

Supporting Information

New facile synthesis of 3-substituted 7,8-dihydroquinolin-5(6*H*)-ones and [1]benzopyrano[4,3-*b*]pyridin-5-ones using 2-(hetero)aryl-vinamidinium salts

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Experimental

General Methods.

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. Reactions were performed in oven-dried round bottom flasks. TLC analysis was performed using pre-coated glass plates. NMR spectra were recorded with 400 MHz spectrometer for ^1H and 100 MHz for ^{13}C , TMS was used as internal standard. All the reactions were monitored by TLC.

1) General procedure for the preparation of 2-(hetero)aryl-vinamidinium salts **1**

Anhydrous DMF (10 mL) were placed in a flask with a magnetic stirring bar. BTC [*bis* (trichloromethyl) Carbonate] (3 mmol) was added and stirred at 0 °C for 1.5h. Then the temperature was risen to 25 °C for 0.5h. (hetero)aryl acetic acids (3 mmol) was added and the mixture was stirred at 80 °C for 3 h. After the reaction was completed (as showed by TLC), mixture was cooled to room temperature. 30% NaClO_4 (3mmol) were successively added dropwise to the mixture. The 2-arylvinamidinium salts **1** was collected by filtration, and recrystallized by $\text{CH}_3\text{CH}_2\text{OH}$.

2) General procedure for the preparation of 7,8-Dihydroquinolin-5(6*H*)-ones **4a-4f**

A mixture of 3-amino-2-cyclohexen-1-one **2a** (1.0mmol), 2-arylvinamidinium salts **1** (1.2mmol), NaH (3.0mmol) and anhydrous DMF (10mL) were placed in a nitrogen-protected flash equipped with a magnetic stirring bar. The mixture was subsequently stirred at 10 °C for 0.5h. After the reaction was complete (as showed by TLC), the solvent was removed *in vacuo*. The residue was dissolved by 50 mL dichloromethane, then it was washed with water (3×20mL). The organic phase was dried by anhydrous Na_2SO_4 , filtered and evaporated. The remaining mixture was purified by column chromatography (petroleum ether: ethyl acetate = 1 : 1) to give products **4a-4f**.

3) General procedure for the preparation of 7,8-Dihydroquinolin-5(6*H*)-ones **4g-4l**

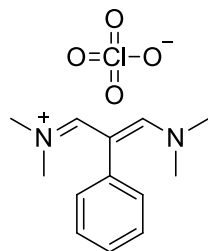
A mixture of 3-amino-5,5-dimethylcyclohex-2-enone **2b** (1.0mmol), 2-arylvinamidinium salts **1** (1.2mmol), NaOCH_3 (3.0mmol) and anhydrous DMF (10mL) were placed in a nitrogen-protected flash equipped with a magnetic stirring bar. The mixture was subsequently stirred at 10 °C for 2h. After the reaction was complete (as showed by TLC), the solvent was removed *in vacuo*. The residue was dissolved by 50 mL dichloromethane, then it was washed with water (3×20mL). The organic phase was dried by anhydrous Na_2SO_4 , filtered and evaporated. The remaining mixture

was purified by column chromatography (petroleum ether: ethyl acetate = 1 : 1) to give products **4g-4l**.

4) General procedure for the preparation of [1]benzopyrano[4,3-*b*]pyridine-5-ones **5**

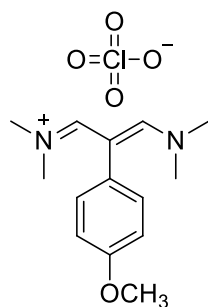
A mixture of 4-Aminocoumarine **3** (1.0mmol), 2-arylvinamidinium salts **1** (1.2mmol), NaOCH₃ (3.0mmol) and anhydrous DMF (10mL) were placed in a nitrogen-protected flash equipped with a magnetic stirring bar. The mixture was subsequently stirred at 10 °C for 3h. After the reaction was complete (as showed by TLC), the solvent was removed *in vacuo*. The residue was dissolved by 50 mL dichloromethane, then it was washed with water (3×20mL). The organic phase was dried by anhydrous Na₂SO₄, filtered and evaporated. The remaining mixture was purified by column chromatography (petroleum ether: ethyl acetate = 1 : 1) to give products **5a-5e**.

¹H and ¹³C NMR data



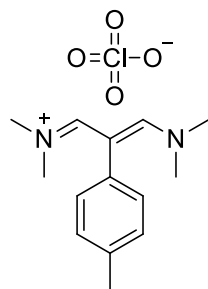
2-Phenyl-1,3-bis(dimethylamino)trimethinmium perchlorate (1a)

White solid; mp: 199.3-200.5 °C [lit.¹ 198 °C], ¹H NMR (400 MHz, CDCl₃): δ = 2.47 (s, 6H), 3.34 (s, 6H), 7.29-7.27 (m, 2H), 7.42-7.38 (m, 3H), 7.88-7.82 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 49.0, 105.5, 128.9, 129.2, 132.4, 133.1 163.4. MS (ESI) *m/z* = 203 [M- H]⁺.



2-(4-Methoxyphenyl)-1,3-bis(dimethylamino)trimethinmium perchlorate (1b)

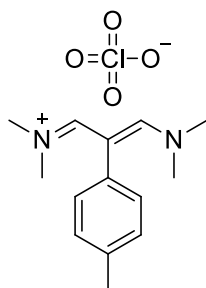
Brown yellow solid; mp: 132-134.6 °C [lit.² 134-135 °C], ¹H NMR (400 MHz, CDCl₃): δ = 2.50 (s, 6H), 3.32 (s, 6H), 3.82 (s, 3H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 7.78-7.75 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 39.6, 49.2, 55.4, 105.6, 114.2, 123.7, 133.3, 160.1, 164.3. MS (ESI) *m/z* = 233.2 [M-H]⁺.



2-(4-Methylphenyl)-1,3-bis(dimethylamino)trimethinmium perchlorate (1c)

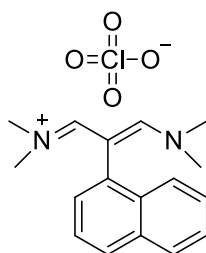
Yellow solid; mp: 161.2-163.4 °C [lit.³ 150-152°C], ¹H NMR (400 MHz, CDCl₃): δ = 2.34 (s, 3H),

2.43 (s, 6H), 3.23 (s, 6H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.25 (d, $J = 7.8$ Hz, 2H), 7.78 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 26.0, 53.7, 110.2, 134.2, 134.7, 137.2, 143.3, 168.3$. MS (ESI) m/z : 217.1 $[\text{M}-\text{H}]^+$.



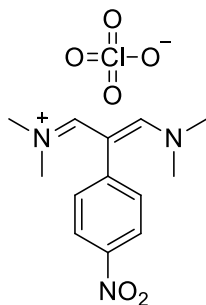
2-(4-Chlorophenyl)-1,3-bis(dimethylamino)trimethinmium perchlorate (1d)

Light yellow solid; mp: 234.5-245.3 °C [lit.³ 244-245 °C], ^1H NMR (400 MHz, CDCl_3): $\delta = 2.45$ (s, 6H), 3.25 (s, 6H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.82 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 34.5, 49.0, 104.0, 128.8, 132.1, 163.5, 134.0, 134.4$. MS (ESI) $m/z = 237.2$ $[\text{M}-\text{H}]^+$.



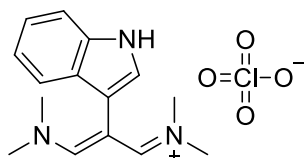
2-β-naphthyl-1,3-bis(dimethylamino)trimethinmium perchlorate (1e)

Brown solid; mp: 189.5-192.2 °C, ^1H NMR (400 MHz, CDCl_3): $\delta = 2.20$ (s, 6H), 3.34 (s, 6H), 7.41 (t, $J = 6.8$ Hz, 1H), 7.50 (t, $J = 7.0$ Hz, 1H), 7.57 (t, $J = 7.7$ Hz, 1H), 7.64 (t, $J = 6.9$ Hz, 1H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.91 (t, $J = 8.2$ Hz, 2H), 8.15 (s, 2H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 34.1, 44.8, 98.1, 120.4, 121.1, 122.3, 123.3, 124.1, 125.0, 125.2, 125.7, 128.5, 129.3, 160.1$. MS (ESI) $m/z = 253.3$ $[\text{M}-\text{H}]^+$.



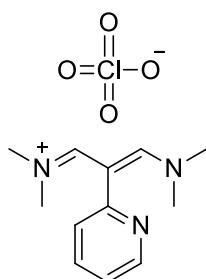
2-(4-Nitrophenyl)-1,3-bis(dimethylamino)trimethinium perchlorate (1f)

Yellow solid; mp: 227.0-229.6 °C [lit.¹ 226 °C], ¹H NMR (400 MHz, CDCl₃): δ = 2.47 (s, 6H), 3.28 (s, 6H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.79 (s, 2H), 8.26 (d, *J* = 8.7 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 49.1, 103.0, 123.6, 133.7, 141.0, 147.7, 163.2. MS (ESI) *m/z* = 248.2 [M-H]⁺.



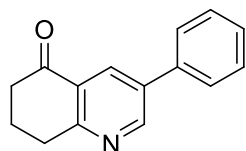
2-(1-Indolyl)-1,3-bis(dimethylamino)trimethinium hexafluorophosphate (1g)

Brown solid; mp: 189.5-191.2 °C, [lit.⁴ 196-198 °C], ¹H NMR (400 MHz, CDCl₃): δ = 2.48 (s, 6H), 3.29 (s, 6H), 7.17 (d, *J* = 4.0 Hz, 1H), 7.21 (t, *J* = 8 Hz, 1H), 7.28 (d, *J* = 8 Hz, 1H), 7.46-7.40 (m, 2H), 7.75 (s, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 40.0, 49.2, 94.0, 116.5, 119.9, 125.9, 126.5, 128.8, 130.9, 132.3, 165.9. MS (ESI) *m/z* = 241.2 [M-H]⁺.



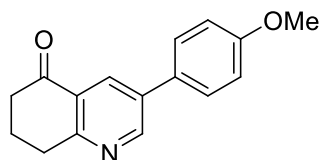
1,1,5,5-Tetramethyl-3-(2-pyridyl)-1,5-diazapentadienium hexafluorophosphate (1h)

Light yellow solid; mp: 177.7-180.9 °C, ¹H NMR (400 MHz, CDCl₃): δ = 2.43 (s, 6H), 3.34 (s, 6H), 7.37-7.34 (m, 1H), 7.46 (d, *J* = 8 Hz, 1H), 7.65 (s, 2H), 7.78 (dt, *J* = 4, 8 Hz, 1H), 8.68 (d, *J* = 4 Hz, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 40.0, 49.1, 105.9, 123.9, 128.5, 137.0, 149.6, 152.2, 163.4. MS (ESI) *m/z* = 203.1 [M-H]⁺.



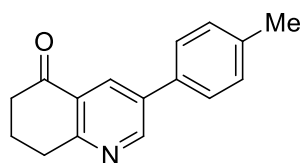
3-Phenyl-7,8-dihydroquinolin-5(6H)-one (4a)

Yellow solid; mp: 79.6-81.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.20-2.27 (m, 2H), 2.73 (t, *J* = 8 Hz, 2H), 3.20 (t, *J* = 8 Hz, 2H), 7.38-7.42 (m, 1H), 7.47 (t, *J* = 8Hz, 2H), 7.60 (d, *J* = 8Hz, 2H), 8.46 (s, 1H), 8.90 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.9, 32.2, 38.6, 126.8, 127.6, 128.1, 128.9, 132.6, 135.1, 136.5, 151.5, 161.9, 197.6. MS(ESI): *m/z* = 224.2 [M+H]⁺. HRMS- ESI: calcd for C₁₅H₁₄NO [M+H]⁺: 224.1070; found: 224.1075.



3-(4-Methoxyphenyl)-7,8-dihydroquinolin-5(6H)-one (4b)

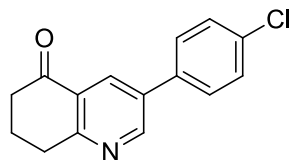
Yellow solid; mp: 124.3-125.7 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.20-2.26 (m, 2H), 2.73 (t, *J* = 8 Hz, 2H), 3.19 (t, *J* = 8 Hz, 2H), 3.86 (s, 3H), 7.01 (d, *J* = 8 Hz, 2H), 7.55 (d, *J* = 8 Hz, 2H), 8.41 (s, 1H), 8.87 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 22.0, 32.3, 38.7, 55.4, 114.5, 127.6, 128.0, 129.0, 132.1, 134.8, 151.2, 159.7, 161.3, 197.9. MS (ESI): *m/z* = 254.1 [M+H]⁺. HRMS-ESI: calcd for C₁₆H₁₆NO₂ [M+H]⁺: 254.1182; found: 254.1176.



3-p-Tolyl-7,8-dihydroquinolin-5(6H)-one (4c)

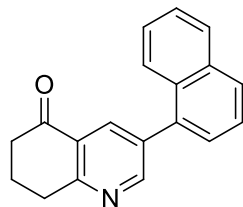
Yellow solid; mp: 111.8-112.6 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.20-2.26 (m, 2H), 2.40 (s, 3H), 2.72 (t, *J* = 8.0 Hz, 2H), 3.19 (t, *J* = 8 Hz), 7.28 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 8.43 (s, 1H), 8.88 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 21.9, 32.2, 38.6, 126.5, 127.5,

129.6, 132.2, 133.5, 134.9, 138.0, 151.3, 161.5, 197.6. MS (ESI): $m/z = 238.1$ $[M+H]^+$. HRMS-ESI: calcd for $C_{16}H_{16}NO$ $[M+H]^+$: 238.1226; found: 238.1232.



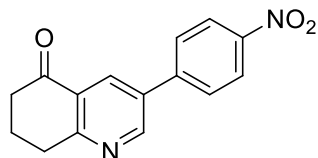
3-(4-Chlorophenyl)-7,8-dihydroquinolin-5(6H)-one (4d)

Green solid; mp: 127.1-127.7 °C. 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.21$ -2.27 (m, 2H), 2.74 (t, $J = 8.0$ Hz, 2H), 3.20 (t, $J = 8.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 8.42 (s, 1H), 8.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.9$, 32.3, 38.6, 127.7, 128.0, 129.2, 132.5, 134.0, 134.5, 135.0, 151.2, 162.3, 197.5. MS (ESI): $m/z = 258.1$ $[M+H]^+$, HRMS-ESI: calcd for $C_{15}H_{13}ClNO$ $[M+H]^+$: 258.0680; found: 258.0675.



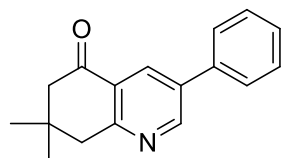
3-(Naphthalen-1-yl)-7,8-dihydroquinolin-5(6H)-one (4e)

Yellow solid; mp: 111.5-112.4 °C. 1H NMR (400 MHz, $CDCl_3$): $\delta = 2.26$ -2.32 (m, 2H), 2.77 (t, $J = 8.0$ Hz, 2H), 3.27 (t, $J = 8.0$ Hz, 2H), 7.39-7.55 (m, 4H), 7.76 (d, $J = 12.0$ Hz, 1H), 7.89-7.92 (m, 2H), 8.42 (s, 1H), 8.80 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 22.0$, 32.4, 38.7, 124.8, 125.2, 126.0, 126.6, 127.3, 127.5, 128.4, 128.6, 131.1, 133.6, 134.9, 135.1, 135.7, 154.0, 162.1, 197.6. MS (ESI): $m/z = 274.2$ $[M+H]^+$, HRMS-ESI: calcd for $C_{19}H_{16}NO$ $[M+H]^+$: 274.1226; found: 274.1216.



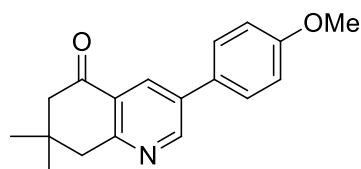
3-(4-Nitrophenyl)-7,8-dihydroquinolin-5(6H)-one (4f)

Yellow solid; mp: 176.9-177.6 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.24-2.30 (m, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 3.24 (t, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 12.0 Hz, 2H), 8.35 (d, *J* = 8.0 Hz, 2H), 8.51 (s, 1H), 8.95 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.8, 32.4, 38.6, 124.3, 127.7, 127.8, 133.0, 133.2, 143.0, 147.6, 151.4, 163.6, 197.3. MS (ESI): *m/z* = 269.1 [M+H]⁺, HRMS-ESI: calcd for C₁₅H₁₃N₂O₃ [M+H]⁺: 269.0921; found: 269.0925.



7,7-Dimethyl-3-phenyl-7,8-dihydroquinolin-5(6H)-one (4g)

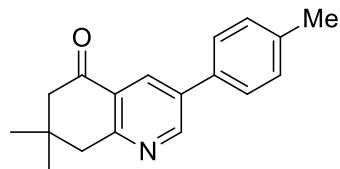
White solid; mp: 119.3-120.1 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.15 (s, 6H), 2.59 (s, 2H), 3.09 (s, 2H), 7.38-7.43 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 8.45 (s, 1H), 8.93 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 28.4, 33.2, 46.2, 52.2, 126.8, 126.9, 128.2, 129.0, 132.3, 135.1, 136.6, 151.9, 160.6, 197.8. MS (ESI): *m/z* = 252.3 [M+H]⁺. HRMS-ESI: calcd for C₁₇H₁₈NO [M+H]⁺: 252.1383; found: 252.1390.



3-(4-Methoxyphenyl)-7,7-dimethyl-7,8-dihydroquinolin-5(6H)-one (4h)

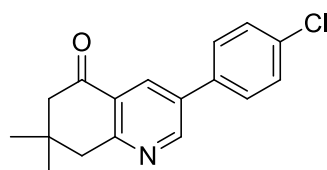
Yellow solid; mp: 95.6-96.6 °C. ¹H NMR (400 MHz, CDCl₃): δ = 1.14 (s, 6H), 2.58 (s, 2H), 3.07 (s, 2H), 3.85 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 8.39 (s, 1H), 8.88 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 28.4, 33.1, 46.1, 52.2, 55.4, 114.5, 126.7, 128.0, 129.0, 131.7,

134.8, 151.5, 159.7, 159.9, 197.9. MS (ESI): $m/z = 282.2$ $[M+H]^+$. HRMS-ESI: calcd for HRMS-ESI: calcd for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1489; found: 282.1497.



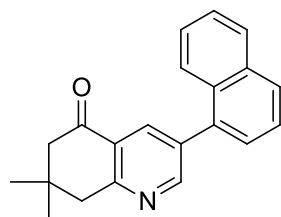
7,7-Dimethyl-3-p-tolyl-7,8-dihydroquinolin-5(6H)-one (4i)

Yellow solid; mp: 103.0-104.2 °C. 1H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (s, 6H), 2.41 (s, 3H), 2.59 (s, 2H), 3.08 (s, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 8.42 (s, 1H), 8.91 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.3, 28.4, 33.1, 46.1, 52.2, 126.7, 129.7, 132.0, 133.6, 135.0, 138.2, 151.8, 160.2, 197.9$. MS (ESI): $m/z = 266.0$ $[M+H]^+$. HRMS-ESI: calcd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found: 266.1547.



