Supporting Information

$PhI(OAc)_2/Pd(OAc)_2$ Promoted the formation of 8-Hydroxyquinoline Derivatives from Benzoxazoles and alcohols

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Table of contents

1. General information 2
2. General procedure for the synthesis of 8-hydroxyquinoline derivatives 2
3. Characterization data for products 2
4. Crystal data 12
5. The GC-Ms spectra of the reaction of 1a and 2a under the optimized conditions 14
6. ^{1}H NMR and ^{13}C NMR spectrum of target compounds 16
7. References 37

1. General information

All reagents and solvents were obtained from commercial suppliers and were used without further purification. All solvents were used directly without drying. All reactions were carried out in air and monitored by analytical thin layer chromatography on 0.20 mm silica gel plates (Anhui Liangchen Chem. Company, Ltd.); spots were detected by UV absorption. Silica gel (200–300 mesh; Qingdao Ocean Chemical Company, Ltd.) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 500 MHz. Chemical shifts are reported in ppm relative to tetramethylsilane (0.00 ppm), and multiplicity of signals are denoted as: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet. High-resolution mass spectra were recorded on Thermo Exactive or SCIEX TripleTOF 5600+ System.

The substituted benzoxazoles **1j**[1], **1l**[1], **1o**[2] and **5a**[3] were prepared according to the literatures and the NMR spectra of these compounds are consistent with the literatures.

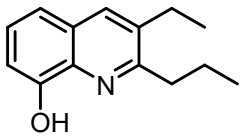
2. General procedure for the synthesis of 8-hydroxyquinoline derivatives

Benzoxazoles **1a-1o** (0.2 mmol, 1.0 eq.), PIDA (0.4 mmol, 2.0 eq.) and $Pd(OAc)_2$ (0.01 mmol, 0.05 eq.) in 2 mL alcohol were heated at 80°C for 6 h to 8 h. The mixture

was filtered and then concentrated under reduced pressure to give the crude product, which was purified by column chromatography (PE/EA = 40:1 to 20:1, v/v) to afford the desired product.

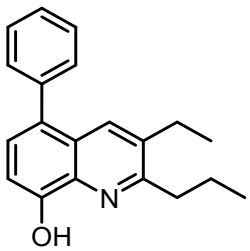
3. Characterization data for products

3-ethyl-2-propylquinolin-8-ol (3aa)



The desired product **3aa** was obtained in 73% yield (31.4 mg) as yellow oil from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 8.2 Hz, 1H), 7.10 (d, *J* = 6.3 Hz, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.85 (q, *J* = 7.8 2H), 1.97 – 1.89 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 151.7, 136.5, 136.2, 133.8, 127.4, 126.6, 117.0, 108.6, 36.9, 25.2, 21.8, 14.4, 14.2. HRMS (ESI) calculated for $C_{14}H_{18}NO$ $[M + H]^+$:216.1383, found 216.1390.

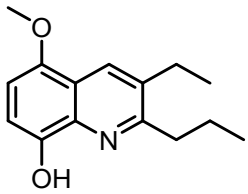
3-ethyl-5-phenyl-2-propylquinolin-8-ol (3ba)



The desired product **3ba** was obtained in 78% yield (45.4 mg) as white solid from 5-phenylbenzo[d]oxazole (39.0 mg, 0.2 mmol) **1b** and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.54 – 7.46 (m, 4H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 2.98 (t, *J* = 7.5 Hz 2H), 2.79 (q, *J* = 7.2 Hz 2H), 1.99 – 1.91 (m, 2H), 1.26 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 151.2, 139.9, 136.6, 136.2,

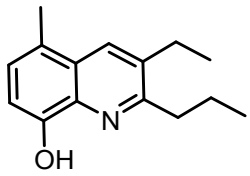
132.5, 130.1, 130.0, 128.4, 127.3, 127.0, 125.4, 108.2, 36.8, 25.5, 21.9, 14.7, 14.2. HRMS (ESI) calculated for $C_{20}H_{22}NO$ $[M + H]^+$: 292.1696, found 292.1702.

3-ethyl-5-methoxy-2-propylquinolin-8-ol (3ca)



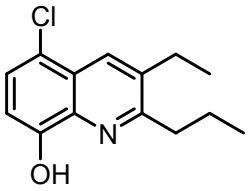
The desired product **3ca** was obtained in 78% yield (39.2 mg) as brown solid from 5-methoxybenzo[d]oxazole **1c** (29.8 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 2.96 (t, *J* = 7.3 Hz 2H), 2.85 (q, *J* = 7.4 Hz 2H), 1.96 – 1.88 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 147.3, 145.5, 136.4, 135.6, 129.2, 119.5, 107.3, 104.0, 55.8, 36.9, 25.4, 21.8, 14.6, 14.2. HRMS (ESI) calculated for $C_{15}H_{20}NO_2$ $[M + H]^+$: 246.1489, found 246.1495.

3-ethyl-5-methyl-2-propylquinolin-8-ol (3da)



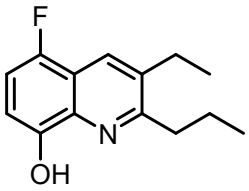
The desired product **3da** was obtained in 74% yield (33.9 mg) as brown solid from 5-methylbenzo[d]oxazole **1d** (26.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 2.97 (t, *J* = 7.3 Hz 2H), 2.88 (q, *J* = 7.3 Hz 2H), 2.58 (s, 3H), 1.97 – 1.90 (m, 2H), 1.38 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 150.0, 136.4, 135.9, 131.0, 126.5, 126.4, 123.5, 108.0, 36.8, 25.5, 21.9, 17.8, 14.8, 14.2. HRMS (ESI) calculated for $C_{15}H_{20}NO$ $[M + H]^+$: 230.1539, found 230.1529.

5-chloro-3-ethyl-2-propylquinolin-8-ol (3ea)



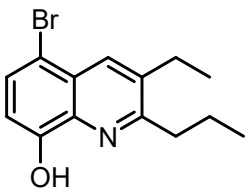
The desired product **3ea** was obtained in 71% yield (35.5 mg) as yellow oil from 5-chlorobenzo[d]oxazole **1e** (30.7 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.02 (d, J = 8.1 Hz, 1H), 2.98 (t, J = 7.5 Hz 2H), 2.89 (q, J = 7.5 Hz 2H), 1.96 – 1.89 (m, 2H), 1.39 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 150.8, 137.5, 136.4, 131.2, 126.4, 125.1, 119.7, 108.8, 36.7, 25.4, 21.7, 14.4, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}ClNO$ $[M + H]^+$: 250.0993, found 250.0984.

3-ethyl-5-fluoro-2-propylquinolin-8-ol (3fa)



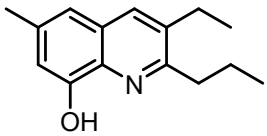
The desired product **3fa** was obtained in 64% yield (29.9 mg) as brown oil from 5-fluorobenzo[d]oxazole **1f** (27.4 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.07 – 7.01 (m, 1H), 6.97 (dd, J = 8.4, 4.6 Hz, 1H), 2.98 (t, J = 7.7 Hz, 2H), 2.88 (q, J = 7.5 Hz, 2H), 1.97 – 1.89 (m, 2H), 1.38 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ160.6, 150.5 (d, J_F = 244.7 Hz), 147.9 (d, J_F = 3.3 Hz), 136.7 (d, J_F = 2.3 Hz), 135.9 (d, J_F = 4.0 Hz), 127.3 (d, J_F = 2.4 Hz), 117.7 (d, J_F = 18.3 Hz), 109.5 (d, J_F = 20.6 Hz), 107.04 (d, J_F = 7.8 Hz), 36.9, 25.3, 21.7, 14.2, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}FNO$ $[M + H]^+$: 234.1289, found 234.1276.

5-bromo-3-ethyl-2-propylquinolin-8-ol (3ga)



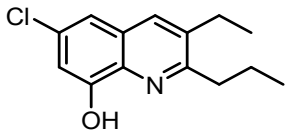
The desired product **3ga** was obtained in 69% yield (40.6 mg) as brown oil from 5-bromobenzo[d]oxazole **1g** (39.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 2.98 (t, *J* = 7.3 Hz 2H), 2.90 (q, *J* = 7.5 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.39 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 151.5, 137.9, 136.7, 133.6, 129.9, 126.4, 109.4, 109.0, 36.6, 25.3, 21.8, 14.4, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}BrNO$ $[M + H]^+$: 294.0488 found 294.0482.

3-ethyl-6-methyl-2-propylquinolin-8-ol (3ha)



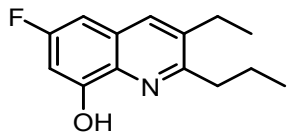
The desired product **3ha** was obtained in 72% yield (33.0 mg) as yellow solid from 6-methylbenzo[d]oxazole **1h** (26.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.04 (s, 1H), 6.96 (s, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.83 (q, *J* = 7.5 Hz, 2H), 2.49 (s, 3H), 1.95 – 1.88 (m, 2H), 1.35 (t, *J* = 7.5 Hz, 3H), 1.08 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 151.2, 136.8, 136.4, 134.8, 133.2, 127.3, 116.0, 110.7, 36.8, 25.2, 22.2, 21.8, 14.4, 14.2. HRMS (ESI) calculated for $C_{15}H_{20}NO$ $[M + H]^+$: 230.1539, found 230.1531.

6-chloro-3-ethyl-2-propylquinolin-8-ol (3ia)



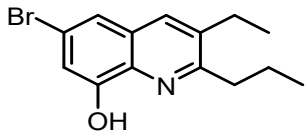
The desired product **3ia** was obtained in 75% yield (37.5 mg) as brown solid from 6-chlorobenzo[d]oxazole **1i** (30.7 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.61 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 1H), 2.99 (t, *J* = 7.5 Hz, 2H), 2.90 (q, *J* = 7.1 Hz, 2H), 1.96 – 1.89 (m, 2H), 1.40 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 151.5, 137.9, 136.7, 133.5, 129.8, 126.4, 109.4, 109.0, 36.7, 25.3, 21.7, 14.4, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}ClNO$ $[M + H]^+$: 250.0993, found 250.0986.

3-ethyl-6-fluoro-2-propylquinolin-8-ol (3ja)



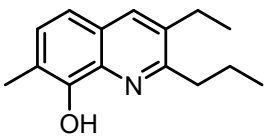
The desired product **3ja** was obtained in 78% yield (30.3 mg) as brown solid from 6-fluorobenzo[d]oxazole **1j** (27.4 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.88 (d, J = 9.7 Hz, 2H), 2.94 (t, J = 7.8 Hz, 2H), 2.84 (q, J = 7.5 Hz, 2H), 1.95-1.87 (m, 2H),1.35 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 160.1, 158.64 (d, J_F = 2.7 Hz), 153.29 (d, J_F = 14.6 Hz), 137.7, 133.5, 133.35 (d, J_F = 5.6 Hz), 127.31 (d, J_F = 11.9 Hz), 100.25 – 99.42 (m). 36.7, 25.2, 21.7, 14.3, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}FNO$ $[M + H]^+$: 234.1289, found 234.1280.

6-bromo-3-ethyl-2-propylquinolin-8-ol (3ka)



The desired product **3ka** was obtained in 70% yield (41.2 mg) as brown oil from 6-bromobenzo[d]oxazole **1k** (39.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 2.99 (t, J = 7.8 Hz, 2H), 2.90 (q, J = 7.5 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.40 (t, J = 7.5 Hz, 3H), 1.09 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 151.5, 137.9, 136.7, 133.6, 129.9, 126.4, 109.4, 109.0, 36.6, 25.3, 21.8, 14.4, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}BrNO$ $[M + H]^+$: 294.0488 found 294.0480.

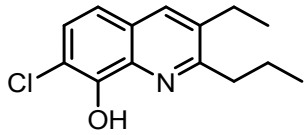
3-ethyl-7-methyl-2-propylquinolin-8-ol (3la)



The desired product **3la** was obtained in 72% yield (33.0 mg) as yellow oil from 7-methylbenzo[d]oxazole **1l** (26.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to

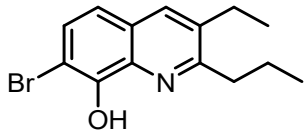
general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.26 (d, *J* = 8.3 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.83 (q, *J* = 7.5 Hz, 2H), 2.47 (s, 3H), 1.96 – 1.88 (m, 2H), 1.35 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 148.8, 136.4, 135.3, 133.7, 129.6, 125.6, 118.8, 116.1, 36.9, 25.1, 21.8, 15.5, 14.4, 14.2. HRMS (ESI) calculated for $C_{15}H_{20}NO$ $[M + H]^+$: 230.1539, found 230.1531.

7-chloro-3-ethyl-2-propylquinolin-8-ol (3ma)



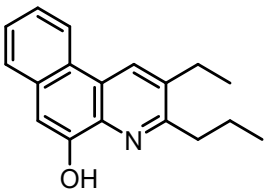
The desired product **3ma** was obtained in 71% yield (35.5 mg) as yellow from 7-chlorobenzo[d]oxazole **1m** (30.7 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.84 (q, *J* = 7.4 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 147.7, 136.6, 136.4, 133.9, 127.8, 125.8, 117.3, 114.3, 36.8, 25.1, 21.8, 14.2, 14.2. HRMS (ESI) calculated for $C_{14}H_{17}ClNO$ $[M + H]^+$: 250.0993, found 250.0988.

7-bromo-3-ethyl-2-propylquinolin-8-ol (3na)



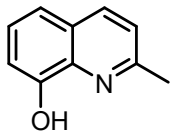
The desired product **3na** was obtained in 79% yield (46.5 mg) as brown solid from 7-bromobenzo[d]oxazole **1n** (39.6 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 2.97 (t, *J* = 7.7 Hz, 2H), 2.85 (q, *J* = 7.6 Hz, 2H), 1.95 – 1.87 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 149.2, 136.8, 136.3, 133.9, 130.1, 126.2, 117.8, 102.5, 36.8, 25.1, 21.7, 14.2, 14.1. HRMS (ESI) calculated for $C_{14}H_{17}BrNO$ $[M + H]^+$: 294.0488 found 294.0480.

2-ethyl-3-propylbenzo[f]quinolin-5-ol (3oa)



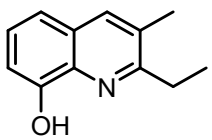
The desired product **3oa** was obtained in 80% yield (42.5 mg) as brown solid from naphtho[2,3-d]oxazole **1o** (33.8 mg, 0.2 mmol) and n-butanol **2a** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.53 – 7.49 (m, 1H), 7.32 (s, 1H), 3.03 (t, *J* = 7.7 Hz, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 2.01 – 1.92 (m, 2H), 1.43 (t, *J* = 7.5 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 149.4, 137.9, 136.5, 133.0, 130.8, 127.4, 127.1, 124.6, 124.0, 123.9, 122.3, 106.2, 36.6, 25.6, 22.0, 14.9, 14.2. HRMS (ESI) calculated for $C_{18}H_{20}NO$ $[M + H]^+$: 266.1539 found 266.1533.

2-methylquinolin-8-ol (3ab)



The desired product **3ab** was obtained in 28% yield (8.9 mg) as light yellow solid from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and ethanol **2b** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 151.7, 137.7, 136.1, 126.7, 126.6, 122.7, 117.6, 109.8, 24.9. HRMS (ESI) calculated for $C_{14}H_{12}NO$ $[M + H]^+$: 210.0913 found 210.0910.

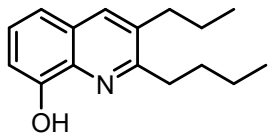
2-ethyl-3-methylquinolin-8-ol (3ac)



The desired product **3ac** was obtained in 77% yield (28.9 mg) as light yellow solid from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and n-propanol **2c** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.37 (t, *J* = 7.7 Hz,

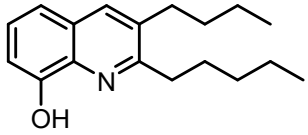
1H), 7.24 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 2.98 (q, *J* = 7.4 Hz, 2H), 2.49 (s, 3H), 1.44 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 151.7, 136.3, 135.5, 130.5, 127.3, 126.7, 116.8, 108.7, 28.6, 19.0, 11.9. HRMS (ESI) calculated for $C_{16}H_{16}NO$ $[M + H]^+$: 238.1226 found 238.1234.

2-butyl-3-propylquinolin-8-ol (3ad)



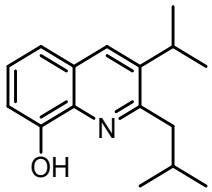
The desired product **3ad** was obtained in 79% yield (38.4 mg) as light yellow solid from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and n-pentanol **2d** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.09 (d, *J* = 6.3 Hz, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.80 – 1.69 (m, 2H), 1.56 – 1.46 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H), 1.02 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 151.6, 136.3, 135.0, 134.8, 127.2, 126.6, 117.0, 108.6, 34.7, 34.4, 30.8, 23.5, 22.8, 14.1, 14.1. HRMS (ESI) calculated for $C_{20}H_{24}NO$ $[M + H]^+$: 294.1852 found 294.1845.

3-butyl-2-pentylquinolin-8-ol (3ae)



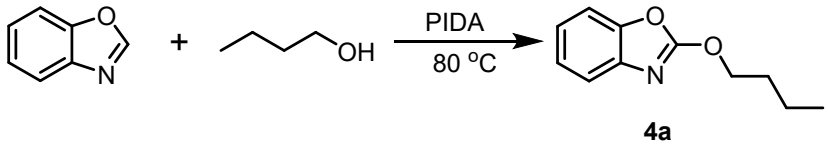
The desired product **3ae** was obtained in 77% yield (36.4mg) as light yellow solid from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and n-hexanol **2e** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.81 (t, *J* = 8.4 Hz, 2H), 1.93 – 1.84 (m, 2H), 1.74 – 1.65 (m, 2H), 1.54 – 1.42 (m, 6H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 151.6, 136.1, 135.2, 134.8, 127.2, 126.6, 116.9, 108.3, 34.9, 32.6, 32.0, 31.9, 28.4, 22.7, 14.1, 14.0, 1.5. HRMS (ESI) calculated for $C_{22}H_{28}NO$ $[M + H]^+$: 322.2165 found 322.2160.

