Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Effects of silylene ligands on performance of carbonyl hydrosilylation catalyzed by cobalt phosphine complexes

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1. Crystallographic Details

Table S1. Crystallographic data for complexes **3 – 4**

	3	**4**
formula	$C_{15}H_{35}ClCoP_3Si$	$C_{39}H_{63}Cl_3CoN_4PSi_3$
Mz	430.81	868.45
crystal system	Monoclinic	Monoclinic
space group	I2/c	$P2_1/n$
a/Å	27.1266(7)	15.27681(17)
b/Å	12.8624(3)	19.2189(3)
c/Å	12.9099(3)	15.42856(19)
α/°	90	90
β/°	92.062(2)	95.7072(11)
γ/°	90	90
V [Å3]	4501.52(19)	4507.43(10)
T [K]	173(2)	173(2)
Z	8	4
μ[mm-1]	9.529	5.959
total reflns	13144	28041
unique reflns	3996	8920
Rint	0.0485	0.0511
R1[I>2σ(I)]	0.0548	0.0450
wR(F2)[I>2σ(I)]	0.1410	0.1079
R1(all data)	0.0623	0.0548
wR(F2)(all data)	0.1470	0.1120
GOF on F2	0.859	1.061

2. IR, ^{1}H, ^{31}P, ^{13}C and ^{29}Si NMR spectra of complexes 3 - 4

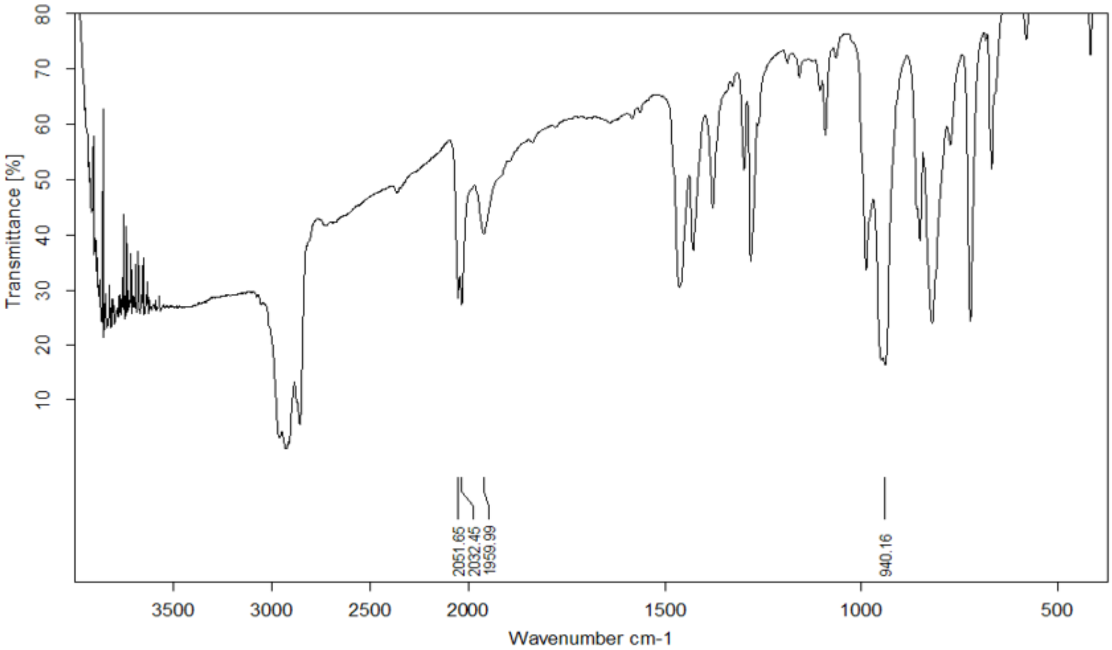


Figure S1. The IR Spectrum of complex **3**

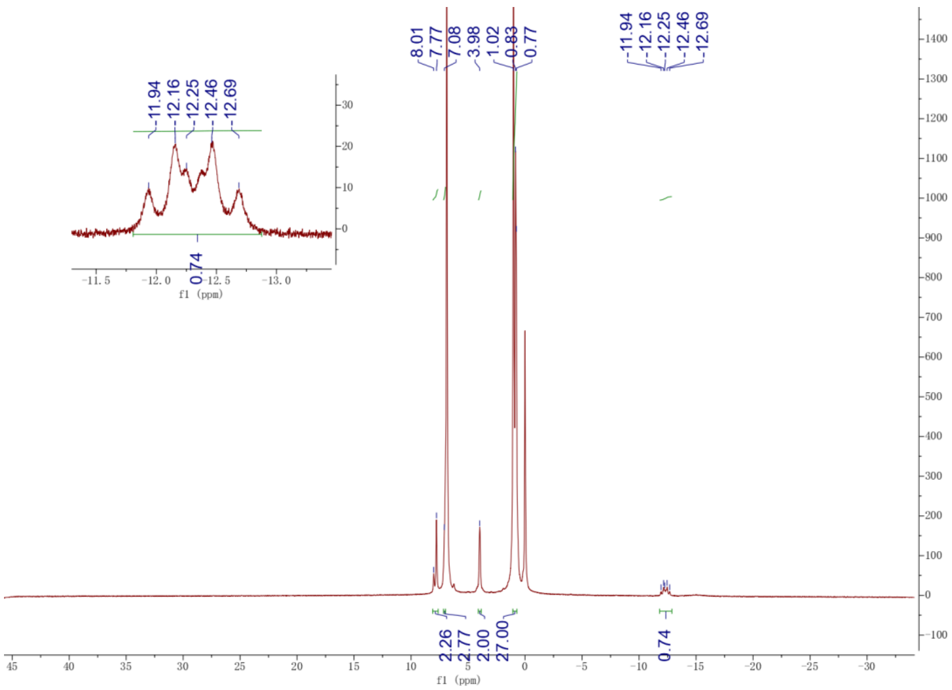


Figure S2. The ^{1}H NMR spectrum of complex **3** in C_6D_6

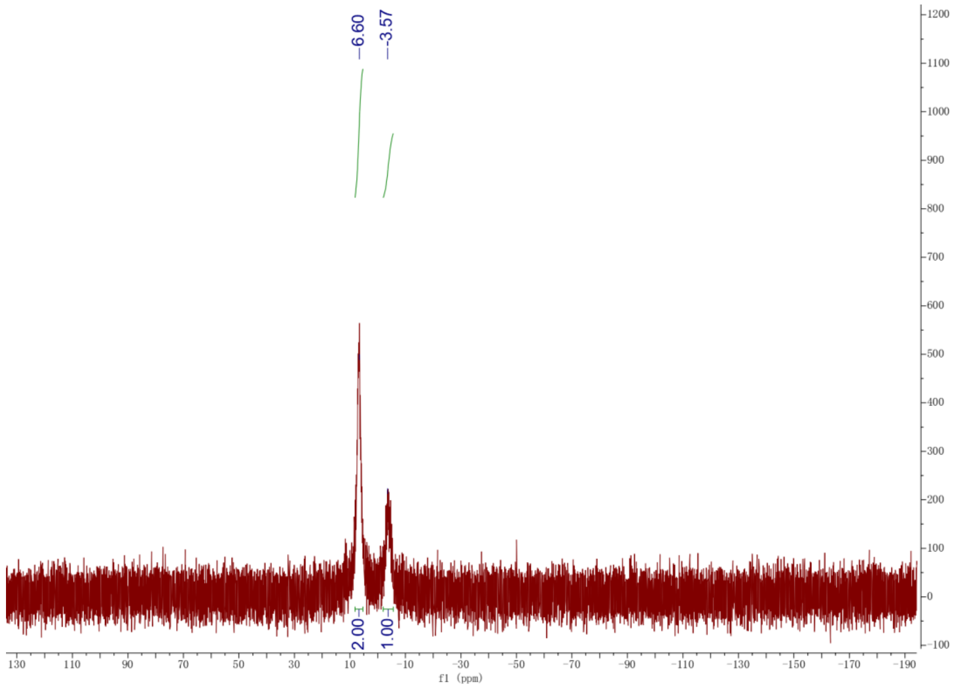


Figure S3. The ^{31}P NMR spectrum of complex **3** in C_6D_6

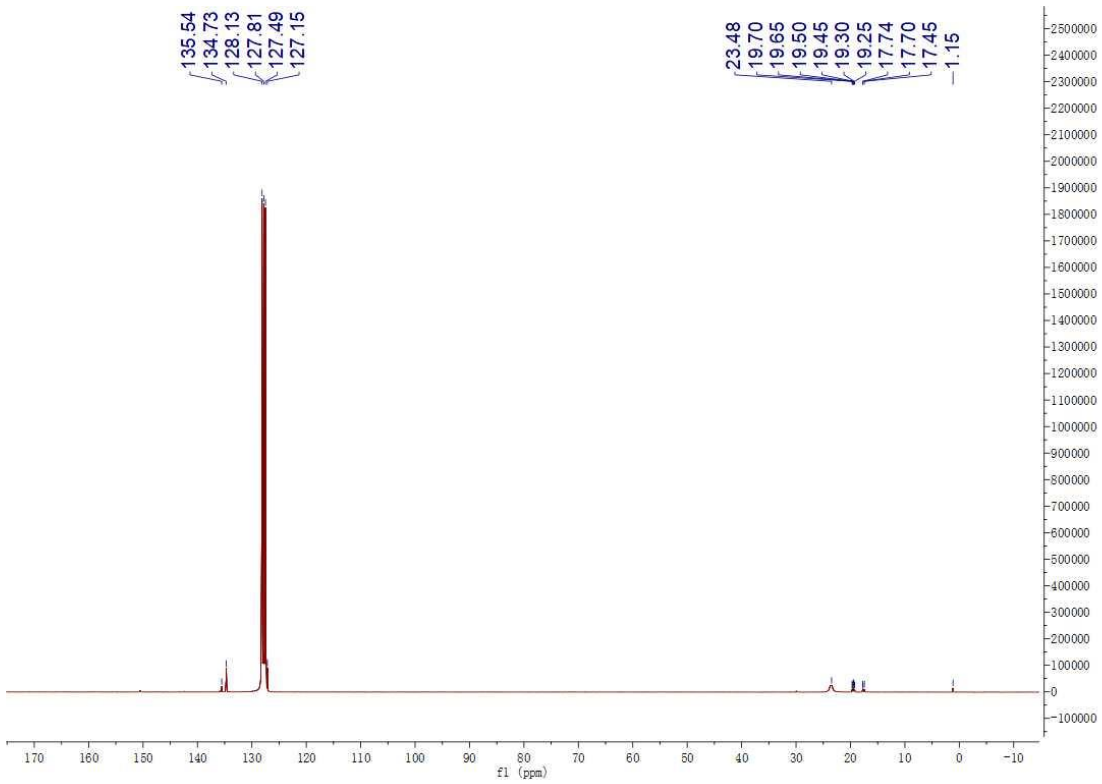


Figure S4. The ^{13}C NMR spectrum of complex **3** in C_6D_6

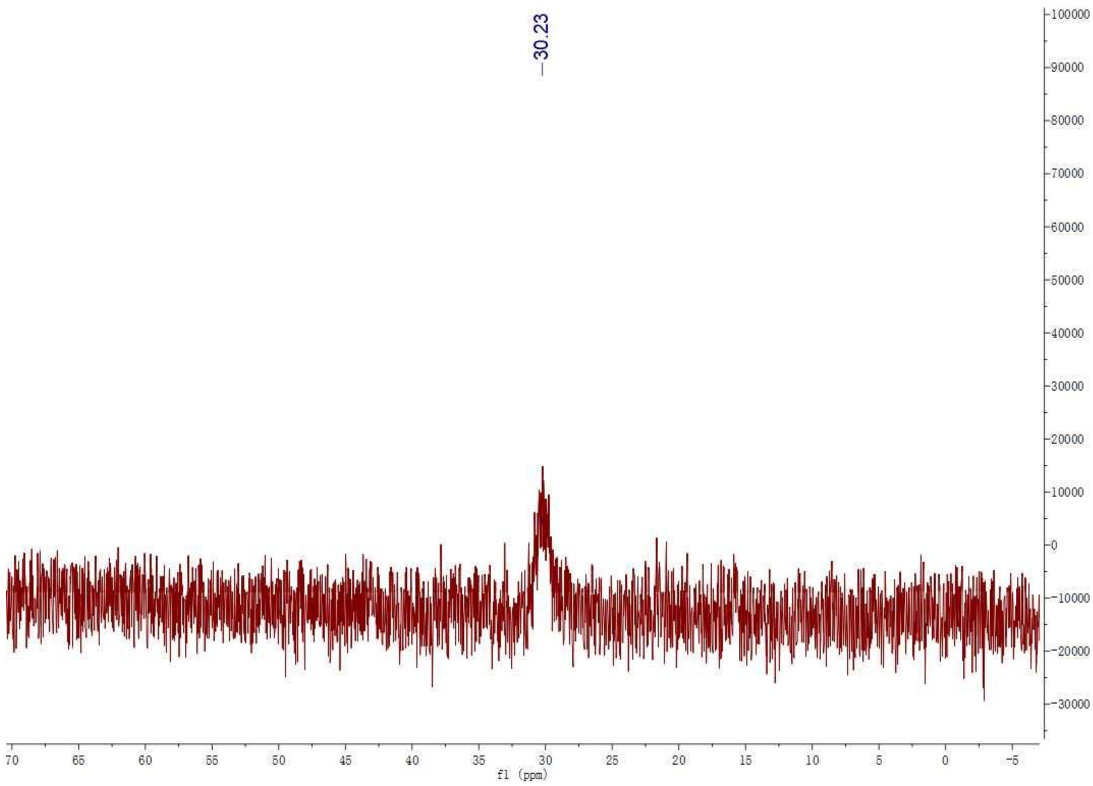


Figure S5. The ^{29}Si NMR spectrum of complex **3** in C_6D_6

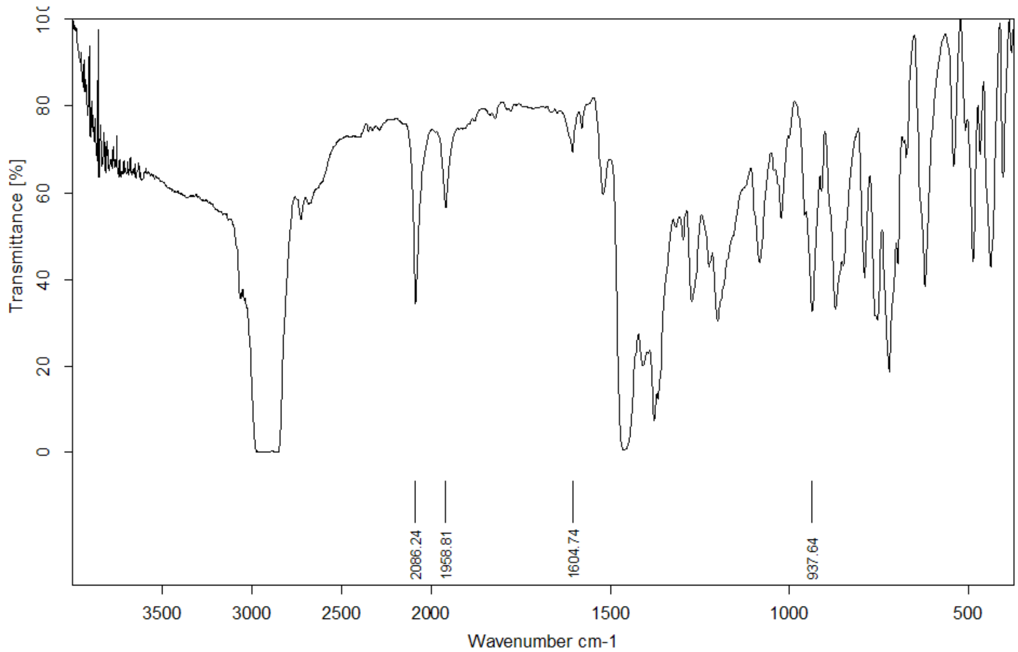


Figure S6. The IR spectrum of complex **4**

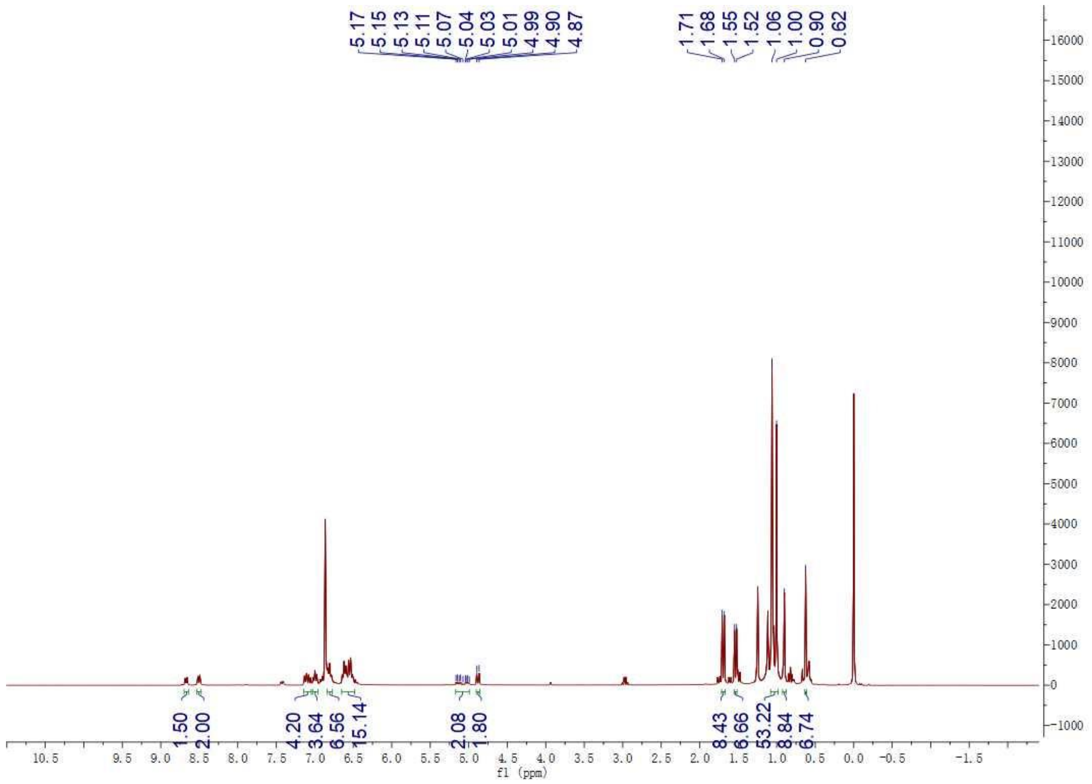


