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Physicochemical properties of Urea/Zinc chloride eutectic mixture and its improved effect on the fast and high yield synthesis of indeno[2,1-*c*]quinolones

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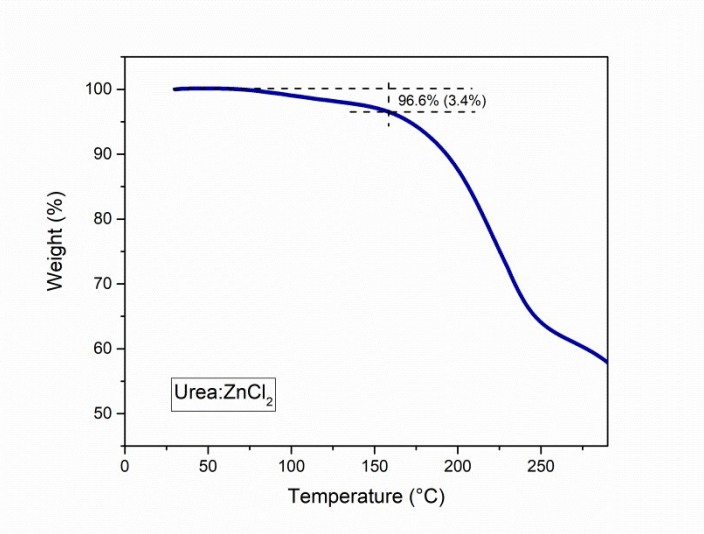
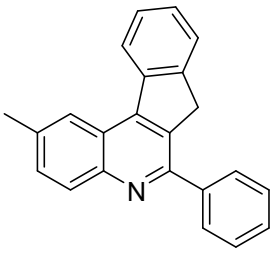
1. TGA of urea/zinc chloride DES



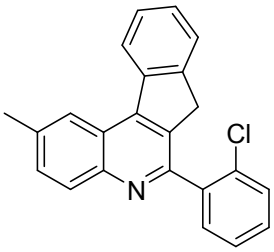
2. General experimental details and characterization data

General procedure for the synthesis of indeno[2,1-*c*]quinolines (9-44). 1.6 g of urea/zinc chloride DES (3.5:1) was heated to 60 °C to obtain a clear melt. To this melt a mixture of amine (1 mmol), aldehyde (1 mmol) and indene (1 mmol) was added and the reaction was stirred at 110 °C for 60 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by adding water while still hot, cooled to room temperature and the crude mixture was filtered. The resulting solid was purified by column chromatography on silica gel (60–120 mesh) using a mixture of petroleum ether–ethyl acetate as eluent to afford the pure product.

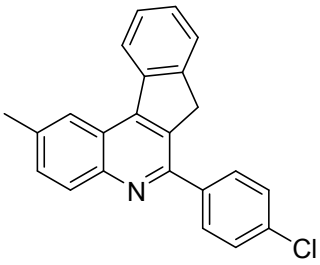


2-Methyl-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (9). White solid; mp: 215-218 °C, reported 216-218 °C.[1] IR ν_{max}/cm^{-1}: 3429, 1654, 1354. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (d, *J* = 7.9 Hz, 2H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 3H), 7.56 (m, 2H), 4.18 (s, 2H), 2.70 (s, 3H). ^{13}C-NMR (101 MHz, $CDCl_3$): δ (ppm) 145.1,

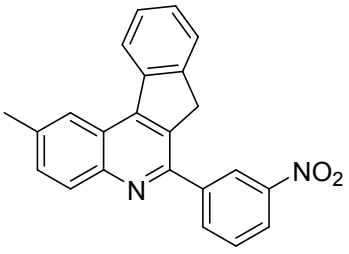
140.8, 136.7, 134.3, 131.1, 130.0, 128.8, 128.6, 128.2, 127.3, 125.1, 124.4, 123.9, 122.4, 37.6, 22.1. Anal. calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56; found: C, 89.73; H, 5.48; N, 4.52.



6-(2-Chlorophenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinoline (10): White solid; mp: 173-175 °C. IR ν_{max}/cm^{-1}: 3434, 1650, 1351. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 7.5 Hz, 2H), 7.51 (m, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (m, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.99 (m, 3H), 4.11 (s, 2H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 148.3, 147.6, 145.9, 144.3, 141.9, 140.4, 139.3, 136.9, 135.5, 134.1, 131.9, 131.0, 128.5, 126.4, 125.9, 124.4, 123.1, 121.9, 119.6, 30.2, 23.7. Anal. calcd for $C_{23}H_{16}ClN$: C, 80.81; H, 4.72; N, 4.10; found: C, 80.78; H, 4.69; N, 4.07.

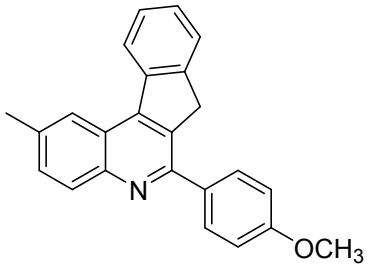


6-(4-Chlorophenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinoline (11): yellow solid; mp: 130-132 °C, reported 130 °C.[2] IR ν_{max}/cm^{-1}: 3430, 1649, 1352. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 7.7, 3.3 Hz, 4H), 7.49 (dd, *J* = 7.6, 3.3 Hz, 4H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 1H), 4.16 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.7, 146.6, 145.6, 144.5, 143.8, 141.6, 141.4, 138.5, 136.9, 134.0, 133.2, 132.2, 130.8, 130.6, 128.8, 127.4, 126.2, 124.2, 123.5, 30.3, 22.9. Anal. calcd for $C_{23}H_{16}ClN$: C, 80.81; H, 4.72; N, 4.10; found: C, 80.74; H, 4.67; N, 4.05.

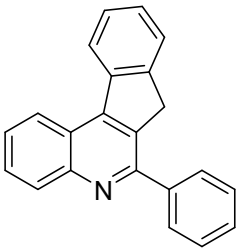


2-Methyl-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (12): Yellow solid; mp: 149-151 °C. IR ν_{max}/cm^{-1}: 3428, 1653, 1356. ^{1}H NMR (400 MHz, DMSO): δ 8.20 (s, 1H), 7.71 (s, 1H), 7.57 (ddd, *J* = 7.9, 7.0, 3.8 Hz, 3H), 7.27 (m, 1H), 7.22 (m, 2H), 7.00 (m, 1H), 6.94 (m, 2H), 4.11 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 152.4, 148.4, 146.9, 145.2, 142.4, 139.9, 137.6,

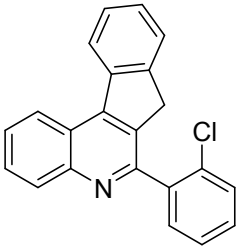
135.6, 133.6, 132.5, 131.1, 130.8, 129.2, 129.2, 128.7, 125.9, 123.3, 122.0, 119.6, 118.6, 30.2, 20.7. Anal. calcd for $C_{23}H_{16}N_2O_2$: C, 78.39; H, 4.58; N, 7.95; found: C, 78.35; H, 4.53; N, 7.91.



6-(4-Methoxyphenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinoline (13): Yellow solid; mp: 198-201 °C. IR ν_{max}/cm^{-1}: 3429, 1652, 1358. ^1H NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 8.8, 6.9 Hz, 2H), 7.62 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.46 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.11 (t, *J* = 6.6 Hz, 2H), 7.05 (m, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.91 (dd, *J* = 7.3, 5.3 Hz, 2H), 3.79 (s, 2H), 3.77 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.4, 150.0, 147.5, 145.6, 143.0, 141.1, 139.0, 136.8, 134.2, 133.2, 130.8, 130.4, 129.7, 127.2, 125.9, 123.4, 121.5, 120.0, 119.1, 118.1, 32.4, 21.75. Anal. calcd for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15; found: C, 85.38; H, 5.63; N, 4.11.

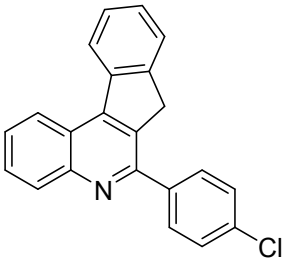


6-Phenyl-7*H*-indeno[2,1-*c*]quinoline (14): Light brown solid; mp: 197-199 °C, reported 196 °C.[1] IR ν_{max}/cm^{-1}: 3429, 1648, 1354. ^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.38 (m, 4H), 7.28 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 2H), 4.06 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 137.4, 136.0, 134.8, 131.8, 129.7, 128.0, 126.6, 126.3, 125.8, 125.1, 124.4, 124.1, 121.3, 120.3, 117.6, 117.1, 117.0, 116.8, 21.9. Anal. calcd for $C_{22}H_{15}N$: C, 90.07; H, 5.15; N, 4.77; found: C, 89.94; H, 5.11; N, 4.70.

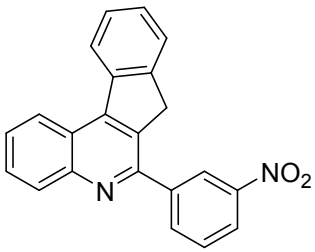


6-(2-Chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (15): Light yellow solid; mp: 117-119 °C. IR ν_{max}/cm^{-1}: 3440, 1647, 1348. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 2H), 7.39 (d, *J* = 7.8 Hz, 4H), 7.21 (t, *J* = 7.9 Hz, 4H), 6.95 (t, *J* = 7.4 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.3, 147.5, 142.1, 137.5, 136.0,

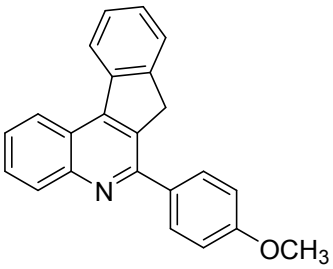
133.2, 131.0, 128.5, 128.4, 127.5, 126.6, 126.3, 125.8, 125.5, 124.9, 121.2, 120.3, 117.5, 117.1, 35.4. Anal. calcd for $C_{22}H_{14}ClN$: C, 80.61; H, 4.30; N, 4.27; found: C, 80.57; H, 4.28; N, 4.25.



6-(4-Chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (16): Light brown solid; mp: 138-140 °C, reported 138 °C.[2] IR ν_{max}/cm^{-1}: 3429, 1650, 1354. ^1H NMR (400 MHz, $CDCl_3$): δ 8.15 (s, 2H), 7.38 (d, *J* = 7.6 Hz, 4H), 7.21 (t, *J* = 7.6 Hz, 4H), 6.96 (t, *J* = 7.2 Hz, 2H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.4, 145.3, 143.6, 141.9, 139.5, 137.3, 134.3, 132.4, 130.4, 128.8, 127.3, 126.6, 126.3, 125.6, 123.8, 121.3, 120.4, 117.6, 117.3, 33.1. Anal. calcd for $C_{22}H_{14}ClN$: C, 80.61; H, 4.30; N, 4.27; found: C, 80.55; H, 4.23; N, 4.27.

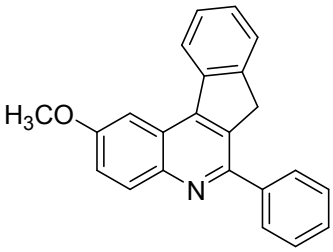


6-(3-Nitrophenyl)-7*H*-indeno[2,1-*c*]quinolone (17): Yellow solid; mp: 108-110 °C. IR ν_{max}/cm^{-1}: 3429, 1652, 1354. ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.22 (t, *J* = 7.9 Hz, 4H), 6.97 (t, *J* = 7.4 Hz, 3H), 5.53 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.6, 149.7, 148.4, 146.7, 144.6, 143.4, 142.0, 139.5, 138.0, 136.1, 135.1, 132.8, 132.0, 130.8, 129.5, 127.4, 125.3, 124.4, 122.1, 34.4. Anal. calcd for $C_{22}H_{14}N_2O_2$: C, 78.09; H, 4.17; N, 8.28; found: C, 77.98; H, 4.15; N, 8.21.

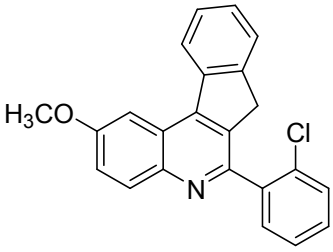


6-(4-Methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (18): yellow solid; mp: 171-173 °C. IR ν_{max}/cm^{-1}: 3428, 1645, 1351. ^1H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.38 (d, *J* = 9.5 Hz, 4H), 7.23 (t, *J* = 8.0 Hz, 4H), 6.97 (t, *J* = 7.4 Hz, 2H), 5.75 (s, 2H), 5.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 150.6, 148.0, 145.6, 142.5, 139.9, 137.2, 135.9, 135.0, 134.0, 133.3, 129.8, 126.7,

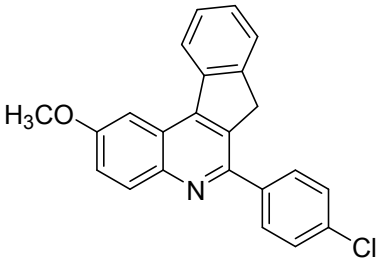
126.7, 125.4, 124.4, 123.5, 120.5, 117.4, 53.4, 32.4. Anal. calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33; found: C, 85.39; H, 5.28; N, 4.30.



2-Methoxy-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (19): Light purple solid; mp: 118-120 °C. IR ν_{max}/cm^{-1}: 3431, 1648, 1355. ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.48 – 7.43 (m, 2H), 7.35 (dd, *J* = 8.2, 5.4 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 4H), 6.79 (d, *J* = 8.9 Hz, 3H), 3.99 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.1, 144.9, 140.0, 136.3, 132.3, 129.8, 129.1, 128.1, 127.7, 127.4, 126.9, 126.8, 126.2, 125.8, 120.7, 112.9, 111.9, 53.0. Anal. calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33; found: C, 85.37; H, 5.27; N, 4.28.

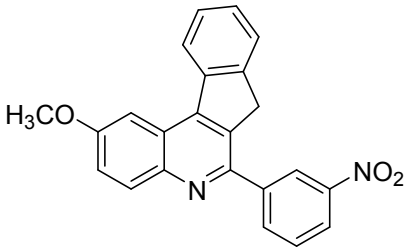


6-(2-Chlorophenyl)-2-methoxy-7*H*-indeno[2,1-*c*]quinoline (20): Green solid; mp: 225-228 °C. IR ν_{max}/cm^{-1}: 3445, 1637, 1352. ^1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, J=8.0, 1H), 7.76 (m, 1H), 7.57 (m, 1H), 7.41 (m, 4H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.24 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.6, 144.6, 143.8, 135.8, 135.2, 133.5, 132.4, 132.1, 131.7, 130.8, 130.1, 129.9, 128.8, 128.3, 127.0, 125.0, 122.5, 114.4, 55.5, 32.2. Anal. calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91; found: C, 77.17; H, 4.48; N, 3.85.

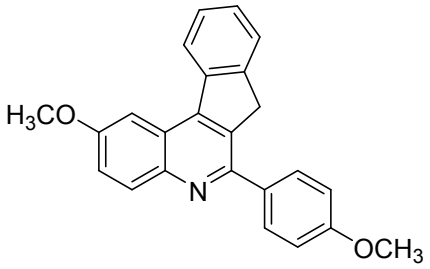


6-(4-Chlorophenyl)-2-methoxy-7*H*-indeno[2,1-*c*]quinoline (21): Light purple solid; mp: 126-129 °C, reported 125-127 °C.[3] IR ν_{max}/cm^{-1}: 3429, 1653, 1349. ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.5 Hz, 2H), 7.59 (m, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 (m, 3H), 6.96 (d, *J* = 8.9 Hz, 3H), 4.24 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.7, 147.7, 144.5,

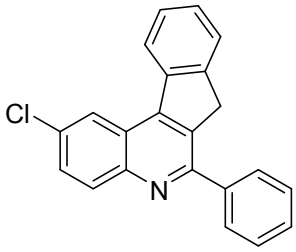
142.2, 139.4, 136.9, 135.2, 133.1, 130.8, 129.7, 129.0, 128.8, 126.1, 124.4, 122.2, 120.2, 118.3, 114.4, 55.5, 33.7. Anal. calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91; found: C, 77.15; H, 4.47; N, 3.87.



2-Methoxy-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (22): brown solid; mp: 128-130 °C, reported 127-129 °C.[3] IR ν_{max}/cm^{-1}: 3445, 1639, 1354. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 2H), 7.84 (t, *J* = 7.9 Hz, 1H), 7.32 (dd, *J* = 10.3, 3.4 Hz, 1H), 7.22 (d, *J* = 9.0 Hz, 4H), 6.79 (d, *J* = 9.0 Hz, 3H), 4.12 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 156.6, 148.2, 146.5, 140.0, 138.3, 135.4, 132.9, 132.3, 130.56 (s), 129.8, 129.2, 128.5, 126.3, 122.4, 121.8, 121.8, 120.7, 119.6, 112.0, 111.9, 53.0, 34.2. Anal. calcd for $C_{23}H_{16}N_2O_3$: C, 74.99; H, 4.38; N, 7.60; found: C, 74.93; H, 4.37; N, 7.54.

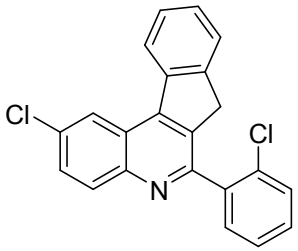


2-Methoxy-6-(4-methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (23): Brown solid; mp: 174-176 °C. IR ν_{max}/cm^{-1}: 3442, 1653, 1348. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 2H), 7.73 (d, *J* = 6.5 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.11 (m, 2H), 4.24 (s, 2H), 3.93 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 156.0, 150.5, 141.9, 140.7, 139.2, 137.2, 135.3, 134.0, 133.1, 131.0, 129.6, 127.2, 123.0, 122.1, 120.2, 119.1, 118.0, 117.2, 56.9, 33.6. Anal. calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96; found: C, 81.49; H, 5.38; N, 3.94.

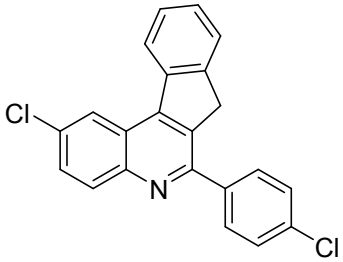


2-Chloro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (24): White solid; mp: 187-189 °C. IR ν_{max}/cm^{-1}: 3440, 1654, 1359. ^{1}H NMR (400 MHz, DMSO): δ

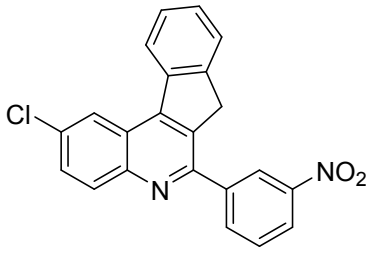
8.49 (s, 2H), 7.81 (m, 1H), 7.64 (m, 1H), 7.55 (m, 1H), 7.33 (d, *J* = 8.7 Hz, 3H), 7.09 (d, *J* = 8.9 Hz, 4H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 149.9, 145.7, 142.4, 141.3, 139.2, 138.4, 136.5, 134.8, 132.3, 131.1, 130.3, 128.7, 128.5, 127.3, 125.7, 124.9, 123.2, 121.4, 119.6, 34.7. Anal. calcd for $C_{22}H_{14}ClN$: C, 80.61; H, 4.30; N, 4.27; found: C, 80.53; H, 4.27; N, 4.21.



2-Chloro-6-(2-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (25): Light brown solid; mp: 156-158 °C. IR ν_{max}/cm^{-1}: 3448, 1643, 1343. ^{1}H NMR (400 MHz, DMSO): δ 8.52 (s, 2H), 7.81 (d, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 7.6, 3.4 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 4H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 148.3, 146.1, 144.2, 142.1, 139.3, 138.2, 136.4, 135.3, 133.6, 131.4, 130.3, 128.5, 127.5, 125.7, 123.8, 122.7, 121.6, 120.5, 119.6, 33.0. Anal. calcd for $C_{22}H_{13}Cl_2N$: C, 72.94; H, 3.62; N, 3.87; found: C, 72.88; H, 3.60; N, 3.83.

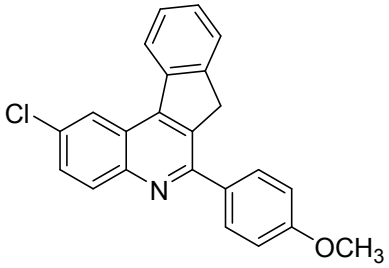


2-Chloro-6-(4-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (26): Light brown solid; mp: 131-133 °C. IR ν_{max}/cm^{-1}: 3438, 1648, 1353. ^{1}H NMR (400 MHz, DMSO): δ 8.48 (s, 2H), 7.86 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 3.9 Hz, 4H), 7.16 (m, 2H), 4.11 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 150.4, 147.5, 145.2, 142.5, 140.8, 139.3, 136.6, 134.3, 131.2, 131.2, 128.7, 128.5, 126.1, 125.6, 124.0, 123.5, 123.0, 122.0, 120.9, 119.6, 33.8. Anal. calcd for $C_{22}H_{13}Cl_2N$: C, 72.94; H, 3.62; N, 3.87; found: C, 72.85; H, 3.58; N, 3.84.

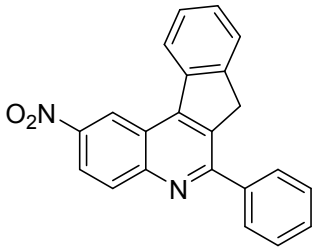


2-Chloro-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (27): Yellow solid; mp: 176-178 °C. IR ν_{max}/cm^{-1}: 3437, 1642, 1343. ^{1}H NMR (400 MHz, DMSO): δ 8.46 (s, 1H), 7.76 (dd, *J* = 7.0, 2.7 Hz,

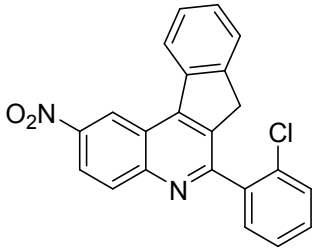
2H), 7.58 (dd, *J* = 8.1, 3.3 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 3H), 7.09 (d, *J* = 8.8 Hz, 3H), 4.11 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 148.6, 147.3, 145.7, 144.3, 143.3, 142.0, 140.6, 139.2, 137.8, 136.3, 135.0, 132.3, 131.1, 129.7, 128.6, 128.4, 125.8, 124.0, 121.9, 119.6, 30.2. Anal. calcd for $C_{22}H_{13}ClN_2O_2$: C, 70.88; H, 3.51; N, 7.51; found: C, 70.81; H, 3.44; N, 7.46.



2-Chloro-6-(4-methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (28): Light yellow solid; mp: 202-204 °C. IR ν_{max}/cm^{-1}: 3445, 1646, 1354. ^{1}H NMR (400 MHz, DMSO): δ 7.68 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 3H), 7.18 (m, 4H), 4.11 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 156.4, 145.4, 144.5, 143.0, 142.5, 140.5, 139.1, 137.0, 134.9, 133.0, 132.0, 130.2, 128.4, 127.5, 125.9, 124.7, 123.4, 119.6, 56.7, 34.1. Anal. calcd for $C_{23}H_{16}ClNO$: C, 77.20; H, 4.51; N, 3.91; found: C, 77.12; H, 4.50; N, 3.86.

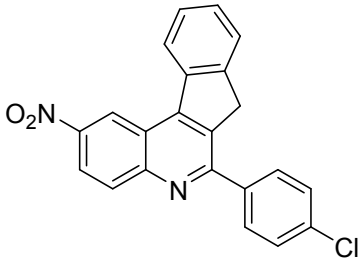


2-Nitro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (29): Light yellow solid; mp: 233-235 °C. IR ν_{max}/cm^{-1}: 3510, 1645, 1356. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.56 (d, *J* = 8.9 Hz, 3H), 8.33 (d, *J* = 8.8 Hz, 3H), 7.90 (dd, *J* = 7.2 Hz, 2H), 7.33 – 7.24 (m, 3H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.2, 143.2, 142.8, 140.5, 140.1, 138.4, 135.3, 135.0, 131.6, 130.8, 128.8, 128.5, 125.8, 125.7, 125.5, 123.7, 123.6, 123.1, 33.2. Anal. calcd for $C_{22}H_{14}N_2O_2$: C, 78.09; H, 4.17; N, 8.28; found: C, 78.11; H, 4.16; N, 8.26.

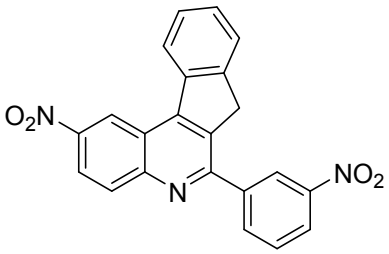


6-(2-Chlorophenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (30): Yellow solid; mp: 183-185 °C. IR ν_{max}/cm^{-1}: 3495, 1654, 1360. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.12 (d, *J* = 9.2 Hz, 2H), 7.93 (d, *J* = 8.5 Hz,

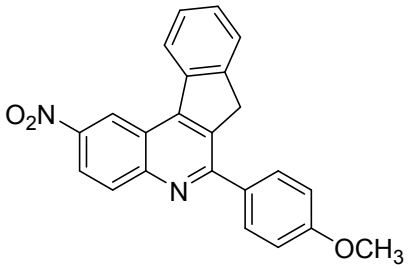
2H), 7.71 (m, 2H), 7.21 (m, 4H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.6, 142.6, 141.3, 140.0, 138.2, 136.7, 135.5, 133.2, 131.1, 129.3, 127.8, 126.4, 124.7, 122.7, 120.7, 118.3, 117.1, 115.3, 33.7. Anal. calcd for $C_{22}H_{13}ClN_2O_2$: C, 70.88; H, 3.51; N, 7.51; found: C, 70.83; H, 3.47; N, 7.46.



6-(4-Chlorophenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (31): Light yellow solid; mp: 178-180 °C. IR ν_{max}/cm^{-1}: 3499, 1654, 1356. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.12 (d, *J* = 9.2 Hz, 3H), 7.67 (d, *J* = 10.3 Hz, 4H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.21 (m, 2H), 4.11 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.0, 144.6, 142.9, 141.4, 140.5, 139.2, 137.7, 136.5, 135.8, 134.7, 133.4, 131.9, 129.9, 128.9, 127.8, 126.7, 125.4, 123.6, 122.5, 33.1. Anal. calcd for $C_{22}H_{13}ClN_2O_2$: C, 70.88; H, 3.51; N, 7.51; found: C, 70.80; H, 3.45; N, 7.47.

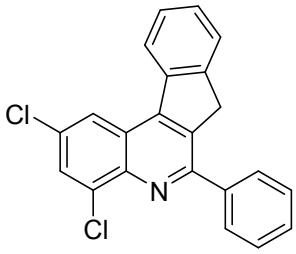


2-Nitro-6-(3-nitrophenyl)-7H-indeno[2,1-c]quinoline (32): Yellow solid; mp: 187-189 °C. IR ν_{max}/cm^{-1}: 3483, 1649, 1354. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.13 (d, *J* = 9.2 Hz, 3H), 7.65 (d, *J* = 9.0 Hz, 3H), 7.57 (s, 1H), 7.32 (m, 3H), 4.04 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 145.7, 144.5, 142.9, 141.7, 140.3, 137.8, 135.0, 133.4, 131.9, 130.1, 128.2, 126.0, 125.1, 122.7, 121.3, 119.2, 116.9, 115.3, 34.5. Anal. calcd for $C_{22}H_{13}N_3O_4$: C, 68.93; H, 3.42; N, 10.96; found: C, 68.88; H, 3.37; N, 10.90.

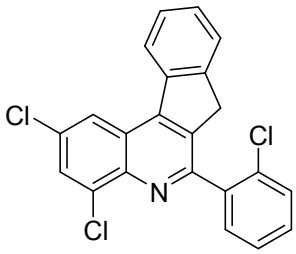


6-(4-Methoxyphenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (33): Yellow solid; mp: 186-198 °C. IR ν_{max}/cm^{-1}: 3484, 1653, 1354. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.12 (d, *J* = 9.2 Hz, 2H), 7.93 (d, *J* = 9.2 Hz, 1H), 7.80 (s, 1H), 7.69 (d, *J* = 9.2 Hz, 2H), 7.26

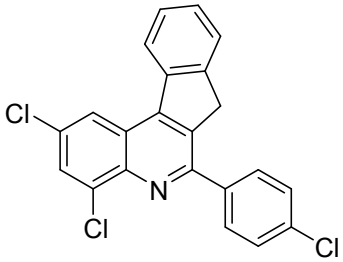
(m, 4H), 4.10 (s, 2H), 3.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.2, 142.7, 141.8, 138.3, 135.7, 133.9, 132.5, 131.2, 129.8, 127.9, 126.7, 125.3, 124.0, 122.6, 120.9, 117.1, 115.2, 56.5. Anal. calcd for $C_{23}H_{16}N_2O_3$: C, 74.99; H, 4.38; N, 7.60; found: C, 47.85; H, 4.31; N, 7.58.



2,4-Dichloro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (34): White solid; mp: 285-287 °C. IR ν_{max}/cm^{-1}: 3499, 1654, 1360. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 4H), 7.76 (s, 1H), 7.69 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.20 (dd, *J* = 9.0, 2.4 Hz, 2H), 4.08 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 146.9, 145.3, 143.8, 142.4, 141.3, 140.2, 138.5, 135.7, 133.4, 131.3, 128.9, 126.2, 125.3, 123.1, 121.2, 119.9, 34.0. Anal. calcd for $C_{22}H_{13}Cl_2N$: C, 72.94; H, 3.62; N, 3.87; found: C, 72.90; H, 3.57; N, 3.84.