2-isobutyl-3-isopropylquinolin-8-ol (3af)



The desired product **3af** was obtained in 25% yield (12.2 mg) as light yellow solid from benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol) and 3-methyl-1-butanol **2f** (2 mL) according to general procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.37 (d, *J* = 15.7 Hz, 1H), 7.27 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 3.37 – 3.31 (m, 1H), 2.92 (d, *J* = 7.2 Hz, 2H), 2.39 – 2.30 (m, 1H), 1.36 (d, *J* = 6.9 Hz, 6H), 1.03 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 151.7, 141.8, 136.0, 131.6, 127.3, 126.7, 117.1, 108.5, 43.7, 28.8, 28.7, 23.8, 22.7. HRMS (ESI) calculated for $C_{20}H_{24}NO$ [M + H]$^{+}$: 294.1852 found 294.1848.

2-butoxybenzo[d]oxazole (4a)



4a

Benzo[d]oxazole **1a** (23.6 mg, 0.2 mmol, 1.0 eq), n-butanol **2a** (2 mL) in the presence of PIDA (128 mg, 0.4 mmol, 2.0 eq) was heated at 80^{o}C for 6 h. The mixture was filtered and then concentrated under reduced pressure to give the crude product, which was purified by column chromatography (PE/EA = 40:1 to 20:1, v/v) to afford 4a (21.56 mg, 57%) as light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.1 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 4.58 (t, *J* = 6.6 Hz, 2H), 1.91 – 1.85 (m, 2H), 1.57 – 1.50 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.8, 148.5, 141.3, 124.2, 122.8, 117.9, 109.7, 72.2, 30.7, 18.9, 13.7. HRMS (ESI) calculated for $C_{11}H_{14}NO_2$ [M + H]$^{+}$: 192.1019 found 192.1024.

4. Crystal data

The purified compound **3ca** was dissolved in n-hexane, and placed in a dark cabinet to slowly evaporate. After several days, a brown bulk crystal was obtained. The X-ray crystal-structure determinations were obtained on a Bruker APEX-II CCD diffractometer at 296.15 K.

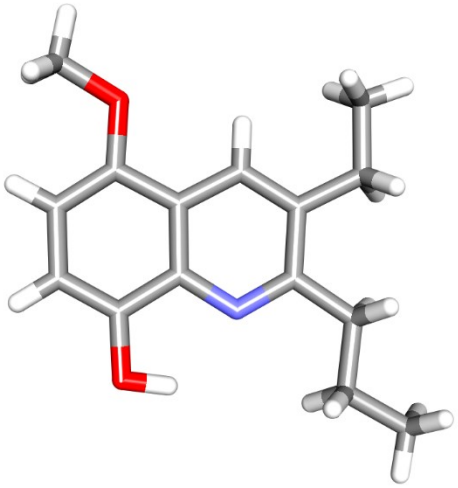


Fig. S1. X-ray crystal structure of compound **3ca**. Ellipsoid plot (50% probability) using Discovery Studio 2019 Client

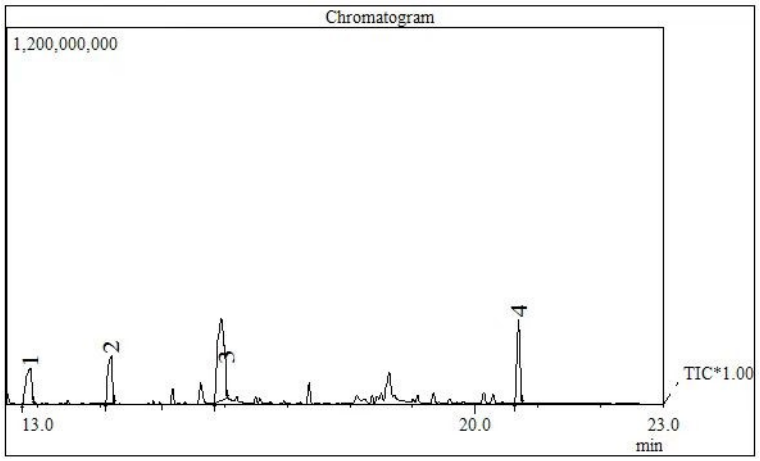
Table S1. Crystal data and structure refinement for **3ca**

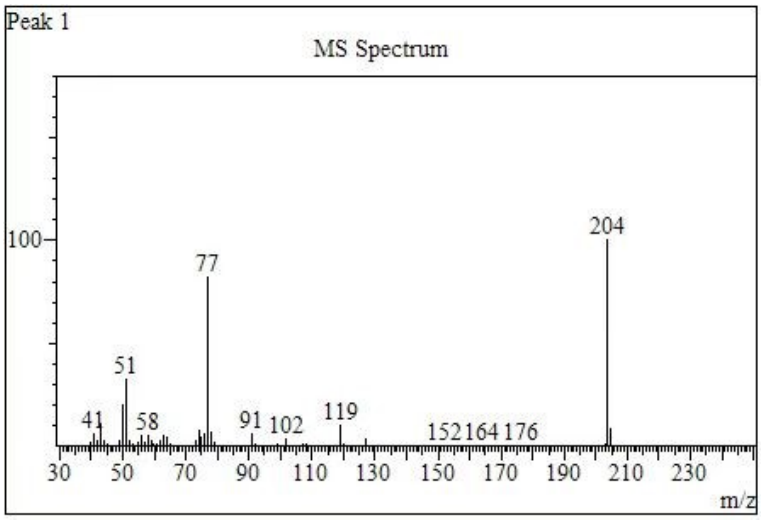
Empirical formula	$C_{15}H_{19}NO_2$
Formula weight	245.31
Temperature (k)	296.15
Crystal system	triclinic
space group	P-1
a (Å)	8.342(3)
b (Å)	12.518(5)
c (Å)	13.597(5)
α (deg)	87.692(5)
β (deg)	75.650(6)
γ (deg)	77.497(6)
Volume ($Å^3$)	1342.8(9)
Z	4
ρ_{calc}g (cm^3)	1.213
μ (mm^{-1})	0.080
Crystal size (mm^3)	0.18 × 0.16 × 0.1
F (000)	528.0
2Θ range for data (deg)	3.092 to 55.156

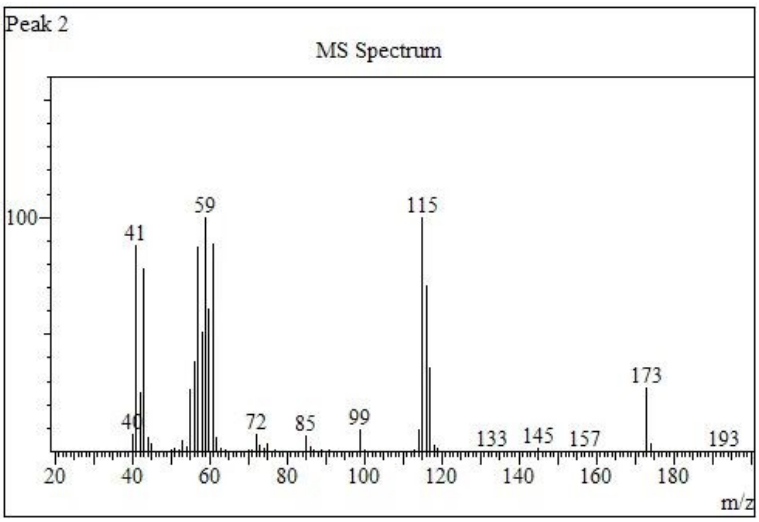
Index ranges	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-13 \leq l \leq 17$
Reflections collected	8412
Independent reflections	5985 [$R_{int} = 0.0257$, $R_{sigma} = 0.0625$]
Data/restraints/parameters	5985/0/331
Goodness-of-fit on F^2	0.973
Final R indexes [I>=2σ (I)]	$R_1 = 0.0552$, $wR_2 = 0.1215$
Final R indexes [all data]	$R_1 = 0.1067$, $wR_2 = 0.1471$
Largest diff. peak/hole ($e \cdot Å^{-3}$)	0.17/-0.20
CCDC#	2194995

5. The GC-Ms spectra of the reaction of 1a and 2a under the optimized conditions.

Peak 1 is PhI, Peak 2 is dibutyl carbonate (DBC), peak 3 is quinoline that was used as the internal standard, and peak 4 is the target product.







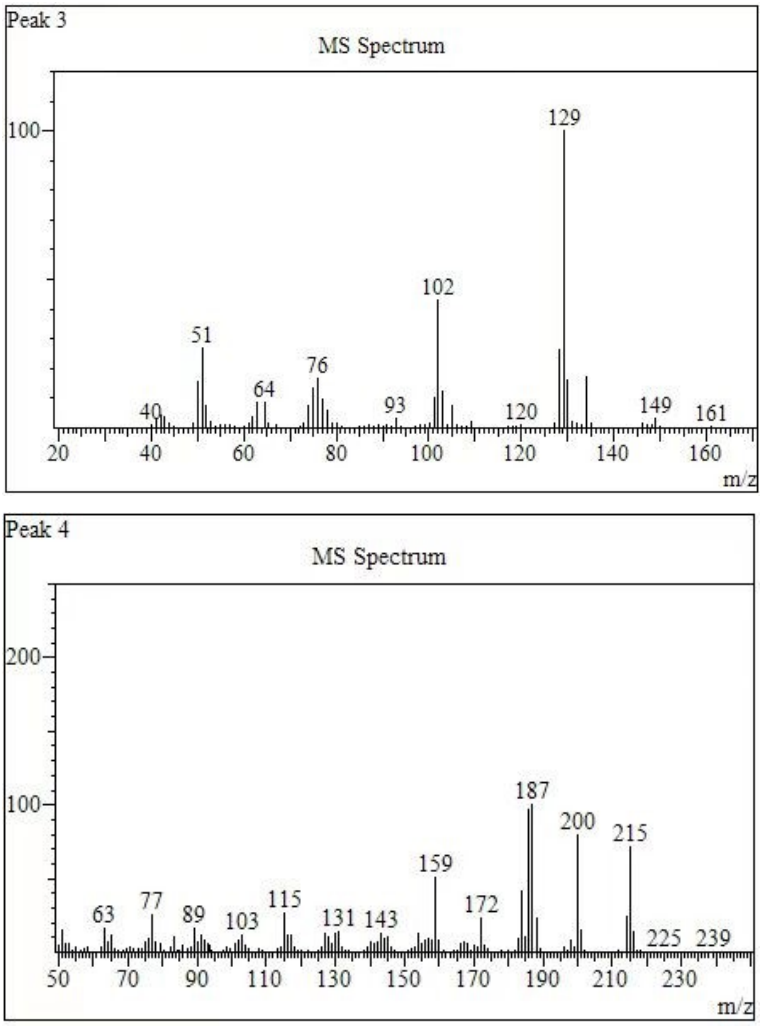
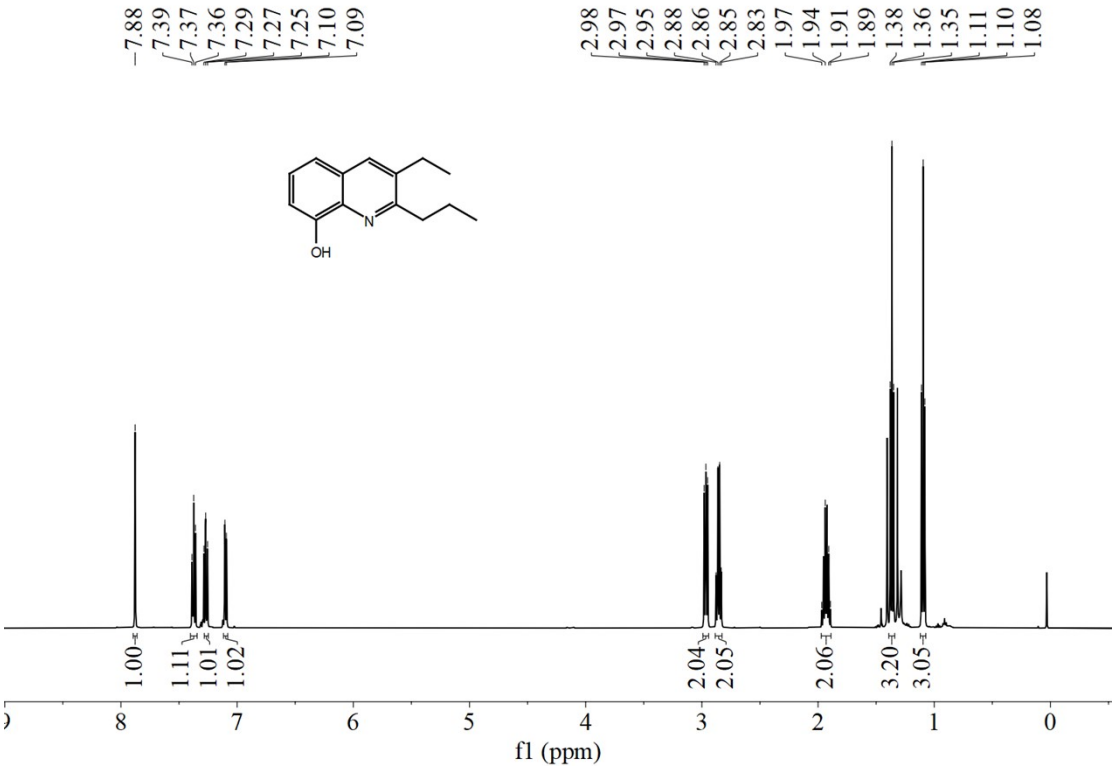


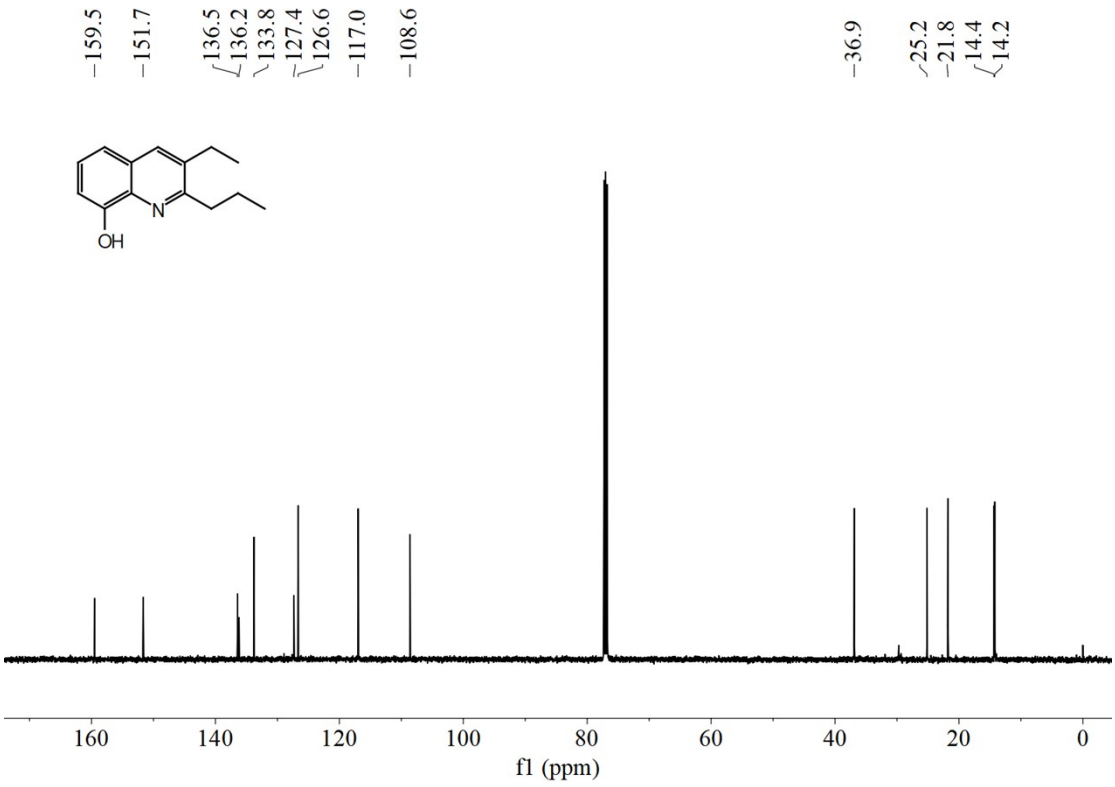
Figure S1. The spectra of GC-Ms of the reaction under the optimized conditions.

