

Synthesis of Silyl Iron Hydride via Si-H Activation and its Double Catalytic Application in Hydrosilylation of Carbonyl Compounds and Dehydration of Benzamides

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1. Table S1. Crystallographic Data for Complex 2b

	2b
empirical formula	C ₂₆ H ₃₉ FeP ₃ Si
fw	528.42
cryst syst	Monoclinic
space group	P2(1)/n
<i>a</i> , Å	10.5677(9)
<i>b</i> , Å	17.7146(15)
<i>c</i> , Å	15.1486(14)
β , deg	90.232(2)
<i>V</i> , Å ³	2835.8(4)
<i>Z</i>	4
<i>D_x</i> , gcm ⁻³	1.238
no. of reflns collected	13959
no. of unique data	5029
<i>R_{int}</i>	0.0495
$\theta_{\max}$, deg	27.51
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0464
<i>wR</i> ₂ (all data)	0.1117

2. IR, ¹H NMR, ³¹P NMR and ¹³C NMR spectrum of complex 2.

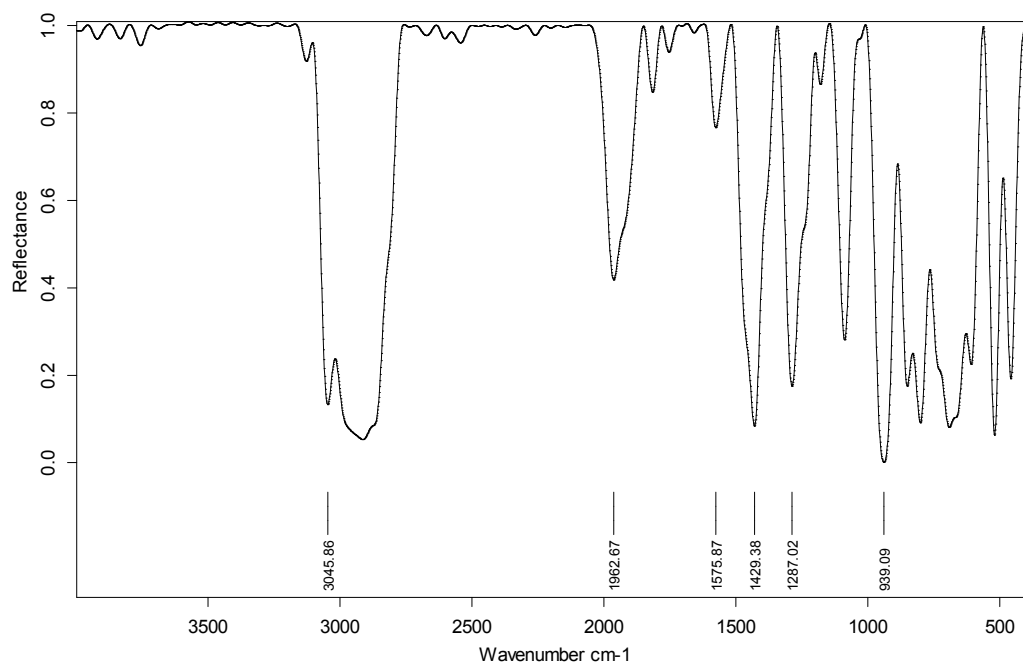


Fig S1 IR spectrum of **2**

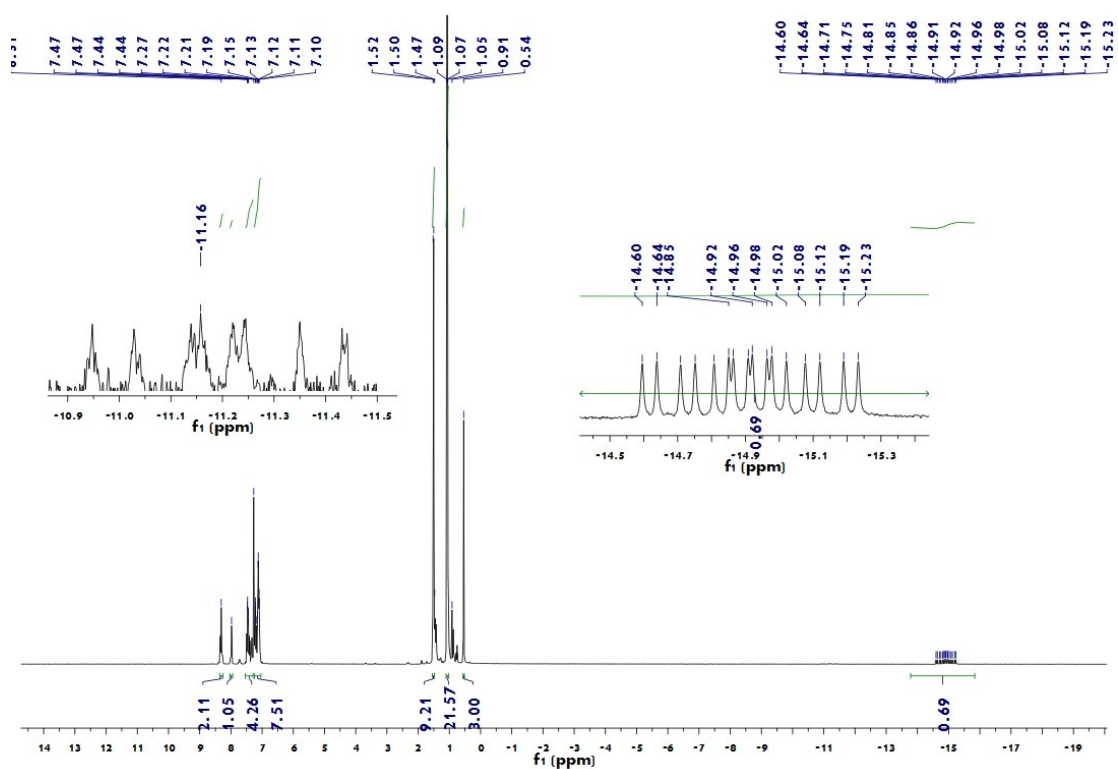


Fig S2 ^1H NMR spectrum of **2**(evidence for the existence of **2b** at -11.19 ppm)

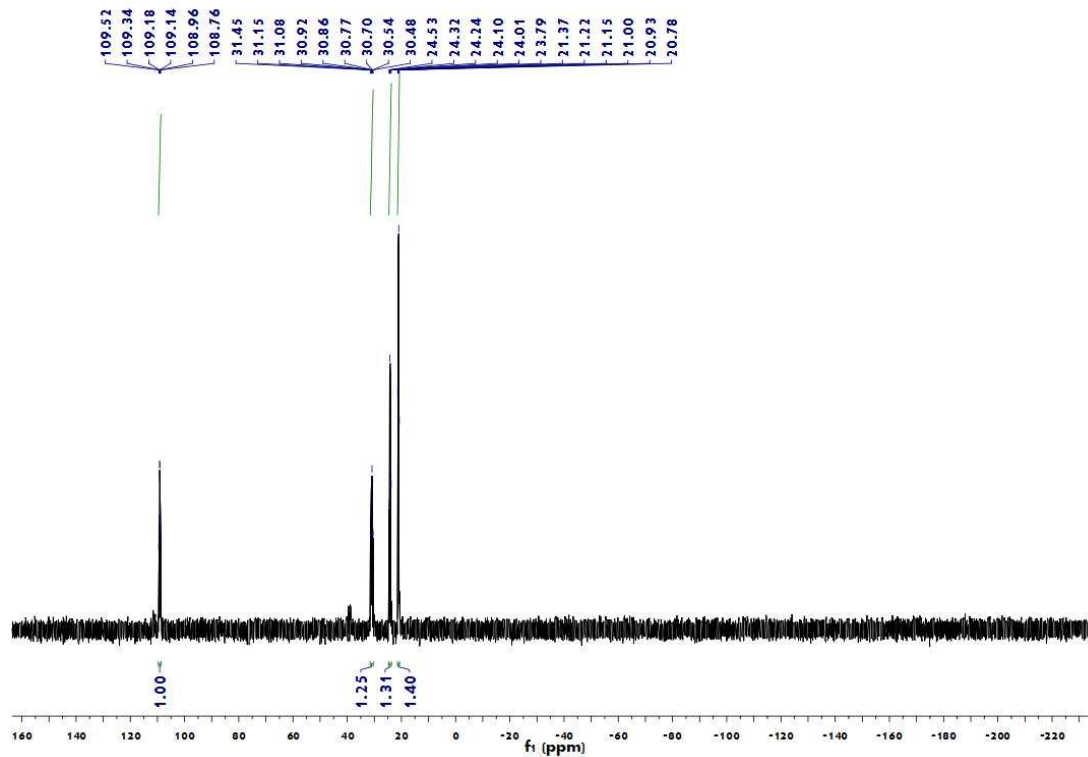


Fig S3 ^{31}P NMR spectrum of **2**

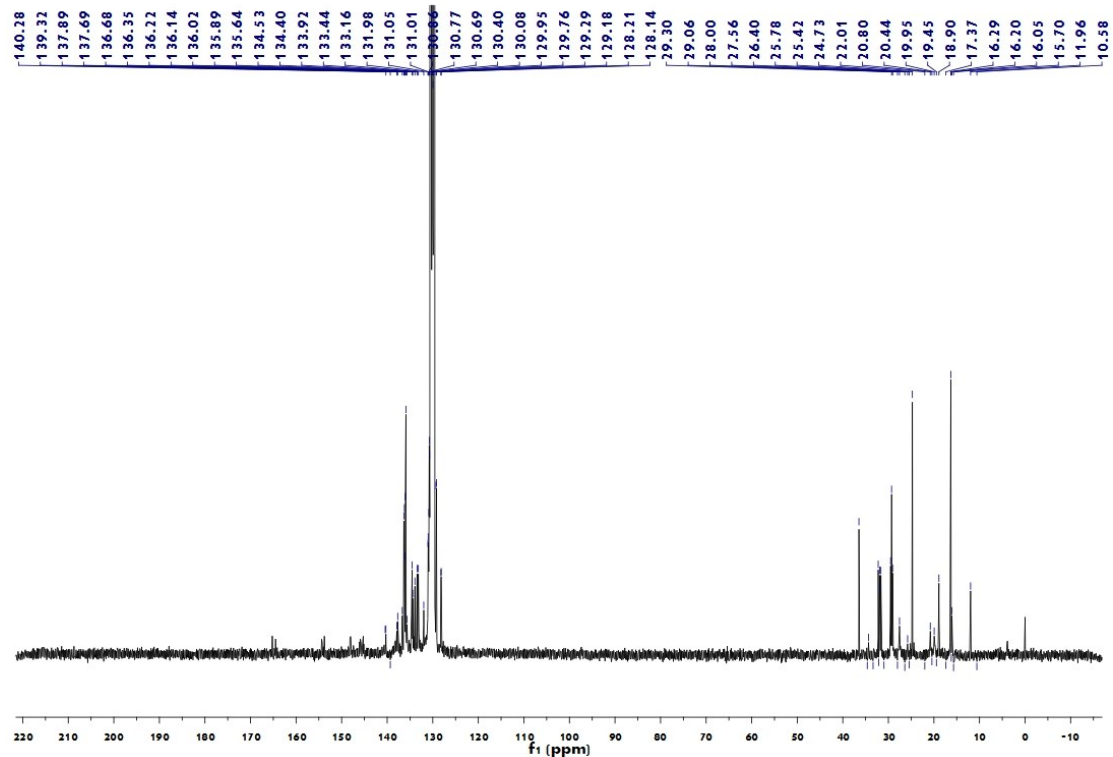


Fig S4 ^{13}C NMR spectrum of **2**

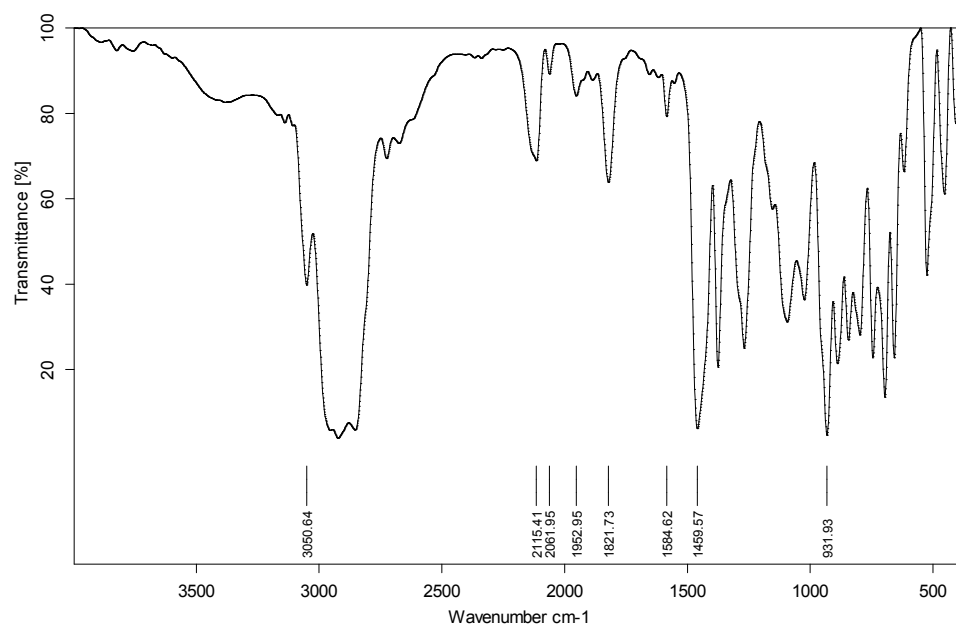
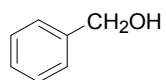
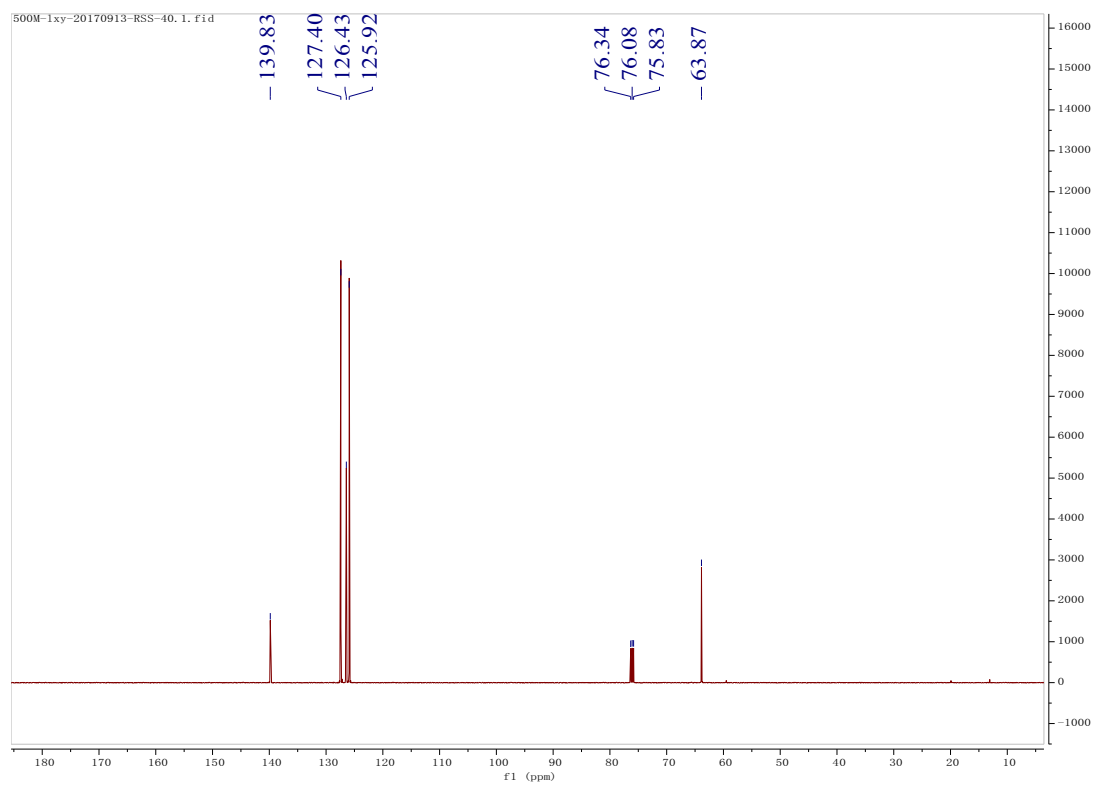
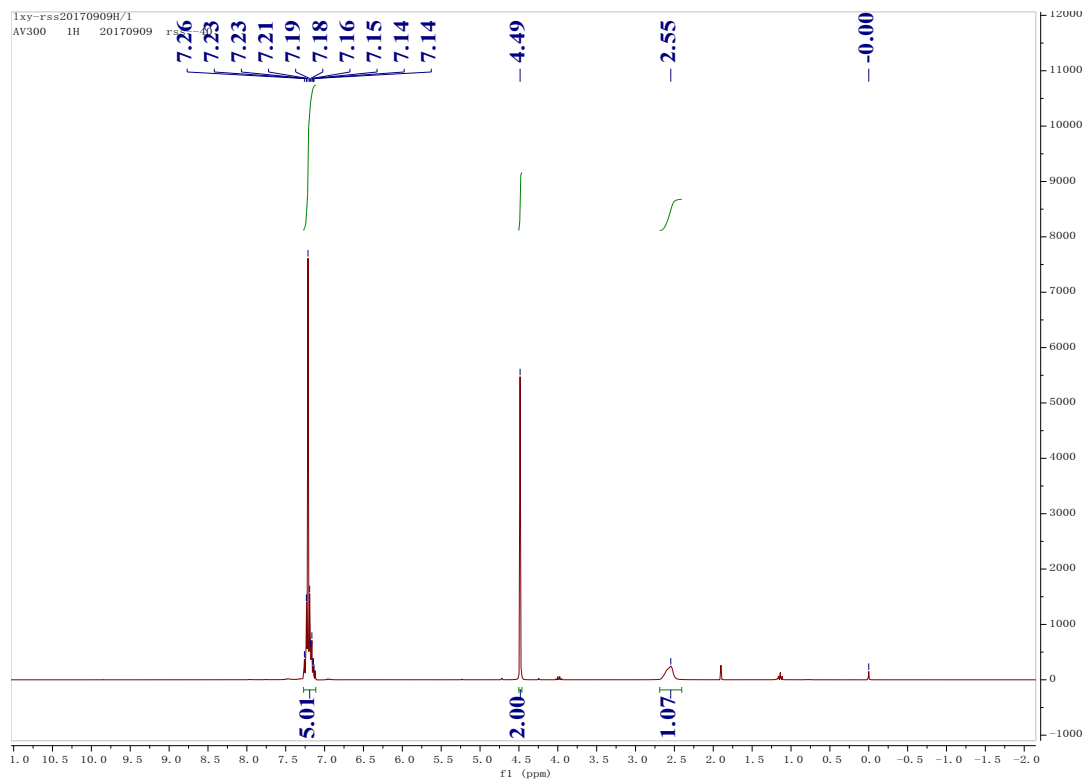


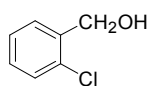
Fig S5 *in situ* IR spectrum of reaction (1).
(pentane solution, after stirring at room temperature for 3 h)

3 ^1H NMR and ^{13}C NMR spectrum of alcohols

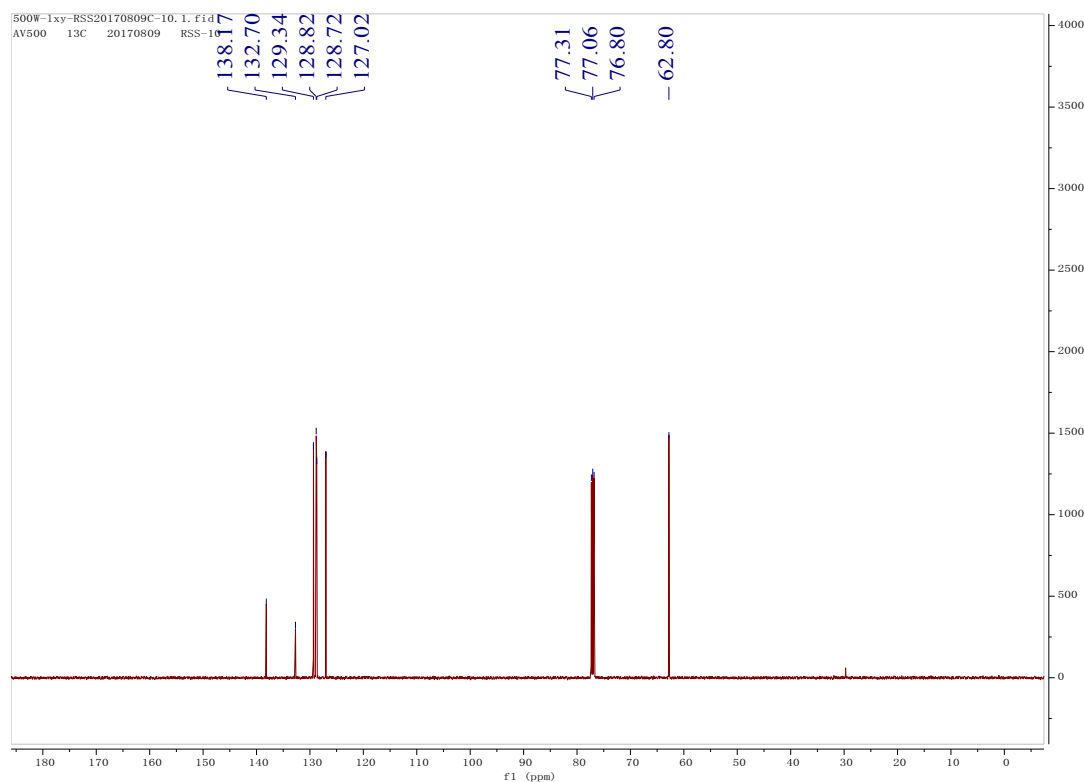
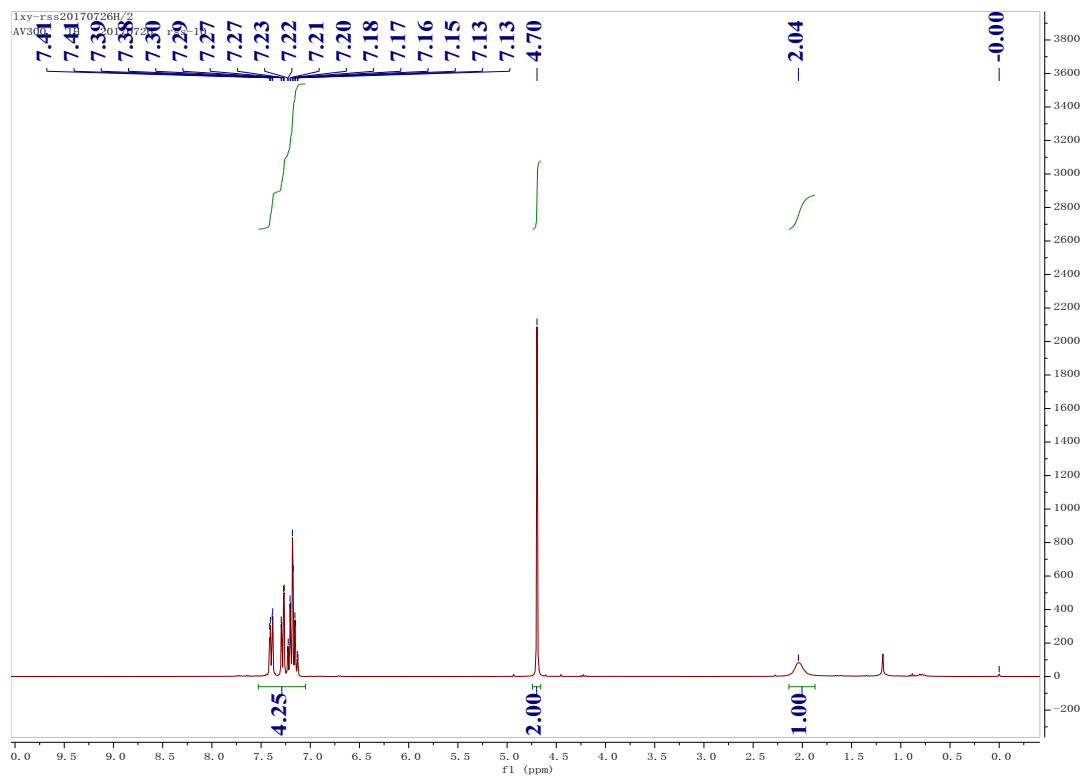


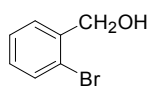
^1H NMR (300 MHz, CDCl_3 , δ): 7.26–7.14 (m, *Ar*, 5H), 4.49 (s, CH_2 , 2H), 2.55 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 139.83, 127.40, 126.43, 125.92 (Ar-C), 63.87 (CH_2).