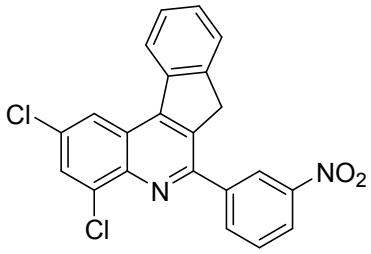


2,4-Dichloro-6-(2-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (35): White solid; mp: 186-188 °C. IR ν_{max}/cm^{-1}: 3494, 1653, 1362. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.07 (m, 4H), 7.76 (s, 1H), 7.34 (s, 1H), 7.21 (d, *J* = 8.8, 2H), 4.05 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.9, 141.6, 140.8, 139.7, 138.5, 137.7, 136.6, 135.9, 134.5, 133.6, 132.8, 131.6, 130.5, 128.6, 127.6, 126.2, 125.2, 124.4, 120.3, 119.8, 33.2. Anal. calcd for $C_{22}H_{12}Cl_3N$: C, 66.61; H, 3.05; N, 3.53; found: C, 66.58; H, 2.99; N, 3.48.

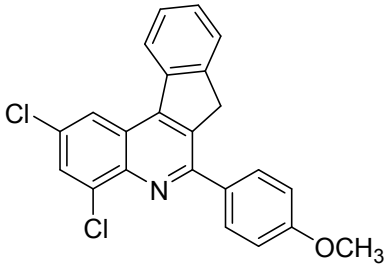


2,4-Dichloro-6-(4-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (36): White solid; mp: 254-256 °C. IR ν_{max}/cm^{-1}: 3496, 1652, 1360. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.0 Hz, 2H), 7.76 (s, 2H), 7.71 (s, 1H), 7.40 (m, 2H), 7.33 (s, 1H), 7.20 (m, 2H), 4.15 (s, 2H). ^{13}C NMR (101

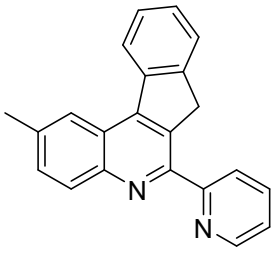
MHz, $CDCl_3$): δ 144.8, 143.5, 142.5, 140.8, 139.6, 137.7, 136.3, 134.5, 133.5, 131.9, 131.3, 129.9, 128.2, 126.2, 125.3, 124.0, 122.0, 120.3, 119.8, 33.7. Anal. calcd for $C_{22}H_{12}Cl_3N$: C, 66.61; H, 3.05; N, 3.53; found: C, 66.56; H, 2.97; N, 3.49.



2,4-Dichloro-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (37): Light yellow solid; mp: 164-166 °C. IR ν_{max}/cm^{-1}: 3491, 1653, 1359. ^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.0 Hz, 2H), 8.06 (m, 4H), 7.77 (s, 1H), 7.34 (s, 1H), 7.21 (dd, *J* = 9.0, 2.4 Hz, 2H), 4.20 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.1, 146.9, 145.5, 144.4, 143.1, 141.6, 139.9, 138.6, 136.8, 135.2, 133.6, 132.3, 130.6, 128.4, 126.2, 125.2, 124.4, 122.8, 120.3, 119.8, 35.5. Anal. calcd for $C_{22}H_{12}Cl_2N_2O_2$: C, 64.88; H, 2.97; N, 6.88; found: C, 64.83; H, 2.91; N, 6.85.

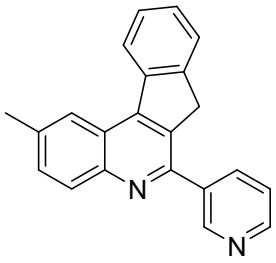


2,4-dichloro-6-(4-methoxyphenyl)-7H-indeno[2,1-c]quinoline (38): White solid; mp: 183-185 °C. IR ν_{max}/cm^{-1}: 3495, 1657, 1360. ^1H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H), 7.70 (s, 1H), 7.42 (m, 4H), 7.33 (s,1H), 7.20 (dd, *J* = 9.0, 2.4 Hz, 2H), 4.22 (s, 2H), 4.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.4, 148.5, 147.4, 146.1, 144.2, 142.5, 140.3, 137.9, 136.5, 135.1, 133.5, 131.8, 130.0, 127.5, 126.2, 125.3, 123.7, 121.1, 119.8, 118.1, 56.4, 33.7. Anal. calcd for $C_{23}H_{15}Cl_2NO$: C, 70.42; H, 3.85; N, 3.57; found: C, 70.39; H, 3.82; N, 3.51.

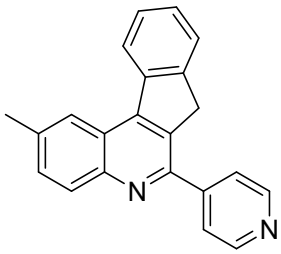


2-Methyl-6-(pyridin-2-yl)-7*H*-indeno[2,1-*c*]quinoline (39): light yellow solid; mp: 189-191 °C,[4] IR ν_{max}/cm^{-1}: 3045, 2915, 1586, 1554. ^1H NMR (500 MHz, $CDCl_3$): δ 8.79 (d, *J* = 6.3 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.48 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.18 (d, *J* = 8.6 Hz, 1H), 7.89 (td, *J* = 7.7, 1.8 Hz, 1H),

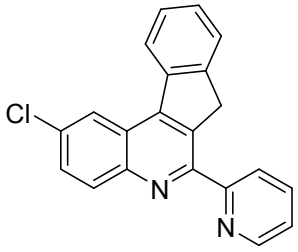
7.71 (d, *J* = 7.4 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.46 (td, *J* = 7.4, 1.0 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.57 (s, 2H), 2.66 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.3, 151.9, 148.5, 146.2, 145.2, 140.4, 136.8, 136.5, 135.2, 130.6, 130.3, 127.8, 126.7, 125.0, 124.0, 123.3, 123.2, 122.4, 38.9, 22.1. Anal. calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08; found: C, 85.67; H, 5.19; N, 9.02.



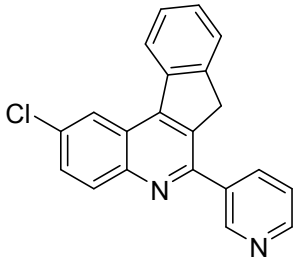
2-Methyl-6-(pyridin-3-yl)-7*H*-indeno[2,1-*c*]quinoline (40): light yellow solid; mp: 203-205 °C,[4] IR ν_{max}/cm^{-1}: 3050, 2900, 1575, 1557. ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.18 (s, 1H), 8.71 (d, *J* = 3.0 Hz, 1H), 8.40 (d, *J* = 7.1 Hz, 2H), 8.25 (d, *J* = 6.2 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.57 (dd, *J* = 8.7, 1.4 Hz, 1H), 7.55 – 7.41 (m, 3H), 4.07 (s, 2H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.9, 149.5, 147.1, 146.8, 145.1, 144.6, 140.4, 136.9, 136.2, 133.9, 131.1, 130.2, 128.2, 127.2, 125.0, 124.2, 123.9, 123.5, 122.4, 37.3, 22.1. Anal. calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08; found: C, 85.63; H, 5.17; N, 9.03.



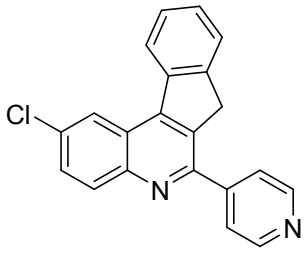
2-Methyl-6-(pyridin-4-yl)-7*H*-indeno[2,1-*c*]quinoline (41): Yellow solid; mp: 218-220 °C,[4] IR ν_{max}/cm^{-1}: 3024, 2918, 1596, 1557. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (d, *J* = 5.6 Hz, 2H), 8.43 (m, 2H), 8.15 (d, *J* = 8.6 Hz, 1H), 7.85 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.59 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.49 – 7.44 (m, 2H), 4.09 (s, 2H), 2.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.9, 149.9, 149.4, 147.8, 146.7, 145.3, 144.5, 140.3, 137.4, 133.7, 131.3, 130.4, 128.35, 127.3, 125.1, 124.3, 123.3, 122.4, 37.2, 22.1. Anal. calcd for $C_{22}H_{16}N_2$: C, 85.69; H, 5.23; N, 9.08; found: C, 85.60; H, 5.20; N, 9.01.



2-Chloro-6-(pyridin-2-yl)-7*H*-indeno[2,1-*c*]quinoline (42): Yellow solid; mp: 238-239 °C,[4] IR ν_{max}/cm^{-1}: 3046, 3005, 1586, 1550. ^{1}H NMR (500 MHz, DMSO): δ 8.86-8.84 (m, 2H), 8.63 (d, *J* = 7.1 Hz, 1H), 8.59 (d, *J* = 7.9 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 8.07 (td, *J* = 7.7, 1.8 Hz, 1H), 7.89 (dd, *J* = 8.9, 2.2 Hz, 1H), 7.86 (d, *J* = 6.6 Hz, 1H), 7.62-7.56 (m, 3H), 4.66 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 158.1, 152.8, 148.5, 147.6, 146.3, 146.0, 140.2, 136.6, 135.2, 130.6, 128.4, 128.0, 126.9, 125.0, 124.5, 124.0, 123.5, 123.4, 39.0. Anal. calcd for $C_{21}H_{13}ClN_2$: C, 76.71; H, 3.99; N, 8.52; found: C, 76.65; H, 3.94; N, 8.47.

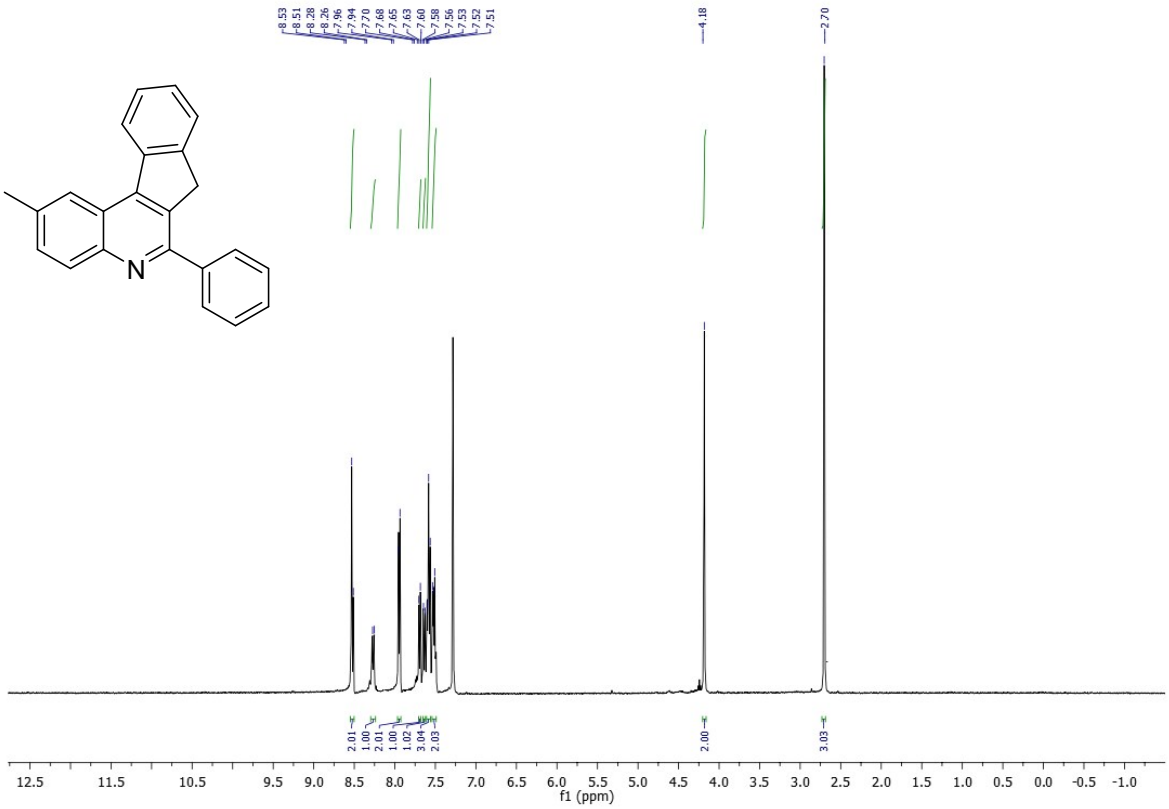


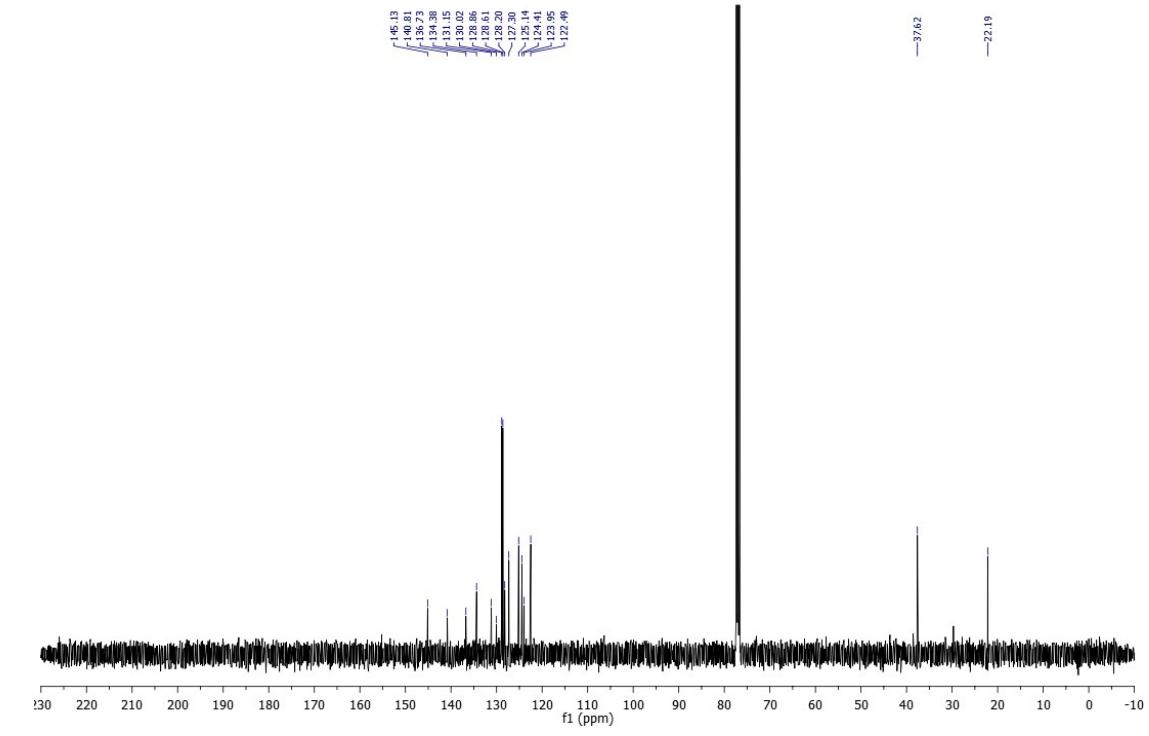
2-Chloro-6-(pyridin-3-yl)-7*H*-indeno[2,1-*c*]quinoline (43): Yellow solid; mp: 258-259 °C,[4] IR ν_{max}/cm^{-1}: 3052, 2905, 1586, 1556. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.22 (s, 1H), 8.75 (d, *J* = 4.3 Hz, 1H), 8.67 (s, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.29 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.71-7.66 (m, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52-7.47 (m, 2H), 4.17 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 153.2, 150.0, 149.7, 146.8, 145.3, 144.6, 139.9, 136.2, 135.7, 134.9, 132.2, 129.8, 128.7, 127.6, 125.2, 124.1, 123.5, 122.6, 37.5. Anal. calcd for $C_{21}H_{13}ClN_2$: C, 76.71; H, 3.99; N, 8.52; found: C, 76.67; H, 3.91; N, 8.43.



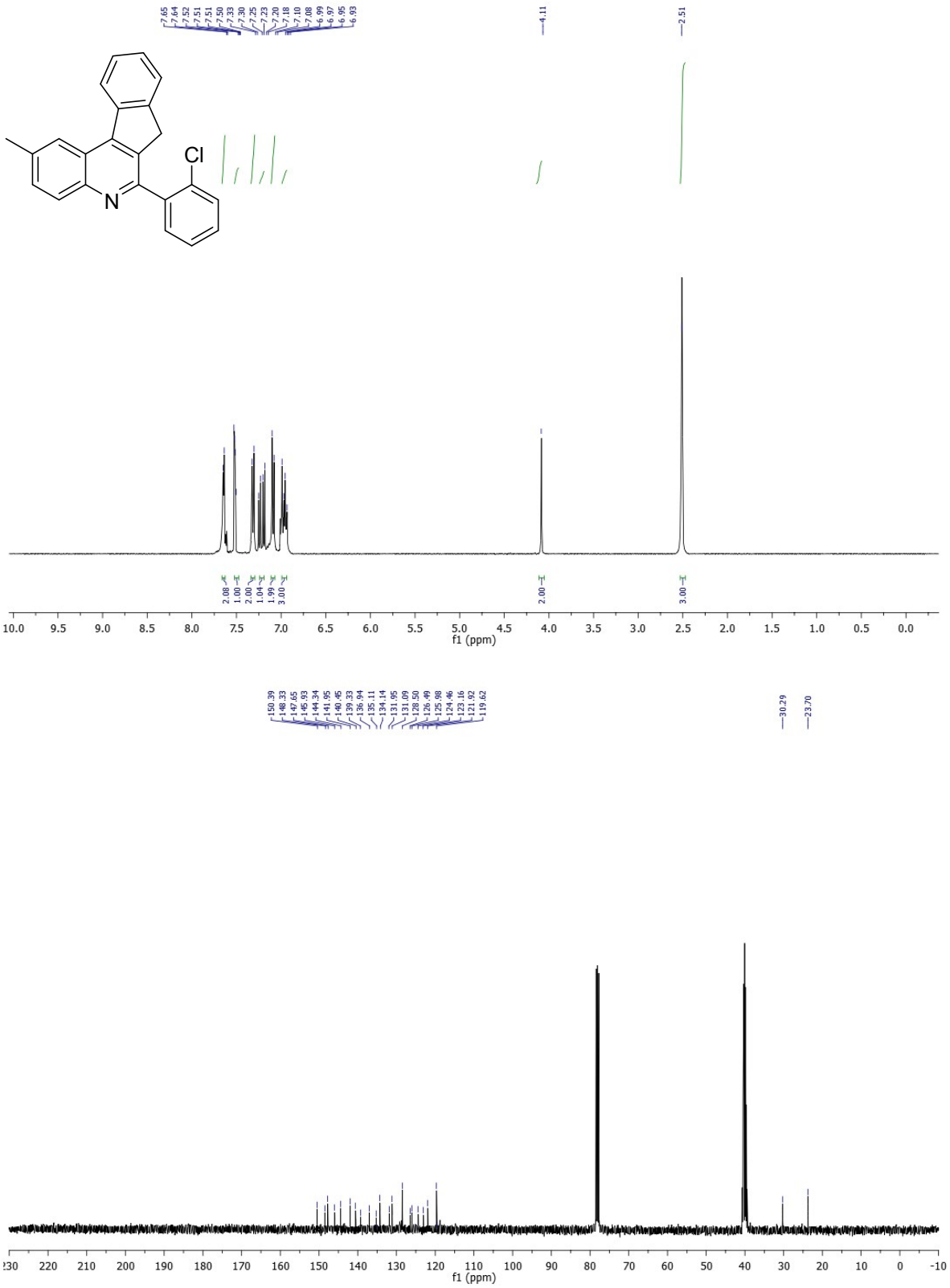
2-Chloro-6-(pyridin-4-yl)-7*H*-indeno[2,1-*c*]quinoline (44): Pale yellow solid; mp: 268-270 °C,[4] IR ν_{max}/cm^{-1}: 3046, 3005, 1597, 1559. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.77 (d, *J* = 6.0 Hz, 2H), 8.23 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 9.3 Hz, 1H), 7.87-7.77 (m, 3H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.52-7.44 (m, 2H), 7.41-7.37 (m, 1H), 4.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.4, 150.0, 147.6, 144.4, 144.1, 140.2, 134.0, 132.1, 128.1, 127.3, 125.0, 123.7, 123.1, 121.6, 121.2, 37.2.

2-Methyl-6-phenyl-7H-indeno[2,1-c]quinoline (9)

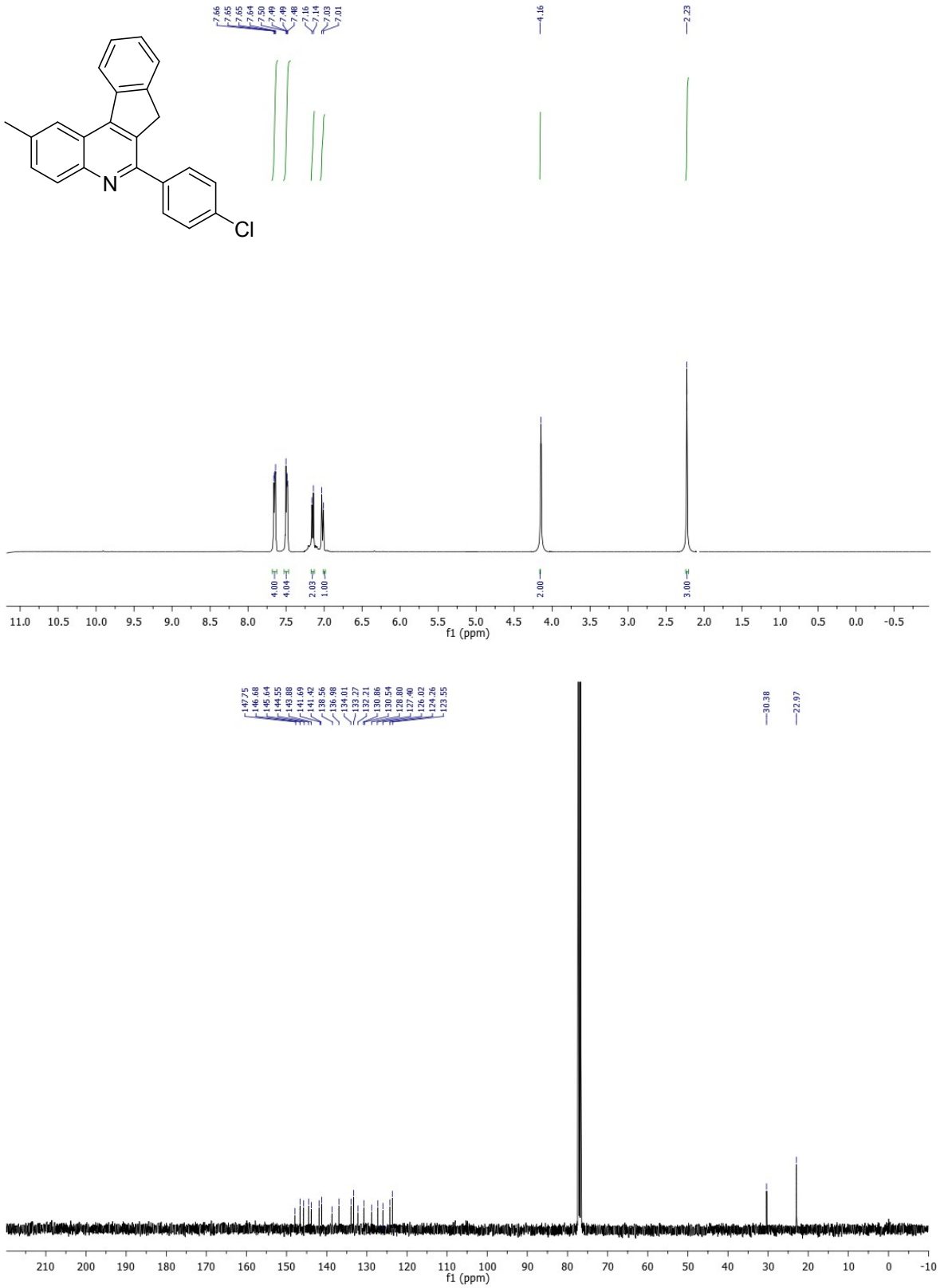




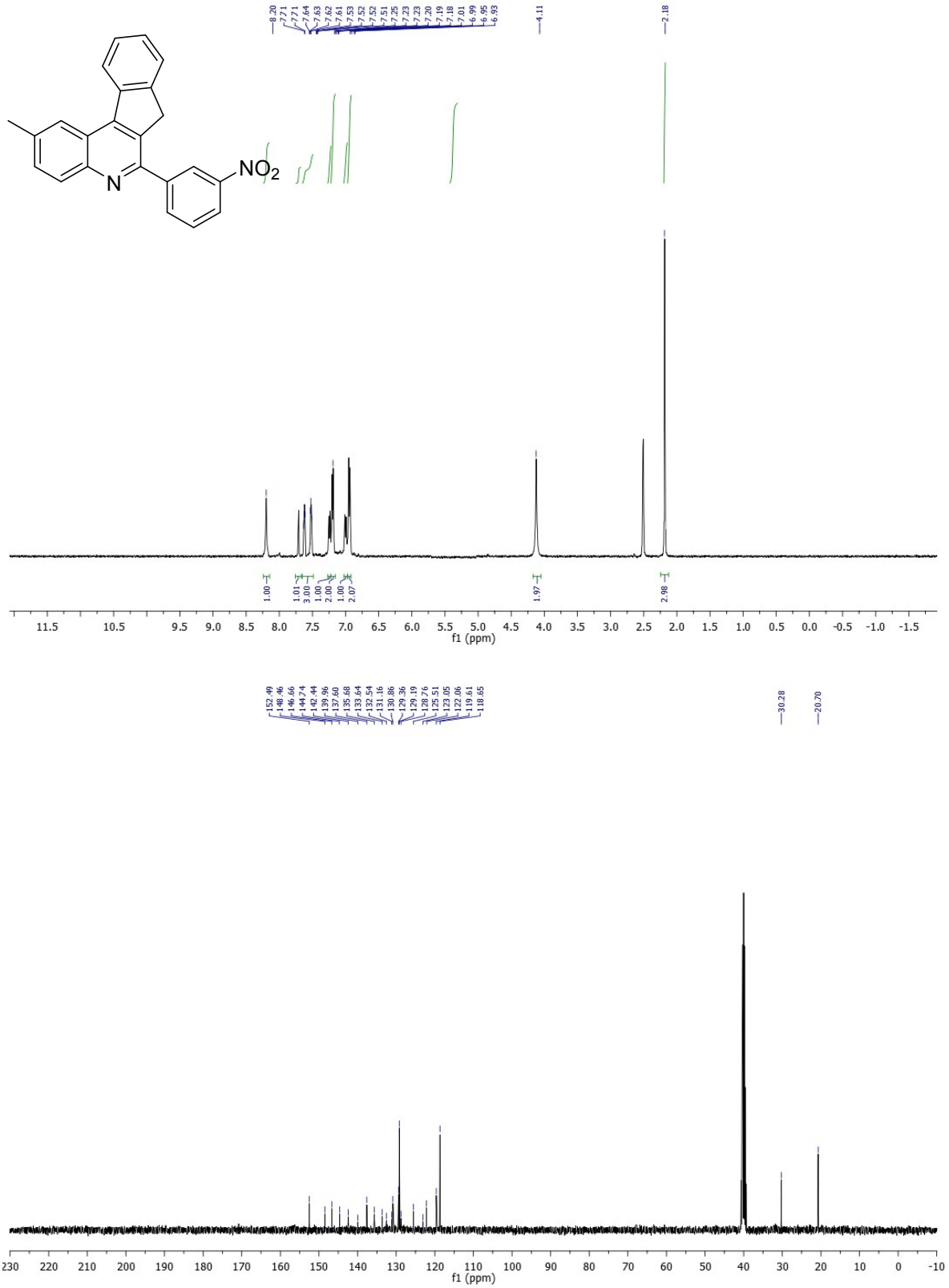
6-(2-Chlorophenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinolone (10)