Figure S7-A. The [1]H NMR spectrum of complex **4** in C_6D_6

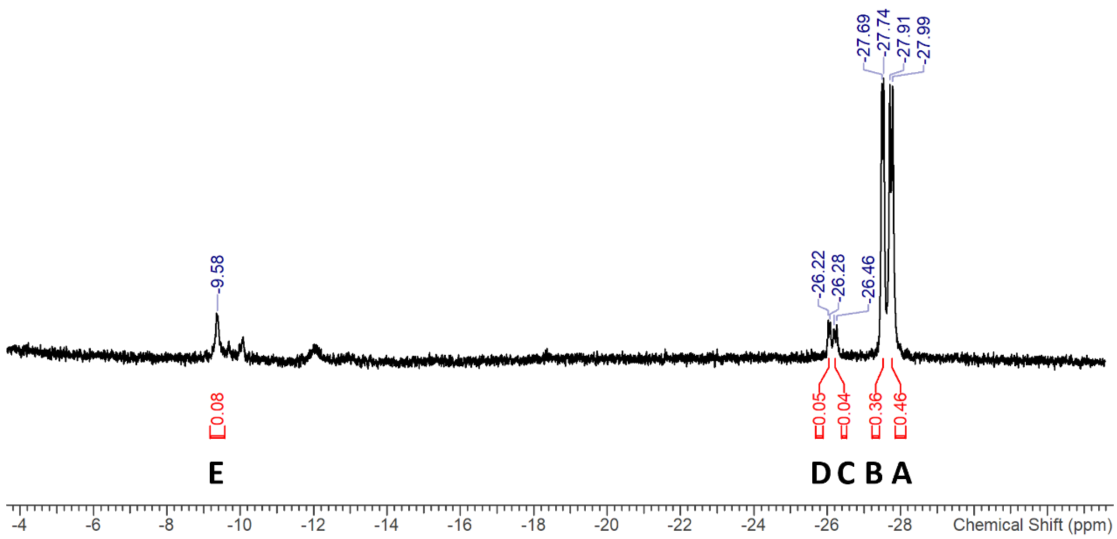


Figure S7-B. Hydride signals **A-E** in [1]H NMR spectrum of **4** in C_6D_6

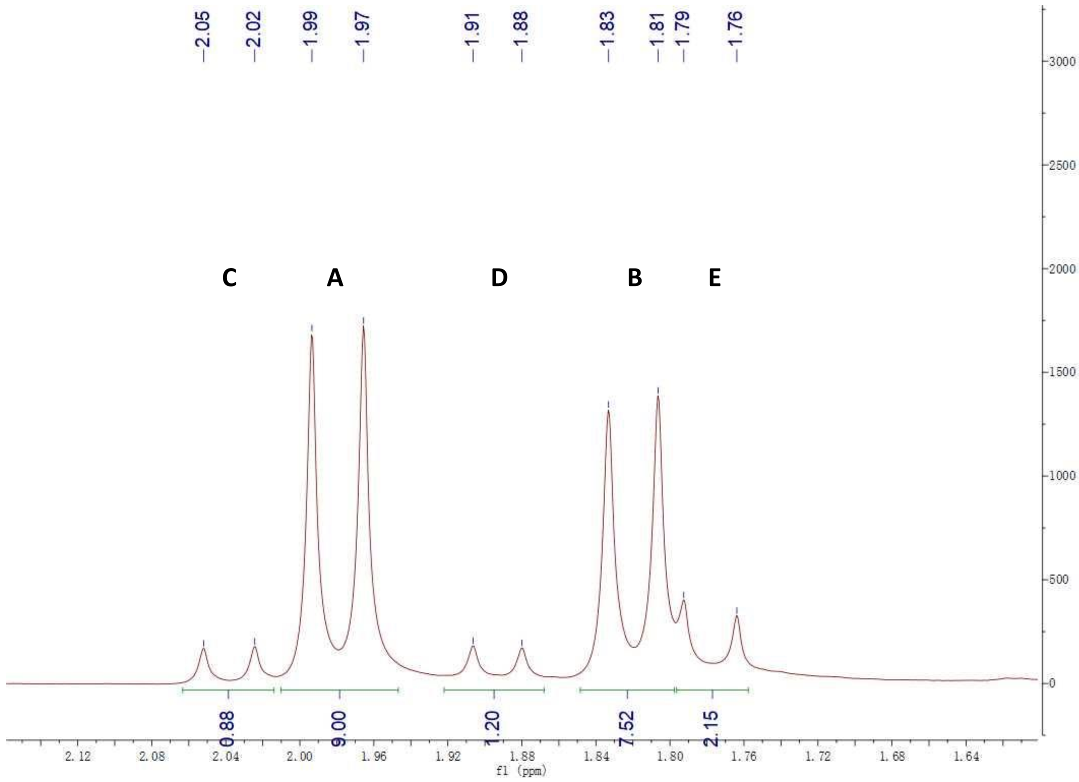


Figure S7-C. PMe_3 doublets **A-E** in ^1H NMR spectrum of **4** in C_6D_6

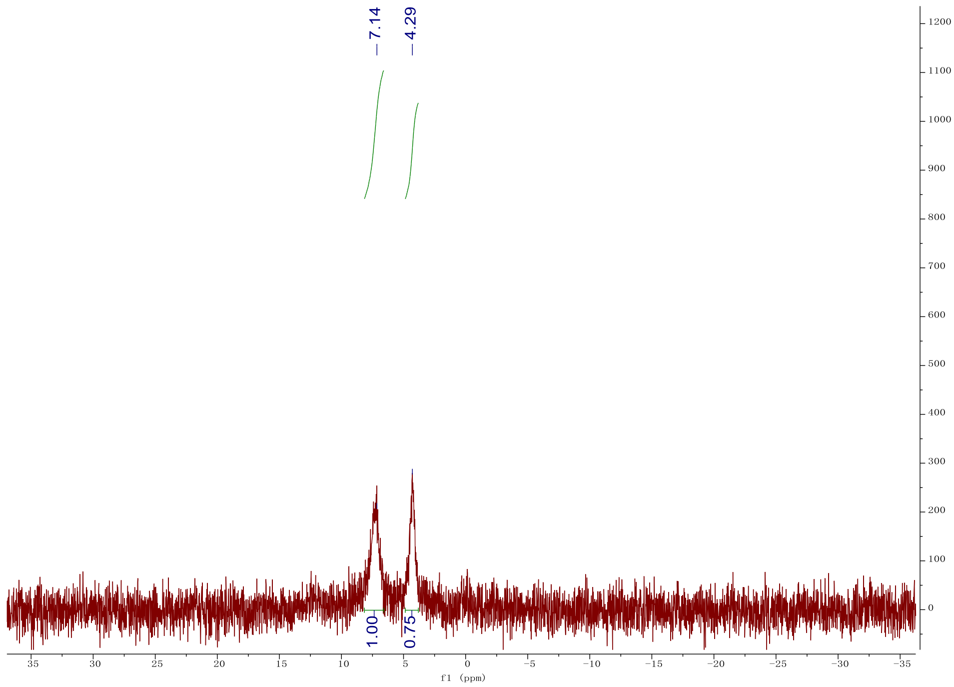


Figure S8-A. The ^{31}P NMR of complex **4** in C_6D_6

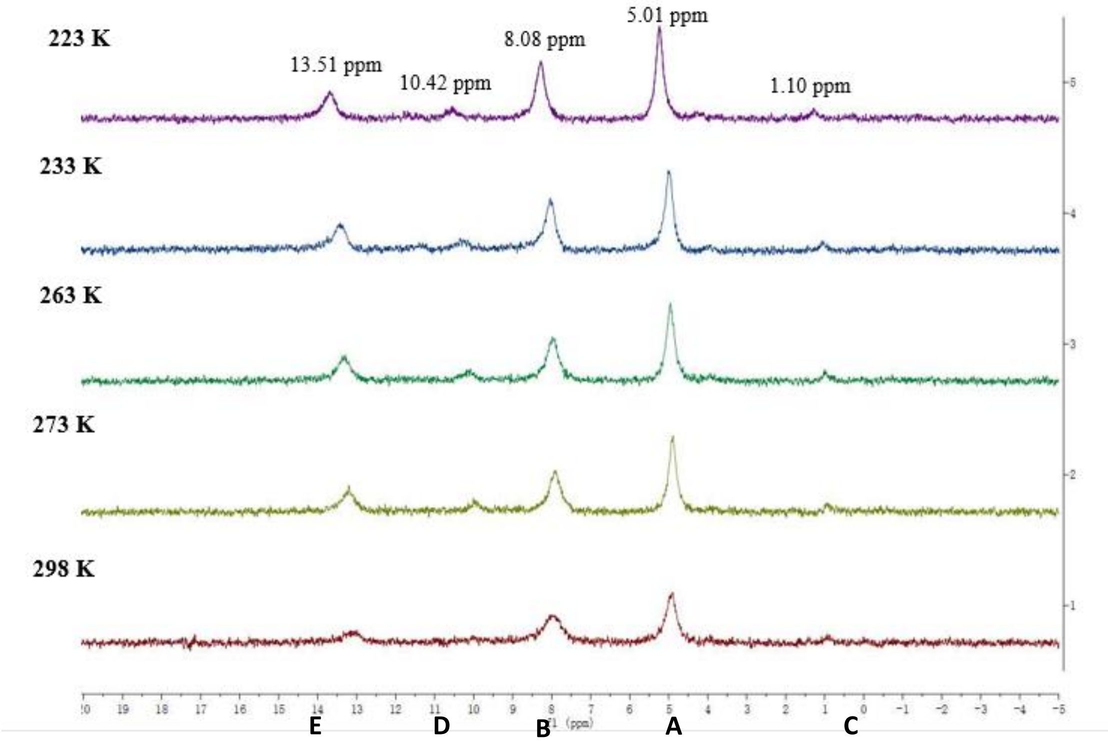


Figure S8-B. The VT-^{31}P NMR of complex **4 A-E** in D_8-THF

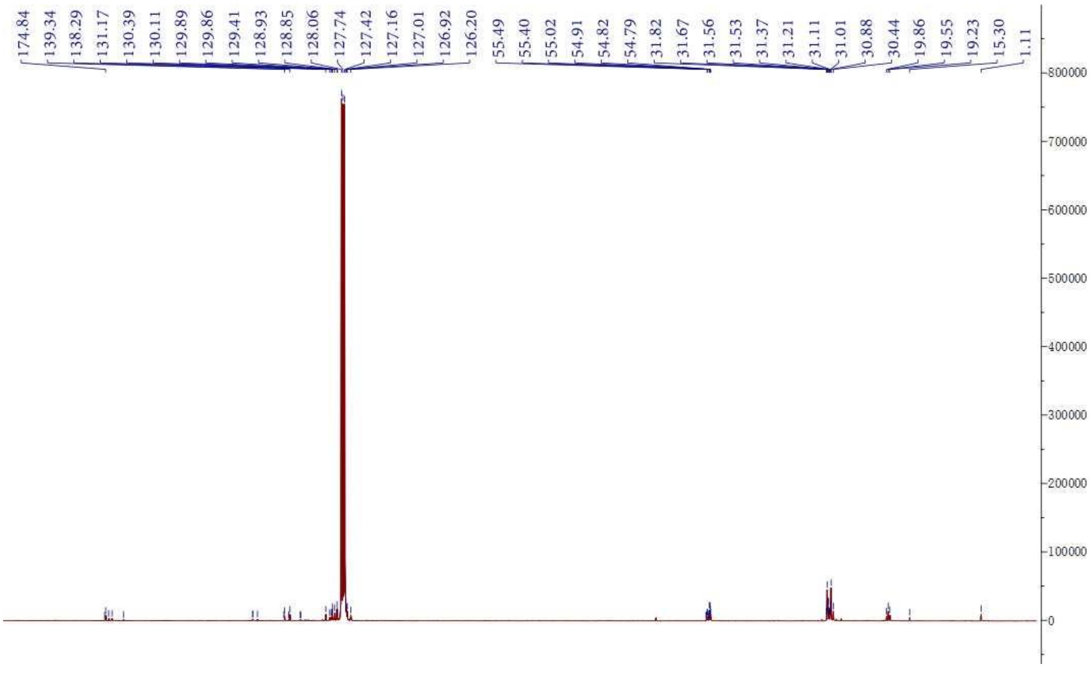


Figure S9. The ^{13}C NMR spectrum of complex **4** in C_6D_6

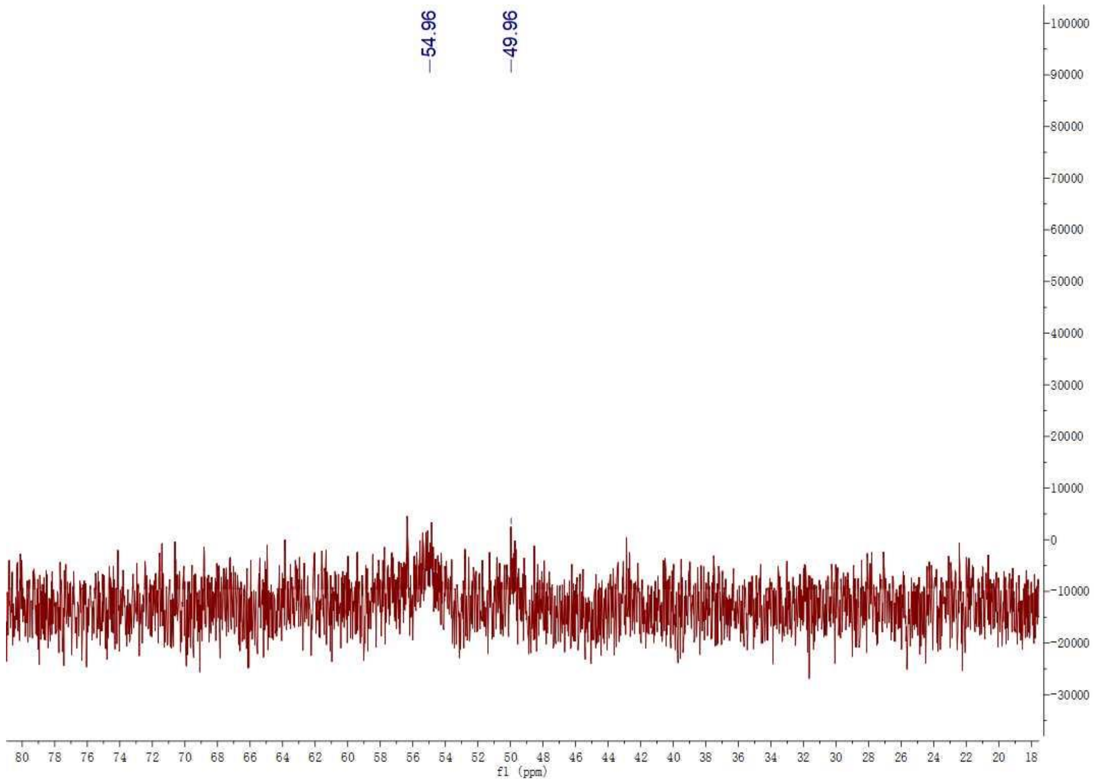
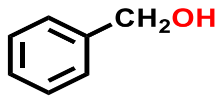


Figure S10. The ^{29}Si NMR of complex **4** in C_6D_6

3. ^{1}H and ^{13}C NMR spectra for the alcohol product



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.17 - 7.26 (m, Ar-*H*, 5H), 4.48 (s, CH_2, 2H), 2.70 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 140.91 (Ar-*C*), 128.55 (Ar-*C*), 127.59 (Ar-*C*), 127.05 (Ar-*C*), 65.07 (*C*H_2).

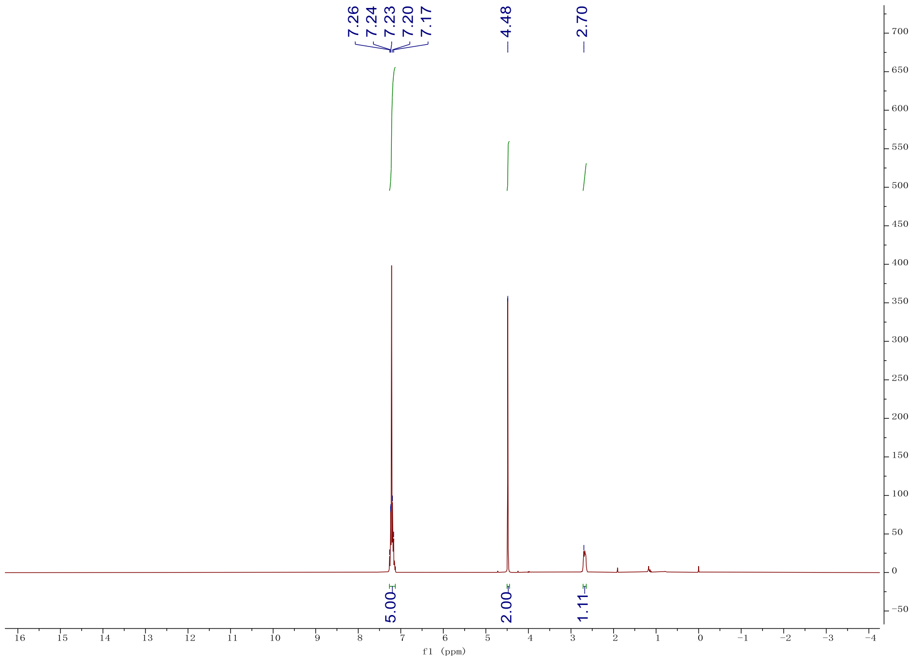


Figure S11. ^{1}H NMR spectrum of **2a** in $CDCl_3$

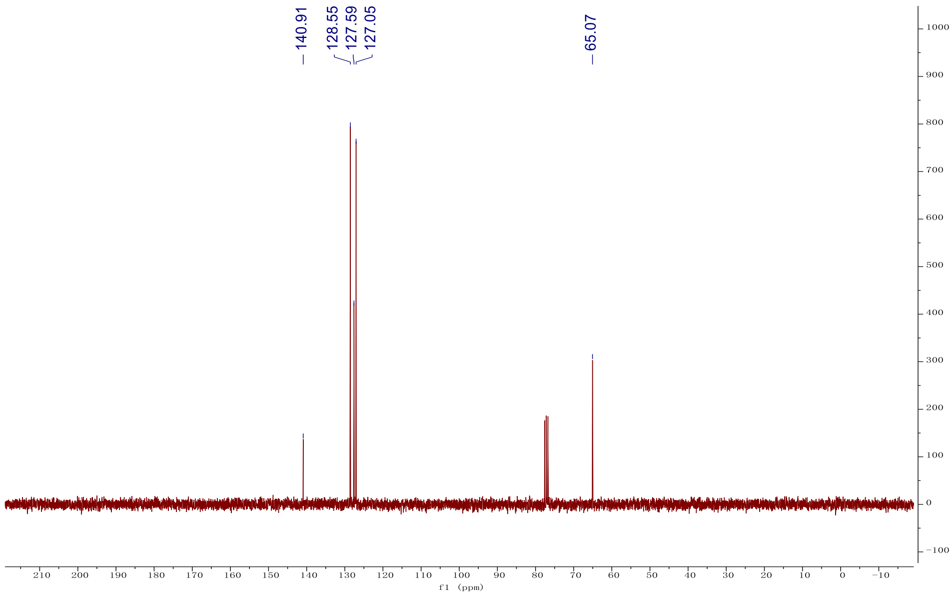
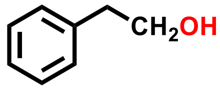


Figure S12. ^{13}C NMR spectrum of **2a** in $CDCl_3$



^{1}**H NMR** (300 MHz, $CDCl_3$, δ): 7.14 - 7.22 (m, Ar-*H*, 5H), 3.70 (t, CH_2, 2H), 3.51 (s, O*H*, 1H), 2.74 (t, CH_2, 2H). ^{13}**C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 138.94 (Ar-*C*), 129.18 (Ar-*C*), 128.60 (Ar-*C*), 126.45 (Ar-*C*), 63.51(*C*H_2), 39.27 (*C*H_2).

