Electronic Supplementary Material (ESI)
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Supporting information

Efficient and environmentally-benign three-component synthesis of quinolines and *bis*-quinolines catalyzed by recyclable potassium dodecatungstocobaltate trihydrate under microwave irradiation

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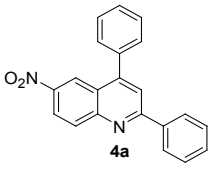
General information:

$K_5CoW_{12}O_{40}\cdot 3H_2O$ was prepared according to the reported procedure.[16d] Melting points were determined using Stuart Scientific SMP2 apparatus. FT-IR spectra were recorded over the 400–4000 cm^{-1} range with a Nicolet-Impact 400D instrument. ^1H and ^{13}C NMR (500 and 125 MHz) spectra were recorded with a Bruker-AC 500 spectrometer. Mass spectra were recorded with a Platform II spectrometer from Micromass. EI mode at 70 eV. Elemental analysis was carried out with a LECO, CHNS-932 instrument. The microwave system used in these experiments includes the following items: Micro-SYNTH labstation, equipped with a glass door, a dual magnetron system with pyramid-shaped diffuser, 1000 W delivered power, exhaust system, magnetic stirrer, "quality pressure" sensor for flammable organic solvents, and a ATCFO fibre optic system for automatic temperature control.

Microwave-assisted synthesis of quinolines; General procedure:

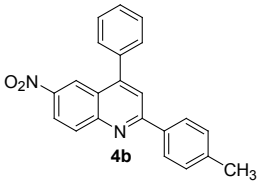
A mixture of arylamine **1** (1 mmol) and arylaldehyde **2** (1 mmol) was irradiated for 30 second and then phenylacetylene **3** (1 mmol) and $K_5WCo_{12}O_{40}\cdot 3H_2O$ (11 mol%) were added. The resulting mixture was subjected to microwave irradiation under solvent-free conditions for the appropriate time according to Table 2. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/ethyl acetate: 7/3). After completion of the reaction, the mixture was cooled to room temperature and EtOH (20 ml) was added. The residue was filtered, the filtrate was evaporated and the crude product was purified by recrystallization from EtOH to give the pure product in 87-98% yields.

Spectroscopic data of the products:

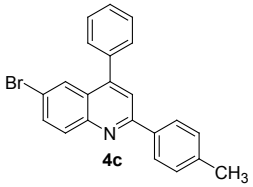


4a

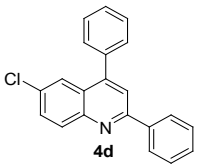
2,4-Diphenyl-6-nitroquinoline (**4a**): Mp: 265-266 °C (Lit.[10f] 264 °C). IR (KBr): ν_{max} = 2922, 2852, 1595, 1440, 1382, 1338, 883, 846, 771, 752 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.54-7.64 (m, 8H), 7.99 (s, 1H), 8.26 (d, J = 7.0 Hz, 2H), 8.35 (d, J = 9.2 Hz, 1H), 8.50 (dd, J = 9.2, 2.4 Hz, 1H), 8.87 (d, J = 2.4 Hz, 1H). MS: m/z = 326.11 ($[M]^+$, 3.20), 244.02 (13.24), 203.06 (10.96), 146.58 (27.40), 100.66 (25.11), 78.08 (29.68), 77.04 (81.28), 55.10 (100.00) .



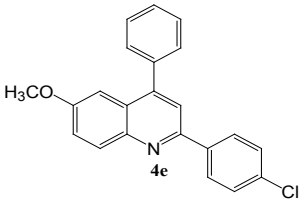
6-Nitro-4-phenyl-2-*p*-tolylquinoline (4b): Mp: 201-202 °C (Lit.[18d] 202-203 °C). IR (KBr): ν_{max} = 2922, 2850, 1593, 1548, 1483, 1336, 1180, 819, 746 cm^{-1}. ^1H NMR (500M Hz, $CDCl_3$): δ = 2.46 (s, 3H), 7.37 (d, J = 8.0 Hz, 2H), 7.56-7.64 (m, 5H), 7.97 (s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 8.32 (d, J = 9.2 Hz, 1H), 8.48 (dd, J = 9.2, 2.5 Hz, 1H), 8.85 (d, J = 2.5 Hz, 1H). MS: m/z = 340.07 ($[M]^+$, 100.00), 310.09 (7.43), 294.10 (25.54), 293.10 (60.75), 202.05 (24.60), 176.02 (45.16), 145.72 (38.17), 139.18 (19.35), 91.04 (11.96), 77.03 (8.60), 57.01 (50.54).



6-Bromo-4-phenyl-2-p-tolylquinoline (4c): Mp 103-105 °C. IR (KBr): ν_{max} = 2923, 2853, 1589, 1537, 1481, 878, 834, 770, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3H), 7.34 (d, J = 7.9 Hz, 2H), 7.54-7.58 (m, 5H), 7.78-7.82 (m, 2H), 8.02-8.03 (m, 1H), 8.09-8.10 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4, 119.9, 120.2, 126.9, 127.4, 127.8, 128.7, 128.8, 129.5, 129.7, 131.8, 132.9, 136.4, 137.8, 139.8, 147.5, 148.3, 157.2. MS: m/z = 374.92 ($[M+1]^+$, 97.37), 373.91 ($[M]^+$, 93.86), 372.91 ($[M-1]^+$, 100.00), 371.90 (81.58), 294.02 (63.16), 201.95 (34.21), 146.91 (61.40), 138.98 (37.94), 76.91 (12.94). Anal. calcd for $C_{22}H_{16}BrN$: C, 76.60; H, 4.31; N, 3.74%. Found: C, 76.46; H, 4.27; N, 3.81%.

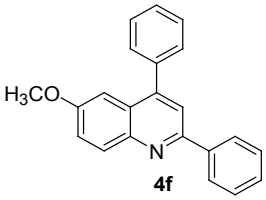


6-Chloro-2,4-diphenylquinoline (4d): Mp: 98-99 °C (Lit.[11f] 98 °C). IR (KBr): ν_{max} = 2922, 2852, 1587, 1543, 1481, 887, 823, 779, 700 cm^{-1}. ^1H NMR (500M Hz, $CDCl_3$): δ = 7.47-7.50 (m, 1H), 7.53-7.60 (m, 7H), 7.68 (dd, J = 9.0, 2.2 Hz, 1H), 7.85 (s, 1H), 7.87 (d, J = 2.0 Hz, 1H), 8.17-8.20 (m, 3H). MS: m/z = 317.08 ($[M+2]^+$, 2.15), 315.03 ($[M]^+$, 8.10), 280.11 (6.22), 238.08 (2.63), 103.05 (20.24), 77.05 (100.00), 51.09 (57.09).



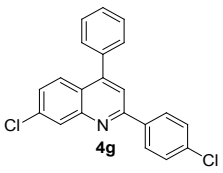
4e

2-(4-Chlorophenyl)-6-methoxy-4-phenylquinoline (4e): Mp 124-125 °C. IR (KBr): ν_{max} = 2923, 1616, 1590, 1488, 1391, 1223, 1090, 831, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.41 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.48 (d, *J* = 11.1 Hz, 2H), 7.52-7.58 (m, 5H), 7.73 (s, 1H), 8.11-8.14 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 55.5, 103.7, 119.2, 122.1, 126.8, 128.5, 128.6, 128.8, 129.0, 129.4, 131.6, 135.2, 138.2, 138.6, 144.9, 148.0, 153.3, 158.0. MS: *m*/*z* = 347.06 ($[M+2]^+$, 35.04), 345.06 ($[M]^+$, 100.00), 330.03 (34.15), 314.05 (11.66), 266.07 (12.39), 218.05 (28.35), 190.05 (31.47), 165.07 (25.22), 138.98 (25.56), 132.52 (29.24), 119.46 (17.41), 74.97 (10.44). Anal. calcd for $C_{22}H_{16}ClNO$: C, 76.41; H, 4.66; N, 4.05%. Found: C, 76.50; H, 4.70; N, 3.97%.



4f

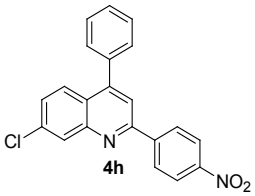
6-Methoxy-2,4-diphenylquinoline (4f): Mp 108-110 °C. IR (KBr): ν_{max} = 3056, 2829, 1619, 1590, 1547, 1489, 1358, 1224, 829, 759, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.81 (s, 3H), 7.20-7.21 (m, 1H), 7.40-7.46 (m, 2H), 7.51-7.60 (m, 7H), 7.79 (s, 1H), 8.15-8.18 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 55.5, 103.7, 119.7, 121.8, 126.7, 127.3, 128.4, 128.7, 128.8, 129.0, 129.4, 131.6, 138.8, 139.8, 140.5, 144.9, 147.8, 154.7, 157.8. MS: *m*/*z* = 313.02 ($[M+2]^+$, 27.84), 311.98 ($[M+1]^+$, 90.59), 310.98 ($[M]^+$, 100.00), 309.95 (96.47), 295.95 (94.12), 279.98 (73.33), 266.99 (72.55), 217.95 (72.55), 189.92 (87.06), 164.97 (70.98), 148.07 (100.00), 133.57 (100.00), 76.91 (76.47). Anal. calcd for $C_{22}H_{17}NO$: C, 84.86; H, 5.50; N, 4.50%. Found: C, 84.96; H, 5.55; N, 4.43%.



4g

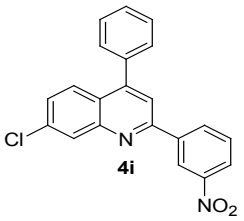
7-Chloro-2-(4-chlorophenyl)-4-phenylquinoline (**4g**): Mp: 125-127 °C (Lit.[10e] 124 °C). IR (KBr): ν_{max} = 2922, 2854, 1588, 1415, 1351, 1094, 882, 834, 766, 697. ^1H NMR (500 MHz, $CDCl_3$): *δ* = 7.43 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.50-7.60 (m, 7H), 7.79 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 8.15 (d, *J* = 8.5 Hz , 2H), 8.22 (d, *J* = 2.0 Hz, 1H). MS: *m*/*z* = 352.89 ($[M+2]^+$, 43.14), 351.89 ($[M+1]^+$, 75.29), 350.89 ($[M]^+$, 89.80), 349.85 (94.51), 347.85 (96.86), 315.91 (65.49), 313.90 (89.41), 278.00 (50.20), 235.96 (45.10), 200.97

(71.76), 175.93 (80.39), 156.94 (86.27), 139.22 (100.00), 124.93 (84.17), 111.94 (49.02), 76.91 (46.27), 74.92 (71.76), 50.97 (59.22).



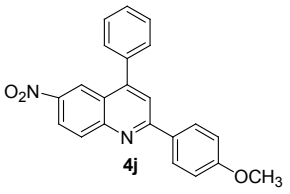
4h

7-Chloro-2-(4-nitrophenyl)-4-phenylquinoline (4h): Mp 218-220 °C. IR (KBr): ν_{max} = 2922, 1587, 1512, 1345, 1073, 860, 740, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.49 (dd, J = 9.0 Hz, 1.7, 1H), 7.54-7.60 (m, 5H), 7.87-7.90 (m, 2H), 8.27 (d, J = 1.5 Hz, 1H), 8.40 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 119.2, 124.1, 124.7, 127.2, 128.2, 128.4, 128.9, 129.0, 129.2, 129.4, 136.1, 137.5, 145.0, 146.2, 149.4, 150.0, 155.1. MS: m/z = 362.06 ($[M+2]^+$, 4.53), 361.04 ($[M+1]^+$, 12.58), 360.10 ($[M]^+$, 22.40), 359.04 (11.53), 330.08 (13.47), 314.09 (7.79), 279.14 (12.91), 265.10 (6.90), 201.10 (19.48), 176.00 (36.36), 149.99 (23.38), 76.94 (63.96), 57.08 (83.12), 50.99 (100.00). Anal. calcd for $C_{21}H_{13}ClN_2O_2$: C, 69.91; H, 3.63; N, 7.76%. Found: C, 70.05; H, 3.69; N, 7.67%.



4i

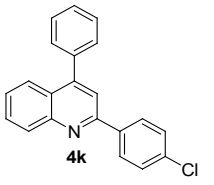
7-Chloro-2-(3-nitrophenyl)-4-phenylquinoline (4i): Mp 149-151 °C. IR (KBr): ν_{max} = 2920, 1579, 1533, 1486, 1349, 1105, 1079, 928, 883, 765, 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.42 (m, 1H), 7.46-7.49 (m, 2H), 7.55-7.60 (m, 2H), 7.67-7.74 (m, 2H), 7.82 (s, 1H), 7.87-7.90 (m, 1H), 8.22-8.27 (m, 1H), 8.33 (d, J = 8.9 Hz, 1H), 8.57-8.60 (m, 1H), 9.06-9.07 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 118.8, 122.0, 122.5, 124.2, 127.2, 127.8, 128.1, 128.9, 129.1, 129.5, 129.6, 129.9, 130.1, 133.3, 140.8, 149.8, 153.5. MS: m/z = 360.11 ($[M]^+$, 4.48), 325.10 (5.64), 313.93 (2.59), 279.17 (2.02), 278.19 (6.08), 201.91 (4.48), 175.98 (6.53), 149.04 (7.80), 76.87 (50.88), 57.04 (100.00). Anal. calcd for $C_{21}H_{13}ClN_2O_2$: C, 69.91; H, 3.63; N, 7.76%. Found: C, 70.02; H, 3.67; N, 7.69%.



