Supporting Information

Gold/Copper-Cocatalyzed Tandem Reactions of 2-Alkynylanilines: A Synthetic Strategy for the C2-Quaternary Indolin-3-ones

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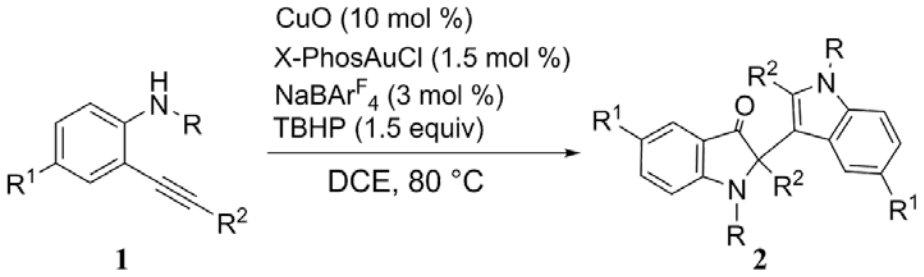
I. General Information

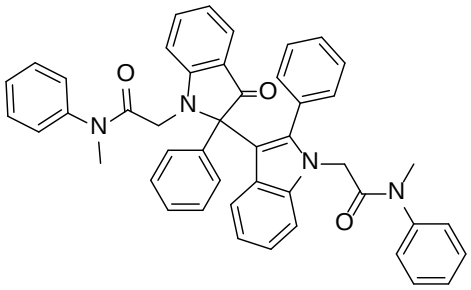
Unless stated otherwise, all reactions were carried out in glassware under atmosphere. All glassware and stirrers were dried in an oven at 85 °C overnight. All reagents were commercially available without further purification. The substrates were prepared according to the previous method reported. Elevated temperatures were maintained by an IKA heating block for 1 dram vials. The chromatographic purification of the products was performed on silica gel 300–400 mesh. NMR-spectra were measured in the given solvent at room temperature on a *Bruker Avance* (600 MHz, ^{1}H; 151 MHz, ^{13}C) or *Varian* (500 MHz, ^{1}H; 126 MHz, ^{13}C) instrument. Data for ^{1}H NMR and ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI). The compounds **2a** was glued on a glass fiber. Data were collected at 293 Kusing graphite-monochromated Mo Kα radiation (λ = 0.71073Å) and IP technique inthe range 2.19° < θ < 27.48°. Empirical absorption correction was applied. Thestructures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXS 97 crystallographic software package.Anisotropic thermal parameters were used to refine all non-hydrogen atoms.Hydrogen atoms were located from difference Fourier maps.

II. General Procedure for the Preparation of 2 (2a as Example):



To a solution of **1a** (136.2 mg, 0.4 mmol) in DCE (2.0 mL) was added CuO (3.2 mg, 0.04 mmol), X-PhosAuCl (4.3 mg, 0.006 mmol), $NaBAr^F_4$ (10.6 mg, 0.012 mmol) and TBHP (60 μL, 0.6 mmol). Then the mixture was stirred for 15 minutes at 80 ℃. After the complete consumption of **1a** (TLC), the mixture was treated with brine (50 mL) and extracted with DCM (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure to remove the solvent. Then the given residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:50 - 1:30, V/V) to afford **2a** (97.3 mg, 70% yield) as a yellow solid.

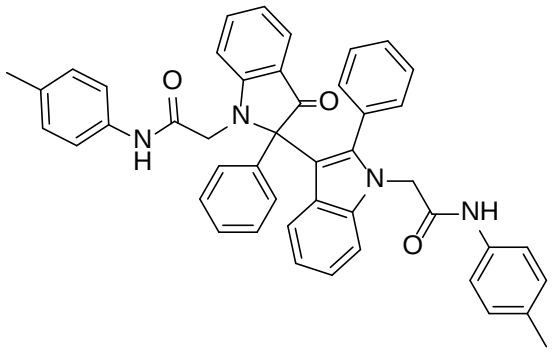
2,2'-(3-Oxo-2,2'-diphenyl-2,3'-biindoline-1,1'-diyl)bis(*N*-methyl-*N*-phenylacetamide (2a):



97.3 mg, 70% yield; yellow solid, mp. 270 – 272 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.41 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.22 (m, 10H), 7.18 (t, *J* = 6.5 Hz, 2H), 7.13 (d, *J* = 5.7 Hz, 4H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 5.6 Hz, 1H), 6.83 – 6.8 (m, 1H), 6.77 (s, 2H), 6.70 – 6.65 (m, 2H), 6.63 – 6.58 (m, 2H), 6.40 (d, *J* = 8.0 Hz, 1H), 4.31 – 4.05 (m, 2H), 3.72 (d, *J* = 17.7 Hz, 1H), 3.16 (s, 4H), 2.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 199.09, 167.02, 166.91, 159.23, 142.26, 139.05, 138.33, 137.50, 136.47, 131.75, 131.21, 130.84, 130.51, 129.92, 129.67, 128.73, 128.16, 127.92, 127.71, 127.54, 127.39, 127.28, 127.21, 126.95, 126.88, 124.67, 122.56,

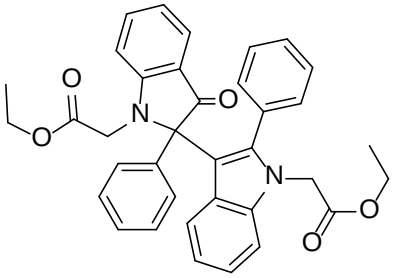
121.74, 119.60, 119.10, 116.84, 109.66, 109.44, 109.08, 76.44, 45.68, 45.20, 37.41, 37.04. HRMS (ESI) calculated for $C_{46}H_{39}N_4O_3^+$ $[M + H]^+$ 695.3022, found 695.3030.

2,2'-(3-Oxo-2,2'-diphenyl-2,3'-biindoline-1,1'-diyl)bis(*N*-p-tolylacetamide) (2b):



90.3 mg, 65% yield; yellow solid, mp. 190 – 192 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 9.93 (s, 1H), 9.58 (s, 1H), 7.59 (s, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 4H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.24 (s, 3H), 7.20 (dd, *J* = 9.1, 5.6 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 3H), 7.10 (d, *J* = 8.3 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 3H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.2 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 7.8 Hz, 1H), 4.64 (dd, *J* = 17.1 Hz, 2H), 4.39 (d, *J* = 17.4 Hz, 1H), 3.90 (d, *J* = 17.3 Hz, 1H), 2.24 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 198.64, 166.74, 166.35, 159.49, 138.79, 137.54, 137.32, 136.47, 136.43, 132.97, 132.56, 131.56, 131.19, 131.12, 129.61, 129.34, 128.89, 128.82, 128.14, 127.66, 127.33, 127.27, 124.30, 121.88, 121.30, 119.89, 119.81, 119.79, 119.14, 117.50, 110.69, 110.46, 110.07, 76.40, 47.55, 47.20, 20.92, 20.89. HRMS (ESI) calculated for $C_{46}H_{39}N_4O_3^+$ $[M + H]^+$ 695.3022, found 695.3031.

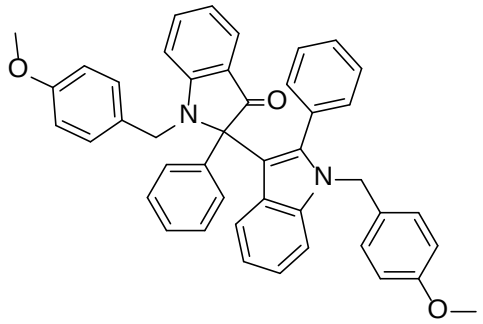
Diethyl 2,2'-(3-oxo-2,2'-diphenyl-2,3'-biindoline-1,1'-diyl)diacetate (2c):



60.7 mg, 53% yield; yellow solid, mp. 165 – 167 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 6.0 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.27 (d, *J* =

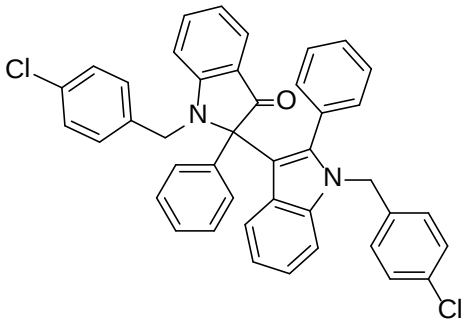
7.3 Hz, 2H), 7.25 – 7.17 (m, 5H), 7.17 – 7.11 (m, 2H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.64 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 4.49 (q, *J* = 7.5 Hz, 2H), 4.15 – 4.07 (m, 3H), 3.72 (tt, *J* = 14.3, 7.1 Hz, 1H), 3.66 (d, *J* = 4.3 Hz, 1H), 3.63 (dd, *J* = 10.6, 7.1 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.90, 168.97, 168.55, 158.50, 139.35, 137.86, 137.01, 136.87, 131.25, 130.88, 130.76, 130.09, 128.93, 128.59, 127.92, 127.77, 127.64, 127.21, 127.15, 126.59, 125.01, 122.31, 122.19, 120.07, 119.49, 117.61, 110.22, 109.04, 108.73, 76.26, 61.47, 60.72, 45.50, 45.25, 14.10, 13.73. HRMS (ESI) calculated for $C_{36}H_{33}N_2O_5^+$ $[M + H]^+$ 573.2389, found 573.2378.

1,1'-Bis(4-methoxybenzyl)-2,2'-diphenyl-2,3'-biindolin-3-one (2d):



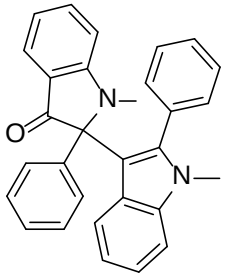
89.7 mg, 70% yield; yellow solid, mp. 118 – 120 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.52 (s, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.21 (m, 4H), 7.20 – 7.11 (m, 5H), 7.11 – 7.07 (m, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.77 – 6.69 (m, 6H), 6.63 (d, *J* = 8.7 Hz, 2H), 6.56 (dd, *J* = 7.8, 6.0 Hz, 2H), 6.52 (t, *J* = 5.7 Hz, 2H), 5.04 (q, *J* = 16.3 Hz, 2H), 4.66 (d, *J* = 16.2 Hz, 1H), 4.37 (d, *J* = 15.8 Hz, 1H), 3.73 (s, 3H), 3.67 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.97, 158.68, 158.62, 158.37, 139.68, 138.54, 136.97, 136.49, 131.39, 131.30, 130.86, 130.50, 130.07, 129.78, 128.98, 128.73, 128.33, 127.74, 127.64, 127.60, 127.51, 127.28, 127.06, 126.09, 125.14, 121.99, 121.82, 119.67, 119.49, 116.83, 114.21, 113.88, 113.46, 110.89, 110.44, 108.72, 77.23, 55.17, 55.12, 48.20, 46.73. HRMS (ESI) calculated for $C_{44}H_{37}N_2O_3^+$ $[M + H]^+$ 641.2804, found 641.2806.

1,1'-Bis(4-chlorobenzyl)-2,2'-diphenyl-2,3'-biindolin-3-one (2e):



103.7 mg, 80% yield; yellow solid, mp. 133 – 135 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.47 (s, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.11 (m, 10H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 5.4 Hz, 1H), 6.92 – 6.87 (m, 4H), 6.81 (s, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 3H), 6.44 (d, *J* = 8.3 Hz, 1H), 5.06 – 4.94 (m, 2H), 4.66 (d, *J* = 16.6 Hz, 1H), 4.24 (d, *J* = 16.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 198.92, 158.53, 139.39, 138.18, 137.21, 136.49, 136.44, 136.13, 132.93, 132.41, 131.27, 131.04, 130.53, 130.00, 129.01, 128.90, 128.70, 128.54, 128.46, 128.29, 128.10, 127.88, 127.82, 127.76, 127.52, 127.34, 127.20, 126.54, 125.27, 122.19, 119.97, 119.34, 117.32, 110.73, 110.19, 108.54, 76.99, 47.77, 46.63. HRMS (ESI) calculated for $C_{42}H_{31}Cl_2N_2O^+$ $[M + H]^+$ 649.1813, found 649.1806.

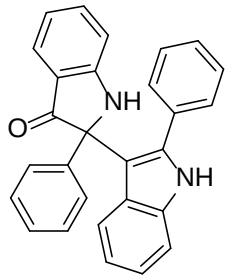
1,1'-Dimethyl-2,2'-diphenyl-2,3'-biindolin-3-one (2f):



65.1 mg, 76% yield; yellow solid, mp. 253 – 255 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (s, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 5H), 7.18 (d, *J* = 6.5 Hz, 3H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.88 (q, *J* = 7.5 Hz, 2H), 6.79 (d, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 6.55 (d, *J* = 8.3 Hz, 1H), 6.52 (t, *J* = 7.6 Hz, 1H), 3.44 (s, 3H), 2.77 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.07, 159.37, 139.96, 138.42, 137.15, 136.79, 131.37, 131.31, 130.67, 128.24, 127.69, 127.55, 127.50, 126.89, 125.14, 121.86, 121.49, 119.45, 119.39, 116.37, 109.71, 109.38, 107.71, 76.19, 30.55,

29.62. HRMS (ESI) calculated for $C_{30}H_{24}N_2NaO^+$ $[M + Na]^+$ 451.1786, found 451.1779.

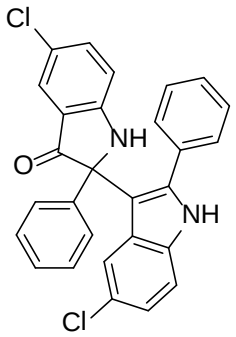
2,2'-Diphenyl-2,3'-biindolin-3-one (2g):



To a solution of **1g** (1.54 g, 8.0 mmol) in DCE (40 mL) in a flask was added CuO (63.6 mg, 0.8 mmol), X-PhosAuCl (85.0 mg, 0.12 mmol), $NaBAr^F_4$ (212.7 mg, 0.24 mmol) and TBHP (1.2 mL, 12.0 mmol). Then the mixture was stirred for 40 minutes at 80 ℃. After the complete consumption of **1g** (TLC), the mixture was treated with brine (100 mL) and extracted with DCM (3 × 30 mL). The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure to remove the solvent. Then the given residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:50 - 1:30, V/V) to afford **2g** (1.02 g, 64% yield).