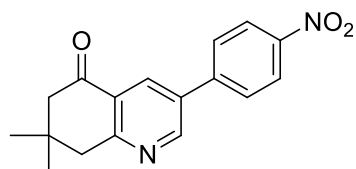
3-(4-Chlorophenyl)-7,7-dimethyl-7,8-dihydroquinolin-5(6H)-one (4j)

Yellow solid; mp: 146.3-147.0°C. 1H NMR (400 MHz, $CDCl_3$): $\delta = 1.15$ (s, 6H), 2.59 (s, 2H), 3.09 (s, 2H), 7.46 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 8.41 (s, 1H), 8.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 28.4, 33.1, 46.2, 52.1, 126.8, 128.1, 129.3, 132.2, 134.0, 134.5, 135.1, 151.7, 161.0, 197.7$. MS (ESI): $m/z = 286.1$ $[M+H]^+$. HRMS-ESI: calcd for $C_{17}H_{17}ClNO$ $[M+H]^+$: 286.0993; found: 286.0999.



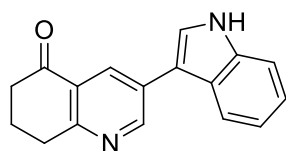
7,7-Dimethyl-3-(naphthalen-1-yl)-7,8-dihydroquinolin-5(6H)-one (4k)

Yellow solid; mp: 72.0-72.6°C. ¹H NMR (400 MHz, CDCl₃): δ = 1.20 (s, 6H), 2.62 (s, 2H), 3.15 (s, 2H), 7.40-7.56 (m, 4H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.90-7.93 (m, 2H), 8.39 (s, 1H), 8.81 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): 28.5, 33.2, 46.3, 52.2, 124.8, 125.2, 126.0, 126.5, 126.6, 127.4, 128.4, 128.7, 131.1, 133.6, 134.8, 135.1, 135.3, 154.4, 160.7, 197.7. MS (ESI): *m/z* = 302.2 [M+H]⁺. HRMS-ESI: calcd for C₂₁H₂₀NO [M+H]⁺: 302.1539; found: 302.1550.



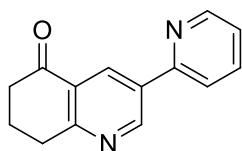
7,7-Dimethyl-3-(4-nitrophenyl)-7,8-dihydroquinolin-5(6H)-one (4l)

Yellow solid; mp: 170.4-171.3°C. ¹H NMR (400 MHz, CDCl₃): δ = 1.16 (s, 6H) 2.62 (s, 2H), 3.13 (s, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.36 (d, *J* = 12 Hz), 8.50 (s, 1H), 8.96 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 28.4, 46.2, 33.1, 52.1, 124.3, 126.9, 127.7, 132.7, 132.9, 143.0, 147.6, 151.7, 162.2, 197.3, MS (ESI): *m/z* = 297.1 [M+H]⁺. HRMS-ESI: calcd for C₁₇H₁₇N₂O₃ [M+H]⁺: 297.1234; found: 297.1239.



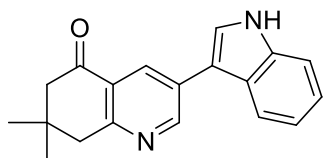
3-(1H-indol-3-yl)-7,8-dihydroquinolin-5(6H)-one (4m)

Yellow solid; mp: 189.0-190.1°C. ¹H NMR (400 MHz, CDCl₃) δ 2.27-2.20 (m, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 3.20 (t, *J* = 8.0 Hz, 2H), 7.18-7.27 (m, 2H), 7.42-7.44 (m, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 8.52 (s, 1H), 9.00 (s, 1H), 9.04 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 22.0, 32.2, 38.7, 111.6, 113.3, 119.1, 120.7, 122.5, 122.7, 125.1, 127.9, 130.4, 132.3, 136.6, 151.6, 160.3, 198.1. MS (ESI): *m/z* = 263.3 [M+H]⁺. HRMS-ESI: calcd for C₁₇H₁₅N₂O [M+H]⁺: 263.1179; found: 263.1179.



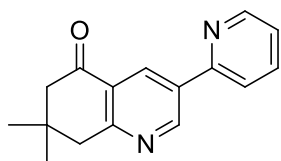
3-(pyridin-2-yl)-7,8-dihydroquinolin-5(6H)-one (4n)

Yellow solid; mp: 91.7-93.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.27-2.21 (m, 2H), 2.74 (t, *J* = 8.0 Hz, 2H), 3.22 (t, *J* = 8.0 Hz, 2H), 7.27-7.30 (m, 1H), 7.75-7.80 (m, 2H), 8.60-8.70 (m, 1H), 8.77 (s, 1H), 9.34 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 21.9, 32.4, 38.6, 120.4, 122.9, 127.6, 132.5, 133.4, 136.8, 149.8, 151.8, 153.7, 163.4, 197.4. MS (ESI): *m/z* = 225.3 [M+H]⁺. HRMS-ESI: calcd for C₁₄H₁₃N₂O [M+H]⁺: 225.1022; found: 225.1018.



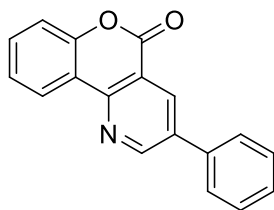
3-(1H-indol-3-yl)-7,7-dimethyl-7,8-dihydroquinolin-5(6H)-one (4o)

Yellow solid; mp: 168.0-168.8°C. ¹H NMR (400 MHz, CDCl₃) δ 1.16 (s, 6H), 2.60 (s, 2H), 3.09 (s, 2H), 7.19-7.28 (m, 2H), 7.43-7.45 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.50 (s, 1H), 8.77 (s, 1H), 9.03 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 28.4, 33.2, 46.3, 52.2, 111.6, 113.5, 119.1, 120.8, 122.5, 122.7, 125.1, 126.9, 130.3, 132.0, 136.6, 151.9, 158.9, 198.2. MS (ESI): *m/z* (%) = 291.3 [M+H]⁺. HRMS-ESI: calcd for C₁₉H₁₉N₂O [M+H]⁺: 291.1492; found: 291.1499.



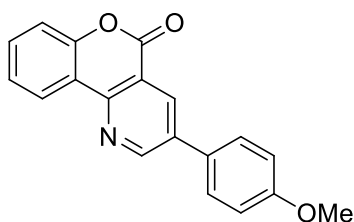
7,7-dimethyl-3-(pyridin-2-yl)-7,8-dihydroquinolin-5(6H)-one (4p)

White solid; mp: 82.0-83.5°C. ¹H NMR (400 MHz, CDCl₃) δ 1.14 (s, 6H), 2.59 (s, 2H), 3.01 (s, 2H), 7.27-7.31 (m, 1H), 7.76-7.81 (m, 2H), 8.71 (d, *J* = 4.0 Hz, 1H), 8.76 (s, 1H), 9.36 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 28.3, 33.0, 46.3, 52.1, 120.4, 122.8, 126.6, 132.1, 133.4, 136.8, 149.8, 152.2, 153.8, 162.1, 197.5. MS (ESI): *m/z* = 253.2 [M+H]⁺. HRMS-ESI: calcd for C₁₆H₁₇N₂O: 253.1335 [M+H]⁺; found: 253.1339.



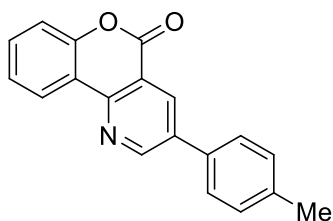
3-Phenyl-5H-chromeno[4,3-b]pyridin-5-one (5a)

White solid; mp: 187.1-187.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 7.39-7.61 (m, 6H), 7.71 (d, *J* = 8.0 Hz, 2H), 8.61 (d, *J* = 8.0 Hz, 1H), 8.79 (s, 1H), 9.25 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 117.1, 119.0, 124.5, 124.8, 126.9, 128.8, 129.2, 131.9, 135.4, 135.8, 136.6, 150.1, 152.2, 154.0, 161.1. MS (ESI): *m/z* = 274.2 [M+H]⁺. HRMS-ESI: calcd for C₁₈H₁₂NO₂ [M+H]⁺: 274.0863; found: 274.0852.



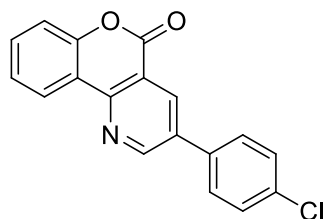
3-(4-Methoxyphenyl)-5H-chromeno[4,3-b]pyridin-5-one (5b)

White solid; mp: 229.9-230.8 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.88 (s, 3H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 8.60 (d, *J* = 8 Hz, 1H), 8.74 (s, 1H), 9.22 (s, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 55.5, 114.8, 117.1, 119.1, 124.4, 124.9, 128.1, 128.2, 131.8, 134.7, 136.4, 149.5, 152.2, 153.6, 160.2, 161.2. MS (ESI): *m/z* = 304.1 [M+H]⁺. HRMS-ESI: calcd for C₁₉H₁₄NO₃ [M+H]⁺: 304.0968; found: 304.0973.



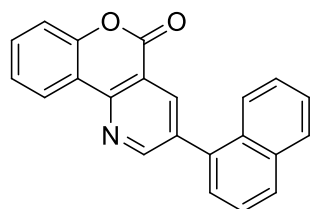
3-*p*-Tolyl-5H-chromeno[4,3-b]pyridin-5-one (5c)

White solid; mp: 193.7-194.4 °C. ^1H NMR (400 MHz, CDCl_3): δ = 2.44 (s, 3H), 7.35 (d, J = 8.0 Hz, 1H), 7.39-7.44 (m, 2H), 7.56-7.61 (m, 3H), 8.60 (d, J = 8 Hz, 1H), 8.77 (s, 1H), 9.24 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 21.3, 117.1, 119.2, 124.5, 124.8, 126.8, 130.0, 131.8, 133.0, 135.0, 136.6, 138.9, 149.9, 152.2, 153.9, 161.1. MS (ESI): m/z = 288.2 $[\text{M}+\text{H}]^+$. HRMS- ESI: calcd for $\text{C}_{19}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 288.1019; found: 288.1013.



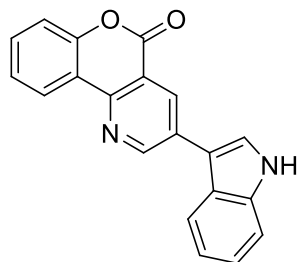
3-(4-Chlorophenyl)-5H-chromeno[4,3-b]pyridin-5-one (5d)

White solid; mp: 259.3-260.3°C. ^1H NMR (400 MHz, CDCl_3): δ = 7.40-7.45 (m, 2H), 7.52 (d, J = 8.0 Hz, 2H), 7.58-7.64 (m, 3H), 8.64 (d, J = 8.0 Hz, 1H), 8.78 (s, 1H), 9.22 (s, 1H). MS (ESI): m/z = 308.1 $[\text{M}+\text{H}]^+$. HRMS-ESI: calcd for $\text{C}_{18}\text{H}_{11}\text{ClNO}_2$ $[\text{M}+\text{H}]^+$: 308.0473; found: 308.0459.



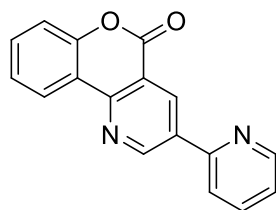
3-(Naphthalen-1-yl)-5H-chromeno[4,3-b]pyridin-5-one (5e)

White solid; mp: 220.8-221.3 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.42-7.63 (m, 7H), 7.81 (d, J = 8.0 Hz), 7.94-7.97 (m, 2H), 8.68 (d, J = 8 Hz, 1H), 8.76 (s, 1H), 9.16 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 116.9, 117.1, 119.1, 124.6, 124.9, 125.3, 126.2, 126.9, 127.7, 128.5, 129.2, 131.0, 132.1, 133.7, 136.7, 138.5, 150.4, 152.4, 156.5, 161.0. MS (ESI): m/z = 324.2 $[\text{M}+\text{H}]^+$. HRMS-ESI: calcd for $\text{C}_{22}\text{H}_{14}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 324.1019; found: 324.1028.



3-(1*H*-indol-3-yl)-5*H*-chromeno[4,3-*b*]pyridin-5-one (5f)

Yellow solid; mp: 248.7-249.6°C. ¹H NMR (400 MHz, *d*₆-DMSO) δ 7.17-7.21 (m, 2H), 7.40-7.43 (m, 2H), 7.49-7.51 (m, 1H), 7.57-7.62 (m, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 8.10 (s, 1H), 8.44 (dd, *J* = 8.3, 1.7 Hz, 1H), 8.67 (s, 1H), 9.43 (s, 1H), 11.73 (s, 1H). ¹³C NMR (100 MHz, *d*₆-DMSO) δ 110.6, 112.2, 116.7, 117.0, 118.4, 118.9, 120.3, 121.9, 123.4, 124.3, 124.6, 125.4, 131.3, 131.9, 132.4, 136.8, 146.9, 151.4, 153.3, 160.3. MS (ESI): *m/z* (%) = 311.5 [M-H]⁻. HRMS-ESI: *m/z* [M+Na]⁺ calcd for C₂₀H₁₂N₂NaO₂: 335.0791; found: 335.0791.



3-(pyridin-2-yl)-5*H*-chromeno[4,3-*b*]pyridin-5-one (5g)

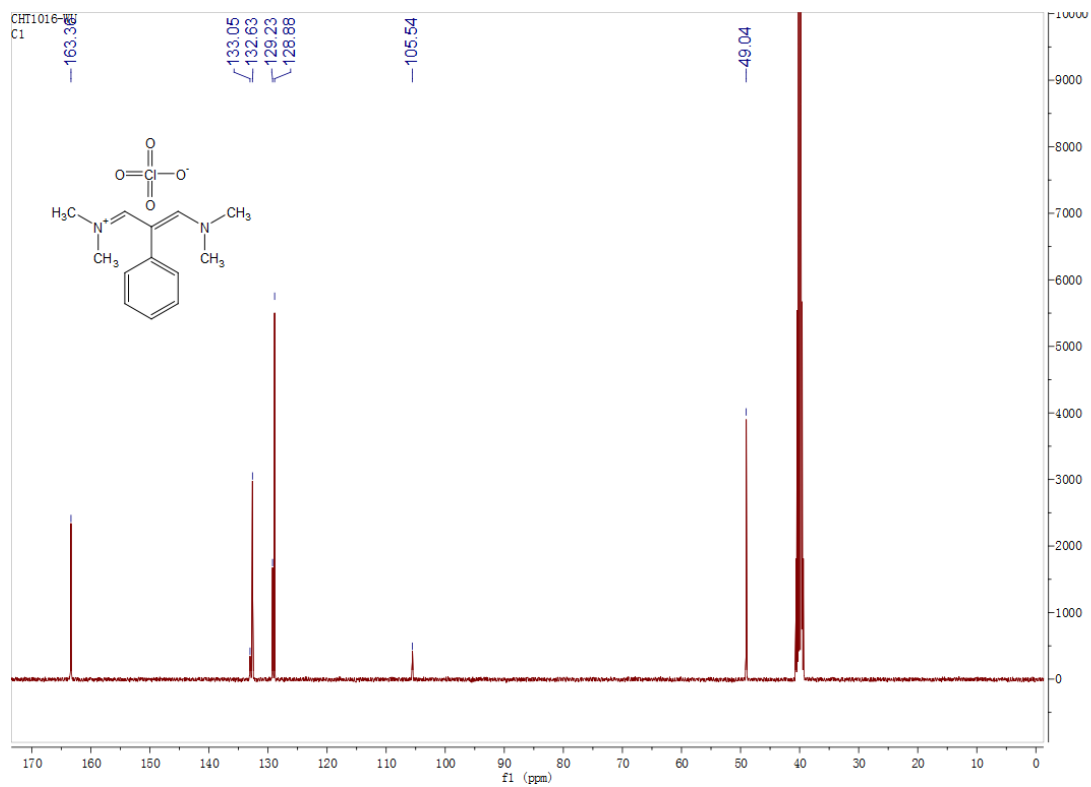
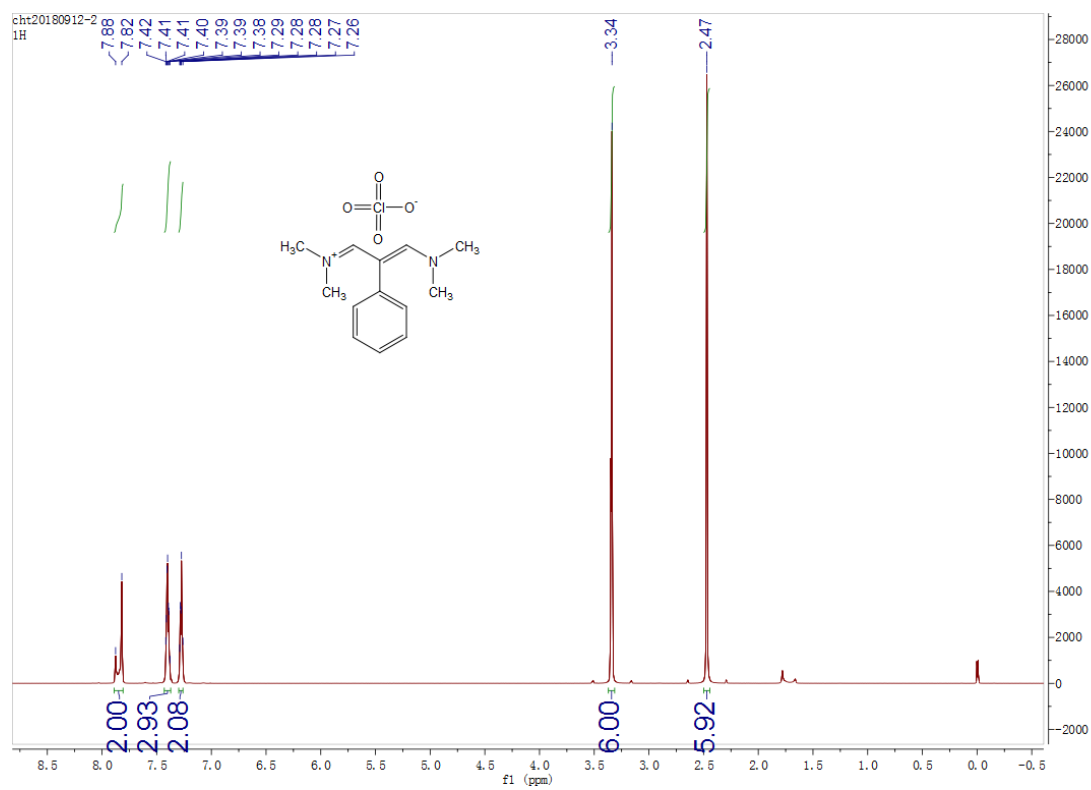
White solid; mp: 189.6-191.6°C. ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.41 (m, 3H), 7.55-7.59 (m, 1H), 7.81-7.85 (m, 2H), 8.58 (t, *J* = 8.0 Hz, 1H), 8.74 (t, *J* = 4.0 Hz, 1H), 9.10 (s, 1H), 9.67 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 116.9, 117.0, 119.0, 120.5, 123.3, 124.8, 132.1, 134.6, 135.4, 137.0, 150.0, 151.3, 152.4, 152.9, 154.2, 160.9. MS (ESI): *m/z* = 275.3 [M+H]⁺. HRMS-ESI: calcd for C₁₇H₁₀N₂NaO₂ [M+Na]⁺: 297.0634; found: 297.0635.