4j

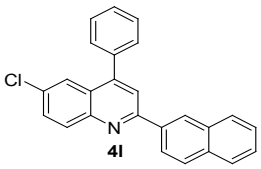
2-(4-Methoxyphenyl)-6-nitro-4-phenylquinoline (**4j**): Mp: 220-221 °C (Lit.[18d] 221 °C). IR (KBr): ν_{max} = 2922, 2852, 1643, 1593, 1479, 1253, 1095, 954, 796, 761 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.91 (s, 3H), 7.07 (d, J = 8.8, 2H), 7.56-7.64

(m, 5H), 7.94 (s, 1H), 8.24 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 9.3 Hz, 1H), 8.47 (dd, J = 9.3, 2.5 Hz, 1H), 8.80 (d, J = 2.5 Hz, 1H). MS: m/z = 356.10 ($[M]^+$, 100.00), 326.06 (2.85), 309.09 (25.00), 267.11 (6.84), 241.11 (5.38), 202.09 (8.29), 176.08 (12.95), 169.68 (8.10), 132.79 (16.58), 120.54 (9.20), 63.03 (8.00), 57.11 (4.81).



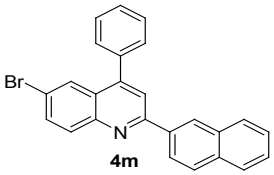
4k

2-(4-Chlorophenyl)-4-phenylquinoline (4k): Mp: 98-100 °C (Lit.[12a] 98 °C). IR (KBr): ν_{max} = 2928, 1618, 1508, 1487, 1277, 1177, 1089, 1013, 819, 755 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 6.63 (d, J = 9.5 Hz, 3H), 6.72 (d, J = 9.0 Hz, 2H), 6.79 (t, J = 9.0 Hz, 1H), 6.89 (d, J = 9.5 Hz, 3H), 7.06 (d, J = 9.5 Hz, 2H), 7.19 (t, J = 9.0 Hz, 1H), 7.24-7.28 (m, 2H).



4l

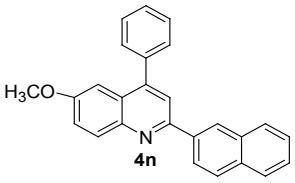
6-Chloro-2-(naphthalen-3-yl)-4-phenylquinoline (4l): Mp: 143-145 °C (Lit.[12a] 143 °C). IR (KBr): ν_{max} = 2921, 2851, 1588, 1541, 1480, 1360, 1151, 875, 838, 744, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.54-7.61 (m, 7H), 7.70 (dd, J = 9.0, 2.1 Hz, 1H), 7.89-7.92 (m, 2H), 7.98-8.02 (m, 3H), 8.23 (d, J = 9.0 Hz, 1H), 8.40 (d, J = 8.6 Hz, 1H), 8.64 (s, 1H). MS: m/z = 366.98 ($[M+2]^+$, 74.51), 365.98 ($[M+1]^+$, 77.65), 364.98 ($[M]^+$, 90.59), 363.96 (85.49), 330.04 (55.29), 328.02 (45.10), 235.97 (21.67), 200.95 (34.12), 164.50 (100.00), 162.97 (65.88), 149.93 (40.00), 76.88 (17.65).



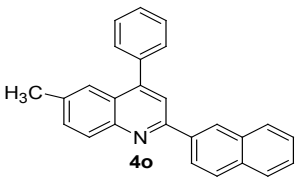
4m

6-Bromo-2-(naphthalen-2-yl)-4-phenylquinoline (4m): Mp 151-153 °C. IR (KBr): ν_{max} = 3050, 1587, 1536, 1507, 1481, 1362, 1188, 1130, 1068, 809, 767, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.54-7.63 (m, 7H), 7.83 (dd, J = 7.8, 2.1 Hz, 1H), 7.90-7.92 (m, 1H), 7.98-8.02 (m, 3H), 8.06 (d, J = 2.3 Hz, 1H), 8.16 (d, J = 8.9 Hz, 1H), 8.40 (dd, J = 8.5, 1.7 Hz, 1H), 8.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.2, 120.5, 124.9, 126.5, 126.9, 127.3, 127.8, 127.9, 128.7, 128.8, 128.9, 129.5, 131.9, 133.1, 133.5,

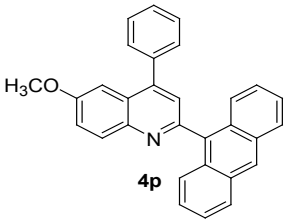
134.0, 136.5, 137.8, 147.5, 148.5, 157.0. MS: *m/z* = 411.13 ($[M+2]^+$, 97.73), 409.12 ($[M]^+$, 100.00), 330.18 (42.33), 328.16 (39.49), 201.18 (22.73), 164.96 (49.15), 164.09 (55.68), 150.07 (24.72), 77.07 (15.41). Anal. calcd for $C_{22}H_{16}BrN$: C, 73.18; H, 3.93; N, 3.41%. Found: C, 73.07; H, 3.88; N, 3.48%.



6-Methoxy-2-(naphthalen-2-yl)-4-phenylquinoline (4n): Mp 119-120 °C. IR (KBr): ν_{max} = 3050, 2931, 1621, 1589, 1553, 1493, 1370, 1227, 1029, 856, 815, 746, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 3H), 7.45 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.53-7.65 (m, 7H), 7.90-7.92 (m, 1H), 7.96-8.01 (m, 3H), 8.23 (d, *J* = 9.1 Hz, 1H), 8.42 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.64 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 55.5, 103.8, 119.8, 121.9, 125.0, 126.3, 126.6, 126.7, 127.8, 128.4, 128.6, 128.8, 129.5, 131.7, 133.6, 133.8, 137.1, 138.8, 145.1, 147.9, 154.4, 157.9. MS: *m/z* = 362.10 ($[M+1]^+$, 74.88), 361.08 ($[M]^+$, 100.00), 346.05 (79.80), 317.07 (18.10), 289.03 (8.62), 218.06 (28.20), 190.07 (36.95), 164.03 (64.53), 157.58 (41.38), 144.53 (21.31), 77.02 (13.92). Anal. calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88%. Found: C, 86.36; H, 5.26; N, 3.92%.

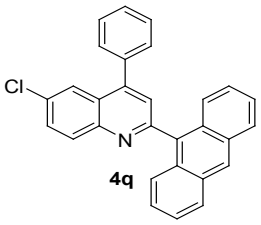


6-Methyl-2-(naphthalen-2-yl)-4-phenylquinoline (4o): Mp 161-163 °C. IR (KBr): ν_{max} = 3046, 2917, 2854, 1587, 1508, 1434, 1128, 1030, 885, 864, 820, 760, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.51 (s, 3H), 7.53-7.63 (m, 8H), 7.70 (s, 1H), 7.90-7.92 (m, 1H), 7.96 (s, 1H), 7.99-8.02 (m, 2H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.42 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.65 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 21.9, 119.6, 124.5, 125.1, 126.3, 126.6, 127.0, 127.8, 128.4, 128.6, 128.7, 128.8, 129.6, 129.9, 131.9, 133.6, 136.4, 137.1, 138.7, 147.6, 148.5, 155.8. MS: *m/z* = 346.12 ($[M+2]^+$, 65.64), 345.08 ($[M]^+$, 100.00), 344.09 (88.72), 330.08 (79.49), 328.06 (18.21), 268.09 (9.36), 216.10 (24.10), 172.67 (33.33), 165.02 (90.77), 164.07 (70.77), 118.07 (40.00), 114.06 (56.41), 74.07 (69.23). Anal. calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05%. Found: C, 90.33; H, 5.58; N, 4.01%.



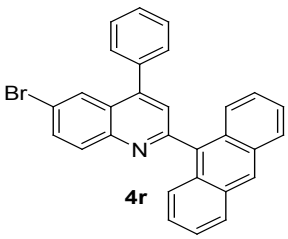
4p

2-(Anthracen-9-yl)-6-methoxy-4-phenylquinoline (4p): Mp 234-236 °C. IR (KBr): ν_{max} = 3047, 2928, 2826, 1617, 1586, 1488, 1399, 1265, 1221, 1030, 884, 846, 733, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.90 (s, 3H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 2.7 Hz, 1H), 7.46-7.56 (m, 6H), 7.58 (s, 1H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 8.24 (d, *J* = 9.1 Hz, 1H), 8.58 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 55.6, 103.9, 122.1, 125.2, 126.0, 126.2, 126.6, 127.7, 128.5, 128.6, 128.8, 129.6, 130.3, 131.5, 131.8, 135.3, 138.3, 145.1, 147.3, 155.9, 158.3. MS: *m/z* = 412.12 ($[M+2]^+$, 71.36), 411.09 ($[M+1]^+$, 95.45), 410.07 ($[M]^+$, 100.00), 394.04 (12.27), 367.05 (67.27), 334.05 (59.09), 291.05 (15.00), 189.05 (64.55), 76.95 (11.93). Anal. calcd for $C_{30}H_{21}NO$: C, 87.56; H, 5.14; N, 3.40%. Found: C, 87.68; H, 5.08; N, 3.49%.



4q

2-(Anthracen-9-yl)-6-chloro-4-phenylquinoline (4q): Mp 224-226 °C. IR (KBr): ν_{max} = 3049, 2923, 1589, 1542, 1479, 1441, 1377, 1311, 886, 827, 734, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.52–7.57 (m, 3H), 7.62-7.66 (m, 3H), 7.69 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 1H), 8.08-8.11 (m, 3H), 8.27 (d, *J* = 8.9 Hz, 1H), 8.60 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 124.7, 125.3, 125.6, 125.9, 126.2, 126.4, 128.0, 128.6, 128.9, 129.7, 130.1, 130.7, 131.5, 131.9, 133.0, 134.7, 137.2, 147.4, 147.9, 158.8. MS: *m/z* = 417.25 ($[M+1]^+$, 8.97), 415.20 ($[M]^+$, 26.63), 378.23 (5.43), 340.16 (5.30), 338.12 (7.34), 302.26 (6.39), 224.13 (2.45), 201.04 (11.35), 176.09 (18.21), 150.10 (14.13), 99.05 (7.47), 76.99 (100.00). Anal. calcd for $C_{29}H_{18}ClN$: C, 83.75; H, 4.36; N, 3.37%. Found: C, 83.89; H, 4.40; N, 3.42%.

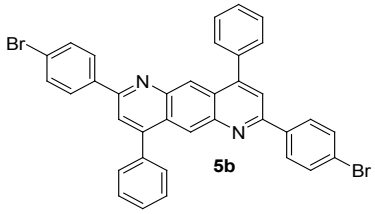


4r

2-(Anthracen-9-yl)-6-bromo-4-phenylquinoline (4r): Mp 207-209 °C. IR (KBr): ν_{max} = 2922, 2850, 1585, 1538, 1448, 1143, 877, 780, 735, 700 cm^{-1}. ^1H NMR

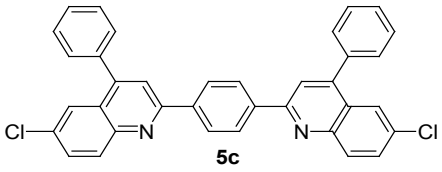
(500 MHz, $CDCl_3$): δ = 7.38-7.41 (m, 2H), 7.47-7.58 (m, 5H), 7.61-7.63 (m, 3H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.90 (dd, *J* = 8.9, 2.1 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.9 Hz, 1H), 8.27 (d, *J* = 2.1 Hz, 1H), 8.60 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): *δ* = 118.7, 121.2, 125.2, 125.6, 125.9, 126.2, 126.9, 128.0, 128.6, 128.9, 129.7, 130.1, 131.5, 132.0, 133.3, 134.7, 137.2, 147.6, 147.8, 159.0. MS: *m*/*z* = 462.20 ($[M+2]^+$, 9.23), 461.18 ($[M+1]^+$, 32.48), 460.18 ($[M]^+$, 44.63), 458.18 (38.55), 378.21 (26.40), 310.23 (17.06), 202.16 (21.50), 191.21 (100.00), 189.37 (75.70), 188.36 (34.58), 176.09 (20.09), 105.09 (47.43), 77.06 (91.59). Anal. calcd for $C_{22}H_{18}BrN$: C, 75.66; H, 3.94; N, 3.04%. Found: C, 75.53; H, 3.99; N, 3.08%.

2,7-Bis(2,4-dichlorophenyl)-4,9-diphenylpyrido[2,3-g]quinoline (5a): Mp 325-327 °C. IR (KBr): ν_{max} = 3059, 2921, 2852, 1585, 1536, 1473, 1385, 890, 858, 827, 788, 761, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.60 (s, 2H), 6.77 (s, 2H), 7.05-7.06 (m, 4H), 7.18-7.19 (m, 2H), 7.44 (s, 4H), 7.57 (s, 2H), 7.92 (d, *J* = 7.6 Hz, 2H), 8.25 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.8, 123.8, 126.8, 127.4, 127.7, 130.1, 132.4, 132.7, 133.3, 135.5, 137.1, 140.7, 149.1, 150.1, 155.3. Anal. calcd for $C_{36}H_{20}Cl_4N_2$: C, 69.47; H, 3.24; N, 4.50%. Found: C, 69.59; H, 3.28; N, 4.41%.



5b

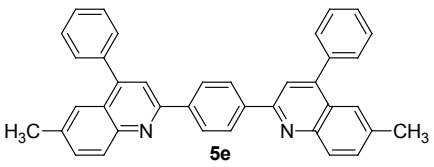
2,7-Bis(4-bromophenyl)-4,9-diphenylpyrido[2,3-g]quinoline (5b): Mp 235-236 °C. IR (KBr): ν_{max} = 2916, 2875, 1615, 1584, 1561, 1492, 1400, 1360, 1189, 1063, 846, 819, 707 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11 (d, *J* = 8.4 Hz, 2H), 7.32 (s, 4H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 6H), 7.75-7.84 (m, 6H), 8.49 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 121.3, 121.9, 126.0, 129.6, 130.2, 130.3, 131.0, 131.5, 132.1, 132.2, 132.5, 135.1, 149.8, 158.4, 160.3. Anal. calcd for $C_{38}H_{22}Br_2N_2$: C, 67.31; H, 3.45; N, 4.36%. Found: C, 67.45; H, 3.49; N, 4.28%.



