Supporting information

New Pyridinium Based Ionic Liquid as an Excellent Solvent-Catalyst System for the One-Pot Three-Component Synthesis of 2,3-Disubstituted Quinolines

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Experimental Section:

General information

Melting points were determined using a Stuart Scientific SMP2 apparatus without correction. FT-IR spectra were obtained as KBr pellets using a Jasco 6300 instrument in the range of 400–4000 cm^{-1}. ^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded on a Bruker-AC 500 spectrometer in $CDCl_3$ solution. Mass spectra were recorded on a Platform II spectrometer from Micromass; EI mode at 70 eV. Elemental analysis was carried out on a LECO, CHNS-932 instrument.

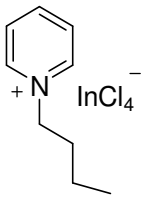
Preparation of [bpy][$InCl_4$]

A mixtre of pyridine (0.096 g, 1.2 mmol) and 1-chlorobutane (0.105 g,1.1 mmol) was stirred under reflux conditions for 72 h in dark. The reaction mixture was cooled and the resulting solid was recrystallized from MeCN/EtOAc (1:1), filtered under vacuum and washed with EtOAc. The excess solvent was then removed under vacuum at 70 ^{o}C. The IL was prepared by stirring [bpy]Cl (0.171 g,1 mmol,) with $InCl_3$ (0.219 g, 1 mmol) at room temperature for 10 min.

General Procedure for Synthesis of 2,3-Disubstituted Quinolines

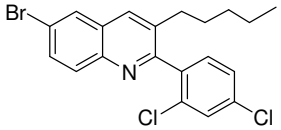
To a mixture of arylamine (1 mmol), arylaldehyde (1 mmol) and aliphatic aldehyde (1 mmol), was added [bpy][$InCl_4$] (1 mmol). The reaction mixture was stirred at 70 ^{o}C for 30-45 min (Table 2). The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtOAc: 9/1). After completion of the reaction, the mixture was diluted with 5 mL water and 5 mL EtOAc, and shaken vigorously. The organic layer was separated from the IL. The IL was dried at 60-70 ^{o}C under vacuum to remove water and reused. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by recrystallization from EtOH to obtain the pure product in 83-97% yields.

SpectroscopicData of the Catalyst and Products



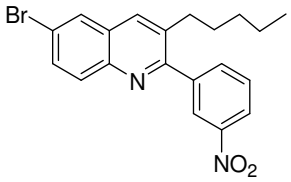
[bpy][InCl$_4$]

mp 68-70 °C. IR (KBr): ν_{max} = 3130, 3085, 2963, 2935, 2877, 1633, 1487, 1466, 1178, 769, 681 cm^{-1}. ^{1}H NMR(500 MHz, $CDCl_3$): δ = 0.76 (t, J = 7.2 Hz, 3H), 1.16-1.22 (m, 2H), 1.80-1.86 (m, 2H), 4.45 (t, J = 7.6 Hz, 2H), 7.89 (t, J = 7.2 Hz, 2H), 8.37 (t, J = 7.6 Hz, 1H), 7.68 (d, J = 5.6 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.57, 18.63, 32.49, 61.66, 128.09, 144.12, 145.37. Anal. Calcd for $C_9H_{14}Cl_4InN$: C, 27.52; H, 3.59; N, 3.57. Found: C, 27.60; H, 3.50; N, 3.65.



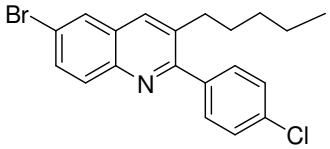
6-Bromo-2-(2,4-dichlorophenyl)-3-pentylquinoline (4{1,1,1})

mp 133-134 °C. IR (KBr): ν_{max} = 2923, 2854, 1593, 1468, 1376, 1344, 1099, 817, 644 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.75 (t, J = 6.8 Hz, 3H), 1.14-1.16 (m, 4H), 1.47-1.46 (m, 2H), 2.44-2.60 (m, 2H), 7.27 (d, J = 8.0 Hz, 1H), 7.33 (dd, ^1J = 8.0 Hz, ^2J = 2.0 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.69 (dd, ^1J = 9.2 Hz, ^2J = 2.0 Hz, 1H), 7.93-7.95 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.86, 18.36, 22.29, 29.59, 31.34, 120.85, 127.33, 129.11, 129.15, 129.47, 130.84, 131.23, 132.53, 133.65, 134.44, 134.96, 135.70, 137.72, 144.72, 158.00. MS: m/z = 423.17 ([M]$^+$, 94.20), 422.04 (62.80), 388.04 (64.73), 330.94 (65.70), 250.00 (77.78), 113.87 (91.79), 77.89 (5.28), 55.92 (32.37) . Anal. Calcd for $C_{20}H_{18}BrCl_2N$: C, 56.76; H, 4.29; N, 3.31. Found: C, 56.87; H, 4.22; N, 3.21.



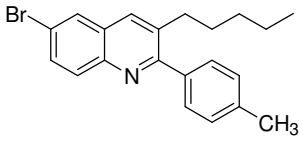
6-Bromo-2-(3-nitrophenyl)-3-pentylquinoline (4{1,2,1})

mp 128-129 °C. IR (KBr): ν_{max} = 2929, 2860, 1591, 1531, 1471, 1348, 1264, 817, 728 cm^{-1}. ^1H NMR (500M Hz, $CDCl_3$): δ = 0.75 (t, J = 6.8 Hz, 3H), 1.15-1.18 (m, 4H), 1.46-1.53 (m, 2H), 2.71 (t, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.73 (dd, ^1J = 8.8 Hz, ^2J = 2.0 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.97 (s, 1H), 8.03-8.06 (m, 2H), 8.29 (dd, ^1J = 7.6 Hz, ^2J = 2.0 Hz, 1H), 8.39 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.85, 18.25, 22.26, 30.25, 31.36, 120.92, 121.62, 123.73, 124.10, 129.02, 129.13, 129.63, 129.89, 133.52, 135.01, 135.12, 136.45, 136.65, 148.11, 158.11. MS: m/z = 399.28 ($[M]^+$, 78.04), 397.00 (65.88), 356.98 (92.55), 354.97 (94.90), 310.99 (57.65), 293.99 (69.02), 228.08 (67.84), 151.10 (45.88), 99.10 (62.75), 95.04 (89.41), 77.03 (37.25), 57.03 (100.00). Anal. Calcd for $C_{20}H_{19}BrN_2O_2$: C, 60.16; H, 4.80; N, 7.02. Found: C, 60.05; H, 4.87; N, 7.12.



6-Bromo-2-(4-chlorophenyl)-3-pentylquinoline (4{1,3,1})

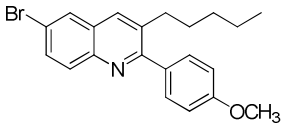
mp 102-104°C. IR (KBr): ν_{max} = 2959, 2927, 2854, 1595, 1468, 1348, 1086, 1004, 824, 727 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.75 (t, J = 6.8 Hz, 3H), 1.14-1.18 (m, 4H), 1.42-1.50 (m, 2H), 2.67 (t, J = 8.0 Hz, 2H), 7.38-7.43 (m, 4H), 7.66 (dd, ^1J = 9.0 Hz, ^2J = 2.0 Hz, 1H), 7.88-7.93 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.90, 22.31, 30.17, 31.43, 32.73, 120.61, 128.63, 128.80, 128.99, 130.20, 130.71, 132.63, 134.62, 135.08, 135.20, 144.57, 145.07, 159.64. MS: m/z = 389.01 ($[M+1]^+$, 79.83), 387.99 ($[M]^+$, 75.21), 386.99 ($[M-1]^+$, 74.37), 345.96 (89.92), 331.94 (58.40), 296.97 (68.91), 216.14 (80.25), 127.12 (83.19), 95.17 (75.63), 77.15 (34.87), 57.15 (92.86). Anal. Calcd for $C_{20}H_{19}BrClN$: C, 76.60; H, 4.31; N, 3.74. Found: C, 76.70; H, 4.38; N, 3.64.



6-Bromo-3-pentyl-2-p-tolylquinoline (4{1,4,1})

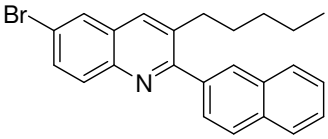
mp 135-137 °C. IR (KBr): ν_{max} = 2953, 2923, 2853, 1588, 1474, 1375, 1008, 906, 829, 726 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.76 (t, J = 6.8 Hz, 3H), 1.15-1.18 (m, 4H), 1.49-1.51(m, 2H),

2.39 (s, 3H), 2.78 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 6.8 Hz, 2H), 7.46 (d, J = 6.4 Hz, 2H), 7.80(d, J = 8.0 Hz, 1H), 8.01 (s, 1H), 8.18 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.92, 22.34, 22.54, 30.15, 30.94, 31.42, 113.81, 119.91, 120.08, 123.89, 128.89, 130.08, 130.94, 132.14, 134.59, 143.18, 144.11, 144.91, 159.23. MS: m/z = 368.03 ([M]$^+$, 41.51), 367.05 (44.34), 324.02 (75.94), 231.18 (38.21), 216.14 (61.79), 125.21 (72.64), 97.19 (91.51), 77.16 (18.07), 51.17 (25.47). Anal. Calcd for $C_{21}H_{22}BrN$: C, 68.48; H, 6.02; N, 3.80. Found: C, 68.57; H, 6.05; N, 3.85.



6-Bromo-2-(4-methoxyphenyl)-3-pentylquinoline (4{1,5,1})

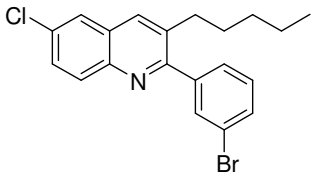
mp 100-102 °C . IR (KBr): ν_{max} = 2955, 2926, 2854, 1606, 1513, 1420, 1249, 1177, 1033, 836, 789 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.80 (t, J = 6.8 Hz, 3H), 1.45-1.48 (m, 6H), 2.71 (t, J = 8.0 Hz, 2H), 3.81 (s, 3H), 6.94 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.62-7.65 (m, 1H), 7.84-7.90 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.92, 22.34, 30.15, 30.94, 31.48, 55.40, 113.79, 119.94, 120.07, 125.89, 128.89, 130.07, 130.97, 132.11, 134.58, 143.17, 143.58, 145.17, 159.24. MS: m/z = 386.02 ([M+2]$^+$, 52.11), 384.11 ([M]$^+$, 88.73), 383.03 (91.08), 342.05 (93.43), 328.07 (50.23), 284.09 (19.37), 247.05 (21.71), 167.07 (23.00), 153.98 (31.46), 139.52 (39.44), 121.46 (100.00), 97.97 (85.45), 77.45 (12.09), 55.56 (17.37). Anal. Calcd for $C_{21}H_{22}BrNO$: C, 65.63; H, 5.77; N, 3.64. Found: C, 65.70; H, 5.71; N, 3.60.



6-Bromo-2-(naphthalen-3-yl)-3-pentylquinoline (4{1,6,1})

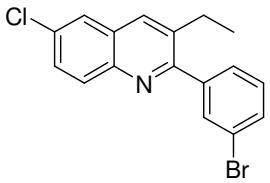
mp 110-112 °C. IR (KBr): ν_{max} = 2924, 2857, 1593, 1493, 1363, 1317, 1268, 1158, 1078, 813, 751 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (t, J = 7.2 Hz, 3H), 1.10-1.14 (m, 4H), 1.48-1.49 (m, 2H), 2.76 (t, J = 8.0 Hz, 2H), 7.45-7.50 (m, 2H), 7.59 (dd, ^1J = 8.4 Hz, ^2J = 1.6 Hz, 1H), 7.69 (dd, ^1J = 9.0 Hz, ^2J = 1.6 Hz, 1H), 7.85 (t, J = 4.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 1H), 7.94-7.98 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.92, 22.34, 30.15, 30.94, 31.48, 120.14, 123.54,

124.34, 124.54, 126.61, 128.15, 128.65, 128.74, 128.80, 129.29, 129.69, 129.78, 129.91, 130.15, 132.61, 134.92, 135.28, 145.82, 158.91. MS: *m/z* = 405.07 ($[M+1]^+$, 4.51), 404.11 ($[M]^+$, 4.61), 376.25 (2.12), 360.03 (8.20), 322.24 (2.90), 265.17 (2.66), 205.25 (3.07), 181.19 (6.56), 165.21 (8.94), 149.18 (13.39), 111.16 (55.74), 97.15 (89.62), 76.08 (4.51), 55.14 (97.81). Anal. Calcd for $C_{24}H_{22}BrN$: C, 71.29; H, 5.48; N, 3.46. Found: C, 71.38; H, 5.42; N, 3.39.



2-(3-Bromophenyl)-6-chloro-3-pentylquinoline (4{2,7,1})

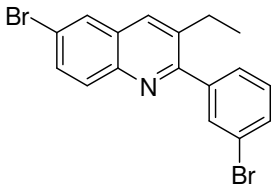
mp 135-138 °C. IR (KBr):ν_{max} = 2959, 2920, 2859, 1600, 1511, 1426, 1249, 1176, 1029, 867, 778 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 6.8 Hz, 3H), 1.93-1.94 (m, 6H), 2.67 (t, *J* = 8.0 Hz, 2H), 7.39 (dt, ^1J = 8.0 Hz, ^2J = 1.2 Hz, 1H), 7.45(s, 1H), 7.50-7.55 (m, 2H), 7.63 (t, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.89 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.92, 22.54, 30.15, 30.94, 31.48, 120.74, 122.59, 126.69, 128.90, 129.01, 129.91, 130.85, 131.55, 131.81, 132.75, 134.42, 136.14, 142.02, 144.52, 159.21. MS: *m/z* = 389.03 ($[M]^+$, 15.52), 388.04 (12.93), 387.03 (12.19), 345.96 (36.45), 216.16 (40.89), 193.28 (22.54), 179.28 (30.91), 169.17 (43.35), 151.28 (56.16), 139.26 (63.05), 125.25 (83.25), 111.22 (94.09), 97.22 (98.03), 83.20 (98.52), 77.21 (39.90), 55.19 (99.51). Anal. Calcd for $C_{20}H_{19}BrClN$: C, 61.79; H, 4.93; N, 3.60. Found: C, 61.88; H, 4.86; N, 3.69.



2-(3-Bromophenyl)-6-chloro-3-ethylquinoline (4{2,7,2})

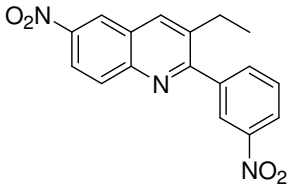
mp 128-129 °C. IR (KBr):ν_{max} = 2967, 2932, 2874, 1589, 1563, 1476, 1326, 1262, 1071, 912, 835, 781, 711 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.2 Hz, 3H), 2.80 (q, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.49 (dt, ^1J = 7.6 Hz , ^2J = 1.6 Hz, 1H), 7.59-7.64 (m, 2H), 7.73 (t, *J* = 2.0 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.99 (s, 1H), 7.38 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.57, 25.92, 122.57, 125.66, 127.35, 128.43, 129.91, 130.06, 130.78,

131.46, 131.81, 132.46, 134.36, 136.15, 142.27, 144.51, 159.12. MS: *m/z* = 346.99 ([M+2]$^+$, 90.08), 345.98 ([M+1]$^+$, 95.98), 344.98 ([M]$^+$, 89.99), 343.89 (11.53), 330.96 (50.65), 266.11 (89.02), 251.09 (78.82), 216.13 (82.35), 153.16 (62.75), 126.12 (100.00), 95.06 (96.86), 75.06 (87.06), 55.14 (74.90), 50.11 (79.22). Anal. Calcd for $C_{17}H_{13}BrClN$: C, 58.90; H, 3.78; N, 4.04. Found: C, 58.99; H, 3.82; N, 4.10.



6-Bromo-2-(3-bromophenyl)-3-ethylquinoline (4{1,7,2})

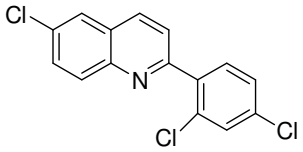
mp 155-157 °C. IR (KBr): ν_{max} = 2967, 2933, 2878, 1586, 1557, 1473, 1434, 1259, 1058, 912, 835, 781, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.22 (t, *J* = 7.6 Hz, 3H), 2.81 (q, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.49 (dt, ^1J = 8.0 Hz , ^2J = 1.2 Hz, 1H), 7.61 (dq, ^1J = 8.0 Hz , ^2J = 1.2 Hz, 1H), 7.72-7.77 (m, 2H), 7.99-8.04 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.57, 25.91, 120.72, 122.56, 127.35, 128.95, 129.04, 129.92, 130.76, 131.53, 131.79, 132.66, 134.41, 136.18, 142.06, 144.55, 159.17. MS: *m/z* = 392.90 ([M+4]$^+$, 62.35), 390.90 ([M+2]$^+$, 73.70), 388.90 ([M]$^+$, 63.50), 375.78 (5.64), 373.56 (2.59), 310.34 (2.02), 295.72 (6.08), 230.54 (4.48), 216.60 (6.53), 148.38 (7.80), 125.33 (50.88), 115.65 (100.00), 85.23 (75.69), 81.74 (15.20), 69.74 (13.73), 57.76 (10.69). Anal. Calcd for $C_{17}H_{13}Br_2N$: C, 52.51; H, 3.35; N, 3.58. Found: C, 52.60; H, 3.40; N, 3.47.



3-Ethyl-6-nitro-2-(3-nitrophenyl)quinoline (4{3,2,2})

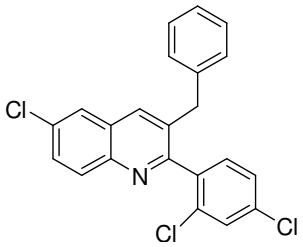
mp 171-172 °C . IR (KBr): ν_{max} = 2970, 2874,1609, 1525, 1478, 1348, 1084, 925, 835, 738, 680 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.2 Hz, 3H), 2.90 (q, *J* = 7.2 Hz, 2H), 7.74-7.78 (m, 1H), 7.97-7.99 (m, 1H), 8.27-8.41 (m, 3H), 8.49-8.52 (m, 2H), 8.87 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.41, 25.96, 122.92, 123.85, 123.93, 124.01, 126.78, 129.70, 130.90, 134.84, 137.17, 137.55, 141.05, 145.94, 147.96, 148.24, 161.13. MS: *m/z* = 323.05 ([M]$^+$,

39.80), 322.03 (64.90), 276.09 (32.65), 230.13 (22.45), 216.12 (23.21), 203.14 (15.43), 137.18 (25.64), 125.18 (49.49), 111.16 (86.73), 97.16 (94.39), 57.15 (100). Anal. Calcd for $C_{17}H_{13}N_3O_4$: C, 63.17; H, 4.05; N, 13.00. Found: C, 63.25; H, 4.00; N, 13.09.



6-Chloro-2-(2,4-dichlorophenyl)quinoline (4{2,1,3})

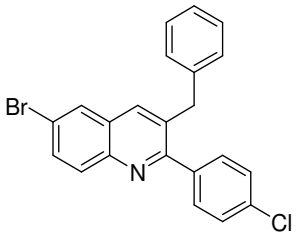
mp 220 °C. IR (KBr) : ν_{max} = 2923, 2854,1593, 1546, 1476, 1383, 1072, 876, 821, 777, 686 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36 (s, 1H), 7.48 (s, 1H), 7.64 (d, J = 7.0 Hz, 2H), 7.72 (d, J = 7.2 Hz, 1H), 7.82 (s, 1H), 8.12 (d, J = 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 125.81, 126.31, 127.90, 128.81, 129.12, 129.72, 130.92, 131.42, 132.82, 133.22, 135.52, 136.94, 139.09, 145.22, 158.31. MS: m/z = 310.95 ($[M+2]^+$, 57.14), 309.97 ($[M+1]^+$, 32.90), 308.97 ($[M]^+$, 80.09), 274.02 (73.59), 272.02 (82.68), 237.06 (74.89), 201.10 (63.20), 151.17 (45.02), 137.07 (97.40), 111.10 (93.94), 99.07 (90.48), 77.09 (16.45), 55.06 (95.24). Anal. Calcd for $C_{15}H_8Cl_3N$: C, 58.38; H, 2.61; N, 4.54. Found: C, 58.45; H, 2.58; N, 4.44.



3-Benzyl-6-chloro-2-(2,4-dichlorophenyl)quinoline (4{2,1,4})

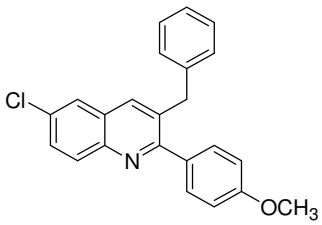
mp 136-140 °C. IR (KBr): ν_{max} = 3085, 3033, 2932, 2849, 1612, 1578, 1476, 1398, 1329, 1334, 1189, 1110, 967, 845, 812, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.87 (s, 2H), 6.97 (dd, ^1J = 7.8 Hz, ^2J = 2.0 Hz, 2H), 7.13 (s, 1H), 7.24-7.31 (m,4H), 7.54 (d, J = 2.0 Hz, 1H), 7.65 (dd, ^1J = 9.0 Hz, ^2J = 2.0 Hz, 1H), 7.78 (d, J = 2.0 Hz, 1H), 7.85 (s, 1H), 8.06 (d, J = 9.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 38.76, 125.95, 126.25, 127.36, 127.63, 128.43, 128.65, 129.06, 129.30, 129.96, 130.90, 131.30, 132.64, 132.82, 133.55, 134.92, 135.53, 137.74, 144.88, 157.87. MS: m/z = 400.98 ($[M+2]^+$, 13.73), 402.14 ($[M+2]^+$, 11.18), 398.96 ($[M]^+$, 31.76), 362.00 (32.55), 284.00 (20.59), 268.18 (47.06), 252.20 (59.22), 164.22 (48.63), 134.19 (100.00), 117.19

(87.84), 92.17 (92.94), 78.20 (71.37). Anal. Calcd for $C_{22}H_{14}Cl_3N$: C, 58.38; H, 2.61; N, 4.54. Found: C, 58.30; H, 2.68; N, 4.48.



