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Supporting Information

Pyridine N-oxide promoted hydrosilylation of carbonyl compounds catalyzed by [PSiP]-pincer iron hydrides

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1. **Table S1.** Crystallographic Data for Complex **3**

complex	**3**
Empirical formula	$C_{48}H_{52}FeP_4Si$
Formula weight	836.71
Temperature/K	180.0
Crystal system	orthorhombic
Space group	Pnma
a/Å	18.4493(2)
b/Å	21.2072(2)
c/Å	10.7787(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4217.25(13)
Z	4
ρ_{calc}g/cm^3	1.318
μ/mm^{-1}	3.197
F(000)	1760.0
Crystal size/mm^3	0.35 × 0.34 × 0.33
Radiation	GaKα (λ = 1.34143)
2Θ range for data collection/°	8.266 to 124.994
Index ranges	$-24 \leq h \leq 8$, $-27 \leq k \leq 28$, $-14 \leq l \leq 13$
Reflections collected	22903
Independent reflections	5184 [R_{int} = 0.0189, R_{sigma} = 0.0144]
Data/restraints/parameters	5184/0/267
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0282, wR_2 = 0.0764
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.0789
Largest diff. peak/hole / e Å^{-3}	0.30/-0.34

2. IR, ^{1}H, ^{31}P, and ^{13}C NMR spectra of complex **3**

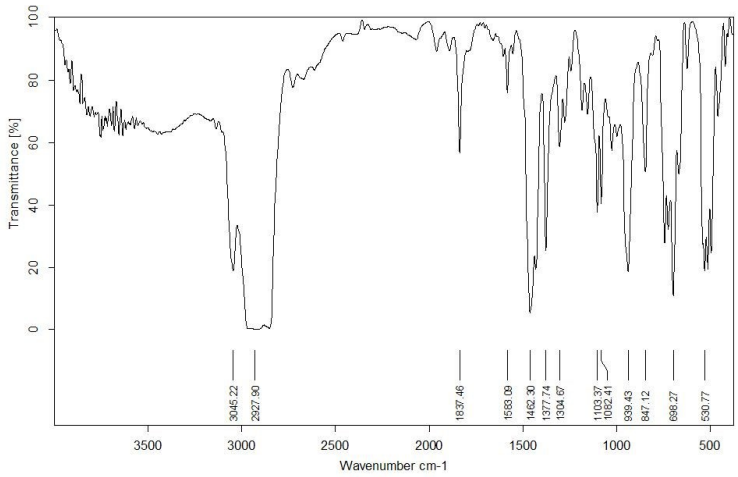


Fig.S1 IR spectrum of complex **3**

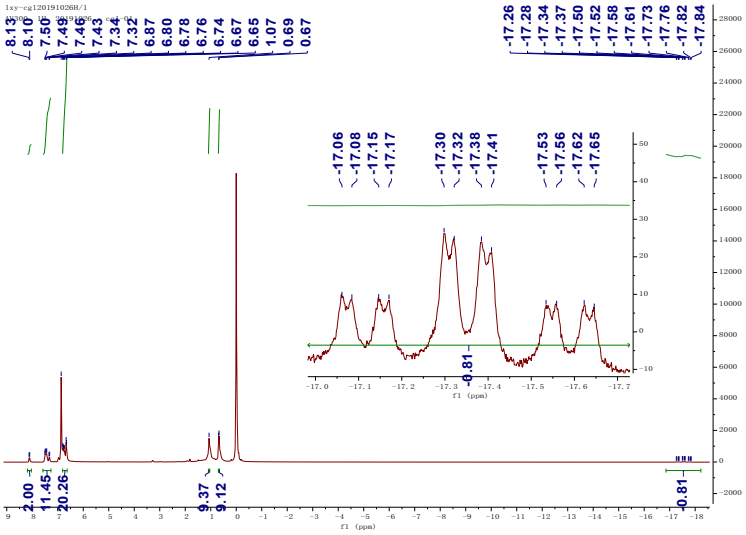


Fig.S2 ^{1}H NMR spectrum of complex **3**

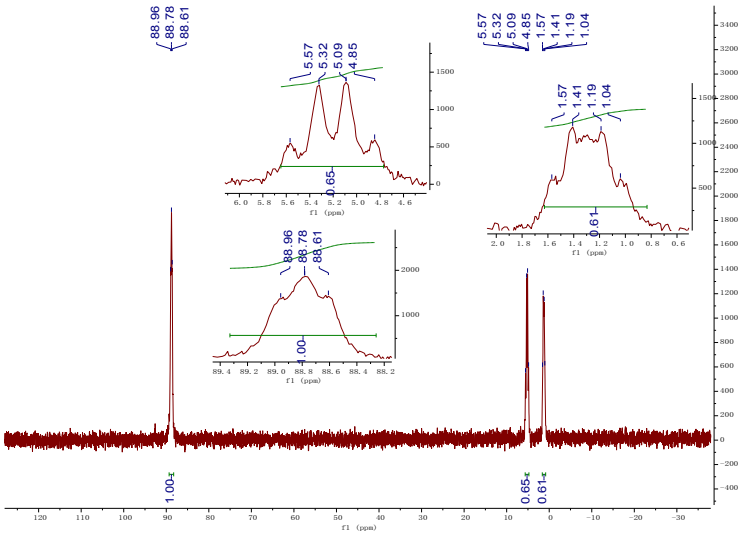


Fig.S3 ^{31}P NMR spectrum of complex **3**

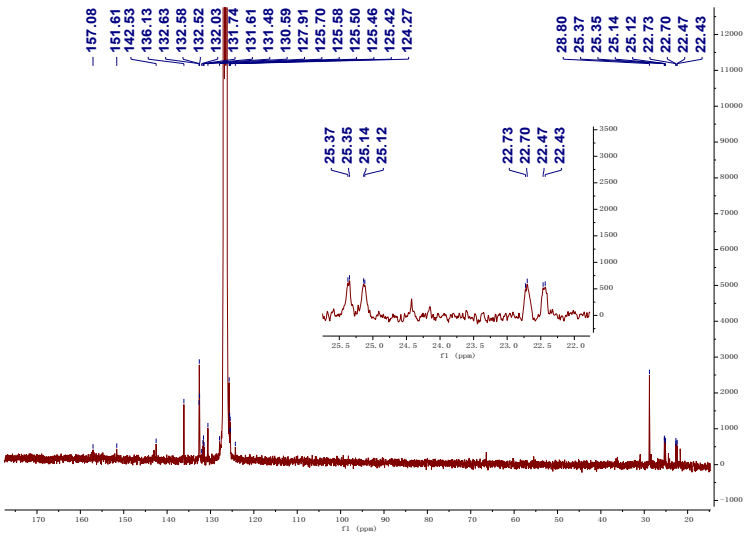
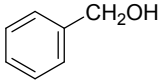


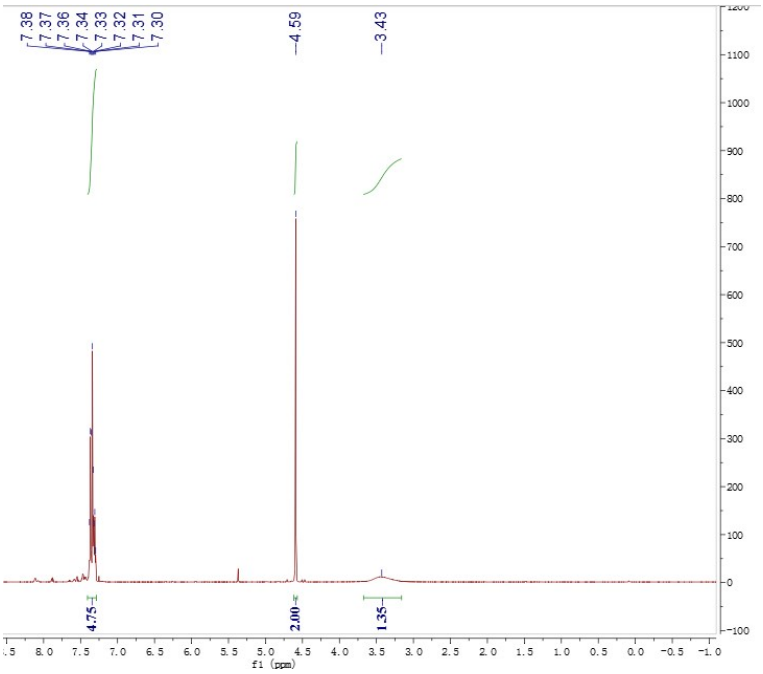
Fig.S4 ^{13}C NMR spectrum of complex **3**

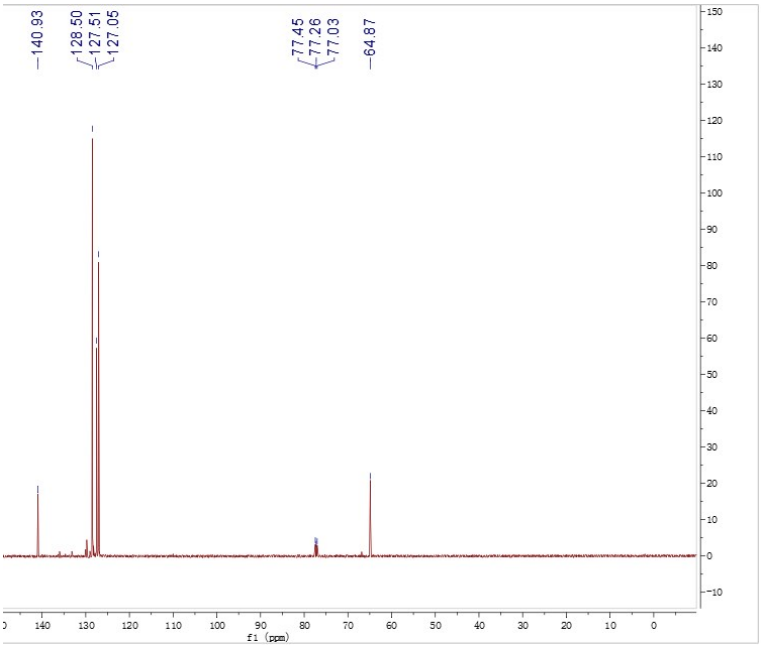
(note: the signal at 28.80 ppm belongs to high vacuum fat)

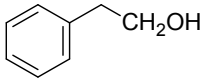
3. ^{1}H and ^{13}C NMR data for the alcohol products.



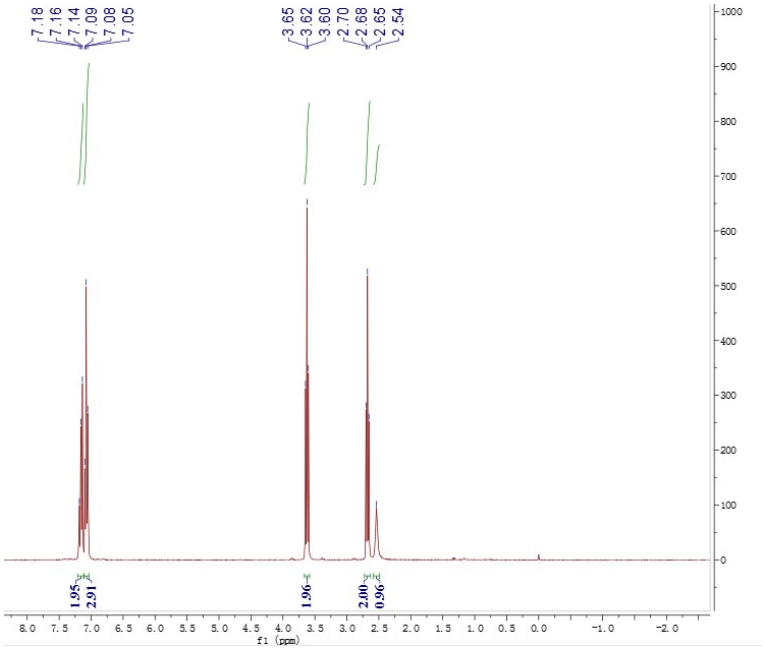
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.30-7.38(m, Ar-*H*, 5H), 4.59(s, C*H*$_2$, 2H), 3.43(s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 140.93(Ar-*C*), 128.50(Ar-*C*), 127.51(Ar-*C*), 127.05(Ar-*C*), 64.87 (*C*H$_2$).

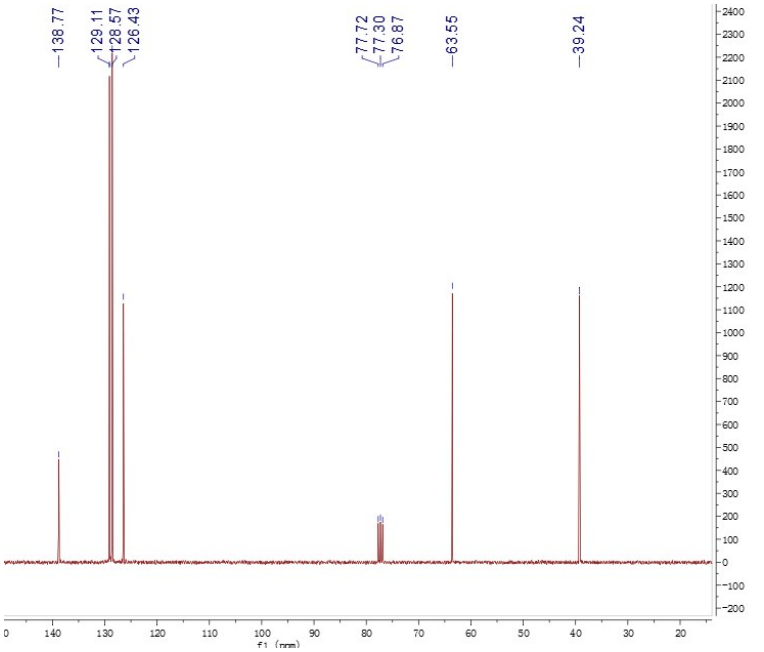


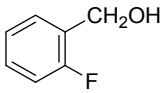




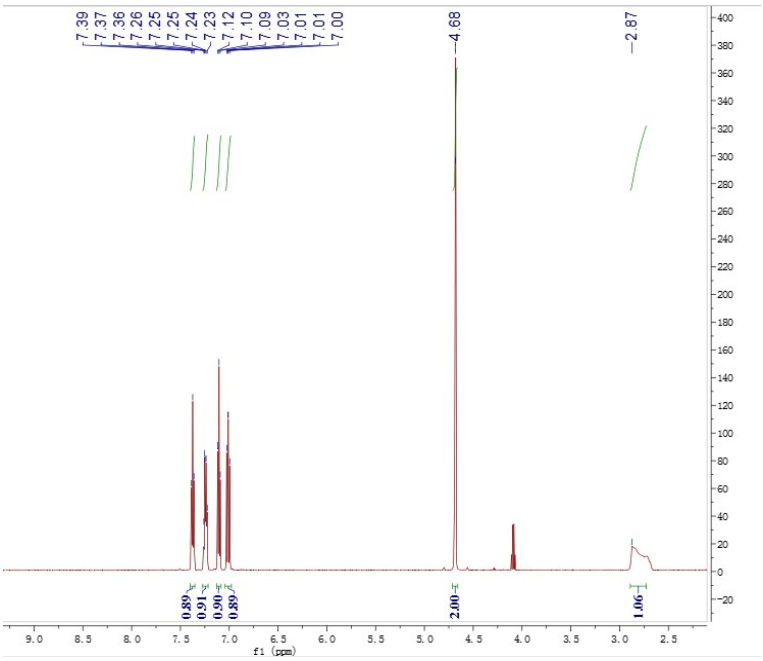
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.05-7.18 (m, Ar-*H*, 5H), 3.62 (t, *J* = 6 Hz, C*H*$_2$, 2H), 2.54 (s, O*H*, 1H) ,2.68 (t, C*H*$_2$, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 138.77(Ar-*C*), 129.11(Ar-*C*), 128.57(Ar-*C*), 126.43 (Ar-*C*), 63.55 (*C*H$_2$), 39.24 (*C*H$_2$).