5c

6-Chloro-2-(4-(6-chloro-4-phenylquinolin-2-yl)phenyl)-4-phenylquinoline (5c): Mp 266-268 °C. IR (KBr): ν_{max} = 2922, 2852, 1585, 1544, 1483, 1348, 1153, 1066, 881, 832, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 7.55-7.62 (m, 10H), 7.70 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.89 (d, *J* = 2.0 Hz, 2H), 7.93 (s, 2H), 8.22 (d, *J* = 8.9 Hz, 2H), 8.38 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 120.0, 124.6, 126.7, 128.0, 128.8, 128.9, 129.5, 130.6, 131.8, 132.4, 135.3, 137.8, 138.6, 148.6, 156.3. MS: *m*/*z* = 554.29 ($[M+1]^+$, 19.90), 553.36 ($[M]^+$, 17.09), 552.29 ($[M-1]^+$, 27.55), 517.33 (2.97), 339.12 (5.29), 278.10 (25.26), 238.07 (15.24), 202.08 (52.04), 176.02 (100.00), 151.02 (35.97), 76.98 (45.41), 57.05 (38.78), 55.07 (74.49). Anal. calcd for $C_{36}H_{22}Cl_2N_2$: C, 78.12; H, 4.01; N, 5.06%. Found: C, 77.99; H, 4.05; N, 5.13.

6-Methoxy-2-(4-(6-methoxy-4-phenylquinolin-2-yl)phenyl)-4-phenylquinoline (5d): Mp 144-146 °C. IR (KBr): ν_{max} = 2923, 2850, 1619, 1542, 1482, 1221, 1030, 816, 765, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.82 (s, 6H) , 7.25-7.26 (m, 2H), 7.42 (td, *J* = 9.0, 2.7 Hz, 4H), 7.51-7.60 (m, 10H), 7.64 (s, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 8.13 (d, *J* = 9.1 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.5, 103.7, 122.1, 123.1, 126.8, 127.5, 128.5, 128.8, 129.4, 129.9, 131.6, 132.7, 135.0, 138.3, 146.9, 153.4, 158.3. MS: *m*/*z* = 544.57 ($[M]^+$, 4.87), 339.19 (3.00), 284.02 (2.08), 280.08 (4.93), 240.10 (2.61), 239.14 (4.82), 193.06 (3.56), 176.05 (7.17), 164.02 (13.88), 104.96 (21.10), 91.02 (18.58), 76.98 (47.25), 57.08 (52.06), 55.05 (100.00). Anal. calcd for $C_{38}H_{28}N_2O_2$: C, 83.80; H, 5.18; N, 5.14%. Found: C, 83.69; H, 5.14; N, 5.07%.



5e

6-Methyl-2-(4-(6-methyl-4-phenylquinolin-2-yl)phenyl)-4-phenylquinoline (5e): Mp 275-277 °C. IR (KBr): ν_{max} = 3046, 2922, 2853, 1589, 1546, 1487, 1461, 1346, 1073, 876, 836, 820, 764, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 6H), 7.19-7.21 (m, 2H), 7.55-7.67 (m, 13H), 7.86 (s, 2H), 8.18 (d, *J* = 8.7 Hz, 2H), 8.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.8, 119.4, 120.9, 124.5, 125.9,

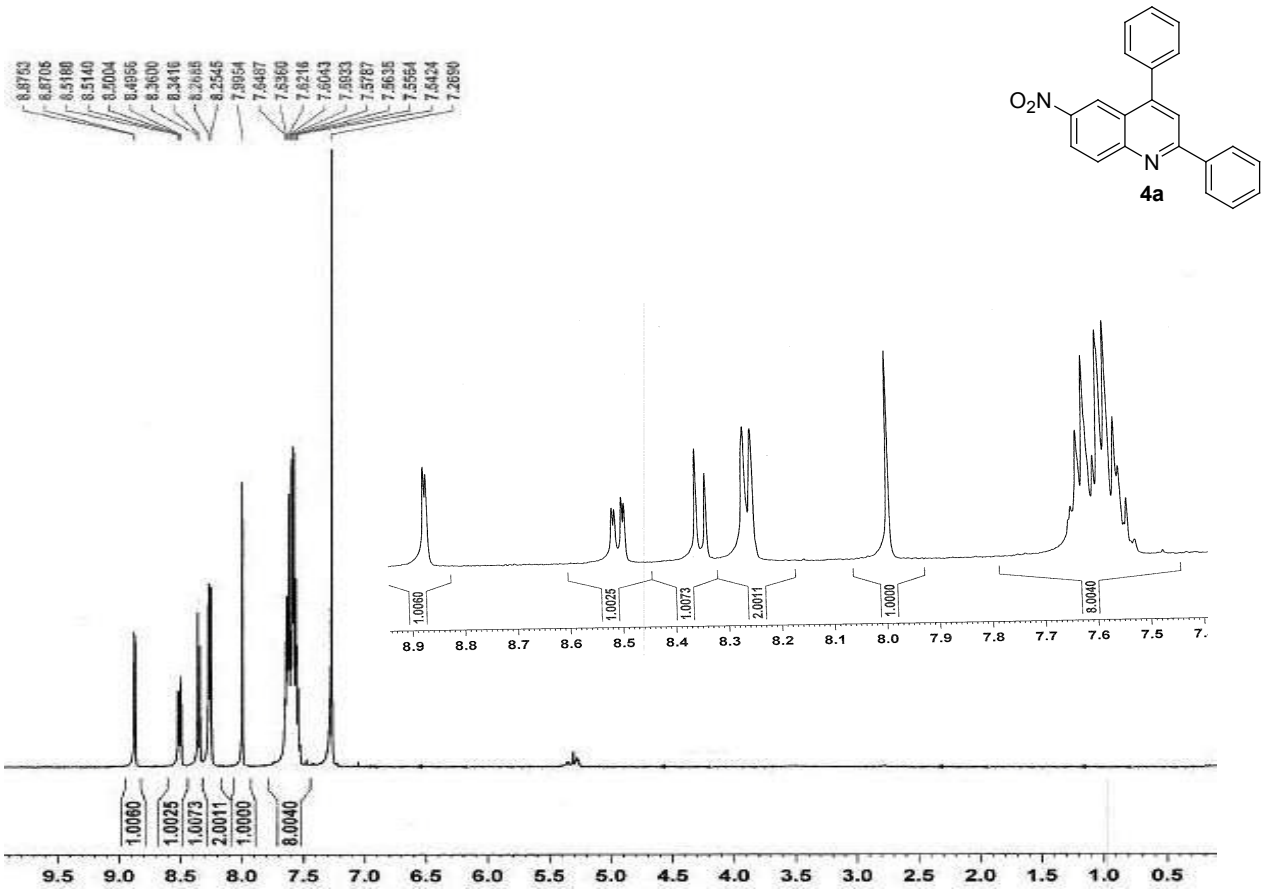
127.9, 128.6, 129.6, 129.9, 131.9, 136.5, 138.7, 140.3, 147.5, 148.6, 155.4. Anal. calcd for $C_{38}H_{28}N_2$: C, 89.03; H, 5.51; N, 5.46%. Found: C, 88.92; H, 5.47; N, 5.51%.

(*10e*) S. Rotzoll, B. Willy, J. Schoenhaber, T. J. Mueller, F. Rominger, *Eur. J. Org. Chem.,* 2010, 3516.

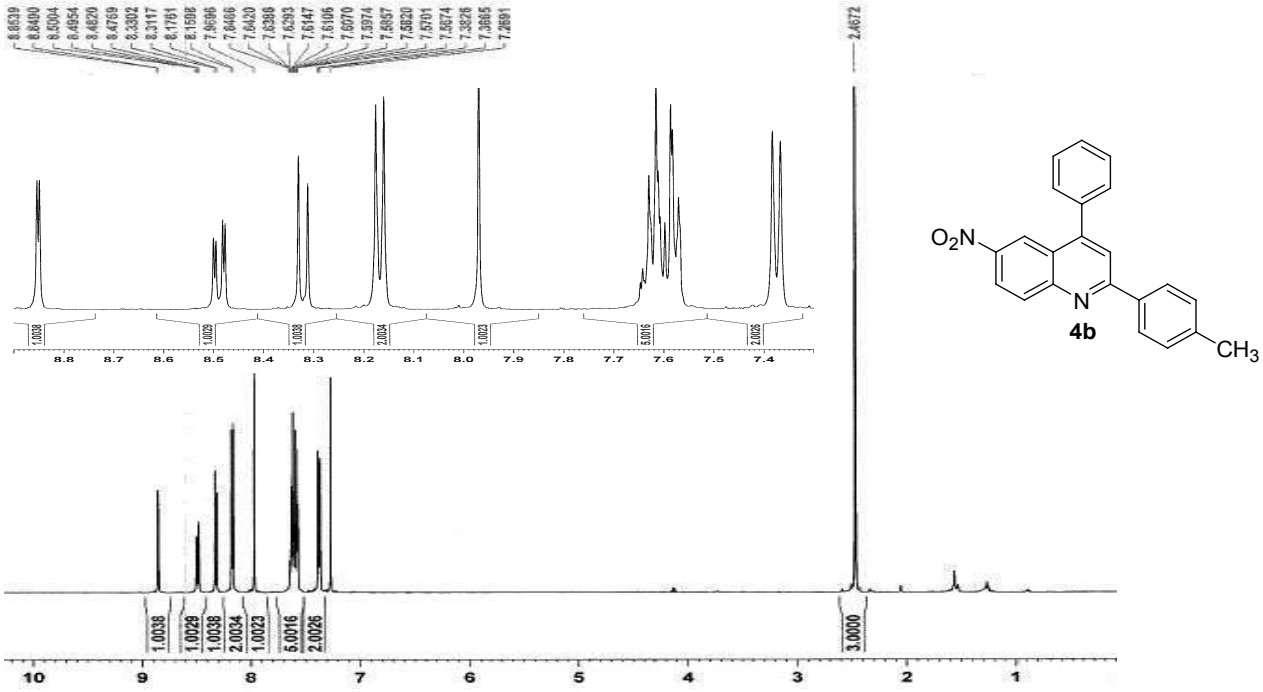
(*10f*) R. Leardini, D. Nanni, A. Tundo, G. Zanardi, F. Ruggieri, *J. Org. Chem.*, 1992, **57**, 1843.

(*12a*) H. M. Mack, E. A. Davis, B. Kadkhodayan, R. A. Taylor, D. C. Duncan, C. F. Beam, *J. Heterocycl. Chem*., 1987, **24**, 1733;

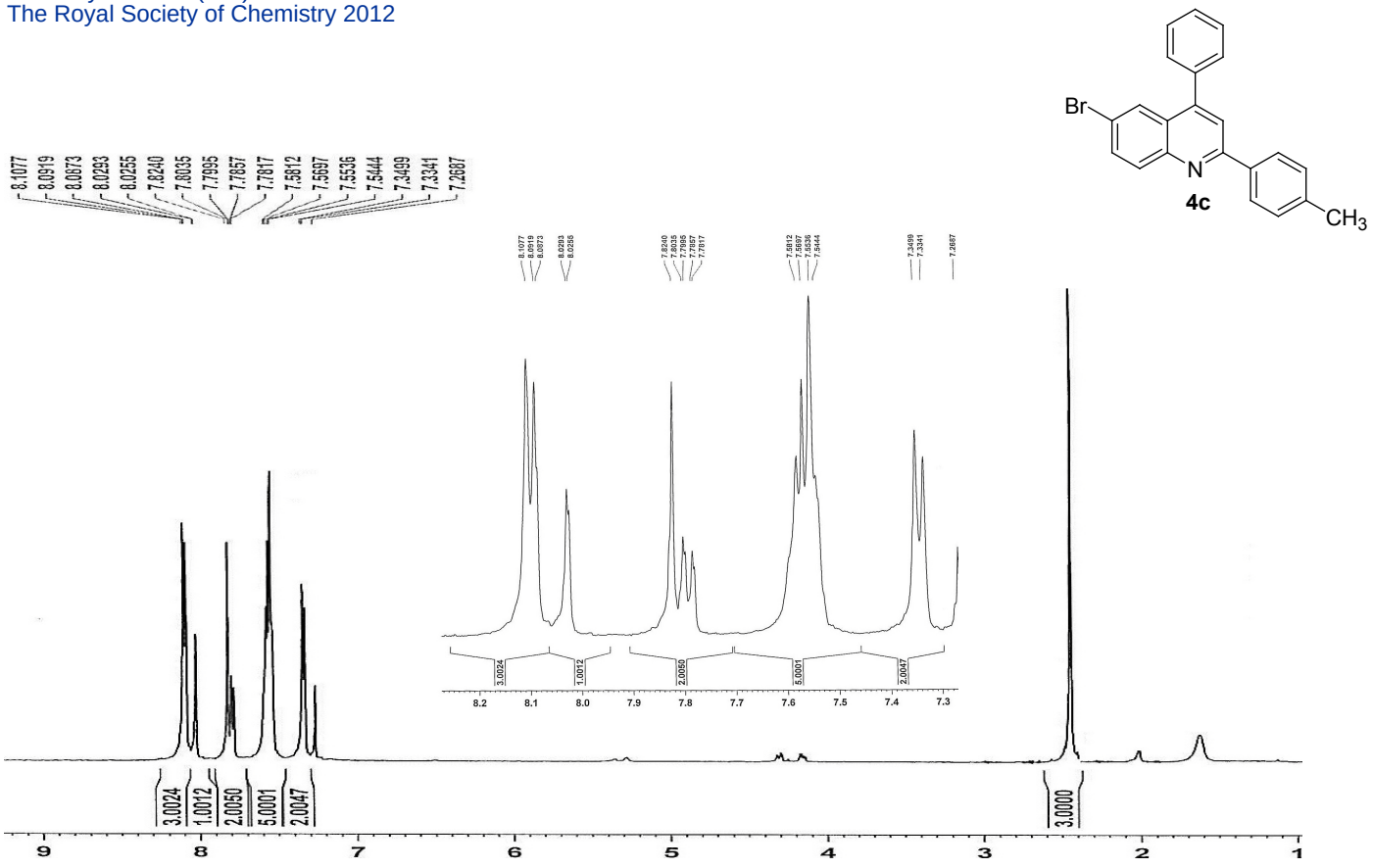
(*18d*) I. Mohammadpoor-Baltork, S. Tangestaninejad, M. Moghadam, V. Mirkhani, S. Anvar and A. Mirjafari, *Synlett,* 2010, 3104;



