Supporting Information

Synthesis of [POCOP]-Pincer Iron and Cobalt Complexes via C_{sp3}-H Activation and Catalytic Application of Iron Hydride in Hydrosilylation Reactions

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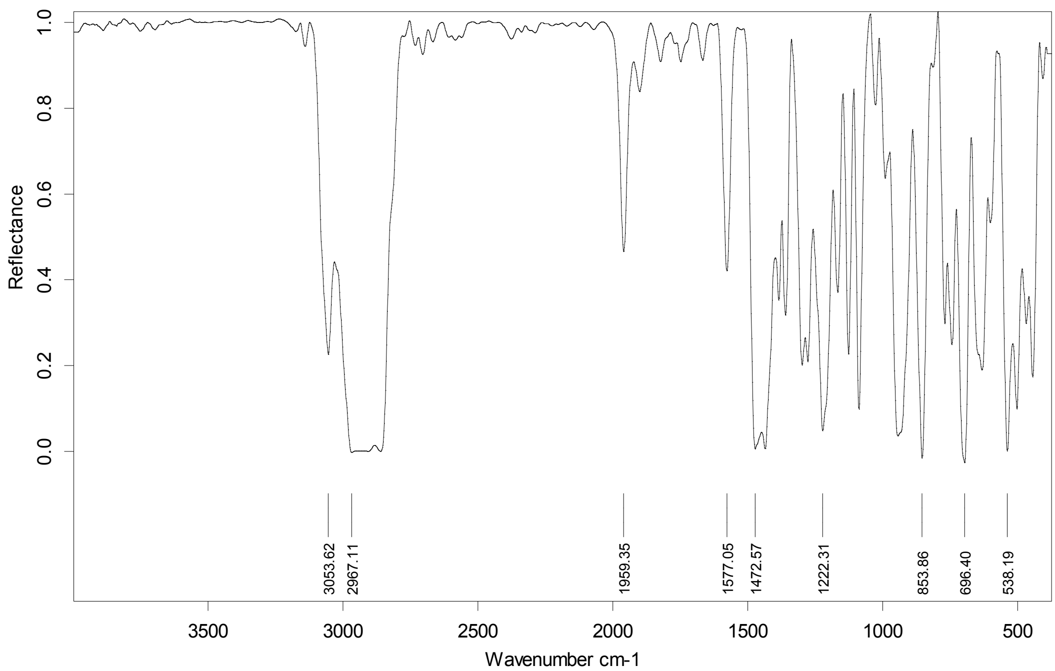
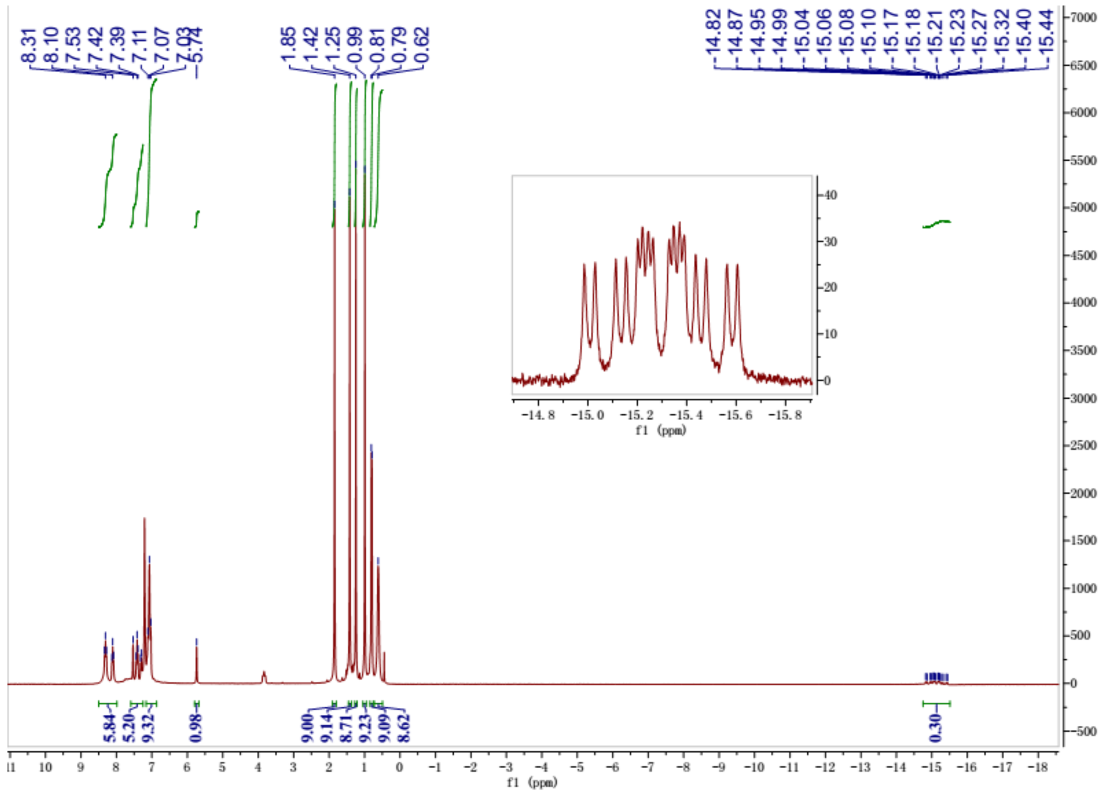
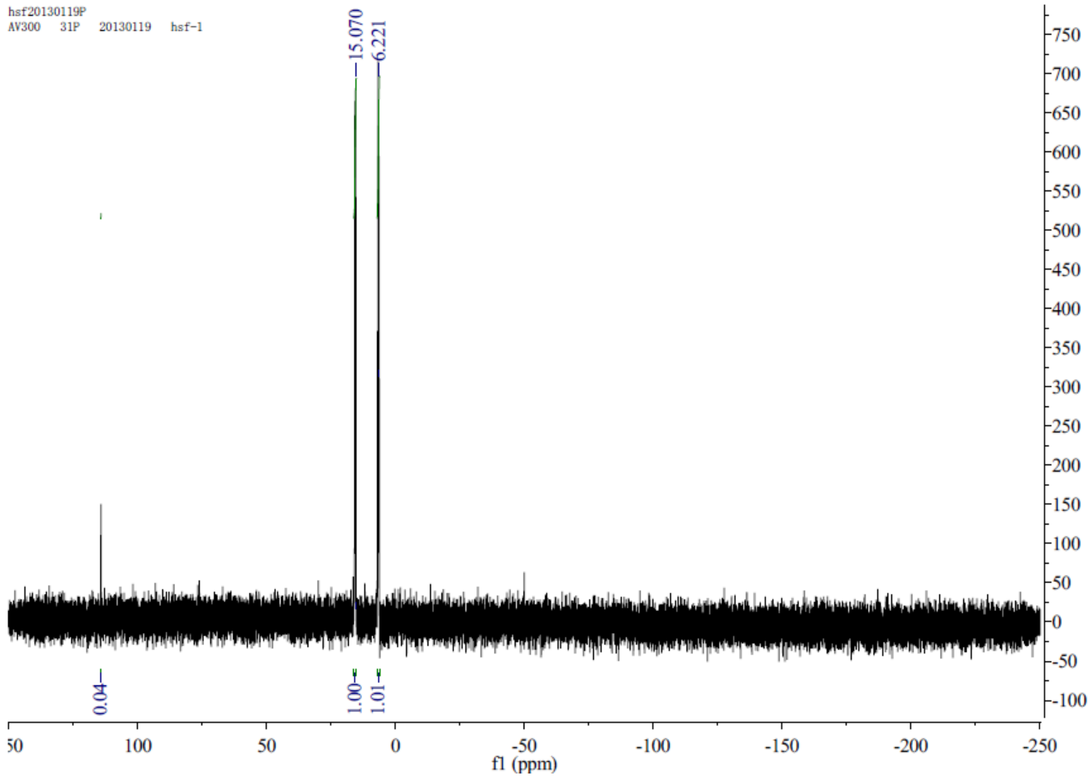
IR and NMR spectra of complexes 2, 3, 4, and 5