References

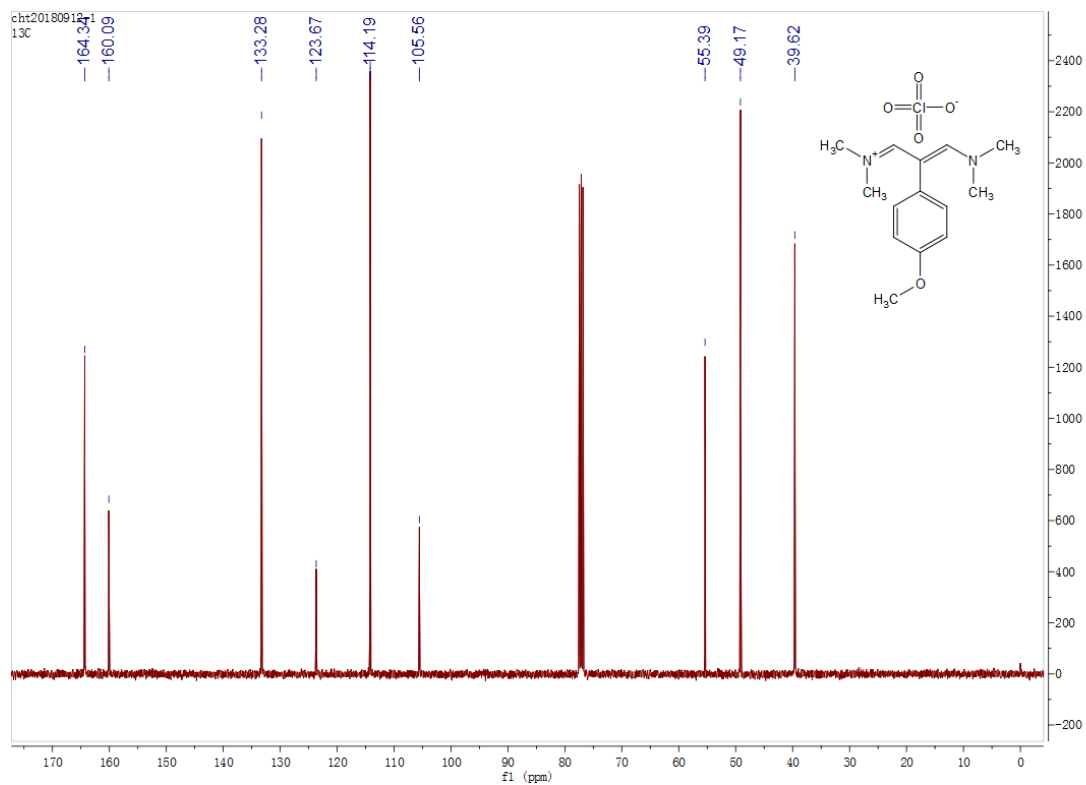
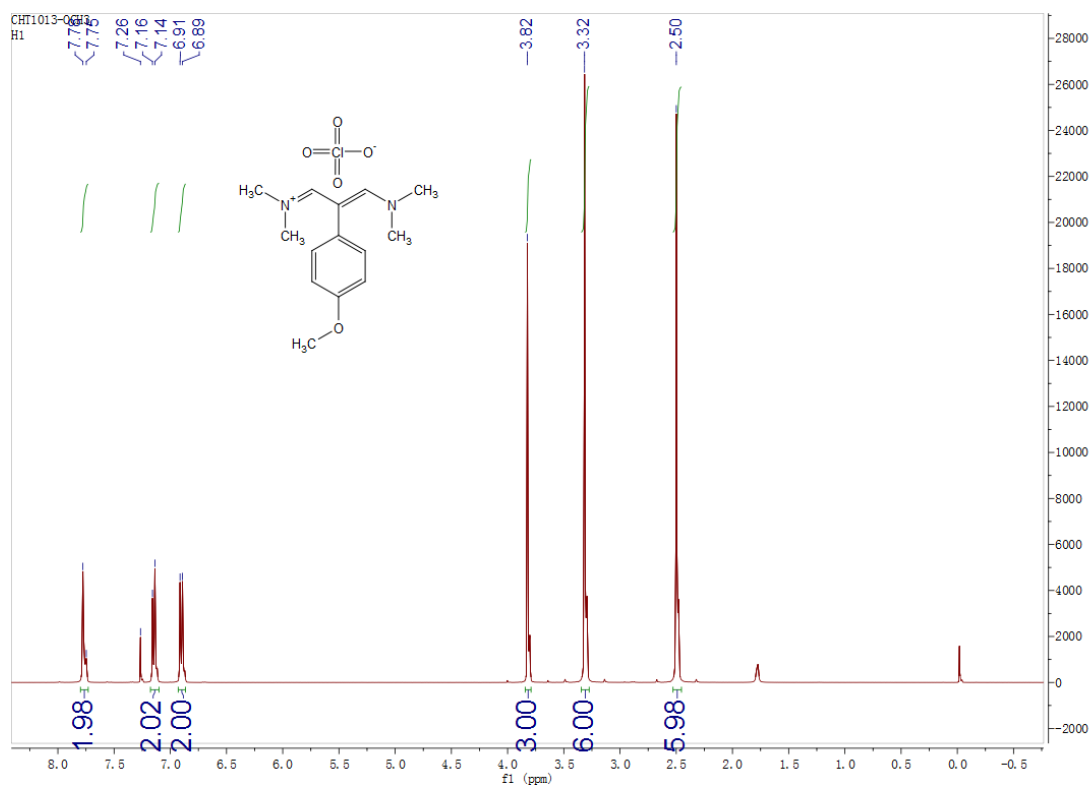
1. S. Selvi, P. T. Perumal, *Tetrahedron Lett.*, **1997**, 38: 6263.
2. H. Zäschke, S. Arndt, V. Wagner, H. Schubert, *Zeitschrift fuer Chemie*, **1977**, 8: 193.
3. D. Lloyd, K. S. Tucker, D. R. Marshall, Diazepines. Part 25. *J. Chem. Soc.* **1998**, 3: 726.
4. J.T. Gupton, N. Telang, D.F. Gazzo, et.al., *Tetrahedrom* **2013**, 69: 5829

Copies of ^1H and ^{13}C NMR Spectra

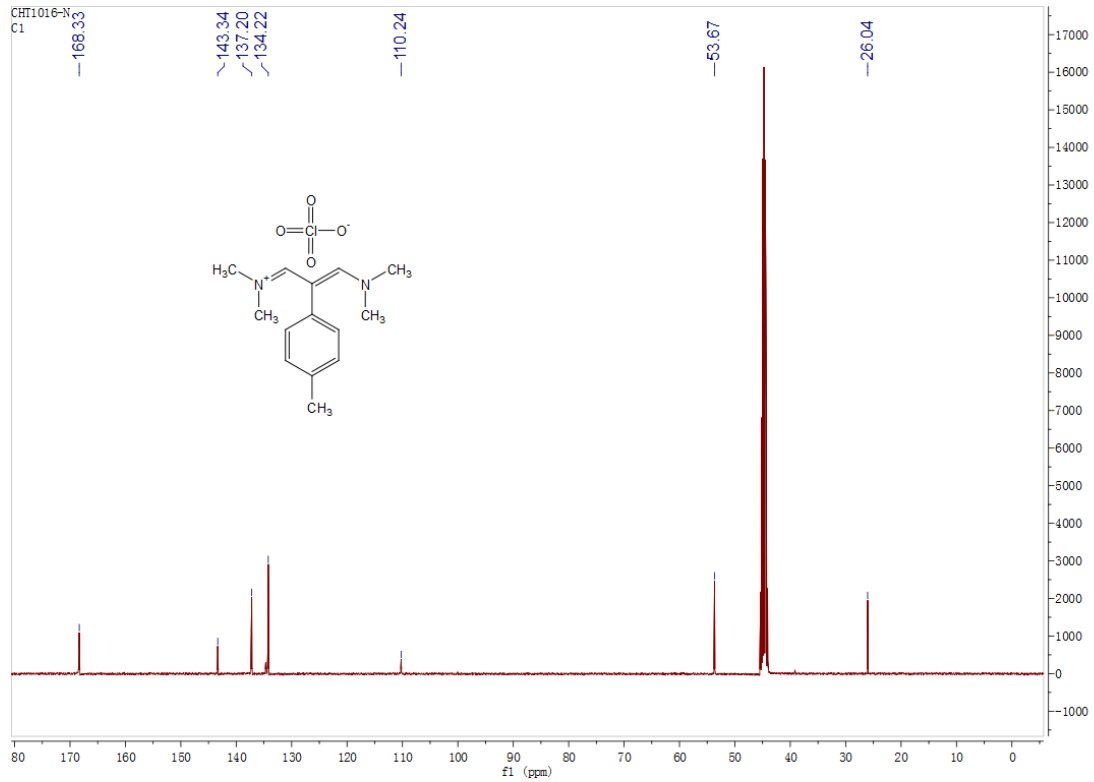
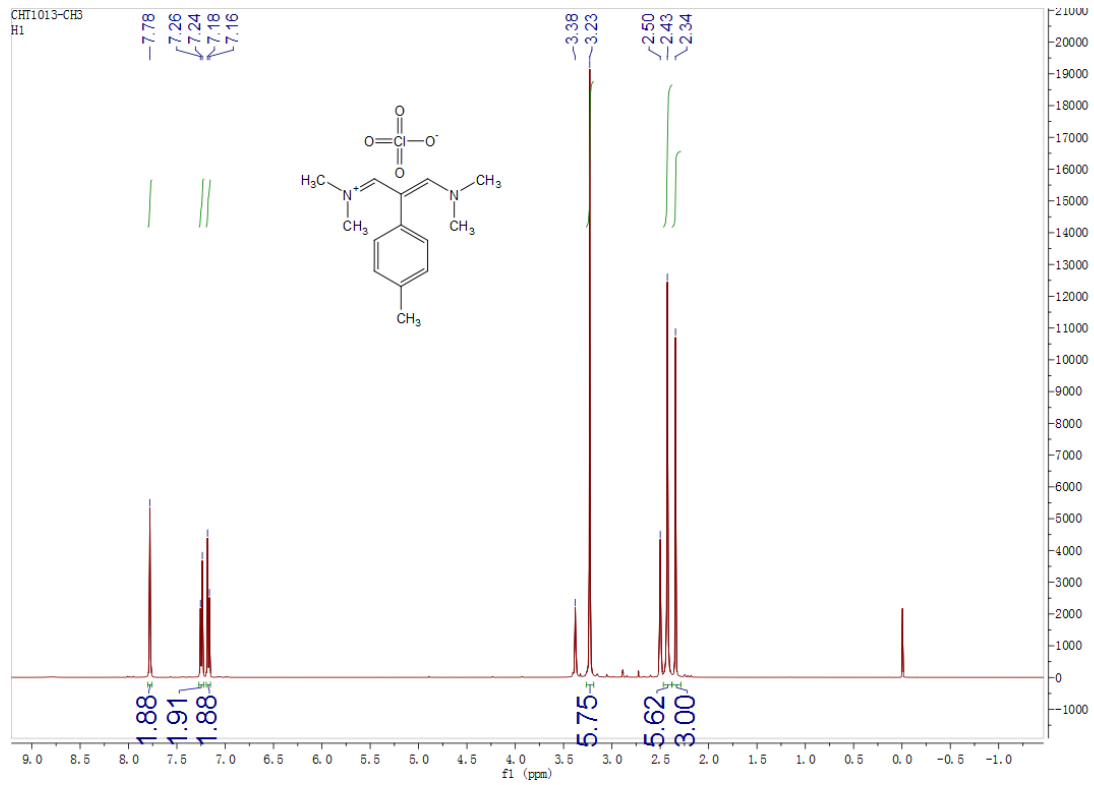
2-Phenyl-1,3-bis(dimethylamino)trimethinium perchlorate (1a)



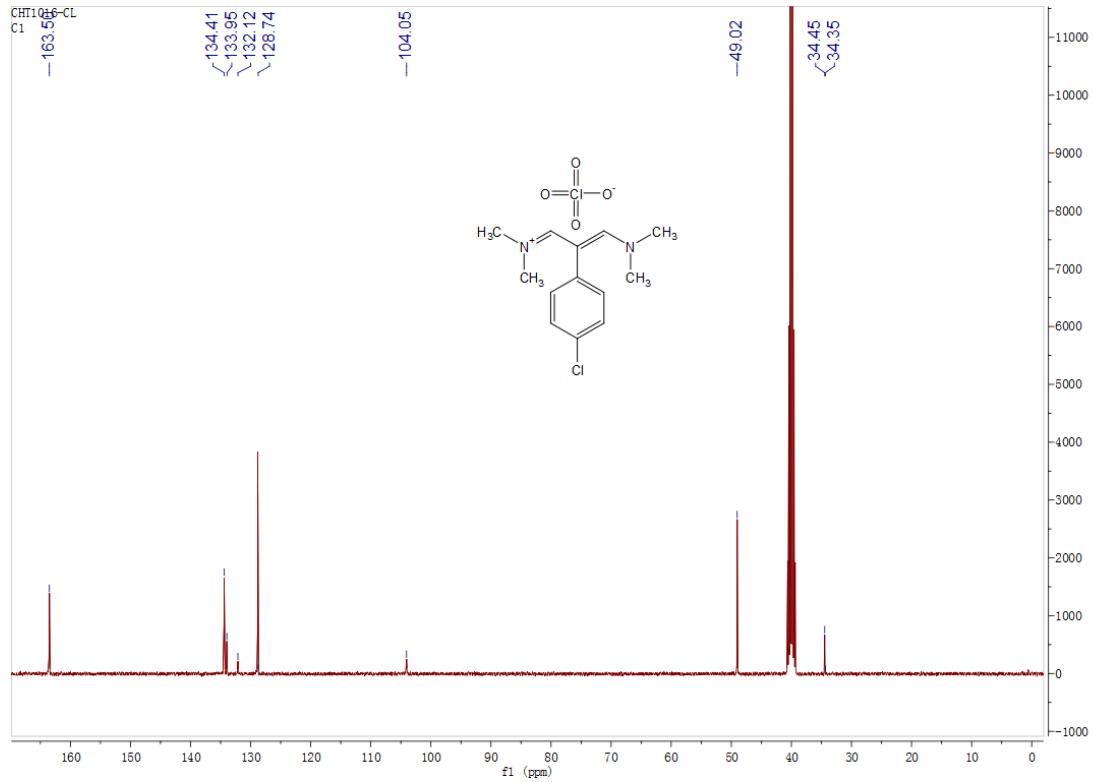
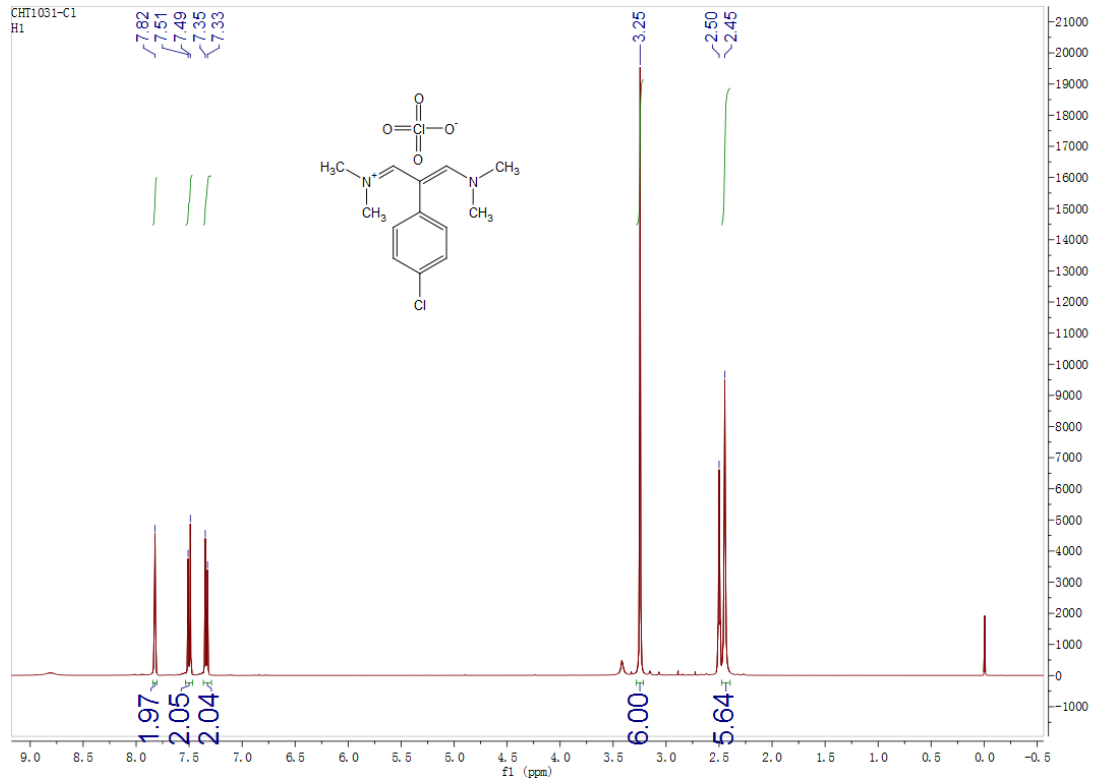
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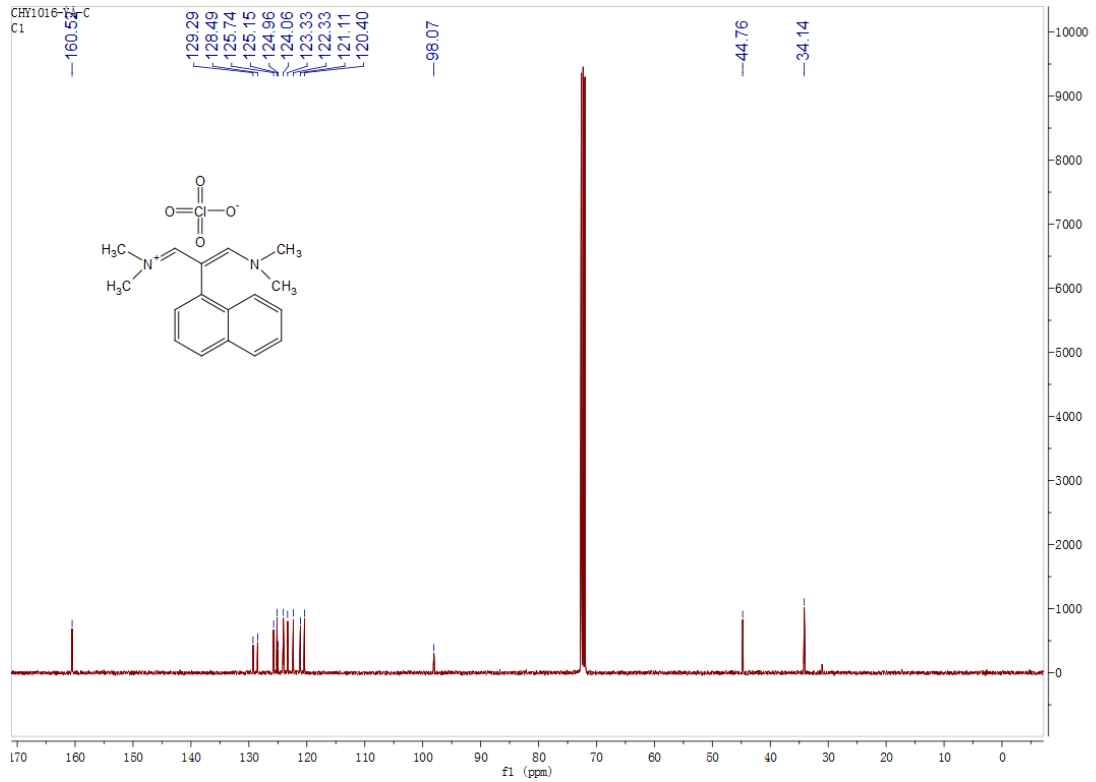
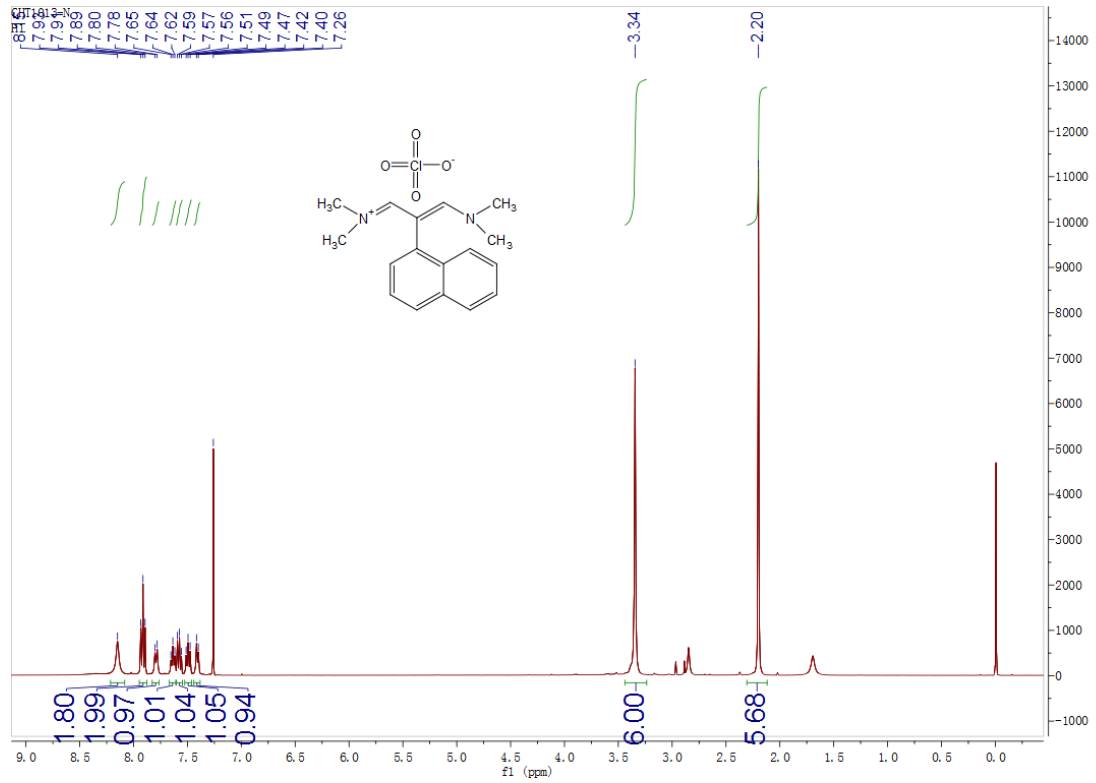
2-(4-Methylphenyl)-1,3-bis(dimethylamino)trimethinium perchlorate (1c)