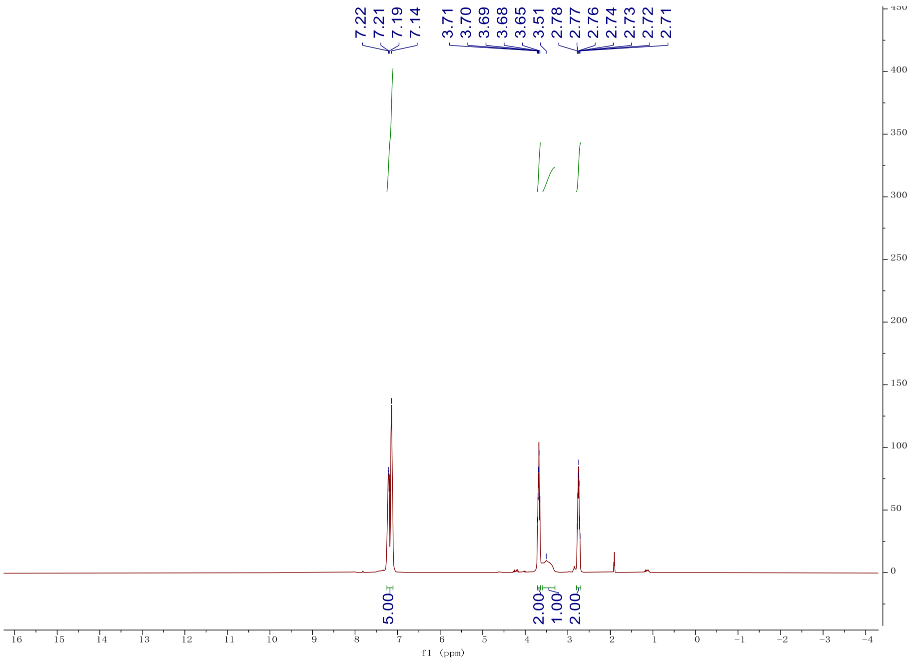


Figure S13. ^{1}H NMR spectrum of **2b** in $CDCl_3$

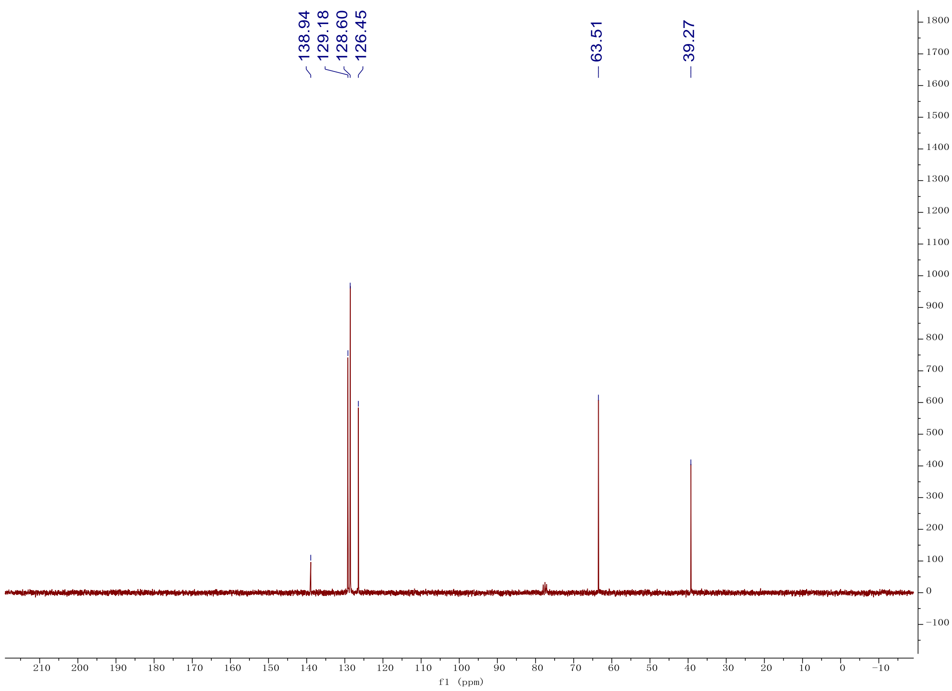
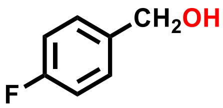


Figure S14. ^{13}C NMR spectrum of **2b** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 6.91-7.25 (m, *Ar*, 4H), 4.54 (s, CH_2, 2H), 2.03 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 160.68 (s, Ar-*C*), 136.24 (s, Ar-*C*), 128.76 (d, Ar-*C*), 115.37 (d, Ar-*C*), 64.56 (*C*H_2).

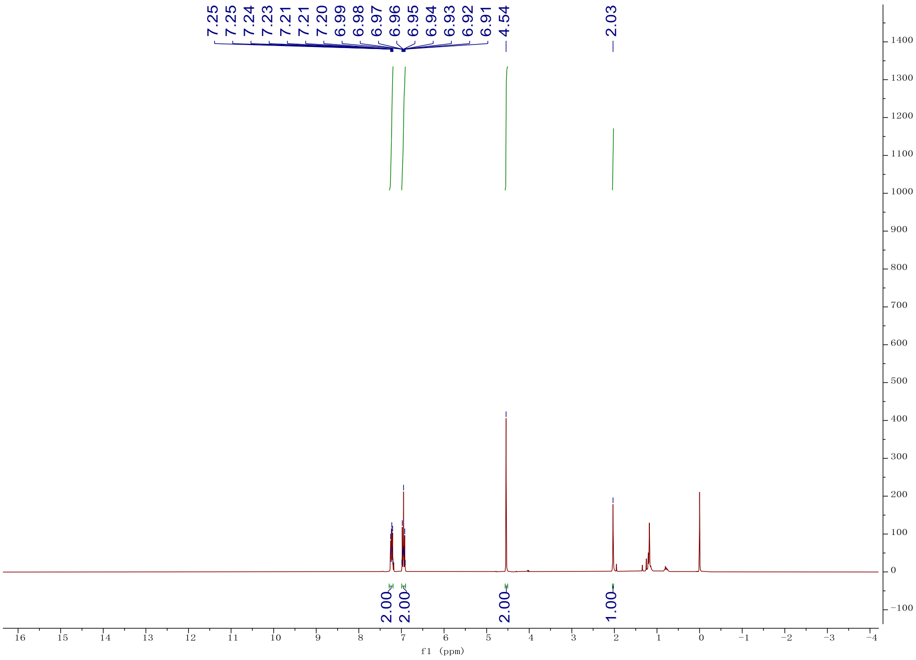


Figure S15. ^{1}H NMR spectrum of **2c** in $CDCl_3$

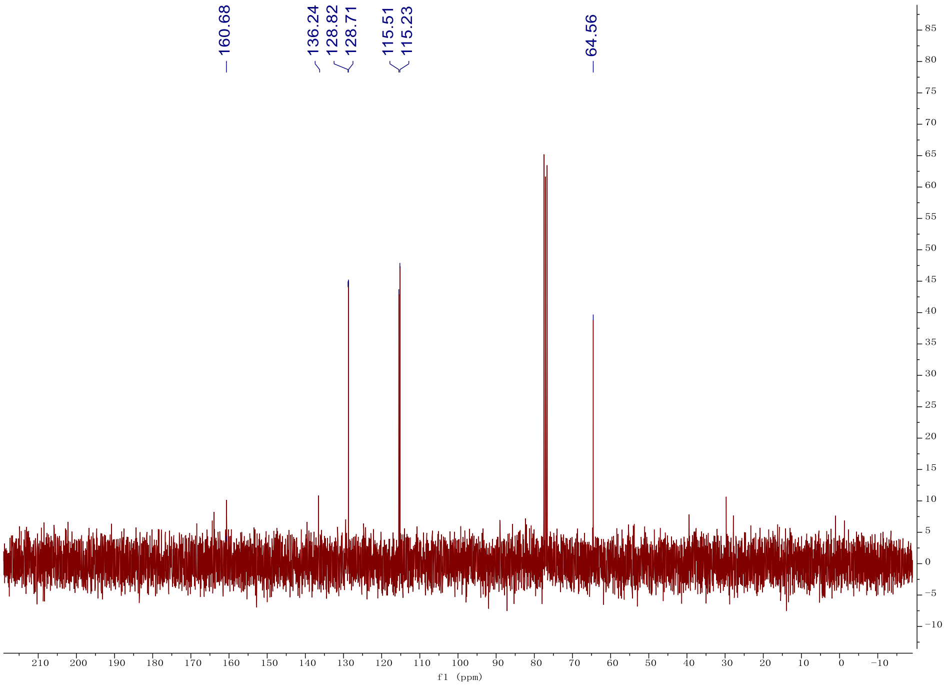
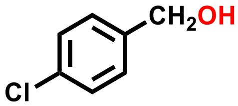


Figure S16. ^{13}C NMR spectrum of **2c** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.15-7.25 (m, *Ar*, 4H), 4.51 (s, C*H*$_2$, 2H), 2.29 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 139.95 (Ar-*C*), 134.03 (Ar-*C*), 129.37 (Ar-*C*), 128.99 (Ar-*C*), 65.12 (*C*H$_2$).

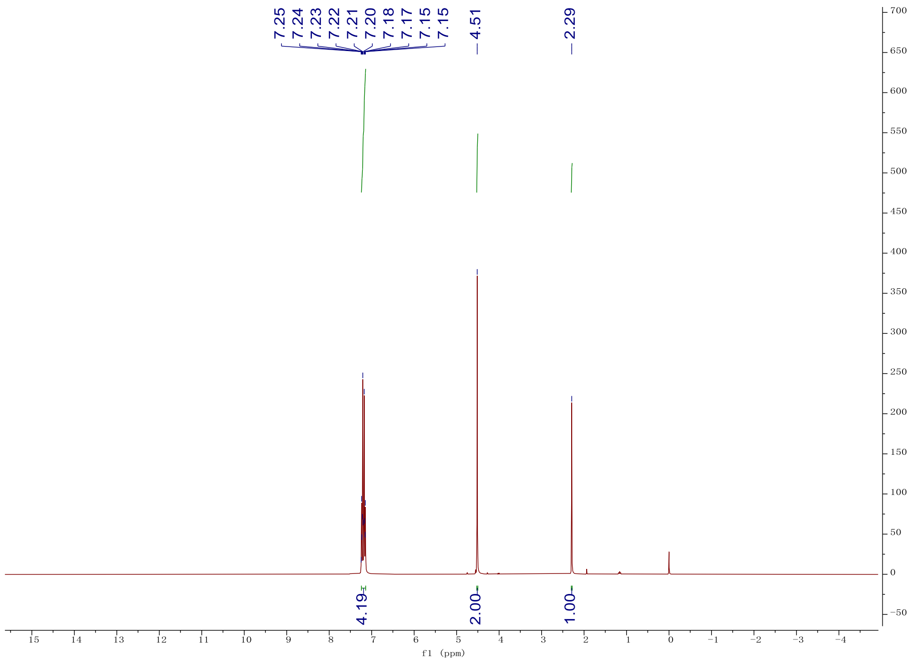


Figure S17. ^{1}H NMR spectrum of **2d** in $CDCl_3$

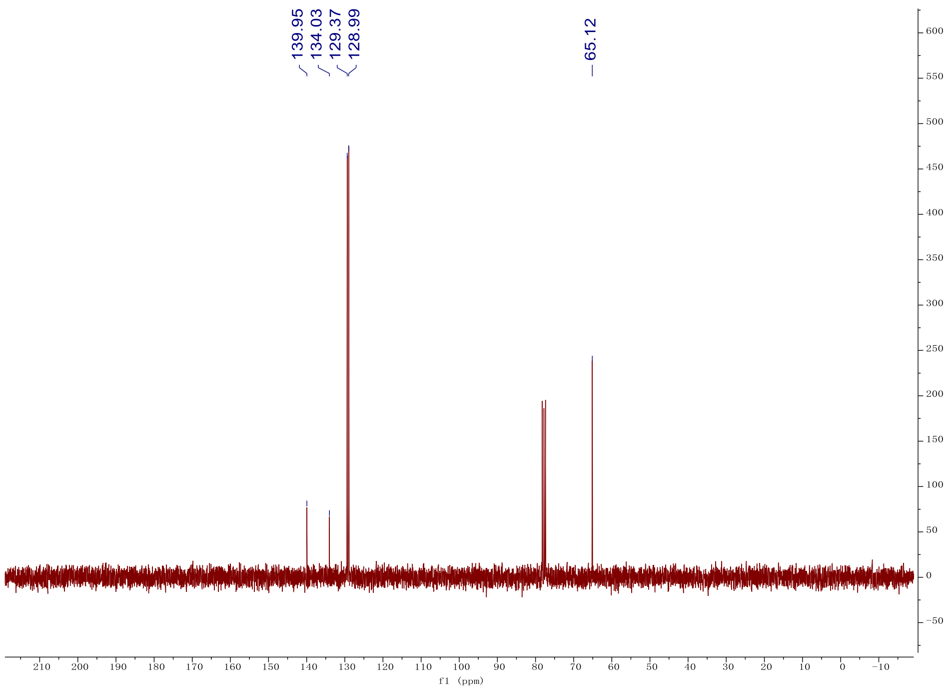
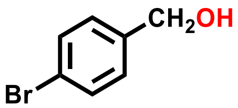


Figure S18. ^{13}C NMR spectrum of **2d** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.19-7.37 (m, *Ar*, 4H), 4.41 (s, C*H*$_2$, 2H), 2.33 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 131.71 (Ar-*C*), 128.52 (Ar-*C*), 128.35 (Ar-*C*), 122.56 (Ar-*C*), 51.55 (*C*H$_2$).

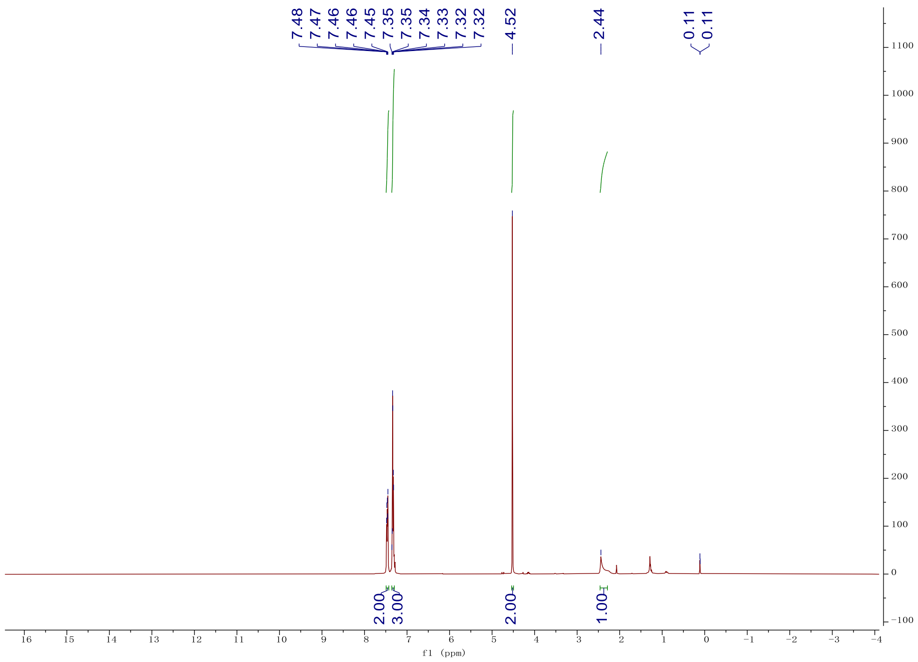


Figure S19. ^{1}H NMR spectrum of **2e** in $CDCl_3$

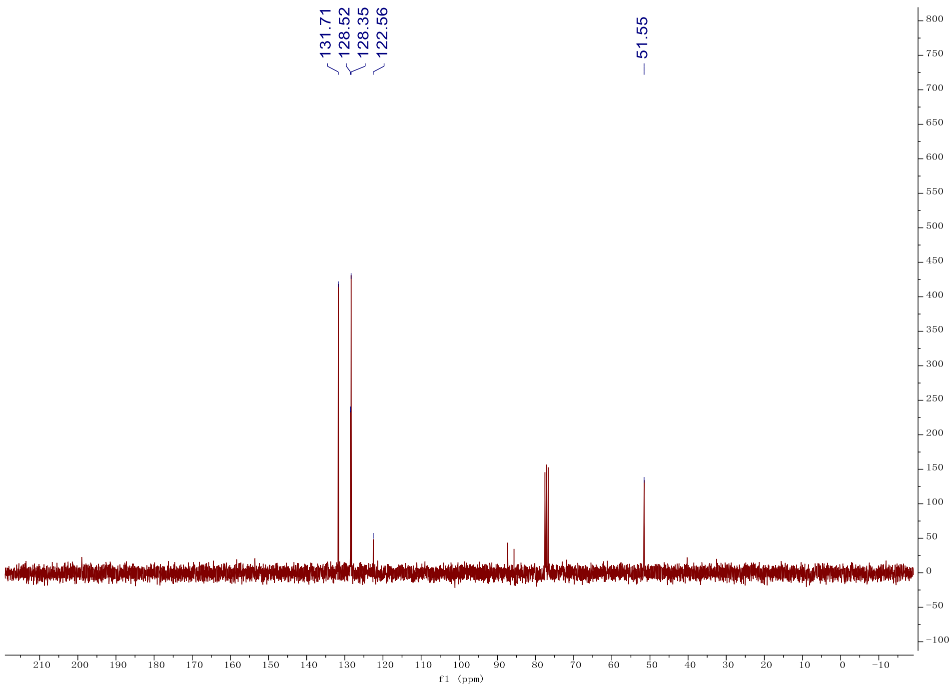
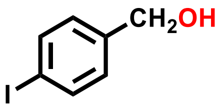


Figure S20. ^{13}C NMR spectrum of **2e** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.59 (d, Ar-*H*, 2H), 7.01 (d, Ar-*H*, 2H), 4.53 (s, C*H*$_2$, 2H), 1.97 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 140.42 (Ar-*C*), 137.59 (Ar-*C*), 128.82 (Ar-*C*), 93.01 (Ar-*C*), 64.59 (*C*H_2).

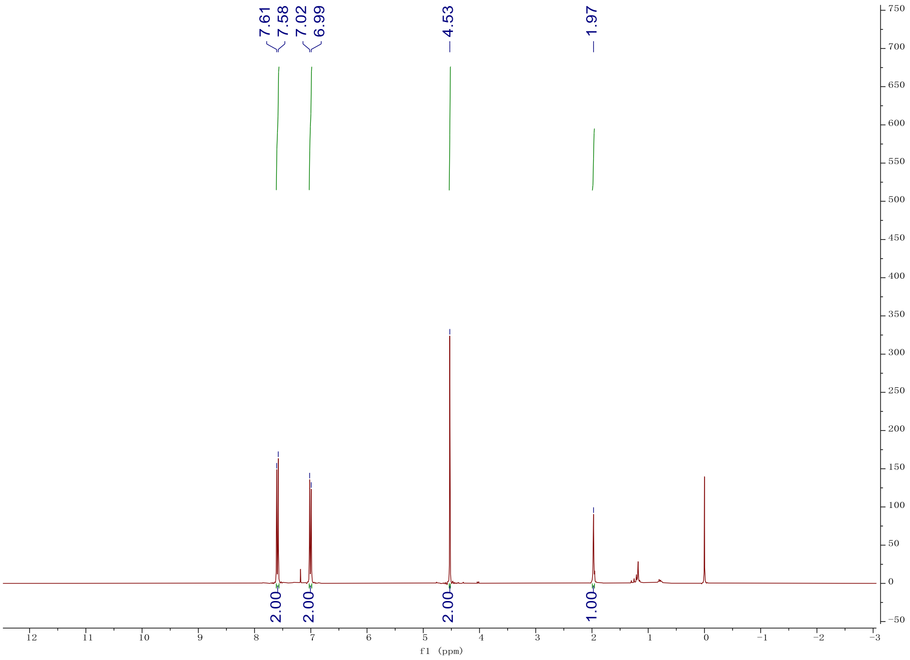


Figure S21. ^{1}H NMR spectrum of **2f** in $CDCl_3$

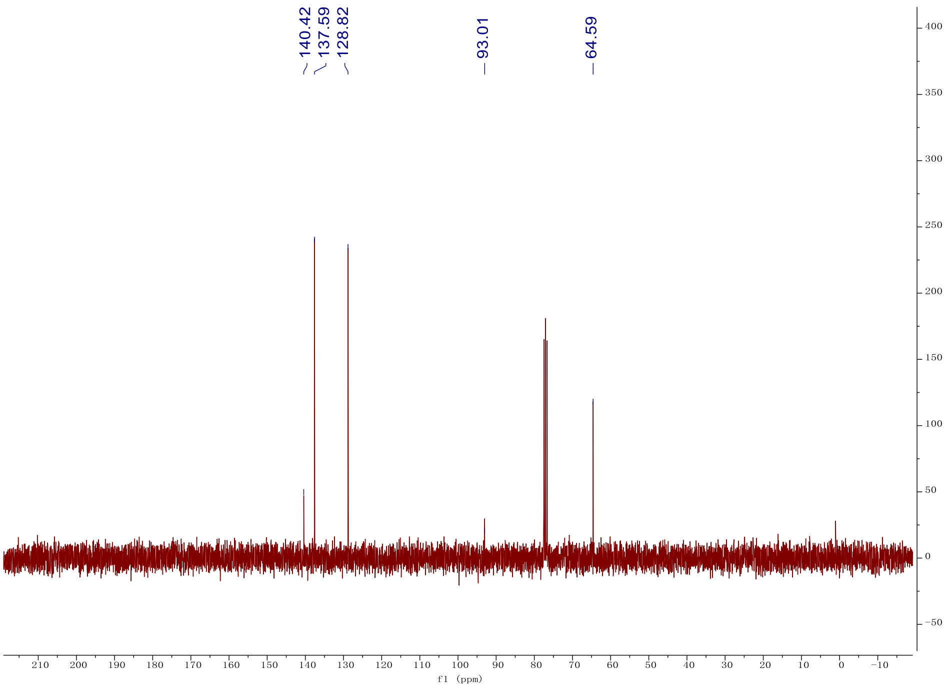
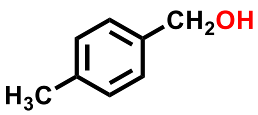


Figure S22. ^{13}C NMR spectrum of **2f** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 7.25 (d, Ar-*H*, 2H), 7.17 (d, Ar-*H*, 2H), 4.64 (s, C*H*$_2$, 2H), 2.35 (s, C*H*$_3$, 3H), 1.66 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 137.93 (Ar-*C*), 137.41 (Ar-*C*), 129.25 (Ar-*C*), 127.12 (Ar-*C*), 65.29 (*C*H_2), 21.14 (*C*H_2).

