Room temperature hydroamination of alkynes with anilines catalyzed by anti-Bredt di(amino)carbene gold(I) complexes.

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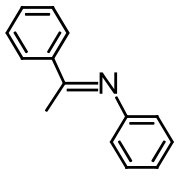
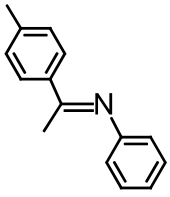
Index:

1. ^{13}C NMR, ^{1}H NMR and MS data for the hydroamination products



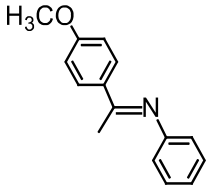
3a

^{13}C NMR (75 MHz, C_6D_6) δ 164.43, 152.13, 139.46, 130.22, 128.93, 128.10, 127.29, 123.04, 119.38, 16.48. ^{1}H NMR (300 MHz, C_6D_6) δ 7.95 – 7.92 (t, 2H), 7.22 – 7.17(m,5H), 6.97 – 6.92(t, 1H), 6.76 – 6.74(d, 2H), 1.84(s, 3H). MS calculated m/e for $C_{14}H_{13}N$: 195.1, found: 195.3 (Relative abundance: 48%). Calculated [M-CH_3]: 108.1, found: 108.3 (Relative abundance: 100%).



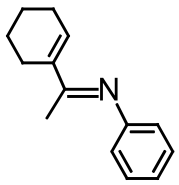
3b

^{13}C NMR (75 MHz, C_6D_6) δ 164.50, 152.18, 140.36, 136.91, 128.92, 128.89, 127.34, 122.97, 119.50, 20.90, 16.53. ^{1}H NMR (300 MHz, C_6D_6) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.00 – 7.03 (m, 3H), 6.75 (d, *J* = 7.5 Hz, 2H), 2.10 (s, 3H), 1.87 (s, 3H). MS calculated m/e for $C_{15}H_{15}N$: 209.1, found: 209.2 (Relative abundance: 43%). Calculated [M-CH_3]: 194.1, found: 194.2 (Relative abundance: 100%).



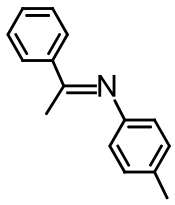
3c

^{13}C NMR (75 MHz, C_6D_6) δ 163.72, 161.71, 152.32, 132.15, 128.99, 128.92, 122.87, 119.65, 113.49, 54.56, 16.40. ^{1}H NMR (300 MHz, C_6D_6) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 4H), 3.31 (s, 3H), 1.89 (s, 3H). MS calculated m/e for $C_{15}H_{15}NO$: 225.1, found: 225.2 (Relative abundance: 40%). Calculated [M-CH_3]: 210.1, found: 210.2 (Relative abundance: 100%).



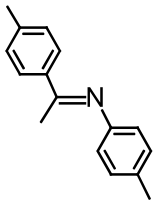
3d

^{13}C NMR (75 MHz, C_6D_6) δ 165.88, 152.52, 139.46, 133.30, 128.79, 122.62, 119.35, 26.01, 24.71, 22.59, 22.07, 15.22. ^{1}H NMR (300 MHz, C_6D_6) δ 7.19 – 7.14 (m, 2H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.2 Hz, 2H), 6.16 (t, *J* = 4.0 Hz, 1H), 2.60 – 2.56 (m, 2H), 2.00 – 1.95 (m, 2H), 1.69 (s, 3H), 1.59~1.51 (m, 2H), 1.48~1.40 (m, 2H). MS calculated m/e for $C_{14}H_{17}N$: 199.1, found: 199.3 (Relative abundance: 30%). Calculated [M-C_6H_9]: 118.1, found: 118.1 (Relative abundance: 100%).



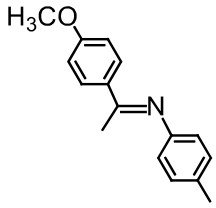
4a

^{13}C NMR (75 MHz, C_6D_6) δ 164.46, 149.55, 139.66, 132.19, 130.12, 129.53, 128.09, 127.25, 119.45, 20.51, 16.45. ^{1}H NMR (300 MHz, C_6D_6) δ 7.95 (br, 2H), 7.24 – 7.15 (m, 3H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.70 (d, *J* = 7.8 Hz, 2H), 2.16 (s, 3H), 1.89 (s, 3H). MS calculated m/e for $C_{15}H_{15}N$: 209.1, found: 209.3 (Relative abundance: 53%). Calculated [M-CH_3]: 194.1, found: 194.3 (Relative abundance: 100%).



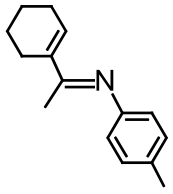
4b

^{13}C NMR (75 MHz, C_6D_6) δ 164.16, 149.71, 140.18, 137.10, 131.99, 129.51, 128.86, 127.33, 119.55, 20.91, 20.53, 16.41. ^{1}H NMR (300 MHz, C_6D_6) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 7.6 Hz, 2H), 6.71 (d, *J* = 8.0 Hz, 2H), 2.16 (s, 3H), 2.12 (s, 3H), 1.93 (s, 3H). MS calculated m/e for $C_{16}H_{17}N$: 223.1, found: 223.2 (Relative abundance: 38%). Calculated [M-CH_3]: 208.1, found: 208.2 (Relative abundance: 100%).



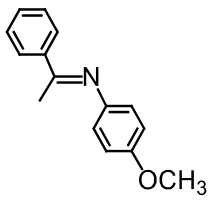
4c

^{13}C NMR (75 MHz, C_6D_6) δ 163.58, 161.62, 149.79, 132.37, 131.92, 129.52, 128.94, 119.68, 113.47, 54.55, 20.52, 16.33. ^{1}H NMR (300 MHz, C_6D_6) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.72 (d, *J* = 7.8 Hz, 2H), 3.33 (s, 3H), 2.17 (s, 3H), 1.93 (s, 3H). MS calculated m/e for $C_{16}H_{17}NO$: 239.1, found: 239.2 (Relative abundance: 41%). Calculated [M-CH_3]: 224.1, found: 224.1 (Relative abundance: 100%).



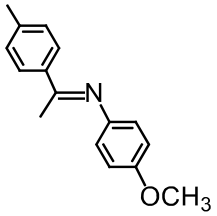
4d

^{13}C NMR (75 MHz, C_6D_6) δ 165.62, 150.04, 139.70, 132.85, 131.60, 129.37, 119.37, 26.03, 24.77, 22.64, 22.14, 20.47, 15.11. ^{1}H NMR (300 MHz, C_6D_6) δ 6.99 (d, *J* = 8.0 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.18 (t, *J* = 4.0 Hz, 1H), 2.62 (br, 2H), 2.15 (s, 3H), 2.01 – 1.98 (m, 2H), 1.74 (s, 3H), 1.61 – 1.53 (m, 2H), 1.49 – 1.44 (m, 2H). MS calculated m/e for $C_{15}H_{19}N$: 213.2, found: 213.3 (Relative abundance: 26%). Calculated [M-C_6H_9]: 132.1, found: 132.1 (Relative abundance: 100%).



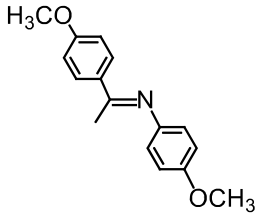
5a

^{13}C NMR (75 MHz, C_6D_6) δ 164.56, 156.22, 145.09, 139.80, 130.08, 128.10, 127.23, 120.79, 114.32, 54.71, 16.42. ^{1}H NMR (300 MHz, C_6D_6) δ 8.09 – 7.92 (m, 2H), 7.26 – 7.16 (m, 3H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 3.37 (s, 3H), 1.92 (s, 3H). MS calculated m/e for $C_{15}H_{15}NO$: 225.1, found: 225.2 (Relative abundance: 59%). Calculated [M-CH_3]: 210.1, found: 210.2 (Relative abundance: 100%).



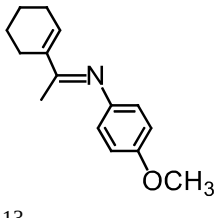
5b

^{13}C NMR (75 MHz, C_6D_6) δ 164.35, 156.11, 145.25, 140.14, 137.24, 128.87, 127.30, 120.86, 114.29, 54.70, 20.91, 16.40. ^{1}H NMR (300 MHz, C_6D_6) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.38 (s, 3H), 2.12 (s, 3H), 1.95 (s, 3H). MS calculated m/e for $C_{16}H_{17}NO$: 239.1, found: 239.2 (Relative abundance: 48%). Calculated [M-CH_3]: 224.1, found: 224.1 (Relative abundance: 100%).



5c

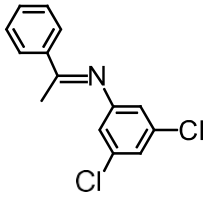
^{13}C NMR (75 MHz, $CDCl_3$) δ 164.94, 161.48, 155.84, 145.01, 132.47, 128.77, 120.92, 114.25, 113.60, 55.48, 55.37, 17.11. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.6 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 9.0 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 2.24 (s, 3H). MS calculated m/e for $C_{16}H_{17}NO_2$: 255.1, found: 255.2 (Relative abundance: 50%). Calculated [M-CH_3]: 240.1, found: 240.2 (Relative abundance: 100%).



5d

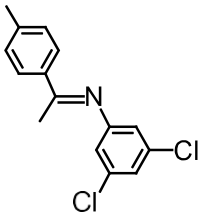
^{13}C NMR (75 MHz, C_6D_6) δ 165.69, 155.83, 145.68, 139.86, 132.68, 120.60, 114.17, 54.68, 26.05, 24.81, 22.68, 22.18, 15.05. ^{1}H NMR (300 MHz, C_6D_6) δ 6.78 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.21 – 6.18 (m, 1H), 3.38 (s, 3H), 2.65 – 2.62 (m, 2H), 2.05 – 1.95 (m, 2H), 1.77 (s, 3H), 1.60 – 1.55 (m, 2H), 1.50 – 1.44 (m, 2H). MS

calculated m/e for $C_{15}H_{19}NO$: 229.2, found: 229.3 (Relative abundance: 26%). Calculated [M-C_6H_9]: 148.1, found: 148.1 (Relative abundance: 100%).



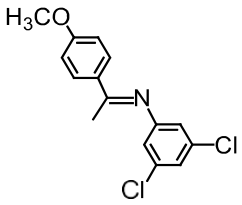
6a

^{13}C NMR (75 MHz, C_6D_6) δ 166.43, 153.91, 138.47, 135.23, 130.81, 128.18, 127.29, 122.85, 117.90, 16.63. ^{1}H NMR (300 MHz, C_6D_6) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.18 (br, 3H), 6.93 (s, 1H), 6.49 (s, 2H), 1.59 (s, 3H). MS calculated m/e for $C_{14}H_{11}Cl_2N$: 263.0, found: 263.1 (Relative abundance: 42%). Calculated [M-CH_3]: 248.0, found: 248.1 (Relative abundance: 100%).



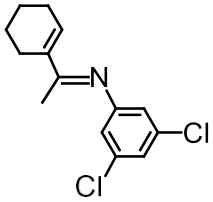
6b

^{13}C NMR (75 MHz, C_6D_6) δ 166.06, 154.16, 141.11, 135.90, 135.15, 128.96, 127.37, 122.65, 118.01, 20.96, 16.59. ^{1}H NMR (300 MHz, C_6D_6) δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (s, 1H), 6.51 (s, *1*H), 6.51 (s, *1*H), 2.12 (s, 3H), 1.65 (s, 3H). MS calculated m/e for $C_{15}H_{13}Cl_2N$: 277.0, found: 277.2 (Relative abundance: 42%). Calculated [M-CH_3]: 262.0, found: 262.1 (Relative abundance: 100%).



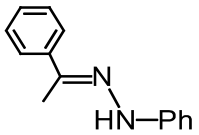
6c

^{13}C NMR (75 MHz, C_6D_6) δ 165.49, 162.11, 154.24, 135.15, 131.13, 129.12, 122.59, 118.21, 113.55, 54.59, 16.51. ^{1}H NMR (300 MHz, C_6D_6) δ 7.80 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 1H), 6.77 (d, *J* = 8.7 Hz, 2H), 6.54 (s, 2H), 3.34 (s, 3H), 1.66 (s, 3H). MS calculated m/e for $C_{15}H_{13}Cl_2NO$: 293.0, found: 293.2 (Relative abundance: 30%). Calculated [M-CH_3]: 278.0, found: 278.1 (Relative abundance: 100%).



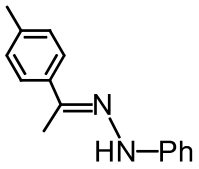
6d

^{13}C NMR (75 MHz, C_6D_6) δ 167.14, 154.59, 138.89, 135.02, 134.76, 122.23, 117.84, 26.05, 24.45, 22.44, 21.93, 15.25. ^{1}H NMR (300 MHz, C_6D_6) δ 6.90 (s, 1H), 6.46 (s, 1H), 6.47 (s, 1H), 6.12 (t, *J* = 4.0 Hz, 1H), 2.43 – 2.40 (m, 2H), 1.55 – 1.52 (m, 2H), 1.47 (s, 3H), 1.45 – 1.41 (m, 2H). MS calculated m/e for $C_{14}H_{15}Cl_2N$: 267.1, found: 267.2 (Relative abundance: 100%). Calculated [M-C_6H_9]: 186.0, found: 186.0 (Relative abundance: 41%).



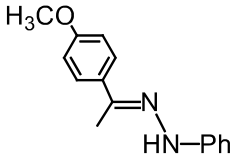
2a

^{13}C NMR (75 MHz, C_6D_6) δ 145.54, 140.80, 139.32, 129.24, 128.26, 128.22, 125.56, 120.13, 113.39, 10.76. ^{1}H NMR (300 MHz, C_6D_6) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.28 – 7.21 (m, 3H), 7.18 – 7.12 (m, *J* = 5.3 Hz, 3H), 6.86 (t, *J* = 7.0 Hz, 2H), 1.45 (s, 3H). MS calculated m/e for $C_{14}H_{14}N_2$: 210.1, found: 210.1 (Relative abundance: 100%). Calculated [M-C_6H_6N]: 118.1, found: 118.1 (Relative abundance: 52%).



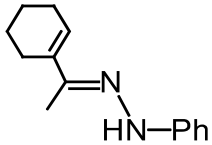
2b

^{13}C NMR (75 MHz, C_6D_6) δ 145.68, 141.08, 137.42, 136.65, 129.20, 128.96, 125.54, 119.98, 113.37, 20.83, 10.80. ^{1}H NMR (300 MHz, C_6D_6) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.21 (m, 2H), 7.18 – 7.15 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.85 (t, *J* = 7.2 Hz, 1H), 2.14 (s, 3H), 1.51 (s, 3H). MS calculated m/e for $C_{15}H_{16}N_2$: 224.1, found: 224.2 (Relative abundance: 92%).



2c

^{13}C NMR (75 MHz, C_6D_6) δ 159.84, 145.86, 140.76, 132.11, 129.20, 126.87, 119.91, 113.70, 113.34, 54.49, 10.80. ^{1}H NMR (300 MHz, C_6D_6) δ 7.73 (d, *J* = 8.9 Hz, 2H), 7.26 – 7.19 (m, 4H), 6.90 – 6.87 (m, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 3.33 (s, 3H), 1.50 (s, 3H). MS calculated m/e for $C_{15}H_{16}N_2O$: 240.1, found: 240.1 (Relative abundance: 100%). Calculated [M-C_6H_6N]: 148.0, found: 148.0 (Relative abundance: 86%).

