Exceptionally Mild Palladium(II)-Catalyzed Dehydrogenative C–H/C–H Arylation of Indolines at the C-7 Position under Air

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Supporting Information

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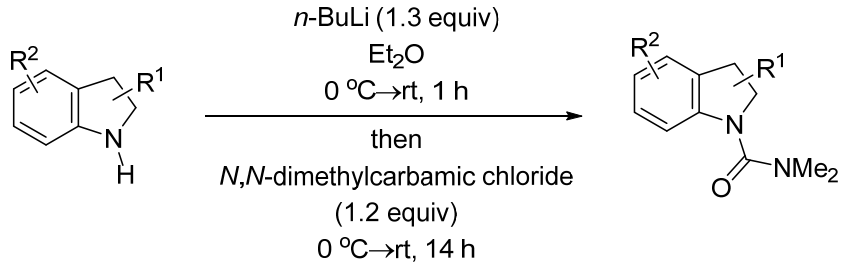
1 General Information

Reactions involving air were conducted open to atmosphere (open flask); other reactions were however performed in flame-dried glassware using conventional Schlenk techniques under a static pressure of nitrogen. Liquids and solutions were transferred with syringes. Solvents were purified and dried following standard procedures. Technical grade solvents for extraction and chromatography (cyclohexane, ethyl acetate, diethyl ether, dichloromethane, *tert*-butyl methyl ether, and pentane) were distilled prior to use. Compounds **1a**–**1e**, **3a**, **5a**–**7a**, and **10a** were prepared according to reported procedures.[S1] Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} glass plates from *Merck*. Flash column chromatography was performed on silica gel 60 (40–63 *μ*m, 230–400 mesh, ASTM) by *Grace GmbH* using the indicated solvents. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ on *Bruker* AV 400 and *Bruker* AV 500 instruments. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 ppm for ^{1}H and $CDCl_3$: δ = 77.16 ppm for ^{13}C). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on an *Agilent Technologies* Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported (br = broad, vw = very weak, w = weak, m = medium, s = strong) in wavenumbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on an *Agilent Technologies* 7820A gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) by *Agilent Technologies* using the following program: N_2 carrier gas, injection temperature 250 °C, detector temperature 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C/min, end temperature 280 °C for 10 min. Melting points (m.p.) were determined with a *Stuart* SMP20 apparatus and are not corrected. High resolution mass spectrometry (HRMS) analyses were performed by the Analytical Facility at the Institut für Chemie of the Technische Universität Berlin.

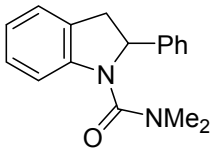
2 Experimental Details for the Synthesis of Indolines

2.1 General Procedure for the Preparation of *N*-Carbamoyl Indolines (GP1)



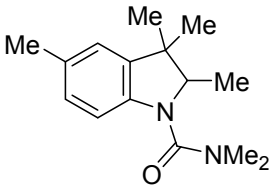
To a stirred solution of indoline (1.0 equiv) in anhydrous diethyl ether (0.2 M) is added dropwise a solution of *n*-BuLi in hexane (1.3 equiv) in an ice bath. The resulting mixture is stirred at room temperature under N_2 for 1 h. The mixture is then cooled to 0 °C and *N*,*N*-dimethylcarbamoyl chloride (1.2 equiv) is added dropwise. After being stirred at room temperature for 14 h, the reaction is quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2 (3 ×). The combined organic phases are washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of cyclohexane and ethyl acetate as eluents affords the analytically pure product.

2.2 Characterization Data of *N*-Carbamoyl Indolines



4a
$C_{17}H_{18}N_2O$
M = 266.34 g/mol

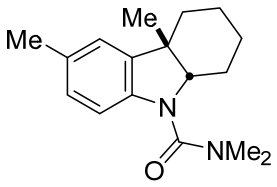
***N*,*N*-Dimethyl-2-phenylindoline-1-carboxamide** (**4a**, Scheme 3): Prepared from 2-phenylindoline (196 mg, 1.0 mmol, 1.00 equiv) and *N*,*N*-dimethylcarbamoyl chloride (130 mg, 1.2 mmol, 1.20 equiv) according to the **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1) afforded the analytically pure product (244 mg, 92%) as a white solid (**m.p.** = 93–94 °C). $\mathbf{R_f}$ = 0.70 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2922 (br), 2850 (w), 1657 (s), 1600 (m), 1475 (s), 1457 (m), 1361 (m), 1241 (m), 1196 (m), 1056 (w), 1002 (w), 944 (w), 842 (vw), 745 (s), 704 (m). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.93 (s, 6H), 3.02 (dd, *J* = 15.7 Hz, *J* = 9.7 Hz, 1H), 3.45 (dd, *J* = 15.7 Hz, *J* = 9.3 Hz, 1H), 5.42 (t, *J* = 9.7 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.90 (dd, *J* = 7.4 Hz, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.16 (dd, *J* = 7.7 Hz, *J* = 7.4 Hz, 1H), 7.23–7.26 (m, 1H), 7.31 (dd, *J* = 7.2 Hz, *J* = 7.2 Hz, 2H), 7.38 (dd, *J* = 8.3 Hz, *J* = 1.1 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 37.7, 38.9, 65.8, 111.6, 121.4, 124.9, 126.6, 127.5, 127.5, 128.7, 129.4, 142.9, 145.3, 159.4 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{17}H_{19}N_2O$): calcd *m/z* 267.1492, found: 267.1482. **GLC** (HP-5): t_R = 20.4 min.



8a
$C_{15}H_{22}N_2O$
M = 246.35 g/mol

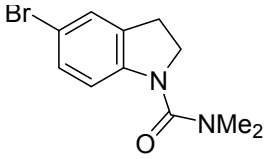
***N*,*N*,2,3,3,5-Hexamethylindoline-1-carboxamide** (**8a**, Scheme 3): Prepared from 2,3,3,5-tetramethylindoline (200 mg, 1.14 mmol, 1.00 equiv) and *N*,*N*-dimethylcarbamoyl chloride (147 mg, 1.37 mmol, 1.20 equiv) according to the **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1) afforded the analytically pure product (257 mg, 92%)

as a yellow solid (**m.p.** = 60–61 °C). $\mathbf{R_f}$ = 0.36 (cyclohexane:ethyl acetate = 3:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2955 (w), 2921 (w), 2863 (w), 1637 (s), 1482 (s), 1445 (m), 1385 (s), 1325 (m), 1262 (m), 1185 (s), 1106 (w), 1040 (w), 943 (w), 895 (w), 820 (m), 771 (w), 716 (w), 686 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.08 (s, 3H), 1.25 (d, *J* = 6.3 Hz, 3H), 1.28 (s, 3H), 2.29 (s, 3H), 2.96 (s, 6H), 3.90 (q, *J* = 6.3 Hz, 1H), 6.57 (d, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.91 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 13.1, 21.0, 23.1, 25.9, 37.8, 42.3, 67.6, 111.4, 123.2, 127.5, 130.6, 140.1, 141.1, 159.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{15}H_{23}N_2O$): calcd *m/z* 247.1805, found: 247.1797. **GLC** (HP-5): t_R = 16.8 min.



9a
$C_{17}H_{24}N_2O$
M = 272.39 g/mol

***cis*-*N*,*N*,4a,6-Tetramethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide** (**9a**, Scheme 3): Prepared from *cis*-4a,6-dimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-carbazole (230 mg, 1.14 mmol, 1.00 equiv) and *N*,*N*-dimethylcarbamoyl chloride (147 mg, 1.37 mmol, 1.20 equiv) according to the **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 2:1→1.5:1) afforded the analytically pure product (279 mg, 90%) as a white solid (**m.p.** = 91–92 °C). $\mathbf{R_f}$ = 0.41 (cyclohexane:ethyl acetate = 1:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2914 (s), 2873 (w), 1658 (s), 1481 (s), 1444 (m), 1383 (s), 1334 (m), 1239 (m), 1188 (s), 1156 (m), 1058 (m), 991 (w), 885 (w), 811 (s), 688 (w). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 1.28 (s, 3H), 1.35–1.43 (m, 4H), 1.50–1.55 (m, 1H), 1.60–1.65 (m, 1H), 1.83–1.87 (m, 2H), 2.30 (s, 3H), 2.96 (s, 6H), 3.80 (t, *J* = 5.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 6.91 (dd, *J* = 8.1 Hz, *J* = 0.5 Hz, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 21.1, 21.8, 21.8, 24.0, 24.9, 35.6, 37.8, 42.1, 68.4, 112.3, 122.6, 127.3, 130.6, 140.4, 141.1, 159.7 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{17}H_{25}N_2O$): calcd *m/z* 273.1961, found: 273.1953. **GLC** (HP-5): t_R = 17.3 min.

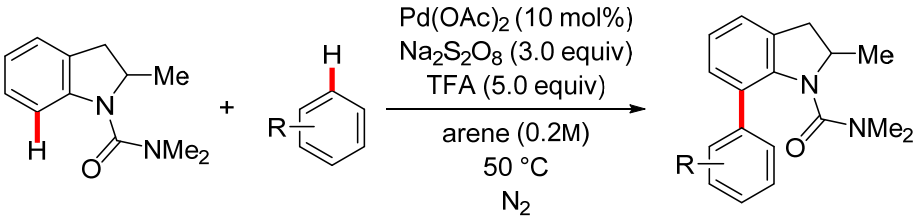


11a
$C_{11}H_{13}BrN_2O$
M = 269.14 g/mol

5-Bromo-*N*,*N*-dimethylindoline-1-carboxamide (**11a**, Scheme 3): Prepared from 5-bromo-indoline (650 mg, 3.28 mmol, 1.00 equiv) and *N*,*N*-dimethylcarbamoyl chloride (1.17 g, 3.93 mmol, 1.20 equiv) according to the **GP1**. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1) afforded the analytically pure product (653 mg, 74%) as a light yellow solid (**m.p.** = 65–66 °C). $\mathbf{R_f}$ = 0.40 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2887 (br), 1646 (s), 1465 (s), 1355 (s), 1248 (m), 1177 (m), 1091 (w), 1053 (w), 1001 (w), 929 (vw), 872 (w), 802 (m), 760 (m), 660 (m). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 2.92 (s, 6H), 3.02 (t, *J* = 8.4 Hz, 2H), 3.90 (t, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.21–7.24 (m, 1H), 7.26–7.27 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 28.1, 38.3, 50.6, 113.6, 115.0, 128.0, 129.9, 133.8, 143.8, 160.1 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{11}H_{14}BrN_2O$): calcd *m/z* 269.0284, found: 269.0277. **GLC** (HP-5): t_R = 15.5 min.

3 Experimental Details for the Palladium(II)-Catalyzed Dehydrogenative C–H/C–H Arylation of Indolines at the C-7 Position under Air

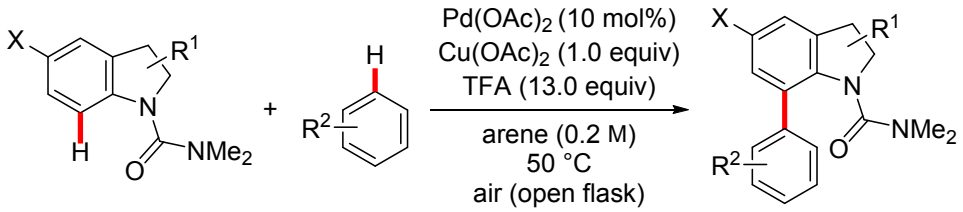
Table S1. C–H/C–H Cross-Coupling of Indoline **2a** and Various Arenes using $Na_2S_2O_8$ as Oxidant



entry	arene	time (h)	conversion (%)[a]	yield (%)
1	***o*-xylene**	**18**	**99**	**83**[b]
2	*p*-xylene	18	85	<5[c]
3	*m*-xylene	18	92	<10[c]
4	benzene	18	97	<19[c]
5	toluene	18	97	<10[c]
6	mesitylene	18	92	<10[c]
7	biphenyl	18	84	<10[c]
8	veratrol	18	78	—[c]
9	*N*,*N*-dimethyl-*o*-toluidine	18	32	—[c]

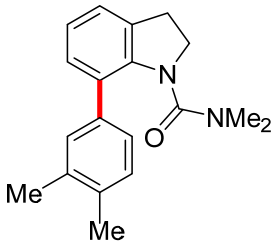
[a]Determined by GLC analysis with tetracosane as internal standard. [b]Isolated yield after purification by flash column chromatography. [c]Decomposition.

3.1 General Procedure for the C-7 Arylation of Indolines (GP2)



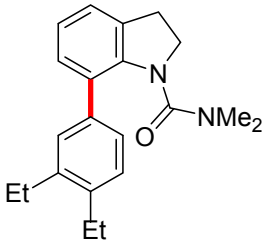
A reaction tube equipped with a magnetic stir bar is successively charged with the indoline (0.20 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.020 mmol, 10 mol %), $Cu(OAc)_2$ (0.20 mmol, 1.0 equiv), trifluoroacetic acid (TFA, 2.6 mmol, 13.0 equiv), and tetracosane (10 mg) as internal standard in the corresponding arene (1.0 mL, 0.2 M). The reaction mixture is stirred at 50 °C in the open air for the indicated reaction time. After complete consumption of the indoline, as monitored by GLC analysis, the reaction mixture is diluted with ethyl acetate (25 mL). The crude reaction mixture is washed with saturated aqueous Na_2CO_3 (8 mL) and H_2O (5 mL). The organic phase is dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using mixtures of cyclohexane and ethyl acetate as eluents affords the analytically pure title product. The regioisomeric ratio was determined by GLC analysis.

3.2 Characterization Data of C-7 Arylation Indolines



2aa
$C_{19}H_{22}N_2O$
M = 294.40 g/mol

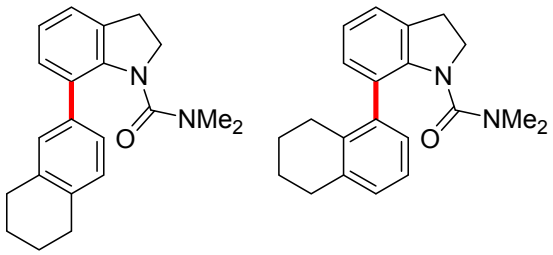
7-(3,4-Dimethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2aa**, Table 1, entries 1–15, Schemes 2–4): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 18 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1.5→1:2) afforded the analytically pure product (48 mg, 81%) as a brown solid (**m.p.** = 132–133 °C). $\mathbf{R_f}$ = 0.21 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2916 (br), 2849 (br), 1653 (s), 1589 (w), 1434 (m), 1376 (s), 1257 (m), 1165 (m), 1102 (w), 1061 (w), 1004 (w), 884 (vw), 811 (w), 776 (m), 761 (s), 677 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.26 (s, 3H), 2.28 (s, 3H), 2.61 (s, 6H), 3.10 (t, *J* = 7.8 Hz, 2H), 3.97 (t, *J* = 7.8 Hz, 2H), 7.01 (dd, *J* = 7.5 Hz, *J* = 7.4 Hz, 1H), 7.11–7.14 (m, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.24 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.6, 20.0, 29.9, 36.9, 52.0, 123.1, 123.4, 124.4, 128.2, 129.0, 129.2, 129.6, 133.7, 135.0, 136.2, 137.9, 142.4, 159.9 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{19}H_{23}N_2O$): calcd *m/z* 295.1805, found: 295.1805. **GLC** (HP-5): t_R = 22.1 min.