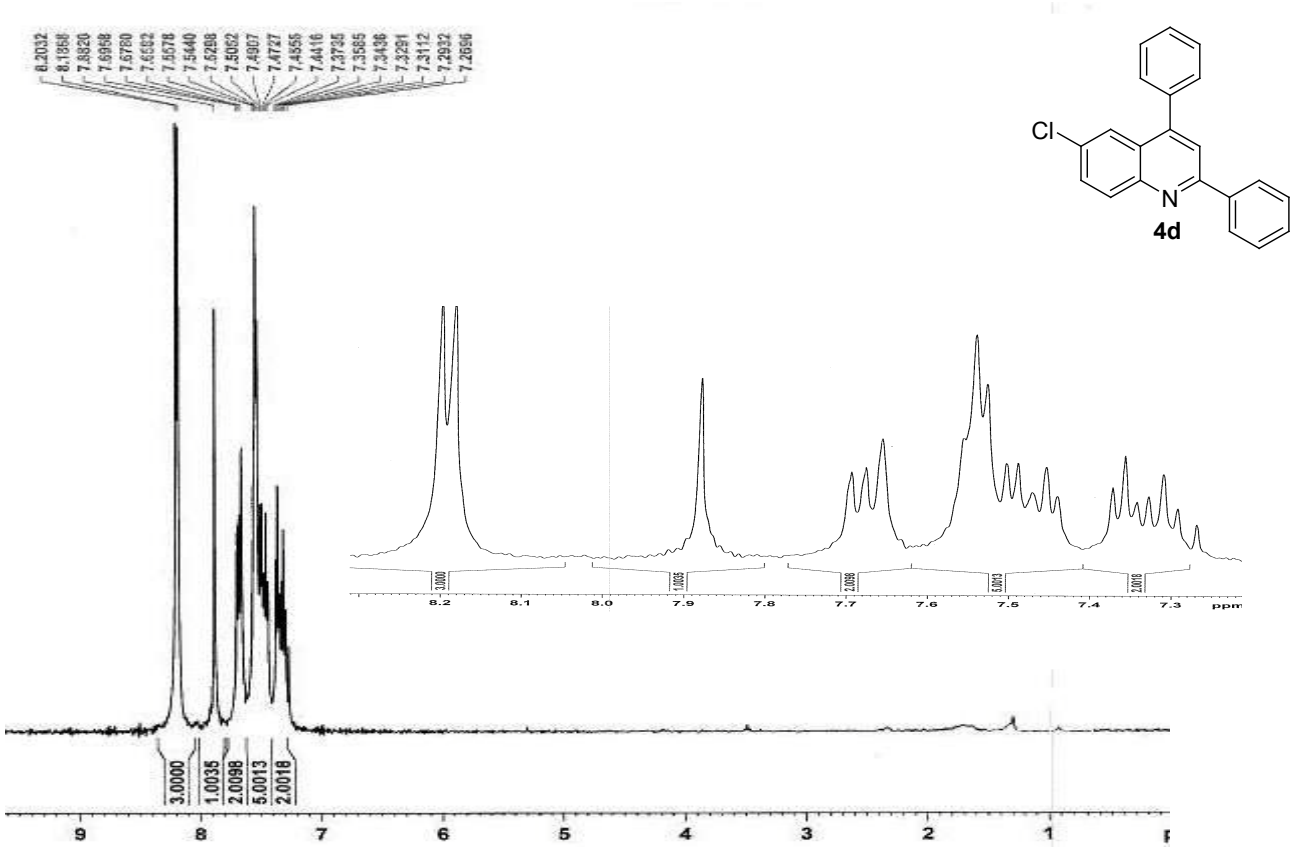
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4a



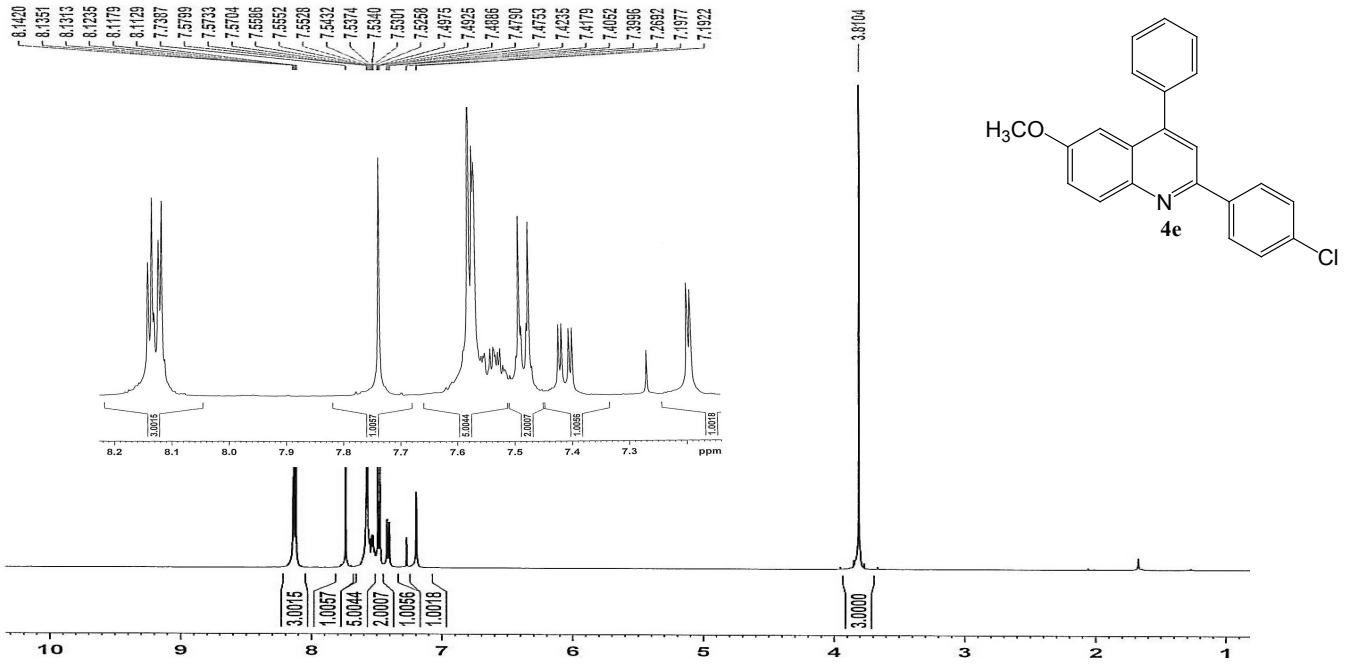
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4b



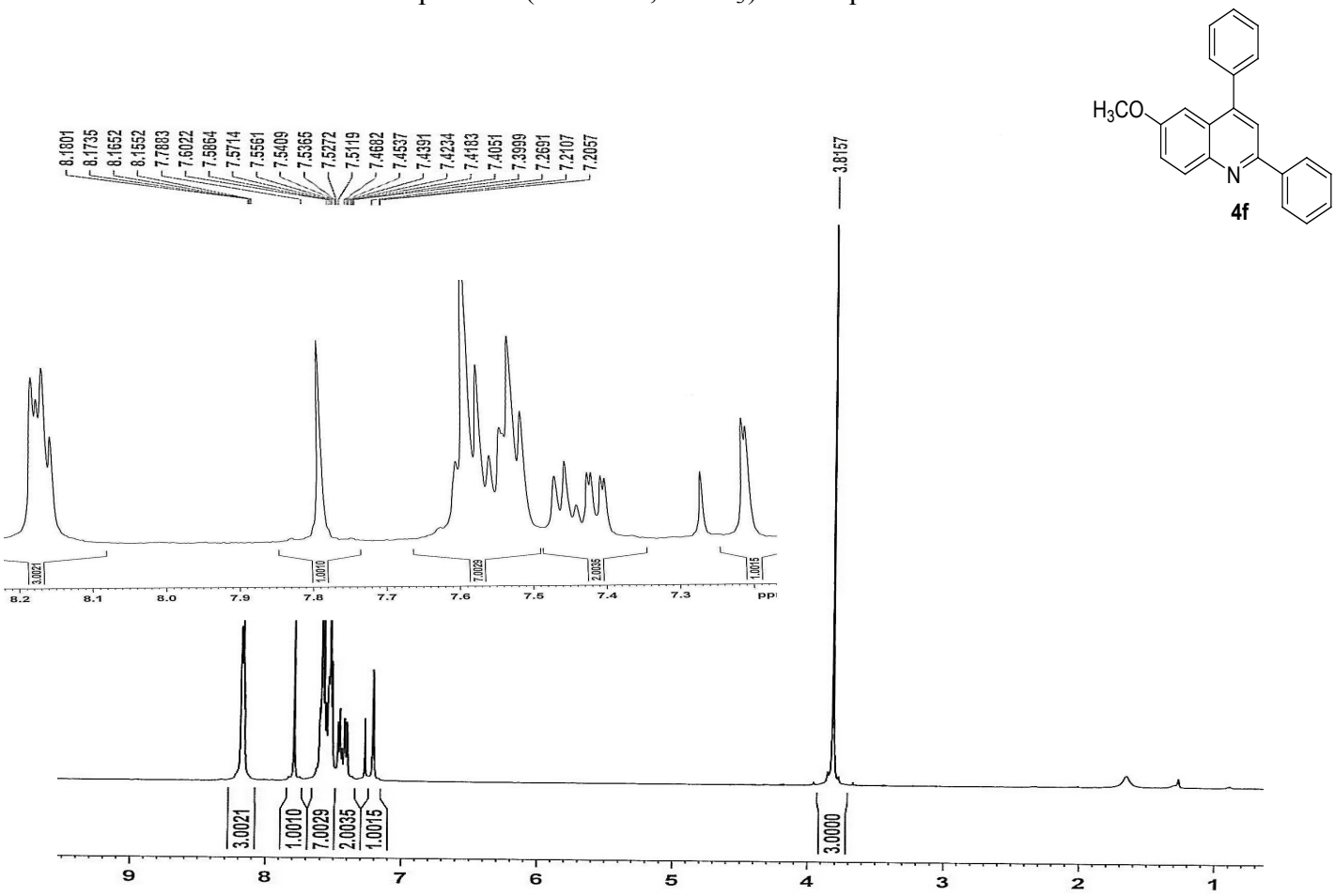
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4c



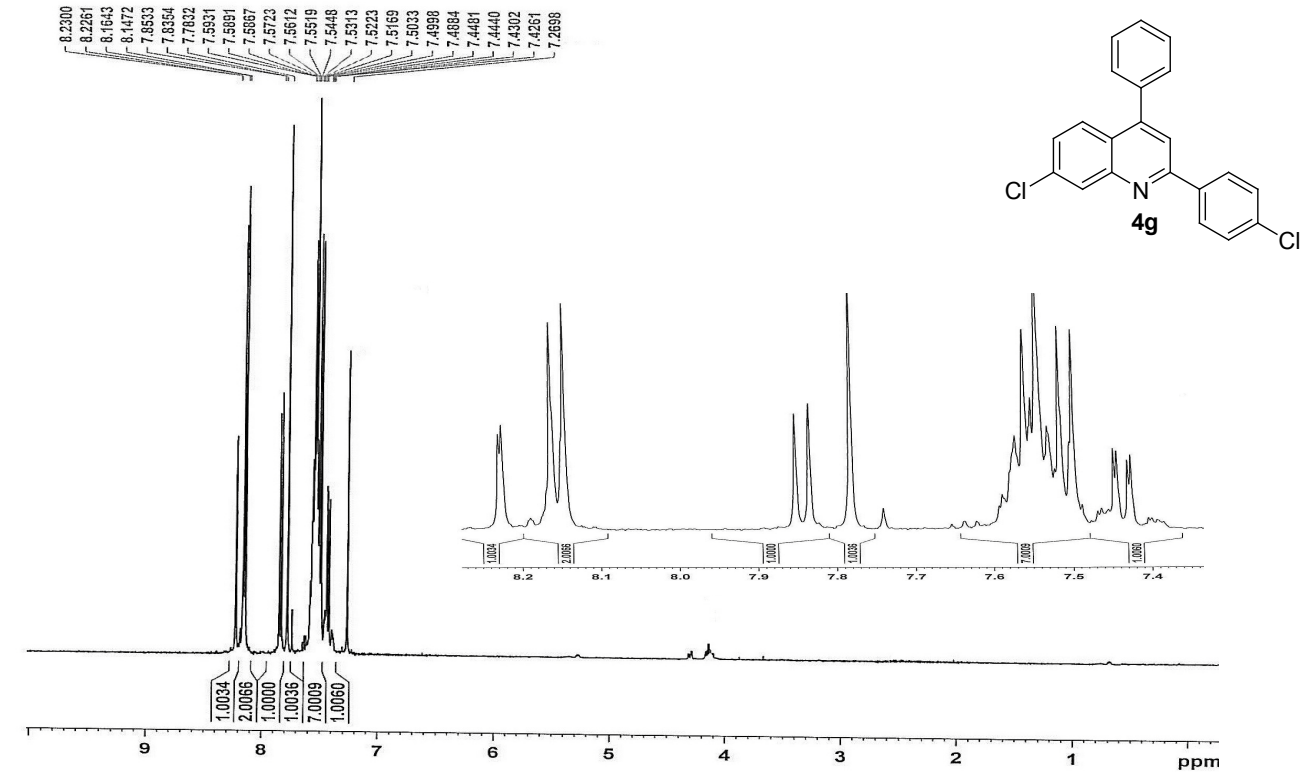
^{13}C NMR Spectrum (125 MHz, $CDCl_3$) of compound 4d



