Supporting Information

Regioselective synthesis of 4-substituted indoles via C-H activation: A Ruthenium catalyzed novel directing group strategy

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General experimental

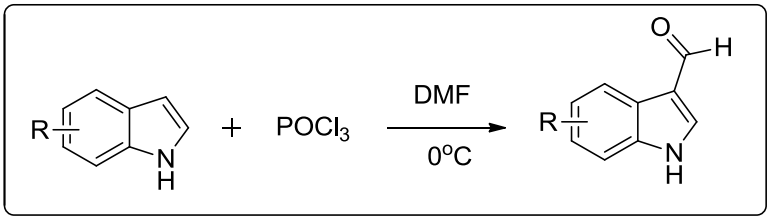
NMR spectra were recorded on BRUKER-AV400 spectrometer in $CDCl_3$, Tetramethylsilane (TMS; δ = 0.00 ppm) served as an internal standard for ^1H NMR. The corresponding residual non-deuterated solvent signal ($CDCl_3$; δ = 77.00 ppm) was used as internal standard for ^{13}C NMR. IR spectra were measured using a JASCO FT/IR-410 spectrometer and Perkin-Elmer FT/IR Spectrum BX, GX. Mass spectra were measured with Micromass Q-Tof (ESI-HRMS). Column chromatography was carried out on Silica gel 100-200 mesh (commercial suppliers) and thin-layer chromatography was carried out using SILICA GEL GF-254. Ruthenium and Silver catalysts are purchased from Alfa Aesar. Some of starting materials were synthesized from commercially available reagent. Other reagents and solvents were purchased from commercial supplier and used without further purification, except acrolein (distilled).

1. ***Typical experimental procedure for the C4- alkenylated indoles*:**

*To a well-stirred solution of 1-benzyl-1H-indole-3-carbaldehyde derivative (**1**, 0.21mmol, 50 mg, 1 equiv), $[Ru(p\text{-}cymene)Cl_2]_2$ (10 mol %, 6 mg), $AgSbF_6$ (20 mol %, 14.5 mg) and $Cu(OAc)_2{\cdot}H_2O$ (0.10mmol, 21.3 mg, 0.5 equiv) in dichloroethane (2 mL) was added methyl acrylate (**2a,** 0.85mmol, 73.5mg, 4 equiv.) (in the case of olefins **2b** and **2j-2o,** 1 equiv of $Cu(OAc)_2{\cdot}H_2O$ was used). Then, the reaction mixture was stirred at 120 ^oC (oil bath temperature) and an efficient cold water circulation was maintained, in an open air atmosphere for 8 – 12 h (monitored by TLC). After the completion of the reaction, the reaction mixture was cooled to room temperature, and diluted with 50% EtOAc/hexane (5 mL), passed through a short silica gel (100-200 mesh size) bed, and washed with 50% EtOAc/ hexane (20 mL x 3 times). The combined organic layer was concentrated under reduced pressure and the crude product was purified on a silica gel column using EtOAc/hexane mixture.*

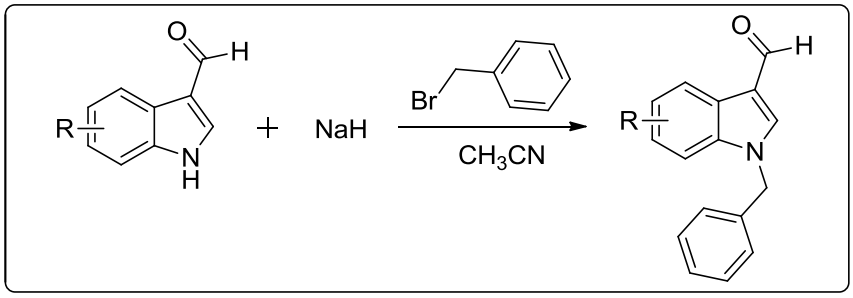
2. **Preparation of starting materials.**

(i) **General Procedure for the Synthesis of indole-3-carboxaldehyde derivatives:**



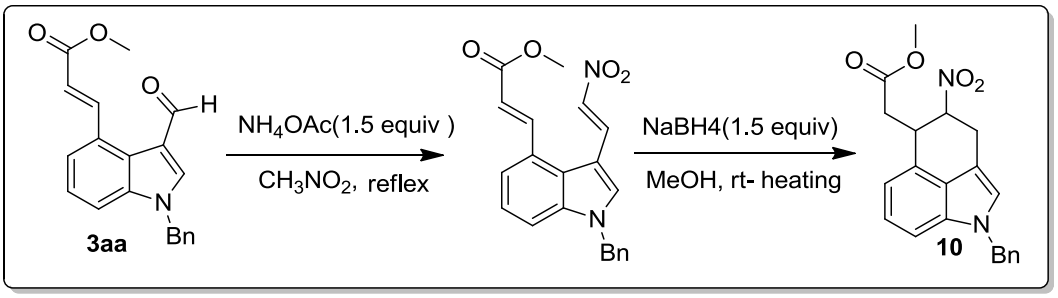
Starting materials, indole-3-carboxaldehyde, were prepared by Vilsmeier-Haack reaction according to a literature method from indoles .[1] To a well- stirred solution of indole derivatives (8.55 mmol, 1g, 1equiv) in anhydrous DMF (10ml) under dry argon atmosphere, phosphorus chloride oxide (25.6 mmol, 2.4 ml, 3.0 equiv.) was added at 0 ºC and the resulting mixture was stirred at room temperature. After being stirred for 1h, the reaction mixture was poured into cold saturated $NaHCO_3$ solution (aqueous) and stirred for 30 min. The reaction mixture was extracted by EtOAc for several times. The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, concentrated under reduced pressure and purified by silica gel flash column chromatography to provide desired products in moderate to excellent yields (52–93%).

(ii) **Preparation of N-substituted indole-3-carboxaldehyde.**[2]



N-substituted indole-3-carboxaldehyde was prepared by the treatment of indole-3-carboxaldehyde (6.89 mmol, 1g, 1 equiv) with NaH (10.3 mmol, 248 mg, 1.5 equiv) in CH_3CN (7 mL) followed by the addition of alkyl/acyl/tosyl halides (10.3 mmol, 1.23 ml, 1.5 equiv). After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (50 mL) and extracted by EtOAc (25mL x 3 times). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered, concentrated under pressure and purified by silica gel flash column chromatography.

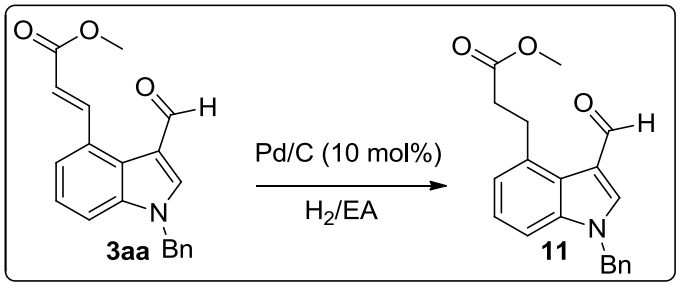
3. Synthesis of methyl 2-(1-benzyl-4-nitro-1,3,4,5-tetrahydrobenzo[cd]indol-5-yl)acetate (10).[3,4]



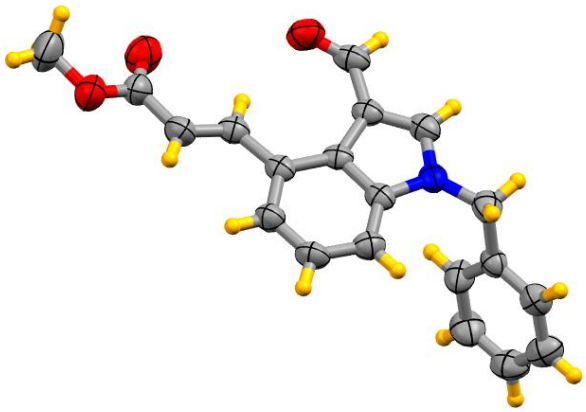
(E)-Methyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (**3aa**, 319 mg, 0.31 mmol), glacial CH_3COOH (470.2 mg, 0.78 mmol), NH_4OAc (50.9 mg, 0.78 mmol) in 0.4 ml of CH_3NO_2 was sonicated at room temperature for 4.5 h according to reported procedure[3], which produces corresponding nitroaldol product ((E)-methyl 3-(1-benzyl-3-((E)-2-nitrovinyl)-1H-indol-4-yl)acrylate) in 75% isolated yield.

(E)-Methyl 3-(1-benzyl-3-((E)-2-nitrovinyl)-1H-indol-4-yl)acrylate (70 mg, 0.193 mmol), was dissolved in a methanol (2 mL) and $NaBH_4$ (11.0 mg, 0.29 mmol) was added slowly. After the addition, the reaction mixture was heated at 65 °C for 15 h, followed by aqueous work up the product **10** was isolated in 90% (in 50:50 diastereomeric mixture. The spectral data of the compound is matching with the reported one.[4]

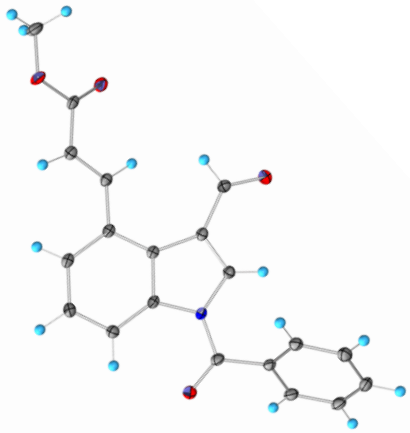
4. Selective reduction of Olefin.



(E)-Methyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (**3aa**, 30 mg, 0.094 mmol) dissolved in EtOAc (2 mL) and was hydrogenated uisng a hydrogen baloon for 2 h at RT with 10% Pd/C (10 mg, 0.0094 mmol) as a catalyst. The reaction mixture was filtered, passed through Celite pad and was concentrated in vacuum. The crude product was purified by flash chromatography using EtOAc/hexana as eluent, which yielded 98% of **11** (29.4 mg).



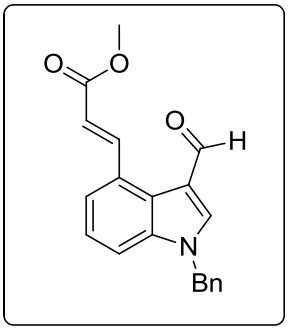
ORTEP diagram for 3aa.



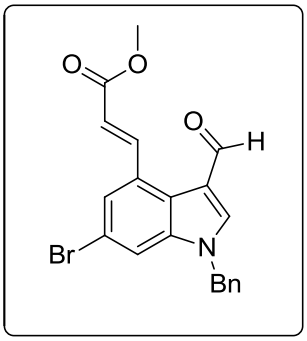
ORTEP diagram for 6.

Characterization data for C4- alkenylated indoles:

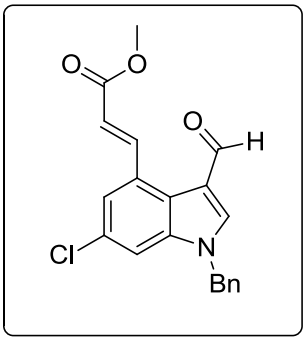
1. **(E)-Methyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3aa)**: Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black crystals; **Yield**: 47.5 mg, (70%); ***mp***: 133 - 137 °C; *Rf* (40 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3446, 1713, ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 9.28 (d, *J* = 16.0 Hz, 1H), 7.82 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.33-7.23 (m, 5H), 7.15 (d, *J* = 6.8 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.33 (s, 2H), 3.83 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.4, 167.4, 145.3, 142.2, 138.6, 134.8, 129.4, 129.0, 128.3, 127.1, 124.4, 124.0, 120.8, 119.4, 118.5, 112.1, 51.6, 50.9; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{17}NO_3$ (M + Na): 342.1106, found (M + Na): 342.1103.



2. (E)-Methyl 3-(1-benzyl-6-bromo-3-formyl-1H-indol-4-yl)acrylate (3ba): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow solid; **Yield**: 47 mg, (80%); ***mp***: 125 - 127 °C; *Rf* (40 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3435, 1691; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 9.14 (d, *J* = 15.9 Hz, 1H), 7.79 (s, 1H), 7.66 (s, 1H), 7.49 (d, *J* = 1.0 Hz, 1H), 7.40-7.37 (m, 3H), 7.18-7.17 (m, 2H), 6.41 (d, *J* = 15.9 Hz, 1H), 5.33 (s, 2H), 3.85 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.3, 167.1, 143.8, 142.2, 139.4, 134.2, 131.2, 129.3, 128.7, 127.2, 123.9, 123.4, 120.0, 119.6, 117.8, 114.7, 51.8, 51.1; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{16}NO_3Br$ (M + Na): 420.0211, found (M + Na): 420.0214.

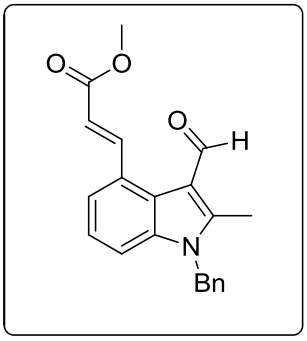


3. (E)-Methyl 3-(1-benzyl-6-chloro-3-formyl-1H-indol-4-yl)acrylate (3ca): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as orange solid; **Yield**: 38 mg, (58%); ***mp***: 122 – 125 °C; *Rf* (40 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3440, 1717; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.89 (s, 1H), 9.14 (d, *J* = 15.9 Hz, 1H), 7.82 (s, 1H), 7.52 (s, 1H), 7.38-.736 (m, 3H), 7.32 (s, 1H), 7.17 (d, *J* = 6.5Hz, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 5.33 (s, 2H), 3.85 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.3, 167.2, 143.9, 142.5, 139.1, 134.3, 130.9, 130.2, 129.3, 128.7, 127.2, 123.1, 121.2, 119.9, 119.6, 111.7, 51.8,

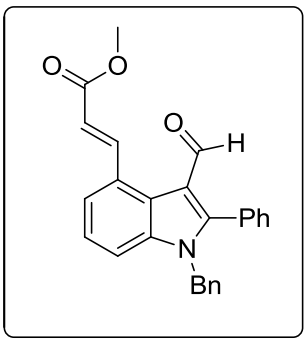


51.1; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{16}ClNO_3$ (M + Na): 376.0716, found (M + Na): 376.0717.

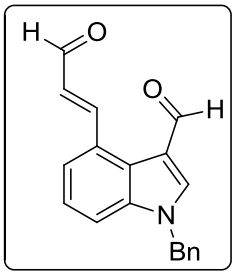
4. **(E)-Methyl 3-(1-benzyl-3-formyl-2-methyl-1H-indol-4-yl)acrylate (3da)**: Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dirty white solid; **Yield**: 52 mg, (75%); ***mp***: 168 - 170 °C; *Rf* (35 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3418, 1715; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.30 (s, 1H), 8.99 (d, *J* = 15.9 Hz, 1H), 7.48 (d, *J* = 7.4 Hz, 1H), 7.31-7.20 (m, 5H), 6.97 (d, *J* = 6.6 Hz, 2H), 6.40 (d, *J* = 15.9 Hz, 1H), 5.37 (s, 2H), 3.85 (s, 3H), 2.72 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 184.6, 167.4, 149.1, 145.3, 137.5, 135.2, 129.1, 128.7, 127.9, 125.8, 124.8, 123.2, 121.5, 119.1, 115.5, 111.4, 51.7, 46.6, 11.6; **HRESI-MS** *(m/z)*: Calculated for $C_{21}H_{19}NO_3$ (M + Na): 356.1263, found (M + Na): 356.1257.



5. (E)-Bethyl 3-(1-benzyl-3-formyl-2-phenyl-1H-indol-4-yl)acrylate (3ea): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as pale yellow solid; **Yield**: 53 mg, (83%); ***mp***: 68 - 75 °C; *Rf* (40 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3448, 1717; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.66 (s, 1H), 9.54 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 6.5 Hz, 1H), 7.52 (q, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40-7.38 (m, 2H), 7.30-7.25 (m, 5H), 6.95-6.93 (m, 2H), 6.43 (d, *J* = 16.0 Hz, 1H), 5.26 (s, 2H), 3.86 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 185.7, 167.7, 154.9, 146.3, 138.0, 136.0, 130.8, 130.2, 129.9, 128.9, 128.6, 128.5, 127.8, 125.8, 124.4, 124.2, 121.5, 118.2, 117.2, 112.4, 51.7, 47.8; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{21}NO_3$ (M + Na): 418.1419, found (M + Na): 418.1419.

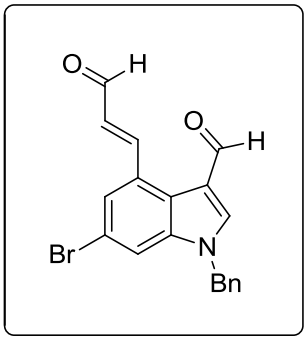


6. (E)-1-Benzyl-4-(3-oxoprop-1-en-1-yl)-1H-indole-3-carbaldehyde (3ab): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dark yellow crystals; **Yield**: 47 mg, (77%); ***mp***: 138 - 139 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3443, 1672; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.88 (d, *J* = 7.8 Hz, 1H), 9.85 (s, 1H), 9.46 (d, *J* = 15.6 Hz, 1H), 7.87 (s, 1H), 7.67 (d, *J* = 7.4 Hz, 1H), 7.42-7.33 (m,

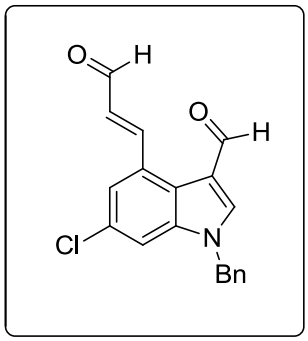


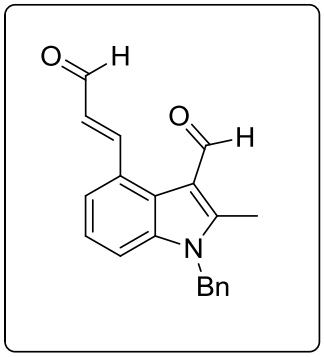
5H), 7.20 (d, *J* = 7.4 Hz, 2H), 6.72 (dd, *J* = 7.8, 15.6 Hz, 1H), 5.40 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.9, 183.3, 154.1, 143.9, 139.1, 134.6, 129.2, 129.0, 128.6, 127.2, 124.8, 124.4, 121.4, 119.7, 113.0, 51.1; **HRESI-MS** *(m/z)*: Calculated for $C_{19}H_{15}NO_2$ (M + Na): 312.1000, found (M + Na): 312.1002.

7. (E)-1-Benzyl-6-bromo-4-(3-oxoprop-1-en-1-yl)-1H-indole-3-carbaldehyde (3bb): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dark yellow crystals; **Yield**: 47 mg, (80%); ***mp***: 163 - 165 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3448, 1671; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.88 (d, *J* = 8.3 Hz, 1H), 9.87 (s, 1H), 9.35 (d, *J* = 16.2 Hz, 1H), 7.83 (s, 1H), 7.75 (s, 1H), 7.55 (s, 1H), 7.41-7.36 (m, 3H), 7.20-7.18 (m, 2H), 6.68 (dd, *J* = 7.8Hz, 1H), 5.36 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ194.4, 183.1, 152.3, 144.0, 139.8, 134.0, 130.8, 129.9, 129.4, 128.9, 127.2, 124.3, 123.5, 119.7, 118.1, 115.5, 51.2; **HRESI-MS** *(m/z)*: Calculated for $C_{19}H_{14}NO_2Br$ (M + Na): 390.0106, found (M + Na): 390.0104.

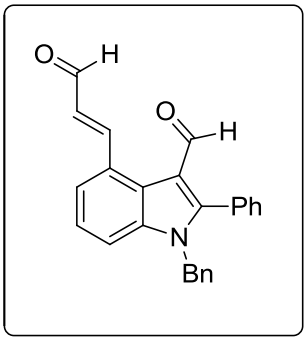


8. (E)-1-Benzyl-6-chloro-4-(3-oxoprop-1-en-1-yl)-1H-indole-3-carbaldehyde (3cb): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black solid; **Yield**: 51 mg, (85%); ***mp***: 161 - 163 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3448, 1671; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.87 (d, *J* = 7.8 Hz, 1H), 9.82 (s, 1H), 9.35 (d, *J* = 15.7 Hz, 1H), 7.86 (s, 1H), 7.59 (s, 1H), 7.39-7.36 (m, 4H), 7. 19 (d, *J* = 7.8 Hz, 2H), 6.67 (dd, *J* = 7.8 Hz, 1H), 5.36 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ194.4, 183.1, 152.4, 144.2, 139.5, 134.1, 130.6, 130.4, 129.9, 129.4, 128.9, 127.2, 123.2, 121.5, 119.7, 112.6, 51.2; **HRESI-MS** *(m/z)*: Calculated for C19H14ClNO2 (M + Na): 346.0611, found (M + Na): 346.0612.

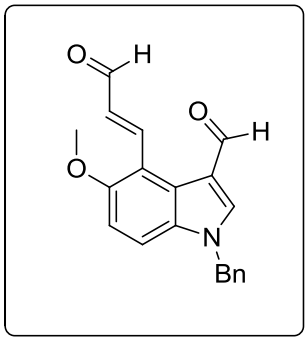




9. (E)-1-Benzyl-2-methyl-4-(3-oxoprop-1-en-1-yl)-1H-indole-3-carbaldehyde (3db): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black solid; **Yield**: 47.4 mg, (78%); ***mp***: 171 - 173 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3446, 1648; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 10.17 (s, 1H), 9.87 (d, *J* = 8.0 Hz, 1H), 9.41 (d, *J* = 16 Hz, 1H), 7.60 (d, *J* = 7.6Hz, 1H), 7.35-7.26 (m, 5H), 6.99-6.97 (m, 2H), 6.69 (dd, *J* = 8 Hz, 1H), 5.4 (s, 2H), 2.72 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 194.8, 183.6, 154.7, 151.4, 138.1, 134.9, 129.2, 128.9, 128.5, 128.1, 125.7 124.7, 123.7, 121.8, 115.6, 112.3, 46.8, 11.1; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{17}NO_2$ (M + Na): 326.1157, found (M + Na): 326.1158.



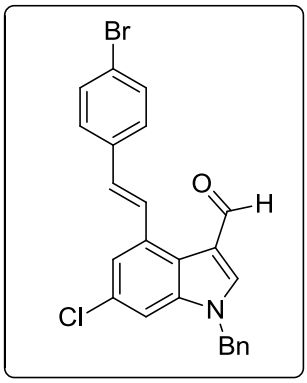
10. (E)-1-Benzyl-4-(3-oxoprop-1-en-1-yl)-2-phenyl-1H-indole-3-carbaldehyde (3eb): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dark orange crystals; **Yield**: 53.9 mg, (92%); ***mp***: 169 - 171 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3447, 1665; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.90 (d, *J* = 7.9 Hz, 1H), 9.65 (d, *J* = 15.8 Hz, 1H), 9.62 (s, 1H), 7.69 (t, *J* = 4.3 Hz, 1H), 7.56 (t, *J* = 6.7 Hz, 5H), 7.50 (t, *J* = 6.6 Hz, 2H), 7.42-7.40 (m, 2H), 7.33 (d, *J* = 4.3 Hz, 2H), 7.28-7.25 (m, 3H), 6.95-6.93 (m, 2H), 6.73 (dd, *J* = 8.4 Hz, 1H), 5.29 (s, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 195.0, 185.9, 155.9, 154.9, 138.1, 135.7, 130.7, 130.3, 129.2, 129.0, 128.9, 128.7, 128.2, 127.9, 125.8, 124.6, 124.5, 121.9, 117.1, 113.5, 47.9; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{19}NO_2$ (M + Na): 388.1313, found (M + Na): 388.1312.



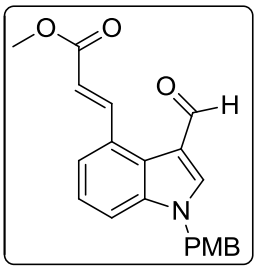
11. (E)-1-Benzyl-5-methoxy-4-(3-oxoprop-1-en-1-yl)-1H-indole-3-carbaldehyde (3fb): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dark orange solid; **Yield**: 41.5 mg, (69%); ***mp***: 149 - 152 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3440, 1661; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.87 (d, *J* = 7.6 Hz, 1H), 9.83 (s, 1H), 9.39 (d, *J* = 15.9 Hz, 1H), 7.83 (s, 1H), 7.38-7.36 (m, 3H), 7.31 (d, *J* = 9.0 Hz, 1H), 7. 24 (dd,

J = 7.8 Hz, 1H), 7.19-7.17 (m, 2H), 7.01 (d, *J* = 15.9 Hz, 1H), 5.36 (s, 2H), 3.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.2, 183.1, 157.0, 151.2, 144.5, 134.6, 133.7, 132.6, 129.2, 128.6, 127.2, 127.1, 119.6, 116.9, 113.5, 109.5, 56.2, 51.2; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{17}NO_3$ (M + Na): 342.1106, found (M + Na): 342.1107.

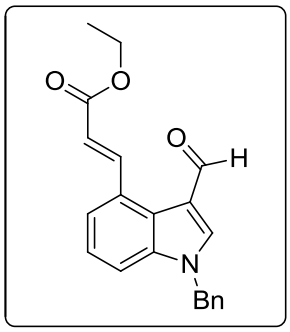
12. (E)-1-Benzyl-4-(4-bromostyryl)-6-chloro-1H-indole-3-carbaldehyde (3cm): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow solid; **Yield**: 28.6 mg, (35%); ***mp***: 193 - 195 °C; *Rf* (40 % EtOAc/Hexane) 0.4; **IR** (KBr, cm^{-1}): 3448, 1667; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.87 (s, 1H), 8.80 (d, *J* = 16.2 Hz, 1H), 7.76 (s, 1H), 7.61-7.50 (m, 5H), 7.38-7.36 (m, 3H), 7.22 (s, 1H), 7.17 (d, *J* = 6.3 Hz, 2H), 7.04 (d, *J* = 16.2 Hz, 1H), 5.31 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.4, 143.1, 139.4, 136.5, 134.5, 133.9, 131.8, 130.7, 129.3, 128.9, 128.7, 128.4, 127.2, 122.4, 121.5, 120.0, 119.5, 109.5, 51.1; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{17}BrClNO$ (M + Na): 472.0080, found (M + Na): 472.0078.



13 (E)-Methyl 3-(3-formyl-1-(4-methoxybenzyl)-1H-indol-4-yl)acrylate (4): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as Thick liquid; **Yield**: 44.7 mg, (68%); *Rf* (30 % EtOAc/Hexane) 0.4; **IR** (Neat, cm^{-1}): 3615, 2949, 1715, 1699, 1669; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.83 (s, 1H), 9.30 (d, *J* = 16.0 Hz, 1H), 7.77 (s, 1H), 7.54 (d, *J* = 6.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 6.8 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.24 (s, 2H), 3.82 (s, 3H), 3.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.3, 167.4, 159.5, 145.3, 142.2, 138.5, 129.3, 128.7, 126.4, 124.4, 123.8, 120.6, 119.1, 118.2, 114.3, 112.1, 55.1, 51.5, 50.3; **HRESI-MS** *(m/z)*: Calculated for $C_{21}H_{19}NO_4$ (M + Na): 372.1212, found (M + Na): 372.1210.

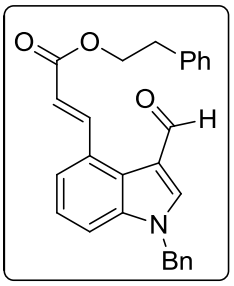


14. (E)-Ethyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ac): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow crystals; **Yield**: 51 mg, (72%); ***mp***: 132 - 135 °C; *Rf* (35 % EtOAc/Hexane)

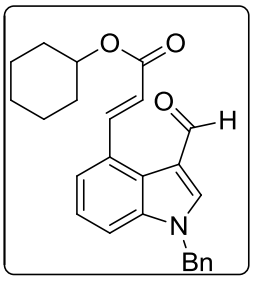


0.3; **IR** (KBr, cm^{-1}): 3412, 1702; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.96 (s, 1H), 9.24 (d, *J* = 15.9 Hz, 1H), 7.84 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.36-7.27 (m, 5H), 7.17 (dd, J_1 = 2.2, J_2 = 7.2 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.36 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.5, 167.1, 144.9, 141.7, 138.7, 134.8, 129.8, 129.2, 128.5, 127.2, 124.6, 124.1, 121.0, 119.6, 119.3, 111.9, 60.4, 51.1, 14.3; **HRESI-MS** *(m/z)*: Calculated for $C_{21}H_{19}NO_3$ (M + Na): 356.1263, found (M + Na): 356.1262.

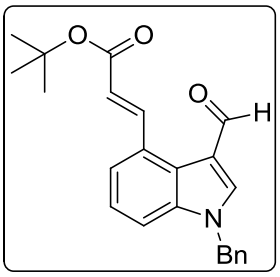
15. (E)-Phenethyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ad): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black thick liquid; **Yield**: 54 mg, (62%); *Rf* (40 % EtOAc/Hexane) 0.2; **IR** (Neat, cm^{-1}): 3414, 1706; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 9.24 (d, *J* = 16.0 Hz, 1H), 7.85 (s, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.36-7.28 (m, 9H), 7.24-7.21 (m, 1H), 7.18 (dd, J_1 = 2.5, J_2 = 7.8 Hz, 2H), 6.44 (d, *J* = 16.0 Hz, 1H), 5.37 (s, 2H), 4.46 (t, *J* = 7.1 Hz, 2H), 3.08 (t, *J* = 7.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.5, 166.9, 145.2, 141.6, 138.7, 138.1, 134.8, 129.8, 129.2, 129.0, 128.5, 128.4, 127.2, 126.4, 124.7, 124.1, 121.0, 119.7, 119.2, 112.0, 65.1, 51.1, 35.3; **HRESI-MS** *(m/z)*: Calculated for $C_{27}H_{23}NO_3$ (M + Na): 432.1576, found (M + Na): 432.1590.



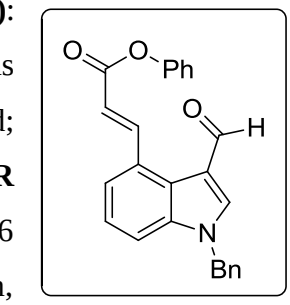
16. (E)-Cyclohexyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ae): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black viscous liquid; **Yield**: 49 mg, (60%); *Rf* (30% EtOAc/Hexane) 0.2; **IR** (Neat, cm^{-1}): 3422, 1700; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 9.22 (d, *J* = 15.9 Hz, 1H), 7.84 (s, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.38-7.28 (m, 5H), 7.18-7.16 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 5.36 (s, 2H), 4.9 (sept, *J* = 4.4 Hz, 1H), 1.97 – 1.94 (m, 2H). 1.83-1.80 (m, 3H), 1.60-1.54 (m, 3H), 1.44-1.41 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.5, 166.5, 144.6, 141.6, 138.6, 134.8, 129.9, 129.2, 128.5, 127.2, 124.6, 124.1, 120.9, 120.0, 119.7, 111.9, 72.6, 51.1, 31.7, 25.5, 23.7; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{25}NO_3$ (M + Na): 410.0732, found (M + Na): 410.1732.



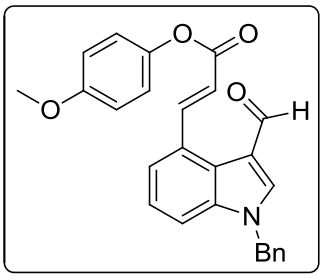
17. (E)-*tert*-Butyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3af): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as Thick liquid; **Yield**: 36 mg, (50%); *Rf* (30 % EtOAc/Hexane) 0.4; **IR** (Neat, cm-1): 3463, 2977, 1698, 1670; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 9.16 (d, *J* = 16 Hz, 1H), 7.81 (s, 1H), 7.57 (d, *J* = 3.8 Hz, 1H), 7.34-7.20 (m, 5H), 7.17-7.15 (m, 2H), 6.38 (d, *J* = 16 Hz, 1H), 5.34 (s, 2H), 1.59 (s, 9H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.5, 166.4, 143.9, 141.7, 138.6, 134.8, 129.8, 129.1, 128.4, 127.1, 124.6, 124.0, 121.1, 120.7, 119.6, 111.8, 80.2, 51.0, 28.2; **HRESI-MS** *(m/z)*: Calculated for $C_{23}H_{23}NO_3$(M + Na): 384.1576, found (M + Na): 384.1578.



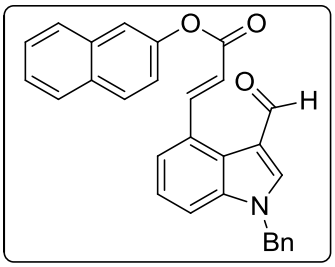
18. (E)-Phenyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ag): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as dark yellow solid; **Yield**: 45 mg, (56%); ***mp***: 138 - 140 °C; *Rf* (30 % EtOAc/Hexane) 0.2; **IR** (Kbr, cm^{-1}): 3452, 1723; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 9.56 (d, *J* = 16.0 Hz, 1H), 7.81 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.39-7.19 (m, 10H), 7.14-7.13 (m, 2H), 6.60 (d, *J* = 16Hz, 1H), 5.32 (s, 2H),; ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.3, 165.4, 150.9, 147.2, 142.6, 138.7, 134.8, 129.3, 129.2, 129.1, 128.4, 127.1, 125.4, 124.6, 124.1, 121.7, 121.0, 119.5, 117.8, 112.5, 50.9; **HRESI-MS** *(m/z)*: Calculated for $C_{25}H_{19}NO_3$ (M + Na): 404.1263, found (M + Na): 404.1263.



