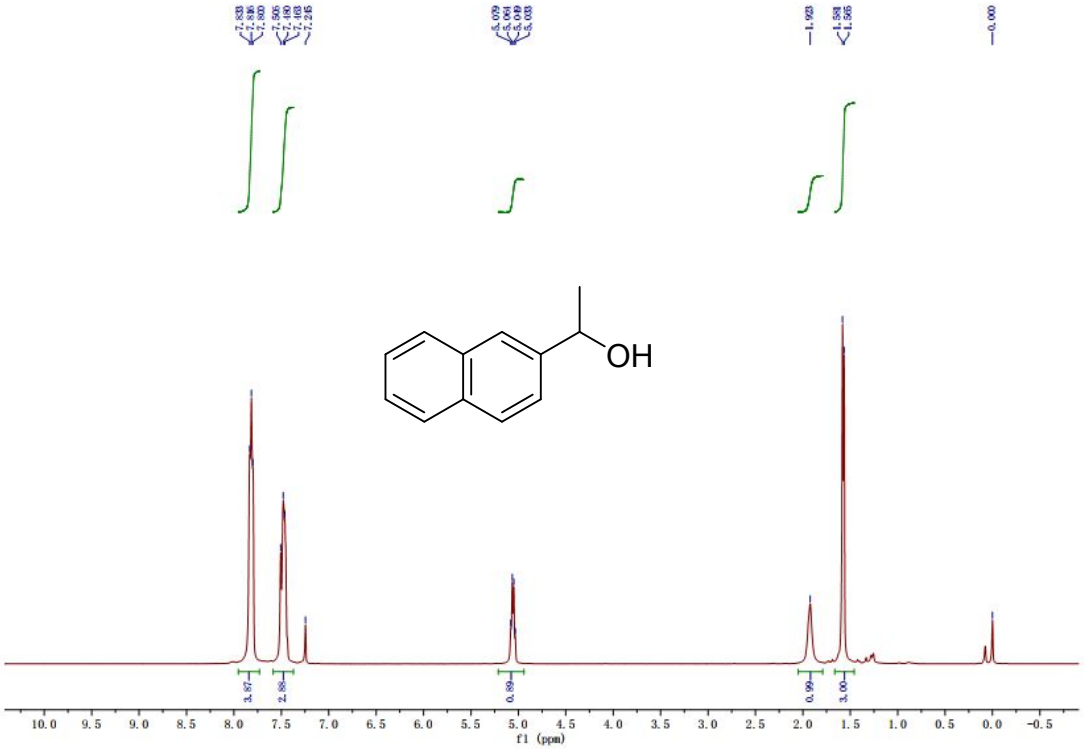
^{1}H NMR spectra of **5j** (400 MHz, $CDCl_3$):



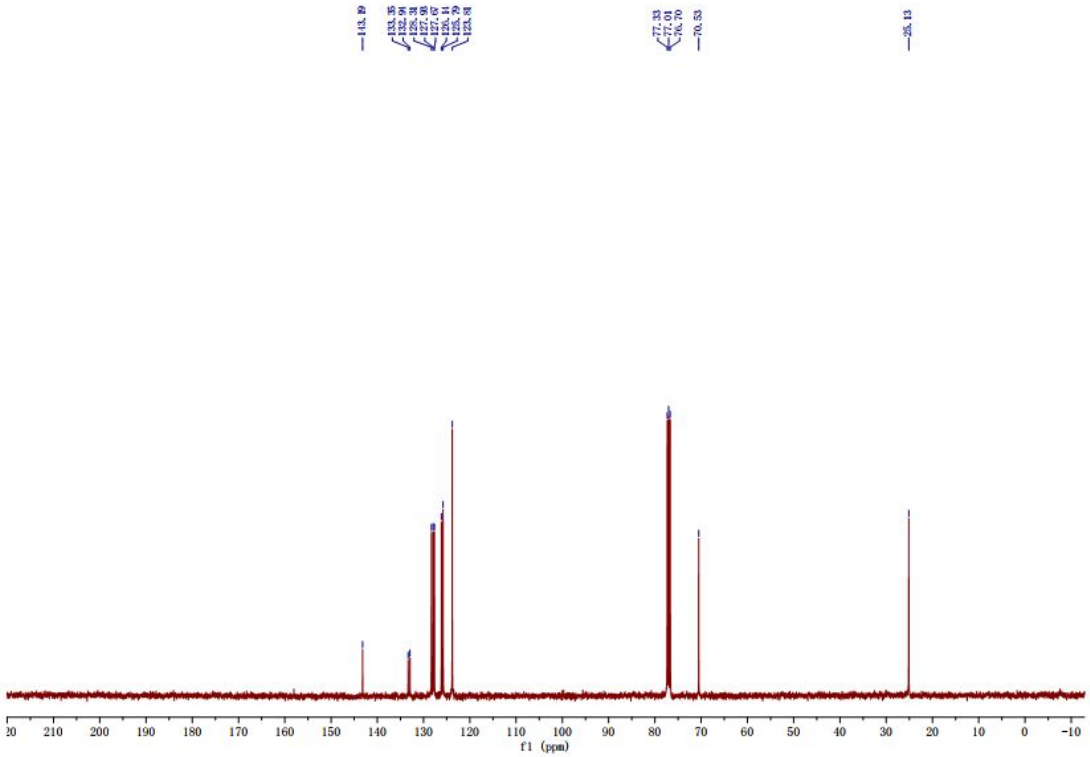
$^{13}C\{1H\}$ NMR spectra of **5j** (100 MHz, $CDCl_3$):



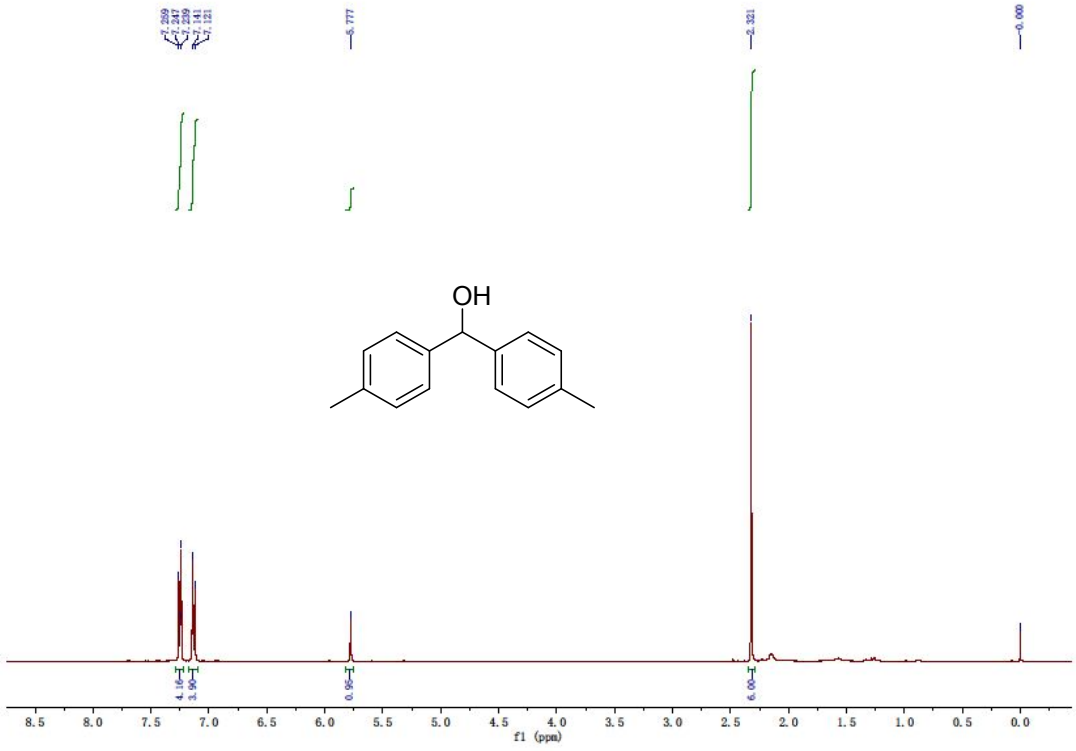
^{1}H NMR spectra of **5j** (400 MHz, $CDCl_3$):



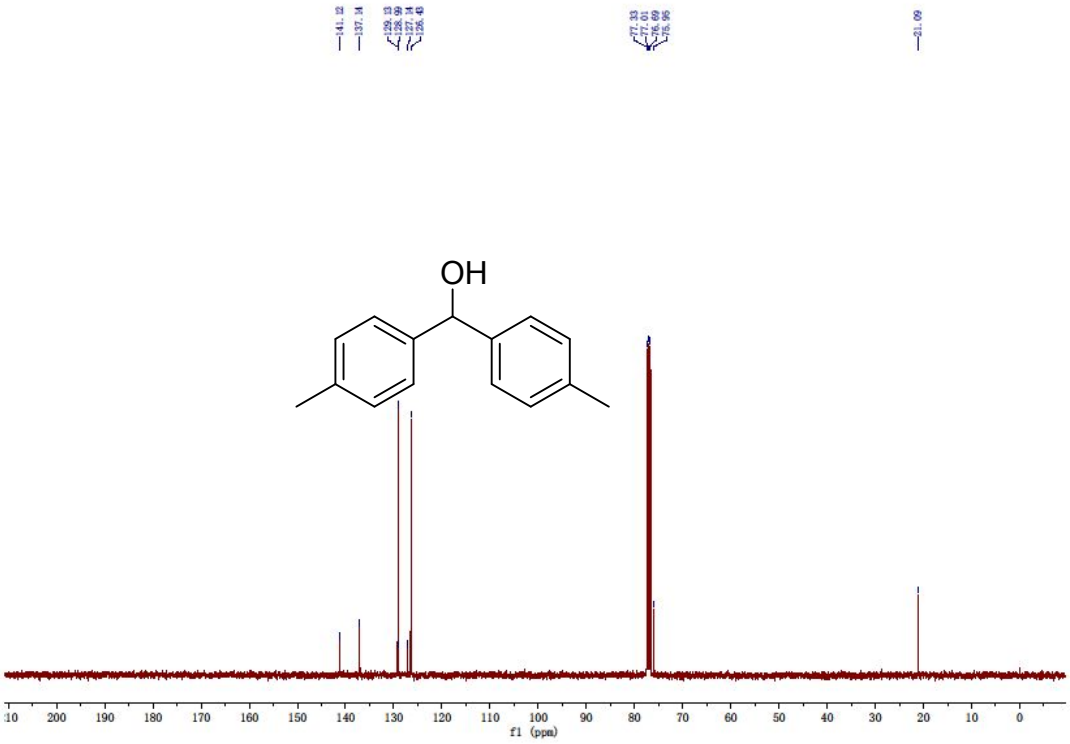
$^{13}C\{1H\}$ NMR spectra of **5k** (100 MHz, $CDCl_3$):



