Electronic Supplementary Material (ESI) for Chemical Communications


# Schischkiniin support studies:

# Synthetic access to 1,1′-bisindoles

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# SUPPORTING INFORMATION

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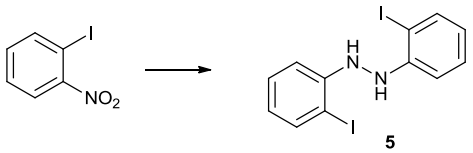
## Experimental

### General

All reactions were carried out in oven-dried or flame-dried glassware under a nitrogen atmosphere unless otherwise stated. Analytical thin layer chromatography was performed using 0.2 mm Kieselgel F254 (Merck) silica plates and compounds were visualized under 365 nm ultraviolet irradiation followed by staining with either alkaline permanganate or ethanolic vanillin solution. Infrared spectra were obtained using a Perkin Elmer spectrum One Fourier Transform Infrared spectrometer as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers ($cm^{-1}$). Optical rotations were measured using a Perkin-Elmer 341 polarimeter at $\lambda$ = 598 nm and are given in $10^{-1}$ deg $cm^2$ $g^{-1}$. Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded as indicated on either a Bruker DRX-400 spectrometer operating at 400 MHz for $^1H$ nuclei and 100 MHz for $^{13}C$ nuclei or on a Bruker Avance 300 spectrometer operating at 300 MHz and 75 MHz for $^1H$ and $^{13}C$ nuclei, respectively. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak recorded as $\delta$ 0.00 ppm in $CDCl_3$/ TMS solvent, or the residual chloroform ($\delta$ 7.26 ppm), DMSO ($\delta$ 2.50 ppm) or acetone ($\delta$ 2.05 ppm) peaks. The $^{13}C$ NMR values were referenced to the residual chloroform ($\delta$ 77.1 ppm), DMSO ($\delta$ 39.5 ppm) or acetone ($\delta$ 29.8 ppm) peaks. $^{13}C$ NMR values are reported as chemical shift $\delta$, multiplicity and assignment. $^1H$ NMR shift values are reported as chemical shift $\delta$, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet, p, pentet; m, multiplet), coupling constant (*J* in Hz) and assignment. Assignments are made with the aid of DEPT 135, COSY, NOESY and HSQC experiments. High resolution mass spectra were recorded on a VG-70SE mass spectrometer at a nominal accelerating voltage of 70 eV.

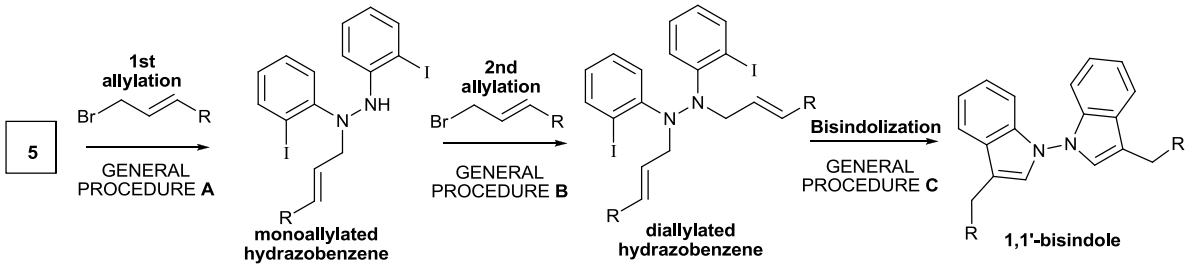
**1,2-Bis(2-iodophenyl)hydrazine (5)**




**5**

A mixture of 1-iodo-2-nitrobenzene (6 g, 24 mmol) and 50% aq. NaOH (1.5 mL) was heated at 60 °C until complete dissolution of the solid. Zinc dust (4.5 g, 68.8 mmol) was added in small portions such that the temperature remained at 70 – 80 °C. The sludge was diluted with water (30 mL) and 20% aq. NaOH (18 mL) followed by immediate addition of zinc (6 g, 91.8 mmol) in one portion. The mixture was heated at 80 °C for 30 min then cooled to room temperature and poured slowly onto 10% sulfuric acid (100 mL) at 0 °C. The mixture was stirred for 20 min then extracted with diethyl ether (3 × 150 mL). The combined organic extracts were washed with water (2 × 200 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on basic alumina eluting with *n*-hexanes: ethyl acetate (39:1) to give the *title compound* as an orange solid (2.83 g, 6.48 mmol, 54%); m.p. 123 - 127 °C; $\nu_{max}$ (neat)/$cm^{-1}$ 3357, 3298, 3064, 2926, 2581, 1935, 1897, 1859, 1775, 1588, 1494, 1477, 1445, 1432, 1290, 1230, 1157, 1102, 1043, 1019, 972, 930; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.68 (2 H, dd, *J* 7.6, 1.2, 2 × ArH), 7.20 (2 H, td, *J* 8.0, 1.6, 2 × ArH), 7.05 (2 H, br s, 2 × NH), 6.68 (2 H, dd, *J* 8.0, 1.6, 2 × ArH), 6.55 (2 H, td, *J* 7.6, 1.2, 2 × ArH); $\delta_c$ (100 MHz, DMSO-$d_6$) 144.8 (2 × C), 138.8 (2 × CH), 129.1 (2 × CH), 120.7 (2 × CH), 112.6 (2 × CH), 81.3 (2 × C); *m/z* (ESI) 435 (54%, $[M]^+$), 308 (100), 207 (45), 181 (80); HRMS (ESI, $[MNa]^+$) Found 458.8823. $[C_{12}H_{10}I_2N_2 + Na]^+$ requires 458.8826.

## Synthesis of 1,1′–bisindoles: General Procedures




### General Procedure A (1st allylation)

A solution of 1,2-bis(2-iodophenyl)hydrazine **5** (87.2 mg, 0.2 mmol) in THF (0.5 mL) was added dropwise to a freshly prepared solution of lithium diisopropylamide (0.25 mmol, 0.31 mL, 0.8 M in THF) at -78 °C. Allyl bromide (0.3 - 0.5 mmol, neat or else specified) was added immediately and the mixture was warmed to 0 °C for 10 min. The reaction was quenched with water (5 mL) and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The monoallylated hydrazobenzene was used in the next step without further purification.

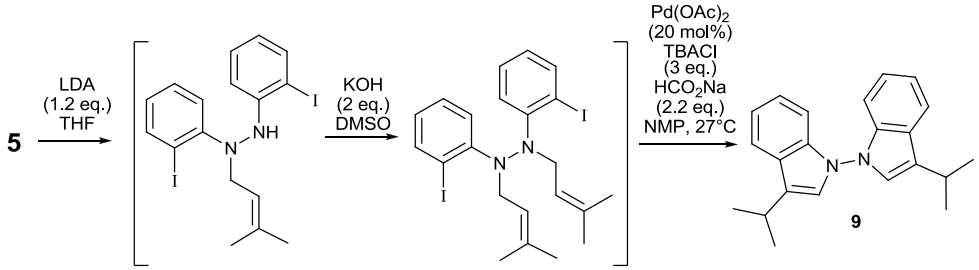
### General Procedure B (2nd allylation)

A solution of monoallylated hydrazobenzene (ca. 0.2 mmol) in anhydrous DMSO (1 mL) was added dropwise to a suspension of KOH (22.4 mg, 0.4 mmol) in anhydrous DMSO (1 mL). The mixture was stirred at r.t. for 15 min and allyl bromide (0.1 - 0.5 mmol) was added. The reaction mixture was stirred at r.t. for another 20 – 30 min and quenched with saturated aqueous $NH_4Cl$ (10 mL). The aqueous solution was extracted with diethyl ether (2 × 10 mL) and the combined organic extracts were washed with water (15 mL), brine (15 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The diallylated hydrazobenzene was used in the next step without further purification.

### General Procedure C (Bisindolization)

In a 4-dram vial equipped with a stirring bar and Teflon-lined screwcap, diallylated hydrazobenzene (ca. 0.2 mmol) in *N*-methyl-2-pyrrolidone (3 mL) was purged with nitrogen for 30 min. Sodium formate (29.9 mg, 0.44 mmol), tetrabutylammonium chloride monohydrate (166.7 mg, 0.6 mmol) and palladium acetate (8.98 mg, 0.04 mmol, 20 mol %) were added sequentially to the solution. The reaction mixture was stirred at 27 °C for 16 – 36 h and quenched with saturated aqueous $NH_4Cl$ (10 mL). The slurry was extracted with diethyl ether (2 × 20 mL). The combined organic extracts were washed with water (25 mL) and brine (25 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified with flash-chromatography on silica gel eluting with *n*-hexanes: dichloromethane (9:1) affording the desired 1,1′-bisindole. The overall yield is calculated over the three general procedures **A**-**C** from 1,2-bis(2-iodophenyl)hydrazine (**5**).

**3,3'-Diisopropyl-1,1'-bisindole (9)**

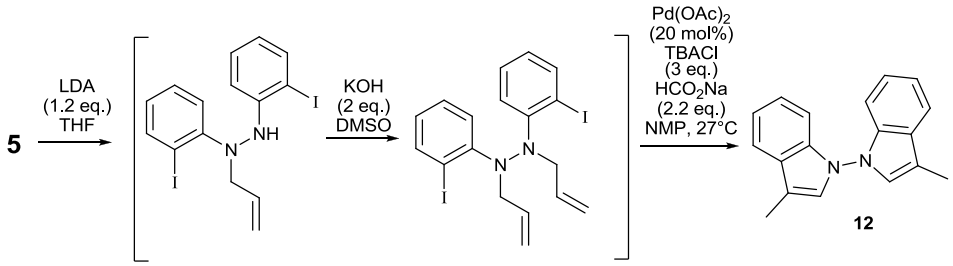



According to general procedure **A**, using 3,3-dimethylallyl bromide (44.7 mg, 0.039 mL, 0.3 mmol), the monoallylated hydrazobenzene **1,2-bis(2-iodophenyl)-1-(3-methylbut-2-en-1-yl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 3058, 2920, 2852, 1584, 1488, 1451, 1007, 748; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.85 (1 H, d, *J* 7.6, ArH), 7.61 (1 H, d, *J* 8.4, ArH), 7.39 – 7.37 (2 H, m, 2 × ArH), 7.19 – 7.17 (2 H, m, 2 × ArH), 6.90 – 6.87 (1 H, m, ArH), 6.57 (1 H, br s, NH), 6.50 – 6.46 (1 H, m, ArH), 5.27 (1 H, t, *J* 7.2, CH), 3.82 (2 H, d, *J* 6.8, $CH_2$); 1.67 (3 H, s, Me), 1.58 (3 H, s, Me); $\delta_c$ (100 MHz, DMSO-$d_6$) 151.5 (C), 146.5 (C), 139.4 (CH), 138.5 (CH), 137.5 (C), 129.0 (CH), 128.8 (CH), 126.4 (CH), 122.6 (CH), 120.4 (CH), 118.3 (CH), 114.3 (CH), 95.6 (C), 81.4 (C), 54.4 ($CH_2$), 25.7 (Me), 18.0 (Me); *m/z* (ESI) 504 (50%, $[MH]^+$), 448 (100), 378 (85), 309 (40), 286 (25); HRMS (ESI, $[MH]^+$) Found 504.9625. $[C_{17}H_{18}I_2N_2 + H]^+$ requires 504.9632.

According to general procedure **B**, using 3,3-dimethylallyl bromide (44.7 mg, 0.039 mL, 0.3 mmol), the diallylated hydrazobenzene **1,2-bis(2-iodophenyl)-1,2-bis(3-methylbut-2-en-1-yl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 3392, 2919, 2853, 1594, 1498, 1450, 1308, 1006, 743; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.77 (2 H, dd, *J* 7.6, 1.2, 2 × ArH), 7.29 (2 H, td, *J* 8.4, 1.2, 2 × ArH), 7.05 (2 H, dd, *J* 7.6, 0.8, 2 × ArH), 6.84 (2 H, td, *J* 7.6, 1.2, 2 × ArH), 5.02 (2 H, t, *J* 6.4, 2 × CH), 4.05 (4 H, d, *J* 6.0, 2 × $CH_2$), 1.56 (6 H, s, 2 × Me), 1.51 (6 H, s, 2 × Me); $\delta_c$ (100 MHz, DMSO-$d_6$) 148.2 (2 × C), 139.5 (2 × CH), 133.7 (2 × CH), 127.7 (2 × CH), 126.6 (2 × CH), 125.2 (2 × CH), 120.6 (2 × CH), 101.5 (2 × C), 48.7 (2 × $CH_2$), 25.5 (2 × Me), 18.0 (2 × Me); *m/z* (ESI) 573 (30%, $[MH]^+$), 503 (90), 446 (70), 378 (90), 309 (100), 250 (15); HRMS (ESI, $[MH]^+$) Found 573.0245. $[C_{22}H_{26}I_2N_2 + H]^+$ requires 573.0258.

According to general procedure **C**, 3,3'-diisopropyl-1,1'-bisindole **9** was obtained (19 mg, 0.06 mmol, 30% from **5**) as a colourless solid; m.p. 88 – 92 °C; $\nu_{max}$ (neat)/cm$^{-1}$ 2959, 2923, 2868, 1452, 1221, 1137, 737; $\delta_H$ (400 MHz, $CDCl_3$) 7.73 (2 H, dd, *J* 6.8, 1.6, 2 × ArH), 7.17 (4 H, pd, *J* 7.2, 1.2, 4 × ArH), 7.05 (2 H, br s, H – 2, H – 2′), 6.89 (2 H, dd, *J* 7.2, 1.6, 2 × ArH), 3.26 (2 H, pd, *J* 7.2, 0.8, 2 × CH), 1.41 (12 H, dd, *J* 6.8, 1.6, 4 × Me); $\delta_c$ (100 MHz, $CDCl_3$) 137.7 (2 × C), 125.6 (2 × C), 123.6 (2 × C), 123.5 (2 × CH), 123.1 (2 × CH), 120.5 (2 × CH), 119.9 (2 × CH), 109.3 (2 × CH), 25.6 (2 × CH), 23.4 (2 × Me), 23.2 (2 × Me); *m/z* (ESI) 317 (20%, $[MH]^+$), 158 (100); HRMS (ESI, $[MH]^+$) Found 317.2014. $[C_{22}H_{24}N_2 + H]^+$ requires 317.2012.

**3,3'-Dimethyl-1,1'-bisindole (12)**

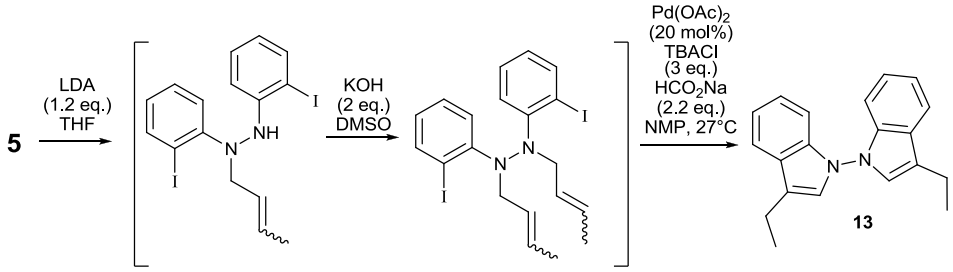



According to general procedure **A**, using allyl bromide (60.5 mg, 0.043 mL, 0.5 mmol), the monoallylated hydrazobenzene **1-allyl-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 2920, 2850, 1584, 1491, 1450, 1007, 931, 742; $\delta_H$ (400 MHz, Acetone-$d_6$) 7.89 (1 H, dd, *J* 7.6, 1.2, ArH), 7.62 (1 H, dd, *J* 8.0, 1.6, ArH), 7.46 (1 H, dd, *J* 8.0, 1.2, ArH), 7.38 (1 H, td, *J* 6.8, 1.2, ArH), 7.32 (1 H, dd, *J* 8.0, 1.6, ArH), 7.22 (1 H, td, *J* 8.4, 1.2, ArH), 6.90 (1 H, td, *J* 7.2, 1.6, ArH), 6.52 (1 H, td, *J* 8.0, 1.6, ArH), 6.36 (1 H, br s, NH), 6.00 – 5.93 (1 H, m, allyl CH), 5.35 (1 H, dq, *J* 16.0, 1.6, allyl $CH_2$), 5.27 – 5.24 (1 H, m, allyl $CH_2$), 3.89 (2 H, dd, *J* 4.0, 0.8, $CH_2$); $\delta_c$ (100 MHz, Acetone-$d_6$) 152.4 (C), 147.3 (C), 140.7 (CH), 139.5 (CH), 133.2(CH), 130.0 (CH), 129.9 (CH), 127.4 (CH), 123.4 (CH), 121.6 (CH), 120.8 ($CH_2$), 116.0 (CH), 95.4 (C), 81.8 (C), 61.2 ($CH_2$); *m/z* (ESI) 498 (25%, $[MNa]^+$), 372 (24), 349 (100), 280 (80), 222 (10); HRMS (ESI, $[MNa]^+$) Found 498.9148. $[C_{15}H_{14}I_2N_2 + Na]^+$ requires 498.9139.

According to general procedure **B**, using allyl bromide (60.5 mg, 0.043 mL, 0.5 mmol), the diallylated hydrazobenzene **1,2-diallyl-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 2921, 1584, 1495, 1458, 1430, 1209, 1087, 968, 745; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.77 (2 H, dd, *J* 7.9, 1.5, 2 × ArH), 7.28 (2 H, td, *J* 8.0, 1.5, 2 × ArH), 7.08 (2 H, dd, *J* 8.0, 1.4, 2 × ArH), 6.86 (2 H, td, *J* 7.6, 1.5, 2 × ArH), 5.77 – 5.71 (2 H, m, 2 × allyl CH), 5.10 (2 H, dd, *J* 17.4, 1.8, allyl $CH_2$), 4.94 (2 H, dd, *J* 10.4, 1.8, allyl $CH_2$), 4.16 (4 H, d, *J* 6.1, 2 × $CH_2$); $\delta_c$ (100 MHz, DMSO-$d_6$) 147.3 (2 × C), 139.6 (2 × CH), 134.5 (2 × CH), 127.8 (2 × CH), 127.0 (2 × CH), 125.7 (2 × CH), 117.9 (2 × $CH_2$), 102.2 (2 × C), 53.5 (2 × $CH_2$); *m/z* (ESI) 515 (40%, $[M]^+$), 474 (100), 348 (48), 306 (41), 221 (56); HRMS (ESI, $[M]^+$) Found 515.9562. $[C_{18}H_{18}I_2N_2]^+$ requires 515.9554.

According to general procedure **C**, 3,3'-dimethyl-1,1'-bisindole **12** was obtained (32.8 mg, 0.13 mmol, 63% from **5**) as a colourless solid; m.p. 123 – 126 °C; $\nu_{max}$ (neat)/cm$^{-1}$ 2914, 2856, 1582, 1448, 1223, 1118, 735; $\delta_H$ (400 MHz, $CDCl_3$) 7.65 (2 H, dd, *J* 7.2, 0.2, 2 × ArH), 7.22 - 7.14 (4 H, m, 4 × ArH), 7.05 (2 H, d, *J* 1.2, H – 2, H – 2′), 6.87 (2 H, dd, *J* 8.0, 1.2, 2 × ArH), 2.39 (6 H, d, *J* 0.8, 2 × Me); $\delta_c$ (100 MHz, $CDCl_3$) 137.5 (2 × C), 127.0 (2 × C), 125.7 (2 × CH), 123.2 (2 × CH), 120.6 (2 × CH), 119.3 (2 × CH), 111.5 (2 × C), 109.1 (2 × CH), 9.73 (2 × Me); *m/z* (ESI) 261 (50%, $[MH]^+$), 130 (100); HRMS (ESI, $[MH]^+$) Found 261.1388. $[C_{18}H_{16}N_2 + H]^+$ requires 261.1386.

