Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Data

Synthesis of substituted 4-hydroxalkyl-quinoline derivatives by a three-component reaction using CuCl/AuCl as sequential catalysts

Kun-Ming Jiang,[a],‡ Jing-An Kang,[a],‡ Yi Jin,[a],* and Jun Lin,[a],*

[a] Key Laboratory of Medicinal Chemistry for Natural Resource (Yunnan University), Ministry Education, School of Chemical Science and Technology, Yunnan University, Kunming, 650091, P. R. China.

‡ The authors contributed equally to this work.

* Corresponding author. Tel./fax: +86-871-6503-3215 (J. L.).

*E-mail: jinyi@ynu.edu.cn.
*E-mail: linjun@ynu.edu.cn.

Contents

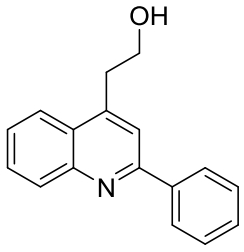
1. General considerations 2
2. General procedure for synthesis of quinoline derivatives 2
3. Computational data 19
3. Copies of ^{1}H NMR and ^{13}C NMR Spectra 29
References 61

1. General considerations

All compounds were fully characterized by IR, NMR, and LC/MS. NMR spectra were recorded on a Bruker DRX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) using deuterated $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts (δ) are expressed in ppm and J values given in Hz. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. Reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined using a XT-4A melting point apparatus and were uncorrected. HRMS (High Resolution Mass Spectrometry) were performed on an Agilent LC/MSD TOF instrument. All chemicals and solvents were used as received without further purification, unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh). Substituted benzaldehyde, substituted aniline, substituted alkyne, CuCl and $AuCl_3$ were purchased from Adamas-Beta Corporation Limited.

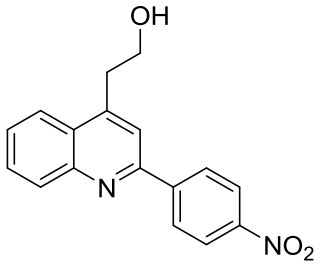
2. General procedure for synthesis of quinoline derivatives

Substituted aniline (1 mmol), substituted benzaldehyde (1.1 mmol) and substituted alkyne (1.1 mmol) were dissolved in 25 mL THF into a 50 mL round-bottom flask. Then, 0.1 mmol CuCl and 0.05 mmol AuCl were added to reaction bottle. The mixture was stirred at reflux temperature for 6 h and monitored by TLC. Upon completion, the solvent was removed by rotary evaporator, then water was added to the residue, extracted with ethyl acetate, dried over Na_2SO_4, and concentrated by rotary evaporator to yield quinoline derivatives (64 to 93% yields).



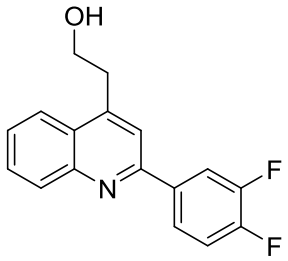
2-(2-Phenylquinolin-4-yl)ethan-1-ol (5a).

Yellowish-brown solid; m.p. = 93.1-93.4 ℃; IR (KBr): 3308, 3061, 2933, 2866, 1713, 1595, 1545, 1501, 1448, 1408, 1353, 1221, 1155, 1039, 846, 761, 695, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.4 Hz, 1H, ArH), 7.93-7.92 (m, 2H, ArH), 7.58 (d, J = 8.0 Hz, 1H, ArH), 7.68 (d, J = 6.0 Hz, 1H, ArH), 7.57 (s, 1H, CH), 7.43 (d, J = 7.2 Hz, 4H, ArH), 3.92 (s, 2H, CH_2), 3.25 (s, 2H, CH_2); ^{13}C NMR (100 MHz，$CDCl_3$): δ = 156.3, 148.2, 145.6, 139.2, 130.2, 129.4, 129.3, 128.7, 127.5, 126.5, 123.3, 119.9, 62.1, 35.9; HRMS (ESI^+): m/z calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226; found 250.1227.



2-(2-(4-Nitrophenyl)quinolin-4-yl)ethan-1-ol (5b).

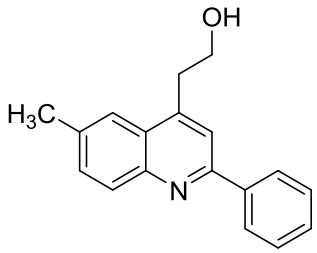
Yellowish-brown solid; m.p. = 155.1-155.8 ℃; IR (KBr): 3274, 2930, 2352, 1599, 1512, 1432, 1341, 1087, 1039, 845, 763, 697, 462 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.37 (s, 2H, ArH), 8.28 (s, 2H, ArH), 8.23 (d, J = 8.4 Hz, 1H, ArH), 8.07 (d, J = 8.4 Hz, 1H, ArH), 7.79 (d, J = 7.6 Hz, 2H, ArH), 7.64-7.59 (m, 1H, CH), 4.10 (d, J = 8.8 Hz, 2H, CH_2), 3.43 (d, J = 12.8 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 148.5, 148.3, 146.2, 145.3, 130.7, 130.0, 128.3, 127.3, 127.0, 124.0, 123.4, 120.0, 62.2, 35.7; HRMS (ESI^+): m/z calcd. for $C_{17}H_{15}N_2O_3$ $[M+H]^+$ 295.1077; found 295.1072.



2-(2-(3,4-Difluorophenyl)quinolin-4-yl)ethan-1-ol (5c).

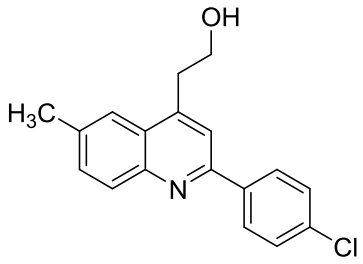
Yellow solid; m.p. = 122.0-122.8 ℃; IR (KBr): 3311, 3070, 2946, 2880, 1601, 1512,

1440, 1357, 1271, 1179, 1116, 1051, 925, 826, 766, 716 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.4 Hz, 1H, ArH), 8.00-7.90 (m, 2H, ArH), 7.82-7.74 (m, 2H, ArH), 7.64 (s, 1H, CH), 7.58-7.54 (m, 1H, ArH), 7.31-7.24 (m, 1H, ArH), 4.06 (t, J = 6.0 Hz, 2H, CH_2), 3.38 (t, J = 6.0 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.4, 148.3, 145.9, 136.5, 130.4, 129.8, 126.6, 123.5, 123.3, 119.2, 117.5, 117.4, 116.6, 116.4, 62.2, 35.8; HRMS (ESI^+): m/z calcd. for $C_{17}H_{14}F_2NO$ $[M+H]^+$ 286.1038; found 286.1041.



2-(6-Methyl-2-phenylquinolin-4-yl)ethan-1-ol (5d).

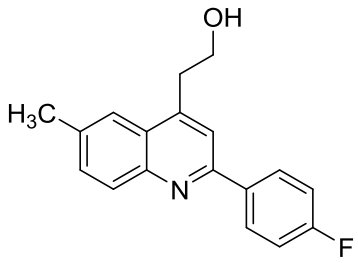
Yellow solid; m.p. = 187.1-187.4 ℃; IR (KBr): 3305, 3050, 2930, 2864, 1596, 1550, 1499, 1448, 1354, 1224, 1046, 824, 774, 701, 651 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.24 (d, J = 7.6 Hz, 2H, ArH), 7.78-7.16 (m, 3H, ArH), 7.60-7.46 (m, 4H, ArH), 4.88 (s, 1H, OH), 3.82 (d, J = 4.4 Hz, 2H, CH_2), 3.23 (t, J = 6.4 Hz, 2H, CH_2), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.1, 146.8, 146.3, 139.4, 136.1, 132.0, 130.0, 129.7, 129.2, 127.5, 126.9, 123.2, 119.7, 61.4, 35.7, 21.9; HRMS (ESI^+): m/z calcd. for $C_{18}H_{18}NO$ $[M+H]^+$ 264.1383; found 264.1380.



2-(2-(4-Chlorophenyl)-6-methylquinolin-4-yl)ethan-1-ol (5e).

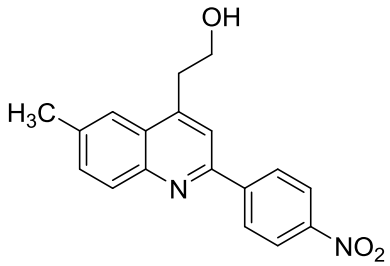
Yellow solid; m.p. = 185.7-185.9 ℃; IR (KBr): 3287, 2926, 2873, 1595, 1550, 1499, 1493, 1410, 1359, 1224, 1088, 964 , 827, 712, 649 cm^{-1}; ^{1}H NMR (400 MHz,

DMSO-d_6): δ = 8.26 (d, J = 8.4 Hz, 2H, ArH), 7.95 (t, J = 7.2 Hz, 3H, ArH), 7.59 (d, J = 8.4 Hz, 3H, ArH), 4.87 (t, J = 5.2 Hz, 1H, OH), 3.84-3.79 (m, 2H, CH_2), 3.27 (t, J = 6.8 Hz, 2H, CH_2), 2.52 (d, J = 11.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.8, 146.7, 146.6, 138.1, 136.4, 134.6, 132.1, 130.0, 129.2, 127.0, 123.2, 119.4, 61.4, 35.7, 21.9; HRMS (ESI$^+$): m/z calcd. for $C_{18}H_{17}ClNO$ $[M+H]^+$ 298.0993; found 298.0996.



2-(2-(4-Fluorophenyl)-6-methylquinolin-4-yl)ethan-1-ol (5f).

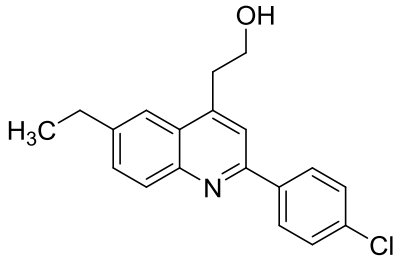
Yellow solid; m.p. = 180.8-181.2 ℃; IR (KBr): 3303, 2929, 2863, 1598, 1506, 1448, 1358, 1218, 1156, 1048, 833, 728, 598cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03-7.96 (m, 3H, ArH), 7.67 (s, 1H, CH), 7.56-7.54 (m, 2H, ArH), 7.16-7.12 (m, 2H, ArH), 4.00 (t, J = 6.4 Hz, 2H, CH_2), 3.00 (t, J = 6.4 Hz, 2H, CH_2), 2.54 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.8, 146.8, 144.7, 136.2, 135.5, 131.8, 129.9, 129.7, 129.3, 129.2, 126.3, 122.3, 119.5, 115.7, 115.5, 62.2, 35.8, 21.9; HRMS (ESI$^+$): m/z calcd. for $C_{18}H_{17}FNO$ $[M+H]^+$ 282.1289; found 282.1286.



2-(6-Methyl-2-(4-nitrophenyl)quinolin-4-yl)ethan-1-ol (5g).

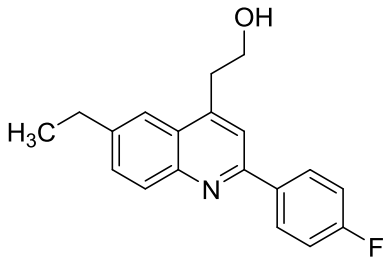
Yellow solid; m.p. = 184.4-185.2 ℃; ^{1}H NMR (400 MHz, DMSO-d_6)： δ = 8.50 (d, J = 8.8 Hz, 2H, ArH), 8.37 (d, J = 8.8 Hz, 2H, ArH), 8.08 (s, 1H, CH), 8.02-7.97 (m, 2H, ArH), 7.65-7.63 (m, 1H, ArH), 4.86 (t, J = 5.6 Hz, 1H, OH), 4.88-4.85 (m, 2H, CH_2),

3.50 (t, J = 6.4 Hz, 2H, CH_2), 2.55 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.2, 148.2, 147.0, 146.8, 145.2, 137.2, 132.4, 130.7, 128.6, 127.5, 124.4, 123.3, 120.0, 61.3, 35.7, 21.9; HRMS (ESI^+): m/z calcd. for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1234; found 309.1232.



2-(2-(4-Chlorophenyl)-6-ethylquinolin-4-yl)ethan-1-ol (5h).

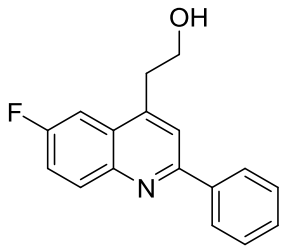
Yellow solid; m.p. = 101.7-102.1 ℃; IR (KBr): 3316, 2928, 1735, 1598, 1555, 1508, 1420, 1361, 1312, 1224, 1156, 1048, 884, 835, 777, 651 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 8.27 (d, J = 8.4 Hz, 2H, ArH), 7.99 (d, J = 8.0 Hz, 2H, ArH), 7.94 (s, 1H, CH), 7.65 (d, J = 8.8 Hz, 1H, ArH), 7.60 (d, J = 8.4 Hz, 2H, ArH), 4.87 (s, 1H, OH), 3.83 (s, 2H, CH_2), 3.29 (t, J = 6.4 Hz, 2H, CH_2), 2.87-2.81 (m, 2H, CH_2), 1.30 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.9, 146.9, 146.8，142.6, 138.1, 134.6, 131.0, 130.2, 129.2, 127.0, 122.0, 119.4, 61.4, 35.7, 29.0, 16.1; HRMS (ESI^+): m/z calcd. for $C_{19}H_{19}ClNO$ $[M+H]^+$ 312.1150; found 312.1149.



2-(6-Ethyl-2-(4-fluorophenyl)quinolin-4-yl)ethan-1-ol (5i).

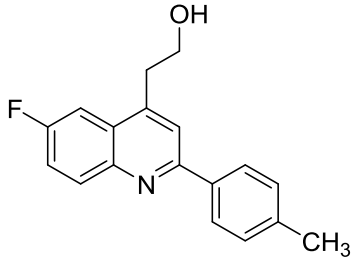
Yellow solid; m.p. = 115.9-116.3 ℃; IR (KBr): 3265, 2948, 2878, 1598, 1506, 1425, 1362, 1224, 1158, 1048, 889, 777, 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (d, J = 8.4 Hz, 1H, ArH), 7.84-7.80 (m, 2H, ArH), 7.57-7.43 (m, 2H, ArH), 7.52 (s, 1H, CH), 7.07 (t, J = 8.8 Hz, 2H, ArH), 3.92 (t, J = 6.0 Hz, 2H, CH_2), 3.46 (s, 1H, OH),

3.22 (t, J = 6.0 Hz, 2H, CH_2), 2.82-2.76 (m, 2H, CH_2), 1.31 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 162.3, 154.6, 146.8, 145.1, 142.3, 135.3, 130.6, 129.8, 129.2, 129.1, 126.3, 121.0, 119.6, 115.6, 115.4, 61.9, 35.9, 29.1, 15.4; HRMS (ESI$^+$): m/z calcd. for $C_{19}H_{19}FNO$ $[M+H]^+$ 296.1445; found 296.1446.



2-(6-Fluoro-2-phenylquinolin-4-yl)ethan-1-ol (5j)

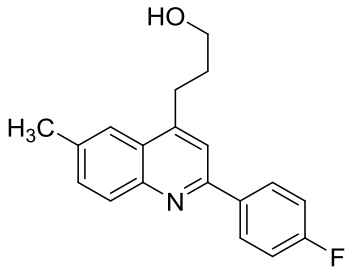
Yellow solid; m.p. = 101.5-102.3 ℃; IR (KBr): 3429, 3233, 3175, 2921, 1648, 1593, 1518, 1316, 1349, 1281, 1124, 1112, 1047, 755 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27-8.11 (m, 2H), 7.87 (s, 1H), 7.61 (dd, J = 8.8, 4.8 Hz, 1H), 7.50 (dd, J = 9.7, 2.4 Hz, 1H), 7.47-7.35 (m, 4H), 4.04 (td, J = 6.6, 3.0 Hz, 2H), 3.25 (t, J = 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 162.2, 155.7, 145.1, 139.4, 137.6, 131.9, 129.4, 128.3, 128.3, 124.9, 122.6, 121.0, 115.1, 62.8, 36.0; HRMS (ESI$^+$): m/z calcd. for $C_{17}H_{15}FNO$ $[M+H]^+$ 268.1132; found 268.1131.



2-(6-Fluoro-2-(p-tolyl)quinolin-4-yl)ethan-1-ol (5k)

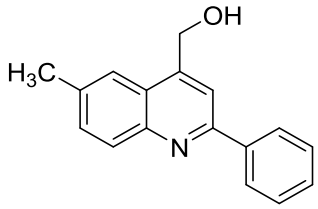
Yellow solid; m.p. = 146.1-147.9 ℃; IR (KBr): 3493, 3329, 3236, 3166, 2939, 1649, 1598, 1532, 1473, 1409, 1233, 1130, 995 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16-8.04 (m, 2H), 7.80 (t, J = 1.0 Hz, 1H), 7.61 (dd, J = 8.8, 4.8 Hz, 1H), 7.55-7.38 (m, 2H), 7.36-7.27 (m, 2H), 4.04 (td, J = 6.6, 3.1 Hz, 2H), 3.25 (dd, J = 7.0, 6.2 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 162.2, 155.9, 145.1, 141.4,

139.4, 136.3, 131.9, 128.6, 127.4, 124.4, 122.6, 121.0, 115.1, 62.8, 36.0, 21.8; HRMS (ESI^+): m/z calcd. for $C_{18}H_{17}FNO$ $[M+H]^+$ 282.1289; found 282.1286.



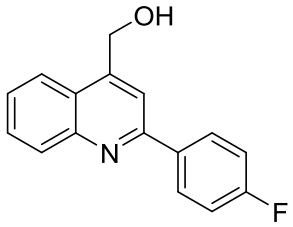
3-(2-(4-Fluorophenyl)-6-methylquinolin-4-yl)propan-1-ol (5l)

Yellow solid; m.p. = 164.9-166.1 ℃; IR (KBr): 3593, 3529, 3137, 3076, 1643, 1593, 1520, 1400, 1220, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.07-7.99 (m, 2H), 7.90 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.56 (d, *J* = 0.9 Hz, 1H), 7.11-7.02 (m, 2H), 3.77 (td, *J* = 6.3, 4.9 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.51 (s, 3H), 2.14 (td, *J* = 6.7, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 161.8, 157.9, 146.3, 142.6, 137.9, 132.7, 129.5, 129.5, 128.9, 127.1, 126.8, 122.5, 115.3, 62.1, 35.6, 29.7, 20.6; HRMS (ESI^+): m/z calcd. for $C_{19}H_{19}FNO$ $[M+H]^+$ 296.1445; found 296.1448.



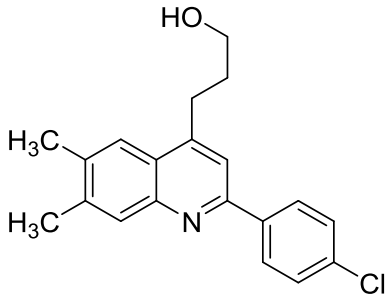
(6-Methyl-2-phenylquinolin-4-yl)methanol (5m)

Yellow solid; m.p. = 99.9-100.3 ℃; IR (KBr): 3243, 3063, 2313, 1742, 1648, 1594, 1511, 1467, 1301, 1239, 1175, 1032, 824, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24-8.14 (m, 2H), 7.96 (s, 1H), 7.82 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.66-7.59 (m, 1H), 7.54 – 7.44 (m, 2H), 7.42 – 7.32 (m, 1H), 4.78 (d, *J* = 5.3 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 151.7, 141.8, 138.2, 135.7, 129.9, 129.8, 129.0, 128.3, 126.0, 124.6, 122.8, 122.0, 77.7, 77.4, 77.1, 63.2, 18.4; HRMS (ESI^+): m/z calcd. for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226; found 250.1228.



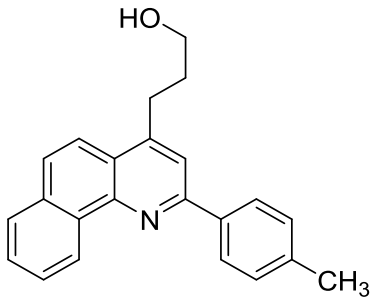
(2-(4-Fluorophenyl)quinolin-4-yl)methanol (5n)

Yellow solid; m.p. = 136.2-138.3 ℃; IR (KBr): 3693, 3529, 3139, 2351, 1646, 1597, 1504, 1452, 1248, 1110, 1041, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.8 Hz, 1H), 8.11-8.02 (m, 2H), 8.01-7.93 (m, 1H), 7.90 (s, 1H), 7.64 (td, J = 7.6, 1.4 Hz, 1H), 7.35 (td, J = 7.7, 1.5 Hz, 1H), 7.24-7.09 (m, 2H), 4.81 (d, J = 5.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 161.8, 157.7, 153.1, 143.5, 138.0, 130.8, 129.9, 129.5, 127.9, 126.0, 125.4, 122.2, 116.4, 63.7; HRMS (ESI^+): m/z calcd. for $C_{16}H_{13}FNO$ $[M+H]^+$ 254.0976; found 254.0979.



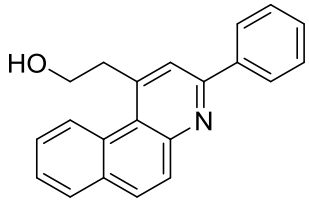
3-(2-(4-Chlorophenyl)-6,7-dimethylquinolin-4-yl)propan-1-ol (5o)

Yellow solid; m.p. = 194.3-195.2 ℃; IR (KBr): 3381, 3261, 2971, 2355, 1637, 1524, 1516, 1325, 1171, 1103, 1051 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-7.96 (m, 2H), 7.74 (d, J = 1.8 Hz, 2H), 7.63-7.51 (m, 2H), 7.40 (d, J = 1.0 Hz, 1H), 3.77 (td, J = 6.3, 4.9 Hz, 2H), 3.28-3.10 (m, 2H), 2.51 (s, 3H), 2.41 (s, 3H), 2.22-2.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.7, 146.7, 143.4, 142.8, 138.0, 133.2, 131.6, 128.5, 128.0, 128.0, 127.0, 126.9, 126.8, 62.1, 57.2, 35.6, 29.8, 21.8, 20.2; HRMS (ESI^+): m/z calcd. for $C_{20}H_{21}ClNO$ $[M+H]^+$ 326.1306; found 326.1309.



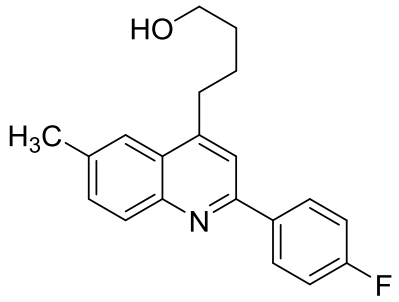
3-(2-(p-Tolyl)benzo[h]quinolin-4-yl)propan-1-ol (5p)

Yellow solid; m.p. = 213.5-214.3 ℃; IR (KBr): 3265, 1651, 1590, 1506, 1469, 1245, 1243, 1036 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.22 (d, J = 8.0 Hz, 1H), 8.53 (d, J = 9.4 Hz, 1H), 8.07 (d, J = 8.3 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 9.3, 0.8 Hz, 1H), 7.56 (d, J = 1.0 Hz, 1H), 7.39 (td, J = 7.6, 1.6 Hz, 1H), 7.34-7.22 (m, 5H), 3.77 (td, J = 6.2, 4.9 Hz, 2H), 3.34-3.20 (m, 2H), 2.41 (s, 3H), 2.28-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.33, 143.66, 142.98, 141.40, 138.33, 130.86, 130.50, 128.95, 128.69, 127.99, 127.79, 127.20, 126.80, 126.35, 123.29, 120.26, 62.10, 35.65, 30.01, 21.80; HRMS (ESI^+): m/z calcd. for $C_{23}H_{22}NO$ $[M+H]^+$ 328.1696; found 328.1694.



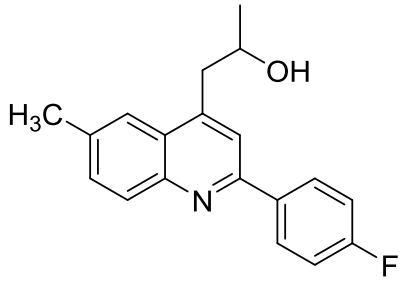
2-(3-Phenylbenzo[*f*]quinolin-1-yl)ethan-1-ol (5q).

Yellow solid; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.19 (s, 1H, ArH), 8.92 (d, J = 8.0 Hz, 1H, ArH), 8.09-8.05 (m, 2H, ArH), 7.90 (d, J = 9.2 Hz, 1H, ArH), 7.80-7.70 (m, 2H, ArH), 7.64 (d, J = 6.8 Hz, 2H, ArH), 7.55-7.42 (m, 3H, ArH) , 4.77 (s, 1H, OH), 3.68 (s, 2H, CH_2), 3.06 (t, J = 6.8 Hz, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.7, 145.9, 140.9, 133.0, 131.7, 131.5, 130.8, 129.6, 129.4, 129.0, 128.5, 128.4, 128.0, 127.8, 127.7, 124.3, 123.9, 61.7, 36.2; HRMS (ESI^+): m/z calcd. for $C_{21}H_{18}NO$ $[M+H]^+$ 300.1383; found 300.1385.



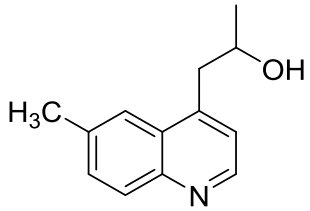
4-(2-(4-Fluorophenyl)-6-methylquinolin-4-yl)butan-1-ol (5r)

Yellow solid; m.p. = 146.9-148.2 ℃; IR (KBr): 3433, 3288, 1646, 1588, 1518, 1243, 1025, 824 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-7.99 (m, 2H), 7.91 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.53 (d, *J* = 0.9 Hz, 1H), 7.14-7.01 (m, 2H), 3.76 (td, *J* = 6.2, 4.5 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.51 (s, 3H), 1.85 (dt, *J* = 7.5, 6.6 Hz, 2H), 1.78-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 161.8, 158.2, 146.7, 142.5, 137.9, 132.7, 129.5, 129.5, 128.8, 127.2, 127.0, 122.5, 115.3, 62.7, 32.4, 31.9, 27.1, 20.6; HRMS (ESI^+): m/z calcd. for $C_{20}H_{21}FNO$ $[M+H]^+$ 310.1602; found 310.1604.



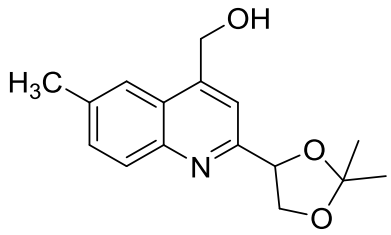
1-(2-(4-Fluorophenyl)-6-methylquinolin-4-yl)propan-2-ol (5s)

Yellow solid; m.p. = 178.1-179.3 ℃; IR (KBr): 3432, 3266, 1648, 1593, 1510, 1411, 1234, 1131 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10-7.99 (m, 2H), 7.92 (s, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 1.0 Hz, 1H), 7.59 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.13-7.00 (m, 2H), 4.44 (dddd, *J* = 10.2, 6.1, 4.8, 1.2 Hz, 1H), 3.22 (dd, *J* = 14.0, 1.5 Hz, 1H), 3.13-3.00 (m, 1H), 2.51 (s, 3H), 1.54-1.41 (m, 1H), 1.41-1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.3, 157.8, 132.8, 129.9, 129.5, 129.5, 128.8, 126.8, 122.6, 115.3, 69.8, 42.0, 22.0, 20.6; HRMS (ESI^+): m/z calcd. for $C_{19}H_{19}FNO$ $[M+H]^+$ 296.1445; found 296.1447.