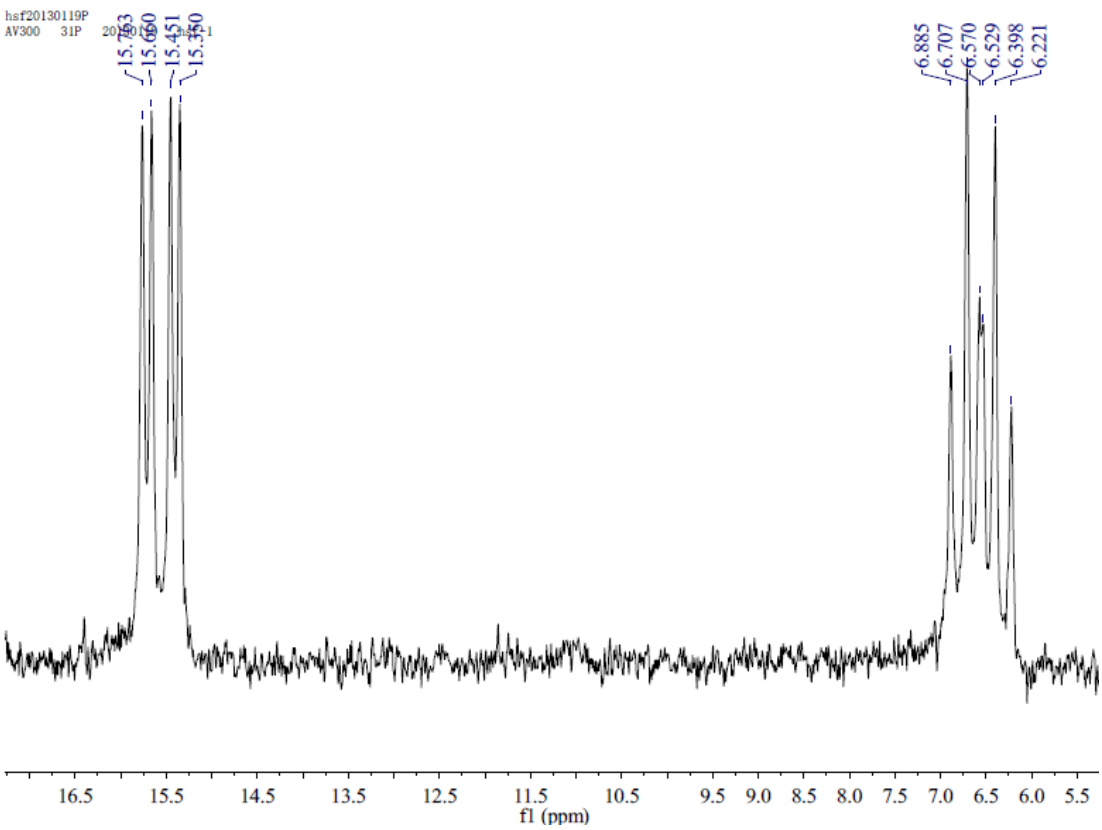
IR spectrum of complex **2**



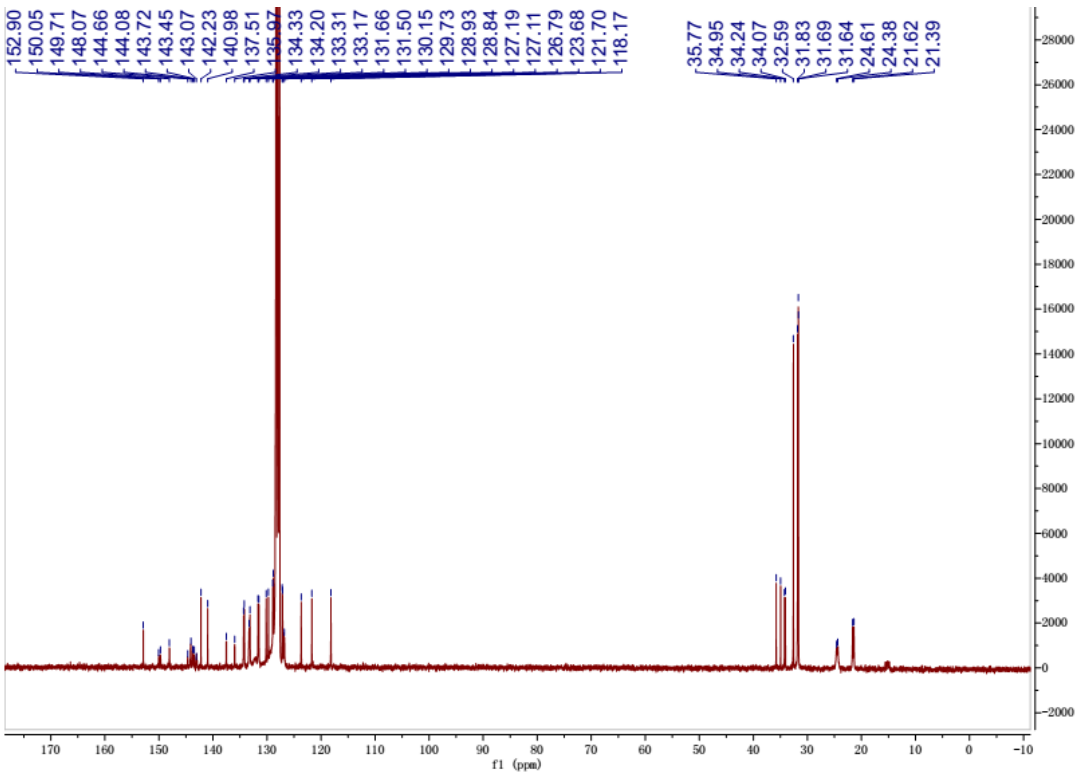
^{1}H NMR spectrum of complex **2**



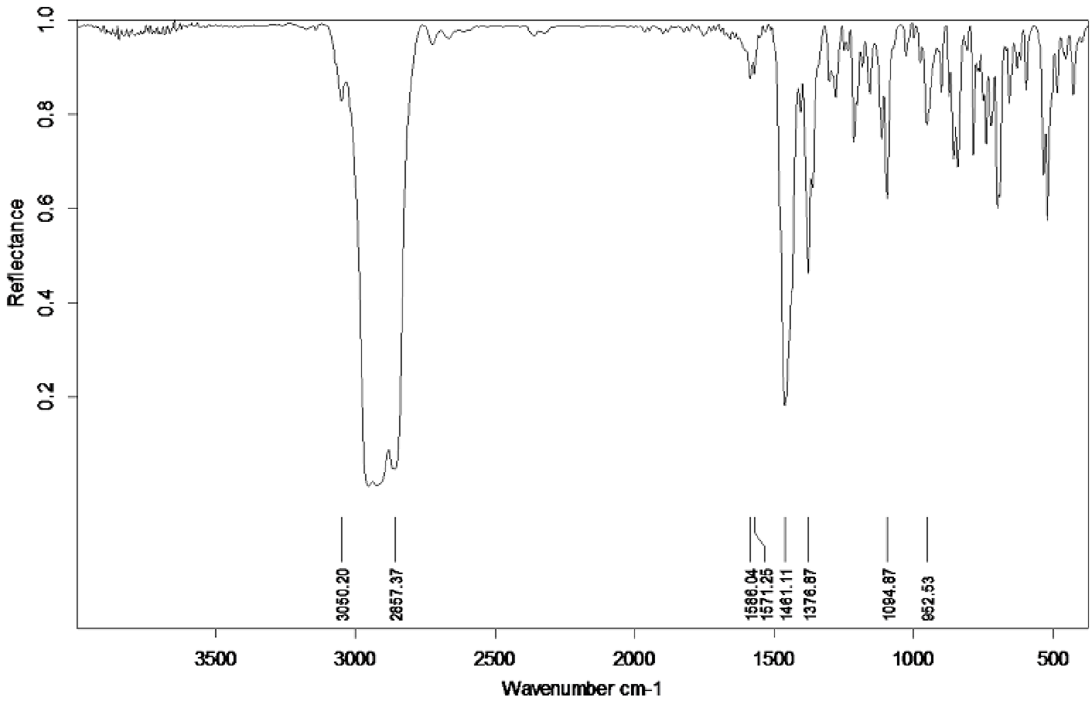
Amplification:



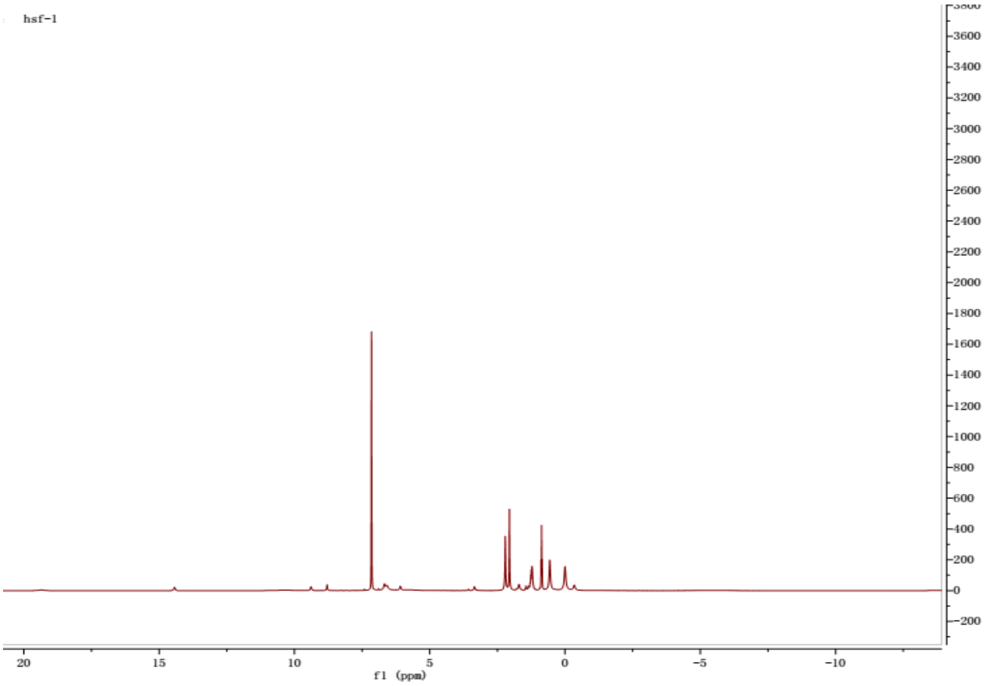
$^{31}P\{^{1}H\}$ NMR spectrum of complex **2**