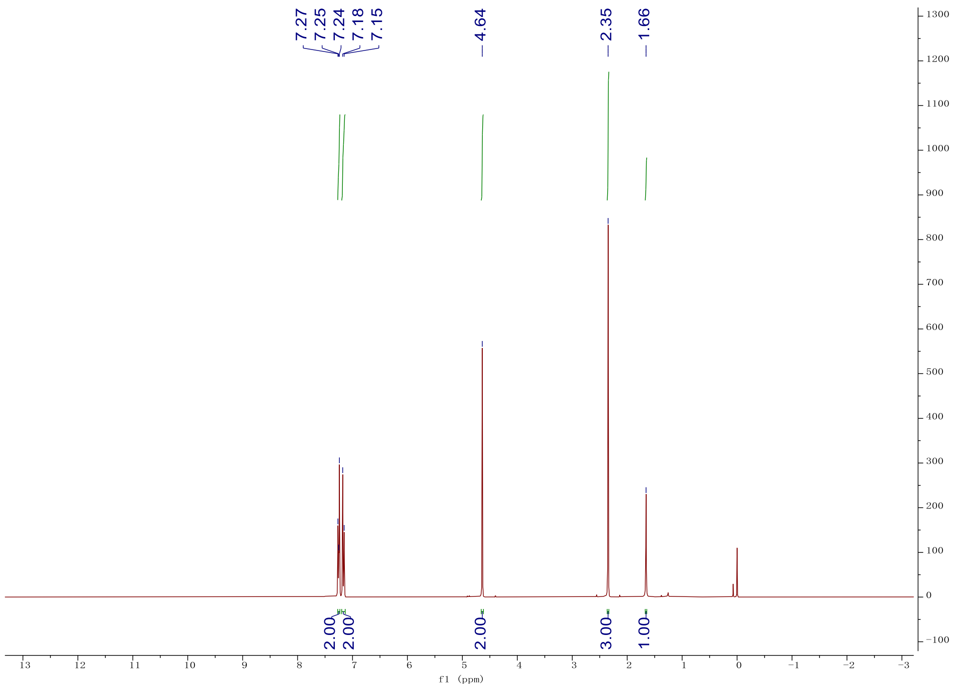


Figure S23. ^{1}H NMR spectrum of **2g** in $CDCl_3$

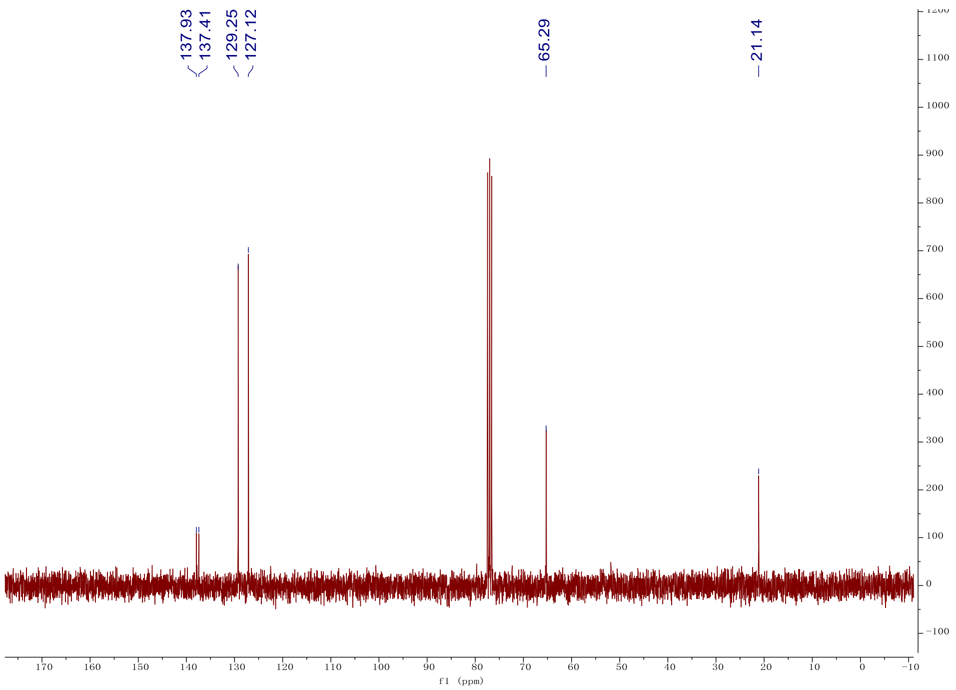
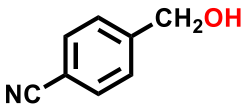


Figure S24. ^{13}C NMR spectrum of **2g** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, *δ*): 7.38–7.56 (m, *Ar*, 4H), 4.68 (s, C*H*$_2$, 2H), 2.32 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 146.42 (Ar-*C*), 132.29 (Ar-*C*), 127.02 (Ar-*C*), 118.90 (Ar-*C*), 110.95 (Ar-*C*), 64.07 (*C*H$_2$).

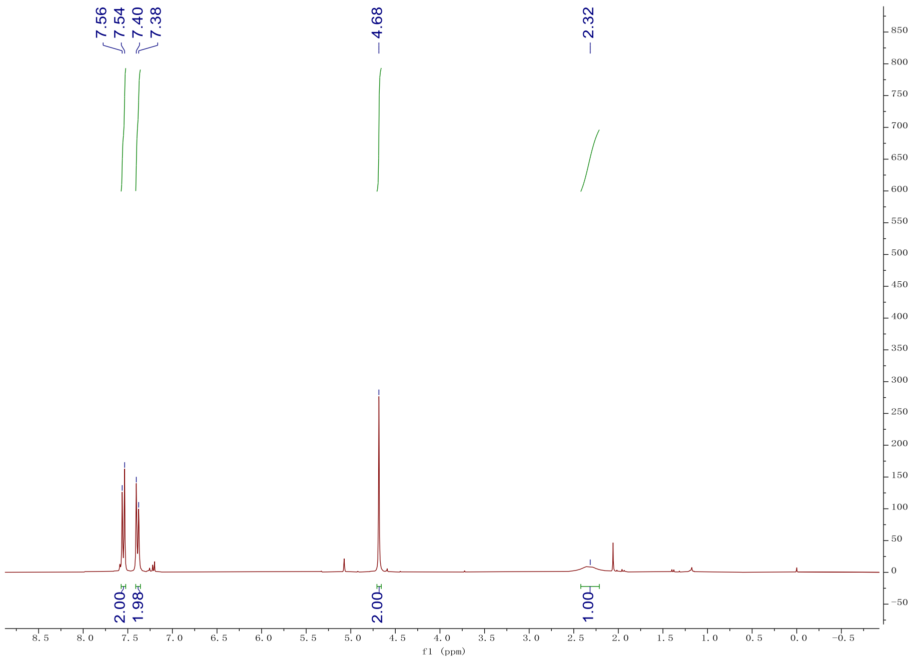


Figure S25. ^{1}H NMR spectrum of **2h** in $CDCl_3$

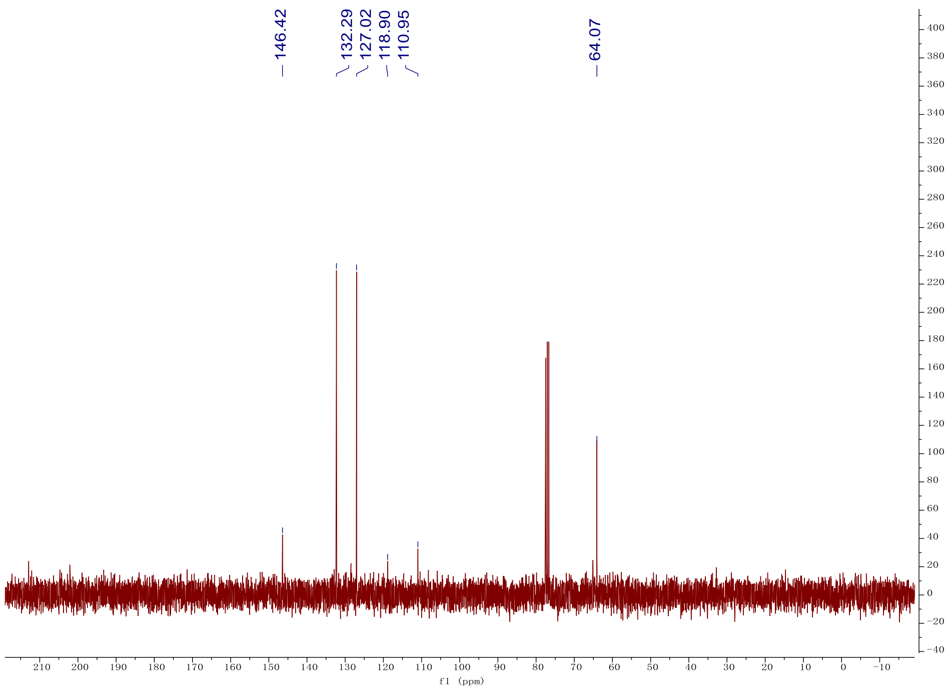
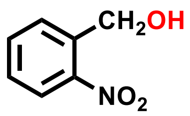


Figure S26. ^{13}C NMR spectrum of **2h** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 8.10 (dd, Ar-*H*, 1H), 7.75 (dd, Ar-*H*, 1H), 7.68 (td, Ar-*H*, 1H), 7.48 (ddd, Ar-*H*, 1H), 4.98 (s, C*H*$_2$, 2H), 2.56 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 136.77 (Ar-*C*), 134.14 (Ar-*C*), 130.02 (Ar-*C*), 128.52 (Ar-*C*), 125.03 (Ar-*C*), 62.57 (*C*H$_2$).

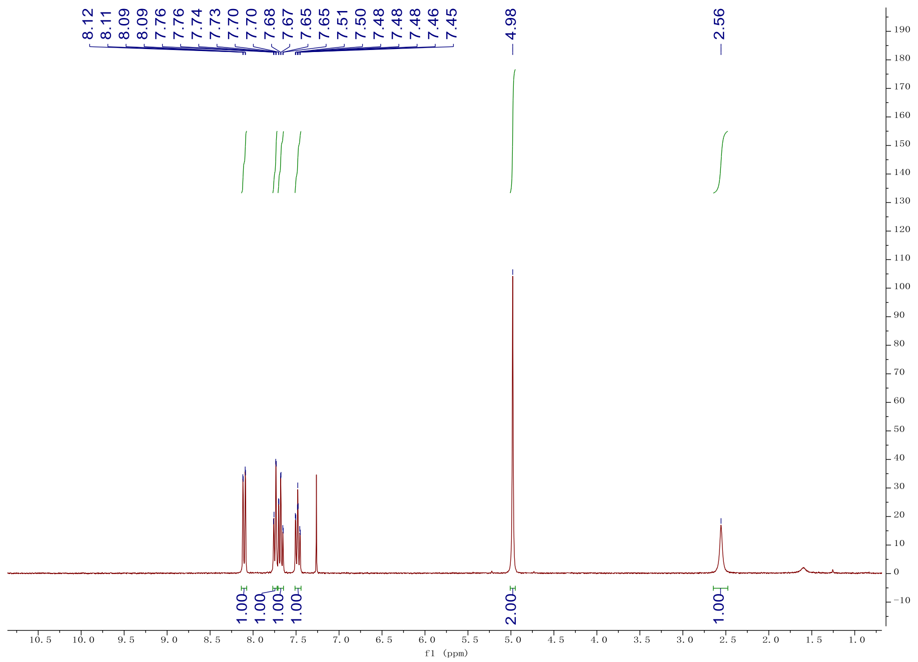


Figure S27. ^{1}H NMR spectrum of **2i** in $CDCl_3$

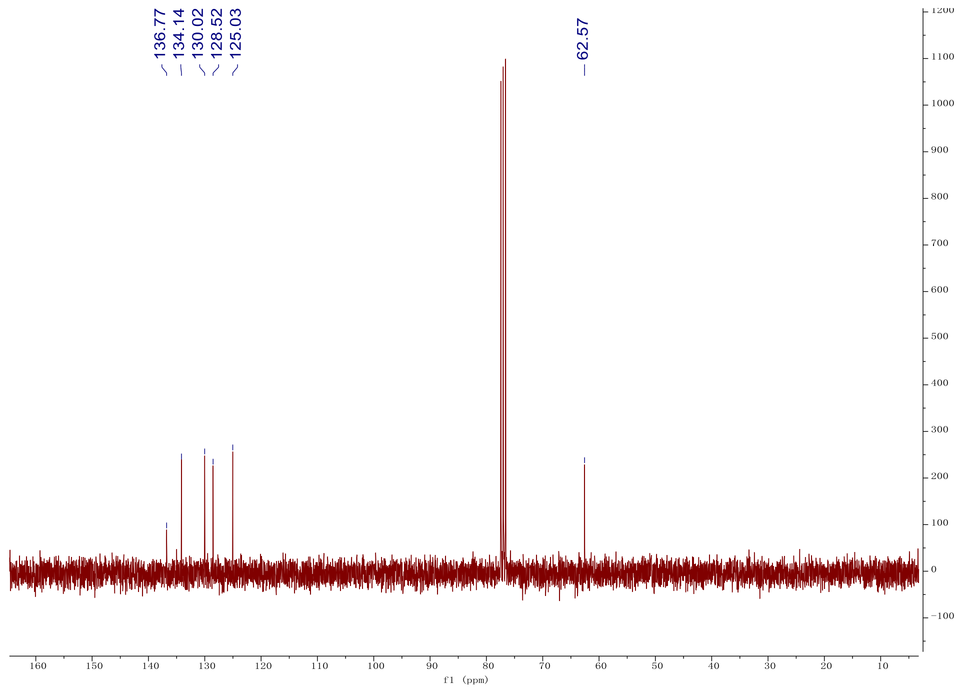
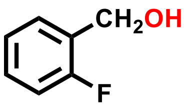


Figure S28. ^{13}C NMR spectrum of **2i** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 6.88 - 7.31 (m, Ar-*H*, 4H), 4.59 (s, C*H*$_2$, 2H), 2.87 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 162.19 (Ar-*C*), 158.93 (Ar-*C*), 129.32 (d, Ar-*C*), 129.24 (d, Ar-*C*), 124.20 (d, Ar-*C*), 115.19 (d, Ar-*C*), 59.00 (d, *C*H$_2$).

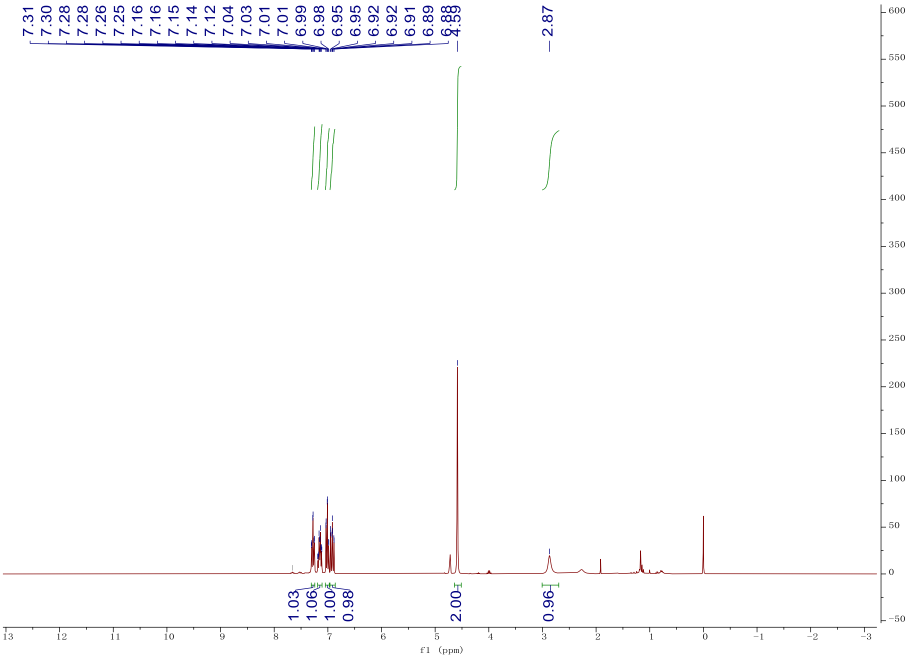


Figure S29. ^{1}H NMR spectrum of **2j** in $CDCl_3$

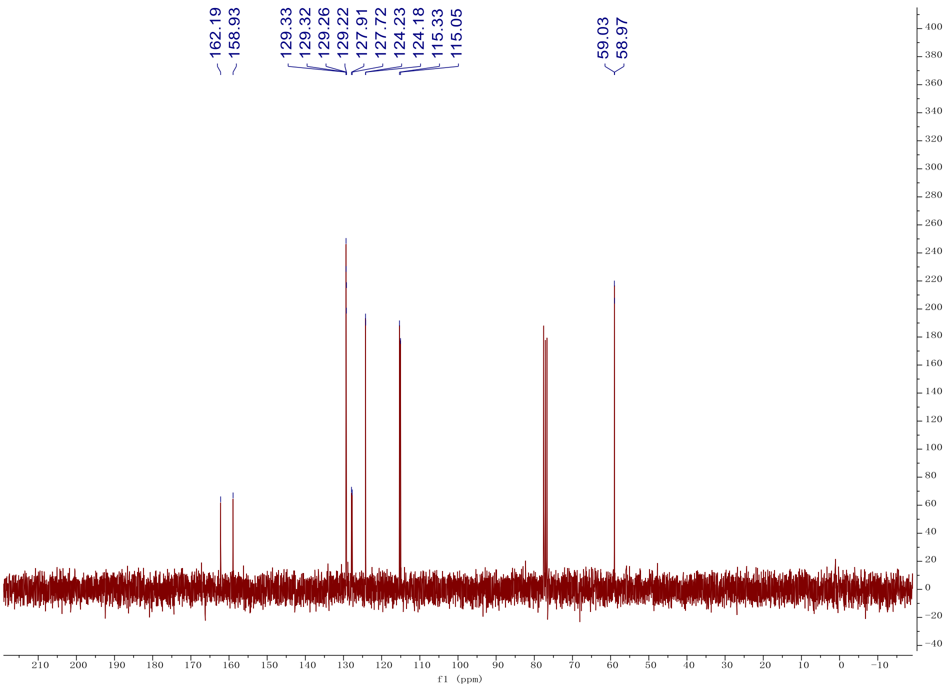
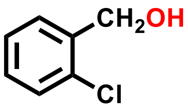


Figure S30. ^{13}C NMR spectrum of **2j** in $CDCl_3$



¹H NMR (300 MHz, $CDCl_3$, δ): 7.12-7.40 (m, *Ar*, 4H), 4.68 (s, C*H*$_2$, 2H), 2.18 (s, O*H*, 1H). **¹³C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 138.16 (Ar-*C*), 132.70 (Ar-*C*), 129.34 (Ar-*C*), 128.83 (Ar-*C*), 128.72 (Ar-*C*), 127.03 (Ar-*C*), 62.80 (*C*H$_2$).