2ab
$C_{21}H_{26}N_2O$
M = 322.45 g/mol

7-(3,4-Diethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ab**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and 1,2-diethylbenzene

(1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 20 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 2:1) afforded the analytically pure product (40 mg, 62%) as a brown oil. $\mathbf{R_f}$ = 0.23 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2962 (w), 2929 (w), 2872 (w), 1640 (s), 1443 (s), 1380 (s), 1293 (m), 1258 (m), 1170 (m), 1059 (w), 907 (w), 832 (w), 721 (s). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.23 (t, *J* = 7.6 Hz, 6H), 2.50 (s, 6H), 2.66 (q, *J* = 7.6 Hz, 4H), 3.08 (t, *J* = 8.1 Hz, 2H), 3.99 (t, *J* = 8.1 Hz, 2H), 6.99 (dd, *J* = 7.6 Hz, *J* = 7.4 Hz, 1H), 7.13–7.17 (m, 2H), 7.18 (s, 1H), 7.21–7.23 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 15.5, 15.6, 25.3, 25.8, 29.7, 36.9, 52.0, 122.9, 123.5, 124.8, 127.1, 128.5, 129.1, 129.3, 133.7, 137.8, 140.3, 141.5, 142.2, 159.4 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{21}H_{27}N_2O$): calcd *m/z* 323.2118, found: 323.2115. **GLC** (HP-5): t_R = 22.3 min.

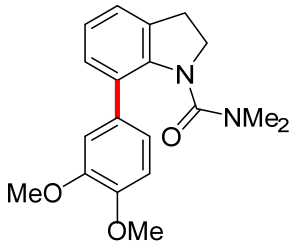


2ac $C_{21}H_{24}N_2O$ M = 320.44 g/mol

2ac' $C_{21}H_{24}N_2O$ M = 320.44 g/mol

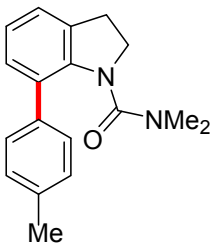
***N,N*-Dimethyl-7-(5,6,7,8-tetrahydronaphthalen-2-yl)indoline-1-carboxamide** (**2ac**, Scheme 2) and *N*,*N*-dimethyl-7-(5,6,7,8-tetrahydronaphthalen-1-yl)indoline-1-carboxamide (**2ac'**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and 1,2,3,4-tetrahydronaphthalene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 44 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1→3:1) afforded the analytically pure product (**2ac**, 12 mg, 18%; ratio of regioisomers: **2ac**:**2ac'** = 89:11; **2ac'** not isolated) as a light green oil. $\mathbf{R_f}$ = 0.35 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2922 (br), 1635 (s), 1588 (m), 1432 (m), 1384 (s), 1255 (m), 1166 (m), 1100 (w), 883 (m), 810 (w), 765 (s), 670 (m). NMR spectroscopic data for **2ac** (major product): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 1.78–1.81 (m, 4H), 2.60 (s, 6H), 2.75–2.78 (m, 4H), 3.09 (t, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.11–7.21 (m, 4H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 23.5, 29.3, 29.7, 29.9, 37.0, 52.3, 123.1, 123.5, 124.3, 127.5, 129.4, 129.2, 129.3, 133.8, 135.8, 136.9, 137.4, 142.4, 159.9 ppm. **HRMS** (APCI)

exact mass for $[M+H]^+$ ($C_{21}H_{25}N_2O$): calcd *m/z* 321.1961, found: 321.1955. **GLC** (HP-5): t_R = 24.6 min (**2ac**), t_R = 23.4 min (**2ac'**).

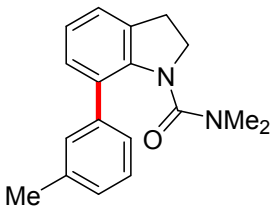


2ad
$C_{19}H_{22}N_2O_3$
M = 326.40 g/mol

7-(3,4-Dimethoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ad**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and veratrol (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 52 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:4) afforded the analytically pure product (12 mg, 18%) as a brown oil. $\mathbf{R_f}$ = 0.17 (cyclohexane:ethyl acetate = 1:3). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2931 (br), 1625 (s), 1516 (m), 1442 (m), 1392 (s), 1245 (m), 1203 (m), 1171 (m), 1136 (s), 1023 (m), 911 (w), 800 (w), 761 (m), 722 (m). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 2.60 (s, 6H), 3.10 (t, *J* = 8.0 Hz, 2H), 3.87 (s, 3H), 3.89 (s, 3H), 3.99 (t, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.95–6.96 (m, 1H), 7.00 (d, *J* = 5.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 7.14 (s, 1H), 7.16 (s, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 29.8, 37.1, 52.1, 56.0, 77.5, 110.5, 111.2, 119.6, 123.3, 123.5, 129.1, 129.1, 133.2, 134.0, 142.1, 148.1, 148.7, 159.9 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{19}H_{23}N_2O_3$): calcd *m/z* 327.1703, found: 327.1699. **GLC** (HP-5): t_R = 23.7 min.



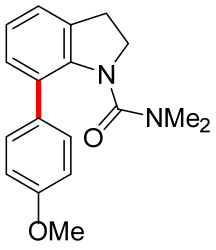
2ae
$C_{18}H_{20}N_2O$
M = 280.37 g/mol



2ae'
$C_{18}H_{20}N_2O$
M = 280.37 g/mol

***N*,*N*-Dimethyl-7-(4-tolyl)indoline-1-carboxamide** (**2ae**, Scheme 2) and ***N*,*N*-dimethyl-7-(3-tolyl)indoline-1-carboxamide** (**2ae'**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and toluene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 24 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:2) afforded the product as a mixture of regioisomers (**2ae**:**2ae'** = 62:38) as a light yellow solid (39 mg, 70% combined yield). $\mathbf{R_f}$ = 0.31 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2920 (br), 1735 (vw), 1656 (s), 1439 (m), 1372 (s), 1273 (m), 1168 (m), 1104 (w), 1063 (w), 998 (w), 907 (w), 823 (w), 762 (m), 737 (m). NMR spectroscopic data for **2ae** (major product): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 2.35 (s, 3H), 2.57 (s, 6H), 3.10 (t, *J* = 8.0 Hz, 2H), 3.96 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 7.13–7.15 (m, 2H), 7.25 (d, *J* = 5.2 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 21.3, 29.9, 37.0, 52.0, 123.1, 123.5, 124.2, 127.0, 127.8, 129.0, 129.1, 129.3, 133.8, 137.5, 159.8 ppm.

NMR spectroscopic data for **2ae'** (minor product): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 2.36 (s, 3H), 2.57 (s, 6H), 3.10 (t, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 7.05–7.08 (m, 1H), 7.14–7.17 (m, 4H), 7.13–7.15 (m, 1H) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 21.7, 29.9, 37.0, 52.0, 123.0, 123.7, 127.6, 128.3, 129.1, 129.2, 129.3, 133.8, 136.4, 137.8, 140.3, 142.4, 159.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{18}H_{21}N_2O$): calcd *m/z* 281.1648, found: 281.1641. **GLC** (HP-5): t_R = 21.3 min (**2ae**), t_R = 21.2 min (**2ae'**).



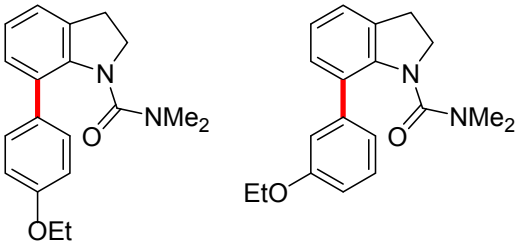
2af

$C_{18}H_{20}N_2O_2$

M = 296.37 g/mol

7-(4-Methoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2af**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and anisol (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 18 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1→1:2) afforded the analytically pure product (40 mg, 68%) as a brown oil. $\mathbf{R_f}$ = 0.24 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2929 (br), 1655 (s), 1641 (s), 1511 (m), 1439 (m), 1379 (s), 1288 (m), 1241 (s), 1173 (m), 1105 (w), 1063 (w),

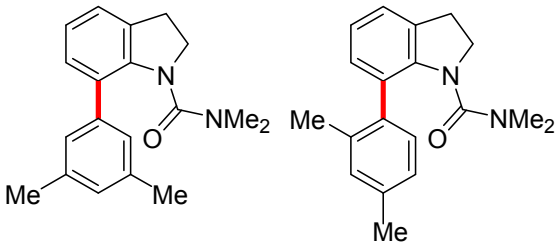
1026 (m), 902 (w), 830 (m), 759 (w), 736 (m). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.59 (s, 6H), 3.09 (t, *J* = 8.0 Hz, 2H), 3.81 (s, 3H), 3.95 (t, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 6.9 Hz, 2H), 7.00 (dd, *J* = 7.3 Hz, *J* = 7.0 Hz, 1H), 7.12 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 6.7 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 29.9, 37.0, 52.0, 55.3, 113.8, 123.2, 123.4, 128.2, 128.9, 129.1, 133.0, 133.8, 142.4, 158.6, 159.9 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{18}H_{21}N_2O_2$): calcd *m/z* 297.1598, found: 297.1589. **GLC** (HP-5): t_R = 22.6 min.



2ag $C_{19}H_{22}N_2O_2$ M = 310.40 g/mol

2ag' $C_{19}H_{22}N_2O_2$ M = 310.40 g/mol

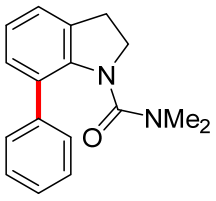
7-(4-Ethoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ag**, Scheme 2) and **7-(3-ethoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide** (**2ag'**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and ethyl benzene ether (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 24 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:2) afforded the product as a mixture of regioisomers (**2ag**:**2ag'** = 94:6) as a light yellow oil (52 mg, 84% combined yield). $\mathbf{R_f}$ = 0.27 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2976 (w), 2927 (w), 2878 (w), 1735 (w), 1655 (s), 1512 (m), 1440 (m), 1376 (s), 1278 (m), 1238 (s), 1172 (m), 1113 (w), 1043 (m), 920 (w), 829 (m), 765 (m), 729 (m), 681 (w). NMR spectroscopic data for **2ag** (major product): **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ = 1.42 (t, *J* = 7.0 Hz, 3H), 2.58 (s, 6H), 3.09 (t, *J* = 8.0 Hz, 2H), 3.96 (t, *J* = 8.0 Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.11–7.14 (m, 2H), 7.34 (d, *J* = 8.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ = 15.0, 29.9, 37.0, 52.0, 63.5, 114.3, 123.1, 123.3, 128.2, 129.0, 129.1, 132.8, 133.8, 142.4, 157.9, 159.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{19}H_{23}N_2O_2$): calcd *m/z* 311.1754, found: 311.1746. **GLC** (HP-5): t_R = 23.1 min (**2ag**), t_R = 22.6 min (**2ag'**).



2ah
$C_{19}H_{22}N_2O$
M = 294.40 g/mol

2ah'
$C_{19}H_{22}N_2O$
M = 294.40 g/mol

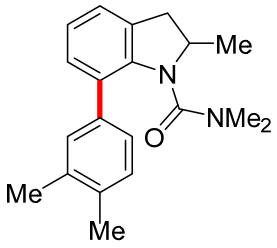
7-(3,5-Dimethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ah**, Scheme 2) and **7-(2,4-dimethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide** (**2ah'**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and *m*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 44 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1→1:2) afforded the product as a mixture of regioisomers (**2ah**:**2ah'** = 69:31) as a white solid (32 mg, 55% combined yield). $\mathbf{R_f}$ = 0.29 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2906 (br), 1735 (vw), 1661 (s), 1588 (w), 1449 (w), 1370 (s), 1287 (w), 1224 (w), 1157 (m), 1082 (w), 1048 (w), 994 (w), 925 (w), 850 (m), 794 (s), 761 (s), 702 (m). NMR spectroscopic data for **2ah** (major product): **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.32 (s, 6H), 2.60 (s, 6H), 3.09 (t, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 8.0 Hz, 2H), 6.89 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 7.08 (s, 2H), 7.13–7.18 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 21.6, 29.9, 37.0, 52.0, 123.0, 123.6, 124.9, 128.5, 129.1, 129.2, 133.8, 137.7, 140.1, 142.4, 159.9 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{19}H_{23}N_2O$): calcd *m/z* 295.1805, found: 295.1797. **GLC** (HP-5): t_R = 21.6 min (**2ah**), t_R = 21.0 min (**2ah'**).



2ak
$C_{17}H_{18}N_2O$
M = 266.34 g/mol

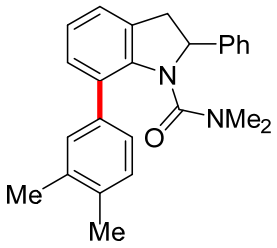
***N*,*N*-Dimethyl-7-phenylindoline-1-carboxamide** (**2ak**, Scheme 2): Prepared from *N*,*N*-dimethylindoline-1-carboxamide (**1a**, 38 mg, 0.20 mmol, 1.0 equiv) and benzene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 20 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1→1:2) afforded the analytically pure product (38 mg, 71%) as a

light yellow solid (**m.p.** = 140–141 °C). $\mathbf{R_f}$ = 0.35 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2917 (br), 1736 (vw), 1650 (s), 1455 (m), 1376 (s), 1265 (m), 1219 (m), 1169 (m), 1102 (s), 1069 (w), 1024 (w), 962 (w), 895 (w), 753 (s), 700 (s). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.54 (s, 6H), 3.10 (t, *J* = 8.0 Hz, 2H), 3.97 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.14–7.18 (m, 2H), 7.24–7.27 (m, 1H), 7.34–7.37 (m, 2H), 7.42–7.45 (m, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 29.8, 36.9, 52.0, 123.1, 123.8, 126.8, 127.2, 128.3, 129.1, 129.2, 133.8, 140.5, 142.5, 159.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{17}H_{19}N_2O$): calcd *m/z* 267.1492, found: 267.1482. **GLC** (HP-5): t_R = 20.6 min.



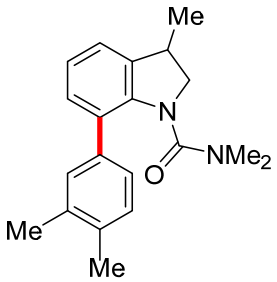
12aa
$C_{20}H_{24}N_2O$
M = 308.43 g/mol

7-(3,4-Dimethylphenyl)-*N*,*N*,2-trimethylindoline-1-carboxamide (**12aa**, Scheme 3): Prepared from *N*,*N*,2-trimethylindoline-1-carboxamide (**3a**, 41 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 18 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1→3:1) afforded the analytically pure product (56 mg, 90%) as a yellow oil. $\mathbf{R_f}$ = 0.35 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2919 (br), 1736 (vw), 1639 (s), 1486 (m), 1434 (s), 1381 (s), 1271 (s), 1212 (m), 1105 (w), 1061 (w), 1031 (w), 959 (w), 886 (w), 821 (w), 772 (m), 744 (m), 687 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.44 (d, *J* = 6.0 Hz, 3H), 2.26 (s, 6H), 2.29 (s, 6H), 2.60 (dd, *J* = 15.3 Hz, *J* = 3.6 Hz, 1H), 3.27 (dd, *J* = 15.3 Hz, *J* = 8.0 Hz, 1H), 4.35–4.41 (m, 1H), 6.95 (dd, *J* = 7.5 Hz, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.11–7.14 (m, 3H), 7.17 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.5, 19.9, 20.5, 36.6, 37.3, 59.3, 122.2, 123.9, 124.7, 128.1, 128.5, 129.4, 129.5, 132.3, 135.2, 136.3, 137.3, 141.3, 158.4 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{20}H_{25}N_2O$): calcd *m/z* 309.1961, found: 309.1956. **GLC** (HP-5): t_R = 21.6 min.