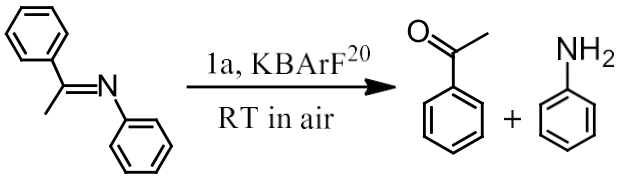


2d

^{13}C NMR (75 MHz, C_6D_6) δ 145.94, 142.93, 137.56, 129.12, 125.66, 119.68, 113.18, 26.01, 24.77, 22.87, 22.57, 9.08. ^{1}H NMR (300 MHz, C_6D_6) δ 7.29 – 7.19 (m, 2H),

7.15 – 7.10 (m, 2H), 6.84 (t, *J* = 7.2 Hz, 1H), 5.80 (t, *J* = 4.2 Hz, 1H), 2.65 – 2.60 (m, 2H), 2.07 – 2.02 (m, 2H), 1.66 – 1.58 (m, 2H), 1.55 – 1.49 (m, 2H), 1.38 (s, 3H). MS calculated m/e for $C_{14}H_{18}N_2$: 214.2, found: 214.2 (Relative abundance: 100%). Calculated [M-C_6H_6N]: 122.1, found: 122.1 (Relative abundance: 23%).

2. Hydrolysis of 3a in air



The C_6D_6 solution of **3a**, 5 mol% catalyst **1a**, and 5 mol% KBArF was kept under air for 24 hours. The following ^{13}C NMR was obtained. It shows that **2a** was partially hydrolyzed to acetophenone and aniline.

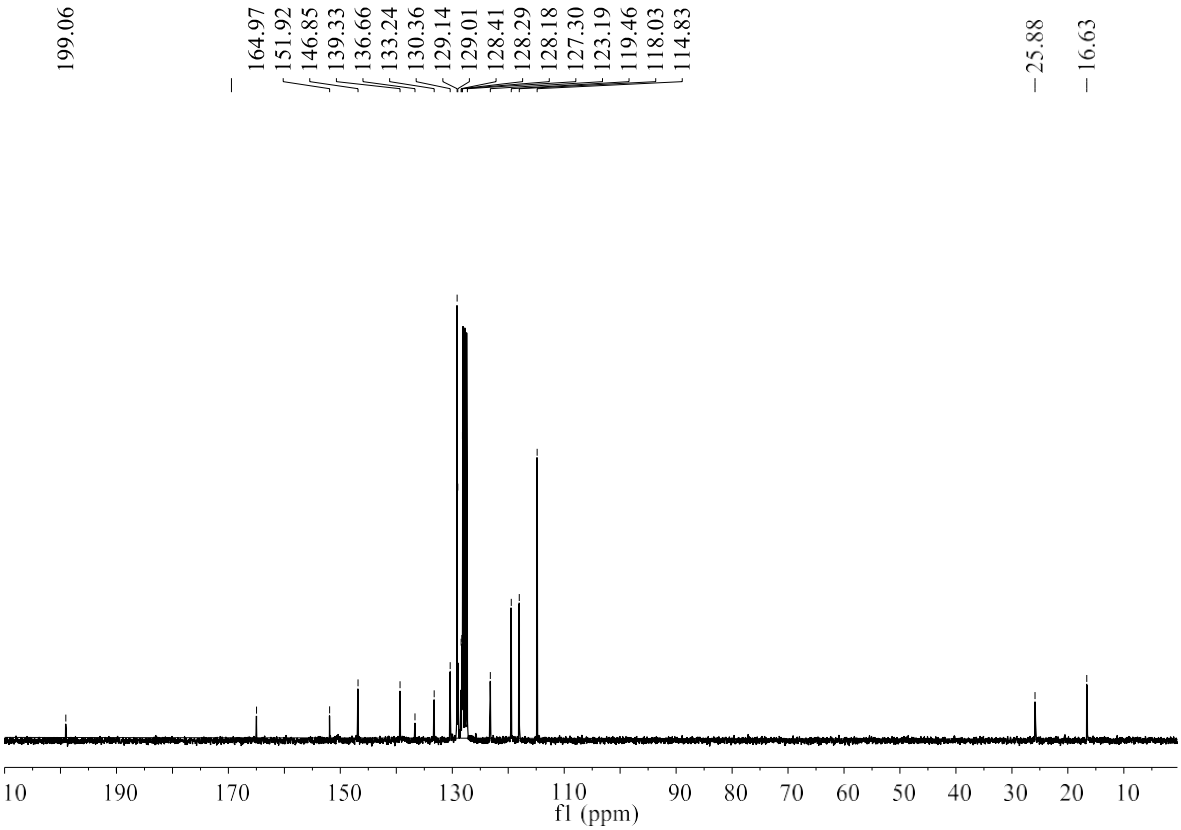
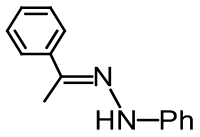


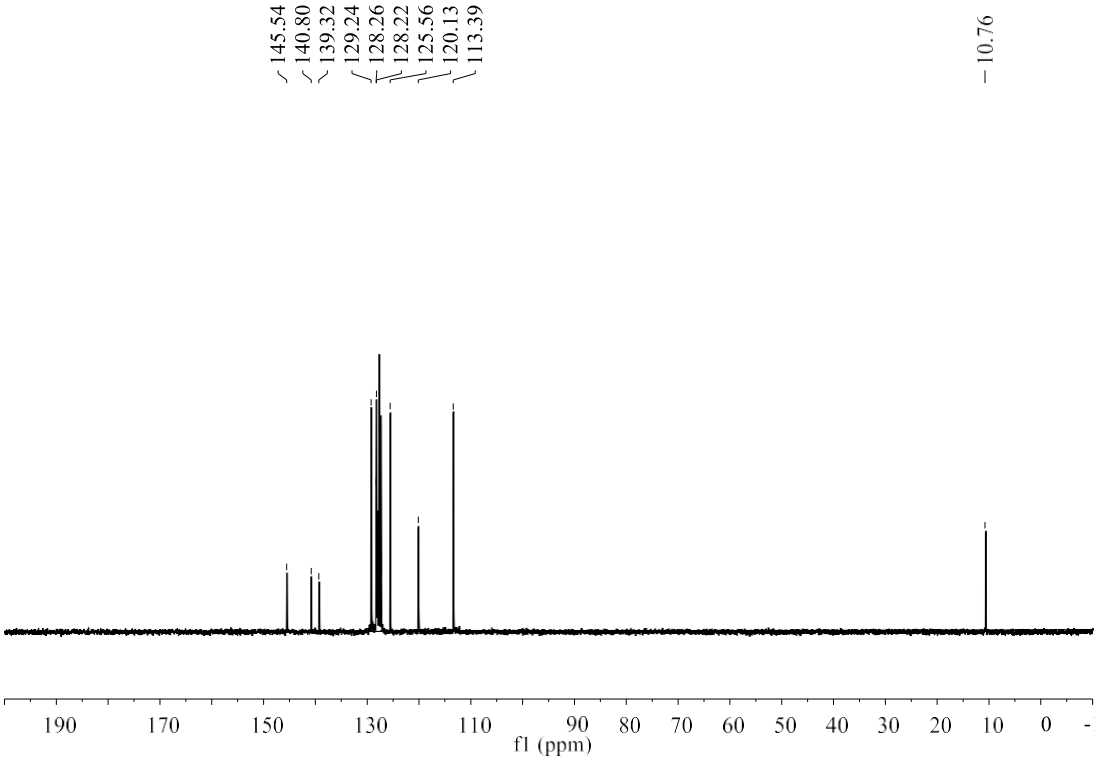
Figure S1. ^{13}C NMR monitoring the hydrolysis of 2a in air.