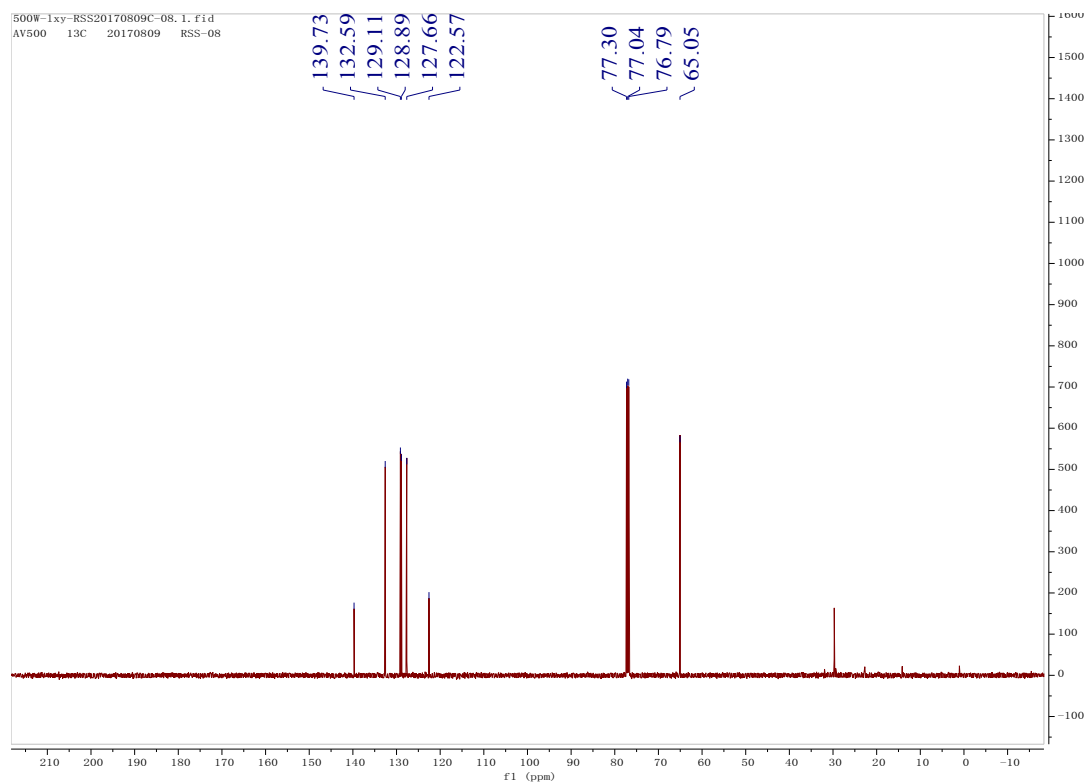
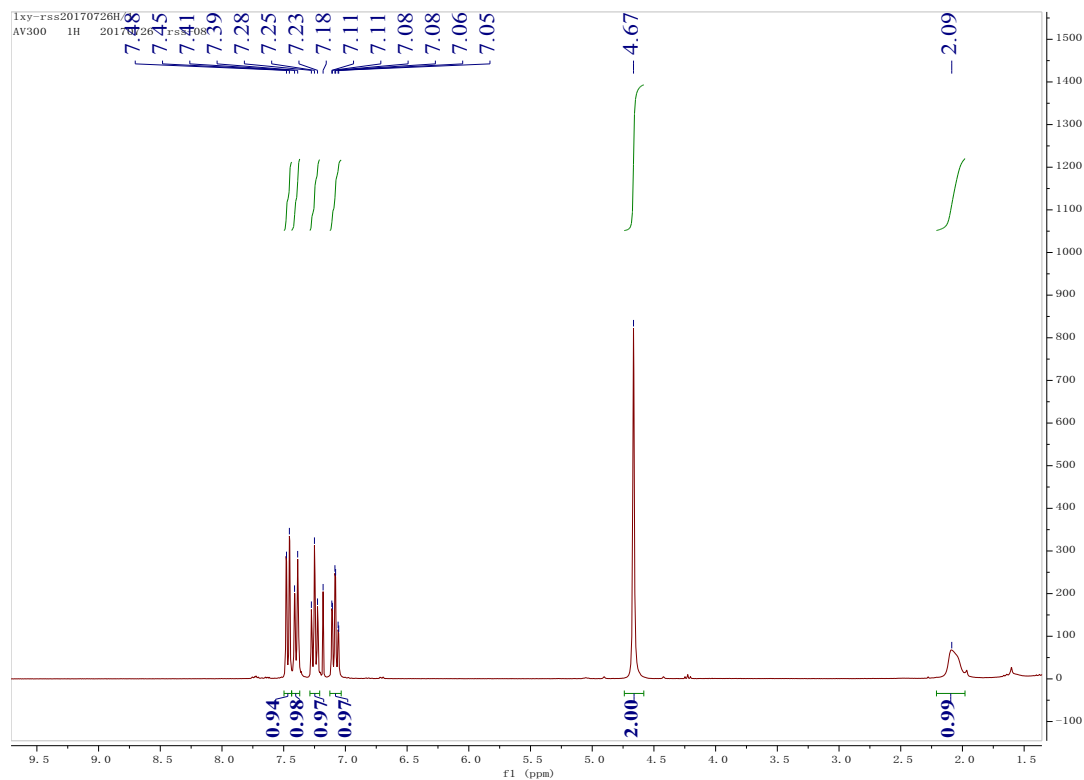


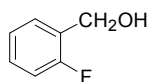
^1H NMR (300 MHz, CDCl_3 , δ): 7.41–7.13 (m, *Ar*, 4H), 4.70 (s, CH_2 , 2H), 2.04 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 138.17, 132.70, 129.34, 128.82, 128.72, 127.02 (Ar-C), 62.80 (CH_2).



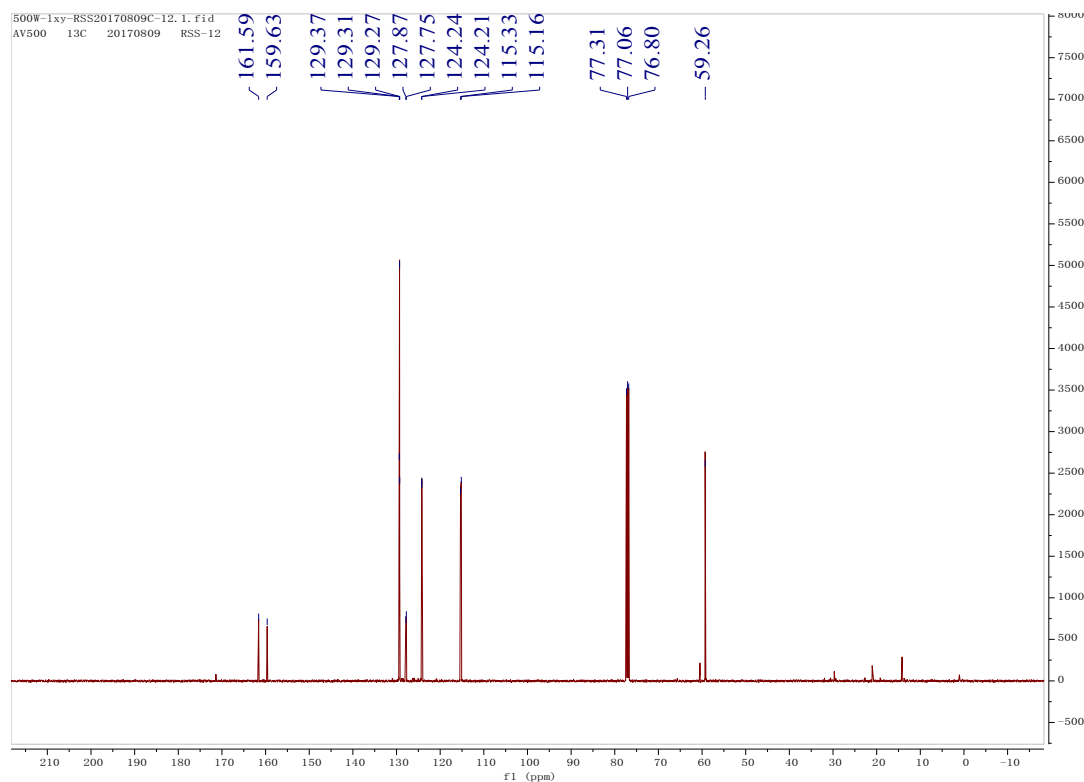
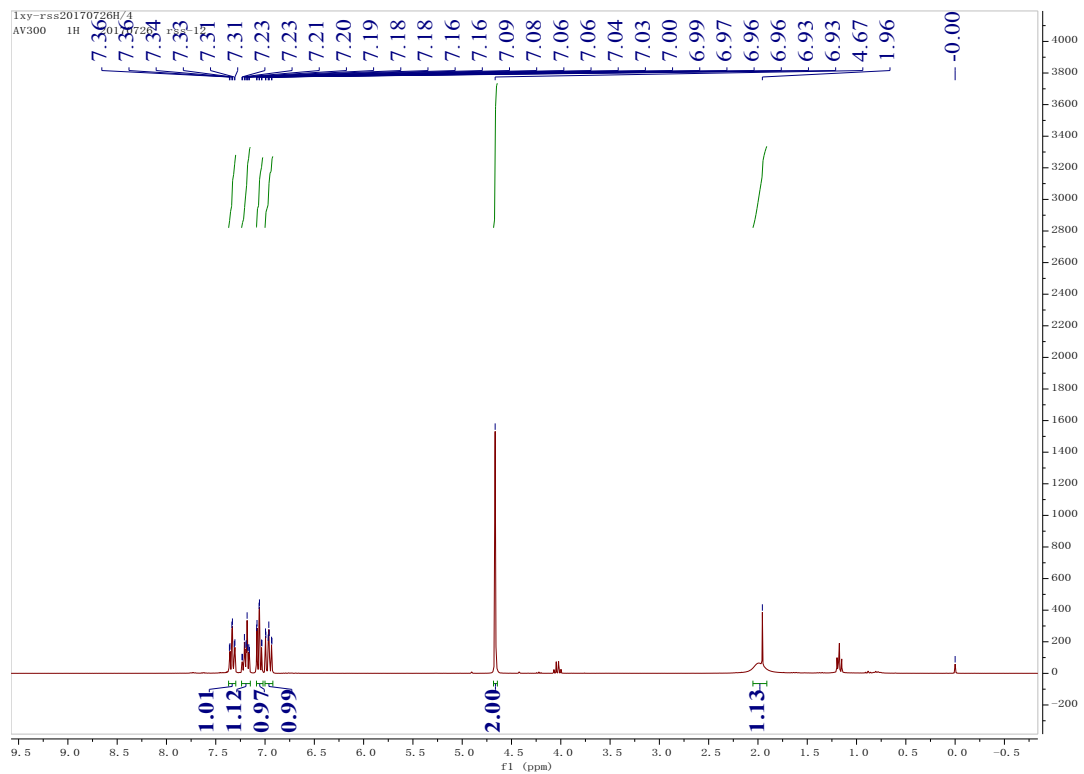


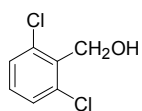
^1H NMR (300 MHz, CDCl_3 , δ): 7.48–7.05 (m, *Ar*, 4H), 4.67 (s, CH_2 , 2H), 2.99 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 139.73, 132.59, 129.11, 128.89, 127.66, 122.57 (Ar-C), 65.05 (CH_2).



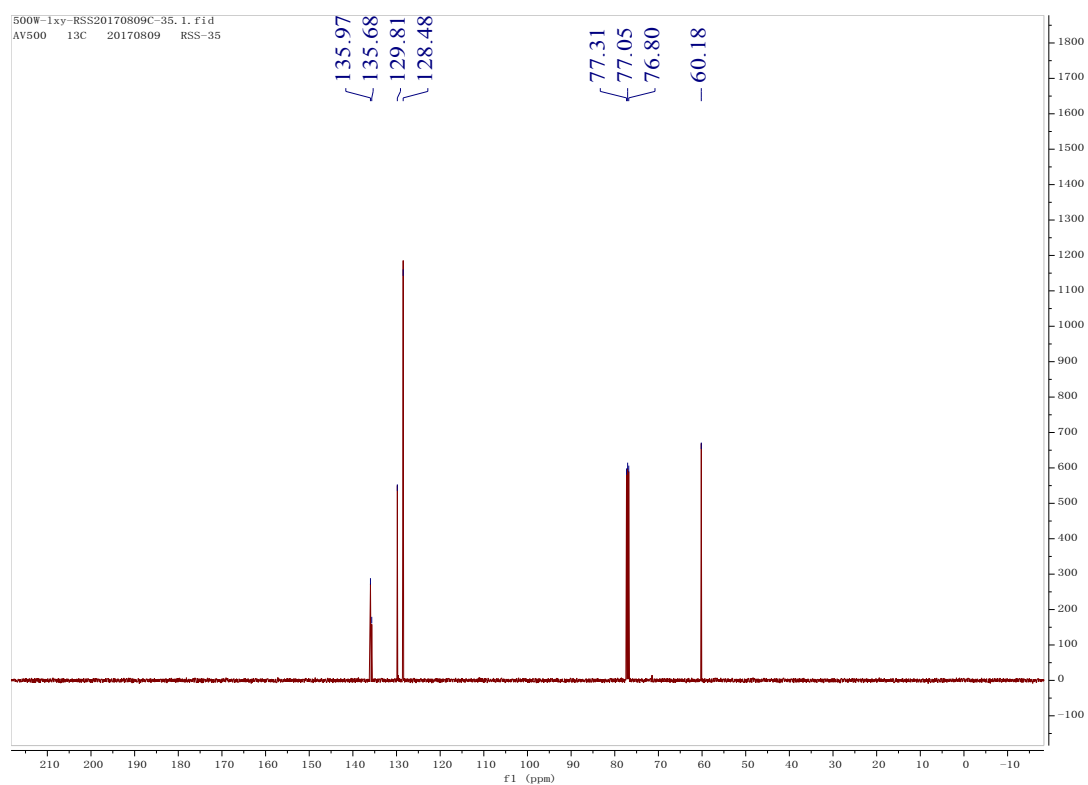
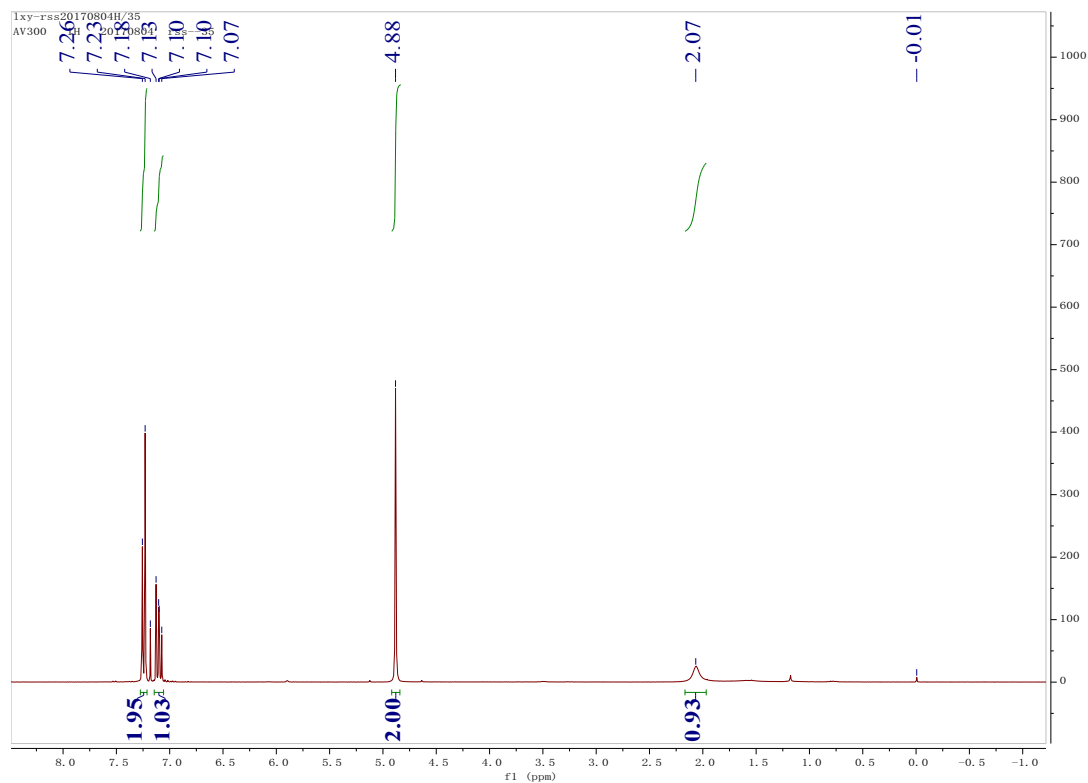


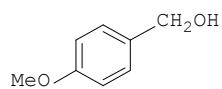
^1H NMR (300 MHz, CDCl_3 , δ): 7.36–6.93 (m, *Ar*, 4H), 4.67 (s, CH_2 , 2H), 1.96 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 160.61 (d, $J = 147$ Hz, Ar-C), 129.31(t, $J = 4.50$ Hz, Ar-C), 127.81(d, $J = 9$ Hz, Ar-C), 124.22 (d, $J = 2.25$ Hz, Ar-C), 115.24(d, $J = 6.38$ Hz, Ar-C), 59.26 (CH_2).



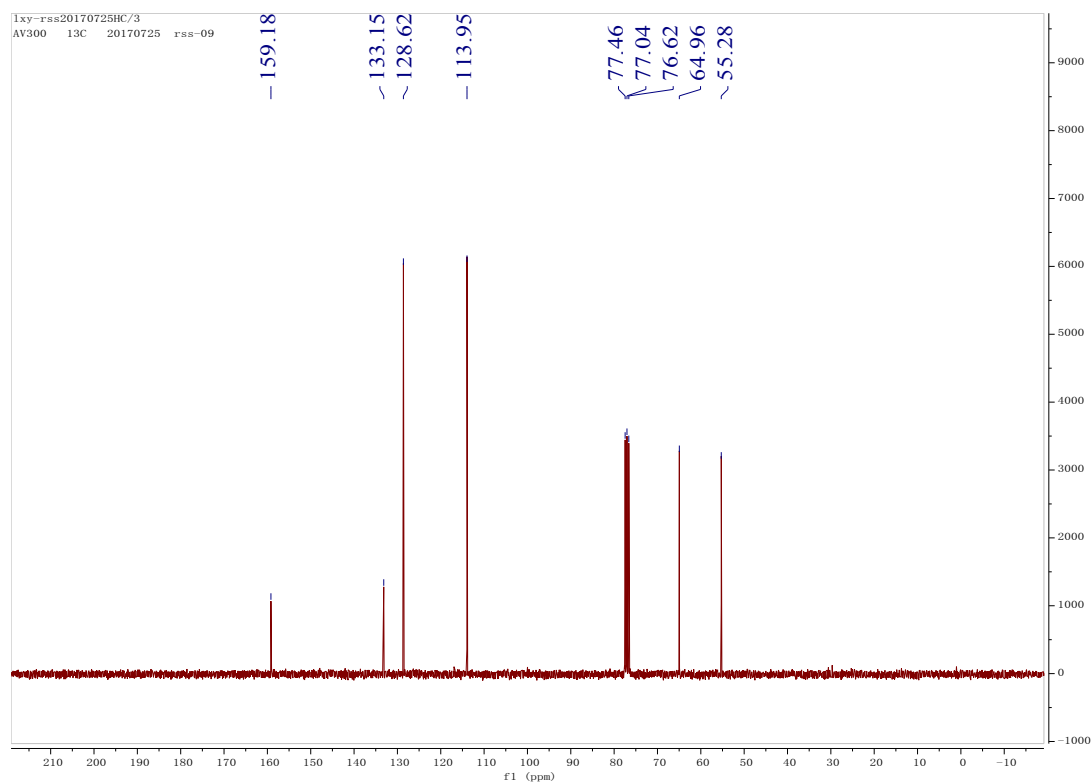
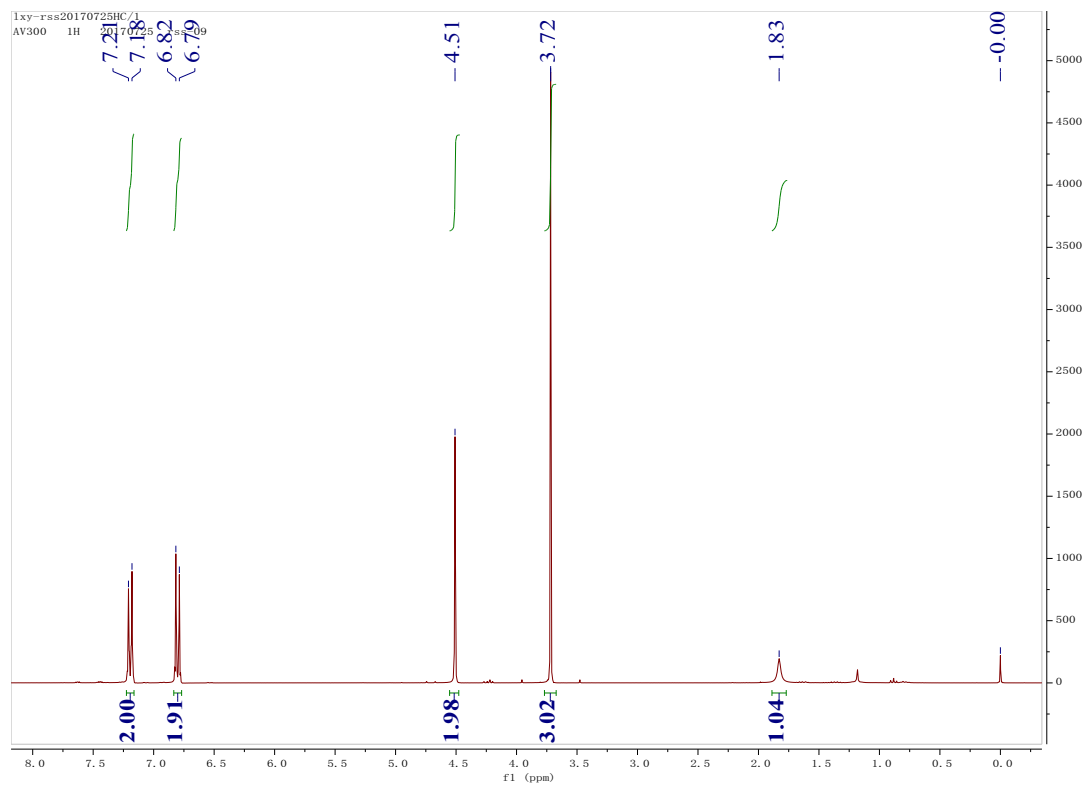


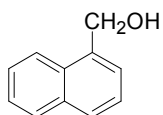
^1H NMR (300 MHz, CDCl_3 , δ): 7.26–7.07 (m, *Ar*, 3H), 4.88 (s, CH_2 , 2H), 2.07 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 135.97, 135.68, 129.81, 128.48 (Ar-C), 60.18 (CH_2).