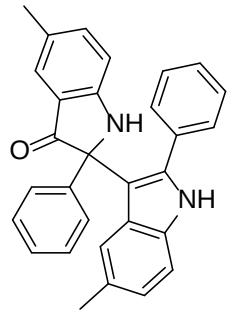
52.8 mg, 66% yield; yellow solid, mp. 271 – 273 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.37 (s, 1H), 8.36 (s, 1H), 7.55 – 7.49 (m, 1H), 7.41 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.10 – 7.02 (m, 6H), 7.00 (d, *J* = 8.3 Hz, 1H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 201.01, 160.54, 140.28, 138.46, 137.98, 136.27, 133.65, 130.01, 128.05, 127.88, 127.81, 127.58, 127.51, 127.46, 124.89, 121.63, 120.79, 119.15, 118.95, 118.00, 112.39, 111.73, 111.51, 71.65. HRMS (ESI) calculated for $C_{28}H_{20}N_2NaO^+$ $[M + Na]^+$ 423.1473, found 423.1464.

5,5'-Dichloro-2,2'-diphenyl-2,3'-biindolin-3-one (2h):



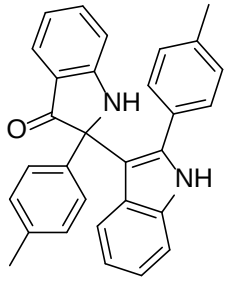
75.1 mg, 80% yield; yellow solid, mp. 257 – 259 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.67 (s, 1H), 8.61 (s, 1H), 7.53 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 7.19 – 7.15 (m, 5H), 7.12 (t, *J* = 7.5 Hz, 2H), 7.06 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 6.44 (d, *J* = 1.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 199.50, 158.76, 139.95, 139.66, 137.78, 134.70, 133.07, 129.98, 128.85, 128.47, 128.38, 127.99, 127.76, 127.41, 123.76, 121.82, 121.64, 119.84, 114.14, 113.32, 111.00, 72.18. HRMS (ESI) calculated for $C_{28}H_{18}Cl_2N_2NaO^+$ $[M + Na]^+$ 491.0694, found 491.0690.

5,5'-Dimethyl-2,2'-diphenyl-2,3'-biindolin-3-one (2i):



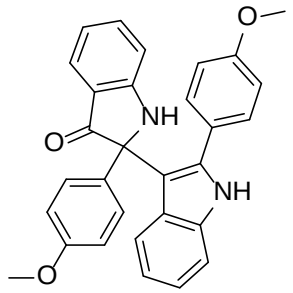
51.4 mg, 60% yield; yellow solid, mp. 300 – 302 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.16 (s, 1H), 8.24 (s, 1H), 7.40 – 7.34 (m, 2H), 7.18 – 7.10 (m, 5H), 7.08 – 7.02 (m, 5H), 6.79 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 8.3 Hz, 1H), 2.35 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 200.11, 160.93, 148.81, 140.60, 137.71, 136.71, 133.84, 130.66, 129.96, 127.93, 127.60, 127.53, 127.50, 127.30, 125.90, 124.65, 120.86, 120.62, 119.76, 116.87, 112.09, 111.46, 111.41, 71.86, 22.61, 21.74. HRMS (ESI) calculated for $C_{30}H_{24}N_2NaO^+$ $[M + Na]^+$ 451.1786, found 451.1776.

2,2'-Dip-tolyl-2,3'-biindolin-3-one (2j):



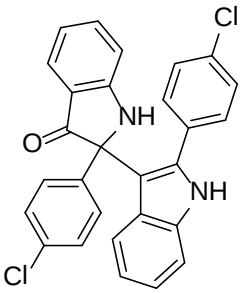
55.7 mg, 65% yield; yellow solid, mp. 196 – 198 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.25 (s, 1H), 8.26 (s, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 3H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.87 (t, *J* = 8.3 Hz, 4H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 1H), 2.22 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 200.98, 160.33, 138.29, 137.80, 137.37, 136.92, 136.54, 136.20, 130.84, 129.83, 128.66, 128.13, 128.02, 127.45, 124.84, 121.43, 120.79, 119.10, 119.01, 117.80, 112.29, 111.60, 111.31, 71.44, 21.25, 21.00. HRMS (ESI) calculated for $C_{30}H_{24}N_2NaO^+$ $[M + Na]^+$ 451.1786, found 451.1788.

2,2'-Bis(4-methoxyphenyl)-2,3'-biindolin-3-one (2k):



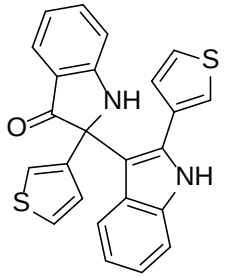
50.7 mg, 55% yield; yellow solid, mp. 207 – 209 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.42 – 7.38 (m, 1H), 7.38 – 7.33 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.11 – 7.04 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 3H), 6.89 – 6.84 (m, 1H), 6.72 (dd, *J* = 7.5, 3.8 Hz, 1H), 6.67 (t, *J* = 8.3 Hz, 3H), 6.52 (d, *J* = 8.7 Hz, 2H), 5.22 (s, 1H), 3.69 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.77, 159.25, 159.07, 158.91, 136.95, 136.83, 135.38, 132.29, 130.81, 128.32, 127.41, 125.35, 125.23, 121.86, 121.25, 120.32, 119.62, 118.81, 113.51, 112.93, 112.11, 111.85, 110.72, 77.21, 76.95, 76.70, 71.52, 55.14, 55.08. HRMS (ESI) calculated for $C_{30}H_{24}N_2NaO_3^+$ $[M + Na]^+$ 483.1685, found 483.1680.

2,2'-Bis(4-chlorophenyl)-2,3'-biindolin-3-one (2l):



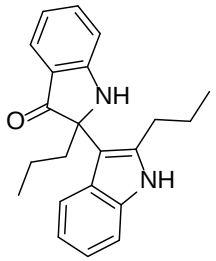
65.7 mg, 70% yield; yellow solid, mp. 151 – 153 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.48 (s, 1H), 8.44 (s, 1H), 7.58 – 7.51 (m, 1H), 7.39 (d, *J* = 8.6 Hz, 3H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.14 (m, 4H), 7.12 (d, *J* = 8.7 Hz, 2H), 7.08 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 200.86, 160.73, 139.11, 138.35, 137.30, 136.26, 132.85, 132.47, 132.31, 131.81, 129.43, 128.03, 127.58, 127.45, 124.99, 122.05, 120.57, 119.51, 118.66, 118.43, 112.56, 111.92, 111.77, 71.13. HRMS (ESI) calculated for $C_{28}H_{18}Cl_2N_2NaO^+$ $[M + Na]^+$ 491.0694, found 491.070.

2,2'-Di(thiophen-3-yl)-2,3'-biindolin-3-one (2m):



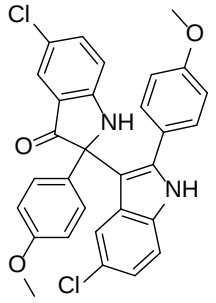
41.3 mg, 50% yield; yellow solid, mp. 142 – 144 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.31 (s, 1H), 8.31 (s, 1H), 7.53 – 7.48 (m, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.29 (m, 3H), 7.21 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.18 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.06 – 7.01 (m, 1H), 6.98 (dd, *J* = 4.9, 1.2 Hz, 1H), 6.94 (d, *J* = 8.3 Hz, 1H), 6.84 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.81 – 6.76 (m, 1H), 6.75 – 6.71 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 200.74, 160.48, 141.26, 138.01, 135.90, 133.66, 133.61, 129.11, 128.39, 127.47, 126.14, 125.18, 125.01, 124.94, 121.95, 121.66, 120.36, 119.27, 118.62, 117.95, 112.36, 111.61, 111.15, 69.98. HRMS (ESI) calculated for $C_{24}H_{17}N_2OS_2^+$ $[M + H]^+$ 413.0782, found 413.0788.

2,2'-Dipropyl-2,3'-biindolin-3-one (2n):



49.9 mg, 75% yield; yellow solid, mp. 177 – 179 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 10.83 (s, 1H), 7.75 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.90 – 6.84 (m, 1H), 6.66 (t, *J* = 7.3 Hz, 1H), 2.83 (ddd, *J* = 15.5, 9.9, 5.9 Hz, 1H), 2.71 – 2.62 (m, 1H), 2.34 (td, *J* = 13.0, 4.2 Hz, 1H), 2.03 (td, *J* = 13.1, 4.7 Hz, 1H), 1.50 (ttd, *J* = 15.6, 13.1, 5.9 Hz, 2H), 1.34 – 1.15 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 203.60, 161.03, 137.85, 137.72, 135.70, 127.30, 124.51, 121.17, 120.45, 119.24, 118.66, 117.14, 111.83, 110.97, 107.80, 70.65, 30.17, 24.21, 17.43, 14.63, 14.50. HRMS (ESI) calculated for $C_{22}H_{25}N_2O^+$ $[M + H]^+$ 333.1967, found 333.1976.

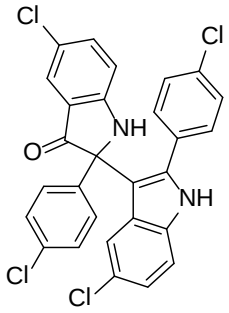
5,5'-Dichloro-2,2'-bis(4-methoxyphenyl)-2,3'-biindolin-3-one (2o):



65.6 mg, 62% yield; yellow solid, mp. 270 – 272 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.56 (s, 1H), 8.52 (s, 1H), 7.52 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.06 (d, *J* = 8.7 Hz, 2H), 7.04 (dd, *J* = 8.6, 2.0 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 1H), 6.76 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.44 (d, *J* = 1.9 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 199.92, 159.38, 159.30, 158.63, 139.81, 137.61, 134.53, 131.28, 128.95, 128.64, 125.30, 123.75, 123.65, 121.62, 121.36, 119.95, 119.72, 114.04, 113.96,

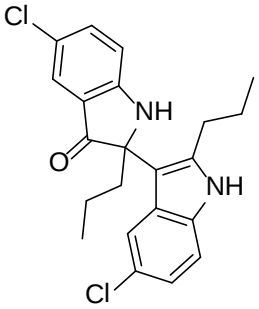
113.19, 113.14, 111.08, 71.65, 55.58. HRMS (ESI) calculated for $C_{30}H_{22}Cl_2N_2NaO_3^+$ $[M + Na]^+$ 551.0905, found 551.0911.

5,5'-Dichloro-2,2'-bis(4-chlorophenyl)-2,3'-biindolin-3-one (2p):



92.6 mg, 86% yield; yellow solid, mp. 187 – 189 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.77 (s, 1H), 8.67 (s, 1H), 7.57 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.41 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.22 – 7.15 (m, 6H), 7.10 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.60 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 199.46, 170.78, 159.07, 138.90, 138.36, 138.20, 134.72, 133.40, 132.93, 131.82, 131.69, 129.32, 128.38, 127.73, 124.12, 123.88, 122.36, 122.10, 119.59, 119.45, 114.33, 113.57, 111.09, 71.76. HRMS (ESI) calculated for $C_{28}H_{16}Cl_4N_2NaO^+$ $[M + Na]^+$ 560.9885, found 560.9878.

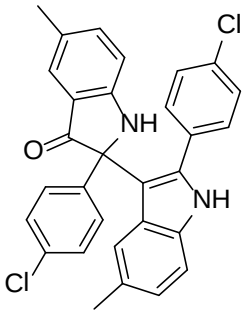
5,5'-Dichloro-2,2'-dipropyl-2,3'-biindolin-3-one (2q):



53.0 mg, 66% yield; yellow solid, mp. 175 – 177 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.11 (s, 1H), 8.03 (s, 1H), 7.75 (s, 1H), 7.49 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.39 (d, *J* = 2.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 2H), 2.93 – 2.83 (m, 1H), 2.75 – 2.66 (m, 1H), 2.26 (td, *J* = 13.1, 4.9 Hz, 1H), 2.01 (td, *J* = 13.3, 5.3 Hz, 1H), 1.63 – 1.51 (m, 1H), 1.52 – 1.41 (m, 1H), 1.31 – 1.15 (m, 2H), 0.85 (dt, *J* = 14.9, 7.3 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 202.33, 159.47, 139.93, 137.62, 134.21, 128.09, 123.61, 123.43, 121.20, 120.49, 120.31, 120.00, 113.63, 112.46, 107.34,

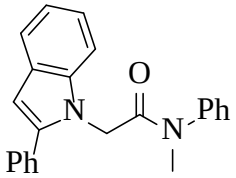
71.43, 39.89, 30.19, 24.06, 17.41, 14.51, 14.43. HRMS (ESI) calculated for $C_{22}H_{23}Cl_2N_2O^+$ $[M + H]^+$ 401.1187, found 401.1188.