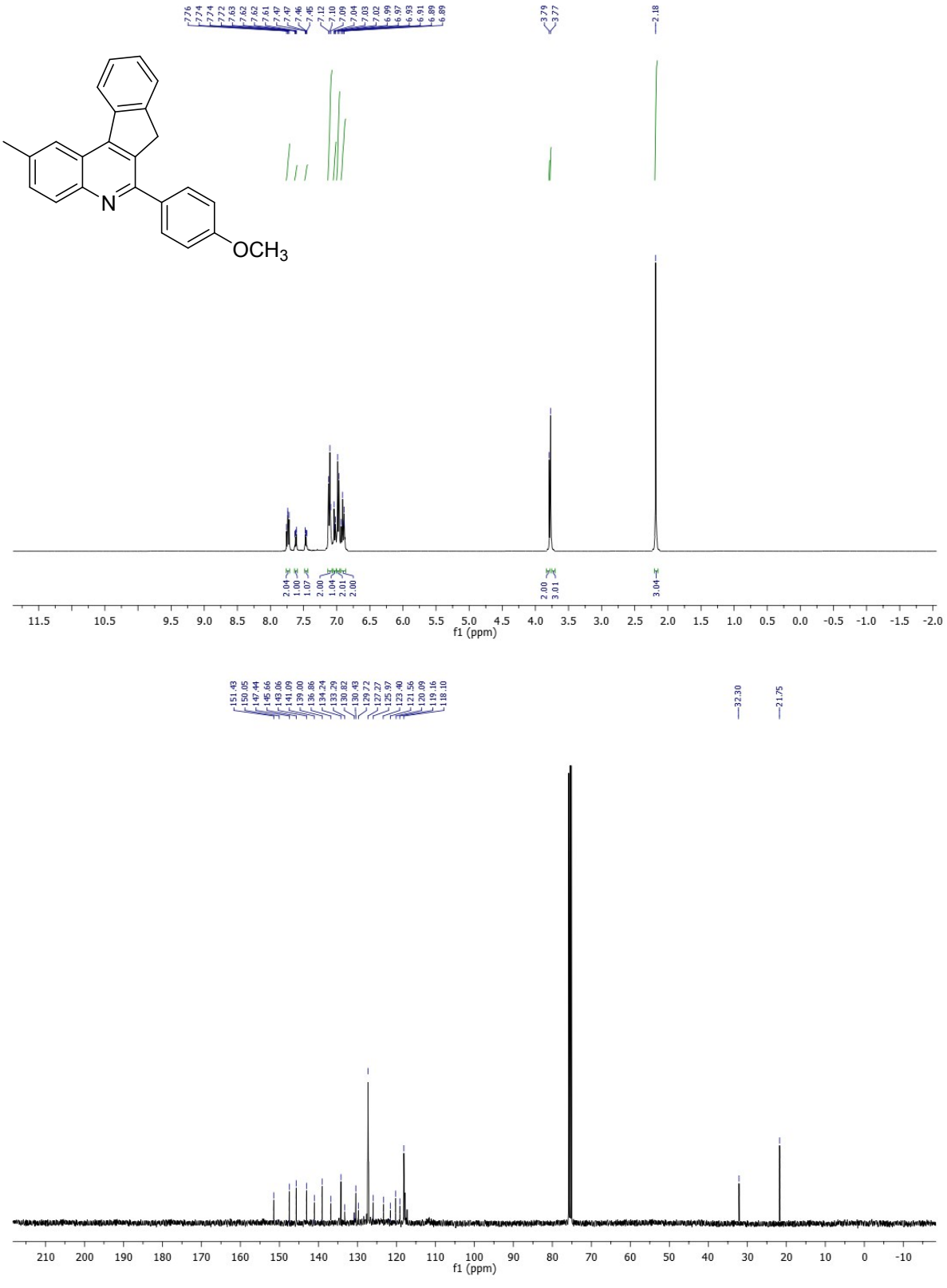
6-(4-Chlorophenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinoline (11)



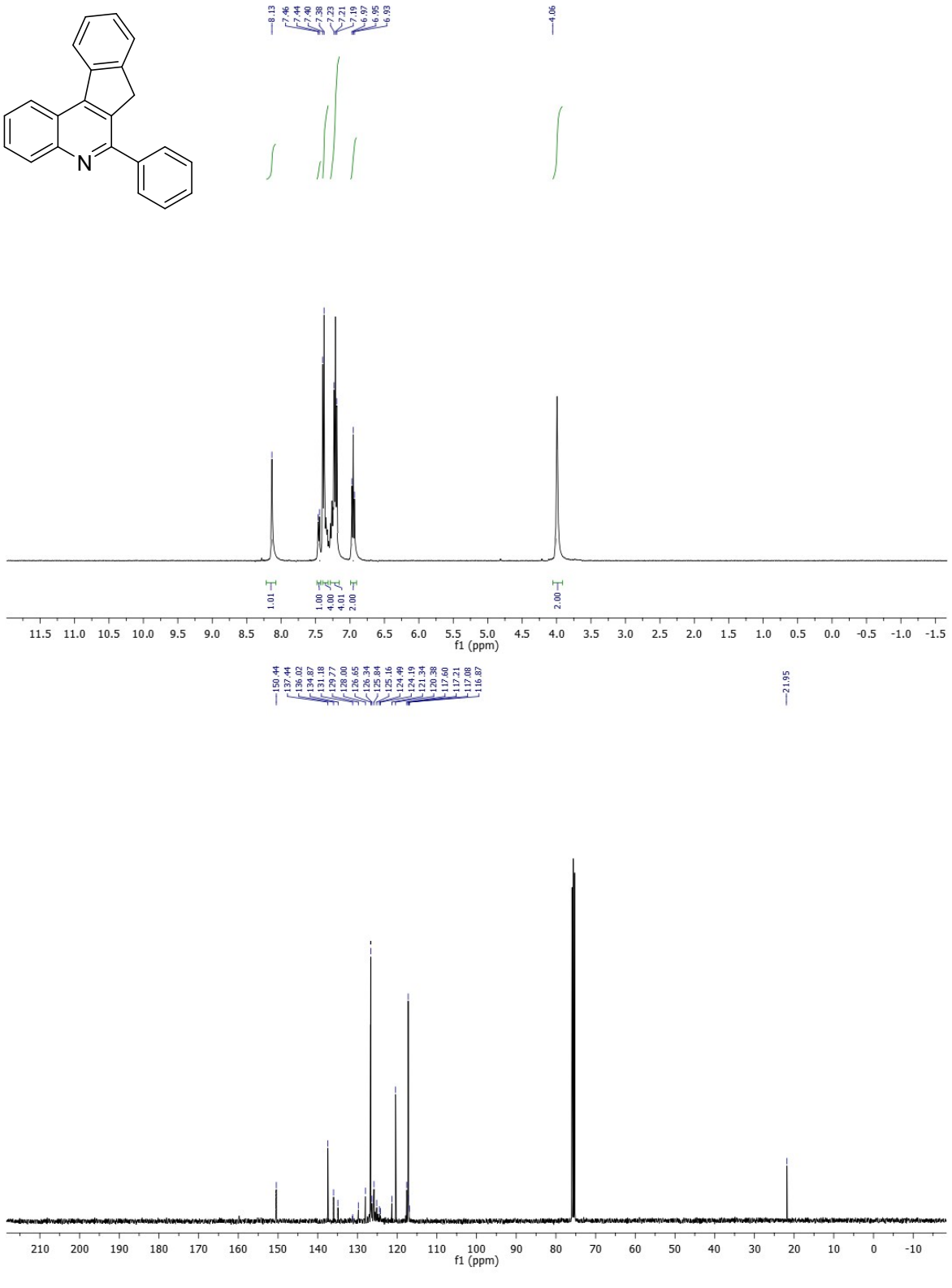
2-Methyl-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (12)



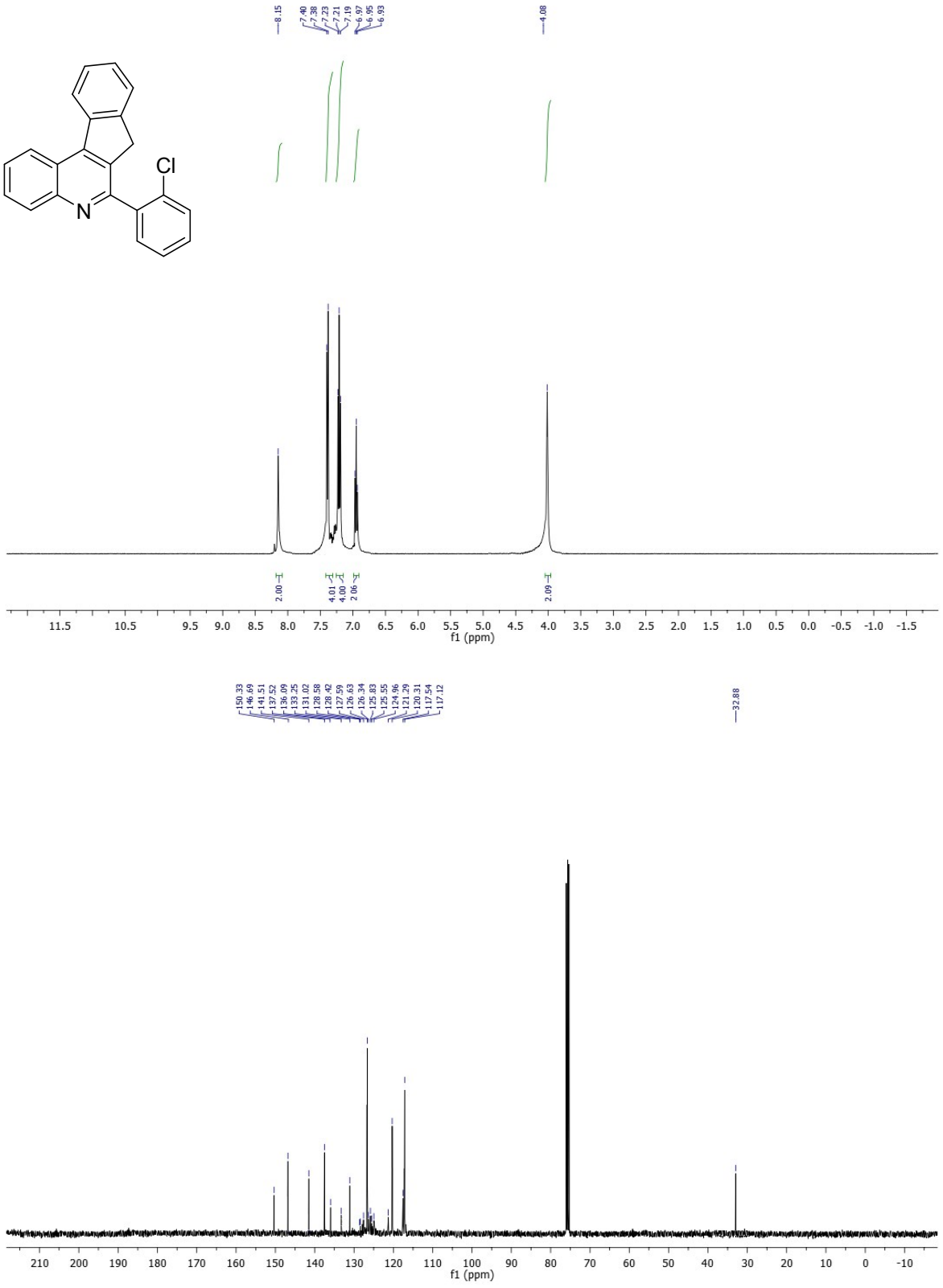
6-(4-Methoxyphenyl)-2-methyl-7*H*-indeno[2,1-*c*]quinoline (13)



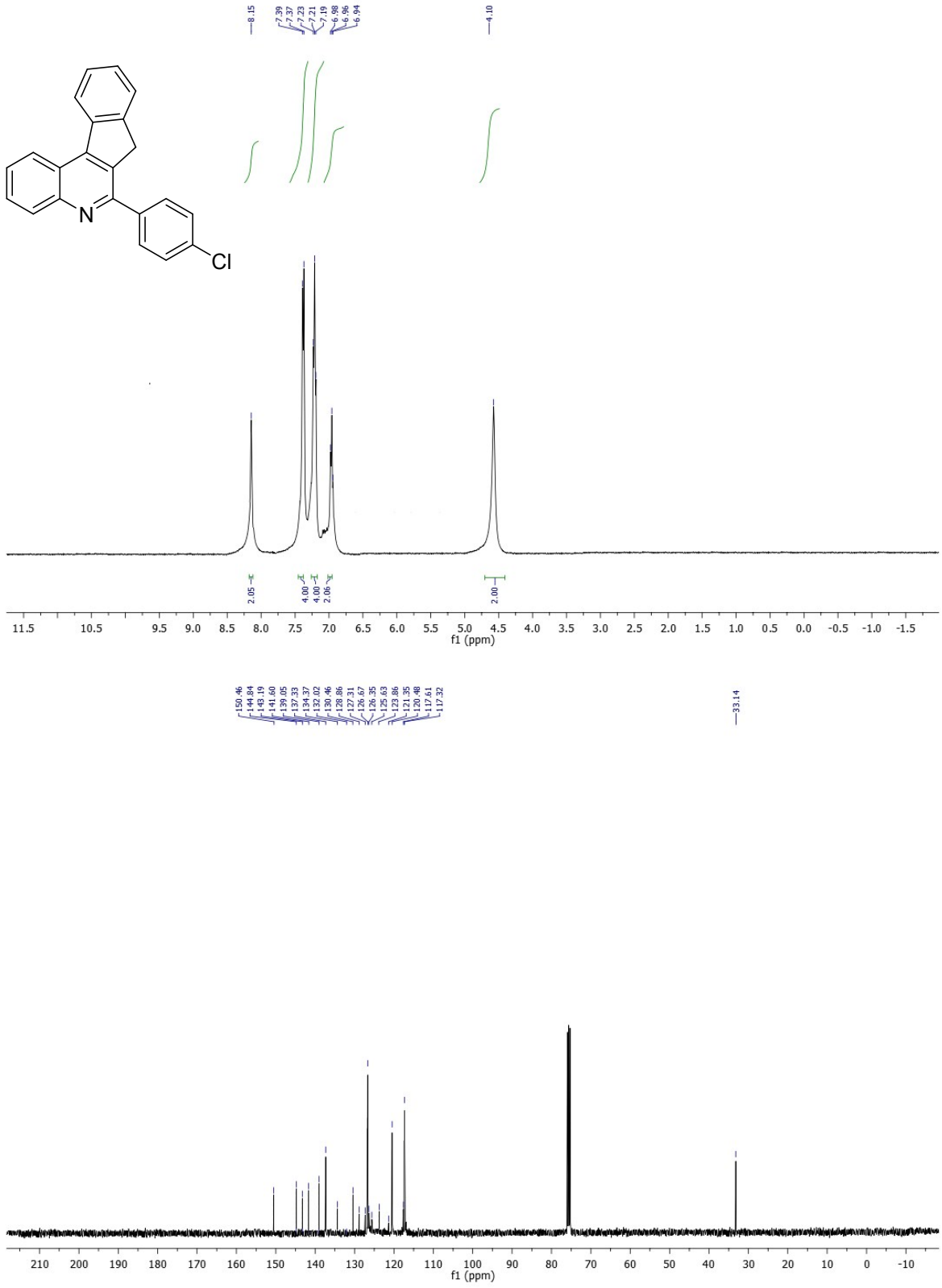
6-Phenyl-7*H*-indeno[2,1-*c*]quinoline (14)



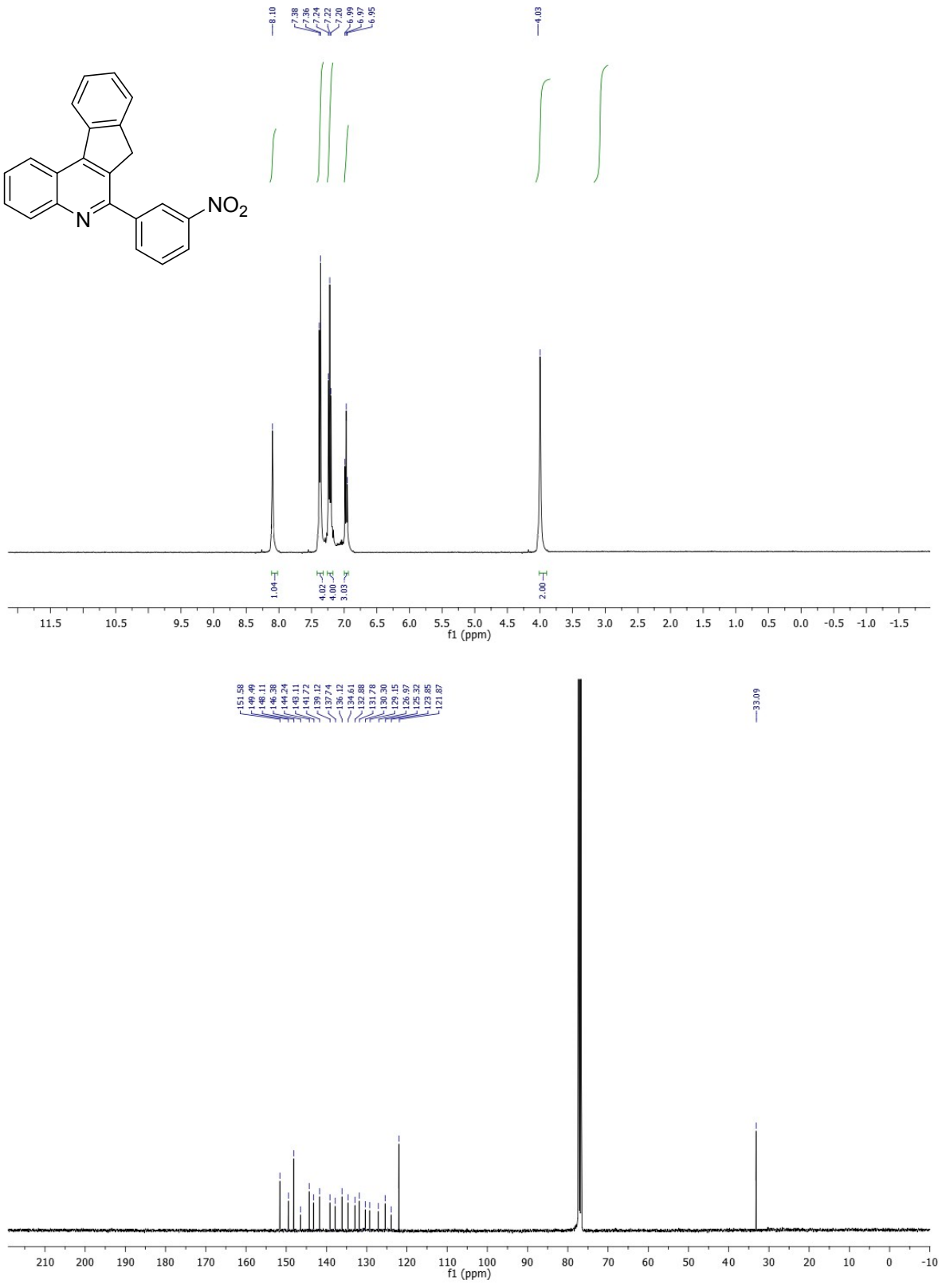
6-(2-Chlorophenyl)-7H-indeno[2,1-c]quinoline (15)



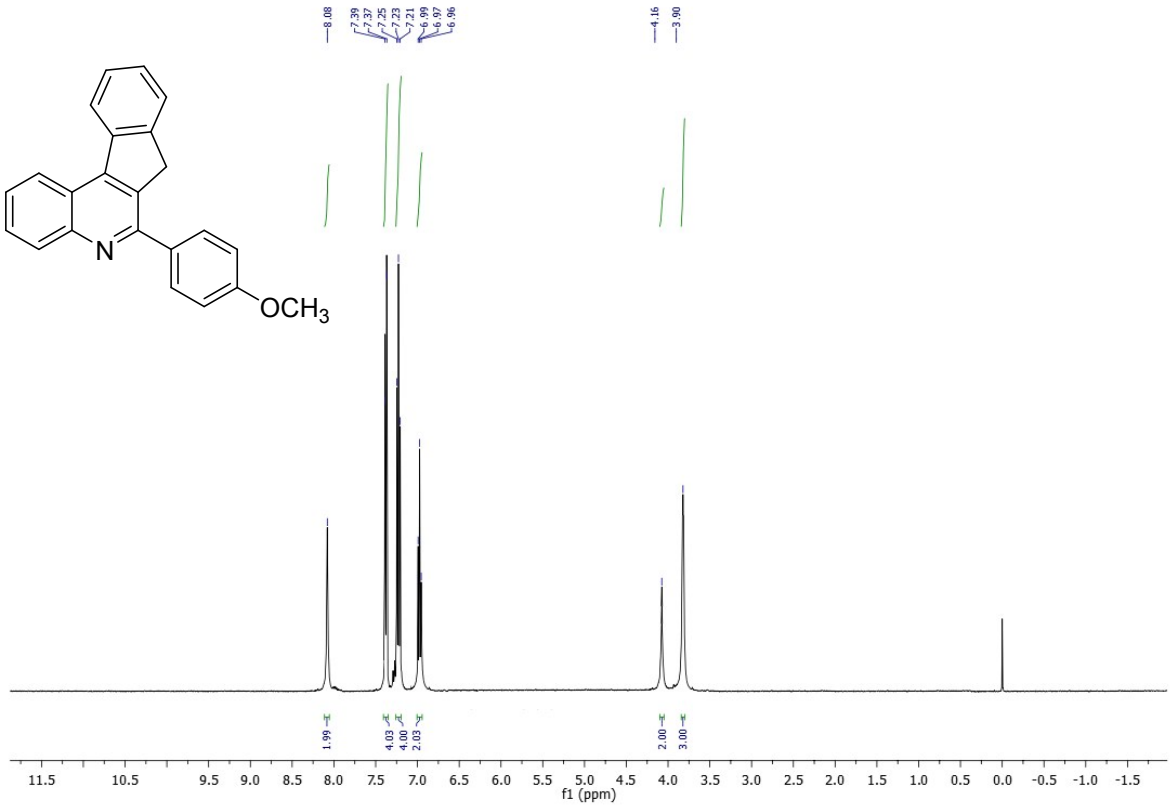
6-(4-Chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (16)

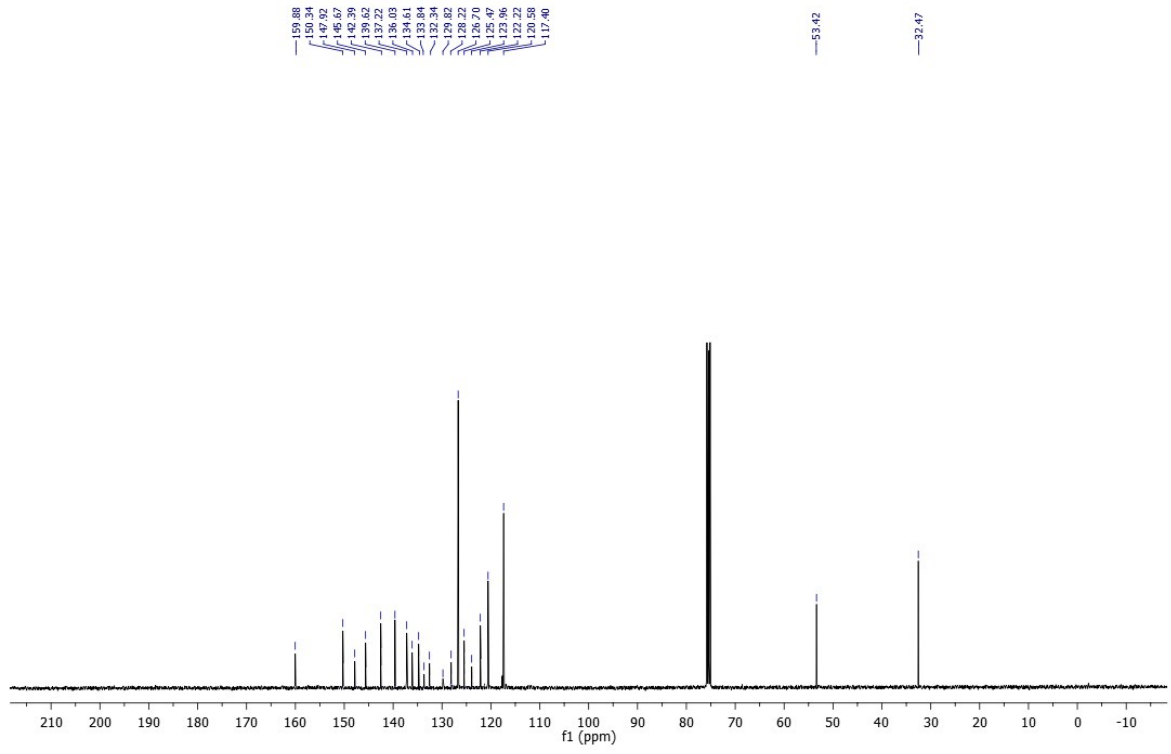


6-(3-Nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (17)

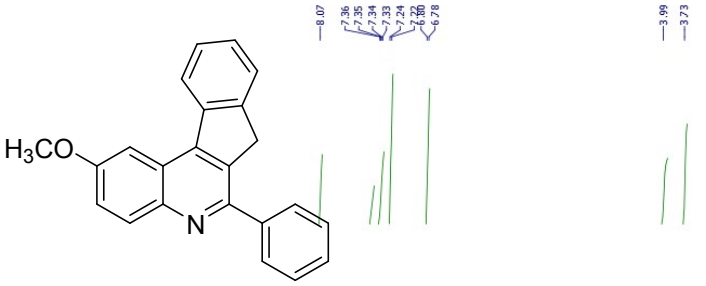


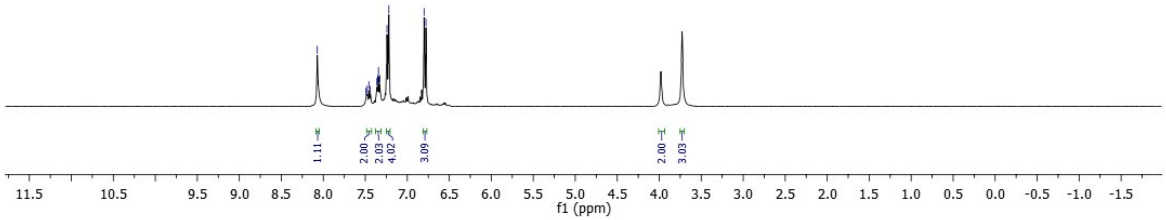
6-(4-Methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (18)

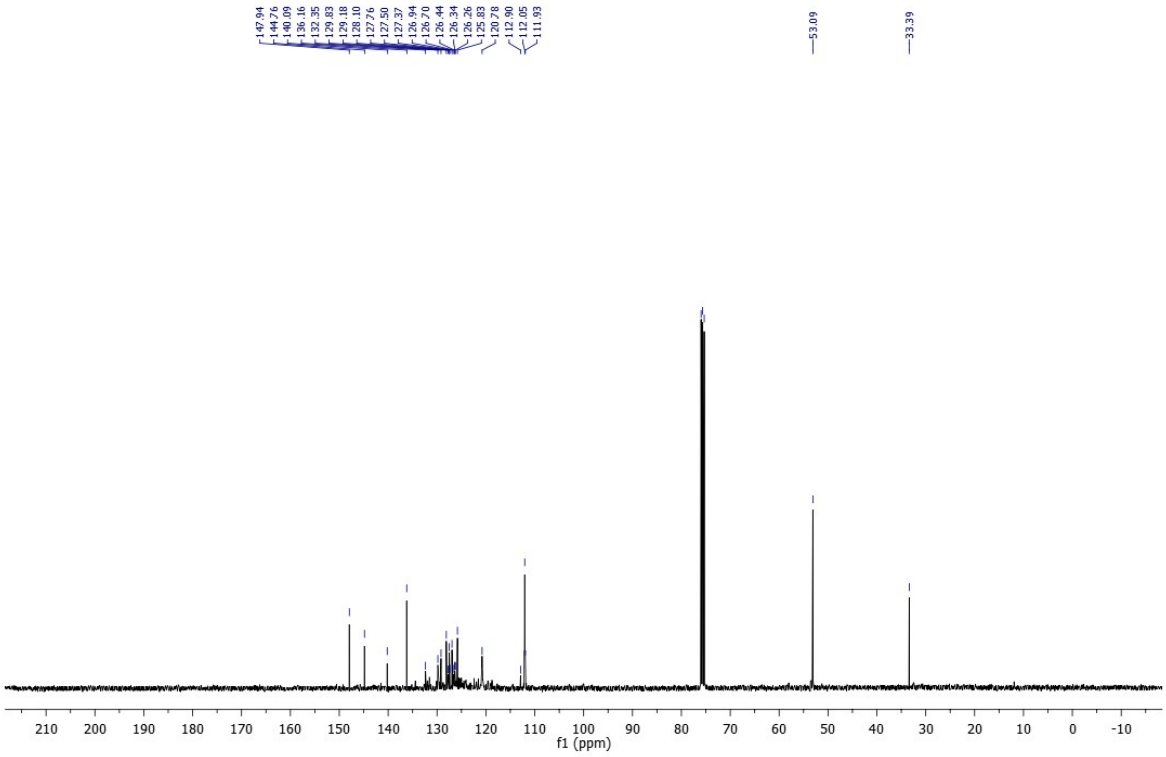

8.08
7.39
7.37
7.25
7.23
7.21
6.99
6.97
6.96
4.16
3.90
N
OCH3
1.99
4.03
4.00
2.03
2.00
3.00
f1 (ppm)


159.88
150.34
147.92
145.67
142.39
139.62
137.22
136.03
134.61
133.84
132.34
129.82
128.22
126.70
125.47
123.96
122.22
120.58
117.40
53.42
32.47
f1 (ppm)