6. ^{1}H NMR and ^{13}C NMR spectrum of target compounds

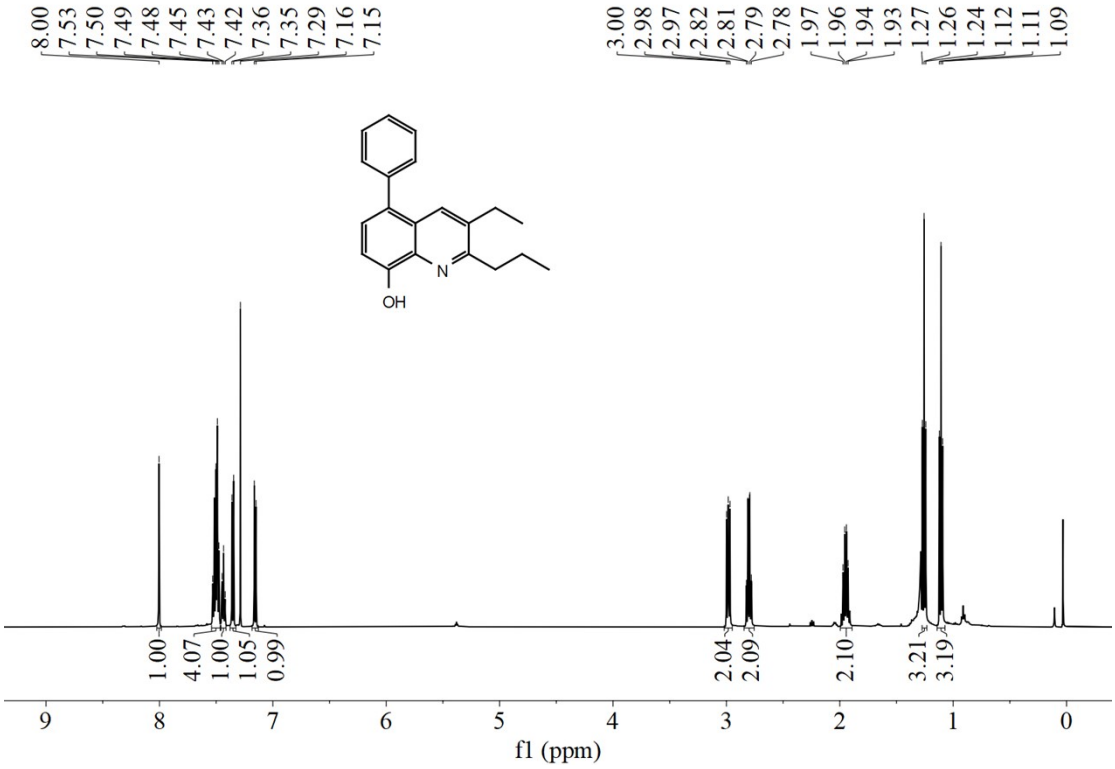
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3aa**



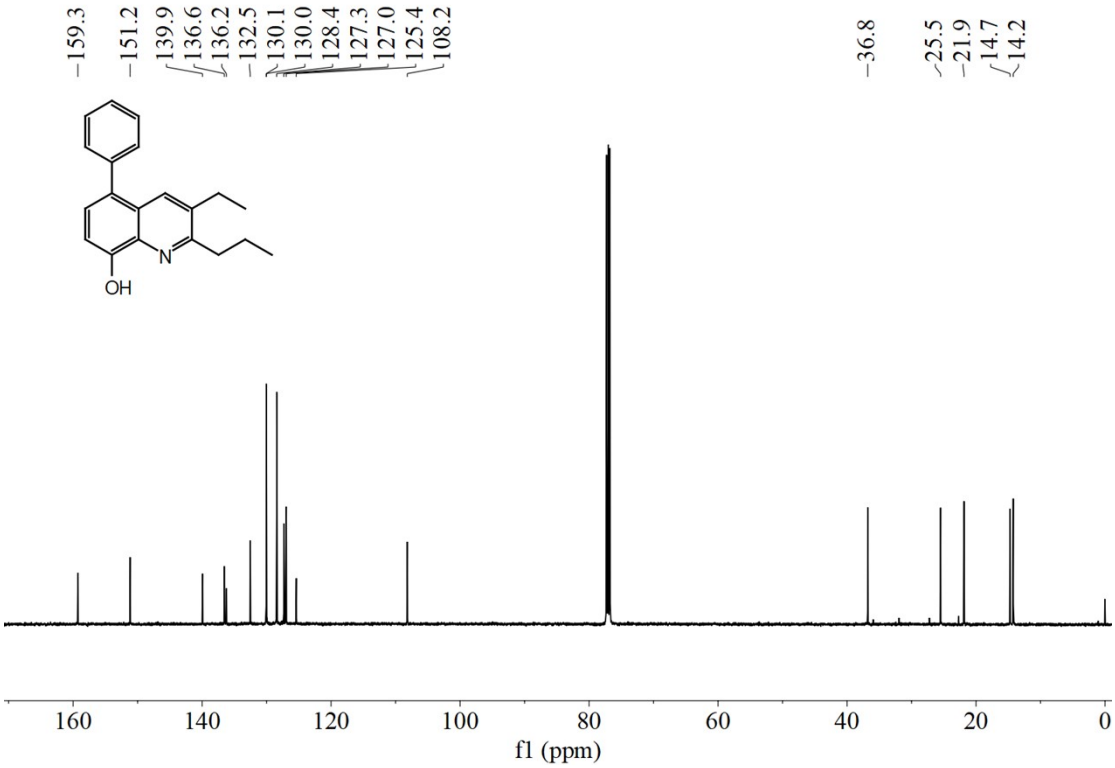
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3aa**



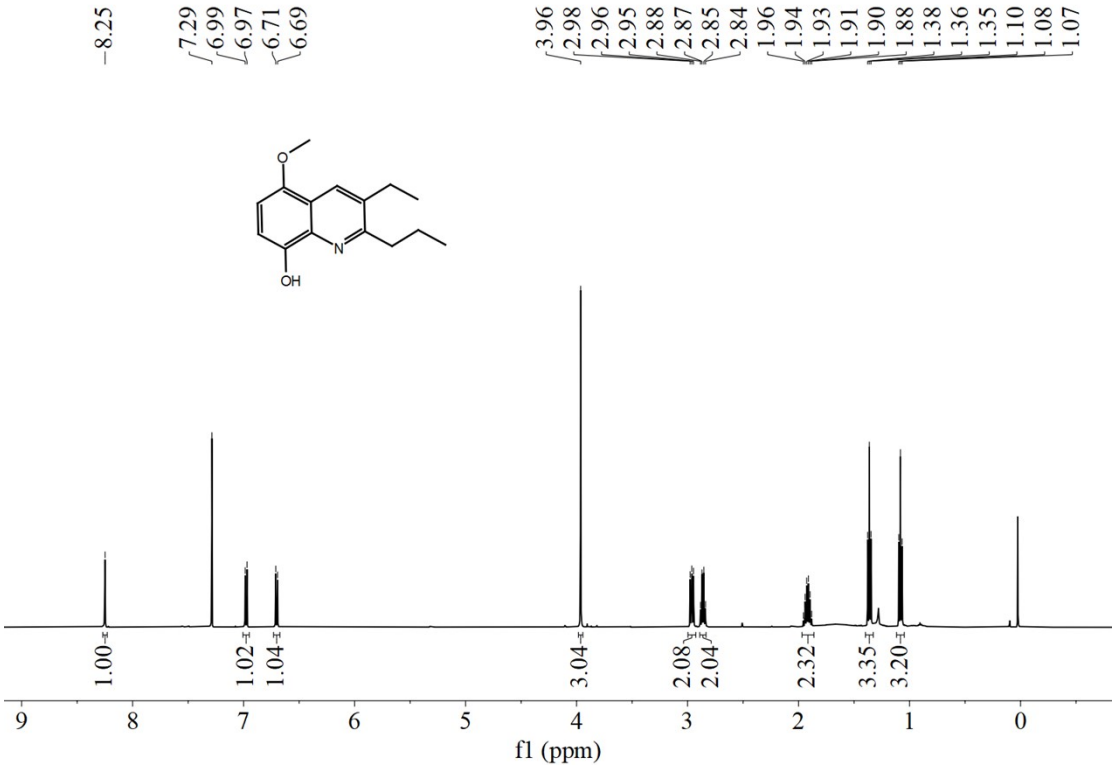
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ba**



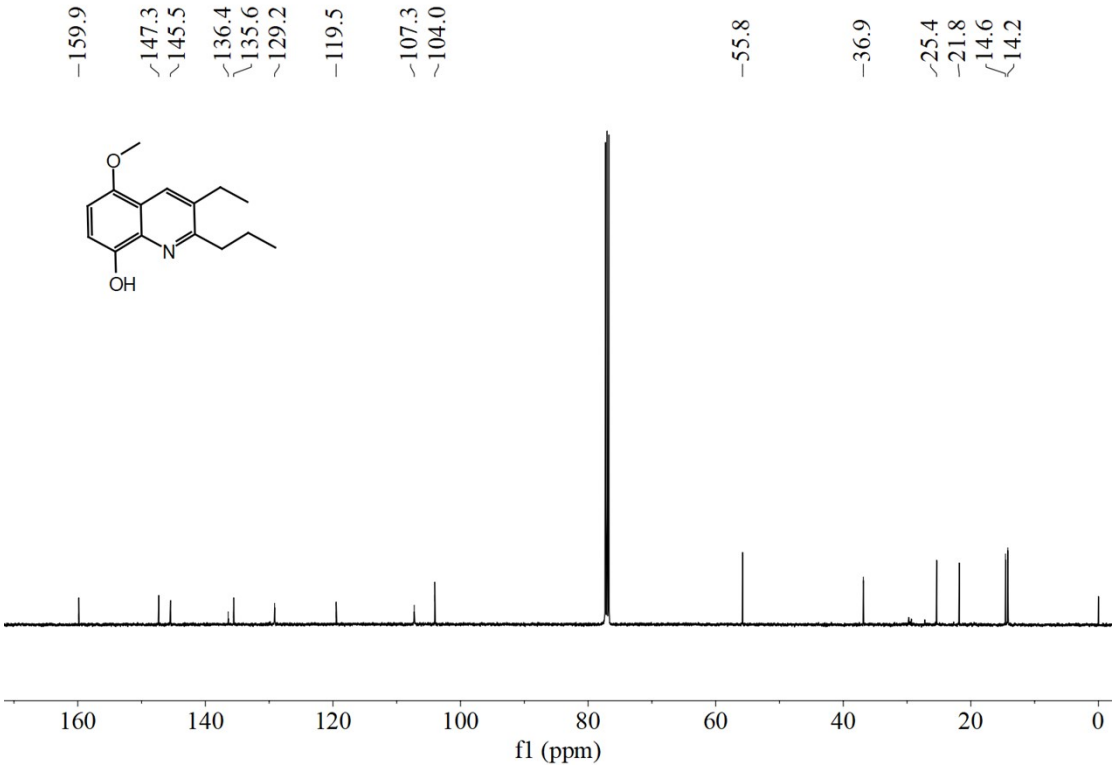
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ba**



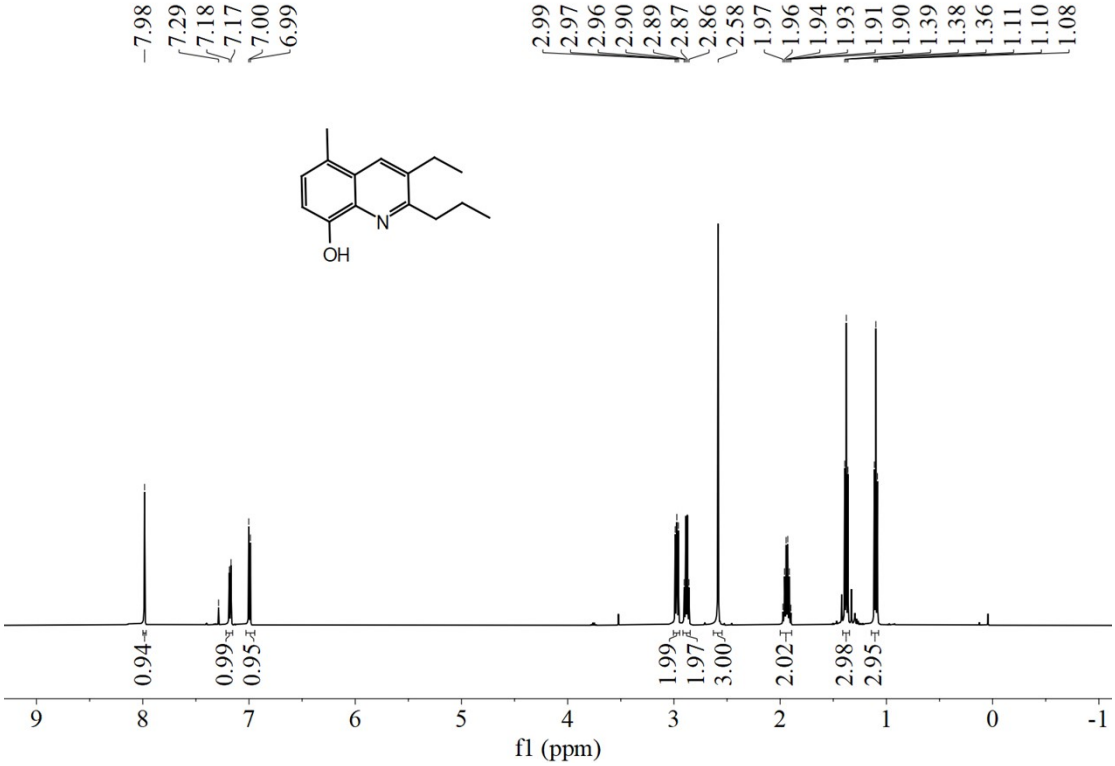
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ca**



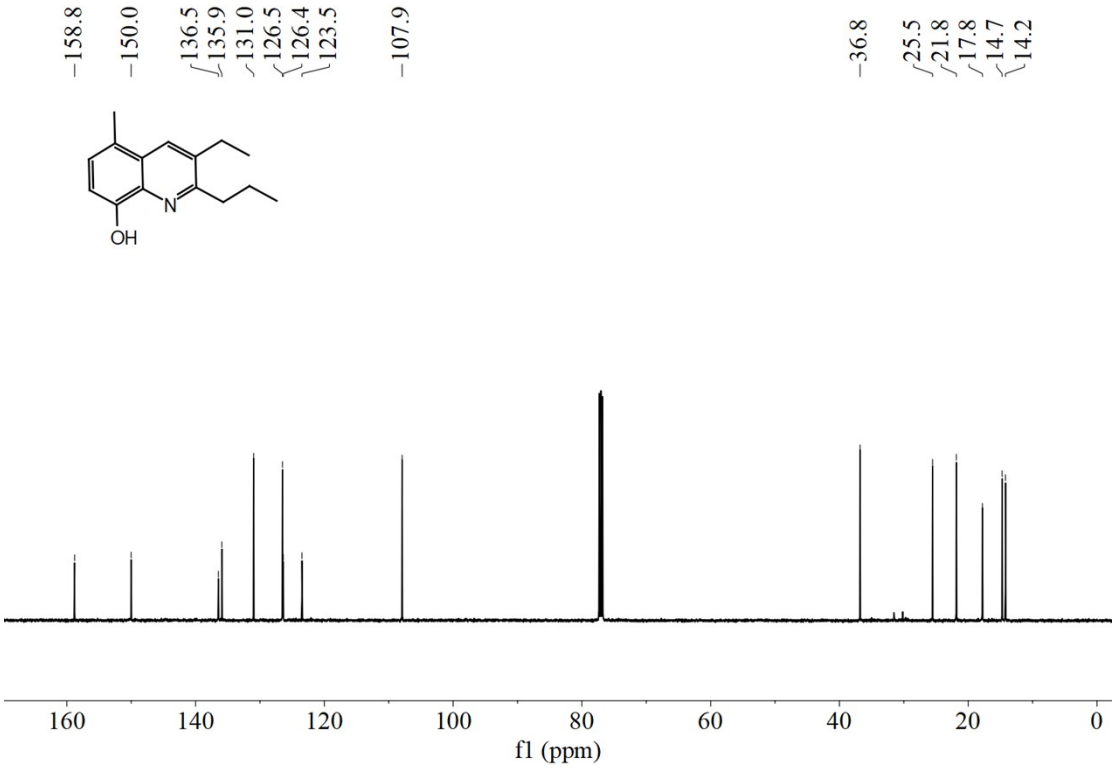
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ca**



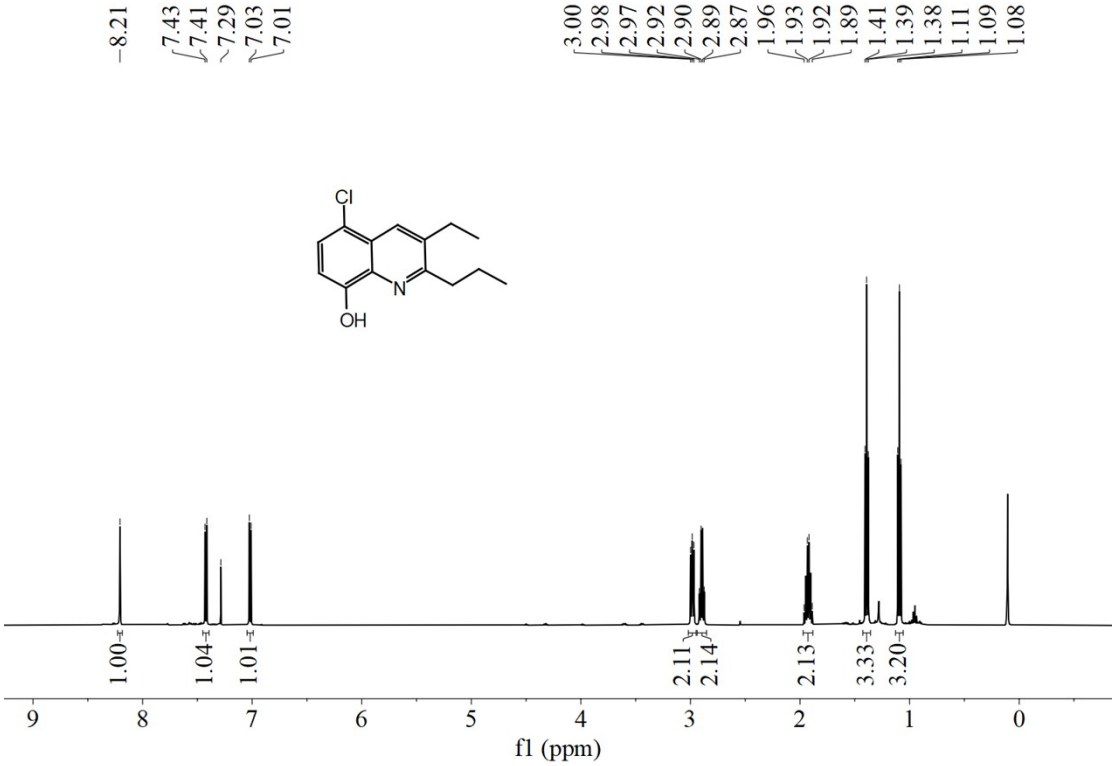
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3da**