2,2'-Bis(4-chlorophenyl)-5,5'-dimethyl-2,3'-biindolin-3-one (2r):



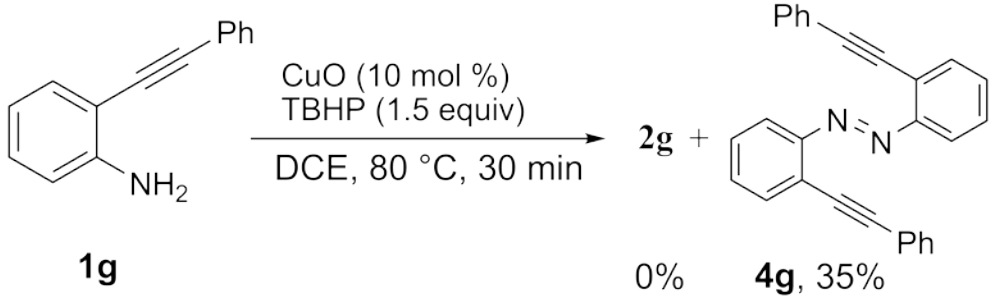
59.7 mg, 60% yield; yellow solid, mp. 301 – 303 ℃. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 11.27 (s, 1H), 8.32 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 1H), 7.14 (s, 4H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.80 (s, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.62 – 6.57 (m, 2H), 2.36 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ: 199.91, 161.09, 149.32, 139.43, 136.71, 136.51, 132.63, 132.49, 132.31, 131.74, 131.16, 129.39, 127.91, 127.53, 125.48, 124.74, 121.22, 120.39, 120.20, 116.56, 112.24, 111.72, 111.56, 71.33, 22.61, 21.74. HRMS (ESI) calculated for $C_{30}H_{22}Cl_2N_2NaO^+$ $[M + Na]^+$ 519.1007, found 519.1011.

***N*-Methyl-*N*-phenyl-2-(2-phenyl-1H-indol-1-yl)acetamide (3a):**



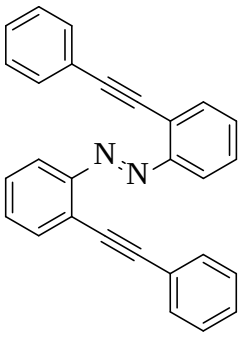
6.1 mg, 9% yield; white solid, mp. 170 – 172 ℃. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.60 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.41 – 7.36 (m, 3H), 7.35 – 7.29 (m, 1H), 7.23 – 7.18 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 3H), 6.54 (s, 1H), 4.54 (s, 2H), 3.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 167.67, 142.46, 141.57, 138.37, 132.68, 130.21, 129.41, 128.51, 128.45, 128.24, 128.00, 127.04, 121.96, 120.71, 120.12, 109.33, 102.46, 46.41, 37.72. HRMS (ESI) calculated for $C_{23}H_{21}N_2O^+$ $[M + H]^+$ 341.1654, found 341.1669.

III. Control Experiments for Mechanistic Studies:

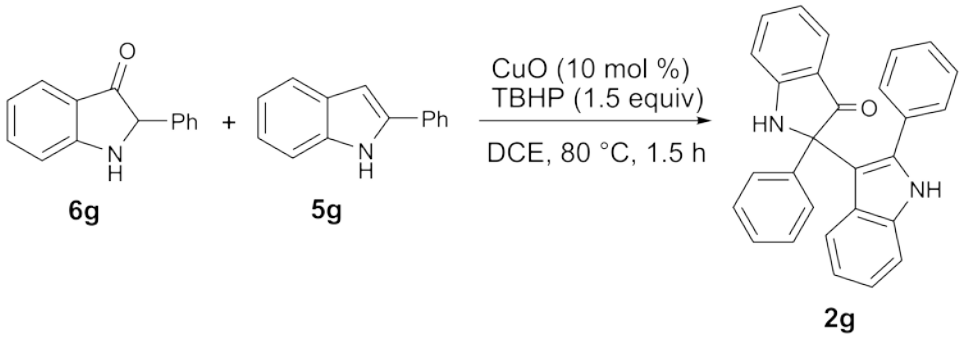


To a solution of **1g** (77.3 mg, 0.4 mmol) in DCE (2.0 mL) was added CuO (3.2 mg, 0.04 mmol) and TBHP (60 μL, 0.6 mmol). Then the mixture was stirred for 30 minutes at 80 ℃. After the complete consumption of **1g**, the resulting mixture was treated with brine (50 mL) and extracted with DCM (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure to remove the solvent. Then the given residue was purified by silica gel column chromatography (Et_2O/ petroleum ether = 1:100 - 1:50, V/V) to afford **4g** (26.8 mg, 35% yield) as a yellow oil.

(*E*)-1,2-Bis(2-(phenylethynyl)phenyl)diazene (4g):

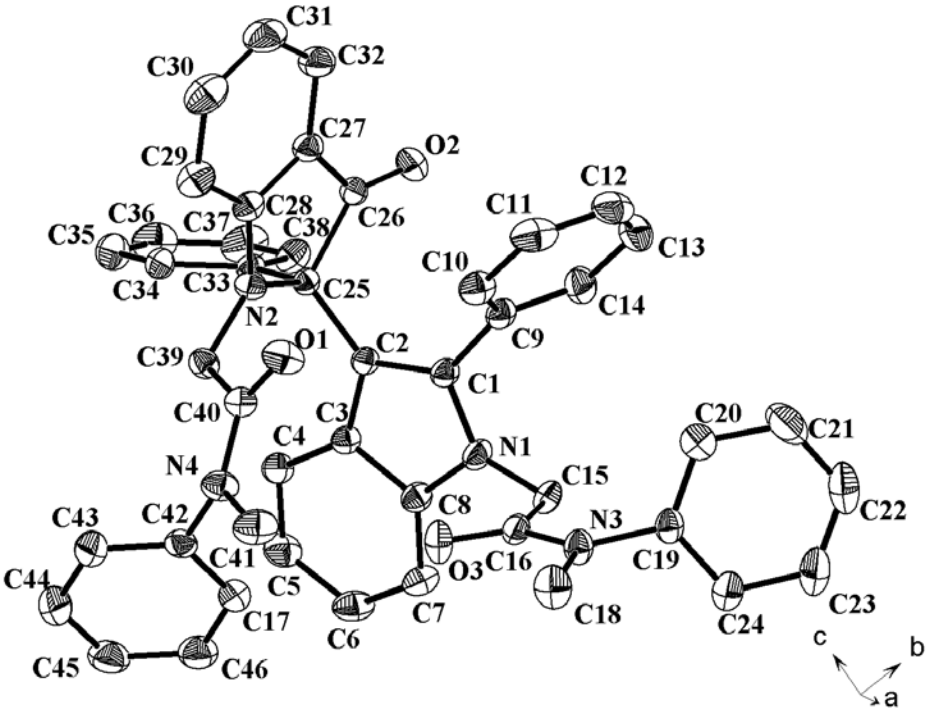


26.8 mg, 35% yield; yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.08 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.72 (dd, *J* = 7.8, 1.2 Hz, 2H), 7.59 (ddd, *J* = 7.7, 5.8, 1.6 Hz, 6H), 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 149.70, 134.58, 132.78, 132.04, 129.24, 128.52, 128.46, 124.73, 122.43, 118.82, 97.18, 84.76. HRMS (ESI) calculated for $C_{28}H_{19}N_2^+$ $[M + H]^+$ 383.1548, found 383.1529.



To a solution of **6g** (41.8 mg, 0.2 mmol) and **5g** (38.6 mg, 0.2 mmol) in DCE (2.0 mL) was added CuO (1.6 mg, 0.02 mmol) and TBHP (30 μL, 0.3 mmol). Then the mixture was stirred for 1.5 h at 80 ℃. After the complete consumption of **6g**, the resulting mixture was treated with brine (50 mL) and extracted with DCM (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, and evaporated under reduced pressure to remove the solvent. Then the given residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1:50 - 1:30, V/V) to afford **2g** (48.1 mg, 60% yield) as a yellow solid.

IV. Crystal ORTEP drawing of compound 2a:



V. ^{1}H NMR and ^{13}C NMR Spectra of 2, 3a and 4g:

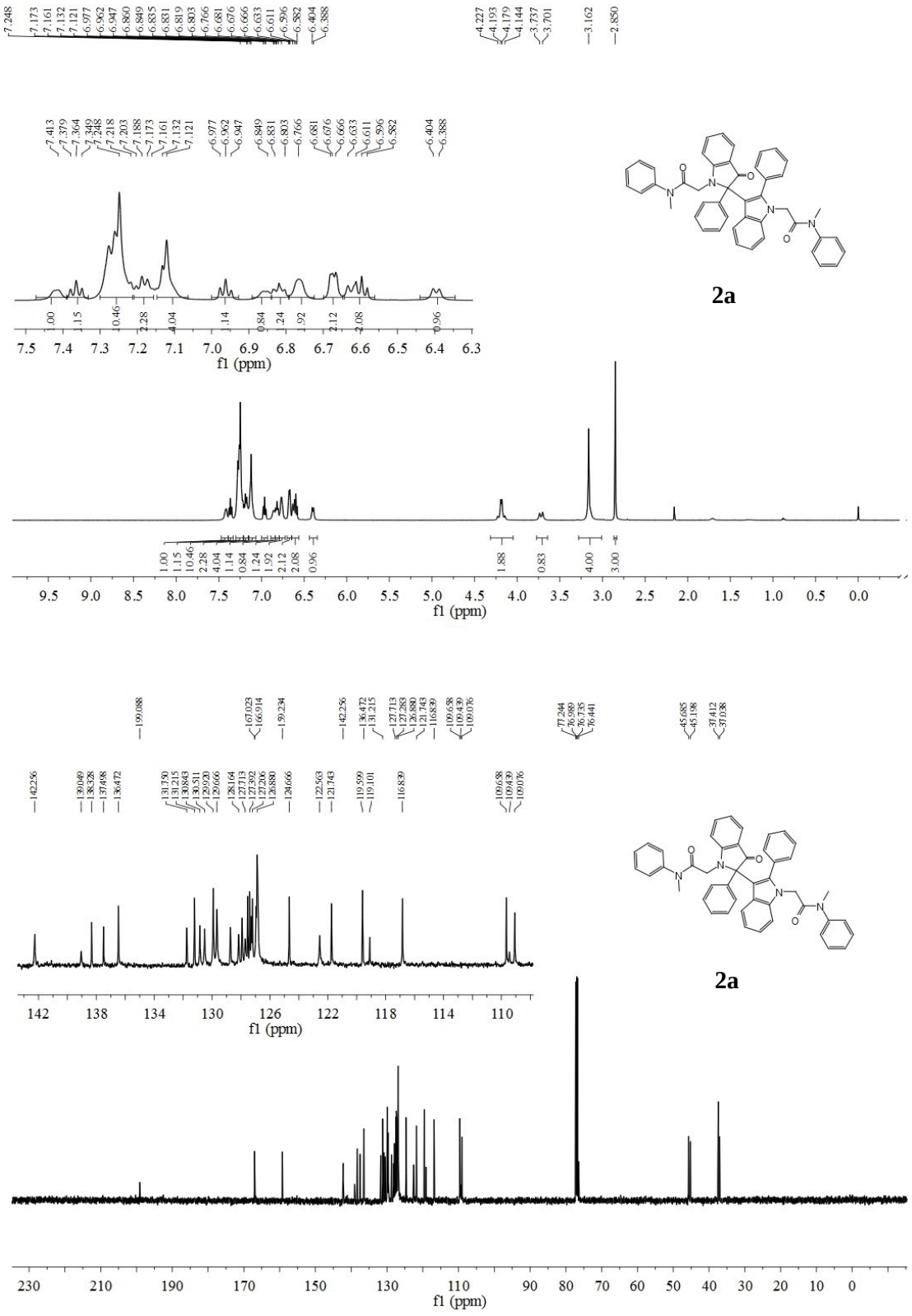


Figure 1. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2a**.

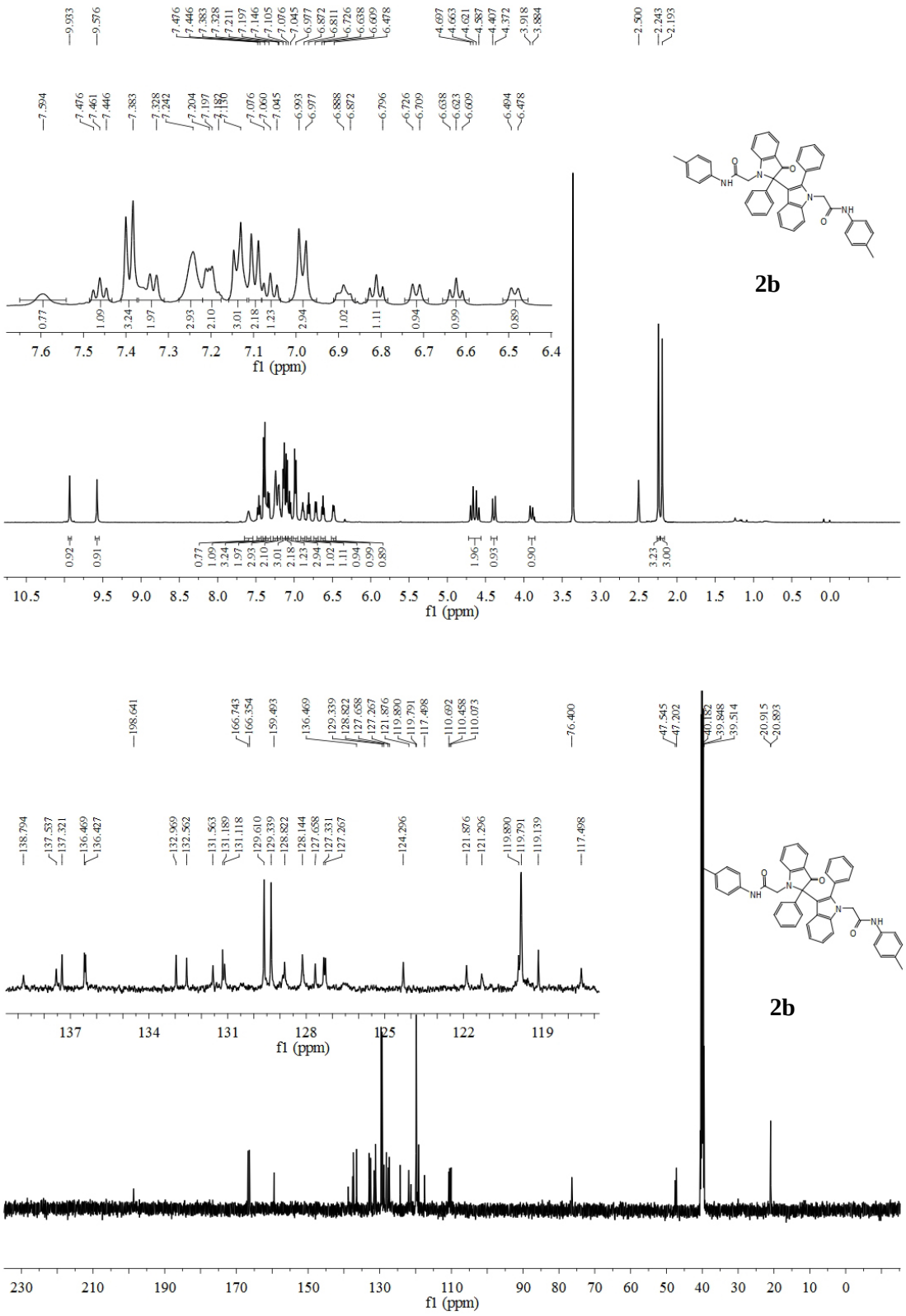


Figure 2. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2b**.

