Supporting Information

External oxidant-free alkylation of quinoline and pyridine derivatives

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Contents

1. General information

All manipulations were carried out in glass reaction tube equipped with a magnetic stir bar under air atmosphere unless otherwise noted. Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used as received. Analytical thin-layer chromatography was performed using silica gel 60 GF254 plates. Flash column chromatography was performed using silica gel (60-Å pore size, 32-63 μm, standard 15 grade).

Mass spectra and HPLC yields were measured on a LC-MSD-Trap-XCT instrument. ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Bruker DPX 400 instrument by using tetramethylsilane (TMS) as the internal standard. All coupling constants (*J*) are reported in hertz (Hz). Melting points were measured with an XT4A microscopic apparatus. The high resolution mass spectrum was received via Agilent Technologies 6540 UHD Accurate-mass Q-Tof LC/MS, with ESI as ion source. Preparative TLC was performed on silica gel plates and developed with ethyl acetate/petroleum ether. Quinoline N-oxides were prepared according to literature.[1]

2. General experimental procedures.

2.1. General Procedures for Synthesis of N-methoxyquinoline-1-ium tetrafluoroborate salts.[2]

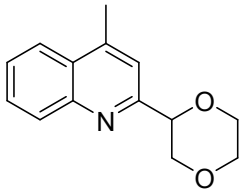
A mixture of 1.1 equiv of trimethyloxonium tetrafluoroborate and 1.0 equiv of the quinoline N-oxide was stirred in dichloromethane for 4h. Then the reaction mixture was concentrated in vacuo, and the crude product was recrystallized in EtOAc to obtained the N-methoxyquinoline-1-ium tetrafluoroborate salts.

2.2. General Procedures for Synthesis of alkylated pyridine and quinoline derivatives.

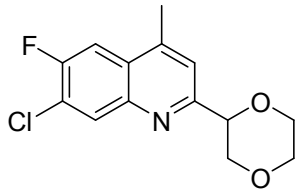
A dried glass reaction tube equipped with a magnetic stir bar was charged with 1(0.2 mmol, 1.0 equiv), 2 (3.0 mL), K_3PO_4 (0.6 mmol, 3.0 equiv), and DCM (2.0 mL). The resulting mixture was then stirred at 30 °C under argon for 4h. The crude production was extracted with ethyl acetate (3 × 10 mL). The combined organic layers dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by flash column chromatograph to give the pure products. The products were characterized by ^{1}H

NMR, ^{13}C NMR, MS.

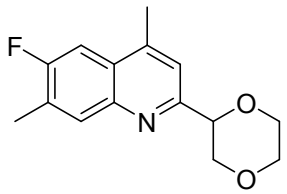
3. Characterization data of the Products.



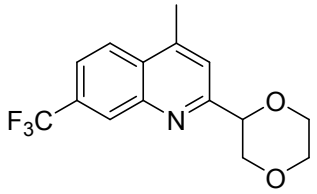
2-dioxanyl-4-methylquinoline (3aa) [3]**:** (33.9 mg, yield 74%) yellow solid; m. p. 82–83 °C. ^1H NMR (400 MHz, $CDCl_3$): 8.07 (like d, 1H), 7.97 (like d, 1H), 7.71-7.67 (m, 1H), 7.56-7.52 (m, 1H), 7.45 (s, 1H), 4.89 (dd, *J*=2.9 Hz, 10.1 Hz, 1H), 4.22 (dd, *J*=2.84 Hz, 11.6 Hz, 1H). 4.05-3.96 (m, 2H), 3.86-3.75 (m, 2H), 3.63 (like t, 1H), 2.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 157.9, 147.4, 145.3, 129.9, 129.4, 127.7, 126.2, 123.8, 119.2, 78.9, 71.2, 67.1, 66.5, 19.0 ppm. MS (ESI) (m/z): 230.1 $[M + H]^+$.



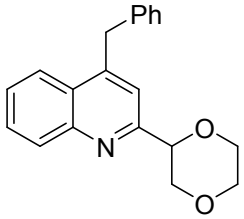
7-chloro-2-(1, 4-dioxan-2-yl)-6-fluoro-4-methylquinoline (3ba): (43.2 mg, yield 77%); yellow solid; m. p 130-131 °C. ^1H NMR (400 MHz, $CDCl_3$): 8.13 (d, 7.2 Hz, 1H), 7.63 (d, 10.5 Hz, 1H), 7.47 (s, 1H), 4.83 (dd, *J*=2.8 Hz, 10.1 Hz, 1H), 4.19 (dd, *J*=2.9 Hz, 11.5 Hz, 1H), 4.04-3.94 (m, 2H), 3.86-3.73 (m, 2H), 3.60 (like t, 1H), 2.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 158.5 (d, *J* =2.8 Hz), 155.9 (d, *J*=250.4 Hz), 144.7 (d, *J*=5.9 Hz), 144.5, 131.6, 127.1 (d, *J*=8.0 Hz), 124.7 (d, *J*=21 Hz), 120.0, 108.7 (d, *J*=22.0), 78.4, 71.0, 67.2, 66.5, 19.0 ppm. HRMS (ESI): m/z calcd for $C_{14}H_{13}ClFNO_2$ $[M+H]^+$: 282.0692, found: 282.0694.



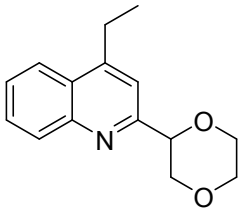
2-(1, 4-dioxan-2-yl)-6-fluoro-4, 7-dimethylquinoline (3ca): (44.9 mg, 86%); yellow solid; m. p. 107-108 °C. ^1H NMR (400 MHz, $CDCl_3$): 7.87 (d, 7.6 Hz, 1H), 7.47 (d, *J*=10.7 Hz, 1H), 7.39 (s, 1H), 4.83 (dd, *J*=2.8 Hz, 10.4 Hz, 1H), 4.19 (dd, *J*=2.9 Hz, 11.5 Hz, 1H), 4.02-3.94 (m, 2H), 3.85-3.74 (m, 2H), 3.61 (like t, 1H), 2.62 (s, 3H), 3.28 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 160.0 (d, *J*=250 Hz), 157.1 (d, *J*=2.6 Hz), 144.5 (d, *J*=5.6 Hz), 144.4, 131.9 (d, *J*=6.3 Hz), 129.6 (d, *J*=21 Hz), 127.0 (d, *J*=9.2 Hz), 119.0, 106.8 (d, *J*=23.2 Hz), 78.7, 71.1, 67.1, 66.5, 18.9, 15.5 (d, *J*=3.3 Hz) ppm. HRMS (ESI): m/z calcd for $C_{15}H_{16}FNO_2$ $[M+H]^+$: 262.1243, found: 262.1242.



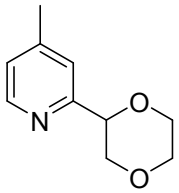
2-(1, 4-dioxan-2-yl)-4-methyl-7-(trifluoromethyl)quinoline (3da)： (39.2 mg, 66%). white solid; m. p. 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 8.37 (s, 1H), 8.07 (d, *J*=8.7 Hz, 1H), 7.70-7.68 (m, 1H), 7.56 (s, 1H), 4.88 (dd, *J*=2.8 Hz, 10.4 Hz, 1H), 4.25 (dd, *J*=2.9 Hz, 11.8 Hz, 1H), 4.05-3.95 (m, 2H), 3.86-3.74 (m, 2H), 3.62 (like t, 1H), 2.73 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 159.6, 146.5, 145.4, 131.2 (q, *J*=33.1 Hz), 129.2, 127.7 (q, *J*=3.6 Hz), 125.1, 124.1 (q, *J*=270 Hz), 121.9 (q, *J*=3.2 Hz), 121.0, 78.4, 71.0, 67.2, 66.5, 18.9 ppm. HRMS (ESI): m/z calcd for $C_{15}H_{14}F_3NO_2$ $[M+H]^+$: 298.1049, found: 298.1048.



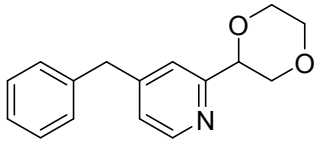
4-benzyl-2-(1, 4-dioxan-2-yl) quinoline (3ea): (37.8 mg, yield 62%); yellow liq uid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.09 (like d, 1H), 7.97 (like d, 1H), 7.68-7. 64 (m, 1H), 7.49-7.45 (m, 1H), 7.44 (s, 1H), 7.30-7.25 (m, 2H), 7.23-7.17 (m, 3H), 4.89 (dd, *J*=2.9 Hz, 10.1 Hz, 1H), 4.44 (s, 2H), 4.24 (dd, *J*=2.84 Hz, 11. 6 Hz, 1H) 4.02-3.93 (m, 2H), 3.84-3.73 (m, 2H), 3.64 (like t, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 158.1, 147.9, 147.3, 138.9, 130.1, 129.4, 128.8, 127. 1, 126.7, 126.6, 124.1, 119.6, 78.8, 71.2, 67.2, 66.5, 38.7 ppm. HRMS (ESI): m/z calcd for $C_{20}H_{19}NO_2$ $[M+H]^+$: 306.1494, found: 306.1492.



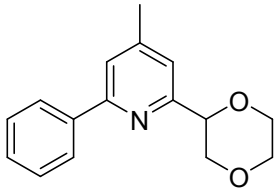
2-(1, 4-dioxan-2-yl)-4-ethylquinoline(3fa): (36.5 mg, yield 75%), yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (like d, 1H), 8.02 (like d, 1H), 7.71-7.67 (m, 1H), 7.56-7.52 (m, 1H), 7.47 (s, 1H), 4.90 (dd, *J*=2.9 Hz, 10.1 Hz, 1H), 4.24 (dd, *J*=2.88 Hz, 11.6 Hz, 1H), 4.05-3.97 (m, 2H), 3.87-3.76 (m, 2H), 3.65 (like t, 1H), 3.13（q, *J*=7.5 Hz, 2H), 1.41 (t, *J*=7.52, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 158.1, 151.0, 147.7, 130.1, 129.3, 126.9, 126.3, 123.5, 117.2, 79.0, 71.3, 67.2, 66.6, 25.5, 14.3 ppm. HRMS (ESI): m/z calcd for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332, found: 244.1331.



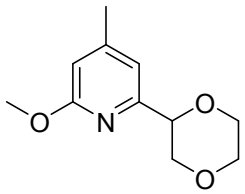
2-(1, 4-dioxan-2-yl)-4-methylpyridine (3ga) [3]**:** (26.8 mg, 75%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.38 (d, *J*=5 Hz, 1H), 7.27 (s, 1H), 7.01 (d, *J*= 4.84 Hz, 1H), 4.70 (dd, *J*=2.8 Hz, 10.1 Hz, 1H), 4.12(dd, *J*=2.8 Hz, 11.6 Hz, 1H), 3.97-3.89 (m, 2H), 3.82-3.69 (m, 2H), 3.50 (like d, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 148.9, 148.1, 123.8, 121.7, 78.3, 71.4, 67. 1, 66.5, 21.2ppm.MS (ESI) (m/z):180.2 $[M + H]^+$.



4-benzyl-2-(1,4-dioxan-2-yl)pyridine (3ha*)*: The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to provide the product **3ha** as a colourless liquid (32.1 mg, yield 63%). ^{1}H NMR (400 MHz, $CDCl_3$):8.42 (d, *J*=5.0Hz, 1H), 7.33-7.22 (m, 5H), 7.18-7.16 (m, 1H), 7.00-6.99 (m, 1H), 4.71 (dd, *J*=2.8 Hz, 7.4 Hz, 1H), 4.13 (dd, *J*=2.8 Hz, 8.6 Hz, 1H), 3.97 (s, 2H), 3.95-3.89 (m, 2H), 3.91-3.69 (m, 2h), 3.51 (like d, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): 157.9, 150.9, 149.0, 129.0, 128.7, 126.6, 123.2, 121.1, 78.0, 71.2, 66.9, 66.3, 41.4 ppm. HRMS (ESI-TOF): m/z calcd for $C_{16}H_{18}NO_3$ $[M+H]^+$: 256.1332, found: 256.1334.

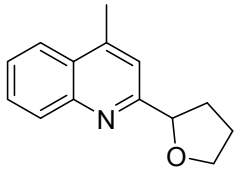


2-(1,4-dioxan-2-yl)-4-methyl-6-phenylpyridine (3ia): The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to provide the product **3ia** as a colourless liquid (16.7 mg, yield 40%). ^{1}H NMR (400 MHz, $CDCl_3$): 7.98-7.96 (m, 2H), 7.46-7.36 (m, 4H), 7.24(s, 1H), 4.79 (dd, *J*=2.8 Hz, 7.4 Hz, 1H), 4.30 (dd, *J*=2.8 Hz, 8.7 Hz, 1H), 3.98-3.95(m, 2H), 3.83-3.70 (m, 2H), 3.57 (like d, 1H), 2.40(s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): 157.7,156.3, 148.4, 139.2, 128.8, 128.6, 126.9, 120.3, 119.7, 78.2, 71.4, 67.0, 66.4, 21.3 ppm. HRMS (ESI-TOF): m/z calcd for $C_{16}H_{18}NO_3$ $[M+H]^+$: 256.1332, found: 256.1334.

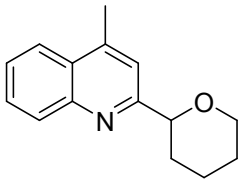


2-(1, 4-dioxan-2-yl)-6-methoxy-4-methylpyridine (3ja): (16.7 mg, yield 40%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 6.87 (s, 1H), 6.44 (s, 1H), 4.60 (dd,

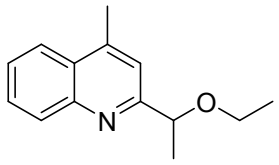
J=2.8 Hz, 10.1 Hz, 1H), 4.12 (dd, *J*=2.8 Hz, 11.6 Hz, 1H), 3.97-3.89 (m, 2H), 3.82-3.69 (m, 2H), 3.50 (like d, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 157.7, 148.9, 148.1, 123.8, 121.7, 78.3, 71.4, 67.1, 66.5, 21.2 ppm. HRMS (ESI): m/z calcd for $C_{11}H_{15}NO_3$ $[M+H]^+$: 210.1125, found: 210.1126.



