Supplementary Information for

A *N*-Heterocyclic Carbene - Catalyzed Approach to the indirect Friedländer Quinoline Synthesis

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1 Experimental

1.1 General Remarks

All of the reagents and solvents were commercially available and used without further purification. GC analyses were performed on an Agilent 7890A instrument. ^{1}H NMR and ^{13}C NMR were recorded on Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. The ^{1}H NMR spectroscopic data of these precatalysts and products are in agreement with those reported in the literatures.

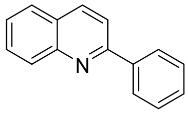
1.2 General procedure for the synthesis of quinolines (**3**).

To a solution of catalyst precursor **B** (0.02 mmol), **1** (1 mmol) and **2** (2 mmol) in toluene (2 mL) was added the KOH (1 mmol) and then the mixture was stirred and heated at 60 °C for an appropriate time. Then, the mixture was quenched by the addition of a saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent removed under reduced pressure. The resulting residue was purified by flash chromatography to afford the corresponding product.

1.3 General method for the one-pot synthesis of polysubstituted quinolines (**7**).

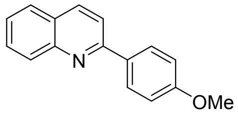
To a solution of catalyst precursor **A** (0.002 mmol) and KOH (0.5 mmol) in toluene (1.5 mL) was added the corresponding ketone (0.5 mmol) followed by the corresponding alcohol (0.6 mmol). The mixture was stirred and heated at 110 °C for an appropriate time. After the reaction was completed and cooled to rt, 2-aminobenzyl alcohol (0.25 mmol), precursor **B** (2 mol %) and KOH (0.25 mmol) were added. After the reaction was completed, the mixture was quenched by the addition of a saturated NH_4Cl solution (20 mL) and extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and the solvent removed under reduced pressure. The resulting residue was purified by flash chromatography to afford the corresponding product.

2. Characterization Data



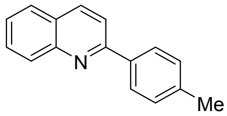
3a [1]

White solid; m. p. 82-83 °C; 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 1.6 Hz, 1H), 8.21 (d, *J* = 1.2 Hz, 2H), 8.19 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.72 (m, 1H), 7.58 – 7.51 (m, 3H), 7.52 – 7.46 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.36, 147.18, 138.56, 135.96, 128.79, 128.67, 128.44, 127.91, 126.66, 126.52, 126.22, 125.38, 118.08; MS (M^+), found 205; Anal. calcd for $C_{15}H_{11}N$: C, 87.77; H, 5.40; N, 6.82 Found: C, 87.45, H,5.38, N, 6.80.



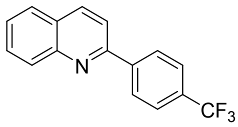
3b [1]

White solid; m. p. 122-123 °C; 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 5.4 Hz, 1H), 8.16 (t, *J* = 2.6 Hz, 2H), 8.15 – 8.13 (m, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.80 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.07 – 7.02 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.94, 155.85, 147.09, 135.83, 131.02, 128.70, 128.39, 127.99, 126.45, 125.93, 125.01, 117.59, 113.28, 54.42; MS (M^+), found 235; Anal. calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.54, H,5.59, N, 5.97.



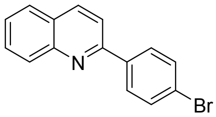
3c [1]

White solid; m. p. 80-81 ºC; 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.20 (d, *J* = 5.5 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.55 – 7.48 (m, 1H), 7.34 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.29, 147.03, 138.59, 135.93, 135.60, 128.74, 128.62, 128.48, 126.54, 126.47, 126.12, 125.21, 117.94, 20.38; MS (M^+), found 219; Anal. calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.85, H,5.96, N, 6.41.



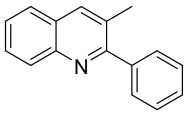
3d [5]

Colorless oil; 83% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 2H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.95 – 7.84 (m, 2H), 7.82 – 7.72 (m, 3H), 7.59 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.64, 147.21, 141.86, 136.21, 130.52, 130.27, 130.01, 129.75, 129.05, 128.82, 126.88, 126.54, 126.47, 125.90, 124.76, 124.32, 122.15, 117.78; MS (M^+), found 273; Anal. calcd for $C_{16}H_{10}F_3N$: C, 70.33; H, 3.69; F, 20.86; N, 5.13. Found: C, 70.48, H,3.70, N, 5.15.



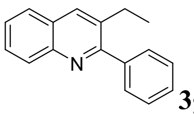
3e [7]

Colorless oil; 86% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (t, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.80 (dd, *J* = 8.2, 5.2 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.00, 147.15, 137.39, 136.09, 131.00, 128.94, 128.65, 128.14, 126.53, 126.27, 125.59, 123.02, 117.53; MS (M^+), found 283; Anal. calcd for $C_{15}H_{10}BrN$: C, 63.40; H, 3.55; N, 4.93. Found: C, 63.28, H,3.56, N,4.95.



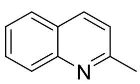
3f [1]

Colorless oil; 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.50 (ddd, *J* = 13.1, 6.9, 1.1 Hz, 3H), 7.46 – 7.41 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.54, 145.66, 139.89, 135.80, 128.33, 128.24, 127.91, 127.80, 127.35, 127.24, 126.64, 125.76, 125.45, 19.66; MS (M^+), found 219; Anal. calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.92, H,5.96, N, 6.41.



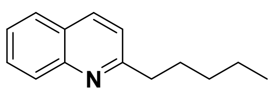
3g [8]

Colorless oil; 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 1H), 8.02 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.57 (dt, *J* = 3.0, 1.8 Hz, 2H), 7.49 (dd, *J* = 14.7, 7.6 Hz, 3H), 7.44 (dd, *J* = 8.5, 6.0 Hz, 1H), 2.79 (q, *J* = 7.5 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.65, 145.41, 139.95, 134.32, 134.02, 128.30, 127.89, 127.82, 127.37, 127.17, 126.80, 126.03, 125.45, 25.08, 13.80; MS (M^+), found 233; Anal. calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.82, H,6.44, N, 6.02.



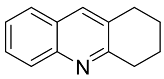
3h [6]

Colorless oil; 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 10.5, 8.8 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.57 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.21 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.93, 146.80, 135.18, 128.42, 127.56, 126.47, 125.48, 124.66, 120.97, 24.29; MS (M^+), found 143; Anal. calcd for $C_{10}H_9N$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.64, H,6.32, N, 9.75.



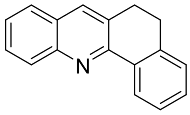
3i [3]

Colorless oil; 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.07 (s, 1H), 7.77 (m, *J* = 8.1, 1.4 Hz, 1H), 7.68 (m, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 3.04 – 2.92 (m, 2H), 1.87 – 1.75 (m, 2H), 1.43 – 1.31 (m, 4H), 0.93 – 0.84 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.11, 146.59, 135.50, 128.51, 127.60, 126.52, 125.73, 124.78, 120.42, 38.21, 30.78, 28.83, 21.60, 13.06; MS (M^+), found 199; Anal. calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.70, H,8.57, N,7.01.



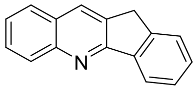
3j [1]

Colorless oil; 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 3.12 (t, *J* = 6.6 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.07 – 1.93 (m, 2H), 1.91 – 1.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.26, 145.40, 134.17, 130.00, 127.60, 127.11, 126.21, 125.90, 124.61, 32.46, 28.23, 22.19, 21.89; MS (M^+), found 183; Anal. calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.01, H,7.18, N, 7.67.



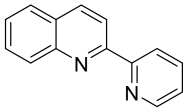
3k [3]

White solid; m. p. 64-65 °C; 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 7.6 Hz, 1H), 8.17 (d, *J* = 8.3 Hz, 1H), 7.92 (s, 1H), 7.73 (dd, *J* = 12.7, 5.7 Hz, 1H), 7.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.38 (td, *J* = 7.4, 1.4 Hz, 1H), 7.30 – 7.24 (m, 1H), 3.15 – 3.09 (m, 2H), 3.01 (dd, *J* = 8.3, 5.6 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.34, 146.46, 138.48, 133.54, 132.91, 129.64, 128.81, 128.30, 127.78, 126.97, 126.90, 126.38, 125.94, 125.16, 27.85, 27.42; MS (M^+), found 231; Anal. calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.45, H,5.69, N, 6.04.



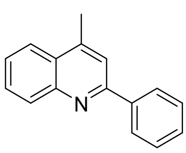
3l [4]

Colorless oil; 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 – 8.28 (m, 1H), 8.21 (d, *J* = 7.7 Hz, 2H), 7.85 – 7.80 (m, 1H), 7.72 – 7.67 (m, 1H), 7.63 – 7.59 (m, 1H), 7.53 – 7.46 (m, 3H), 4.05 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.66, 146.96, 144.14, 133.66, 130.30, 129.06, 128.04, 127.92, 126.79, 126.59, 126.42, 124.75, 124.49, 121.20, 33.06; MS (M^+), found 217; Anal. calcd for $C_{16}H_{11}N$: C, 88.45; H, 5.10; N, 6.45. Found: C, 88.80, H,5.12, N, 6.43.



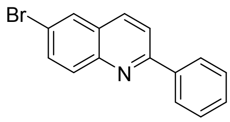
3m [3]

White solid; m. p. 98-99 °C; 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.65 (s, 1H), 8.55 (s, 1H), 8.27 (d, *J* = 7.1 Hz, 1H), 8.19 (d, *J* = 6.4 Hz, 1H), 7.85 (t, *J* = 7.1 Hz, 2H), 7.72 (s, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.34 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.24, 148.15, 146.92, 136.02, 135.83, 128.84, 128.57, 127.27, 126.69, 125.82, 123.10, 120.93, 118.01; MS (M^+), found 206; Anal. calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.32, H,4.90, N, 13.61.



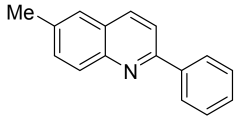
3n [9]

Yellow oil; 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 7.4 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 14.1, 5.6 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 3H), 7.43 (t, *J* = 7.3 Hz, 1H), 2.70 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.17, 148.23, 144.97, 139.93, 130.38, 129.47, 129.34, 128.91, 127.69, 127.38, 126.16, 123.75, 119.88, 19.11; MS (M^+), found 219; Anal. calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.93, H,5.96, N, 6.38.



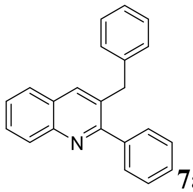
3o [10]

Yellow oil; 79% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.10 (m, 3H), 8.04 (d, J = 9.0 Hz, 1H), 7.98 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 9.0, 2.1 Hz, 1H), 7.54 (t, J = 7.4 Hz, 2H), 7.48 (dd, J = 8.4, 6.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.80, 146.97, 139.31, 135.86, 133.21, 131.56, 129.72, 129.61, 129.02, 128.36, 127.63, 120.15, 119.89, 29.82; MS (M^+), found 283; Anal. calcd for $C_{15}H_{10}BrN$: C, 63.40; H, 3.55; N, 4.93. Found: C, 63.29, H,3.56, N,4.91.



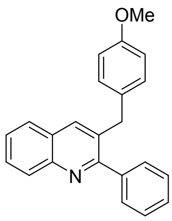
3p [5]

Yellow oil; 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (dd, J = 11.6, 4.5 Hz, 3H), 8.03 (d, J = 8.6 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.41 (t, J = 7.3 Hz, 1H), 2.51 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.65, 146.99, 139.93, 136.20, 132.04, 129.51, 129.22, 128.91, 127.58, 127.31, 126.43, 119.11, 21.70; MS (M^+), found 219; Anal. calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.45, H,5.96, N, 6.37.



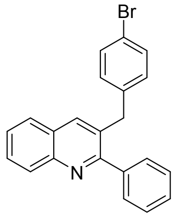
7a [2]

Yellow solid; 85% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 8.5 Hz, 1H), 7.93 (s, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.69 (dd, J = 11.2, 4.1 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.44 (dt, J = 11.8, 4.2 Hz, 3H), 7.24 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.00 (d, J = 7.2 Hz, 2H), 4.14 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.76, 145.66, 139.67, 138.98, 136.02, 131.53, 128.32, 128.16, 128.02, 127.87, 127.50, 127.30, 127.21, 126.55, 126.12, 125.50, 125.27, 38.12; MS (M^+), found 295; Anal. calcd for $C_{22}H_{17}N$: C, 89.46; H, 5.80; N, 4.74. Found: C, 89.10 H,5.78, N, 4.75.



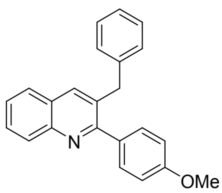
7b [2]

Yellow solid; 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.4 Hz, 1H), 7.90 (s, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.49 (dd, J = 8.0, 1.5 Hz, 3H), 7.43 (t, J = 4.8 Hz, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.06 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.76, 157.11, 145.64, 139.74, 135.85, 132.00, 131.01, 129.01, 128.32, 128.12, 127.91, 127.31, 127.21, 126.60, 126.14, 125.49, 112.95, 54.26, 37.29; MS (M $^+$), found 325; Anal. calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30; O, 4.92. Found: C, 85.19, H,5.91, N, 4.31.



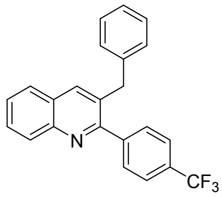
7c (**new compound**)

Yellow oil; 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.90 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.69 (dd, *J* = 8.2, 7.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43 (s, 4H), 7.33 (d, *J* = 8.4 Hz, 3H), 6.83 (d, *J* = 8.2 Hz, 2H), 4.07 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.63, 145.73, 139.48, 137.93, 136.00, 130.90, 130.57, 130.44, 129.70, 129.24, 128.37, 127.80, 127.57, 127.38, 126.13, 125.68, 119.19, 37.64; MS (M $^+$), found 373; Anal. calcd for $C_{22}H_{16}BrN$: C, 70.60, H, 4.31, N, 3.74. Found: C, 70.38, H,4.30, N, 3.75.



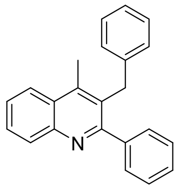
7d [2]

Yellow solid; 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.89 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.22 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 4.15 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.42, 158.73, 145.75, 139.16, 136.06, 132.25, 131.57, 129.29, 128.27, 128.01, 127.52, 126.42, 126.08, 125.30, 125.28, 112.78, 54.41, 38.20; MS (M $^+$), found 325; Anal. calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 85.17, H,5.87, N, 4.28.



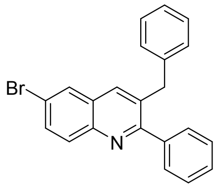
7e [2]

Off-white solid; 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.98 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (d, *J* = 8.4 Hz, 3H), 7.23 – 7.16 (m, 3H), 6.95 (d, *J* = 7.0 Hz, 2H), 4.10 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.25, 145.67, 143.20, 138.53, 136.46, 131.09, 128.51, 128.30, 128.09, 128.02, 127.87, 127.59, 127.37, 126.69, 126.20, 125.97, 125.45, 125.30, 125.11, 125.00, 124.26, 38.06; MS (M $^+$), found 363; Anal. calcd for $C_{23}H_{16}F_3N$: C, 76.02; H, 4.44; N, 3.85. Found: C, 76.28, H,4.43, N, 3.84.



7f (**new compound**)

Yellow oil; 68% yield. [1]H NMR (300 MHz, CDCl3) δ 8.04 (d, J = 9.1 Hz, 1H), 7.84 (s, 1H), 7.55 – 7.39 (m, 7H), 7.28 – 7.18 (m, 3H), 7.00 (d, J = 7.8 Hz, 2H), 4.12 (s, 2H), 2.53 (s, 3H). [13]C NMR (75 MHz, CDCl3) δ 160.73, 146.17, 141.77, 141.14, 137.47, 133.47, 132.53, 130.06, 129.96, 129.52, 129.32, 129.15, 128.60, 127.27, 127.00, 40.13, 22.66; MS (M^+), found 309; Anal. calcd for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53. Found: C, 88.93, H, 6.21, N, 4.54.



7g [3]

Yellow oil; 72% yield. [1]H NMR (300 MHz, CDCl3) δ 8.00 (d, J = 8.9 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 7.0 Hz, 1H), 7.74 (dd, J = 8.9, 2.1 Hz, 1H), 7.55 – 7.40 (m, 5H), 7.32 – 7.19 (m, 3H), 6.99 (d, J = 7.5 Hz, 2H), 4.13 (s, 2H). [13]C NMR (75 MHz, CDCl3) δ 162.16, 146.11, 141.28, 140.58, 136.99, 134.75, 133.67, 132.08, 130.21, 130.08, 129.84, 129.66, 129.45, 127.50, 121.40, 40.15; MS (M^+), found 373; Anal. calcd for $C_{22}H_{16}BrN$: C, 70.60, H, 4.31, N, 3.74. Found: C, 70.45, H,4.32, N, 3.73.