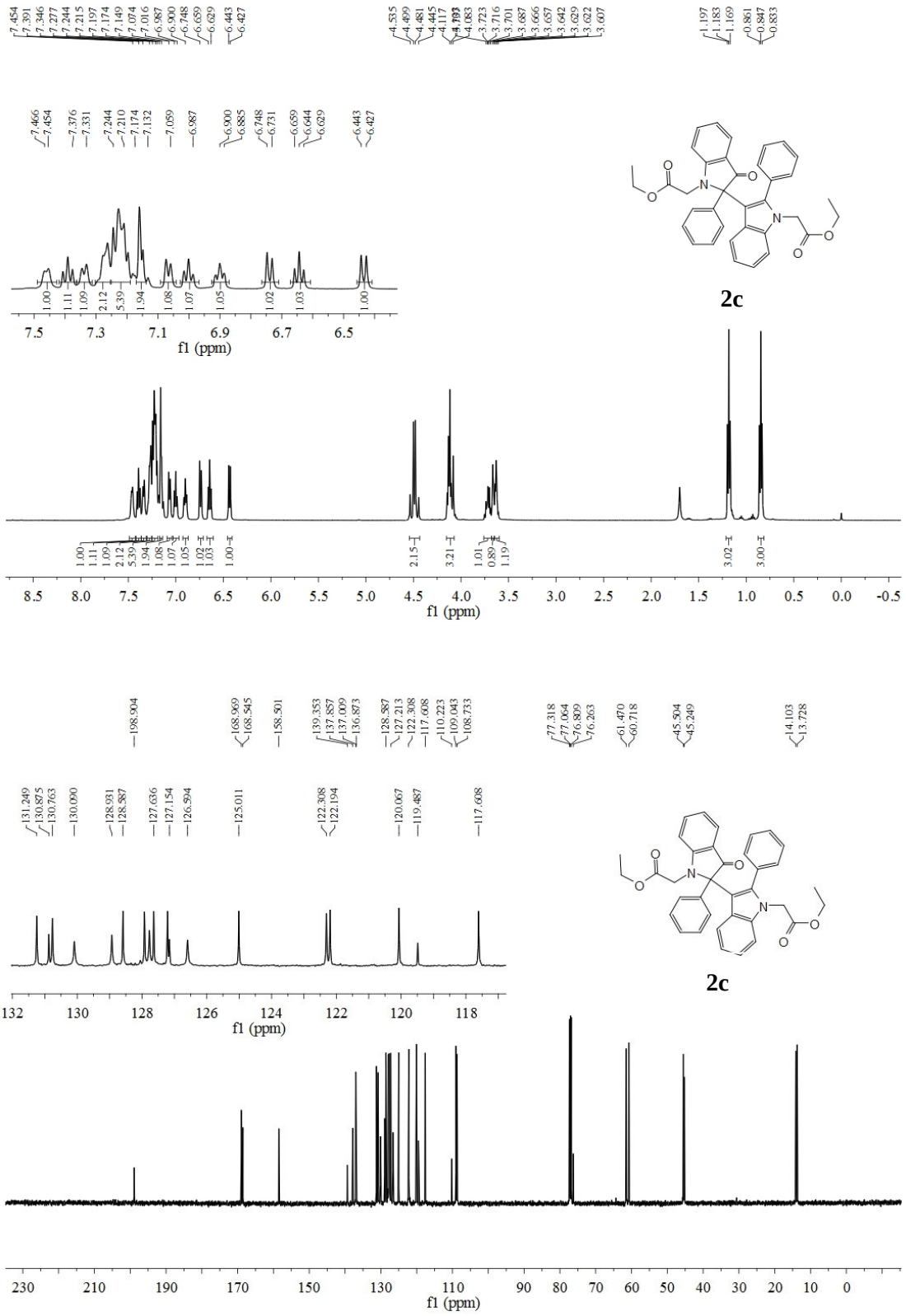


Figure 3. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2c**.

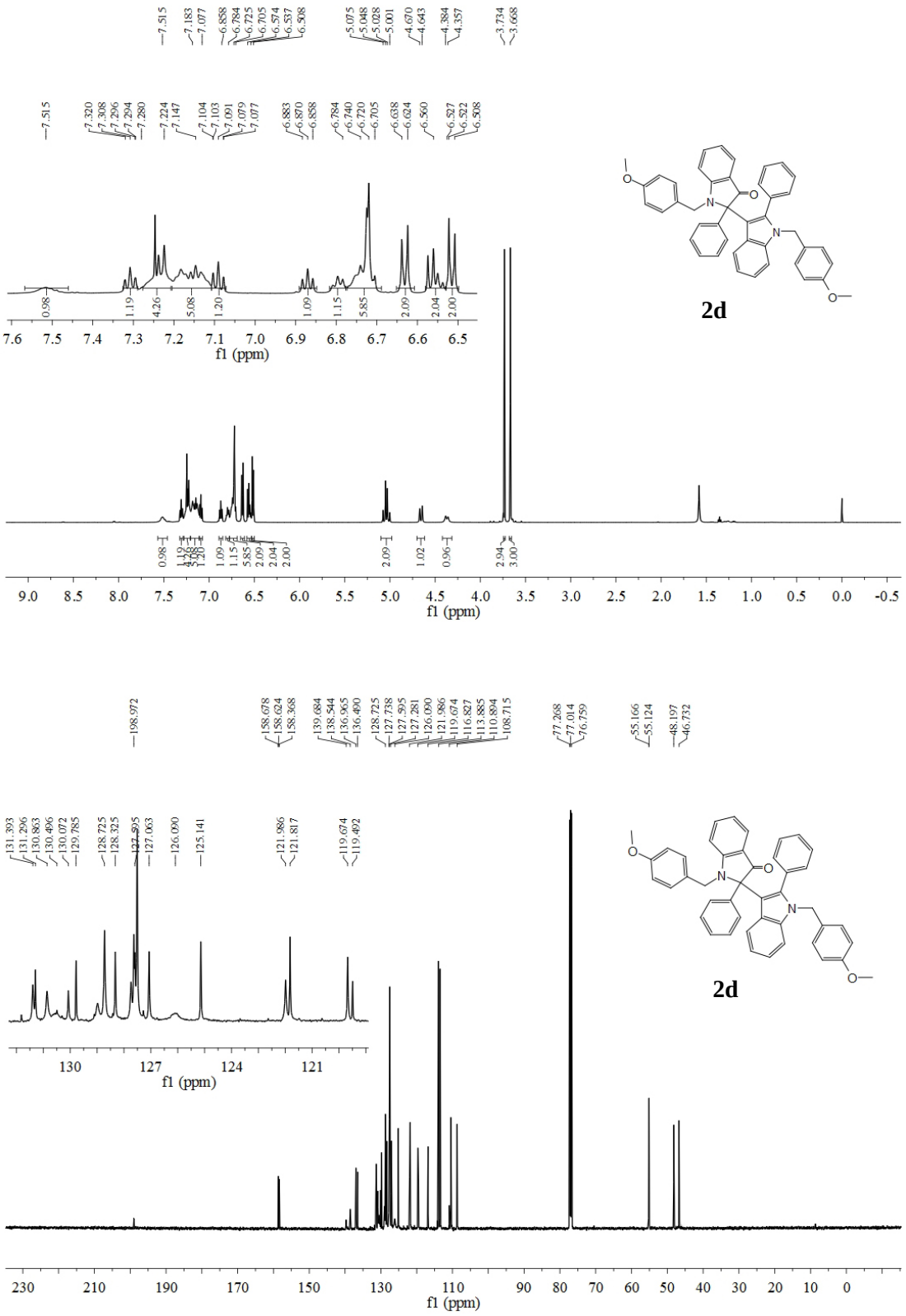


Figure 4. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2d**.

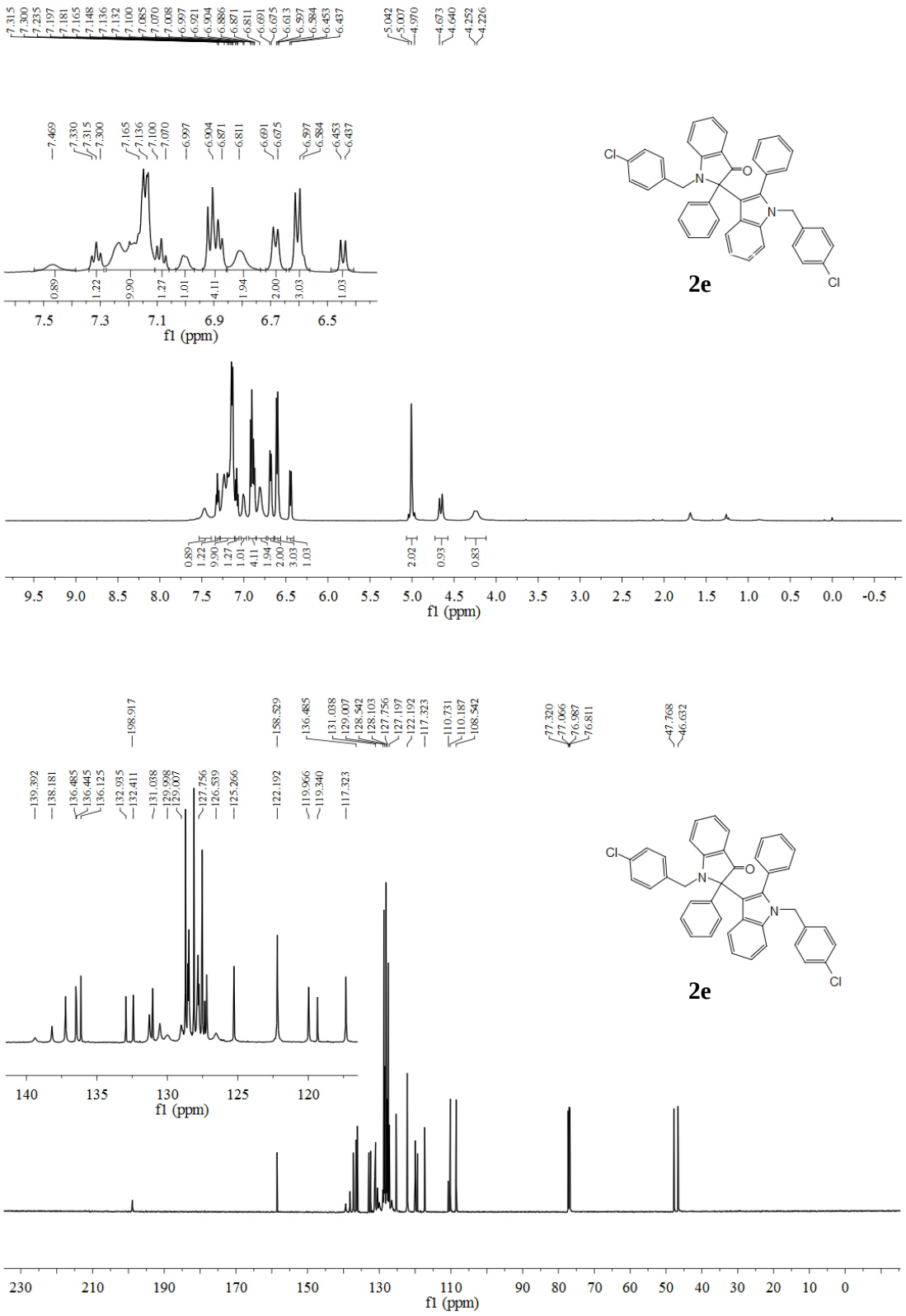


Figure 5. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2e**.

