Electronic Supplementary Material (ESI) for ChemComm.


# E.S.I.

## Step and Redox Efficient Nitroarene to Indole Synthesis

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## Summary

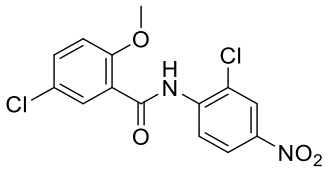


## General information

All reactions were carried out in 50 mL reaction vials containing a Teflon-coated stirring bar with sealed aluminous headspace caps under nitrogen, unless otherwise specified. Substrates were purchased either from Sigma Aldrich, Acros, ABCR, chemPUR or TCI if not further specified, and engaged directly. Degassed acetic acid (stored over molecular sieves 3Å and argon atmosphere) was used. Acetonitrile was purified by the Pure Solvent PS-MD-5 solvent drying system from Innovative Technology. NMR spectra were recorded at ambient temperature either on Varian V-NMRS 400, Varian V-NMRS 600, Bruker Avance Neo 400 or Bruker Avance Neo 600 using $CDCl_3$ or DMSO-$d_6$ as solvents. Chemical shifts are given in ppm and coupling constants (J) in Hz. For spectra with $CDCl_3$ as a solvent, $^1H$ spectra were calibrated in relation to the reference measurement of TMS (0.00 ppm), $^{13}C$ spectra were calibrated in relation to deuterated solvent, namely $CDCl_3$ (77.16 ppm). The following abbreviations were used for $^1H$ NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. Flash chromatography was performed on silica gel (60 M, 0.04-0.063 mm) by standard technique. High resolution mass spectra (HRMS) were recorded on ThermoFisher Scientific LTQ Orbitrap XL spectrometer. IR spectra were measured on a PerkinElmer 100 FT-IR spectrometer with an UATR Diamond KRS-5 unit.

## Synthesis of starting materials

### 5-Chloro-*N*-(2-chloro-4-nitrophenyl)-2-methoxybenzamide (920)




Preparation of the methoxylated derivative was prepared based on a known procedure.[1] A solution of niclosamide (5 mmol, 1.64 g) in acetone (50 mL) was prepared and potassium carbonate (6.5 mmol, 0.9 g) and methyl iodide (6.5 mmol, ~0.4 mL) were added. The mixture was heated to reflux and stirred overnight (15 h). The reaction was quenched with saturated ammonium chloride solution (50 mL) and the residue was filtered. The solid was washed with water (50 mL), ethanol (50 mL) and pentante (50 mL), leaving a pure yellow powder to collect as the product.
Isolated yield: 1.60 g, 4.69 mmol, 94 %.
Due to high insolubility of the compound, only a proton NMR at 100 °C is provided.

**$^1$H-NMR (400 MHz at 100 °C, DMSO-d$_6$)**: $\delta$ (ppm) = 10.73 (s, NH), 8.72 (d, $^3J$= 9.2 Hz, 1H), 8.39 (d, $^4J$= 2.6 Hz, 1H), 8.26 (dd, $^3J$= 9.2 Hz, $^4J$= 2.6 Hz, 1H), 8.01 (d, $^4J$= 2.8 Hz, 1H), 7.66 (dd, $^3J$= 8.9 Hz, $^4J$= 2.8 Hz, 1H), 7.37 (d, $^3J$= 8.9 Hz, 1H), 4.12 (s, 3H).

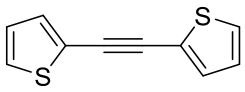
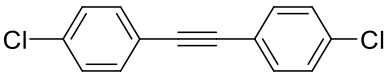
**APCI-TOF-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{14}H_{11}Cl_2N_2O_4]^+$ 341.00904, found 341.00883.

### Synthesis of alkynes

Alkynes were prepared according to the known procedure.[2]

$Pd(PPh_3)_2Cl_2$ (105 mg, 0.15 mmol), 1,4-bis(diphenylphosphino)butane (128 mg, 0.30 mmol), aryl halides (6.00 mmol), and propiolic acid (212 mg, 3.0 mmol) or 2-butynedioic acid (342 mg, 3.0 mmol) were combined with DBU (913 mg, 6.0 mmol) in a 50 mL reaction vial. DMSO (15.0 mL) was added, and the flask was sealed with an aluminous headspace cap. The resulting mixture was heated to 80 °C (for propiolic acid) or 110 °C (for 2-butynedioic acid) for 3 h. All reactions were set twice according to this protocol and combined for further work-up. Both reaction mixtures were poured into 50 mL of saturated aqueous ammonium chloride and extracted with $Et_2O$ (4 x 50 mL). The combined ether extracts were washed with brine (200 mL), dried over $MgSO_4$, and filtered. The solvent was removed under vacuum, and the resulting crude product was purified by flash chromatography on silica gel.

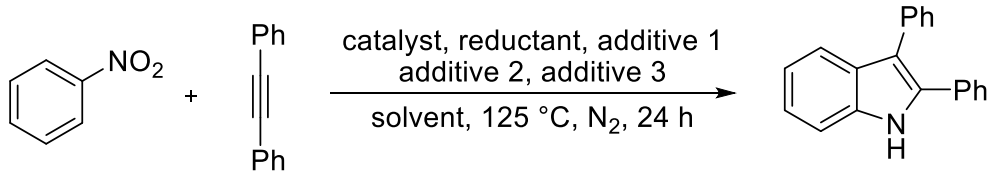
**Table S 1:** Alkynes according to literature.

| | | |
|---|---|---|
| **1,2-di(thiophen-2-yl)ethyne (CHB-682)**<br>  | Made from 2-butynedioic acid. Column chromatography with hexane/EA (19:1). Isolated: 775 mg, 4.01 mmol, 68%. | **$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 7.32-7.28 (m, 4H), 7.03-7.01 (m, 2H).<br><br>Spectroscopic data are in accordance with literature.[2] |
| **1,2-bis(4-chlorophenyl)ethyne (CHB-690)**<br>  | Made from propiolic acid. Column chromatography with hexane/EA (9:1). Isolated: 1.14 g, 4.61 mmol, 77%. | **$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 7.45 (second order d, $^3J$ ~ 8.6 Hz, 2H), 7.33 (second order d, $^3J$ ~ 8.5 Hz, 2H).<br><br>Spectroscopic data are in accordance with literature.[3] |

## Screening of the reaction conditions

Unless otherwise stated, the Nitro-compound (0.5 mmol), alkyne (0.6 mmol) and all solids were added to the reaction vial and closed by a rubber septum. The vial was brought into nitrogen atmosphere by standard Schlenk-technique. Then the liquids were added, starting with the solvent and then the additives. At last, the vial was quickly sealed by an aluminous headspace cap and heated to 125 °C for 20 h. Then the reaction was allowed to cool down, *n*-dodecan (100 µL) was added and worked up by adding ethyl acetate and filtering over silica. A diluted sample of this filtrate was injected directly into the GC. For GC-yields, a response factor was determined by utilizing different concentrations (0.1; 0.2; 0.3; 0.4; 0.5 mmol/mL) of the pure corresponding sample with the same amount of n-dodecane (100 µL) for all samples.

**Table S 2:** Screening experiments for the formation of 2,3-diphenylindole out of nitrobenzene and diphenylacetylene, GC yields (Yields in parentheses = isolated yields)




**3a**

| # | Catalyst (mol%) | Reductant (equiv.) | Additive 1 (equiv.) | Additive 2 (equiv.) | Additive 3 (equiv.) | Solvent (mL) | Yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | 7 |
| 2 | - | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |
| 3 [a] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | 6 |
| 4 | $[(Rh(C_2H_4)_2Cl]_2$ (1) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |
| 5 | $[(RhCp^*(MeCN)_3)](SbF_6)_2$ (2) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | 6 |
| 6 [b] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | trace |
| 7 [c] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (1) | AcOH (1.5) | - | - | MeCN (2.5) | 8 |
| 8 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (1) | - | - | - | MeCN (2.5) | trace |
| 9 [d] | $[(RhCp^*Cl)_2]_2$ (1) | - | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |
| 10 [d] | $[(RhCp^*Cl)_2]_2$ (1) | Fe (1) | AcOH (1.5) | - | - | MeCN (2.5) | trace |
| 11 [d] | $[(RhCp^*Cl)_2]_2$ (1) | $NaBH_4$ (1) | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |
| 12 [d] | $[(RhCp^*Cl)_2]_2$ (1) | $B_2pin_2$ (1) | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 13 | $[(RhCp^*Cl)_2]_2$ (1) | Mn (1) | AcOH (1.5) | - | - | MeCN (2.5) | n.d. |
| 14 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | MeCN (2.5) | 10 |
| 15 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | Chlorobenzene (2.5) | n.d. |
| 16 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | 1,2 Chlorobenzene (2.5) | n.d. |
| 17 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | *Iso*-butylnitrile (2.5) | trace |
| 18 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | Benzonitrile (2.5) | trace |
| 19 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | 1,4-Dioxane (2.5) | n.d. |
| 20 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | Toluene (2.5) | n.d. |
| 21 [e] | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | - | - | NMP (2.5) | n.d. |
| 22 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | *Iso*-butylnitrile (2.5) | trace |
| 23 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | Benzonitrile (2.5) | trace |
| 24 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | Water (2.5) | n.d. |
| 25 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | Ethanol (2.5) | n.d. |
| 26 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | MeCN + Water (1.25 + 1.25) | n.d. |
| 27 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | - | - | MeCN + Ethanol (1.25 + 1.25) | n.d. |
| 28 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | TFA (1.5) | - | MeCN (2.5) | 12 |
| 29 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | TFA (1.5) | - | MeCN (2.5) | 6 |
| 30 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | MS 3Å (70 mg) | - | MeCN (2.5) | 15 |
| 31 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | MS 3Å (70 mg) | - | MeCN (2.5) | 13 |
| 32 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | - | MeCN (2.5) | 21 |
| 33 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | TMSCl (1.5) | - | MeCN (2.5) | 2 |
| 34 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | - | MeCN (2.5) | 5 |
| 35 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | TMSCl (1.5) | - | MeCN (2.5) | 2 |
| 36 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | HFIP (1.5) | - | MeCN (2.5) | 11 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 37 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | HFIP (1.5) | - | MeCN (2.5) | n.d. |
| 38 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | $AgSbF_6$ (1.5) | - | MeCN (2.5) | 15 |
| 39 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | $AgSbF_6$ (1.5) | - | MeCN (2.5) | trace |
| 40 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | $Si(Me)_2Cl_2$ (1.5) | - | MeCN (2.5) | 3 |
| 41 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | $Si(Me)_2Cl_2$ (1.5) | - | MeCN (2.5) | trace |
| 42 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | $NH_4Cl$ (1.5) | - | MeCN (2.5) | 13 |
| 43 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | $NH_4Cl$ (1.5) | - | MeCN (2.5) | n.d. |
| 44 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | $NH_4Cl$ (1.5) | - | MeCN (2.5) | 13 |
| 45 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | $NH_4Cl$ (1.5) | - | MeCN (2.5) | n.d. |
| 46 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | LiCl (1.5) | - | MeCN (2.5) | n.d. |
| 47 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | - | LiCl (1.5) | - | MeCN (2.5) | n.d. |
| 48 | $Pd(CH_3CN)_2Cl_2$ (5) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | - | MeCN (2.5) | n.d. |
| 49 | $[(Rh(COE)_2Cl]_2$ (1) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | - | MeCN (2.5) | trace |
| 50 | $[(RhCp^*(MeCN)_3)](SbF_6)_2$ (2) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | - | MeCN (2.5) | 18 |
| 51 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | TMSCl (1.5) | MS 3Å (70 mg) | MeCN (2.5) | 50 (25) |
| 52 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (3) | AcOH (1.5) | TMSCl (1.5) | MS 3Å (70 mg) | MeCN (2.5) | 8 |
| 53 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.5) | TMSCl (2) | MS 3Å (70 mg) | MeCN (2.5) | 29 |
| 54 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (2) | TMSCl (1.5) | MS 3Å (70 mg) | MeCN (2.5) | 36 |
| 55 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 45 |
| 56 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (2) | TMSCl (1.5) | MS 3Å (70 mg) | MeCN (2.5) | 36 |
| 57 | $[(RhCp^*Cl)_2]_2$ (1) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 45 |
| 58 | $[(RhCp^*Cl)_2]_2$ (1.5) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 42 |
| 59 | $[(RhCp^*Cl)_2]_2$ (2) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 51 (42) |
| 60 | $[(RhCp^*Cl)_2]_2$ (2.5) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 50 |
| 61 | $[(RhCp^*Cl)_2]_2$ (3) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2.5) | 37 |

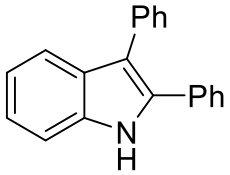
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 62 | $[(RhCp^*Cl)_2]_2$ (2) | Zn (2) | AcOH (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2) | 55 |
| 63 | $[(RhCp^*Cl)_2]_2$ (2) | Zn (2) | AcOH (over MS 4Å) (1.25) | TMSCl (1) | MS 3Å (70 mg) | MeCN (2) | 58 |
| 64 | $[(RhCp^*Cl)_2]_2$ (2) | Zn (2) | AcOH (over MS 4Å) (1.25) | TMSCl (1) | MS 3Å (150 mg) | MeCN (2) | 70 (39) |
| 65 [c] | $[(RhCp^*Cl)_2]_2$ (2) | Zn (2) | AcOH (over MS 4Å) (1.25) | TMSCl (1) | MS 3Å (150 mg) | MeCN (2) | (46) |

[a] reaction under air. [b] reaction carried out at 100 °C [c] reaction time: 24 h [d] reactions were carried out with 3-trifluoromethylnitrobenzene; detection by $^{19}$F-NMR [e] reactions were carried out with 4-fluoronitrobenzene; detection by $^{19}$F-NMR.

## Experimental Procedure for the synthesis of indoles and characterization

Unless otherwise stated, the Nitro-compound (0.5 mmol), $[Rh(Cp^*)Cl_2]_2$ (2 mol%), zinc (1mmol), molsieves 3Å (~150 mg) and alkyne (0.6 mmol) were added to the reaction vial and closed by a rubber septum. The vial was brought into nitrogen atmosphere by standard Schlenk-technique. The liquid compounds were added one after the other in the following order: first acetonitrile (2 mL), then TMSCl (0.5 mmol), and finally acetic acid (1.25 mmol). If one of the starting materials was liquid, they were added last. In the end, the vial was quickly sealed by an aluminous headspace cap and heated to 125 °C for 24h. The reaction was allowed to cool to room temperature. The crude was directly engaged on SiO2 gel column chromatography for purification, including the molsieves of the reaction mixture. In most cases, the expected product can be easily detected under 365 nm UV-light on TLC plates.

**2,3-Diphenyl-1*H*-indole (3a, 848)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 61.4 mg, 0.23 mmol, 46% (brown crystals).

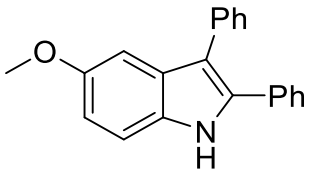
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.20 (s, NH), 7.85 (d, $^3J$= 8.0 Hz, 1H), 7.59-7.58 (m, 2H), 7.52-7.46 (m, 5H), 7.43-7.35 (m, 5H), 7.31-7.29 (m, 1H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 135.96 (s, $C_{quat}$), 135.17 (s, $C_{quat}$), 134.18 (s, $C_{quat}$), 132.70 (s, $C_{quat}$), 130.24 (s, CH), 128.81 (s, $C_{quat}$), 128.71 (s, CH), 128.63 (s, CH), 128.28 (s, CH), 127.74 (s, CH), 126.31 (s, CH), 122.74 (s, CH), 120.50 (s, CH), 119.75 (s, CH), 115.04 (s, $C_{quat}$), 111.08 (s, CH).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{20}H_{16}N]^+$ 270.12773, found 270.12701.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3391, 3053, 1600, 1502, 1448, 1371, 1325, 1246, 1150, 1068, 1027, 965, 919, 828, 747, 694.

**5-Methoxy-2,3-diphenyl-1*H*-indole (3b, 850)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:9). Isolated yield: 67.0 mg, 0.23 mmol, 45% (yellow solid).

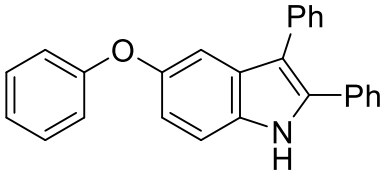
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.19 (s, NH), 7.47-7.45 (m, 2H), 7.43-7.40 (m, 4H), 7.34-7.28 (m, 5H), 7.16 (d, $^4J$= 2.2 Hz, 1H), 6.92 (dd, $^4J$= 2.4 Hz, $^3J$= 8.7 Hz, 1H), 3.84 (s, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 154.88 (s, $C_{quat}$), 135.35 (s, $C_{quat}$), 135.09 (s, $C_{quat}$), 132.84 (s, $C_{quat}$), 131.19 (s, $C_{quat}$), 130.21 (s, CH), 129.28 (s, $C_{quat}$), 128.76 (s, CH), 128.73 (s, CH), 128.20 (s, CH), 127.72 (s, CH), 126.31 (s, CH), 115.03 (s, $C_{quat}$), 113.12 (s, CH), 111.85 (s, CH), 101.33 (s, CH), 56.05 (s, $CH_3$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}ON]^+$ 300.13829, found 300.13752.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3406, 3060, 2935, 2834, 1893, 1732, 1592, 1456, 1299, 1222, 1155, 1118, 1069, 1027, 929, 835, 793, 759, 695.

**5-Phenoxy-2,3-diphenyl-1*H*-indole (3c, 895)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:9). Isolated yield: 95.0 mg, 0.26 mmol, 53 % (yellowish solid).

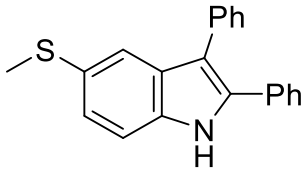
**$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.16 (s, NH), 7.37-7.31 (m, 6H), 7.28 (s, 1H), 7.26-7.22 (m, 3H), 7.22-7.16 (m, 4H), 6.93-6.86 (m, 4H).

**$^{13}$C{$^1$H}-NMR (101 MHz, $CDCl_3$)**: $\delta$ (ppm) = 159.64 (s, $C_{quat}$), 150.50 (s, $C_{quat}$), 135.62 (s, $C_{quat}$), 134.82 (s, $C_{quat}$), 133.13 (s, $C_{quat}$), 132.68 (s, $C_{quat}$), 130.13 (s, CH), 129.74 (s, $C_{quat}$), 129.63 (s, CH), 128.90 (s, CH), 128.73 (s, CH), 128.32 (s, CH), 128.04 (s, CH), 126.48 (s, CH), 121.95 (s, CH), 117.10 (s, CH), 116.80 (s, CH), 115.38 (s, $C_{quat}$), 111.97 (s, CH), 110.98 (s, CH).

**ESI-HRMS**: $[M+Na]^+$ m/z: calculated for $[C_{26}H_{19}NONa]^+$ 384.13589, found 384.13498.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3405, 3051, 1586, 1474, 1373, 1311, 1215, 1150, 1070, 1024, 975, 951, 912, 854, 800, 759, 692.

**5-(Methylthio)-2,3-diphenyl-1*H*-indole (3d, 882)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:9). Isolated yield: 73.2 mg, 0.23 mmol, 46 % (yellow resin).

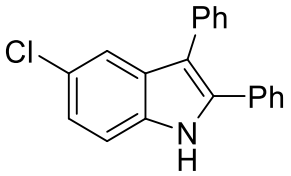
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.24 (s, NH), 7.68 (d, $^4J$= 1.6 Hz, 1H), 7.43-7.34 (m, 8H), 7.34-7.27 (m, 5H), 2.49 (s, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 134.95 (s, $C_{quat}$), 134.81 (s, $C_{quat}$), 134.75 (s, $C_{quat}$), 132.56 (s, $C_{quat}$), 130.25 (s, CH), 129.64 (s, $C_{quat}$), 128.88 (s, CH), 128.77 (s, CH), 128.25 (s, CH), 128.00 (s, CH), 126.53 (s, CH), 124.88 (s, CH), 120.60 (s, CH), 114.82 (s, $C_{quat}$), 111.58 (s, CH), 19.04 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}NS]^+$ 316.11545, found 316.11508.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3399, 3064, 3021, 2924, 1879, 1756, 1601, 1550, 1501, 1450, 1308, 1282, 1097, 1064, 1025, 966, 919, 863, 836, 791, 762, 694.

**5-Chloro-2,3-diphenyl-1*H*-indole (3e, 859)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:9). Isolated yield: 66.5 mg, 0.22 mmol, 44% (yellow solid).

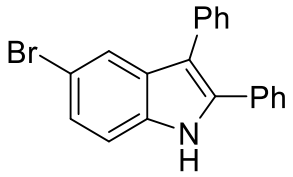
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.24 (s, NH), 7.65 (d, $^4J$= 2.0 Hz, 1H), 7.42-7.39 (m, 6H), 7.35-7.30 (m, 5H), 7.20 (dd, $^4J$= 2.0 Hz, $^3J$= 8.6 Hz, 1H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 135.53 (s, $C_{quat}$), 134.49 (s, $C_{quat}$), 134.32 (s, $C_{quat}$), 132.29 (s, $C_{quat}$), 130.16 (s, CH), 130.03 (s, $C_{quat}$), 128.90 (s, CH), 128.81 (s, CH), 128.25 (s, CH), 128.17 (s, CH), 126.68 (s, CH), 126.29 (s, $C_{quat}$), 123.06 (s, CH), 119.25 (s, CH), 114.89 (s, $C_{quat}$), 112.04 (s, CH).

**APCI-TOF-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{20}H_{15}ClN]^+$ 304.08875, found 304.08907.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3458, 3062, 2921, 2852, 1879, 1739, 1602, 1504, 1452, 1367, 1305, 1283, 1238, 1175, 1127, 1062, 1028, 968, 922, 872, 787, 761, 731, 691.

**5-Bromo-2,3-diphenyl-1*H*-indole (3f, 869)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 57.1 mg, 0.16 mmol, 33% (yellow solid).

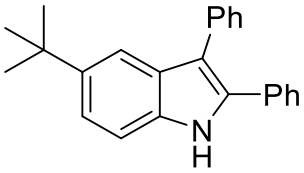
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.27 (s, NH), 7.80 (s, 1H), 7.42-7.38 (m, 6H), 7.35-7.28 (m, 6H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 135.35 (s, $C_{quat}$), 134.59 (s, $C_{quat}$), 134.45 (s, $C_{quat}$), 132.23 (s, $C_{quat}$), 130.66 (s, CH), 130.17 (s, CH), 128.89 (s, CH), 128.81 (s, CH), 128.25 (s, CH), 128.17 (s, CH), 126.70 (s, CH), 125.60 (s, CH), 122.30 (s, CH), 114.78 (s, $C_{quat}$), 113.83 (s, $C_{quat}$), 112.47 (s, CH).

**APCI-TOF-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{20}H_{15}NBr]^+$ 348.03824, found 348.03935.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3414, 3058, 2924, 1883, 1714, 1601, 1503, 1457, 1365, 1308, 1284, 1243, 1216, 1179, 1096, 1070, 1052, 1028, 965, 921, 868, 796, 758, 696.

**5-*tert*-butyl-2,3-diphenyl-1*H*-indole (3g, 864)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 88.2 mg, 0.27 mmol, 54% (white solid).

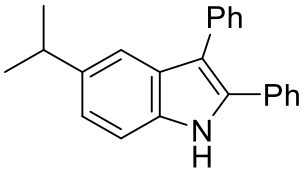
**$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.08 (s, NH), 7.59 (s, 1H), 7.38 (d, $^3J$= 7.1 Hz, 2H), 7.34-7.28 (m, 6H), 7.26-7.20 (m, 4H), 7.19 (s, 1H), 1.31 (s, 9H).

**$^{13}$C{$^1$H}-NMR (101 MHz, $CDCl_3$)**: $\delta$ (ppm) = 143.66 (s, $C_{quat}$), 135.42 (s, $C_{quat}$), 134.54 (s, $C_{quat}$), 134.23 (s, $C_{quat}$), 133.09 (s, $C_{quat}$), 130.37 (s, CH), 128.80 (s, CH), 128.68 (s, CH), 128.60 (s, $C_{quat}$), 128.30 (s, CH), 127.70 (s, CH), 126.27 (s, CH), 121.21 (s, CH), 115.45 (s, $C_{quat}$), 115.34 (s, $C_{quat}$), 110.55 (s, CH), 34.87 (s, $C_{quat}$), 32.06 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{24}H_{24}N]^+$ 326.19033, found 326.18961.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3383, 3051, 2956, 2864, 1863, 1735, 1602, 1502, 1467, 1424, 1361, 1303, 1255, 1202, 1154, 1097, 1070, 1026, 971, 913, 889, 841, 805, 758, 695.

**5-Isopropyl-2,3-diphenyl-1*H*-indole (3h, 884)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 89.2 mg, 0.29 mmol, 57 % (white solid).

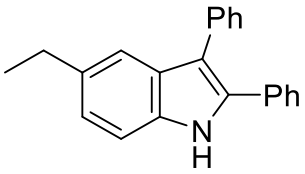
**$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.05 (s, NH), 7.44 (s, 1H), 7.39-7.28 (m, 7H), 7.26-7.16 (m, 4H), 7.08 (d, $^3J$= 8.2 Hz, 1H), 2.95 (sept, , $^3J$= 6.9 Hz, 1H), 1.23 (d, $^3J$= 6.9 Hz, 6H).

**$^{13}$C{$^1$H}-NMR (101 MHz, $CDCl_3$)**: $\delta$ (ppm) = 141.47 (s, $C_{quat}$), 135.43 (s, $C_{quat}$), 134.65 (s, $C_{quat}$), 134.50 (s, $C_{quat}$), 133.04 (s, $C_{quat}$), 130.37 (s, CH), 128.94 (s, $C_{quat}$), 128.79 (s, CH), 128.66 (s, CH), 128.28 (s, CH), 127.71 (s, CH), 126.28 (s, CH), 121.96 (s, CH), 116.74 (s, CH), 115.10 (s, $C_{quat}$), 110.86 (s, CH), 34.55 (s, CH), 19.04 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{23}H_{22}N]^+$ 312.17468, found 312.17468.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3389, 3050, 2956, 2925, 2866, 1734, 1602, 1551, 1504, 1472, 1452, 1427, 1363, 1309, 1261, 1096, 1067, 1028, 970, 940, 912, 885, 842, 805, 755, 694.

**5-Ethyl-2,3-diphenyl-1*H*-indole (3i, 876)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 88.7 mg, 0.30 mmol, 59% (yellow resin).

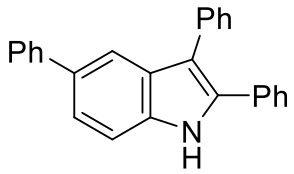
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.15 (s, NH), 7.48 (s, 1H), 7.45-7.37 (m, 6H), 7.35-7.26 (m, 5H), 7.11 (dd, $^4J$= 1.3 Hz, $^3J$= 8.2 Hz, 1H), 2.74 (q, $^3J$= 7.6 Hz, 2H), 1.27 (t, $^3J$= 7.6 Hz, 3H).

**$^{13}$C{$^1$H}-NMR (150 MHz, $CDCl_3$)**: $\delta$ (ppm) = 136.75 (s, $C_{quat}$), 135.41 (s, $C_{quat}$), 134.54 (s, $C_{quat}$), 134.42 (s, $C_{quat}$), 133.01 (s, $C_{quat}$), 130.36(s, CH), 129.10 (s, $C_{quat}$), 128.80 (s, CH), 128.65 (s, CH), 128.25 (s, CH), 127.72 (s, CH), 126.30 (s, CH), 123.44 (s, CH), 118.23 (s, CH), 114.97 (s, $C_{quat}$), 110.83 (s, CH), 29.32 (s, $CH_2$), 16.78 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{22}H_{20}N]^+$ 298.15903, found 298.15878.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3389, 3053, 2961, 2927, 2861, 1814, 1745, 1600, 1549, 1502, 1472, 1450, 1371, 1311, 1251, 1153, 1092, 1069, 1027, 963, 911, 883, 842, 807, 757, 694.

**6-Methyl-2,3-diphenyl-1*H*-indole (3j, 914)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 94.8 mg, 0.27 mmol, 55 % (yellow resin).

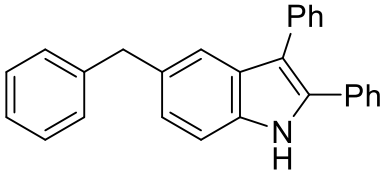
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.27 (s, NH), 7.89 (s, 1H), 7.64 (d, $^3J$= 7.2 Hz, 2H), 7.53-7.40 (m, 10H), 7.36-7.31 (m, 5H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 142.63 (s, $C_{quat}$), 135.55 (s, $C_{quat}$), 135.07 (s, $C_{quat}$), 134.91 (s, $C_{quat}$), 134.27 (s, $C_{quat}$), 132.74 (s, $C_{quat}$), 130.35 (s, CH), 129.43 (s, $C_{quat}$), 128.86 (s, CH), 128.75 (s, CH), 128.28 (s, CH), 127.92 (s, CH), 127.57, 126.54 (s, CH), 126.48 (s, CH), 122.74 (s, CH), 118.33 (s, CH), 115.57 (s, $C_{quat}$), 111.26 (s, CH).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{26}H_{20}N]^+$ 346.15903, found 346.15897.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3410, 3050, 1738, 1597, 1459, 1369, 1312, 1253, 1173, 1072, 1028, 963, 911, 885, 808, 755, 691.

**5-Benzyl-2,3-diphenyl-1*H*-indole (3k, 875)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 80.9 mg, 0.23 mmol, 45% (yellowish resin).

**$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.08 (s, NH), 7.47 (s, 1H), 7.37-7.26 (m, 6H), 7.24-7.06 (m, 9H), 6.98 (dd, $^4J$= 1.4 Hz, $^3J$= 8.3 Hz, 1H), 4.00 (s, 2H).

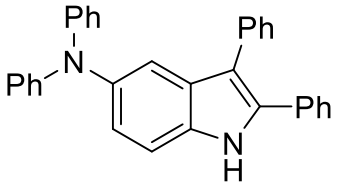
**$^{13}$C{$^1$H}-NMR (101 MHz, $CDCl_3$)**: $\delta$ (ppm) = 142.46 (s, $C_{quat}$), 135.26 (s, $C_{quat}$), 134.76 (s, $C_{quat}$), 134.58 (s, $C_{quat}$), 133.33 (s, $C_{quat}$), 132.94 (s, $C_{quat}$), 130.32 (s, CH), 129.10 (s, $C_{quat}$), 128.92 (s, CH), 128.83 (s,

$C_{quat}$), 128.68 (s, CH), 128.47 (s, CH), 128.29 (s, CH), 127.80 (s, CH), 126.35 (s, CH), 125.93 (s, CH), 124.43 (s, CH), 119.78 (s, CH), 115.08 (s, $C_{quat}$), 111.09 (s, CH), 42.32 (s, $CH_2$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{27}H_{22}N]^+$ 360.17468, found 360.17456.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3404, 3021, 2891, 1813, 1600, 1474, 1448, 1368, 1317, 1249, 1183, 1153, 1069, 1027, 975, 944, 925, 877, 811, 759, 738, 694.

***N,N*,2,3-tetraphenyl-1*H*-indol-5-amine (3l, CHB-605)**




The crude product was purified by flash column chromatography on silica gel with ethyl acetate:hexane (1:9). Isolated yield: 87.4 mg, 0.20 mmol, 40% (beige solid).

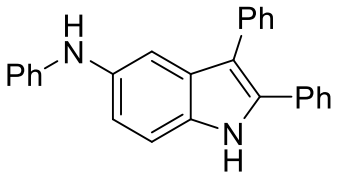
**$^1$H-NMR (400 MHz, DMSO-$d_6$):** δ (ppm) = 11.64 (s, NH), 7.48-7.19 (m, 16H), 6.96-6.88 (m, 7H).

**$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-$d_6$):** δ (ppm) = 148.08 (s, $C_{quat}$), 139.61 (s, $C_{quat}$), 135.28 (s, $C_{quat}$), 134.93 (s, $C_{quat}$), 133.73 (s, $C_{quat}$), 132.27 (s, $C_{quat}$), 129.58 (s, CH), 129.12 (s, CH), 128.84 (s, $C_{quat}$), 128.64 (s, CH), 128.50 (s, CH), 128.16 (s, CH), 127.64 (s, CH), 126.12 (s CH), 122.31 (s, CH), 121.81 (s, CH). 121.33 (s, CH), 116.59 (s, CH), 113.29 (s, $C_{quat}$), 112.88 (s, CH).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{32}H_{25}N_2]^+$: 437.20123, measured: 437.20129.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3387, 3040, 1739, 1585, 1480, 1280, 1172, 1067, 1035, 962, 882, 812, 757, 696.

***N*,2,3-triphenyl-1*H*-indol-5-amine (3m, CHB-604)**




The crude product was purified by flash column chromatography on silica gel with toluene:dichloromethane (19:1). Isolated yield: 76.1 mg, 0.21 mmol, 42% (pale brown solid).

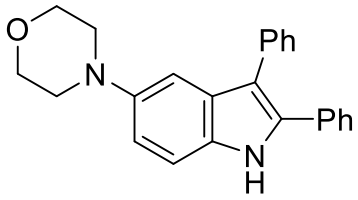
**$^1$H-NMR (400 MHz, DMSO-$d_6$):** δ (ppm) = 11.42 (s, NH), 7.81 (s, NH), 7.45-7.43 (m, 2H), 7.40-7.26(m, 9H), 7.22 (d, $^4J$ = 2.0 Hz, 1H), 7.12 (t, $^3J$= 7.8 Hz, 2H), 7.01 (dd, $^3J$ = 8.6 Hz, $^4J$ = 2.0 Hz, 1H), 6.92-6.90 (m. 2H), 6.65 (t, $^3J$ = 7.3 Hz, 1H).
**$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-$d_6$):** δ (ppm) = 146.61 (s, $C_{quat}$), 136.13 (s, $C_{quat}$), 135.94 (s, $C_{quat}$), 135.03 (s, $C_{quat}$), 133.04 (s, $C_{quat}$), 132.74 (s, $C_{quat}$), 130.15 (s, CH), 129.48 (s, CH), 129.11 (s, $C_{quat}$), 129.07 (s,

CH), 128.95 (s, CH), 128.50 (s, CH), 127.89 (s, CH), 126.45 (s, CH), 118.16 (s, CH), 117.65 (s, CH), 114.80 (s, CH), 113.37 (s, $C_{quat}$), 112.46 (s, CH), 109.18 (s, CH).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{26}H_{21}N_2]^+$: 361.16993, measured: 361.17020.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3383, 3046, 1732, 1594, 1500, 1365, 1298, 1169, 1071, 1029, 983, 952, 917, 873, 800, 752, 690.

**4-(2,3-diphenyl-1*H*-indol6-yl)-morpholine (3n, 899)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane → ethyl acetate:dichloromethane (1:4). Isolated yield: 104.5 mg, 0.29 mmol, 59 % (yellow resin).

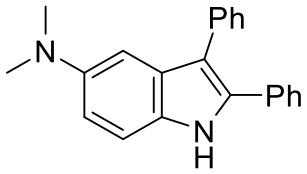
**$^1$H-NMR (600 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 11.33 (s, NH), 7.42-7.38 (m, 4H), 7.35-7.32 (m, 5H), 7.28-7.26 (m, 2H), 6.96 (dd, $^4J$= 2.1 Hz, $^3J$= 6.0 Hz), 6.92 (d, $^4J$= 1.9 Hz, 1H), 3.73 (t, $^3J$= 4.6 Hz, 4H), 2.99 (t, $^3J$= 4.6 Hz, 4H).

**$^{13}$C{$^1$H}-NMR (151 MHz, DMSO-$d_6$):** $\delta$ (ppm) = 145.90 (s, $C_{quat}$), 135.57 (s, $C_{quat}$), 134.36 (s, $C_{quat}$), 132.64 (s, $C_{quat}$), 131.50 (s, $C_{quat}$), 129.73 (s, CH), 128.67 (s, $C_{quat}$), 128.44 (s, CH), 128.25 (s, $C_{quat}$), 127.99 (s, CH), 127.30 (s, CH), 125.93 (s, CH), 114.88 (s, $C_{quat}$), 113.15 (s, $C_{quat}$), 111.93 (s, CH), 104.11 (s, CH), 66.37 (s, $CH_2$) 51.02 (s, $CH_2$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{24}H_{23}N_2O]^+$ 355.18049, found 355.18137.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3325, 3047, 2867, 1735, 1598, 1455, 1375, 1306, 1229, 1170, 1108, 1063, 950, 899, 843, 806, 758, 692.

***N,N*-Dimethyl-2,3-diphenyl-1*H*-indol-5-amine (3o, 898)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:9). Isolated yield: 97.5 mg, 0.31 mmol, 62 %.

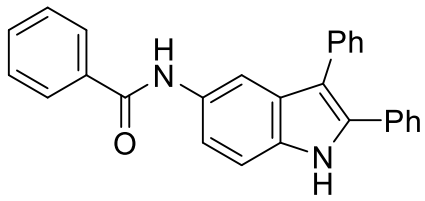
**$^{1}$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.07 (s, NH), 7.46-7.38 (m, 6H), 7.34-7.26 (m, 5H), 7.06 (d, $^{3}J$= 1.6 Hz, 1H), 6.96 (dd, $^{4}J$= 2.2 Hz, $^{3}J$= 8.8 Hz, 1H), 2.91 (s, 6H).

**$^{13}$C{$^{1}$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 146.83 (s, $C_{quat}$), 135.61 (s, $C_{quat}$), 134.79 (s, $C_{quat}$), 133.09 (s, $C_{quat}$), 130.46 (s, $C_{quat}$), 130.28 (s, CH), 129.50 (s, $C_{quat}$), 128.74 (s, CH), 128.67 (s, CH), 128.20 (s, CH), 127.59 (s, CH), 126.15 (s, CH), 114.77 (s, $C_{quat}$), 113.78 (s, CH), 111.45 (s, CH), 103.67 (s, CH), 43.02 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{22}H_{21}N_2]^+$ 313.16993, found 313.17075.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3126, 3029, 2938, 2826, 2740, 1733, 1597, 1453, 1427, 1379, 1296, 1171, 1122, 1030, 954, 921, 861, 762, 691.

***N*-(2,3-diphenyl-1*H*-indol-5-yl)benzamide (3p, 902.2-F2)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:4). Isolated yield: 123.5 mg, 0.32 mmol, 64 % (yellowish solid).

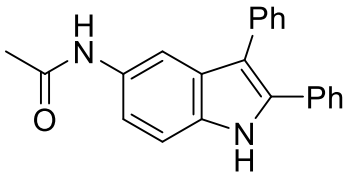
**$^{1}$H-NMR (600 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 11.55 (s, NH), 10.15 (s, NH), 8.01 (s, 1H), 7.98 (d, $^{3}J$= 7.6 Hz, 2H), 7.60-7.41 (m, 9H), 7.37-7.29 (m, 6H).

**$^{13}$C{$^{1}$H}-NMR (151 MHz, DMSO-$d_6$):** $\delta$ (ppm) = 165.00 (s, $C_{quat}$), 135.40 (s, $C_{quat}$), 135.29 (s, $C_{quat}$), 134.71 (s, $C_{quat}$), 133.14 (s, $C_{quat}$), 132.44 (s, $C_{quat}$), 132.00 (s, $C_{quat}$), 131.25 (s, CH), 129.80 (s, CH), 128.70 (s, CH), 128.54 (s, CH), 128.31 (s, CH), 128.08 (s, CH), 127.88 (s, $C_{quat}$), 127.54 (s, CH), 126.13 (s, CH), 116.92 (s, $CH_t$), 113.47 (s, $C_{quat}$), 111.20 (s, CH), 110.42 (s, CH).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{27}H_{20}N_2ONa]^+$ 411.14678, found 411.14786.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3421, 3288, 3055, 2921, 1741, 1653, 1536, 1437, 1378, 1315, 1258, 1182, 1073, 1027, 973, 914, 847, 809, 760, 695.

***N*-(2,3-diphenyl-1H-indol-5-yl)acetamide (3q, 885-F2)**



The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:1). Isolated yield: 126.7 mg, 0.39 mmol, 78 % (white solid).

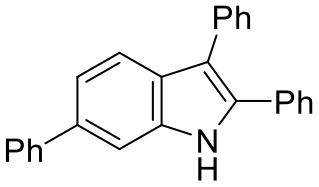
**$^1$H-NMR (600 MHz, DMSO-d$_6$)**: $\delta$ (ppm) = 11.48 (s,NH), 9.78 (s, NH), 7.81 (s, 1H), 7.44-7.39 (m, 4H), 7.37-7.28 (m, 8H), 2.01 (s, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, DMSO-d$_6$)**: $\delta$ (ppm) = 167.62 (s, $C_{quat}$), 135.44 (s, $C_{quat}$), 134.66 (s, $C_{quat}$), 132.77 (s, $C_{quat}$), 132.48 (s, $C_{quat}$), 132.37 (s, $C_{quat}$), 129.77 (s, CH), 128.69 (s, CH), 128.54 (s, CH), 128.09 (s, CH), 127.90 (s, CH), 127.52 (s, $C_{quat}$), 126.11 (s, CH), 115.69 (s, CH), 113.34 (s, $C_{quat}$), 111.31 (s, CH), 108.82 (s, CH), 23.96 (s, $CH_3$).

