

Supporting Information

Transition Metal/Brønsted Acid Cooperative Catalysis Enabled Facile Synthesis of 8-hydroxyquinolines through One-pot Reactions of *ortho*-Aminophenol, Aldehydes and Alkynes

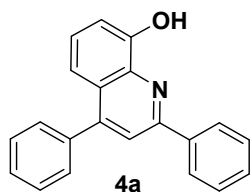
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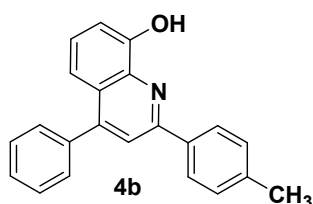
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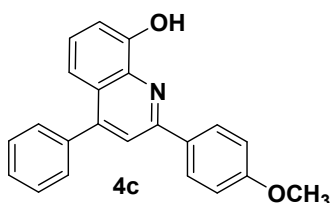
1. Characterization data of 8-hydroxyquinoline compounds



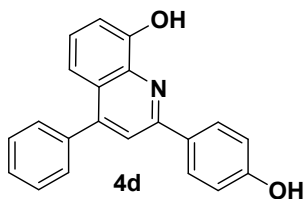
Light yellow solid; m.p.107-109°C; ¹H NMR (600 MHz, CDCl₃): δ 8.60 (s, 1H), 8.19-8.21 (m, 2H), 7.87 (s, 1H), 7.49-7.59 (m, 8H), 7.40-7.41 (m, 2H), 7.23 (d, *J* = 8.7 Hz, 1H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ 152.0, 150.2, 147.3, 136.4, 136.2, 135.9, 127.2, 127.1, 126.5, 126.2, 126.2, 125.0, 125.0, 123.6, 117.5, 113.6, 107.6 ppm.



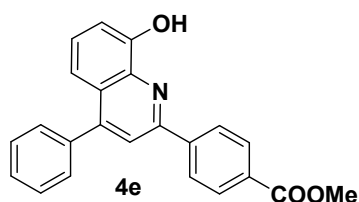
Light yellow solid; m.p.116-117°C; ¹H NMR (600 MHz, CDCl₃): δ 8.60 (s, 1H), 8.10 (d, *J* = 8.2 Hz, 2H), 7.85 (s, 1H), 7.58 (dd, *J* = 11.4, 4.4 Hz, 5H), 7.34-7.39 (m, 4H), 7.21 (dd, *J* = 6.1, 2.6 Hz, 1H), 2.46 (s, 3H) ppm; ¹³C NMR (150 MHz, CDCl₃): δ 153.4, 151.4, 148.5, 138.7, 137.5, 137.3, 134.9, 128.6, 128.4, 127.5, 127.5, 126.2, 126.1, 124.8, 118.7, 114.9, 108.8, 20.3 ppm.



Light yellow solid; m.p.114-117°C; ¹H NMR (600 MHz, CDCl₃): δ 8.59 (s, 1H), 8.16 (d, *J* = 8.9 Hz, 2H), 7.81 (s, 1H), 7.51-7.58 (m, 5H), 7.36-7.37 (m, 2H), 7.20 (dd, *J* = 6.3, 2.4 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 161.1, 154.1, 152.4, 149.6, 138.6, 138.4, 131.3, 129.5, 128.8, 128.6, 128.5, 126.9, 125.7, 119.5, 116.0, 114.3, 109.9, 55.4 ppm.

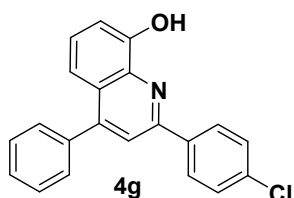


Orange solid; m.p.: 185-187°C; ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.79 (s, 1H), 7.53 (dd, *J* = 14.1, 6.7 Hz, 5H), 7.31-7.40 (m, 2H), 7.19 (dd, *J* = 5.8, 2.6 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 157.2, 154.0, 152.3, 149.6, 138.5, 138.3, 129.5, 129.0, 128.6, 127.0, 125.7, 119.5, 116.1, 115.8, 109.9 ppm.

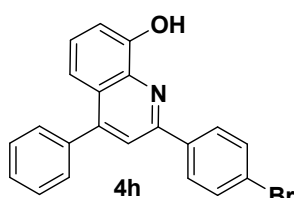


Light yellow solid; m.p.206-208°C; ¹H NMR (600 MHz, CDCl₃) δ 8.51 (s, 1H), 8.25 (d, *J* = 8.3 Hz, 2H),

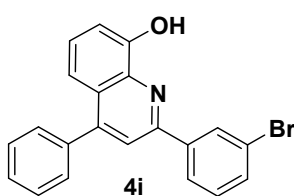
8.19 (d, $J = 8.4$ Hz, 2H), 7.88 (s, 1H), 7.55 (m, 5H), 7.41 (d, $J = 6.5$ Hz, 2H), 7.23 (dd, $J = 6.1, 2.5$ Hz, 1H), 3.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 166.8, 153.1, 152.6, 150.0, 142.8, 138.6, 138.0, 130.9, 130.1, 129.5, 128.7, 128.6, 128.0, 127.3, 126.3, 119.9, 116.1, 110.3, 52.3 ppm.



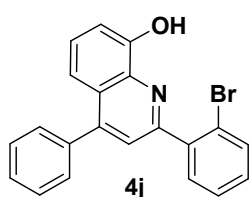
Light yellow solid; m.p.148-149°C; ^1H NMR (400 MHz, CDCl_3): δ 8.51 (s, 1H), 8.16 (d, $J = 8.6$ Hz, 2H), 7.84 (s, 1H), 7.52-7.61 (m, 7H), 7.41-7.45 (m, 2H), 7.25 (dd, $J = 5.1, 3.6$ Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 152.1, 151.4, 148.9, 137.5, 137.02, 136.1, 134.8, 128.4, 128.0, 127.6, 126.5, 125.0, 118.4, 115.0, 109.1 ppm.



Light yellow solid; m.p.163-164°C; ^1H NMR (600 MHz, CDCl_3) δ 8.49 (s, 1H), 8.06 (d, $J = 8.3$ Hz, 2H), 7.81 (s, 1H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.55 (d, $J = 5.4$ Hz, 5H), 7.40 (d, $J = 6.0$ Hz, 2H), 7.21 (d, $J = 2.4$ Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 153.2, 152.5, 150.0, 138.5, 138.1, 137.6, 132.1, 129.5, 128.9, 128.7, 128.7, 127.7, 126.1, 119.5, 116.1, 110.2 ppm.

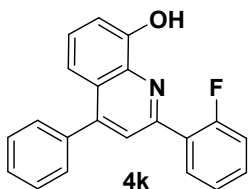


Light yellow solid; m.p.153-154°C; ^1H NMR (600 MHz, CDCl_3): δ 8.48 (s, 1H), 8.34 (t, $J = 1.6$ Hz, 1H), 8.10 (d, $J = 7.8$ Hz, 1H), 7.81 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.56-7.57 (m, 3H), 7.52-7.54(m, 1H), 7.41 (dd, $J = 8.8, 6.2$ Hz, 3H), 7.23 (dd, $J = 6.0, 2.7$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 152.8, 152.6, 150.1, 140.8, 138.6, 138.1, 132.5, 130.4, 129.5, 128.7, 127.8, 126.2, 125.9, 123.2, 119.7, 116.1, 110.3 ppm.