13aa
$C_{25}H_{26}N_2O$
M = 370.50 g/mol

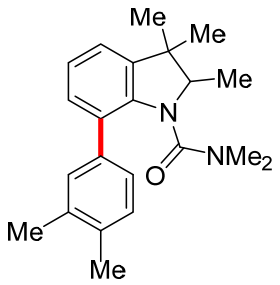
7-(3,4-Dimethylphenyl)-*N*,*N*-dimethyl-2-phenylindoline-1-carboxamide (**13aa**, Scheme 3): Prepared from *N*,*N*-dimethyl-2-phenylindoline-1-carboxamide (**4a**, 53 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 48 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 3:1→2:1) afforded the analytically pure product (14 mg, 18%) as a yellow oil. $\mathbf{R_f}$ = 0.31 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 3025 (w), 2922 (br), 1735 (w), 1661 (s), 1489 (m), 1438 (s), 1380 (s), 1261 (m), 1181 (m), 1063 (w), 1018 (w), 881 (w), 799 (w), 769 (m), 700 (m). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.25 (s, 3H), 2.26 (s, 3H), 2.41 (s, 6H), 2.99 (dd, *J* = 16.0 Hz, *J* = 4.8 Hz, 1H), 3.68 (dd, *J* = 15.2 Hz, *J* = 8.8 Hz, 1H), 5.21 (dd, *J* = 9.1 Hz, *J* = 4.3 Hz, 1H), 7.03 (dd, *J* = 7.6 Hz, *J* = 7.4 Hz, 1H), 7.11 (dd, *J* = 7.7 Hz, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.23–7.27 (m, 2H), 7.30–7.34 (m, 3H), 7.39 (d, *J* = 7.3 Hz, 2H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.6, 20.0, 37.1, 39.9, 67.2, 123.3, 123.8, 124.7, 126.2, 127.5, 128.6, 128.8, 128.9, 129.5, 129.6, 132.0, 135.2, 136.3, 137.6, 143.1, 143.7, 160.1 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{25}H_{27}N_2O$): calcd *m/z* 371.2118, found: 371.2112. **GLC** (HP-5): t_R = 26.0 min.



14aa
$C_{20}H_{24}N_2O$
M = 308.43 g/mol

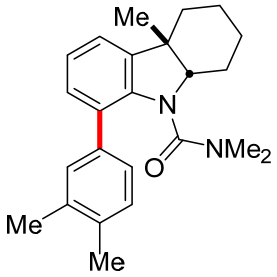
7-(3,4-Dimethylphenyl)-*N*,*N*,3-trimethylindoline-1-carboxamide (**14aa**, Scheme 3): Prepared from *N*,*N*,3-trimethylindoline-1-carboxamide (**5a**, 53 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0

mL, 0.2 M) according to the **GP2** at 50 °C for 26 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1→1:1.5) afforded the analytically pure product (41 mg, 67%) as a yellow oil. $\mathbf{R_f}$ = 0.36 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2921 (br), 2864 (w), 1782 (vw), 1652 (s), 1437 (s), 1377 (s), 1276 (m), 1173 (m), 1128 (w), 1162 (w), 906 (w), 786 (s), 727 (s). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.34 (d, *J* = 6.6 Hz, 3H), 2.26 (s, 3H), 2.27 (s, 3H), 2.57 (s, 6H), 3.40 (dd, *J* = 14.5 Hz, *J* = 7.5 Hz, 1H), 3.55 (dd, *J* = 10.0 Hz, *J* = 7.9 Hz, 1H), 4.08 (dd, *J* = 9.7 Hz, *J* = 8.5 Hz, 1H), 7.03 (dd, *J* = 7.5 Hz, *J* = 7.3 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 7.16–7.20 (m, 2H), 7.23 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 18.9, 19.6, 20.0, 36.4, 37.0, 59.9, 122.2, 123.2, 124.5, 128.3, 129.2, 129.2, 129.7, 135.1, 136.3, 137.9, 138.9, 142.0, 159.8 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{20}H_{25}N_2O$): calcd *m/z* 309.1961, found: 309.1956. **GLC** (HP-5): t_R = 22.2 min.



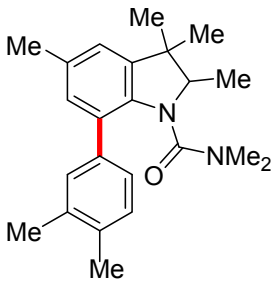
15aa
$C_{22}H_{28}N_2O$
M = 326.48 g/mol

7-(3,4-Dimethylphenyl)-*N*,*N*,2,3,3-pentamethylindoline-1-carboxamide (**15aa**, Scheme 3): Prepared from *N*,*N*,2,3,3-pentamethylindoline-1-carboxamide (**6a**, 46 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 24 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 3:1→2:1) afforded the analytically pure product (46 mg, 71%) as a brown oil. $\mathbf{R_f}$ = 0.36 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2961 (w), 2921 (w), 2863 (w), 1775 (vw), 1639 (s), 1488 (m), 1431 (s), 1383 (s), 1281 (w), 1206 (w), 1165 (m), 1036 (w), 908 (w), 822 (w), 789 (w), 728 (s). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.21 (br s, 3H), 1.28 (s, 3H), 1.36 (d, *J* = 6.6 Hz, 3H), 2.24 (br s, 6H), 2.27 (s, 3H), 2.29 (s, 3H), 3.97 (q, *J* = 6.6 Hz, 1H), 6.99 (dd, *J* = 7.5 Hz, *J* = 7.3 Hz, 1H), 7.05–7.11 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 14.7, 19.5, 19.9, 21.8, 36.5, 37.8, 43.2, 69.6, 121.3, 122.4, 124.8, 127.6, 128.7, 129.5, 129.7, 129.9, 135.3, 136.3, 137.2, 141.6, 158.1 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{22}H_{29}N_2O$): calcd *m/z* 327.2274, found: 327.2267. **GLC** (HP-5): t_R = 22.3 min.



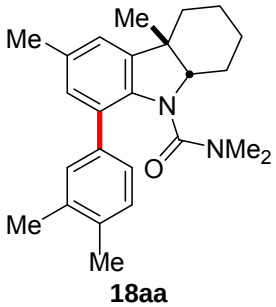
16aa
$C_{24}H_{30}N_2O$
M = 363.52 g/mol

***cis*-8-(3,4-Dimethylphenyl)-*N*,*N*,4a-trimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide** (**16aa**, Scheme 3): Prepared from *cis*-*N*,*N*,4a-trimethyl-2,3,4,4a-tetrahydro-1*H*-carbazole-9(9a*H*)-carboxamide (**7a**, 52 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 24 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1→3:1) afforded the analytically pure product (55 mg, 75%) as a brown oil. $\mathbf{R_f}$ = 0.45 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 3016 (w), 2922 (w), 2854 (w), 1637 (s), 1488 (m), 1431 (s), 1383 (s), 1265 (m), 1180 (m), 1064 (w), 987 (w), 908 (w), 824 (w), 787 (w), 727 (s). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.23 (s, 3H), 1.25–1.31 (m, 3H), 1.51–1.59 (m, 4H), 2.04–2.08 (m, 1H), 2.26 (s, 3H), 2.29 (s, 3H), 2.30 (br s, 6H), 3.83 (dd, *J* = 8.1 Hz, *J* = 5.7 Hz, 1H), 7.00 (dd, *J* = 7.3 Hz, *J* = 7.3 Hz, 1H), 7.04 (dd, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 7.09 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 7.12 (s, 1H), 7.12–7.14 (m, 1H), 7.16 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.5, 19.9, 22.2, 22.7, 26.8, 28.0, 34.2, 36.6, 43.4, 70.3, 120.6, 122.4, 124.8, 128.6, 128.6, 129.4, 129.5, 135.2, 136.2, 137.3, 140.3, 140.9, 158.2 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{24}H_{31}N_2O$): calcd *m/z* 363.2431, found: 363.2424. **GLC** (HP-5): t_R = 24.6 min.



17aa
$C_{23}H_{30}N_2O$
M = 350.51 g/mol

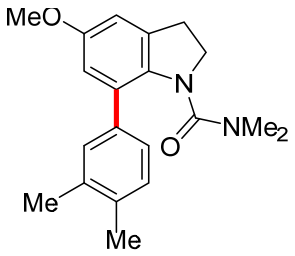
7-(3,4-Dimethylphenyl)-*N*,*N*,2,3,3,5-hexamethylindoline-1-carboxamide (**17aa**, Scheme 3): Prepared from *N*,*N*,2,3,3,5-hexamethylindoline-1-carboxamide (**8a**, 49 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 44 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1→3:1) afforded the analytically pure product (31 mg, 44%) as a brown oil. $\mathbf{R_f}$ = 0.40 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2919 (w), 2859 (w), 1639 (s), 1444 (m), 1381 (s), 1282 (m), 1229 (m), 1171 (m), 1114 (w), 1030 (w), 961 (w), 859 (w), 820 (w), 751 (w), 719 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.20 (s, 3H), 1.26 (s, 3H), 1.35 (d, *J* = 6.1 Hz, 3H), 2.22 (br s, 6H), 2.26 (s, 3H), 2.28 (s, 3H), 2.32 (s, 3H), 3.94 (q, *J* = 6.3 Hz, 1H), 6.87 (s, 1H), 6.89 (s, 1H), 7.08–7.13 (m, 3H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.5, 19.9, 21.1, 21.8, 27.5, 36.3, 36.5, 43.2, 69.8, 122.1, 124.9, 127.4, 128.7, 129.4, 130.0, 131.8, 131.8, 135.2, 136.2, 137.3, 141.7, 158.2 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{23}H_{31}N_2O$): calcd *m/z* 351.2431, found: 351.2427. **GLC** (HP-5): t_R = 22.9 min.



18aa
$C_{25}H_{32}N_2O$
M = 376.54 g/mol

***cis*-8-(3,4-Dimethylphenyl)-*N*,*N*,4a,6-tetramethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide** (**18aa**, Scheme 3): Prepared from *cis*-*N*,*N*,4a,6-tetramethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide (**9a**, 54 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0

mL, 0.2 M) according to the **GP2** at 50 °C for 17 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 4:1→3:1) afforded the analytically pure product (64 mg, 85%) as a light brown oil. $\mathbf{R_f}$ = 0.35 (cyclohexane:ethyl acetate = 2:1). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2921 (w), 2854 (w), 1635 (s), 1488 (m), 1441 (s), 1383 (s), 1264 (w), 1222 (w), 1180 (m), 1063 (w), 1030 (w), 987 (w), 908 (m), 858 (m), 820 (m), 726 (s), 679 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 1.19 (s, 3H), 1.20–1.31 (m, 3H), 1.51–1.58 (m, 3H), 1.67–1.77 (m, 1H), 2.06–2.10 (m, 1H), 2.26 (s, 3H), 2.28 (s, 3H), 2.29 (br s, 6H), 2.33 (s, 3H), 3.82 (dd, *J* = 8.0 Hz, *J* = 5.9 Hz, 1H), 6.86 (s, 1H), 6.91 (s, 1H), 7.10–7.13 (m, 2H), 7.15 (s, 1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.5, 19.9, 21.1, 22.2, 22.8, 27.0, 27.1, 34.1, 36.6, 43.5, 70.4, 121.4, 124.8, 128.4, 128.6, 129.4, 129.8, 132.0, 135.1, 136.1, 137.3, 137.9, 141.0, 158.4 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{25}H_{33}N_2O$): calcd *m/z* 377.2587, found: 377.2579. **GLC** (HP-5): t_R = 25.1 min.



19aa
$C_{20}H_{24}N_2O_2$
M = 324.42 g/mol

7-(3,4-Dimethylphenyl)-5-methoxy-*N*,*N*-dimethylindoline-1-carboxamide (**19aa,** Scheme 2): Prepared from 5-methoxy-*N*,*N*-dimethylindoline-1-carboxamide (**10a**, 44 mg, 0.20 mmol, 1.0 equiv) and *o*-xylene (1.0 mL, 0.2 M) according to the **GP2** at 50 °C for 48 h. Purification by flash column chromatography on silica gel (cyclohexane:ethyl acetate = 1:1→1:2) afforded the analytically pure product (19 mg, 30%) as a brown oil. $\mathbf{R_f}$ = 0.28 (cyclohexane:ethyl acetate = 1:2). **IR** (ATR): $\tilde{\nu}$ /cm^{-1} = 2921 (br), 1734 (w), 1663 (s), 1608 (s), 1438 (s), 1377 (s), 1275 (m), 1234 (m), 1189 (w), 1155 (w), 1097 (w), 1041 (w), 996 (w), 829 (m), 766 (w), 701 (w). **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 2.25 (s, 3H), 2.27 (s, 3H), 2.63 (s, 6H), 3.06 (t, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 3.95 (t, *J* = 8.0 Hz, 2H), 6.73 (dd, *J* = 6.4 Hz, *J* = 2.1 Hz, 2H), 7.11 (d, *J* = 6.7 Hz, 1H), 7.21 (dd, *J* = 7.8 Hz, *J* = 1.1 Hz, 1H), 7.27 (s,1H) ppm. **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): δ = 19.6, 20.0, 30.5, 37.1, 52.4, 55.9, 110.1, 113.6, 124.4, 128.2, 129.8, 130.2, 135.3, 135.5, 136.0, 136.4, 137.9, 156.5, 160.6 ppm. **HRMS** (APCI) exact mass for $[M+H]^+$ ($C_{20}H_{25}N_2O_2$): calcd *m/z* 325.1911, found: 325.1907. **GLC** (HP-5): t_R = 24.0 min.