3-Benzyl-6-bromo-2-(4-chlorophenyl)quinoline (4{1,3,4})

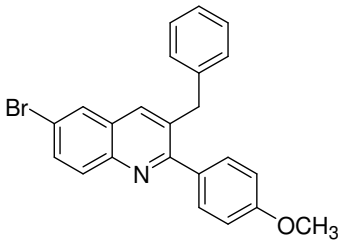
mp 145-147 °C. IR (KBr): ν_{max} = 3024, 2912, 2839, 1596, 1550, 1491, 1474, 1339, 1094, 1006, 914, 838, 732, 696 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 4.13 (s, 2H), 7.00 (d, J = 6.5 Hz, 2H), 7.23-7.30 (m, 3H), 7.41-7.48 (m, 4H), 7.77 (dd, ^1J = 9.0 Hz, ^2J = 2.0 Hz, 1H), 7.85 (s,1H), 7.94-8.00 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.08, 120.61, 126.56, 128.41, 128.65, 128.68, 128.90, 129.18, 130.24, 130.99, 132.81, 133.37, 134.62, 136.23, 138.65, 139.29, 145.19, 159.84. MS: m/z = 410.00 ($[M+2]^+$, 79.15), 409.00 ($[M+1]^+$, 93.36), 407.99 ($[M]^+$, 100.00), 373.99 (33.65), 371.98 (45.02), 327.04 (34.60), 292.10 (45.02), 216.15 (49.76), 167.29 (25.12), 134.17 (81.04), 97.23 (86.26), 71.21 (80.57), 57.23 (67.77). Anal. Calcd for $C_{22}H_{15}BrClN$: C, 64.65; H, 3.70; N, 3.43. Found: C, 64.74; H, 3.74; N, 3.50.



3-Benzyl-6-chloro-2-(4-methoxyphenyl)quinoline (4{2,5,4})

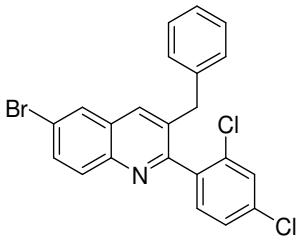
mp 120-122 °C. IR(KBr): ν_{max} = 3059, 3025, 2952, 2926, 2857, 1601, 1495, 1452, 1368, 1318, 1193, 1125, 1060, 917, 749 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 2H), 4.35 (s, 3H), 7.21-7.23 (m, 4H), 7.24 (s, 4H), 7.30 (s, 2H), 7.32 (s, 2H), 7.34 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.63, 55.64, 125.95, 128.26, 128.29, 128.32, 128.35, 128.38, 128.42, 128.50, 128.53, 128.56, 128.62, 128.62, 128.65, 141.33, 148.32, 158.92. MS: m/z = 361.13 ($[M+1]^+$, 6.96), 359.80 ($[M]^+$, 4.26), 357.10 (7.16), 280.16 (5.29), 269.19 (45.49), 252.20 (63.14), 193.27

(9.41), 164.19 (65.49), 134.21 (100.00), 93.20 (73.33) 77.14 (80.78), 56.19 (62.75). Anal. Calcd for $C_{23}H_{18}ClNO$: C, 76.77; H, 5.04; N, 3.89. Found: C, 76.70; H, 5.10; N, 3.95.



3-Benzyl-6-bromo-2-(4-methoxyphenyl)quinoline (4{1,5,4})

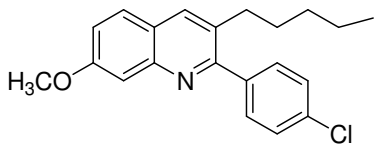
mp 132-133 °C. IR (KBr): ν_{max} = 3060, 3025, 2926, 2857, 1601, 1495, 1452, 1368, 1193, 1125, 1061, 917, 749, 697 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 2H), 4.24 (s, 3H), 7.20-7.22 (m, 4H), 7.24 (s, 4H), 7.30-7.32 (m, 4H), 7.33 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.16, 55.24, 125.95, 128.16, 128.42, 128.46, 128.51, 128.53, 128.54, 128.56, 128.69, 128.81, 128.89, 128.95, 129.11, 141.33, 148.32, 156.82. MS: *m/z* = 403.05 ($[M]^+$, 17.75), 402.07 (15.59), 401.01 (16.76), 310.01 (8.14), 269.18 (50.98), 252.20 (60.78), 181.29 (10.69), 164.20 (58.43), 134.22 (100.00), 118.21 (87.84), 93.20 (67.84), 78.16 (92.55). Anal. Calcd for $C_{23}H_{18}BrNO$: C, 68.33; H, 4.49; N, 3.46. Found: C, 68.40; H, 4.55; N, 3.51.



3-Benzyl-6-bromo-2-(2,4-dichlorophenyl)quinoline (4{1,1,4})

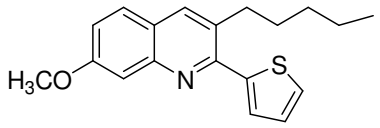
mp 140-142 °C. IR (KBr): ν_{max} = 3081, 3032, 2923, 2853, 1651, 1585, 1469, 1384, 1338, 1317, 1185, 1104, 985, 855, 822, 774, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.03 (s, 2H), 7.12-7.14 (m, 3H), 7.40 (d, J = 2.0 Hz, 3H), 7.58 (d, J = 8.4 Hz, 3H), 7.96-8.00 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.62, 125.94, 126.91, 127.62, 128.29, 128.41, 128.74, 129.29, 129.78, 130.17, 131.53, 132.56, 133.88, 135.08, 136.04, 136.70, 138.36, 138.82, 141.82, 158.91. MS: *m/z* = 445.91 ($[M+2]^+$, 23.33), 444.92 ($[M+1]^+$, 53.33), 442.92 ($[M]^+$, 72.16), 440.91 (60.39), 407.96 (65.49), 371.93 (57.25), 334.91 (90.59), 272.05 (52.55), 236.11 (54.12), 216.16 (60.78),

199.07 (63.92), 171.09 (77.65), 134.16 (84.71), 91.05 (100.00), 78.19 (66.67). Anal. Calcd for $C_{22}H_{14}BrCl_2N$: C, 59.62; H, 3.18; N, 3.16. Found: C, 59.70; H, 3.11; N, 3.25.



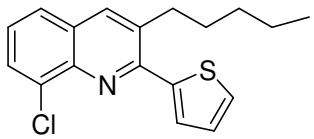
2-(4-Chlorophenyl)-7-methoxy-3-pentylquinoline (4{4,3,1})

mp 190-192 °C. IR (KBr): ν_{max} = 2965, 2935, 2910, 2878, 1643, 1479, 1368, 1234, 1160, 1020, 825, 712 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, J = 7.2 Hz, 3H), 1.37-1.46 (m, 4H), 1.66-1.74 (m, 2H), 2.77 (t, J = 7.6 Hz, 2H), 3.87 (s, 3H), 7.19-7.22 (m, 1H), 7.43-7.46 (m, 4H), 7.50-7.51 (m, 1H), 7.56-7.58 (m, 1H), 7.74 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.00, 22.35, 29.72, 31.43, 32.42, 58.69, 120.70, 122.55, 127.58, 129.18, 130.28, 132.37, 132.98, 134.21, 136.05, 141.21, 146.12, 160.37. Anal. Calcd for $C_{21}H_{22}ClNO$ (339.14): C, 74.21; H, 6.52; N, 4.12. Found: C, 73.89; H, 6.45; N, 4.20.



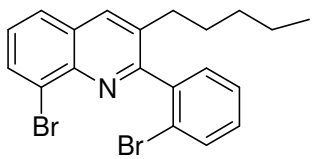
7-Methoxy-3-pentyl-2-(thiophen-2-yl)quinoline (4{4,9,1})

mp 185-187 °C. IR (KBr): ν_{max} = 2955, 2924, 2923, 2851, 1621, 1461, 1380, 1258, 1168, 1030, 817, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.47-1.66 (m, 5H), 1.94-2.00 (m, 2H), 2.22-2.28 (m, 2H), 2.91 (t, J = 7.6 Hz, 2H), 3.88 (s, 3H), 7.07-7.10 (m, 1H), 7.25 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.37-7.40 (m, 1H), 7.45-7.47 (m, 1H), 7.57 (d, J = 9.2 Hz, 1H), 7.85 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.24, 23.08, 29.96, 31.43, 32.66, 57.22, 124.76, 125.31, 125.86, 126.72, 127.34, 128.01, 128.38, 129.73, 130.10, 133.41, 134.64, 139.98, 155.39. Anal. Calcd for $C_{19}H_{21}NOS$ (311.13): C, 73.27; H, 6.80; N, 4.50; S, 10.30. Found: C, 73.35; H, 6.72; N, 4.59; S, 10.37.



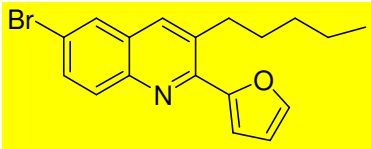
8-Chloro-3-pentyl-2-(thiophen-2-yl)quinoline (4{5,9,1})

mp 200-202 °C. IR (KBr): ν_{max} = 2954, 2926, 2855, 1618, 1455, 1428, 1385, 1257, 1113, 963 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.60-1.76 (m, 5H), 1.78-1.84 (m, 2H), 1.90-1.97 (m, 2H), 2.72 (t, J = 7.6 Hz, 2H), 70.08-7.10 (m, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.55-7.60 (m, 2H), 7.64 (dd, ^1J = 7.1 Hz, ^2J = 1.2 Hz, 1H), 7.63 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.01, 22.56, 29.65, 31.81, 33.60, 125.35, 125.99, 126.14, 127.76, 127.81, 128.33, 128.99, 129.06, 130.51, 134.83, 136.86, 141.43, 145.03. Anal. Calcd for $C_{18}H_{18}ClNS$ (315.08): C, 68.45; H, 5.74; N, 4.43; S, 10.15. Found: C, 68.38; H, 5.68; N, 4.51; S, 10.20.



8-Bromo-2-(2-bromophenyl)-3-pentylquinoline (4{6,8,1})

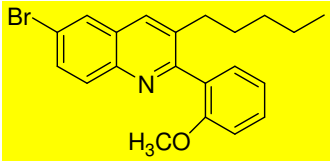
mp 210-212 °C. IR (KBr): ν_{max} = 3054, 2954, 2926, 2857, 1595, 1472, 1434, 1340, 1219, 1057, 915, 827, 754 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, J = 6.8 Hz, 3H), 1.23-1.28 (m, 4H), 1.51-1.58 (m, 2H), 2.51-2.69 (m, 2H), 7.34 (dt, ^1J = 7.8 Hz, ^2J = 2.0 Hz, 1H), 7.39 (dd, ^1J = 7.8 Hz, ^2J = 1.6 Hz, 1H), 7.47 (dt, ^1J = 7.4 Hz, ^2J = 1.2 Hz, 1H), 7.71 (d, J = 8.0 Hz,1H), 7.76 (dd, ^1J = 8.8 Hz, ^2J = 2.4 Hz, 1H), 7.98-8.02 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.89, 22.29, 29.51, 31.39, 32.36, 120.59, 122.50, 127.50, 129.09, 129.15, 129.82, 132.29, 131.05, 132.31, 132.75, 134.22, 135.59, 141.15, 144.73, 160.42. Anal. Calcd for $C_{20}H_{19}Br_2N$ (430.99): C, 55.45; H, 4.42; N, 3.23. Found: C, 55.37; H, 4.37; N, 3.30.



6-Bromo-2-(furan-2-yl)-3-pentylquinoline ({1,10,1)}

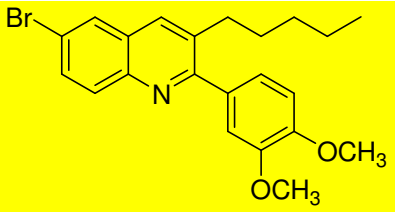
mp 167-169 °C. IR (KBr): ν_{max} = 2967, 2934, 2910, 2834, 1676, 1432, 1387, 1209, 1178, 1054, 900, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82-0.86 (m, 3H), 1.25-1.35 (m, 4H), 1.57-1.64 (m, 2H), 2.99 (t, J = 7.6 Hz, 2H), 6.53 (s, 1H), 7.05 (s, 1H), 7.58-7.59 (m,1H), 7.63 (dd, ^1J = 8.8 HZ, ^2J = 2.4 Hz, 1H), 7.81 (s, 1H), 7.83-7.84 (m,1H), 7.88 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.10, 22.52, 30.02, 31.78, 33.54, 11.83, 112.21, 112.46, 120.18, 128.41, 128.85, 129.01,

130.86, 132.37, 132.53, 134.25, 135.67, 143.77. Anal. Calcd for $C_{18}H_{18}BrNO$ (343.06): C, 62.80; H, 5.27; N, 4.07. Found: C, 62.88; H, 5.20; N, 4.13.



6-Bromo-2-(2-methoxyphenyl)-3-pentylquinoline ({1,11,1})

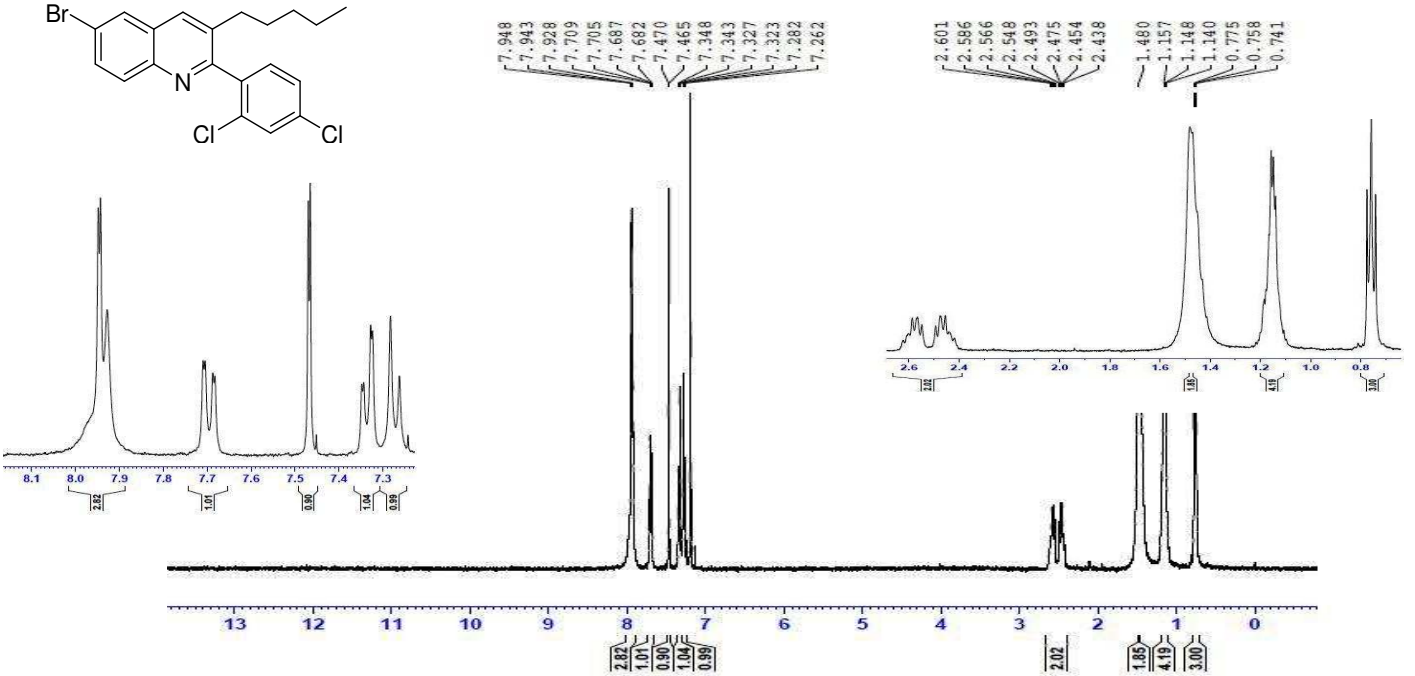
mp 189-191 °C. IR (KBr): ν_{max} = 2932, 2922, 2912, 2823, 1623, 1425, 1357, 1211, 1190, 1021, 881, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86-0.88 (m, 3H), 1.31-1.36 (m, 4H), 1.66-1.74 (m, 2H), 2.87 (t, J = 8.4 Hz, 2H), 3.79 (s, 3H), 7.12 (d, J = 7.2 Hz, 1H), 7.40- 7.45 (m, 3H), 7.59 (d, J = 8.8 Hz, 1H), 7.67 (s, 1H), 7.79-7.81 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.53, 29.42, 31.71, 32.39, 35.89, 57.08, 124.14, 128.19, 128.93, 129.34, 129.91, 130.32, 130.96, 131.70, 132.21, 132.78, 133.32, 133.76, 134.60, 135.24, 160.49. Anal. Calcd for $C_{21}H_{22}BrNO$ (383.09): C, 65.63; H, 5.77; N, 3.64. Found: C, 65.70; H, 5.71; N, 3.70.



6-Bromo-2-(3,4-dimethoxyphenyl)-3-pentylquinoline ({1,12,1})

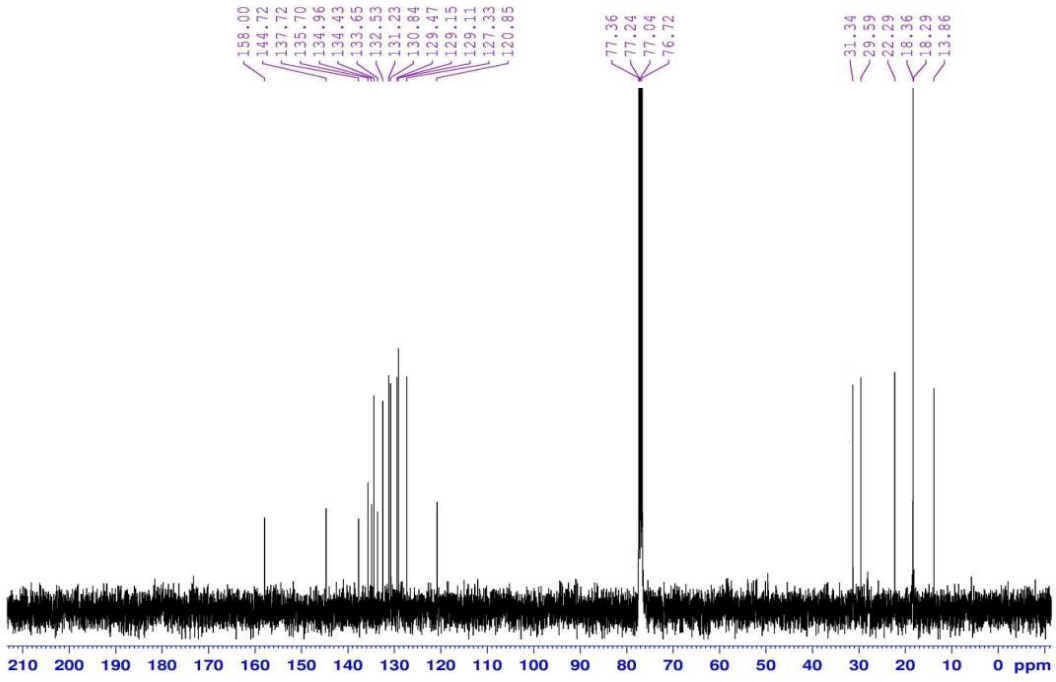
mp 198-200 °C. IR (KBr): ν_{max} = 2955, 2915, 2900, 2888, 1659, 1482, 1361, 1214, 1165, 1029, 889, 720 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84-0.88 (m, 3H), 1.31-1.37 (m, 4H), 1.67-1.74 (m, 2H), 2.68-2.89 (m, 2H), 3.62 (s, 3H), 3.68 (s, 3H), 6.93 (s, 1H), 7.25 (d, J = 7.2 Hz, 1H), 7.46 (d, J = 9.2 Hz, 1H), 7.59 (dd, ^{1}J = 10.4 Hz, ^{2}J = 3.6 Hz, 1H), 7.67 (s, 1H), 7.78-7.90 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.74, 29.63, 30.14, 31.80, 32.31, 56.64, 56. 87, 119.26, 128.21, 128.49, 129.00, 129.29, 130.26, 130.71, 132.37, 133.11, 133.62, 134.25, 134.87, 135.27, 162.85, 163.25. Anal. Calcd for $C_{22}H_{24}BrNO_2$ (414.34): C, 63.77; H, 5.84; N, 3.38. Found: C, 63.86; H, 5.79; N, 3.45.