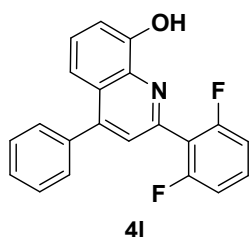


Light yellow oil; ^1H NMR (600 MHz, CDCl_3): δ 8.48 (s, 1H), 7.71-7.75 (m, 2H), 7.70 (dd, $J = 7.6, 1.6$ Hz, 1H), 7.59-7.61 (m, 2H), 7.47-7.55 (m, 3H), 7.32-7.35 (m, 3H), 7.24 (td, $J = 7.8, 1.7$

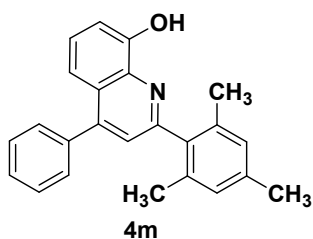
Hz, 1H), 7.23 (dd, $J = 7.1, 1.5$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 155.7, 152.7, 148.6, 140.8, 138.5, 138.0, 133.6, 131.9, 130.2, 129.6, 128.7, 128.0, 127.7, 125.9, 123.6, 121.9, 116.0, 110.1 ppm.



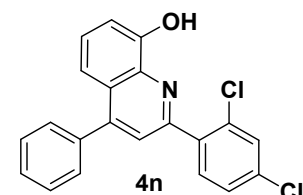
Light yellow solid; m.p.120-121°C; ^1H NMR (600 MHz, CDCl_3): δ 8.51 (s, 1H), 8.12 (t, $J = 7.6$ Hz, 1H), 7.90 (s, 1H), 7.50-7.6 0 (m, 5H), 7.41-7.47 (m, 3H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.22 (dd, $J = 12.4, 6.8$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 159.6, 152.6, 151.2, 149.2, 131.4, 129.6, 128.6, 127.8, 124.7, 116.6, 116.4, 116.0, 109.9, 100.0 ppm.



Green oil; ^1H NMR (600 MHz, CDCl_3): δ 8.43 (s, 1H), 7.57-7.59 (m, 3H), 7.50-7.55 (m, 3H), 7.44 (dd, $J = 21.1, 6.5$ Hz, 4H), 7.23 (t, $J = 4.4$ Hz, 1H), 7.07 (t, $J = 8.0$ Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 162.0, 161.9, 159.5, 159.4, 152.6, 149.1, 147.0, 138.7, 137.8, 129.6, 128.6, 128.3, 124.2, 116.0, 112.1, 112.0, 111.9, 111.8, 110.0 ppm.

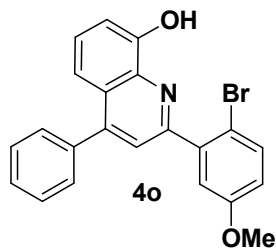


Brown solid; m.p.142°C-143°C; ^1H NMR (600 MHz, CDCl_3) δ 7.55-7.58(m, 2H), 7.53 (t, $J = 7.3$ Hz, 2H), 7.47-7.51 (m, 2H), 7.41-7.45 (m, 1H), 7.35 (s, 1H), 7.19-7.22 (m, 1H), 7.01 (s, 2H), 2.37 (s, 3H), 2.11 (s, 6H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 156.6, 151.5, 147.9, 137.0, 136.9, 134.8, 128.5, 127.5, 127.5, 127.4 126.4, 124.4, 108.7, 20.1, 19.3 ppm.

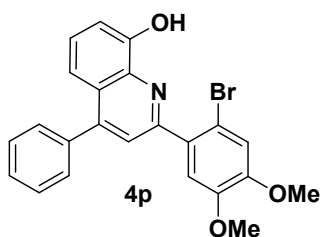


White solid; m.p.132-133°C; ^1H NMR (600 MHz, CDCl_3) δ 8.40 (s, 1H), 7.70-7.74 (m, 2H), 7.57 (dd, $J = 12.5, 7.4$ Hz, 6H), 7.45-7.46 (m, 2H), 7.43 (dd, $J = 9.1\text{Hz}, 1.1$ Hz, 1H), 7.23 (dd, $J = 5.6\text{Hz}, 2.5$ Hz, 1H) ppm; ^{13}C NMR (150 MHz,

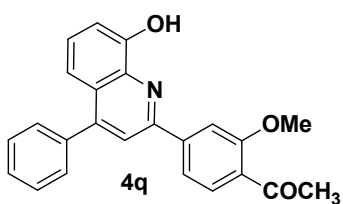
CDCl₃): δ 153.2, 152.5, 148.8, 138.5, 137.8, 135.4, 133.2, 132.7, 130.1, 129.5, 128.6, 128.1, 127.5, 125.9, 123.3, 116.0, 110.1 ppm.



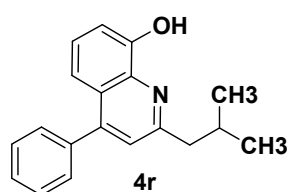
White solid; m.p.166-168°C; ¹H NMR (400 MHz, CDCl₃) δ 8.41 (d, *J* = 1.9 Hz, 1H), 8.15 (d, *J* = 10.4 Hz, 1H), 7.80 (s, 1H), 7.54-7.62 (m, 5H), 7.41 (d, *J* = 4.3 Hz, 2H), 7.24 (t, *J* = 4.3 Hz, 1H), 7.06 (d, *J* = 8.6 Hz, 1H), 4.02 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 159.1, 155.6, 152.7, 148.6, 141.6, 138.4, 138.0, 134.3, 129.6, 128.6, 128.0, 126.0, 123.6, 117.1, 116.3, 116.0, 112.3, 110.0, 55.7 ppm.



Brown oil; ¹H NMR (600 MHz, CDCl₃) δ 8.46 (s, 1H), 7.75 (s, 1H), 7.58-7.60(m, 2H), 7.54 (t, *J*=7.3 Hz, 2H), 7.51 (d, *J* =7.2 Hz, 1H), 7.41-7.46 (m, 2H), 7.24 (s, 1H), 7.22 (dd, *J* =7.0, 1.6 Hz, 1H), 7.18 (s, 1H), 3.95 (d, *J* =11.0 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 155.5, 152.6, 150.1, 148.7, 148.4, 138.0, 129.6, 128.6, 127.8, 125.8, 123.8, 116.2, 116.0, 114.3, 112.3, 110.0, 56.4, 56.3 ppm.

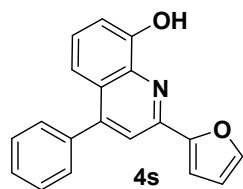


White solid; m.p.205-208°C; ¹H NMR (600 MHz, CDCl₃) δ 8.51 (s, 1H), 7.81-7.82(m, 2H), 7.72 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.52-7.57 (m, 5H), 7.36-7.41(m, 2H), 7.19-7.23 (m, 2H), 3.98 (s, 3H), 2.37 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 169.0, 153.8, 152.5, 151.6, 149.9, 141.2, 138.2, 137.8, 129.5, 128.7, 126.1, 123.2, 120.1, 119.9, 116.8, 111.5, 110.1, 56.2, 20.7 ppm.

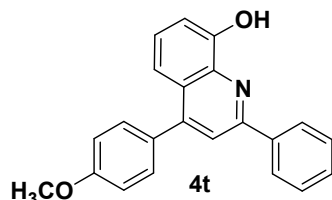


Light yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.46-7.52 (m, 5H), 7.32-37(m, 2H), 7.23 (s, 1H), 7.15 (d, *J* = 7.0 Hz, 1H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.27 (dt, *J* = 13.5, 6.7 Hz, 1H), 1.00 (d, *J* = 6.6 Hz, 6H) ppm; ¹³C NMR (150MHz, CDCl₃): δ

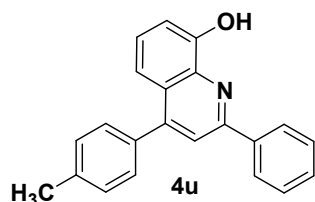
158.8, 151.4, 148.2, 137.6, 137.5, 128.9, 127.8, 127.7, 125.9, 124.7, 122.4, 47.1, 29.2, 28.5, 21.9 ppm.