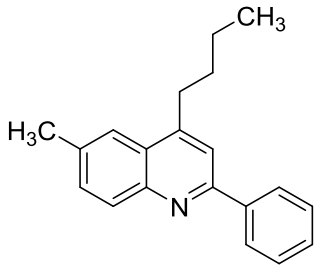
1-(6-Methylquinolin-4-yl)propan-2-ol (5t)

Yellow solid; m.p. = 125.5-127.4 ℃; IR (KBr): 3393, 3147, 1649, 1594, 1516, 1448, 1286, 1247, 1042, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (d, J = 4.4 Hz, 1H), 7.89 (s, 1H), 7.77 (d, J = 8.6 Hz, 1H), 7.62-7.53 (m, 1H), 7.32 (d, J = 4.5 Hz, 1H), 4.45 (dt, J = 10.8, 5.7 Hz, 1H), 3.23-2.96 (m, 2H), 2.51 (d, J = 0.8 Hz, 3H), 1.76 (s, 1H), 1.41 (d, J = 6.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7, 146.2, 139.9, 132.9, 129.6, 127.5, 126.9, 122.8, 121.6, 70.0, 41.2, 22.2, 20.6; HRMS (ESI^+): m/z calcd. for $C_{13}H_{16}NO$ $[M+H]^+$ 202.1226; found 202.1229.



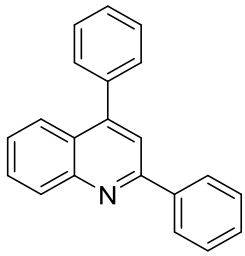
(2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-6-methylquinolin-4-yl)methanol (5u)

Yellow solid; m.p. = 186.1-187.3 ℃; IR (KBr): 3290, 1647, 1589, 1530, 1519, 1250, 1120 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 1.5 Hz, 1H), 7.80 (d, J = 2.1 Hz, 2H), 7.73 (s, 1H), 5.43-5.29 (m, 1H), 4.77 (d, J = 5.3 Hz, 2H), 4.48-4.32 (m, 1H), 3.94-3.80 (m, 1H), 2.56 (s, 3H), 1.48 (d, J = 1.0 Hz, 3H), 1.43 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.0, 149.1, 141.9, 136.7, 130.1, 129.6, 126.1, 125.0, 120.1, 108.9, 82.4, 76.8, 70.3, 70.3, 62.0, 26.3, 24.9, 18.4; HRMS (ESI^+): m/z calcd. for $C_{16}H_{20}NO_3$ $[M+H]^+$ 274.1438; found 274.1441.



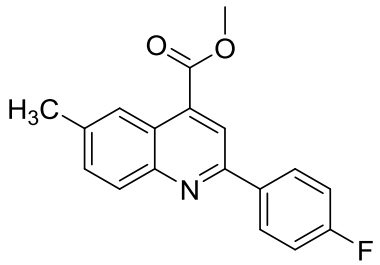
4-Butyl-6-methyl-2-phenylquinoline (5v).

Yellow solid; m.p. = 79.0-81.2 ℃; IR (KBr): 3452, 2955, 2864, 1594, 1551, 1448, 1219, 874, 777, 596 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.0 Hz, 2H, ArH), 8.05 (d, J = 8.0 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 7.60 (s, 1H, CH), 7.75-6.35 (m, 4H, ArH), 3.10 (t, J = 6.8 Hz, 2H, CH_2), 3.60 (s, 3H, CH_3), 1.85-1.75 (m, 2H, CH_2), 1.55-1.45 (m, 2H, CH_2), 1.00 (t, J = 6.9 Hz , 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0, 148.3, 146.9, 139.9, 135.5, 131.2, 130.1, 129.6, 128.8, 128.6, 127.3, 126.4, 122.2, 118.4, 32.1, 29.6, 22.7, 21.8, 13.8; HRMS (ESI^+): m/z calcd. for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747; found 276.1751.



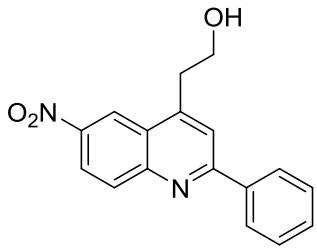
2, 4-Diphenylquinoline (5w).

Yellow solid; m.p. = 124.1-125.6 ℃; IR (KBr): 1634, 1588, 1519, 1489, 1446, 1343, 1260, 967, 768, 701, 596 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$)：δ = 8.24 (d, J = 8.4 Hz, 1H, ArH), 8.19 (d, J = 6.8 Hz, 2H, ArH), 7.89 (d, J = 8.0 Hz, 1H, ArH), 7.82 (s, 1H, ArH), 7.75-7.74 (m, 1H, ArH), 7.55-7.45 (m, 9H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9, 149.2, 148.8, 139.6, 138.4, 130.1, 129.6, 129.5, 129.3, 128.8, 128.6, 128.4, 127.6, 126.3, 125.6, 119.3; HRMS (ESI^+): m/z calcd. for $C_{21}H_{16}N$ $[M+H]^+$ 282.1277; found 282.1270.



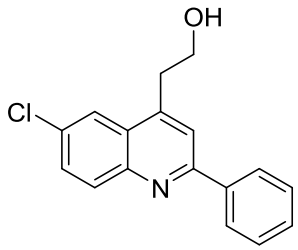
Methyl 2-(4-fluorophenyl)-6-methylquinoline-4-carboxylate (5x)

Yellow solid; m.p. = 136.9-138.3 ℃; IR (KBr): 3395, 2982, 2312, 1640, 1524, 1049, 899, 777, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.28 (s, 1H), 8.16-8.04 (m, 2H), 7.99 (d, J = 8.6 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.17-6.97 (m, 2H), 3.97 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1, 164.3, 161.8, 158.2, 146.1, 137.7, 136.7, 132.5, 132.4, 129.3, 128.9, 127.6, 126.0, 124.9, 115.2, 114.1, 77.6, 51.9, 21.1; HRMS (ESI^+): m/z calcd. for $C_{18}H_{15}FNO_2$ $[M+H]^+$ 296.1081; found 296.1084.



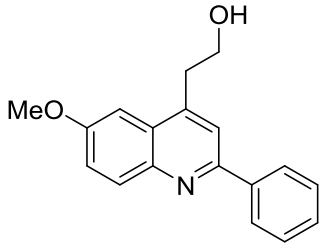
2-(6-nitro-2-phenylquinolin-4-yl)ethan-1-ol (5y)

Yellow solid; m.p. = 143.3-145.1 ℃; IR (KBr): 3206, 1678, 1614, 1549, 1465, 1427, 1275, 751 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.85 (d, J = 2.2 Hz, 1H), 8.45 (dd, J = 9.2, 2.2 Hz, 1H), 8.24 – 8.15 (m, 2H), 8.04 – 7.95 (m, 2H), 7.44 – 7.34 (m, 3H), 4.13 (td, J = 6.7, 4.1 Hz, 2H), 3.38 (dd, J = 7.2, 6.1 Hz, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 155.97, 152.68, 146.23, 145.09, 137.58, 129.57, 128.65, 128.41, 128.30, 125.53, 124.82, 122.76, 77.45, 77.13, 76.81, 62.30, 35.01; HRMS (ESI^+): m/z calcd. for $C_{17}H_{14}N_2O_3$ $[M+H]^+$ 295.1077; found 295.1080.



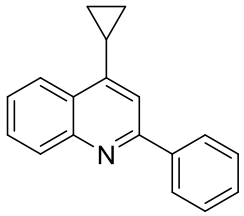
2-(6-chloro-2-phenylquinolin-4-yl)ethan-1-ol (5z)

White solid; m.p. = 127.3-126.9 ℃; IR (KBr): 3274, 2912, 2873, 1561, 1550, 1493, 1410, 1349, 1222, 1078, 961 , 827, 701, 639 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.23 – 8.16 (m, 2H), 7.96 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 0.7 Hz, 1H), 7.82 (d, *J* = 2.2 Hz, 1H), 7.58 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.44 – 7.33 (m, 3H), 4.07 (td, *J* = 6.7, 4.1 Hz, 2H), 3.21 (td, *J* = 6.5, 6.0, 0.9 Hz, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 156.00, 147.78, 141.98, 137.58, 131.75, 129.94, 129.57, 128.41, 128.30, 127.48, 124.56, 122.65, 77.45, 77.13, 76.81, 62.28, 36.20; HRMS (ESI^+): m/z calcd. for $C_{17}H_{14}ClNO$ $[M+H]^+$ 284.0837; found 284.0834.



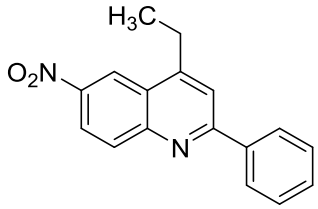
2-(6-methoxy-2-phenylquinolin-4-yl)ethan-1-ol (5aa)

White solid; m.p. = 174.7-176.3 ℃; IR (KBr): 3410, 3073, 2953, 2882, 1601, 1532, 1440, 1365, 1270, 1159, 1113, 1051, 823, 766, 715 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.20 (d, *J* = 2.1 Hz, 1H), 8.18 (t, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 7.84 (s, 1H), 7.46 – 7.35 (m, 4H), 7.31 (d, *J* = 2.2 Hz, 1H), 4.07 – 4.01 (m, 2H), 3.99 (s, 3H), 3.27 (dd, *J* = 7.2, 6.1 Hz, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 160.48, 155.89, 144.52, 137.58, 136.35, 129.57, 128.41, 128.30, 128.04, 126.62, 124.59, 121.74, 99.49, 77.39, 77.07, 76.75, 62.55, 56.20, 36.31; HRMS (ESI^+): m/z calcd. for $C_{18}H_{17}NO_2$ $[M+H]^+$ 280.1332; found 280.1337.



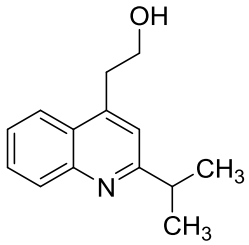
4-cyclopropyl-2-phenylquinoline (5ab)

White solid; m.p. = 151.5-153.1 ℃; IR (KBr): 3230, 3051, 1674, 1583, 1531, 1417, 1343, 1257, 761, 690 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.27 – 8.20 (m, 1H), 8.20 – 8.13 (m, 2H), 8.10 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.68 (s, 1H), 7.61 (td, *J* = 7.5, 1.3 Hz, 1H), 7.33 (dtd, *J* = 8.6, 7.5, 1.4 Hz, 2H), 7.07 – 6.97 (m, 2H), 2.49 – 2.35 (m, 1H), 1.30 – 1.20 (m, 2H), 1.17 – 1.06 (m, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 154.62, 149.72, 144.48, 137.76, 132.80, 131.19, 130.82, 129.26, 128.80, 128.30, 127.11, 125.19, 118.59, 77.46, 77.14, 76.82, 22.55, 11.34; HRMS (ESI^+): m/z calcd. for $C_{18}H_{15}N$ $[M+H]^+$ 246.1277; found 246.1280.



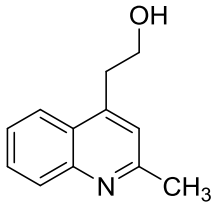
4-ethyl-6-nitro-2-phenylquinoline (5ac)

White solid; m.p. = 184.1-186.1 ℃; IR (KBr): 3796, 3438, 3262, 1644, 1581, 1515, 1415, 1287, 1221, 763 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.82 (d, *J* = 2.2 Hz, 1H), 8.45 (dd, *J* = 9.2, 2.2 Hz, 1H), 8.23 – 8.15 (m, 2H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.90 (d, *J* = 0.8 Hz, 1H), 7.46 – 7.33 (m, 3H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.23 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 152.66, 149.33, 146.18, 137.53, 129.57, 128.73, 128.60, 128.41, 128.30, 125.51, 122.95, 122.76, 77.80, 77.76, 77.48, 77.44, 77.16, 77.11, 23.63, 15.37; HRMS (ESI^+): m/z calcd. for $C_{17}H_{14}N_2O_2$ $[M+H]^+$ 279.1128; found 279.1131.



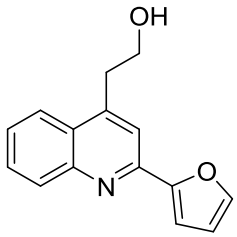
2-(2-isopropylquinolin-4-yl)ethan-1-ol (5ad)

White solid; m.p. = 142.6-145.1 ℃; IR (KBr): 3723, 3432, 3271, 2927, 1648, 1592, 1518, 1415, 1349, 1280, 1224, 1115, 1047, 753 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.01 (dd, J = 7.8, 1.5 Hz, 1H), 7.88 (dt, J = 8.0, 0.9 Hz, 1H), 7.54 (td, J = 7.4, 1.4 Hz, 1H), 7.44 (ddd, J = 8.0, 7.2, 1.6 Hz, 1H), 6.96 (d, J = 0.8 Hz, 1H), 3.94 (td, J = 6.7, 4.1 Hz, 2H), 3.30 – 3.19 (m, 2H), 2.99 (p, J = 6.9 Hz, 1H), 1.27 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 162.33, 148.29, 139.94, 128.58, 127.65, 126.12, 125.68, 125.42, 122.35, 77.43, 77.11, 76.80, 62.50, 37.81, 35.33, 22.32; HRMS (ESI^+): m/z calcd. for $C_{14}H_{17}NO$ $[M+H]^+$ 216.1383; found 216.1380.



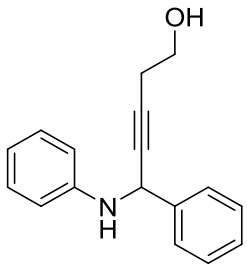
2-(2-methylquinolin-4-yl)ethan-1-ol (5ae)

White solid; m.p. = 140.2-142.0 ℃; IR (KBr): 3791, 3725, 3436, 3263, 2939, 1646, 1598, 1517, 1453, 1402, 1233, 1133, 992 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.00 – 7.93 (m, 1H), 7.93 – 7.86 (m, 1H), 7.61 – 7.50 (m, 2H), 7.28 (s, 1H), 4.05 (td, J = 6.7, 4.2 Hz, 2H), 3.19 (dd, J = 7.2, 6.2 Hz, 2H), 2.59 (d, J = 0.7 Hz, 3H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 158.35, 146.95, 141.08, 128.75, 128.19, 127.24, 126.99, 124.99, 123.46, 77.39, 77.07, 76.75, 62.54, 35.67, 24.39; HRMS (ESI^+): m/z calcd. for $C_{12}H_{13}NO$ $[M+H]^+$ 188.1070; found 188.1074.



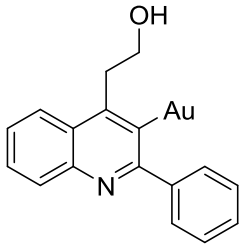
2-(2-(furan-2-yl)quinolin-4-yl)ethan-1-ol (5af)

Yellow solid; m.p. = 173.7-175.6 ℃; IR (KBr): 3436, 3243, 1647, 1528, 1112, 621 cm^{-1}; ^{1}H NMR (400 MHZ, $CDCl_3$): δ = 8.18 (dd, *J* = 8.0, 1.4 Hz, 1H), 8.04 (dd, J = 7.6, 1.6 Hz, 1H), 7.89 (d, *J* = 0.8 Hz, 1H), 7.71 (ddd, J = 8.1, 7.2, 1.6 Hz, 1H), 7.62 (td, *J* = 7.4, 1.4 Hz, 1H), 7.39 (dd, *J* = 2.1, 0.9 Hz, 1H), 6.98 (dd, *J* = 3.2, 1.0 Hz, 1H), 6.53 (dd, *J* = 3.3, 2.0 Hz, 1H), 4.07 (td, *J* = 6.7, 4.2 Hz, 2H), 3.25 (td, *J* = 6.5, 6.1, 0.9 Hz, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$): δ = 13C NMR (101 MHz,) δ 154.57, 152.13, 151.13, 145.61, 144.90, 131.35, 131.27, 129.05, 127.43, 124.48, 121.30, 113.89, 113.72, 77.67, 77.37, 77.05, 76.73, 62.52, 36.85; HRMS (ESI^+): m/z calcd. for $C_{15}H_{13}NO_2$ $[M+H]^+$ 240.1019; found 240.1023.



5-Phenyl-5-(phenylamino)pent-3-yn-1-ol (4a).

Yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.75 (d, *J* = 7.2 Hz, 2H, ArH), 7.36 (t, *J* = 7.6 Hz, 2H, ArH), 7.27 (t, *J* = 7.2 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 2H, ArH), 6.69 (d, *J* = 7.6 Hz, 2H, ArH), 6.55 (t, *J* = 7.2 Hz, 1H, ArH), 6.62 (d, *J* = 8.0 Hz, 1H, NH), 5.36 (d, *J* = 8.0 Hz, 1H, CH), 4.80 (t, *J* = 5.6 Hz, 1H, OH), 3.50-3.36 (m, 2H, CH_2), 2.36-2.32 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 147.6, 141.3, 129.3, 129.1, 128.8, 127.8, 127.6, 117.0, 113.8, 82.3, 81.5, 60.3, 48.7, 23.2; HRMS (ESI^+): m/z calcd. for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383; found 252.1386.



(4-(2-Hydroxyethyl)-2-phenylquinolin-3-yl)gold (10)

Yellow solid; m.p. = 215.2-216.7 ℃; IR (KBr): 3434, 3287, 1640, 1519, 1464, 1402, 1242, 1044, 833, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19-8.13 (m, 2H), 8.09 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.98 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.58 (td, *J* = 7.5, 1.4 Hz, 1H), 7.50-7.42 (m, 1H), 7.42-7.30 (m, 3H), 3.92 (td, *J* = 6.8, 3.0 Hz, 2H), 3.25 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.0, 140.4, 137.8, 131.0, 130.6, 130.3, 129.9, 128.6, 128.1, 127.8, 126.5, 122.1, 77.6, 62.3, 36.4; HRMS (ESI^+): m/z calcd. for $C_{17}H_{15}AuNO$ $[M+H]^+$ 446.0814; found 446.0815.

3. Computational data

Computational methods:

DFT calculations were used to investigate the energetics of our proposed mechanism, the geometry optimizations and transitions state searches were performed on the B3LYP level with 6-31+G(d) basis set for C, H, N, O, Cl atoms and LanL2DZ with relativistic effective core potentials for gold.[1] Single point calculations were performed at the M06 level with a mixed basis set of SDD for gold and 6-311+G(d,p) for all other atoms.[2] Solvation energy corrections were calculated using SMD model and with THF as solvent. All calculations were performed with Gaussian 09 program packages.[3] All transition states were confirmed by intrinsic reaction coordinate (IRC) toward a set of pre- and postreaction complexes.[4] Computed structures are displayed with CYLview.

Optimized Geometries:

Propargyl amine **4a**

E+zero-point Energies= -787.300468 Hartree

Free Energies= -787.345096 Hartree

H	-3.86591	-1.56543	-3.66210
C	-3.56745	-0.89501	-2.85370
H	-5.53052	-0.00621	-2.64260
H	-1.52119	-1.59259	-2.83744
C	-4.50043	-0.02181	-2.28065
C	-2.24767	-0.90654	-2.39624
H	0.23185	-0.40288	-1.70497
C	-4.10722	0.83752	-1.25169
C	-1.84479	-0.04056	-1.36767
H	-4.82880	1.52525	-0.80623
H	2.20390	-0.88110	-0.86547
C	-2.78348	0.82952	-0.79737
C	-0.40821	-0.11857	-0.85528
C	0.10598	1.18003	-0.32631
H	1.93312	4.50407	0.03155
H	4.25003	-1.83102	0.11725
H	-2.47873	1.51225	0.00032
C	2.13225	-1.44578	0.06529
H	3.15246	3.21437	0.28265
N	-0.32134	-1.18755	0.14238
C	0.64774	2.04386	0.37313
C	3.29586	-1.98484	0.62589
C	2.38056	3.82716	0.78333
C	0.88889	-1.63282	0.69757
H	-1.09952	-1.16548	0.80325
H	3.56423	5.19835	1.53192
C	1.29096	2.91409	1.36147
O	2.92090	4.55356	1.89081
C	3.25075	-2.70849	1.82225
H	0.53588	3.54088	1.86403
C	0.85006	-2.35608	1.90769
H	4.16421	-3.12062	2.25427
H	1.74449	2.27188	2.13561
C	2.01666	-2.88770	2.45909
H	-0.11045	-2.50995	2.40956
H	1.95643	-3.44612	3.39535

TS1

E+zero-point Energies= -1383.051153 Hartree

Free Energies= -1383.102447 Hartree

Imaginary frequency: -26.6 cm^{-1}

H	-2.34005	-2.63537	-1.87084
H	4.77895	-0.31503	-1.73738
H	-0.76788	2.89935	-1.84400
H	-4.78197	-2.68979	-1.43261
H	2.43137	0.46843	-1.48102
O	-2.01468	5.15275	-0.98360
C	4.10096	-0.83836	-1.05434
C	-2.74206	-2.18454	-0.96169
H	-2.27979	2.53022	-0.94987
H	-1.89566	6.04267	-0.58683
C	2.79021	-0.39786	-0.91607
C	-4.11418	-2.21756	-0.71216
C	-1.22053	2.84186	-0.82714
H	5.57093	-2.29182	-0.43857
H	-0.09878	-2.51534	-0.61956
C	4.54050	-1.95811	-0.33327
C	-1.24517	4.23906	-0.17652
H	-0.20416	4.60400	-0.05799
N	-0.47029	-1.64681	-0.24885
C	0.46543	-0.64200	-0.19762
C	1.87882	-1.08040	-0.10280
C	-1.87066	-1.57824	-0.03966
C	0.11343	0.73158	0.05384
C	-0.59041	1.86292	0.10913
C	-4.63758	-1.65243	0.45835
H	-5.71733	-1.66758	0.64192
C	3.64460	-2.64678	0.49835
C	2.31824	-2.22180	0.61354
H	-1.67096	4.13579	0.83737
H	3.99892	-3.51765	1.07233
Au	1.66121	2.45845	0.83992
C	-2.39281	-1.01504	1.13857
Cl	3.55324	3.85429	1.46049
H	0.38830	0.30891	1.12996
H	1.63068	-2.75300	1.27974
C	-3.76826	-1.06097	1.38154
H	-1.72553	-0.58923	1.88545
H	-4.15764	-0.65660	2.31613

8a

E+zero-point Energies= -1383.094031 Hartree

Free Energies= -1383.137506 Hartree

H	-4.05531	0.45404	-2.36227
Cl	3.47493	-3.68503	-1.69698
H	-1.62992	0.55683	-1.85100
C	-3.72177	0.90592	-1.42521
H	-1.12107	-1.77411	-1.22995
H	3.78738	3.66109	-0.91065
C	-2.35565	0.94407	-1.13423
H	-5.72095	1.44303	-0.78252
H	1.42788	2.88090	-0.91287
H	-1.50834	-4.30274	-0.77845
Au	1.70338	-2.26886	-0.79594
C	-4.65453	1.46701	-0.54559
C	3.52415	2.73000	-0.40400
C	2.19552	2.29832	-0.39898
C	-0.67279	-1.73977	-0.22354
H	5.55657	2.30450	0.20520
H	0.02248	-4.49505	0.12180
C	4.51729	1.96784	0.22109
C	-1.90516	1.52969	0.06258
C	-1.04469	-4.22479	0.22404
C	0.09599	-0.67972	0.10100
C	1.84228	1.09099	0.23163
C	0.43524	0.61709	0.20189
N	-0.52774	1.63644	0.34540
C	-4.20618	2.06657	0.63565
H	-1.52800	-6.00060	0.90117
C	-1.16623	-2.79356	0.74224
C	4.17428	0.77567	0.86568
H	-2.23868	-2.58876	0.91804
C	2.84504	0.34712	0.88141
C	-2.84428	2.09171	0.94577
O	-1.70907	-5.07674	1.16609
H	-4.92240	2.50805	1.33332
H	-0.29150	2.32123	1.06788
H	4.93923	0.17777	1.36447
H	2.57187	-0.56240	1.42273
H	-0.65762	-2.69929	1.71239
H	-2.50361	2.54476	1.88149

TS2

E+zero-point Energies= -1383.049726 Hartree

Free Energies= -1383.087945 Hartree

Imaginary frequency: -31.3 cm^{-1}

H	2.09846	-0.09488	-3.90056
H	4.17531	-1.39863	-3.54141
C	2.25322	-0.63218	-2.96750
C	3.40602	-1.36677	-2.76793
H	0.18829	-0.70025	-2.38796
H	0.24112	1.44738	-2.22847
C	1.20394	-0.63584	-1.98766
H	2.52399	2.28560	-1.71028
H	4.43457	-2.78599	-1.47549
C	3.53647	-2.17541	-1.61063
C	0.65885	1.22895	-1.23116
H	1.20746	3.24261	-0.99362
C	1.74160	2.27078	-0.91106
C	1.39524	-1.40850	-0.79017
C	2.56577	-2.18579	-0.62163
Cl	-3.31663	4.48687	0.16640
C	-0.32861	0.85260	-0.26599
Au	-1.77360	2.60333	-0.08066
H	2.67475	-2.81416	0.26598
H	-1.90559	-2.72489	0.24117
N	0.39177	-1.40927	0.13245
O	3.28885	3.40370	0.49303
C	-0.57887	-0.35926	0.28087
C	2.42607	2.24933	0.46603
H	3.02549	1.31988	0.61204
C	-2.28596	-2.04031	1.00582
H	0.51441	-2.00363	0.95489
H	3.69918	3.44111	1.37904
C	-1.72201	-0.75440	1.13878
H	1.66469	2.31558	1.28270
H	-3.82241	-3.41403	1.65610
C	-3.37376	-2.42793	1.79714
C	-2.25261	0.11712	2.10789
H	-1.80309	1.10328	2.24664
C	-3.89610	-1.54576	2.75087
C	-3.33965	-0.27128	2.89511
H	-4.73901	-1.84851	3.37702
H	-3.72476	0.42097	3.64548

9a

E+zero-point Energies= -1383.141347 Hartree

Free Energies= -1383.182605 Hartree

H	2.46632	-2.38075	-3.37439
O	2.62460	-2.57550	-2.42891
H	0.82851	-1.58046	-1.96705
H	2.31917	-0.59506	-1.81190
C	1.89095	-1.60500	-1.66329
H	-5.06055	-0.37537	-1.31355
H	2.19499	2.84169	-1.34324
H	-2.70927	-1.10447	-1.02825
H	4.59383	2.65232	-0.75434
C	-4.34282	0.29705	-0.83884
H	-5.78062	1.88929	-0.54280
H	-0.05063	1.98605	-0.95411
C	-3.02007	-0.11991	-0.67201
C	-4.74533	1.56712	-0.41026
C	2.52448	2.13296	-0.57939
C	3.86035	2.01843	-0.25049
C	1.99084	-2.02114	-0.20136
H	1.55367	-3.02731	-0.10647
N	0.26762	1.33336	-0.23053
C	-2.07392	0.72110	-0.05843
H	3.05543	-2.10858	0.07049
C	-3.81314	2.41915	0.18986
C	1.57456	1.30934	0.06528
C	-0.66430	0.30407	0.14120
H	-4.11731	3.40738	0.54269
C	-2.49055	2.00079	0.36189
C	4.30905	1.06993	0.72673
H	5.37752	0.99999	0.94377
C	-0.19522	-0.91406	0.53371
Au	-1.46644	-2.72612	0.81956
H	-1.77948	2.66010	0.86788
Cl	-2.88258	-4.70275	1.19701
C	1.27177	-1.09917	0.81334
C	1.96047	0.32253	1.10941
C	3.41968	0.26783	1.37549
H	1.36089	-1.60801	1.78694
H	3.76291	-0.44573	2.12886
H	1.42461	0.61883	2.03973

TS3

E+zero-point Energies= -1383.117269 Hartree

Free Energies= -1383.161251 Hartree

Imaginary frequency: -18.9 cm^{-1}

H	2.43920	-1.84133	-3.40959
O	2.68406	-2.16469	-2.51814
H	0.69819	-1.98997	-1.86570
H	-4.39589	2.51717	-1.38861
H	1.71410	-0.54480	-1.68250
C	1.70731	-1.63676	-1.60786
H	1.73173	2.64988	-1.43506
H	-6.01515	0.65442	-0.86977
H	4.15147	2.78363	-0.90020
C	-4.06347	1.58858	-0.88140
C	-4.97751	0.56681	-0.52142
H	-2.04802	2.33061	-0.67868
C	2.16802	2.06544	-0.61988
C	-2.72068	1.47492	-0.51042
C	3.50613	2.11173	-0.32798
C	2.01464	-2.07141	-0.18586
H	1.65376	-3.10706	-0.07023
H	3.10192	-2.05677	-0.02661
N	0.02584	1.08405	-0.22693
C	-4.57274	-0.46833	0.35927
C	1.29933	1.16074	0.08260
C	-2.24243	0.30133	0.14905
H	-5.29640	-1.16025	0.83349
C	-0.77429	0.06663	0.27409
H	5.18313	1.30879	0.82411
C	4.10127	1.25854	0.67341
C	-3.22020	-0.57133	0.71607
C	-0.18735	-1.13906	0.70483
Au	-1.26299	-3.05428	1.02960
C	1.30670	-1.21171	0.90359
C	1.87008	0.26341	1.14438
C	3.33829	0.37536	1.36300
H	-2.92134	-1.29620	1.48814
H	1.51439	-1.72873	1.85844
H	3.79370	-0.26491	2.12580
H	1.36503	0.54195	2.09165