**ESI-HRMS**: $[M+Na]^+$ m/z: calculated for $[C_{23}H_{22}N_2ONa]^+$ 349.13113, found 349.13159.

**IR** (neat, cm$^{-1}$): $\tilde{\nu}$: 3410, 3177, 3058, 2927, 1882, 1658, 1592, 1527, 1476, 1432, 1371, 1323, 1261, 1216, 1158, 1098, 1068, 1030, 1097, 952, 914, 866, 790, 757, 687.

**2,3,6-triphenyl-1H-indole (3r, CHB-621)**



The crude product was purified by flash column chromatography on silica gel with ethyl acetate:hexane (1:9). Isolated yield: 71.5 mg, 0.21 mmol, 41% (pale-brown solid).

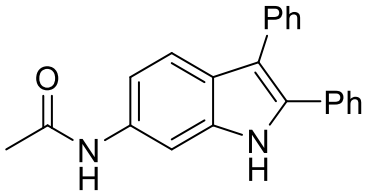
**$^1$H-NMR (400 MHz, DMSO-d$_6$):** δ (ppm) = 11.69 (s, NH), 7.70-7.7.68 (m, 3H), 7.56 (d, $^3J$ = 8.3 Hz, 1H), 7.50-7.28 (m, 14H).

**$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-d$_6$):** δ (ppm) = 141.39 (s, $C_{quat}$), 136.71 (s, $C_{quat}$), 135.14 (s, $C_{quat}$), 134.90 (s, $C_{quat}$), 134.42 (s, $C_{quat}$), 132.34 (s, $C_{quat}$), 129.70 (s, CH), 128.90 (s, CH), 128.65 (s, CH), 128.52 (s, CH), 128.14 (s, CH), 127.61 (s, CH), 127.50 (s, $C_{quat}$), 126.67 (s, CH), 126.64 (s, CH), 126.16 (s, CH), 119.21 (s, CH), 119.07(s, CH), 113.30 (s, $C_{quat}$), 109.49 (s, CH).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{26}H_{20}N]^+$: 346.15903, measured: 346.16013.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3395, 3052, 1732, 1597, 1448, 1500, 1448, 1326, 1250, 1200, 1143, 1071, 1022, 967, 916, 855, 820, 760, 691.

**N-(2,3-diphenyl-1H-indol-6-yl)acetamide (3s, CHB-615)**




The crude product was purified by flash column chromatography on silica gel with ethyl acetate:hexane (1:2 → 1:1). Isolated yield: 78.0 mg, 0.24 mmol, 48% (beige solid).

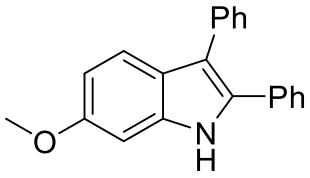
**$^{1}$H-NMR (400 MHz, DMSO-$d_6$):** δ (ppm) = 11.41 (s, NH), 9.90 (s, NH), 8.07 (s, 1H), 7.44-7.05 (m, 11H), 7.07 (dd, $^{3}J$ = 8.6 Hz, $^{4}J$ = 1.6 Hz, 1H), 2.07 (s, 3H).

**$^{13}$C{$^{1}$H}-NMR (101 MHz, DMSO-$d_6$):** δ (ppm) = 167.85 (s, $C_{quat}$), 136.17 (s, $C_{quat}$), 135.30 (s, $C_{quat}$), 134.49 (s, $C_{quat}$), 133.50 (s, $C_{quat}$), 132.54 (s, $C_{quat}$), 129.63 (s, CH), 128.60 (s, CH), 128.46 (s, CH), 127.87 (s, CH), 127.25 (s, $C_{quat}$), 126.02 (s, $C_{quat}$), 124.11 (s, CH), 118.44 (s, CH), 113.25 (s, CH), 112.87 (s, CH), 101.70 (s, CH), 24.05 (s, $CH_3$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{22}H_{19}ON_2]^+$: 327.14919, measured: 327.15005.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3419, 3222, 3058, 2920, 1726, 1662, 1591, 1527, 1417, 1364, 1332, 1248, 1140, 1069, 1017, 958, 912, 862, 801, 761, 691.

**6-Methoxy-2,3-diphenyl-1*H*-indole (3t, CHB-611)**




The crude product was purified by flash column chromatography on silica gel with ethyl acetate:hexane (1:9). Isolated yield: 65.5 mg, 0.22 mmol, 44% (beige solid).

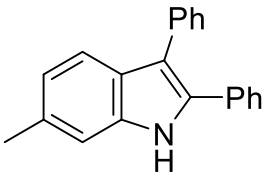
**$^{1}$H-NMR (600 MHz, $CDCl_3$):** δ (ppm) = 8.11 (broad s, NH), 7.55 (d, $^{3}J$ = 8.7 Hz, 1H), 7.44-7-36 (m, 6H), 7.33-7.25 (m, 4H), 6.93 (d, $^{4}J$ =2.2 Hz, 1H), 6.82 (dd, $^{3}J$ = 8.7 Hz, $^{4}J$ = 2.2 Hz, 1H), 3.89 (s, 3H).

**$^{13}$C{1H}-NMR (151 MHz, $CDCl_3$):** δ (ppm) = 157.02 (s, $C_{quat}$), 136.71 (s, $C_{quat}$), 135.17 (s, $C_{quat}$), 132.91 (s, $C_{quat}$), 132.83 (s, $C_{quat}$), 130.08 (s, CH), 128.68 (s, CH), 128.52 (s, CH), 127.87 (s, CH), 127.36 (s, CH), 126.22 (s, CH), 123.31 (s, $C_{quat}$), 120.46 (s, CH), 115.04 (s, $C_{quat}$), 110.31 (s, CH), 94.41 (s, CH), 55.77 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}ON_2]^+$: 300.13829, measured: 300.13806.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$= 3330, 3063, 2960, 295, 1749, 1602, 1497, 1447, 1324, 1254, 1192, 1154, 1116, 1016, 966, 913, 816, 760, 695.

**6-Methyl-2,3-diphenyl-1*H*-indole (3u, 903)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 94.8 mg, 0.33 mmol, 67% (yellowish resin).

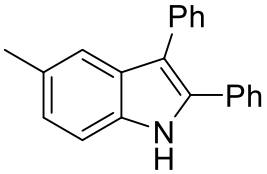
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.09 (s, NH), 7.60 (d, $^3J$= 8.1 Hz, 1H), 7.47 (m, 2H), 7.44-7.39 (m, 4H), 7.35-7.29 (m, 4H), 7.23 (s, 1H), 7.02 (d, $^3J$= 8.2 Hz, 1H), 2.52 (s, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 136.46 (s, $C_{quat}$), 135.37 (s, $C_{quat}$), 133.51 (s, $C_{quat}$), 132.99 (s, $C_{quat}$), 132.75 (s, $C_{quat}$), 130.23 (s, CH), 128.77 (s, CH), 128.62 (s, CH), 128.19 (s, CH), 127.62 (s, CH), 126.78 (s, $C_{quat}$), 126.27 (s, CH), 122.32 (s, CH), 119.49 (s, CH), 115.02 (s, $C_{quat}$), 110.96 (s, CH), 21.89 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}N]^+$ 284.14338, found 284.14407.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$: 3404, 3257, 3053, 2916, 2863, 1720, 1602, 1550, 1500, 1449, 1324, 1248, 1131, 1025, 953, 915, 855, 805, 760, 694.

**5-Methyl-2,3-diphenyl-1*H*-indole (3v, 872)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 78.7 mg, 0.28 mmol, 56% (white solid).

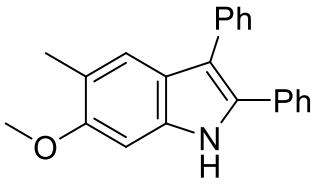
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.12 (s, NH), 7.51-7.40 (m, 6H), 7.40-7.29 (m, 5H), 7.11 (m, 1H), 2.48 (m, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 135.38 (s, $C_{quat}$), 134.33 (s, $C_{quat}$), 132.93 (s, $C_{quat}$), 130.32 (s, CH), 129.85 (s, $C_{quat}$), 129.14 (s, $C_{quat}$), 128.76 (s, CH), 128.63 (s, CH), 128.22 (s, CH), 127.68 (s, CH), 126.28 (s, CH), 124.42 (s, CH), 119.35 (s, CH), 114.77 (s, $C_{quat}$), 110.70 (s, $C_{quat}$), 21.68 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}N]^+$ 284.14338, found 284.14285.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3368, 3021, 1741, 1600, 1447, 1367, 1305, 1082, 780, 695.

**6-methoxy-5-methyl-2,3-diphenyl-1*H*-indole (3w, 892)**



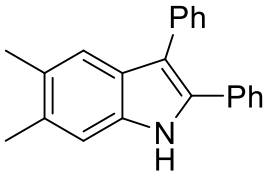

The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 91.2 mg, 0.29 mmol, 59% (white solid).
Due to very broad signals, a $^{13}$C-NMR could not be provided.

**$^1$H-NMR (400 MHz, $CDCl_3$)**: $\delta$ (ppm) = 7.97 (s, NH), 7.43-7.11 (m, 11H), 6.79 (s, 1H), 3.82 (s, 3H), 2.22 (s, 3H).

**ESI-HRMS:** $[M+Na]^+$ m/z: calculated for $[C_{22}H_{19}NONa]^+$ 336.13589, found 336.13654.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3331, 3062, 2925, 1745, 1602, 1558, 1454, 1337, 1291, 1245, 1192, 1134, 1081, 1014, 957, 882, 826, 761, 693.

**5,6-Dimethyl-2,3-diphenyl-1*H*-indole (3x, 871)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 90.8 mg, 0.31 mmol, 61% (yellow solid).

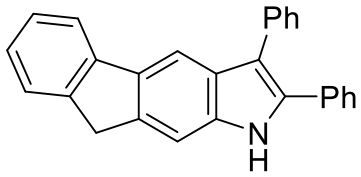
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.05 (s, NH), 7.45-7.37 (m, 7H), 7.32-7.25 (m, 5H), 7.21 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 135.60 (s, $C_{quat}$), 135.04 (s, $C_{quat}$), 133.39 (s, $C_{quat}$), 133.15 (s, $C_{quat}$), 132.04 (s, $C_{quat}$), 130.30 (s, CH), 129.30 (s, $C_{quat}$), 128.76 (s, CH), 128.61 (s, CH), 128.14 (s, CH), 127.51 (s, CH), 127.35 (s, $C_{quat}$), 126.21 (s, CH), 119.79 (s, CH), 114.71 (s, $C_{quat}$), 111.38 (s, $C_{quat}$), 20.64 (s, $CH_3$), 20.29 (s,$CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{22}H_{20}N]^+$ 298.15903, found 298.15823.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3411, 3054, 2923, 1884, 1601, 1544, 1499, 1446, 1382, 1330, 1285, 1248, 1216, 1177, 1096, 1072, 1025, 1001, 961, 915, 849, 801, 758, 695.

**2,3-Diphenyl-1,9-dihyroindeno[1,2-*f*]indole (3y, 874)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (0.5:9.5). Isolated yield: 104.2 mg, 0.29 mmol, 58% (slightly pink solid).

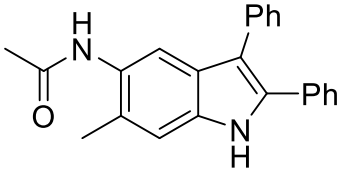
**$^1$H-NMR (600 MHz, $CDCl_3$)**: $\delta$ (ppm) = 8.22 (s, NH), 8.03 (s, 1H), 7.79 (d, $^3J$= 7.6 Hz, 1H), 7.56 (s, 1H), 7.52-7.51 (m, 3H), 7.45-7.43 (m, 4H), 7.36-7.32 (m, 4H), 7.31-7.28 (m, 1H), 7.25-7.23 (m, 1H), 4.02 (s, 2H).

**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$)**: $\delta$ (ppm) = 143.09 (s, $C_{quat}$), 142.57 (s, $C_{quat}$), 139.19 (s, $C_{quat}$), 136.25 (s, $C_{quat}$), 135.61 (s, $C_{quat}$), 135.39 (s, $C_{quat}$), 134.24 (s, $C_{quat}$), 132.90 (s, $C_{quat}$), 130.42 (s, CH), 128.84 (s, CH), 128.79 (s, CH), 128.55 (s, $C_{quat}$), 128.17 (s, CH), 127.74 (s, CH), 126.83 (s, CH), 126.83 (s, CH), 126.47 (s, CH), 125.85 (s, CH), 125.03 (s, CH), 119.53 (s, CH), 115.47 (s, $C_{quat}$), 110.43 (s, CH), 107.40 (s, CH), 36.74 (s, $CH_2$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{27}H_{20}N]^+$ 358.15903, found 358.15900.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3389, 3053, 1600, 1503, 1480, 1449, 1411, 1364, 1278, 1242, 1150, 1115, 1069, 1026, 950, 910, 871, 843, 758, 729, 695.

***N*-(4-Methyl-2,3-diphenyl-1*H*-indol-5-yl)acetamide (3z, 908)**




Due to high insolubility of the compound, the reaction mixture was filtered and washed with cold hexane (3x 50 mL). The residue was dissolved in ethanol and recrystallized. The solid was filtered, washed with pentane (3x 20 mL) and dried. NMR-Analysis showed an unidentified impurity (s at 1.80 ppm in DMSO-$d_6$), which was removed by three portions $SiO_2$ gel column chromatograph with ethyl acetate:dichloromethane (1:4). Isolated yield: 123.2 mg, 0.36 mmol, 72% (beige solid).

**$^1$H-NMR (600 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 11.40 (s, NH), 9.22 (s, NH), 7.44 (d, $^3J$= 7.5 Hz, 2H), 7.40-7.26 (m, 10H), 2.29 (s, 3H), 2.02 (s, 3H).

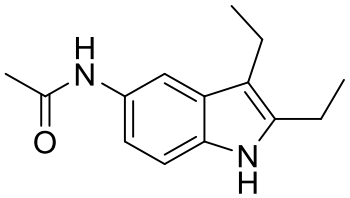
**$^{13}$C{$^1$H}-NMR (151 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 168.29 (s, $C_{quat}$), 135.40 (s, $C_{quat}$), 134.44 (s, $C_{quat}$), 133.97 (s, $C_{quat}$), 132.51 (s, $C_{quat}$), 129.61 (s, CH), 128.67 (s, CH), 128.51 (s, CH), 128.13 (s, CH), 128.04 (s,

CH), 127.73 (s, $C_{quat}$), 127.43 (s, CH), 126.30 (s, $C_{quat}$), 126.05 (s, CH), 115.66 and 115.63 (splitted- possibly rotamers, CH), 113.09 (s, $C_{quat}$), 111.93 and 111.91 (splitted- possibly rotamers, CH), 23.16 (s, $CH_3$), 18.56 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{23}H_{20}N_2ONa]^+$ 363.14678, found 363.14670.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3360, 3190, 3050, 2921, 2853, 1745, 1656, 1509, 1438, 1363, 1271, 1176, 1138, 1068, 1001, 915, 859, 761, 690.

***N*-(2,3-diethyl-1*H*-indol-5-yl)benzamide (3za, 925)**



The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:1). Isolated yield: 46.1 mg, 0.20 mmol, 41%.

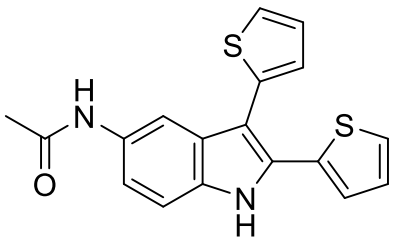
**$^1$H-NMR (600 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 10.53 (s, NH), 9.65 (s, NH), 7.68-7.67 (m, 1H), 7.19-7.09 (m, 2H), 2.66 (q, $^3J$= 7.6 Hz, 2H), 2.59 (q, $^3J$= 7.4 Hz, 2H), 2.01 (s, 3H), 1.21 (t, $^3J$= 7.6 Hz, 3H), 1.19 (t, $^3J$= 7.4 Hz, 3H).

**$^{13}$C{$^1$H}-NMR (151 MHz, DMSO-$d_6$)**: δ (ppm) = 167.41 (s, $C_{quat}$), 137.37 (s, $C_{quat}$), 132.00 (s, $C_{quat}$), 130.72 (s, $C_{quat}$), 127.56 (s, $C_{quat}$), 113.59 (s, CH), 111.11 (s, $C_{quat}$), 110.12 (s, CH), 108.39 (s, CH), 23.91 (s, $CH_3$), 18.83 (s, $CH_2$), 16.89 (s, $CH_2$), 15.91 (s, $CH_3$), 14.66 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{14}H_{18}N_2ONa]^+$ 253.13113, found 253.13130.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3276, 2961, 2867, 1652, 1545, 1468, 1370, 1269, 1129, 1013, 869, 801, 746, 662.

***N*-(2,3-di(thiophen-2-yl)-1*H*-indol-6-yl)acetamide (3zb, CHB-686)**



The crude product was purified by flash column chromatography on silica gel with ethyl acetate: hexane (1:1). Isolated yield: 32.6 mg, 96.5 μmol, 19% (light yellow solid).

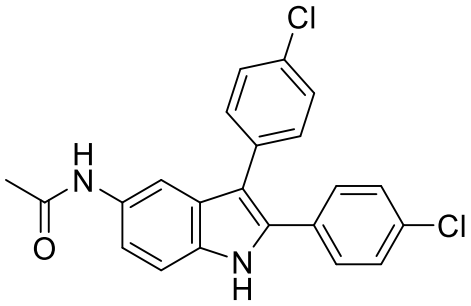
**$^1$H-NMR (400 MHz, DMSO-$d_6$):** δ (ppm) = 11.63 (s, 1H), 9.78 (s, 1H), 7.77 (s, 1H), 7.63 (d, $^3J$ = 5.0 Hz, 1H), 7.52 (d, $^3J$ = 4.9 Hz, 1H), 7.43 (d, $^3J$ = 3.2 Hz, 1H), 7.37-7.31 (m, 2H), 7.20-7.18 (m, 1H), 7.12-7.11 (m, 2H), 2.01 (s, 3H).

**$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-$d_6$):** δ (ppm) = 167.62 (s, $C_{quat}$), 135.25 (s, $C_{quat}$), 133.50 (s, $C_{quat}$), 132.64 (s, $C_{quat}$), 132.27 (s, $C_{quat}$), 130.54 (s, $C_{quat}$), 128.70 (s, $C_{quat}$), 127.65 (s, CH), 127.60 (s, CH), 127.20 (s, CH), 126.80 (s, CH), 126.41 (s, CH), 125.97 (s, CH), 116.08 (s, CH), 111.07 (s, CH), 108.79 (s, CH), 106.05 (s, $C_{quat}$), 23.91 (s, $CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{18}H_{15}ON_2S_2]^+$: 339.06203, measured: 339.06159.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3266, 3068, 2922, 1633, 1528, 1478, 1420, 1365, 1269, 1148, 1077, 1013, 960, 904, 849, 824, 798, 693.

***N*-(2,3-bis(4-chlorophenyl)-1*H*-indol-6-yl)acetamide (3zc, CHB-693)**




The crude product was purified by flash column chromatography on silica gel with dichloromethane:ethyl acetate (7:1→5:1). Isolated yield: 96.2 mg, 0.24 mmol, 49% (colourless solid).

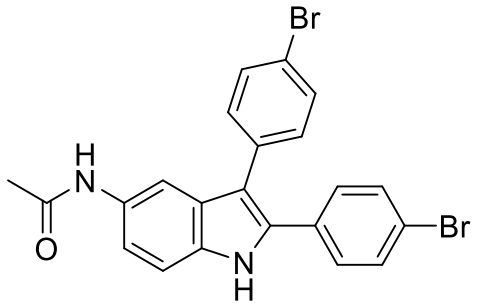
**$^1$H-NMR (400 MHz, DMSO-$d_6$):** δ (ppm) = 11.59 (broad s, NH), 9.78 (broad s, NH), 7.82 (s, 1H), 7.48-7.41 (m, 6H), 7.38-7.30 (m, 4H), 2.01 (s, 3H).

**$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-$d_6$):** δ (ppm) = 167.62 (s, $C_{quat}$), 134.01 (s, $C_{quat}$), 133.65 (s, $C_{quat}$), 132.76 (s, $C_{quat}$), 132.60 (s, $C_{quat}$), 132.28 (s, $C_{quat}$), 131.37 (s, CH), 131.01 (s, $C_{quat}$), 130.82 (s, $C_{quat}$), 129.76 (s, CH), 128.82 (s, CH), 128.69 (s, CH), 127.53 (s, $C_{quat}$), 116.06 (s, CH), 112.40 (s, $C_{quat}$), 111.45 (s, CH), 108.55 (s, CH), 23.90 (s, $CH_3$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{22}H_{17}ON_2Cl_2]^+$: 395.07125, measured: 395.07071.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3425, 3205, 2923, 1667, 1629, 1536, 1501, 1463, 1433, 1378, 1318, 1258, 1172, 1094, 1040, 1014, 963, 937, 835, 805, 748, 722, 670.

***N*-(2,3-bis(4-bromophenyl)-1*H*-indol-6-yl)acetamide (3zd, CHB-650)**




The crude product was purified by flash column chromatography on silica gel with dichloromethane: ethyl acetate (9:1). Isolated yield: 98.0 mg, 0.20 mmol, 40% (off-white solid).

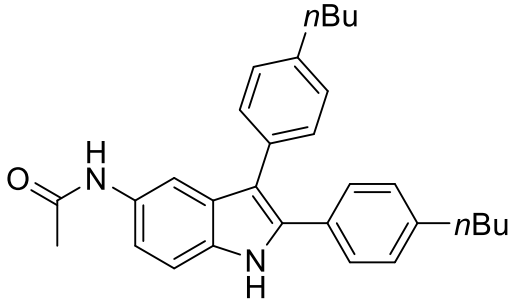
**$^{1}$H-NMR (400 MHz, DMSO-d$_6$):** δ (ppm) = 11.60 (s, NH), 9.77 (s, NH), 7.82 (s, 1H), 7.62-7.58 (m, 4H), 7.37-7.35 (m, 4H), 7.25 (d, $^{3}J$ = 8.2 Hz, 2H), 2.00 (s, 3H).

**$^{13}$C{$^{1}$H}-NMR (101 MHz, DMSO-d$_6$):** δ (ppm) = 167.61 (s, $C_{quat}$), 134.37 (s, $C_{quat}$), 133.66 (s, $C_{quat}$), 132.78 (s, $C_{quat}$), 132.62 (s, $C_{quat}$), 131.71 (s, CH), 131.62 (s, CH), 131.34 (s, CH), 131.34 (s, $C_{quat}$), 130.04 (s, CH), 127.46 (s, $C_{quat}$), 120.93 (s, $C_{quat}$), 119.31 (s, $C_{quat}$), 116.07 (s, CH), 112.42 (s, $C_{quat}$), 111.47 (s, CH), 108.52 (s, CH), 23.90 (s, $CH_3$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{22}H_{17}ON_2Br_2]^+$: 482.97021, measured: 482.97031.

**IR** (neat, cm$^{-1}$): $\tilde{\upsilon}$ = 3422, 3206, 2722, 1867, 1788, 1666, 1628, 1533, 1497, 1462, 1432, 1377, 1316, 1257, 1171, 1092, 1069, 1040, 1009, 961, 936, 858, 831, 803, 739, 711, 667.

***N*-(2,3-bis(4-*n*-butylphenyl)-1*H*-indol-5-yl)acetamide (3ze, 928)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:1). Isolated yield: 113 mg, 0.26 mmol, 51%.

**$^{1}$H-NMR (400 MHz, DMSO-d$_6$)**: $\delta$ (ppm) = 11.31 (s, NH), 9.71 (s, NH), 7.73 (s, 1H), 7.33-7.29 (m, 4H), 7.19-7.16 (m, 4H), 7.14-7.11 (m, 2H), 2.59 (t, $^{3}J$= 5.2 Hz, 2H), 2.55 (t, $^{3}J$= 5.1 Hz, 2H), 1.98 (s, 3H), 1.59

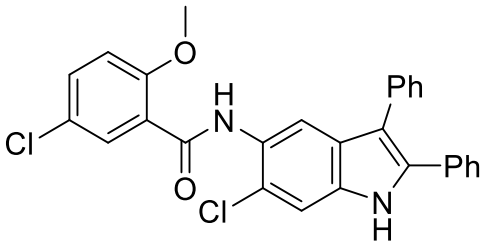
(quint, $^3J$= 5.1 Hz, 2H), 1.54 (quint, $^3J$= 5.3 Hz, 2H), 1.35 (quint, $^3J$= 4.9 Hz, 2H), 1.29 (quint, $^3J$= 4.9 Hz, 2H), 0.91 (t, $^3J$= 4.9 Hz, 3H), 0.88 (t, $^3J$= 4.9 Hz, 3H).

**$^{13}C\{^1H\}$-NMR (101 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 167.50 (s, $C_{quat}$), 141.60 (s, $C_{quat}$), 139.90 (s, $C_{quat}$), 134.54 (s, $C_{quat}$), 132.74 (s, $C_{quat}$), 132.69 (s, $C_{quat}$), 132.17 (s, $C_{quat}$), 129.97 (s, $C_{quat}$), 129.95 (s, CH), 128.47 (s, CH), 128.31 (s, CH), 128.08 (s, $C_{quat}$), 127.82 (s, CH), 115.41 (s, CH), 112.88 (s, $C_{quat}$), 111.05 (s, CH), 108.89 (s, CH), 34.62 (s, $CH_2$), 34.53 (s, $CH_2$), 33.14 (s, $CH_2$), 32.94 (s, $CH_2$), 23.88 (s, $CH_3$), 21.91 (s, $CH_2$), 21.83 (s, $CH_2$), 13.81 (s, $CH_3$), 13.75 (s, $CH_3$).

**APCI-TOF-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{30}H_{35}N_2O]^+$ 439.27439, found 439.27401.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3400, 3280, 3031, 2929, 2861, 1658, 1542, 1466, 1372, 1269, 1176, 1108, 1014, 957, 804, 729.

**5-chloro-*N*-(6-chloro-2,3-diphenyl-1*H*-indol-5-yl)-2-methoxybenzamide (3zf, BOE-921)**




The crude mixture is purified by $SiO_2$ gel column chromatograph with ethyl acetate:hexane (1:4). Isolated yield: 113.2 mg, 0.23 mmol, 47%.

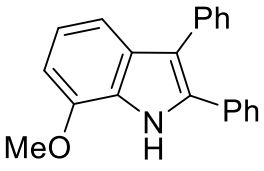
**$^1H$-NMR (600 MHz, DMSO-$d_6$)**: $\delta$ (ppm) = 11.75 (s, NH), 10.45 (s, NH), 8.51 (s, 1H), 8.01-7.96 (m, 1H), 7.63 (dd, $^3J$= 8.7 Hz, $^4J$= 2.8 Hz, 2H), 7.59 (s, 1H), 7.46-7.31 (m, 11H), 4.07 (s, 3H).

**$^{13}C\{^1H\}$-NMR (151 MHz, DMSO-$d_6$)**: δ (ppm) = 161.18 (s, $C_{quat}$), 155.91 (s, $C_{quat}$), 135.84 (s, $C_{quat}$), 134.65 (s, $C_{quat}$), 133.03 (s, $C_{quat}$), 132.79 (s, CH), 131.38 (s, $C_{quat}$), 130.35 (s, CH), 129.73 (s, CH), 128.82 (s, CH), 128.59 (s, CH), 128.10 (s, CH), 127.90 (s, CH), 127.54 (s, $C_{quat}$), 127.10 (s, $C_{quat}$), 126.48 (s, CH), 125.05 (s, $C_{quat}$), 123.11 (s, $C_{quat}$), 119.08 (s, $C_{quat}$), 114.76 (s, CH), 113.65 (s, $C_{quat}$), 112.55 (s, CH), 111.64 (s, CH) 57.06 ($CH_3$).

**ESI-HRMS**: $[M+H]^+$ m/z: calculated for $[C_{28}H_{21}N_2O_2Cl_2]^+$ 487.09746, found 487.09709.

**IR** (neat, $cm^{-1}$): $\tilde{\nu}$: 3269, 3076, 2938, 1681, 1645, 1587, 1538, 1473, 1402, 1345, 1321, 1269, 1235, 1177, 1143, 1115, 1073, 1017, 915, 879, 845, 810, 755, 697, 674.

**7-methoxy-2,3-diphenyl-1H-indole (3zg, CHB-612)**



(CHB-612): The crude product was purified by flash column chromatography on silica gel with ethyl acetate:hexane (1:9). Isolated yield: 58.7 mg, 0.20 mmol, 39% (pale brown solid).

**$^1$H-NMR (600 MHz, $CDCl_3$):** δ (ppm) = 8.45 (broad s, 1H), 7.45-7.44 (m, 4H), 7.38-7.36 (m, 2H), 7.33-7.27 (m, 5H), 7.08 (t, $^3J$ = 7.4 Hz, 1H), 6.71 (d, $^3J$ = 7.7 Hz, 1H), 4.01 (s, 3H).

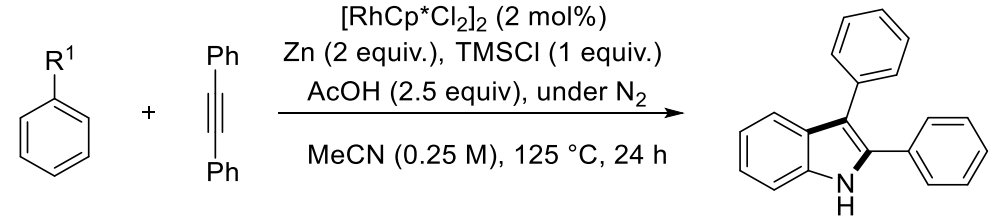
**$^{13}$C{$^1$H}-NMR (151 MHz, $CDCl_3$):** δ (ppm) = 146.18 (s, $C_{quat}$), 135.42 (s, $C_{quat}$), 133.94 (s, $C_{quat}$), 132.93 (s, $C_{quat}$), 130.29 (s, CH), 130.13 (s, $C_{quat}$), 128.80 (s, CH), 128.62 (s, CH), 128.32 (s, CH), 127.76 (s, CH), 126.58 (s, $C_{quat}$), 126.31 (s, CH), 120.92 (s, CH), 115.57 (s, $C_{quat}$), 112.56 (s, CH), 102.69 (s, CH), 55.31 (s, $CH_3$).

**ESI-HRMS:** $[M+H]^+$ m/z: calculated for $[C_{21}H_{18}NO]^+$ m/z calc.: 300.13829, measured: 300.13818.

**IR** (neat, $cm^{-1}$): $\tilde{\upsilon}$ = 3335, 3051, 2944, 1739, 1581, 1490, 1450, 1378, 1317, 1241, 1159, 1068, 983, 911, 857, 768, 689.

**Control experiments**

Reactions were carried out under standard conditions.




**1a** (1 equiv.) **2a** (1.2 equiv.) **3a**

| # | $R^1$ | Isolated yield |
|---|---|---|
| 1 | NHOH | 5% |
| 2 | NH2 | 0% |
| 3 | NO | 14% |
| 4 | ½ NH-NH-Ph | 0% |
| 5 | ½ N=N-Ph | <1% |

## Supplementary References

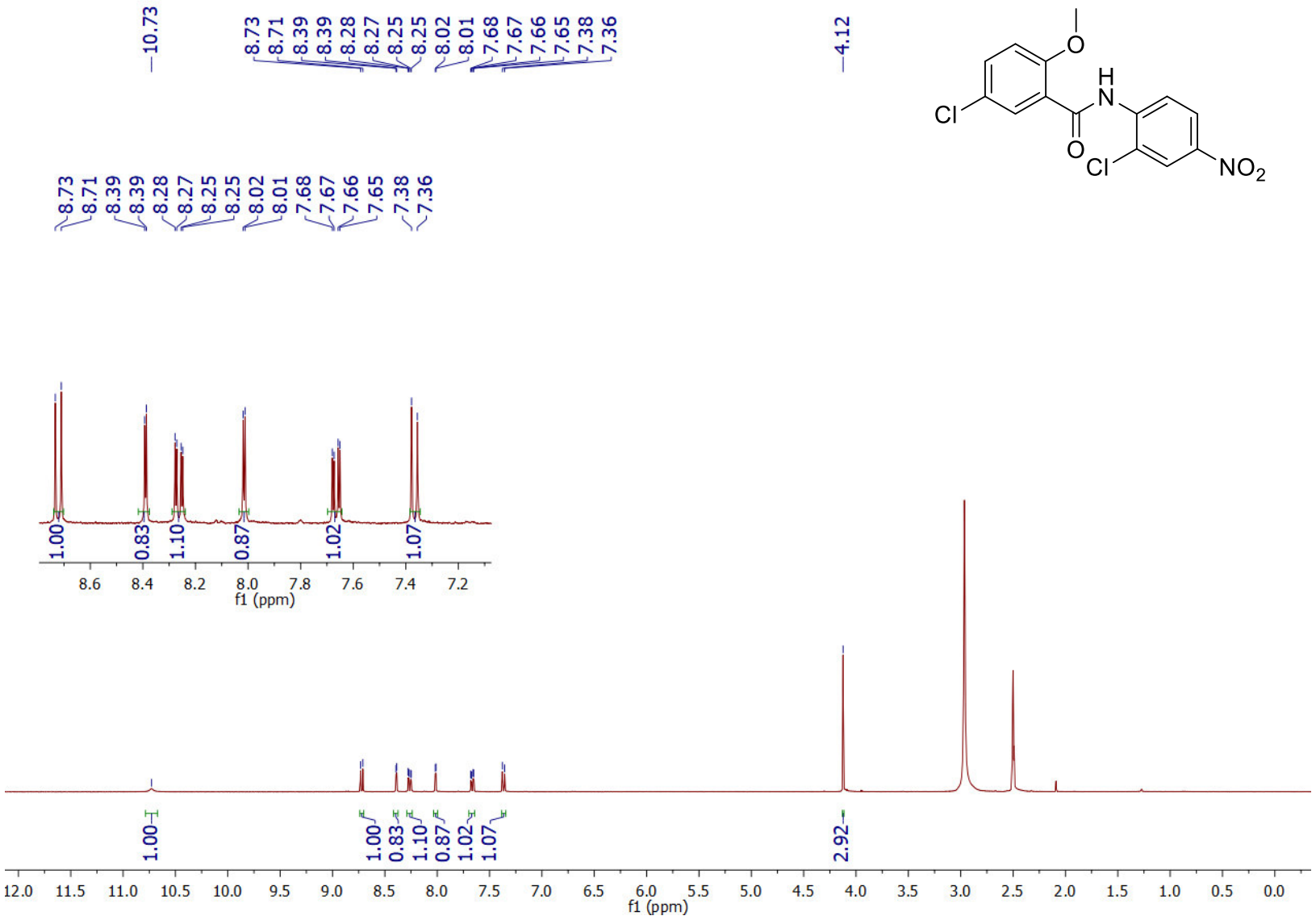

[1] Grecian, S., Wrobleski, A. D. & Aubé, J. Regioselective Single and Double Conjugate Additions to Substituted Cyclohexa-2,5-dienone Monoacetals. *Org. Lett.* **7**, 3167-3170 (2005).

[2] Park, K., Bae, G., Moon, J., Choe, J., Song, K. H. & Lee, S. Synthesis of Symmetrical and Unsymmetrical Diarylalkynes from Propiolic Acid Using Palladium-Catalyzed Decarboxylative Coupling. *J. Org. Chem.* **75**, 6244-6251 (2010).

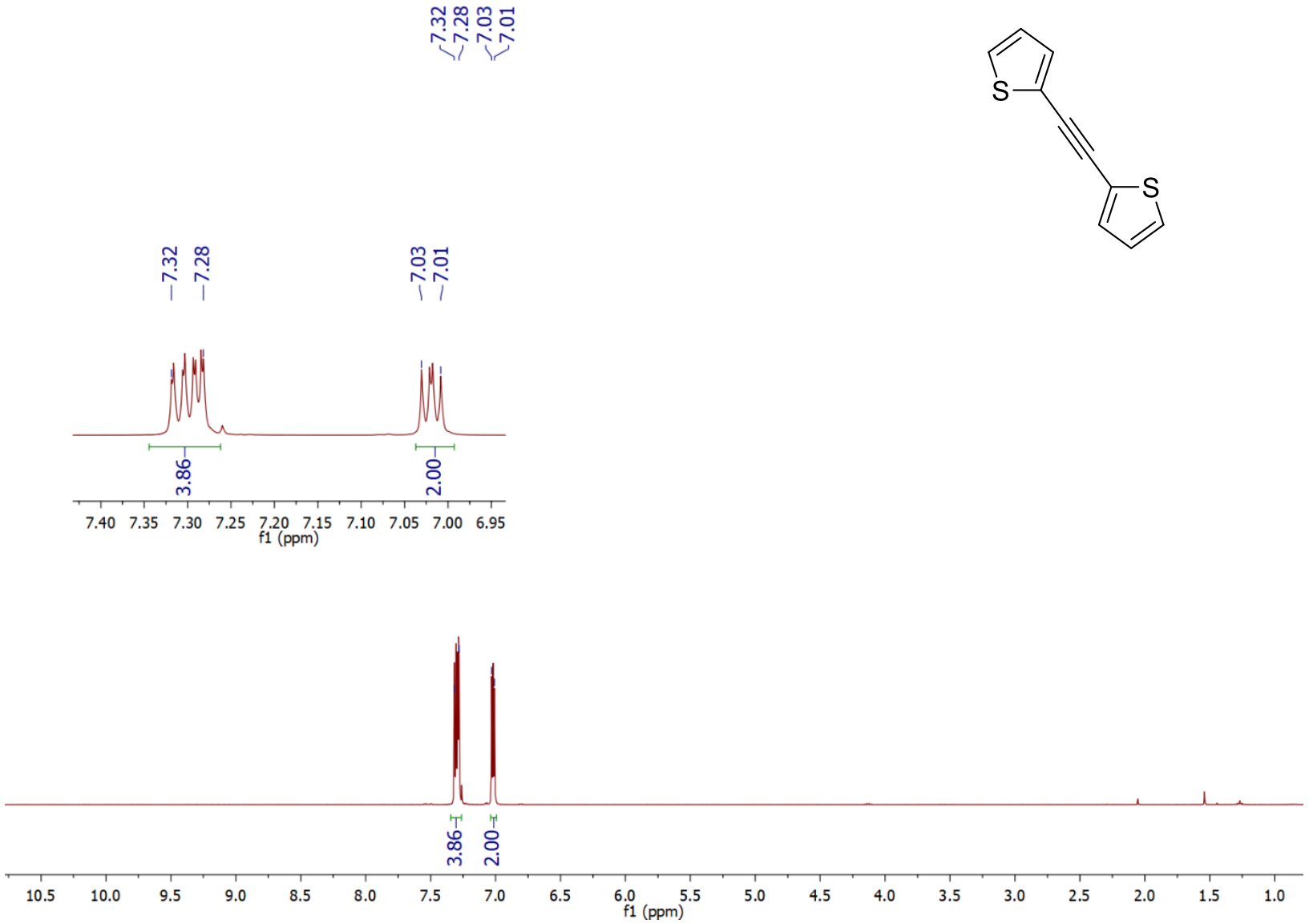
[3] Jia, X., Petrone, D. A. & Lautens, M. A Conjunctive Carboiodination: Indenes by a Double Carbopalladation-Reductive Elimination Domino Process. *Angew. Chem. Int. Ed.* **51**, 9870-9872 (2012).