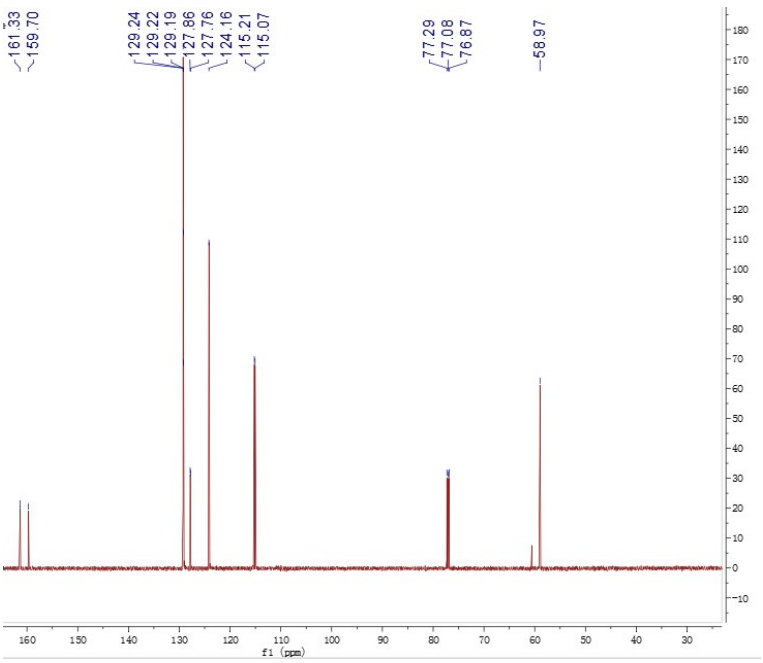


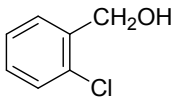




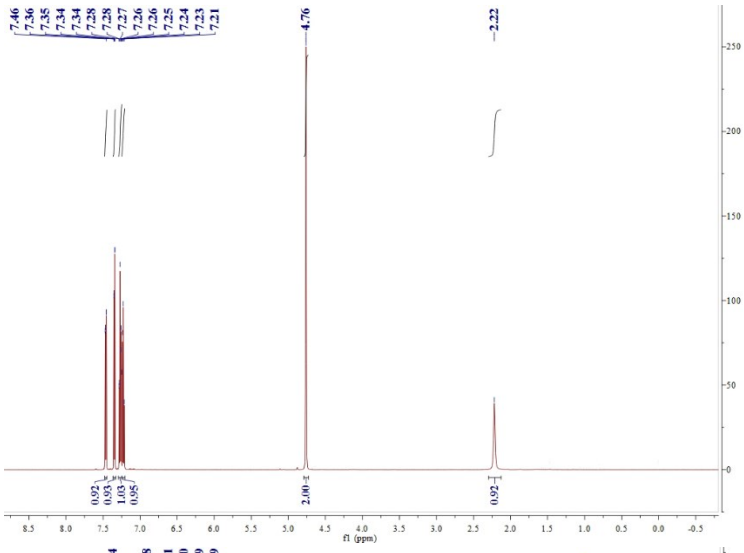
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.38 (td, J = 7.6, 1.8 Hz, Ar-*H*, 1H), 7.27–7.21 (m, Ar-*H*, 1H), 7.11 (td, J = 7.5, 1.1 Hz, Ar-*H*, 1H), 7.01 (ddd, J = 9.6, 8.2, 1.1 Hz, Ar-*H*, 1H), 4.68 (s, CH_2, 2H), 2.87 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 161.33 (s, Ar-*C*), 159.70 (s, Ar-*C*), 129.22(t, J = 3.1 Hz, Ar-*C*), 127.76(d, J = 12.5 Hz, Ar-*C*), 124.16 (s, Ar-*C*), 115.14(d, J = 17.5 Hz, Ar-*C*), 58.97 (CH_2).

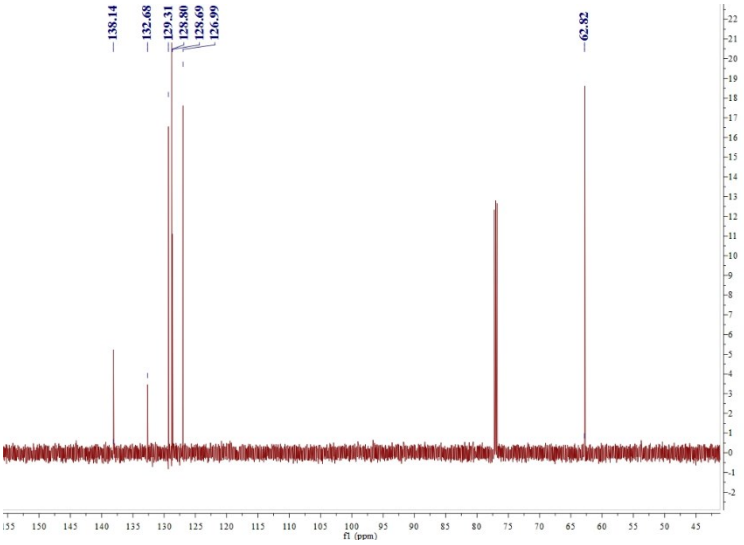


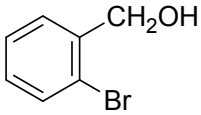




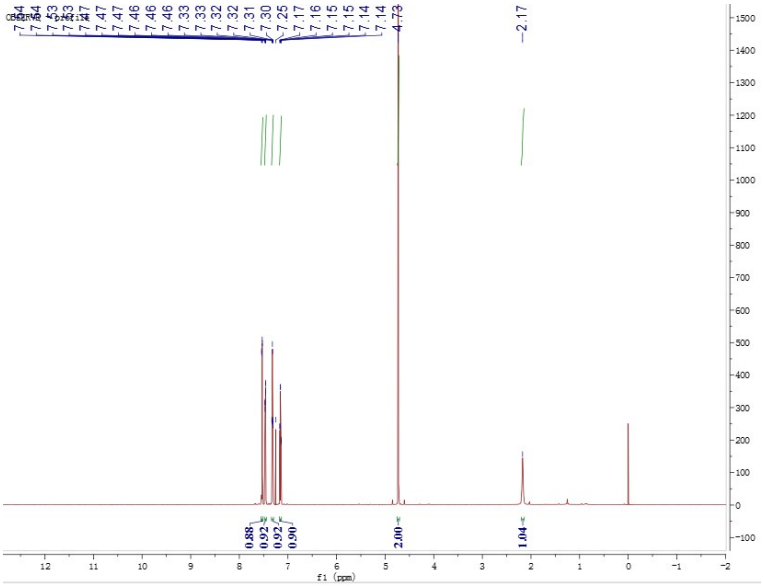
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.46 (dd, J = 7.5, 1.7 Hz, Ar-*H*, 1H), 7.35 (dd, J = 7.8, 1.4 Hz, Ar-*H*, 1H), 7.27 (td, J = 7.5, 1.4 Hz, 1H), 7.23 (td, J = 7.6, 1.8 Hz, 1H), 4.76 (s, CH_2, 2H), 2.22 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 138.14(Ar-*C*), 132.68(Ar-*C*), 129.31(Ar-*C*), 128.80(Ar-*C*), 128.69(Ar-*C*), 126.99 (Ar-*C*), 62.82 (CH_2).

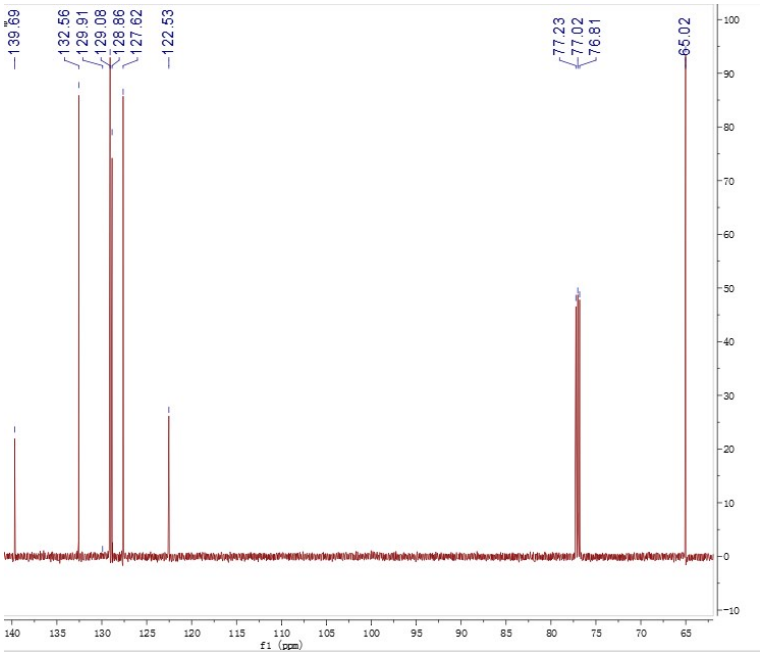


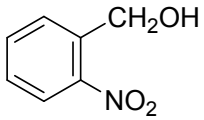




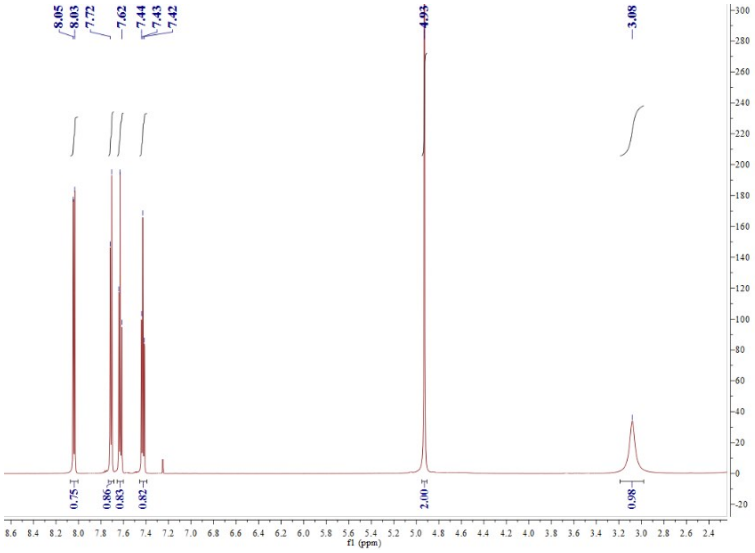
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.53 (dd, J = 8.0, 1.2 Hz, Ar-*H*, 1H), 7.46 (dd, J = 7.6, 1.7 Hz, Ar-*H*, 1H), 7.32 (td, J = 7.5, 1.2 Hz, Ar-*H*, 1H), 7.15 (td, J = 7.7, 1.8 Hz, Ar-*H*, 1H), 4.73 (s, CH_2, 2H), 2.17 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 139.69(Ar-*C*), 132.56(Ar-*C*), 129.91(Ar-*C*), 129.08(Ar-*C*), 128.86(Ar-*C*), 127.62(Ar-*C*), 122.53 (Ar-*C*), 65.02 (CH_2).

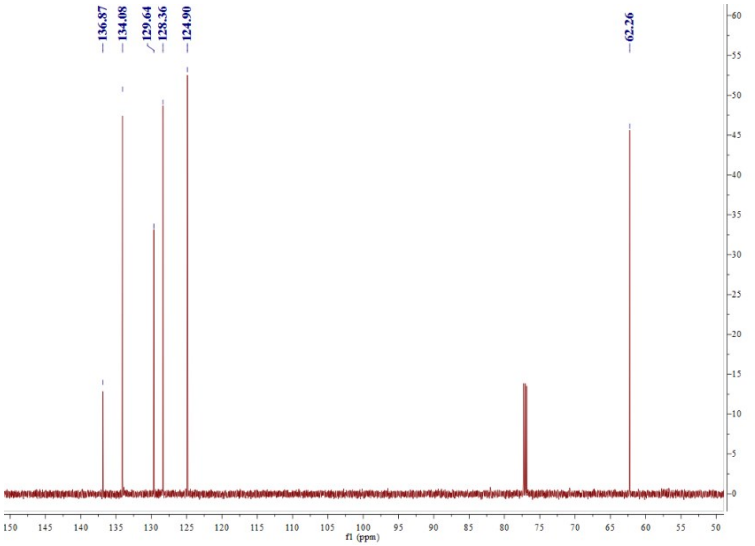


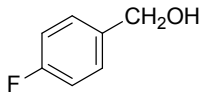




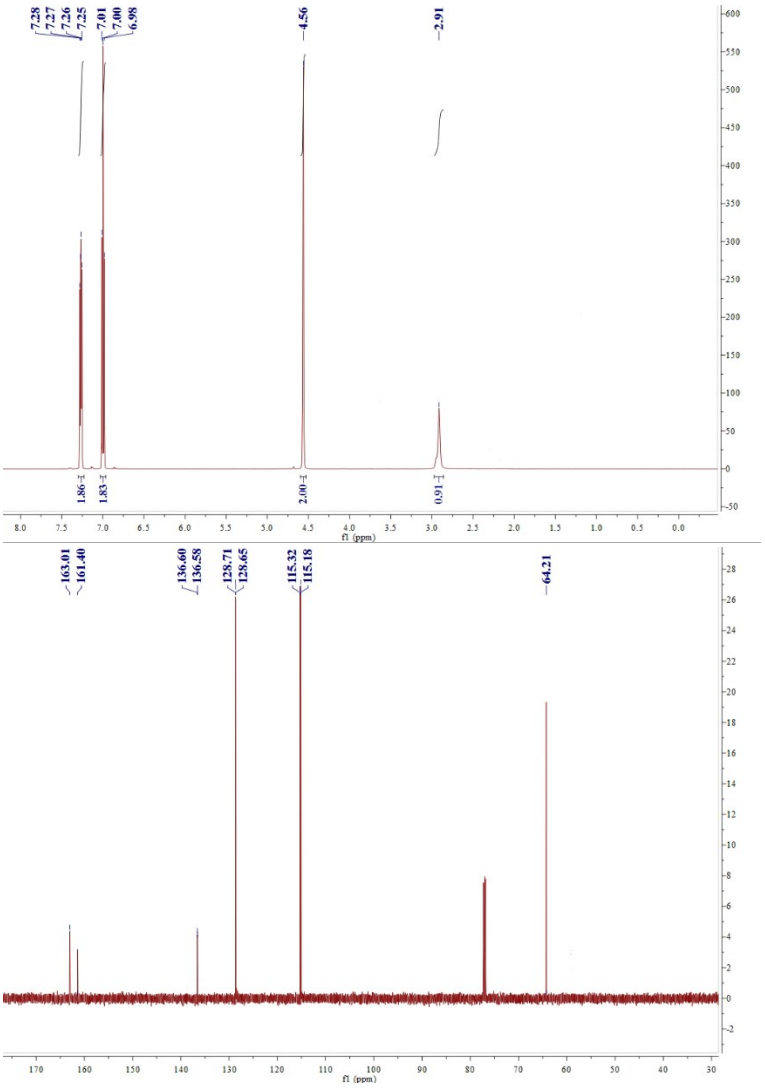
^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.04 (dd, J = 8.2, 1.3 Hz, Ar-*H*, 1H), 7.71 (d, J = 7.7 Hz, Ar-*H*, 1H), 7.63 (td, J = 7.6, 1.3 Hz, Ar-*H*, 1H), 7.46–7.40 (m, Ar-*H*, 1H), 4.93 (s, CH_2, 2H), 3.08 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 139.87(Ar-*C*), 134.08(Ar-*C*), 129.64(Ar-*C*), 128.36(Ar-*C*), 124.90 (Ar-*C*), 62.26 (CH_2).