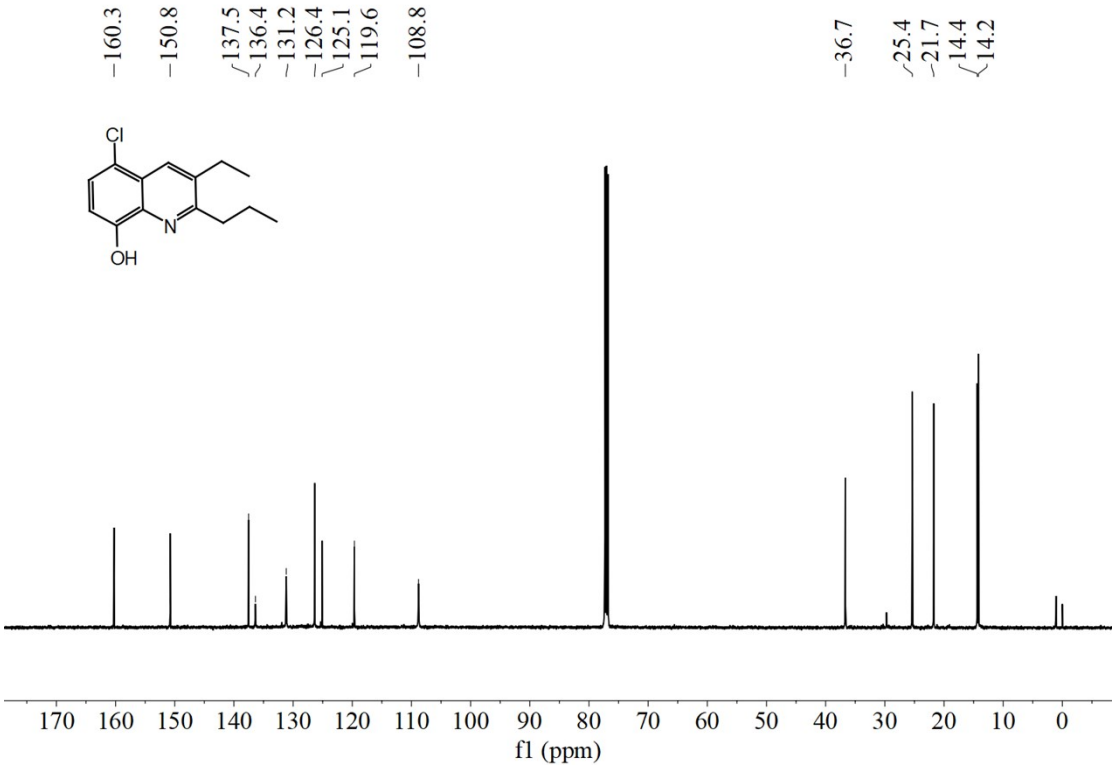
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3da**



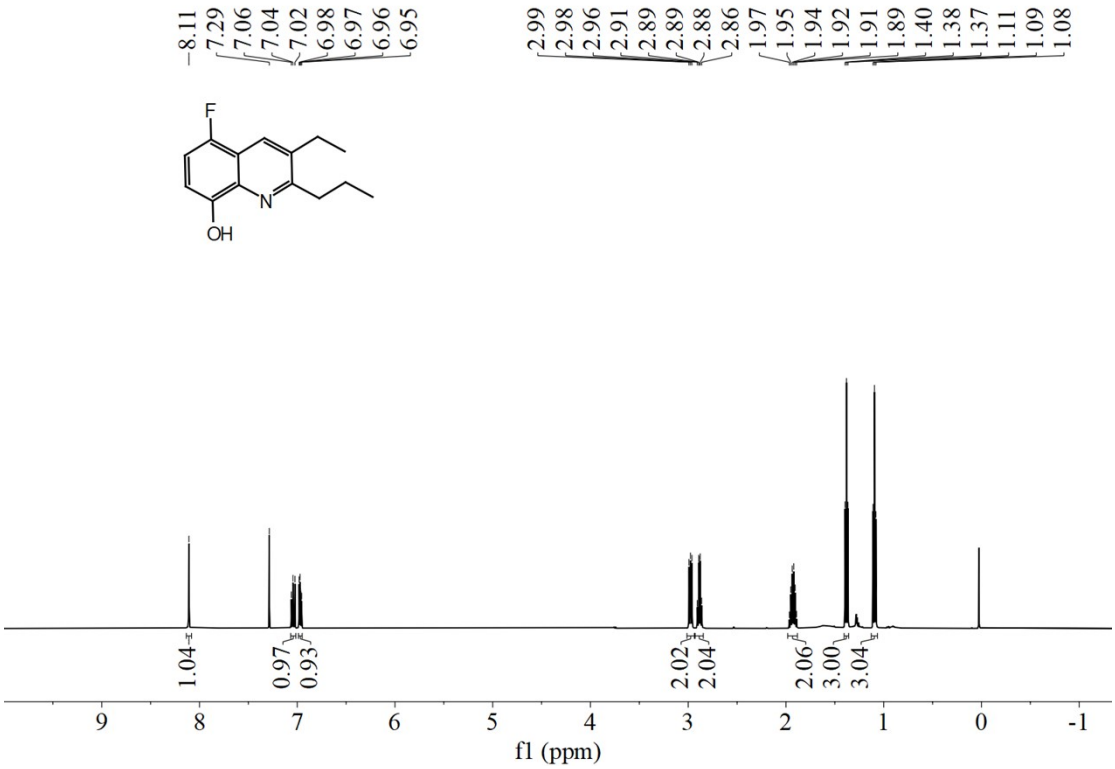
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ea**



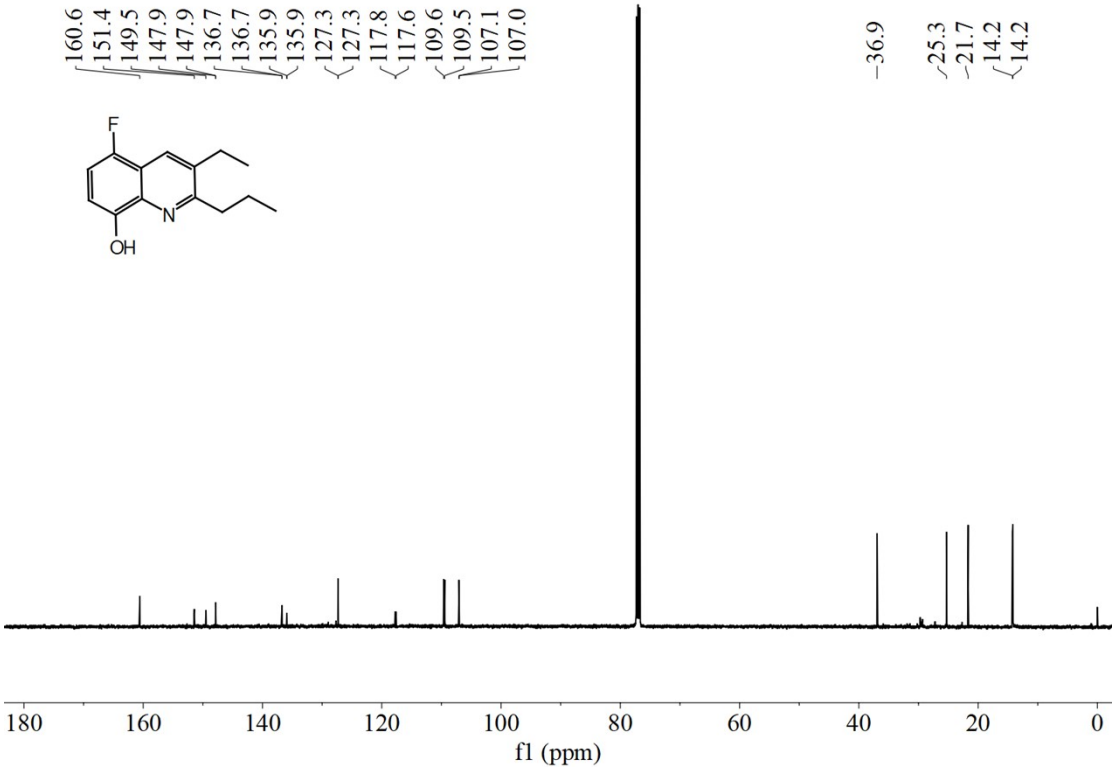
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ea**



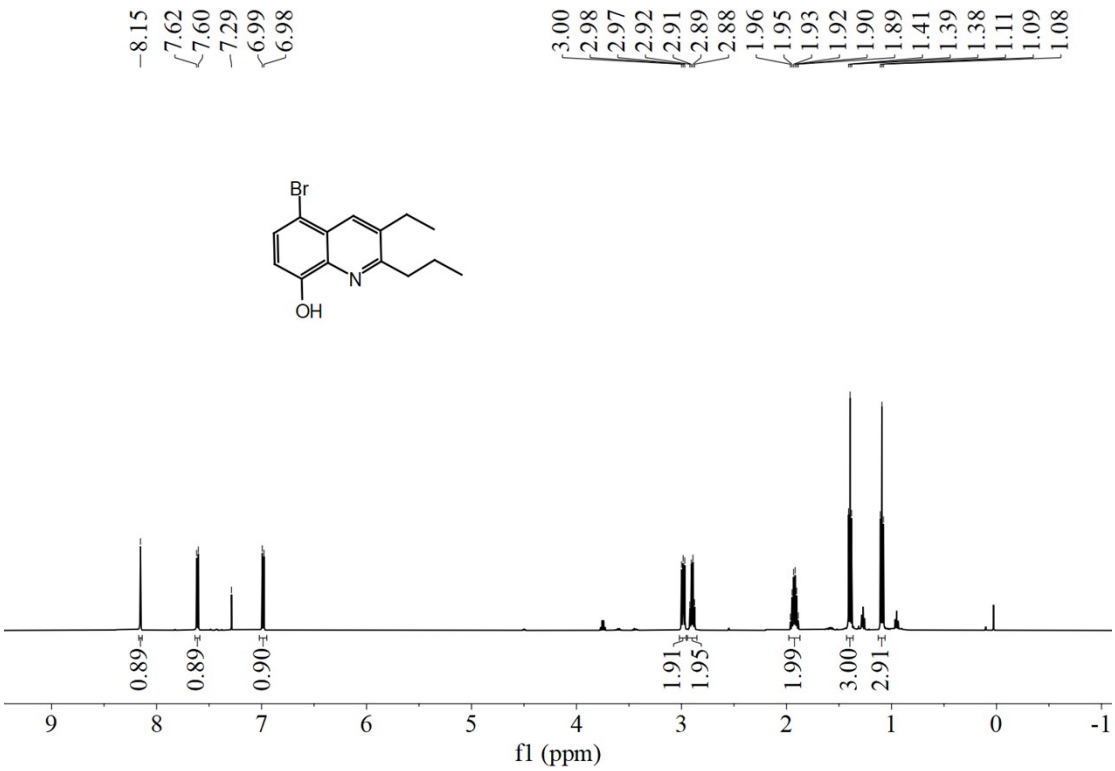
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3fa**



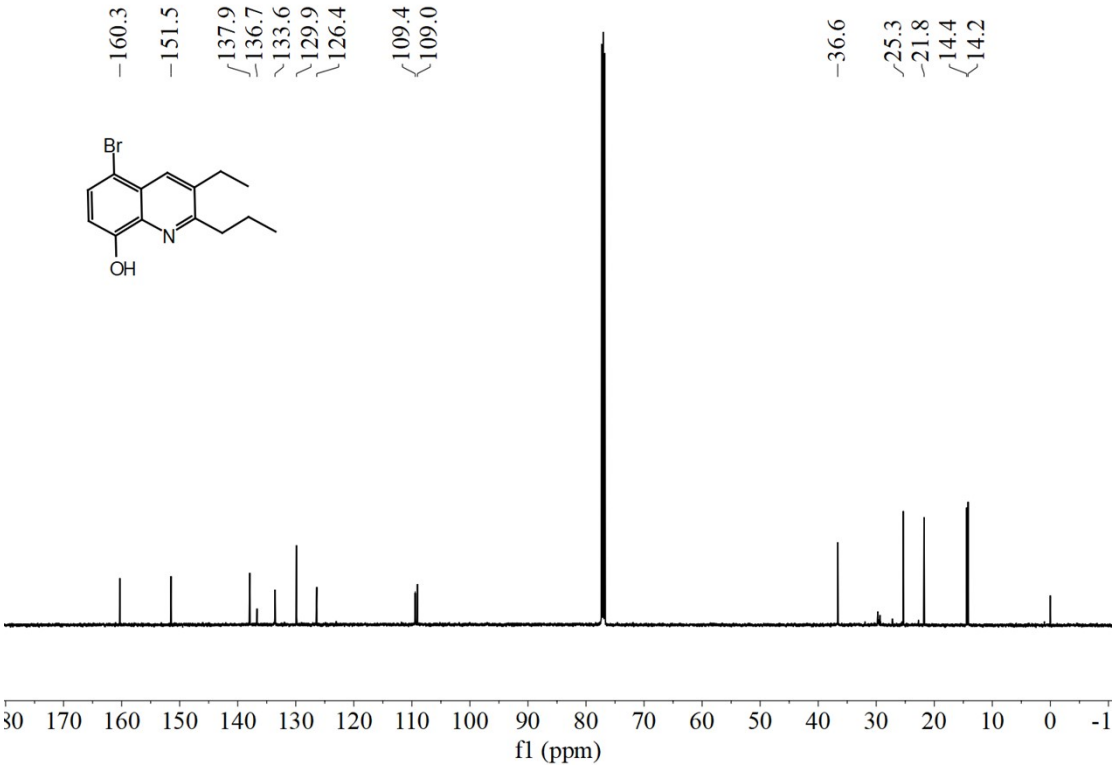
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3fa**



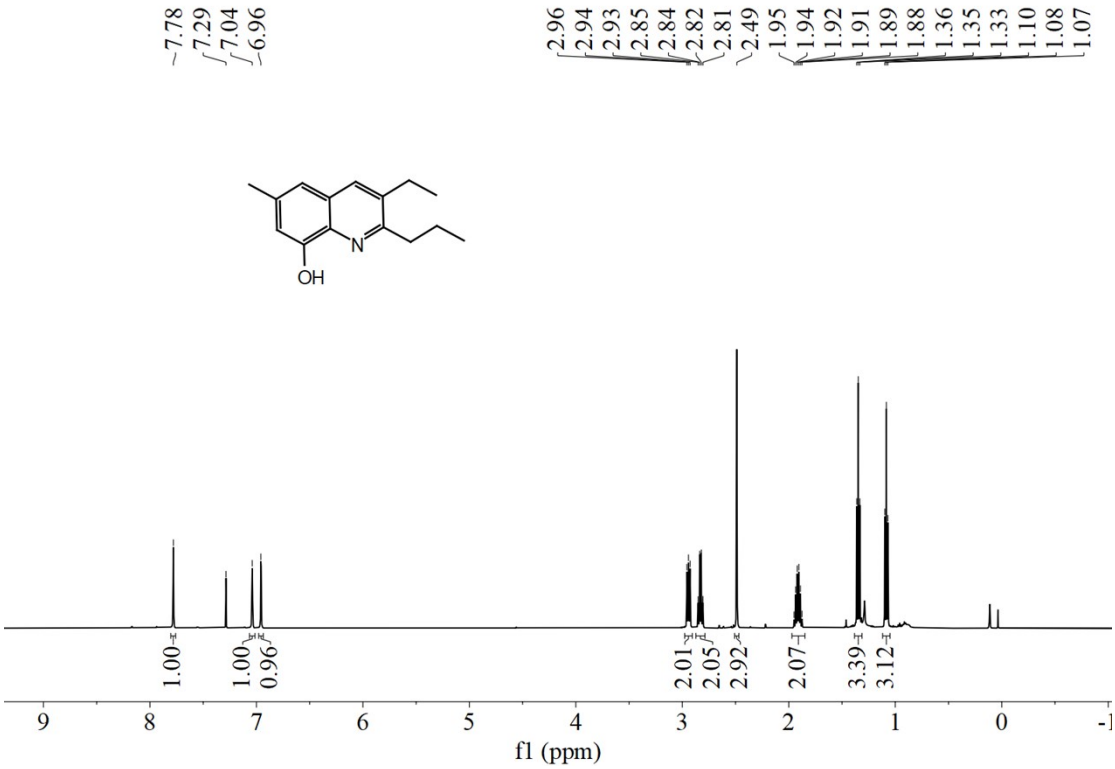
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ga**



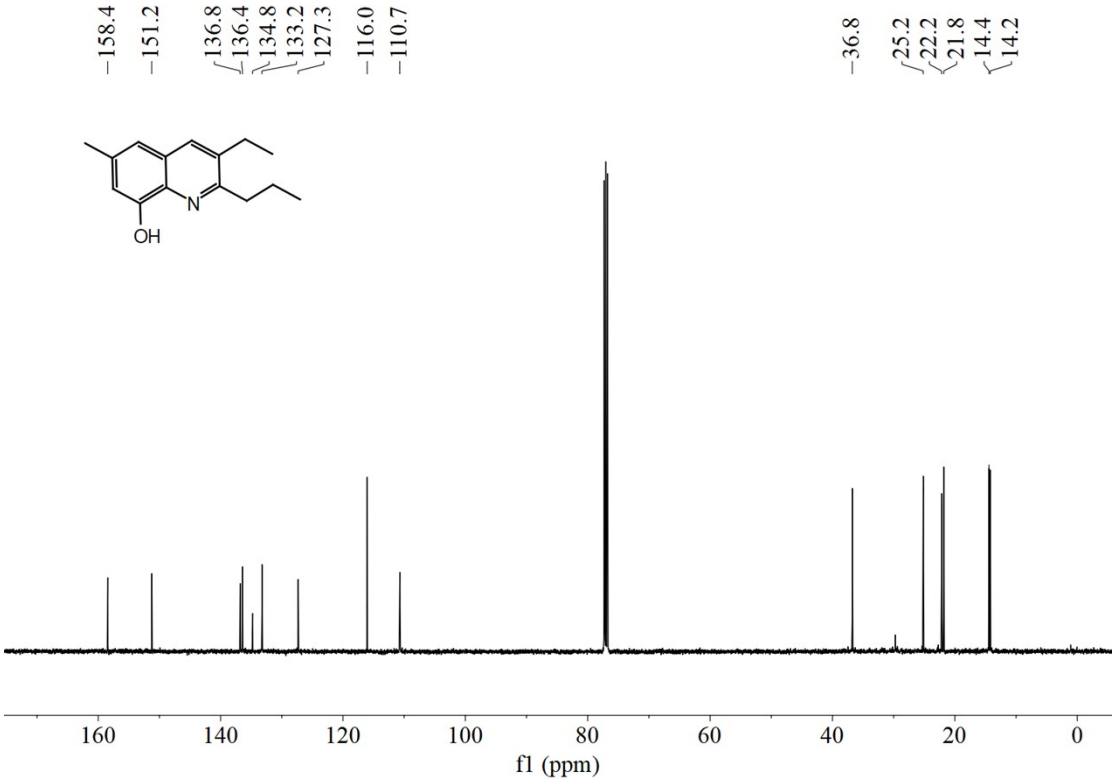
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ga**