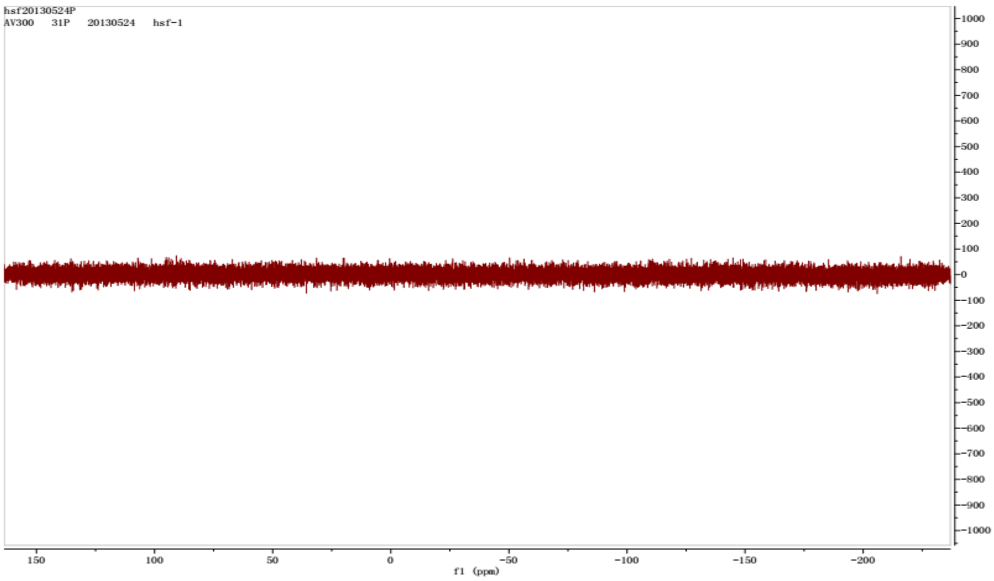
[13]C NMR spectrum of complex **2**



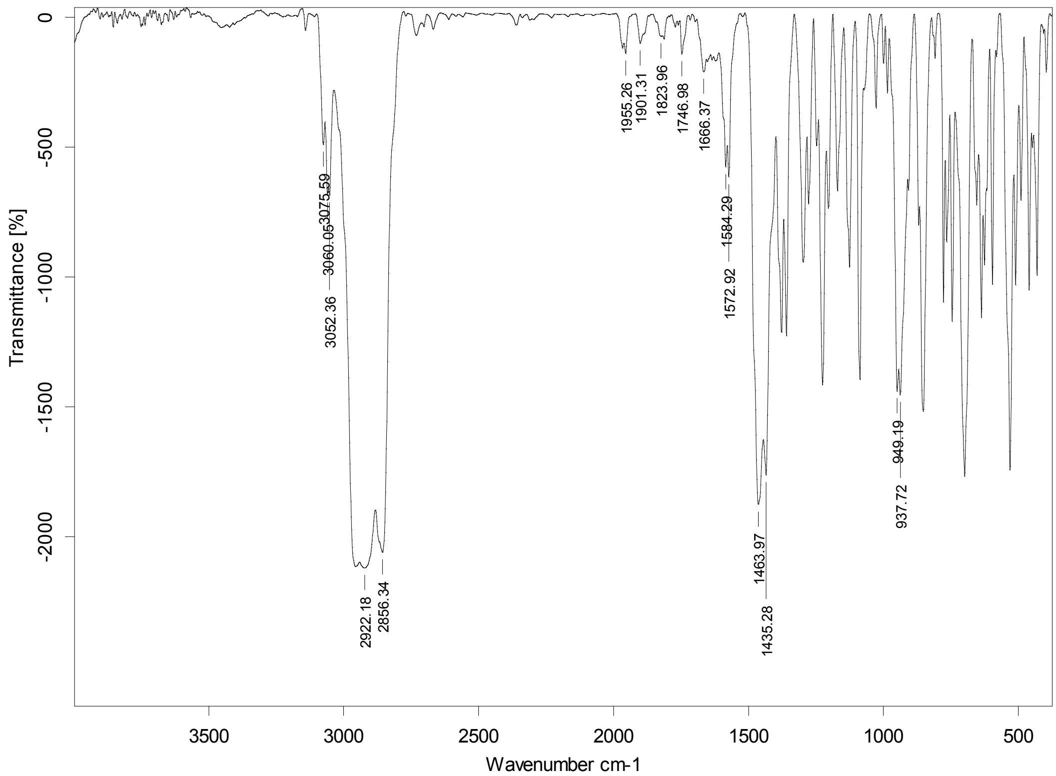
IR spectrum of complex **3**



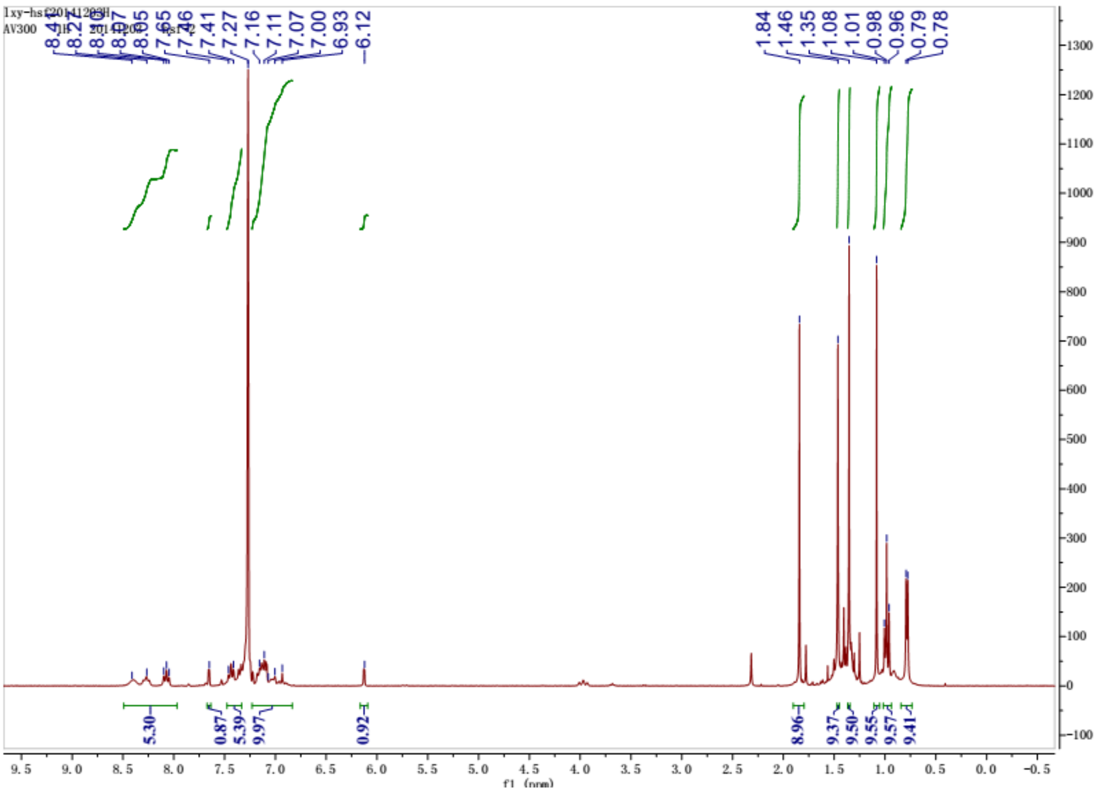
[1]H NMR spectrum of complex **3**



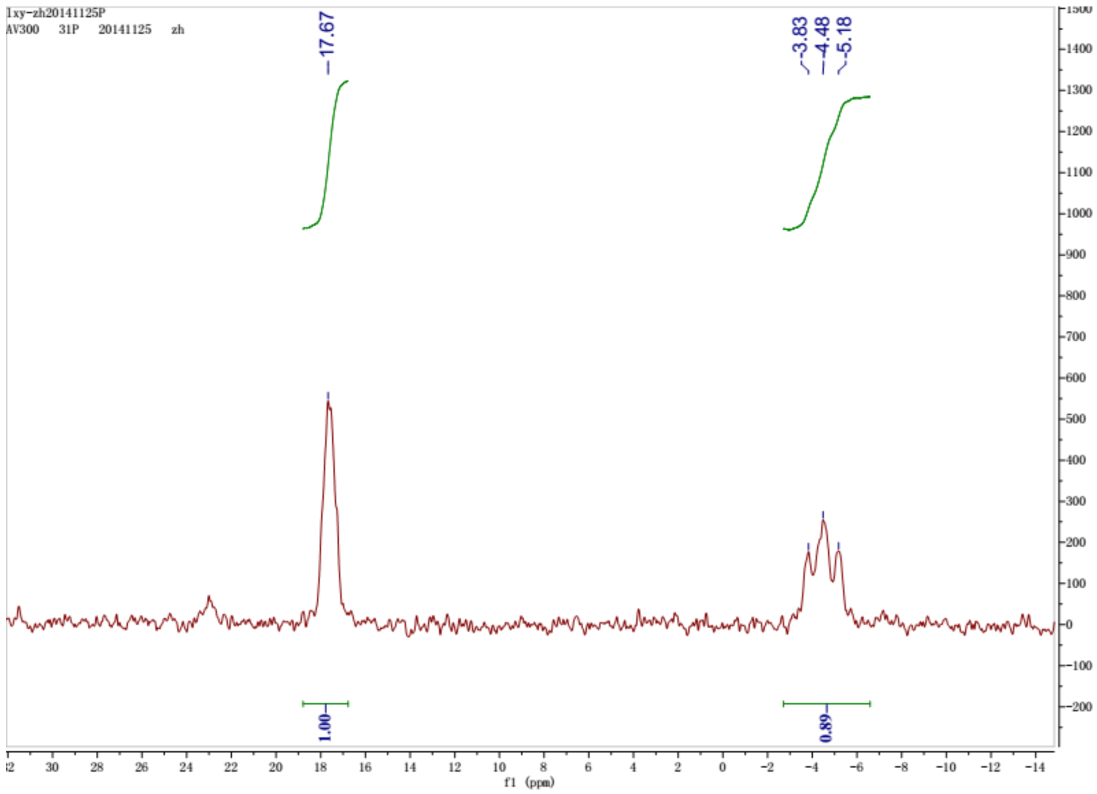
[31]P{[1]H} NMR spectrum of complex **3**



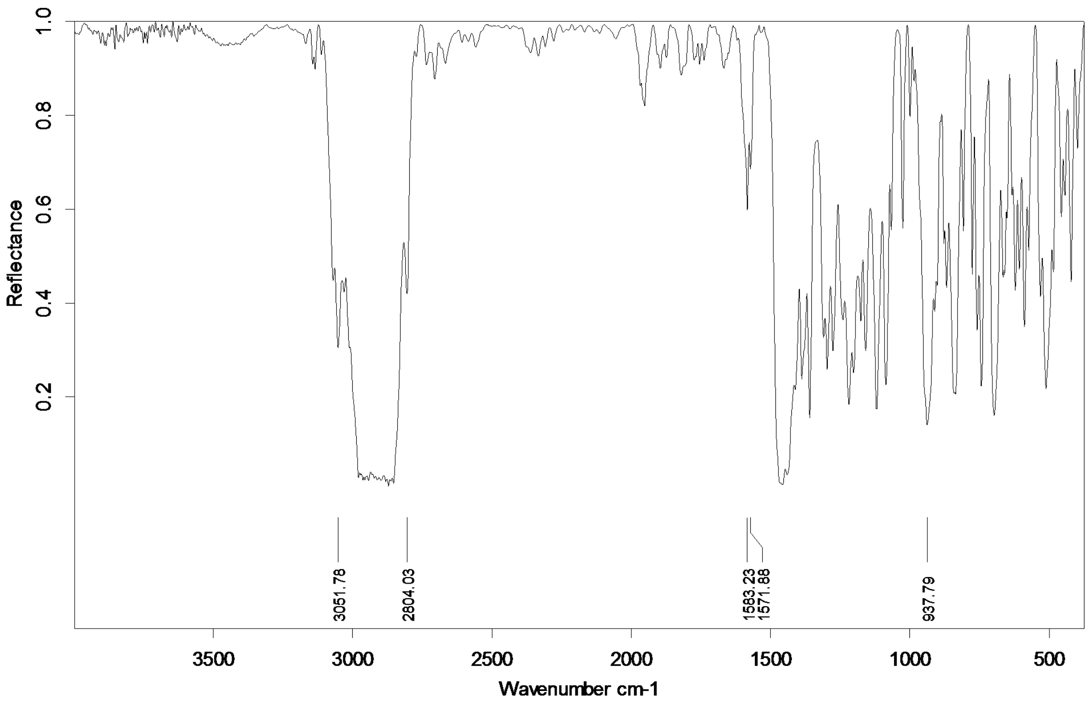
IR spectrum of complex **4**



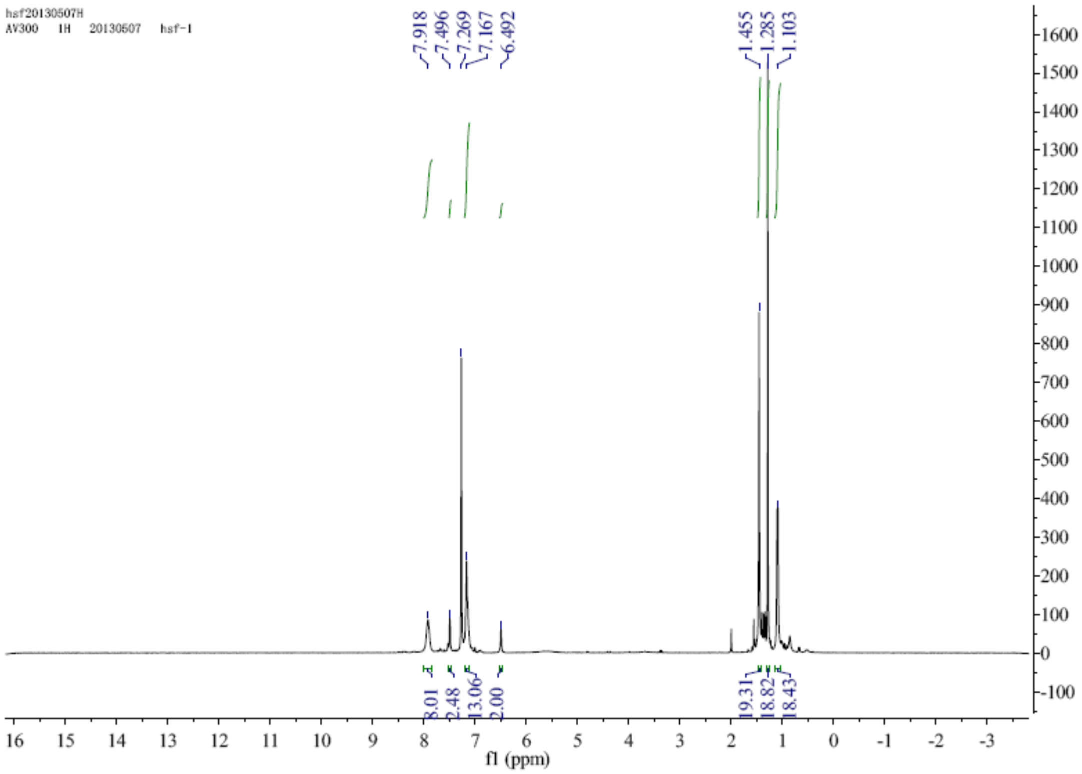
[1]H NMR spectrum of complex **4**



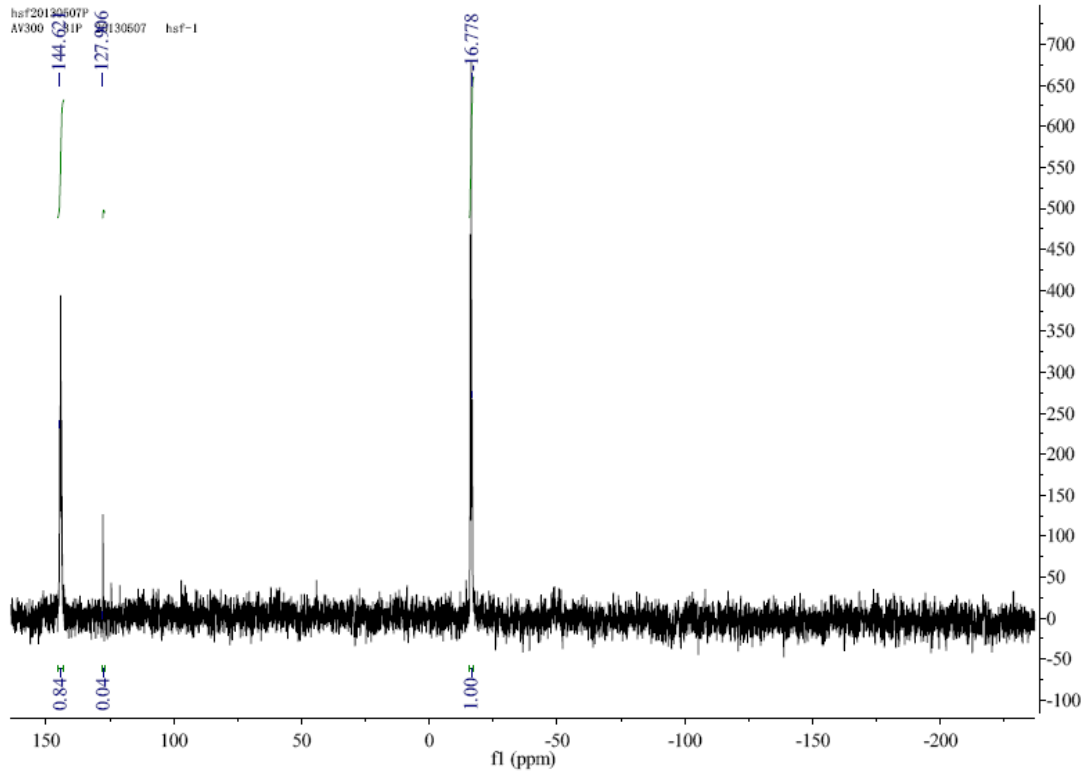
$^{31}P\{^1H\}$ NMR spectrum of complex **4**