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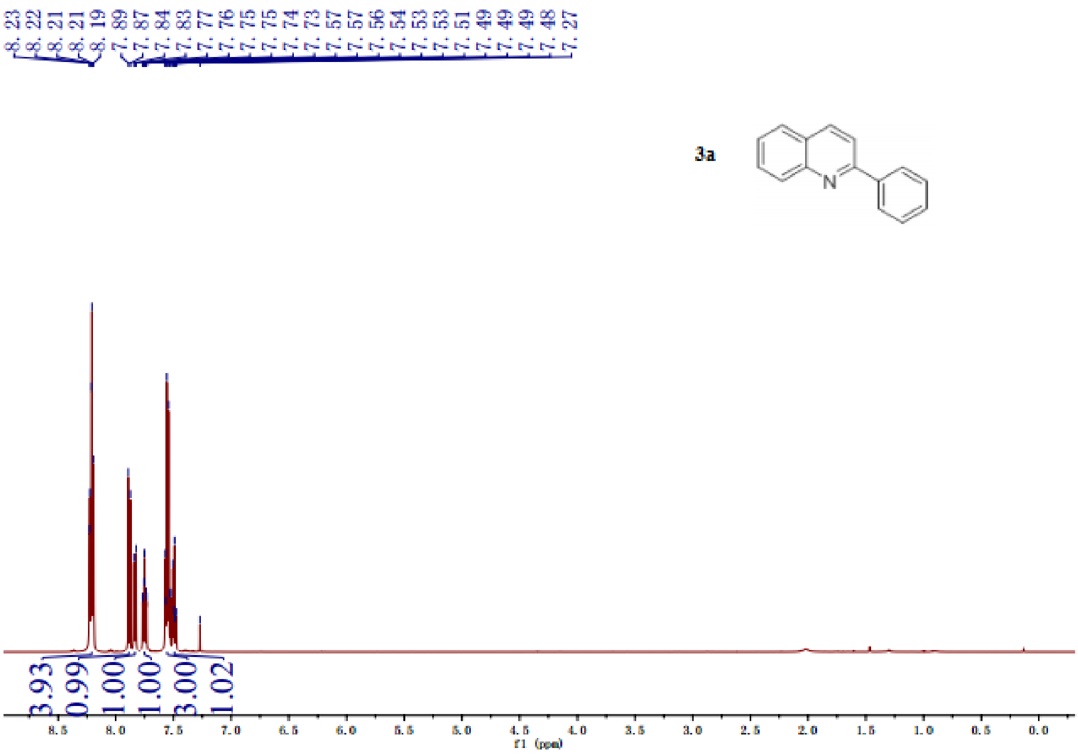
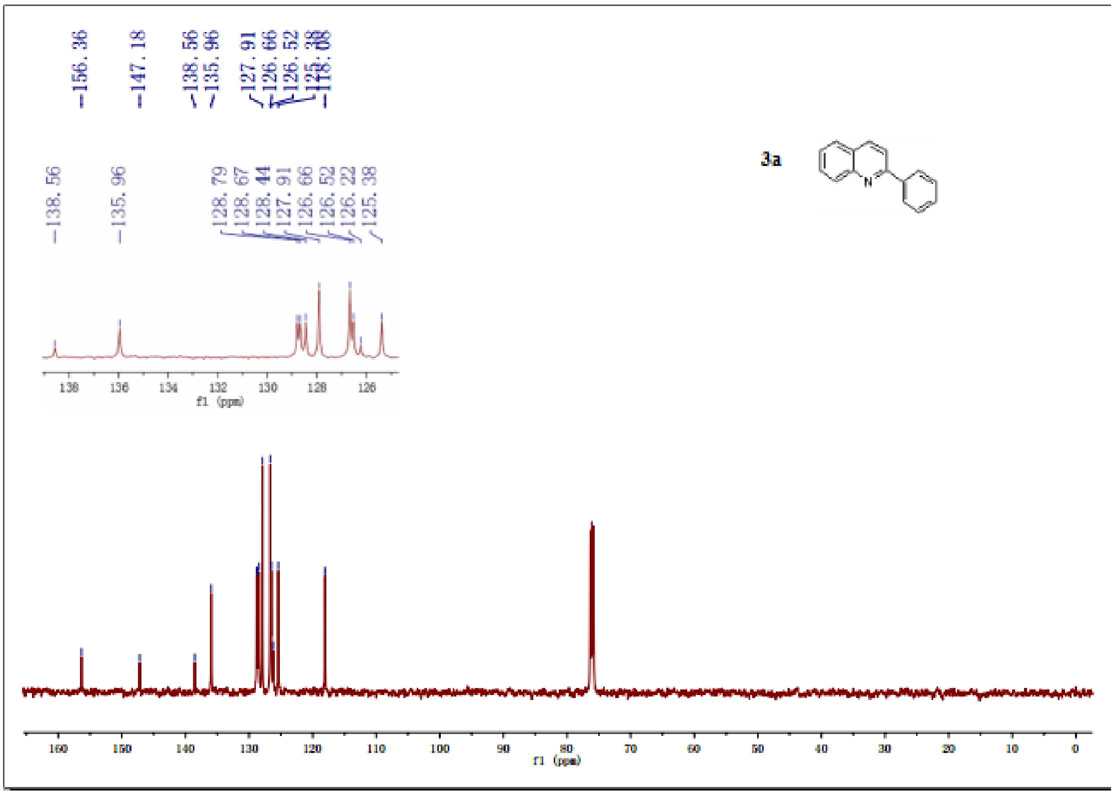
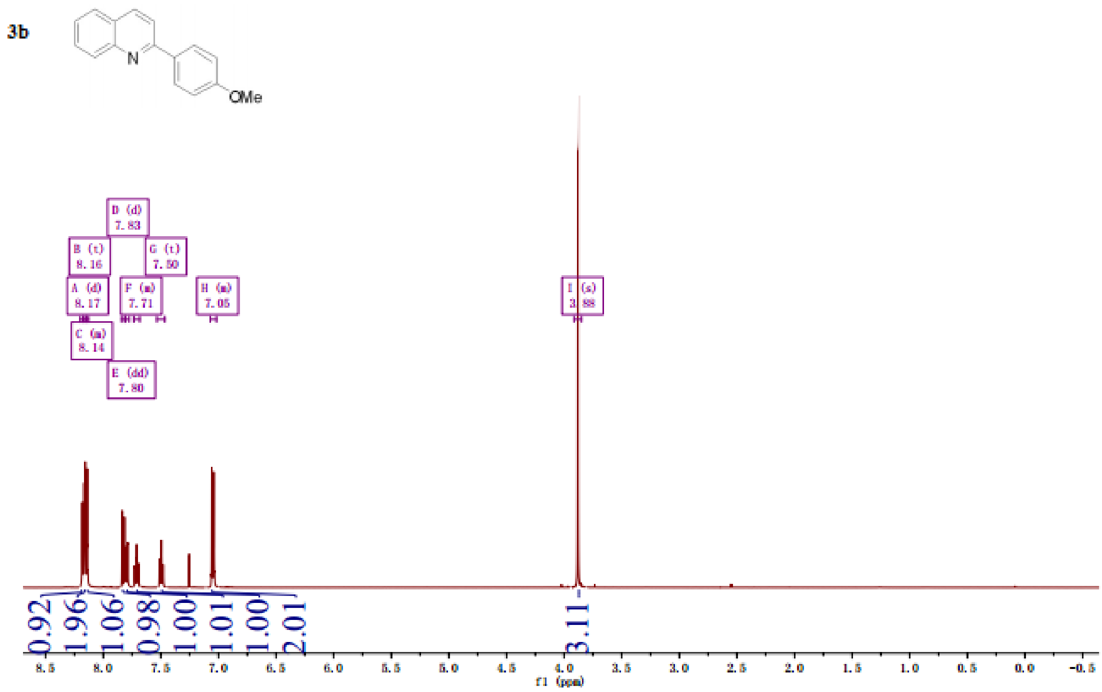
10. X. Zhang, X. f. Xu, L.t. Yu and Q. Zhao, *Tetrahedron Lett.* 2014, **55**, 2280.

3. NMR Spectra of all Products






3b
OMe
D (d) 7.83
B (t) 8.16
G (t) 7.50
A (d) 8.17
F (m) 7.71
H (m) 7.05
I (s) 3.88
C (m) 8.14
E (dd) 7.80
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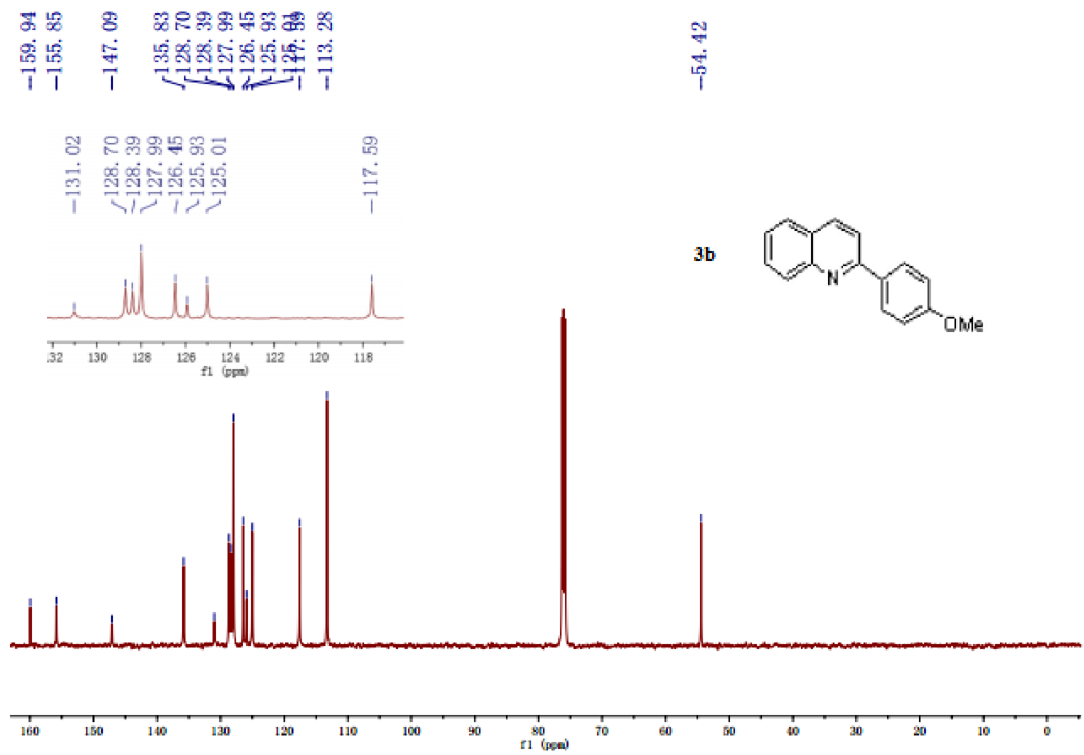
1.96
1.06
0.98
1.00
1.01
1.00
2.01
3.11
f1 (ppm)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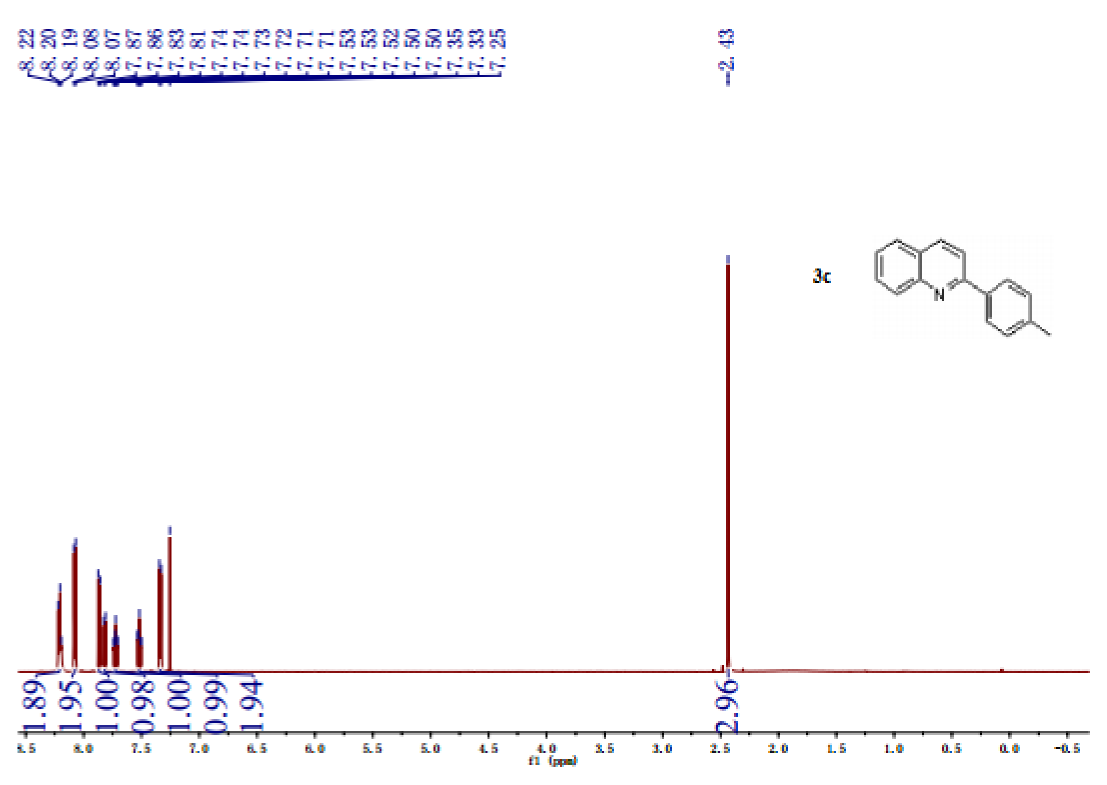
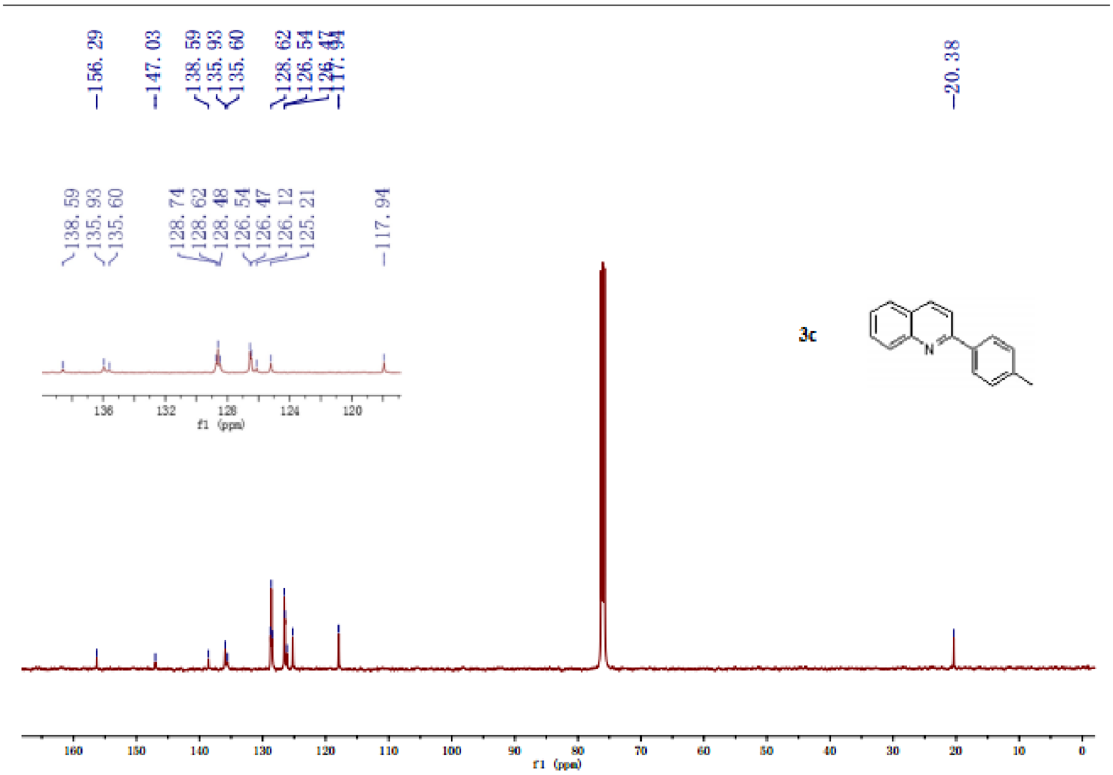
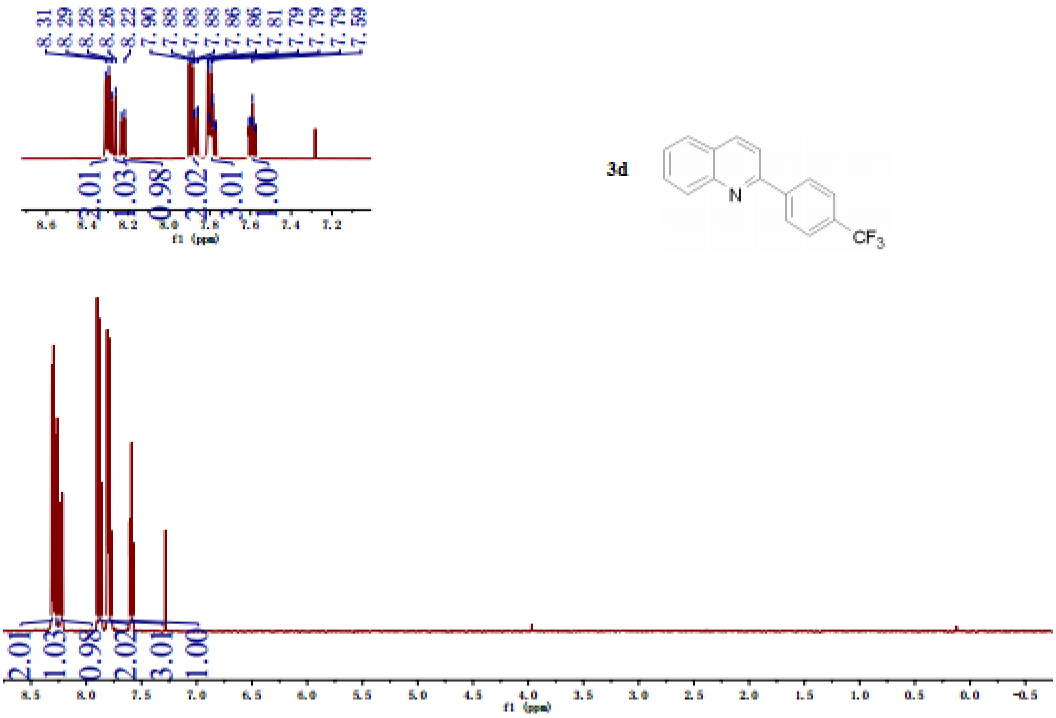
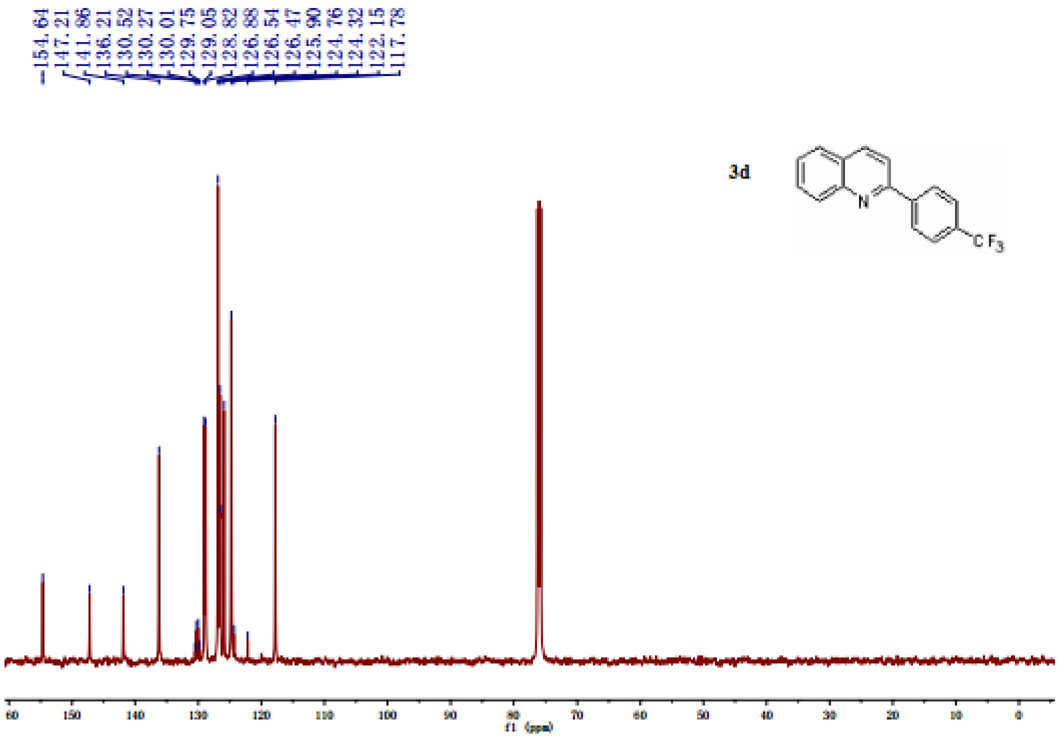
155.85
147.09
135.83
128.70
128.39
127.99
126.45
125.93
117.59
113.28
54.42
131.02
125.01
3b
OMe
f1 (ppm)