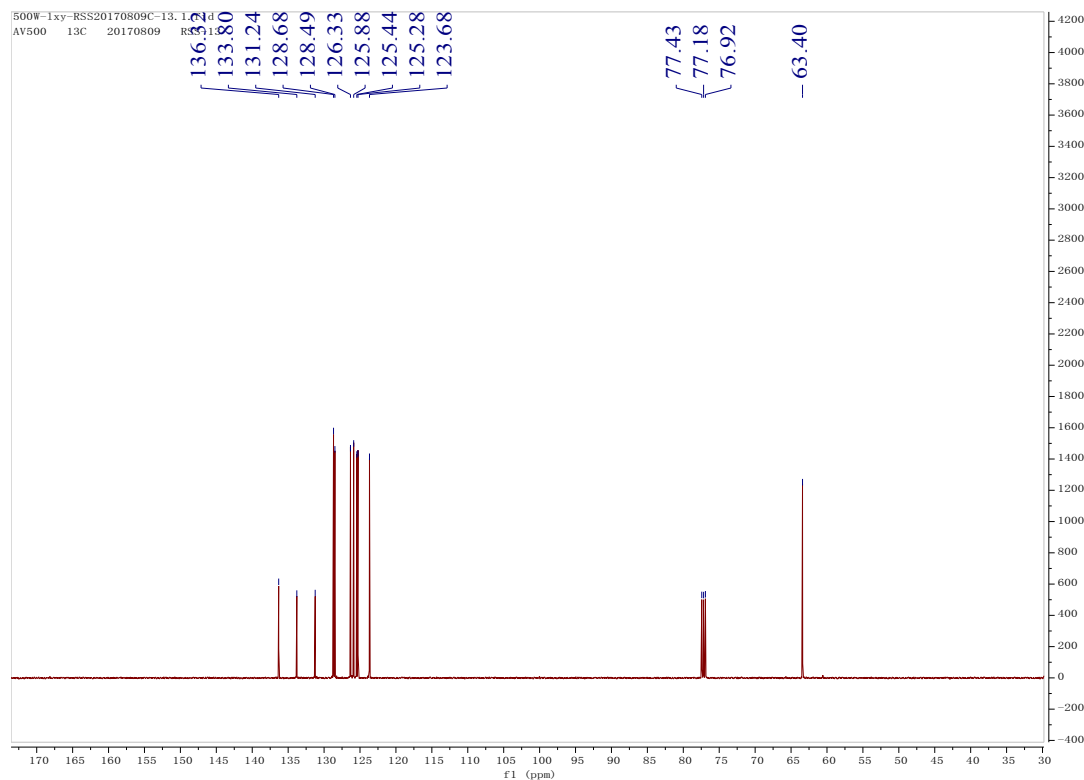
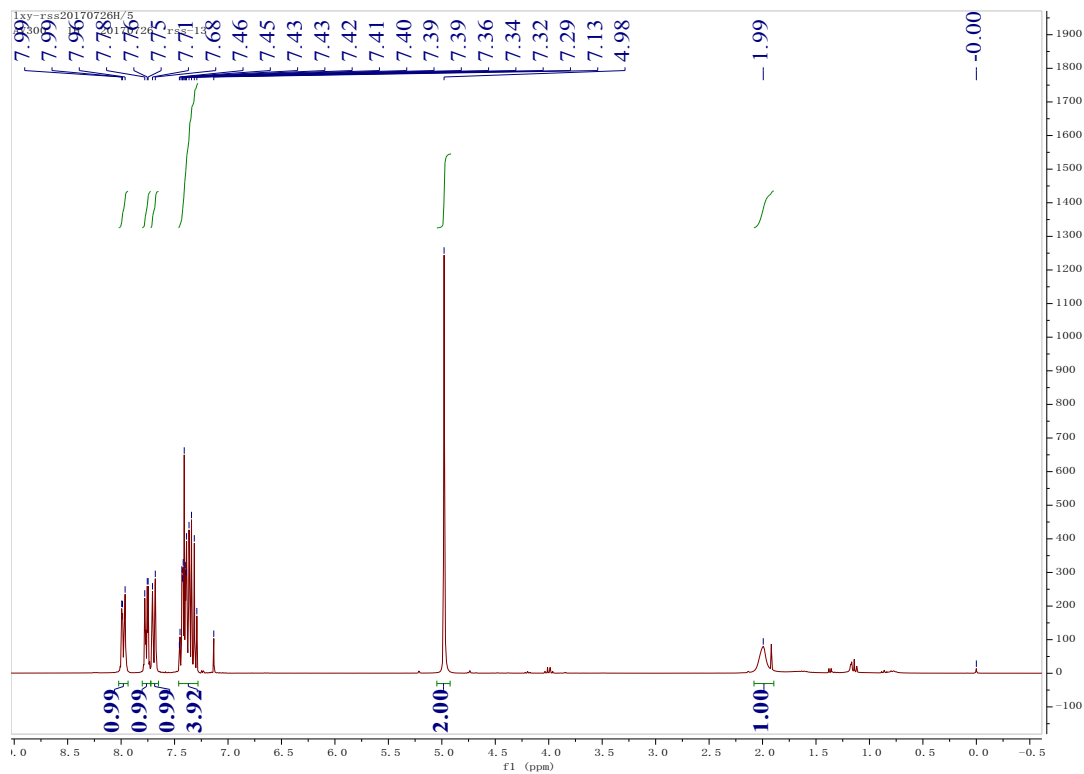


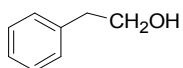
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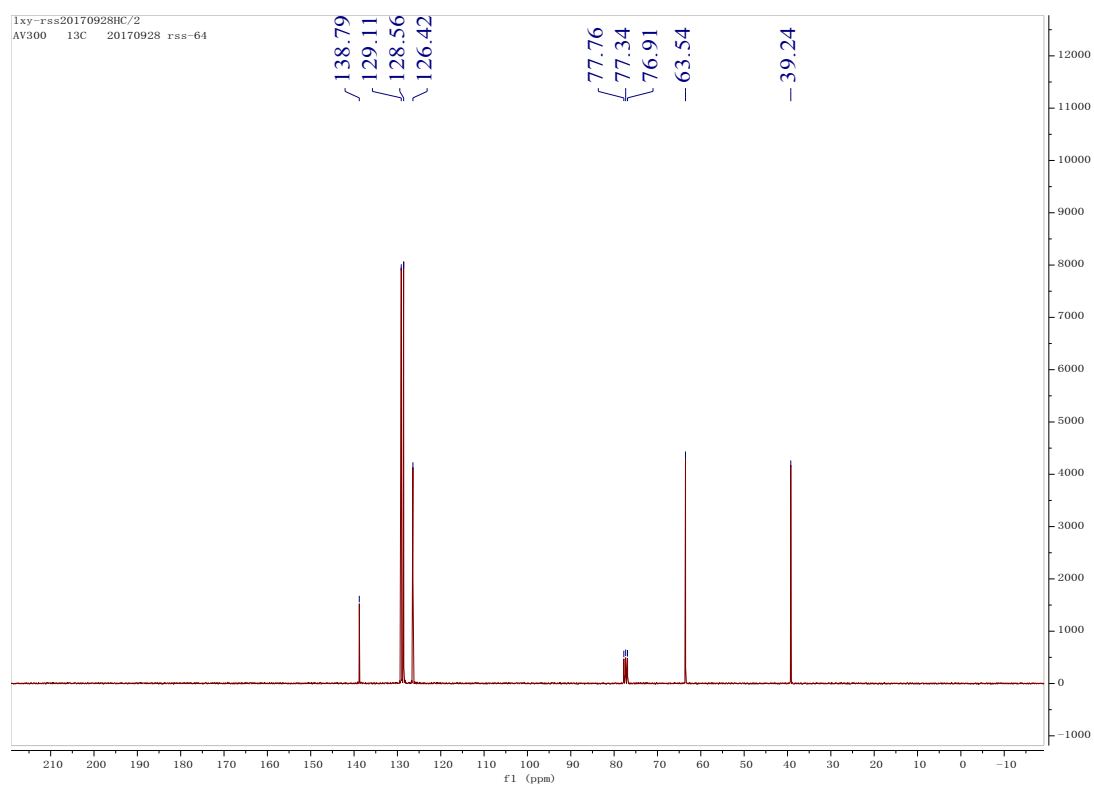
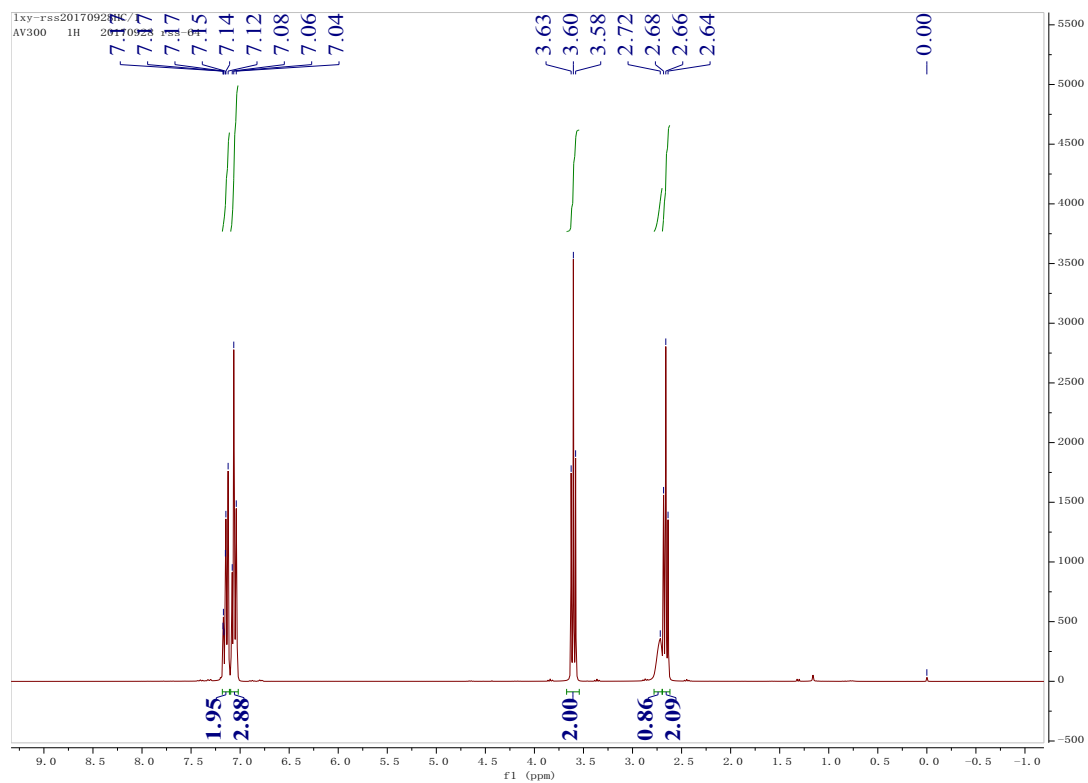


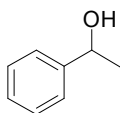
^1H NMR (300 MHz, CDCl_3 , δ): 7.99–7.13 (m, *Ar*, 7H), 4.98 (s, CH_2 , 2H), 1.99 (s, *OH*, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 136.32, 133.80, 131.24, 128.68, 128.49, 126.33, 125.88, 125.44, 125.28, 123.68 (Ar-C), 63.40 (CH_2).



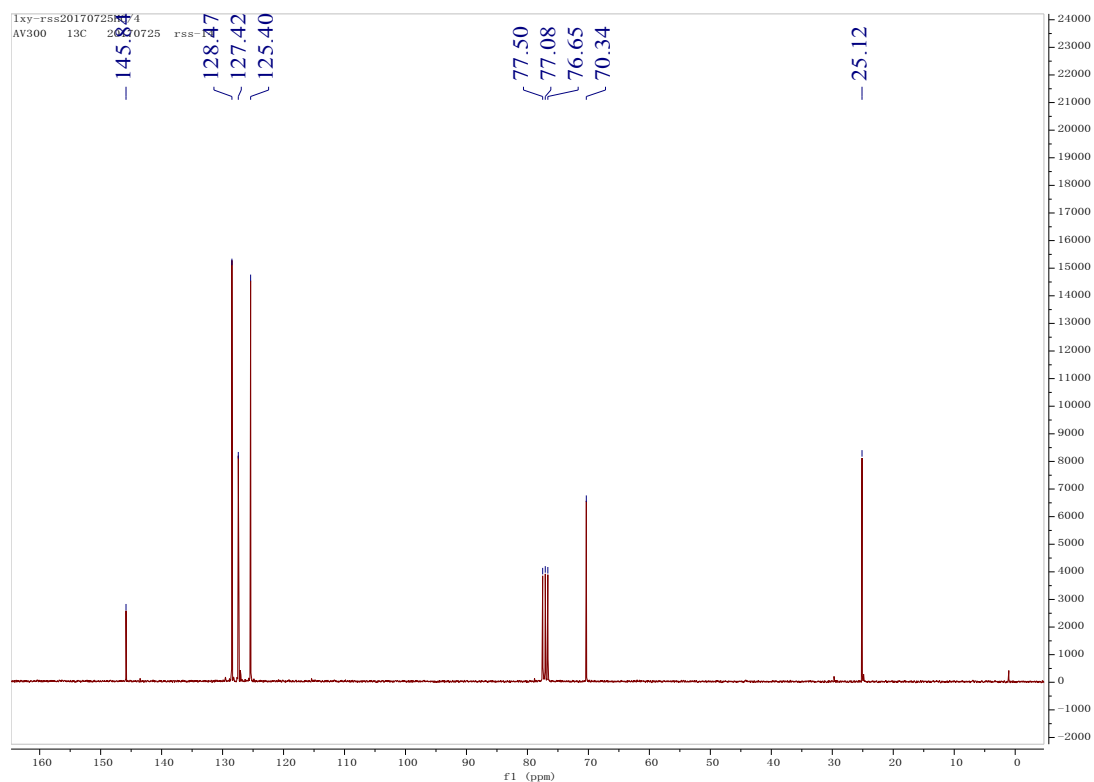
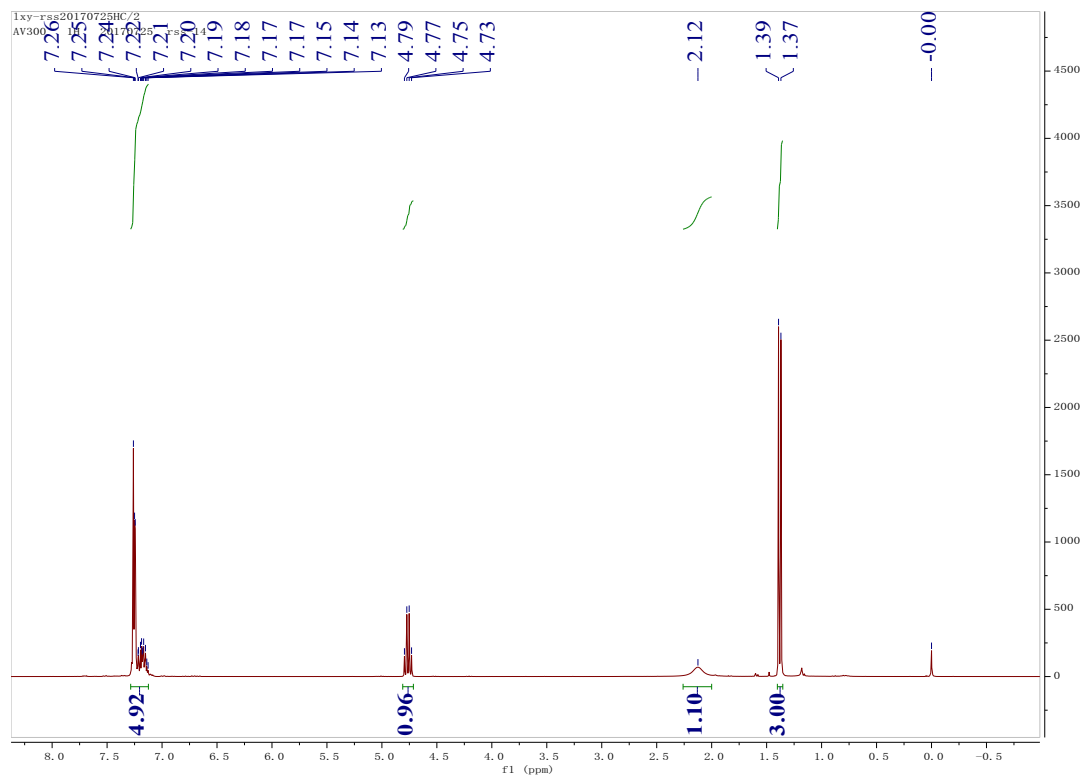


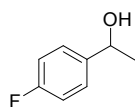
^1H NMR (300 MHz, CDCl_3 , δ): 7.17-7.04 (m, Ar-H, 5H), 3.60 (t, CH_2 , 2H), 2.72 (s, OH, 1H), 2.66 (t, CH_2 , 2H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 138.79, 129.11, 128.56, 126.42 (Ar-C), 63.54 (CH_2), 39.24 (CH_2).



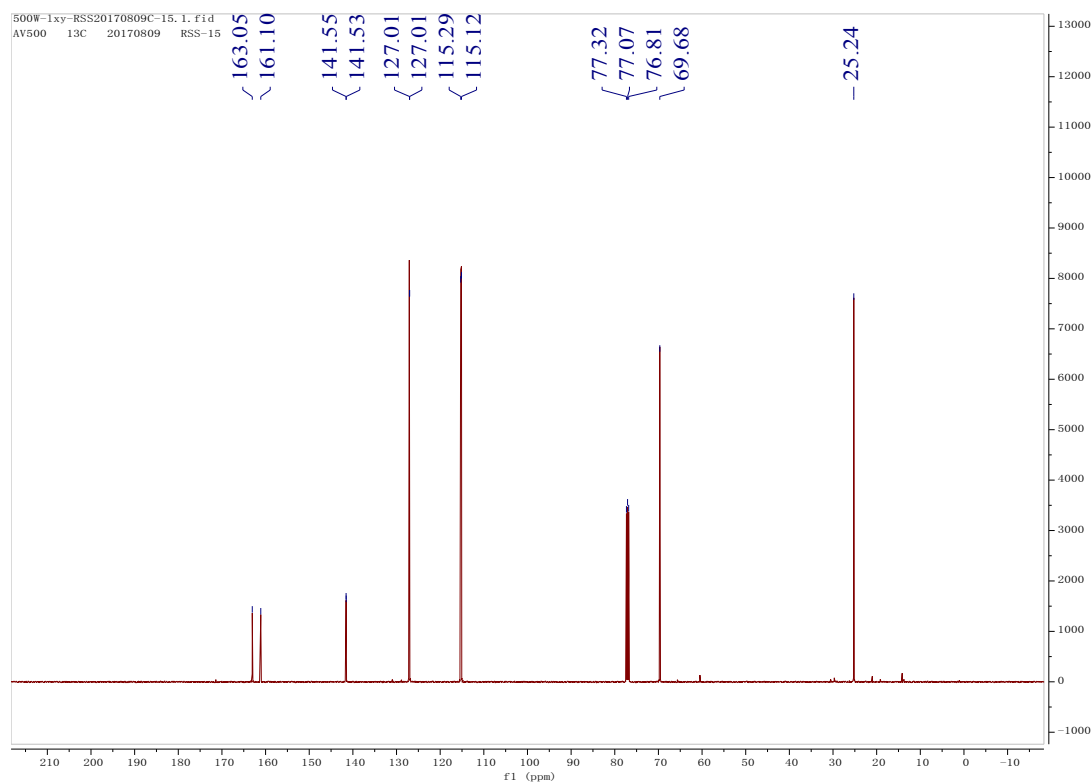
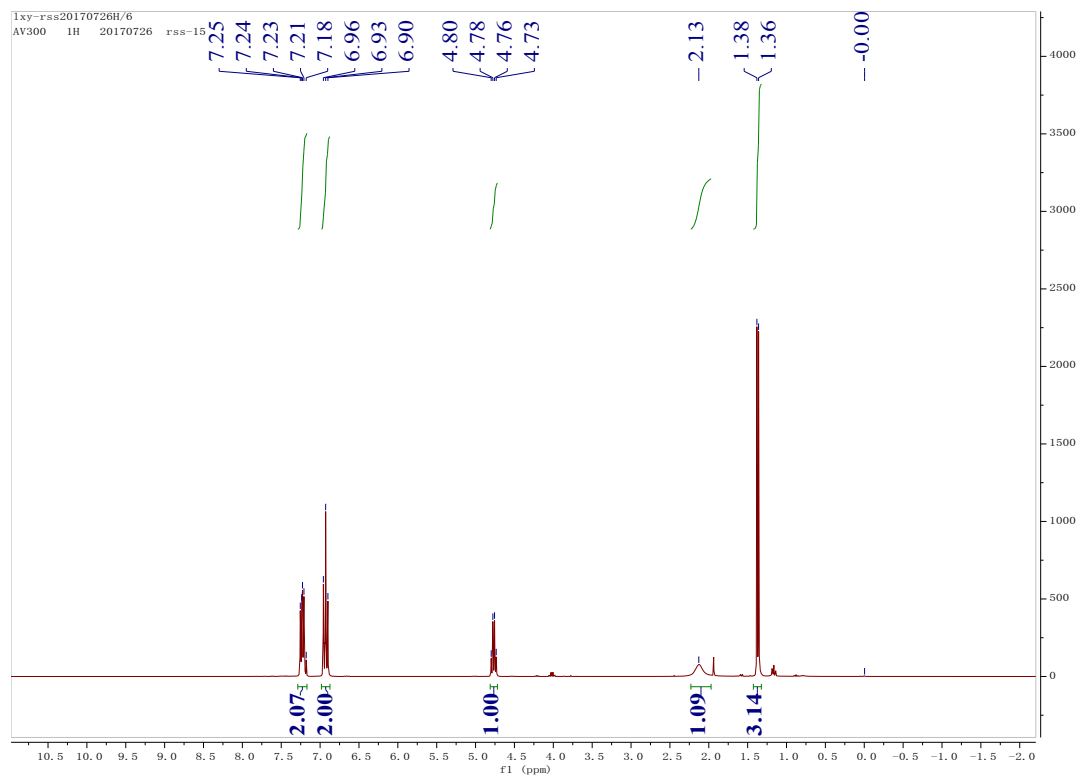


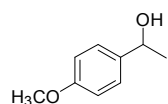
^1H NMR (300 MHz, CDCl_3 , δ): 7.26–7.13 (m, *Ar*, 5H), 4.76 (q, *CH*, 1H), 2.12 (s, *OH*, 1H), 1.38 (d, *CH*₃, 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 145.84, 128.47, 127.40, 125.42 (*Ar-C*), 70.34 (*CH*), 25.12 (*CH*₃).



