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SUPPORTING INFORMATION

Copper-Catalyzed Tandem Reaction of 2-Alkynylanilines with benzoquinones: An efficient access to 3-indolylquinones

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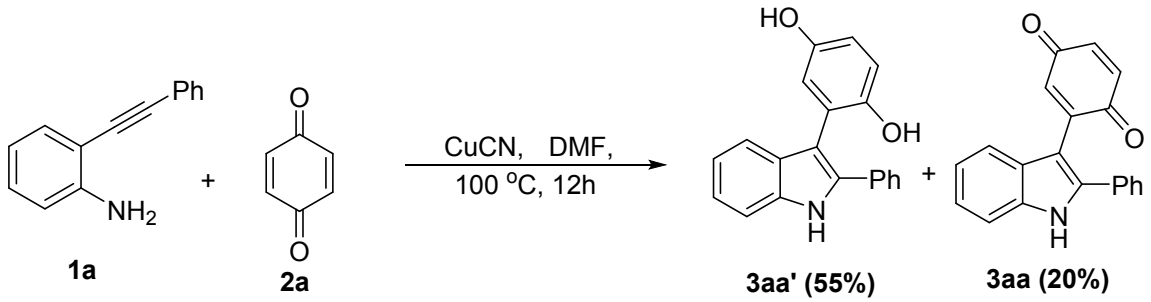
1. General information

Reactions were monitored by using thin-layer chromatography was performed with 0.2 mm coated commercial silica gel (E. Merck, DC-Plastkfolien, Kieselgel 60 F_{254}), and the detection was carried out by either an UV lamp, potassium permanganate solution, or p-anisaldehyde solution. Flash column chromatography was followed the method of Still employing E. Merck silica gel (Kieselgel 60, 70-230 mesh ASTM). Infrared spectra (IR) were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Proton nuclear magnetic resonance spectra (1H NMR) were measured at 400 MHz on a Varian Mucury-400 or Bruker AscendTM 400 and measured as chloroform-d (contains 0.03 % v/v tetramethylsilane or not contains). Chemical shifts were reported in units, parts per million (ppm) downfield from tetramethylsilane, and determined relative to the singlet at 7.26 ppm for chloroform-d. NMR data reported in the following form; chemical shift (multiplicity, coupling constant(s) in Hz, number of hydrogens). Resornances are noted in δ unit downfield from internal Me3SiH as being a singlet (s), a doublet (d), a triplet (t), a quart (q), a quintet (qui), a multiplet (m), or a board singlet (bs). Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were fully decoupled, and chemical shifts were reported in part per million (ppm) downfield from tetramethylsilane and determined relative to the carbon signals of the solvent (chloroform-d, 77.0 ppm), and measured at 100 MHz on a Varian Mucury-400 or Bruker AscendTM 400. High-resolution mass spectra (HRMS) were performed using ESI-Q-TOF mass spectrometer (Bruker Daltonics Inc., Germany) at Organic Chemistry Research Center of Sogang University, Seoul, Korea.

2. Experimental procedures

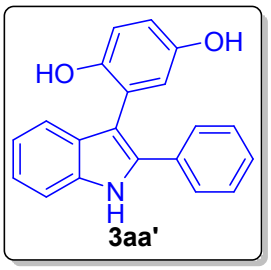
General procedure for the synthesis of 3-indolyl hydroquinones:



A 15 mL tube equipped with a stirring bar was charged with CuCN (0.2 equiv), *o*-alkynyl anilines **1a** (0.2 mmol) and *p*-benzoquinone **2a** (1 equiv), then DMF (2.0 mL) were added via a syringe and the resulting mixture was heated for 12 h at 100 °C with stirring. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1) to afford the targeted product **3aa'**.

Product Characterization 3aa'

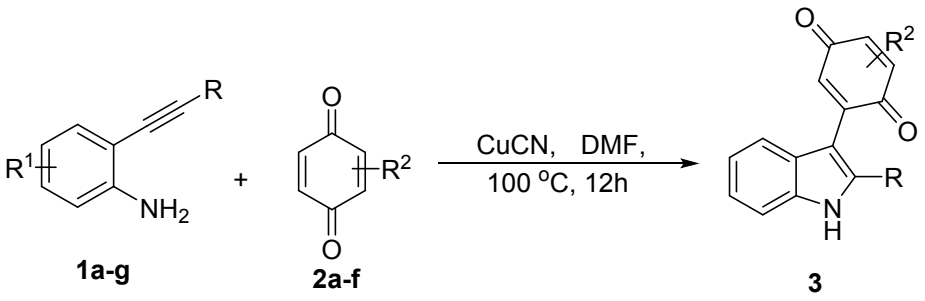
***2-(2-phenyl-1H-indol-3-yl)benzene-1,4-diol* (3aa'):**



Yield 55% (33.1 mg), white solid, m.p. 168-170 °C; R_f = 0.10 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (bs, 1H), 7.48-7.44 (m, 4H), 7.35-7.28 (m, 3H), 7.19-7.15 (m, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.81 (dd, J = 2.8, 5.6 Hz, 1H), 6.75 (d,

J = 2.8 Hz, 1H), 6.71 (s, 1H), 4.88 (bs, 1H), 4.53 (bs, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 149.08, 147.9, 136.1, 135.2, 131.6, 129.0, 128.8, 128.3, 127.0, 123.4, 121.3, 120.9, 119.7, 117.9, 116.2, 116.1, 116.0, 111.1, 107.1 ppm; IR (KBr, cm^{-1}): 3482, 3312, 3052, 1456, 1246, 1120, 814, 767; HRMS (ESI) $[M + Na]^+$ calculated for $C_{20}H_{15}NNaO_2^+$: 324.1000, found 324.0994

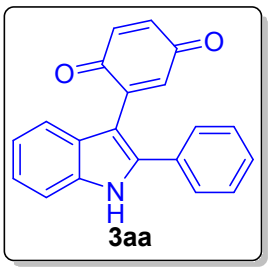
General procedure for the synthesis of 3-indolyl quinones:



A 15 mL tube equipped with a stirring bar was charged with CuCN (0.2 equiv), *o*-alkynyl anilines **1a-g** (0.2 mmol) and *p*-benzoquinone **2a-f** (2 equiv), then DMF (2.0 mL) were added via a syringe and the resulting mixture was heated for 12 h at 100 °C with stirring. After the reaction was complete (as determined by TLC analysis), the reaction was cooled to room temperature and EtOAc (20 mL) was added to the solution and washed with brine, dried over Na_2SO_4, concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4:1) to afford the targeted product **3aa-3ia or 3ab-3ag**.

Product Characterization of 3aa-3ia or 3ab-3ag

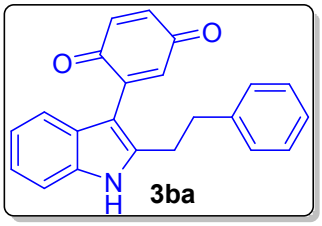
2-(2-phenyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3aa):



3aa

Yield 80% (48.92 mg), blue solid, m.p. 218-220 °C; R_f = 0.12 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.02 (bs, 1H), 7.54-7.50 (m, 3H), 7.47(d, *J* = 6.5 Hz, 1H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 8 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 2.5 hz, 1H), 6.89 (s, 1H), 6.87 (d, *J* = 8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 187.7, 186.6, 143.0, 139.5, 137.5, 137.1, 136.8, 133.5, 132.8, 129.2, 128.6, 128.5, 128.1, 122.9, 120.9, 119.4, 112.2, 105.7 ppm; IR (KBr, cm^{-1}): 3352, 3102, 1690, 1602, 1469, 1365, 1276, 1030, 914, 747; HRMS (ESI) $[M + Na]^+$ calculated for $C_{20}H_{13}NNaO_2^+$: 322.0844, found 322.0848

2-(2-phenethyl-1*H*-indol-3-yl) cyclohexa-2,5-diene-1,4-dione (3ba):

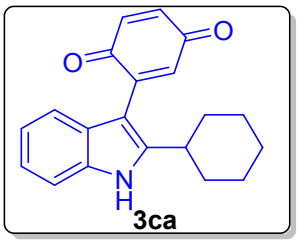


3ba

Yield 72% (47.14 mg), Purple solid, m.p. 192-194 °C; R_f = 0.12 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (bs, 1H), 7.48 (d, *J* = 8 Hz, 1H), 7.31-7.27 (m, 3H), 7.23-7.16 (m, 3H), 7.10 (d, *J* = 6.8 Hz, 2H), 6.85 (s, 1H), 6.82 (dd, *J* = 2.8, 7.6 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 3.07 (t, 6.2 Hz, 2H), 3.00 (t, *J* = 6.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.7, 186.7, 141.8, 140.5, 139.8, 136.9, 136.3, 135.4, 132.6, 128.7, 128.5, 127.2, 126.6, 122.4, 120.9, 119.0, 110.8, 106.7, 35.8, 29.6 ppm; IR (KBr, cm^{-1}): 3258,

3045, 2959, 2925, 1662, 1643, 1440, 1254, 1066, 740; HRMS (ESI) $[M + Na]^+$ calculated for $C_{22}H_{17}NNaO_2^+$: 350.1157, found 350.1151

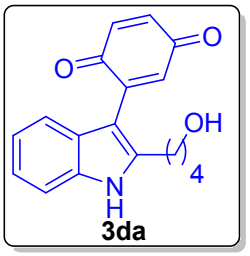
2-(2-cyclohexyl-1*H*-indol-3-yl) cyclohexa-2,5-diene-1,4-dione (3ca):



3ca

Yield 81% (49.5 mg), Purple solid, m.p. 216-218 °C; R_f = 0.21 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (bs, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.35 (d, J = 7.6 Hz, 1H), 7.22-7.13 (m, 2H), 6.94-6.91 (m, 1H), 6.88-6.85 (m, 2H), 2.75-2.74 (m, 1H), 2.08-2.04 (m, 2H), 1.89-1.78 (m, 3H), 1.55-1.44 (m, 2H), 1.41-1.26 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.9, 186.8, 145.6, 142.6, 137.1, 136.4, 135.2, 132.8, 127.3, 122.3, 120.8, 119.1, 110.8, 105.1, 77.3, 77.2, 77.0, 76.7, 36.7, 33.4, 26.4, 25.9 ppm; IR (KBr, cm^{-1}): 3294, 3096, 2912, 2843, 1634, 1596, 1456, 1239, 763; HRMS (ESI) $[M + Na]^+$ calculated for $C_{20}H_{19}NNaO_2^+$: 328.1313, found 328.1307

2-(2-(hydroxymethyl)-1*H*-indol-3-yl) cyclohexa-2,5-diene-1,4-dione (3da):

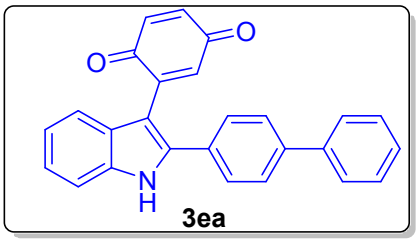


3da

Yield 52% (30.7 mg), Purple liquid, R_f = 0.12 (hexanes/EtOAc = 4:6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (bs, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.6 Hz, 1H), 7.21-7.15 (m, 2H), 6.91-6.83 (m, 3H), 3.71 (t, J = 6 Hz, 2H), 2.78 (t, 7.6 Hz, 2H), 1.86-1.80 (m, 2H), 1.63 (t, J = 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.9, 186.9, 142.5, 141.0, 137.0, 136.5, 135.5, 132.4, 127.4, 122.4, 120.9, 119.1, 110.9, 106.3, 62.2, 31.5, 27.0, 26.9 ppm;

IR (Neat, cm^{-1}): 3512, 3472, 3060, 2962, 2836, 1624, 1596, 1046; HRMS (ESI) $[M + Na]^+$ calculated for $C_{15}H_{11}NNaO_3^+$: 276.0636, found 276.0631

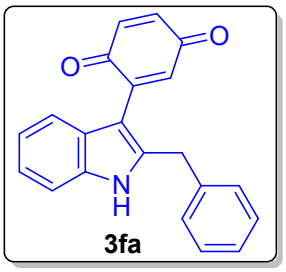
2-(2-([1,1'-biphenyl]-4-yl)-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ea):