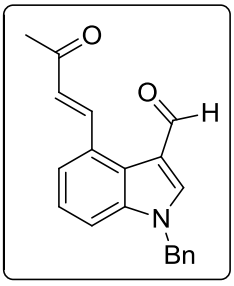
19. (E)-4-Methoxyphenyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ah): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black solid; **Yield**: 62 mg, (71%); ***mp***: 125 - 126 °C; *Rf* (40 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3434, 1720; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 9.50 (d, *J* = 16.0 Hz, 1H), 7.81 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.39-7.30 (m, 5H), 7.18-7.16 (m, 4H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 16.0 Hz, 1H), 5.37 (s, 2H), 3.80 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.4, 165.8, 157.0, 146.9, 144.6, 142.2, 138.8, 134.8, 129.5, 129.2, 128.5, 127.2, 124.7, 124.2, 122.5,



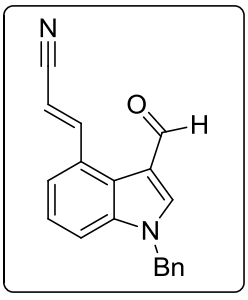
121.1, 119.7, 118.2, 114.3, 112.4, 55.6, 51.1, ; **HRESI-MS** *(m/z)*: Calculated for $C_{26}H_{21}NO_4$ (M + Na): 434.1368, found (M + Na): 434.1365.



20. (E)-Naphthalen-2-yl 3-(1-benzyl-3-formyl-1H-indol-4-yl)acrylate (3ai): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black solid; **Yield**: 60 mg, (65%); ***mp***: 104 - 107 °C; *Rf* (30 % EtOAc/Hexane) 0.2; **IR** (KBr, cm^{-1}): 3442, 1664; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.95 (s, 1H), 9.59 (d, *J* = 15.4 Hz, 1H), 7.88-7.80 (m, 4H), 7.74 (s, 1H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.48-7.45 (m, 2H), 7.42-7.36 (m, 5H), 7.16 (d, *J* = 7.3 Hz, 2H), 6.66 (d, *J* = 15.4 Hz, 1H), 5.35 (s, 2H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 183.4, 165.6, 148.7, 147.3, 142.3, 138.8, 134.7, 133.8 ,131.4, 129.5, 129.2, 128.5, 127.7, 127.2, 126.3, 125.4, 124.8, 124.2, 121.5, 121.2, 119.7, 118.6, 118.1, 112.5, 51.1 ; **HRESI-MS** *(m/z)*: Calculated for $C_{29}H_{21}NO_3$ (M + Na): 454.1419, found (M + Na): 454.1419.



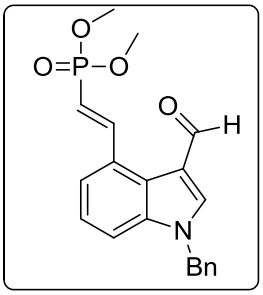
21. (E)-1-Benzyl-4-(3-oxobut-1-en-1-yl)-1H-indole-3-carbaldehyde (3aj): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as pale yellow solid; **Yield**: 21 mg, (32%); ***mp***: 119 - 122 °C; *Rf* (30 % EtOAc/Hexane) 0.2; **IR** (KBr, cm^{-1}): 3441, 1675; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.86 (s, 1H), 9.45 (d, *J* = 16.7 Hz, 1H), 7.85 (s, 1H), 7.65 (d, *J* = 7.2 Hz, 1H), 7.39-7.33 (m, 5H), 7.20-7.18 (m, 2H), 6.65 (d, *J* = 16.7, Hz, 1H), 5.39 (s, 2H), 2.59 (s, 3H); ^{13}**C NMR** (100 MHz, $CDCl_3$): δ 200.6, 183.4, 145.7, 143.8, 138.9, 134.6, 129.9, 129.2, 128.8, 128.6, 127.2, 124.8, 124.5, 120.8, 119.7, 112.3, 51.1, 26.1; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{17}NO_2$ (M + Na): 326.1157, found (M + Na): 326.1158.



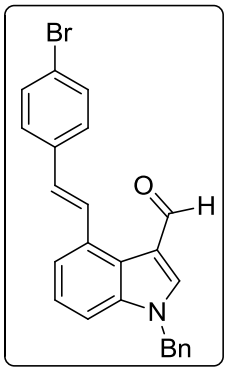
22. (E)-3-(1-Benzyl-3-formyl-1H-indol-4-yl)acrylonitrile (3ak): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow solid; **Yield**: 20 mg, (32%); ***mp***: 124 - 128 °C; *Rf* (30 % EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3450, 1654; ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.84 (s, 1H), 9.24 (d, *J* = 16.9 Hz, 1H), 7.85 (s, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.42-7.30 (m, 5H),

7.19-7.17 (m, 2H), 5.86 (d, *J* = 16.9 Hz, 1H), 5.40 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.1, 151.4, 150.0, 143.4, 138.9, 134.6, 129.2, 128.9, 128.6, 127.2, 124.4, 124.1, 120.1, 119.5, 118.6, 112.9, 96.1, 51.2; **HRESI-MS** *(m/z)*: Calculated for $C_{19}H_{14}N_2O$ (M + Na): 309.1004, found (M + Na): 309.1003.

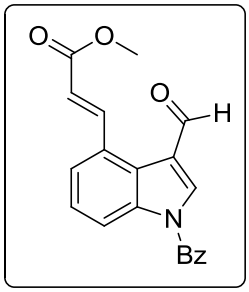
23. (E)-Dimethyl (2-(1-benzyl-3-formyl-1H-indol-4-yl)vinyl)phosphonate (3al): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as black solid; **Yield**: 47 mg, (47%); ***mp***: 127 - 129 °C; *Rf* (EtOAc) 0.6; **IR** (KBr, cm^{-1}): 3448, 1656, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.89 (brs, 1H), 9.05 (dd, J_1 = 17.9 Hz, J_2 = 4.6 Hz, 1H), 7.85 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.36-7.27 (m, 5H), 7.18-7.16 (m, 2H), 6.26 (dd, J_1 = 17.9, J_2 = 1.1 Hz, 1H), 5.38 (s, 2H), 3.88 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.0, 149.2, 149.1, 142.7, 138.7, 134.7, 130.3, 130.0, 129.1, 128.5, 127.1, 124.2, 124.1, 120.6, 114.1, 112.1, 52.8, 52.7, 51.1; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{20}NO_4P$ (M + H): 370.1208, found (M + H): 370.1207.



24. (E)-1-Benzyl-4-(4-bromostyryl)-1H-indole-3-carbaldehyde (3am): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow powder; **Yield**: 35 mg, (40%); ***mp***: 138 - 141 °C; *Rf* (30% EtOAc/Hexane) 0.3; **IR** (KBr, cm^{-1}): 3447, 1654; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.86 (d, *J* = 16.4 Hz, 1H), 7.78 (s, 1H), 7.66 (d, *J* = 7.3 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.35-7.28 (m, 4H), 7.24-7.22 (m, 1H), 7.18-7.16 (m, 2H), 7.04 (d, *J* = 16.4 Hz, 1H), 5.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.6, 142.7, 138.9, 137.0, 135.0, 132.6, 131.7, 130.1, 129.2, 128.5, 128.3, 128.1, 127.2, 124.4, 123.9, 121.0, 120.0, 119.2, 109.8, 51.0; **HRESI-MS** *(m/z)*: Calculated for $C_{24}H_{18}BrNO$ (M + Na): 438.0469, found (M + Na): 438.0469.

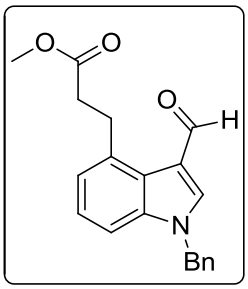


25. (E)-Methyl 3-(1-benzoyl-3-formyl-1H-indol-4-yl)acrylate (6): Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow liquid; **Yield**: 37 mg, (52%); *Rf* (30% EtOAc/Hexane) 0.3; **IR** (Neat, cm^{-1}): 1701; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.00 (s, 1H), 9.05 (d, *J* = 15.8 Hz, 1H), 8.40



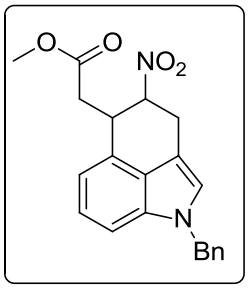
(d, *J* = 8.3 Hz, 1H), 8.06 (s, 1H), 7.78 (d, *J* = 7.81 Hz, 2H), 7.70-7.67 (m, 2H), 7.60 (t, *J* = 7.48 Hz, 2H), 7.47 (t, *J* = 7.81 Hz, 1H), 6.45 (d, *J* = 15.62 Hz, 1H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 184.4, 168.2, 167.2, 144.4, 138.0, 133.3, 129.6, 129.5, 129.1, 126.5, 125.2, 123.4, 123.3, 119.6, 117.5, 51.8.; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{15}NO_4$ (M + Na): 356.0899, found (M + Na): 356.0898.

26. Methyl 3-(1-benzyl-3-formyl-1H-indol-4-yl)propanoate (11):



Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as yellow crystals; **Yield:** 29.5 mg, (98%); ***mp***: 62 - 65 °C; *Rf* (30% EtOAc/Hexane) 0.5; **IR** (KBr, cm^{-1}): 3448, 1645, **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.78 (s, 1H), 7.37-7.25 (m, 3H), 7.21-7.12 (m, 5H), 5.33 (s, 2H), 3.66 (s, 1H), 3.60 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 183.7, 173.6, 140.6, 138.5, 135.7, 135.0, 129.1, 128.4, 127.2, 124.1, 124.0, 123.9, 119.5, 108.8, 51.5, 50.9, 36.1, 31.0; **HRESI-MS** *(m/z)*: Calculated for $C_{20}H_{19}NO_3$ (M + Na): 344.1263, found (M + Na): 344.1261.

27. Methyl 2-(1-benzyl-4-nitro-1,3,4,5-tetrahydrobenzo[cd]indol-5-yl)acetate (10):



Prepared as shown in general procedure. Crude reaction mixture was purified on a silica gel column to obtain the product as Thick liquid; **Yield:** 48 mg (1:1 mixture of diastereomers), (90%); *Rf* (25% EtOAc/Hexane) 0.6; **IR** (Neat, cm^{-1}): 3448, 2931, 2057, 1645, 1380, 1054; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 6H), 7.14-7.10 (m, 8H), 6.95-6.87 (m, 4H), 5.29 (s, 2H), 5.25 (s, 2H), 5.17 (d, *J* = 4.6 Hz, 1H), 5.12-5.08 (m, 1H), 4.38-4.31 (m, 2H), 3.74-3.72 (m, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.55-3.39 (m, 3H), 2.77 (d, *J* = 6.4 Hz, 2H), 2.69 (d, *J* = 5.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.7, 117.5, 137.4, 137.3, 134.5, 129.7, 128.8, 128.8, 127.8, 127.7, 126.9, 125.4, 125.3, 123.2, 123.1, 123.0, 122.8, 116.1, 115.4, 108.7, 108.4, 106.8, 106.6, 85.4, 84.9, 52.0, 51.8, 50.4, 5.3, 38.1, 37.8, 36.9, 35.4, 29.7, 25.5; **HRESI-MS** *(m/z)*: Calculated for $C_{21}H_{20}N_2O_4$ (M + Na): 387.1321, found (M + Na): 387.1325.

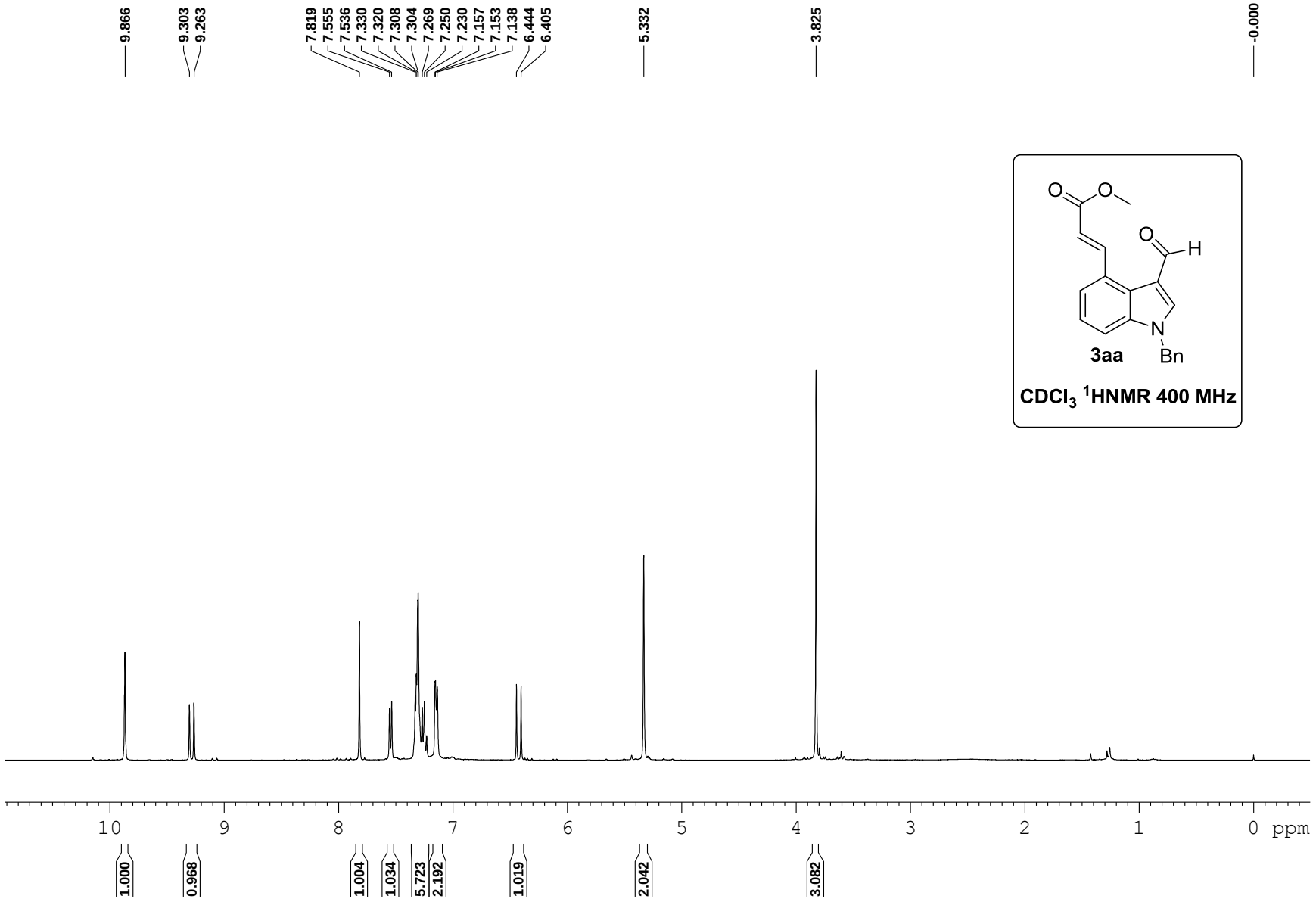
References:

1. Teng, X. ; Degterev, A.; Jagtap, P.; Xing, X.; Choi, S.; Denu, R.; Yuan, J.; Cuny, G. D. *Bioorg. Med. Chem. Lett*. **2005**, *15*, 5039.

2. Singh, P.; Kaur, M.; Holzer, W. *Eur. J. Med. Chem*., **2010**, *45*, 4968.

3. McNulty, J.; Steere, J. A.; Wolf, S. *Tetrahedron Lett*. **1998**, *39*, 8013.

4. Yamada, F.; Makita, Y.; Somei, M. *Heterocycl.Chem.* **2007**, *72*, 599.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9.263
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7.536
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7.320
7.308
7.304
7.269
7.250
7.230
7.157
7.153
7.138
6.444
6.405
5.332
3.825
-0.000
O
O
O
H
N
Bn
3aa
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
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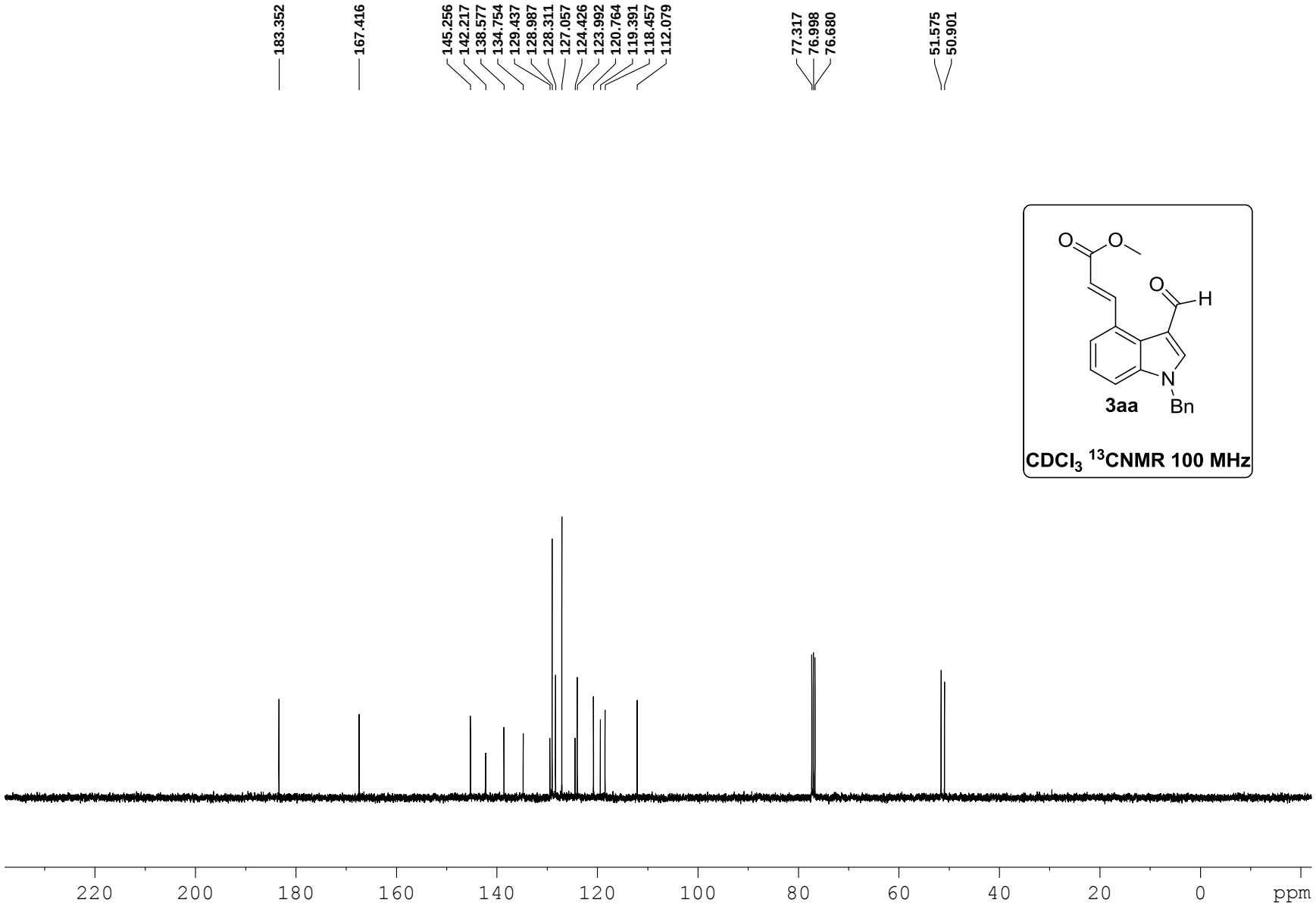
3.082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129.437
128.987
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127.057
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123.992
120.764
119.391
118.457
112.079
77.317
76.998
76.680
51.575
50.901
O
O
O
H
N
Bn
3aa
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200
180
160
140
120
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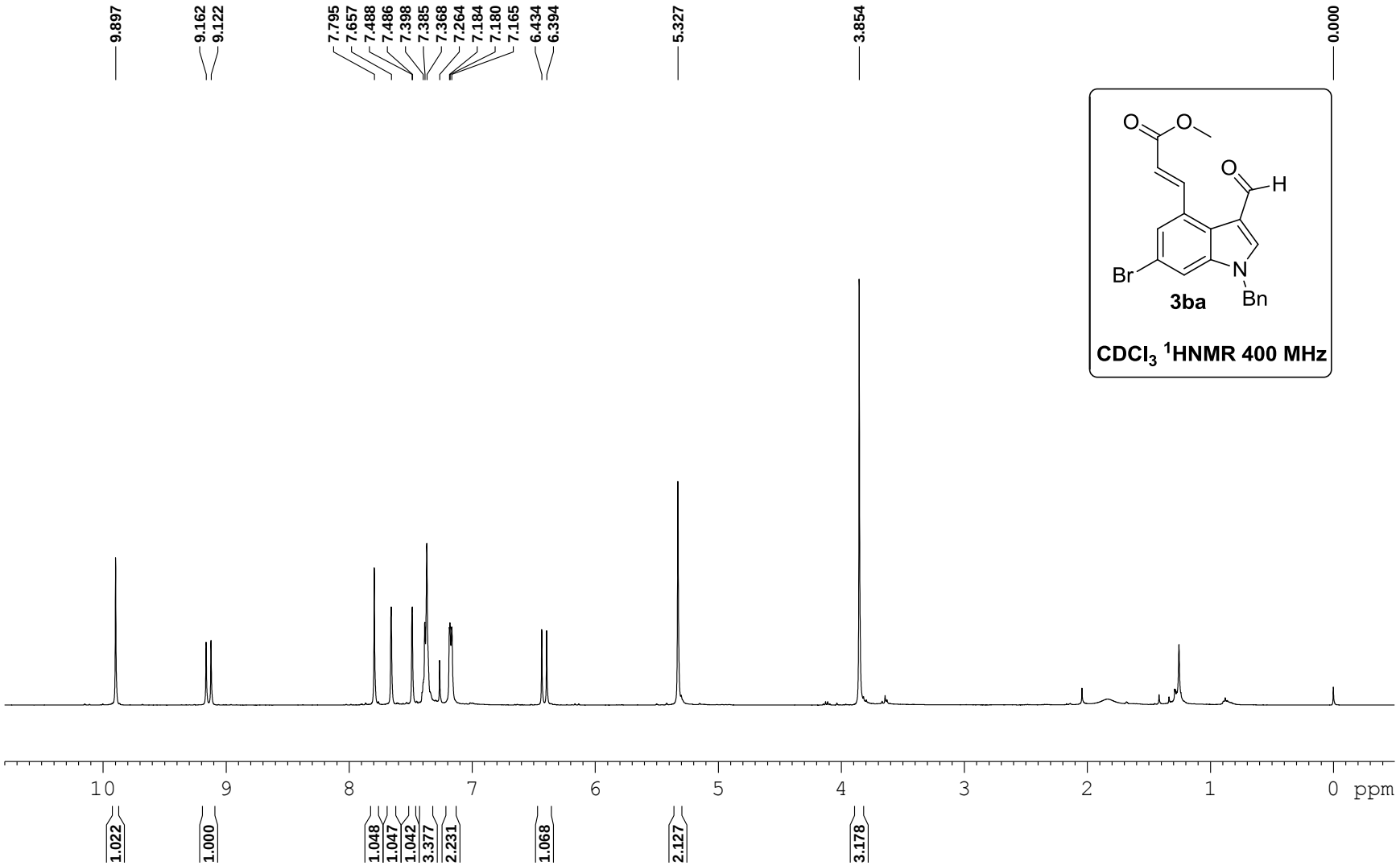
80
60
40
20
0
ppm