3. Original NMR spectra of Hydroamination products

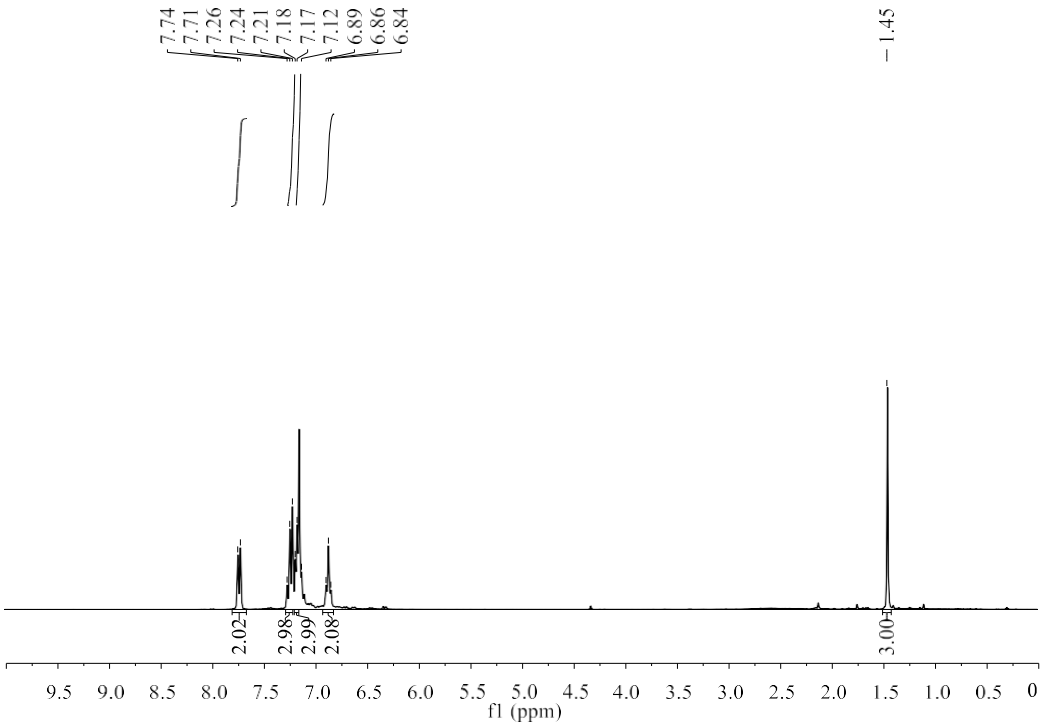


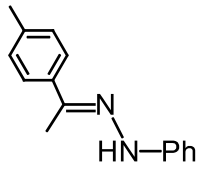
2a

^{13}C NMR



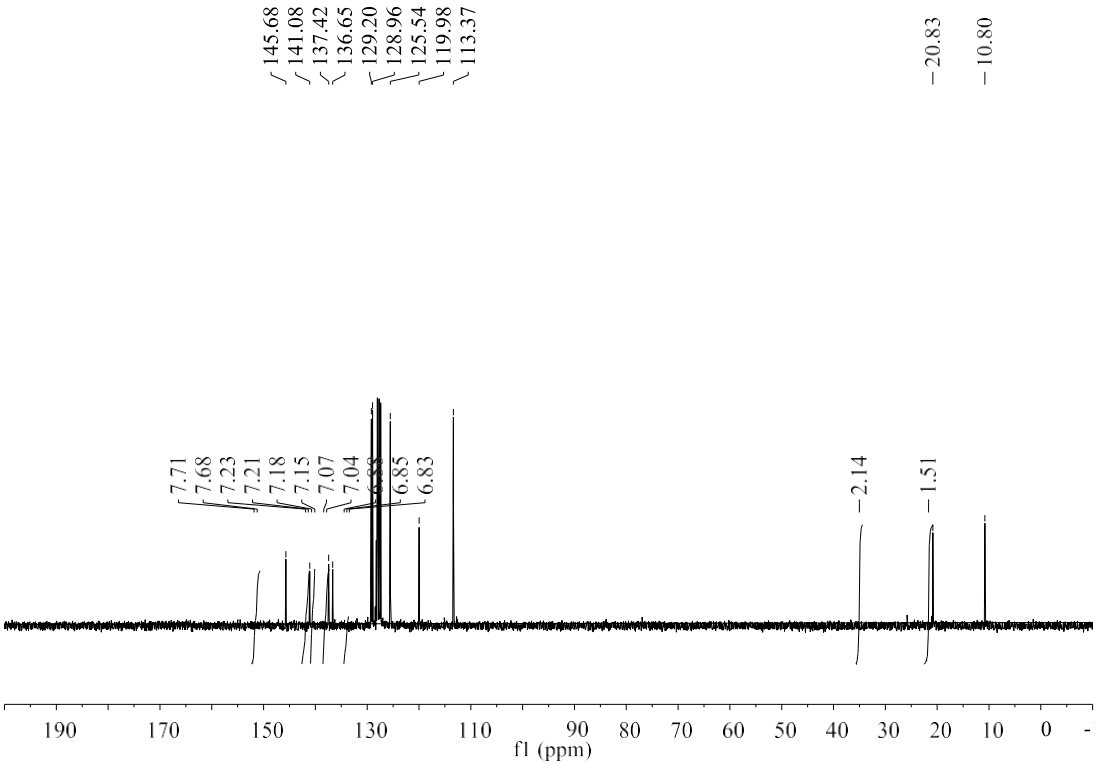
^{1}H NMR



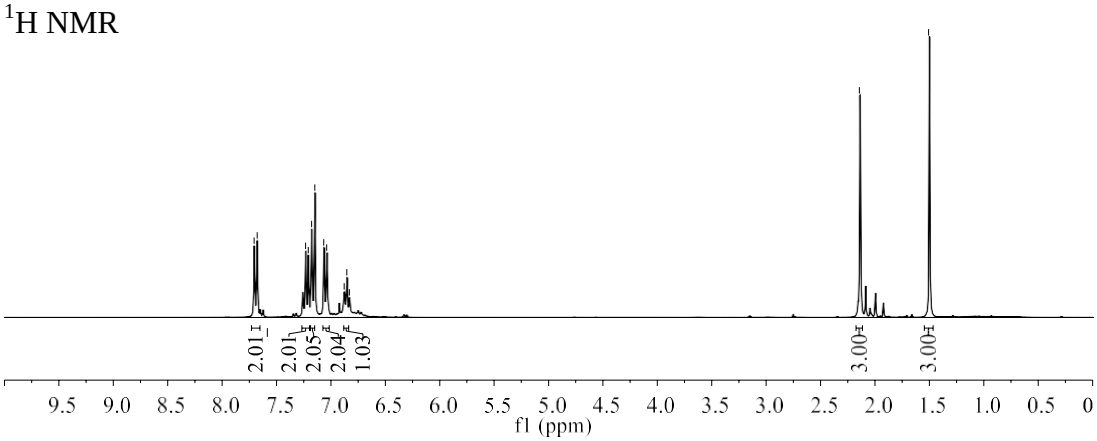


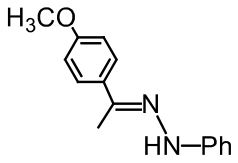
2b

^{13}C NMR



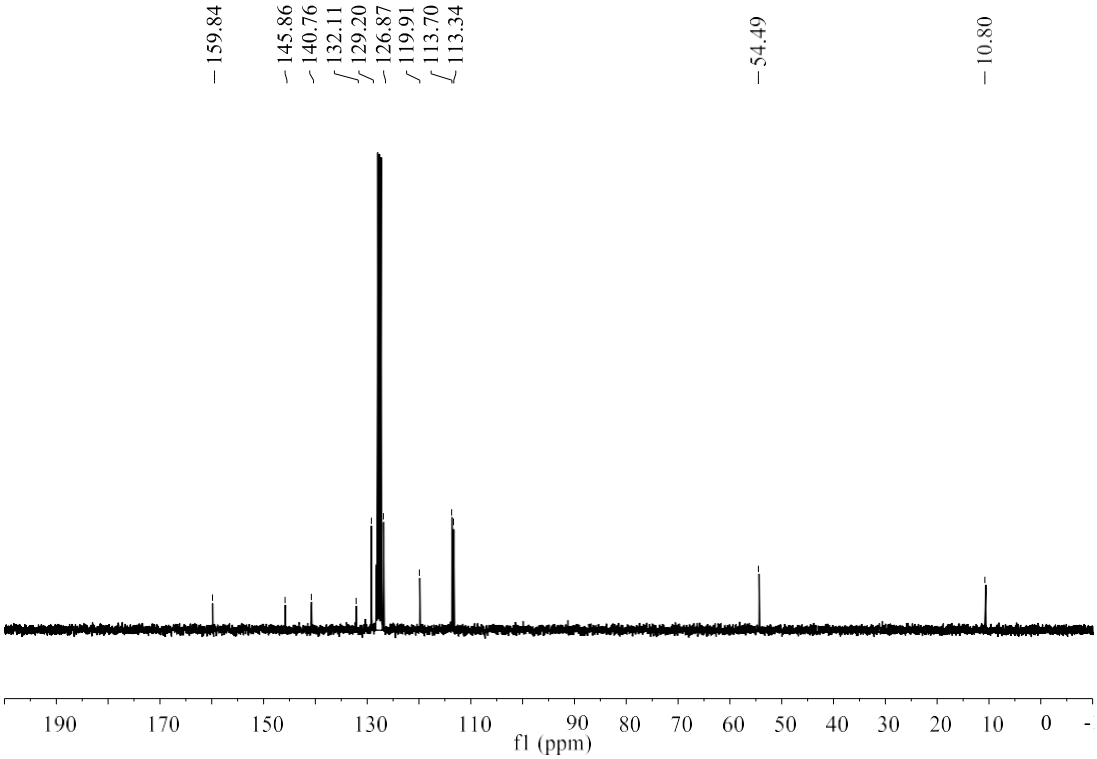
^{1}H NMR



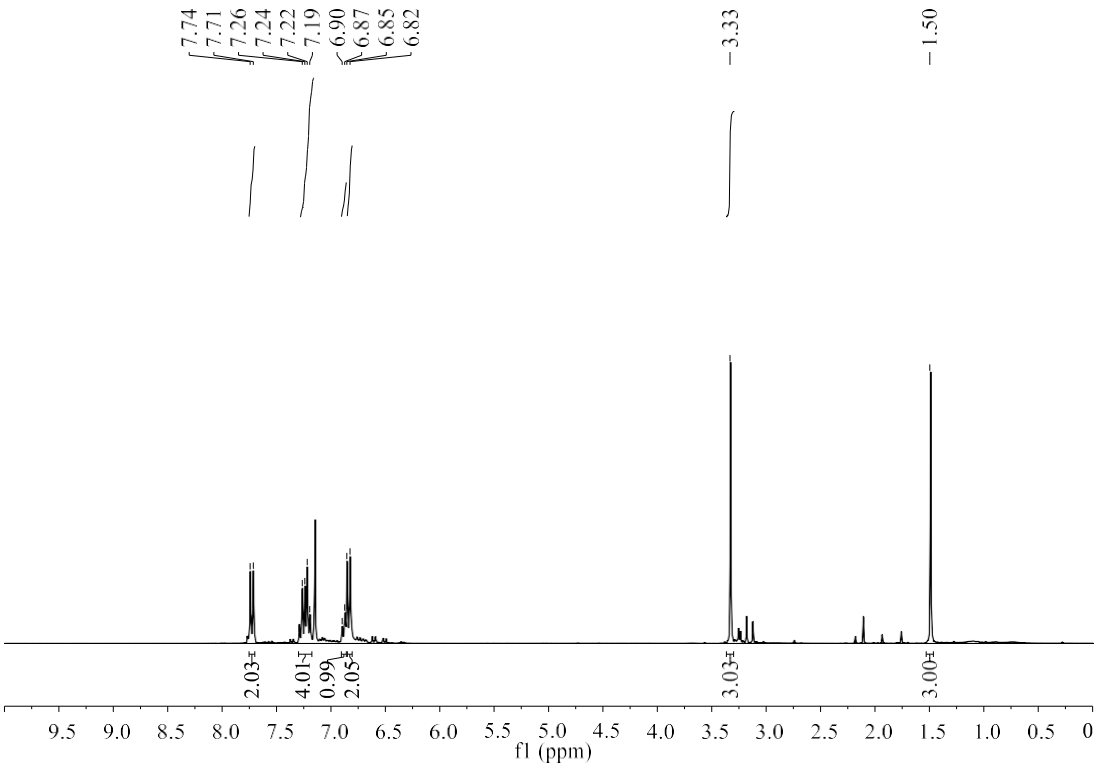


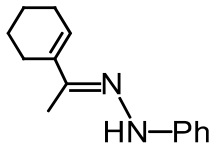
2c

^{13}C NMR



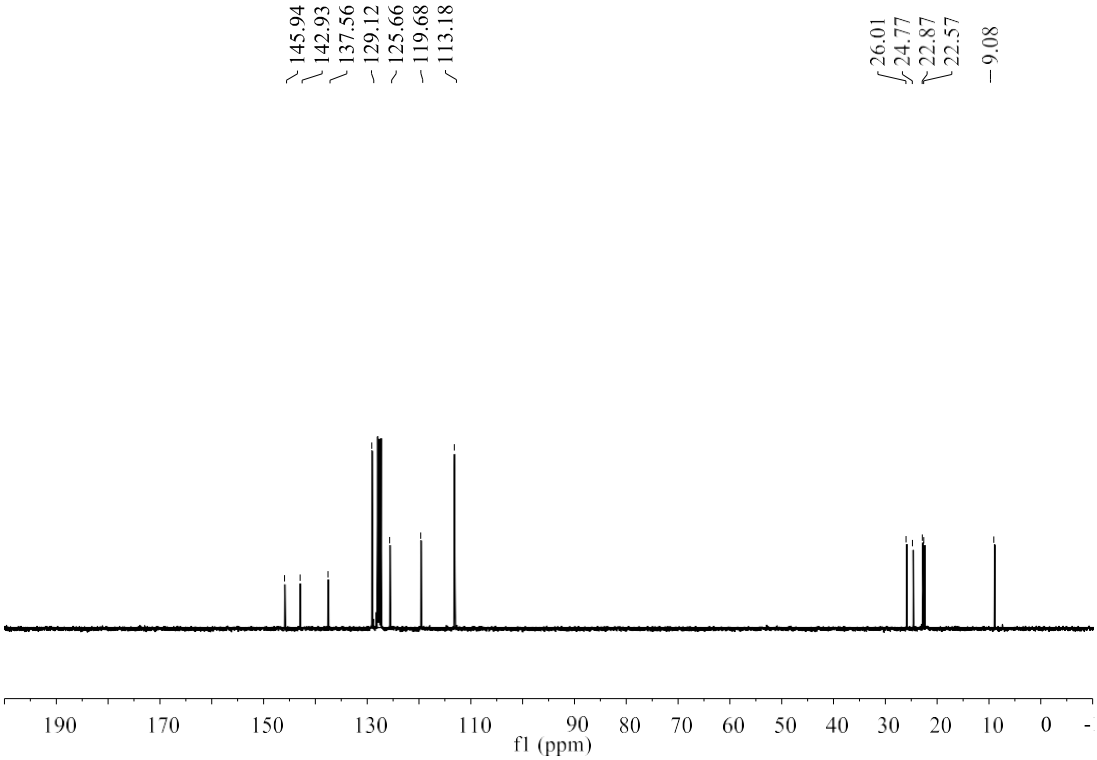
^{1}H NMR



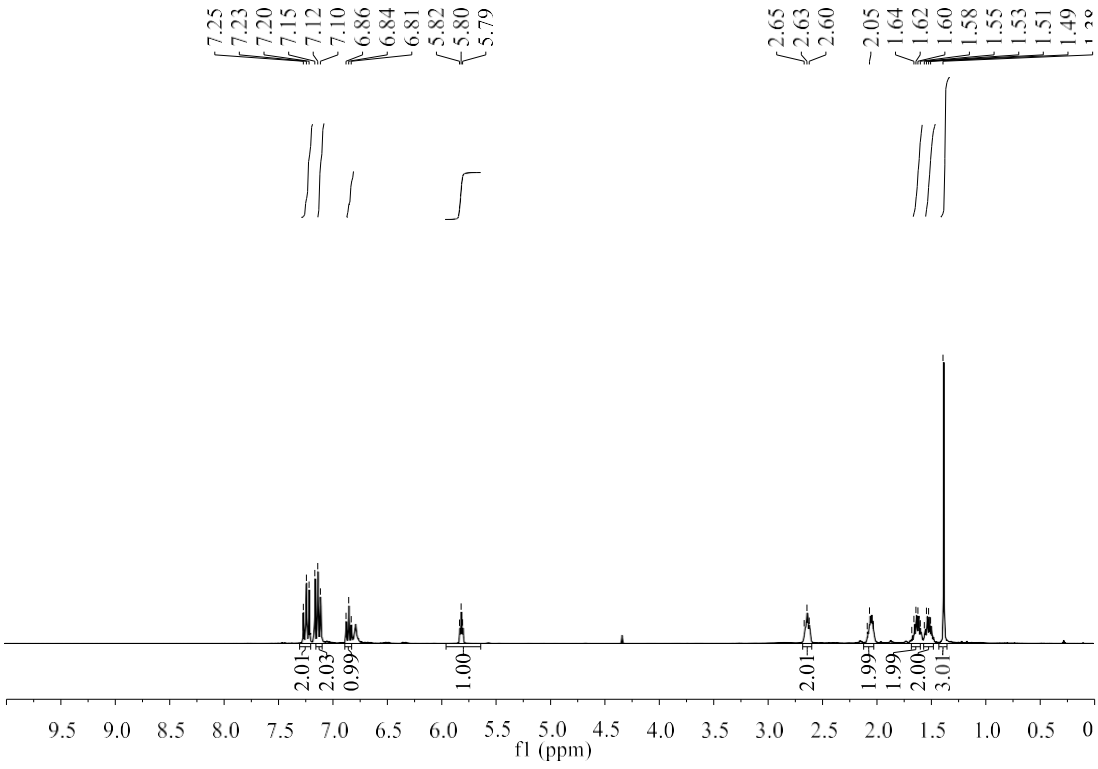


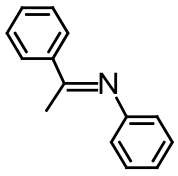
2d

^{13}C NMR



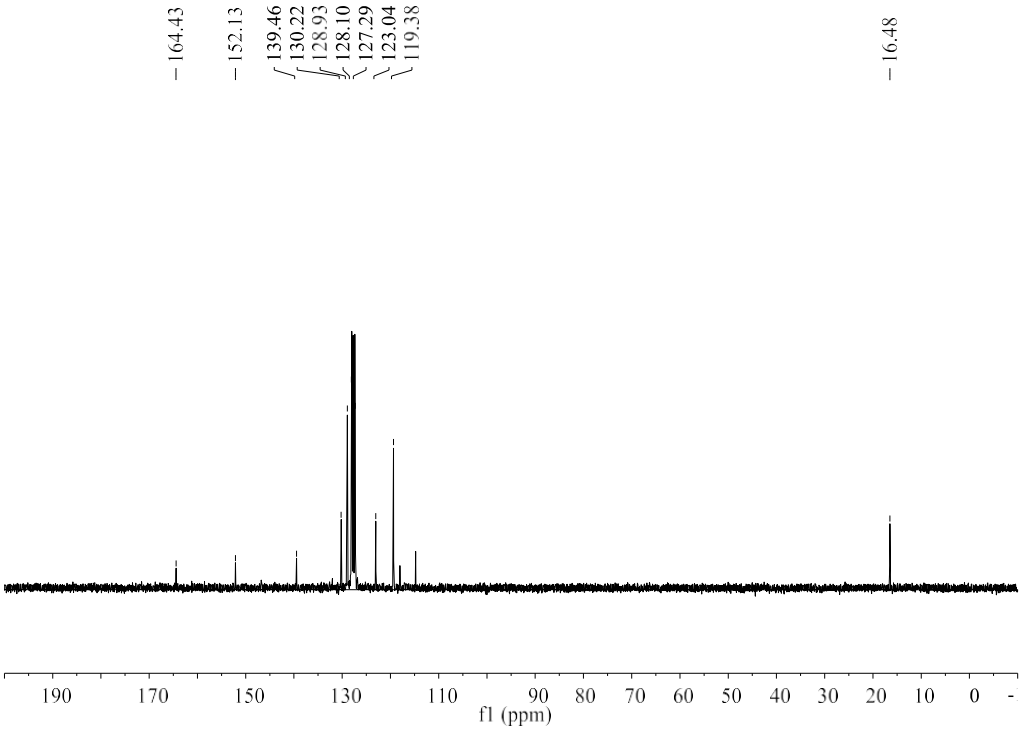
^{1}H NMR