**3,3'-Diethyl-1,1'-bisindole (13)**



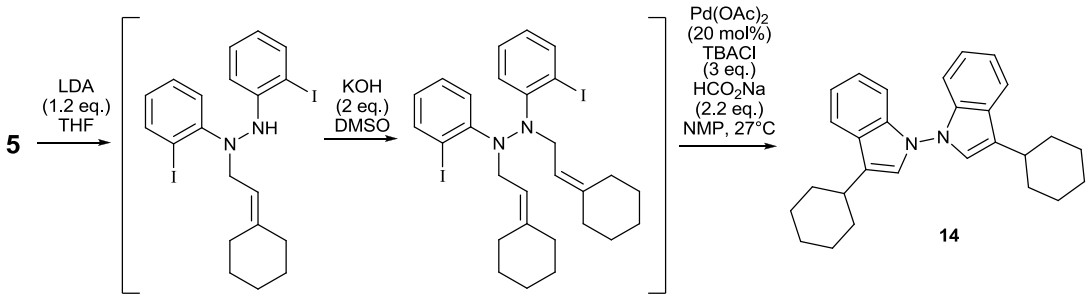

According to general procedure **A** using crotyl bromide (40.5 mg, 0.036 mL, 0.3 mmol), the monoallylated hydrazobenzene **1-(but-2-en-1-yl)-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil and a 3:1 mixture of *E*:*Z* isomers; $\nu_{max}$ (neat)/cm$^{-1}$ 2918, 1582, 1490, 1461, 1450, 1433, 1201, 1088, 965, 747; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.85 (1 H, dd, *J* 8.0, 0.8, ArH), 7.60 (1 H, dd, *J* 7.6, 1.2, ArH), 7.40 - 7.38 (2 H, m, 2 × ArH), 7.20 – 7.15 (2 H, m, 2 × ArH), 6.91 – 6.87 (1 H, m, ArH), 6.71 + 6.60 (1 H, 2 × br s, NH), 6.51 – 6.47 (1 H, m, ArH), 5.73 – 5.70 (1 H, m, CH), 5.55 – 5.50 (1 H, m, CH), 3.91 + 3.76 (2 H, 2 × d, *J* 6.4, *J* 6.8, $CH_2$), 1.65 – 1.63 (3 H, m, Me); $\delta_c$ (100 MHz, DMSO-$d_6$) 151.5 (C), 146.6 (C), 139.4 (CH), 138.5 (CH), 131.1 (CH), 128.93 (CH), 128.91 (CH), 126.51 + 126.46 (CH), 125.0 + 124.8 (CH), 122.7 + 122.6 (CH), 120.4 + 120.3 (CH), 114.6 + 114.2 (CH), 95.5 (C), 81.3 + 81.0 (C), 58.9 + 53.5 ($CH_2$), 17.7 + 13.1 (Me); *m/z* (ESI) 490 (35%, [MH]$^+$), 364 (100), 320 (40), 273 (41), 182 (37); HRMS (ESI, [MH]$^+$) Found 490.9470. [$C_{16}H_{16}I_2N_2$ + H]$^+$ requires 490.9476.

According to general procedure **B**, using crotyl bromide (40.5 mg, 0.036 mL, 0.3 mmol), the diallylated hydrazobenzene **1,2-di(but-2-en-1-yl)-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil and a inconsequential mixture of alkene regioisomers; $\nu_{max}$ (neat)/cm$^{-1}$ 2918, 2852, 1590, 1493, 1456, 1308, 1005, 963, 745; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.77 (2 H, dt, *J* 7.6, 1.6, 2 × ArH), 7.30 – 7.26 (2 H, m, 2 × ArH), 7.07 (2 H, dd, *J* 8.0, 1.2, 2 × ArH), 6.87 – 6.80 (2 H, m, 2 × ArH), 5.55 – 5.49 (2 H, m, CH), 5.39 – 5.34 (2 H, m, CH), 4.14 + 4.07 (4 H, 2 × d, *J* 5.8, *J* 6.0, 2 × $CH_2$), 1.56 + 1.47 (6 H, 2 × dd, *J* 6.4, 1.2, *J* 6.4, 1.2, 2 × Me); $\delta_c$ (100 MHz, DMSO-$d_6$) 148.3 (2 × C), 140.0 + 139.7 (2 × CH), 128.1 (2 × CH), 127.8 + 127.7 (2 × CH), 127.3 (2 × CH), 126.4 + 126.3 (2 × CH), 125.2 (2 × CH), 100.8 (2 × C), 52.5 + 47.6 (2 × $CH_2$), 17.6 + 13.1 (2 × Me); *m/z* (ESI) 544 (42%, [MH]$^+$), 489 (100), 418 (83), 363 (30), 271 (30); HRMS (ESI, [MH]$^+$) Found 544.9924. [$C_{20}H_{22}I_2N_2$ + H]$^+$ requires 544.9945.

According to general procedure **C**, 3,3'-diethyl-1,1'-bisindole **13** was obtained (22.5 mg, 0.078 mmol, 39% from **5**) as colourless solid; m.p. 75 - 79 °C; $\nu_{max}$ (neat)/cm$^{-1}$ 2963, 2851, 1451, 1218, 1136, 737; $\delta_H$ (400 MHz, $CDCl_3$) 7.69 - 7.67 (2 H, m, 2 × ArH), 7.17 (4 H, pd, *J* 7.0, 1.3, 4 × ArH), 7.07 (2 H, t, *J* 1.0, H – 2, H – 2′), 6.90 – 6.87 (2 H, m, 2 × ArH), 2.85 (4 H, qd, *J* 10.0, 1.6, 2 × $CH_2$), 1.38 (6 H, t, *J* 10.0, 2 × Me); $\delta_c$ (100 MHz, $CDCl_3$) 137.6 (2 × C), 126.2 (2 × C), 124.6 (2 × CH), 123.2 (2 × CH), 120.5 (2 × CH), 119.4

(2 × CH), 118.5 (2 × C), 109.2 (2 × CH), 18.4 (2 × $CH_2$), 14.2 (2 × Me); *m/z* (ESI) 288 (60%, $[M]^+$), 144 (100), 130 (55), 115 (30); HRMS (ESI, $[MH]^+$) Found 289.1708. $[C_{20}H_{20}N_2 + H]^+$ requires 289.1699.

**3,3'-Dicyclohexyl-1,1'-bisindole (14)**

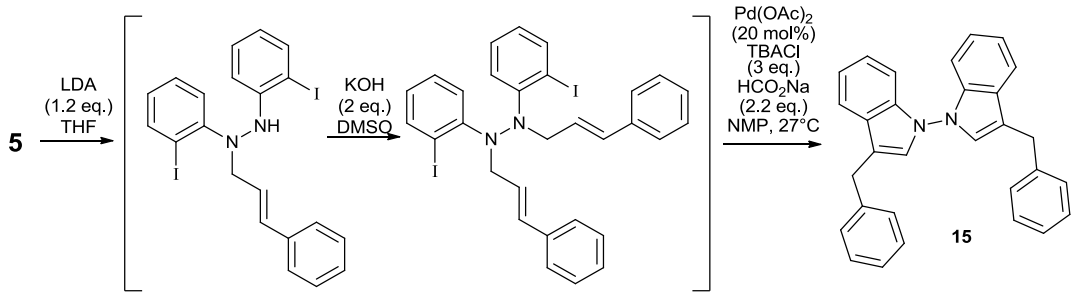



According to general procedure **A** using (2-bromoethylidene)cyclohexane[1,2] (56.7 mg, 0.3 mmol) the monoallylated hydrazobenzene **1-(2-cyclohexylideneethyl)-1,2-bis(2-iodophenyl)hydrazine** was obtained as an unstable crimson oil which was used immediately in the next step.

According to general procedure **B** using (2-bromoethylidene)cyclohexane (24.6 mg, 0.13 mL, 0.13 mmol, 1 M in DMSO), the diallylated hydrazobenzene **1,2-bis(2-cyclohexylideneethyl)-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3055, 2925, 2850, 1953, 1713, 1638, 1585, 1433, 1313, 1279, 1057, 847; $\delta_H$ (400 MHz, Acetone-$d_6$) 7.81 (2 H, dd, *J* 7.6, 1.2, 2 × ArH), 7.30 (2 H, td, *J* 7.2, 1.6, 2 × ArH), 7.18 (2 H, dd, *J* 8.0, 1.6, 2 × ArH), 6.87 (2 H, td, *J* 8.0, 1.6, 2 × ArH), 5.15 (2 H, t, *J* 6.8, 2 × CH), 4.13 (4 H, d, *J* 6.8, 2 × $CH_2$), 2.10 – 2.06 (4 H, m, 2 × $CH_2$), 1.94 – 1.91 (4 H, m, 2 × $CH_2$), 1.46 – 1.42 (4 H, m, 2 × $CH_2$), 1.38 – 1.35 (4 H, m, 2 × $CH_2$), 1.31 – 1.29 (4 H, m, 2 × $CH_2$); $\delta_c$ (100 MHz, Acetone-$d_6$) 149.5 (2 × C), 143.0 (2 × C), 140.6 (2 × CH), 128.7 (2 × CH), 127.7 (2 × CH), 127.2 (2 × CH), 118.3 (2 × CH), 103.4 (2 × C), 49.7 (2 × $CH_2$), 37.8 (2 × $CH_2$), 29.7 (2 × $CH_2$), 29.0 (2 × $CH_2$), 28.2 (2 × $CH_2$), 27.4 (2 × $CH_2$); *m/z* (ESI) 651 (100%, $[MH]^+$), 542 (8), 434 (20), 326 (28); HRMS (ESI, $[MH]^+$) Found 651.0736. $[C_{28}H_{34}I_2N_2 + H]^+$ requires 651.0728.

According to general procedure **C**, 3,3'-dicyclohexyl-1,1'-bisindole **14** was obtained (23 mg, 0.058 mmol, 29% from **5**) as a colourless solid; m.p. 139 – 143 °C; $\nu_{max}$ (neat)/$cm^{-1}$ 2922, 2850, 1714, 1449, 1236, 1134, 735; $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (2 H, dd, *J* 6.4, 1.2, 2 × ArH), 7.16 (4 H, pd, *J* 8.4, 1.2, 4 × ArH), 7.04 (2 H, d, *J* 0.8, H – 2, H – 2′), 6.87 (2 H, dd, *J* 7.2, 1.6, 2 × ArH), 2.90 – 2.87 (2 H, m, 2 × CH), 2.18 – 2.16 (4 H, m, 2 × $CH_2$), 1.88 – 1.86 (4 H, m, 2 × $CH_2$), 1.82 – 1.77 (2 H, m, $CH_2$), 1.50 – 1.47 (8 H, m, 4 × $CH_2$), 1.32 – 1.29 (2 H, m, $CH_2$); $\delta_c$ (100 MHz, $CDCl_3$) 137.6 (2 × C), 125.6 (2 × C), 123.7 (2 × CH), 123.0 (2 × CH), 122.8 (2 × C), 120.4 (2 × CH), 119.8 (2 × CH), 109.3 (2 × CH), 35.5 (2 × CH), 34.1 (2 × $CH_2$), 33.9 (2 × $CH_2$), 27.0 (4 × $CH_2$), 26.6 (2 × $CH_2$); *m/z* (ESI) 419 (100%, $[MNa]^+$), 221 (60); HRMS (ESI, $[MNa]^+$) Found 419.2443. $[C_{28}H_{32}N_2 + Na]^+$ requires 419.2458.

**3,3'-Dibenzyl-1,1'-bisindole (15)**

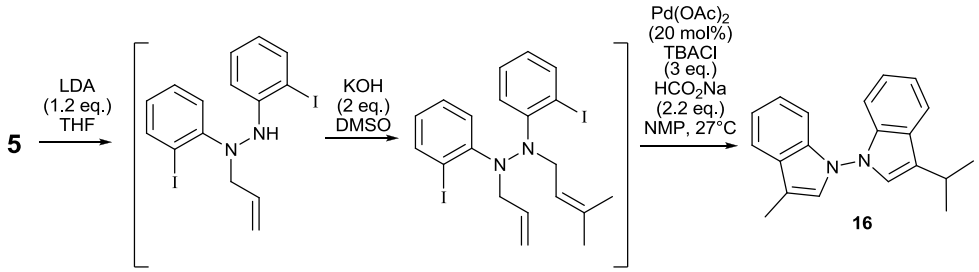



According to general procedure **A** using cinnamyl bromide (69 mg, 0.35 mmol), the monoallylated hydrazobenzene **1-cinnamyl-1,2-bis(2-iodophenyl)hydrazine** was obtained as an unstable crimson oil which was used immediately in the next step.

According to general procedure **B** using cinnamyl bromide (19.7 mg, 0.1 mL, 0.1 mmol, 1 M in DMSO), the diallylated hydrazobenzene **1,2-dicinnamyl-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 3025, 2920, 2850, 1949, 1596, 1493, 1358, 1261, 1067, 1015, 963; $\delta_H$ (400 MHz, DMSO-$d_6$) 7.81 (2 H, dd, *J* 8.0, 1.6, 2 × ArH), 7.28 – 7.22 (10 H, m, 10 × ArH), 7.19 (4 H, d, *J* 6.8, 4 × ArH), 6.83 (2 H, td, *J* 7.6, 1.2, 2 × ArH), 6.50 (2 H, d, *J* 16.0, 2 × CH), 6.22 (2 H, dt, *J* 16.0, 6.4, 2 × CH), 4.37 (4 H, d, *J* 6.4, 2 × $CH_2$); $\delta_c$ (100 MHz, DMSO-$d_6$) 148.0 (2 × C), 139.7 (2 × CH), 136.5 (2 × C), 132.1 (2 × CH), 128.5 (4 × CH), 127.9 (2 × CH), 127.4 (2 × CH), 126.8 (2 × CH), 126.1 (2 × CH), 126.0 (4 × CH), 125.5 (2 × CH), 101.6 (2 × C), 53.2 (2 × $CH_2$); *m/z* (ESI) 669 (50%, $[MH]^+$), 334 (100); HRMS (ESI, $[MH]^+$) Found 669.0257. $[C_{30}H_{26}I_2N_2 + H]^+$ requires 669.0258.

According to general procedure **C**, 3,3'-dibenzyl-1,1'-bisindole **15** was obtained (22.3 mg, 0.054 mmol, 27% from **5**) as a yellow gum; $\nu_{max}$ (neat)/cm$^{-1}$ 2920, 2851, 1493, 1451, 737; $\delta_H$ (400 MHz, $CDCl_3$) 7.58 – 7.57 (2 H, m, 2 × ArH), 7.32 – 7.30 (8 H, m, 8 × ArH), 7.23 – 7.20 (2 H, m, 2 × ArH), 7.17 – 7.14 (4 H, m, 4 × ArH), 6.99 (2 H, s, H – 2, H – 2′), 6.88 – 6.86 (2 H, m, 2 × ArH), 4.15 (4 H, s, 2 × $CH_2$); $\delta_c$ (100 MHz, $CDCl_3$) 140.4 (2 × C), 137.6 (2 × C), 128.9 (4 × CH), 128.6 (4 × CH), 126.3 (2 × CH), 126.2 (2 × CH), 126.1 (2 × C), 123.4 (2 × CH), 120.9 (2 × CH), 119.7 (2 × CH), 115.7 (2 × C), 109.2 (2 × CH), 31.6 (2 × $CH_2$); *m/z* (ESI) 413 (80%, $[MH]^+$), 206 (100); HRMS (ESI, $[MH]^+$) Found 413.1997. $[C_{30}H_{24}N_2 + H]^+$ requires 413.2012.

**3-Isopropyl-3'-methyl-1,1'-bisindole (16)**




According to general procedure **A**, using allyl bromide (60.5 mg, 0.043 mL, 0.5 mmol), the monoallylated hydrazobenzene **1-allyl-1,2-bis(2-iodophenyl)hydrazine** was obtained as a crimson oil, spectroscopic data as described previously during the synthesis of **12**.

According to general procedure **B** using 3,3-dimethylallyl bromide (44.7 mg, 0.039 mL, 0.3 mmol), the diallylated hydrazobenzene **1-allyl-1,2-bis(2-iodophenyl)-2-(3-methylbut-2-en-1-yl)hydrazine** was obtained as a crimson oil; $\nu_{max}$ (neat)/cm$^{-1}$ 2923, 2856, 1592, 1495, 1306, 1004, 748; $\delta_H$ (400 MHz, Acetone-$d_6$) 7.81 (2 H, dt, *J* 8.0, 1.6, 2 × ArH), 7.29 (2 H, tt, *J* 8.0, 1.6, 2 × ArH), 7.13 (2 H, dt, *J* 8.0, 1.6, 2 × ArH), 6.87 (2 H, tt, *J* 8.0, 1.6), 5.89 – 5.82 (1 H, m, allyl CH), 5.13 – 5.11 (2 H, m, 2 × allyl CH), 4.93 (1 H, dt, *J* 12.0, 1.6, CH), 4.24 (2 H, dt, *J* 6.0, 1.6, $CH_2$), 4.14 (2 H, d, *J* 6.4, $CH_2$), 1.61 (3 H, s, Me), 1.54 (3 H, d, *J* 0.8, Me); $\delta_c$ (100 MHz, Acetone-$d_6$) 149.6 (C), 148.8 (C), 140.81 (CH), 140.76 (CH), 135.6 (CH), 135.0 (C), 128.8 (CH), 128.6 (CH), 127.8 (CH), 127.6 (CH), 127.0 (CH), 126.6 (CH), 121.7 (CH), 118.0 (CH), 103.0 (C), 102.8 (C), 55.0 ($CH_2$), 50.3 ($CH_2$), 25.9 (Me), 18.3 (Me); *m/z* (ESI) 544 (26%, $[MH]^+$), 503 (35), 475 (100), 418 (48), 350 (25); HRMS (ESI, $[MH]^+$) Found 544.9949. $[C_{20}H_{22}I_2N_2 + H]^+$ requires 544.9945.