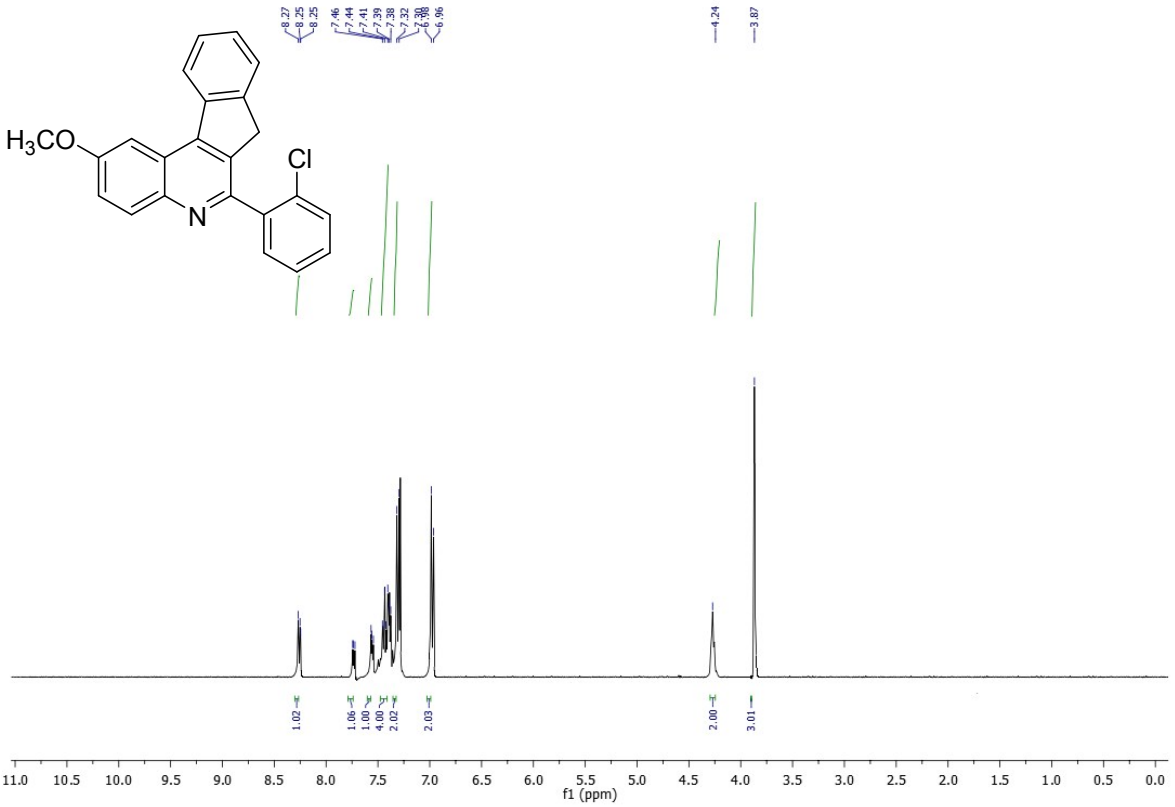
2-Methoxy-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (19)

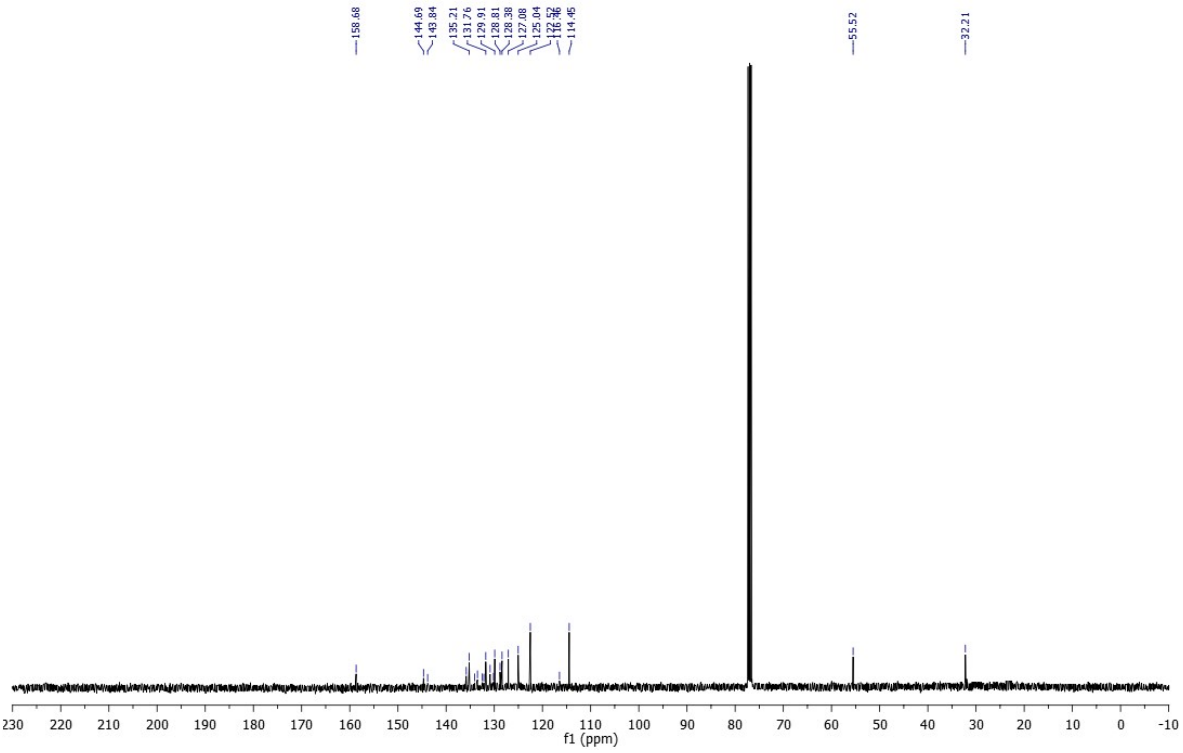




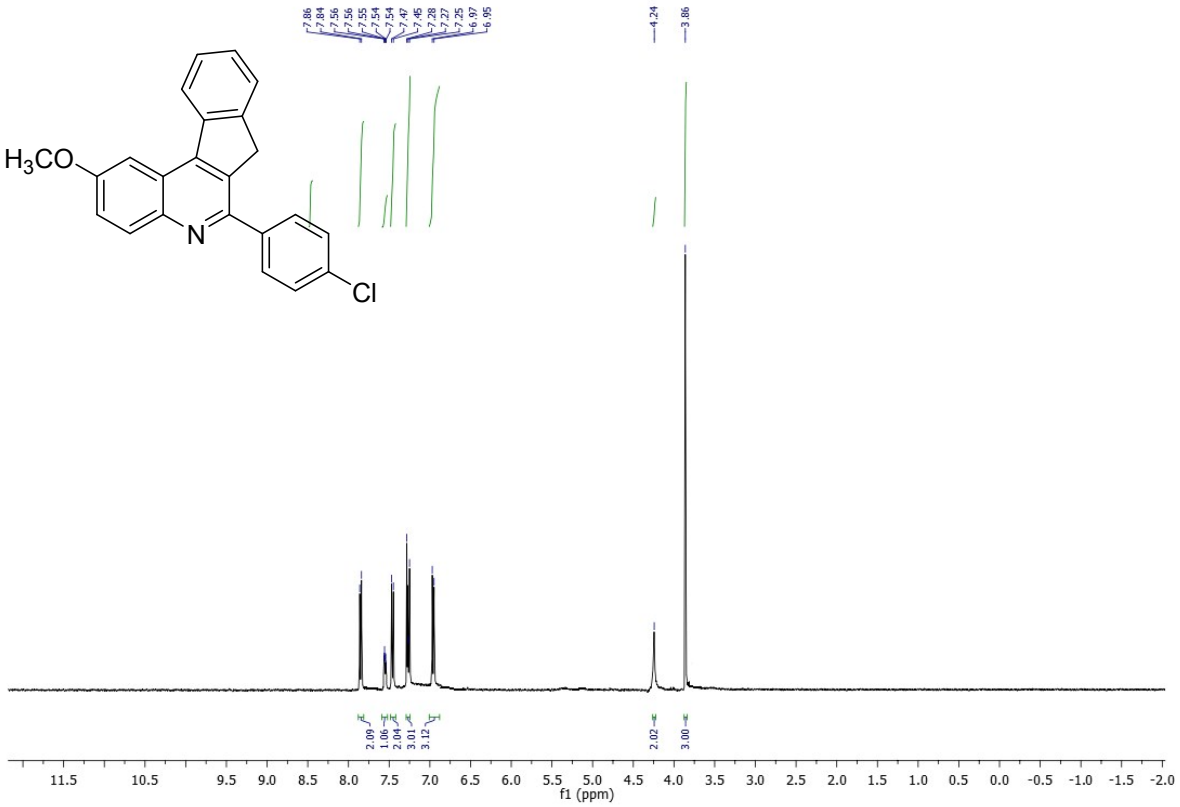


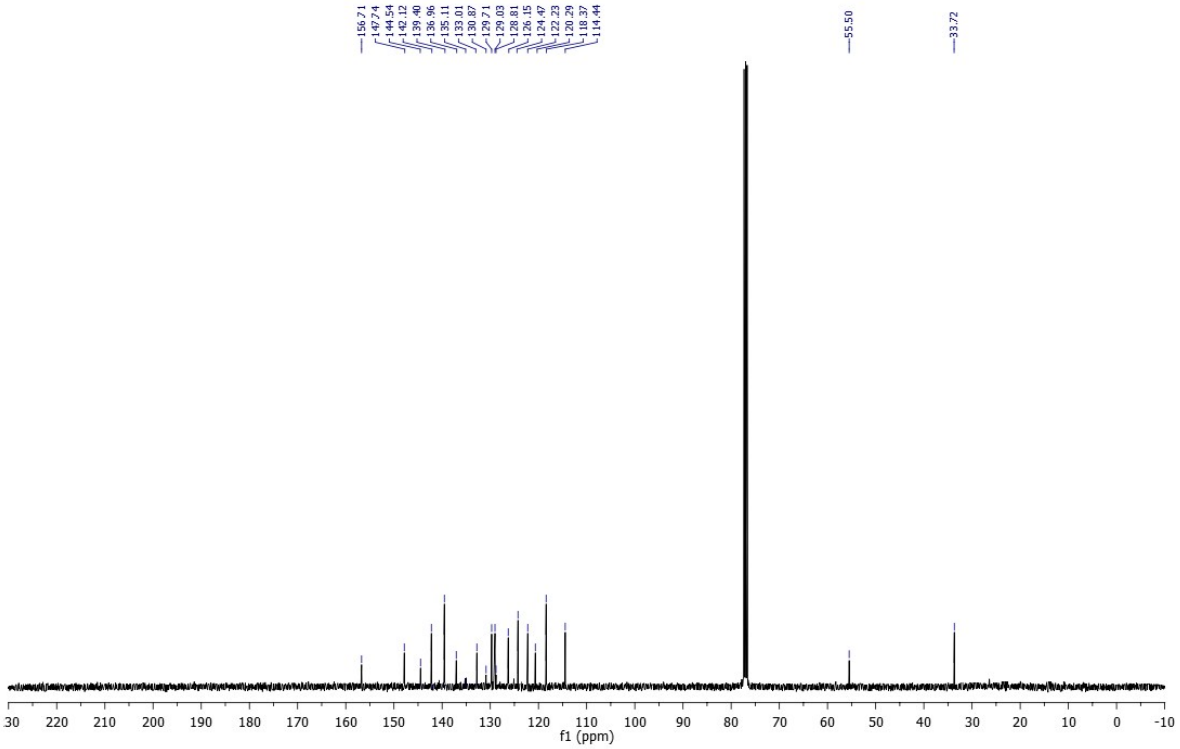
6-(2-Chlorophenyl)-2-methoxy-7*H*-indeno[2,1-*c*]quinoline (20)



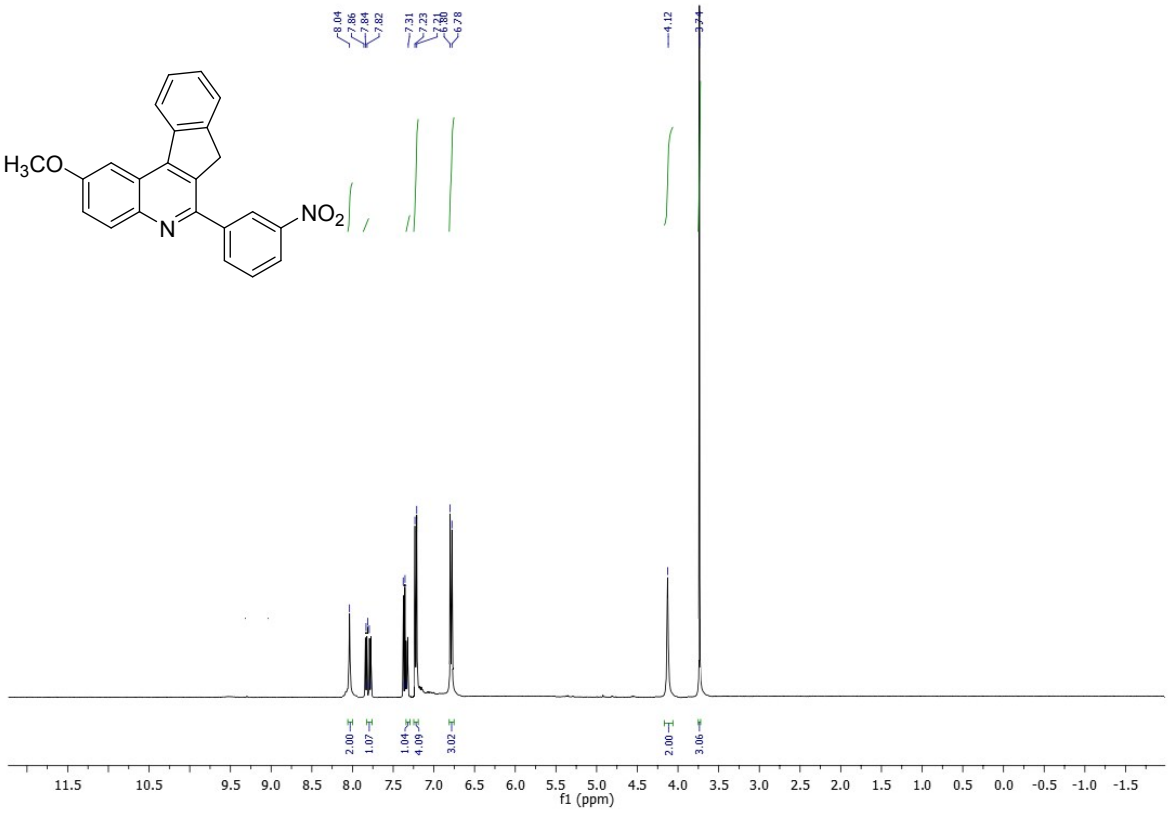


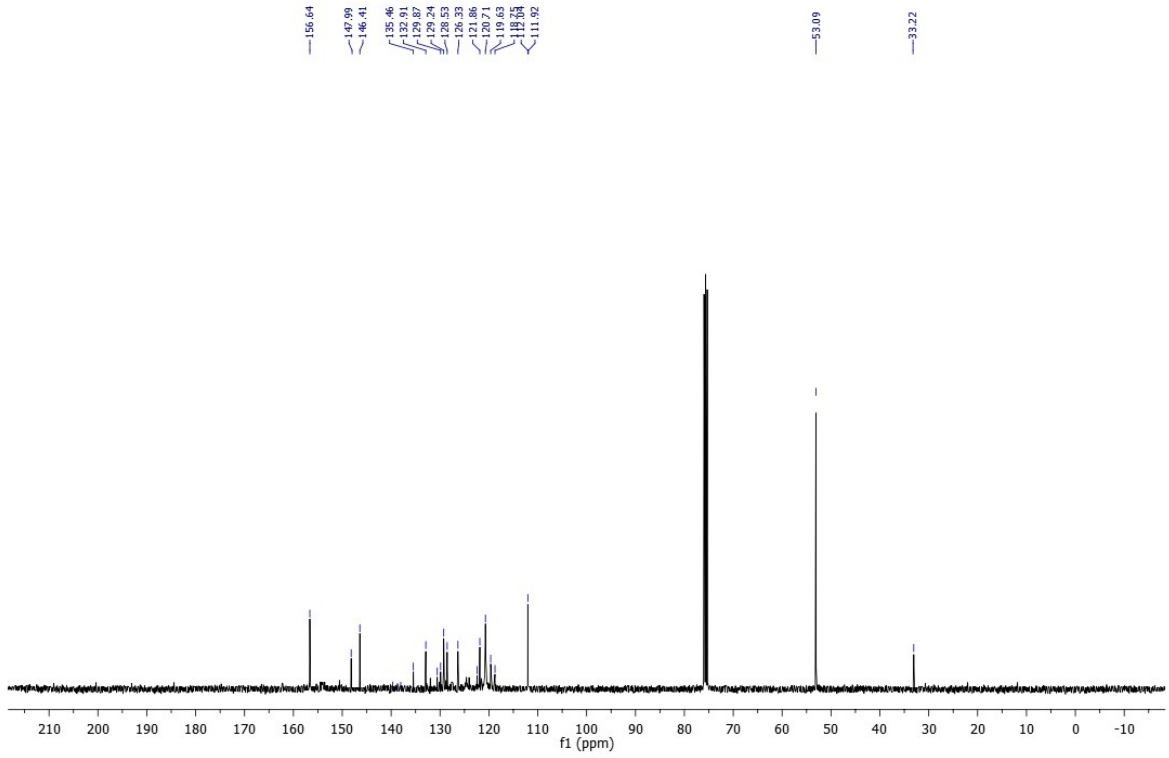
6-(4-Chlorophenyl)-2-methoxy-7*H*-indeno[2,1-*c*]quinoline (21)



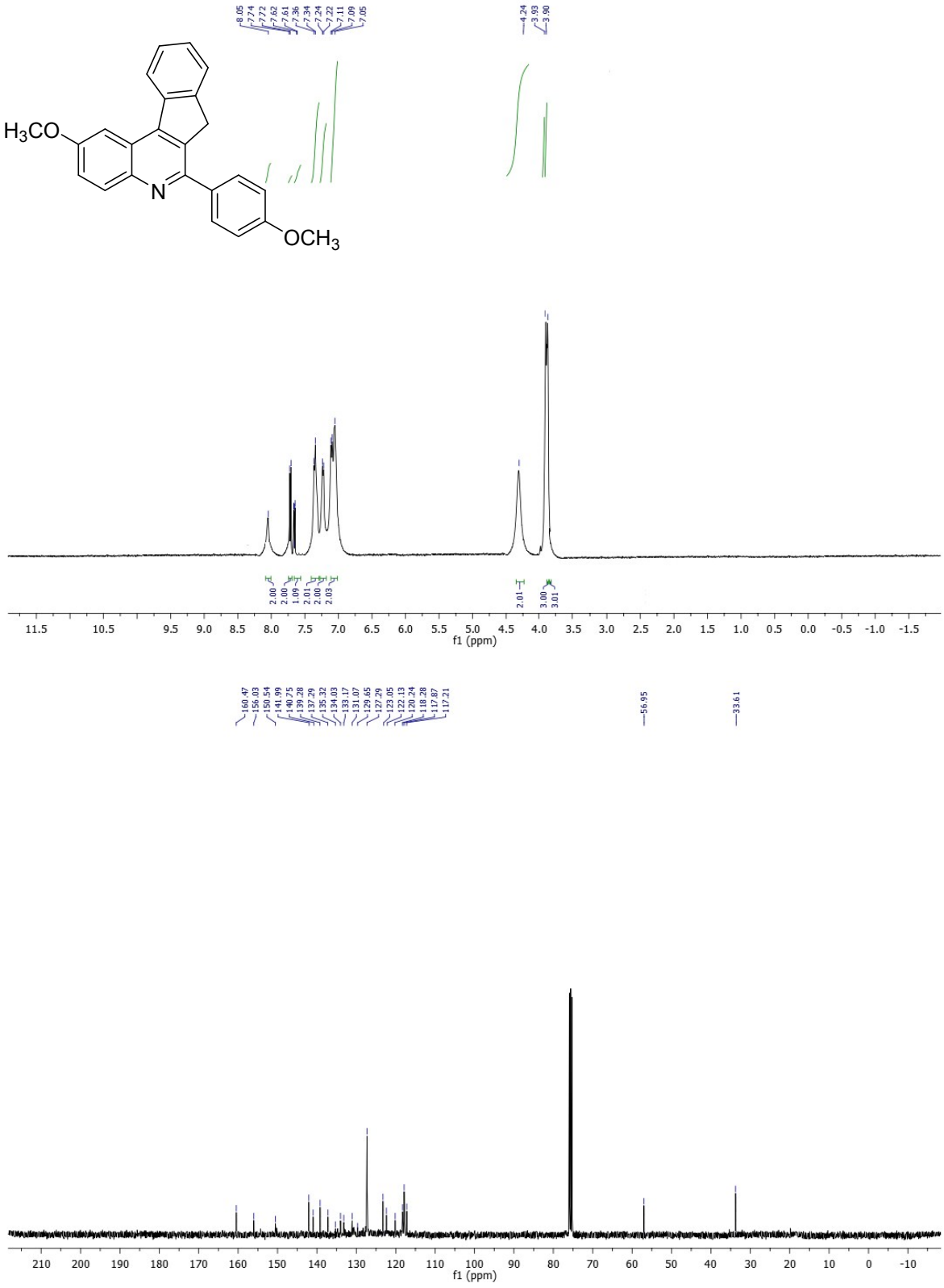


2-Methoxy-6-(3-nitrophenyl)-7H-indeno[2,1-c]quinoline (22)

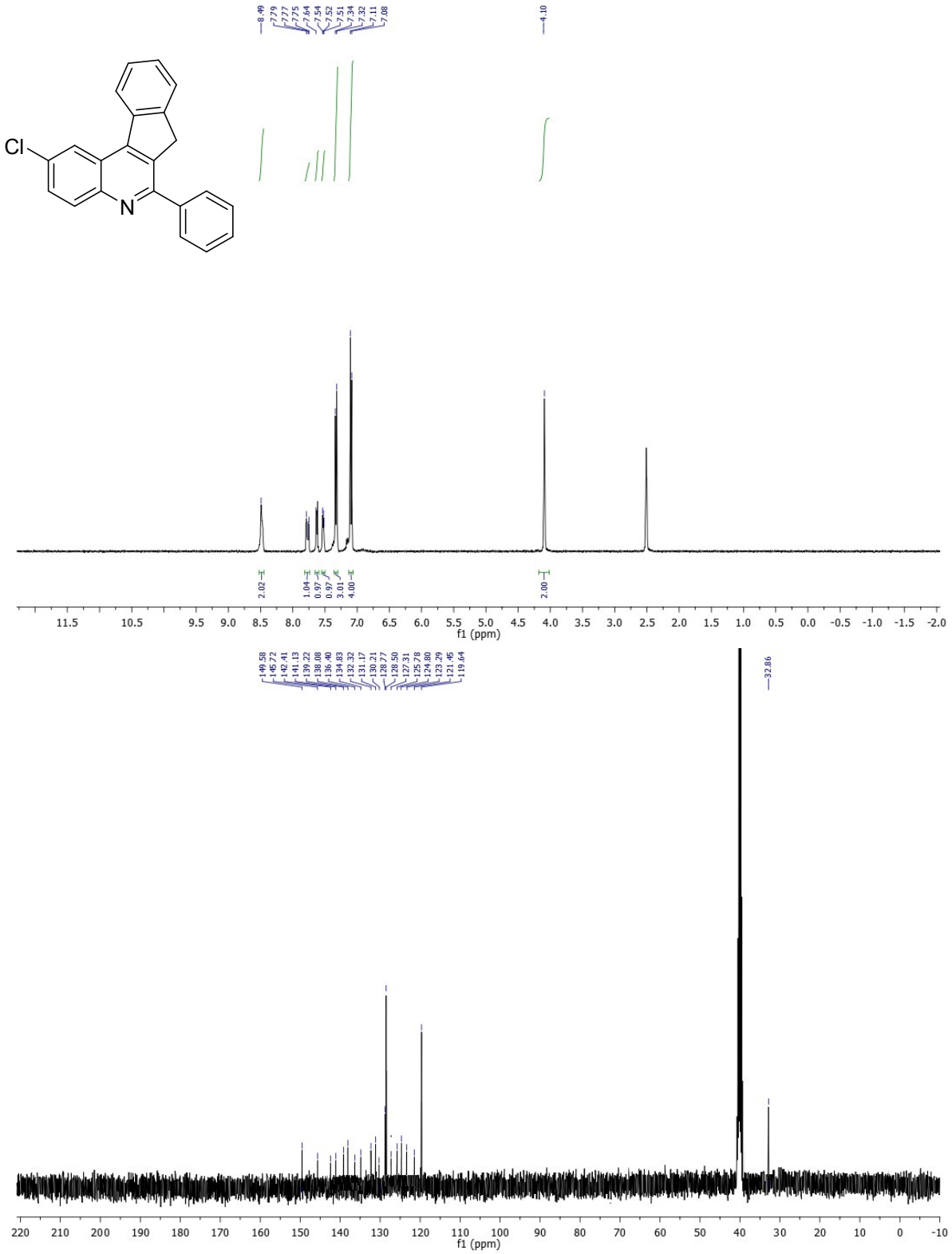




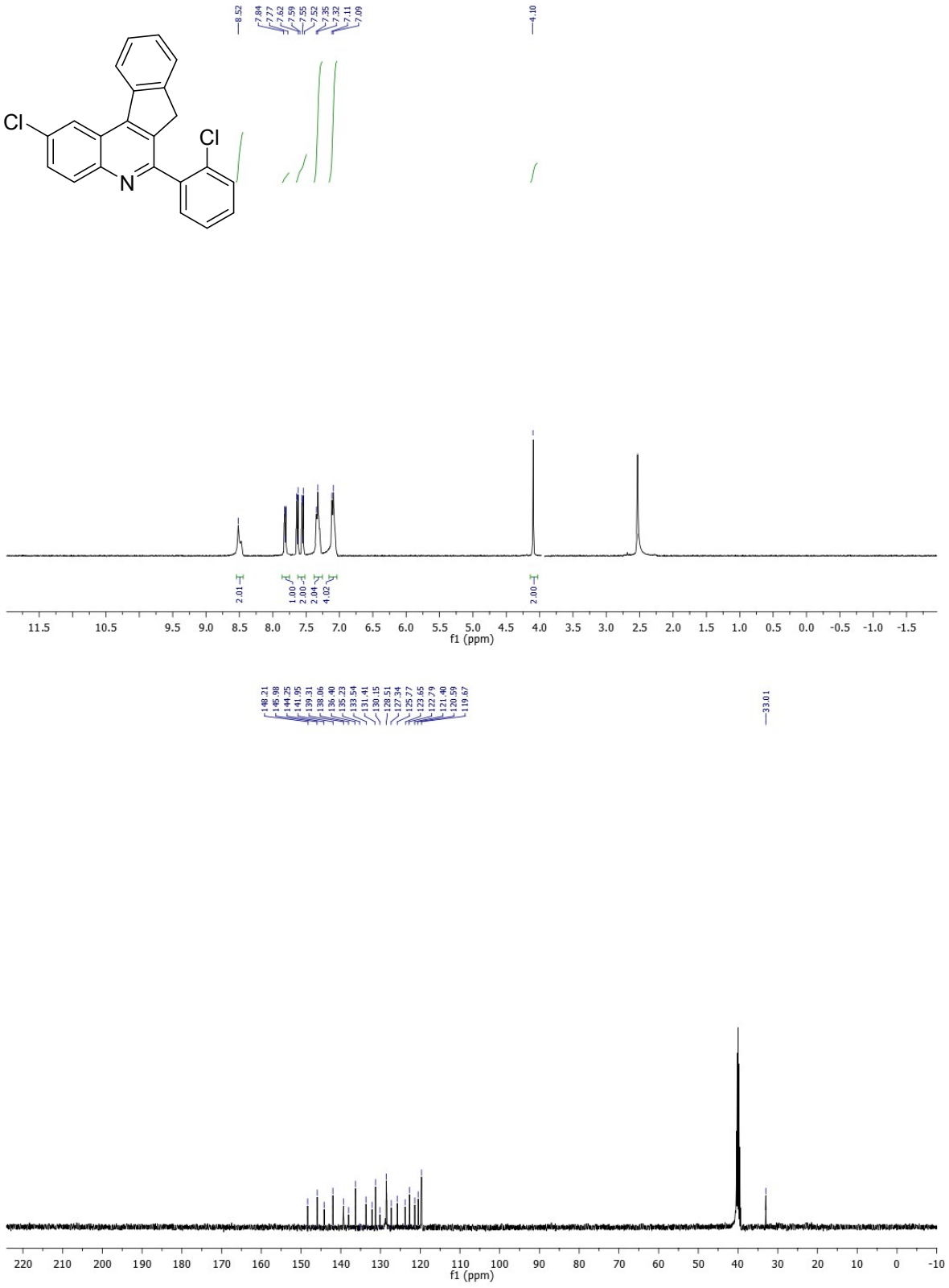
2-Methoxy-6-(4-methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (23)