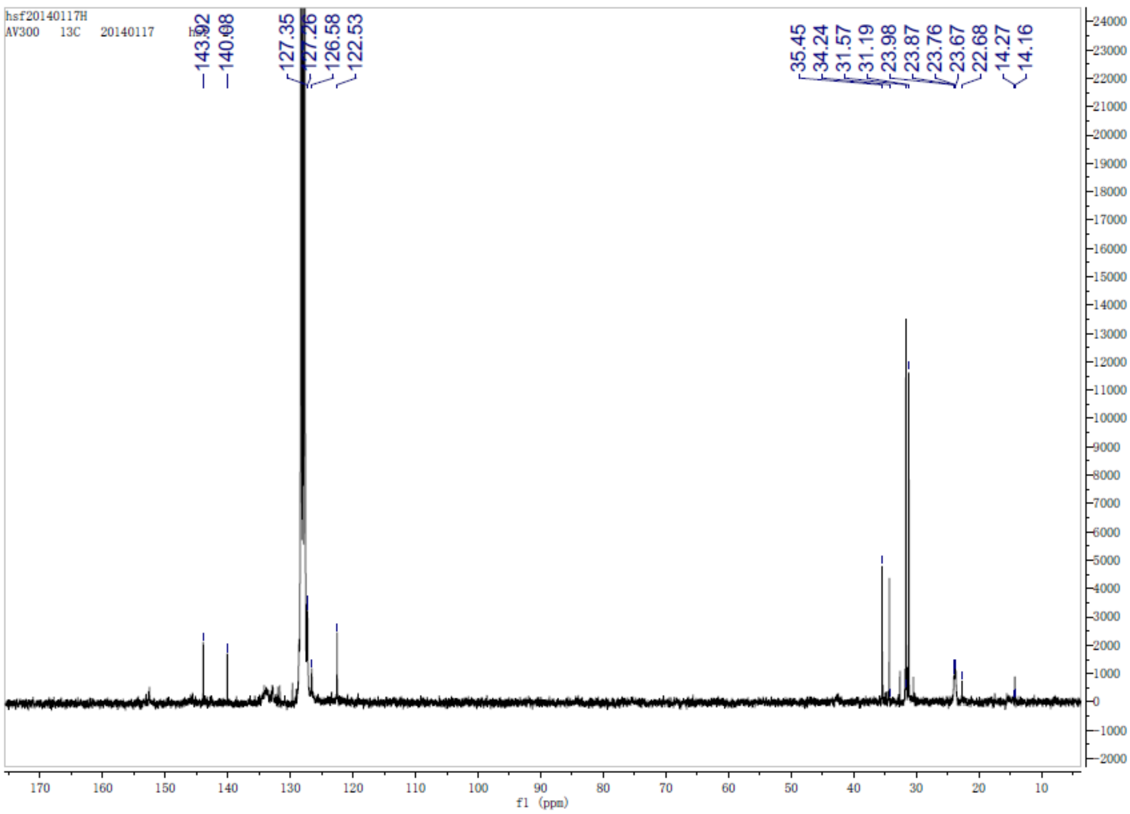
IR spectrum of complex **5**



^{1}H NMR spectrum of complex **5**

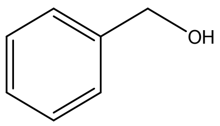


$^{31}P\{^{1}H\}$ NMR spectrum of complex **5**

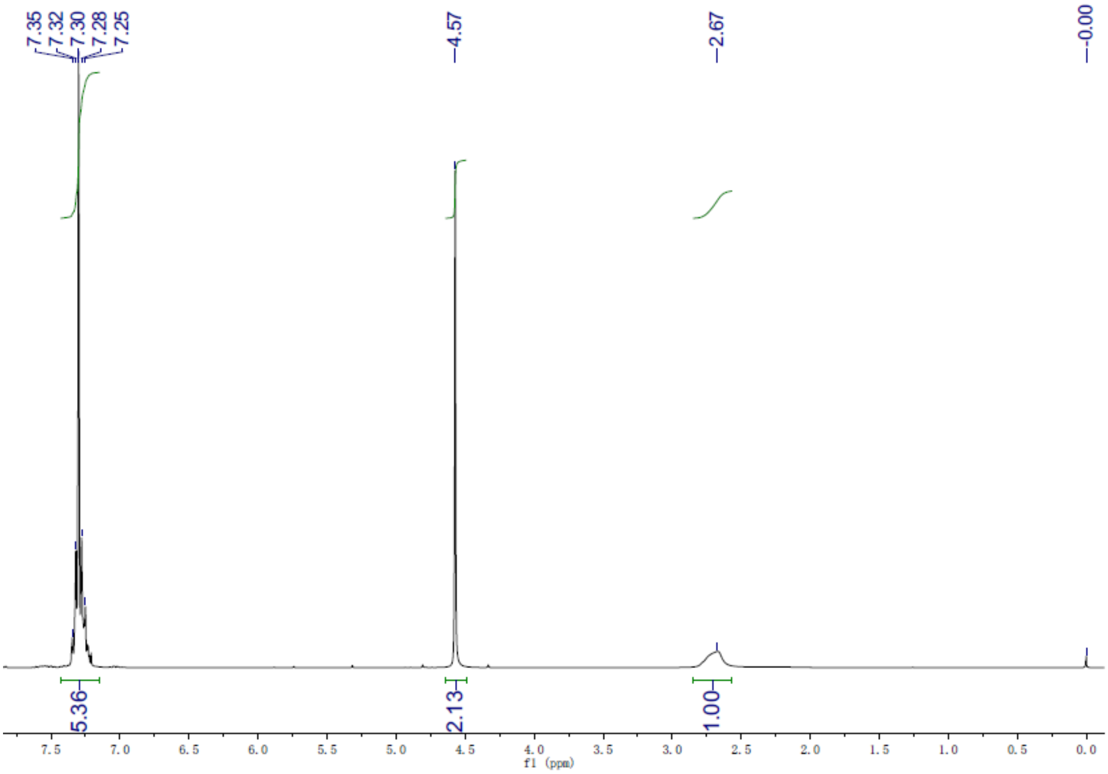


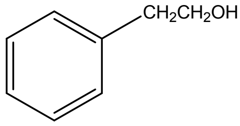
^{13}C NMR spectrum of complex **5**

·NMR data for the alcohol products

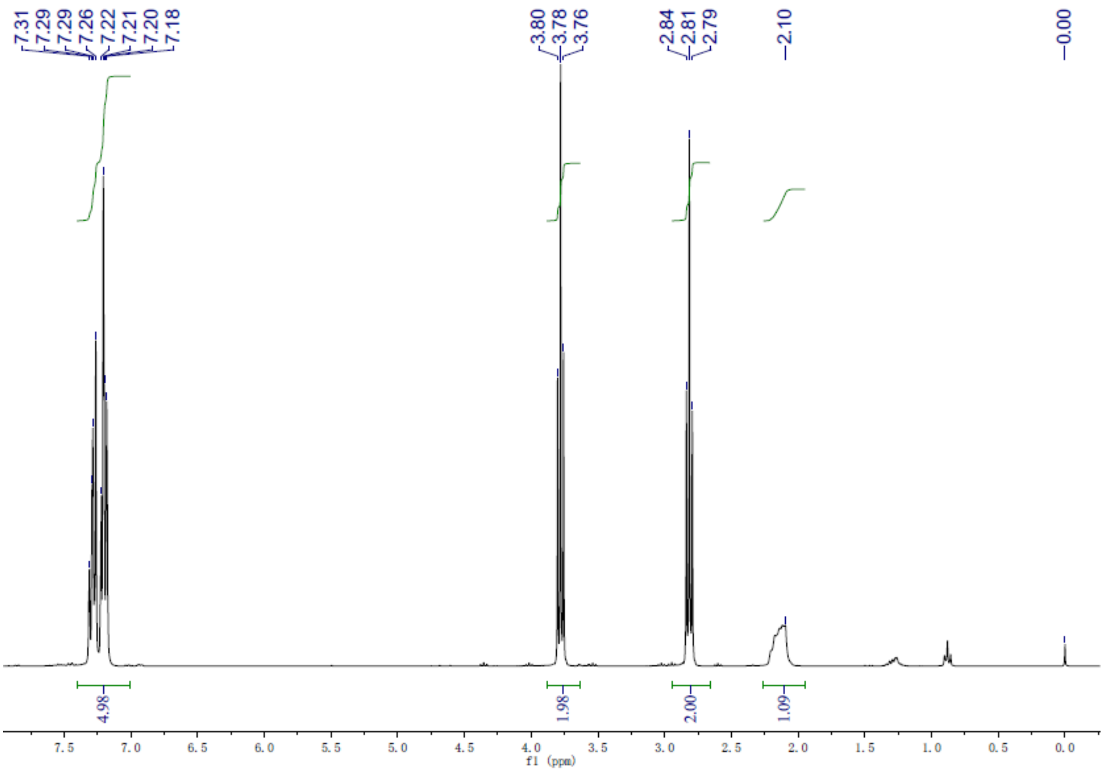


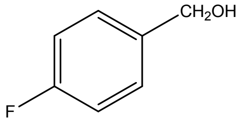
^{1}H NMR (300 MHz, CDCl3, δ): 7.35–7.25 (m, *Ar*, 5H), 4.57 (s, CH_2, 2H), 2.67 (s br, O*H*, 1H).



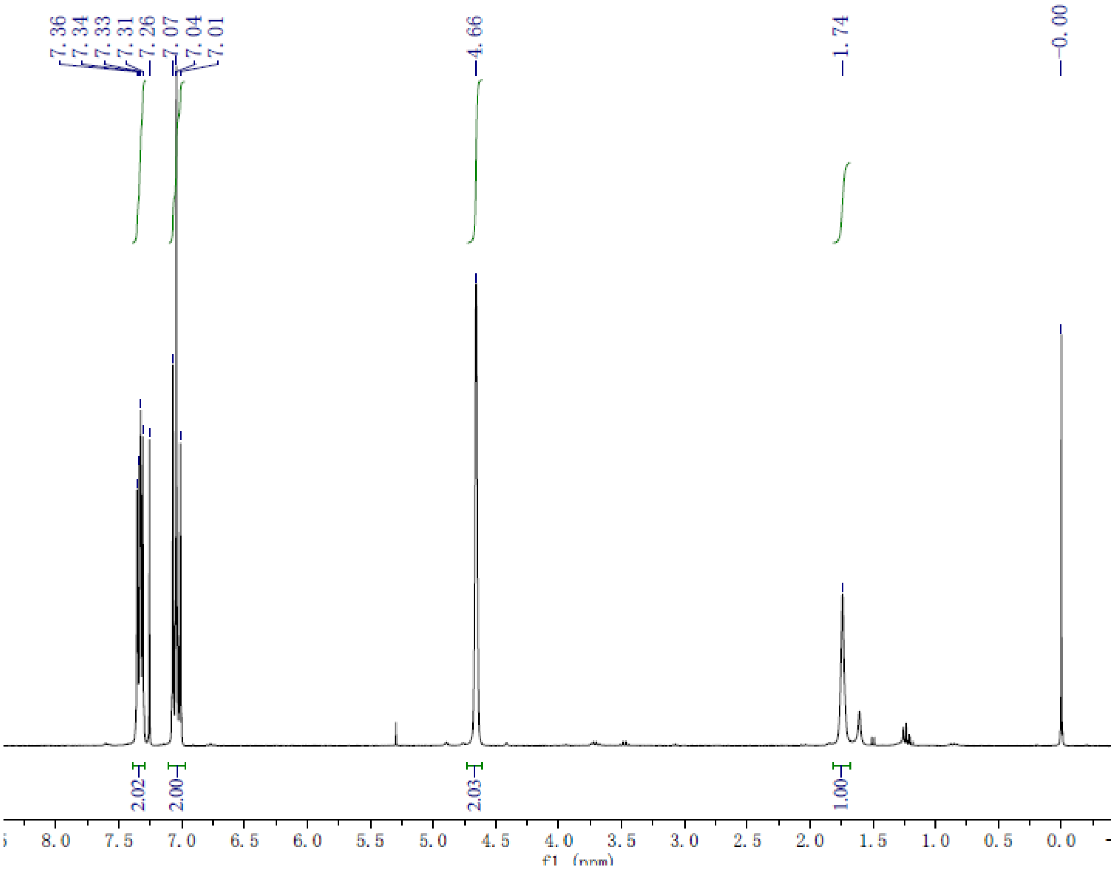


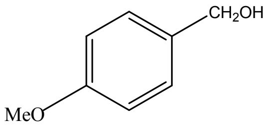
[1]H NMR (300 MHz, CDCl3, δ): 7.31–7.18 (m, *Ar*, 5H), 3.78 (t, CH_2, 2H), 2.81 (t, CH_2, 2H), 2.10 (s br, O*H*, 1H).