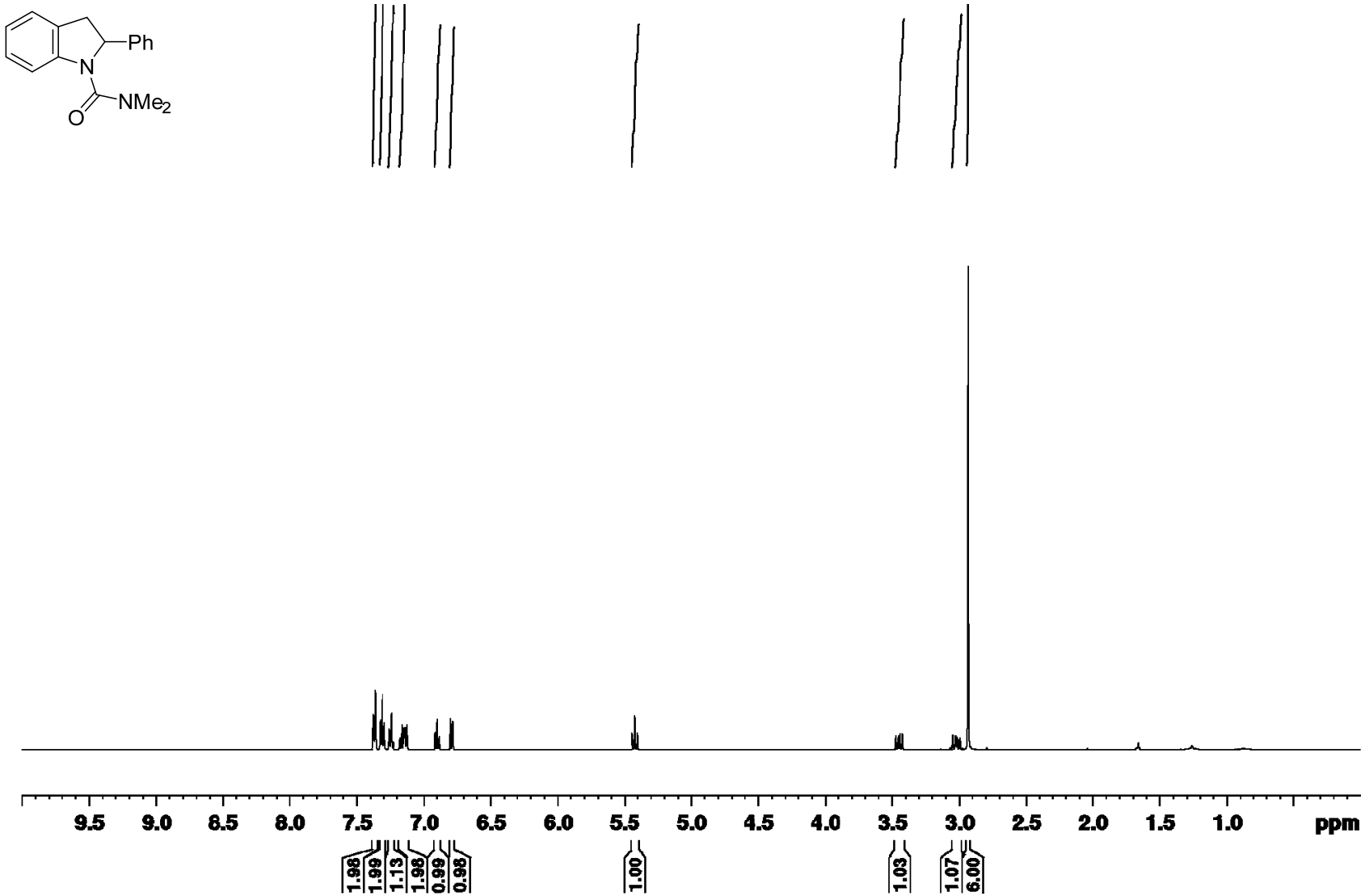
4 References and Footnotes

[S1] Jiao, L.-Y.; Oestreich, M. *Org. Lett*. **2013**, *15*, 5374–5377.

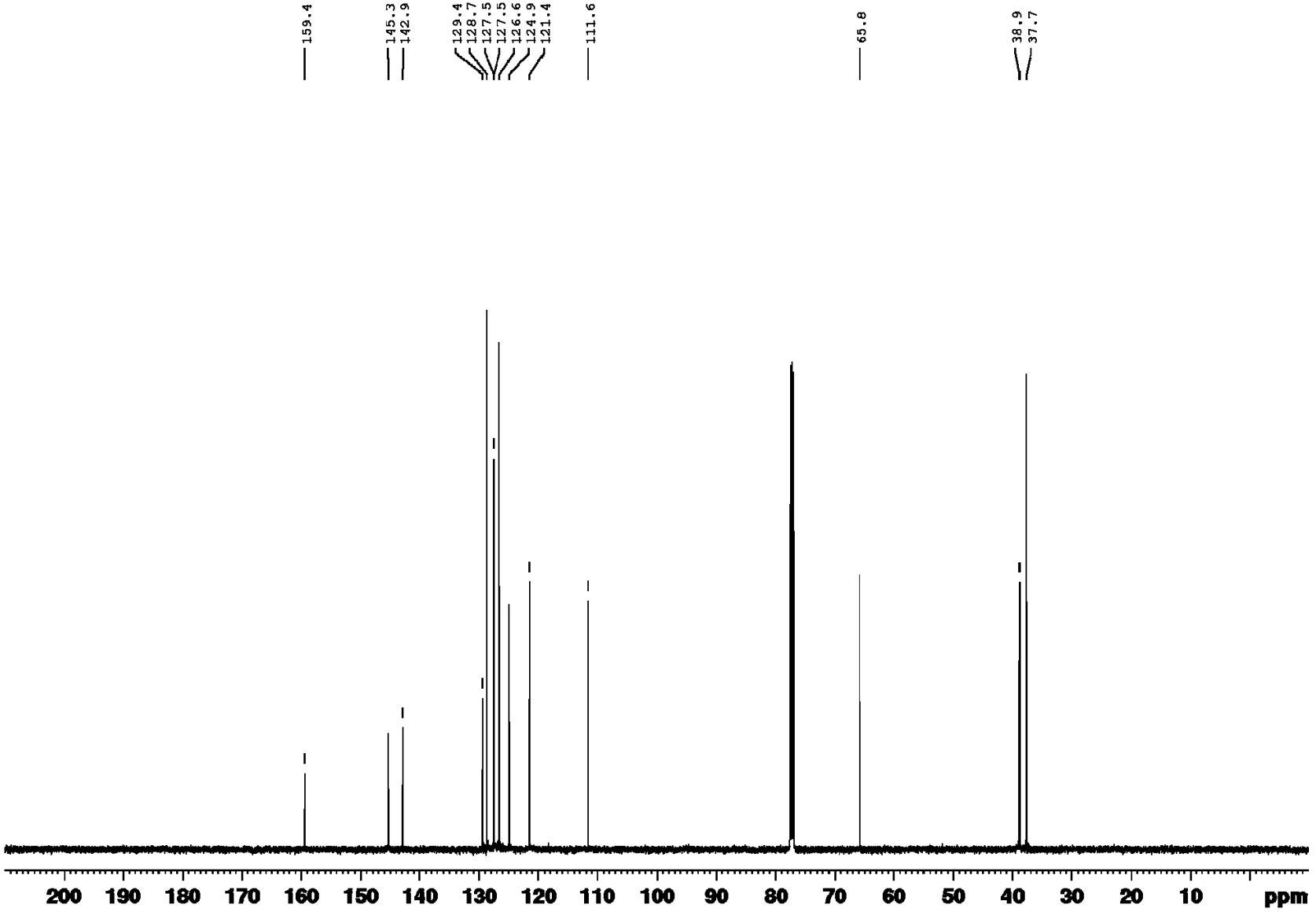
5 ^{1}H and ^{13}C NMR Spectra

_N_,_N_-Dimethyl-2-phenylindoline-1-carboxamide (4a)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

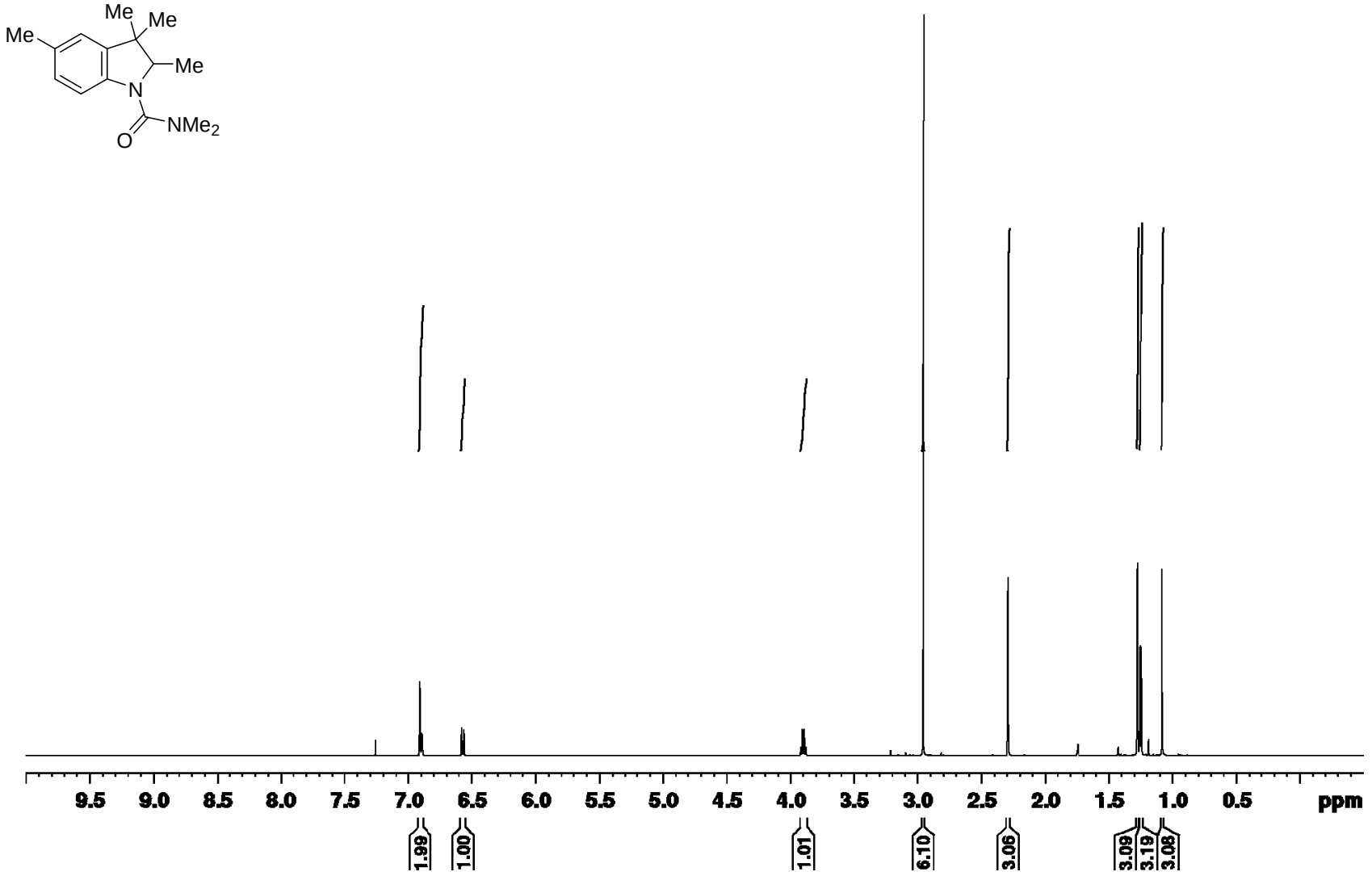


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

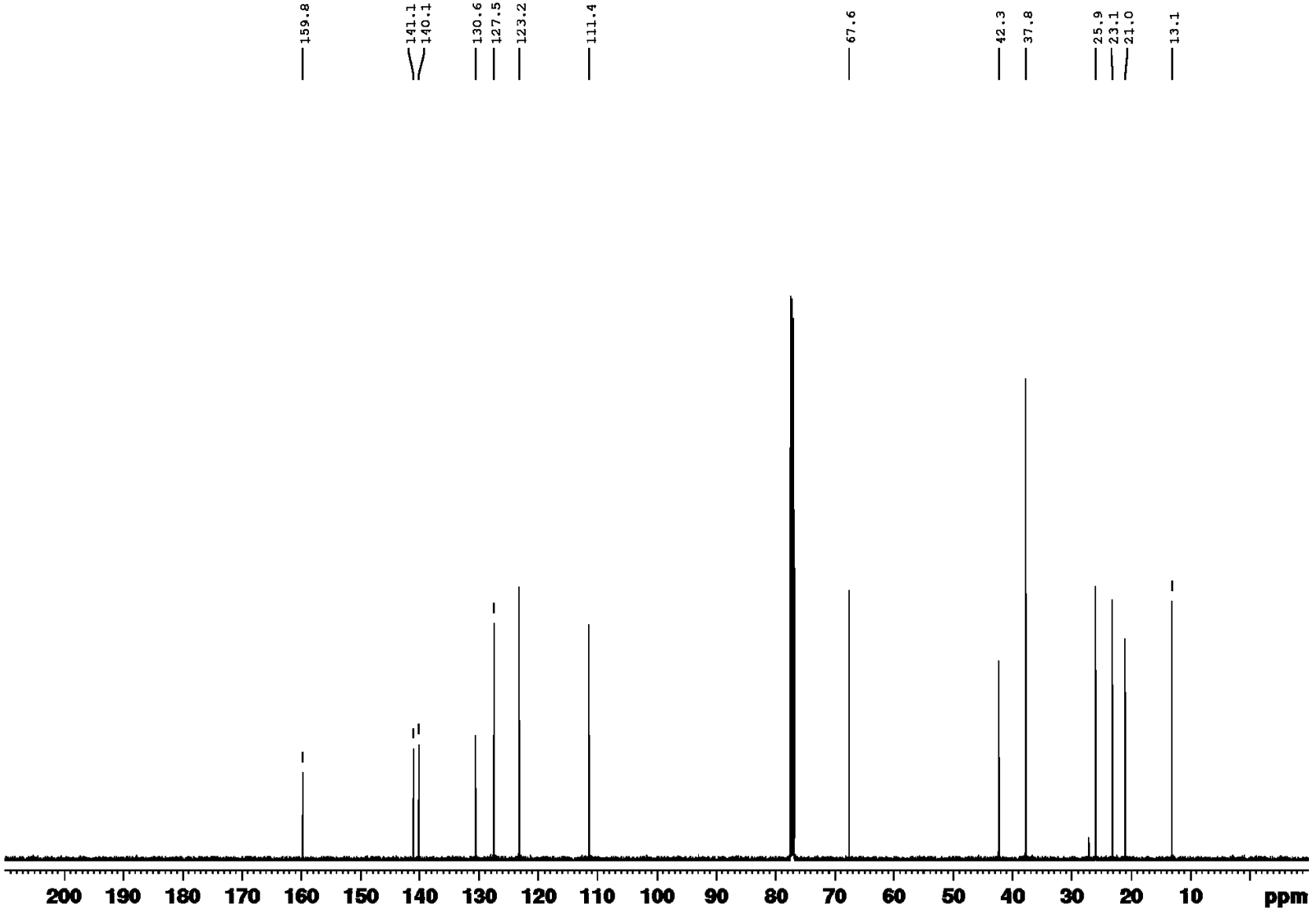


_N_,_N_,2,3,3,5-Hexamethylindoline-1-carboxamide (**8a**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