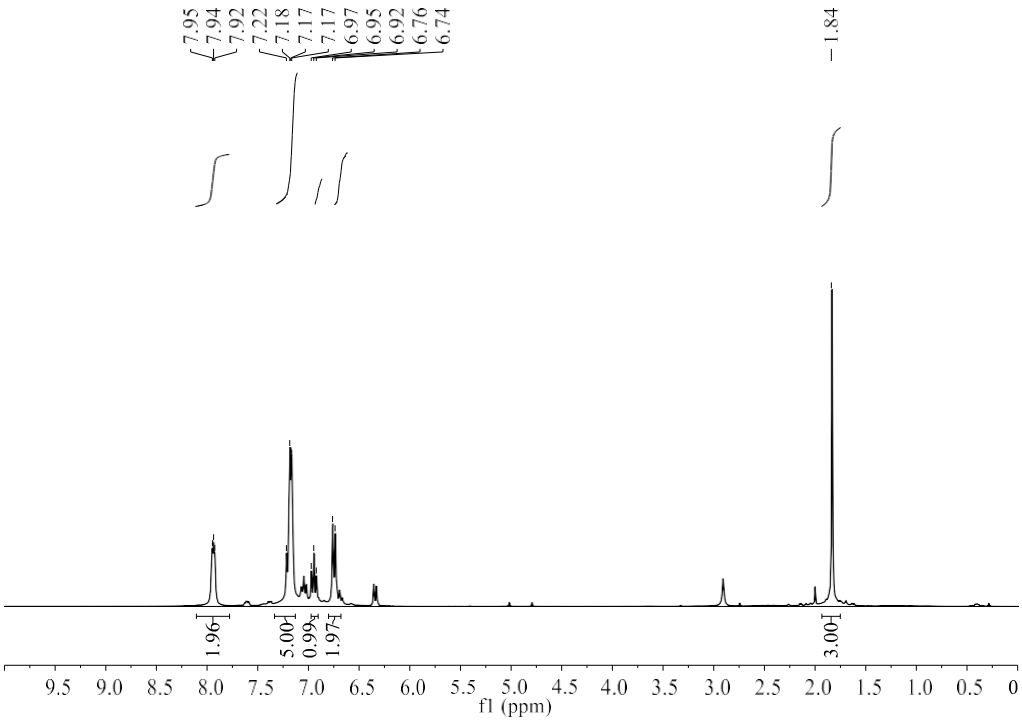


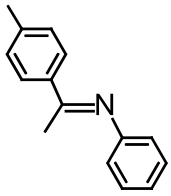
3a

^{13}C NMR



^{1}H NMR





3b

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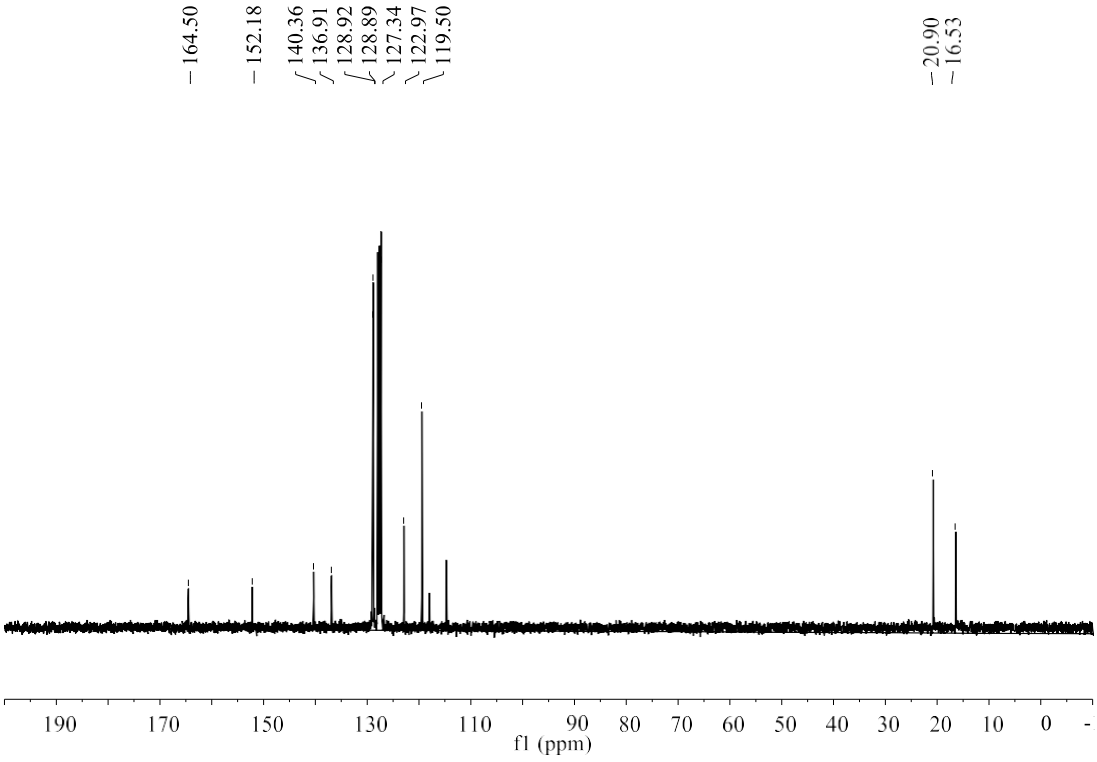

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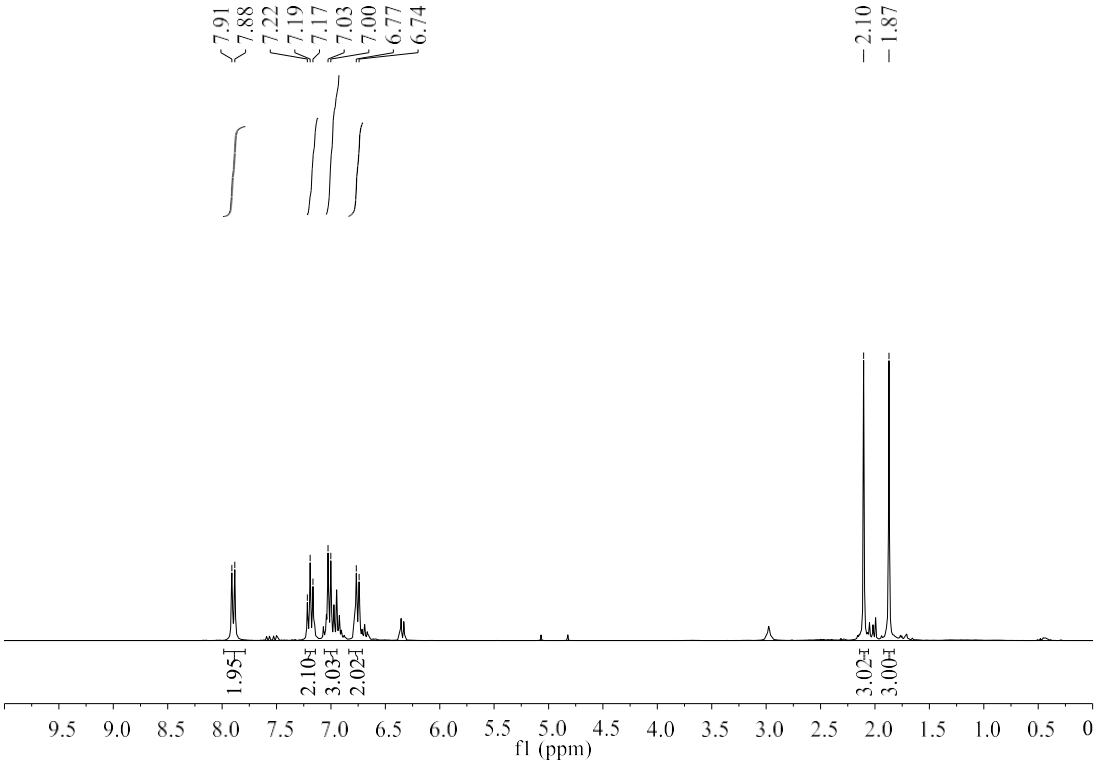
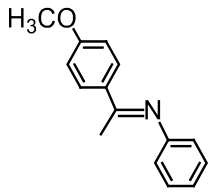
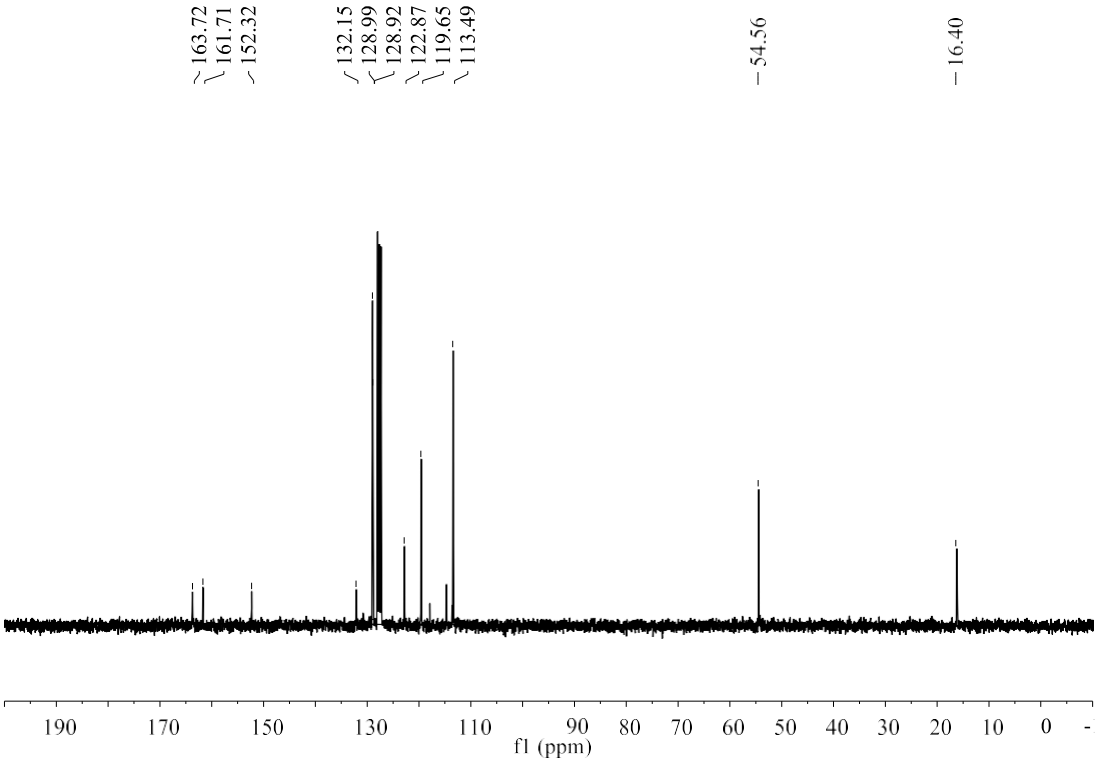


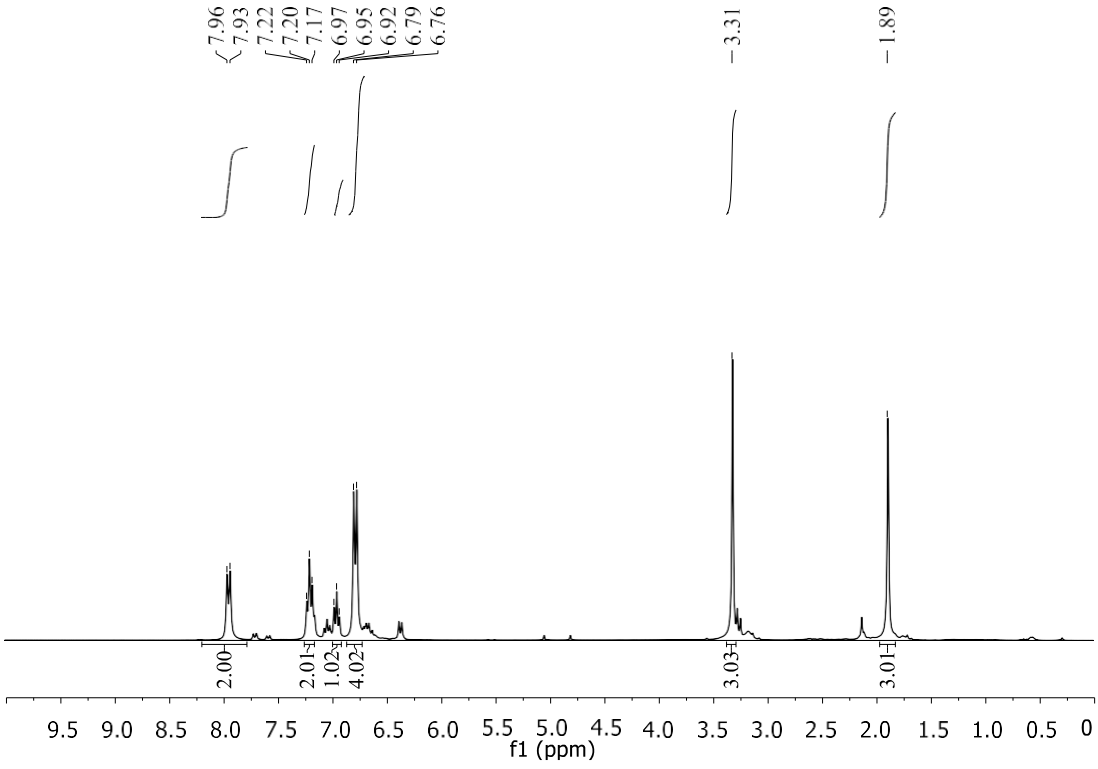


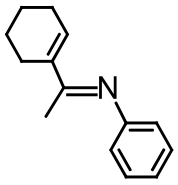
3c

^{13}C NMR



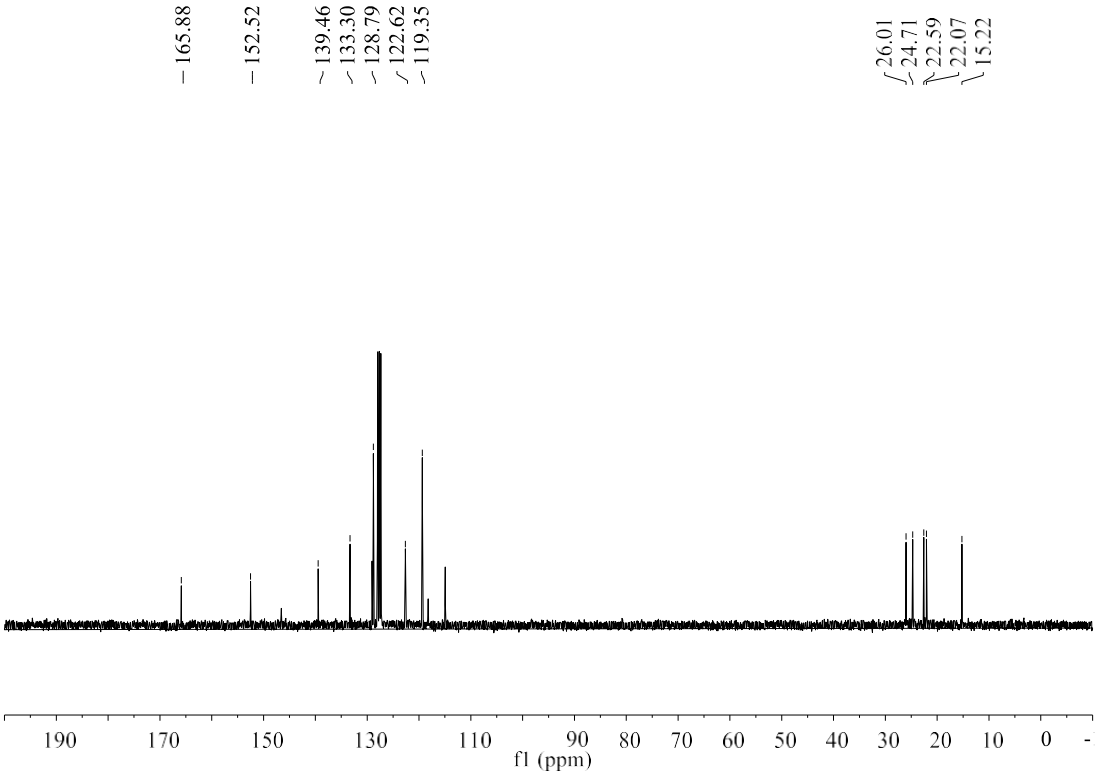
^{1}H NMR





3d

^{13}C NMR



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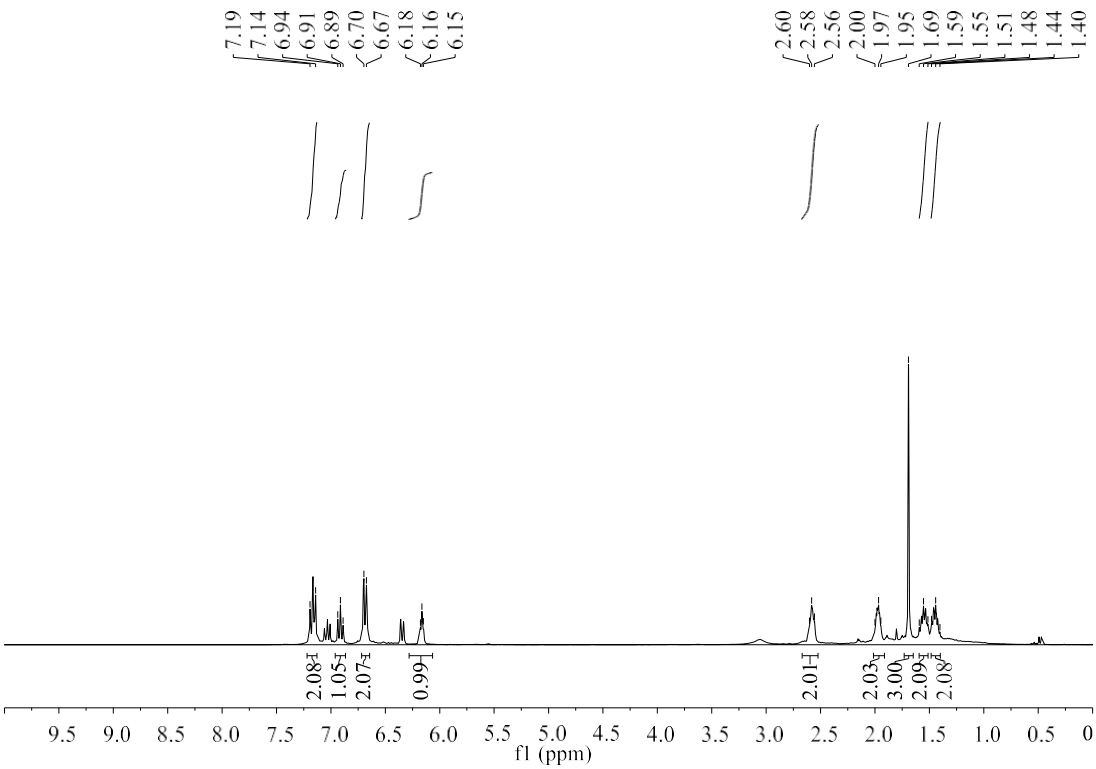

