Supporting Information

Synthesis of [CNN] Pincer Nickel(II) NHC Chlorides and Their Catalytic Effects on Hydrosilylation of Aldehydes and Ketones under Mild Conditions

Shaobo Cao, [a] Shangqing Xie, [a] Qingshuang Li, [a] Xiaoyan Li, [a] Hongjian Sun, [a,*] Olaf Fuhr [b] and Dieter Fenske [b]

[a] *School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250100 Jinan, People's Republic of China*

[b] *Institut für Nanotechnologie (INT) und Karlsruher Nano-Micro-Facility (KNMF), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

Correspondence author: hjsun@sdu.edu.cn

Contents

CONTENTS:

SI Crystallographic Data for Complexes **3a**, **3b** and **5a**

complex	**3a**	**3b**	**5a**
formula	$C_{22}H_{21}ClN_4Ni$	$C_{19}H_{15}Br_{0.07}Cl_{0.95}N_4Ni_{0.96}$	$C_{23}H_{27}Br_{0.11}Cl_{0.89}N_4Ni$
M_z	435.59	395.32	458.42
crystal system	orthorhombic	monoclinic	orthorhombic
space group	$Pca2_1$	P21/c	$P2_12_12_1$
a [Å]	22.2059(5)	7.8582(3)	8.3434(2)
b [Å]	10.1482(2)	24.1174(12)	14.2256(4)
c [Å]	8.5616(2)	17.5914(6)	17.7157(4)
α [°]	90	90	90
β [°]	90	95.976(3)	90
γ [°]	90	90	90
V [Å^3]	1929.36(7)	3315.8(2)	2102.67(9)
T [K]	150.15	150.15	173.15
Z	4	8	4
μ[mm^{-1}]	6.518	7.273	2.735
total reflns	10895	16325	7023
unique reflns	4120	6666	3670
R_{int}	0.0128	0.0268	0.0576
$R_1[I>2\sigma(I)]$	0.0224	0.0546	0.0401
$wR(F^2)[I>2\sigma(I)]$	0.0600	0.1474	0.0928
R_1(all data)	0.0231	0.0630	0.0486
$wR(F^2)$(all data)	0.0604	0.1544	0.0971
GOF on F^2	1.038	1.062	0.987