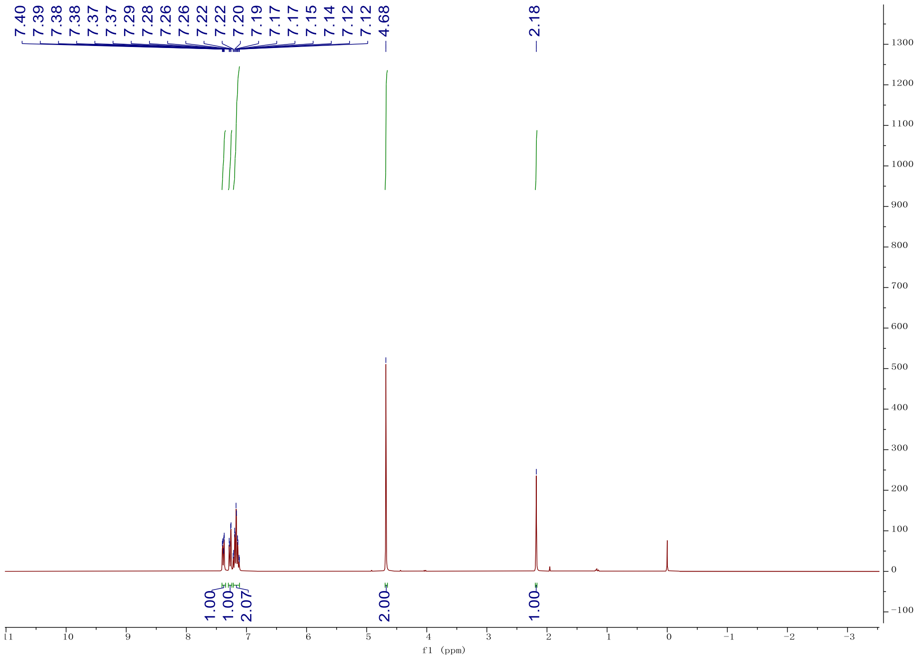


Figure S31. ¹H NMR spectrum of **2k** in $CDCl_3$

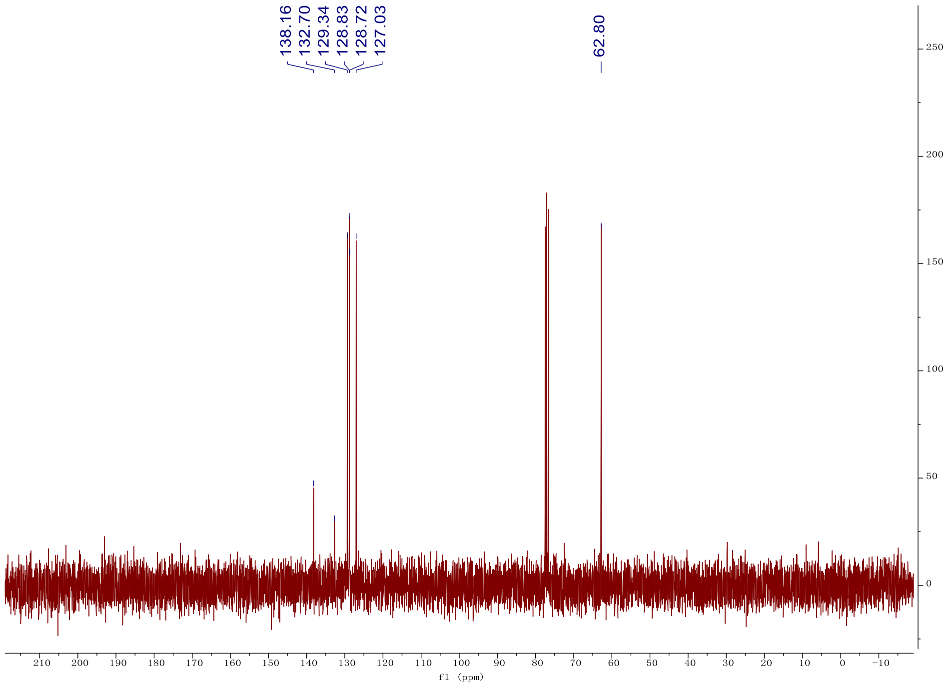
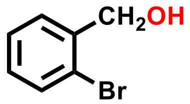


Figure S32. ¹³C NMR spectrum of **2k** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.43 (dd, Ar-*H*, 1H), 7.36 (dd, Ar-*H*, 1H), 7.22 (td, Ar-*H*, 1H), 7.05 (td, Ar-*H*, 1H), 4.61 (s, C*H*$_2$, 2H), 2.51 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 139.72 (Ar-*C*), 132.56 (Ar-*C*), 129.08 (Ar-*C*), 128.81 (Ar-*C*), 127.65 (Ar-*C*), 122.51 (Ar-*C*), 64.92 (*C*H$_2$).

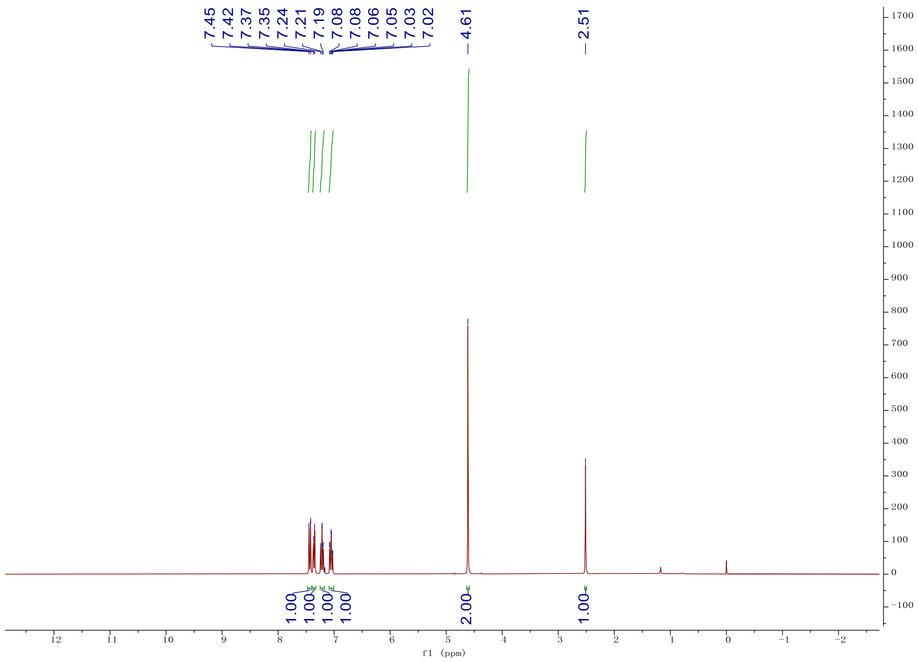


Figure S33. ^{1}H NMR spectrum of **2l** in $CDCl_3$

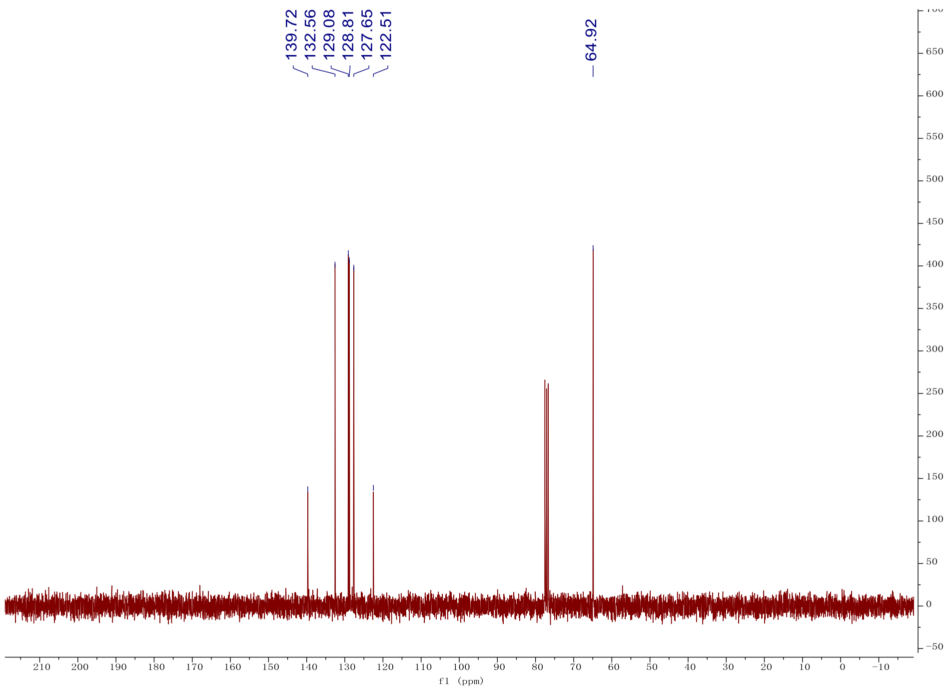
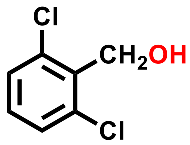


Figure S34. ^{13}C NMR spectrum of **2l** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.23 (d, Ar-*H*, 2H), 7.07 (dd, Ar-*H*, 1H), 4.84 (s, CH_2, 2H), 2.36 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 135.99 (Ar-*C*), 135.66 (Ar-*C*), 129.79 (Ar-*C*), 128.46 (Ar-*C*), 60.08 (*C*H_2).

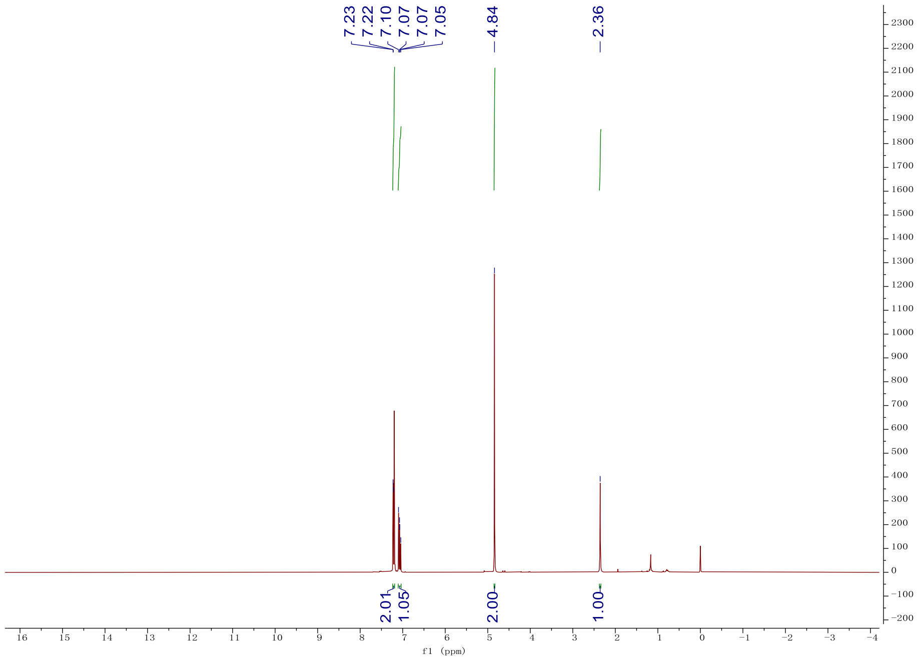


Figure S35. ^{1}H NMR spectrum of **2m** in $CDCl_3$

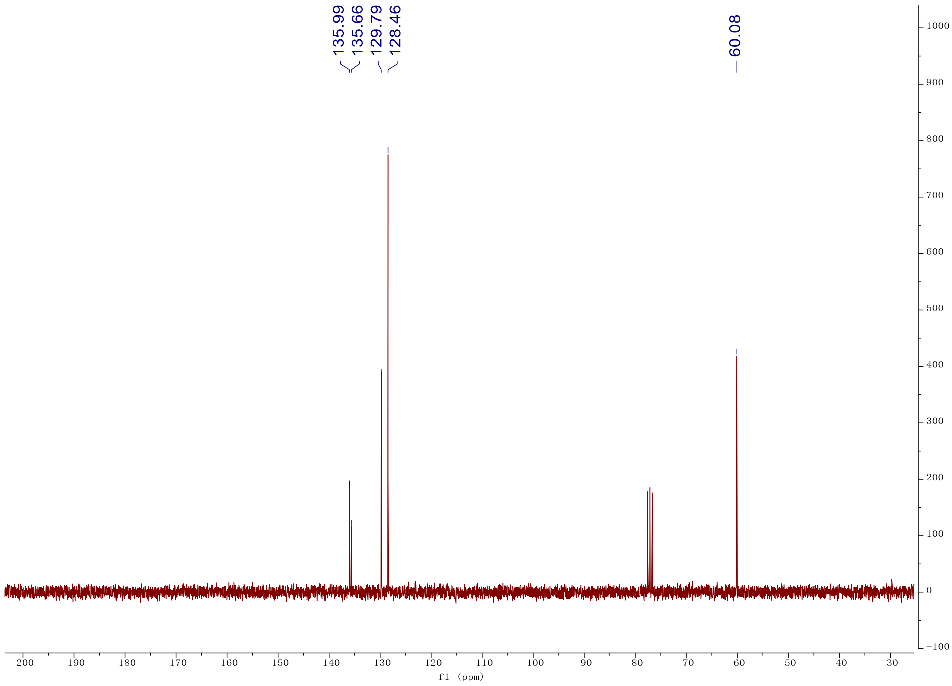
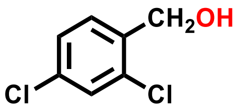


Figure S36. ^{13}C NMR spectrum of **2m** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25 (d, Ar-*H*, 1H), 7.22 (d, Ar-*H*, 1H), 7.10 (dd, Ar-*H*, 1H), 4.55 (s, CH_2, 2H), 3.02 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 136.77 (Ar-*C*), 133.85 (Ar-*C*), 133.20 (Ar-*C*), 129.43 (Ar-*C*), 129.14 (Ar-*C*), 127.29 (Ar-*C*), 62.20 (*C*H_2).

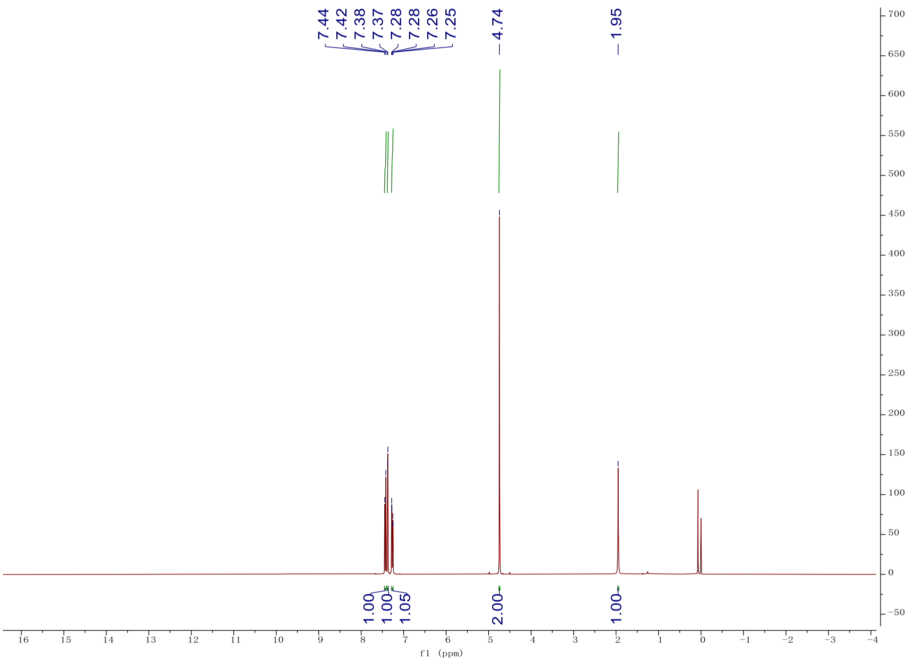


Figure S37. ^{1}H NMR spectrum of **2n** in $CDCl_3$

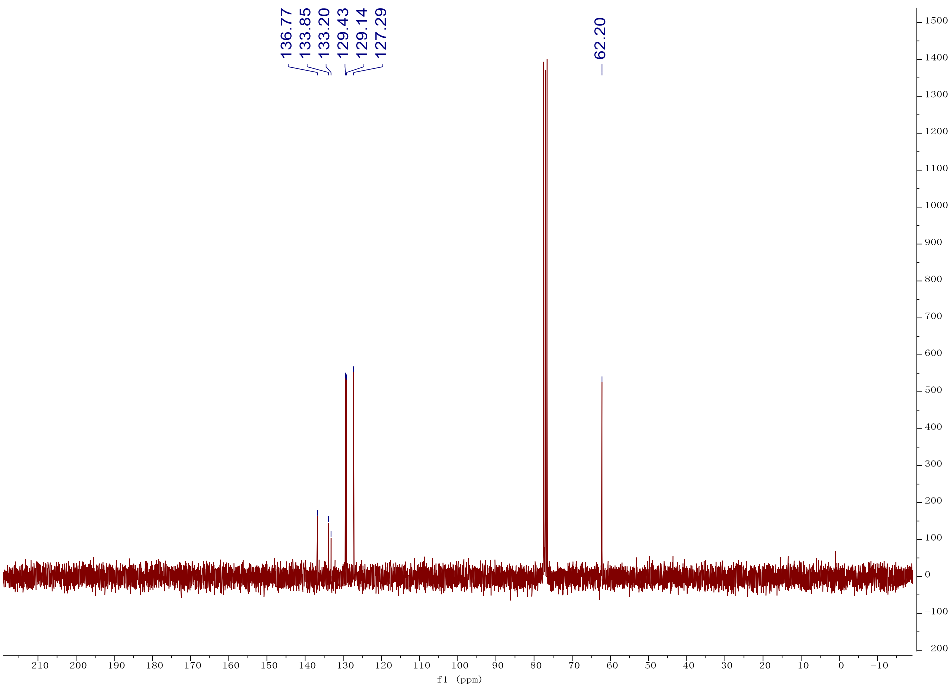
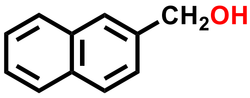


Figure S38. ^{13}C NMR spectrum of **2n** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.16-7.78 (m, Ar-*H*, 7H), 4.71 (s, CH_2, 2H), 2.93 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 136.35 (Ar-*C*), 133.80 (Ar-*C*), 131.26 (Ar-*C*), 128.72 (Ar-*C*), 128.45 (Ar-*C*), 126.33 (Ar-*C*), 125.90 (Ar-*C*), 125.50 (Ar-*C*), 125.27 (Ar-*C*), 123.74 (Ar-*C*), 63.20 (*C*H_2).

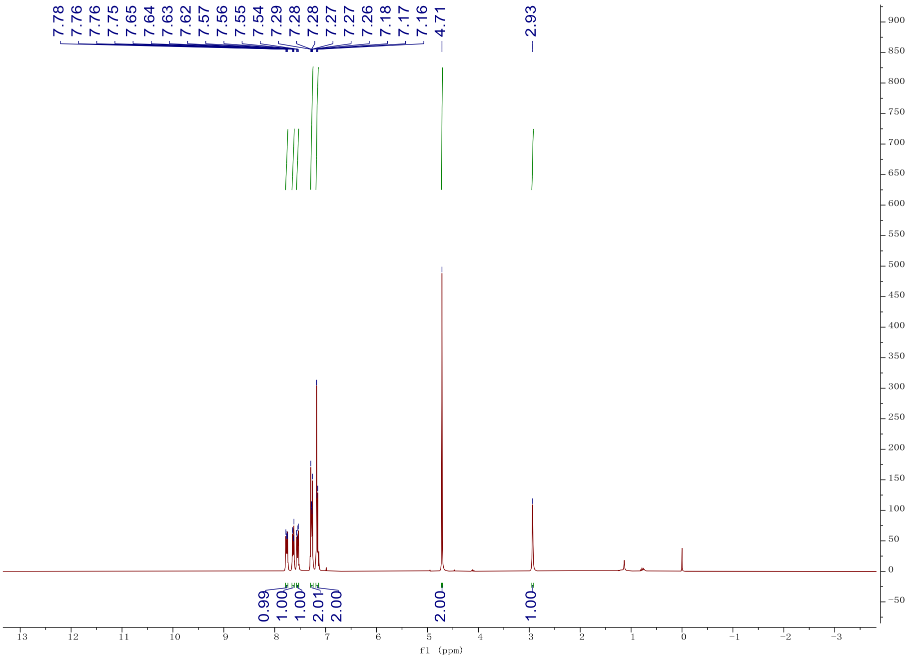


Figure S39. ^{1}H NMR spectrum of **2o** in $CDCl_3$

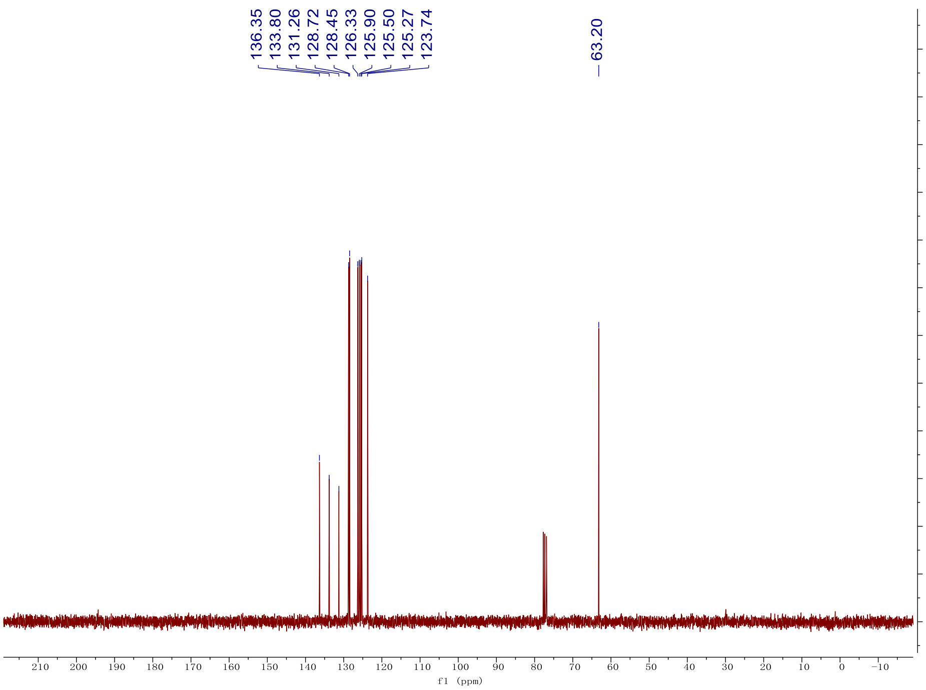
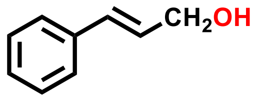


Figure S40. ^{13}C NMR spectrum of **2o** in $CDCl_3$



¹H NMR (300 MHz, $CDCl_3$, δ): 7.14-7.29 (m, Ar-*H*, 5H), 6.50 (d, *H*C=C, 1H), 6.20-6.29 (m, C=C*H*, 1H), 4.19 (dd, CH_2, 2H), 2.31 (s, O*H*, 1H). **¹³C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 136.72 (Ar-*C*), 131.05 (Ar-*C*), 128.63 (Ar-*C*), 128.55 (Ar-*C*), 127.70 (Ar-*C*), 126.50 (*C*=*C*), 63.59 (*C*H_2).