^{1}H NMR and ^{13}C NMR Spectra of the Compounds

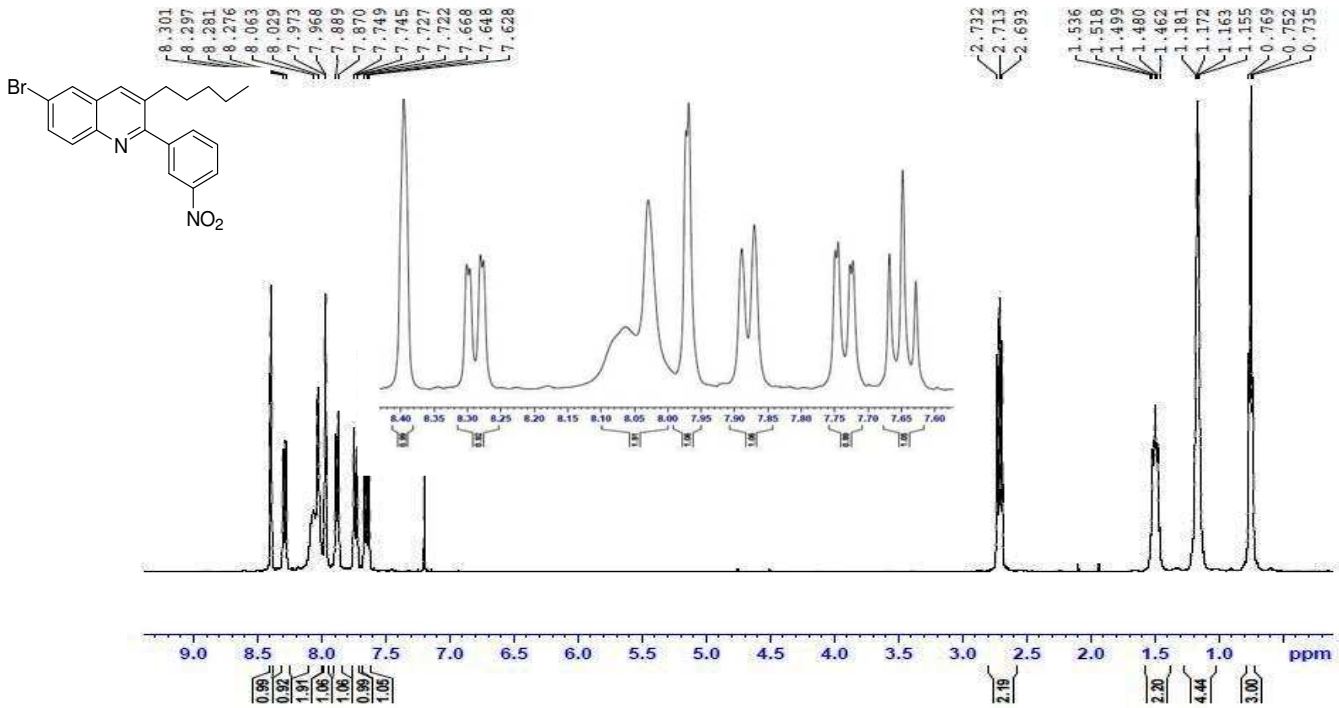


^{1}H

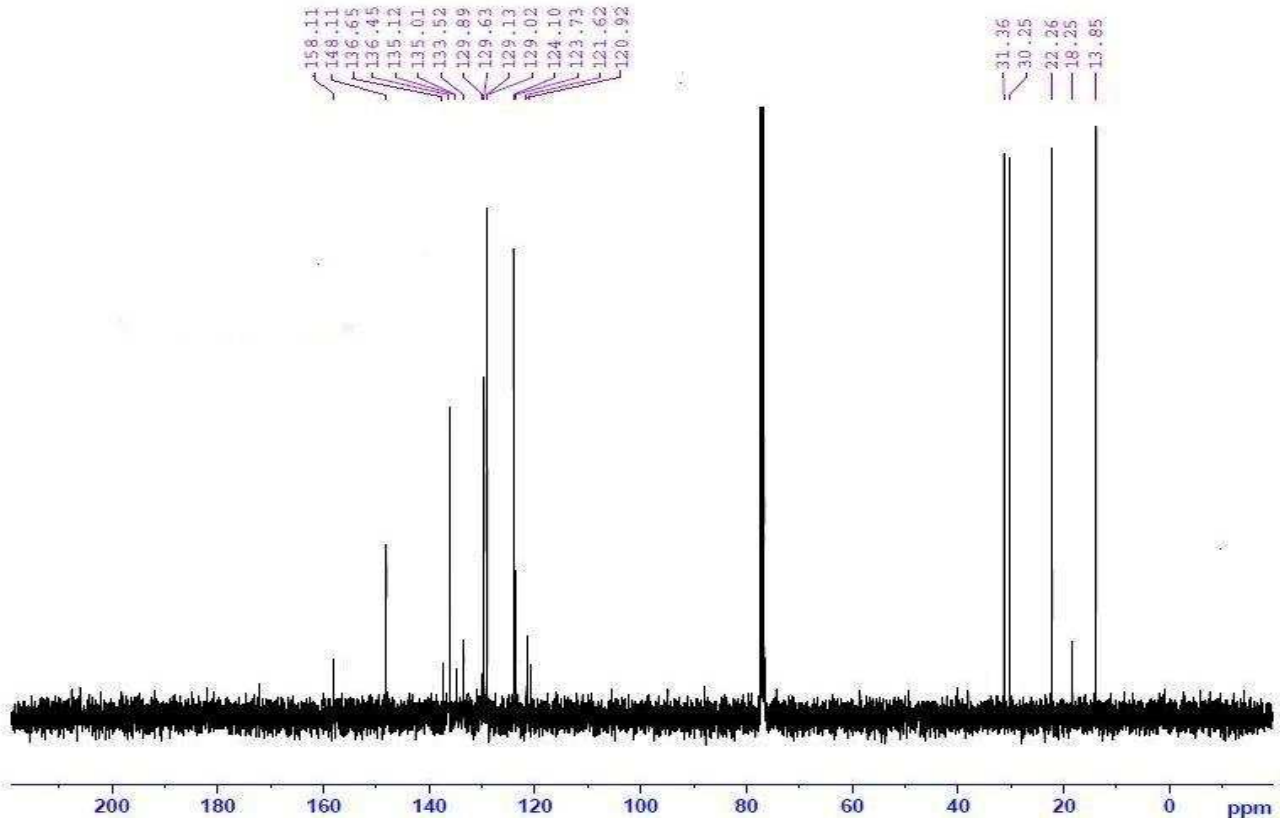
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,1,1}



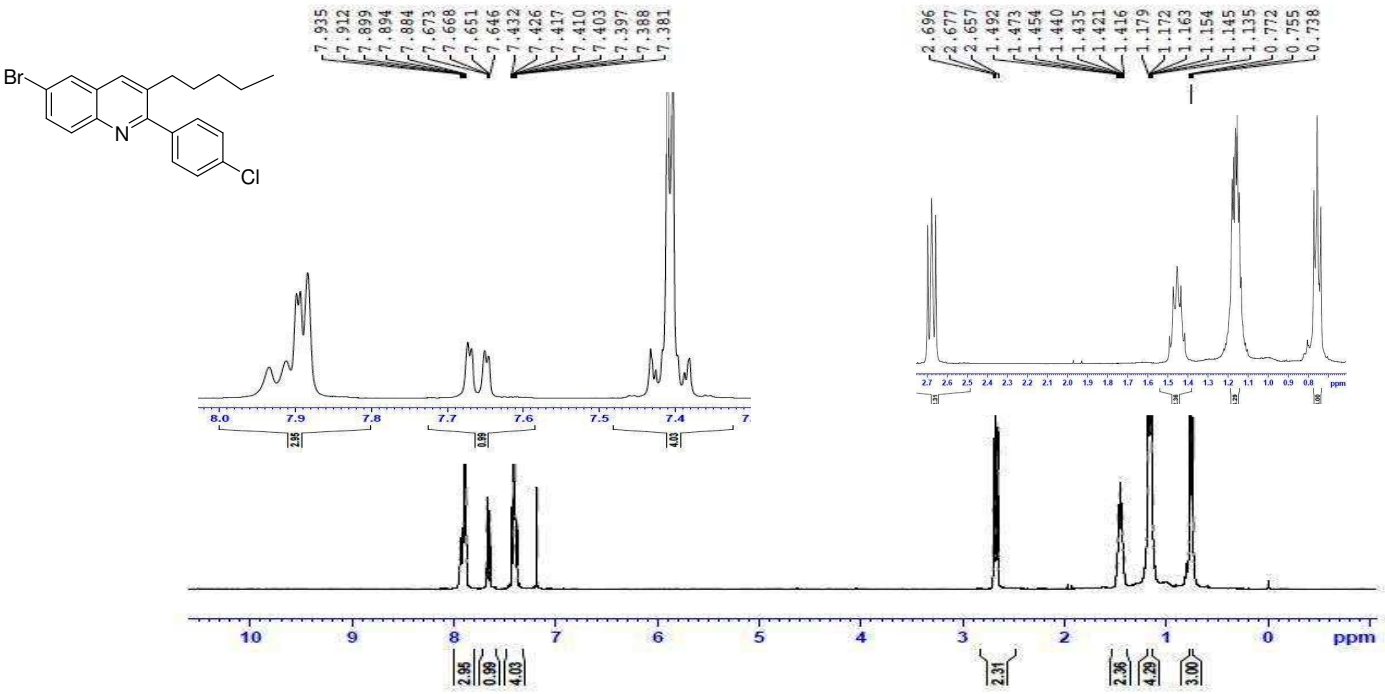
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,1,1}



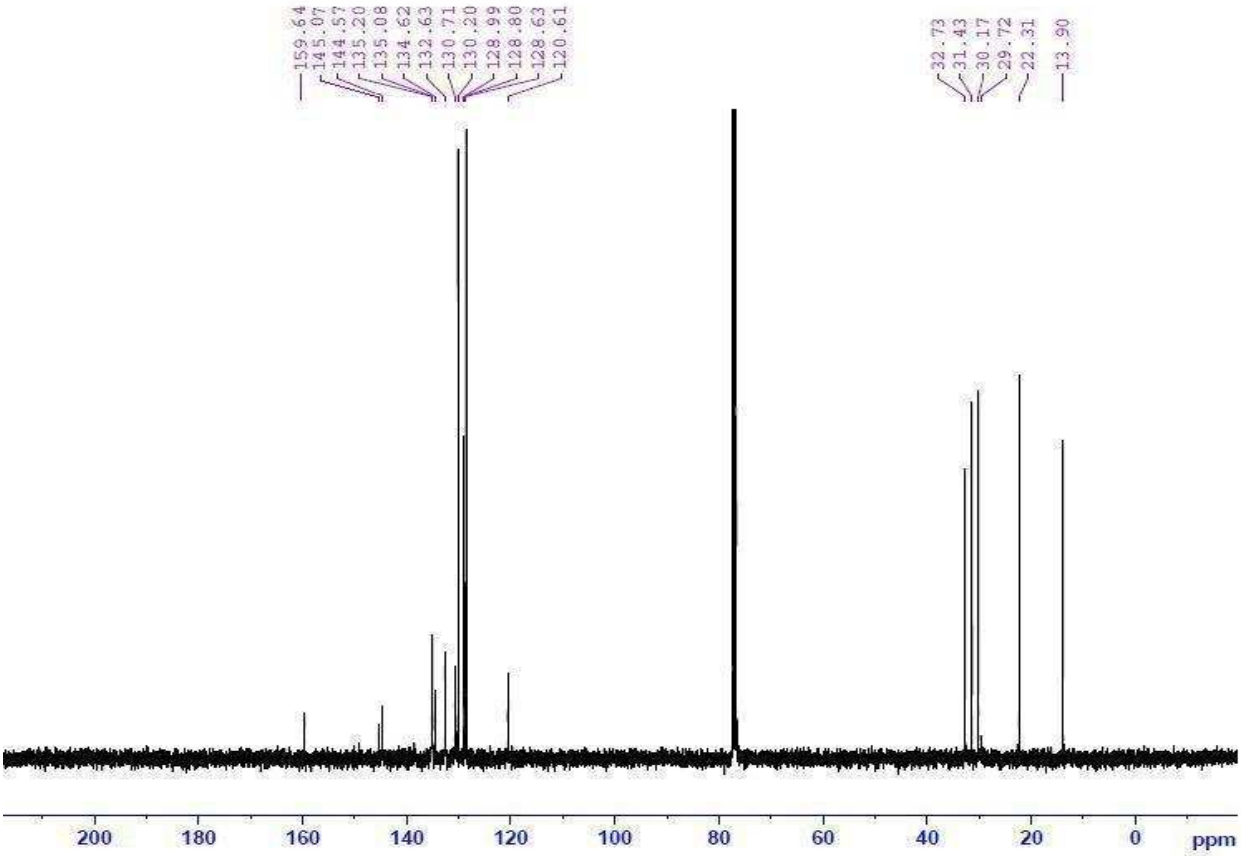
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,2,1}



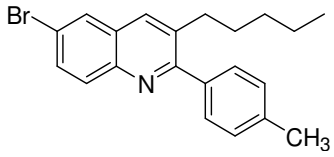
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,2,1}