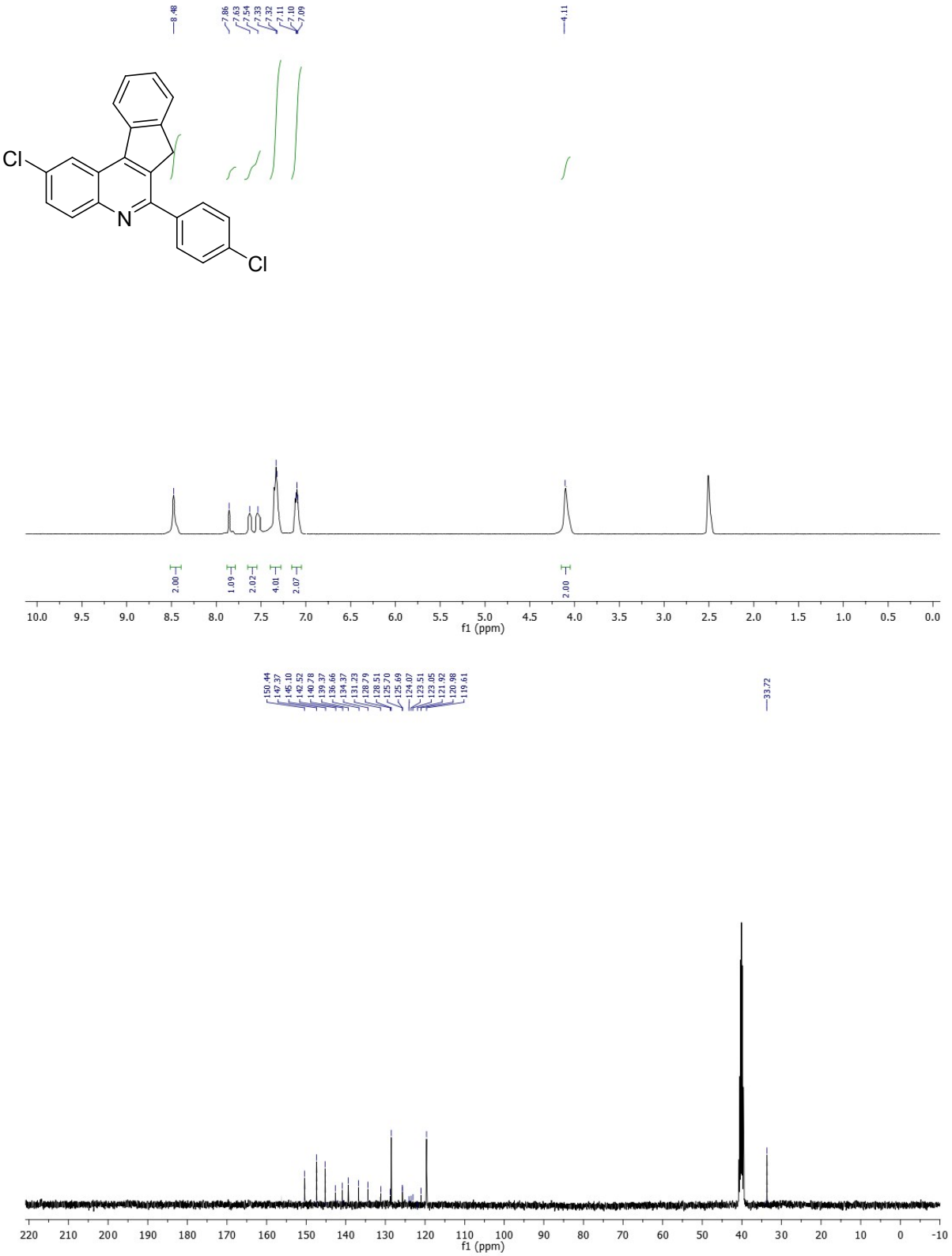
2-Chloro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (24)



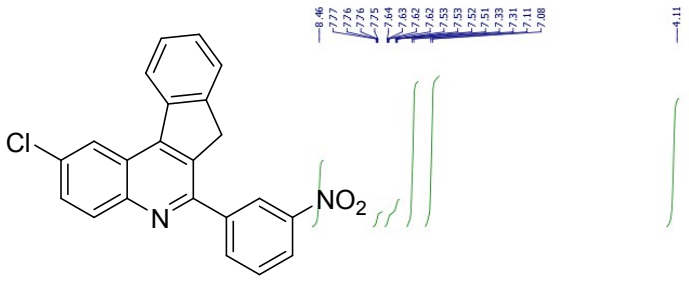
2-Chloro-6-(2-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (25)

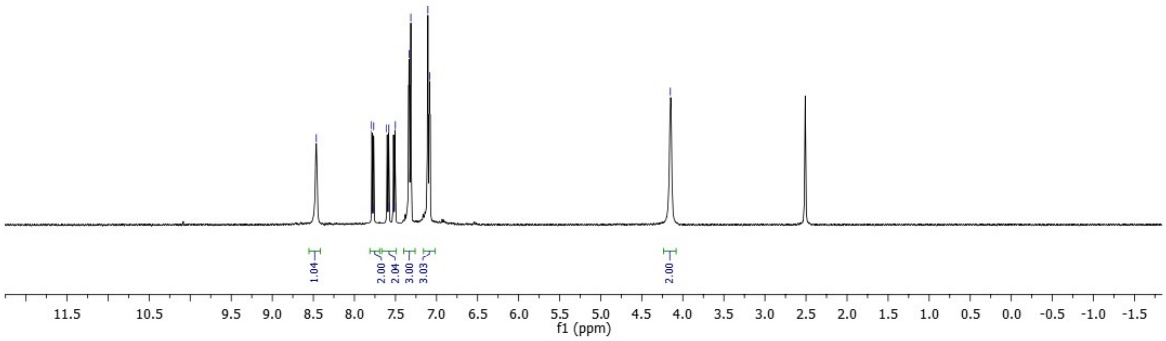


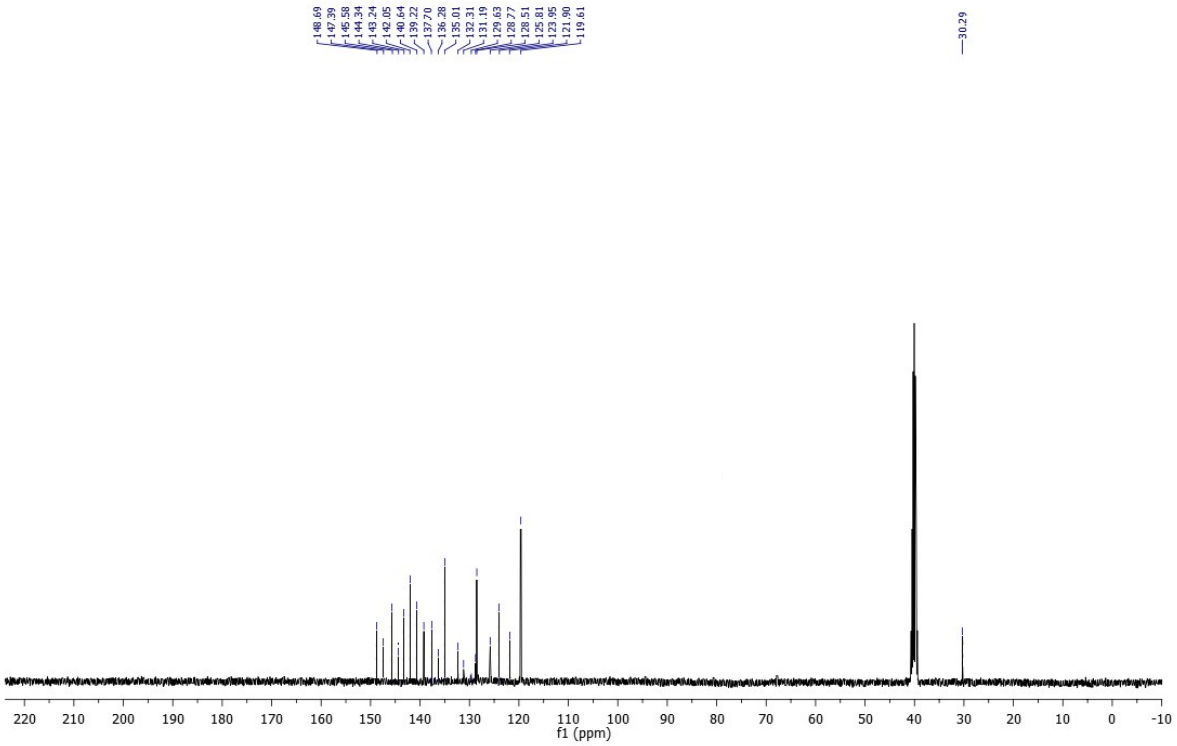
2-Chloro-6-(4-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (26)



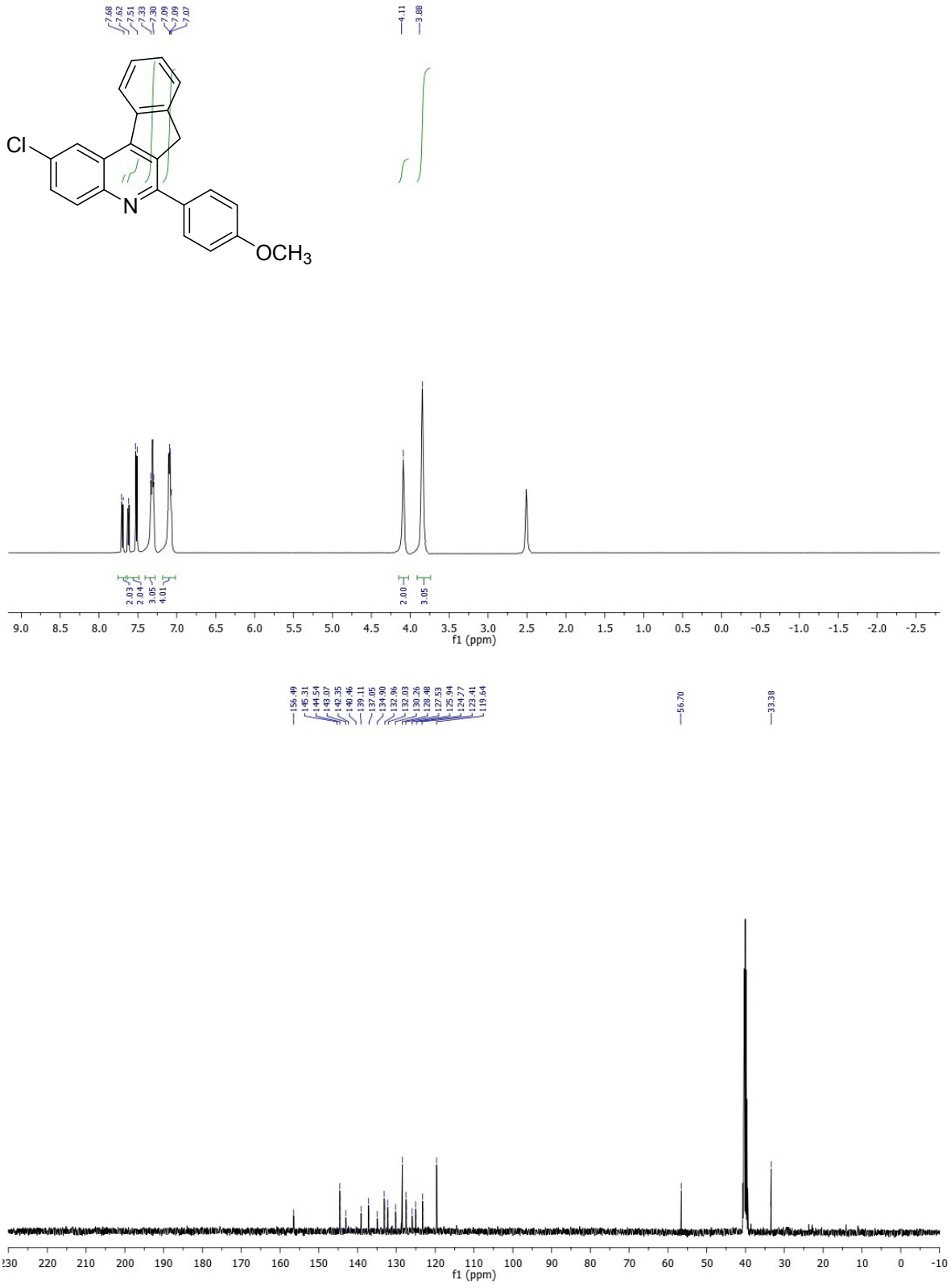
2-Chloro-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (27)



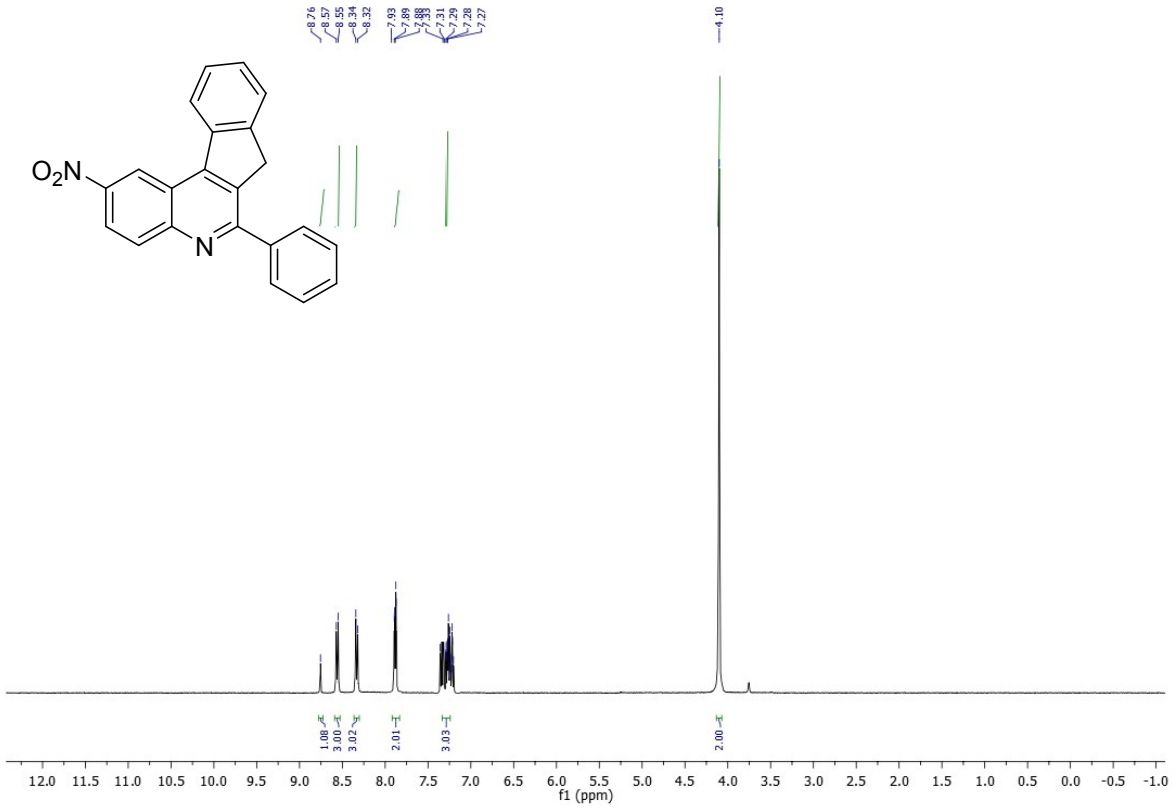


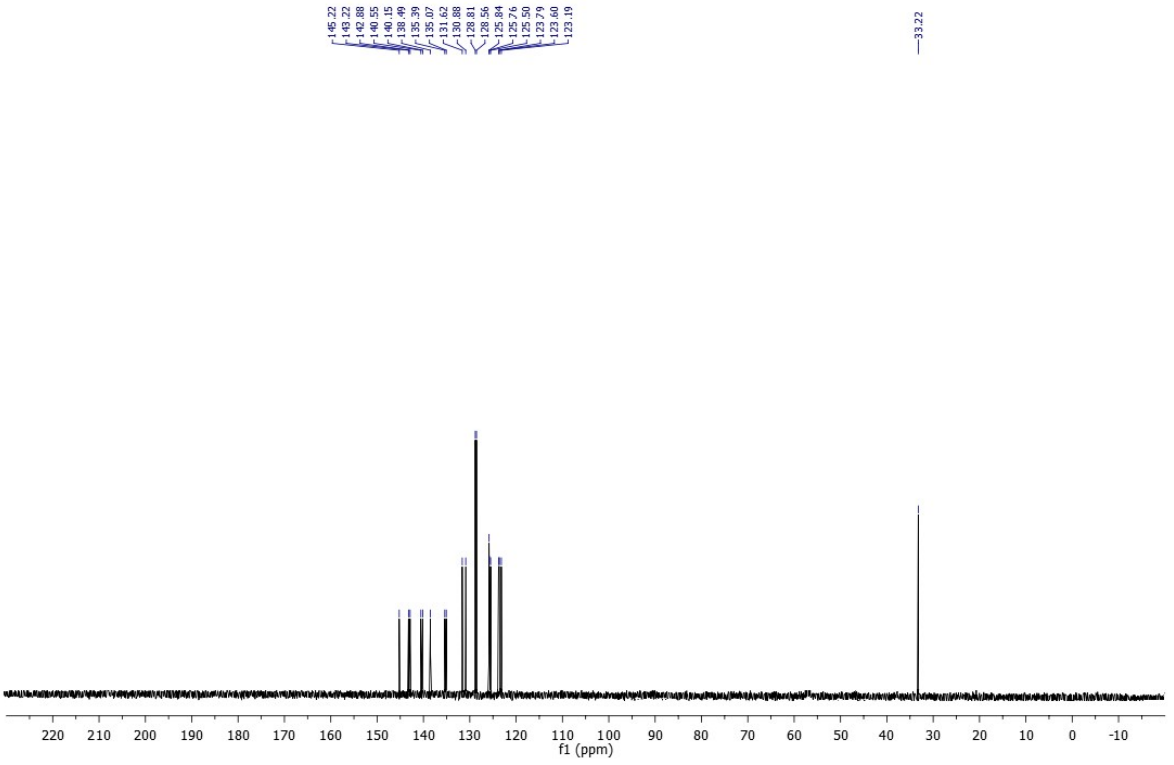


2-Chloro-6-(4-methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (28)

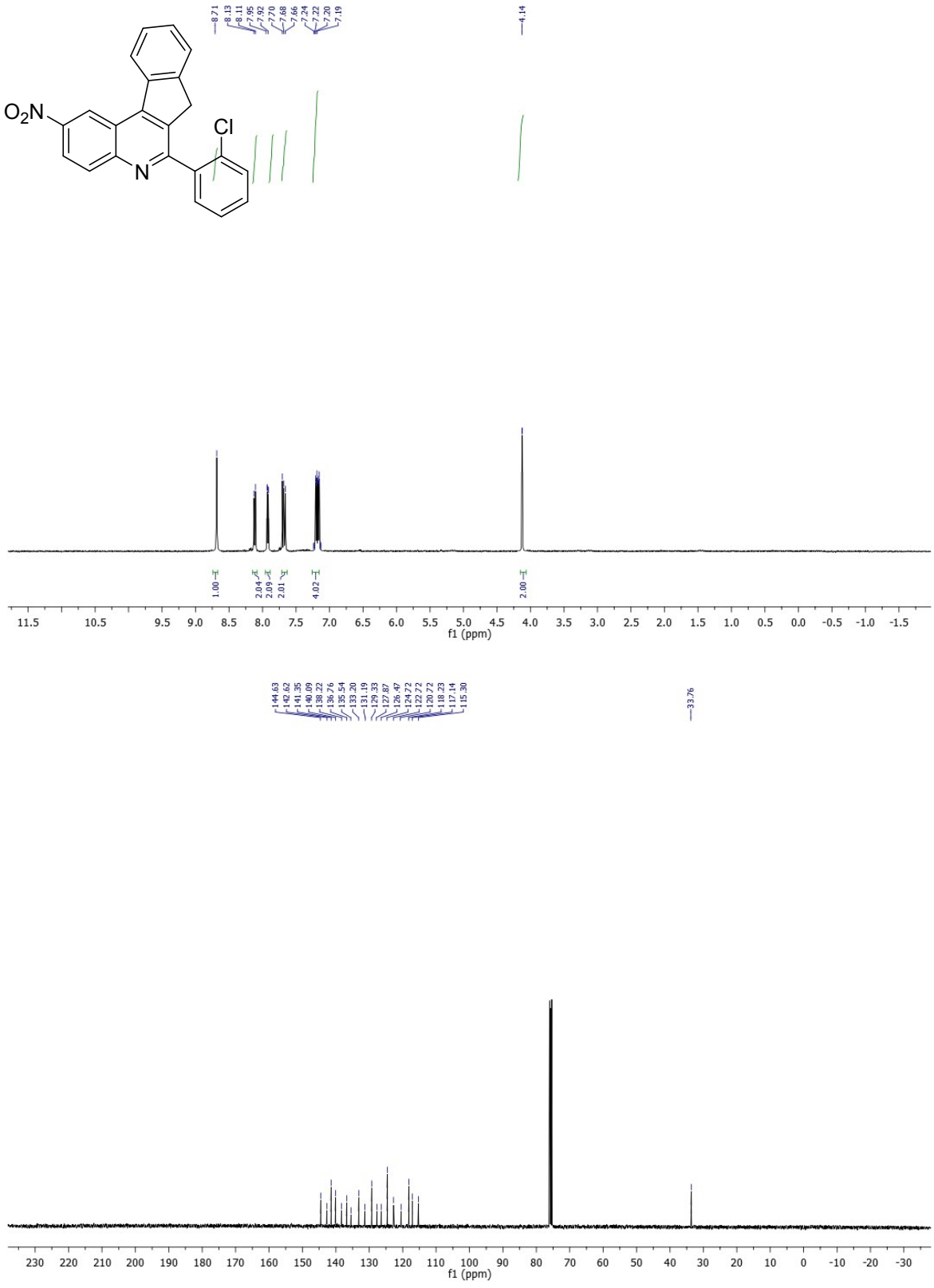


2-Nitro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (29)

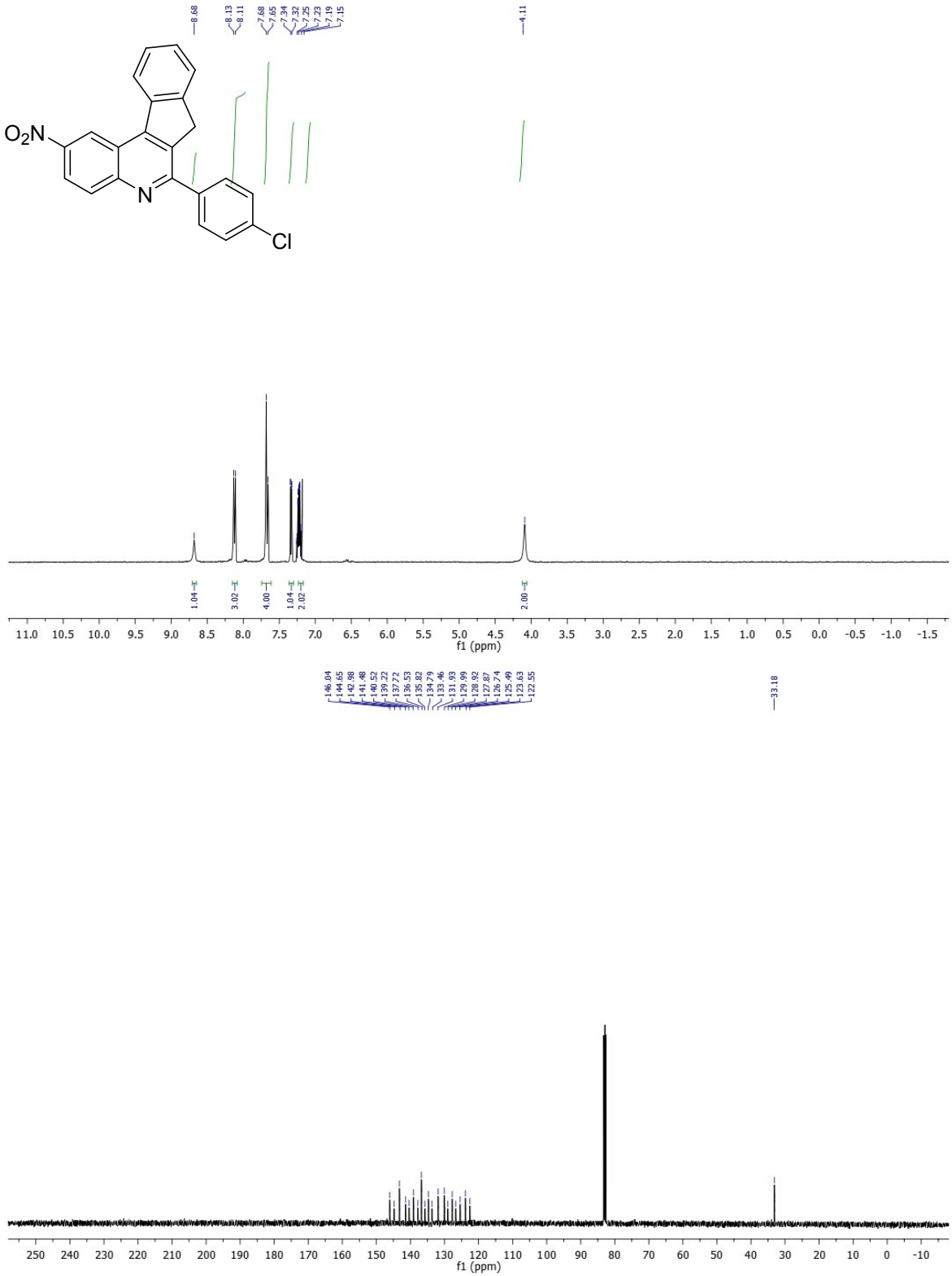




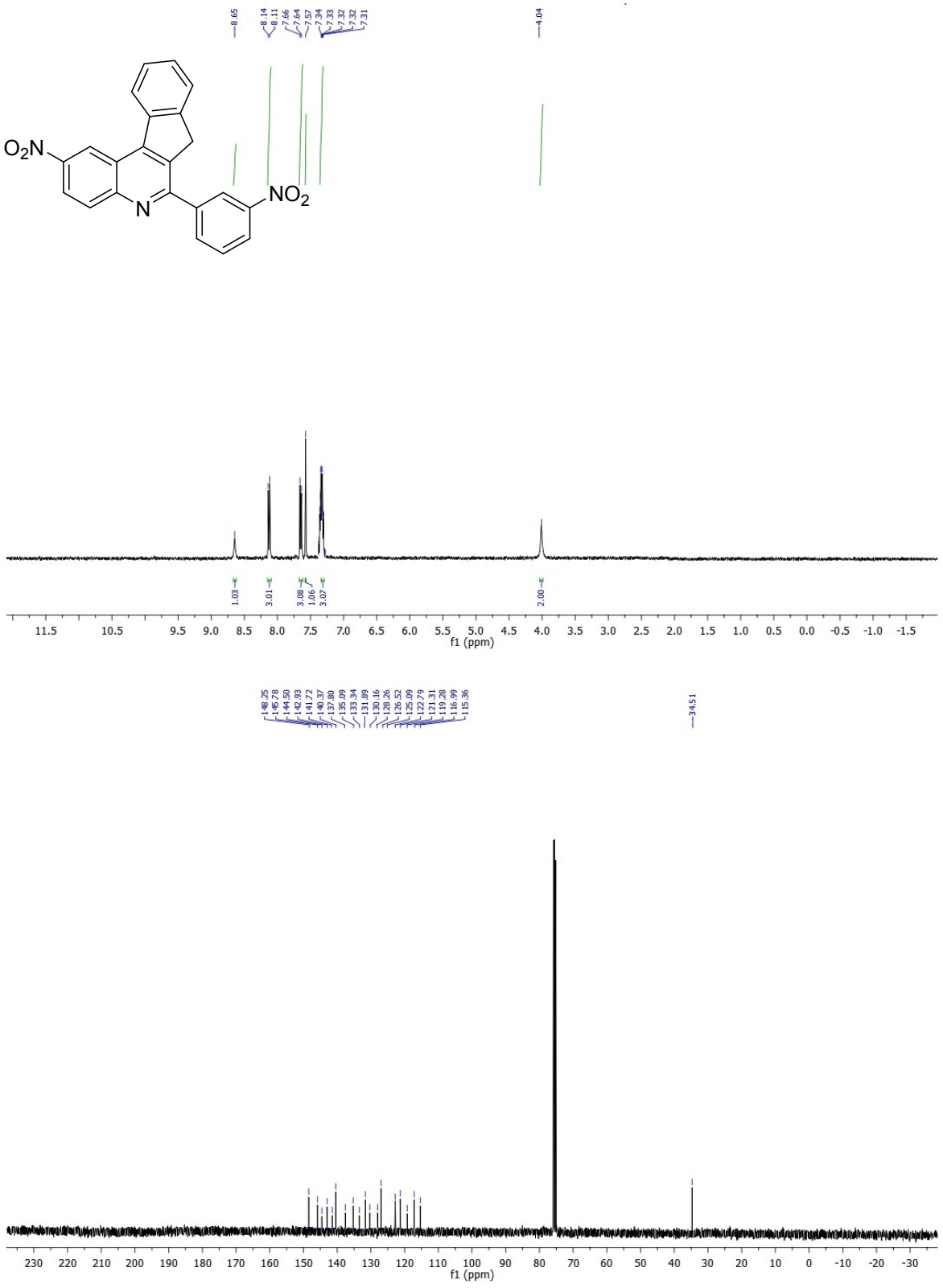
6-(2-Chlorophenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (30)