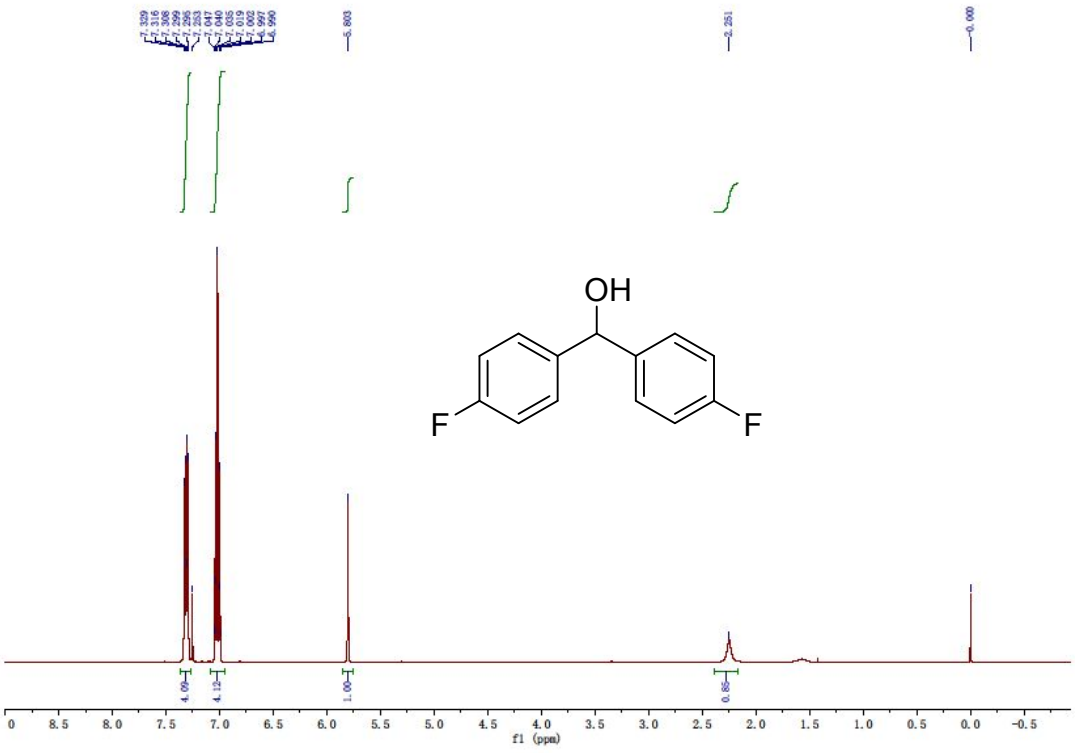
^{1}H NMR spectra of **5l** (400 MHz, $CDCl_3$):



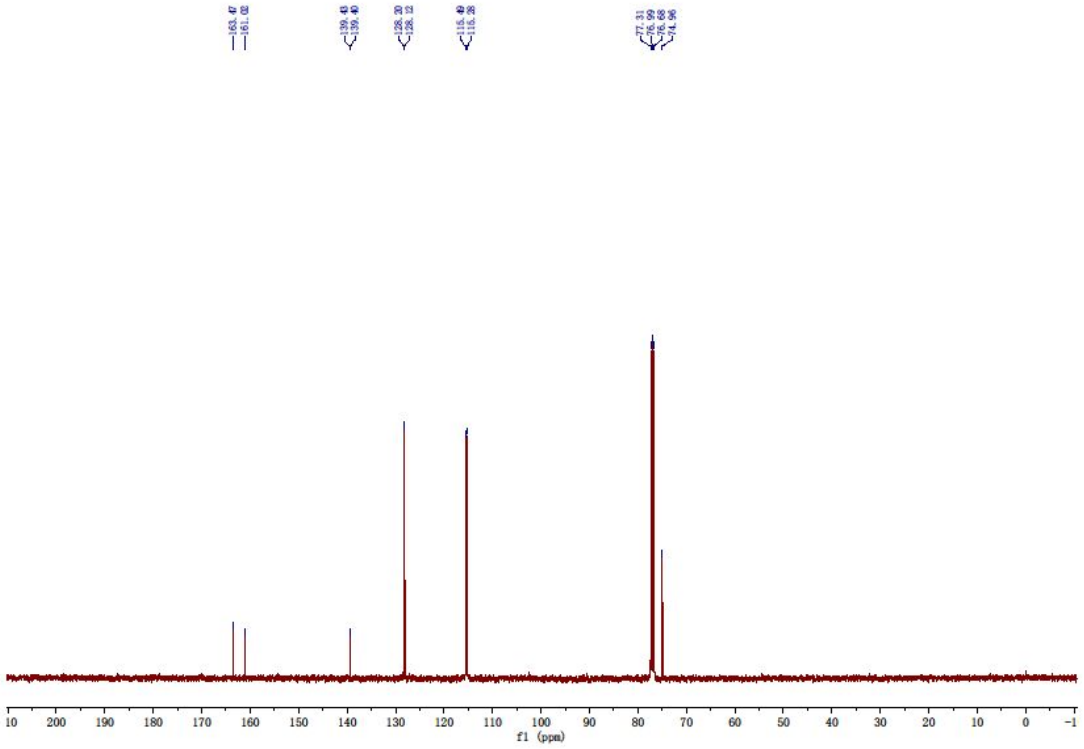
$^{13}C\{1H\}$ NMR spectra of **5l** (100 MHz, $CDCl_3$):



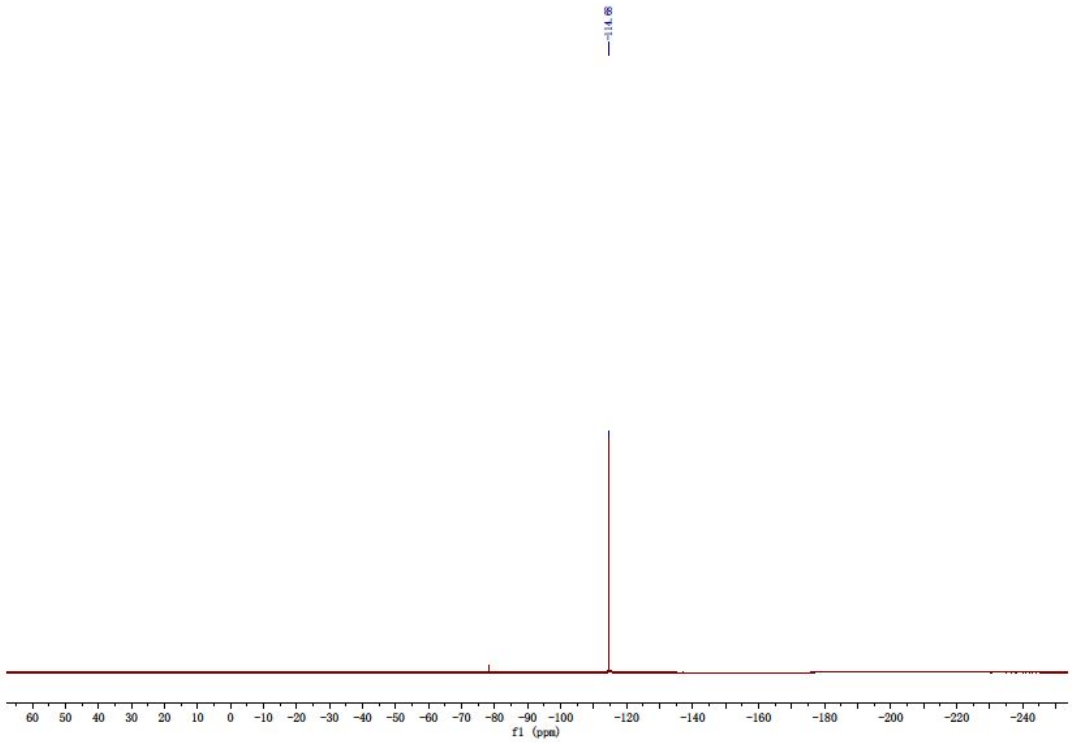
^{1}H NMR spectra of **5m** (400 MHz, $CDCl_3$):



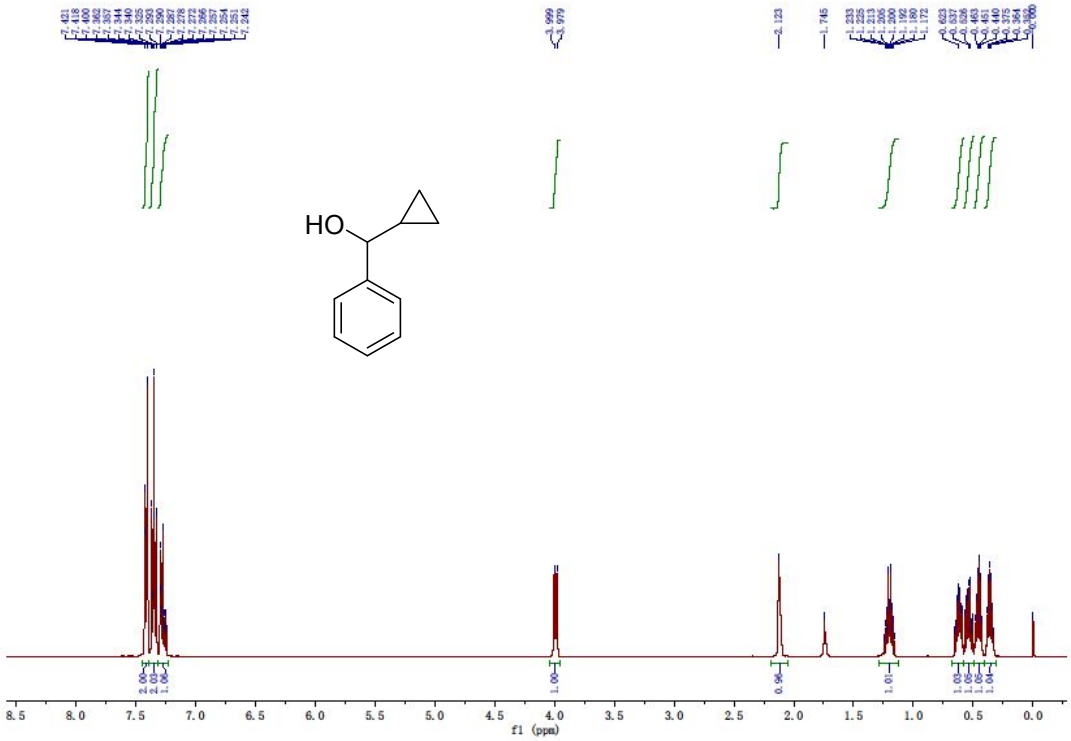
$^{13}C\{1H\}$ NMR spectra of **5m** (100 MHz, $CDCl_3$):



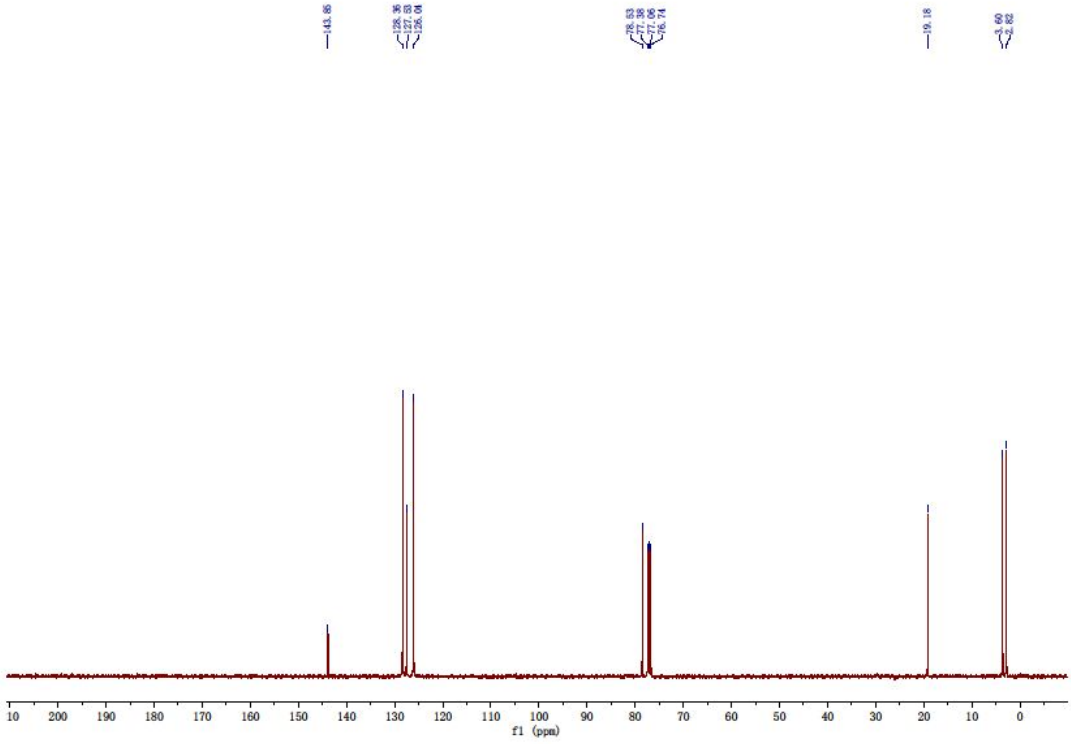
^{19}F NMR spectra of **5m** (377 MHz, $CDCl_3$):