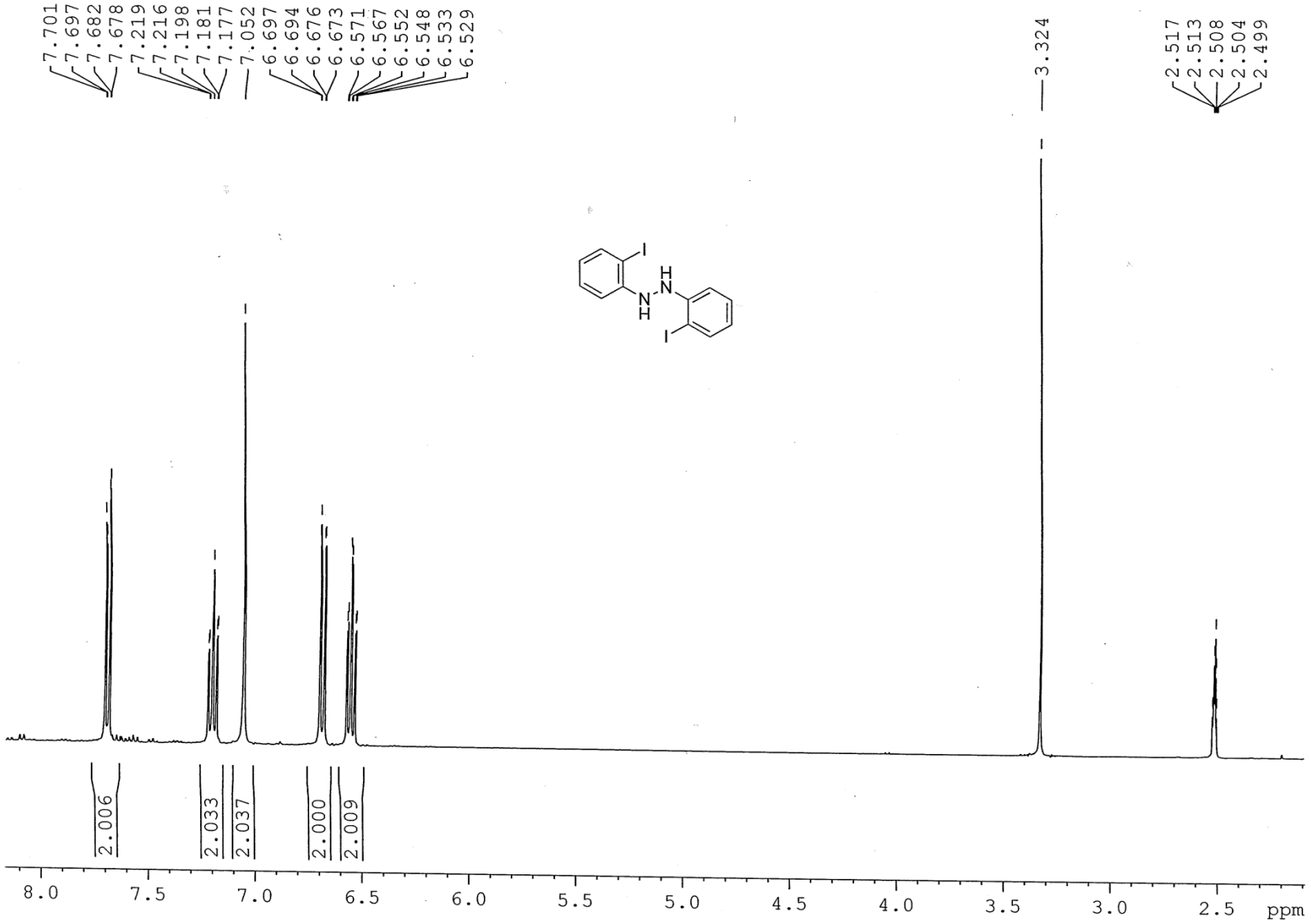
According to general procedure **C**, 3-isopropyl-3'-methyl-1,1'-bisindole **16** was obtained (13.8 mg, 0.048 mmol, 24% from **5**) as a yellow oil**;** $\nu_{max}$ (neat)/cm$^{-1}$ 2960, 2928, 2867, 1455, 1224, 1138, 736; $\delta_H$ (400 MHz, $CDCl_3$) 7.72 (1 H, d, *J* 6.8, ArH), 7.65 (1 H, d, *J* 6.8, ArH), 7.20 – 7.15 (4 H, m, 4 × ArH), 7.07 (1 H, d, *J* 0.8, H – 2), 7.03 (1 H, d, *J* 0.8, H - 2′), 6.90 – 6.87 (2 H, m, 2 × ArH), 3.27 (1 H, pd, *J* 7.2, 0.8, CH), 2.39 (3 H, d, *J* 1.2, Me), 1.40 (6 H, dd, *J* 7.2, 2.2, 2 × Me); $\delta_C$ (100 MHz, $CDCl_3$) 137.7 (C), 137.5 (C), 127.0 (C), 125.7 (CH), 125.6 (C), 123.7 (C), 123.5 (CH), 123.2 (CH), 123.1 (CH), 120.6 (CH), 120.5 (CH), 119.9 (CH), 119.3 (CH), 111.5 (C), 109.3 (CH), 109.2 (CH), 25.6 (CH), 23.35 (Me), 23.26 (Me), 9.73 (Me); *m/z* (ESI) 288 (100%, $[M]^+$), 158 (74), 144 (63), 130 (70); HRMS (ESI, $[MNa]^+$) Found 311.1526. $[C_{20}H_{20}N_2 + Na]^+$ requires 311.1519.

## Reference

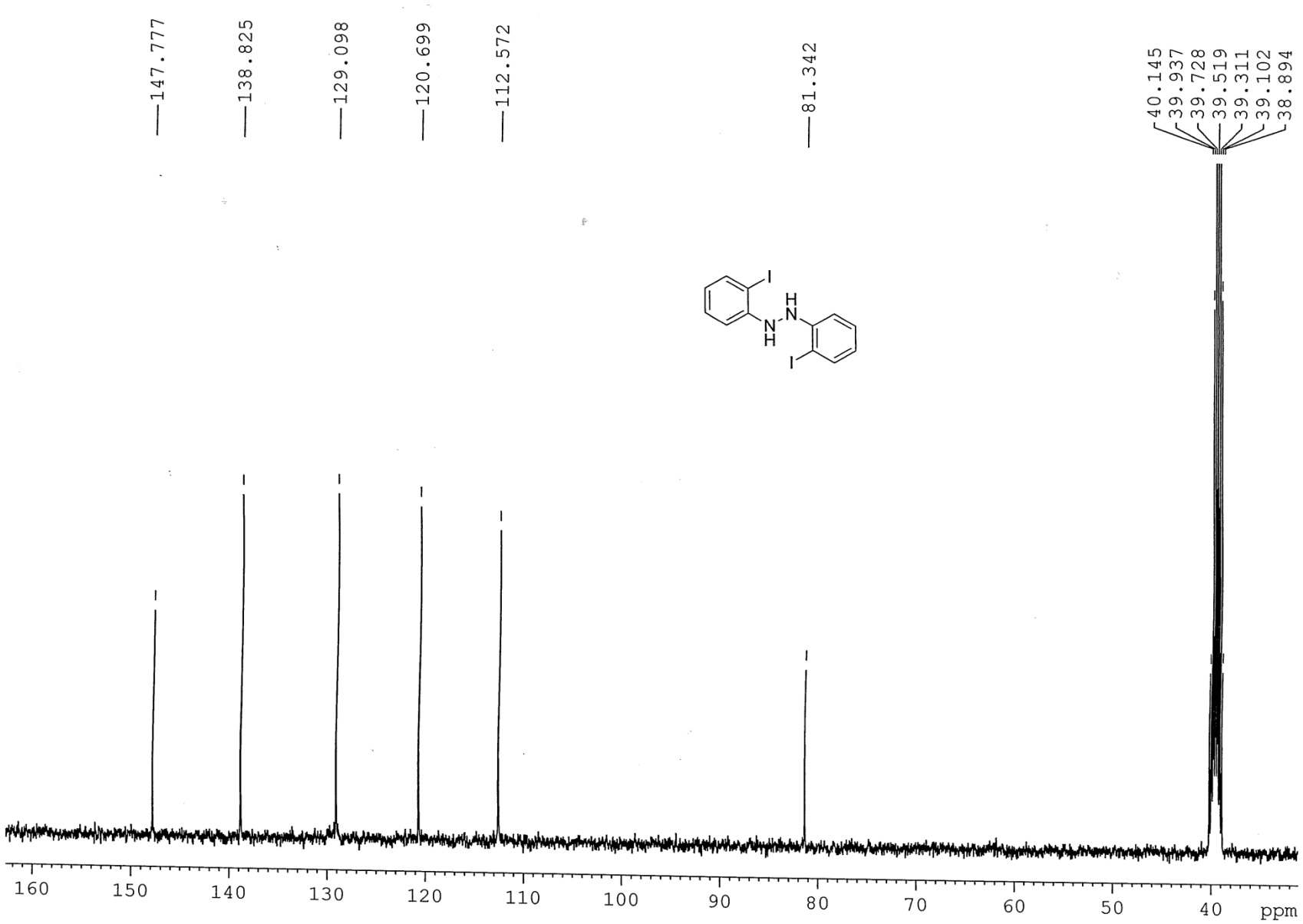
1. Ravikumar, P. C.; Yao, Lihua; Fleming, Fraser F.; *J. Org. Chem.* 2009, **74**, 7294.

2. Chaco, M.C.; Iyer, B. H.; *J. Org. Chem.* 1960, **25**, 186.

**1,2-Bis(2-iodophenyl)hydrazine**



**1,2-Bis(2-iodophenyl)hydrazine**



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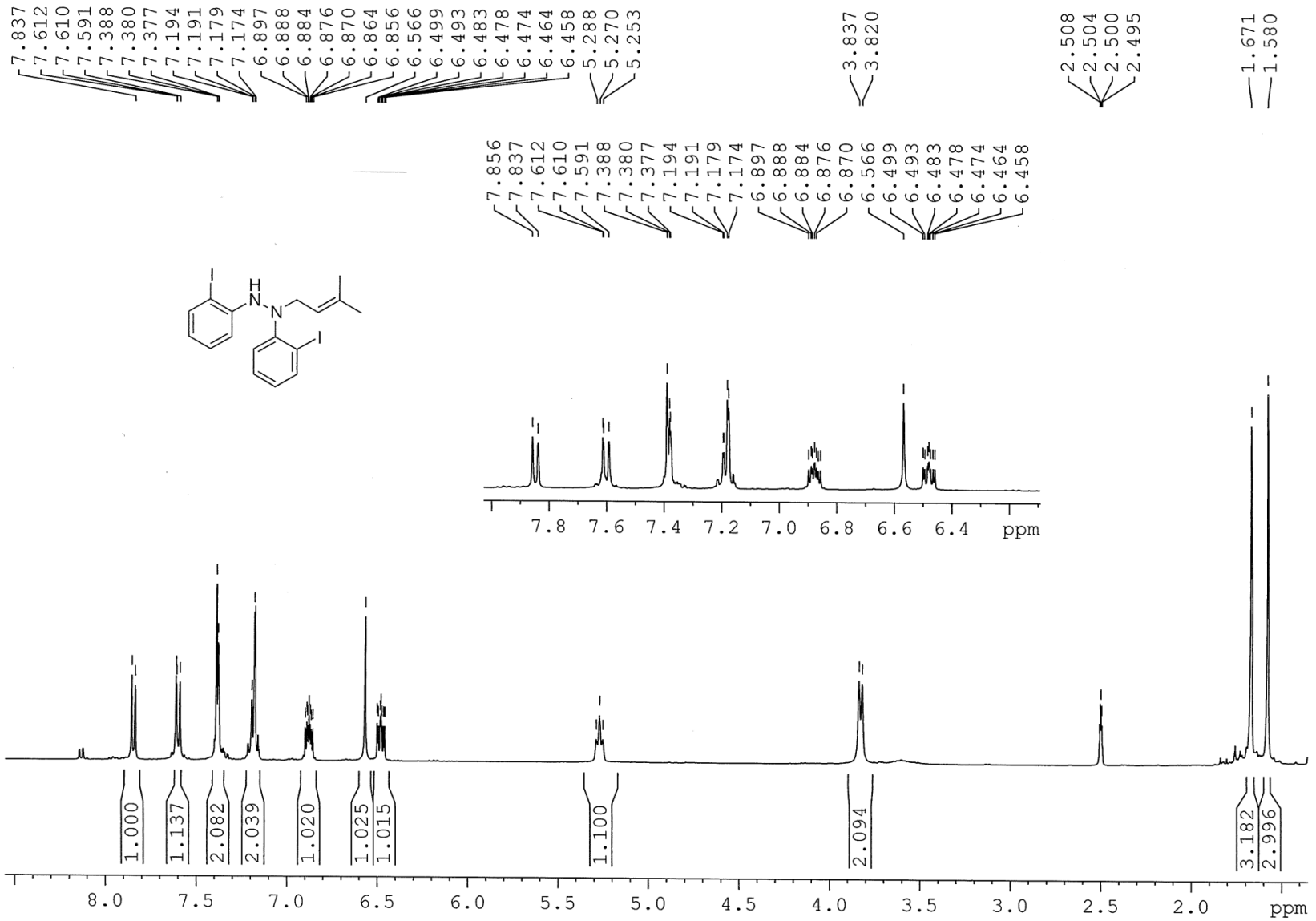

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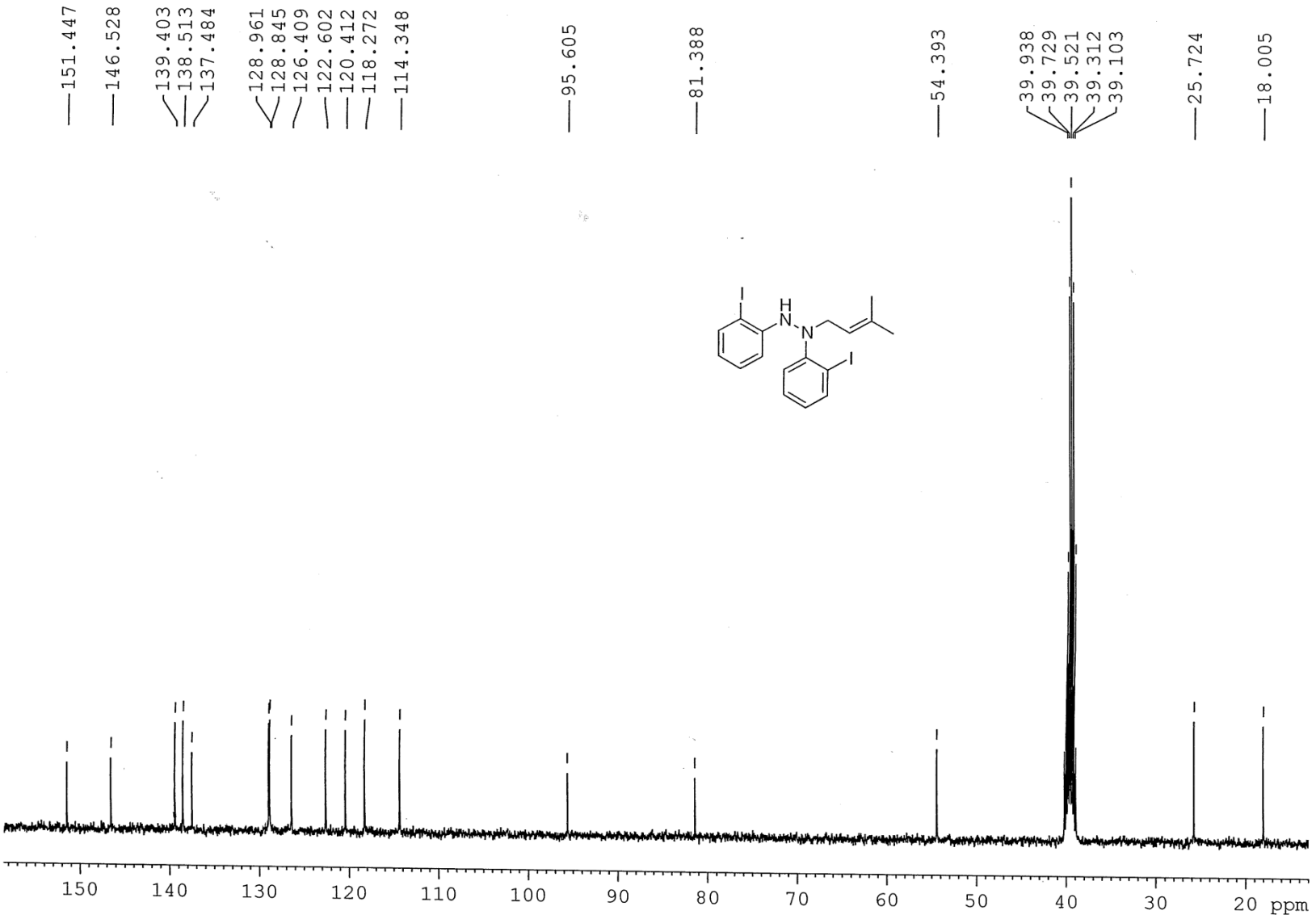

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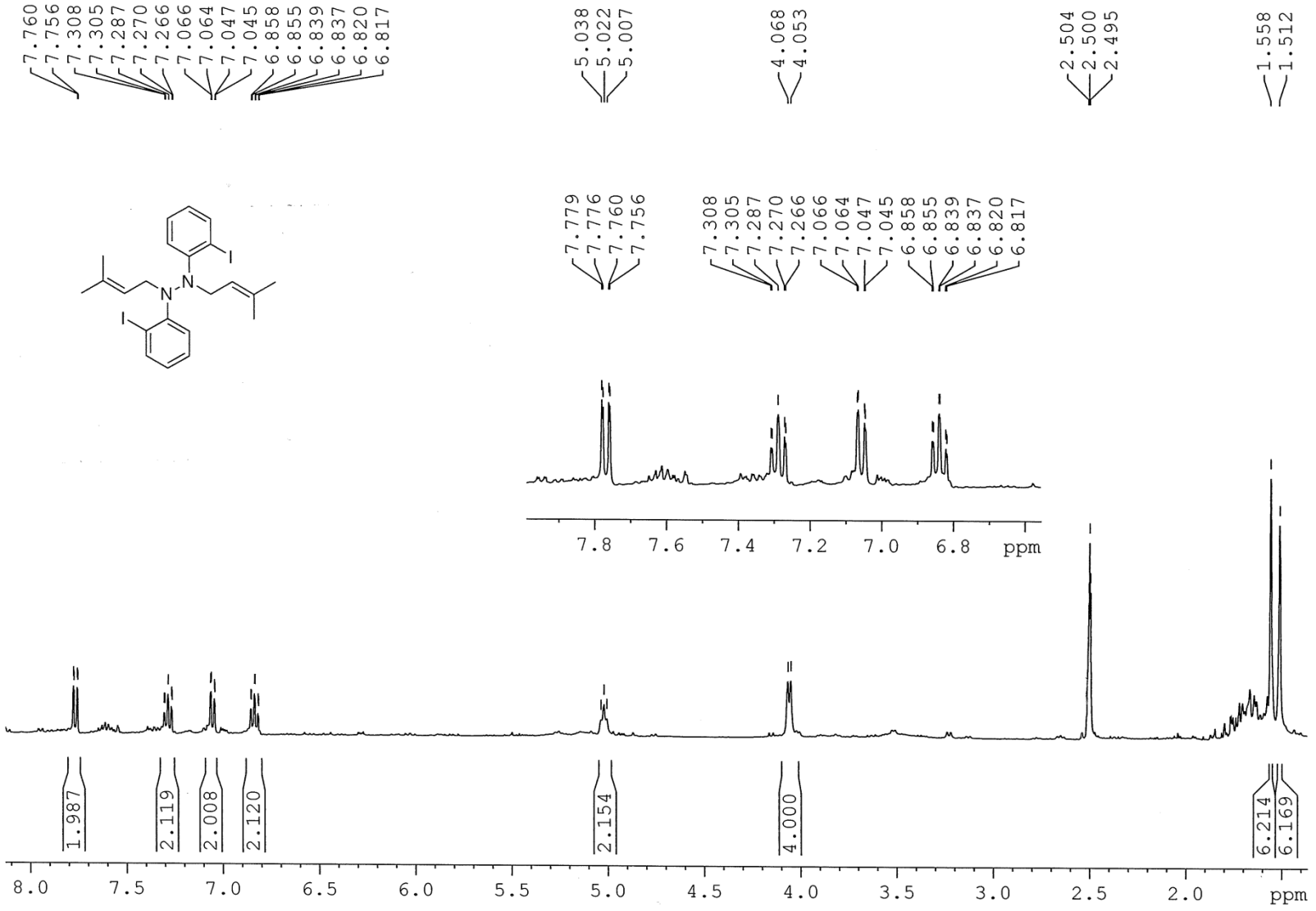