LVR-04043P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7.180
7.165
6.434
6.394
5.327
3.854
0.000
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O
O
H
Br
N
Bn
3ba
CDCl3 1HNMR 400 MHz
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9
8
7
6
5
4
3
2
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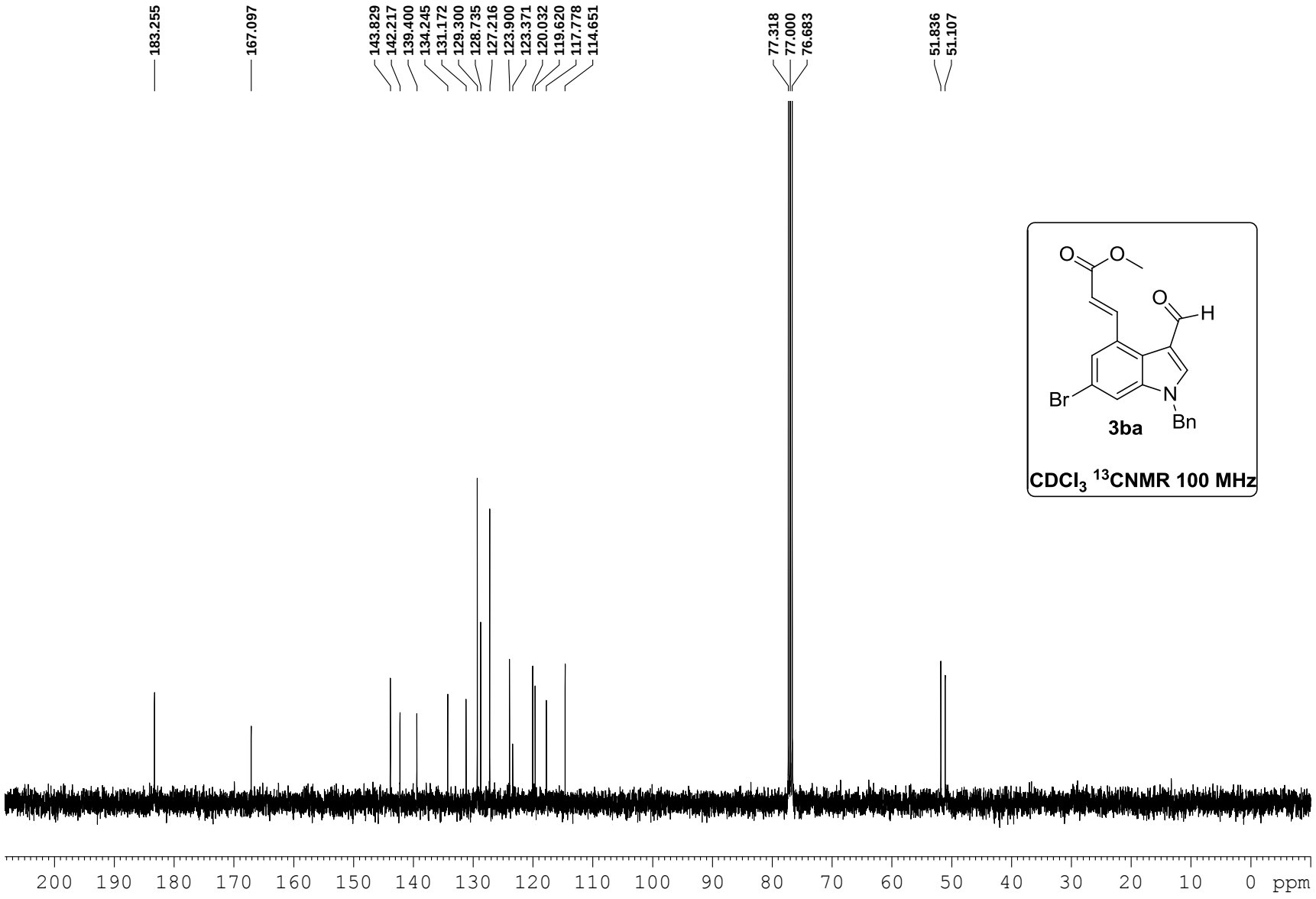
LVR-04043P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139.400
134.245
131.172
129.300
128.735
127.216
123.900
123.371
120.032
119.620
117.778
114.651
77.318
77.000
76.683
51.836
51.107
O
O
O
H
Br
N
Bn
3ba
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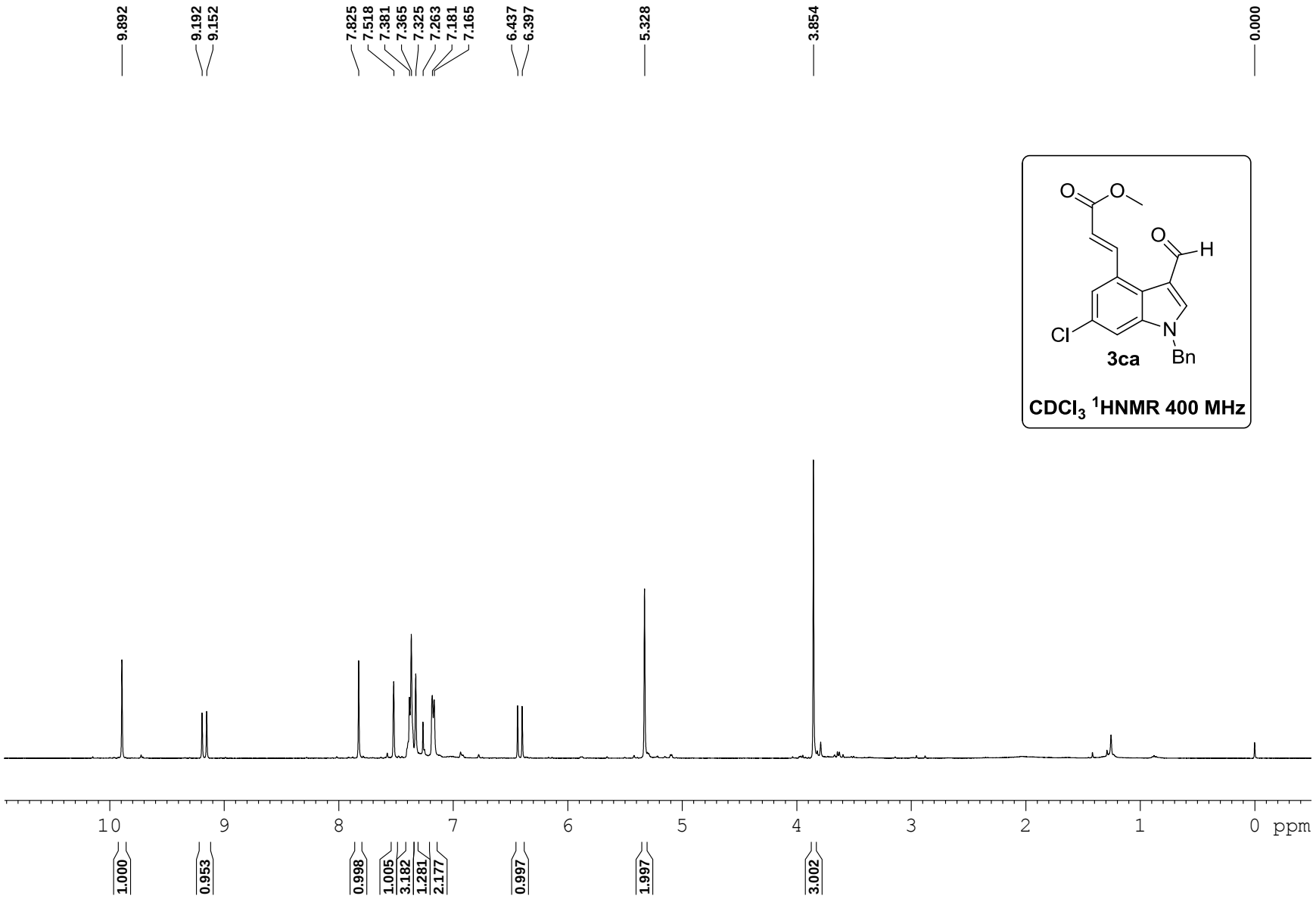
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6.397
5.328
3.854
0.000
O
O
O
H
Cl
N
Bn
3ca
CDCl3 1HNMR 400 MHz
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9
8
7
6
5
4
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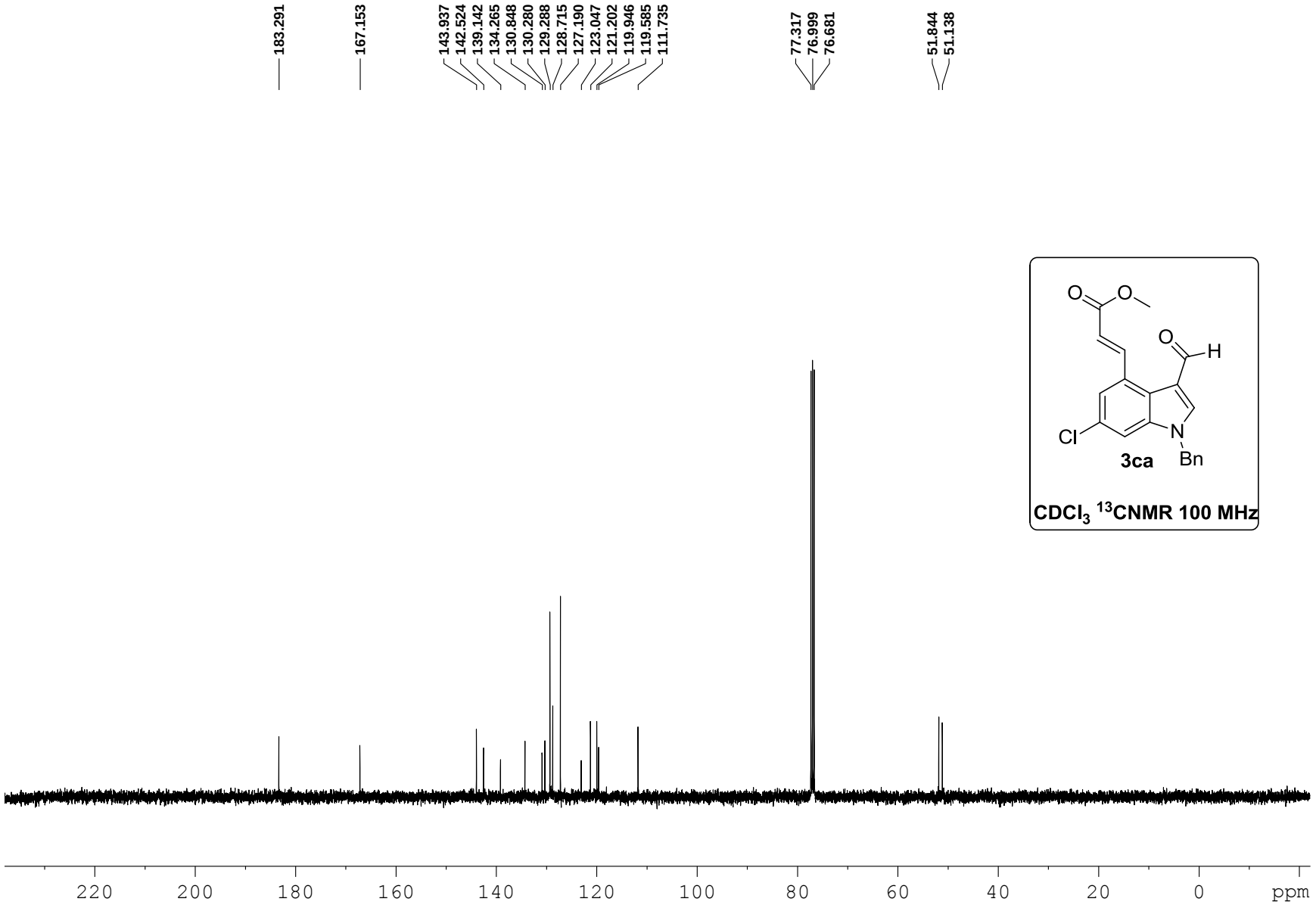
3.002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130.280
129.288
128.715
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121.202
119.946
119.585
111.735
77.317
76.999
76.681
51.844
51.138
O
O
O
H
Cl
N
Bn
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CDCl3 13CNMR 100 MHz
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200
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140
120
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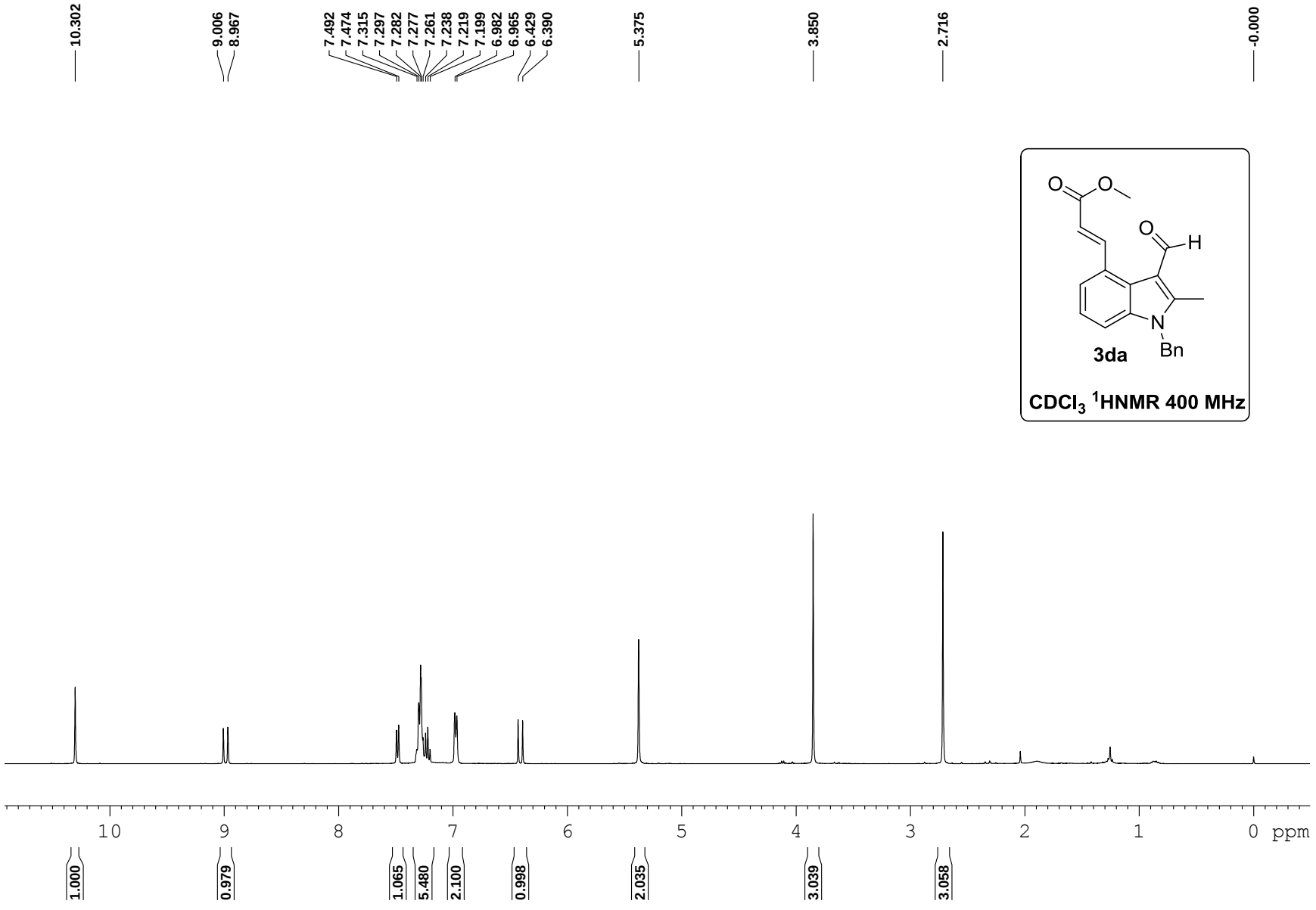
60
40
20
0
ppm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7.199
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6.965
6.429
6.390
5.375
3.850
2.716
-0.000
O
O
O
H
N
Bn
3da
CDCl3 1HNMR 400 MHz
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6
5
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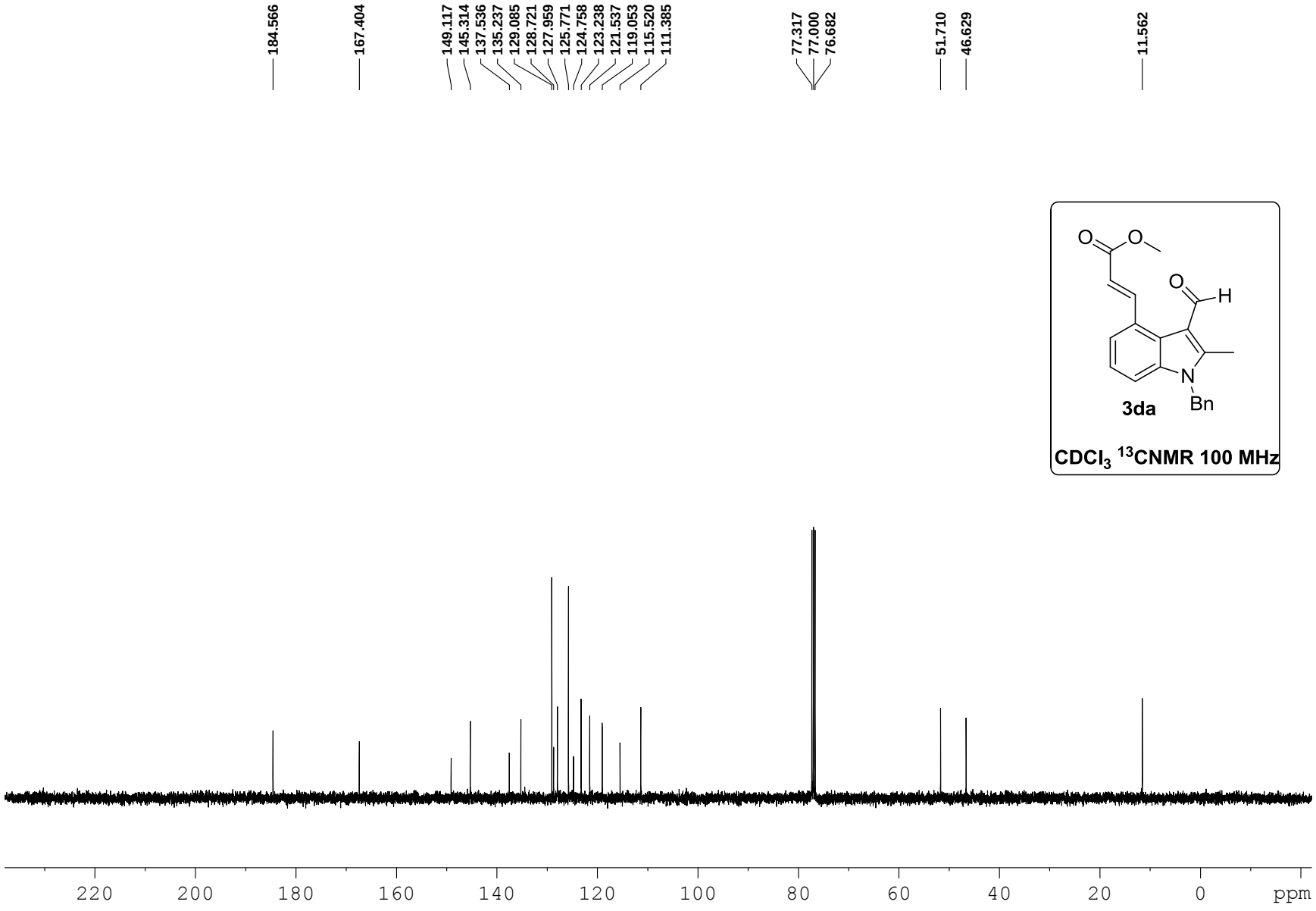
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O
H
N
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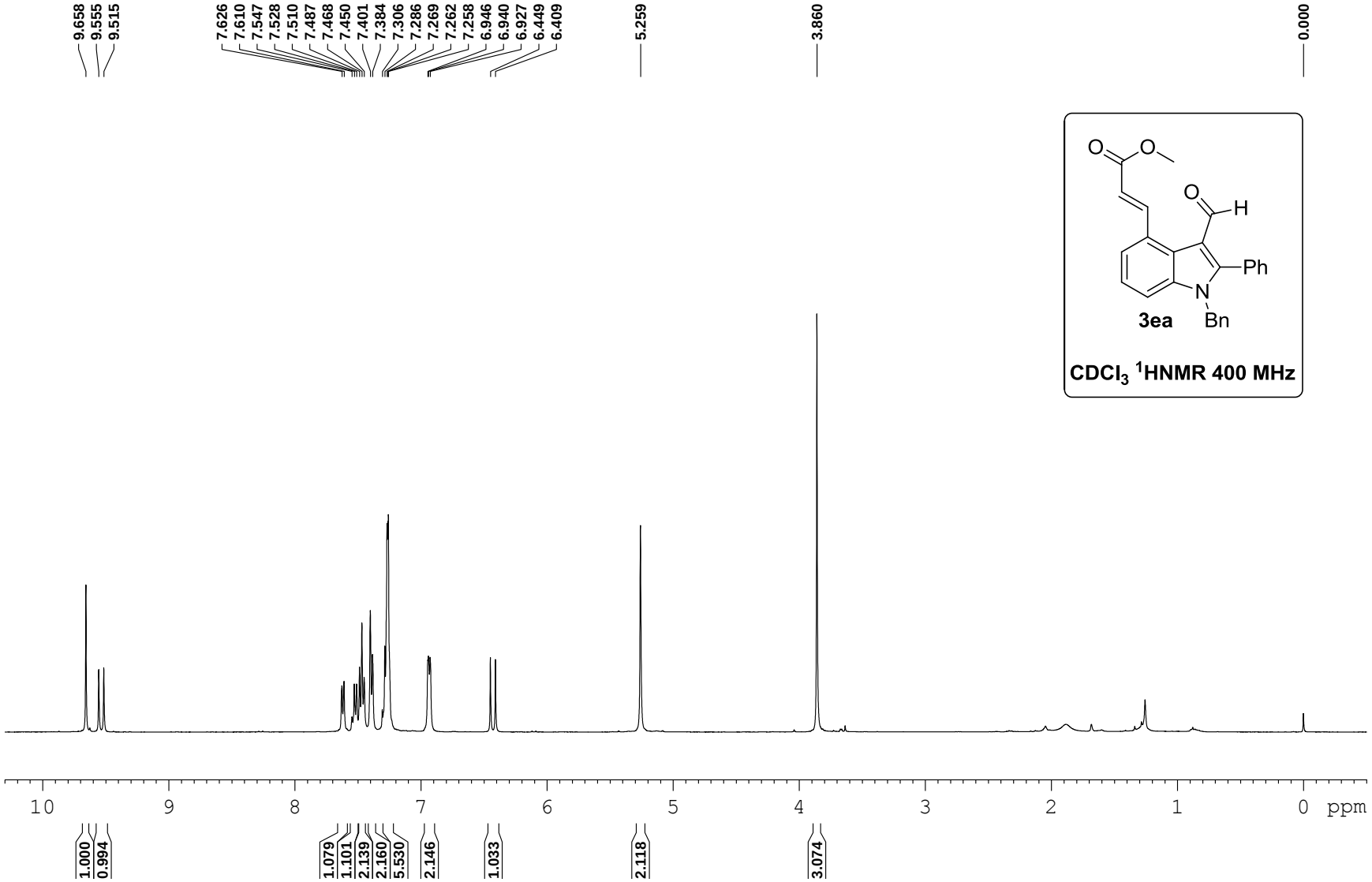
LVR-04058B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7.306
7.286
7.269
7.262
7.258
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6.940
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6.449
6.409
5.259
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N
Bn
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8
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6
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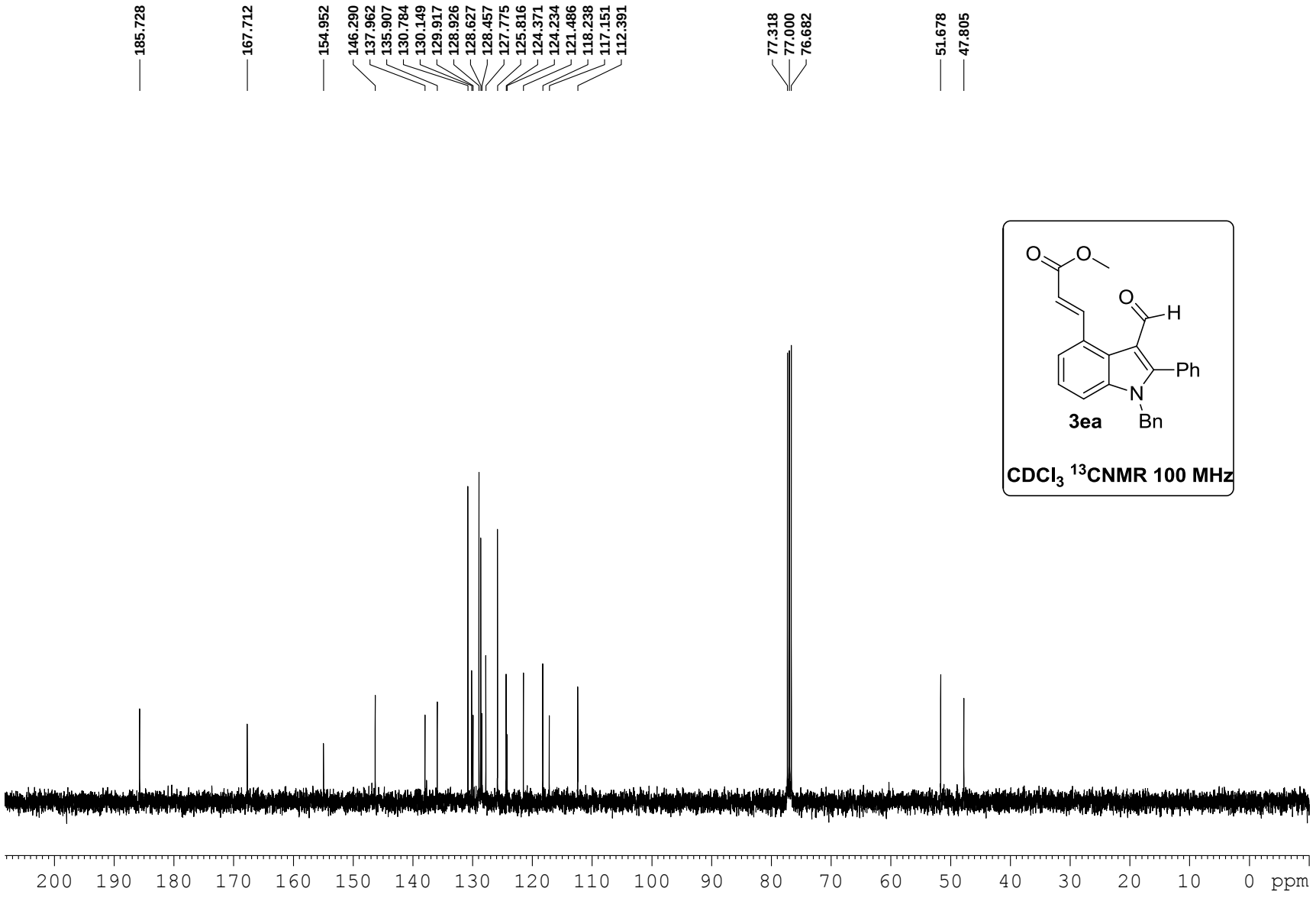
LVR-04058B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117.151
112.391
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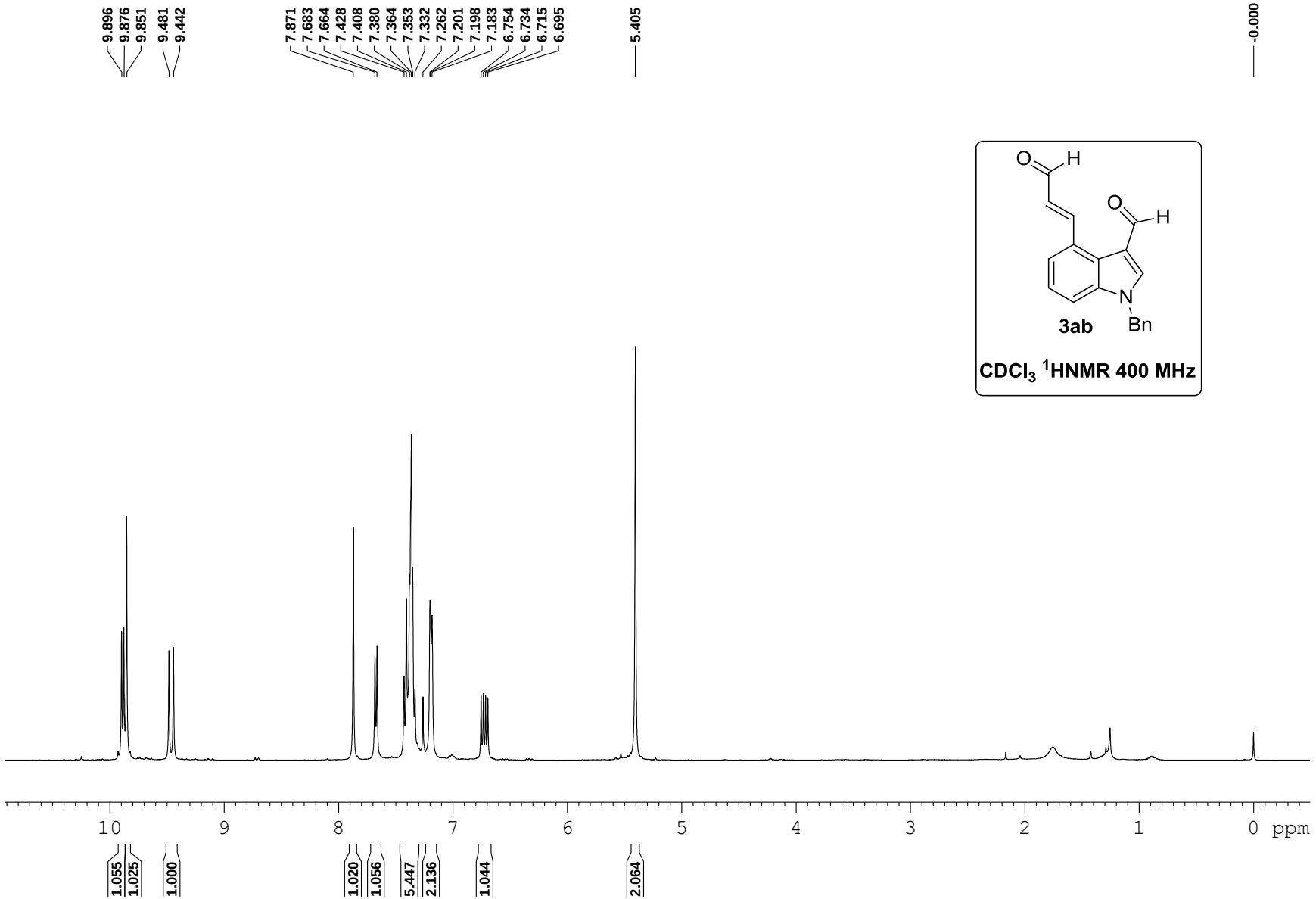
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7.353
7.332
7.262
7.201
7.198
7.183
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6.734
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H
O
H
N
Bn
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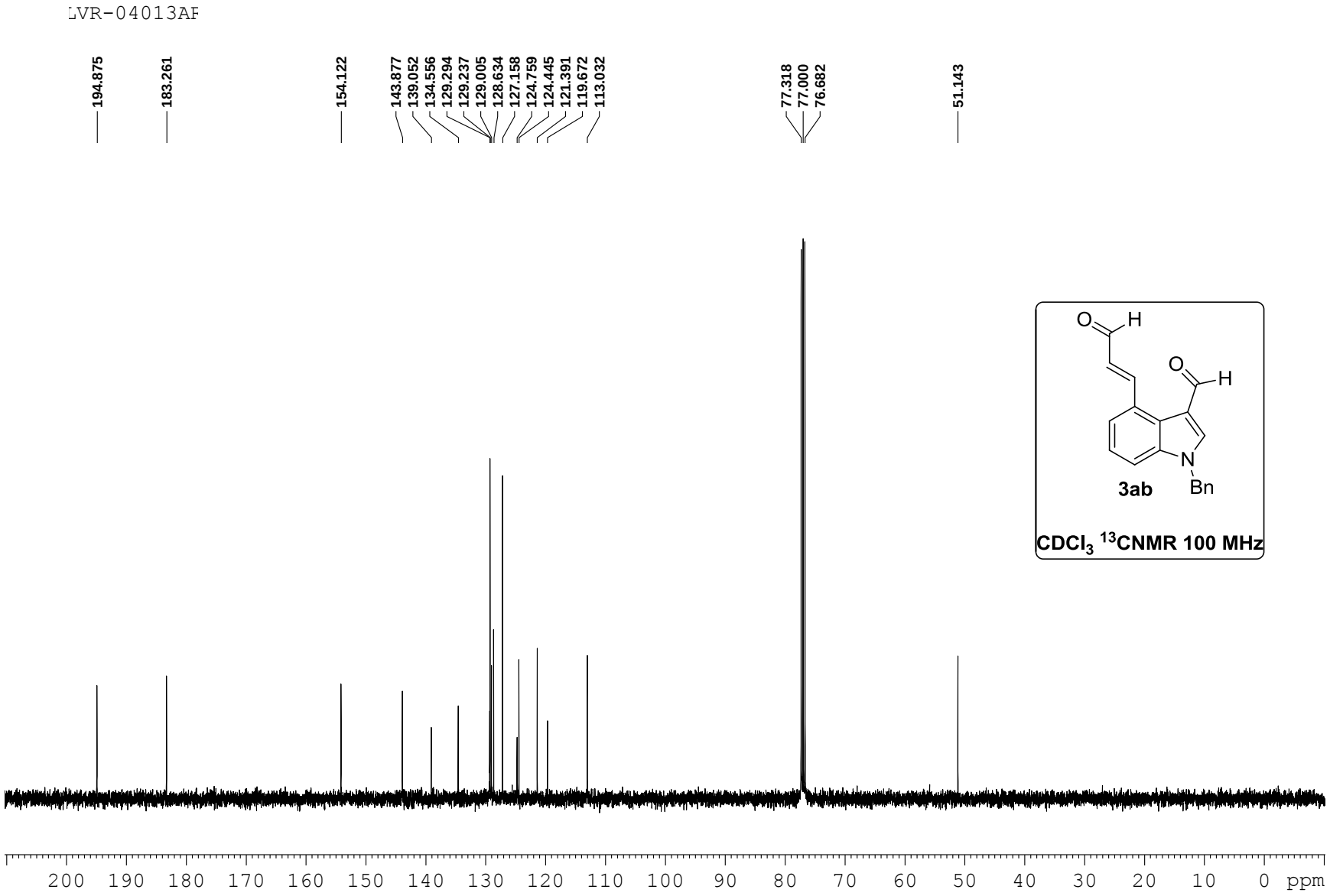
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121.391
119.672
113.032
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77.000
76.682
51.143
O
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H
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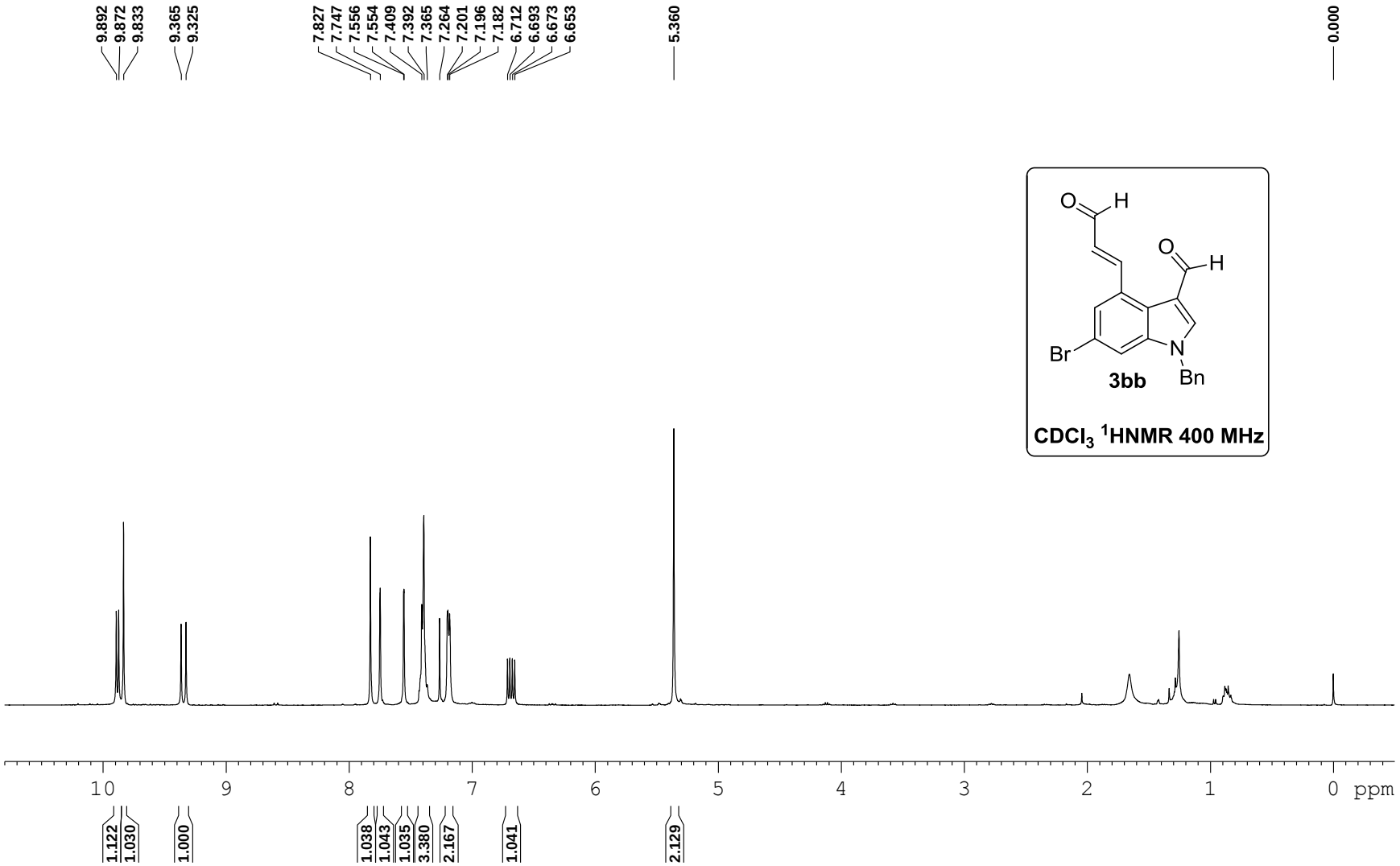
LVR-04042P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O
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Br
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CDCl3 1HNMR 400 MHz
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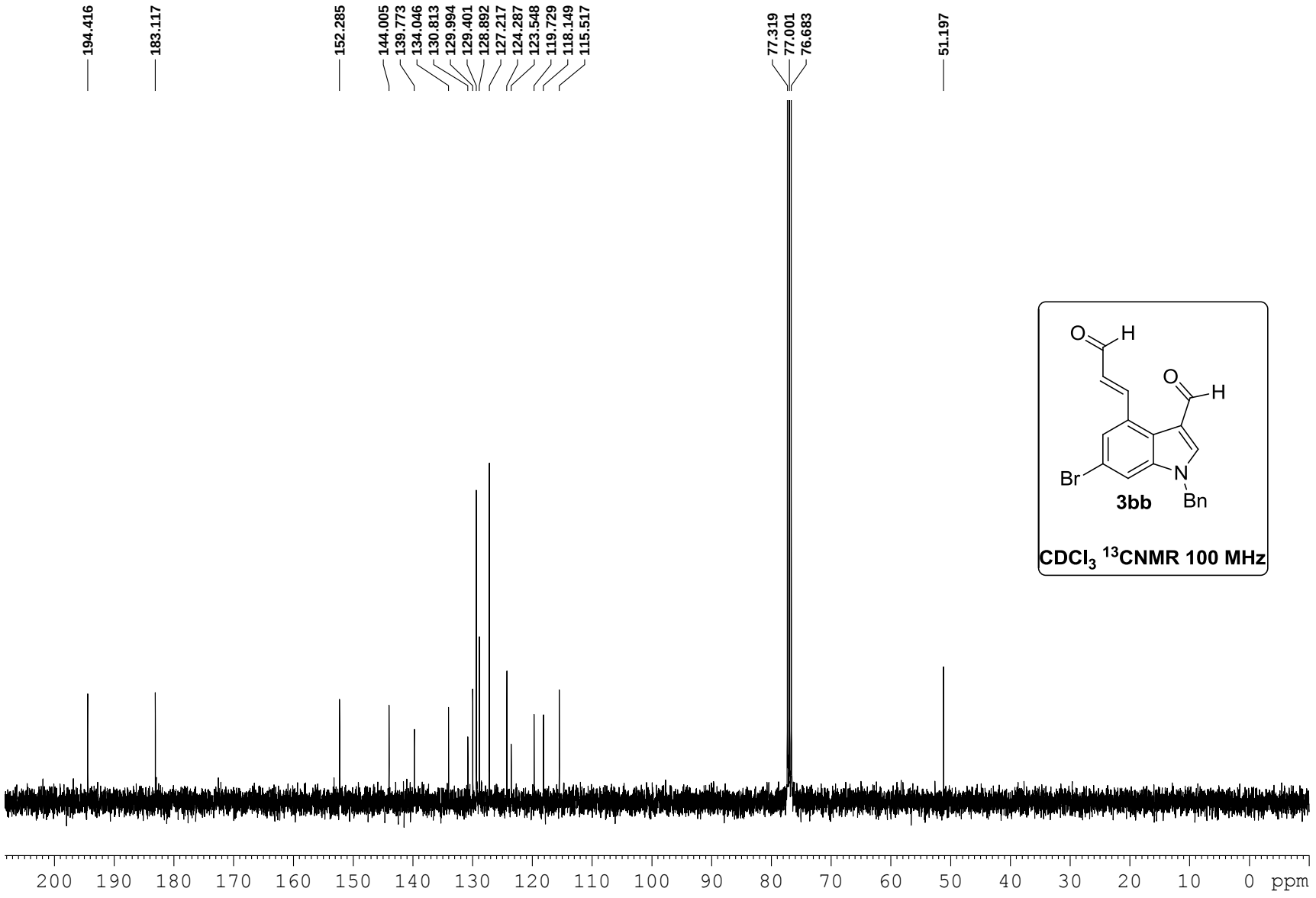
LVR-04042P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H
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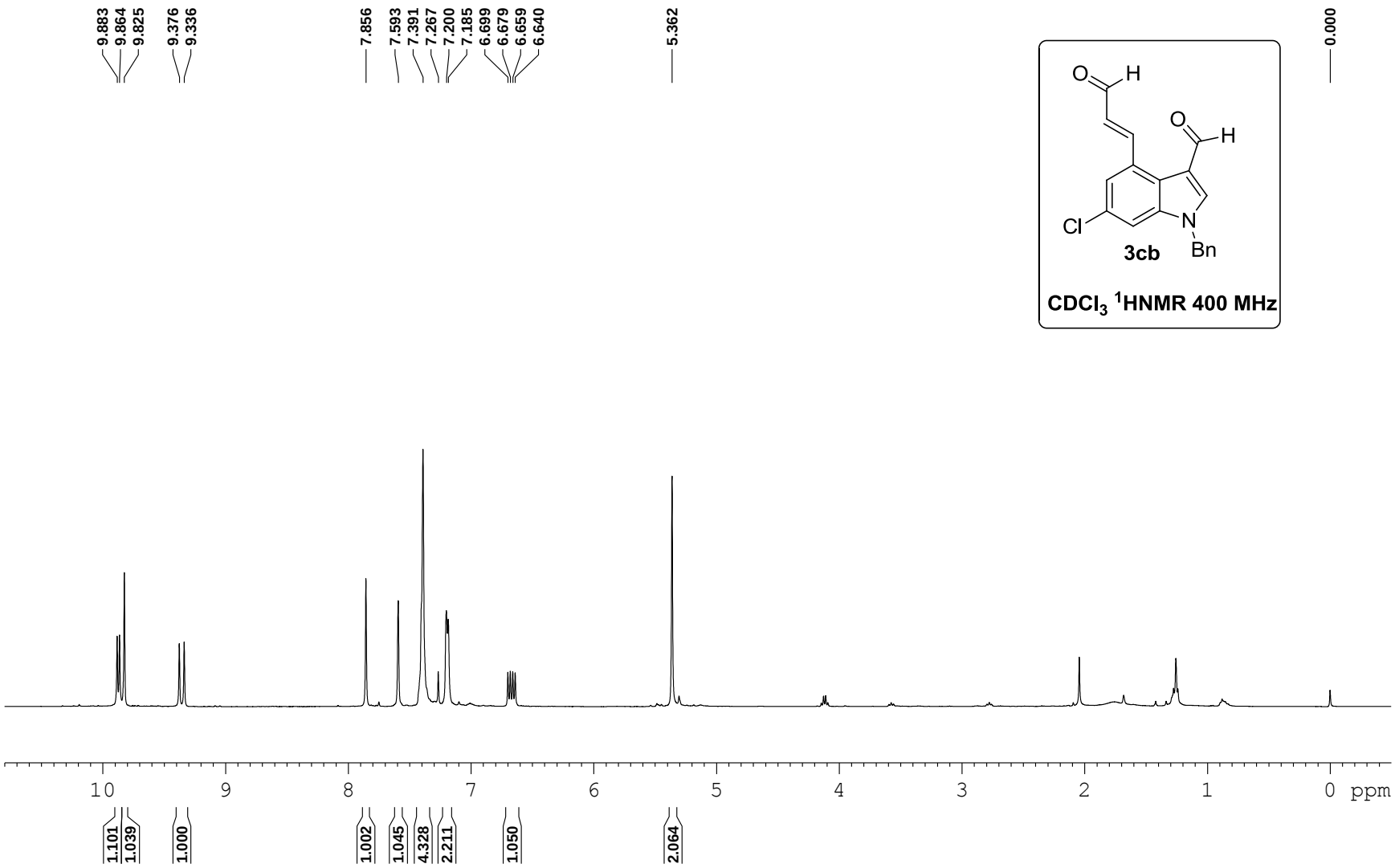
LVR-04031B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7
6
5
4
3
2
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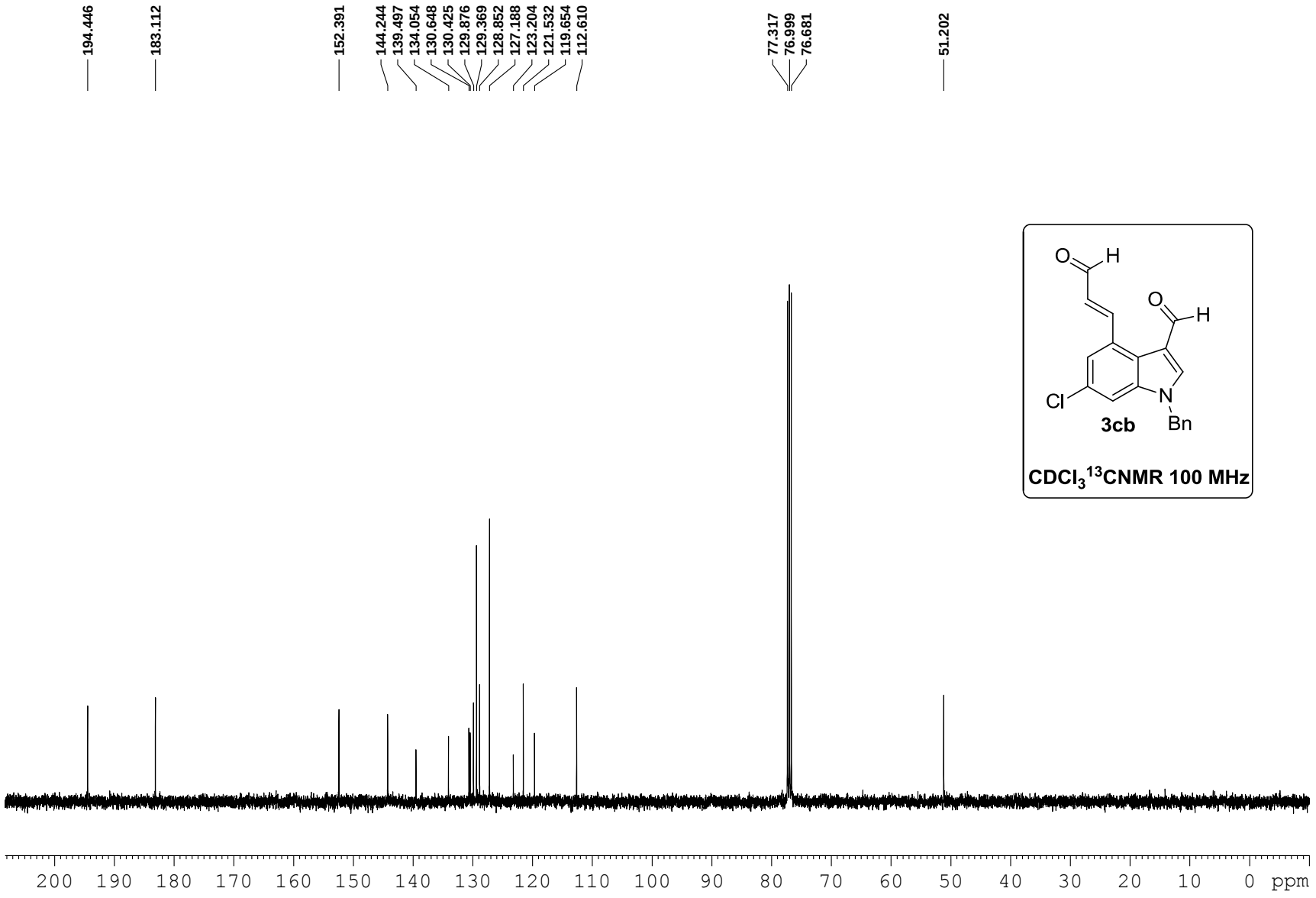
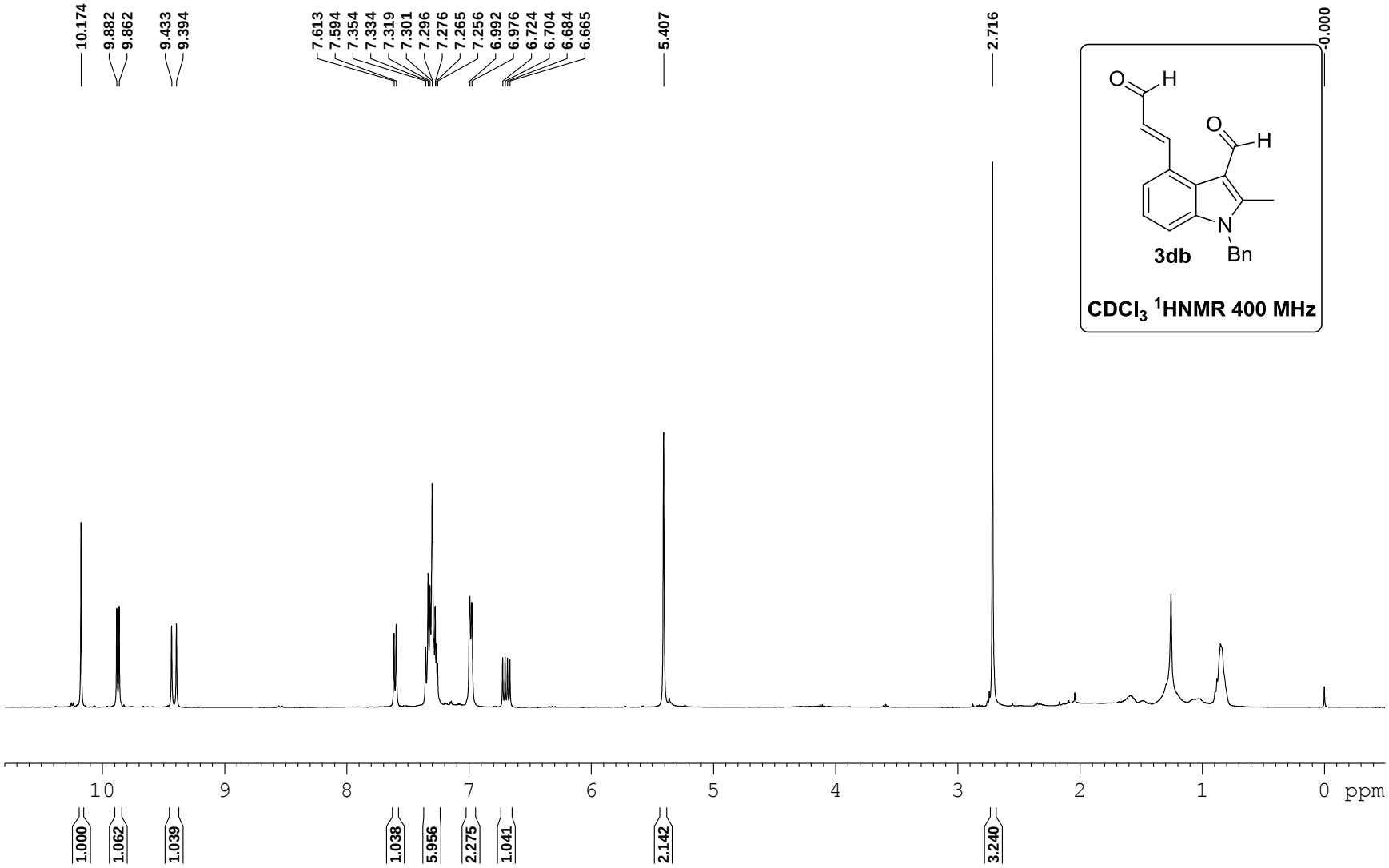
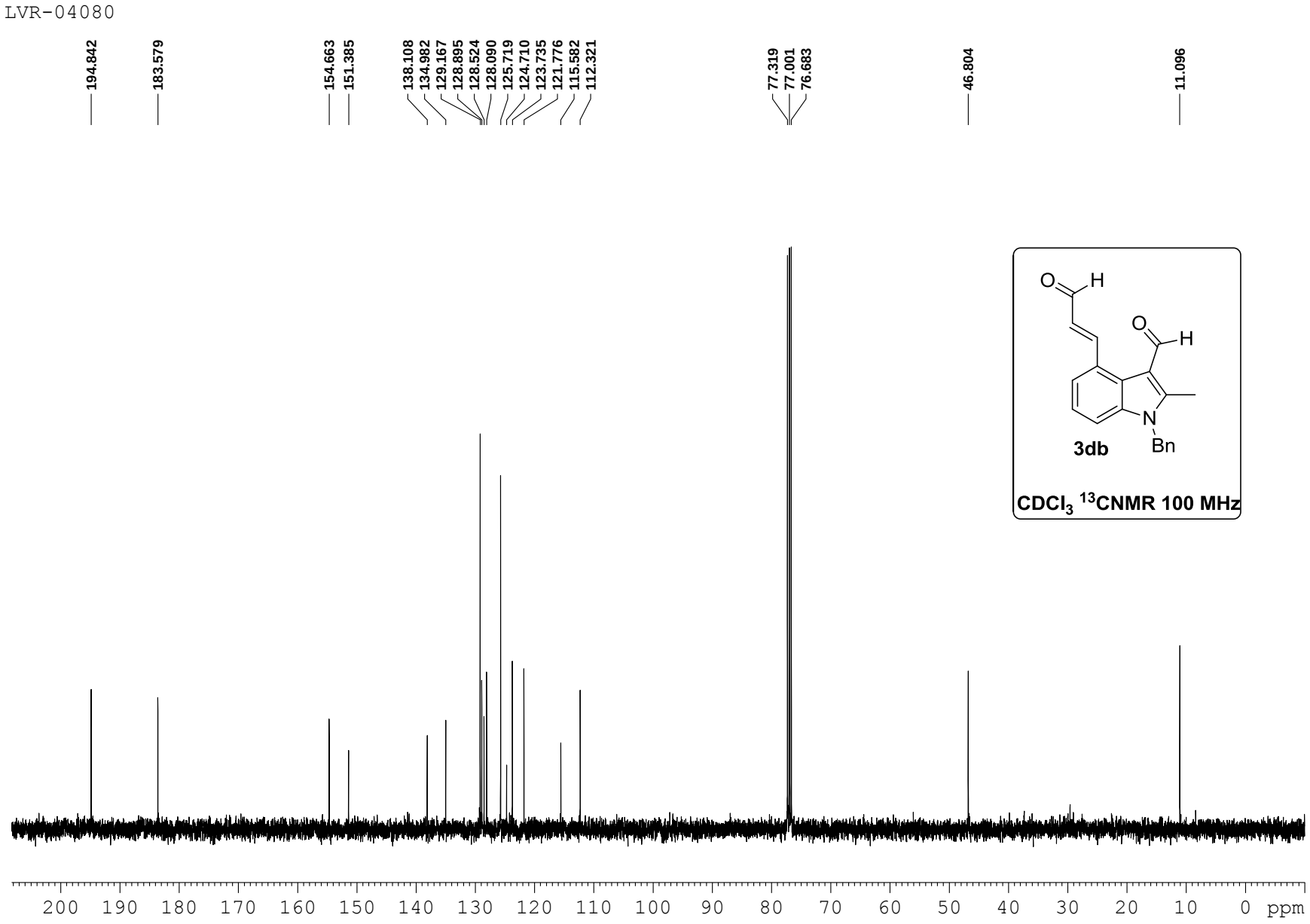
2.211
1.050
2.064