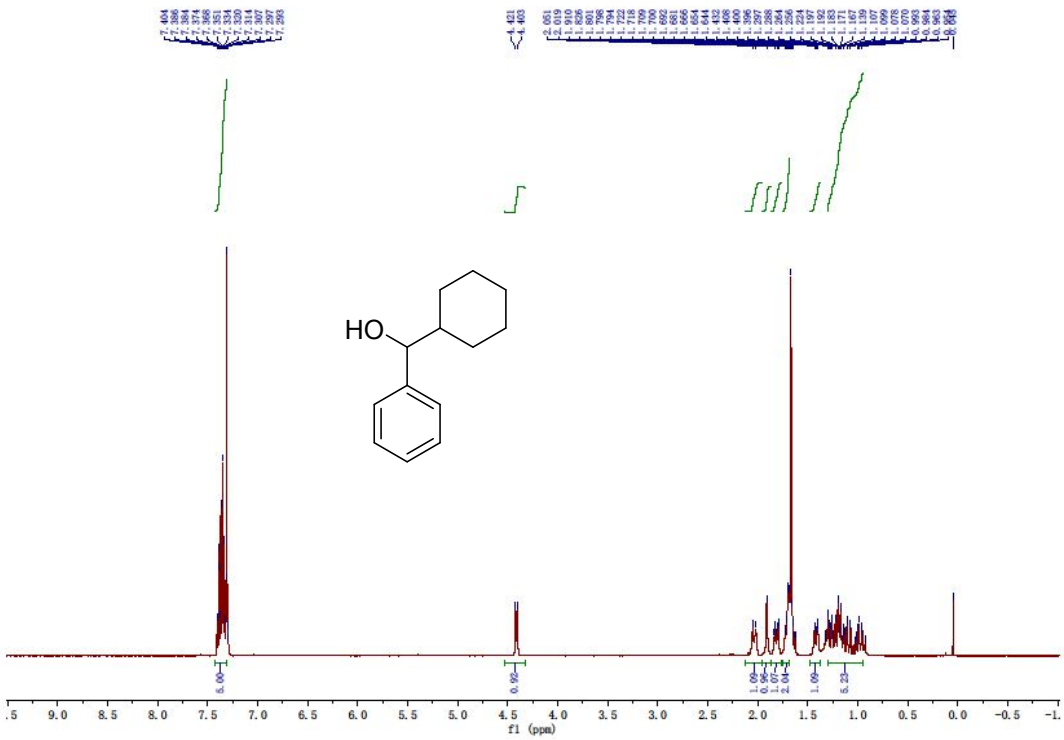
^{1}H NMR spectra of **5n** (400 MHz, $CDCl_3$):



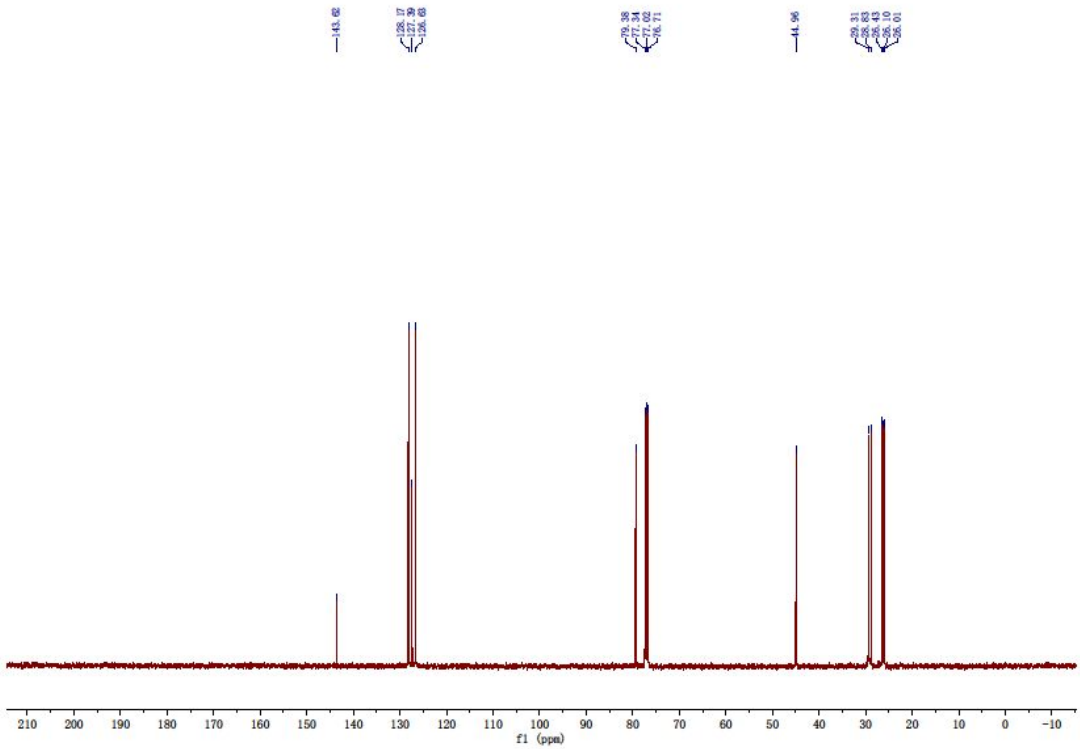
^{13}C{1H} NMR spectra of **5n** (100 MHz, $CDCl_3$):



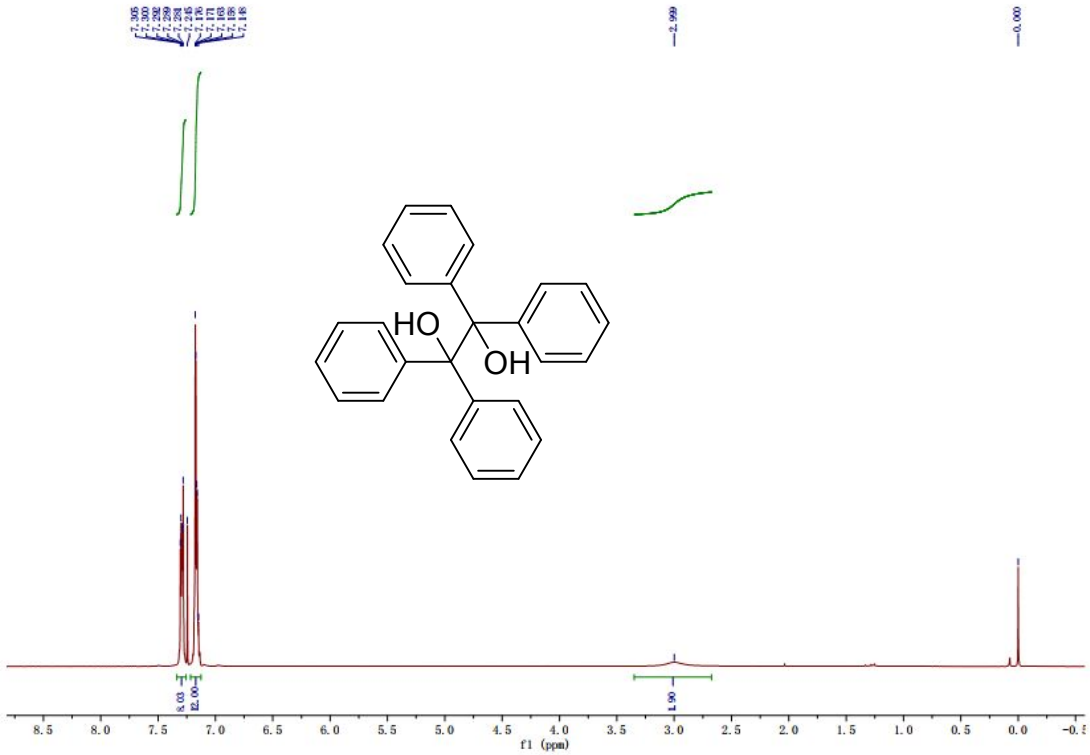
^{1}H NMR spectra of **5o** (400 MHz, $CDCl_3$):



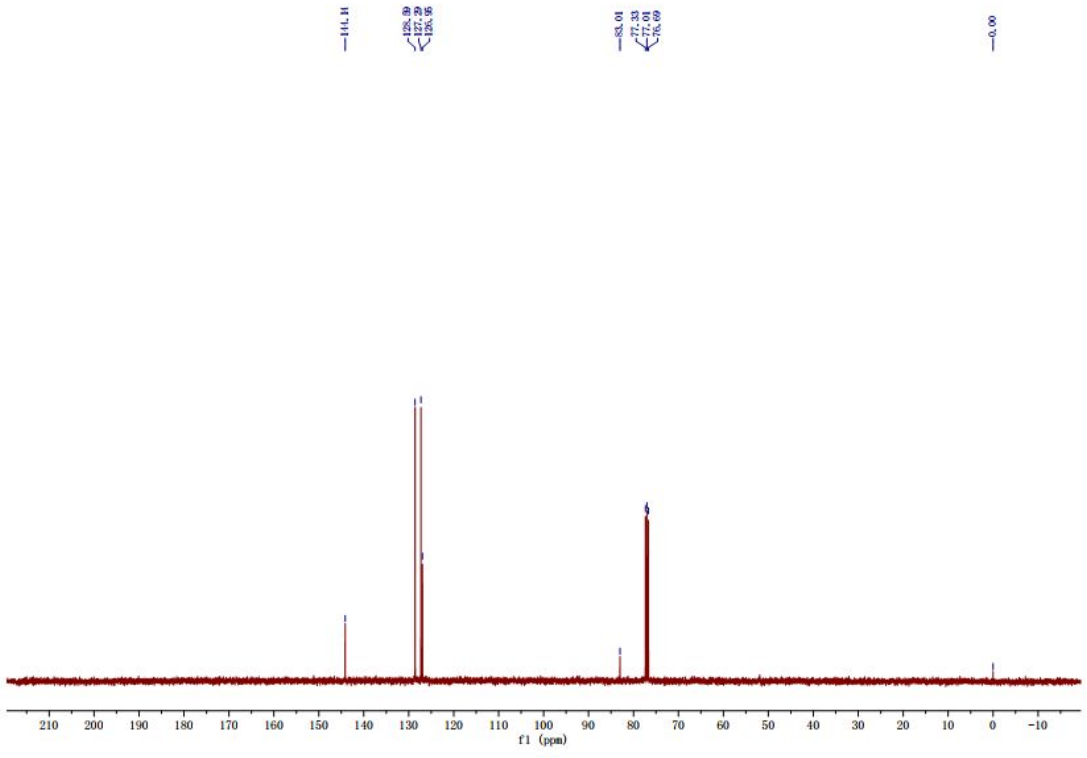
^{13}C{1H} NMR spectra of **5o** (100 MHz, $CDCl_3$):