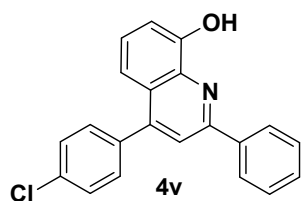
Light yellow solid; m.p.132-133°C; ^1H NMR (600 MHz, CDCl_3) δ 8.41 (s, 1H), 7.75 (s, 1H), 7.51 (s, 1H), 7.41-7.48 (m, 7H), 7.27 (d, $J = 2.6$ Hz, 2H), 7.17-7.19 (m, 2H), 7.10 (dd, $J = 5.9, 2.7$ Hz, 1H), 6.52 (dd, $J = 3.4, 1.7$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 153.5, 152.2, 149.5, 146.4, 144.0, 138.5, 138.1, 129.5, 128.6, 127.2, 126.0, 118.2, 116.2, 112.4, 110.1, 110.8 ppm.



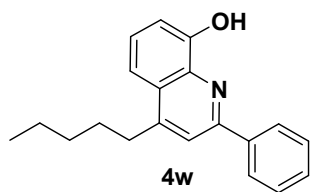
Light yellow solid; m.p.187-189°C; ^1H NMR (600 MHz, CDCl_3) δ 8.54 (s, 1H), 8.18 (d, $J = 7.6$ Hz, 2H), 7.83 (s, 1H), 7.51-7.55 (m, 4H), 7.48 (t, $J = 7.3$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.38 (t, $J = 7.9$ Hz, 1H), 7.20 (d, $J = 7.4$ Hz, 1H), 7.07 (d, $J = 8.5$ Hz, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 160.0, 154.5, 152.6, 149.4, 138.9, 130.7, 130.6, 129.6, 128.9, 127.4, 126.2, 119.9, 116.1, 114.1, 109.9, 55.5 ppm.



Light yellow solid; m.p.127-128°C; ^1H NMR (600 MHz, CDCl_3) δ 8.60 (s, 1H), 8.17 (d, $J = 7.4$ Hz, 2H), 7.84 (s, 1H), 7.53 (t, $J = 7.6$ Hz, 2H), 7.45-7.63 (m, 3H), 7.42 (d, $J = 7.7$ Hz, 1H), 7.33-7.39 (m, 3H), 7.20 (d, $J = 7.3$ Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 154.5, 152.6, 149.8, 138.9, 138.60, 135.4, 129.6, 129.5, 129.4, 128.9, 127.4, 127.3, 126.1, 119.9, 116.1, 109.9, 21.4 ppm.

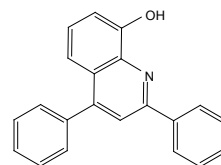
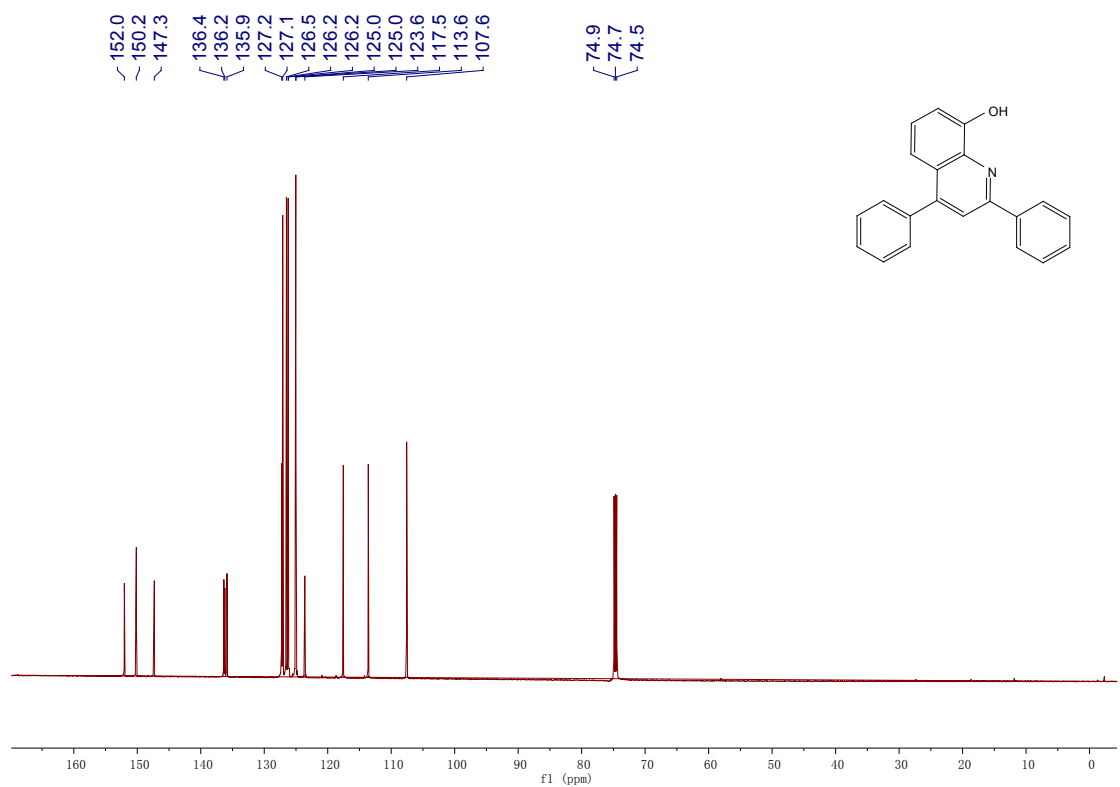
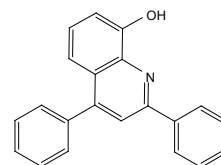
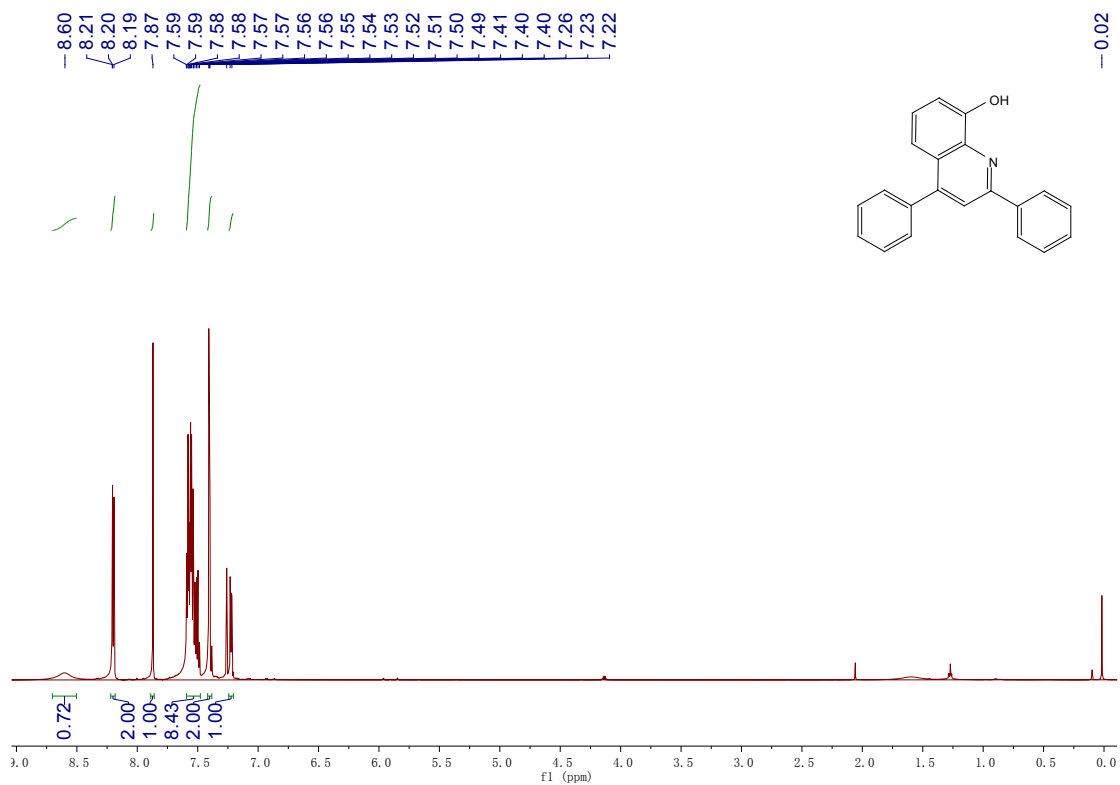