8.22 8.20 8.19 8.08 8.07 7.87 7.86 7.83 7.81 7.74 7.74 7.73 7.72 7.71 7.71 7.53 7.53 7.52 7.50 7.50 7.35 7.33 7.25
2.43
3c
N
1.89 1.95 1.00 0.98 1.00 0.99 1.94
2.96
f1 (ppm)


156.29
147.03
138.59 135.93 135.60
128.62 126.54 126.47 117.94
20.38
138.59 135.93 135.60 128.74 128.62 128.48 126.54 126.47 126.12 125.21 117.94
3c
N
f1 (ppm)


8.31 8.29 8.28 8.26 8.22 7.90 7.88 7.88 7.88 7.86 7.86 7.81 7.79 7.79 7.79 7.59
3.01 1.03 0.98 2.02 3.01 1.00
2.01 1.03 0.98 2.02 3.01 1.00
f1 (ppm)
3d
N
CF3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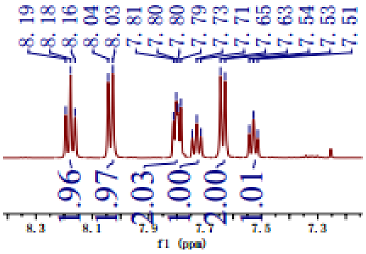
3d
N
CF3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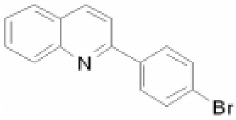
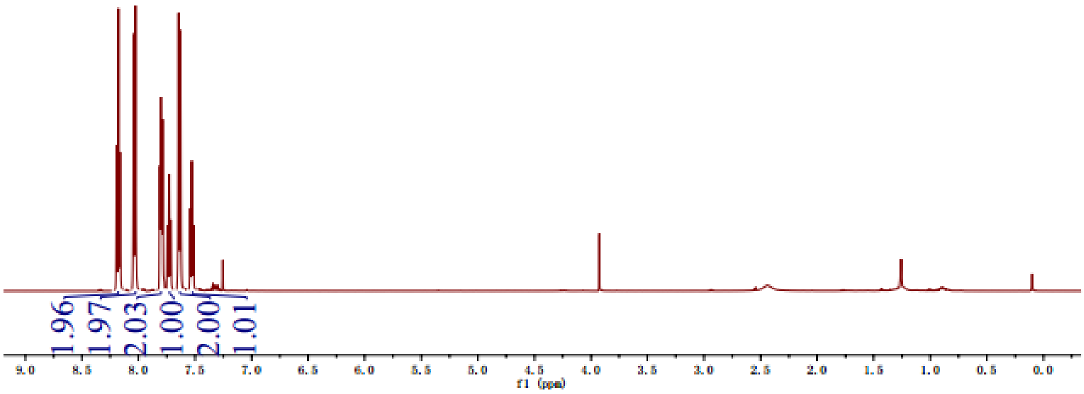
1.96 1.97 2.03 1.00 2.00 1.01
f1 (ppm)

3e


N
Br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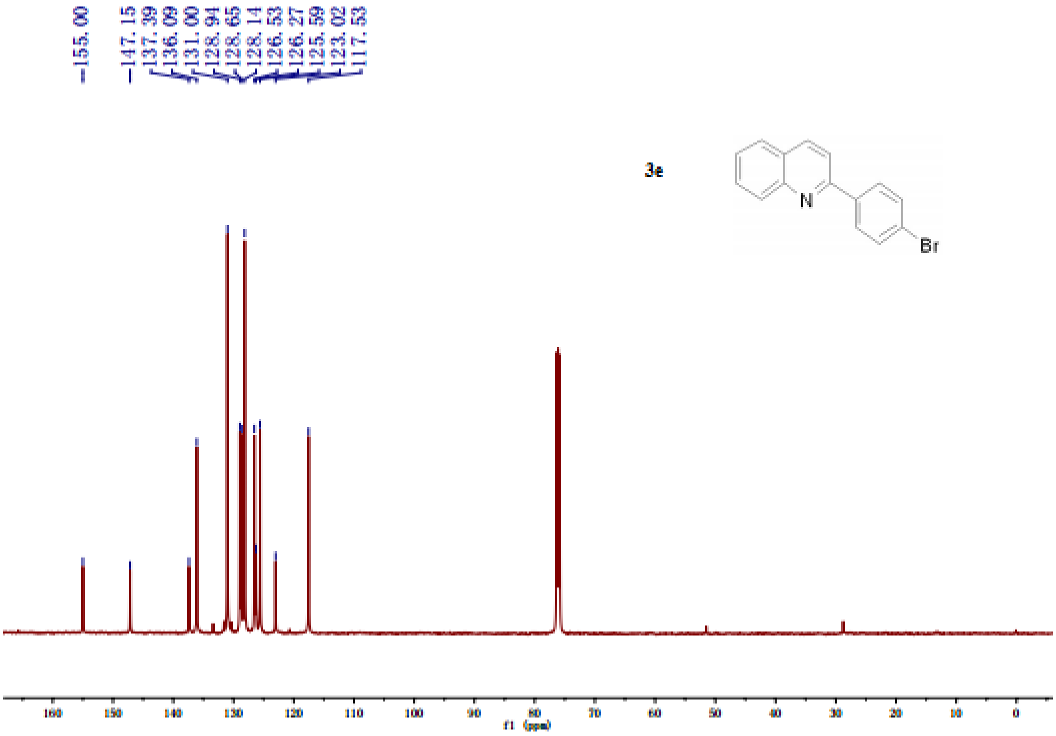
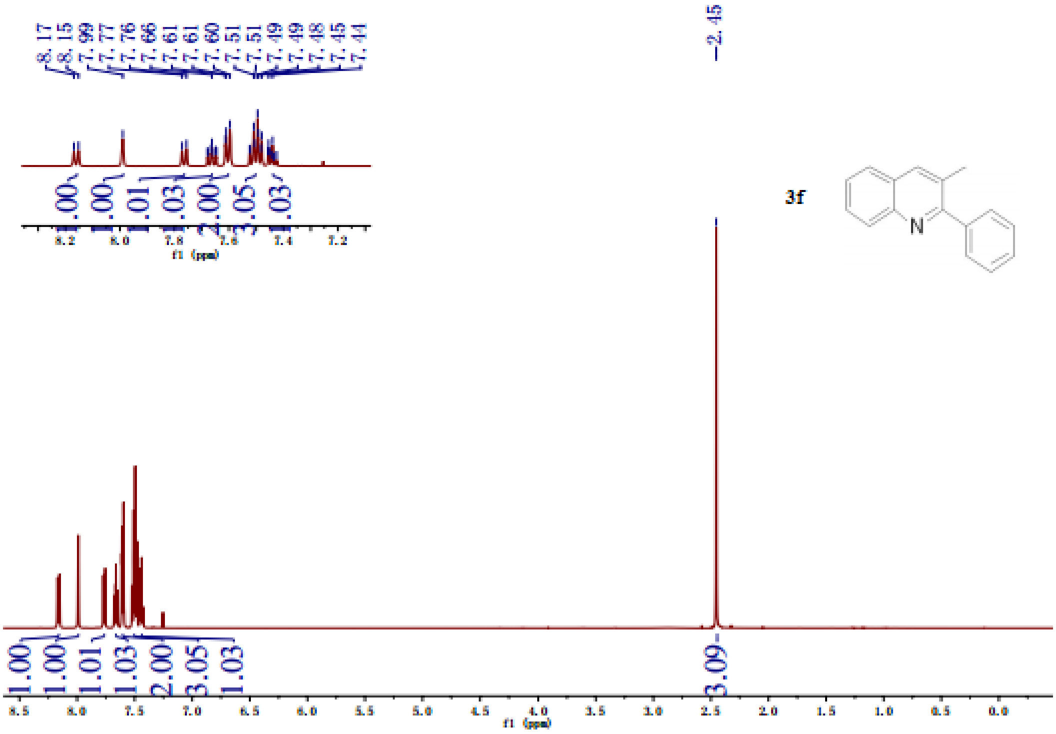
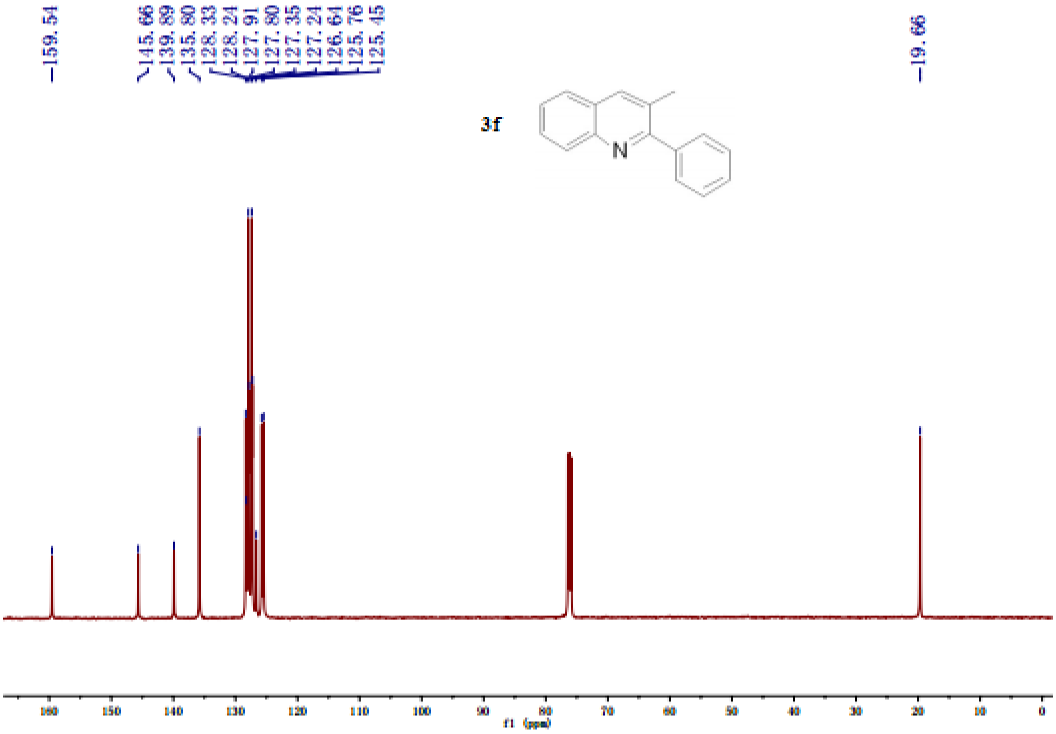
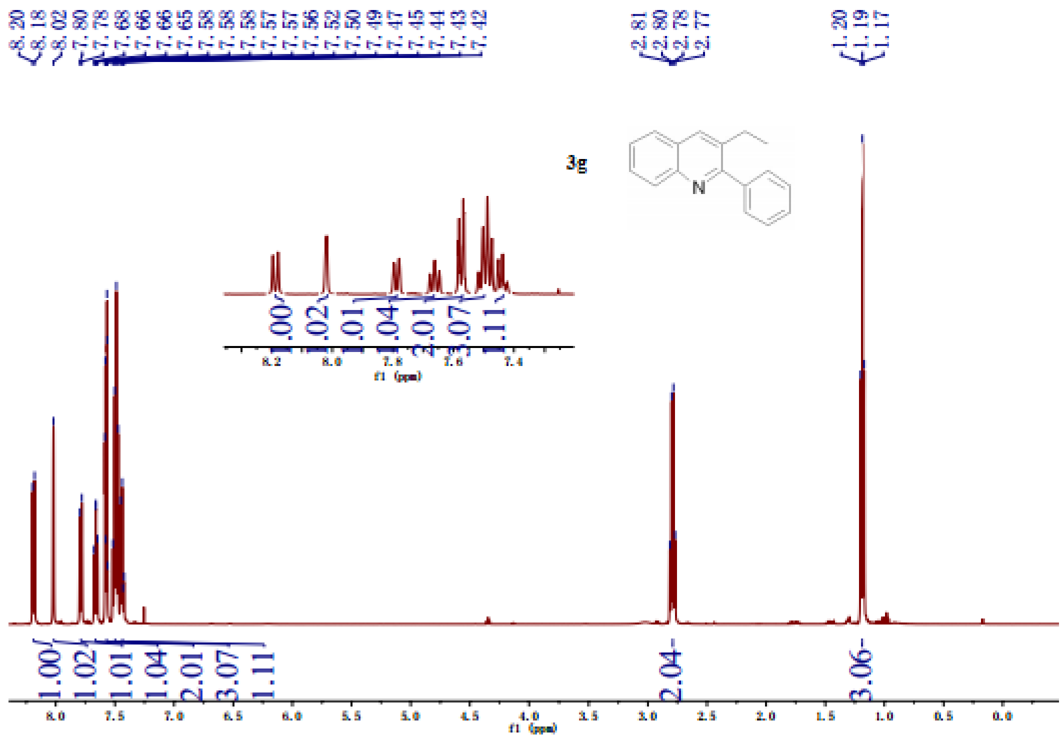
f1 (ppm)


155.00
147.15 137.39 136.09 131.00 128.94 128.65 128.14 126.53 126.27 125.59 123.02 117.53
N
Br
f1 (ppm)

3e







8.20
8.18
8.02
7.80
7.78
7.68
7.66
7.66
7.65
7.58
7.58
7.58
7.57
7.56
7.52
7.50
7.49
7.47
7.45
7.44
7.43
7.42
2.81
2.80
2.78
2.77
1.20
1.19
1.17
3g
N
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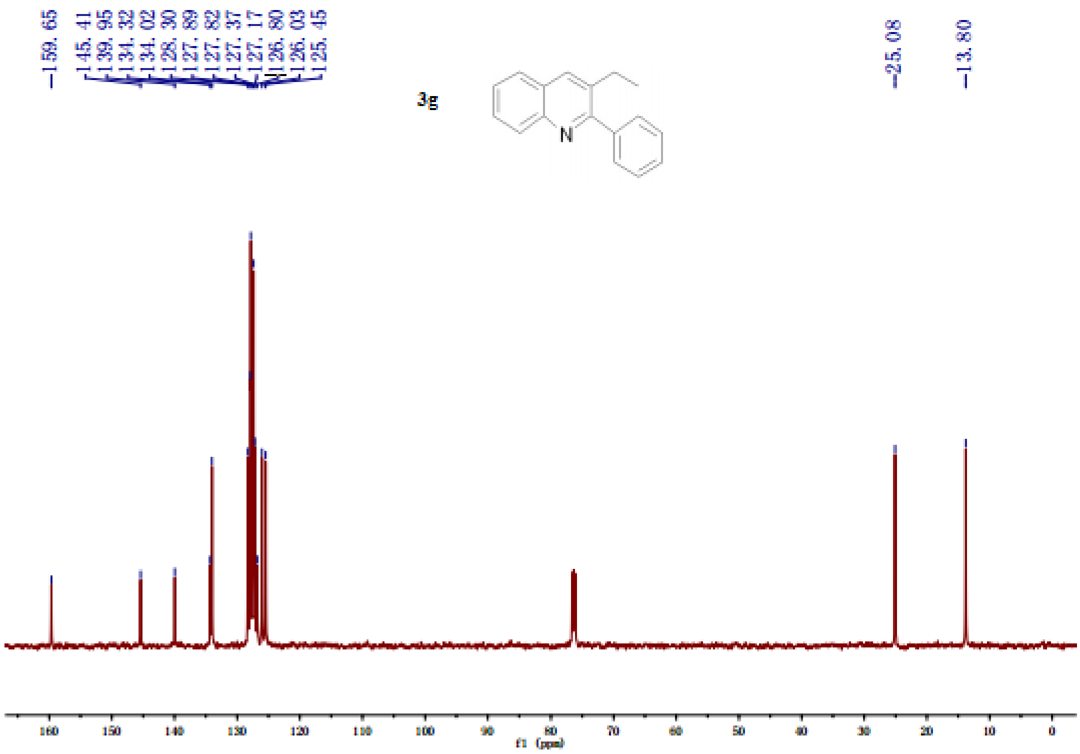
1.02
1.01
1.04
2.01
3.07
1.11
2.04
3.06
f1 (ppm)