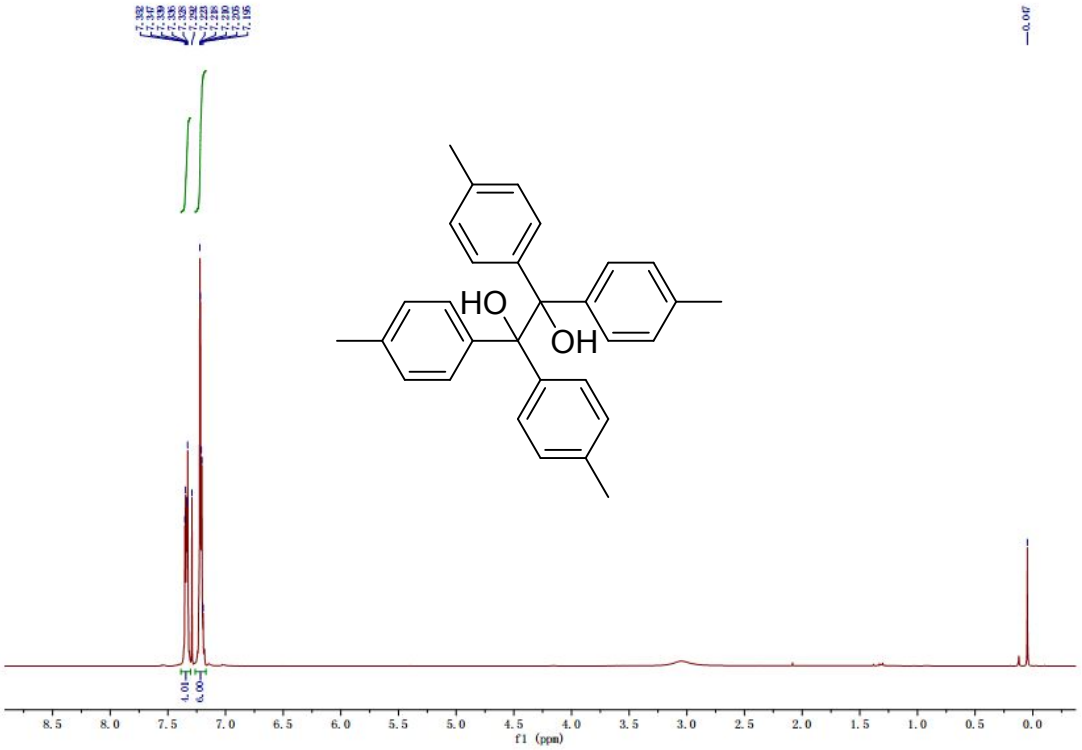
^{1}H NMR spectra of **7a** (400 MHz, $CDCl_3$):



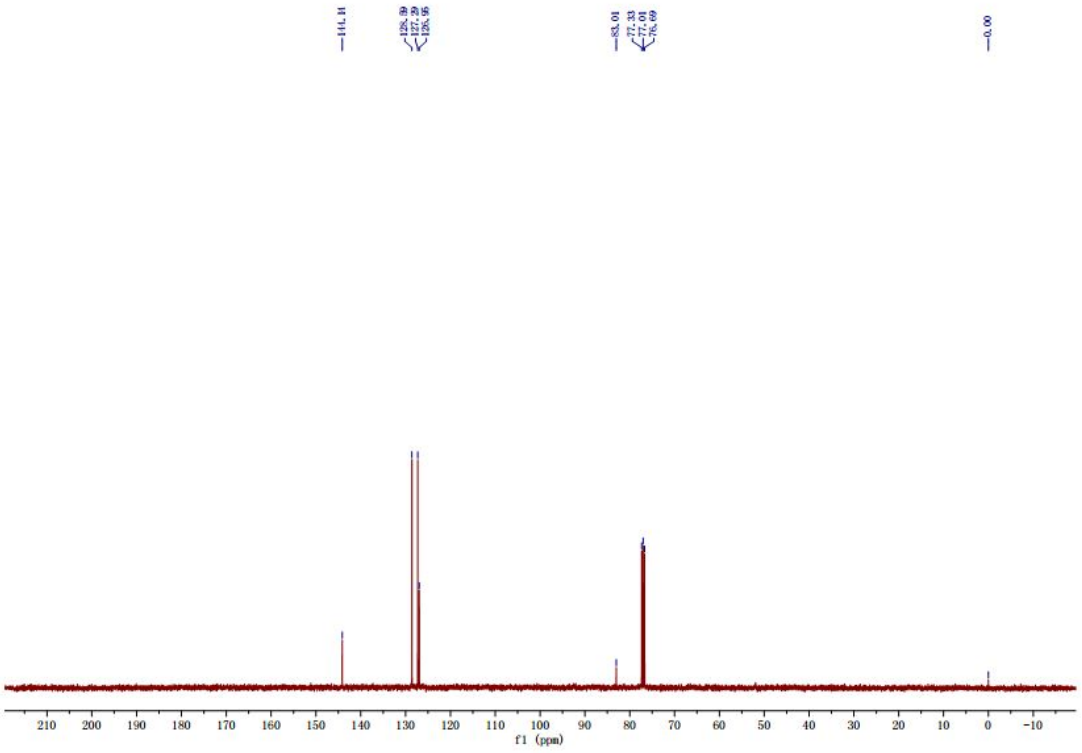
^{13}C{1H} NMR spectra of **7a** (100 MHz, $CDCl_3$):



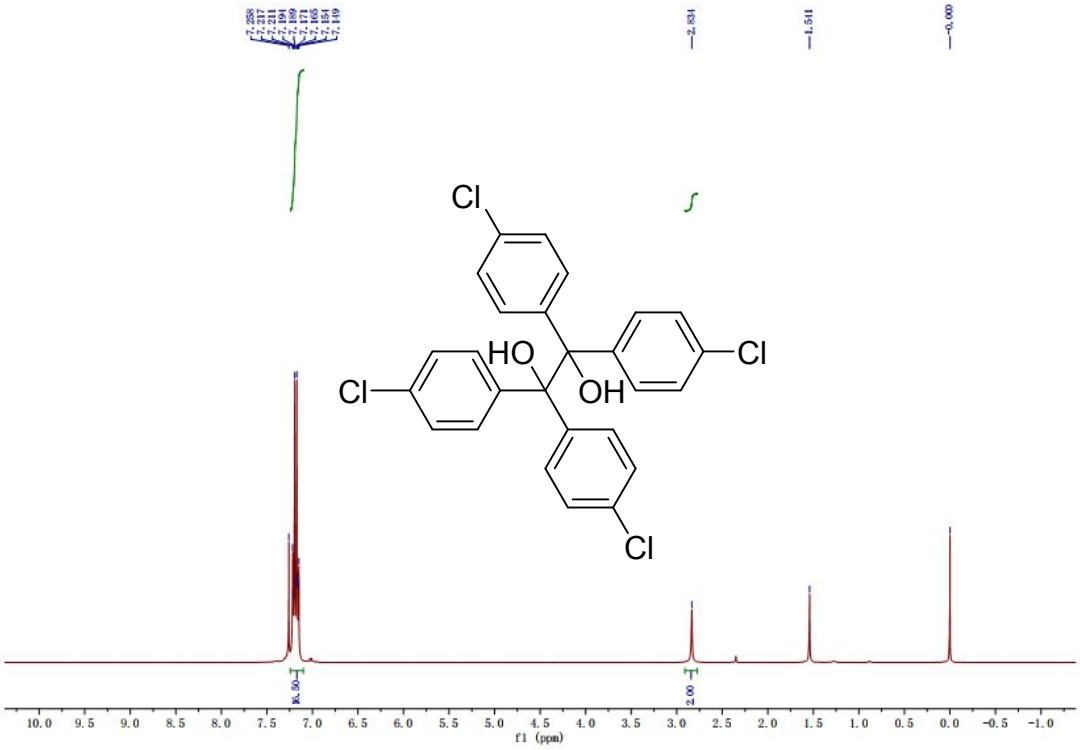
^{1}H NMR spectra of **7b** (400 MHz, $CDCl_3$):



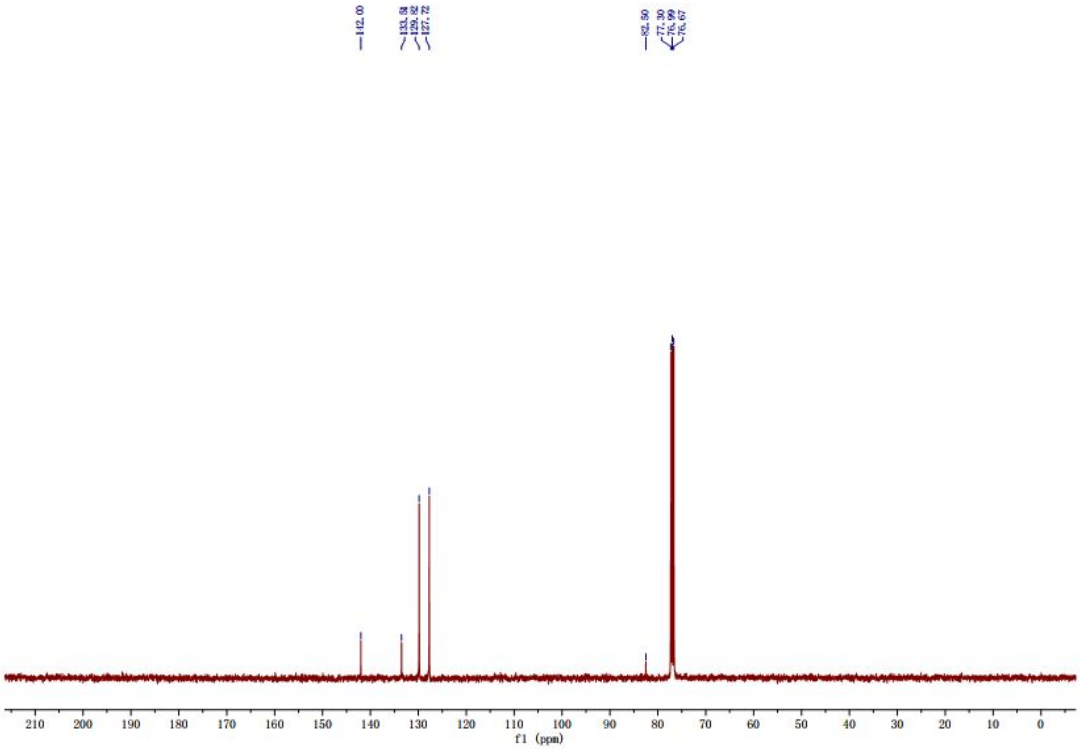
^{13}C{1H} NMR spectra of **7b** (100 MHz, $CDCl_3$):



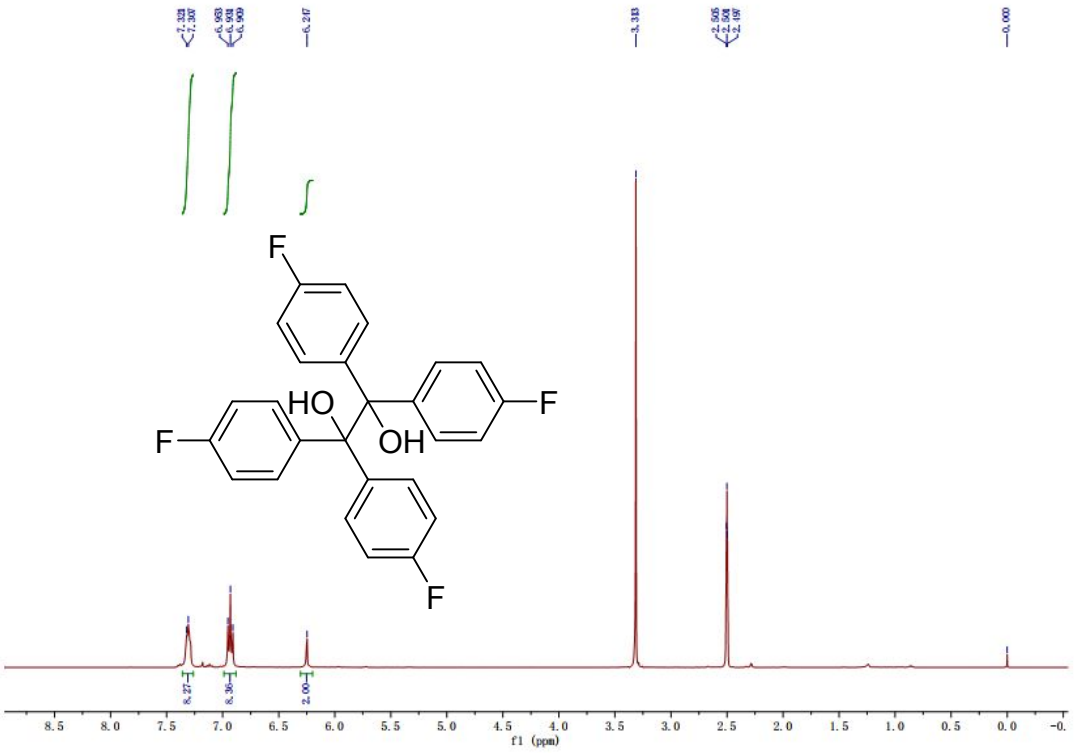
^{1}H NMR spectra of **7c** (400 MHz, $CDCl_3$):