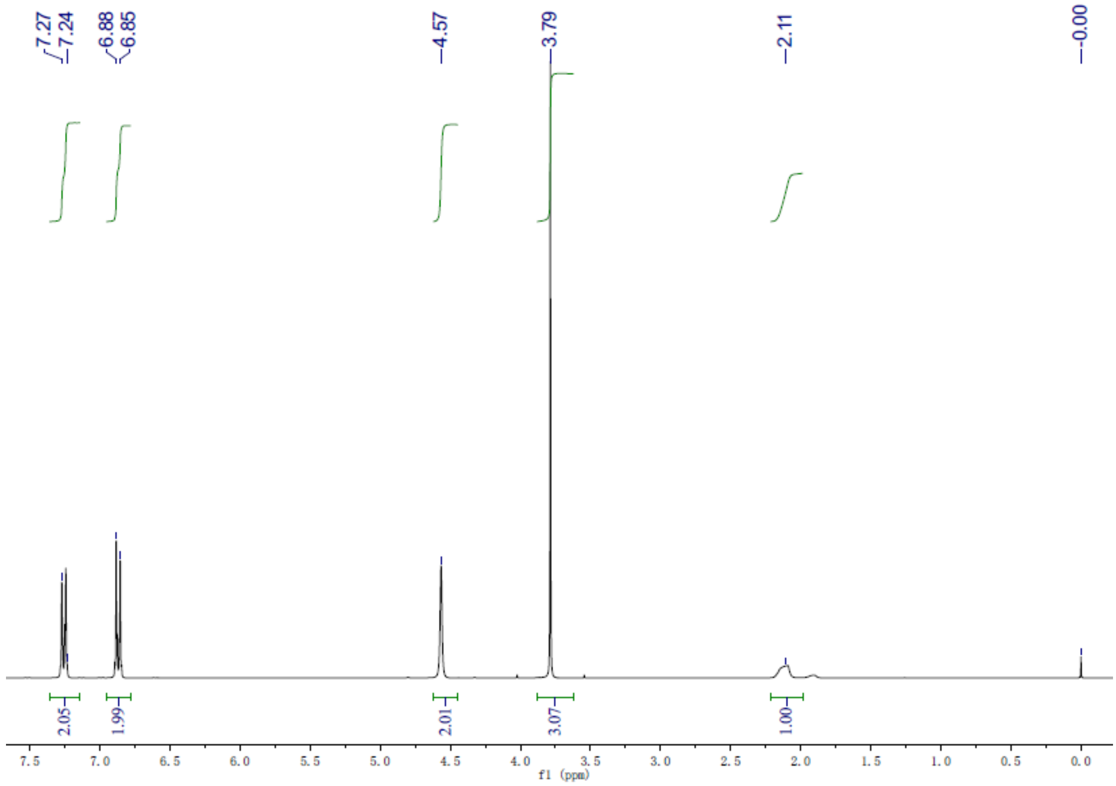


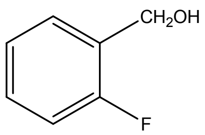
[1]H NMR (300 MHz, CDCl3, *δ*): 7.36–7.26 (m, *Ar*, 2H), 7.07–7.01 (m, *Ar*, 2H), 4.66 (s, CH_2, 2H), 1.74 (s, O*H*, 1H).



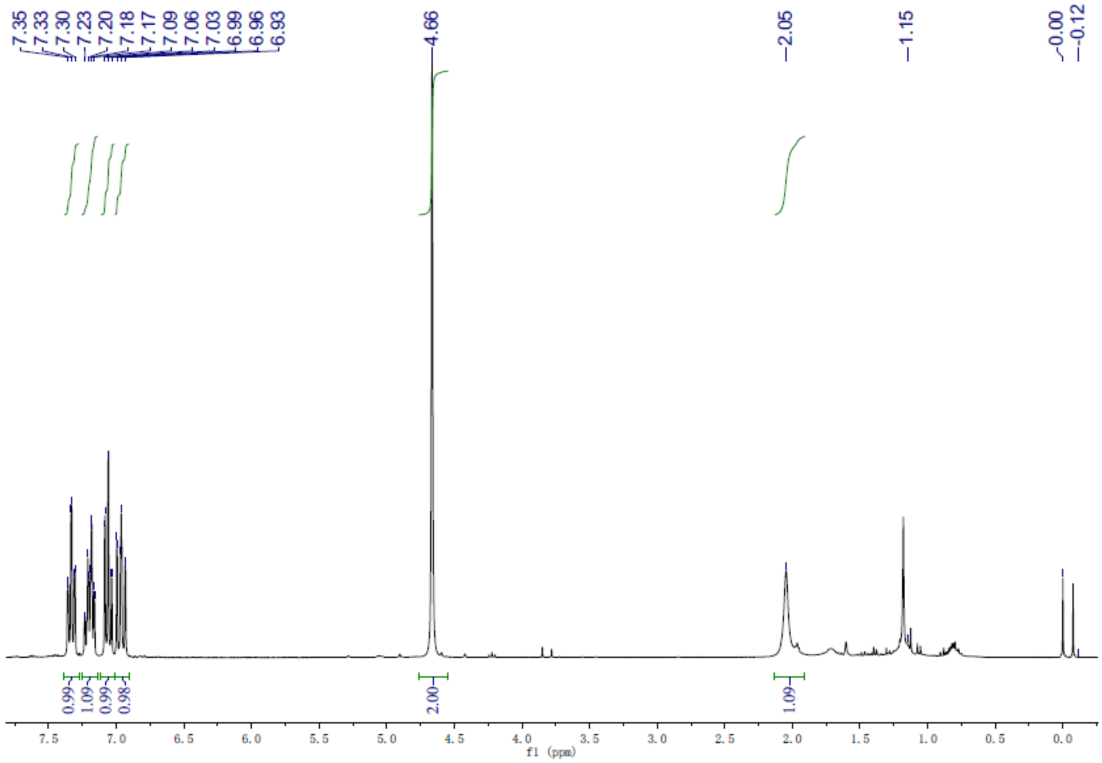


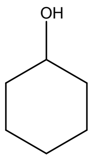
[1]H NMR (300 MHz, CDCl3, *δ*): 7.26 (d, *Ar*, ^3J(HH) = 9.0 Hz, 2H), 6.86 (d, *Ar*, ^3J(HH) = 9.0 Hz, 2H), 4.57 (s, CH_2, 2H), 3.79 (s, OCH_3, 3H), 2.11 (s br, O*H*, 1H).



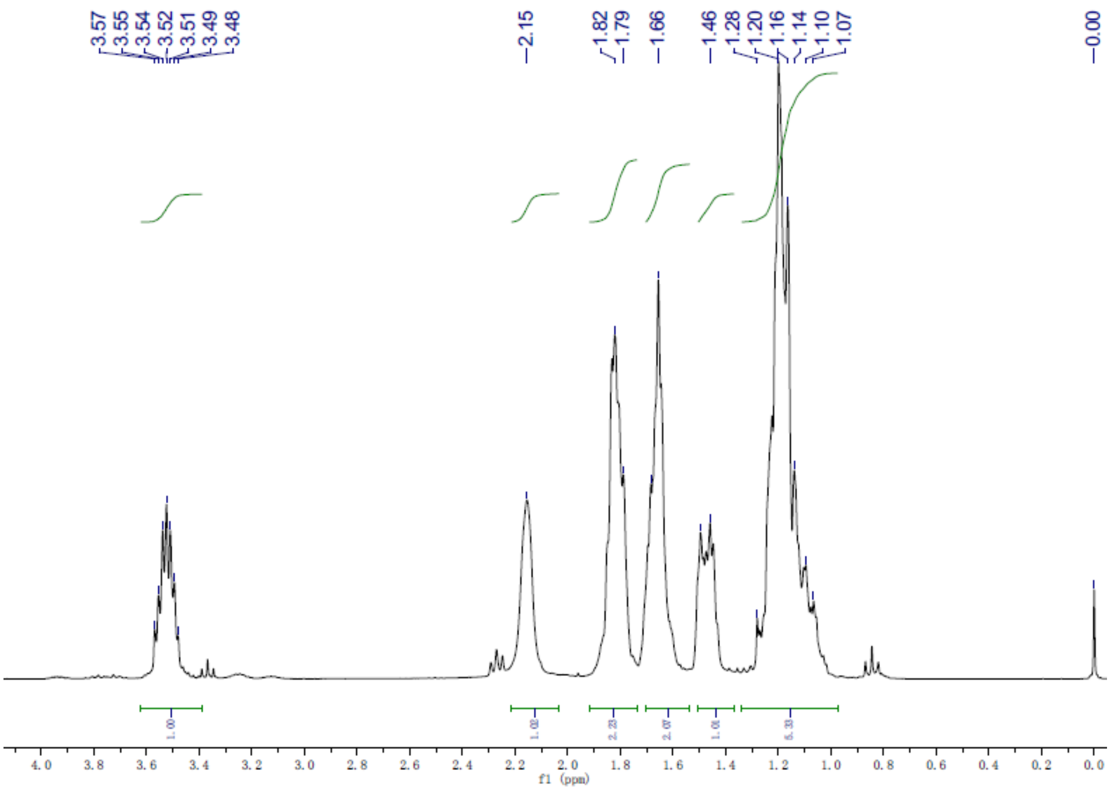


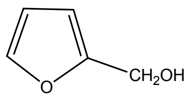
[1]H NMR (300 MHz, CDCl3, δ): 7.34–7.30 (m, *Ar*, 1H), 7.21–7.17 (m, *Ar,* 1H), 7.09–7.03 (m, *Ar*, 1H), 7.00–6.93 (m, *Ar*, 1H), 4.66 (s, C$H_{2,}$ 2H), 2.05 (s, O*H*, 1H).



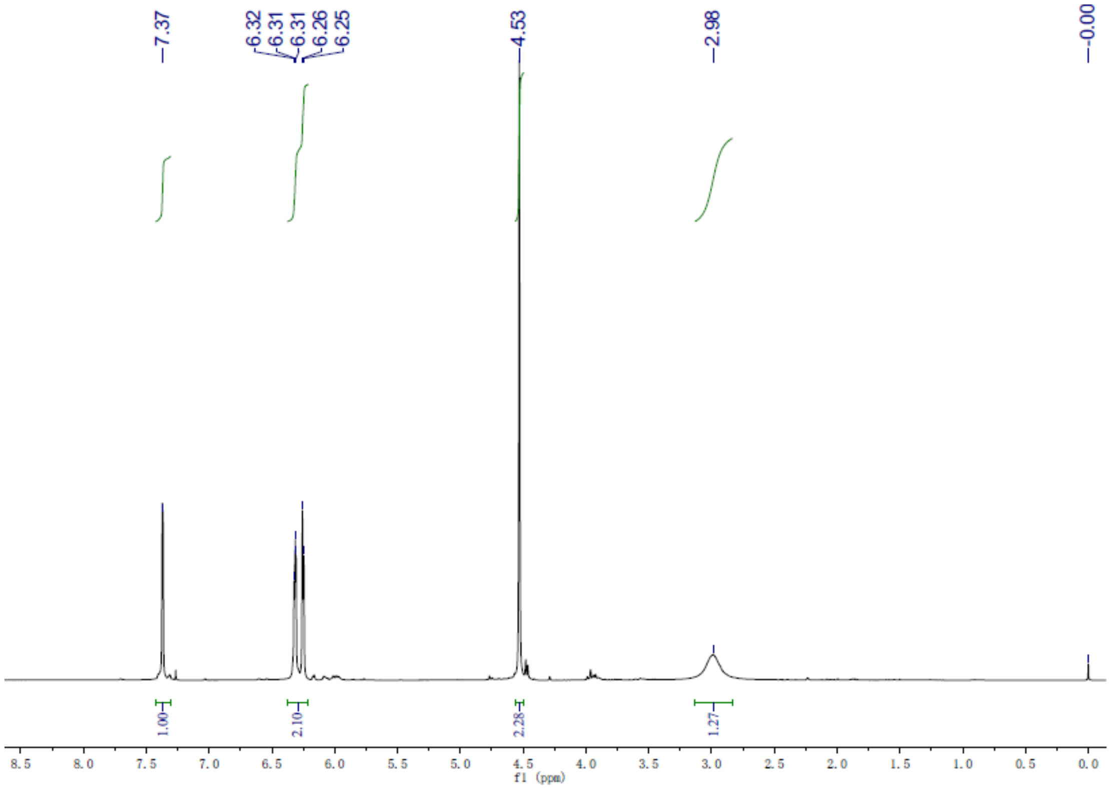


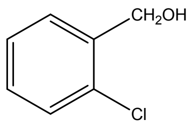
[1]H NMR (300 MHz, CDCl3, *δ*): 3.57–3.48 (m, C*H*OH, 1H), 2.15 (s, 1H), 1.82–1.79 (m, 2H), 1.68–1.66 (m, 2H), 1.50–1.46 (m, 1H), 1.28–1.07 (m, 5H).