SII ^{1}H, ^{13}C NMR spectra of complex **1**

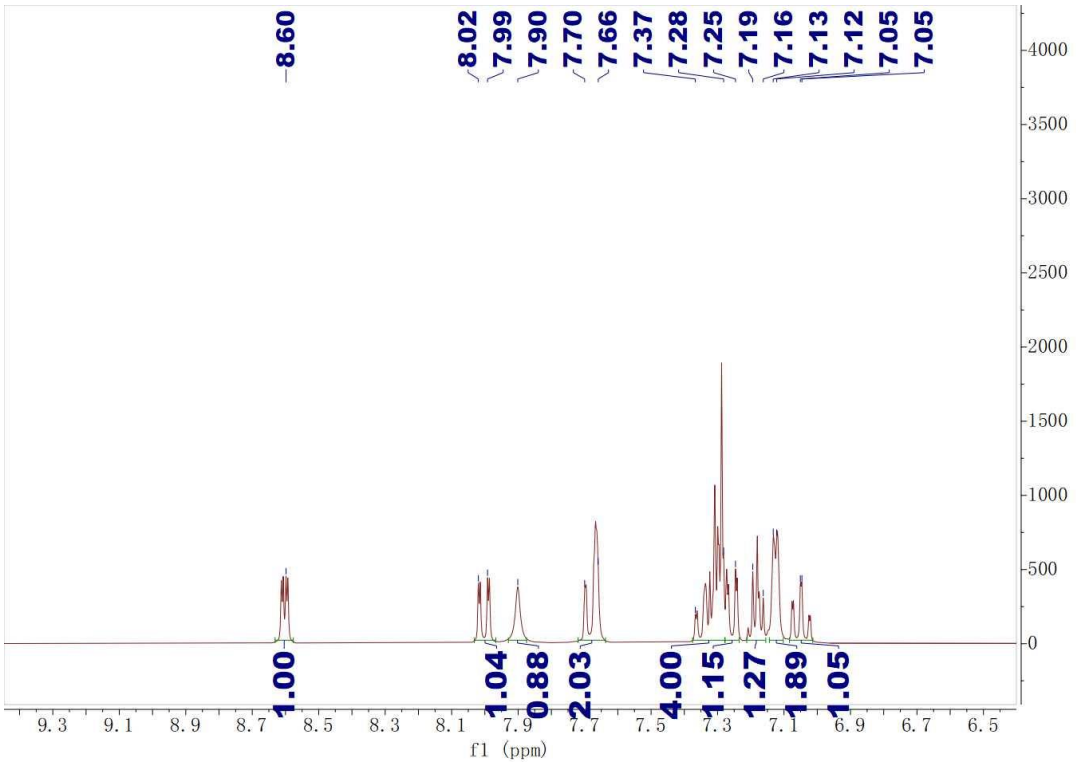


Fig.S2 ^{1}H NMR spectrum of complex **1**（$CDCl_3$）

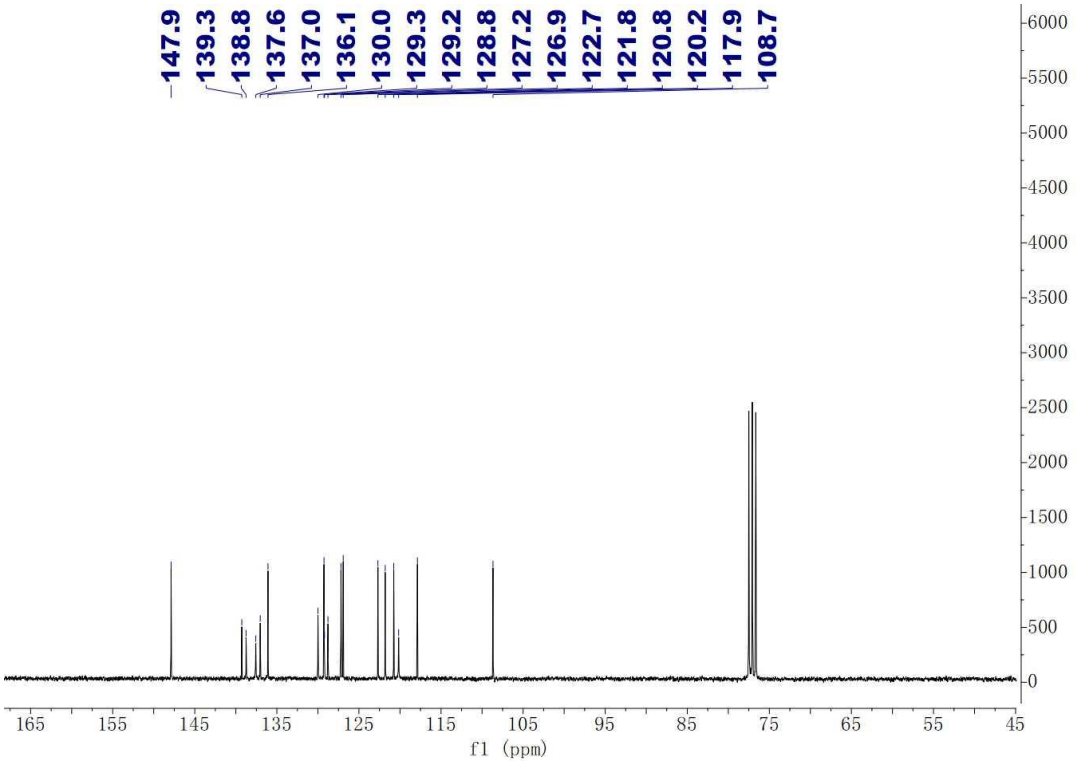


Fig.S3 ^{13}C NMR spectrum of complex **1**（$CDCl_3$）

SIII IR, ^{1}H, ^{13}CNMR spectra of complexes **2a - 2c**

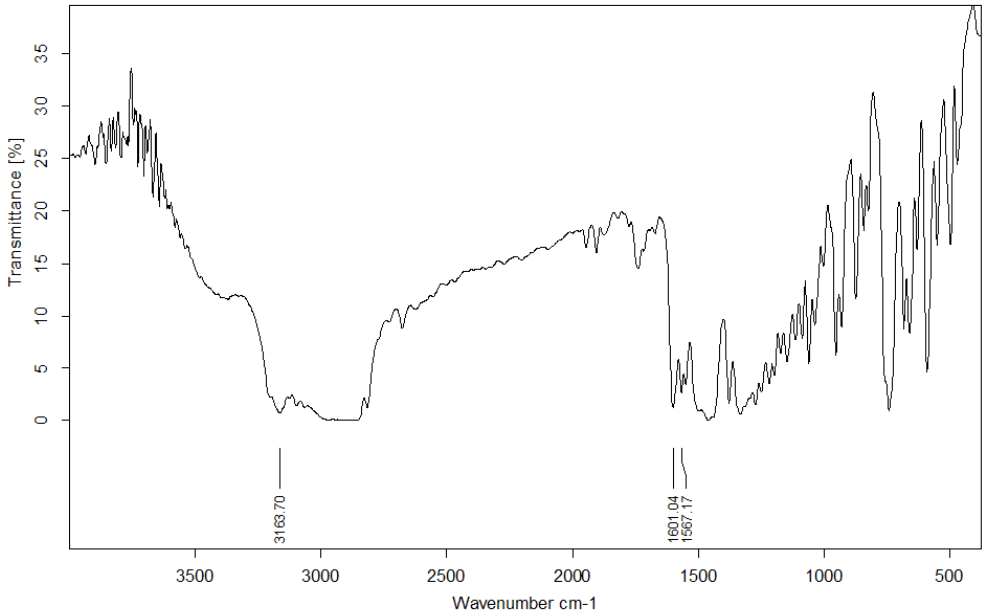


Fig.S4 IR spectrum of complex **2a**

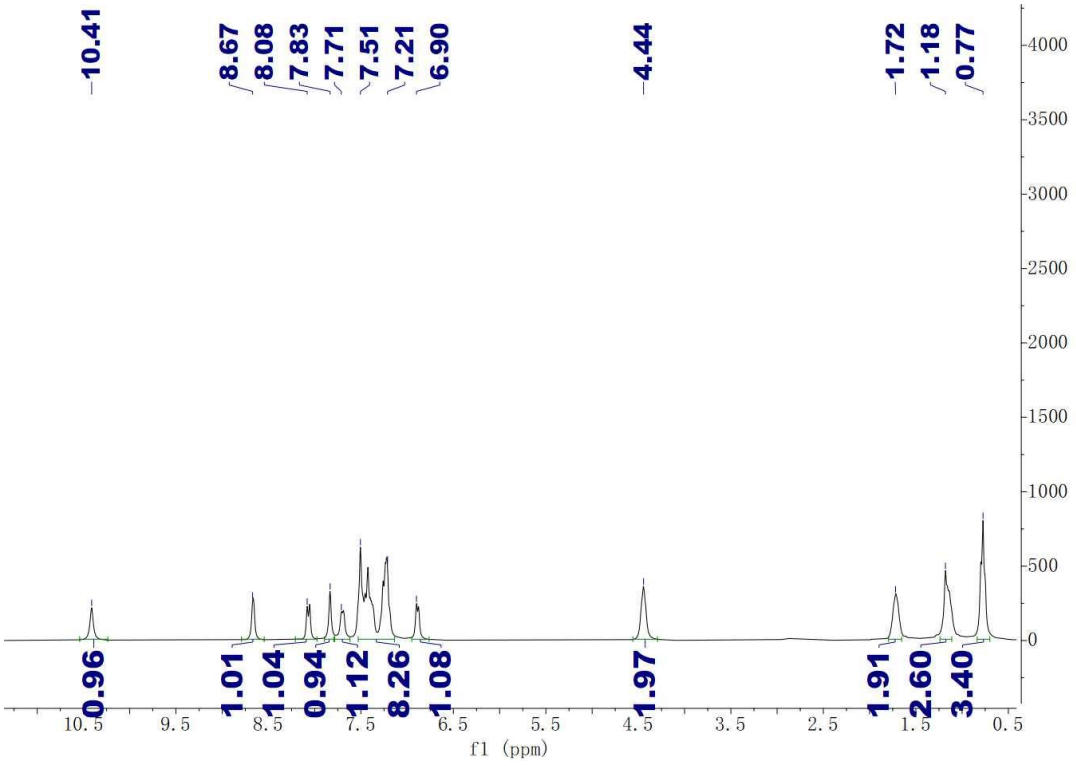


Fig.S5 ^{1}H NMR spectrum of complex **2a**（$CDCl_3$）

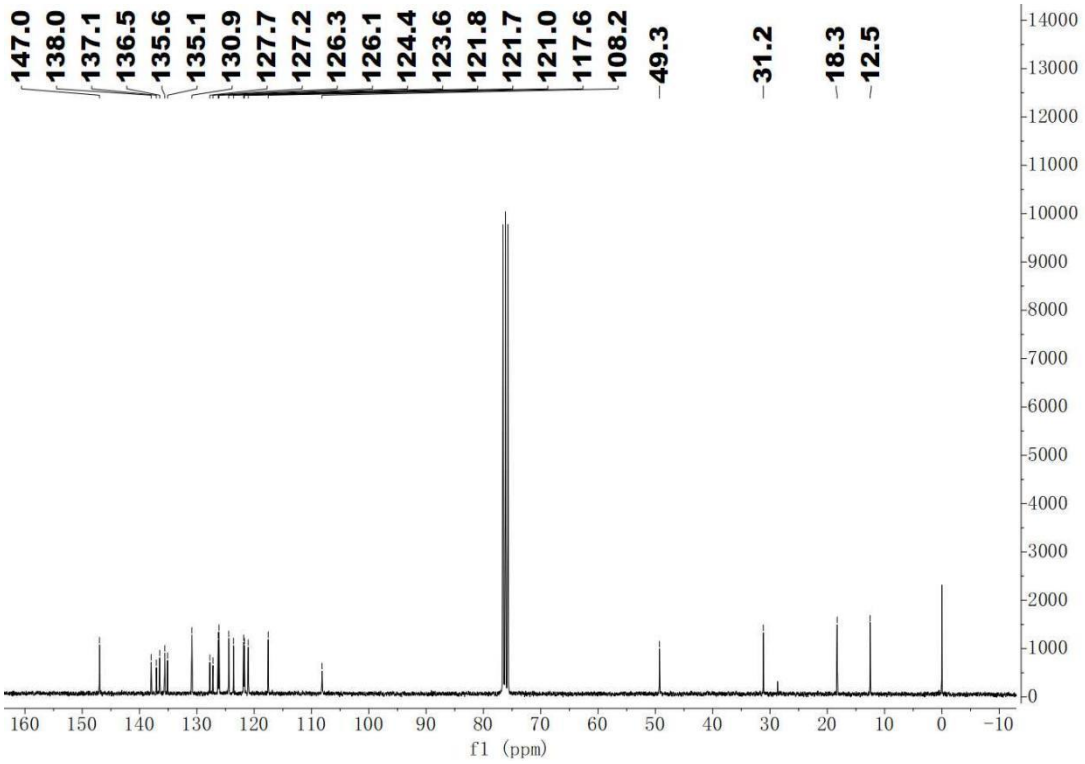


Fig.S6 ^{13}C NMR spectrum of complex **2a**（$CDCl_3$）

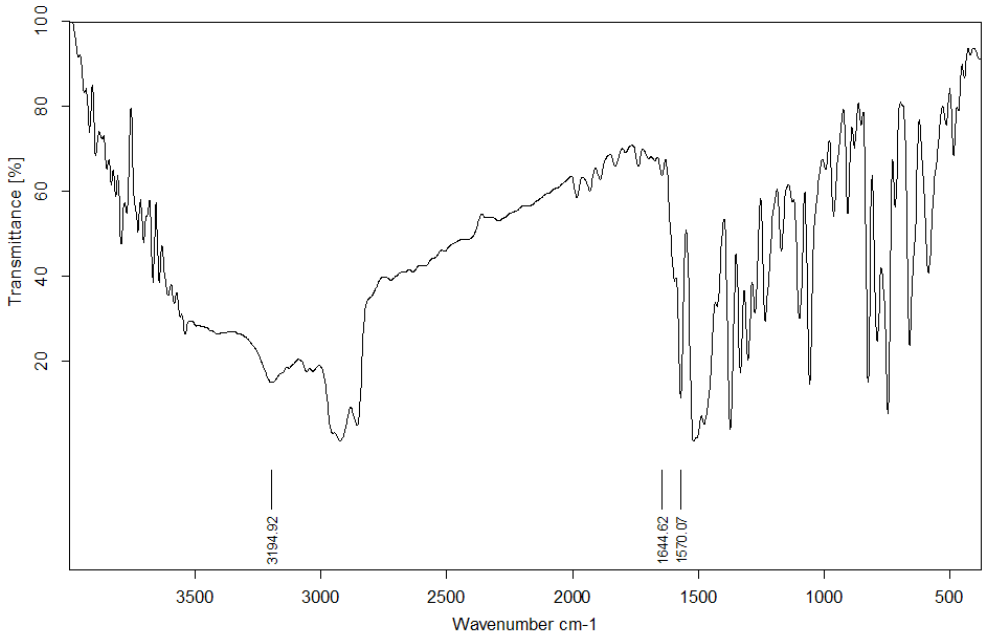


Fig.S7 IR spectrum of complex **2b**

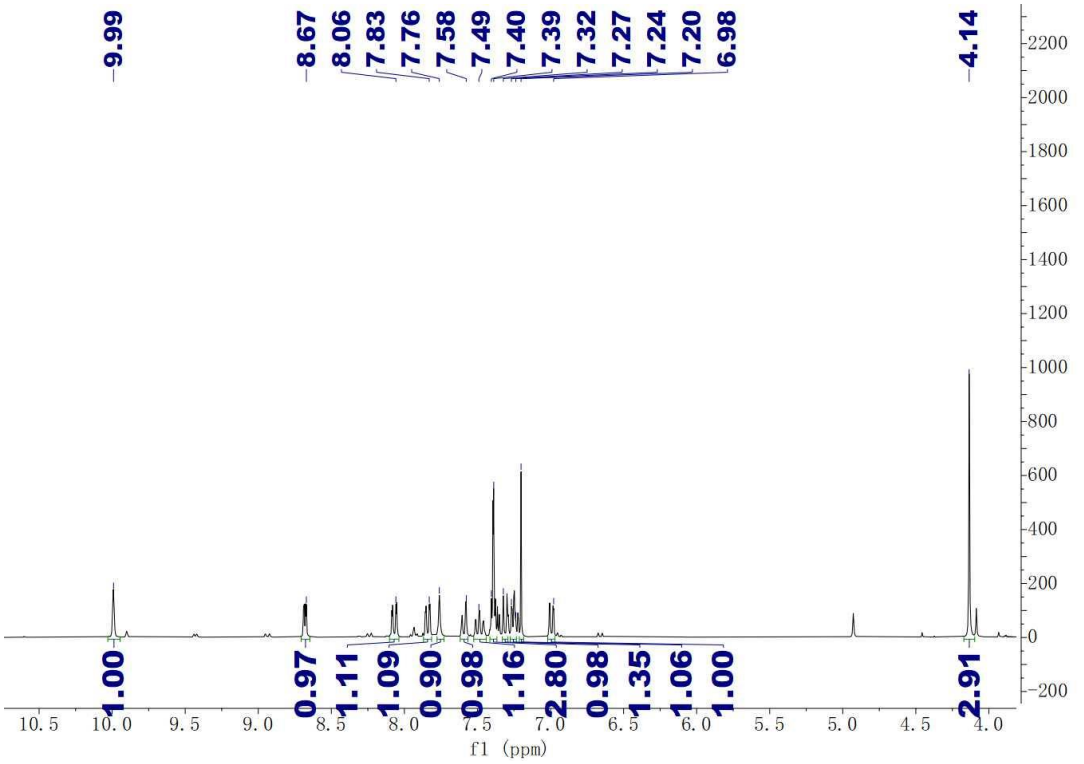


Fig.S8 ^{1}H NMR spectrum of complex **2b**（$CDCl_3$）

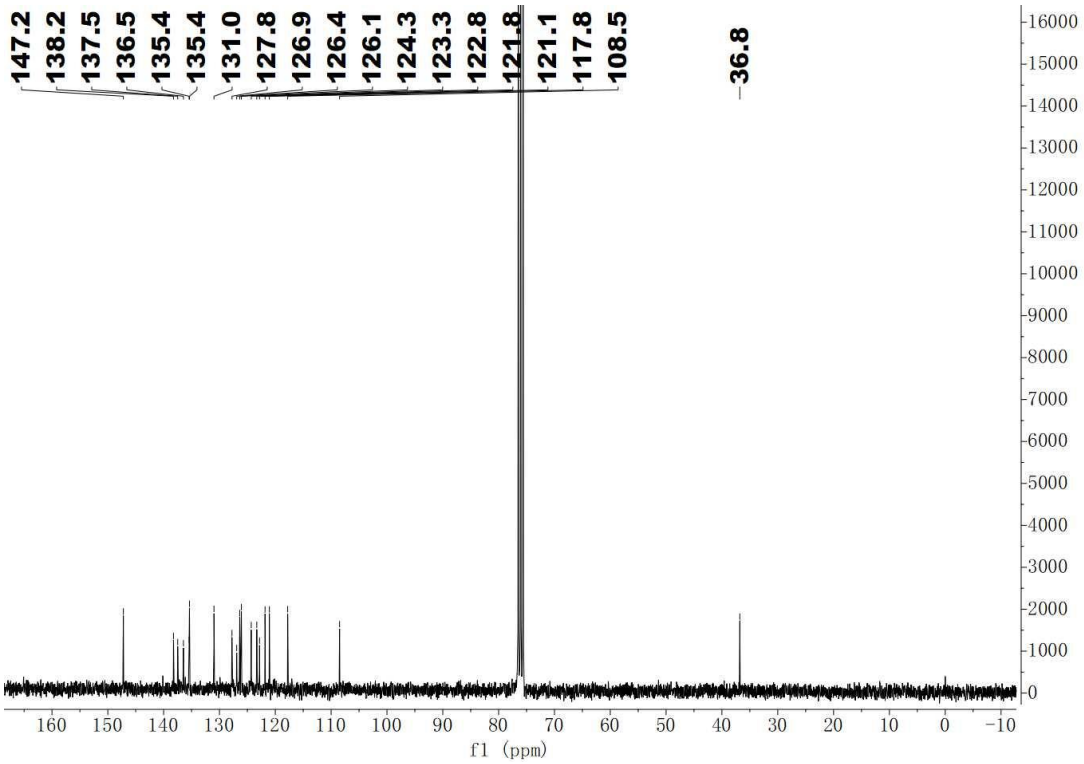


Fig.S9 ^{13}C NMR spectrum of complex **2b**（$CDCl_3$）

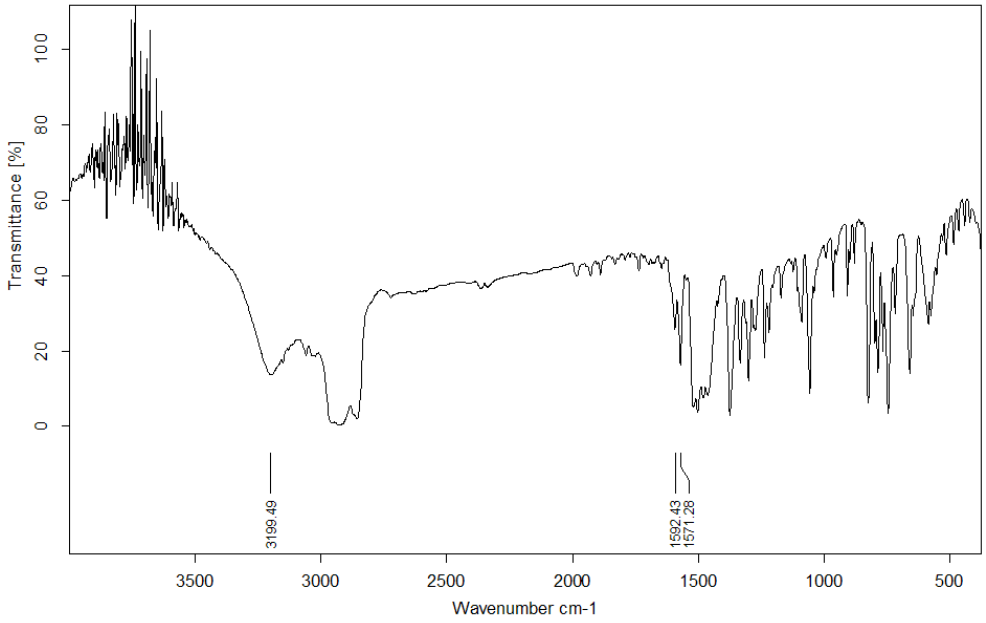


Fig.S10 IR spectrum of complex **2c**

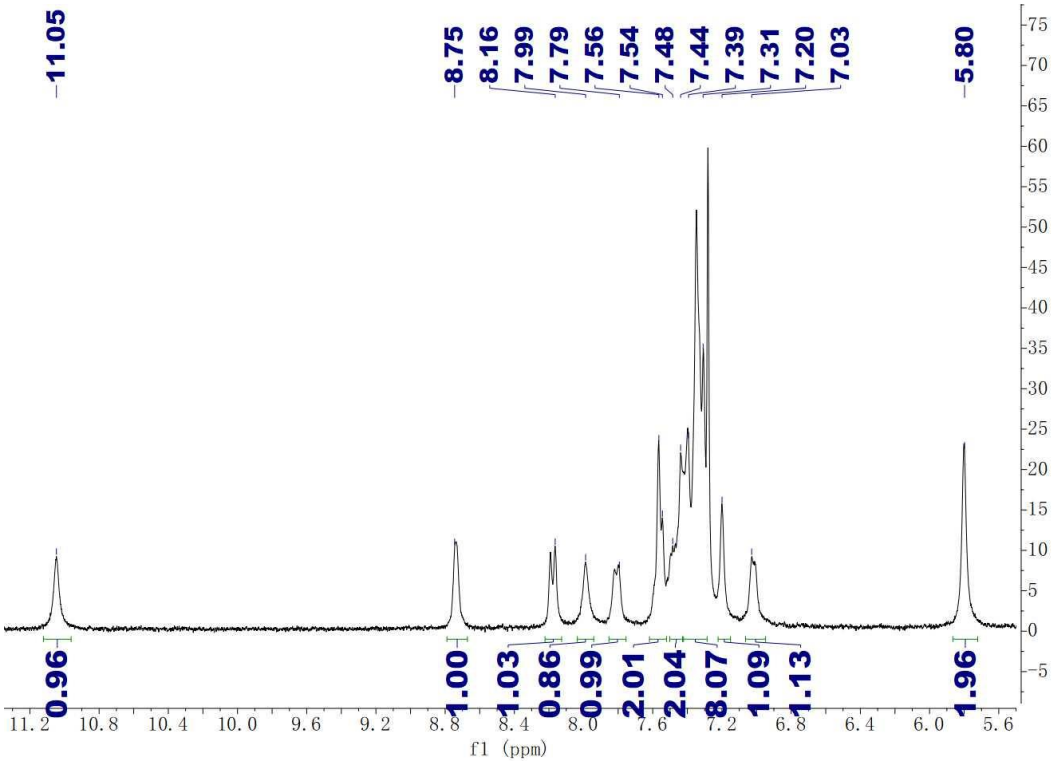


Fig.S11 ^{1}H NMR spectrum of complex **2c**（$CDCl_3$）

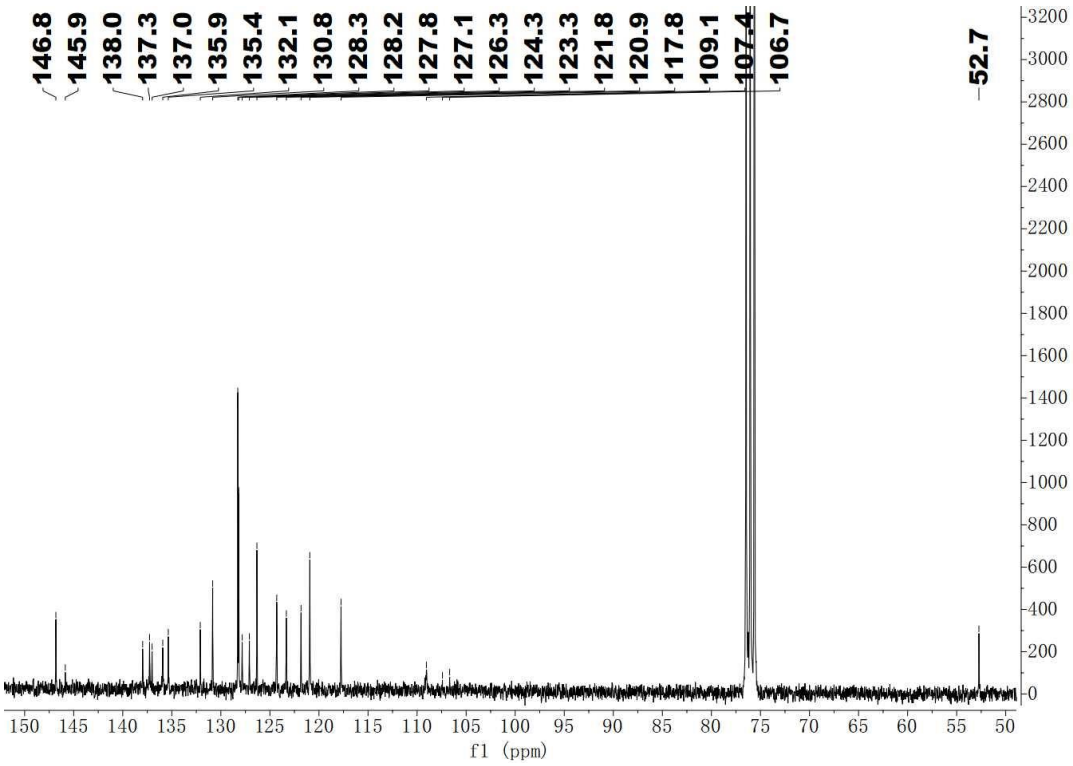


Fig.S12 ^{13}C NMR spectrum of complex **2c**（$CDCl_3$）

SIV IR, ^{1}H, ^{13}C NMR spectra of complexes **3a - 3c** and **5a - 5b**

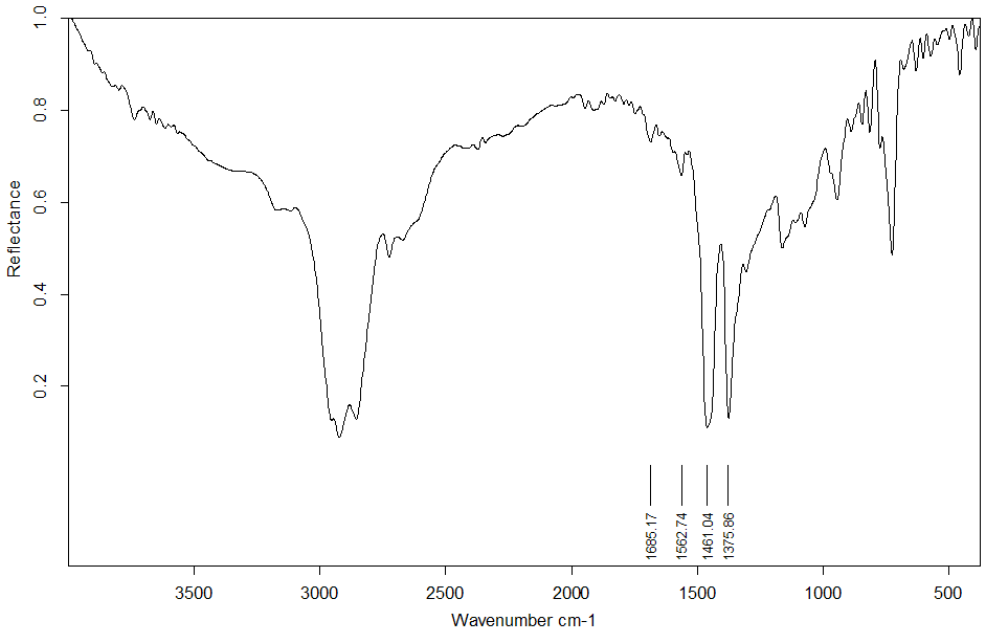


Fig.S13 IR spectrum of complex **3a**

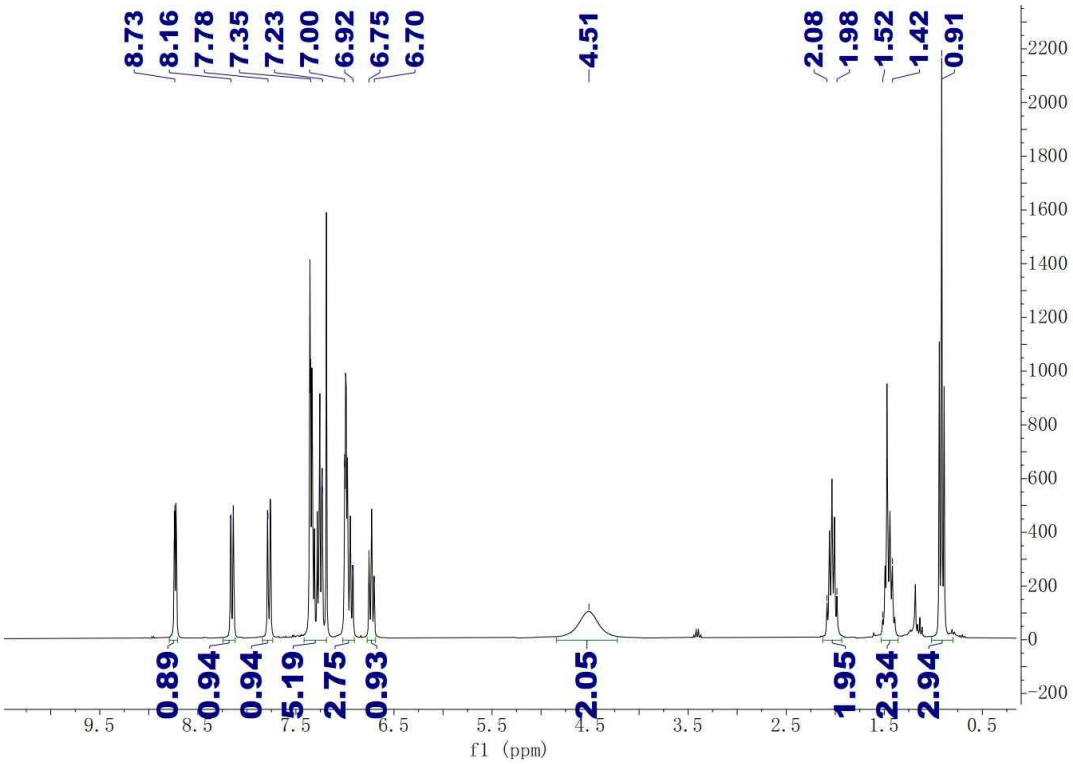


Fig.S14 ^{1}H NMR spectrum of complex **3a**（$CDCl_3$）

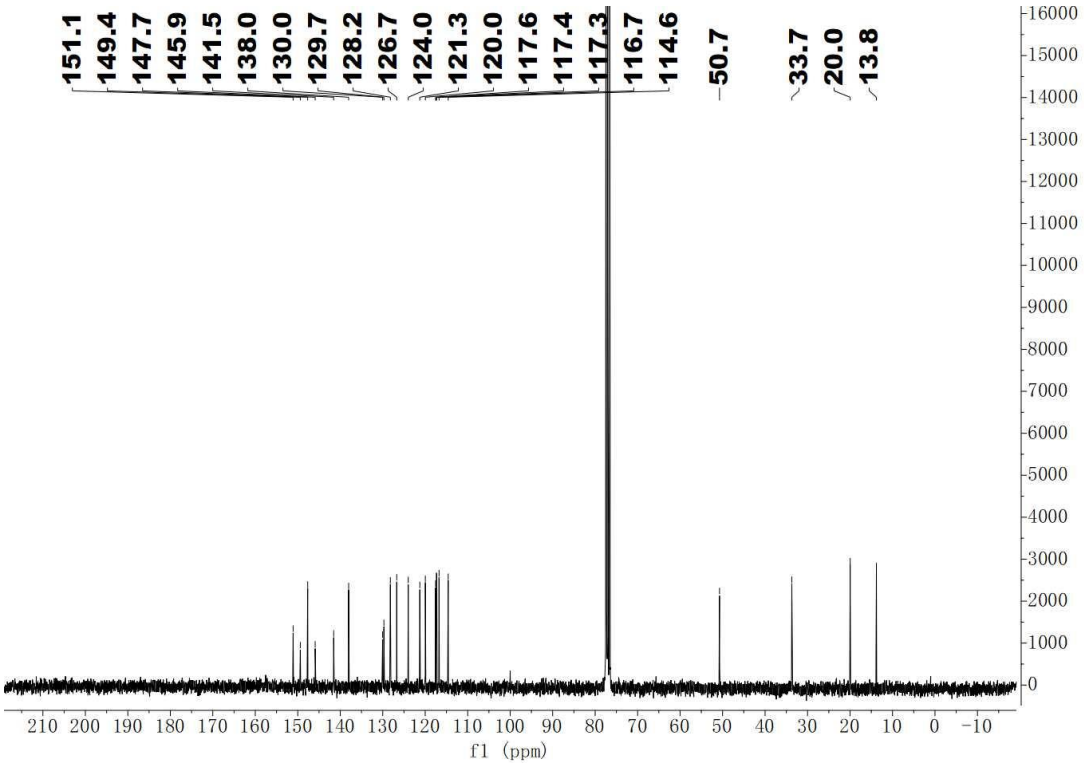


Fig.S15 ^{13}C NMR spectrum of complex **3a**（$CDCl_3$）

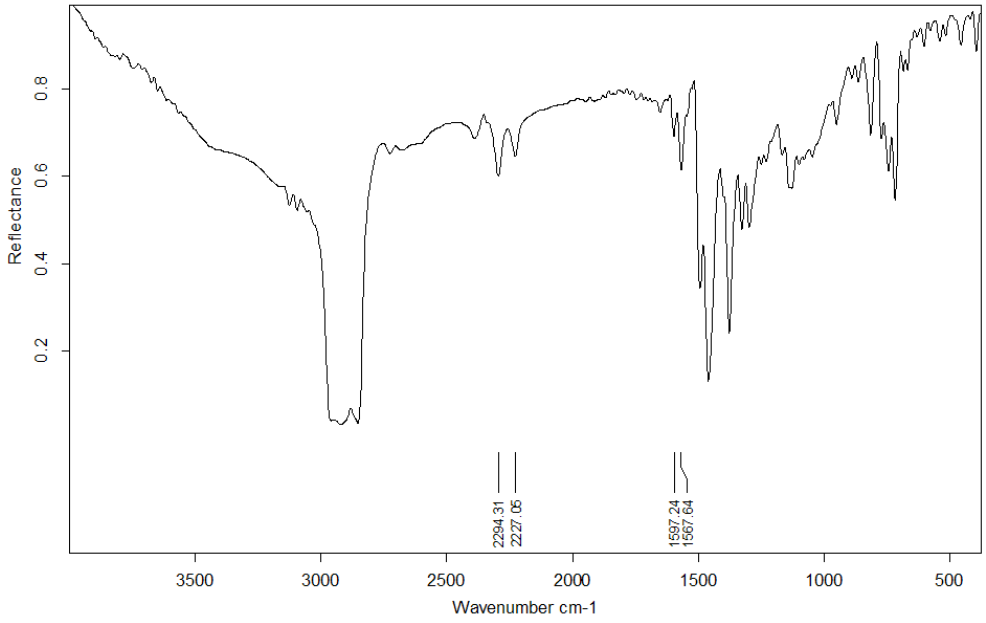


Fig.S16 IR spectrum of complex **3b**（$CDCl_3$）