## Copies of $^{1}H$ and $^{13}C$ Spectra

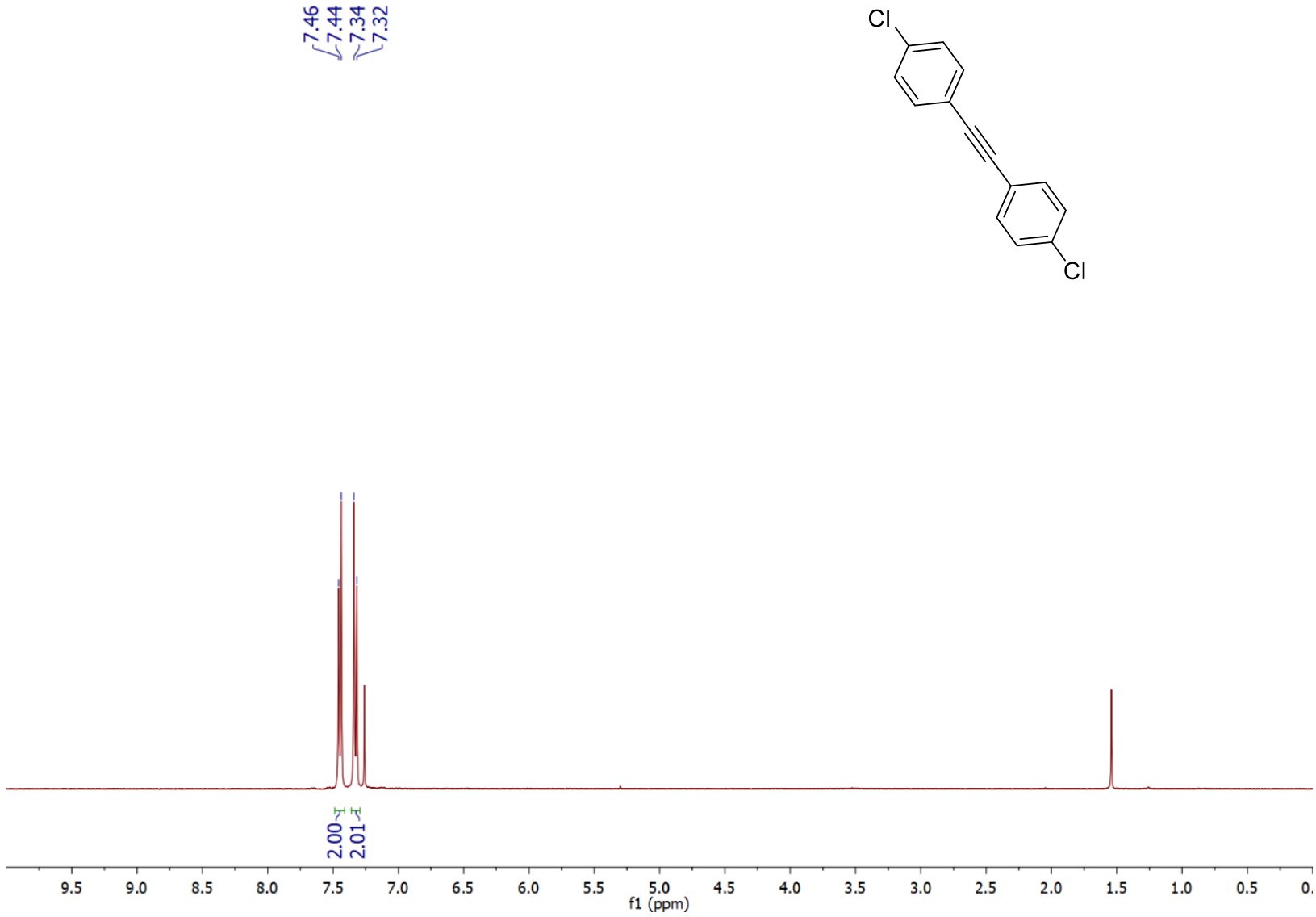
$^{1}H$-NMR at 100 °C (920)



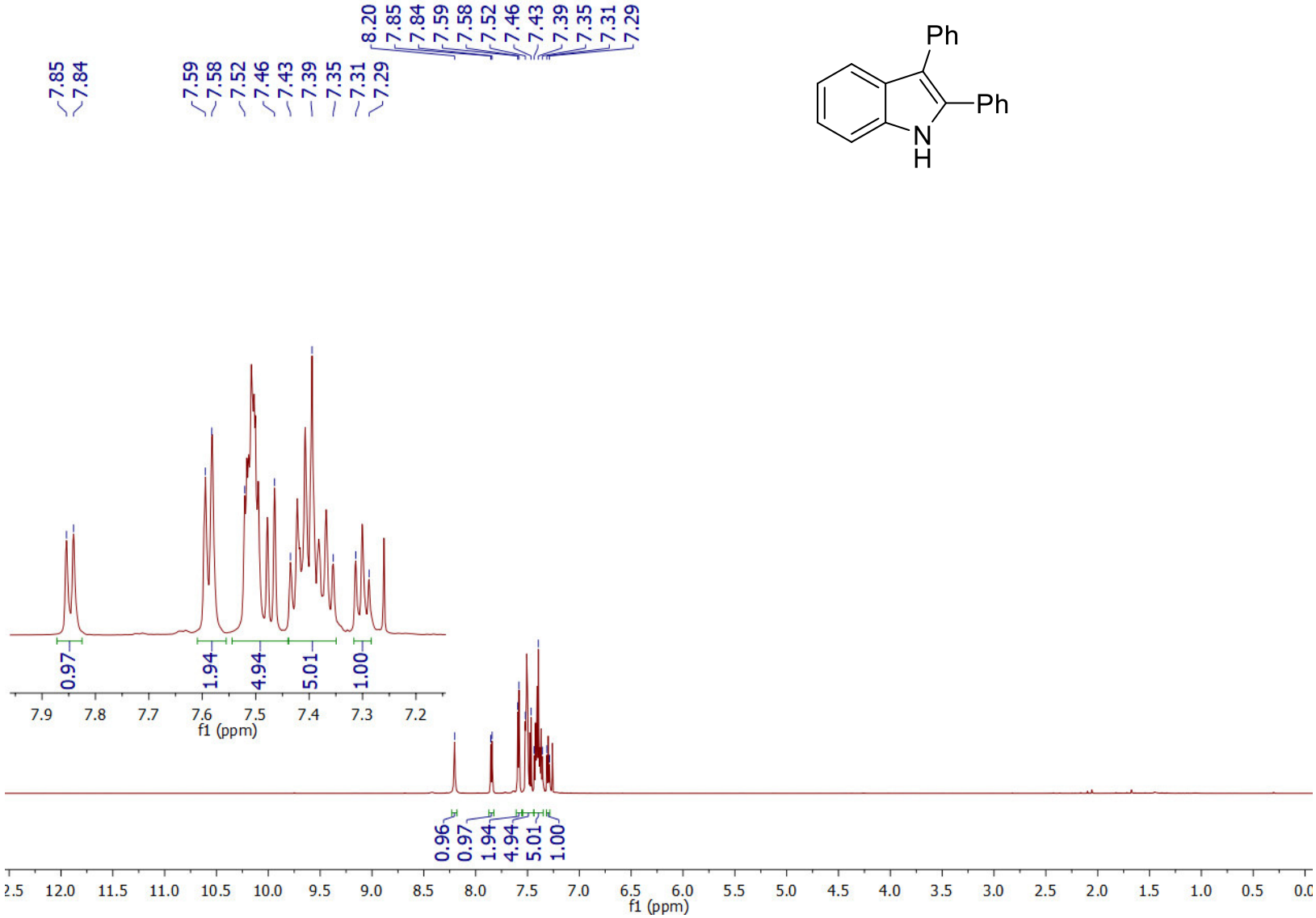
$^{1}$H-NMR (CHB-682)



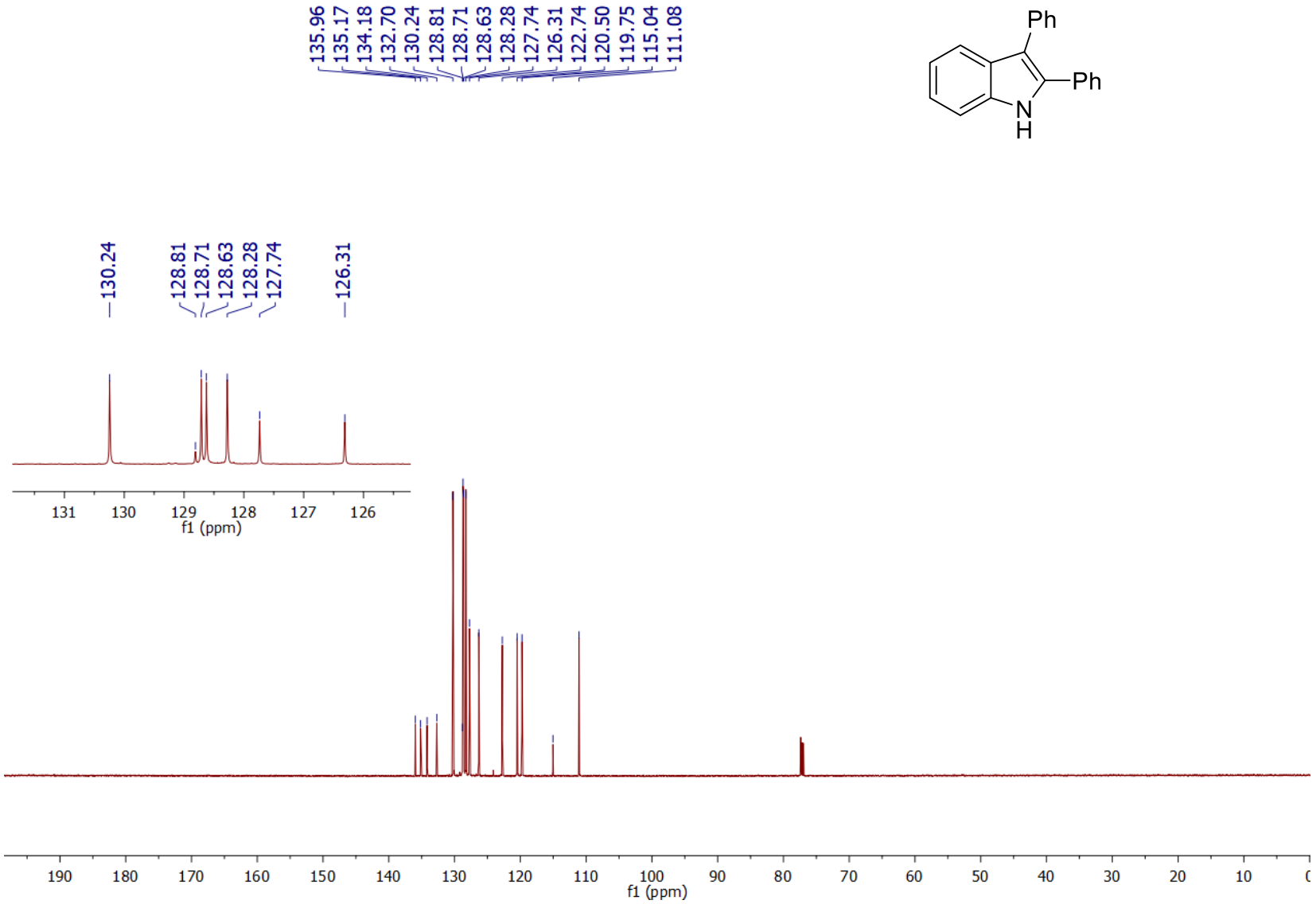
$^{1}$H-NMR (CHB-682)



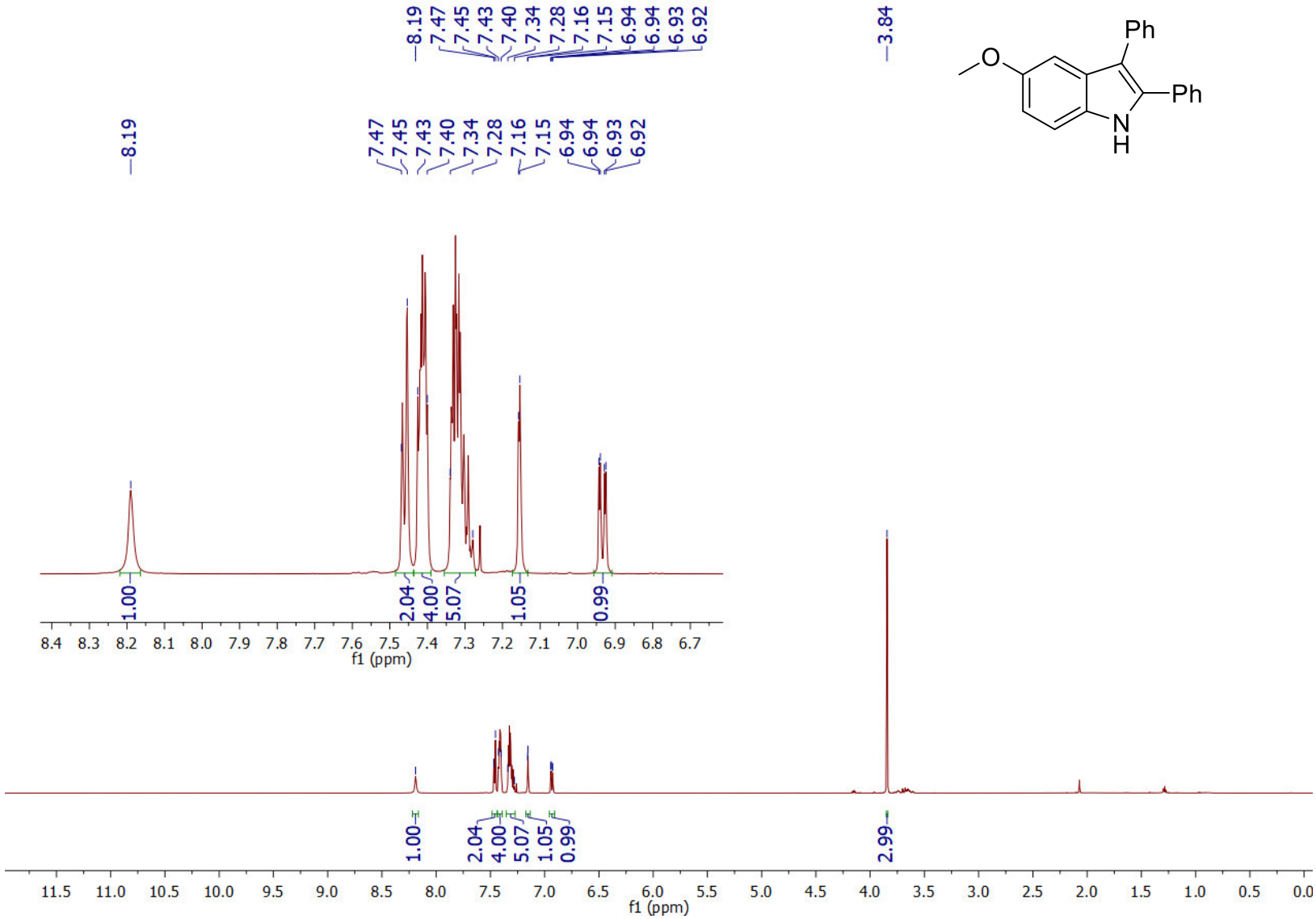
$^{1}$H-NMR (**3a**, 848)


8.20
7.85
7.84
7.59
7.58
7.52
7.46
7.43
7.39
7.35
7.31
7.29
Ph
Ph
N
H
0.97
1.94
4.94
5.01
1.00
f1 (ppm)
0.96
0.97
1.94
4.94
5.01
1.00
f1 (ppm)

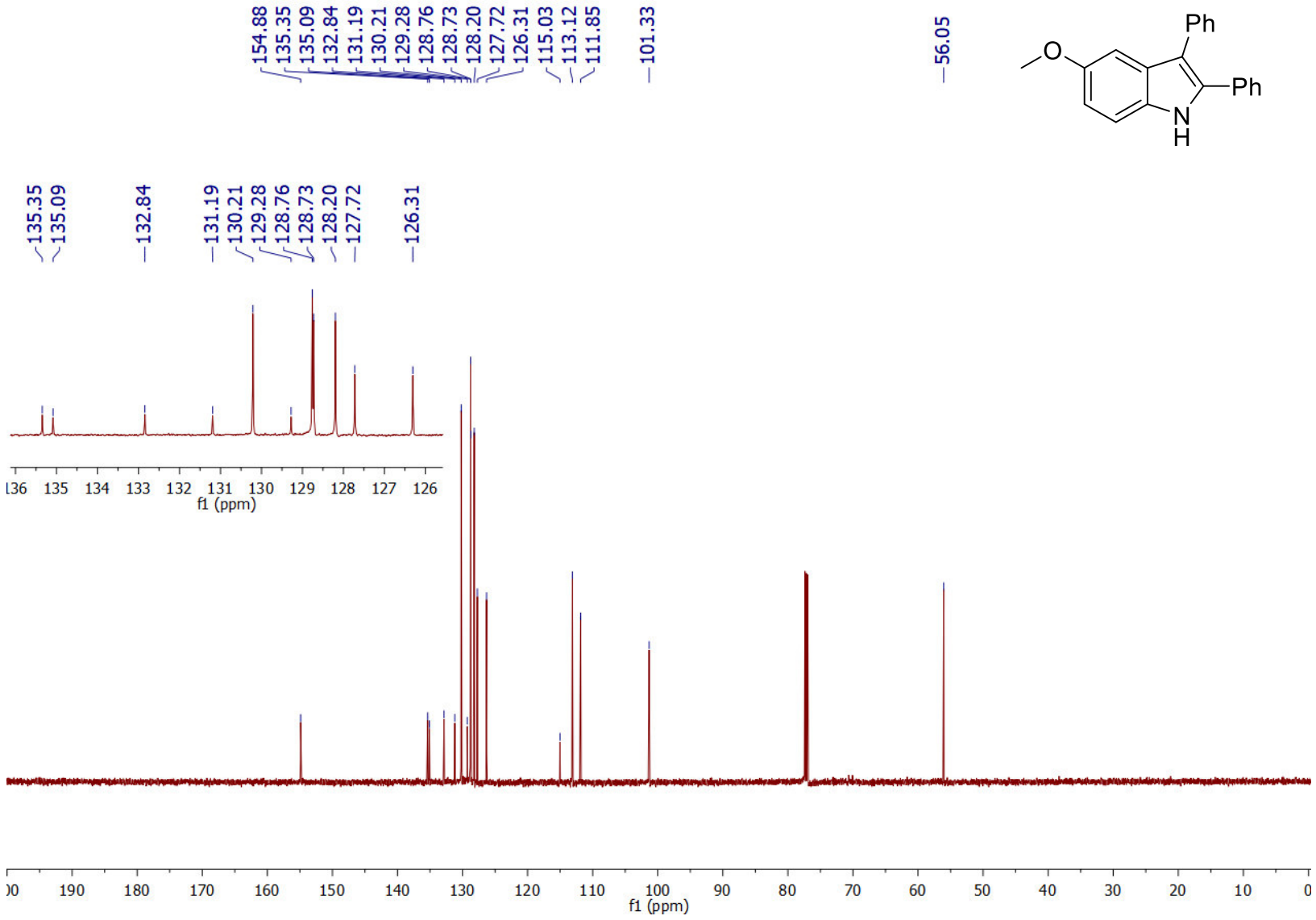
$^{13}$C-NMR (**3a**, 848)



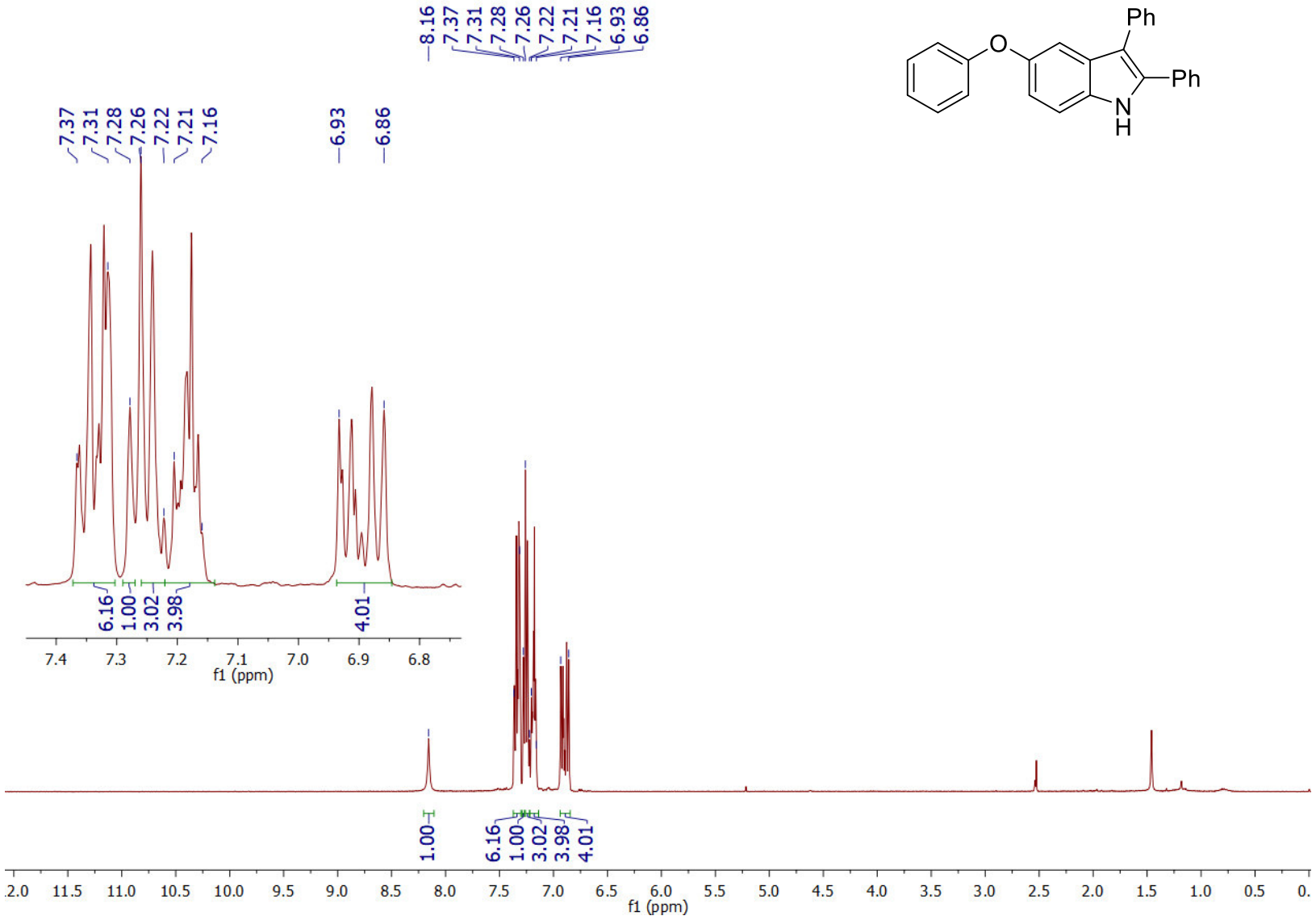
$^{1}$H-NMR (**3b,** 850)


8.19
7.47
7.45
7.43
7.40
7.34
7.28
7.16
7.15
6.94
6.94
6.93
6.92
3.84
Ph
Ph
O
N
H
1.00
2.04
4.00
5.07
1.05
0.99
2.99
f1 (ppm)

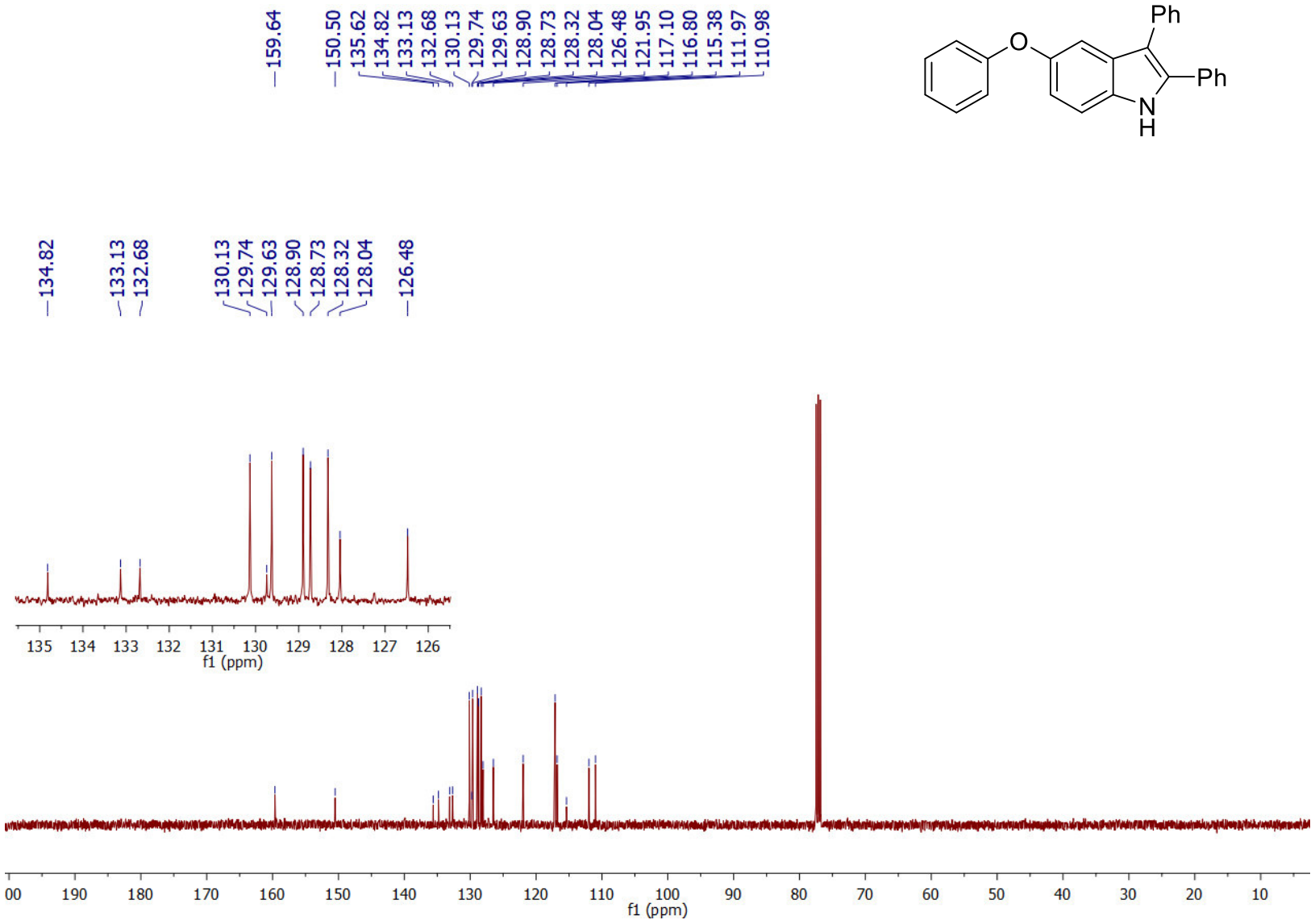
$^{13}$C-NMR (**3b**, 850)



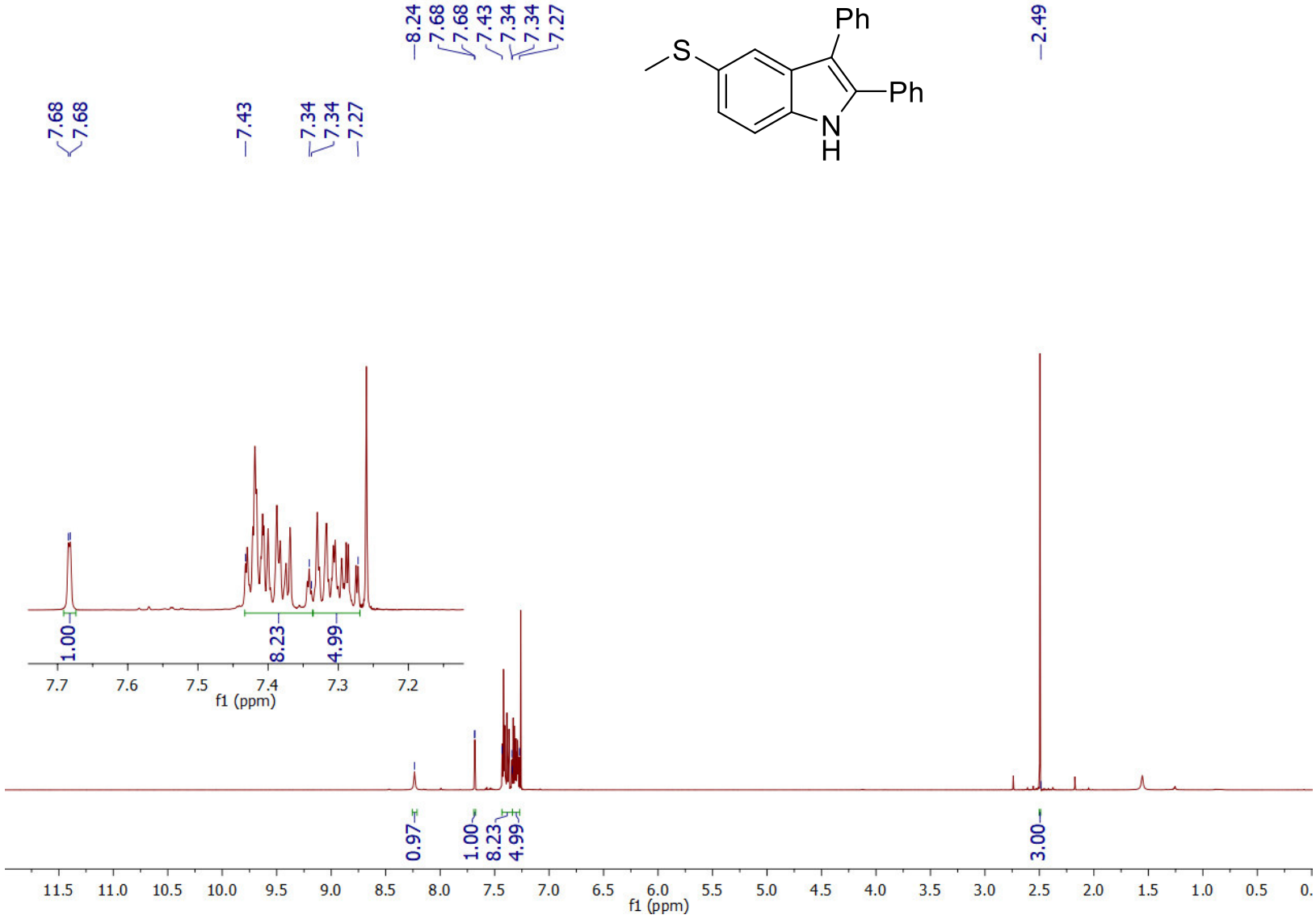
$^{1}$H-NMR (**3c**, 895)


8.16
7.37
7.31
7.28
7.26
7.22
7.21
7.16
6.93
6.86
Ph
O
Ph
N
H
6.16
1.00
3.02
3.98
4.01
f1 (ppm)
1.00
6.16
1.00
3.02
3.98
4.01
f1 (ppm)

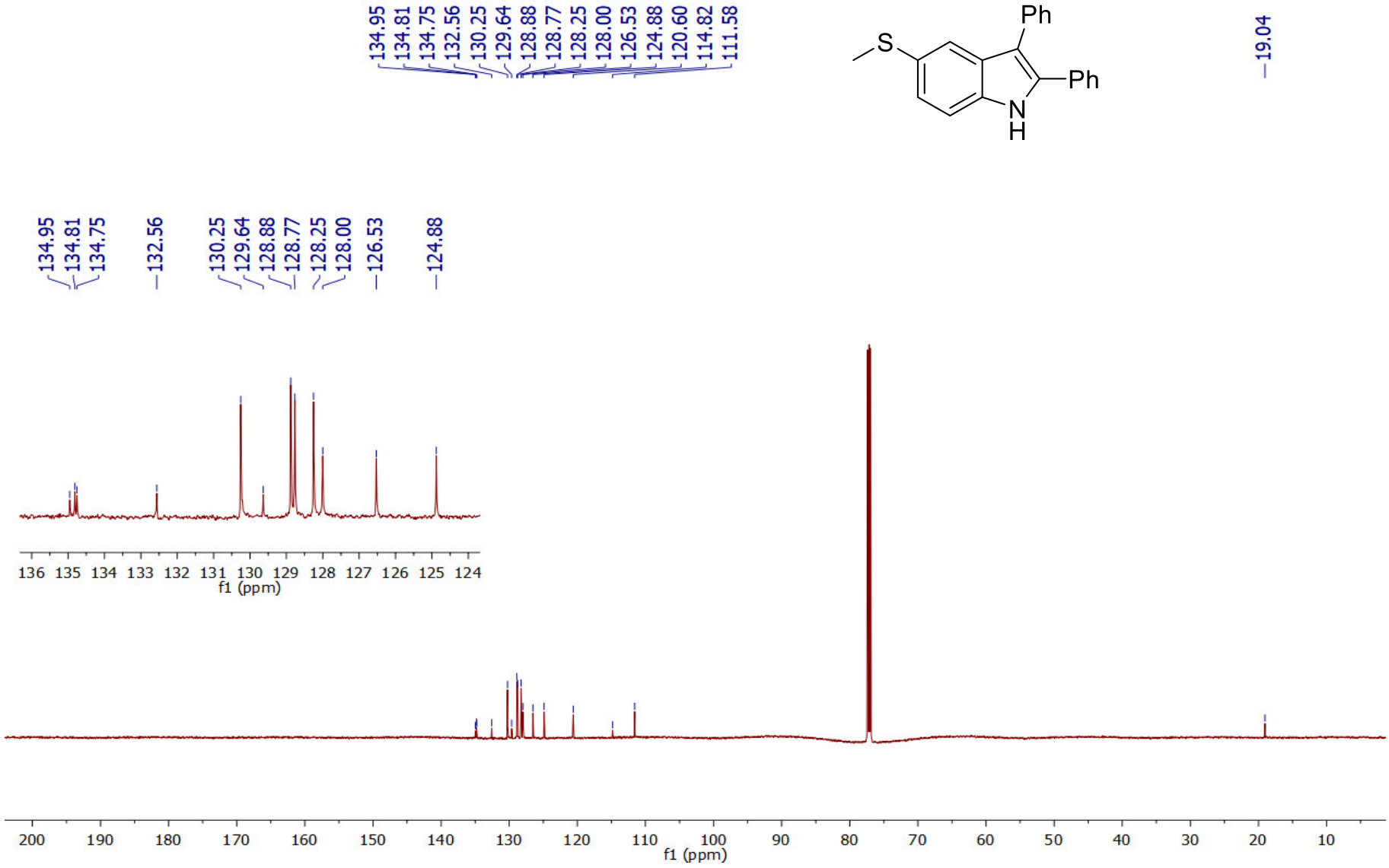
$^{13}$C-NMR (**3c**, 895)



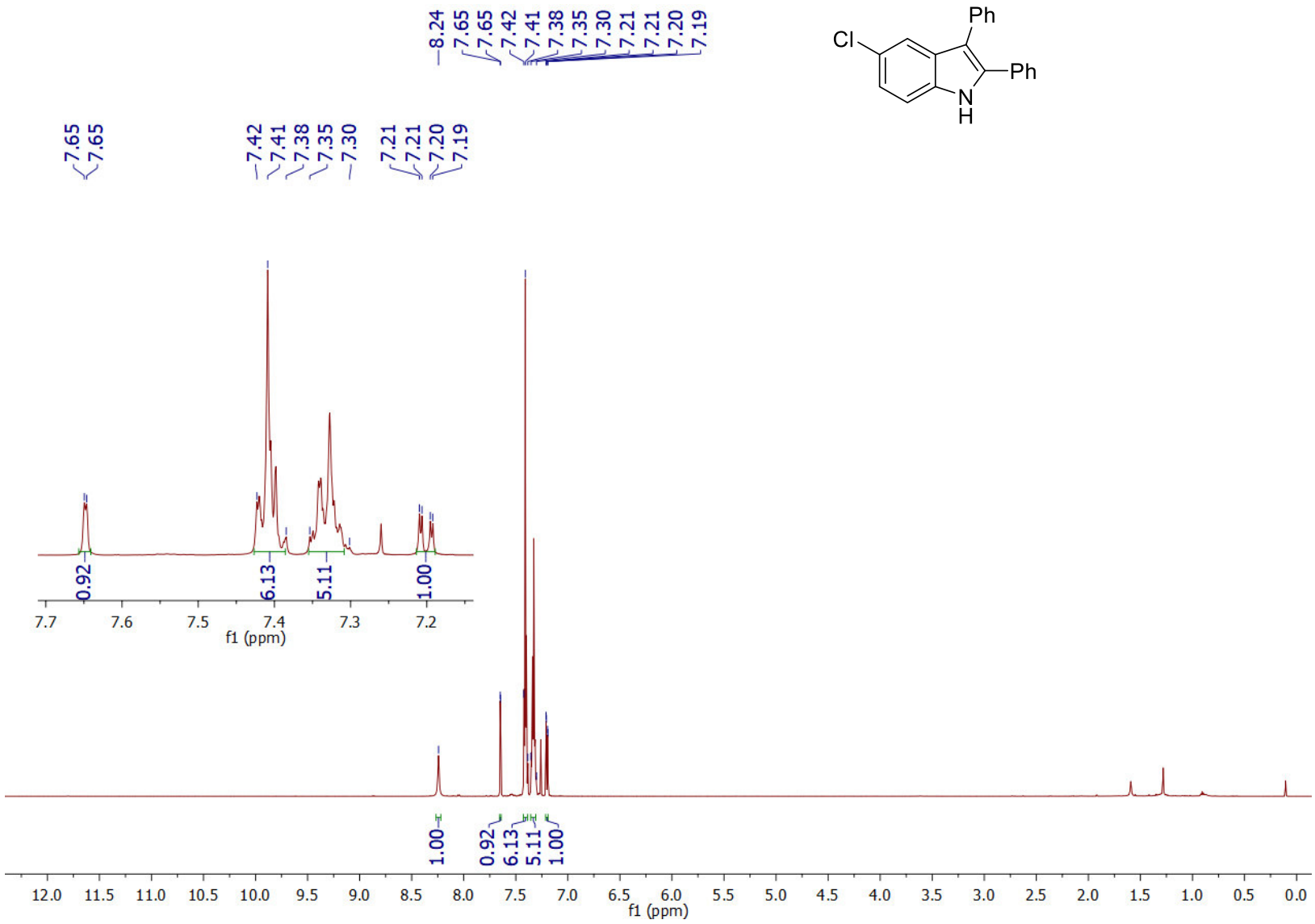
[1]H-NMR (**3d**, 882)


8.24
7.68
7.68
7.43
7.34
7.34
7.27
2.49
Ph
Ph
S
N
H
1.00
8.23
4.99
f1 (ppm)
0.97
1.00
8.23
4.99
3.00
f1 (ppm)

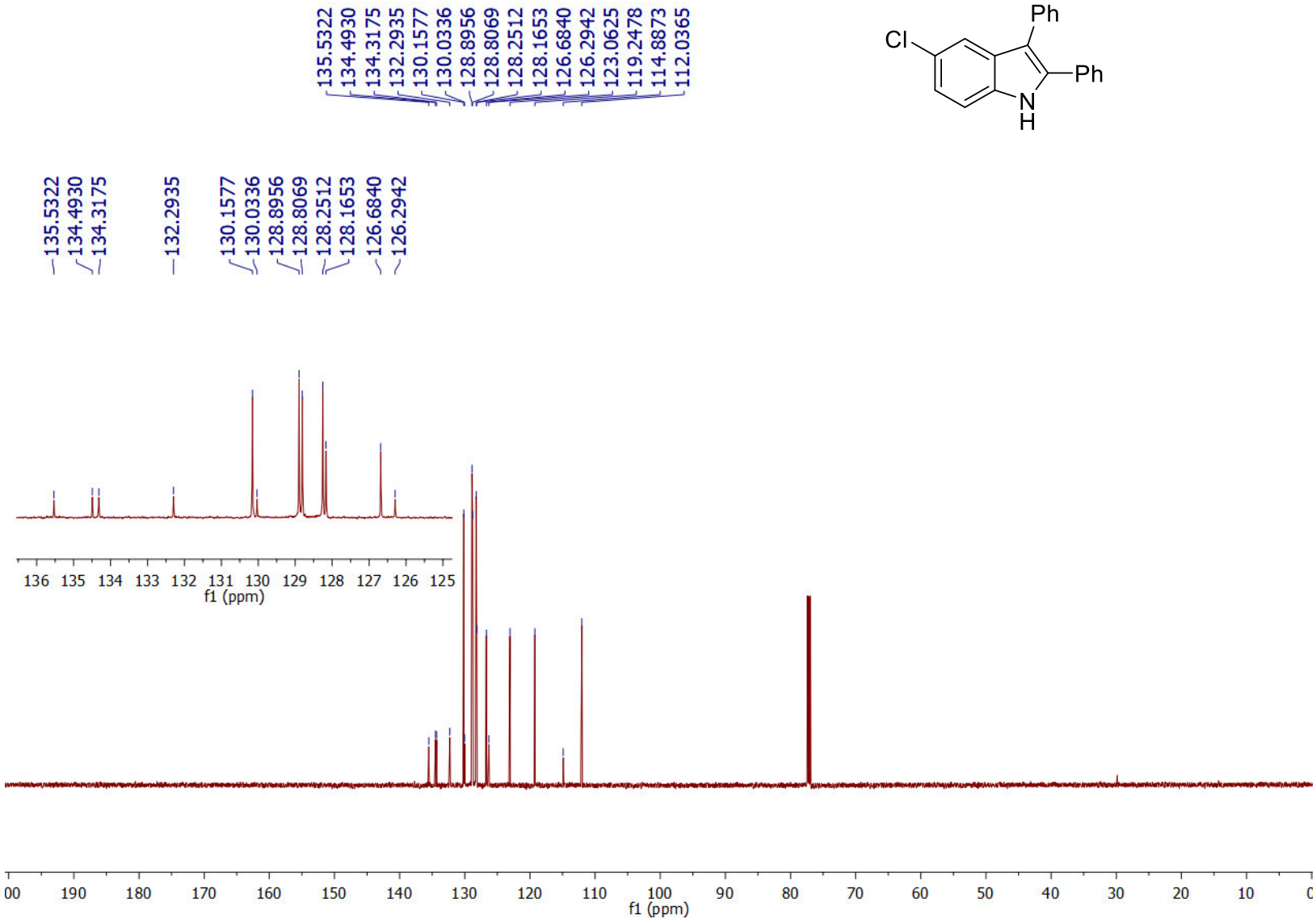
$^{13}$C-NMR (**3d**, 882)