10a

E+zero-point Energies= -1383.166702 Hartree

Free Energies= -1383.219099 Hartree

H	3.68843	0.22581	-3.76562
H	5.04820	1.98073	-2.61995
C	3.34111	0.66783	-2.82892
H	1.50649	-0.46843	-2.81435
C	4.09667	1.65746	-2.19208
C	2.12672	0.25346	-2.27666
Cl	2.72650	-4.58082	-1.69048
C	3.62063	2.24079	-1.00900
Au	1.34377	-2.61559	-1.15452
C	1.64844	0.81145	-1.07141
H	4.20590	3.01728	-0.51103
C	2.40636	1.83098	-0.45922
C	-0.01619	-0.99328	-0.50937
C	0.37940	0.34616	-0.46861
C	-2.29873	-0.12414	0.07825
H	-4.20758	-1.22871	0.31635
C	-1.33914	-1.38508	0.07261
N	-0.32304	1.30578	0.24030
H	2.03218	2.28132	0.46181
C	-3.65060	-0.34974	0.65568
C	-1.56189	1.07101	0.61591
H	-0.77880	-3.17690	1.12014
C	-4.21325	0.53048	1.52383
C	-1.20667	-2.19851	1.39546
C	-2.22551	1.96927	1.51022
H	-5.21980	0.35639	1.91122
H	-2.21227	-2.39340	1.80183
H	-1.67294	2.84861	1.84723
C	-3.50185	1.71202	1.93981
H	0.63817	-1.29823	2.08324
H	-3.99171	2.40673	2.62641
C	-0.33315	-1.62298	2.50111
O	-1.01957	-0.52655	3.12709
H	-0.13249	-2.42219	3.23991
H	-0.37663	-0.07238	3.70605

TS4

E+zero-point Energies= --1383.123288 Hartree

Free Energies= --1383.181649 Hartree

Imaginary frequency: -46.2 cm^{-1}

H	2.80369	-1.42464	-2.90083
H	-3.95020	2.85291	-1.87959
H	2.07075	-3.46817	-1.97262
O	2.85013	-1.53204	-1.93045
H	0.83619	-2.18403	-1.91281
C	1.84325	-2.47769	-1.55307
H	-1.55676	2.35509	-1.41991
C	-3.68638	2.16405	-1.07836
H	-5.73140	1.68598	-0.56969
C	-2.34576	1.88688	-0.83976
C	-4.67953	1.49549	-0.35817
H	2.19916	3.19702	-0.46379
H	4.65312	2.85404	-0.01954
C	2.59548	2.25131	-0.09242
C	1.76937	-2.53201	-0.01563
C	3.94795	2.05326	0.15916
N	0.33616	1.46133	-0.03093
C	-1.97400	0.90932	0.09572
Au	-1.85209	-2.53280	0.21151
H	1.10178	-3.35980	0.27946
C	1.66801	1.21010	0.16172
Cl	-3.64384	-4.21787	0.61550
H	2.77197	-2.70921	0.39783
C	-0.56006	0.51226	0.19460
C	-0.21032	-0.91226	0.24293
C	-4.32195	0.56485	0.62558
C	1.20231	-1.17755	0.42883
C	4.38544	0.85044	0.74727
C	2.14100	-0.06565	0.59061
H	5.41733	0.76587	1.09633
C	-2.97115	0.28659	0.87174
H	-5.08925	0.00496	1.16914
C	3.50600	-0.19802	0.95364
H	3.86986	-1.12991	1.39615
H	0.40089	-1.26078	1.44805
H	-2.71009	-0.42956	1.66571

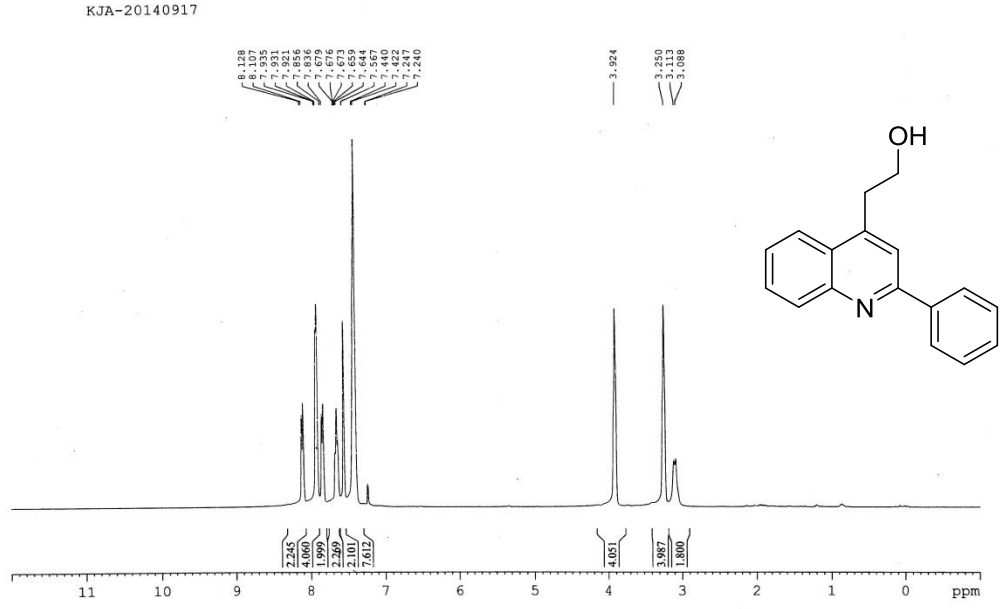
5a

E+zero-point Energies= -787.452450 Hartree

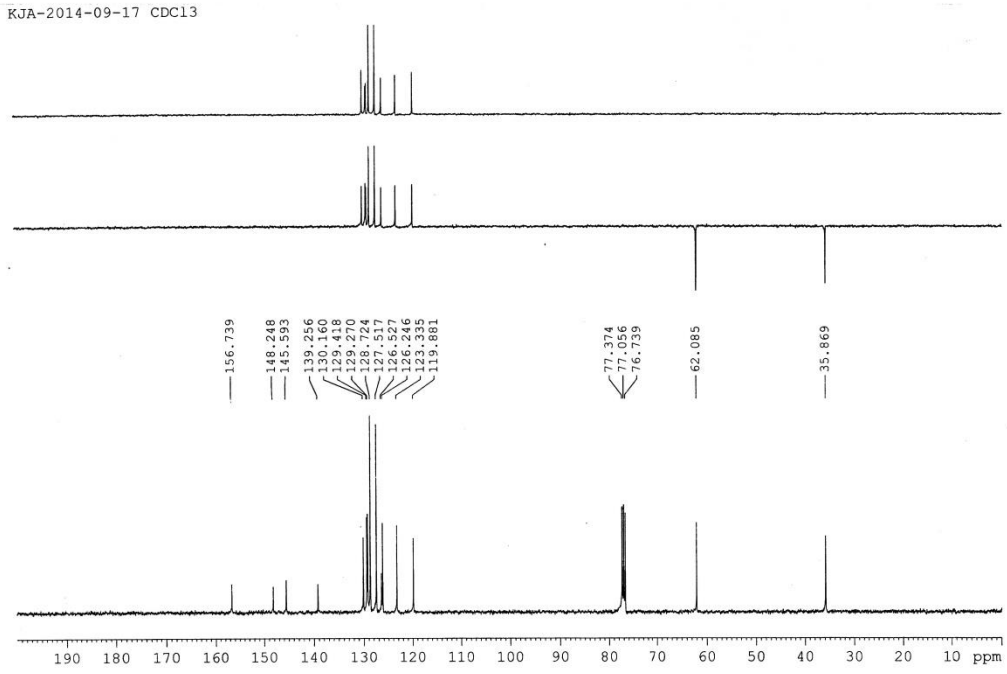
Free Energies= -787.486608 Hartree

H	-1.33076	1.54020	-5.83945
H	-1.39992	-2.82832	-1.66040
H	-2.94815	-2.00006	-1.49263
C	-2.02791	-2.26516	-0.95112
H	5.10583	1.96940	-0.58306
H	2.61349	2.04090	-0.67503
H	0.63186	-1.99637	-0.72178
H	-3.97248	-0.43063	-0.40947
H	-2.76407	-4.16683	-0.25505
C	4.52513	1.08975	-0.29382
C	-1.26998	-1.02638	-0.52512
C	3.12855	1.13302	-0.35684
C	0.11085	-1.07567	-0.44891
C	-3.31429	0.41756	-0.22909
H	6.27185	-0.09536	0.20126
H	-4.94102	1.79234	0.02989
C	-1.90657	0.22110	-0.22619
C	5.18313	-0.06628	0.13362
C	-3.85624	1.66207	0.03196
C	0.86651	0.07912	-0.10010
C	2.34965	0.01545	-0.01716
C	-2.39701	-3.22085	0.18739
C	-1.05743	1.34471	0.07284
C	-3.01795	2.76903	0.30839
N	0.30529	1.26145	0.12694
H	-3.45973	3.74750	0.51239
C	-1.64667	2.61247	0.33322
C	4.42495	-1.18959	0.52381
C	3.01296	-1.15161	0.43533
H	-0.97607	3.44340	0.55779
H	-1.49707	-3.44976	0.78835
H	4.91680	-2.03703	1.01061
H	2.42858	-1.97807	0.84919
O	-3.41296	-2.61019	0.99484
H	-3.60750	-3.22061	1.73378

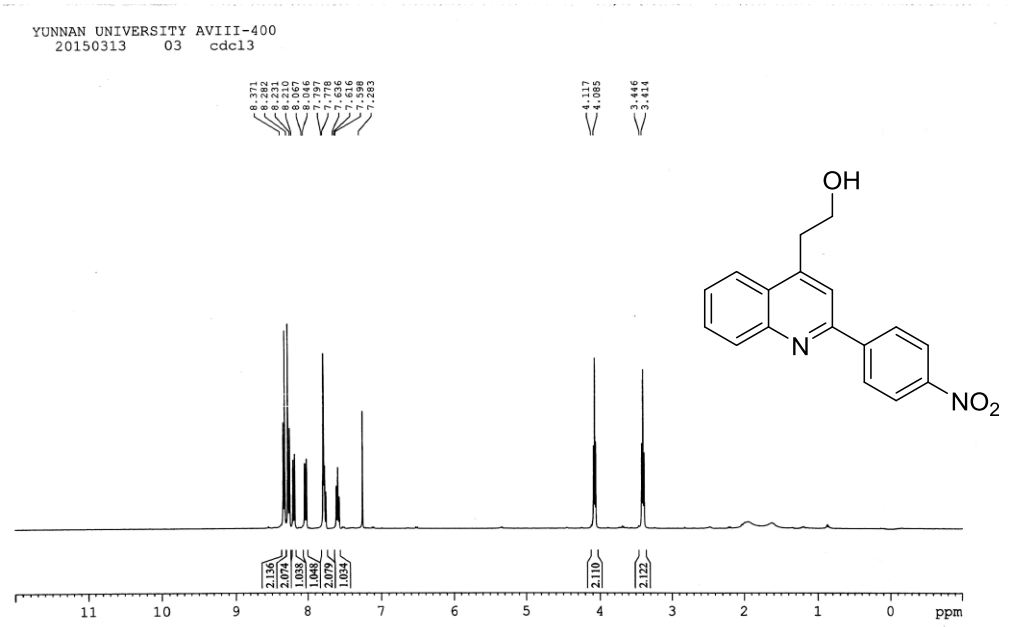
3. Copies of ^{1}H NMR and ^{13}C NMR Spectra