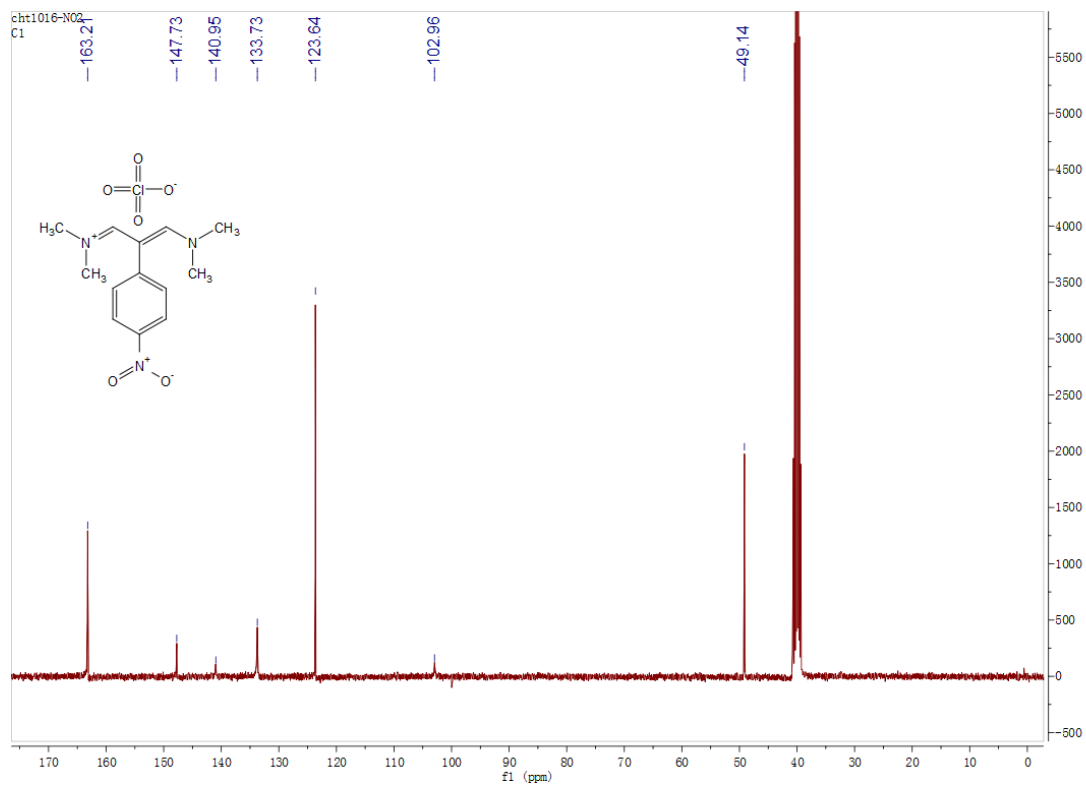
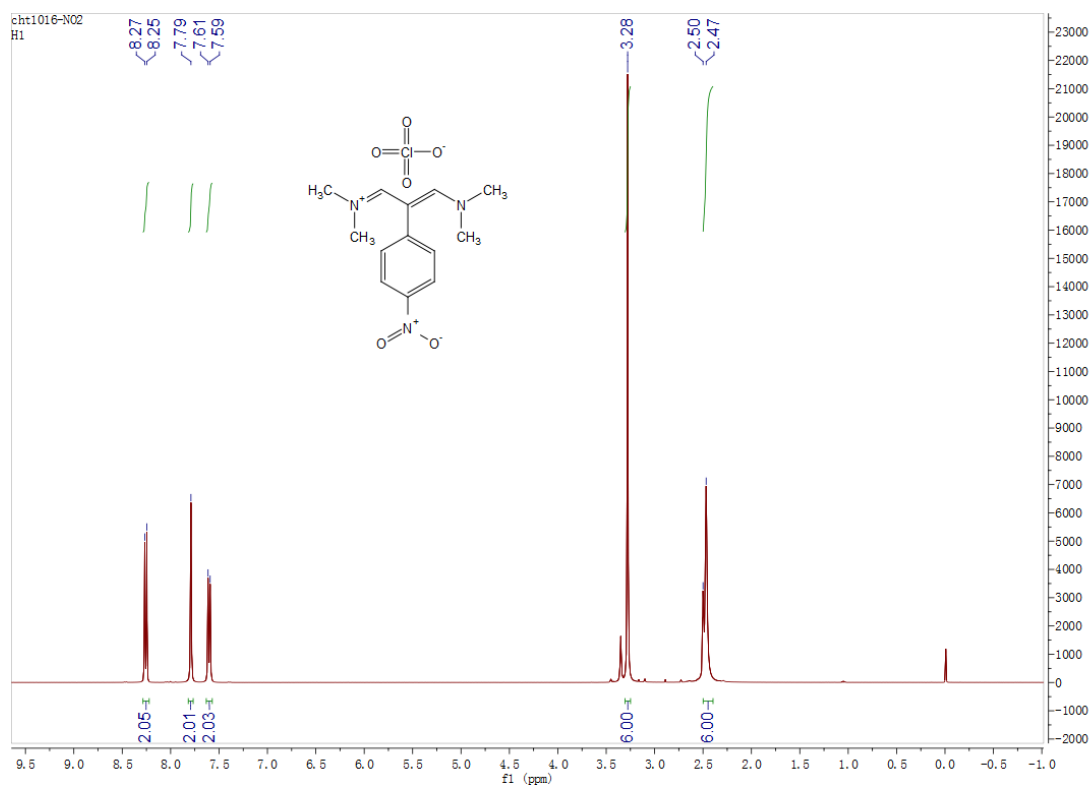
2-(4-Chlorophenyl)-1,3-bis(dimethylamino)trimethiniumium perchlorate (1d)



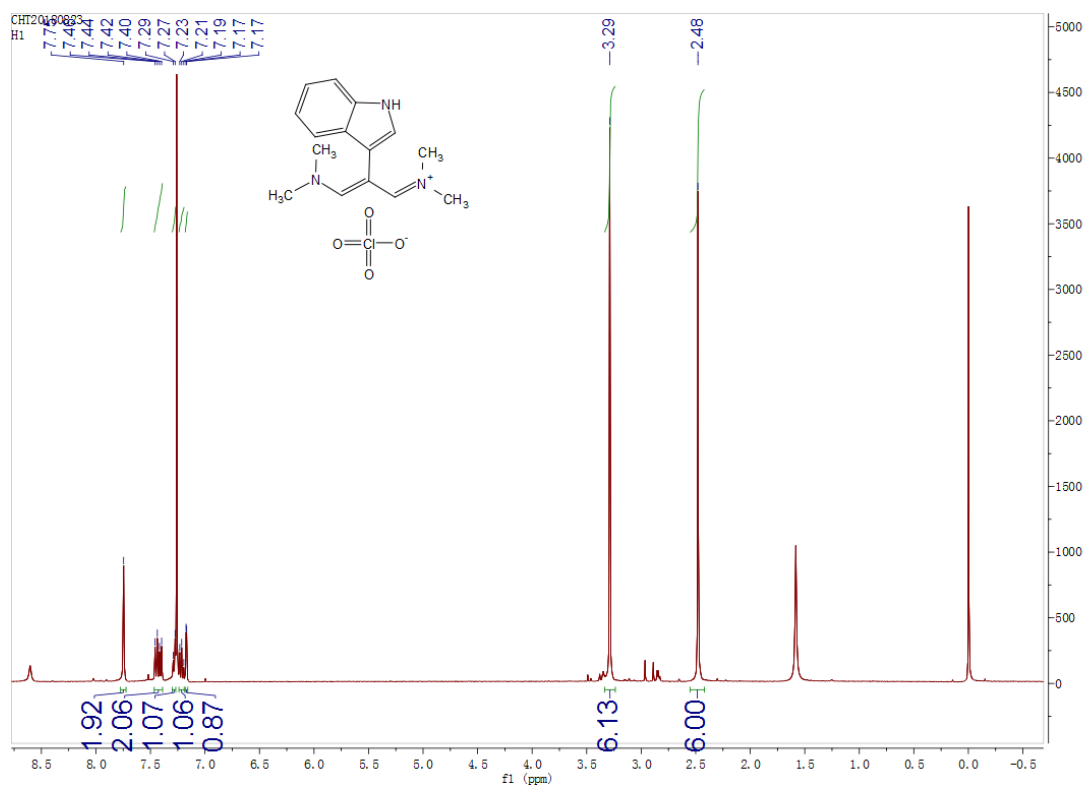
2- β -naphthyl-1,3-bis(dimethylamino)trimethinium perchlorate (1e)



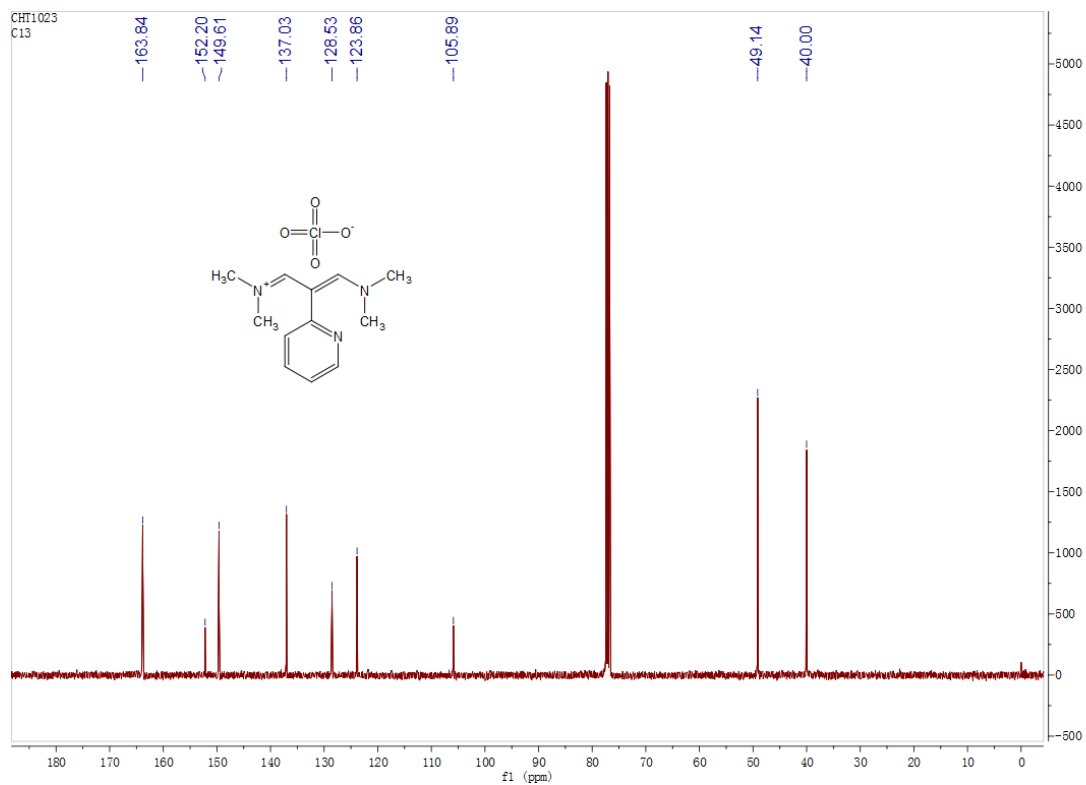
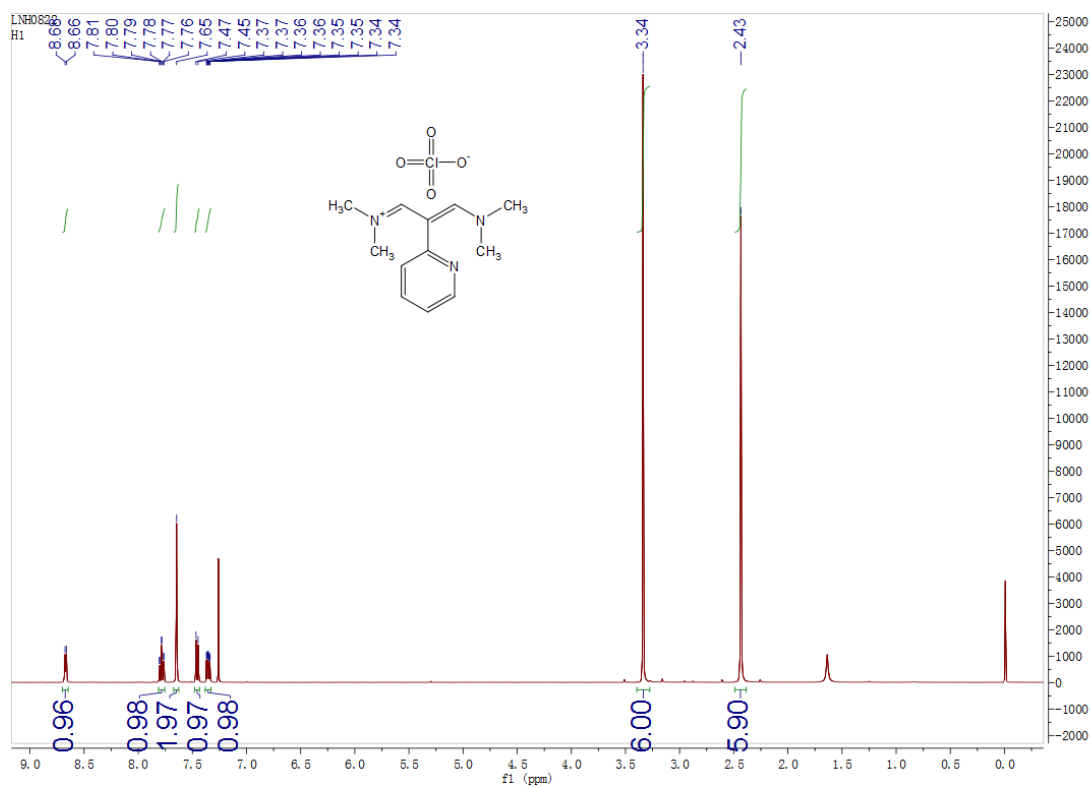
2-(4-Nitrophenyl)-1,3-bis(dimethylamino)trimethinium perchlorate (1f)