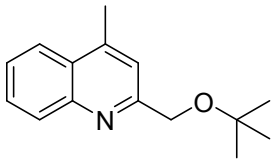
4-methyl-2-(tetrahydrofuran-2-yl) quinoline (3ab) [3]**:** (35.3 mg, yield 83%); yel low liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (like d, 1H), 7.96 (like d, 1H), 7.70-7.66 (m, 1H), 7.54-7.50 (m, 1H), 7.44 (s, 1H), 5.15-5.12 (m, 1H), 4.20-4.15 (m, 1H), 4.06-4.01 (m, 1H), 3.86-3.75 (m, 1H) 2.71 (s, 3H); 2.54-2.45（m, 1H), 2.11-1.95 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.1, 147.3, 145.0, 129.6, 129.1, 127.5, 125.8, 123.7, 118.7, 82.2, 69.4, 33.4, 26.1, 19.0ppm. MS (ESI) (m/z): 214.1 $[M + H]^+$.



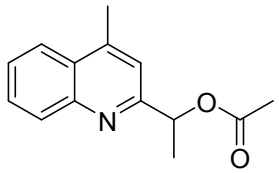
4-methyl-2-(tetrahydro-2H-pyran-2-yl) quinoline (3ac) [3]**:** (30.4 mg, yield 67%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (like d, 1H), 7.96 (like d, 1H), 7.70-7.65 (m, 1H), 7.54-7.50 (m, 1H), 7.47(s, 1H), 4.62 (dd, *J*=2.3 Hz, 11.2 Hz, 1H), 4.23-4.19 (m, 1H); 3.73-3.66 (m, 1H); 2.71(s, 3H), 2.12-2.09 (m, 1H), 2.0-1.97 (m, 1H), 1.82-1.70 (m, 2H), 1.68-1.58 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 162.4, 147.3, 145.3, 129.8, 129.3, 127.8, 126.1, 123.9, 119.1, 81.8, 69.1, 33.0, 26.1, 24.0, 19.1ppm. MS (ESI) (m/z): 228.1 $[M + H]^+$.



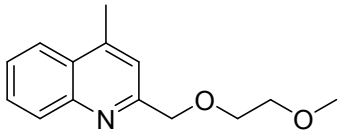
2-(1-ethoxyethyl)-4-methyl quinoline (3ad) [3]**:** (34.4 mg, yield 80%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (like d, 1H), 7.96 (like d, 1H), 7.70-7.66 (m, 1H), 7.54-7.50 (m, 1H), 7.44(s, 1H), 4.67 (q, *J*=6.6 Hz, 1H), 3.54-3.47 (m, 1H), 3.45-3.38 (m, 1H), 2.71 (s, 3H); 1.53 （d, *J*=6.61, 3H), 1.22 (t, *J*=7, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 164.2, 147.4, 145.4, 129.8, 129.3, 127.9, 126.2, 123.9, 118.5, 79.2, 64.8, 22.9, 19.2, 15.7ppm. MS (ESI) (m/z):216.1 $[M + H]^+$.



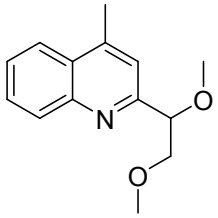
2-(tert-butoxymethyl)-4-methyl quinoline (3ae): (18.3 mg, yield 40%); yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.02 (like d, 1H), 7.97 (like d, 1H), 7.70-7.65 (m, 1H), 7.54-7.52 (m, 1H), 7.51 (s, 1H) , 4.72 (s, 1H), 2.72 (s, 3H); 1.34（s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): 160.6, 147.5, 145.0, 129.6, 129.3, 127.7, 126.0, 123.9, 120.3, 74.3, 66.3, 30.0, 28.0, 19.1 ppm. HRMS (ESI): m/z calcd for $C_{15}H_9NO$ $[M+H]^+$: 230.1539, found: 230.1541.



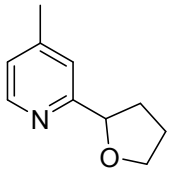
1-(4-methylquinolin-2-yl) ethyl acetate (3af)[4]: (23.3 mg, yield 51%), yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (like d, 1H), 7.98 (like d, 1H), 7.71-7.67 (m, 1H), 7.56-7.52 (m, 1H), 7.42 (s, 1H), 4.67(q, *J*=3.6 Hz, 1H), 3.76-3.67 (m, 2H) 3.41(s, 3H), 3.39(s, 3H), 2.72（s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.5, 147.6, 145.1, 129.8, 129.3, 127.9, 126.3, 123.9, 119.5, 84.7, 75.9, 59.4, 57.8, 19.0 ppm. MS (ESI) (m/z): 230.2 $[M + H]^+$.



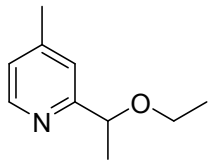
2-((2-methoxyethoxy) methyl)-4-methylquinoline (3ah)[5]: (26.8 mg, yield 58%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (like d, 1H), 7.96 (like d, 1H), 7.70-7.66 (m, 1H), 7.55-7.50 (m, 1H), 7.48 (s, 1H), 4.82 (s, 2H), 3.75-3.73 (m, 2H) 3.64-3.61 (m, 2H), 3.41 (s, 3H); 2.70（s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 158.8, 147.4, 145.1, 129.6, 129.3, 127.7, 126.1, 123.8, 120.2, 74.9, 72.0, 70.2, 59.2, 19.0 ppm. MS (ESI) (m/z): 232.1 $[M + H]^+$.



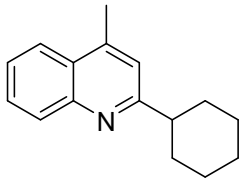
(1, 2-dimethoxyethyl)-4-methylquinoline (3ah')[5]: (14.8 mg, yield 32%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.07 (like d, 1H), 7.98 (like d, 1H), 7.71-7.67 (m, 1H), 7.56-7.52 (m, 1H), 7.42 (s, 1H), 4.66 (q, *J*=3.8 HZ, 1H), 3.76-3.67 (m, 2H), 3.41 (s, 3H); 3.39 (s, 3H), 2.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 159.2, 147.6, 145.1, 129.8, 129.3, 127.9, 126.3, 123.9, 119.5, 84.7, 75.9, 59.4, 57.8, 19.0ppm. MS (ESI) (m/z):232.1 $[M + H]^+$.



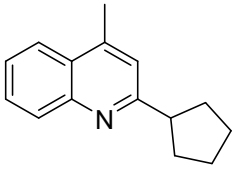
4-methyl-2-(tetrahydrofuran-2-yl)pyridine (3gb) [6]**:** (28.7 mg, yield 88%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.39-8.37 (m, 1H), 7.22 (s, 1H), 6.97-6.96 (m, 1H), 4.99-4.96 (m, 1H), 4.13-4.07 (m, 1H), 3.98-3.93 (m, 1H), 2.44-2.36 (m, 1H), 3.34 (s, 3H), 2.01-1.97 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 162.7, 148.9, 147.8, 123.8, 120.7, 81.4, 69.1, 33.1, 25.8, 21.3 ppm. MS (ESI) (m/z): 164.1 $[M + H]^+$.



2-(1-ethoxyethyl)-4-methylpyridine (3gd): (24.1 mg, yield 73%); colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.35 (d, *J*=5 Hz, 1H), 7.23 (s, 1H), 7.01 (like d, 1H), 4.47 (q, J=6.6 Hz, 1H), 3.49-3.56 (m, 2H), 2.34 (s, 3H), 1.42 (d, *J*=6.6 Hz, 3H), 1.20 (q, *J*=5.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 163.6, 148.7, 148.0, 123.3, 120.6, 79.0, 64.5, 22.7, 21.3, 15.5 ppm. HRMS (ESI): m/z calcd for $C_{10}H_{15}NO$ $[M+H]^+$: 166.1232, found: 166.1626.

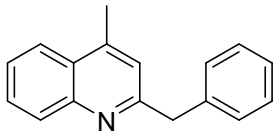


2-cyclohexyl-4-methylquinoline (3ai) [7]**:** (22.1 mg, yield 49%); colorless liquid.
^{1}H NMR (400 MHz, $CDCl_3$): 8.04 (like d, 1H), 7.93 (like d, 1H), 7.68-7.64 (m, 1H), 7.51-7.47 (m, 1H), 7.16 (s, 1H), 2.91-2.83 (m, 1H), 2.68 (s, 3H), 2.03-1.99 (m, 2H), 1.91-1.87 (m, 2H), 1.81-1.76 (m, 1H) ppm, 1.67-1.57 (m, 2H), 1.52-1.41 (m, 2H), 1.39-1.31 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 147.7, 144.4, 129.6, 129.1, 127.2, 125.5, 123.7, 120.4, 47.7, 33.0, 26.7, 26.3, 19.0 ppm. MS (ESI) (m/z): 226.1 $[M + H]^+$.



2-cyclopentyl-4-methylquinoline (3aj) [8]: the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to provide the product **3aj** as a colourless liquid (19.4 mg, yield 46%); ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (like d, 1H), 7.91 (like d, 1H), 7.67-7.63 (m, 1H), 7.49-7.45(m, 1H), 7.16 (s, 1H), 3.38-3.29 (m, 1H), 2.66 (s, 3H), 2.20-2.13 (m, 2H), 1.93-1.84 (m, 4H), 1.79-1.72 (m,

2H), 1.67-1.57 (m, 2H),^{13}C{1H} NMR (100 MHz, CDCl3): 165.8, 147.5, 144.0, 129.4, 128.8, 126.9, 125.2, 123.4, 120.6, 48.7, 33.5, 26.0,18.7 ppm. MS (ESI) (m/z): 212.1 $[M + H]^+$.



2-benzyl-4-methylquinoline (3ak) [7]: the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate =5:1) to provide the product **3ak** as a yellow liquid (15.4 mg, yield 33%); ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (like d, 1H), 7.87 (like d, 1H), 7.66-7.62 (m, 1H), 7.48-7.44 (m, 1H), 7.27-7.23 (m, 4H), 7.19-7.15 (m, 1H), 7.01 (s, 1H), 4.25 (s, 2H), 2.55 (s, 3H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$): 160.8, 147.4, 144.7, 129.6, 129.1, 128.5， 126.8, 126.4, 125.7, 123.6, 122.1, 45.3, 18.6 ppm. MS (ESI) (m/z): 234.1 $[M + H]^+$.

4. References

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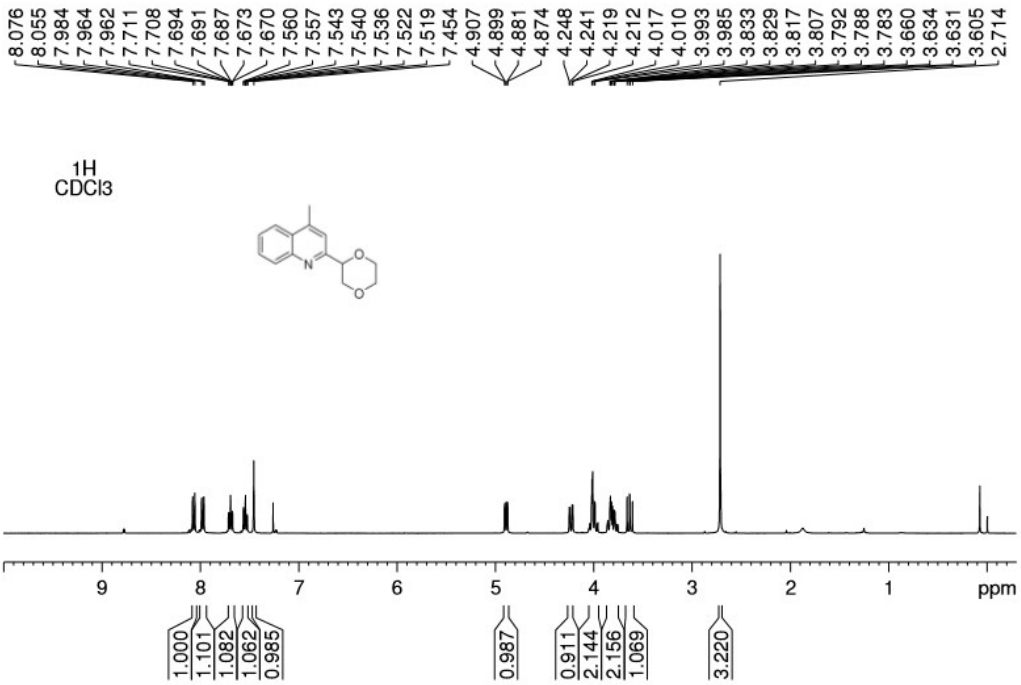
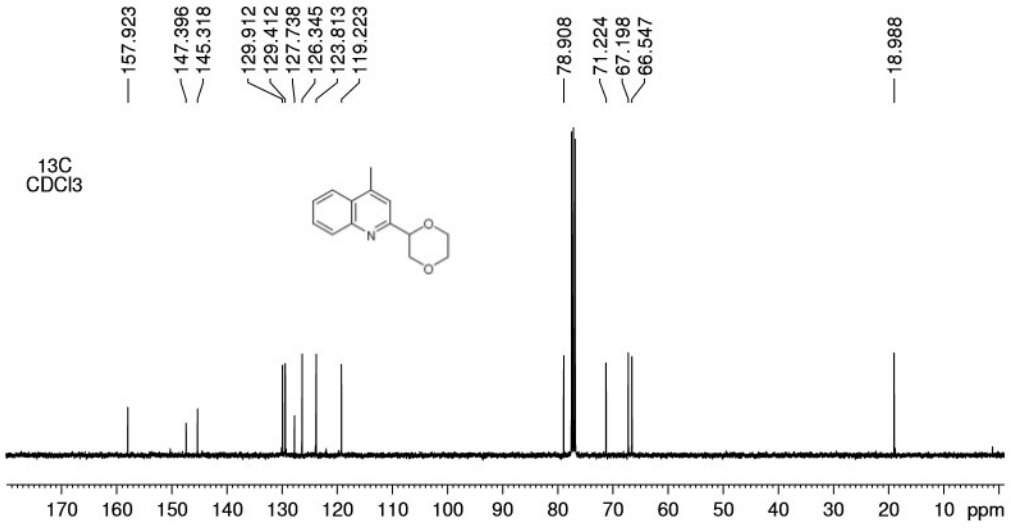
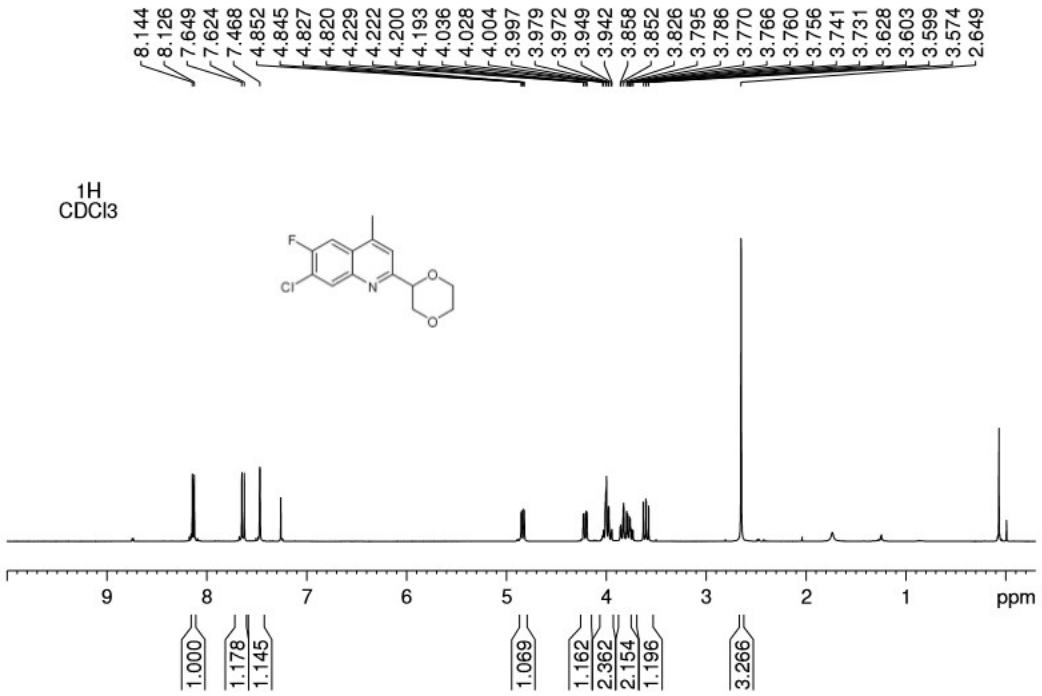
5. ^{1}H NMR and ^{13}C NMR Spectra