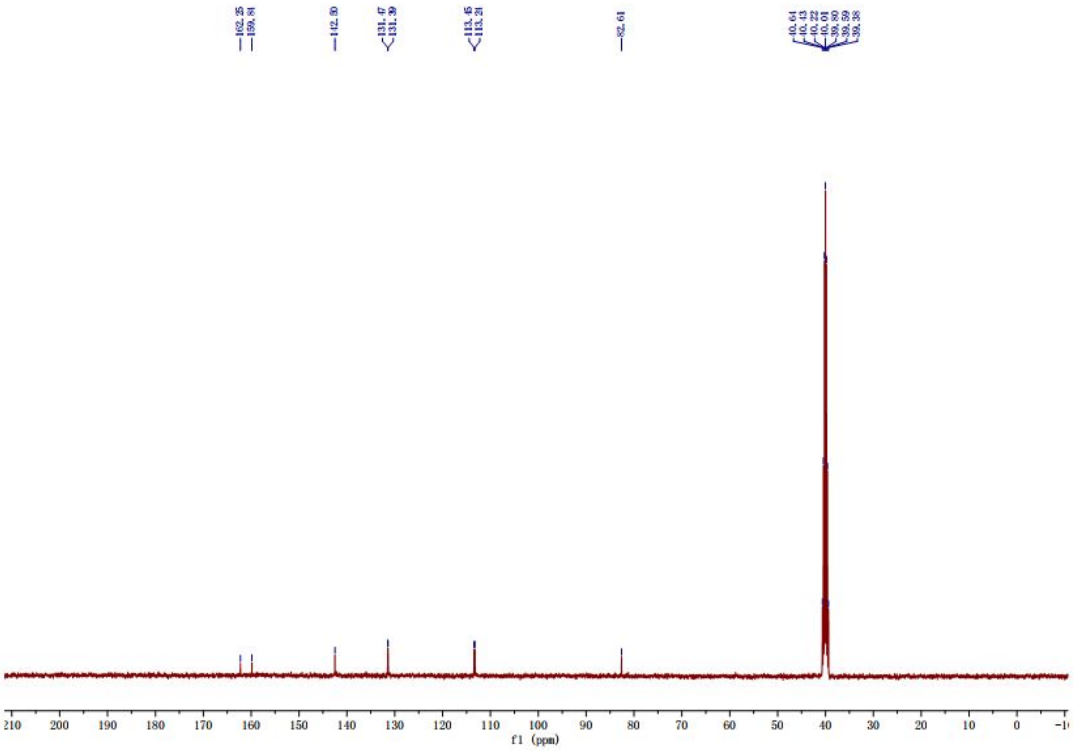
^{13}C{1H} NMR spectra of **7c** (100 MHz, $CDCl_3$):



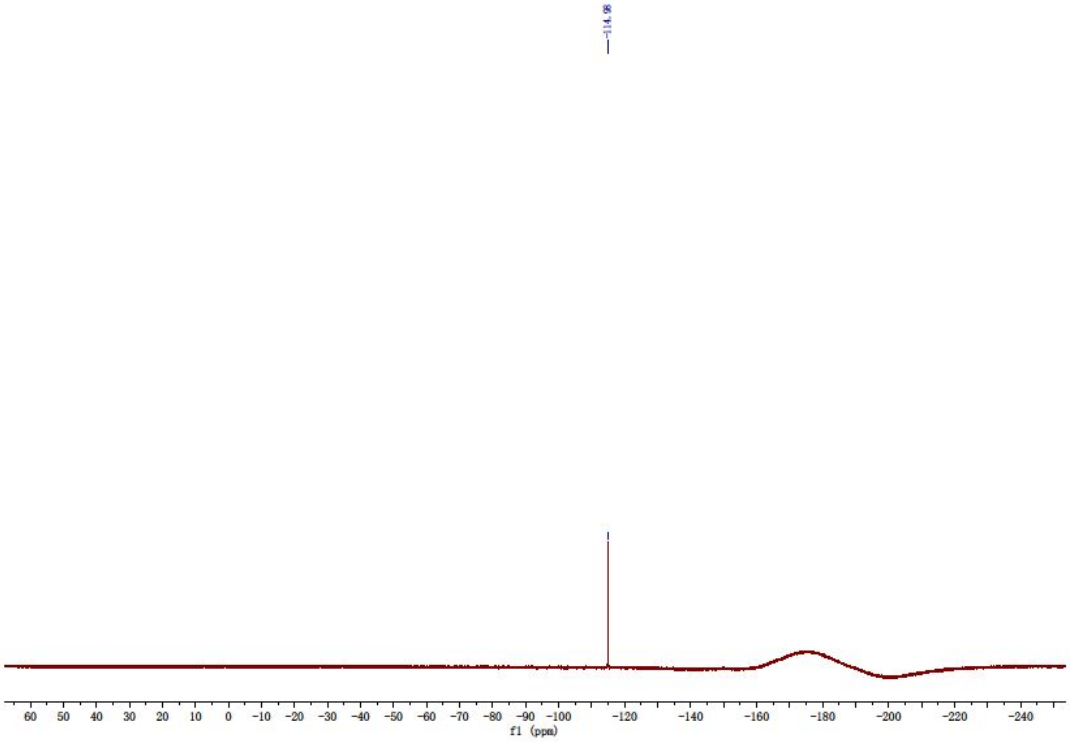
^{1}H NMR spectra of **7d** (400 MHz, $CDCl_3$):



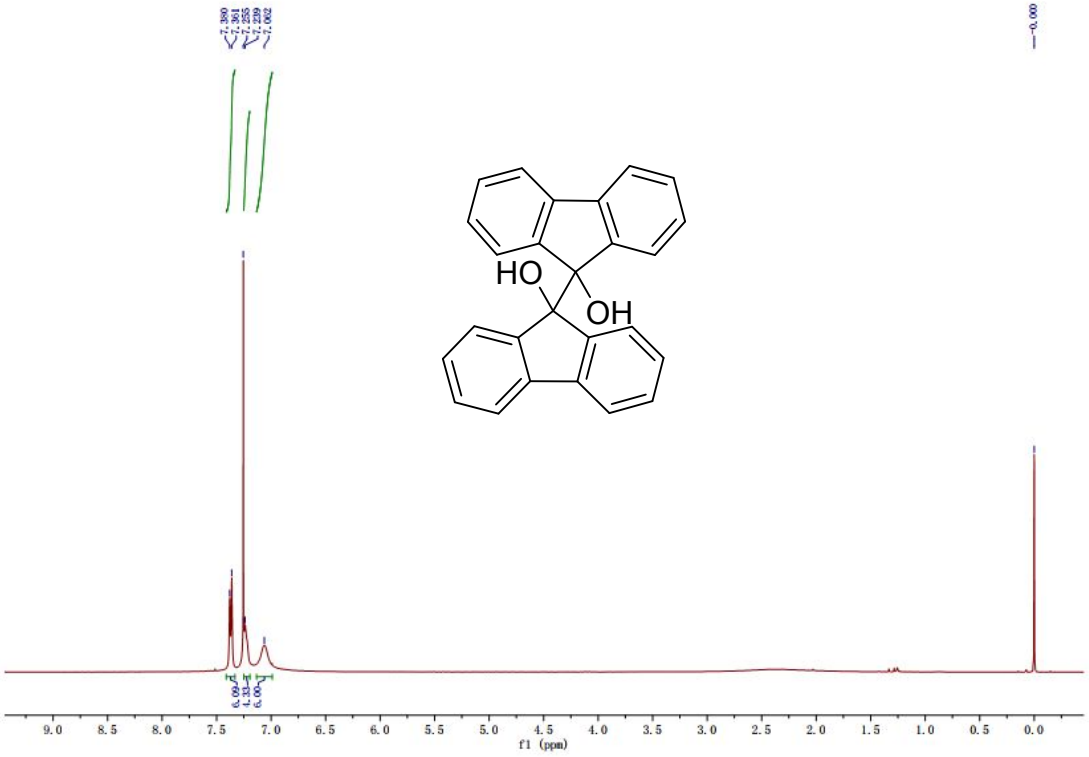
^{13}C{1H} NMR spectra of **7d** (100 MHz, $CDCl_3$):



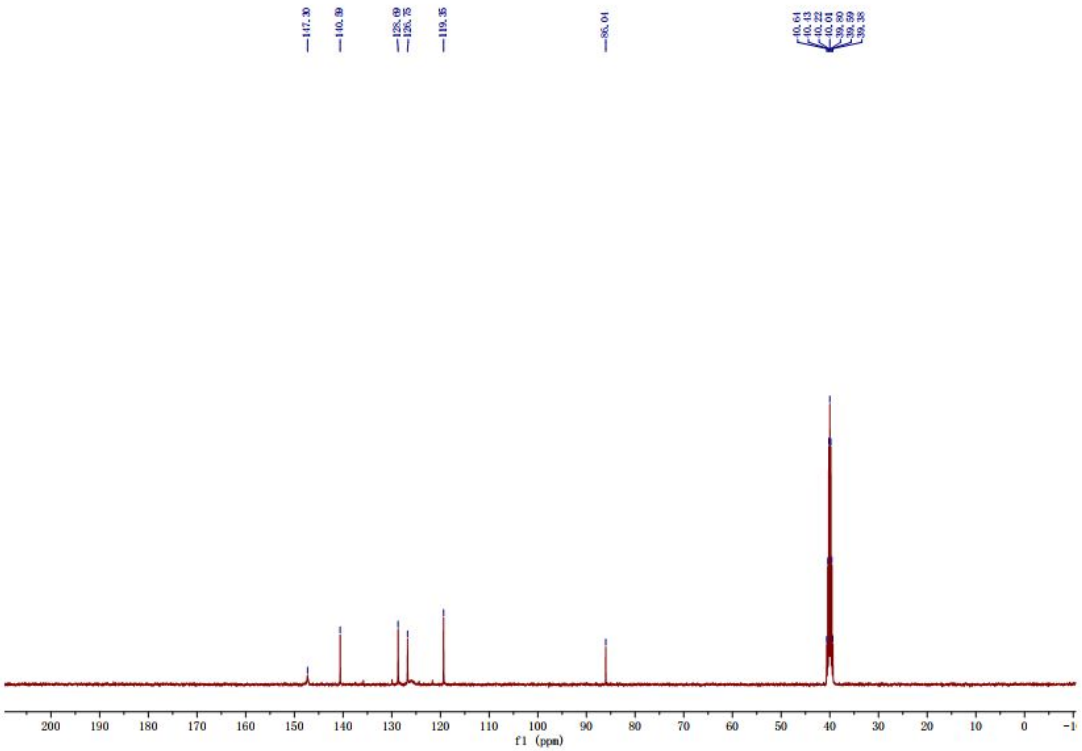
^{19}F NMR spectra of **7d** (377 MHz, $CDCl_3$):