3ea

Yield 85% (63.8 mg), Purple solid, m.p. 188-190 °C; R_f = 0.13 (hexanes/EtOAc = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.53 (bs, 1H), 7.62-7.57 (m, 3H), 7.52-7.43(m, 6H), 7.39 (t, J = 7.2 Hz, 1H), 7.29-7.21 (m, 3H), 7.07 (d, J = 2.4 Hz, 1H), 6.87 (dd, J = 2.4, 7.6 Hz, 1H), 6.80 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.6, 186.1, 142.9, 141.1, 140.0, 138.9, 137.0, 136.7, 136.3, 133.5, 131.2, 128.9, 128.3, 128.1, 127.7, 127.6, 127.0, 123.4, 121.5, 119.2, 111.5, 106.4 ppm; IR (KBr, cm^{-1}): 3412, 3104, 3012, 1596, 1666, 1412, 1005, 916; HRMS (ESI) $[M + Na]^+$ calculated for $C_{26}H_{17}NNaO_2^+$: 398.1157, found 398.1151

2-(2-benzyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3fa):

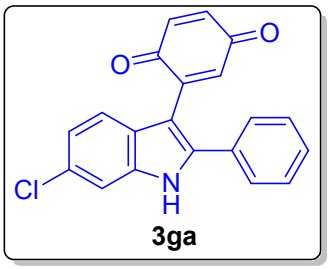


3fa

Yield 90% (56.4 mg), block solid, m.p. 182-184 °C; R_f = 0.12 (hexanes/EtOAc = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.10 (bs, 1H), 7.53-7.51 (m, 1H), 7.35-7.32 (m, 2H), 7.29-7.27 (m, 1H), 7.26-7.22 (m, 3H), 7.18-7.15 (m, 2H), 6.92 (d, J = 2.5 Hz, 1H), 6.87 (s, 1H), 6.82 (d, J = 2.5 Hz, 1H), 4.12 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.8, 186.8, 142.1, 139.0, 137.5, 137.0, 136.5, 135.6, 132.7, 129.1, 129.0, 127.4, 127.2, 122.6, 121.0,

119.2, 110.9, 107.0, 34.0 ppm; IR (KBr, cm^{-1}): 3312, 3054, 1676, 1606, 1046, 746, 576; HRMS (ESI) $[M + Na]^+$ calculated for $C_{21}H_{15}NNaO_2^+$: 336.1000, found 336.1094

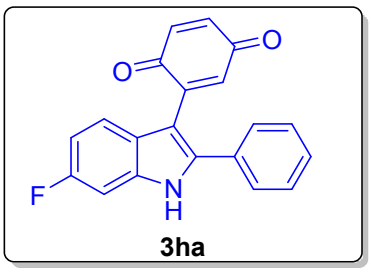
2-(6-chloro-2-phenyl-1*H*-indol-3-yl) cyclohexa-2, 5-diene-1,4-dione (3ga):



3ga

Yield 59% (39.3 mg), purple solid, m.p. 261-263 °C; R_f = 0.10 (hexanes/EtOAc = 8:2); ^{1}H NMR (400 MHz, Acetone-d_6): δ 11.19 (bs, 1H), 7.62-7.54 (m, 4H), 7.47-7.43 (m, 2H), 7.40-7.38 (m, 1H), 7.17 (dd, J = 1.9, 6.6 Hz, 1H), 6.90 (d, J = 2.8 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.82 (s, 1H) ppm; ^{13}C NMR (100 MHz, Acetone-d_6): 187.1, 185.7, 142.5, 139.9, 137.0, 136.5, 134.0, 132.4, 131.1, 128.8, 128.3, 128.2, 127.7, 127.0, 120.9, 120.5, 111.3, 106.0 ppm; IR (KBr, cm^{-1}): 3248, 3050, 2912, 1616, 1598, 1434, 1246, 786; HRMS (ESI) $[M + Na]^+$ calculated for $C_{20}H_{12}ClNNaO_2^+$: 356.0454, found 356.0448

2-(6-fluoro-2-phenyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ha):

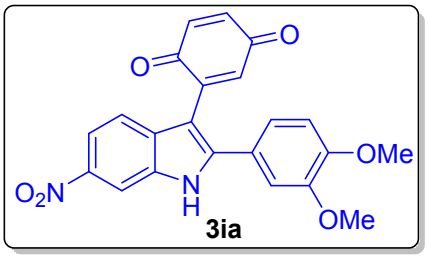


3ha

Yield 63% (40.0 mg), Purple solid, m.p. 218-220 °C; R_f = 0.10 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (bs, 1H), 7.45-7.40 (m, 5H), 7.38-7.34 (m, 1H), 7.24 (dd, J = 2.2 Hz, 1H), 7.05 (td, J = 2.4, 6.5 Hz, 1H), 6.93 (d, J = 2.3 Hz, 1H), 6.82 (d, J = 2.4 Hz, 1H), 6.80 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.5, 185.9, 142.4, 140.8, 136.9, 136.6, 133.5, 132.5, 132.1, 129.1, 128.9, 128.6, 128.5, 128.0, 112.2, 111.8, 104.8,

104.5 ppm; IR (KBr, cm^{-1}): 3312, 3022, 1656, 1602, 1426, 1043, 786, 852; HRMS (ESI) [M + Na]$^+$ calculated for $C_{20}H_{12}FNNaO_2^+$: 340.0749, found 340.0743

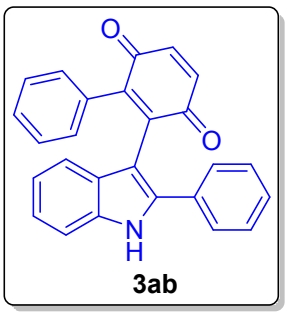
2-(2-(3,4-dimethoxyphenyl)-6-nitro-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3ia):



3ia

Yield 82% (66.3 mg), red solid, m.p. 228-230 °C; R_f = 0.15 (hexanes/EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.28 (bs, 1H), 8.41 (s, 1H), 8.11 (dd, *J* = 2, 7.6 Hz, 1H), 7.41 (d, *J* = 9.2 Hz, 2H), 6.99-6.93 (m, 3H), 6.86 (d, *J* = 6 Hz, 1H), 6.84 (d, *J* = 2.4 Hz, 2H), 3.87(s, 3H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.11, 185.8, 150.0, 149.4, 142.7, 141.9, 141.8, 138.9, 137.0, 136.7, 134.6, 127.6, 123.6, 121.1, 118.5, 116.2, 111.6, 111.4, 110.9, 117.2, 56.0, 55.9 ppm; IR (KBr, cm^{-1}): 3254, 3026, 2936, 2842, 1656, 1598, 1426, 1043, 786; HRMS (ESI) [M + Na]$^+$ calculated for $C_{22}H_{16}N_2NaO_6^+$: 427.0906, found 427.0900.

6-(2-phenyl-1*H*-indol-3-yl)-[1,1'-biphenyl]-2,5-dione (3ab):

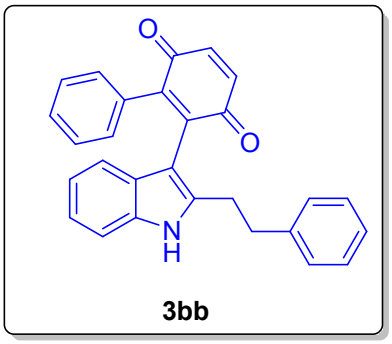


3ab

Yield 78% (58.5 mg), Purple solid, m.p. 210-212 °C; R_f = 0.12 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, CDCl3): δ 8.92 (bs, 1H), 7.49-7.45 (m, 3H), 7.41-7.33 (m, 5H), 7.31-7.24 (m, 4H), 7.14-7.11 (m, 3H), 6.95 (d, *J* = 2.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.5, 186.4, 147.1, 144.1, 139.7, 136.2, 132.8, 132.3, 132.1, 129.9, 129.4, 129.0, 128.5, 128.4, 128.1, 127.8, 123.3, 121.5, 119.3, 111.7, 107.2 ppm; IR (KBr, cm^{-1}): 3303,

3052, 1685, 1593, 1444, 1276, 1030, 914, 676, 643; HRMS (ESI) $[M + Na]^+$ calculated for $C_{26}H_{17}NNaO_2^+$: 398.1157, found 398.1151

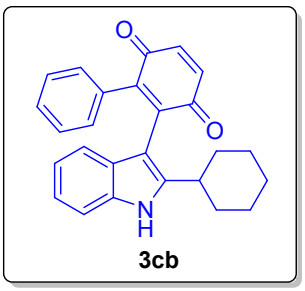
6-(2-phenethyl-1*H*-indol-3-yl)-[1,1'-biphenyl]-2,5-dione (3bb):



3bb

Yield 83% (67.0 mg), Purple solid, m.p. 220-222 °C; R_f = 0.13 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (bs, 1H), 7.56-7.48 (m, 6H), 7.29-7.18 (m, 6H), 7.17-7.07 (m, 2H), 6.90 (d, J = 2.4 Hz, 1H), 6.94 (d, J = 2.8 Hz, 1H), 3.06 (t, J = 6.4 Hz, 2H), 3.02 (t, J = 6.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.8, 186.3, 146.5, 142.3, 139.9, 135.5, 133.6, 132.6, 132.6, 132.2, 129.9, 129.4, 129.3, 128.7, 128.6, 128.5, 127.3, 126.6, 122.4, 120.9, 119.1, 110.9, 107.3, 30.9, 29.7 ppm; IR (KBr, cm^{-1}): 3265, 3046, 2938, 2863, 1609, 1596, 1463, 1206, 786; HRMS (ESI) $[M + Na]^+$ calculated for $C_{28}H_{21}NNaO_2^+$: 426.1470, found 426.1464

6-(2-cyclohexyl-1*H*-indol-3-yl)-[1,1'-biphenyl]-2,5-dione (3cb):

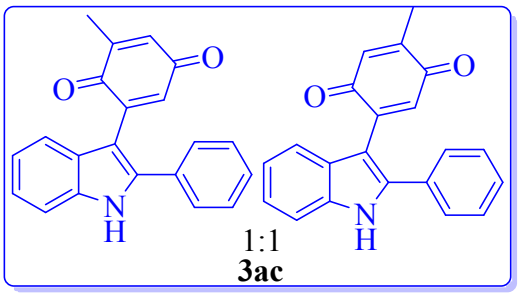


3cb

Yield 82% (62.5 mg), Purple solid, m.p. 165-167 °C; R_f = 0.18 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (bs, 1H), 7.56-7.54 (m, 2H), 7.51-7.47 (m, 4H), 7.32 (d, J = 8.4 Hz, 1H), 7.18-7.15 (m, 2H), 6.97 (d, J = 2.4 Hz, 1H), 6.94 (d, J =

2.8 Hz, 1H), 2.81-2.77 (m, 1H), 2.07-1.77 (m, 3H), 1.51-1.29 (m, 5H) ppm; ^{13}C NMR (100 MHz, CDCl3): 188.0, 186.5, 146.7, 147.6, 143.4, 135.3, 133.6, 132.7, 132.4, 129.9, 129.4, 129.3, 128.6, 127.4, 122.3, 120.9, 119.3, 110.9, 108.7, 37.0, 33.4, 26.5, 26.0 ppm; IR (KBr, cm^{-1}): 3310, 3046, 2956, 2834, 1616, 1587, 1432, 1246, 724; HRMS (ESI) $[M + Na]^+$ calculated for $C_{26}H_{23}NNaO_2^+$: 404.1626, found 404.1621

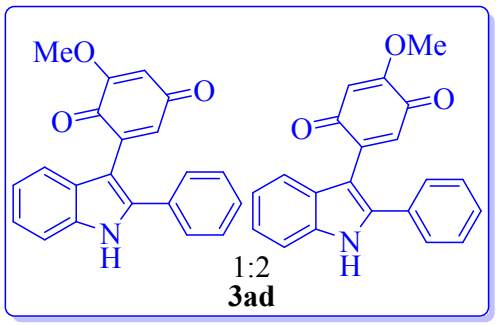
2-methoxy-5-(2-phenyl-1*H*-indol-3-yl) cyclohexa-2,5-diene-1,4-dione and 2-methoxy-6-(2-phenyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (1:1) (3ac):