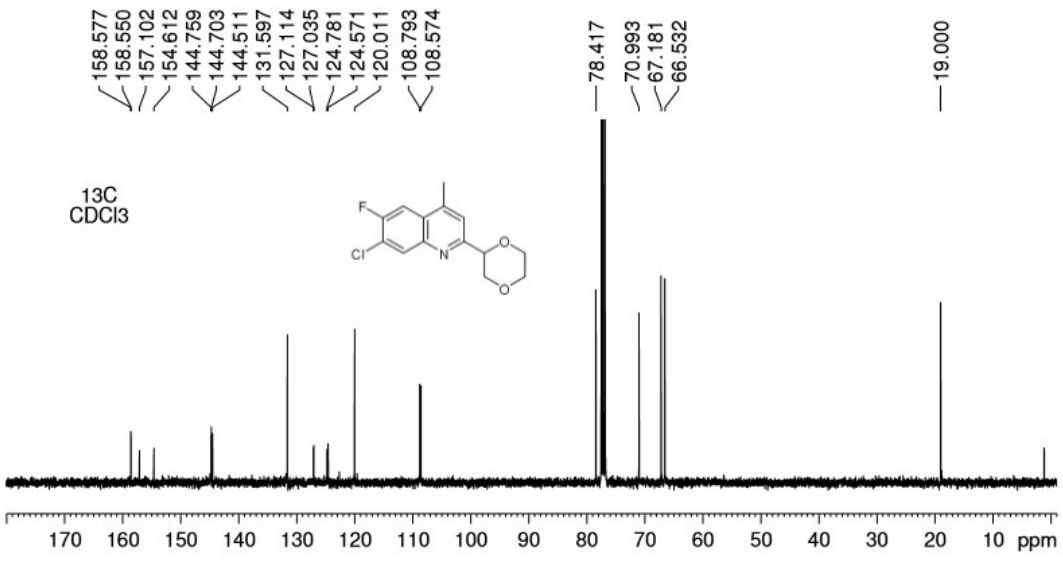
^{1}H NMR spectrum of compound **3aa**



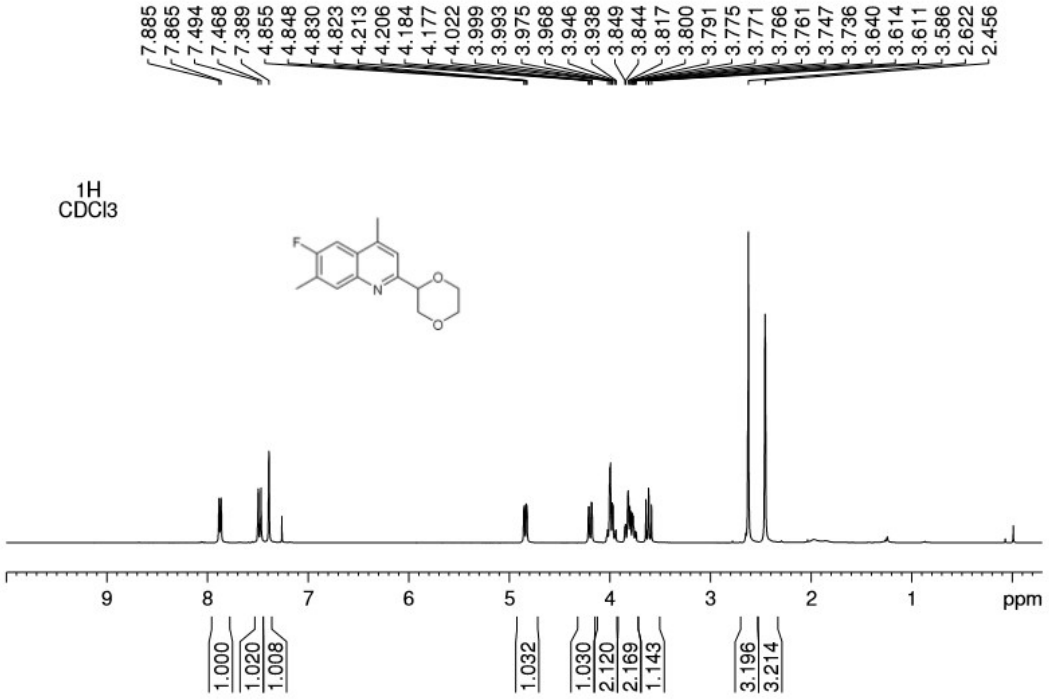
^{13}C NMR spectrum of compound **3aa**



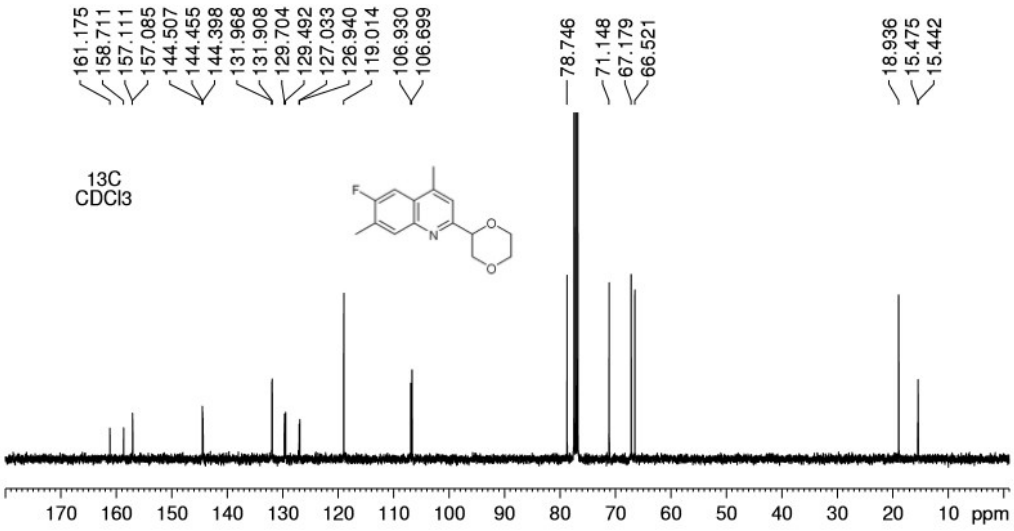
^{1}H NMR spectrum of compound **3ba**



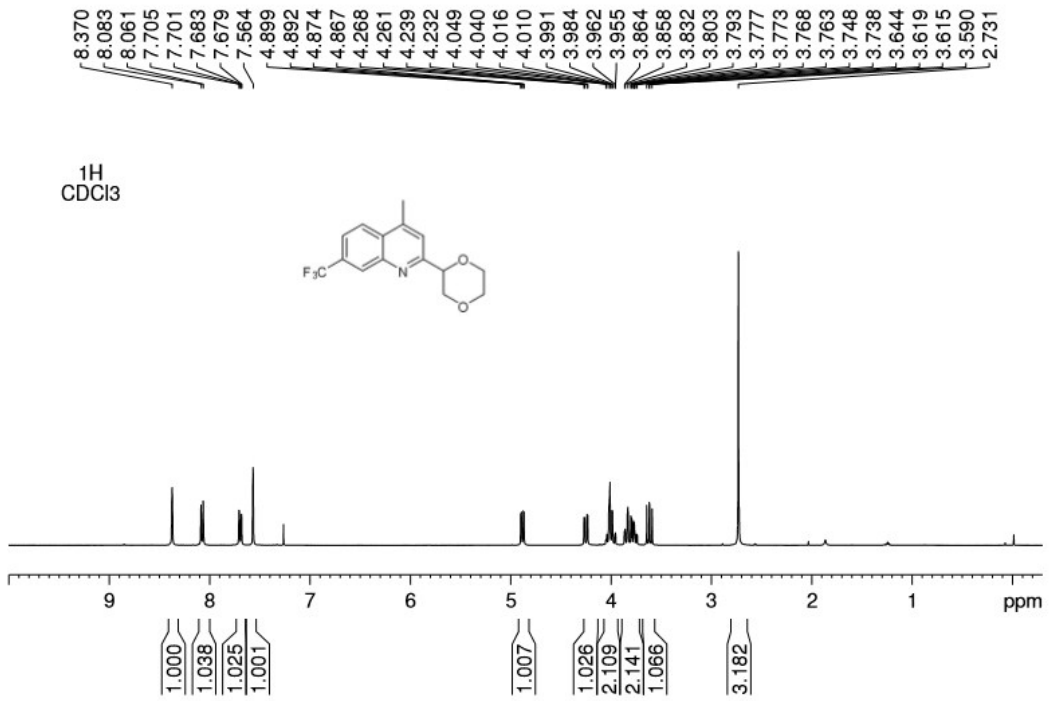
^{13}C NMR spectrum of compound **3ba**



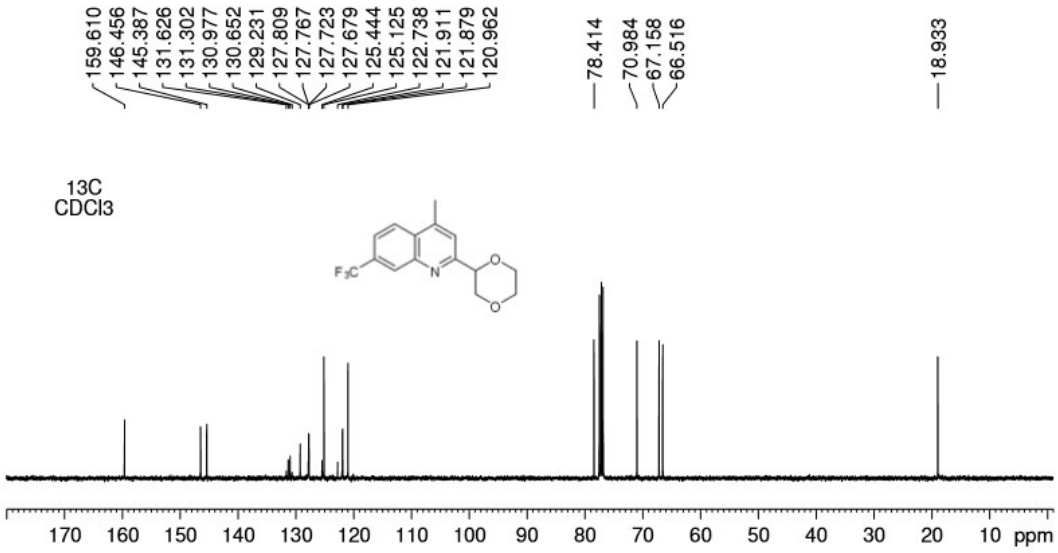
^{1}H NMR spectrum of compound **3ca**



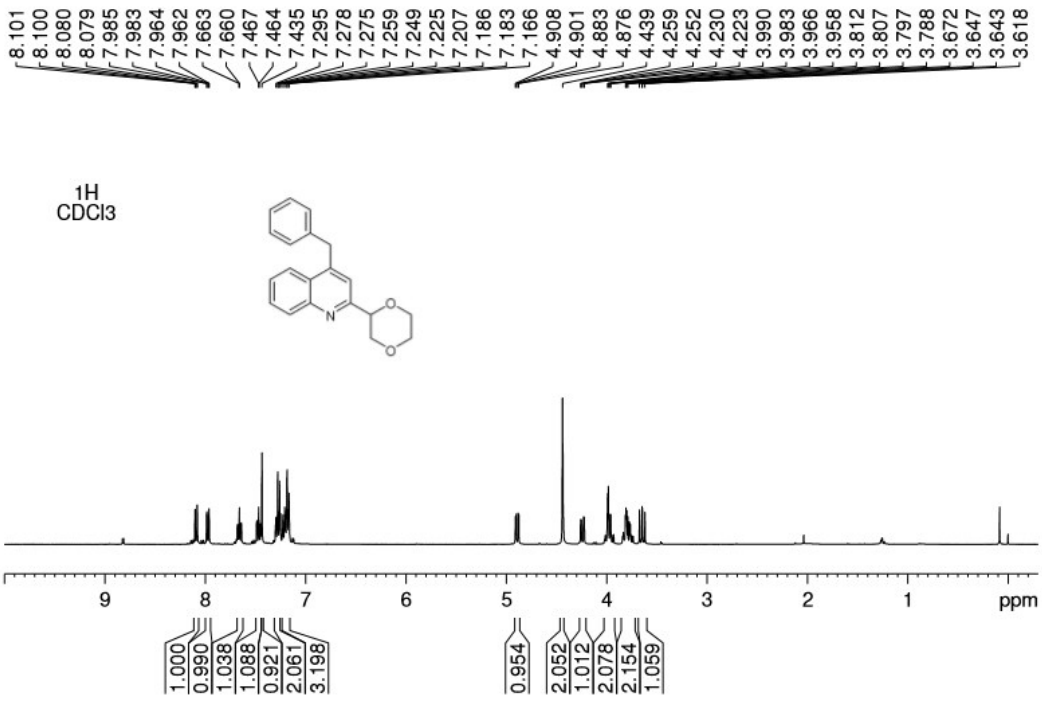
^{13}C NMR spectrum of compound **3ca**



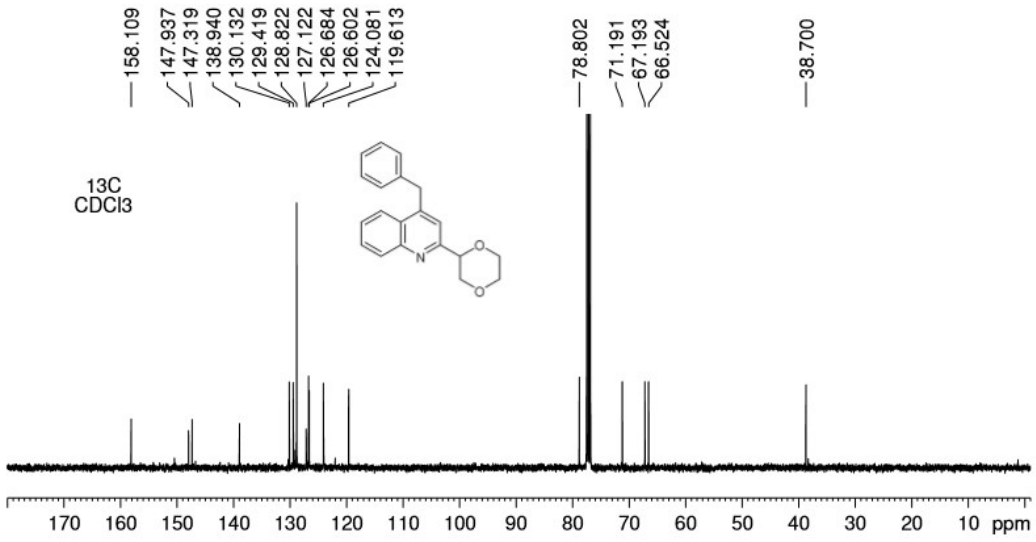
^{1}H NMR spectrum of compound **3da**