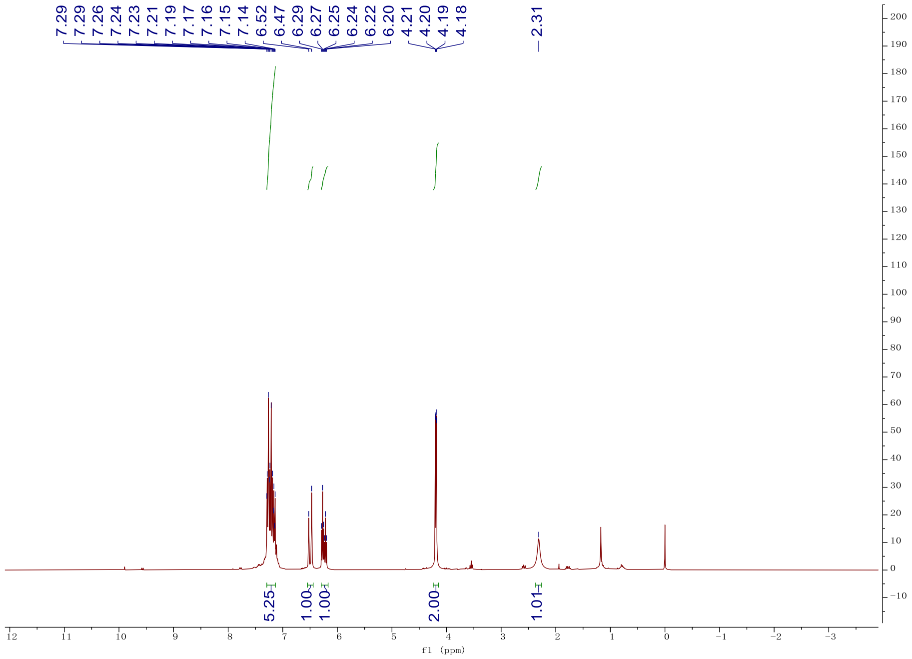


Figure S41. ^{1}H NMR spectrum of **2p** in $CDCl_3$

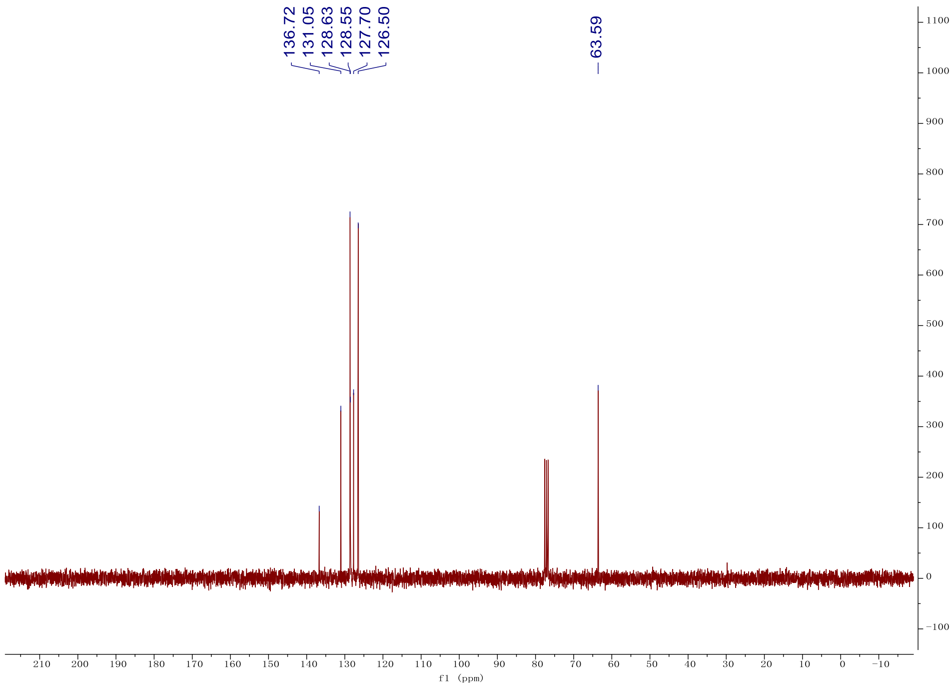
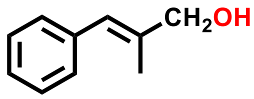


Figure S42. ^{13}C NMR spectrum of **2p** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.08-7.24 (m, Ar-*H*, 5H), 6.41 (d, *H*C=C, 1H), 4.05 (dd, CH_2, 2H), 2.73 (s, O*H*, 1H) ,1.77 (d, CH_3, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 137.70 (Ar-*C*), 137.66 (Ar-*C*), 128.94 (Ar-*C*), 128.20 (Ar-*C*), 126.45 (Ar-*C*), 124.94 (*C*=*C*), 68.77 (*C*H_2), 15.33 (*C*H_3).

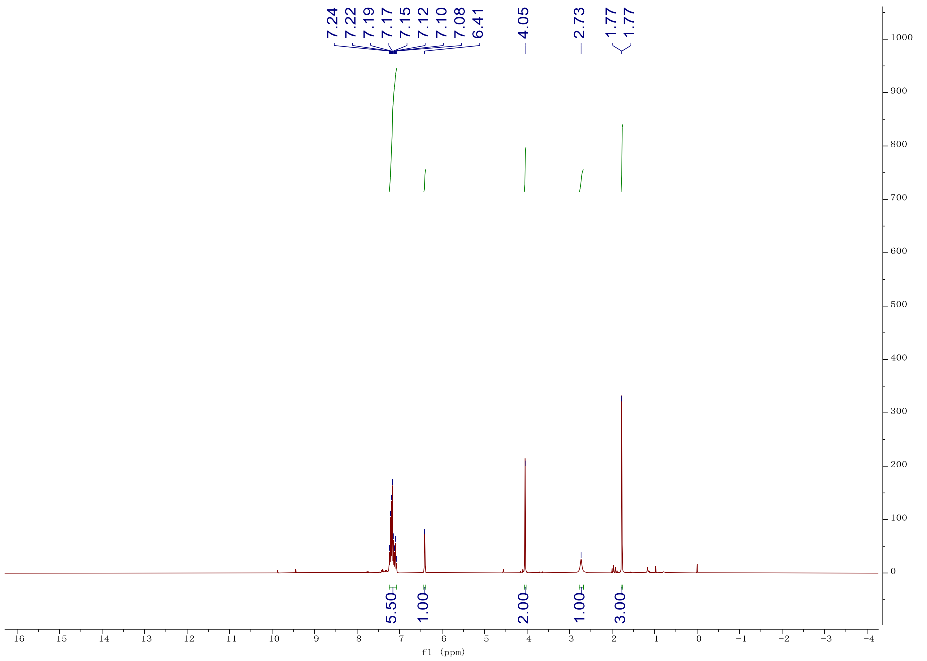


Figure S43. ^{1}H NMR spectrum of **2q** in $CDCl_3$

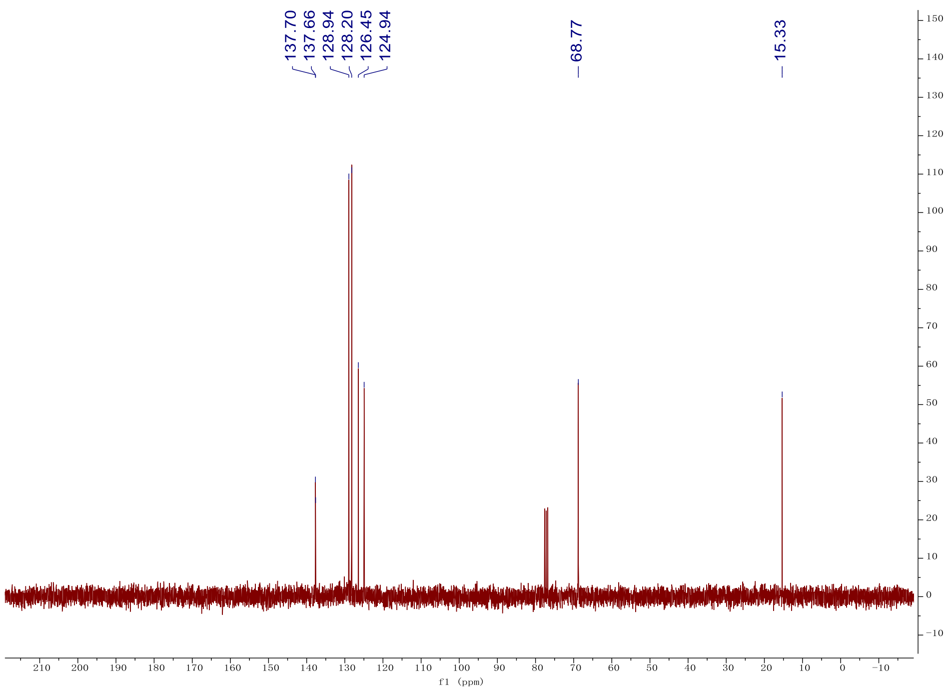
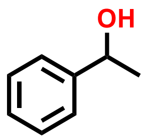


Figure S44. ^{13}C NMR spectrum of **2q** in $CDCl_3$



¹H NMR (300 MHz, $CDCl_3$, δ): 7.12-7.23 (m, Ar-*H*, 5H), 4.71 (q, C*H*, 1H), 2.50 (s, O*H*, 1H), 1.34 (d, CH_3, 3H). **¹³C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 145.89 (Ar-*C*), 128.46 (Ar-*C*), 127.40 (Ar-*C*), 125.45 (Ar-*C*), 70.32 (*C*H), 25.16 (*C*H_3).

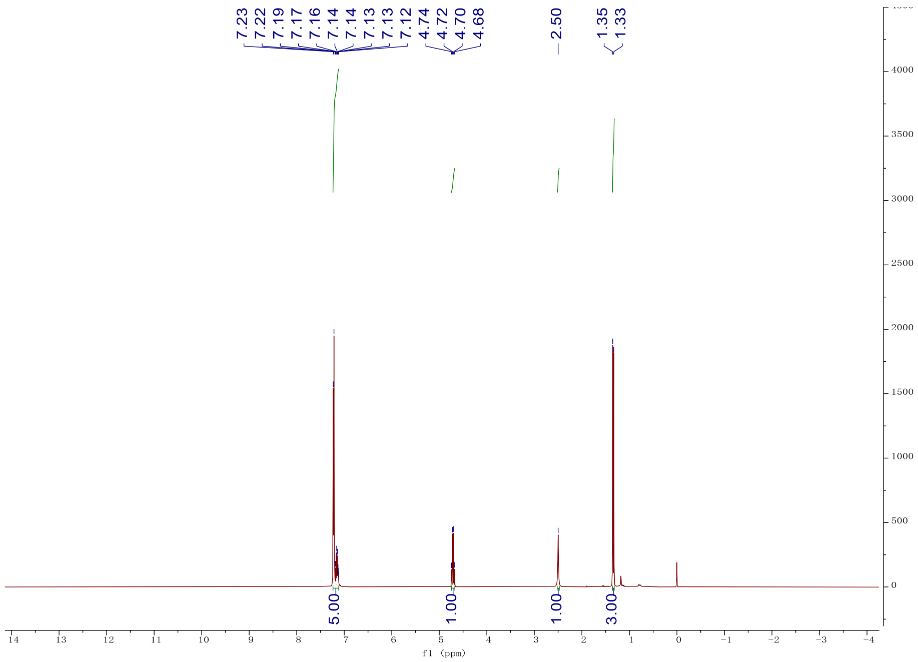


Figure S45. ¹H NMR spectrum of **1a** in $CDCl_3$

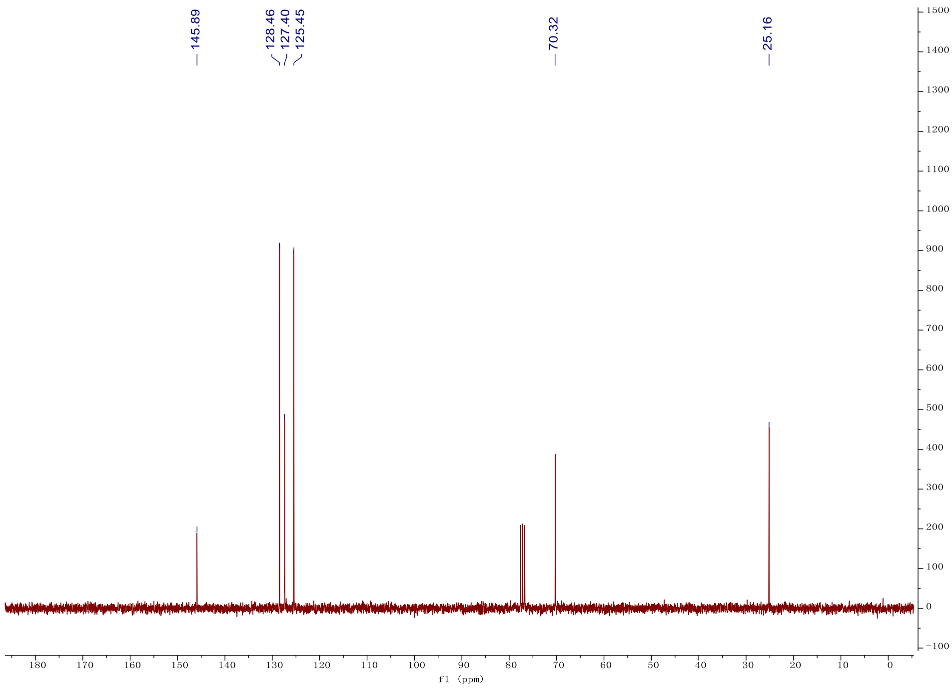
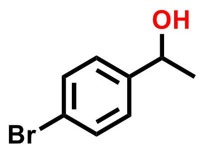


Figure S46. ¹³C NMR spectrum of **1a** in $CDCl_3$



^{1}**H NMR** (300 MHz, $CDCl_3$, δ): 7.02-7.32 (m, Ar-*H*, 4H), 4.61 (q, C*H*, 1H), 3.20 (s, O*H*, 1H), 1.26 (d, C*H*$_3$, 3H). ^{13}**C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 144.79 (Ar-*C*), 131.48 (Ar-*C*), 127.22 (Ar-*C*), 121.05 (Ar-*C*), 69.55 (*C*H), 25.19 (*C*H$_3$).

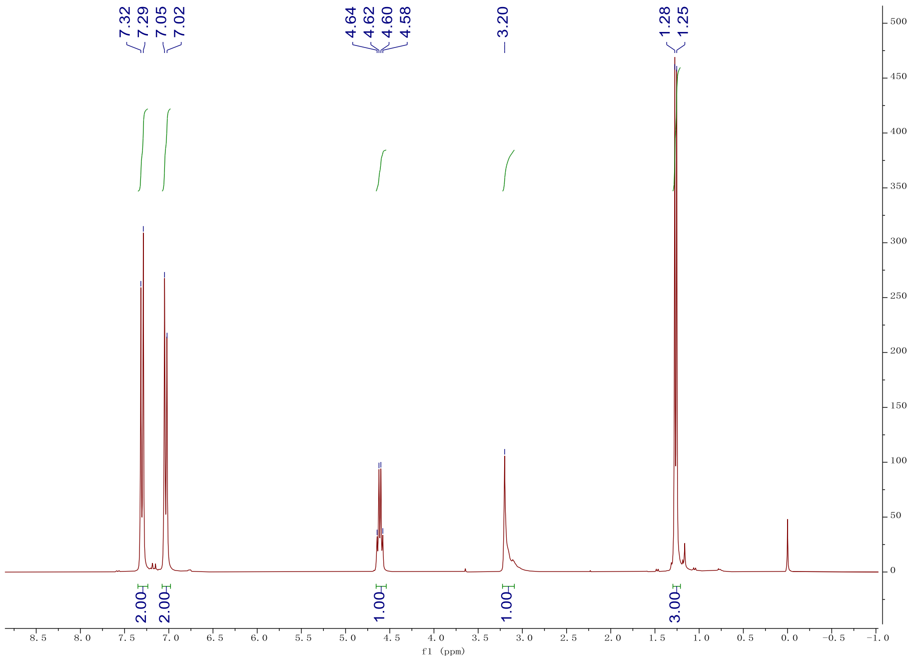


Figure S47. ^{1}H NMR spectrum of **1b** in $CDCl_3$

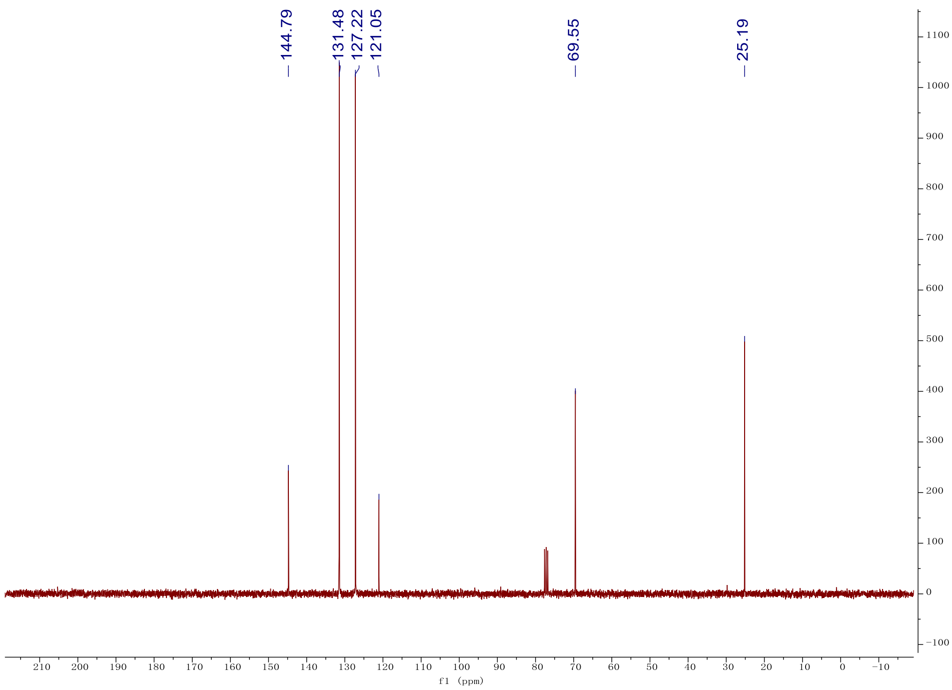
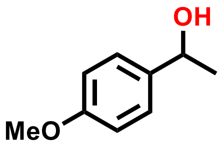


Figure S48. ^{13}C NMR spectrum of **1b** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.09-7.17 (m, Ar-*H*, 2H), 6.70-6.79 (m, Ar-*H*, 2H), 4.68 (q, C*H*, 1H), 3.66 (s, OCH_3, 3H), 2.52 (s, O*H*, 1H), 1.33 (d, CH_3, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 158.85 (Ar-*C*), 138.16 (Ar-*C*), 126.72 (Ar-*C*), 113.78 (Ar-*C*), 69.79 (*C*H), 55.26 (O*C*H_3), 25.07 (*C*H_3).