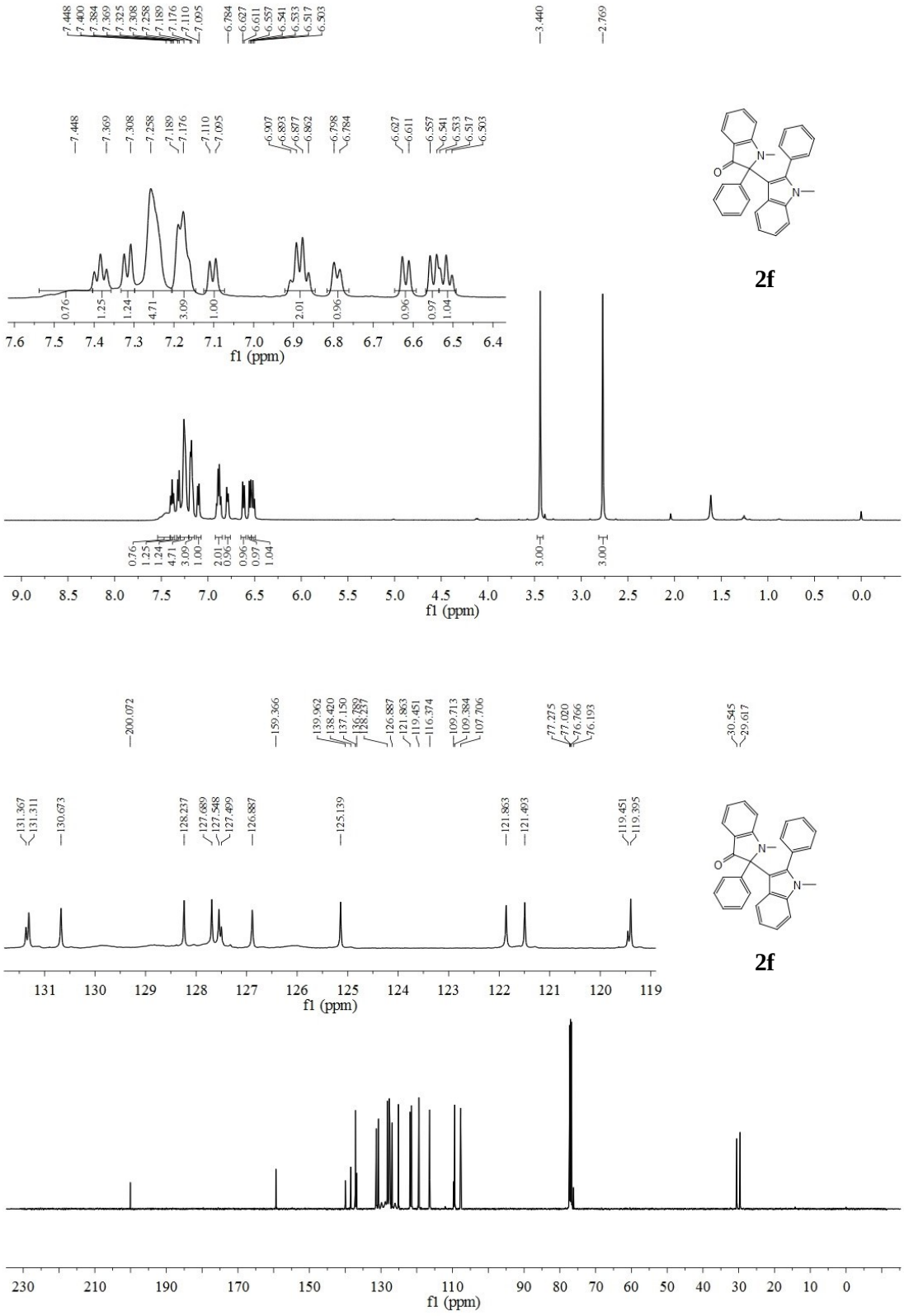


Figure 6. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2f**.

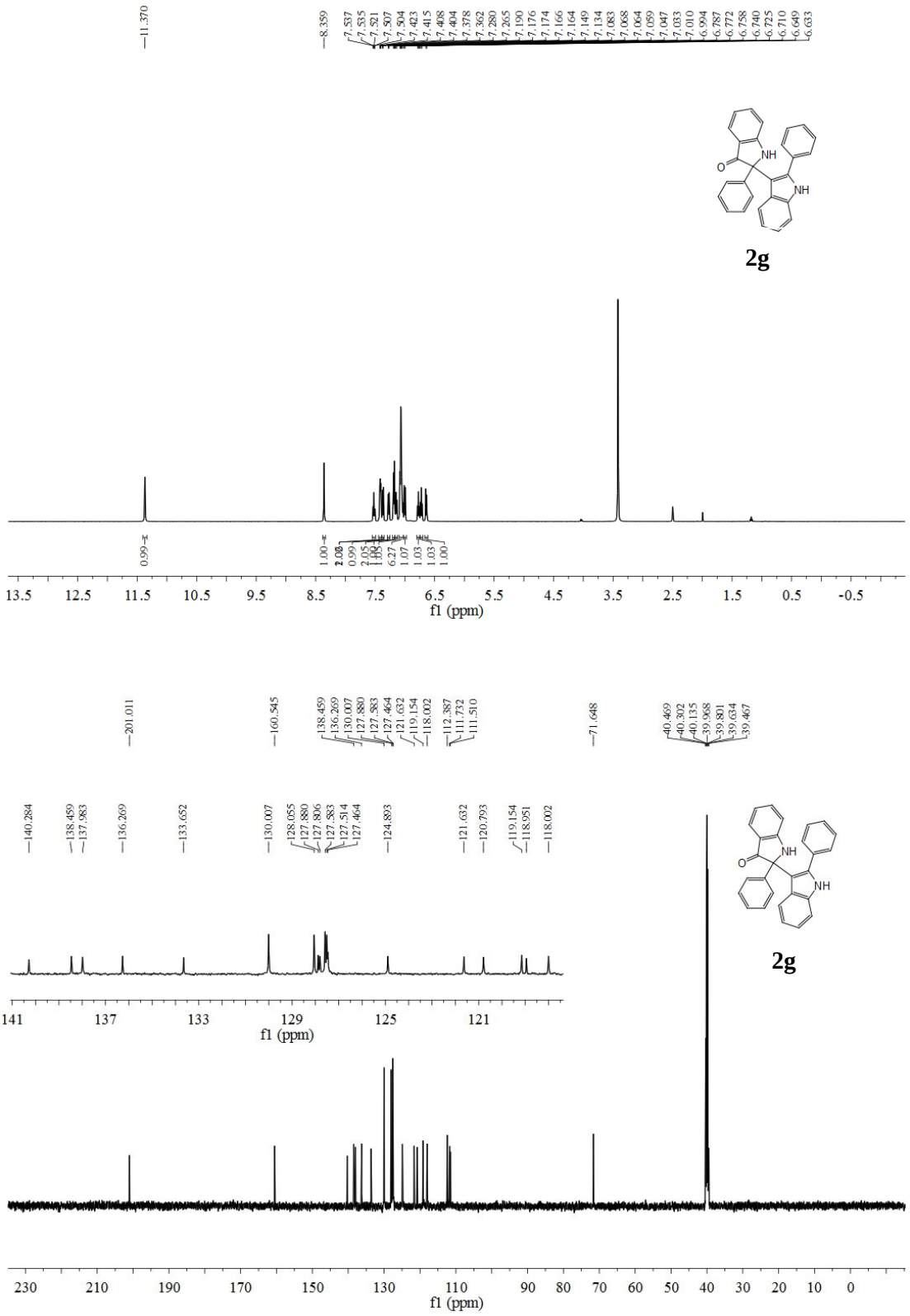


Figure 7. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2g**.

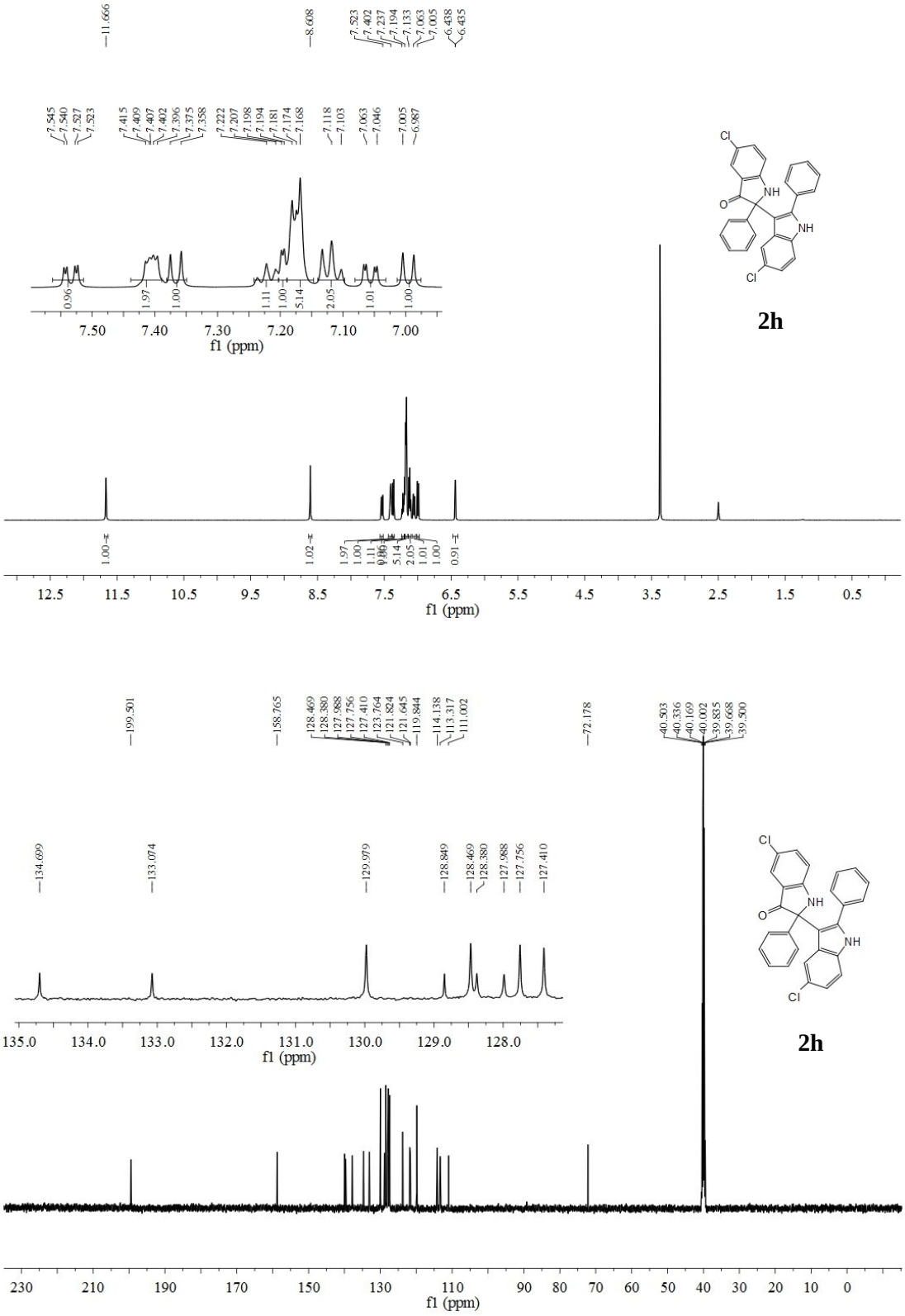


Figure 8. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2h**.

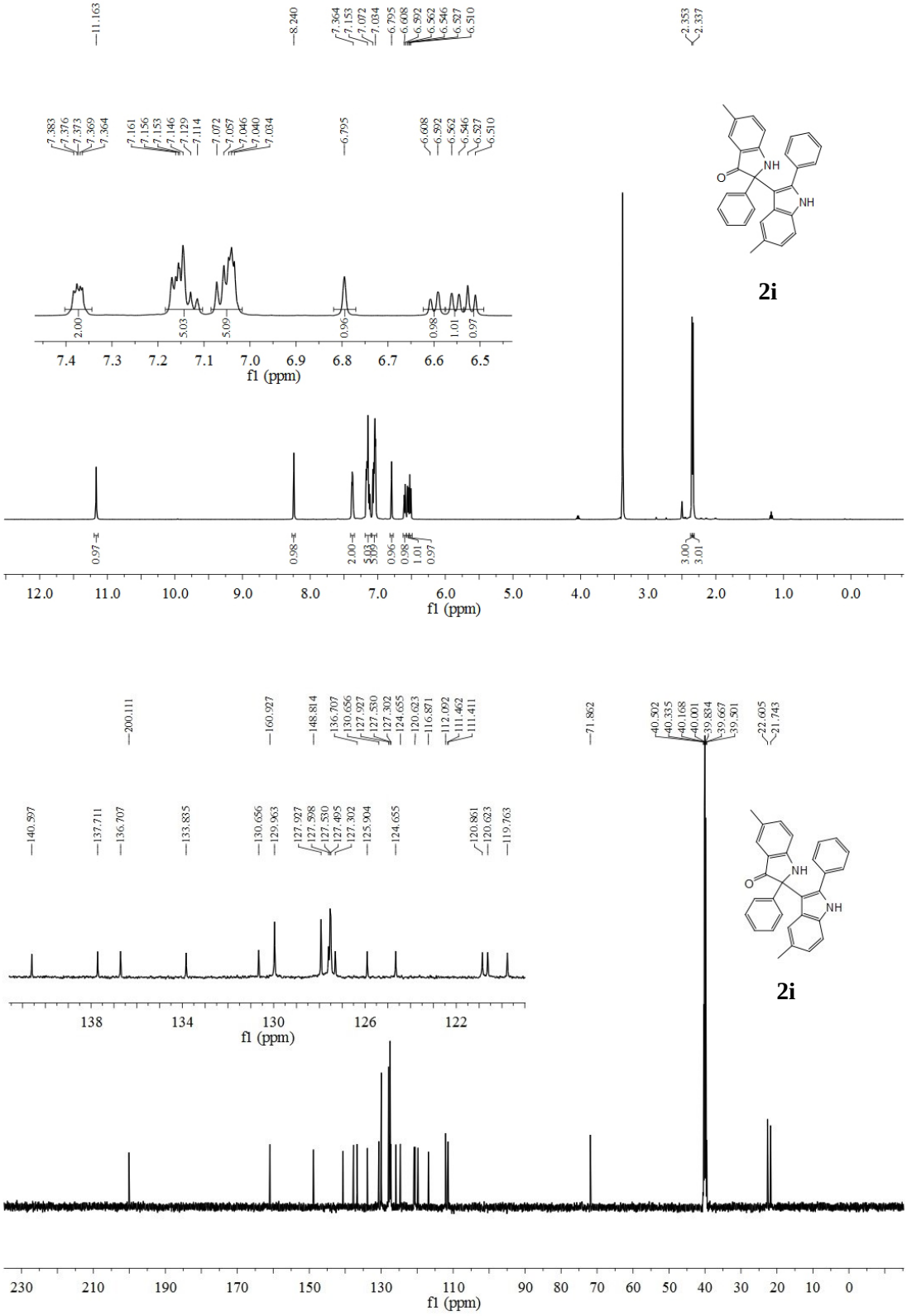


Figure 9. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2i**.