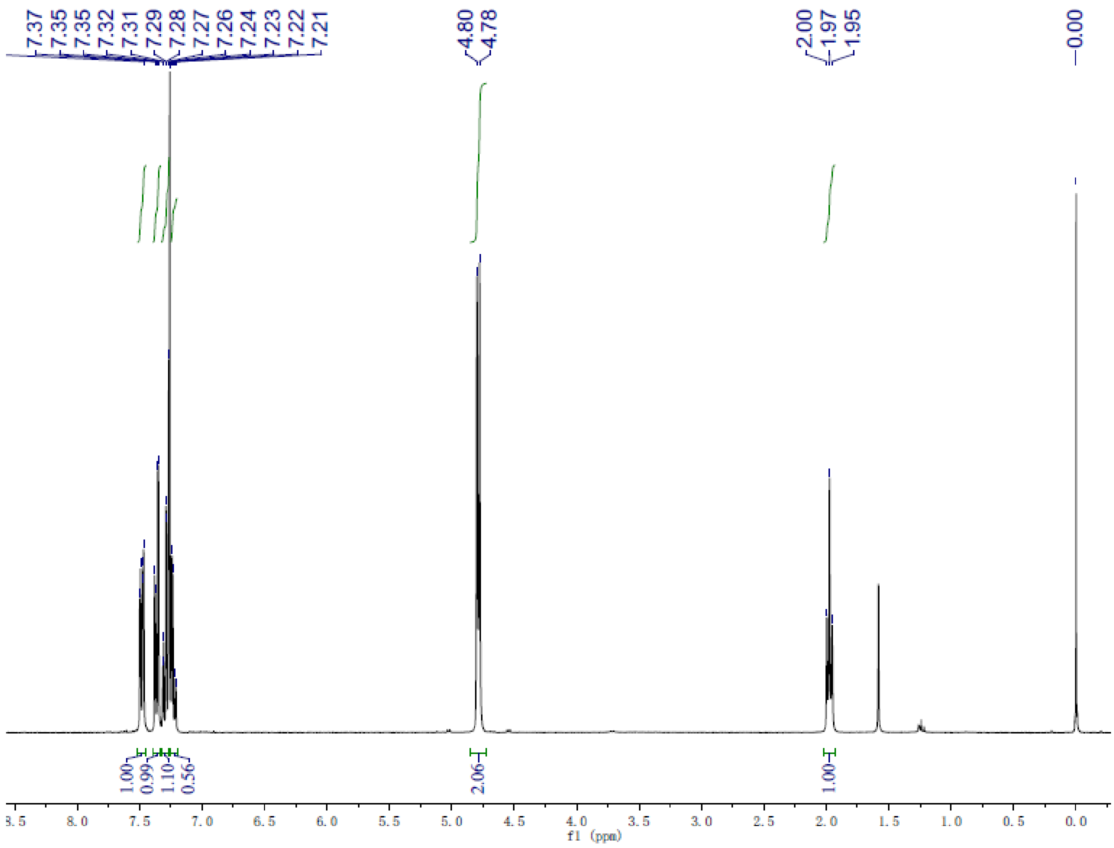


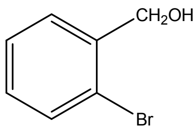
[1]H NMR (300 MHz, CDCl3, δ): 7.37 (br s, *Ar*, 1H), 6.25–6.32 (m, *Ar*, 2H), 4.53 (s, CH_2, 2H), 2.98 (s br, O*H*, 2H).



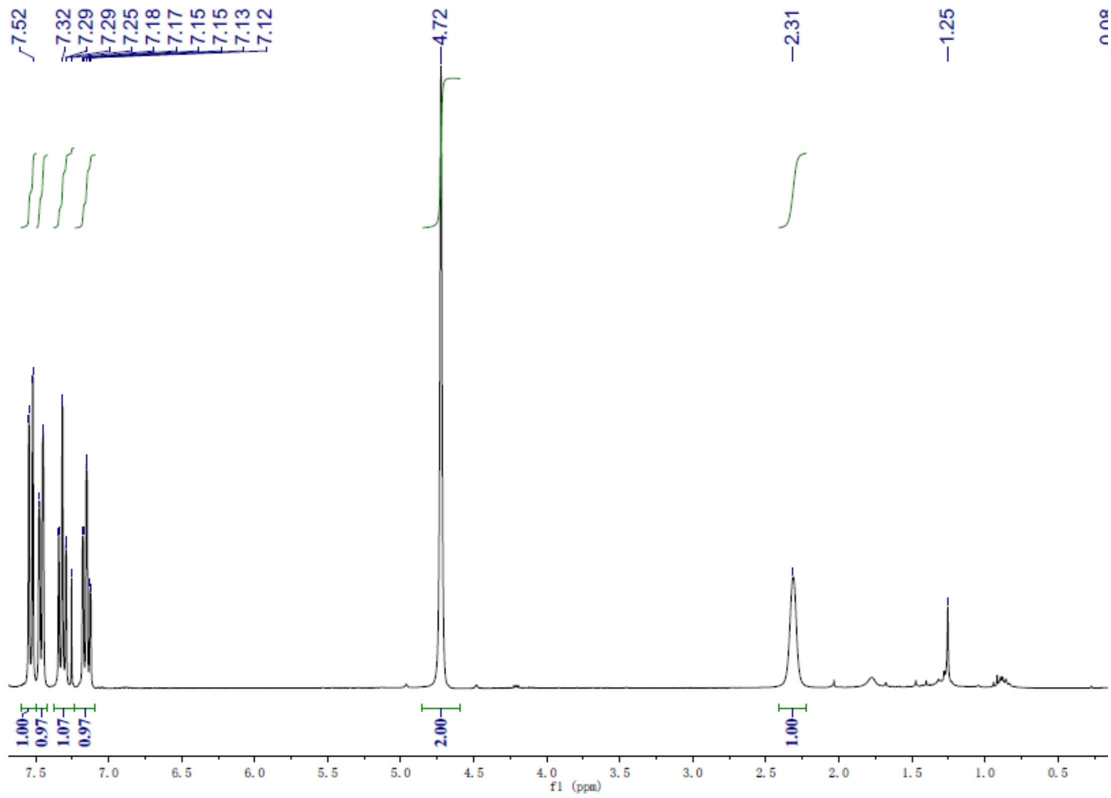


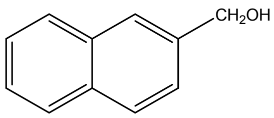
[1]H (300MHZ, CDCl3, δ): 7.47-7.50 (m, *Ar*, 1H), 7.38-7.22 (m, *Ar*, 3H), 4.79 (d, CH_2, 2H, ^3J(HH) =6.0 Hz), 1.97 (t, *OH*, 1H, ^3J(HH) =7.5 Hz).



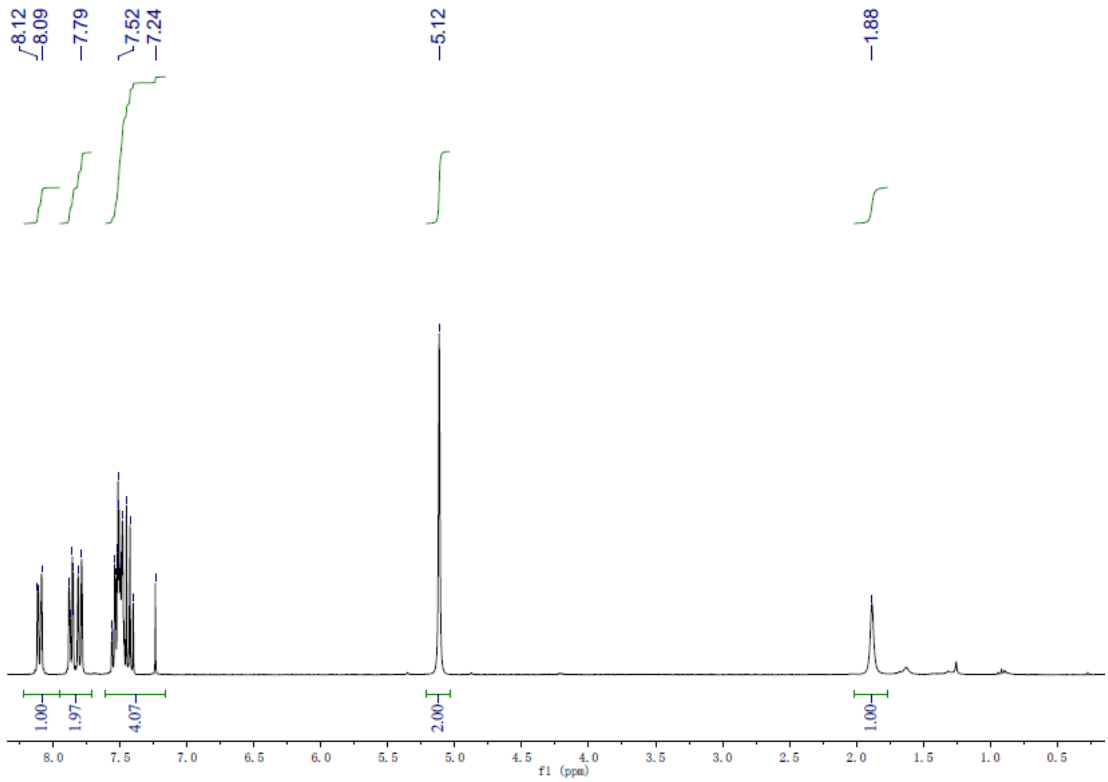


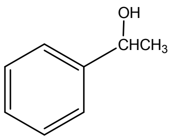
[1]H (300MHZ, CDCl3, *δ*): 7.55-7.45 (m, *Ar*, 2H), 7.34-7.15 (m, *Ar*, 2H), 4.72 (s, *CH_2*, 2H), 2.31 (s, *OH*, 1H).



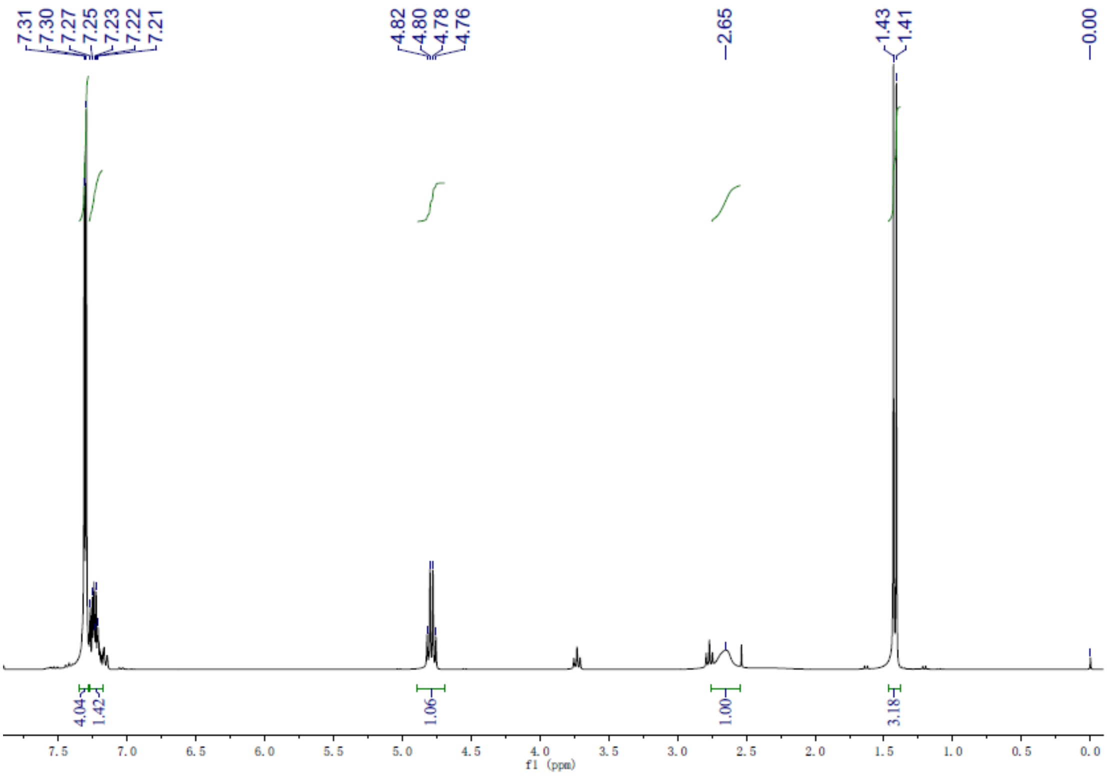


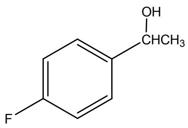
[1]H NMR (300 MHz, CDCl3, δ): 8.12–8.09 (d, *Ar*, 1H), 7.88–7.79 (dd, *Ar*, 2H), 7.54-7.43 (m, *Ar*, 4H), 5.12 (s, C*H*$_2$, 2H), 1.88 (s, O*H*, 1H).