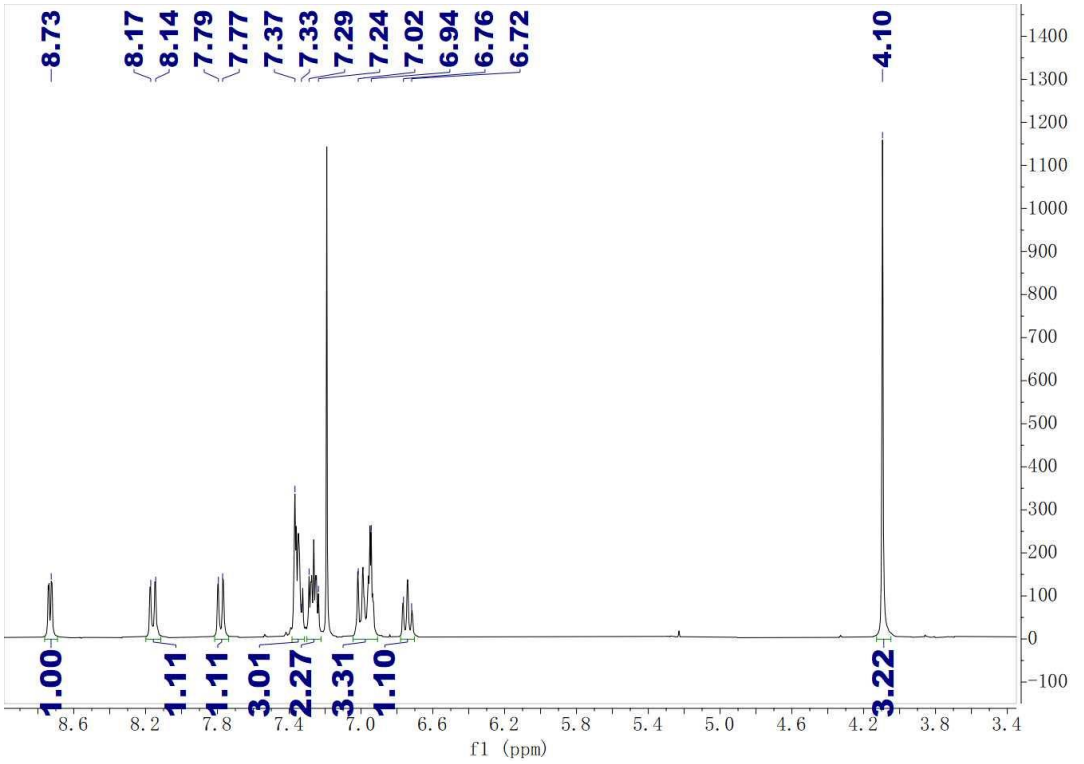


Fig.S17 ^{1}H NMR spectrum of complex **3b**（$CDCl_3$）

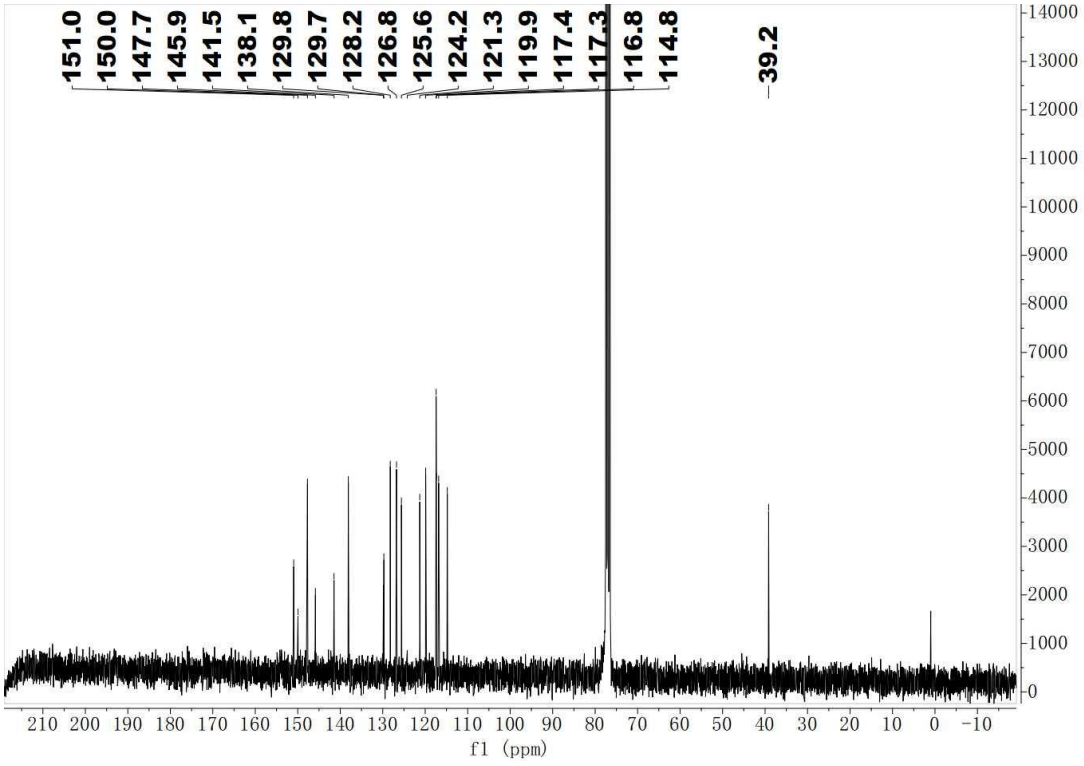


Fig.S18 ^{13}C NMR spectrum of complex **3b**（$CDCl_3$）

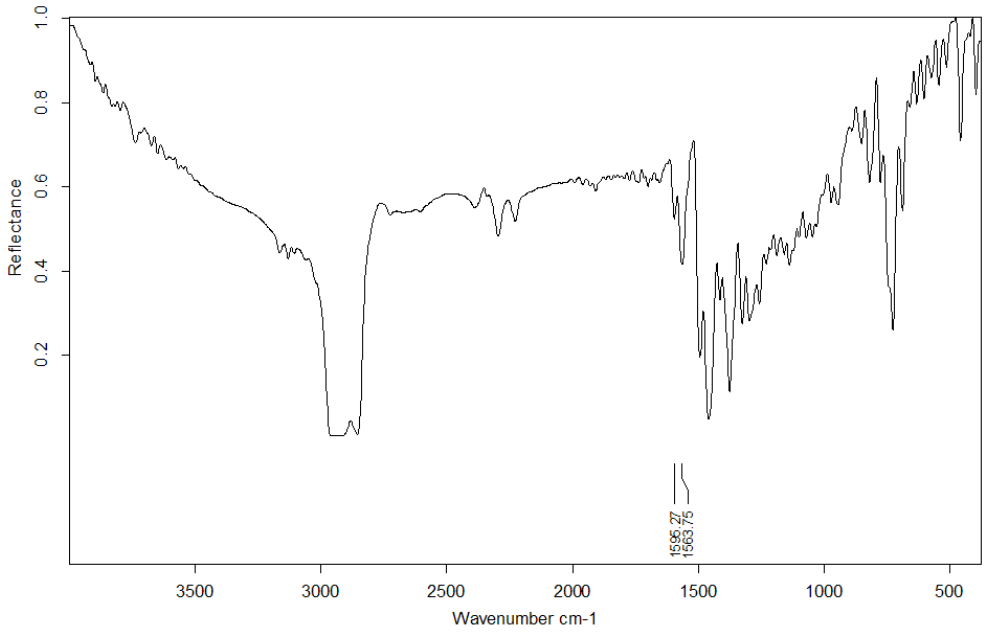


Fig.S19 IR spectrum of complex **3c**

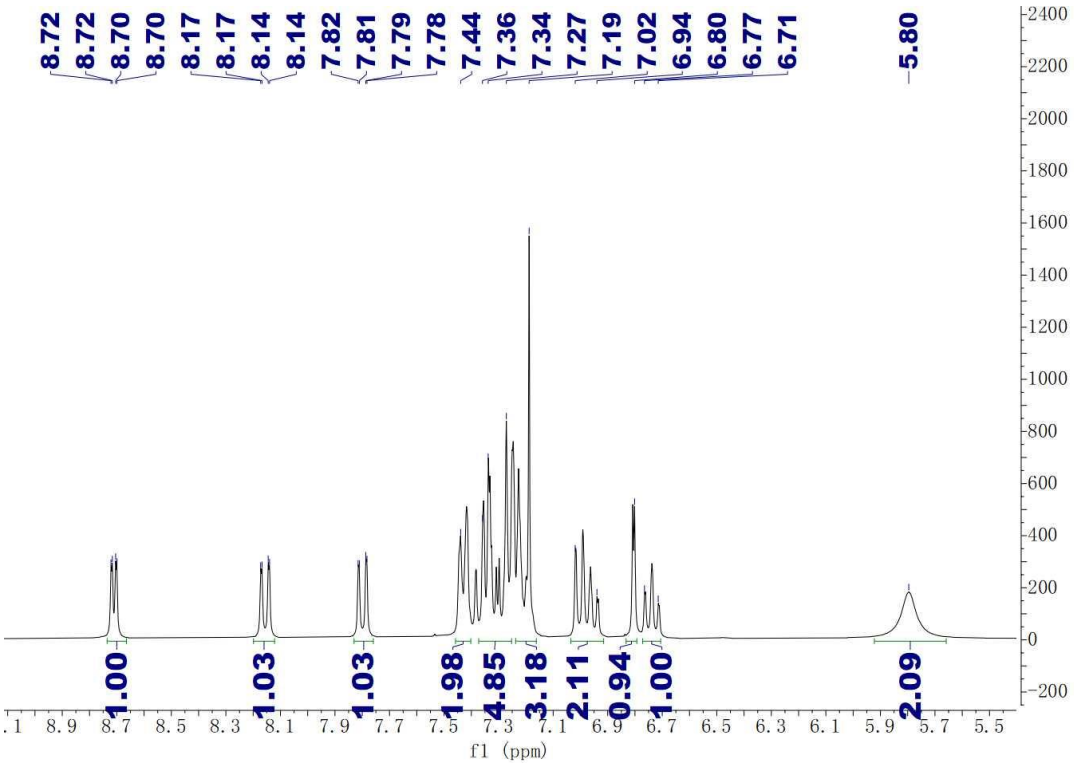


Fig.S20 ^{1}H NMR spectrum of complex **3c**（$CDCl_3$）

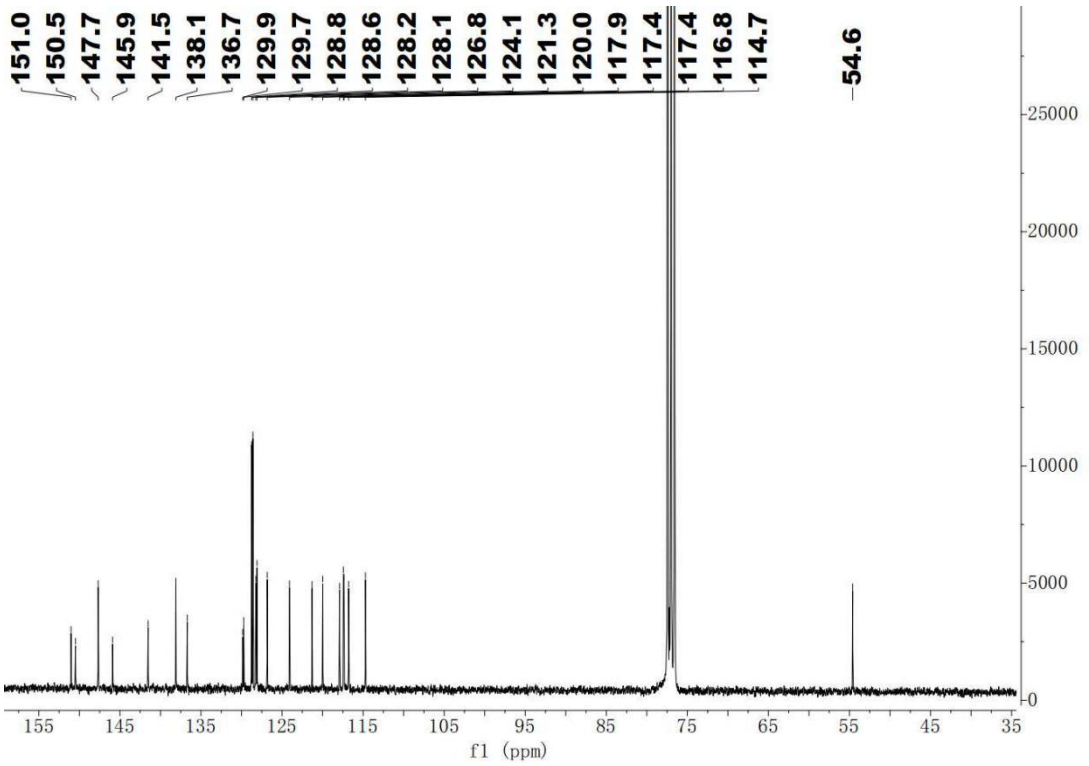


Fig.S21 ^{13}C NMR spectrum of complex **3c**（$CDCl_3$）

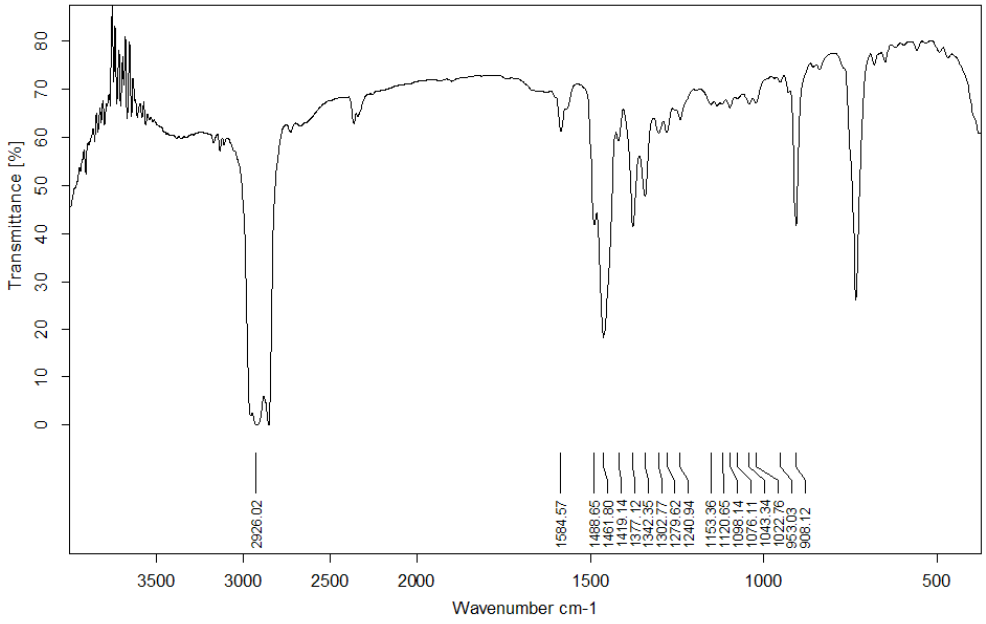


Fig.S22 IR spectrum of complex **5a**

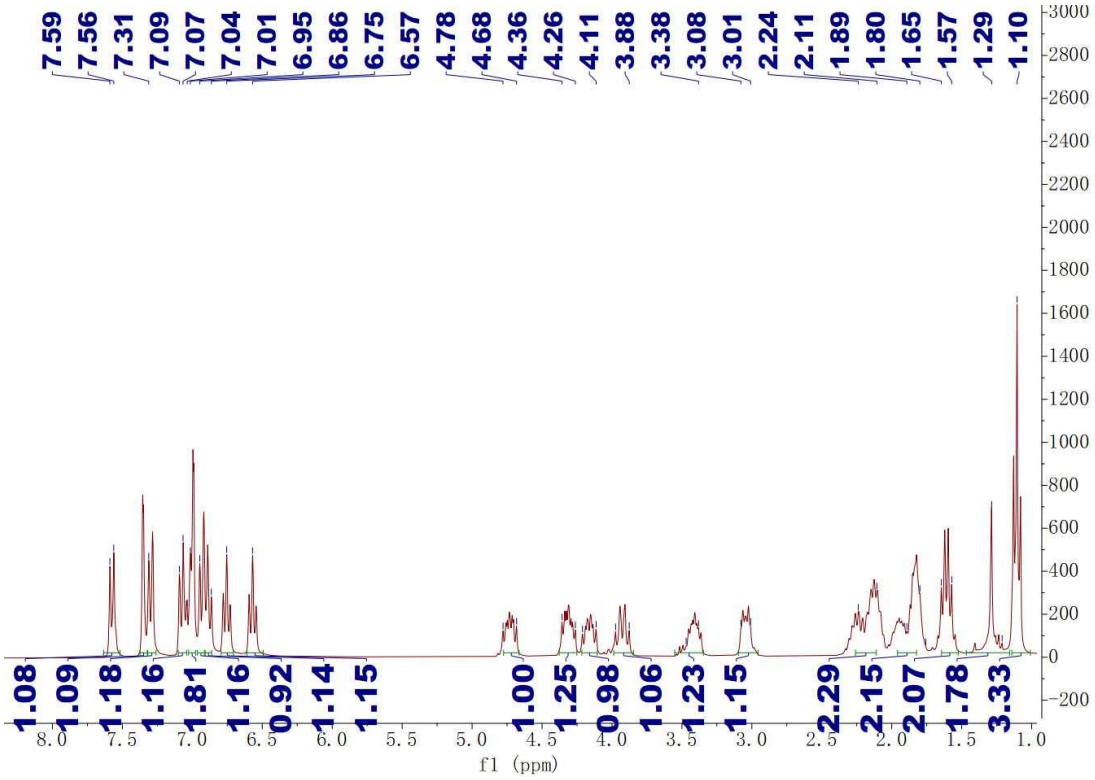


Fig.S23 ^{1}H NMR spectrum of complex **5a**（$CDCl_3$）

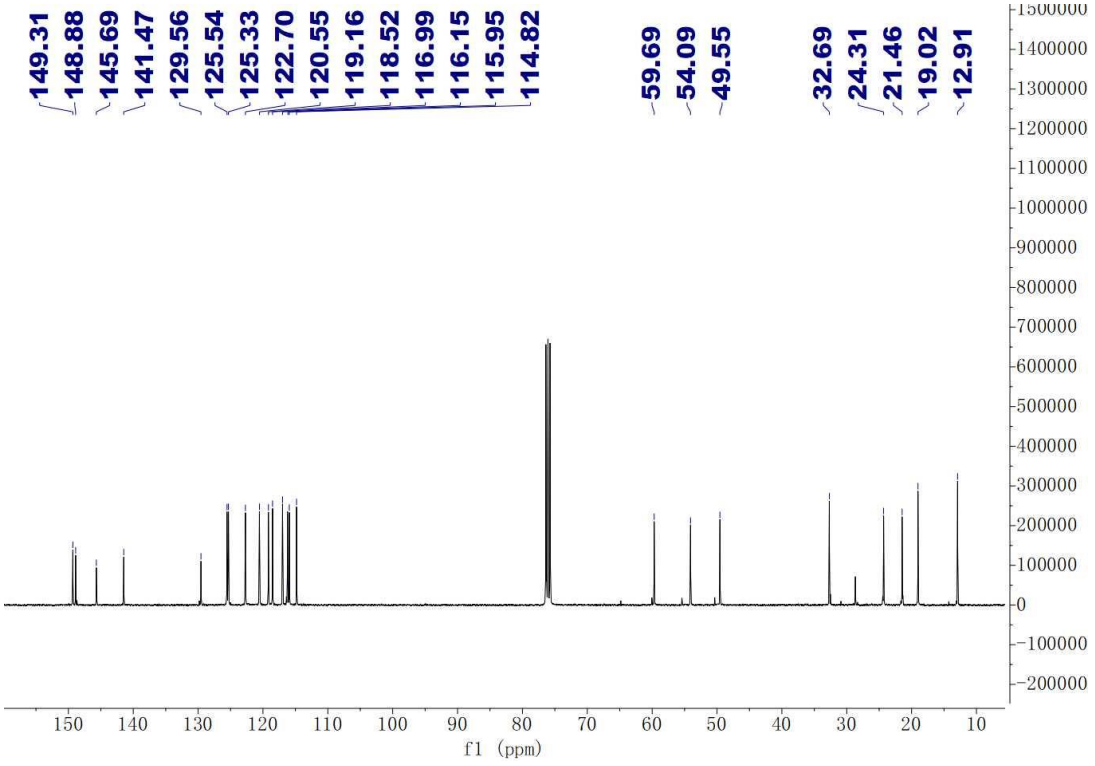


Fig.S24 ^{13}C NMR spectrum of complex **5a**（$CDCl_3$）

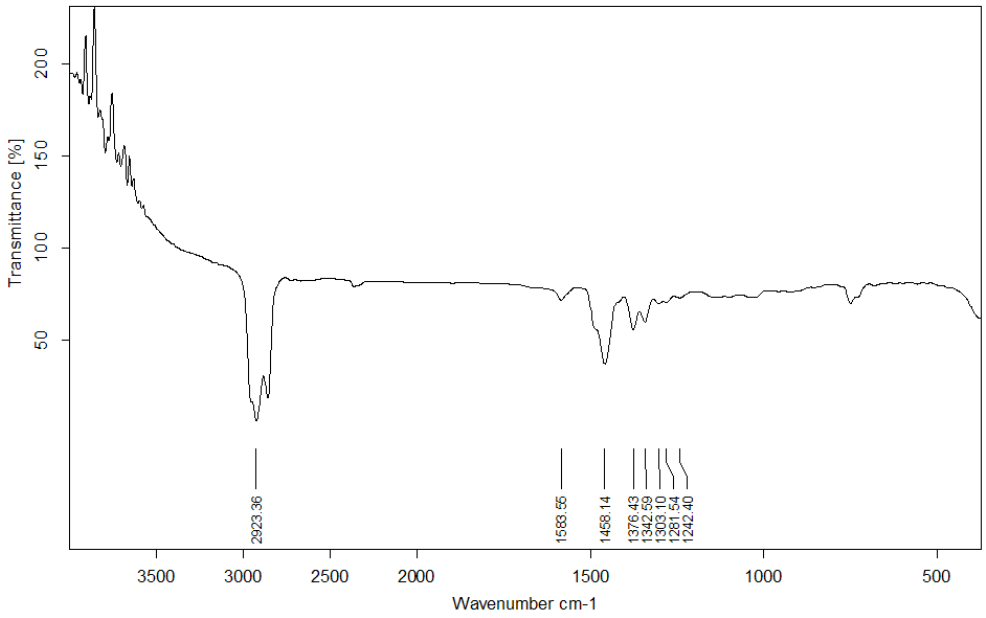


Fig.S25 IR spectrum of complex **5b**

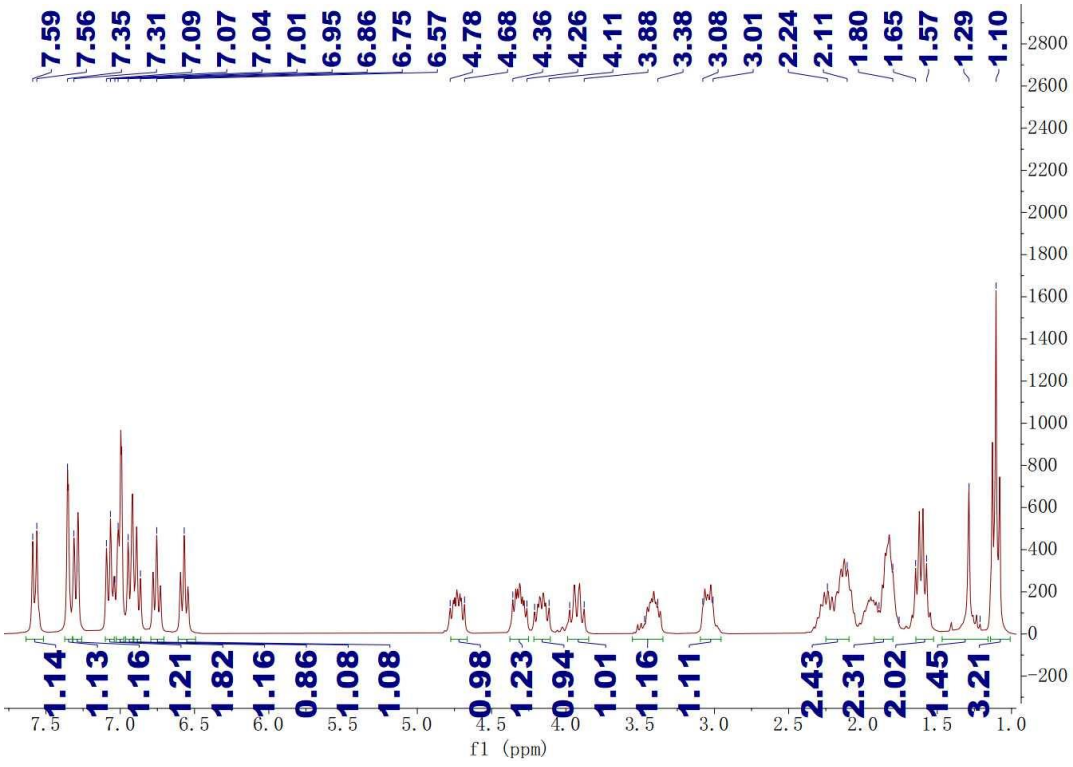


Fig.S26 ^{1}H NMR spectrum of complex **5b**（$CDCl_3$）

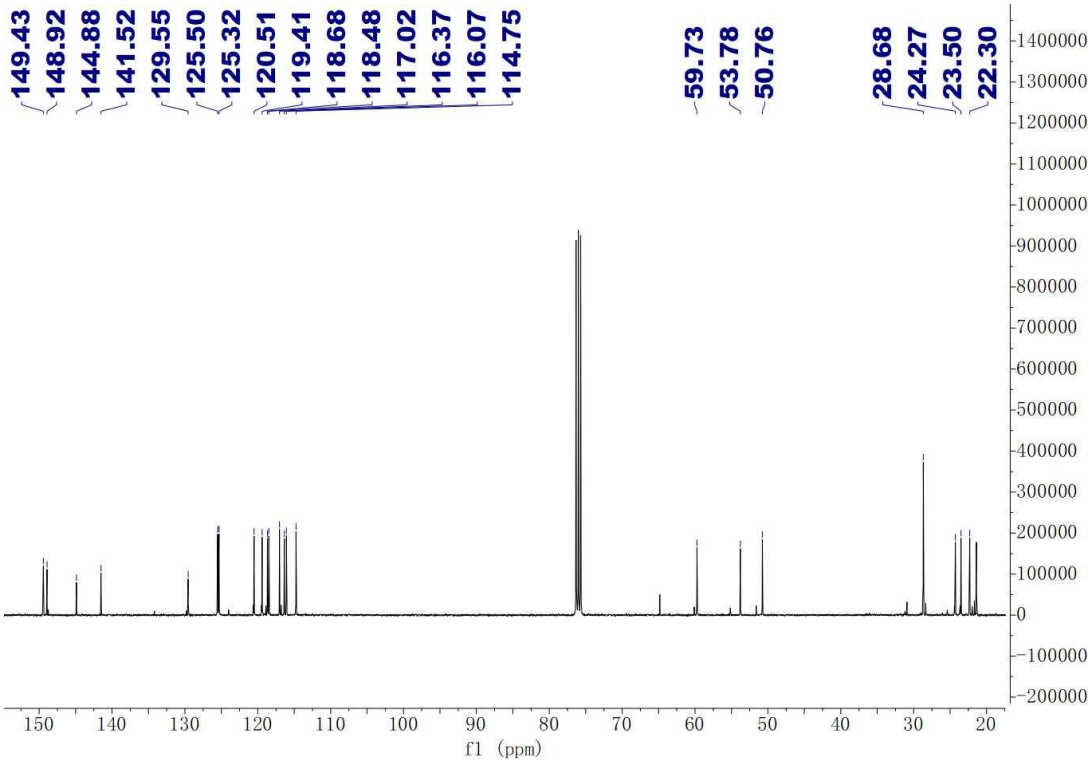


Fig.S27 ^{13}C NMR spectrum of complex **5b**（$CDCl_3$）

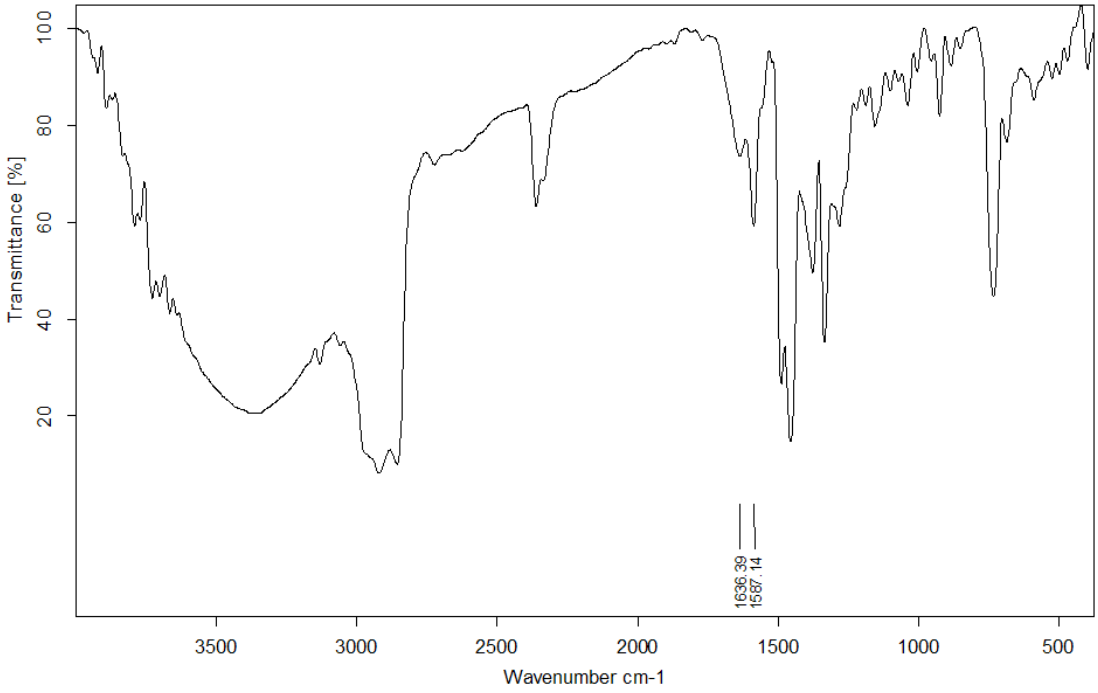


Fig.S28 IR spectrum of complex **5c**

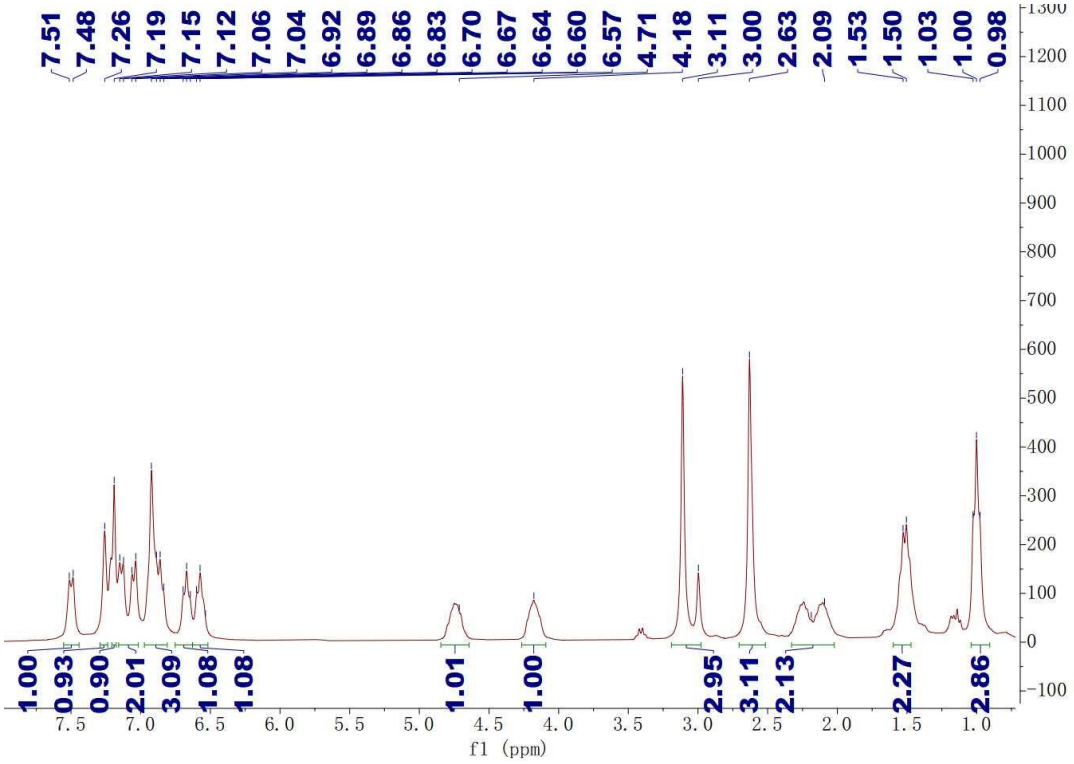


Fig.S29 ^{1}H NMR spectrum of complex **5c**（$CDCl_3$）

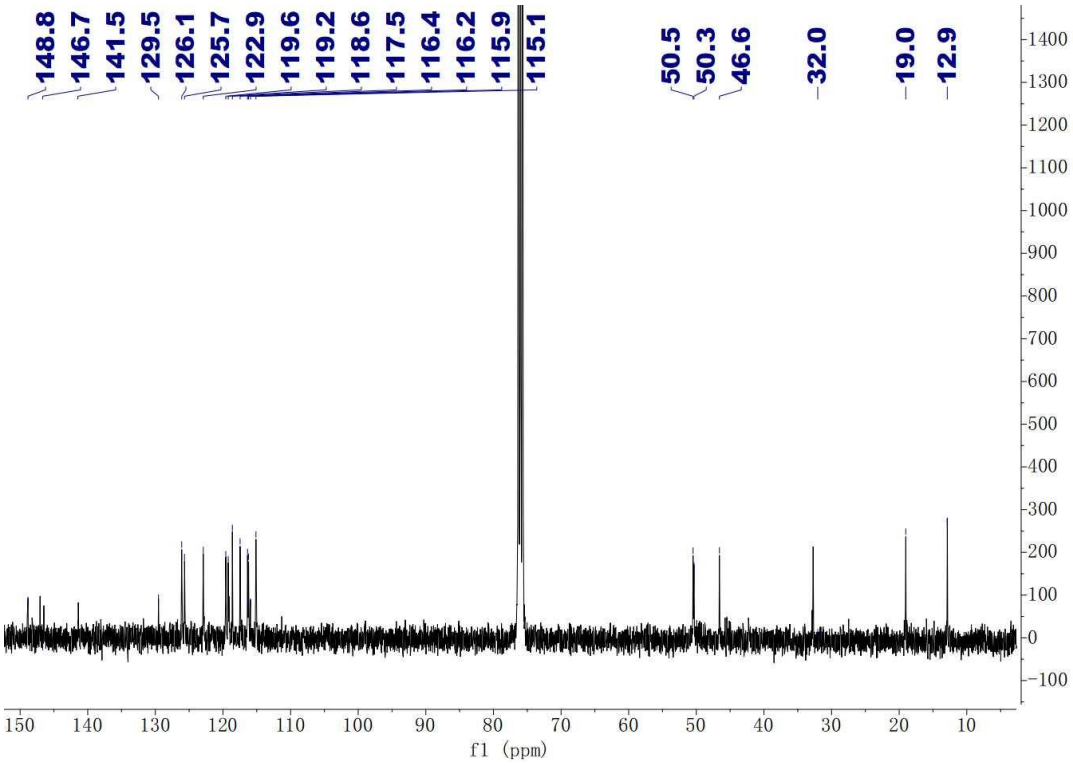


Fig.S30 ^{13}C NMR spectrum of complex **5c**（$CDCl_3$）

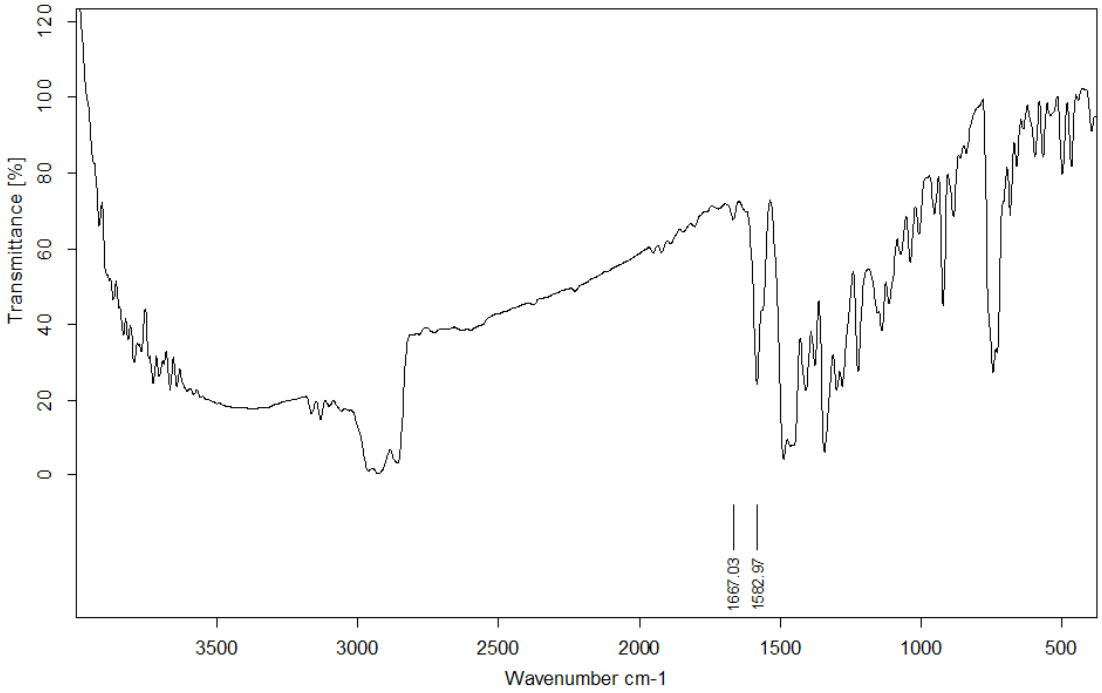


Fig.S31 IR spectrum of complex **5d**

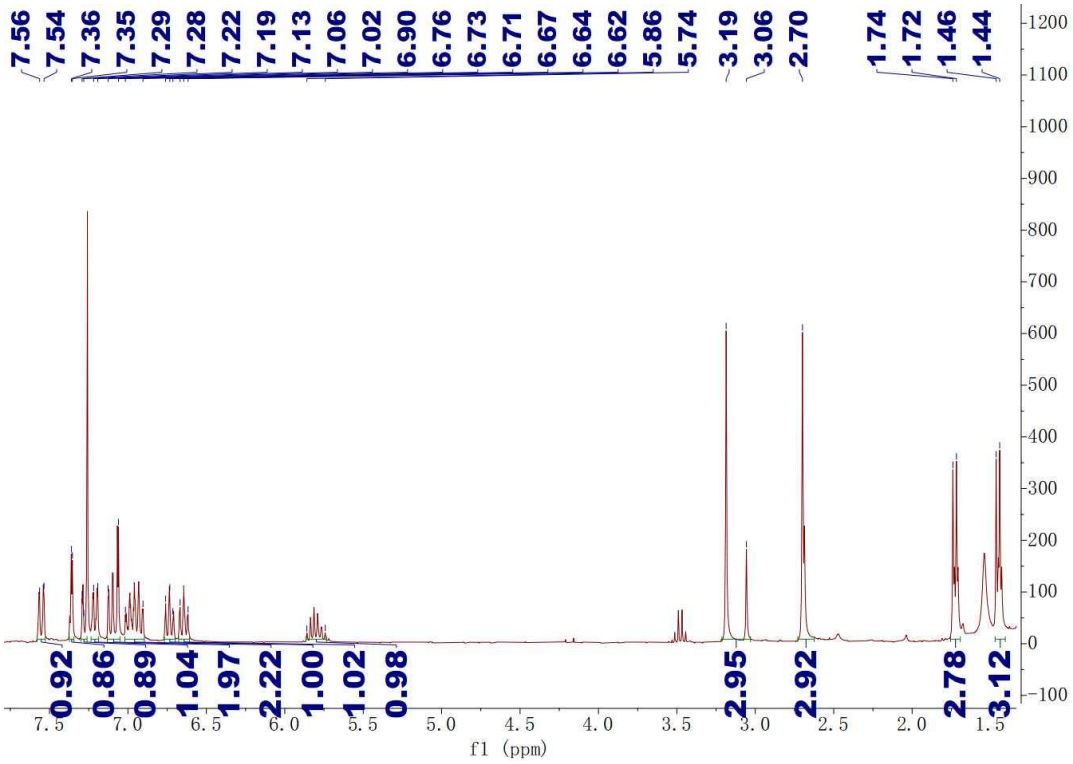


Fig.S32 ^{1}H NMR spectrum of complex **5d**（$CDCl_3$）

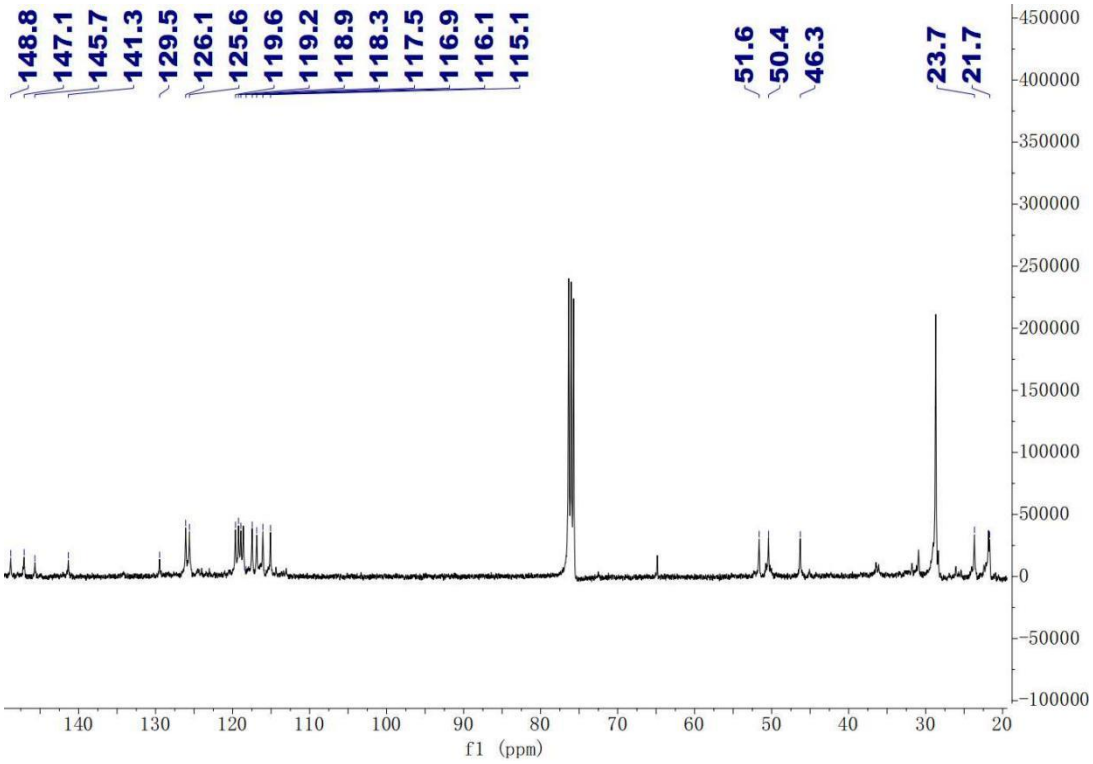
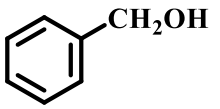