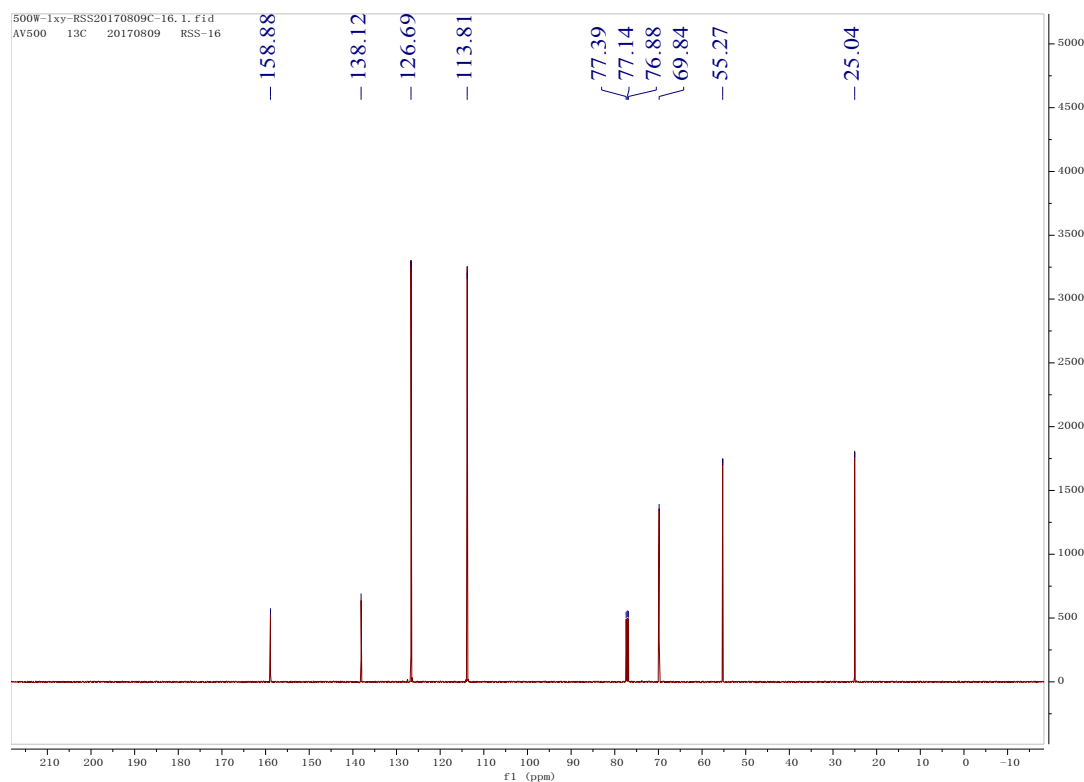
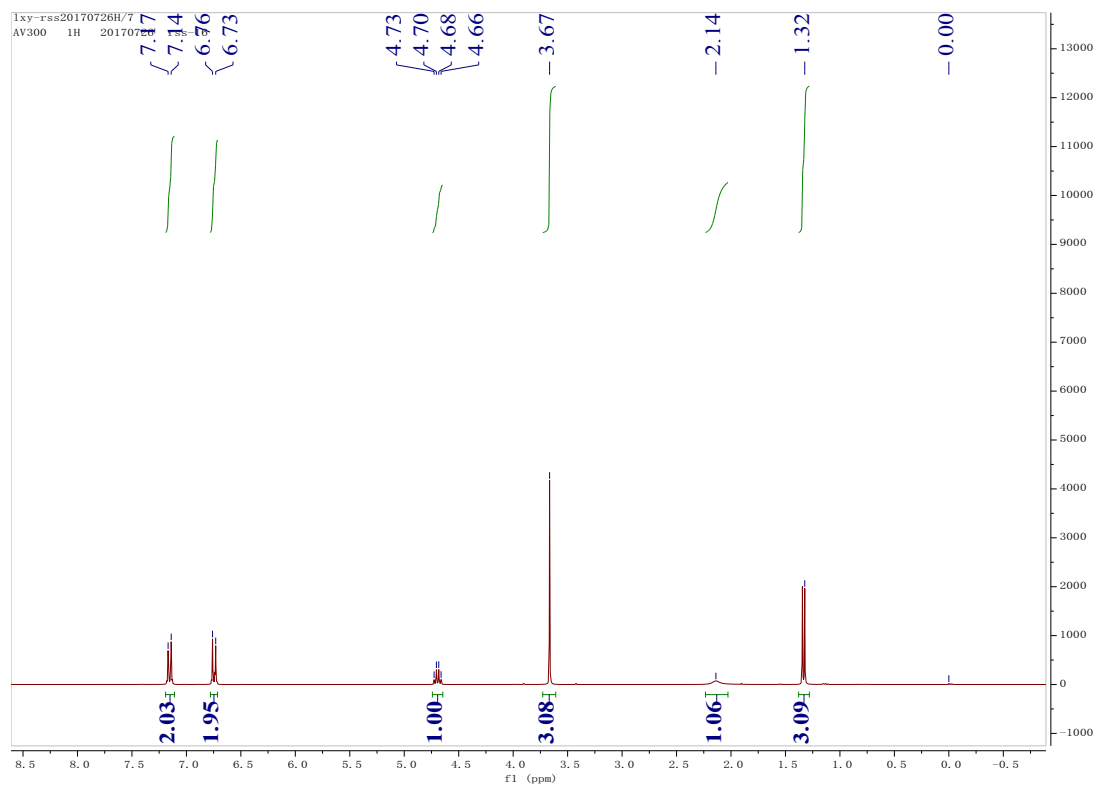


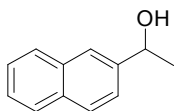
^1H NMR (300 MHz, CDCl_3 , δ): 7.25–6.90 (m, *Ar*, 4H), 4.77 (q, *CH*, 1H), 2.13 (s, *OH*, 1H), 1.37 (d, CH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 162.07 (d, $J = 146.25$ Hz, Ar-C), 141.54 (d, $J = 1.5$ Hz, Ar-C), 127.01 (d, Ar-C), 115.21 (d, $J = 12.75$ Hz, Ar-C), 69.68 (CH), 25.24 (CH_3).



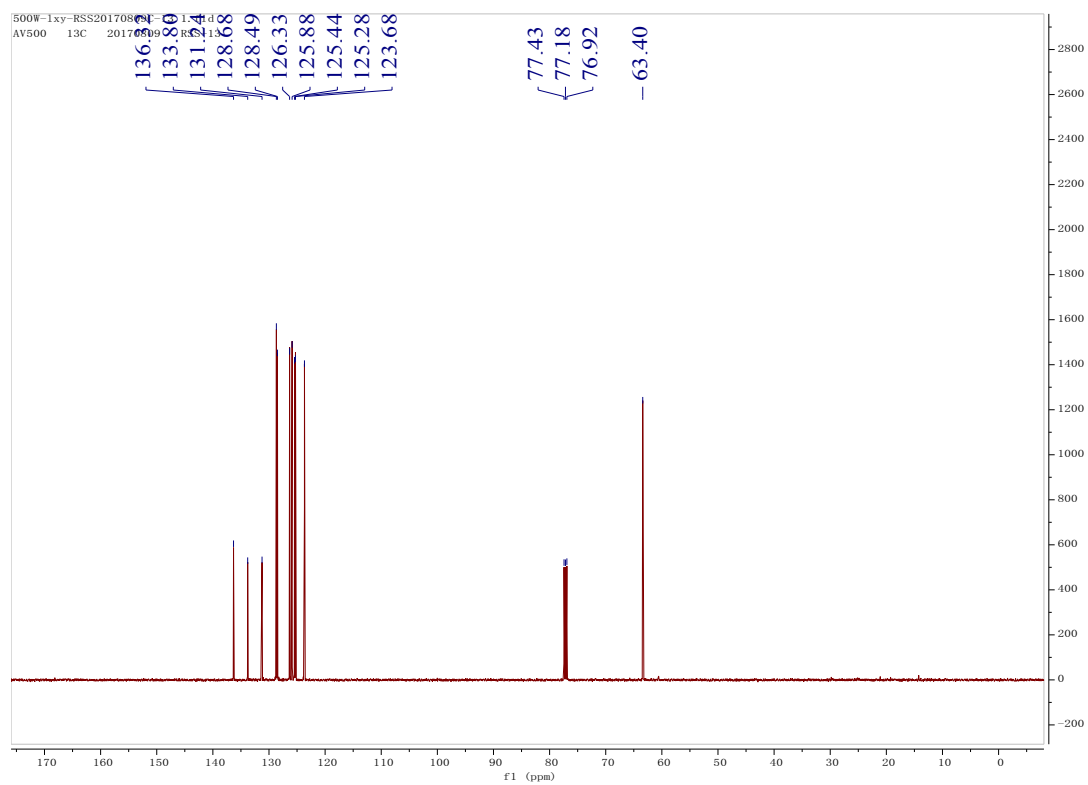
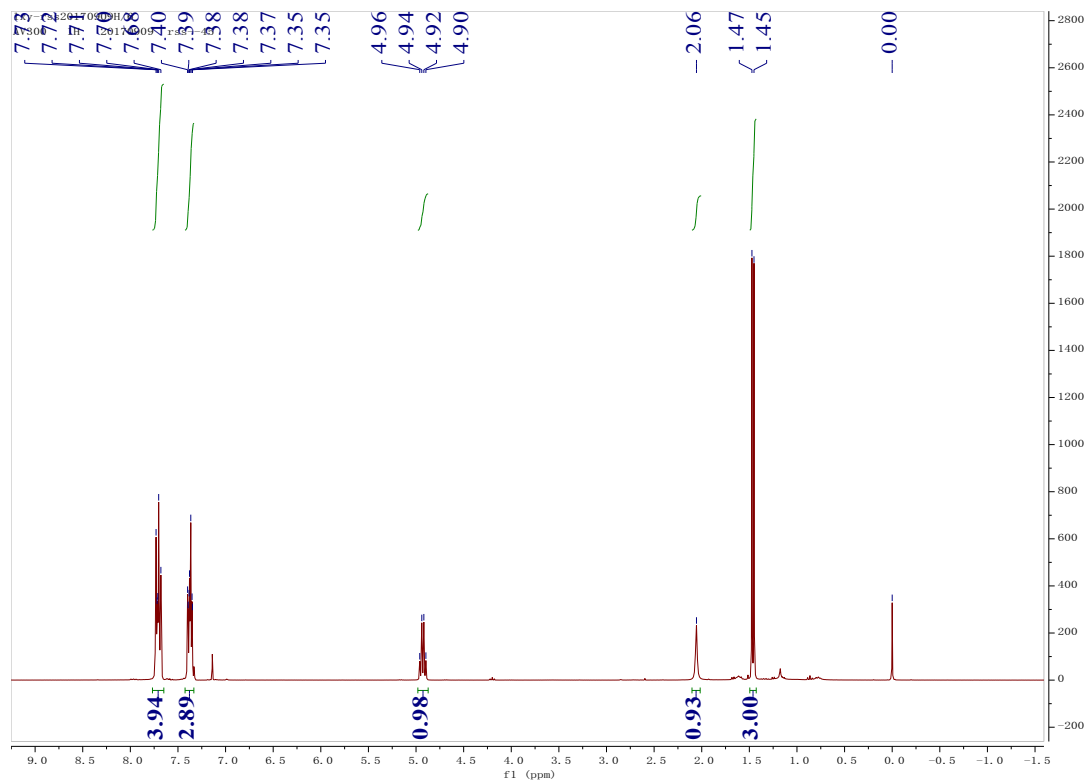


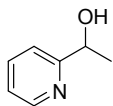
^1H NMR (300 MHz, CDCl_3 , δ): 7.17–6.73 (m, *Ar*, 4H), 4.69 (q, *CH*, 1H), 3.67 (s, OCH_3 , 3H), 2.14 (s, *OH*, 1H), 1.32 (d, CH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 158.88, 138.12, 126.69, 113.81 (*Ar-C*), 69.84 (*CH*), 55.27 (OCH_3), 25.04 (CH_3).



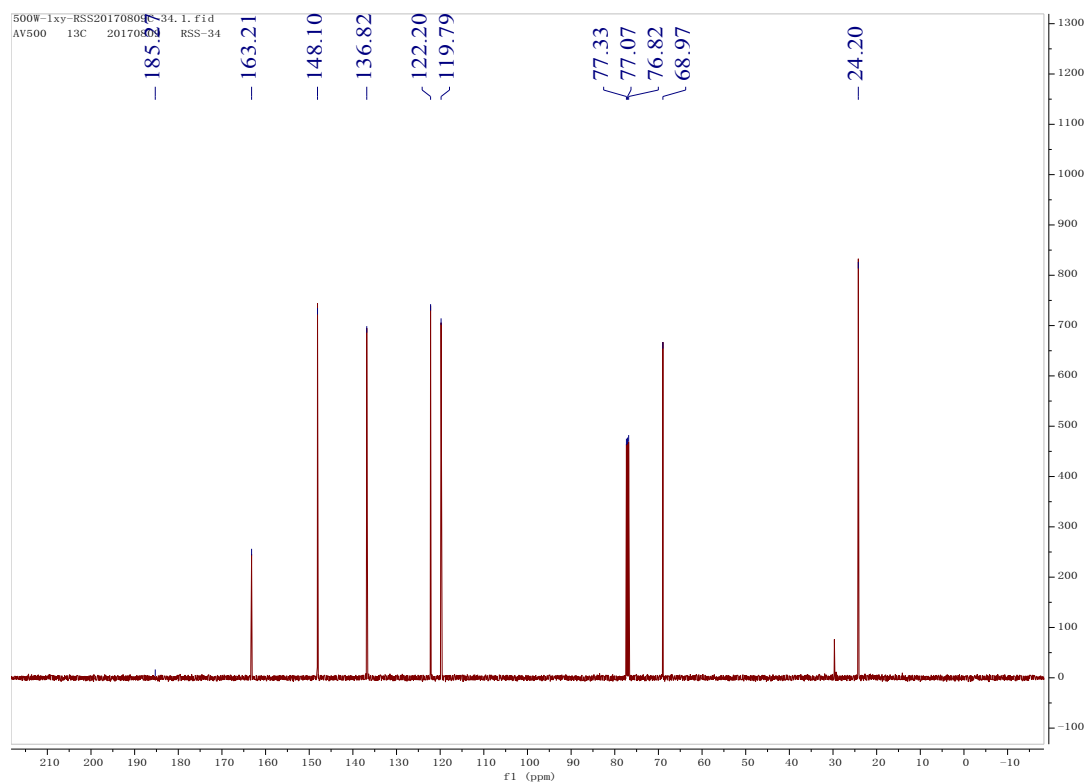
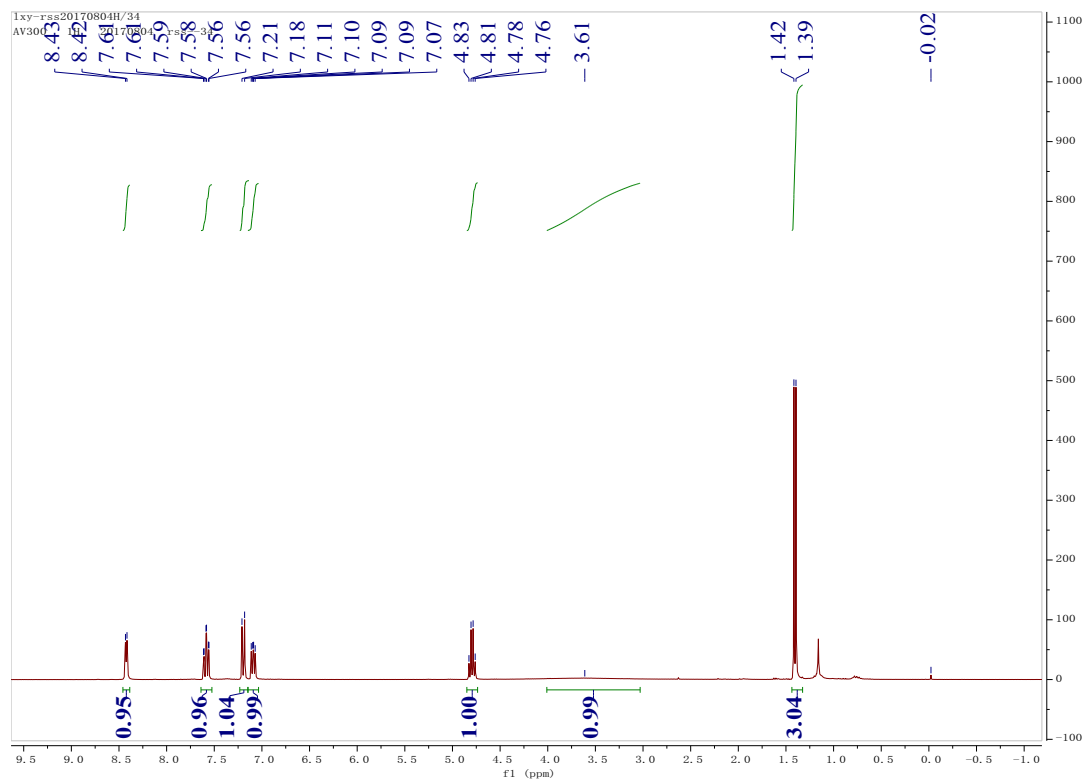


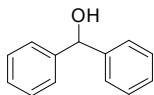
^1H NMR (300 MHz, CDCl_3 , δ): 7.73–7.35 (m, Ar, 7H), 4.93 (q, CH, 1H), 2.06 (s, OH, 1H), 1.46 (d, CH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 136.32, 133.80, 131.24, 128.68, 126.33, 125.88, 125.44, 125.28, 123.68, (Ar-C) 63.40 (CH).



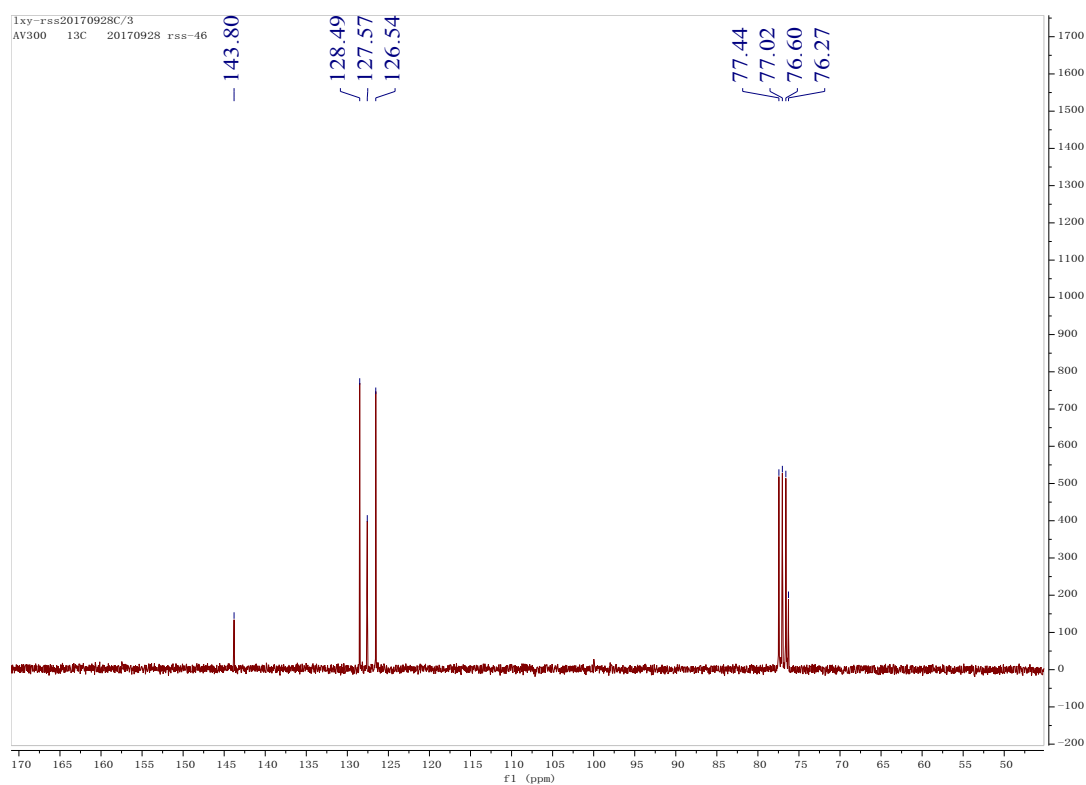
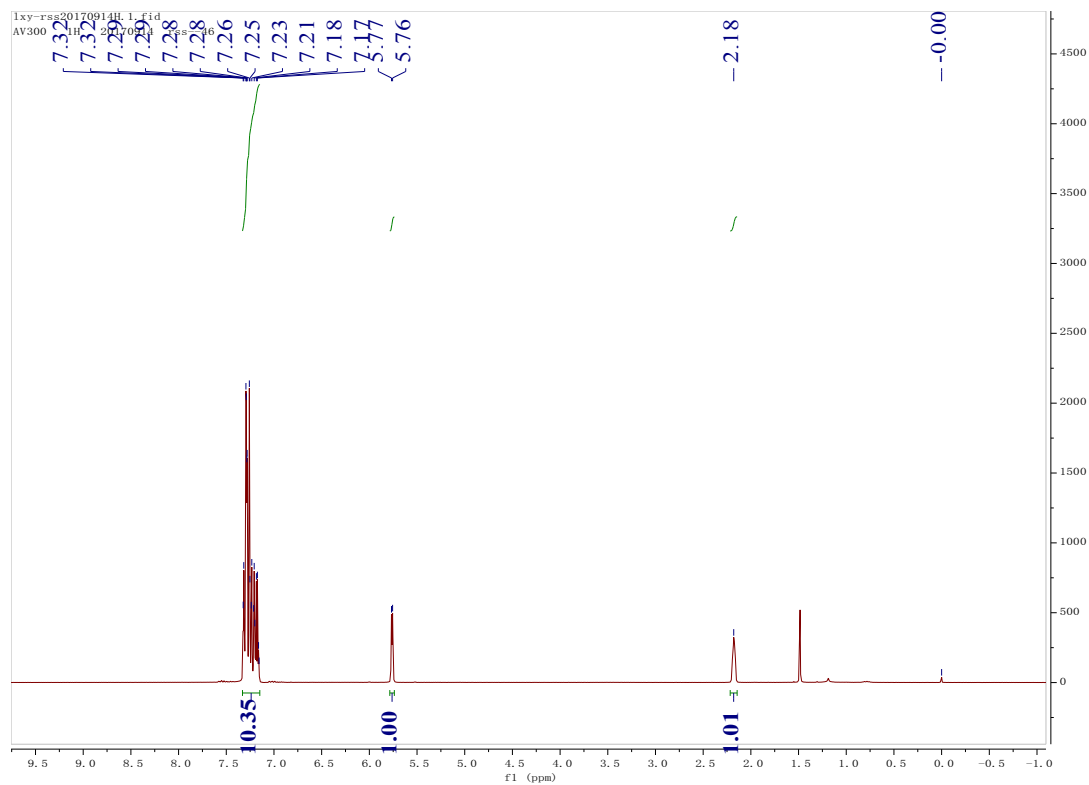


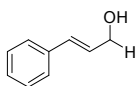
^1H NMR (300 MHz, CDCl_3 , δ): 8.43–7.07 (m, *Ar*, 4H), 4.83–4.76 (q, *CH*, 1H), 3.61 (s, *OH*, 1H), 1.42–1.39 (d, CH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 185.27, 163.21, 148.10, 136.82, 122.20, 119.79 (*Ar-C*), 68.97 (*CH*), 24.20 (CH_3).