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145.41
139.95
134.32
134.02
128.30
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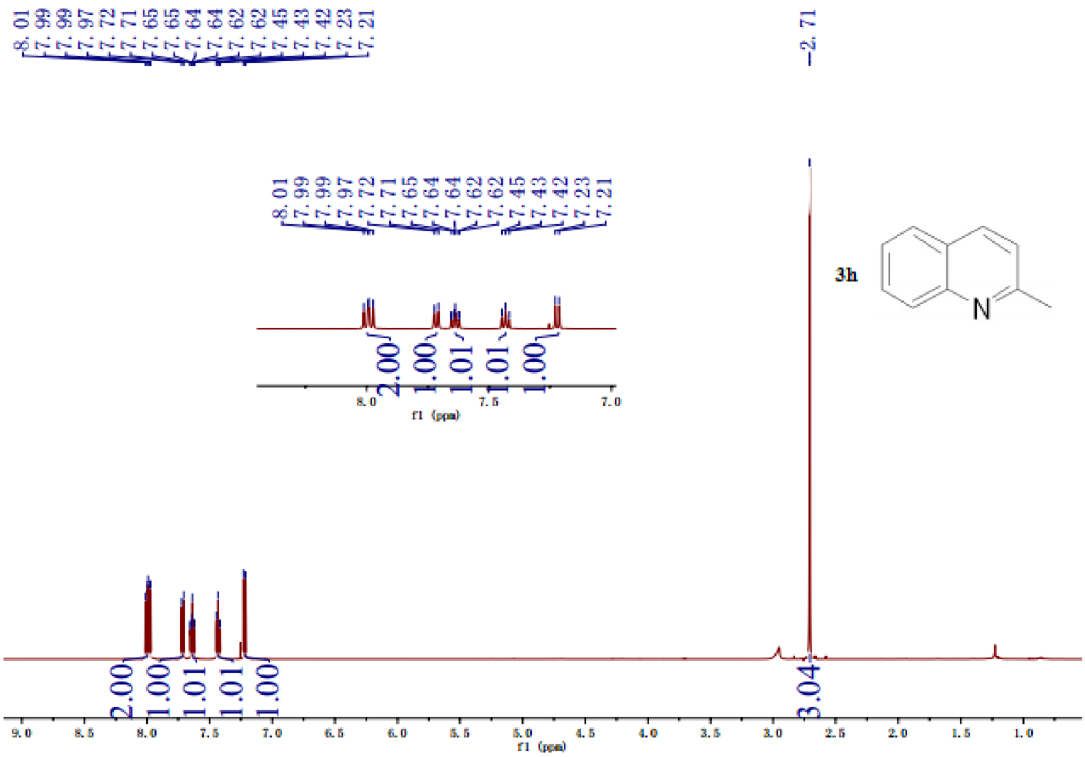
127.37
127.17
126.80
126.03
125.45
25.08
13.80
3g
N
f1 (ppm)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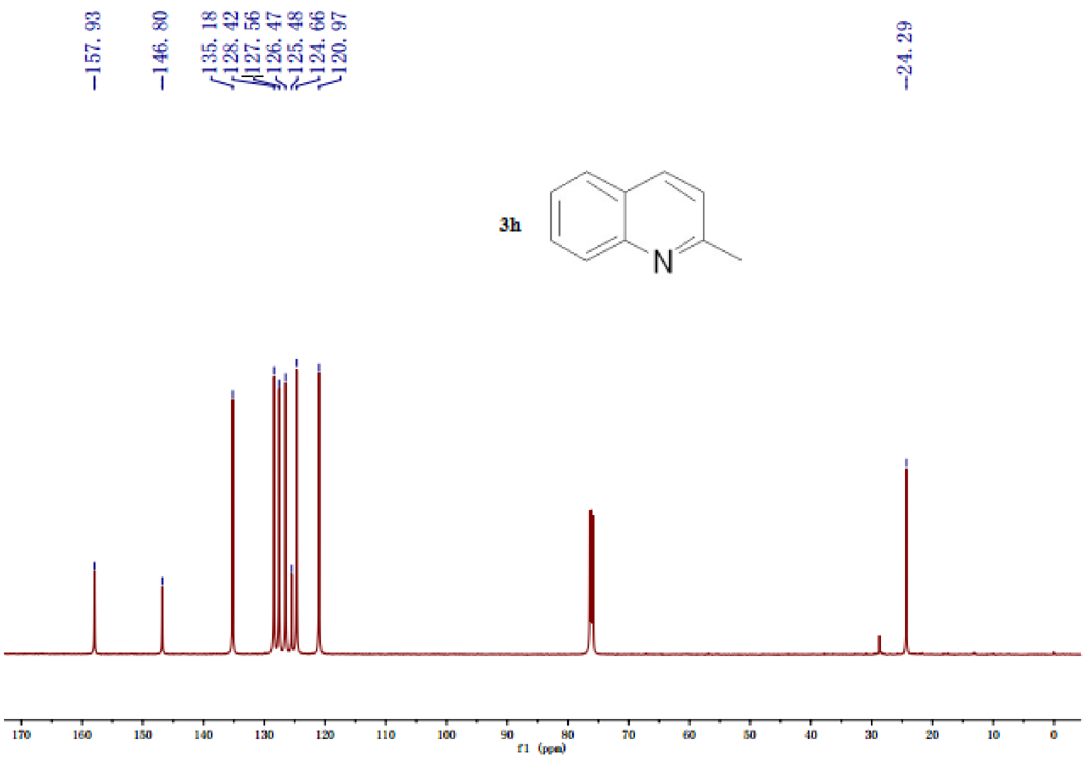
7.65
7.64
7.64
7.62
7.62
7.45
7.43
7.42
7.23
7.21
2.71
3h
N
2.00
1.00
1.01
1.01
1.00
3.04
f1 (ppm)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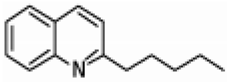
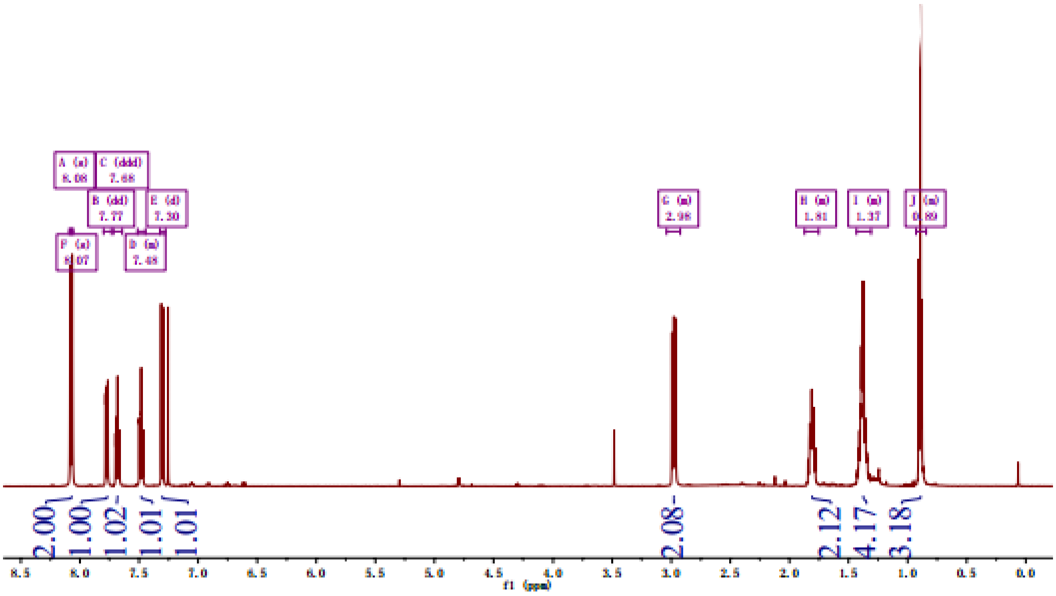
24.29
3h
N
f1 (ppm)



3i



A (s) 8.08
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B (dd) 7.77
E (d) 7.30
F (s) 8.07
D (m) 7.48
G (m) 2.98
H (m) 1.81
I (m) 1.37
J (m) 0.89
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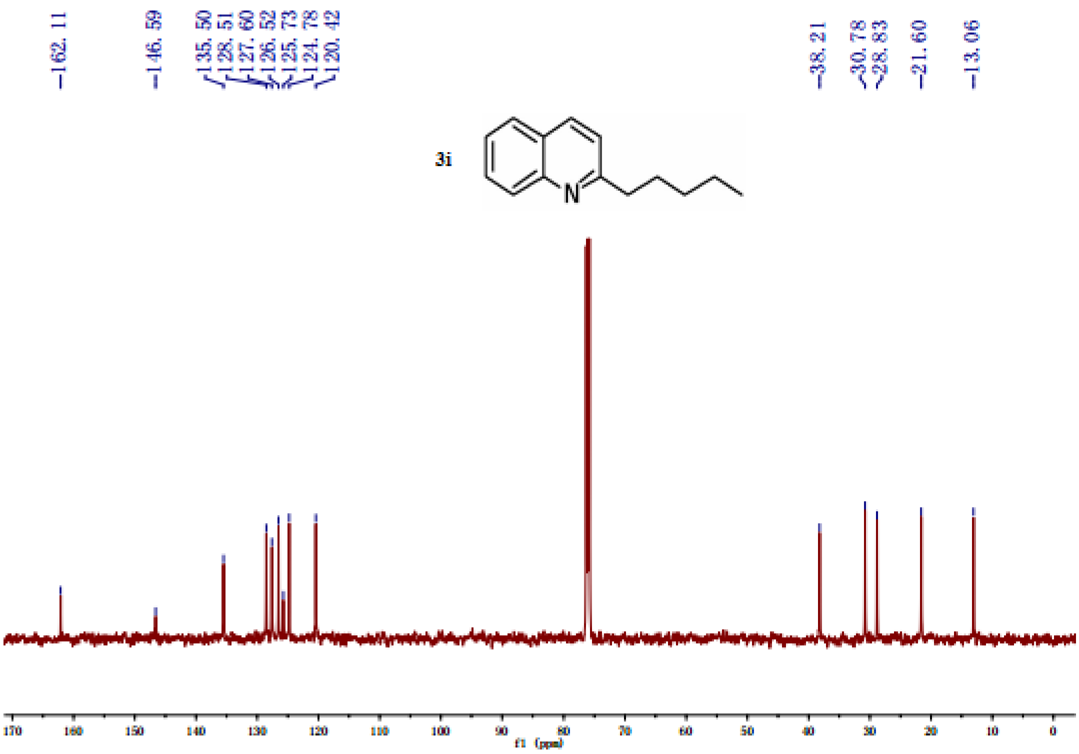
1.00
1.02
1.01
1.01
2.08
2.12
4.17
3.18
f1 (ppm)



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28.83
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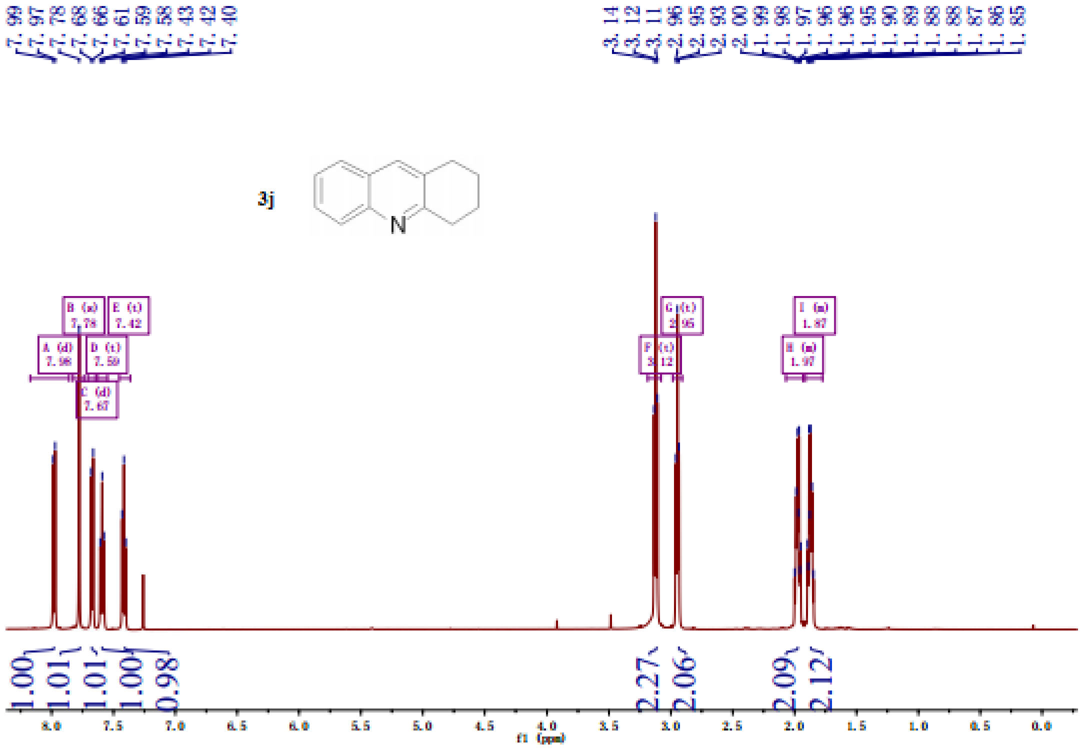
13.06
3i
f1 (ppm)



7.99
7.97
7.78
7.68
7.66
7.61
7.59
7.58
7.43
7.42
7.40
3.14
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1.98
1.97
1.96
1.96
1.95
1.90
1.89
1.88
1.88
1.87
1.86
1.85
3j
N
A (d) 7.98
B (s) 7.78
C (d) 7.67
D (t) 7.59
E (t) 7.42
F (t) 3.12
G (t) 2.95
H (m) 1.97
I (m) 1.87
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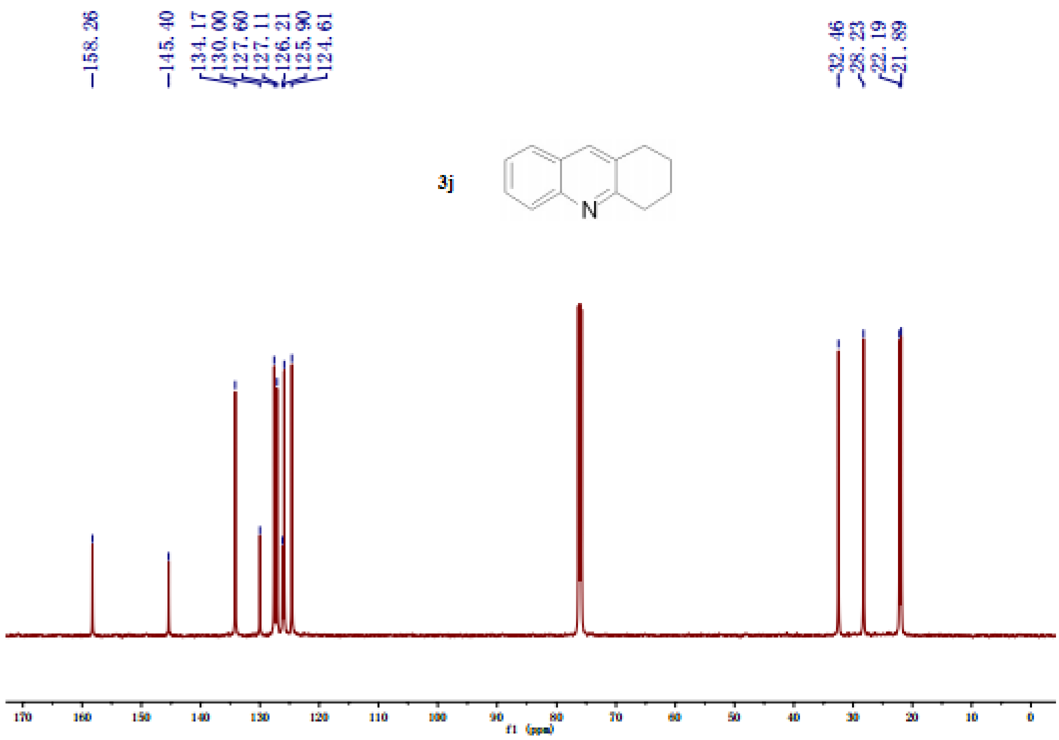
2.06
2.09
2.12
f1 (ppm)