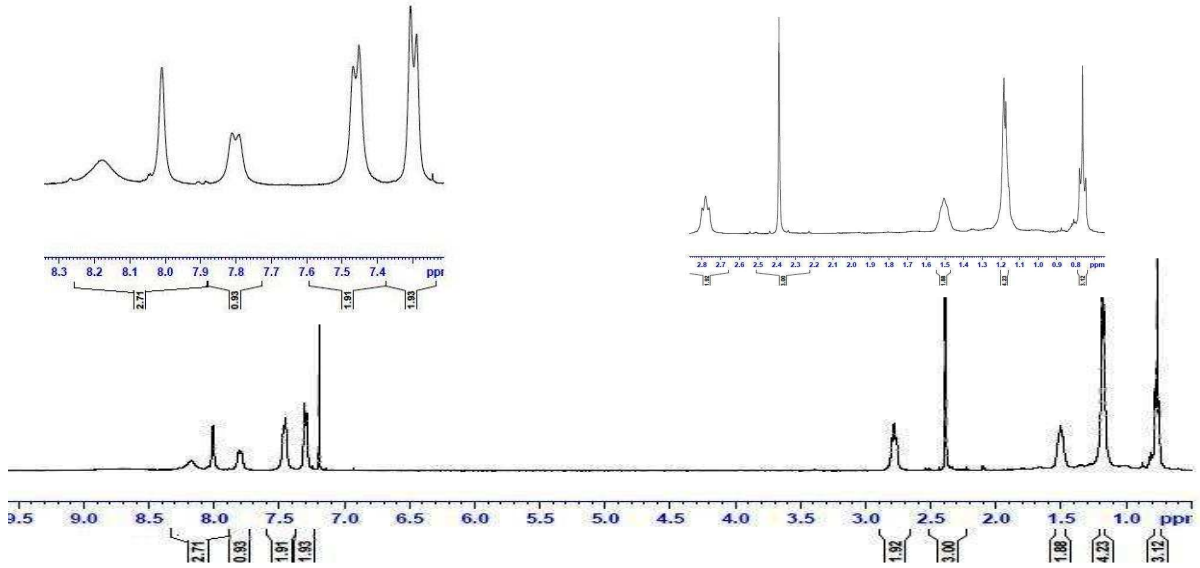


^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,3,1}

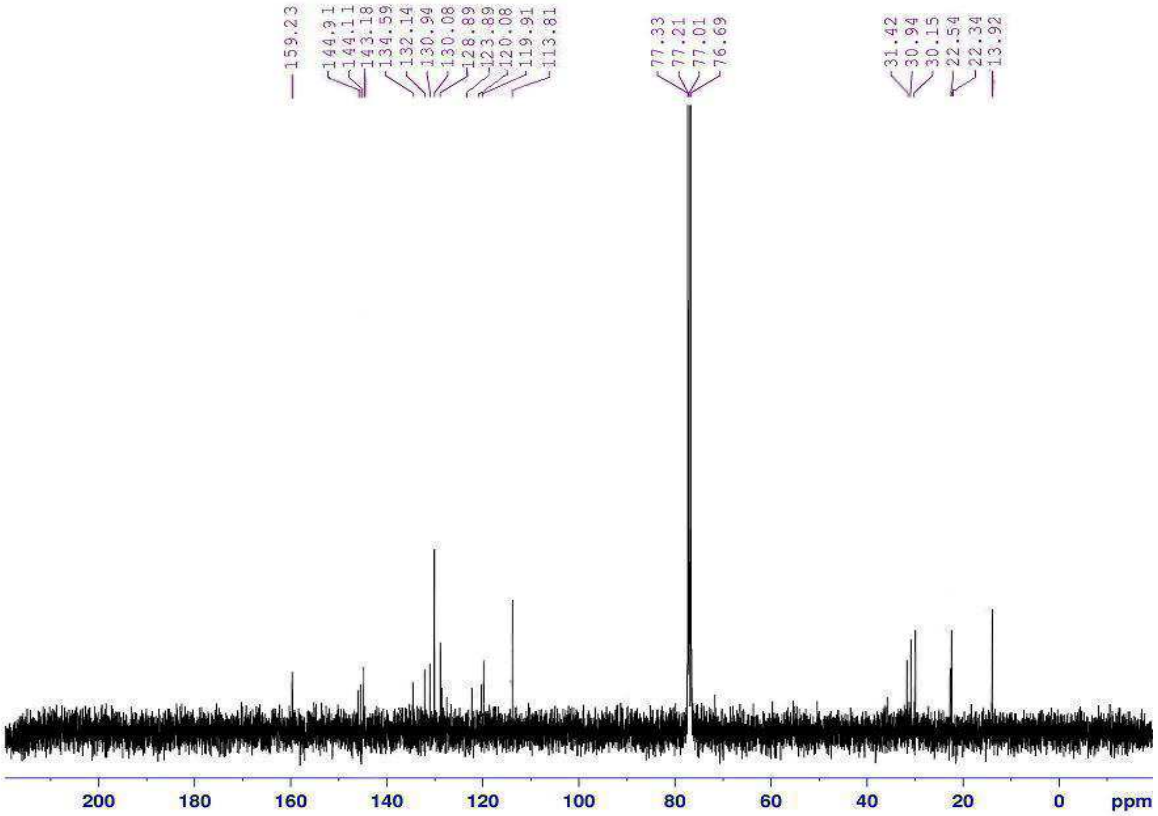


^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,3,1}

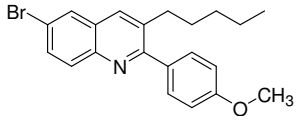


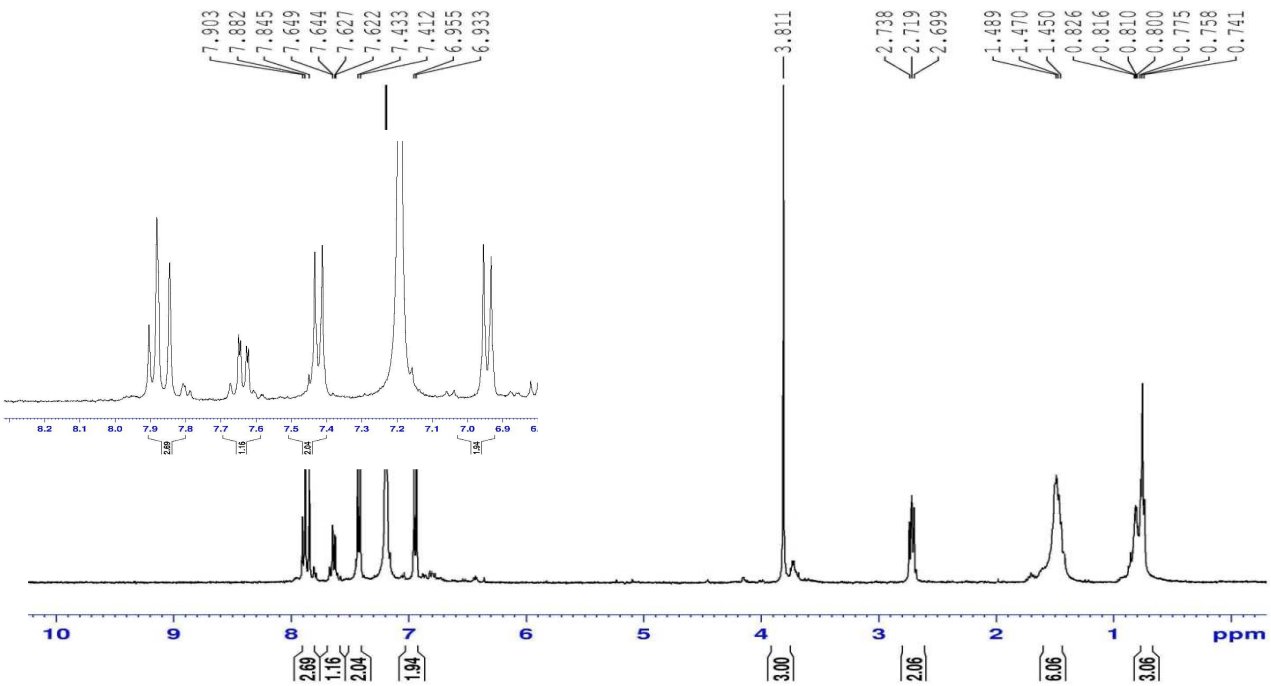


^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,4,1}

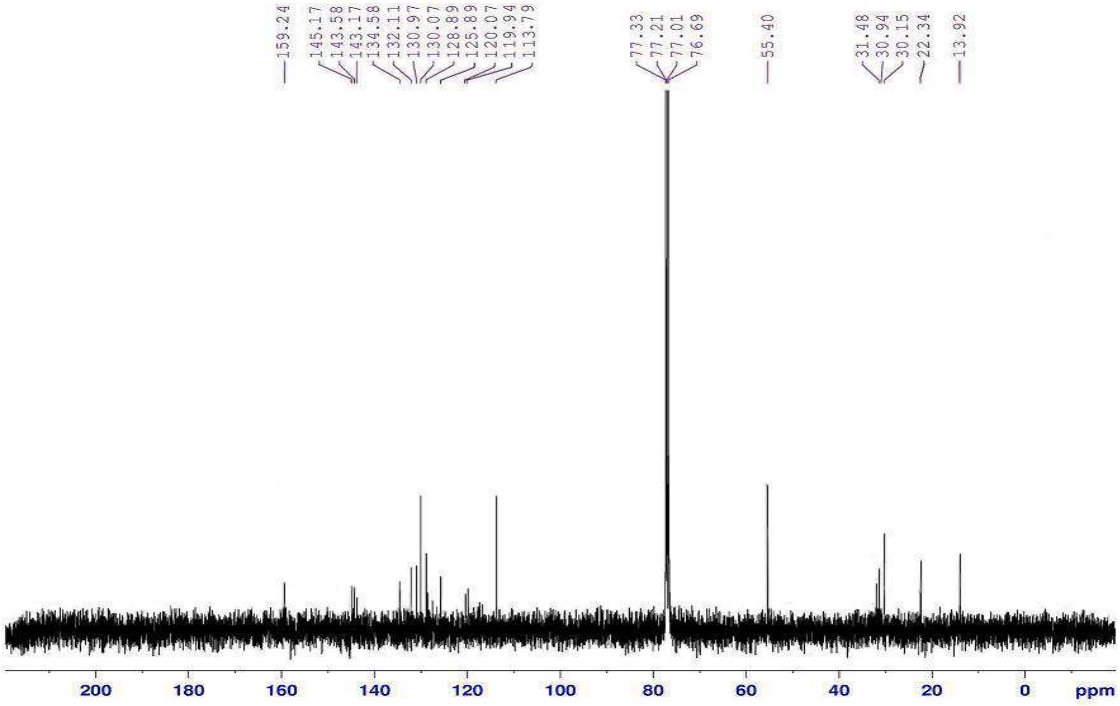


^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,4,1}

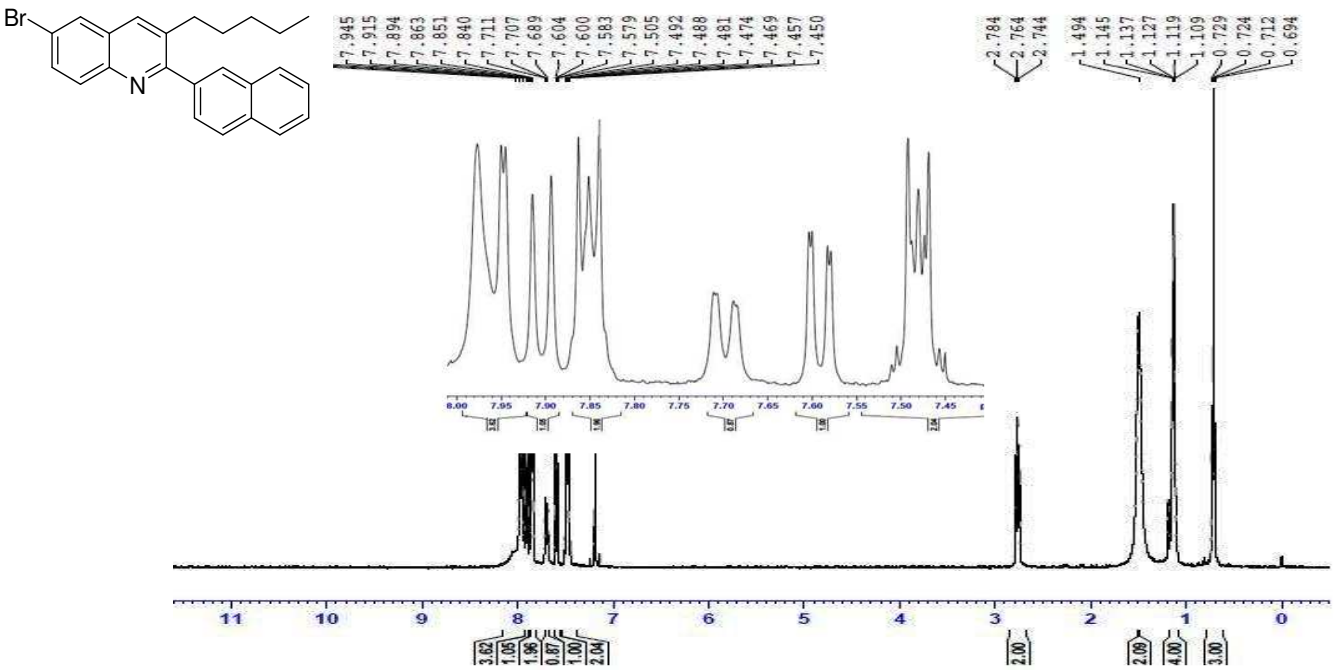




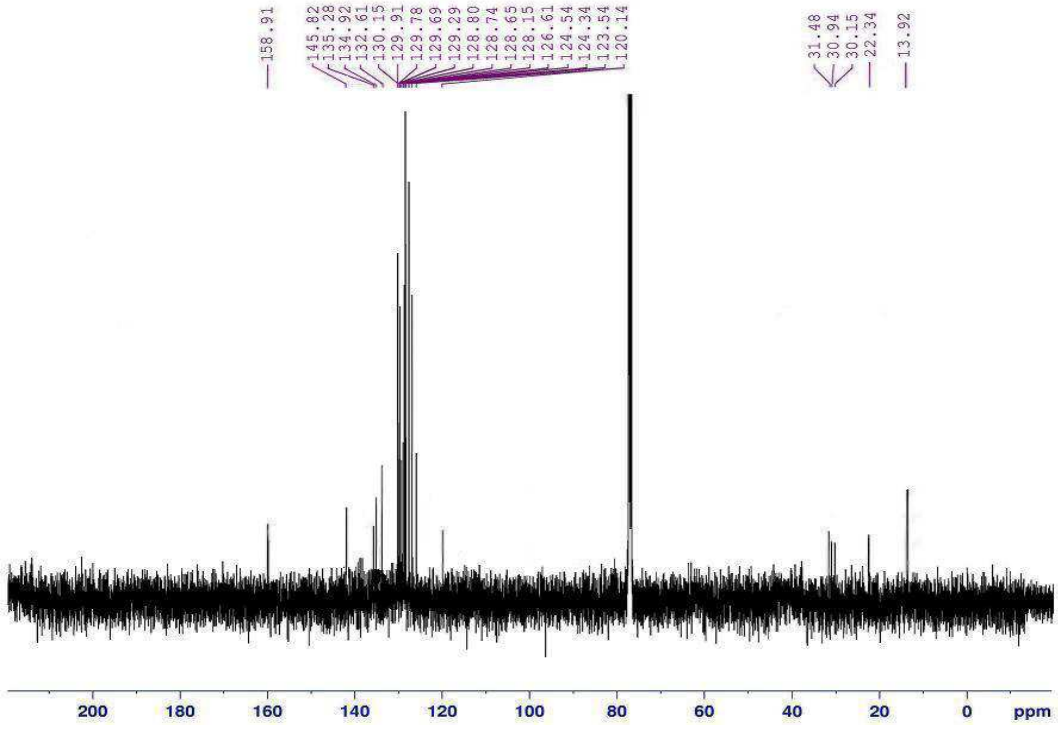
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,5,1}



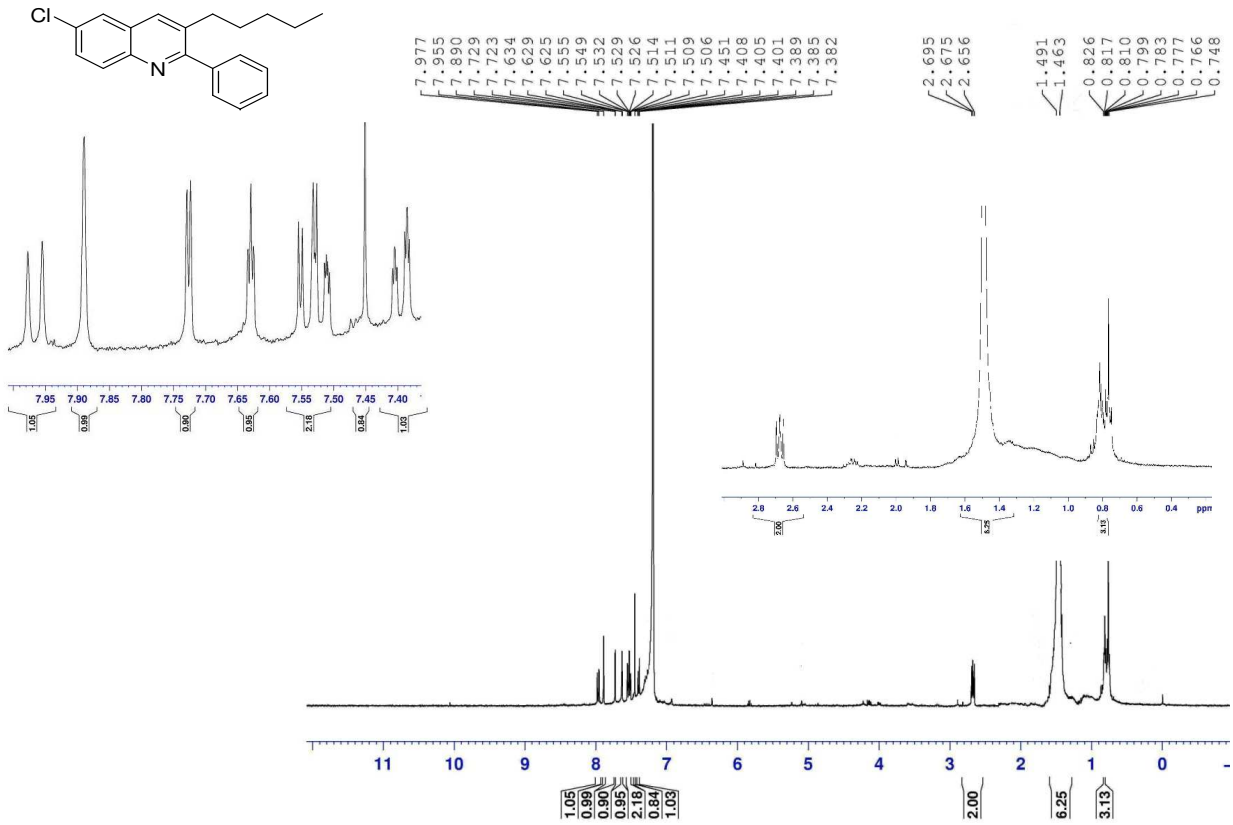
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,5,1}



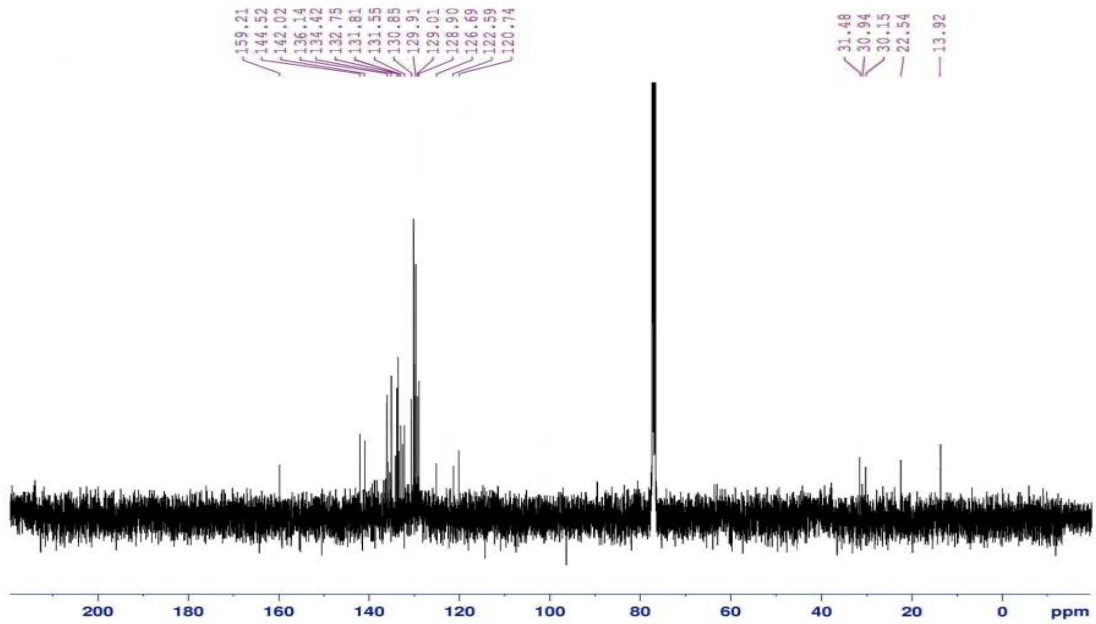
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,6,1}



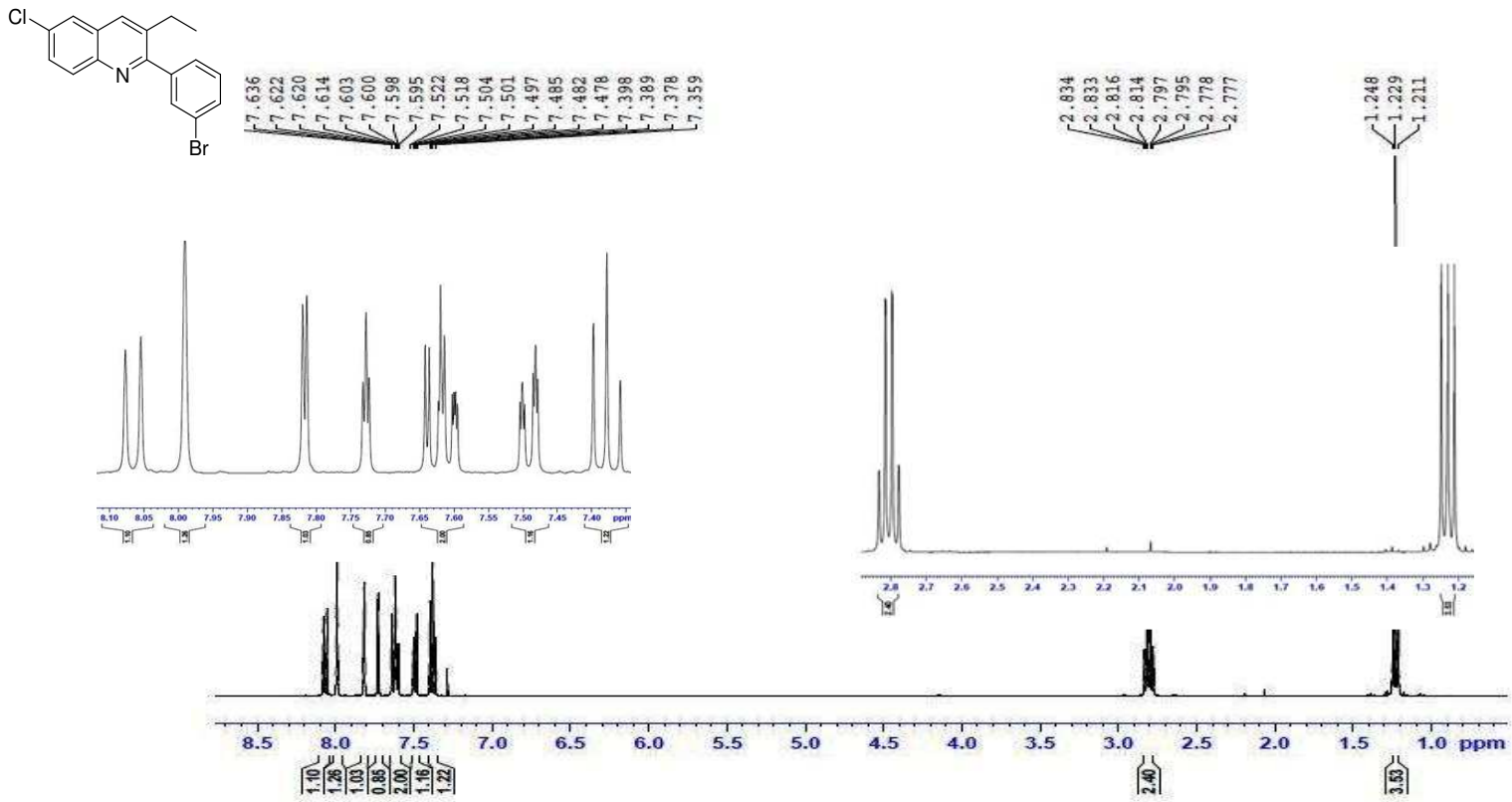
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,6,1}



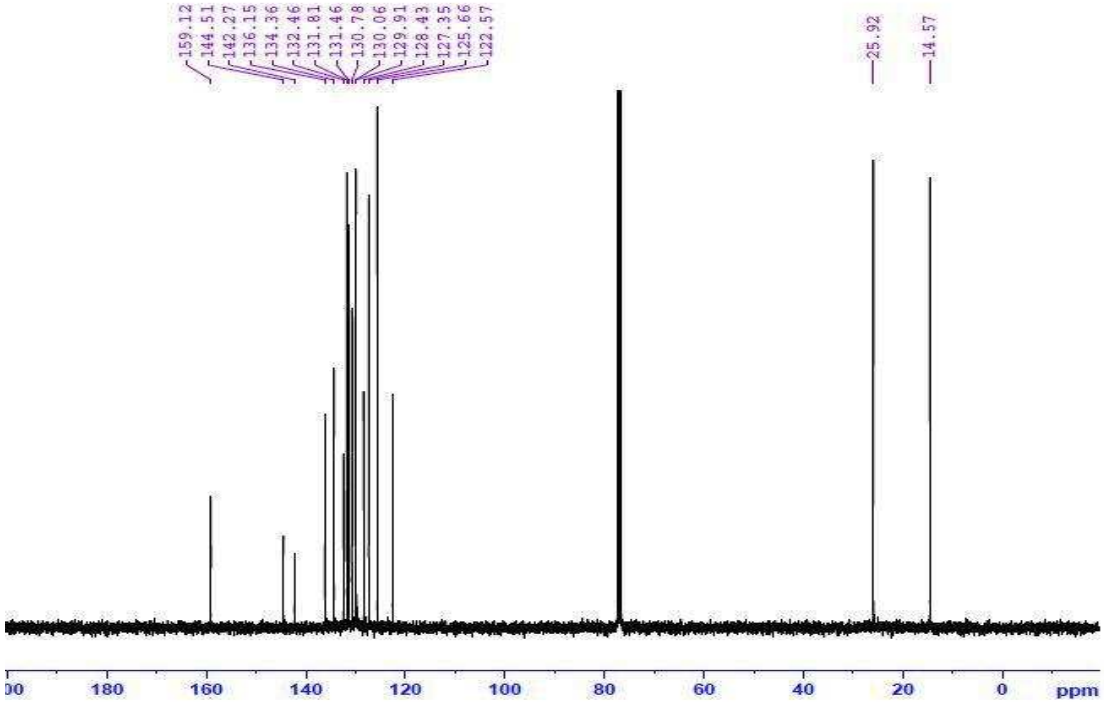
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{2,7,1}



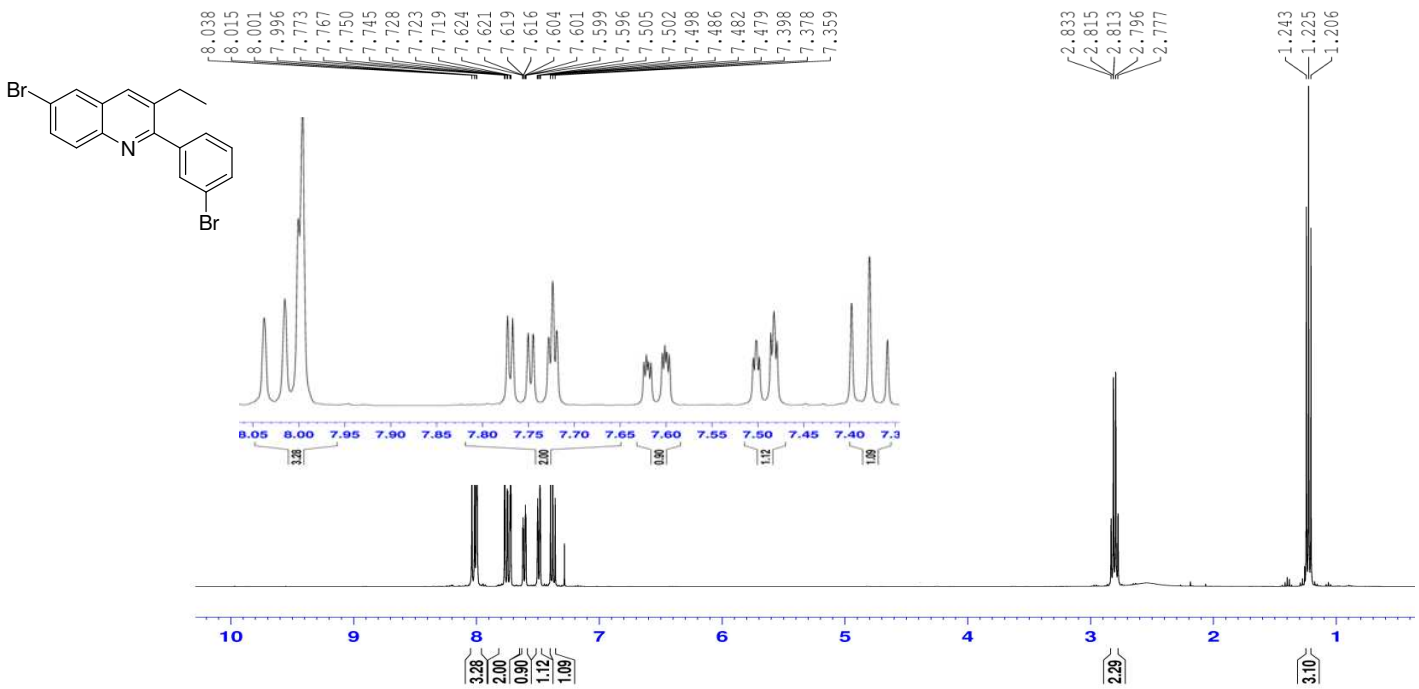
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{2,7,1}



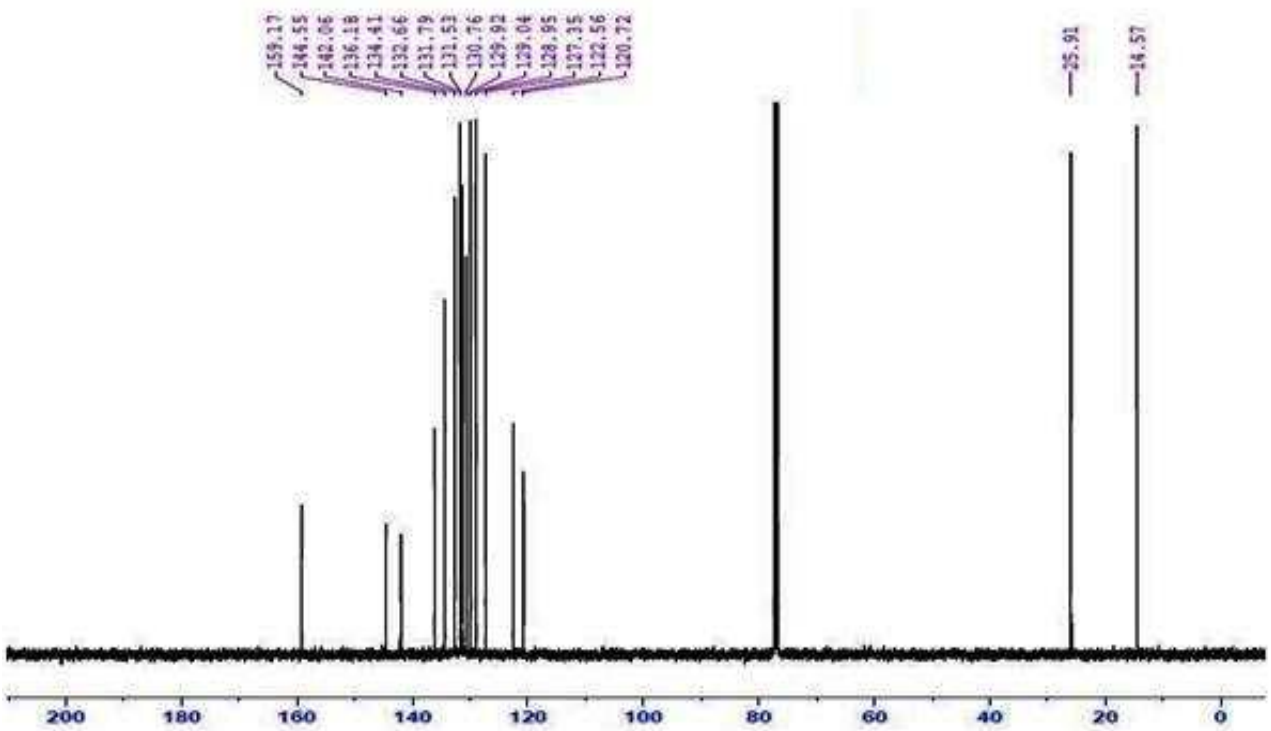
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{2,7,2}