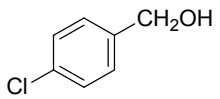




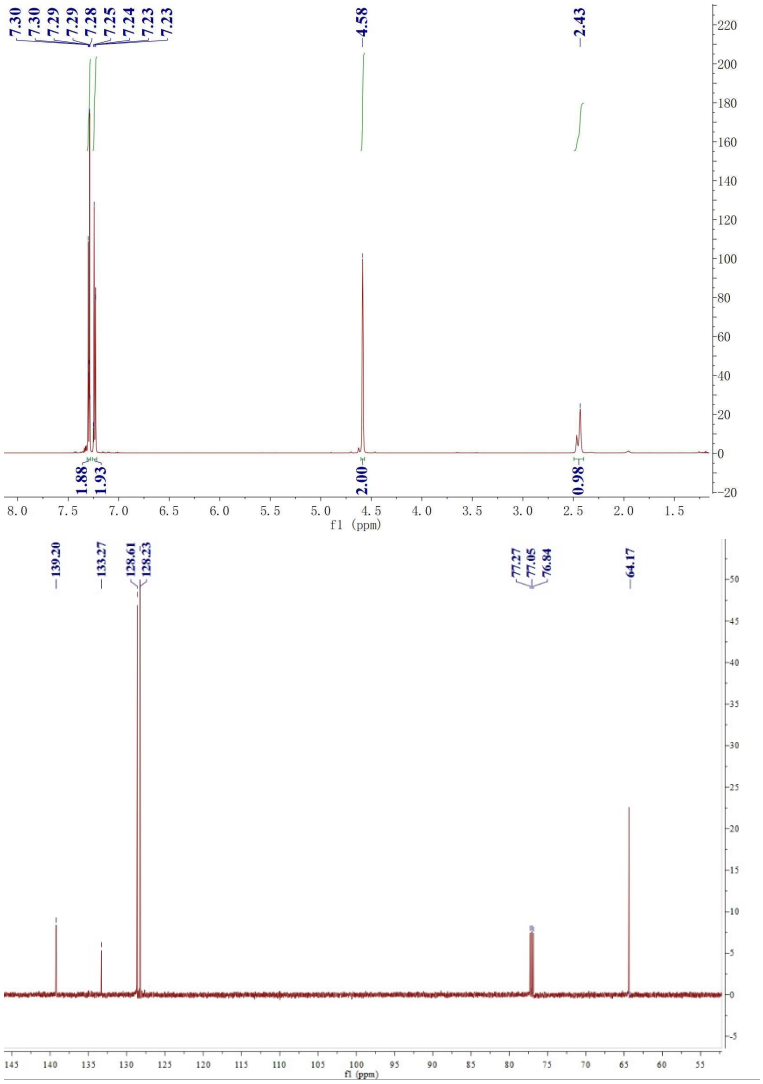


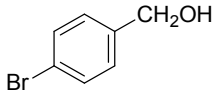
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.27 (dd, J = 8.4, 5.7 Hz, Ar-*H*, 2H), 7.00 (t, J = 8.6 Hz, Ar-*H*, 2H), 4.56 (s, CH_2, 2H), 2.91 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 163.01 (s, Ar-*C*), 161.40 (s, Ar-*C*), 136.59(d, J = 2.5 Hz, Ar-*C*), 128.68 (d, J = 7.7 Hz, Ar-*C*), 115.25(d, J = 17.5 Hz, Ar-*C*), 64.21 (CH_2).



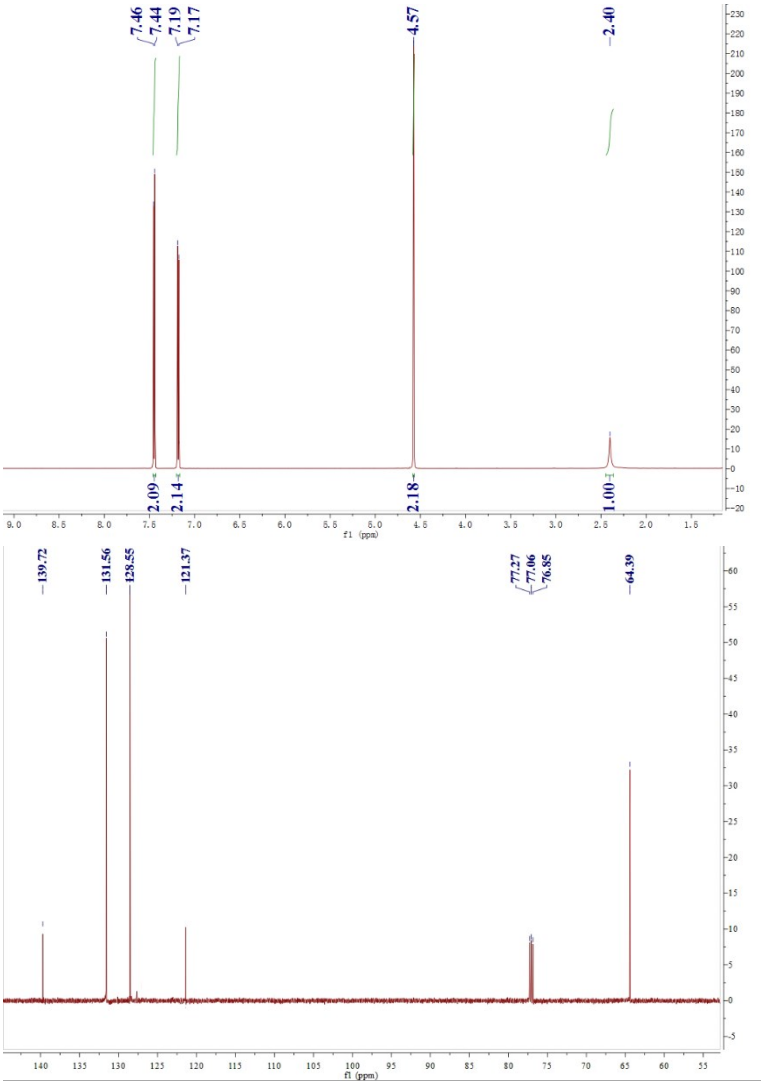


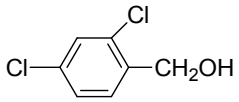
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.23-7.30 (m, Ar-*H*, 4H), 4.58 (s, CH_2, 2H), 2.43 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 139.20(s, Ar-*C*), 133.27(s, Ar-*C*), 128.61 (s, Ar-*C*), 128.23(s, Ar-*C*), 64.17(CH_2).



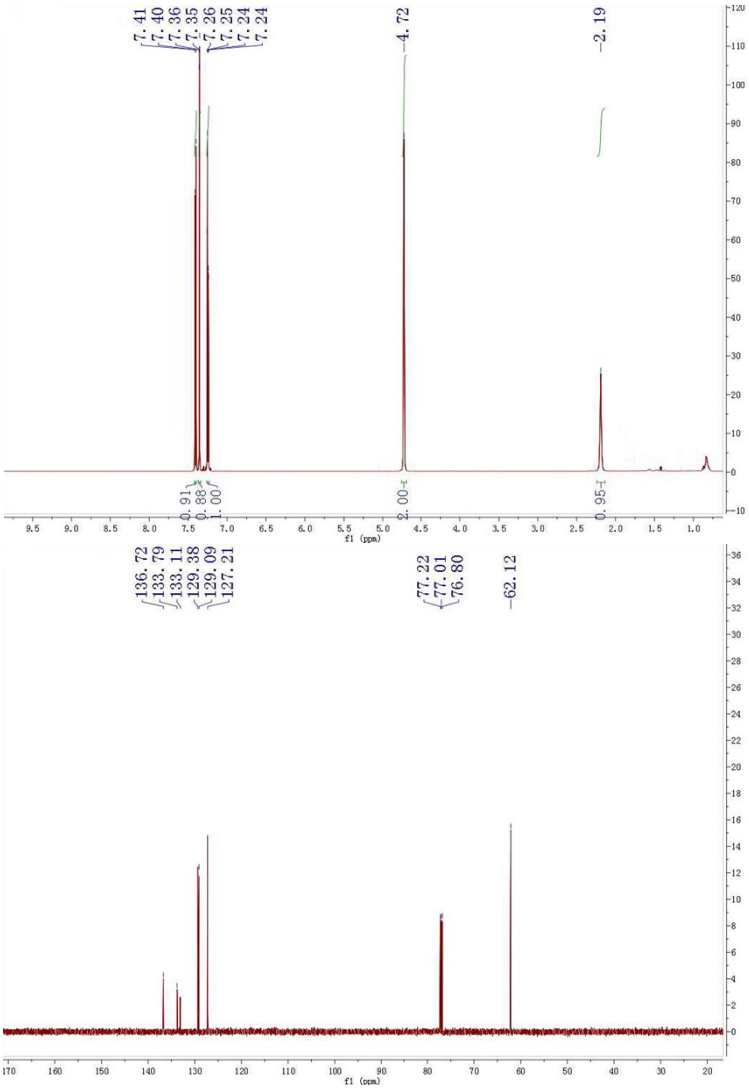


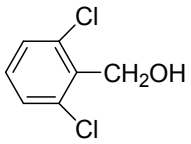
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.46(d, J = 6.0 Hz, Ar-H, 2H), 7.17 (d, J = 6.0 Hz, Ar-H, 2H), 4.57 (s, CH_2, 2H), 2.40 (s, OH, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 139.72(s, Ar-C), 131.56(s, Ar-C), 128.55 (s, Ar-C), 121.37 (s, Ar-C), 64.39 (CH$_2$).



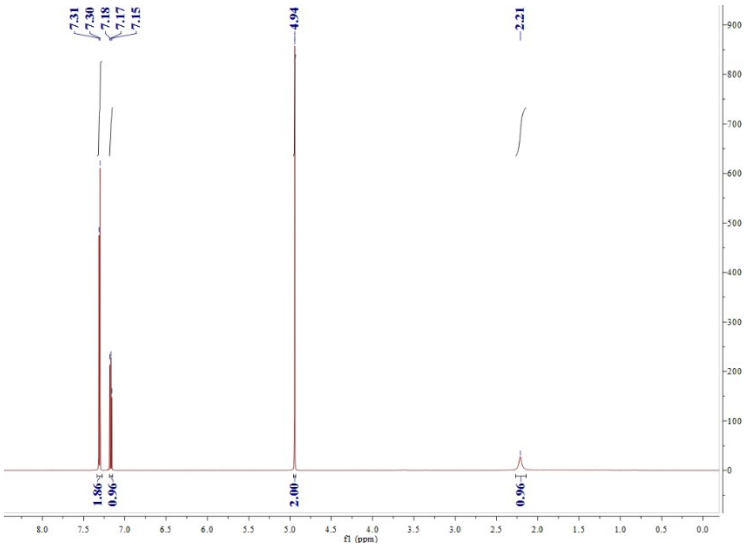


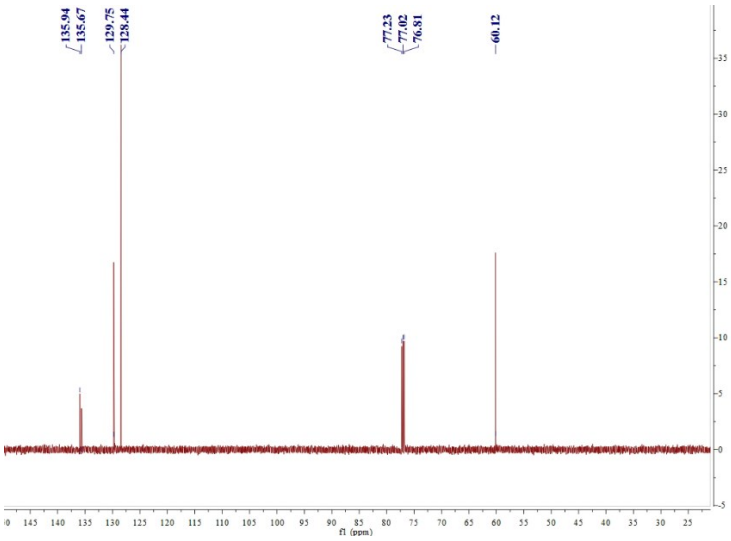
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.41 (d, J = 8.2 Hz, Ar-*H*, 1H), 7.36 (d, J = 2.1 Hz, Ar-*H*, 1H), 7.25 (dd, J = 8.3, 2.1 Hz, Ar-*H*, 1H), 4.72 (s, CH_2, 2H), 2.19 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 136.72 (Ar-*C*), 133.79 (Ar-*C*), 133.11 (Ar-*C*), 129.38 (Ar-*C*), 129.09 (Ar-*C*), 127.21 (Ar-*C*), 62.12 (CH_2).