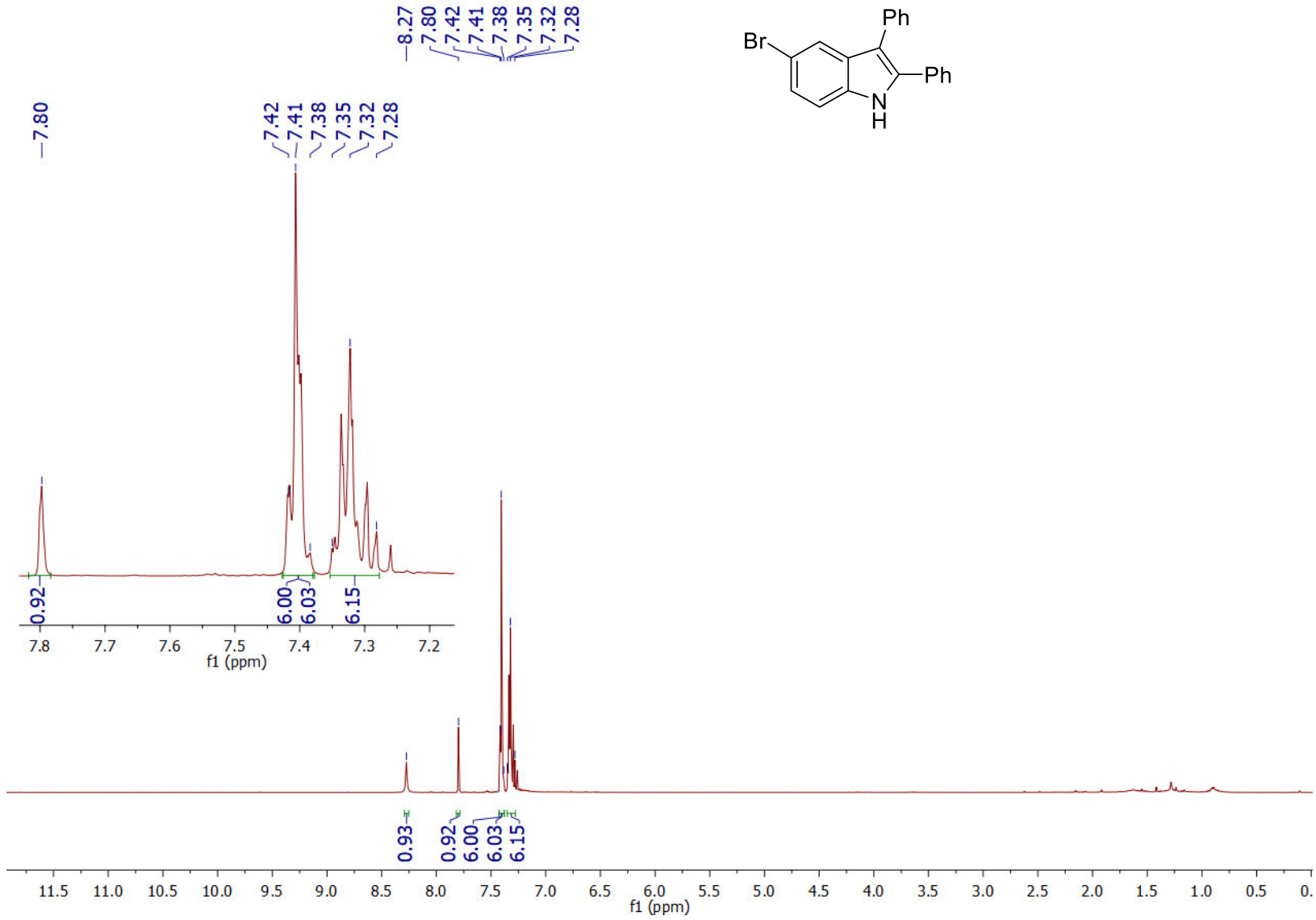
$^{1}$H-NMR (**3e**, 859)


8.24
7.65
7.65
7.42
7.41
7.38
7.35
7.30
7.21
7.21
7.20
7.19
Cl
Ph
Ph
N
H
0.92
6.13
5.11
1.00
f1 (ppm)
1.00
0.92
6.13
5.11
1.00
f1 (ppm)

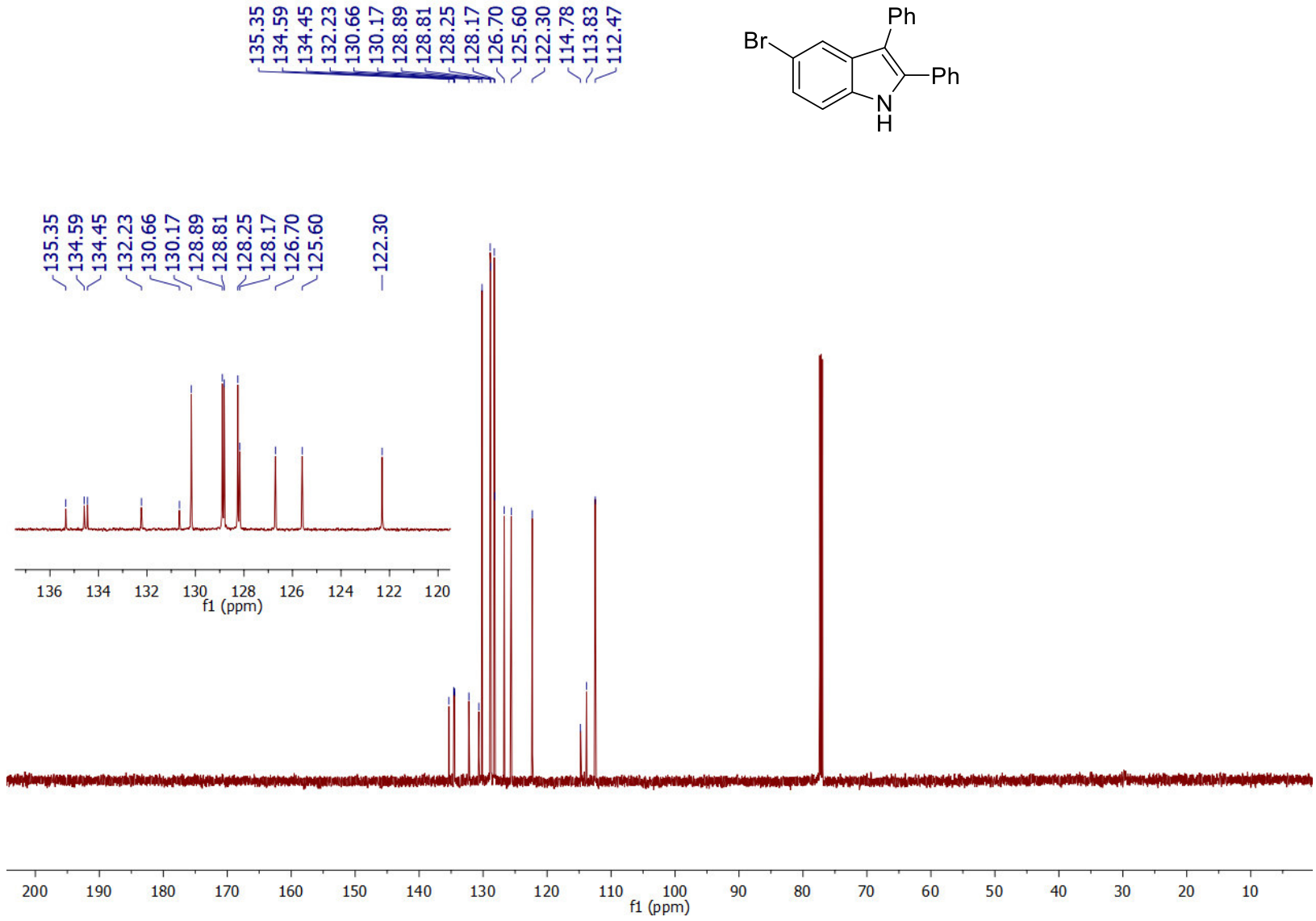
$^{13}$C-NMR (**3e**, 859)



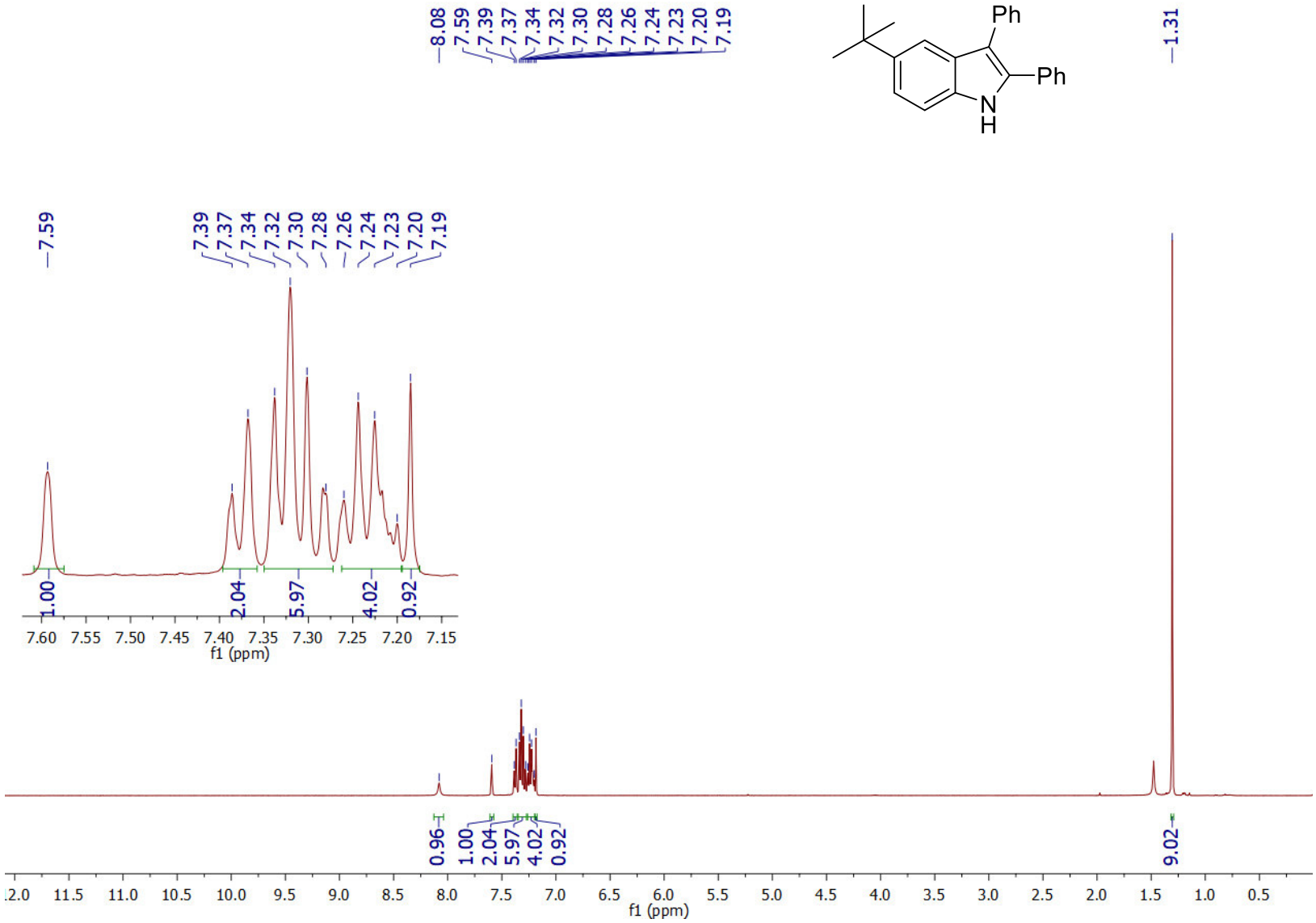
$^{1}$H-NMR (**3f**, 869)


8.27
7.80
7.42
7.41
7.38
7.35
7.32
7.28
Br
Ph
Ph
N
H
0.92
6.00
6.03
6.15
f1 (ppm)
0.93
0.92
6.00
6.03
6.15
f1 (ppm)

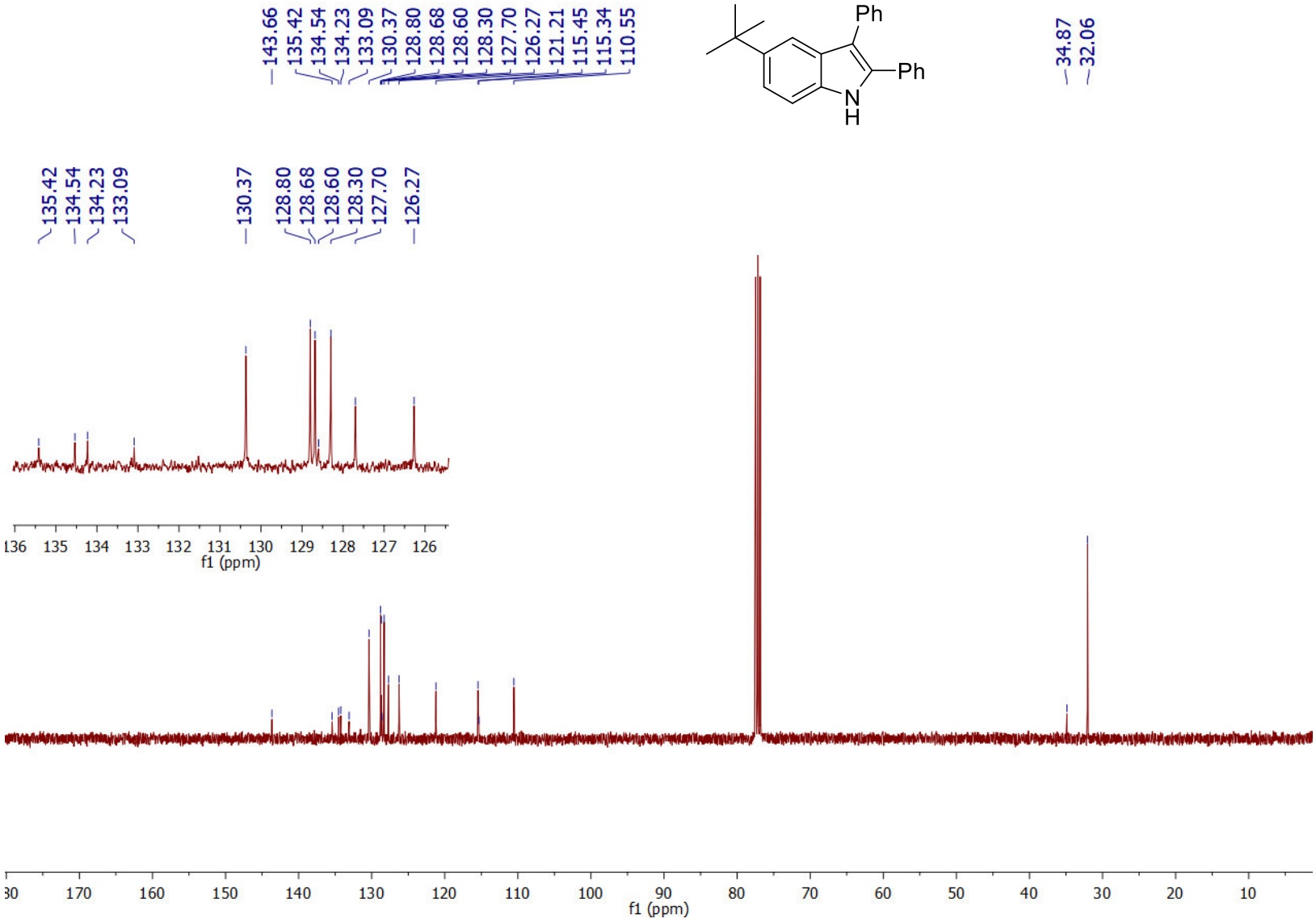
$^{13}$C-NMR (**3f**, 869)



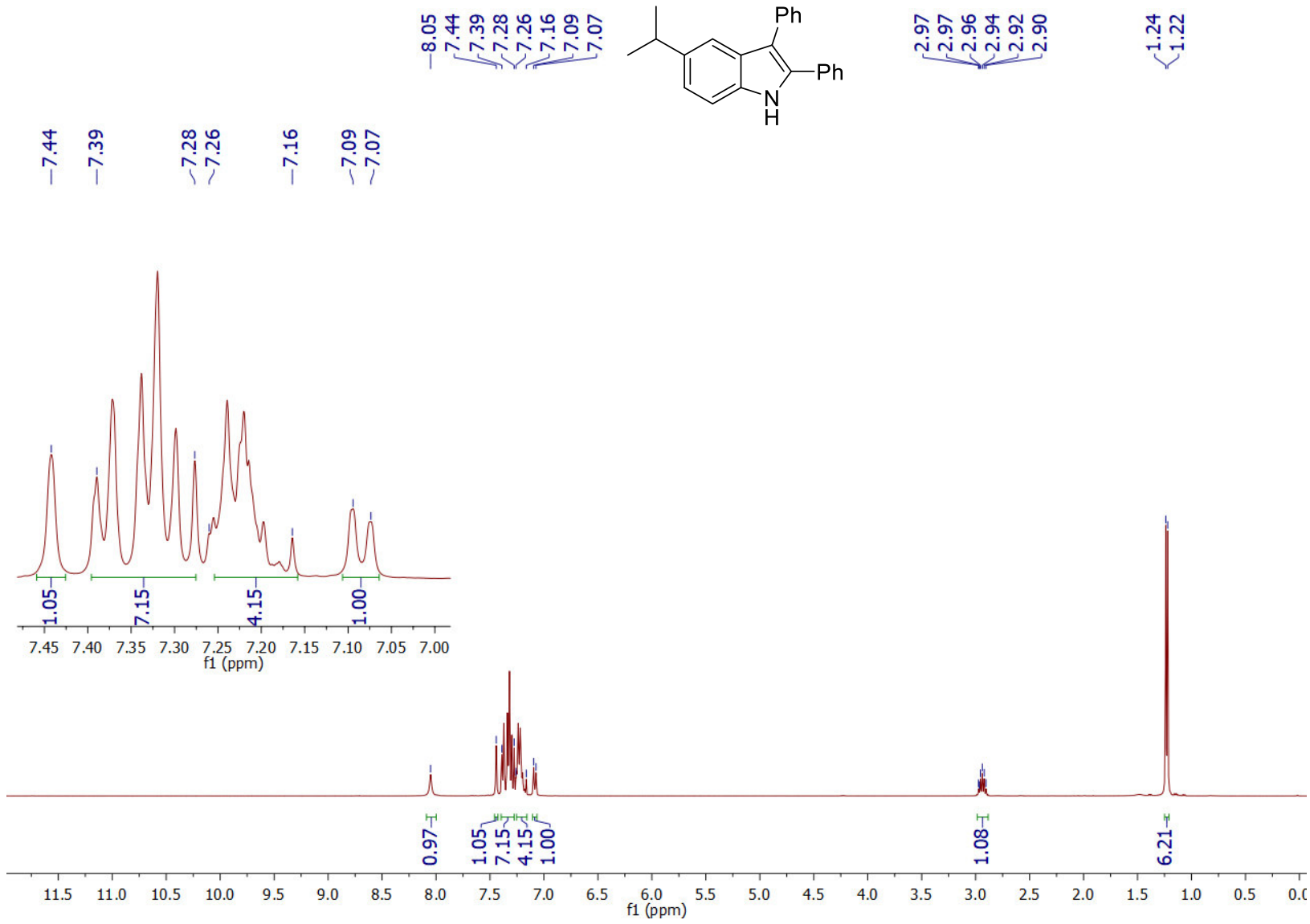
$^{1}$H-NMR (**3g**, 864)


8.08
7.59
7.39
7.37
7.34
7.32
7.30
7.28
7.26
7.24
7.23
7.20
7.19
1.31
Ph
Ph
N
H
7.59
7.39
7.37
7.34
7.32
7.30
7.28
7.26
7.24
7.23
7.20
7.19
1.00
2.04
5.97
4.02
0.92
f1 (ppm)
0.96
1.00
2.04
5.97
4.02
0.92
9.02
f1 (ppm)

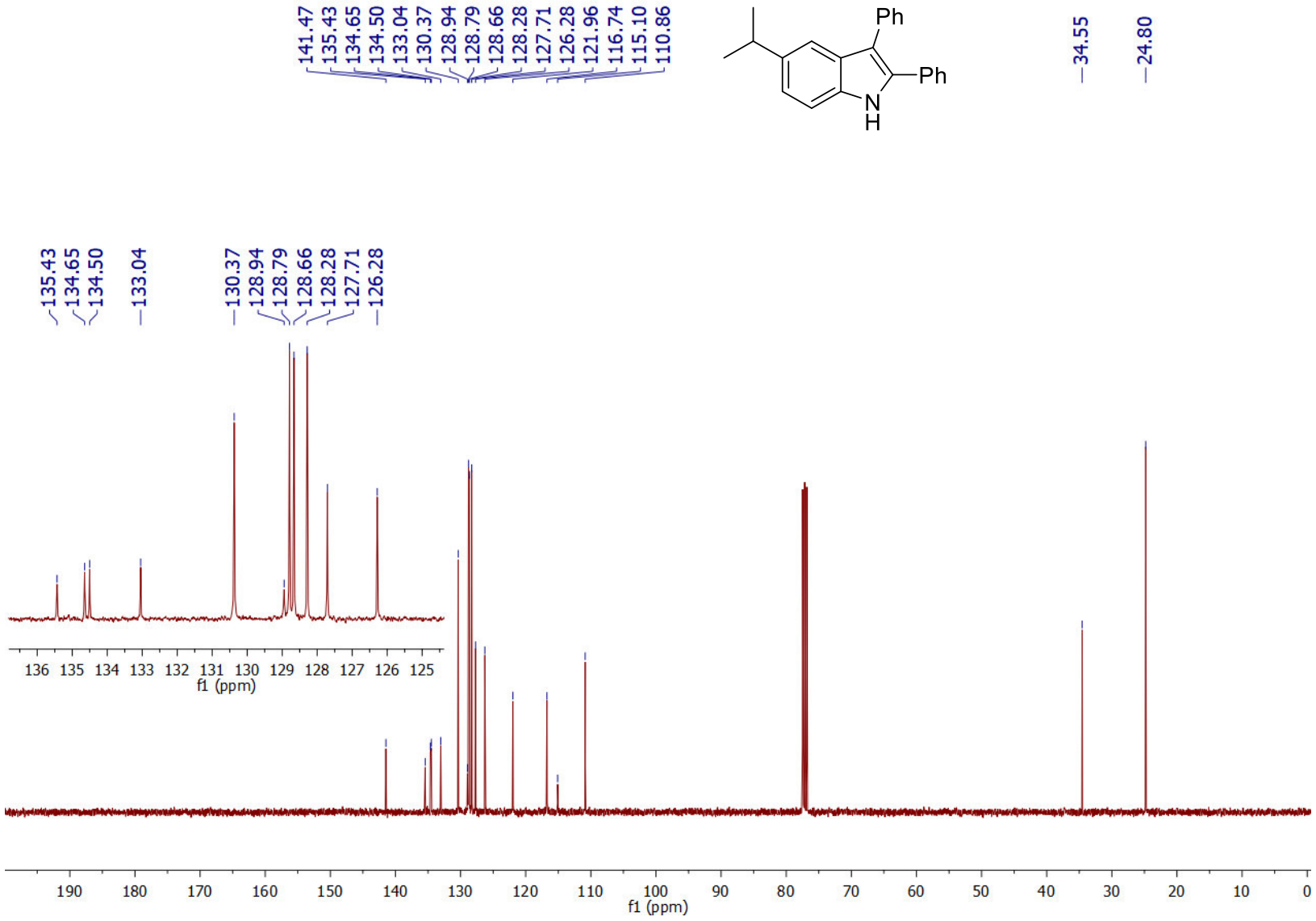
$^{13}$C-NMR (**3g**, 864)



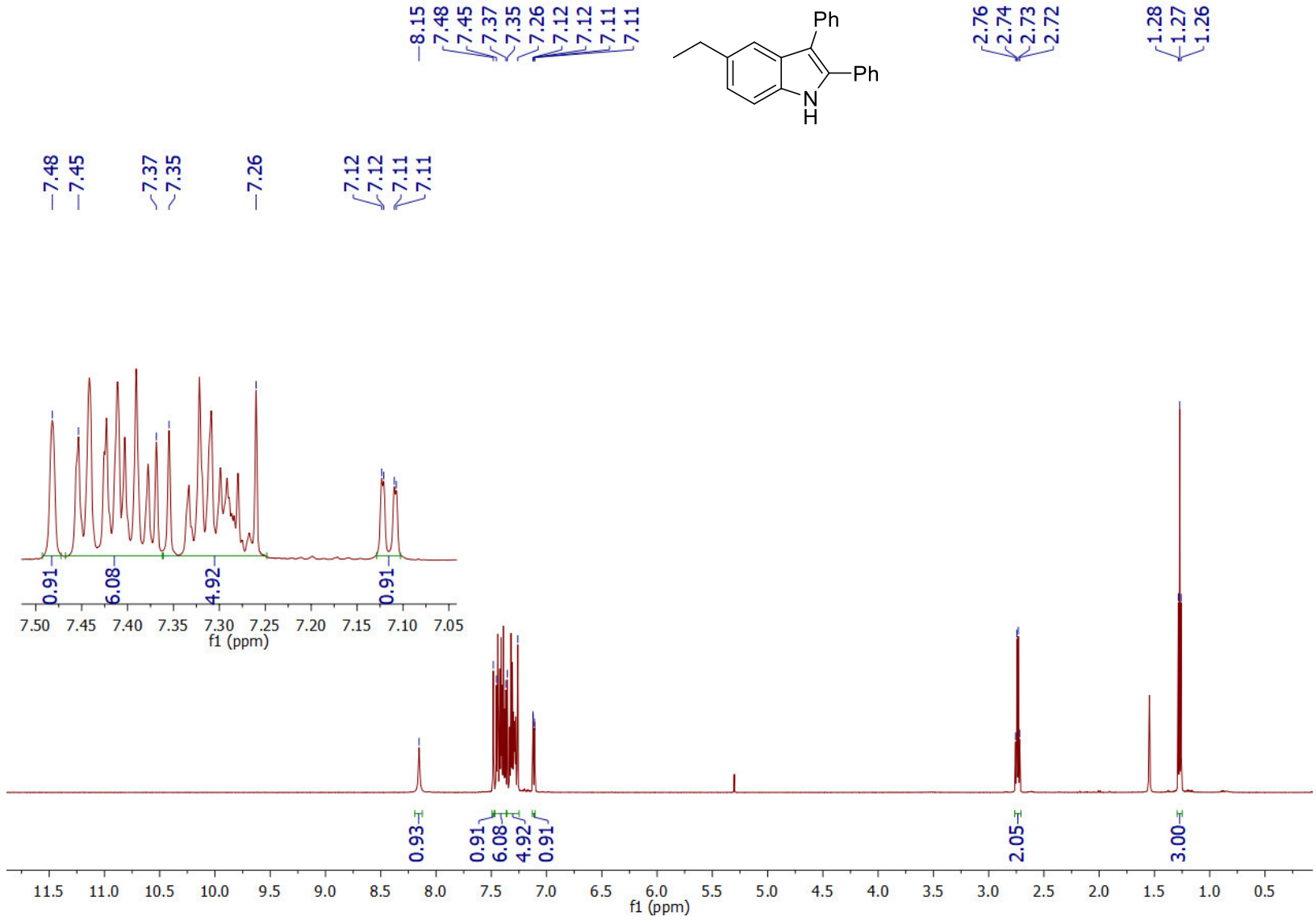
$^{1}$H-NMR (**3h**, 884)


8.05
7.44
7.39
7.28
7.26
7.16
7.09
7.07
2.97
2.97
2.96
2.94
2.92
2.90
1.24
1.22
Ph
Ph
N
H
1.05
7.15
4.15
1.00
f1 (ppm)
0.97
1.05
7.15
4.15
1.00
1.08
6.21
f1 (ppm)

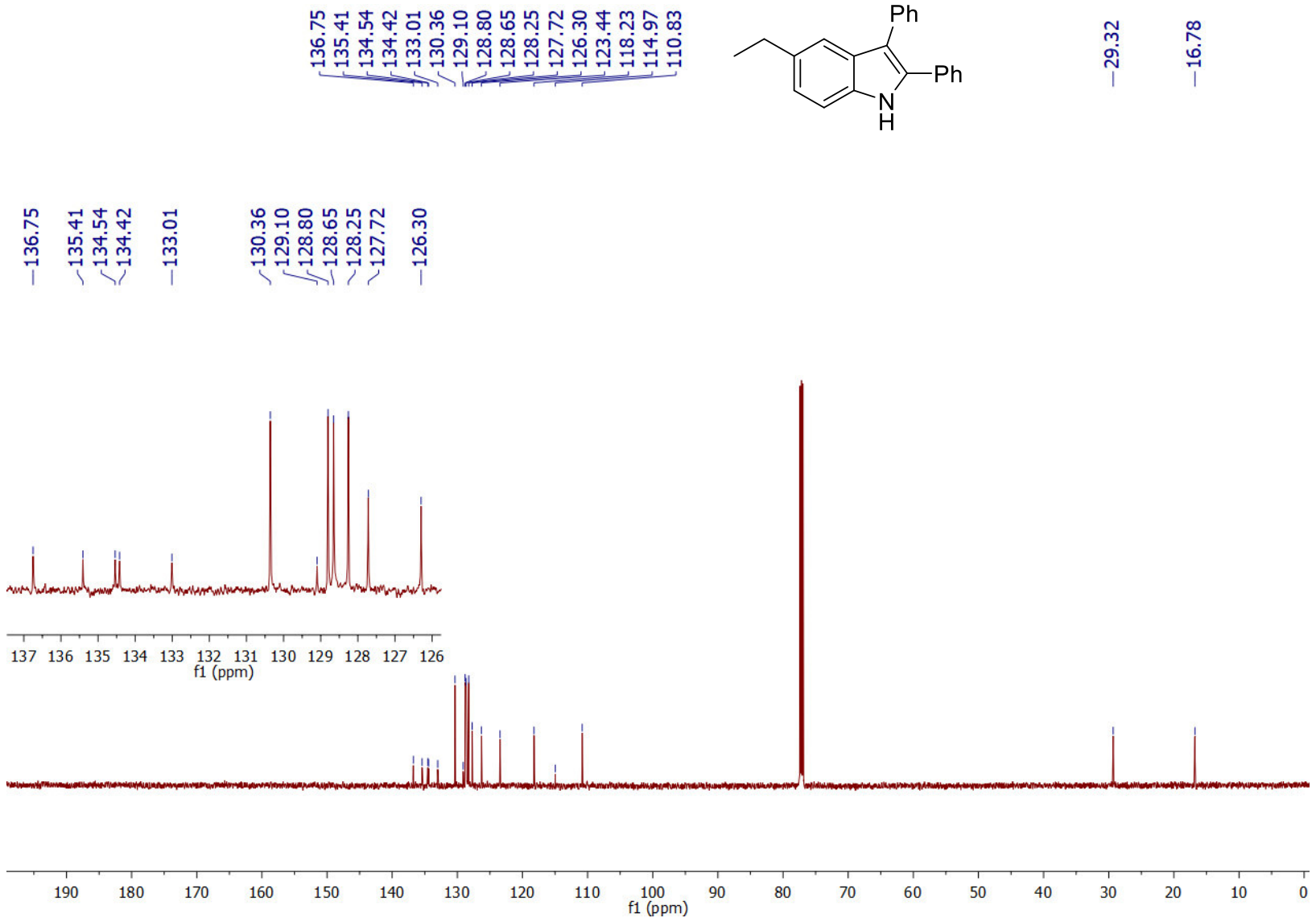
$^{13}$C-NMR (**3h**, 884)



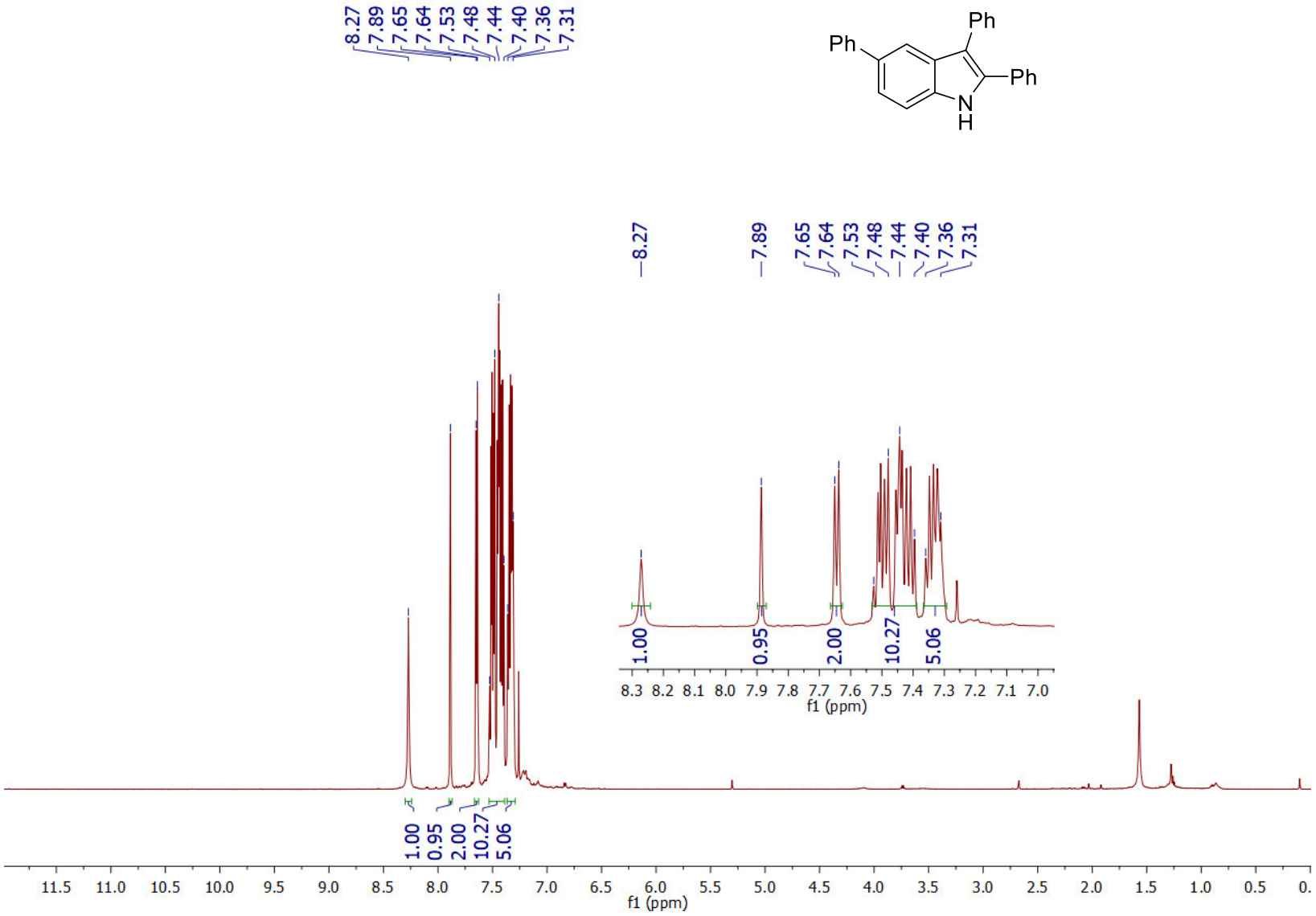
$^{1}$H-NMR (**3i**, 876)


8.15
7.48
7.45
7.37
7.35
7.26
7.12
7.12
7.11
7.11
2.76
2.74
2.73
2.72
1.28
1.27
1.26
Ph
Ph
N
H
0.91
6.08
4.92
0.91
f1 (ppm)
0.93
0.91
6.08
4.92
0.91
2.05
3.00
f1 (ppm)

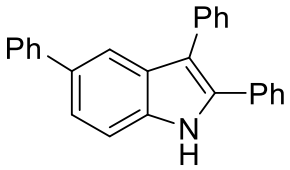
$^{13}$C-NMR (**3i**, 876)

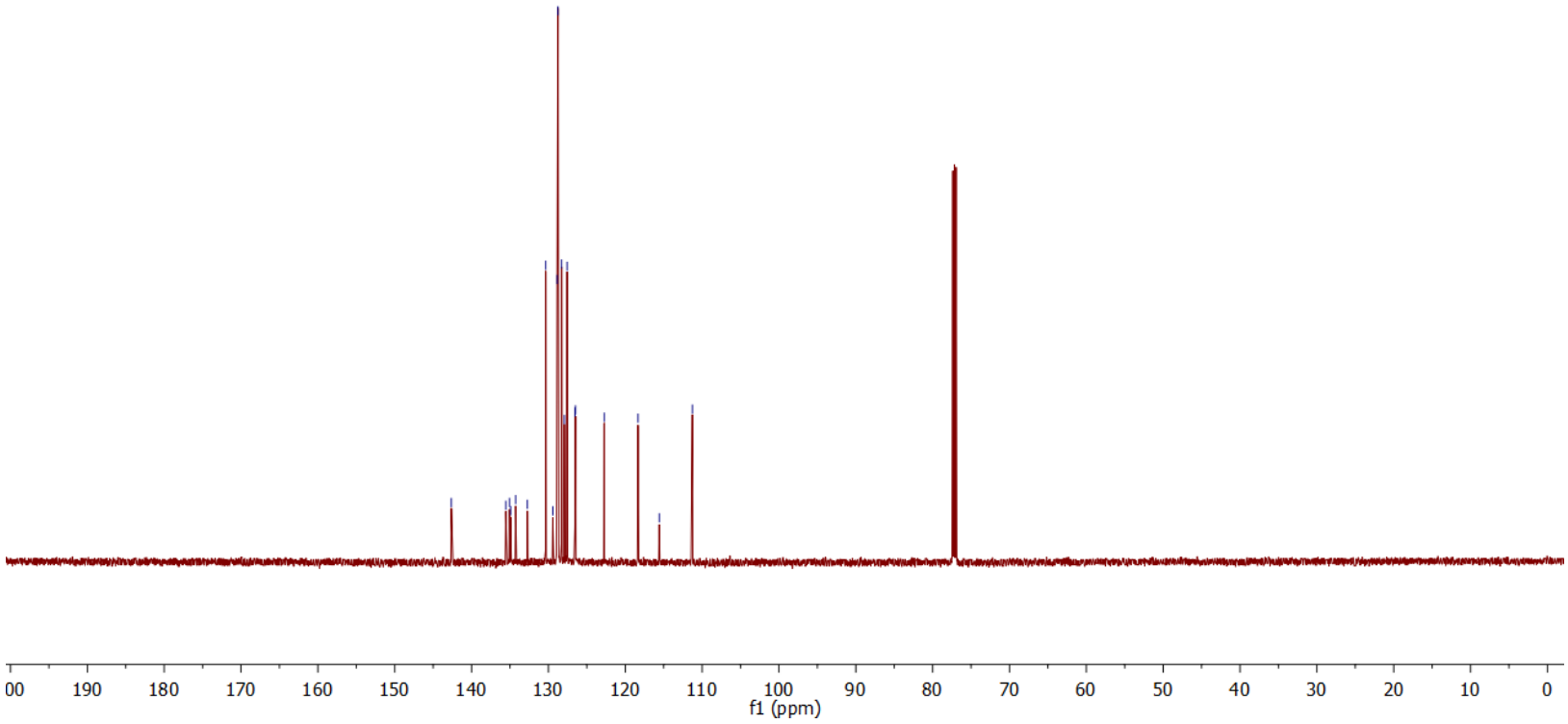


$^{1}$H-NMR (**3j**, 914)