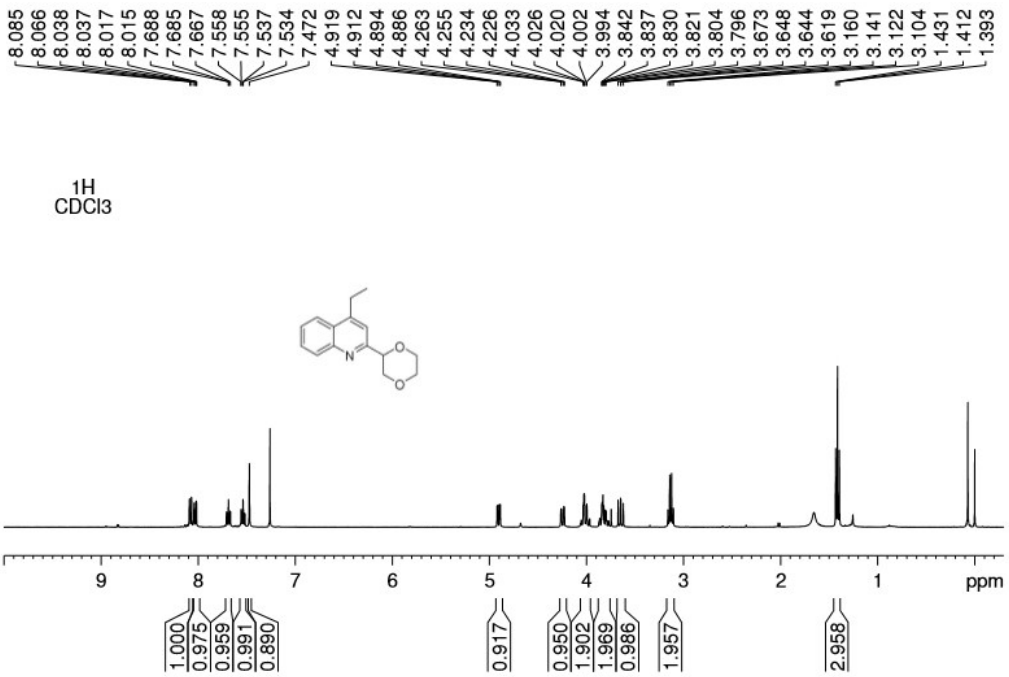
^{13}C NMR spectrum of compound **3da**



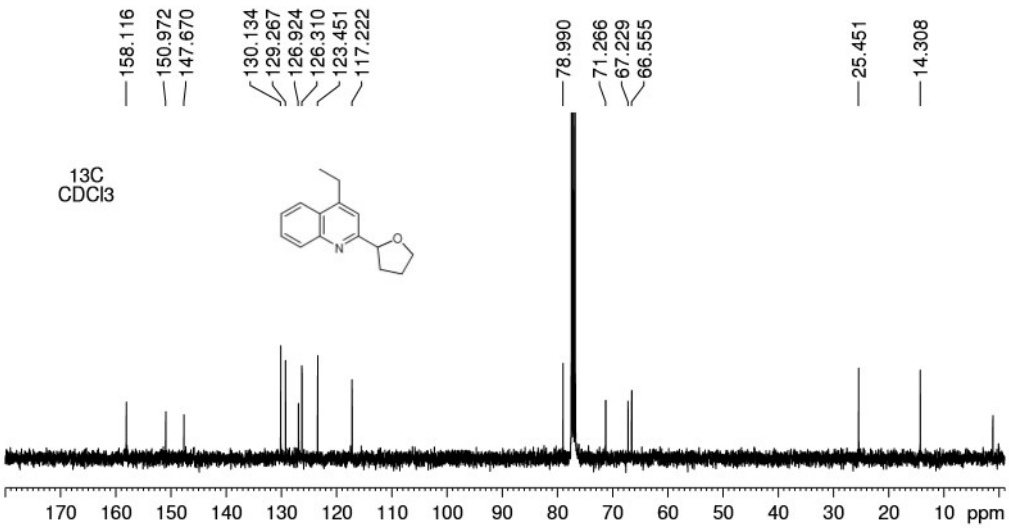
^{1}H NMR spectrum of compound **3ea**



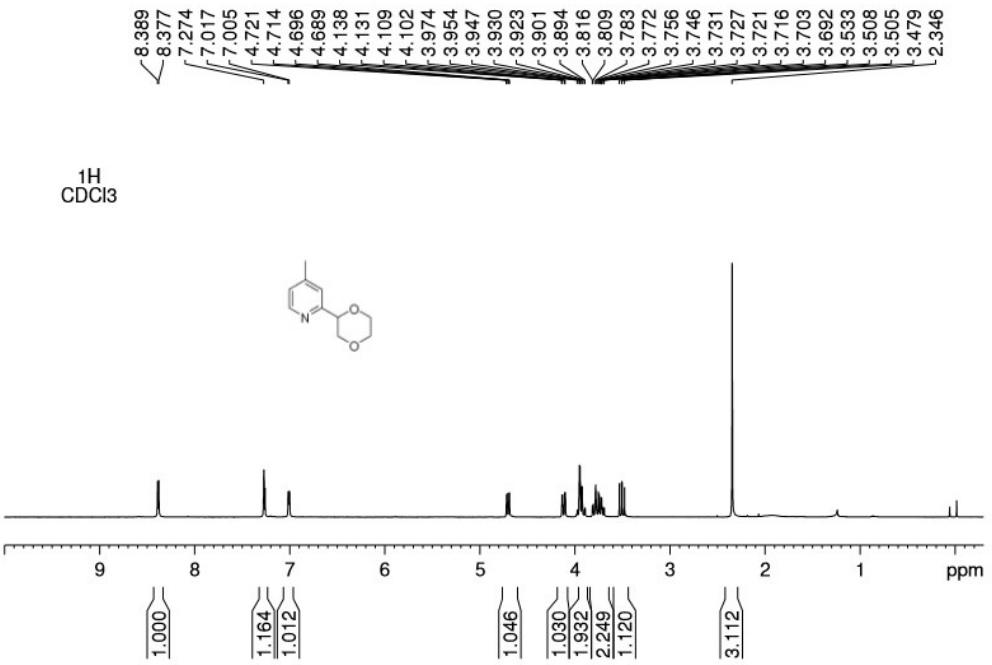
^{13}C NMR spectrum of compound **3ea**



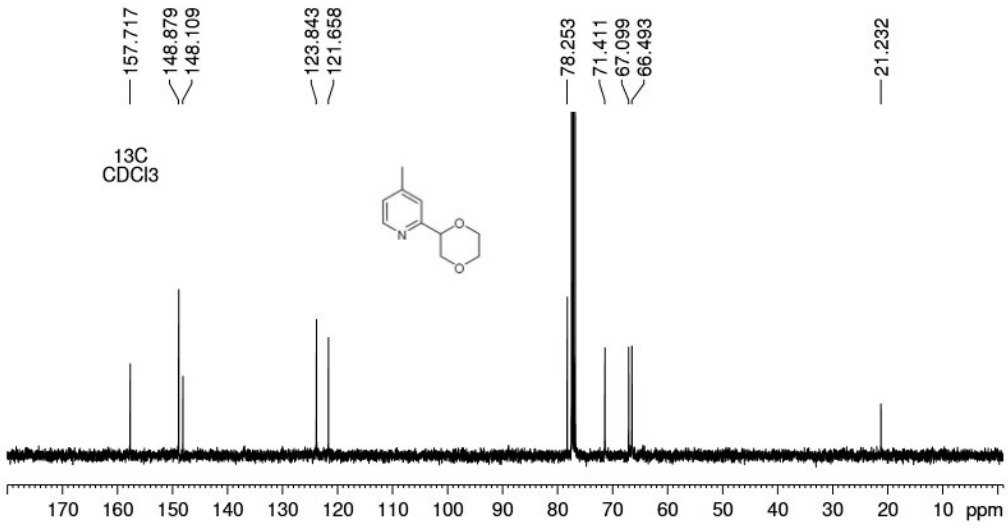
^{1}H NMR spectrum of compound **3fa**



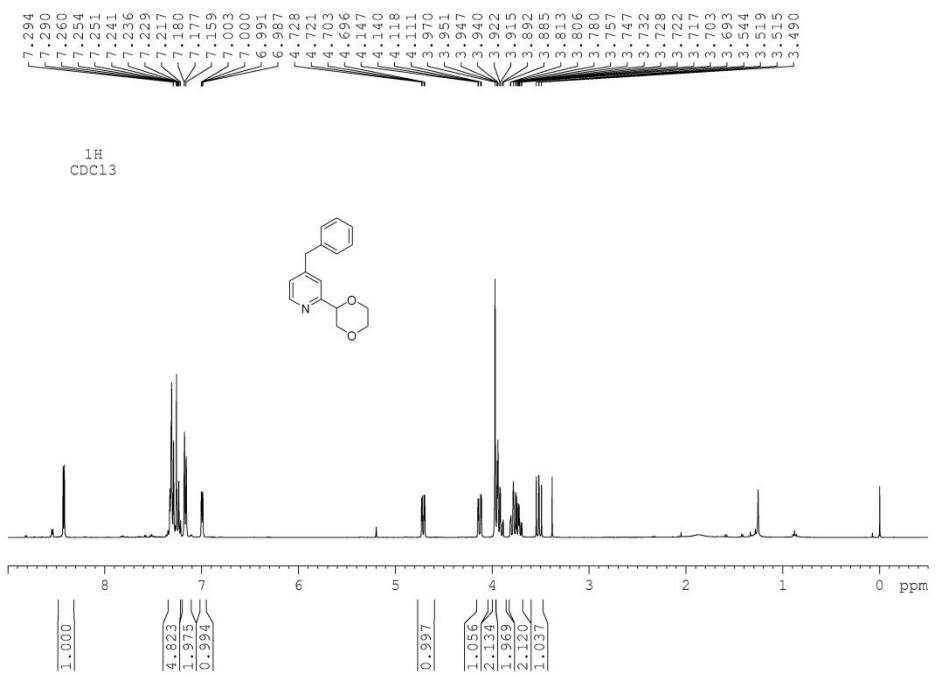
^{13}C NMR spectrum of compound **3fa**



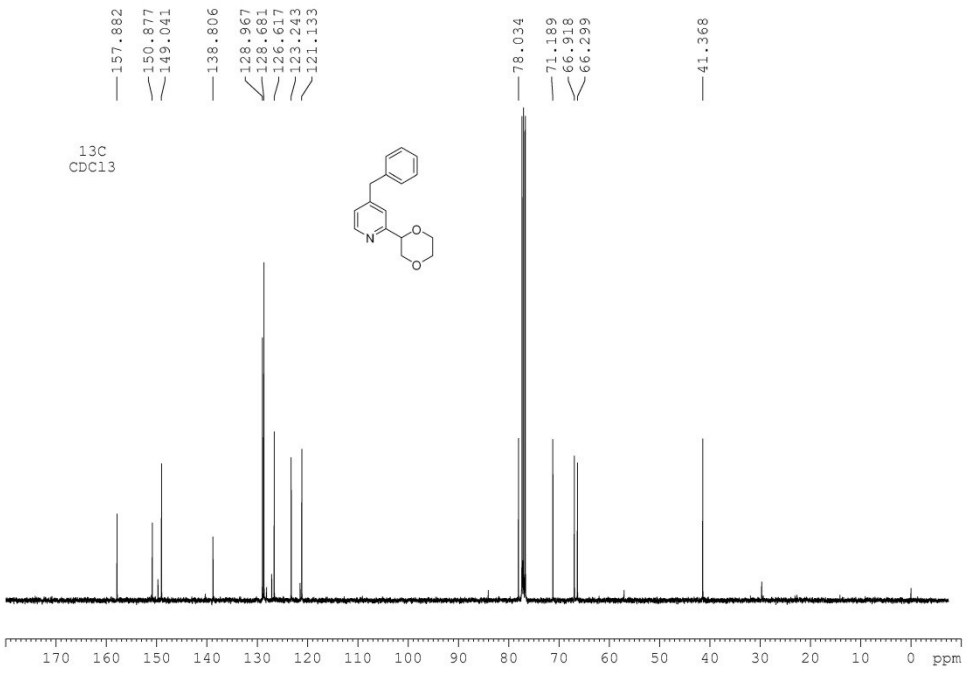
^{1}H NMR spectrum of compound **3ga**



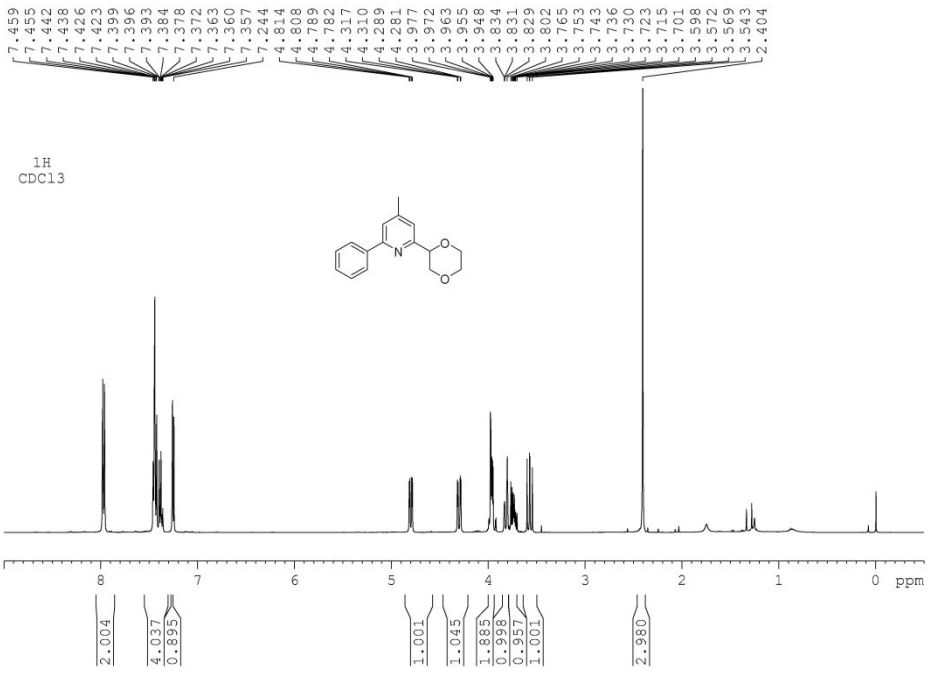