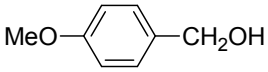




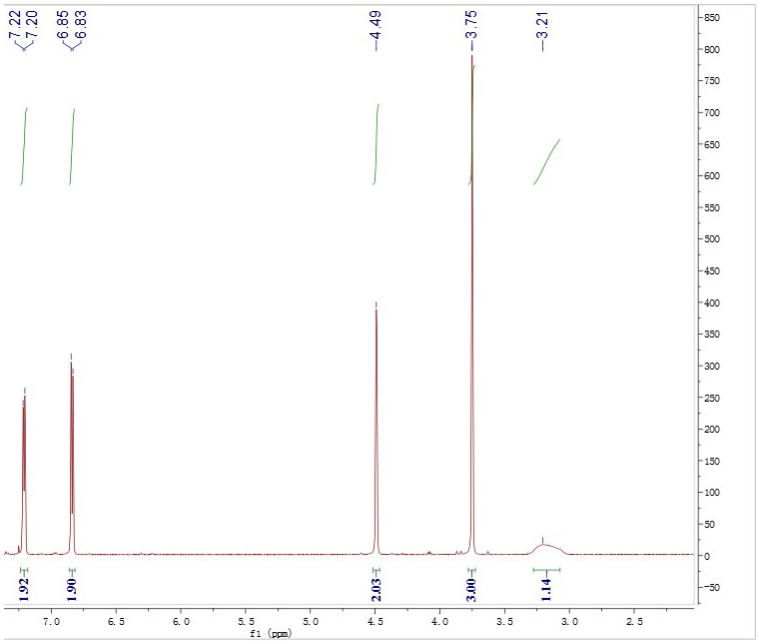
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.31 (d, J = 8.1 Hz, Ar-*H*, 2H), 7.17 (dd, J = 8.4, 7.7 Hz, Ar-*H*, 1H), 4.94 (s, CH_2, 2H), 2.21 (s, O*H*, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 135.94 (Ar-*C*), 135.67 (Ar-*C*), 129.75 (Ar-*C*)，128.44 (Ar-*C*), 60.12 (CH_2).

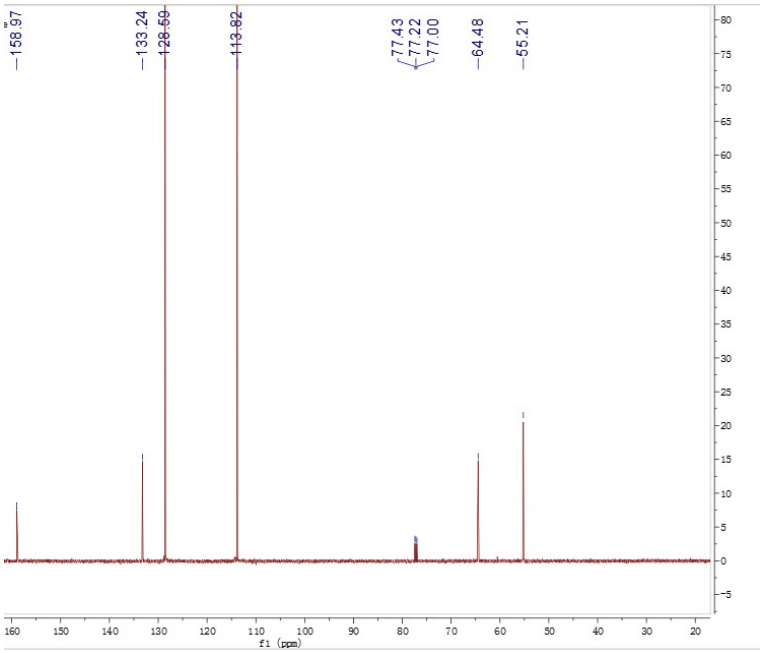


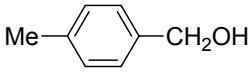




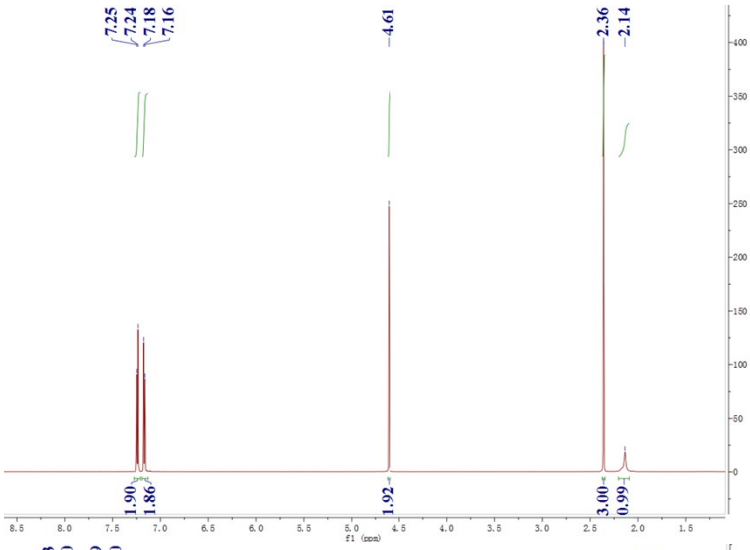
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.21 (d, J = 6 Hz, Ar-H, 2H), 6.84 (d, J = 6 Hz, Ar-H, 2H), 4.49 (s, CH_2, 2H), 3.75 (s, OCH_3, 3H), 3.21 (s, OH, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 158.97 (Ar-C), 133.24 (Ar-C), 128.59 (Ar-C), 113.82 (Ar-C), 64.48 (CH$_2$), 55.21 (OCH$_3$).

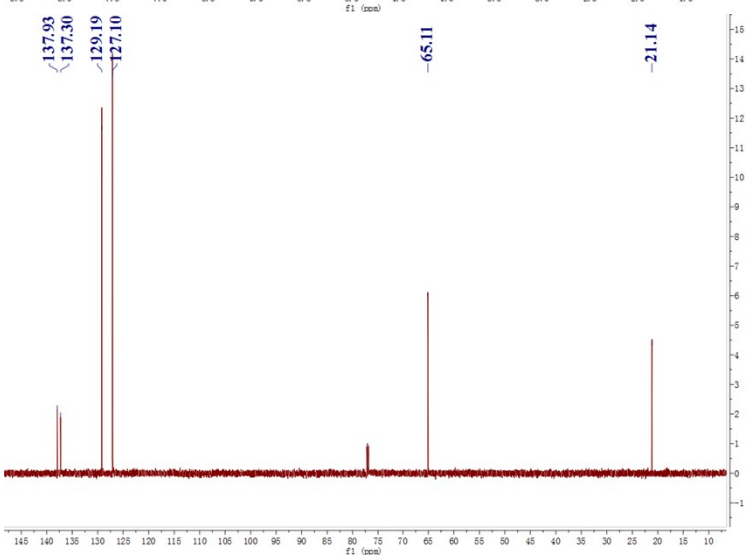


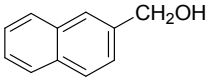




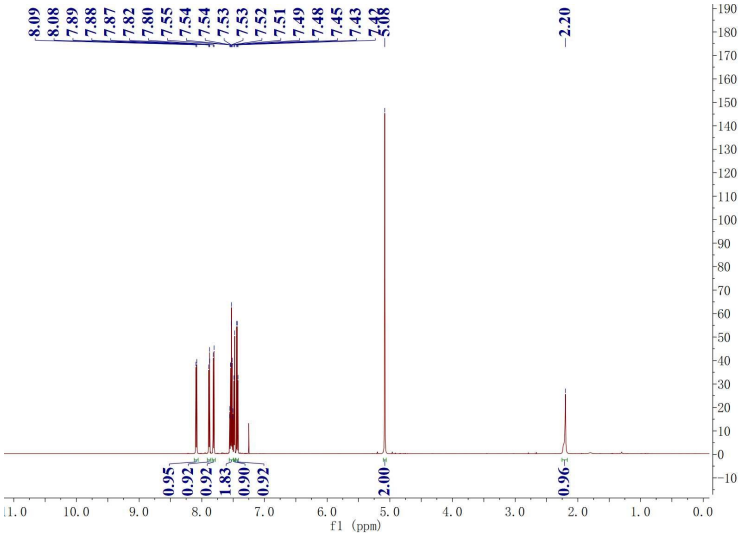
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.24 (d, J = 3 Hz, Ar-H, 2H), 7.17 (d, J = 6 Hz, Ar-H, 2H) 4.61 (s, CH_2, 2H), 2.36 (s, CH_3, 3H), 2.14 (s, OH, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$, 298K, ppm): 137.93 (Ar-C),137.30 (Ar-C), 129.19 (Ar-C), 127.10 (Ar-C), 65.11 (CH$_2$), 21.14 (CH$_3$).

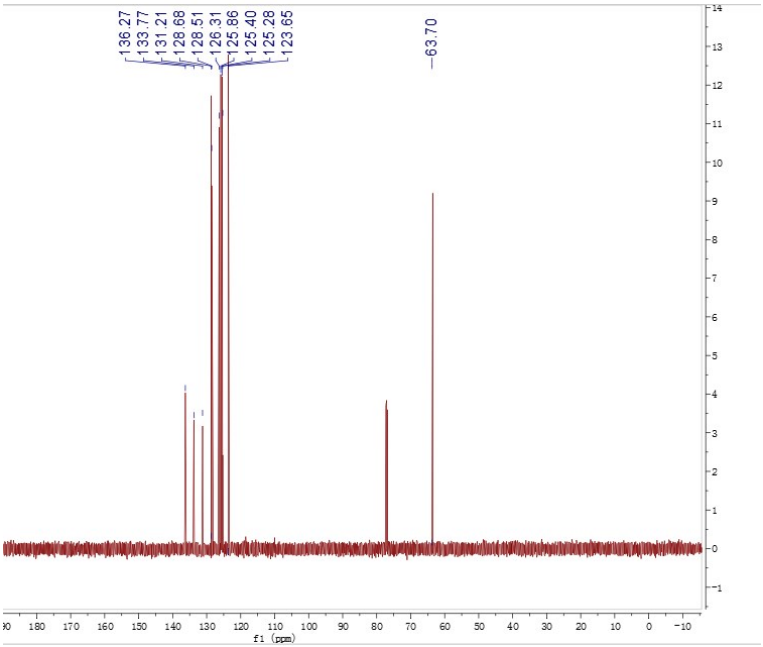


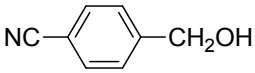




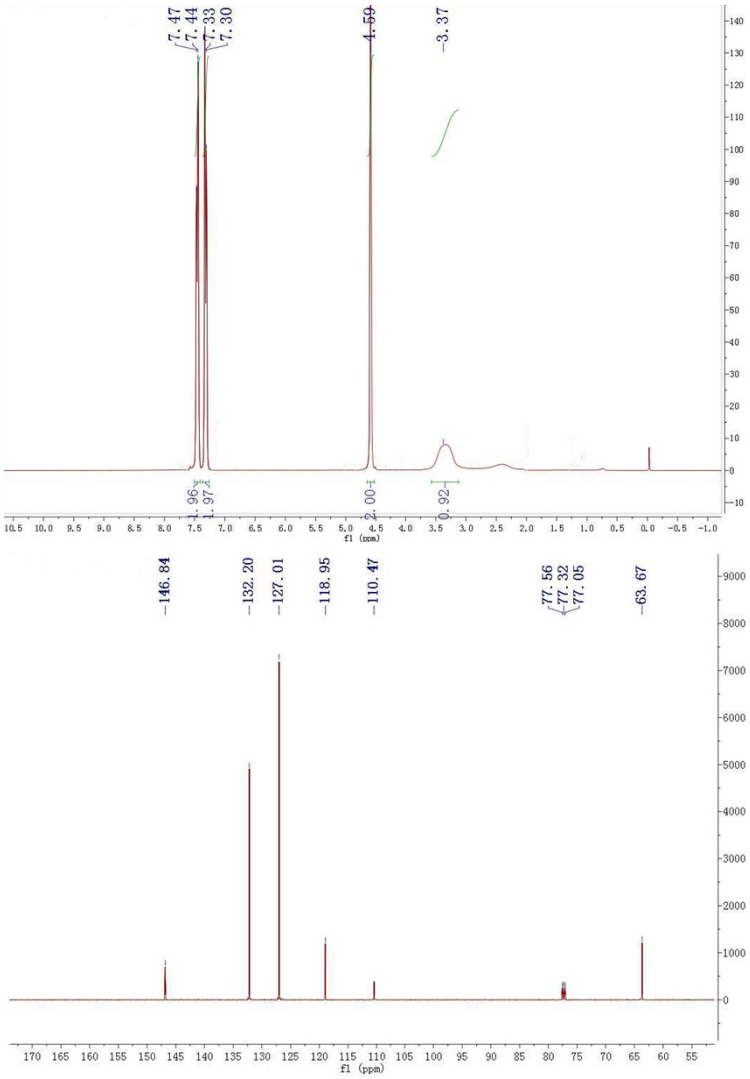
^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.09 (d, J = 8.1 Hz, Ar-H,1H), 7.81 (d, J = 8.1 Hz, Ar-H, 1H), 7.56-7.50 (m, Ar-H, 2H), 7.48 (d, J = 6.9 Hz, Ar-H, 1H), 7.43 (t, J = 6.0 Hz Ar-H, 1H), 5.08 (s, CH_2, 2H), 2.20 (s, OH, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 136.27 (Ar-C), 133.77 (Ar-C), 131.21 (Ar-C), 128.68 (Ar-C), 128.51 (Ar-C), 126.31 (Ar-C), 125.86 (Ar-C), 125.40 (Ar-C), 125.28 (Ar-C), 123.65 (Ar-C), 63.70 (CH$_2$).