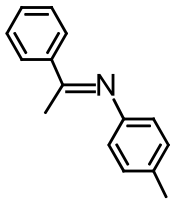

4a

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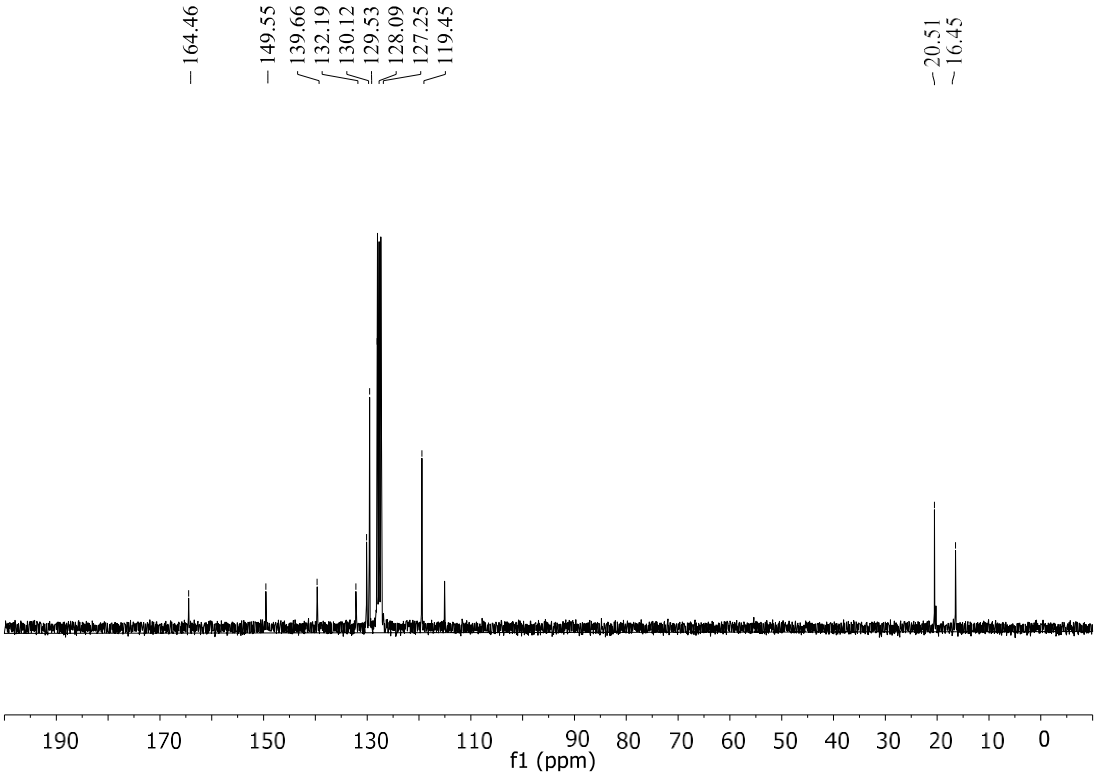
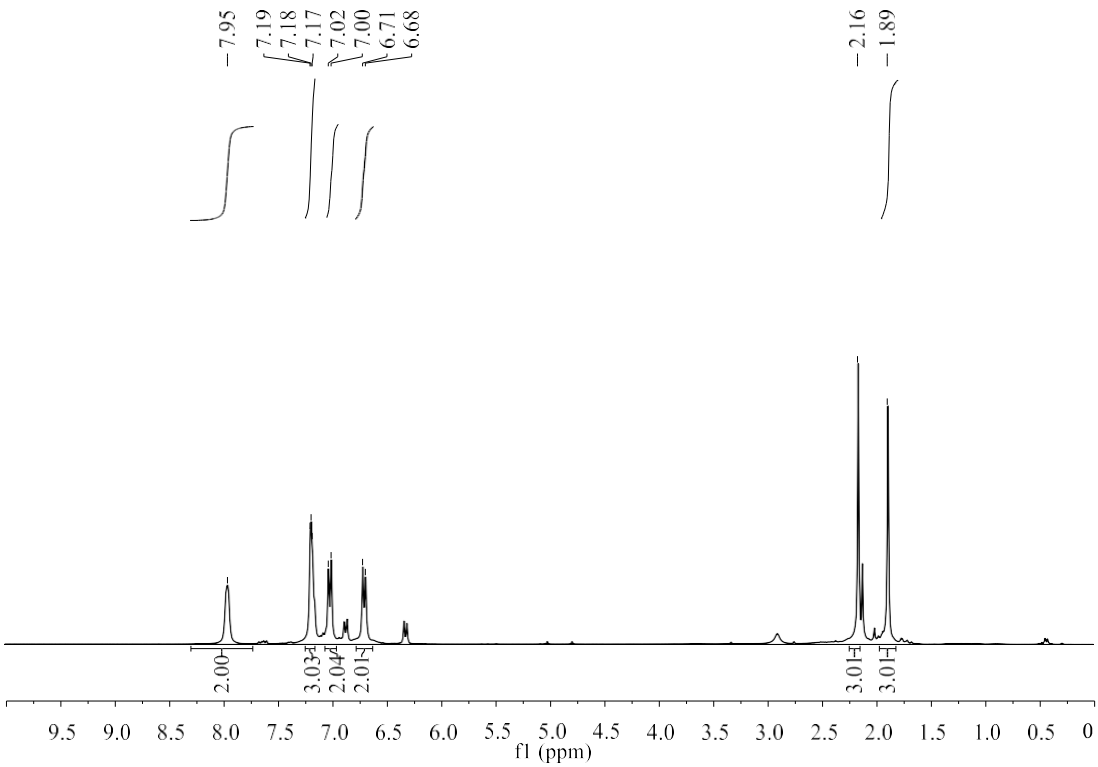
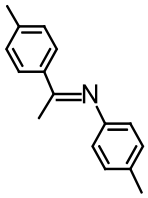