Fig.S33 ^{13}C NMR spectrum of complex **5d**（$CDCl_3$）

SV [1]H NMR Spectra and GC Spectrum of the Alcohol Products



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.14 - 7.29 (m, Ar-*H*, 5H), 4.53 (s, C*H*$_2$, 2H), 2.23 (s, O*H*, 1H).[1]

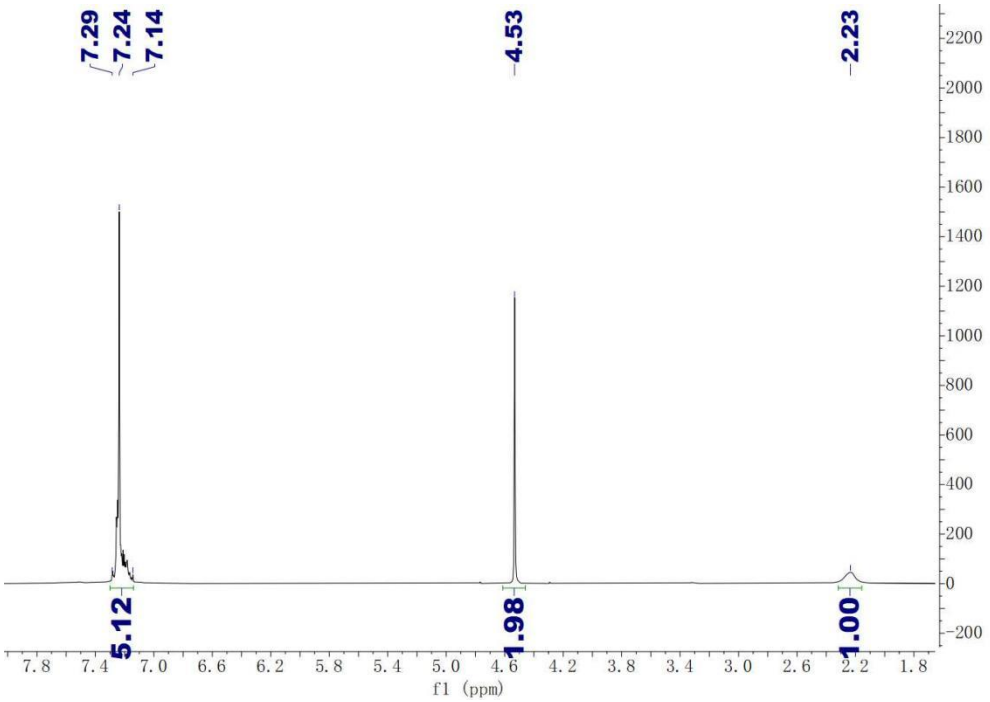
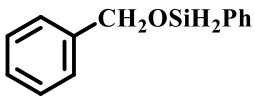


Fig.S34 [1]H NMR spectrum of **6a**（$CDCl_3$）



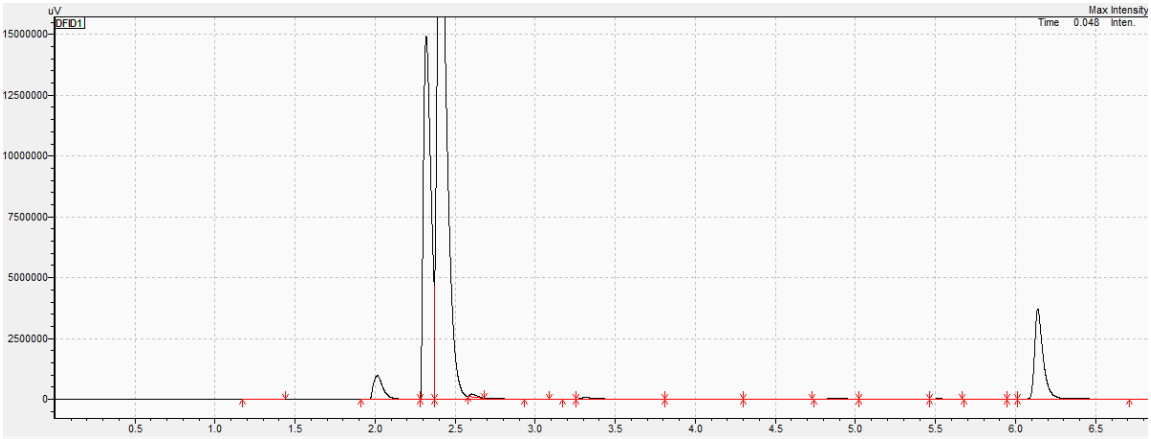
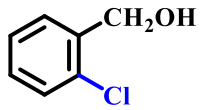


Fig.S35 GC spectrum of **6a**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.14-7.41 (m, Ar-*H*, 4H), 4.71 (s, C*H*$_2$, 2H), 1.92 (s, O*H*, 1H).[1]

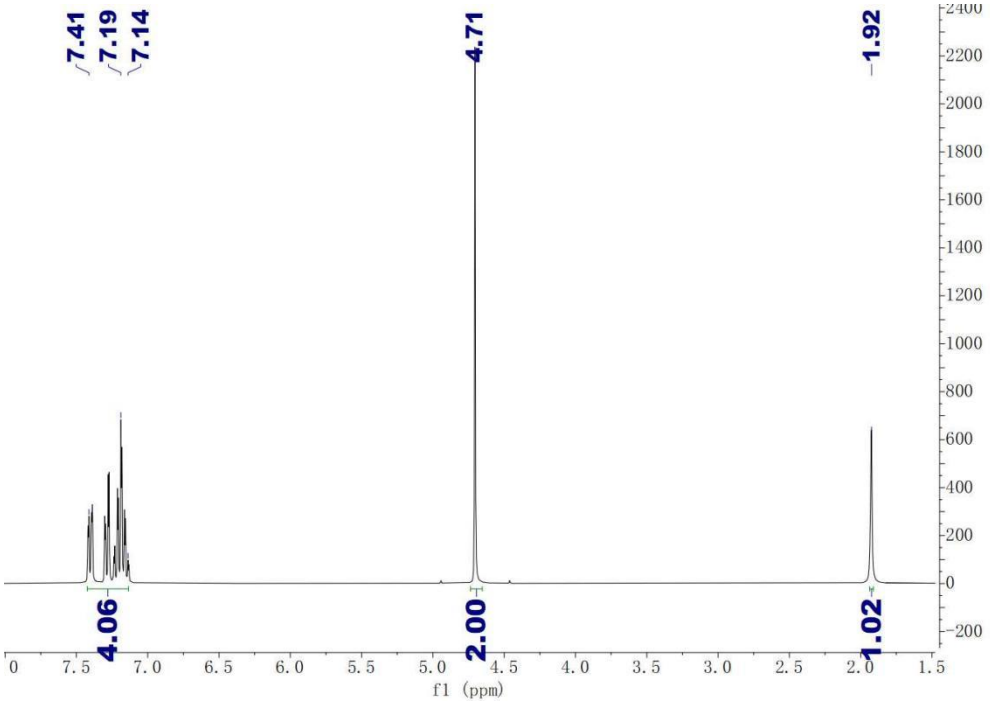
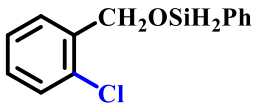


Fig.S36 ^{1}H NMR spectrum of **6b**（$CDCl_3$）



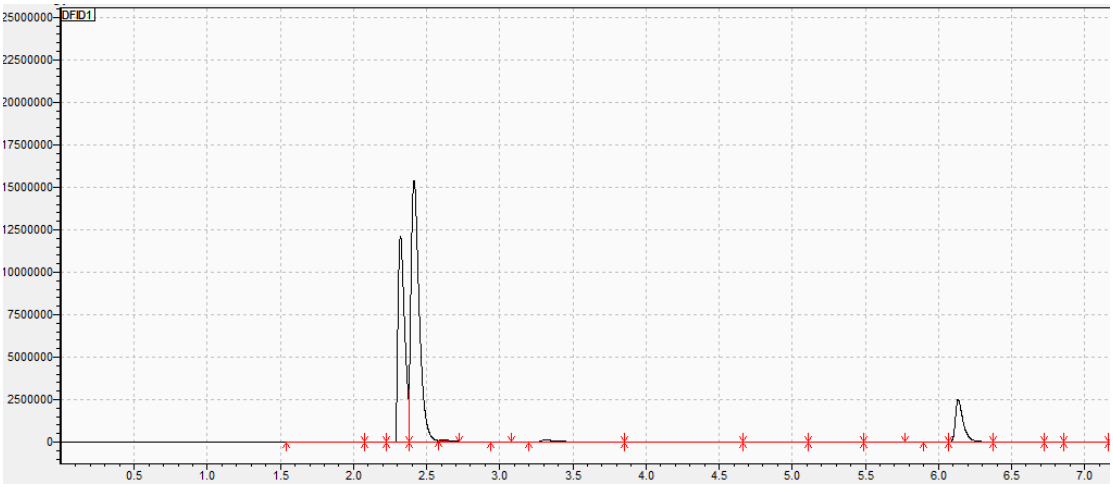
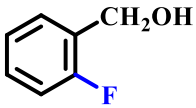


Fig.S37 GC spectrum of **6b**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.91-7.33 (m, Ar-*H*, 4H), 4.63 (s, C*H*$_2$, 2H), 2.33 (s, O*H*, 1H).[2]

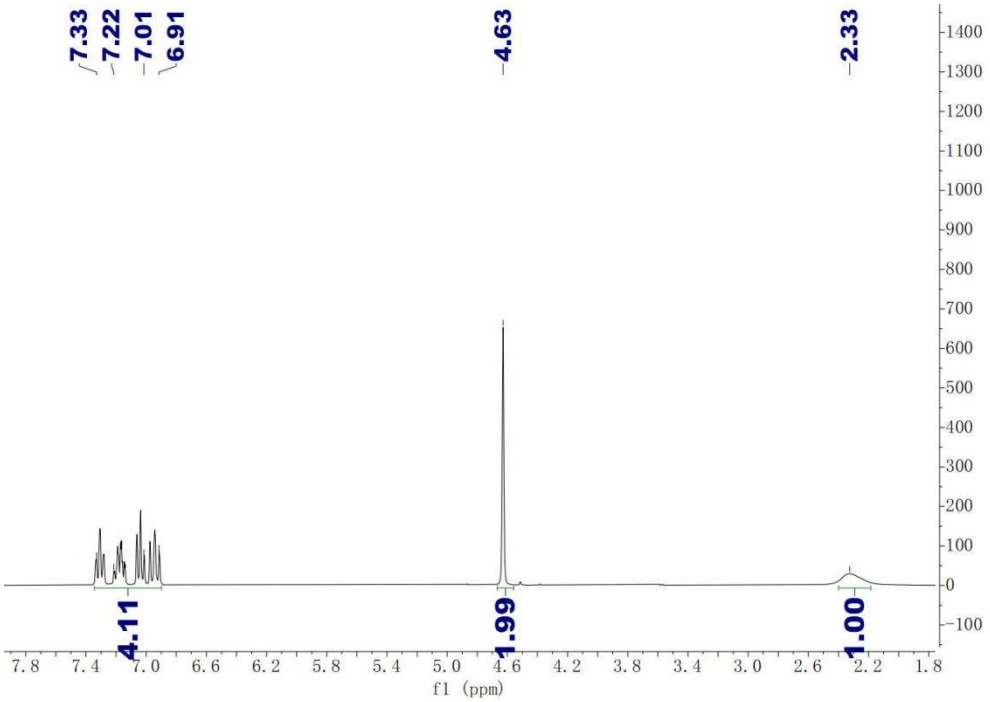
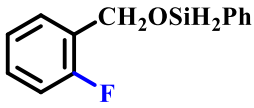


Fig.S38 ^{1}H NMR spectrum of **6c**（$CDCl_3$）



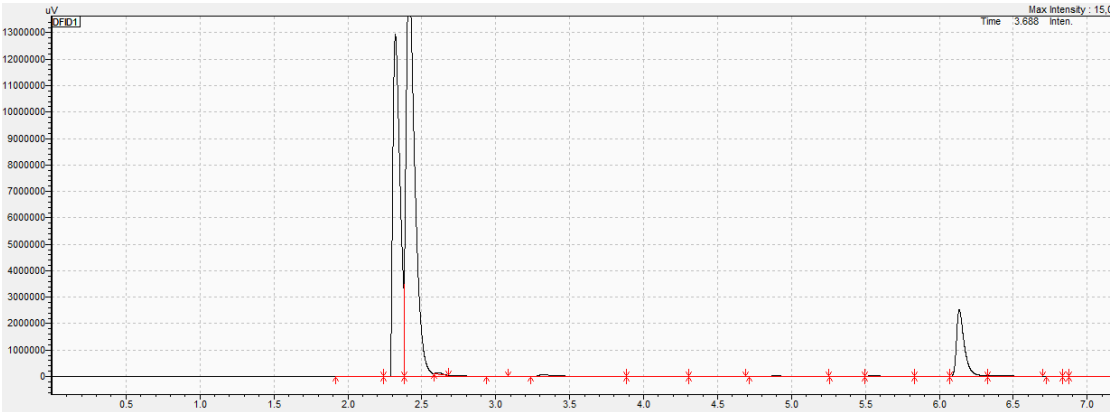
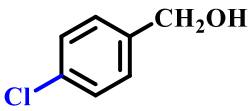


Fig.S39 GC spectrum of **6c**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.26-7.34 (m, Ar-*H*, 4H), 4.66 (s, C*H*$_2$, 2H), 1.78 (s, O*H*, 1H).[3]

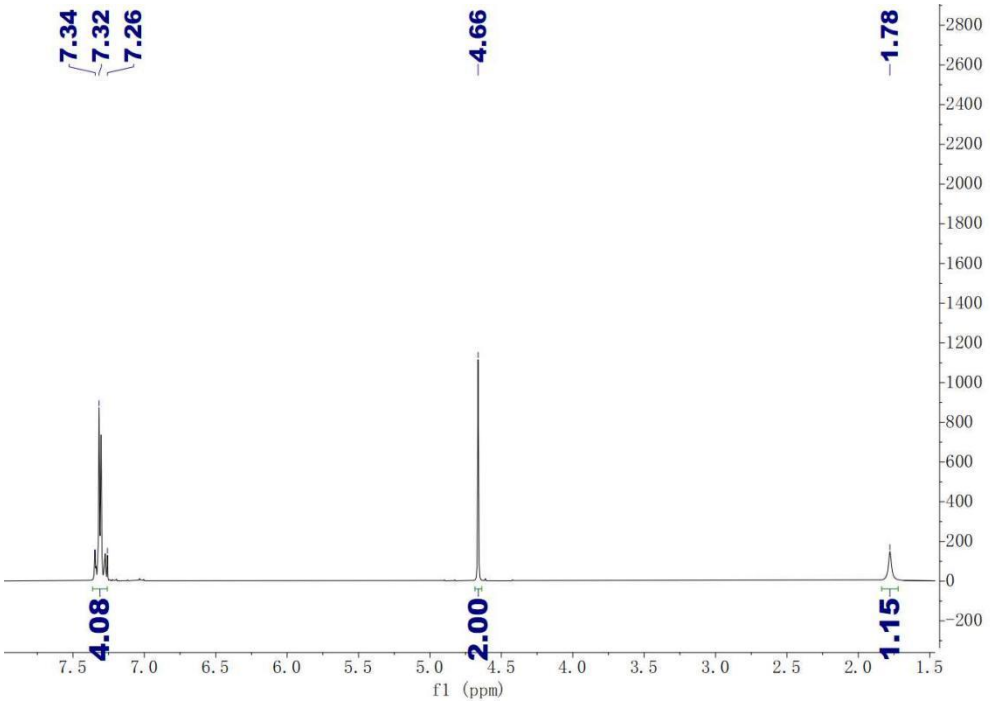
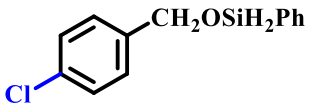


Fig.S40 ^{1}H NMR spectrum of 6**d**（$CDCl_3$）



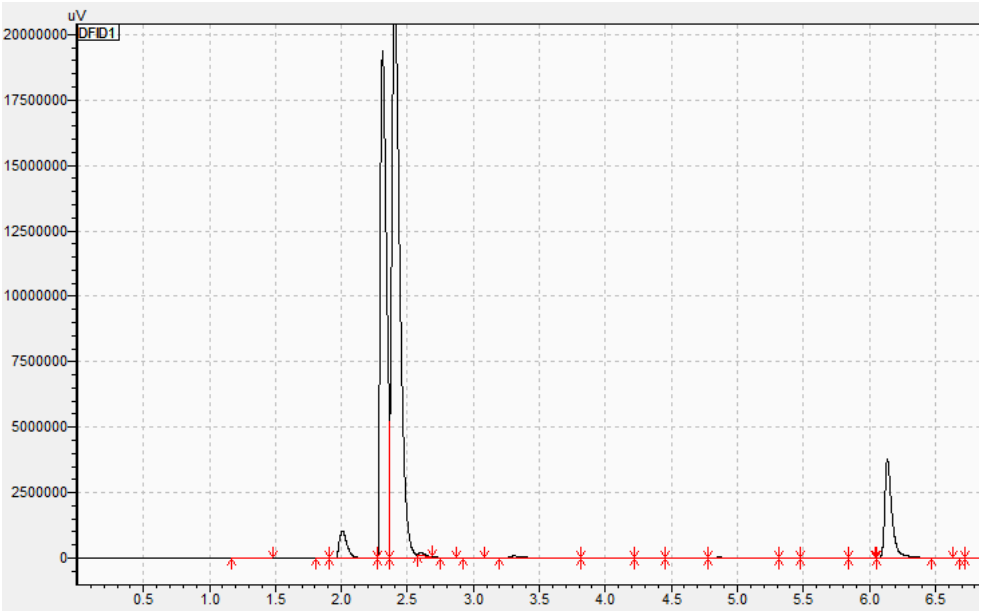
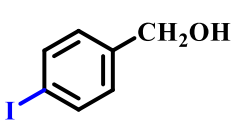


Fig.S41 GC spectrum of **6d**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.54 (d, Ar-*H*, 2H),6.93 (d, Ar-*H*, 2H)， 4.43 (s, CH_2, 2H), 2.71 (s, O*H*, 1H).[1]

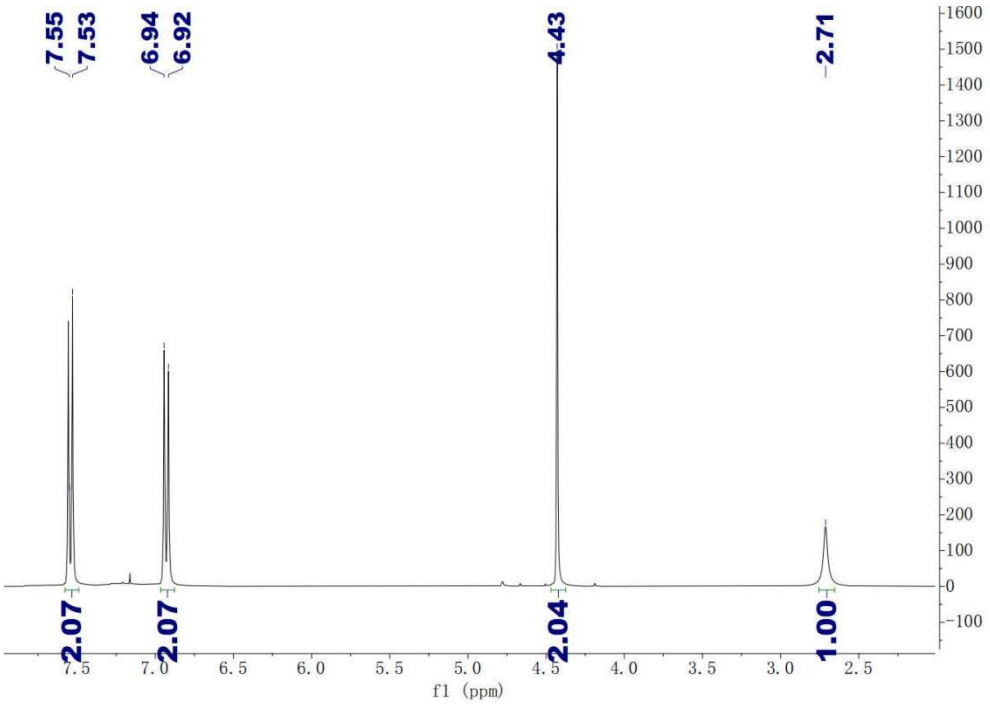
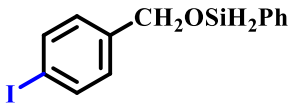


Fig.S42 ^{1}H NMR spectrum of 6**e**（$CDCl_3$）



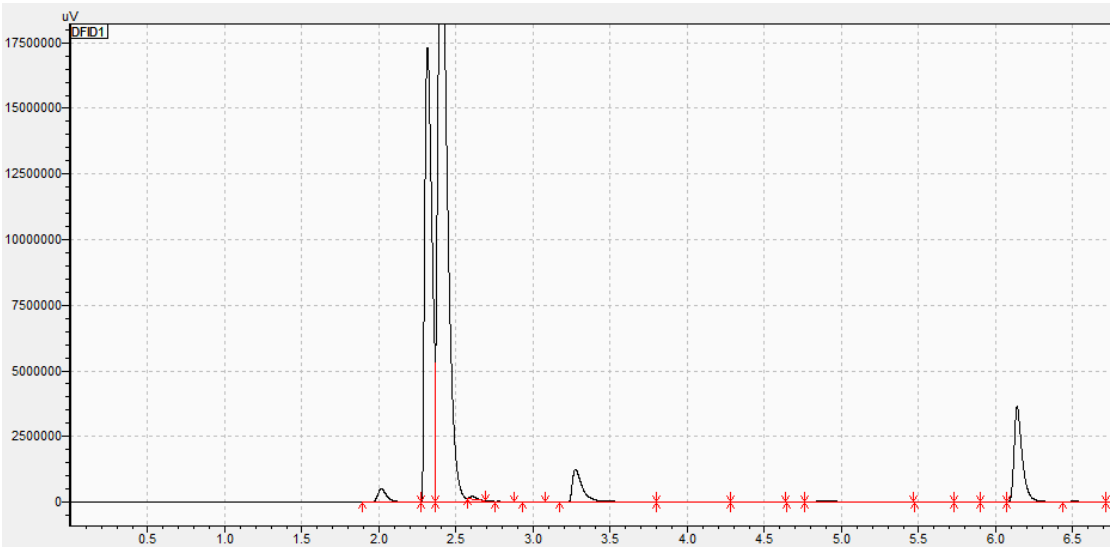
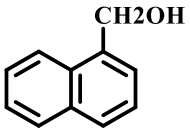


Fig.S43 GC spectrum of **6e**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.21-7.85 (m, Ar-*H*, 7H), 4.83 (s, C*H*$_2$, 2H), 2.45 (s, O*H*, 1H). [2]

.