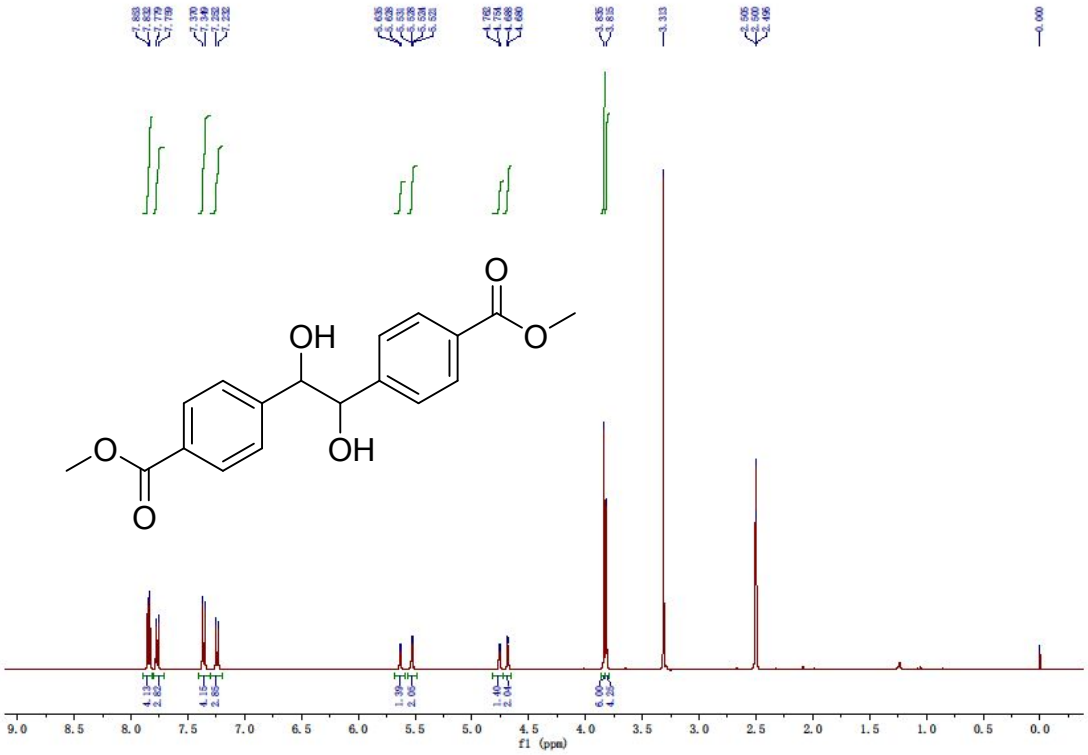
^{1}H NMR spectra of **7e** (400 MHz, $CDCl_3$):



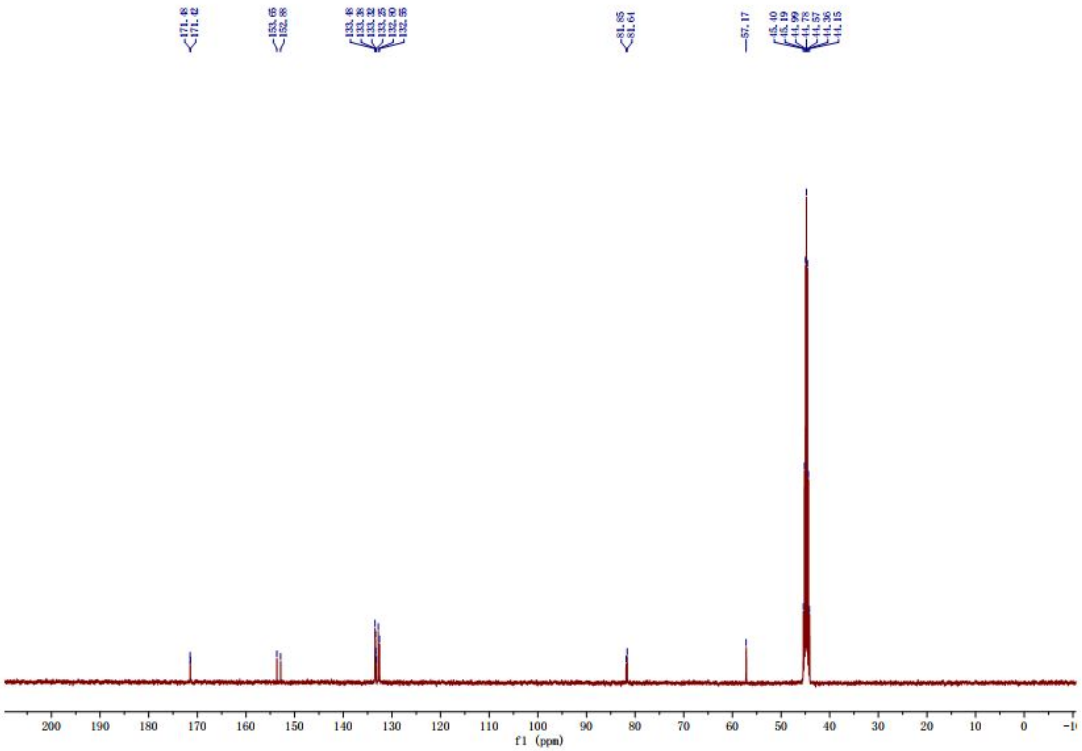
$^{13}C\{1H\}$ NMR spectra of **7e** (100 MHz, $CDCl_3$):



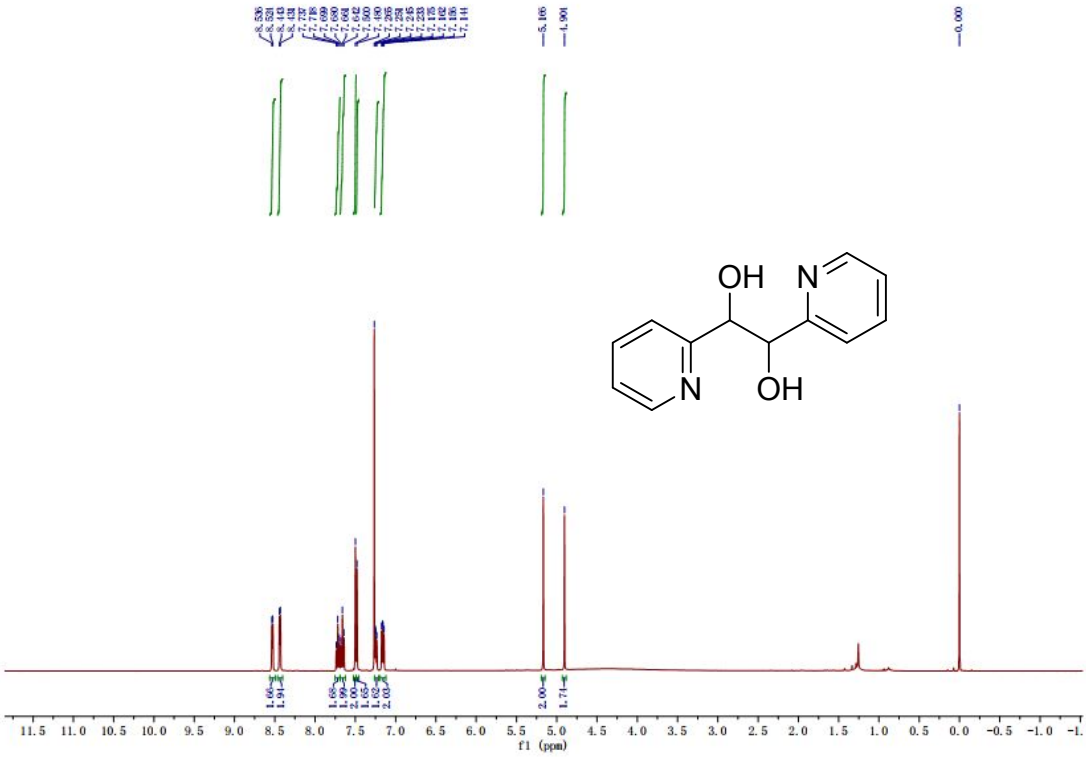
^{1}H NMR spectra of **7f** (400 MHz, $CDCl_3$):



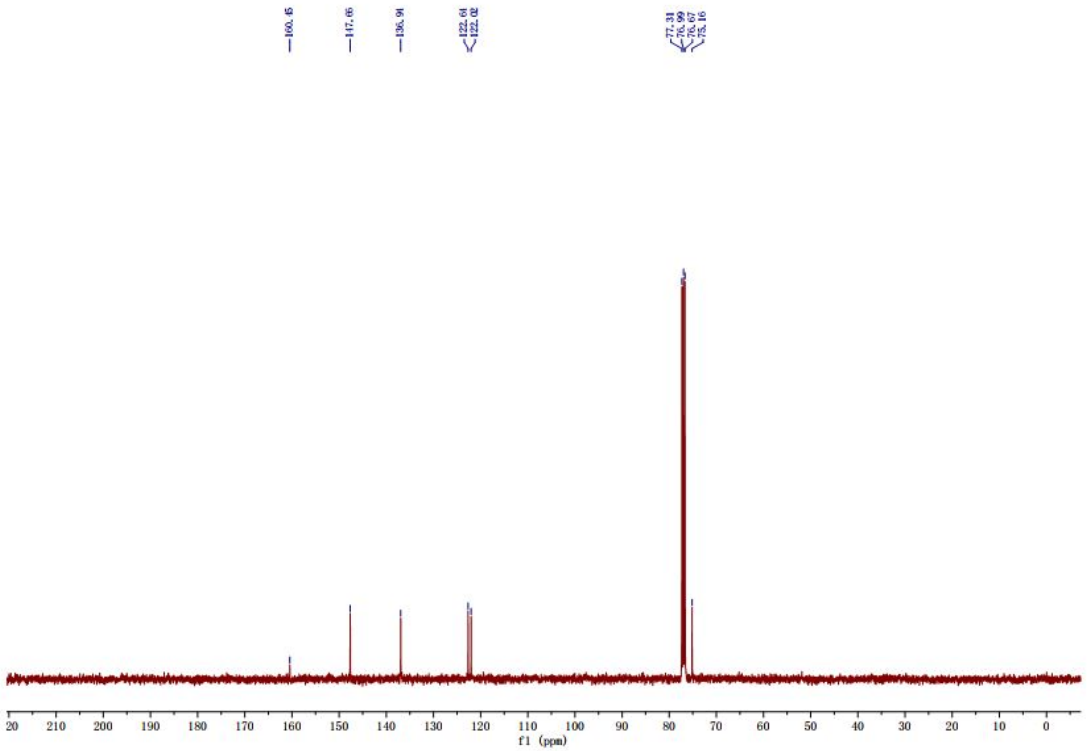
$^{13}C\{1H\}$ NMR spectra of **7f** (100 MHz, $CDCl_3$):