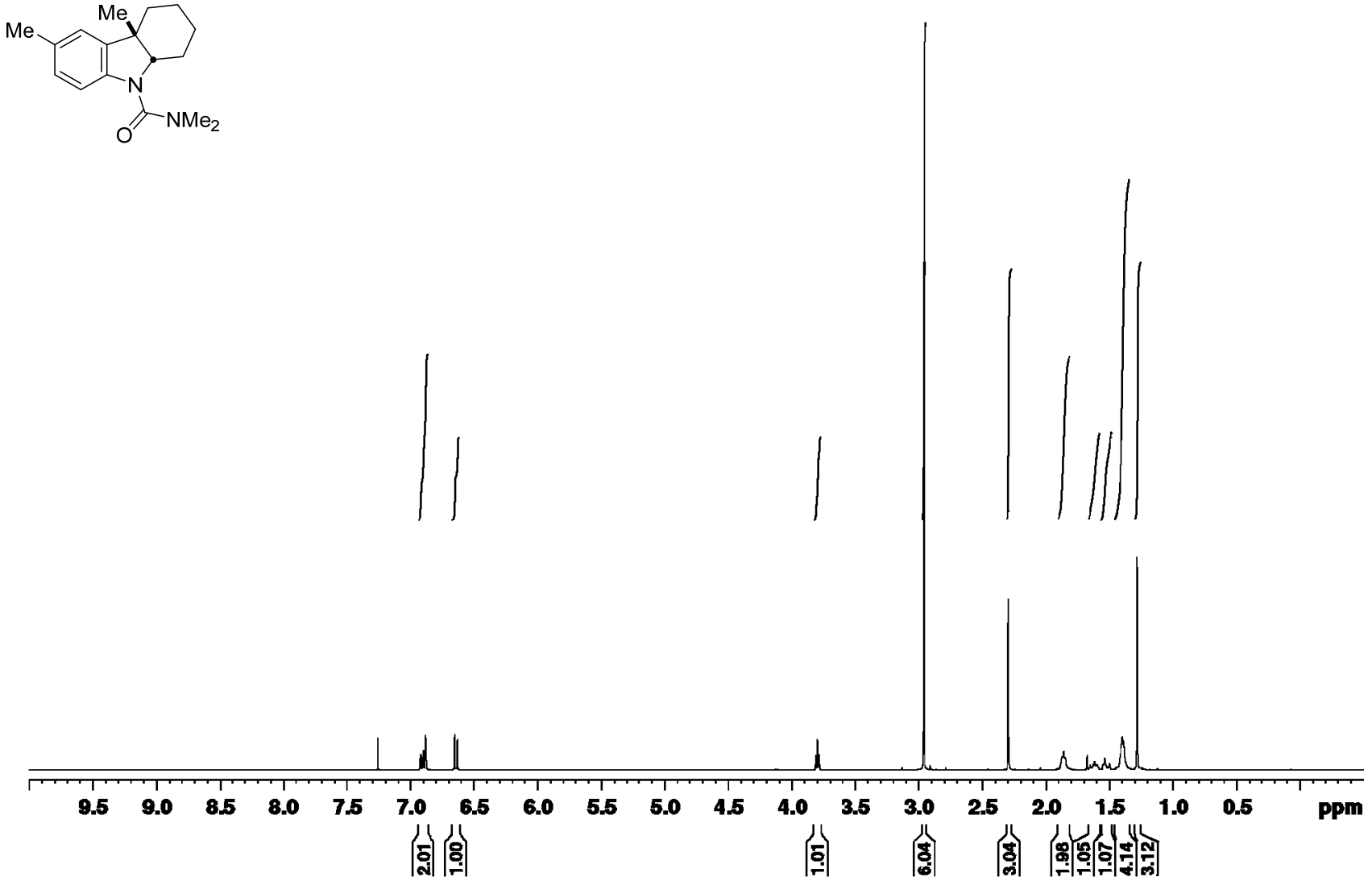


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

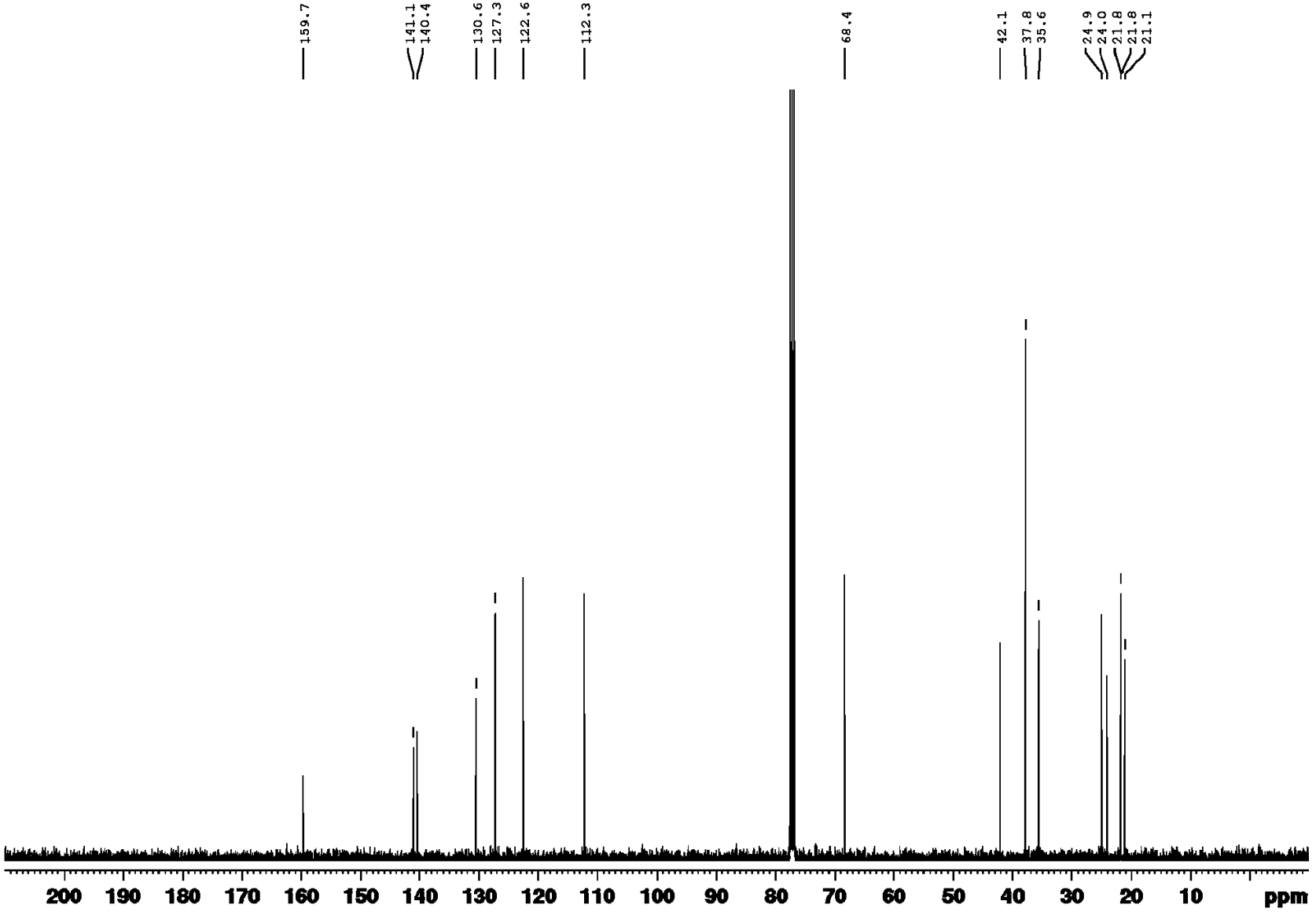


***cis*-*N*,*N*,4a,6-Tetramethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide** (**9a**)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

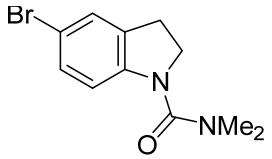


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

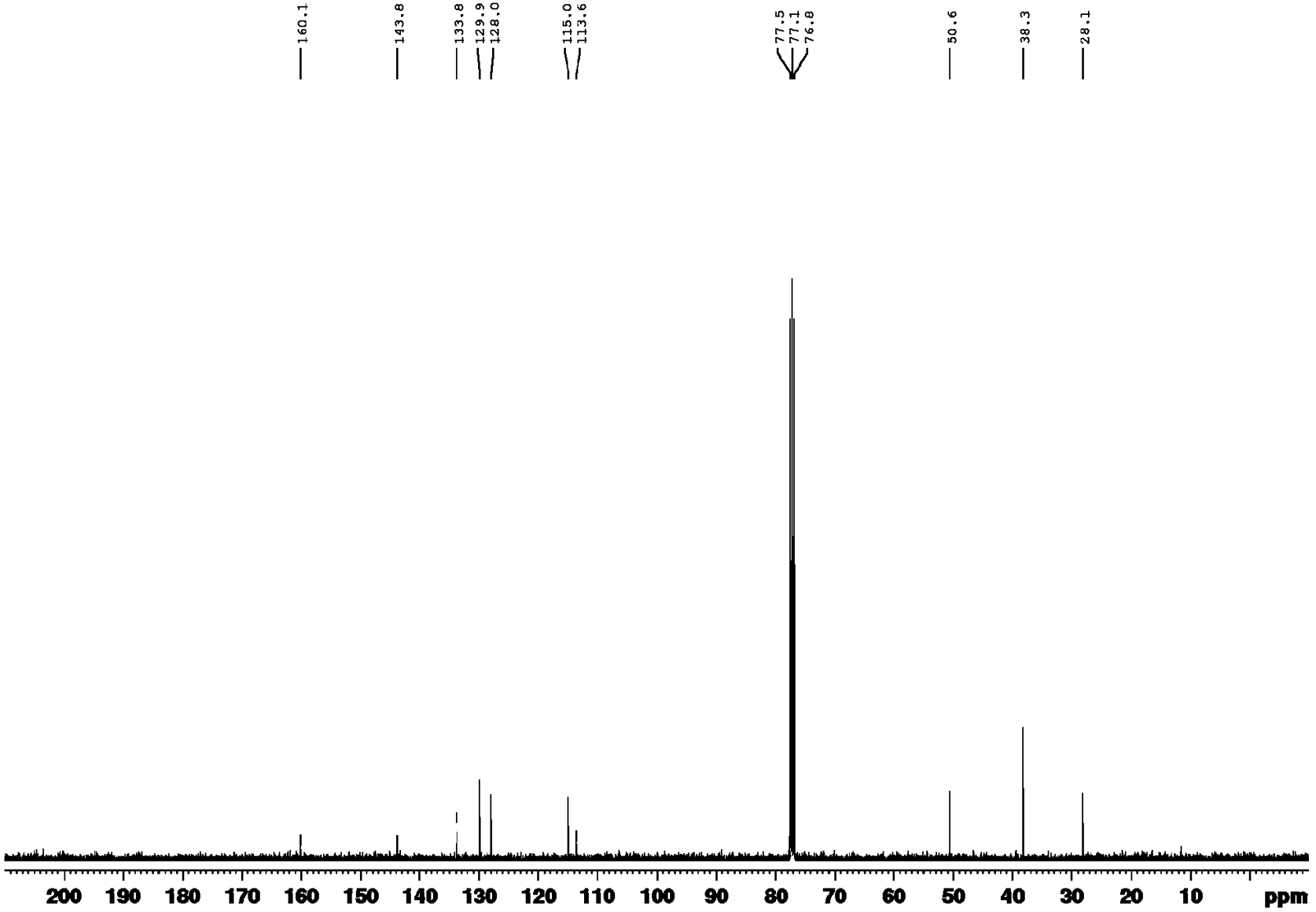


5-Bromo-*N*,*N*-dimethylindoline-1-carboxamide (**11a**)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

