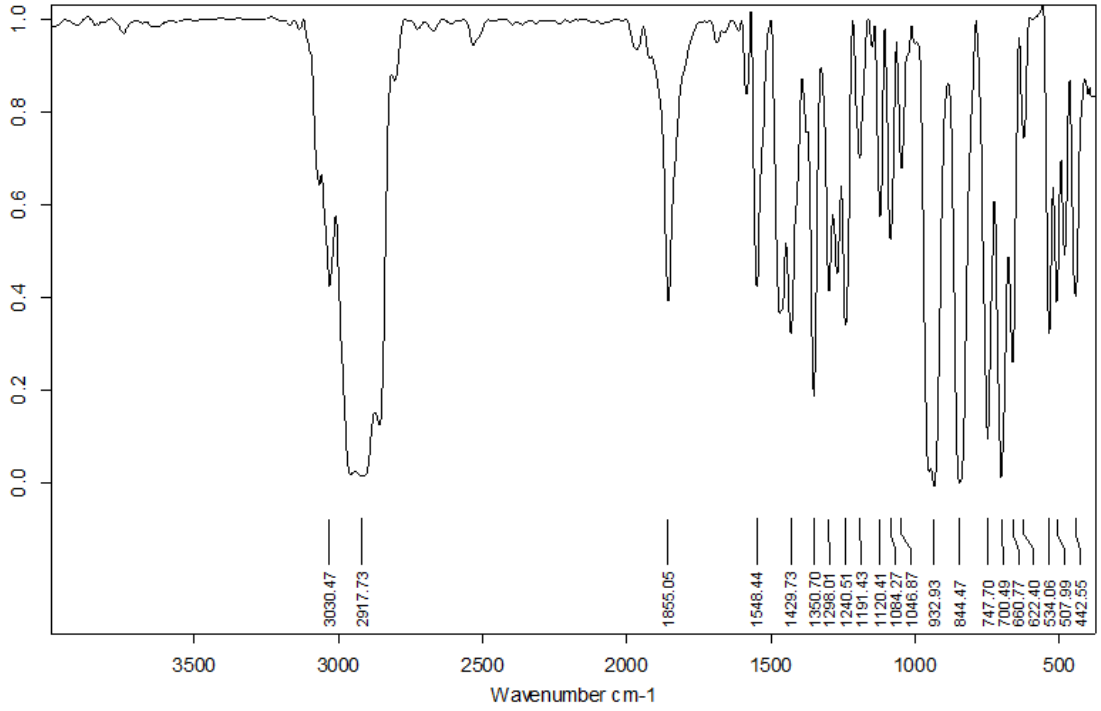
Syntheses and Catalytic Application of Hydrido Iron(II) Complexes with [P,S]-Chelating Ligands in Hydrosilylation of Aldehydes and Ketones

Benjing Xue, Hongjian Sun and Xiaoyan Li*

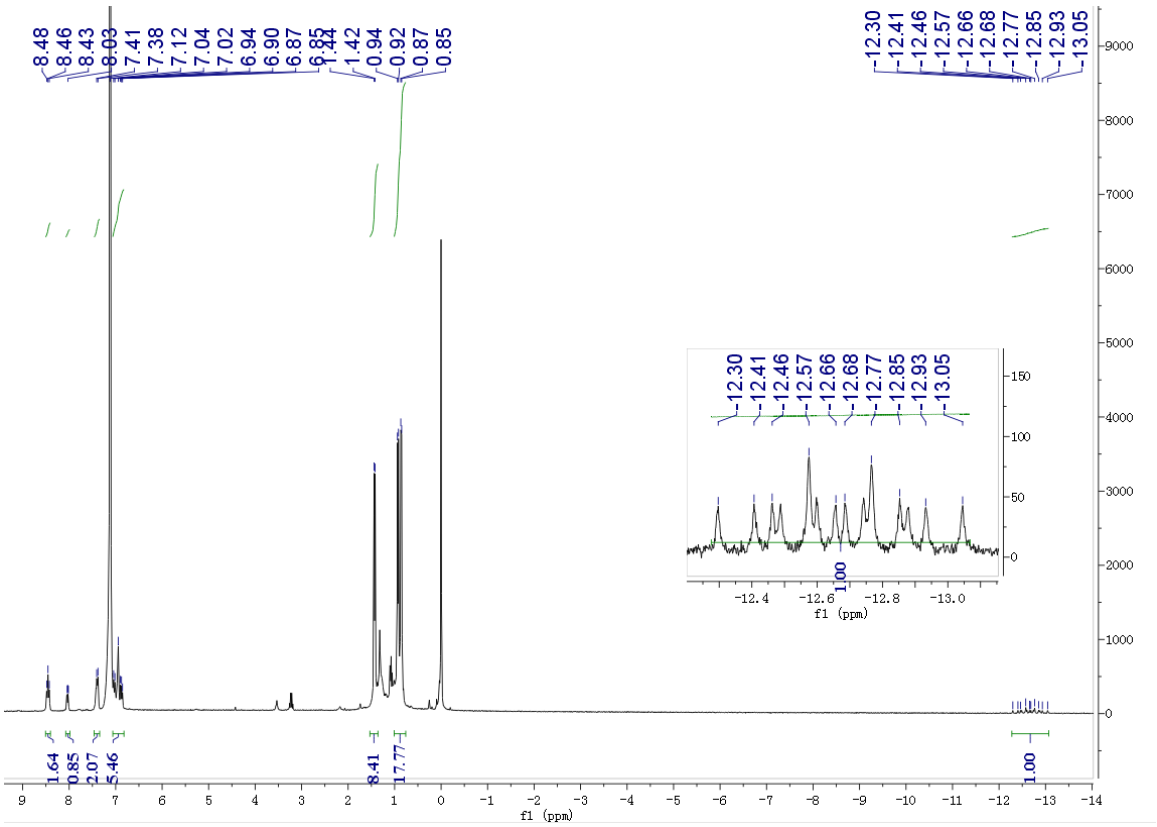
School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, PR China
E-mail: xli63@sdu.edu.cn; Fax: +86 531 88361350