^{13}C NMR spectrum of compound **3ga**



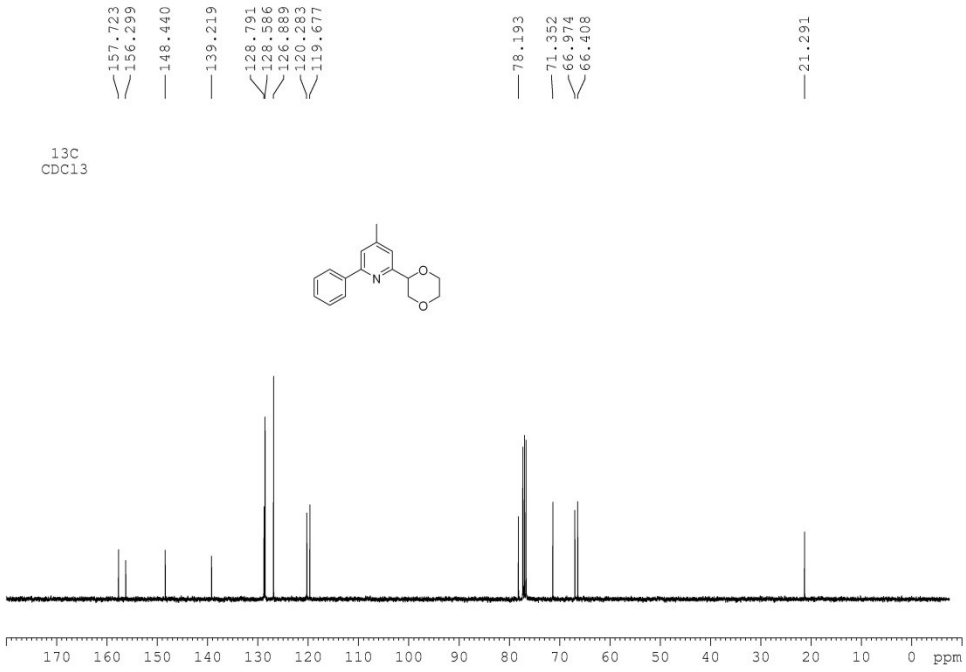
^{1}H NMR spectrum of compound **3ha**



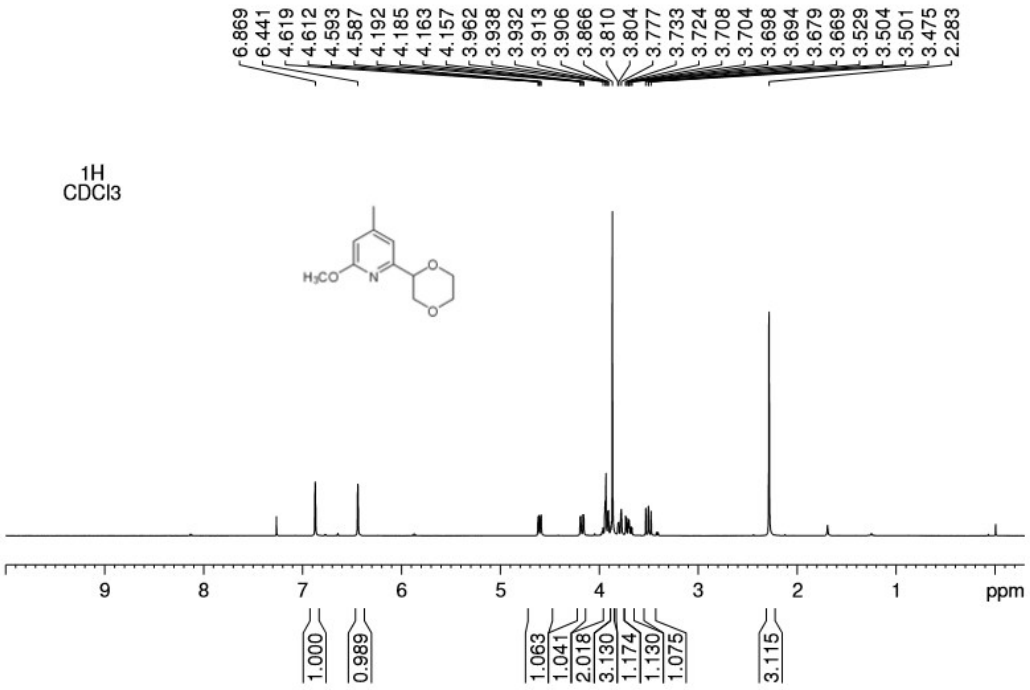
^{13}C NMR spectrum of compound **3ha**



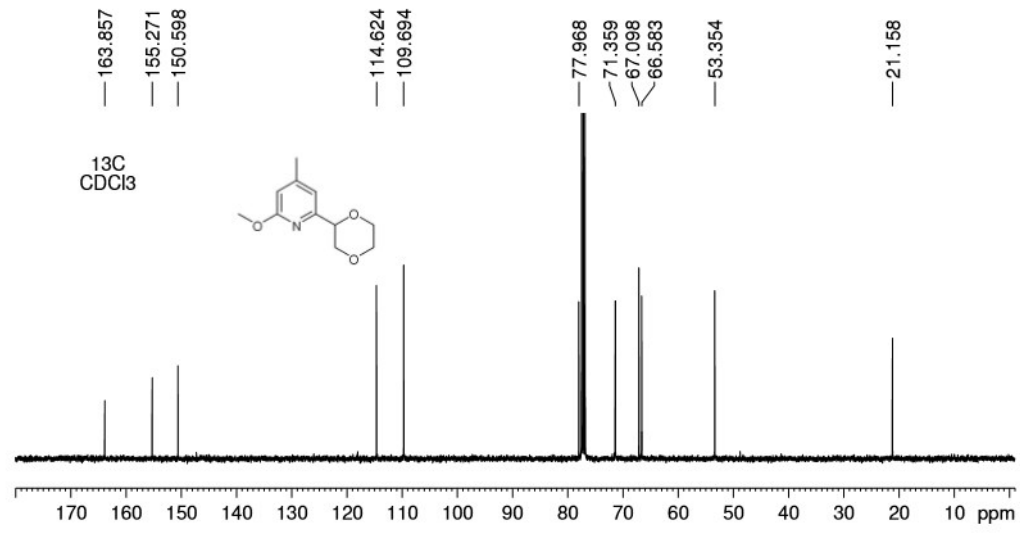
^{1}H NMR spectrum of compound **3ia**



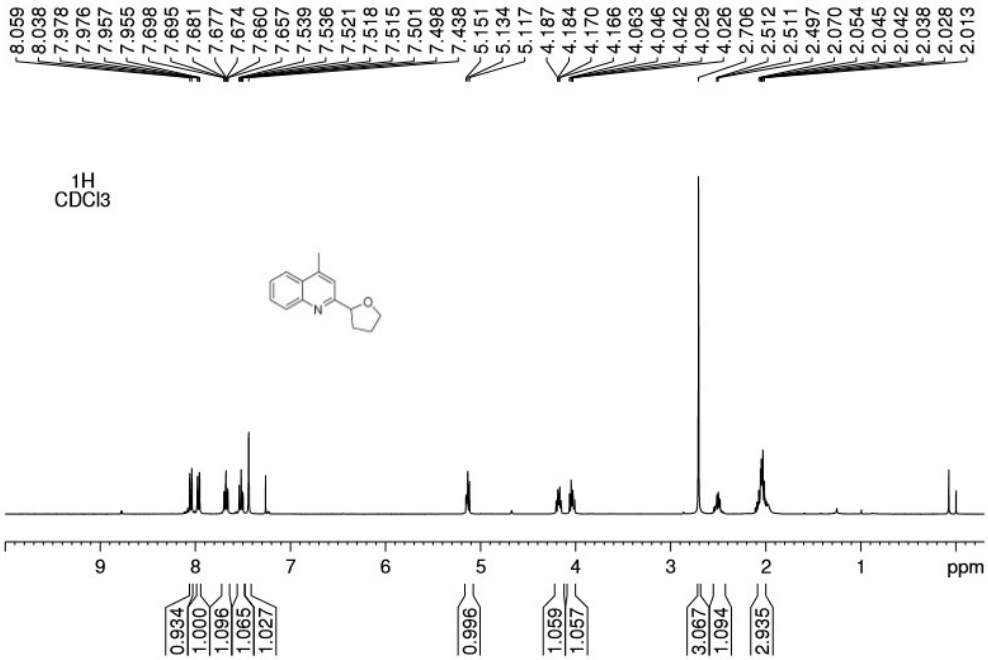
^{13}C NMR spectrum of compound **3ia**



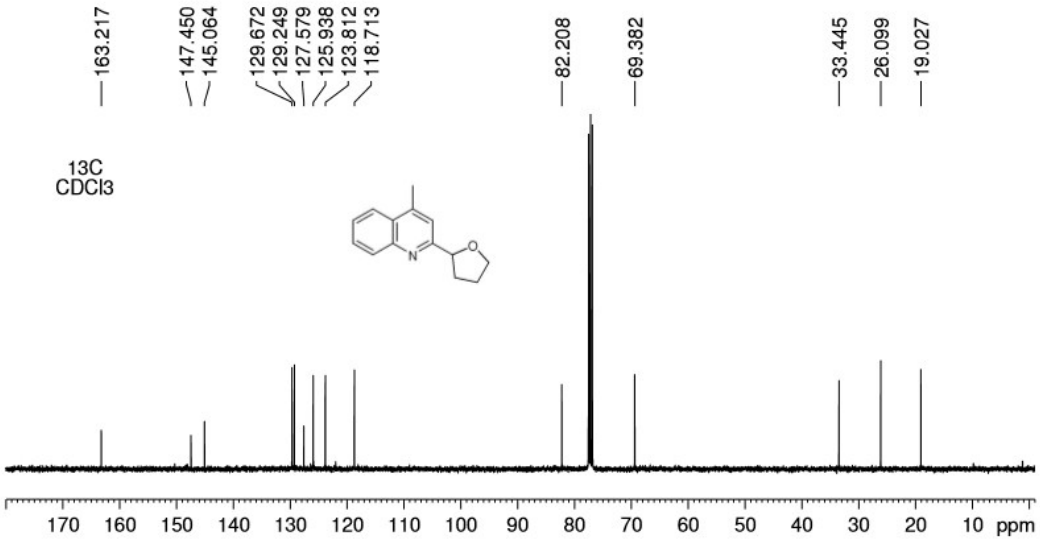
^{1}H NMR spectrum of compound **3ja**



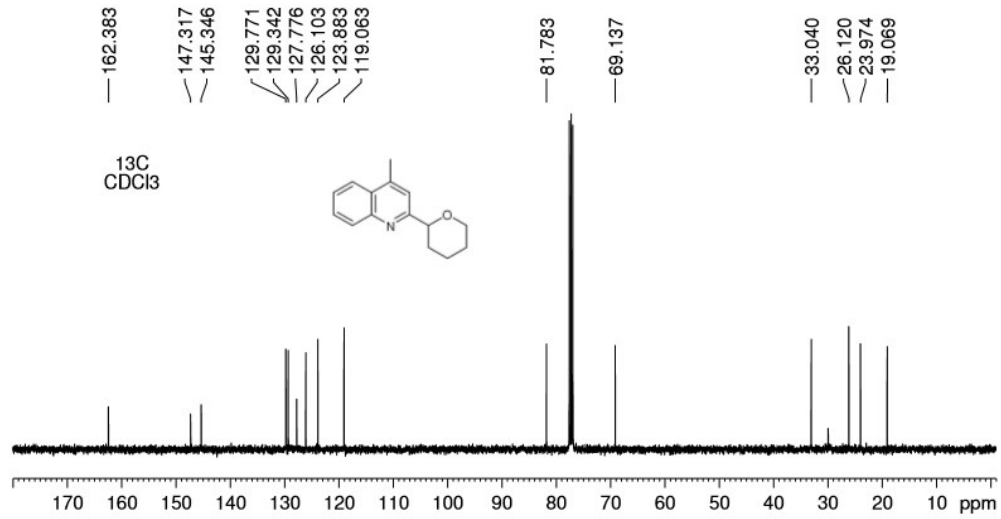
^{13}C NMR spectrum of compound **3ja**



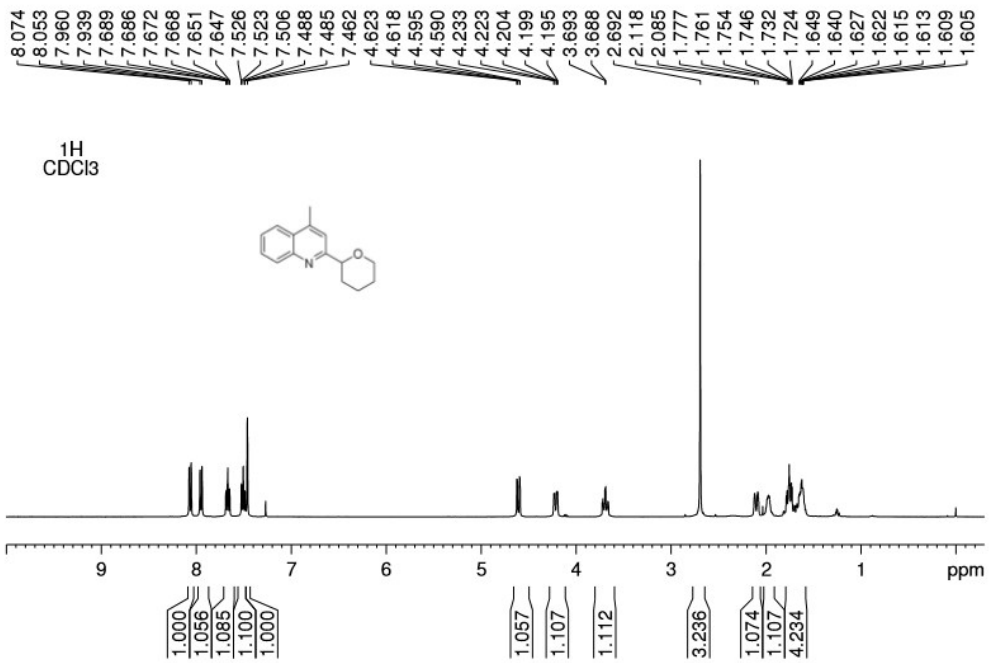