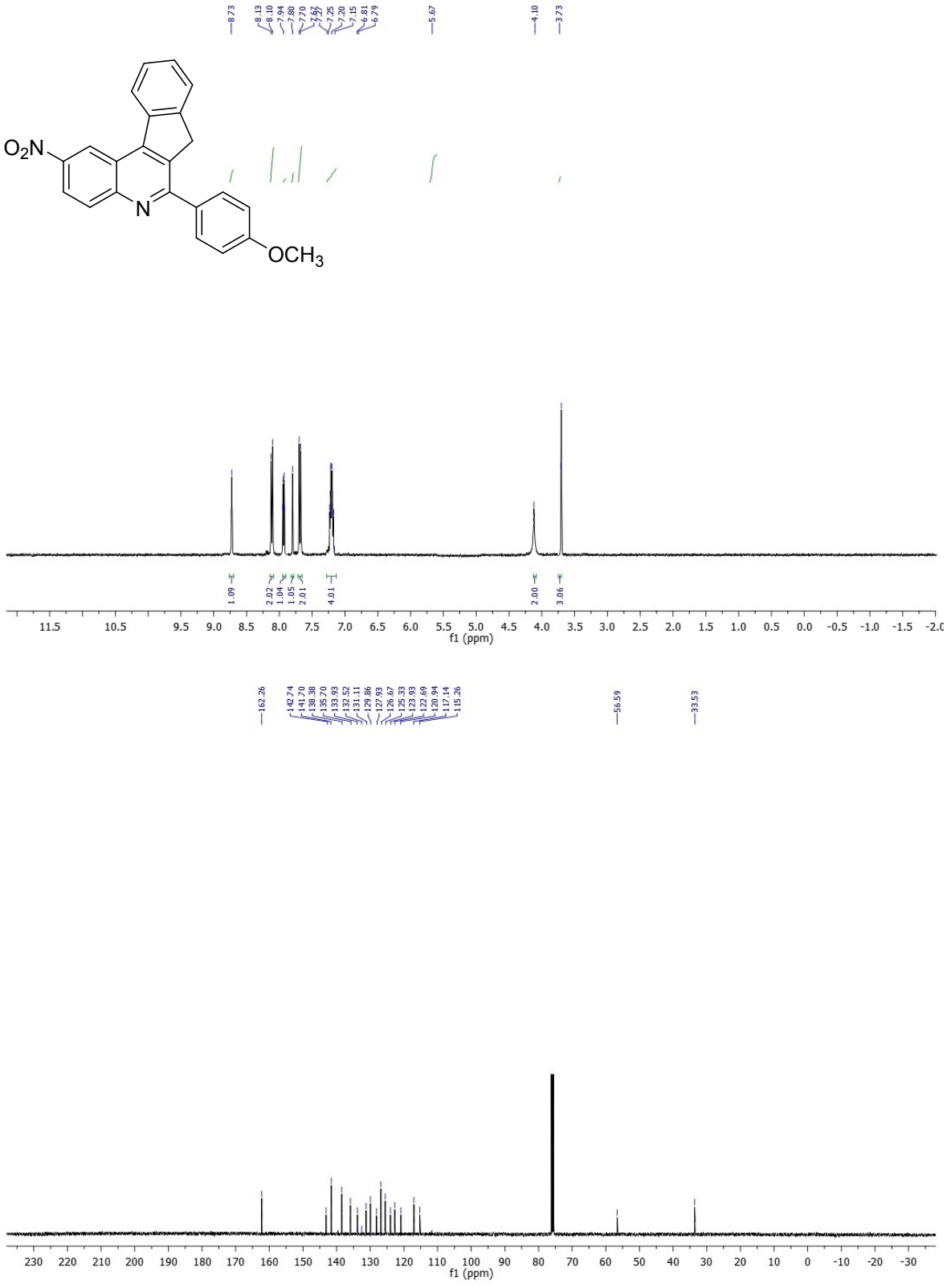
6-(4-Chlorophenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (31)



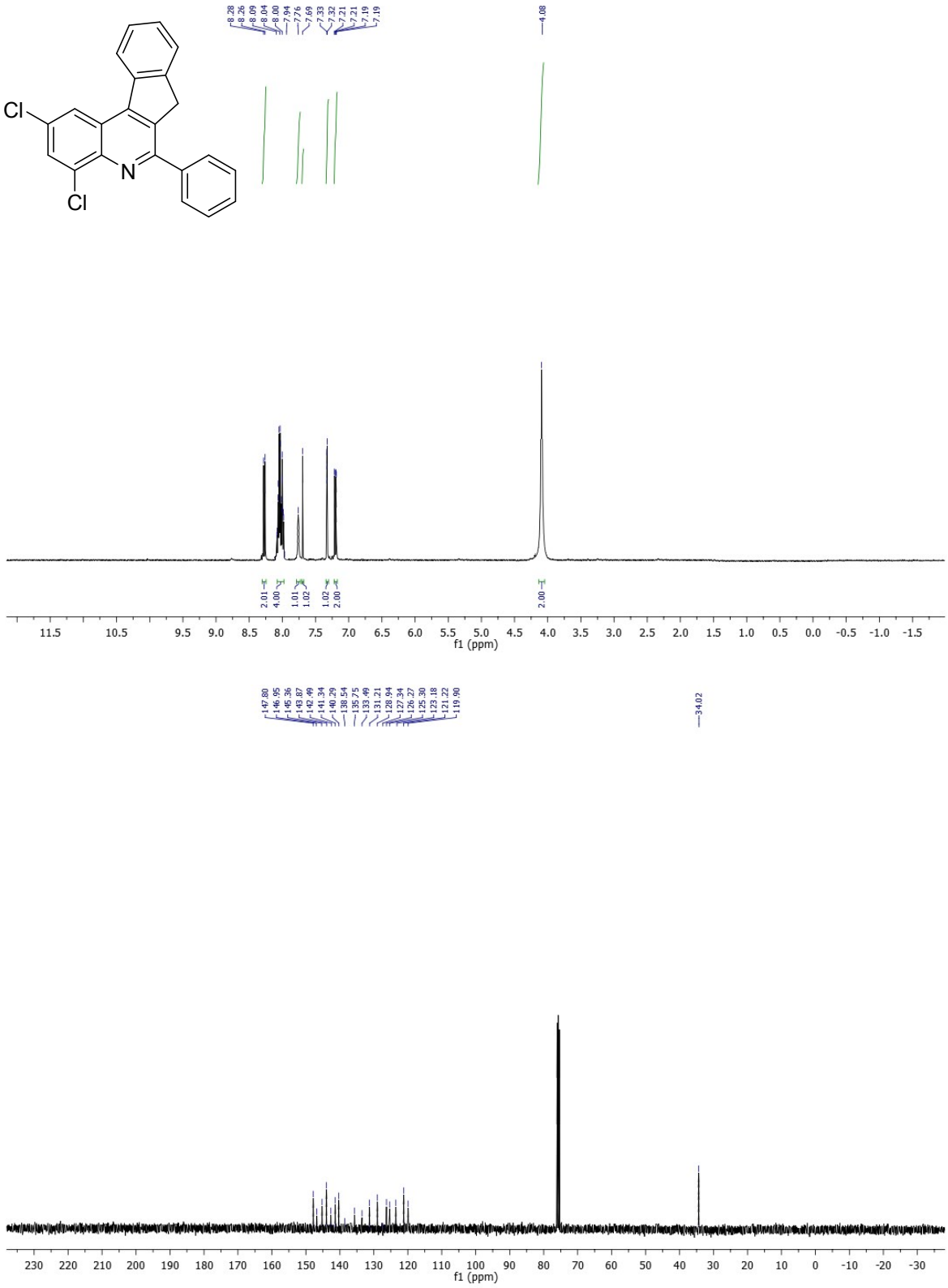
2-Nitro-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (32)



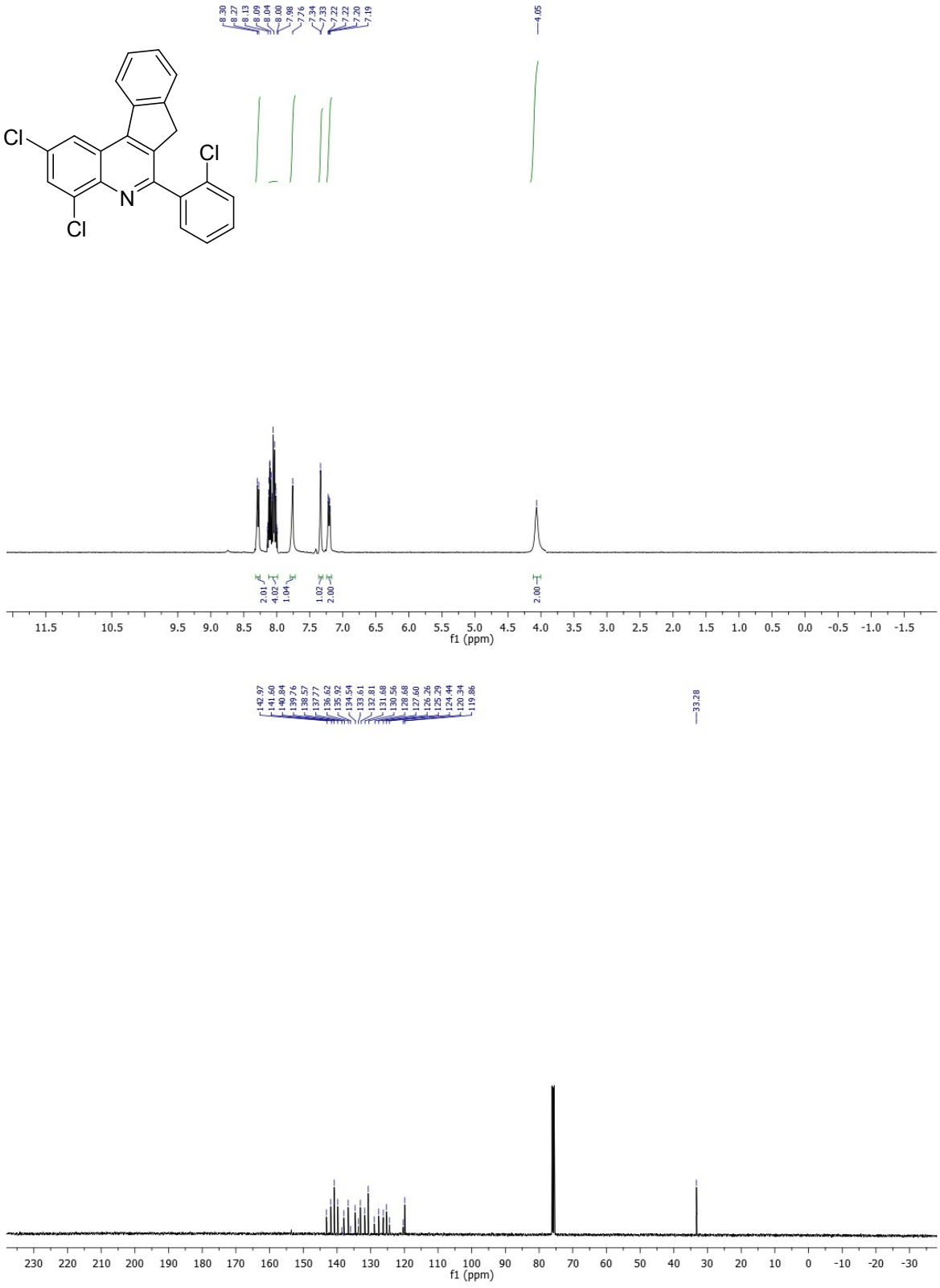
6-(4-Methoxyphenyl)-2-nitro-7*H*-indeno[2,1-*c*]quinoline (33)



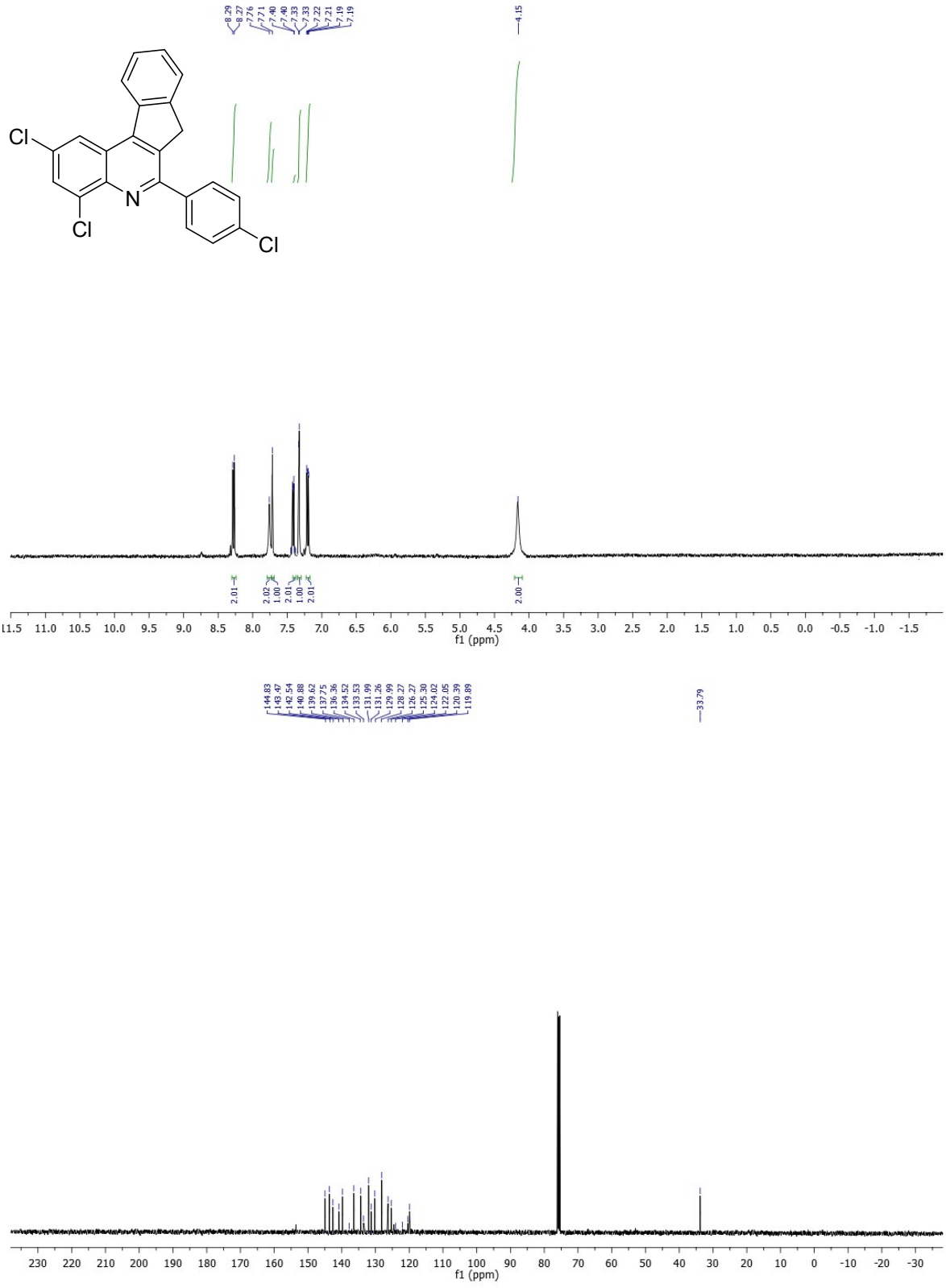
2,4-Dichloro-6-phenyl-7*H*-indeno[2,1-*c*]quinoline (34)



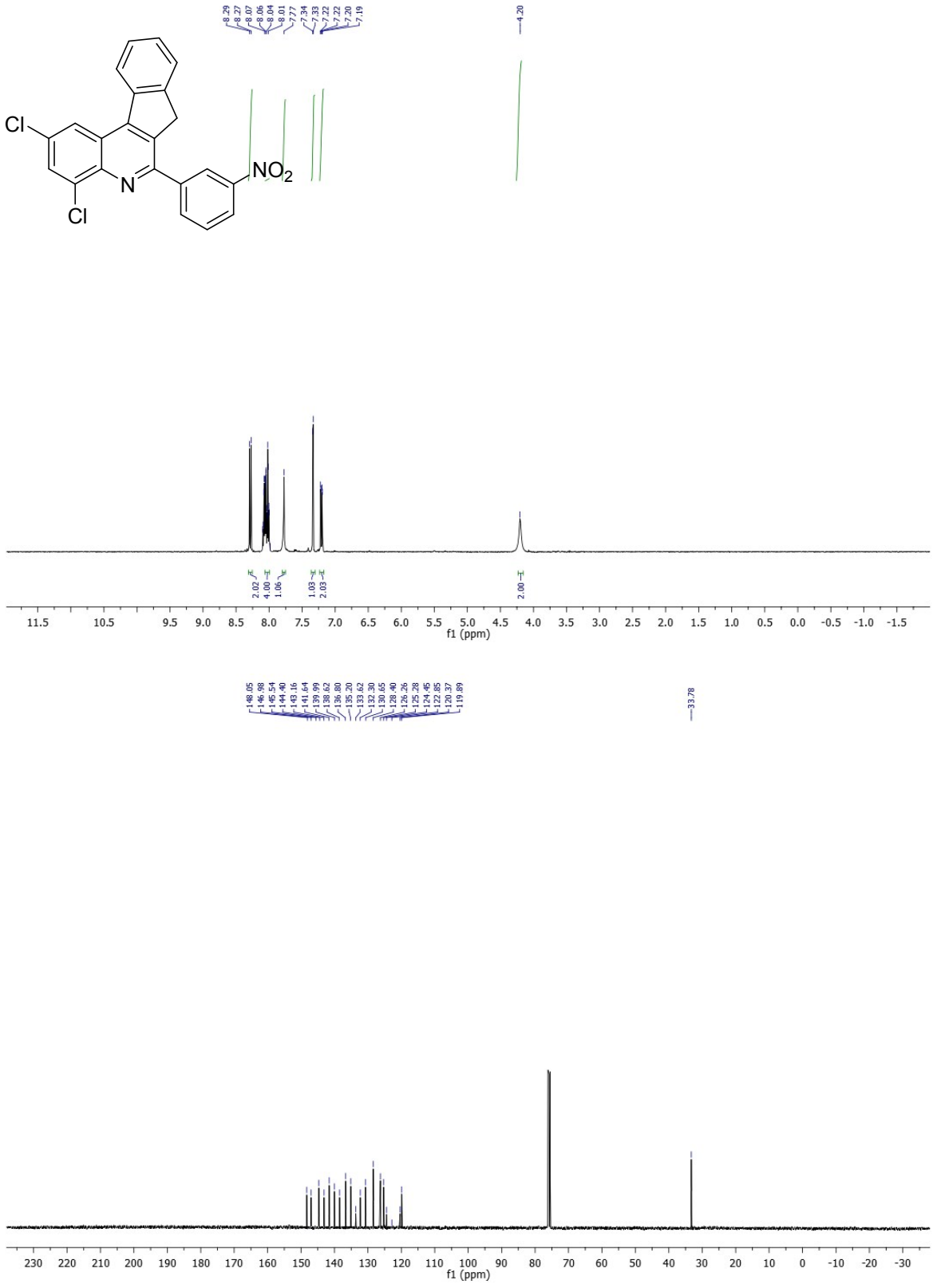
2,4-Dichloro-6-(2-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (35)



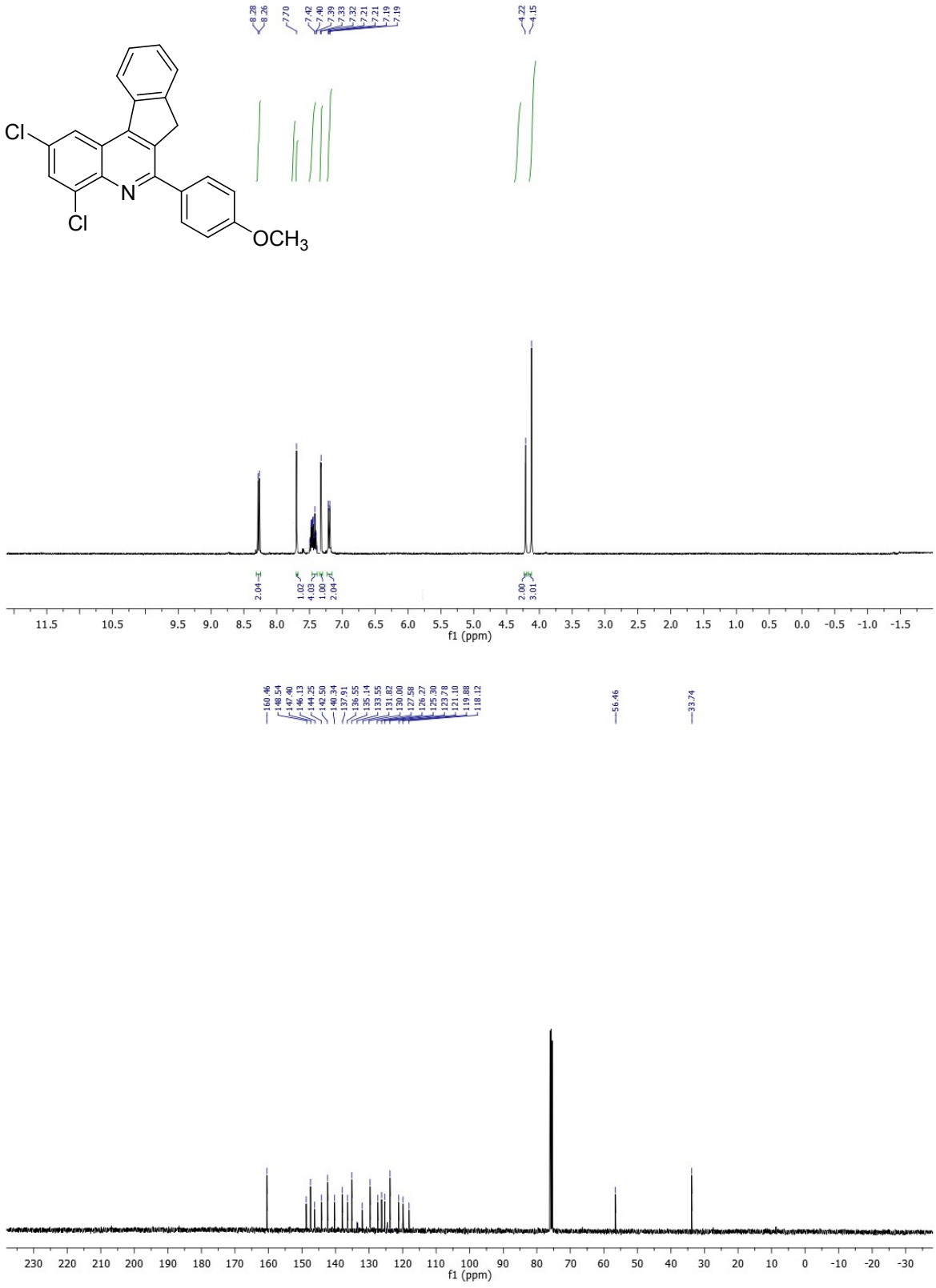
2,4-Dichloro-6-(4-chlorophenyl)-7*H*-indeno[2,1-*c*]quinoline (36)



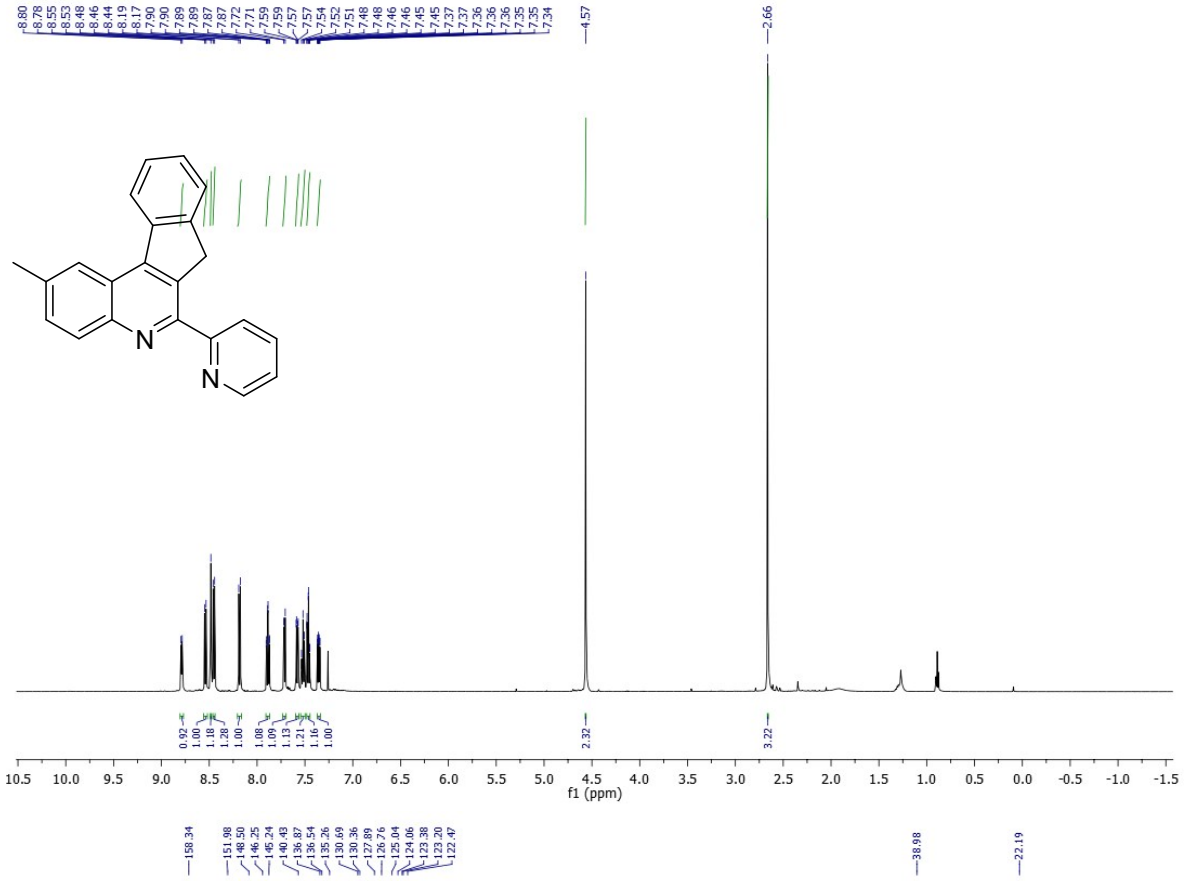
2,4-Dichloro-6-(3-nitrophenyl)-7*H*-indeno[2,1-*c*]quinoline (37)

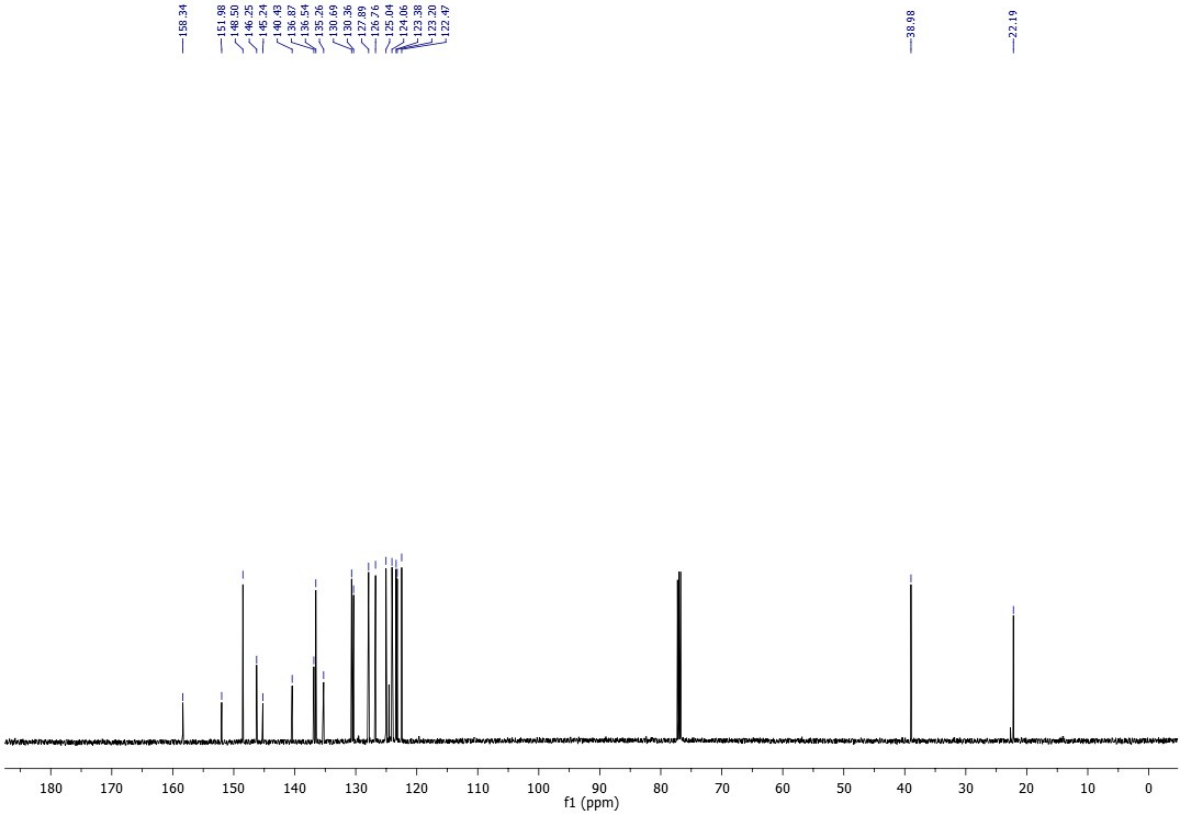


2,4-Dichloro-6-(4-methoxyphenyl)-7*H*-indeno[2,1-*c*]quinoline (38)