1:1
3ac

Yield 80% (50.3 mg), Purple solid, m.p. 215-217 °C; R_f = 0.15 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): 8.70 (bs, 2H), 7.58-7.55 (m, 2H), 7.42-7.38 (m, 4H), 7.38-7.36 (m, 2H), 7.35-7.33 (m, 5H), 7.25-7.24 (m, 1H), 7.23-7.21 (m, 1H), 7.22-7.20 (m, 1H), 6.97 (s, 1H), 6.92 (d, J = 2.7 Hz, 1H), 6.65-6.64 (m, 1H), 6.59 (d, J = 1.6 Hz, 1H), 2.11 (d, J = 1.7 Hz, H), 1.98 (d, J = 1.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 188.0, 187.7, 186.7, 186.3, 146.4, 145.8, 143.1, 142.8, 139.2, 139.0, 136.2, 136.1, 133.8, 133.6, 133.4, 133.3, 132.5, 129.2, 129.0, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 123.2, 121.3, 119.4, 111.4, 106.8, 106.3, 16.4, 15.7 ppm; IR (KBr, cm^{-1}): 3246, 3031, 2984, 28245, 1656, 1599, 1426, 1043, 786; HRMS (ESI) $[M + Na]^+$ calculated for $C_{21}H_{15}NNaO_2^+$: 336.1000, found 336.0994

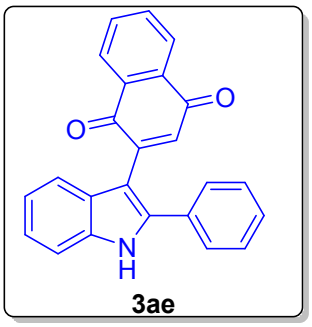
2-methoxy-5-(2-phenyl-1H-indol-3-yl)cyclohexa-2,5-diene-1,4-dione and 2-methoxy-6-(2-phenyl-1H-indol-3-yl)cyclohexa-2,5-diene-1,4-dione(3ad):



3ad

Yield 82% (53.8 mg), Purple solid, m.p. 224-226 °C; R_f = 0.12 (hexanes/EtOAc = 6:4); ^{1}H NMR (400 MHz, $CDCl_3$): 8.83(bs, 1H) 7.57 (d, J = 8 Hz, 1H), 7.40-7.37 (m, 3H), 7.36-7.32 (m, 6H), 7.24-7.20 (m, 2H), 6.92 (s, 1H), 5.91 (s, 1H), 3.81 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 187.6, 186.1, 182.1, 180.7, 158.8, 143.7, 140.9, 139.8, 138.9, 136.3, 136.1, 134.2, 132.5, 132.4, 131.2, 129.0, 128.9, 128.9, 128.5, 128.4, 128.1, 128.1, 128.0, 127.9, 127.0, 123.2, 123.1, 121.4, 121.2, 119.4, 119.3, 111.6, 111.5, 108.2, 107.3, 106.4, 105.6, 60.4, 56.2 ppm; IR (KBr, cm^{-1}): 3316, 3011, 2924, 2835, 1656, 1598, 1416, 1003, 766; HRMS (ESI) $[M + Na]^+$ calculated for $C_{21}H_{15}NNaO_3^+$: 352.0949, found 352.0943

2-(2-phenyl-1*H*-indol-3-yl) naphthalene-1,4-dione (3ae):

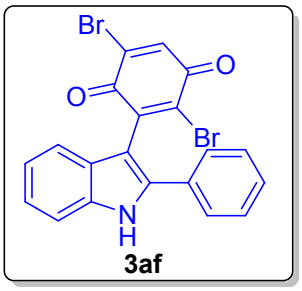


3ae

Yield 60% (11.3 mg), Purple solid, m.p. 215-217 °C; R_f = 0.12 (hexanes/EtOAc = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (bs, 1H), 8.15(dd, J = 1.4, 6.1 Hz, 1H), 8.00 (dd, J = 1.4, 6.1 Hz, 1H), 7.76-7.70 (m, 2H), 7.62 (d, J = 8 Hz, 1H), 7.48-7.43 (m, 4H), 7.36 (dd, J = 1.2, 7.2 Hz, 2H), 7.28 (dd, J =1.4, 6.8 Hz, 1H), 7.23 (d, J = 8 Hz, 1H), 7.19 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 185.1, 184.2, 144.9, 136.1, 136.09, 133.6, 133.5, 133.5, 132.3, 129.0, 128.5, 128.4, 128.2, 128.0, 127.0, 125.9, 123.3, 121.1, 119.7, 111.3, 107.0 ppm; IR

(KBr, cm^{-1}): 3224, 3071, 2958, 2923, 1666, 1623, 1594, 1460, 1439, 1380, 1266, 1108, 1017, 867; HRMS (ESI) $[M + Na]^+$ calculated for $C_{24}H_{15}NNaO_2^+$: 372.1000, found 372.0994

2,5-dibromo-3-(2-phenyl-1*H*-indol-3-yl)cyclohexa-2,5-diene-1,4-dione (3af):



3af

Yield 55% (50.2 mg), blue solid, m.p. 158-160 °C; R_f = 0.17 (hexanes/EtOAc = 4:1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (bs, 1H), 7.55 (s, 1H), 7.42-7.33 (m, 7H), 7.29-7.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 177.7, 175.8, 143.8, 138.8, 137.7, 137.4, 136.6, 135.9, 132.1, 129.2, 128.8, 127.3, 126.7, 123.1, 121.0, 120.3, 111.7, 106.9 ppm; IR (KBr, cm^{-1}): 3294, 3056, 1638, 1576, 1428, 1209, 1001, 765; HRMS (ESI) [M + Na] + calculated for $C_{20}H_{11}Br_2NNaO_2^+$: 477.9054, found 477.9048

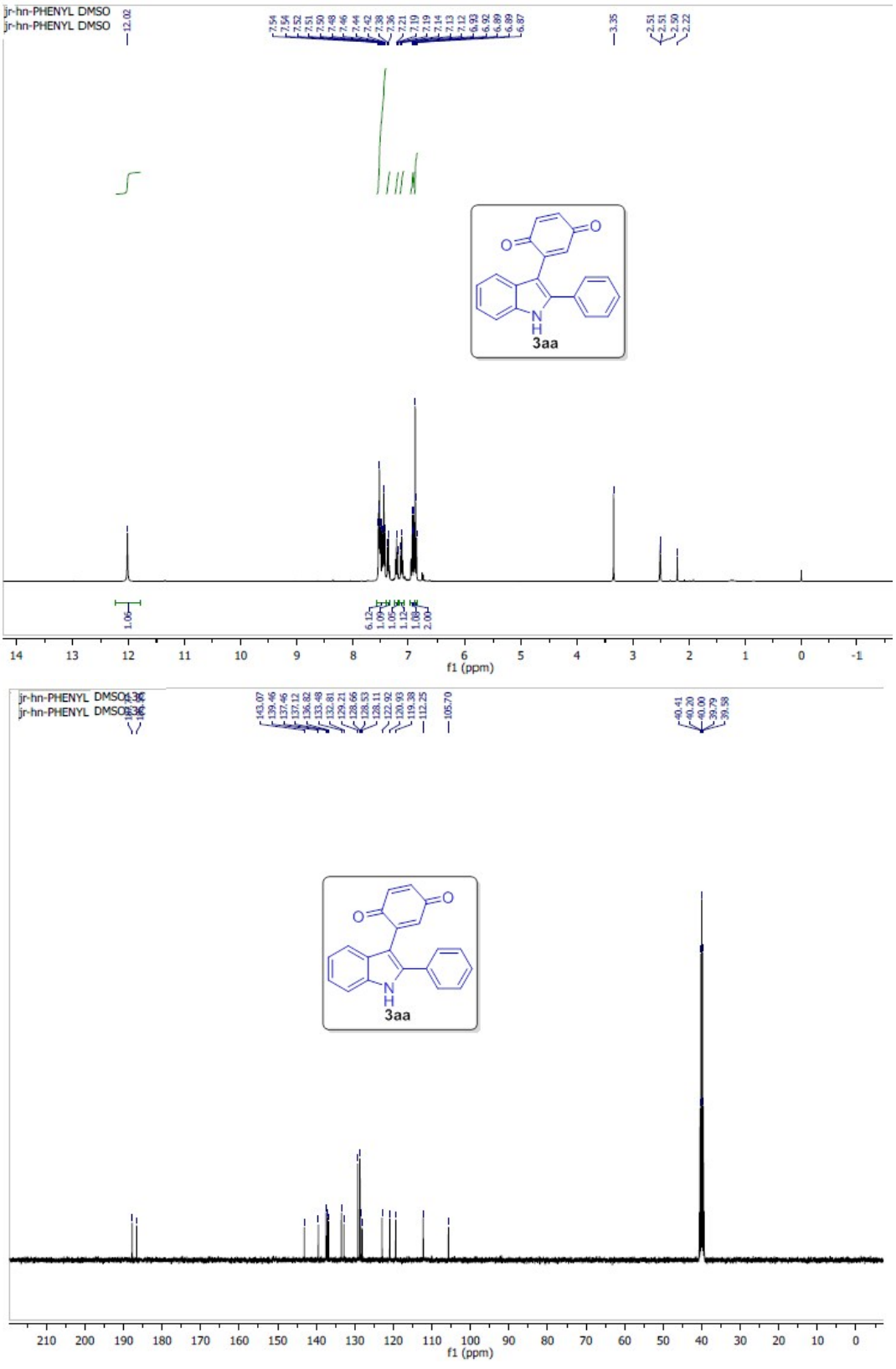


Figure S01. ^{1}H&^{13}C-NMR spectrum of compound **3aa** (DMSO-d_6, 400 MHz)

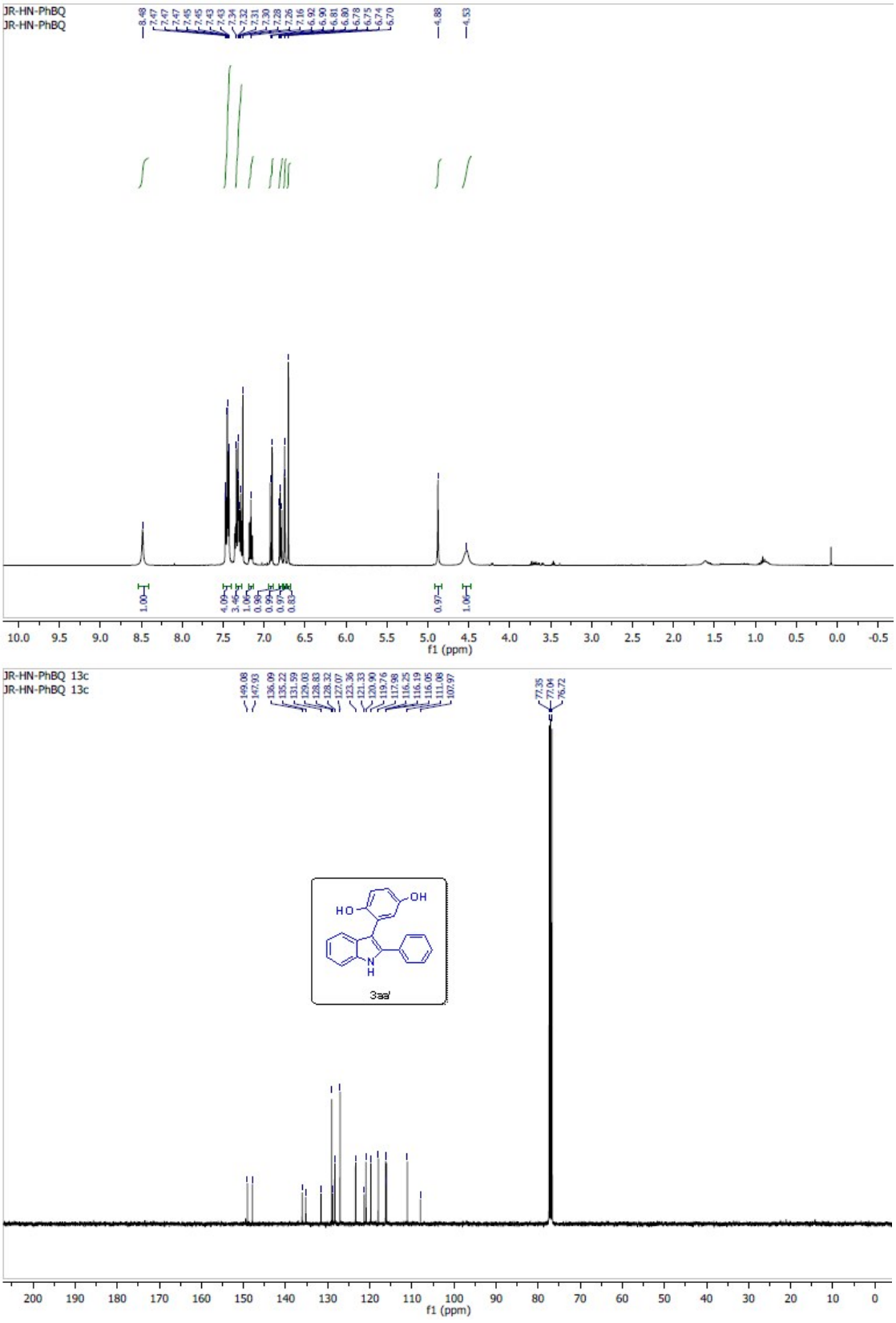


Figure S02. ^{1}H&^{13}C-NMR spectrum of compound **3aa'** ($CDCl_3$, 400 MHz)