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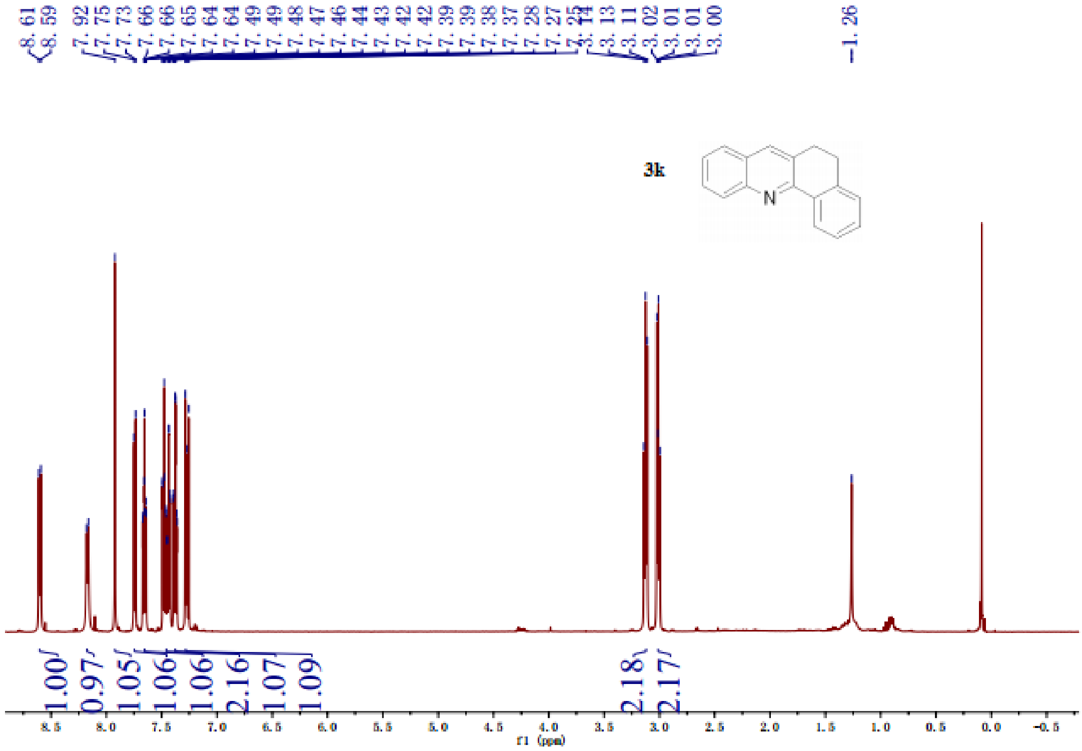
N
f1 (ppm)

3k



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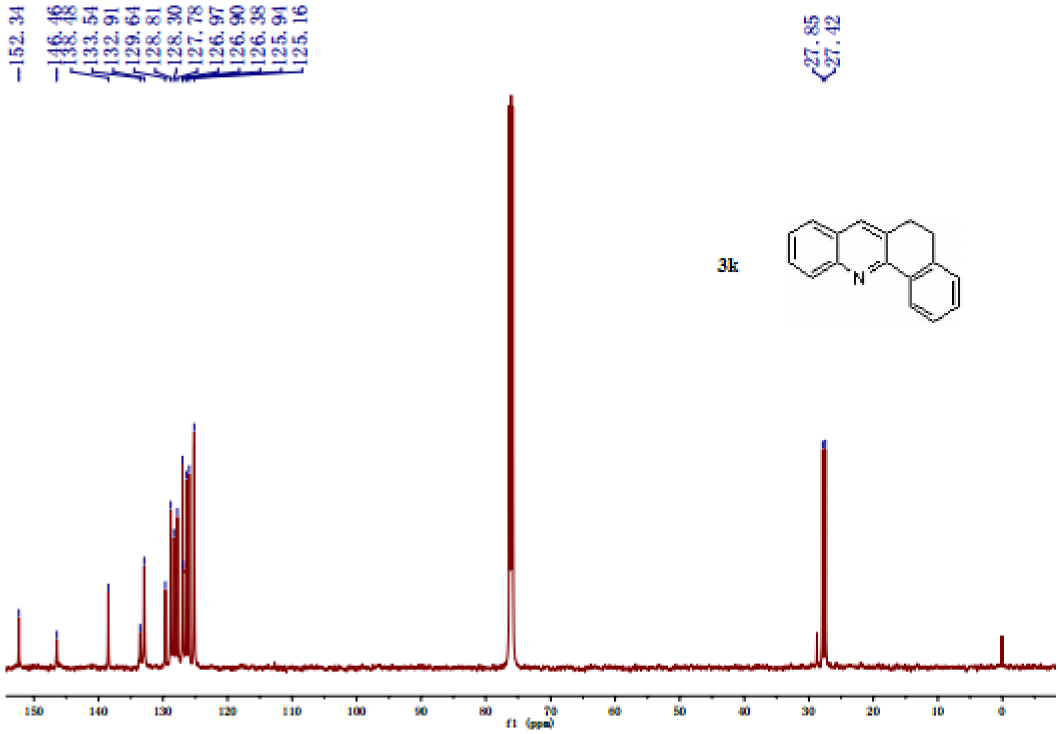

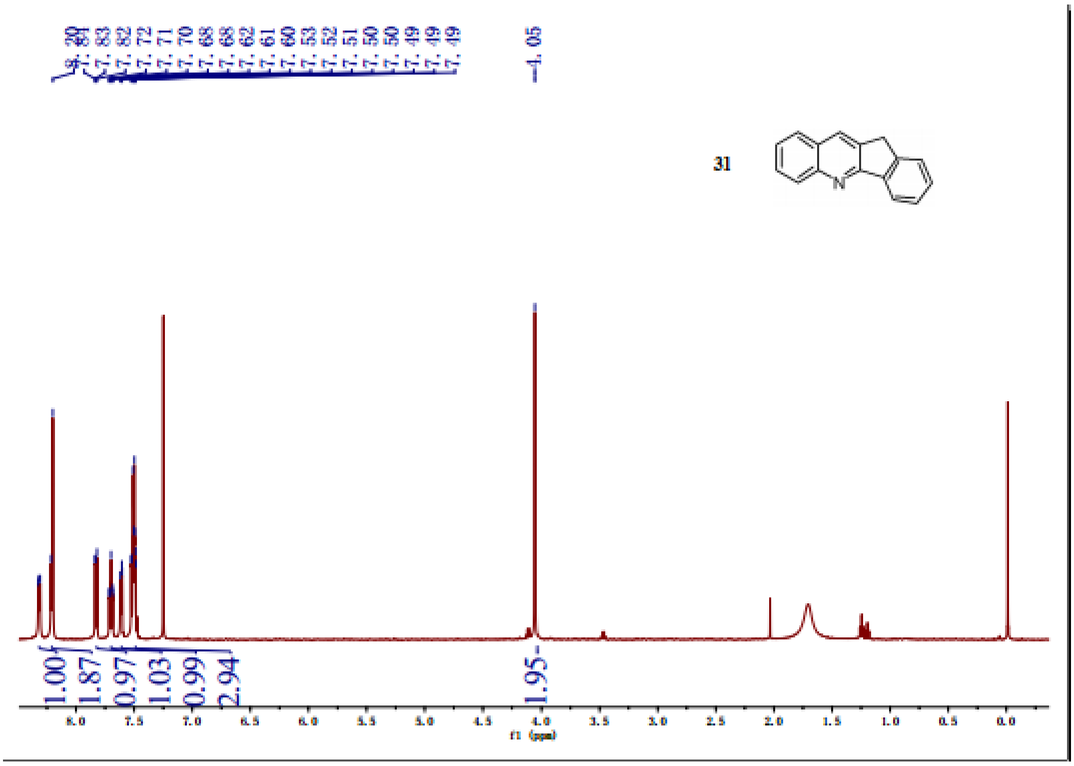

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7.52
7.51
7.50
7.50
7.49
7.49
7.49
4.05
31
N
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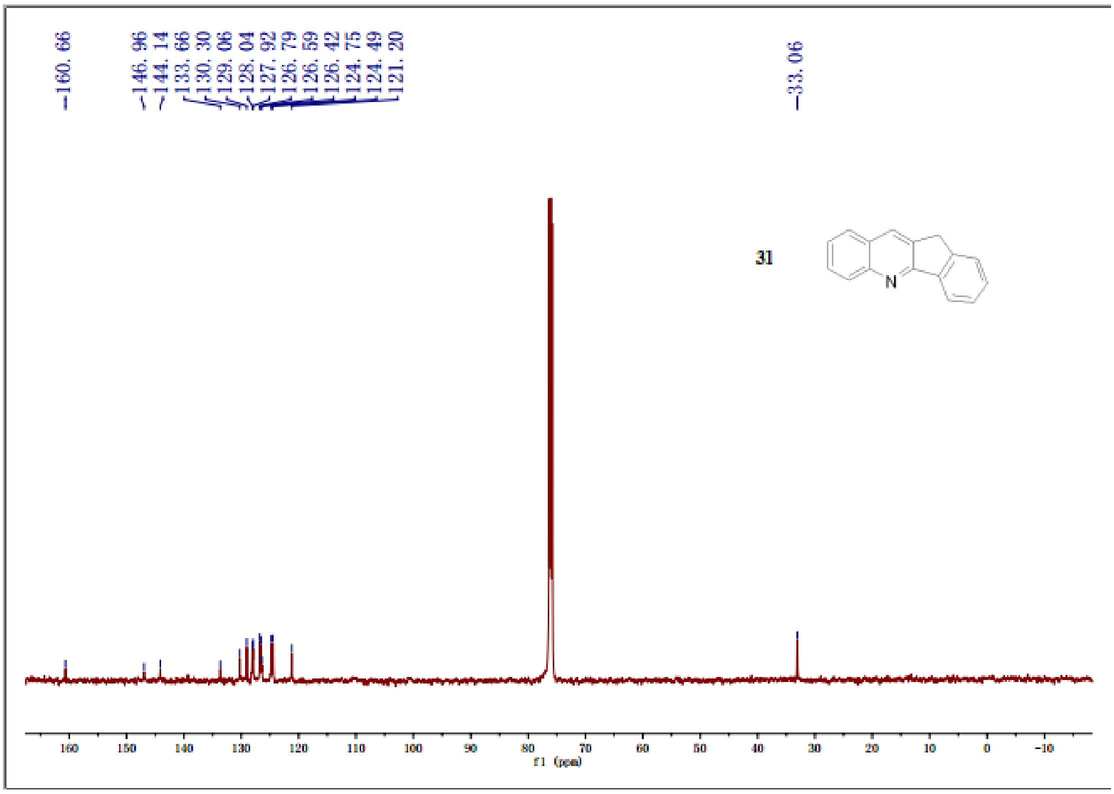
1.87
0.97
1.03
0.99
2.94
1.95
f1 (ppm)



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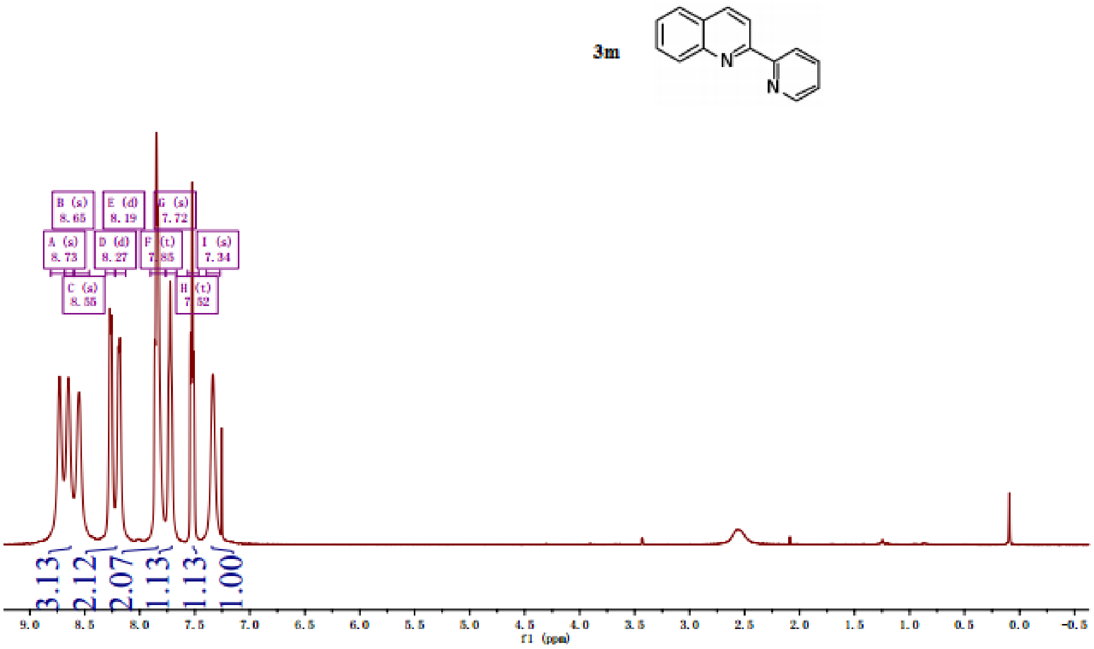
31
N
f1 (ppm)