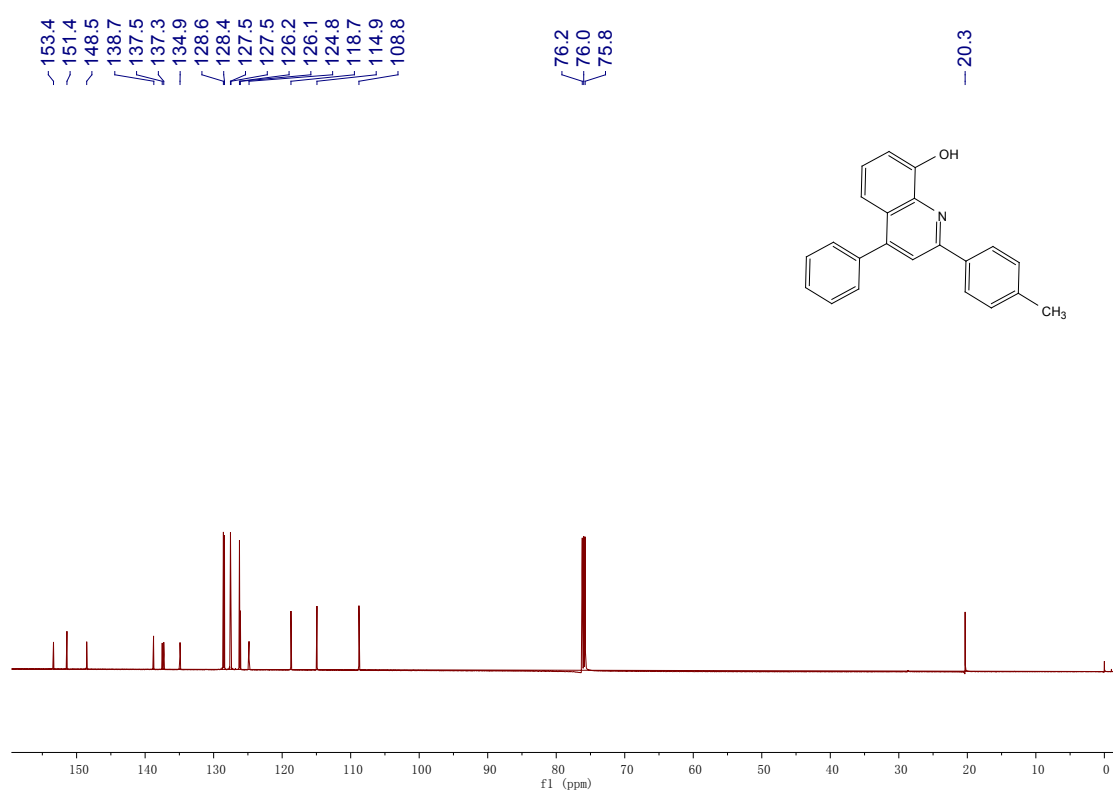
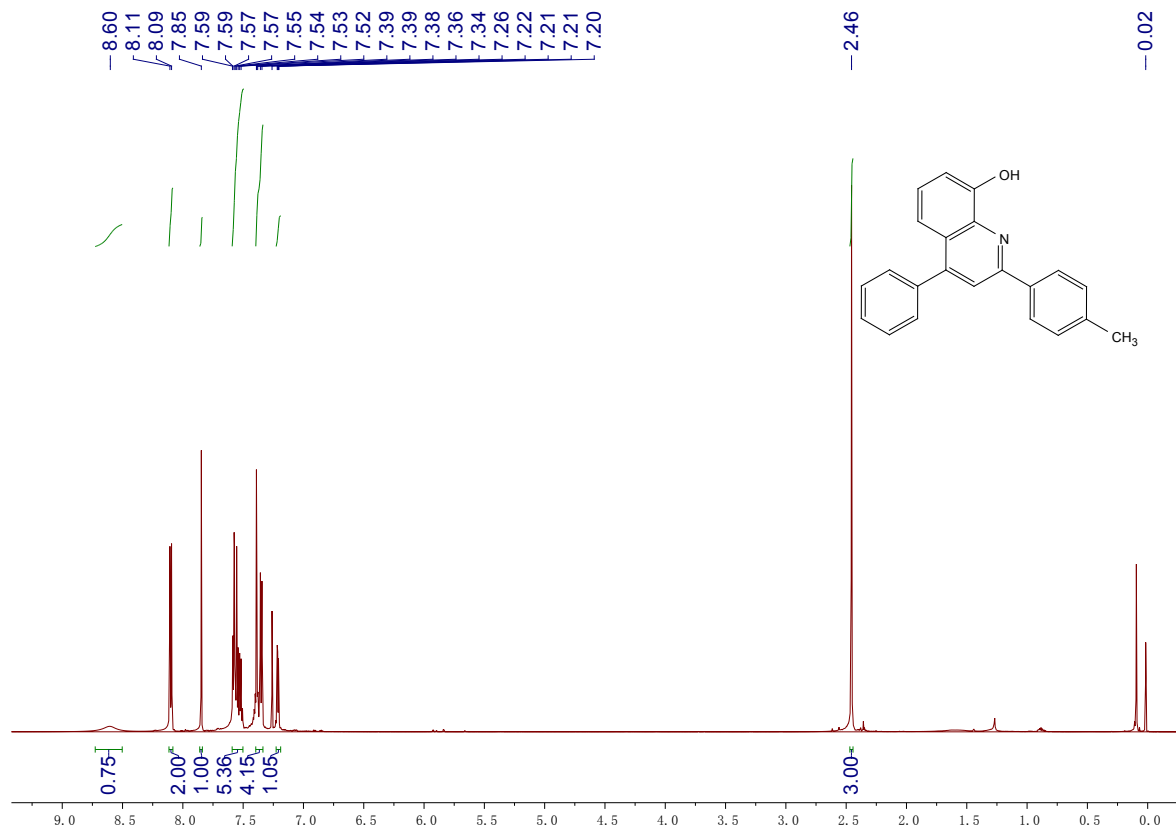
Light yellow solid; m.p.159-161°C; ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 1H), 8.21 (dd, $J = 8.2, 1.3$ Hz, 2H), 7.85 (s, 1H), 7.52-7.61 (m, 7H), 7.41-7.47 (m, 1H), 7.37 (d, $J = 7.2$ Hz, 1H), 7.25 (dd, $J = 7.4, 1.3$ Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 154.4, 152.5, 148.3, 138.5, 136.6, 134.7, 130.7, 129.7, 128.8, 127.6, 127.3, 125.7, 119.8, 115.5, 110.1 ppm.