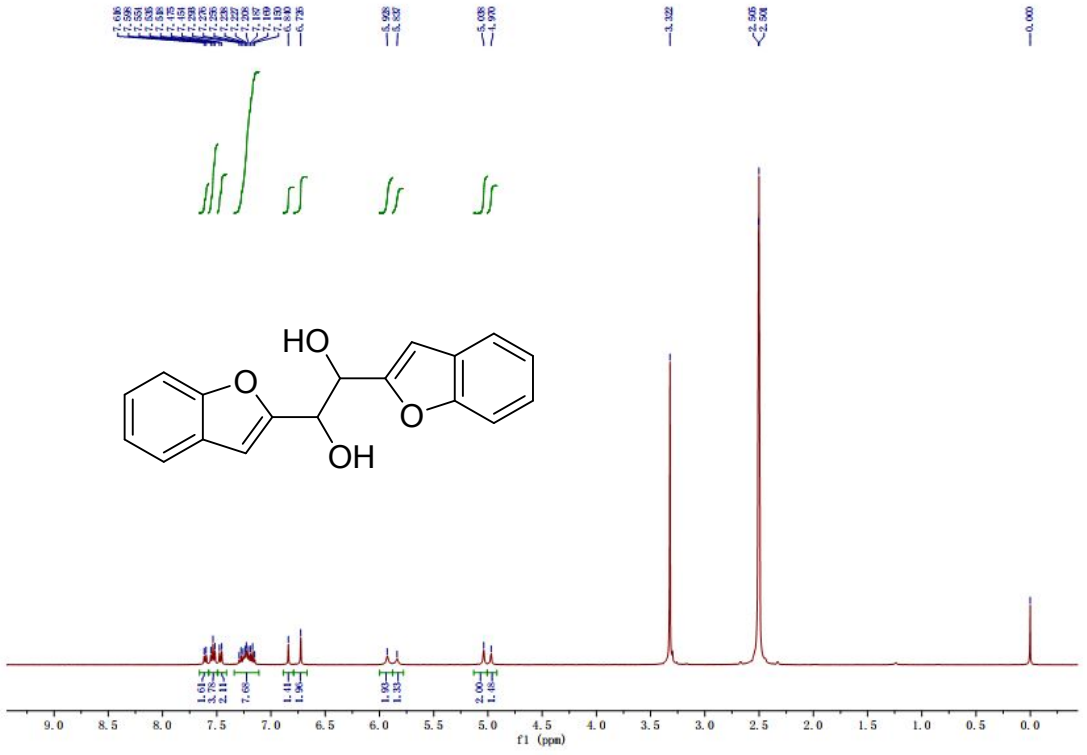
^{1}H NMR spectra of **7g** (400 MHz, $CDCl_3$):



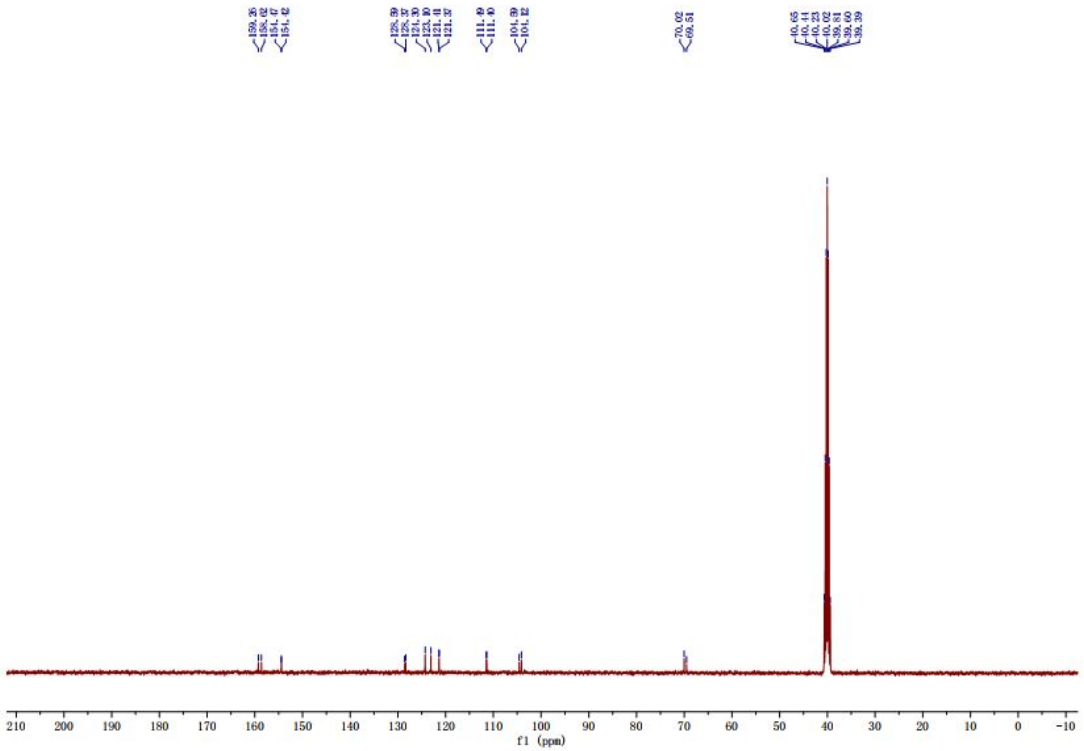
$^{13}C\{1H\}$ NMR spectra of **7g** (100 MHz, $CDCl_3$):



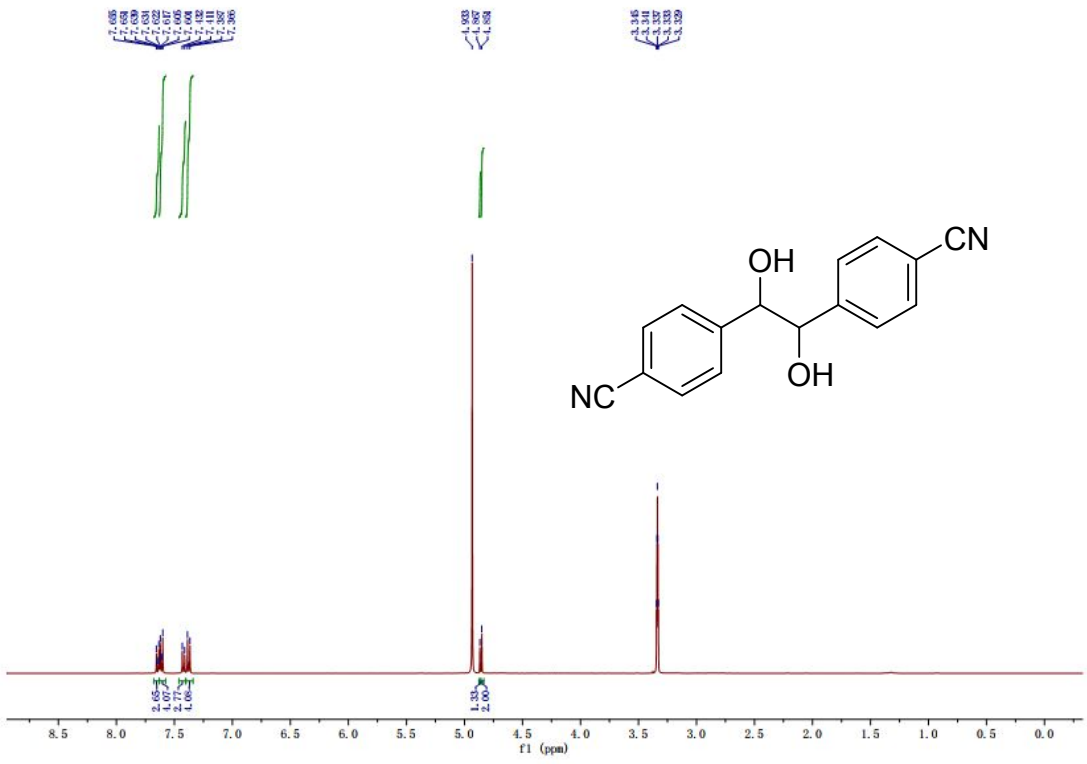
^{1}H NMR spectra of **7h** (400 MHz, $CDCl_3$):



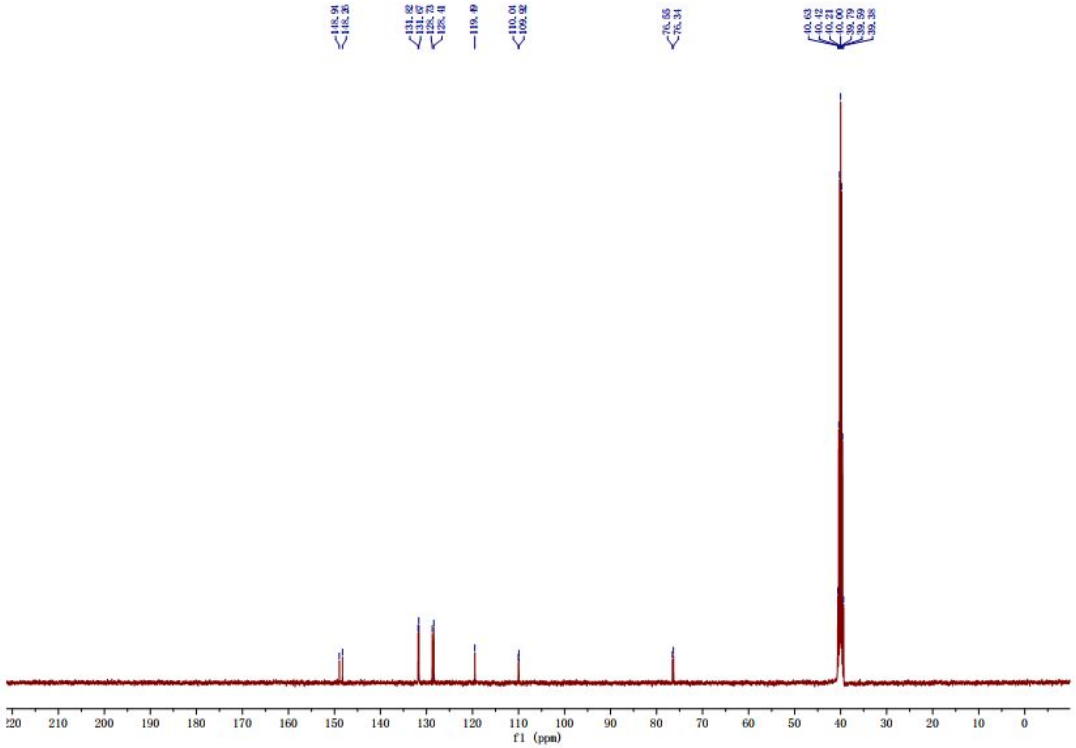
$^{13}C\{1H\}$ NMR spectra of **7h** (100 MHz, $CDCl_3$):



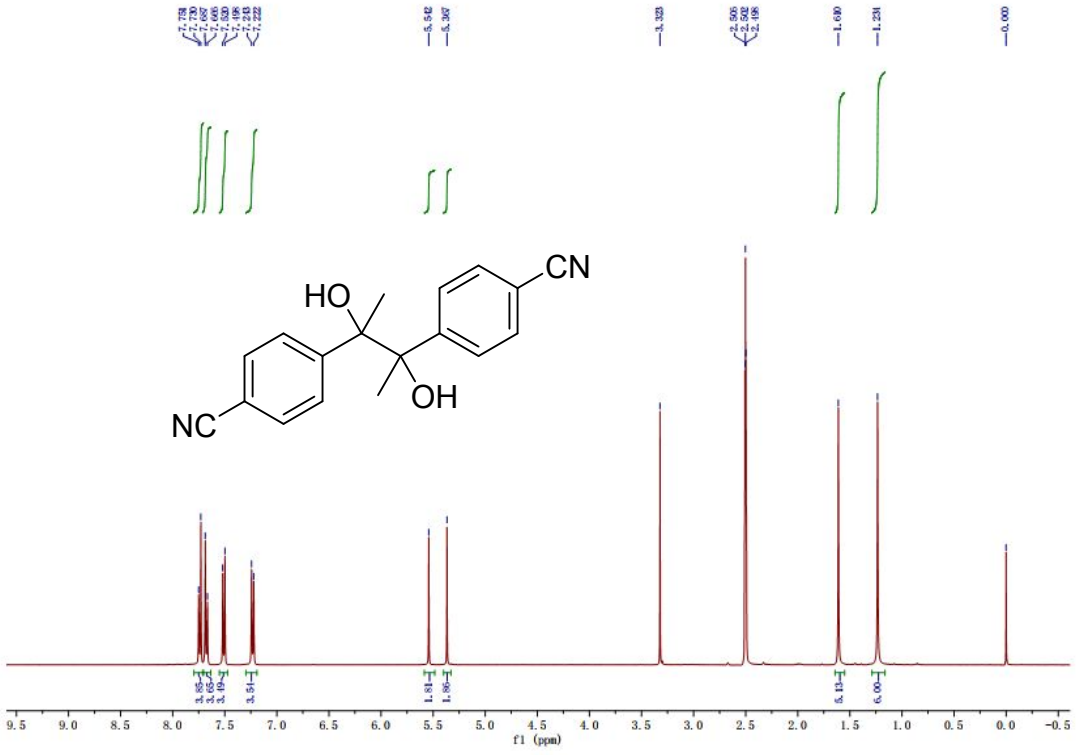
^{1}H NMR spectra of **7i** (400 MHz, $CDCl_3$):