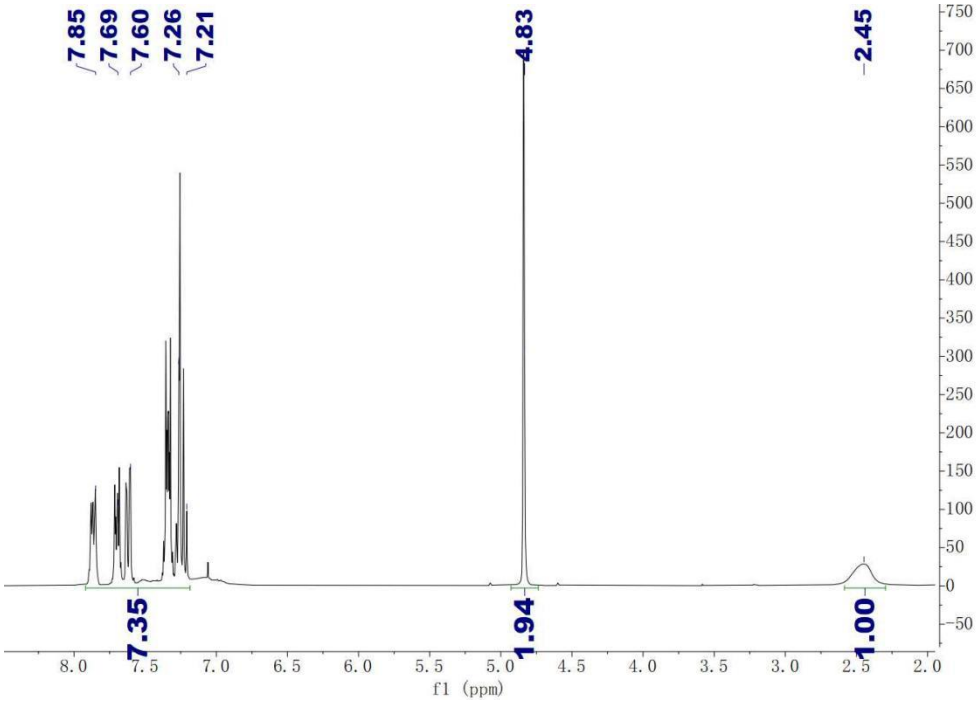
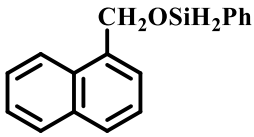


Fig.S44 ^{1}H NMR spectrum of **6f**（$CDCl_3$）



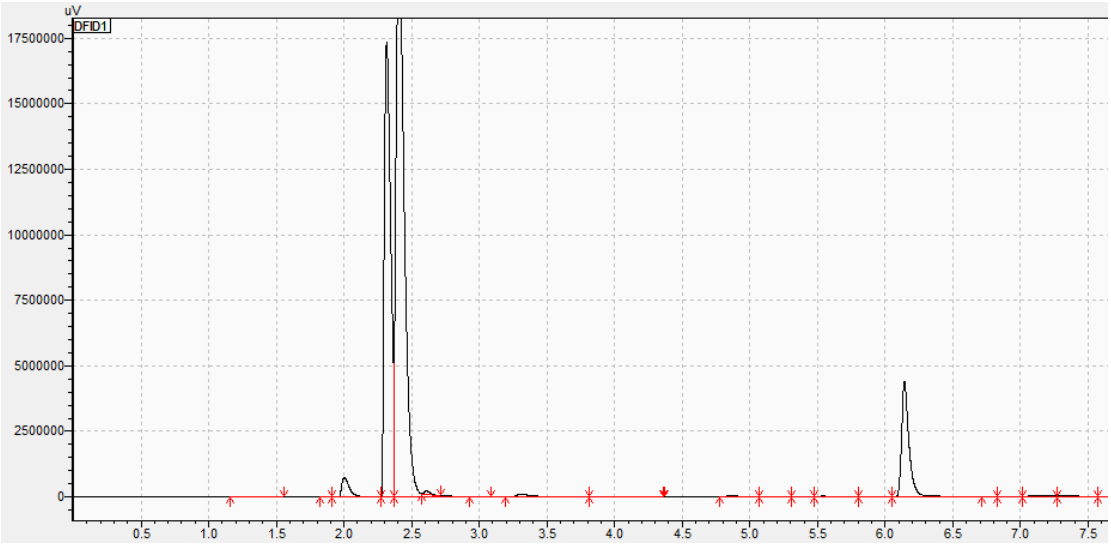


Fig.S45 GC spectrum of **6f**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.18-7.38 (m, Ar-*H*, 3H), 4.69 (s, C*H*$_2$, 2H), 1.75 (s, O*H*, 1H). [1]

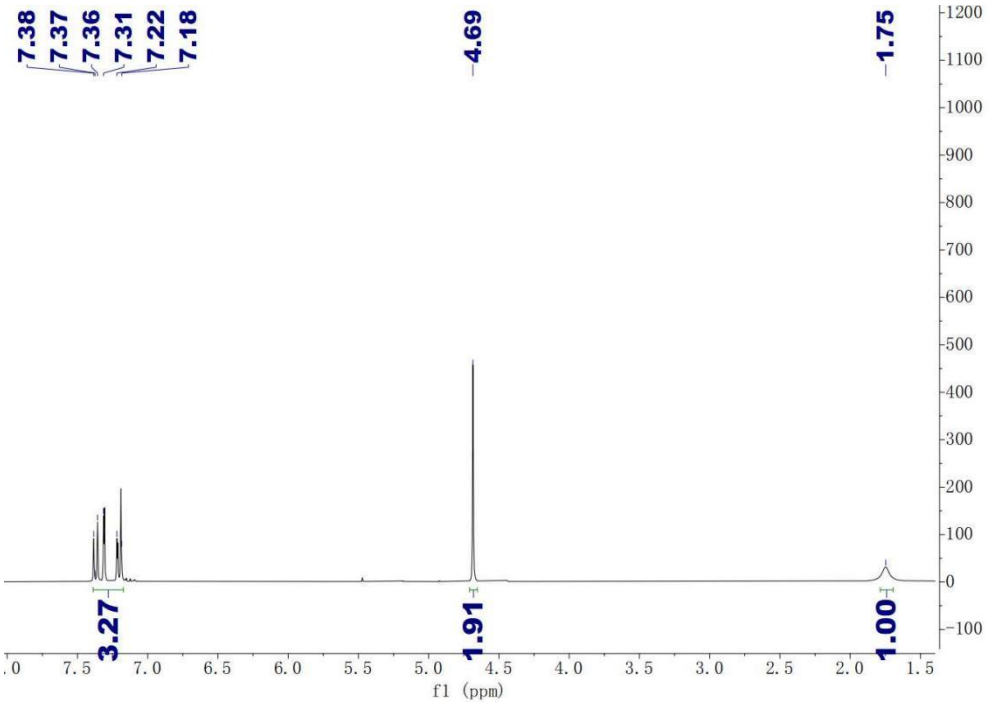
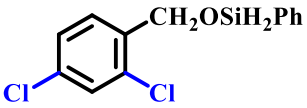


Fig.S46 ^{1}H NMR spectrum of **6g**（$CDCl_3$）



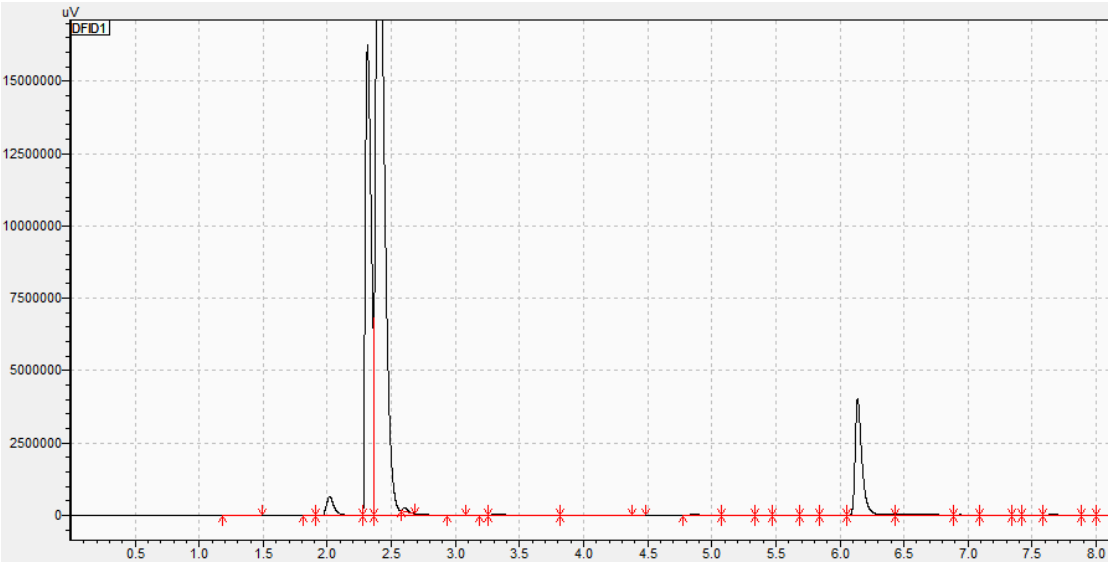
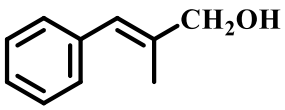


Fig.S47 GC spectrum of **6g**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.12-7.27 (m, Ar-*H*, 5H), 6.44 (d, *H*C=C, 1H), 4.10 (dd, CH_2, 2H), 2.10 (s, O*H*, 1H) ,1.82 (d, CH_3, 3H).[2]

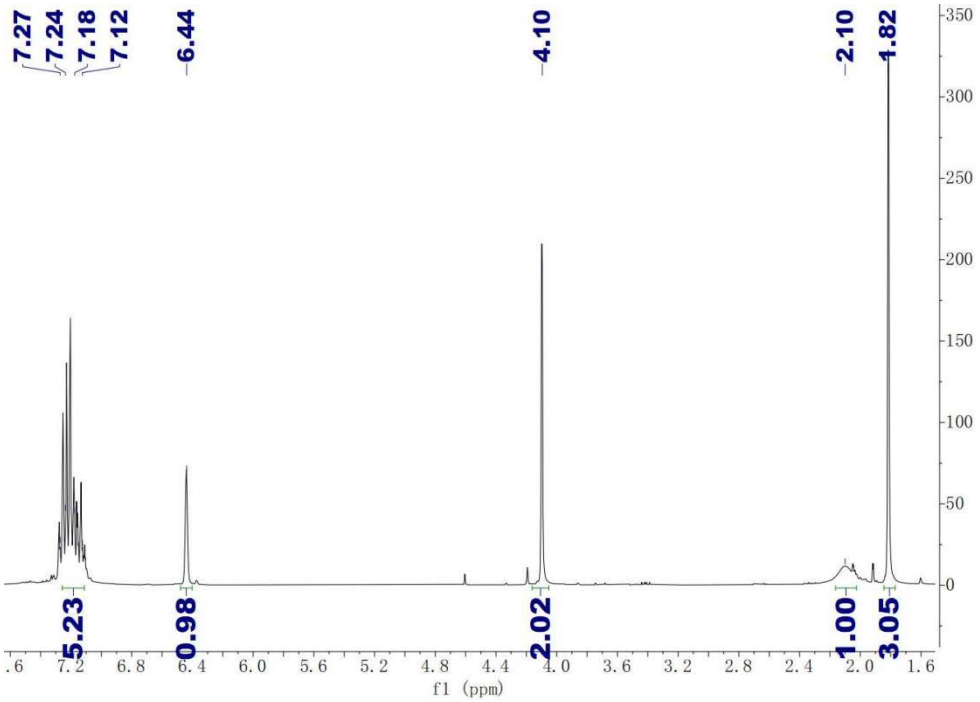
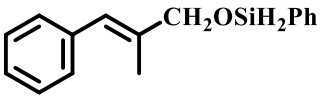


Fig.S48 ^{1}H NMR spectrum of **6h**（$CDCl_3$）



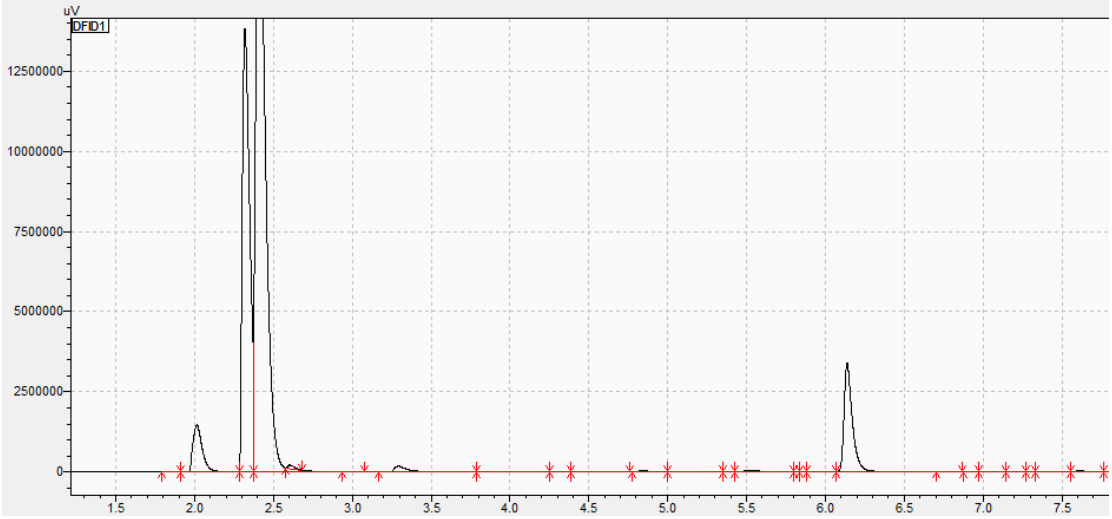
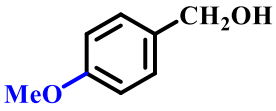


Fig.S49 GC spectrum of **6h**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.16 (d, Ar-*H*, 2H), 6.78 (d, Ar-*H*, 2H), 4.47 (s, CH_2, 2H), 3.69 (s, OCH_3, 3H), 2.21 (s, O*H*, 1H).[1]

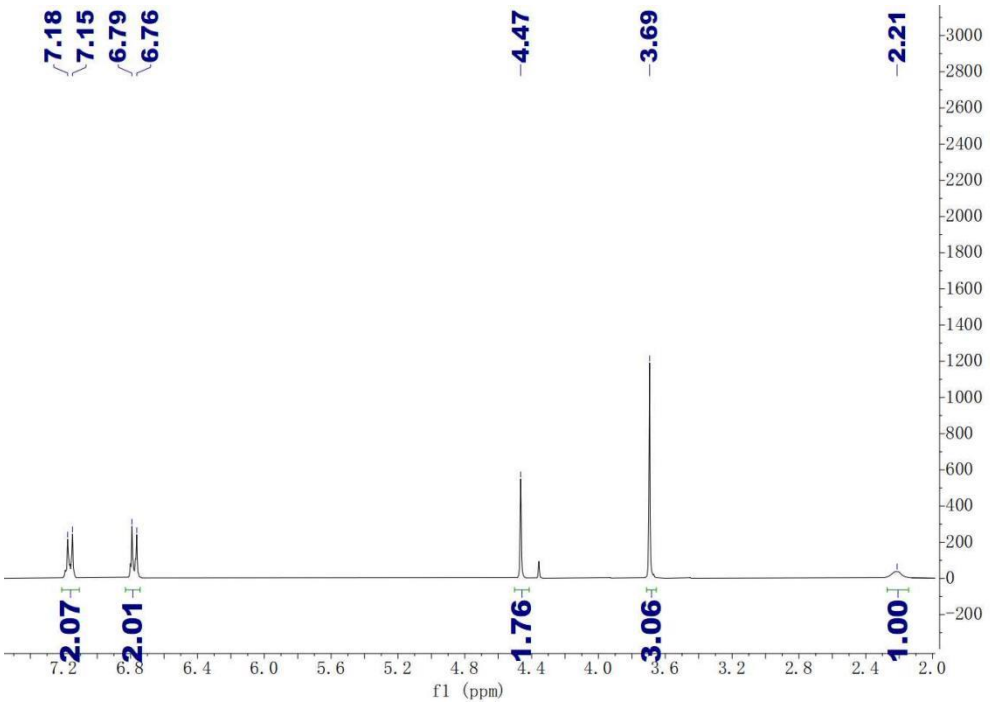
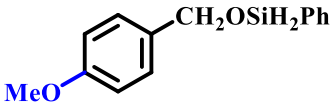


Fig.S50 ^{1}H NMR spectrum of **6i**（$CDCl_3$）



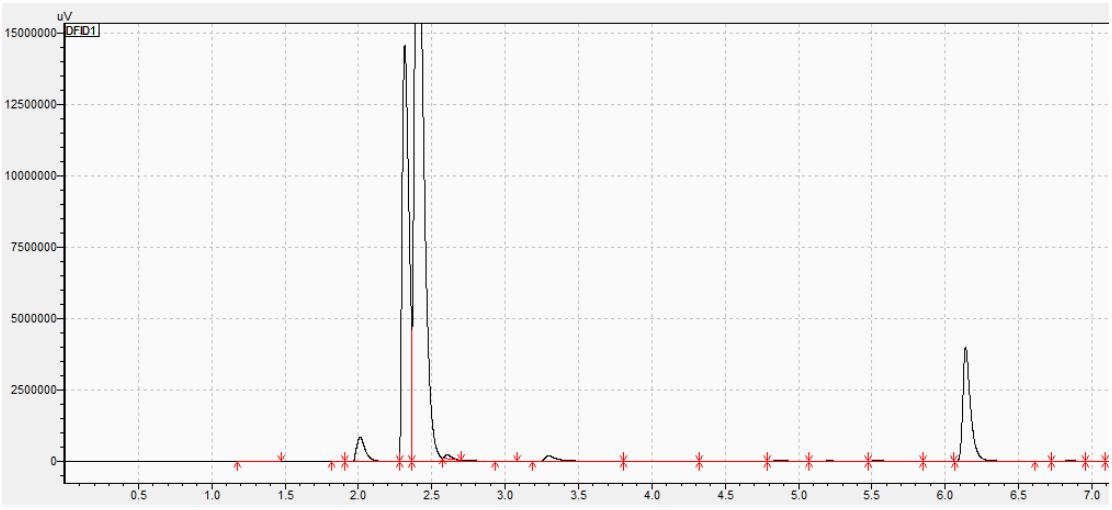
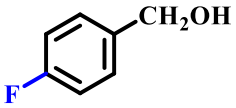


Fig.S51 GC spectrum of **6i**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.93-7.27 (m, Ar-*H*, 4H), 4.57 (s, C*H*$_2$, 2H),1.84 (s, O*H*, 1H).[4]

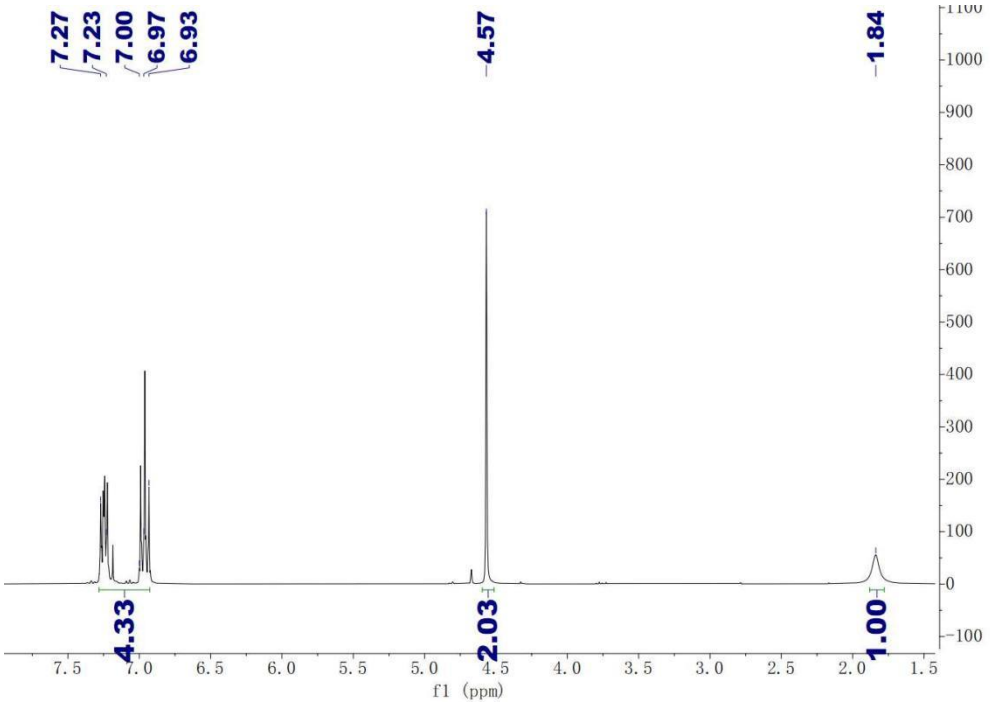
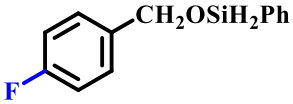


Fig.S52 ^{1}H NMR spectrum of **6j**（$CDCl_3$）



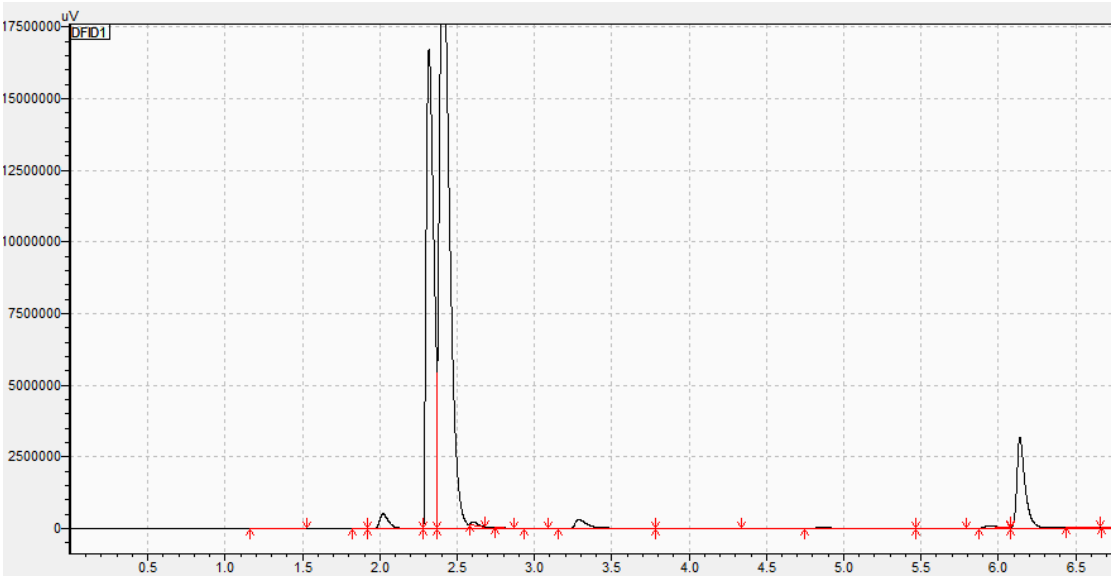
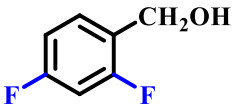


Fig.S53 GC spectrum of **6j**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.26-7.34 (m, Ar-*H*, 1H)，7.69-6.82 (m, Ar-*H*, 2H)，4.61 (s, C*H*$_2$, 2H), 2.01 (s, O*H*, 1H).[]

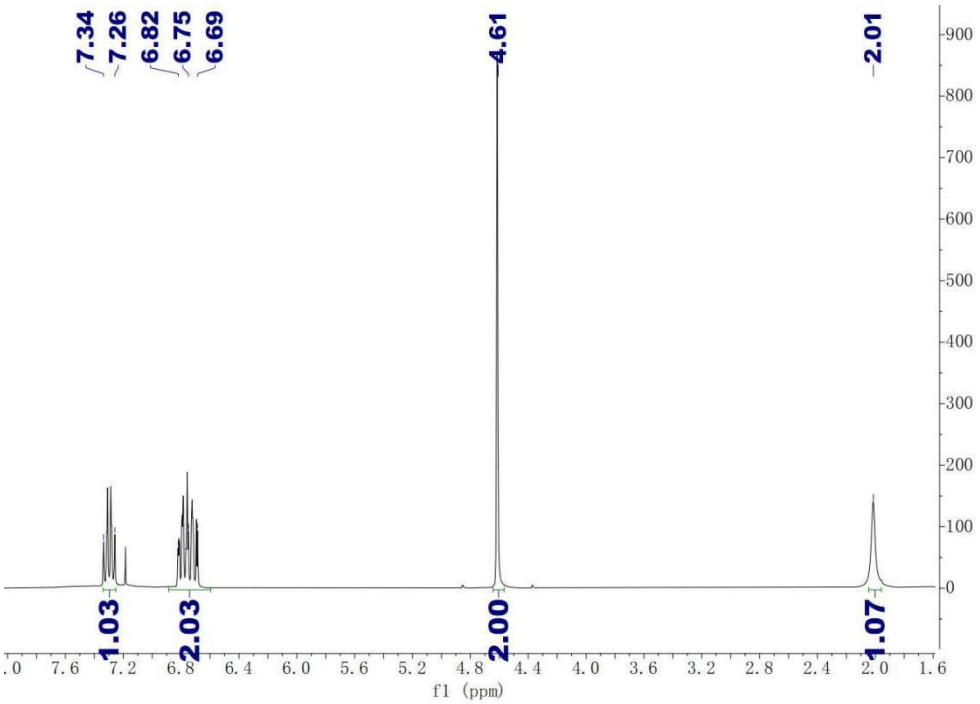
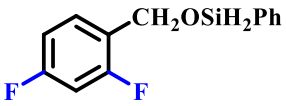


Fig.S54 ^{1}H NMR spectrum of **6k**（$CDCl_3$）



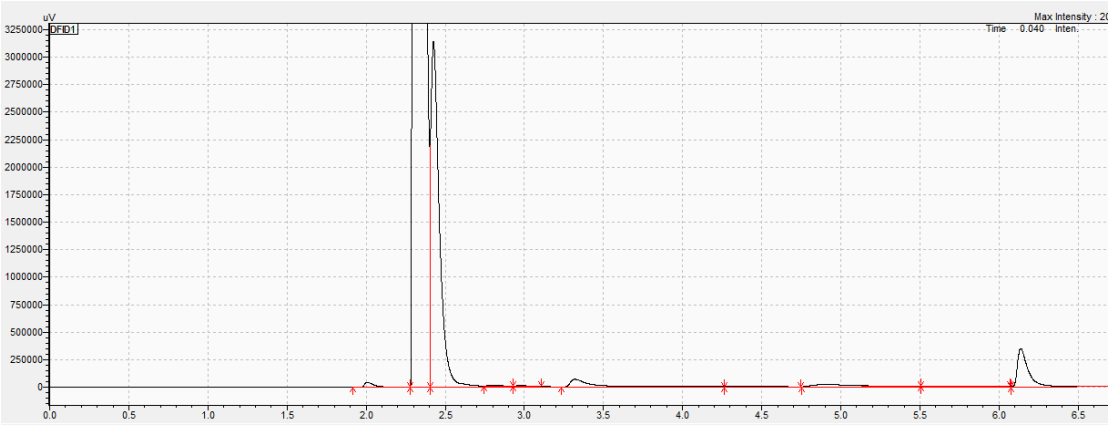
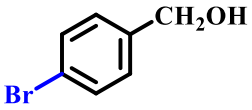


Fig.S55 GC spectrum of **6k**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.47 (d, Ar-*H*, 2H),7.22(d, Ar-*H*, 2H)， 4.63 (s, C*H*$_2$, 2H), 1.91 (s, O*H*, 1H).[3]

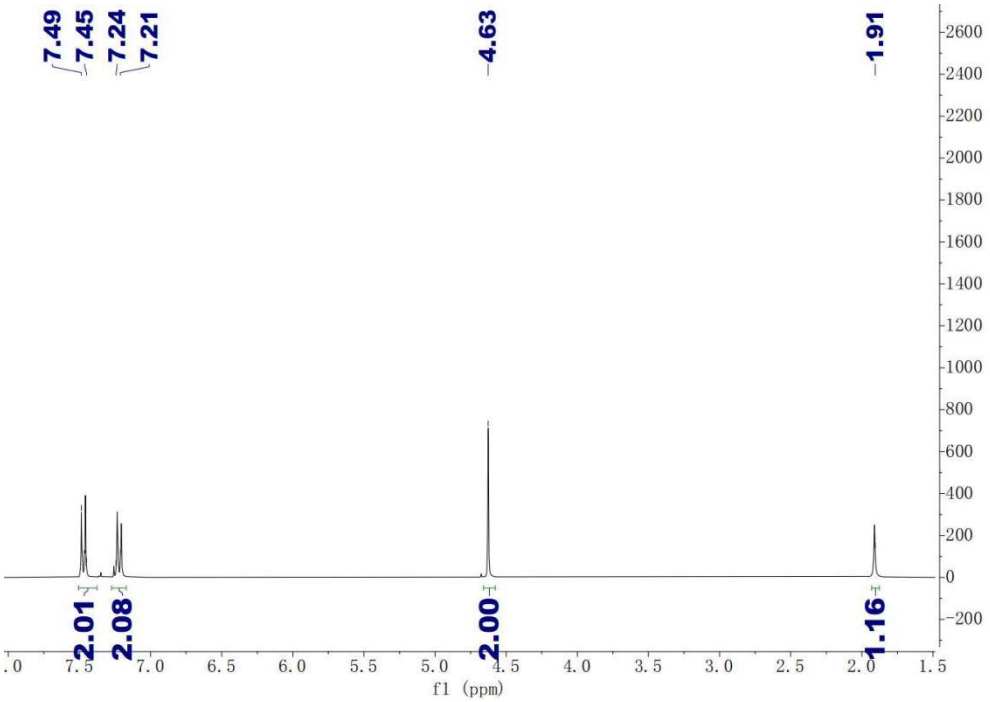
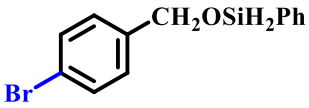


Fig.S56 ^{1}H NMR spectrum of **6l**（$CDCl_3$）



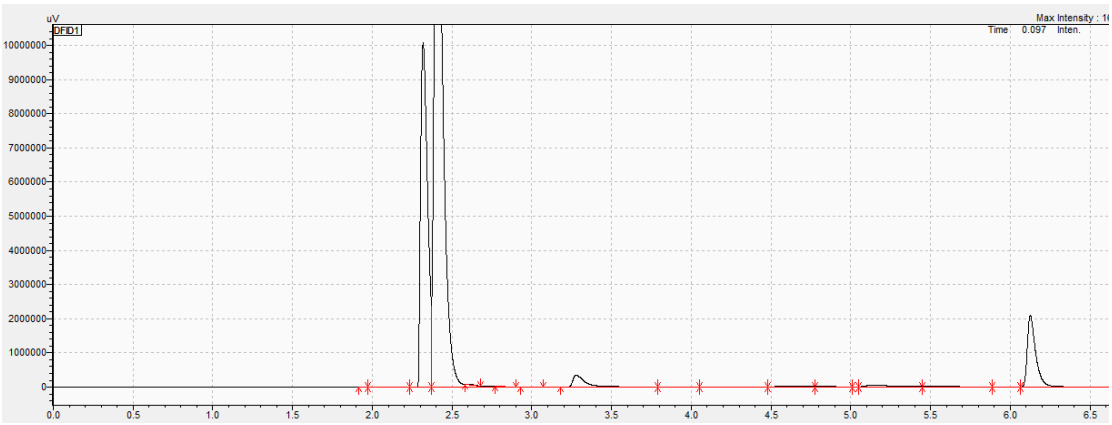


Fig.S57 GC spectrum of **6l**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.48-8.10 (m, Ar-*H*, 4H), 4.98 (s, CH_2, 2H), 2.14 (s, O*H*, 1H).[3]