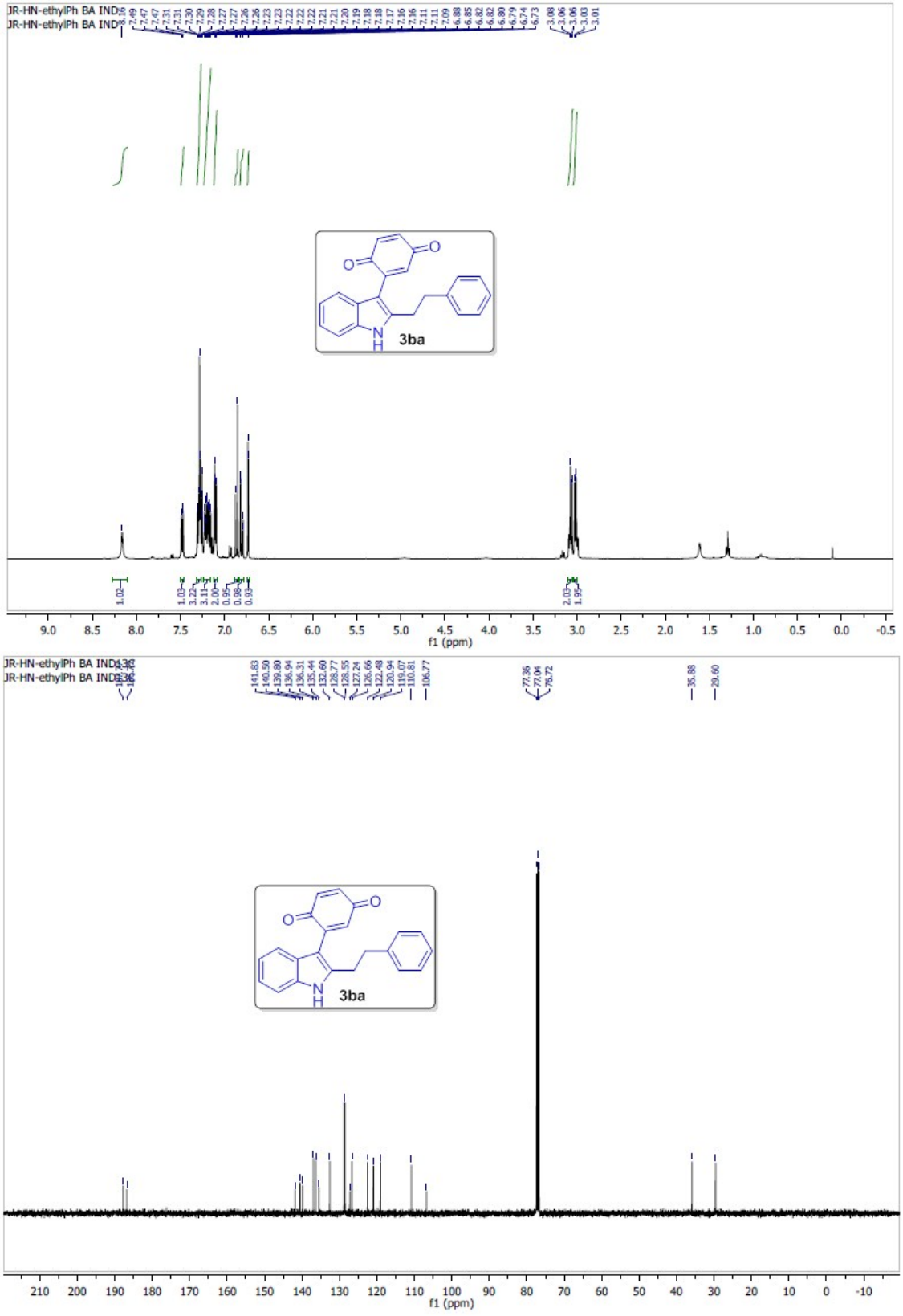


Figure S03. ^{1}H&^{13}C-NMR spectrum of compound **3ba** ($CDCl_3$, 400 MHz)

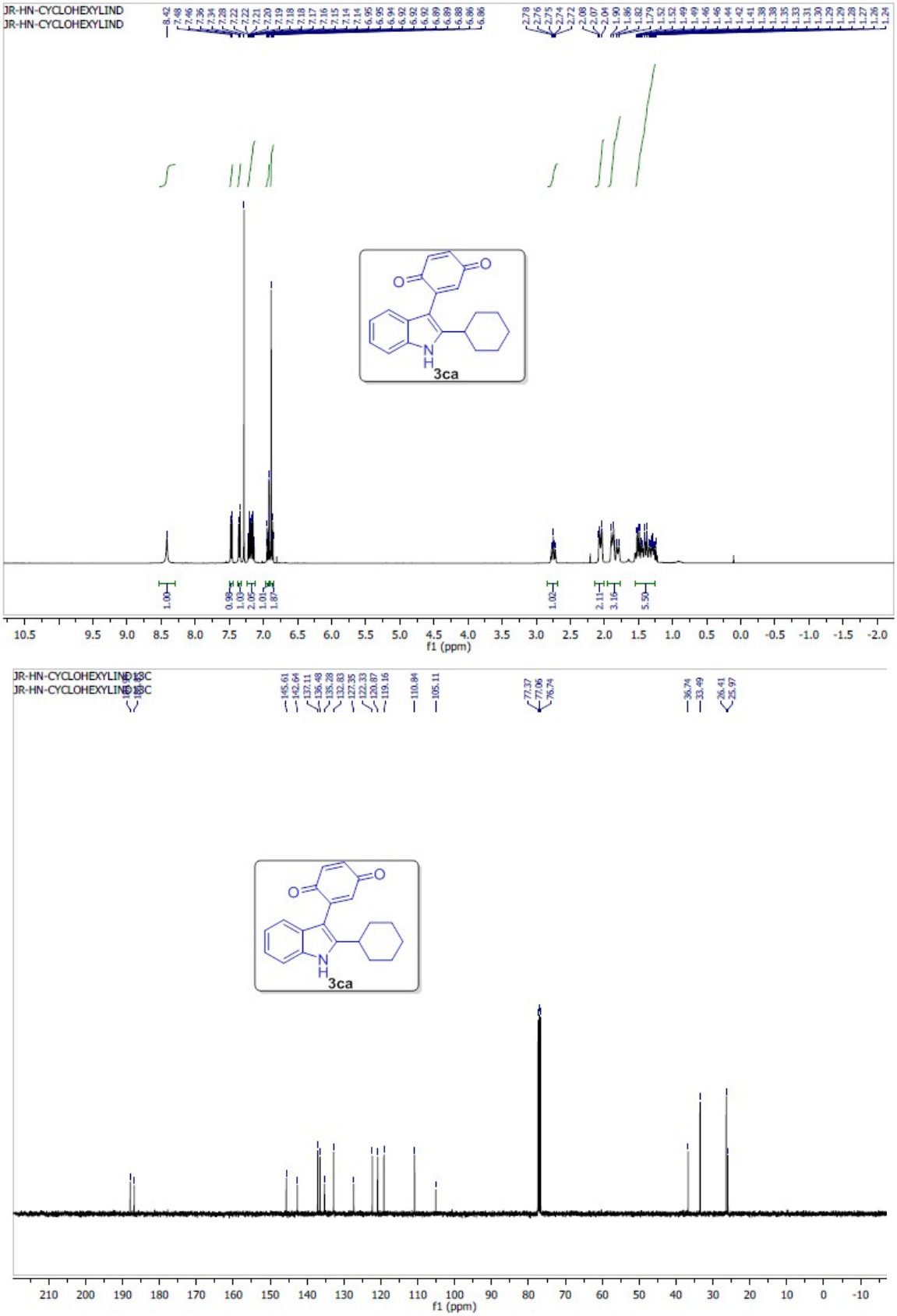


Figure S04. $^{1}H\&^{13}C$-NMR spectrum of compound **3ca** ($CDCl_3$, 400 MHz)

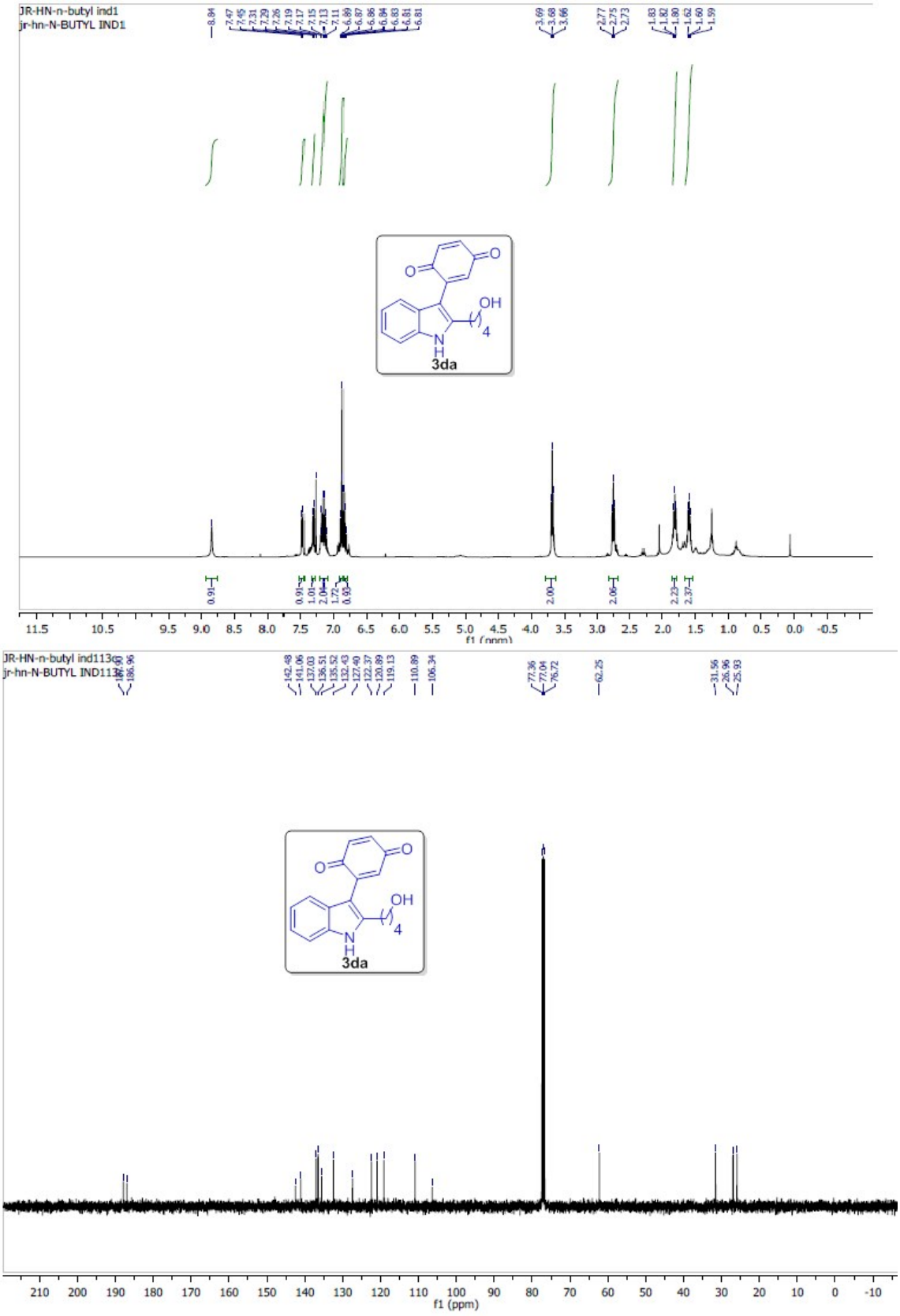


Figure S05. ^{1}H&^{13}C-NMR spectrum of compound **3da** ($CDCl_3$, 400 MHz)