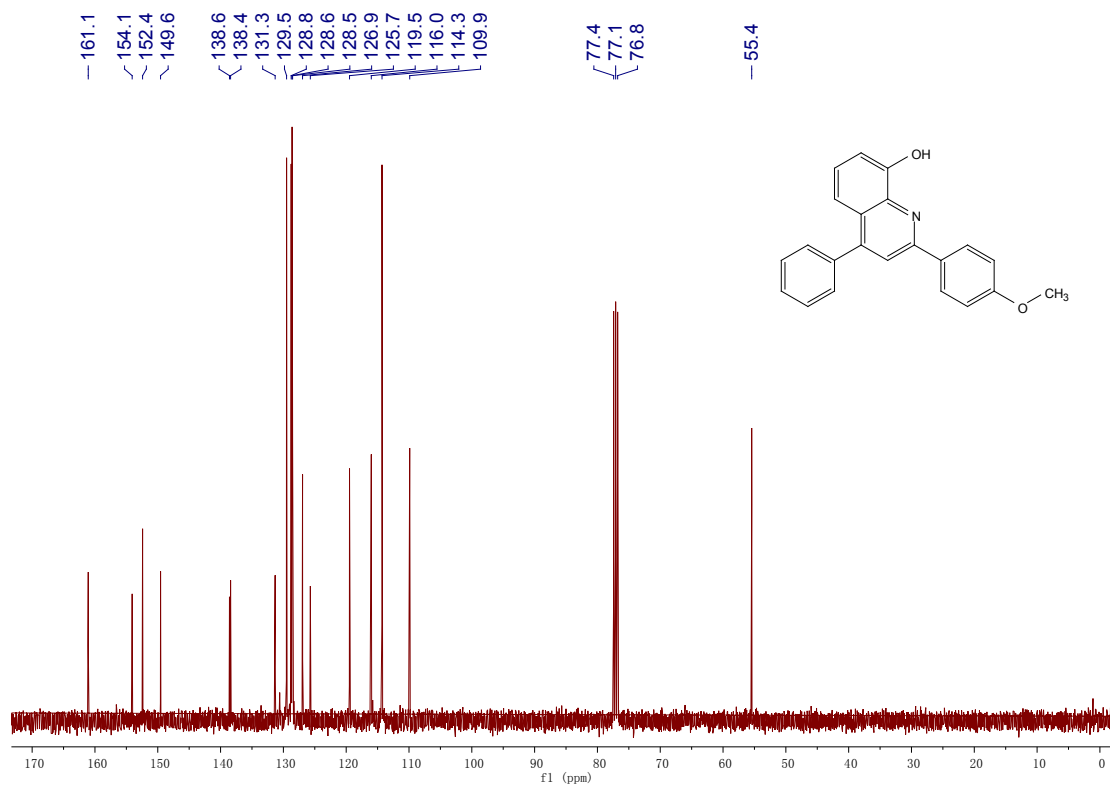
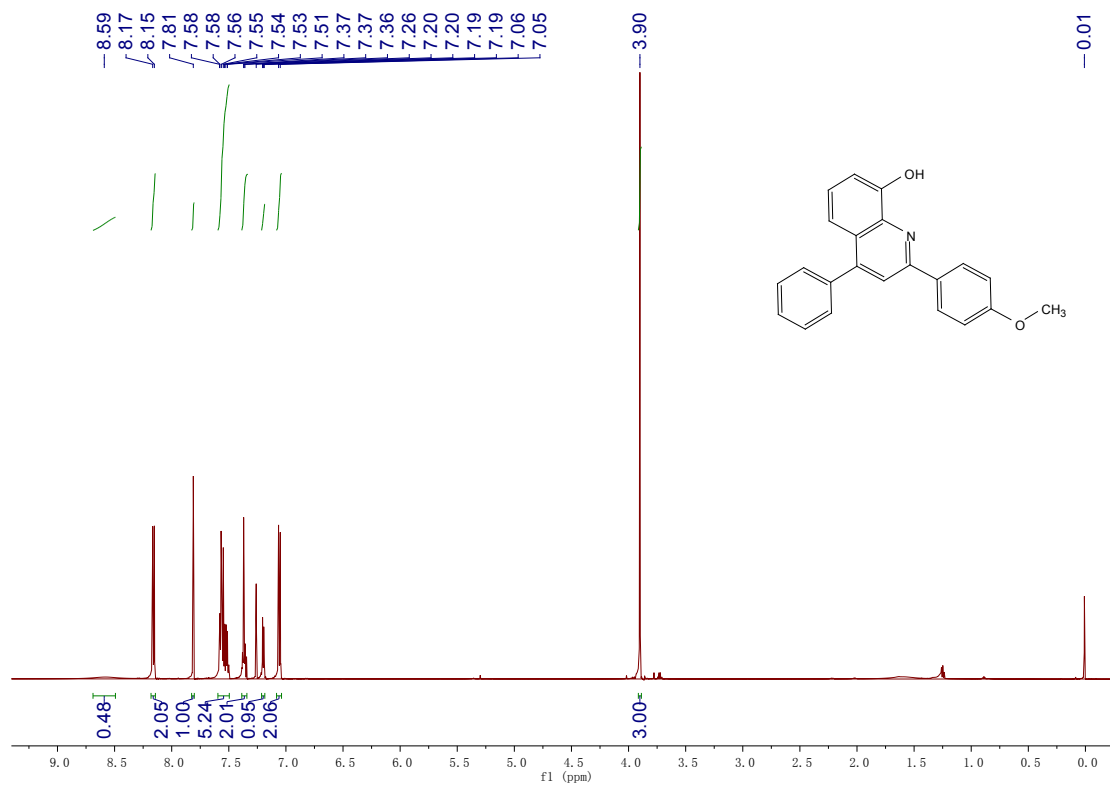