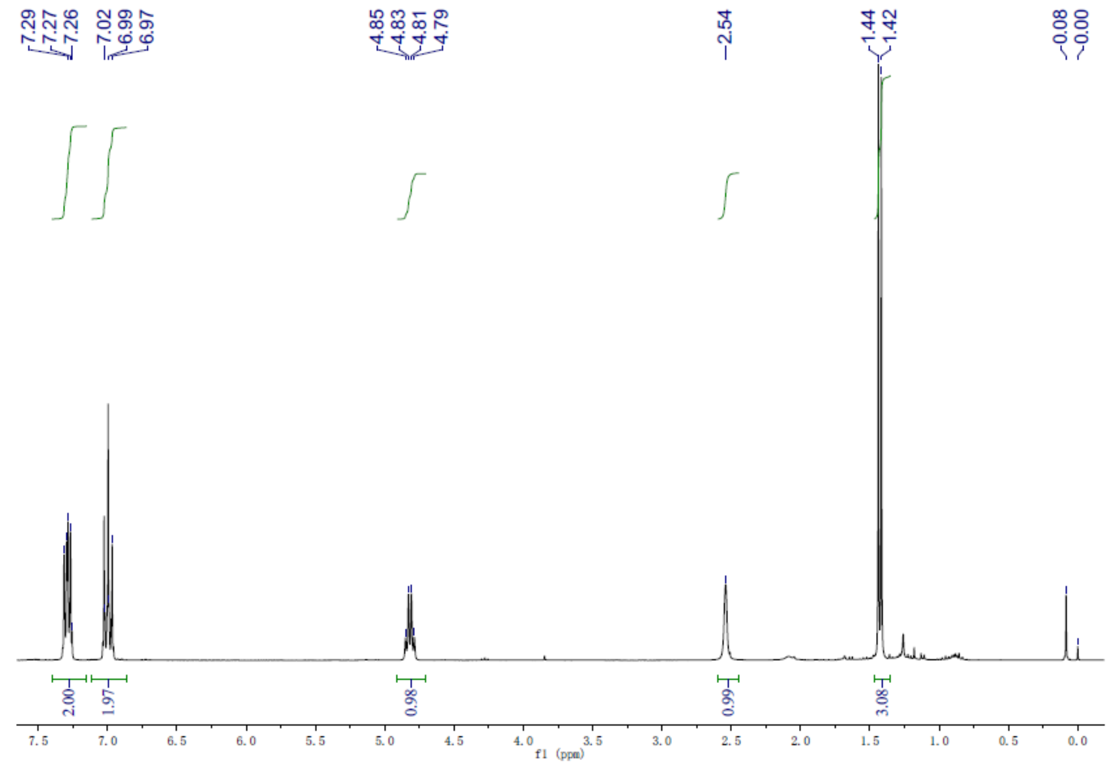


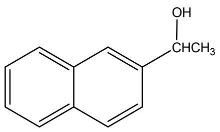
[1]H NMR (300 MHz, CDCl3, δ): 7.31–7.21 (m, *Ar*, 5H), 4.79 (q, C*H*OH, ^3J(HH) = 6.0 Hz, 1H), 2.65 (s br, O*H*, 1H), 1.42 (d, CH_3, ^3J(HH)= 6.0 Hz, 3H).



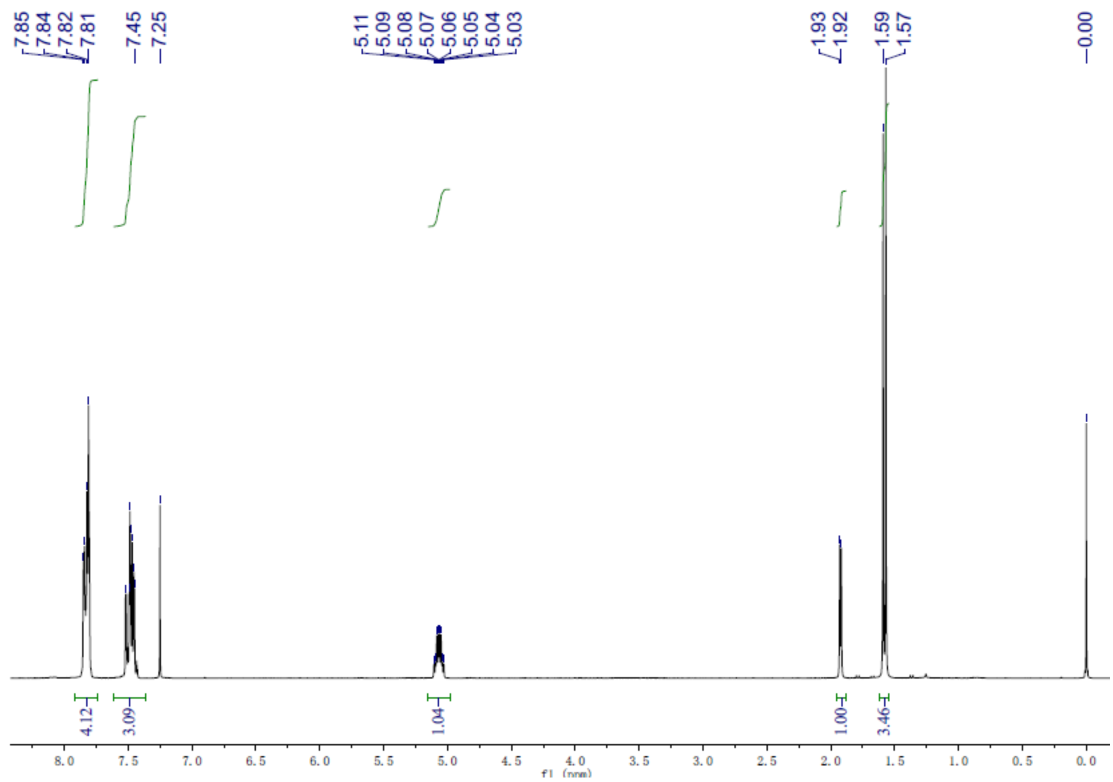


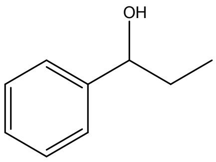
[1]H NMR (300 MHz, CDCl3, δ): 7.31–7.27 (m, *Ar*, 2H), 7.26-6.97 (m, *Ar*, 2H), 4.82 (q, C*H*OH, ^3J(HH) = 6.0 Hz, 1H), 2.54 (s, O*H*, 1H), 1.43 (d, CH_3, ^3J(HH) = 6.0 Hz, 3H).



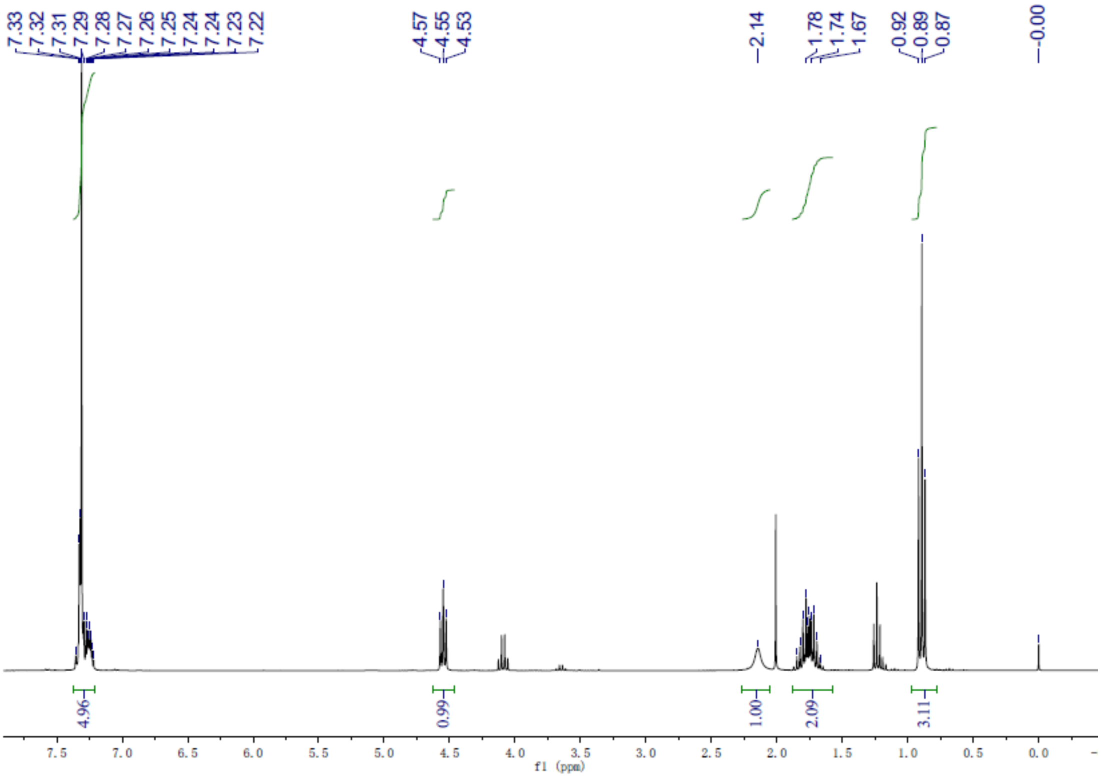


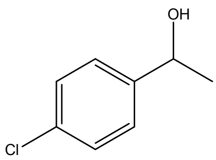
^{1}H NMR (300 MHz, CDCl3, δ): 7.85–7.81 (m, *Ar,* 4H), 7.52–7.45 (m, *Ar*, 3H), 5.07 (m, C*H*OH, 1H), 1.92 (s, O*H*, 1H), 1.58 (d, C*H*$_3$, ^3J(HH) = 6.0 Hz, 3H).



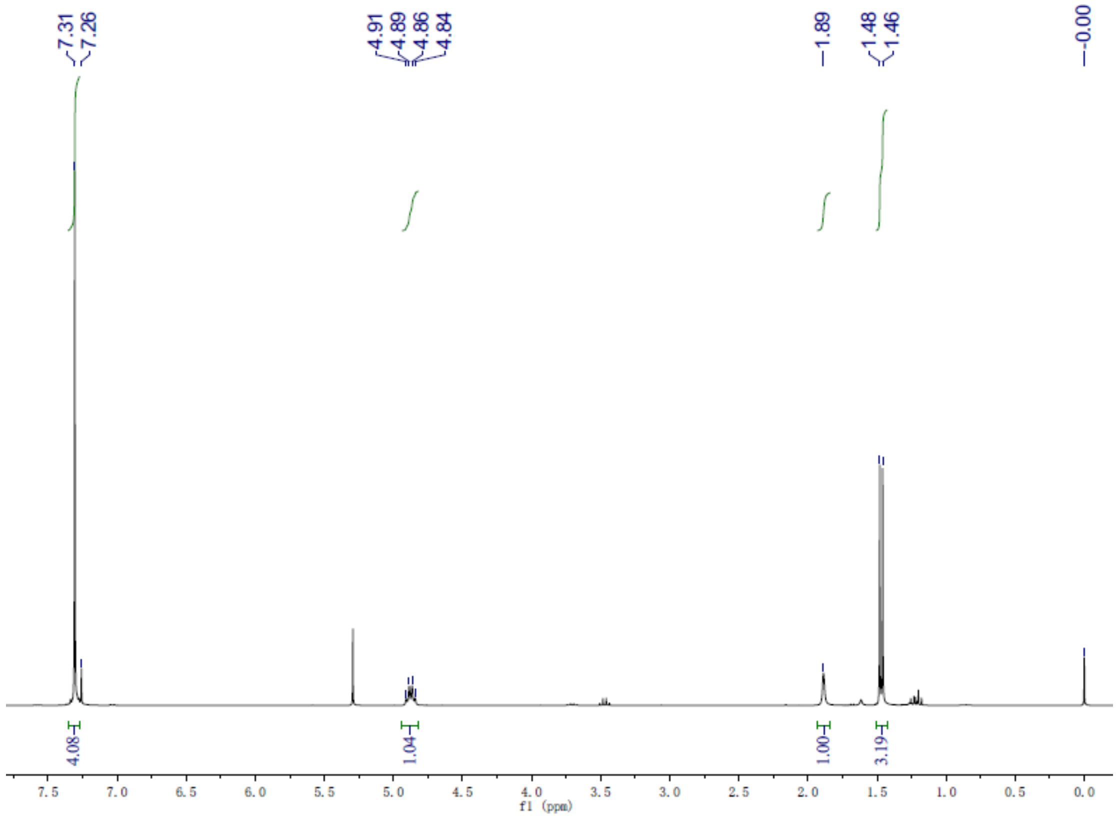


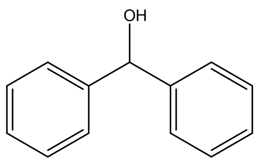
[1]H NMR (300 MHz, CDCl3, *δ*): 7.35-7.22 (m, *Ar*, 5H), 4.55 (t, C*H*OH, 1H, ^3J(HH) =6.0Hz), 2.14 (s, O*H*, 1H), 1.76 (m, CH_2CH_3, 2H),0.89 (t, CH_2CH_3,3H, ^3J(HH)=7.5 Hz).