Table of Contents

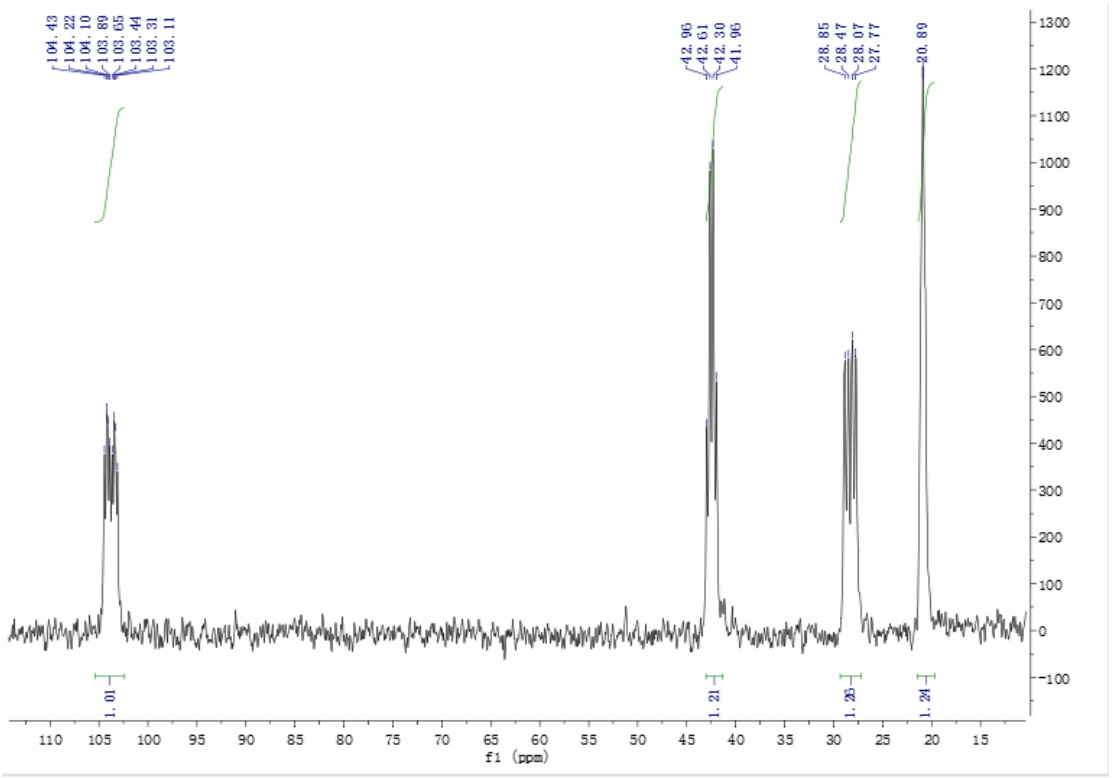
1 IR and NMR data of complexes **2-4**



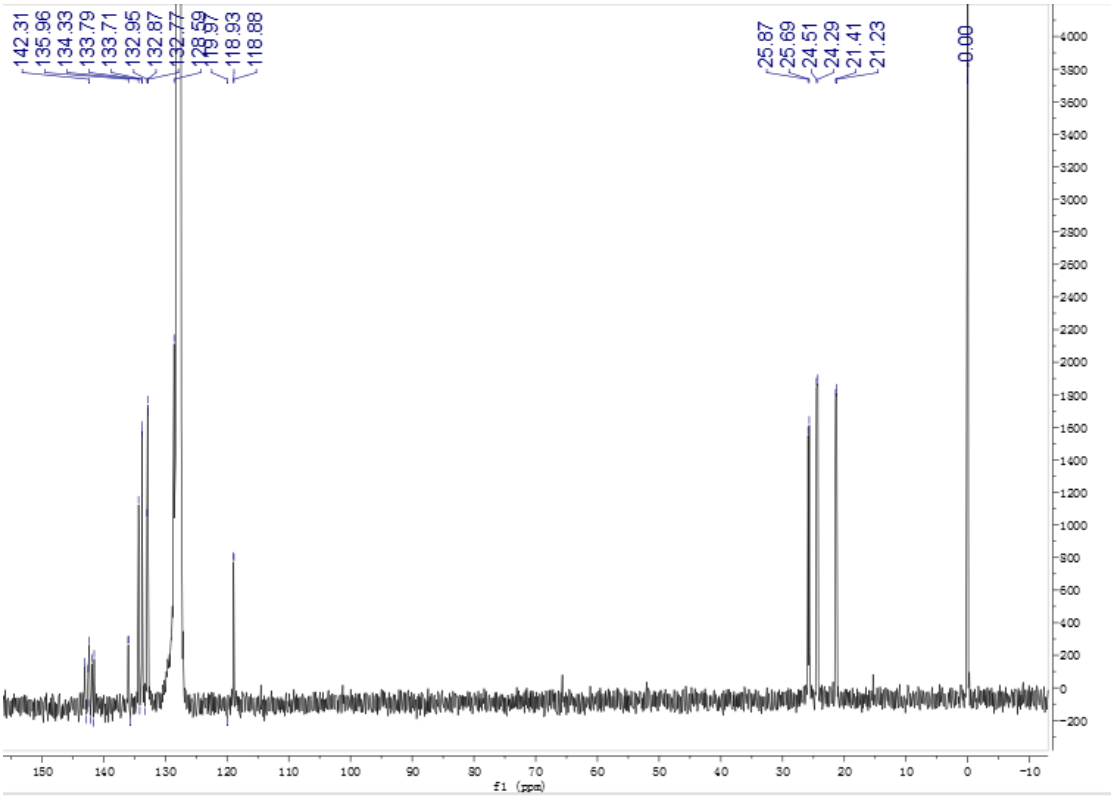
IR spectrum of complex **2**



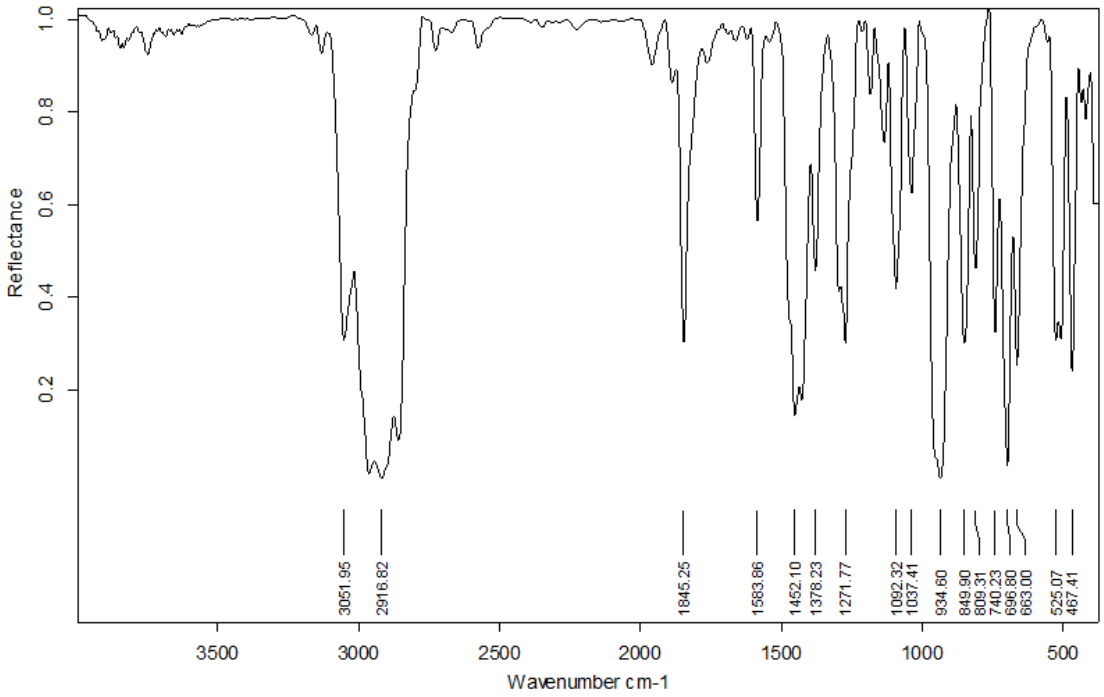
^{1}H NMR spectrum of complex **2**



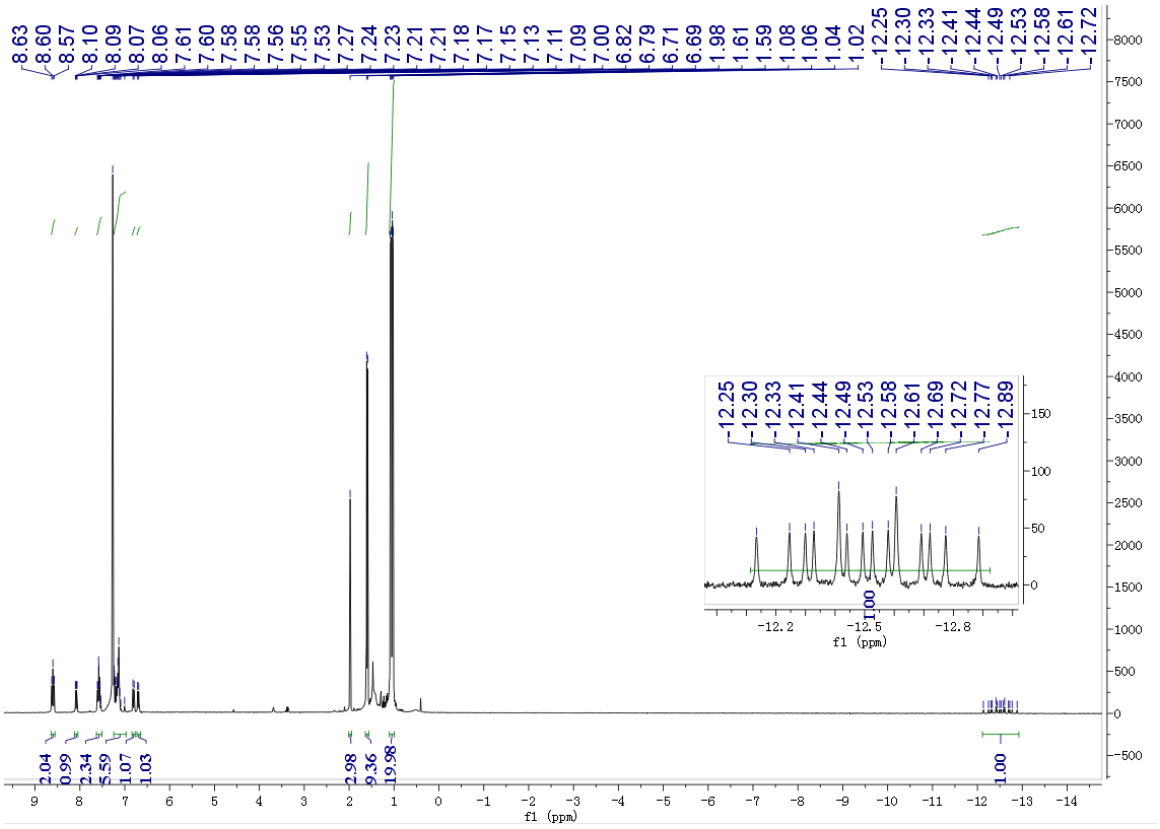
^{31}P NMR spectrum of complex **2**



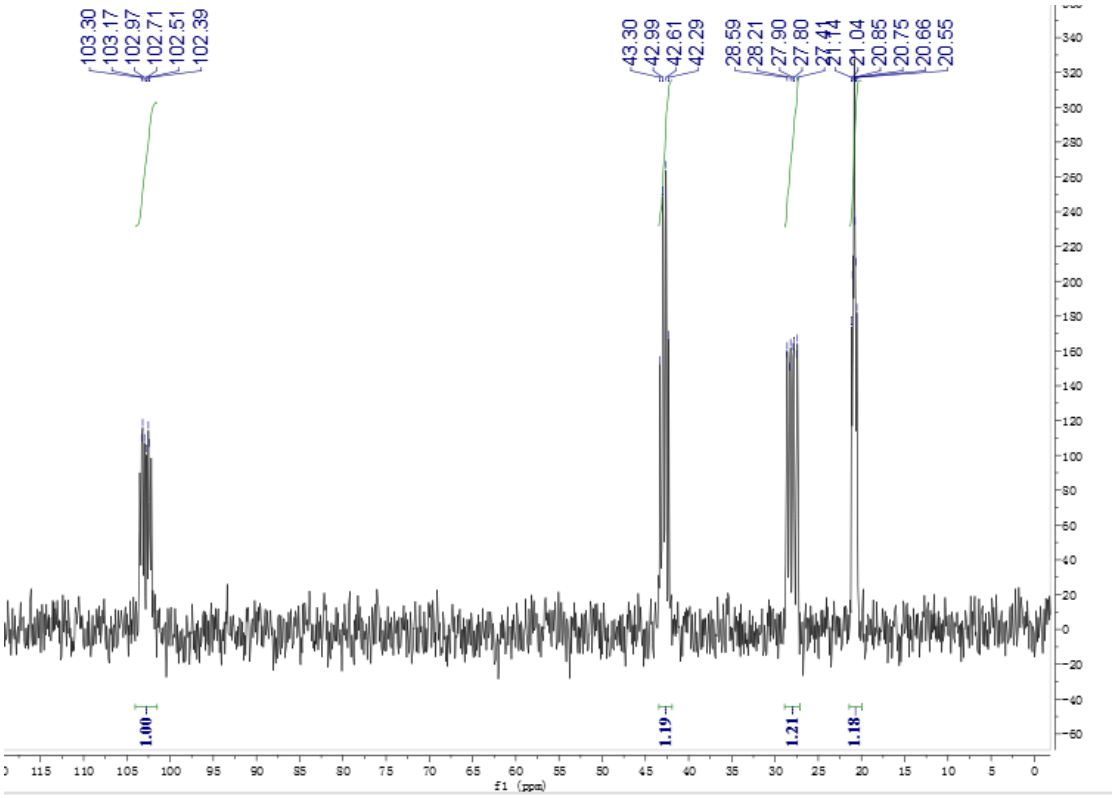
^{13}C NMR spectrum of complex **2**



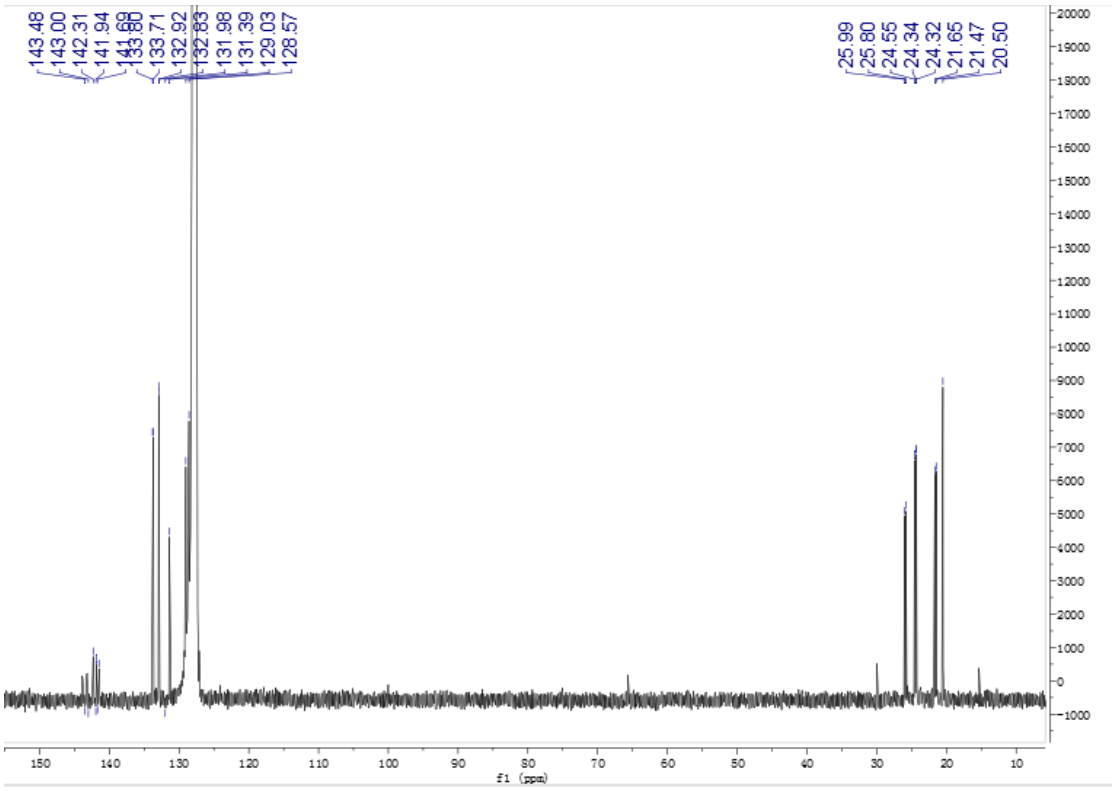
IR spectrum of complex **3**



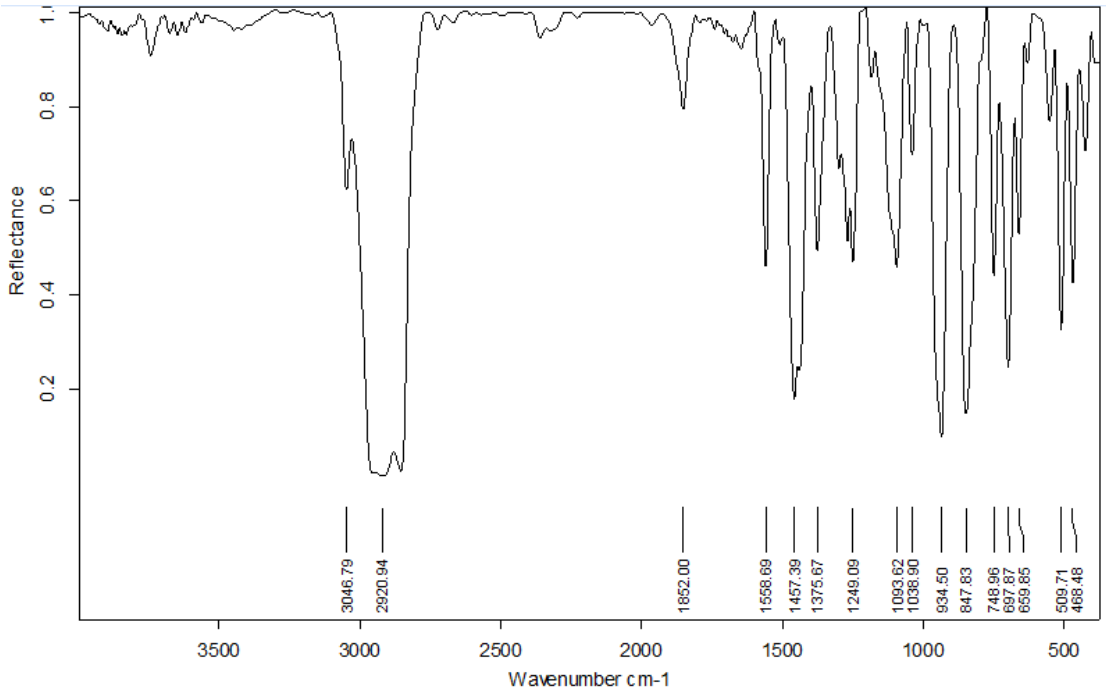
^{1}H NMR spectrum of complex **3**



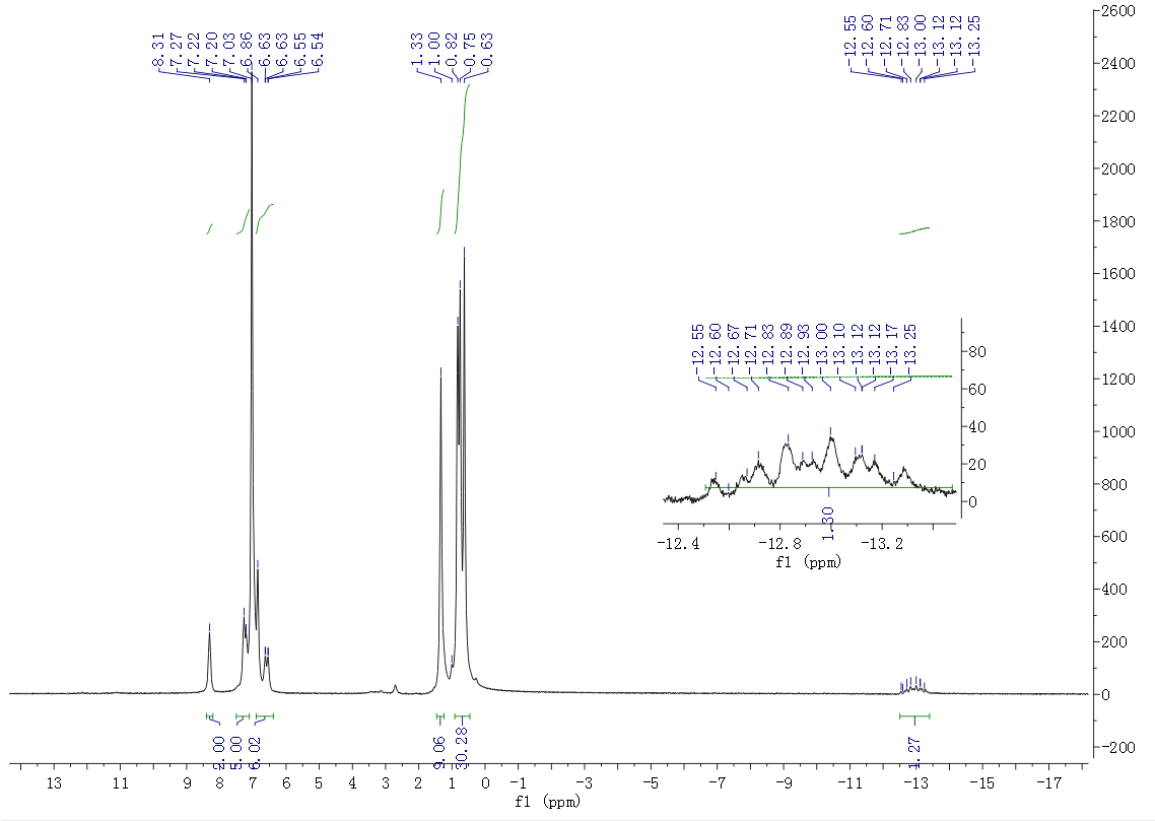
^{31}P NMR spectrum of complex **3**



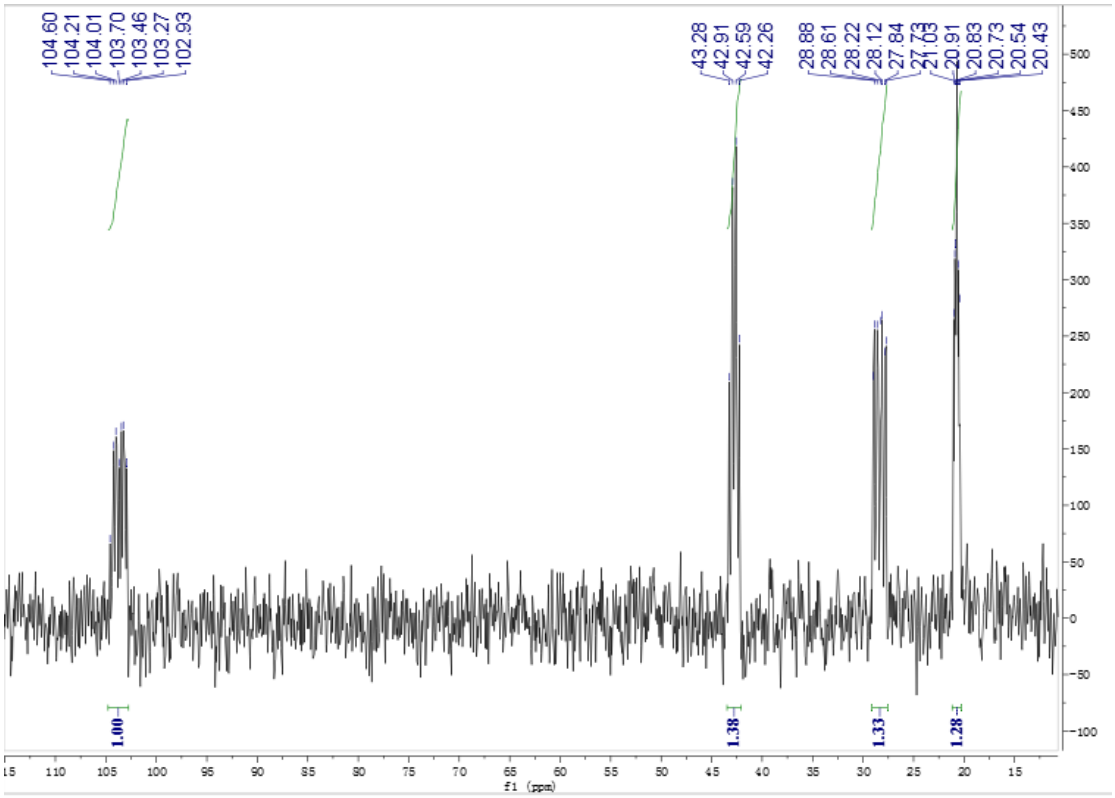
^{13}C NMR spectrum of complex **3**



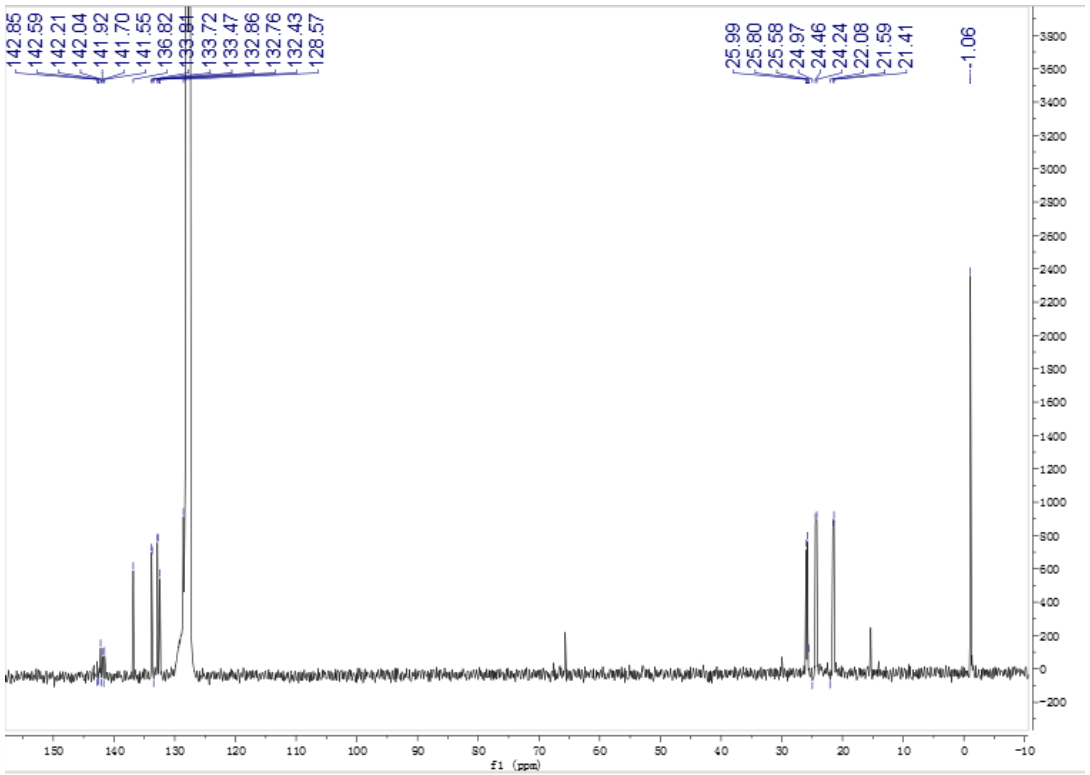
IR spectrum of complex **4**



^{1}H NMR spectrum of complex **4**



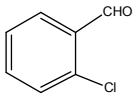
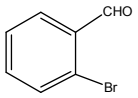
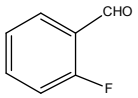
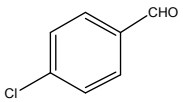
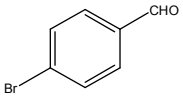
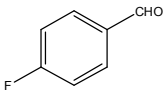
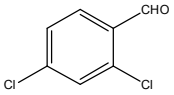
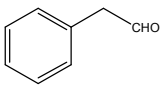
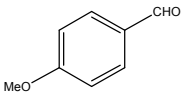
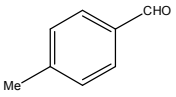
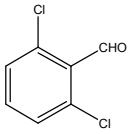
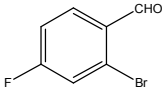
^{31}P NMR spectrum of complex **4**

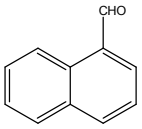
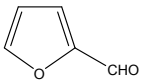