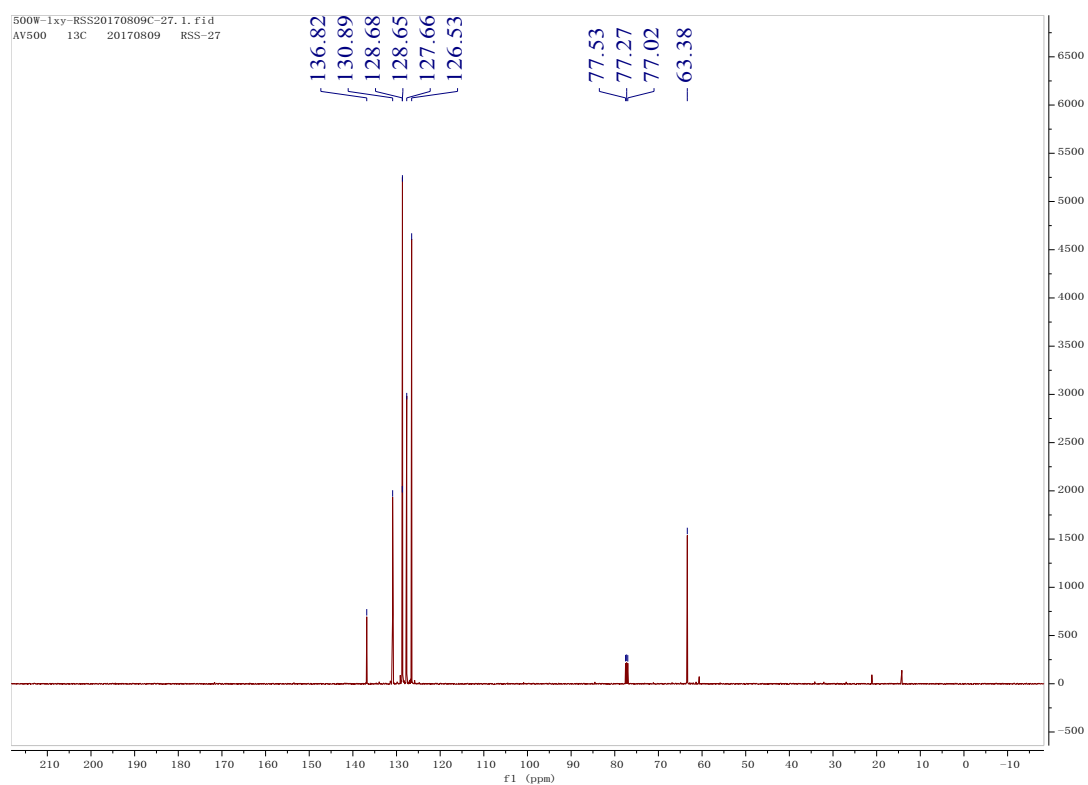
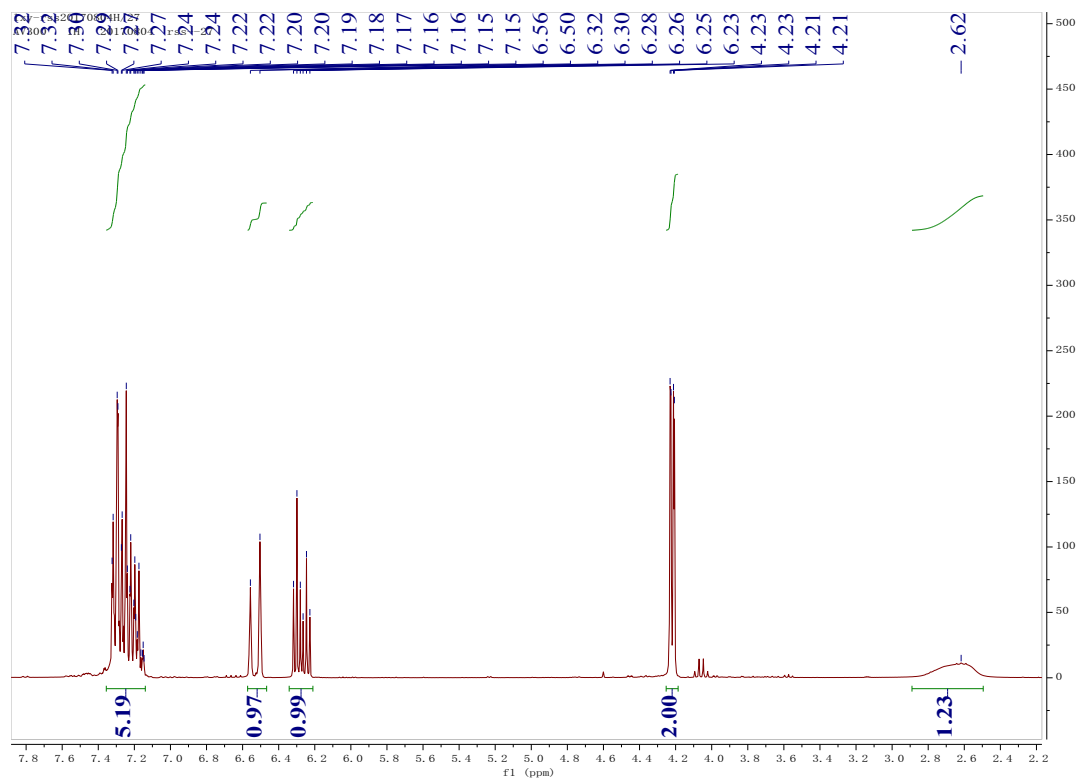


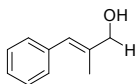
^1H NMR (300 MHz, CDCl_3 , δ): 7.32–7.17 (m, *Ar*, 10H), 5.76 (d, *CH*, 1H), 2.18 (s, *OH*, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 143.80, 128.49, 127.57, 126.54 (Ar-C), 76.27 (CH).



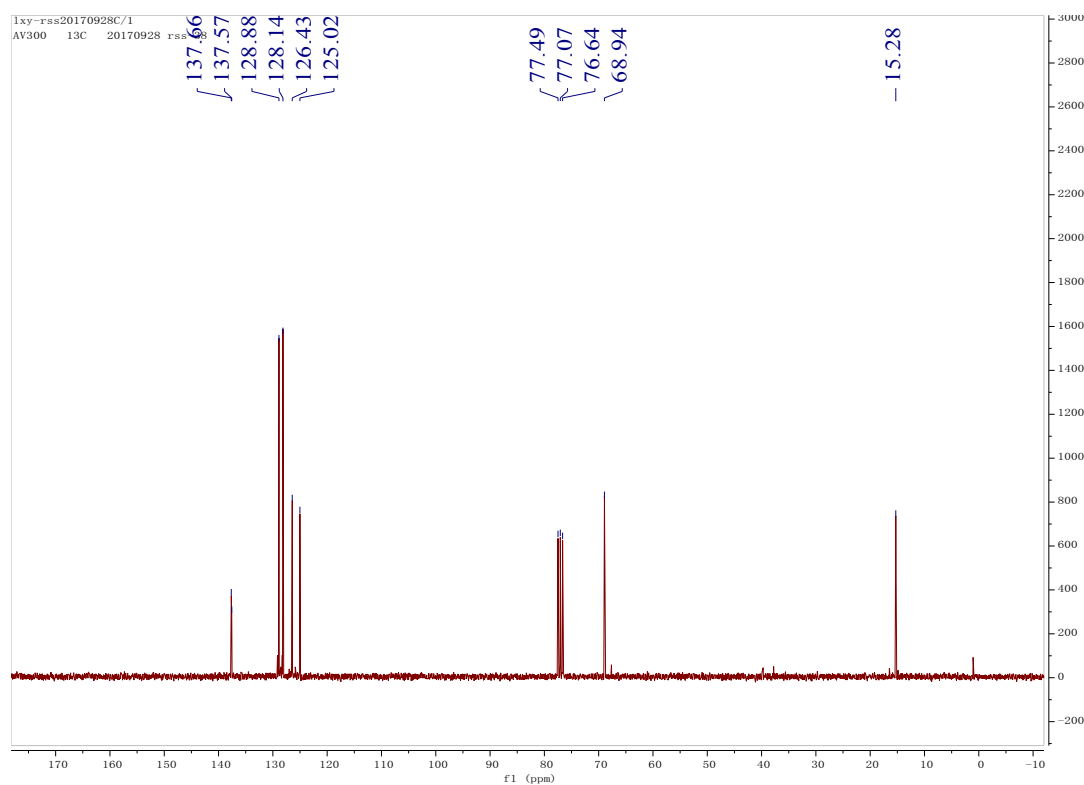
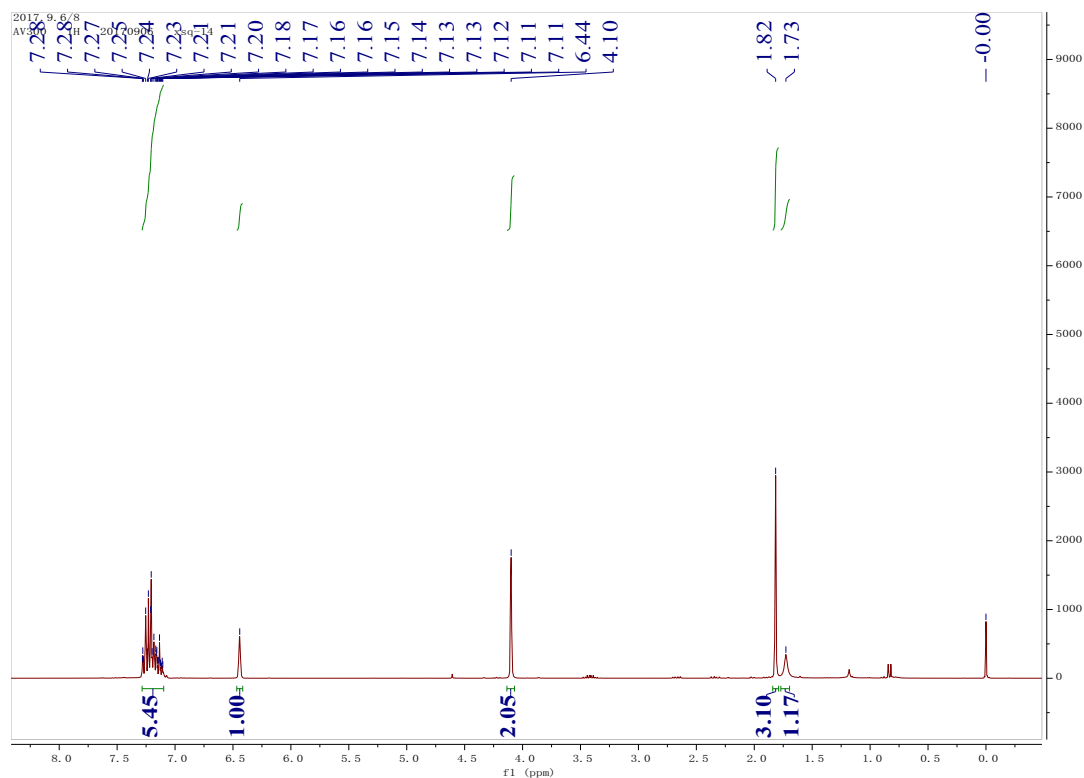


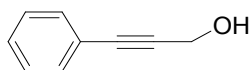
^1H NMR (300 MHz, CDCl_3 , δ): 7.32–7.15 (m, *Ar*, 5H), 6.53 (d, *HC=C*, 1H), 6.27 (m, *C=CH*, 1H), 4.22 (dd, *CH*₂, 2H), 2.62 (s, *OH*, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 136.82, 130.89, 128.68, 128.65 (Ar-C), 127.66, 126.53 (*C=C*), 63.38 (*CH*₂).



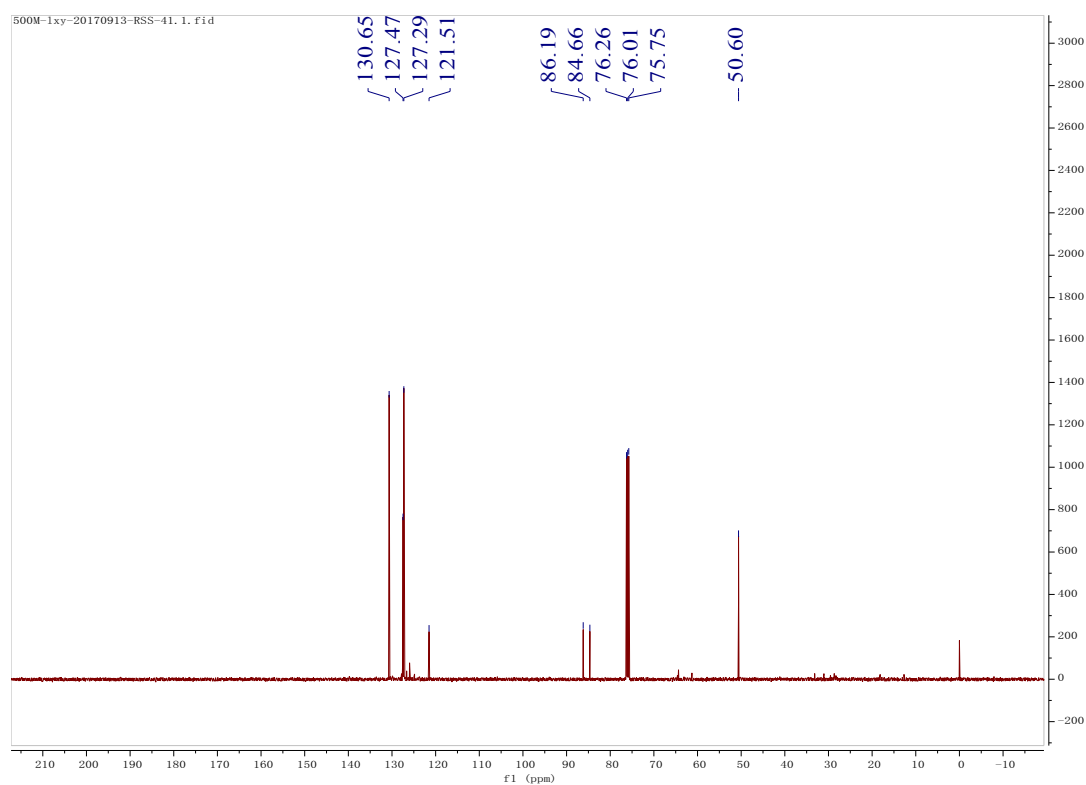
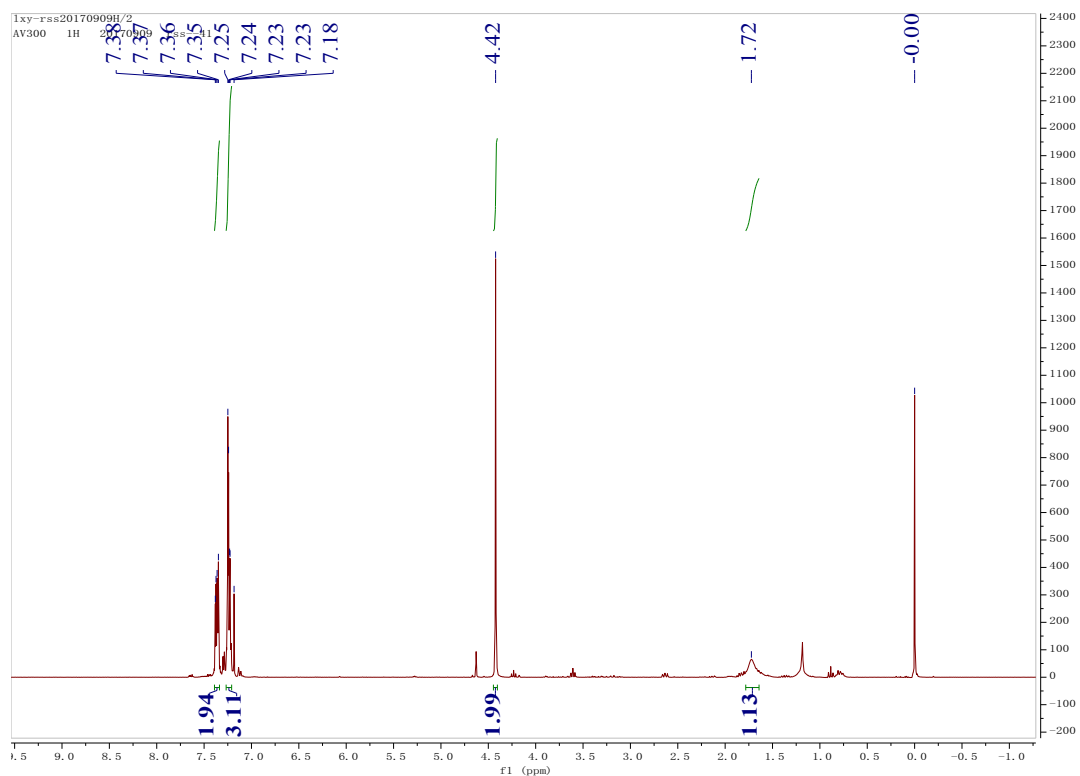


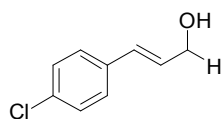
^1H NMR (300 MHz, CDCl_3 , δ): 7.28-7.11 (m, *Ar*, 5H), 6.44 (d, $\text{HC}=\text{C}$, 1H), 4.10 (dd, CH_2 , 2H), 1.82 (s, CH_3 , 3H), 1.73 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 137.66, 137.57, 128.88, 128.14 (*Ar-C*), 126.43, 125.02 ($\text{C}=\text{C}$), 68.94 (CH_2), 15.28 (CH_3).



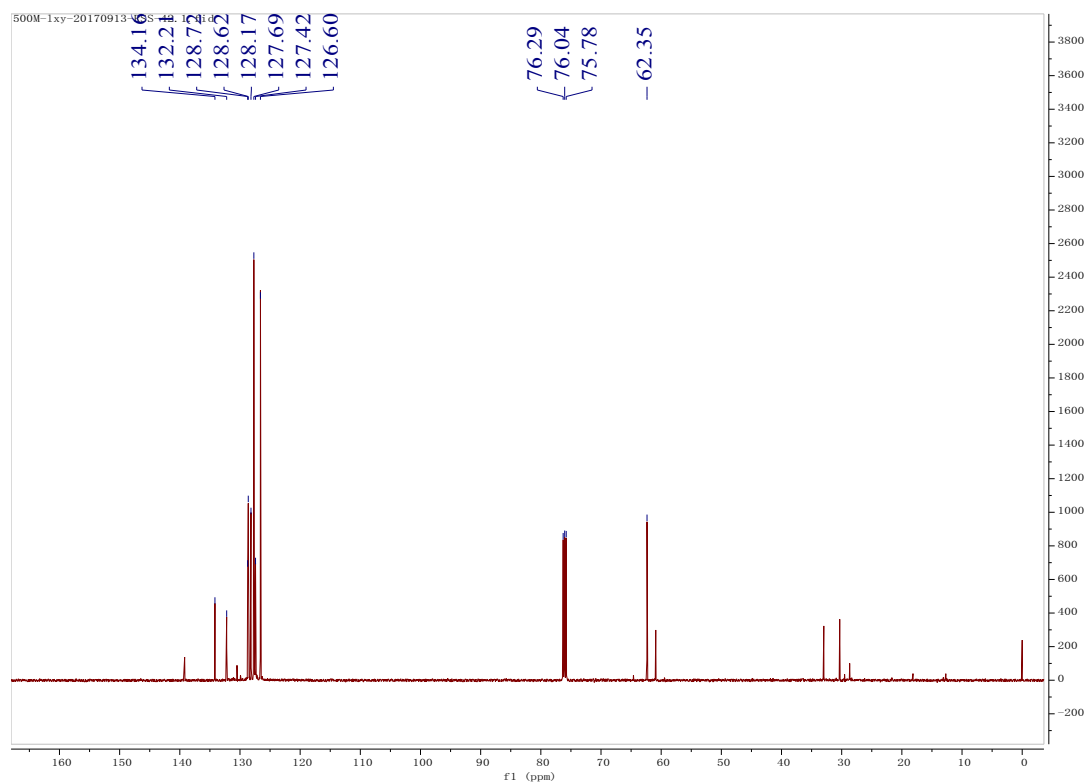
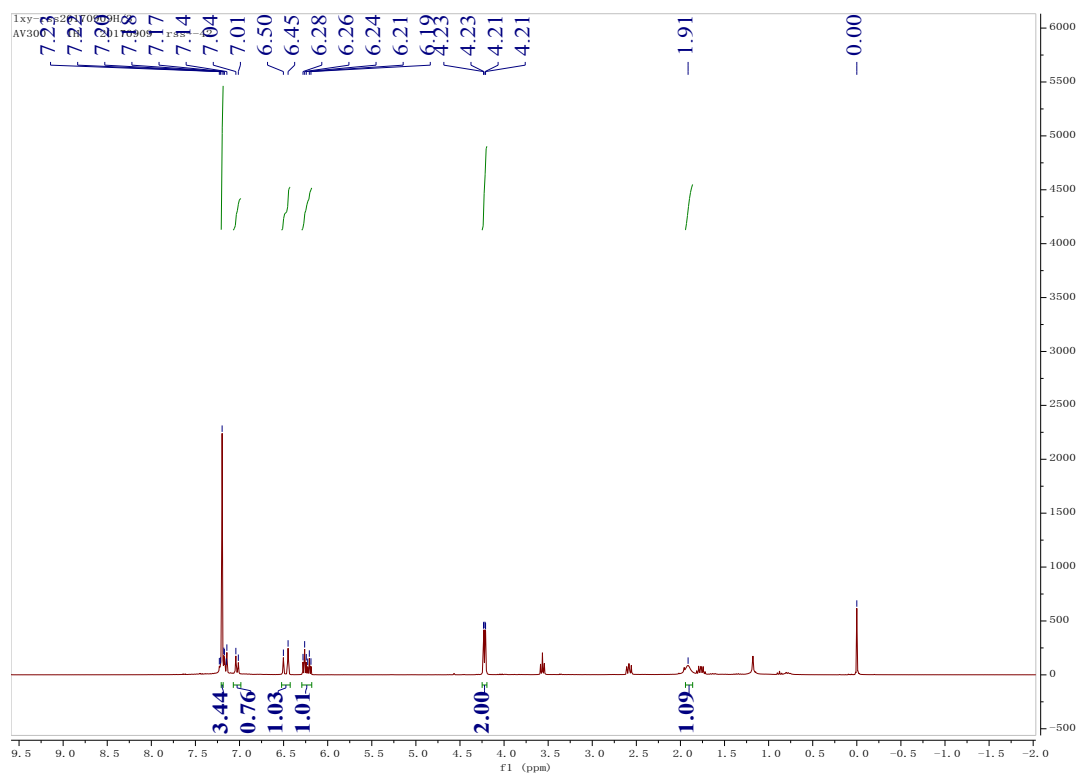


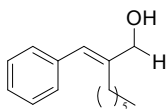
^1H NMR (300 MHz, CDCl_3 , δ): 7.38-7.18 (m, *Ar*, 5H), 4.42 (s, CH_2 , 2H), 1.72 (s, *OH*, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 130.65, 127.47, 127.29, 121.51 (*Ar-C*), 86.19, 84.66 ($\text{C}\equiv\text{C}$), 50.60 (CH_2).