LVR-04031B

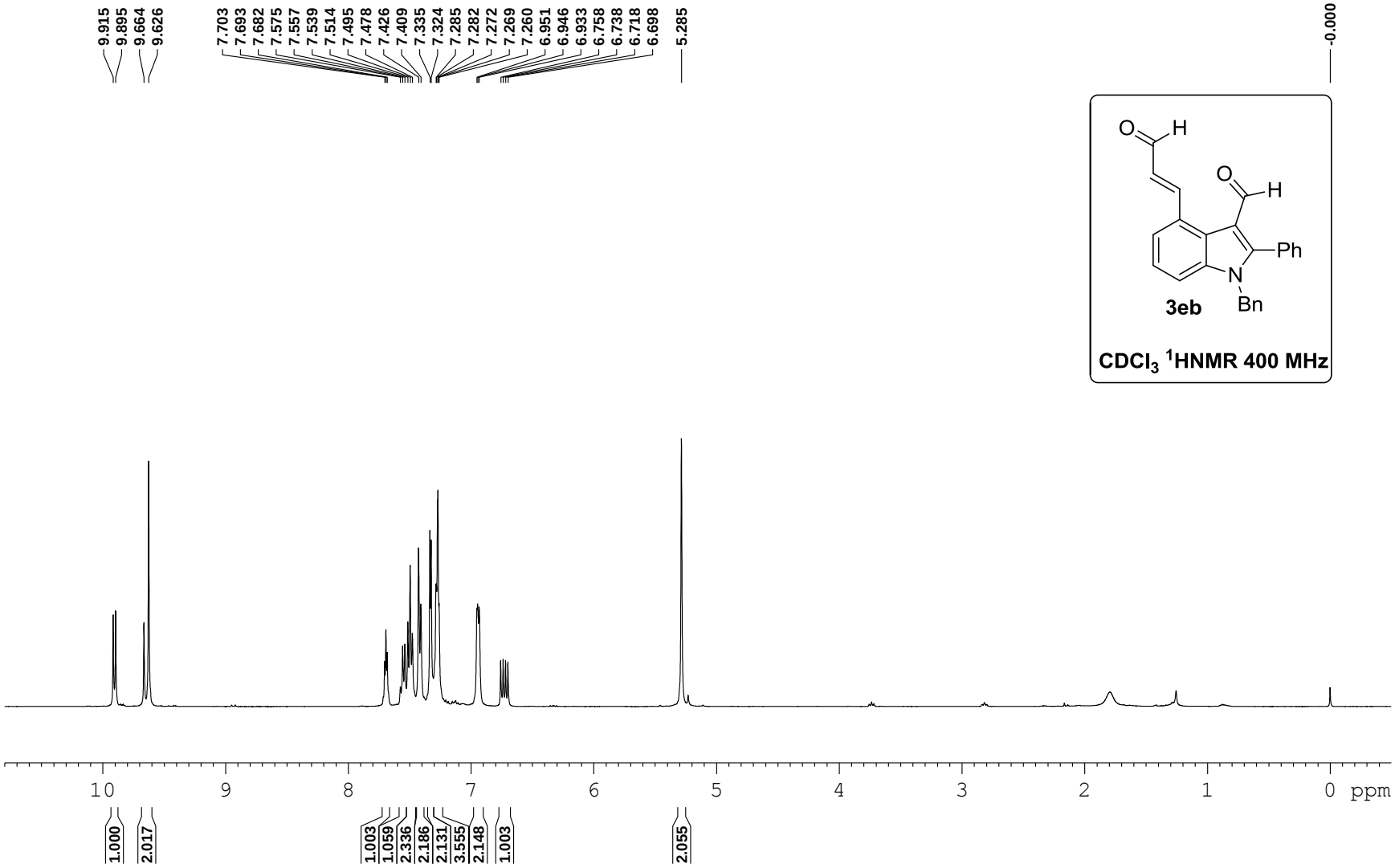

194.446
183.112
152.391
144.244
139.497
134.054
130.648
130.425
129.876
129.369
128.852
127.188
123.204
121.532
119.654
112.610
77.317
76.999
76.681
51.202
O
H
O
H
Cl
N
Bn
3cb
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

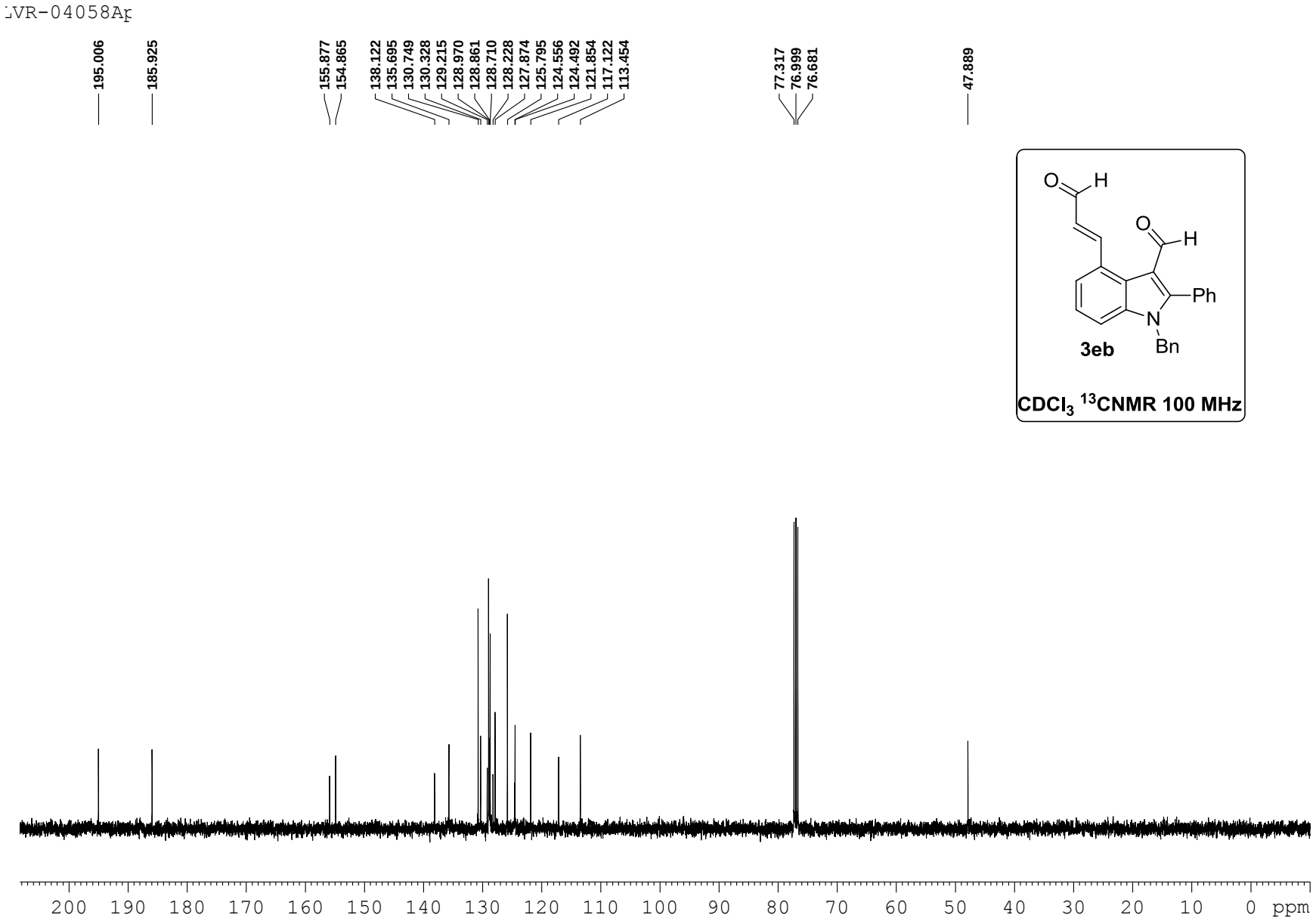
LVR-04080


10.174
9.882
9.862
9.433
9.394
7.613
7.594
7.354
7.334
7.319
7.301
7.296
7.276
7.265
7.256
6.992
6.976
6.724
6.704
6.684
6.665
5.407
2.716
0.000
O
H
O
H
N
Bn
3db
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.062
1.039
1.038
5.956
2.275
1.041
2.142
3.240

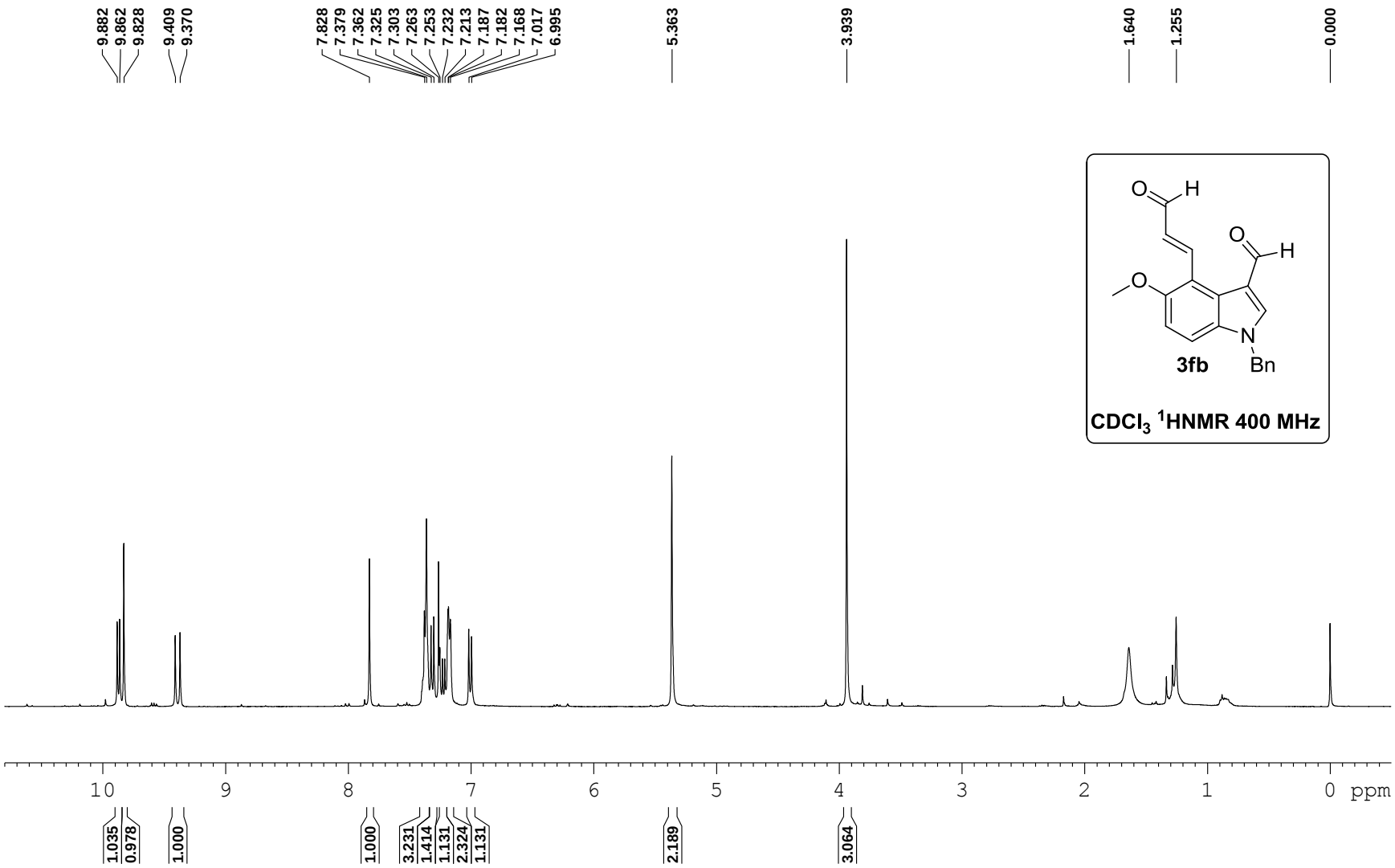

LVR-04080
194.842
183.579
154.663
151.385
138.108
134.982
129.167
128.895
128.524
128.090
125.719
124.710
123.735
121.776
115.582
112.321
77.319
77.001
76.683
46.804
11.096
O
H
O
H
N
Bn
3db
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

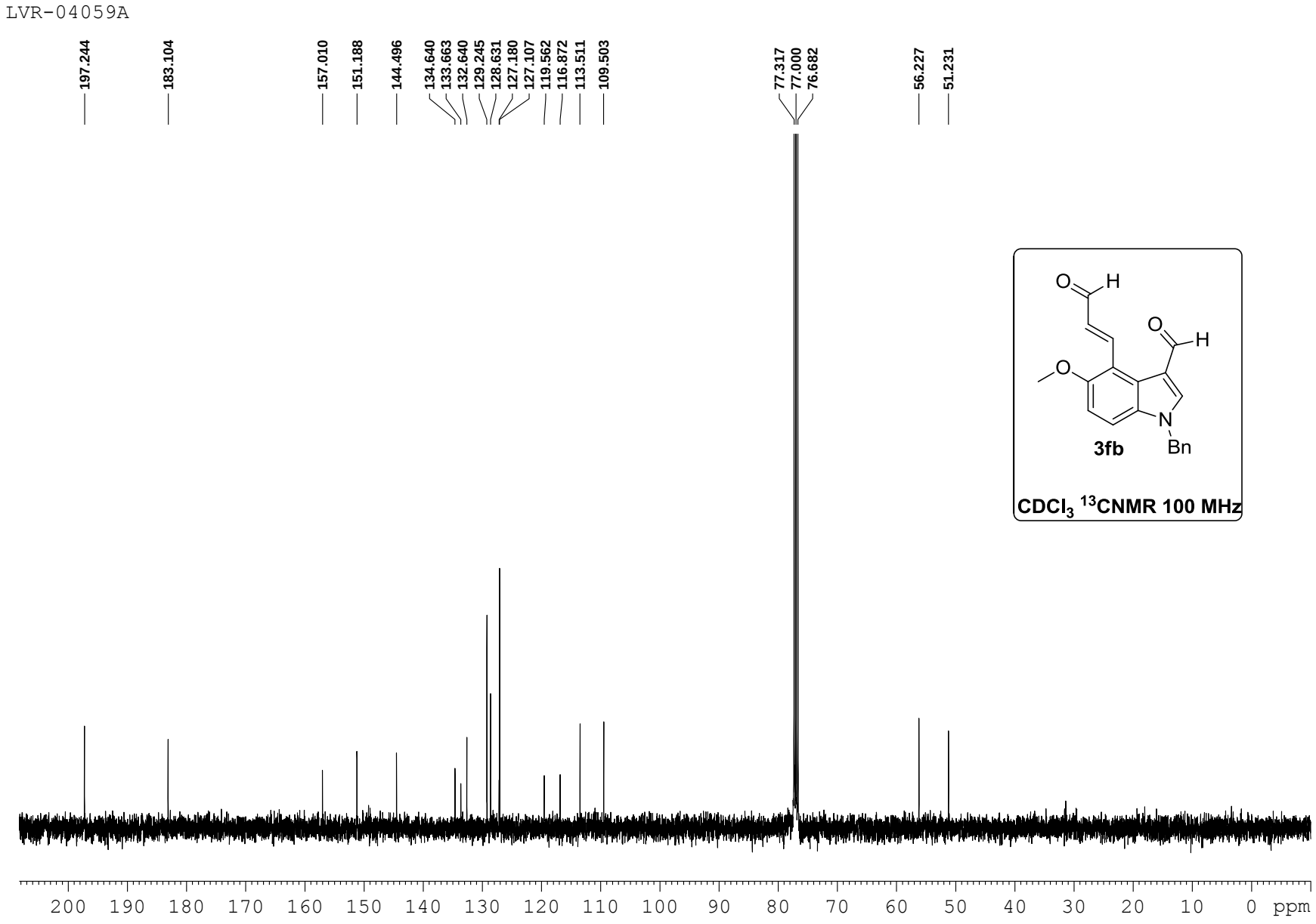
LVR-04058A


9.915
9.895
9.664
9.626
7.703
7.693
7.682
7.575
7.557
7.539
7.514
7.495
7.478
7.426
7.409
7.335
7.324
7.285
7.282
7.272
7.269
7.260
6.951
6.946
6.933
6.758
6.738
6.718
6.698
5.285
-0.000
O
H
O
H
Ph
N
Bn
3eb
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
2.017
1.003
1.059
2.336
2.186
2.131
3.555
2.148
1.003
2.055

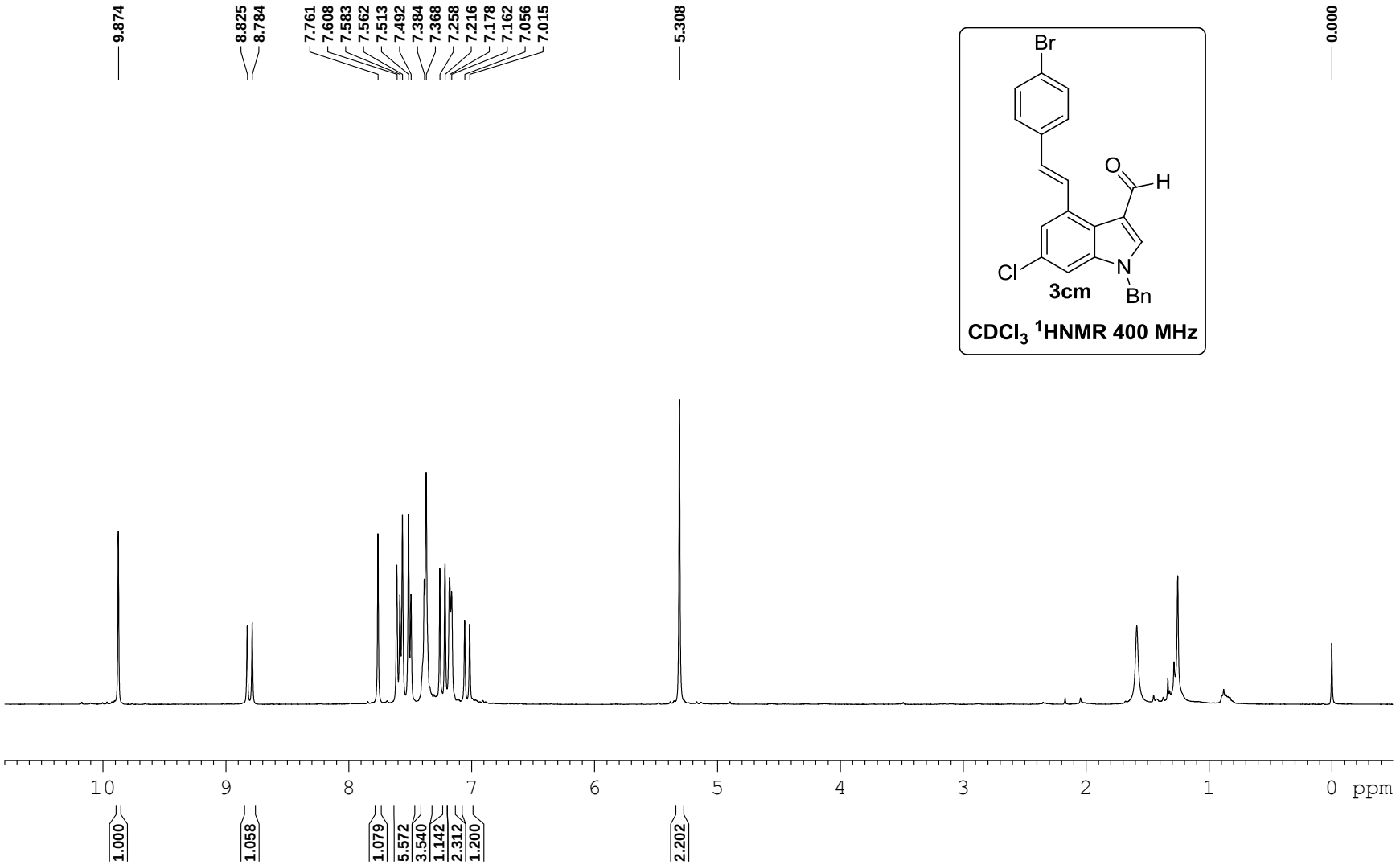

LVR-04058Ap
195.006
185.925
155.877
154.865
138.122
135.695
130.749
130.328
129.215
128.970
128.861
128.710
128.228
127.874
125.795
124.556
124.492
121.854
117.122
113.454
77.317
76.999
76.681
47.889
O
H
O
H
Ph
N
Bn
3eb
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