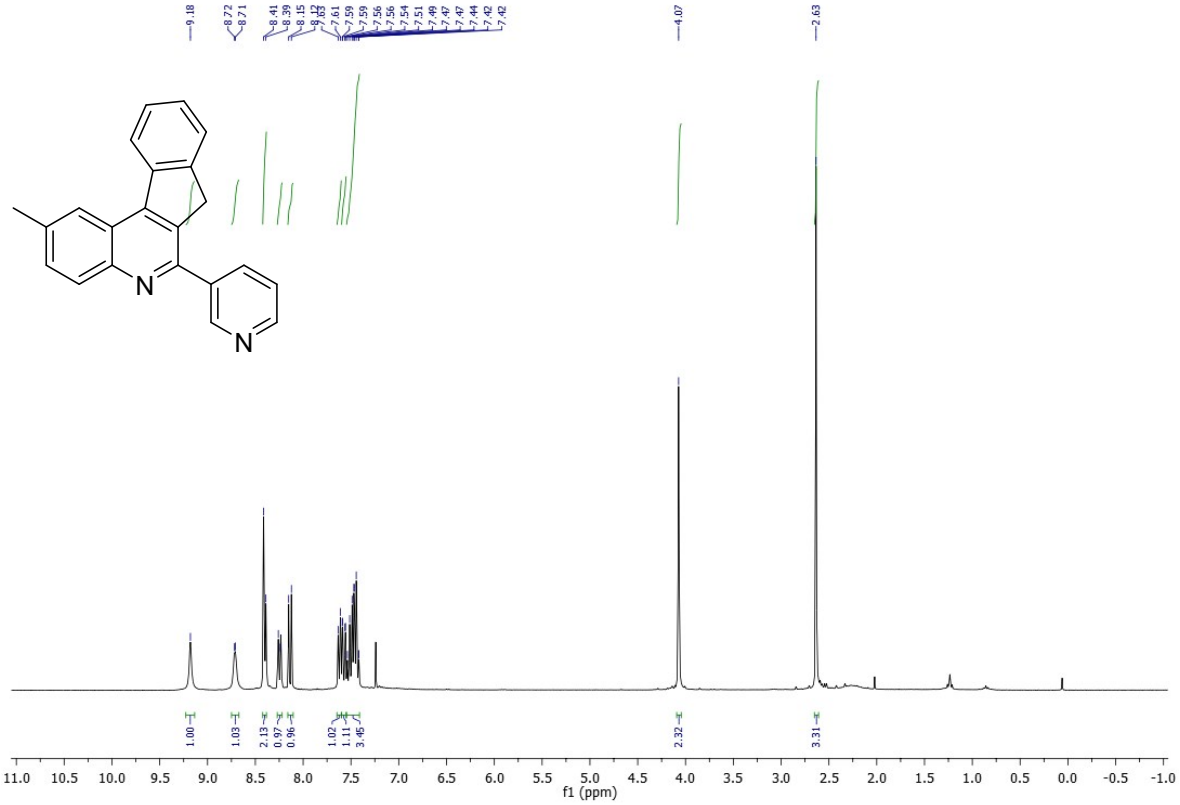


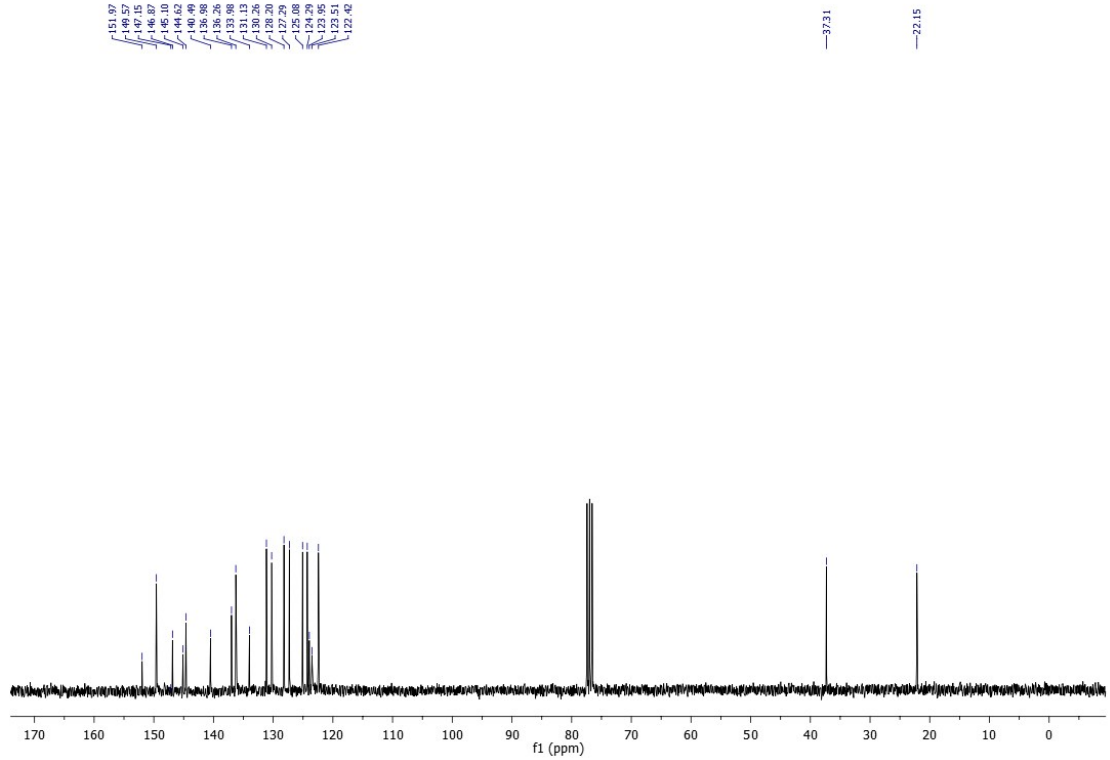
2-Methyl-6-(pyridin-2-yl)-7*H*-indeno[2,1-*c*]quinoline (39)



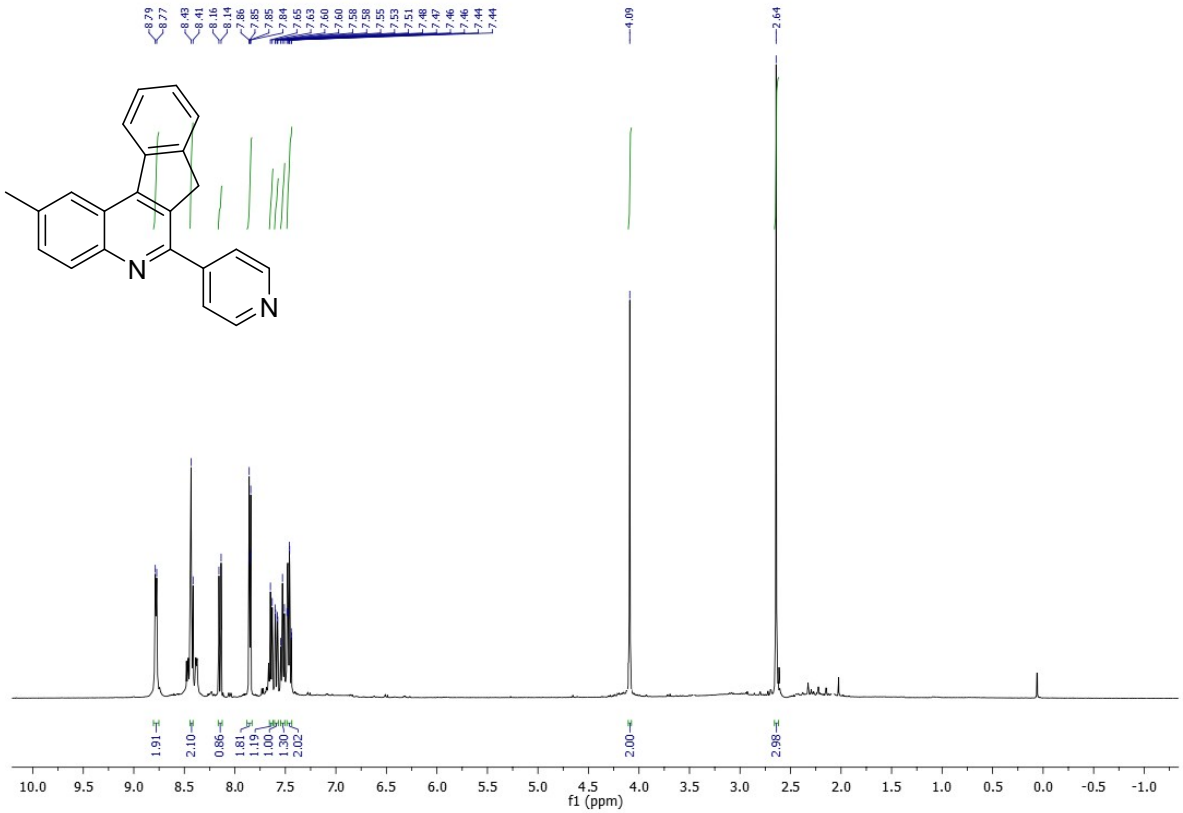


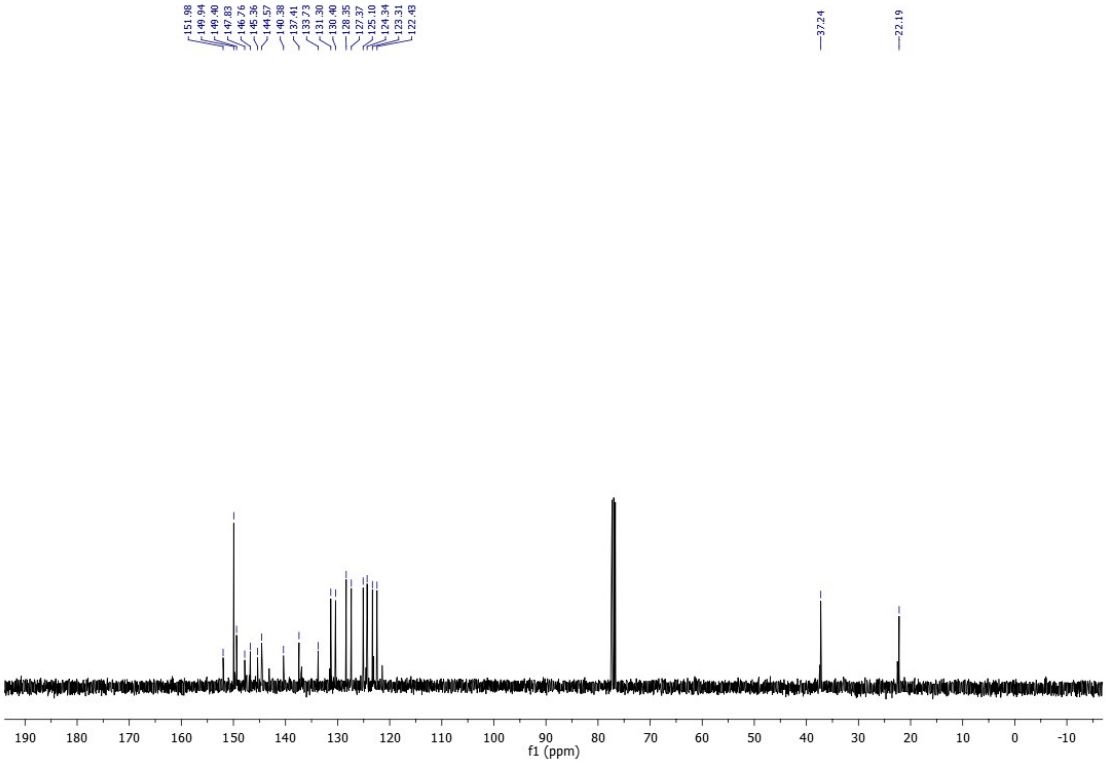
2-Methyl-6-(pyridin-3-yl)-7*H*-indeno[2,1-*c*]quinoline (40)



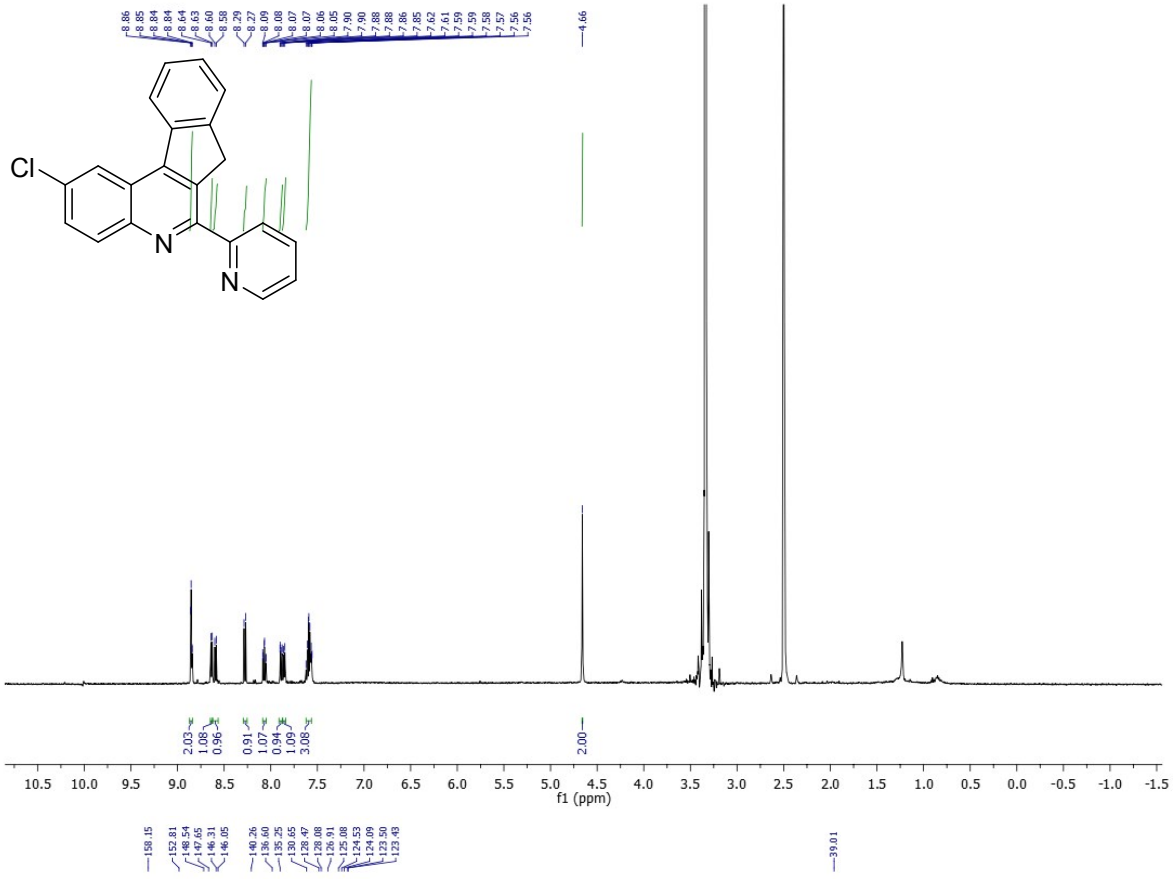


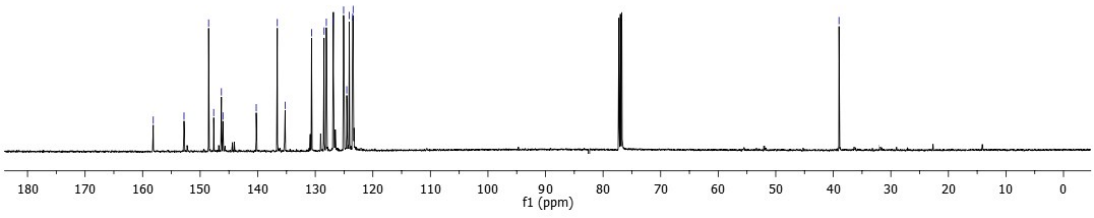
2-Methyl-6-(pyridin-4-yl)-7*H*-indeno[2,1-*c*]quinoline (41)



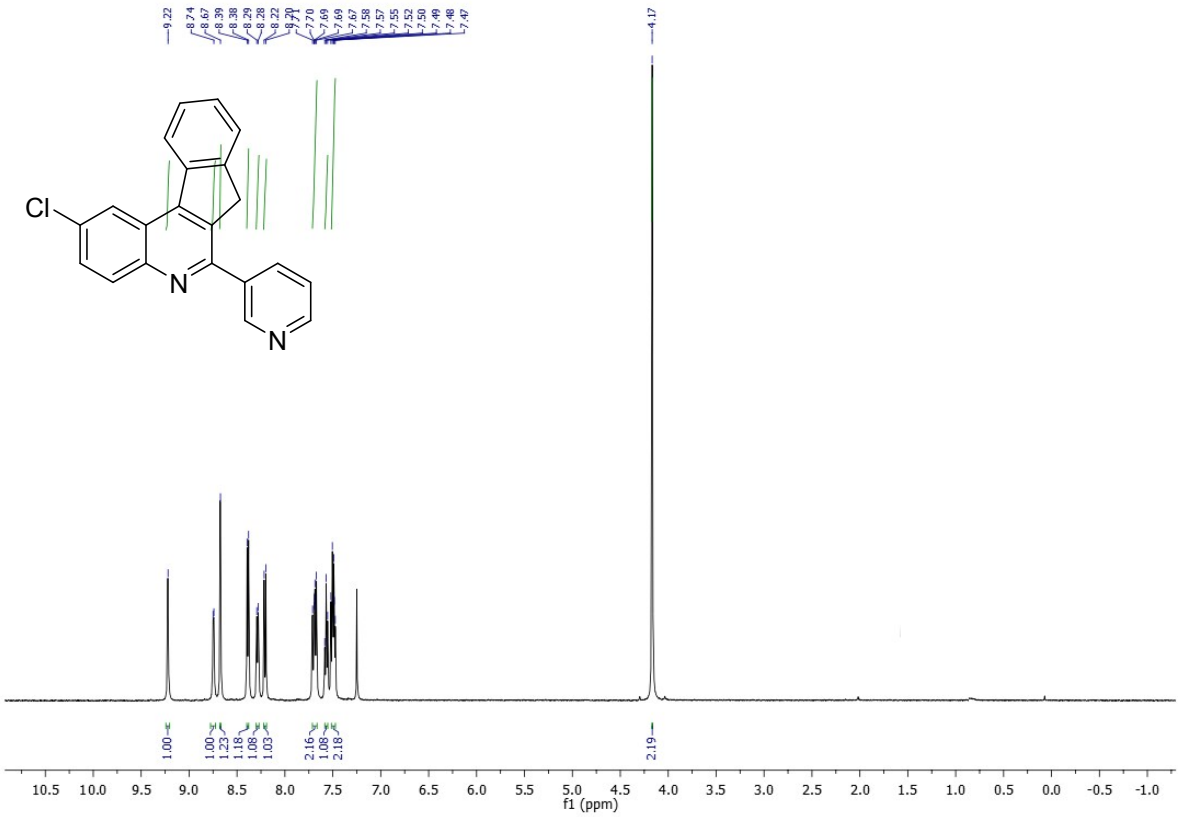


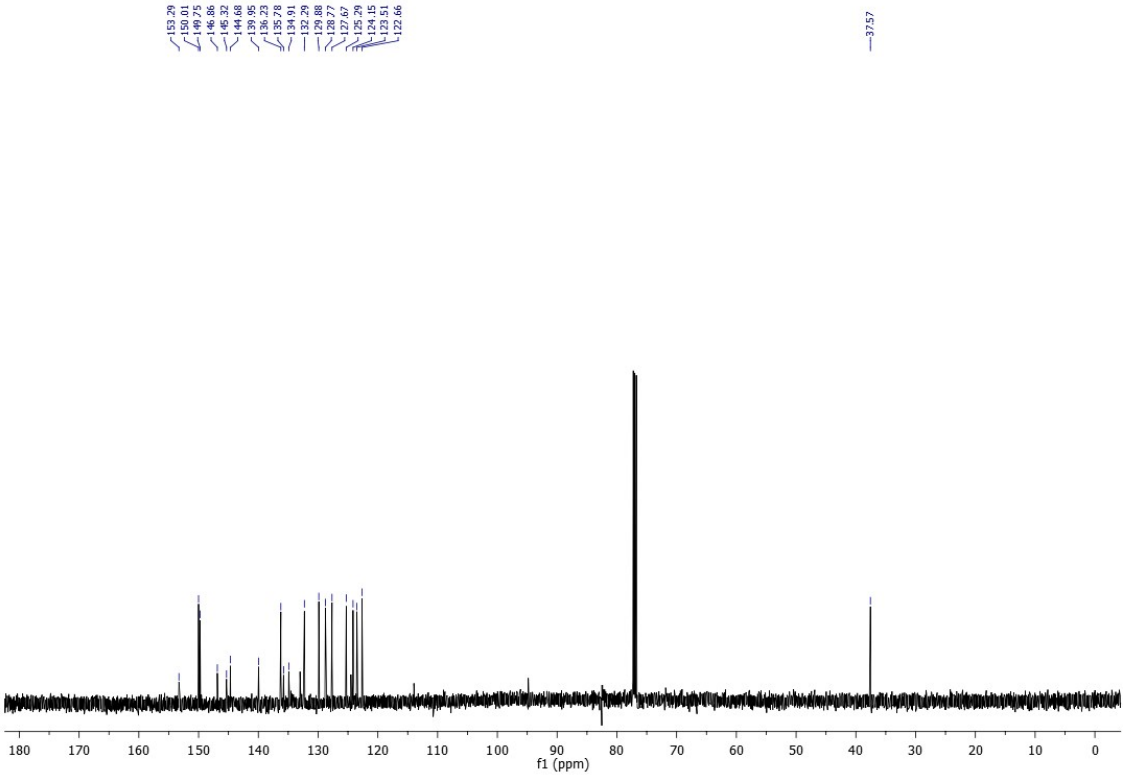
2-Chloro-6-(pyridin-2-yl)-7*H*-indeno[2,1-*c*]quinoline (42)



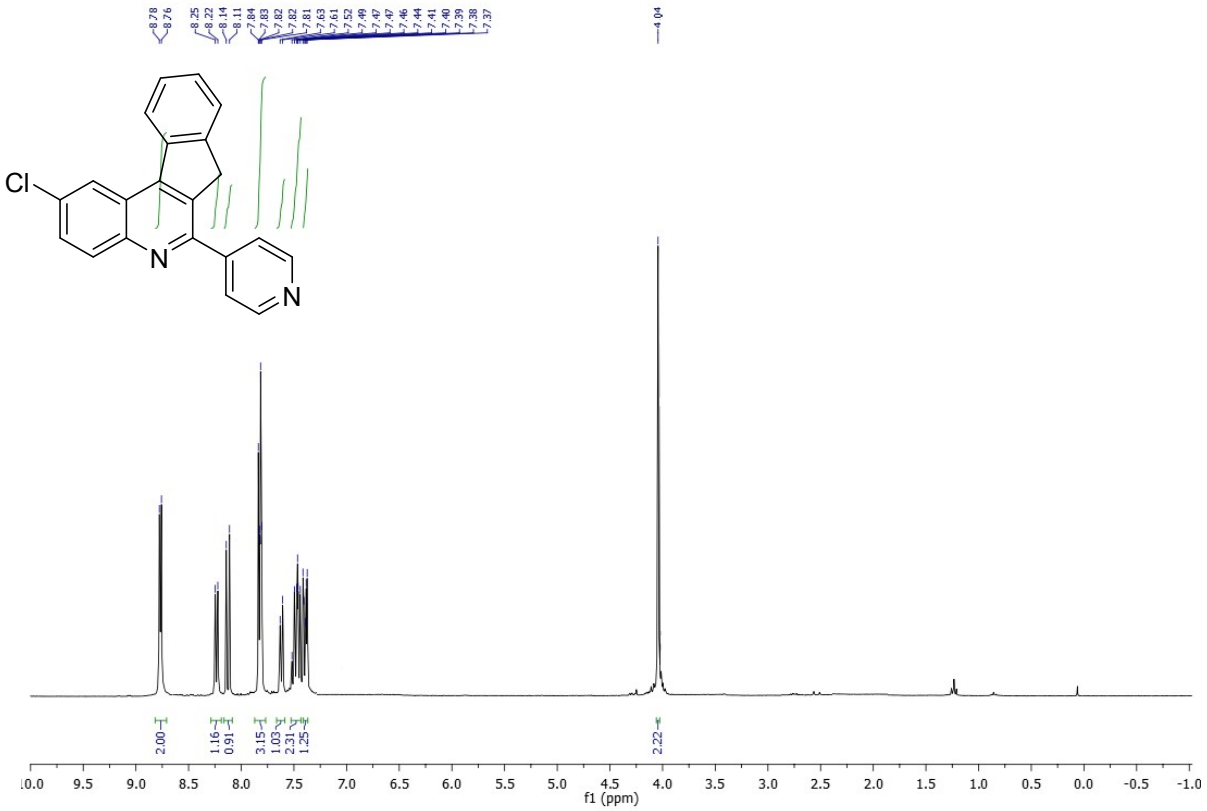


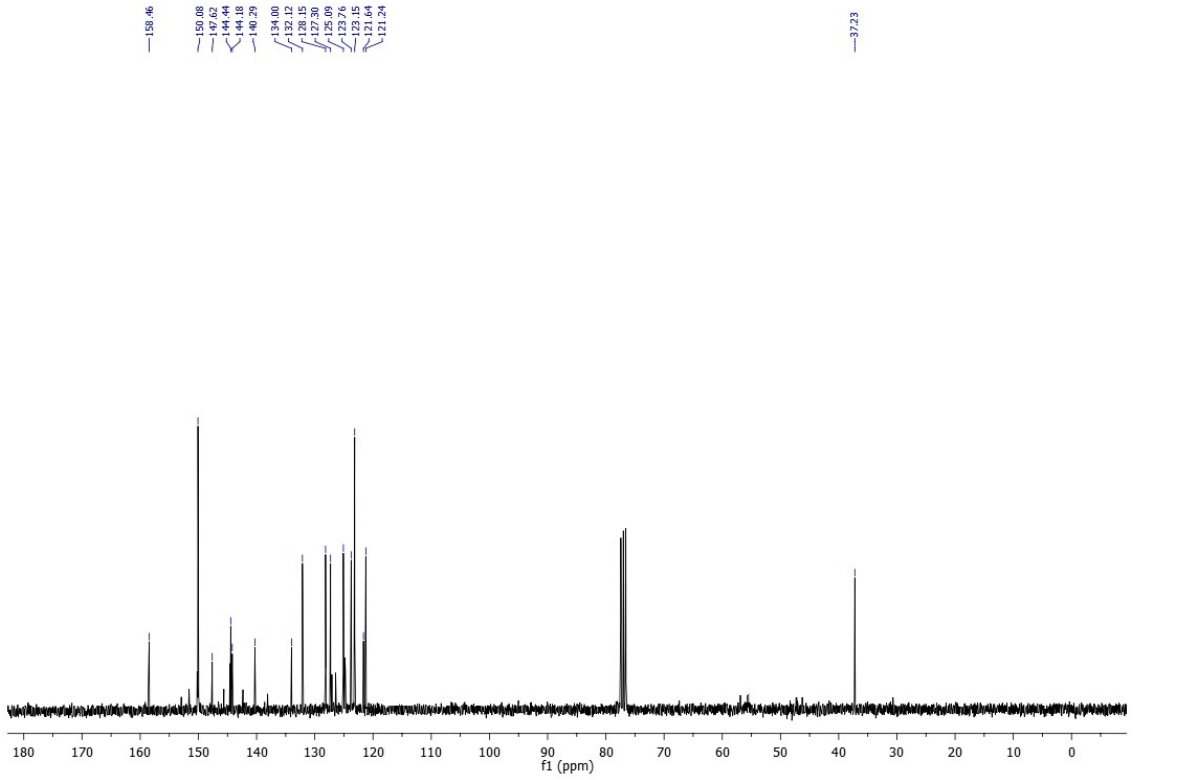
2-Chloro-6-(pyridin-3-yl)-7*H*-indeno[2,1-*c*]quinoline (43)





2-Chloro-6-(pyridin-4-yl)-7*H*-indeno[2,1-*c*]quinoline (44)