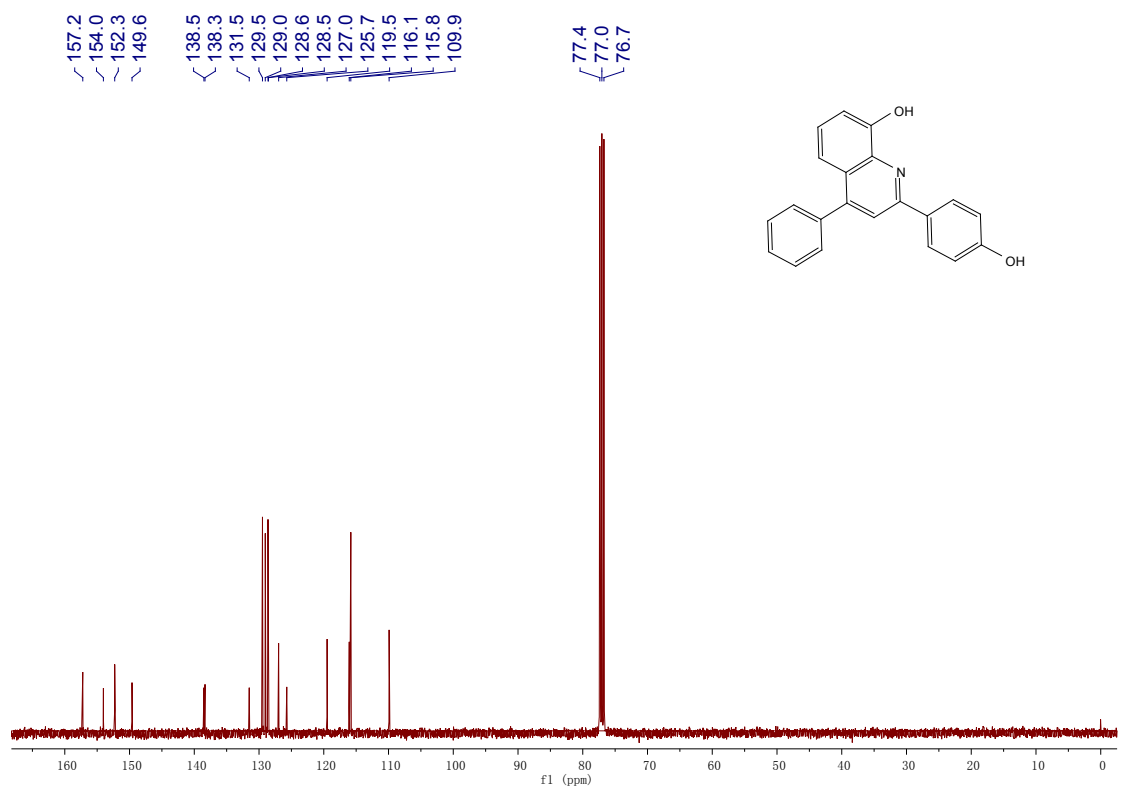
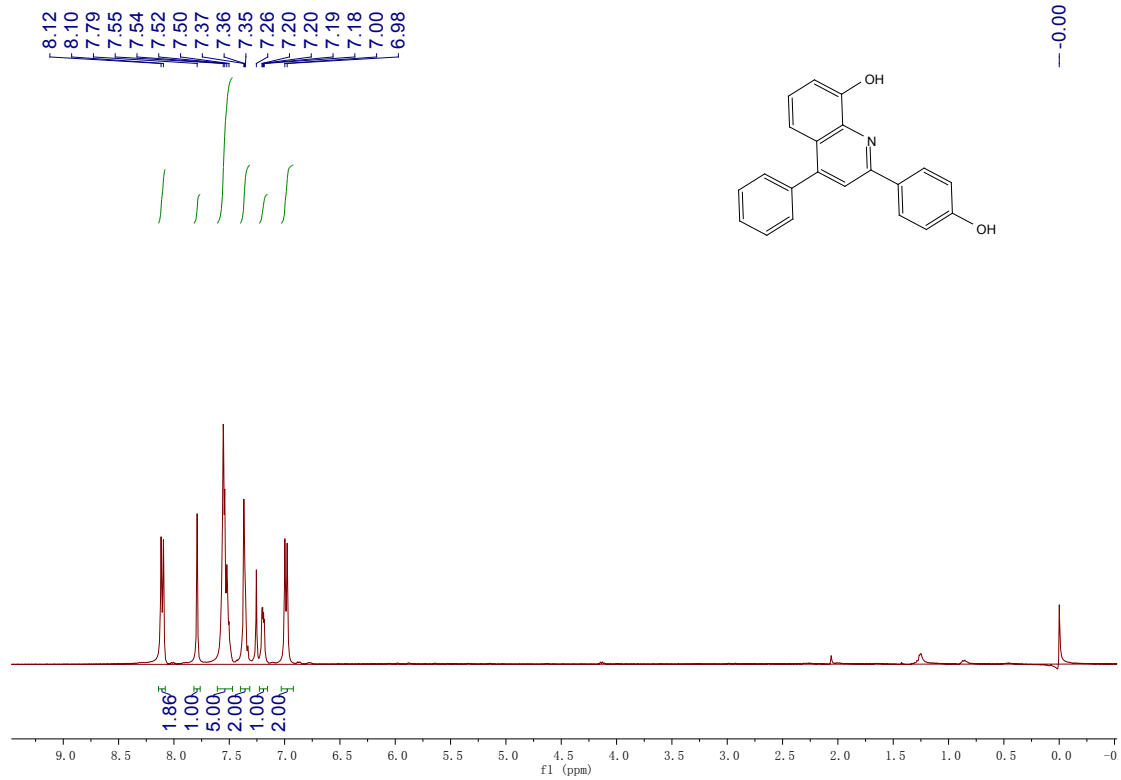
Light yellow oil; ^1H NMR (600 MHz, CDCl_3) δ 8.61 (s, 1H), 8.13-8.16 (m, 2H), 7.73 (s, 1H), 7.41-7.55 (m, 5H), 7.17 (d, $J = 8.5$ Hz, 1H), 3.06-3.10 (m, 2H), 1.80 (dt, $J = 15.5, 7.7$ Hz, 2H), 1.36-1.47 (m, 5H), 1.25 (s, 1H), 0.92 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 154.5, 152.9, 150.3, 139.1, 138.2, 129.5, 128.8, 127.4, 126.9, 119.1, 113.9, 109.7, 32.7, 31.9, 29.8, 22.6, 14.1 ppm.

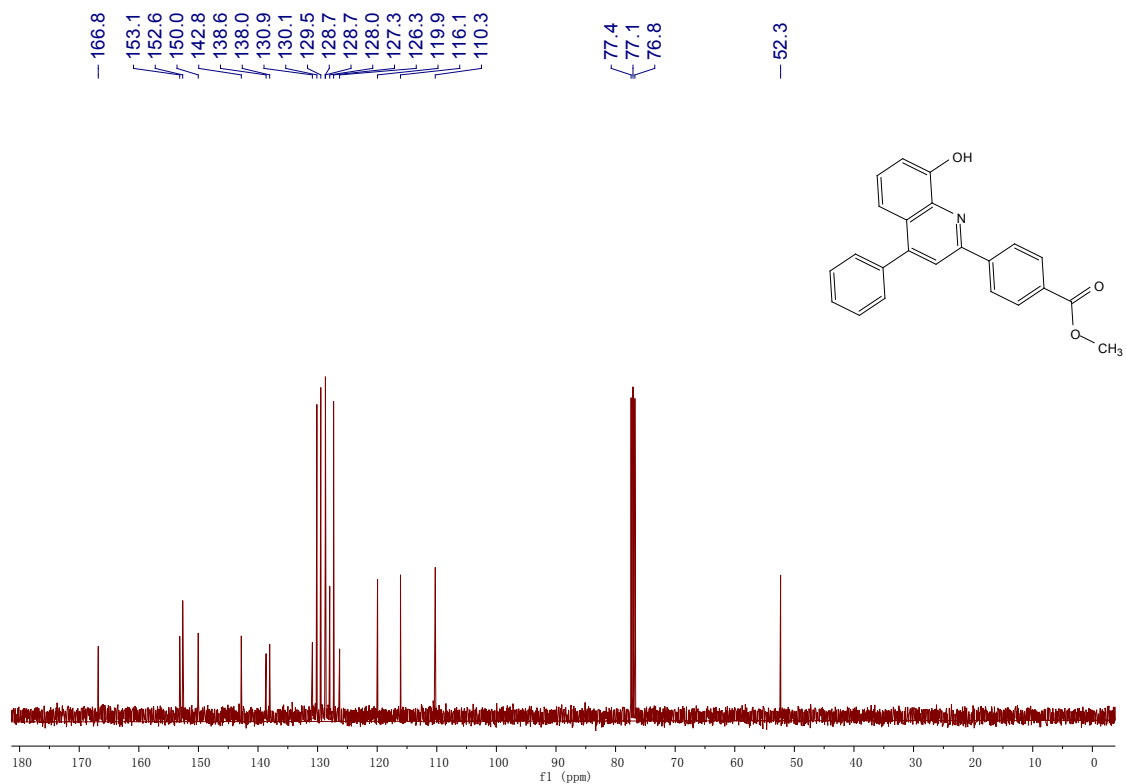
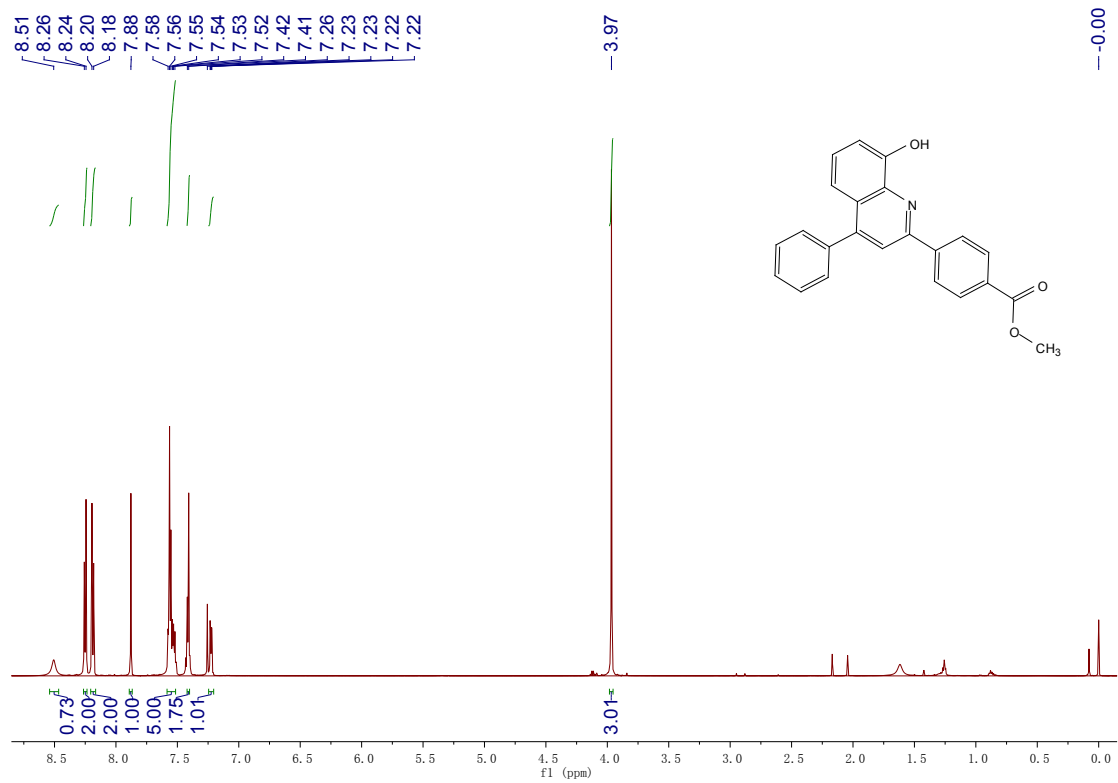
2. ¹H and ¹³C NMR spectra of 8-hydroxyquinoline compounds