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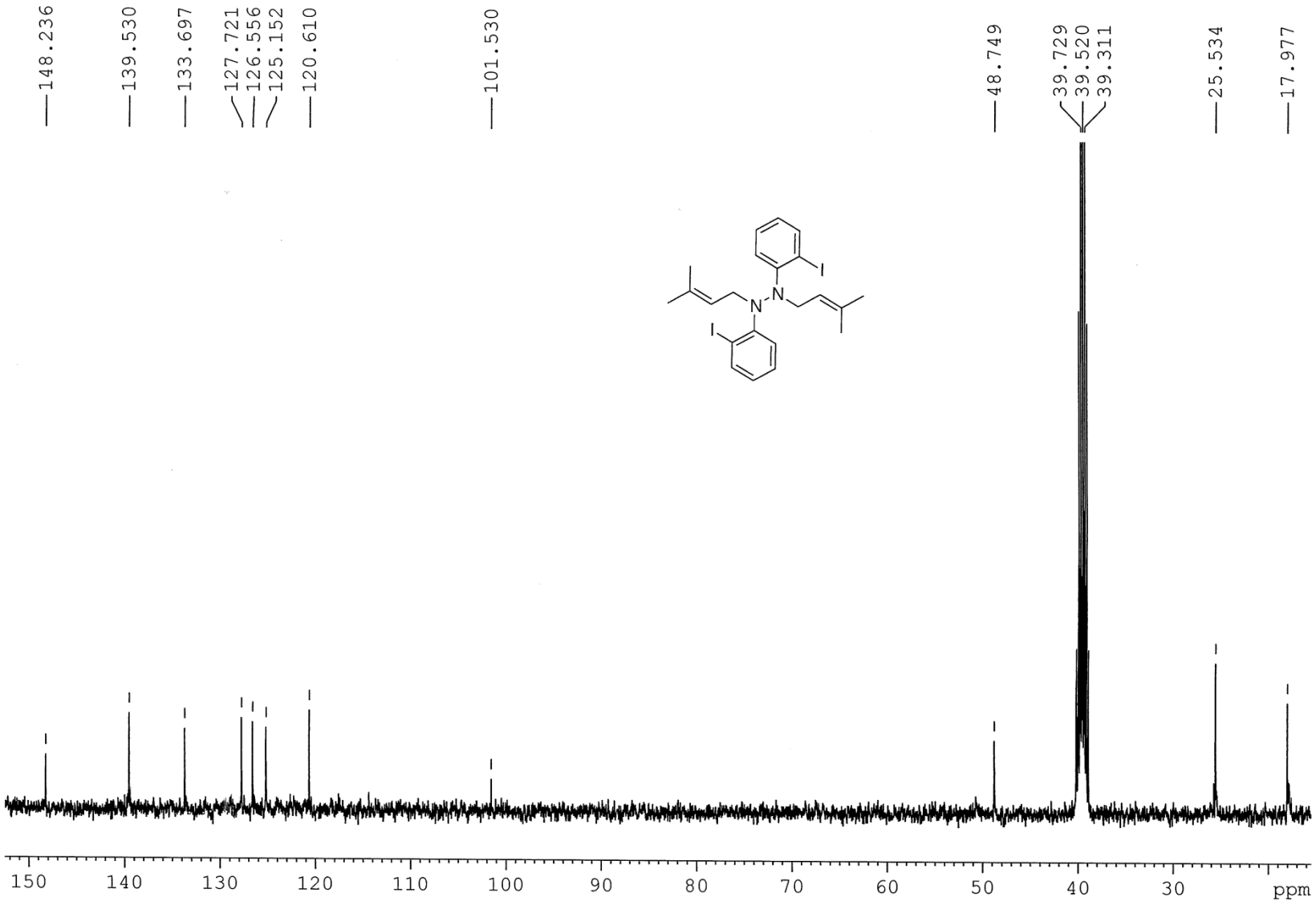
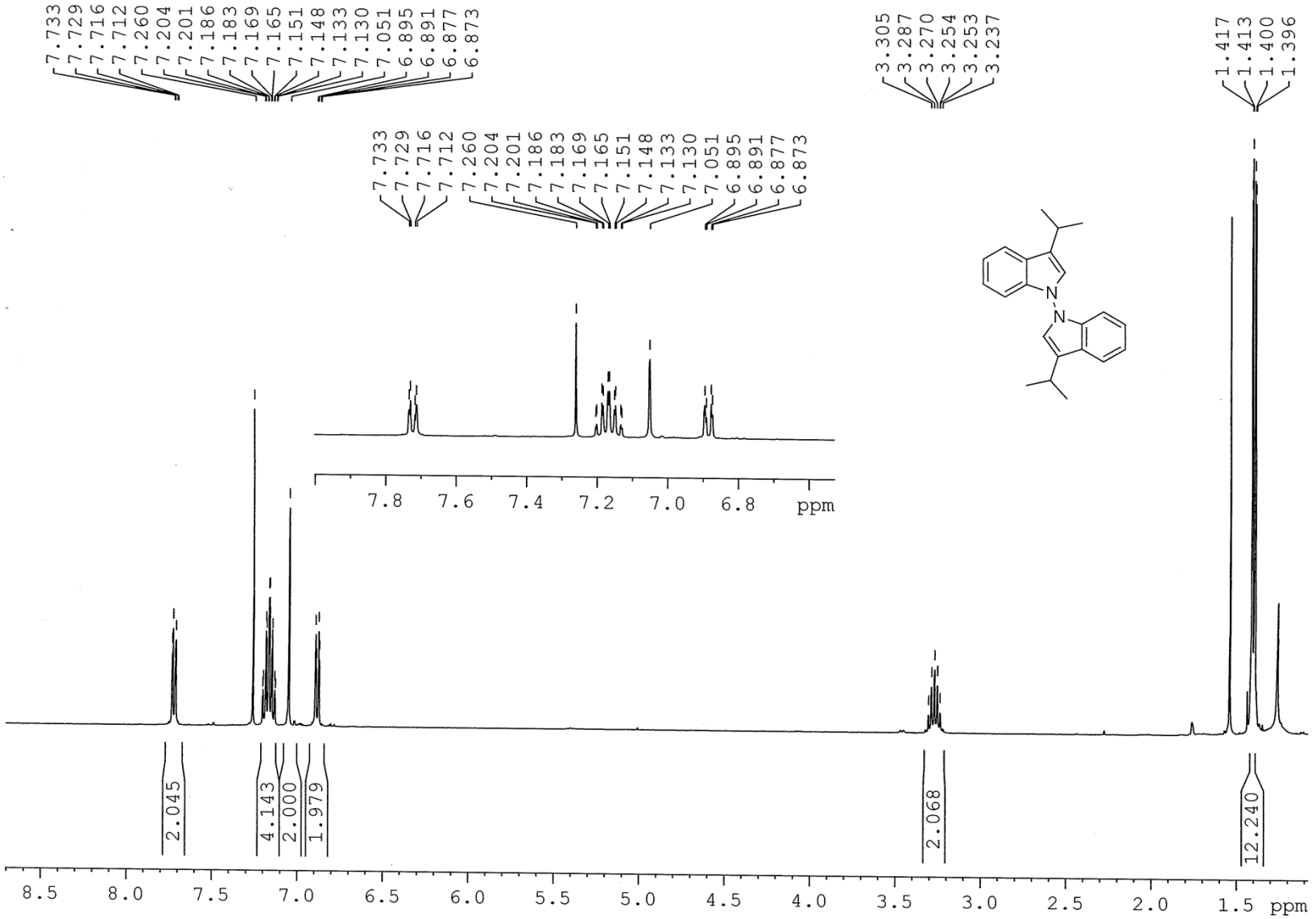
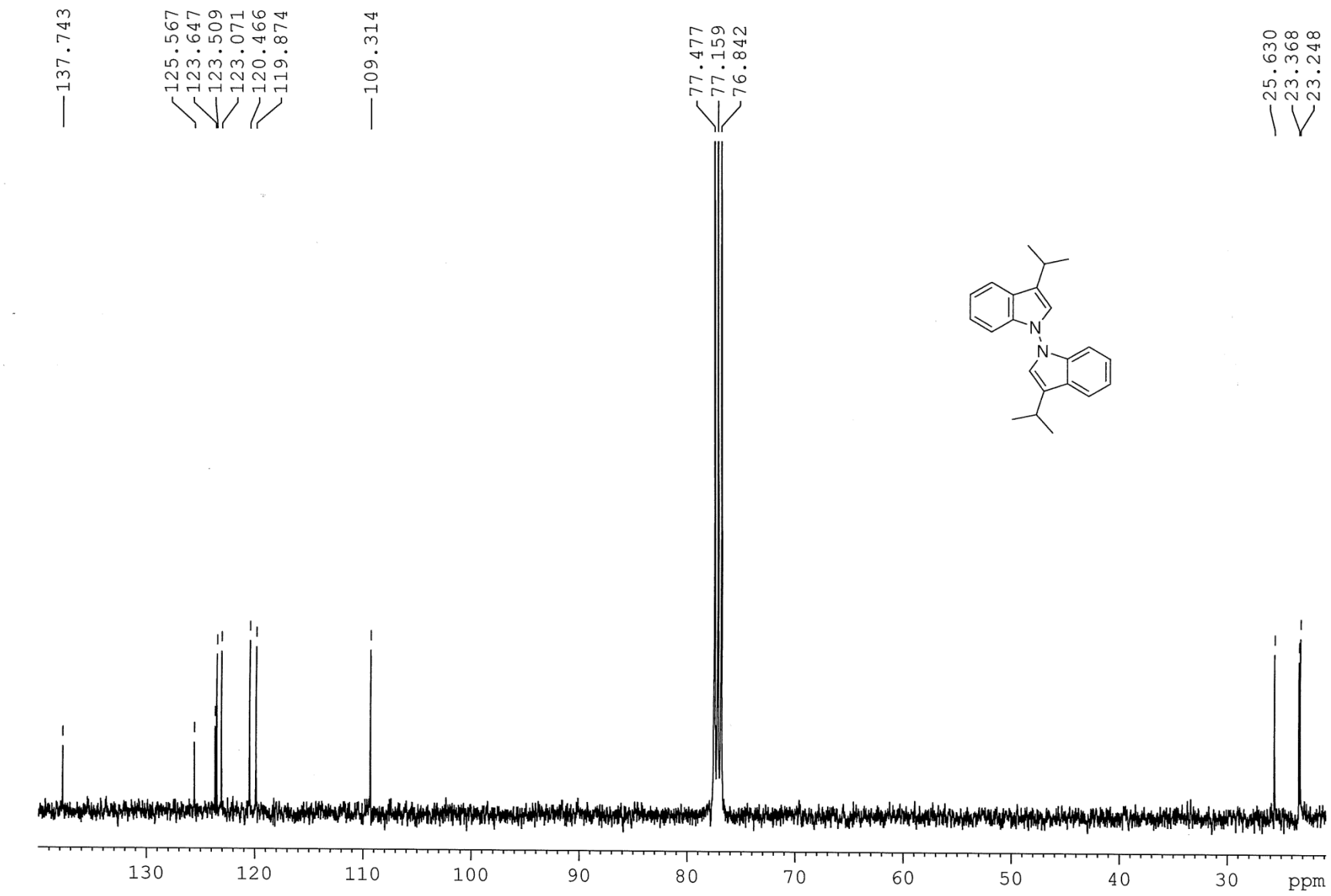


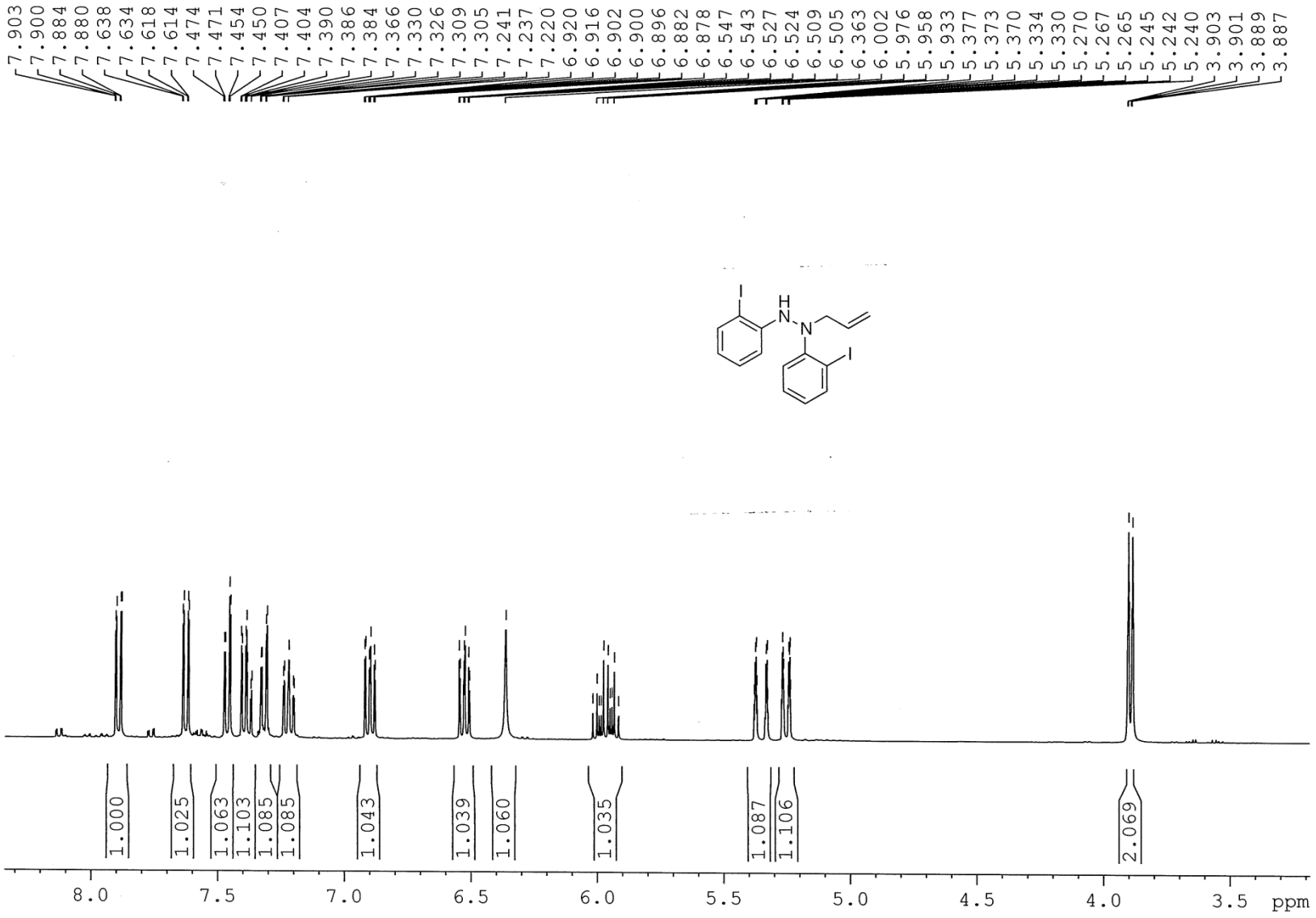
**3,3'-Diisopropyl-1,1'-bisindole**



**3,3'-Diisopropyl-1,1'-bisindole**



**1-Allyl-1,2-bis(2-iodophenyl)hydrazine**



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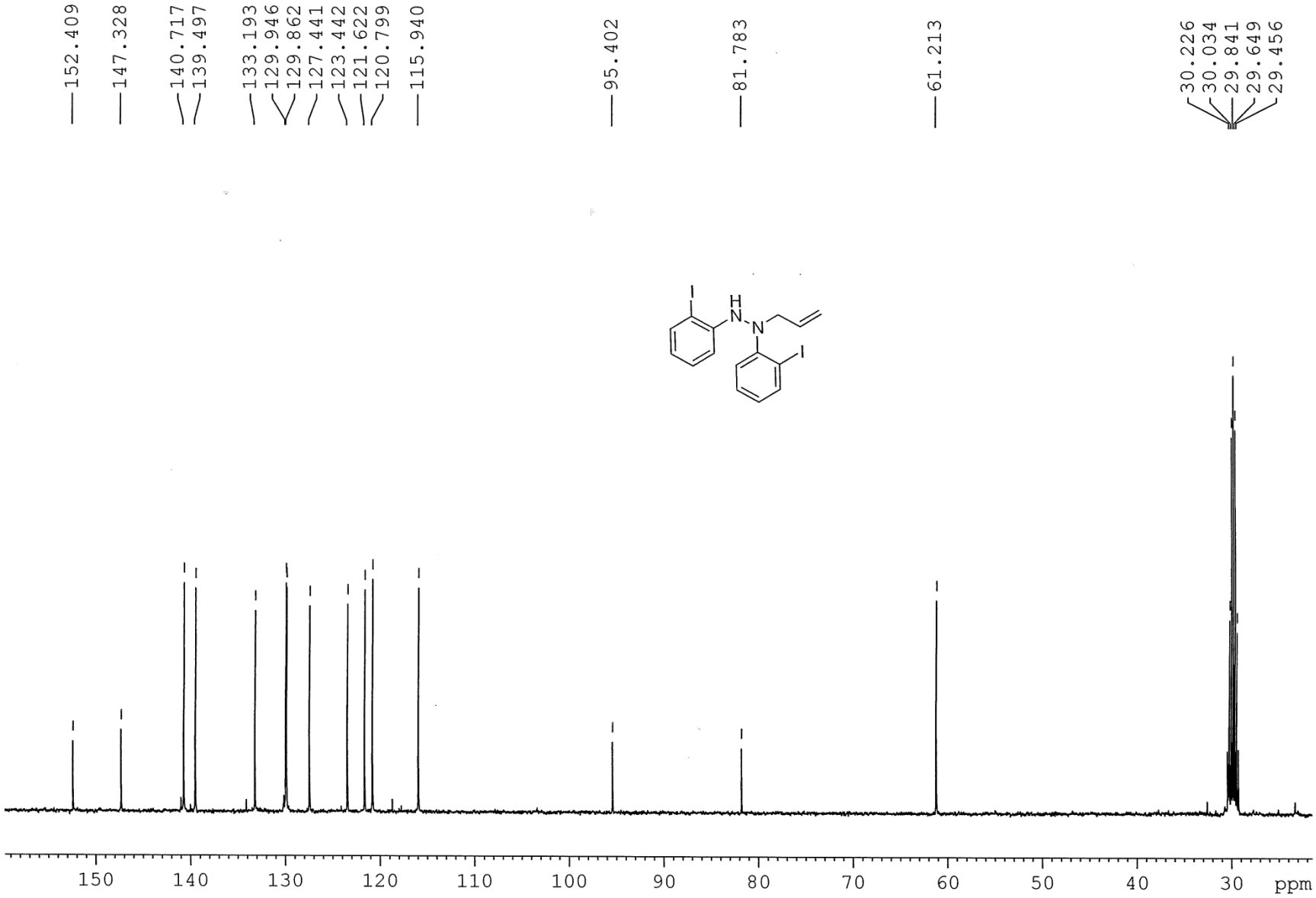