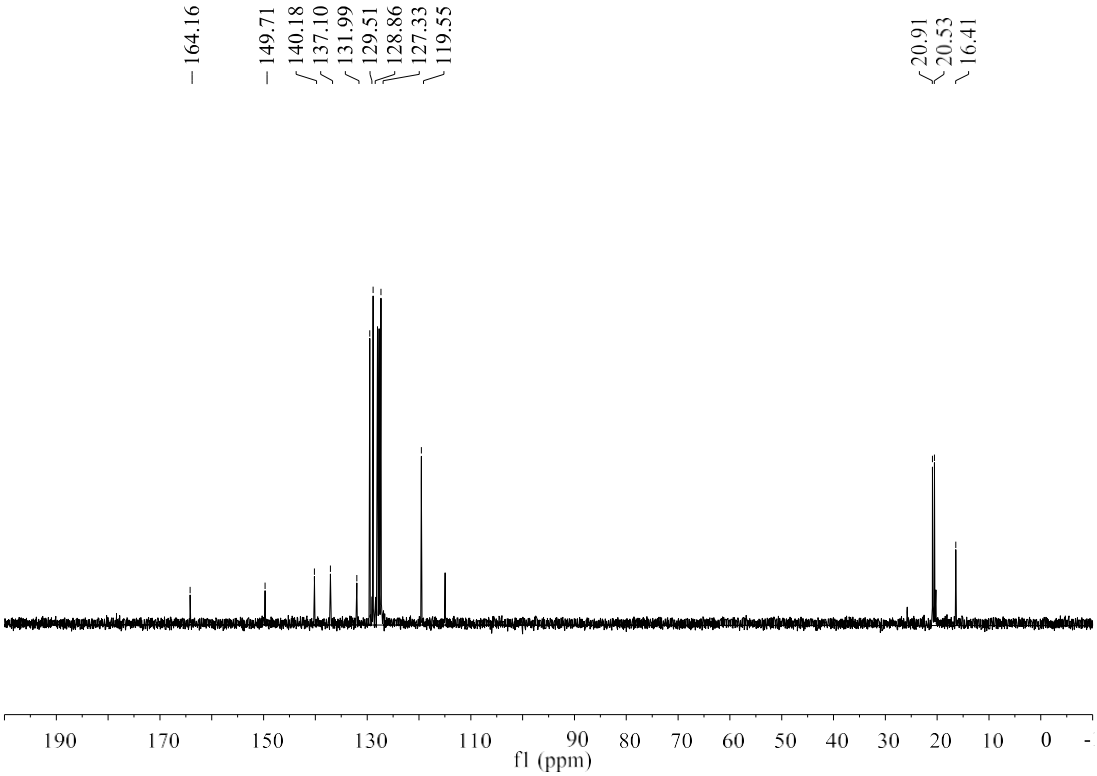
^{1}H NMR



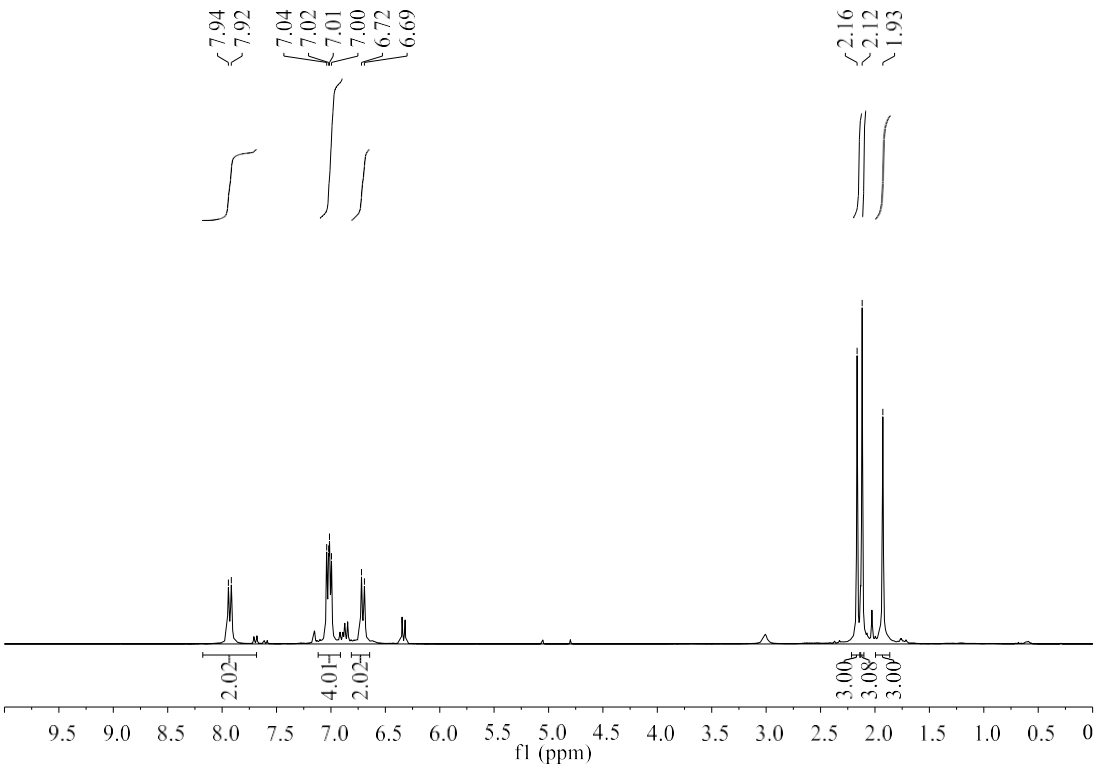


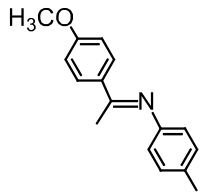
4b

^{13}C NMR



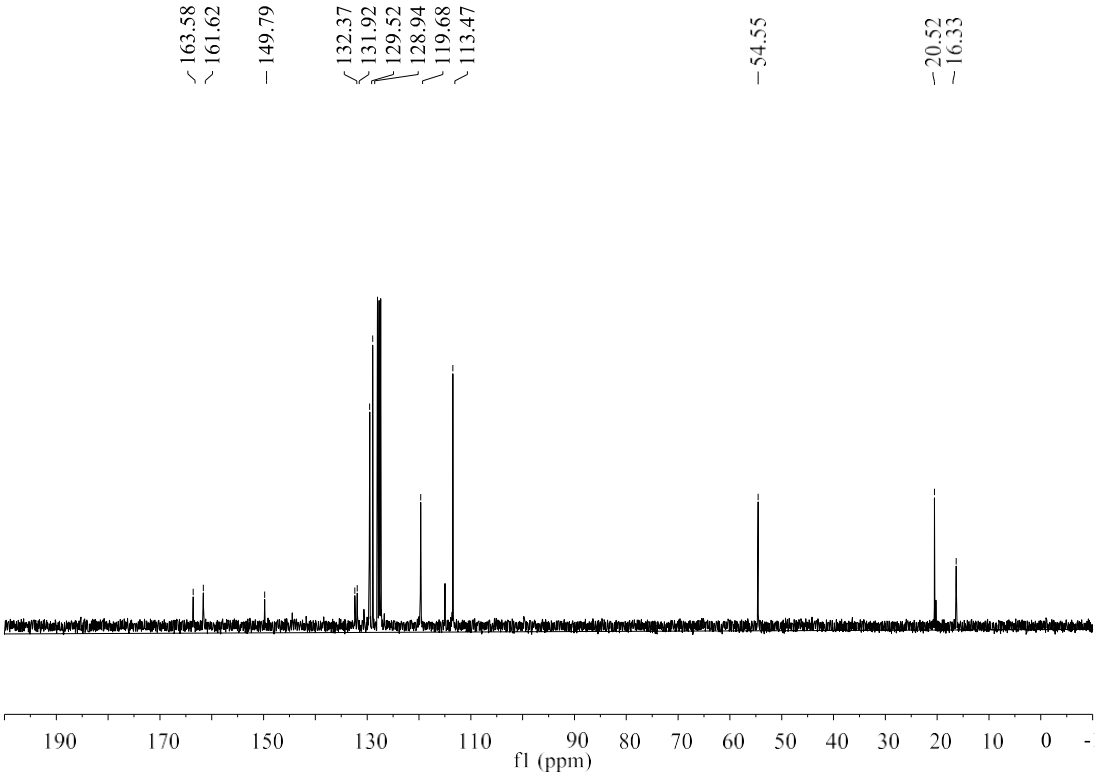
^{1}H NMR



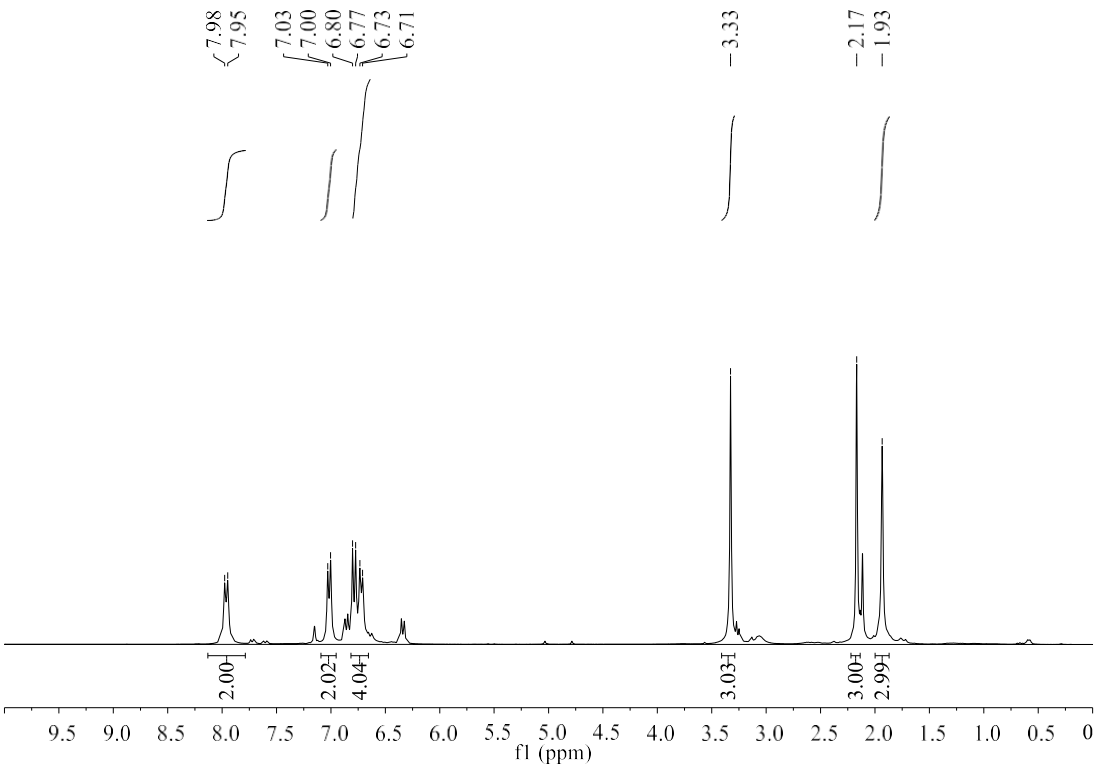


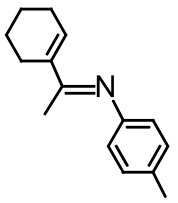
4c

^{13}C NMR



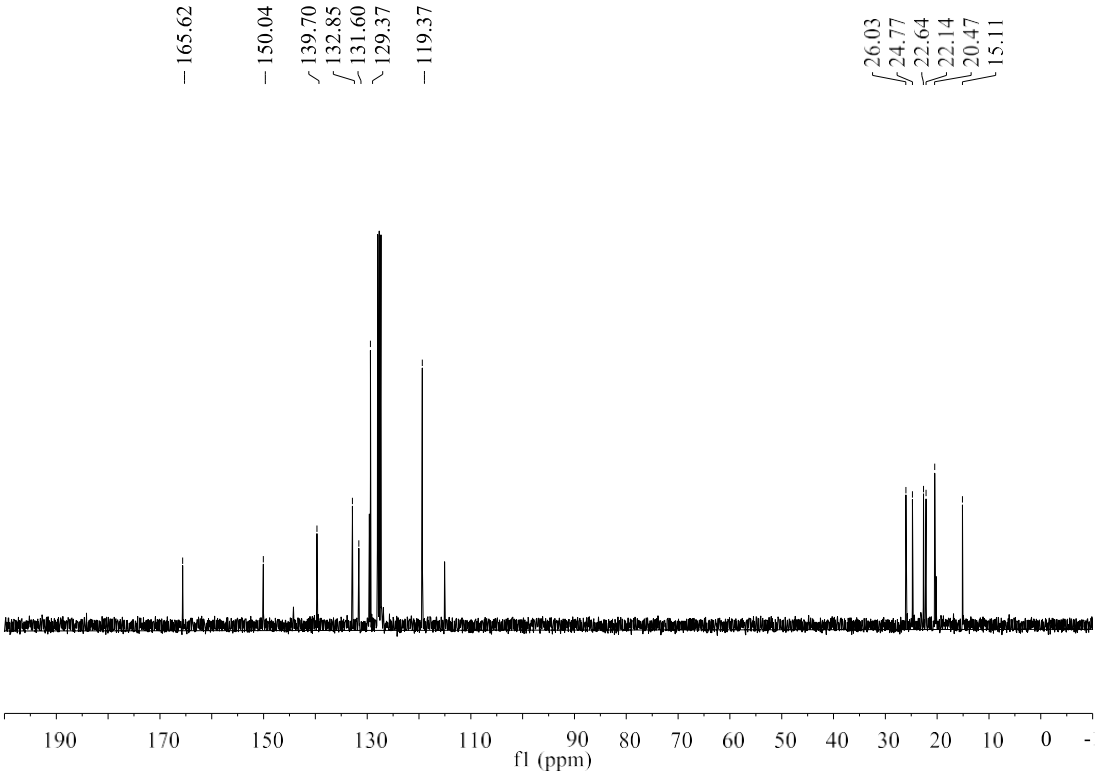
^{1}H NMR



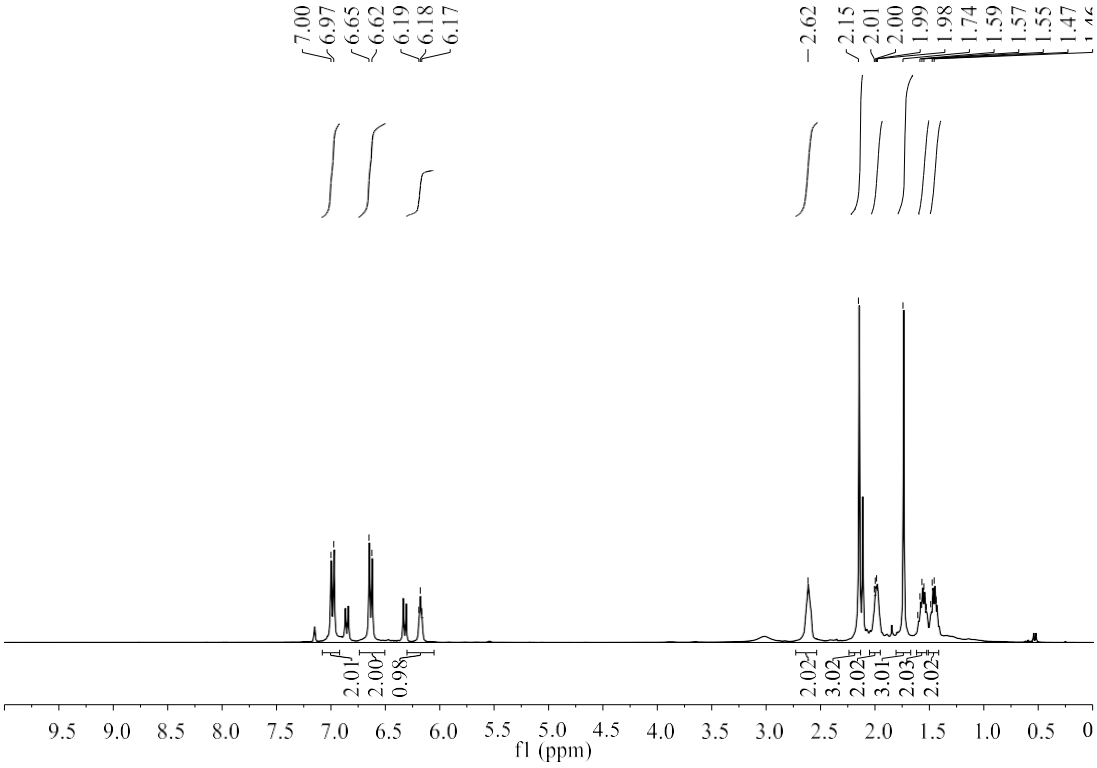


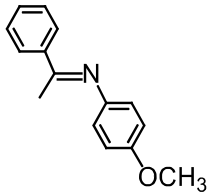
4d

^{13}C NMR



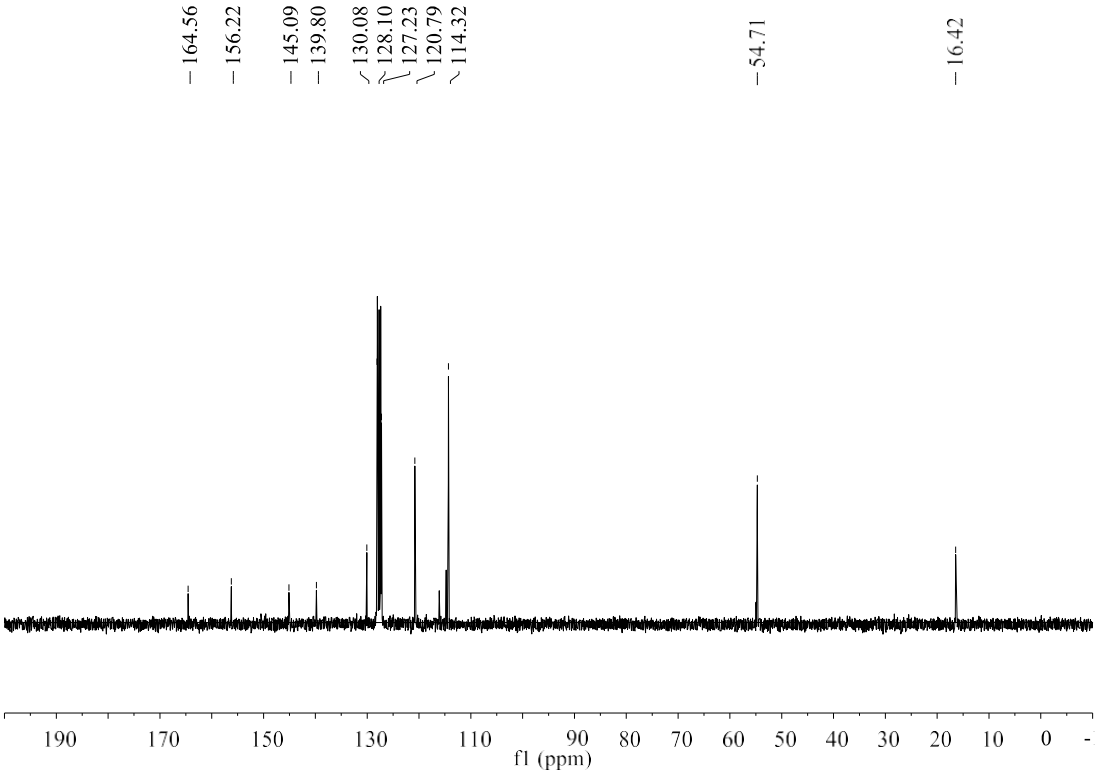
^{1}H NMR



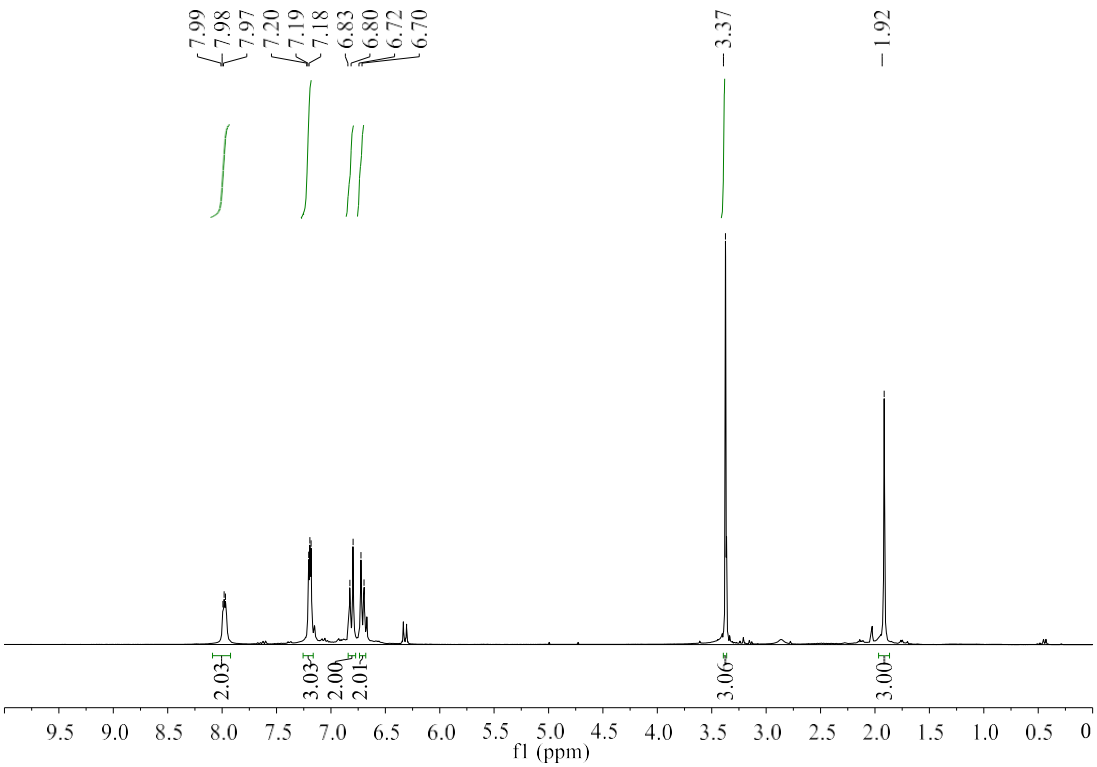


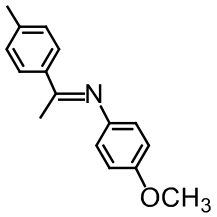