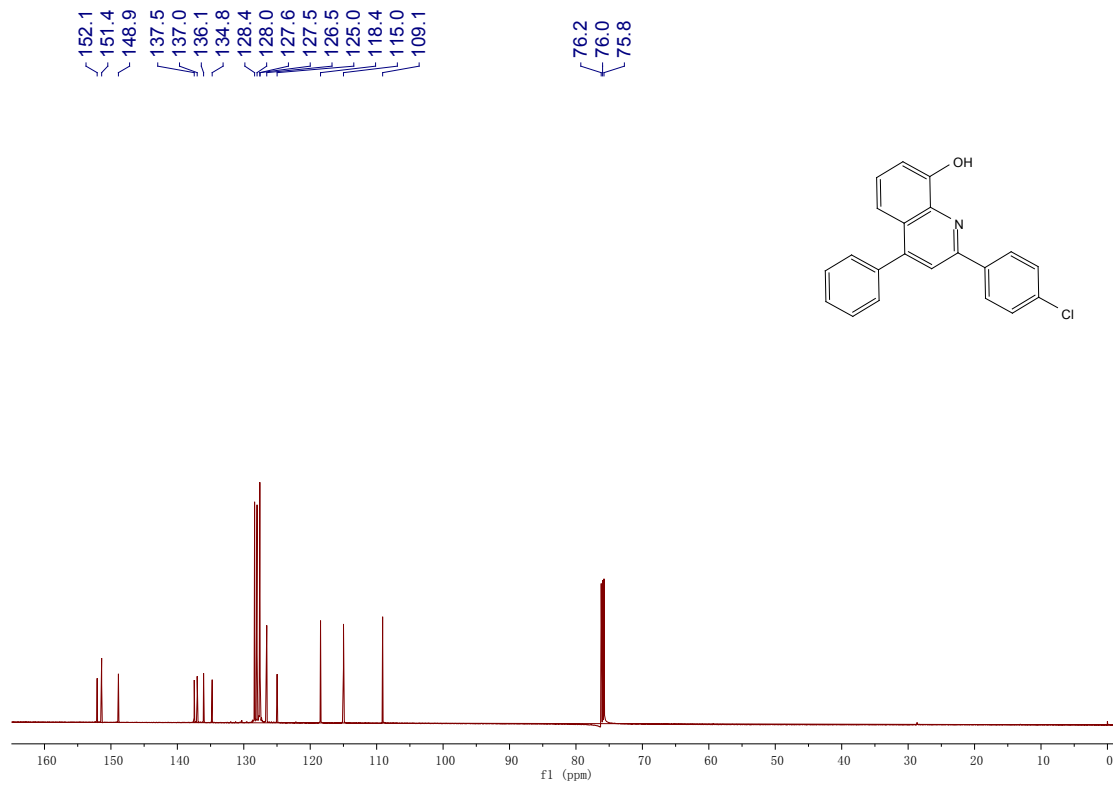
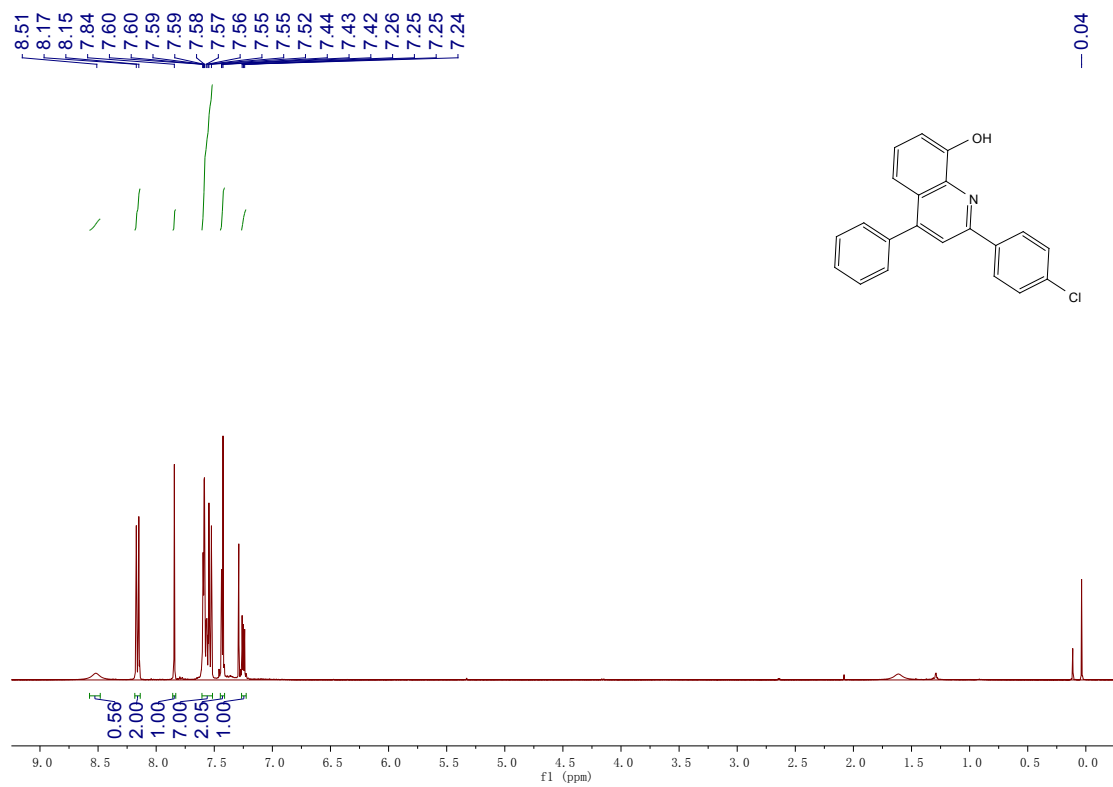