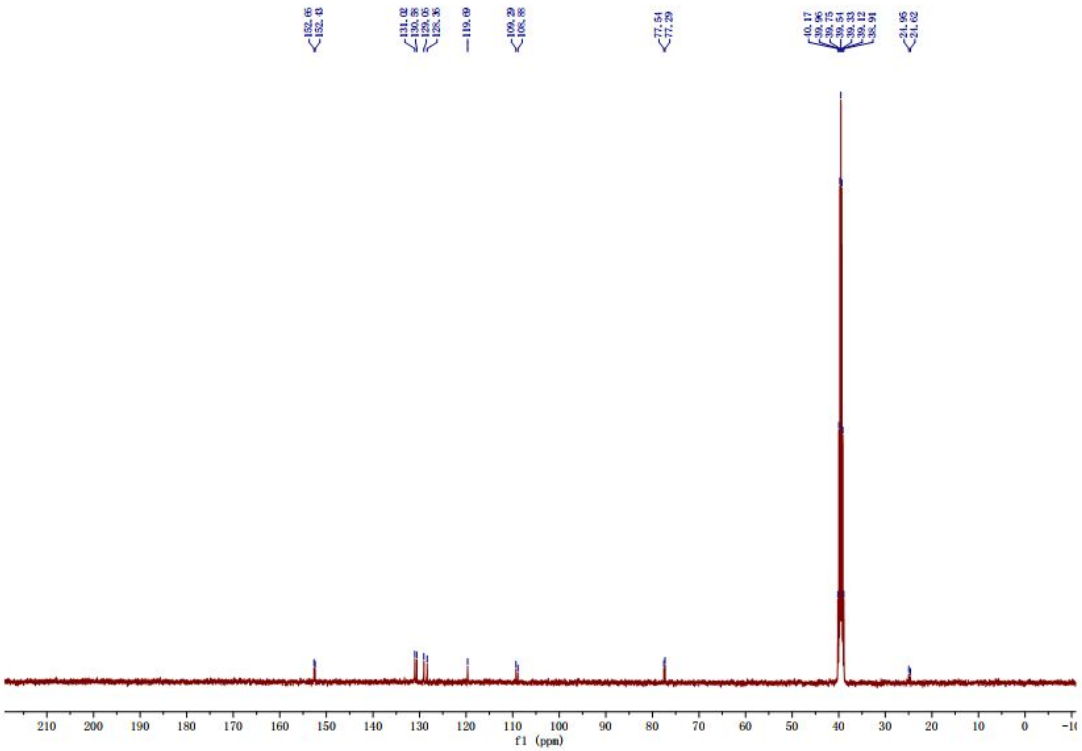
$^{13}C\{1H\}$ NMR spectra of **7i** (100 MHz, $CDCl_3$):



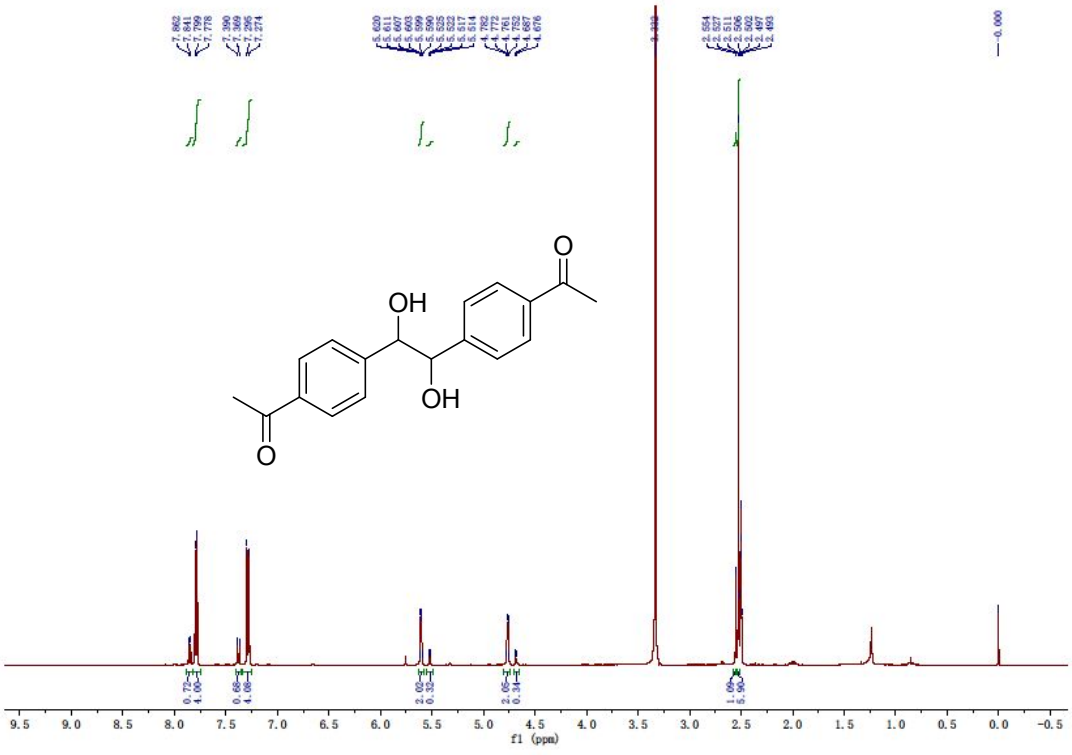
^{1}H NMR spectra of **7j** (400 MHz, $CDCl_3$):



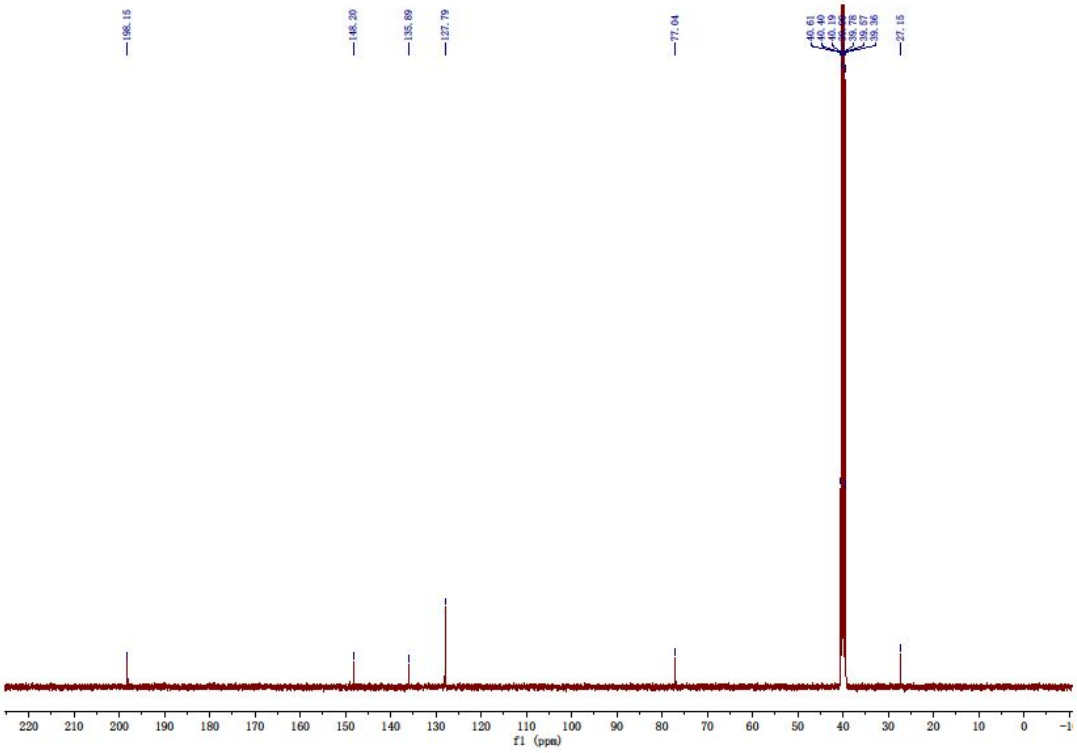
$^{13}C\{1H\}$ NMR spectra of **7j** (100 MHz, $CDCl_3$):



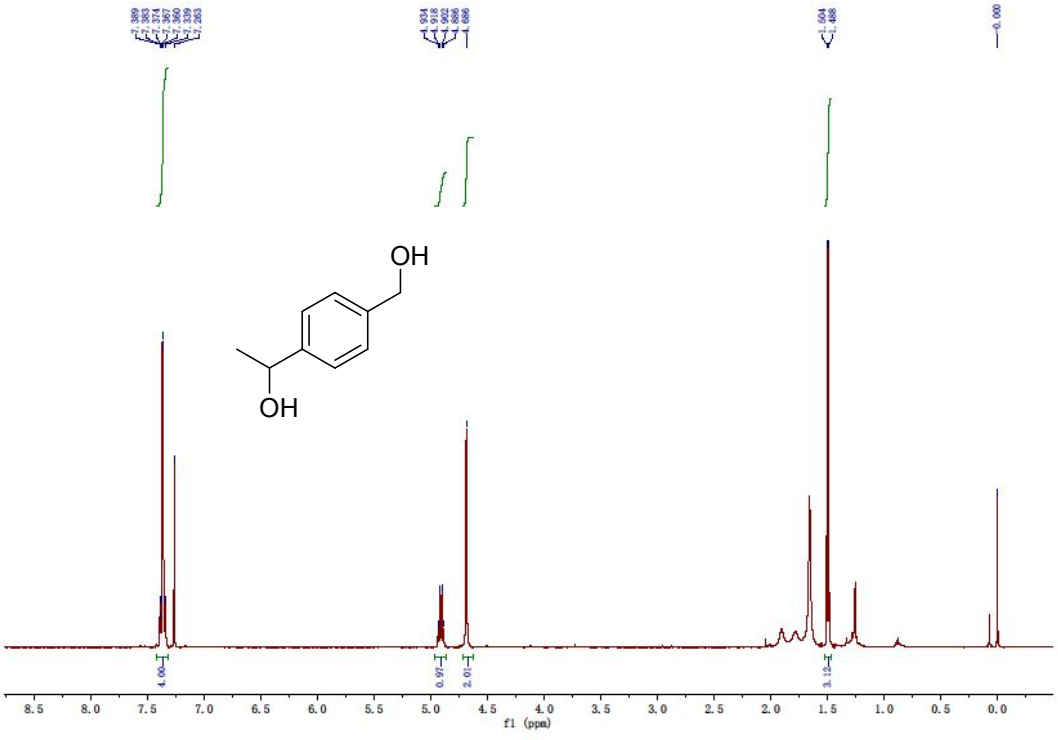
^{1}H NMR spectra of **7k** (400 MHz, $CDCl_3$):



$^{13}C\{1H\}$ NMR spectra of **7k** (100 MHz, $CDCl_3$):



^{1}H NMR spectra of **8** (400 MHz, $CDCl_3$):



$^{13}C\{1H\}$ NMR spectra of **8** (100 MHz, $CDCl_3$):