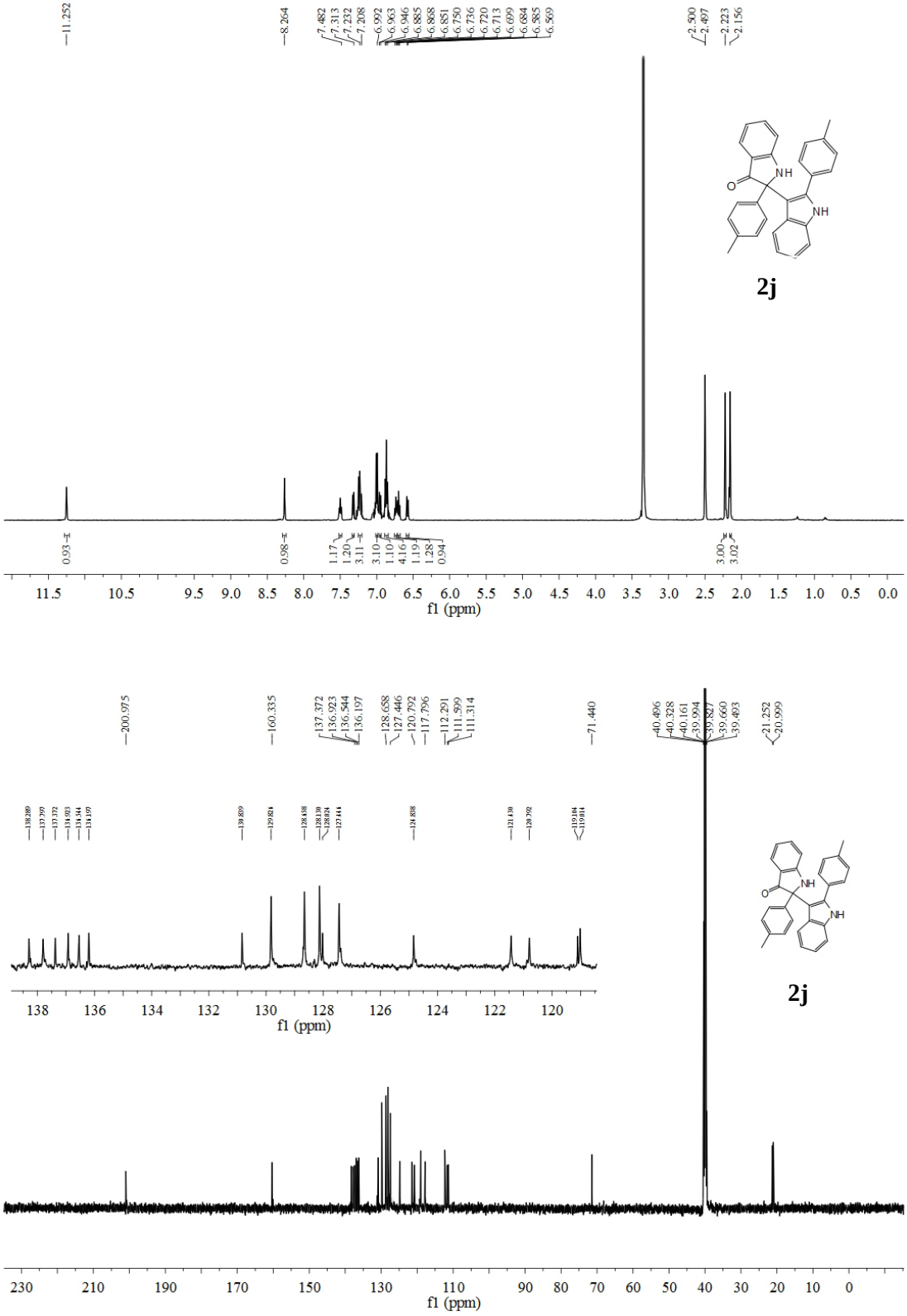


Figure 10. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2j**.

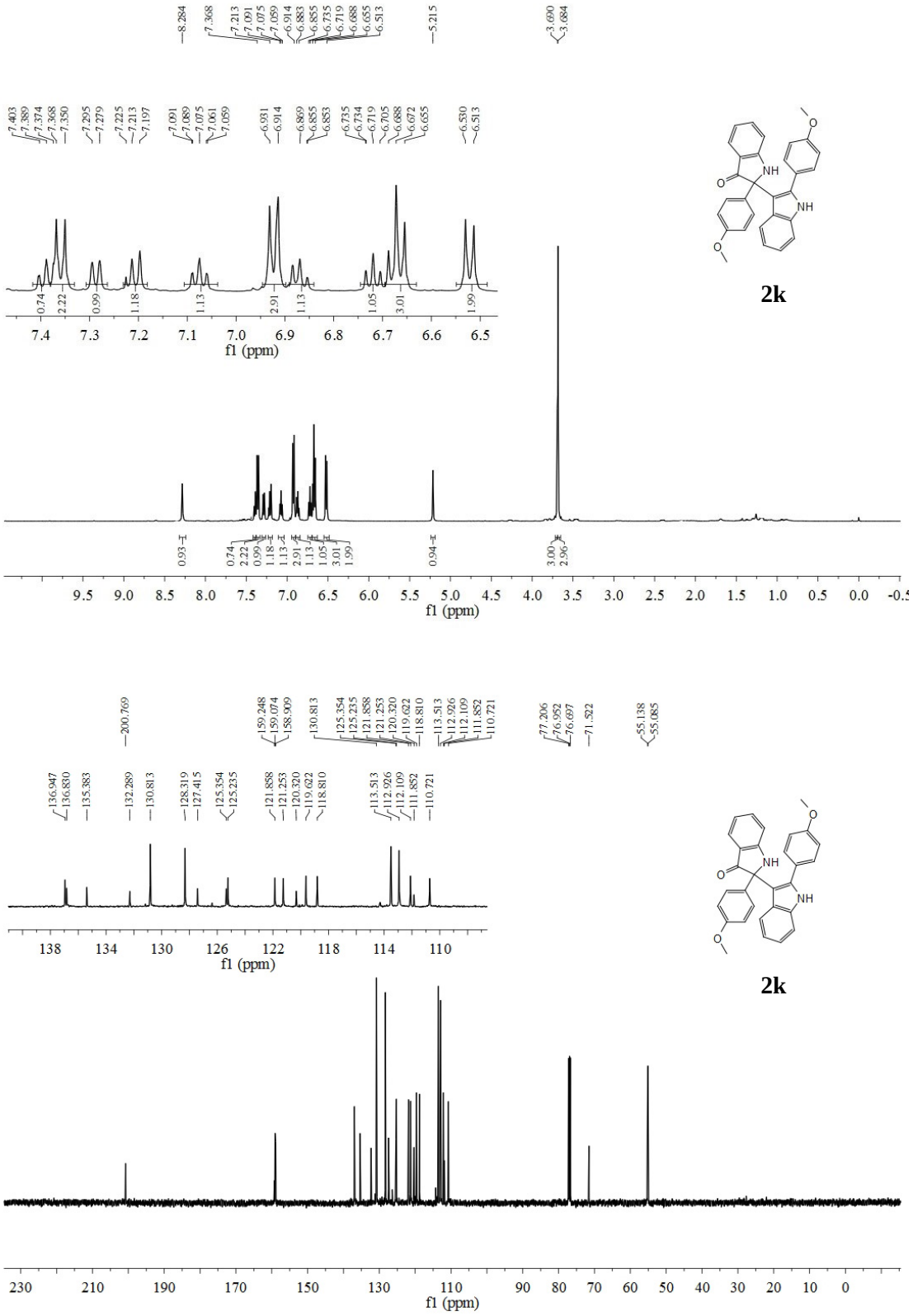


Figure 11. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2k**.

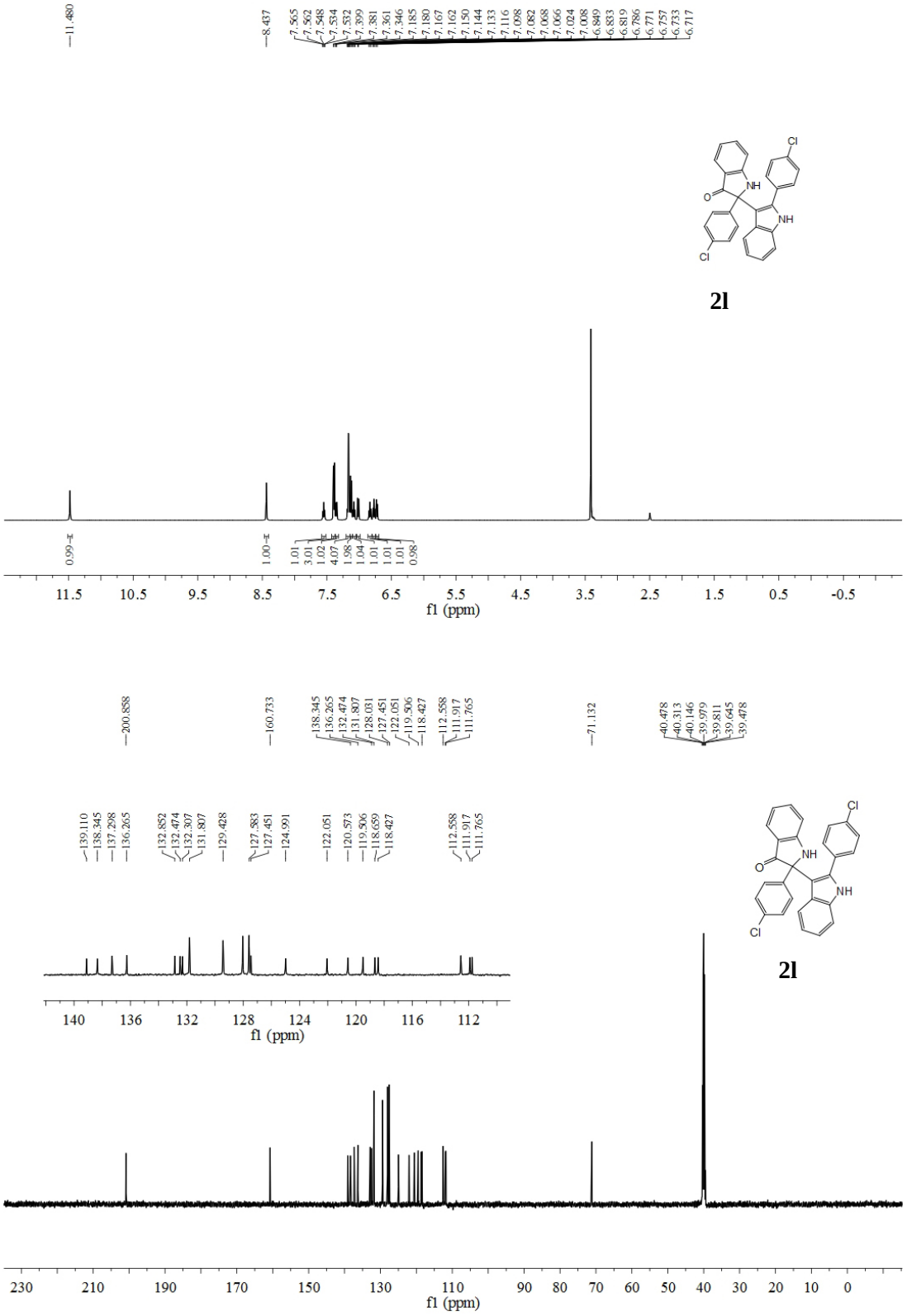


Figure 12. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2l**.

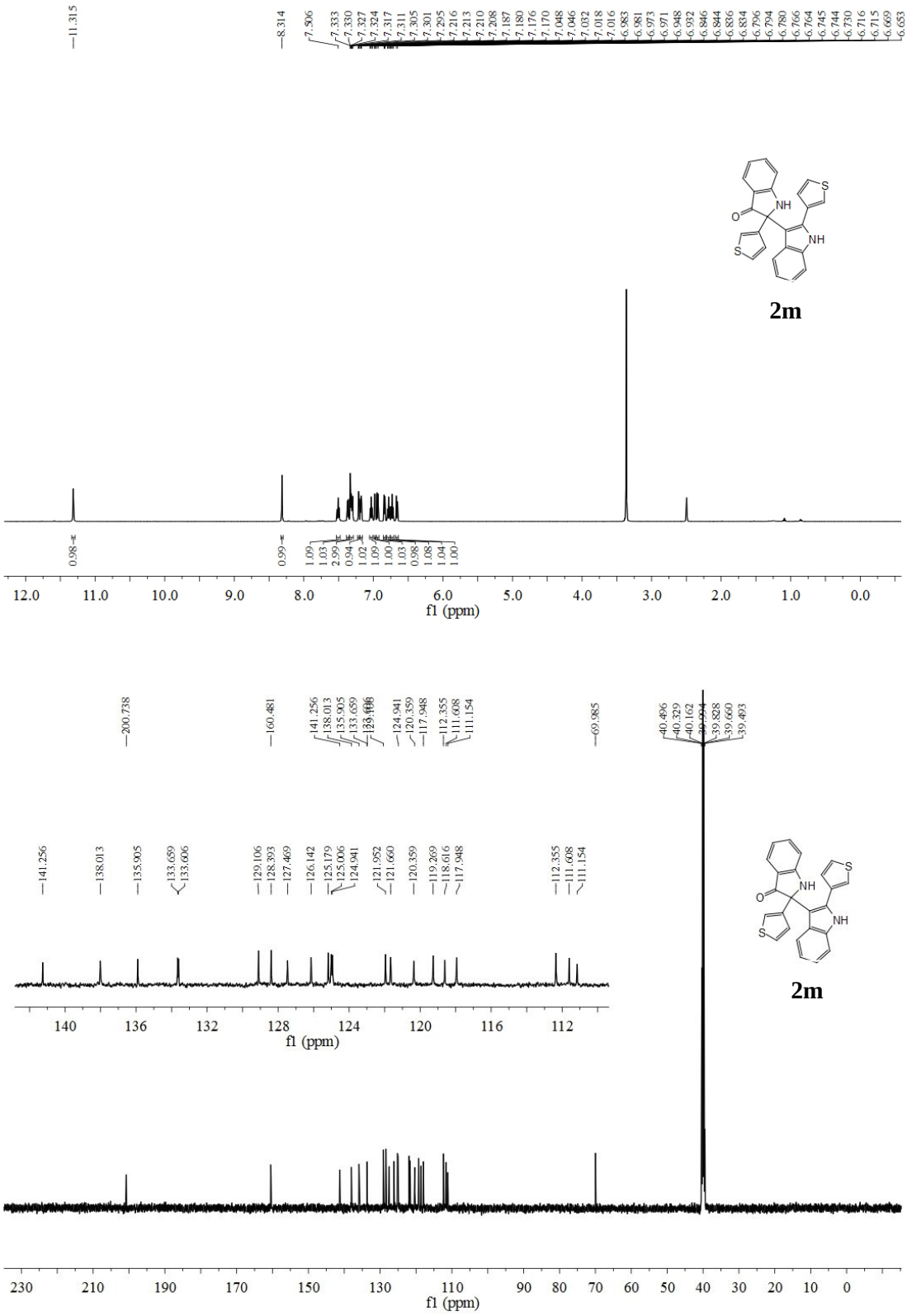


Figure 13. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2m**.