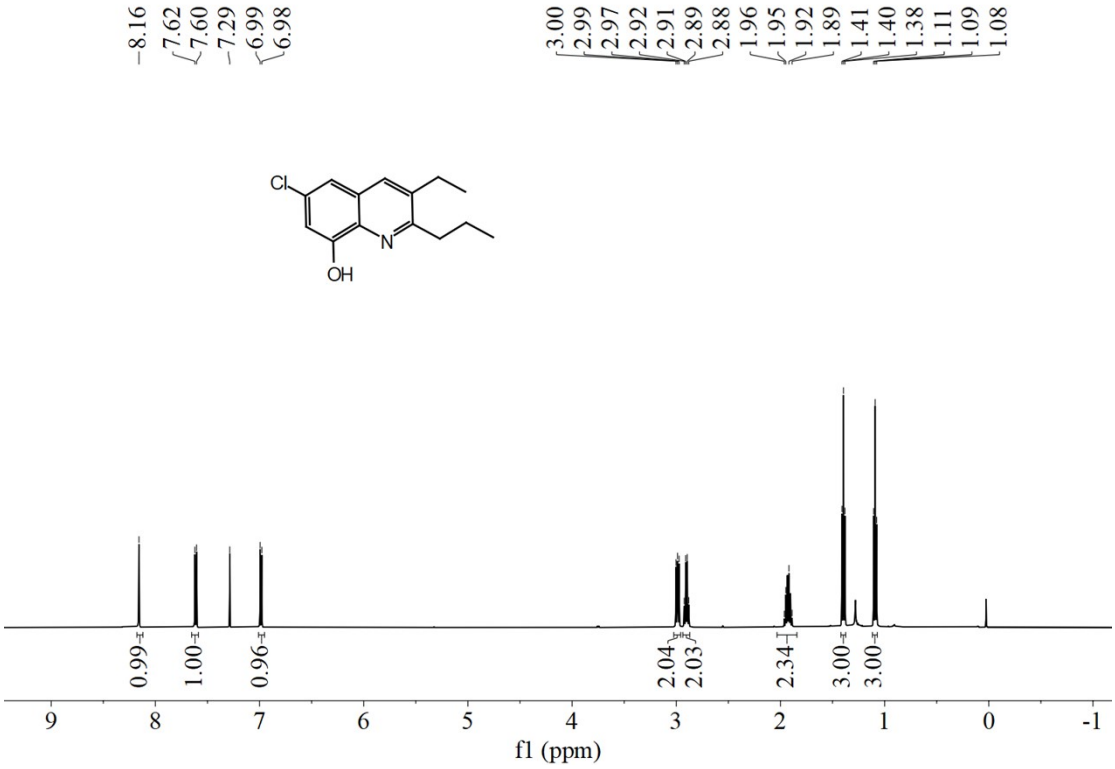
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ha**



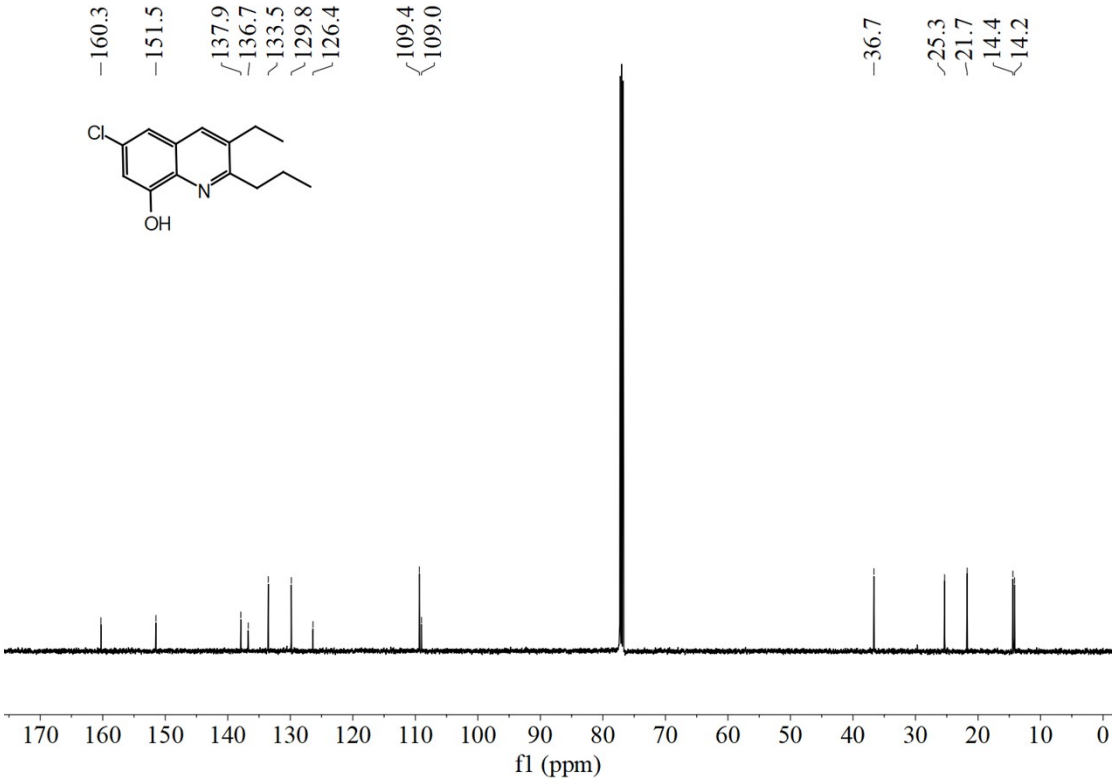
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ha**



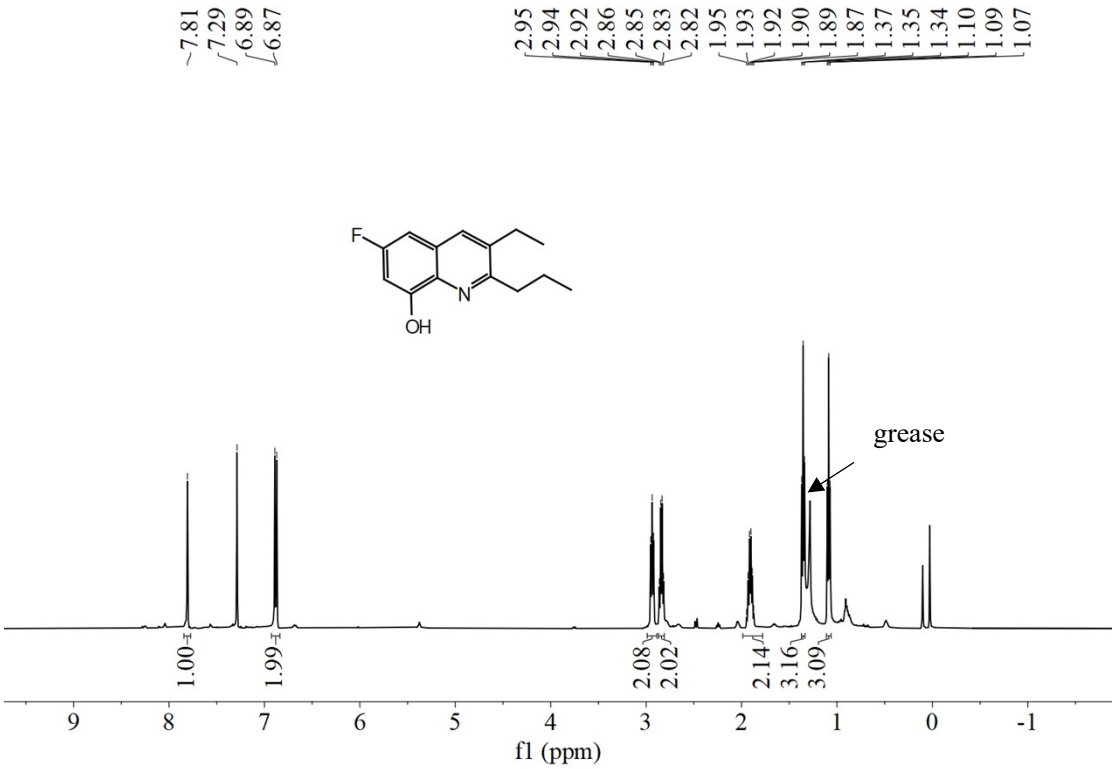
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ia**



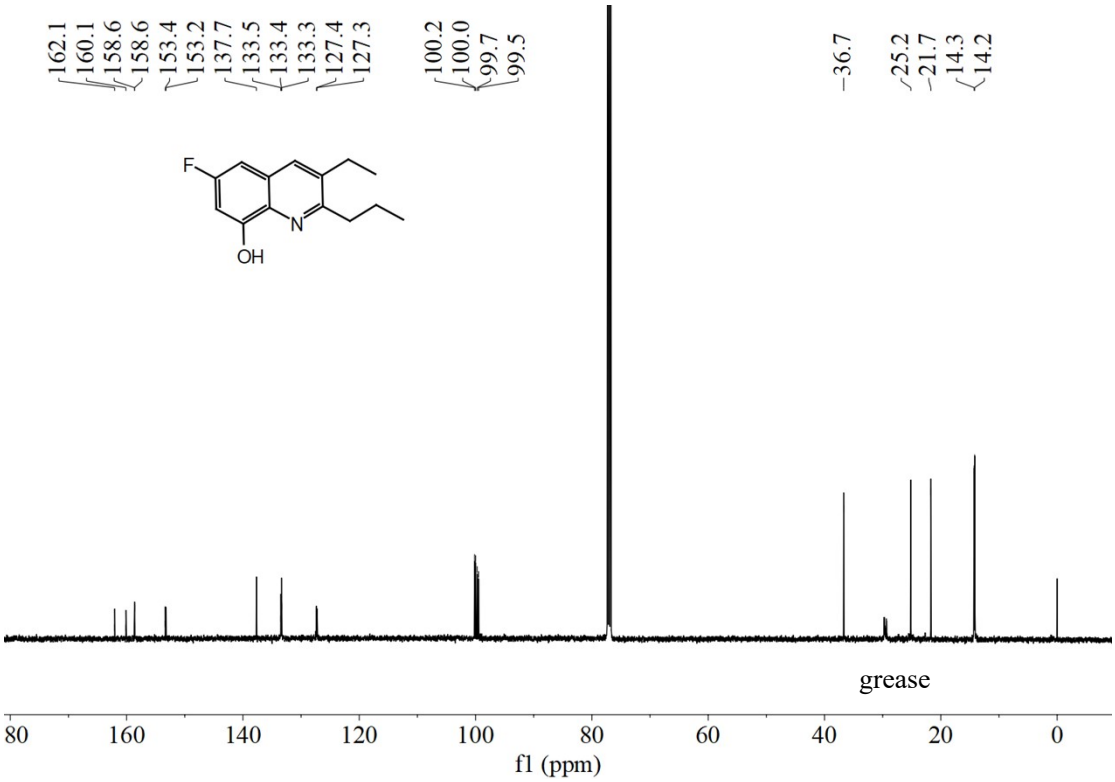
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ia**



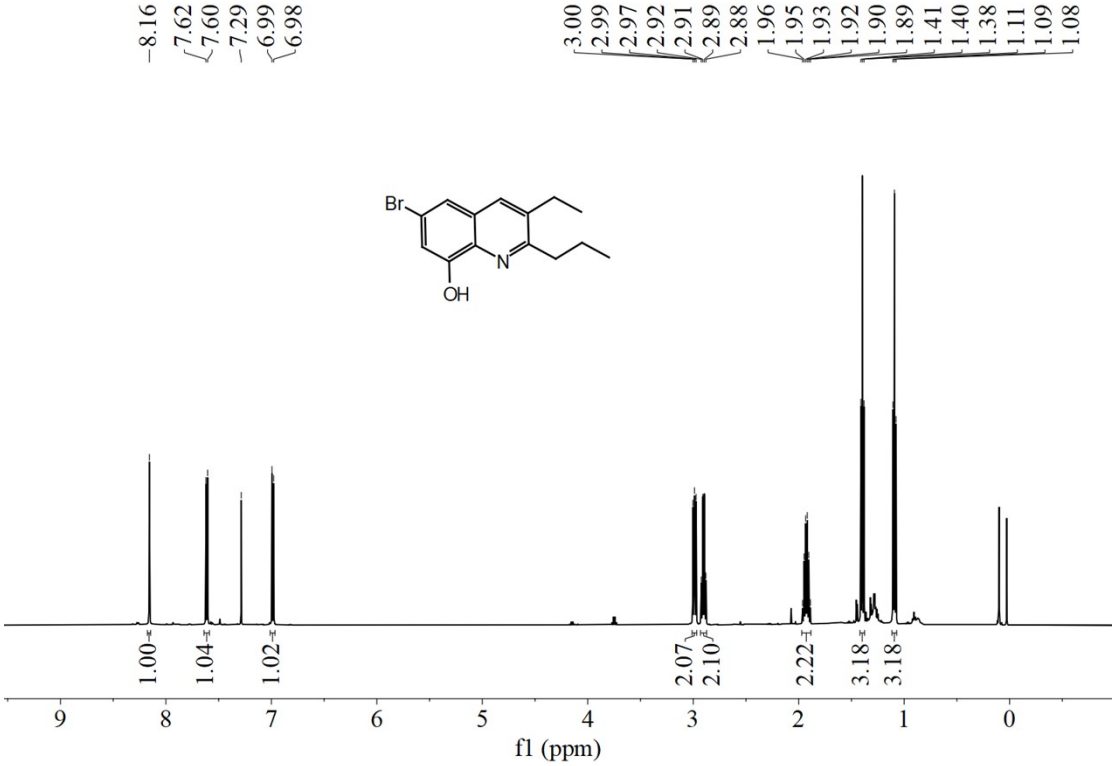
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ja**



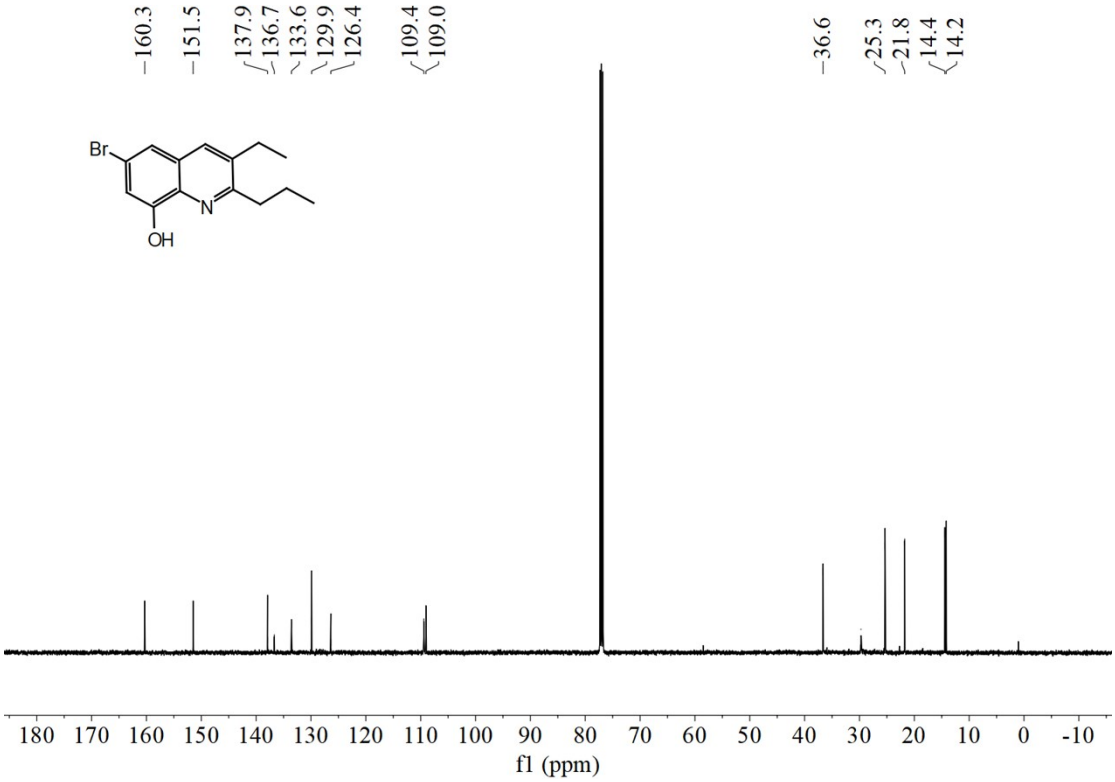
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ja**