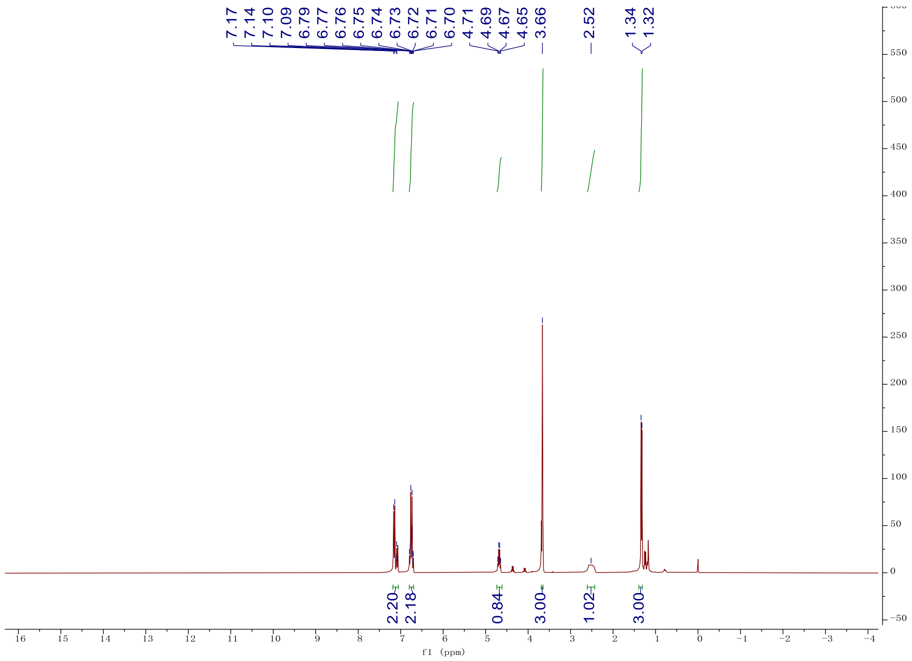


Figure S49. ^{1}H NMR spectrum of **1c** in $CDCl_3$

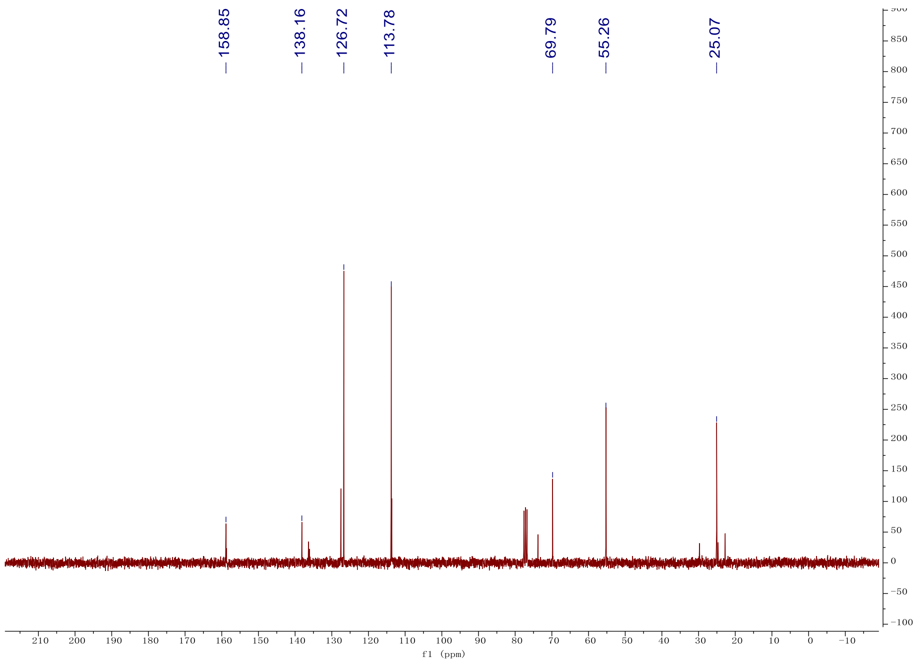
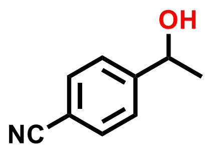


Figure S50. ^{13}C NMR spectrum of **1c** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.36-7.50 (m, Ar-*H*, 4H), 4.82 (q, C*H*, 1H), 3.10 (s, O*H*, 1H), 1.36 (d, C*H*$_3$, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 151.51 (Ar-*C*), 132.25 (Ar-*C*), 126.12 (Ar-*C*), 118.93 (Ar-*C*), 108.33 (Ar-*C*), 69.38 (*C*H), 24.79 (*C*H$_3$).

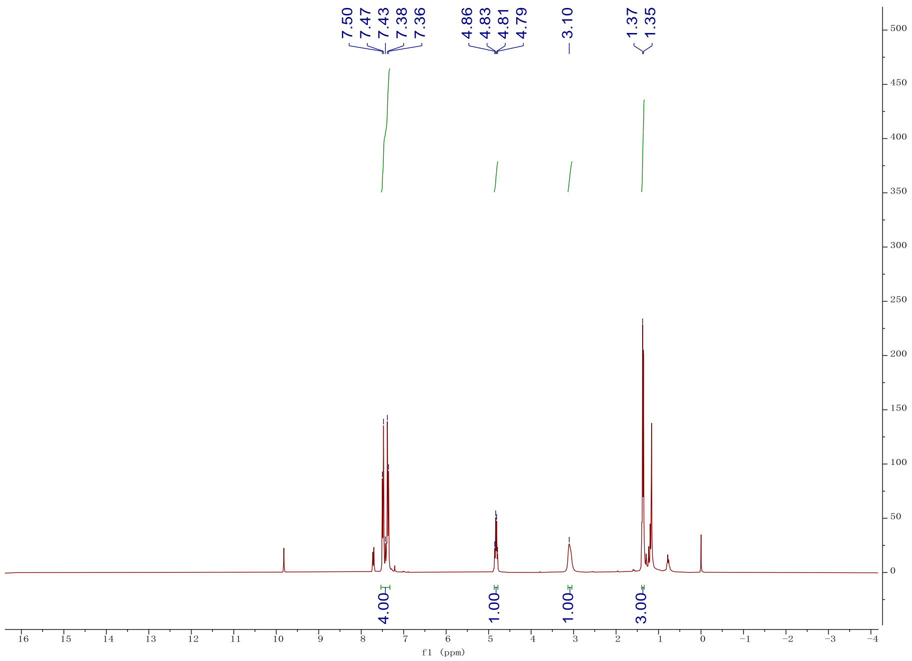


Figure S51. ^{1}H NMR spectrum of **1d** in $CDCl_3$

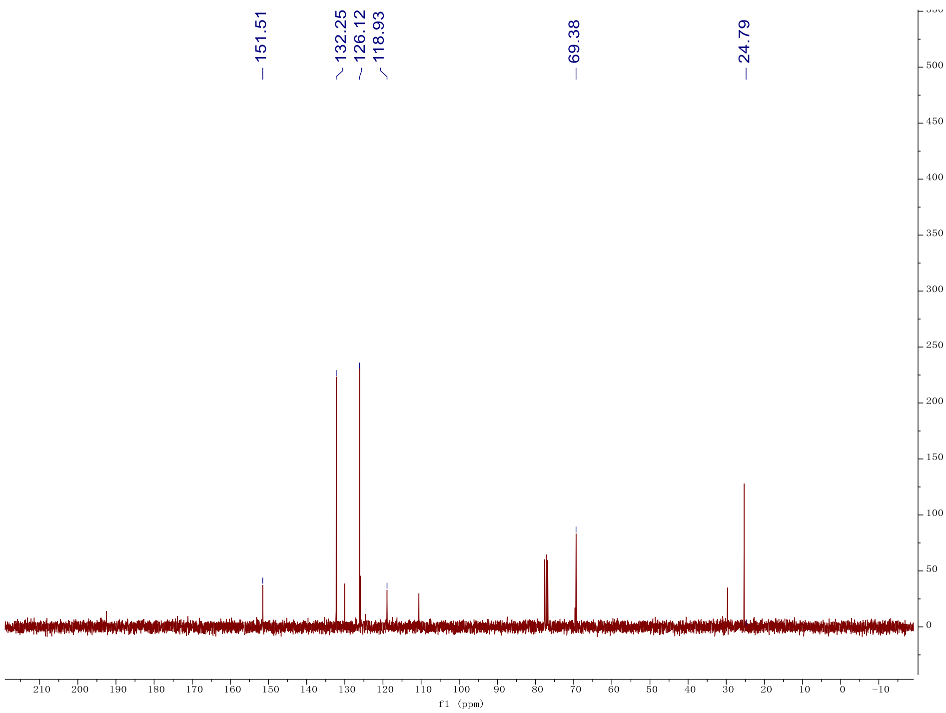
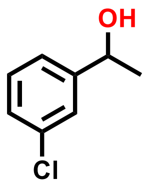


Figure S52. ^{13}C NMR spectrum of **1d** in $CDCl_3$



^{1}H NMR (300 MHz, CDCl3, δ): 7.25 (s, Ar-*H*, 1H), 7.09-7.17 (m, Ar-*H*, 3H), 4.71 (q, C*H*, 1H), 2.50 (s, O*H*, 1H), 1.34 (d, C*H*$_3$, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 147.87 (Ar-*C*), 134.31 (Ar-*C*), 129.79 (Ar-*C*), 127.49 (Ar-*C*), 125.63 (Ar-*C*), 123.58 (Ar-*C*), 69.71 (*C*H), 25.18 (*C*H$_3$).

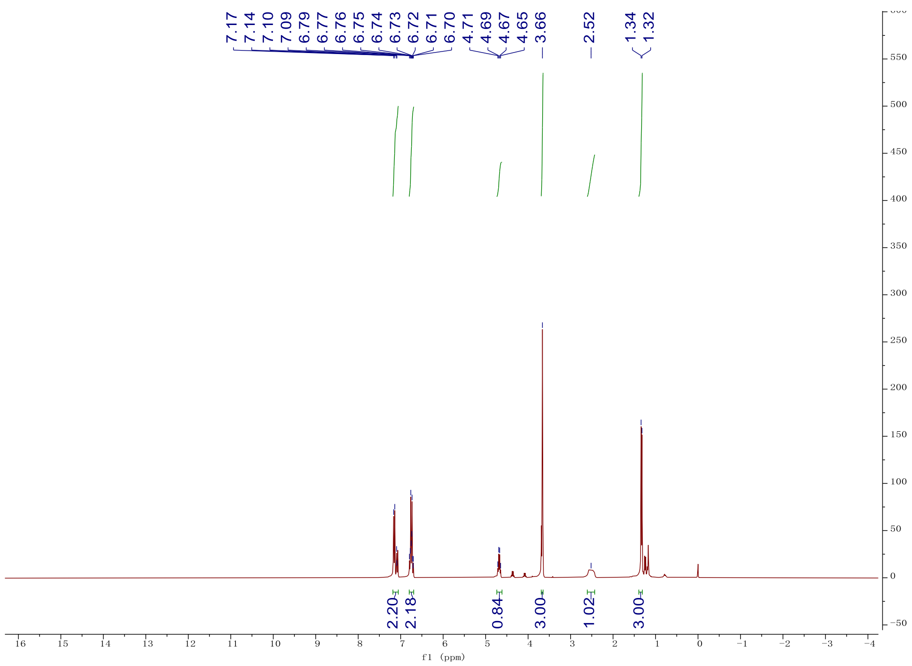


Figure S53. ^{1}H NMR spectrum of **1e** in $CDCl_3$

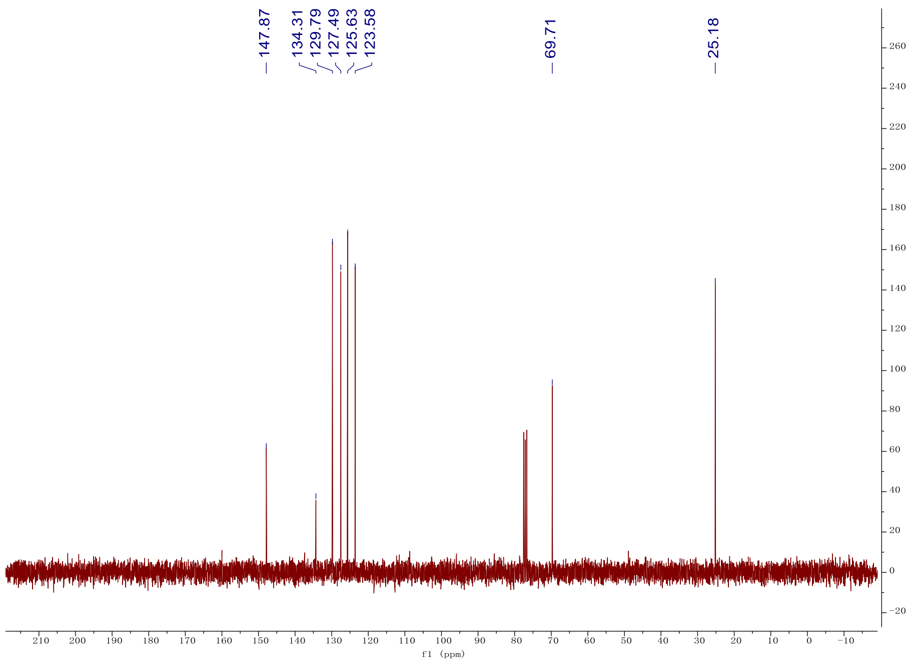
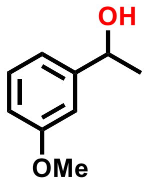


Figure S54. ^{13}C NMR spectrum of **1e** in $CDCl_3$



¹H NMR (300 MHz, $CDCl_3$, δ): 6.66-7.16 (m, Ar-*H*, 4H), 4.69 (q, C*H*, 1H), 3.67 (d, OCH_3, 3H), 2.61 (s, O*H*, 1H), 1.34 (d, CH_3, 3H). **¹³C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 159.68 (Ar-*C*), 147.73 (Ar-*C*), 129.49 (Ar-*C*), 117.76 (Ar-*C*), 112.79 (Ar-*C*), 110.93 (Ar-*C*), 70.16 (*C*H), 55.19 (O*C*H_3), 25.16 (*C*H_3).

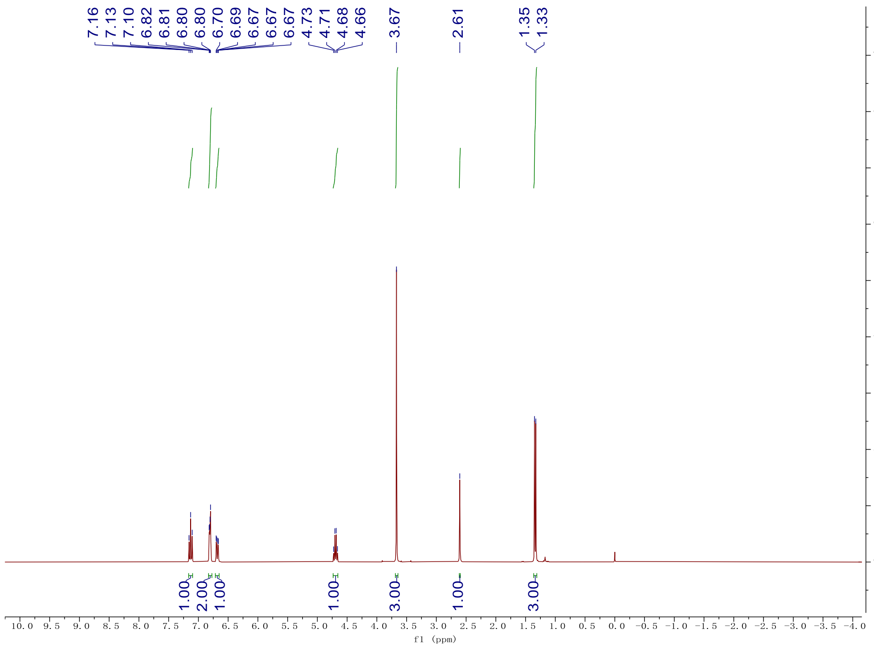


Figure S55. ^{1}H NMR spectrum of **1f** in $CDCl_3$

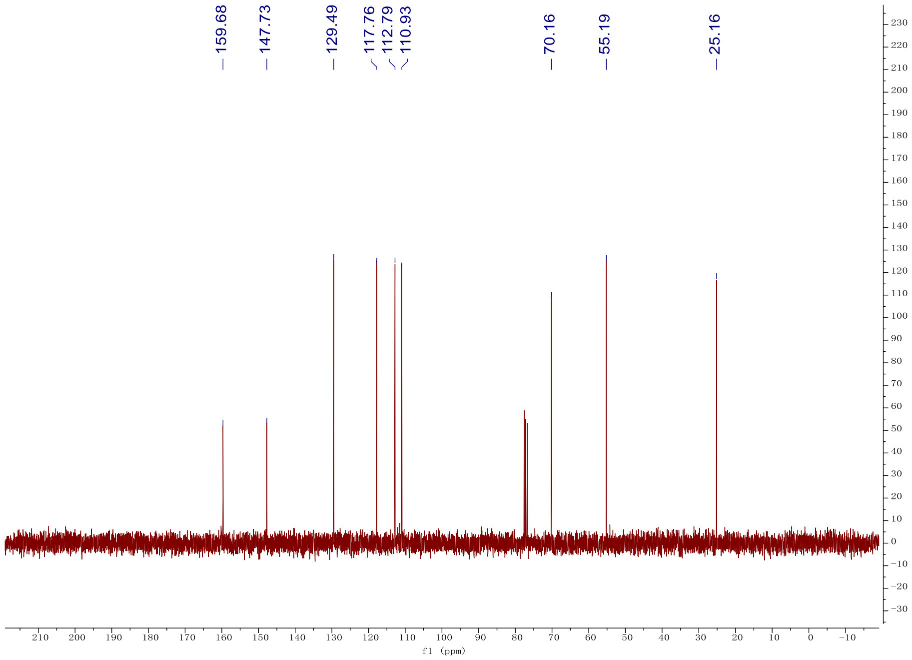
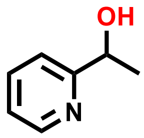


Figure S56. ^{13}C NMR spectrum of **1f** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.40 (d, Ar-*H*, 1H), 7.59 (td, Ar-*H*, 1H), 7.29 (d, Ar-*H*, 1H), 7.09 (m, Ar-*H*, 1H), 4.81 (q, C*H*, 1H), 4.24 (s, O*H*, 1H), 1.41 (d, C*H*$_3$, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 163.46 (Ar-*C*), 148.05 (Ar-*C*), 136.90 (Ar-*C*), 122.19 (Ar-*C*), 119.80 (Ar-*C*), 69.13 (*C*H), 24.15 (*C*H$_3$).