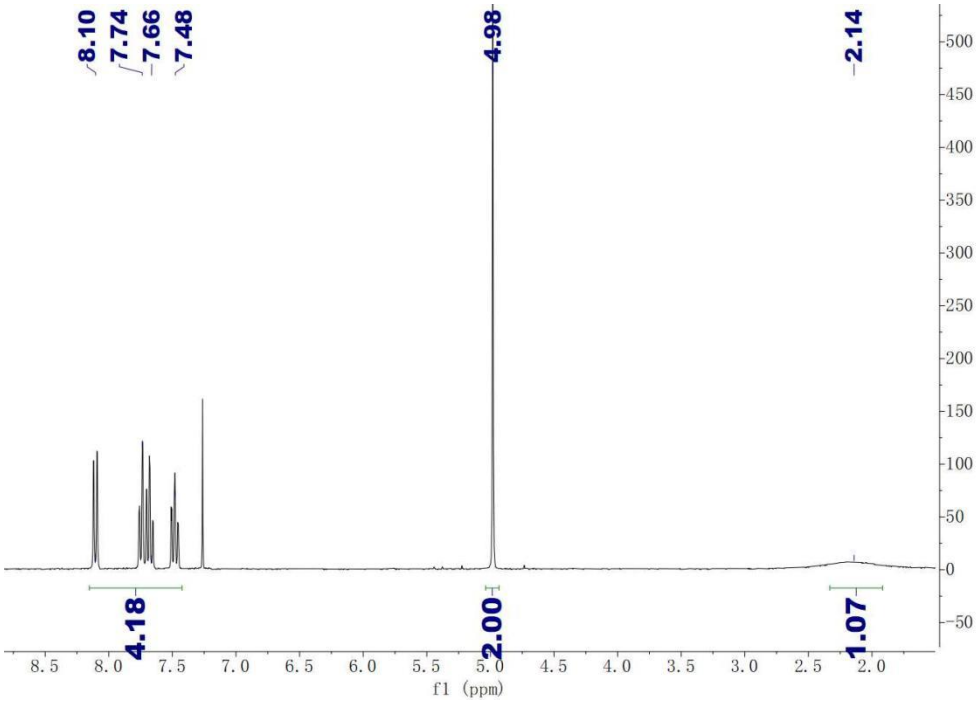
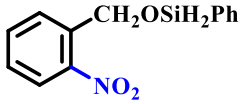


Fig.S58 ^{1}H NMR spectrum of **6m**（$CDCl_3$）



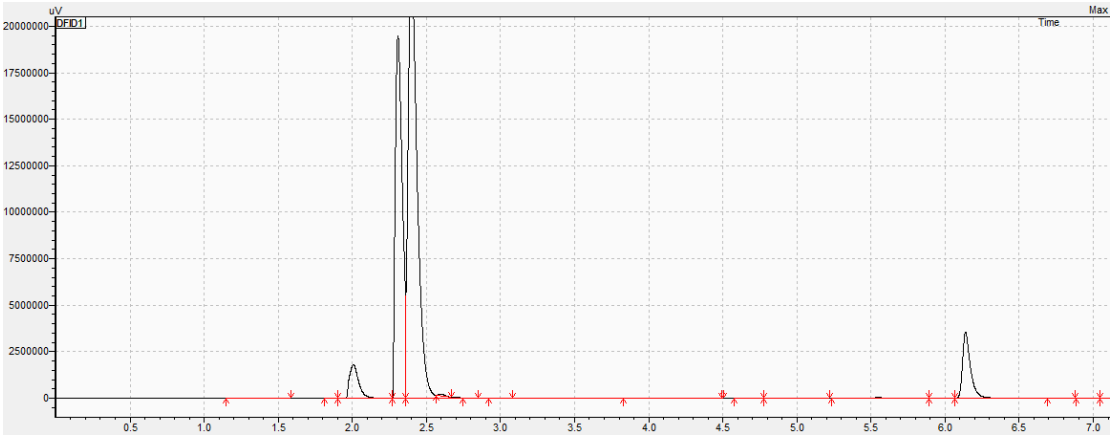
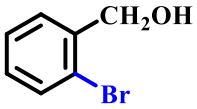


Fig.S59 GC spectrum of **6m**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.14-7.56 (m, Ar-*H*, 4H), 4.75 (s, CH_2, 2H), 1.83 (s, O*H*, 1H).[1]

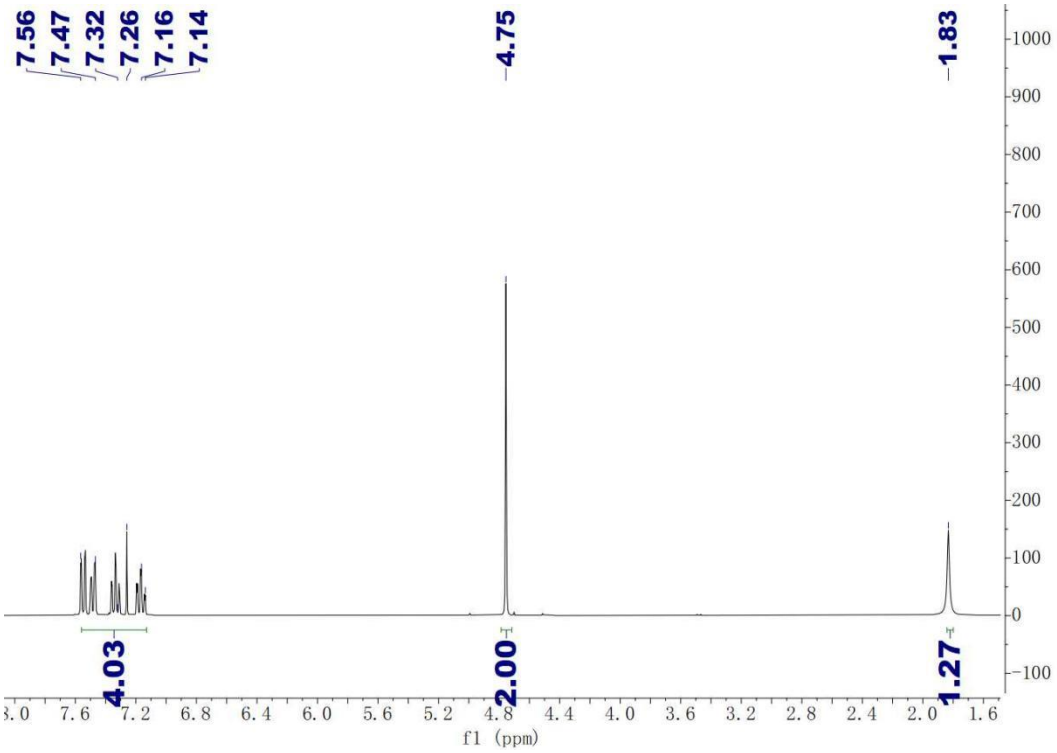
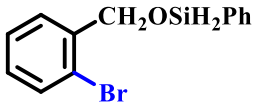


Fig.S60 ^{1}H NMR spectrum of **6n**（$CDCl_3$）



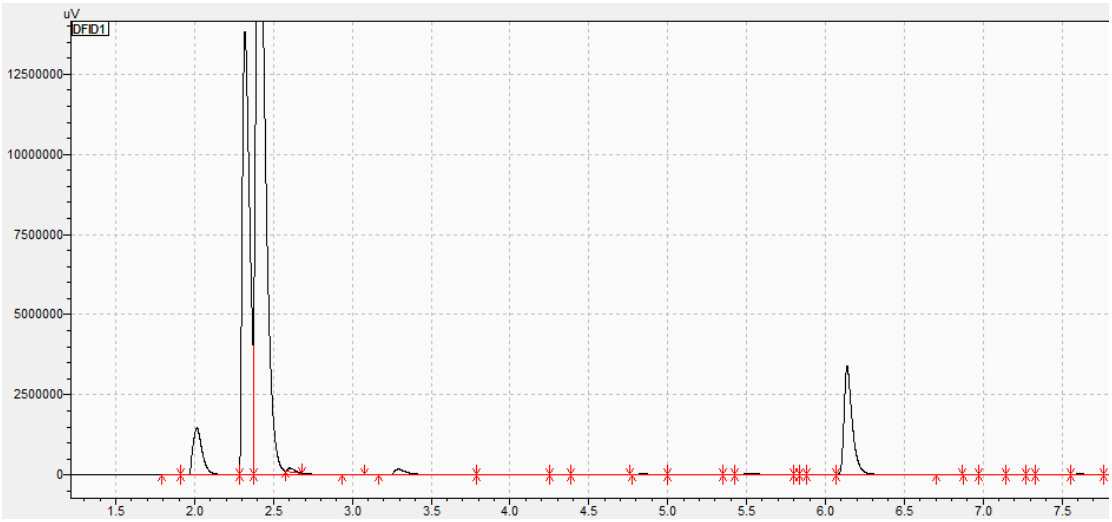
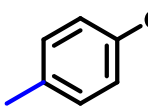


Fig.S61 GC spectrum of **6n**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25 (d, Ar-*H*, 2H),7.16(d, Ar-*H*, 2H)， 4.63 (s, C*H*$_2$, 2H), 2.35 (s, C*H*$_3$, 3*H*), 1.69 (s, O*H*, 1H).[3]

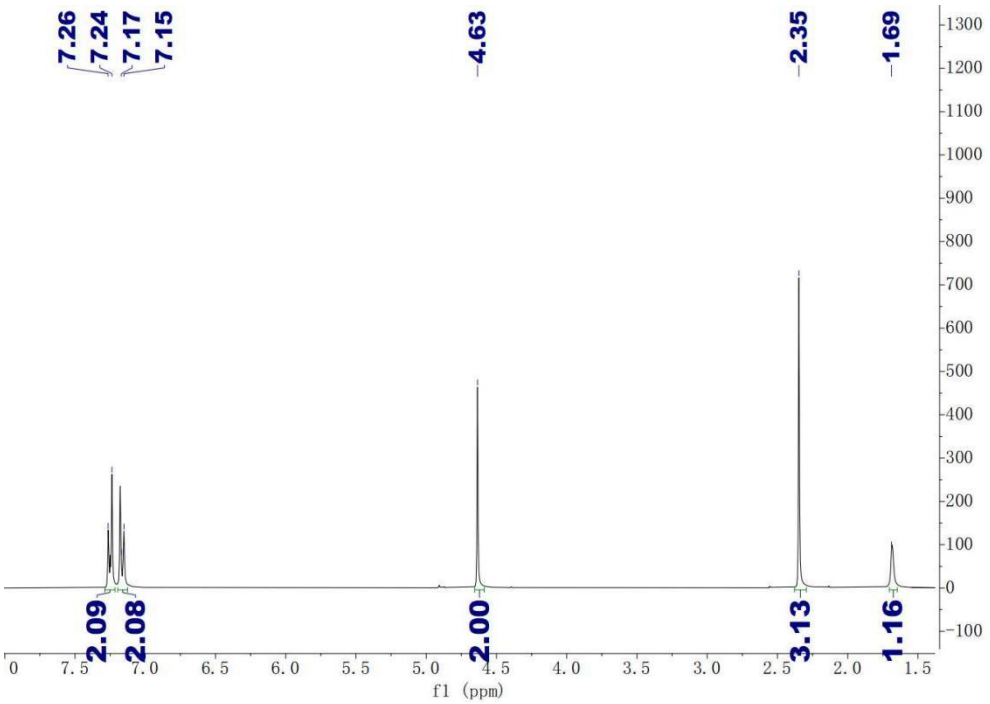
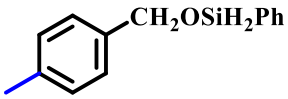


Fig.S62 ^{1}H NMR spectrum of **6o**（$CDCl_3$）



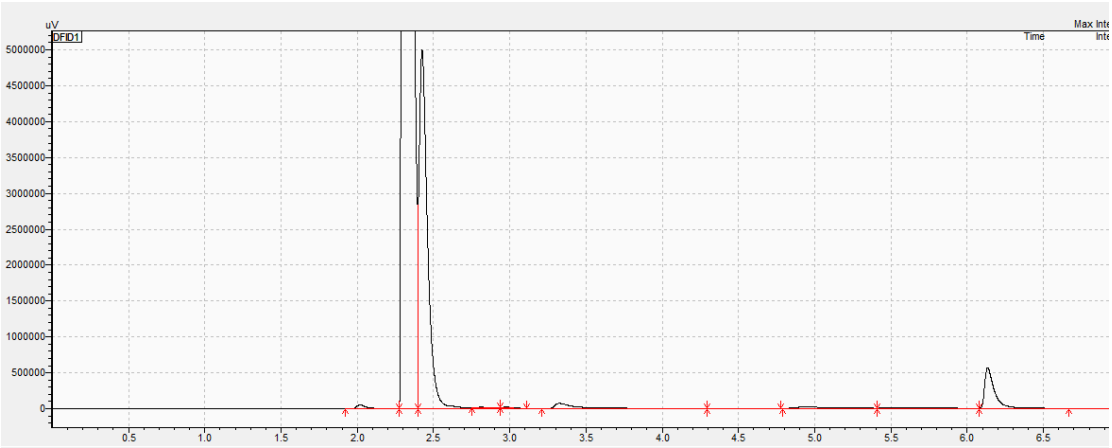
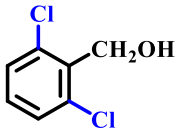


Fig.S63 GC spectrum of **6o**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17-7.34 (m, Ar-*H*, 3H), 4.96 (s, C*H*$_2$, 2H), 2.05 (s, O*H*, 1H).[1]

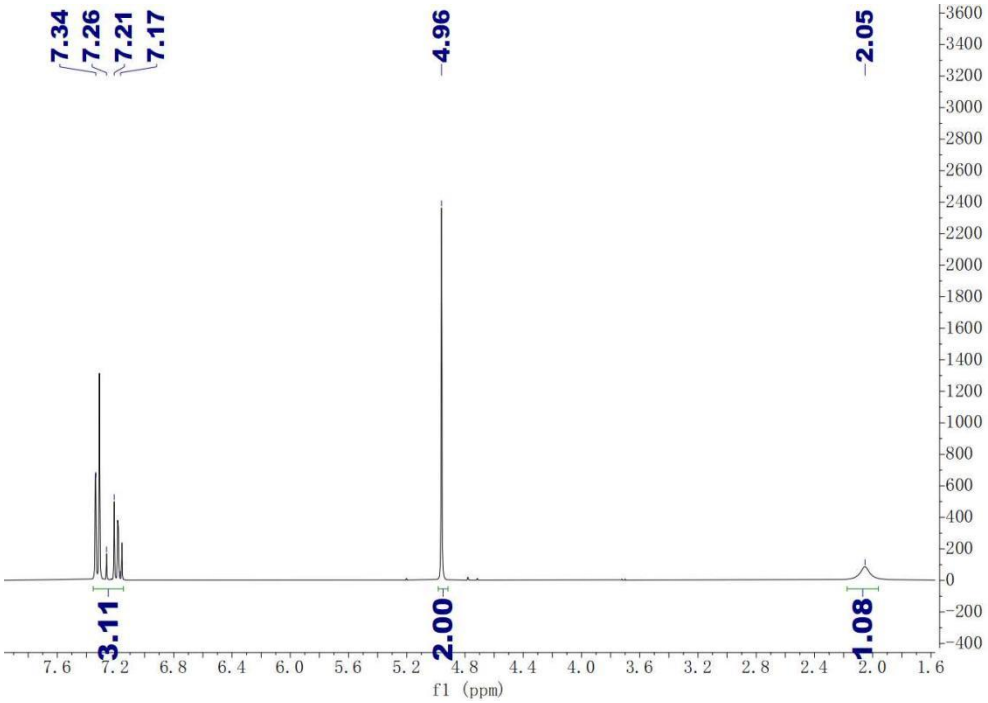
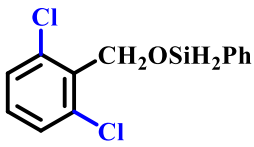


Fig.S64 ^{1}H NMR spectrum of **6p**（$CDCl_3$）



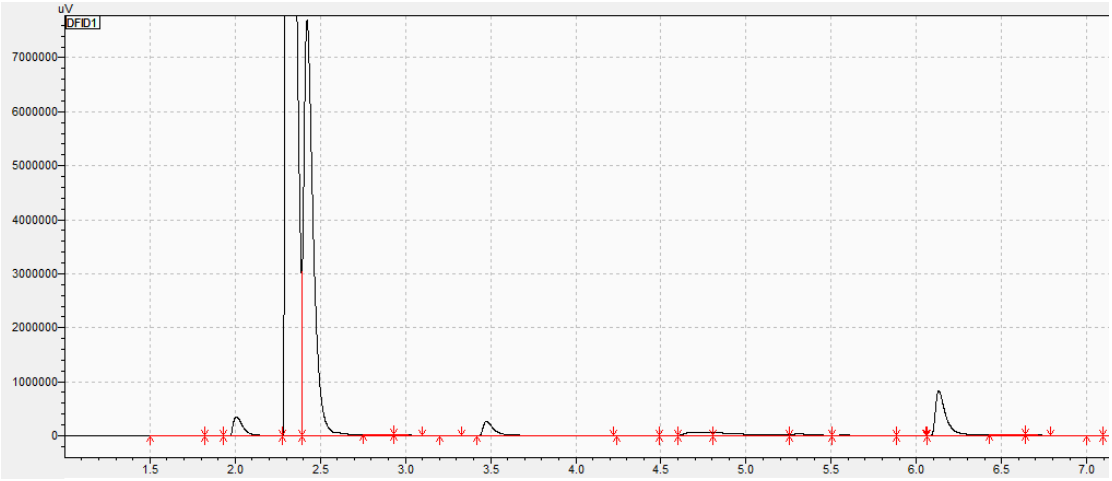
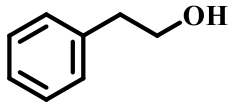


Fig.S65 GC spectrum of **6p**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.10 - 7.22 (m, Ar-*H*, 5H), 3.69 (t, C*H*$_2$, 2H), 2.72 (t, C*H*$_2$, 2H), 2.31 (s, O*H*, 1H).[2]

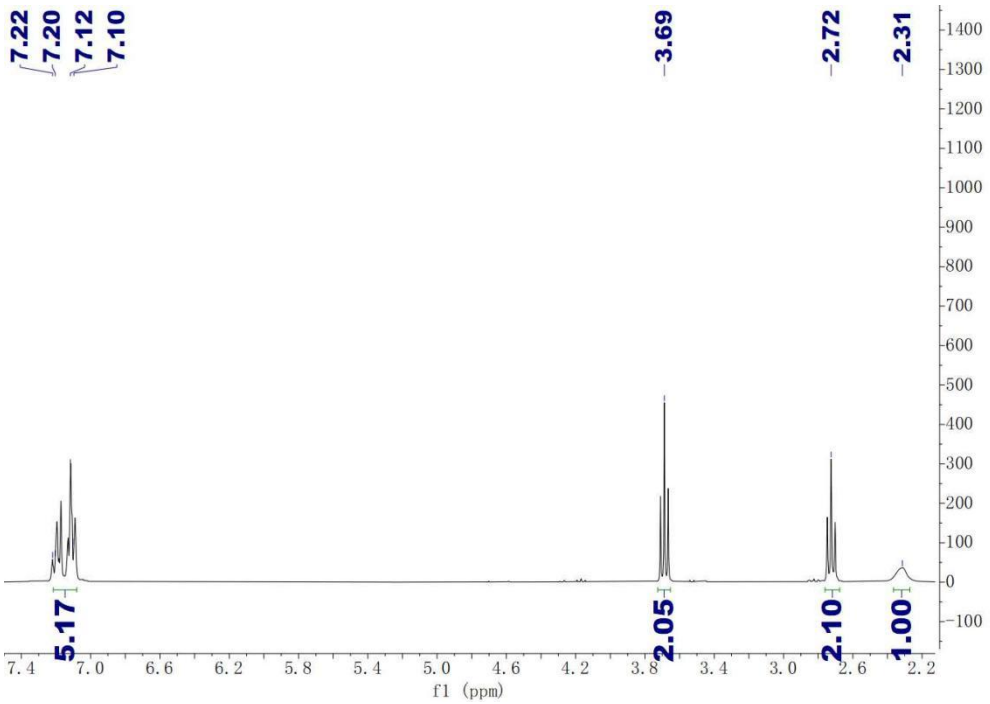
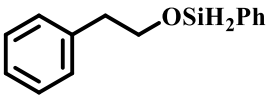


Fig.S66 ^{1}H NMR spectrum of **6q**（$CDCl_3$）



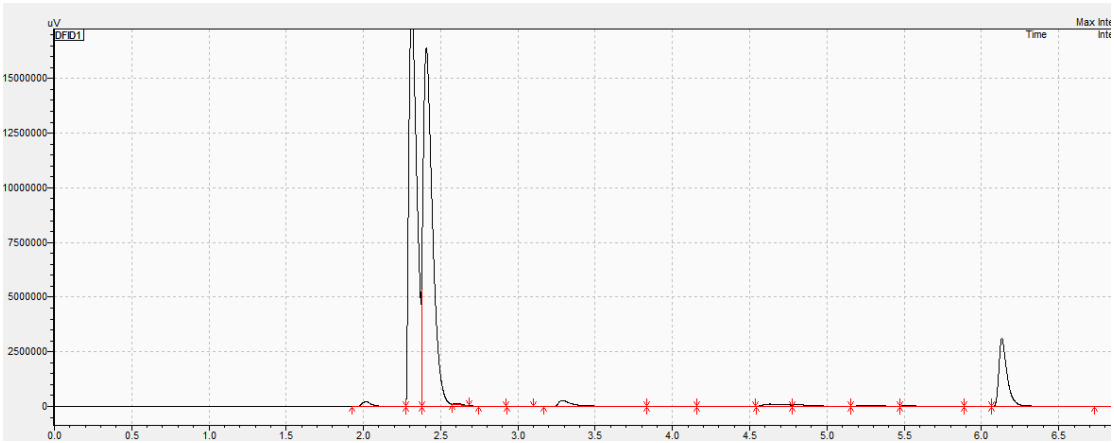
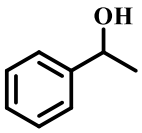


Fig.S67 GC spectrum of **6q**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17-7.27 (m, Ar-*H*, 5H), 4.78 (q, C*H*, 1H), 2.06 (s, O*H*, 1H), 1.40 (d, CH_3, 3H).[1]

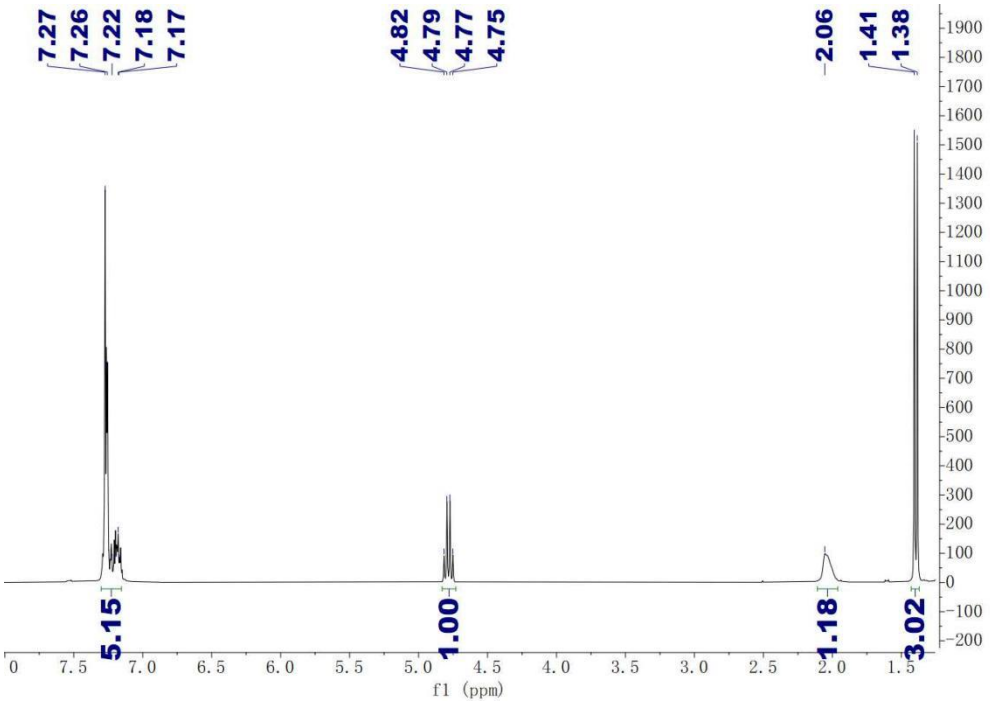
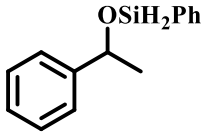


Fig.S68 ^{1}H NMR spectrum of **7a**（$CDCl_3$）



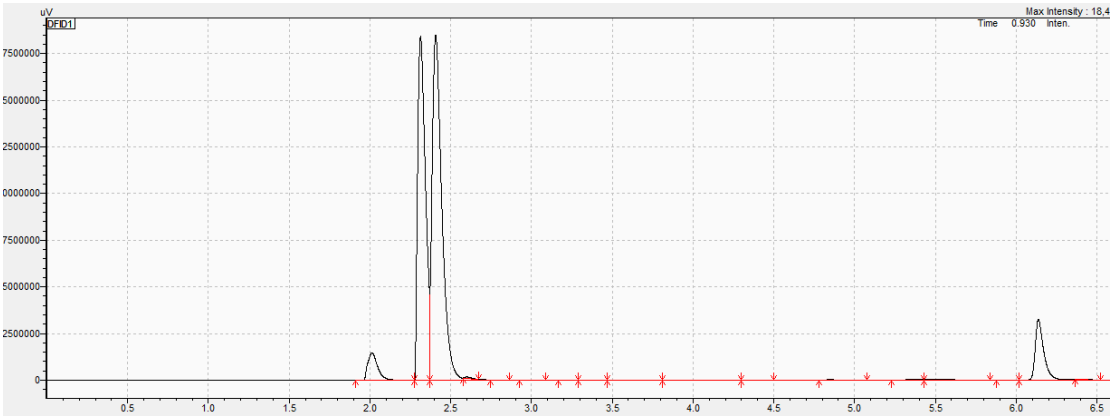
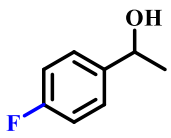


Fig.S69 GC spectrum of **7a**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.89-7.24 (m, Ar-*H*, 4H), 4.75 (q, C*H*, 1H), 2.31 (s, O*H*, 1H), 1.35 (d, CH_3, 3H).[2]