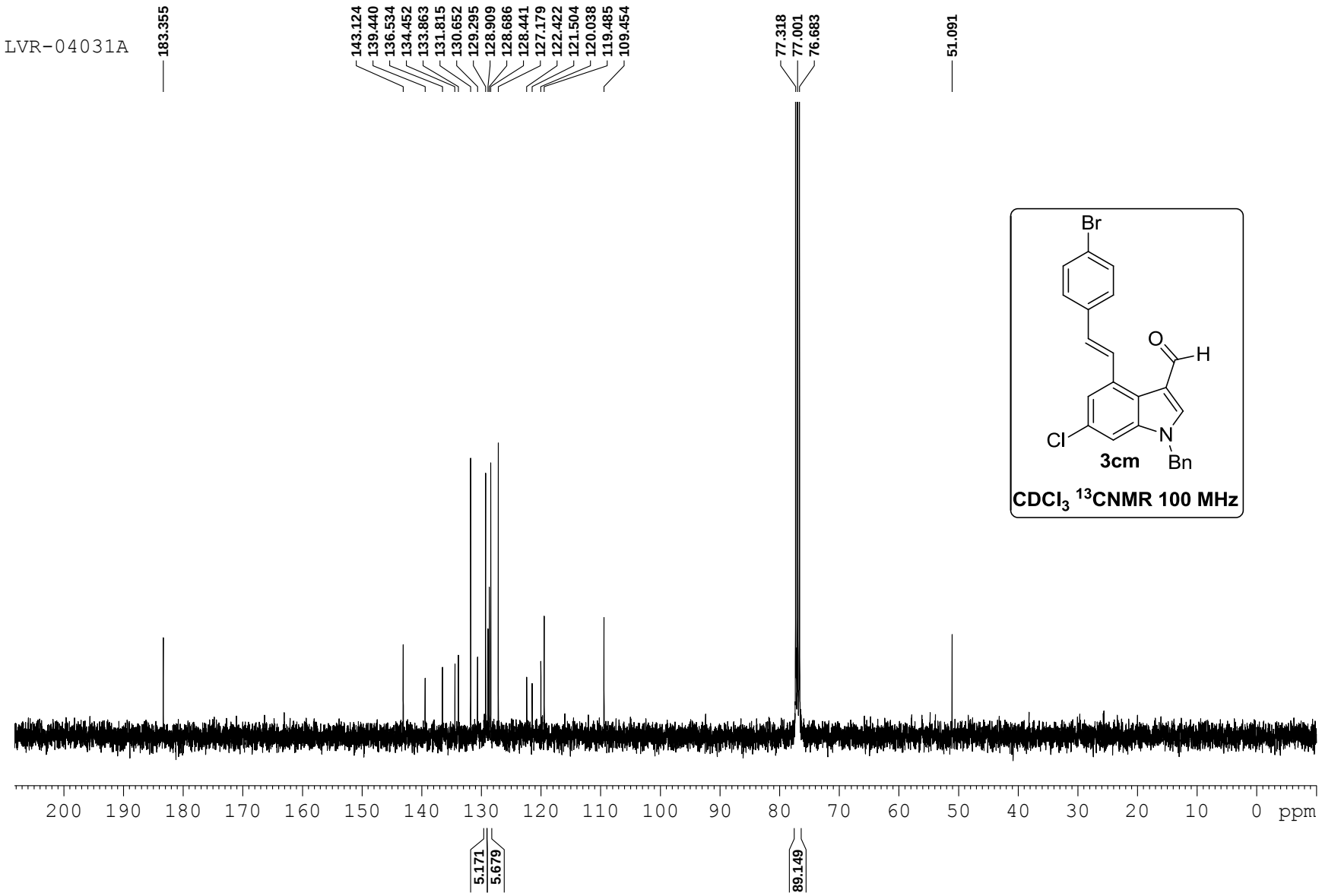
LVR-04059A

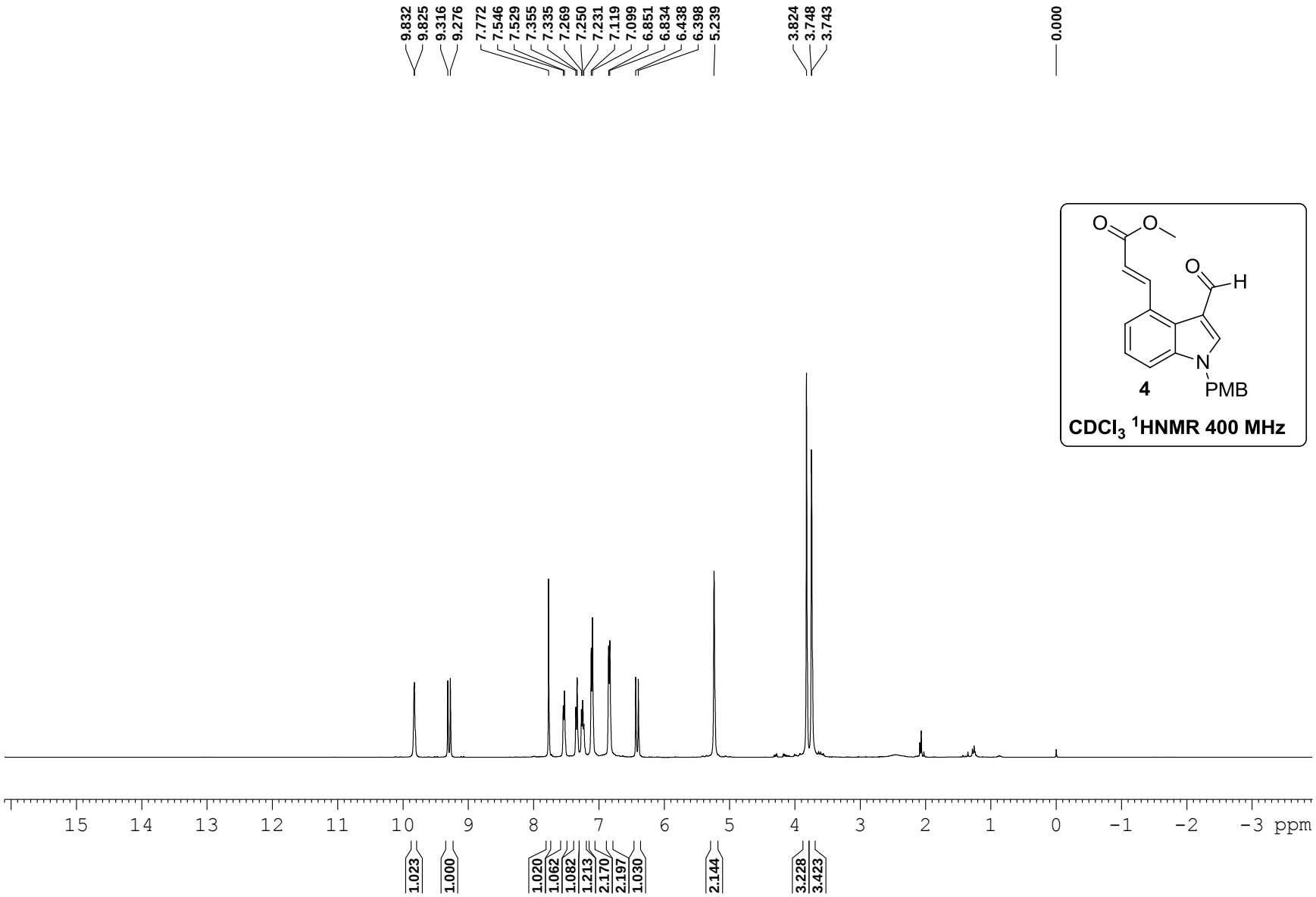

9.882
9.862
9.828
9.409
9.370
7.828
7.379
7.362
7.325
7.303
7.263
7.253
7.232
7.213
7.187
7.182
7.168
7.017
6.995
5.363
3.939
1.640
1.255
0.000
3fb
Bn
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.035
0.978
1.000
1.000
3.231
1.414
1.131
2.324
1.131
2.189
3.064

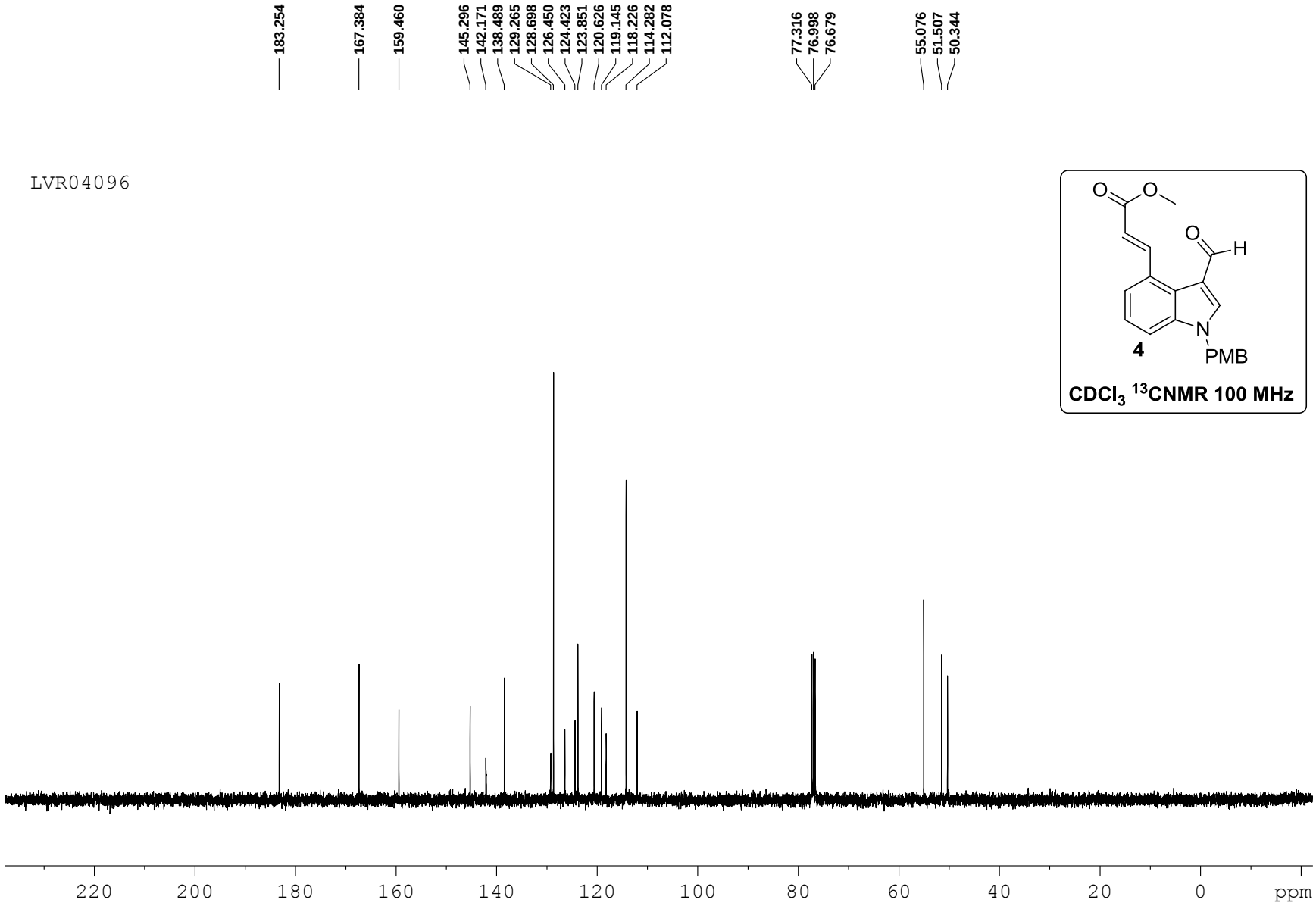

LVR-04059A
197.244
183.104
157.010
151.188
144.496
134.640
133.663
132.640
129.245
128.631
127.180
127.107
119.562
116.872
113.511
109.503
77.317
77.000
76.682
56.227
51.231
O
H
O
H
O
N
Bn
3fb
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

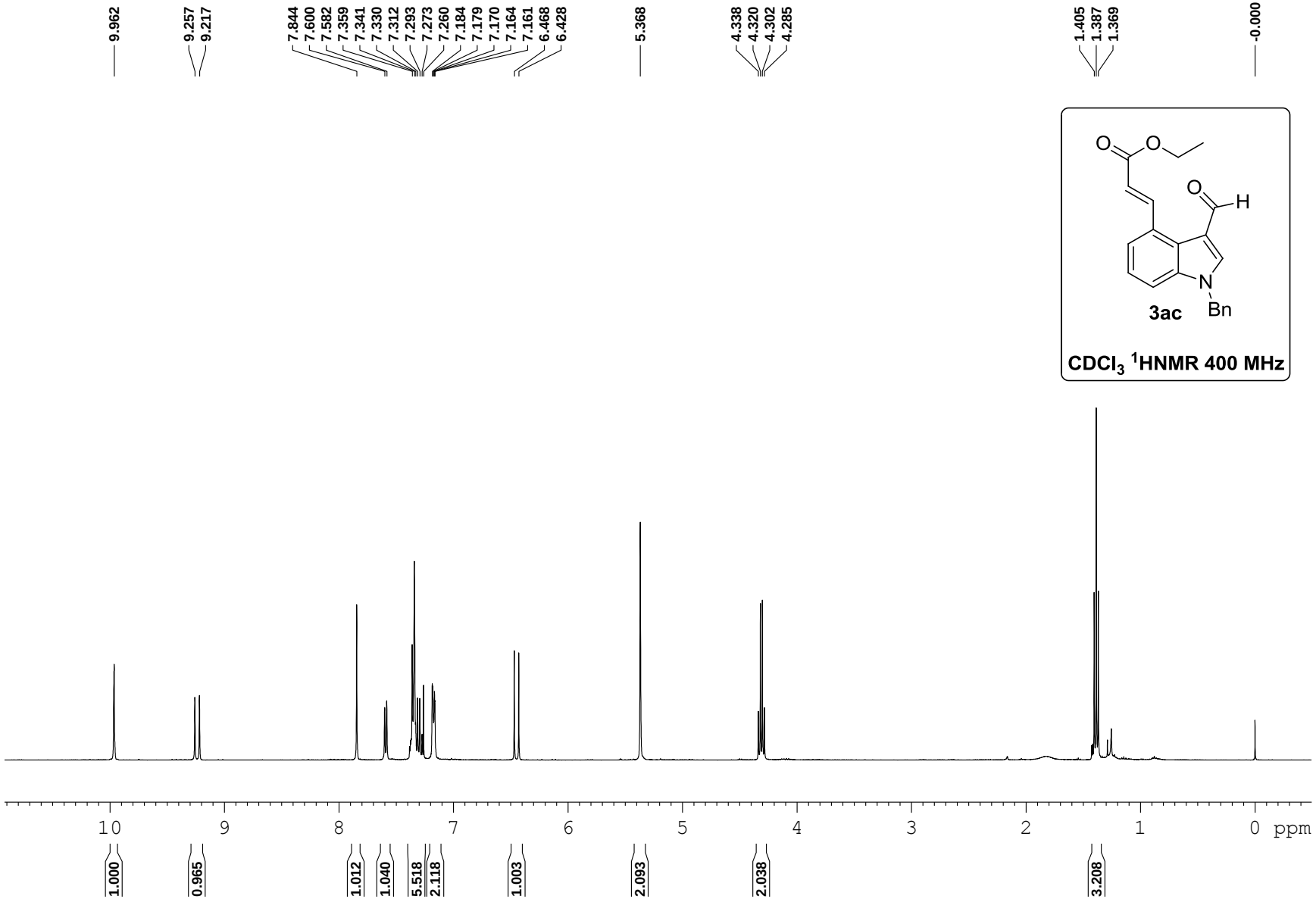
LVR-04031A

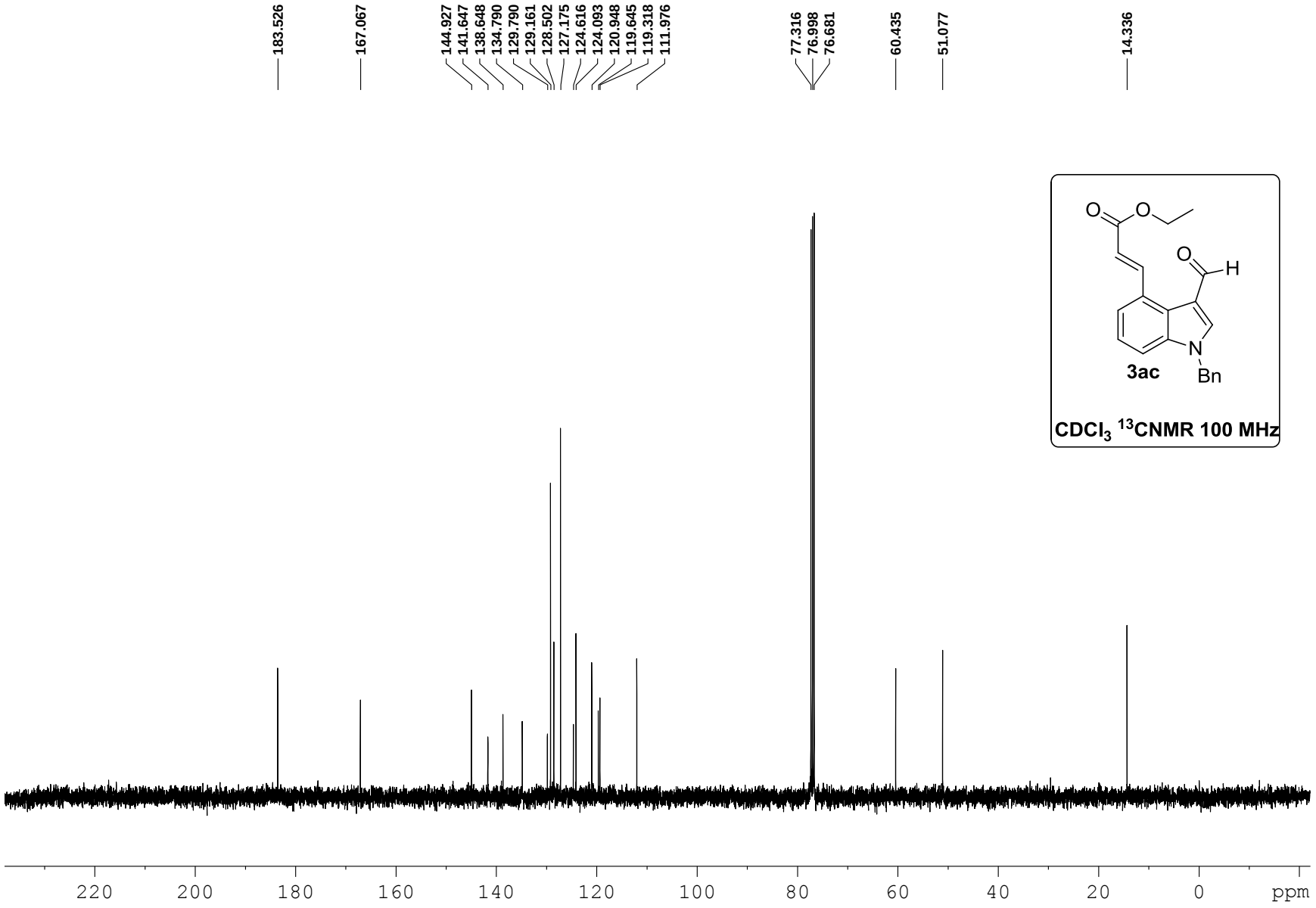

9.874
8.825
8.784
7.761
7.608
7.583
7.562
7.513
7.492
7.384
7.368
7.258
7.216
7.178
7.162
7.056
7.015
5.308
0.000
Br
O
H
Cl
N
Bn
3cm
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.058
1.079
5.572
3.540
1.142
2.312
1.200
2.202

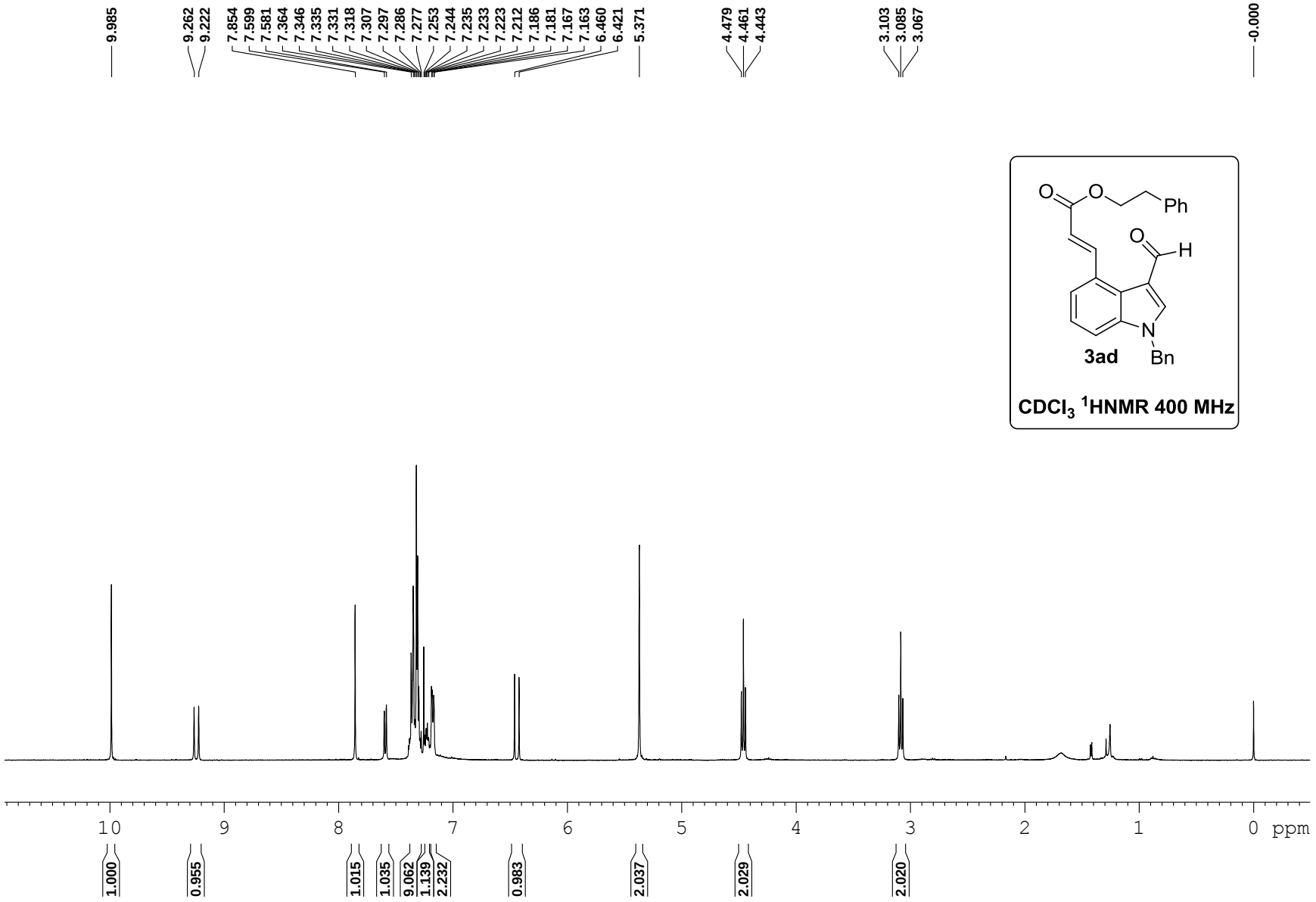

LVR-04031A
183.355
143.124
139.440
136.534
134.452
133.863
131.815
130.652
129.295
128.909
128.686
128.441
127.179
122.422
121.504
120.038
119.485
109.454
77.318
77.001
76.683
51.091
Br
O
H
Cl
N
Bn
3cm
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
5.171
5.679
89.149

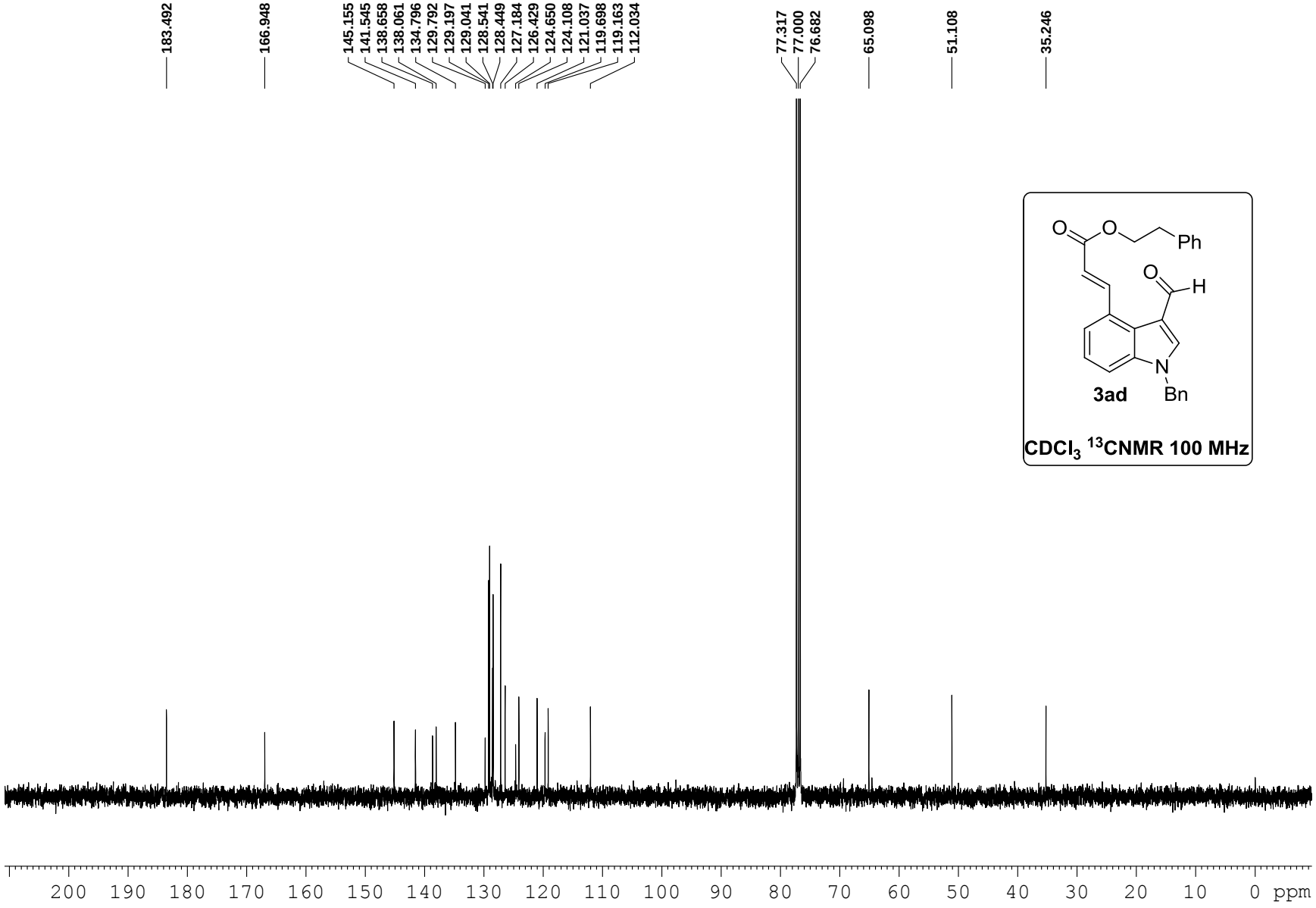

9.832
9.825
9.316
9.276
7.772
7.546
7.529
7.355
7.335
7.269
7.250
7.231
7.119
7.099
6.851
6.834
6.438
6.398
5.239
3.824
3.748
3.743
0.000
O
O
O
H
N
PMB
4
CDCl3 1HNMR 400 MHz
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
1.023
1.000
1.020
1.062
1.082
1.213
2.170
2.197
1.030
2.144
3.228
3.423


183.254
167.384
159.460
145.296
142.171
138.489
129.265
128.698
126.450
124.423
123.851
120.626
119.145
118.226
114.282
112.078
77.316
76.998
76.679
55.076
51.507
50.344
LVR04096
O
O
O
H
N
PMB
4
CDCl3 13CNMR 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0
ppm

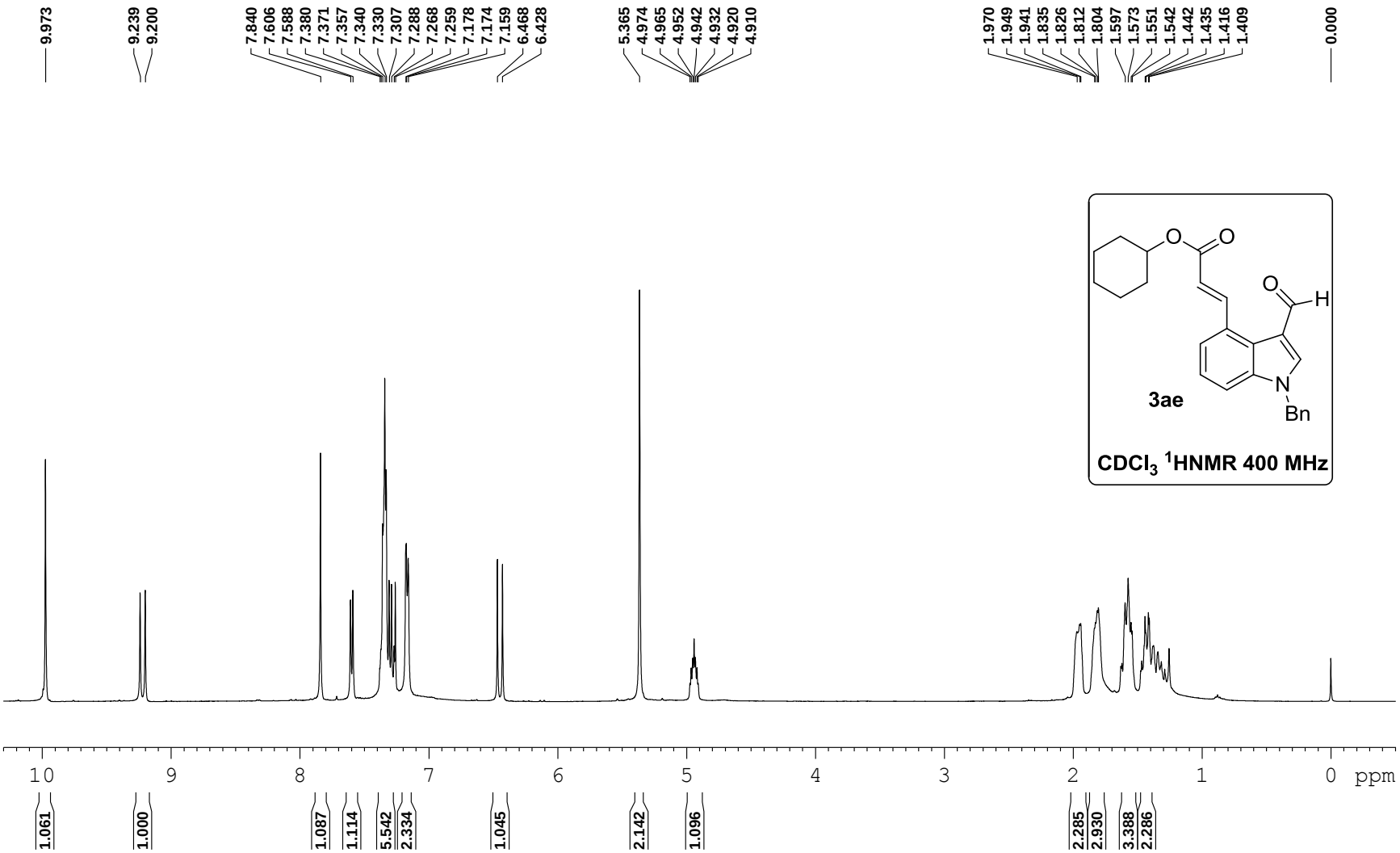

9.962
9.257
9.217
7.844
7.600
7.582
7.359
7.341
7.330
7.312
7.293
7.273
7.260
7.184
7.179
7.170
7.164
7.161
6.468
6.428
5.368
4.338
4.320
4.302
4.285
1.405
1.387
1.369
-0.000
O
O
O
H
N
Bn
3ac
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.965
1.012
1.040
5.518
2.118
1.003
2.093
2.038
3.208