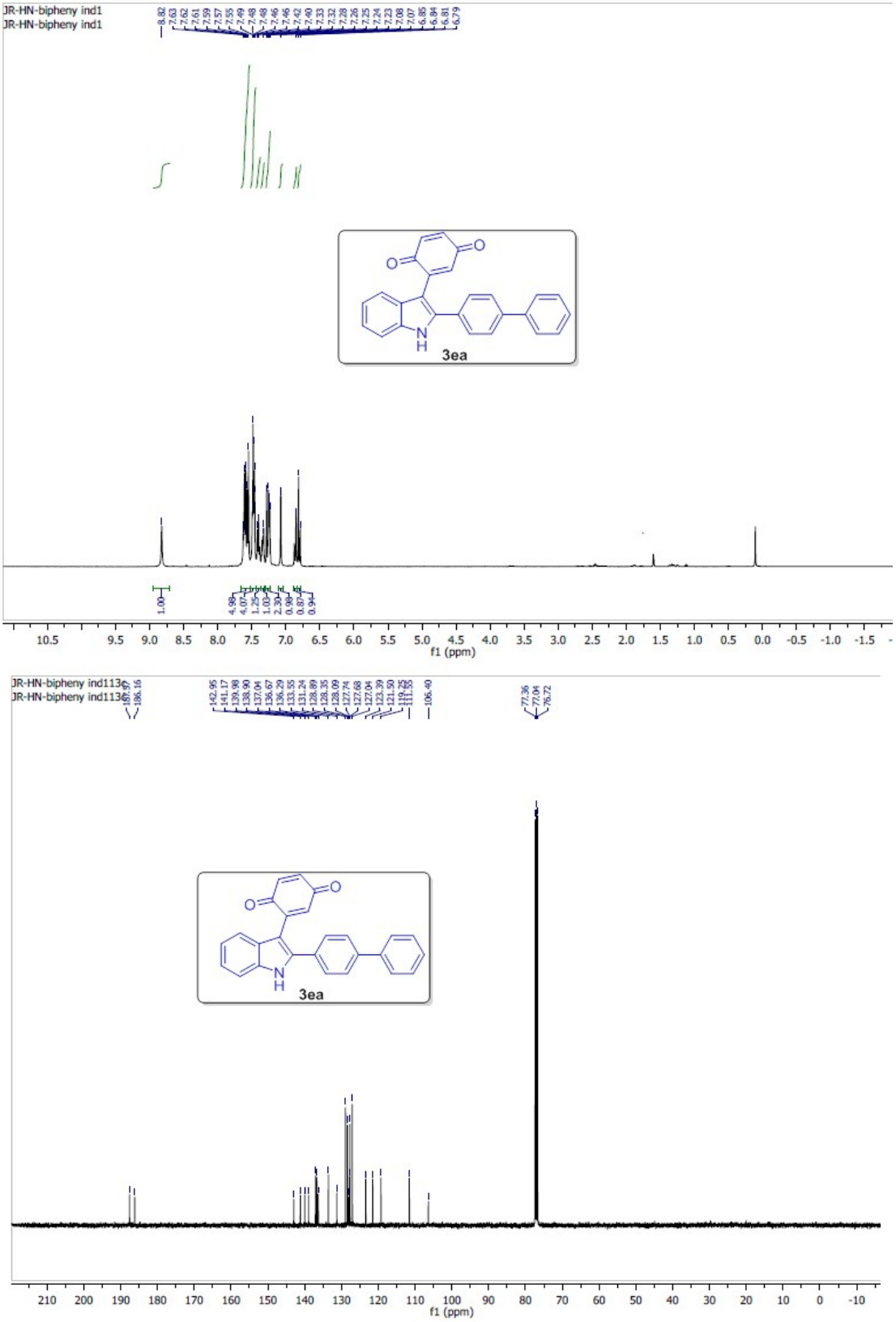


Figure S06. ^{1}H&^{13}C-NMR spectrum of compound **3ea** ($CDCl_3$, 400 MHz)

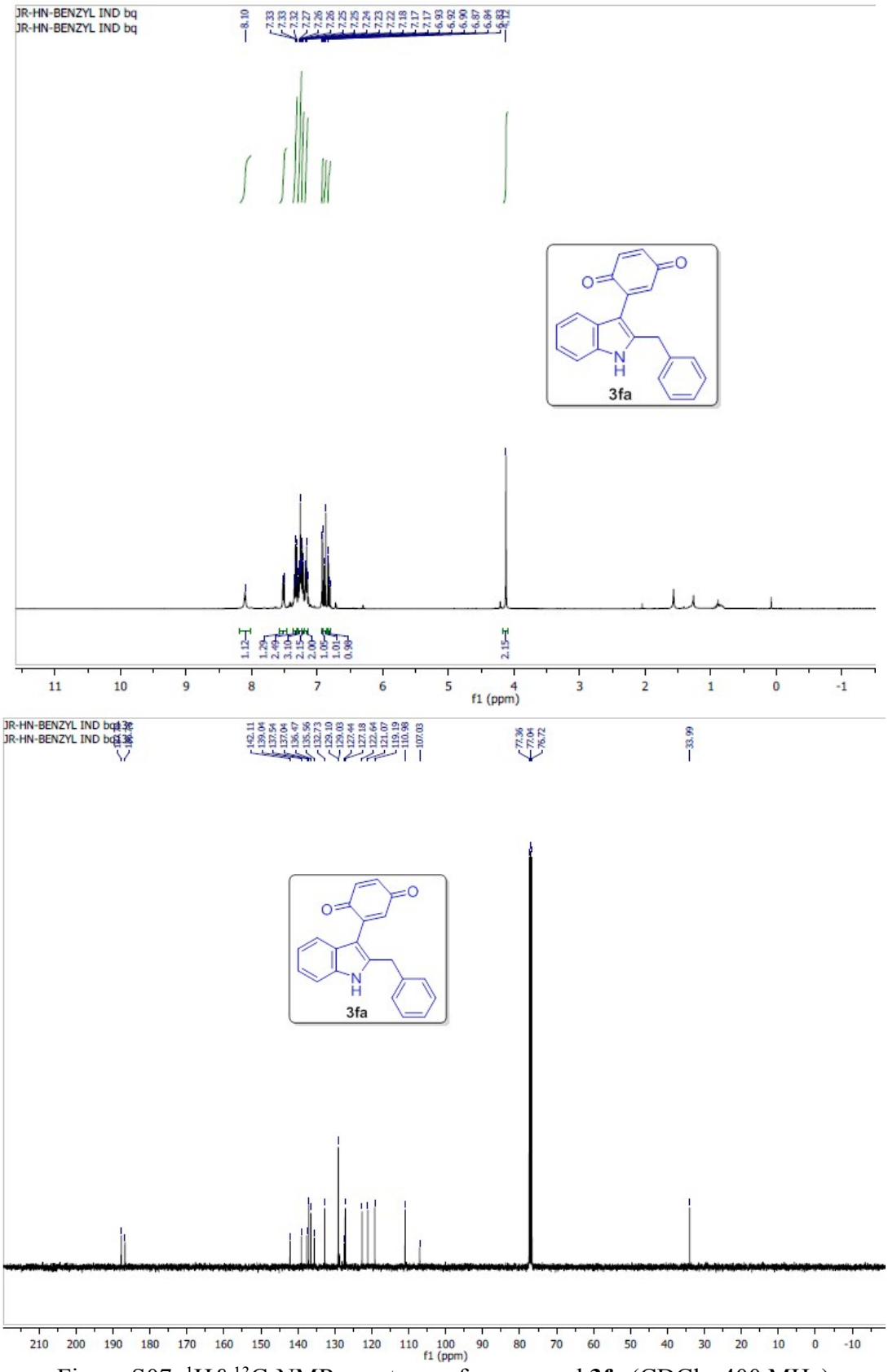


Figure S07. ^{1}H&^{13}C-NMR spectrum of compound **3fa** ($CDCl_3$, 400 MHz)

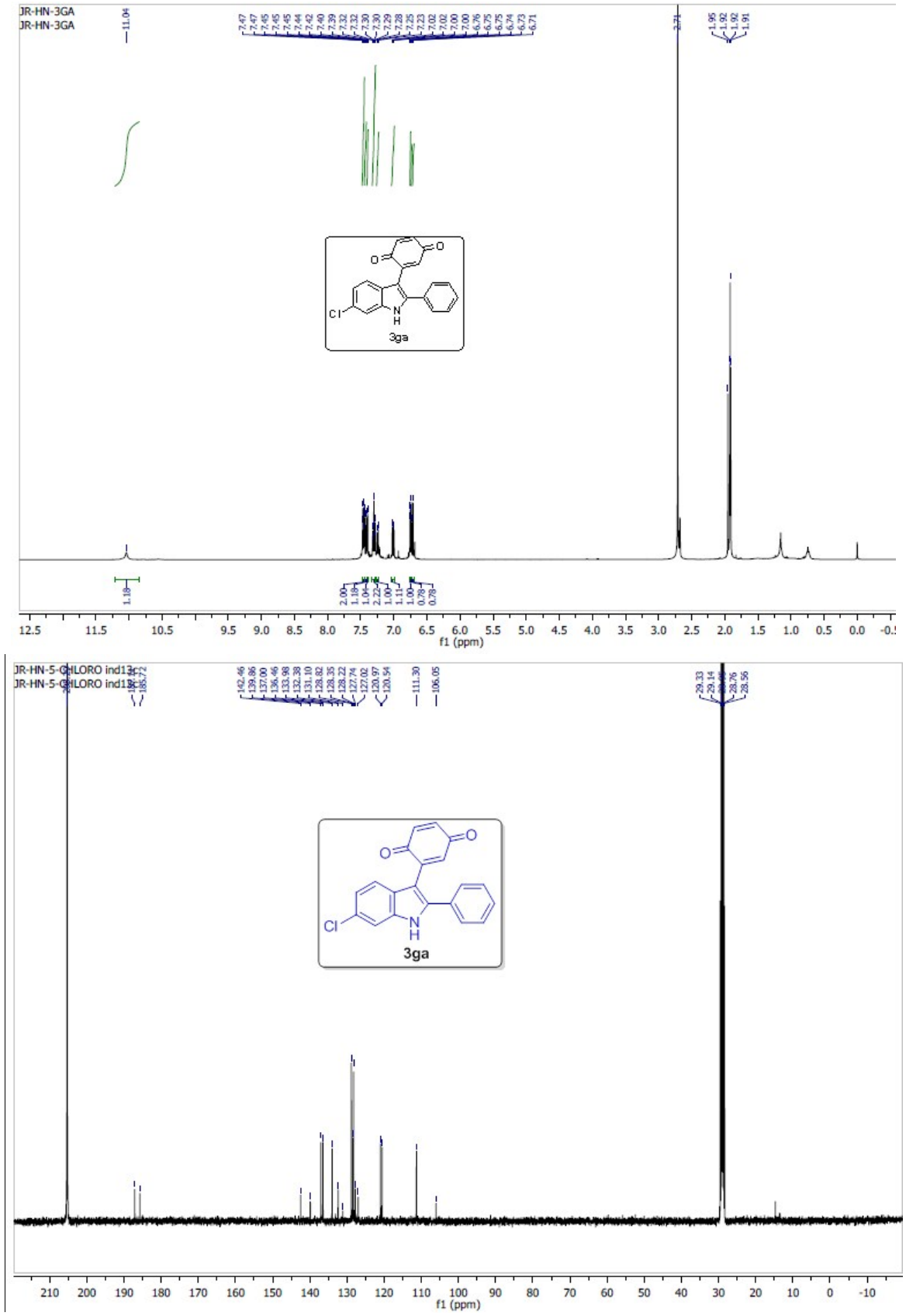


Figure S08. ^{1}H&^{13}C-NMR spectrum of compound **3ga** (Acetone-d_6, 400 MHz)