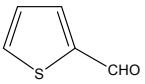


^{13}C NMR spectrum of complex **4**

2 GC data for the catalytic reaction

Table 2 Catalytic Hydrosilylation of Aldehydes with **1** as a Catalyst[a]

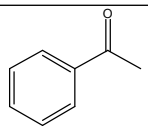
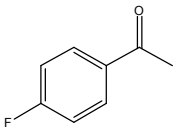
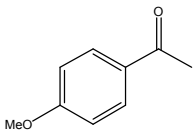
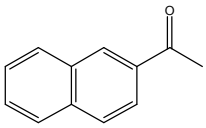
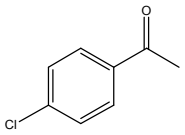
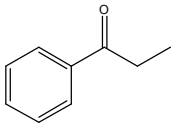
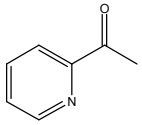
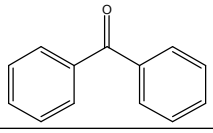
Entry	Substrates	[b]Conversion (%)
1		80
2		80
3		40
4		>99
5		>99
6		>99
7		>99
8		38
9		14
10		21
11		96
12		98

13		92
14		99
15		95

[a]Catalytic reaction conditions: RCHO (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol) and *n*-dodecane (internal standard) (1.0 mmol), 2 ml THF, 50℃, 2h.

[b]Determined by GC analysis.

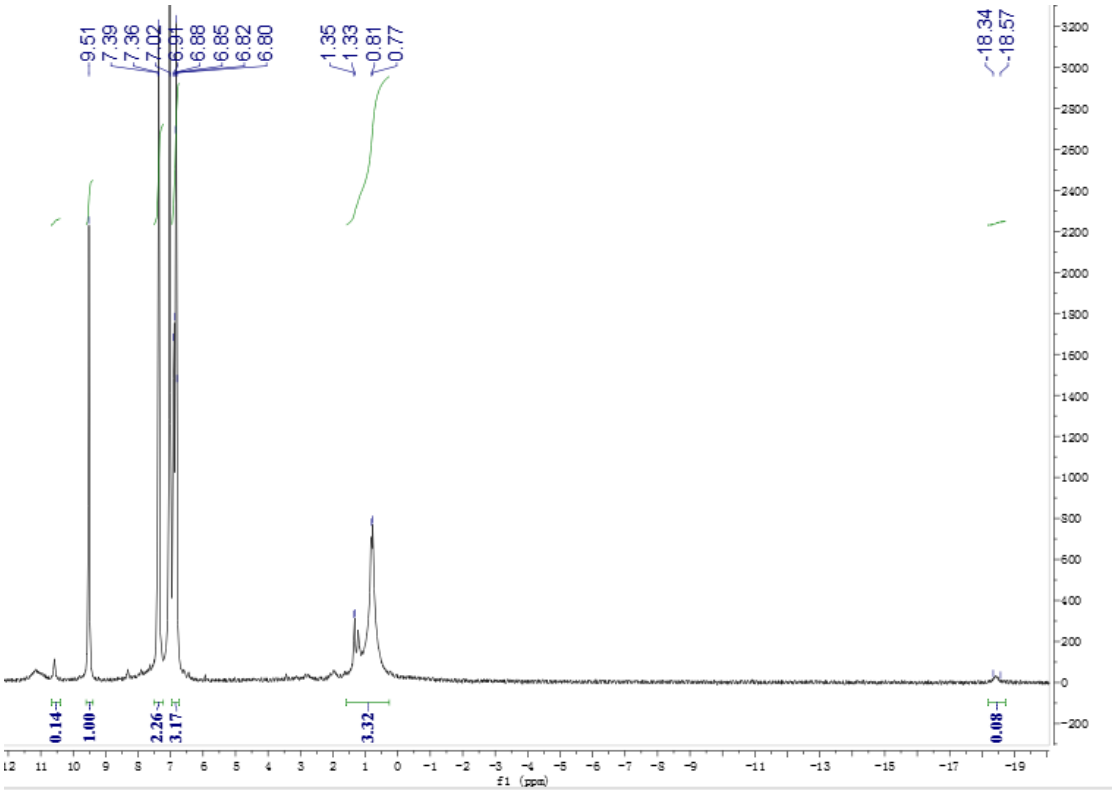
Table 3 Catalytic Hydrosilylation of Ketones with **1** as a Catalyst[a]

Entry	Substrates	[b]Conversion(%)
1		56
2		46
3		57
4		64
5		53
6		37
7		71
8		64

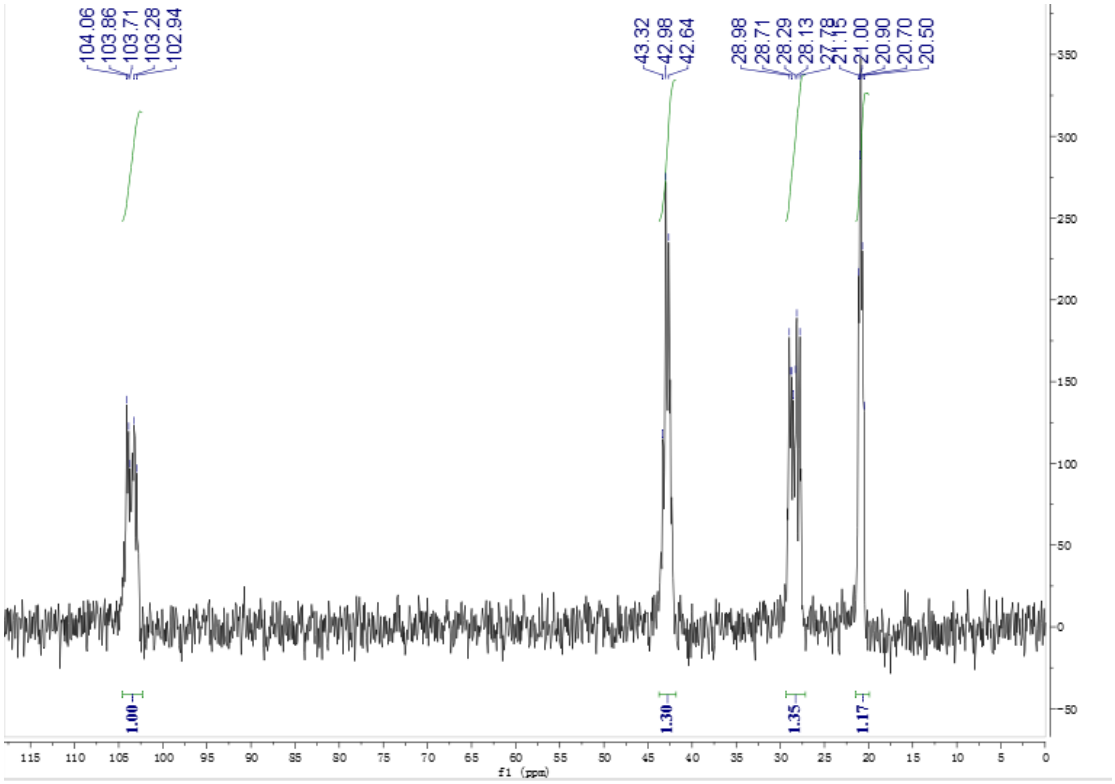
[a]Catalytic reaction conditions: RCOR' (1.0 mmol), $(EtO)_3SiH$ (1.2 mmol) and *n*-dodecane (internal standard) (1.0 mmol), 2 ml THF, 50℃, 24h.

[b]Determined by GC analysis.

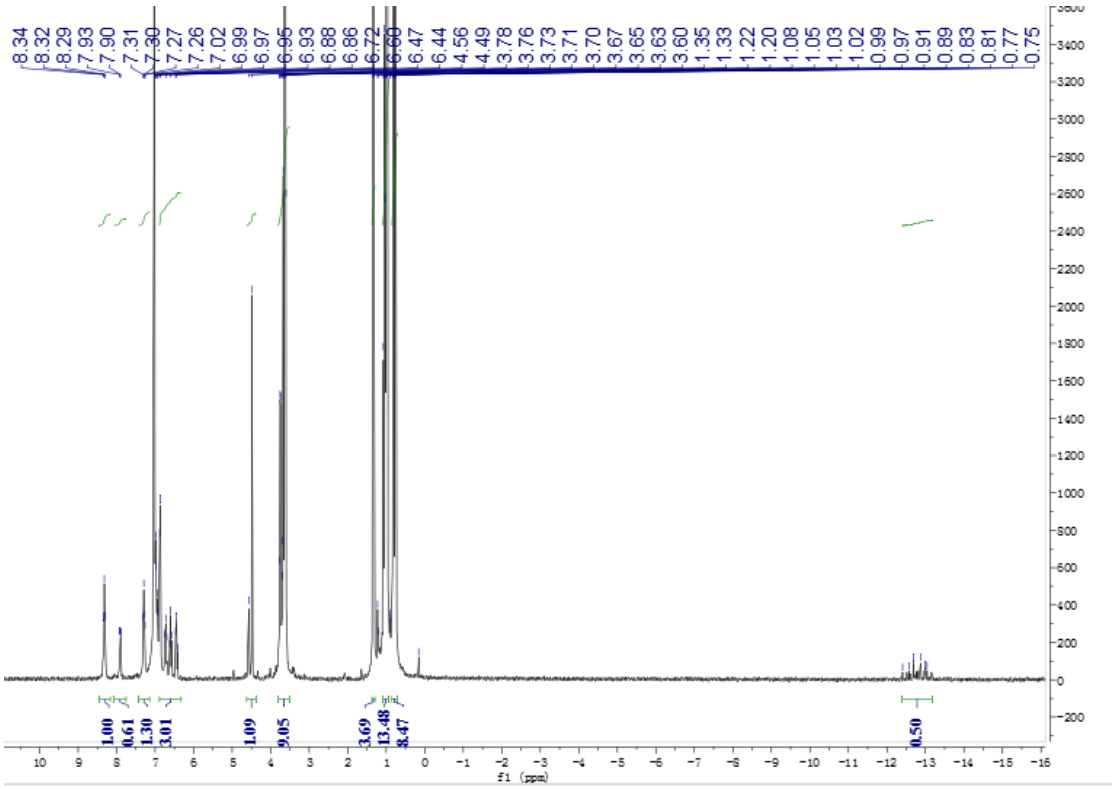
3 NMR data of mechanism study



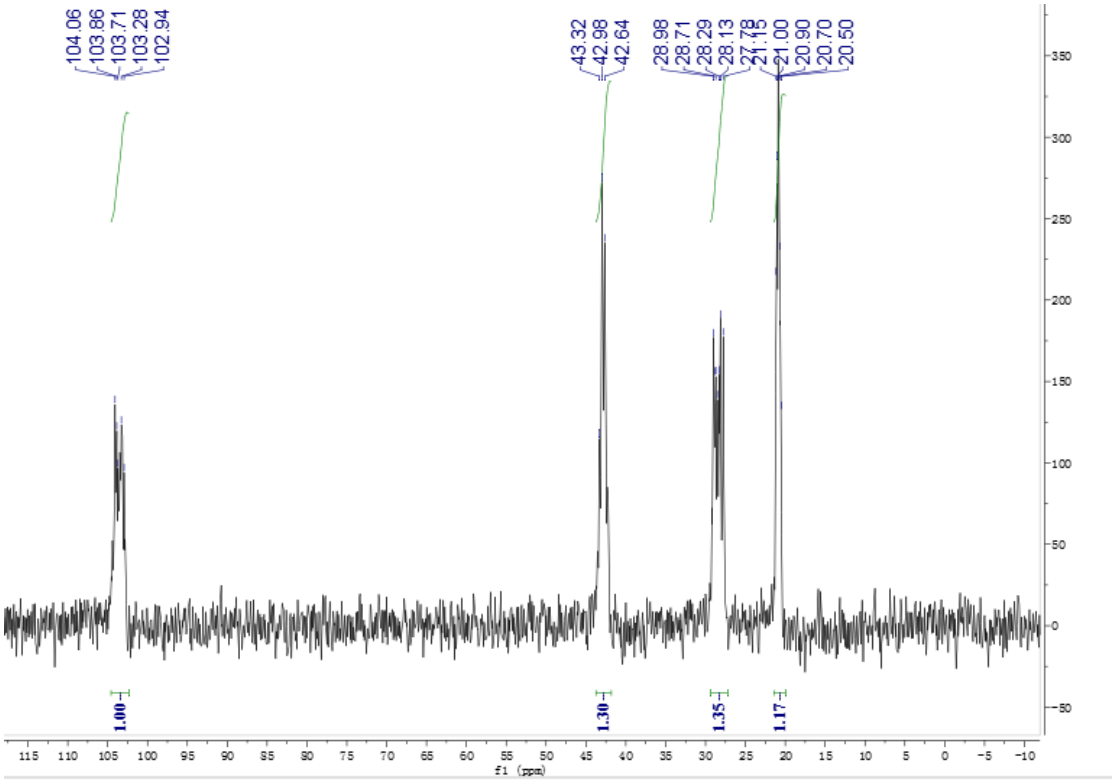
Stoichiometric reactions of complex **1** with benzaldehyde (^{1}H NMR)