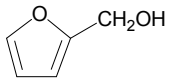




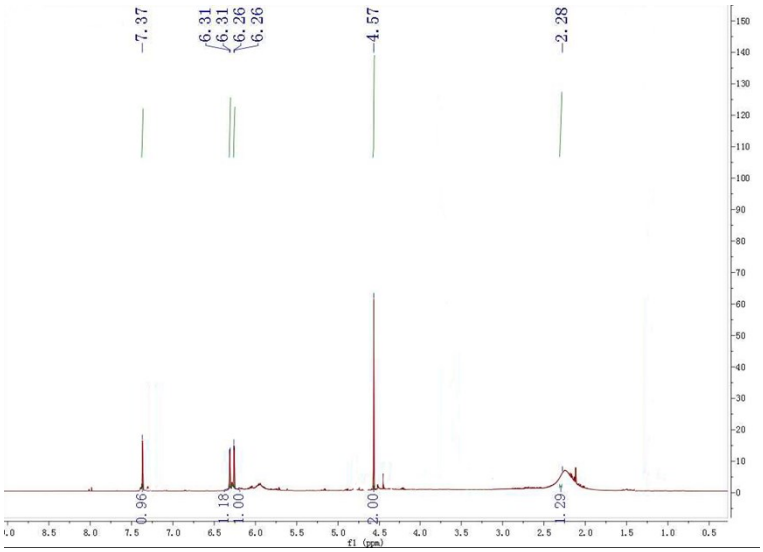


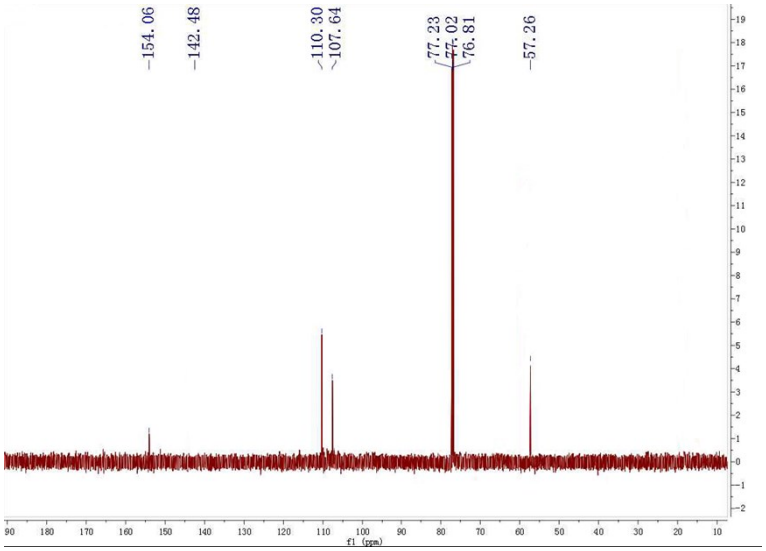
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.44-7.47 (d, *J* = 9 Hz, Ar-*H*, 2H), 7.30-7.33 (d, *J* = 9 Hz, Ar-*H*, 2H), 4.59 (t, C*H*$_2$, 2H), 3.37 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 146.84 (Ar-*C*), 132.20 (Ar-*C*), 127.01 (Ar-*C*), 118.95 (Ar-*C*), 110.47 (Ar-*C*), 63.67 (*C*H$_2$).

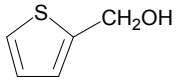




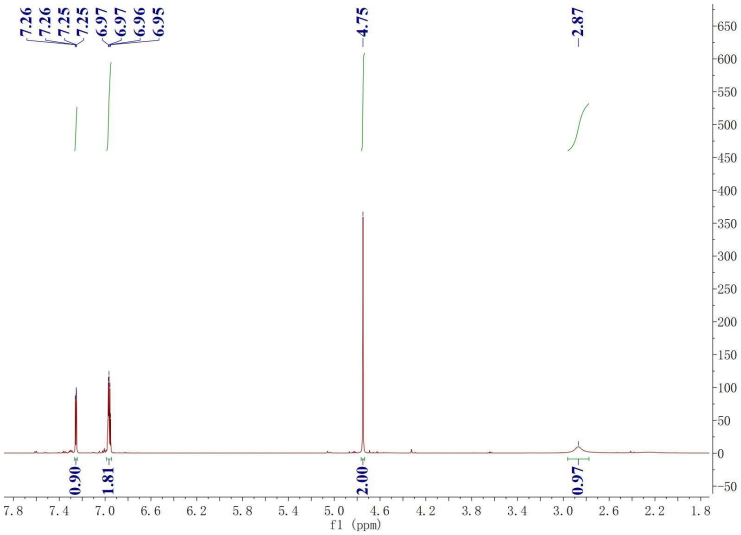
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.37 (s, Ar, 1H), 6.31 (d, J = 3.1 Hz, Ar-H, 1H), 6.26 (d, J = 3.2 Hz, Ar-H 1H), 4.57 (s, CH_2, 2H), 2.28 (s, OH, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 154.06 (Ar-C), 142.48 (Ar-C), 110.30 (Ar-C), 107.64 (Ar-C), 57.26 (CH).

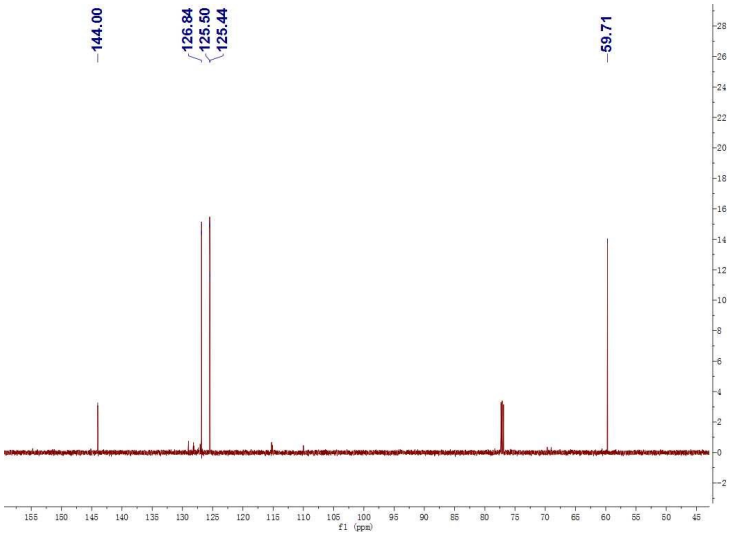


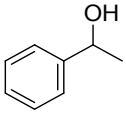




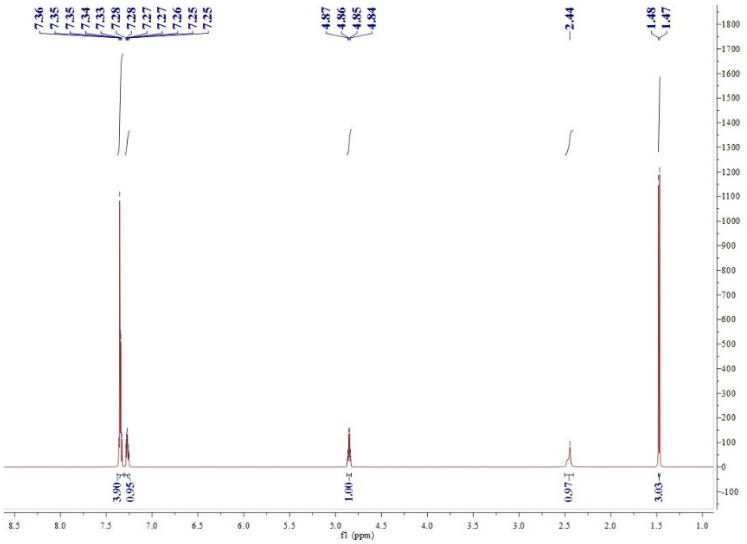
^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.25 (dd, J = 4.9, 1.3 Hz, Ar-*H*, 1H), 6.97-6.95 (m, Ar-*H*, 2H), 4.75 (s, CH_2, 2H), 2.87 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 154.06 (Ar-*C*), 142.48 (Ar-*C*), 110.30 (Ar-*C*), 107.64 (Ar-*C*), 57.26 (*C*H)

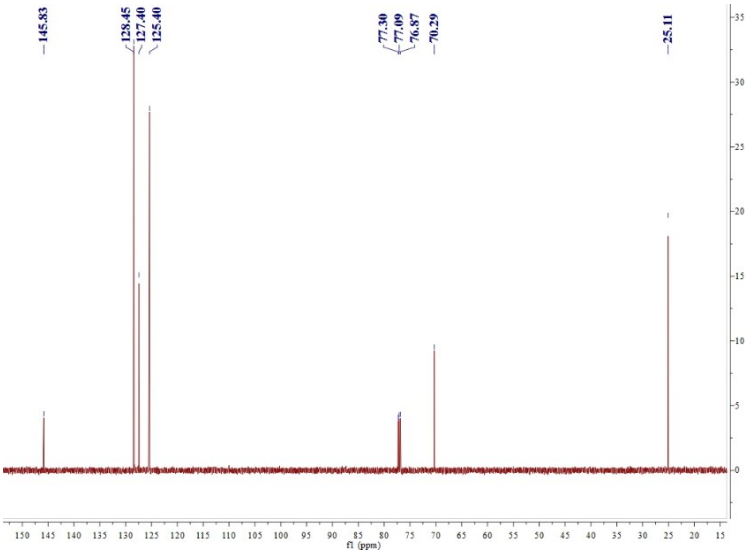


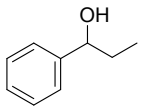




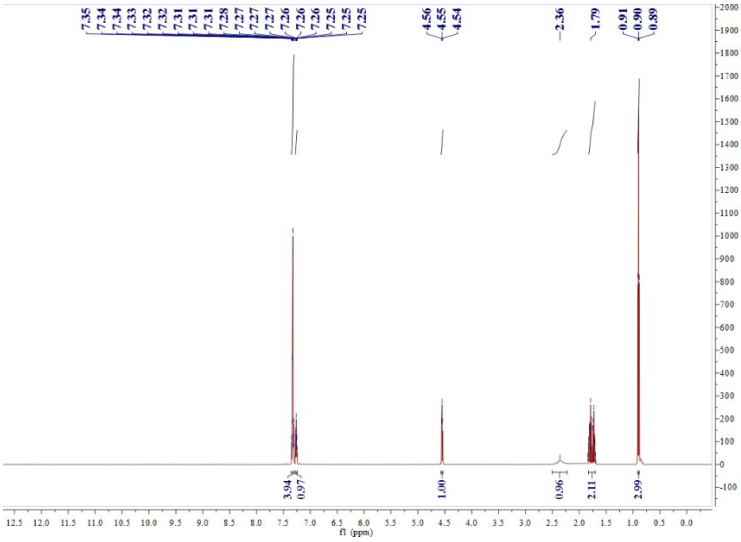
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25-7.36 (m, Ar-*H*, 5H), 4.86 (q, J = 3 Hz, C*H*, 1H), 2.44 (s, O*H*, 1H), 1.48 (d, J = 3 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 145.83 (Ar-*C*), 128.45 (Ar-*C*), 127.40 (Ar-*C*), 125.40 (Ar-*C*), 70.29 (*C*H), 25.11 (*C*H_3).

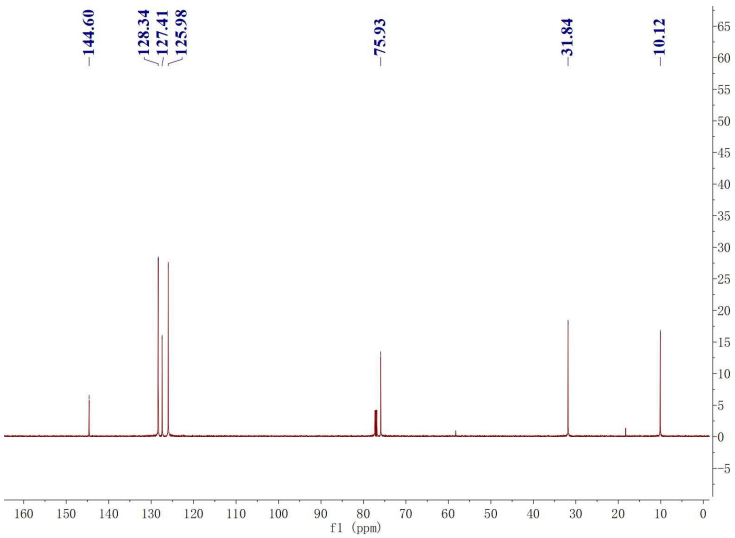


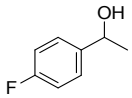




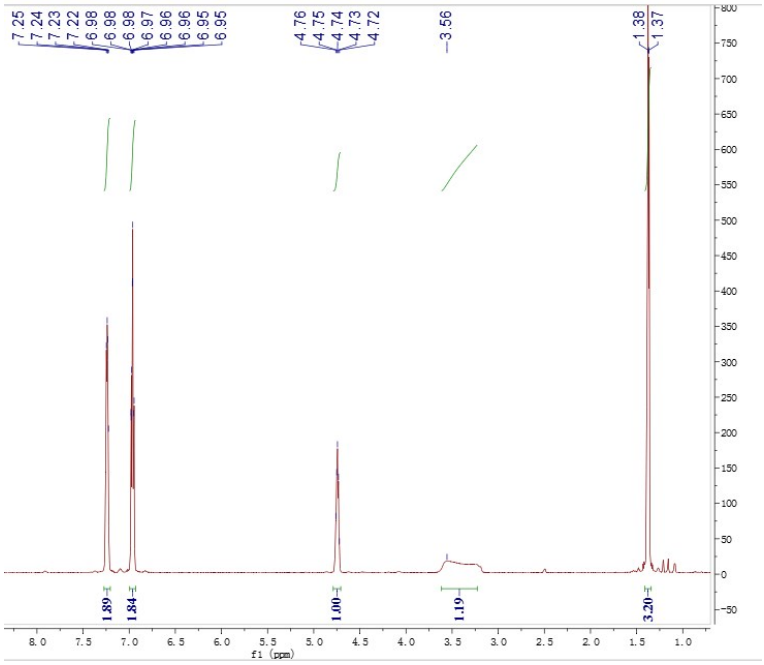
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.25–7.35 (m, Ar-*H*, 5H), 4.55 (t, *J* = 3 Hz, C*H*, 1H), 2.36 (s, O*H*, 1H),1.73-1.79 (m, CH_2, 2H), 0.90 (d, *J* = 3 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 144.60 (s, Ar-*C*), 136.63 (s, Ar-*C*), 131.68 (s, Ar-*C*), 130.50 (s, Ar-*C*), 128.65 (s, Ar-*C*), 128.63 (s, Ar-*C*), 127.81 (s, Ar-*C*), 127.78 (s, Ar-*C*), 126.46 (s, Ar-*C*), 126.04 (s, Ar-*C*), 125.90 (s, Ar-*C*), 75.06 (*C*H), 32.10 (*C*H_3).