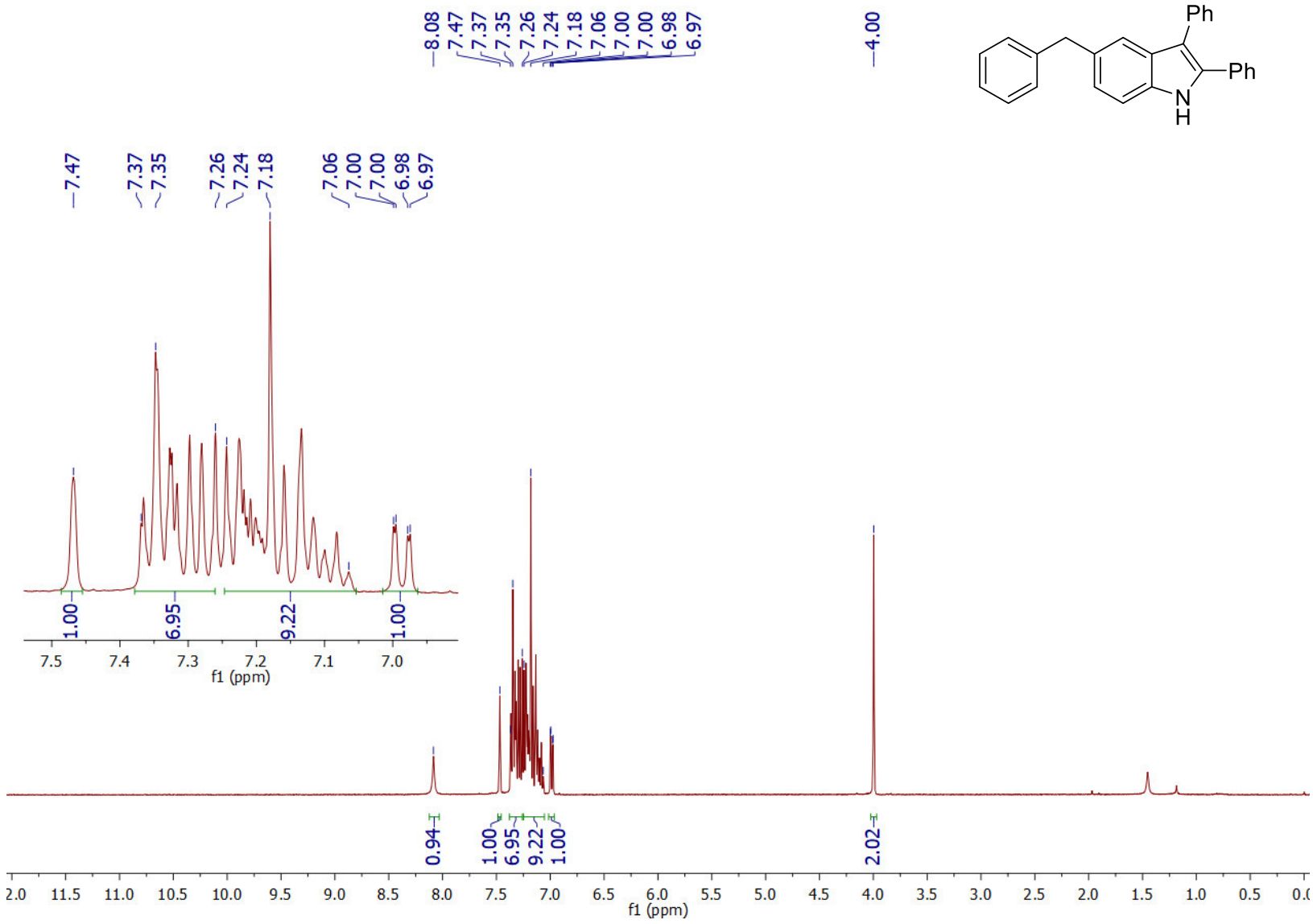

8.27
7.89
7.65
7.64
7.53
7.48
7.44
7.40
7.36
7.31
Ph
Ph
Ph
N
H
1.00
0.95
2.00
10.27
5.06
f1 (ppm)

$^{13}$C-NMR (**3j**, 914)

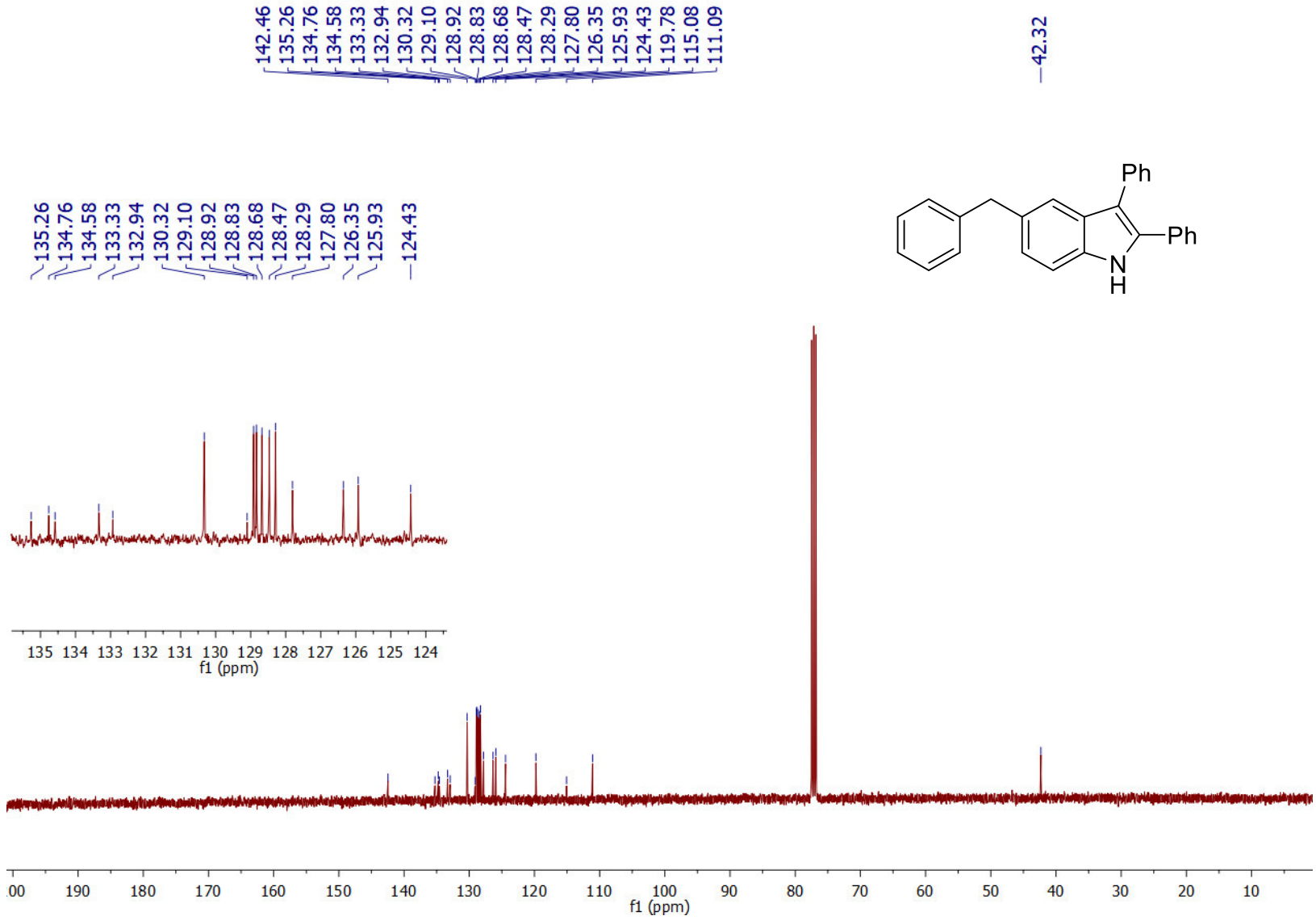



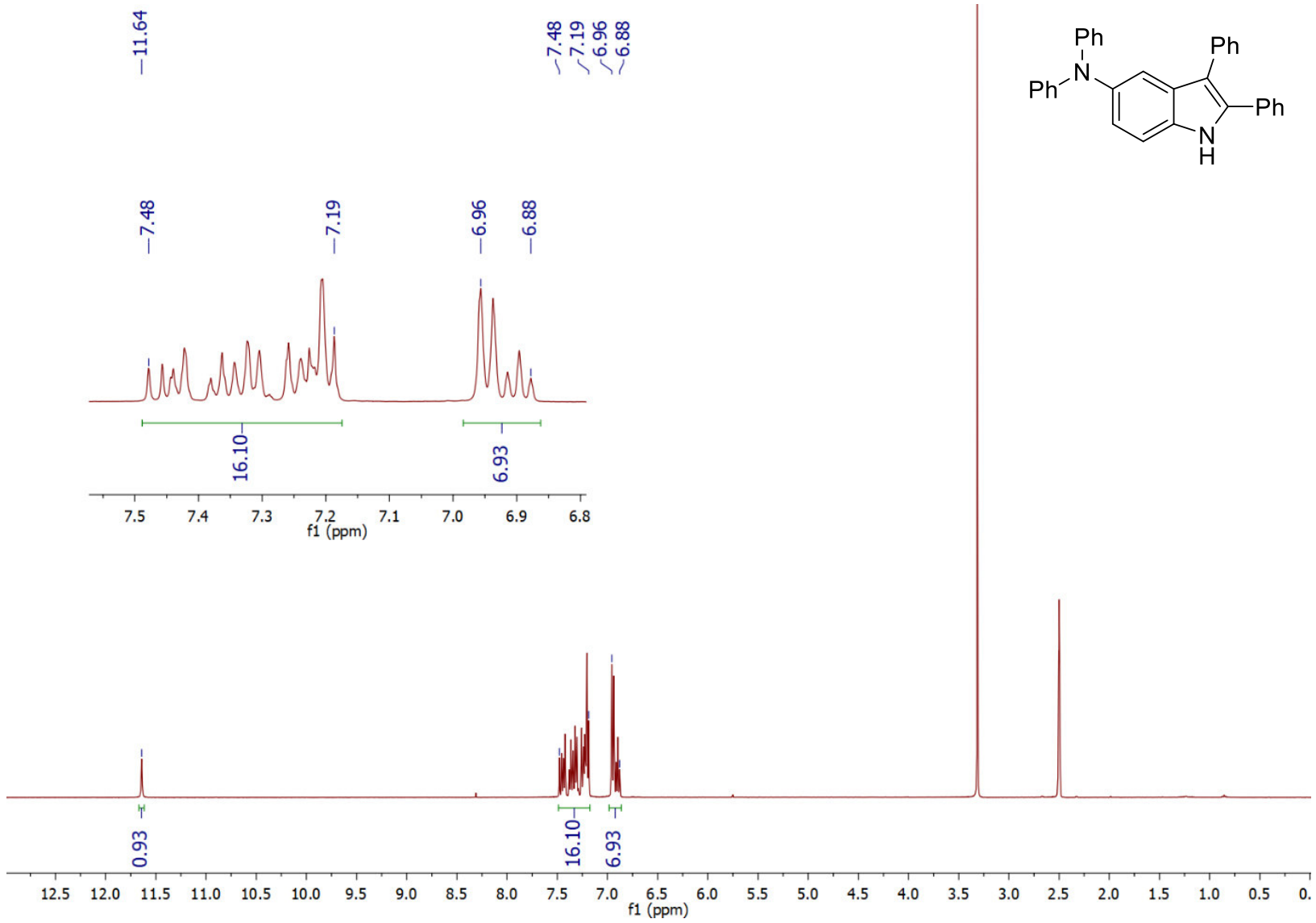
$^{1}$H-NMR (**3k**, 875)


8.08
7.47
7.37
7.35
7.26
7.24
7.18
7.06
7.00
7.00
6.98
6.97
4.00
Ph
Ph
N
H
1.00
6.95
9.22
1.00
f1 (ppm)
0.94
1.00
6.95
9.22
1.00
2.02
f1 (ppm)

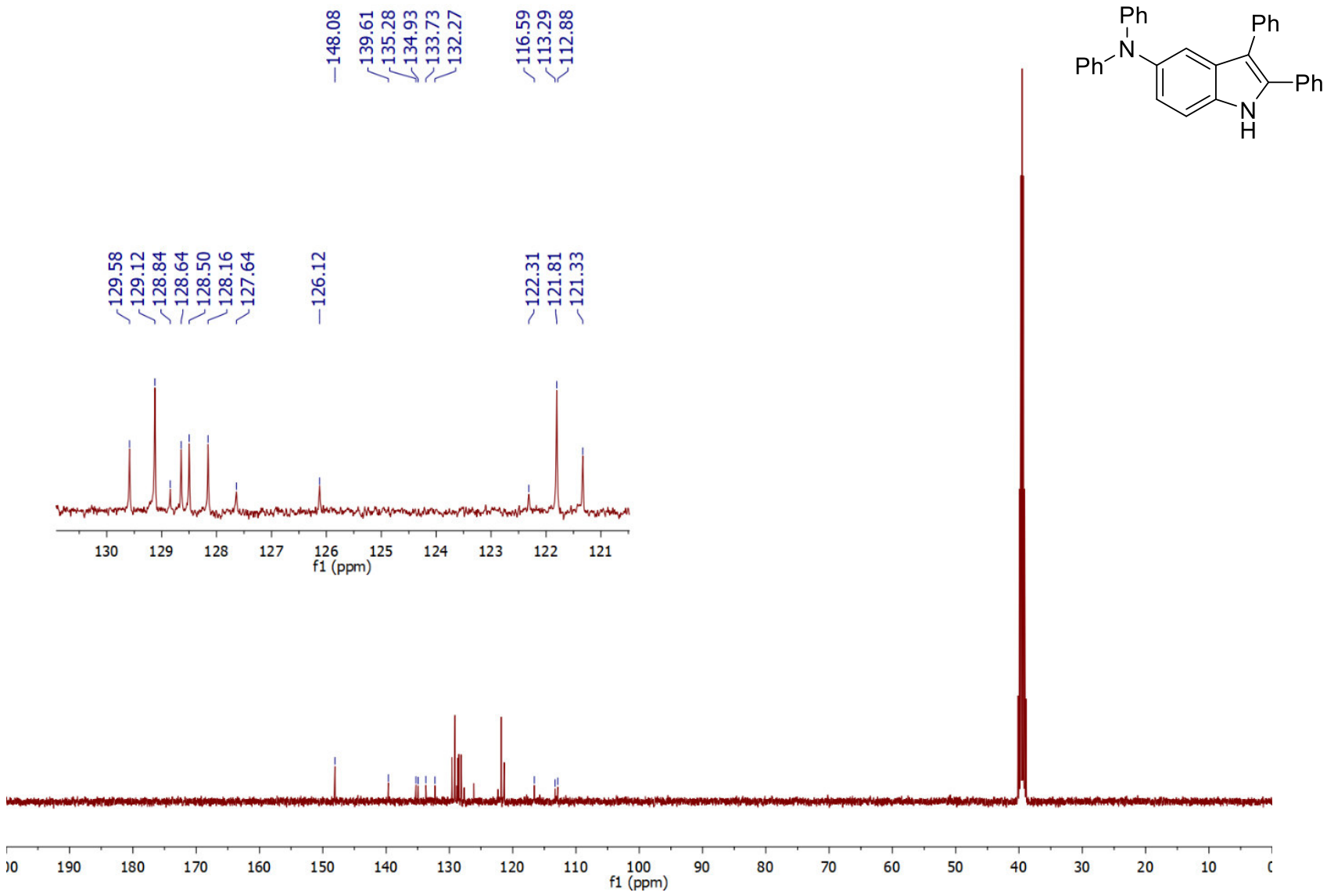
$^{13}$C-NMR (**3k**, 875)



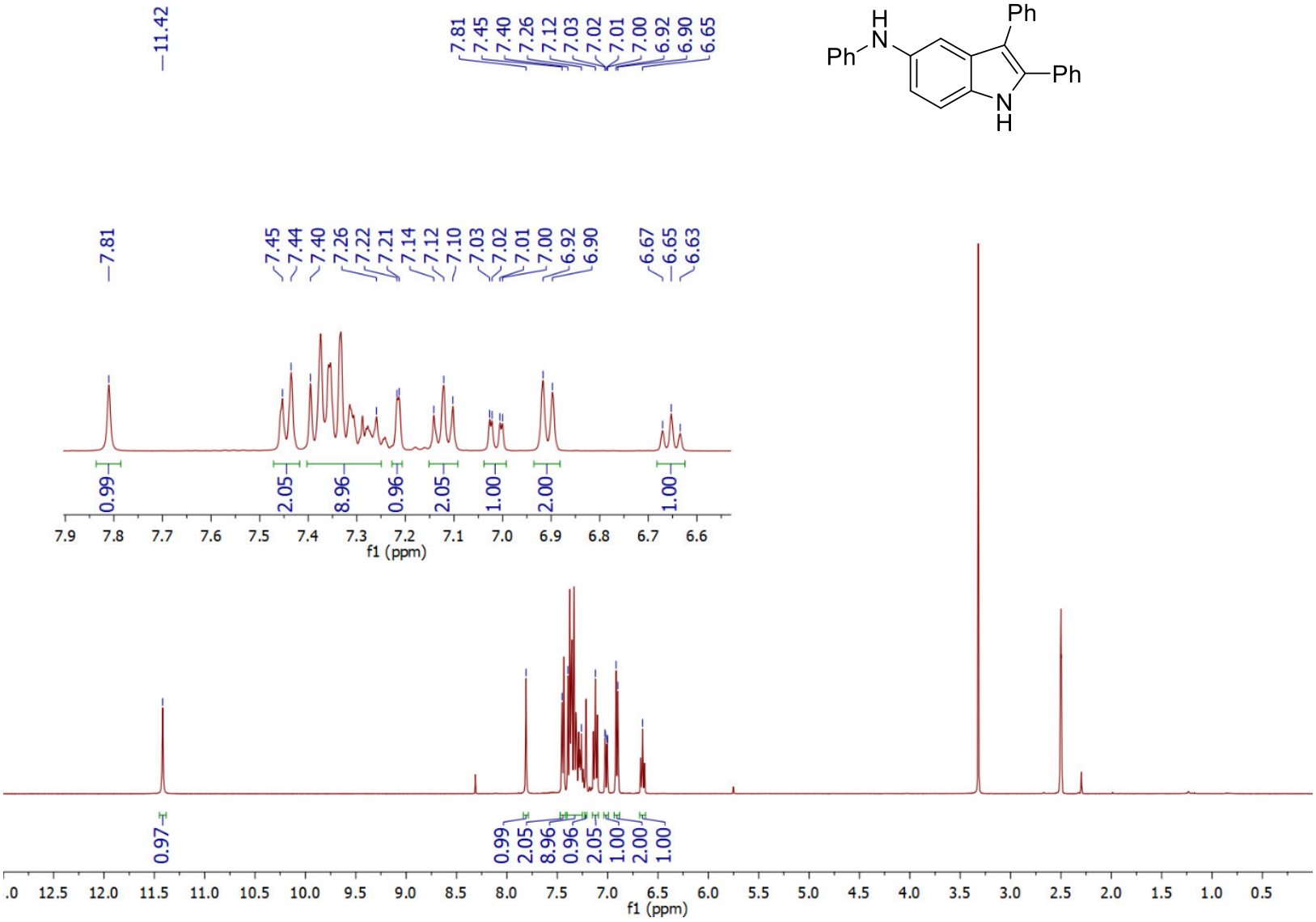
$^{1}$H-NMR (**3l**, CHB-605)



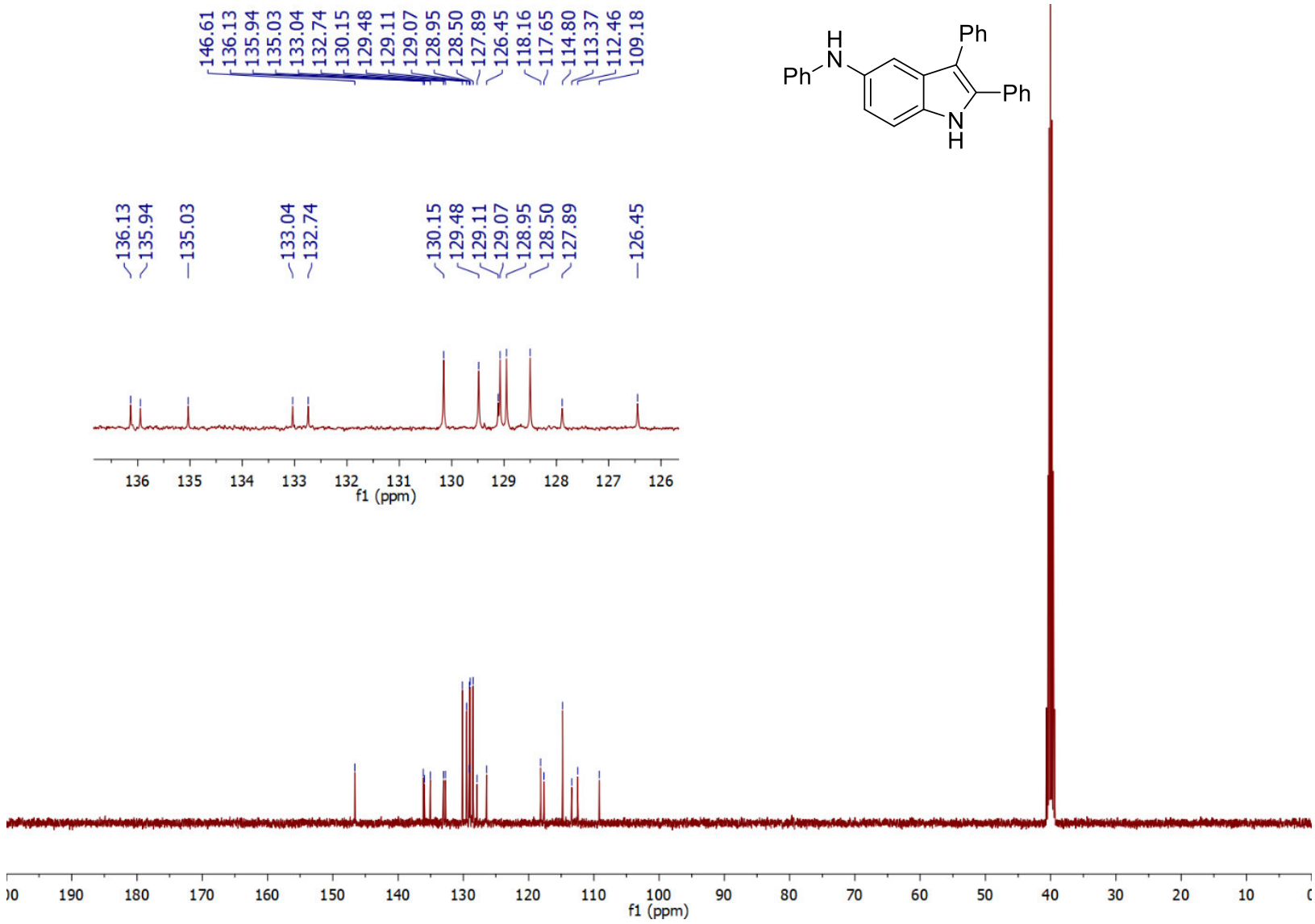
$^{13}$C-NMR (**3l**, CHB-605)



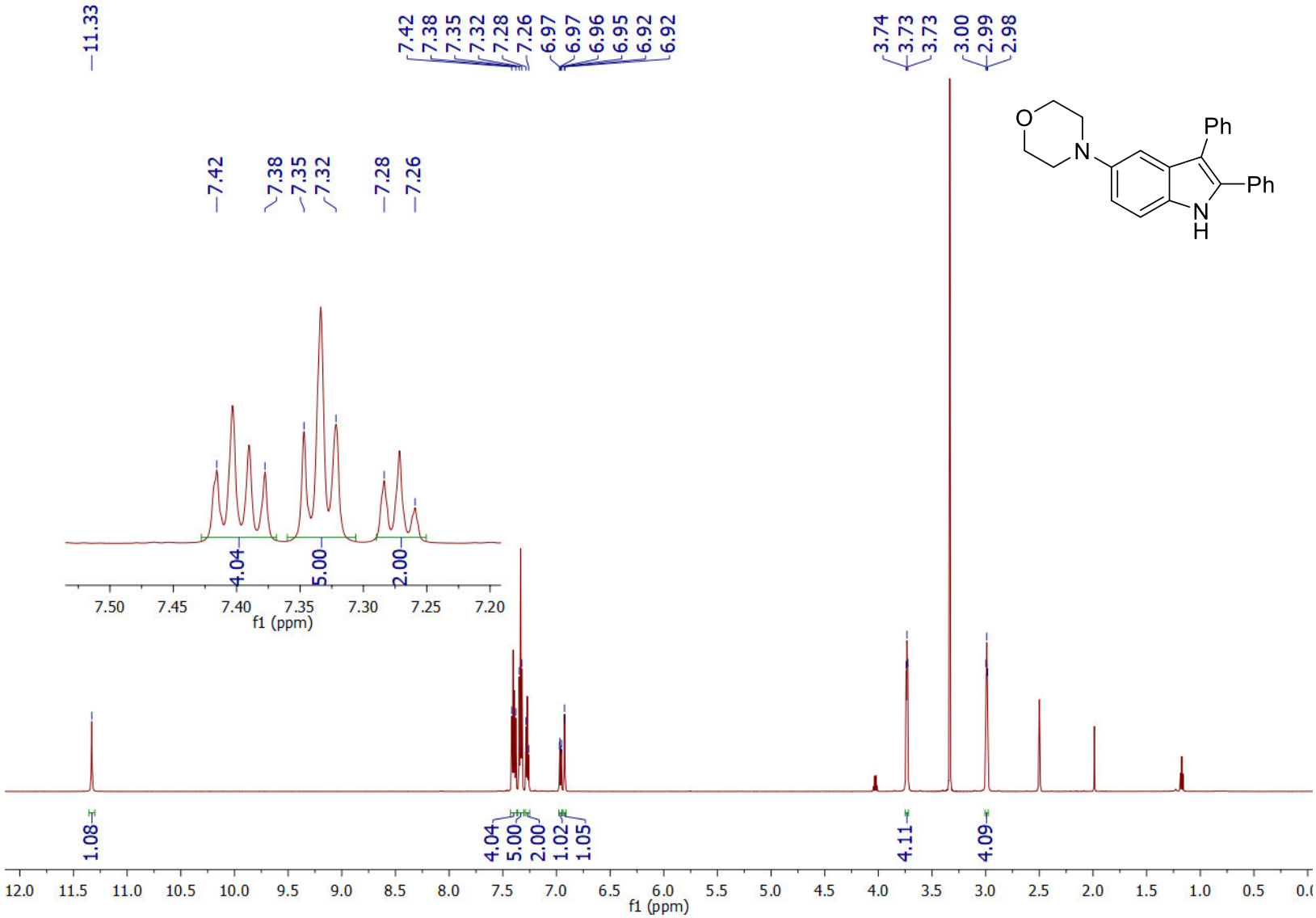
$^{1}$H-NMR (**3m**, CHB-604)



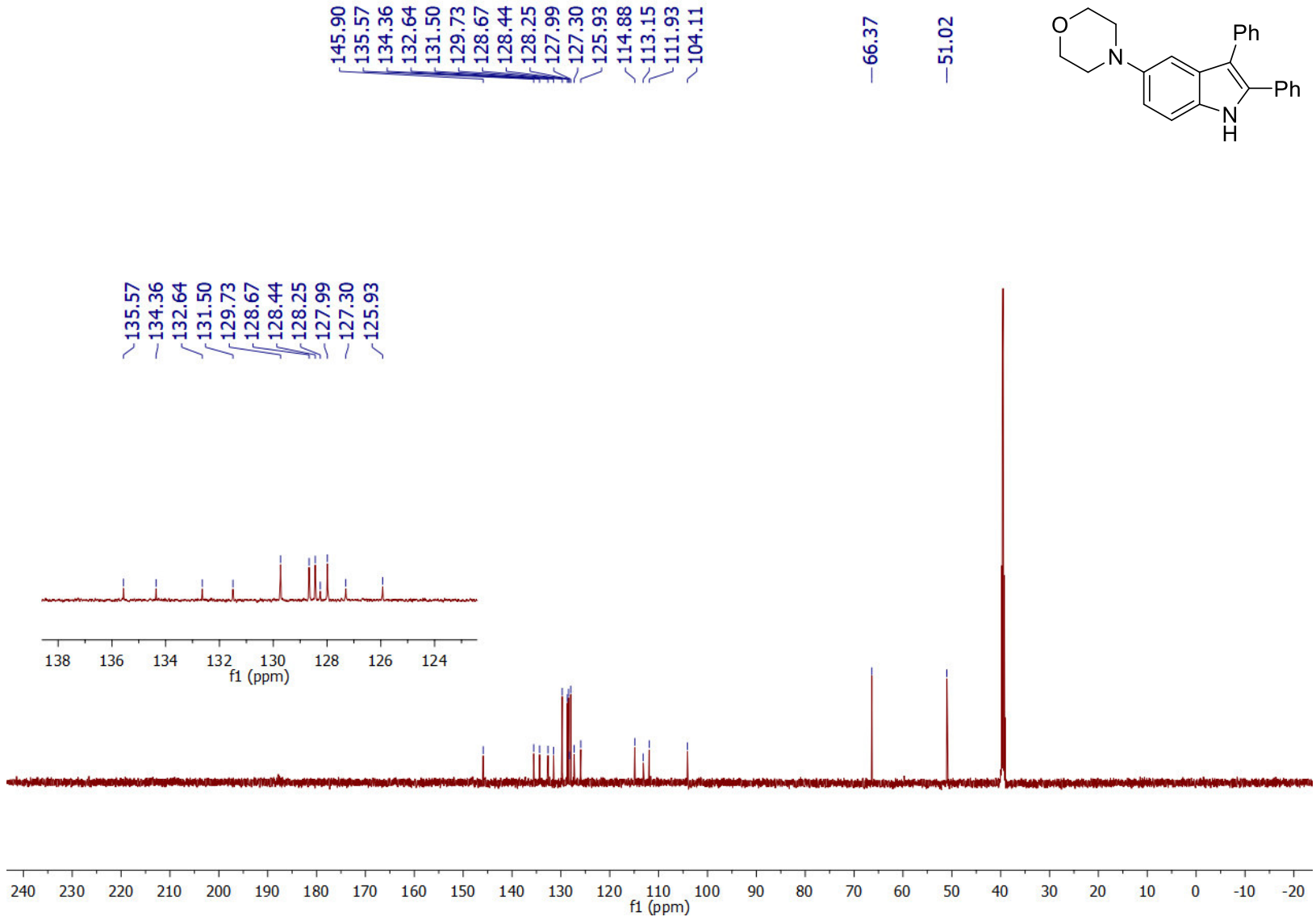
$^{13}$C-NMR (**3m**, CHB-604)



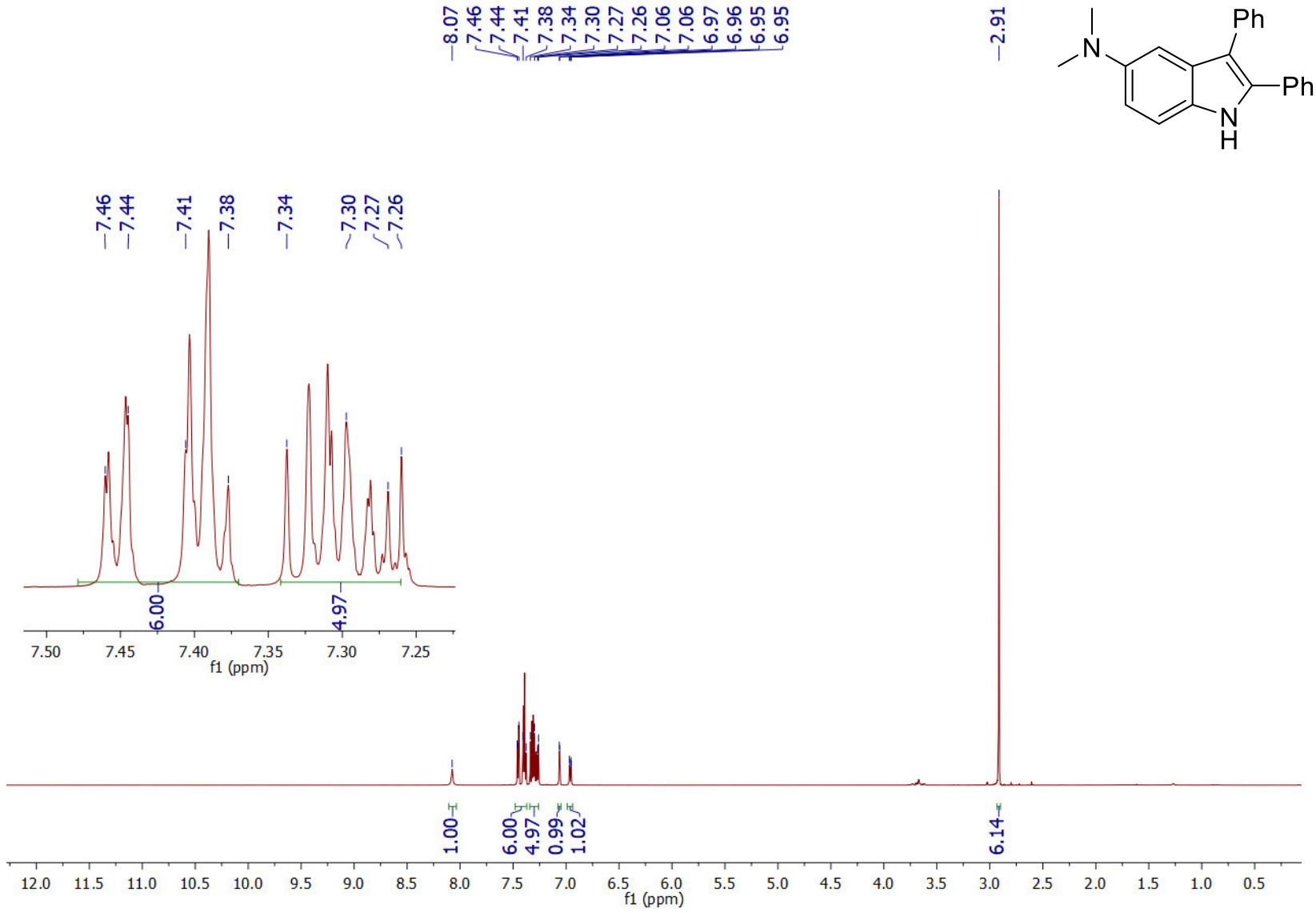
$^{1}$H-NMR (**3n**, 899)


11.33
7.42
7.38
7.35
7.32
7.28
7.26
6.97
6.97
6.96
6.95
6.92
6.92
3.74
3.73
3.73
3.00
2.99
2.98
O
N
Ph
Ph
N
H
4.04
5.00
2.00
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
1.08
4.04
5.00
2.00
1.02
1.05
4.11
4.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

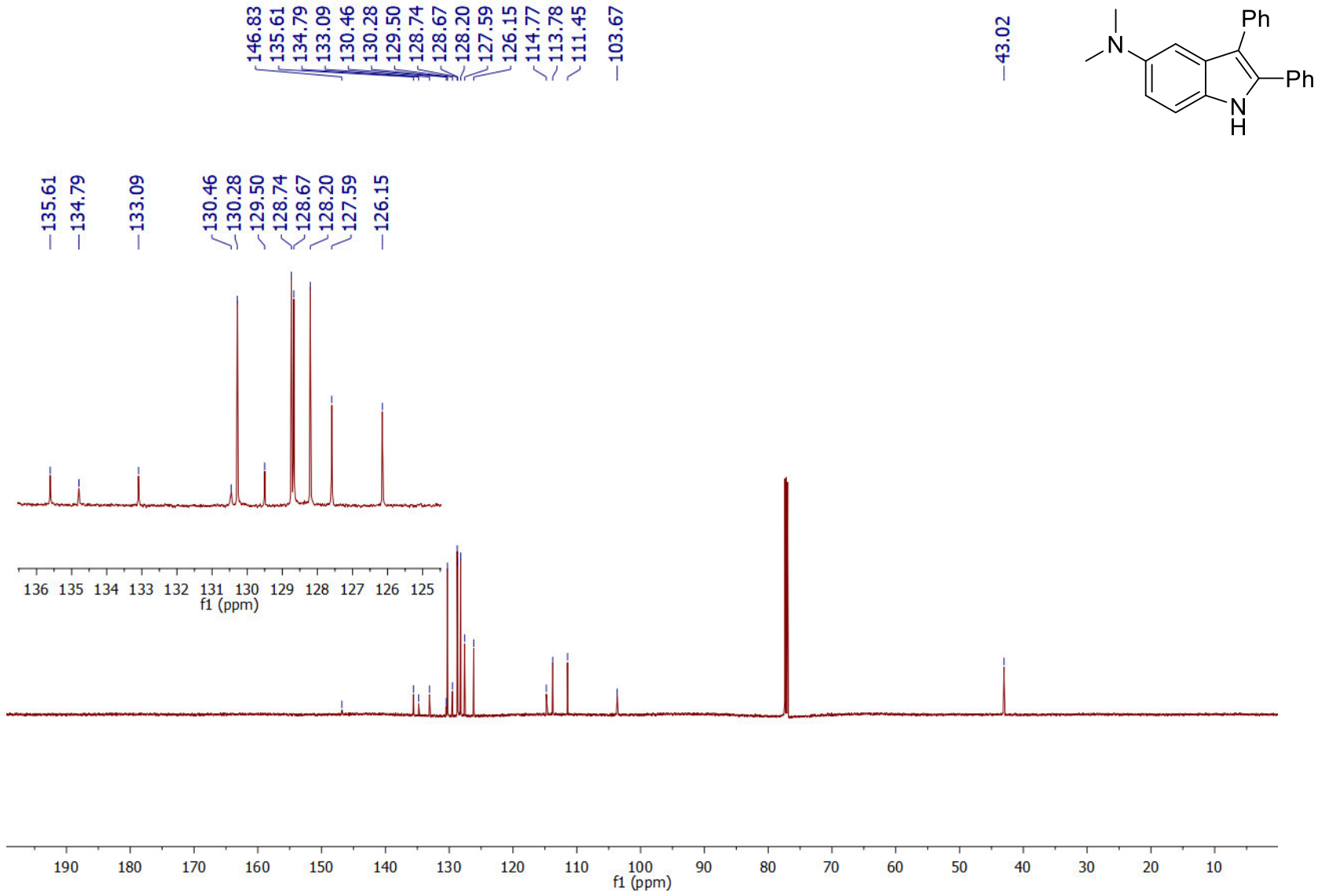
$^{13}$C-NMR (**3n**, 899)



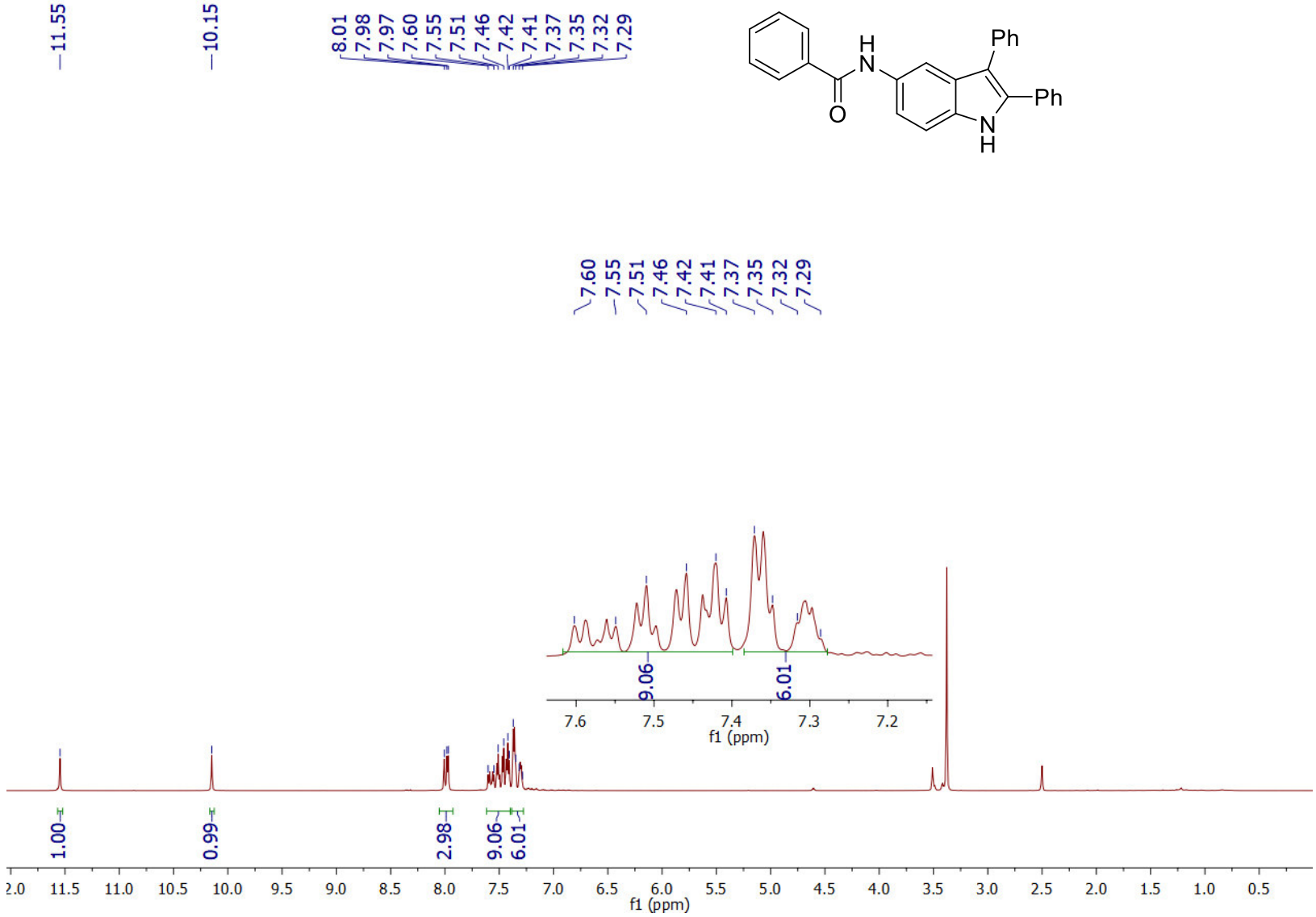
$^{1}$H-NMR (**3o**, 898)


8.07
7.46
7.44
7.41
7.38
7.34
7.30
7.27
7.26
7.06
7.06
6.97
6.96
6.95
6.95
2.91
Ph
Ph
N
H
6.00
4.97
f1 (ppm)
1.00
6.00
4.97
0.99
1.02
6.14
f1 (ppm)