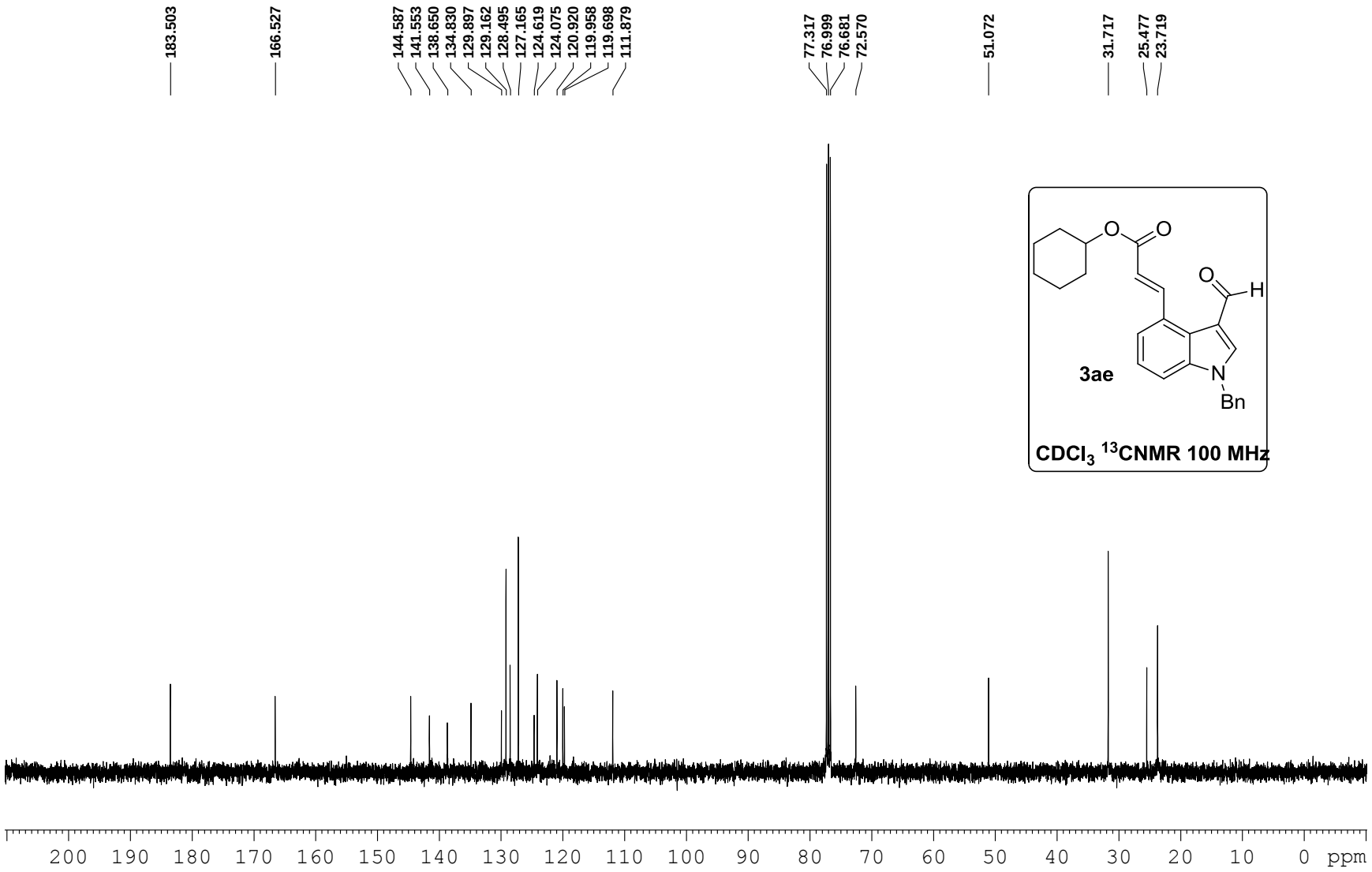

183.526
167.067
144.927
141.647
138.648
134.790
129.790
129.161
128.502
127.175
124.616
124.093
120.948
119.645
119.318
111.976
77.316
76.998
76.681
60.435
51.077
14.336
O
O
O
H
N
Bn
3ac
CDCl3 13CNMR 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0
ppm

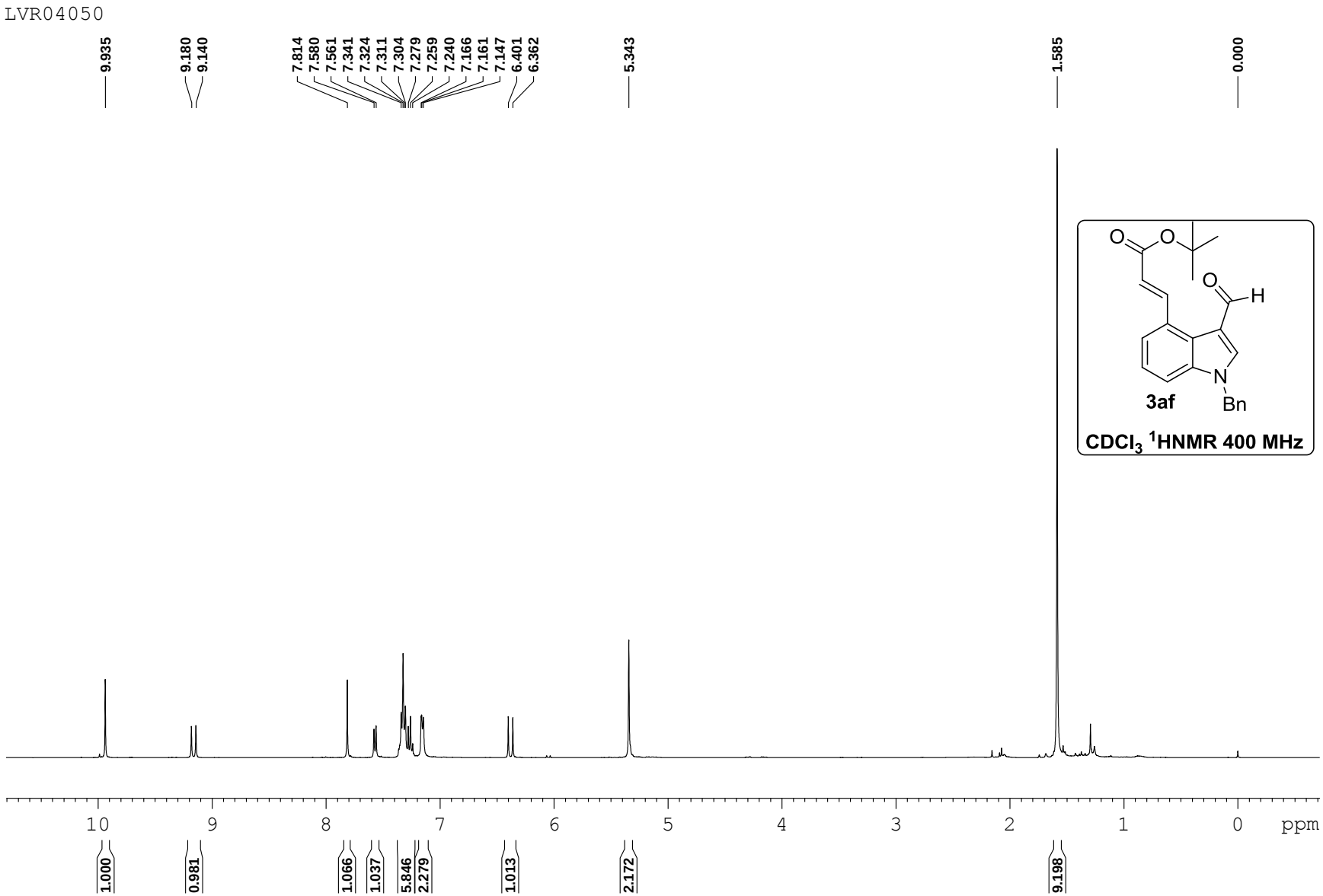

9.985
9.262
9.222
7.854
7.599
7.581
7.364
7.346
7.335
7.331
7.318
7.307
7.297
7.286
7.277
7.253
7.244
7.235
7.233
7.223
7.212
7.186
7.181
7.167
7.163
6.460
6.421
5.371
4.479
4.461
4.443
3.103
3.085
3.067
-0.000
O
O
Ph
O
H
N
Bn
3ad
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.955
1.015
1.035
9.062
1.139
2.232
0.983
2.037
2.029
2.020

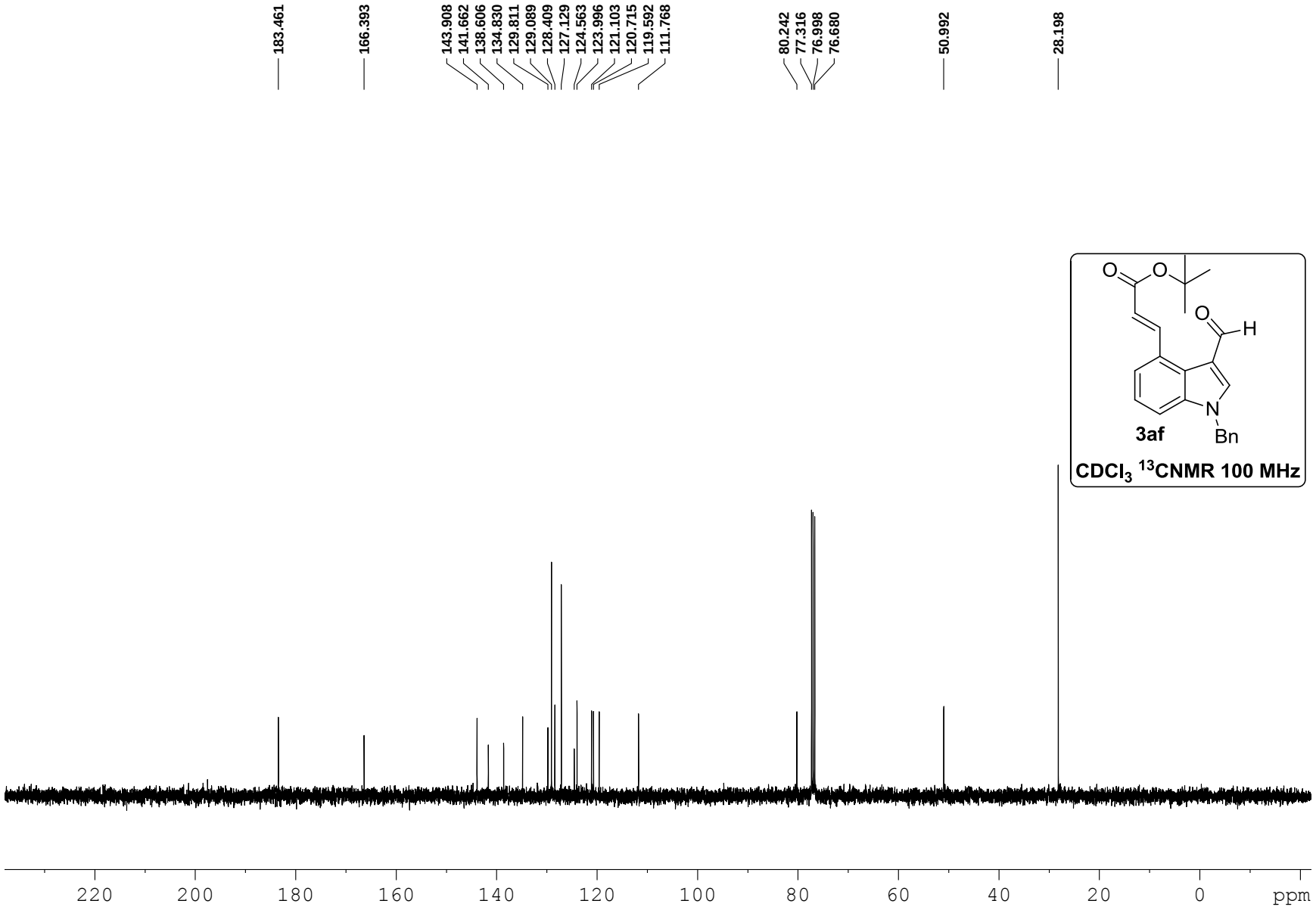

183.492
166.948
145.155
141.545
138.658
138.061
134.796
129.792
129.197
129.041
128.541
128.449
127.184
126.429
124.650
124.108
121.037
119.698
119.163
112.034
77.317
77.000
76.682
65.098
51.108
35.246
O
O
Ph
O
H
N
Bn
3ad
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LVR-03192A

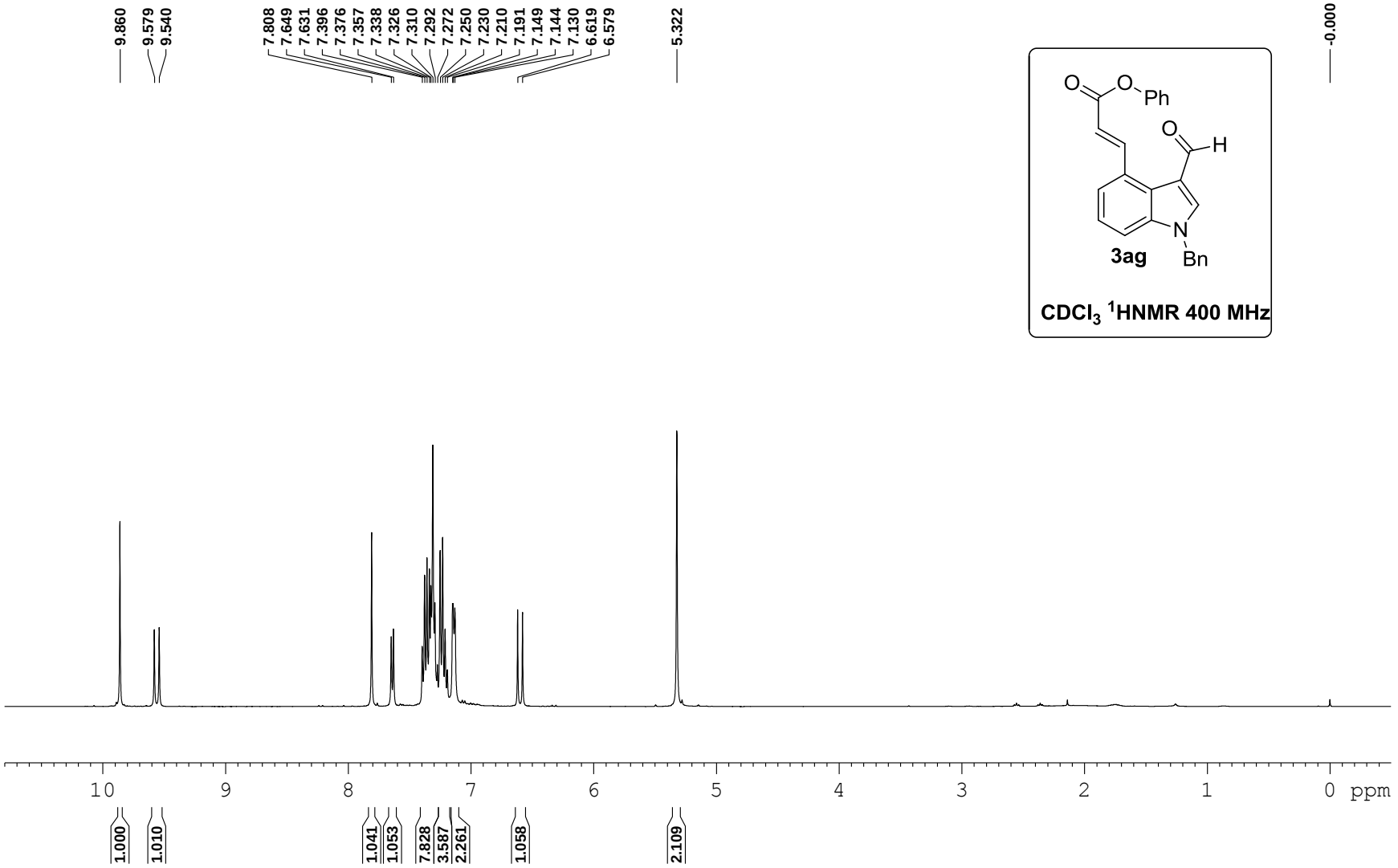

9.973
9.239
9.200
7.840
7.606
7.588
7.380
7.371
7.357
7.340
7.330
7.307
7.288
7.268
7.259
7.178
7.174
7.159
6.468
6.428
5.365
4.974
4.965
4.952
4.942
4.932
4.920
4.910
1.970
1.949
1.941
1.835
1.826
1.812
1.804
1.597
1.573
1.551
1.542
1.442
1.435
1.416
1.409
0.000
O
O
O
H
N
Bn
3ae
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.061
1.000
1.087
1.114
5.542
2.334
1.045
2.142
1.096
2.285
2.930
3.388
2.286

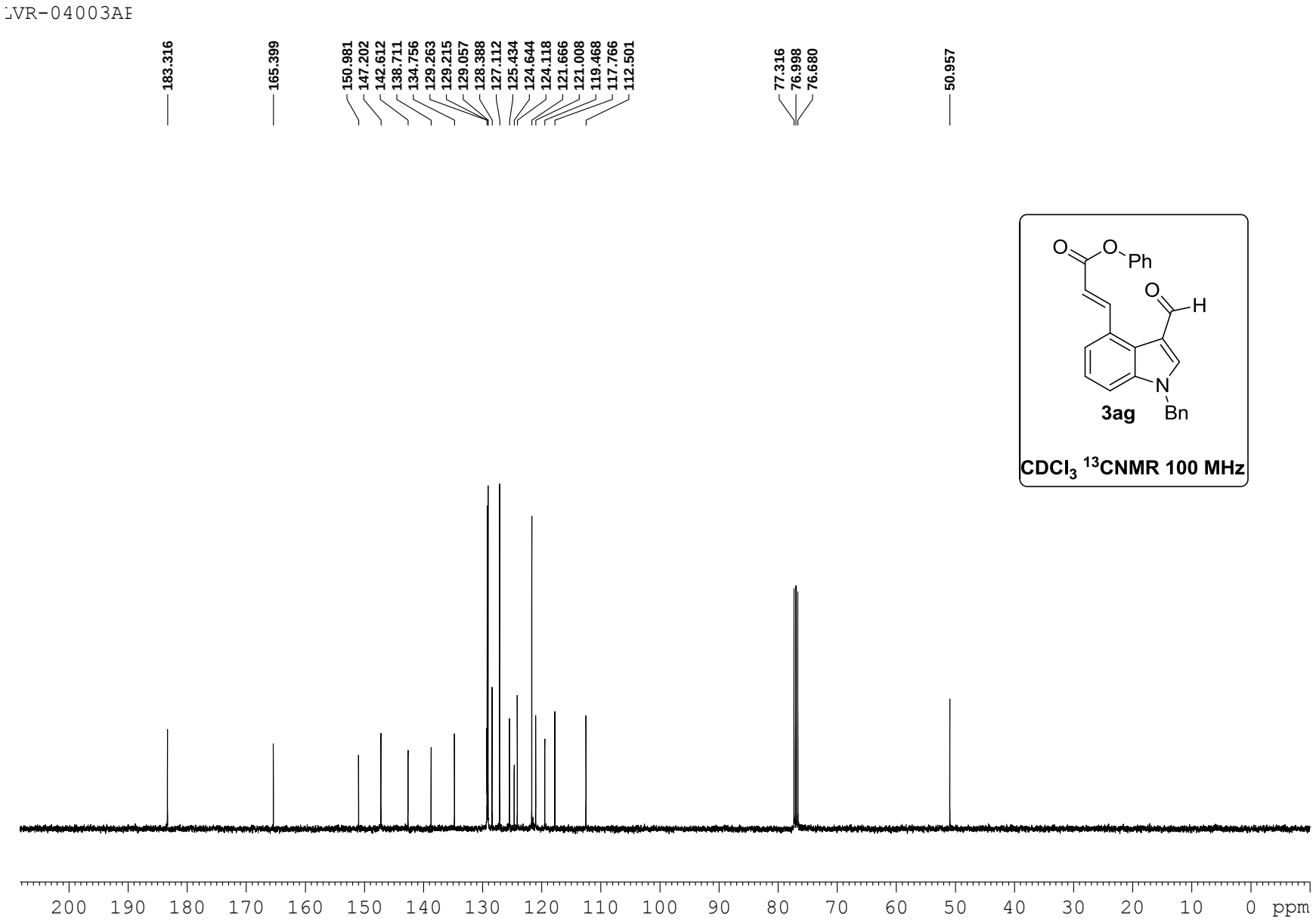

LVR-03192A
183.503
166.527
144.587
141.553
138.650
134.830
129.897
129.162
128.495
127.165
124.619
124.075
120.920
119.958
119.698
111.879
77.317
76.999
76.681
72.570
51.072
31.717
25.477
23.719
O
O
O
H
N
Bn
3ae
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

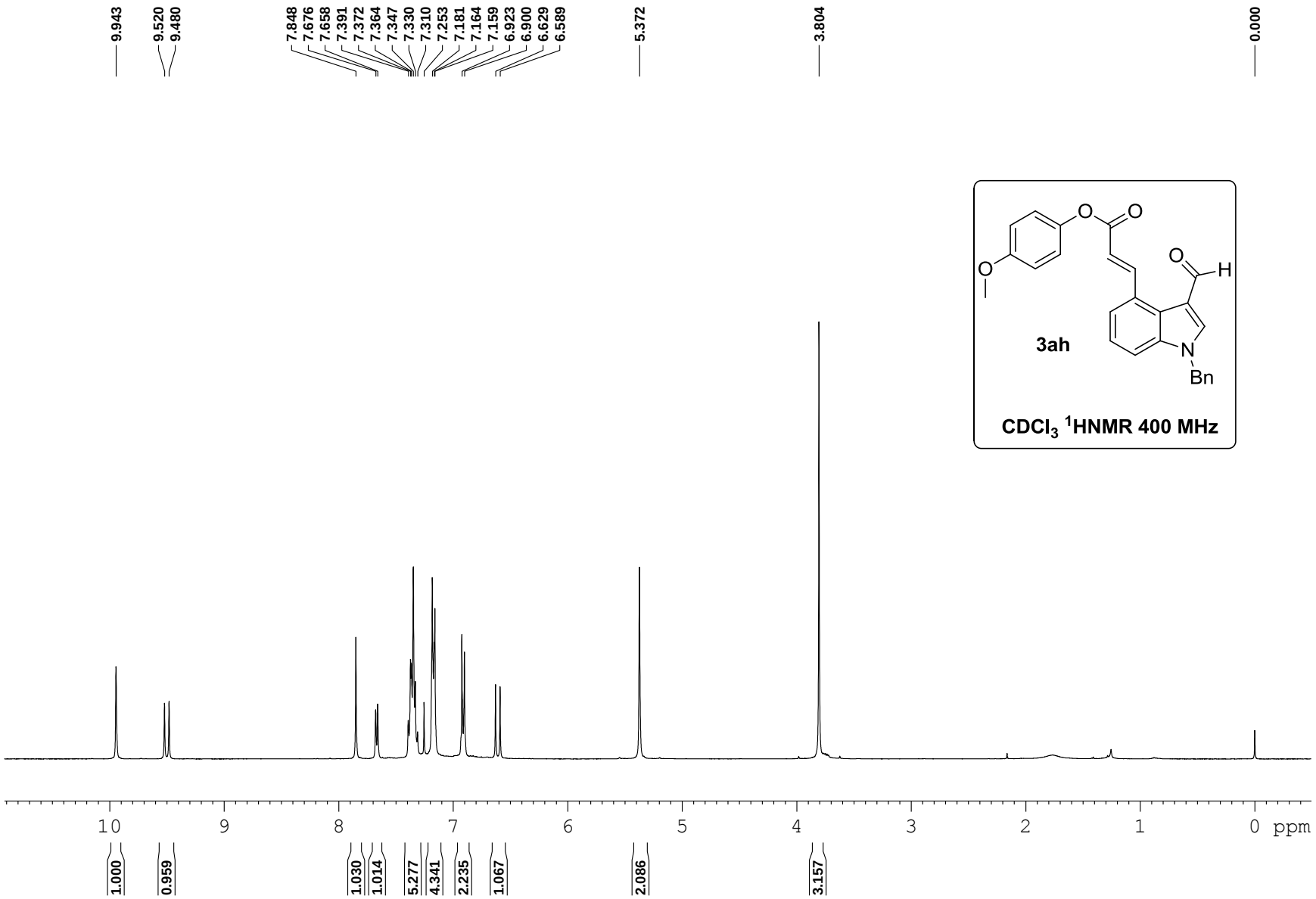

LVR04050
9.935
9.180
9.140
7.814
7.580
7.561
7.341
7.324
7.311
7.304
7.279
7.259
7.240
7.166
7.161
7.147
6.401
6.362
5.343
1.585
0.000
O
O
O
H
N
Bn
3af
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.981
1.066
1.037
5.846
2.279
1.013
2.172
9.198

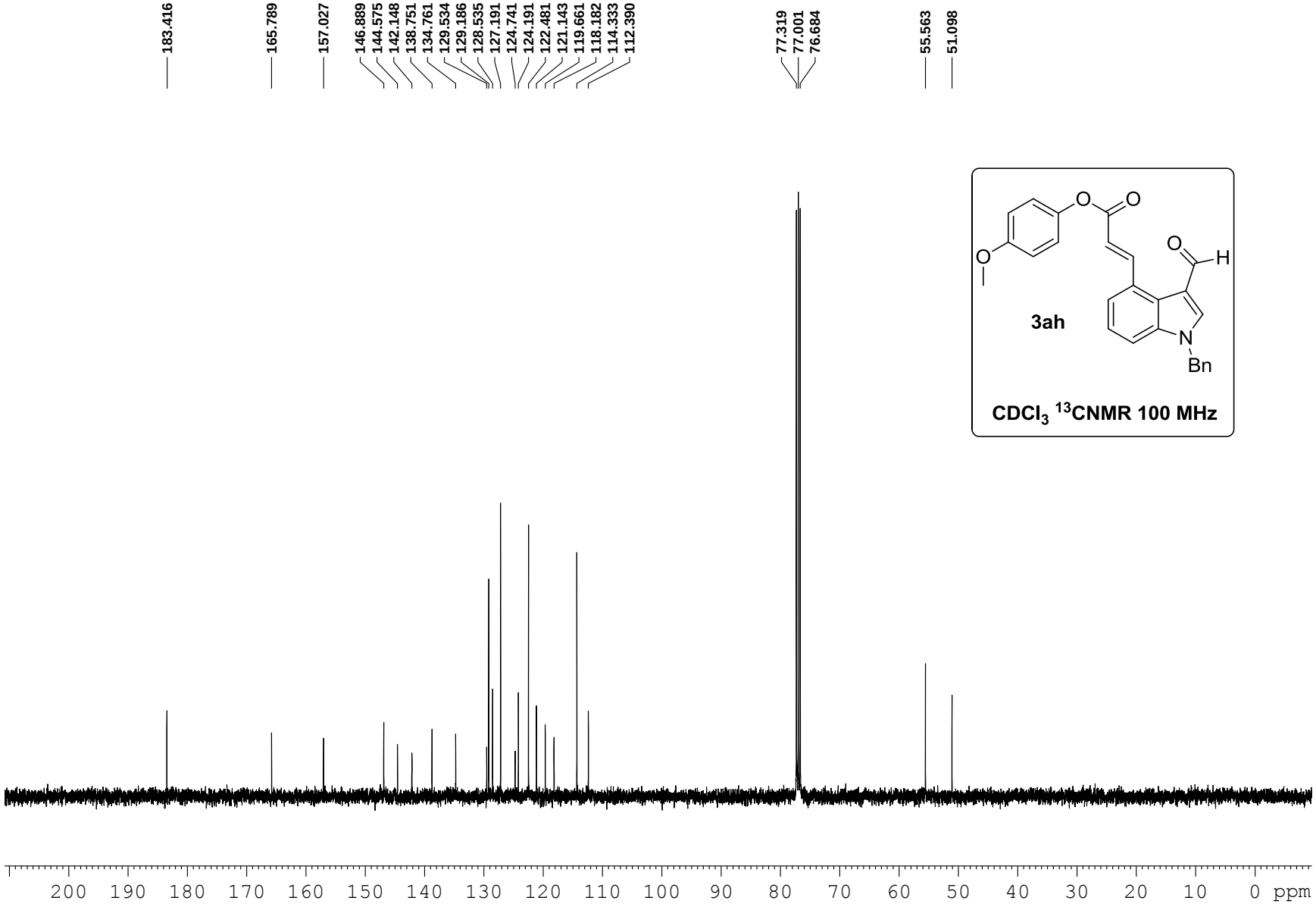

183.461
166.393
143.908
141.662
138.606
134.830
129.811
129.089
128.409
127.129
124.563
123.996
121.103
120.715
119.592
111.768
80.242
77.316
76.998
76.680
50.992
28.198
O
O
O
H
N
Bn
3af
CDCl3 13CNMR 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0
ppm

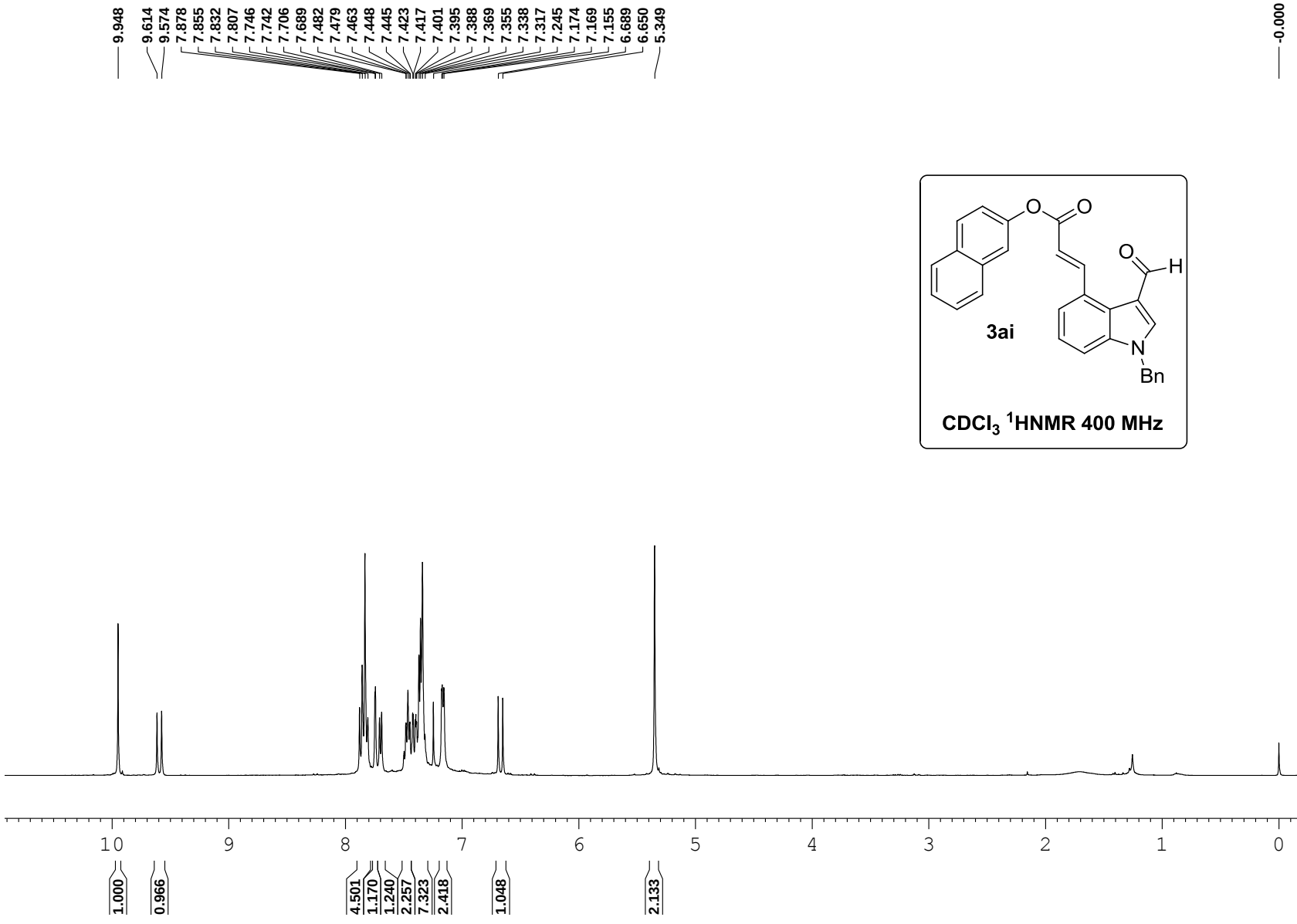
LVR-04003AP

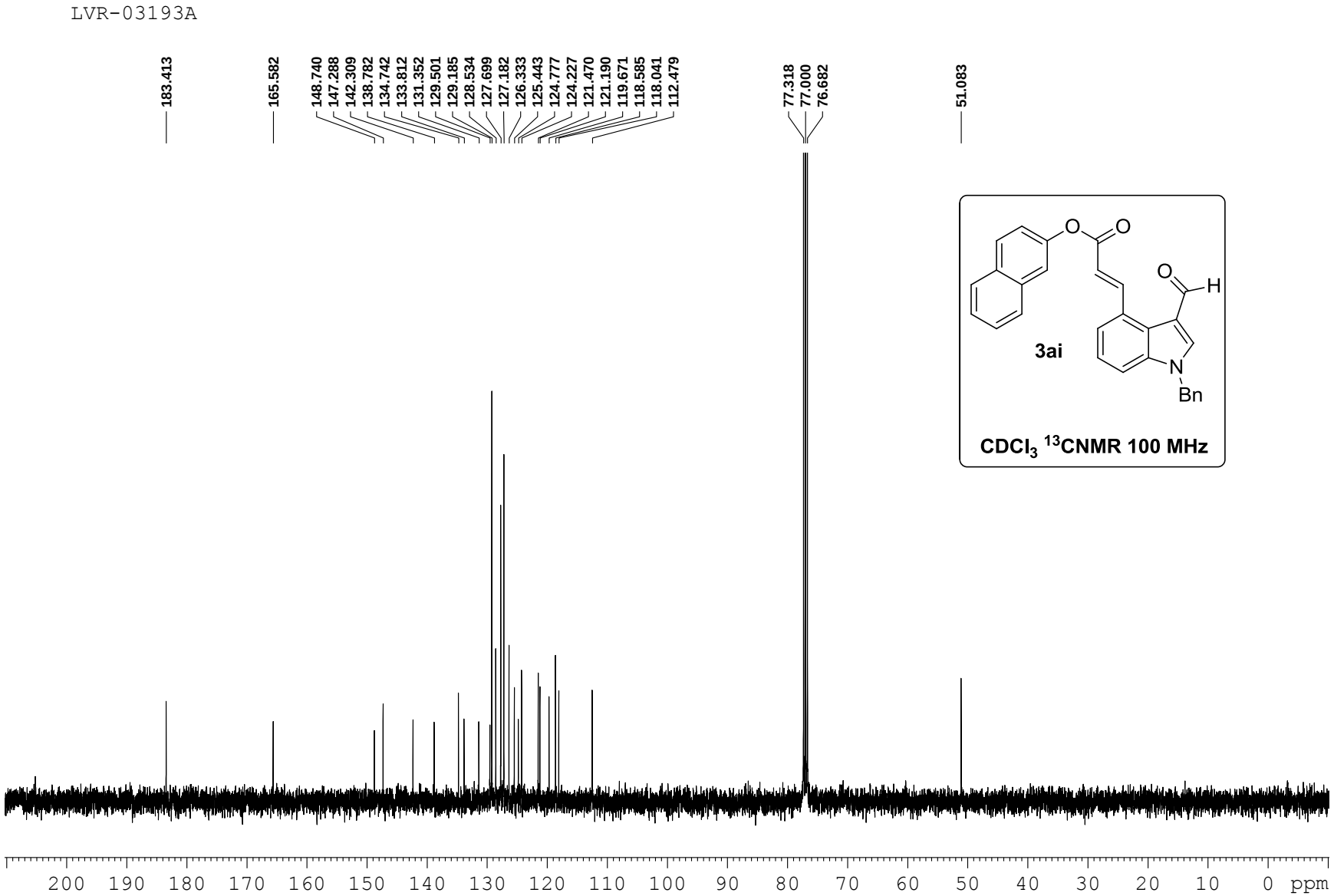

9.860
9.579
9.540
7.808
7.649
7.631
7.396
7.376
7.357
7.338
7.326
7.310
7.292
7.272
7.250
7.230
7.210
7.191
7.149
7.144
7.130
6.619
6.579
5.322
-0.000
O
O
Ph
O
H
N
Bn
3ag
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.010
1.041
1.053
7.828
3.587
2.261
1.058
2.109