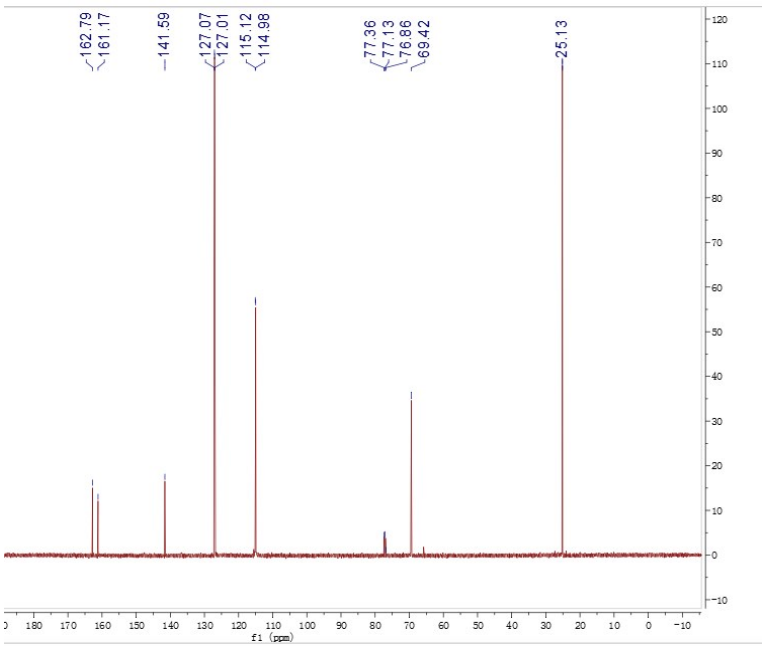


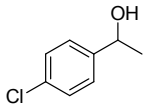




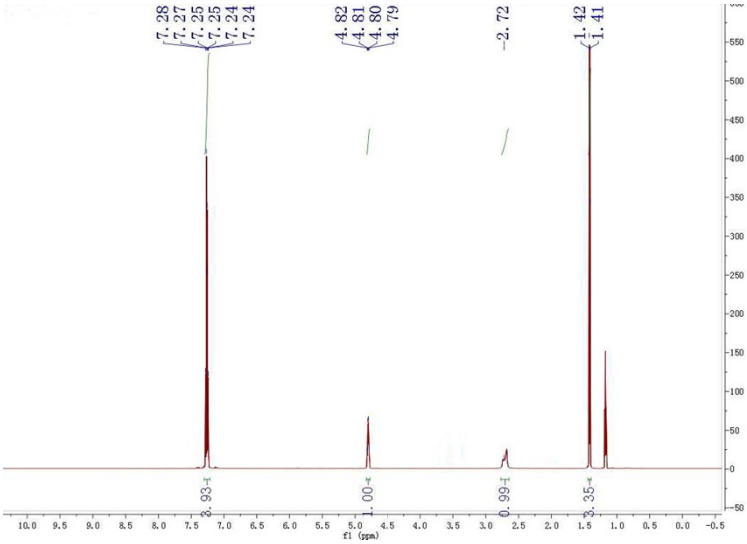
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.22-7.25 (m, Ar-*H*, 2H), 6.95–6.98 (m, Ar-*H*, 2H), 4.74 (q, J = 3 Hz, C*H*, 1H), 3.56 (s, O*H*, 1H), 1.38 (d, J = 3 Hz, CH_3, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$, 298K, ppm): 162.03 (d, J = 245.0 Hz, Ar-*C*), 141.59 (s, Ar-*C*), 127.04 (d, J = 7.5 Hz, Ar-*C*), 115.05 (d, J = 17.5 Hz, Ar-*C*), 69.42 (*C*H), 25.13(*C*H_3).

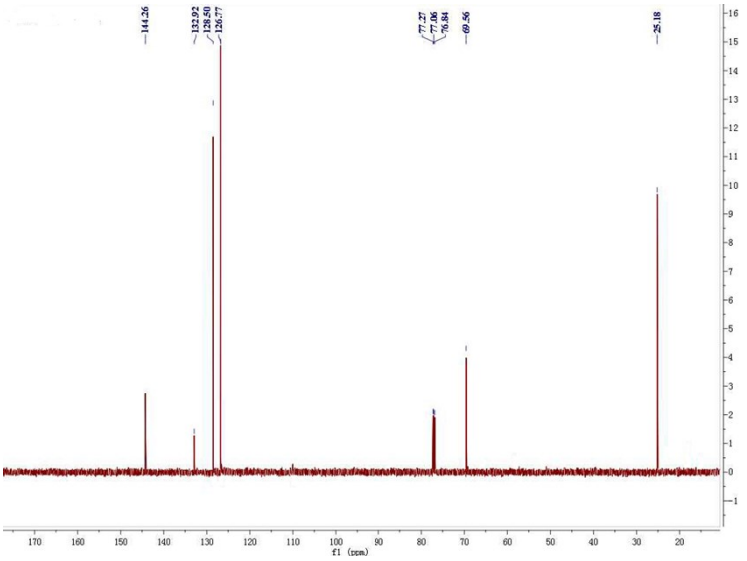


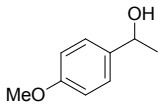




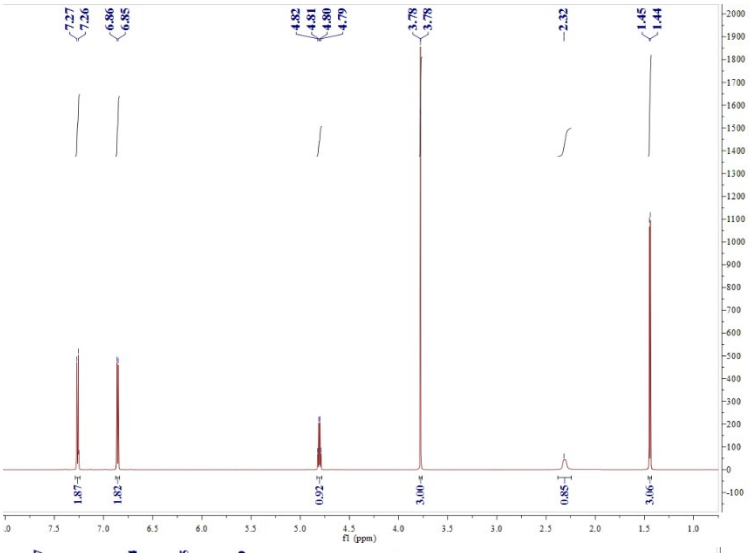
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.24-7.28 (m, Ar-*H*, 4H), 4.81 (q, *J* = 3 Hz, C*H*, 1H), 2.72 (s, O*H*, 1H), 1.42 (d, *J* = 3 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 144.26 (s, Ar-*C*), 132.92 (s, Ar-*C*), 128.50 (s, Ar-*C*), 126.77 (s, Ar-*C*), 69.56 (*C*H), 25.18 (CH_3).

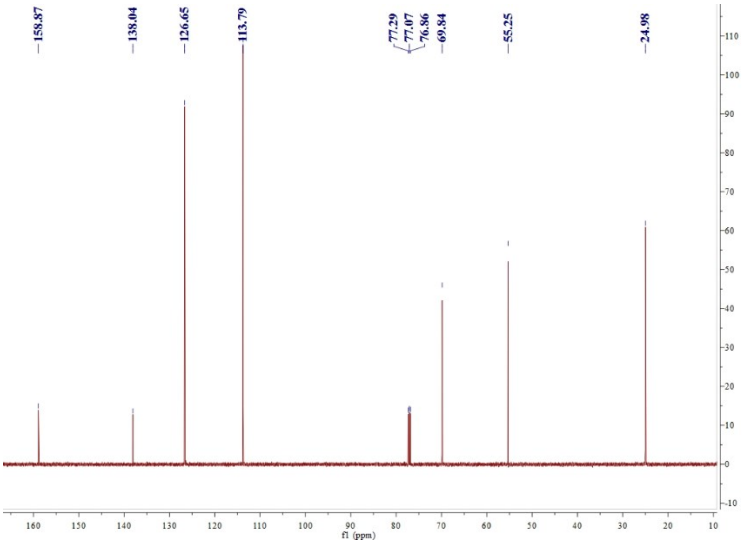


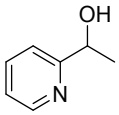




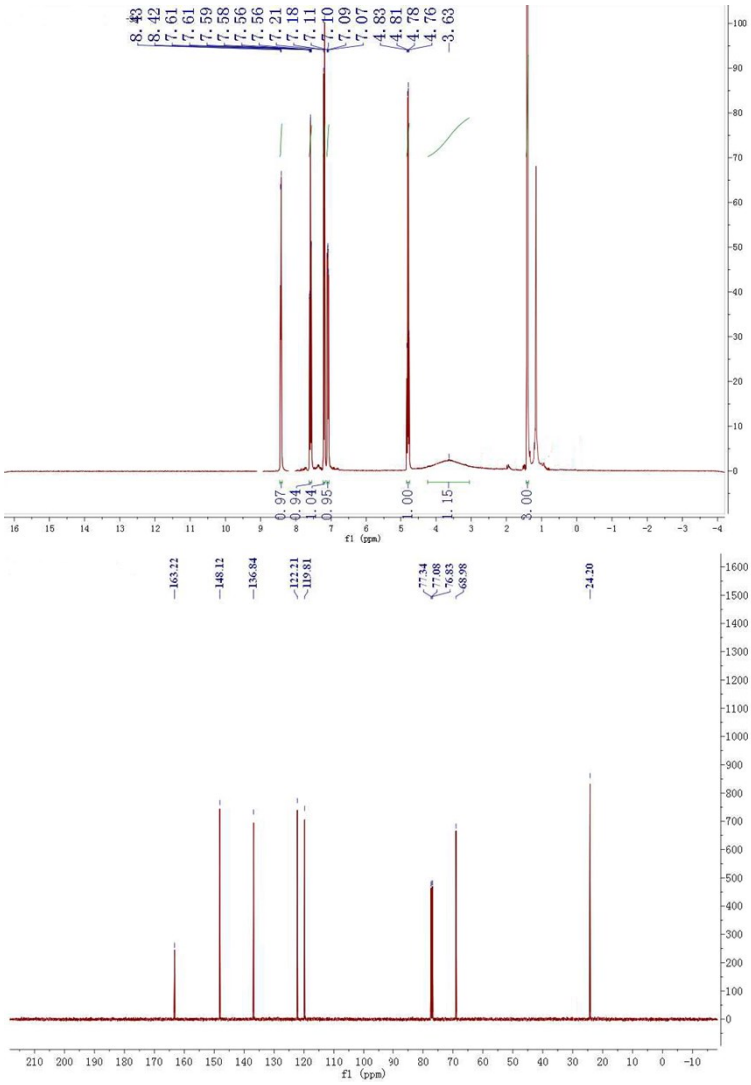
^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.27 (d, J = 8.8 Hz, Ar-*H*, 2H),6.86 (d, J = 8.7 Hz, Ar-*H*, 2H), 4.81 (q, J = 6.4 Hz, C*H*, 1H), 3.78 (d, J = 0.9 Hz, OCH_3, 3H)，2.32 (s, O*H*, 1H), 1.45 (d, J = 6.5 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 158.87 (Ar-*C*), 138.04 (Ar-*C*), 126.65 (Ar-*C*), 113.79 (Ar-*C*), 69.84 (*C*H), 55.25 (O*C*H_3), 24.98(*C*H_3).

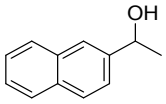




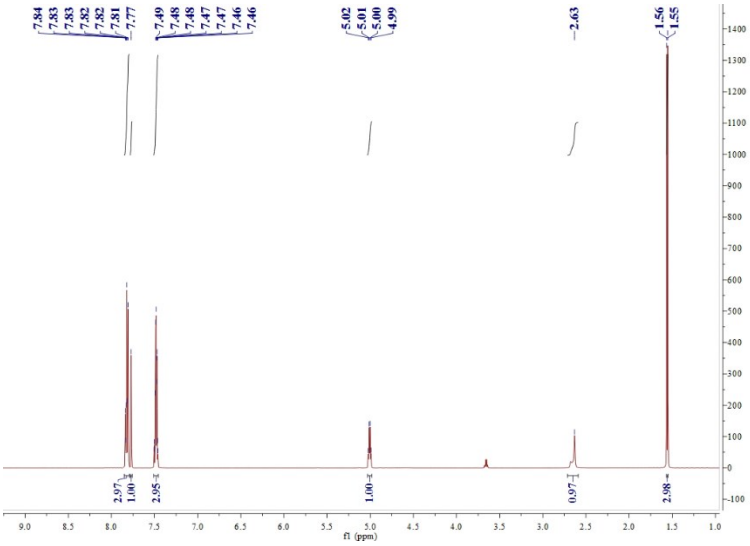


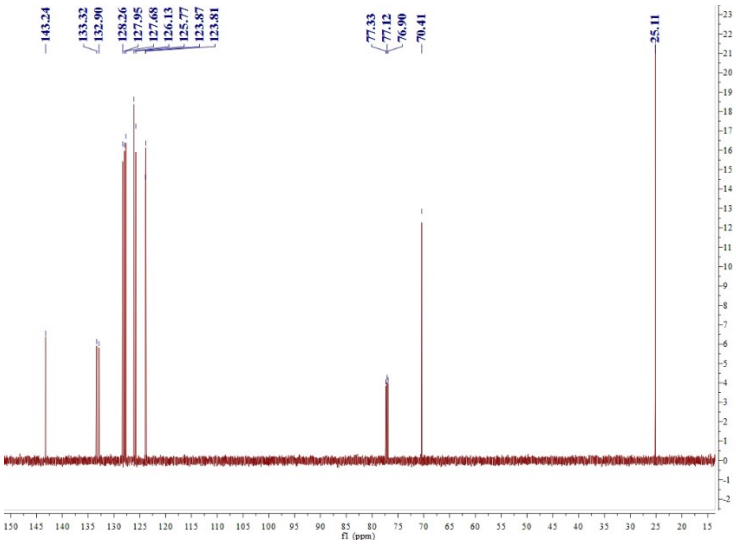
^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.43 (d, J = 3 Hz, Ar-H, 1H), 7.07-7.61 (m, Ar-H, 3H), 4.81 (q, J = 3 Hz, CH, 1H), 3.63 (s, OH, 1H), 1.49 (d, J = 3 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 163.22 (Ar-C), 148.12 (Ar-C), 136.84 (Ar-C), 122.21 (Ar-C), 119.81 (Ar-C), 68.98 (CH), 24.20(CH$_3$).