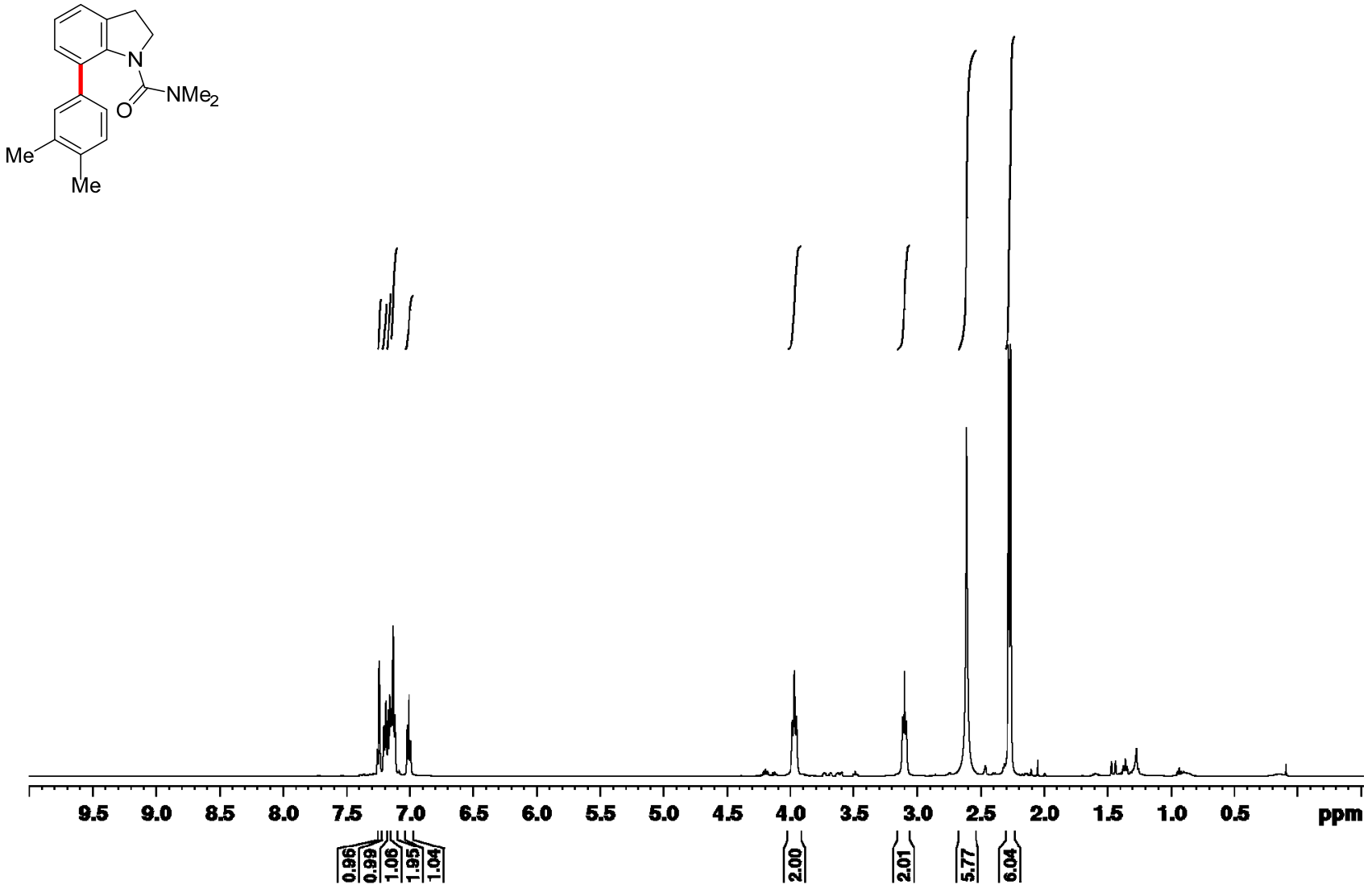


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

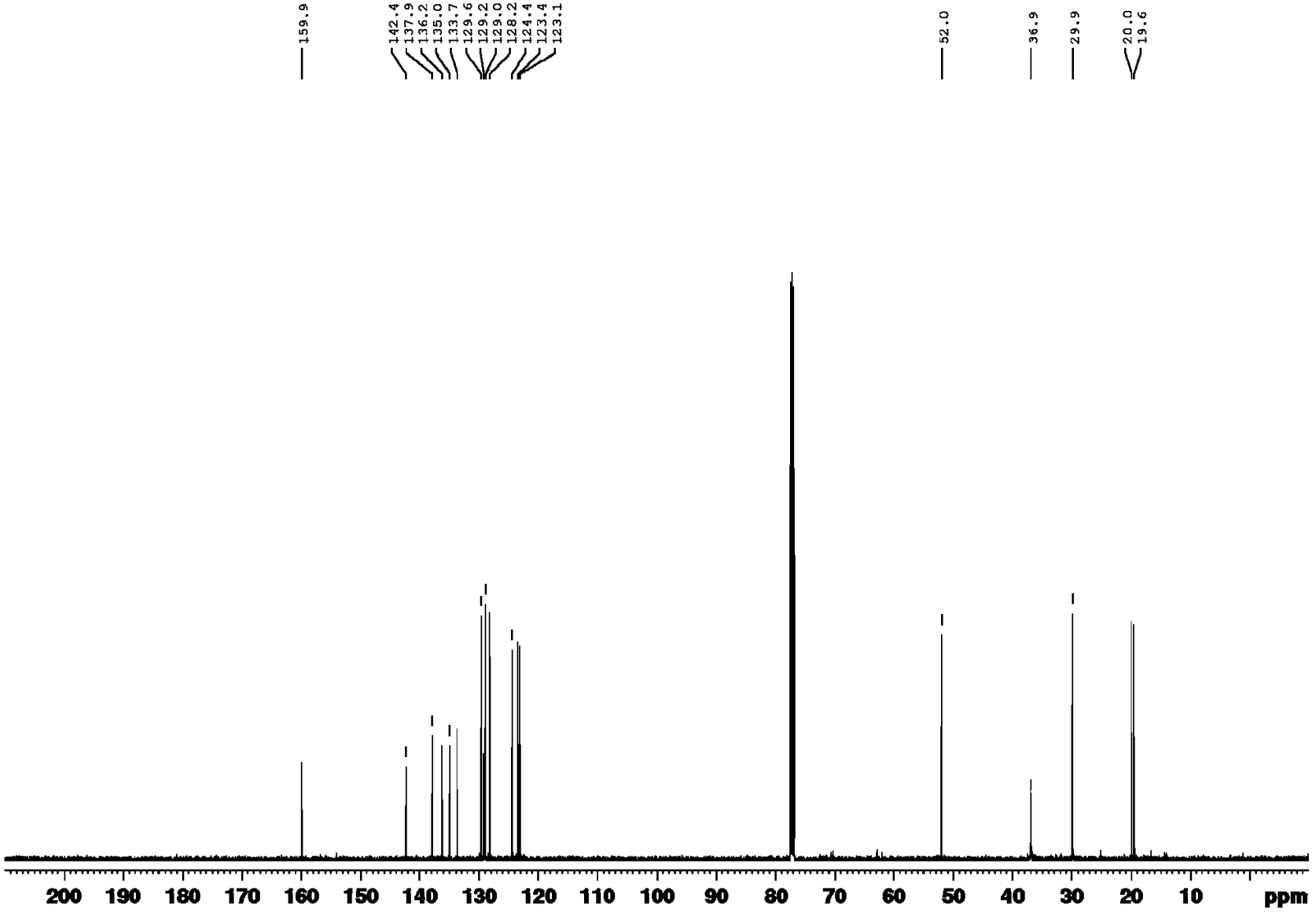


7-(3,4-Dimethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

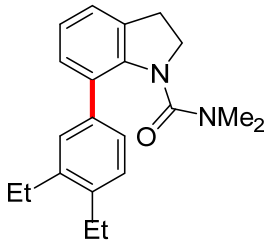


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

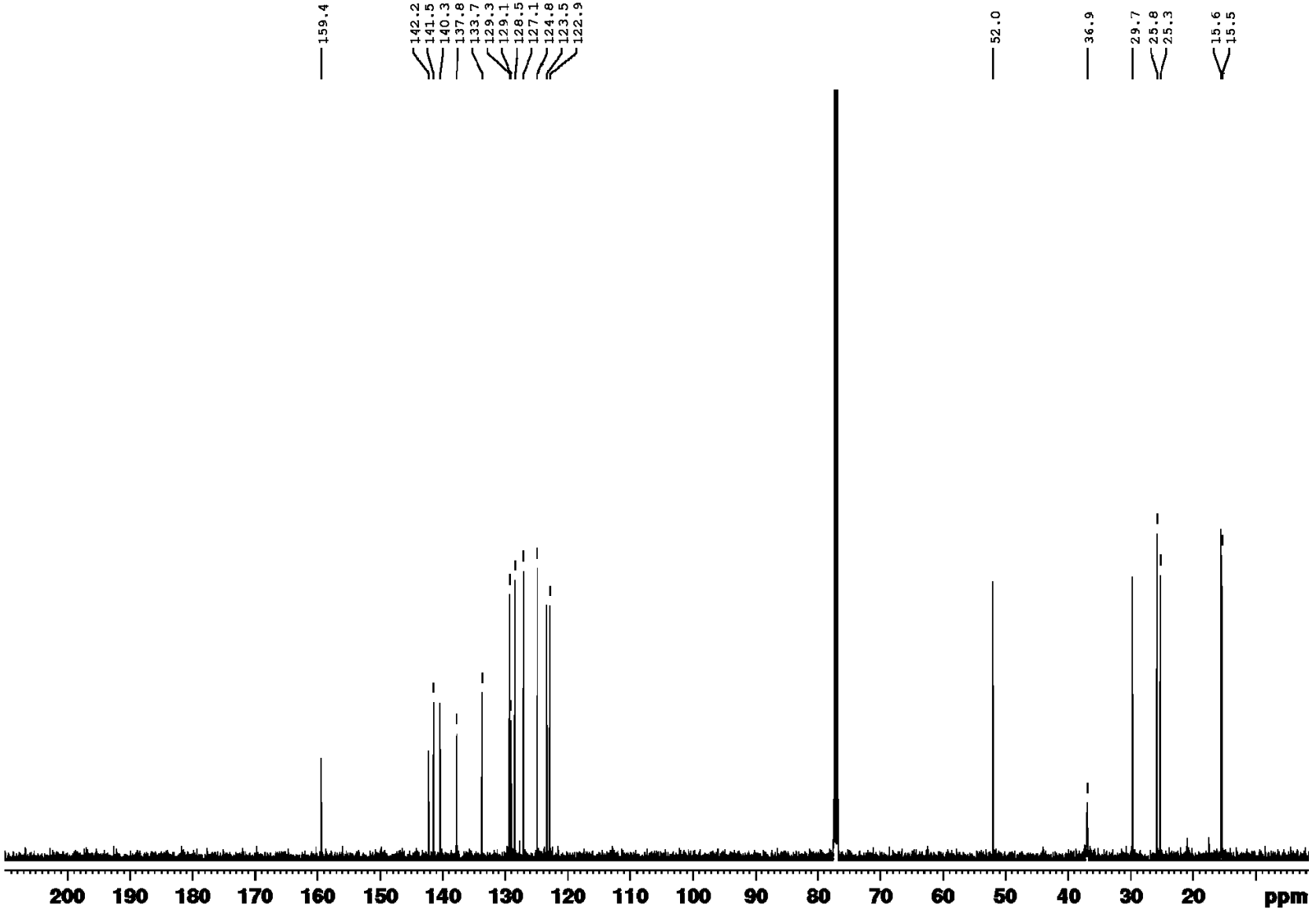


7-(3,4-Diethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ab**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

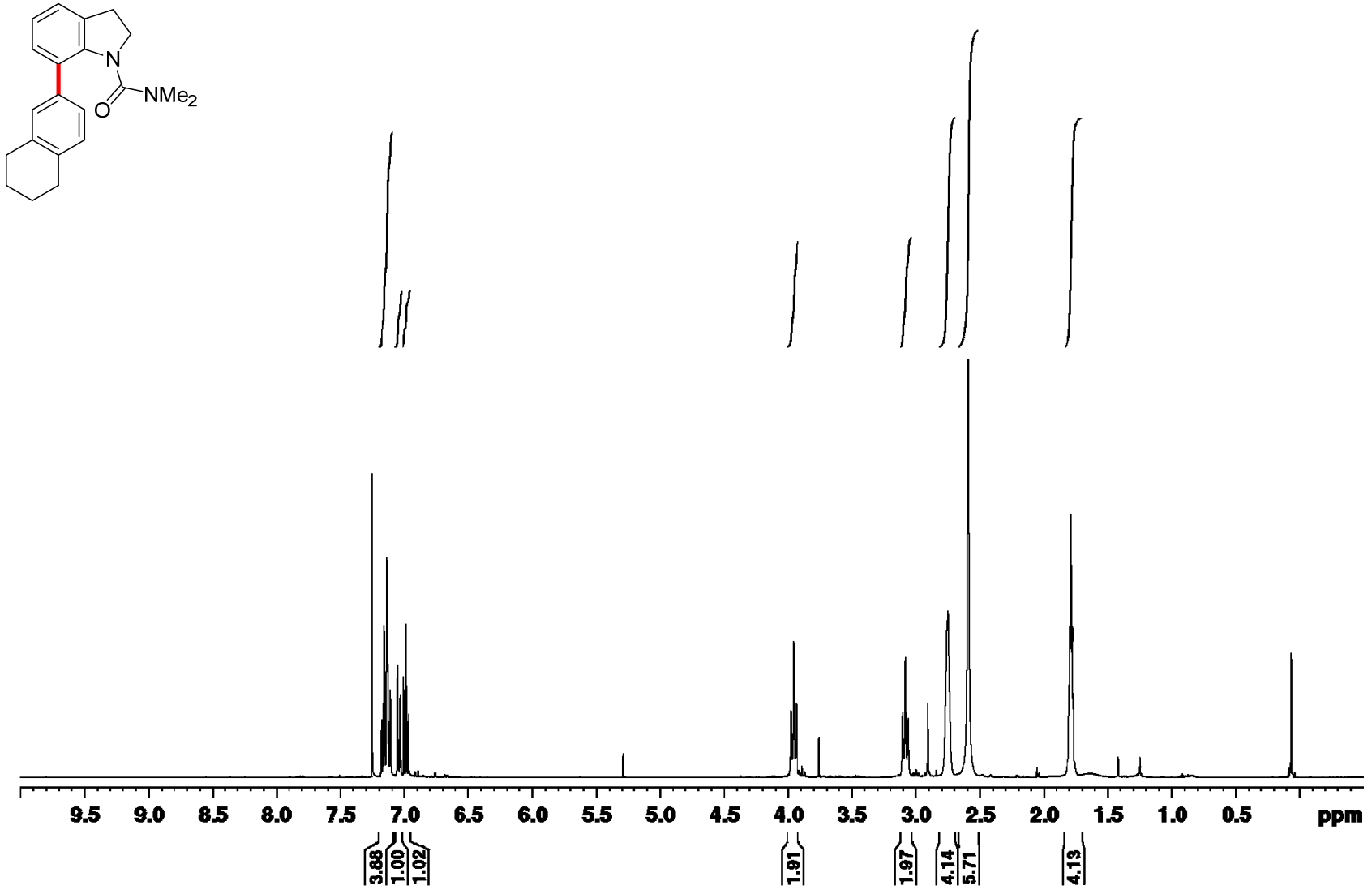


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

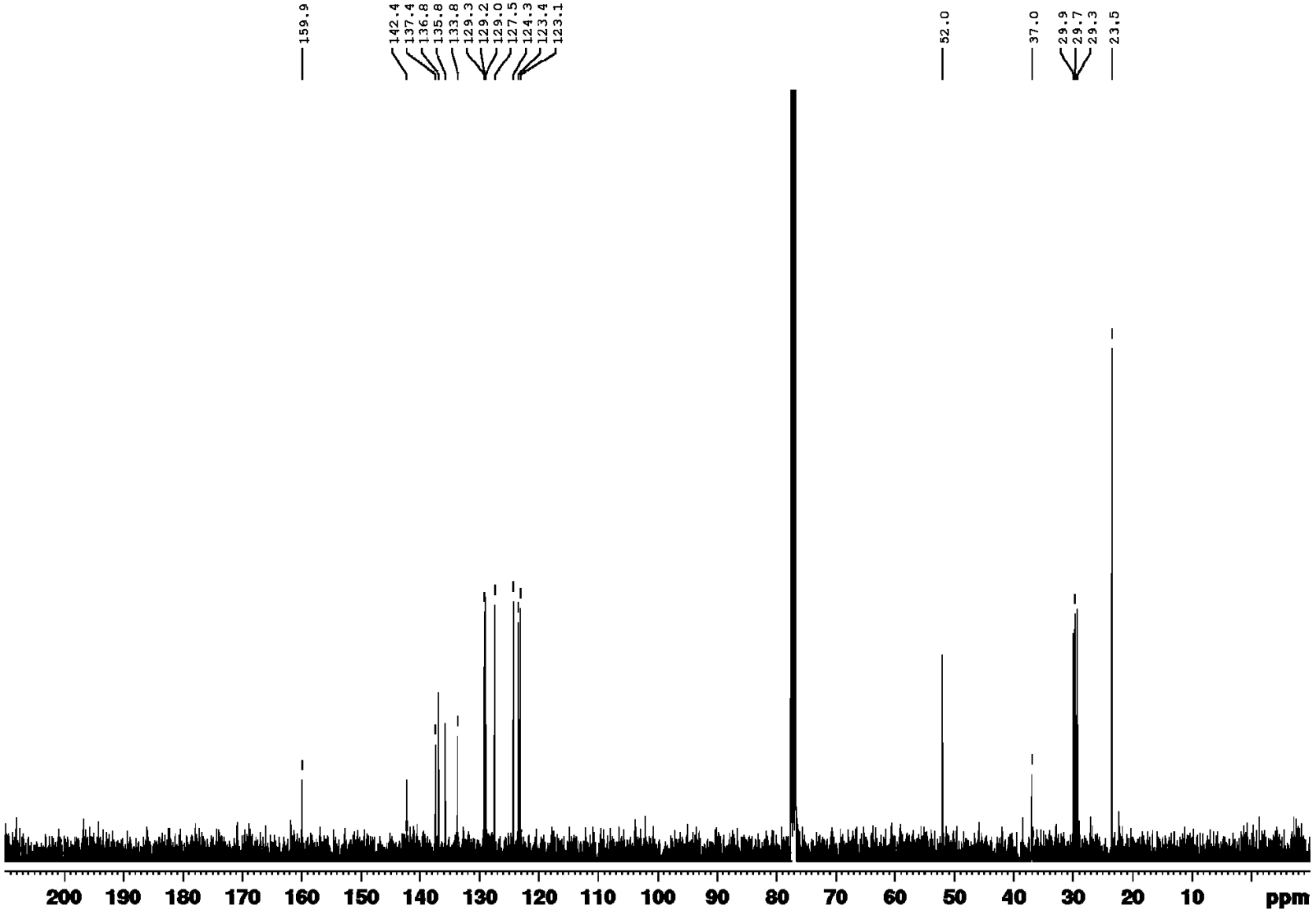


_N,N_-Dimethyl-7-(5,6,7,8-tetrahydronaphthalen-2-yl)indoline-1-carboxamide (2ac)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