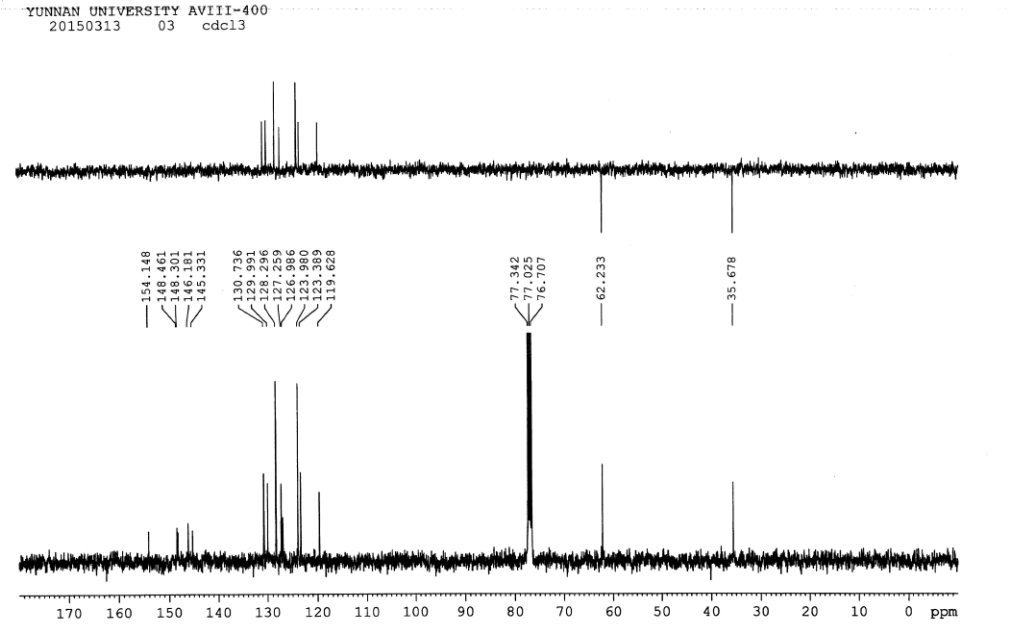
^{1}H-NMR spectrum of **5a**



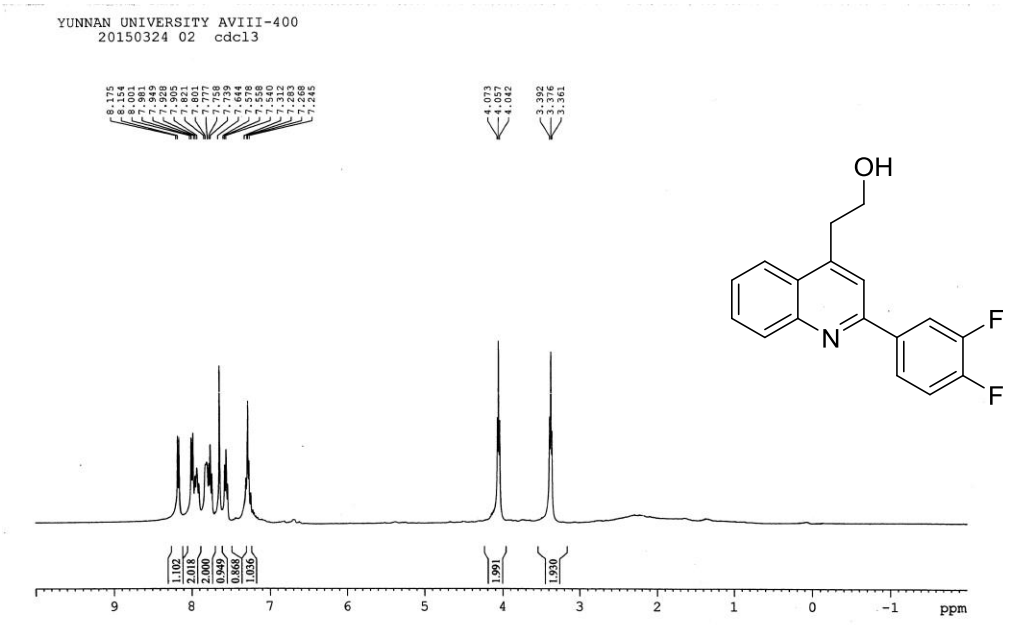
^{13}C-NMR spectrum of **5a**



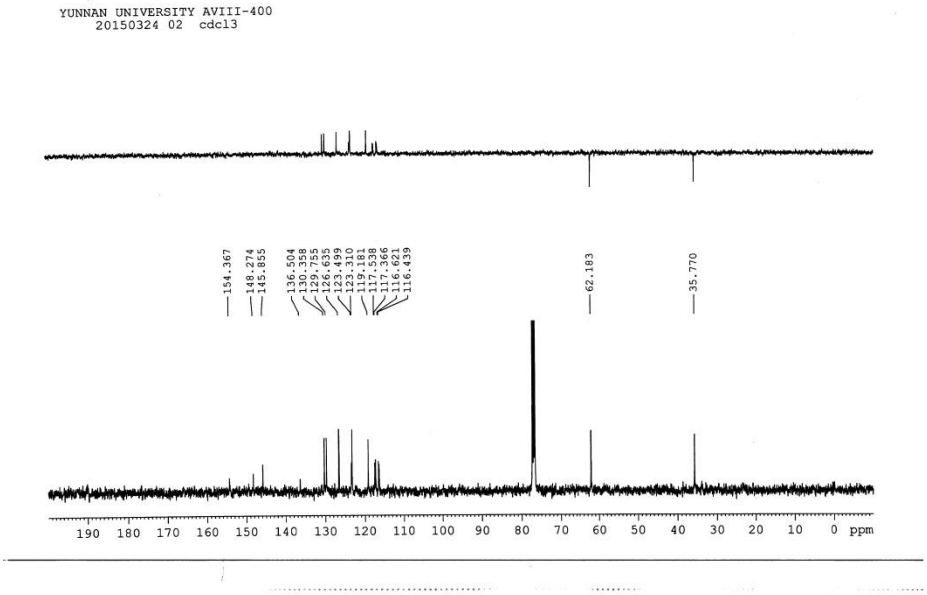
^{1}H-NMR spectrum of **5b**



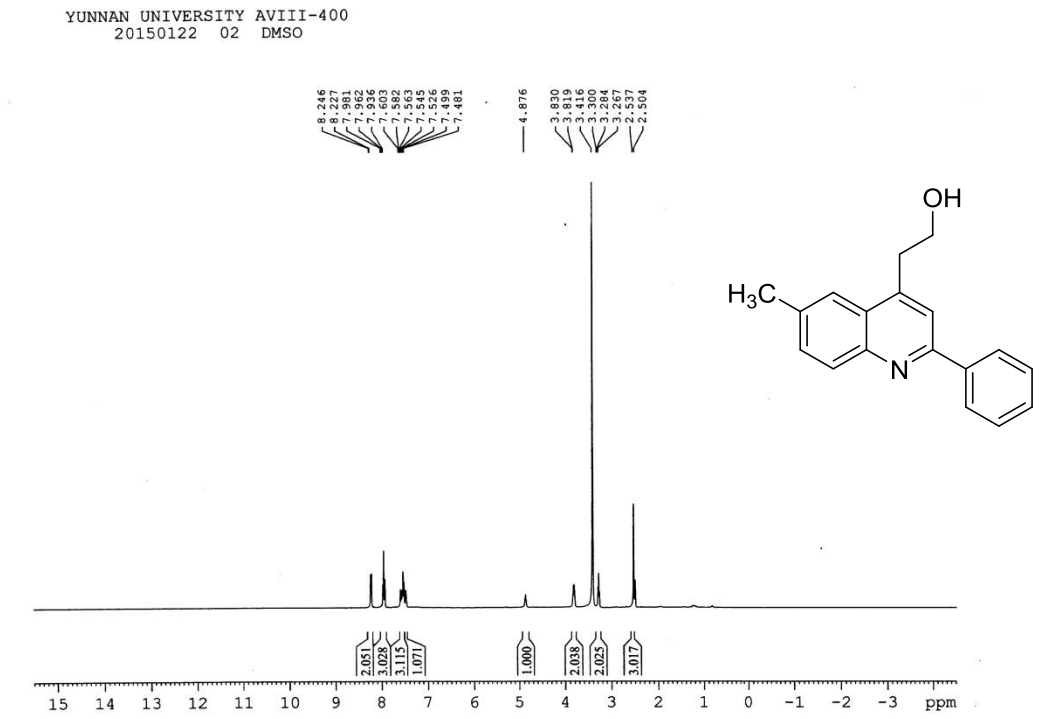
^{13}C-NMR spectrum of **5b**



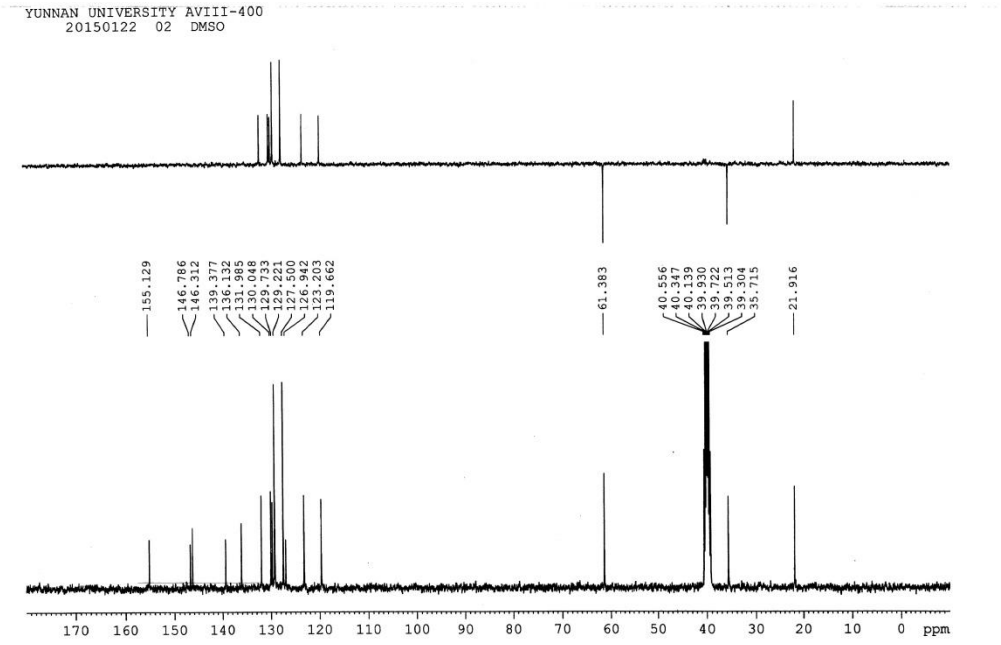
^{1}H-NMR spectrum of **5c**



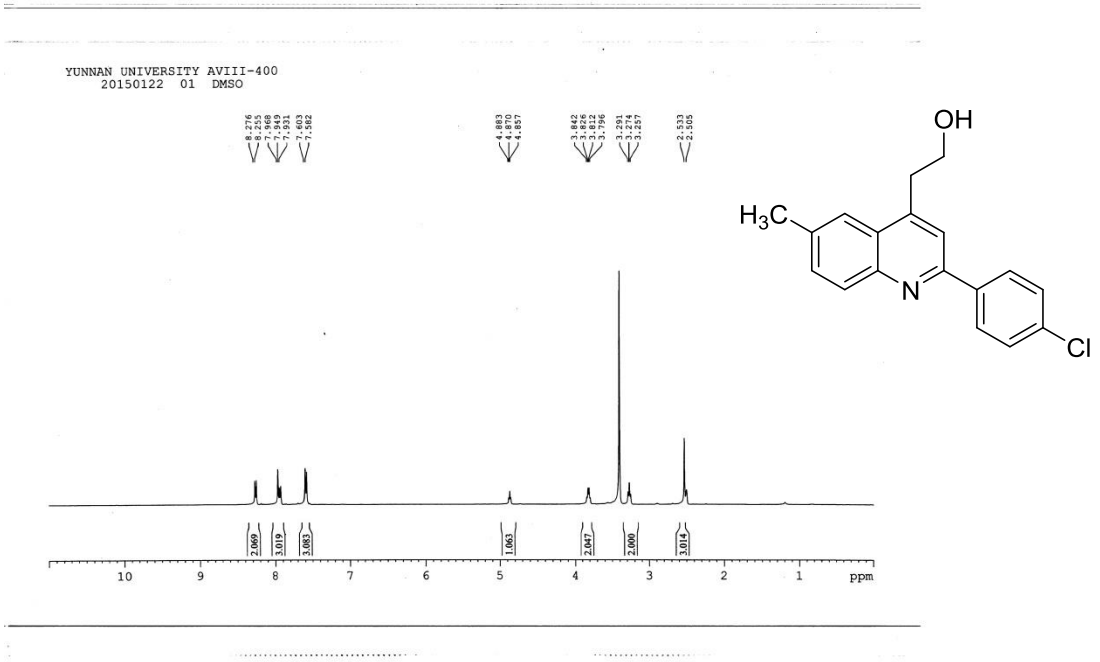
^{13}C-NMR spectrum of **5c**



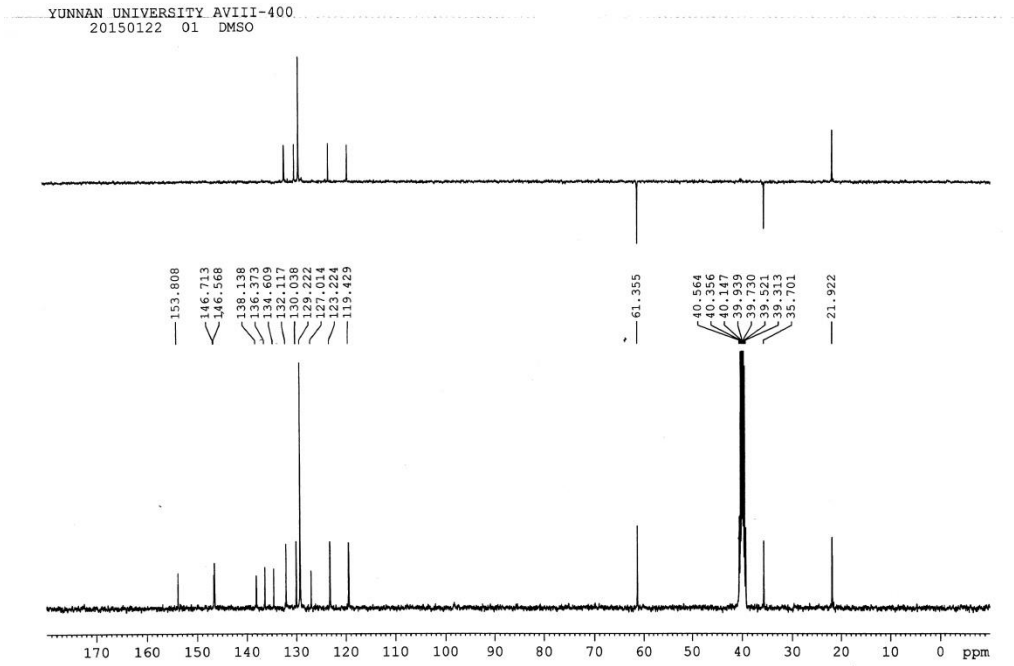
^{1}H-NMR spectrum of **5d**



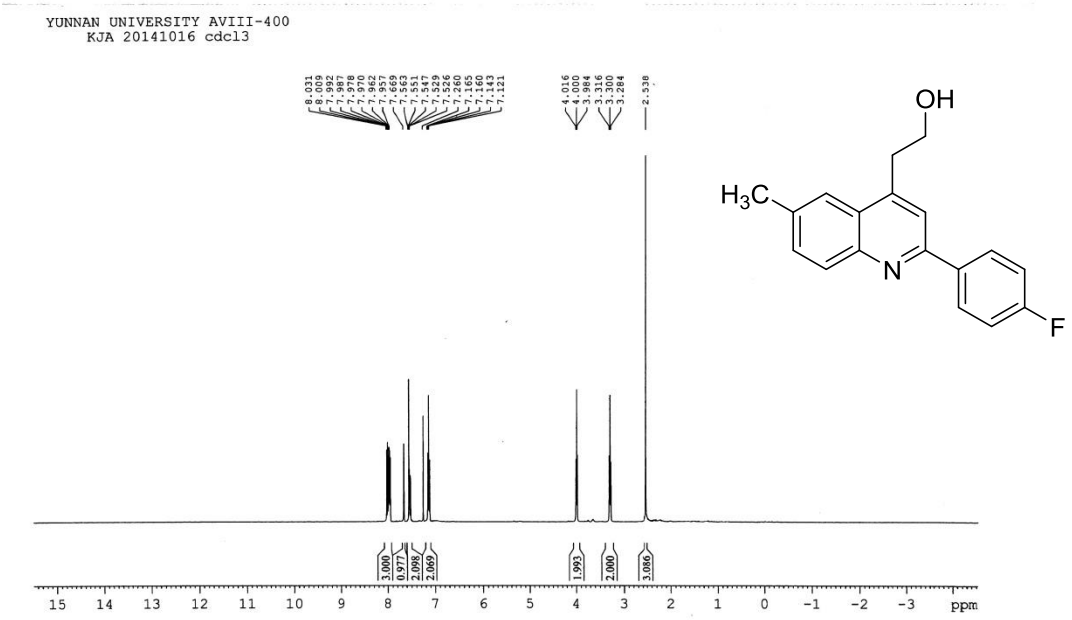
^{13}C-NMR spectrum of **5d**



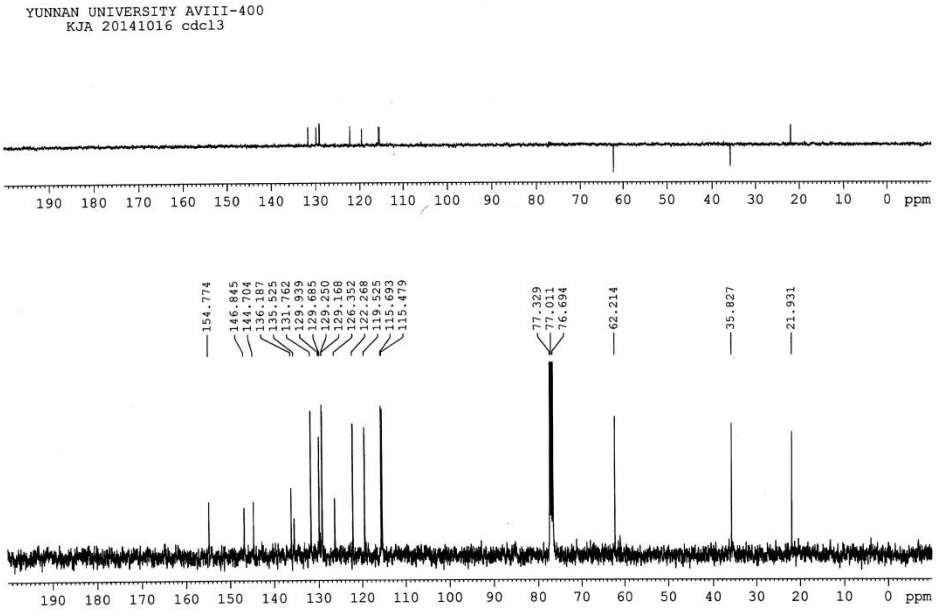
^{1}H-NMR spectrum of **5e**



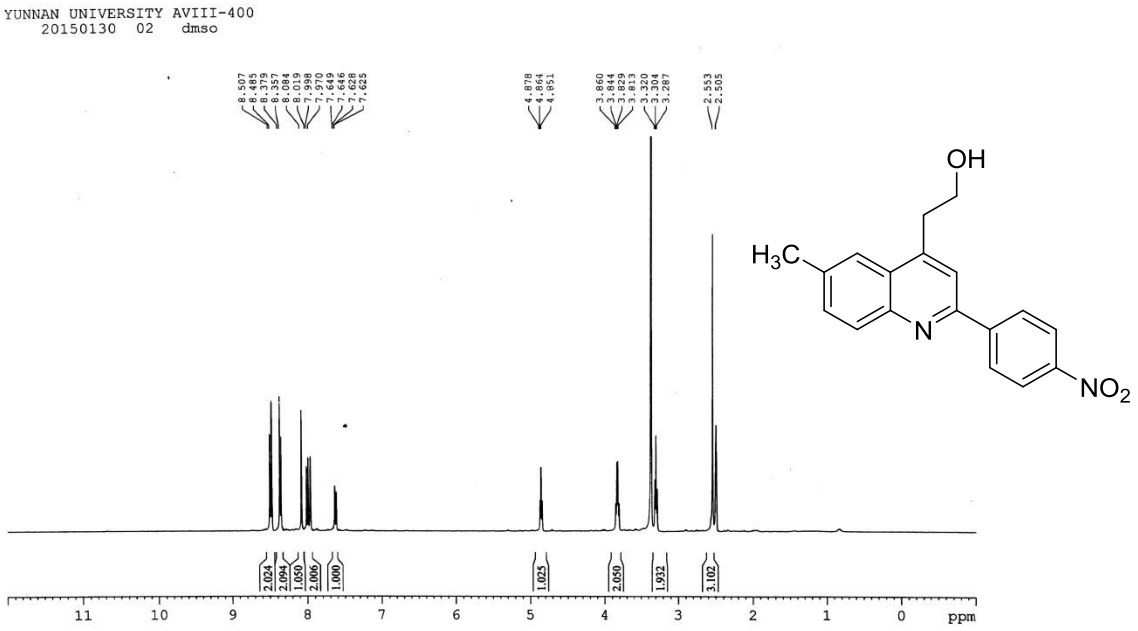
^{13}C-NMR spectrum of **5e**



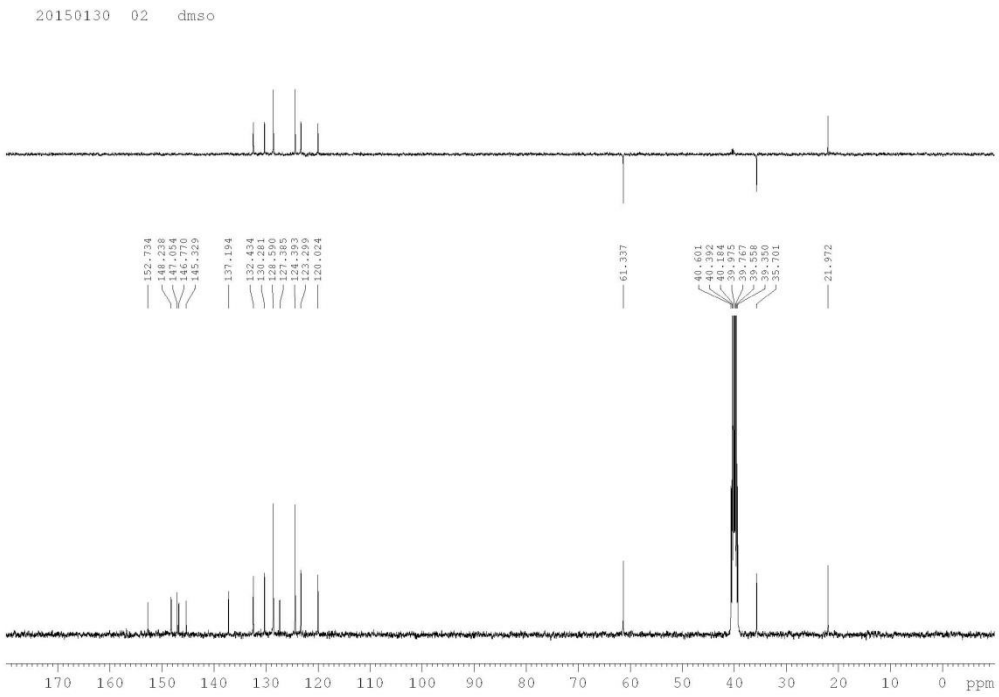
^{1}H-NMR spectrum of **5f**



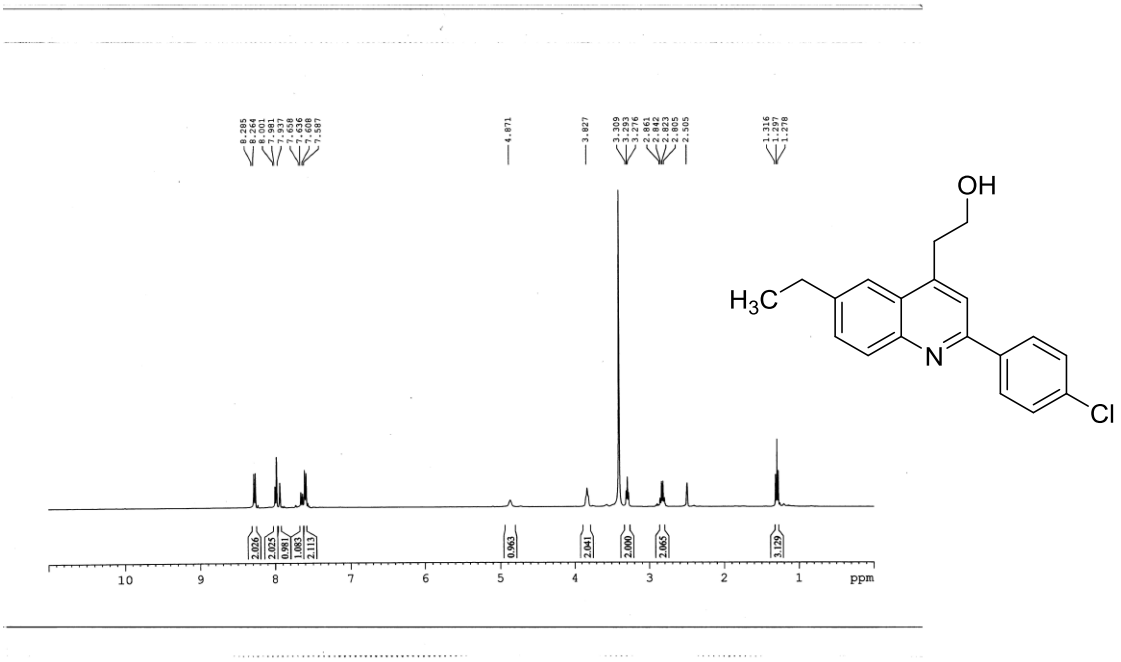
^{13}C-NMR spectrum of **5f**



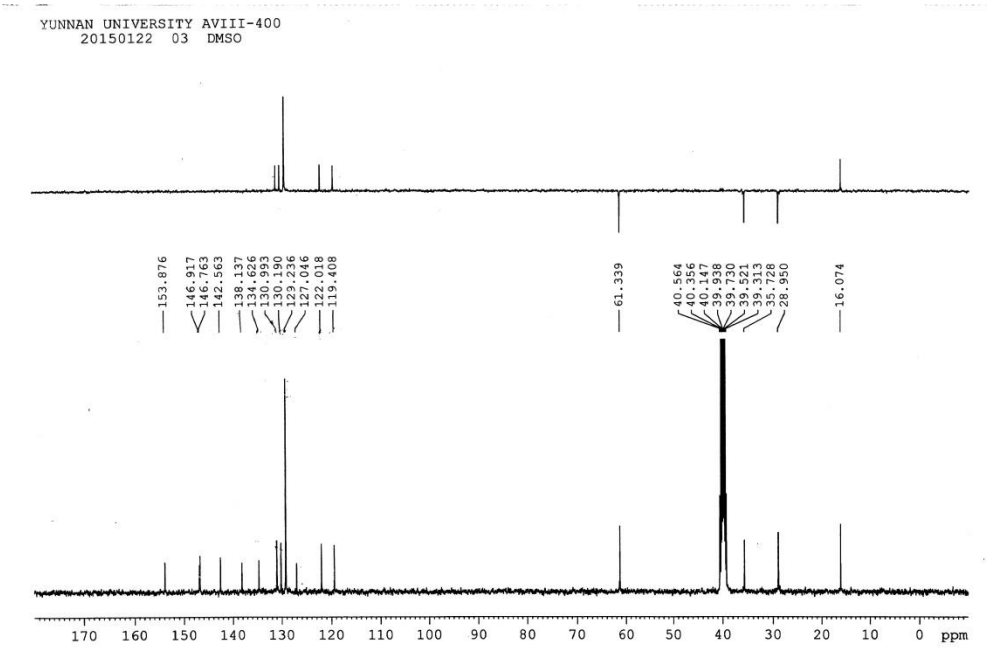
^{1}H-NMR spectrum of **5g**



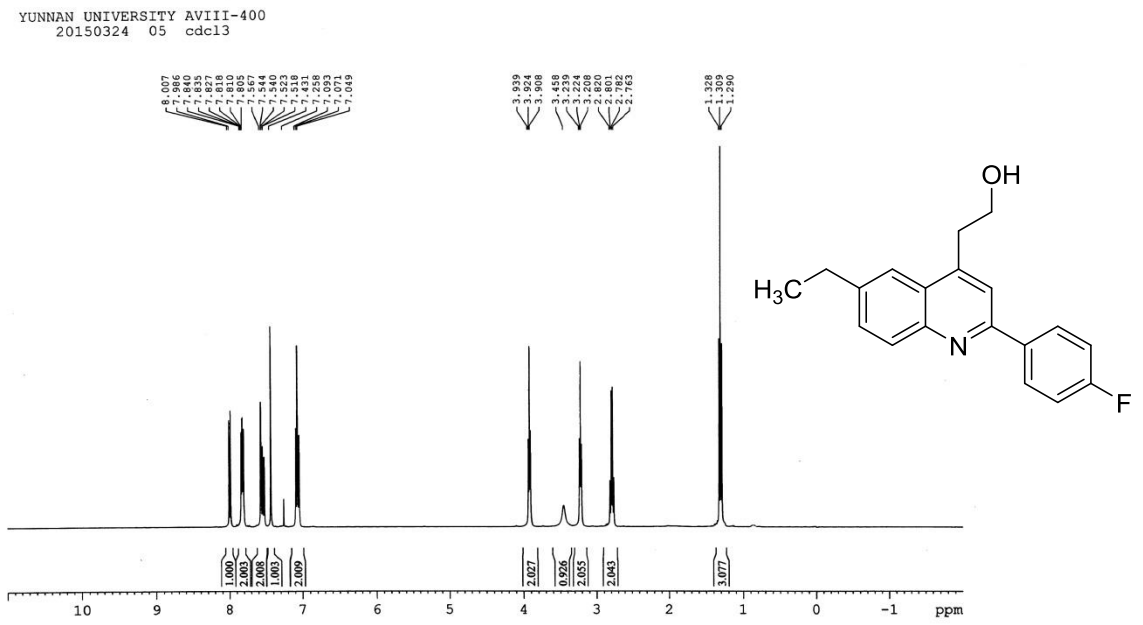