^{1}H NMR spectrum of compound **3ab**



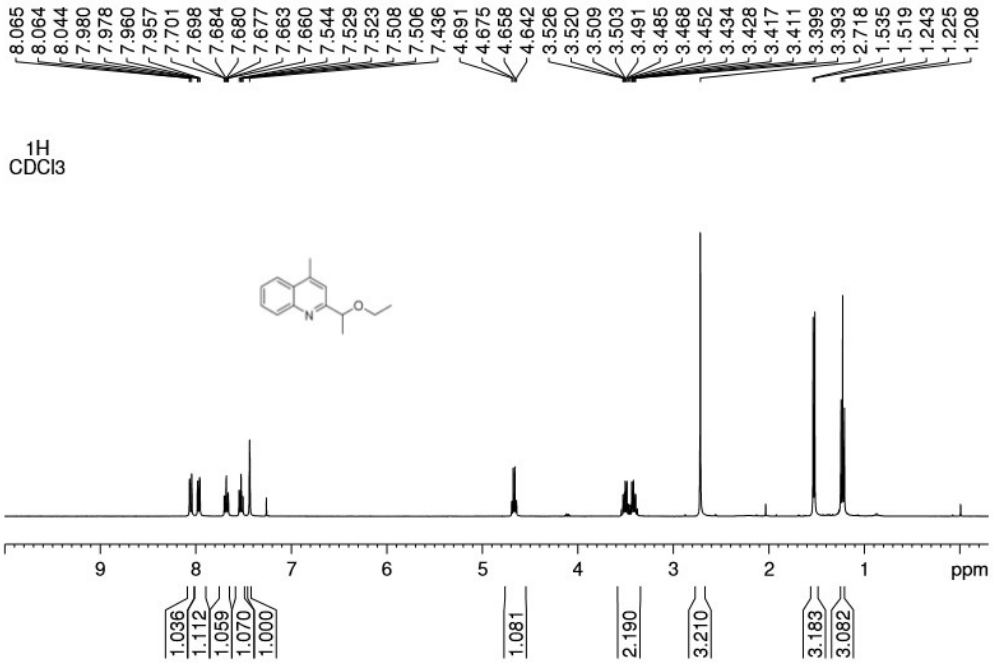
^{13}C NMR spectrum of compound **3ab**



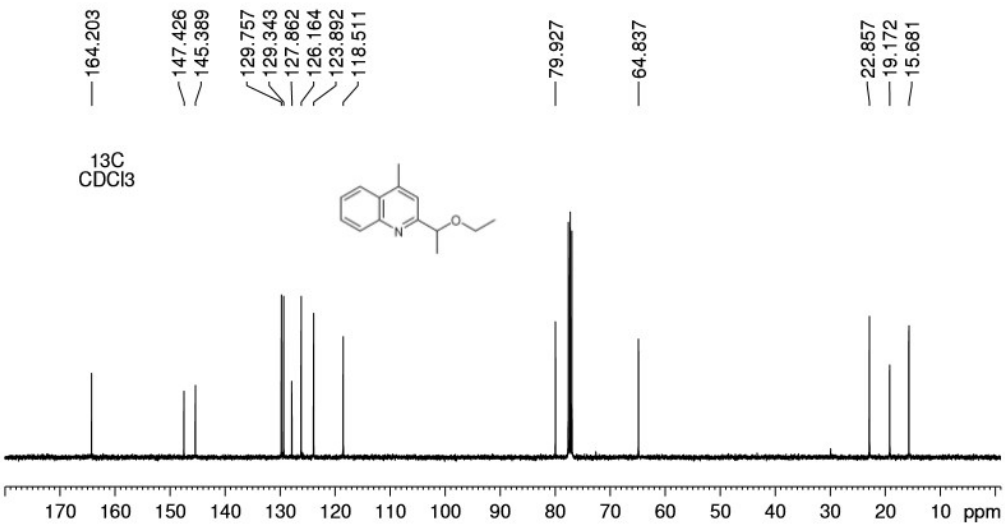
^{1}H NMR spectrum of compound **3ac**



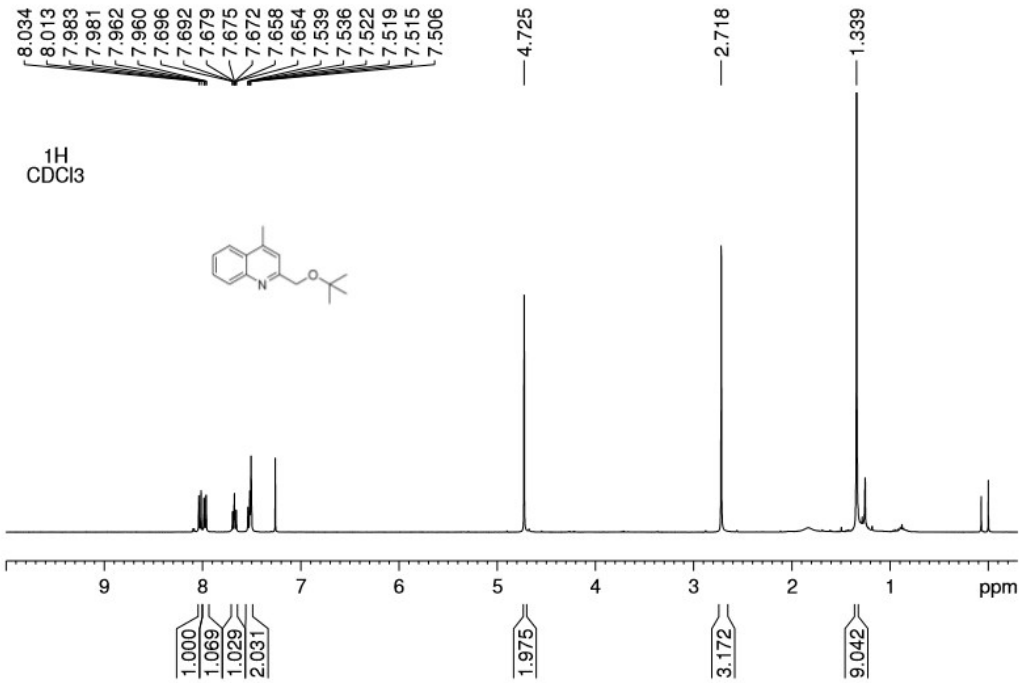
^{13}C NMR spectrum of compound **3ac**



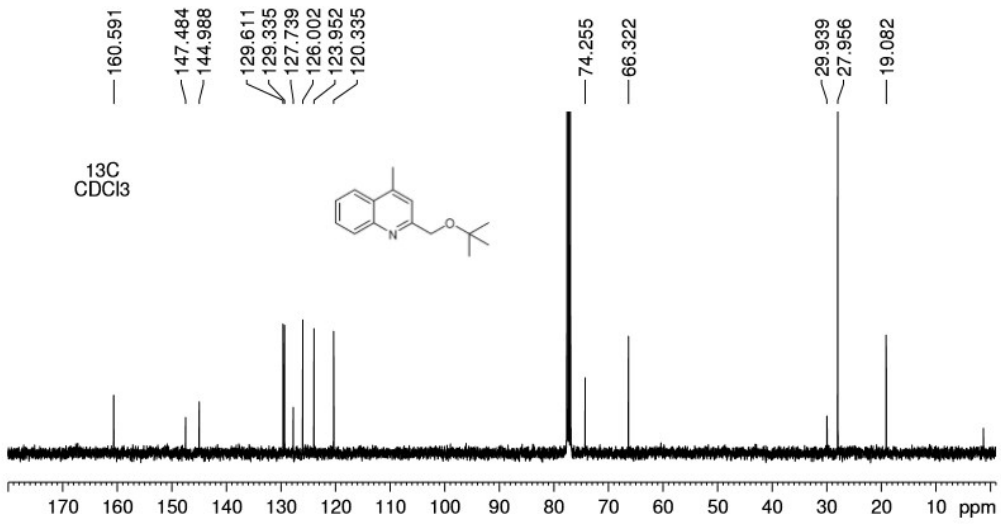
^{1}H NMR spectrum of compound **3ad**



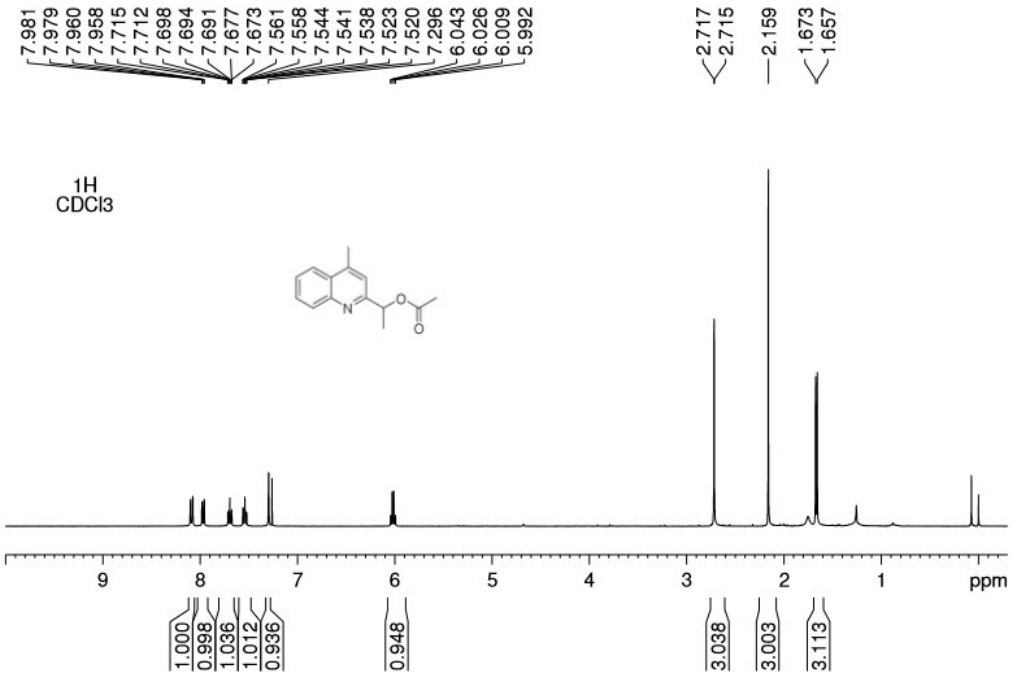
^{13}C NMR spectrum of compound **3ad**



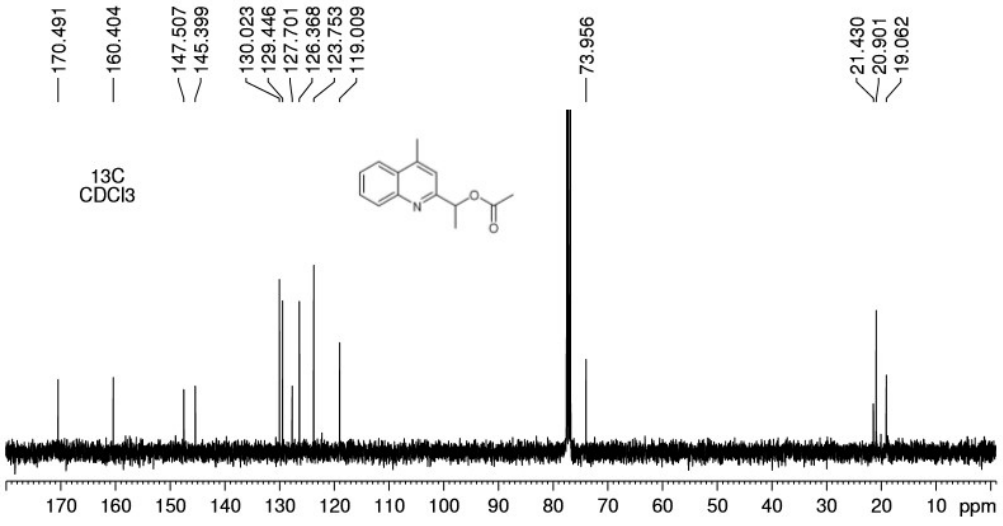
^{1}H NMR spectrum of compound **3ae**