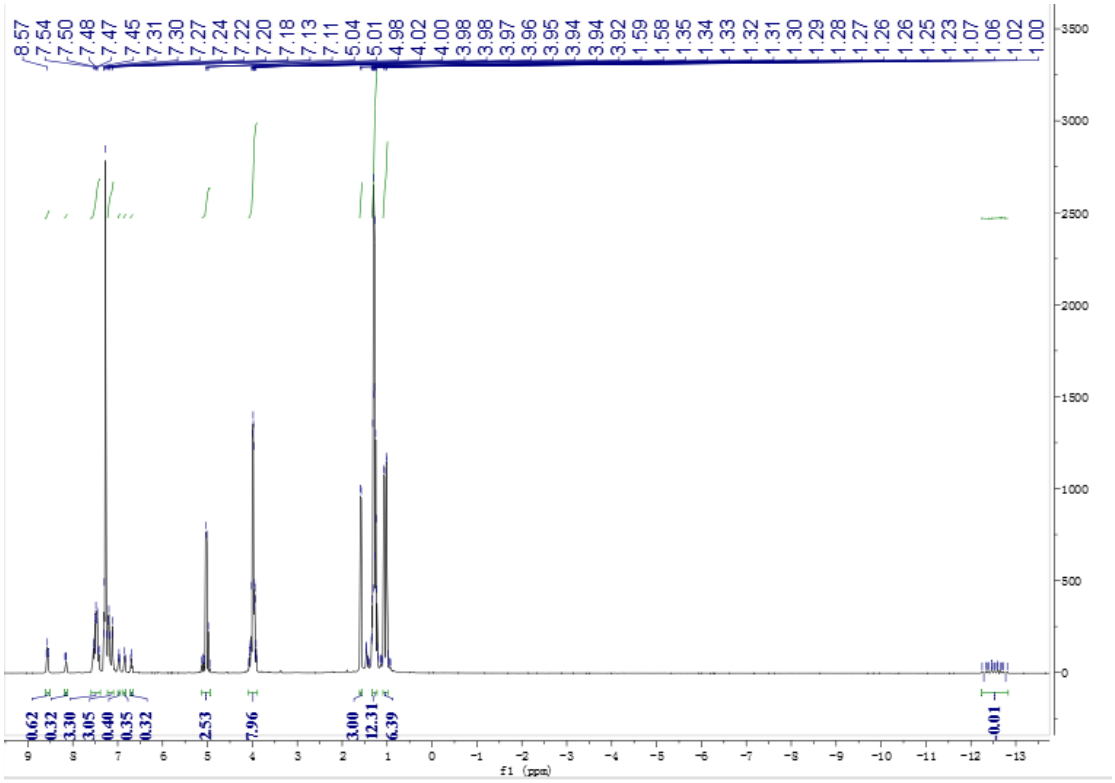
Stoichiometric reactions of complex **1** with benzaldehyde (^{31}P NMR)



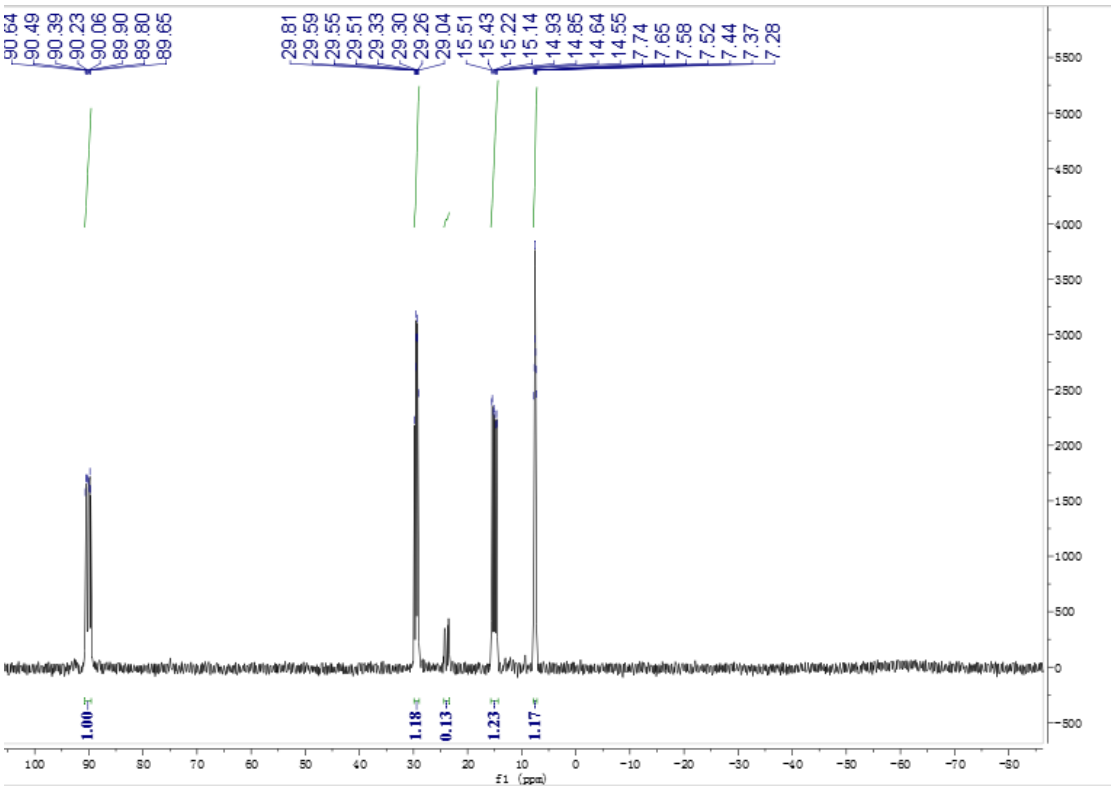
Stoichiometric reactions of complex **1** with triethoxysilane (^{1}H NMR)



Stoichiometric reactions of complex **1** with triethoxysilane (^{31}P NMR)

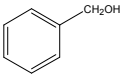


Stoichiometric reactions of complex **1** with benzaldehyde and triethoxysilane (^{1}H NMR)

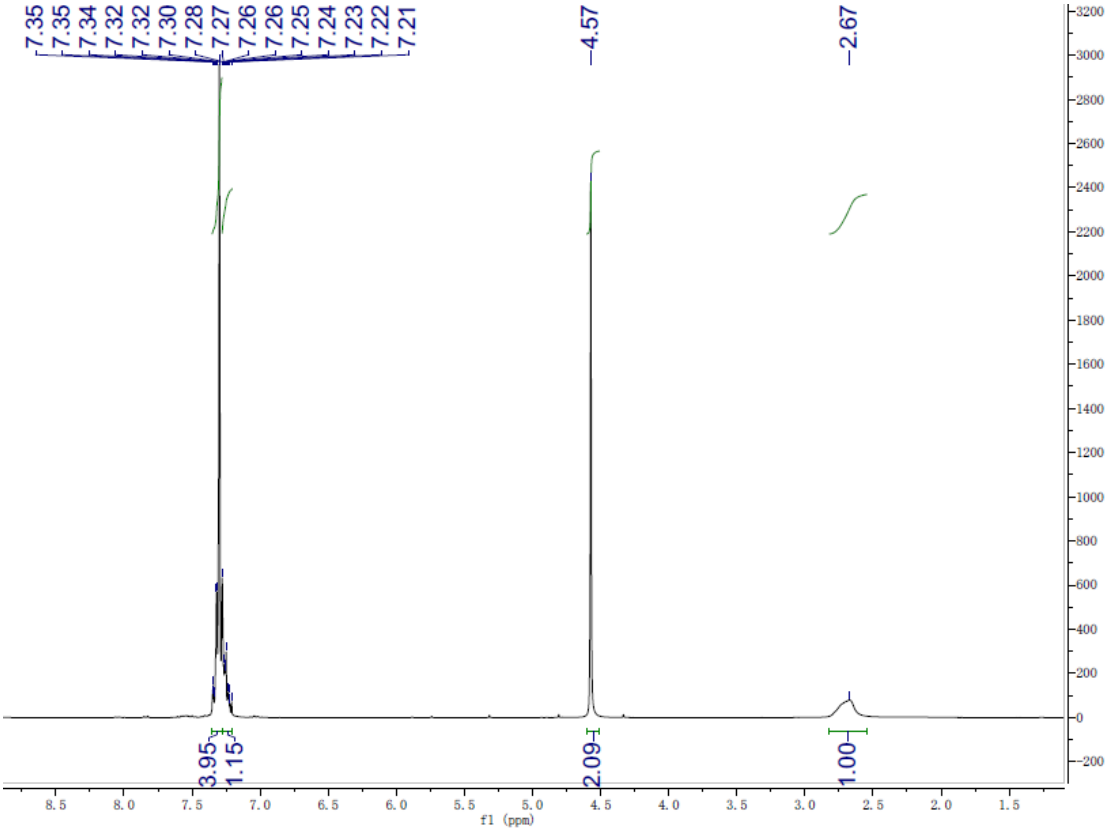


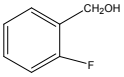
Stoichiometric reactions of complex **1** with benzaldehyde and triethoxysilane (^{31}P NMR)

4 NMR data for the alcohol products

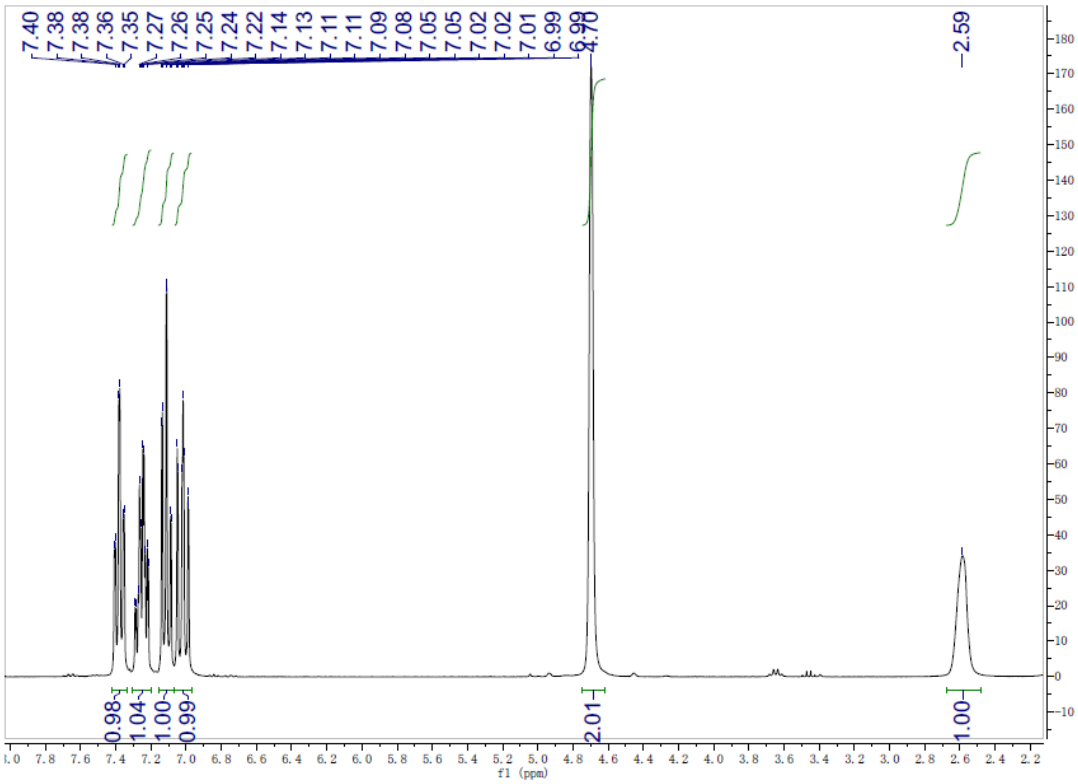


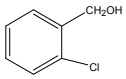
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.35-7.21 (m, Ar, 5H), 4.57 (s, CH_2, 2H), 2.67 (s, OH, 1H).