^{13}C-NMR spectrum of **5g**



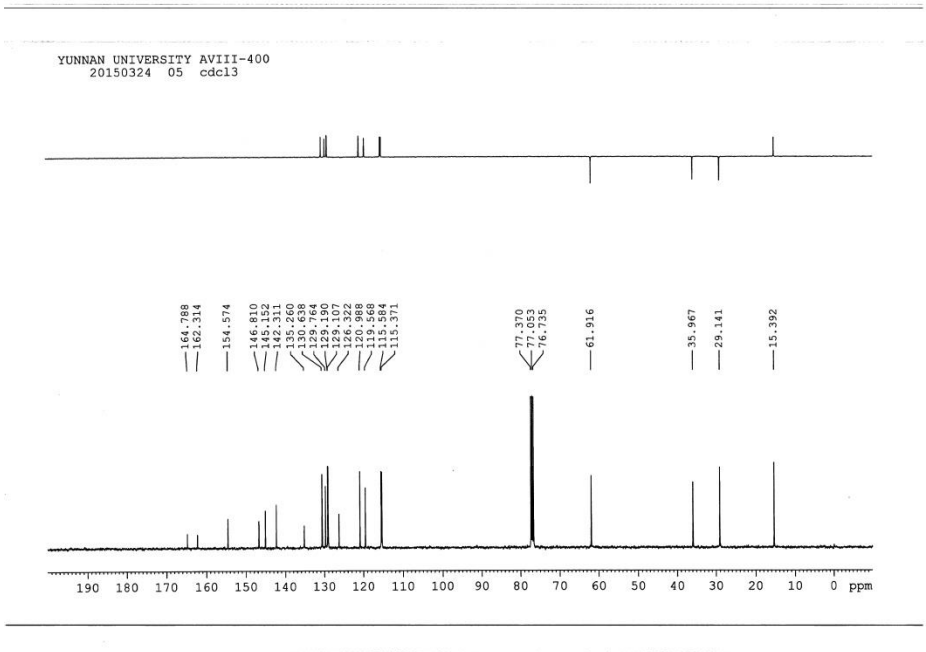
^{1}H-NMR spectrum of **5h**



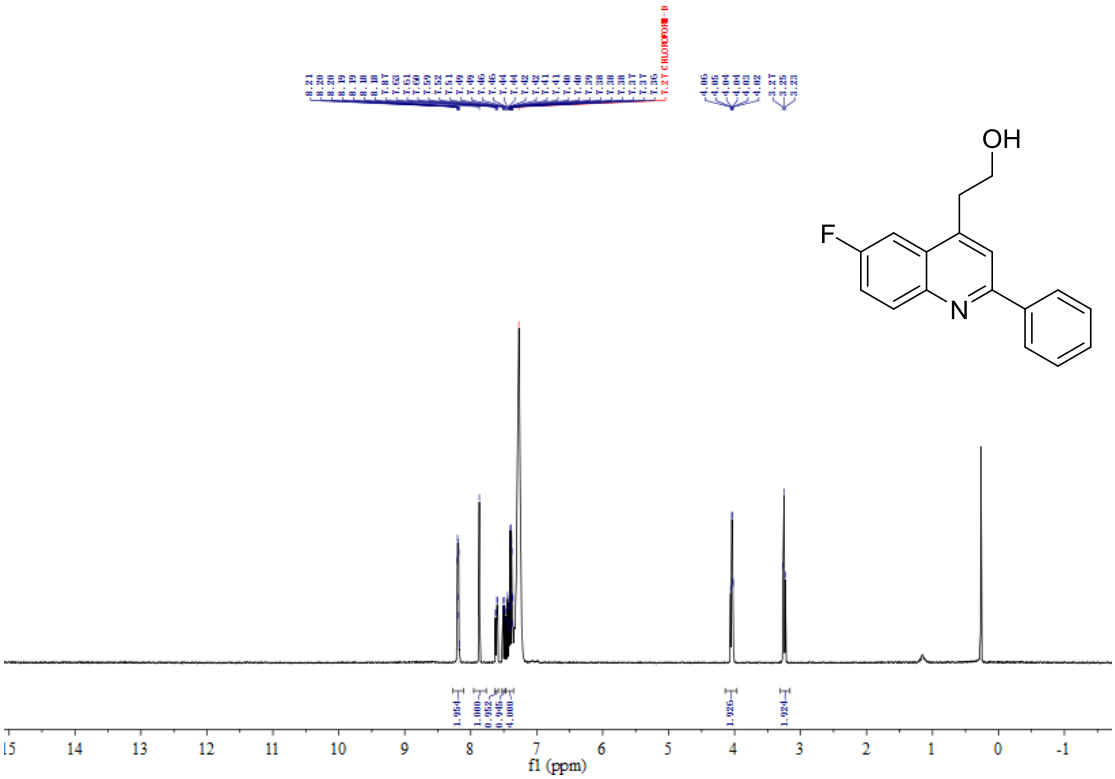
^{13}C-NMR spectrum of **5h**



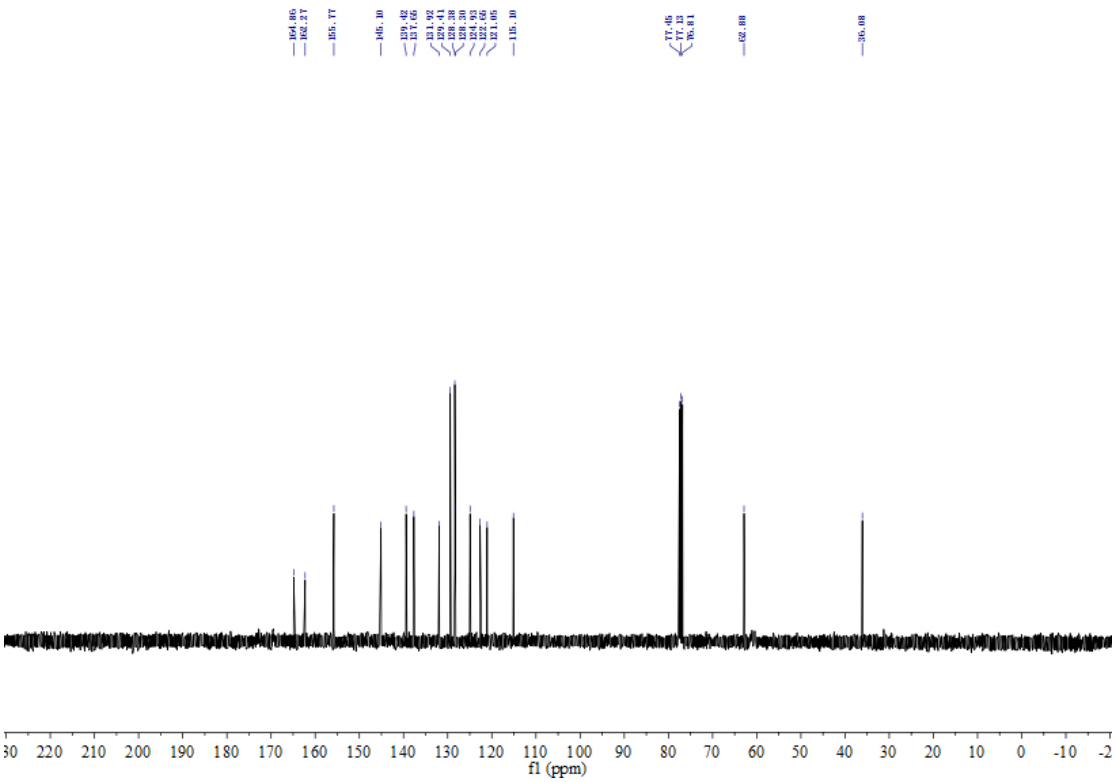
^{1}H-NMR spectrum of **5i**



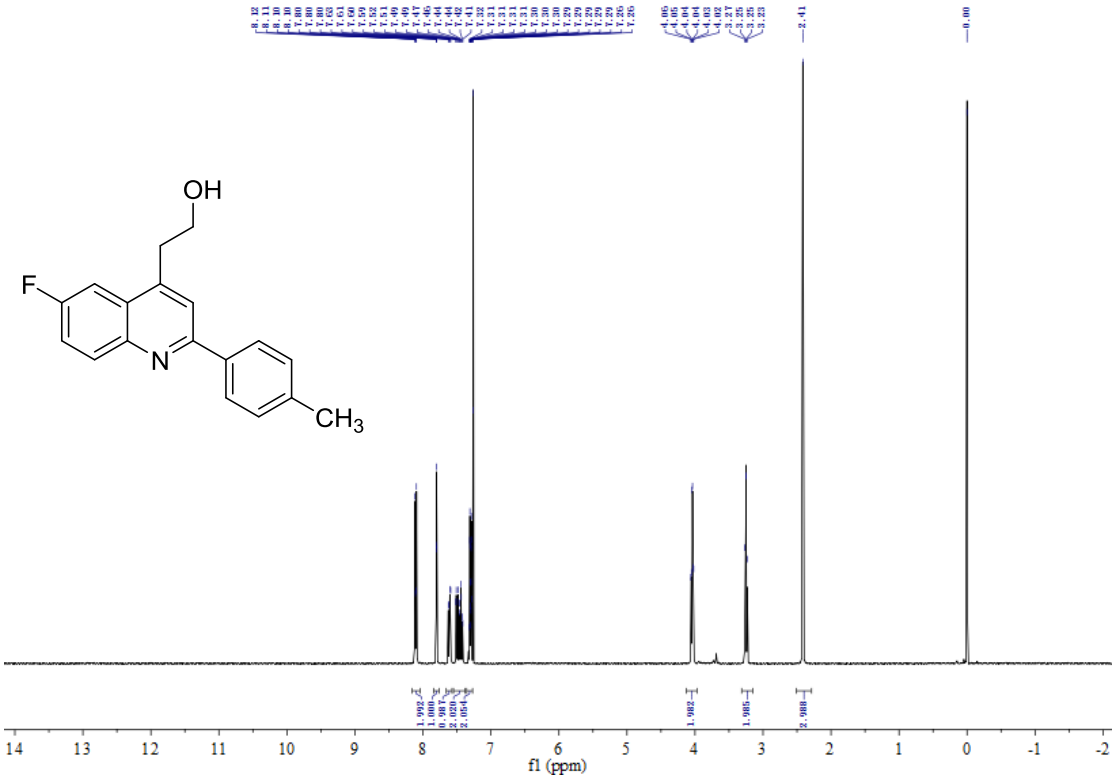
^{13}C-NMR spectrum of **5i**



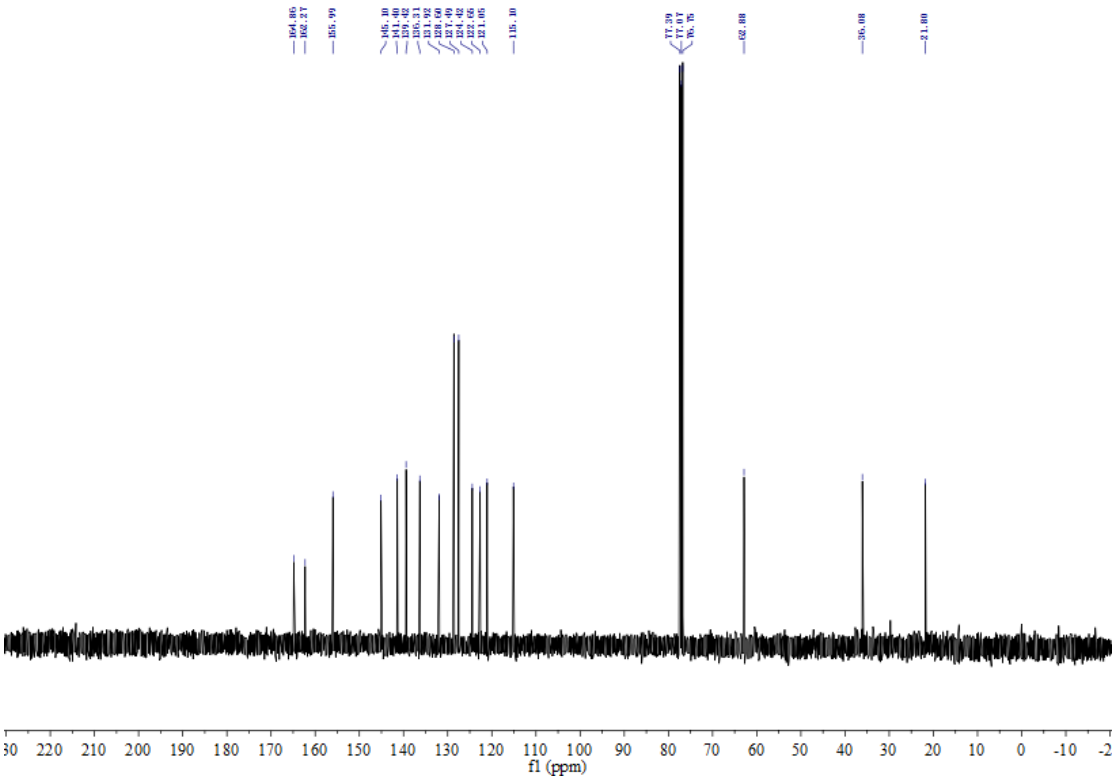
^{1}H-NMR spectrum of **5j**



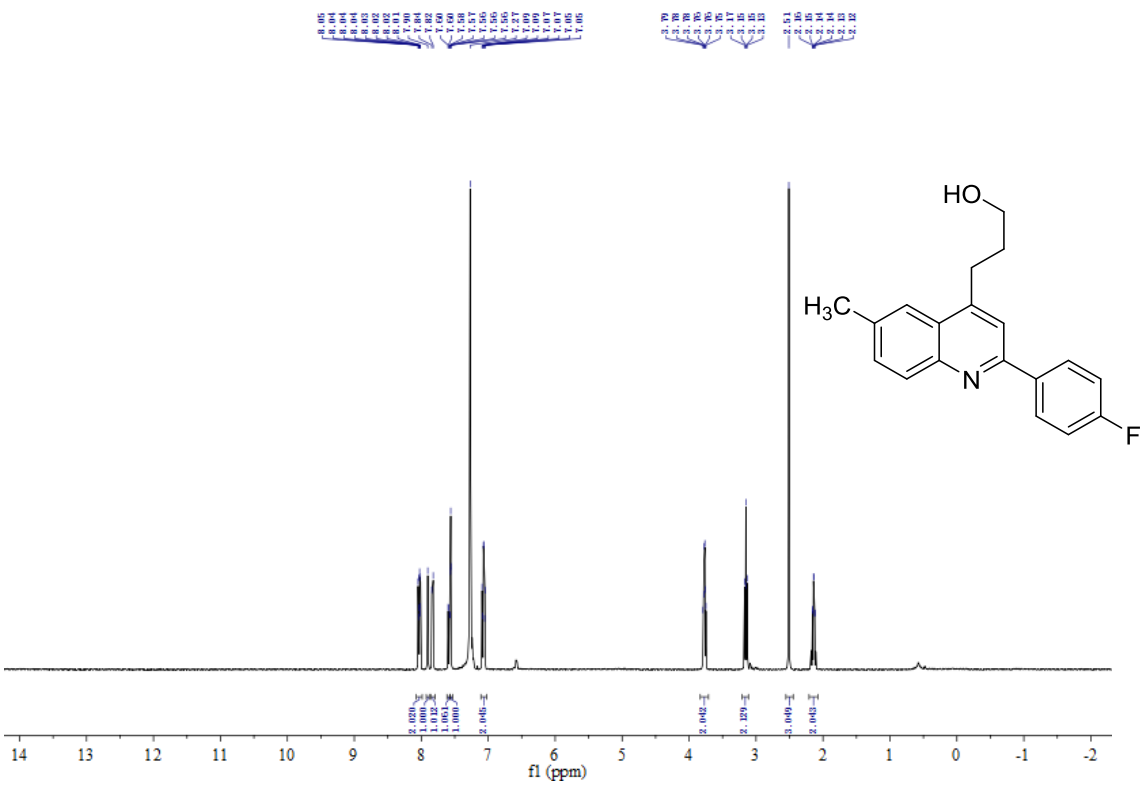
^{13}C-NMR spectrum of **5j**



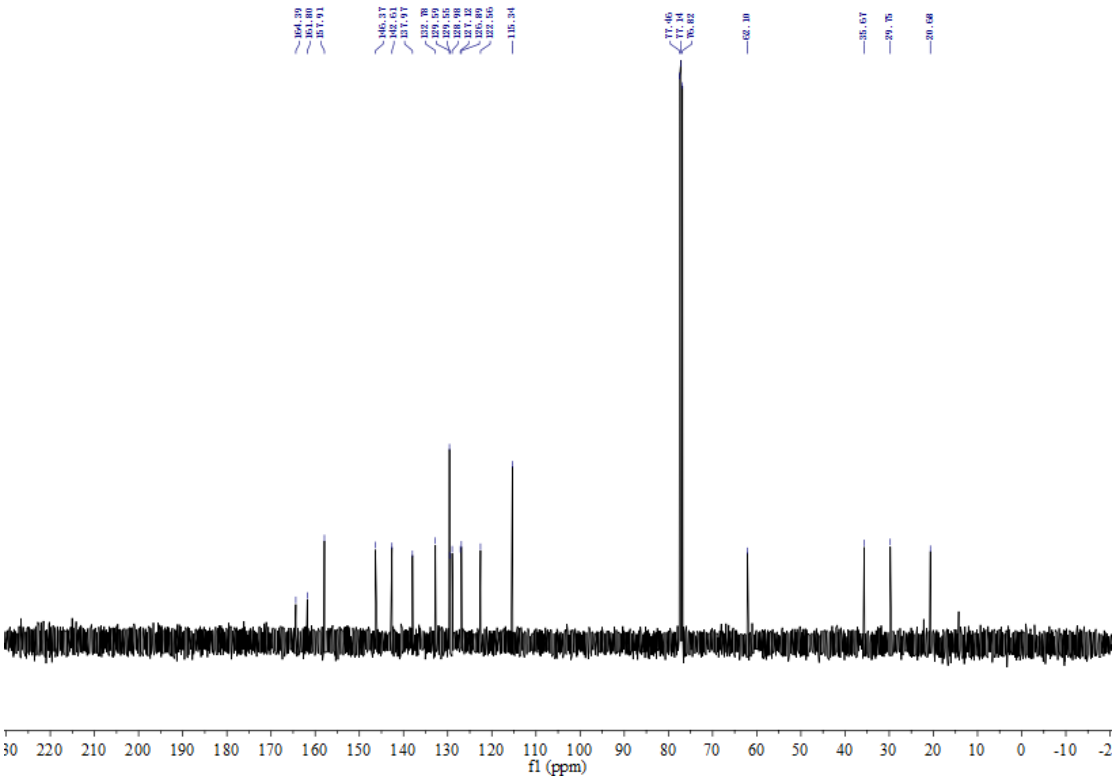
^{1}H-NMR spectrum of **5k**



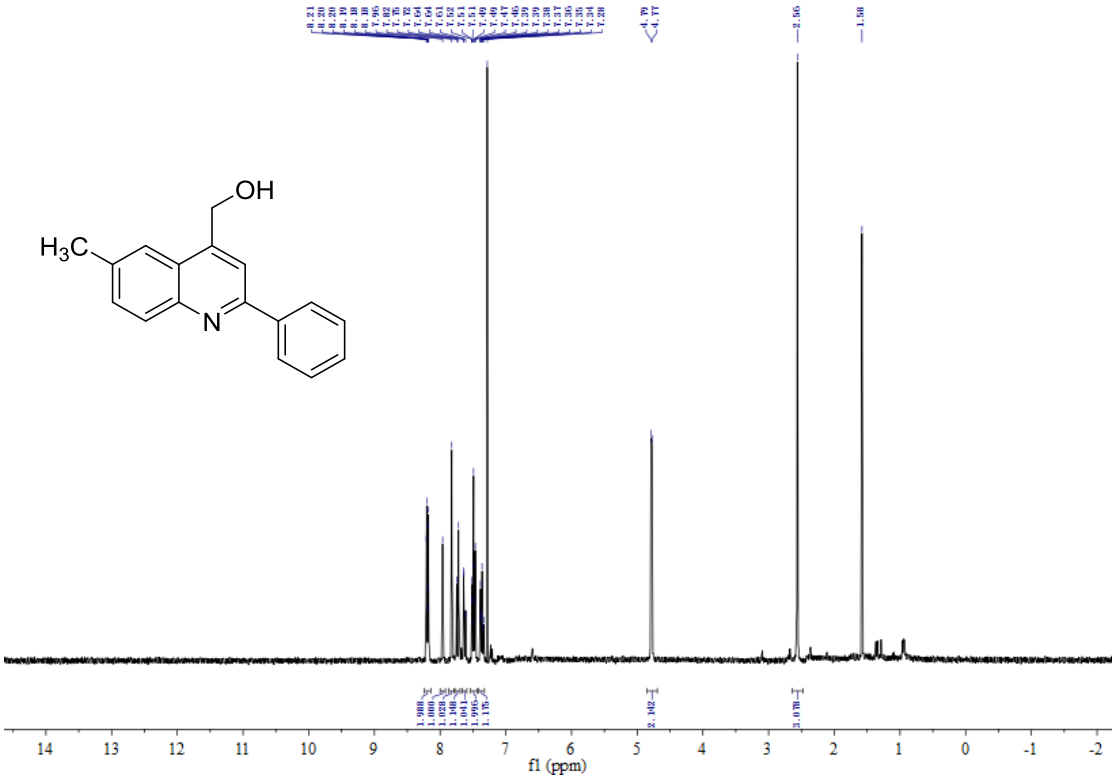
^{13}C-NMR spectrum of **5k**



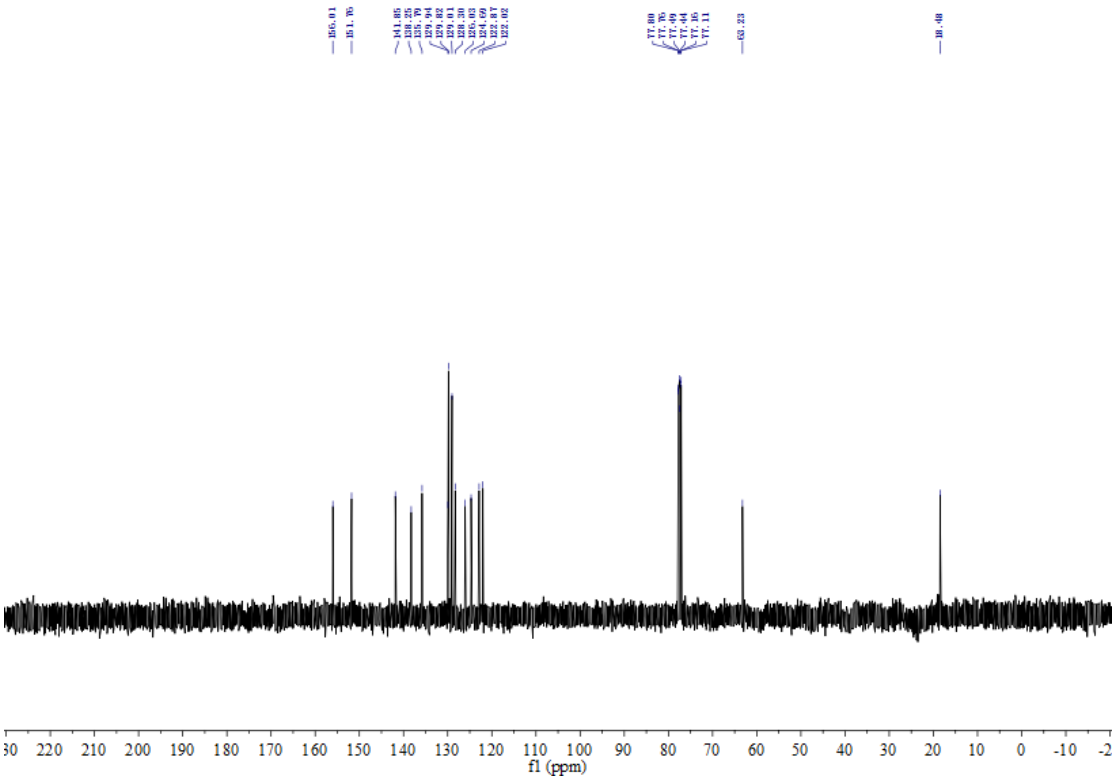
^{1}H-NMR spectrum of **5l**



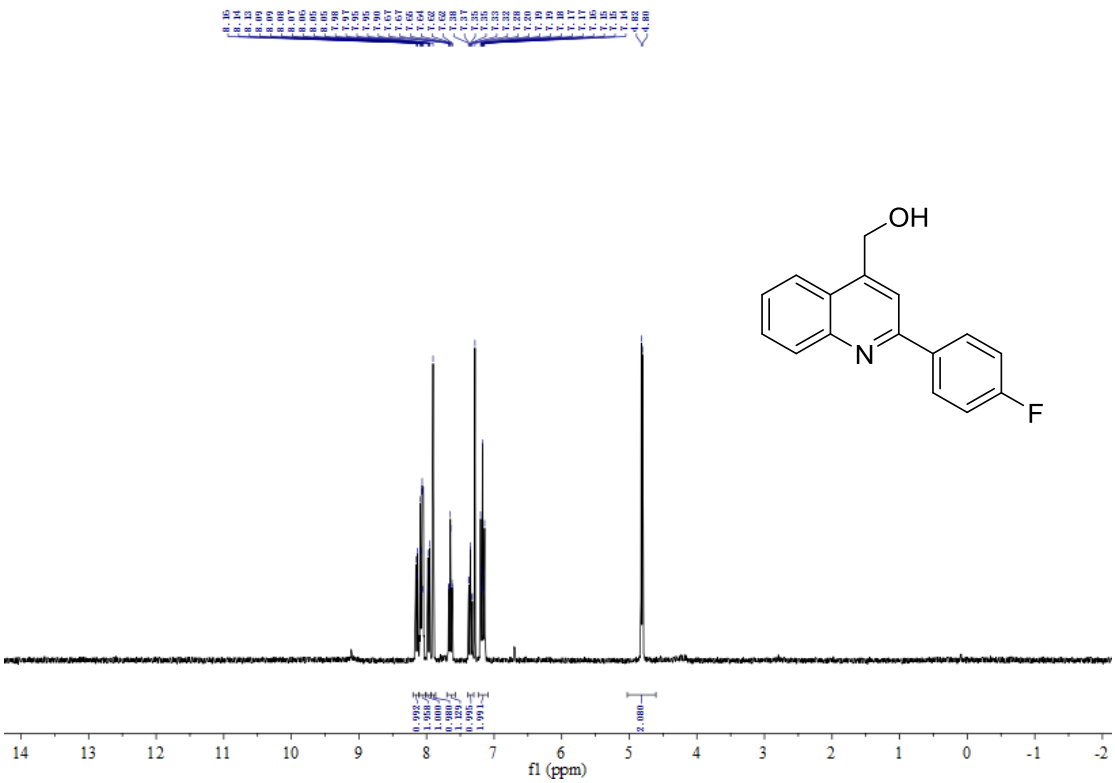
^{13}C-NMR spectrum of **5l**



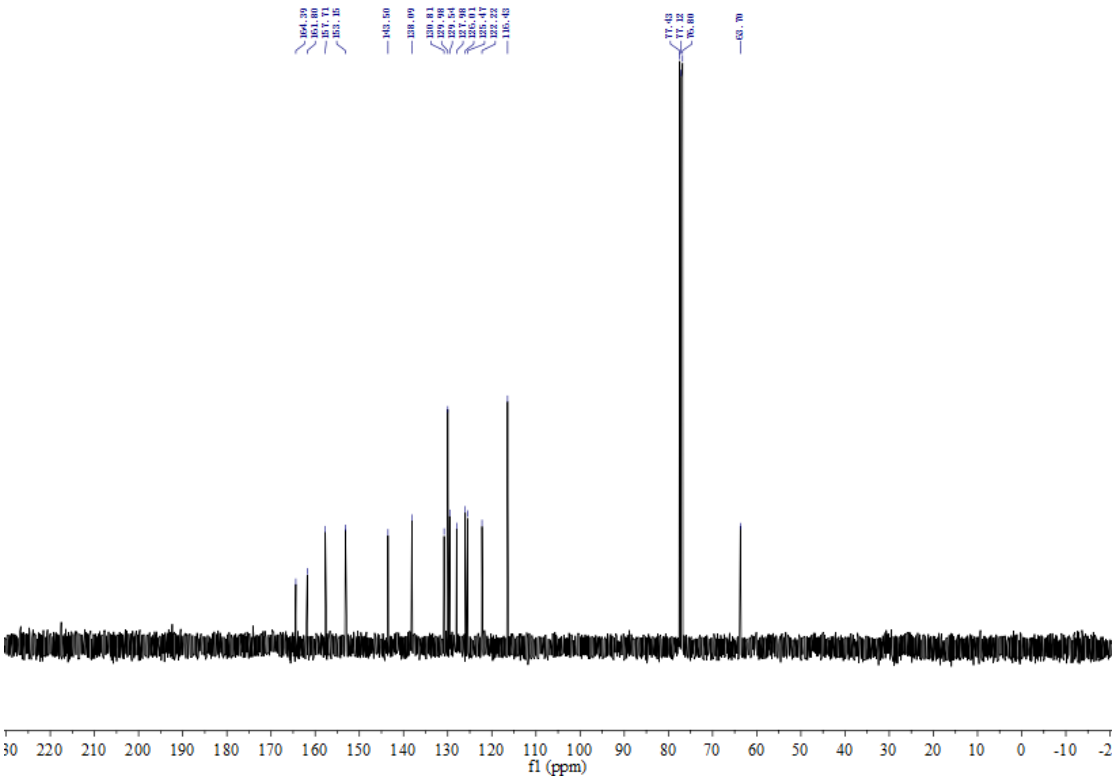
^{1}H-NMR spectrum of **5m**



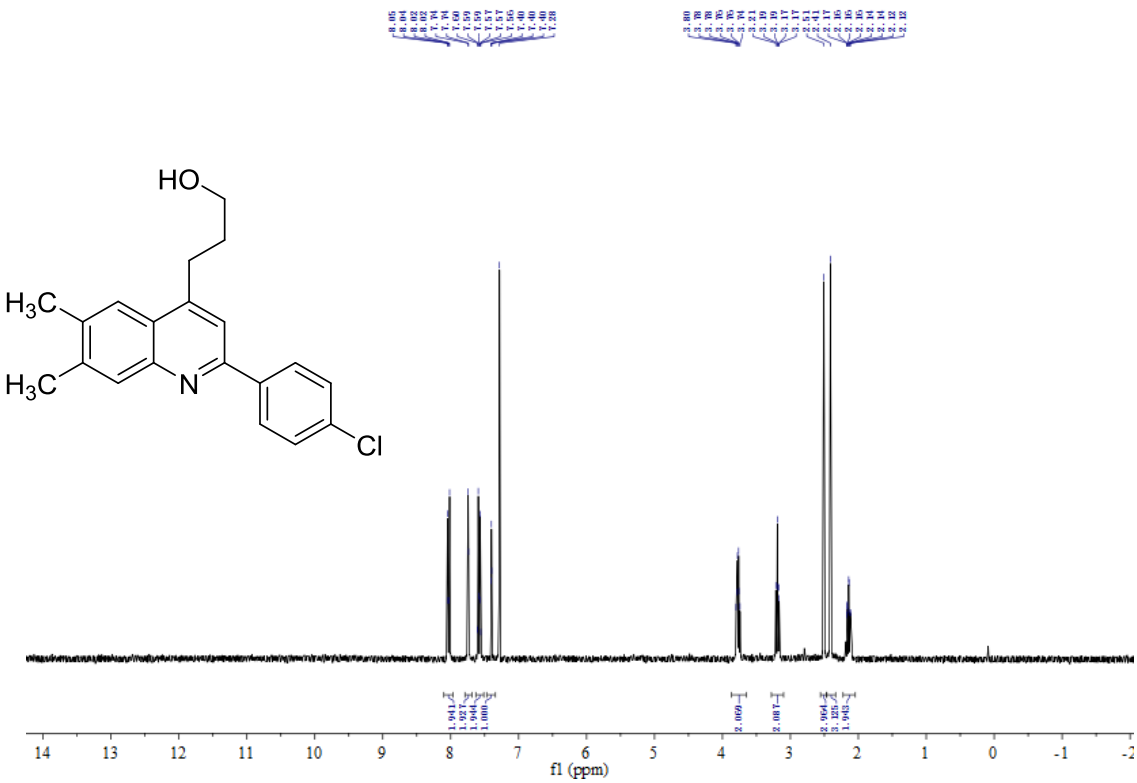
^{13}C-NMR spectrum of **5m**



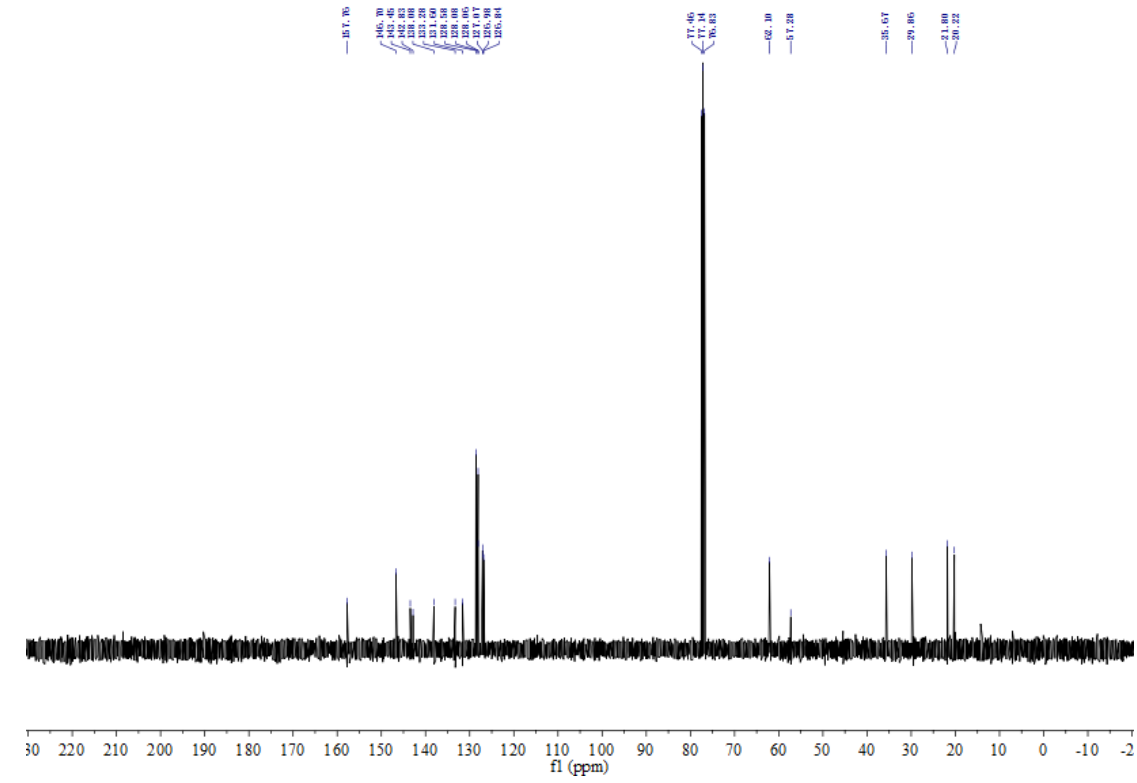
^{1}H-NMR spectrum of **5n**



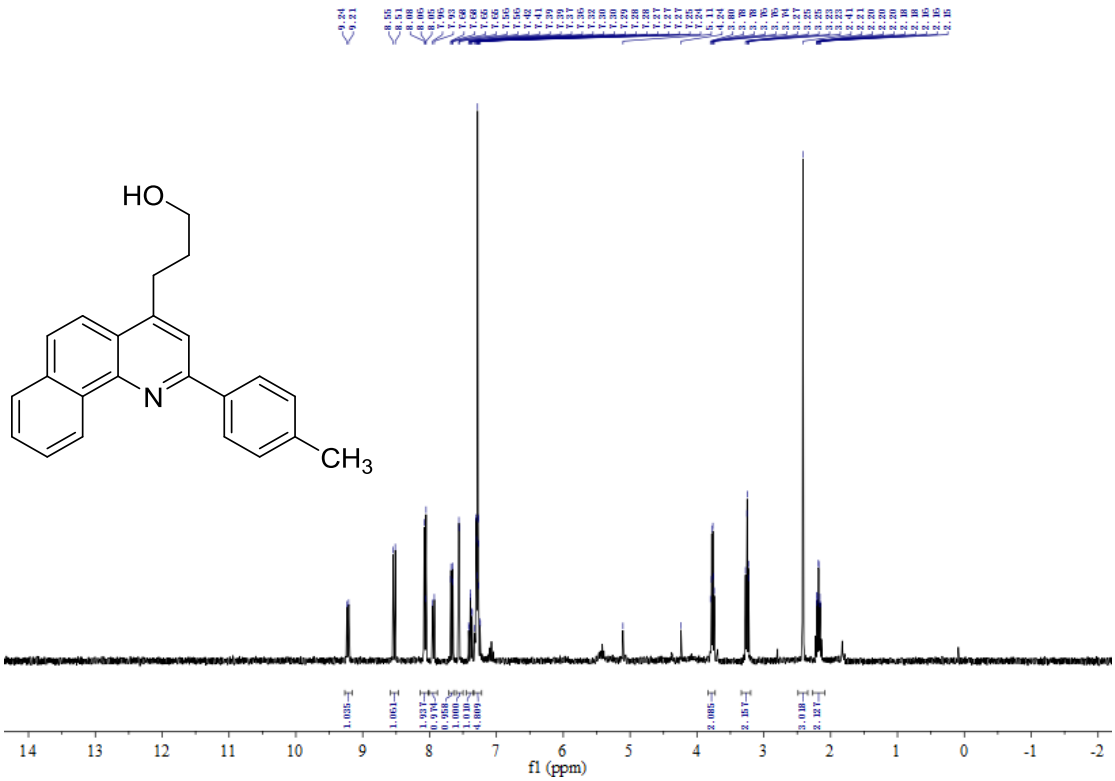