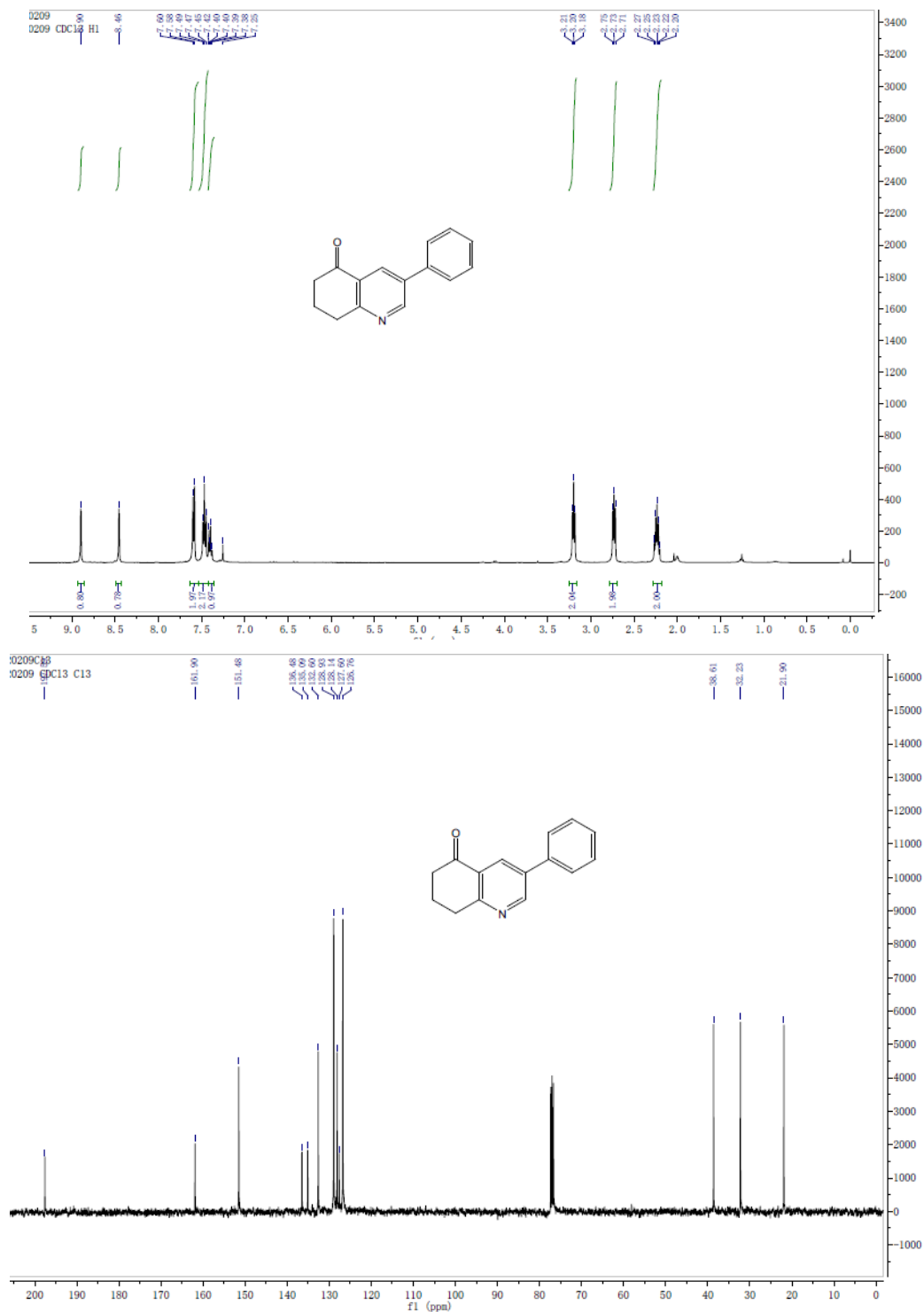
2-(1-Indolyl)-1,3-bis(dimethylamino)trimethinium hexafluorophosphate (1g)



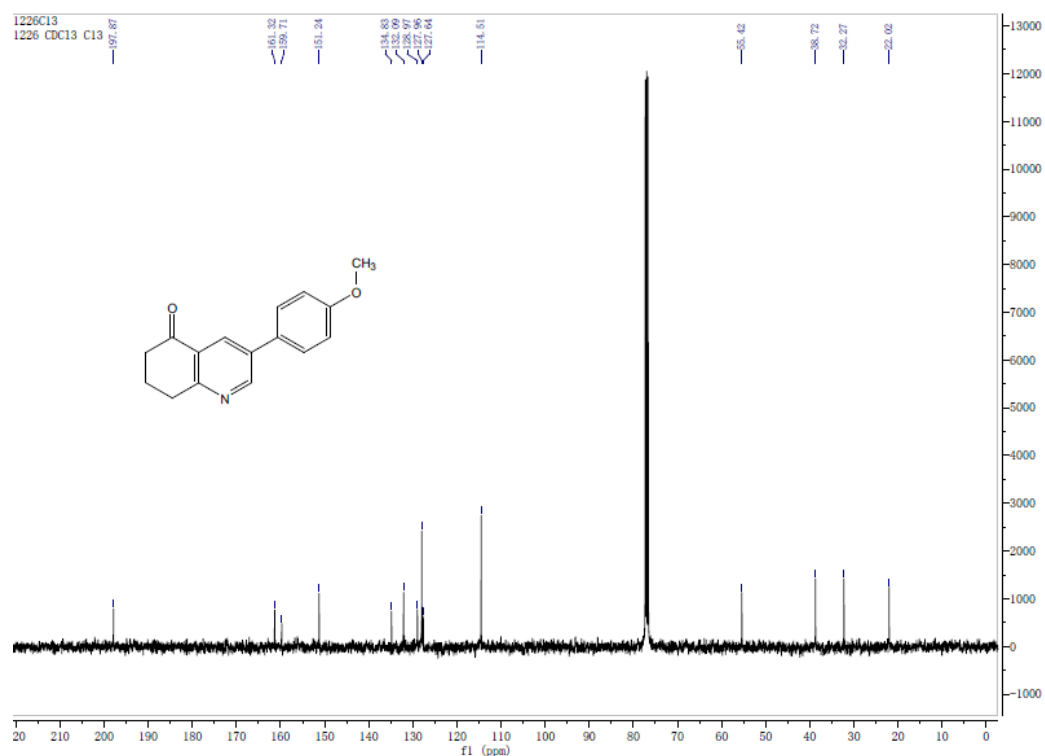
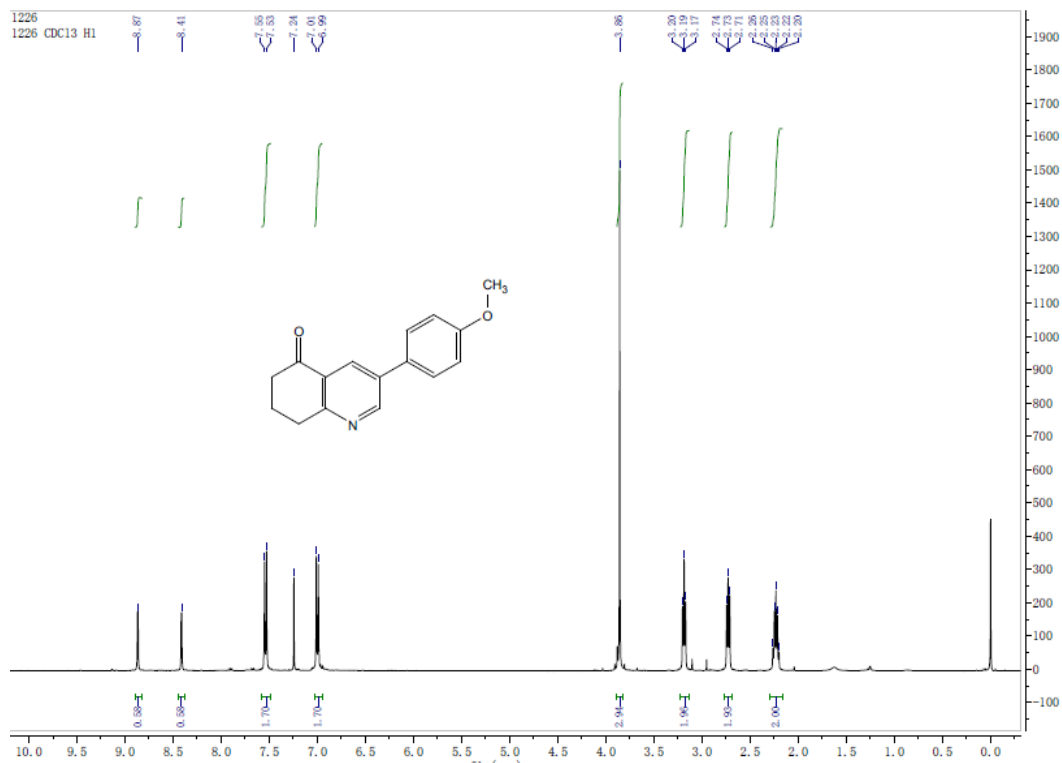
1,1,5,5-Tetramethyl-3-(2-pyridyl)-1,5-diazapentadienium hexafluorophosphate (1h)



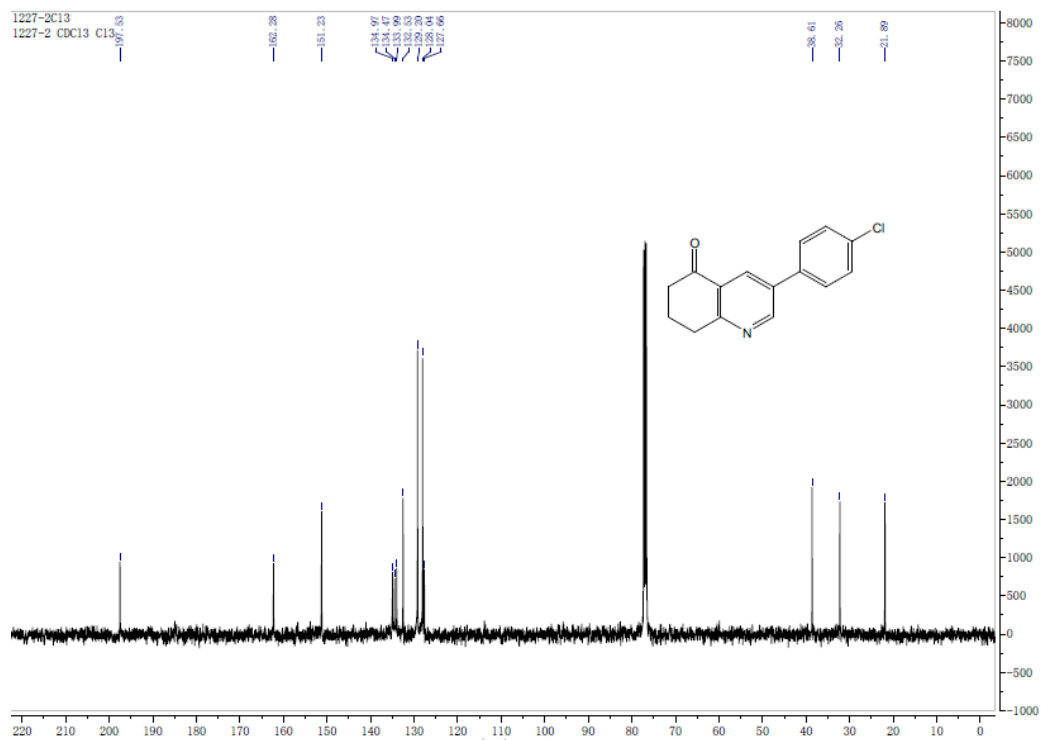
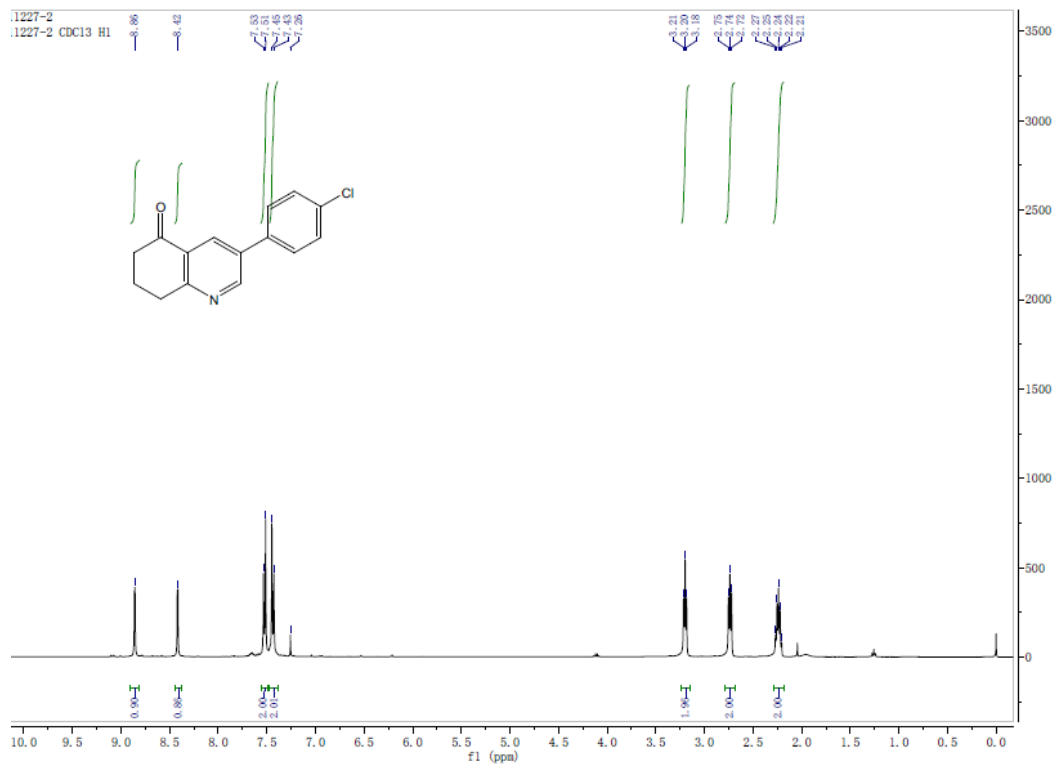
3-Phenyl-7,8-dihydroquinolin-5(6H)-one (4a)



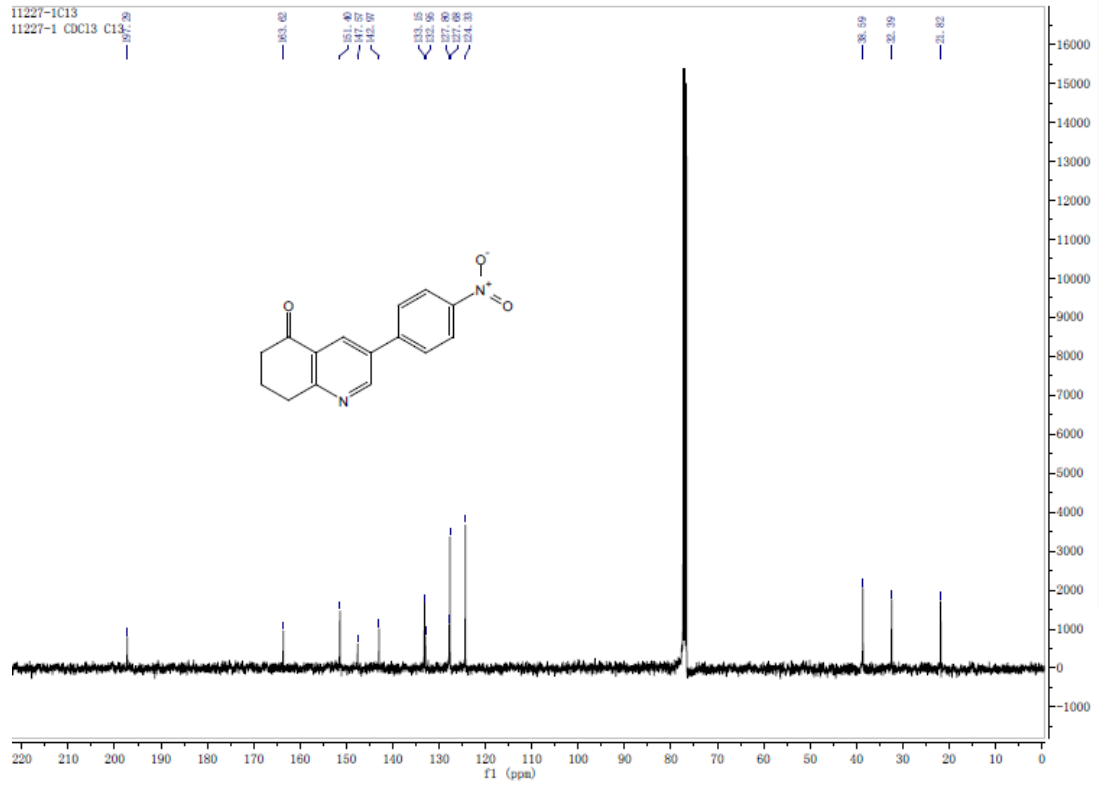
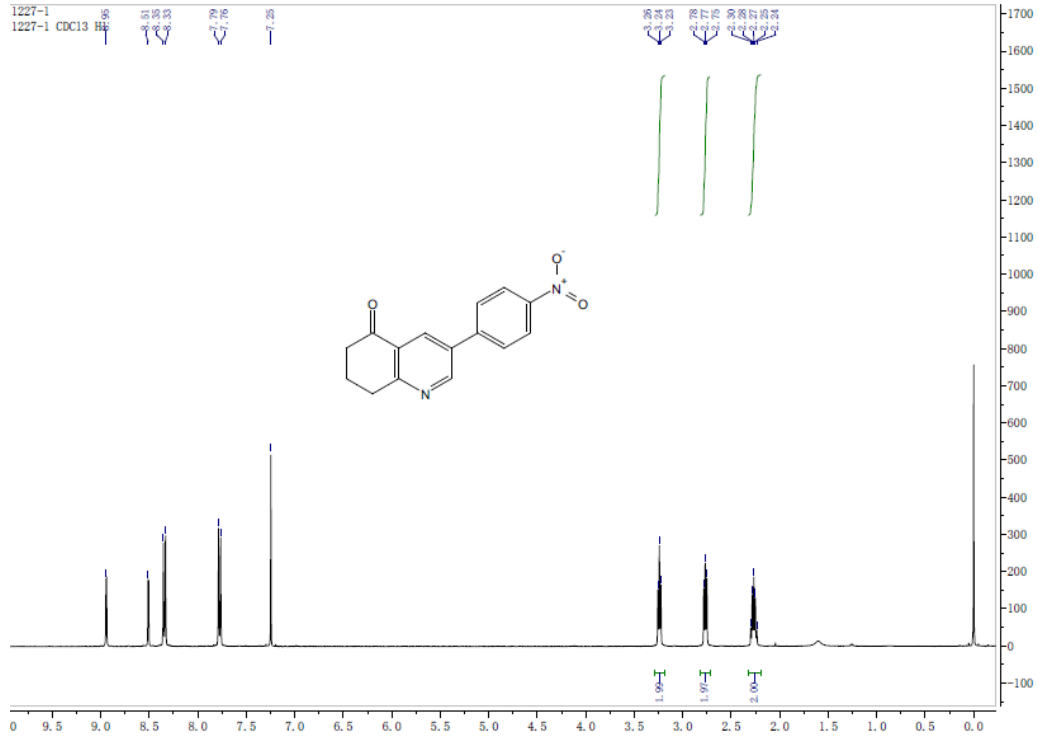
3-(4-Methoxyphenyl)-7,8-dihydroquinolin-5(6H)-one (4b)