Green chemistry metrics analysis

The following formulae were used for calculating Atom Economy (**AE**), Atom Efficiency (**AEf**), Carbon Efficiency (**CE**), Reaction Mass Efficiency (**RME**), Optimum Efficiency (**OE**), Mass Productivity (**MP**), Mass Intensity (**MI**) and Process Mass Intensity (**PMI**), E factor, Solvent and Water Intensity (**SI** and **WI**).[1-4]

$$AE = \frac{Molecular\ weight\ of\ product}{Total\ molecular\ weight\ of\ reactants} x100 \quad \text{(Eq. S1)}$$

$$AEf = AE\ x\ yield\% \quad \text{(Eq. S2)}$$

$$CE = \frac{Amount\ of\ carbon\ in\ the\ product}{total\ carbon\ present\ in\ reactants} x100 \quad \text{(Eq. S3)}$$

$$RME = \frac{Mass\ of\ isolated\ product}{Total\ mass\ of\ reactants} x100 \quad \text{(Eq. S4)}$$

$$OE = \frac{RME}{AE} x100 \quad \text{(Eq. S5)}$$

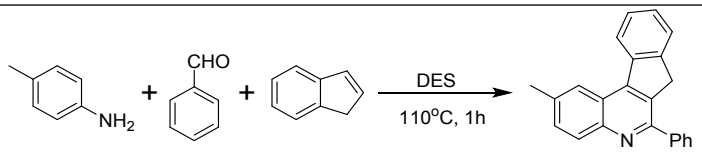
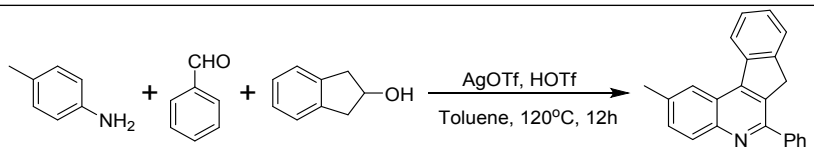
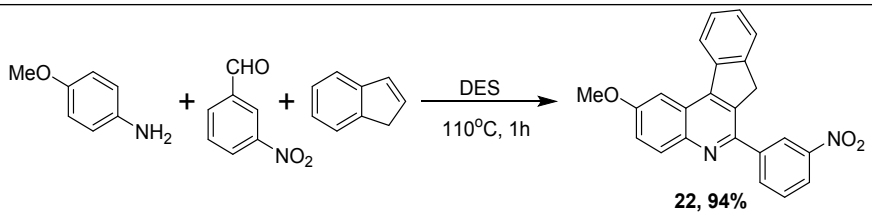
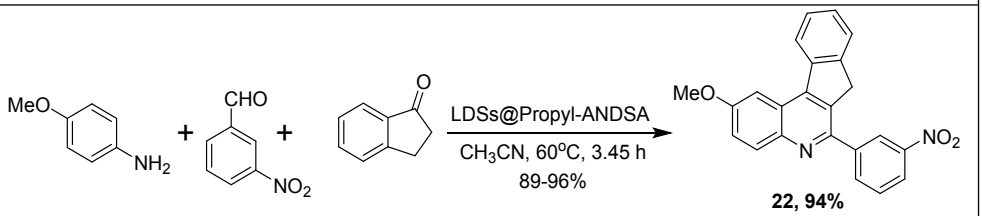
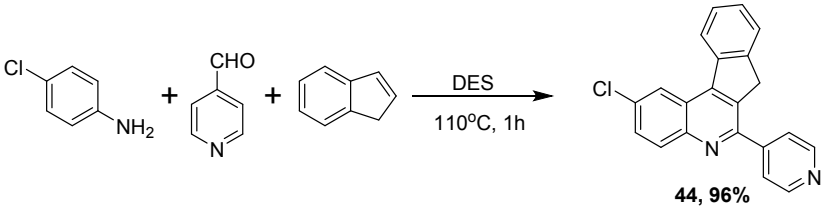
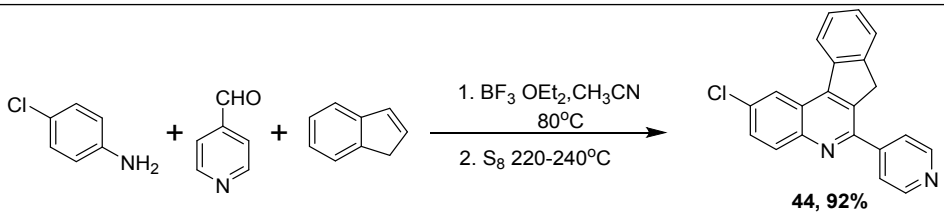
$$PMI = \frac{Total\ mass\ of\ imput\ material\ in\ th\ whole\ process}{mass\ of\ product} \quad \text{(Eq. S6)}$$

$$MP = \frac{1}{PMI} x\ 100 \quad \text{(Eq. S7)}$$

$$E\ Factor = PMI - 1 \quad \text{(Eq. S8)}$$

$$SI = \frac{Total\ mass\ of\ solvents\ excl.\ water\ in\ the\ whole\ process}{Mass\ of\ product} \quad \text{(Eq. S9)}$$

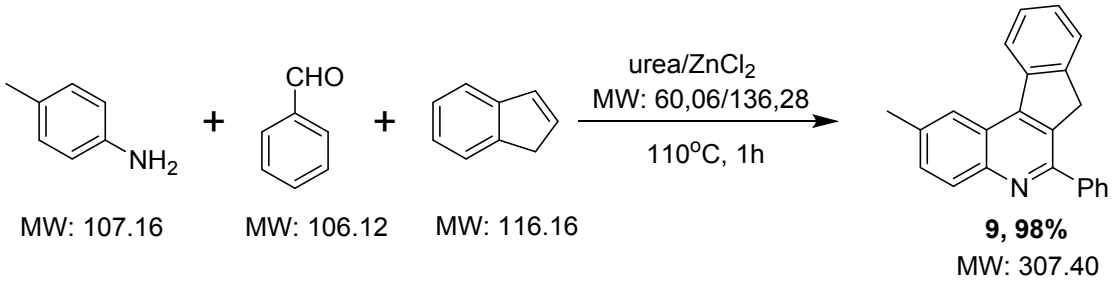
$$WI = \frac{Total\ mass\ of\ water\ used\ in\ the\ whole\ process}{Mass\ of\ product} \quad \text{(Eq. S10)}$$

Compound **9**	
Method A (This work)	 **9, 98%**
Method B (ref. 5)	 **9, 86%**
Compound **22**	
Method A (This work)	 **22, 94%**
Method C (ref. 3)	 **22, 94%**
Compound **44**	
Method A (This work)	 **44, 96%**
Method D (ref. 4)	 **44, 92%**

Compound 9

Method A (this work)

This is a one-step synthesis for the synthesis of compound **9** using commercially available reagents as shown in the following reaction.



Scheme S1. Synthesis of compound **9** in urea/$ZnCl_2$ DES

General experimental procedure: 1.6 g of urea/zinc chloride DES (3.5:1) was heated to 60 °C to obtain a clear melt. To this melt a mixture of amine (1 mmol), aldehyde (1 mmol) and indene (1 mmol) was added and the reaction was stirred at 110 °C for 60 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by adding water while still hot (assuming use of total 5.0 mL), cooled to room temperature and the crude mixture was filtered. The resulting solid was purified by column chromatography on silica gel (60–120 mesh) using a mixture of petroleum ether–ethyl acetate as eluent to afford the quinoline derivative **9**.

Materials used for metrics calculations: *p*-toluidine (1 mmol, 107.15 mg), benzaldehyde (1 mmol, 106.12 mg), indene (1 mmol, 116.16 mg), urea (16.16 mmol, 971.17 mg), $ZnCl_2$ (4.62 mmol, 629.61 mg), water (5 mL, 5 g), compound **9** (0.98 mmol, 301.25 mg).

$$AE = \frac{307.40}{107.15 + 106.12 + 116.16} x100 = 93.31$$ (Eq. S11)

$$AEf = \frac{93.31}{100} x98 = 91.45$$ (Eq. S12)

$$CE = \frac{23x0.98}{(7x1) + (7x1) + (9x1)} x100 = 98$$ (Eq. S13)

$$RME = \frac{301.25}{107.15 + 106.12 + 116.16} x100 = 91.45$$ (Eq. S14)

$$OE = \frac{91.45}{93.31} x100 = 98$$ (Eq. S15)

$$PMI = \frac{107.15 + 106.12 + 116.16 + 971.17 + 629.61 + 5000}{301.25} = 23.00$$ (Eq. S16)

$$MP = \frac{100}{23.00} = 4.34$$ (Eq. S17)

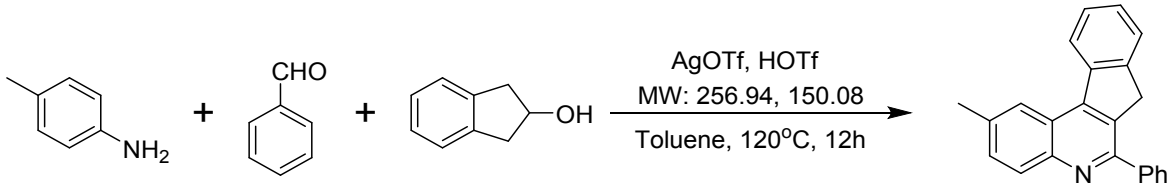
$$E\ Factor = 23 - 1 = 22.00$$ (Eq. S18)

$$SI = \frac{971.17 + 629.61}{301.25} = 5.31$$ (Eq. S19)

$$WI = \frac{5000}{301.25} = 16.59$$ (Eq. S20)

Published synthetic method B (ref. 5)

This is a one-step synthesis, however the reported procedures for the synthesis of compound **9** do not contain all the required information; therefore, some realistic assumptions were used where appropriate. Drying agents, when used, were not included in the calculations.



MW: 107.16 MW: 106.12 MW: 134.18

9, 86%

MW: 307,40

Scheme S2. Synthesis of compound **9** employing AgOTf/HOTf as catalyst.

Experimental procedure: A reaction tube (25 mL) was charged with amine (0.5 mmol, 1 equiv), aldehyde (0.5 mmol, 1 equiv). The mixture was stirred at 100 °C for 5 minutes, and the alcohol (0.75 mmol, 1.5 equiv), AgOTf (0.025 mmol), HOTf (0.05 mmol) and toluene (2 mL) were added. The mixture was stirred at 120 °C for 12 hours, when reaction was cooled down to room temperature, the mixture was quenched by sat. aq. $NaHCO_3$, and diluted with 10 ml dichloromethane and washed with 10 ml H_2O. The aqueous layer was extracted twice with dichloromethane (10 ml) and the combined organic phase was dried over Na_2SO_4. After evaporation of the solvents, the residue was purified by silica gel chromatography (hexane/AcOEt = 20:1).

Materials used for metrics calculations: *p*-toluidine (0.5 mmol, 53.58 mg), benzaldehyde (0.5 mmol, 58.37 mg), 2,3-dihydro-1*H*-inden-2-ol (0.75 mmol, 100.63 mg), AgOTf (0.025 mmol, 6.42 mg), HOTf (0.05 mmol, 7.50 mg), toluene (2 mL, 1.73 g), dichloromethane (30 mL, 39.9 g), water (10 mL, 10 g), compound **9** (0.43 mmol, 132.18 mg).

$$AE = \frac{307.4}{107.16 + 106.12 + 134.18} x100 = 88.47 \quad \text{(Eq. S21)}$$

$$AEf = \frac{62.18}{100} x86 = 53.47 \quad \text{(Eq. S22)}$$

$$CE = \frac{23x0.43}{(7x0.5) + (7x0.5) + (9x0.75)} x100 = 71.92 \quad \text{(Eq. S23)}$$

$$RME = \frac{132.18}{53.58 + 58.37 + 100.63} x100 = 62.17 \quad \text{(Eq. S24)}$$

$$OE = \frac{62.17}{88.47} x100 = 70.27 \quad \text{(Eq. S25)}$$

$$PMI = \frac{53.58 + 58.37 + 100.63 + 6.42 + 7.50 + 1730 + 39900 + 10000}{132.18} = 392.32 \quad \text{(Eq. S26)}$$

$$MP = \frac{100}{392.32} = 0.25$$ (Eq. S27)

$$E\ Factor = 392.32 - 1 = 391.32$$ (Eq. S28)

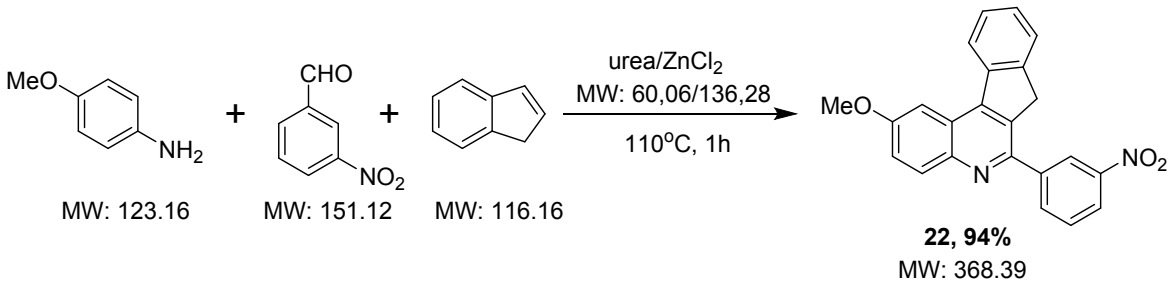
$$SI = \frac{1730 + 39900}{132.18} = 314.95$$ (Eq. S29)

$$WI = \frac{10000}{132.18} = 75.65$$ (Eq. S30)

Compound 22

Method A (this work)

This is a one-step synthesis for the synthesis of compound **22** using commercially available reagents as shown in the following reaction.



Scheme S3. Synthesis of compound **22** in urea/$ZnCl_2$ DES

General experimental procedure: 1.6 g of urea/zinc chloride DES (3.5:1) was heated to 60 °C to obtain a clear melt. To this melt a mixture of amine (1 mmol), aldehyde (1 mmol) and indene (1 mmol) was added and the reaction was stirred at 110 °C for 60 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by adding water while still hot (assuming use of total 5.0 mL), cooled to room temperature and the crude mixture was filtered. The

resulting solid was purified by column chromatography on silica gel (60–120 mesh) using a mixture of petroleum ether–ethyl acetate as eluent to afford the quinoline derivative **22**.

Materials used for metrics calculations: *p*-anisidine (1 mmol, 123.16 mg), *m*-nitrobenzaldehyde (1 mmol, 151.12 mg), indene (1 mmol, 116.16 mg), urea (16.16 mmol, 971.17 mg), $ZnCl_2$ (4.62 mmol, 629.61 mg), water (5 mL, 5 g), compound **22** (0.94 mmol, 346.28 mg).

$$AE = \frac{368.39}{123.16 + 151.12 + 116.16} x100 = 94.35 \quad \text{(Eq. S31)}$$

$$AEf = \frac{94.35}{100} x94 = 88.69 \quad \text{(Eq. S32)}$$

$$CE = \frac{23x0.94}{(7x1) + (7x1) + (9x1)} x100 = 94 \quad \text{(Eq. S33)}$$

$$RME = \frac{346.28}{123.16 + 151.12 + 116.16} x100 = 88.69 \quad \text{(Eq. S34)}$$

$$OE = \frac{88.69}{94.35} x100 = 94.00 \quad \text{(Eq. S35)}$$

$$PMI = \frac{123.16 + 151.12 + 116.16 + 971.17 + 629.61 + 5000}{346.28} = 20.19 \quad \text{(Eq. S36)}$$

$$MP = \frac{100}{20.19} = 4.95 \quad \text{(Eq. S37)}$$

$$E\ Factor = 20.19 - 1 = 19.19 \quad \text{(Eq. S38)}$$

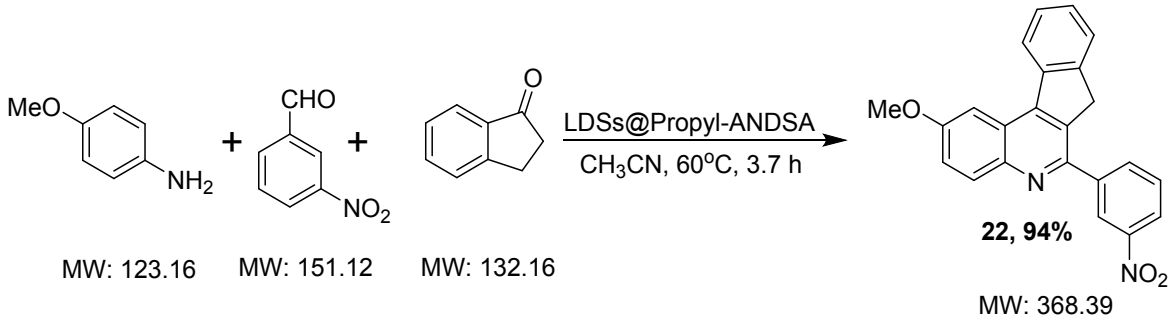
$$SI = \frac{971.17 + 629.61}{346.28} = 4.62 \quad \text{(Eq. S39)}$$

$$WI = \frac{5000}{346.28} = 14.44 \quad \text{(Eq. S40)}$$

Published synthetic method C (ref. 3)

This is a one-step synthesis, however the reported procedures for the synthesis of compound **22** do not contain all the required information such as the preparation of the heterogeneous catalyst, and

therefore this information was not included in the calculations. For solvents, some realistic assumptions were used where appropriate and are italicized in the calculations given below.



Scheme S4. Synthesis of compound **22** employing LDSs@Propyl-ANDSA as catalyst.

Experimental procedure: A mixture of aryl amine (1.0 mmol) and aromatic aldehyde (1.0 mmol) and LDHs@Propyl–ANDSA (0.06 g) in anhydrous CH_3CN (5 mL) was stirred at 60 °C for 30 min. 1-indanone (1.0 mmol) was then added, and the resulting mixture was stirred at 60 °C. After completion of the reaction, as indicated by TLC (*n*-hexane/acetone, 7:3), the catalyst was isolated using filter paper and then, the reaction mixture was dissolved in chloroform (*assuming use of total 2.0 mL*) and added to the *n*-hexane drop drops until solid yellow appeared in the form of a precipitate.

Materials used for metrics calculations: *p*-anisidine (1 mmol, 123.16 mg), *m*-nitrobenzaldehyde (1 mmol, 151.12 mg), 1-indanone (1.0 mmol, 132.16 mg), LDHs@Propyl–ANDSA (60.0 mg), acetonitrile (5 mL, 3.93 g), chloroform (2 mL, 2.98 g), compound **22** (0.94 mmol, 346.28 mg).

$$AE = \frac{368.39}{123.16 + 151.12 + 132.16} x100 = 90.63 \quad \text{(Eq. S41)}$$

$$AEf = \frac{90.63}{100} x94 = 85.19 \quad \text{(Eq. S42)}$$

$$CE = \frac{23x0.94}{(7x1) + (7x1) + (9x1)} x100 = 94 \quad \text{(Eq. S43)}$$

$$RME = \frac{346.28}{123.16 + 151.12 + 132.16} x100 = 85.19$$ (Eq. S44)

$$OE = \frac{85.19}{90.63} x100 = 94.00$$ (Eq. S45)

$$PMI = \frac{123.16 + 151.12 + 132.16 + 60 + 3930 + 2980}{346.28} = 21.30$$ (Eq. S46)

$$MP = \frac{100}{21.30} = 4.69$$ (Eq. S47)

$$E\ Factor = 21.30 - 1 = 20.30$$ (Eq. S48)

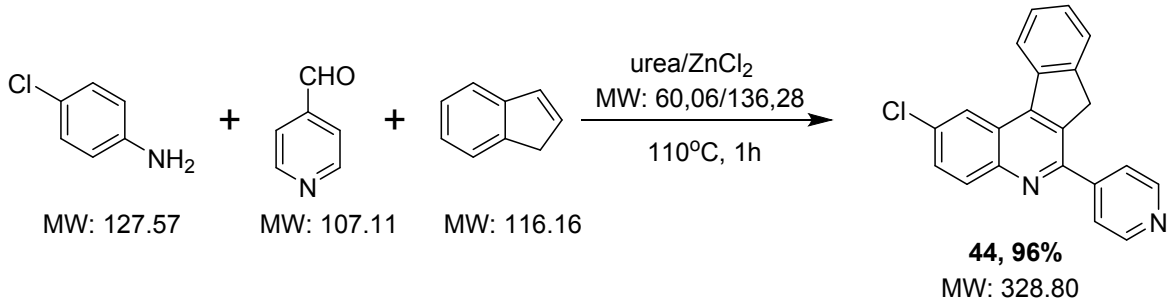
$$SI = \frac{3930 + 2980}{346.28} = 19.95$$ (Eq. S49)

$$WI = \frac{0}{346.28} = 0$$ (Eq. S50)

Compound 44

Method A (this work)

This is a one-step synthesis for the synthesis of compound **44** using commercially available reagents as shown in the following reaction.



Scheme S5. Synthesis of compound **44** in urea/$ZnCl_2$ DES

General experimental procedure: 1.6 g of urea/zinc chloride DES (3.5:1) was heated to 60 °C to obtain a clear melt. To this melt a mixture of amine (1 mmol), aldehyde (1 mmol) and indene (1 mmol) was added and the reaction was stirred at 110 °C for 60 minutes. After completion of the reaction (monitored by TLC), the reaction mixture was quenched by adding water while still hot (assuming use of total 5.0 mL), cooled to room temperature and the crude mixture was filtered. The resulting solid was purified by column chromatography on silica gel (60–120 mesh) using a mixture of petroleum ether–ethyl acetate as eluent to afford the quinoline derivative **44**.

Materials used for metrics calculations: *p*-chloroaniline (1 mmol, 127.57 mg), 4-pyridinecarboxaldehyde (1 mmol, 107.11 mg), indene (1 mmol, 116.16 mg), urea (16.16 mmol, 971.17 mg), $ZnCl_2$ (4.62 mmol, 629.61 mg), water (5 mL, 5 g), compound **44** (0.96 mmol, 315.64 mg).

$$AE = \frac{328.80}{127.57 + 107.11 + 116.16} x100 = 93.72 \quad \text{(Eq. S51)}$$

$$AEf = \frac{93.71}{100} x96 = 89.97 \quad \text{(Eq. S52)}$$

$$CE = \frac{21x0.96}{(6x1) + (6x1) + (9x1)} x100 = 96 \quad \text{(Eq. S53)}$$

$$RME = \frac{315.64}{127.57 + 107.11 + 116.16} x100 = 89.97 \quad \text{(Eq. S54)}$$

$$OE = \frac{89.97}{93.72} x100 = 95.99$$ (Eq. S55)

$$PMI = \frac{127.57 + 107.11 + 116.16 + 971.17 + 629.61 + 5000}{315.64} = 22.02$$ (Eq. S56)

$$MP = \frac{100}{22.02} = 4.54$$ (Eq. S57)

$$E\ Factor = 22.02 - 1 = 21.02$$ (Eq. S58)

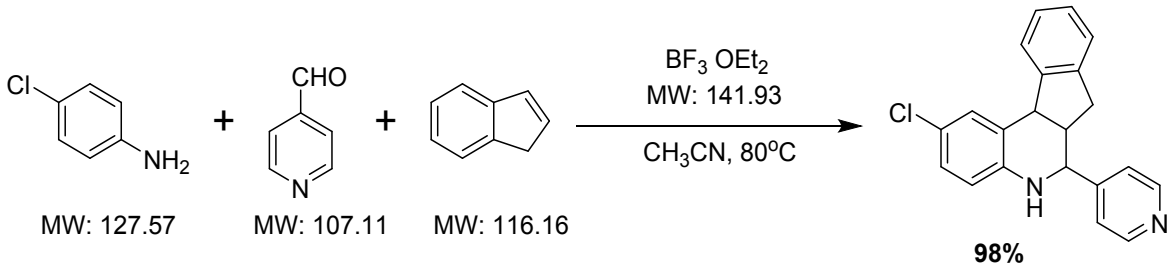
$$SI = \frac{971.17 + 629.61}{315.64} = 5.07$$ (Eq. S59)

$$WI = \frac{5000}{315.64} = 15.84$$ (Eq. S60)

Published synthetic method D (ref. 4)

This is a two-step synthesis; however the reported procedures for the synthesis of compound **44** do not contain all the required information.

Step 1



MW: 127.57 MW: 107.11 MW: 116.16

98%

MW: 332.83

General experimental procedure: A mixture of arylamine (3.6 mmol) and pyridine-4-carbaldehyde (4.0 mmol) in anhyd MeCN (15 mL) was stirred at r.t. for 30 min. $BF_3{\cdot}OEt_2$ (3.6 mmol) was added. Over a period of 20 min, a soln indene (4.0 mmol) in MeCN (10 mL) was added dropwise. The resulting mixture was stirred at 70 °C for 5 h (TLC monitoring). The mixture was diluted with H_2O (30 mL) and extracted with EtOAc (3 × 15 mL). The organic layer was separated, dried (Na_2SO_4), and

concentrated in vacuo and the resulting product was purified by column chromatography (silica gel, PE–EtOAc) to afford pure tetrahydroquinoline.

Materials used for metrics calculations: *p*-chloroaniline (3.6 mmol, 459.25 mg), 4-pyridinecarboxaldehyde (4 mmol, 428.44 mg), indene (4 mmol, 464.64 mg), $BF_3{\cdot}OEt_2$ (3.6 mmol, 510.94 mg), MeCN (10 mL, 7.86 g), water (30 mL, 30 g), EtOAc (15 mL, 13.53 g) tetrahydroquinoline (3.53 mmol, 1.174 g).

$$AE = \frac{332.83}{127.57 + 107.11 + 116.16} x100 = 94.87 \quad \text{(Eq. S61)}$$

$$AEf = \frac{94.87}{100} x98 = 92.97 \quad \text{(Eq. S62)}$$

$$CE = \frac{21x3.53}{(6x3.6) + (6x4) + (9x4)} x100 = 90.79 \quad \text{(Eq. S63)}$$

$$RME = \frac{1174}{459.25 + 428.44 + 464.64} x100 = 86.81 \quad \text{(Eq. S64)}$$

$$OE = \frac{86.81}{94.87} x100 = 91.51 \quad \text{(Eq. S65)}$$

$$PMI = \frac{459.25 + 428.44 + 464.64 + 510.94 + 7860 + 30000 + 13530}{1174} = 45.36 \quad \text{(Eq. S66)}$$

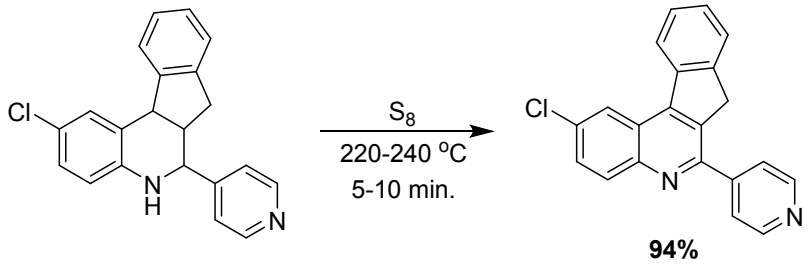
$$MP = \frac{100}{45.36} = 2.20 \quad \text{(Eq. S67)}$$

$$E\ Factor = 2.20 - 1 = 1.20 \quad \text{(Eq. S68)}$$

$$SI = \frac{7860 + 13530}{1174} = 18.21 \quad \text{(Eq. S69)}$$

$$WI = \frac{30000}{1174} = 25.55 \quad \text{(Eq. S70)}$$

Step 2



MW: 332.83 MW: 328.80

General experimental procedure: A mixture of tetrahydroindenoquinoline (0.5 mmol, 164.4 mg) and homogenated elemental sulfur (1.5 mmol, mol. wt. 32 g/mol, 48 mg) was heated at 220–240 °C for 7–10 min. After completion of the reaction as indicated by the complete liberation of H_2S (g), the mixture was directly purified by column chromatography (silica gel, PE–EtOAc) to afford pure indenoquinoline.

Materials used for metrics calculations: terahydroindenoquinoline (0.5 mmol, 164.4 mg), sulfur (1.5 mmol, mol. wt. 32 g/mol, 48 mg), indenoquinoline (0.47 mmol, 154.54 mg)

$$AE = \frac{328.80}{332.83 + 32} x100 = 90.12 \quad \text{(Eq. S71)}$$

$$AEf = \frac{90.12}{100} x94 = 84.72 \quad \text{(Eq. S72)}$$

$$CE = \frac{21x0.47}{21x0.5} x100 = 94 \quad \text{(Eq. S73)}$$

$$RME = \frac{154.54}{164.4 + 48} x100 = 72.76 \quad \text{(Eq. S74)}$$

$$OE = \frac{72.76}{90.12} x100 = 80.74 \quad \text{(Eq. S75)}$$

$$PMI = \frac{164.4 + 48}{154.54} = 1.37 \quad \text{(Eq. S76)}$$

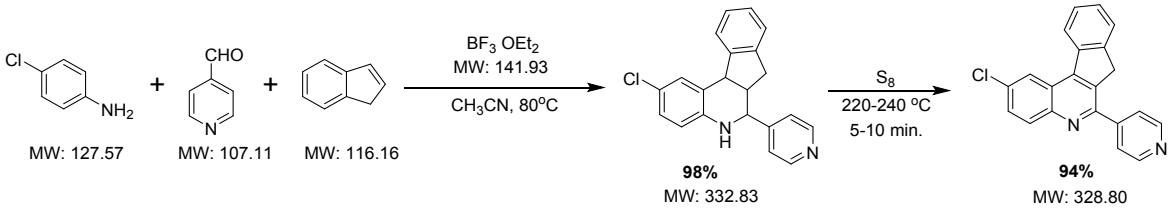
$$MP = \frac{100}{1.37} = 72.99 \quad \text{(Eq. S77)}$$

$$E\ Factor = 72.99 - 1 = 71.99 \quad \text{(Eq. S78)}$$

$$SI = \frac{0}{154.54} = 0$$ (Eq. S79)

$$WI = \frac{0}{154.54} = 0$$ (Eq. S80)

Cumulative metrics for compound 44:



$$AE = \frac{328.80}{127.57 + 107.11 + 116.16} x100 = 93.72$$ (Eq. S81)

$$AEf = \frac{93.72}{100} x94 = 88.10$$ (Eq. S82)

$$CE = \frac{21x0.47x7.2}{(6x3.6) + (6x4) + (9x4)} x100 = 87.09$$ (Eq. S83)

$$RME = \frac{154.54}{(459.25 + 428.44 + 464.64)/7.2} x100 = 82.27$$ (Eq. S84)

$$OE = \frac{82.27}{93.72} x100 = 87.79$$ (Eq. S85)

$$PMI = \frac{\left(\frac{459.25 + 428.44 + 464.64 + 510.94 + 7860 + 30000 + 13530}{7.2}\right) + 48}{154.54} = 48.17$$ (Eq. S86)

$$MP = \frac{100}{48.17} = 2.08$$ (Eq. S87)

$$E\ Factor = 48.17 - 1 = 47.17$$ (Eq. S88)

$$SI = \frac{(7860 + 13530)/7.2}{154.54} = 19.22$$ (Eq. S89)

$$WI = \frac{(30000)/7.2}{154.54} = 26.96$$ (Eq. S90)

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