^{13}C-NMR spectrum of **5n**



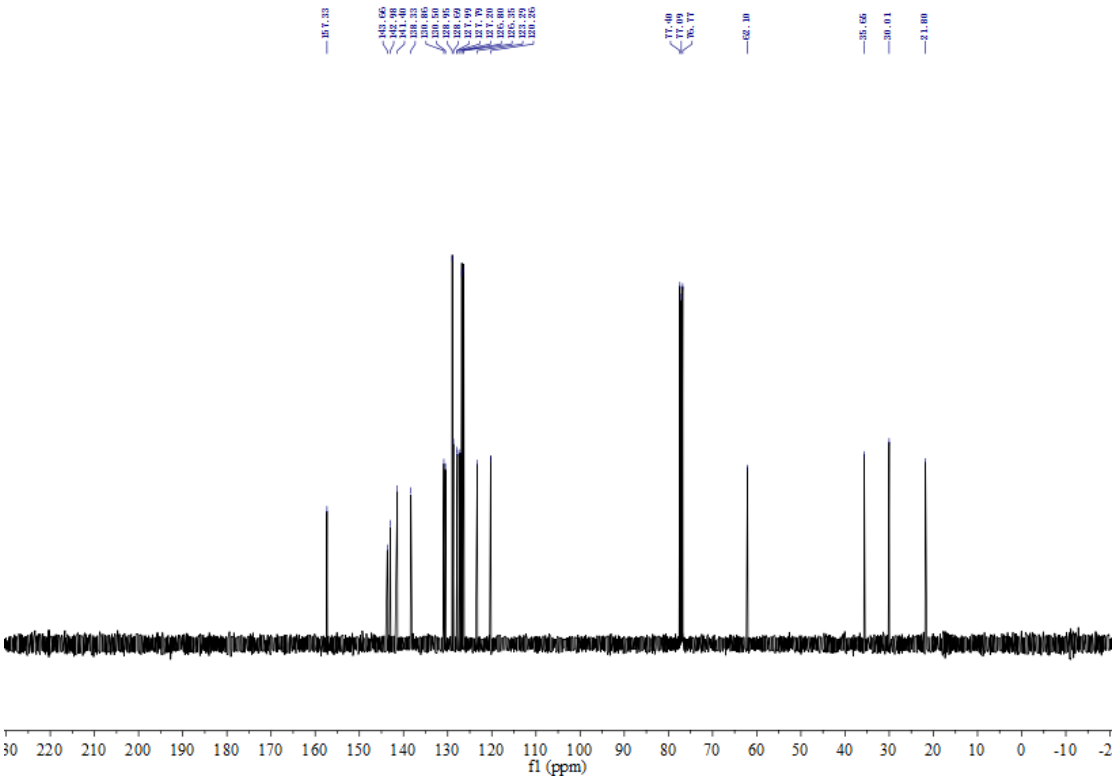
^{1}H-NMR spectrum of **5o**



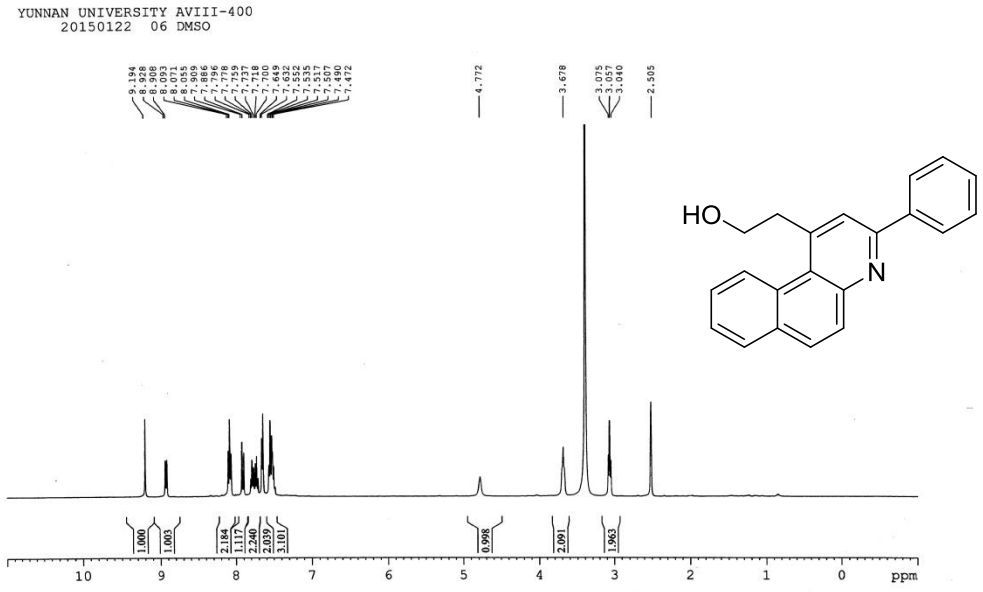
^{13}C-NMR spectrum of **5o**



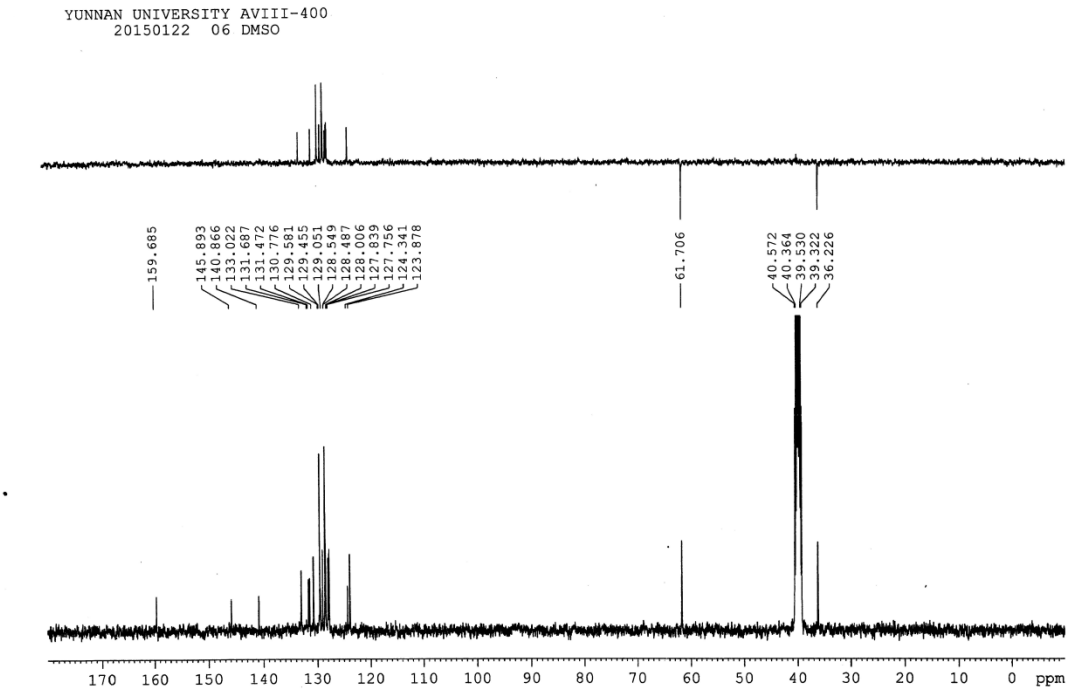
^{1}H-NMR spectrum of **5p**



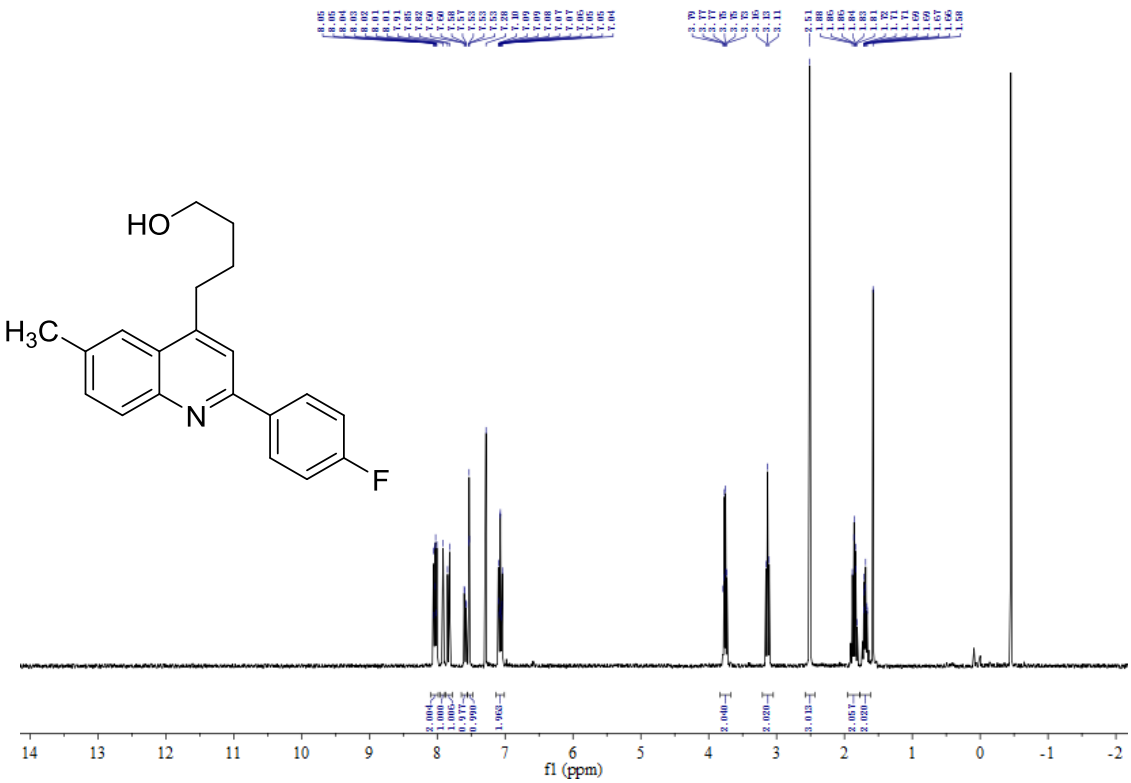
^{13}C-NMR spectrum of **5p**



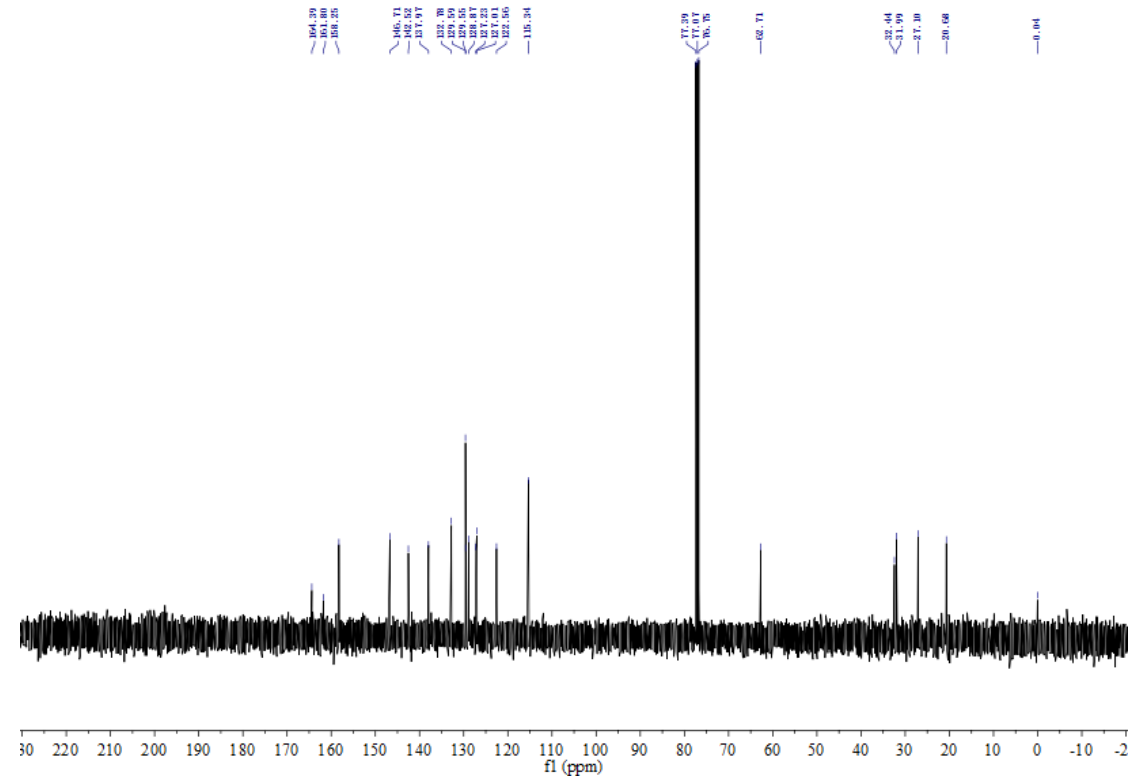
^{1}H-NMR spectrum of **5q**



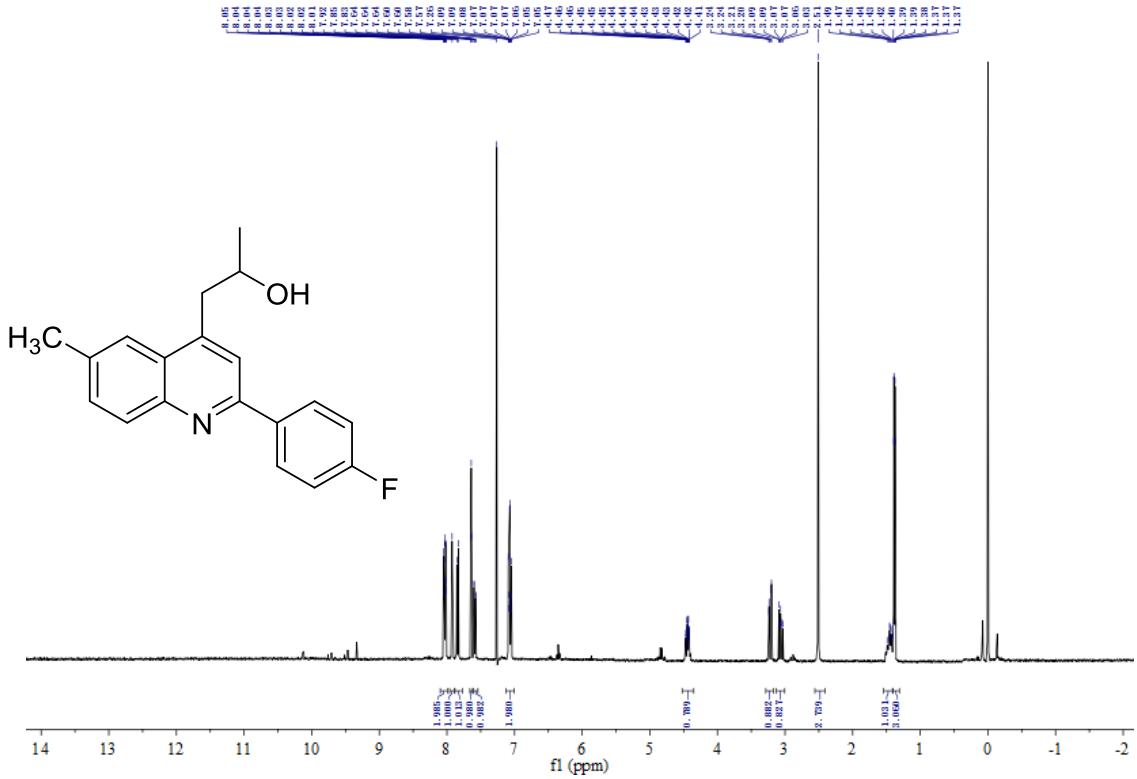
^{13}C-NMR spectrum of **5q**



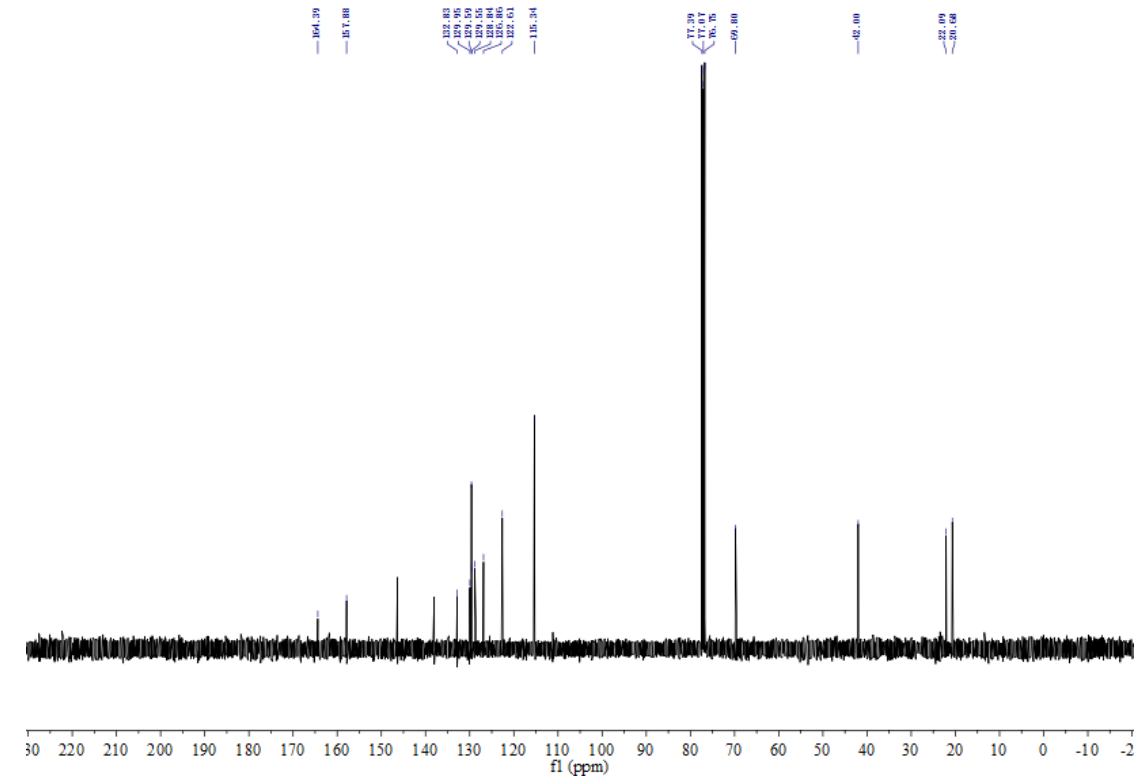
^{1}H-NMR spectrum of **5r**



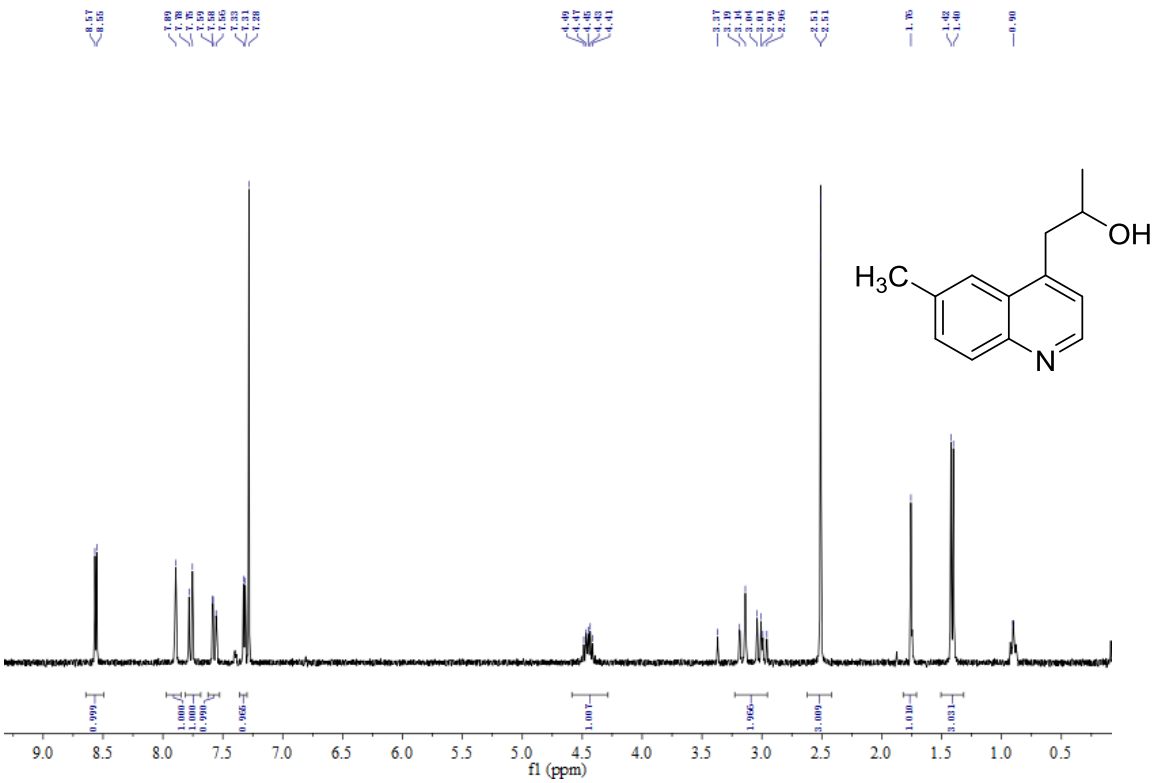
^{13}C-NMR spectrum of **5r**



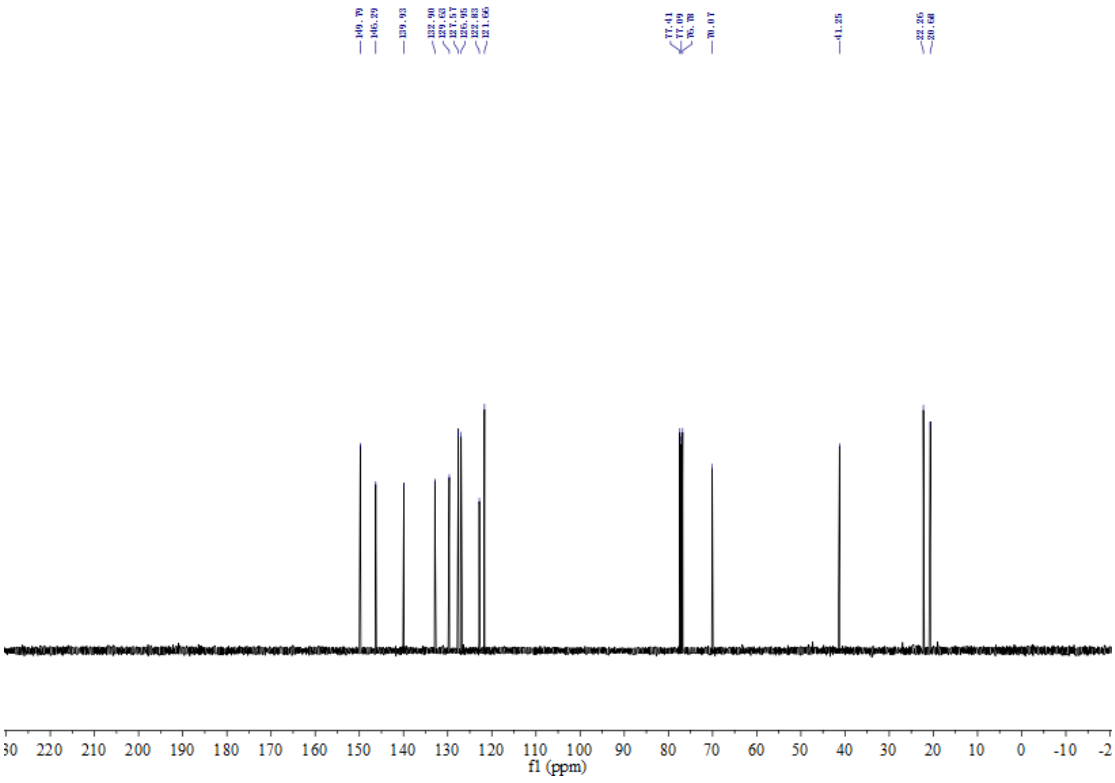
^{1}H-NMR spectrum of **5s**



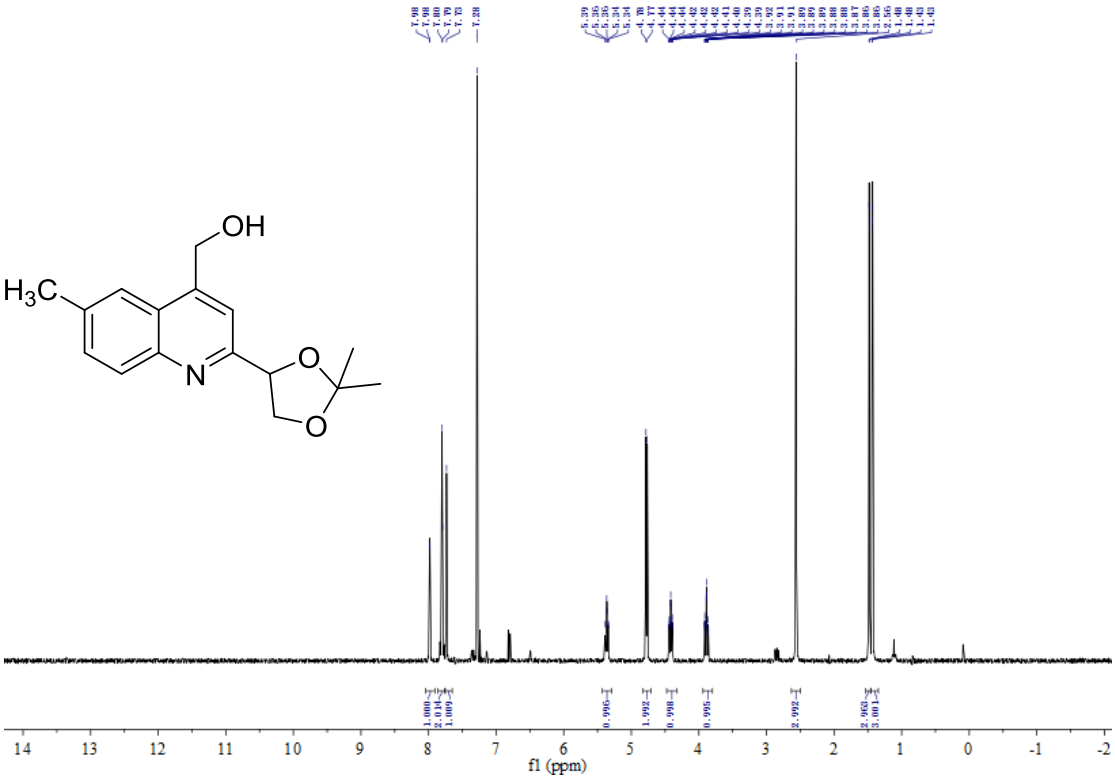
^{13}C-NMR spectrum of **5s**



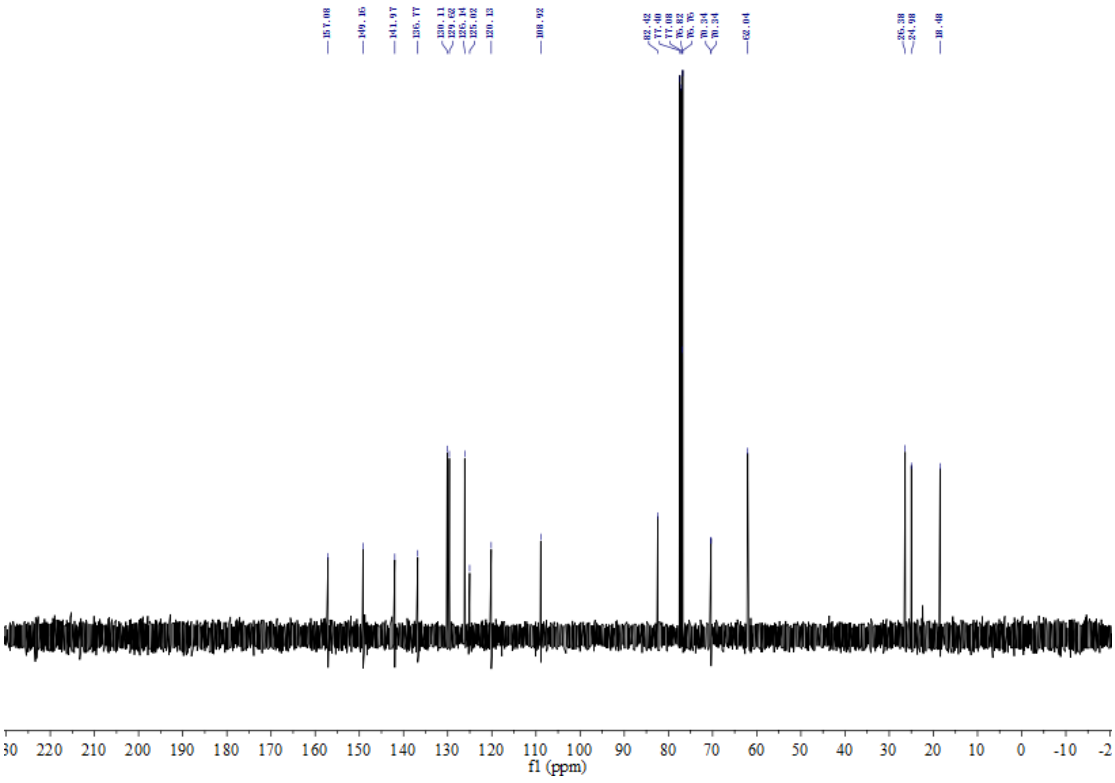
^{1}H-NMR spectrum of **5t**



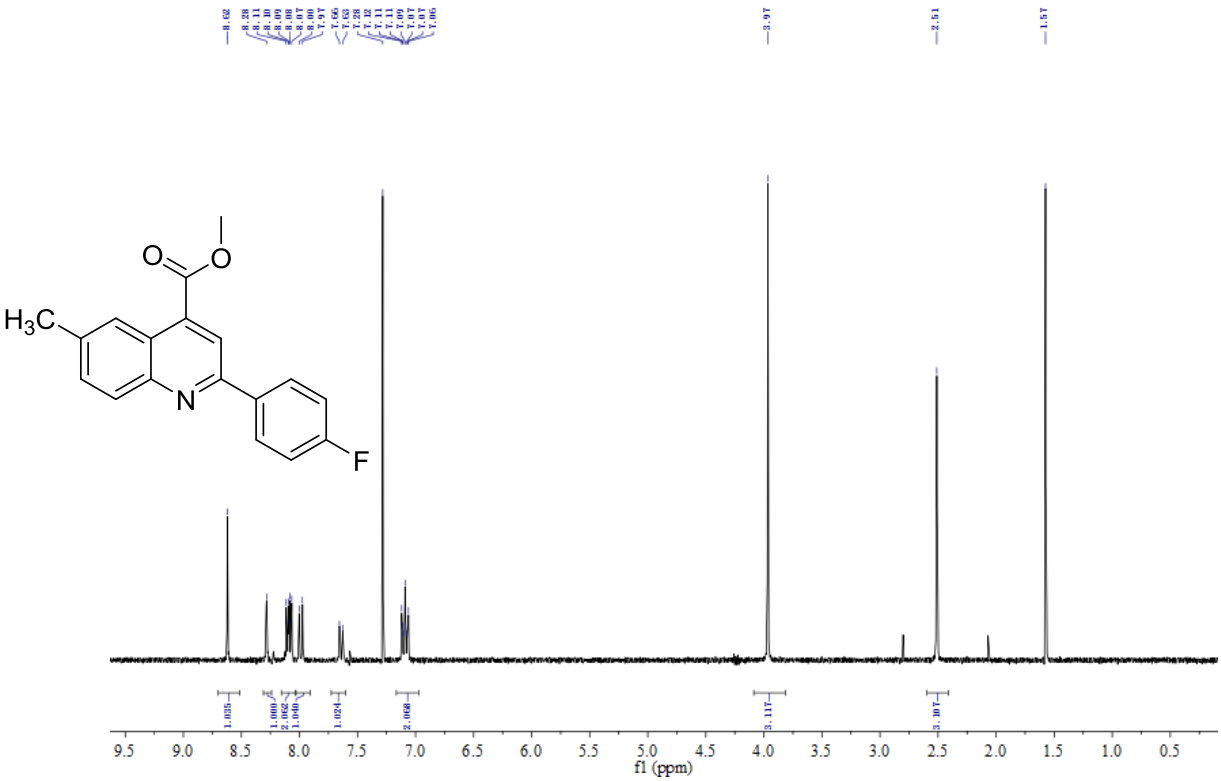
^{13}C-NMR spectrum of **5t**



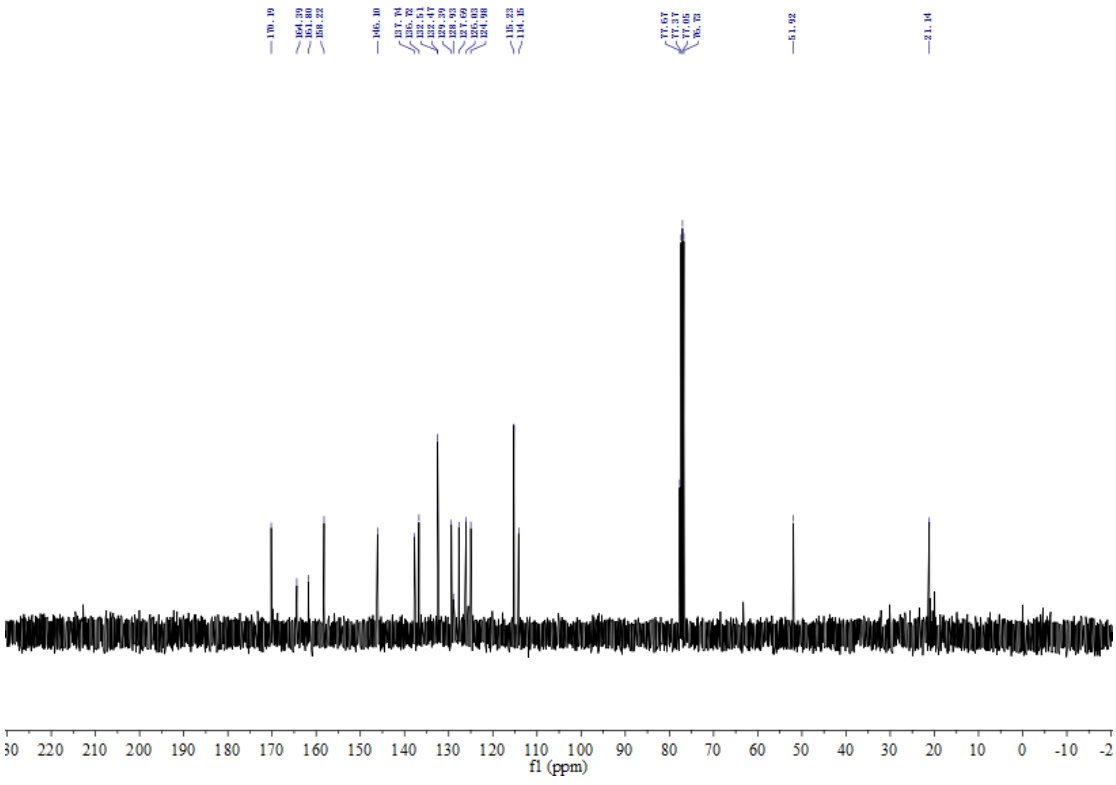
^{1}H-NMR spectrum of **5u**