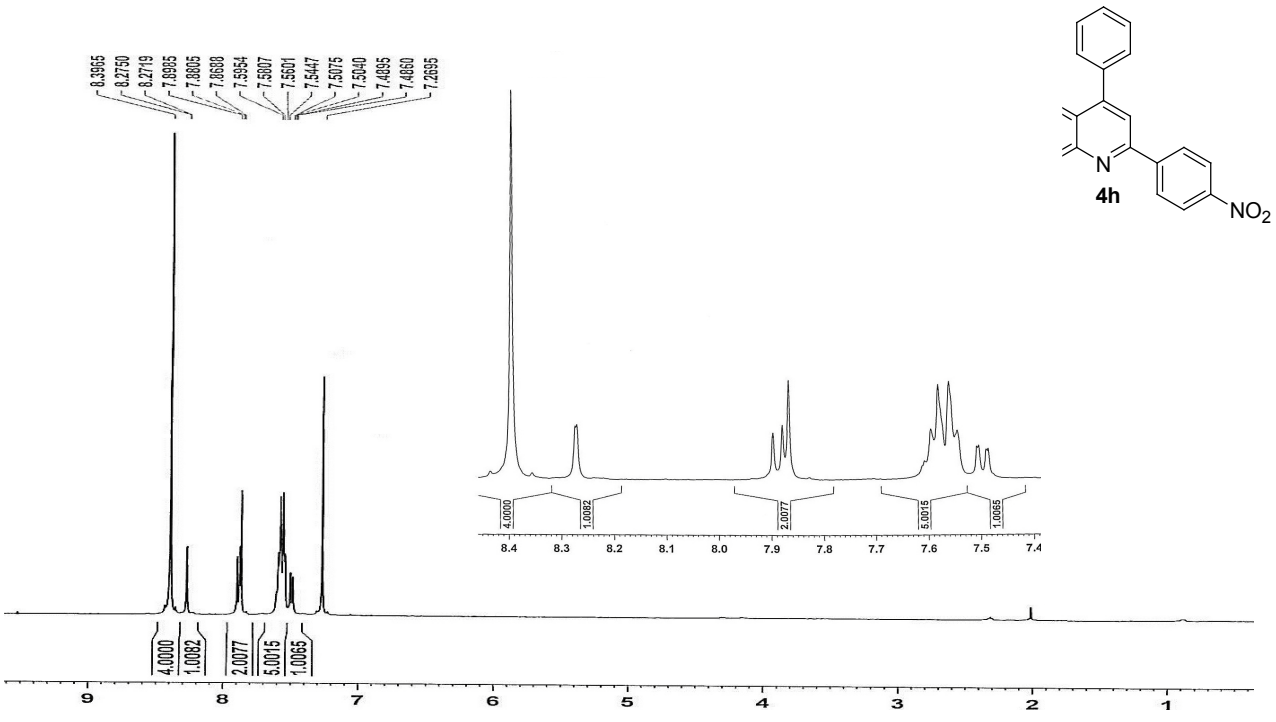
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4e



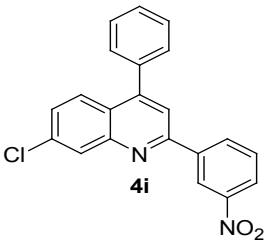
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4f

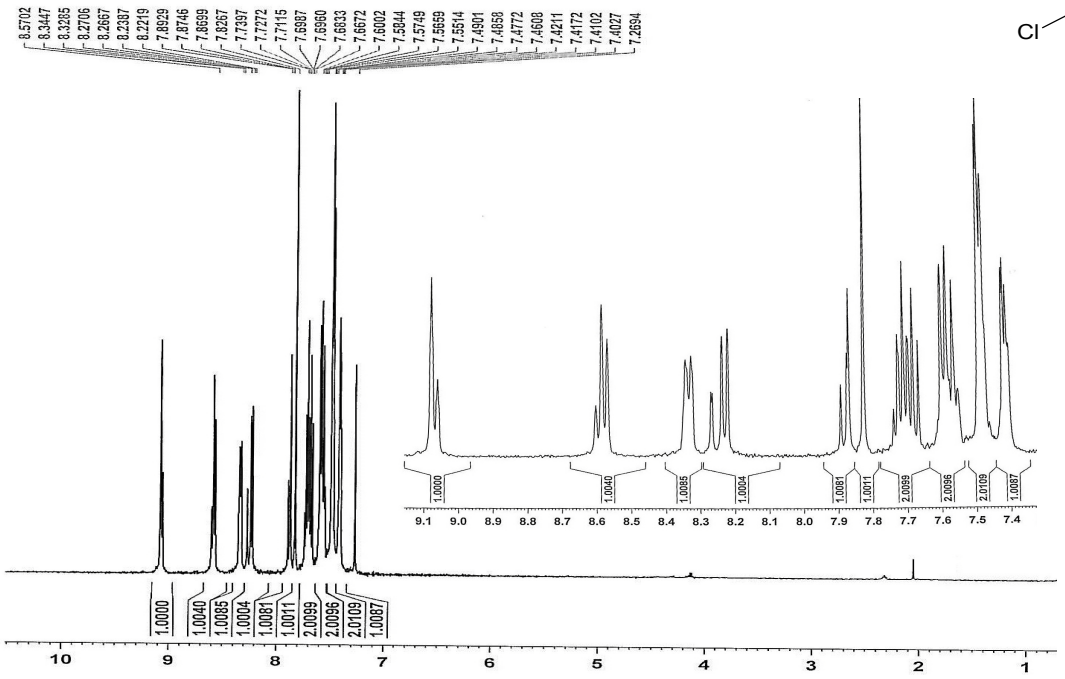


^{1}H NMR Spectrum (500MHz, $CDCl_3$) of compound 4g

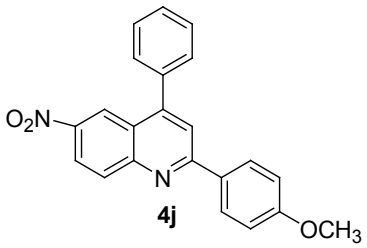


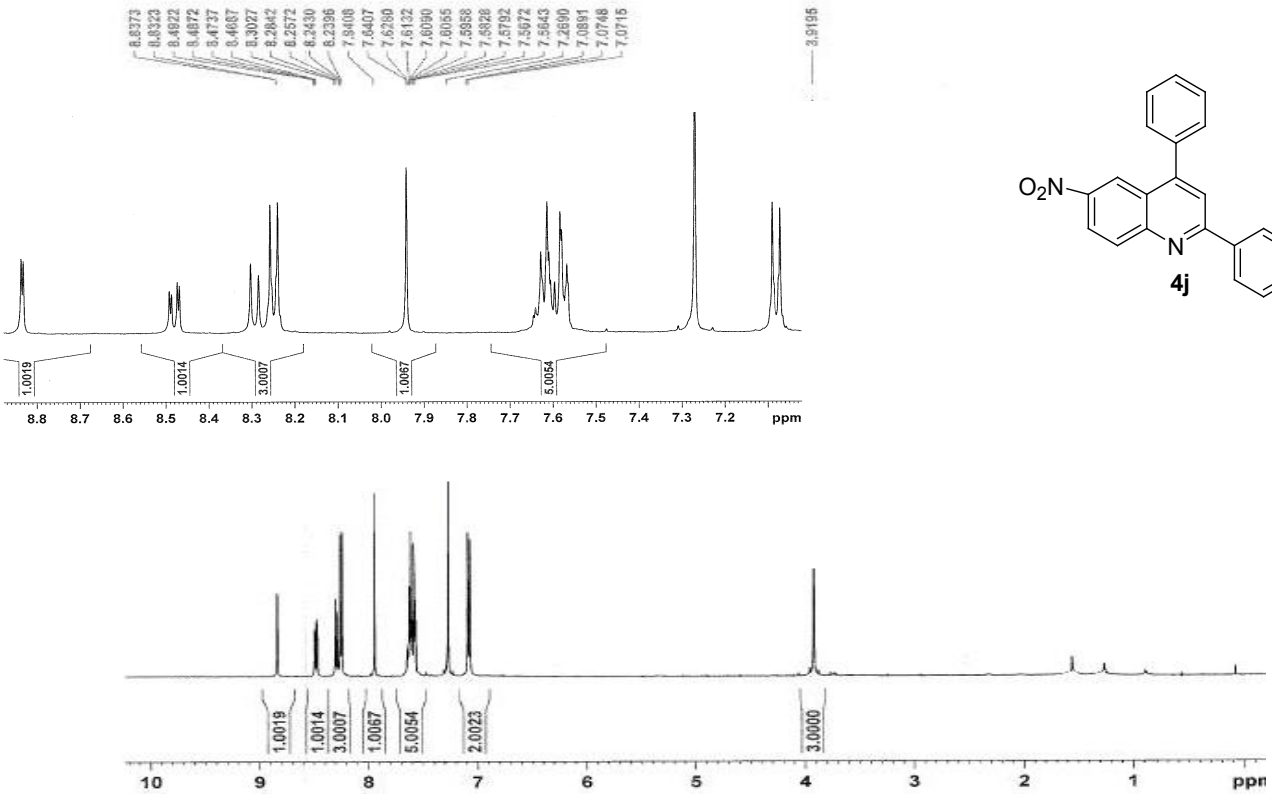
^{1}H NMR Spectrum (500MHz, $CDCl_3$) of compound 4h