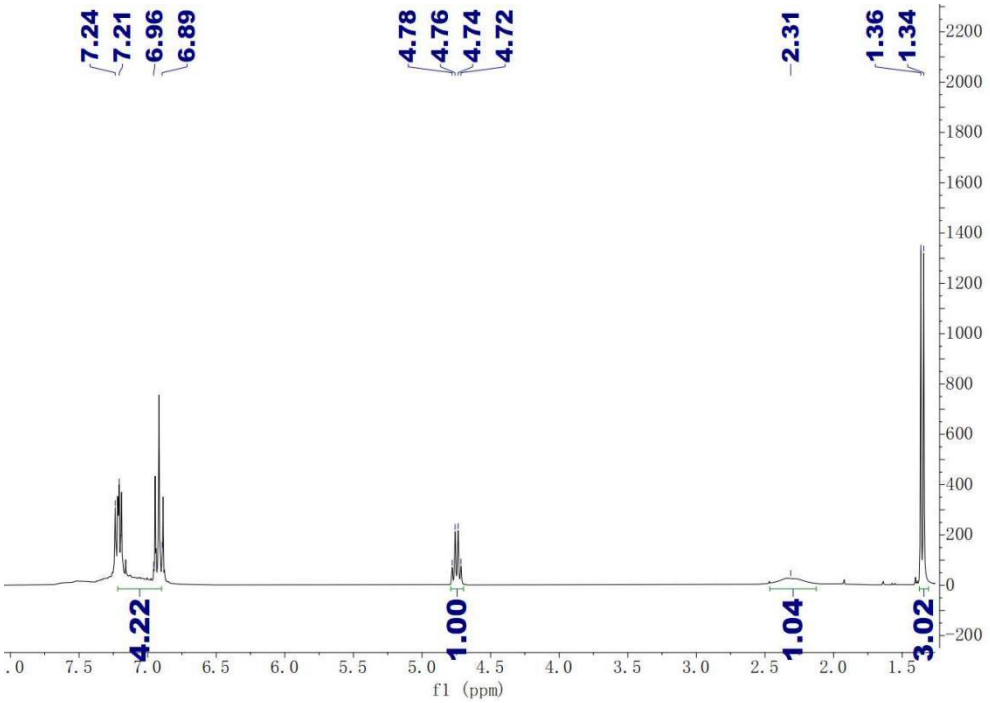
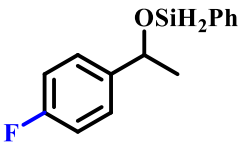


Fig.S70 ^{1}H NMR spectrum of **7b**（$CDCl_3$）



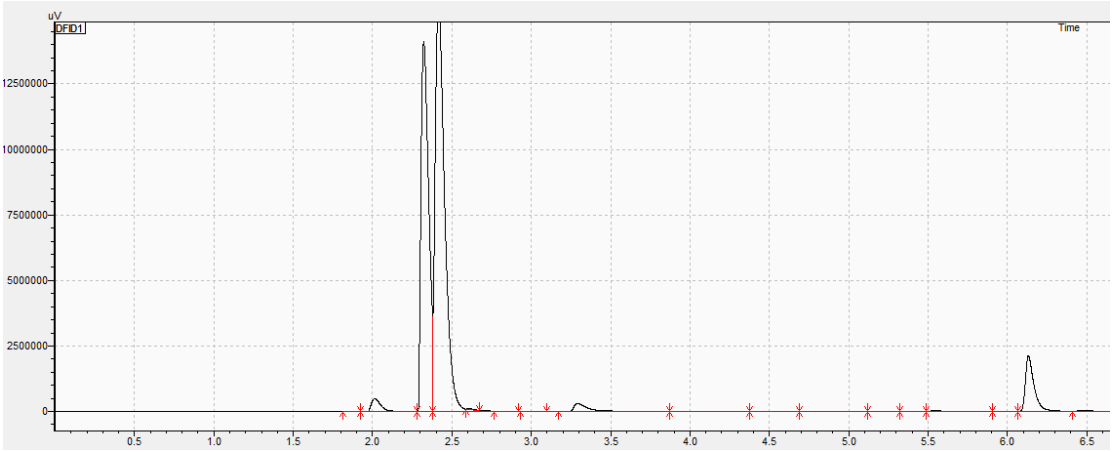
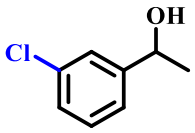


Fig.S71 GC spectrum of **7b**



^{1}H NMR (300 MHz, CDCl3, δ): 7.27 (s, Ar-*H*, 1H), 7.14-7.19 (m, Ar-*H*, 3H), 4.76 (q, C*H*, 1H), 2.12 (s, O*H*, 1H), 1.38 (d, CH_3, 3H).[1]

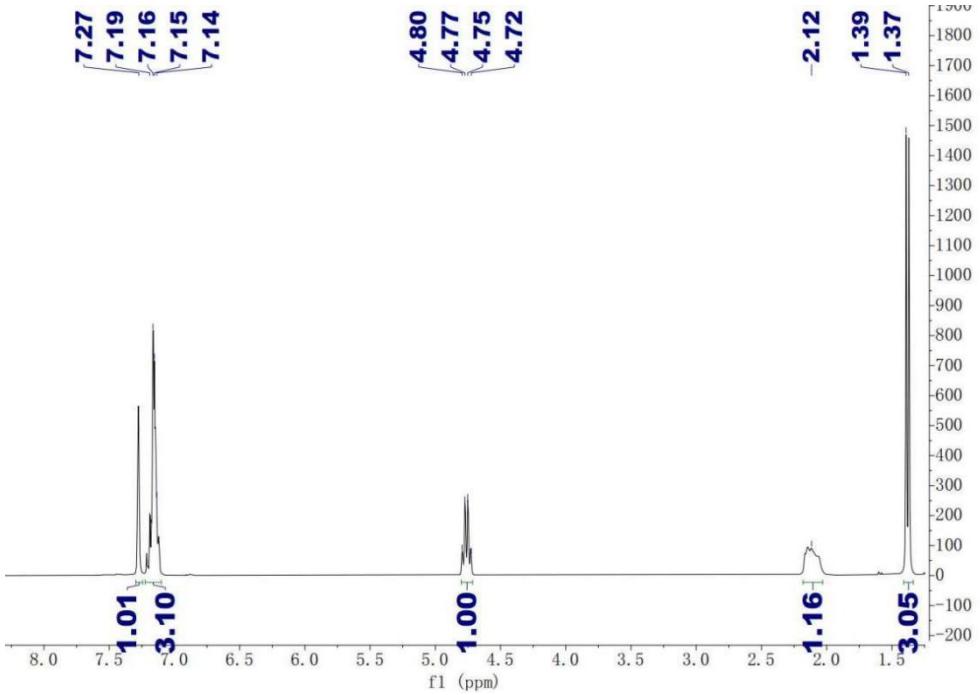
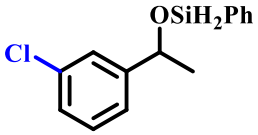


Fig.S72 ^{1}H NMR spectrum of **7c**（$CDCl_3$）



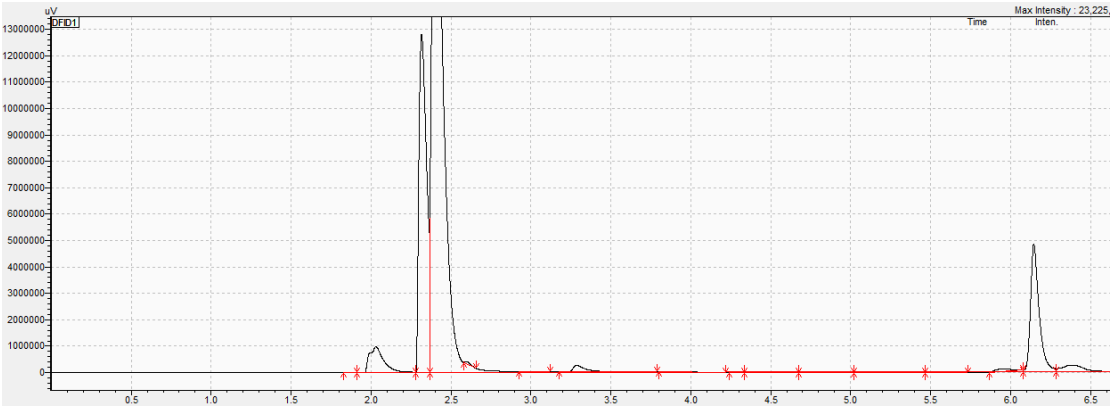
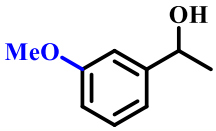


Fig.S73 GC spectrum of **7c**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.71-7.20 (m, Ar-*H*, 4H), 4.76 (q, C*H*, 1H), 3.72 (d, OCH_3, 3H)， 2.02 (s, O*H*, 1H), 1.39 (d, CH_3, 3H).[1]

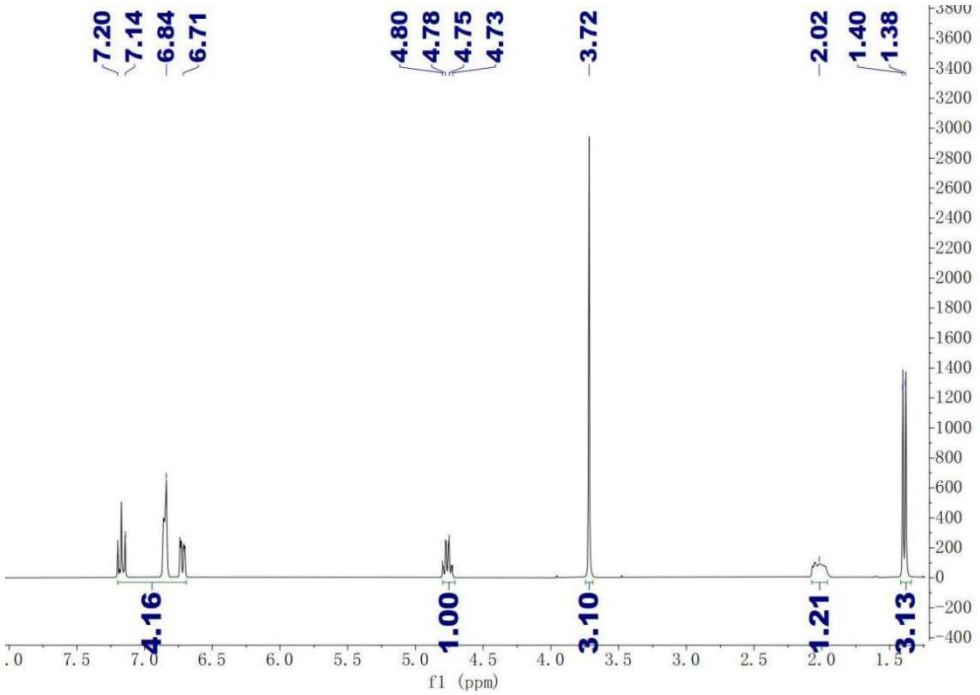
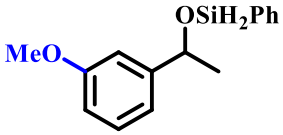


Fig.S74 ^{1}H NMR spectrum of **7d**（$CDCl_3$）



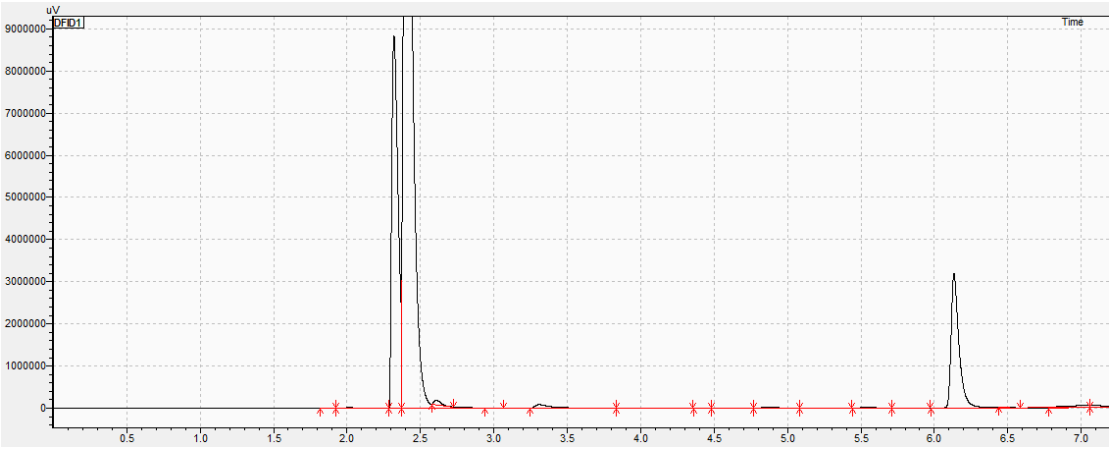
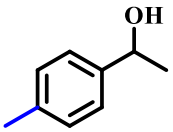


Fig.S75 GC spectrum of **7d**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.16(d, Ar-*H*, 2H), 7.05 (d, Ar-*H*, 2H), 4.74 (q, C*H*, 1H), 2.25(s, C*H*3, 3H)2.00 (s, O*H*, 1H), 1.37 (d, CH_3, 3H).[3]

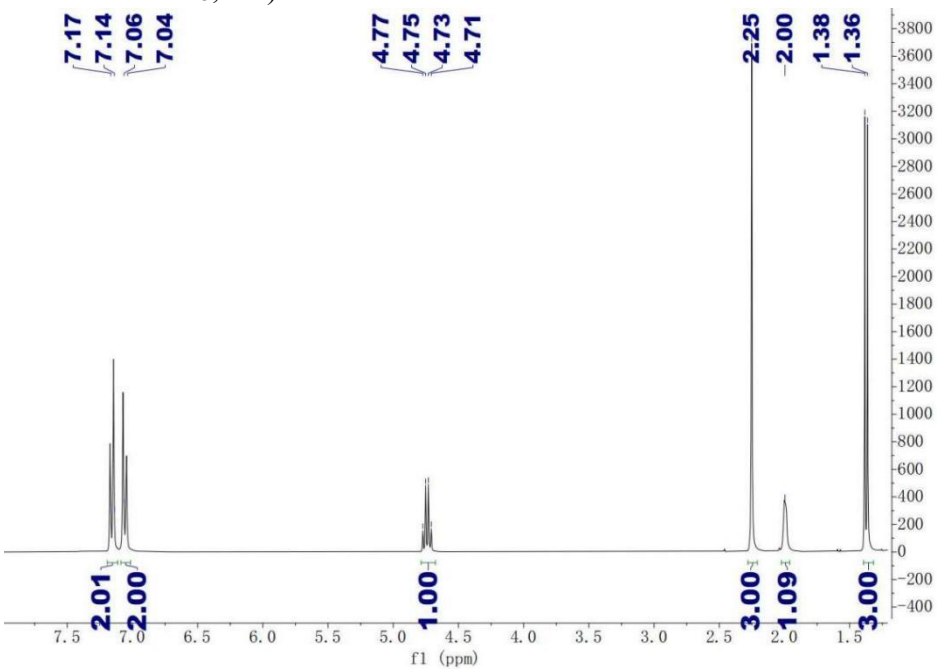
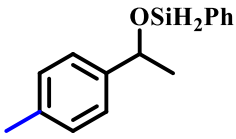


Fig.S76 ^{1}H NMR spectrum of **7e**（$CDCl_3$）



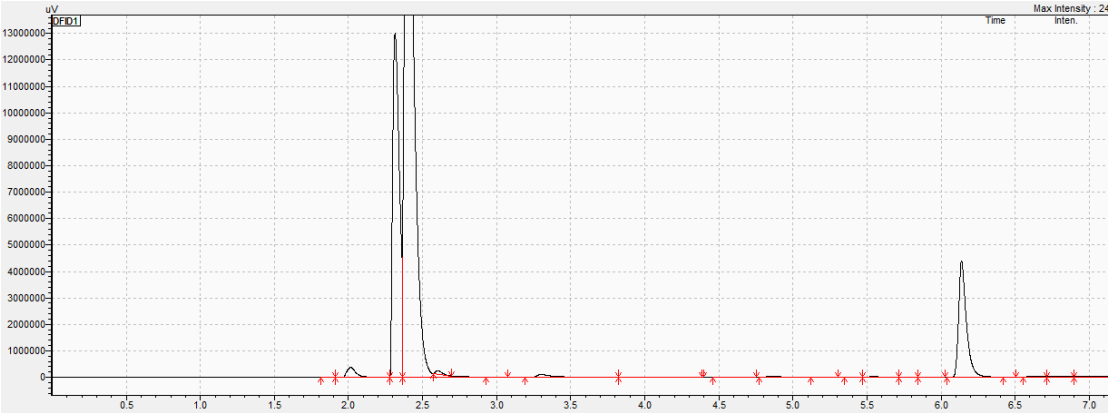
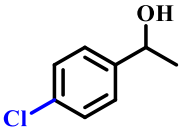


Fig.S77 GC spectrum of **7e**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17-7.24 (m, Ar-*H*, 4H), 4.76 (q, C*H*, 1H), 2.10 (s, O*H*, 1H), 1.36 (d, CH_3, 3H).[1]

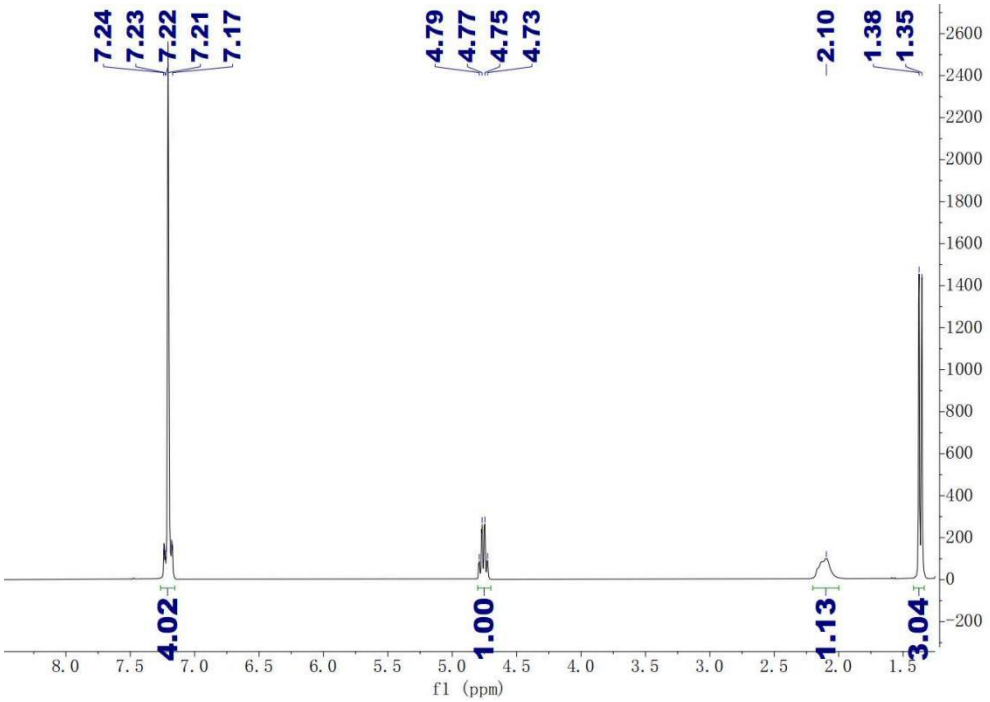
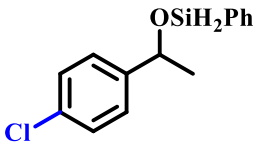


Fig.S78 ^{1}H NMR spectrum of **7f**（$CDCl_3$）



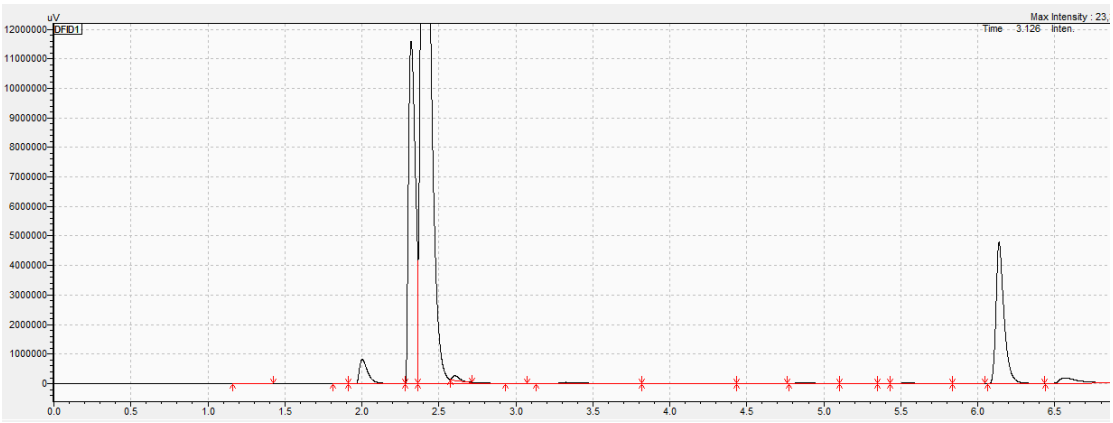
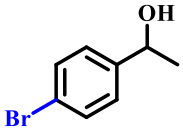


Fig.S79 GC spectrum of **7f**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.38(d, Ar-*H*, 2H), 7.15 (d, Ar-*H*, 2H), 4.77 (q, C*H*, 1H), 1.93 (s, O*H*, 1H), 1.38 (d, CH_3, 3H).[1]

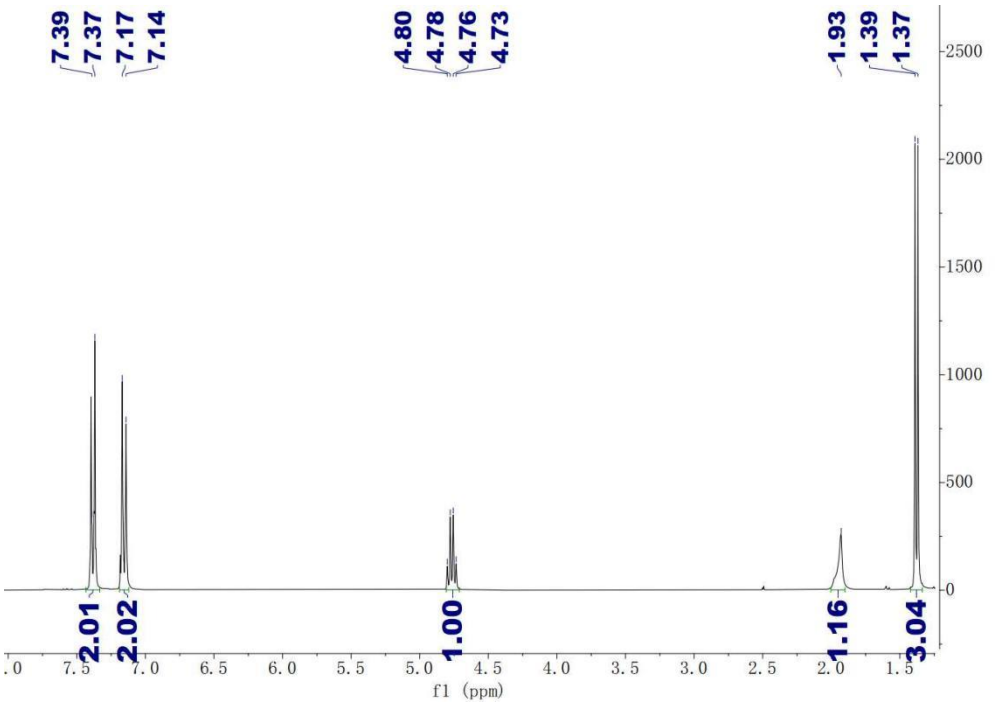
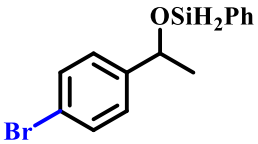


Fig.S80 ^{1}H NMR spectrum of **7g**（$CDCl_3$）



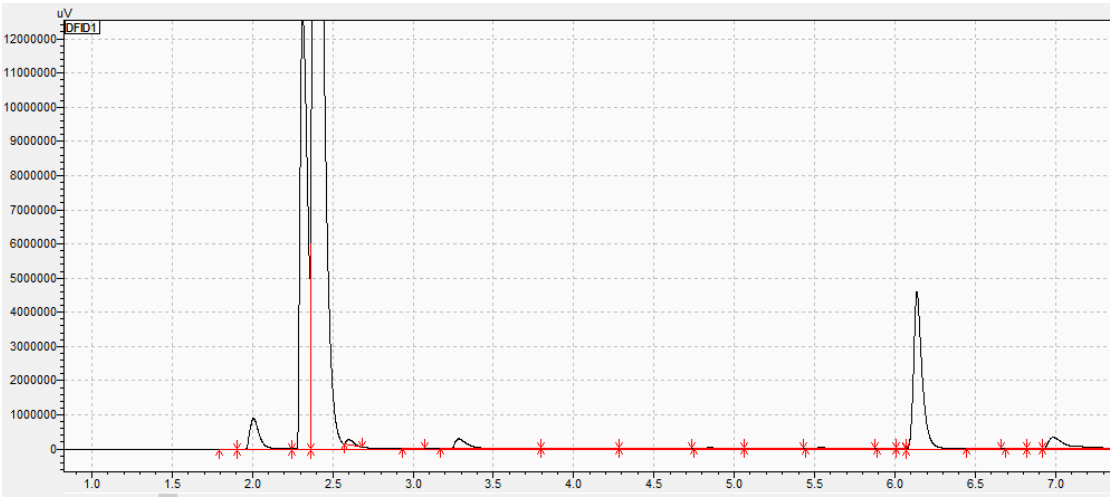
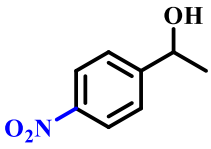


Fig.S81 GC spectrum of **7g**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.10(d, Ar-*H*, 2H), 7.46 (d, Ar-*H*, 2H), 4.93 (q, C*H*, 1H), 2.24 (s, O*H*, 1H), 1.43 (d, CH_3, 3H). [3]

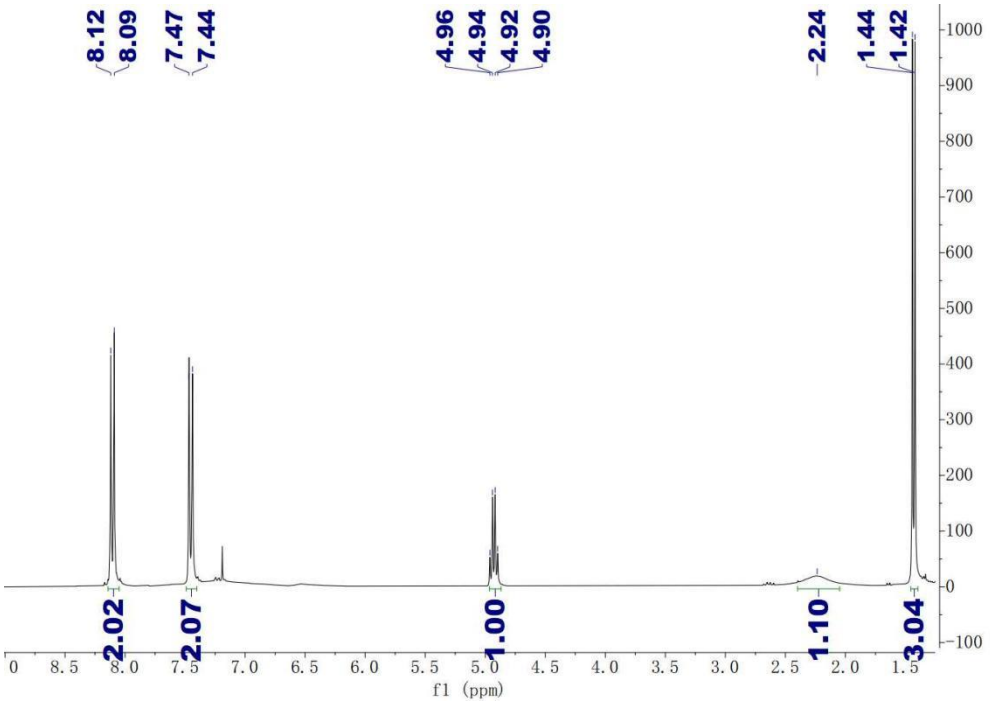
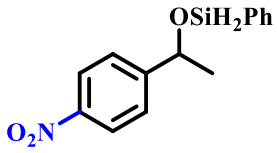