5a

^{13}C NMR



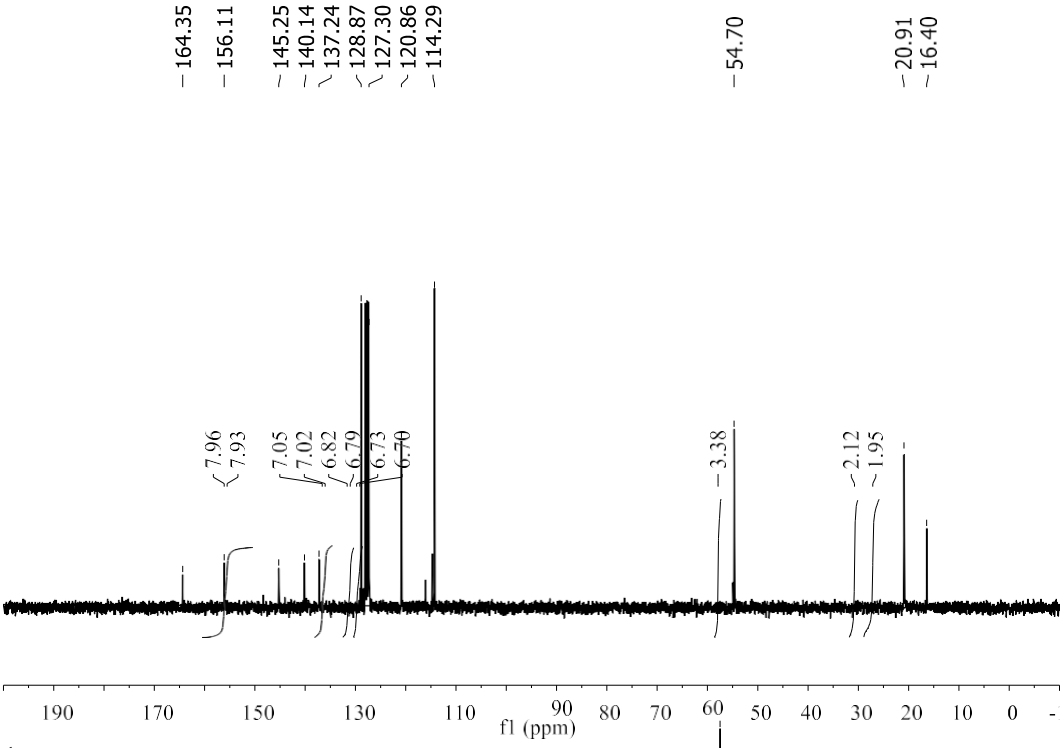
^{1}H NMR



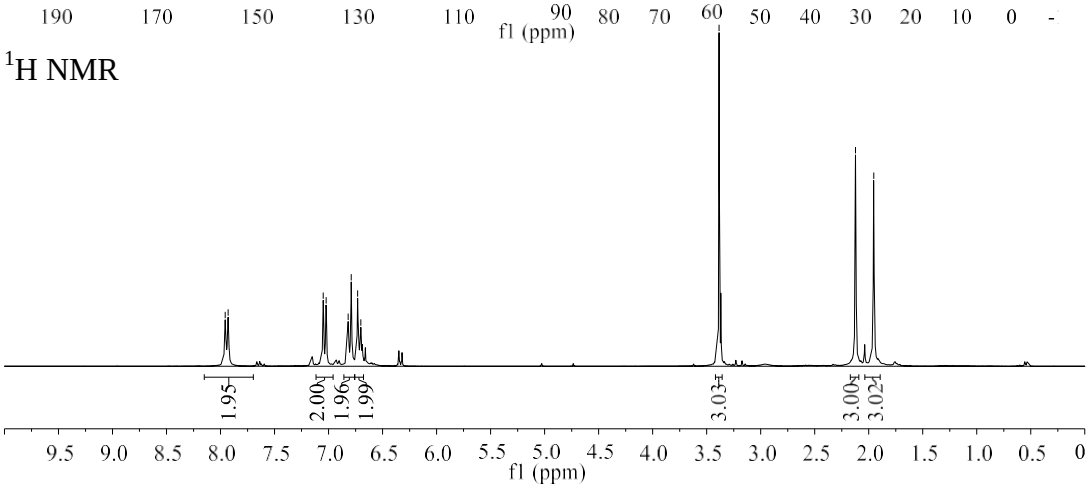


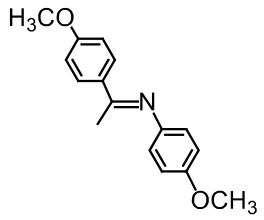
5b

^{13}C NMR



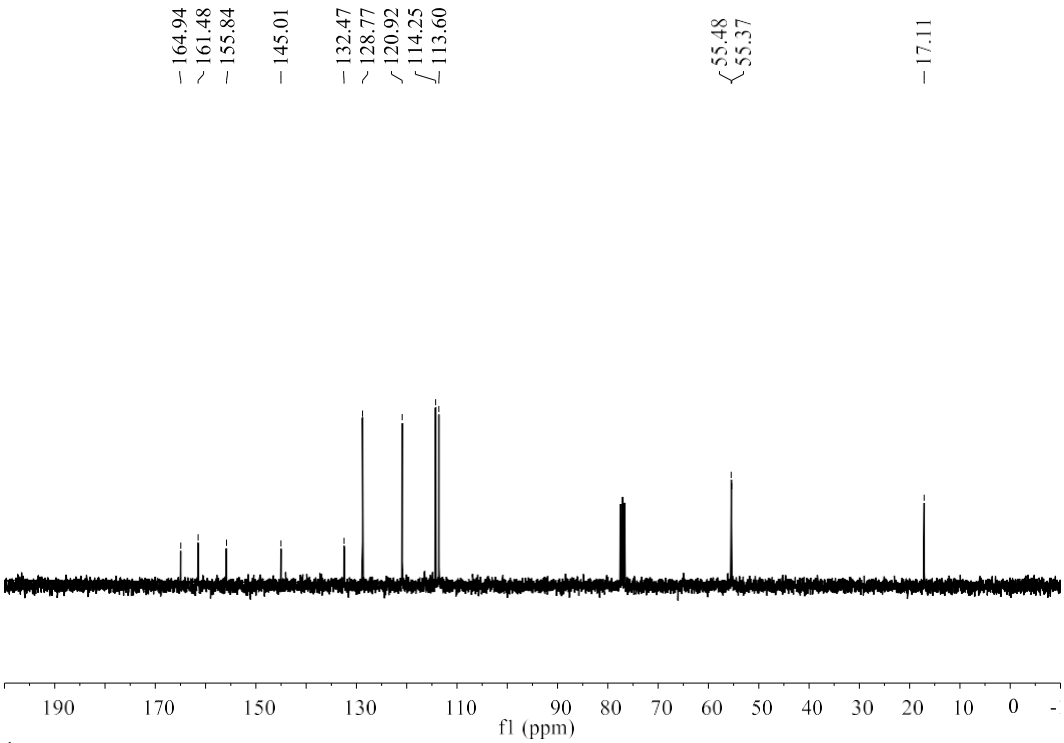
^{1}H NMR



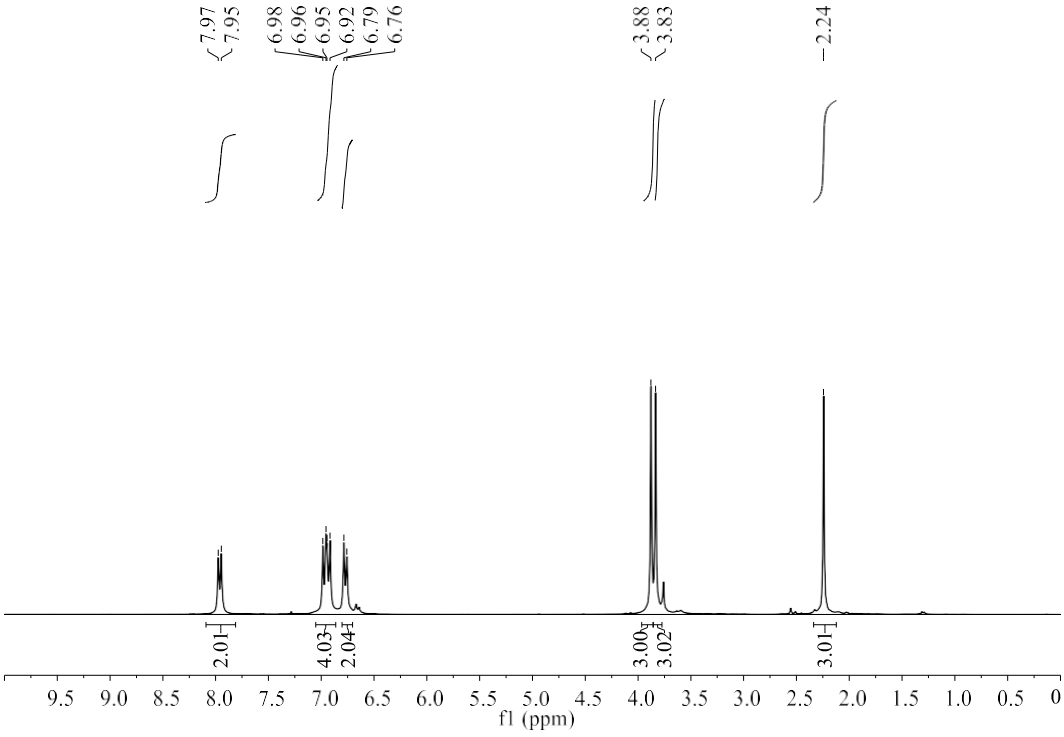


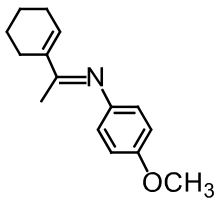
5c

^{13}C NMR



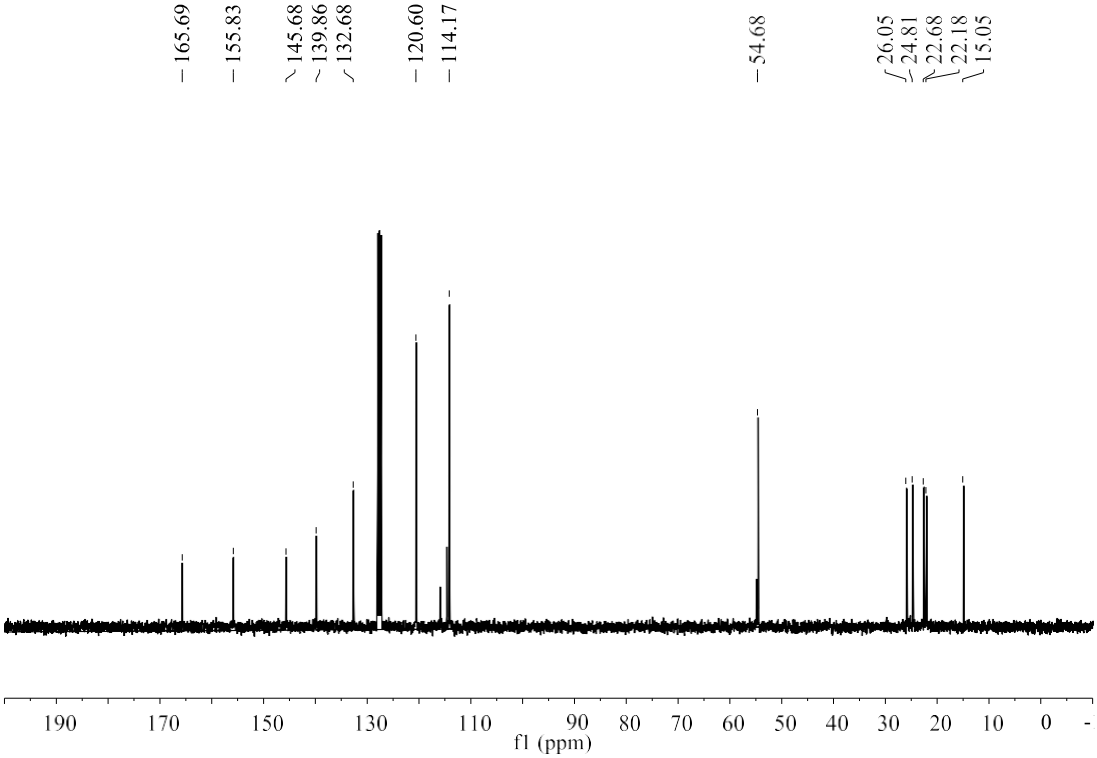
^{1}H NMR



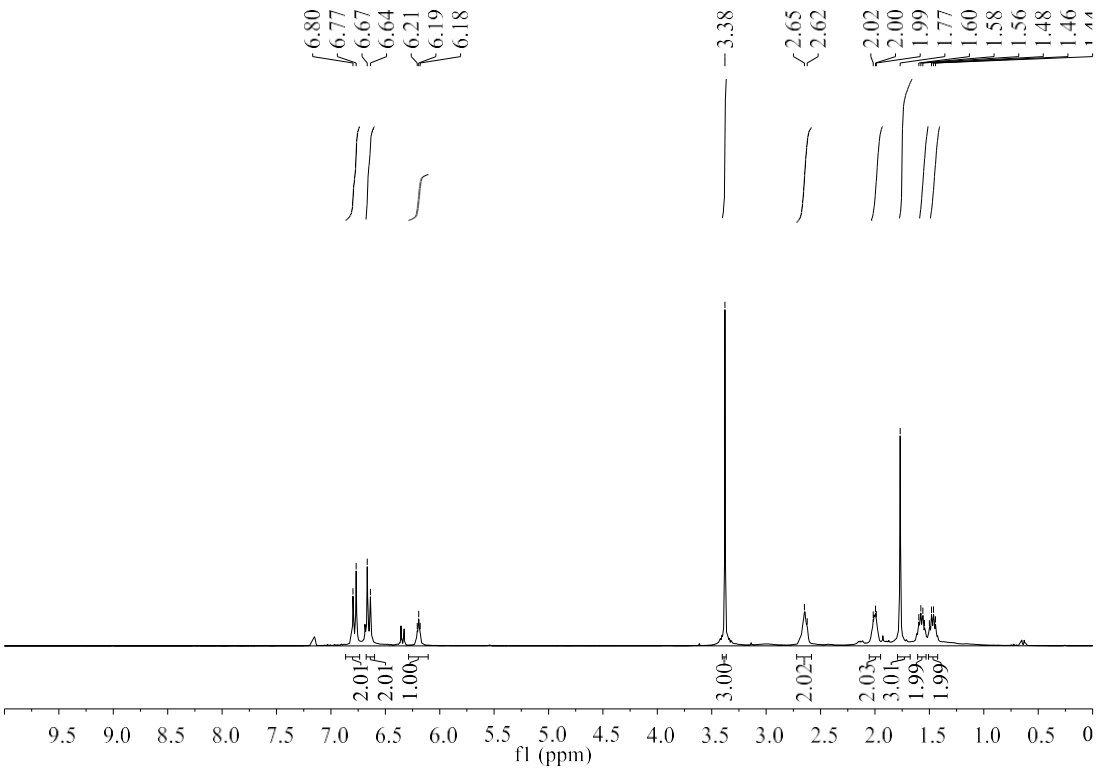


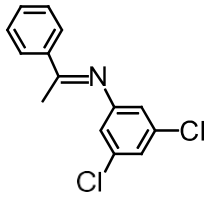
5d

^{13}C NMR



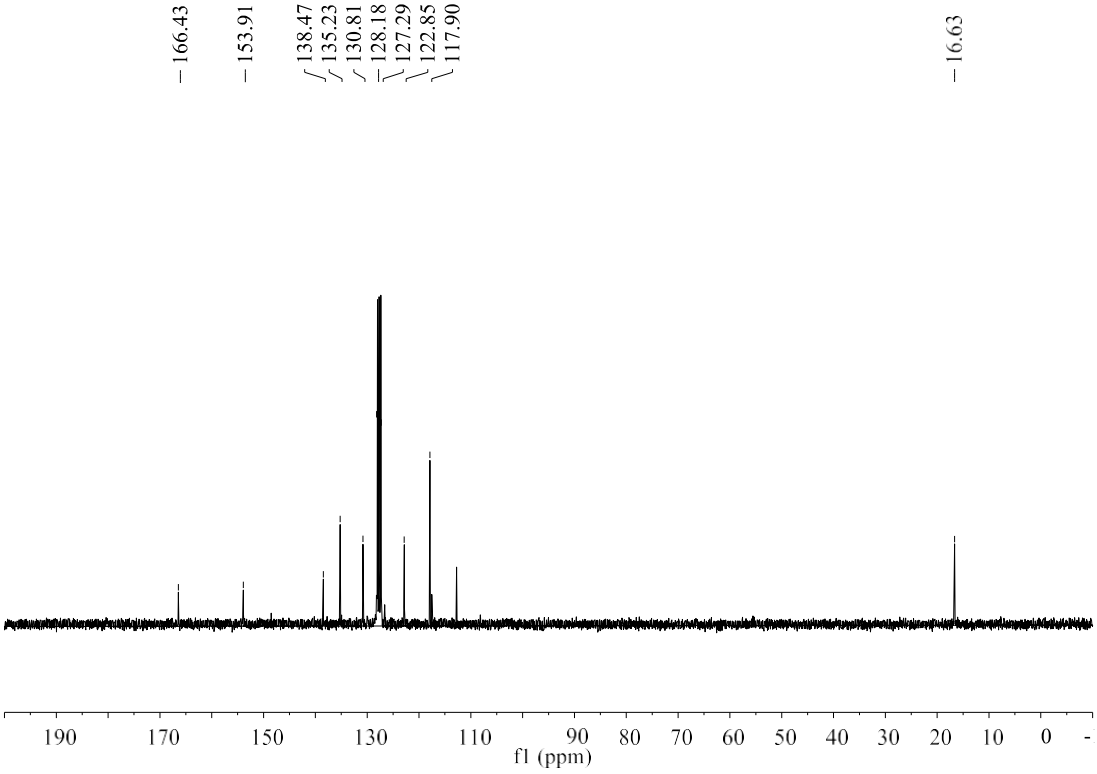
^{1}H NMR



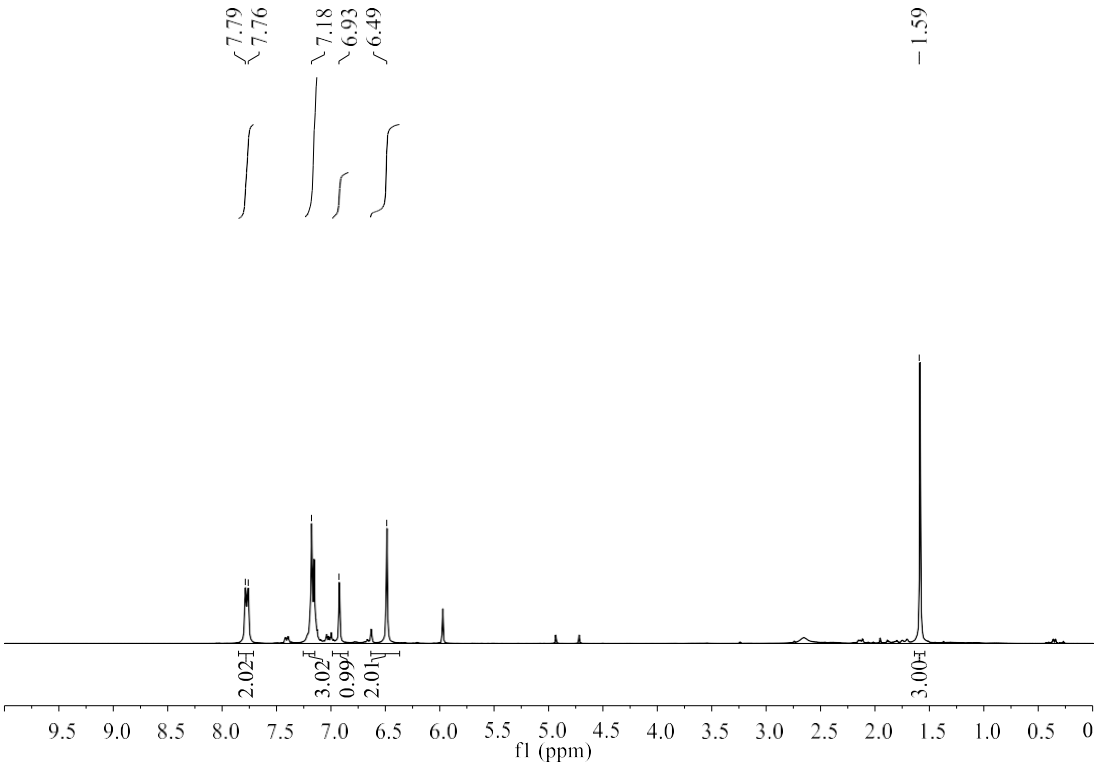