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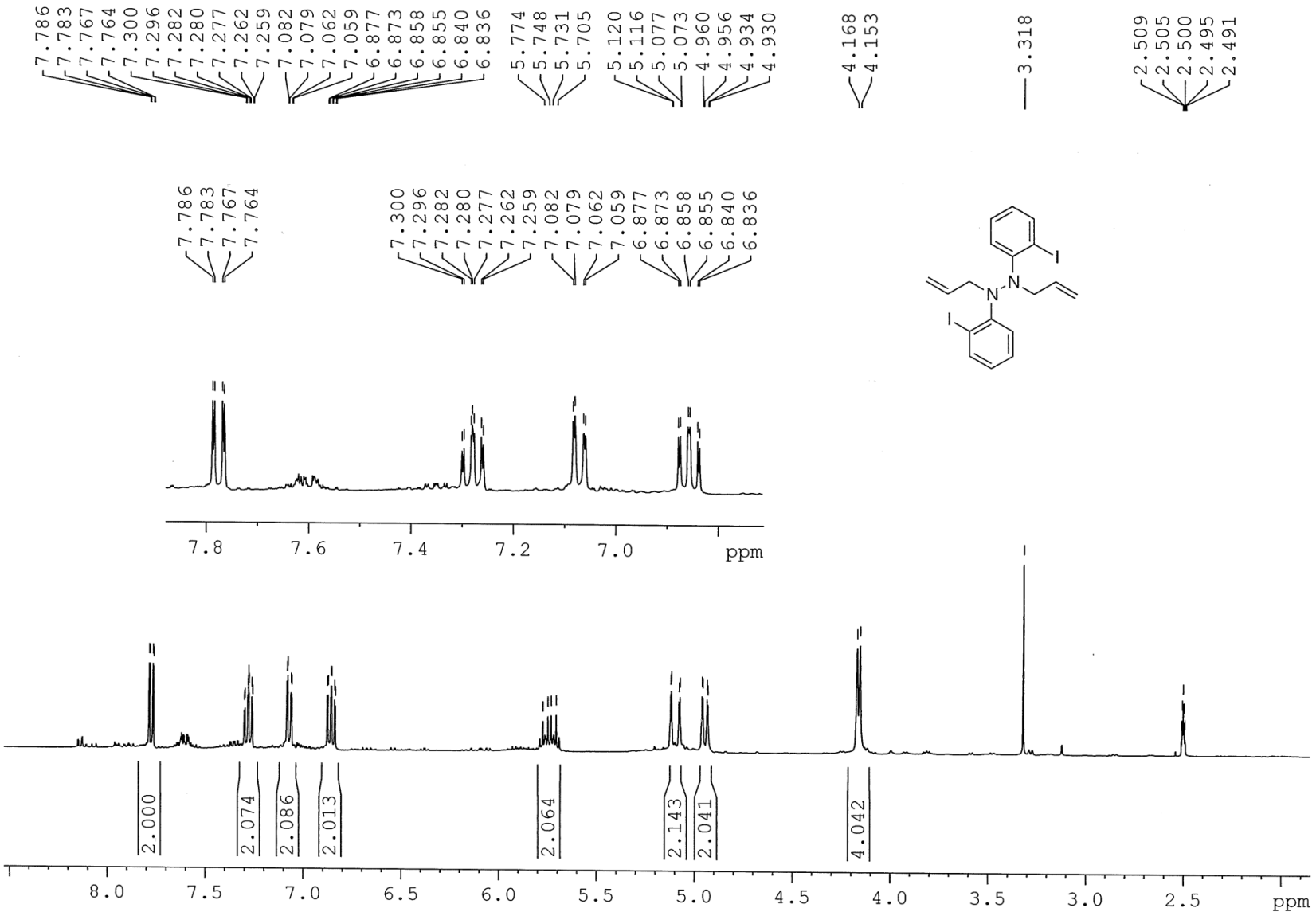

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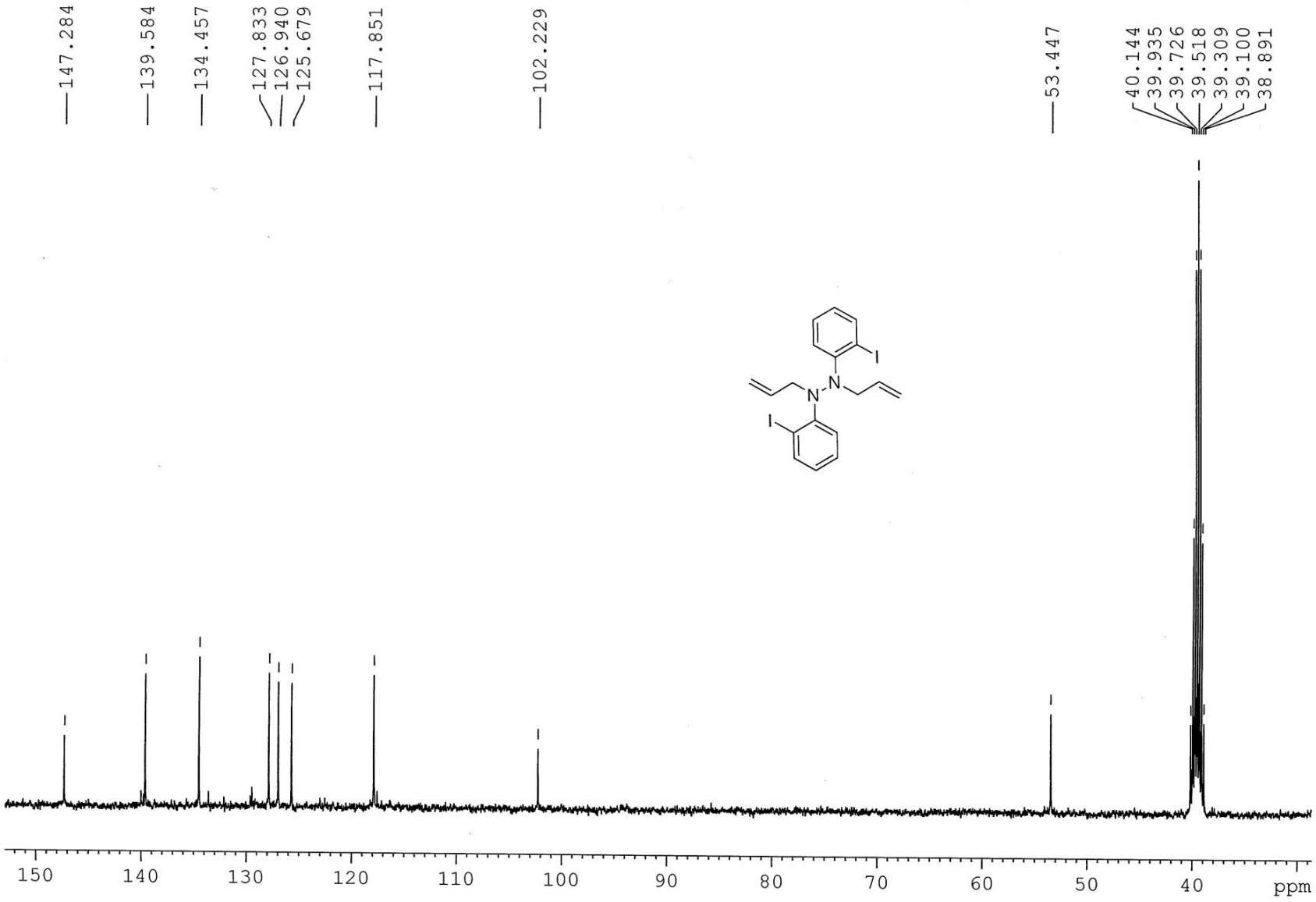

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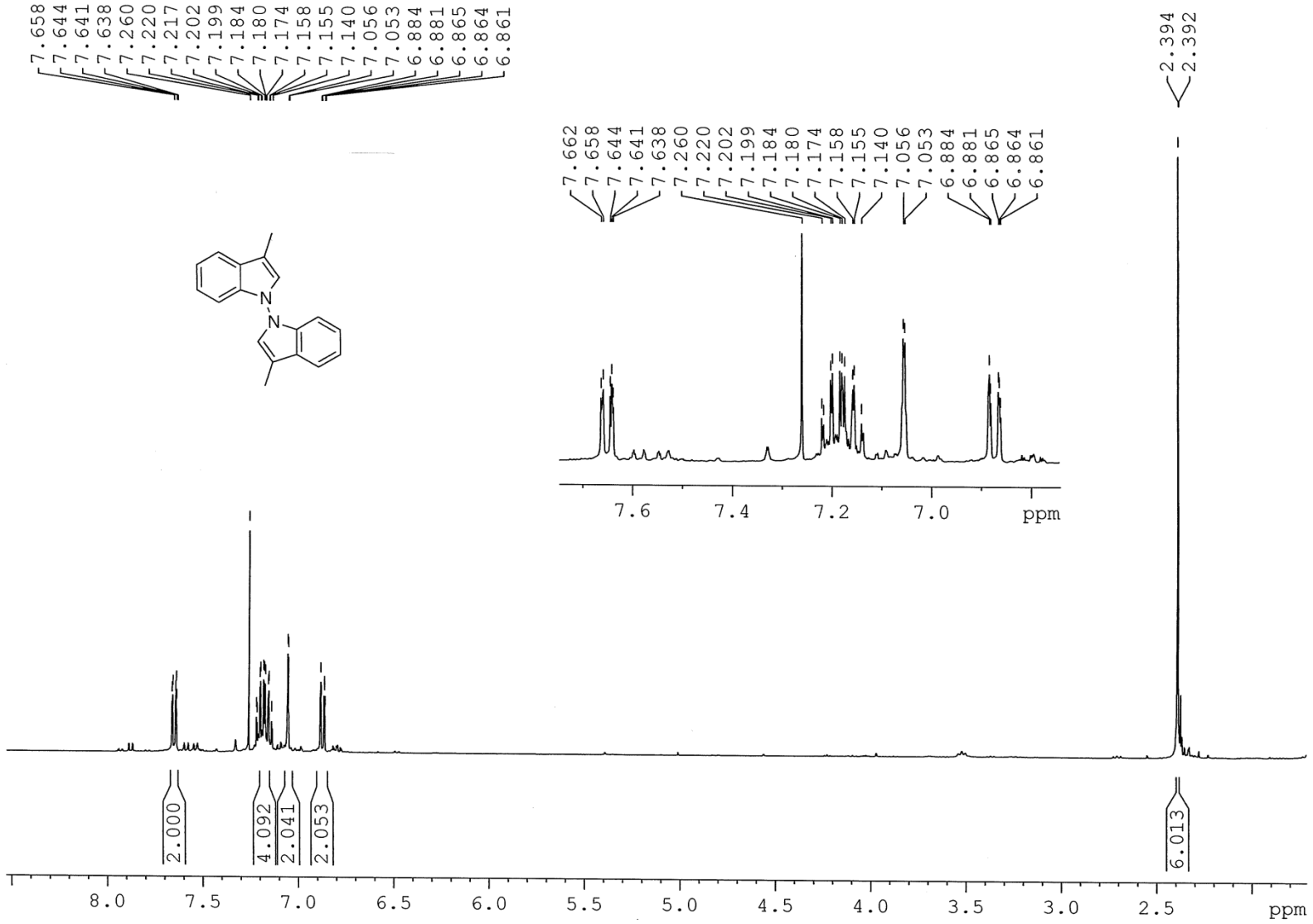
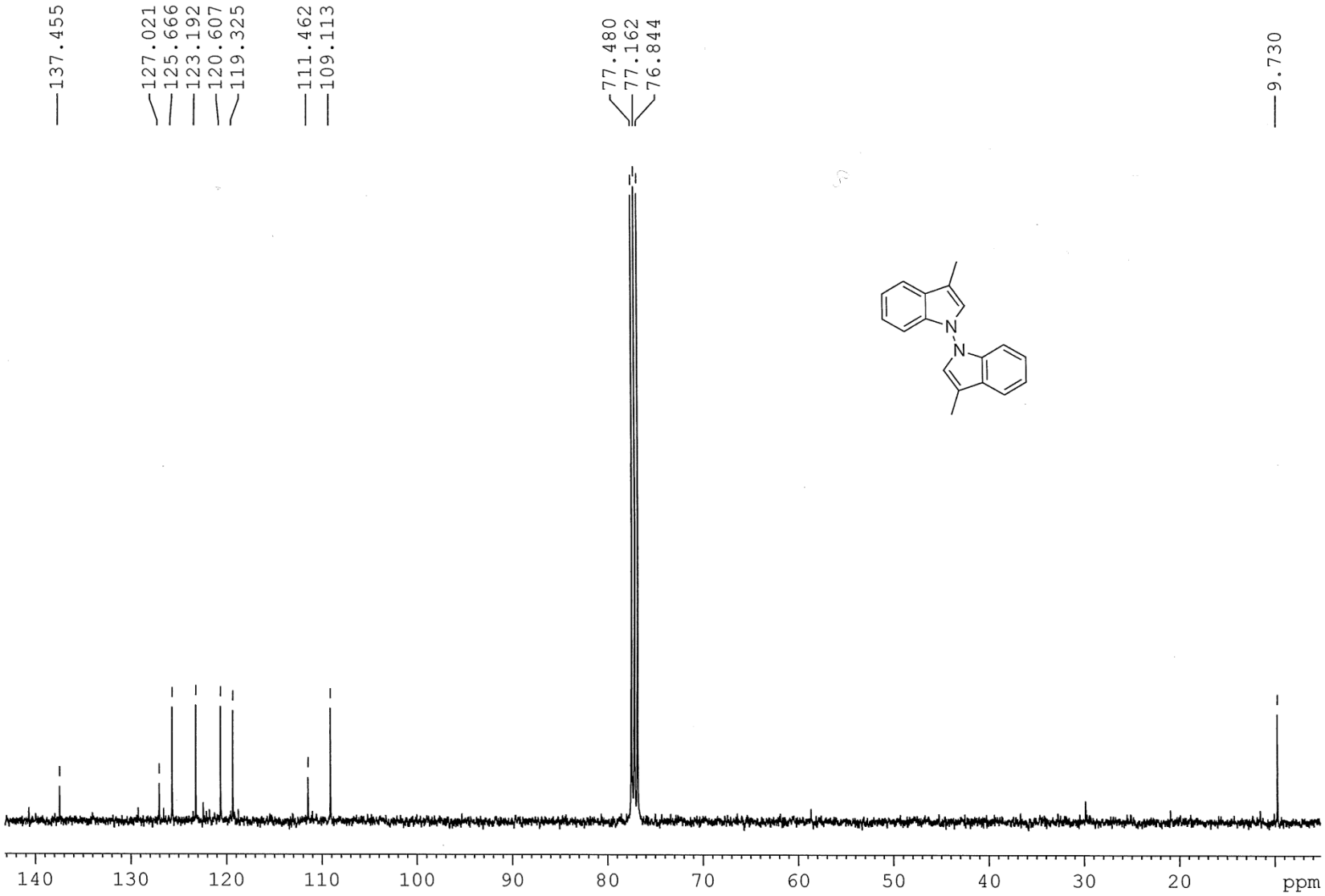
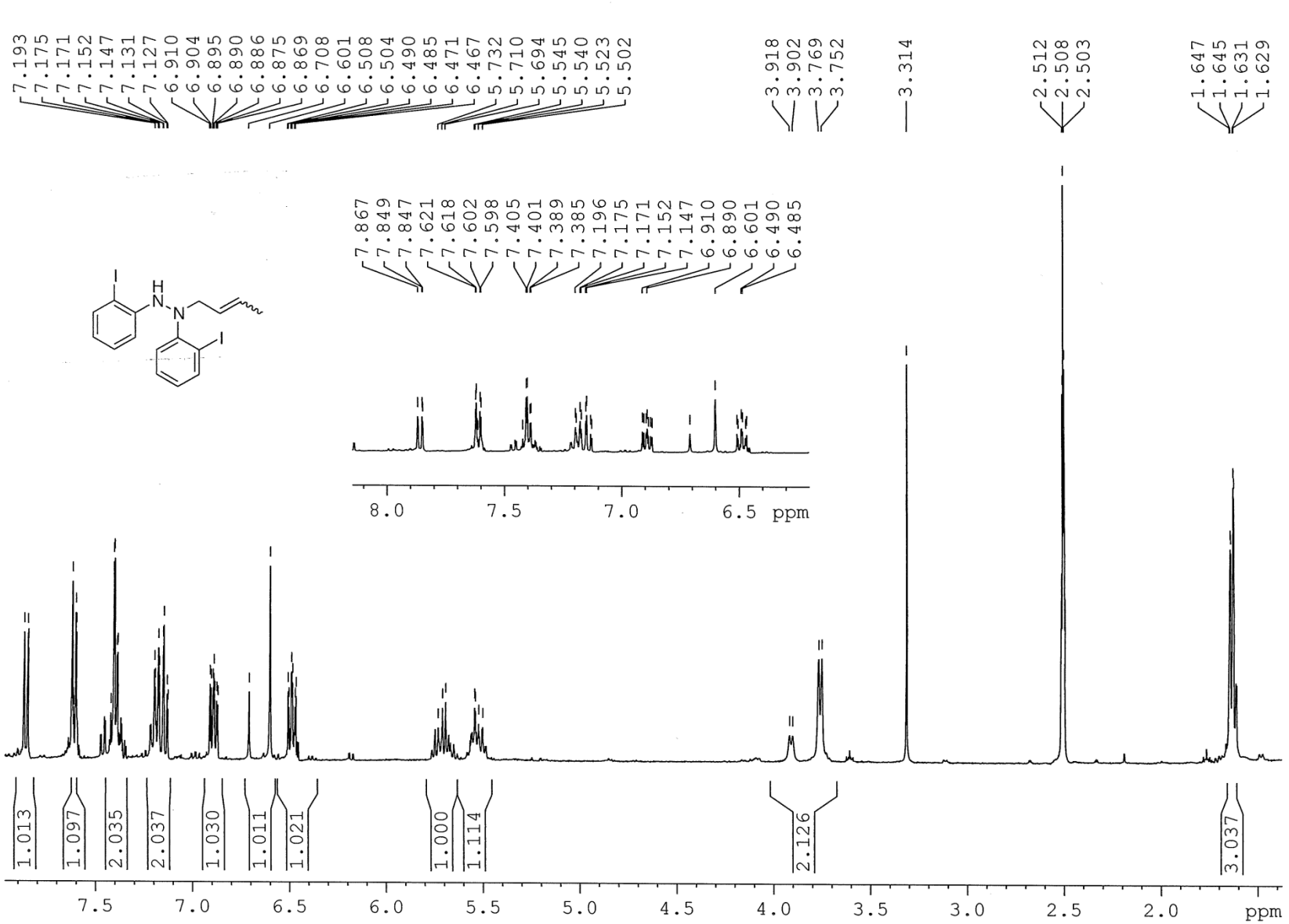