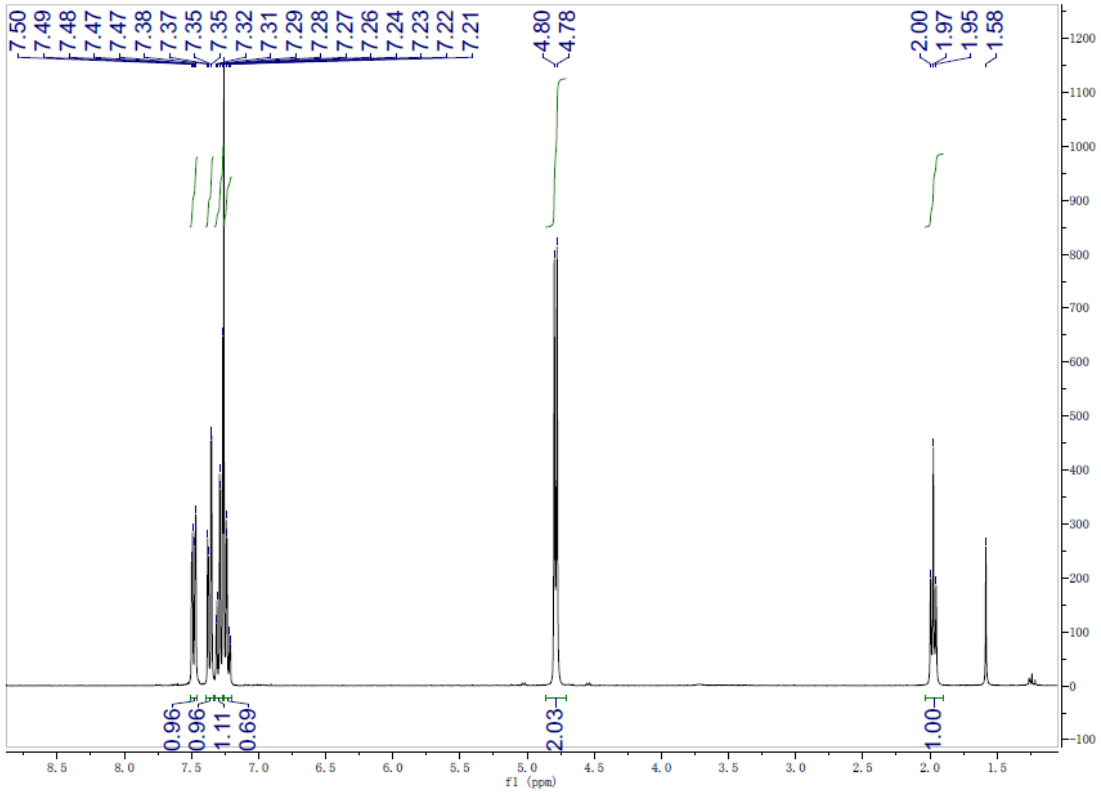


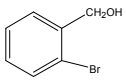
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.40-6.99 (m, Ar, 4H), 4.70 (s, CH_2, 2H), 2.59 (s, OH, 1H).



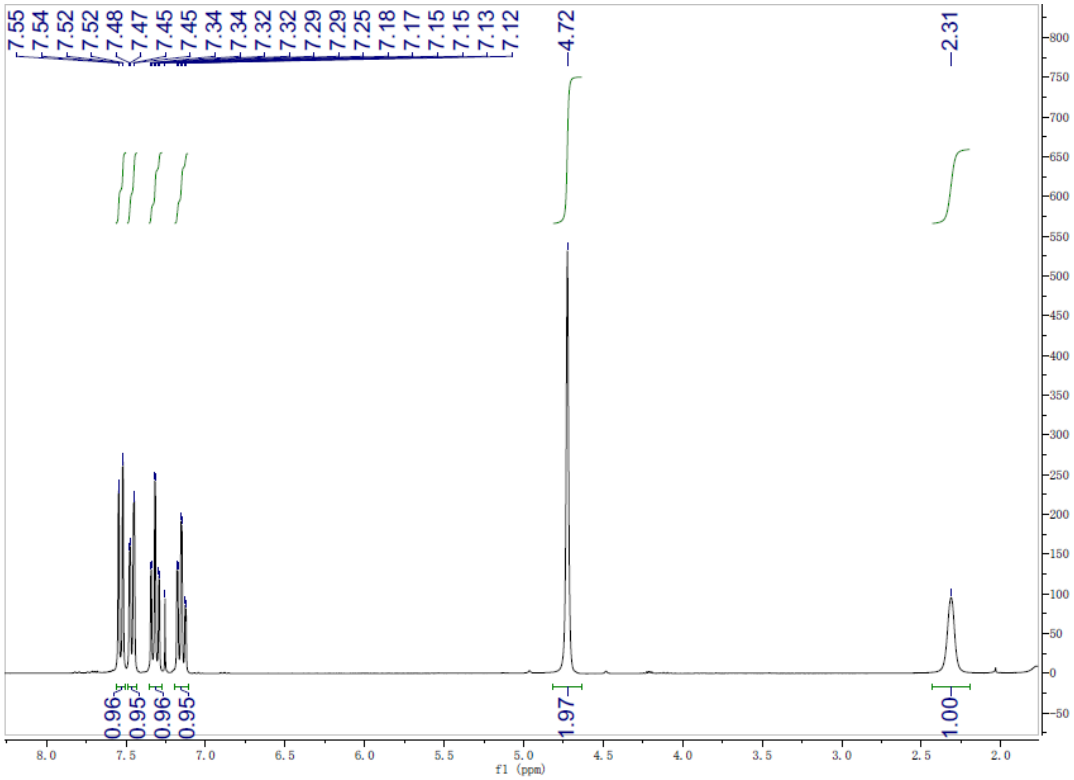


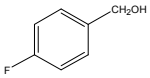
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.50-7.21 (m, Ar, 4H), 4.80-4.78 (d, CH_2, 2H), 1.97 (t, OH, 1H).



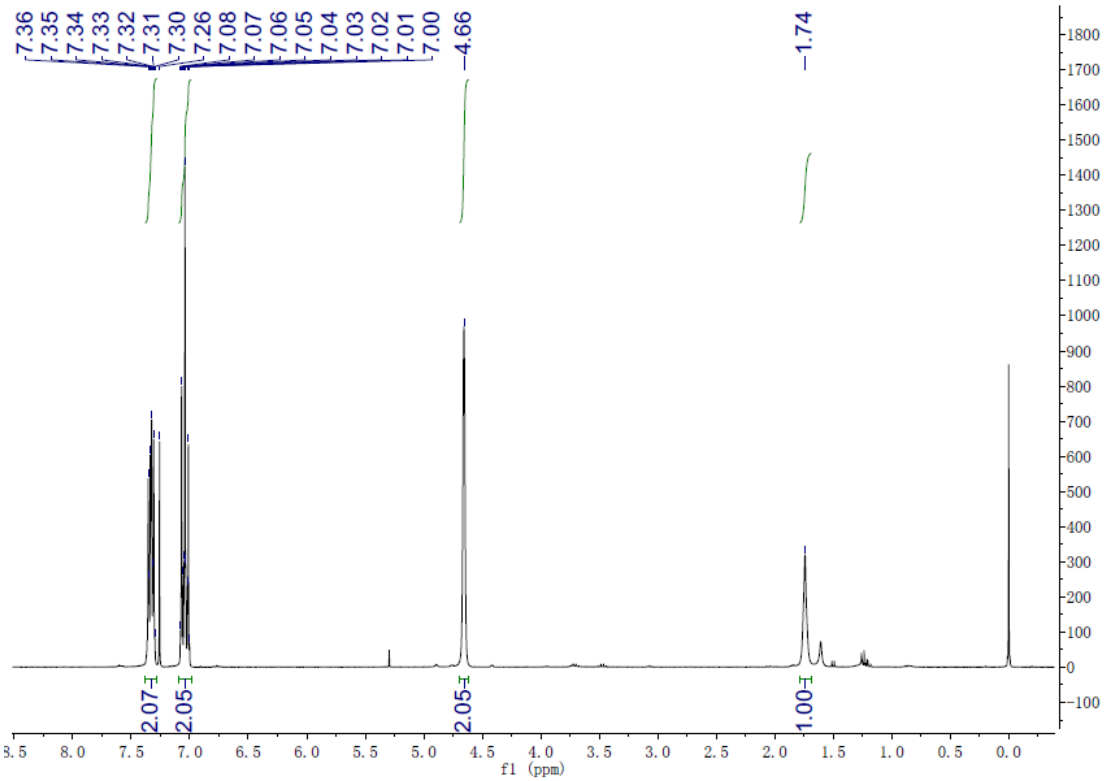


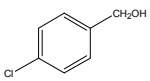
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.55-7.12 (m, Ar, 4H), 4.72 (s, CH_2, 2H), 2.31 (s, OH, 1H).



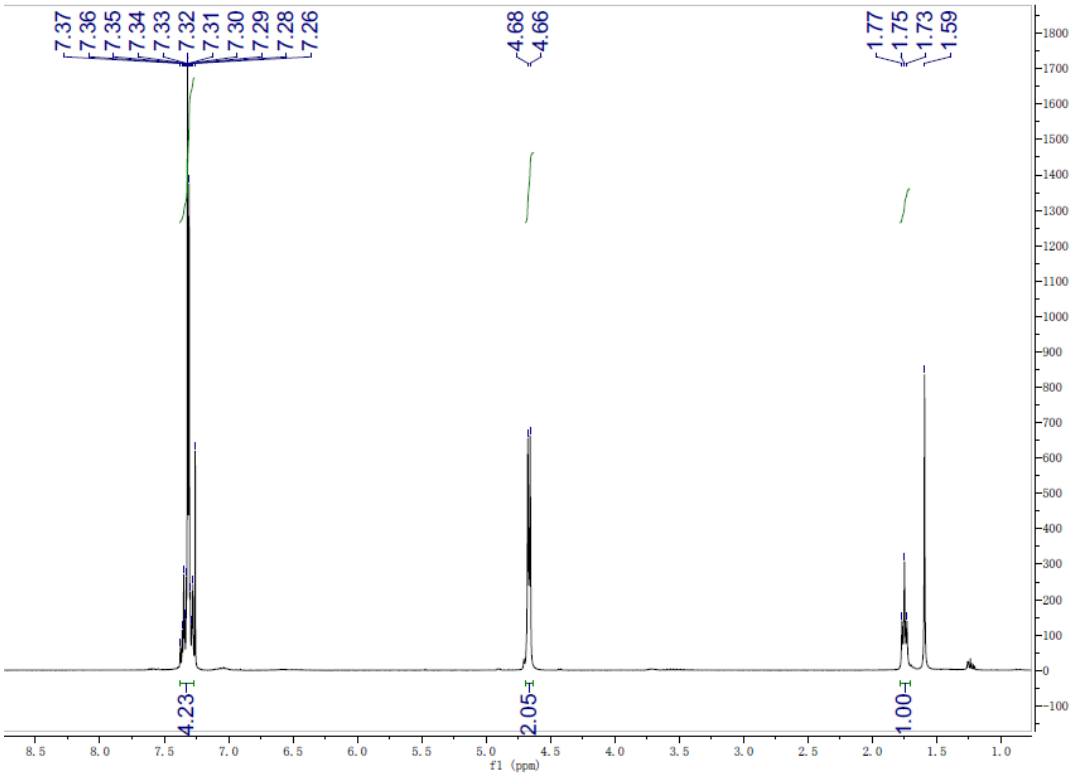


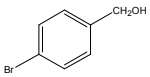
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36-7.00 (m, Ar, 4H), 4.66 (s, CH_2, 2H), 1.74 (s, OH, 1H).



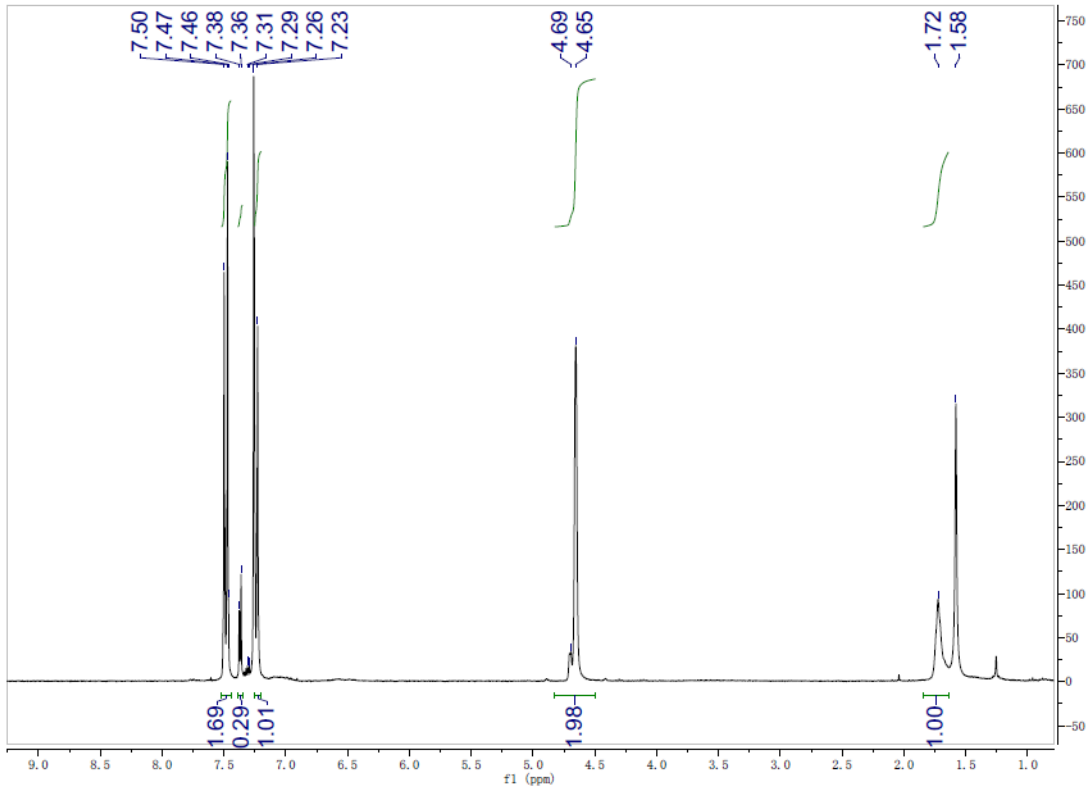


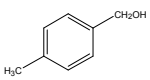
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.37-7.28 (m, Ar, 4H), 4.67 (d, CH_2, 2H), 1.75 (t, OH, 1H).



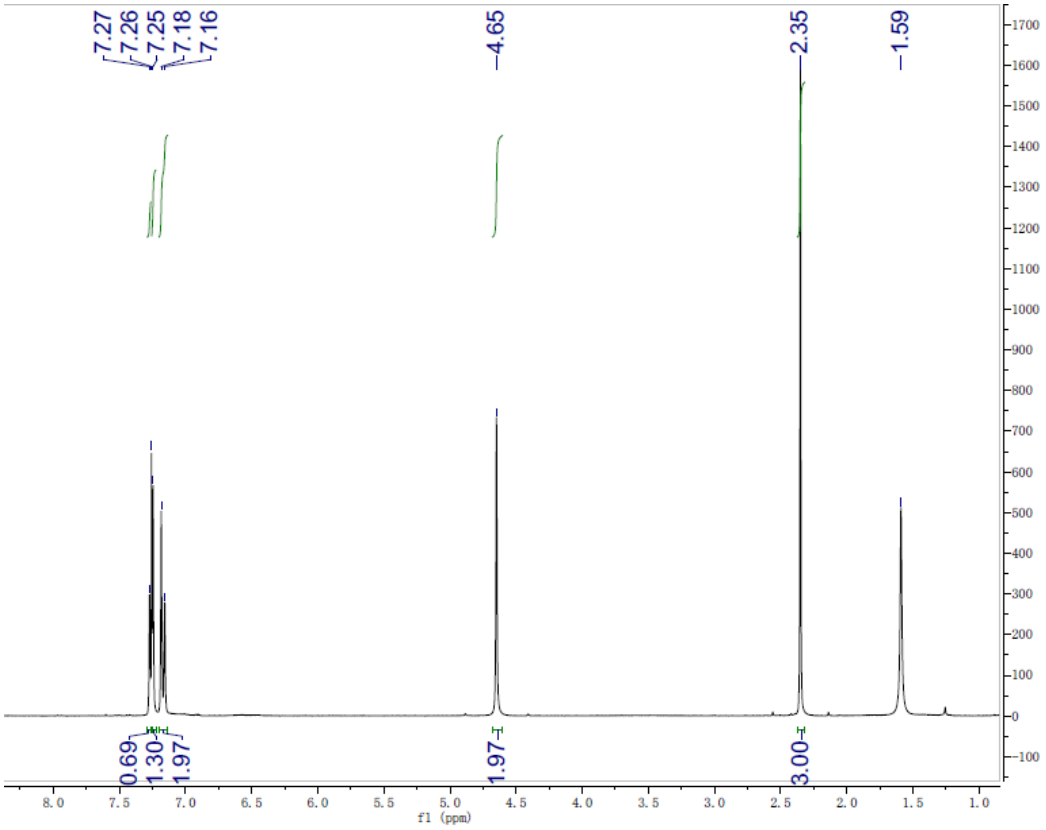


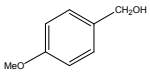
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.50-7.23 (m, Ar, 4H), 4.67 (t, CH_2, 2H), 1.72 (s, OH, 1H).