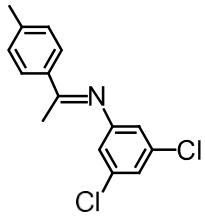
6a

^{13}C NMR



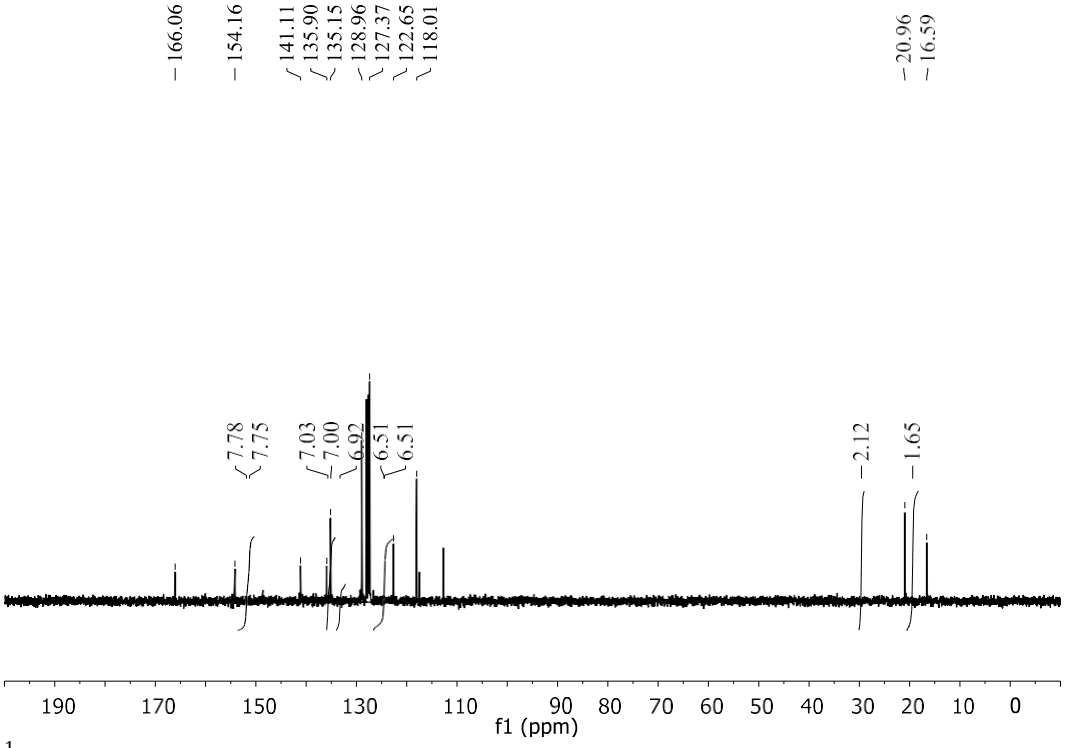
^{1}H NMR



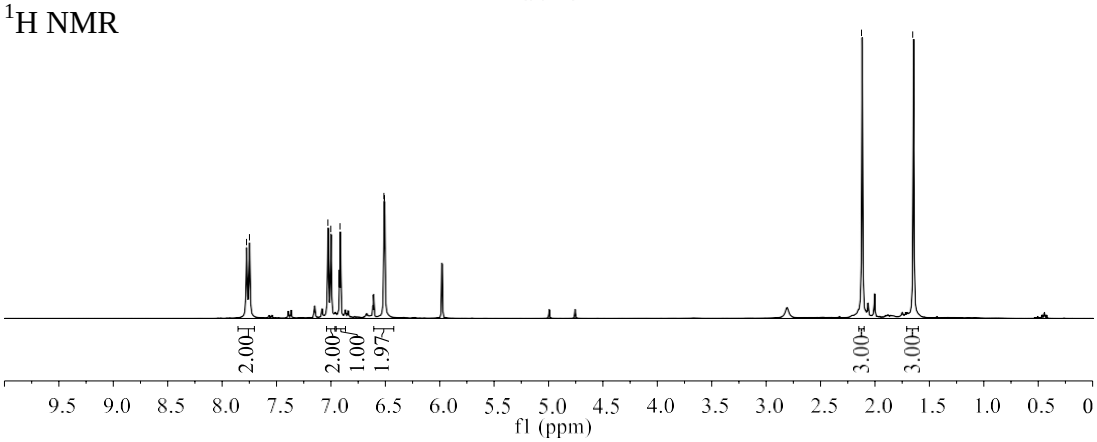


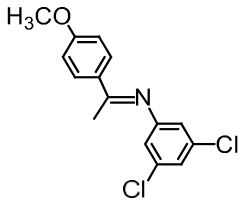
6b

^{13}C NMR



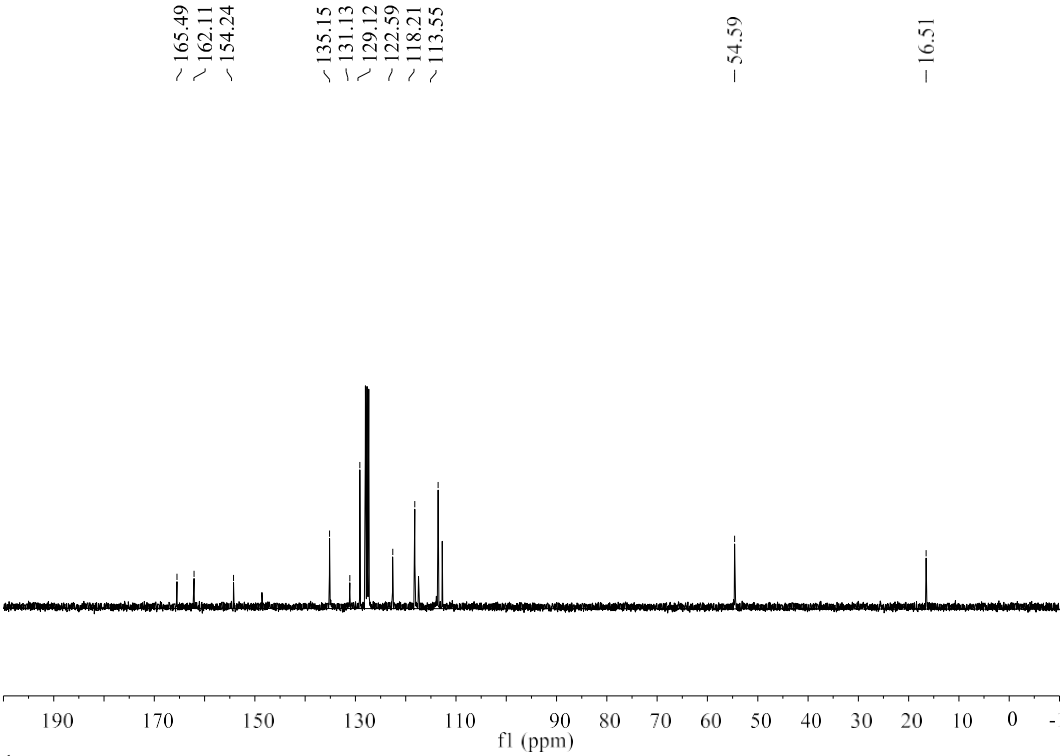
^{1}H NMR



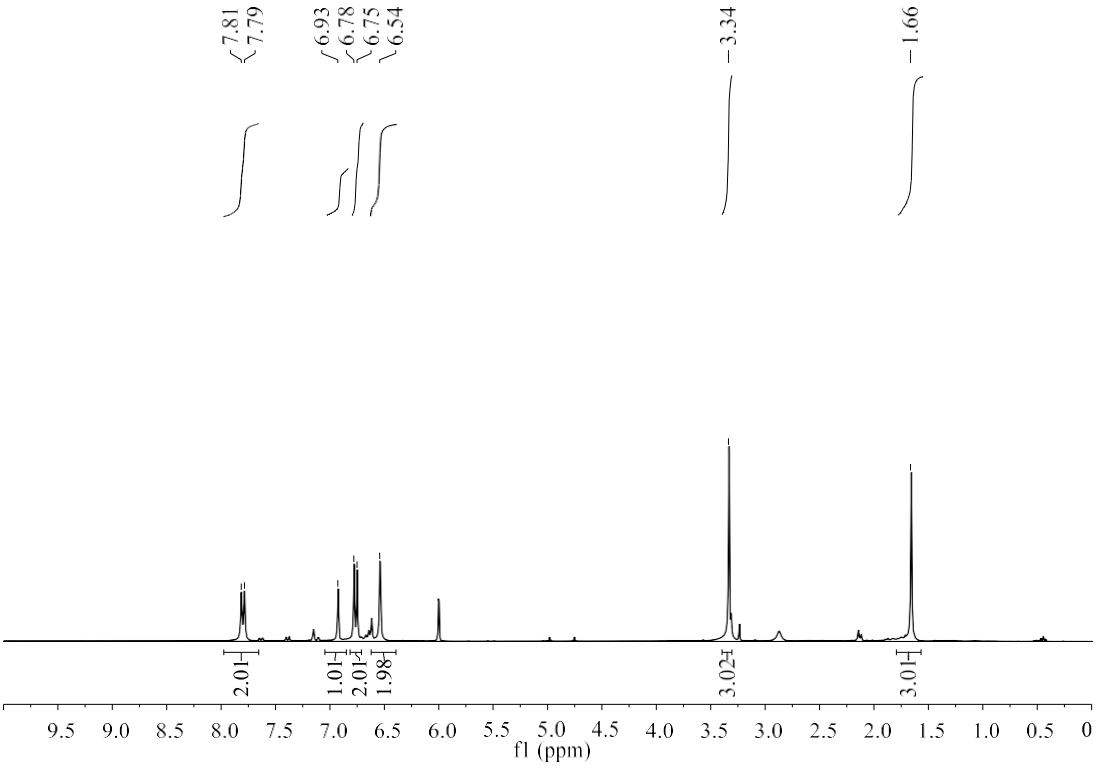


6c

^{13}C NMR



^{1}H NMR



6.90
6.47
6.46
6.14
6.12
6.11

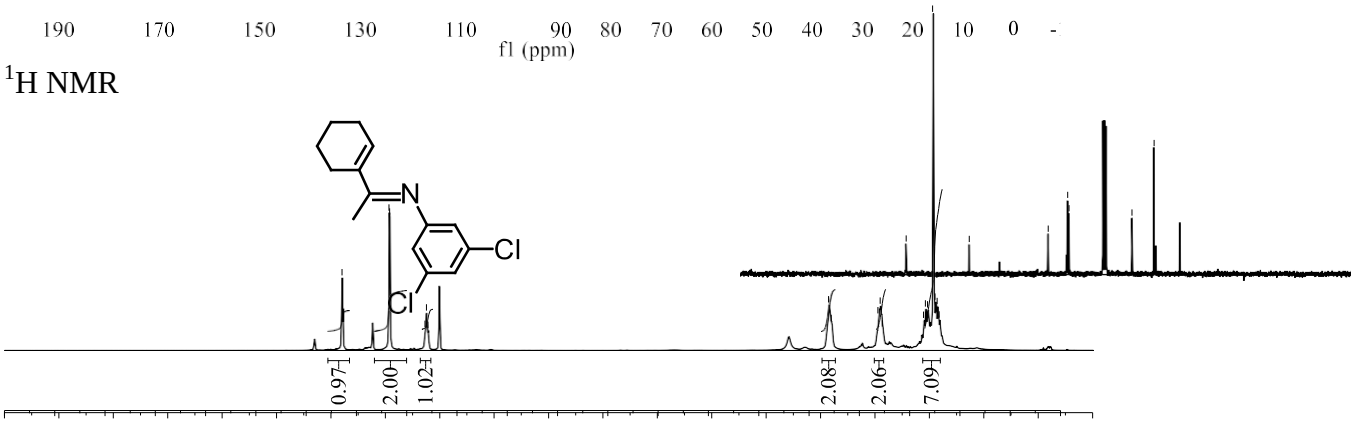
6d

^{13}C NMR

167.14
154.59
138.89
135.02
134.76
122.23
117.84

26.05
24.45
22.44
21.93
15.25

2.43
2.40
1.97
1.95
1.93
1.55
1.54
1.52
1.47
1.45
1.43
1.41



^{1}H NMR