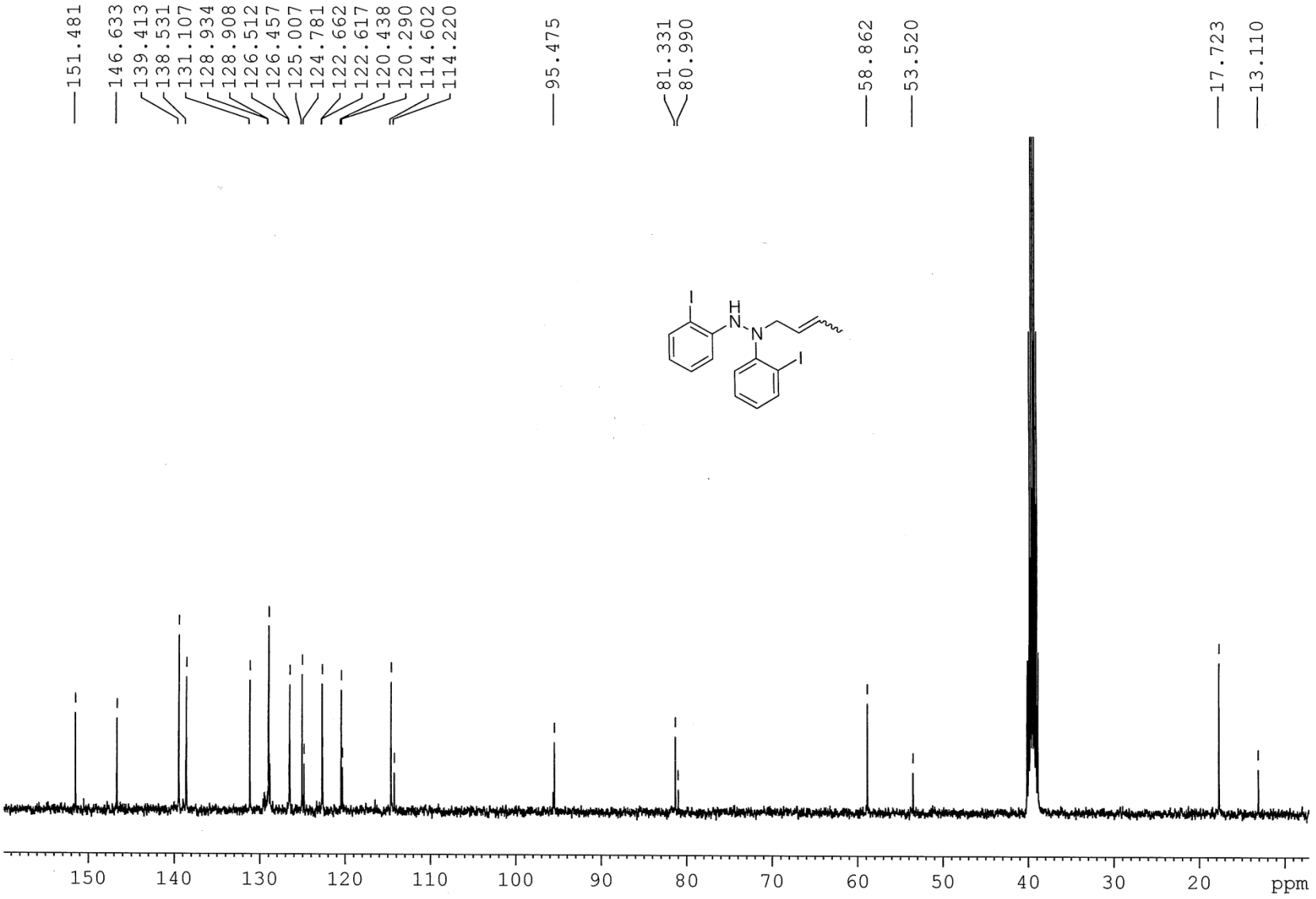
**3,3'-Dimethyl-1,1'-bisindole**



**1-(But-2-en-1-yl)-1,2-bis(2-iodophenyl)hydrazine**



**1-(But-2-en-1-yl)-1,2-bis(2-iodophenyl)hydrazine**



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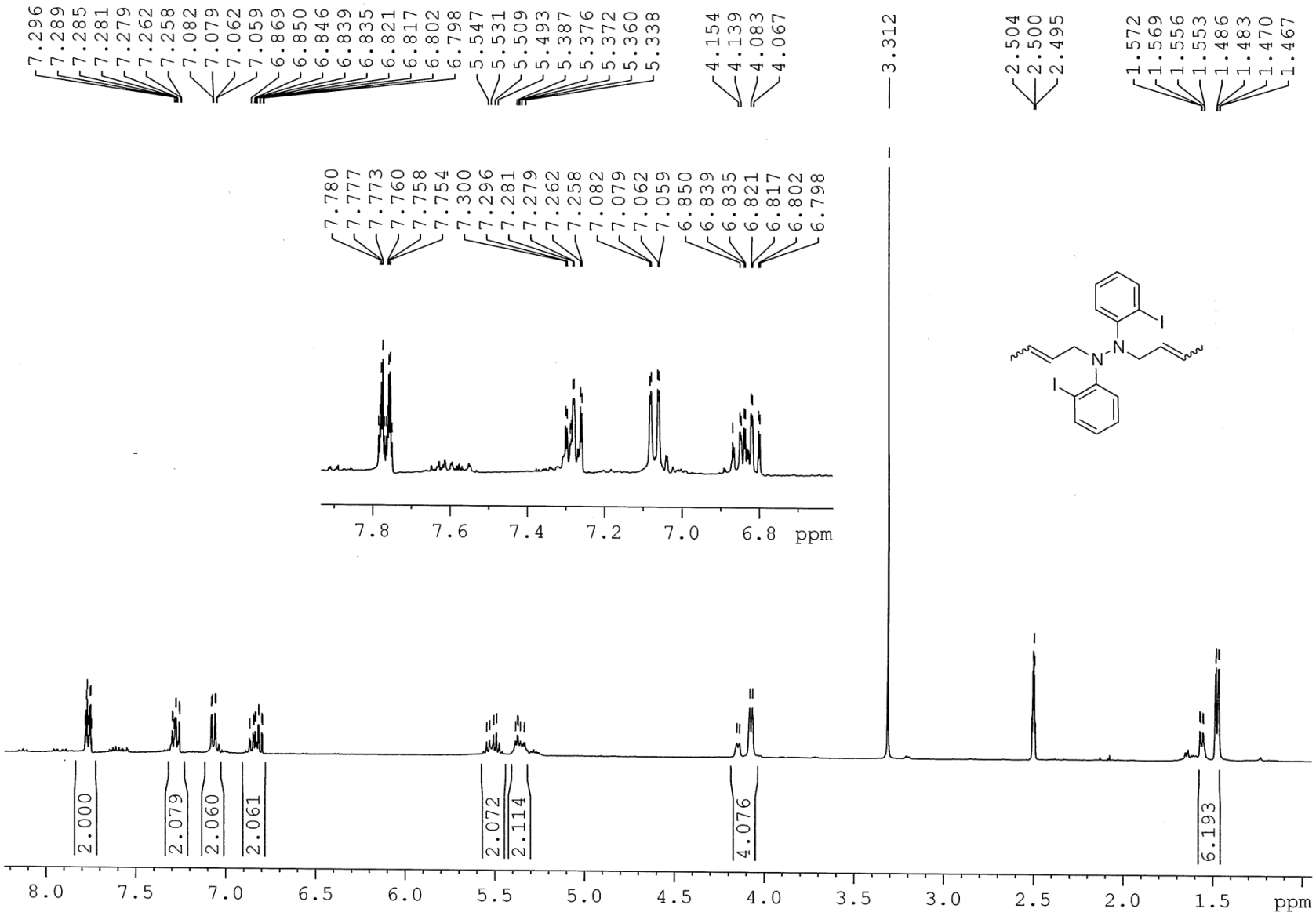

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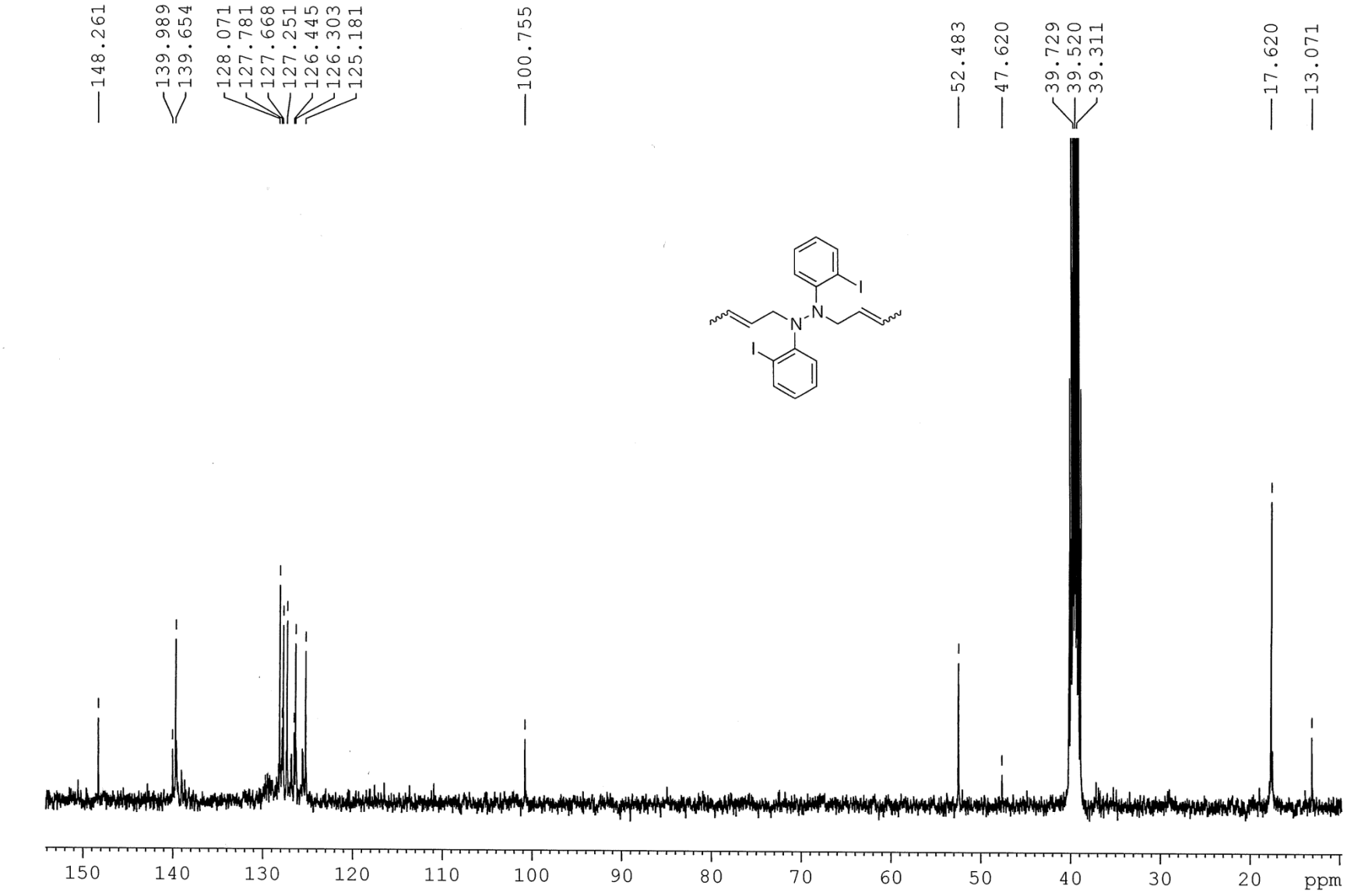

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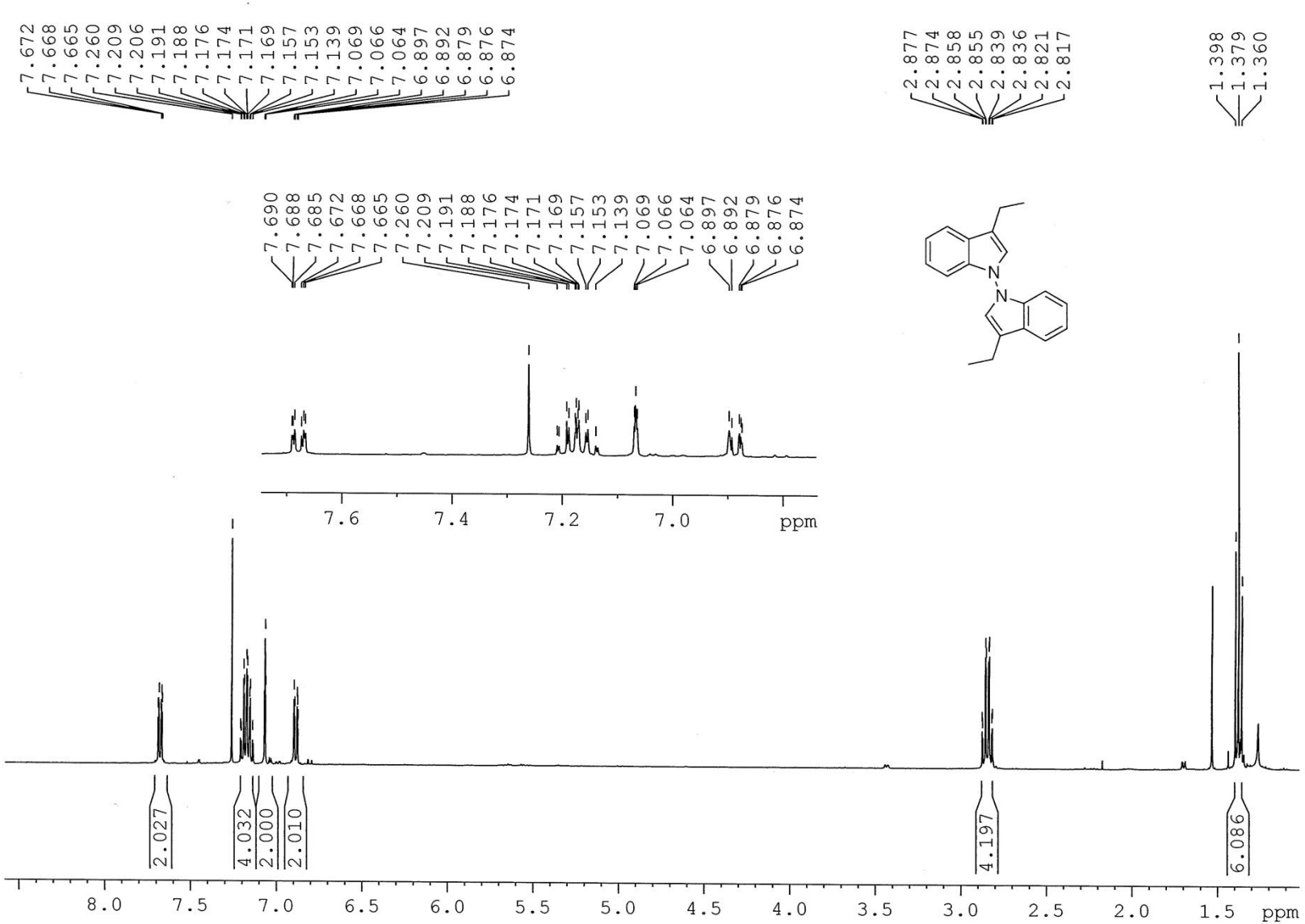
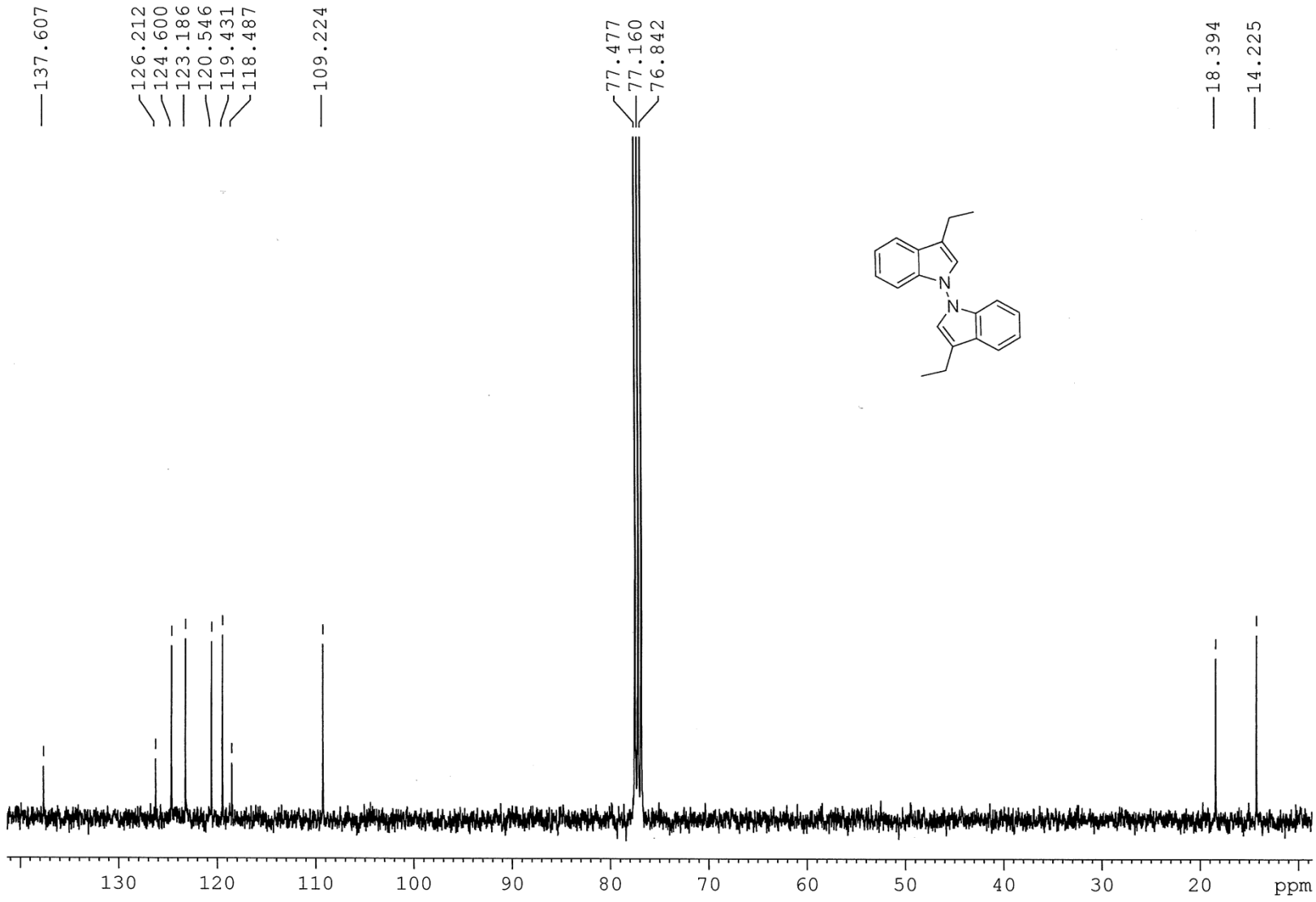
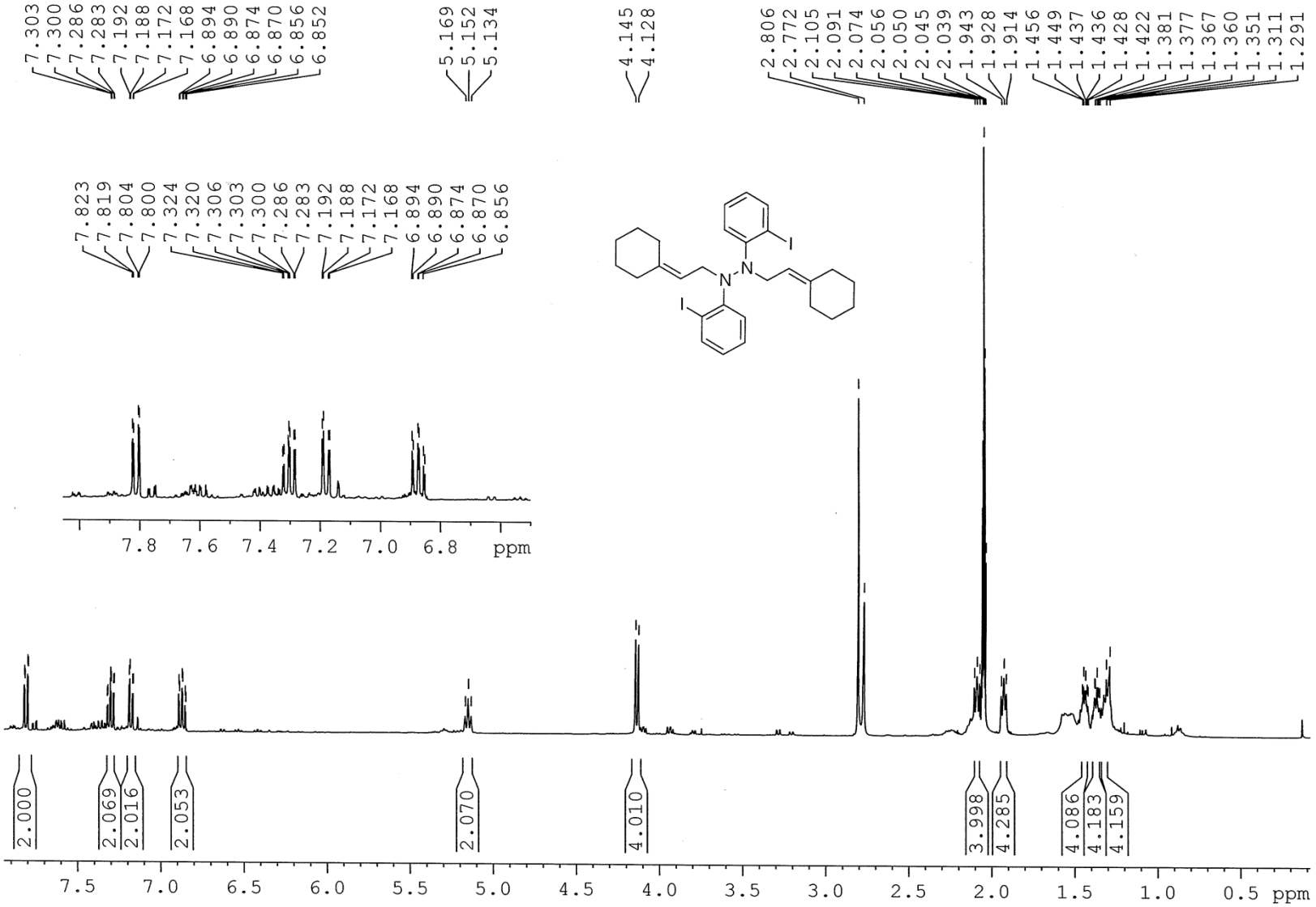