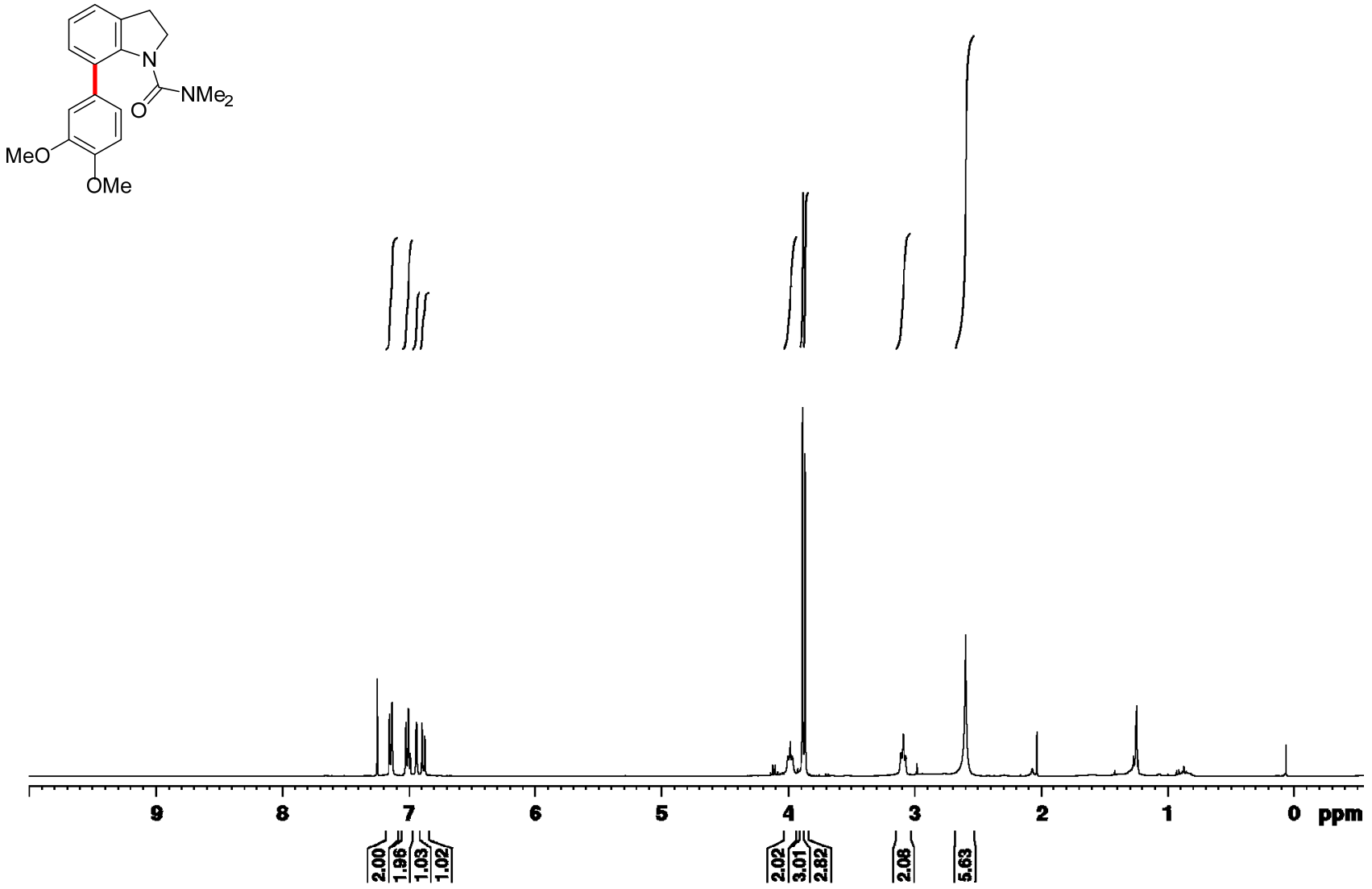


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

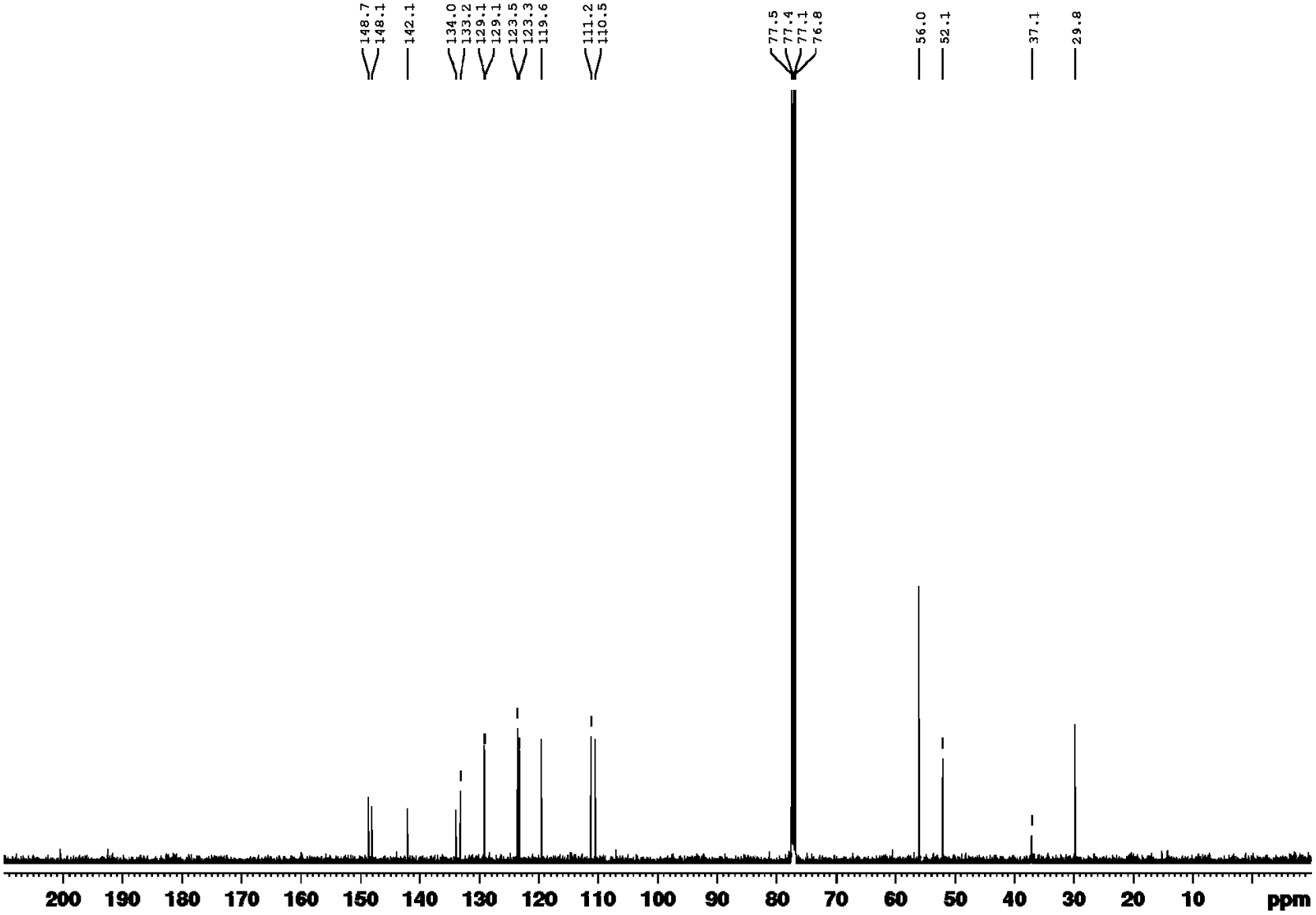


7-(3,4-Dimethoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ad**)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

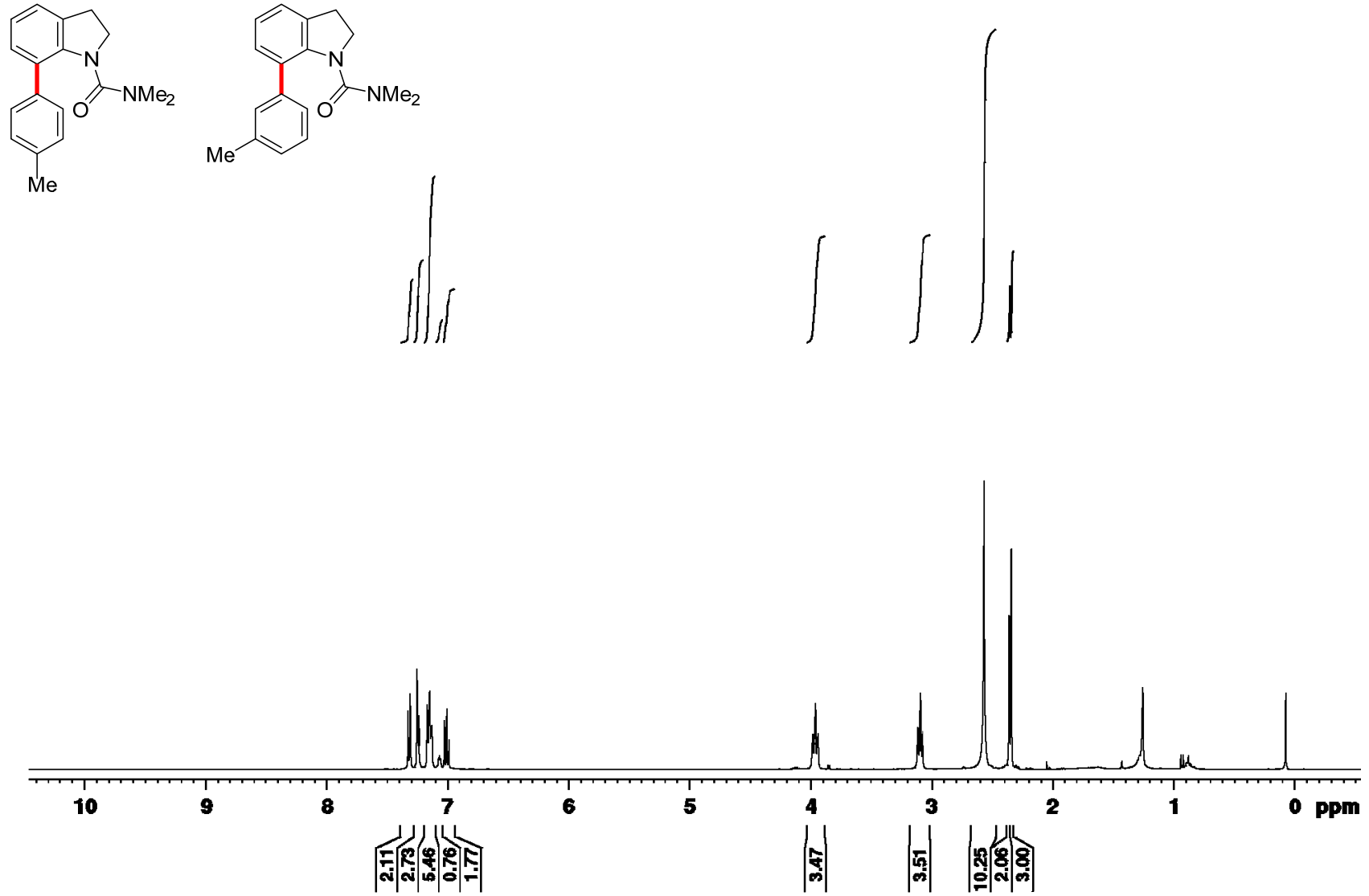


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

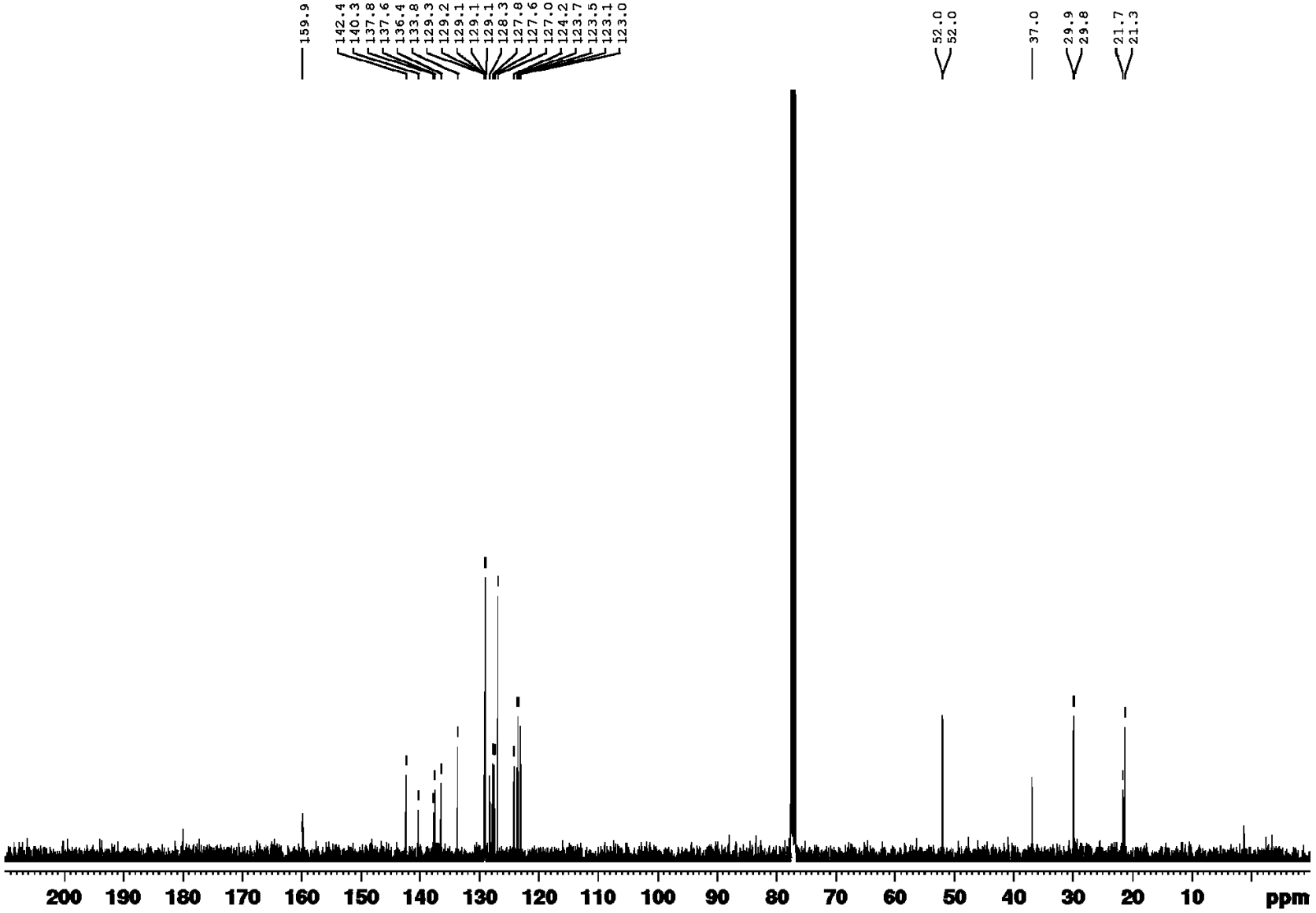


***N*,*N*-Dimethyl-7-(4-tolyl)indoline-1-carboxamide** (**2ae**) and ***N*,*N*-dimethyl-7-(3-tolyl)indoline-1-carboxamide** (**2ae'**)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