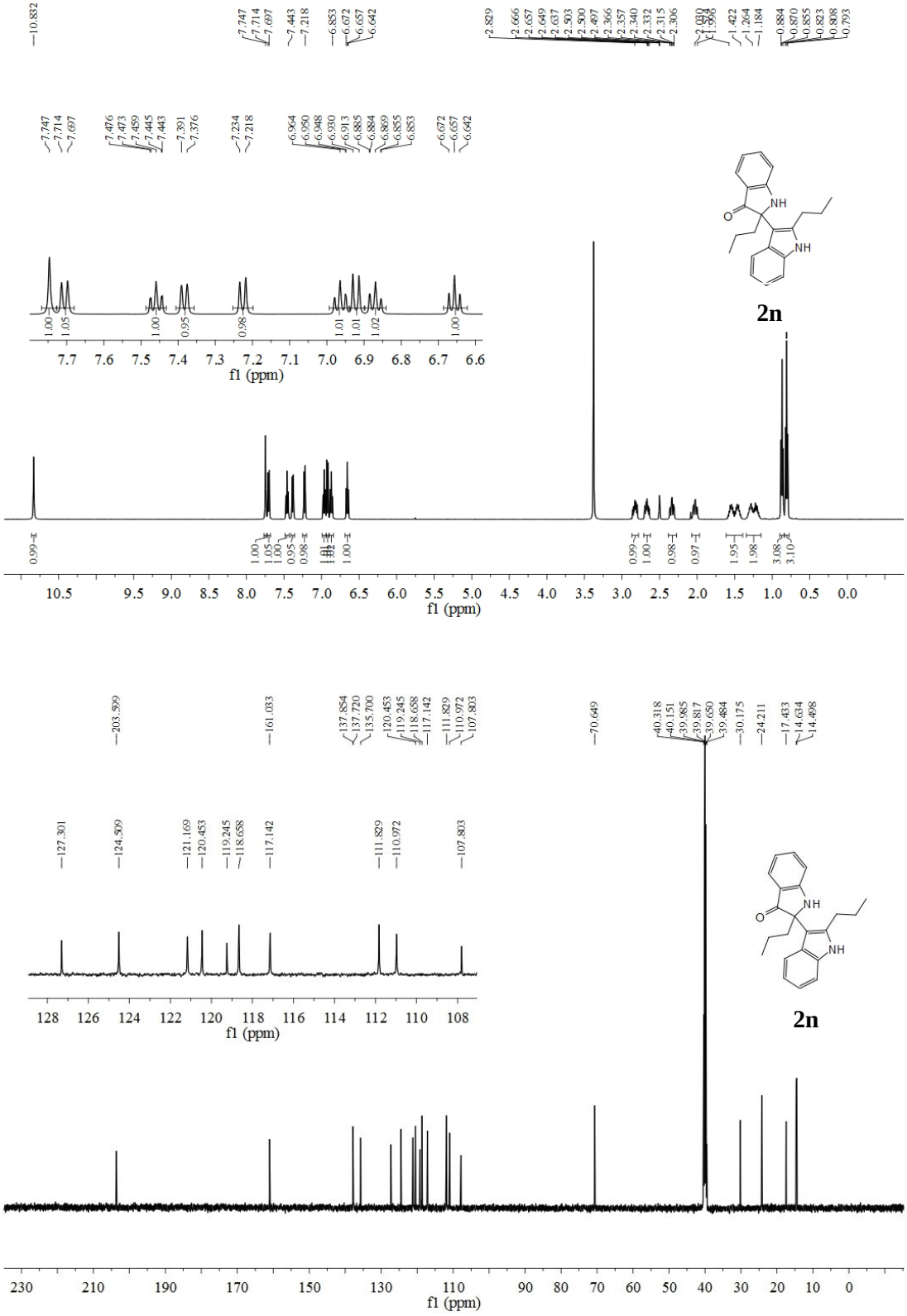


Figure 14. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2n**.

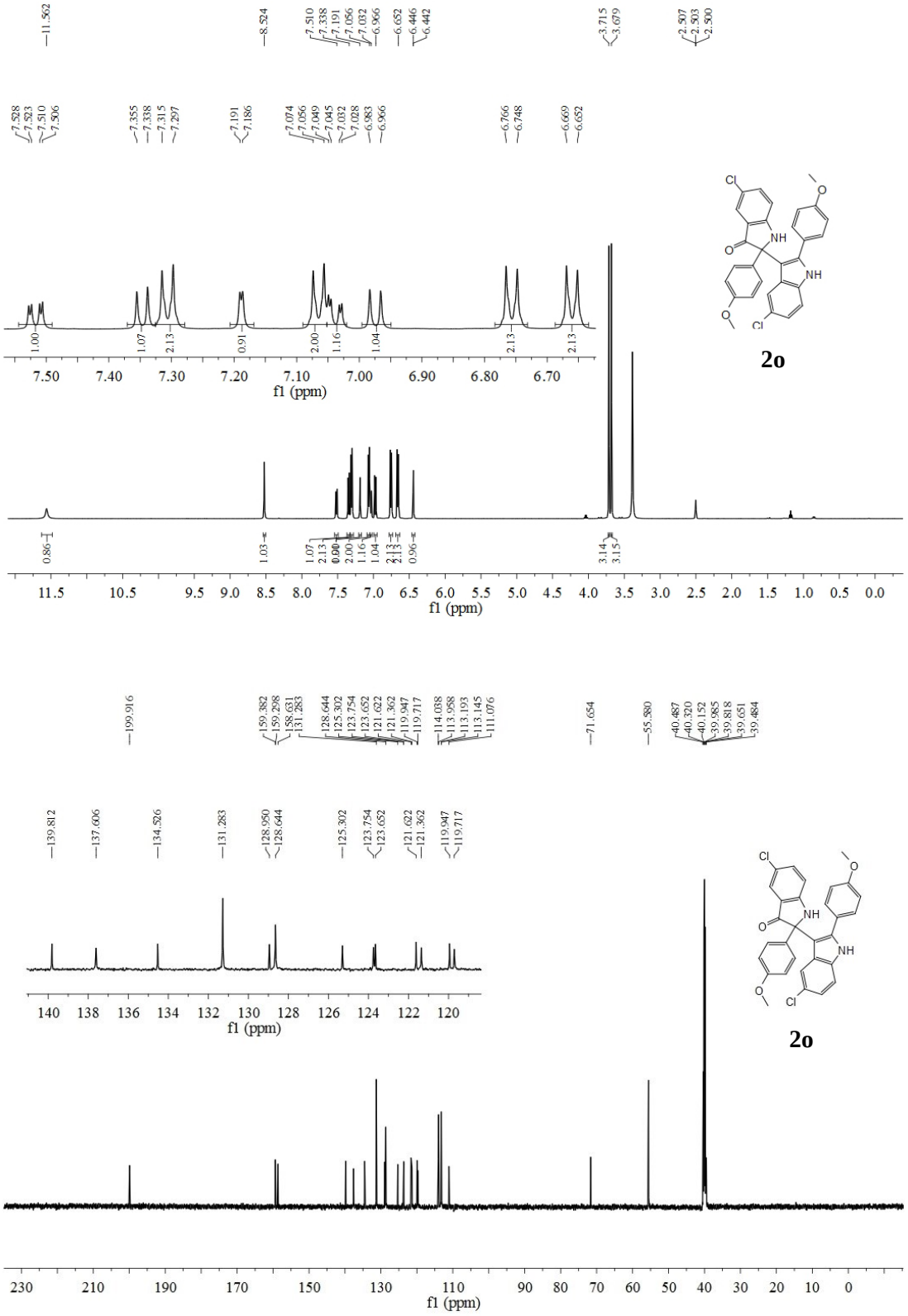


Figure 15. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2o**.

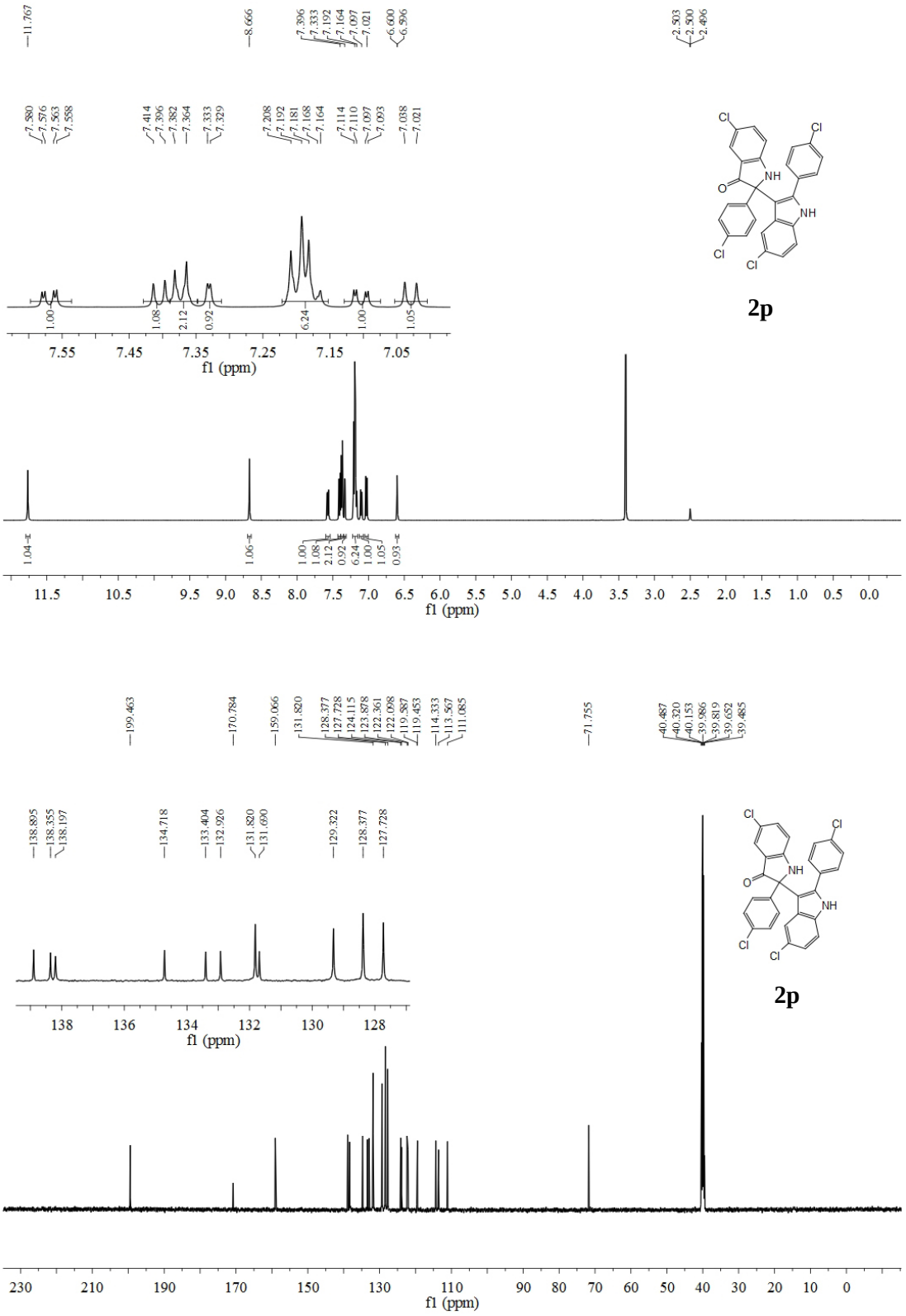


Figure 16. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2p**.