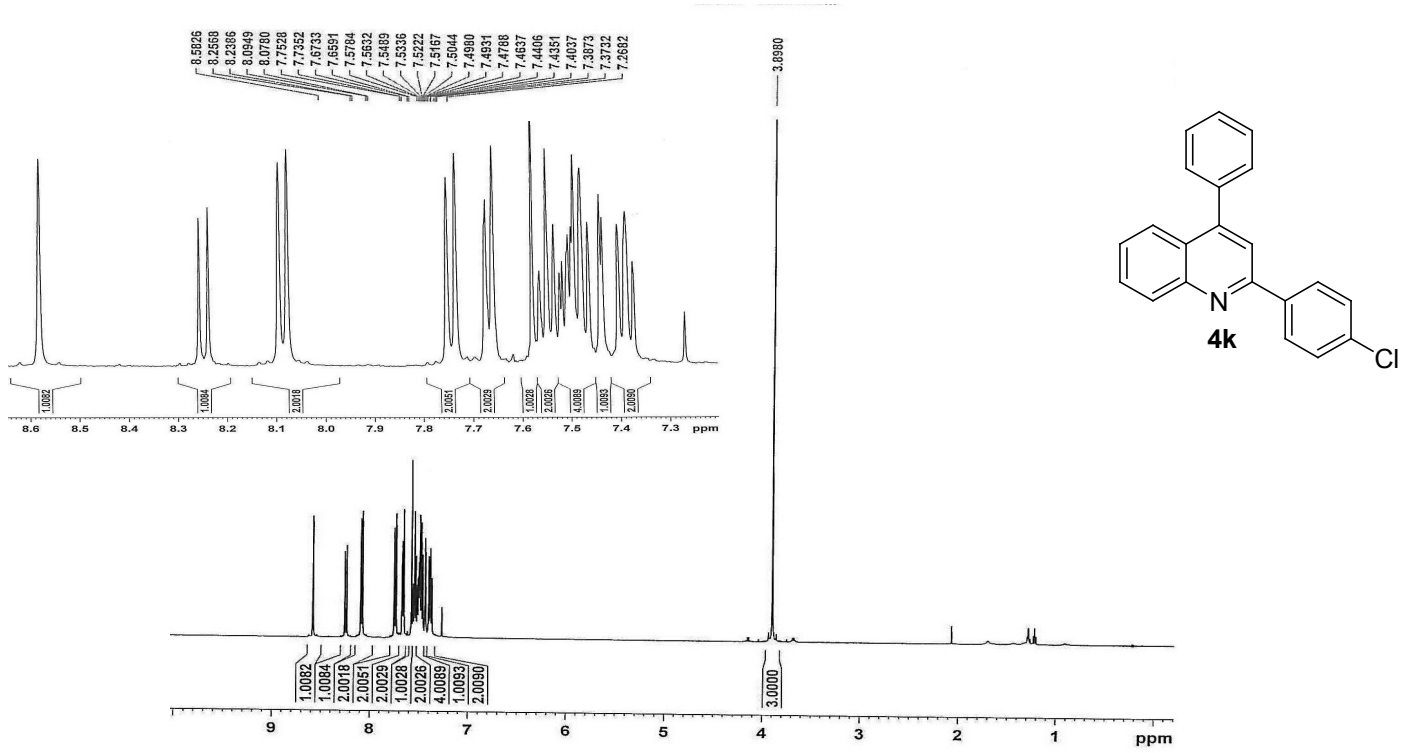


^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4i

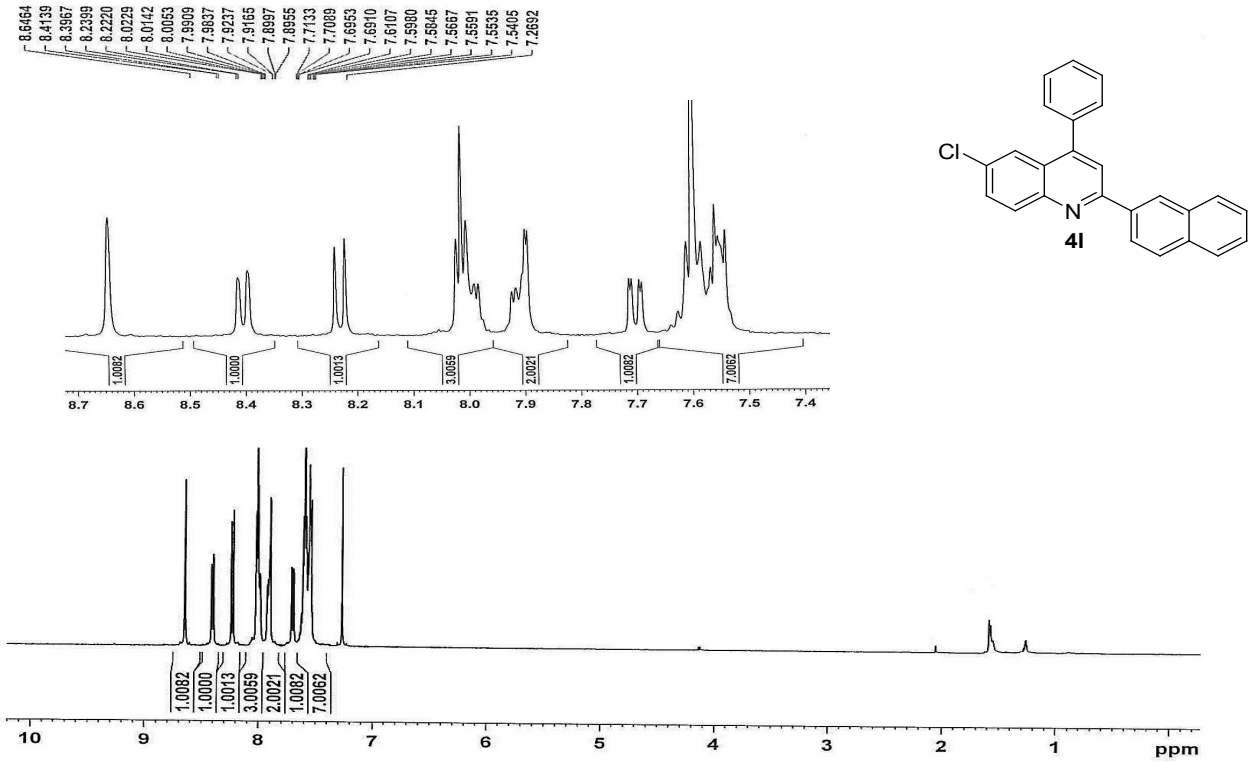




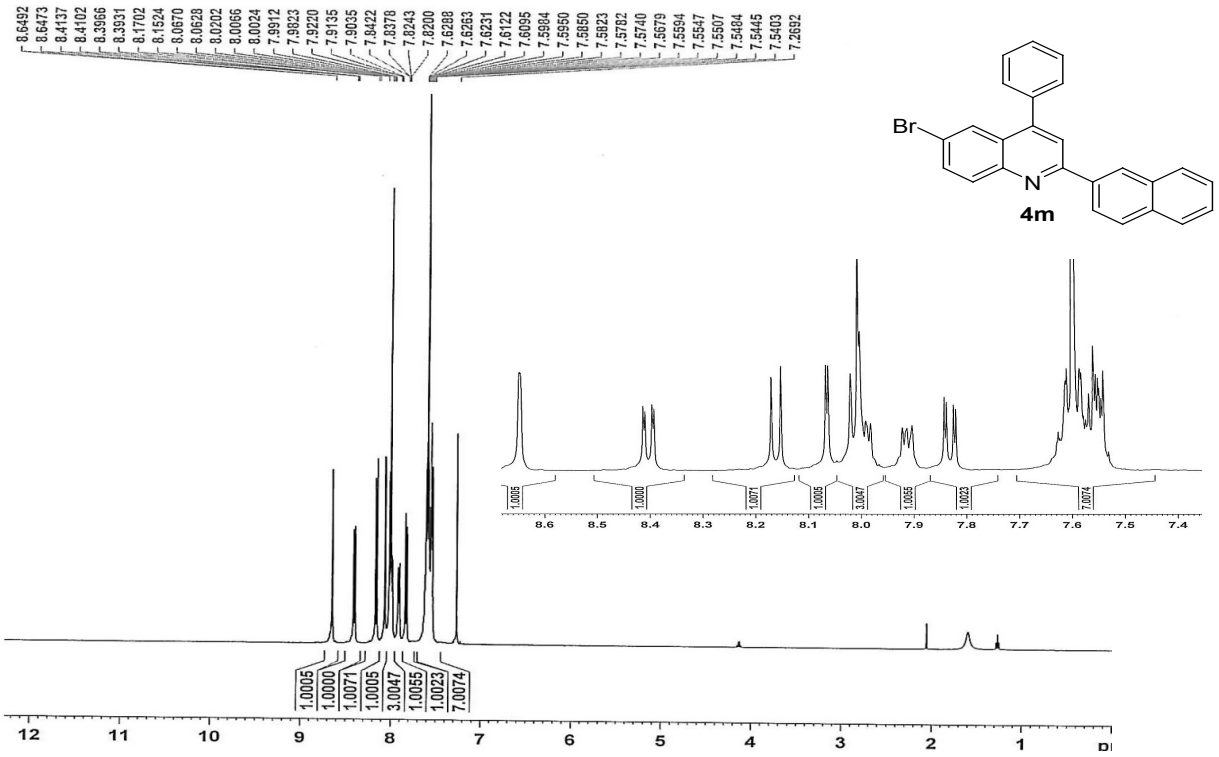
^{1}HNMR Spectrum (125 MHz, $CDCl_3$) of compound 4j



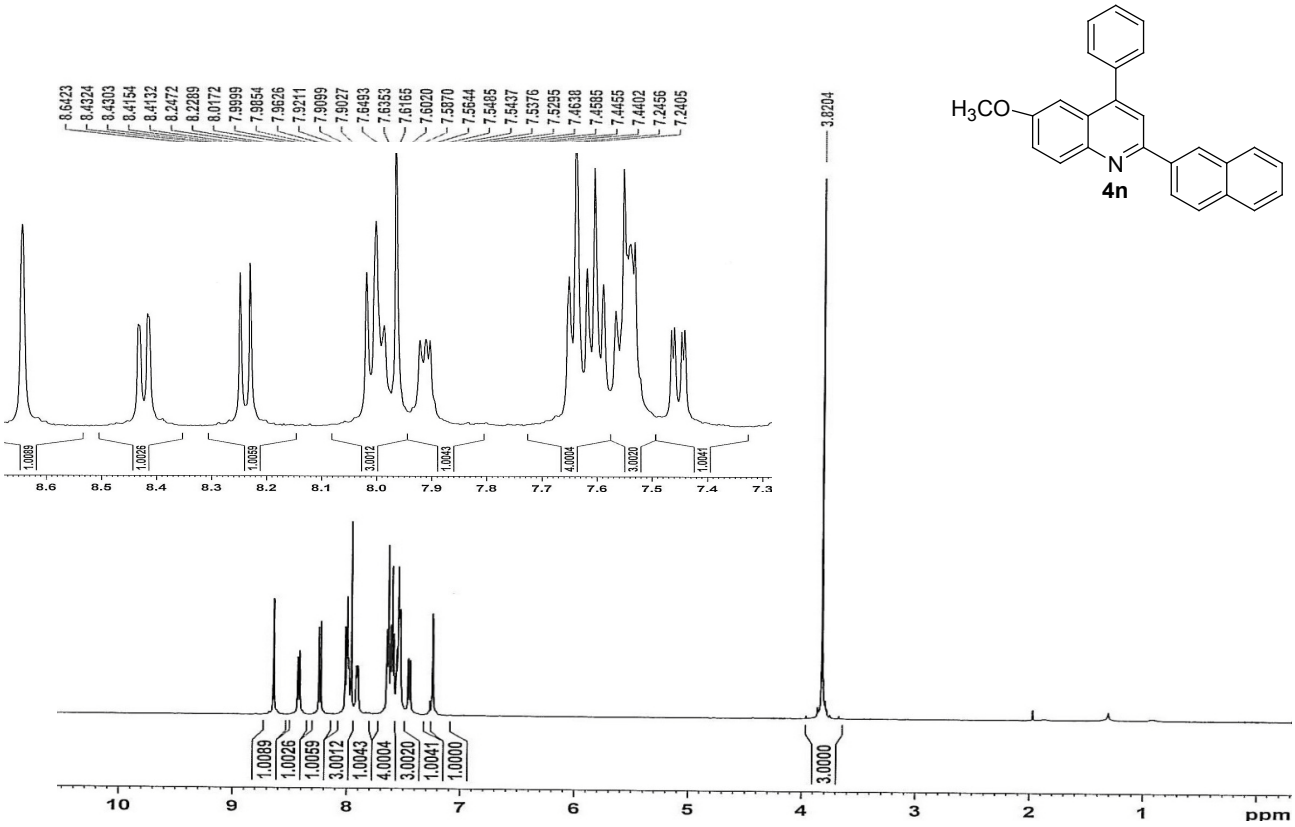
^{1}HNMR Spectrum (125 MHz, $CDCl_3$) of compound 4k



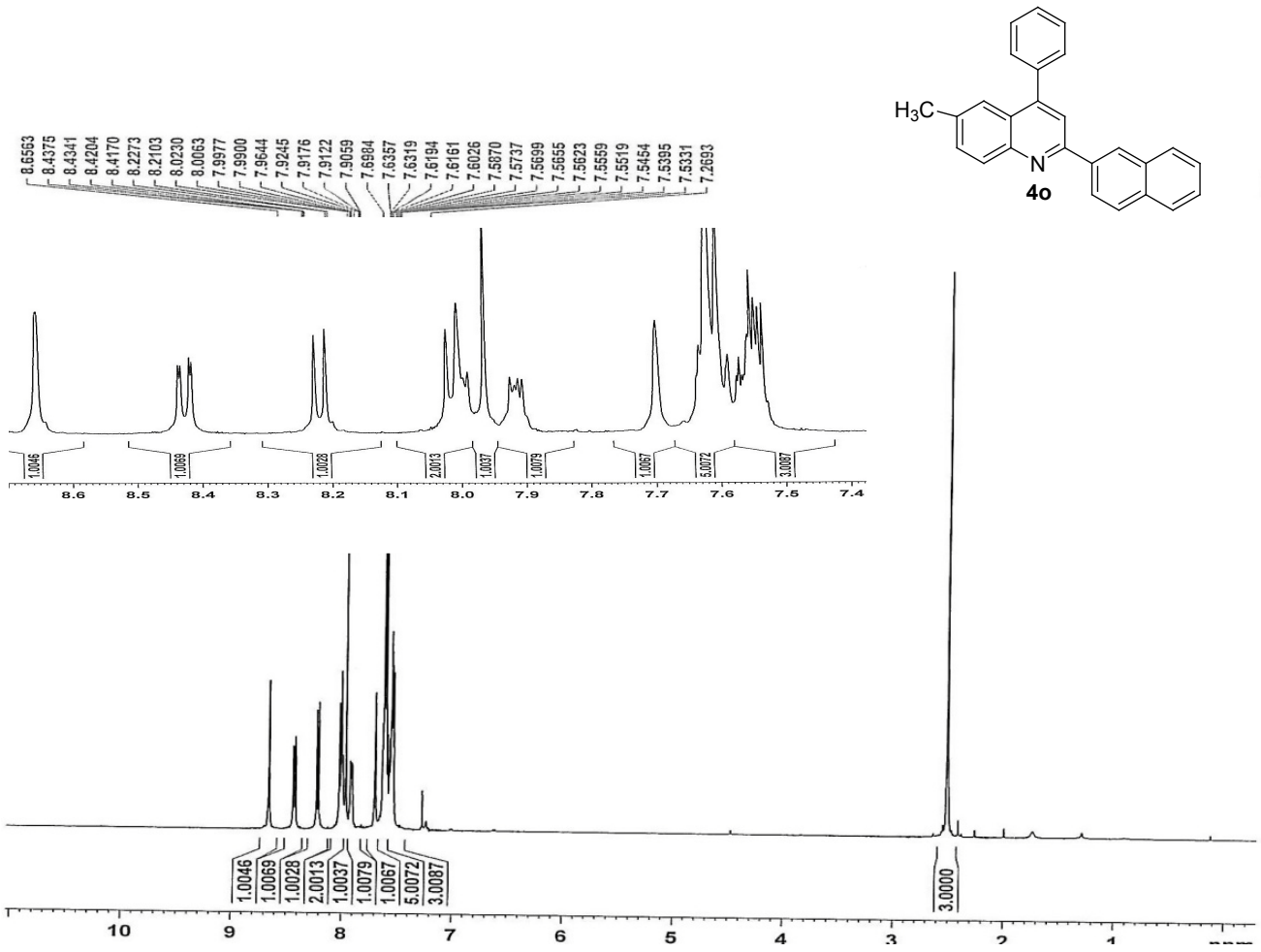
^{1}HNMR Spectrum (125 MHz, $CDCl_3$) of compound 4l



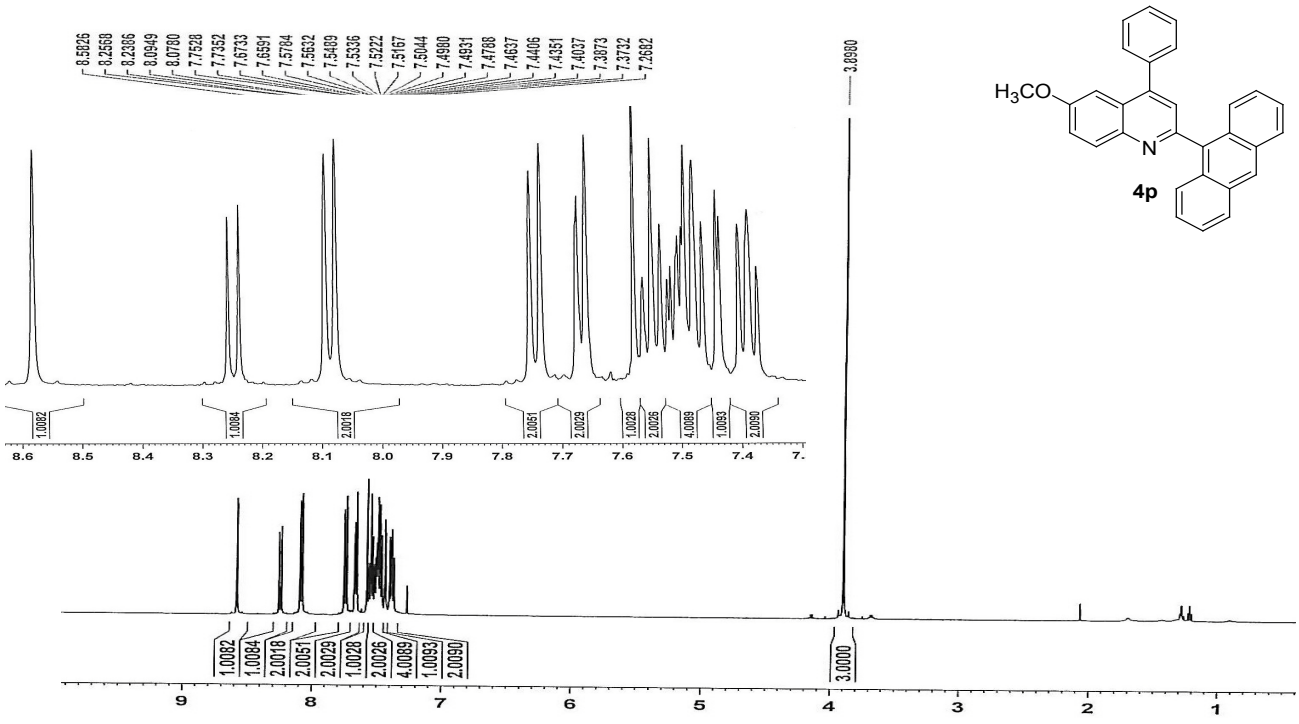
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4m