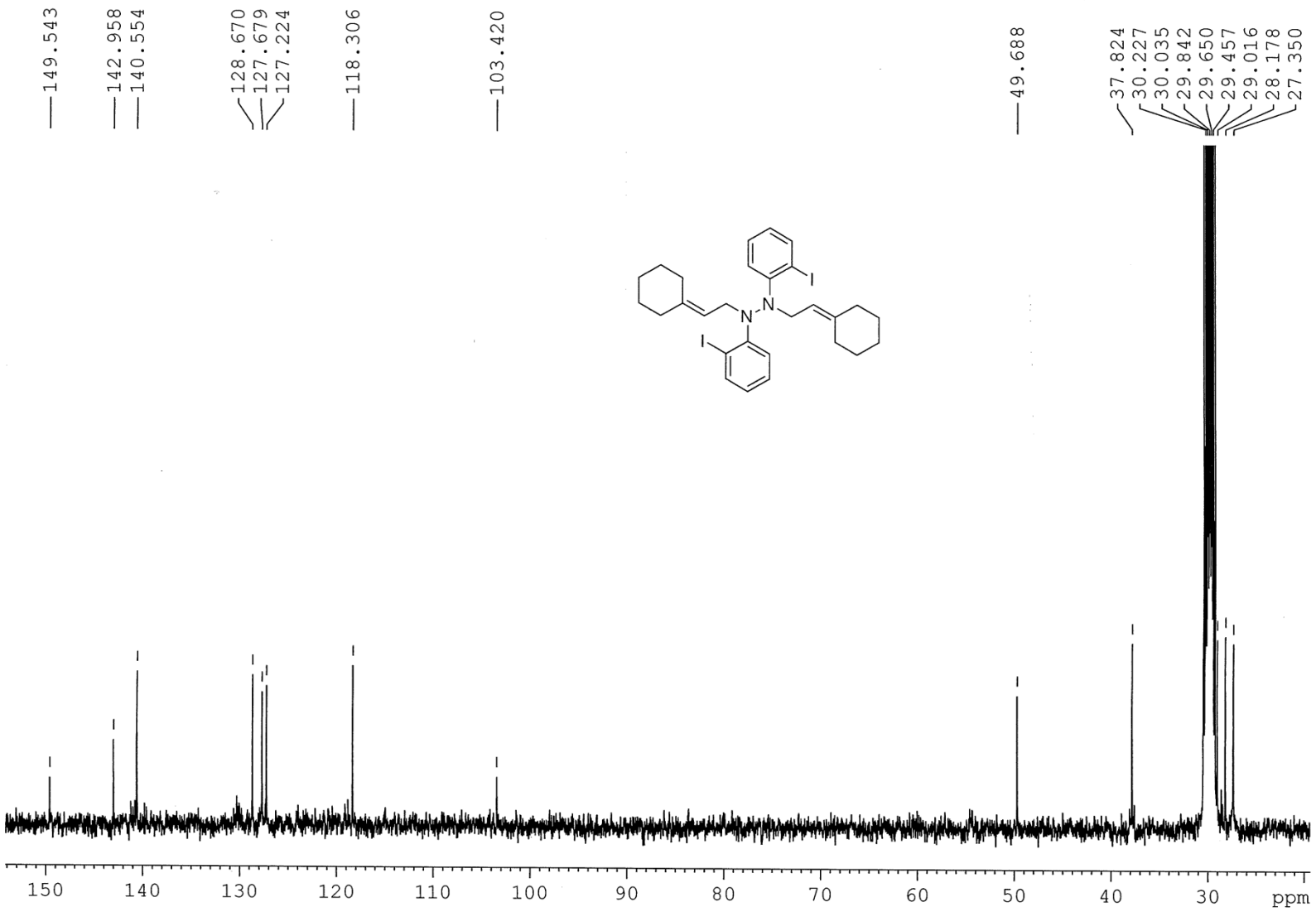
**3,3'-Diethyl-1,1'-bisindole**



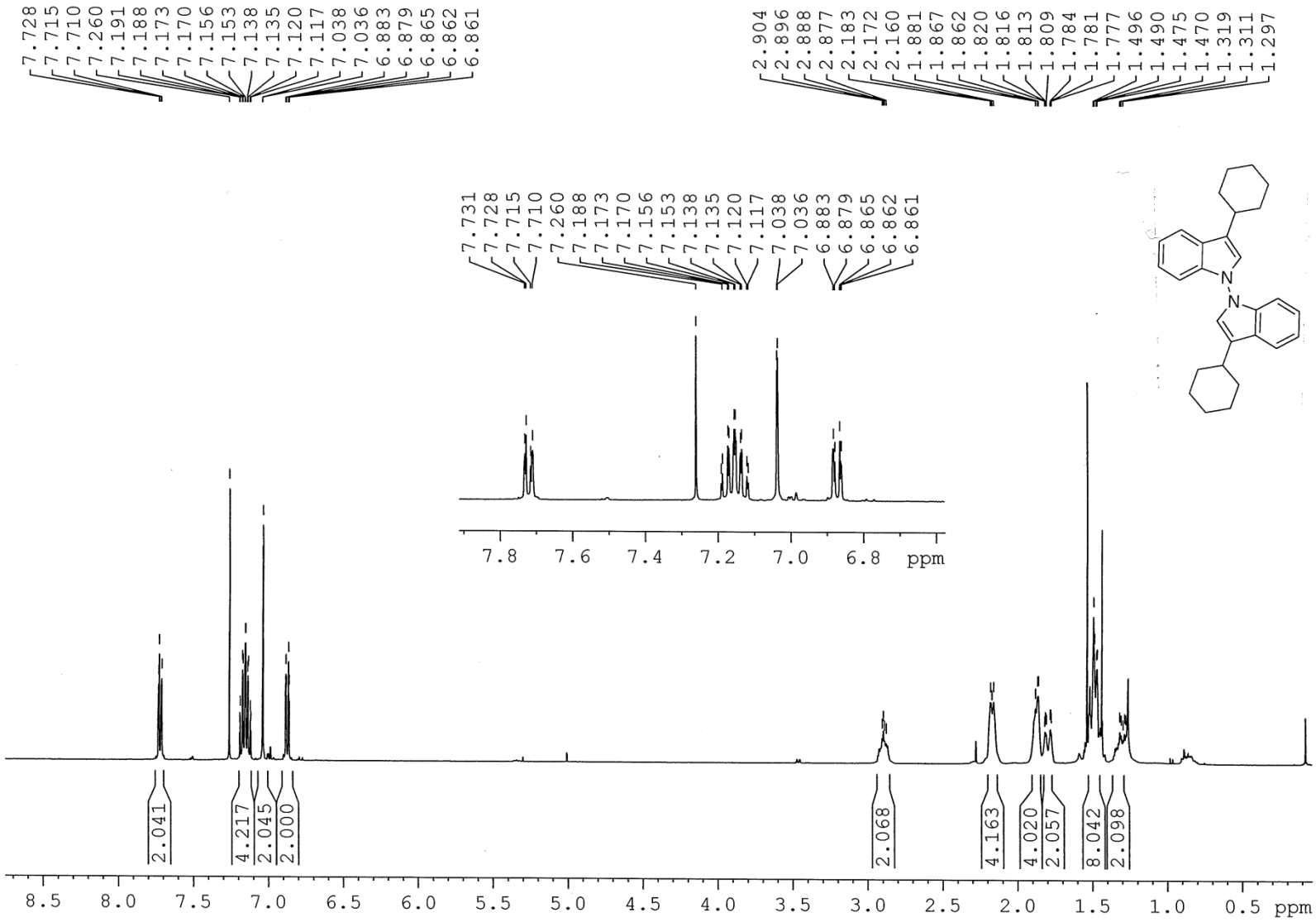
**1,2-Bis(2-cyclohexylideneethyl)-1,2-bis(2-iodophenyl)hydrazine**



**1,2-Bis(2-cyclohexylideneethyl)-1,2-bis(2-iodophenyl)hydrazine**



**3,3'-Dicyclohexyl-1,1'-bisindole**



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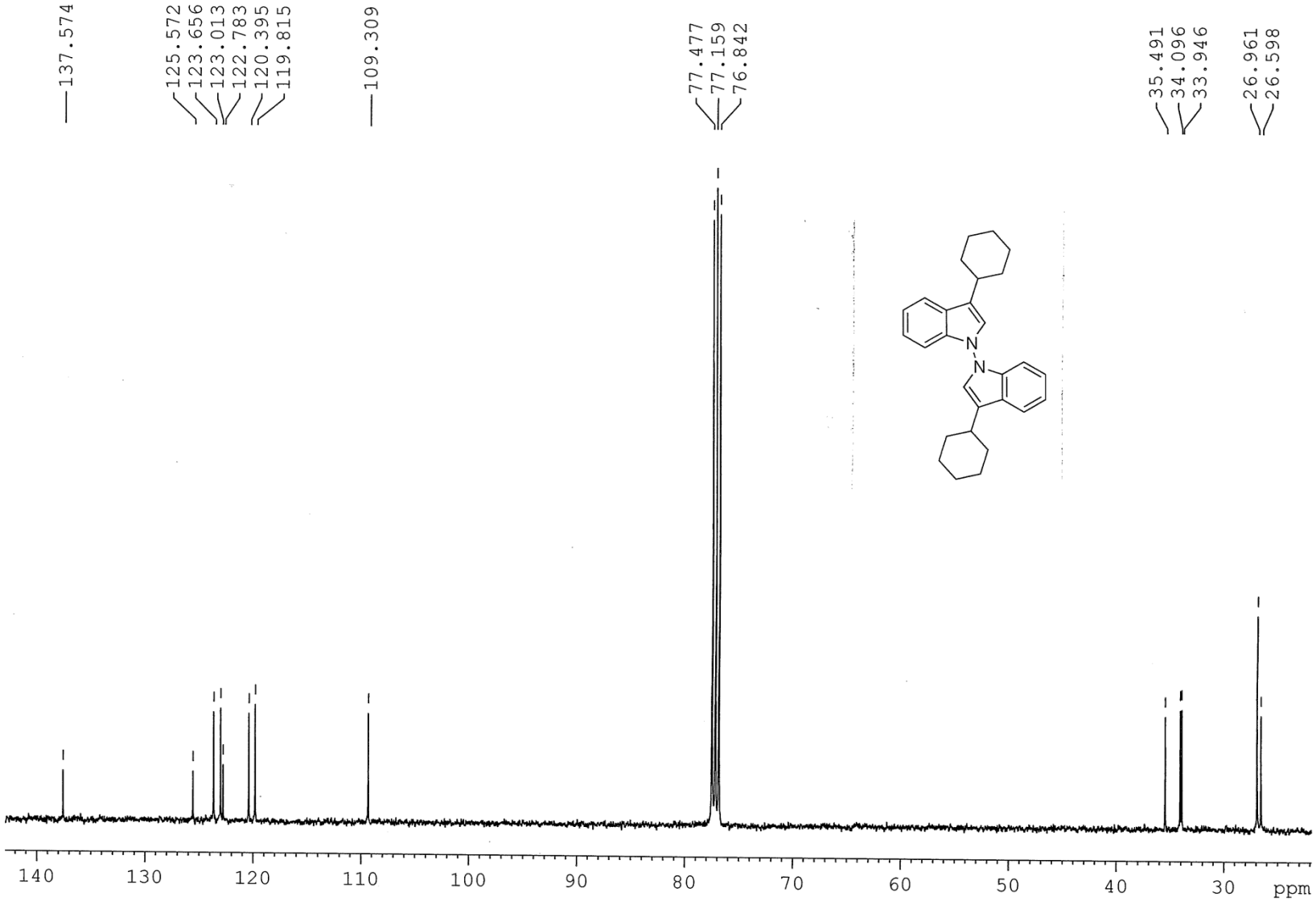
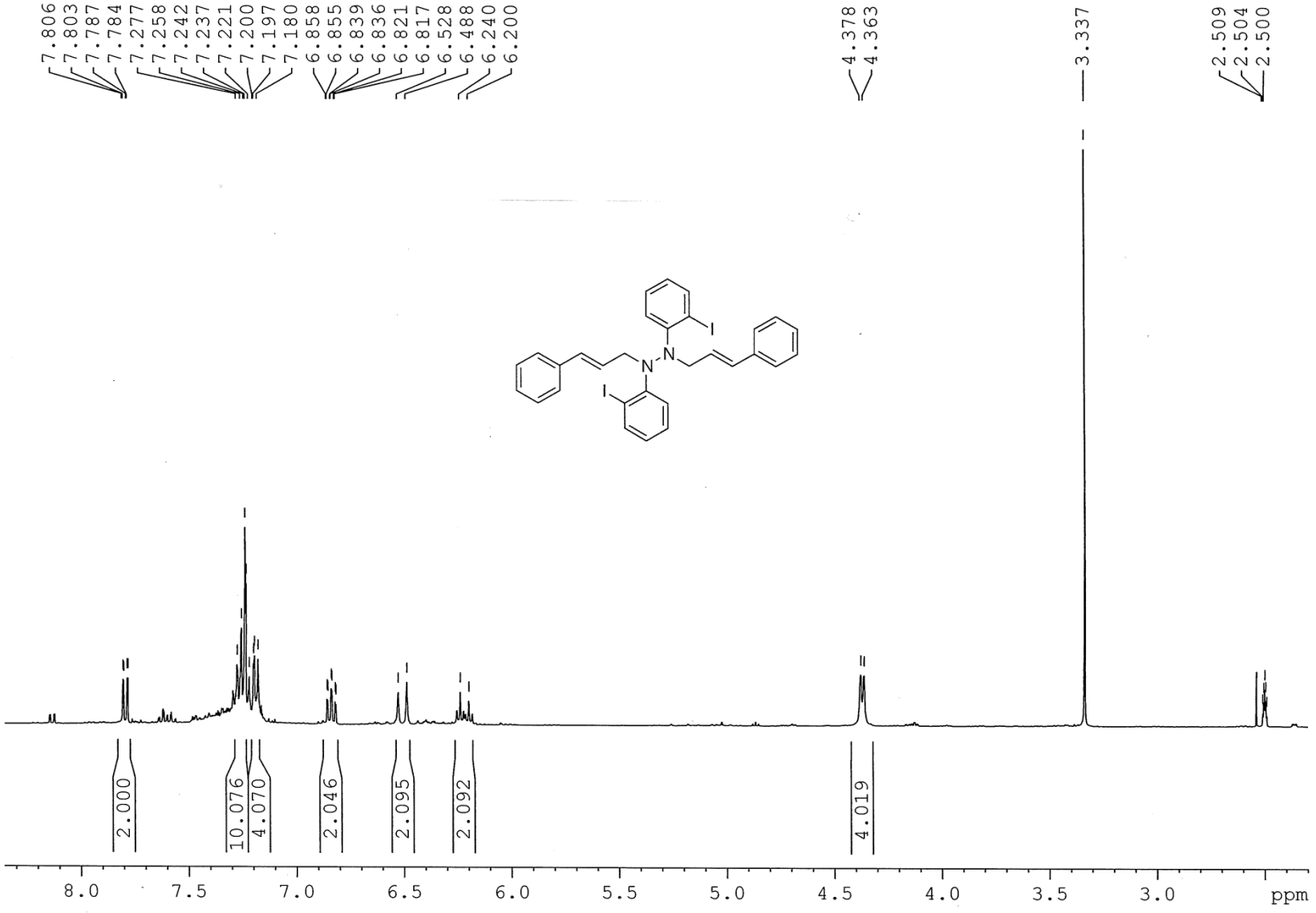


**1,2-Dicinnamyl-1,2-bis(2-iodophenyl)hydrazine**



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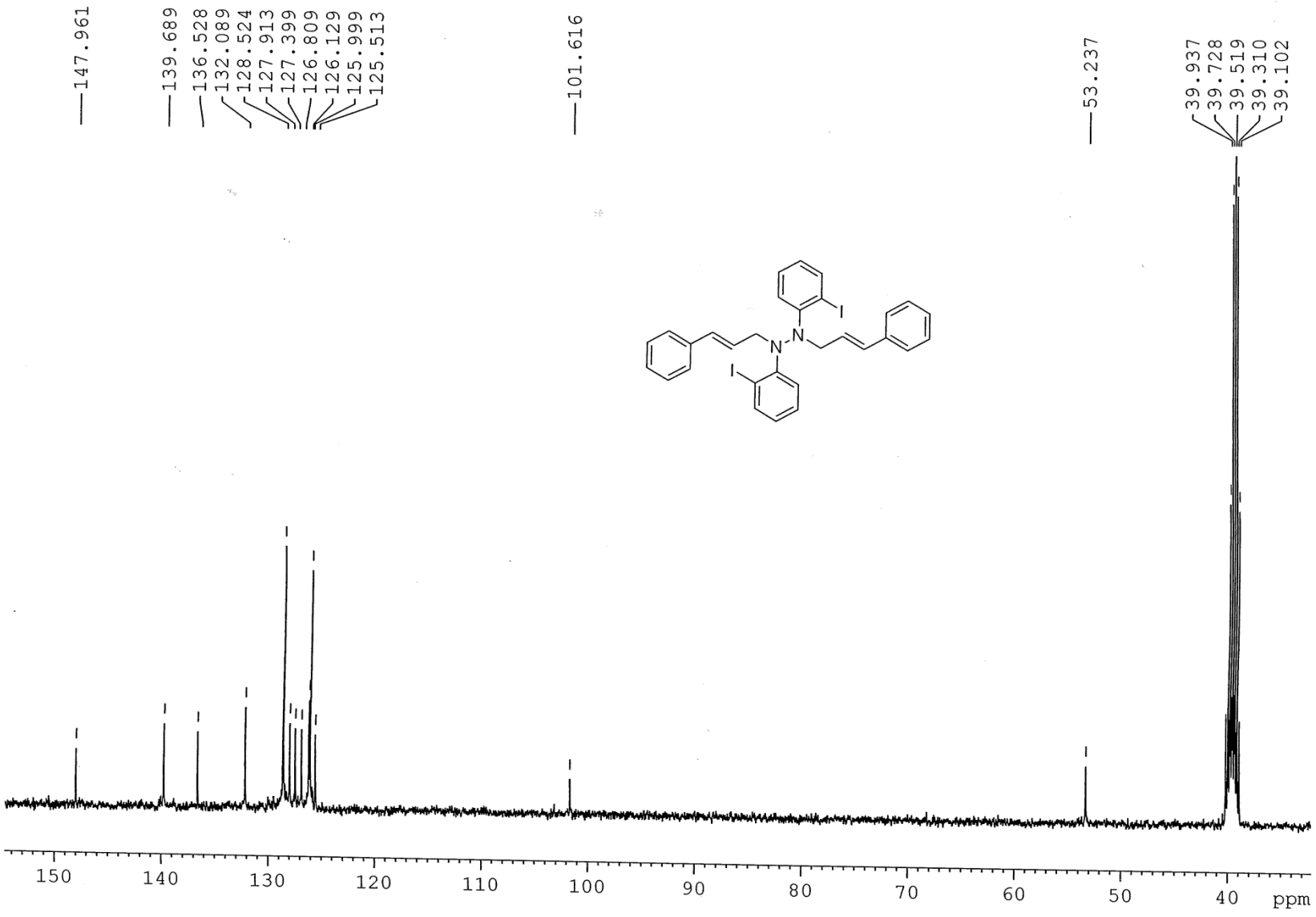