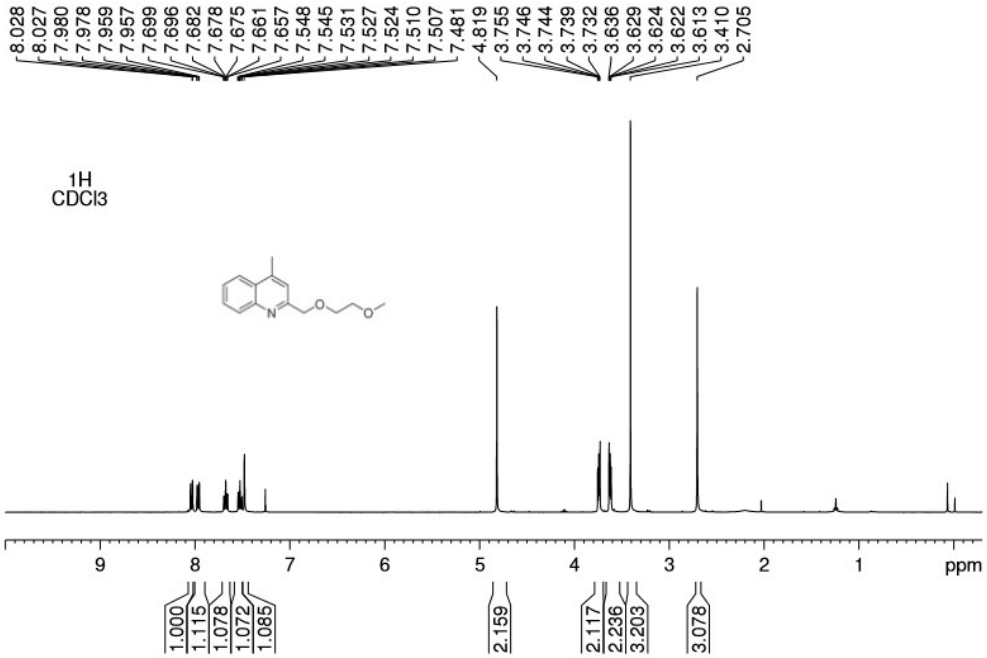
^{13}C NMR spectrum of compound **3ae**



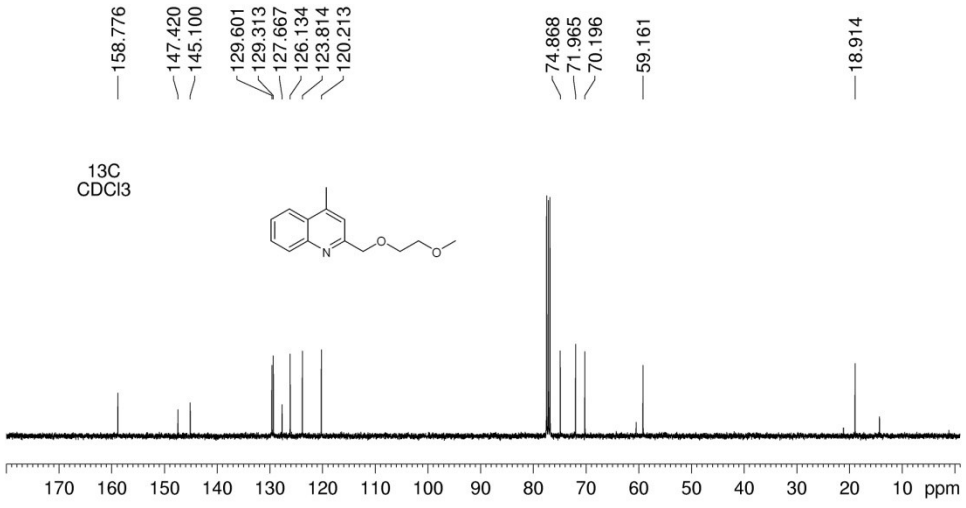
^{1}H NMR spectrum of compound **3af**



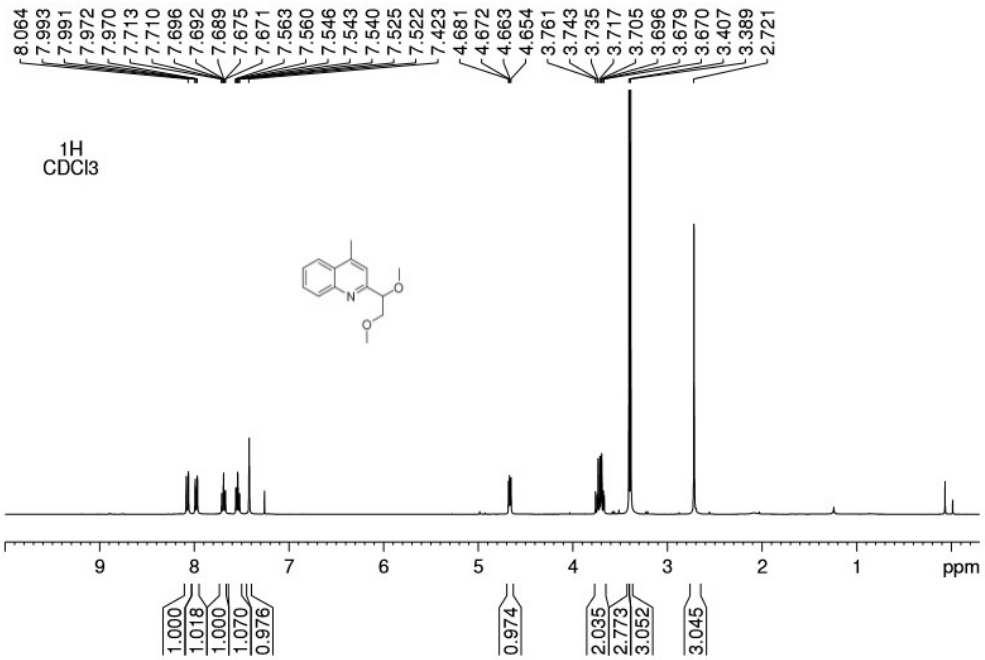
^{13}C NMR spectrum of compound **3af**



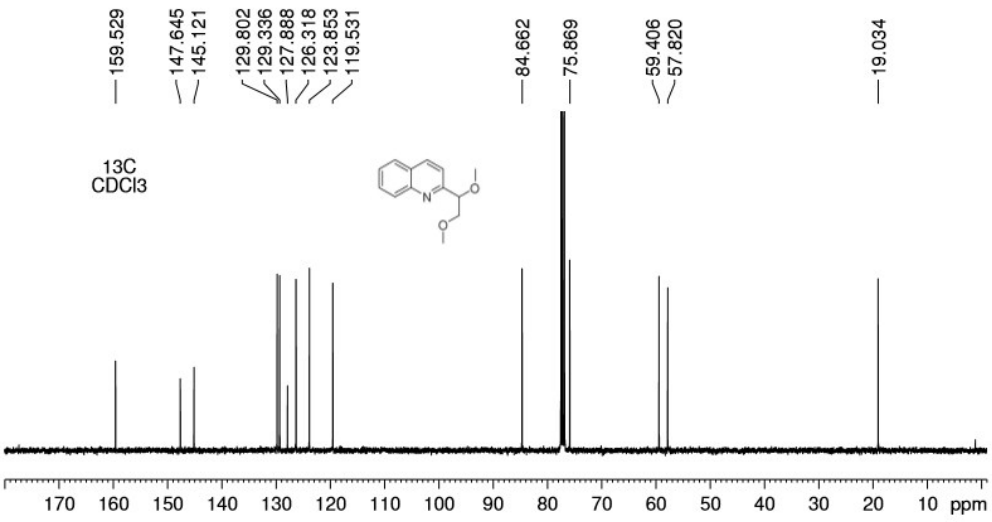
^{1}H NMR spectrum of compound **3ag**



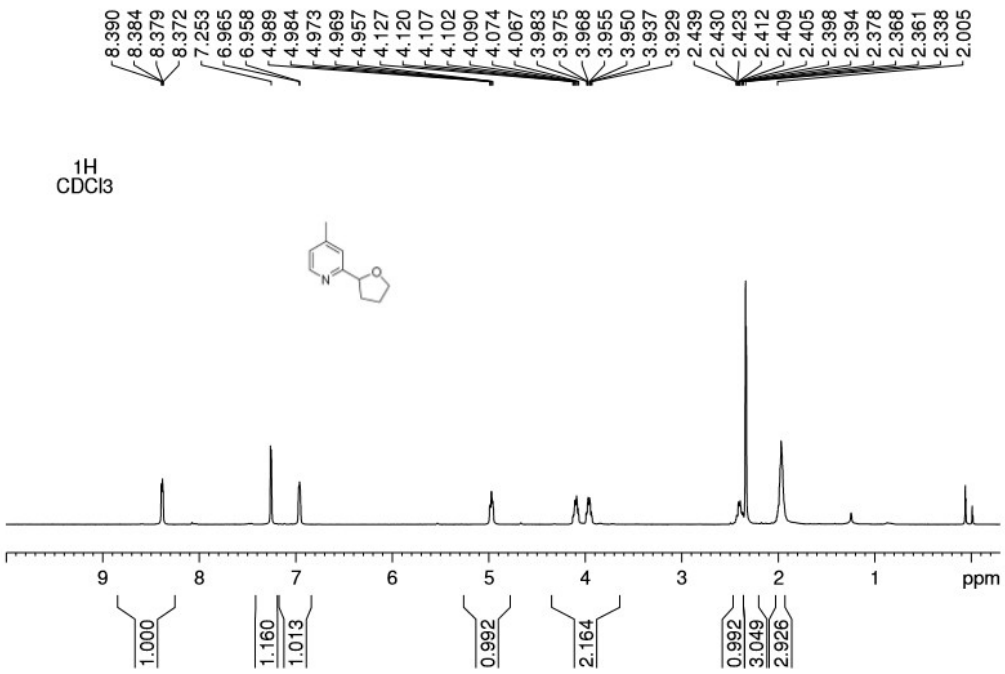
^{13}C NMR spectrum of compound **3ag**



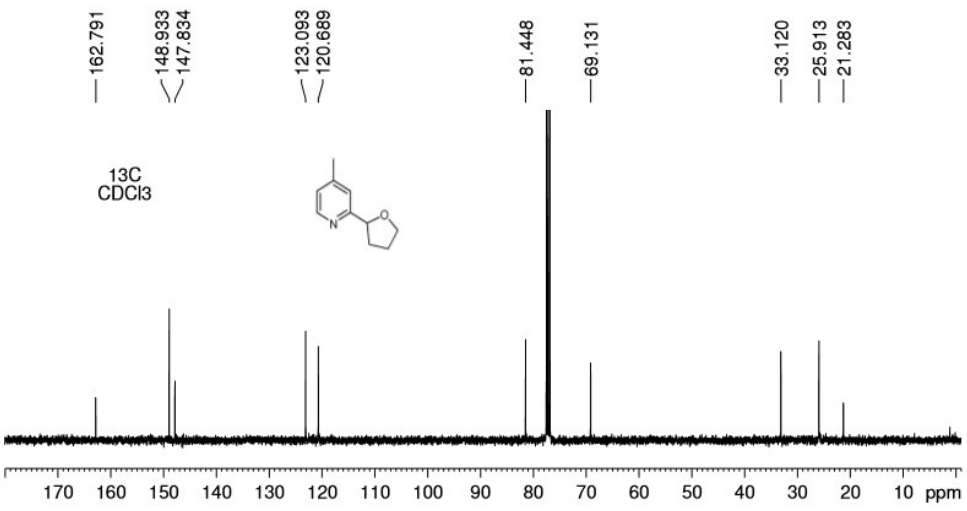
^{1}H NMR spectrum of compound **3ag'**



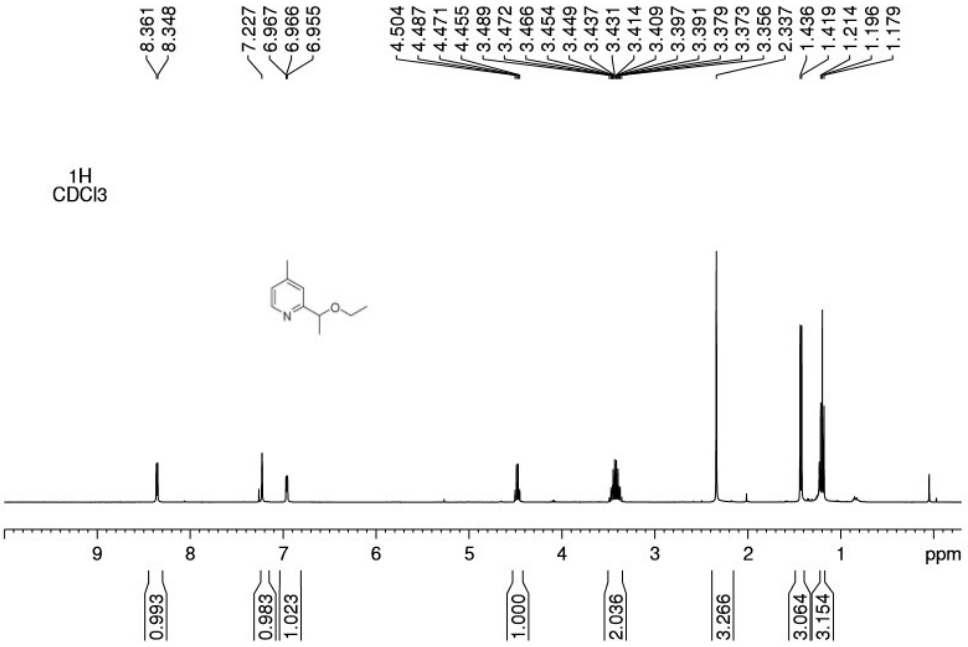
^{13}C NMR spectrum of compound **3ag'**