3m
N
N
B (s) 8.65
E (d) 8.19
G (s) 7.72
A (s) 8.73
D (d) 8.27
F (t) 7.85
I (s) 7.34
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H (t) 7.52
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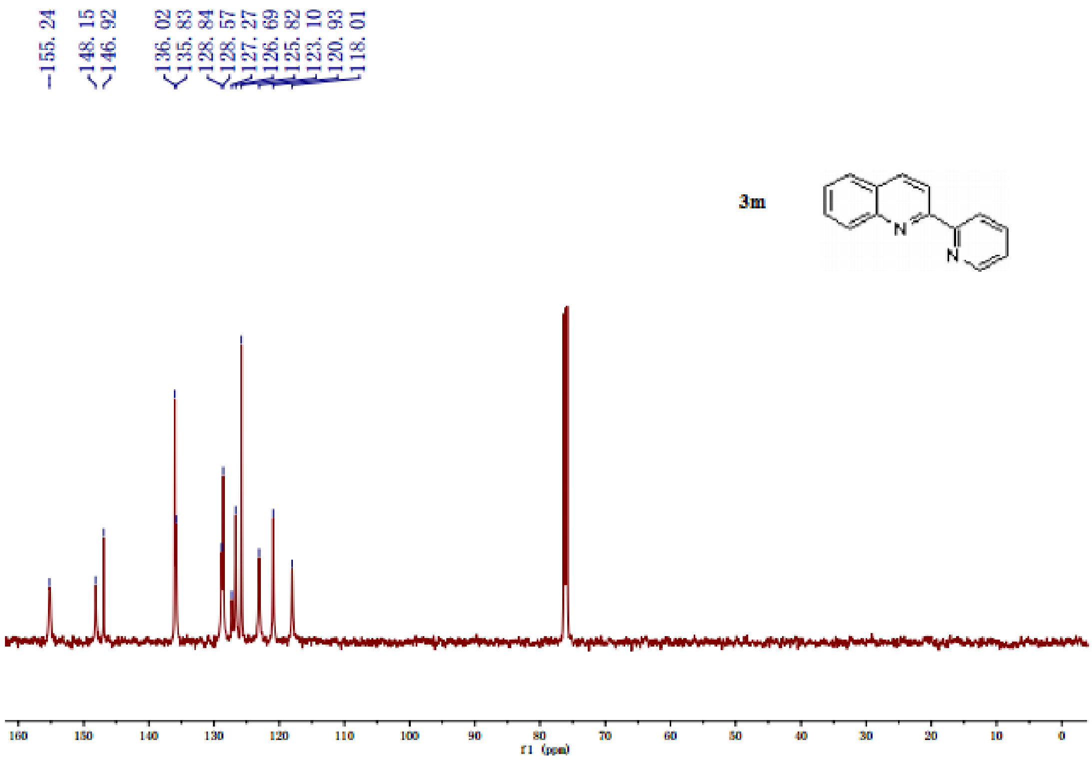
1.00
f1 (ppm)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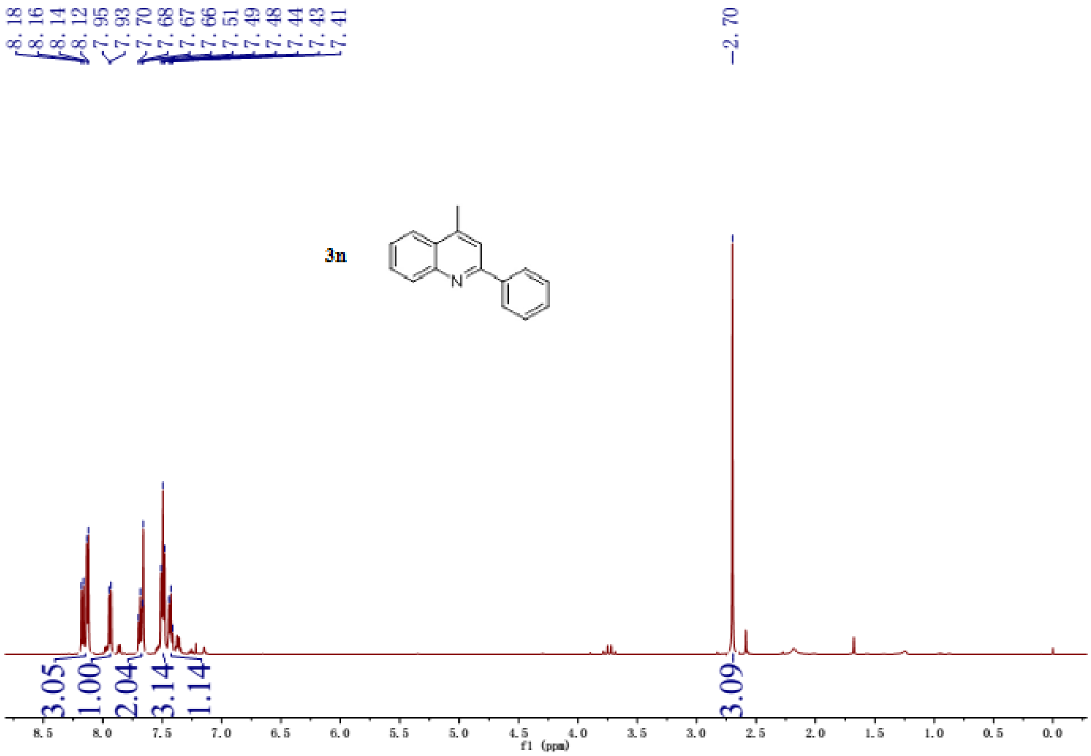
118.01
3m
N
N
f1 (ppm)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7.66
7.51
7.49
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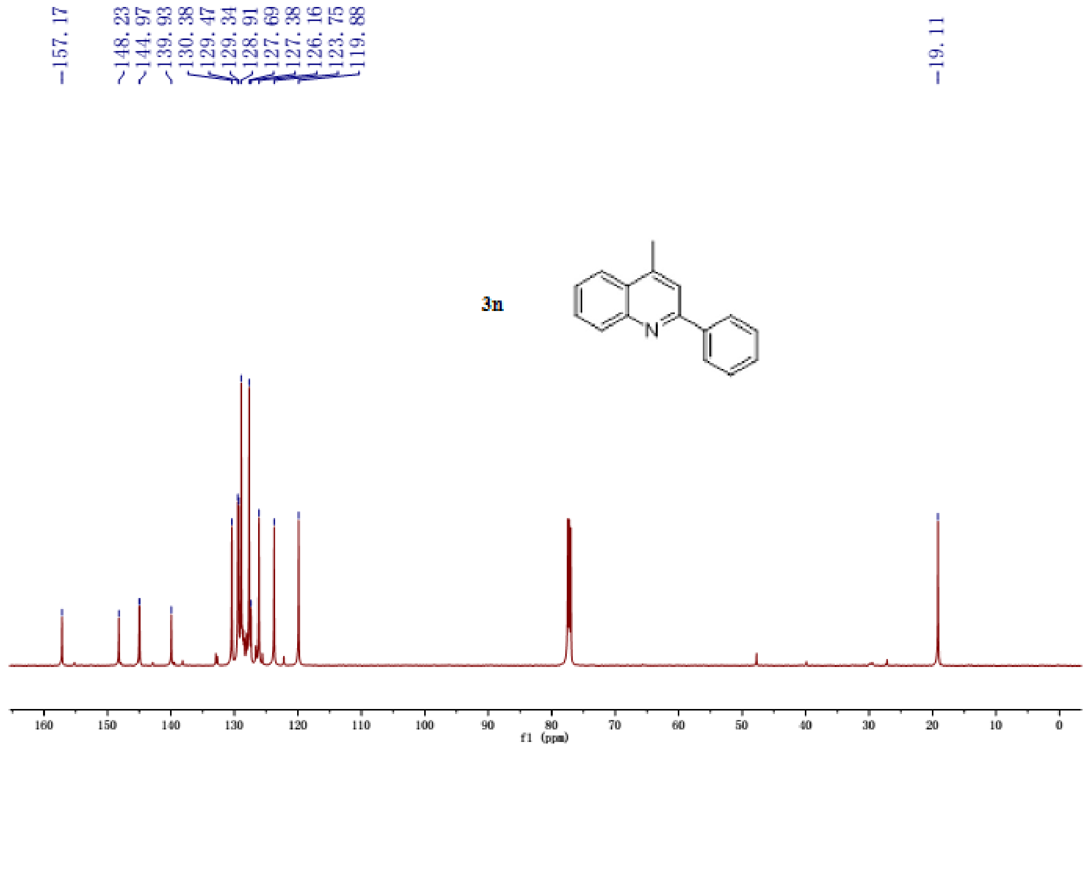
7.44
7.43
7.41
2.70
3n
3.05
1.00
2.04
3.14
1.14
3.09
f1 (ppm)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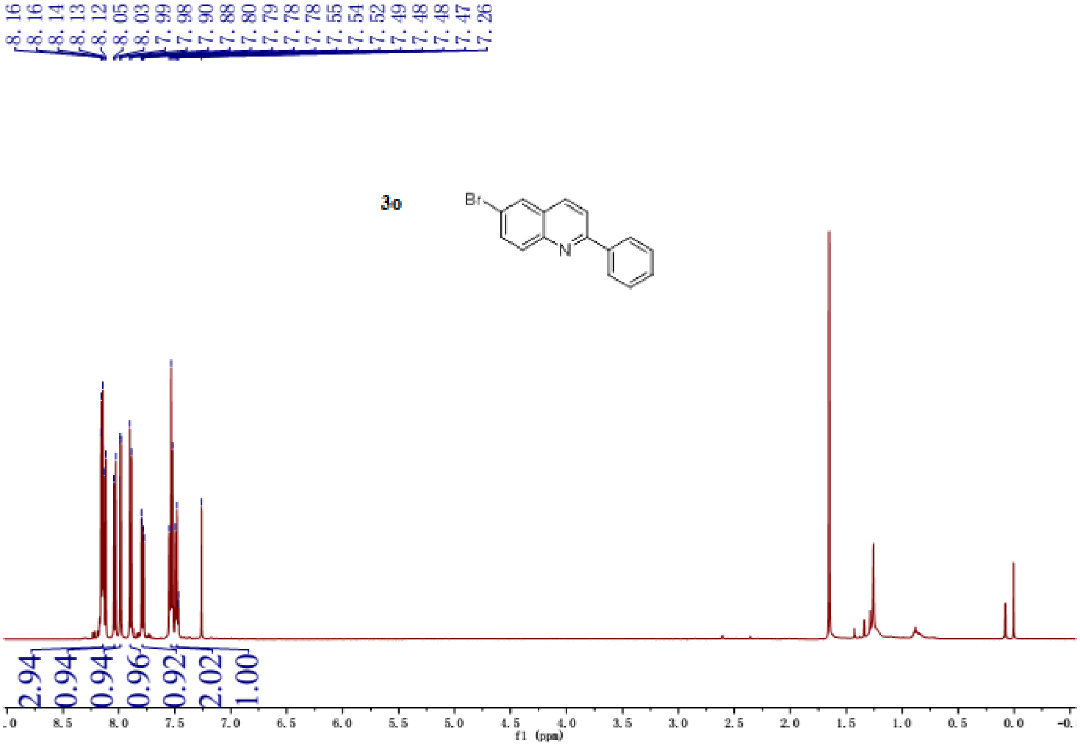
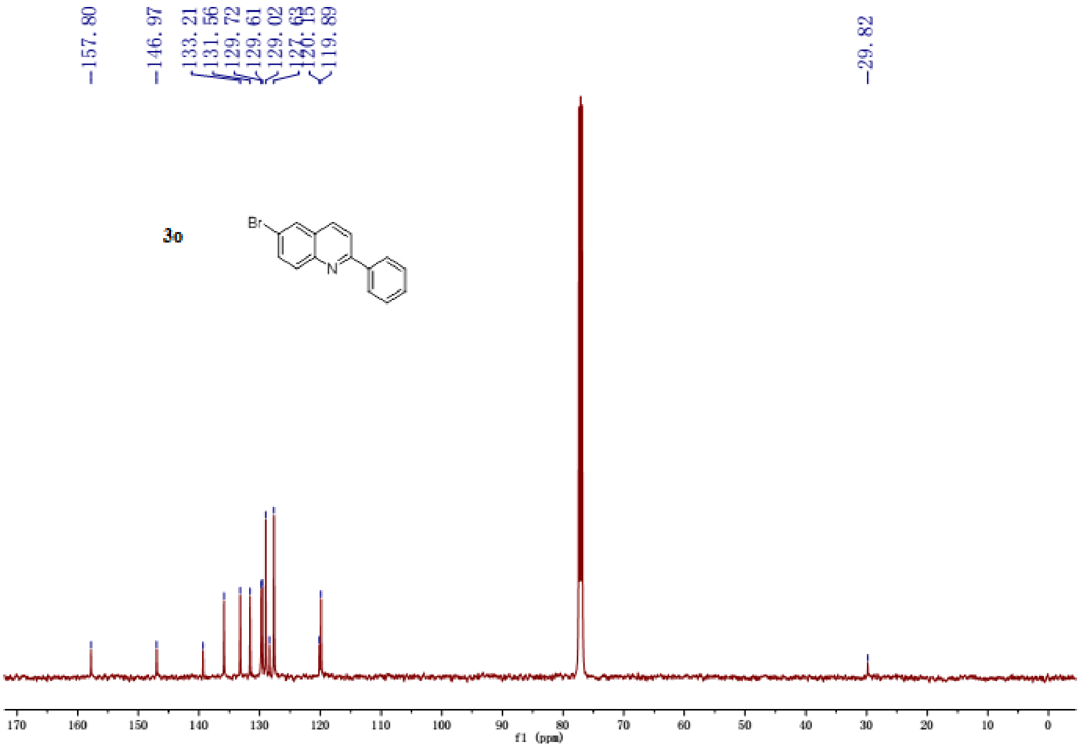
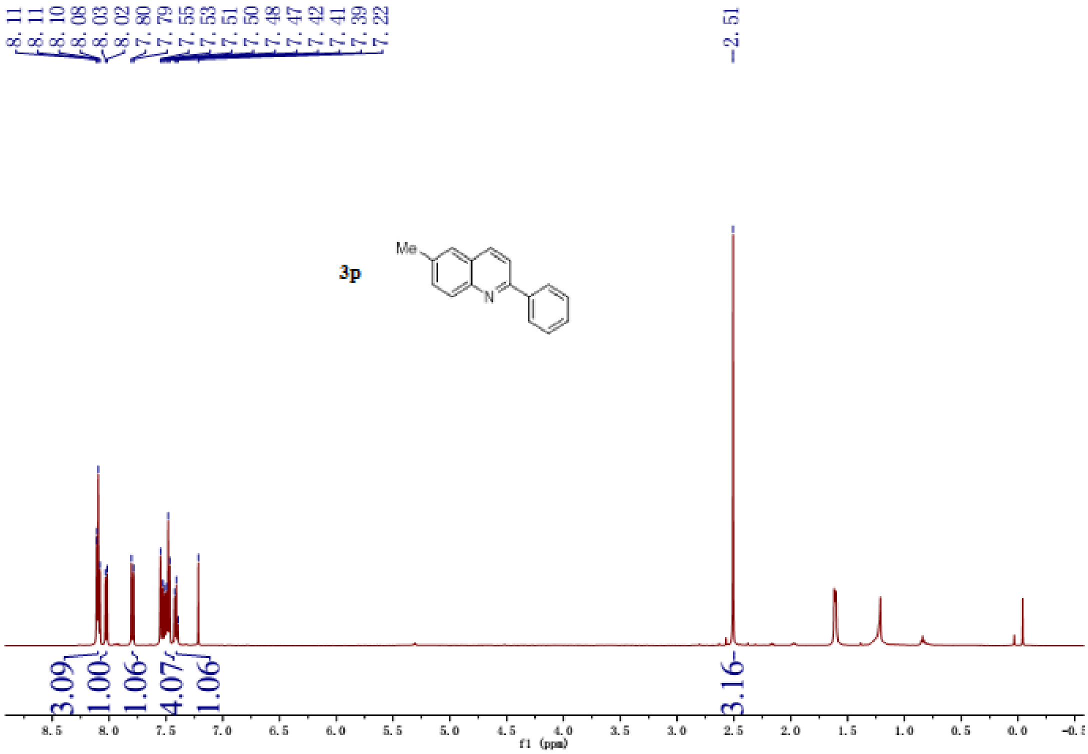
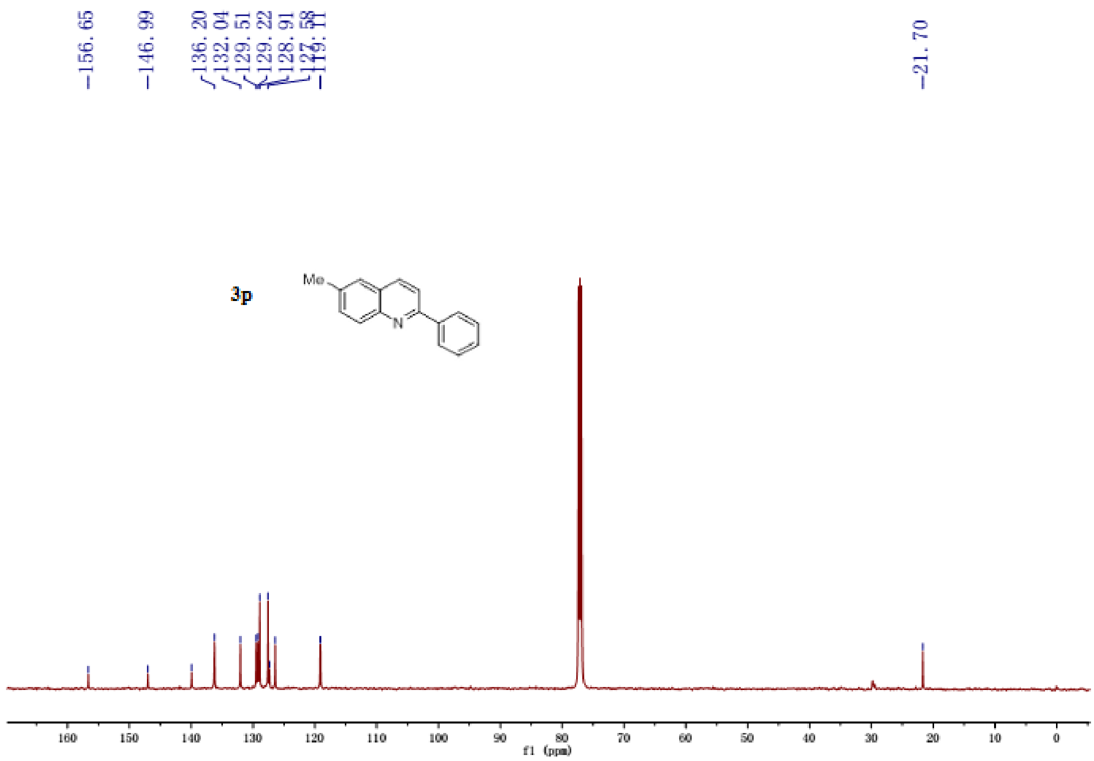
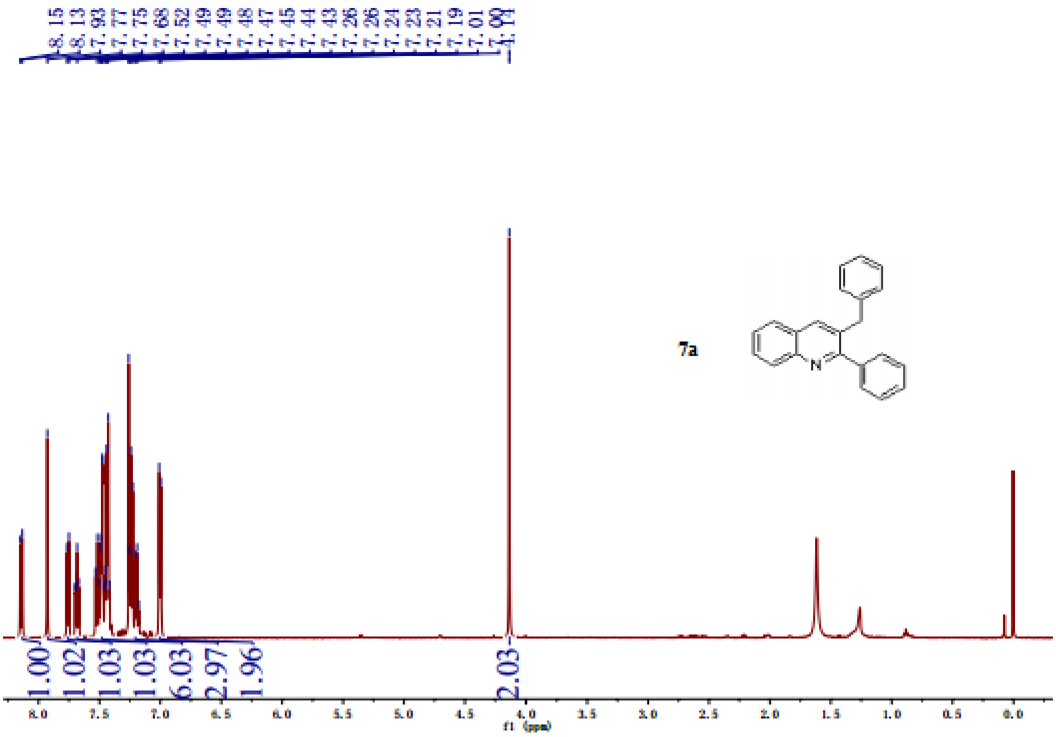
148.23
144.97
139.93
130.38
129.47
129.34
128.91
127.69
127.38
126.16
123.75
119.88
19.11
3n
f1 (ppm)

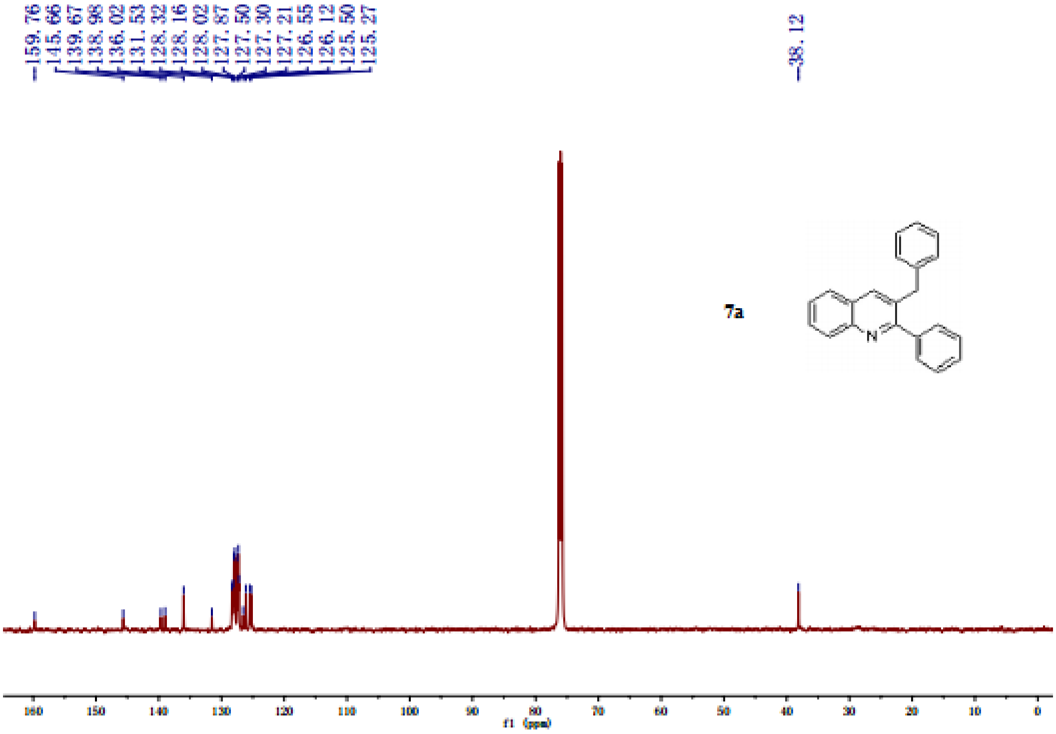

8.16 8.16 8.14 8.13 8.12 8.05 8.03 7.99 7.98 7.90 7.88 7.80 7.79 7.78 7.78 7.55 7.54 7.52 7.49 7.48 7.48 7.47 7.26
3o
Br
N
2.94 0.94 0.94 0.96 0.92 2.02 1.00
f1 (ppm)