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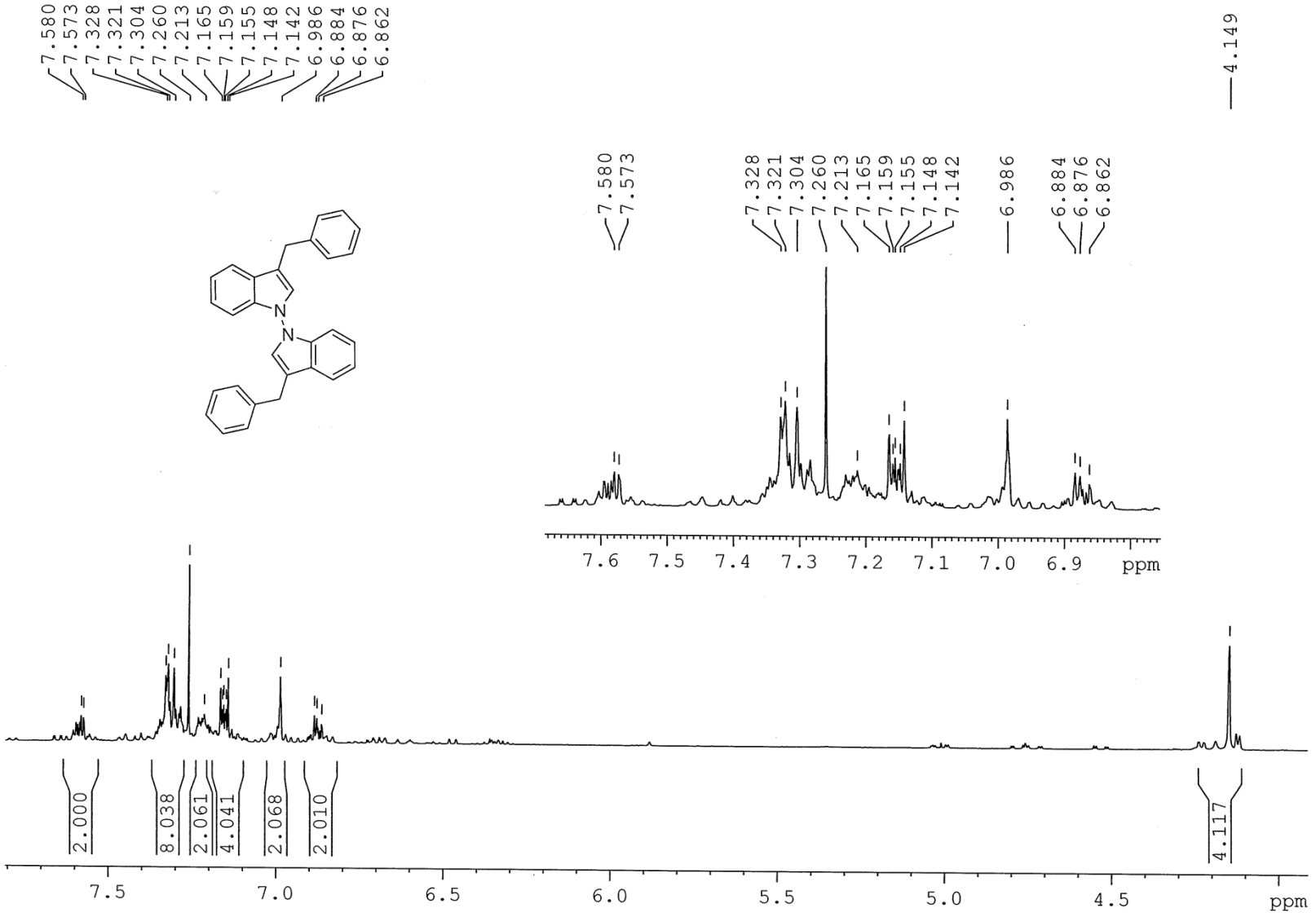

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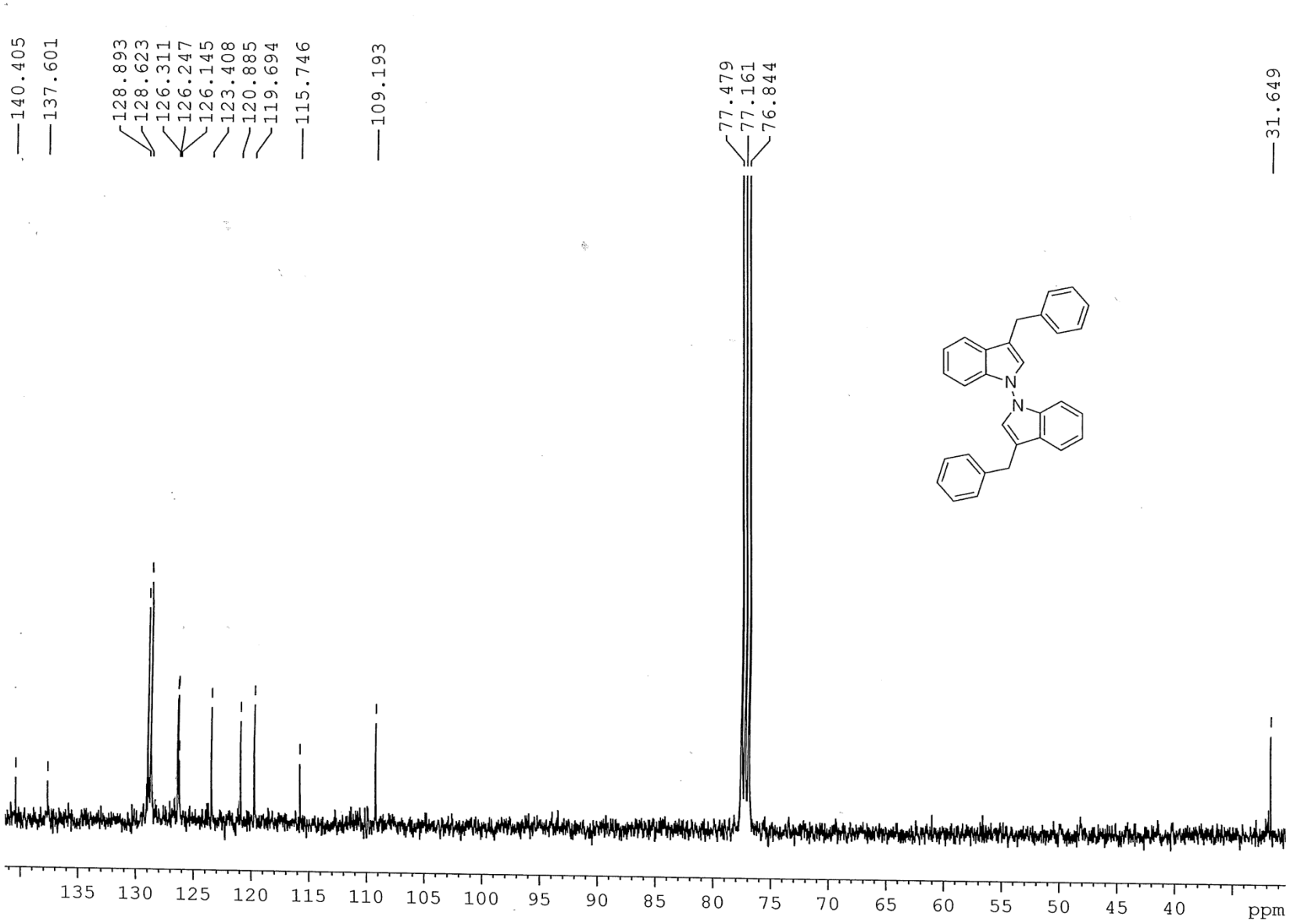
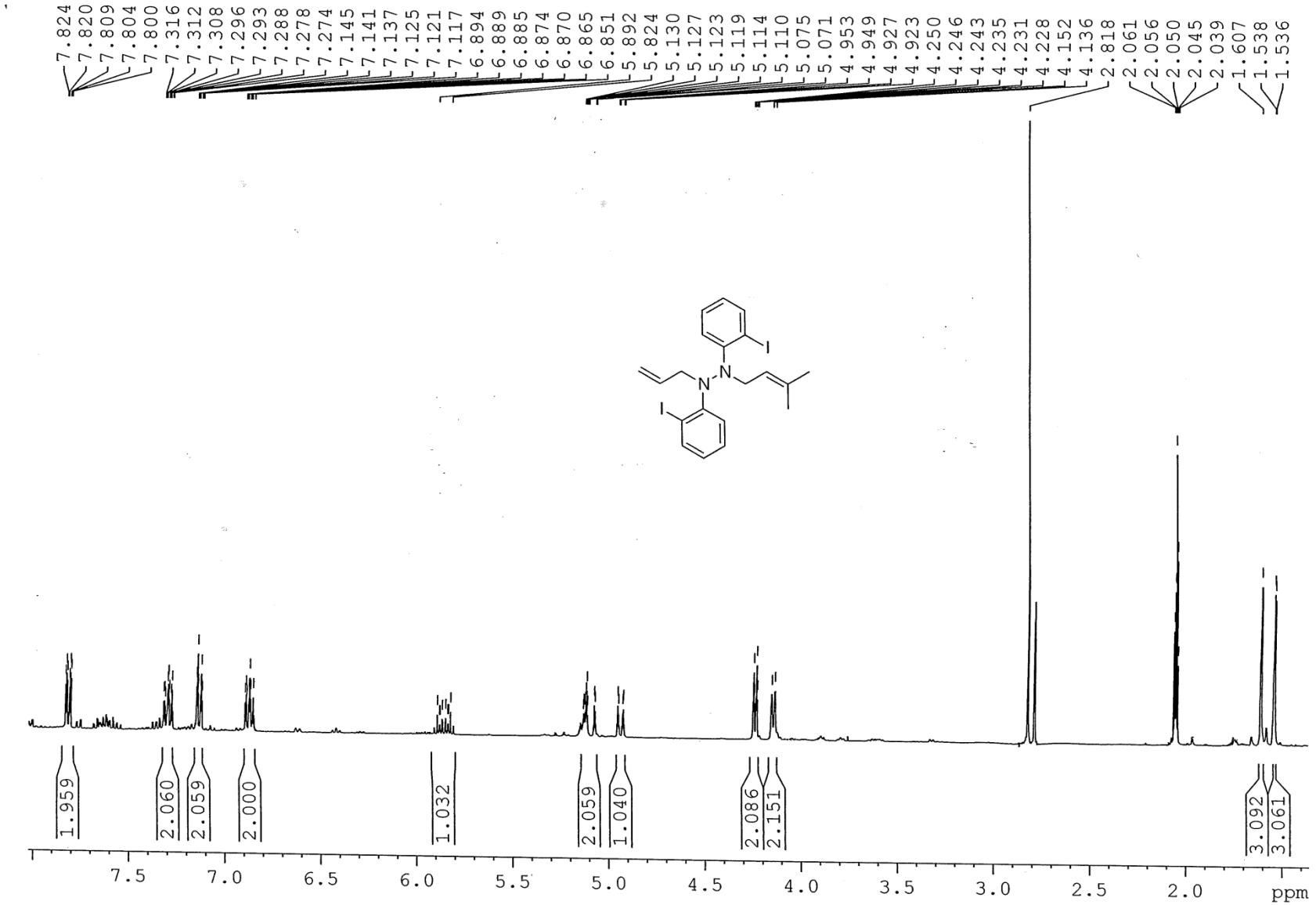
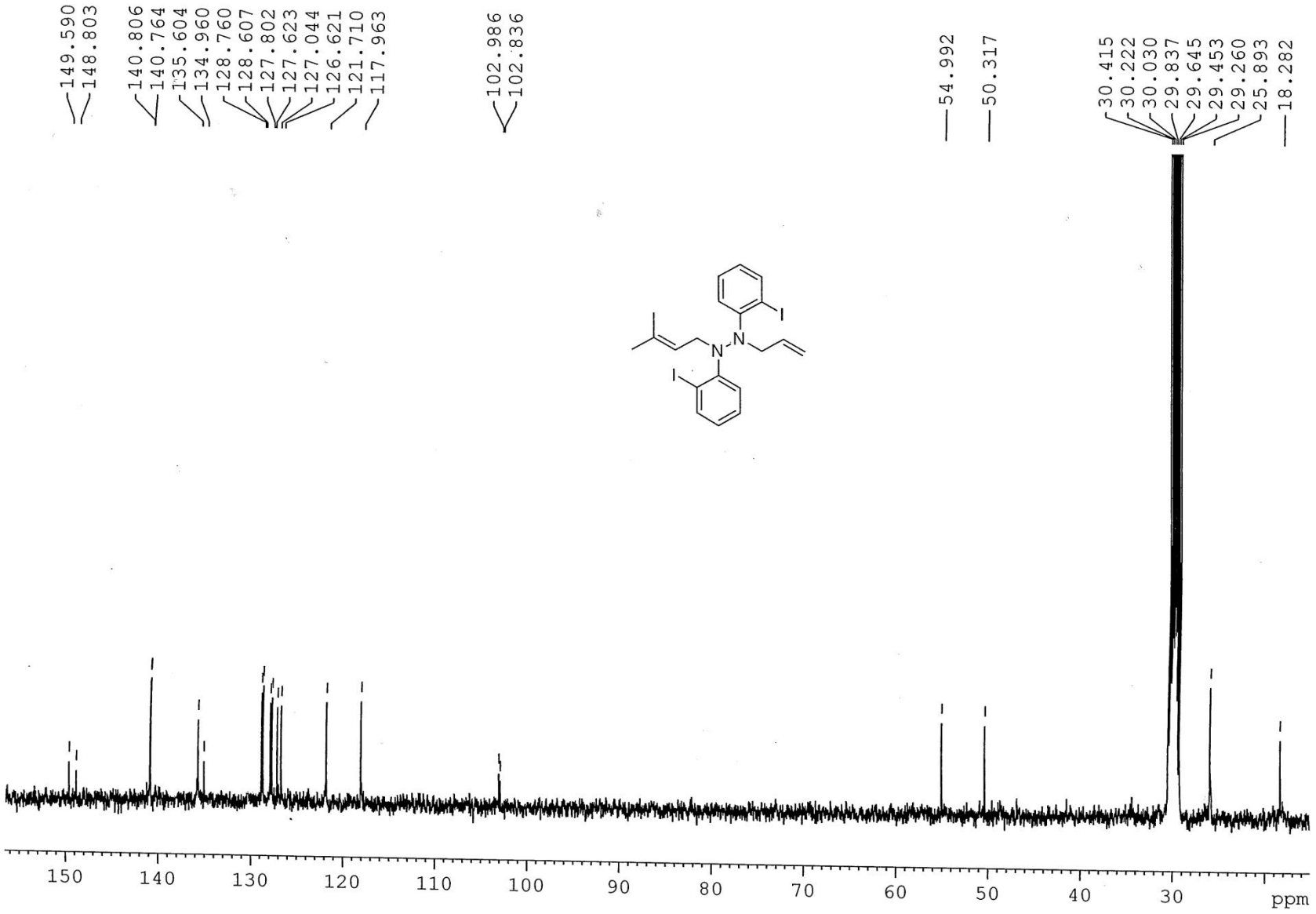


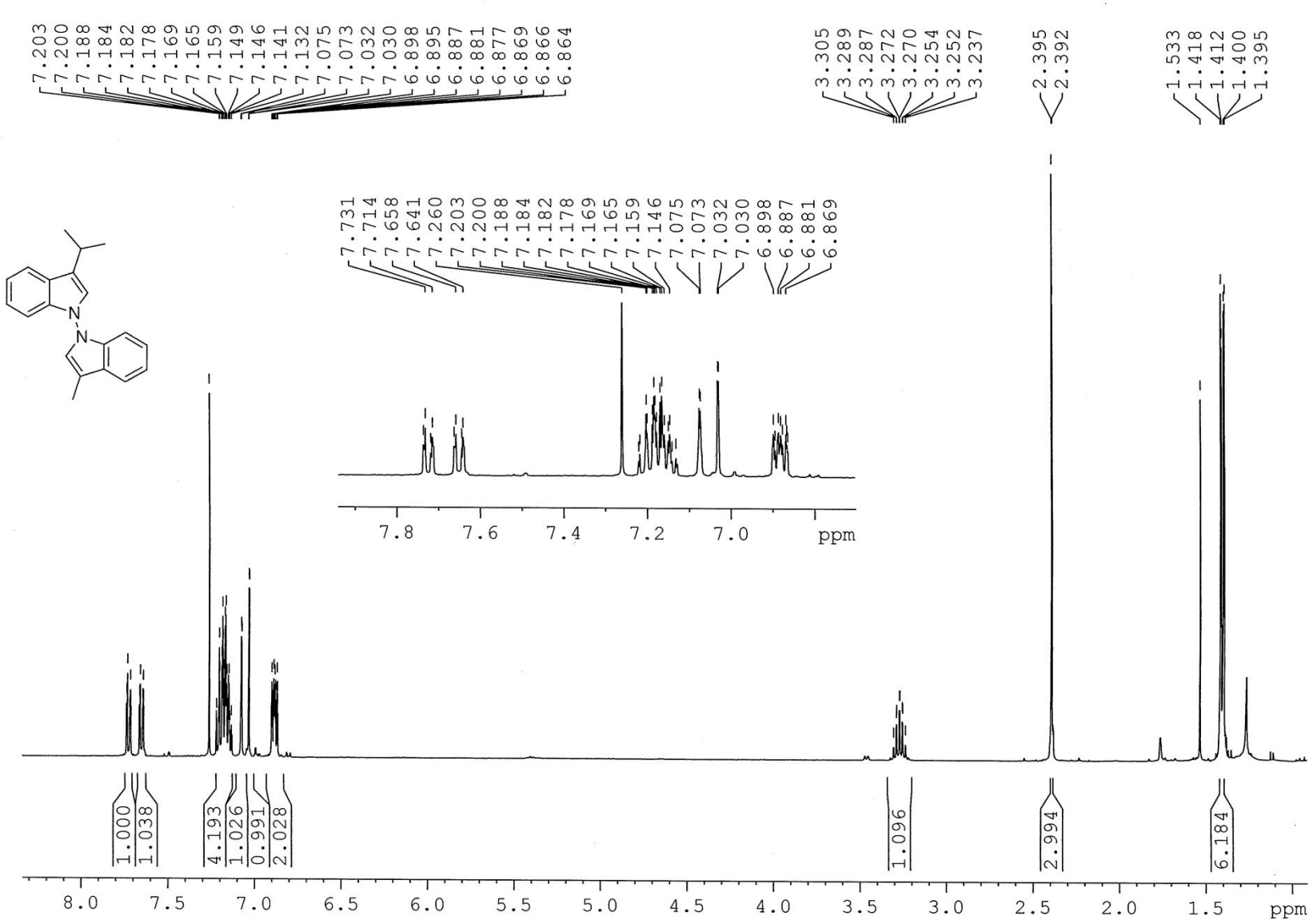
**1-Allyl-1,2-bis(2-iodophenyl)-2-(3-methylbut-2-en-1-yl)hydrazine**



**1-Allyl-1,2-bis(2-iodophenyl)-2-(3-methylbut-2-en-1-yl)hydrazine**



**3-Isopropyl-3'-methyl-1,1'-bisindole**



**3-Isopropyl-3'-methyl-1,1'-bisindole**