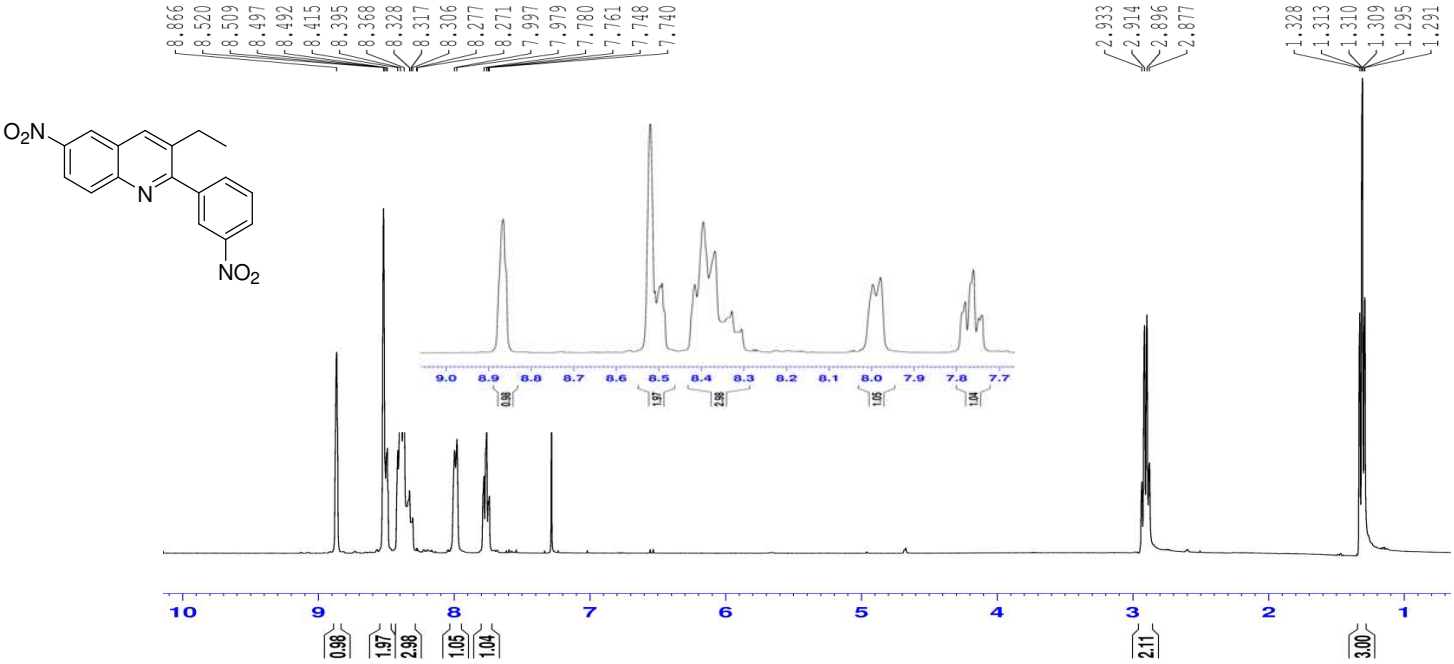
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{2,7,2}



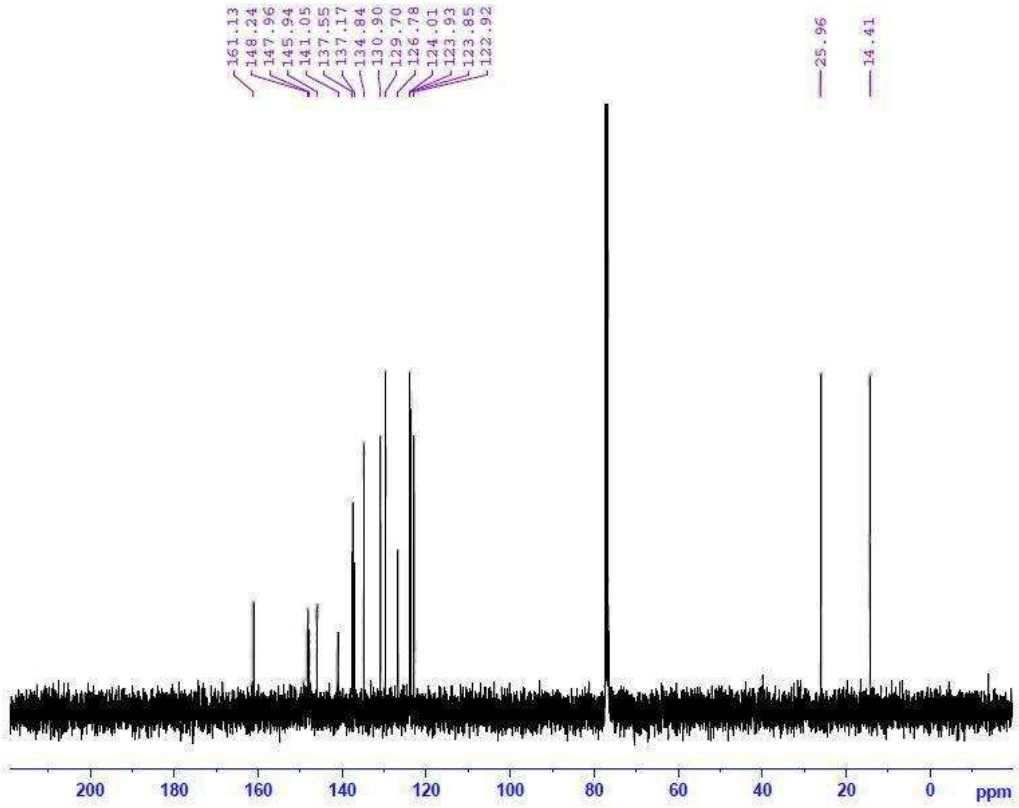
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,7,2}



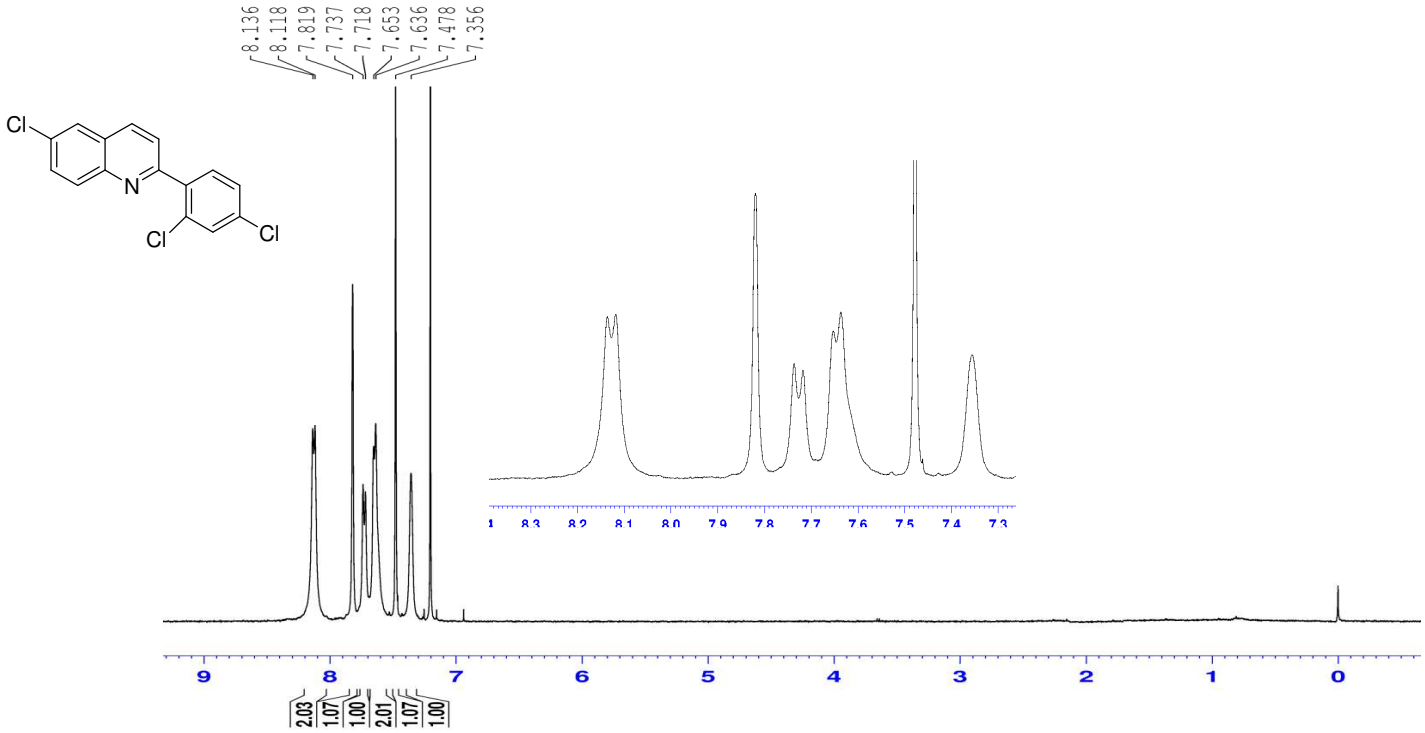
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,7,2}



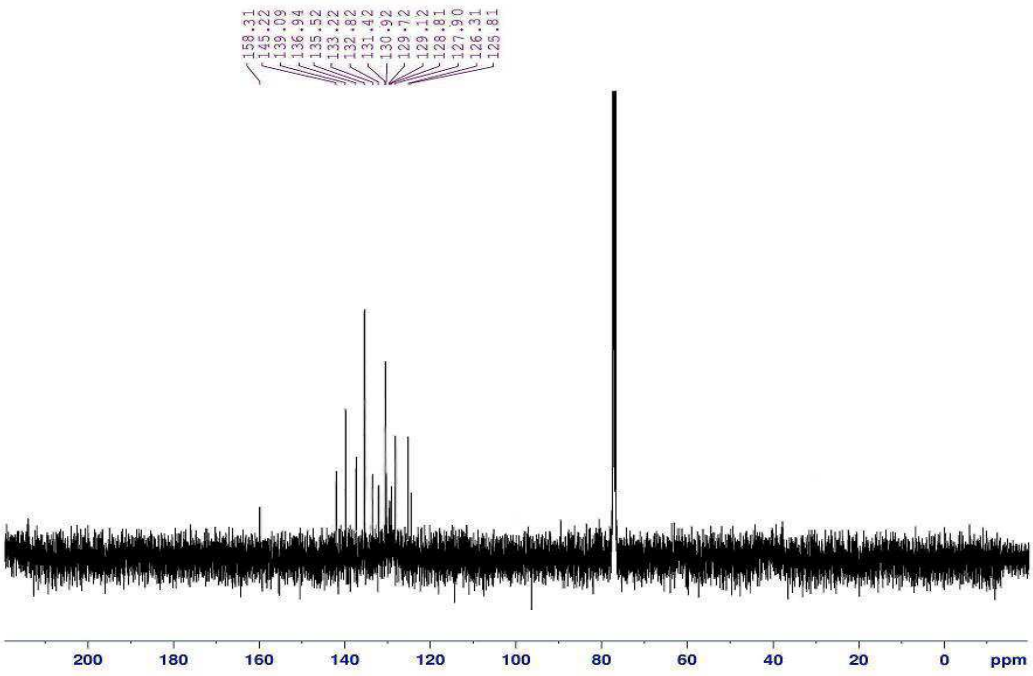
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{3,2,2}



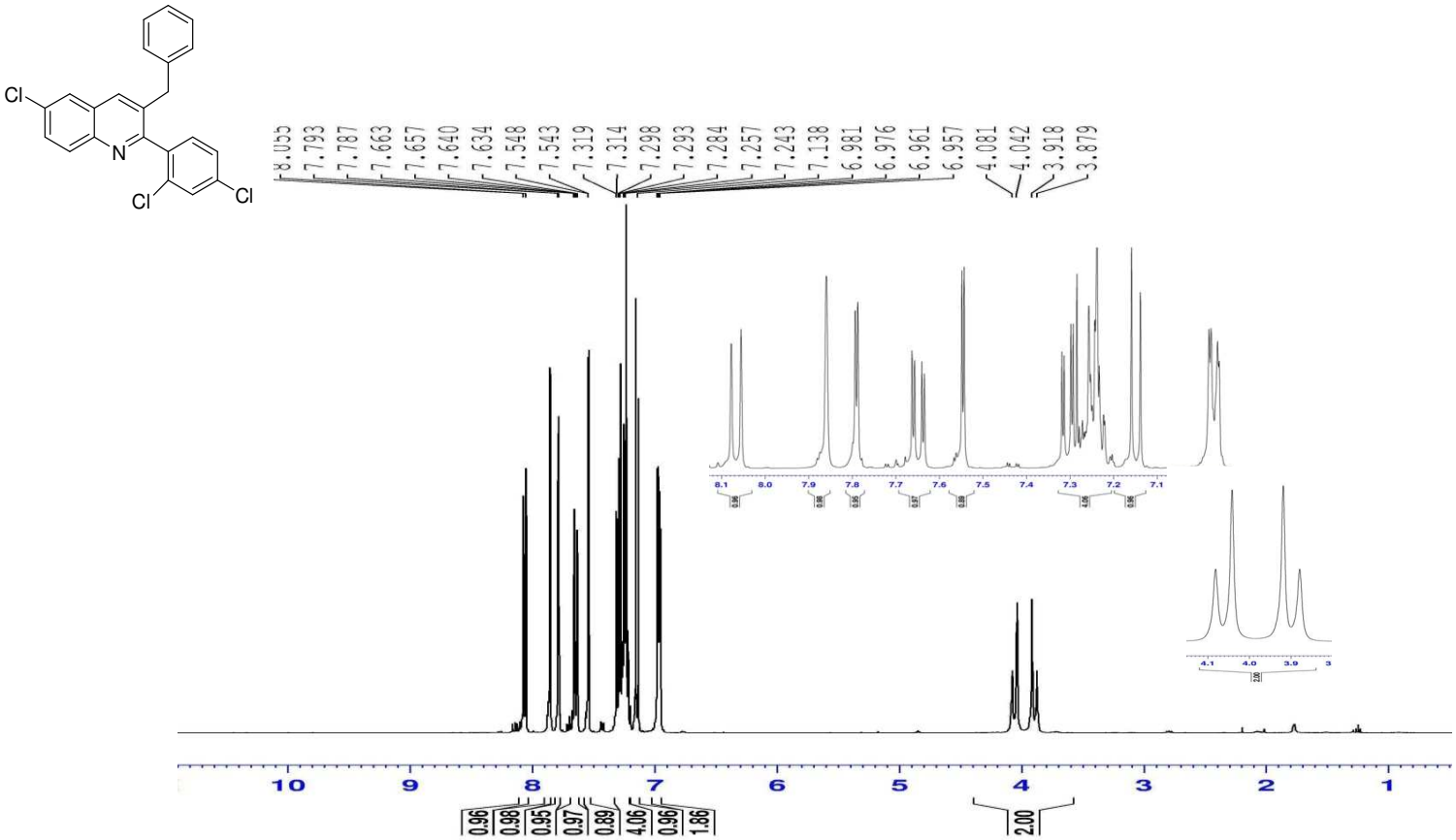
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{3,2,2}



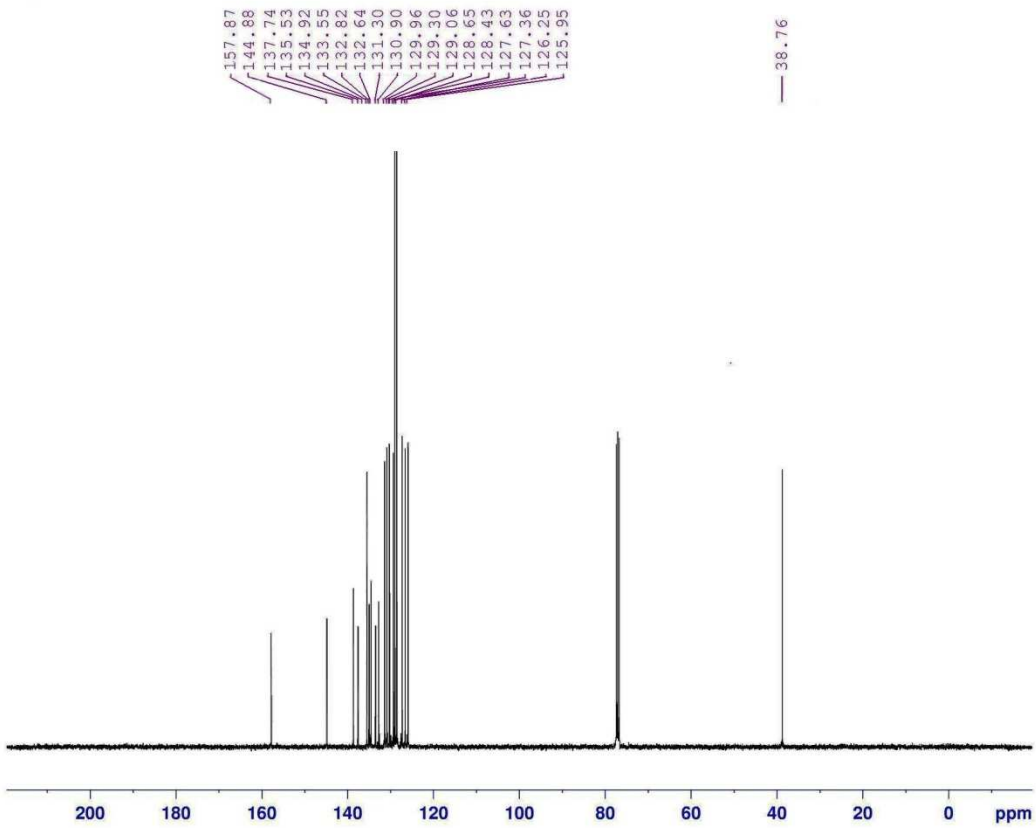
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{2,1,3}



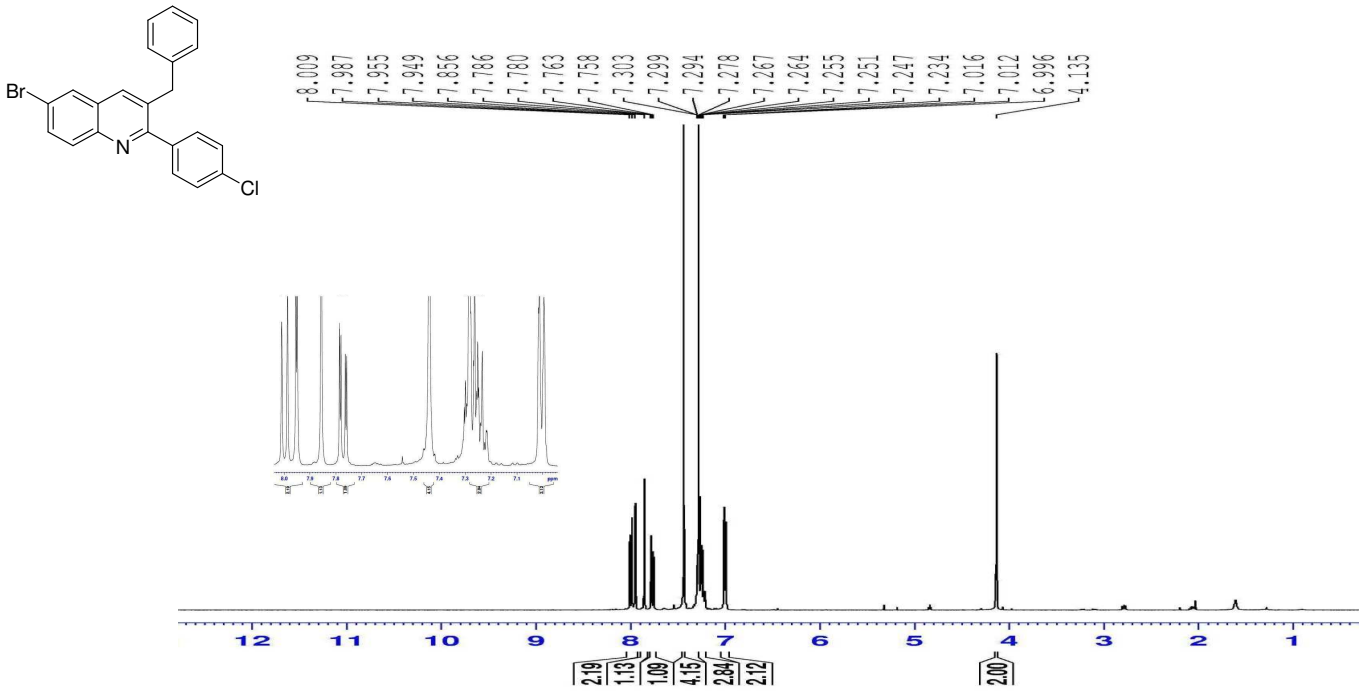
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{2,1,3}