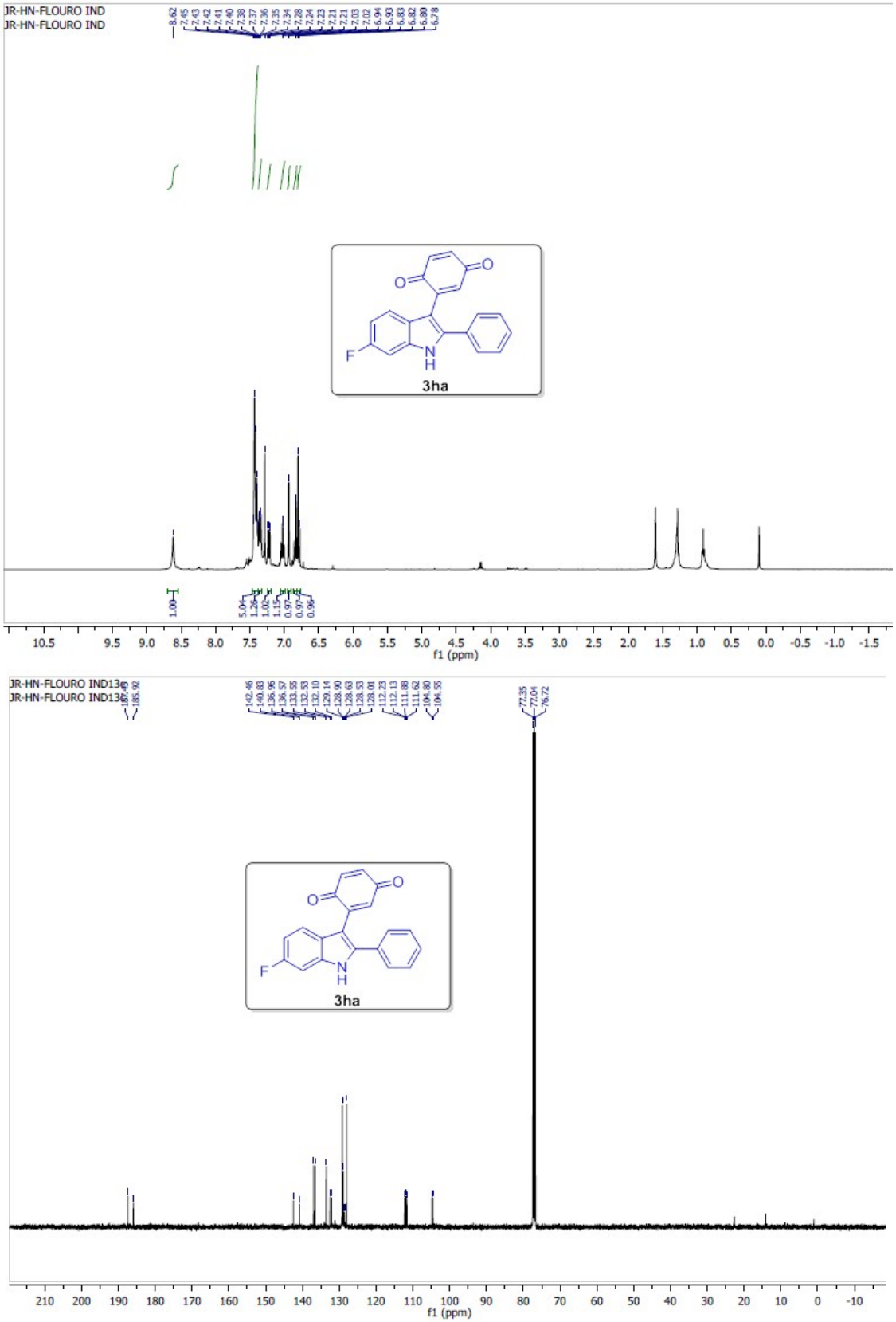


Figure S09. ^{1}H&^{13}C-NMR spectrum of compound **3ha** ($CDCl_3$, 400 MHz)

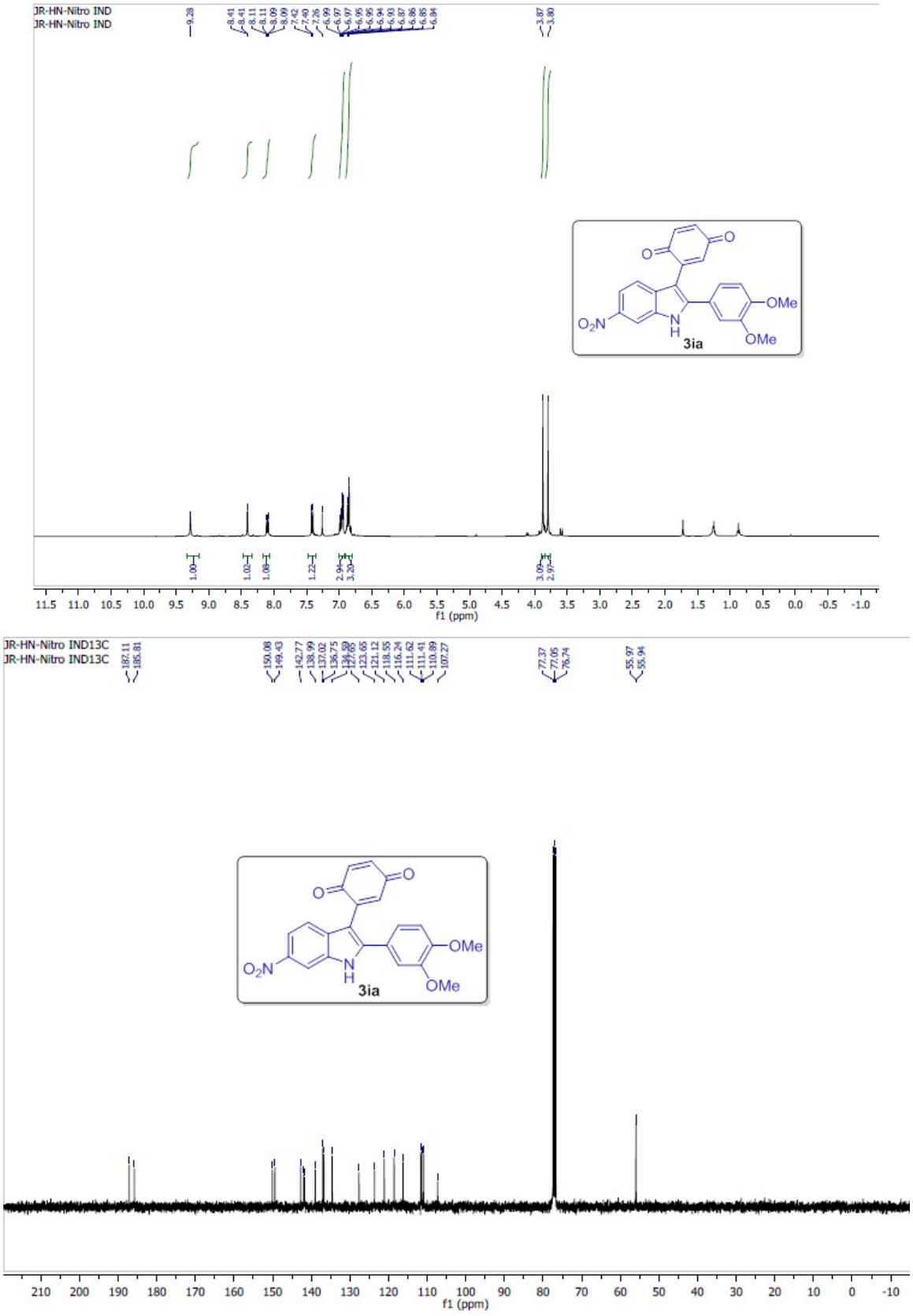


Figure S10. ^{1}H&^{13}C-NMR spectrum of compound **3ia** ($CDCl_3$, 400 MHz)

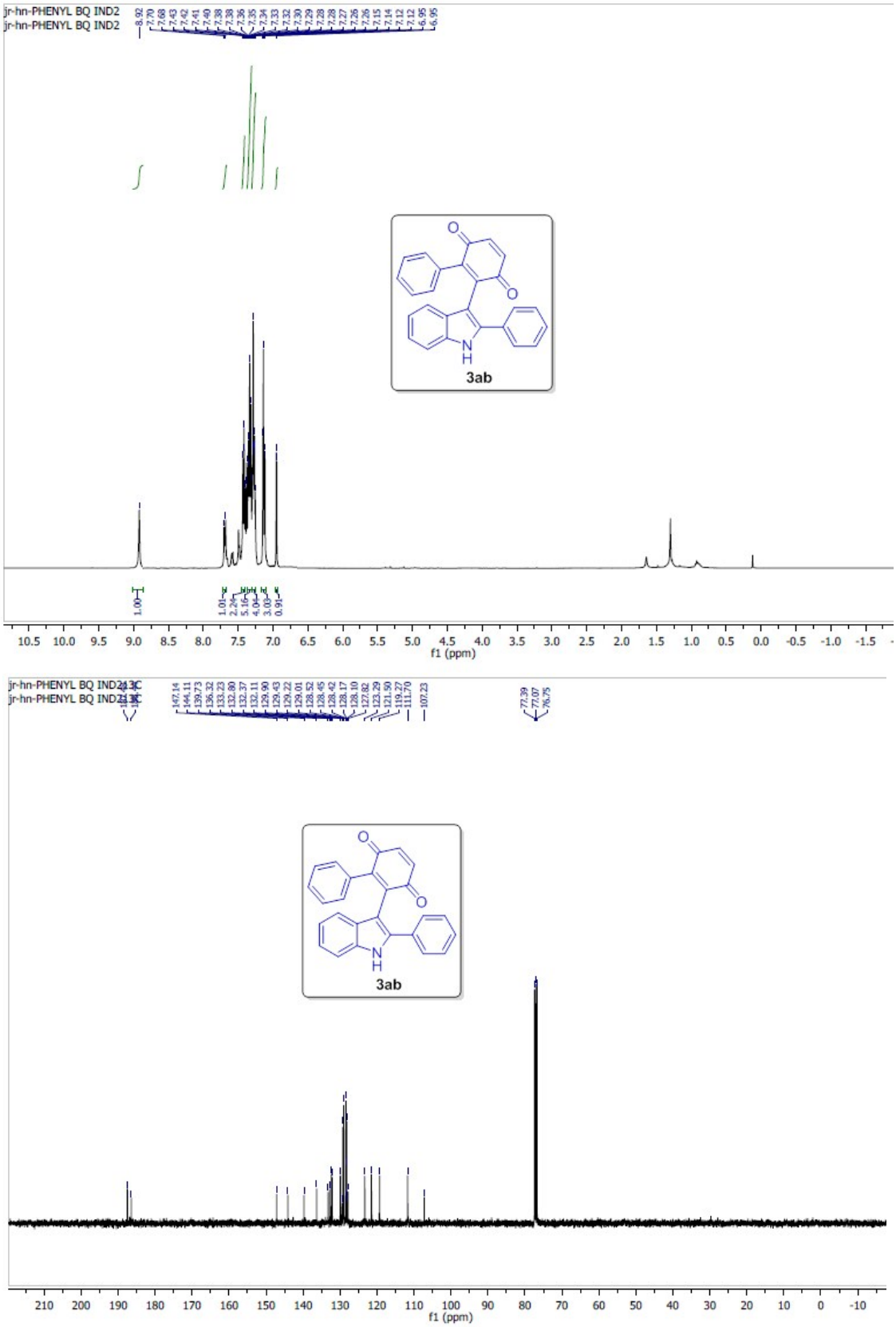


Figure S11. ^{1}H&^{13}C-NMR spectrum of compound **3ab** ($CDCl_3$, 400 MHz)