LVR-04003AE
183.316
165.399
150.981
147.202
142.612
138.711
134.756
129.263
129.215
129.057
128.388
127.112
125.434
124.644
124.118
121.666
121.008
119.468
117.766
112.501
77.316
76.998
76.680
50.957
O
O
Ph
O
H
N
Bn
3ag
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

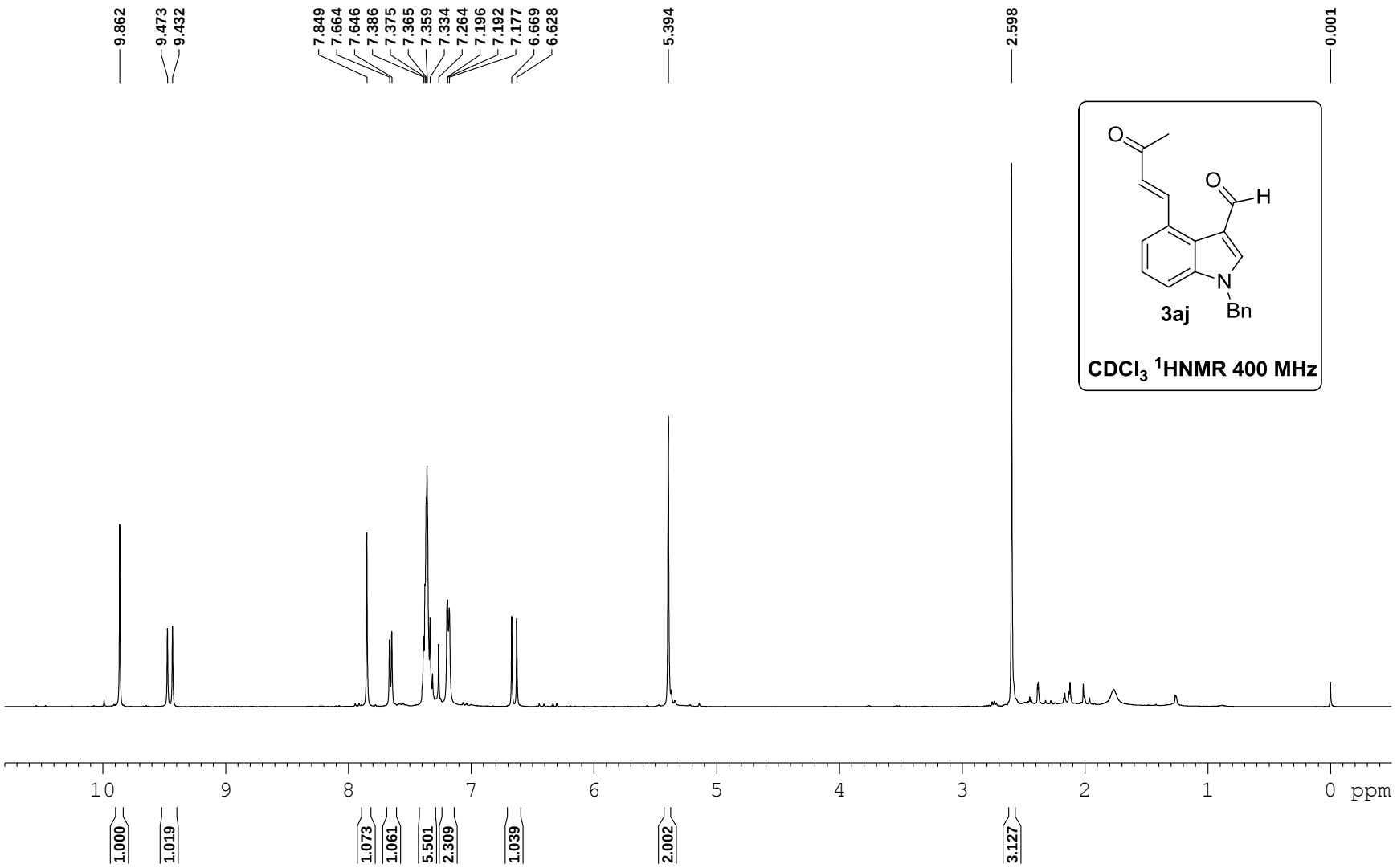

9.943
9.520
9.480
7.848
7.676
7.658
7.391
7.372
7.364
7.347
7.330
7.310
7.253
7.181
7.164
7.159
6.923
6.900
6.629
6.589
5.372
3.804
0.000
3ah
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.959
1.030
1.014
5.277
4.341
2.235
1.067
2.086
3.157

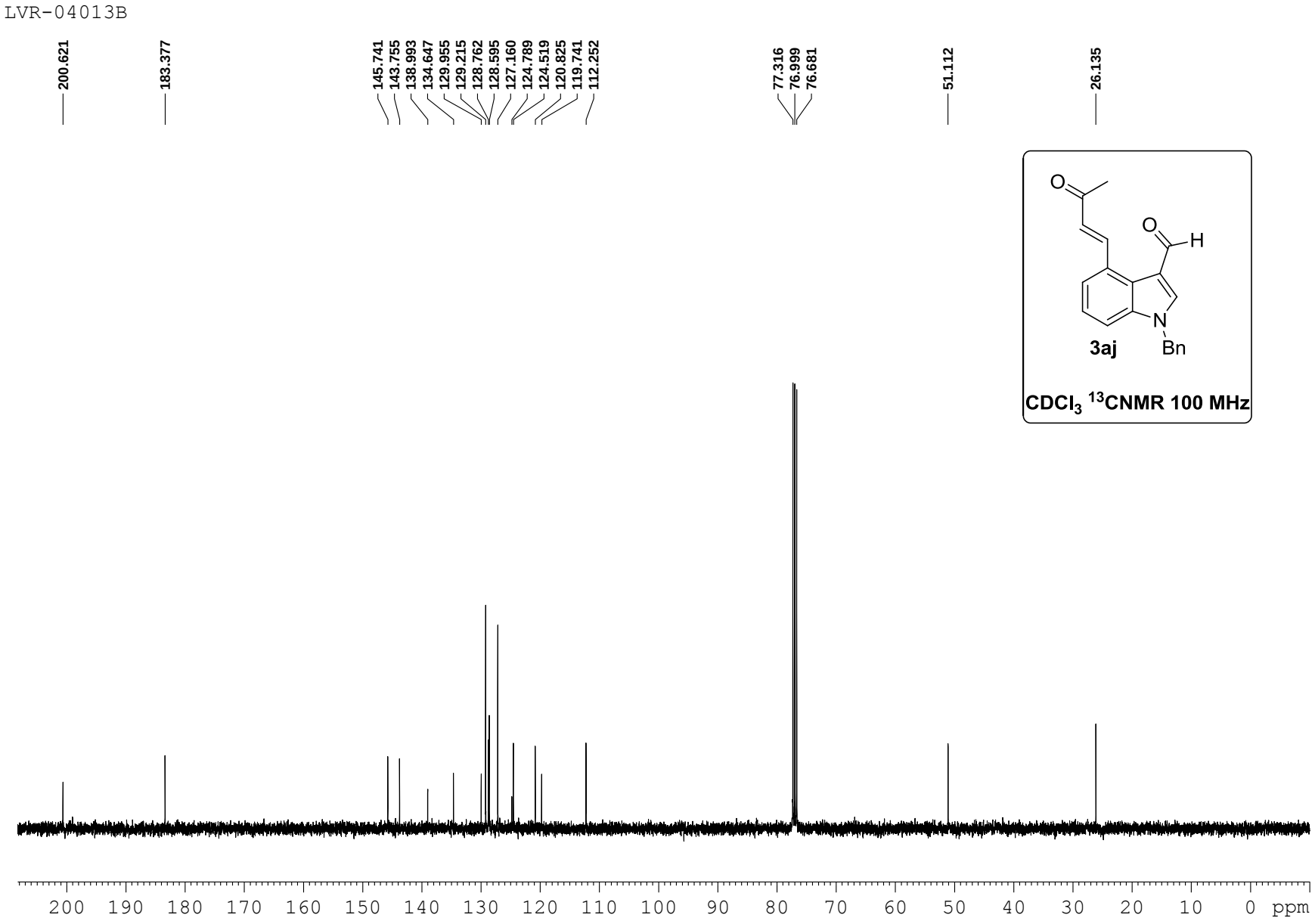

183.416
165.789
157.027
146.889
144.575
142.148
138.751
134.761
129.534
129.186
128.535
127.191
124.741
124.191
122.481
121.143
119.661
118.182
114.333
112.390
77.319
77.001
76.684
55.563
51.098
O
O
O
O
H
3ah
N
Bn
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


9.948
9.614
9.574
7.878
7.855
7.832
7.807
7.746
7.742
7.706
7.689
7.482
7.479
7.463
7.448
7.445
7.423
7.417
7.401
7.395
7.388
7.369
7.355
7.338
7.317
7.245
7.174
7.169
7.155
6.689
6.650
5.349
-0.000
O
O
O
H
3ai
N
Bn
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
0.966
4.501
1.170
1.240
2.257
7.323
2.418
1.048
2.133

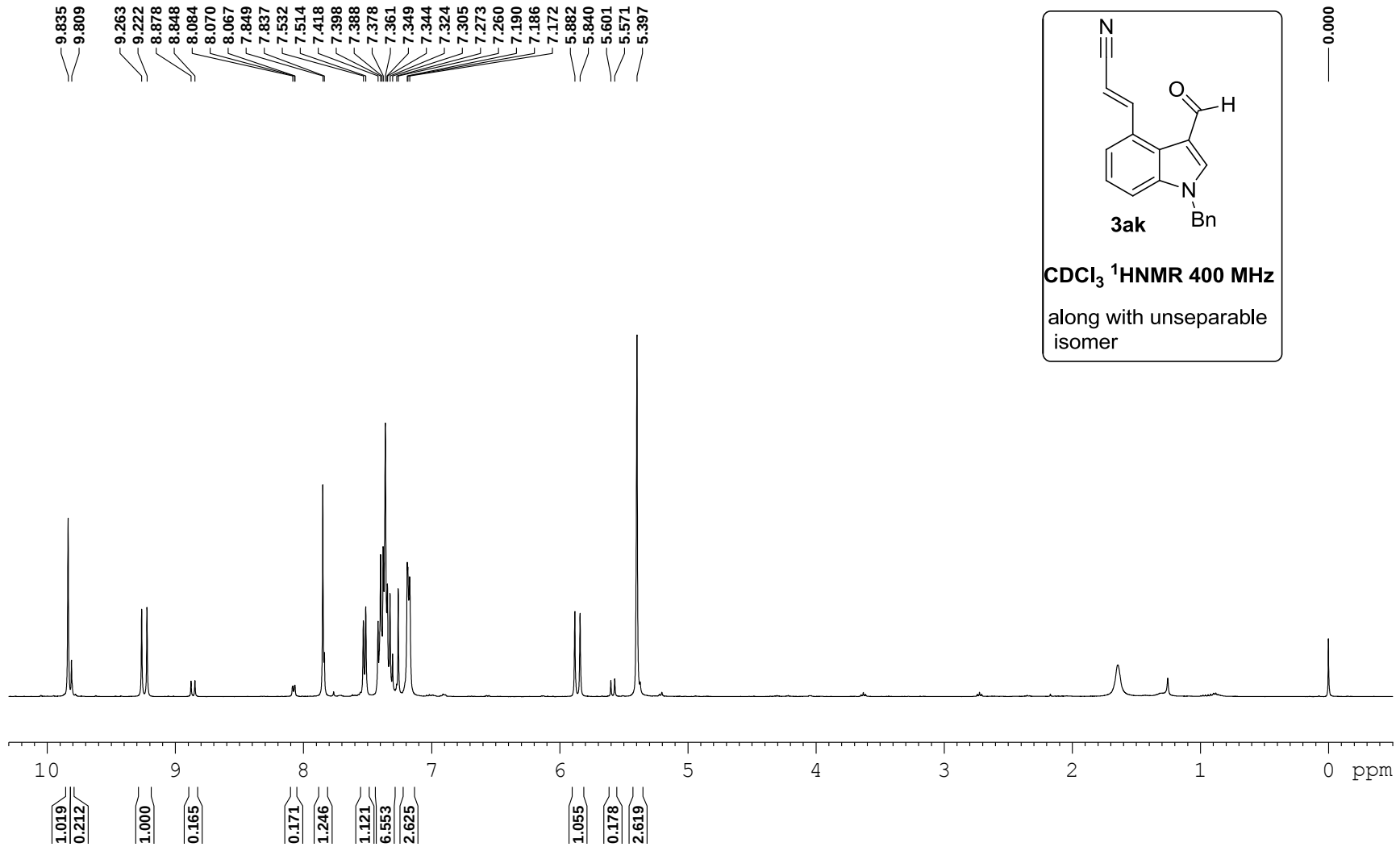

LVR-03193A
183.413
165.582
148.740
147.288
142.309
138.782
134.742
133.812
131.352
129.501
129.185
128.534
127.699
127.182
126.333
125.443
124.777
124.227
121.470
121.190
119.671
118.585
118.041
112.479
77.318
77.000
76.682
51.083
3ai
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

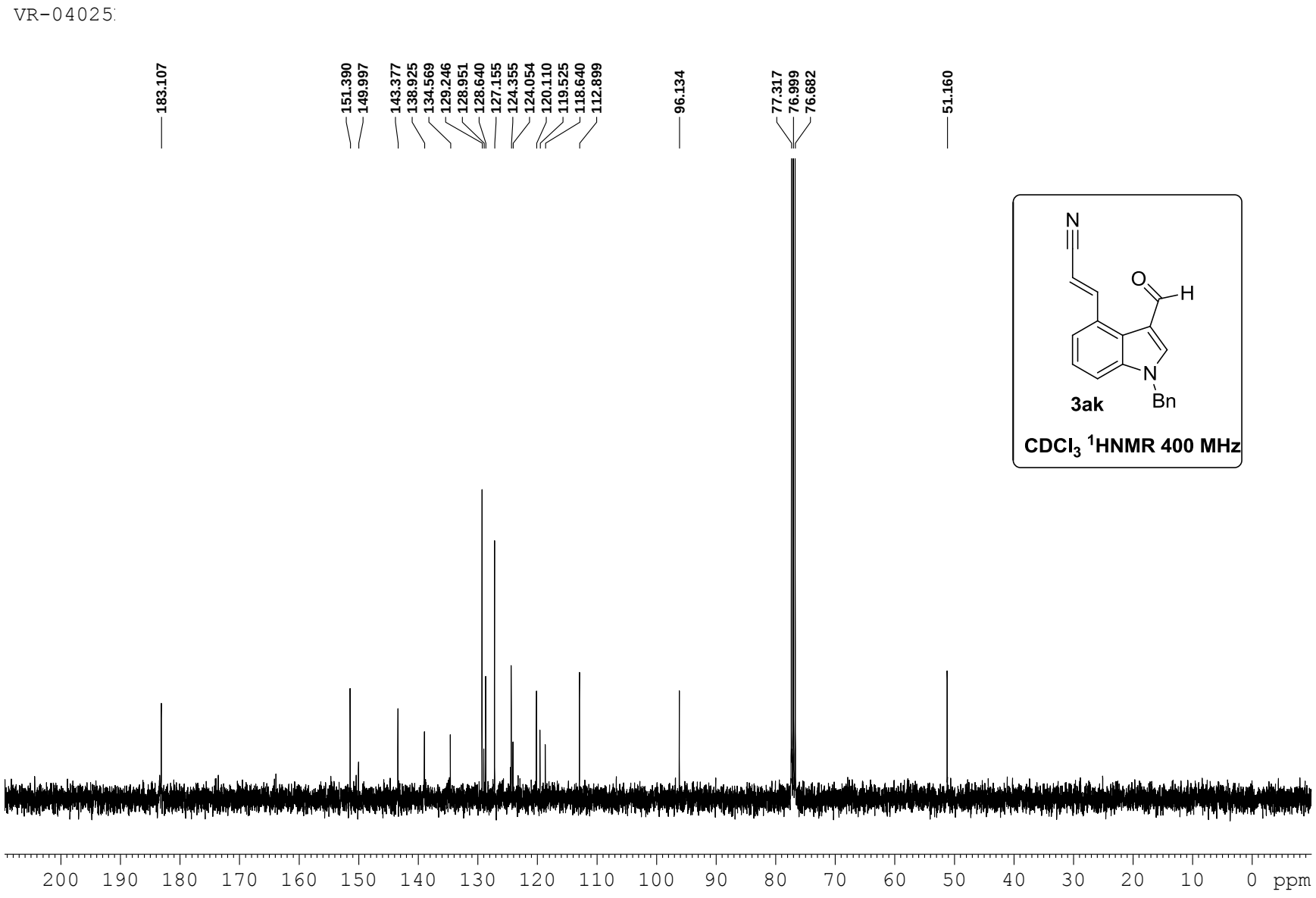
LVR-04013B


9.862
9.473
9.432
7.849
7.664
7.646
7.386
7.375
7.365
7.359
7.334
7.264
7.196
7.192
7.177
6.669
6.628
5.394
2.598
0.001
O
O
H
N
Bn
3aj
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.019
1.073
1.061
5.501
2.309
1.039
2.002
3.127

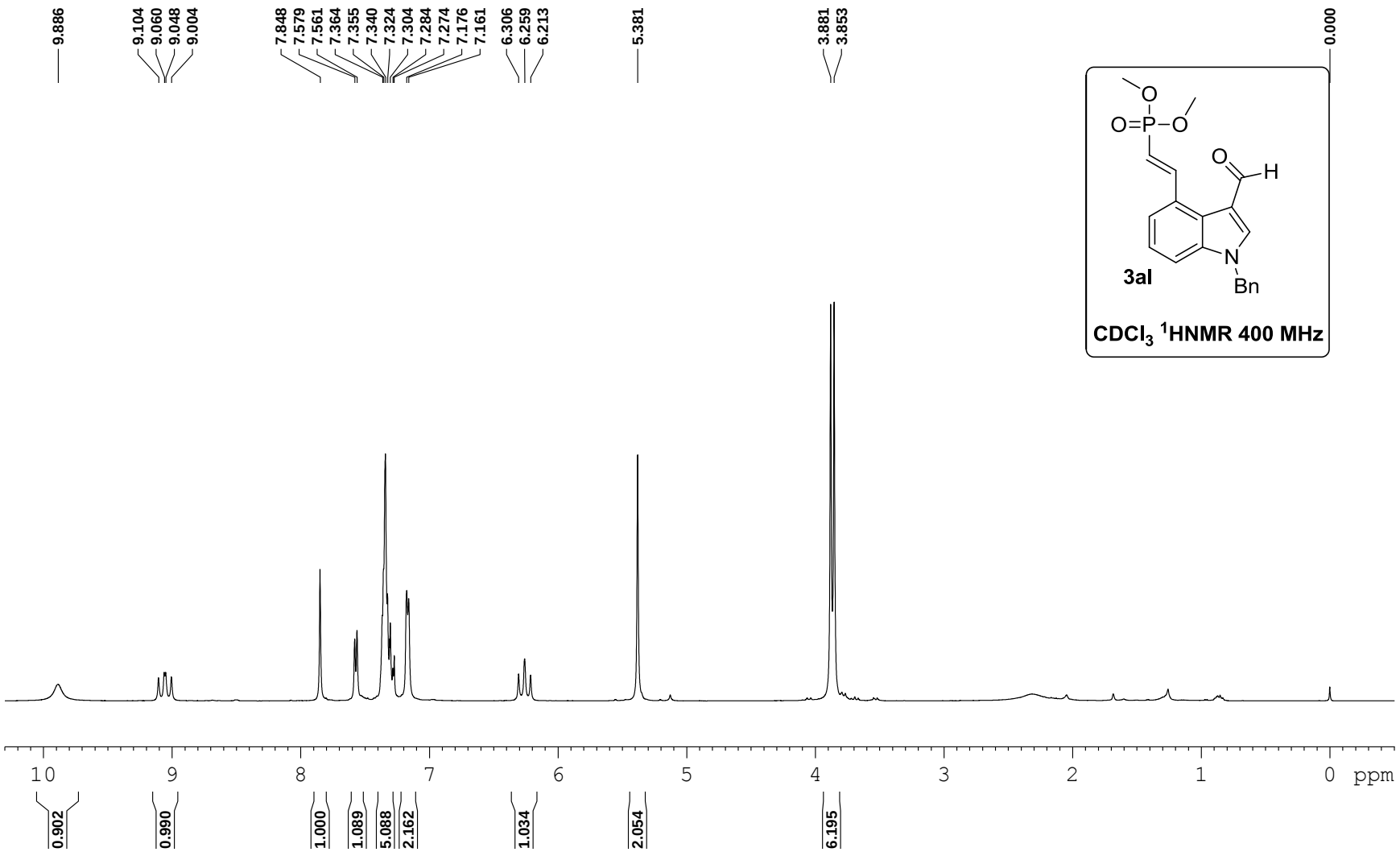

LVR-04013B
200.621
183.377
145.741
143.755
138.993
134.647
129.955
129.215
128.762
128.595
127.160
124.789
124.519
120.825
119.741
112.252
77.316
76.999
76.681
51.112
26.135
O
O
H
N
Bn
3aj
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

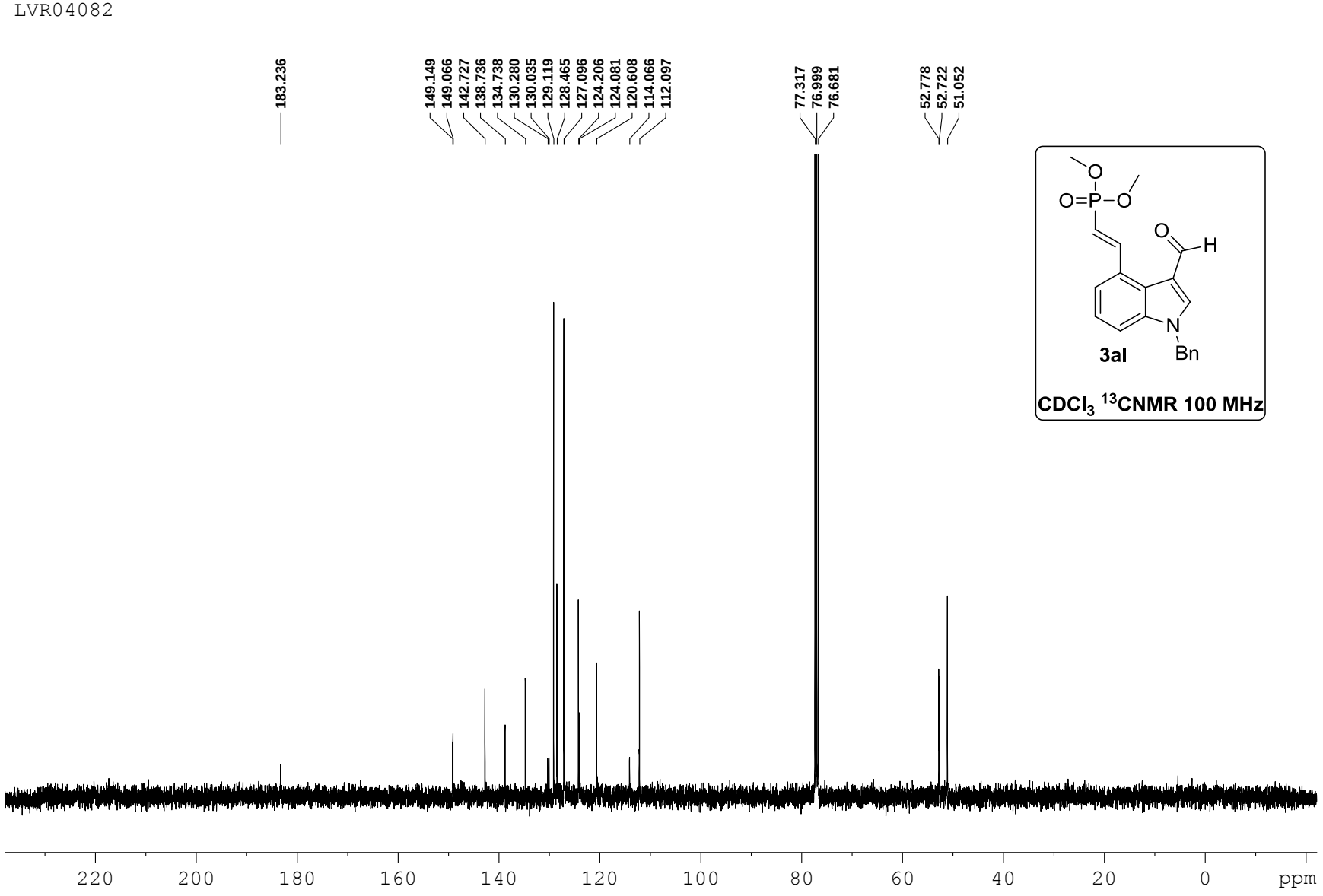
LVR-04025-B


9.835
9.809
9.263
9.222
8.878
8.848
8.084
8.070
8.067
7.849
7.837
7.532
7.514
7.418
7.398
7.388
7.378
7.361
7.349
7.344
7.324
7.305
7.273
7.260
7.190
7.186
7.172
5.882
5.840
5.601
5.571
5.397
0.000
N
O
H
N
Bn
3ak
CDCl3 1HNMR 400 MHz
along with unseparable isomer
10
9
8
7
6
5
4
3
2
1
0
ppm
1.019
0.212
1.000
0.165
0.171
1.246
1.121
6.553
2.625
1.055
0.178
2.619

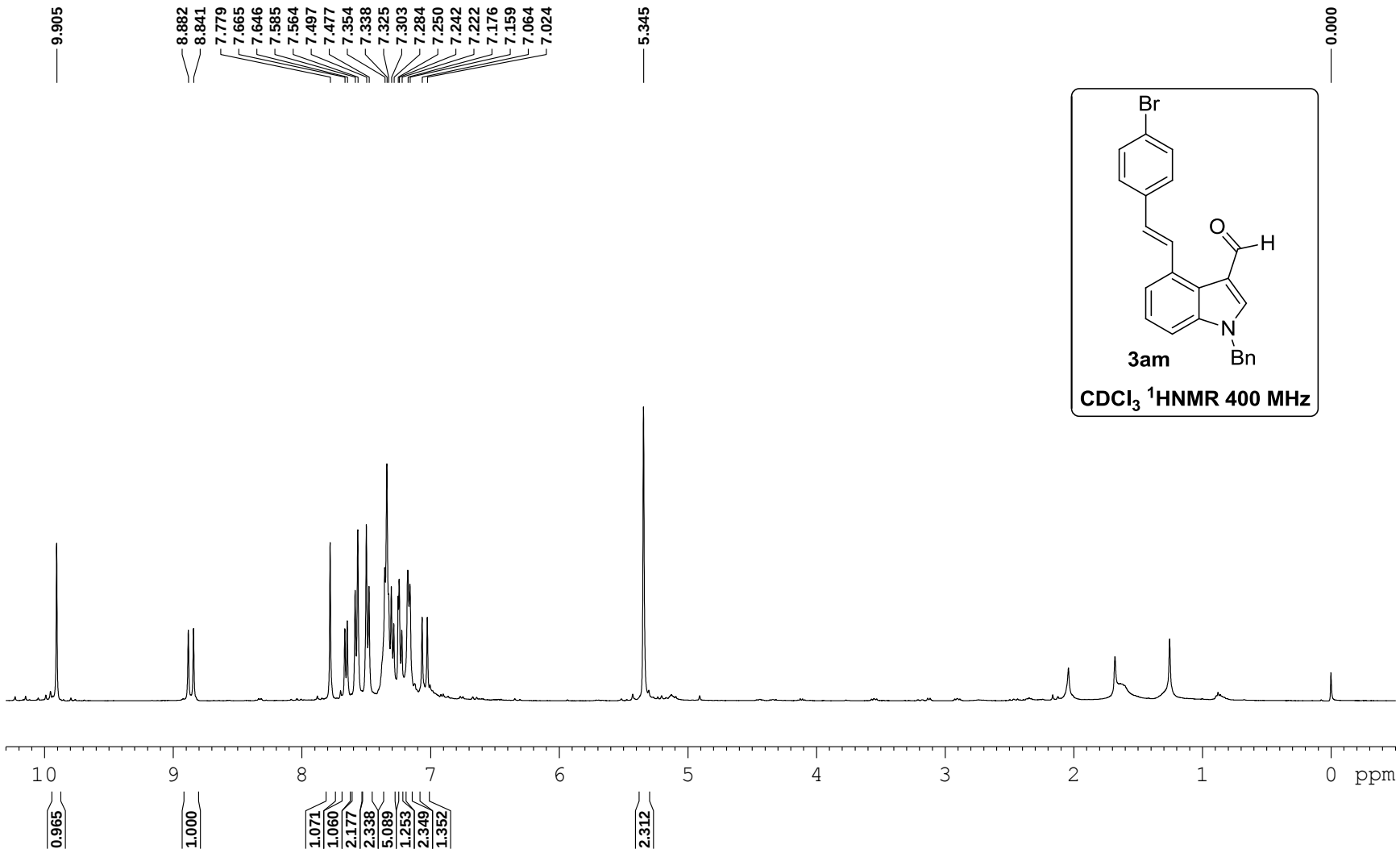

VR-04025
183.107
151.390
149.997
143.377
138.925
134.569
129.246
128.951
128.640
127.155
124.355
124.054
120.110
119.525
118.640
112.899
96.134
77.317
76.999
76.682
51.160
N
O
H
N
Bn
3ak
CDCl3 1HNMR 400 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