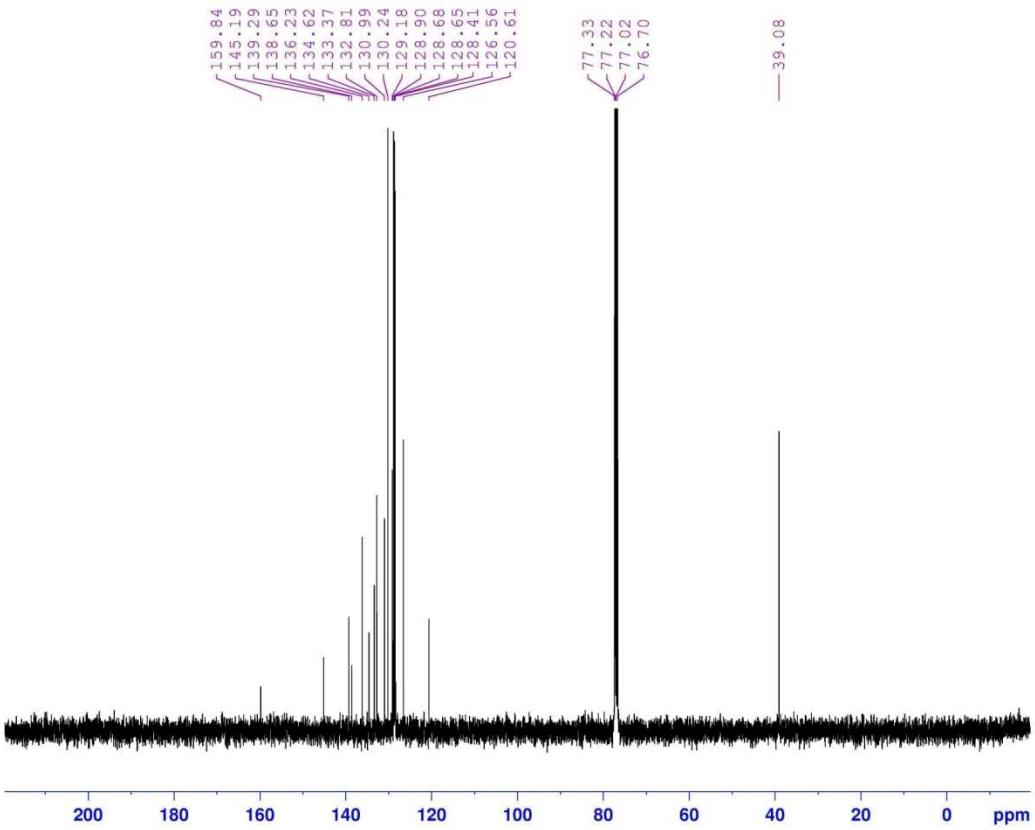
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{2,1,4}



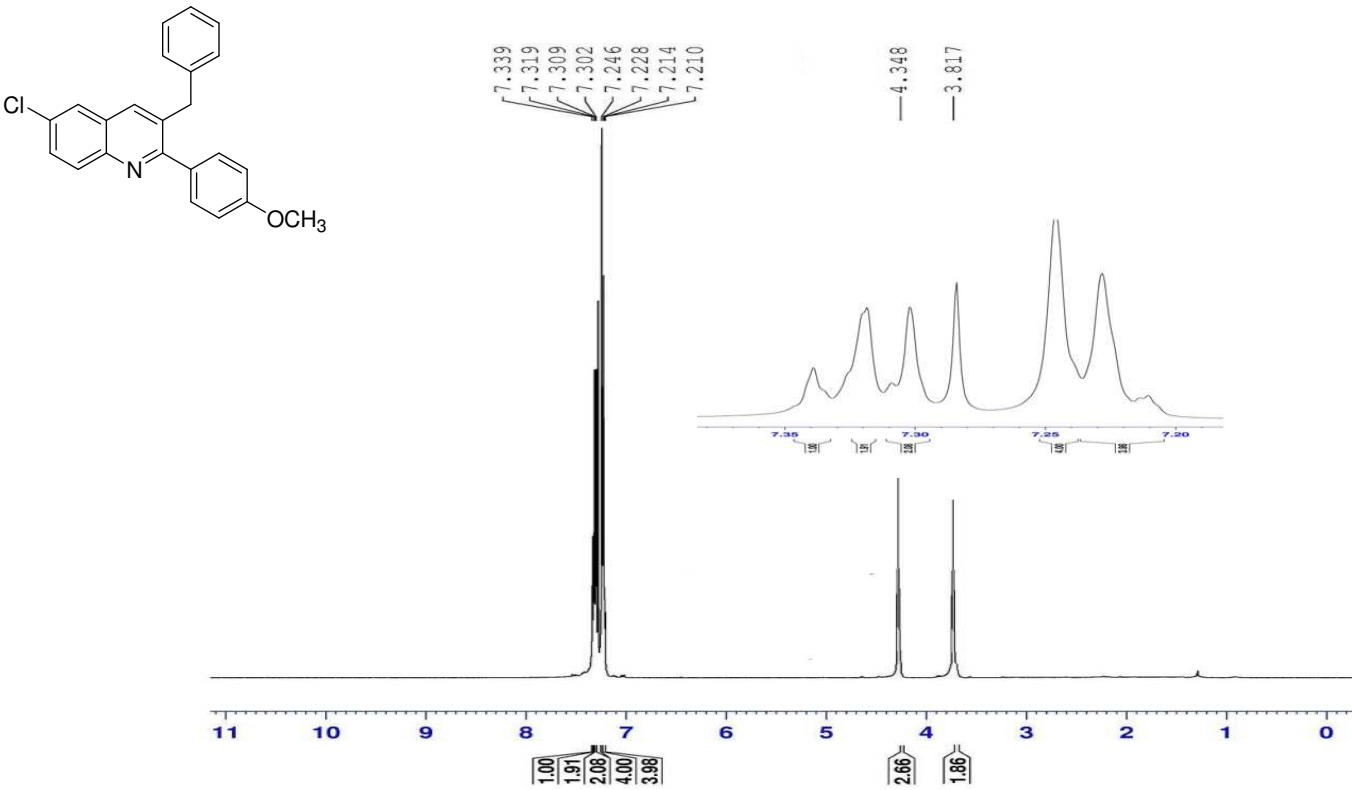
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{2,1,4}



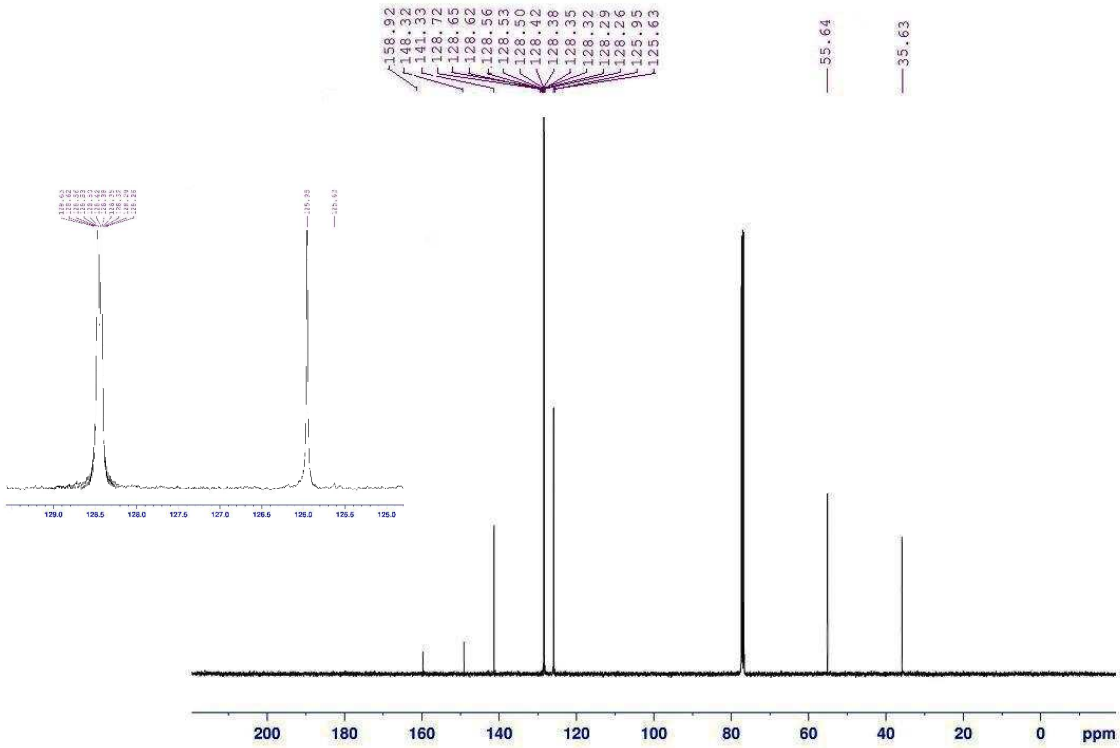
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,3,4}



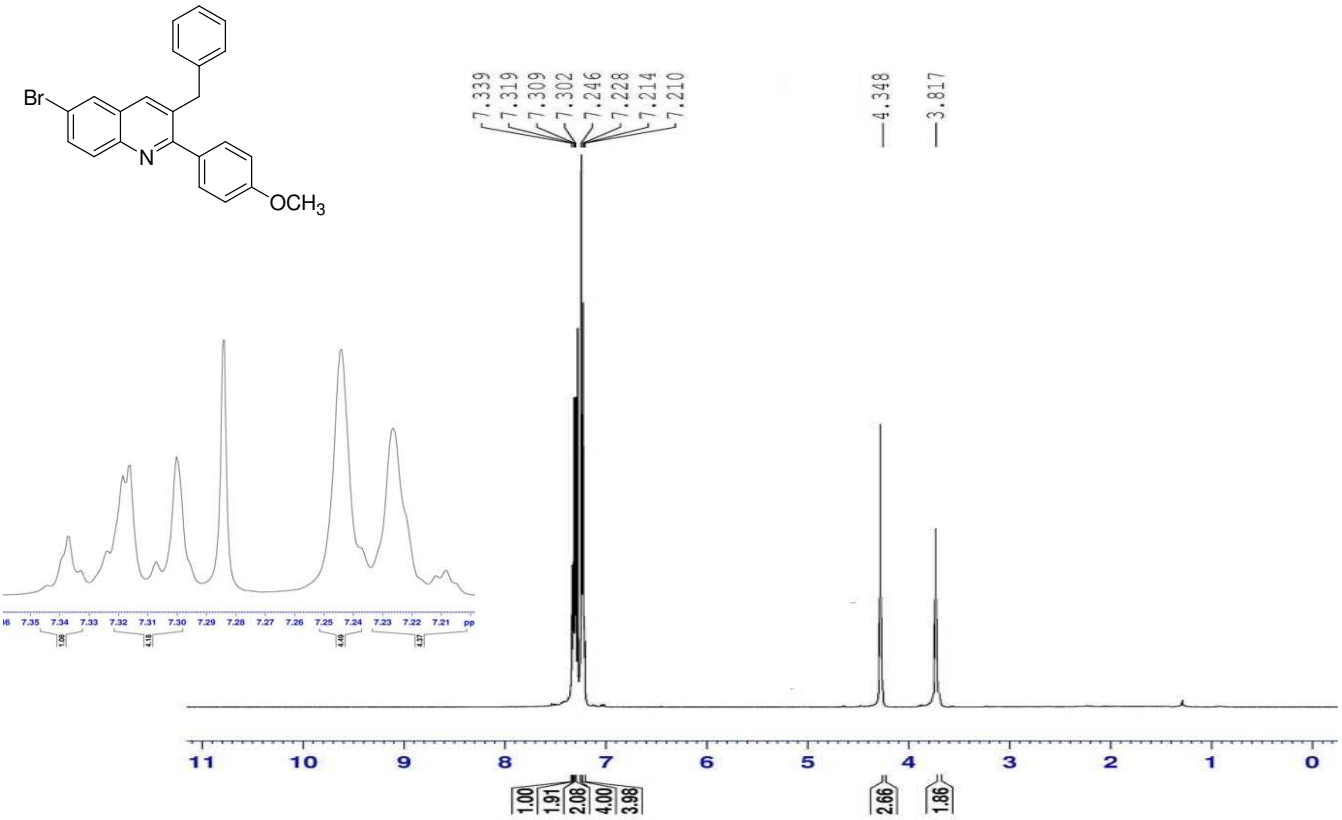
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,3,4}



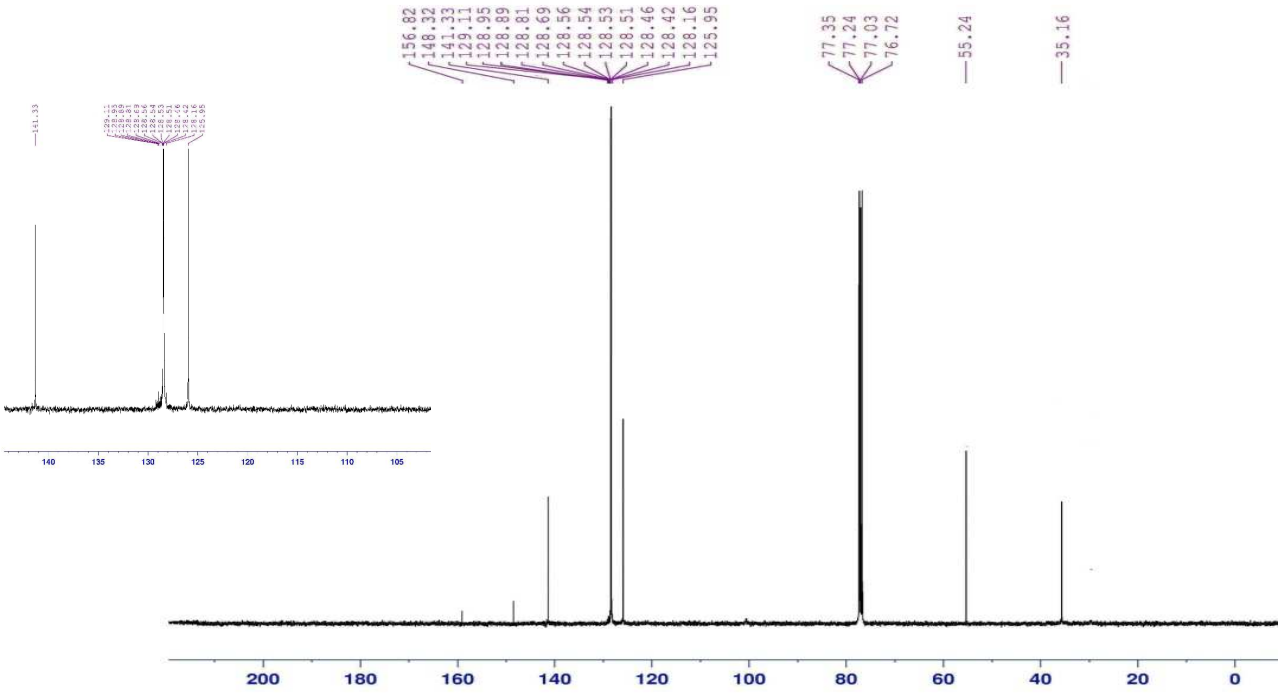
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{2,5,4}



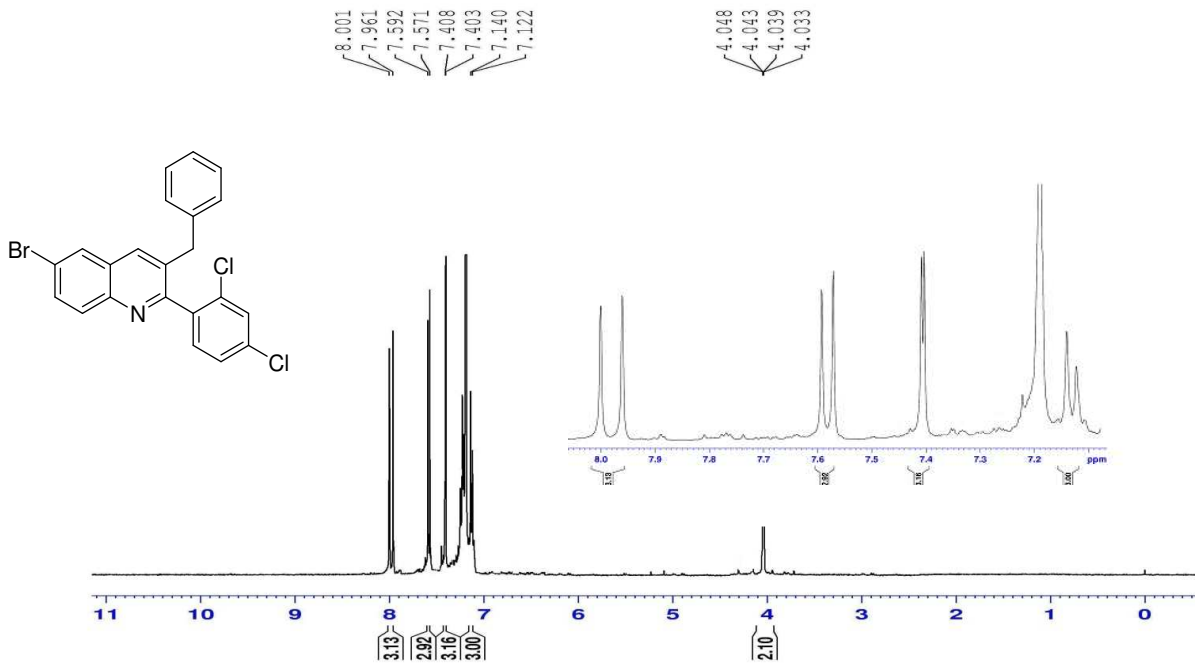
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{2,5,4}



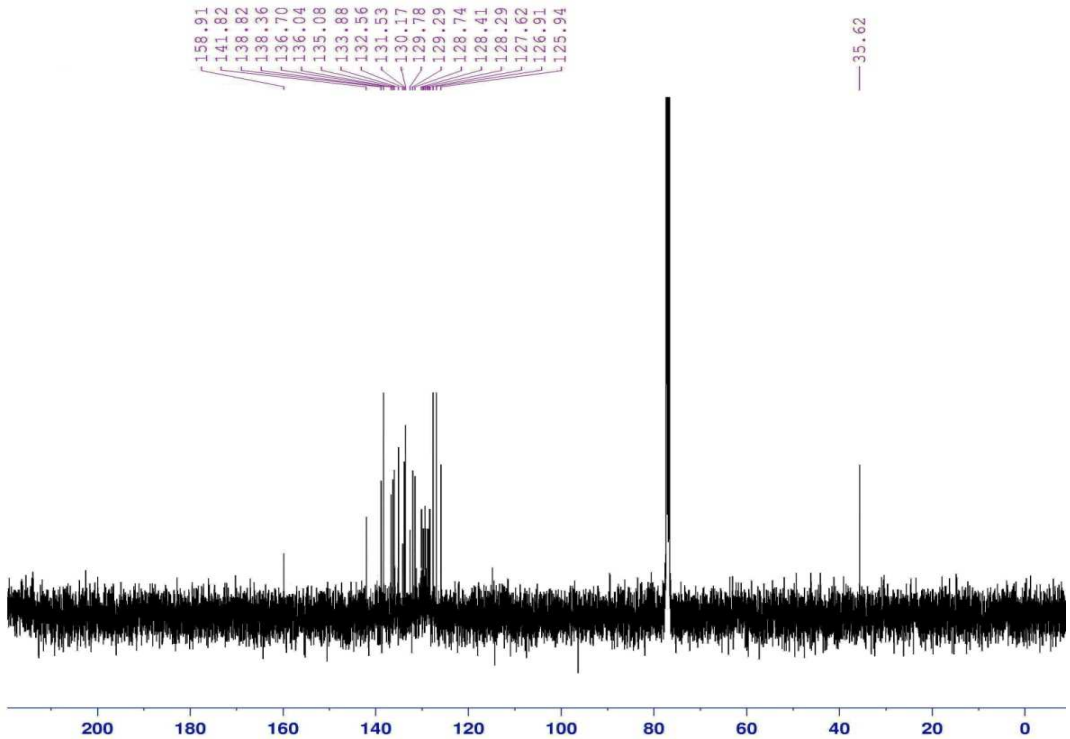
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,5,4}



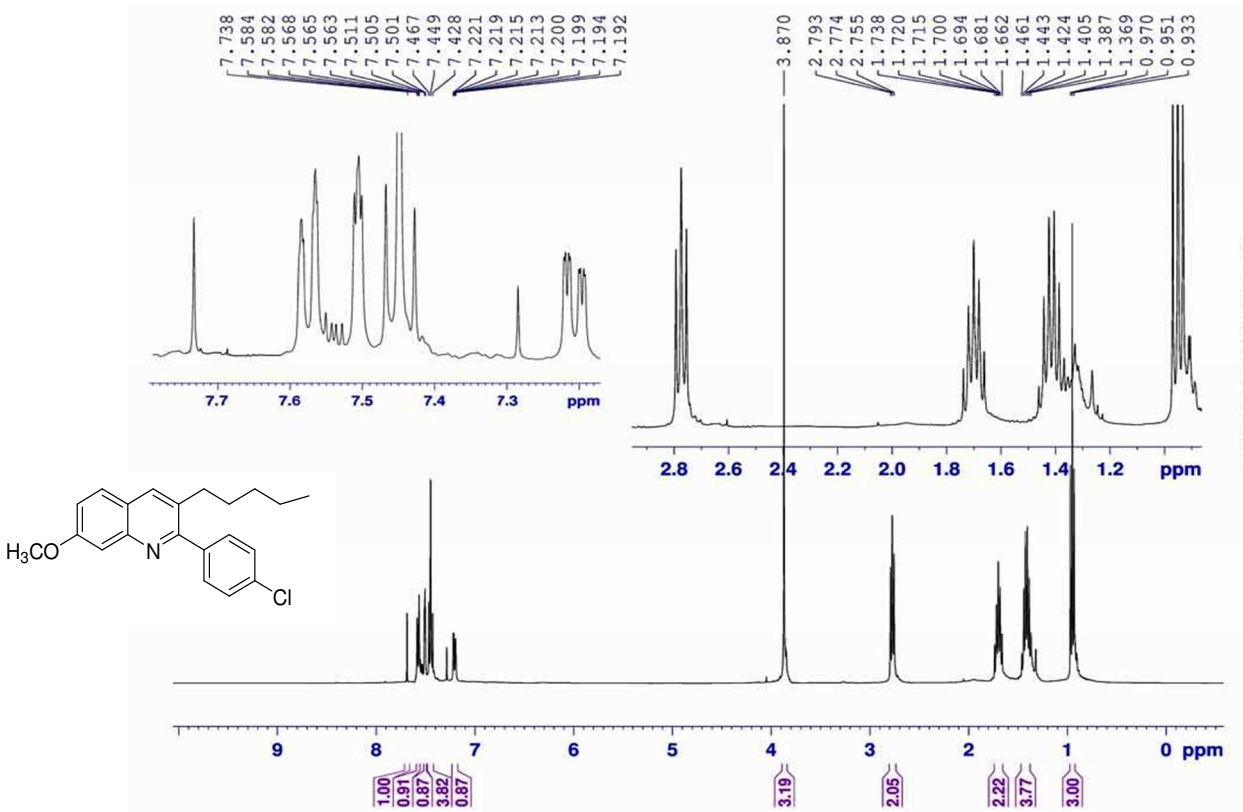
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,5,4}