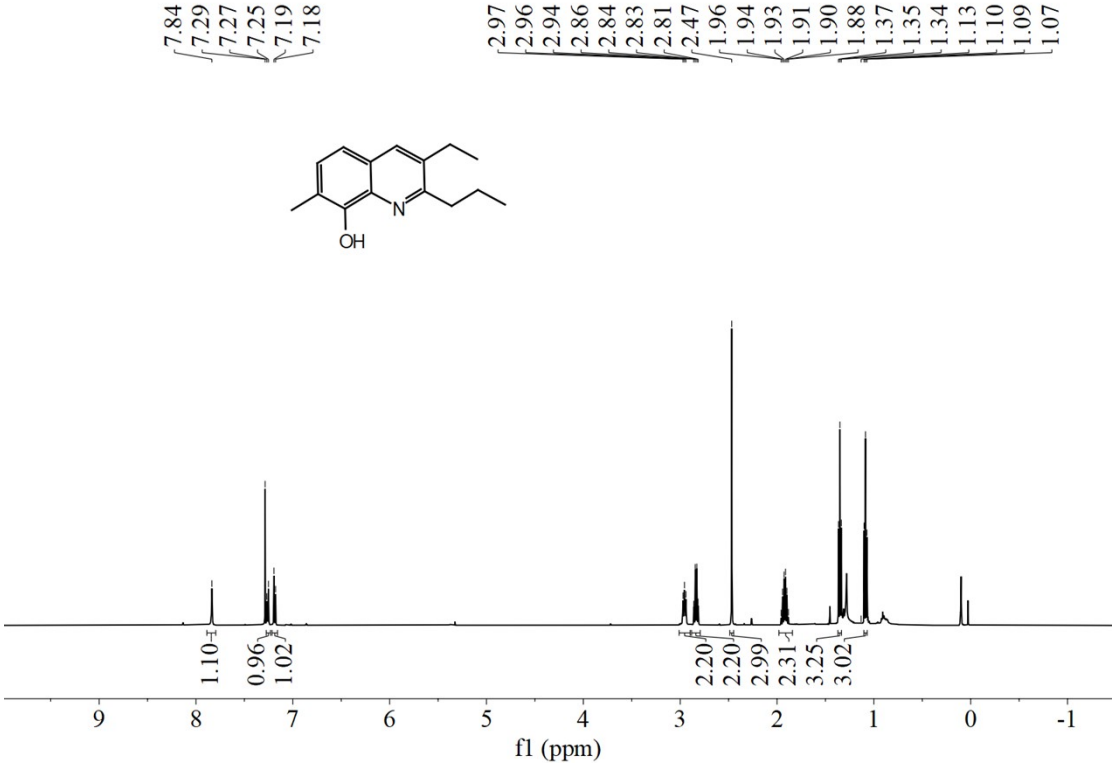
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ka**



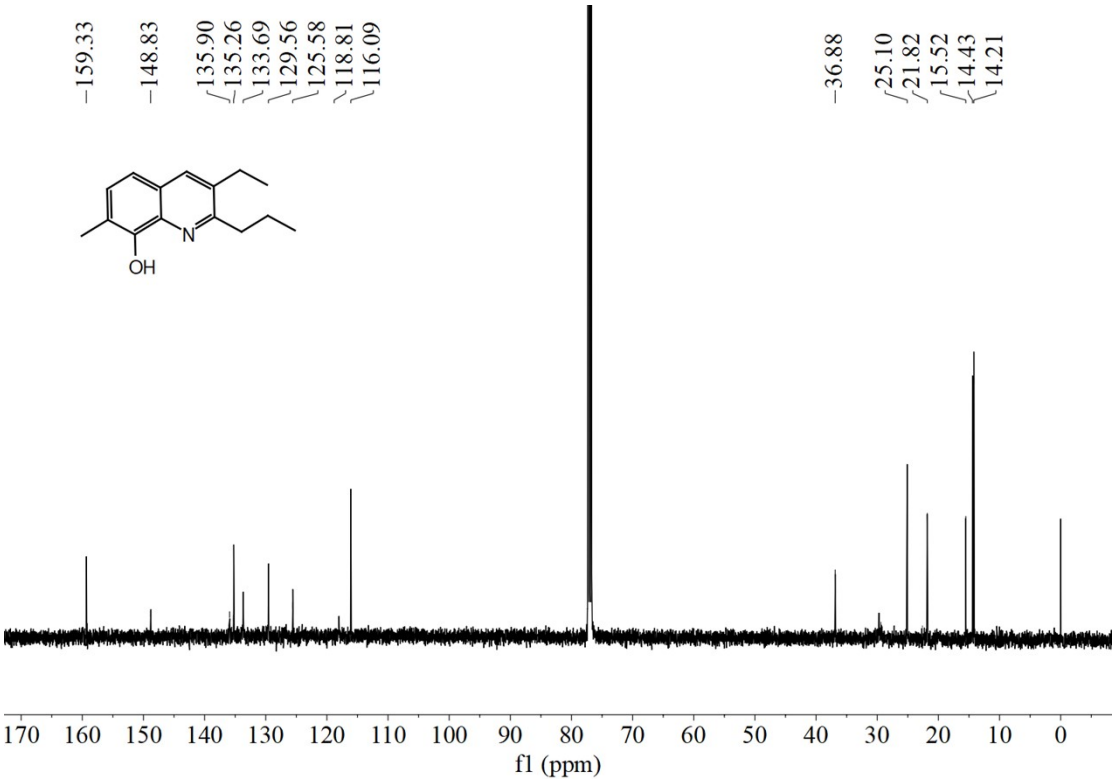
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ka**



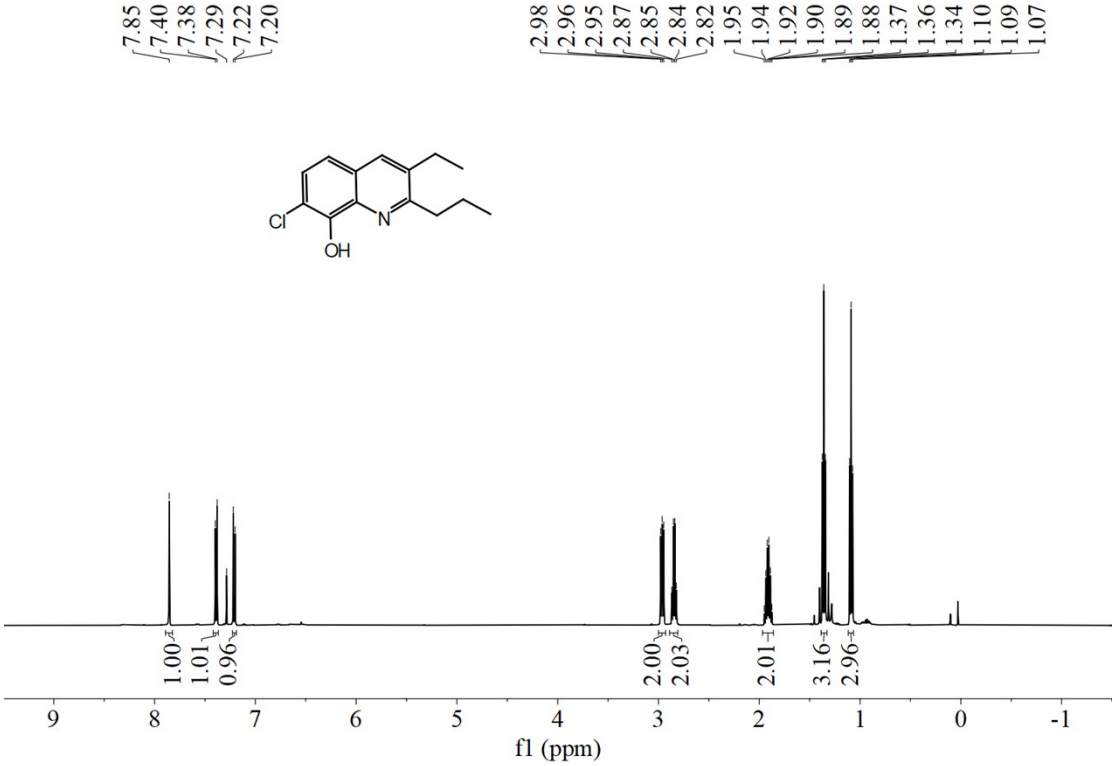
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3la**



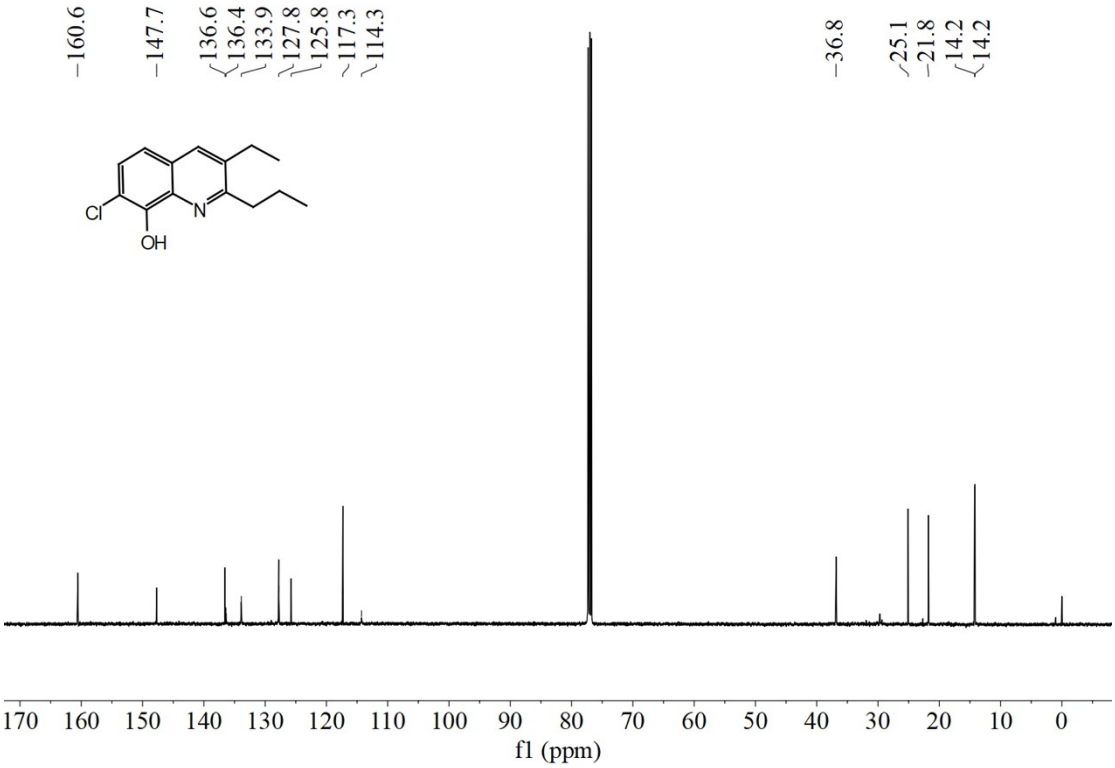
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3la**



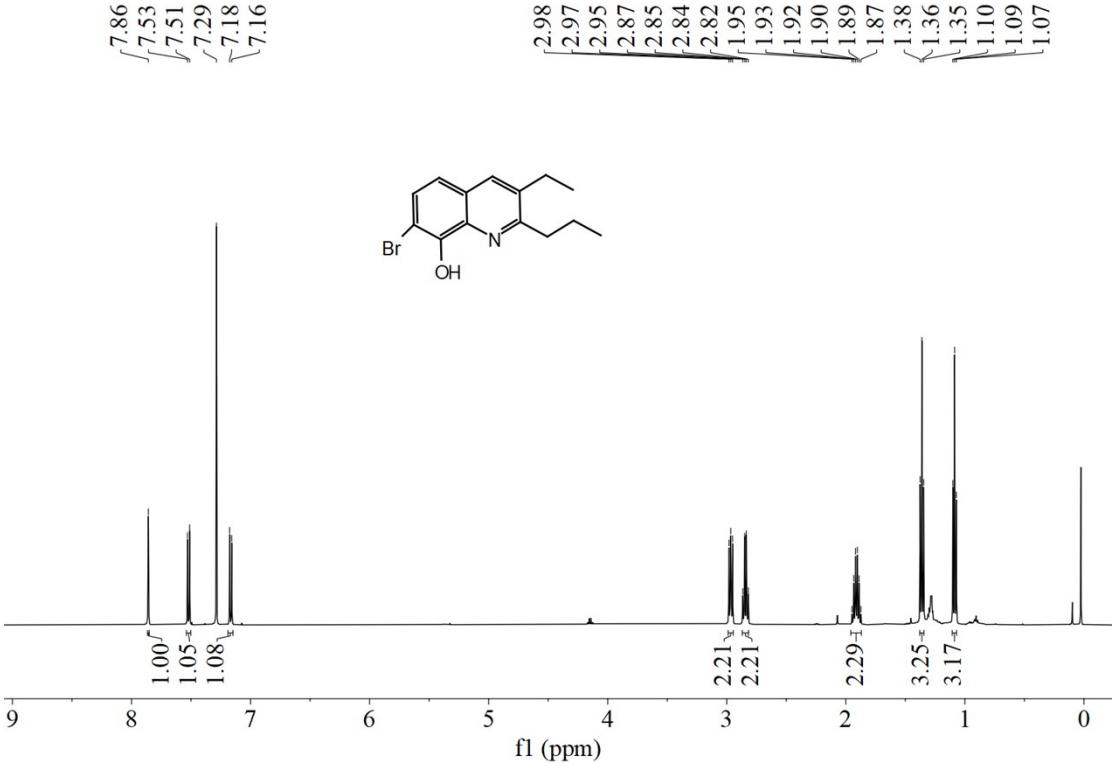
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ma**



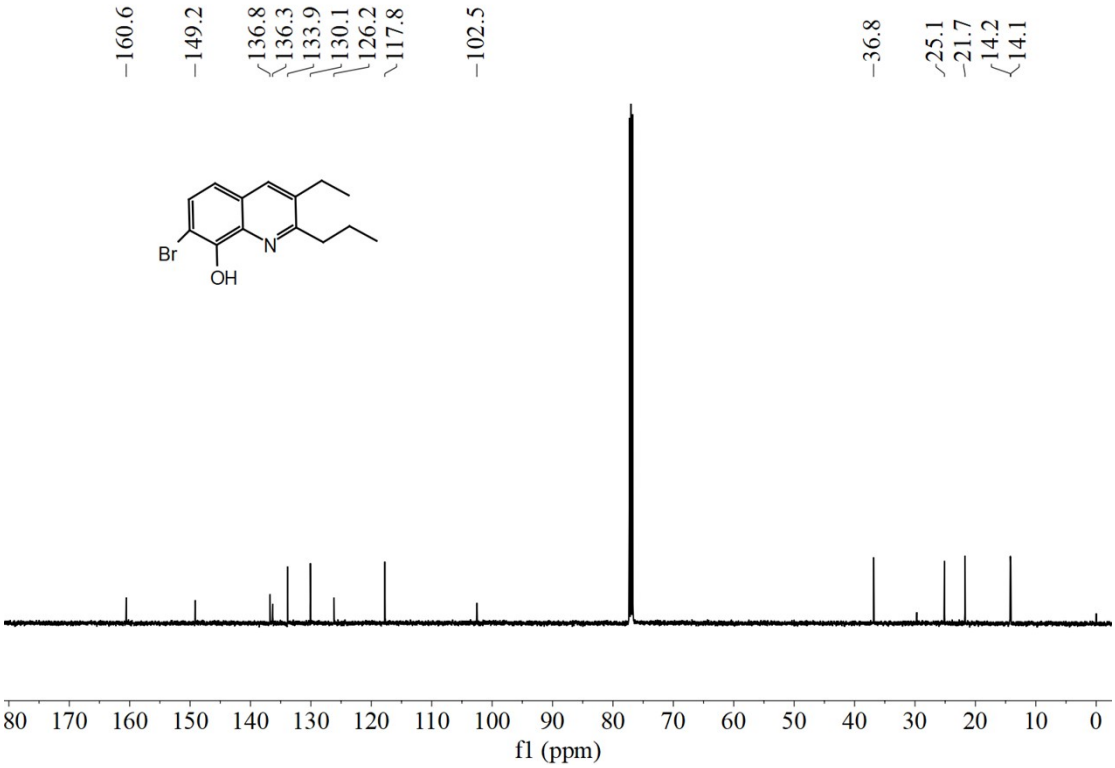
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ma**



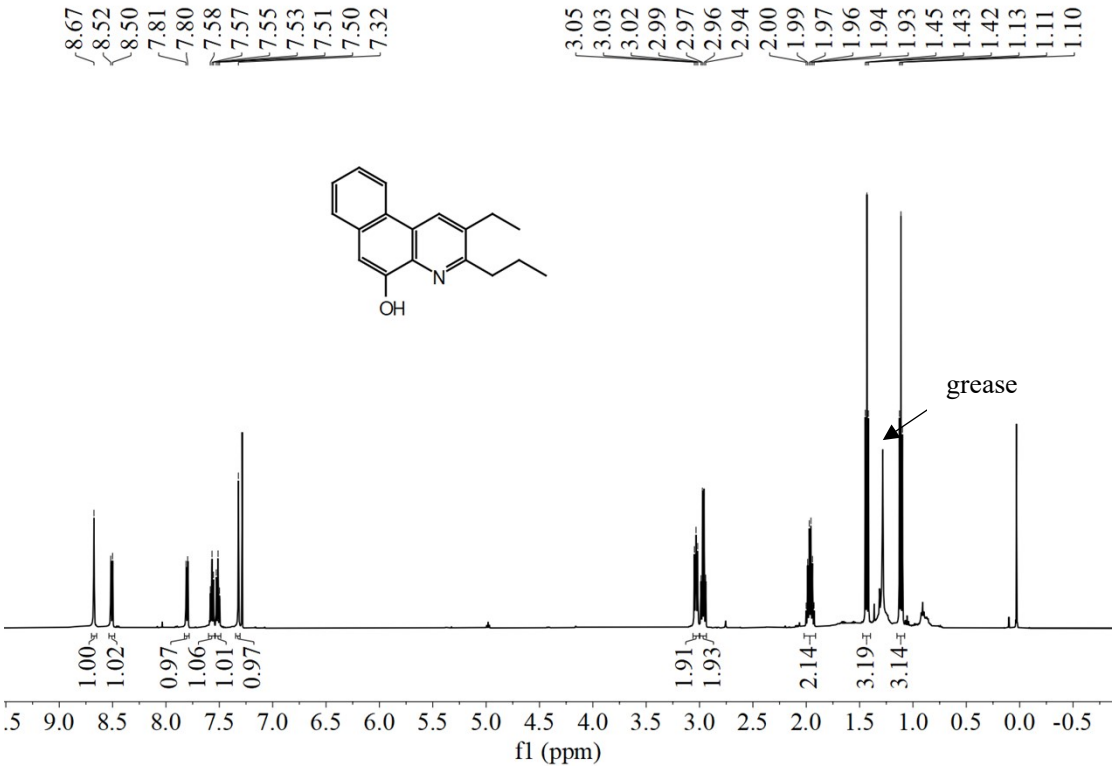
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3na**