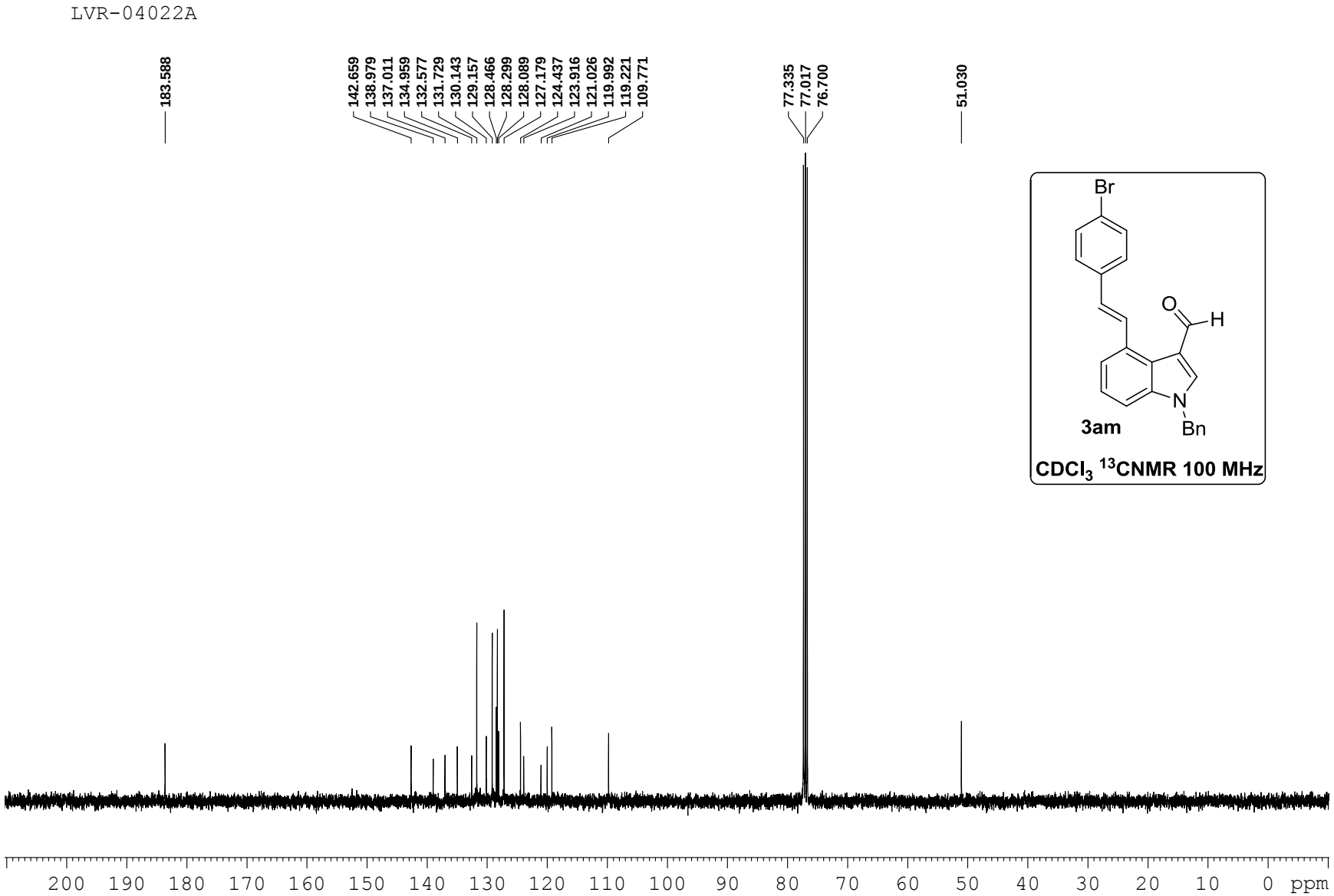
LVR-04082


9.886
9.104
9.060
9.048
9.004
7.848
7.579
7.561
7.364
7.355
7.340
7.324
7.304
7.284
7.274
7.176
7.161
6.306
6.259
6.213
5.381
3.881
3.853
0.000
O
O=P–O
O
H
N
Bn
3al
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0 ppm
0.902
0.990
1.000
1.089
5.088
2.162
1.034
2.054
6.195

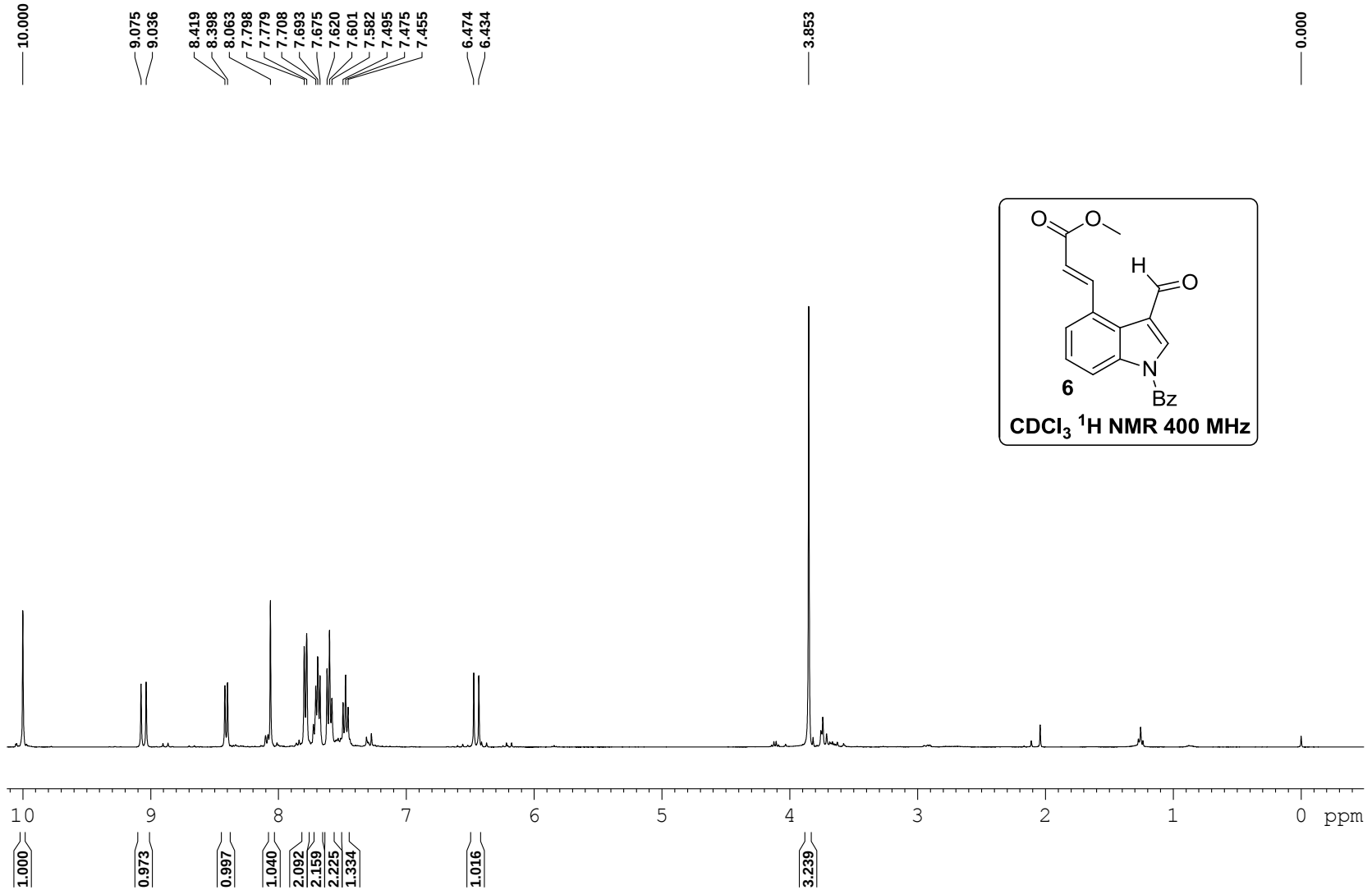

LVR04082
183.236
149.149
149.066
142.727
138.736
134.738
130.280
130.035
129.119
128.465
127.096
124.206
124.081
120.608
114.066
112.097
77.317
76.999
76.681
52.778
52.722
51.052
O
O=P−O
O
H
N
Bn
3aI
CDCl3 13CNMR 100 MHz
220
200
180
160
140
120
100
80
60
40
20
0
ppm

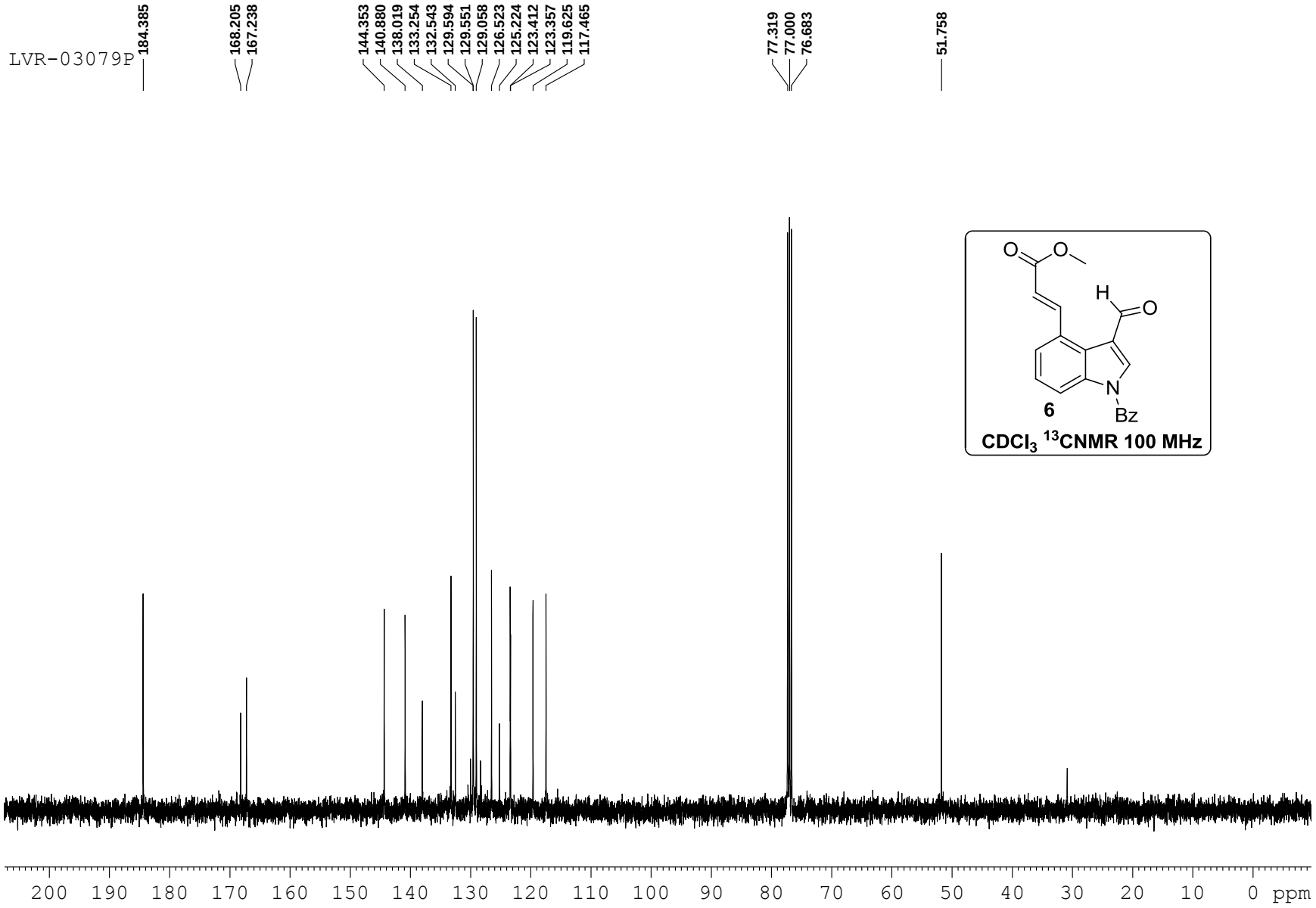
LVR-04022A


9.905
8.882
8.841
7.779
7.665
7.646
7.585
7.564
7.497
7.477
7.354
7.338
7.325
7.303
7.284
7.250
7.242
7.222
7.176
7.159
7.064
7.024
5.345
0.000
Br
O
H
N
Bn
3am
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
0.965
1.000
1.071
1.060
2.177
2.338
5.089
1.253
2.349
1.352
2.312

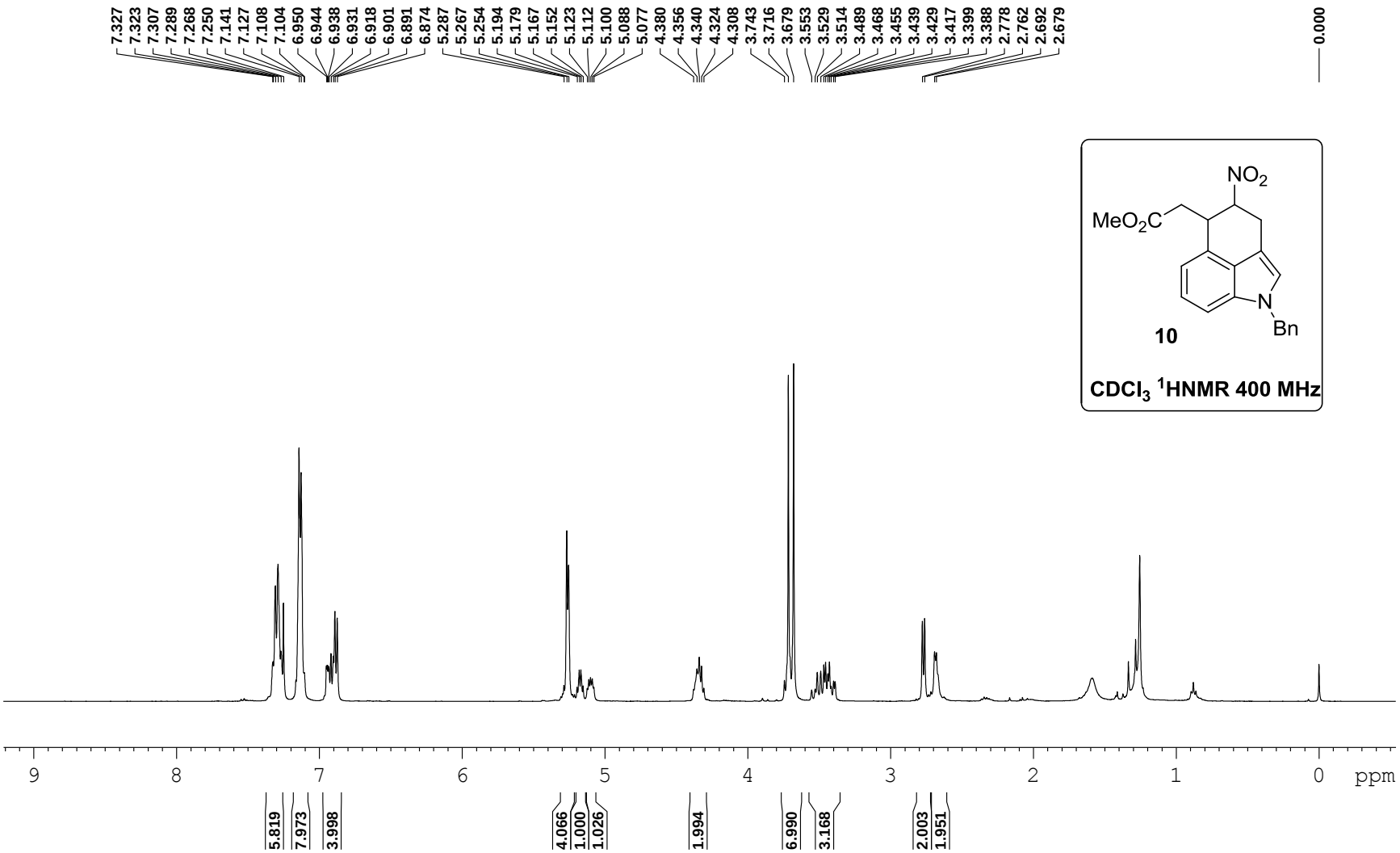

LVR-04022A
183.588
142.659
138.979
137.011
134.959
132.577
131.729
130.143
129.157
128.466
128.299
128.089
127.179
124.437
123.916
121.026
119.992
119.221
109.771
77.335
77.017
76.700
51.030
Br
O
H
N
Bn
3am
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

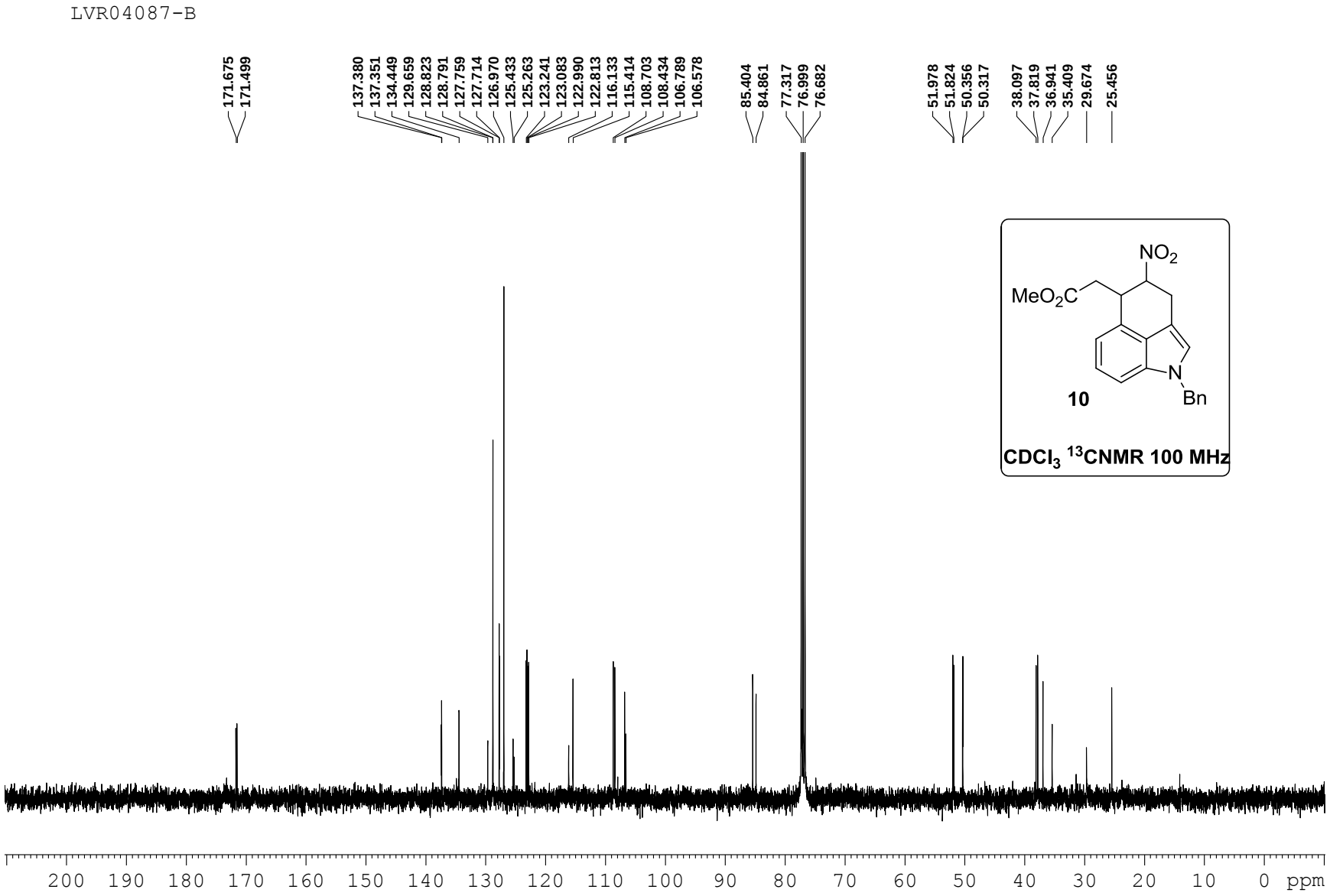
LVR-03079P


10.000
9.075
9.036
8.419
8.398
8.063
7.798
7.779
7.708
7.693
7.675
7.620
7.601
7.582
7.495
7.475
7.455
6.474
6.434
3.853
0.000
O
O
H
O
N
Bz
6
CDCl3 1H NMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.973
0.997
1.040
2.092
2.159
2.225
1.334
1.016
3.239

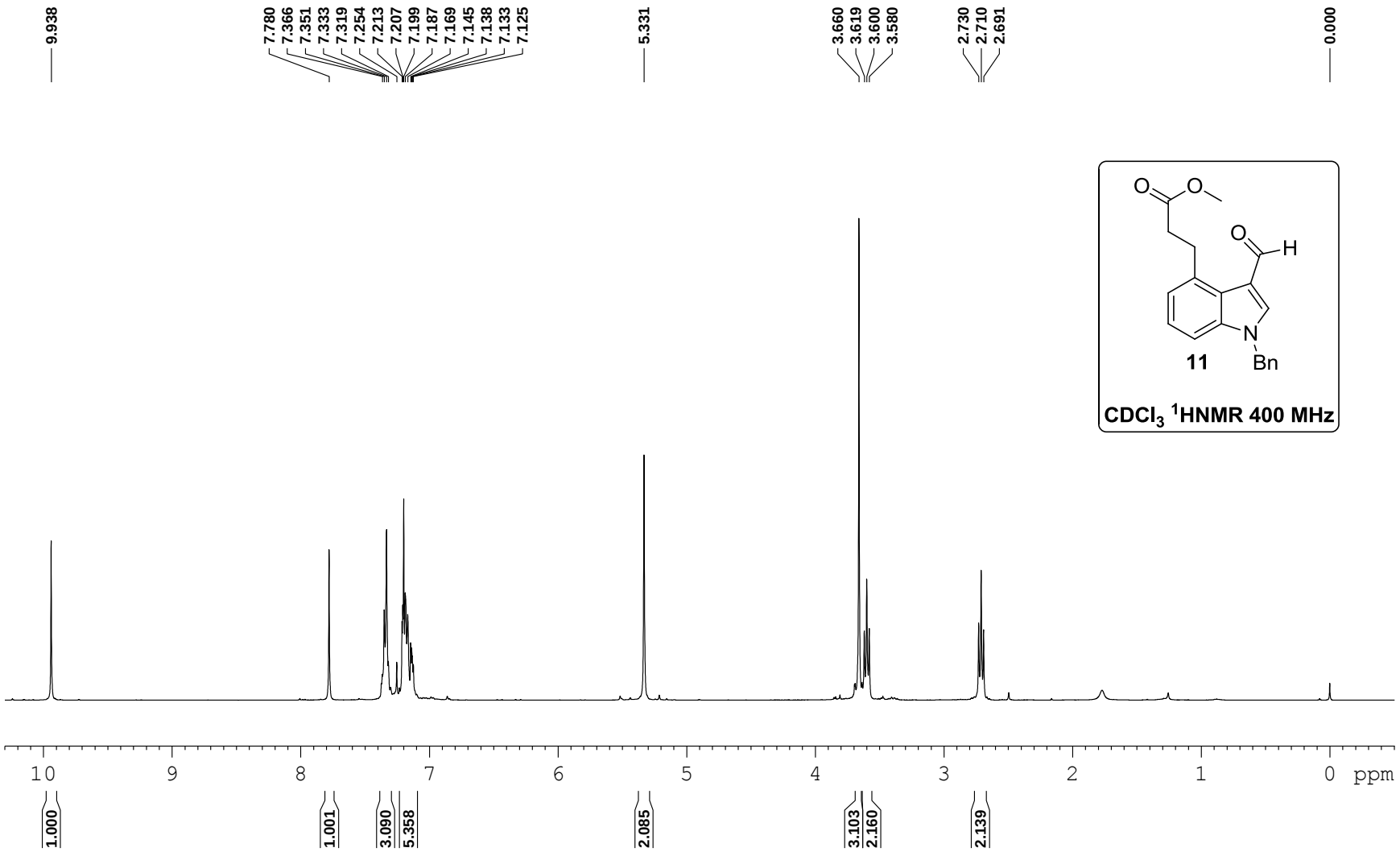

LVR-03079P
184.385
168.205
167.238
144.353
140.880
138.019
133.254
132.543
129.594
129.551
129.058
126.523
125.224
123.412
123.357
119.625
117.465
77.319
77.000
76.683
51.758
O
O
H
O
N
Bz
6
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

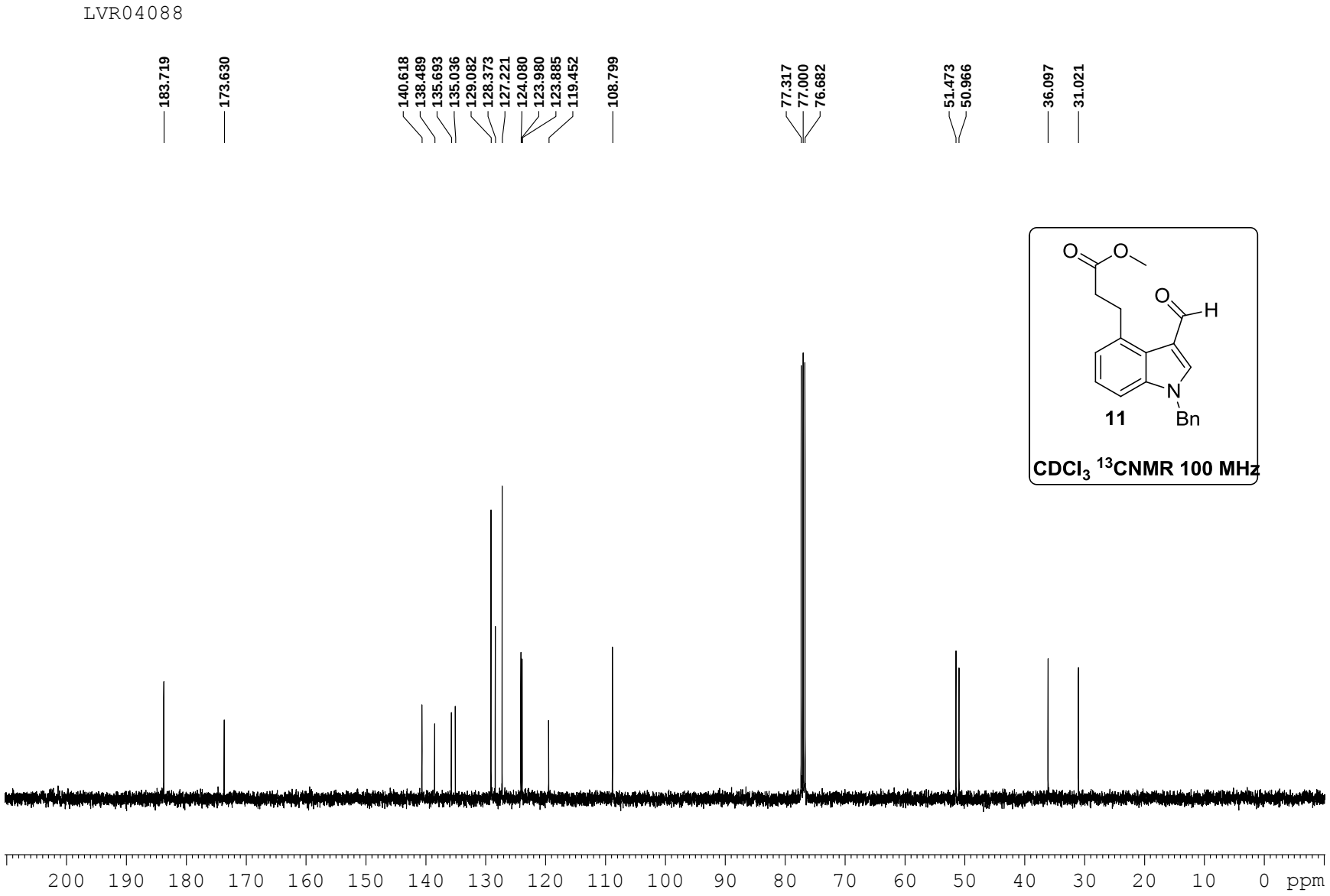
LVR04087-B


7.327
7.323
7.307
7.289
7.268
7.250
7.141
7.127
7.108
7.104
6.950
6.944
6.938
6.931
6.918
6.901
6.891
6.874
5.287
5.267
5.254
5.194
5.179
5.167
5.152
5.123
5.112
5.100
5.088
5.077
4.380
4.356
4.340
4.324
4.308
3.743
3.716
3.679
3.553
3.529
3.514
3.489
3.468
3.455
3.439
3.429
3.417
3.399
3.388
2.778
2.762
2.692
2.679
0.000
NO2
MeO2C
N
Bn
10
CDCl3 1HNMR 400 MHz
9
8
7
6
5
4
3
2
1
0
ppm
5.819
7.973
3.998
4.066
1.000
1.026
1.994
6.990
3.168
2.003
1.951

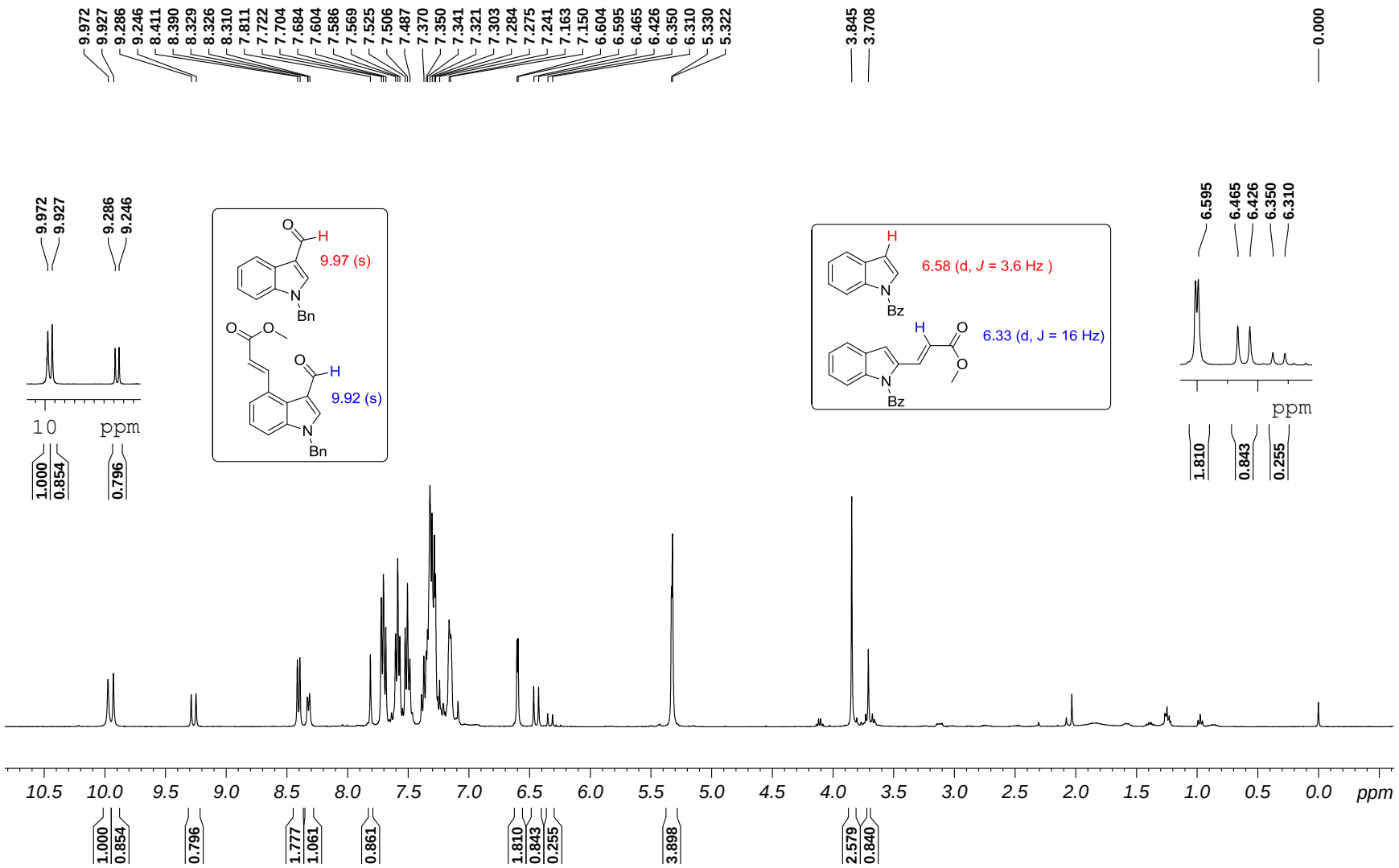

LVR04087-B
171.675
171.499
137.380
137.351
134.449
129.659
128.823
128.791
127.759
127.714
126.970
125.433
125.263
123.241
123.083
122.990
122.813
116.133
115.414
108.703
108.434
106.789
106.578
85.404
84.861
77.317
76.999
76.682
51.978
51.824
50.356
50.317
38.097
37.819
36.941
35.409
29.674
25.456
NO2
MeO2C
N
Bn
10
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LVR04088


9.938
7.780
7.366
7.351
7.333
7.319
7.254
7.213
7.207
7.199
7.187
7.169
7.145
7.138
7.133
7.125
5.331
3.660
3.619
3.600
3.580
2.730
2.710
2.691
0.000
O
O
O
H
N
Bn
11
CDCl3 1HNMR 400 MHz
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.001
3.090
5.358
2.085
3.103
2.160
2.139


LVR04088
183.719
173.630
140.618
138.489
135.693
135.036
129.082
128.373
127.221
124.080
123.980
123.885
119.452
108.799
77.317
77.000
76.682
51.473
50.966
36.097
31.021
O
O
O
H
N
Bn
11
CDCl3 13CNMR 100 MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

LVR-04121A


9.972
9.927
9.286
9.246
8.411
8.390
8.329
8.326
8.310
7.811
7.722
7.704
7.684
7.604
7.586
7.569
7.525
7.506
7.487
7.370
7.350
7.341
7.321
7.303
7.284
7.275
7.241
7.163
7.150
6.604
6.595
6.465
6.426
6.350
6.310
5.330
5.322
3.845
3.708
0.000
9.97 (s)
9.92 (s)
6.58 (d, J = 3.6 Hz)
6.33 (d, J = 16 Hz)
Bn
Bz
ppm
1.000
0.854
0.796
1.777
1.061
0.861
1.810
0.843
0.255
3.898
2.579
0.840