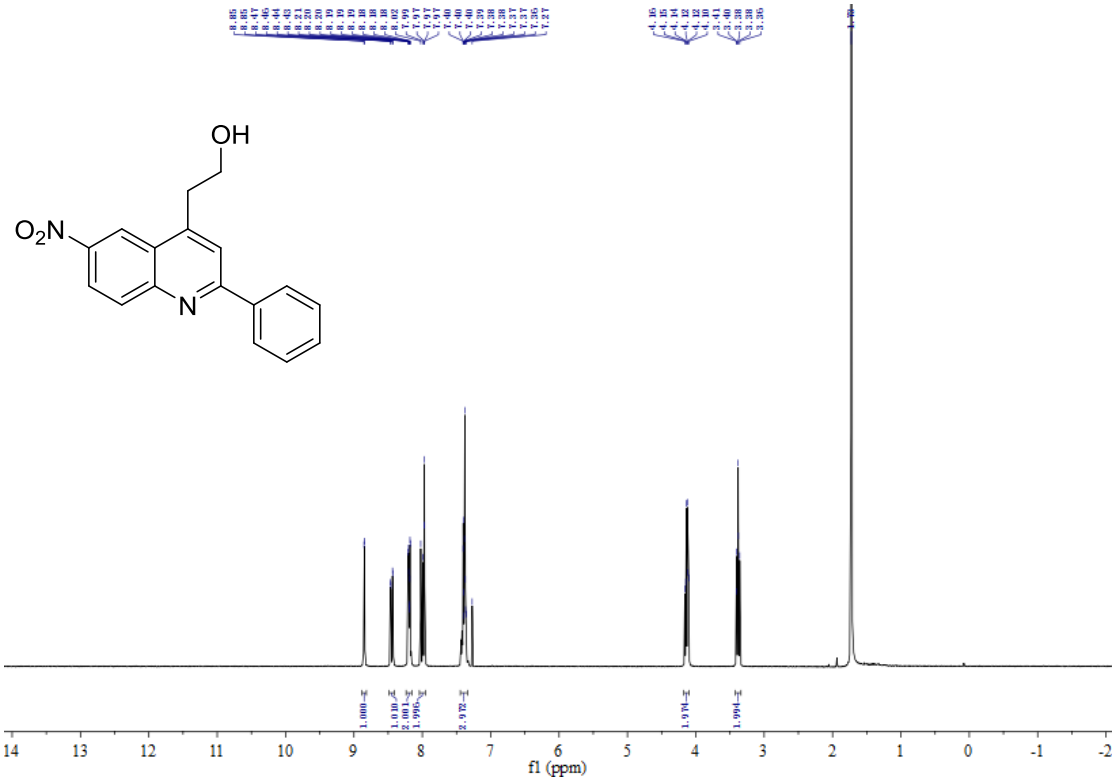
^{13}C-NMR spectrum of **5u**



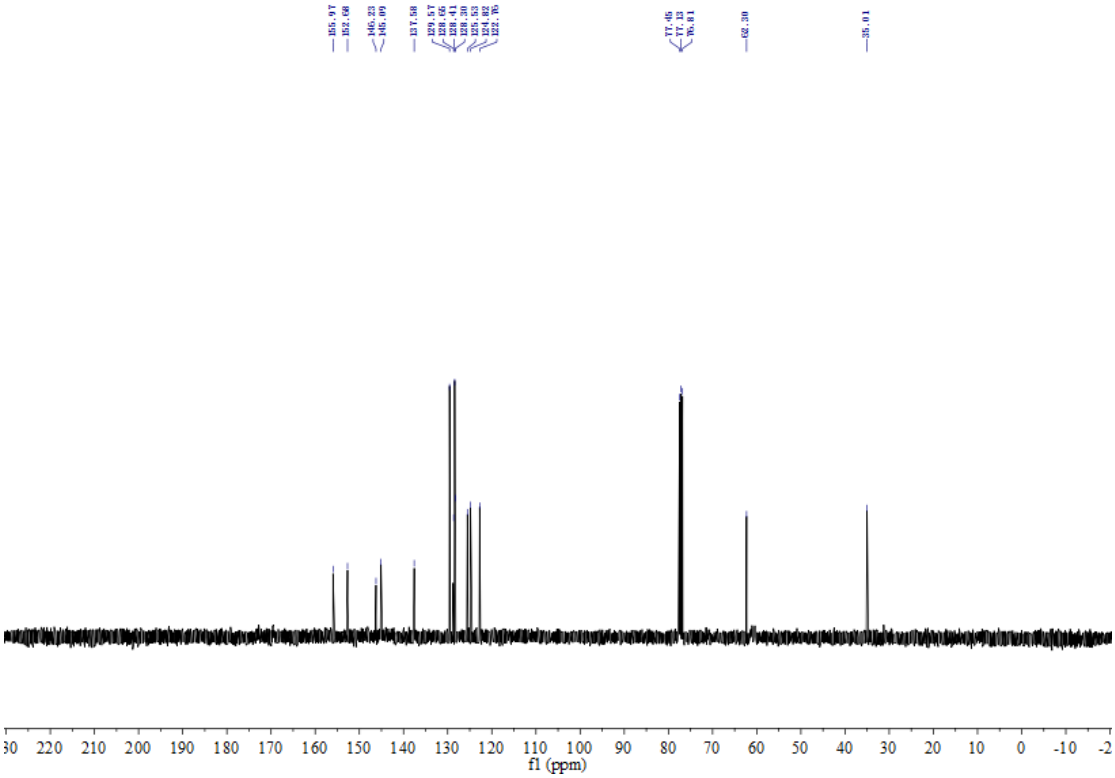
^{1}H-NMR spectrum of **5x**



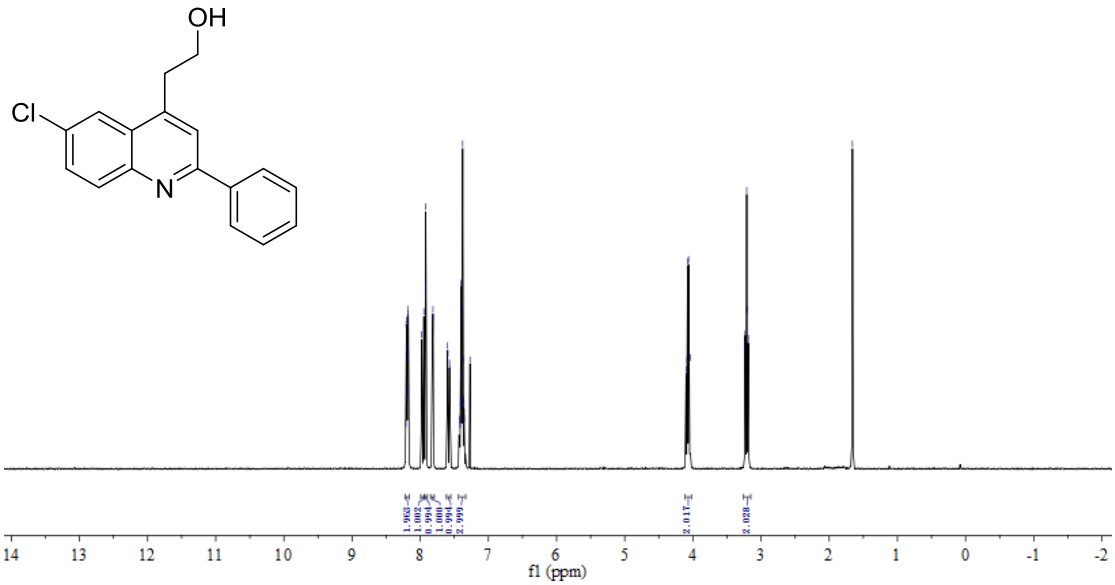
^{13}C-NMR spectrum of **5x**



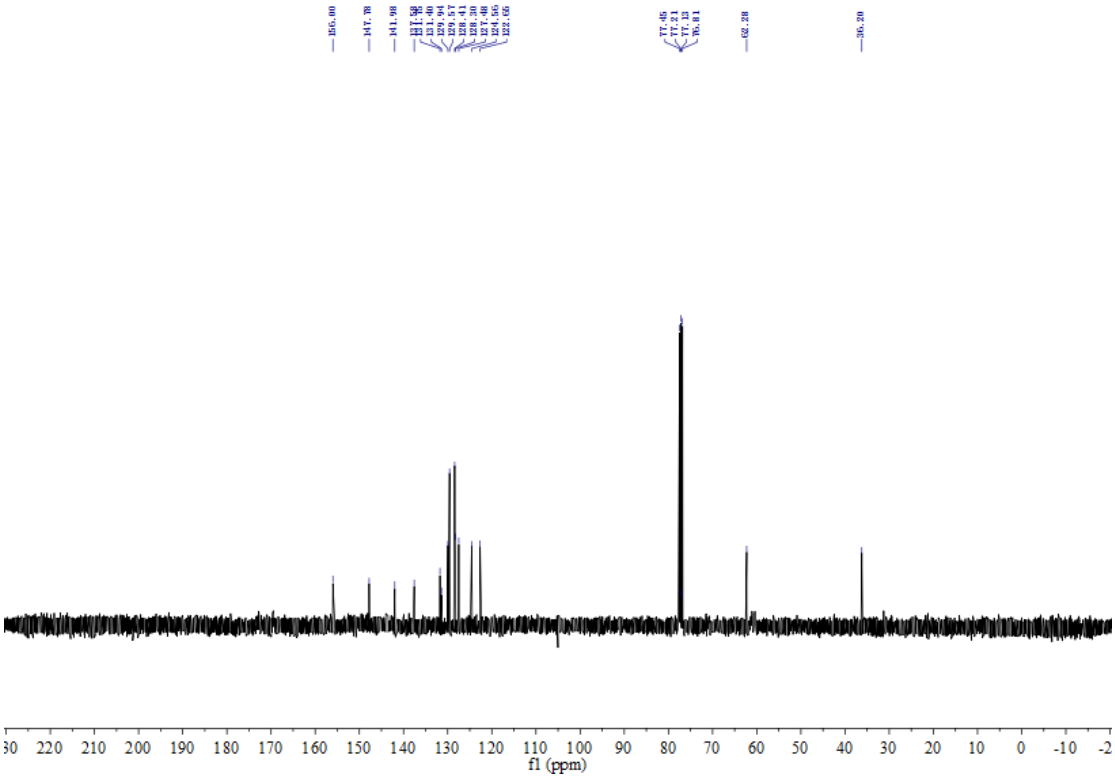
^{1}H-NMR spectrum of **5y**



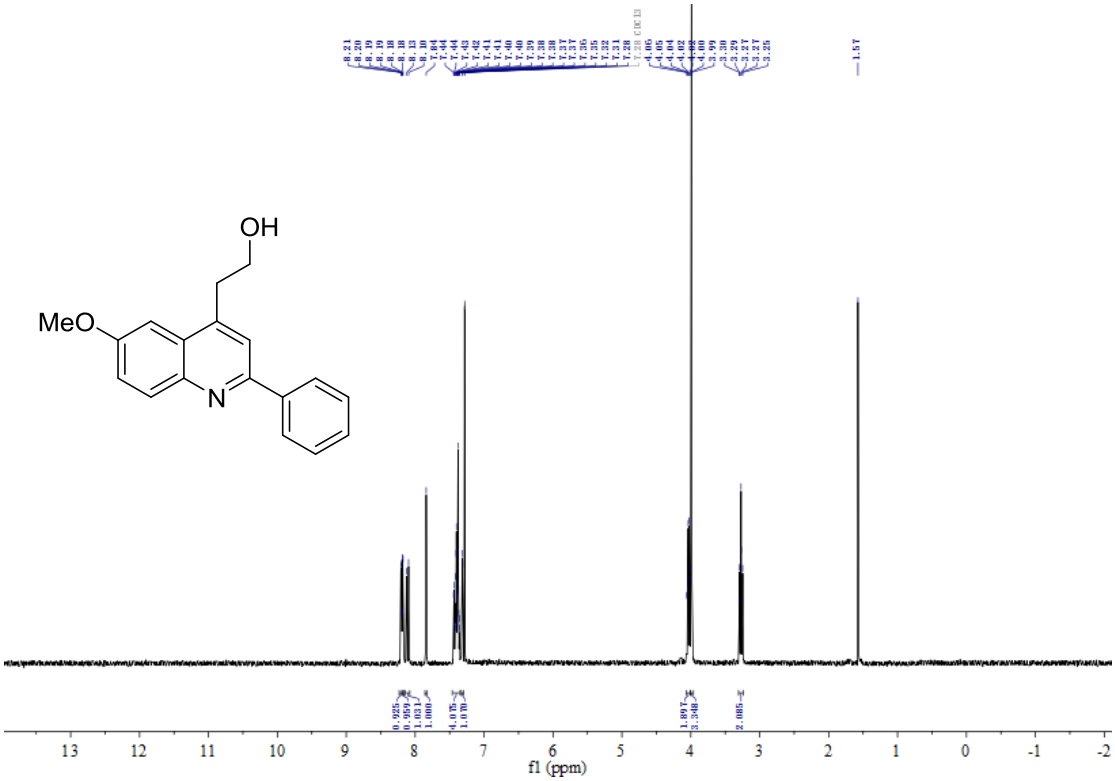
^{13}C-NMR spectrum of **5y**



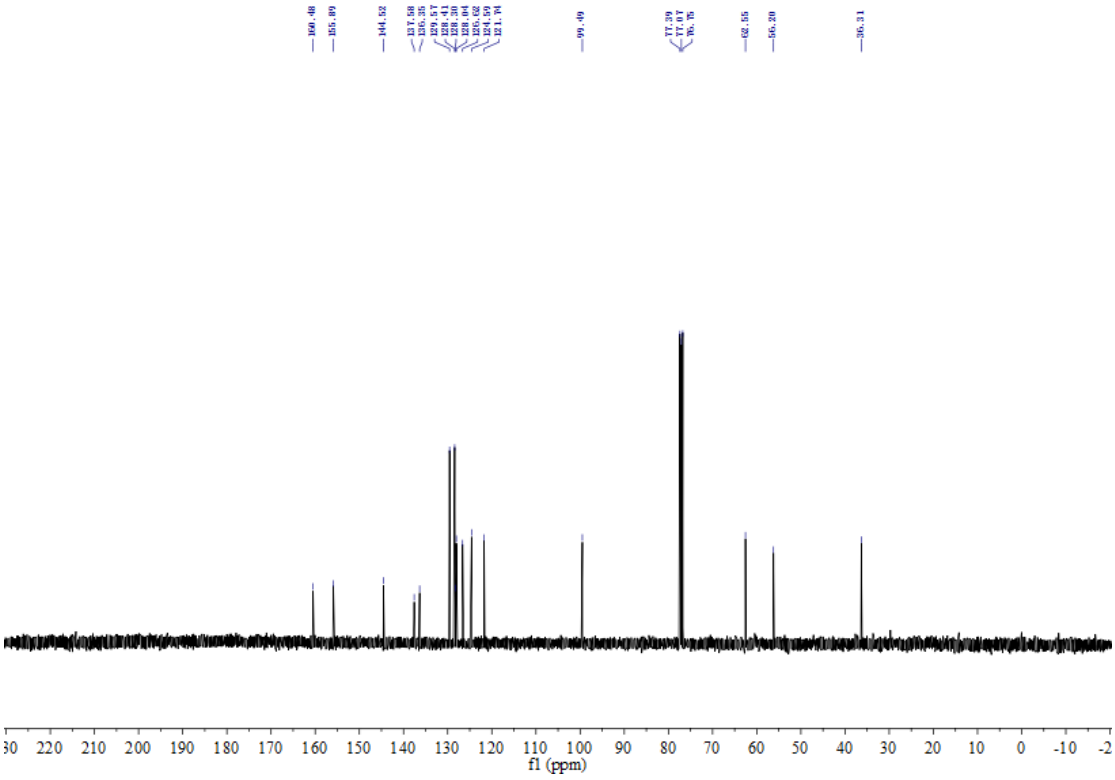
^{1}H-NMR spectrum of **5z**



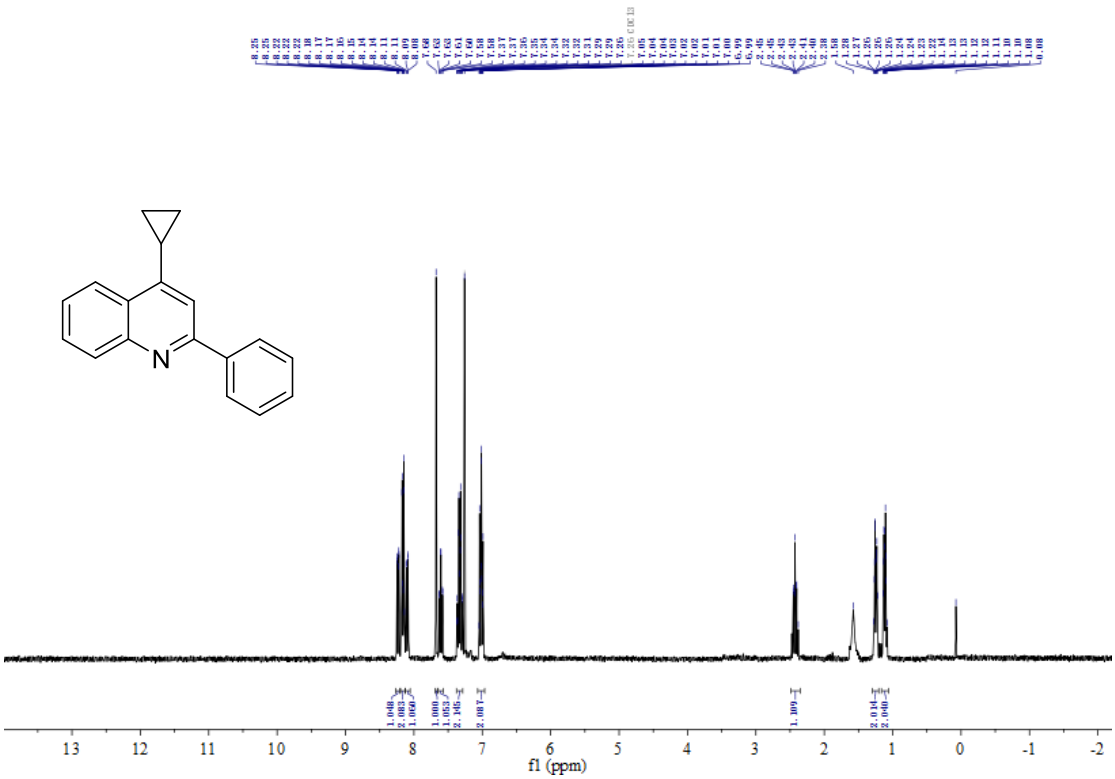
^{13}C-NMR spectrum of **5z**



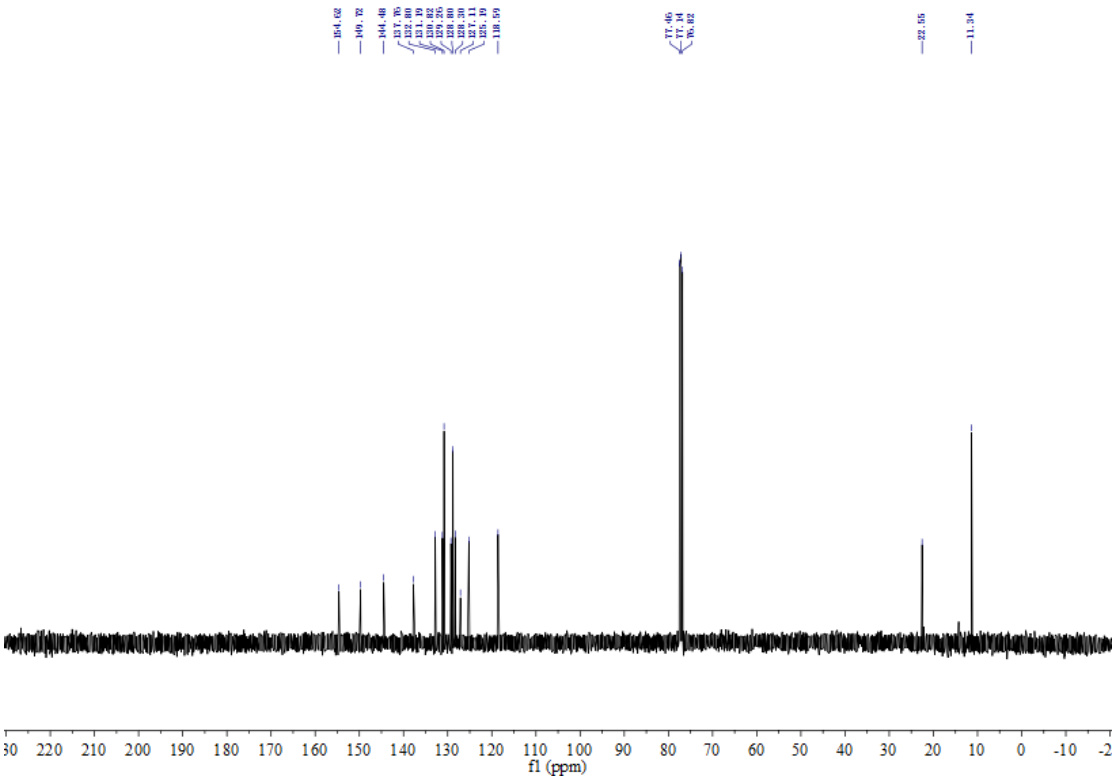
^{1}H-NMR spectrum of **5aa**



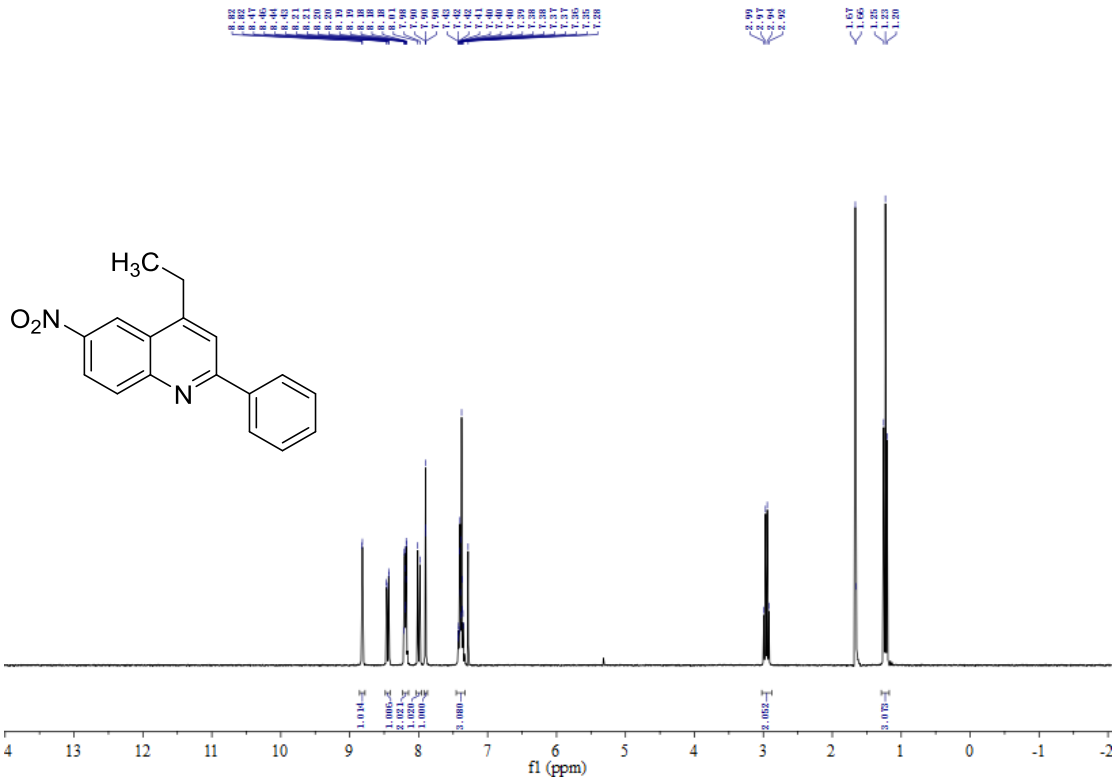
^{13}C-NMR spectrum of **5aa**



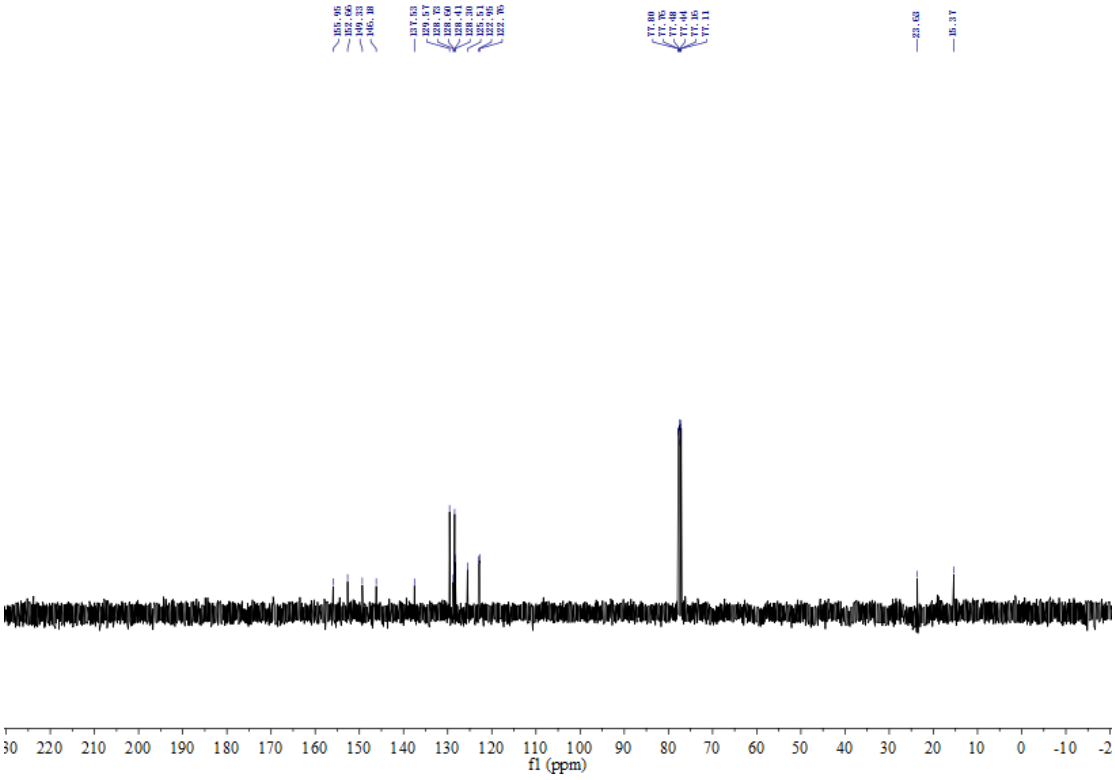
^{1}H-NMR spectrum of **5ab**



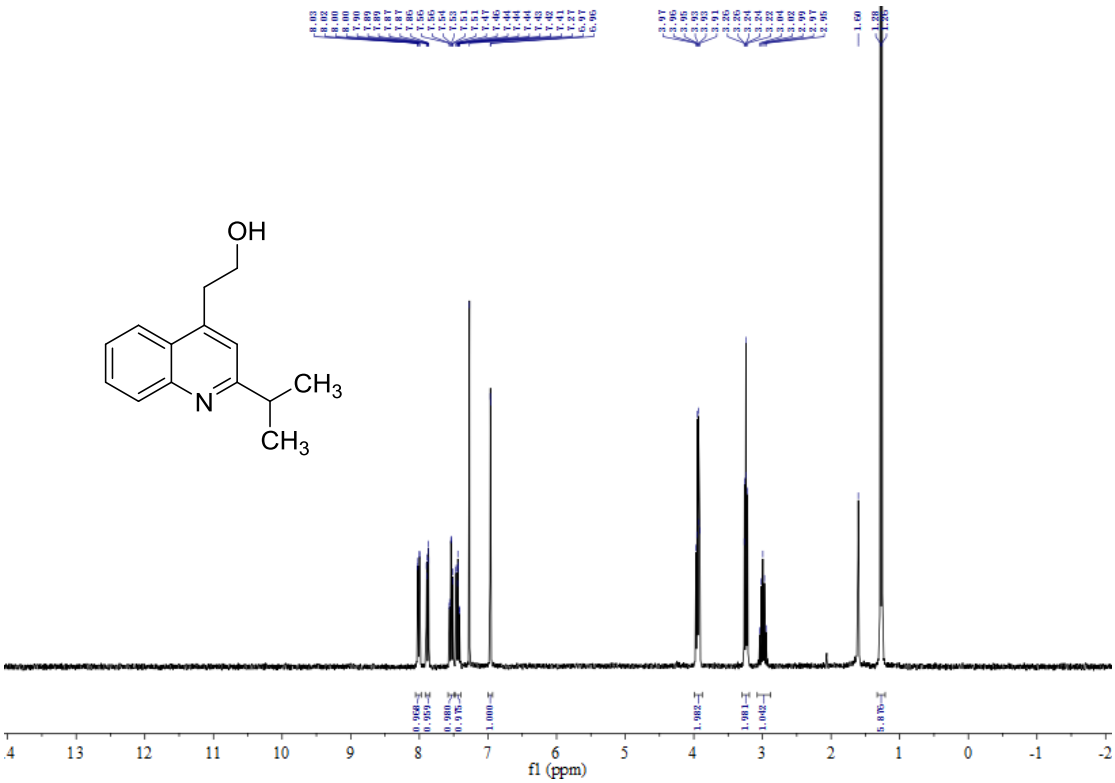
^{13}C-NMR spectrum of **5ab**



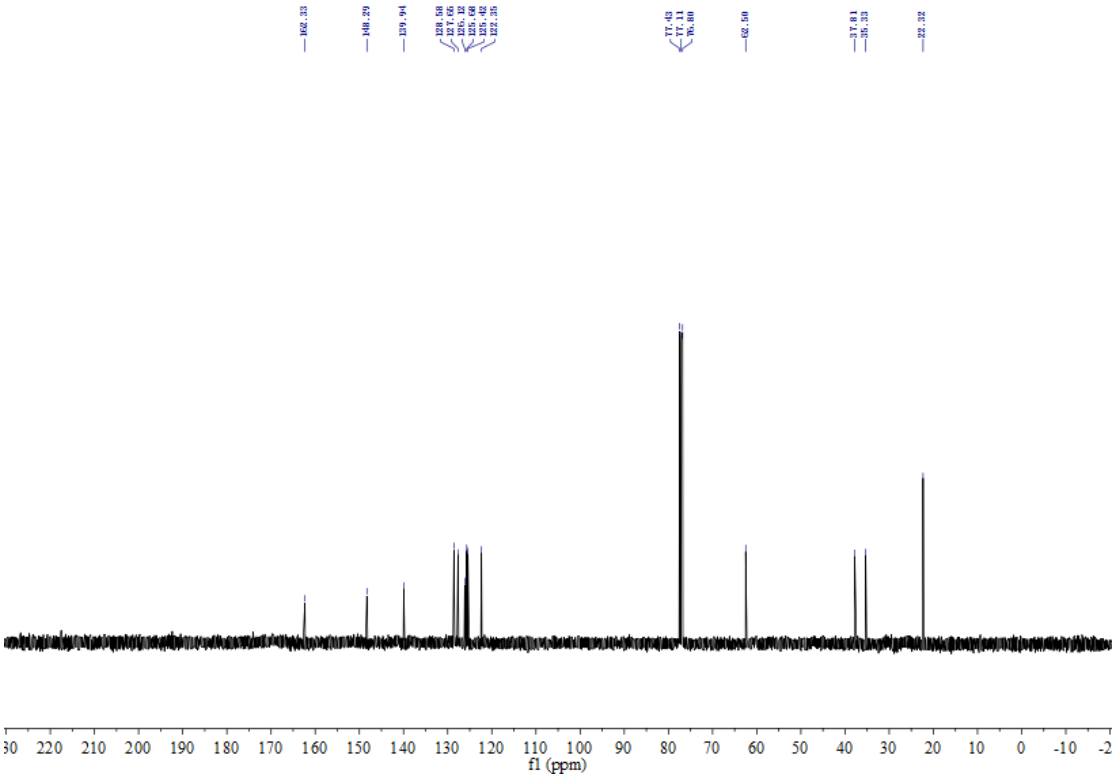
^{1}H-NMR spectrum of **5ac**



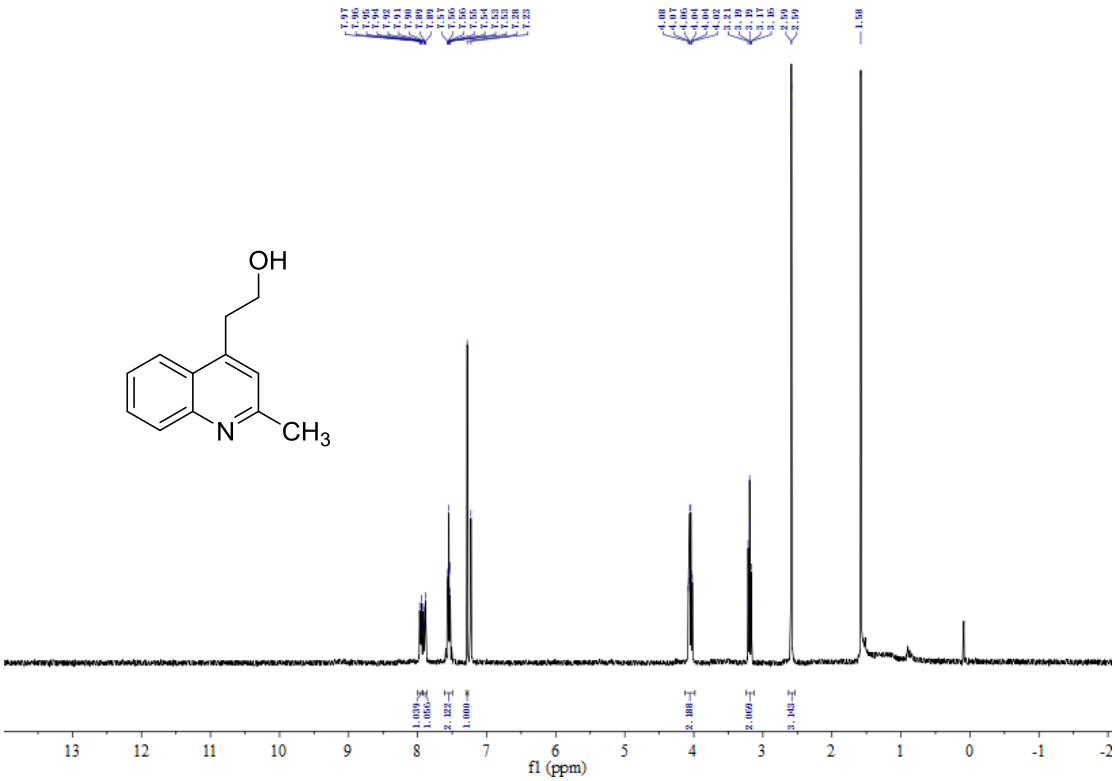
^{13}C-NMR spectrum of **5ac**



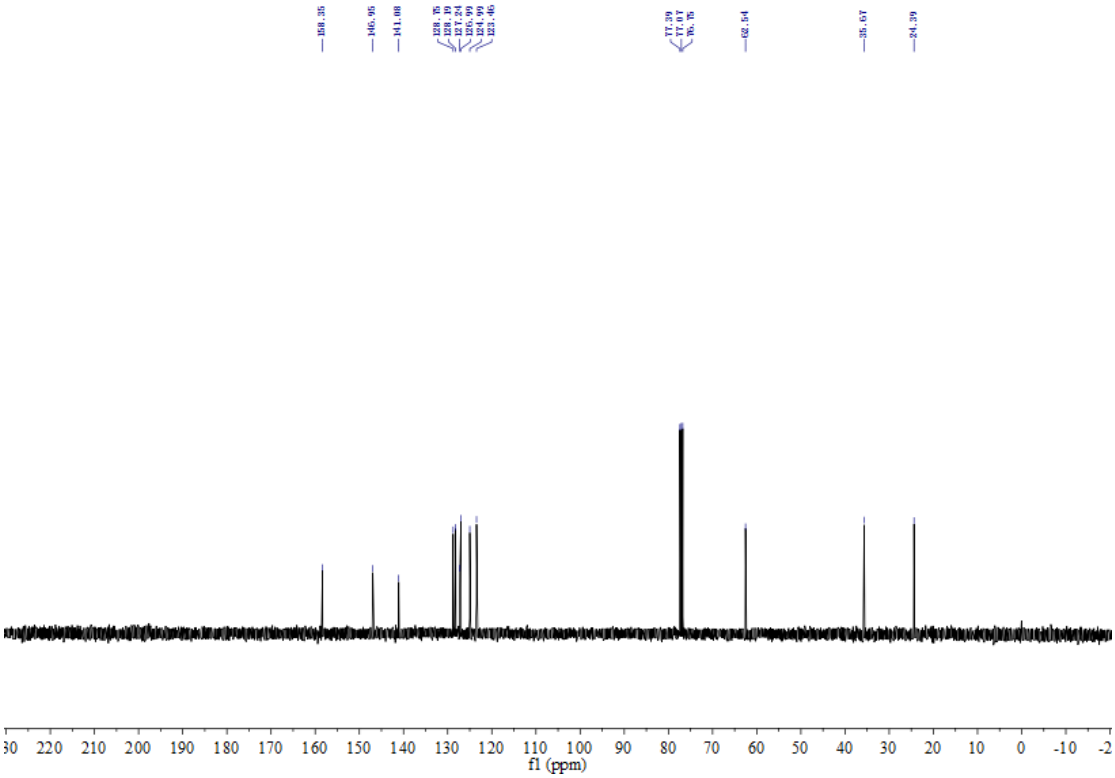
^{1}H-NMR spectrum of **5ad**