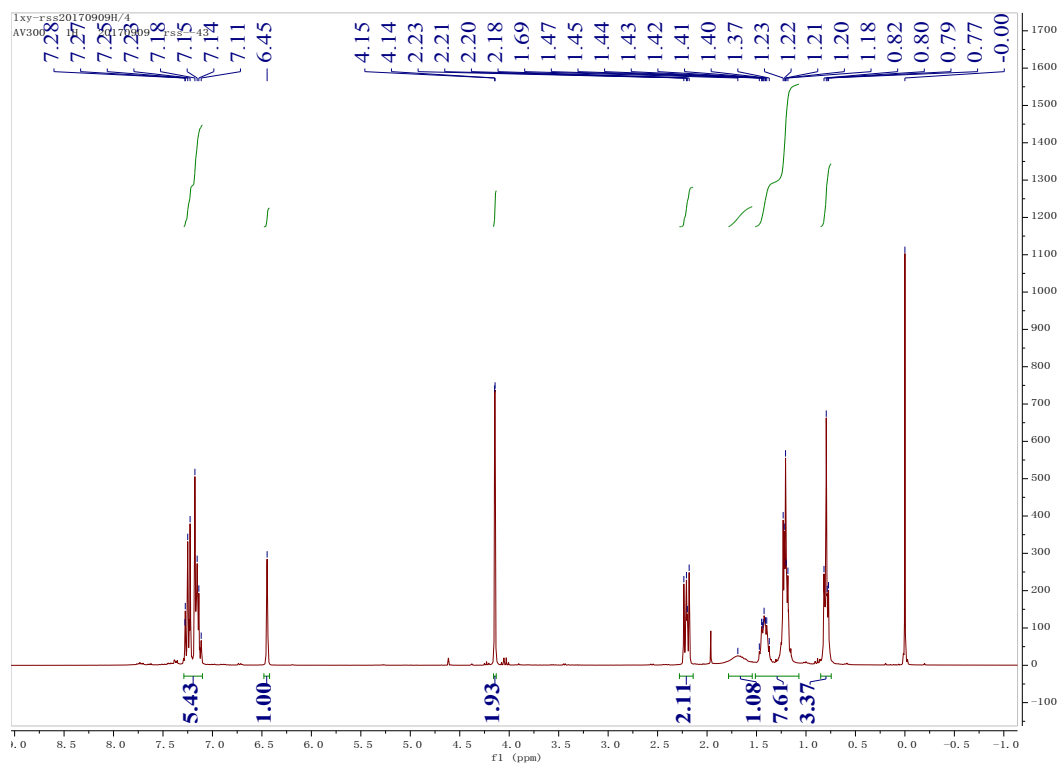


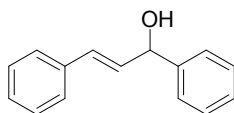
^1H NMR (300 MHz, CDCl_3 , δ): 7.23-7.01 (m, *Ar*, 4H), 6.47 (d, $\text{HC}=\text{C}$, 1H), 6.24 (m, $\text{C}=\text{CH}$, 1H), 4.22 (dd, CH_2 , 2H), 1.91 (s, OH , 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 134.16, 132.21, 128.72, 128.62, 128.17, 127.69 (Ar-C), 127.42, 126.60 ($\text{C}=\text{C}$), 62.35 (CH_2).



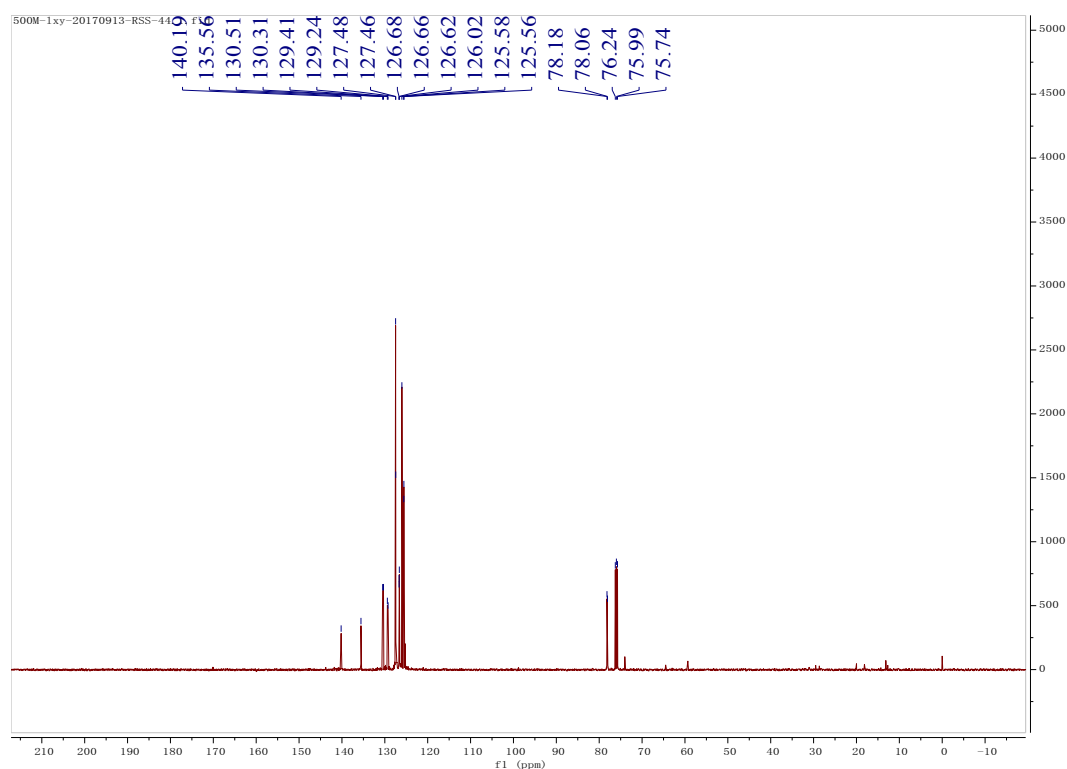
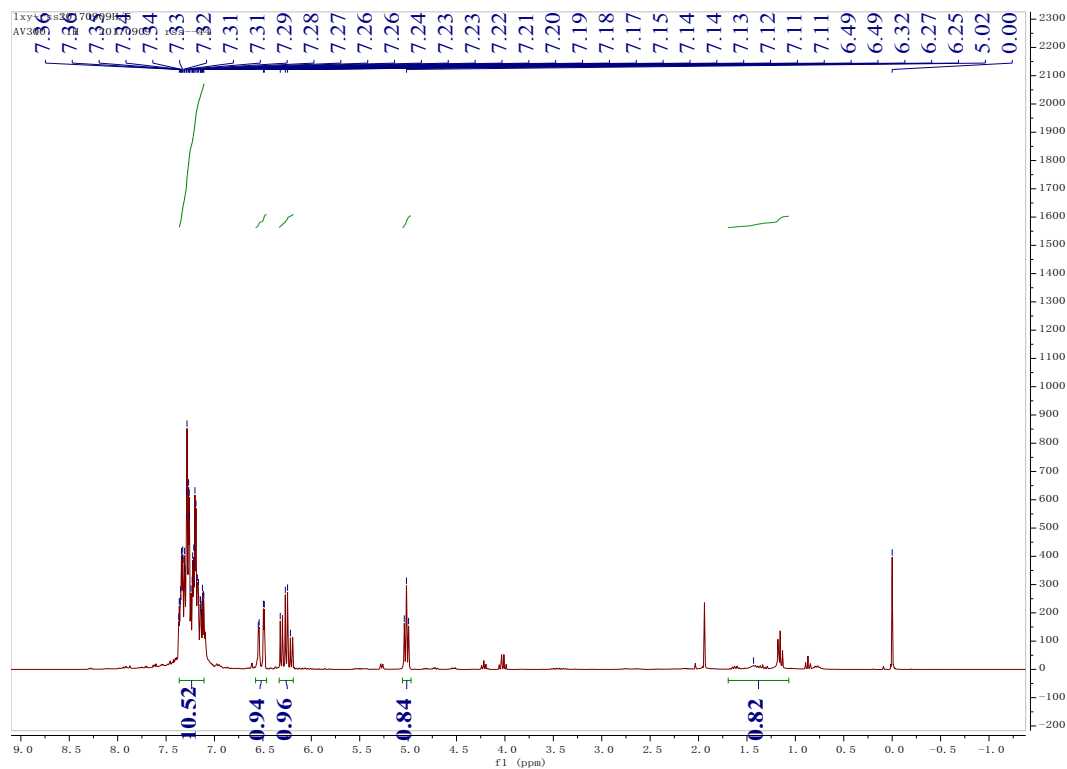


^1H NMR (300 MHz, CDCl_3 , δ): 7.28-7.11 (m, *Ar*, 5H), 6.45 (s, *HC=C*, 1H), 4.14 (s, CH_2 , 2H), 2.20 (m, CH_2 , 2H), 1.69 (s, *OH*, 1H), 1.47 -1.18(m, CH_2 , 8H), 0.79 (s, CH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 141.38, 136.55, 127.60, 127.14 (Ar-C), 125.40, 124.24 ($\text{C}=\text{C}$), 65.98 (CH_2), 31.00, 27.70, 27.04, 21.41, 12.99 (CH_2), 0.00 (CH_3).

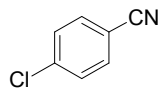




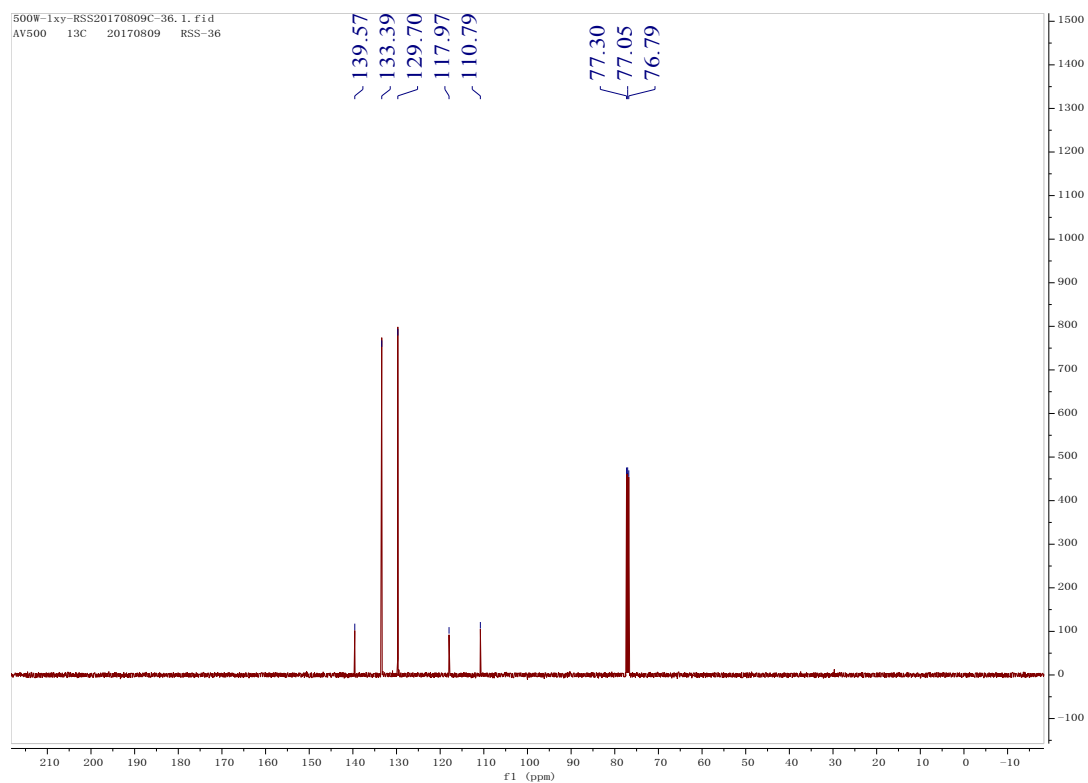
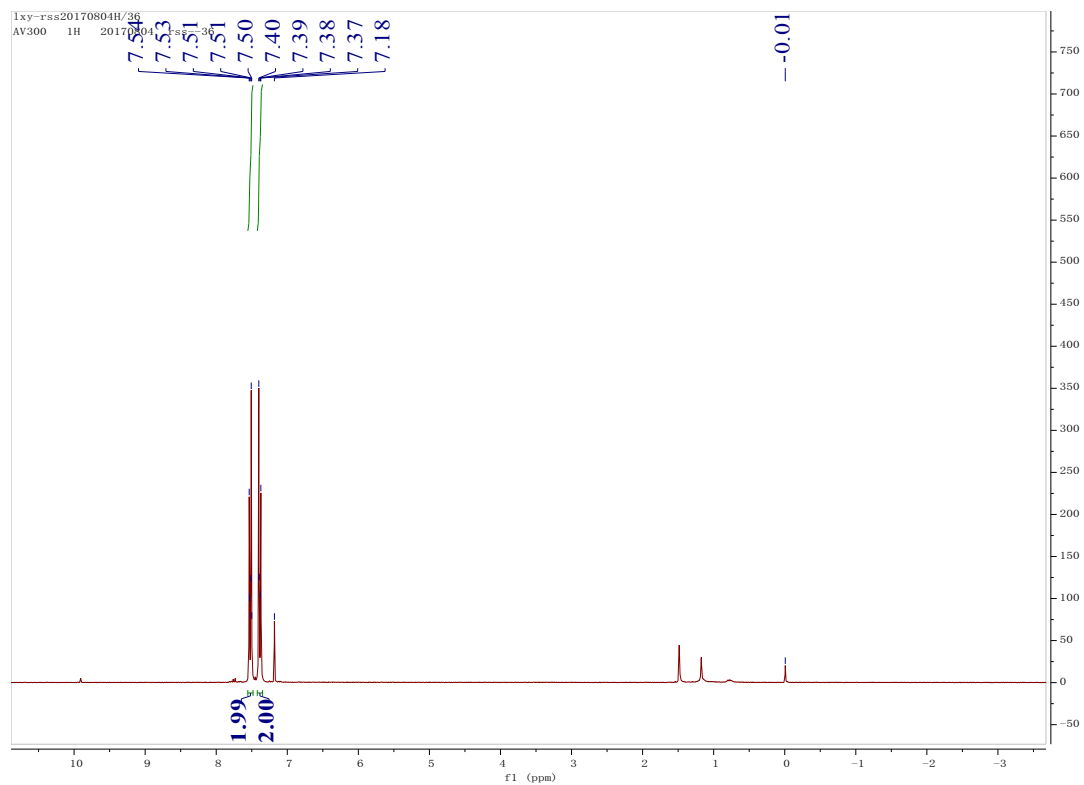
^1H NMR (300 MHz, CDCl_3 , δ): 7.36-7.11 (m, *Ar*, 5H), 6.52 (dd, *HC=C*, 1H), 6.26 (td, *C=CH*, 1H), 5.02 (t, *CH*, 1H), 1.43 (s, *OH*, 1H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 140.19, 135.56, 130.51, 130.31, 129.41, 129.24, 127.47, 126.67, 126.62 (Ar-C), 1276.02, 125.57 (*C=C*), 126.04 (*CH*), 75.74 (CH_2).

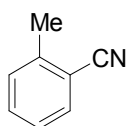


4. ^1H NMR and ^{13}C NMR spectrum of nitriles

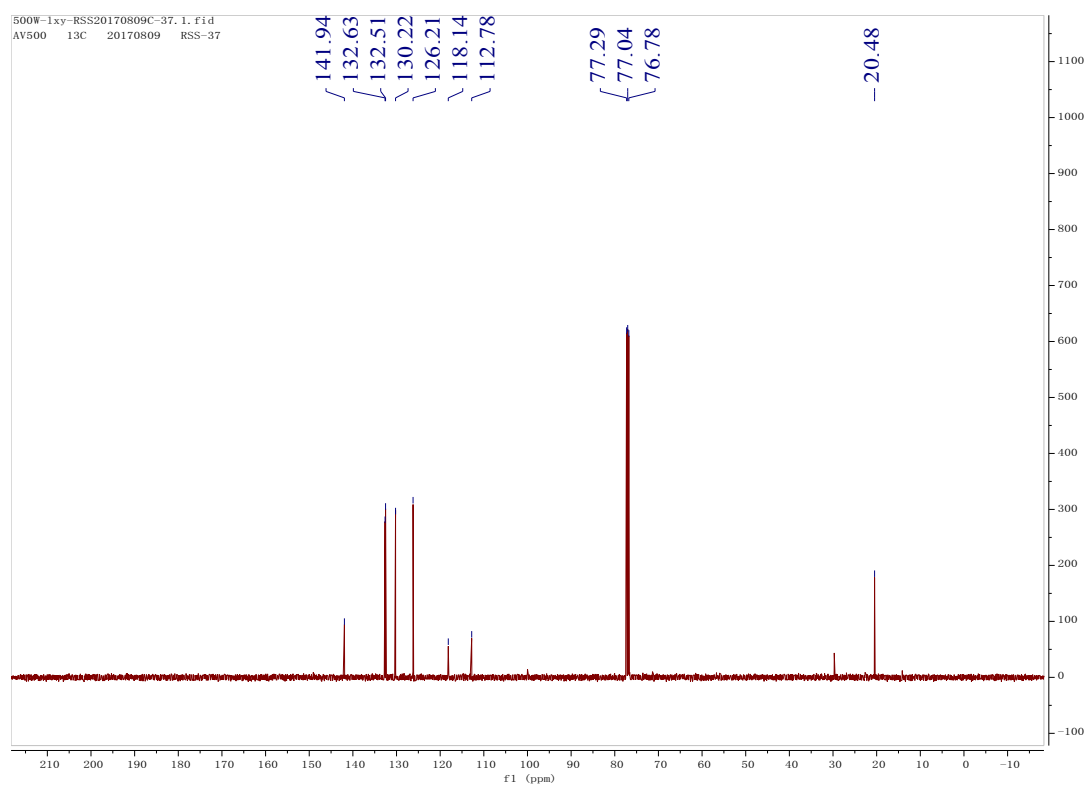
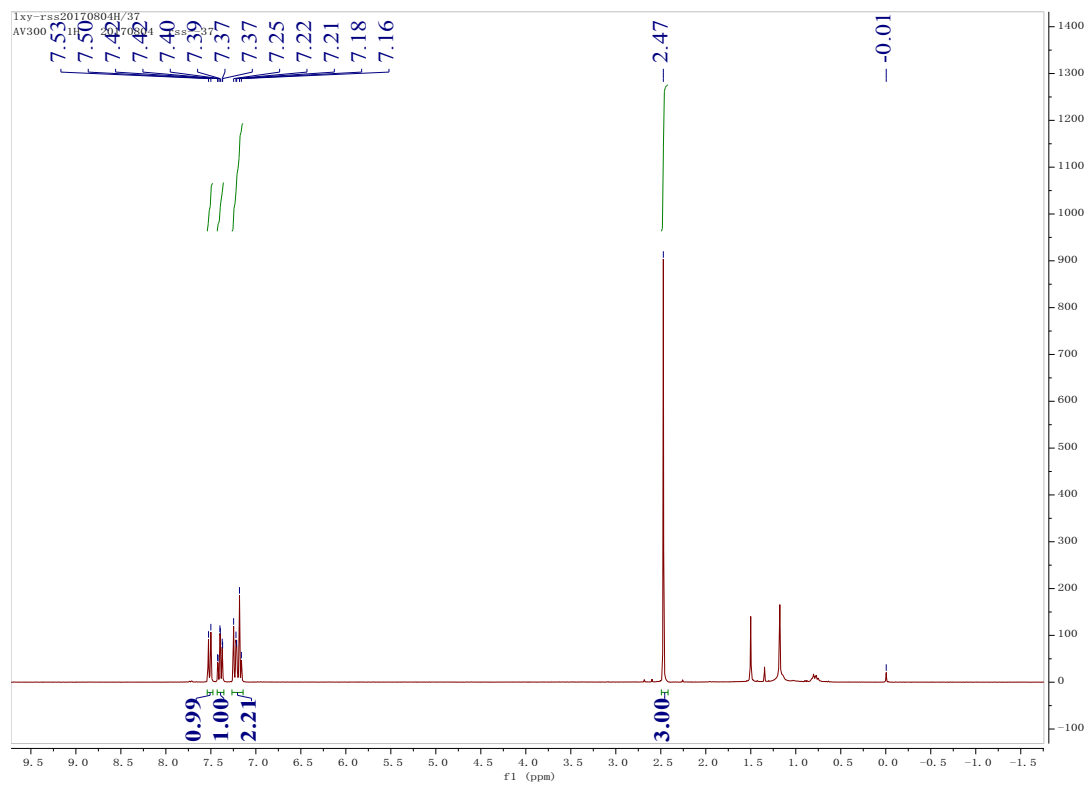


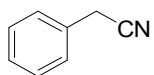
^1H NMR (300 MHz, CDCl_3 , δ): 7.54-7.18 (m, *Ar*, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 139.57, 133.39, 129.70, 117.97 (*Ar-C*), 110.79 (*CN*).