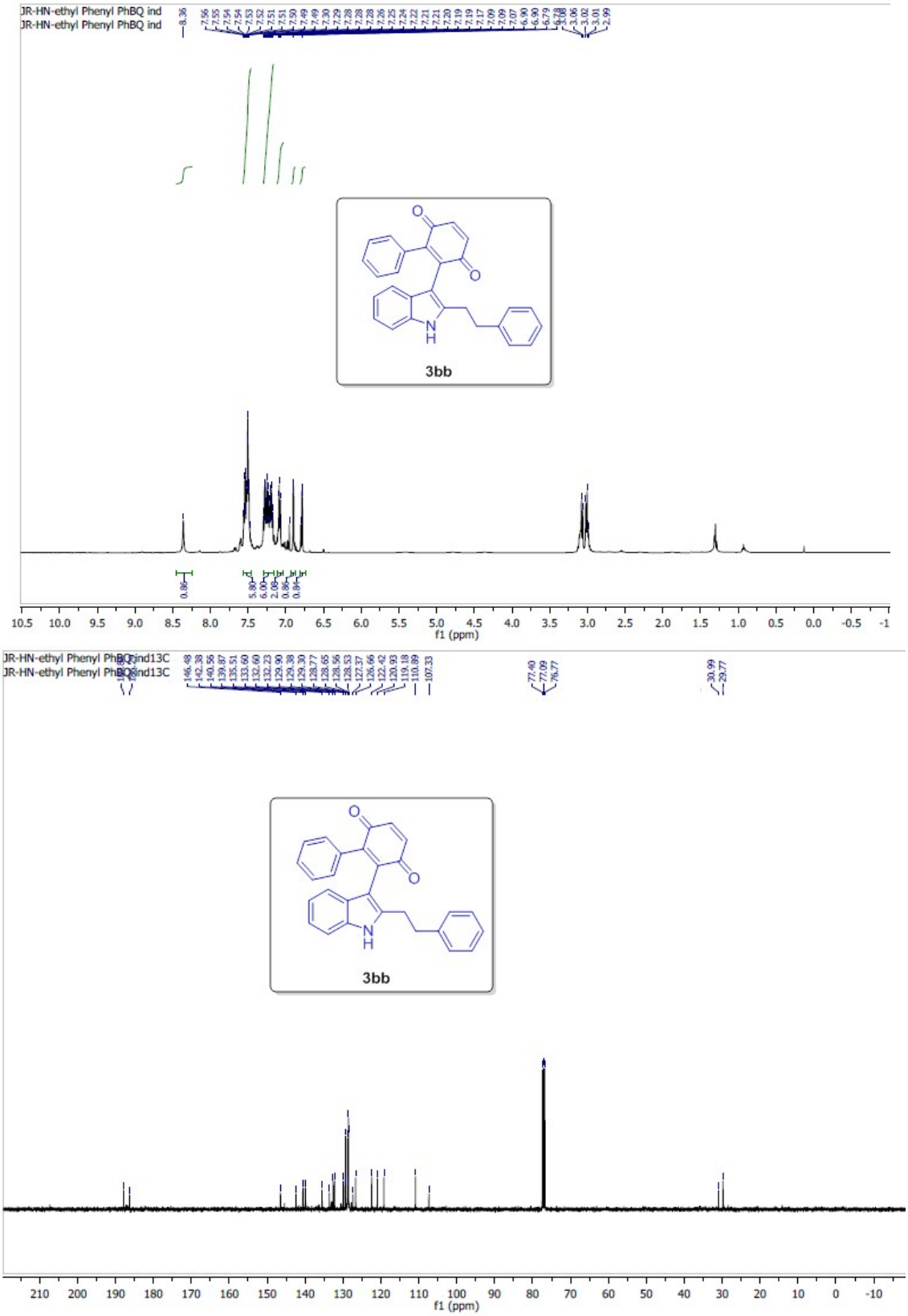


Figure S12. ^{1}H&^{13}C-NMR spectrum of compound **3bb** ($CDCl_3$, 400 MHz)

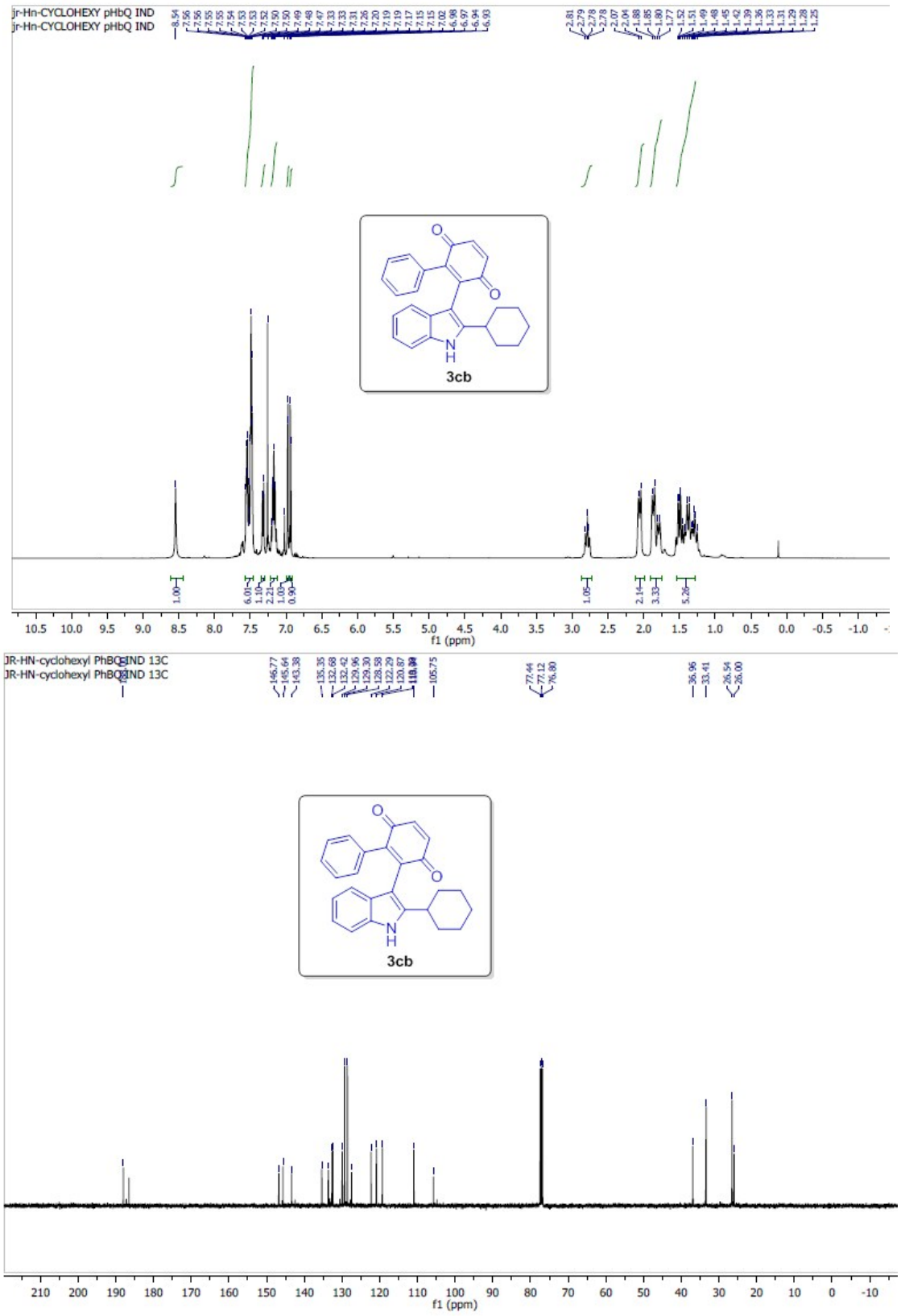


Figure S13. ^{1}H&^{13}C-NMR spectrum of compound **3cb** ($CDCl_3$, 400 MHz)

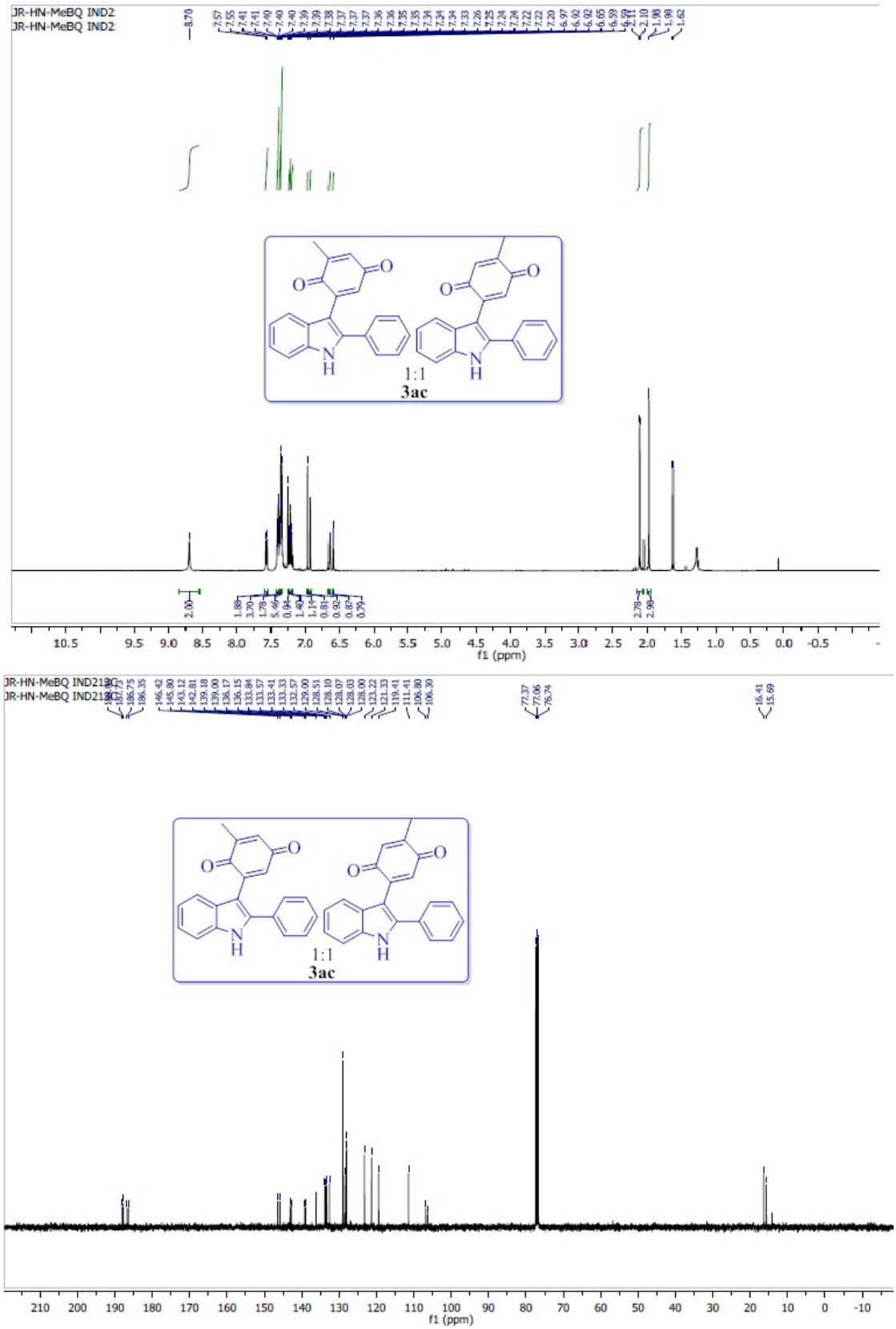


Figure S14. ^{1}H&^{13}C-NMR spectrum of compound **3ac** ($CDCl_3$, 400 MHz)