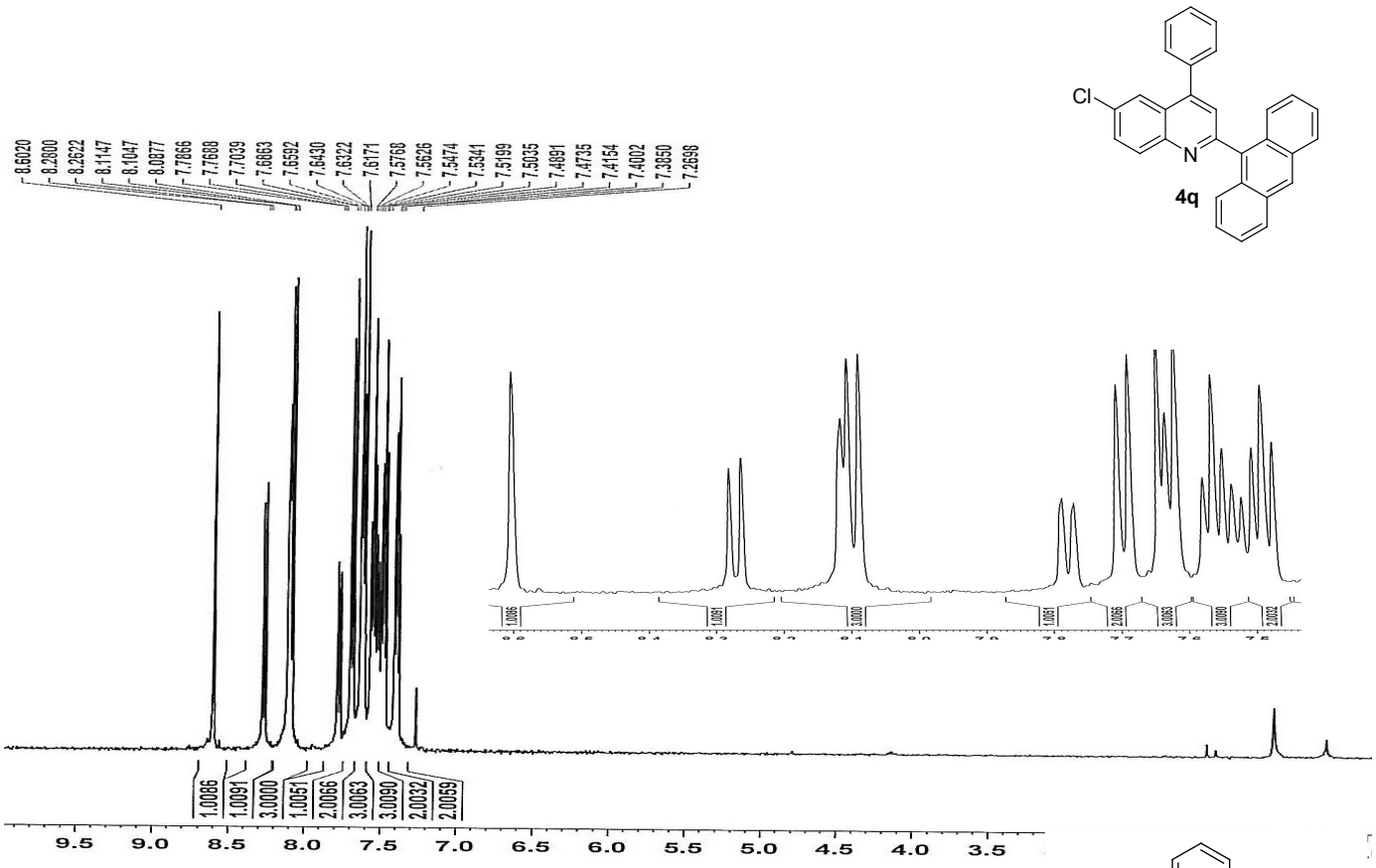
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4n



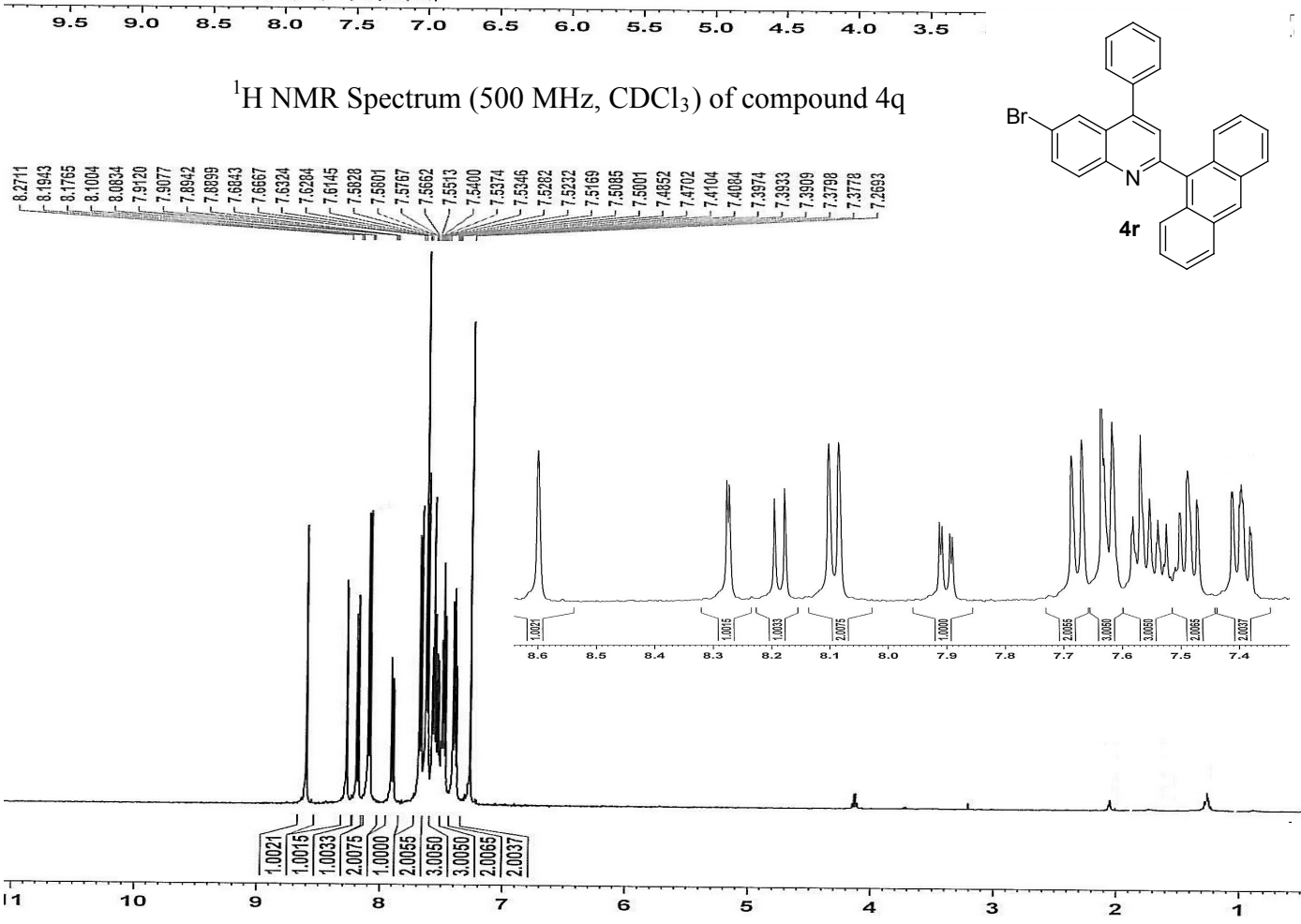
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4o



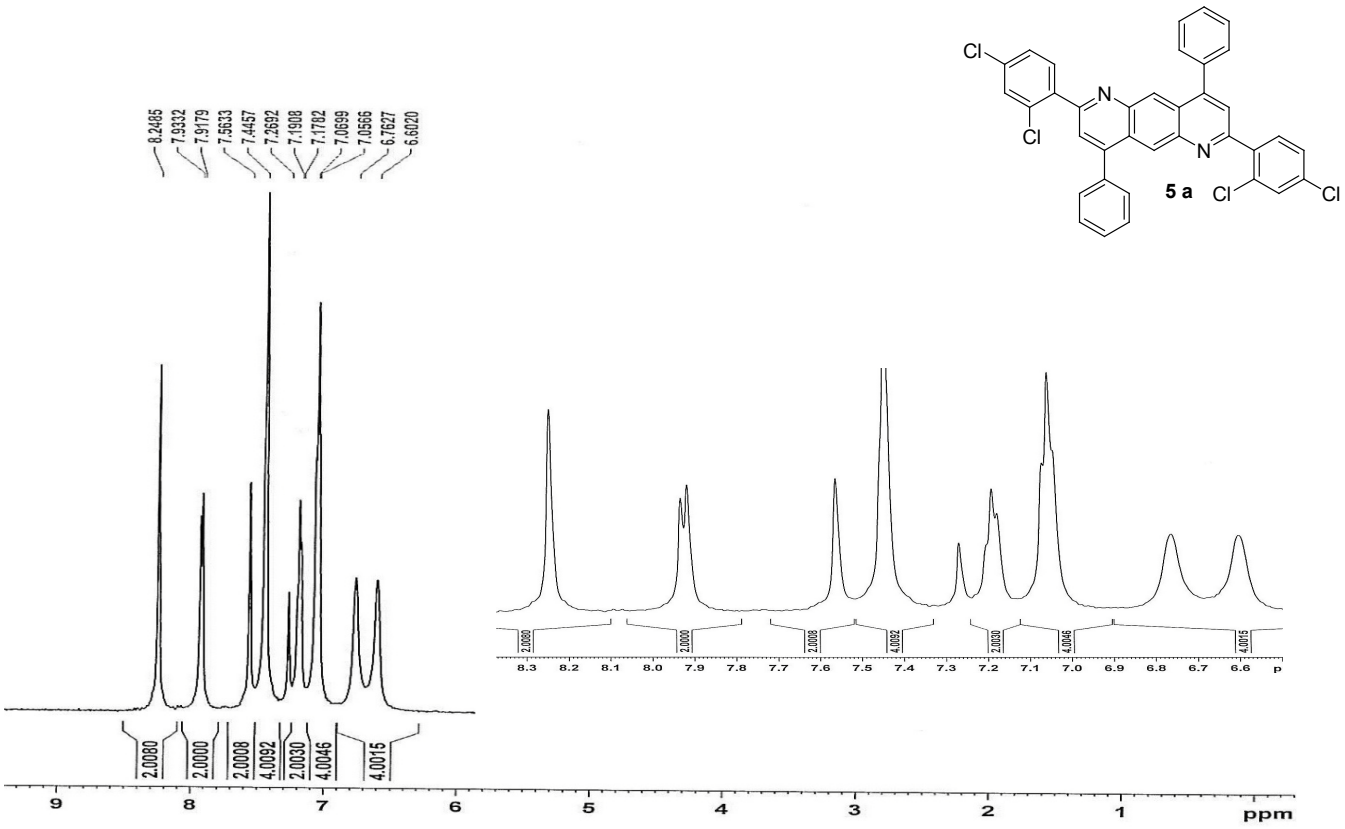
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4p