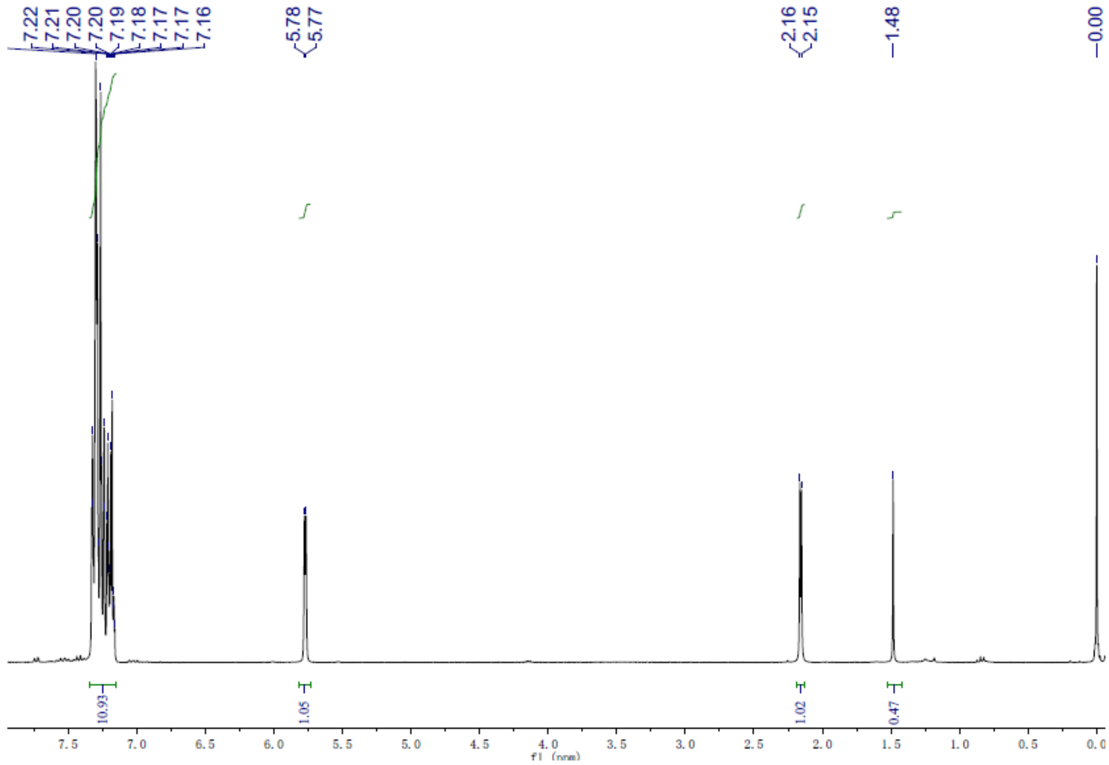


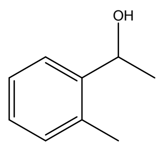
[1]H NMR (300 MHz, CDCl3, *δ*): 7.26-7.31 (m, *Ar*,4H), 4.88 (q, C*H*OH, 1H, ^3J(HH) = 6.0Hz), 1.89 (s, O*H*, 1H), 1.47 (d, CHCH_3, 3H, ^3J(HH) = 3.0Hz).



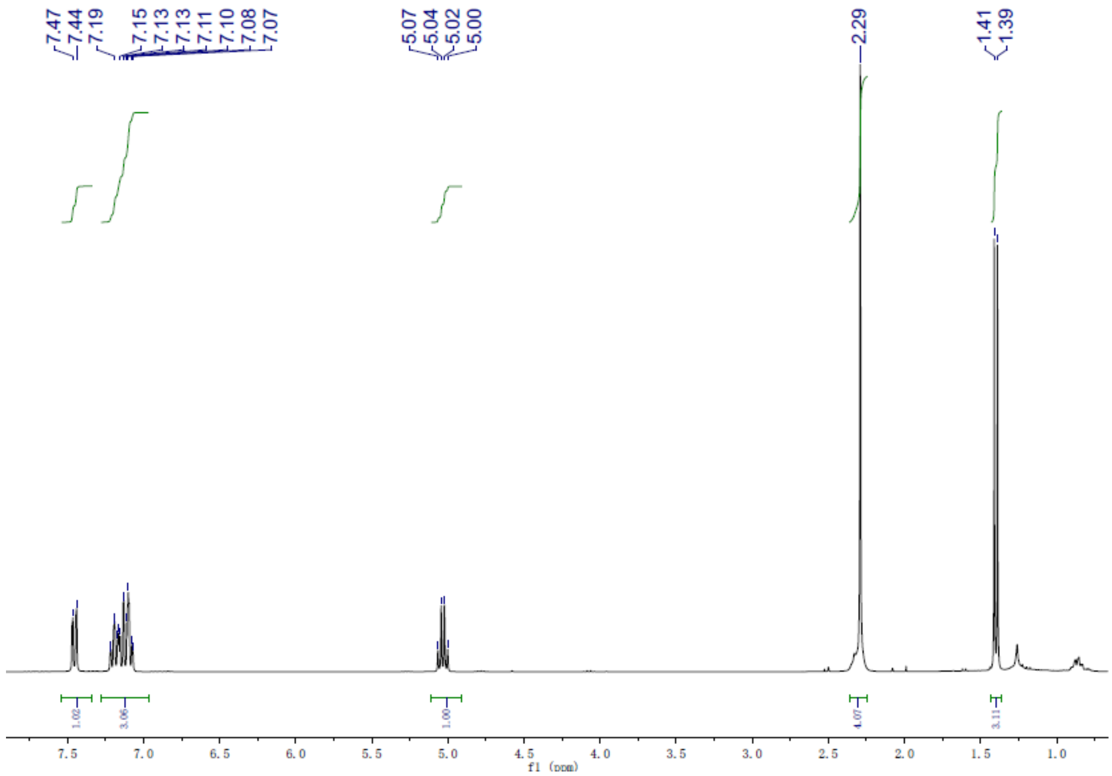


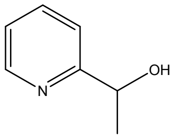
[1]H NMR (300 MHz, CDCl3, *δ*): δ 7.18-7.32 (m, Ar, 10H), 5.78 (s, C*H*(OH), 1H), 2.16 (s br, CH(O*H*), 1H).



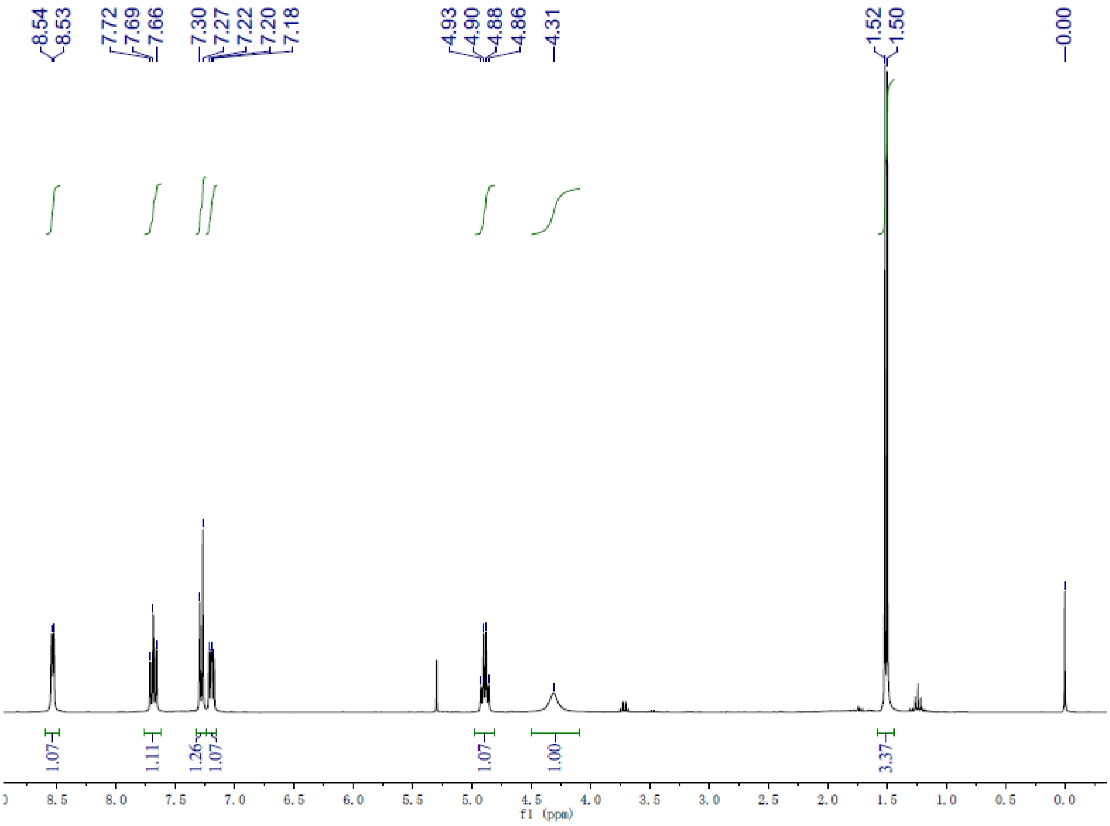


[1]H NMR (300 MHz, CDCl3, *δ*): 7.47-7.44 (m, *Ar,* 1H), 7.22-7.07 (m, *Ar*, 3H), 5.03 (q, C*H*OH, ^3J(HH)=6.0Hz,1H), 2.29 (s, CH_3, 3H), 1.40 (d, CHCH_3, ^3J(HH) = 6.0Hz, 3H).

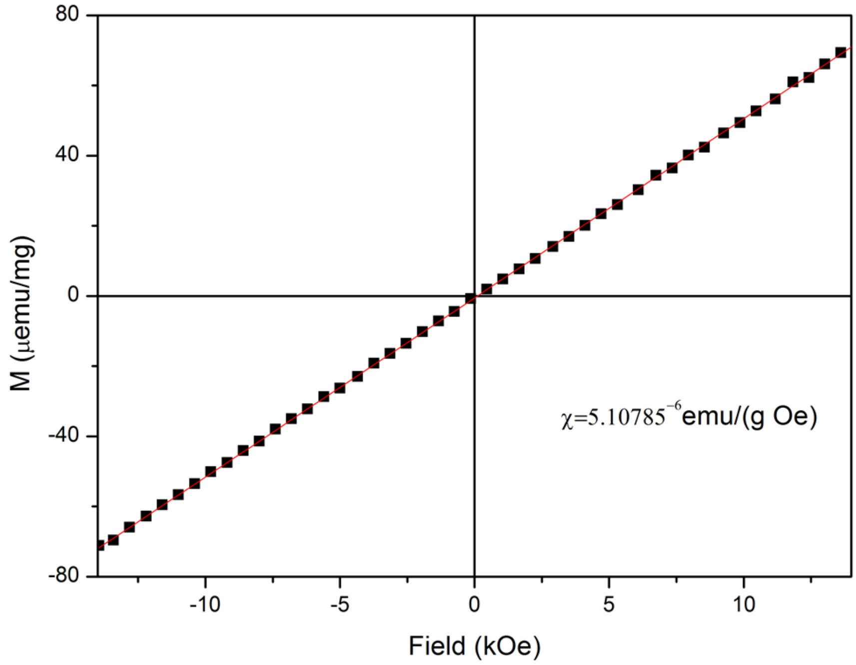




[1]H NMR (300 MHz, CDCl3, δ): 8.54 (d, *Ar*, ^3J(HH) = 3.0 Hz, 1H), 7.72–7.66 (m, *Ar*, 1H), 7.29 (d, *Ar*, ^3J(HH) = 9.0 Hz, 1H), 7.22–7.18 (m, *Ar*, 1H), 4.89 (q, C*H*OH, ^3J(H-H) = 6.0 Hz, 1H), 4.31 (s br, O*H*, 1H), 1.51(d, CH_3, ^3J(H-H) = 6.0 Hz, 3H).



Magnetic susceptibility of complex **3**



$\chi_m = 20\pi * 10^{-9}\ m^3 mol^{-1}$

$\mu_m = 3.16 * 10^{-23}\ JT^{-1}$

n=2.54