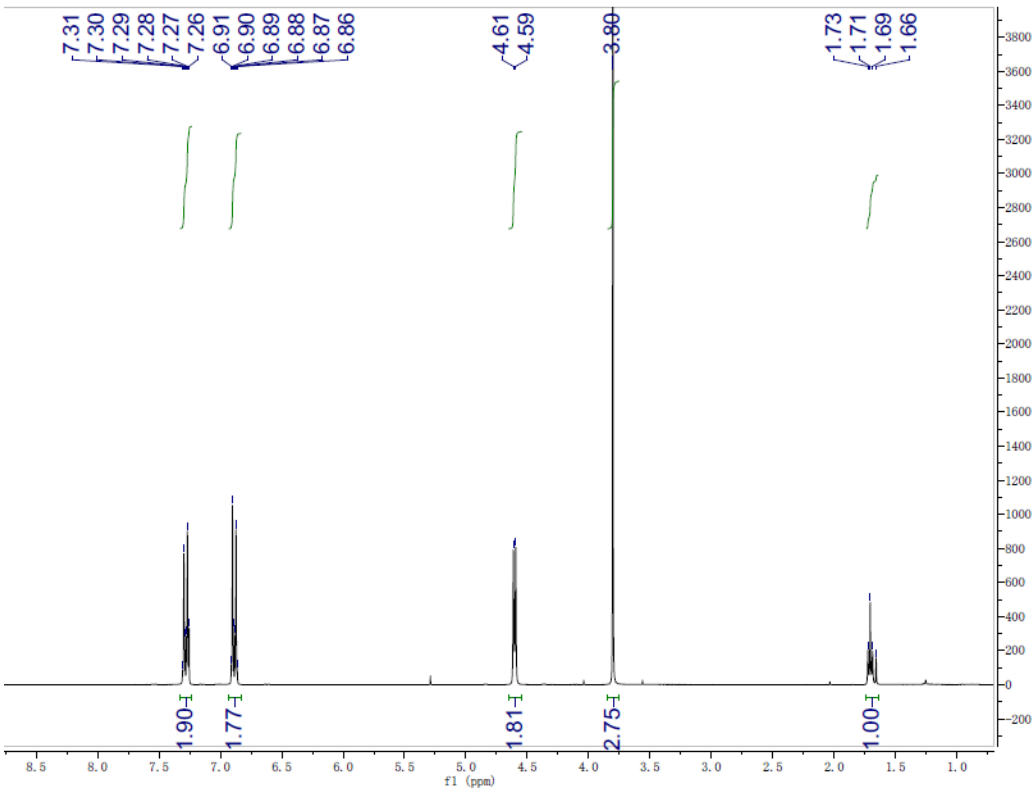


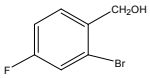
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.27-7.16 (m, Ar, 4H), 4.65 (s, CH_2, 2H), 2.35 (s, CH_3, 3H), 1.70 (s, OH, 1H).



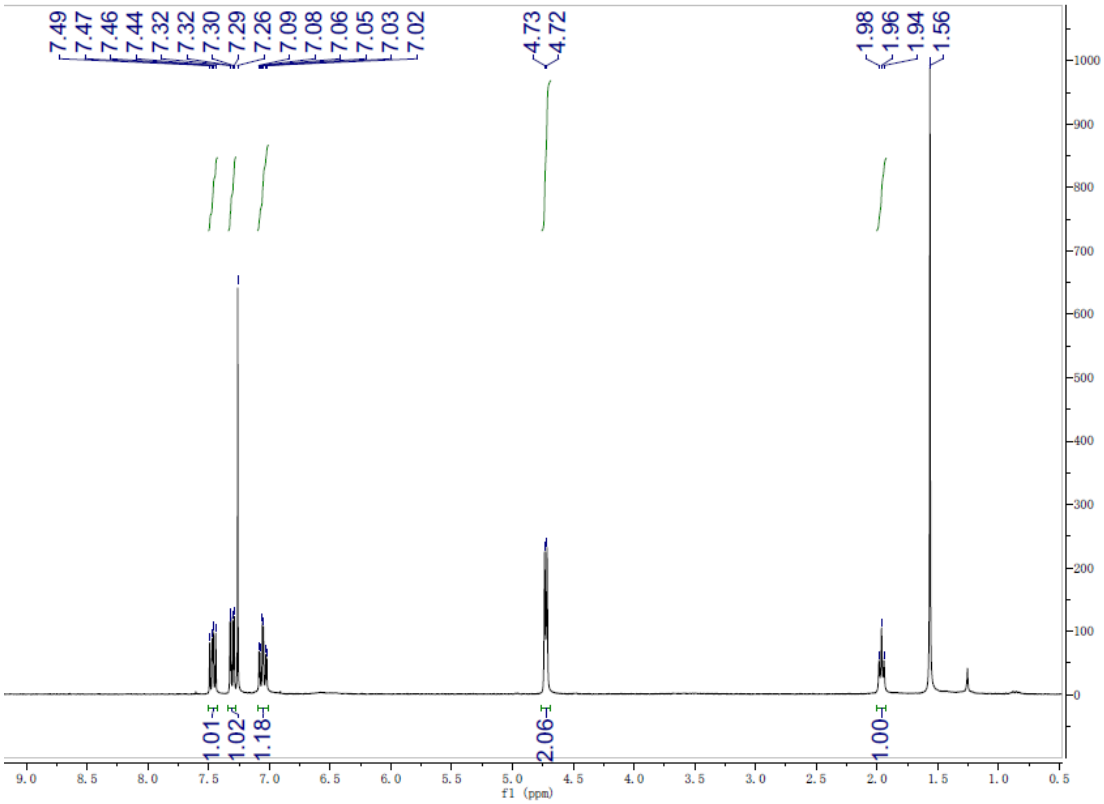


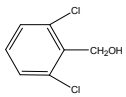
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.31-6.86 (m, Ar, 4H), 4.61-4.59 (d, CH_2, 2H), 3.80 (s, CH_3, 3H), 1.73-1.69 (t, OH, 1H).



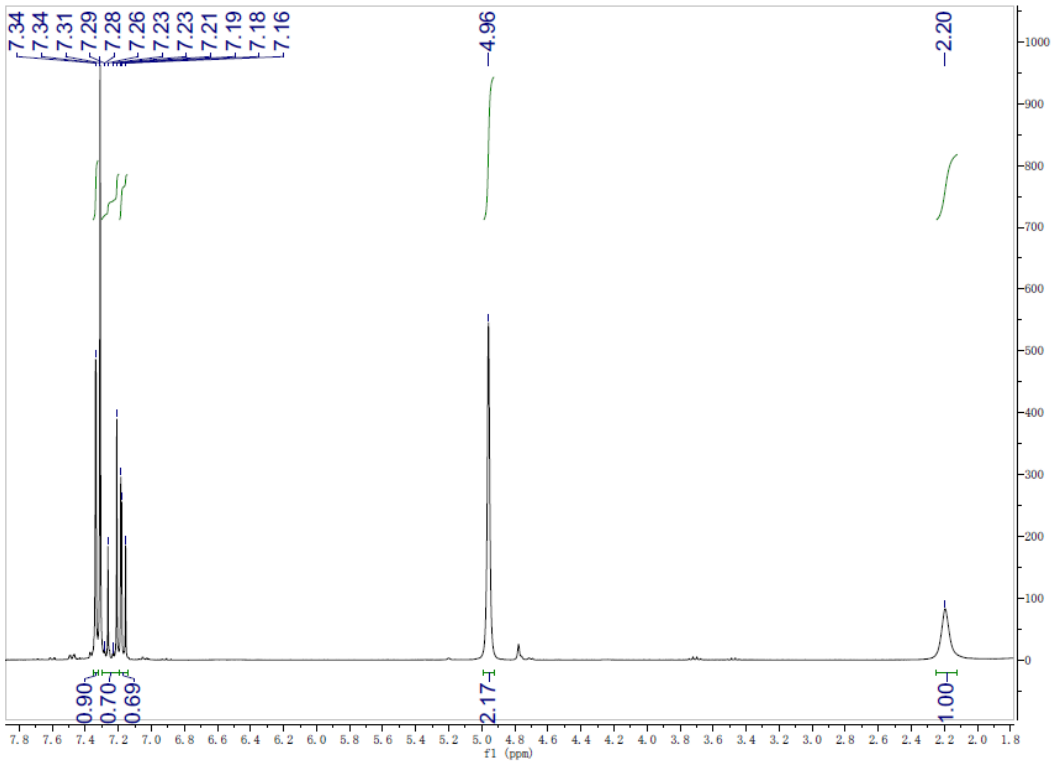


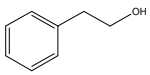
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.49-7.02 (m, Ar, 3H), 4.73-4.72 (d, CH_2, 2H), 1.98-1.94 (t, OH, 1H).



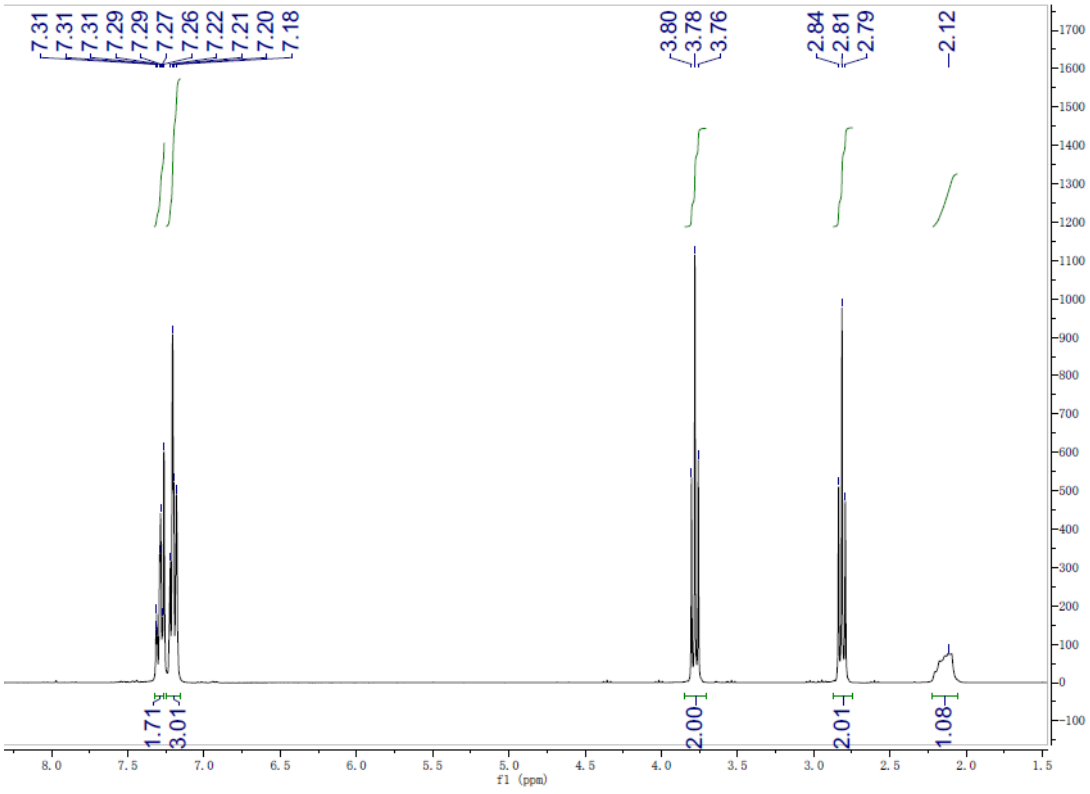


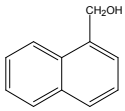
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.34-7.16 (m, Ar, 3H), 4.96 (s, CH_2, 2H), 2.20 (s, OH, 1H).



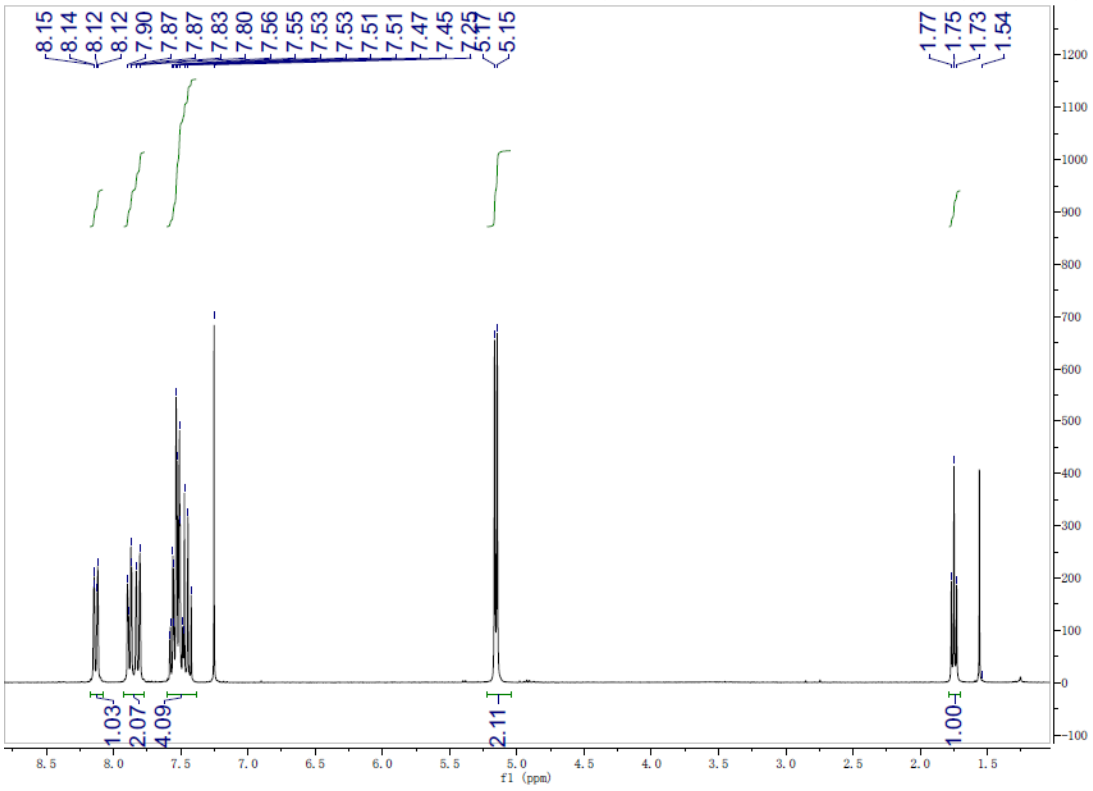


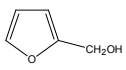
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.31-7.18 (m, Ar, 5H), 3.78 (t, CH_2, 2H), 2.81 (t, CH_2, 2H), 2.12 (s, OH, 1H).