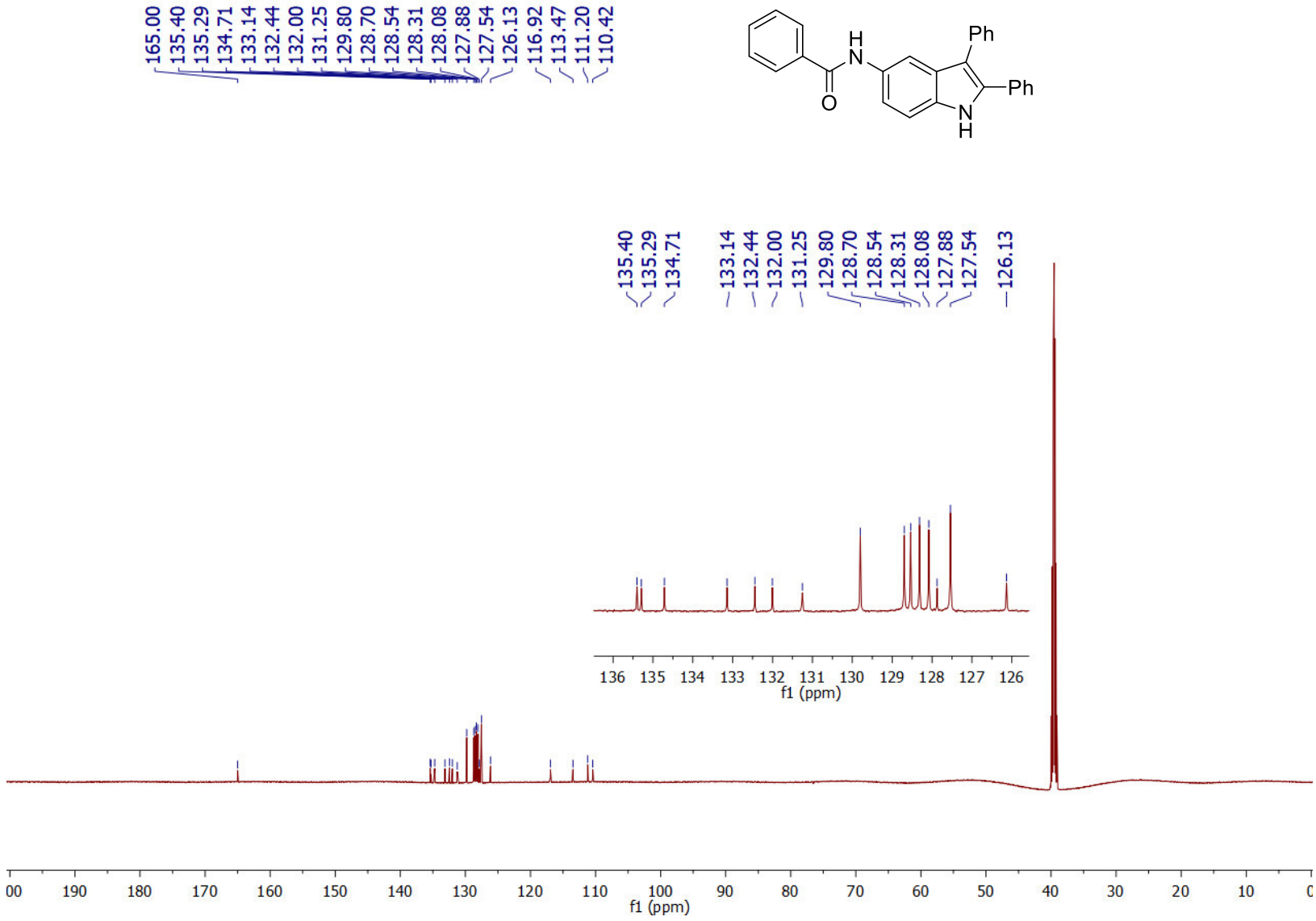
$^{13}$C-NMR (**3o**, 898)



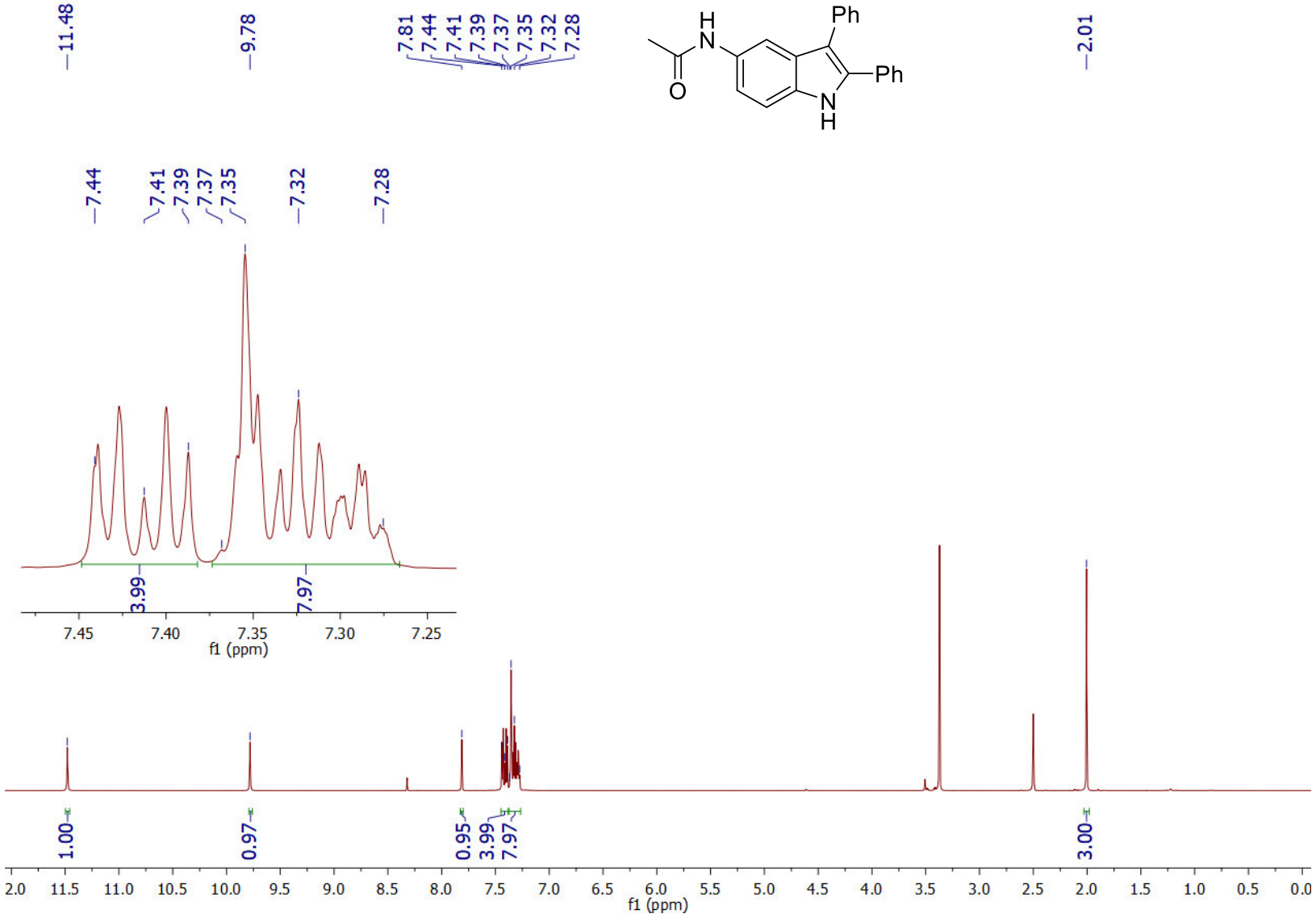
$^{1}$H-NMR (**3p**, 902)


11.55
10.15
8.01
7.98
7.97
7.60
7.55
7.51
7.46
7.42
7.41
7.37
7.35
7.32
7.29
H
N
O
Ph
Ph
N
H
9.06
6.01
f1 (ppm)
1.00
0.99
2.98
9.06
6.01
f1 (ppm)

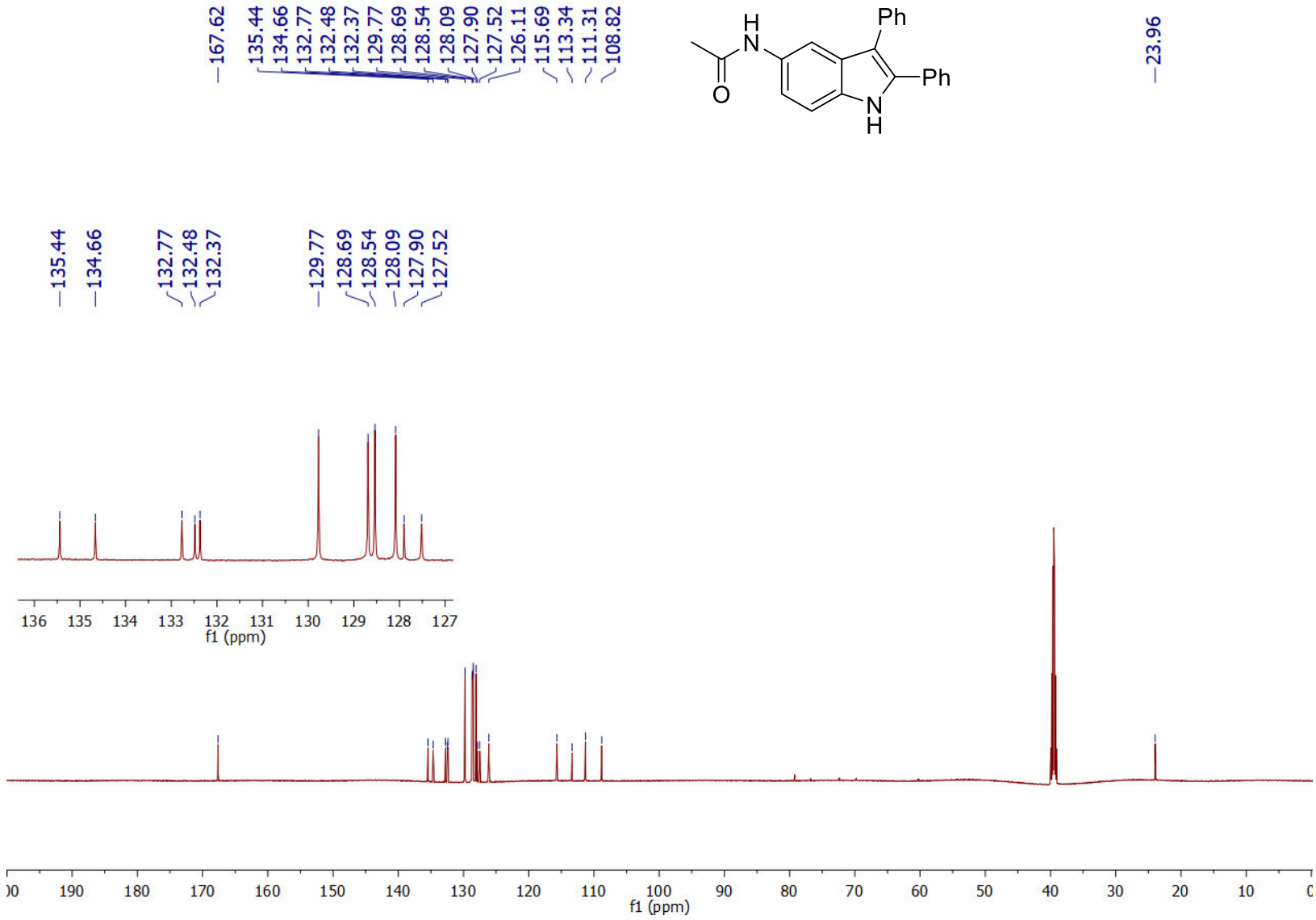
$^{13}$C-NMR (**3p**, 902)



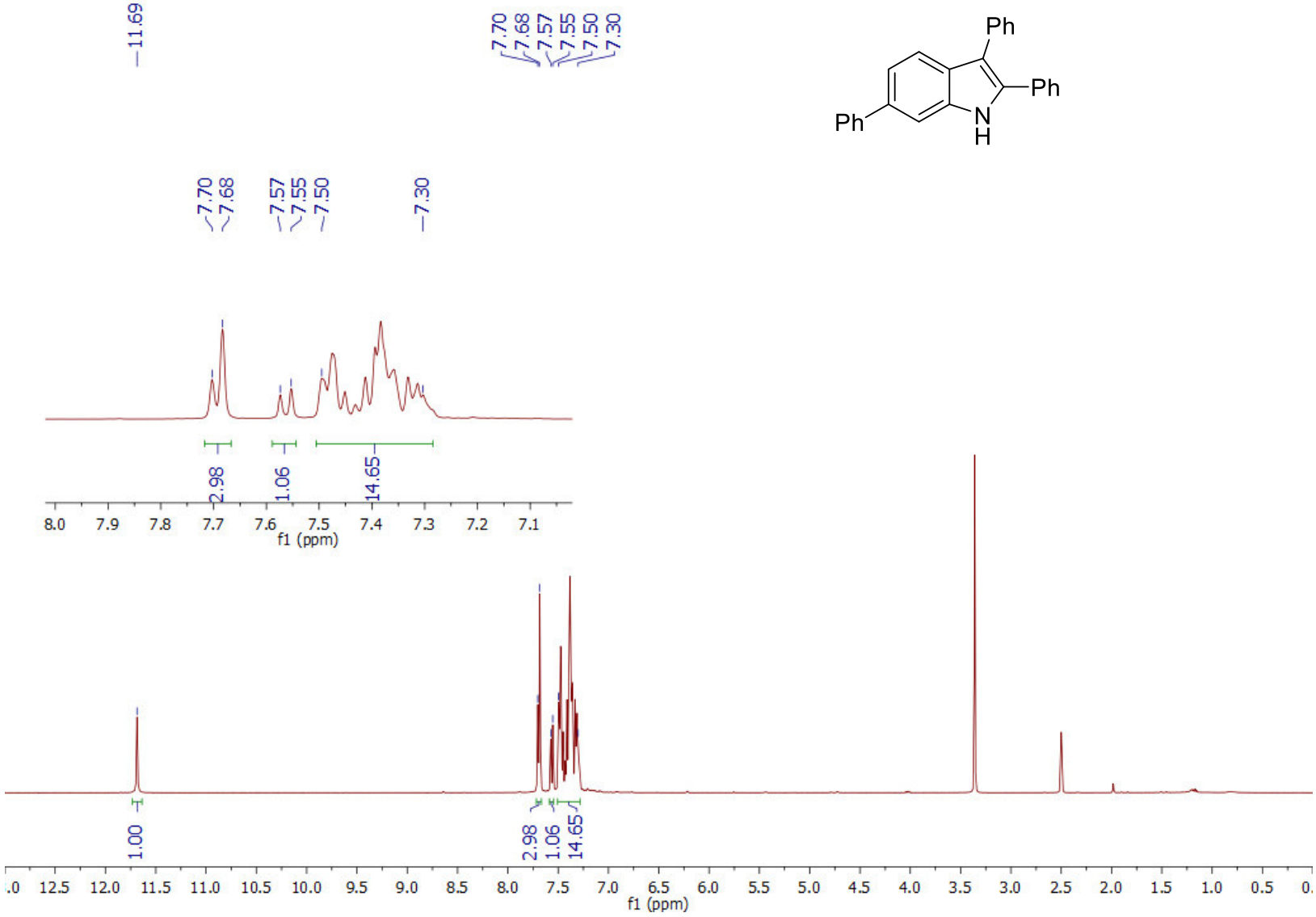
$^{1}$H-NMR (**3q**, 885-F2)



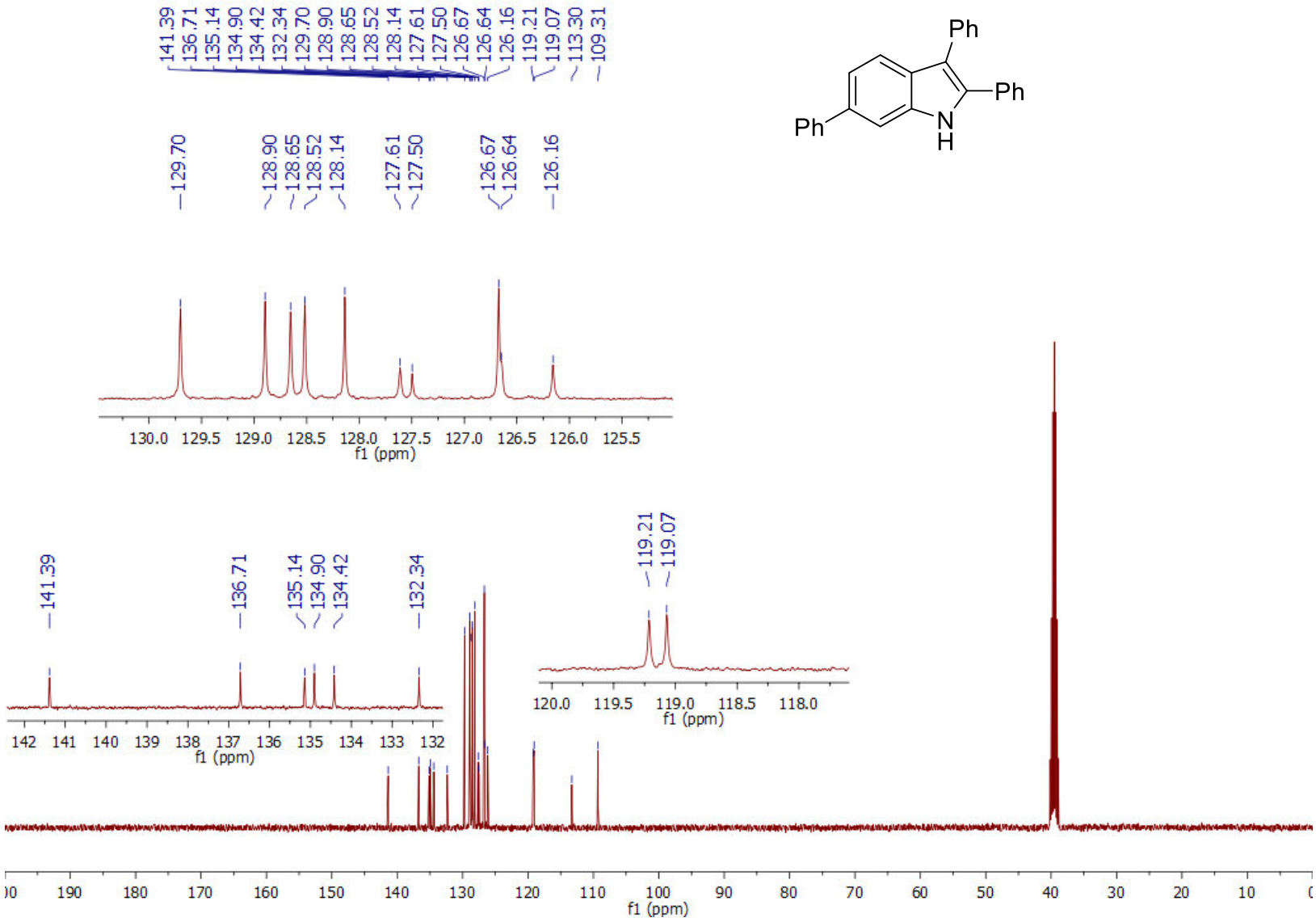
$^{13}$C-NMR (**3q**, 885-F2)



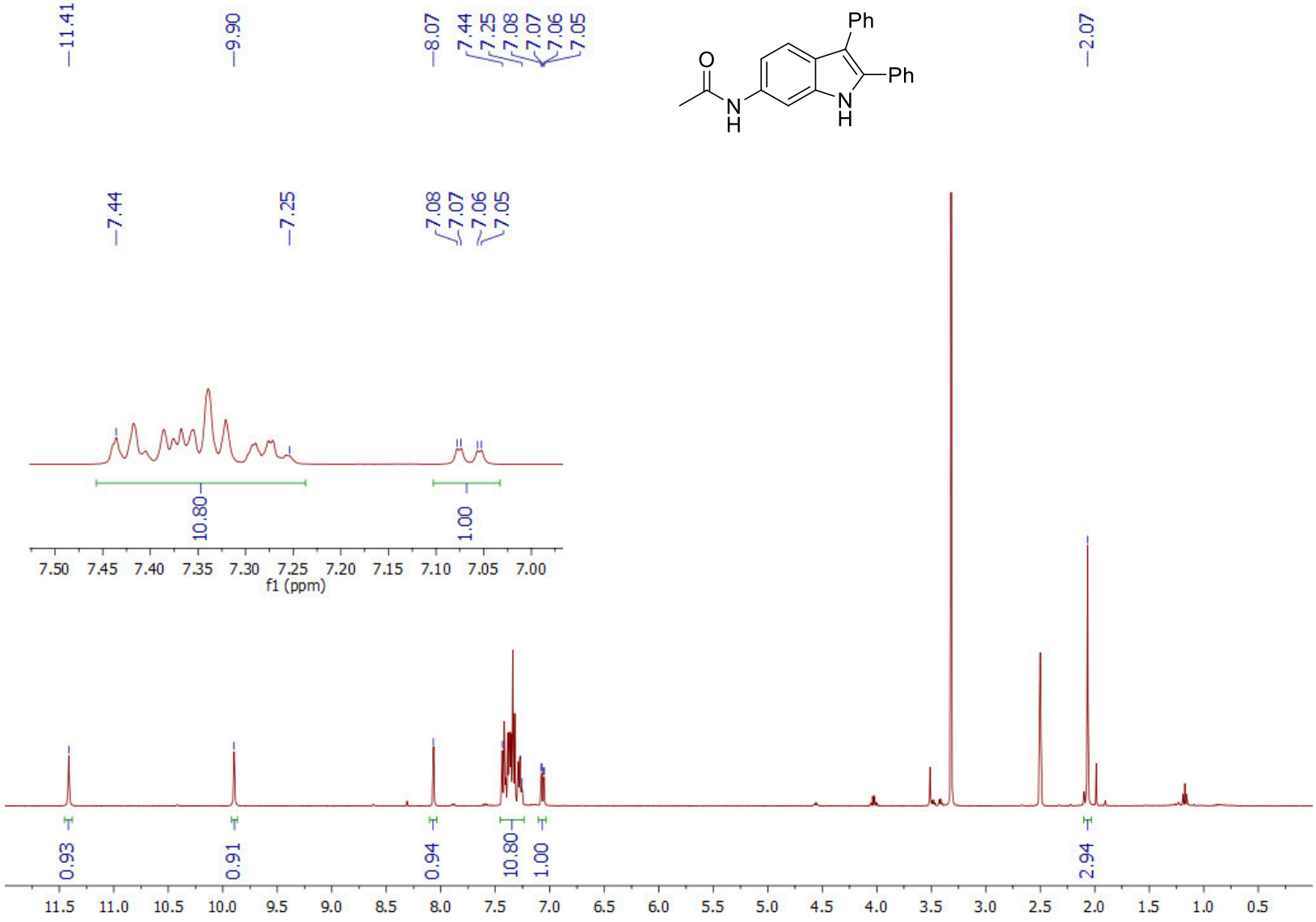
$^{1}$H-NMR (**3r**, CHB-621)



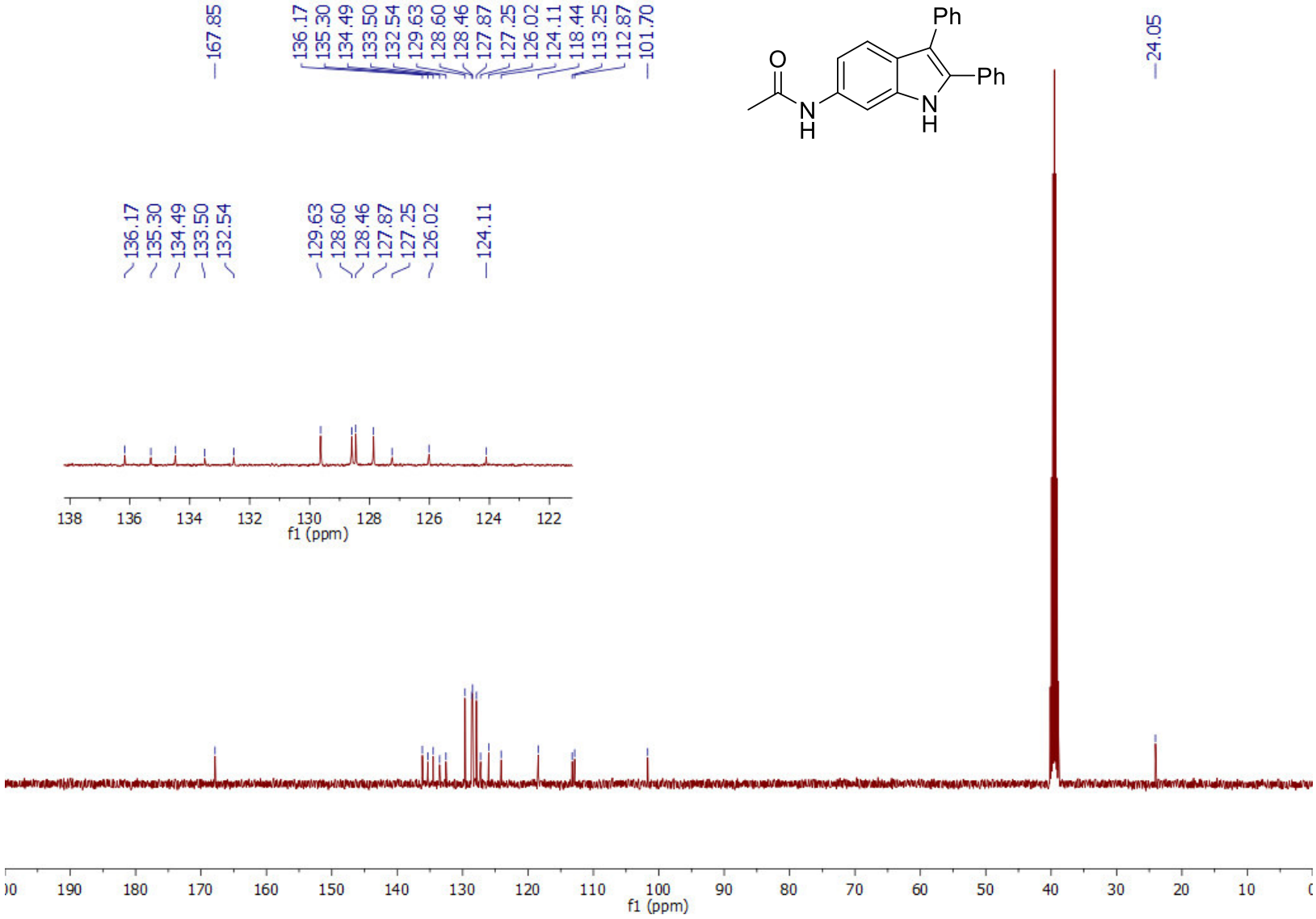
$^{13}$C-NMR (**3r**, CHB-621)



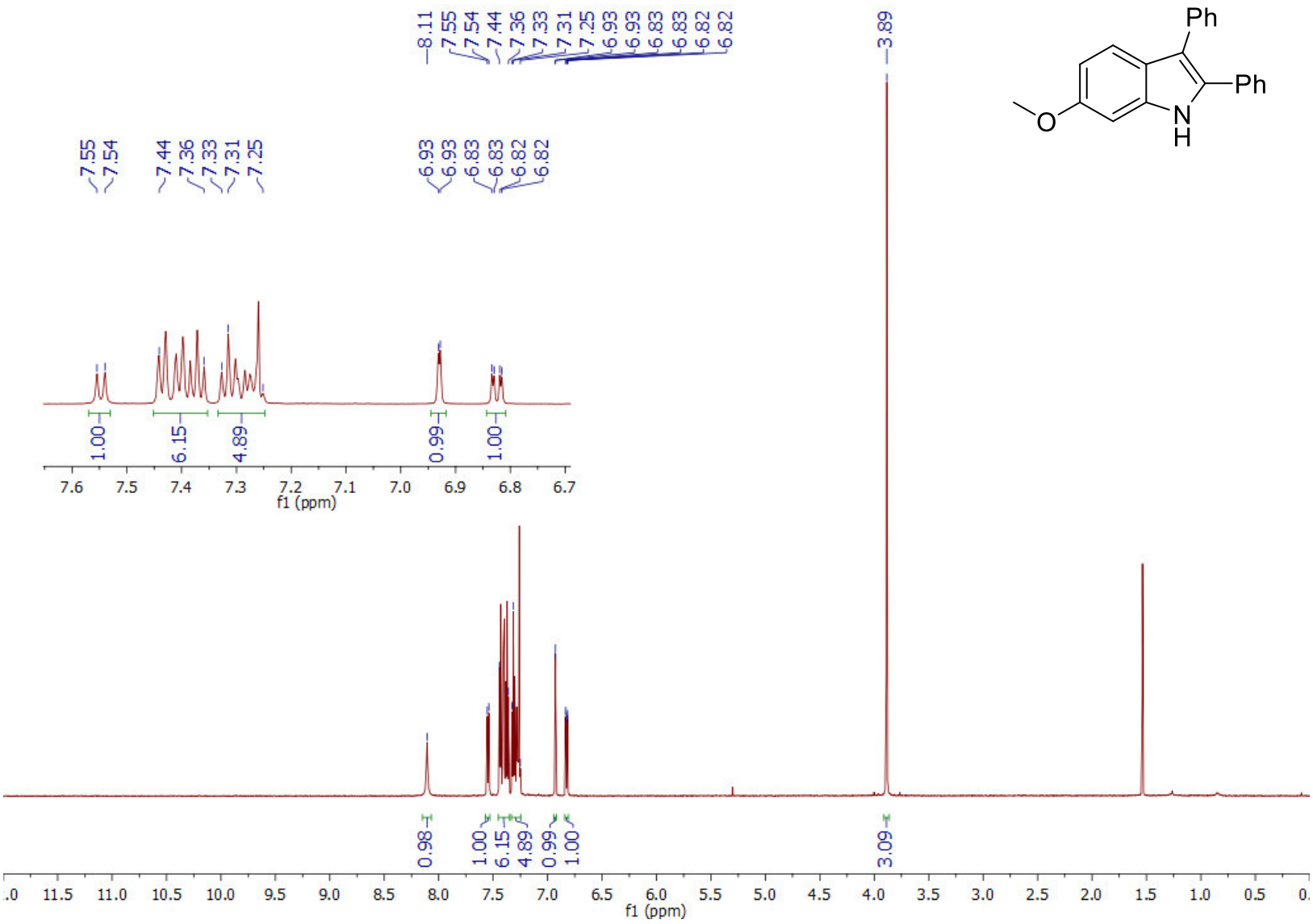
$^{1}$H-NMR (**3s**, CHB-615)



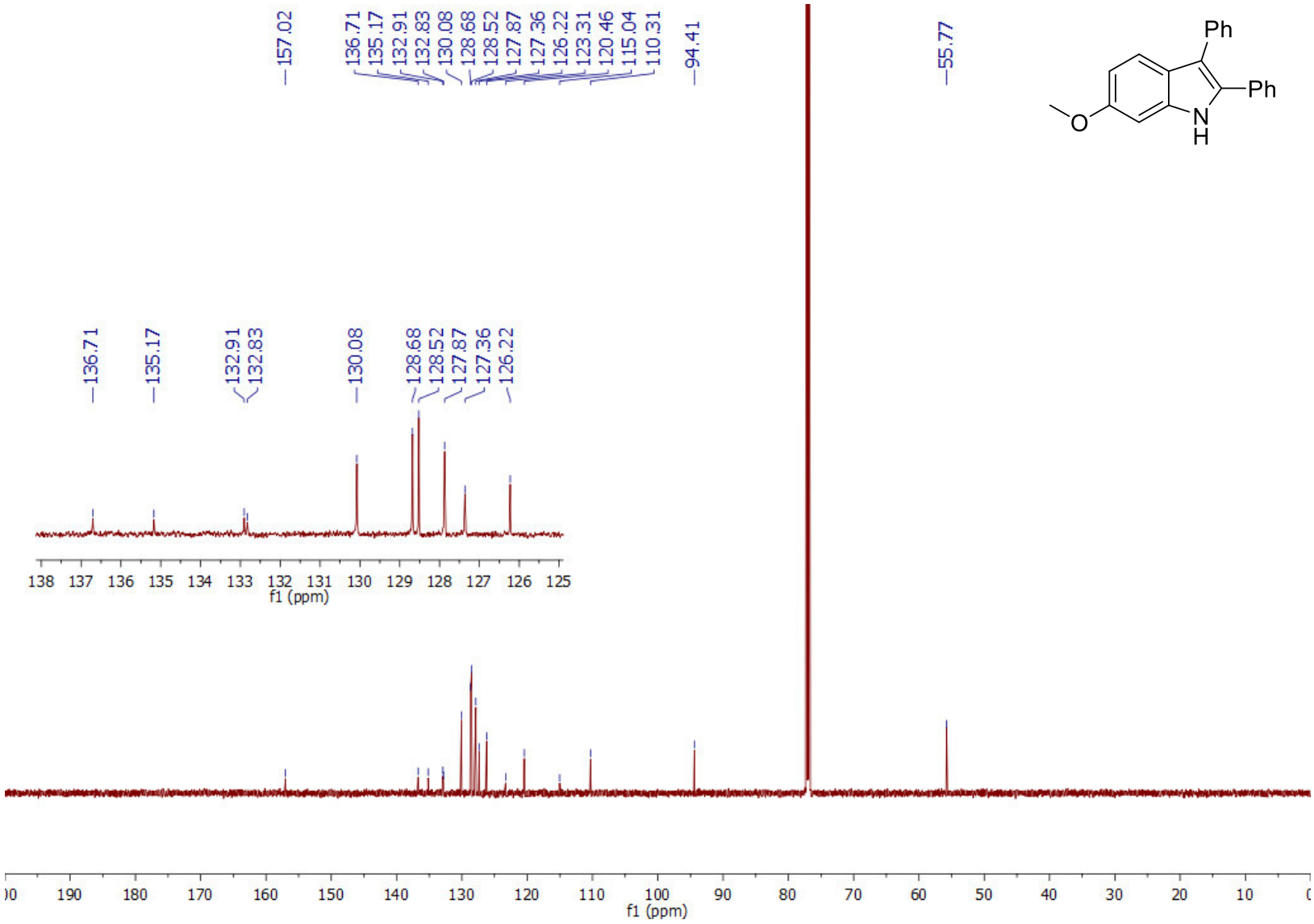
$^{13}$C-NMR (**3s**, CHB-615)



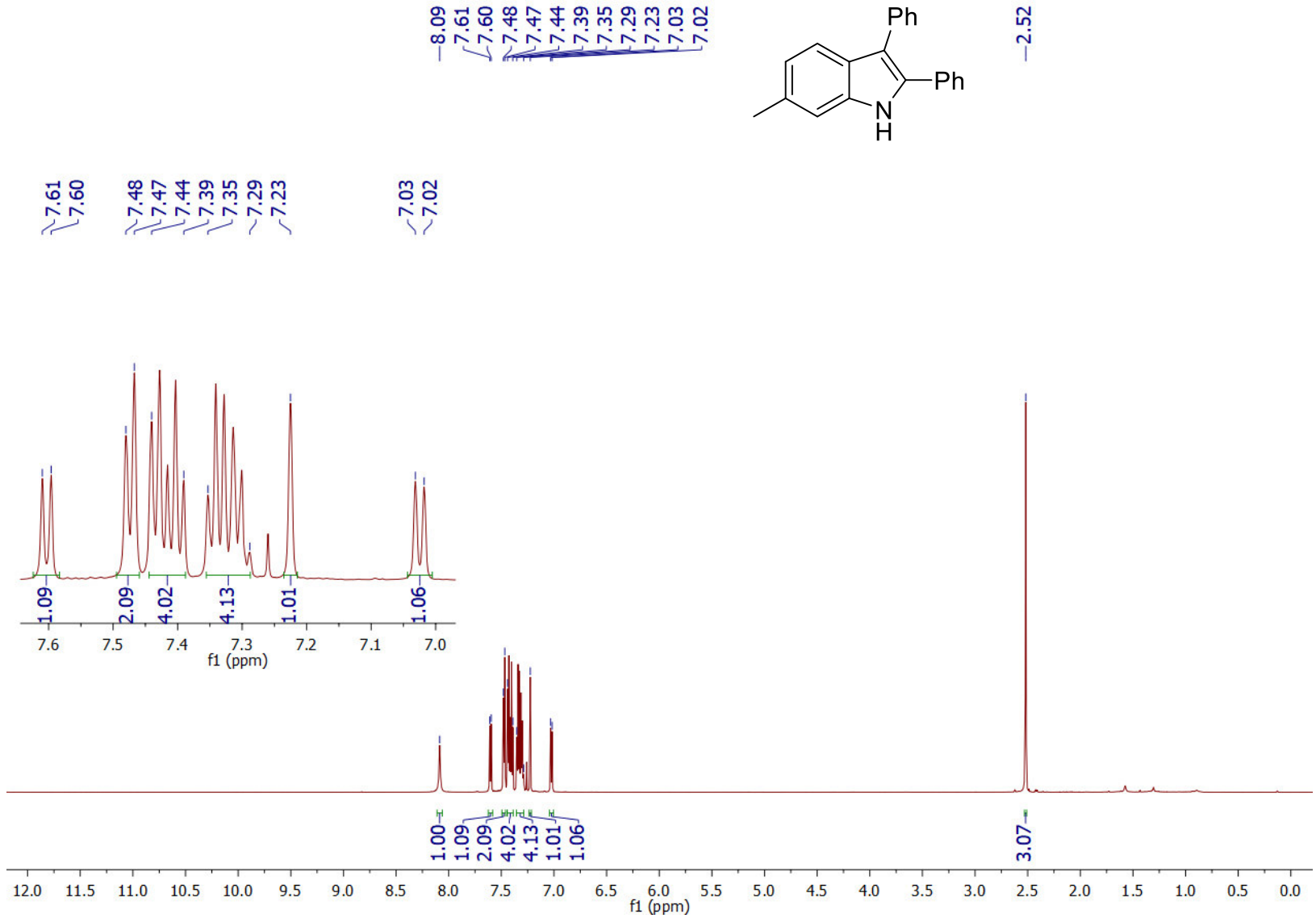
$^{1}$H-NMR (**3t**, CHB-611)



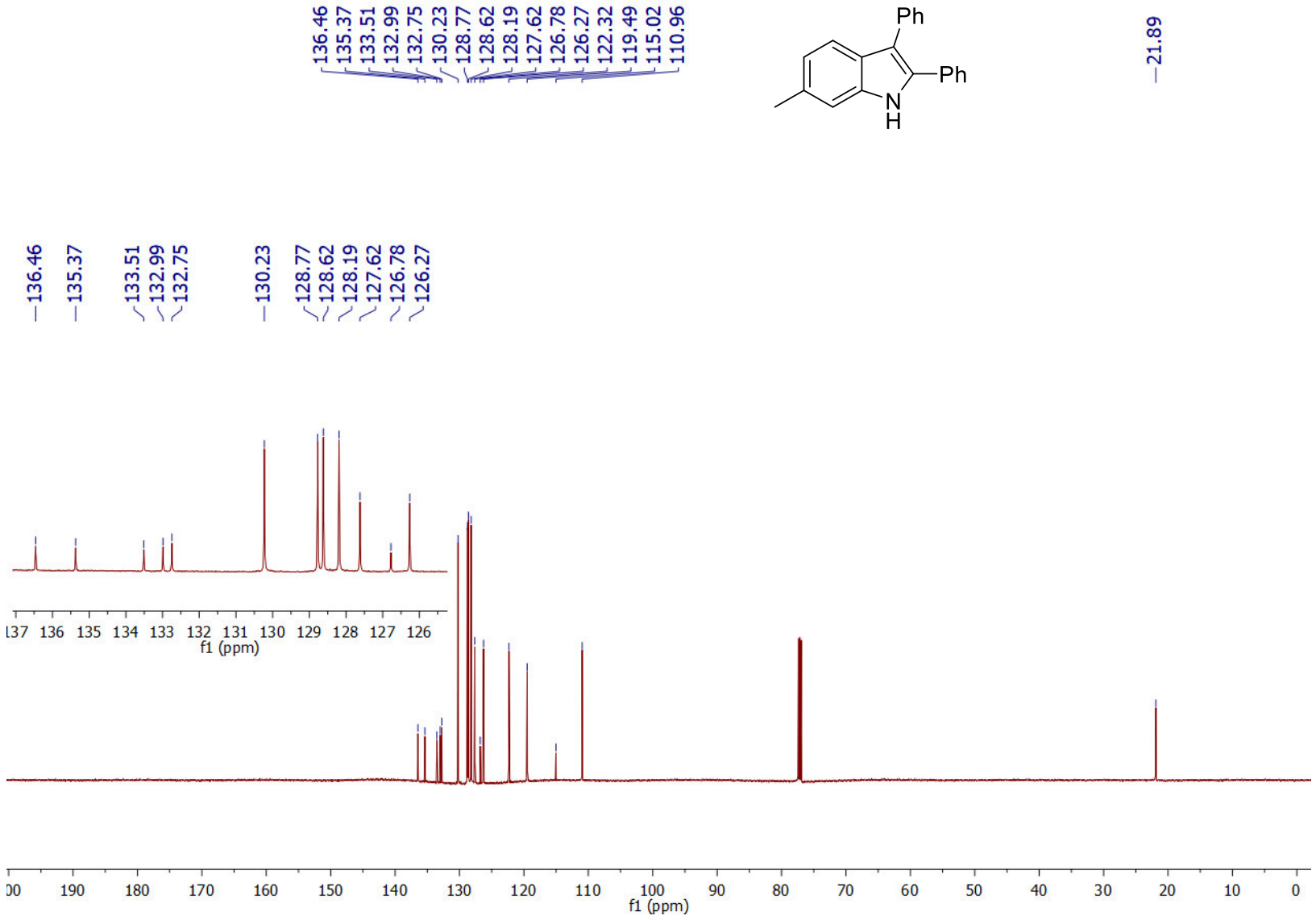
$^{13}$C-NMR (**3t**, CHB-611)