157.80 146.97 133.21 131.56 129.72 129.61 129.02 127.63 120.15 119.89 29.82
3o
Br
N
f1 (ppm)


8.11 8.11 8.10 8.08 8.03 8.02 7.80 7.79 7.55 7.53 7.51 7.50 7.48 7.47 7.42 7.41 7.39 7.22
2.51
3p
Me
N
3.09
1.00
1.06
4.07
1.06
3.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.65
146.99
136.20 132.04 129.51 129.22 128.91
21.70
3p
Me
N
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.15
8.13
7.93
7.77
7.75
7.68
7.52
7.49
7.49
7.48
7.47
7.45
7.44
7.43
7.26
7.26
7.24
7.23
7.21
7.19
7.01
4.14
7a
N
1.00
1.02
1.03
1.03
6.03
2.97
1.96
2.03
f1 (ppm)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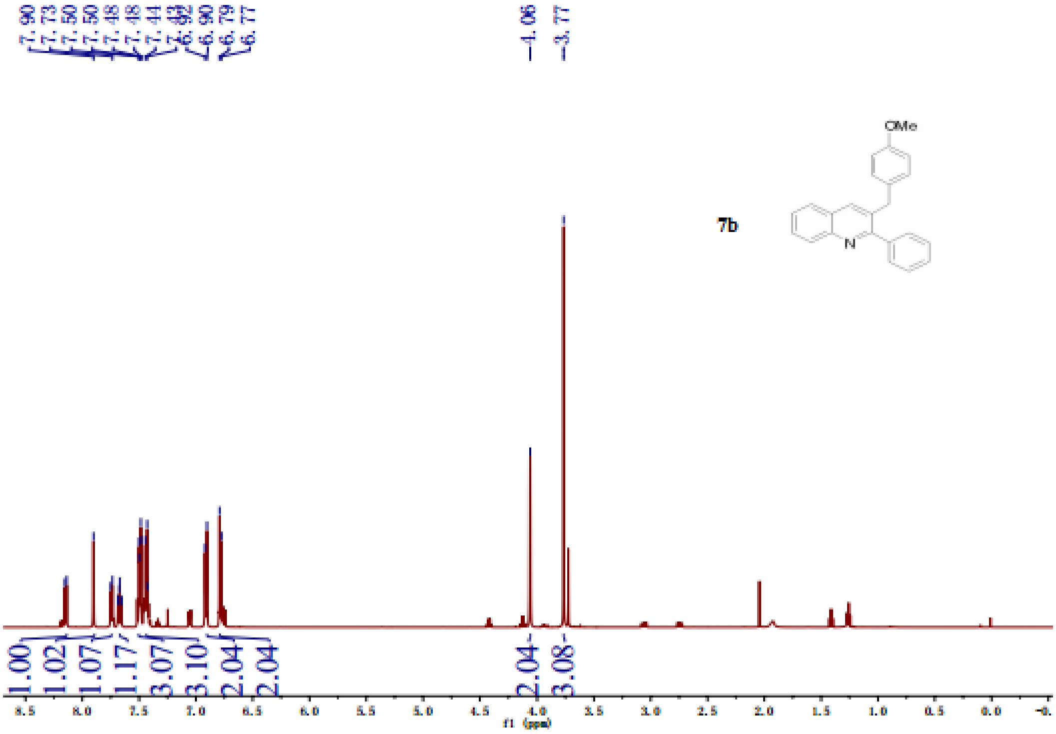
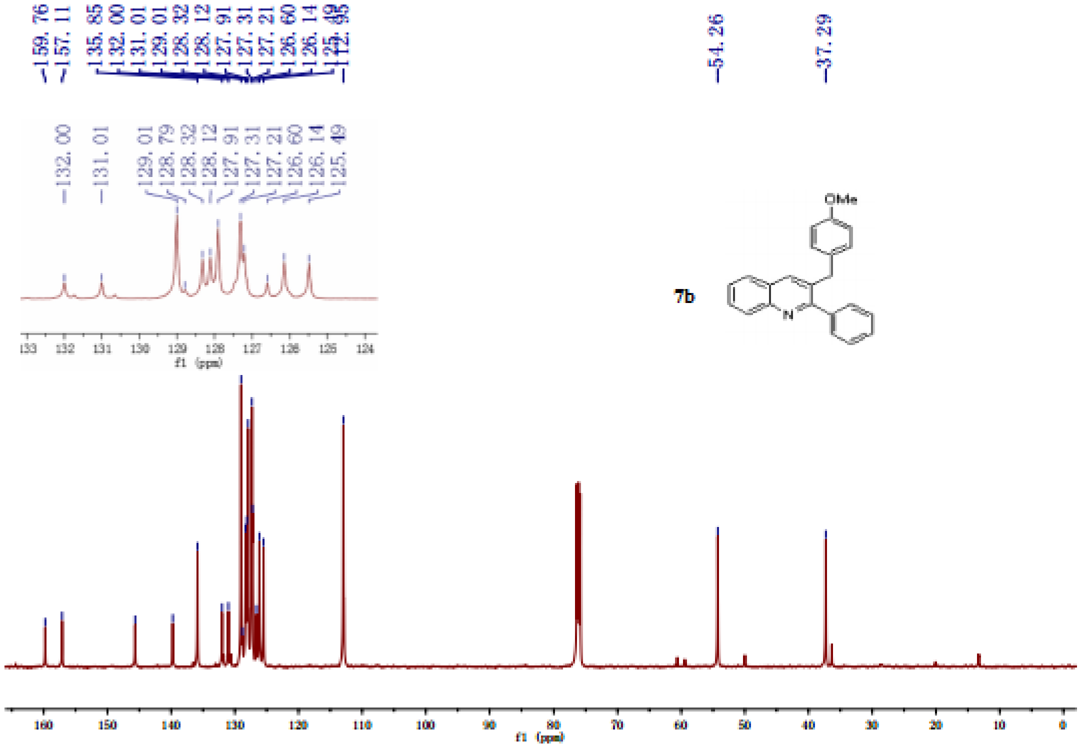
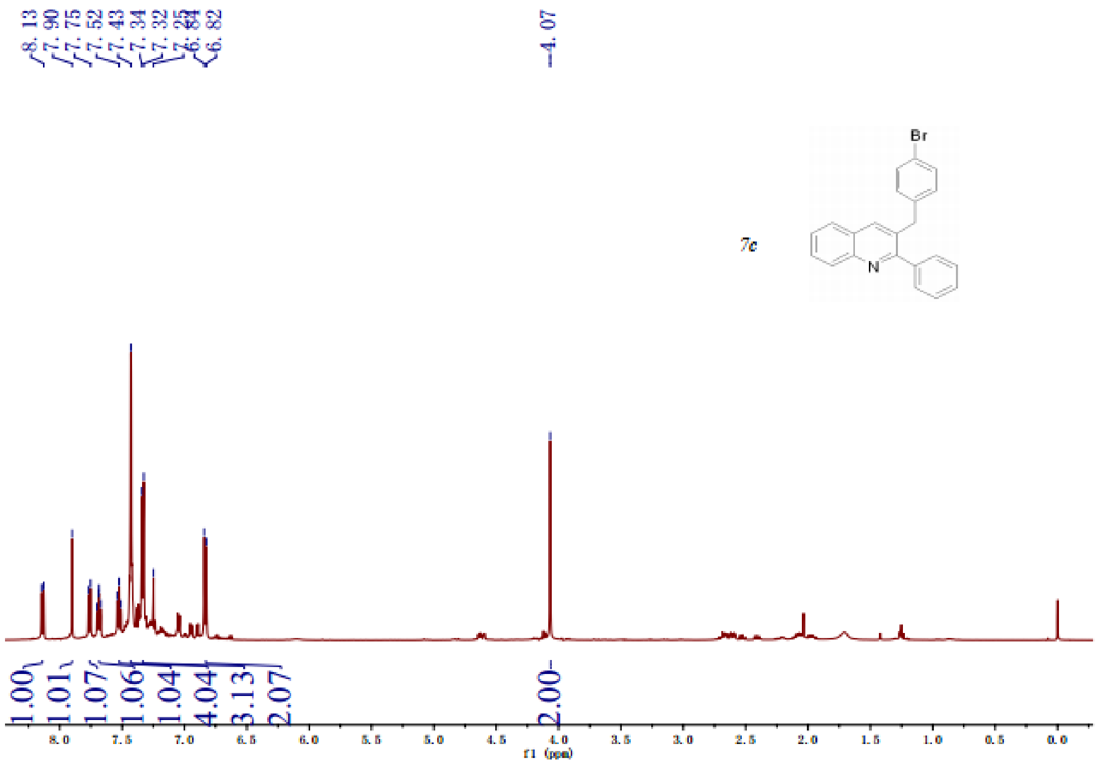
145.66
139.67
138.98
136.02
131.53
128.32
128.16
128.02
127.87
127.50
127.30
127.21
126.55
126.12
125.50
125.27
38.12
7a
N
f1 (ppm)

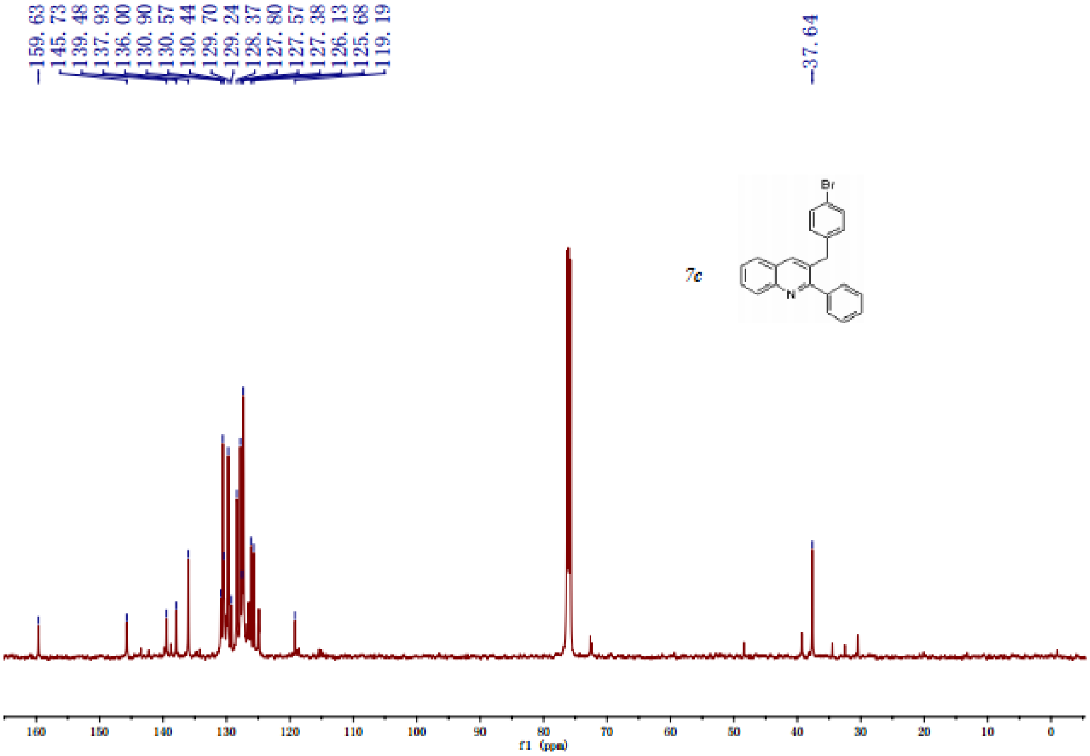


7.90
7.73
7.50
7.50
7.48
7.48
7.44
7.43
6.92
6.90
6.79
6.77
4.06
3.77
OMe
7b
N
1.00
1.02
1.07
1.17
3.07
3.10
2.04
2.04
2.04
3.08
f1 (ppm)



159.76
157.11
135.85
132.00
131.01
129.01
128.32
128.12
127.91
127.31
127.21
126.60
126.14
125.49
112.95
54.26
37.29
132.00
131.01
129.01
128.79
128.32
128.12
127.91
127.31
127.21
126.60
126.14
125.49
f1 (ppm)
OMe
7b
N
f1 (ppm)