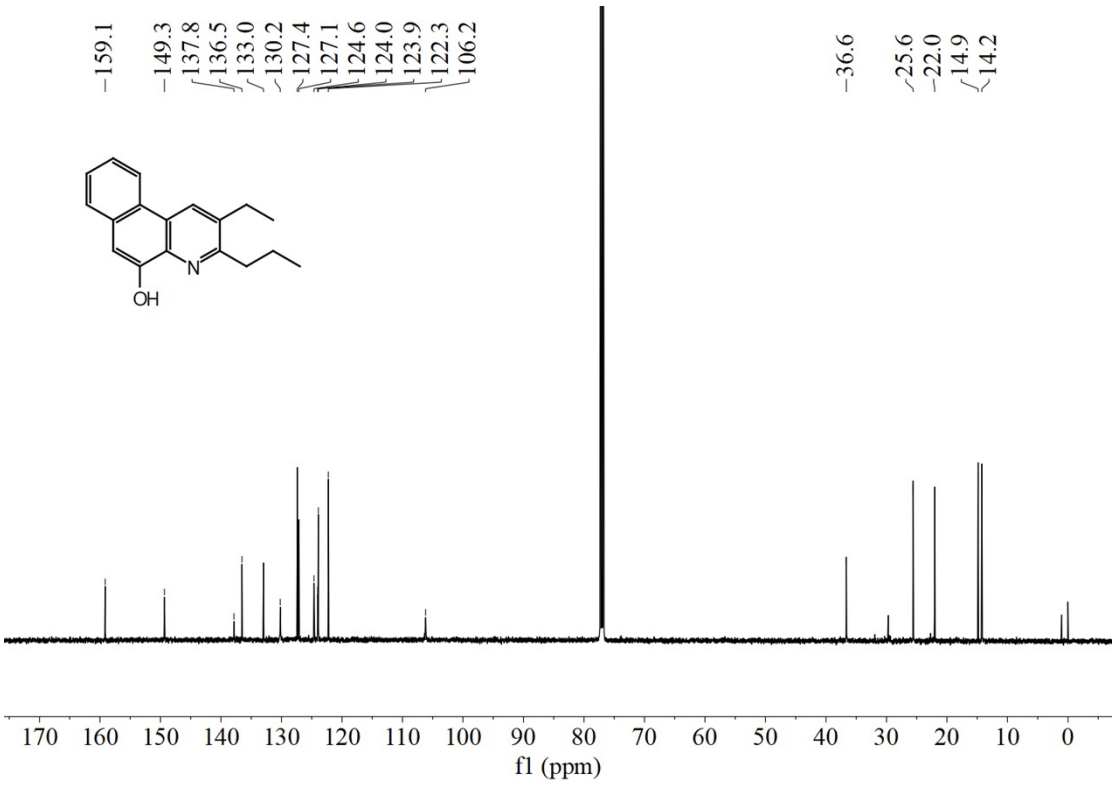
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3na**



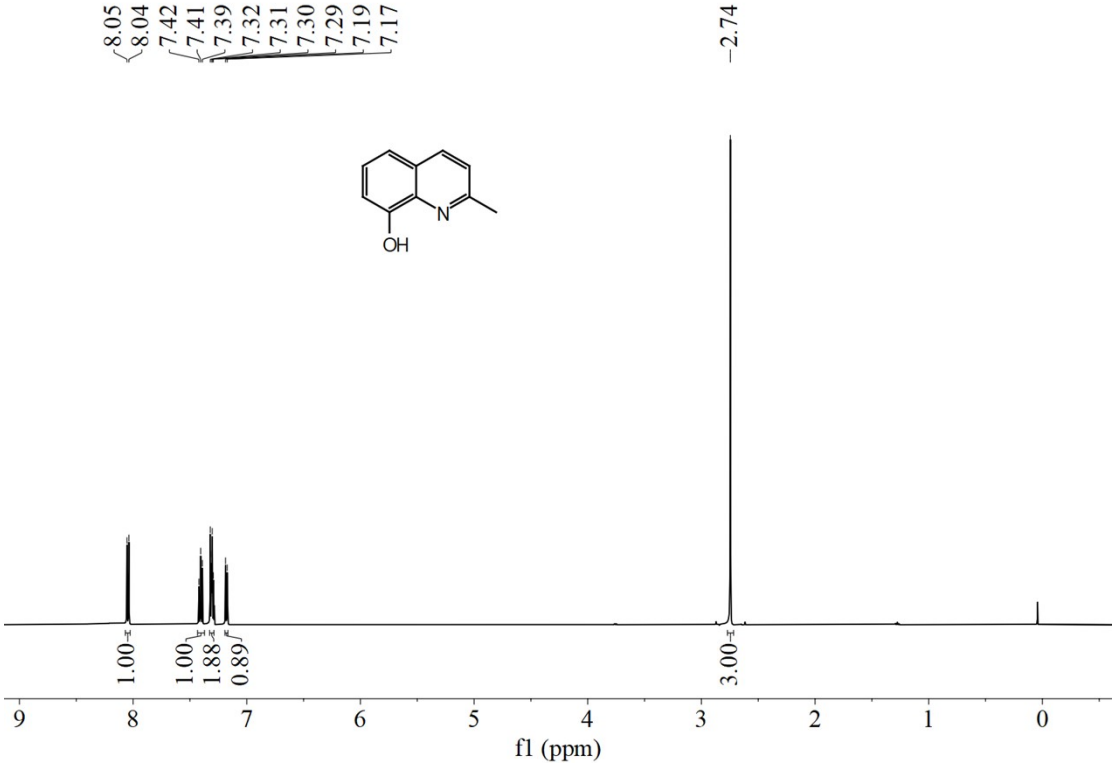
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3oa**



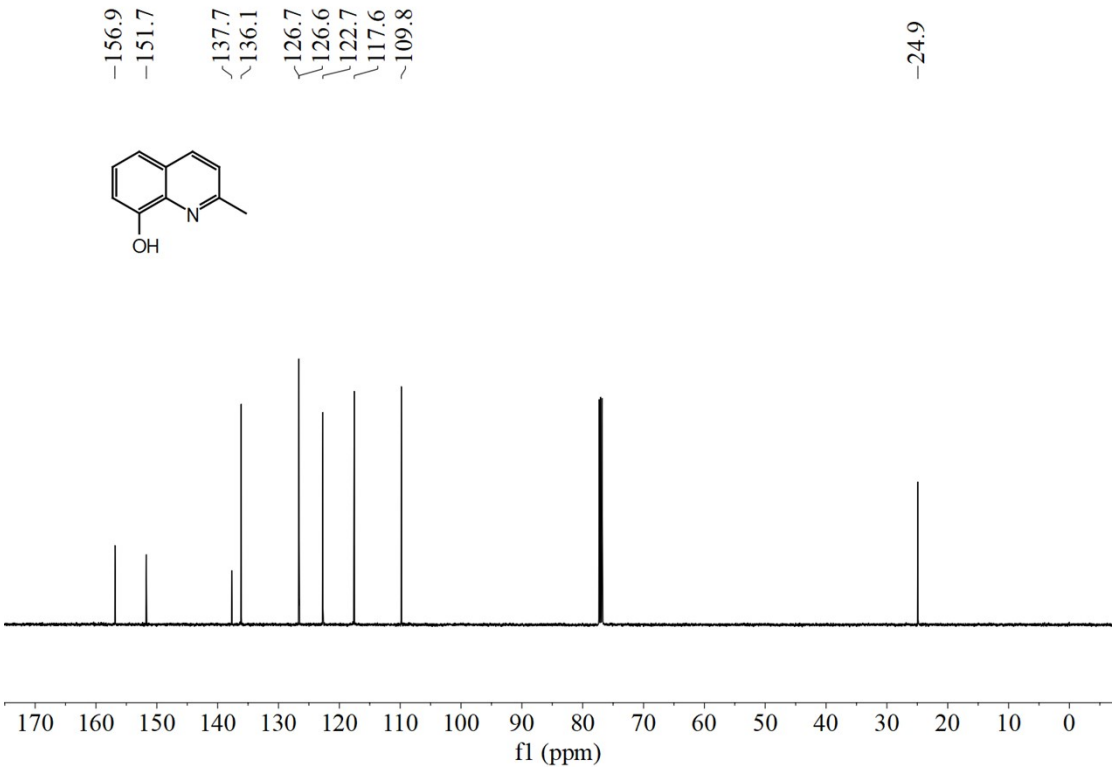
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3oa**



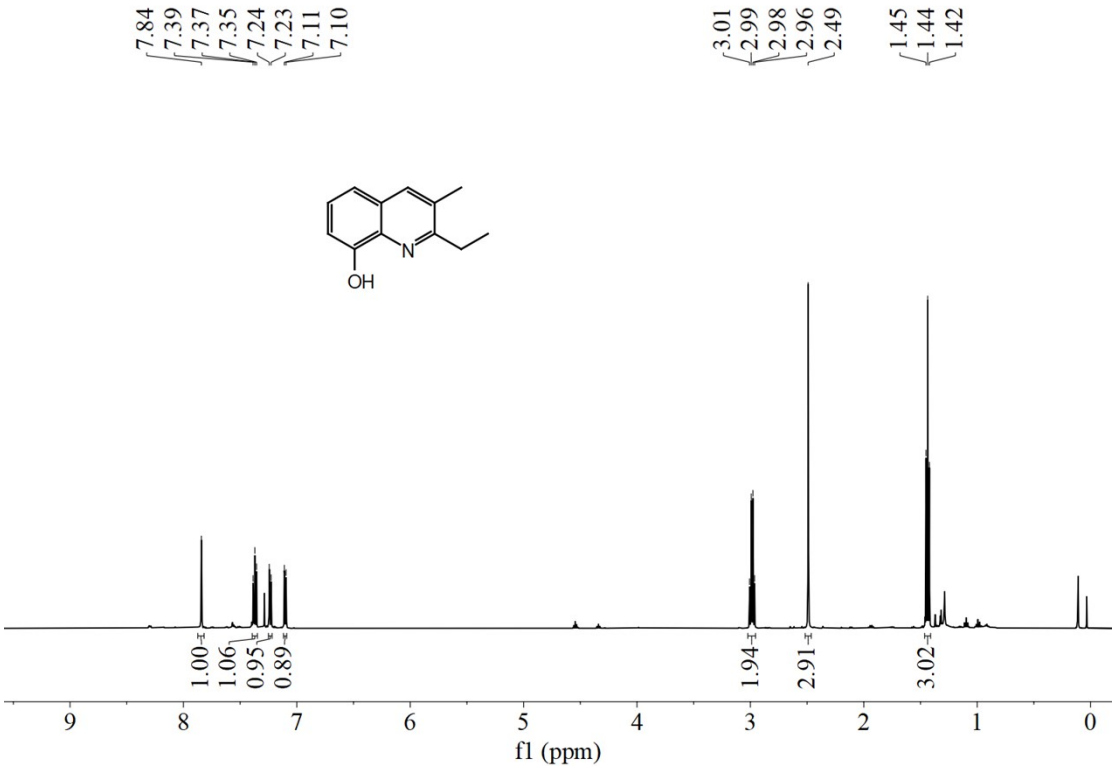
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ab**



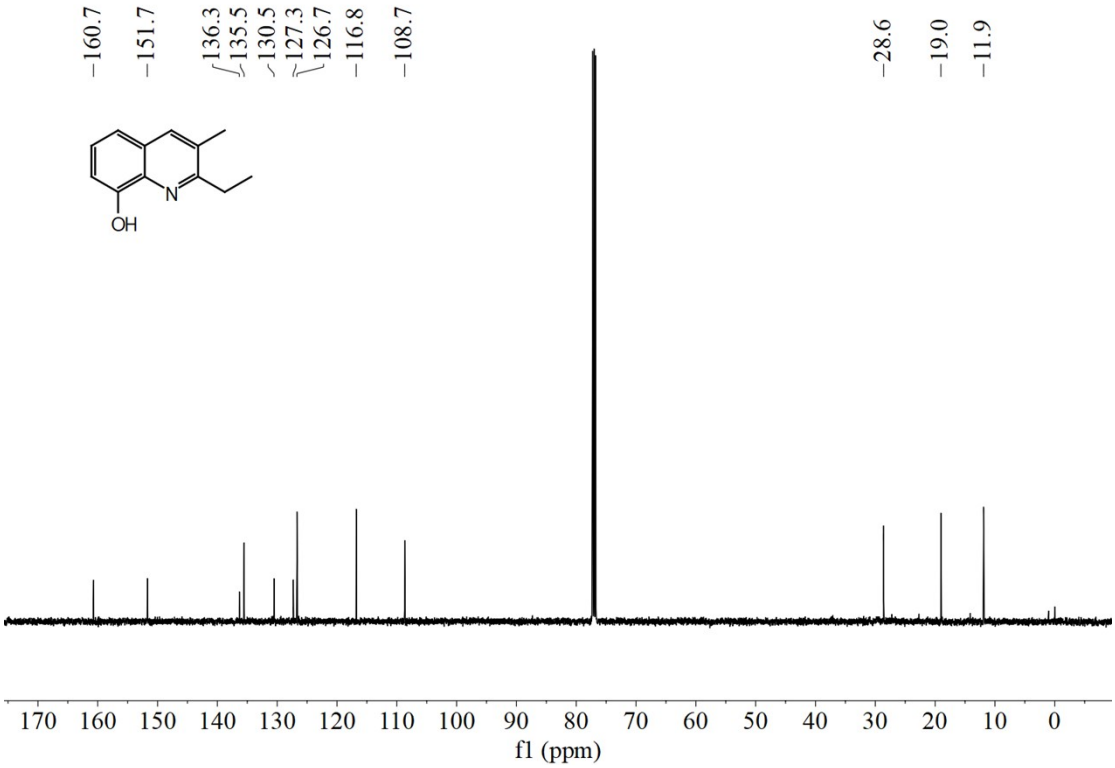
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ab**



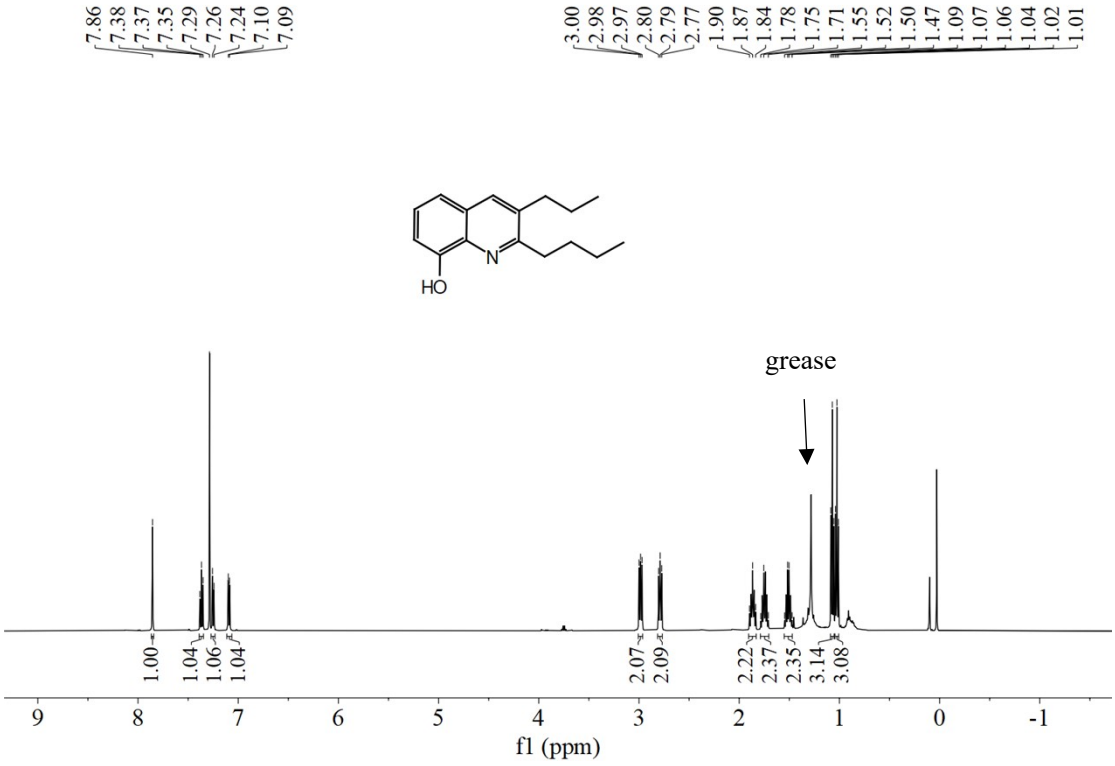
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ac**