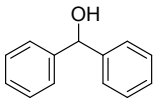




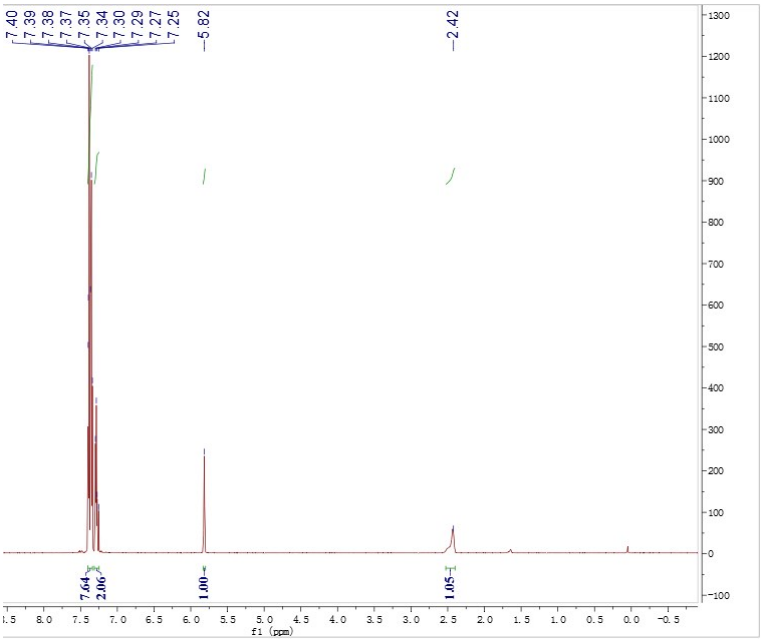
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.81–7.84 (m, Ar-*H*, 3H), 7.77 (s, Ar-*H*, 1H) 7.46–7.49 (m, Ar-*H*, 3H), 5.01 (q, *J* = 3 Hz, C*H*, 1H), 2.63 (s, O*H*, 1H), 1.56 (d, *J* = 3 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 143.24 (Ar-*C*), 133.33 (Ar-*C*), 132.90 (Ar-*C*), 128.26 (Ar-*C*), 127.95 (Ar-*C*), 127.68 (Ar-*C*), 126.13 (Ar-*C*), 125.77 (Ar-*C*), 123.87 (Ar-*C*),123.81 (Ar-*C*), 70.41 (*C*H), 25.11(CH_3).

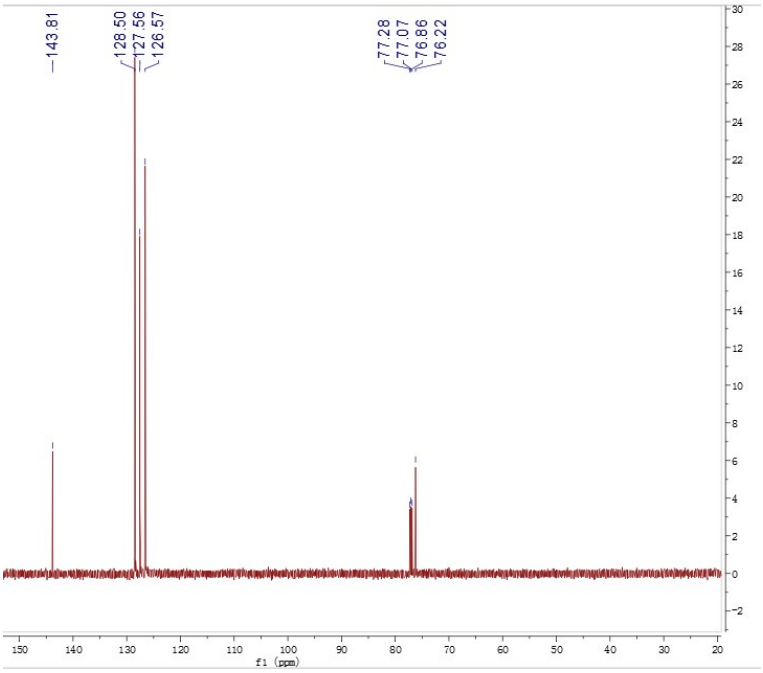


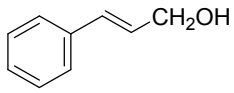




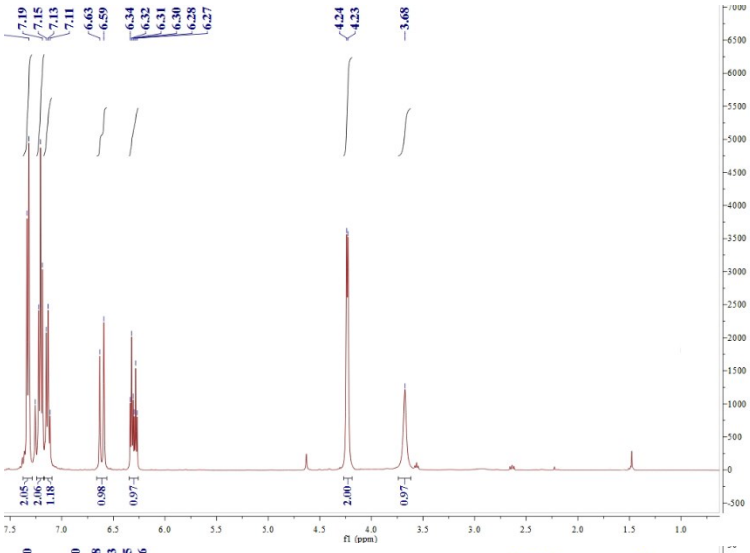
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25-7.40 (Ar-*H*, *Ar*, 10H), 5.82 (s, C*H*, 1H), 2.42 (s, O*H*, 1H).
^{13}C NMR (125 MHz, $CDCl_3$, 298K, ppm): 143.81 (Ar-*C*), 128.50 (Ar-*C*), 127.56 (Ar-*C*),126.57 (Ar-*C*), 76.22 (*C*H).

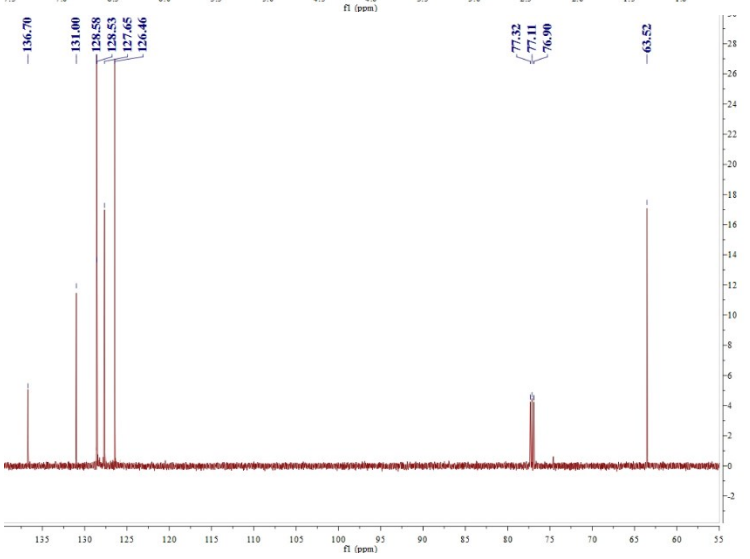


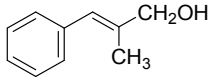




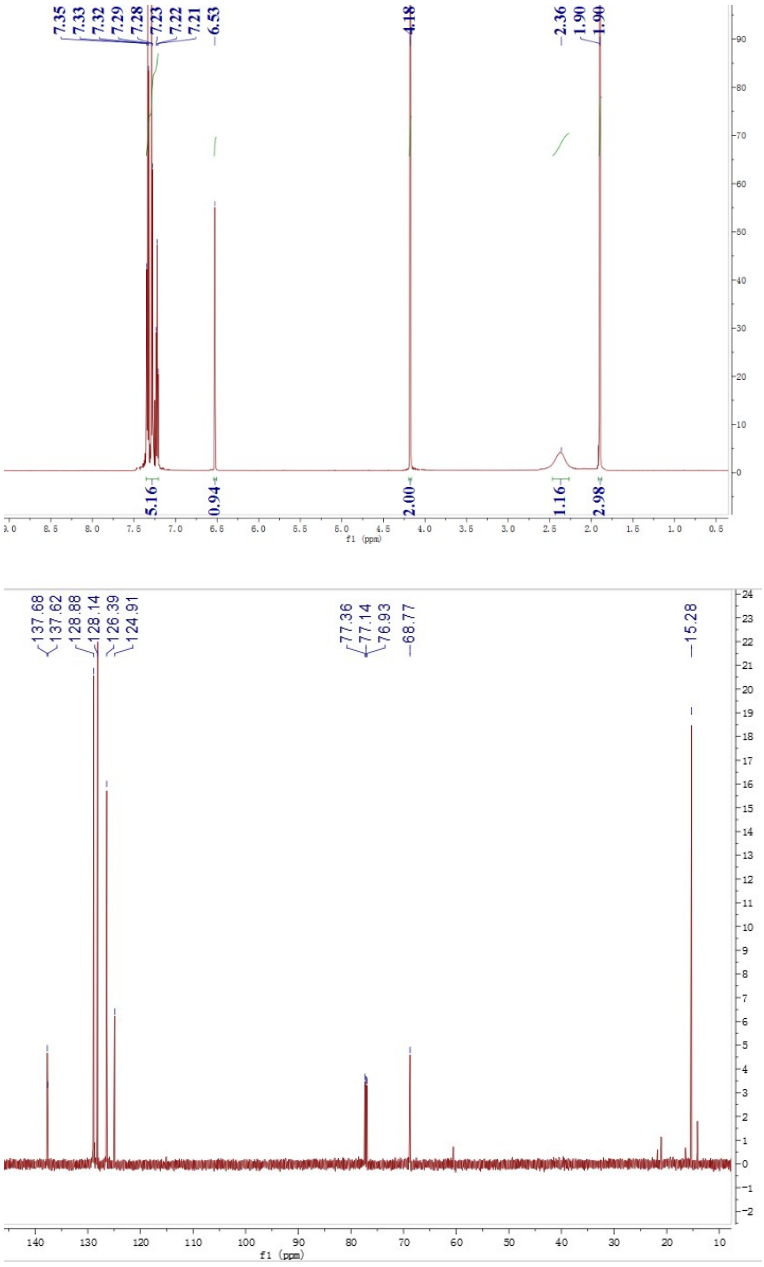
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.11-7.19 (m, Ar-*H*, 5H), 6.61 (d, J = 12 Hz, *H*C=C, 1H), 6.27-6.34 (m, C=C*H*, 1H), 4.24 (d, J = 3 Hz, CH_2, 2H), 3.68 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 136.70 (Ar-*C*), 131.00 (Ar-*C*), 128.58 (Ar-*C*), 128.53 (Ar-*C*), 127.65 (Ar-*C*), 127.69 (Ar-*C*), 126.46 (*C*=*C*), 63.52 (CH_2).

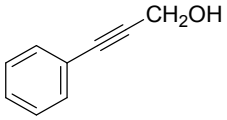




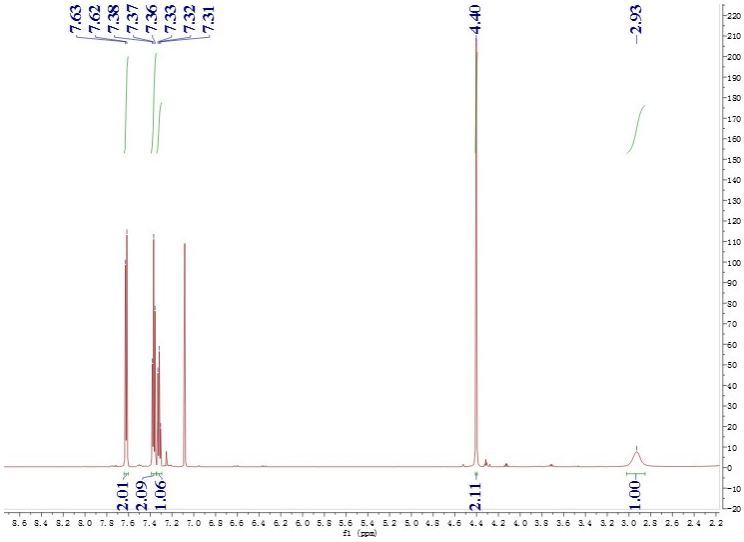


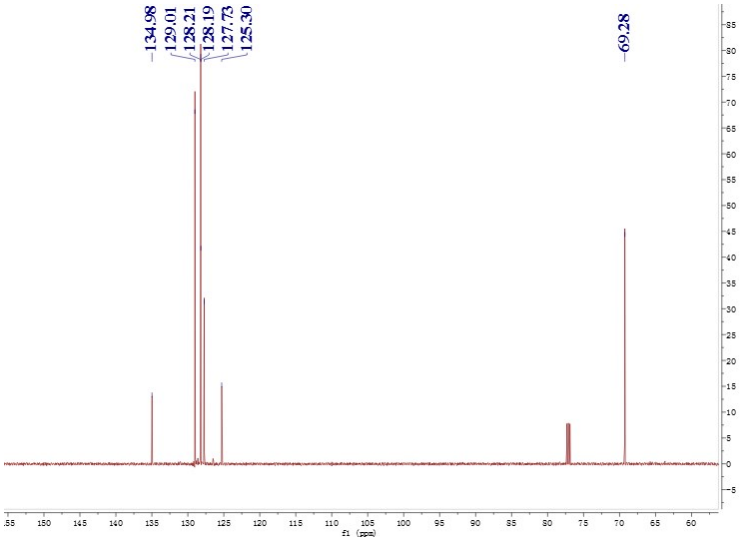
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.21-7.35 (m, Ar-*H*, 5H), 6.53 (d, *H*C=C, 1H), 4.18 (dd, CH_2, 2H), 2.36 (s, O*H*, 1H) ,1.90 (d, J = 1.2 Hz, CH_3, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 137.68 (Ar-*C*), 137.62 (Ar-*C*), 128.88 (Ar-*C*), 128.14 (Ar-*C*), 126.39 (Ar-*C*), 124.91 (*C*=*C*), 68.77 (CH_2), 15.28 (CH_3).

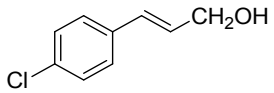




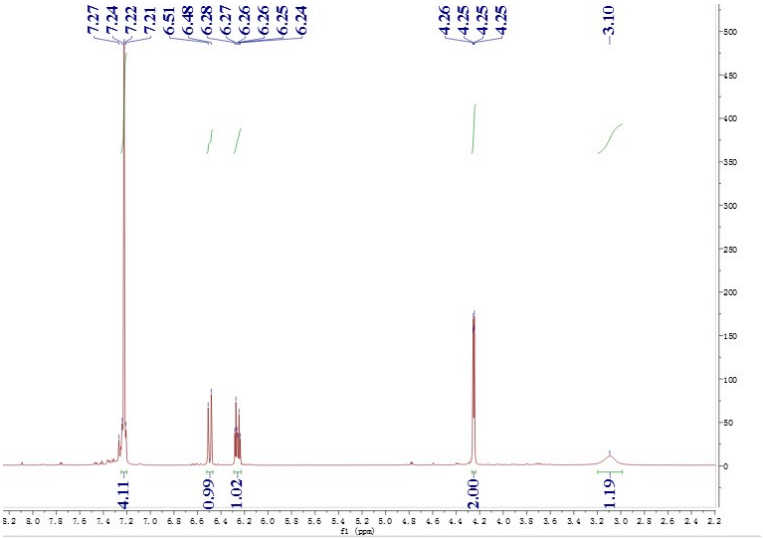
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.62-7.63 (d, J = 3 Hz, Ar-H, 2H), 7.31-7.38 (m, Ar-H, 3H), 4.40 (s, CH_2, 2H), 2.93 (s, OH, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 134.98 (Ar-C), 129.01 (Ar-C), 128.21(Ar-C), 128.19 (Ar-C), 127.73, 125.30 (C≡C), 69.28 (CH$_2$).