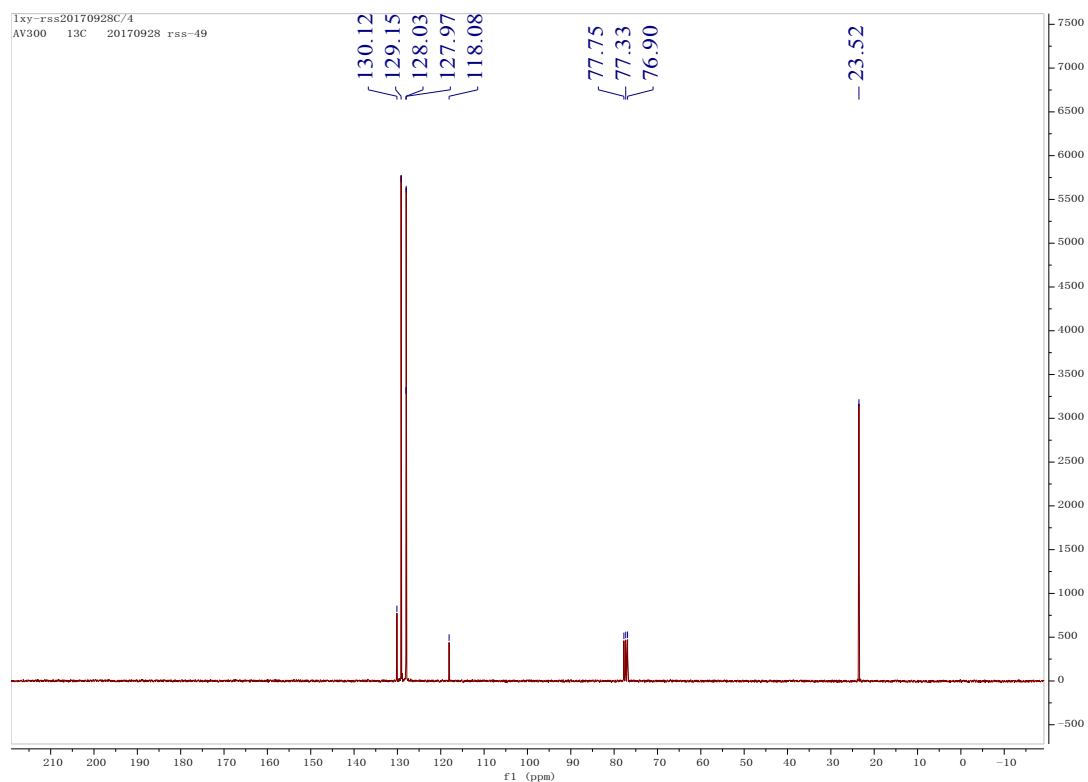
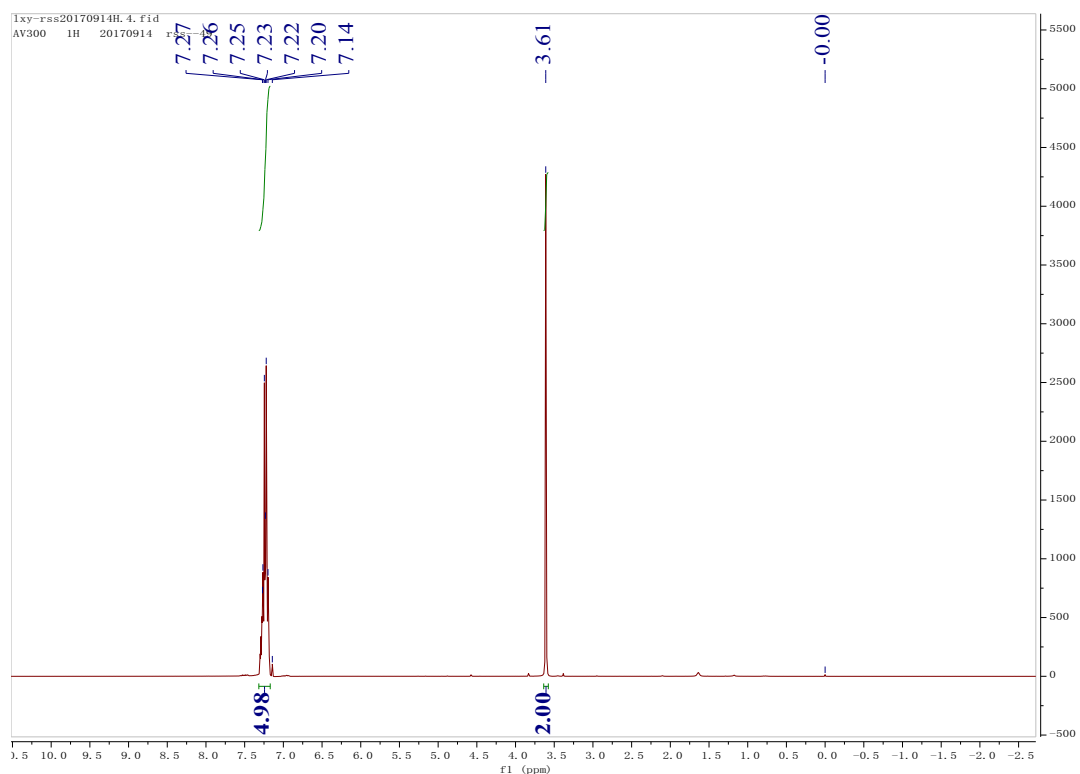


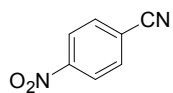
^1H NMR (300 MHz, CDCl_3 , δ): 7.53-7.16 (m, *Ar*, 4H), 2.47(s, CH_3 , 3H) . ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 141.94, 132.57, 130.22, 126.21, 118.14(Ar-C), 112.78 (CN), 20.48 (CH_3).



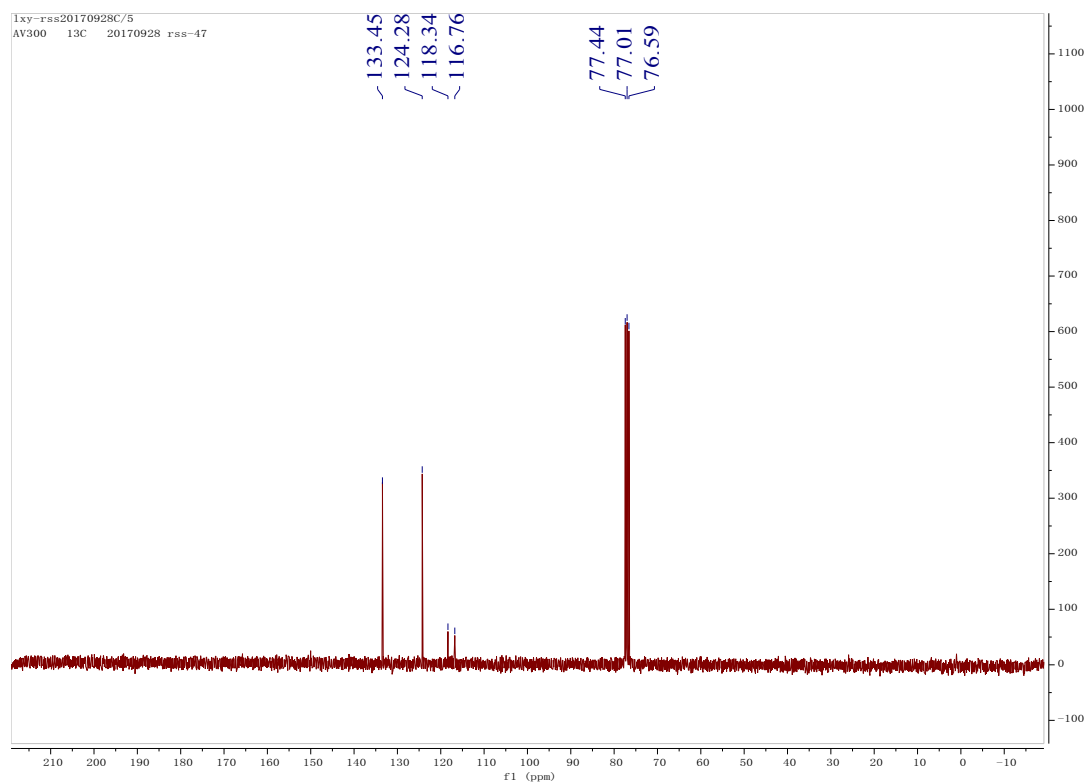
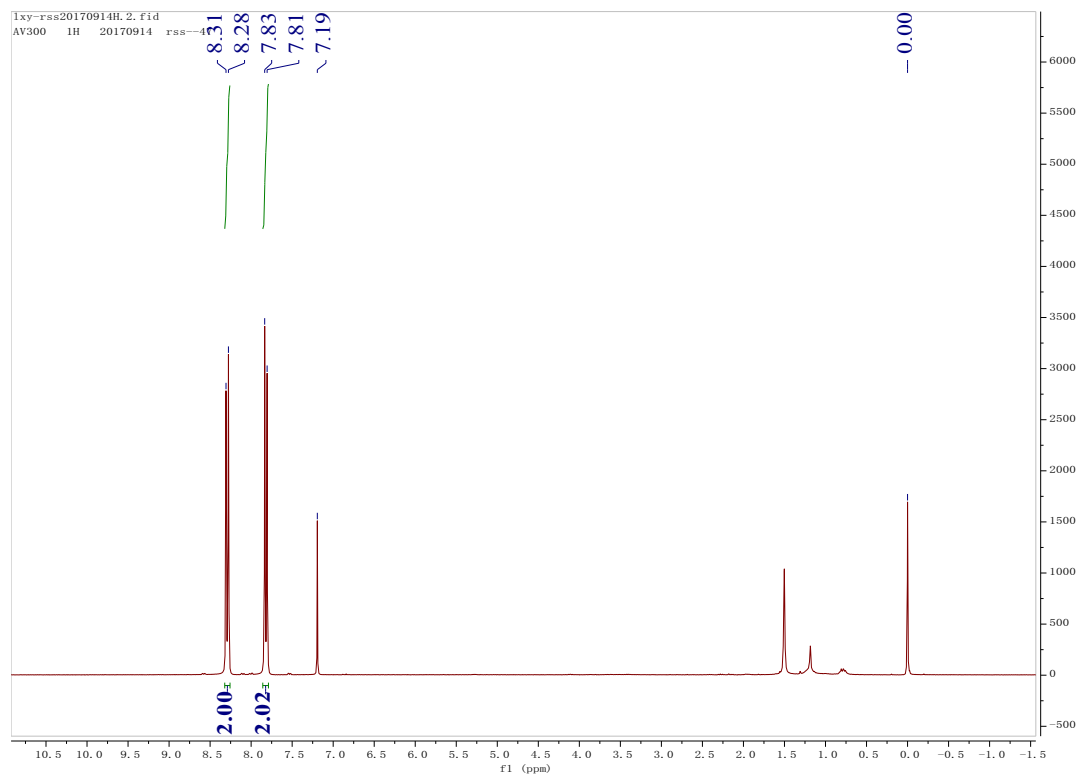


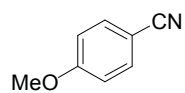
^1H NMR (300 MHz, CDCl_3 , δ): 7.27-7.14 (m, *Ar*, 5H), 3.61 (s, CH_2 , 2H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 130.12, 129.15, 128.03, 127.97 (Ar-C), 118.08 (CN), 77.75, 77.33, 76.90 (CDCl₃), 23.52 (CH_2).



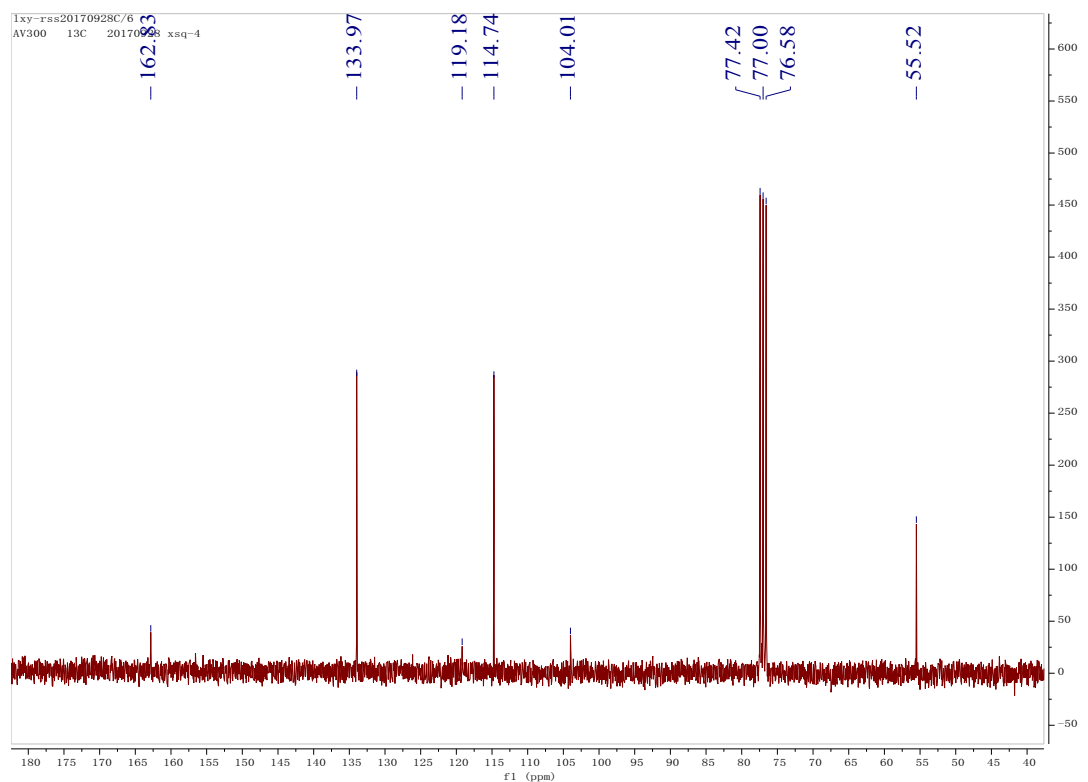
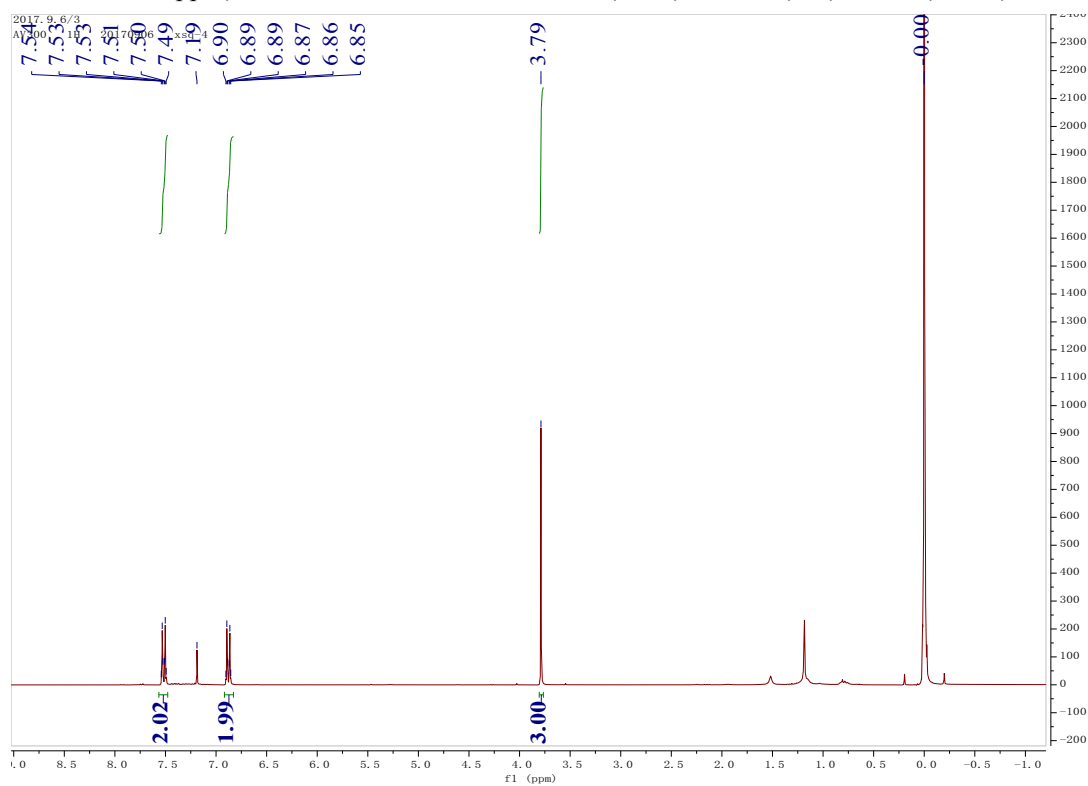


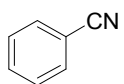
^1H NMR (300 MHz, CDCl_3 , δ): 8.31-7.19 (m, *Ar*, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 133.45, 124.28, 118.34 (*Ar-C*), 116.76 (CN).



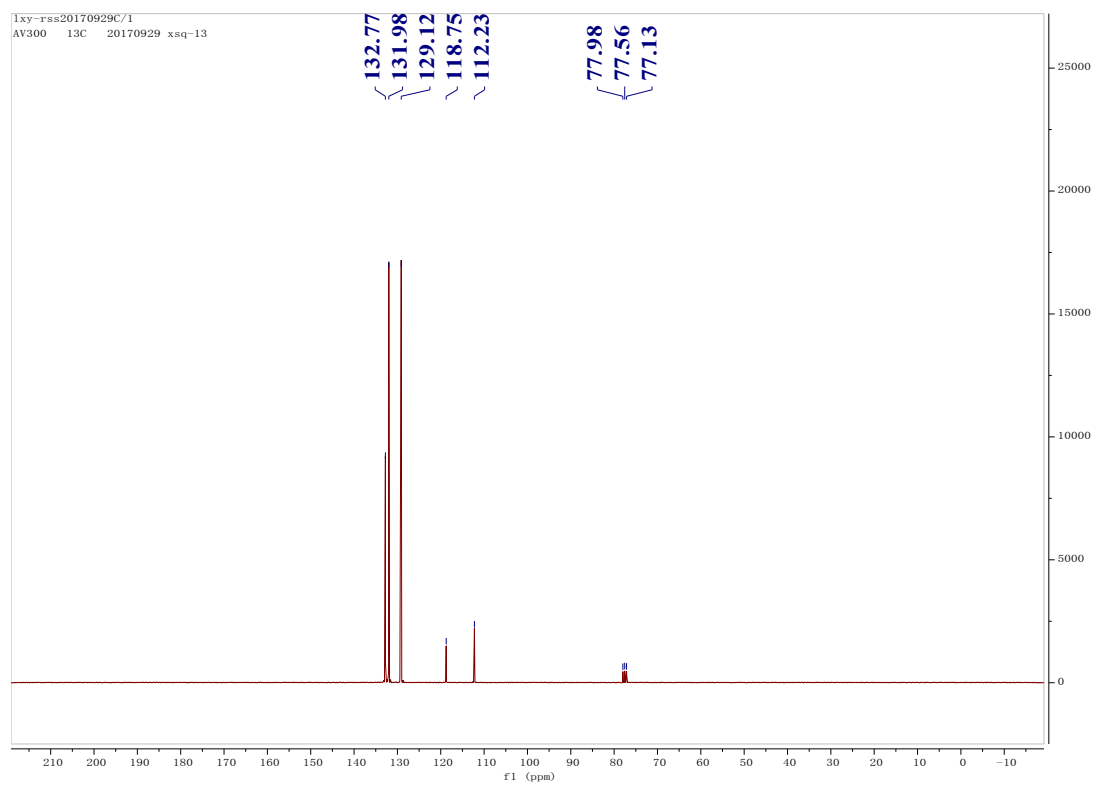
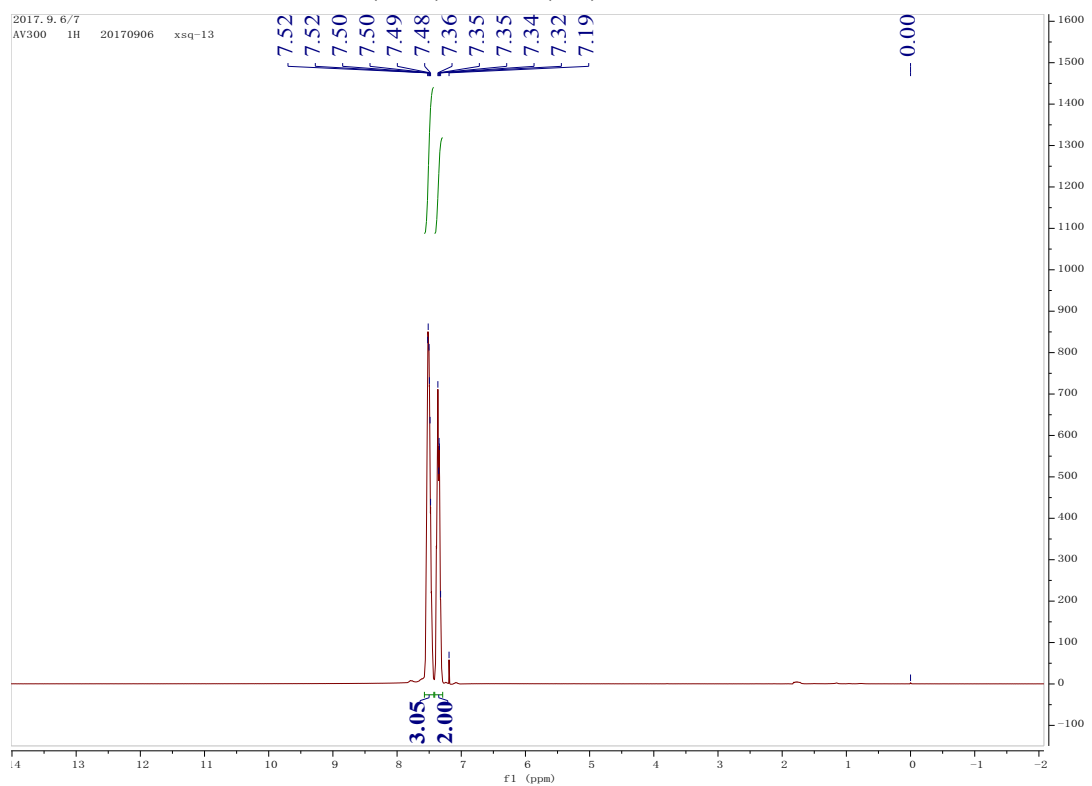


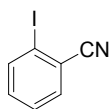
^1H NMR (300 MHz, CDCl_3 , δ): 7.54-6.85 (m, *Ar*, 4H), 3.79 (s, OCH_3 , 3H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 162.83, 133.97, 119.18, 114.74 (Ar-C), 104.01 (CN), 55.52 (OCH_3).