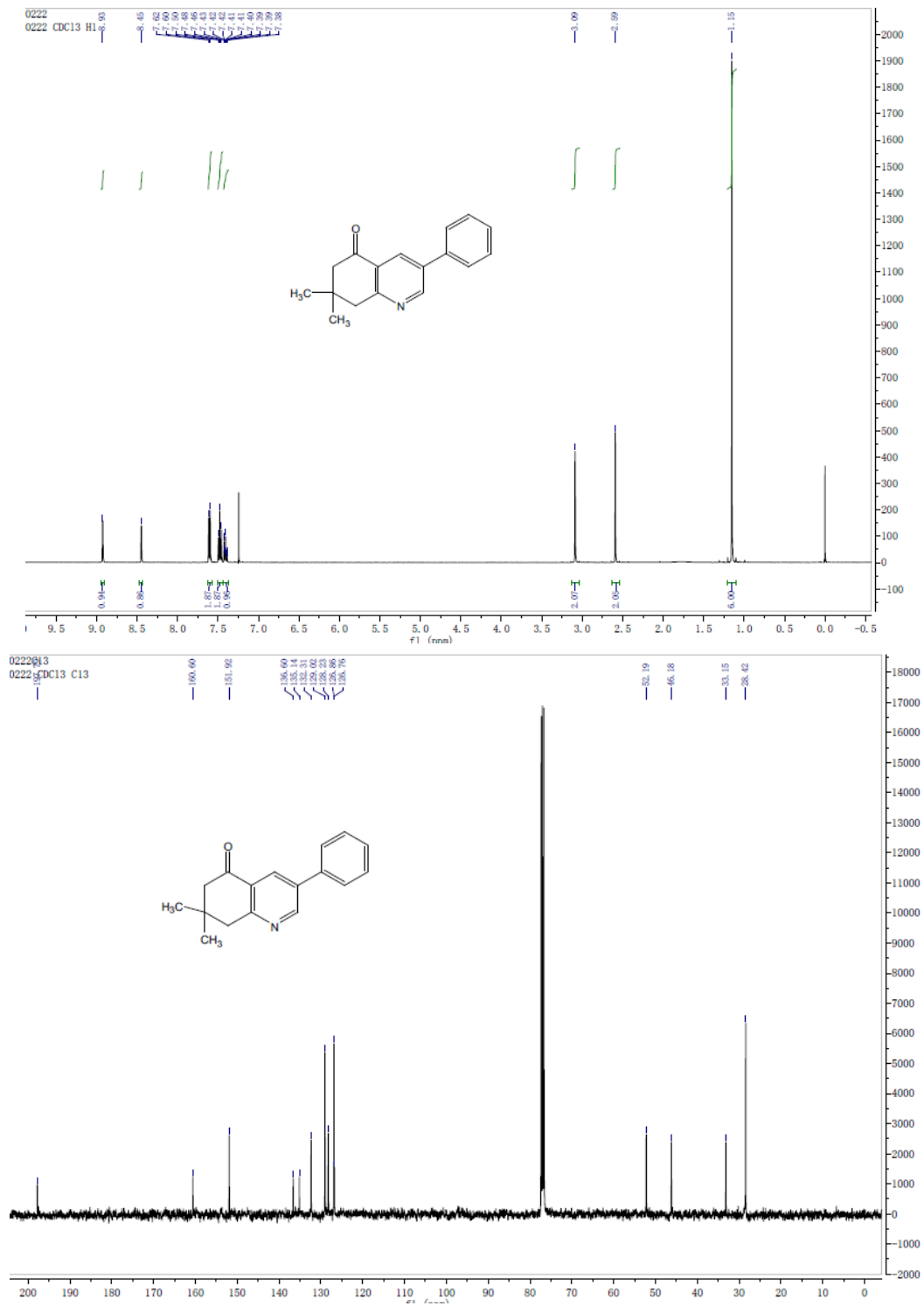
3-(4-Chlorophenyl)-7,8-dihydroquinolin-5(6H)-one (4d)



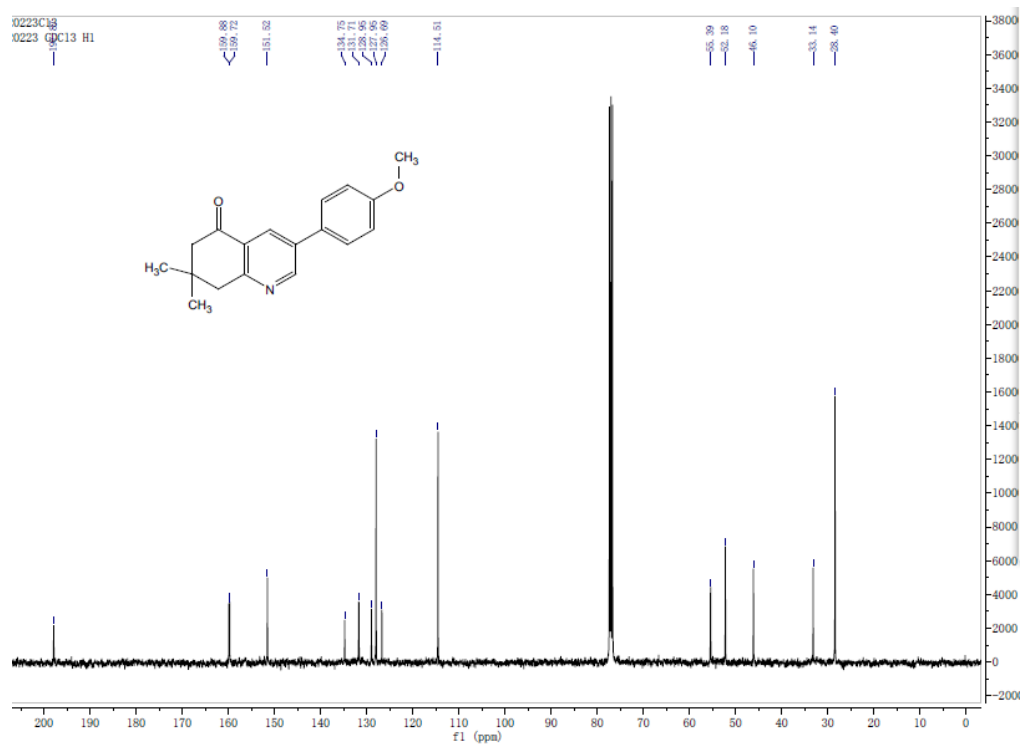
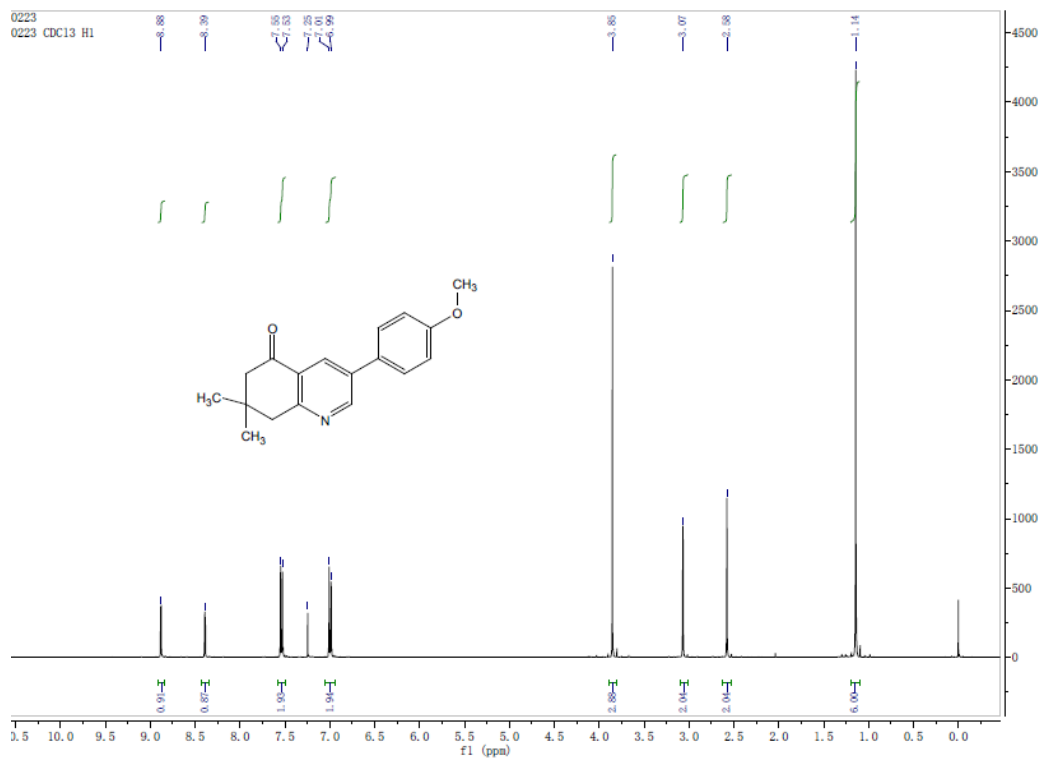
3-(4-Nitrophenyl)-7,8-dihydroquinolin-5(6H)-one (4f)



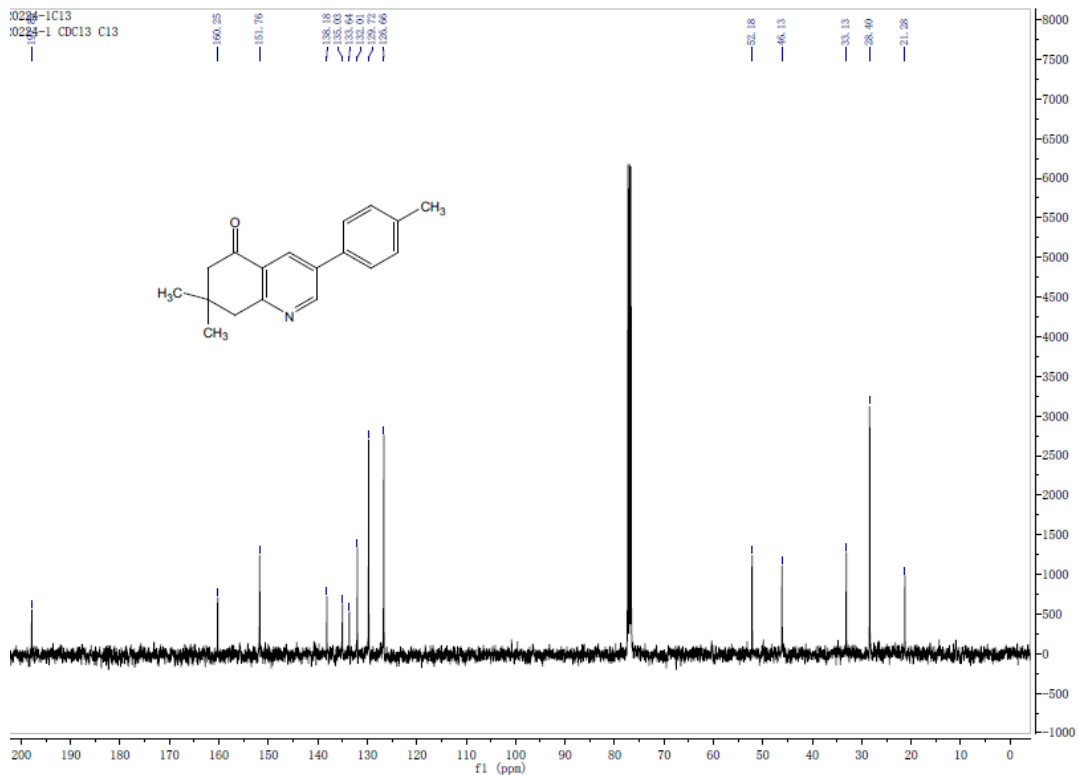
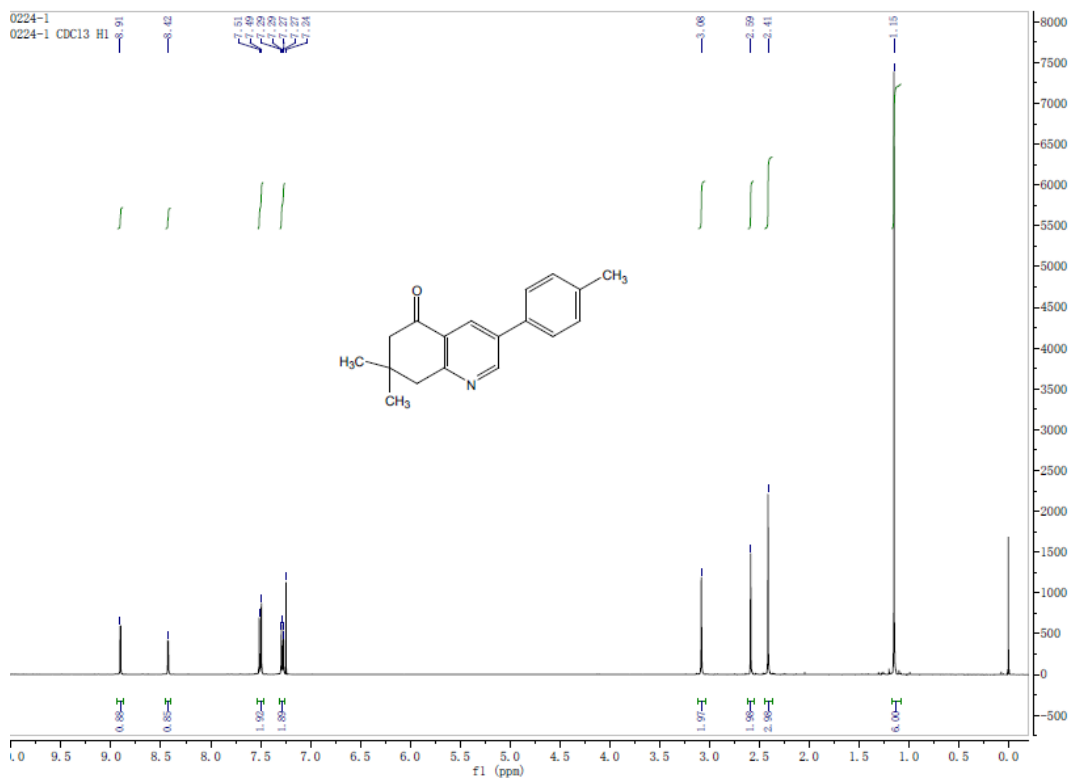
7,7-Dimethyl-3-phenyl-7,8-dihydroquinolin-5(6H)-one (4g)



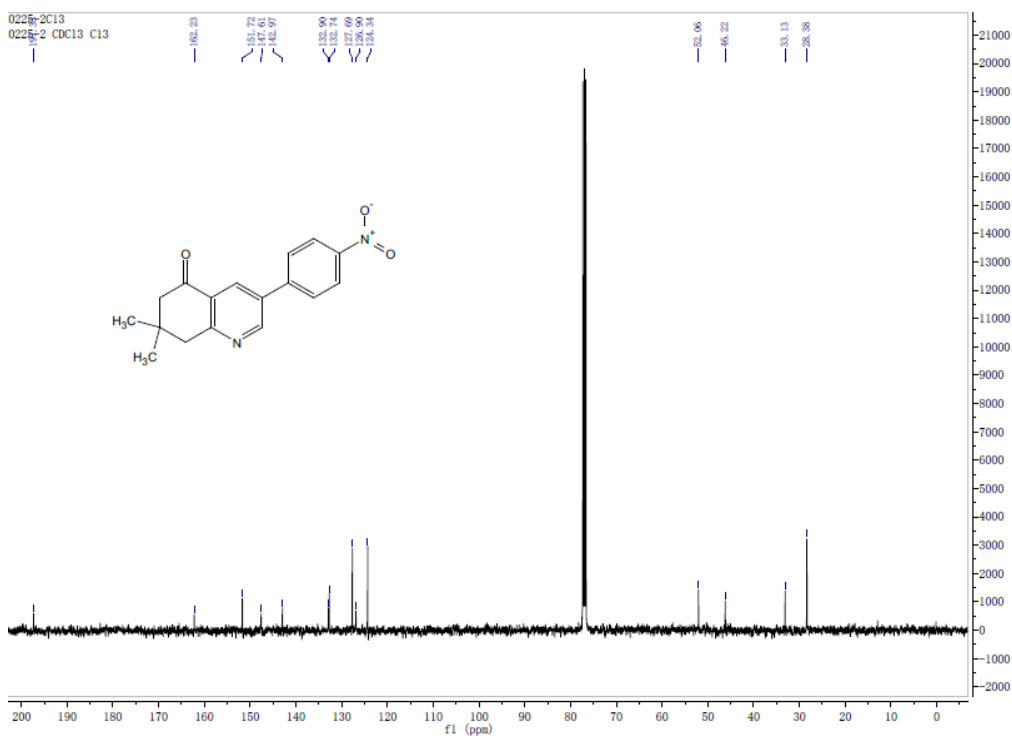
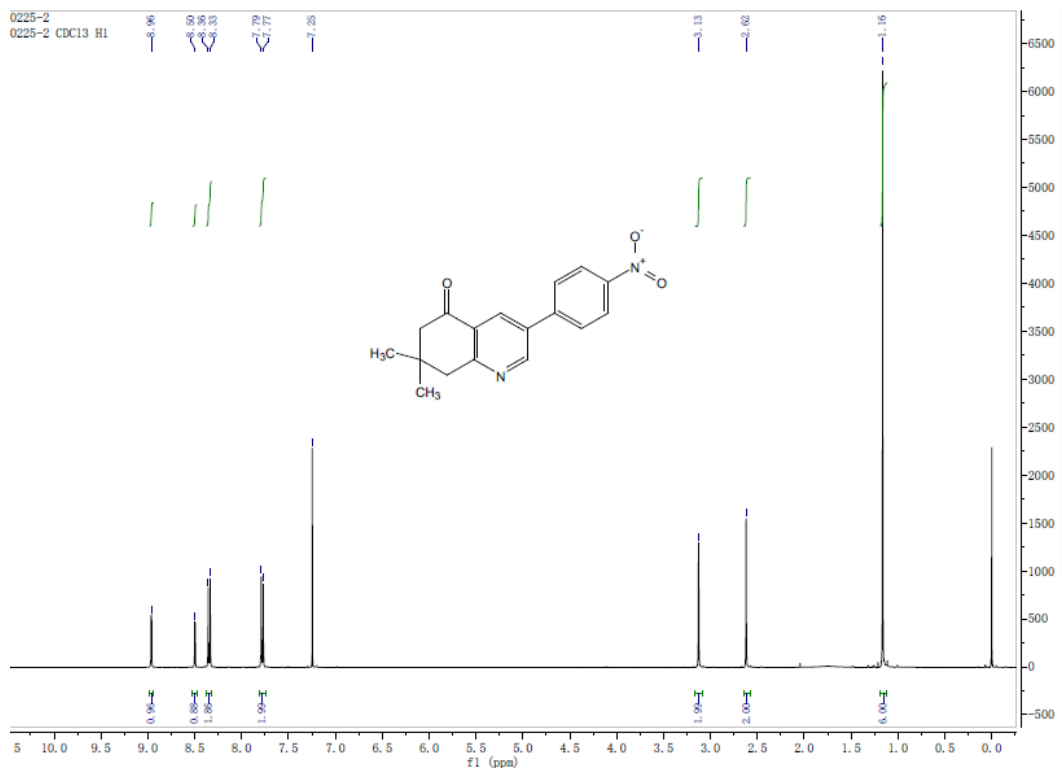
3-(4-Methoxyphenyl)-7,7-dimethyl-7,8-dihydroquinolin-5(6H)-one (4h)