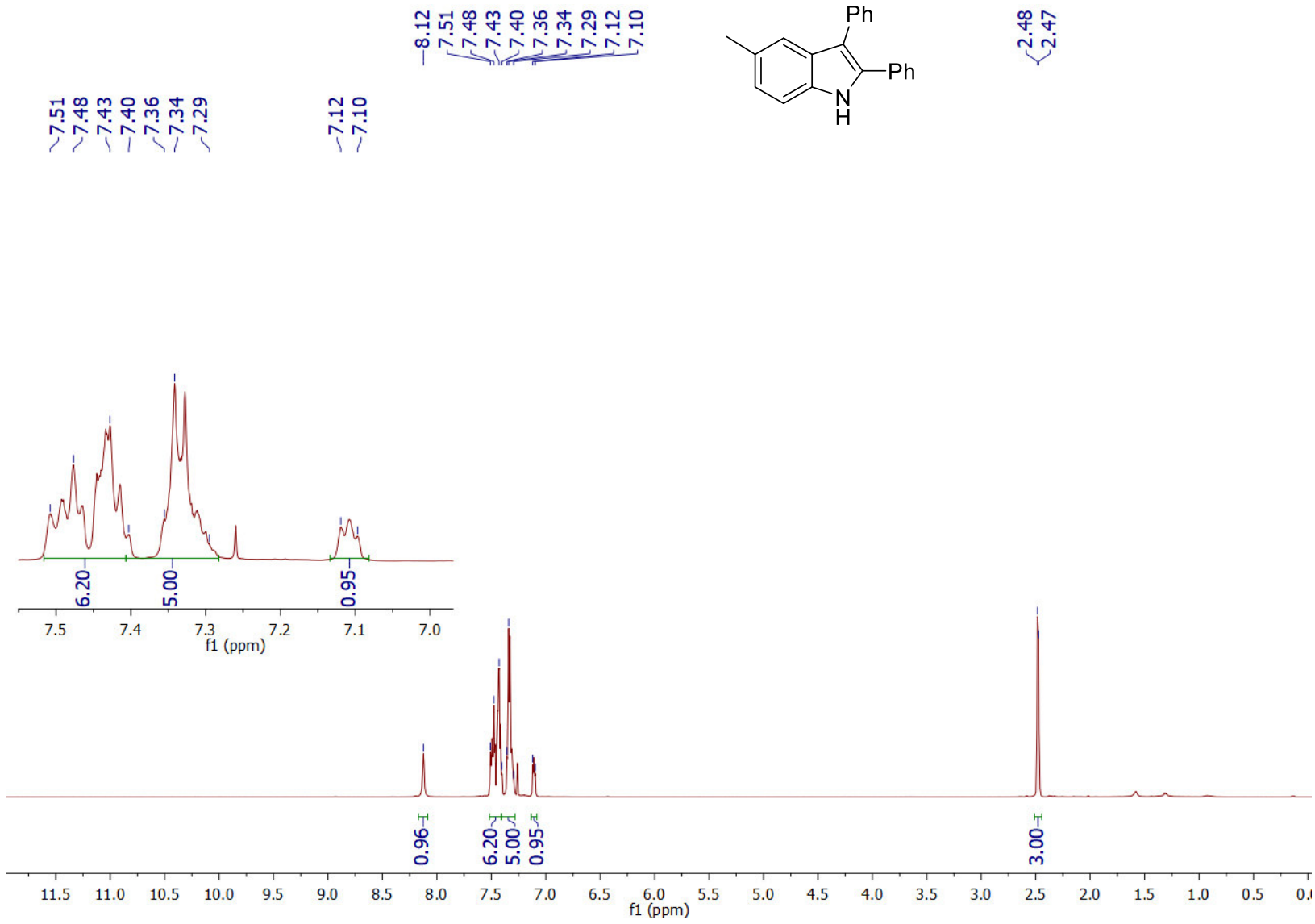
$^{1}$H-NMR (**3u**, 903)


8.09
7.61
7.60
7.48
7.47
7.44
7.39
7.35
7.29
7.23
7.03
7.02
2.52
Ph
Ph
N
H
1.09
2.09
4.02
4.13
1.01
1.06
1.00
3.07
f1 (ppm)

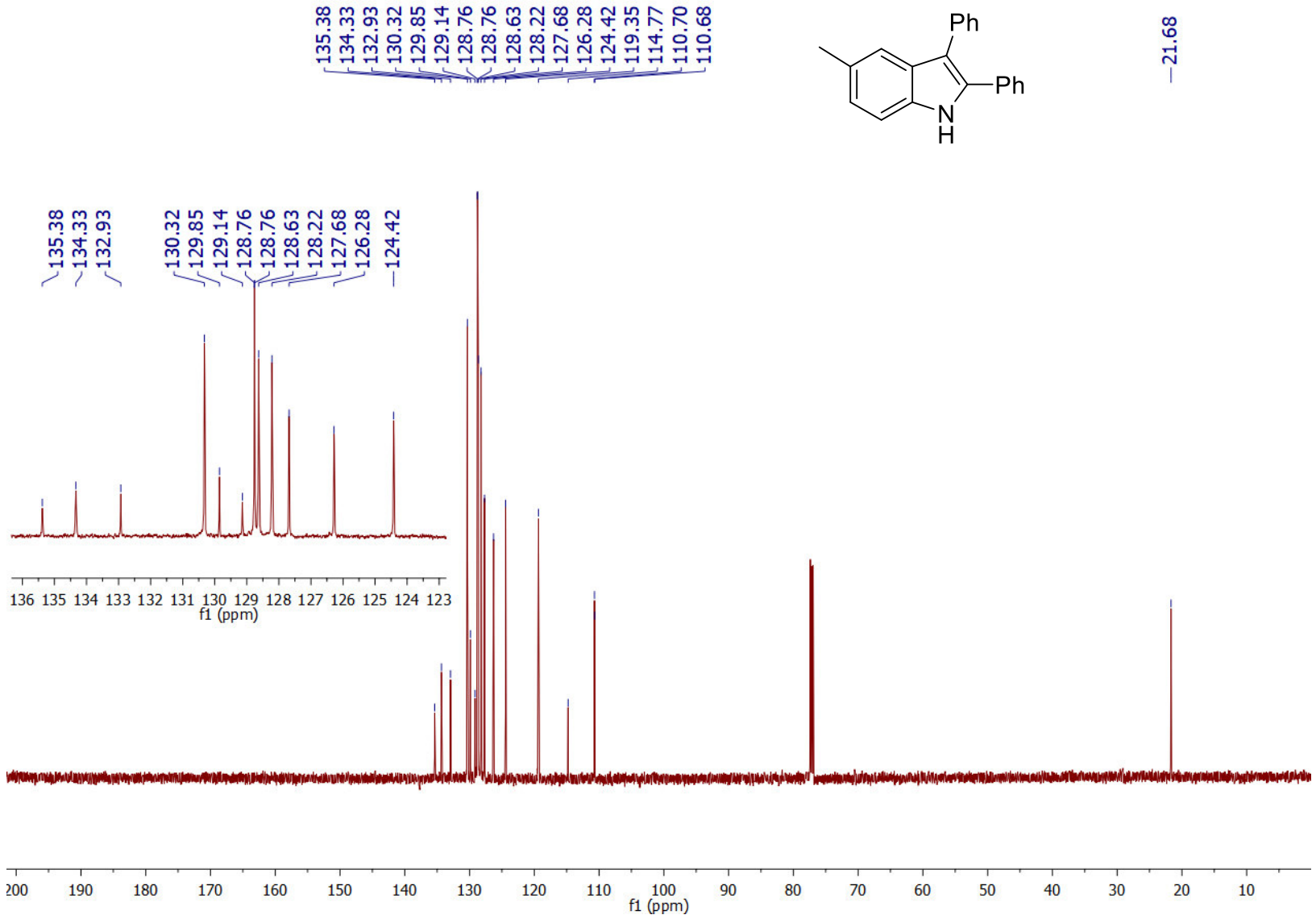
$^{13}$C-NMR (**3u**, 903)



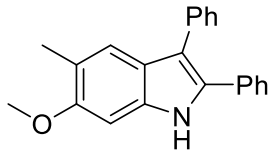
$^{1}$H-NMR (**3v**, 872)


8.12
7.51
7.48
7.43
7.40
7.36
7.34
7.29
7.12
7.10
2.48
2.47
Ph
Ph
N
H
6.20
5.00
0.95
f1 (ppm)
0.96
6.20
5.00
0.95
3.00
f1 (ppm)

$^{13}$C-NMR (**3v**, 872)

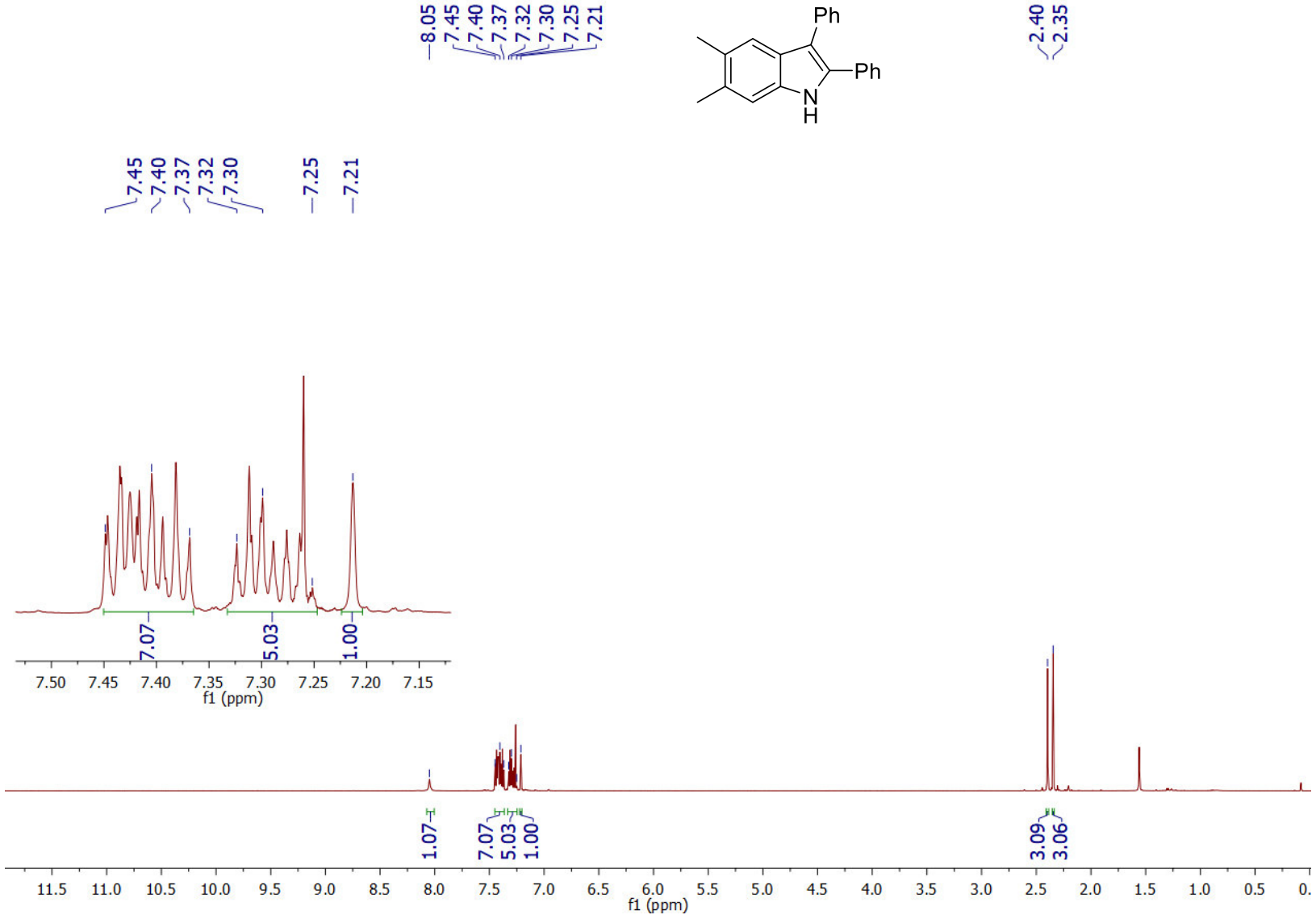


$^{1}$H-NMR (**3w**, 892)

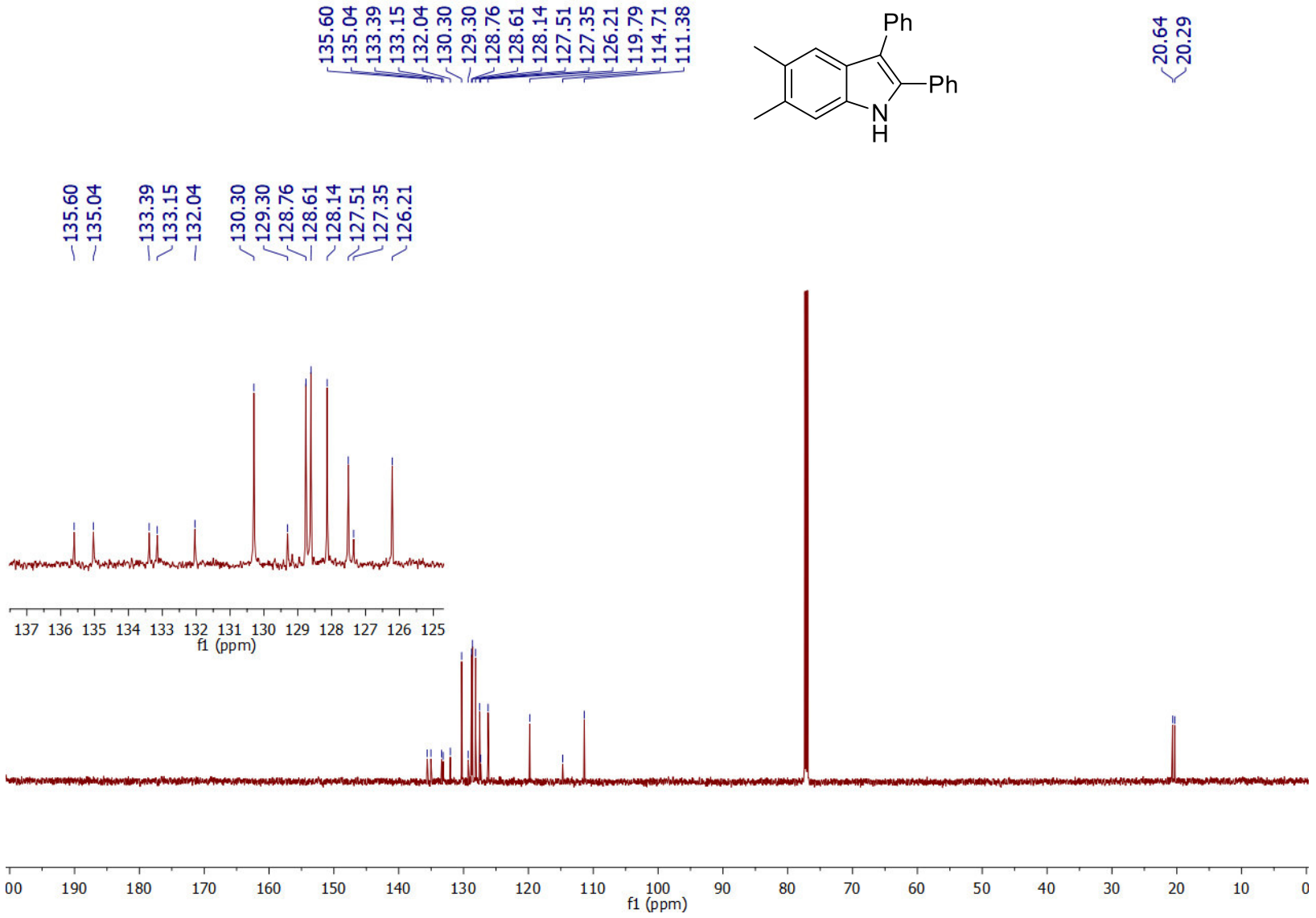

Ph
Ph
O
N
H


7.97
7.43
7.35
7.28
7.22
7.18
7.11
6.79
3.82
2.22
1.04
11.06
1.04
3.00
3.03
f1 (ppm)

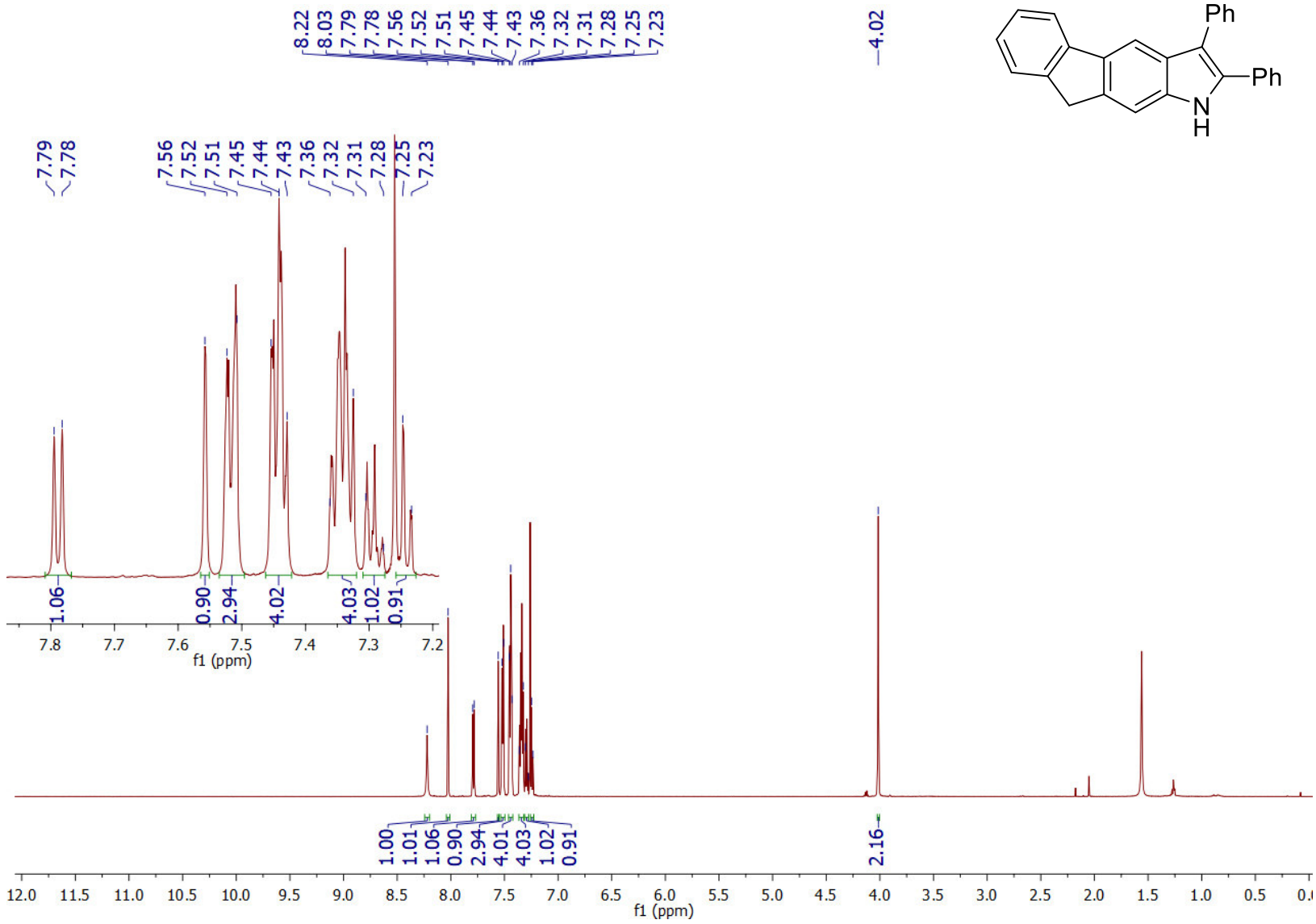
$^{1}$H-NMR (**3x**, 871)


8.05
7.45
7.40
7.37
7.32
7.30
7.25
7.21
2.40
2.35
Ph
Ph
N
H
7.07
5.03
1.00
f1 (ppm)
1.07
7.07
5.03
1.00
3.09
3.06
f1 (ppm)

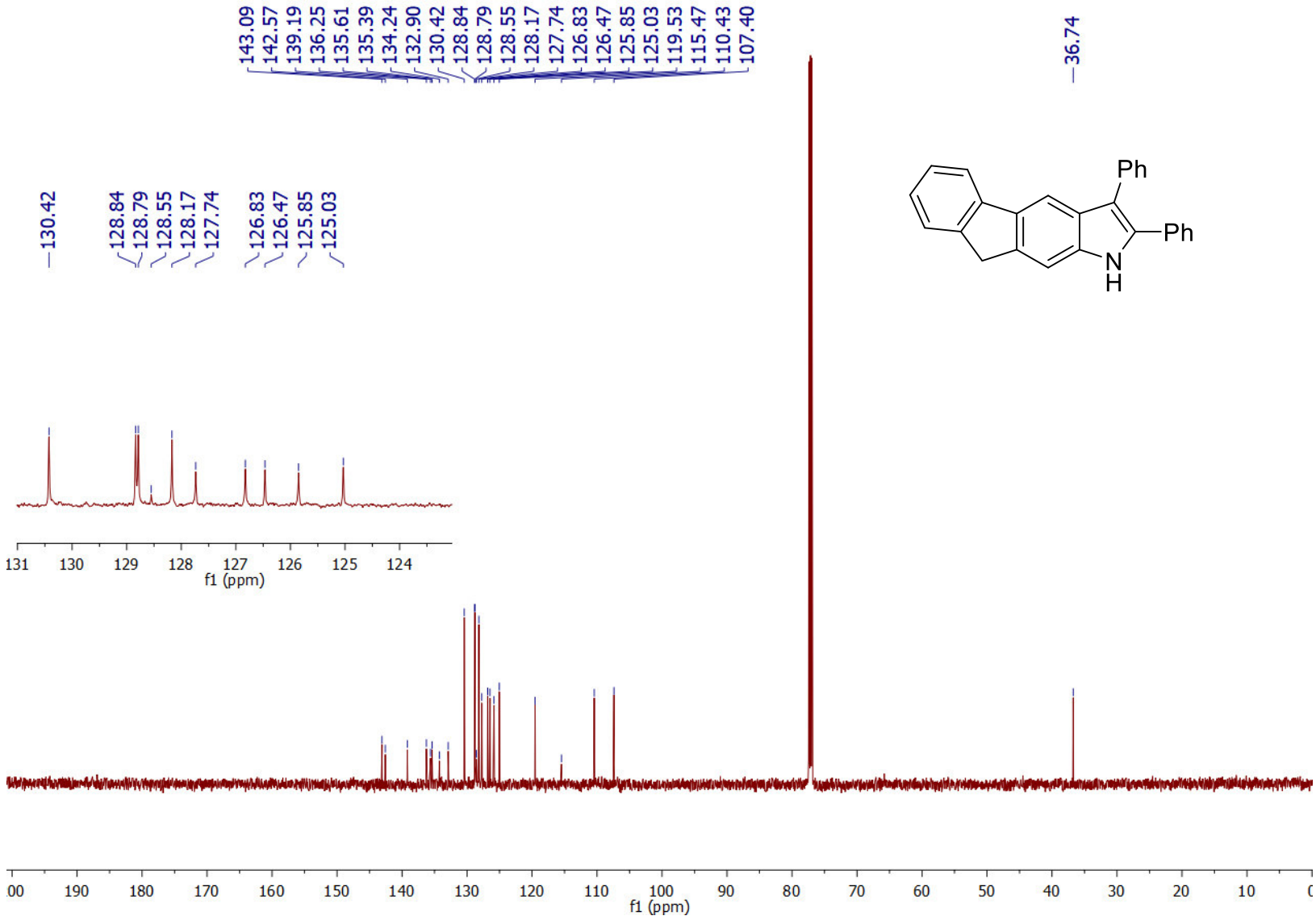
$^{13}$C-NMR (**3x**, 871)



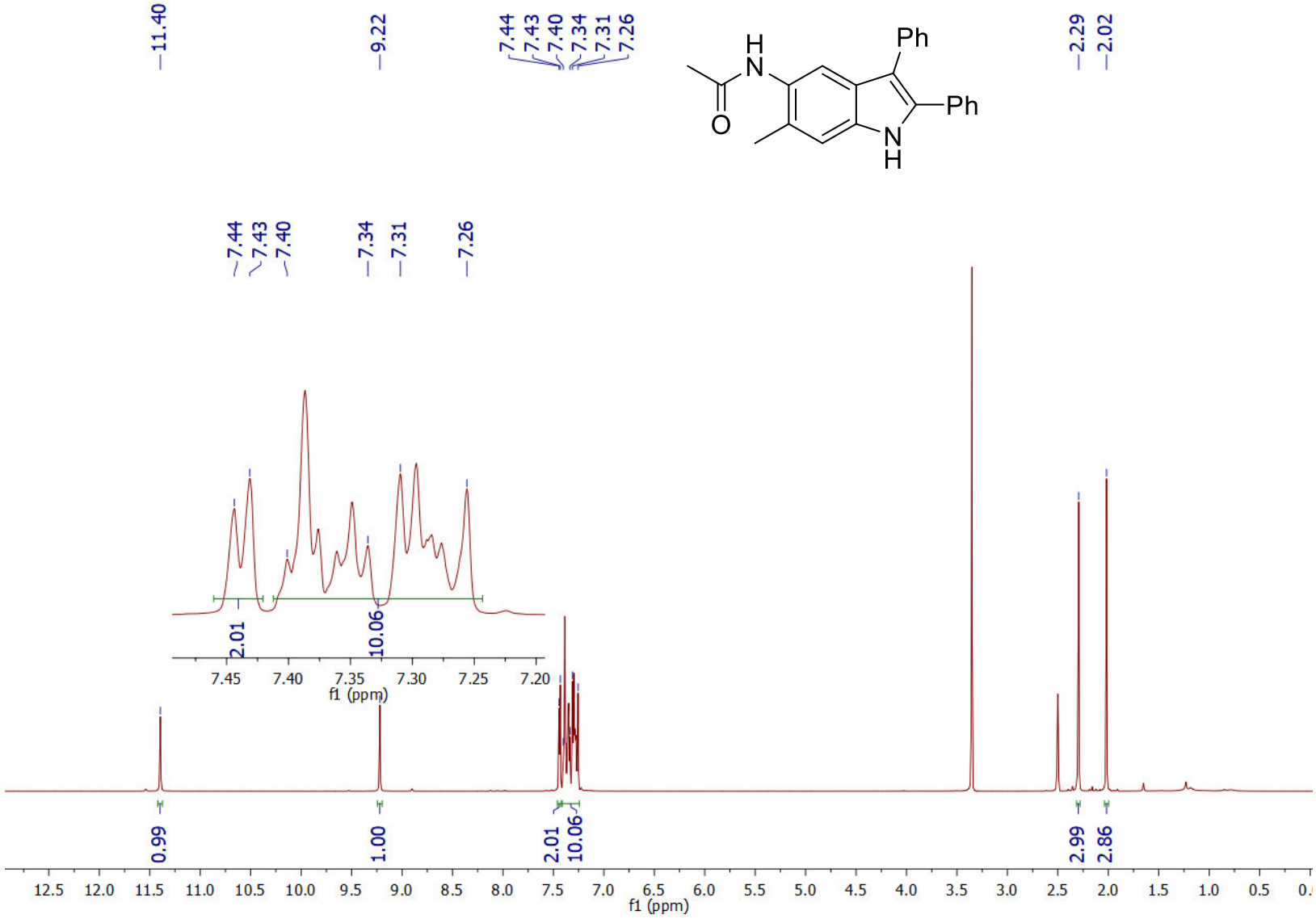
$^{1}$H-NMR (**3y**, 874)


8.22
8.03
7.79
7.78
7.56
7.52
7.51
7.45
7.44
7.43
7.36
7.32
7.31
7.28
7.25
7.23
4.02
Ph
Ph
N
H
1.06
0.90
2.94
4.02
4.03
1.02
0.91
f1 (ppm)
1.00
1.01
1.06
0.90
2.94
4.01
4.03
1.02
0.91
2.16
f1 (ppm)

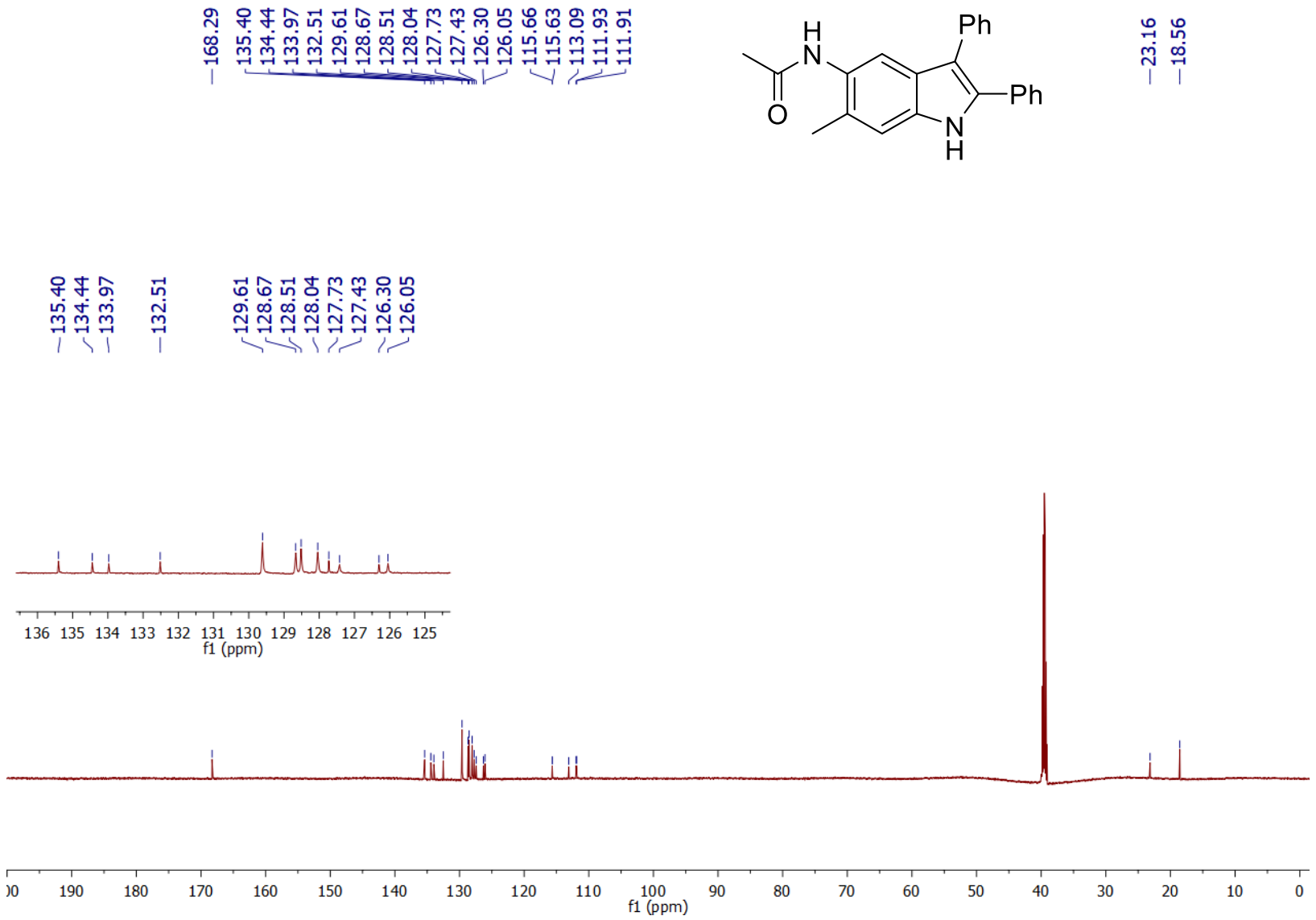
$^{13}$C-NMR (**3y,** 874)



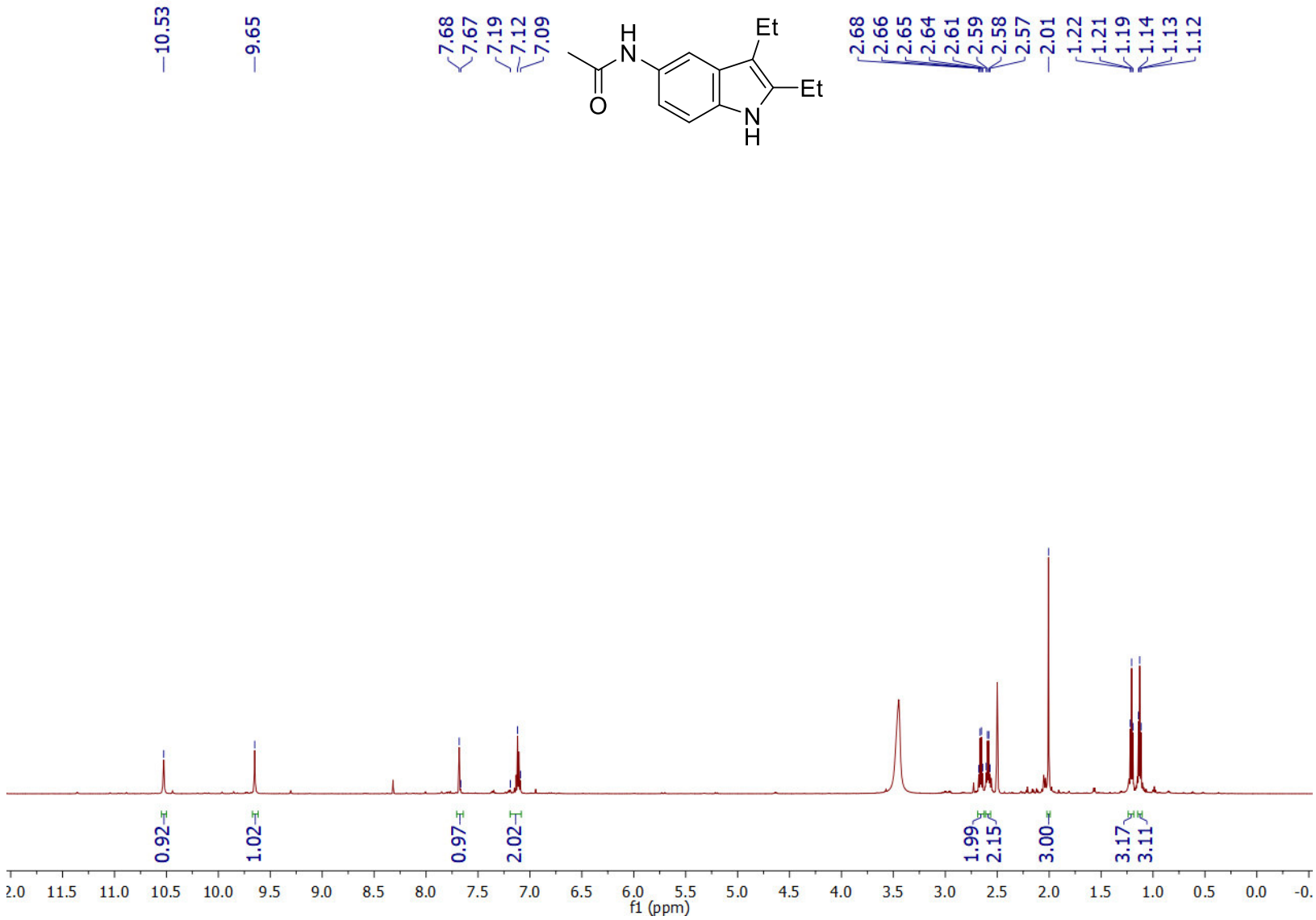
$^{1}$H-NMR (**3z**, 908)


11.40
9.22
7.44
7.43
7.40
7.34
7.31
7.26
2.29
2.02
H
N
O
Ph
Ph
N
H
0.99
1.00
2.01
10.06
2.99
2.86
f1 (ppm)
2.01
10.06
f1 (ppm)

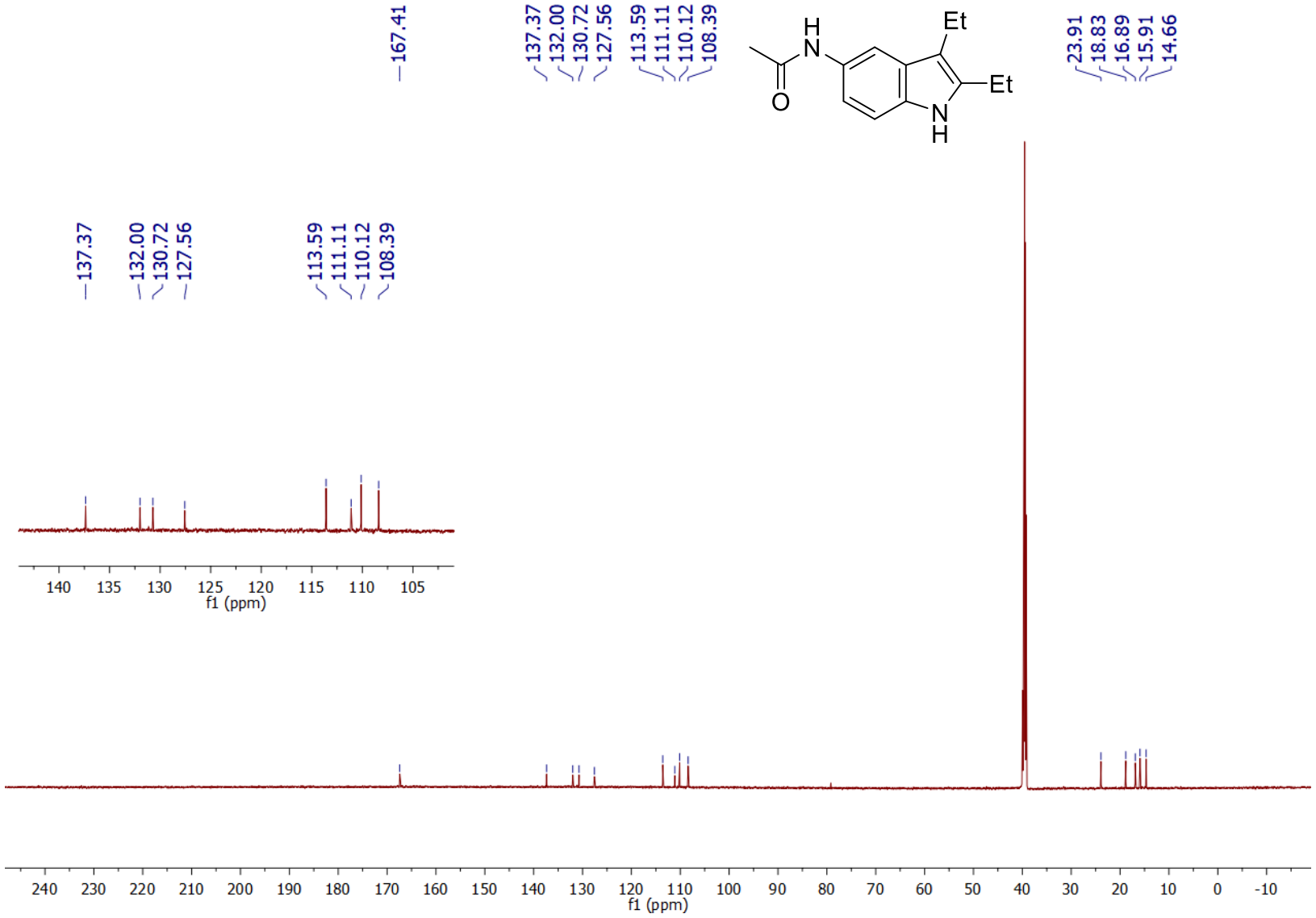
$^{13}$C-NMR (**3z,** 908)