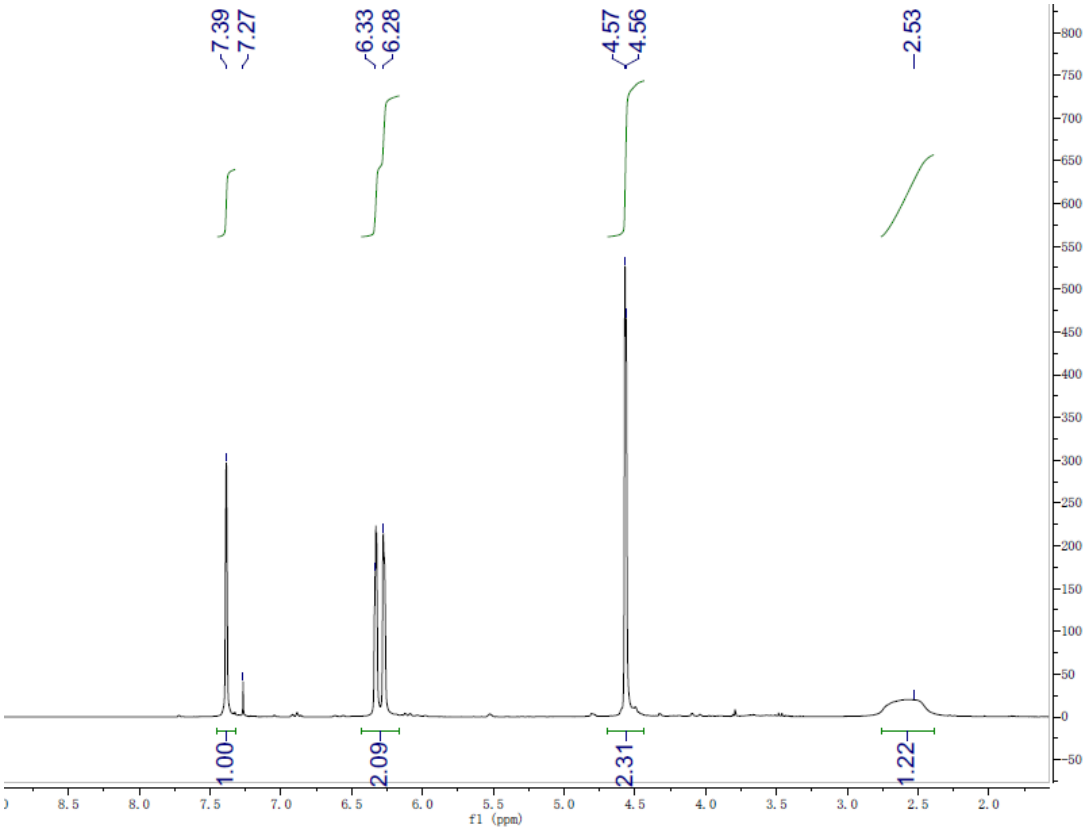


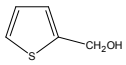
^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.15-7.45 (m, Ar, 7H), 5.17-5.15 (d, CH_2, 2H), 1.75 (t, OH, 1H).



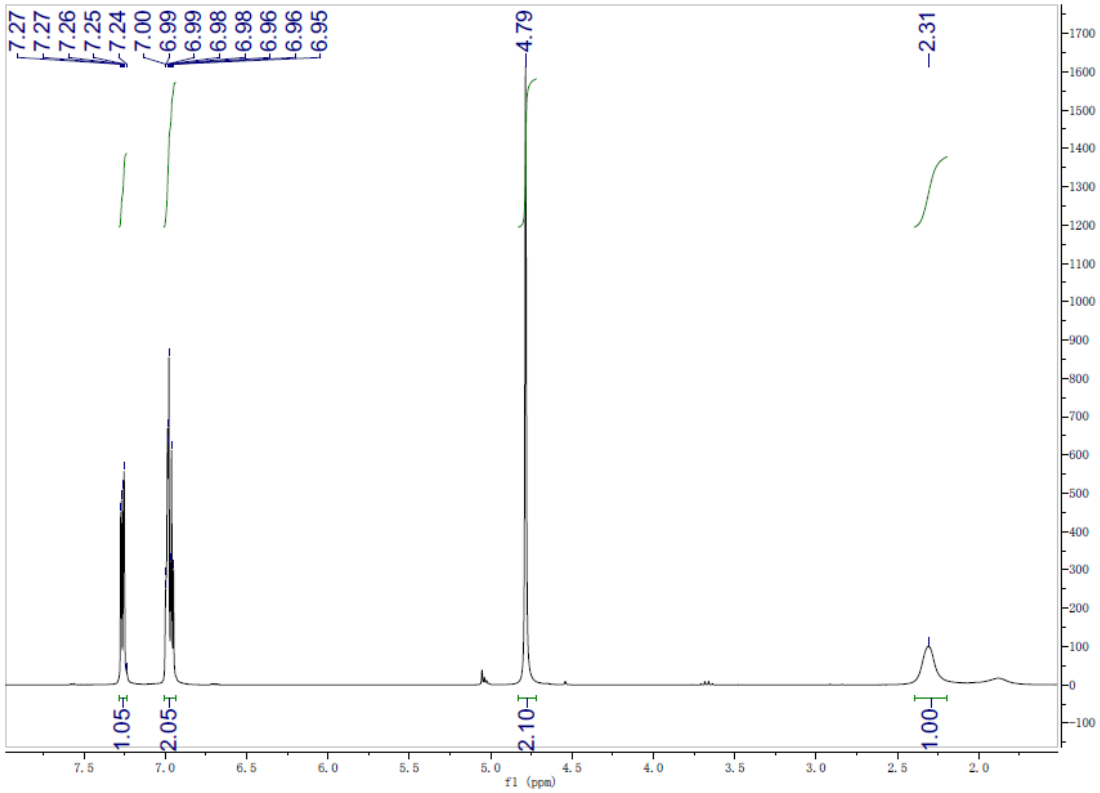


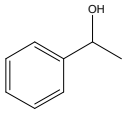
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.39-6.28 (m, Ar, 3H), 4.57 (s, CH_2, 2H), 2.53 (s, OH, 1H).



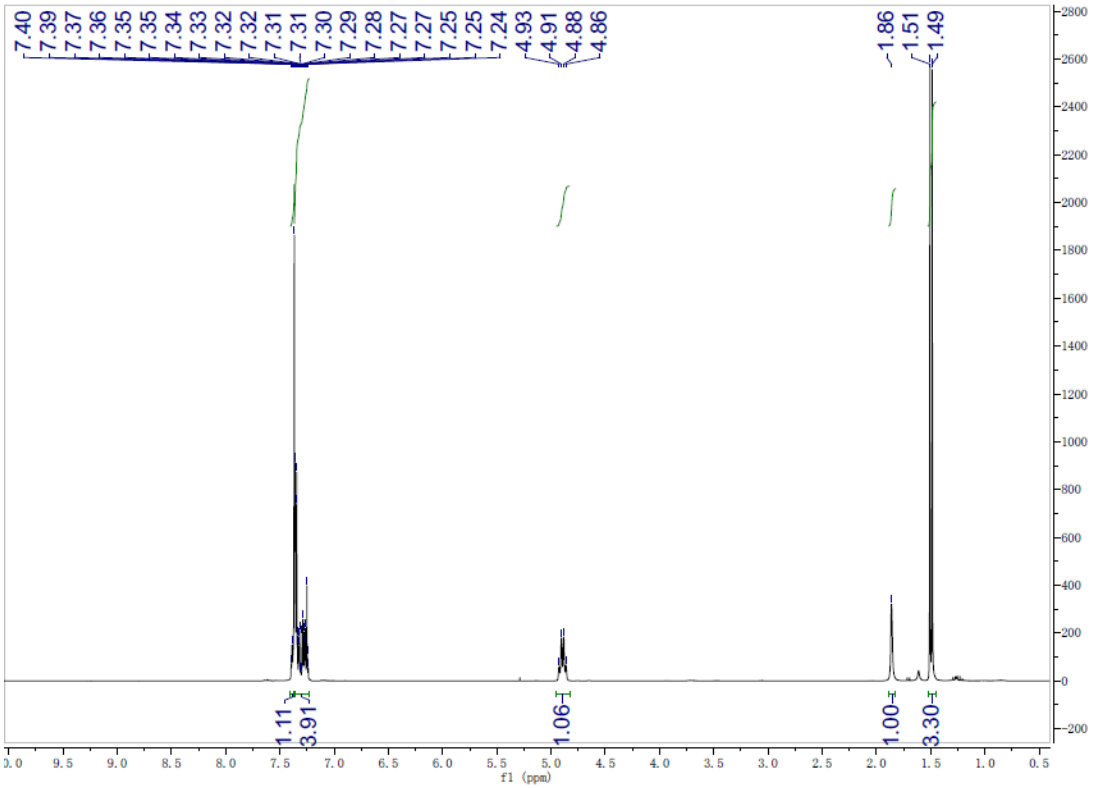


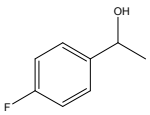
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.27-6.95 (m, Ar, 3H), 4.79 (s, CH_2, 2H), 2.31 (s, OH, 1H).



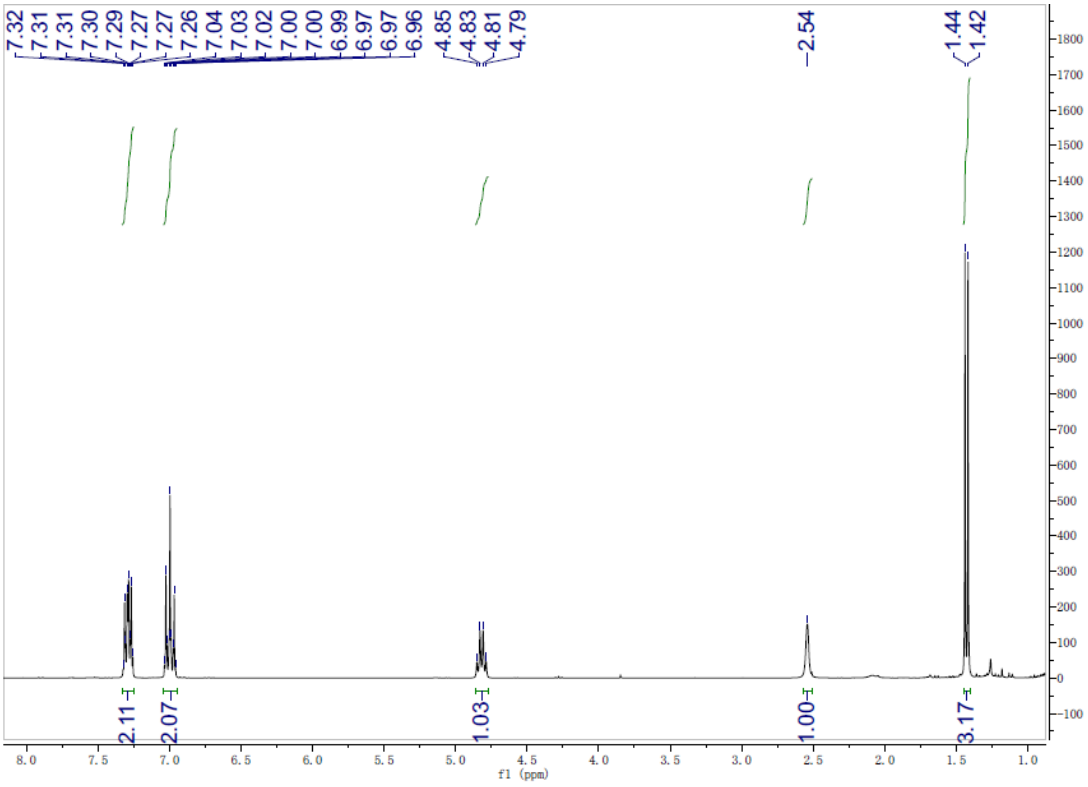


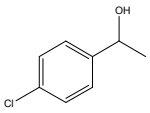
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.40-7.24 (m, Ar, 5H), 4.88 (q, CH, 1H), 1.86 (s, OH, 1H), 1.51 (d, CH_3, 3H).



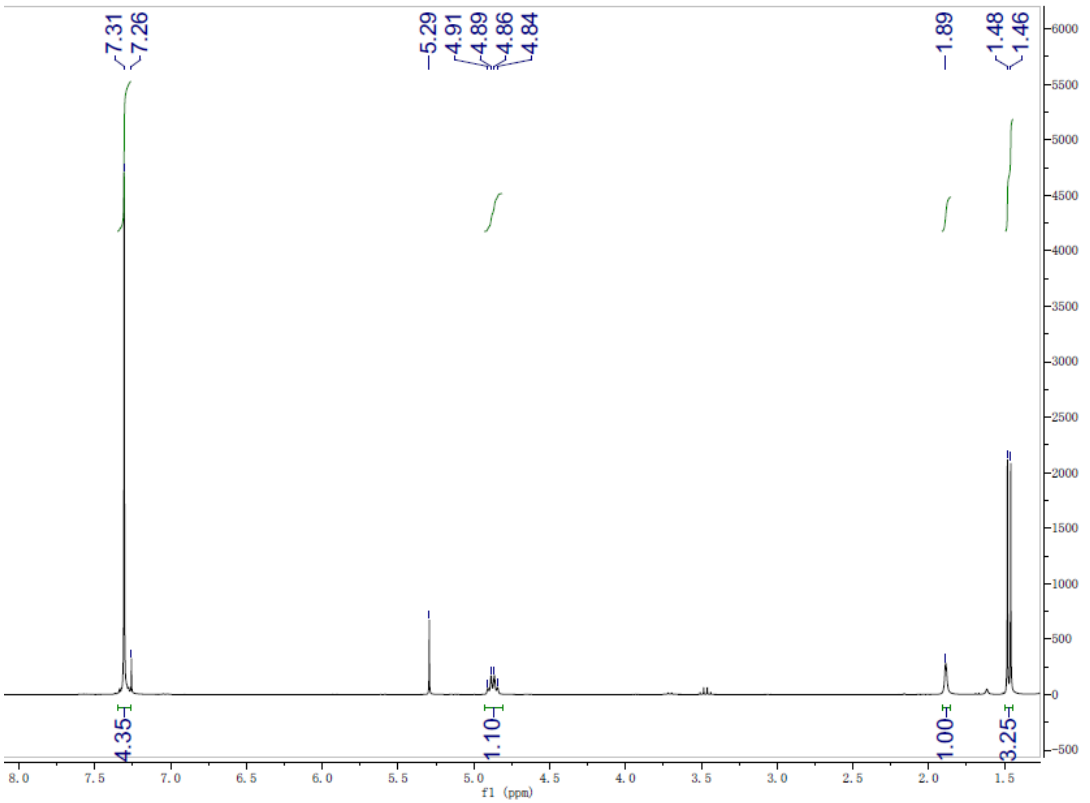


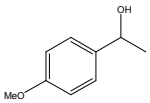
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.32-6.96 (m, Ar, 4H), 4.85-4.79 (q, CH, 1H), 2.54 (s, OH, 1H), 1.43 (d, CH_3, 3H).