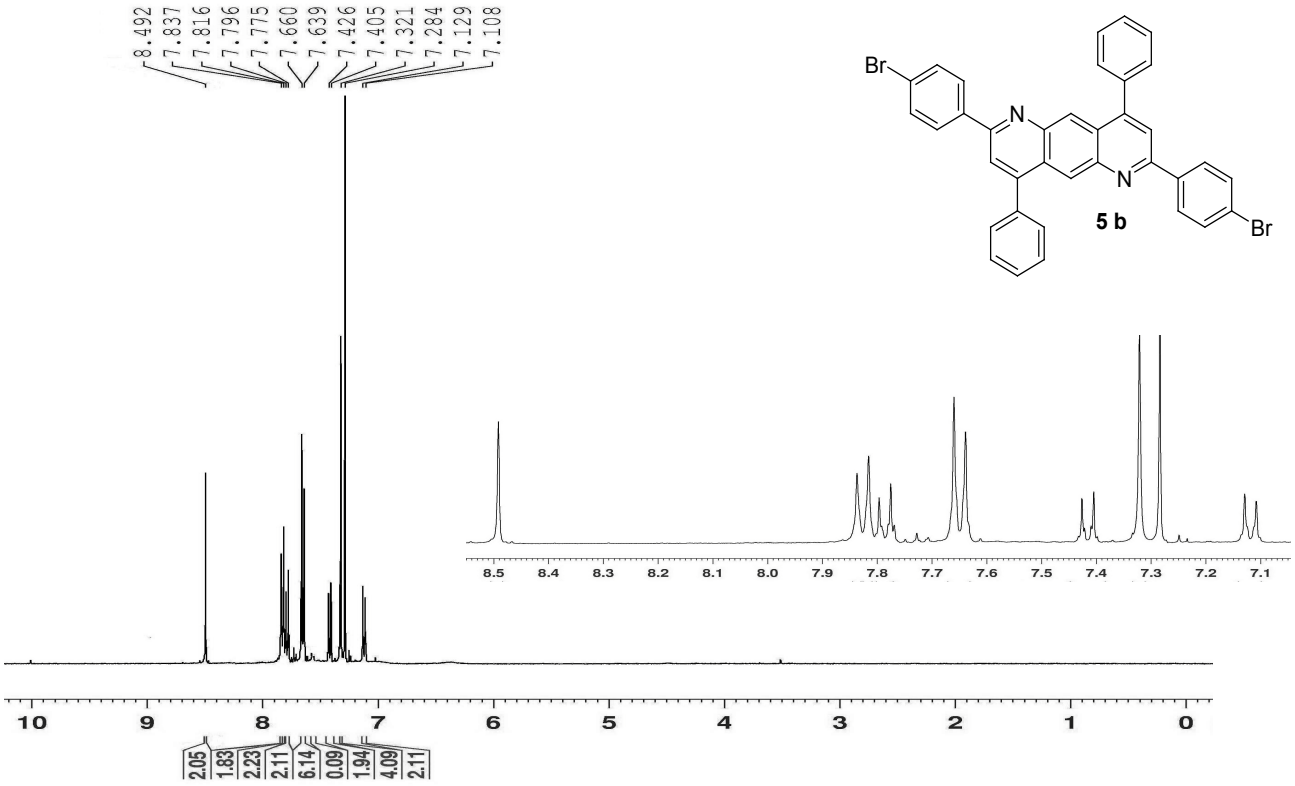
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4q



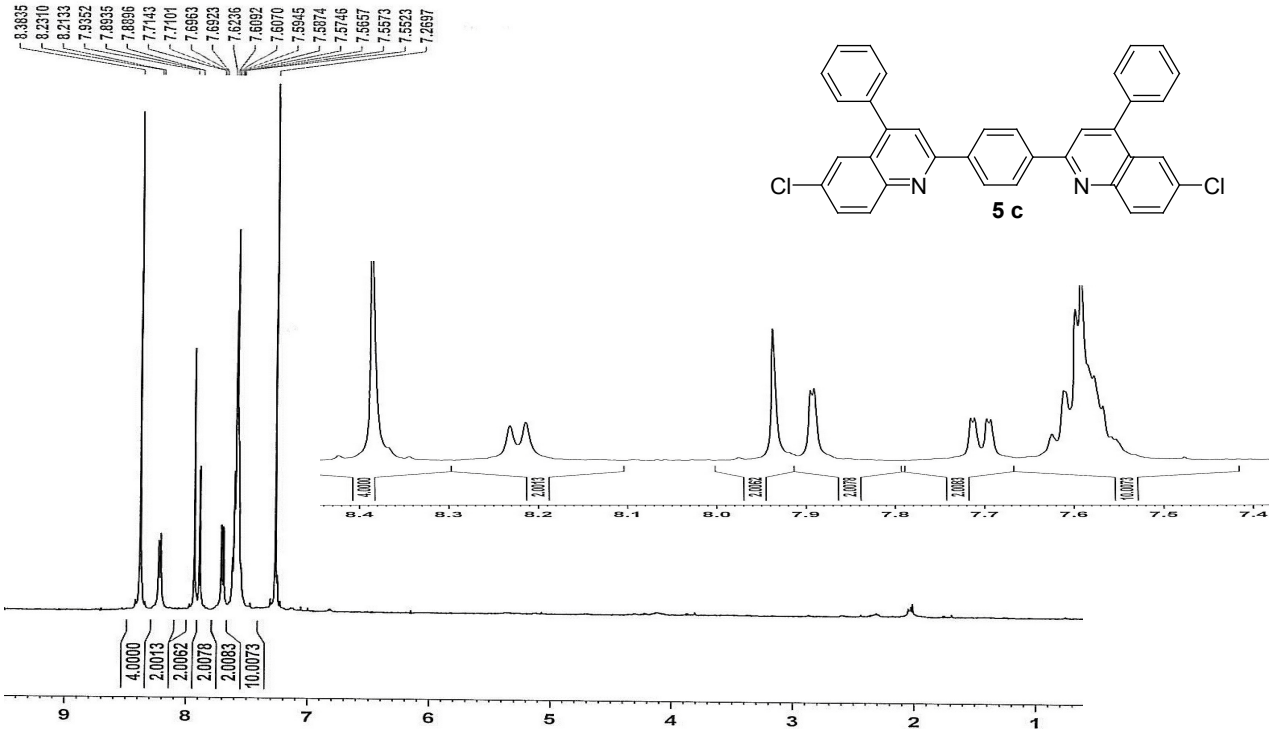
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 4r



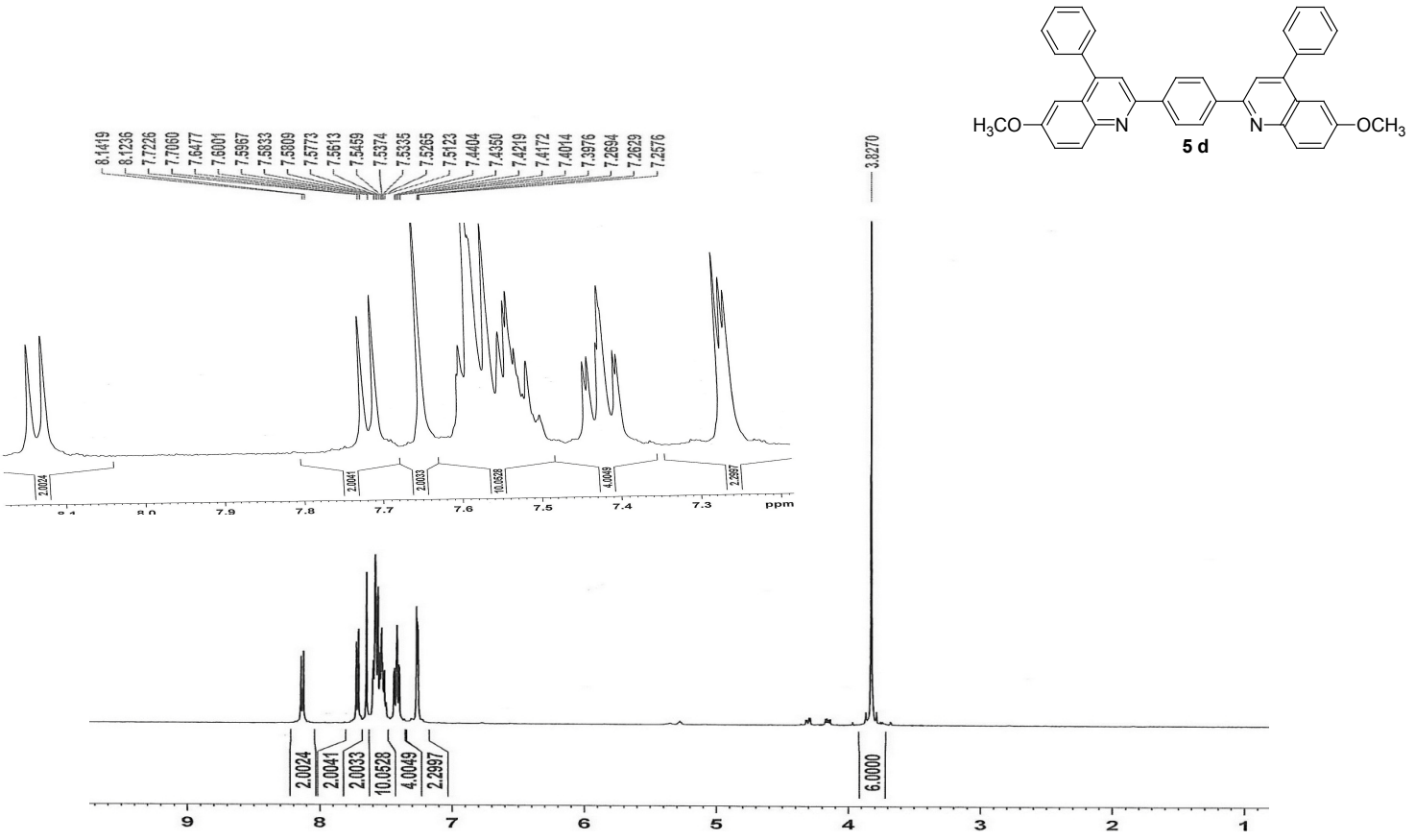
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 5a



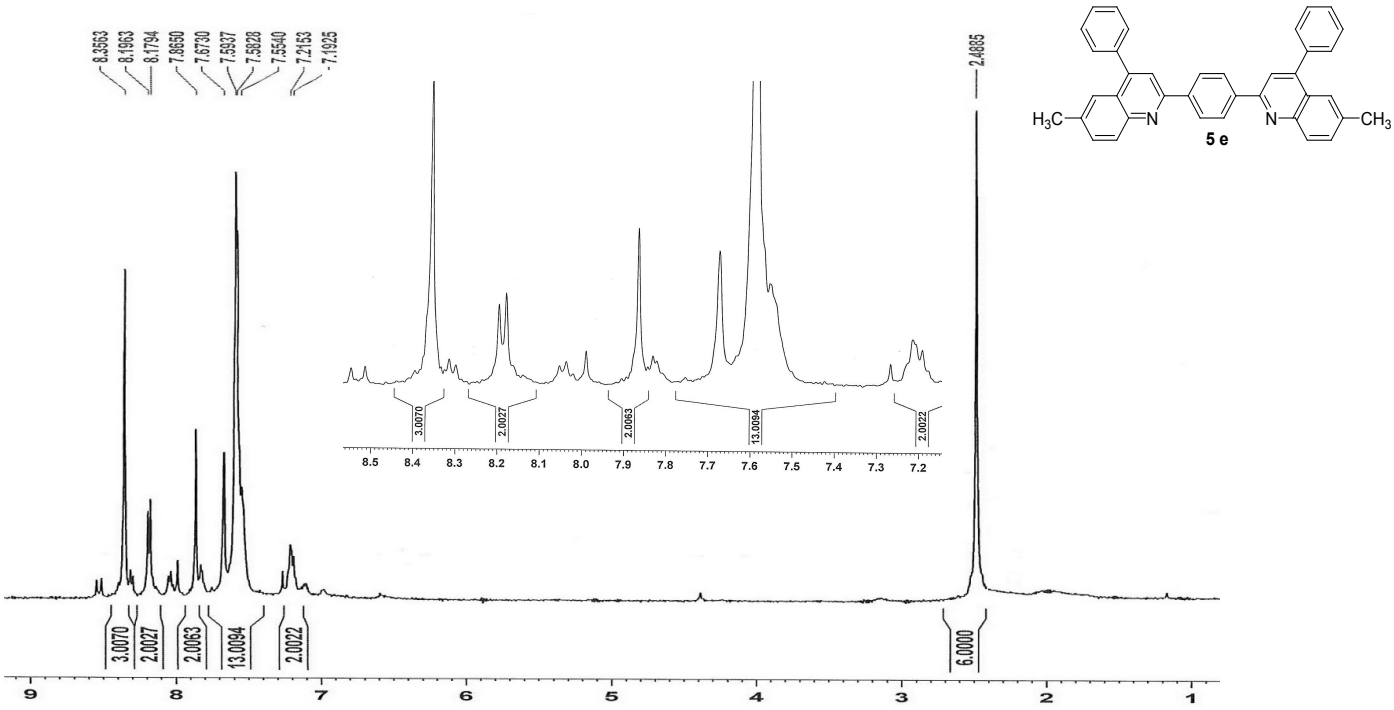
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) of compound 5b



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



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



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

Crystal data and structure refinement for **4p**

Empirical formula	$C_{30}H_{21}NO$	
Formula weight	411.48	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.1823(16) Å	α = 90°
	b = 13.029(3) Å	β = 104.99(3)°
	c = 20.970(6) Å	γ = 90°
Volume	2159.5(9) $Å^3$	
Z	4	
Density (calculated)	1.266 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	864	
Crystal size	0.23 x 0.15 x 0.08 mm^3	
Theta range for data collection	2.01 to 25.50°.	
Index ranges	-9<=h<=9, -15<=k<=13, -25<=l<=25	
Reflections collected	8950	
Independent reflections	3586 [R(int) = 0.0847]	
Completeness to theta = 25.50°	89.3%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9653	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3586 / 0 / 290	
Goodness-of-fit on F^2	0.539	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0411	
R indices (all data)	R1 = 0.1757, wR2 = 0.0556	
Largest diff. peak and hole	0.089 and -0.131e.$Å^3$	

Crystal data and structure refinement for **4q**

Empirical formula	$C_{29}H_{18}ClN$	
Formula weight	415.89	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.218(2) Å	α = 90°
	b = 12.994(3) Å	β = 98.997(19)°
	c = 20.049(5) Å	γ = 90°
Volume	2114.6(9) $Å^3$	
Z	4	
Density (calculated)	1.306 Mg/m^3	
Absorption coefficient	0.197 mm^{-1}	
F(000)	864	
Crystal size	0.42 x 0.25 x 0.11 mm^3	
Theta range for data collection	1.87 to 25.00°.	
Index ranges	-8<=h<=9, -15<=k<=14, -23<=l<=23	
Reflections collected	6630	
Independent reflections	3028 [R(int) = 0.0632]	
Completeness to theta = 25.00°	81.2%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.966	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3028 / 0 / 280	
Goodness-of-fit on F^2	0.514	
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0515	
R indices (all data)	R1 = 0.1389, wR2 = 0.0611	
Largest diff. peak and hole	0.109 and -0.178 e.$Å^3$	