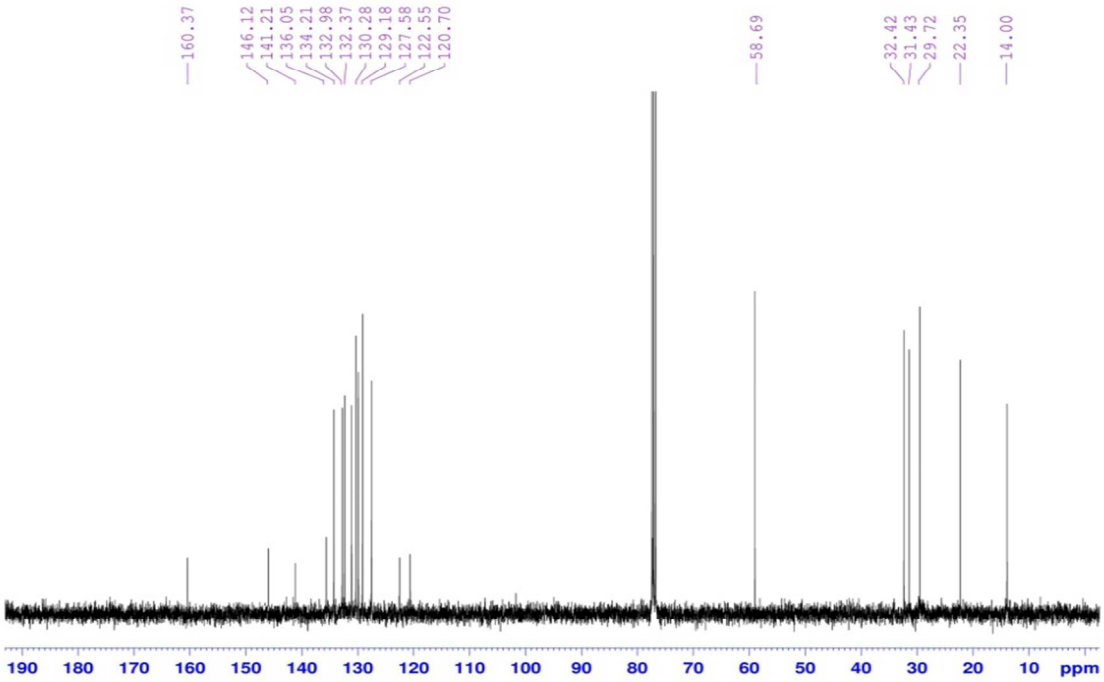
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{1,1,4}



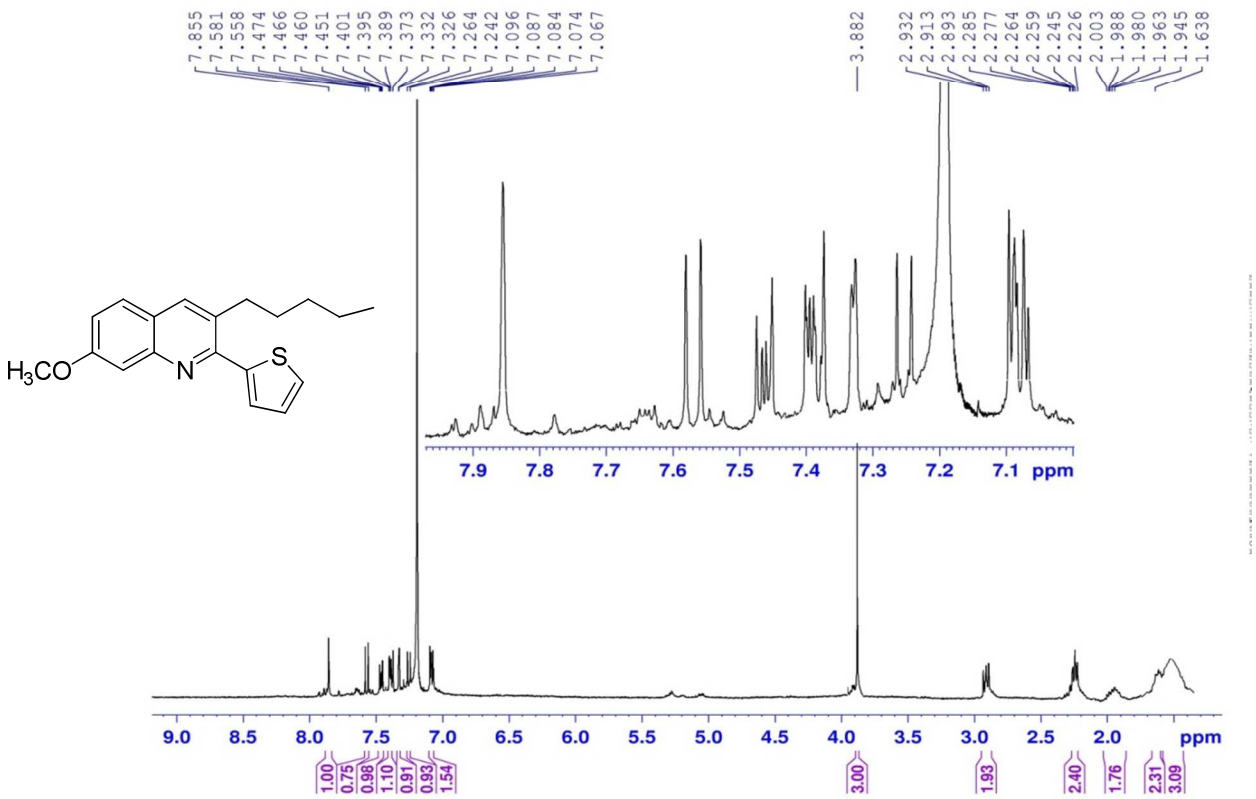
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{1,1,4}



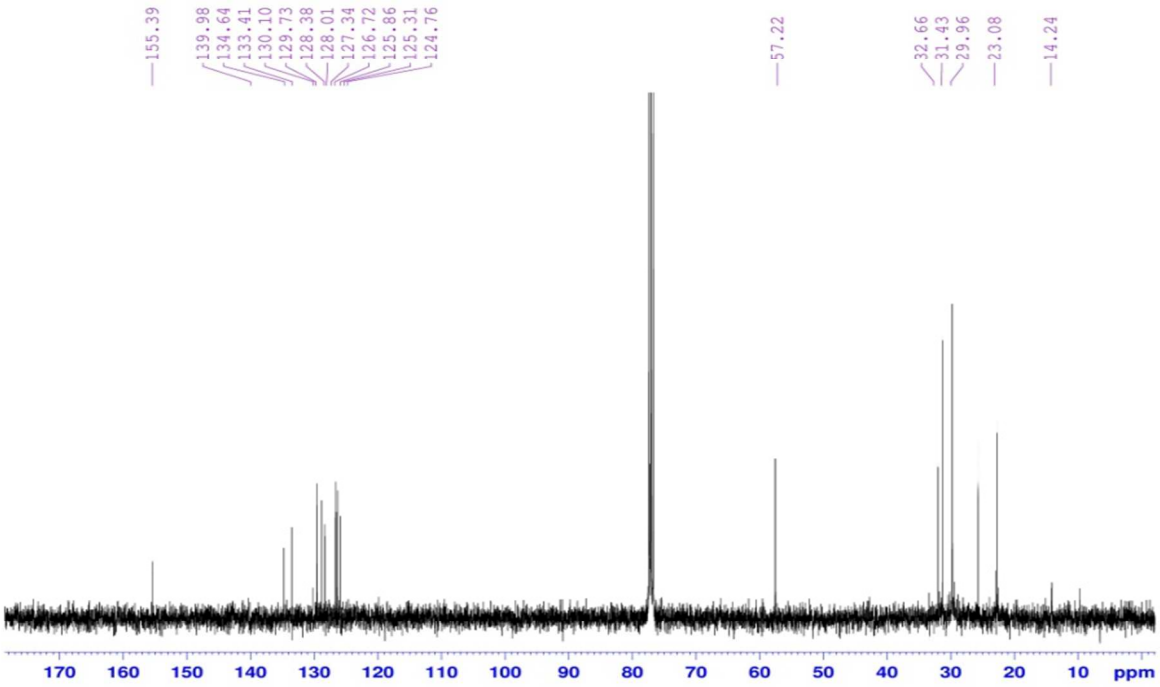
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{4,3,1}



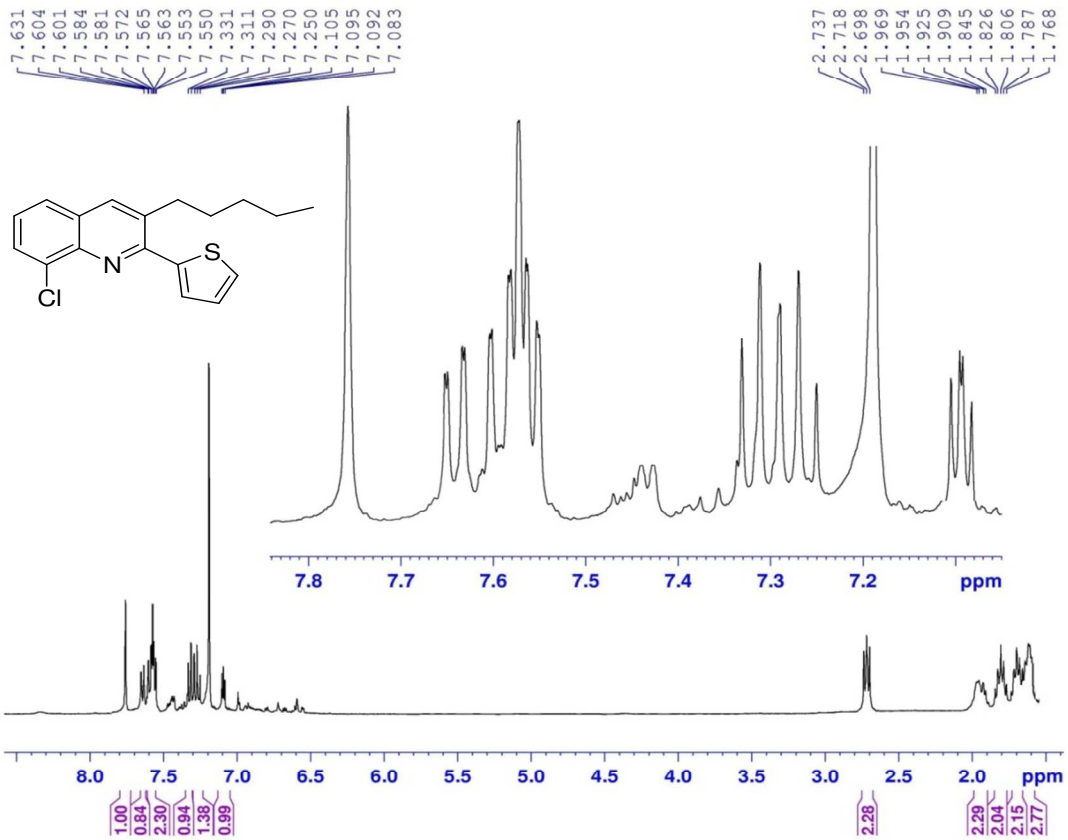
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{4,3,1}



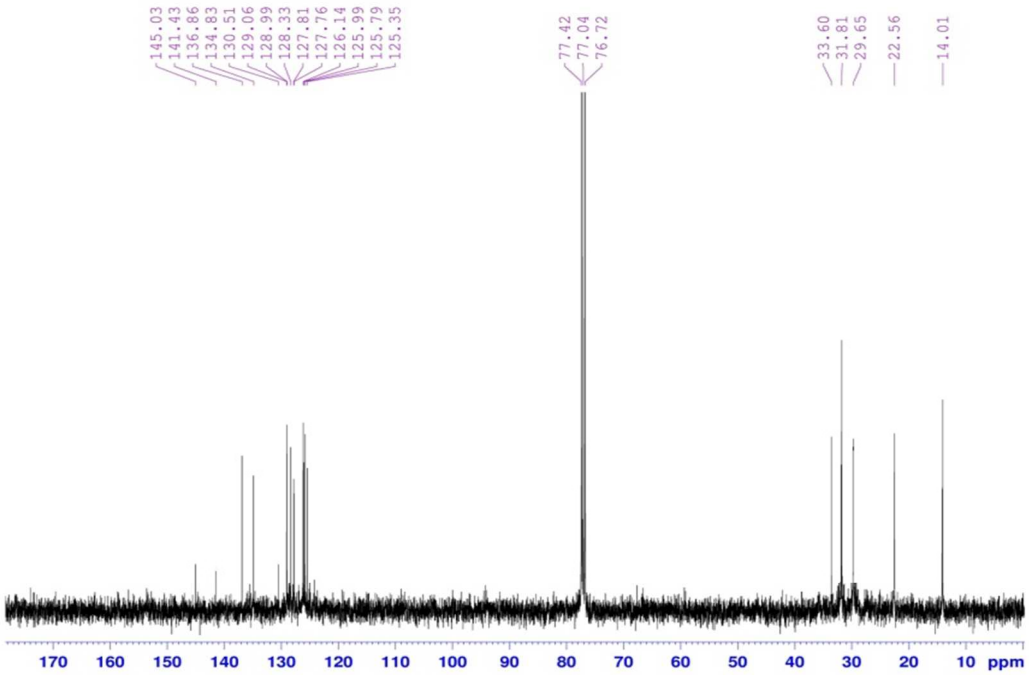
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{4,9,1}



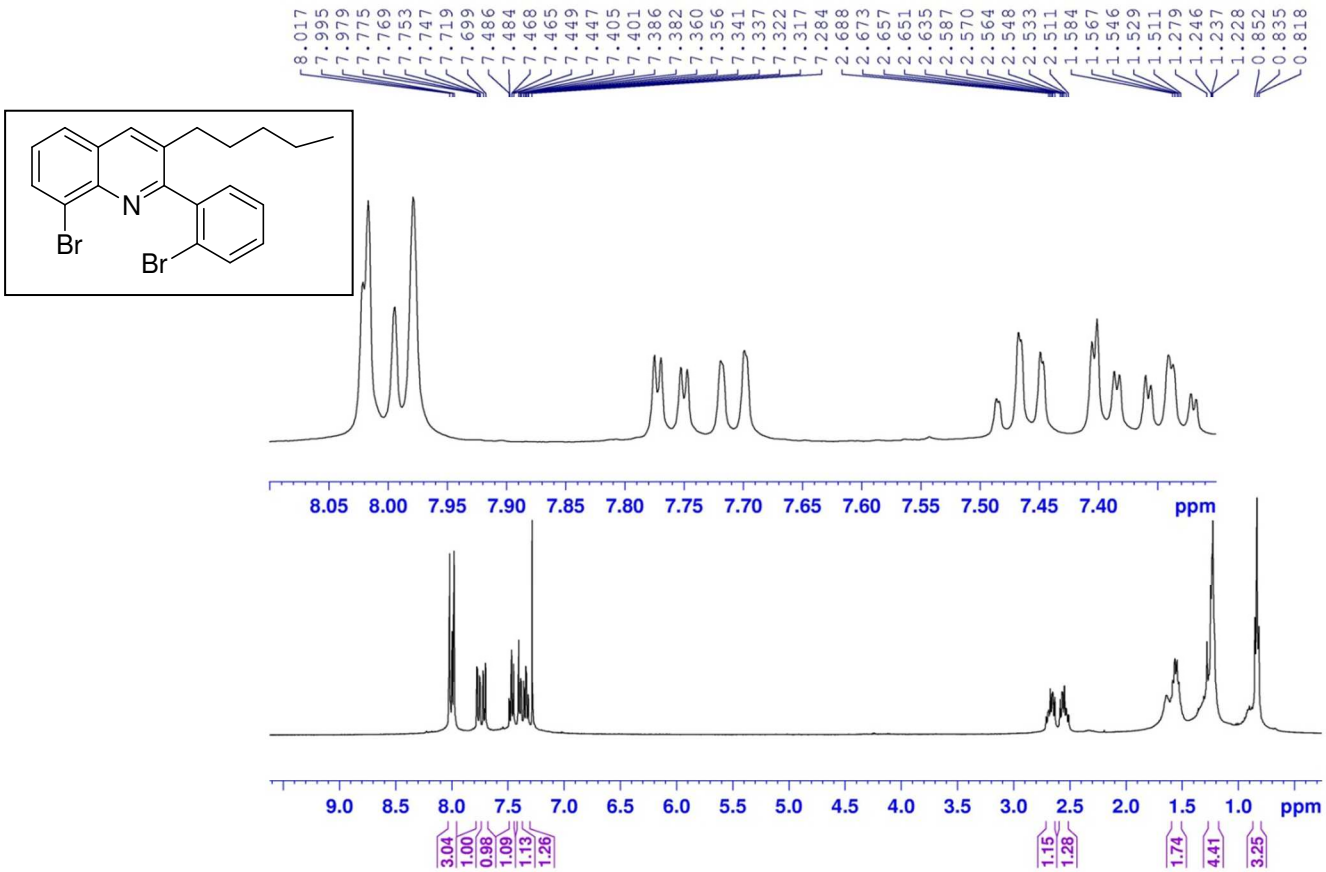
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{4,9,1}



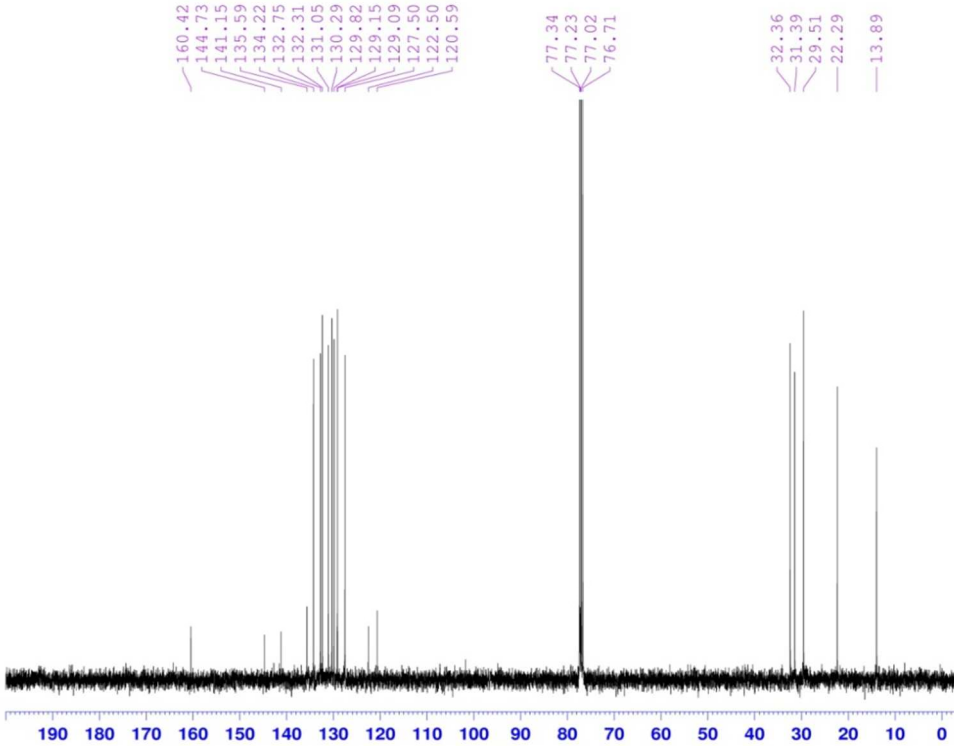
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{5,9,1}



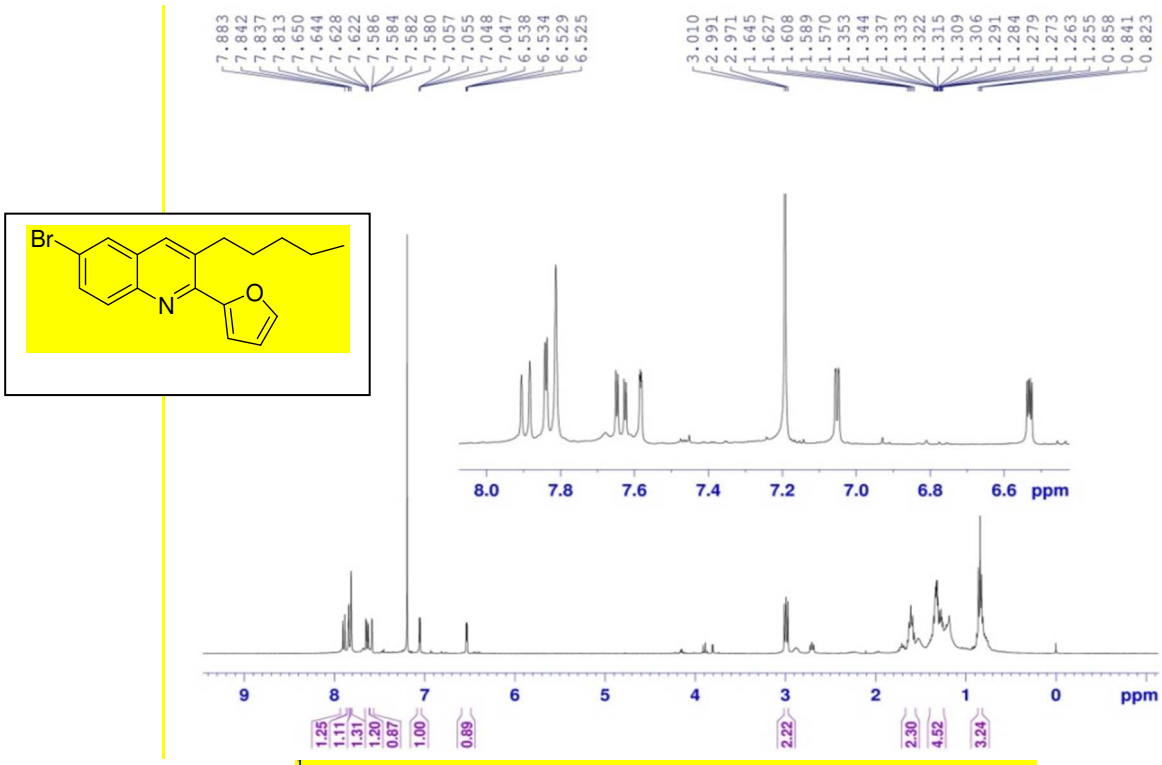
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4{5,9,1}