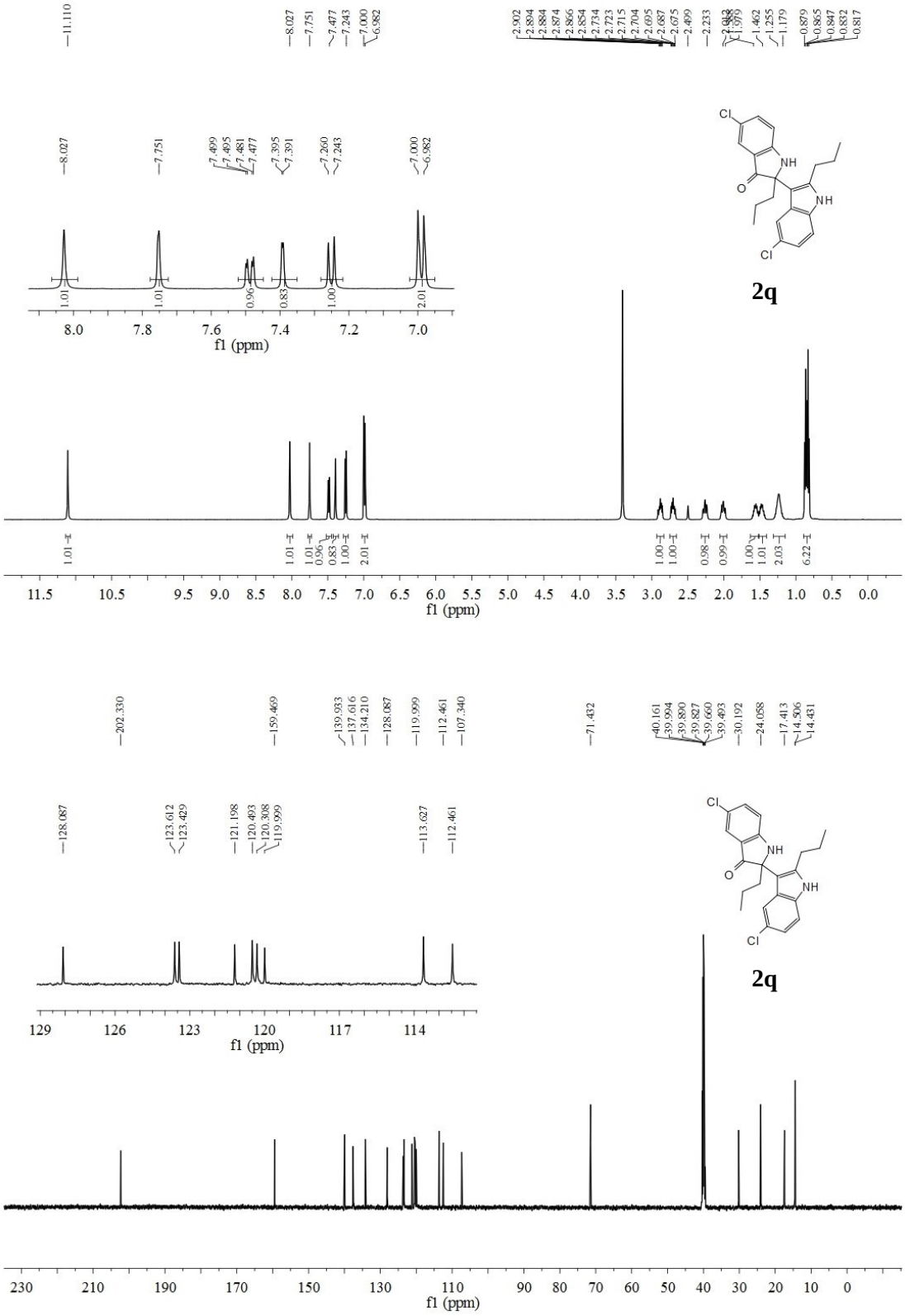


Figure 17. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2q**.

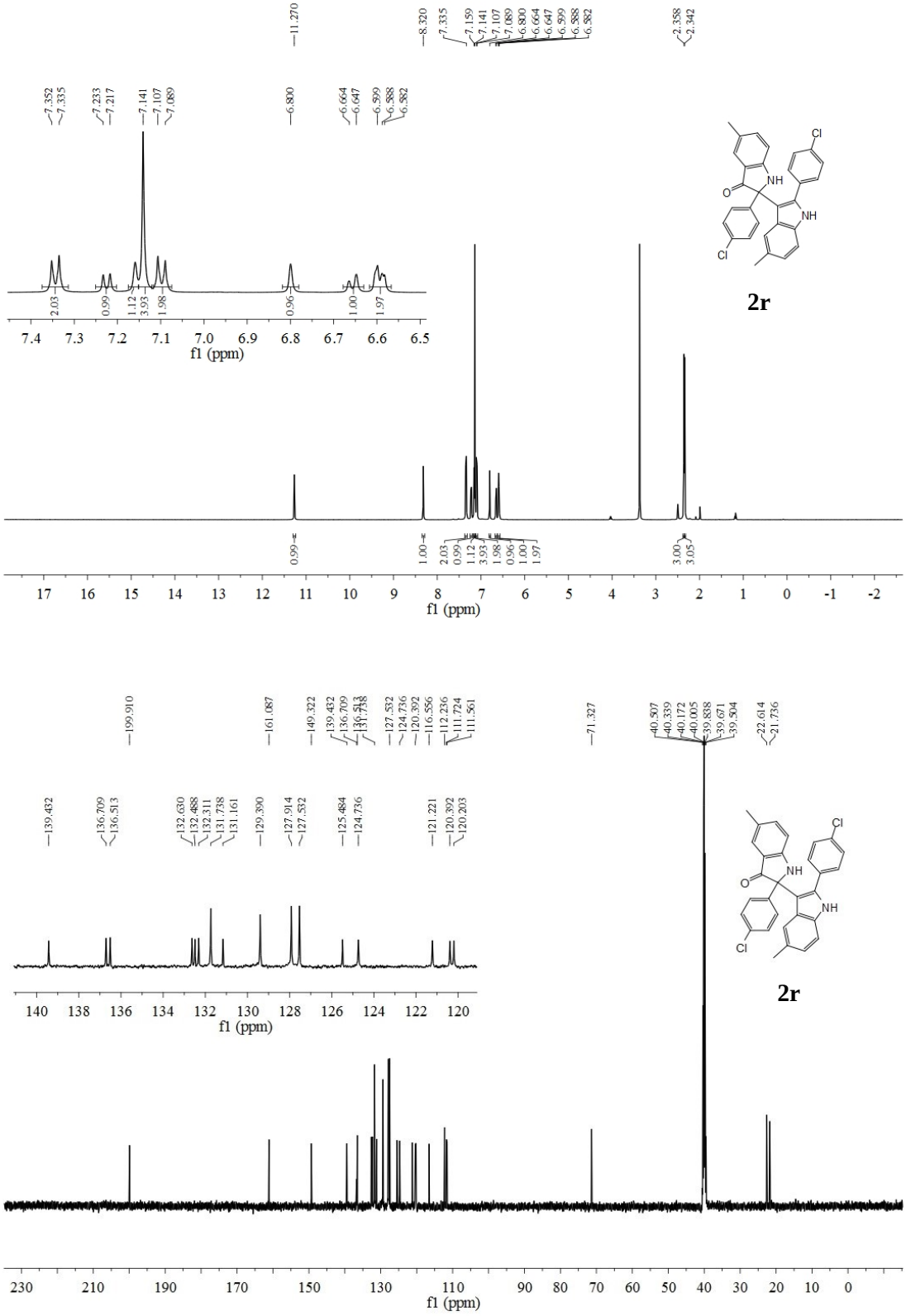
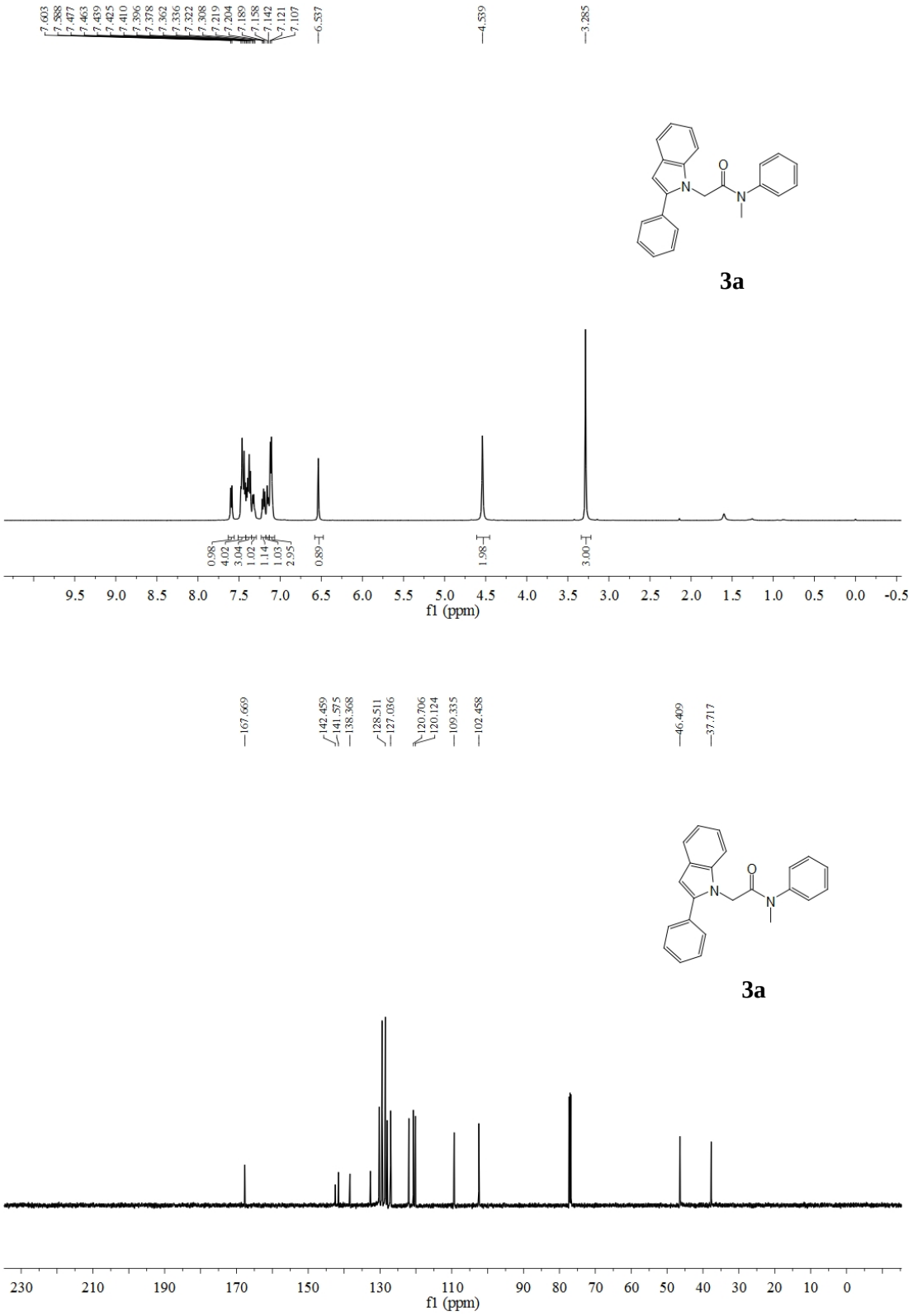


Figure 18. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **2r**.



3a

3a

Figure 19. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **3a**.

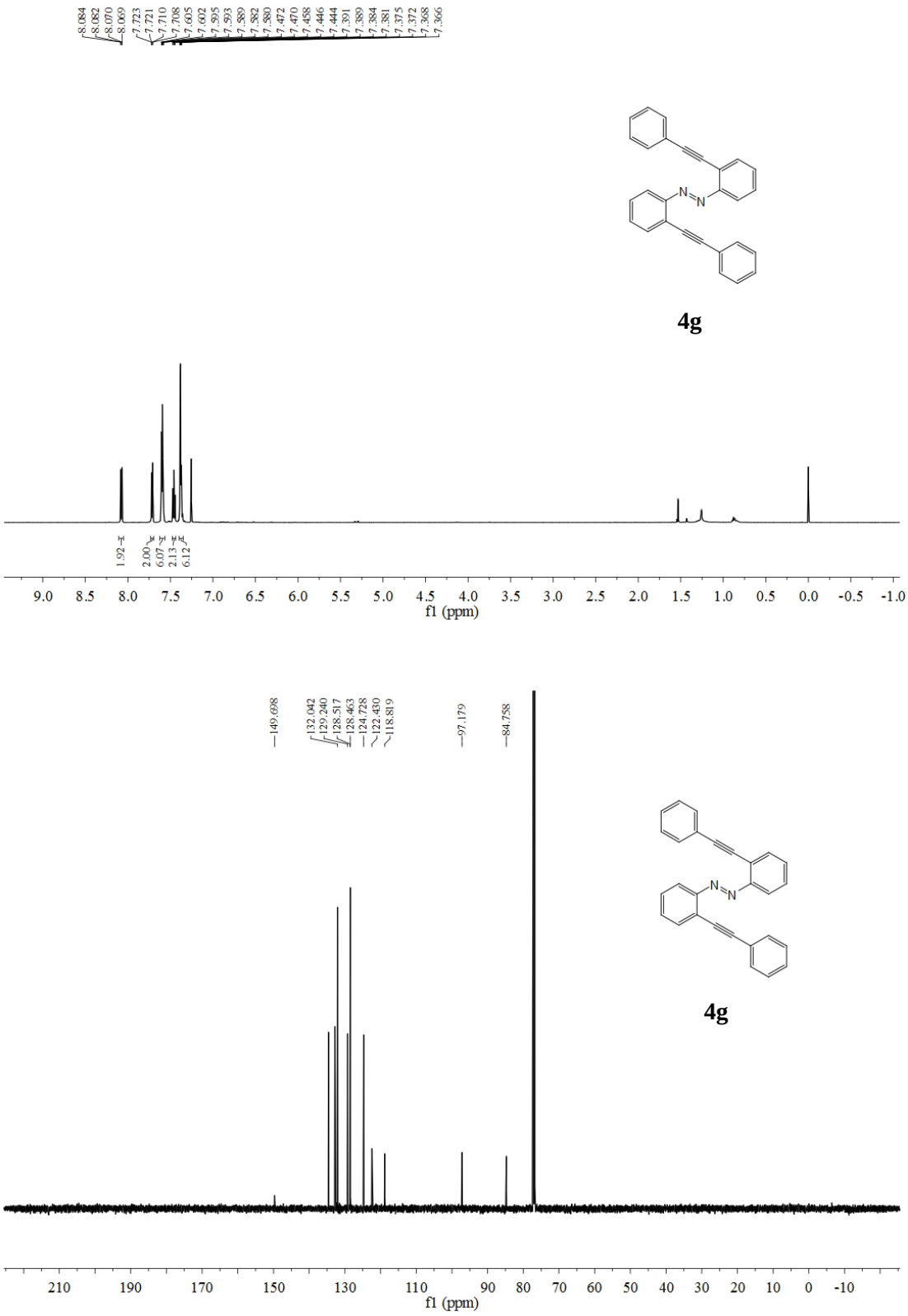


Figure 20. ^{1}H- (upper) and ^{13}C-NMR (lower) spectra of compound **4g**.