8.13
7.90
7.75
7.52
7.43
7.34
7.32
7.25
6.84
6.82
4.07
7c
Br
N
1.00
1.01
1.07
1.06
1.04
4.04
3.13
2.07
2.00
f1 (ppm)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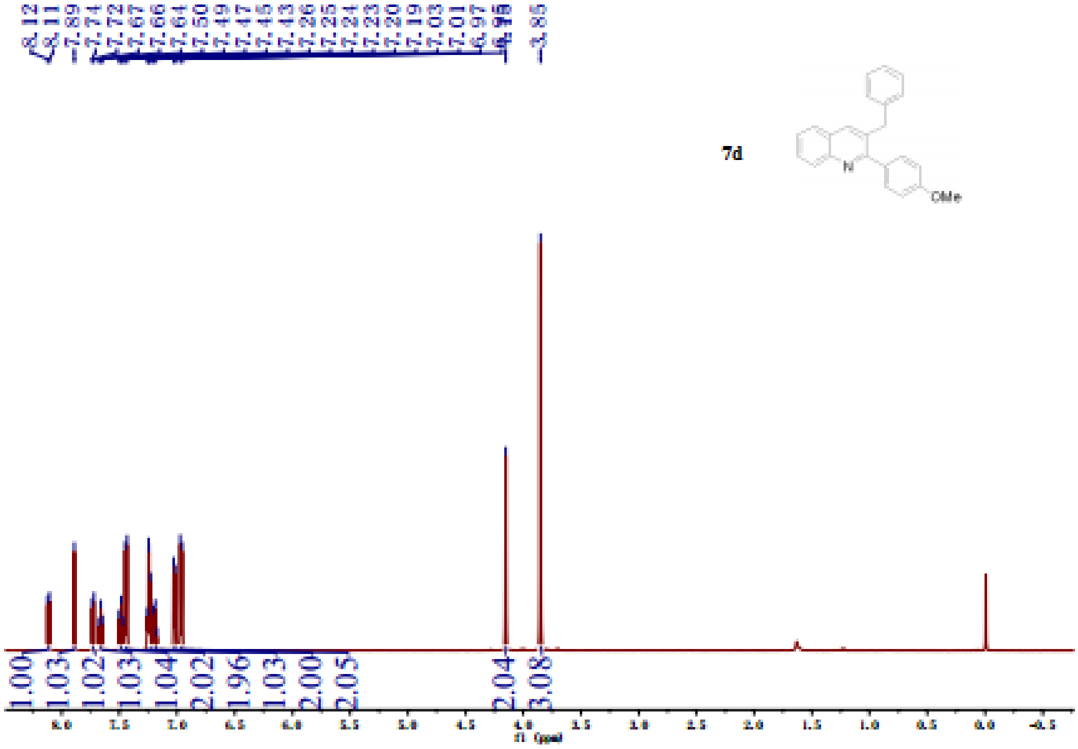
145.73
139.48
137.93
136.00
130.90
130.57
130.44
129.70
129.24
128.37
127.80
127.57
127.38
126.13
125.68
119.19
37.64
7c
Br
N
f1 (ppm)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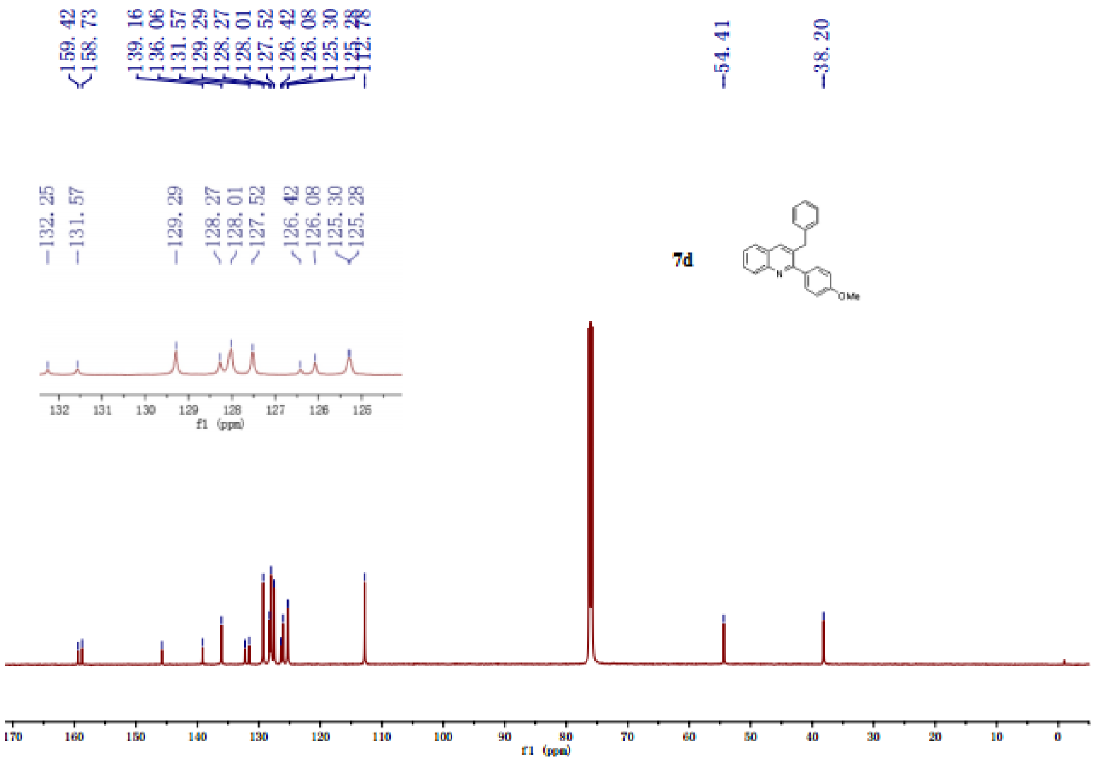
8.11
7.89
7.74
7.72
7.67
7.66
7.64
7.50
7.49
7.47
7.45
7.43
7.26
7.25
7.24
7.23
7.20
7.19
7.03
7.01
6.97
3.85
7d
N
OMe
1.00
1.03
1.02
1.03
1.04
2.02
1.96
1.03
2.00
2.05
2.04
3.08
f1 (ppm)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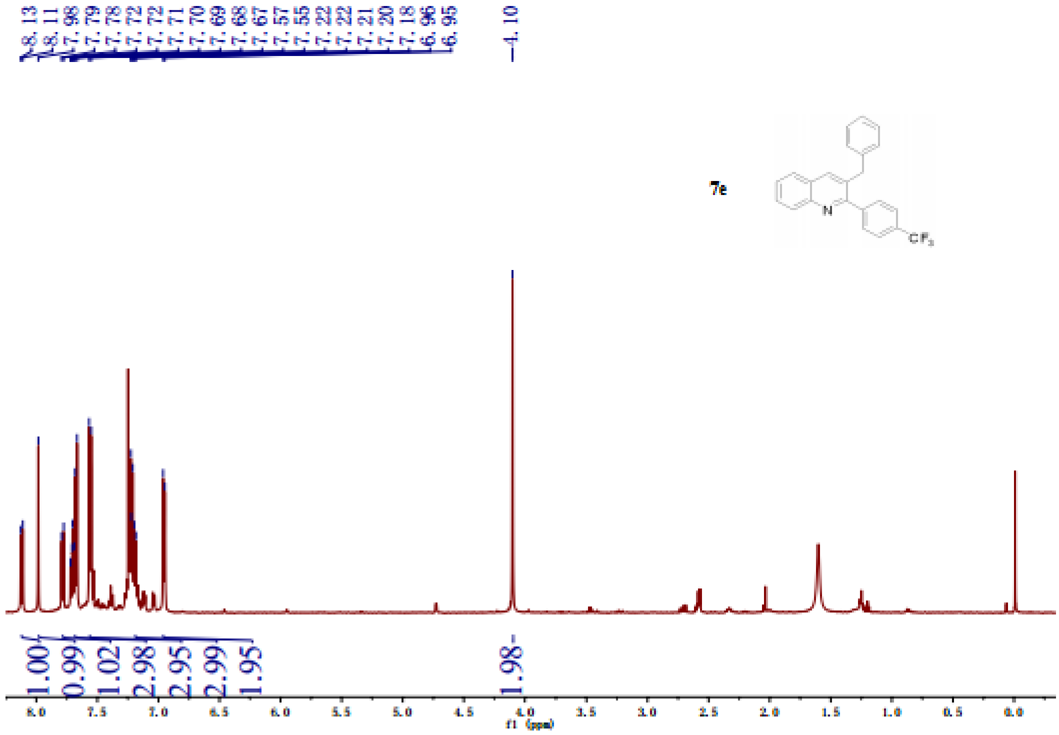
158.73
139.16
136.06
131.57
129.29
128.27
128.01
127.52
126.42
126.08
125.30
54.41
38.20
132.25
131.57
129.29
128.27
128.01
127.52
126.42
126.08
125.30
125.28
7d
N
OMe
f1 (ppm)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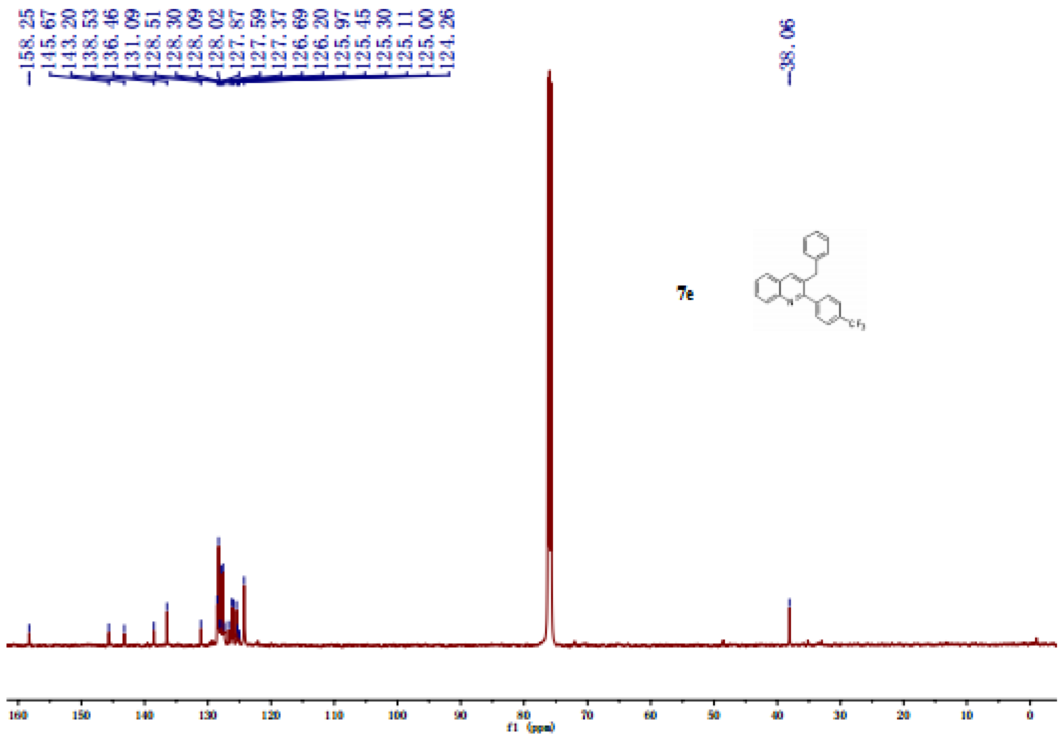
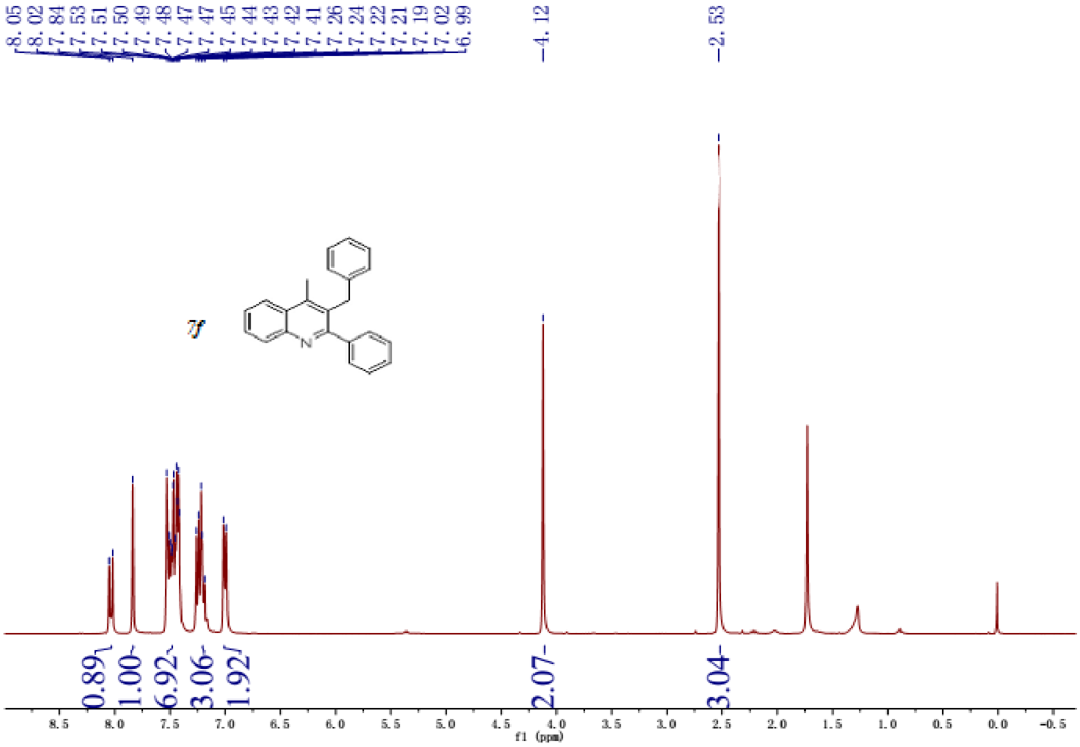
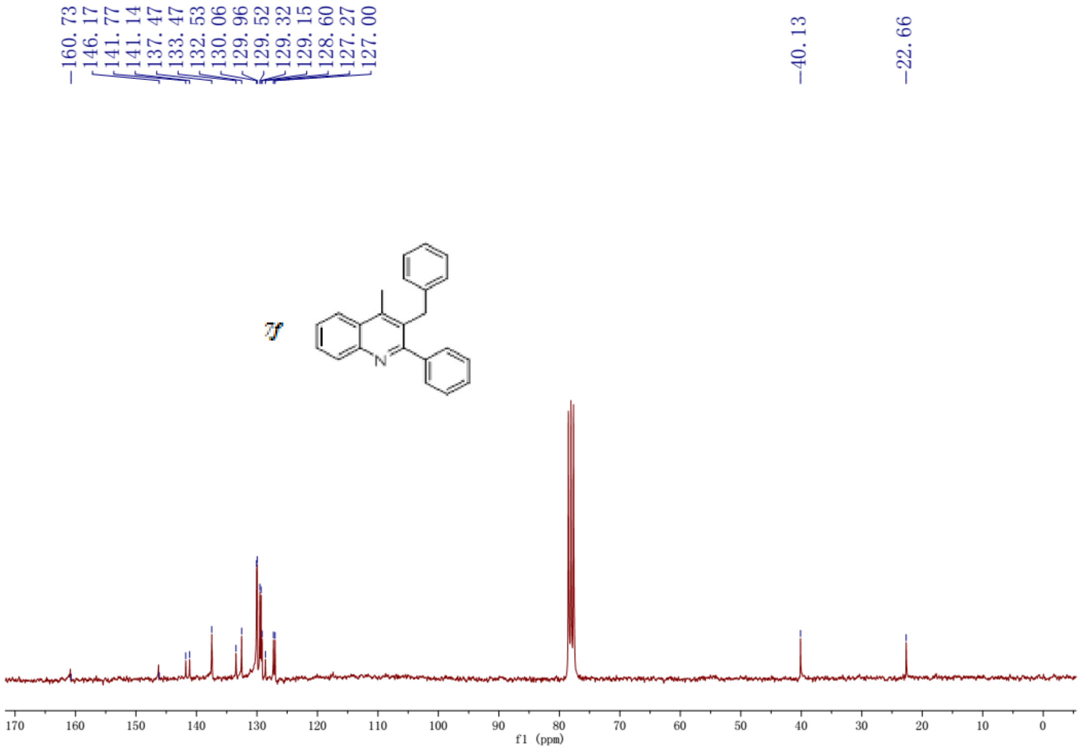
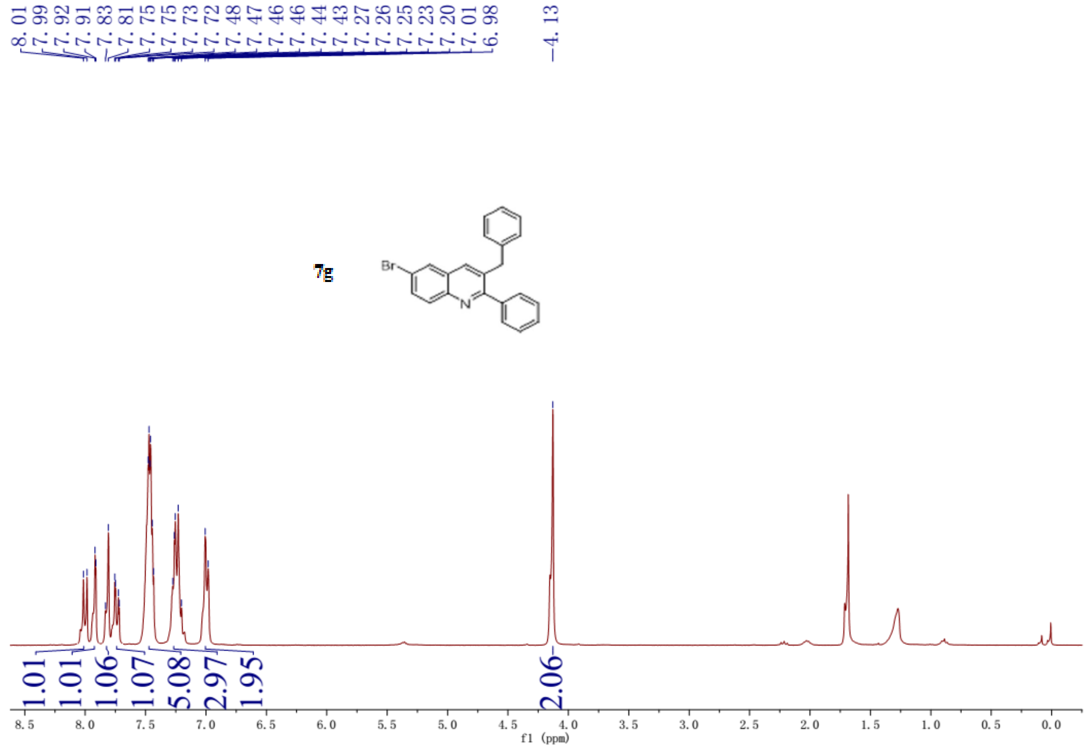
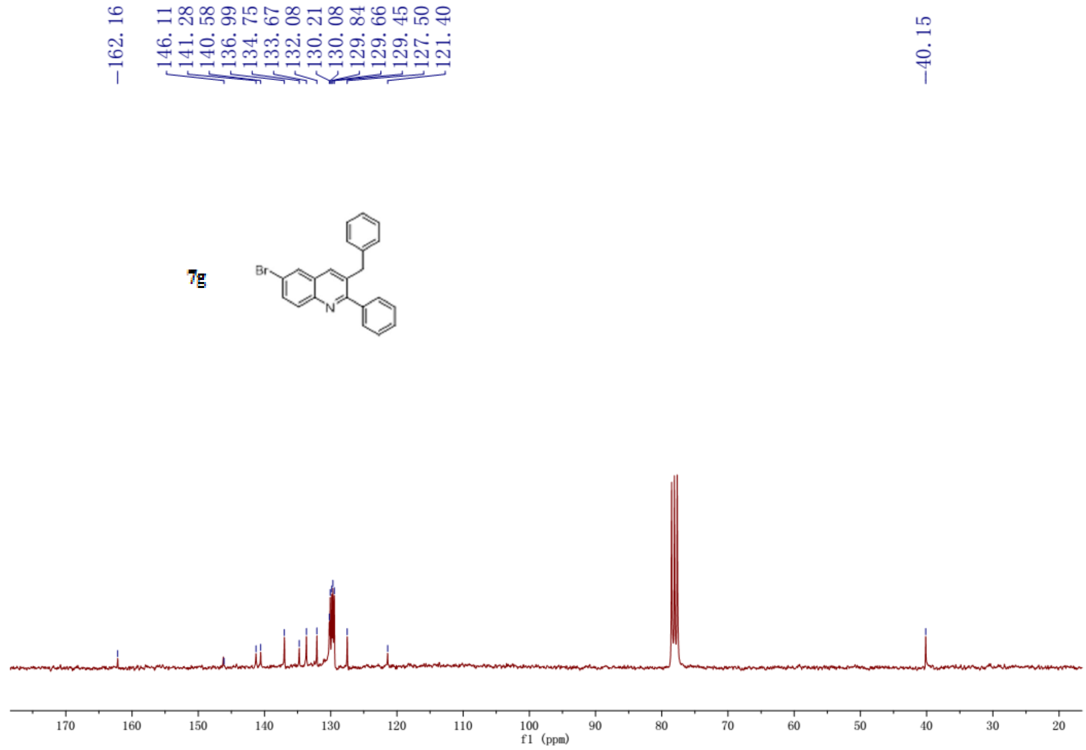
8.11
7.98
7.79
7.78
7.72
7.72
7.71
7.70
7.69
7.68
7.67
7.57
7.55
7.22
7.22
7.21
7.20
7.18
6.96
6.95
4.10
7e
1.00
0.99
1.02
2.98
2.95
2.99
1.95
1.98
f1 (ppm)


158.25
145.67
143.20
138.53
136.46
131.09
128.51
128.30
128.09
128.02
127.87
127.59
127.37
126.69
126.20
125.97
125.45
125.30
125.11
125.00
124.26
38.06
7e
f1 (ppm)


8.05
8.02
7.84
7.53
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.44
7.43
7.42
7.41
7.26
7.24
7.22
7.21
7.19
7.02
6.99
4.12
2.53
7f
N
0.89
1.00
6.92
3.06
1.92
2.07
3.04
f1 (ppm)


160.73
146.17
141.77
141.14
137.47
133.47
132.53
130.06
129.96
129.52
129.32
129.15
128.60
127.27
127.00
40.13
22.66
7f
N
f1 (ppm)


8.01
7.99
7.92
7.91
7.83
7.81
7.75
7.75
7.73
7.72
7.48
7.47
7.46
7.46
7.44
7.43
7.27
7.26
7.25
7.23
7.20
7.01
6.98
4.13
7g
Br
N
1.01
1.01
1.06
1.07
5.08
2.97
1.95
2.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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146.11
141.28
140.58
136.99
134.75
133.67
132.08
130.21
130.08
129.84
129.66
129.45
127.50
121.40
40.15
7g
Br
N
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)