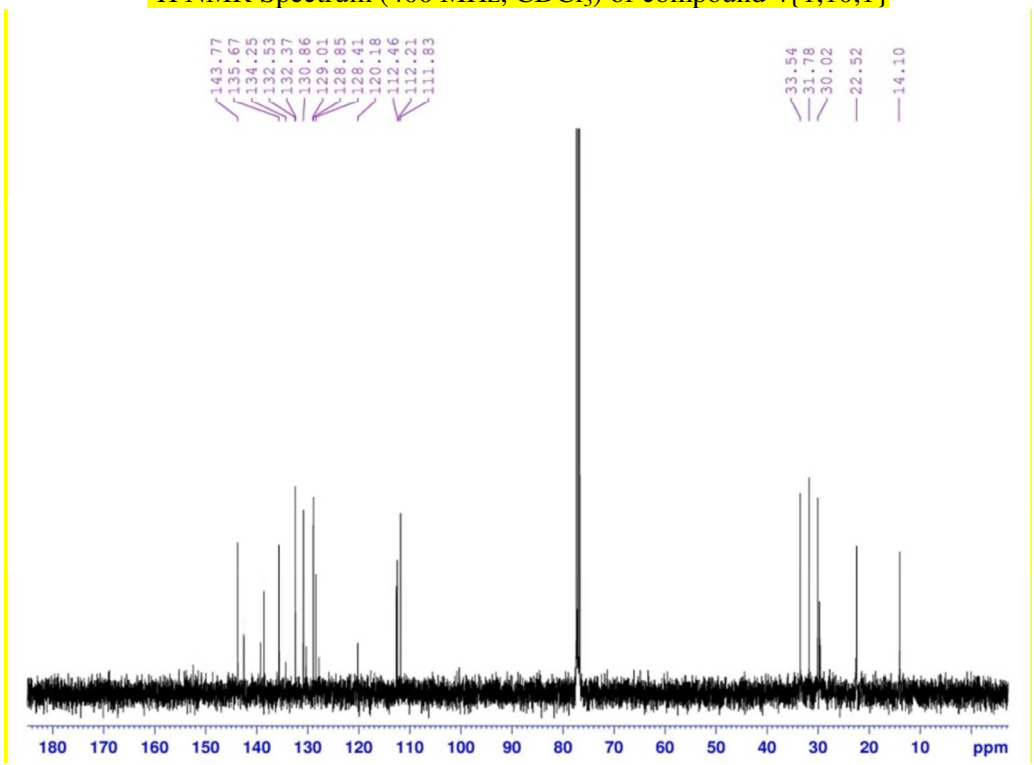
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{6,8,1}



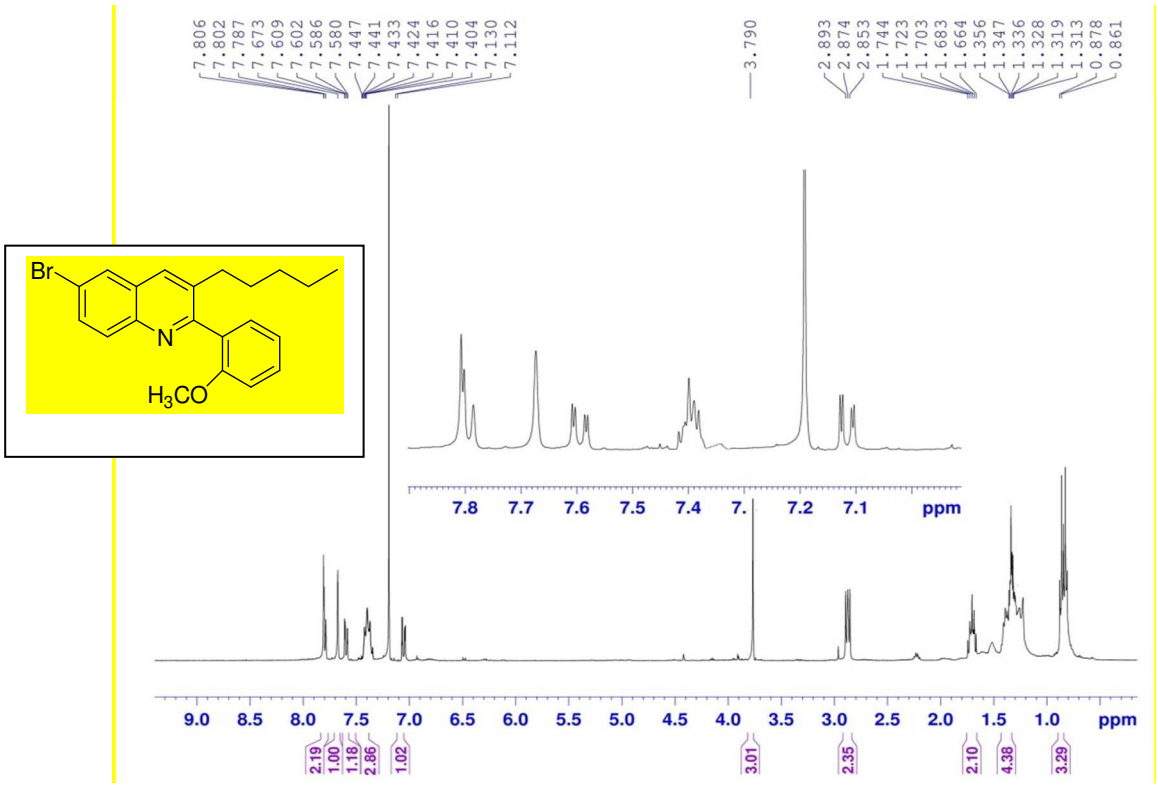
^{13}C NMR Spectrum (500 MHz, $CDCl_3$) of compound 4{6,8,1}



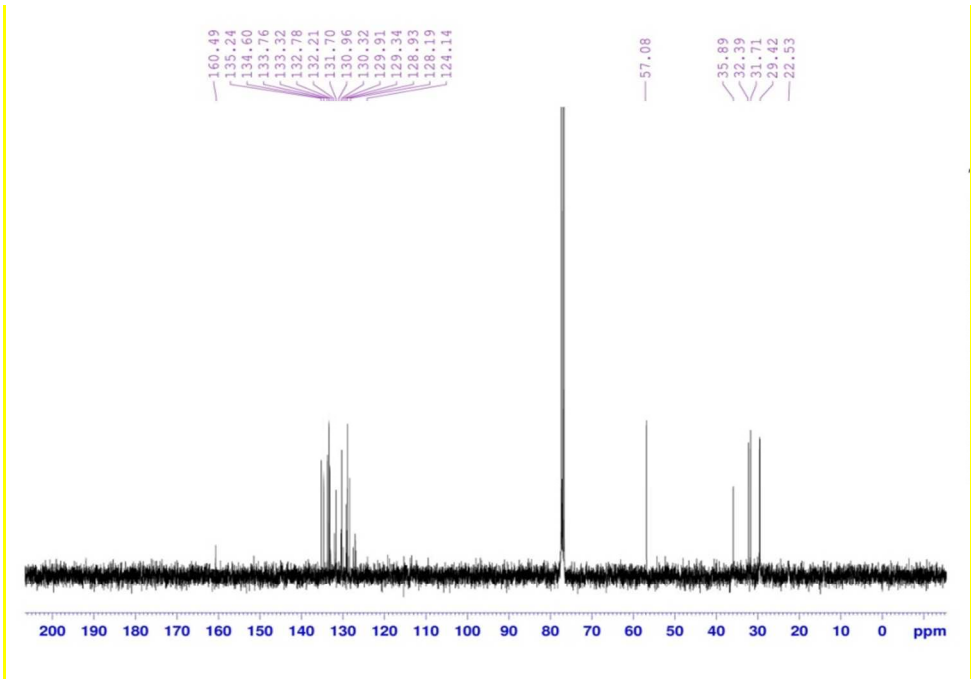
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of compound 4{1,10,1}



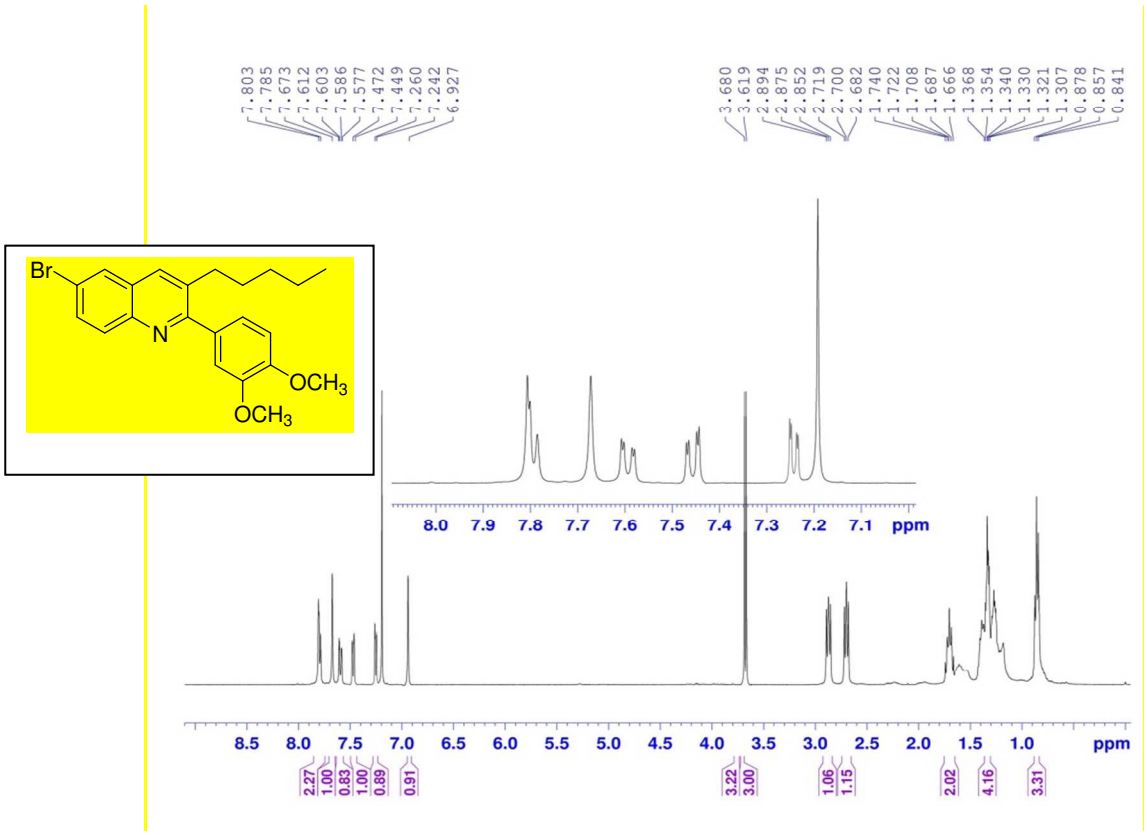
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of compound 4{1,10,1}



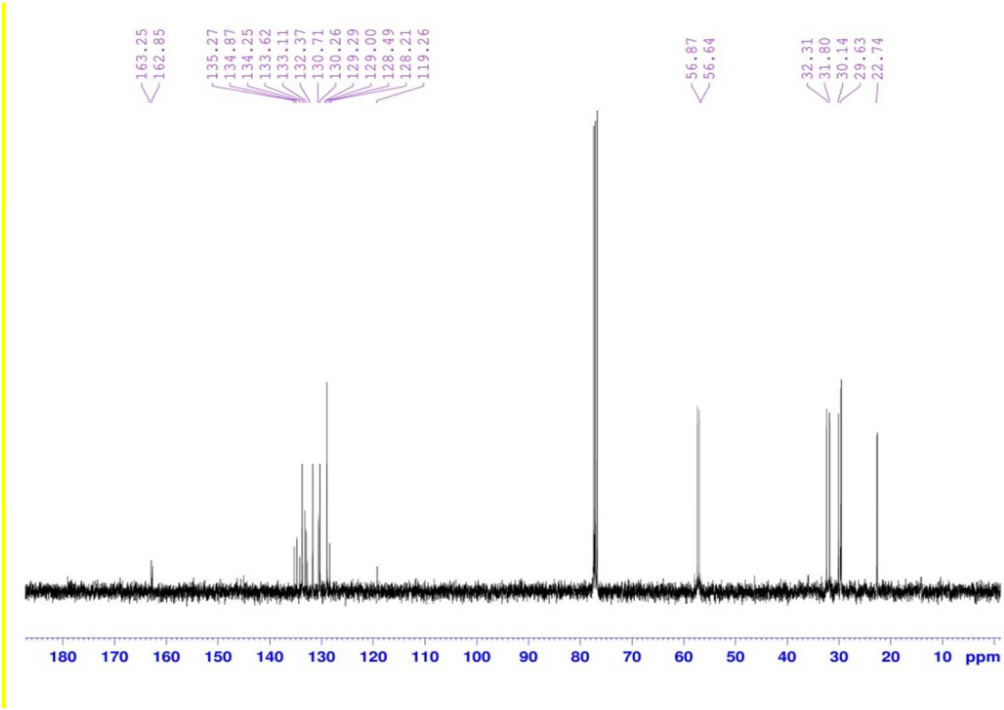
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of compound 4{1,11,1}



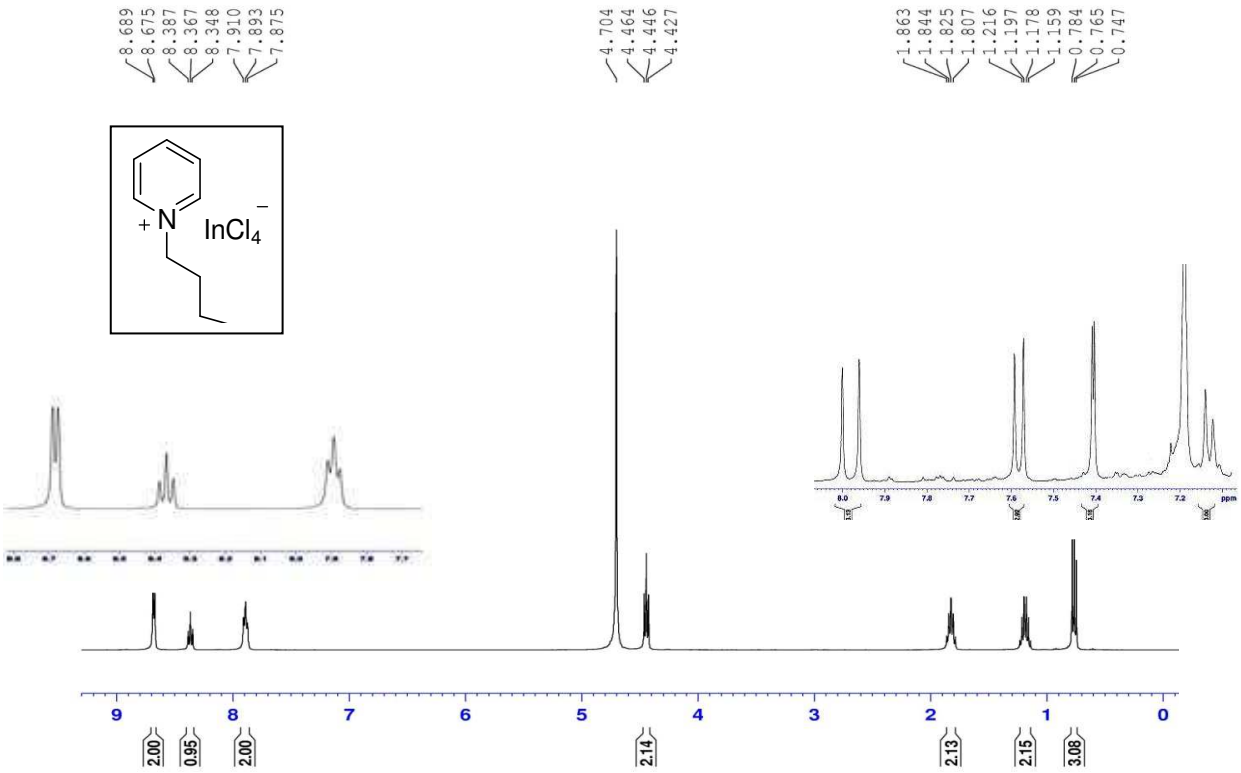
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of compound 4{1,11,1}



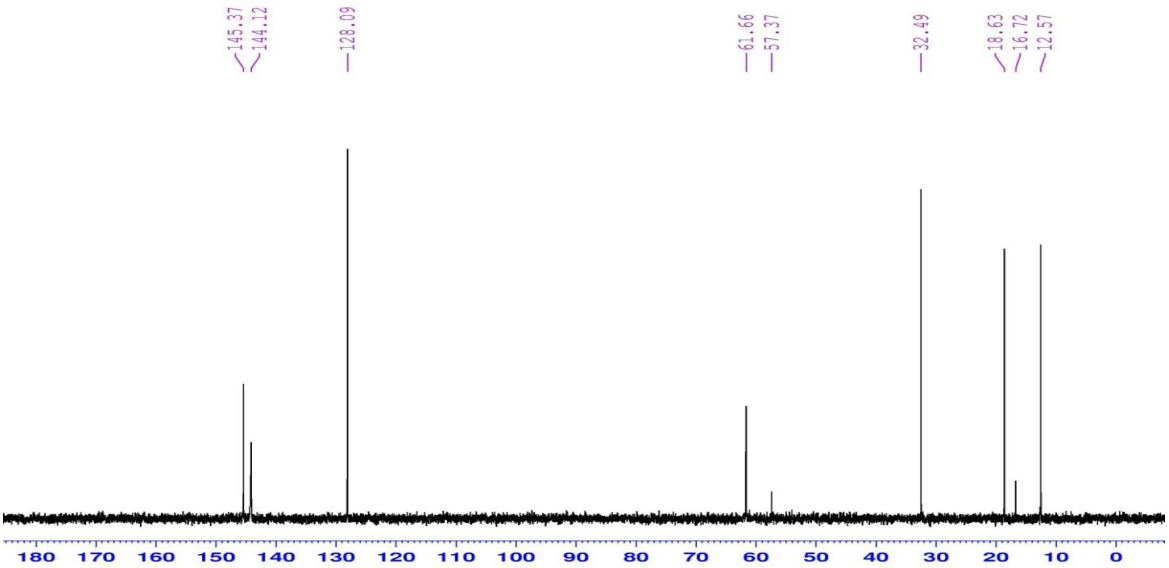
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of compound 4{1,12,1}



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of compound 4{1,12,1}



^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of [bpy][$InCl_4$]



^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of [bpy][$InCl_4$]

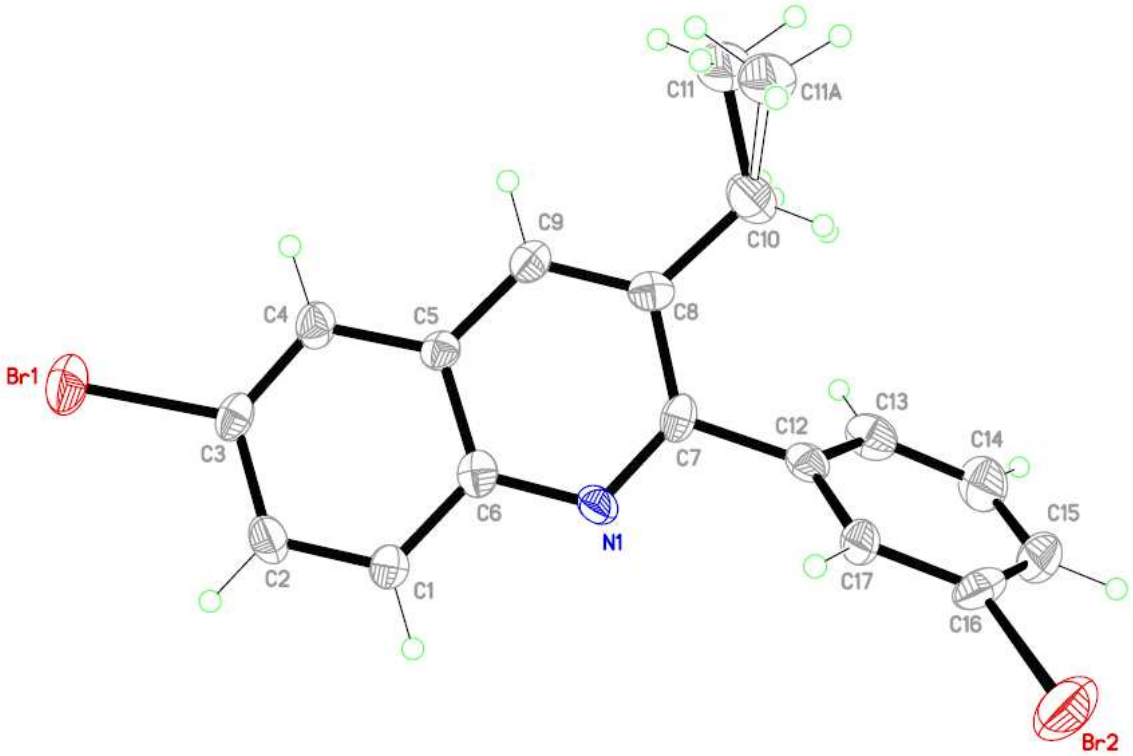


Figure 1. X-ray Crystallography structure of compound **4{1,7,2}**. The methyl segment shows disorder and the minor fragment is shown as open line.

Table 1. Crystal data and structure refinement for compound **4{1,7,2}**

Empirical formula	$C_{17}H_{13}Br_2N$	
Formula weight	391.10	
Temperature	291(2) K	
Wavelength	0.71069Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/c$	
Unit cell dimensions	a = 9.076(5) Å	α = 90.000(5)°
	b = 13.139(5) Å	β = 105.792(5)°
	c = 13.036(5) Å	γ = 90.000(5)°
Volume	1495.9(12) $Å^3$	
Z	4	
Density (calculated)	1.737 Mg/m^3	
Absorption coefficient	5.408 mm^{-1}	
F(000)	768	
Crystal size	0.24 x 0.24 x 0.24 mm^3	
Theta range for data collection	2.24 to 25.00°	
Index ranges	-10<=h<=8, -14<=k<=15, -15<=l<=15	
Reflections collected	6388	
Independent reflections	2370 [R(int) = 0.1159]	
Completeness to theta = 25.00°	90.0%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2370 / 2 / 185	
Goodness-of-fit on F^2	0.818	
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.0850	
R indices (all data)	R1 = 0.1379, wR2 = 0.1029	
Largest diff. peak and hole	0.419 and -0.634 $e.Å^3$	