Fig.S82 ^{1}H NMR spectrum of **7h**（$CDCl_3$）



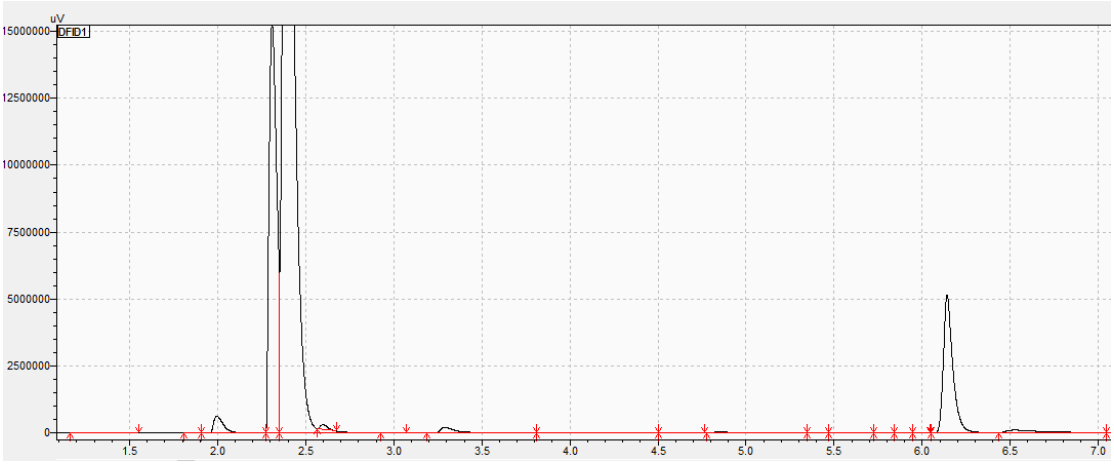
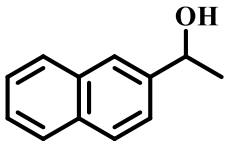


Fig.S83 GC spectrum of **7h**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.63–7.67 (m, Ar-*H*, 3H), 7.61 (s, Ar-*H*, 1H) 7.31–7.33 (m, Ar-*H*, 3H), 4.85 (q, C*H*, 1H), 2.29 (s, O*H*, 1H), 1.40 (d, CH_3, 3H).[1]

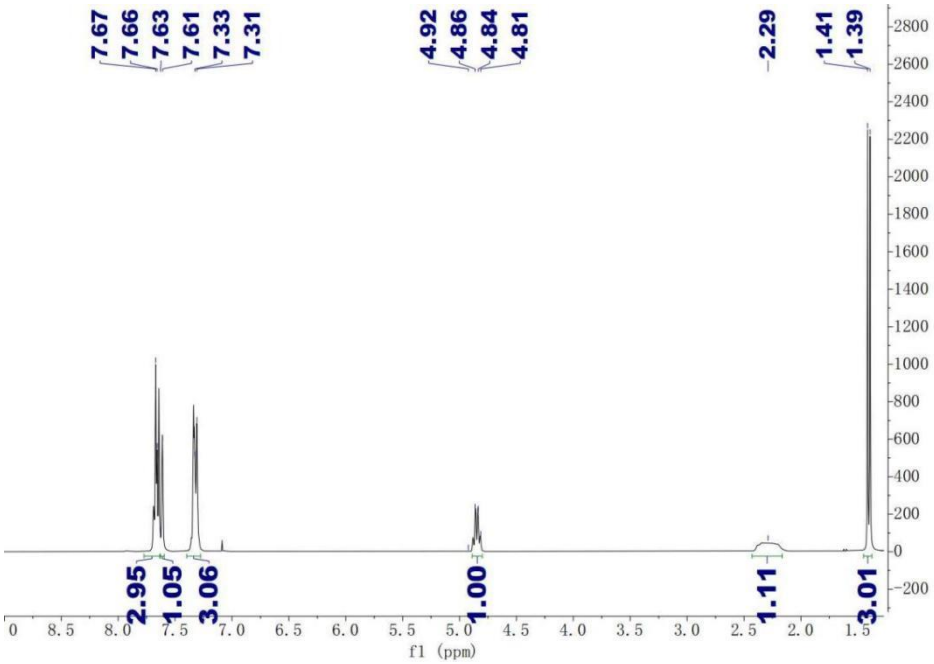
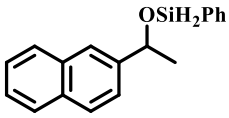


Fig.S84 ^{1}H NMR spectrum of **7i**（$CDCl_3$）



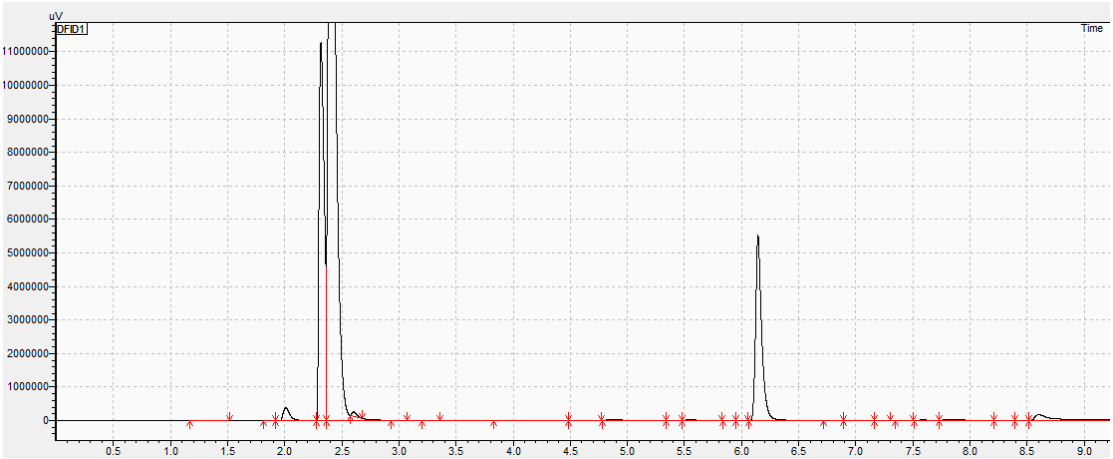
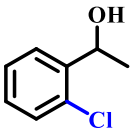


Fig.S85 GC spectrum of **7i**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.07-7.49 (dd, Ar-*H*, 4H), 5.18 (q, C*H*, 1H), 2.21 (s, O*H*, 1H), 1.38 (d, CH_3, 3H).[1]

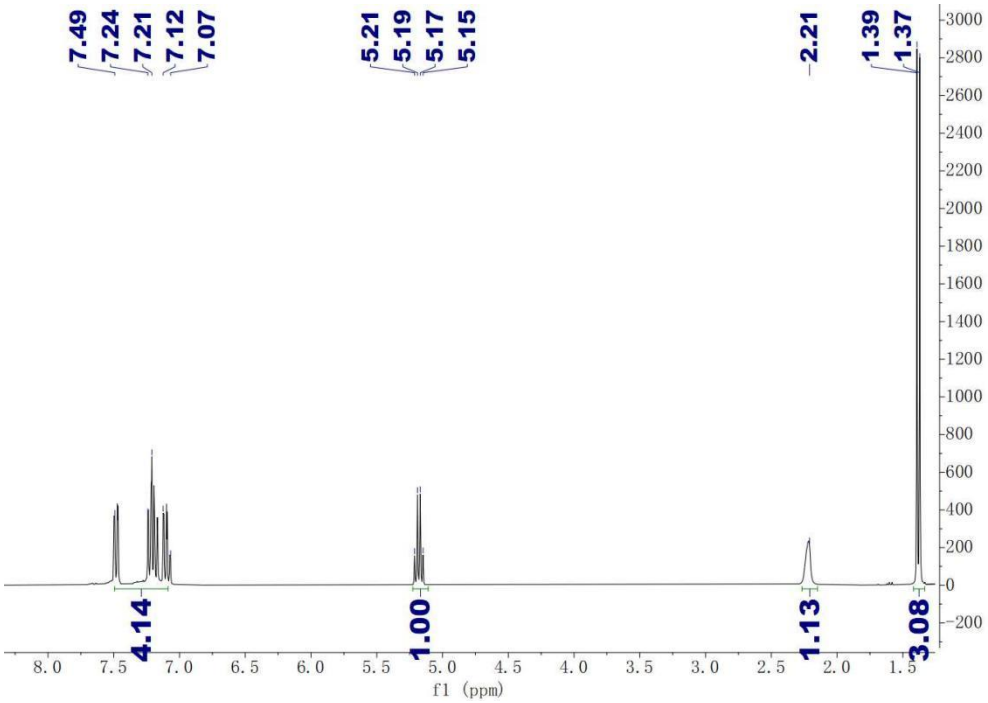
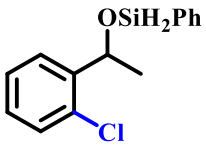


Fig.S86 ^{1}H NMR spectrum of **7j**（$CDCl_3$）



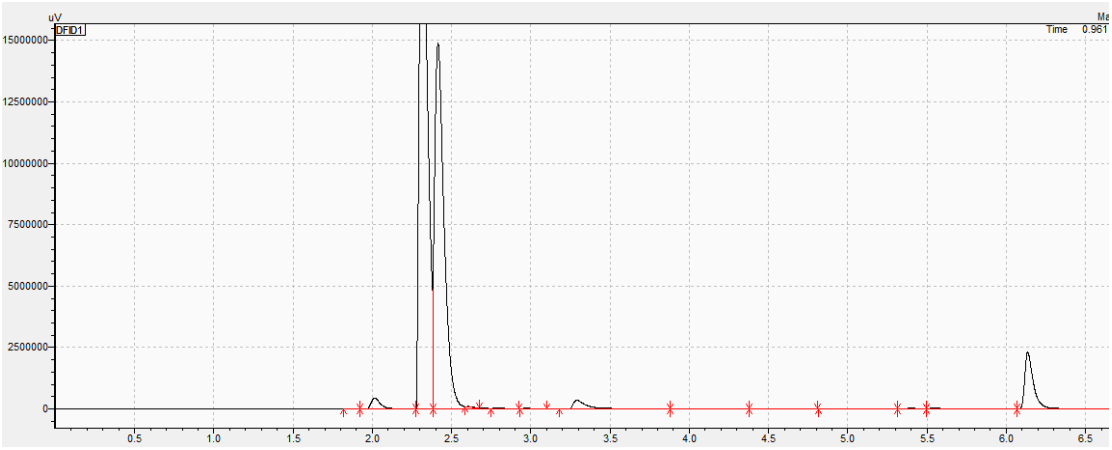
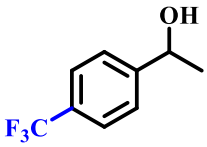


Fig.S87 GC spectrum of **7j**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.50(d, Ar-*H*, 2H), 7.37 (d, Ar-*H*, 2H), 4.84 (q, C*H*, 1H), 2.18 (s, O*H*, 1H), 1.39 (d, CH_3, 3H).[3]

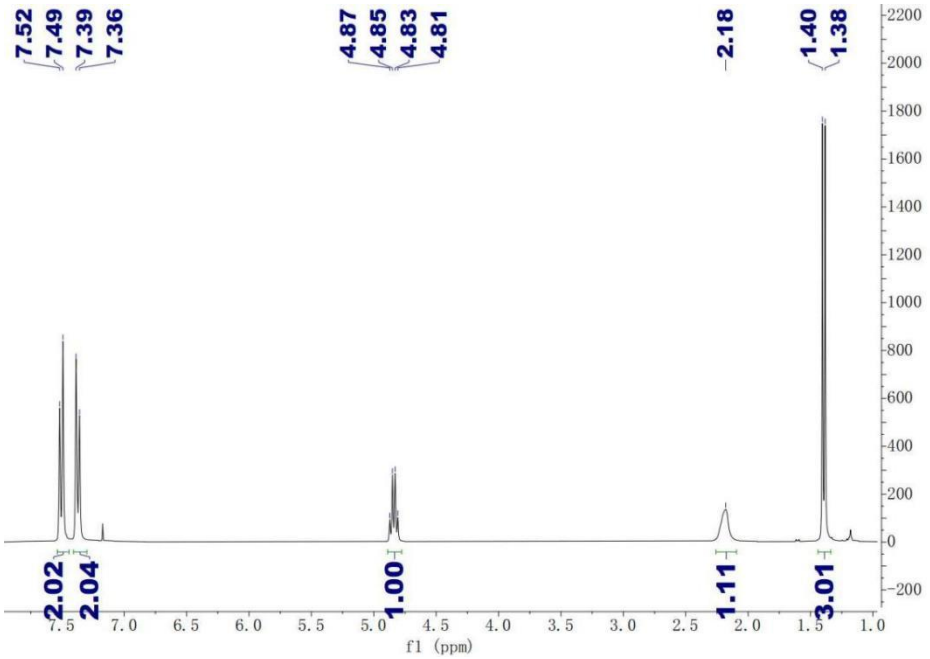
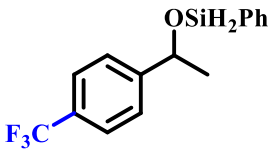


Fig.S88 ^{1}H NMR spectrum of **7k**（$CDCl_3$）



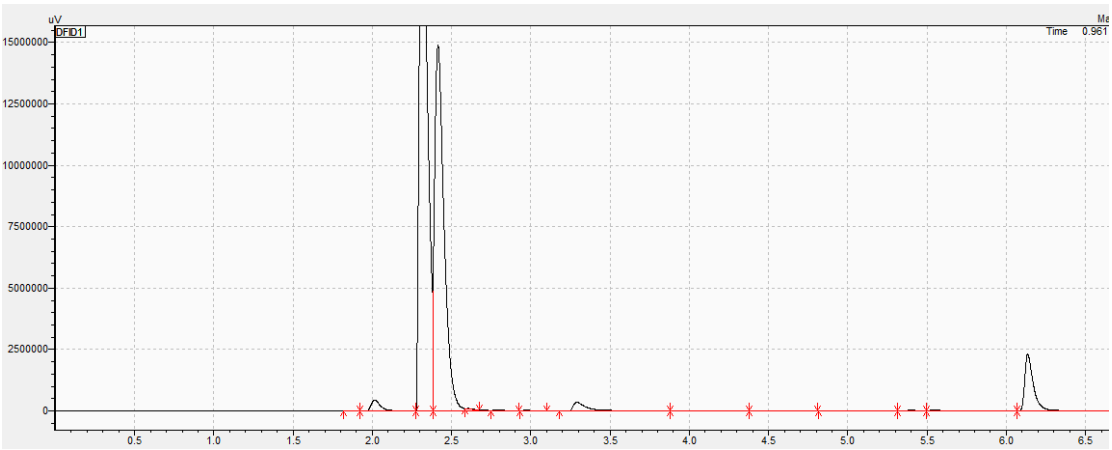
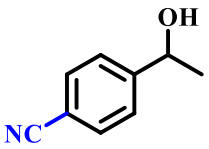


Fig.S89 GC spectrum of **7k**



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.54(d, Ar-*H*, 2H), 7.40 (d, Ar-*H*, 2H), 4.87 (q, C*H*, 1H), 2.27 (s, O*H*, 1H), 1.41 (d, CH_3, 3H).[1]

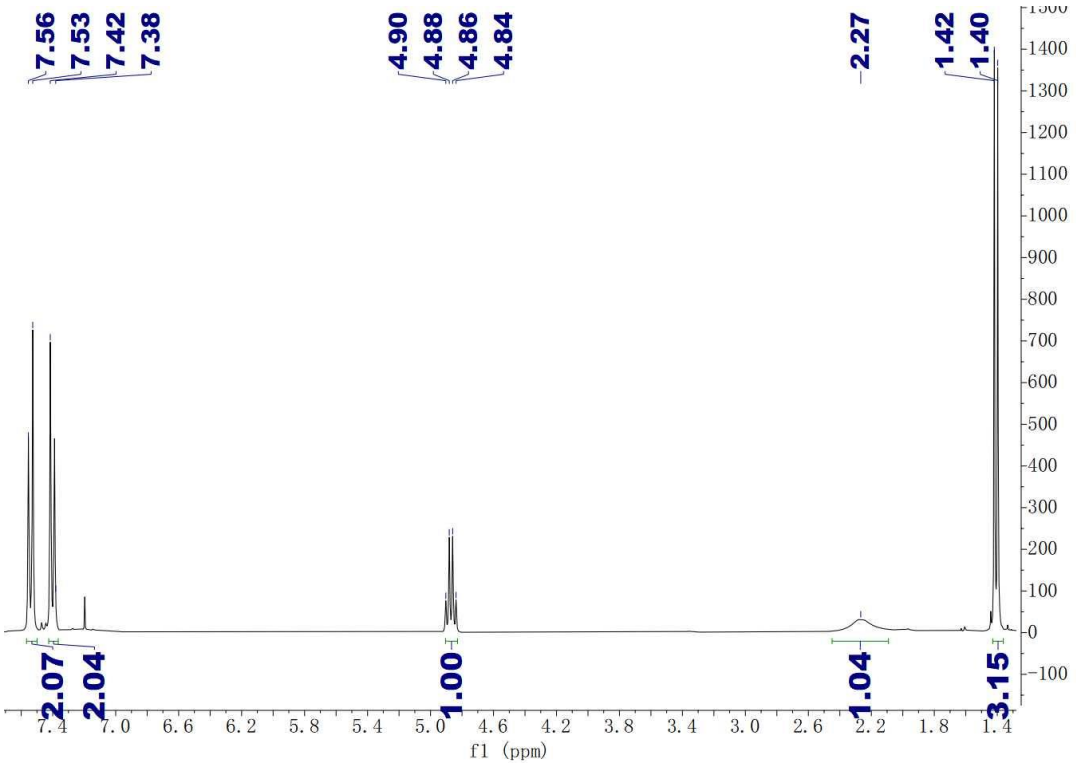
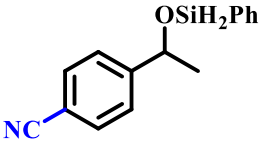


Fig.S90 ^{1}H NMR spectrum of **7l**（$CDCl_3$）



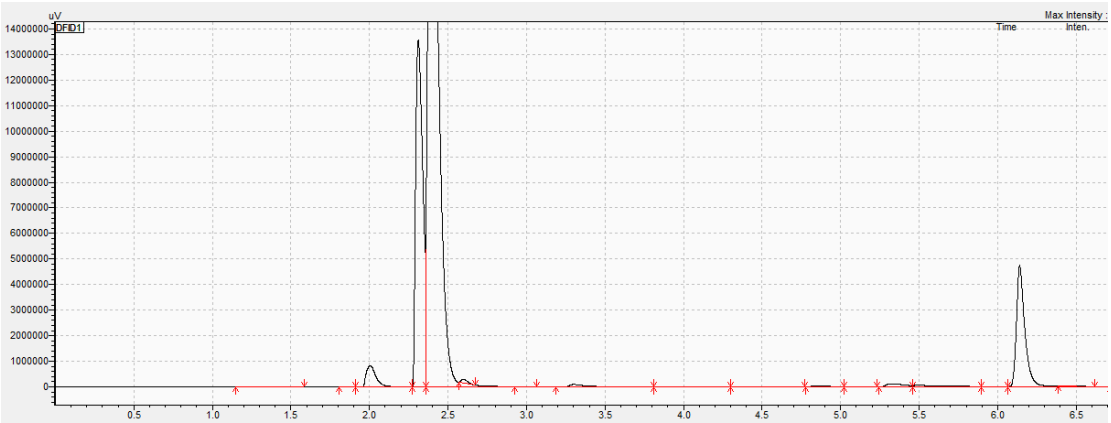
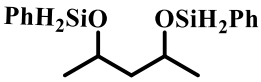


Fig.S91 GC spectrum of **7l**



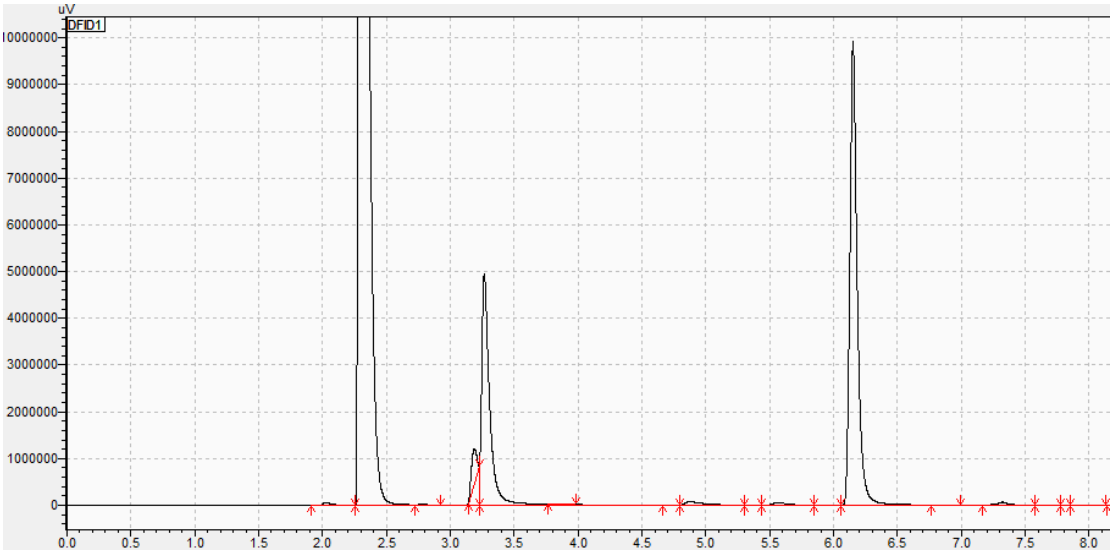
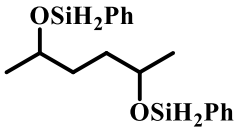


Fig.S92 GC spectrum of **7m**



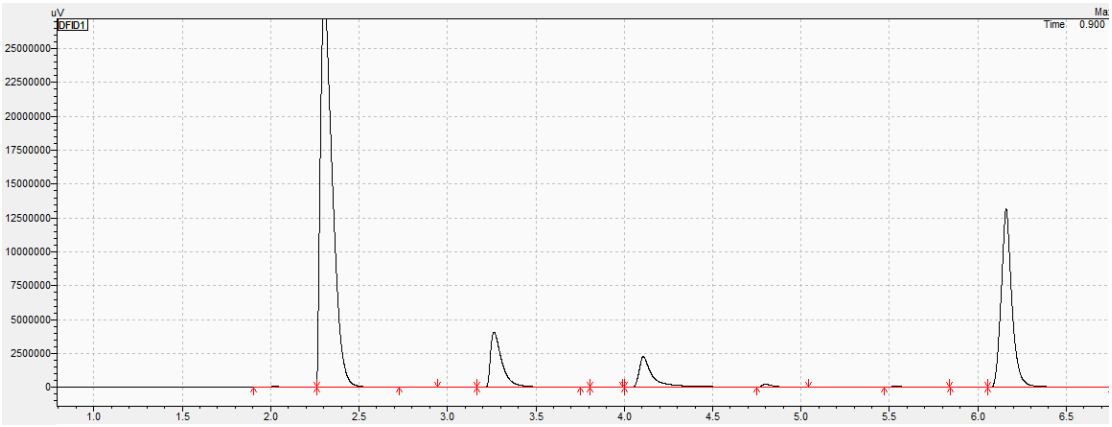
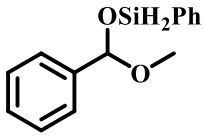


Fig.S93 GC spectrum of **7n**



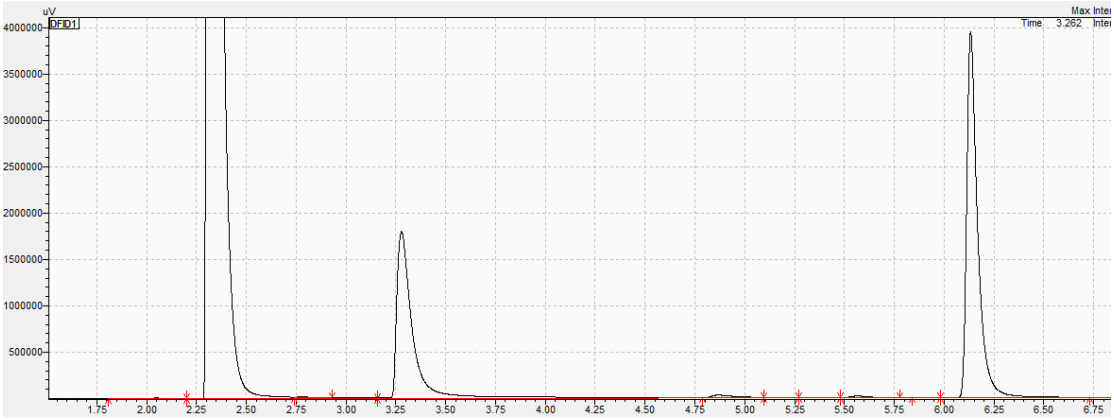
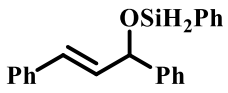


Fig.S94 GC spectrum of **7o**



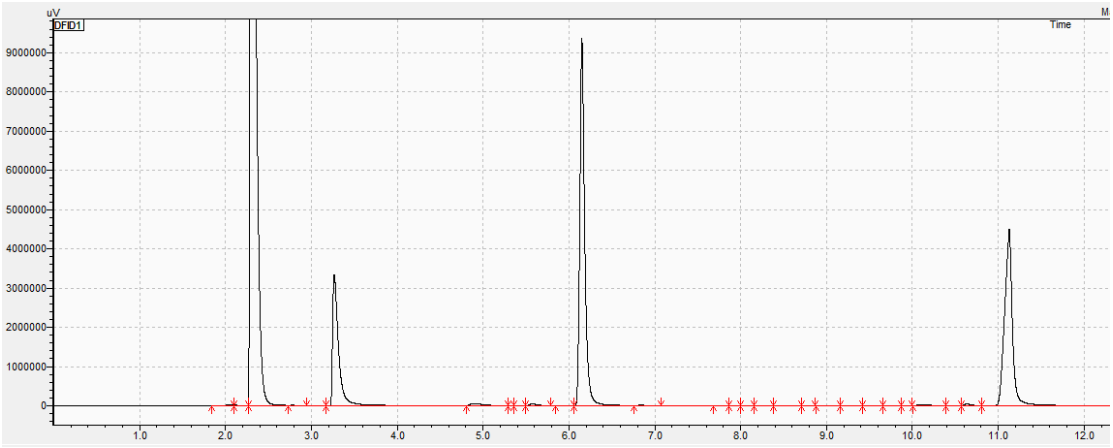


Fig.S95 GC spectrum of **7p**

SVI GC analysis of H_2

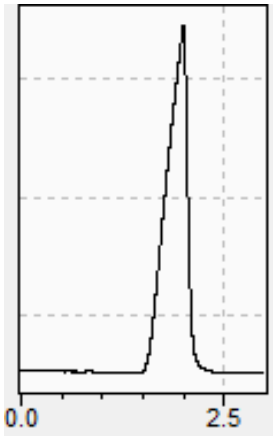


Fig.S96 The GC analysis that shows H_2

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