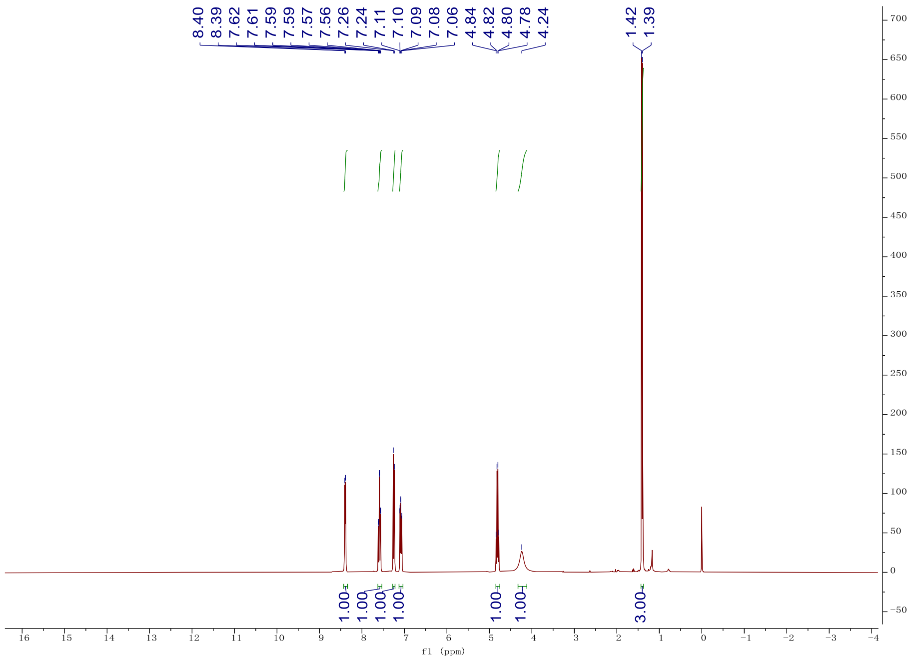


Figure S57. ^{1}H NMR spectrum of **1g** in $CDCl_3$

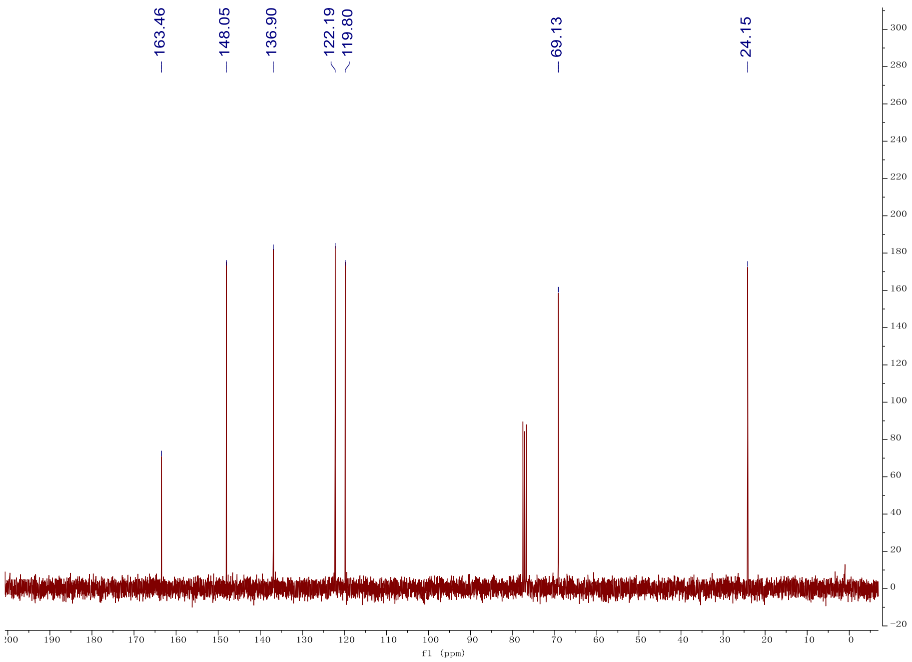
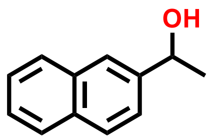


Figure S58. ^{13}C NMR spectrum of **1g** in $CDCl_3$



^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.69–7.72 (m, Ar-*H*, 3H), 7.67 (s, Ar-*H*, 1H) 7.35–7.38 (m, Ar-*H*, 3H), 4.91 (q, C*H*, 1H), 2.12 (s, O*H*, 1H), 1.45 (d, CH_3, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 143.26 (Ar-*C*), 133.37 (Ar-*C*), 132.96 (Ar-*C*), 128.36 (Ar-*C*), 128.01 (Ar-*C*), 127.75 (Ar-*C*), 126.21 (Ar-*C*), 125.86 (Ar-*C*),123.87 (Ar-*C*), 70.54 (*C*H), 25.20 (*C*H_3).

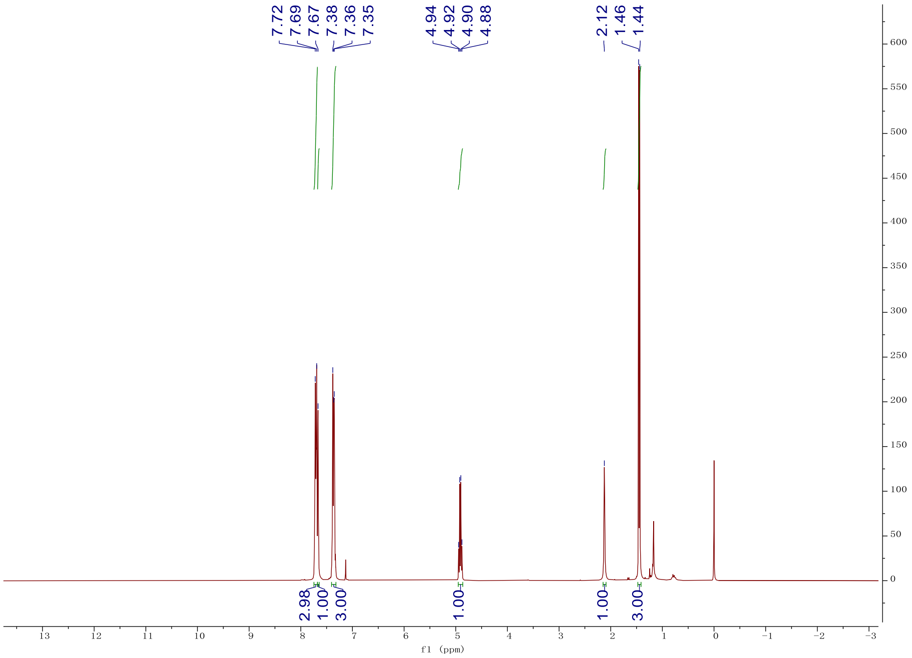


Figure S59. ^{1}H NMR spectrum of **1h** in $CDCl_3$

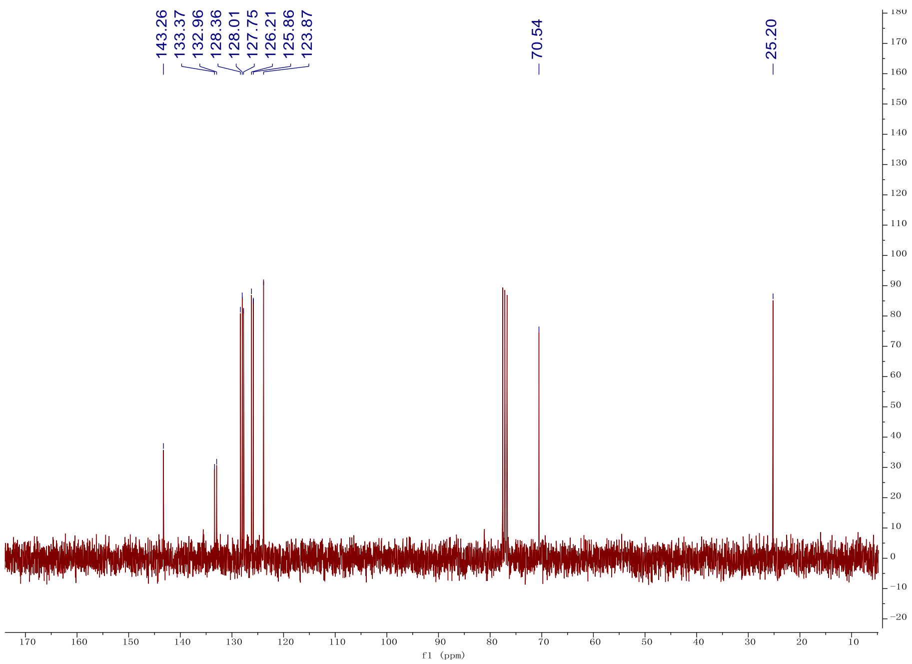


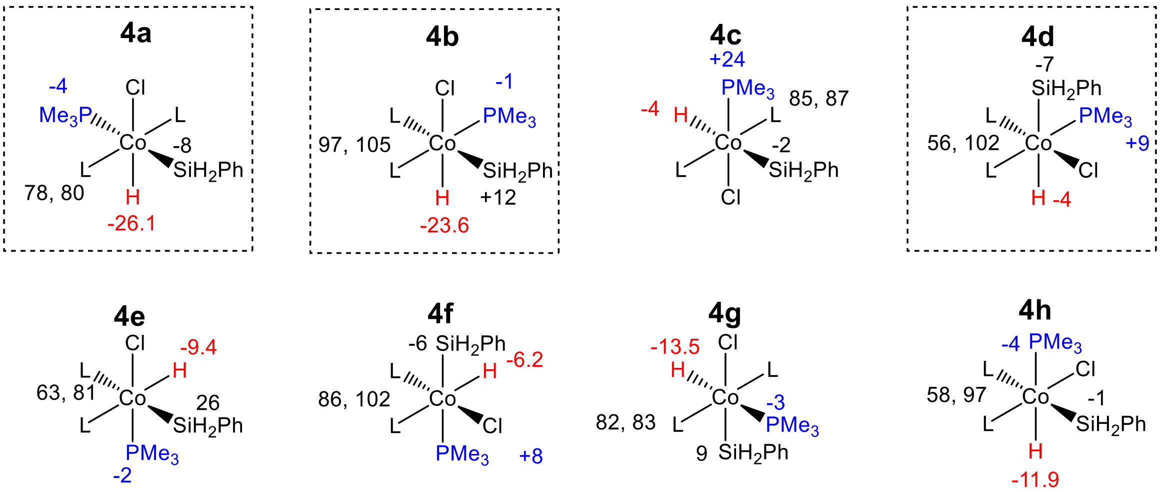
Figure S60. ^{13}C NMR spectrum of **1h** in $CDCl_3$

4. Computational Details

All computations were performed using Gaussian16[1] utilizing the PBE1PBE level of theory, Def2SVP basis sets and empirical dispersion correction (GD3). No solvent corrections were applied. All optimized molecular structures where checked to be minima on the energy hypersurface and possess no imaginary vibrational frequencies.

Table S2. Computed Data for 3 and Isomers of 4

Calcd.				unscaled		obsd.		
	H trans to	ΔG kJ/mol	^{1}H NMR ppm	ν(CoH) cm^{-1}	ν(SiH) cm^{-1}	^{1}H NMR ppm	ν(CoH) cm^{-1}	ν(SiH) cm^{-1}
3	PMe_3	––	-5.6	2063	2101, 2137	-12.30	1960	2032, 2052
4a – A	Cl	0.0	-26.1	2043	2163, 2172	-28.23	1959	2086
4b – B	Cl	17.0	-23.6	2043	2161, 2186	-26.75		
4c	SiH_2	58.2	-4.1	1890	2062, 2183			
4d – E	SiH_2	39.5	-3.5	1773	2107, 2177	-9.6		
4e	L	71.4	-9.4	1937	2077, 2156			
4f	L	49.4	-6.2	1994	2092, 2140			
4g	PMe_3	47.7	-13.5	2017	2123, 2145			
4h	PMe_3	43.2	-11.9	1975	2070, 2146			



Scheme S1 Isomers of complex **4**, assigned species highlighted.

Table S3. Catalysis cycle with 1 and benzaldehyde (S = singlet, T = triplet)

Calcd.	G a.u.	Calcd.	ΔG a.u.	ΔG kJ/mol
PMe_3	-460.540966	B(S) – [A(S) + $PhSiH_3$]	-0.040363	-106.0
$PhSiH_3$	-522.198598	[C(S) + PMe_3] – B(S)	0.045509	119.5
PhCHO	-344.846491	D1(S) – [C(S) + PhCHO]	-0.016913	-44.4
$PhCH_2OSiH_2Ph$	-867.078348	D2(S) – [C(S) + PhCHO]	-0.011702	-30.7
A (S)	-3223.981976	E(S) – D1(S)	-0.010490	-27.5
A (T)	-3224.028007	E(S) – D2(S)	-0.015701	-41.2
B (S)	-3746.220937	F1(S) – [E(S) + PMe_3]	-0.010047	-26.4
C (S)	-3285.634462	F2(S) – E(S)	0.008366	22.0
D1 (S)	-3630.497866	G(S) – F1(S)	0.000267	0.7
D2 (S)	-3630.492655	G(S) – [F2(S) + PMe_3]	0.018146	47.6
E (S)	-3630.492554	[A(S) + $PhCH_2OSiH_2Ph$] – G(S)	0.001222	3.2
F1 (S)	-4091.059369	B(S) – [A(T) + $PhSiH_3$]	0.005668	14.9
F2 (S)	-3630.499990	F2(T) – E(S)	-0.034767	-91.3
F2 (T)	-3630.543123	G(T) – F1(S)	-0.040589	-106.6
G (S)	-4091.059102	[A(T) + $PhCH_2OSiH_2Ph$] – G(T)	-0.006397	-16.8
G (T)	-4091.099958	G(T) – [F2(T)+PMe_3]	-0.015869	-41.7
		A(T) – A(S)	-0.046031	-120.9
		F2(T) – F2(S)	-0.043133	-113.2
		G(T) – G(S)	-0.040856	-107.3

5. The mechanism study for hydrosilylation of benzaldehyde catalyzed by complex 2

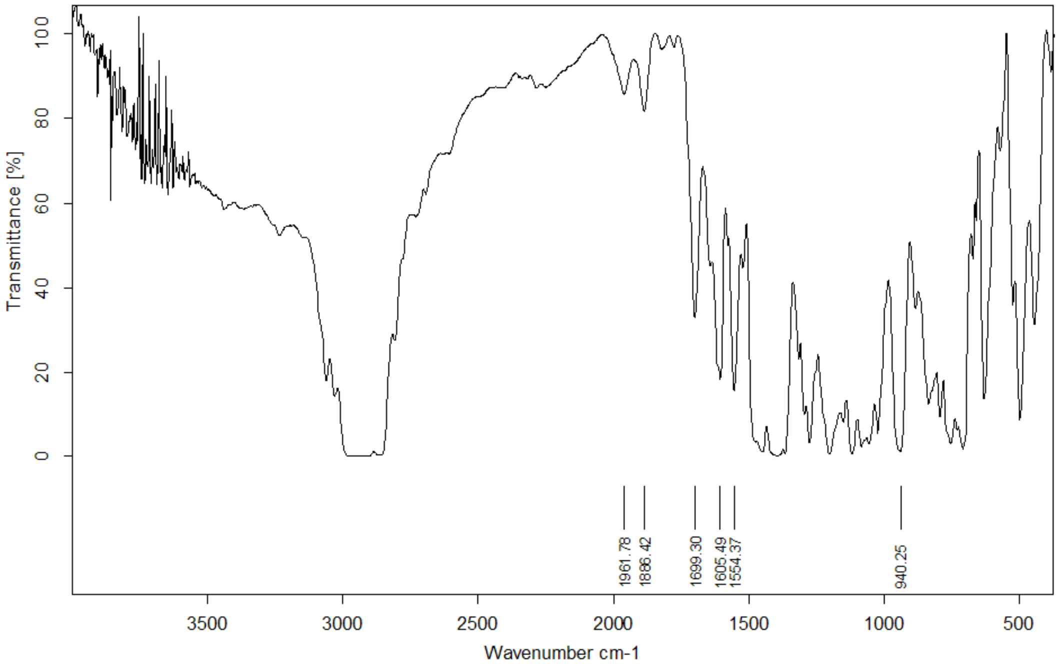


Figure S61. IR spectrum of reaction solution of **2** and benzaldehyde at 40°C for 3 min.

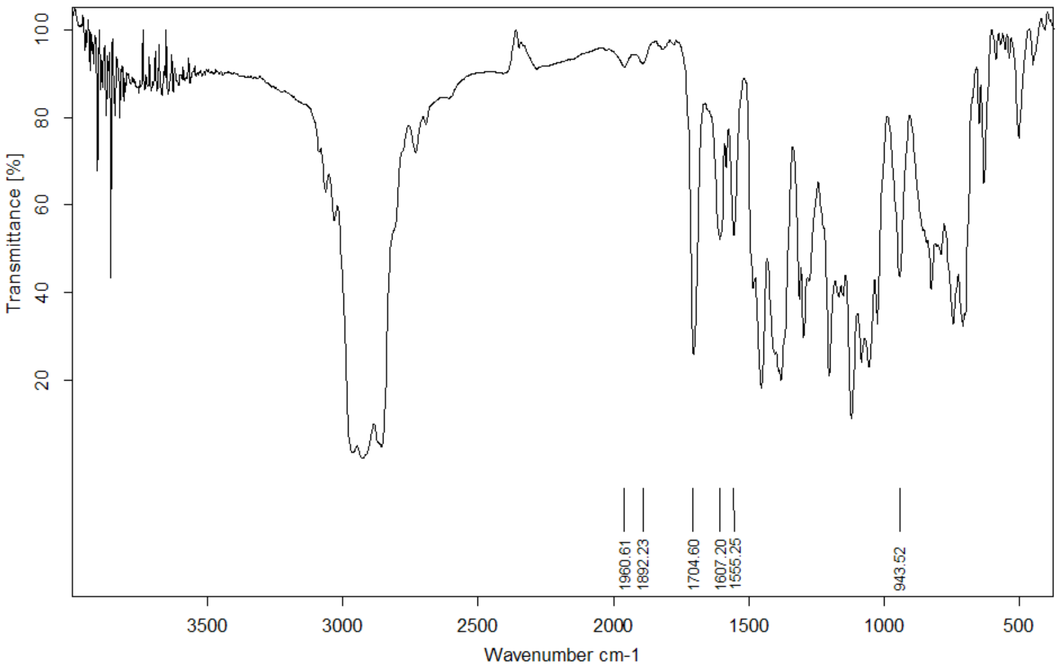


Figure S62. IR spectrum of reaction solution of **2** and benzaldehyde at 40°C for 3 min, then addition of benzaldehyde at 40°C for 15 min.

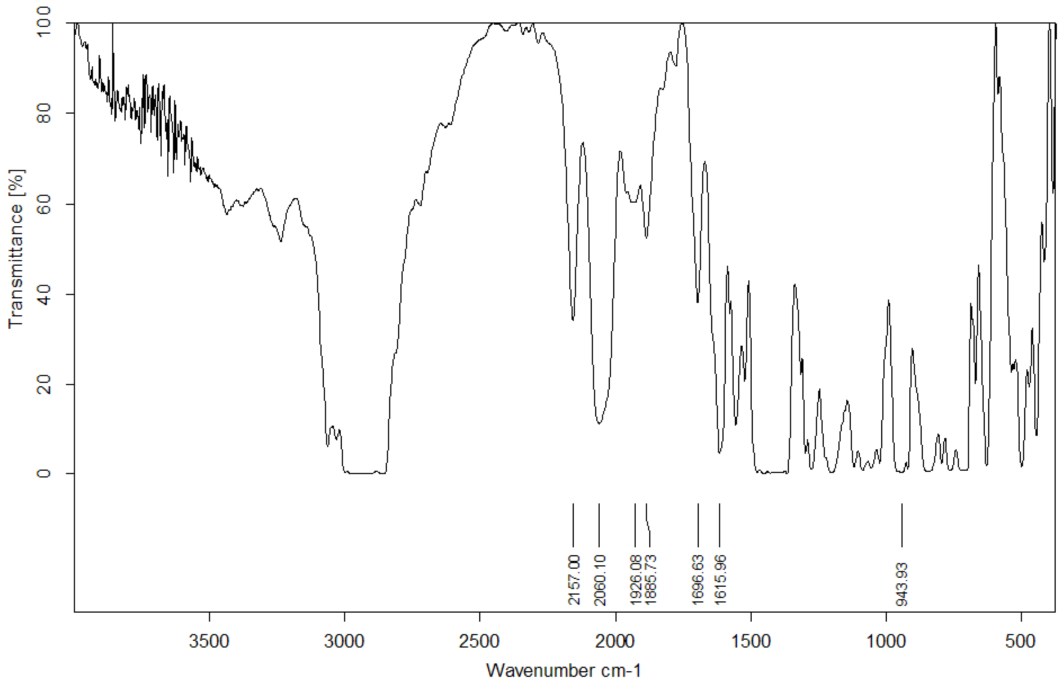


Figure S63. IR spectrum of reaction solution of **2** and benzaldehyde at 40°C for 3 min, then addition of benzaldehyde at 40°C for 15 min, then addition of $PhSiH_3$ at 40°C for 1h.

6. References

1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., *Gaussian16, Revision B.01*, **2016**.