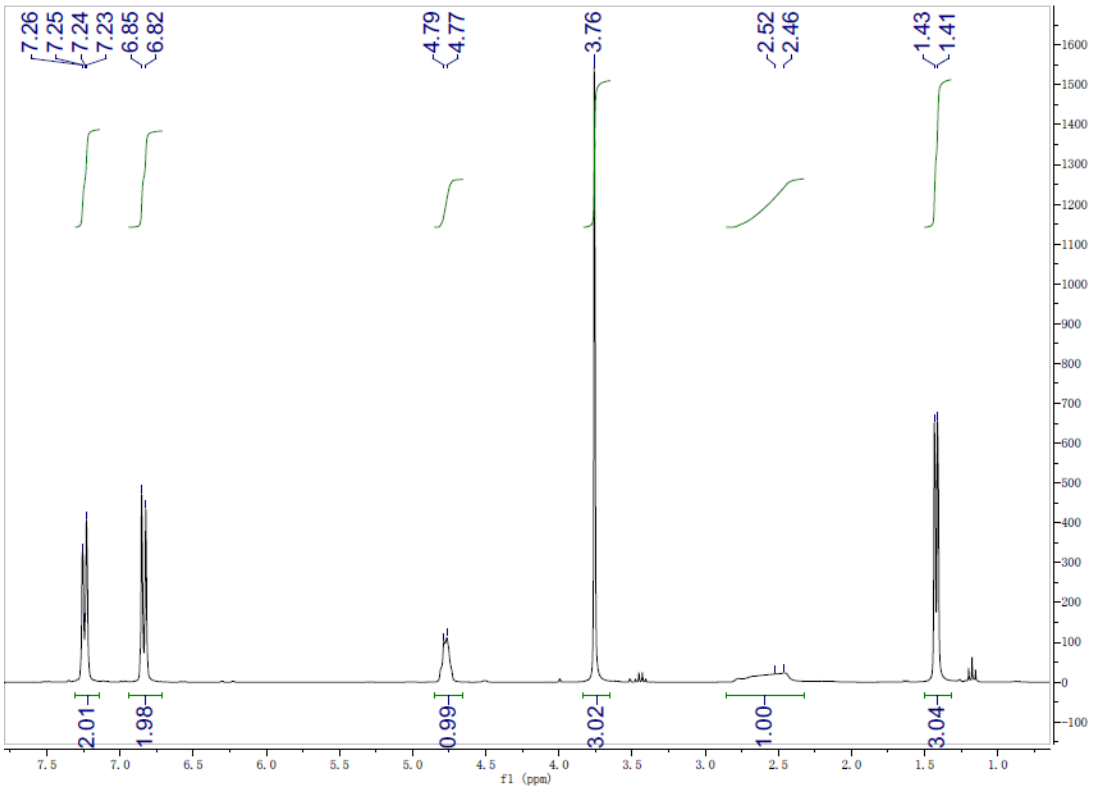


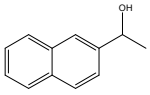
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.31-7.26 (m, Ar, 4H), 4.88 (q, CH, 1H), 1.89 (s, OH, 1H), 1.47 (d, CH_3, 3H).



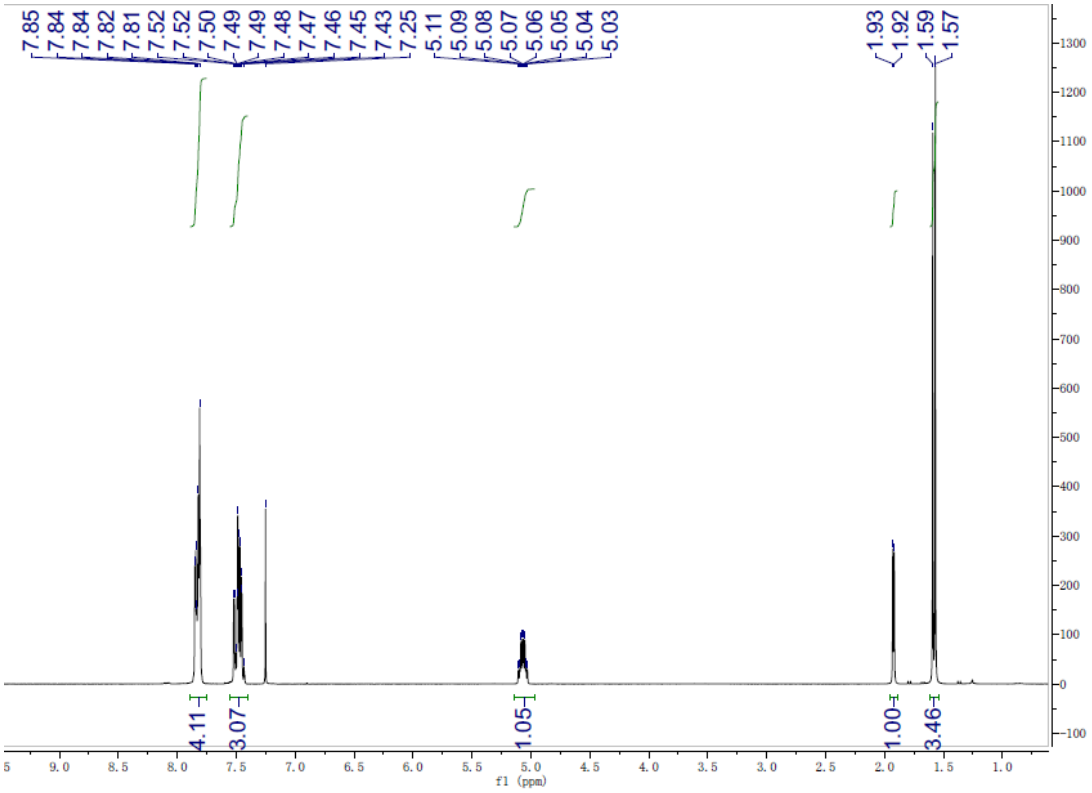


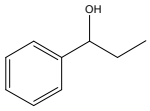
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.26-6.82 (m, Ar, 4H), 4.78 (q, CH, 1H), 3.76 (s, CH_3, 3H), 2.50 (s, OH, 1H), 1.42 (d, CH_3, 3H).



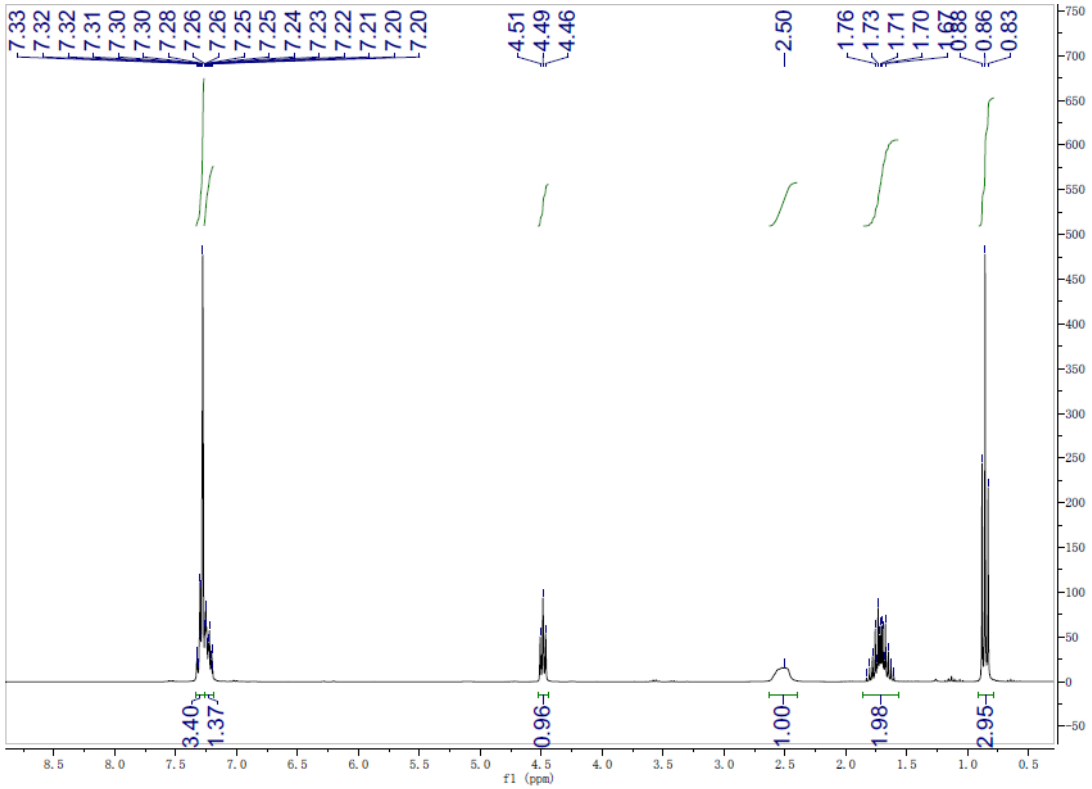


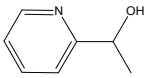
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.85-7.25 (m, Ar, 7H), 5.07 (m, CH, 1H), 1.92 (s, OH, 1H), 1.58 (d, CH_3, 3H).



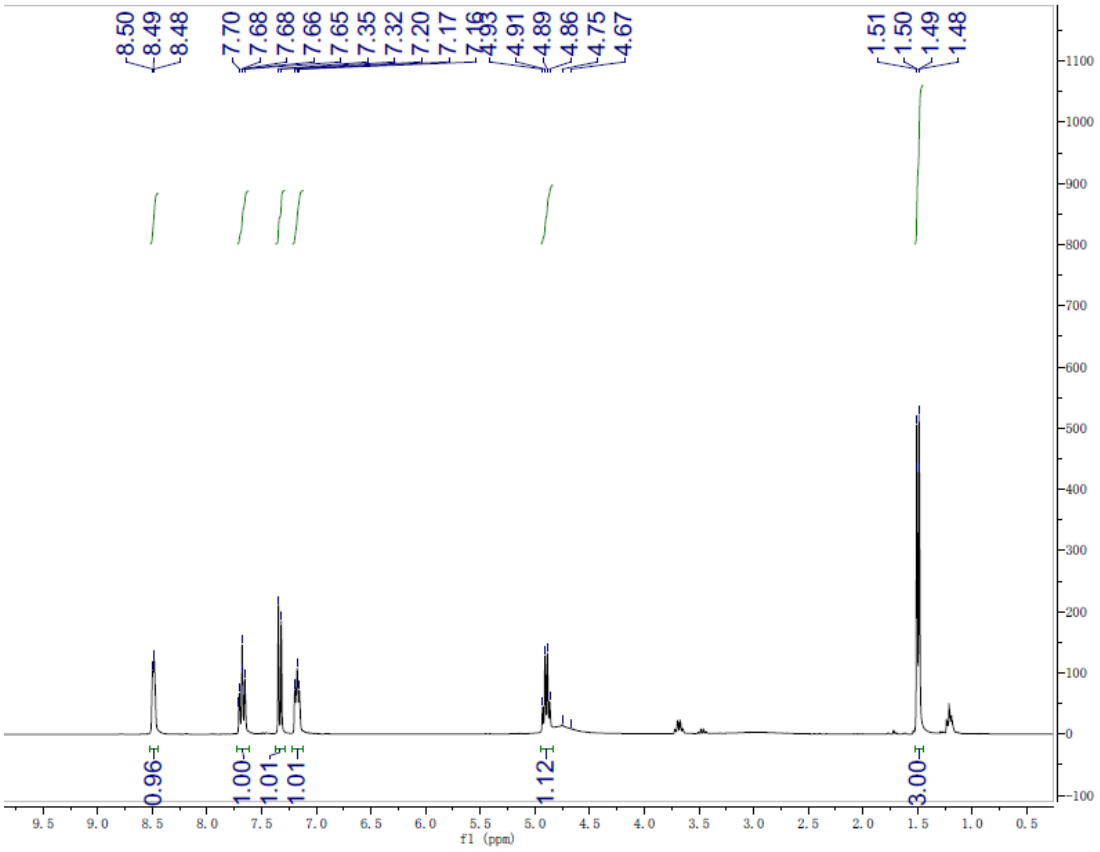


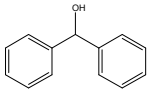
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.33-7.20 (m, Ar, 5H), 4.49 (t, CH, 1H), 2.50 (s, OH, 1H), 1.72 (m, CH_2, 2H), 0.86 (t, CH_3, 3H).



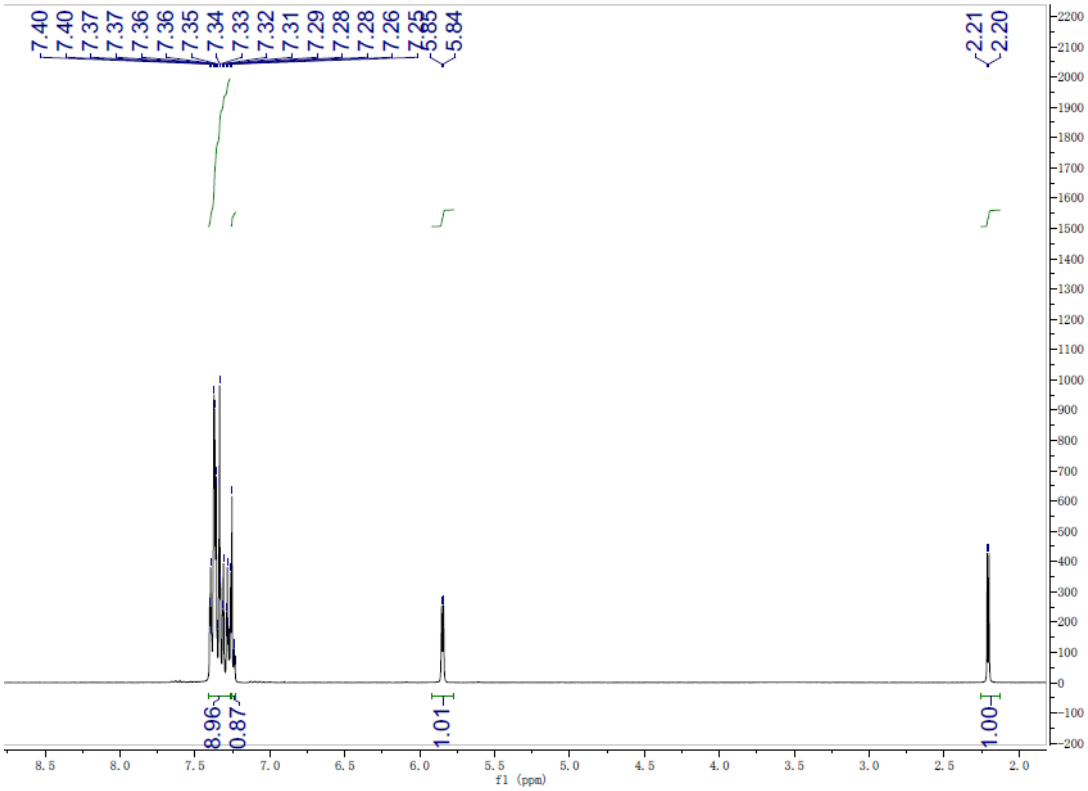


^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.50-7.16 (m, Ar, 4H), 4.90 (q, CH, 1H), 1.50 (d, CH_3, 3H).





^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.40-7.25 (m, Ar, 7H), 5.85 (d, CH, 1H), 2.20 (d, OH, 1H).


7.40
7.40
7.37
7.37
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.29
7.28
7.28
7.26
5.85
5.84
2.21
2.20
8.96
0.87
1.01
1.00
f1 (ppm)