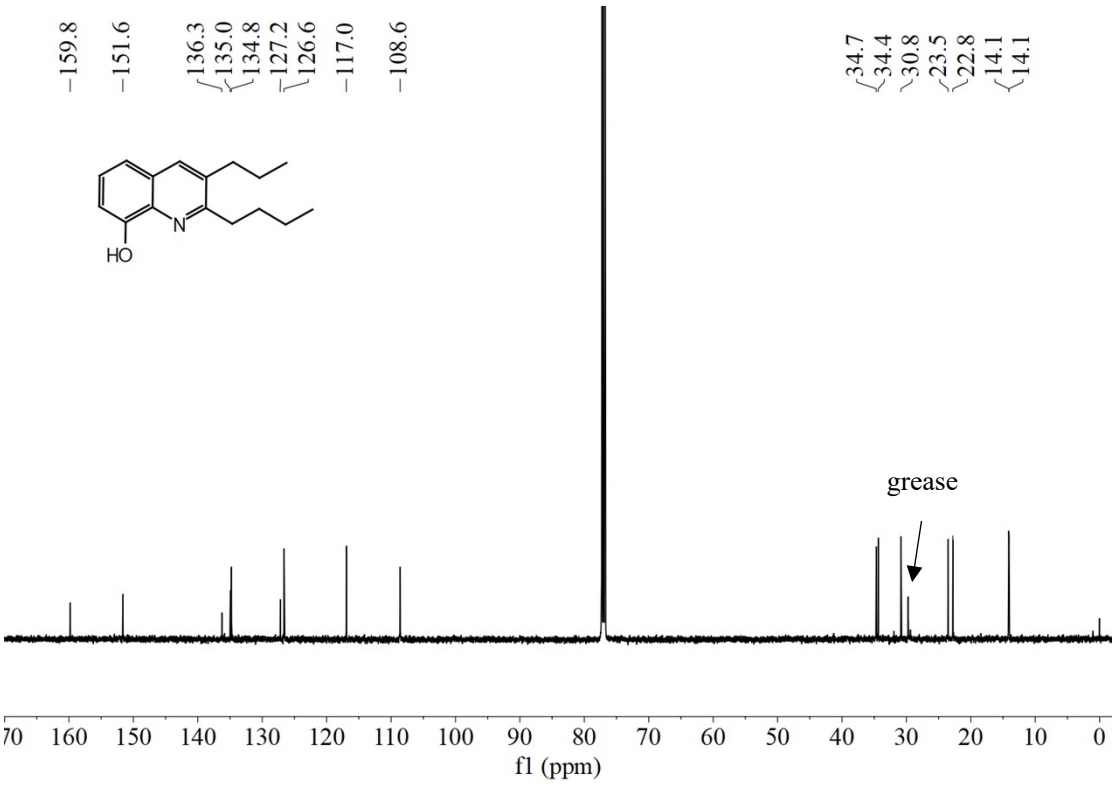
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ac**



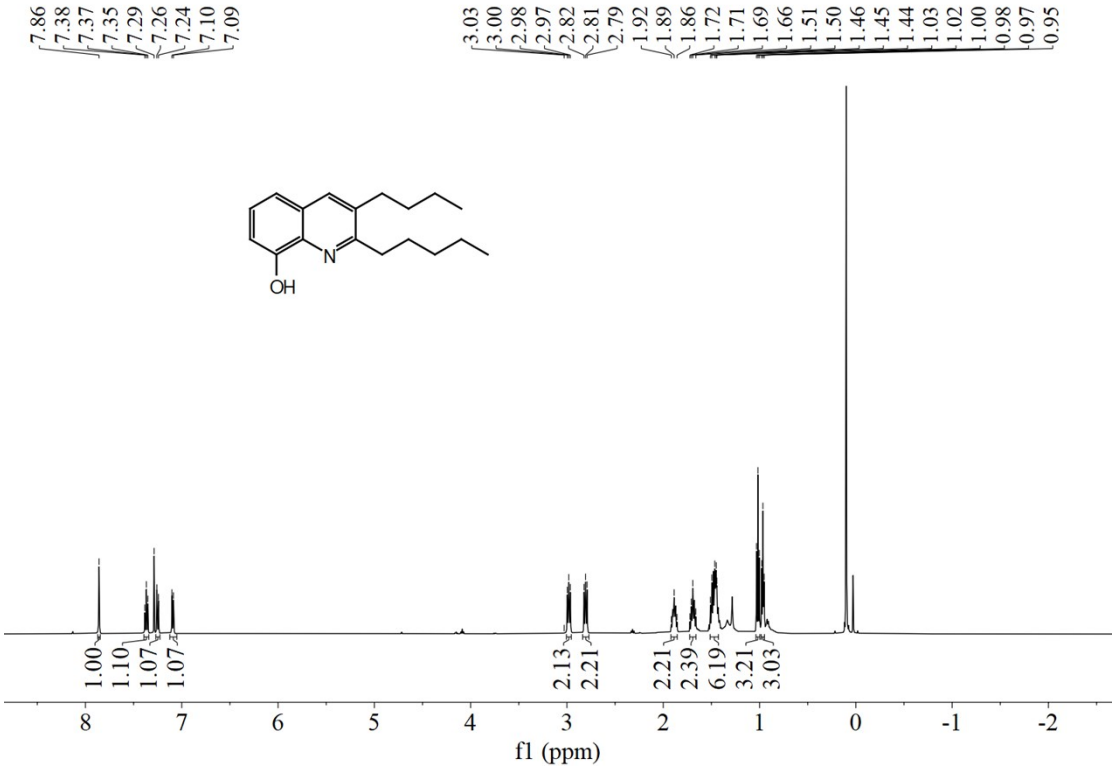
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ad**



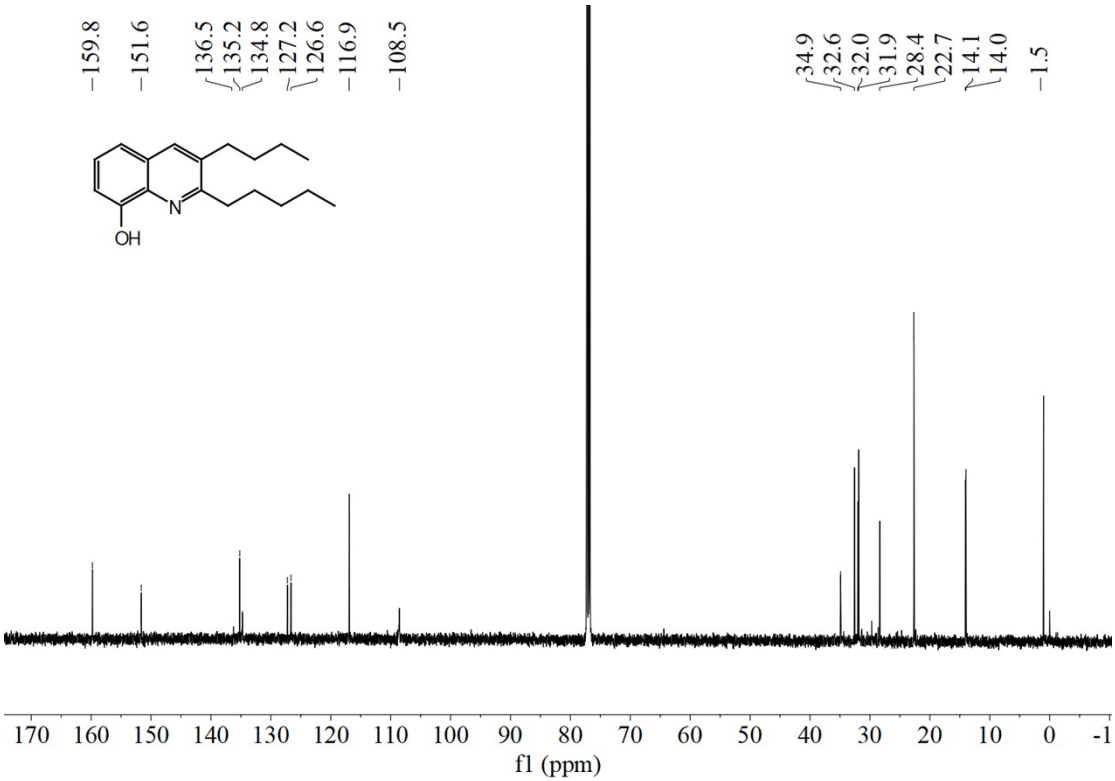
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ad**



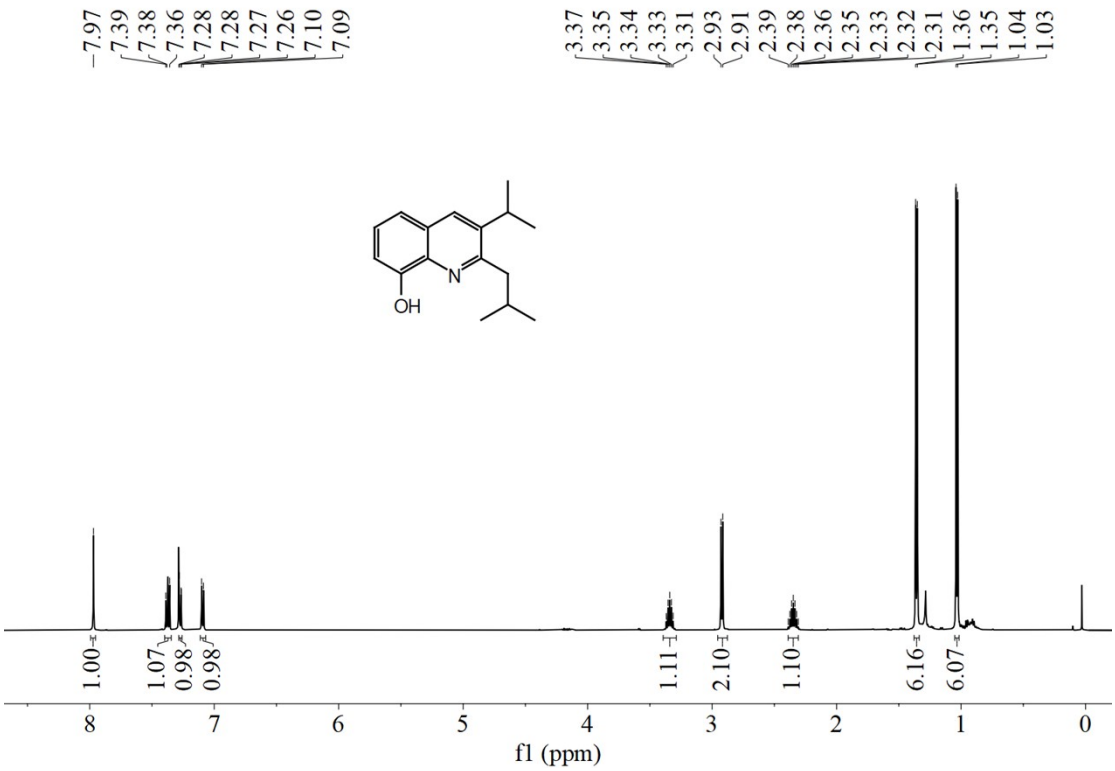
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3ae**



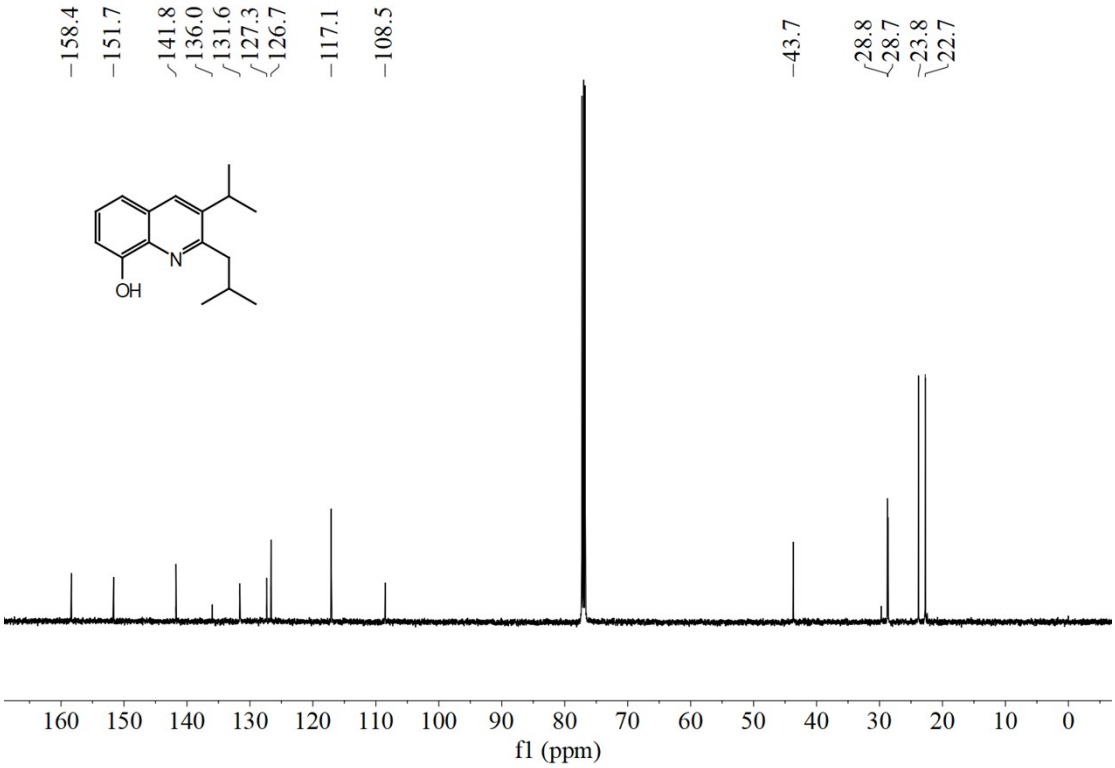
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3ae**



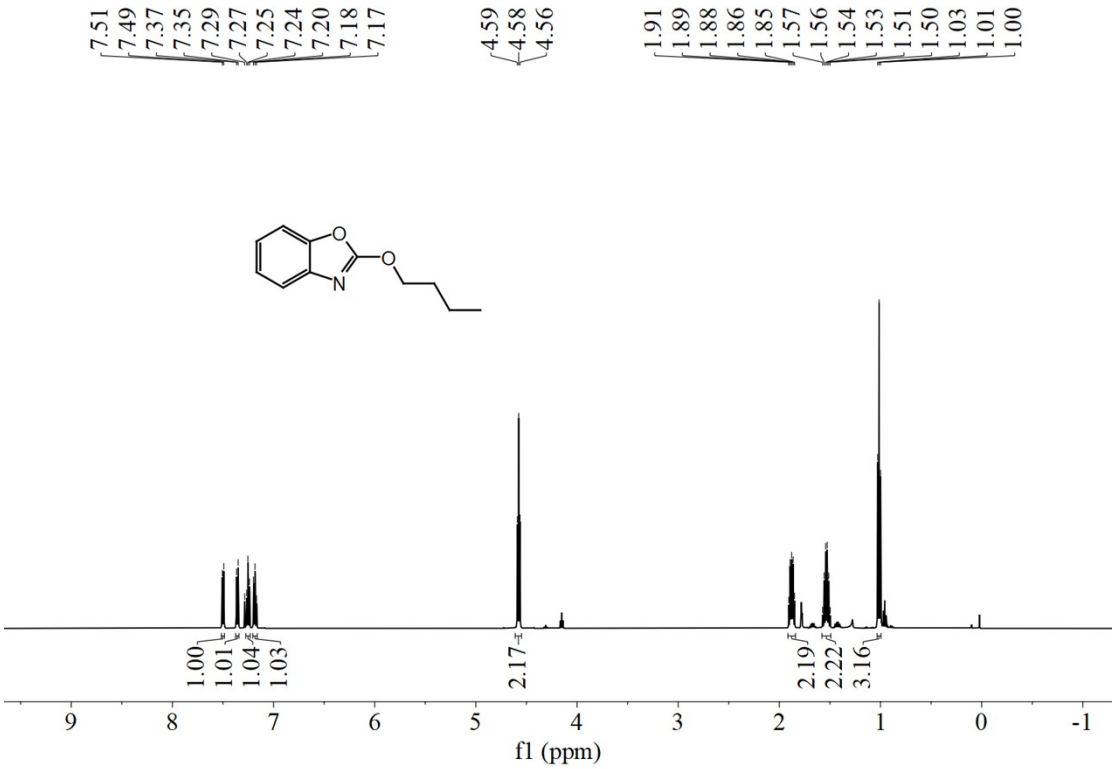
^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **3af**



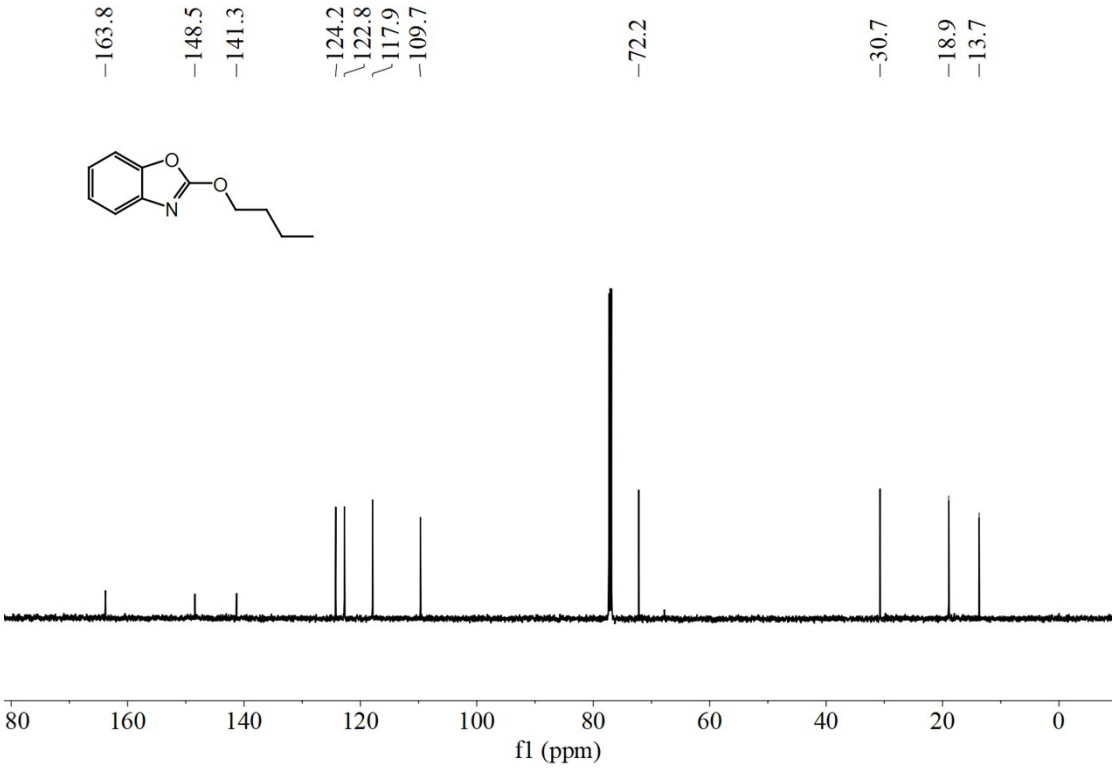
^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **3af**



^{1}H-NMR spectrum (500Hz, $CDCl_3$) of **4a**



^{13}C-NMR spectrum (125Hz, $CDCl_3$) of **4a**



7. References

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