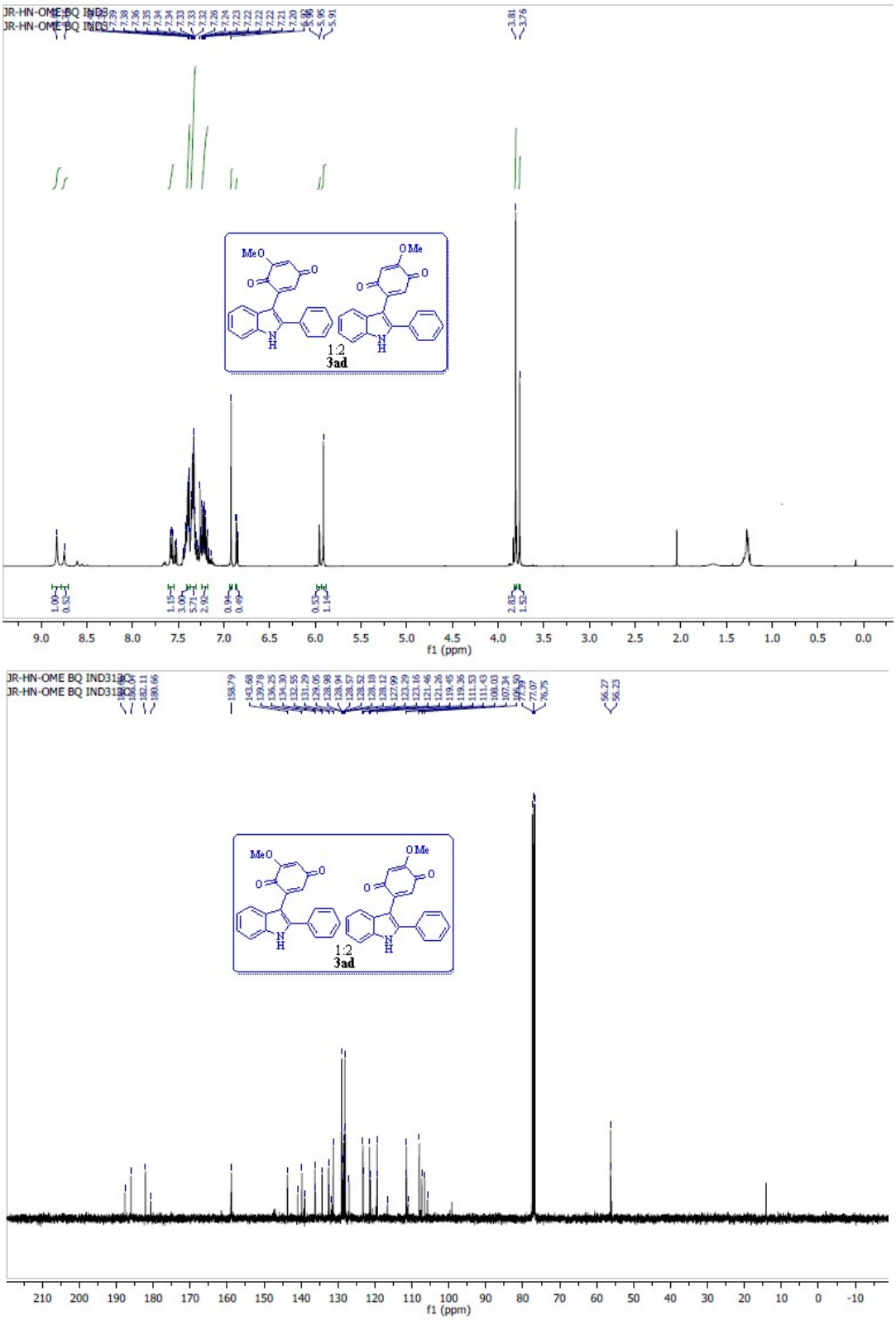


Figure S15. ^{1}H&^{13}C-NMR spectrum of compound **3ad** ($CDCl_3$, 400 MHz)

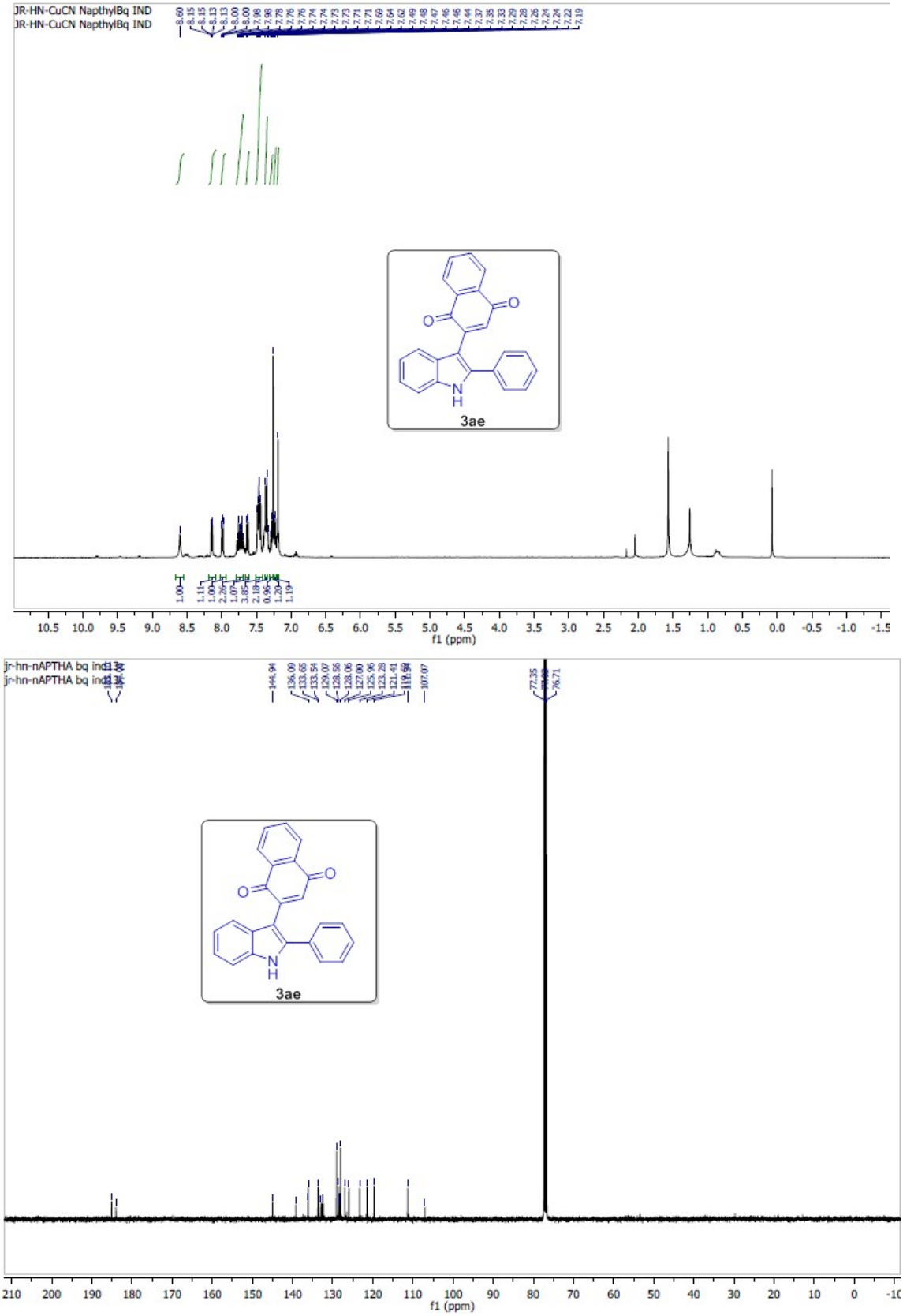


Figure S16. ^{1}H&^{13}C-NMR spectrum of compound **3ae**($CDCl_3$, 400 MHz)

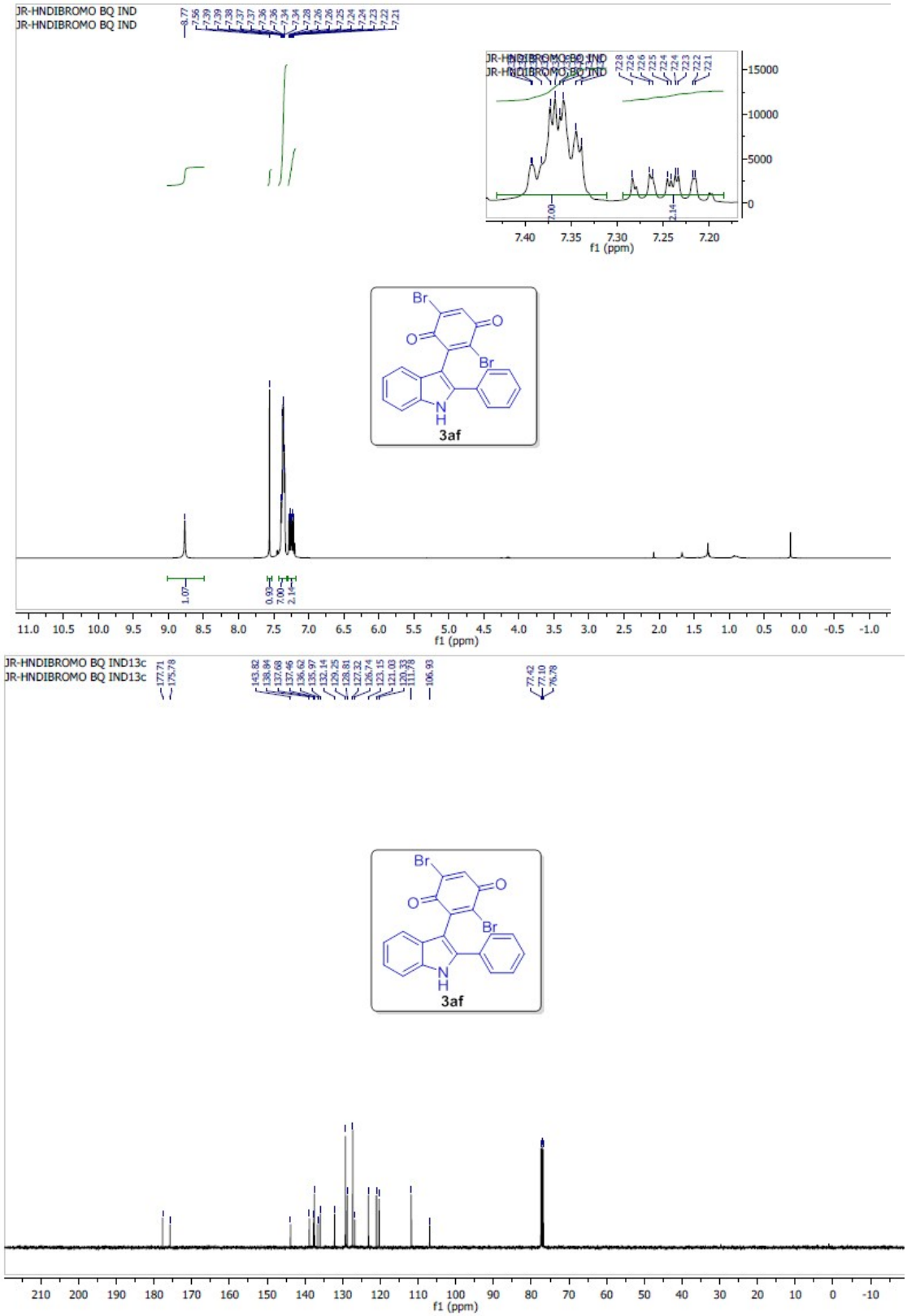


Figure S17. $^{1}H\&^{13}C$-NMR spectrum of compound **3ae**($CDCl_3$, 400 MHz)