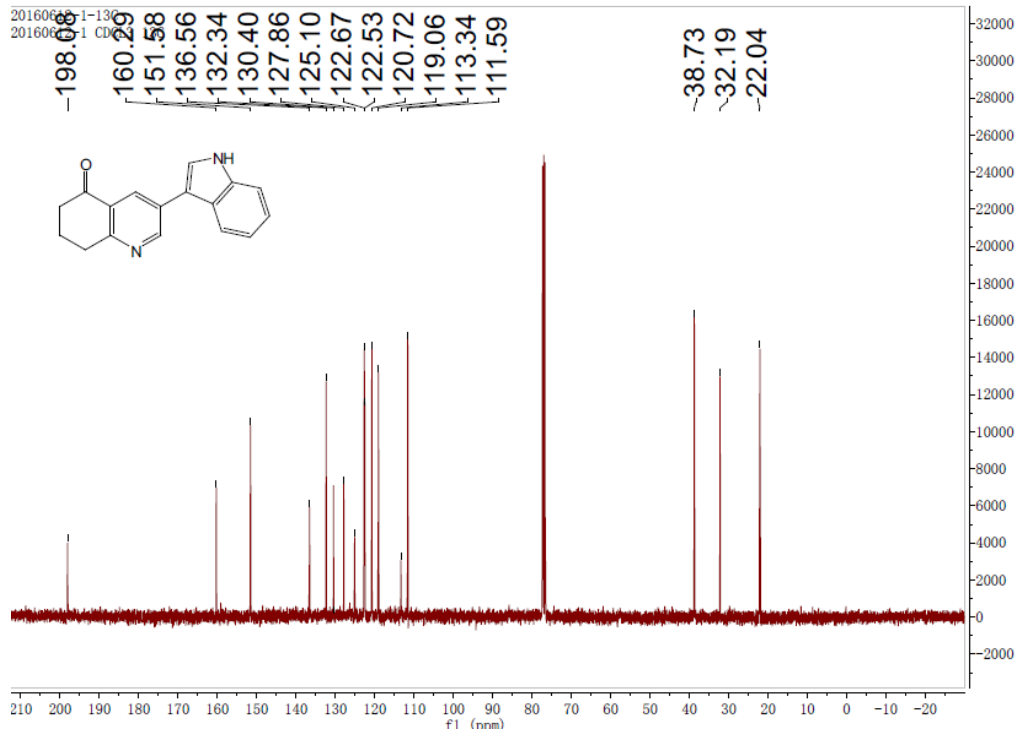
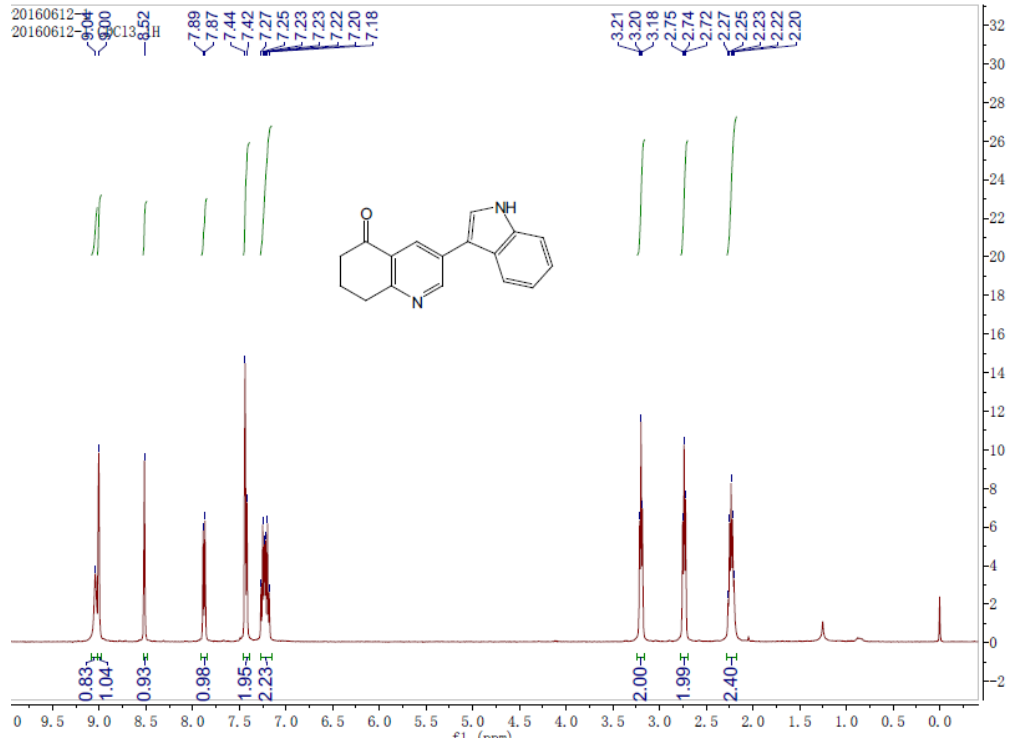
7,7-Dimethyl-3-p-tolyl-7,8-dihydroquinolin-5(6H)-one (4i)



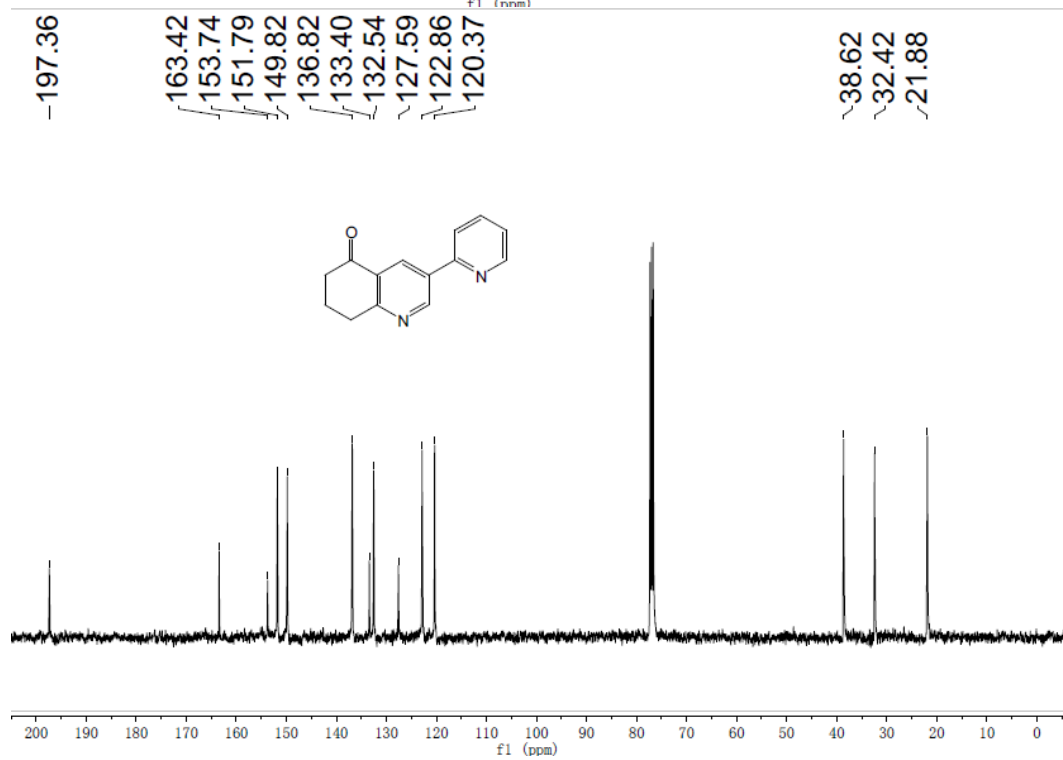
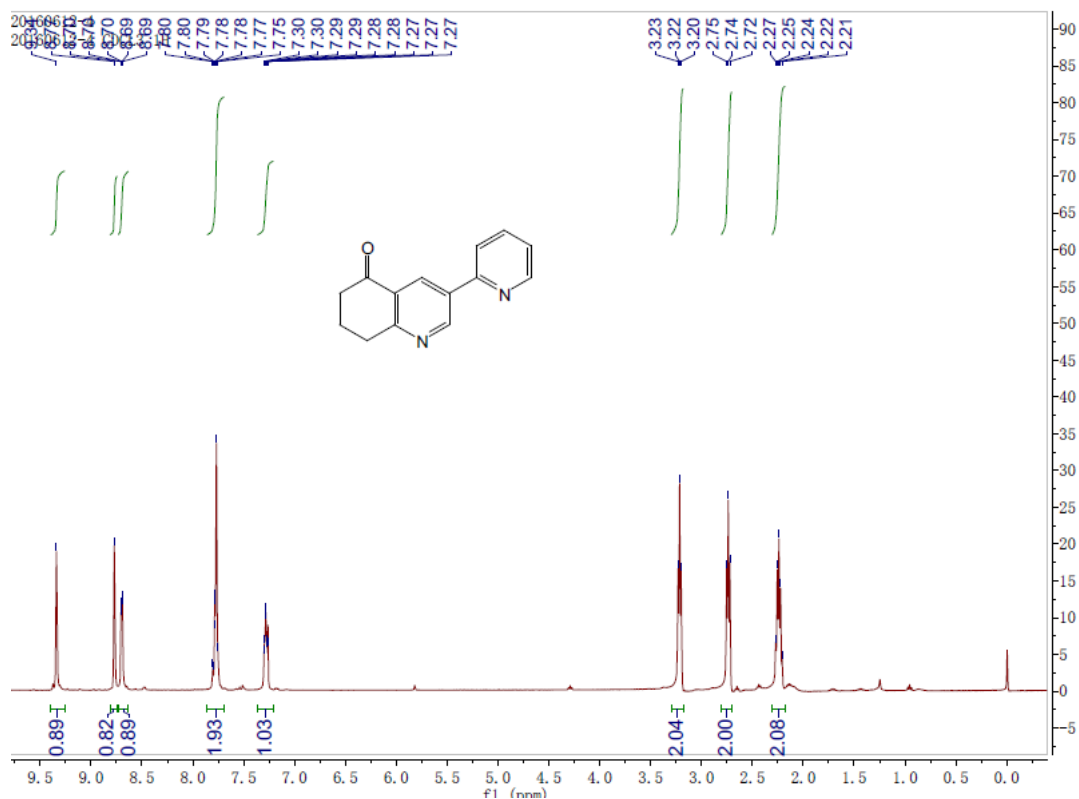
7,7-Dimethyl-3-(4-nitrophenyl)-7,8-dihydroquinolin-5(6H)-one (4I)



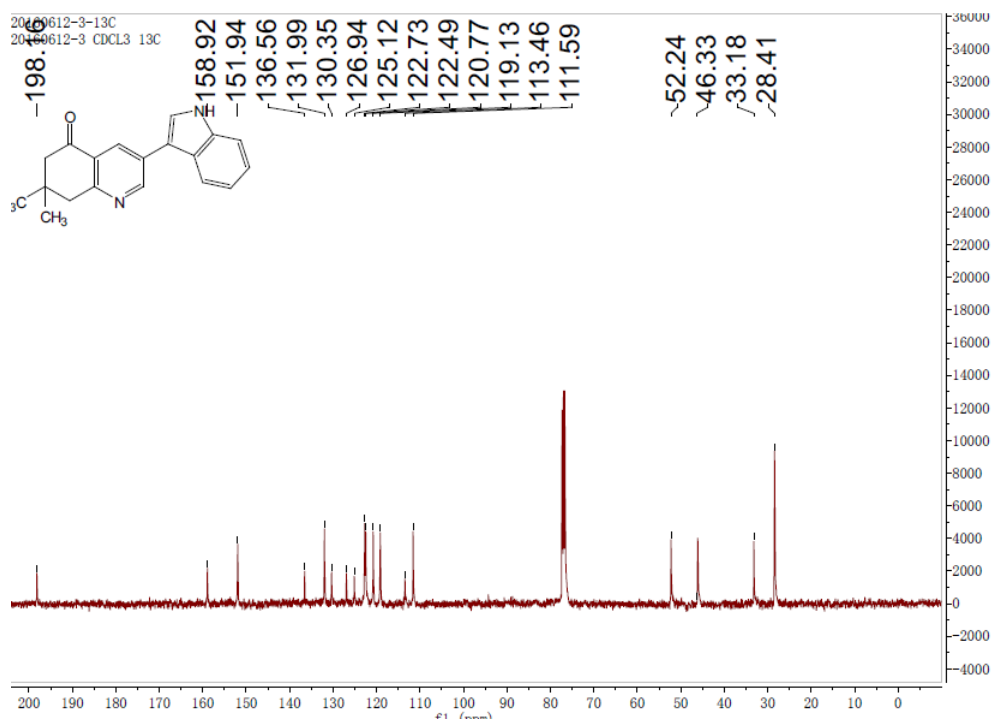
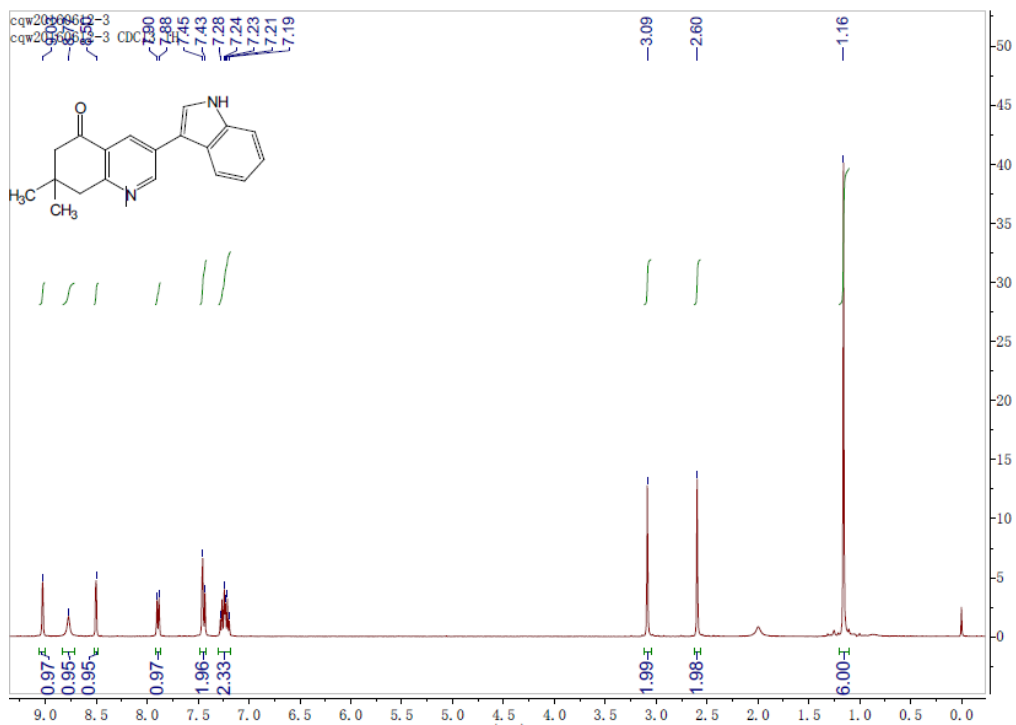
3-(1H-indol-3-yl)-7,8-dihydroquinolin-5(6H)-one (4m)