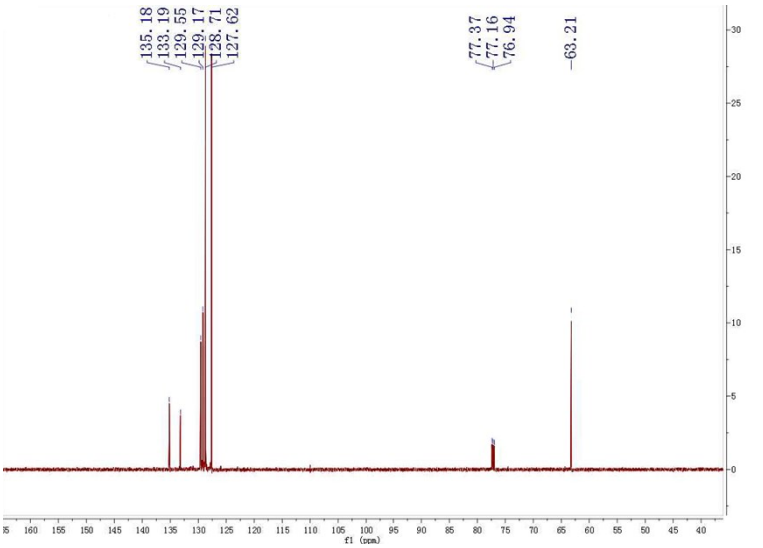


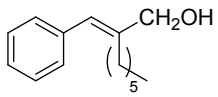




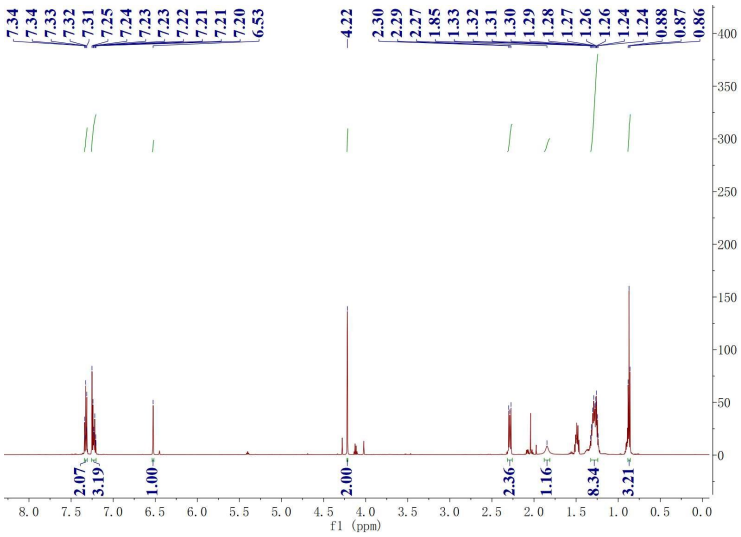
^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.21-7.27 (m, Ar-*H*, 4H), 6.50 (d, *H*C=C, 2H), 6.24 (m, C=C*H*, 1H), 4.25 (dd, CH_2, 2H), 3.10 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 135.18 (Ar-*C*), 133.19 (Ar-*C*),129.55 (Ar-*C*),129.17 (Ar-*C*), 128.71 (Ar-*C*), 127.62 (*C*=*C*), 63.21 (CH_2).

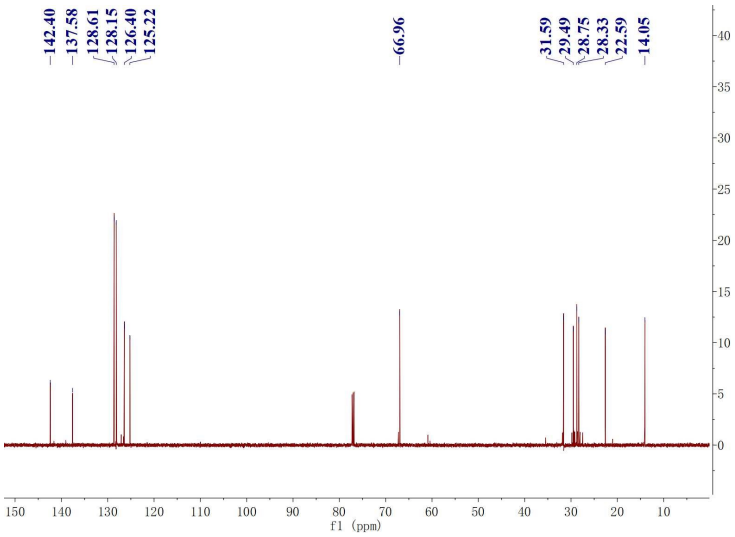


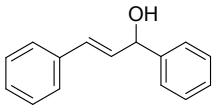




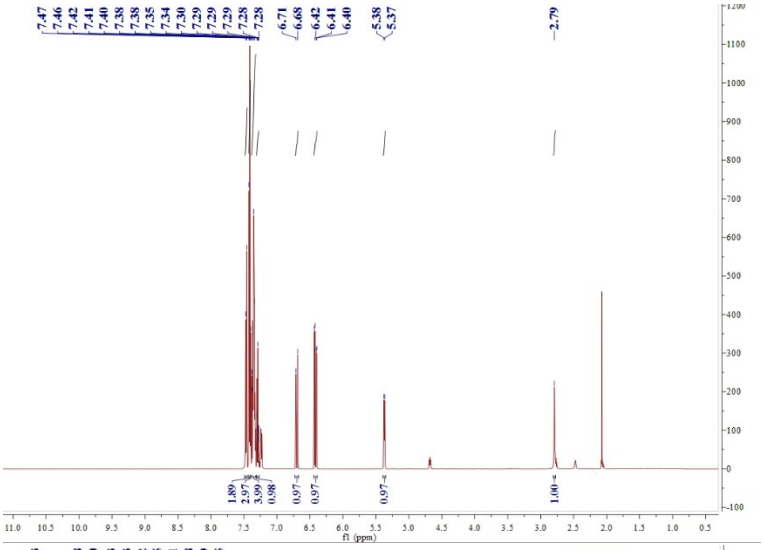
^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.20-7.34 (m, Ar-*H*, 5H), 6.53 (s, *H*C=C, 1H), 4.22 (s, CH_2, 2H), 2.27-2.30 (m, CH_2, 2H), 1.85 (s, O*H*, 1H), 1.33-1.24 (m, CH_2, 8H), 0.88 (q, J = 7.0 Hz, CH_3, 3H).
^{13}C NMR (125 MHz, $CDCl_3$, 298K, ppm): 142.40(Ar-*C*), 137.58(Ar-*C*), 128.61(Ar-*C*), 128.15 (Ar-*C*), 126.40, 125.22(*C*=*C*), 66.96 (*C*H_2), 31.59, 29.49, 28.75, 28.33, 22.59 (*C*H_2), 14.05 (*C*H_3).

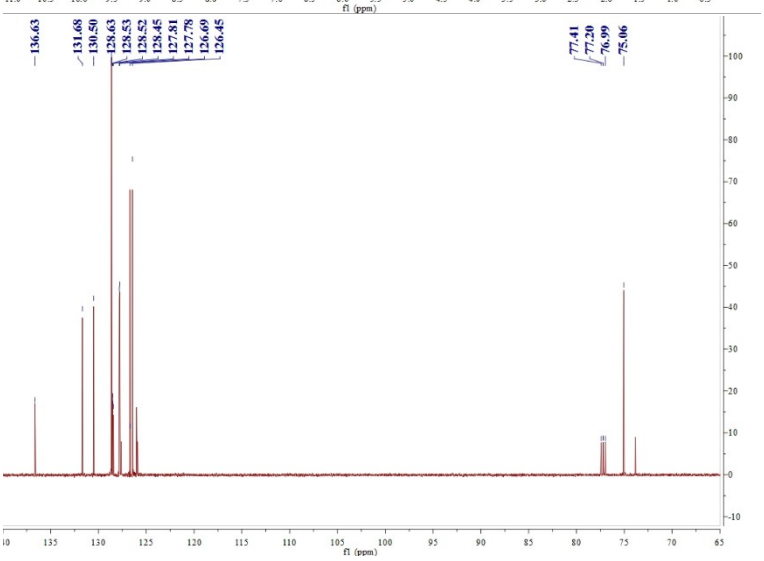




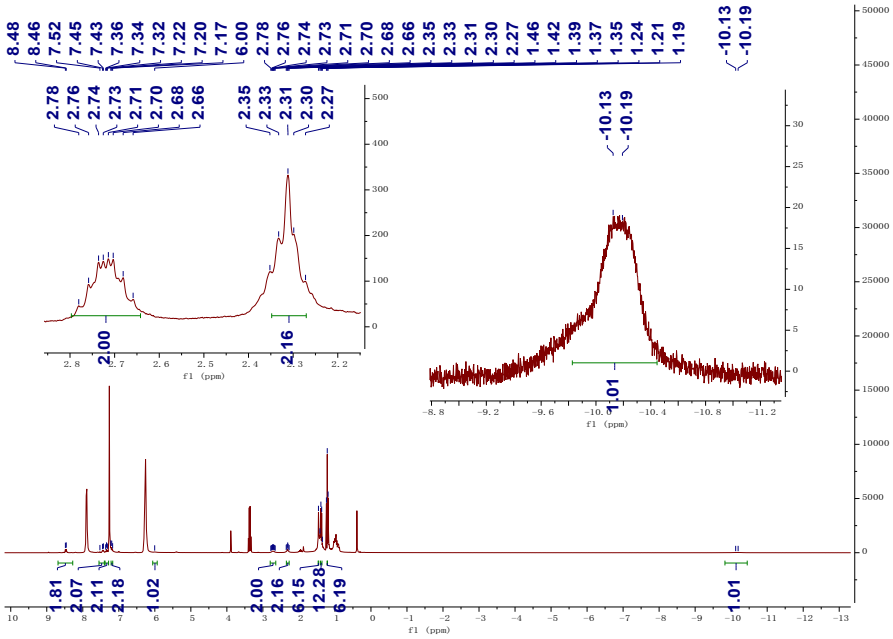


^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.28-7.47 (m, Ar-*H*, 10H), 6.70 (d, *J* = 9 Hz, *H*C=C, 1H), 6.40-6.42 (t, *J* = 3 Hz, C=CH, 1H), 5.38(d, *J* = 3 Hz, C*H*, 1H), 2.79 (s, O*H*, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$, 298K, ppm): 136.63 (Ar-*C*), 131.68 (Ar-*C*), 130.50 (Ar-*C*), 128.63 (Ar-*C*), 128.52 (d, *J* = 12.5 Hz, *H*C=C, 1H), 128.45 (Ar-*C*), 127.78 (Ar-*C*), 126.69, 126.45 (*C*=*C*), 75.06 (C*H*).

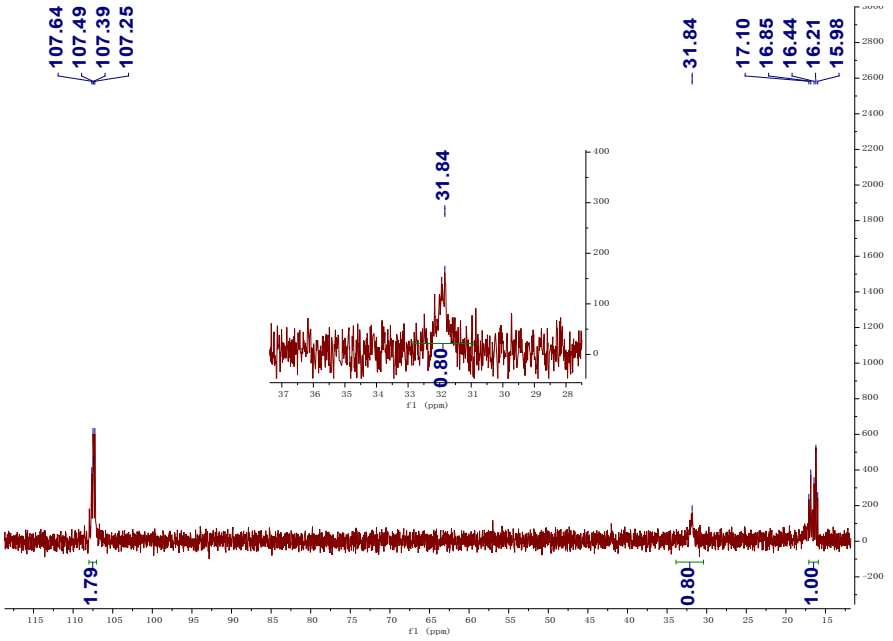




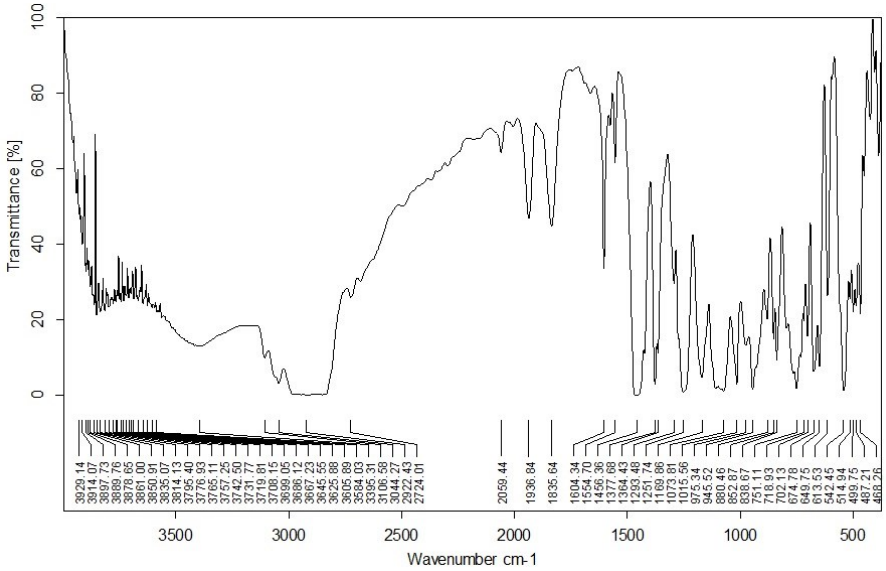
4. The *in situ* NMR and IR spectra for mechanism study



The *in situ* ^{1}H NMR of the reaction of **4** and pyridine N-oxide



The *in situ* ^{31}P NMR of the reaction of **4** and pyridine N-oxide



The *in situ* IR of the reaction of **4** and pyridine N-oxide