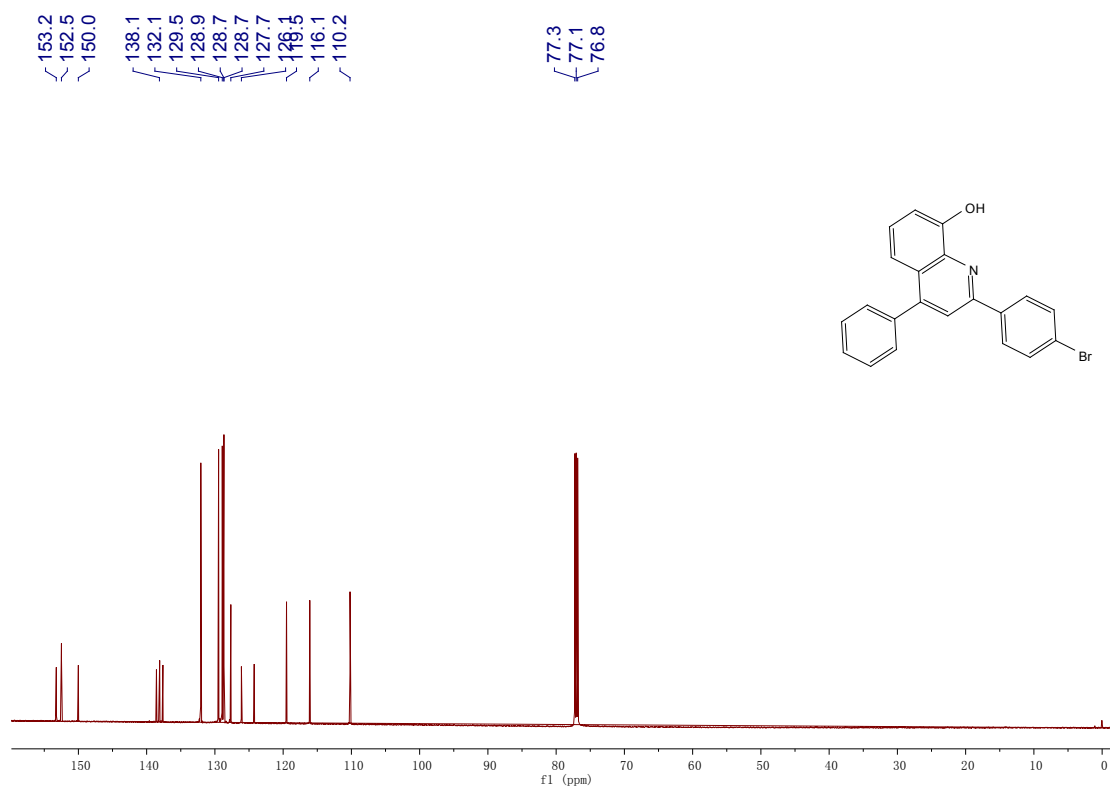
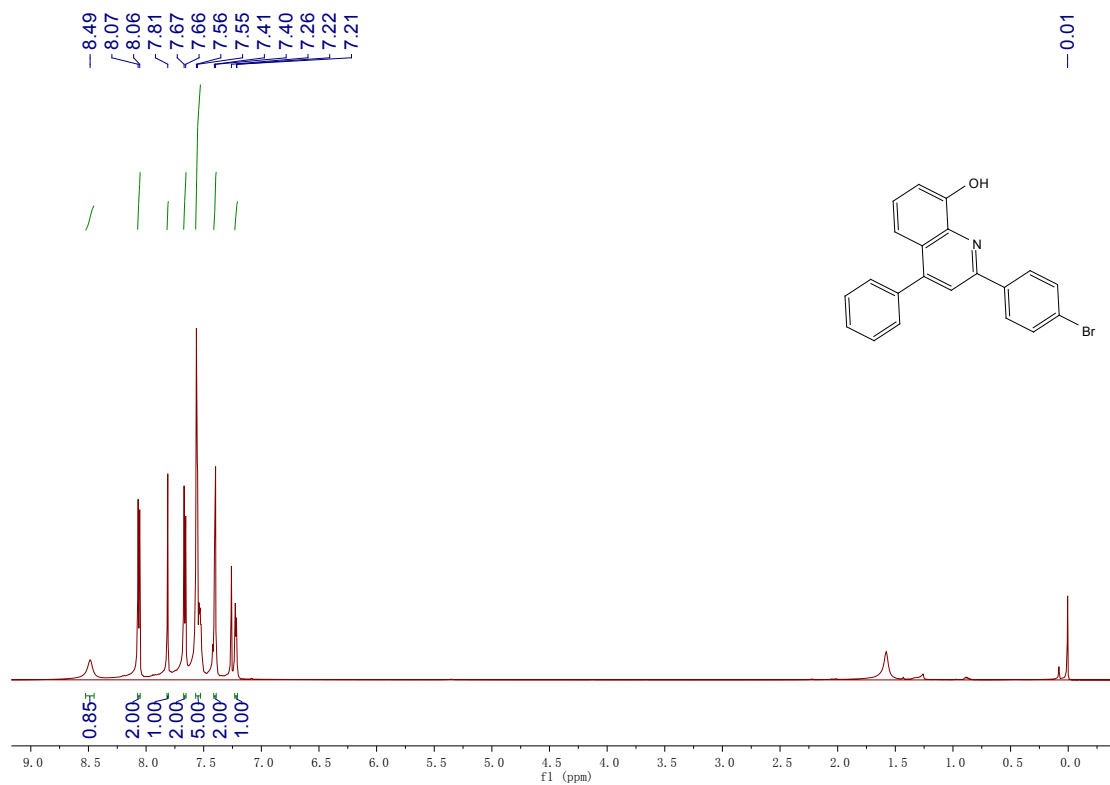






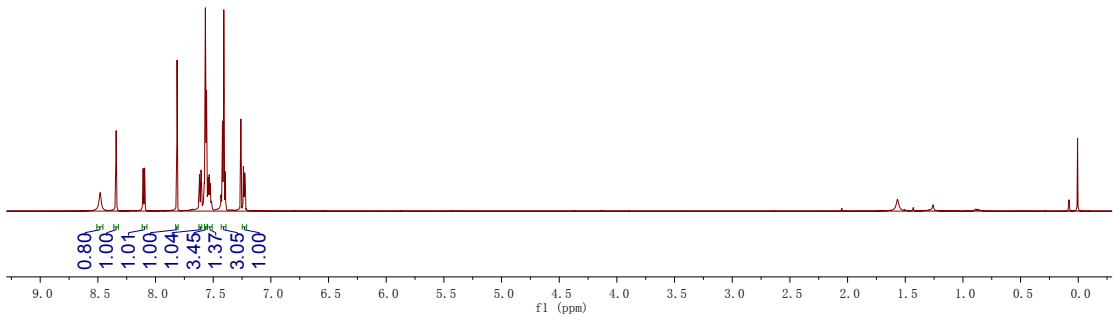
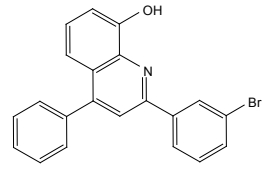






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7.53
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7.52
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7.41
7.41
7.39
7.26
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7.23
7.23
7.22

0.01



152.8
152.6
150.1
140.8
138.6
138.0
132.5
130.4
130.4
129.5
128.7
128.7
127.8
126.2
125.9
123.2
119.7
116.1
110.3

77.4
77.1
76.8