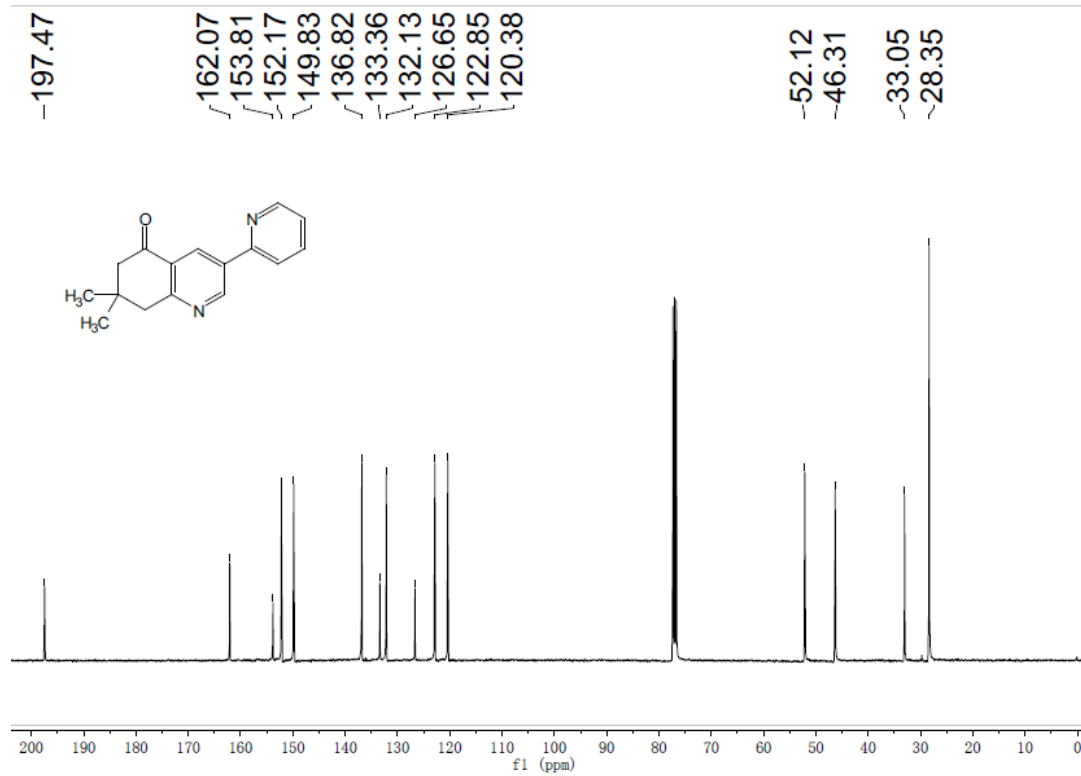
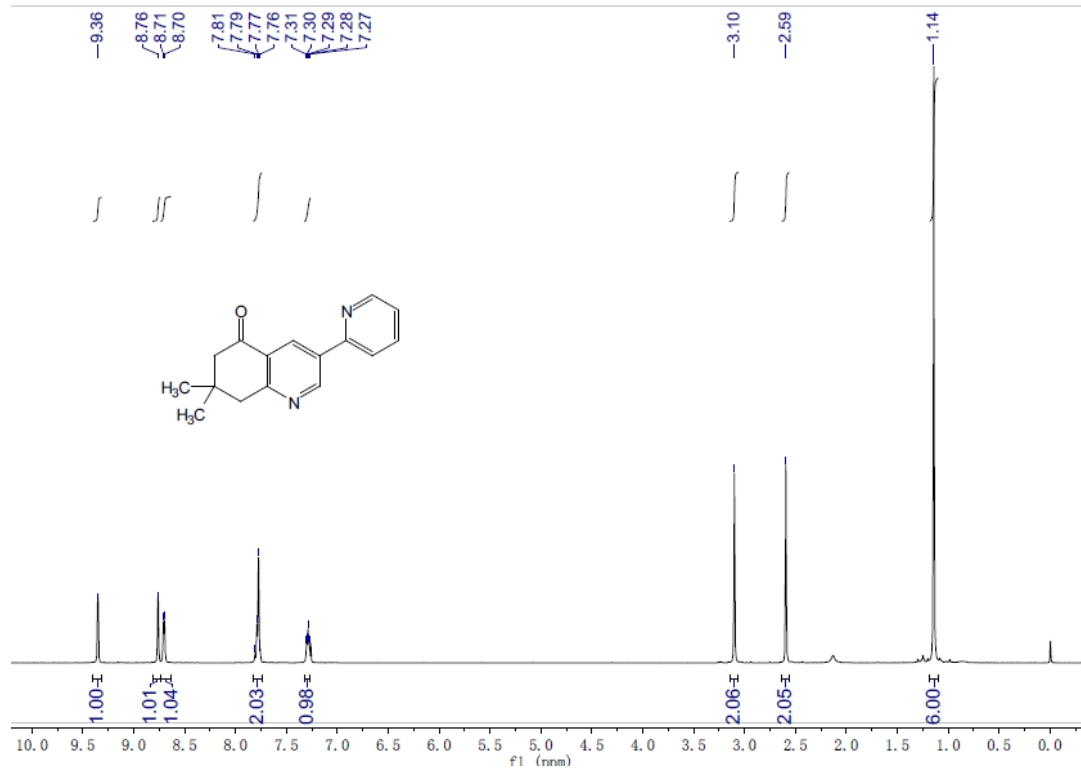
3-(pyridin-2-yl)-7,8-dihydroquinolin-5(6H)-one (4n)



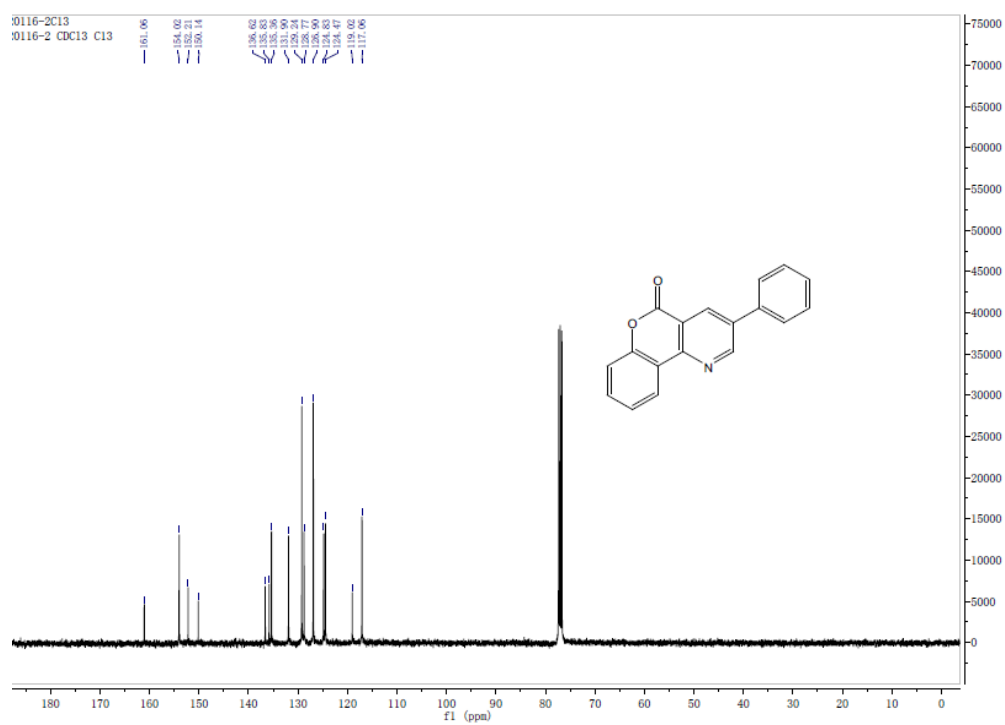
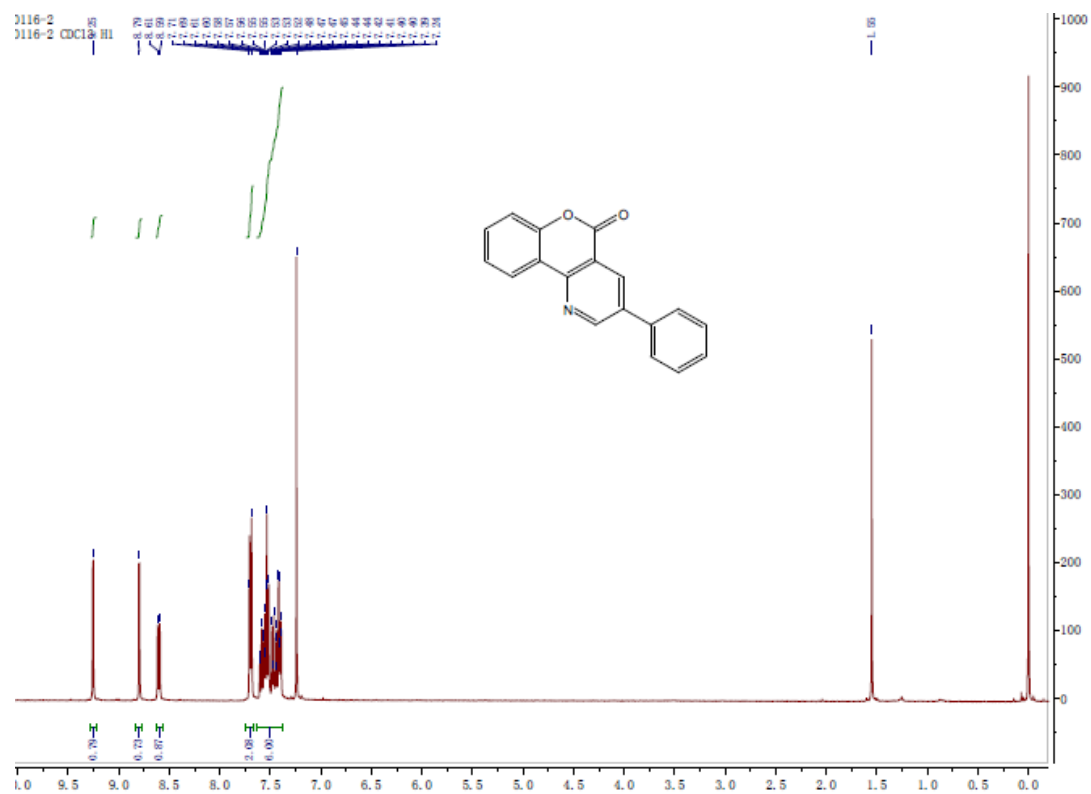
3-(1*H*-indol-3-yl)-7,7-dimethyl-7,8-dihydroquinolin-5(6*H*)-one (4o)



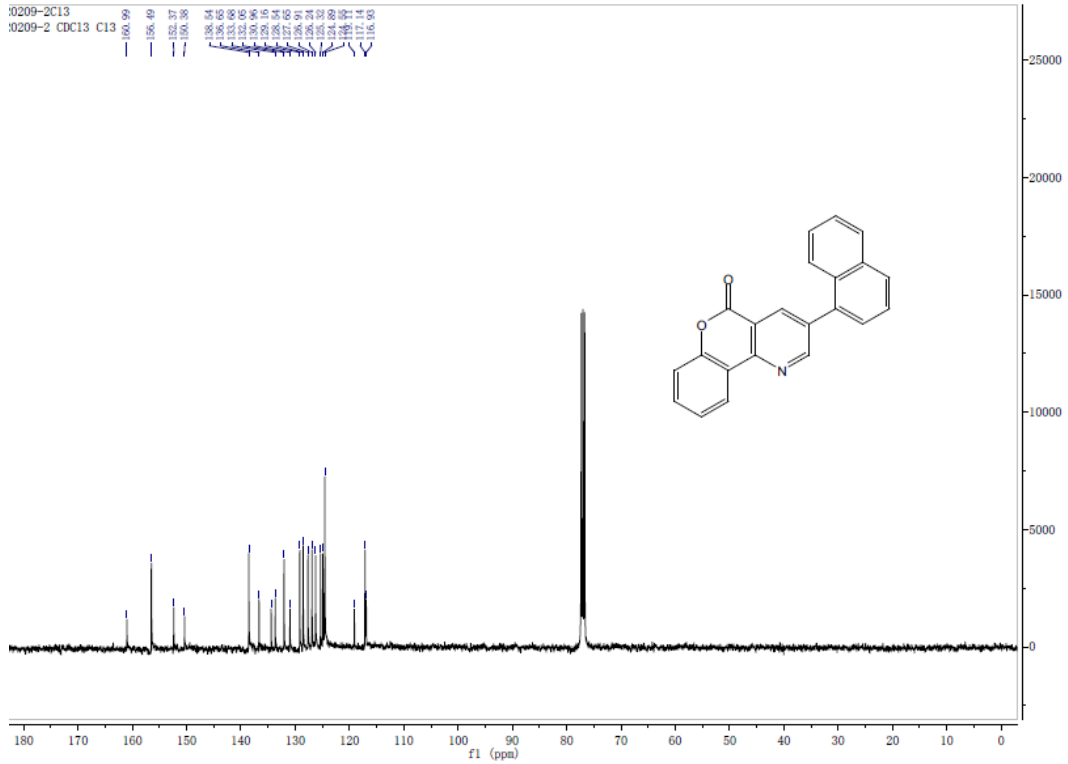
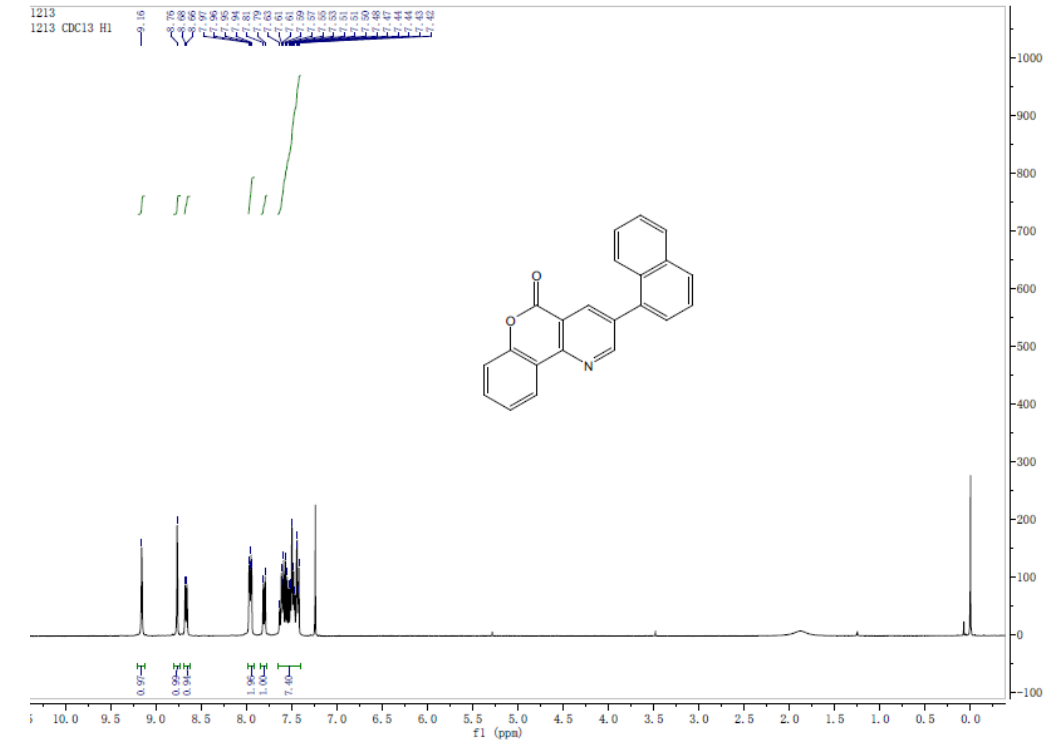
7,7-dimethyl-3-(pyridin-2-yl)-7,8-dihydroquinolin-5(6H)-one (4p)



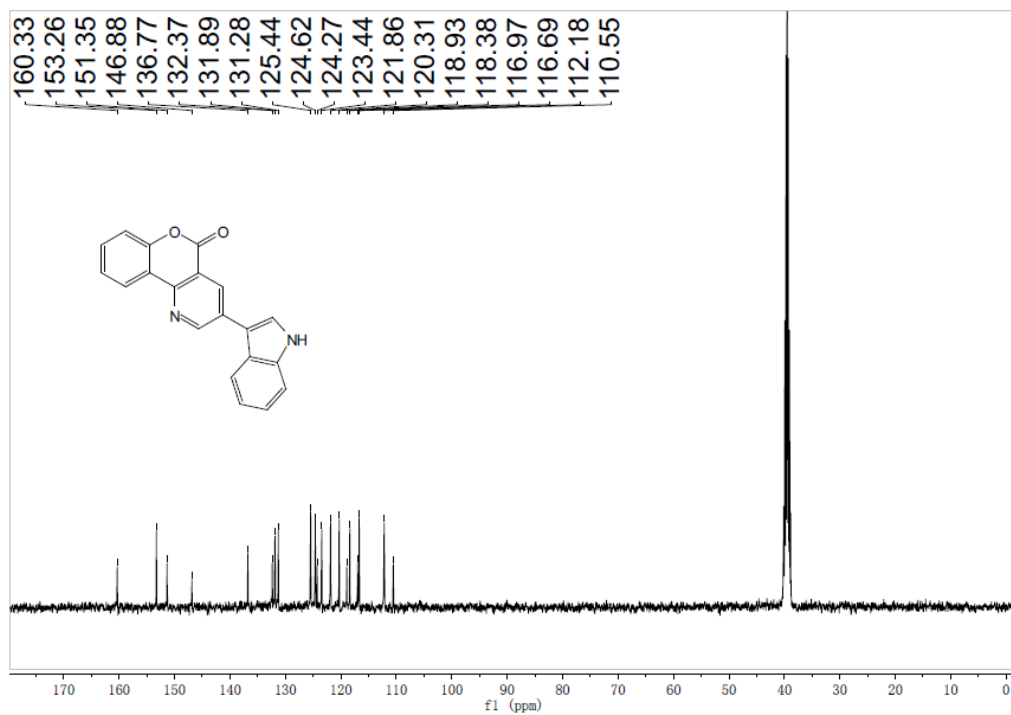
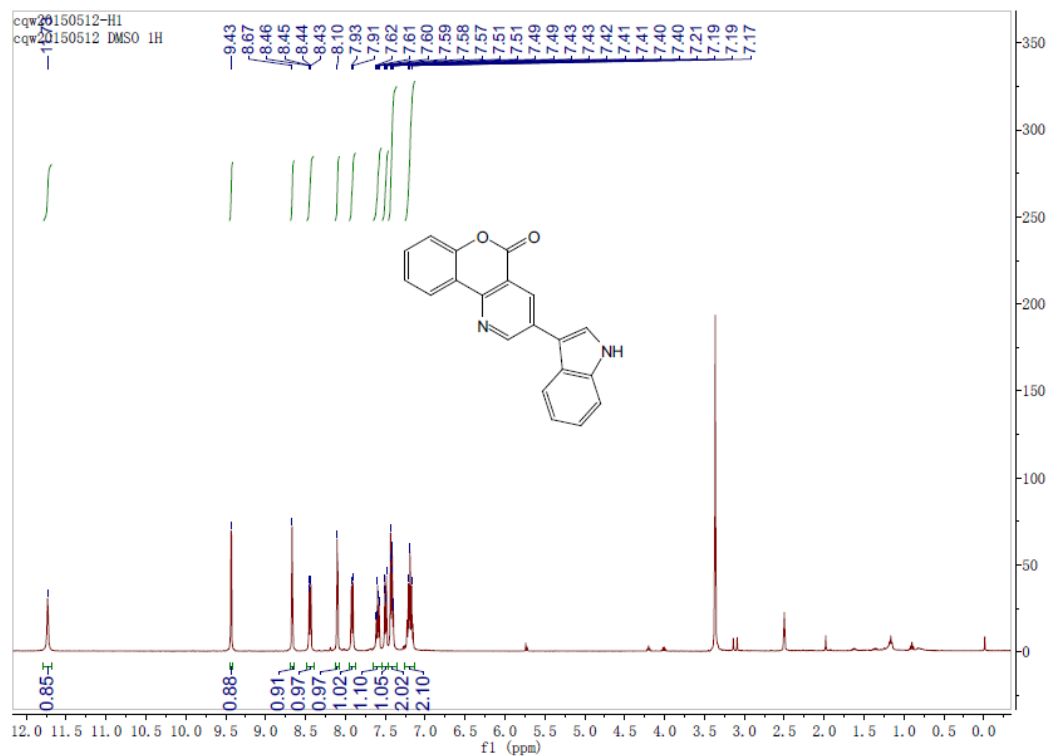
3-Phenyl-5H-chromeno[4,3-b]pyridin-5-one (5a)



3-(Naphthalen-1-yl)-5H-chromeno[4,3-b]pyridin-5-one (5e)



3-(1*H*-indol-3-yl)-5*H*-chromeno[4,3-*b*]pyridin-5-one (5f)



3-(pyridin-2-yl)-5H-chromeno[4,3-b]pyridin-5-one (5g)