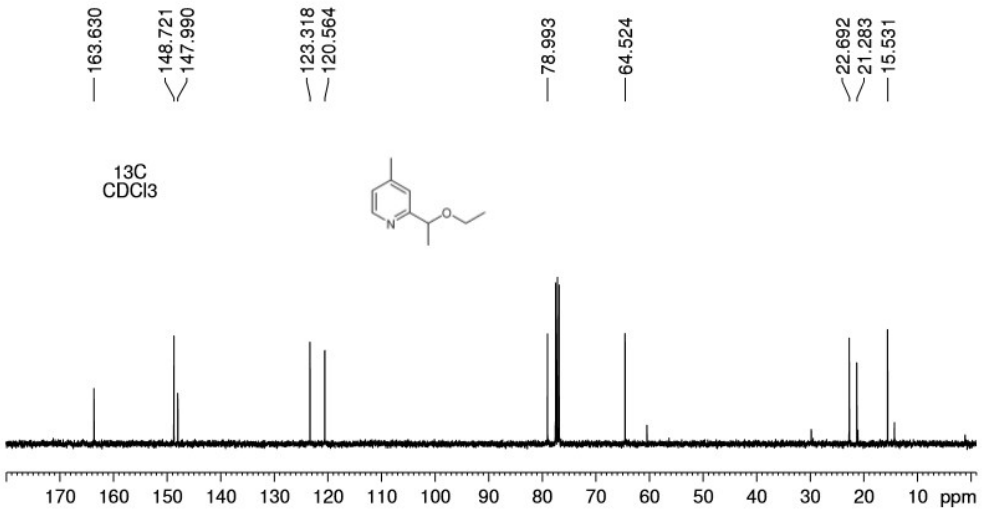
^{1}H NMR spectrum of compound **3gb**



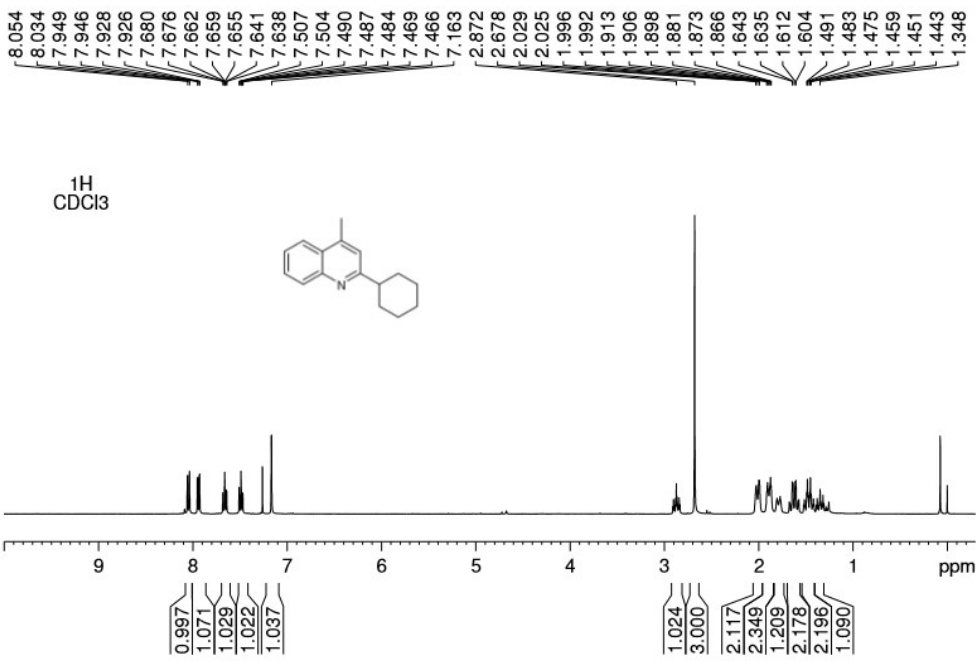
^{13}C NMR spectrum of compound **3gb**



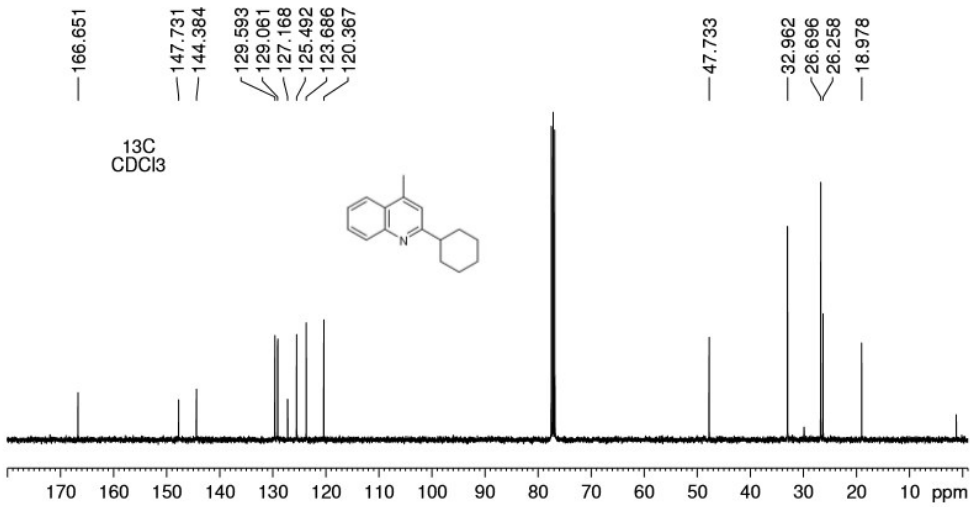
^{1}H NMR spectrum of compound **3gd**



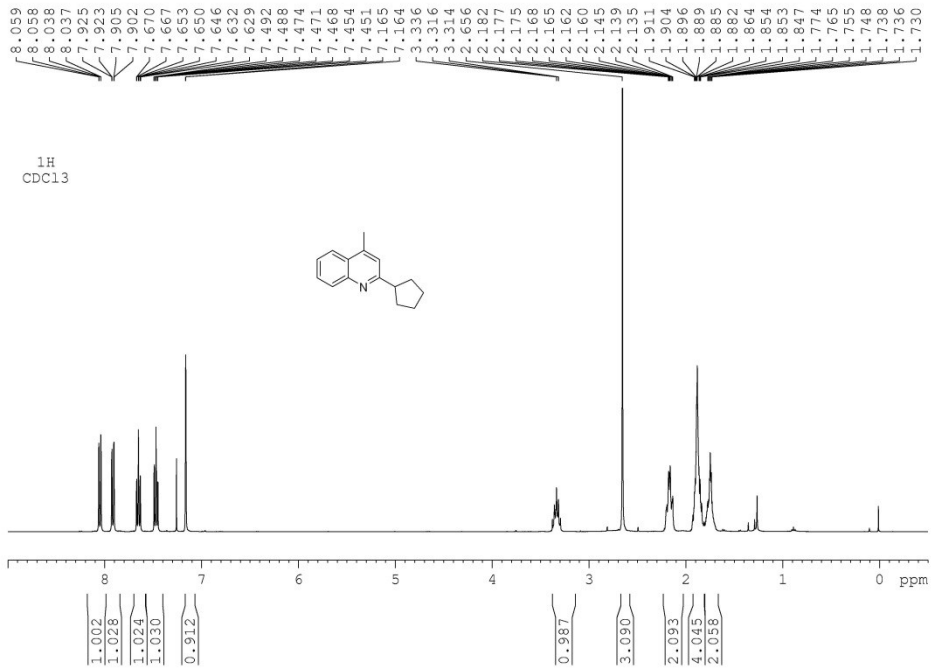
^{13}C NMR spectrum of compound **3gd**



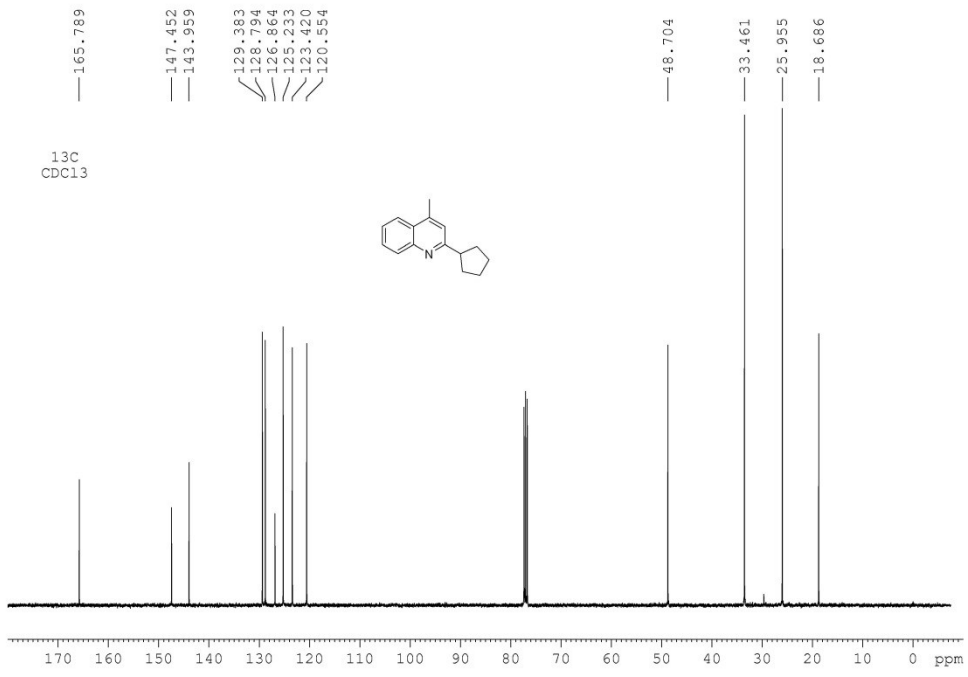
^{1}H NMR spectrum of compound **3ai**



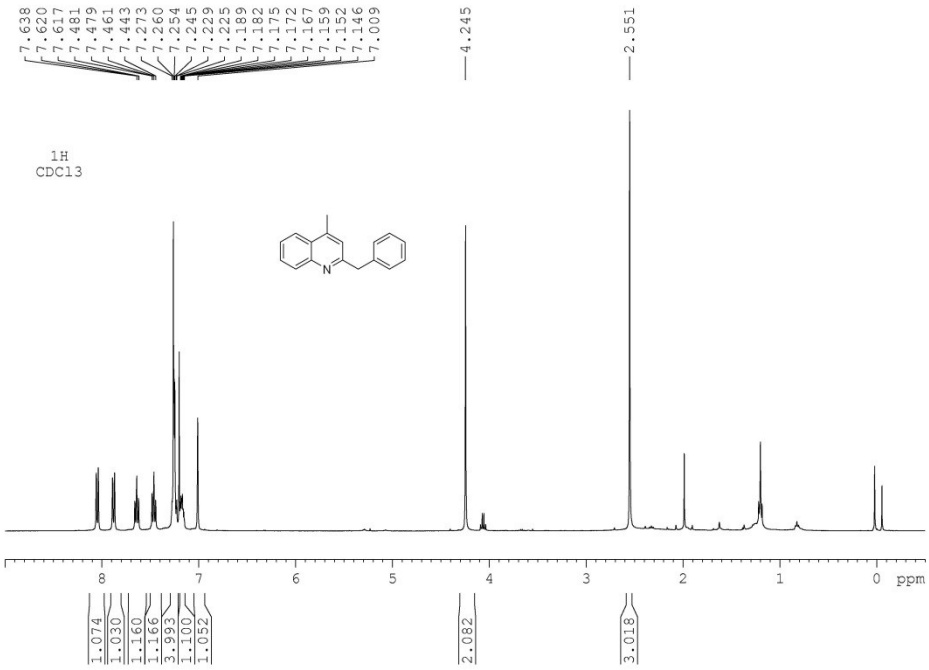
^{13}C NMR spectrum of compound **3ai**



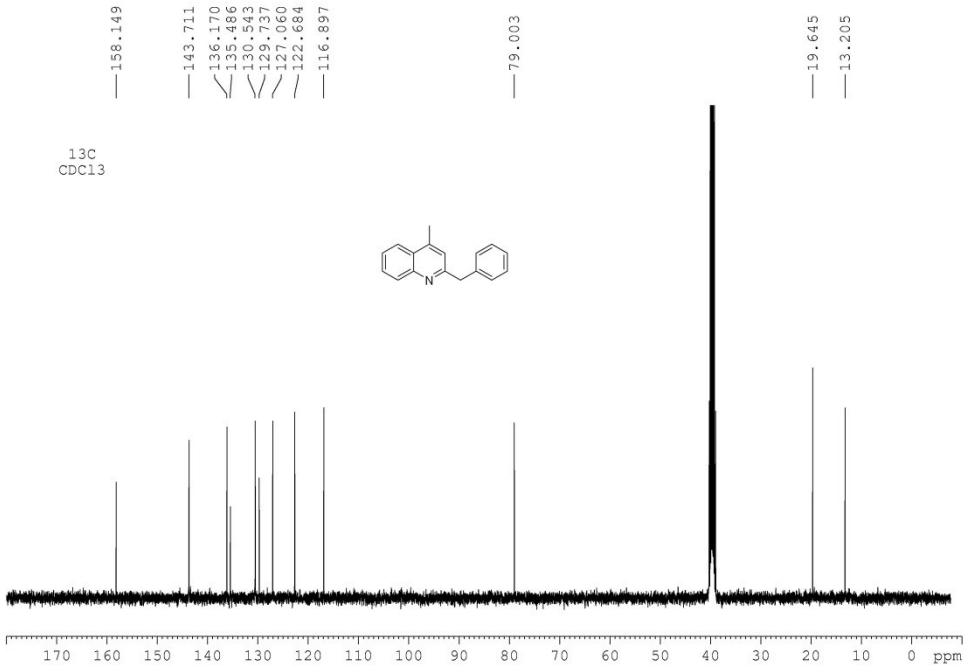
^{1}H NMR spectrum of compound **3aj**



^{13}C NMR spectrum of compound **3aj**



^{1}H NMR spectrum of compound **3ak**



^{13}C NMR spectrum of compound **3ak**