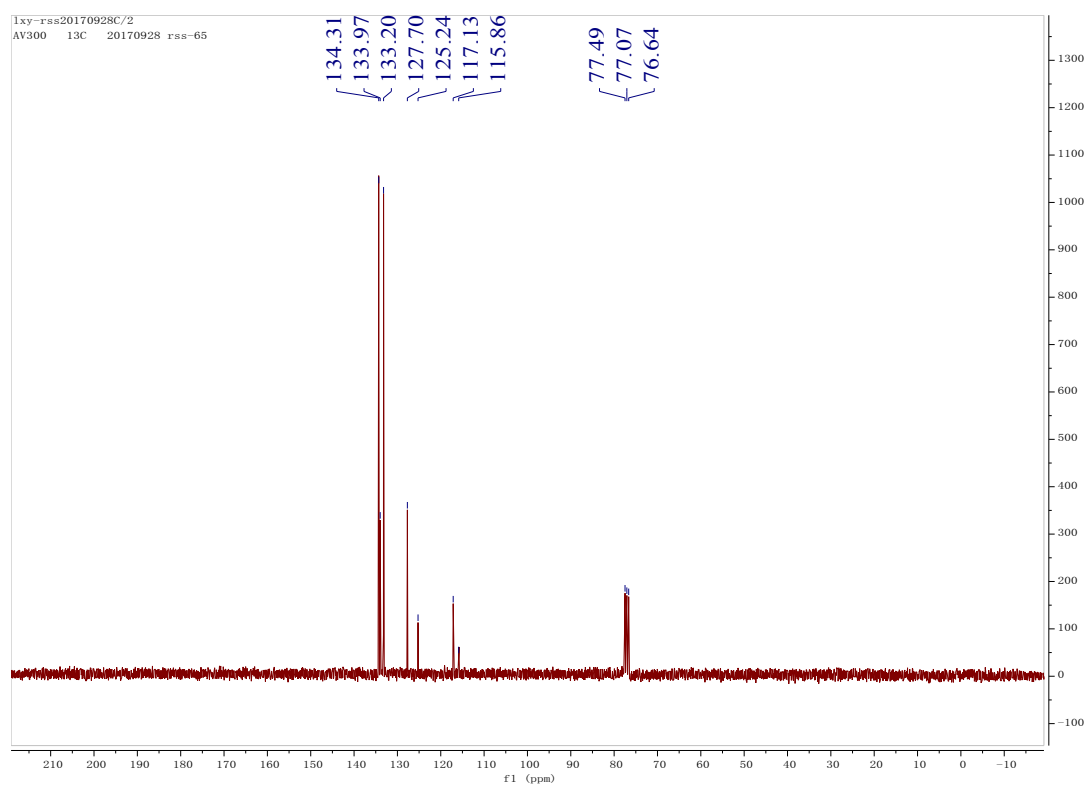
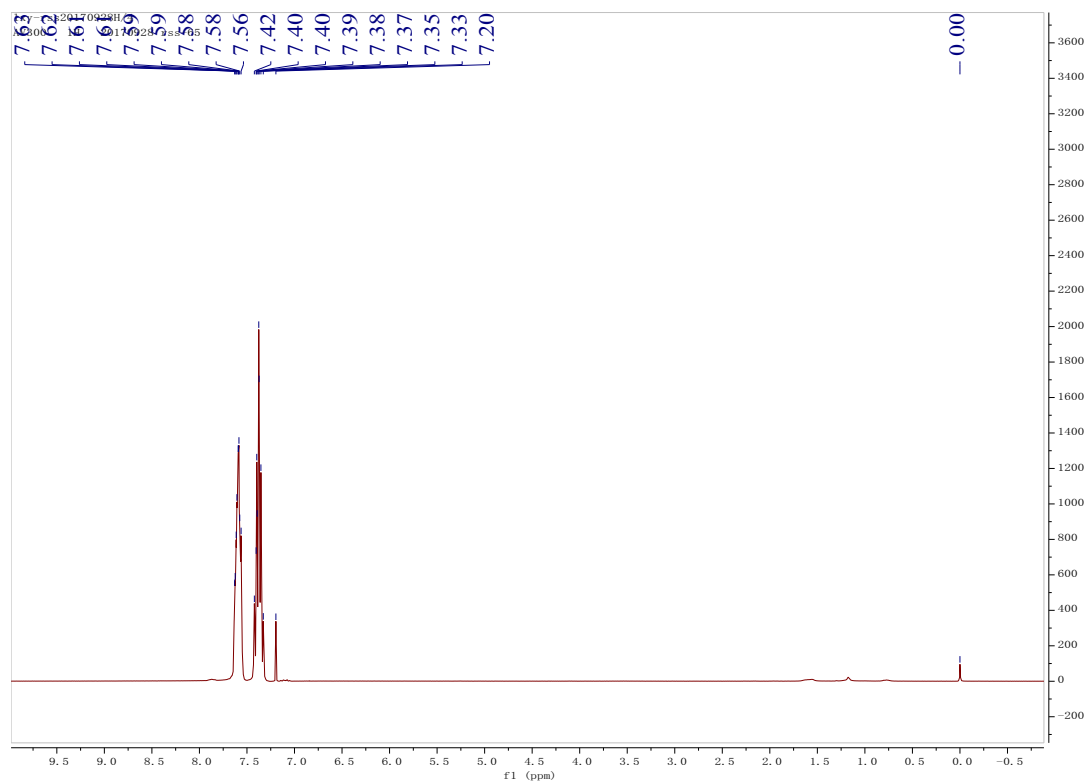


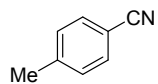
^1H NMR (300 MHz, CDCl_3 , δ): 7.52-7.19 (m, *Ar*, 5H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 132.77, 131.98, 129.12, 118.75 (Ar-C), 112.23 (CN).



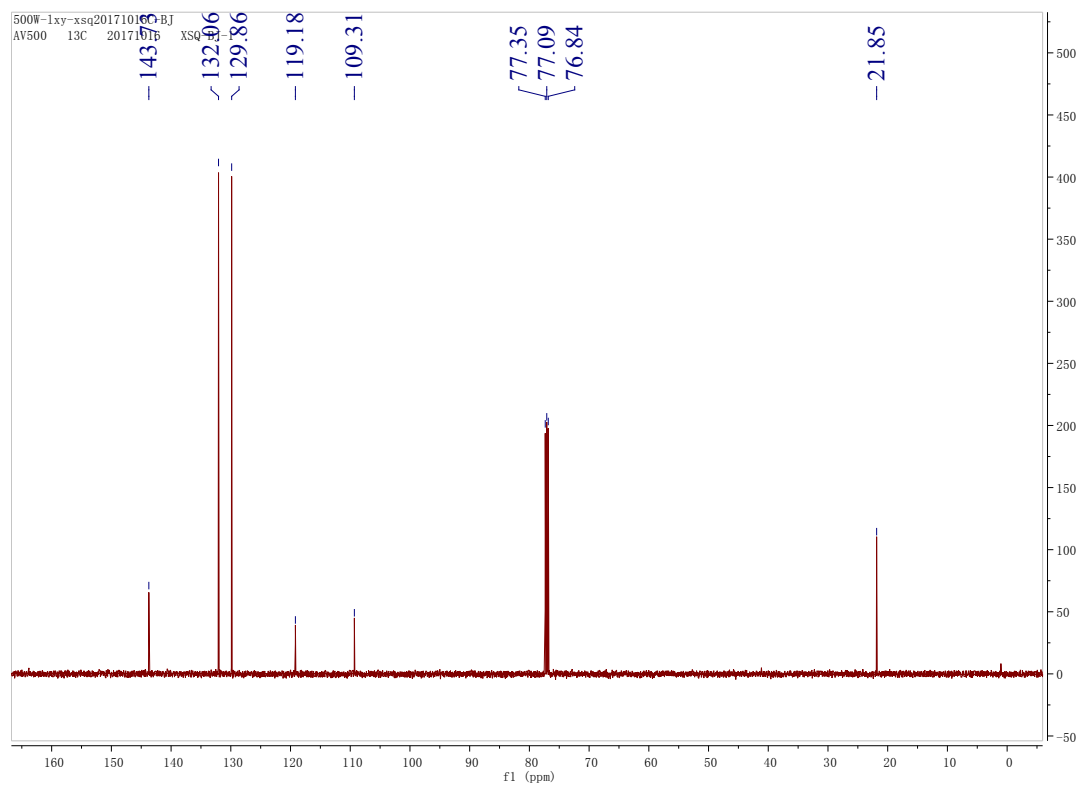
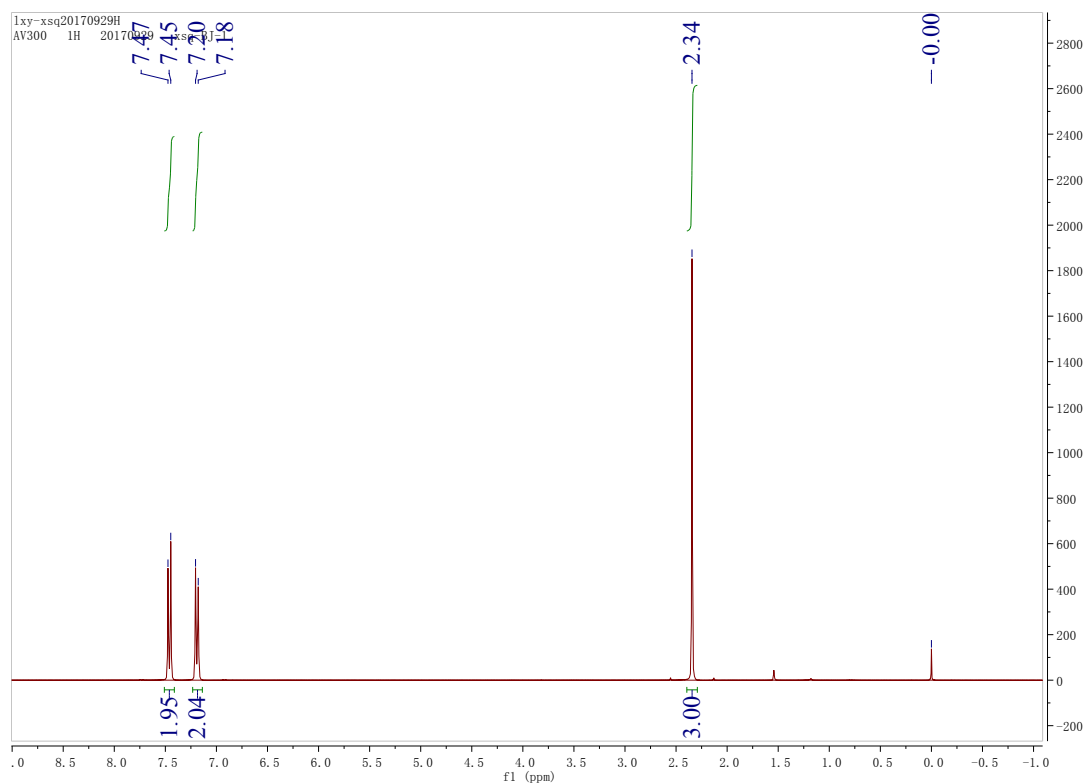


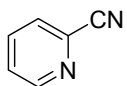
^1H NMR (300 MHz, CDCl_3 , δ): 7.63-7.33 (m, Ar-H, 4H). ^{13}C NMR (75 MHz, CDCl_3 , 298K, ppm): 134.31, 133.97, 133.20, 127.70, 125.24, 117.13 (Ar-C), 115.86 (CN).



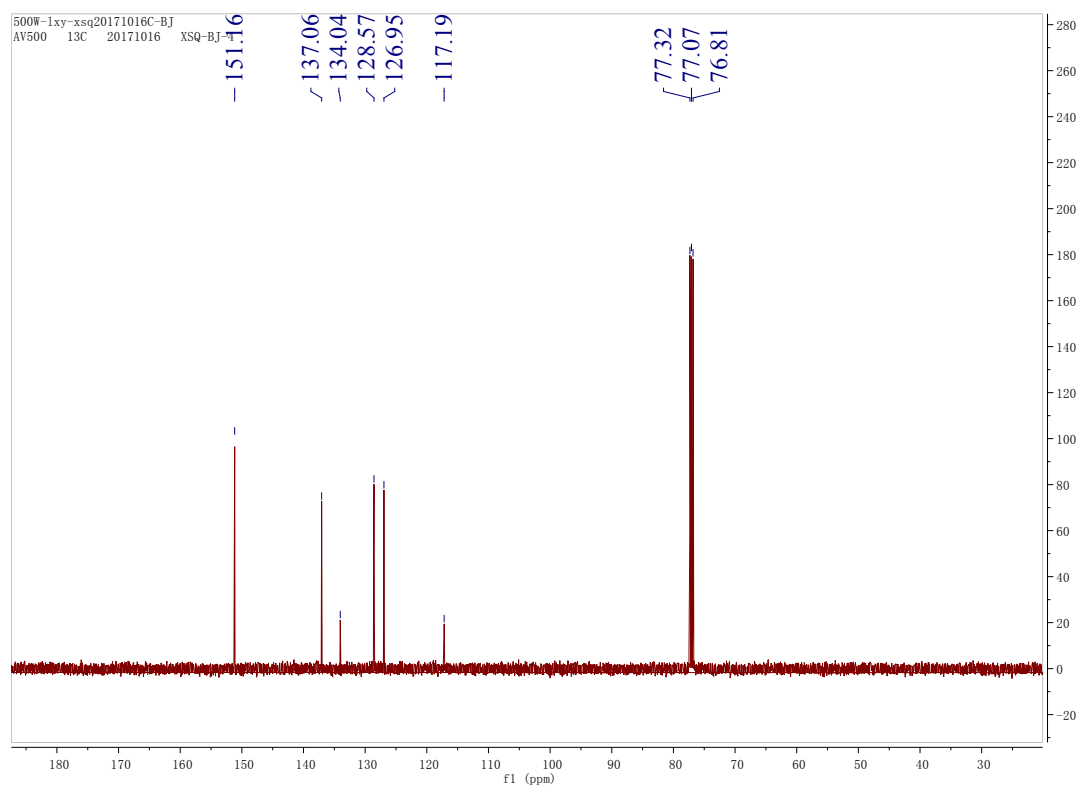
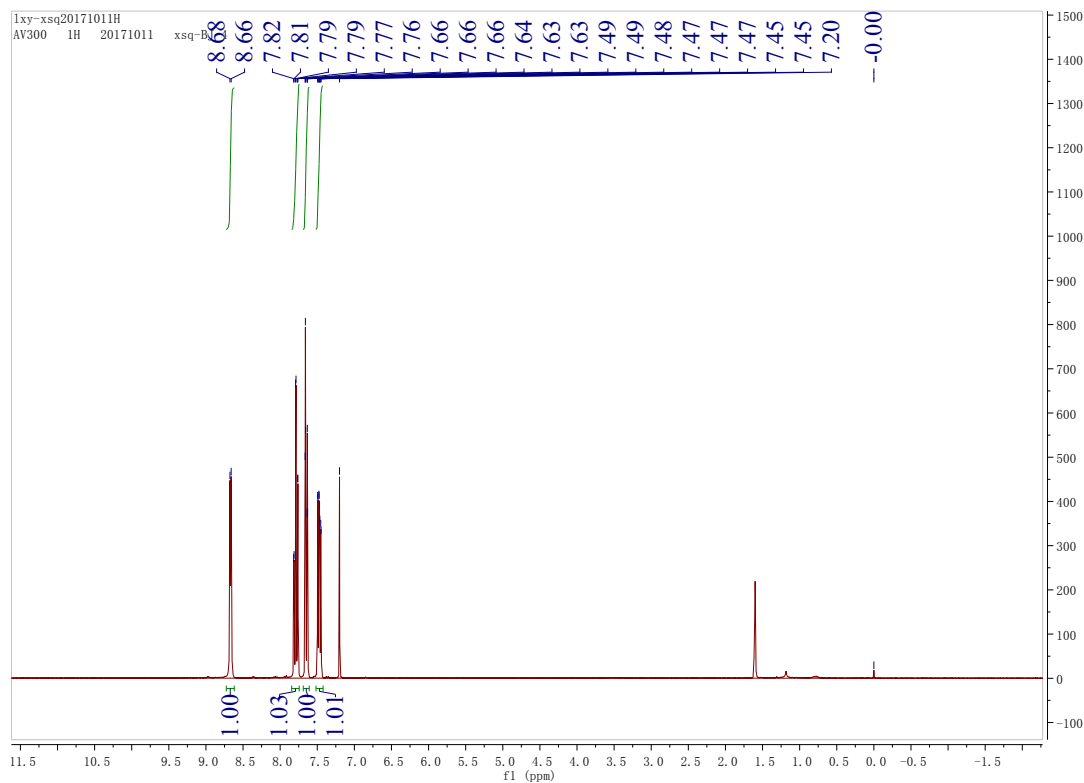


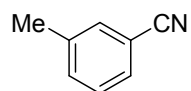
^1H NMR (300 MHz, CDCl_3 , δ): 7.47-7.18 (m, Ar-H, 4H) 2.34(s, CH_3 , 3H). ^{13}C NMR (125 MHz, CDCl_3 , 298K, ppm): 143.73, 132.06, 129.86, 119.18 (Ar-C), 109.31 (CN), 21.85 (CH_3).



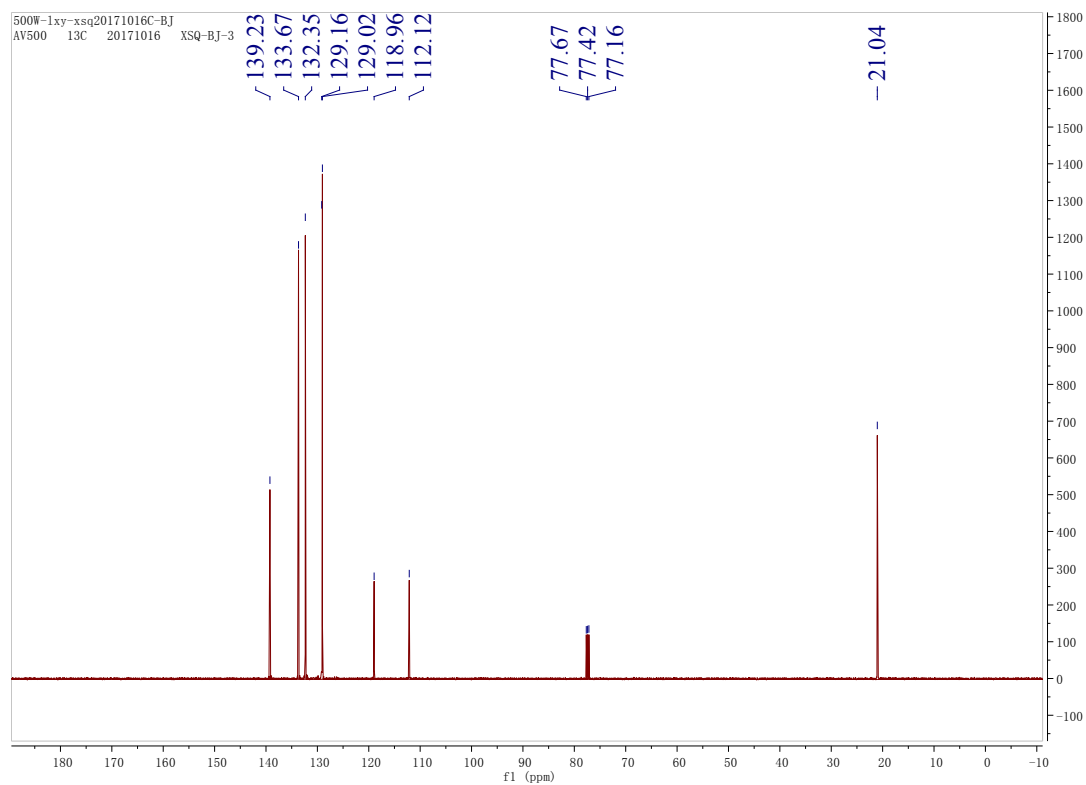
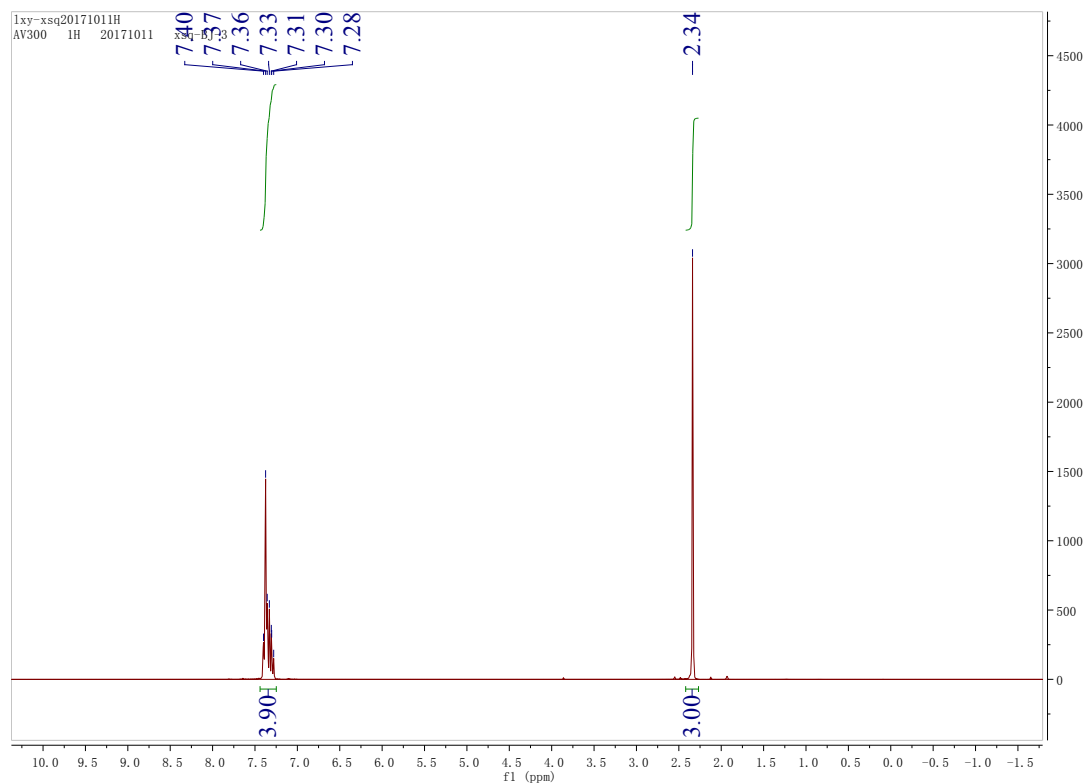


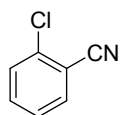
^1H NMR (300 MHz, CDCl_3 , δ): 8.86-7.20 (m, Ar-H, 4H). ^{13}C NMR (125 MHz, CDCl_3 , 298K, ppm): 151.16, 137.06, 134.04, 128.57, 126.95 (Ar-C), 117.19 (CN).





^1H NMR (300 MHz, CDCl_3 , δ): 7.40-7.28 (m, Ar-H, 4H) 2.34(s, CH_3 , 3H). ^{13}C NMR (125 MHz, CDCl_3 , 298K, ppm): 139.23, 133.67, 132.35, 129.16, 129.02, 118.96 (Ar-C), 112.12 (CN), 21.04 (CH_3).





^1H NMR (300 MHz, CDCl_3 , δ): 7.63-7.33 (m, Ar-H, 4H). ^{13}C NMR (125 MHz, CDCl_3 , 298K, ppm): 136.93, 134.04, 133.87, 130.08, 127.15, 115.98, 114.44 (Ar-C), 113.46 (CN).