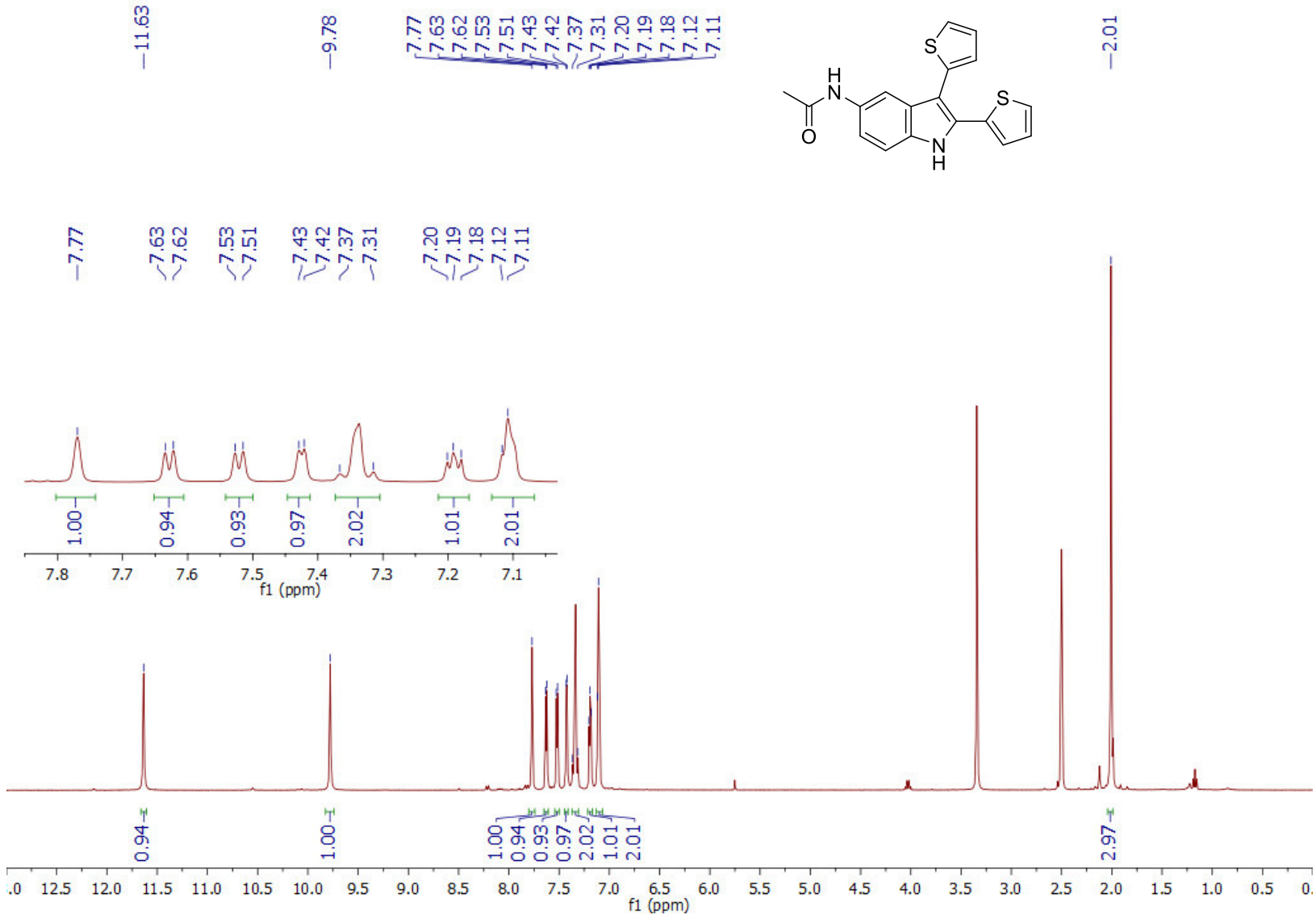
$^{1}$H-NMR (**3za,** 925)



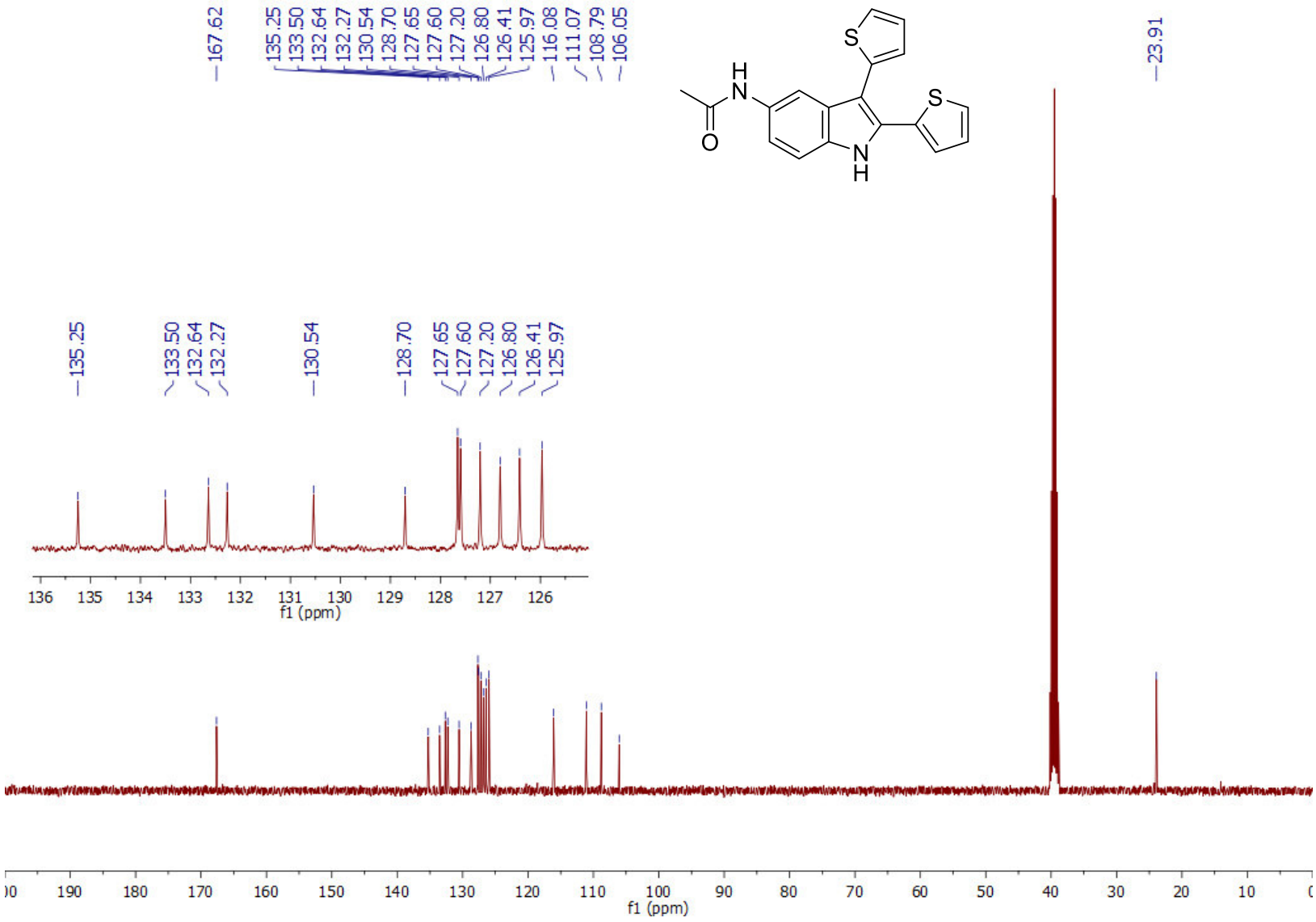
$^{13}$C-NMR (**3za**, 925)



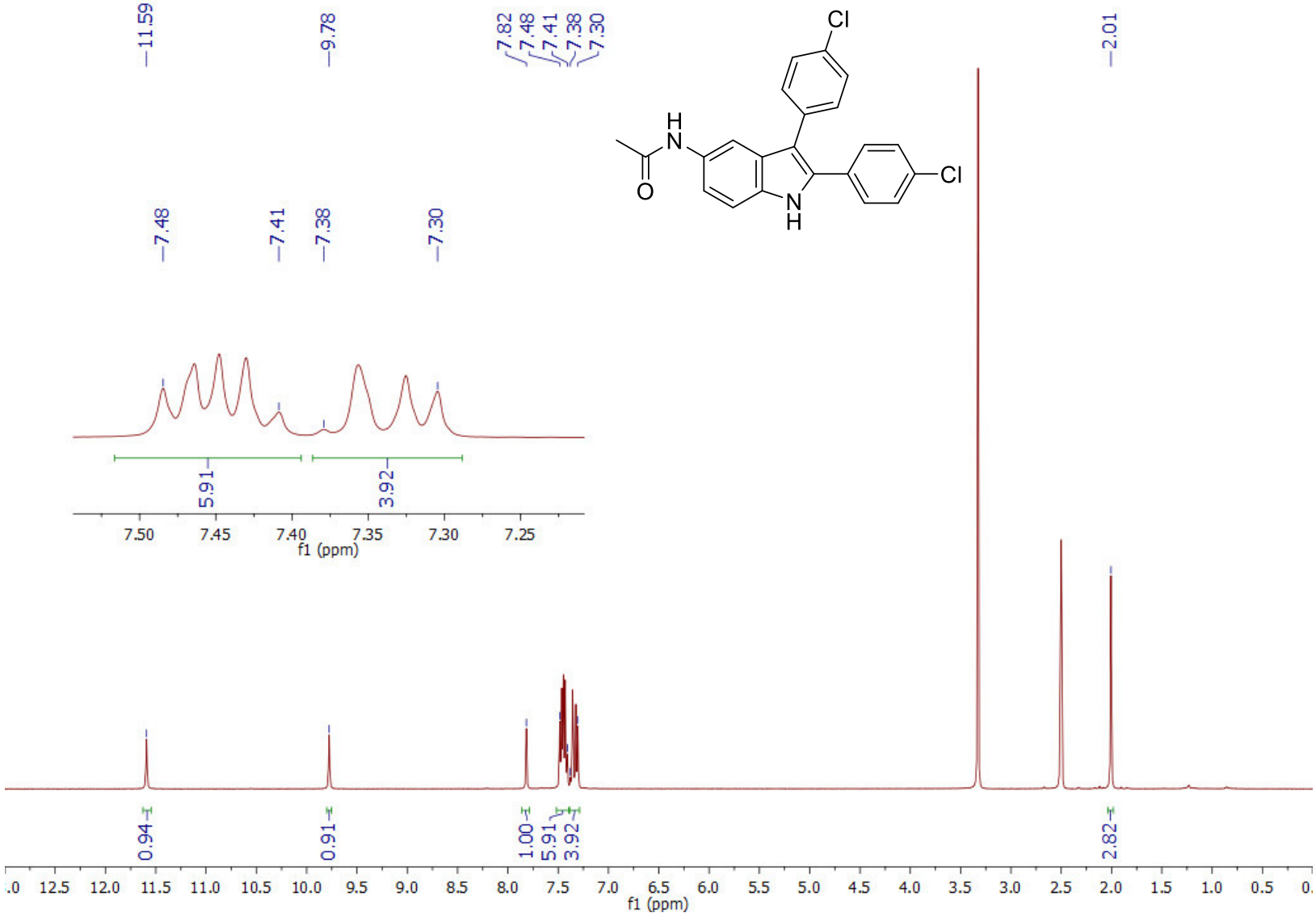
$^{1}$H-NMR (**3zb**, CHB-686)



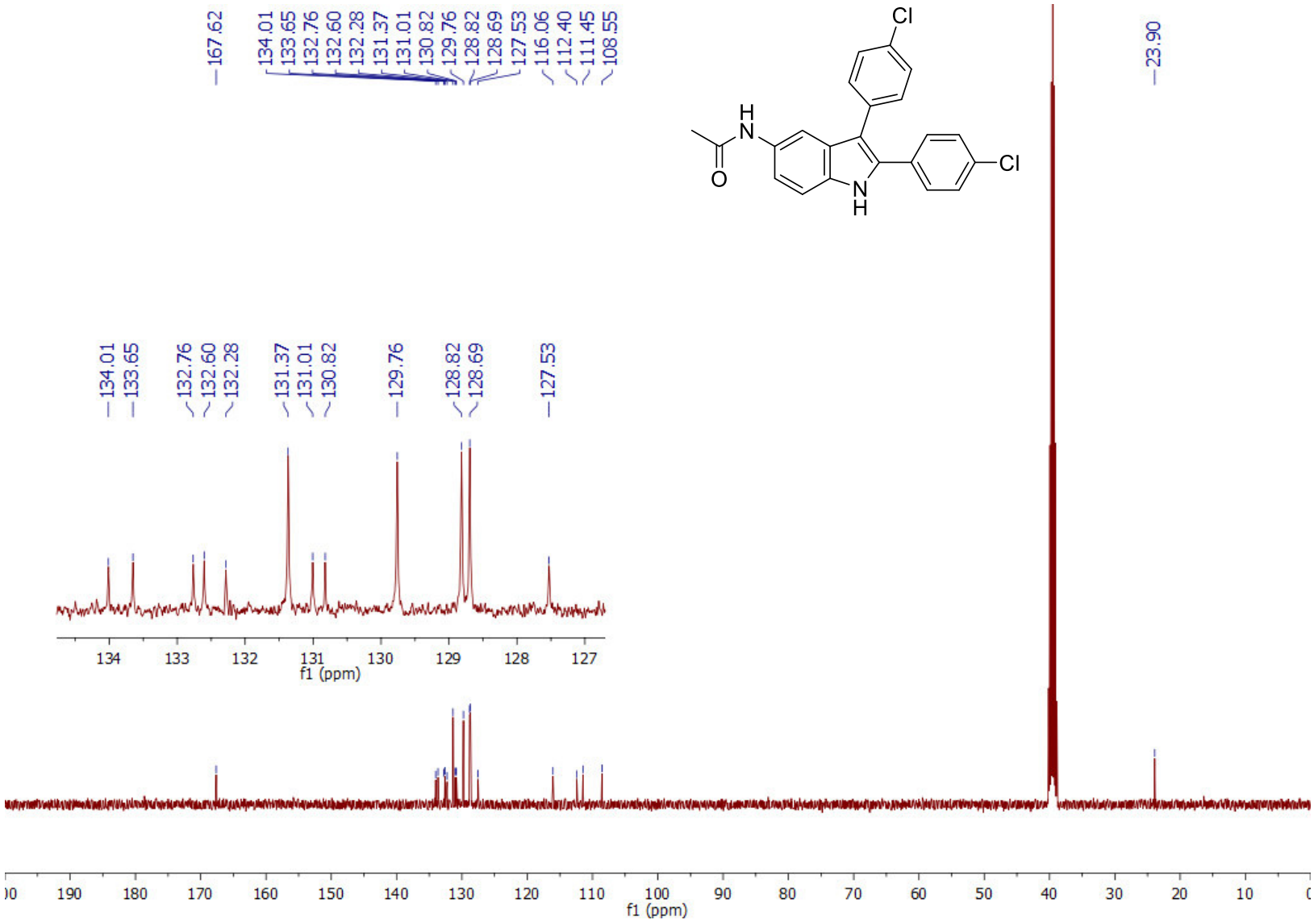
$^{13}$C-NMR (**3zb**, CHB-686)



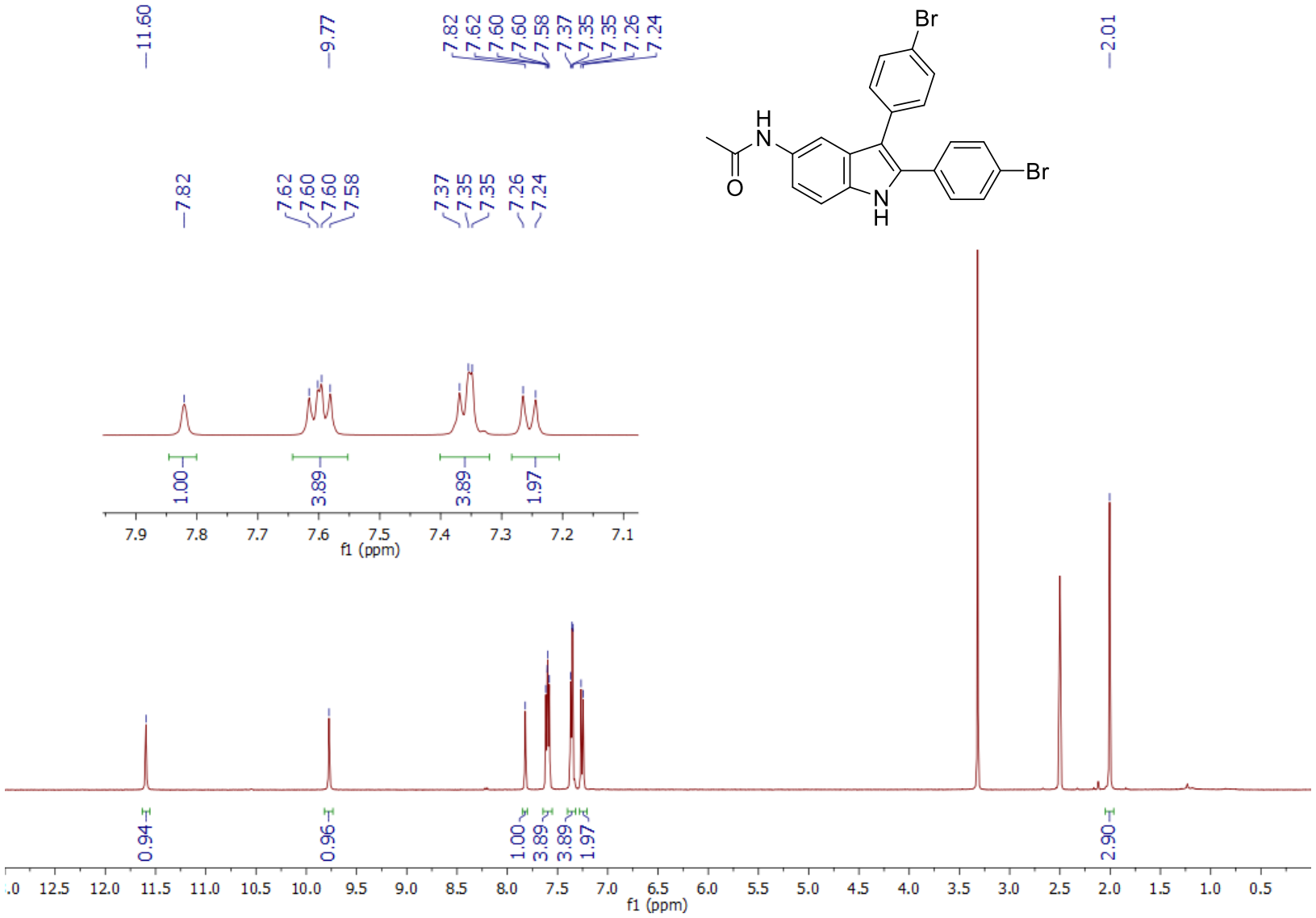
$^{1}$H-NMR (**3zc**, CHB-693)



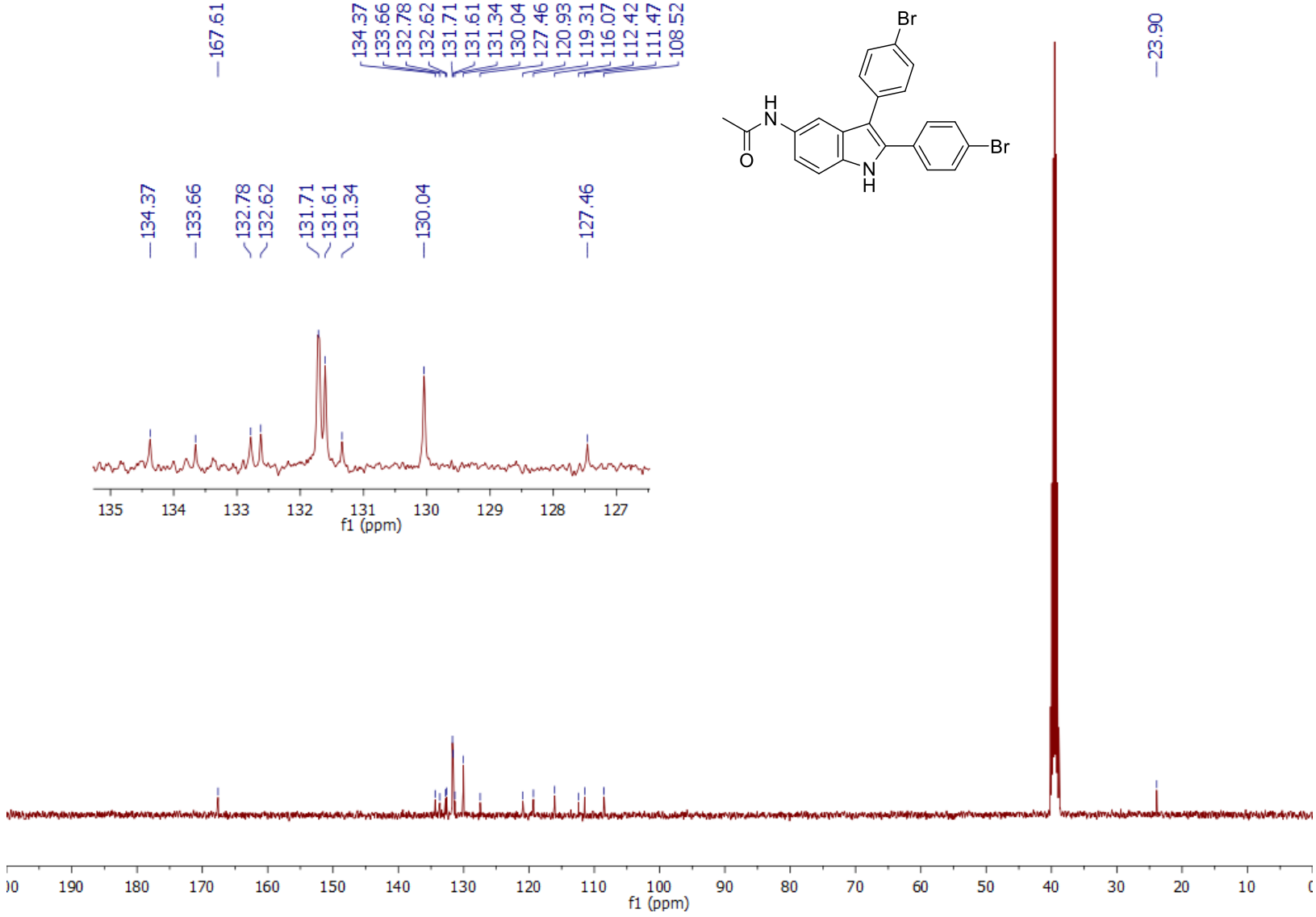
$^{13}$C-NMR (**3zc**, CHB-693)



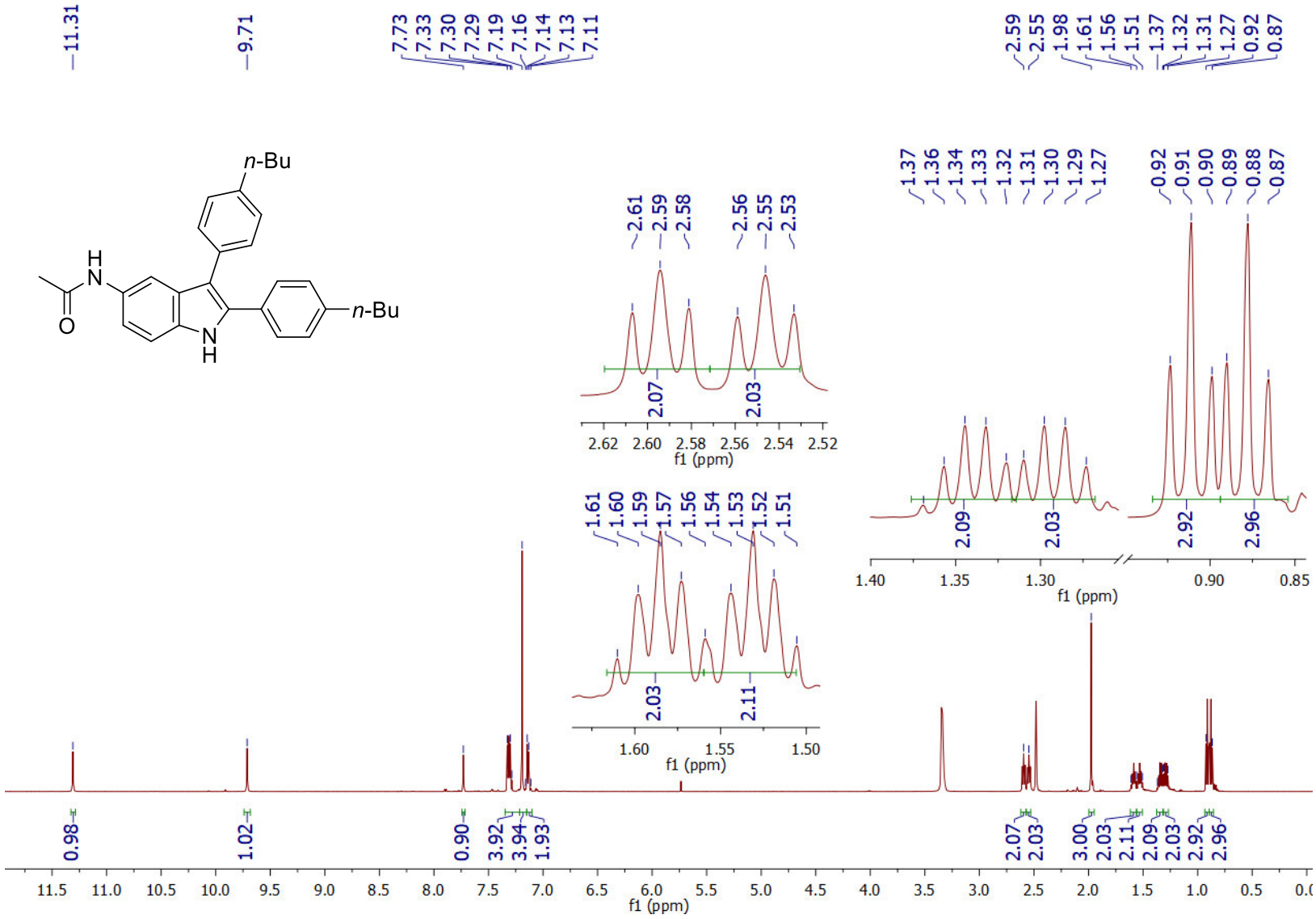
$^{1}$H-NMR (**3zd**, CHB-650)



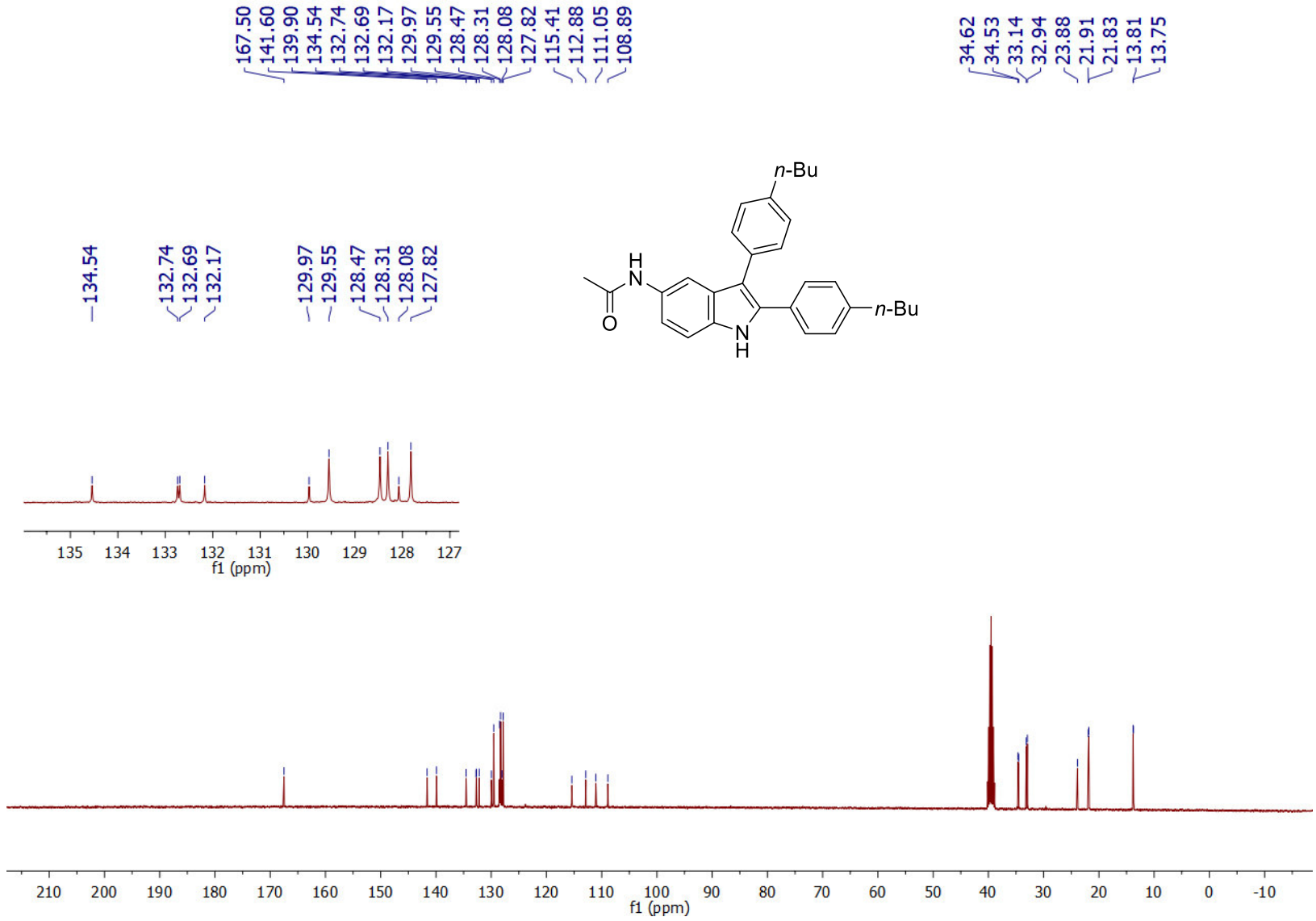
$^{13}$C-NMR (**3zd**, CHB-650)



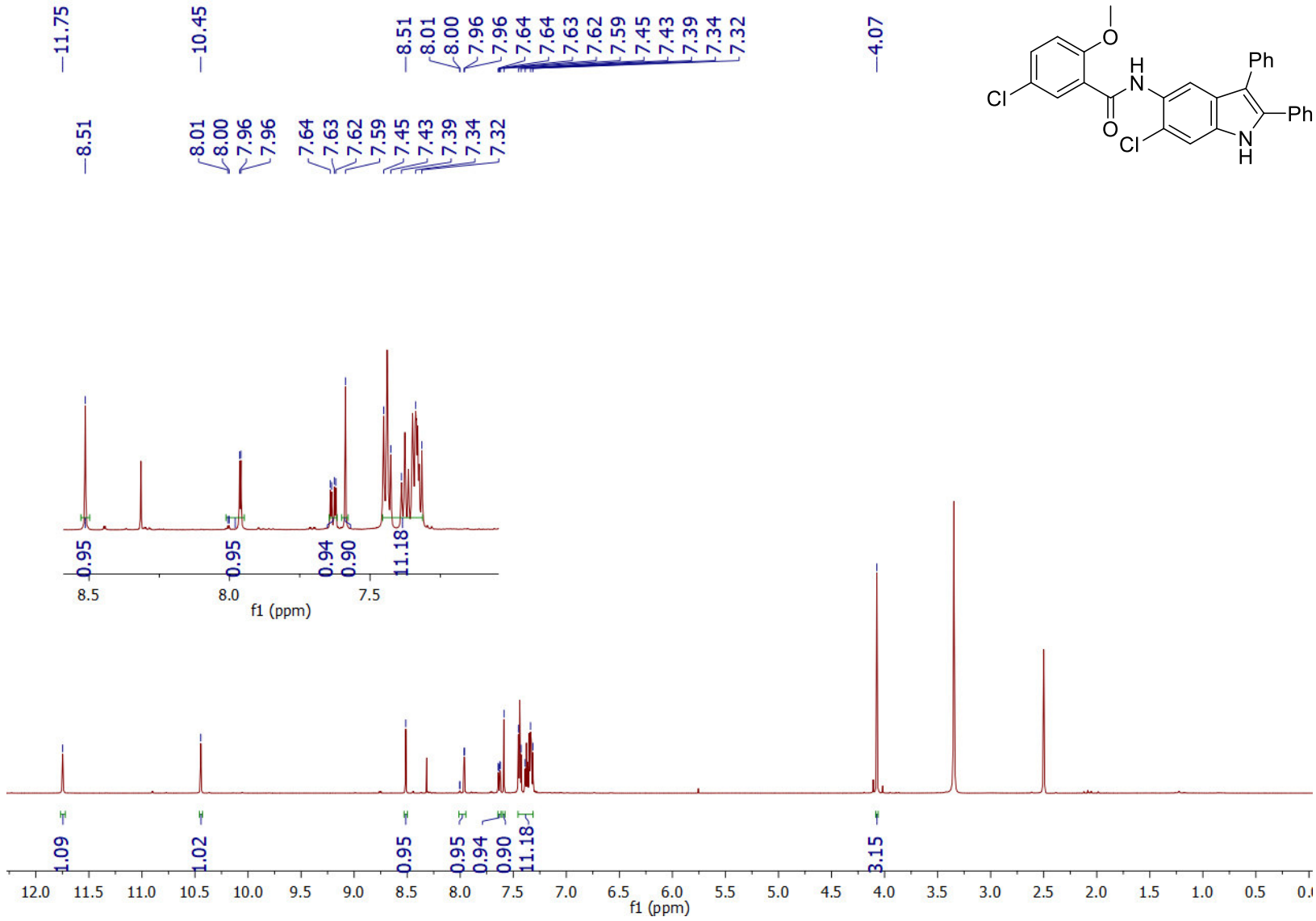
$^{1}$H-NMR (**3ze**, 928)



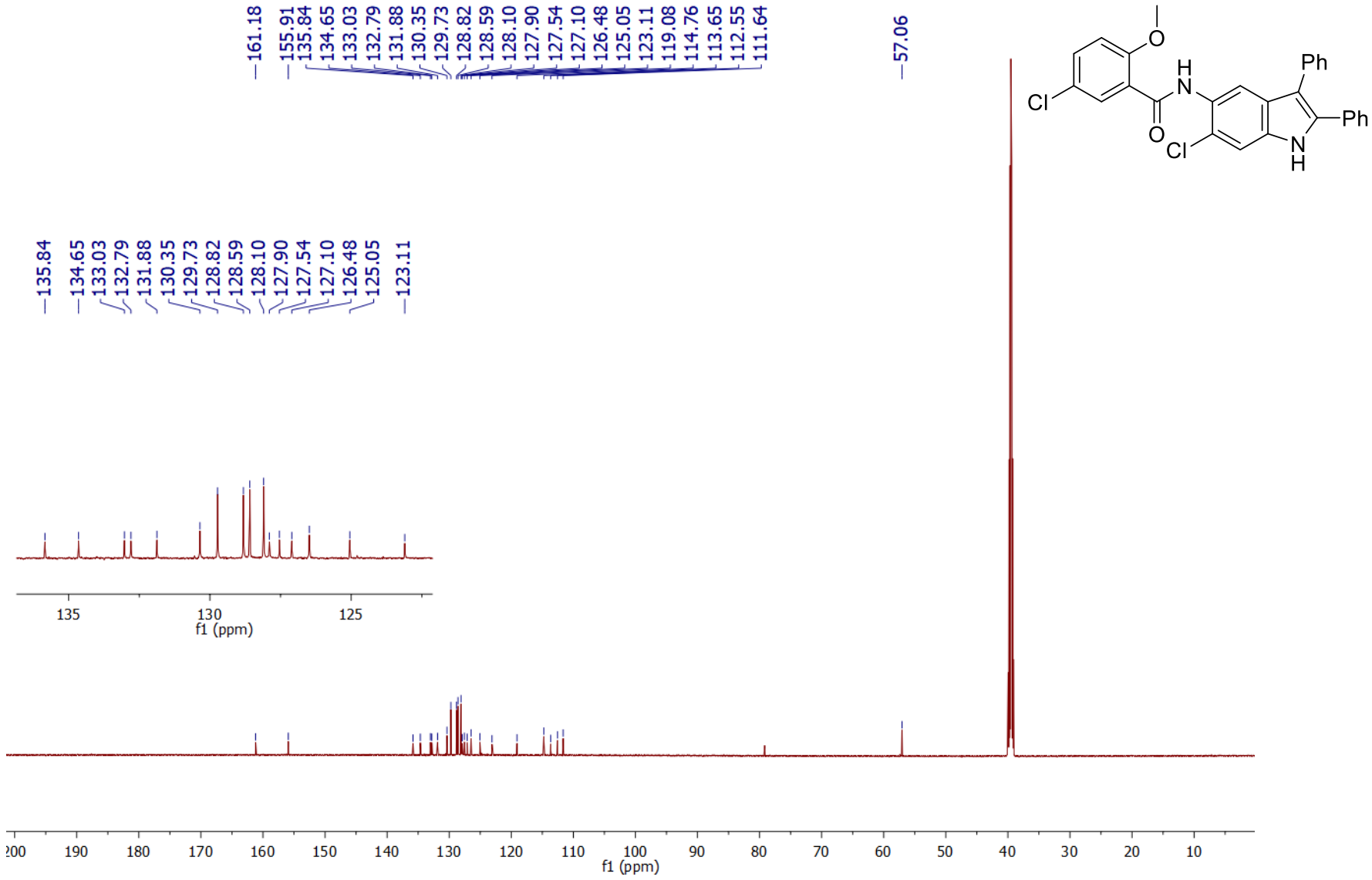
$^{13}$C-NMR (**3ze**, 928)



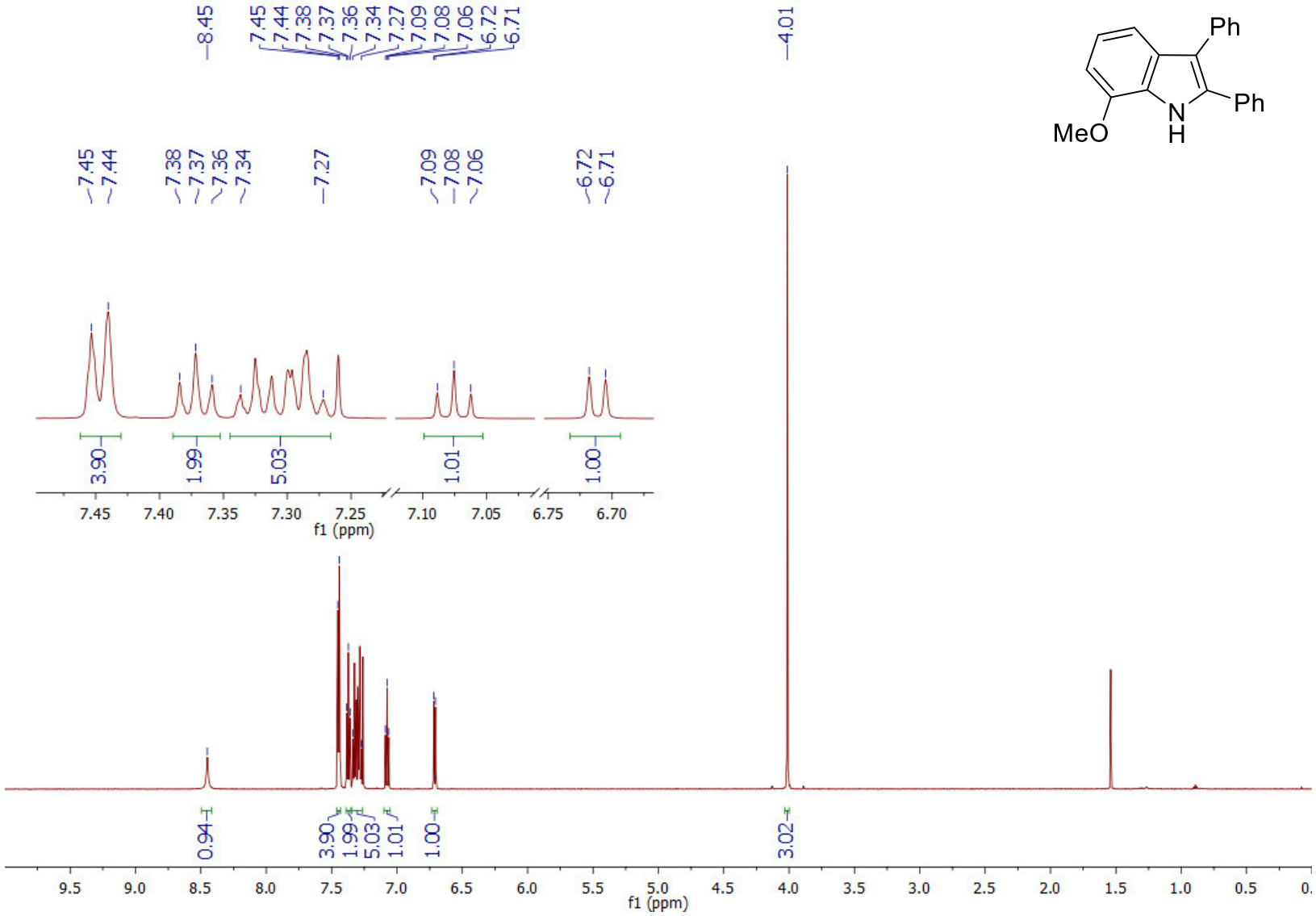
$^{1}$H-NMR (**3zf,** 921)



$^{13}$C-NMR (**3zf**, 912)



$^{1}$H-NMR (**3zg,** CHB-612)



$^{13}$C-NMR (**3zg,** CHB-612)