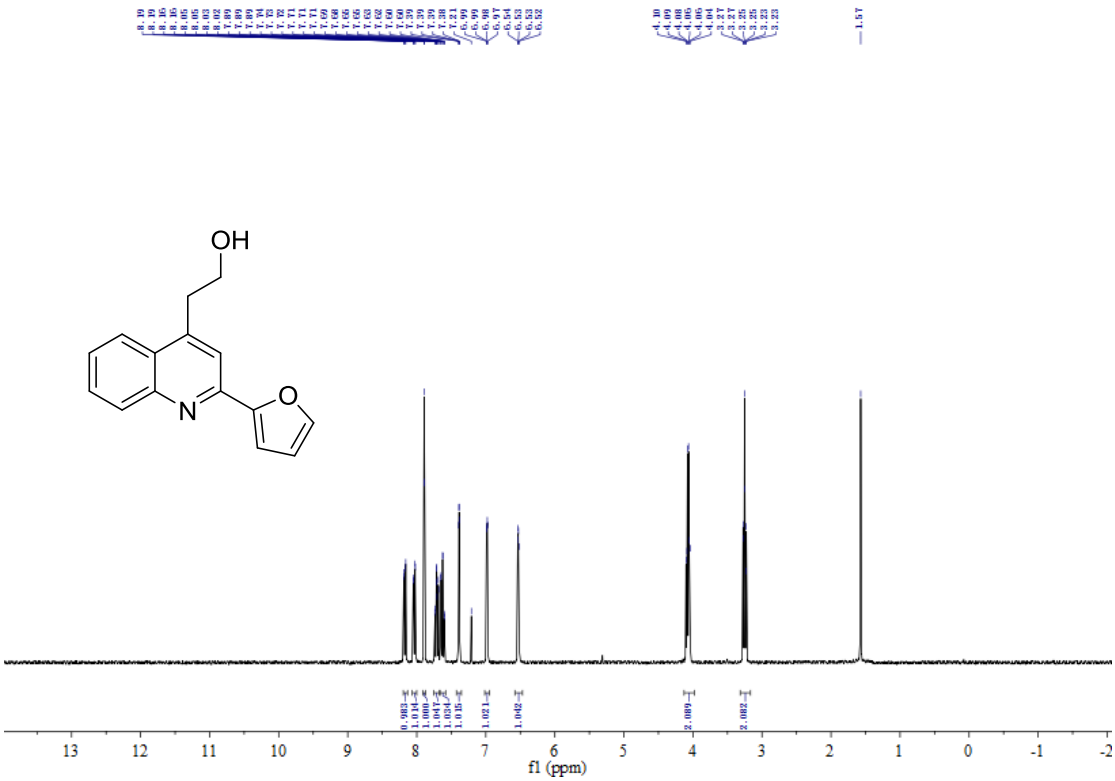
^{13}C-NMR spectrum of **5ad**



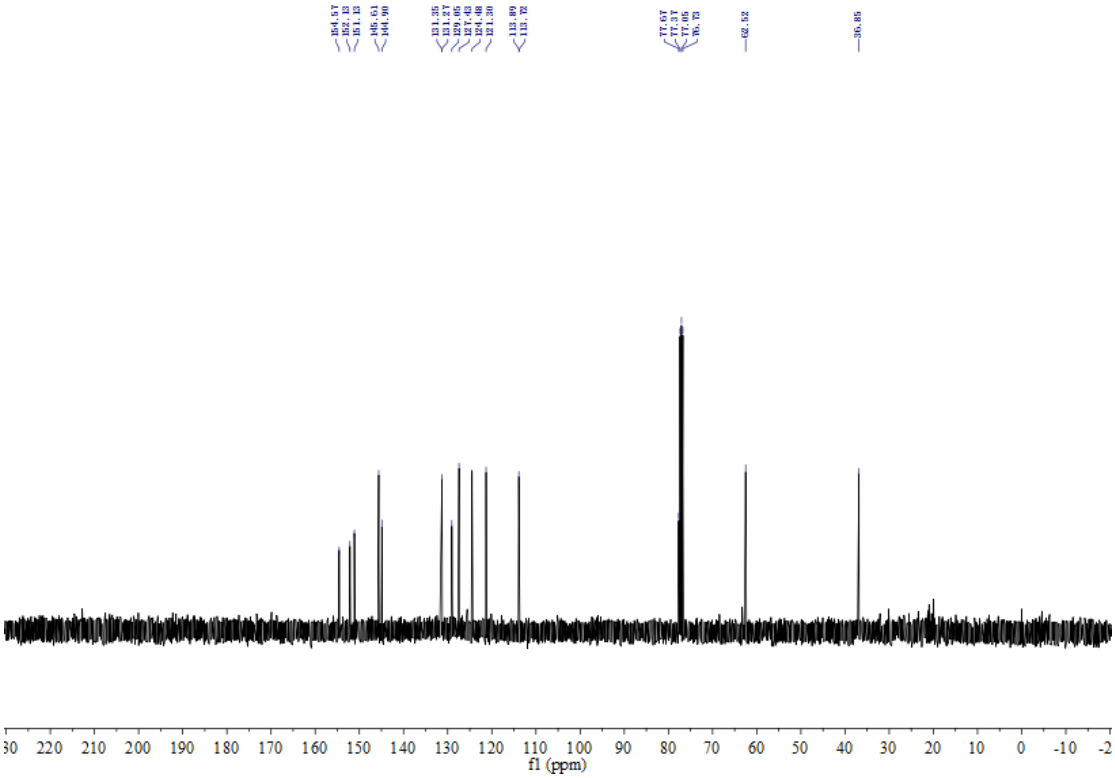
^{1}H-NMR spectrum of **5ae**



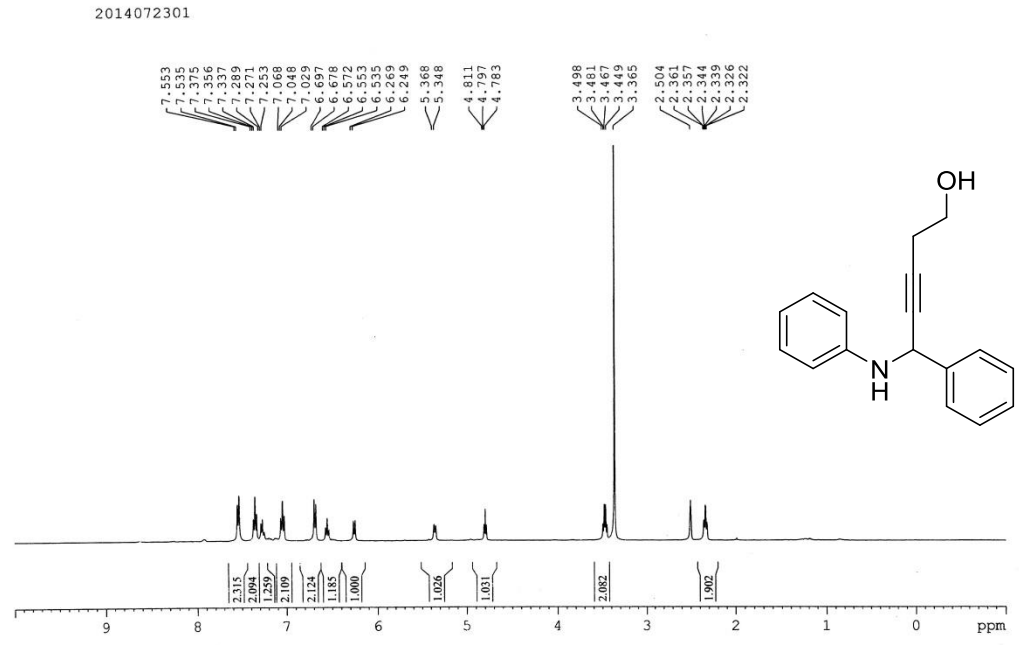
^{13}C-NMR spectrum of **5ae**



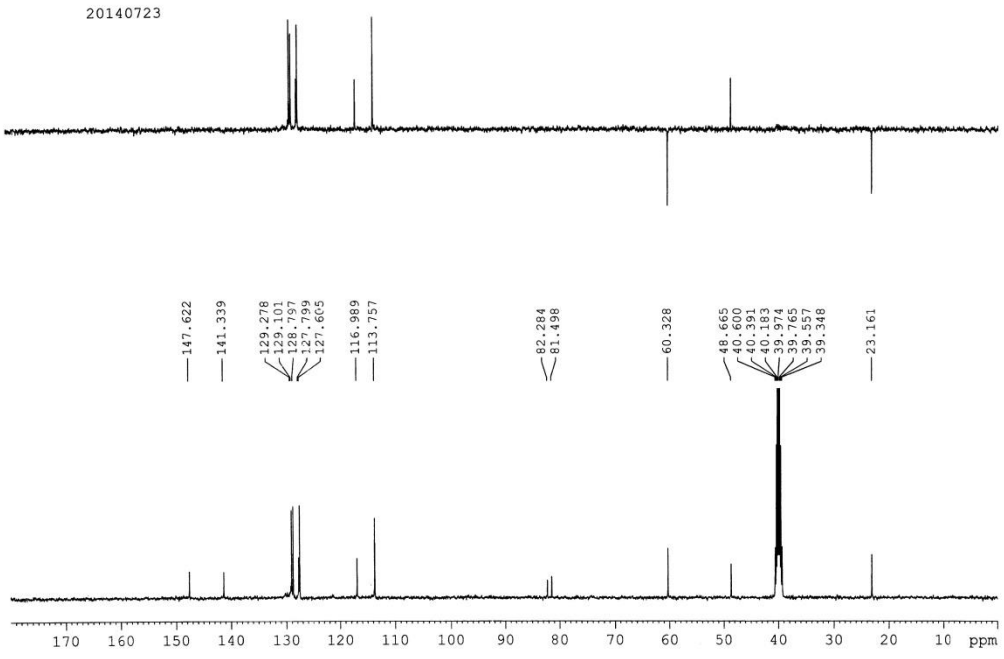
^{1}H-NMR spectrum of **5af**



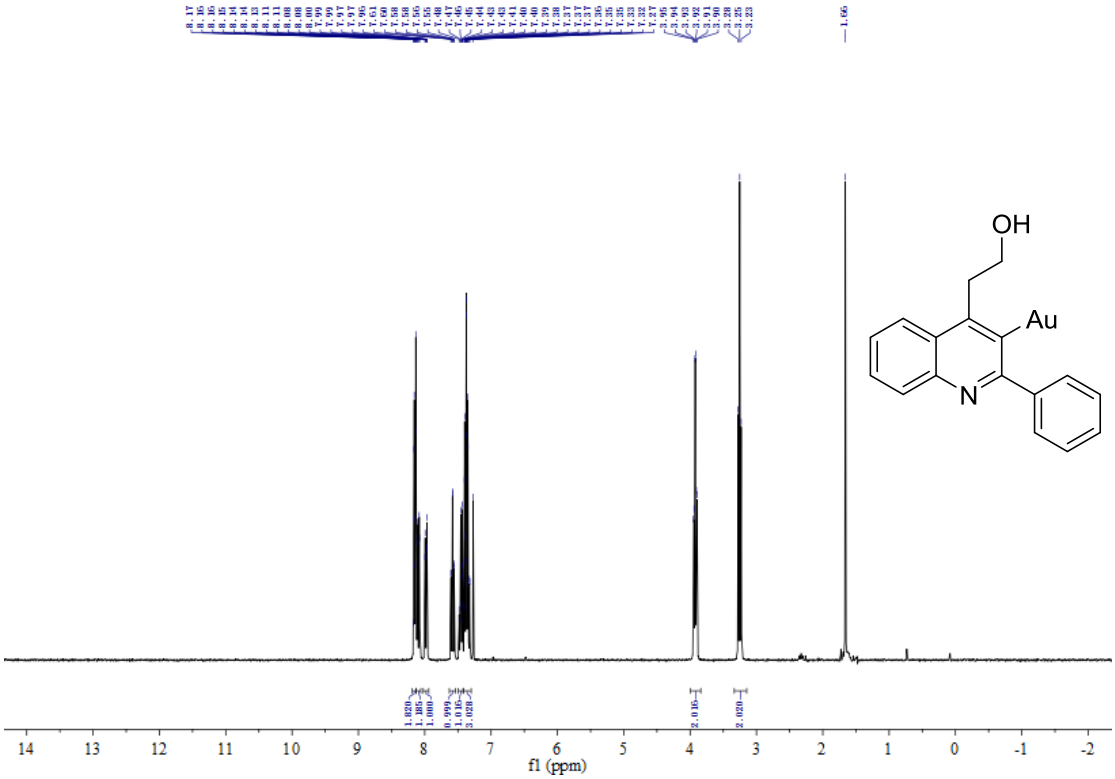
^{13}C-NMR spectrum of **5af**



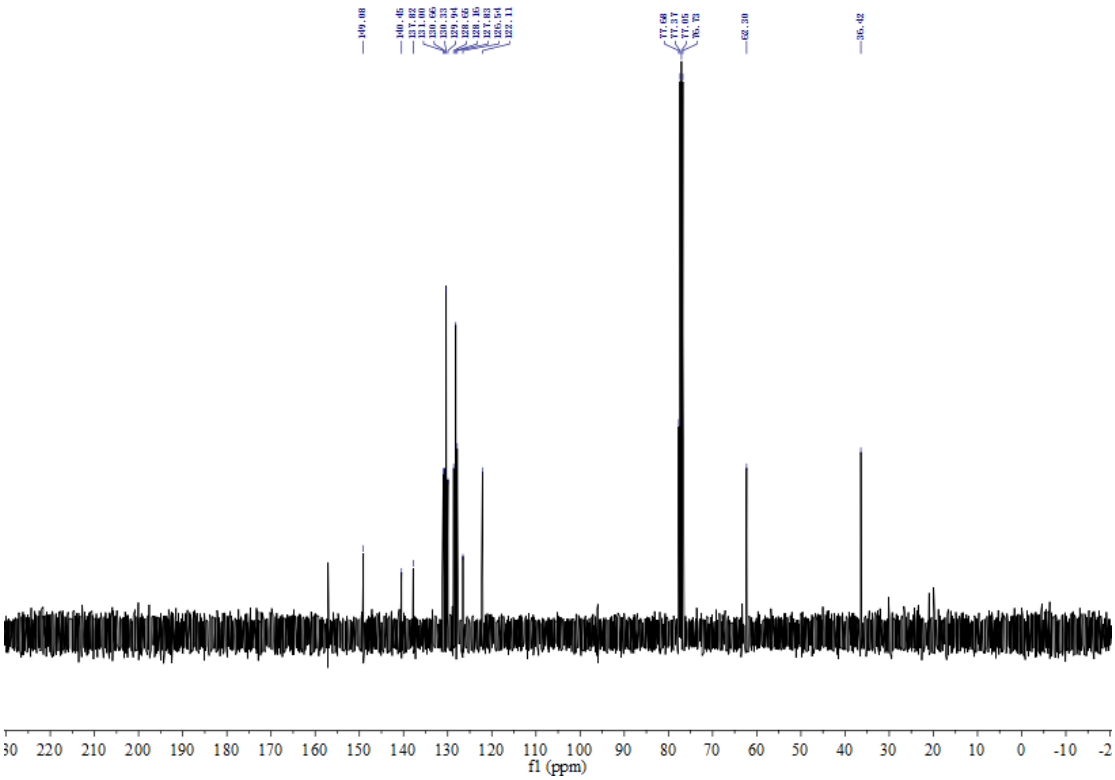
^{1}H-NMR spectrum of **4a**



^{13}C-NMR spectrum of **4a**



^{1}H-NMR spectrum of **10**



^{13}C-NMR spectrum of **10**

4. References

(1). Y. Zhao and D. G. Truhlar, *Theor Chem Acc*, **2008**, *120*, 215-241.

(2). S. E. Wheeler and K. N. Houk, *J Chem Theory Comput*, **2010**, *6*, 395-404.

(3). Y. Zhao and D. G. Truhlar, *Accounts Chem Res*, **2008**, *41*, 157-167.

(4). a) Y. Zhao and D. G. Truhlar, *Phys Chem Chem Phys*, **2008**, *10*, 2813-2818; b) R. F. Ribeiro, A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J Phys Chem B*, **2011**, *115*, 14556-14562.