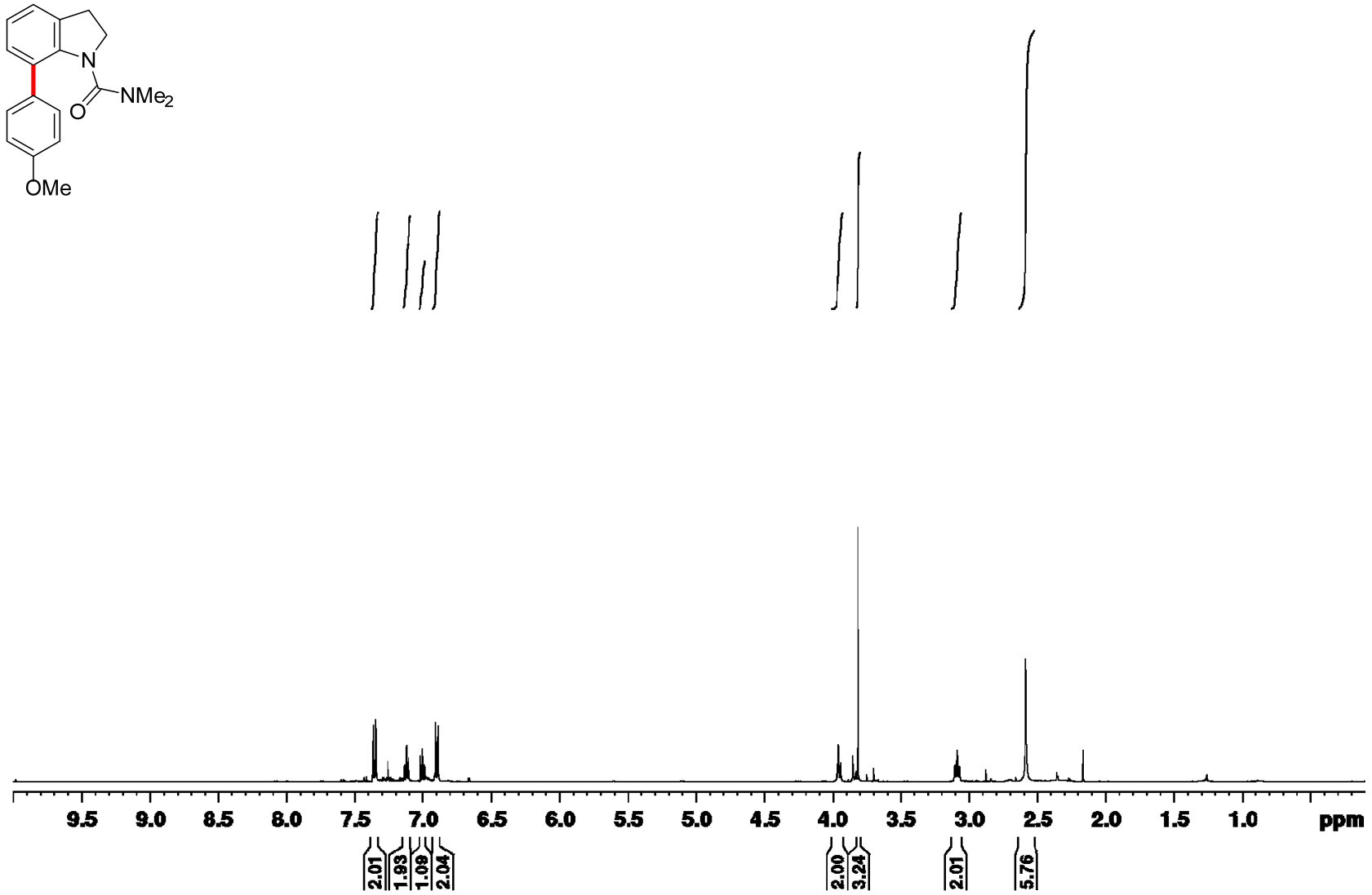


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

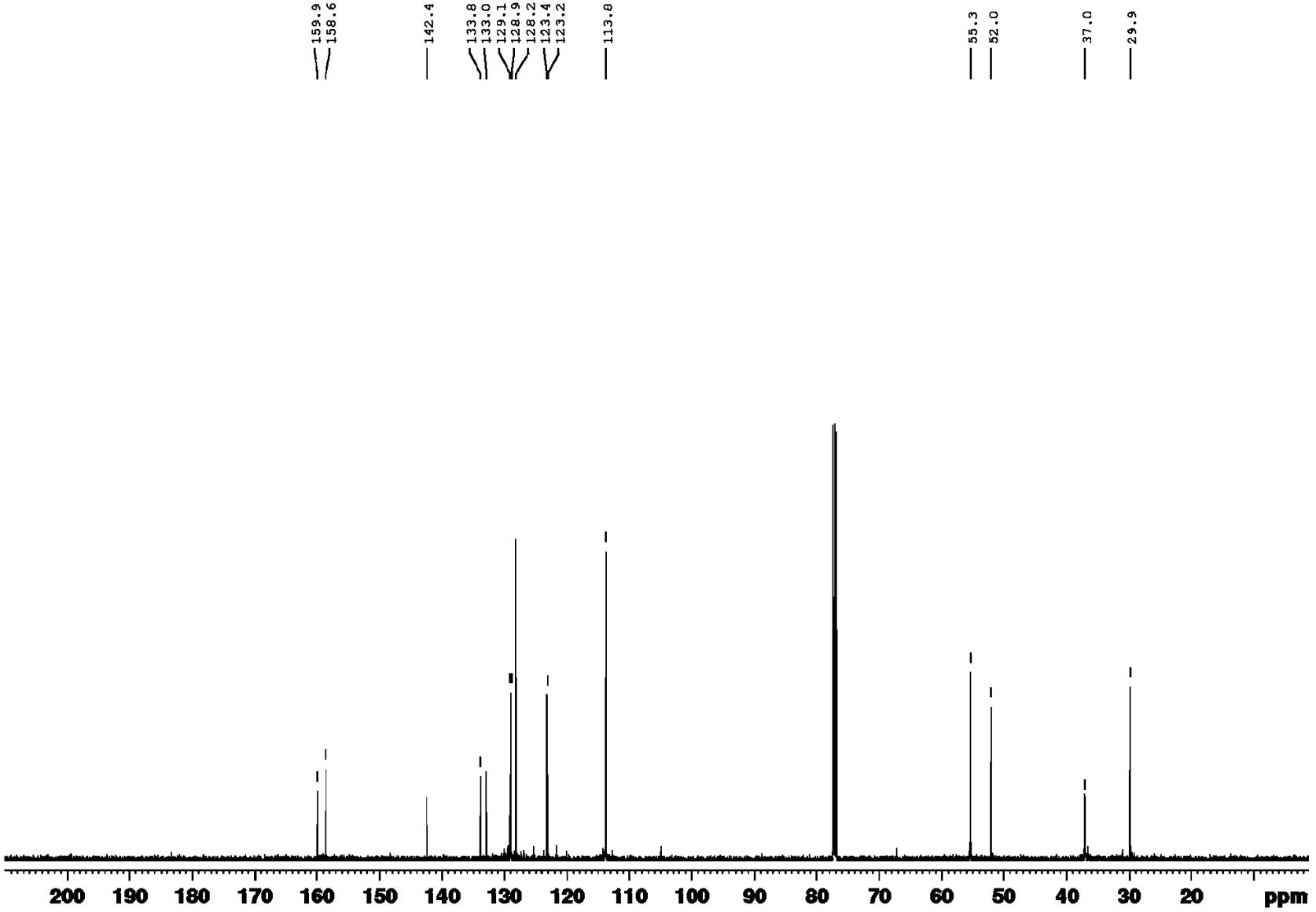


7-(4-Methoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2af**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

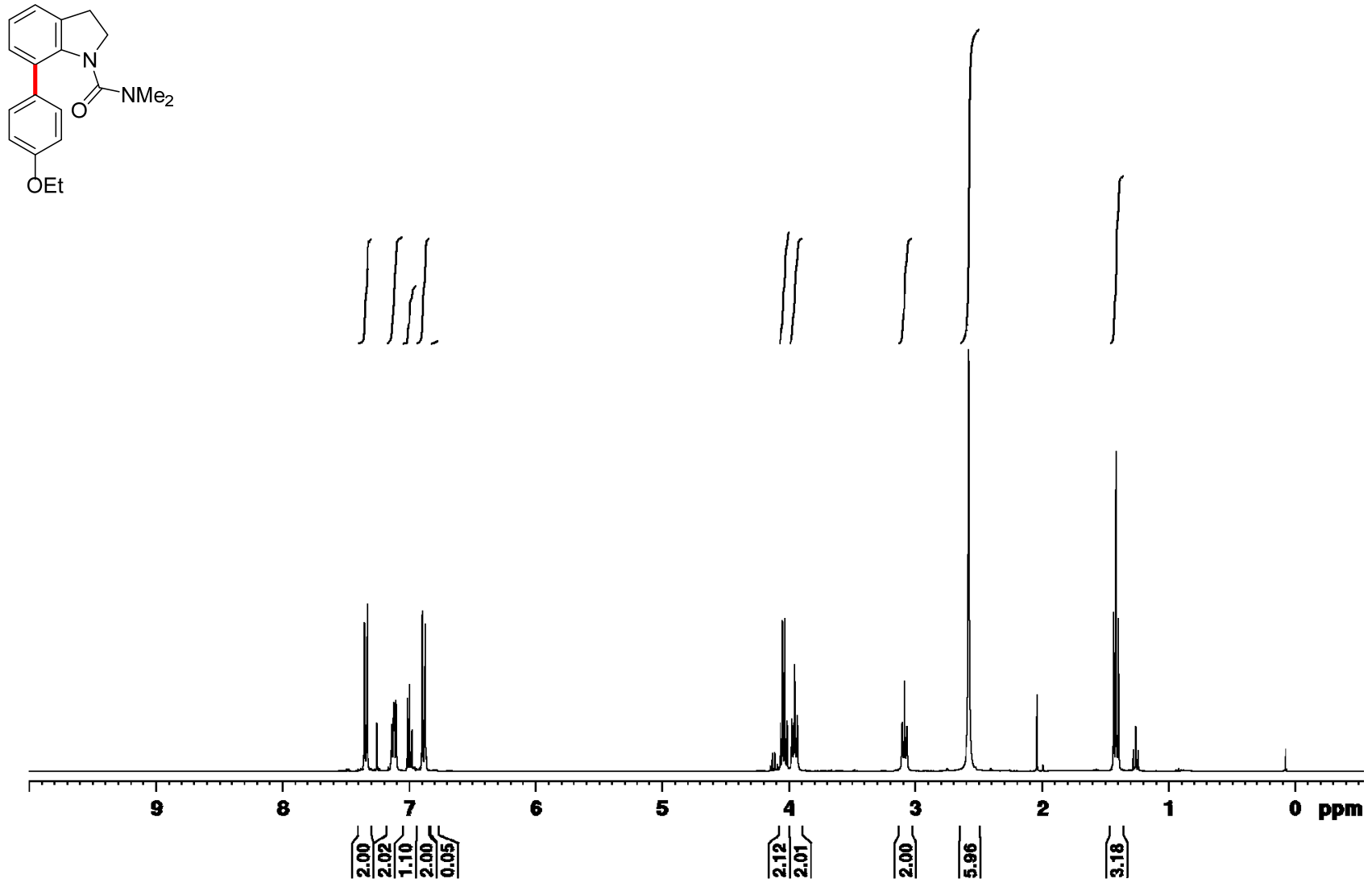


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

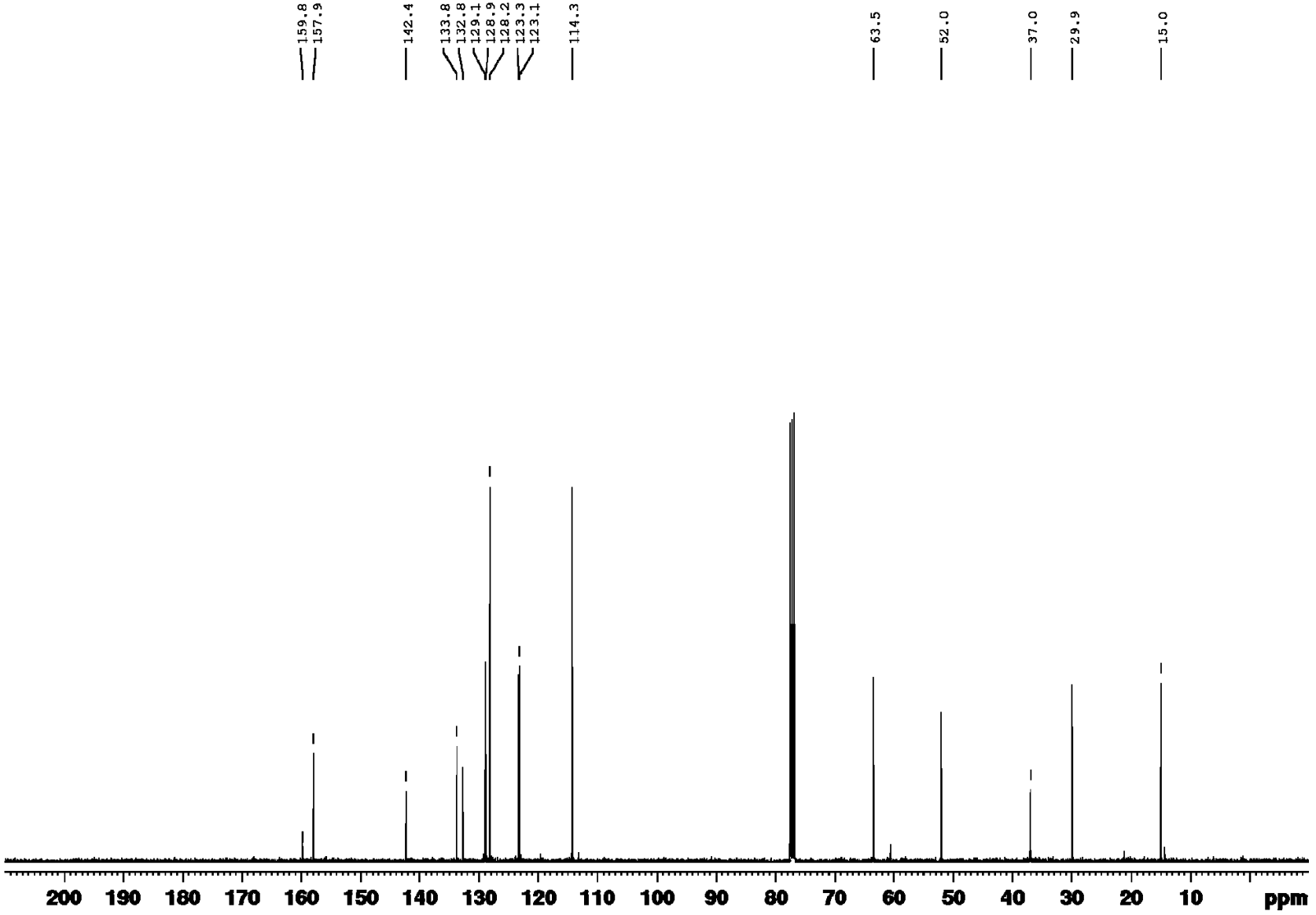


7-(4-Ethoxyphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ag**)

^{1}H NMR (400 MHz, $CDCl_3$, 298 K):

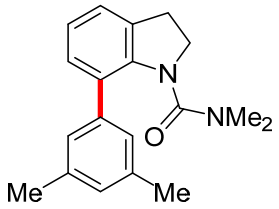


^{13}C NMR (100 MHz, $CDCl_3$, 298 K):

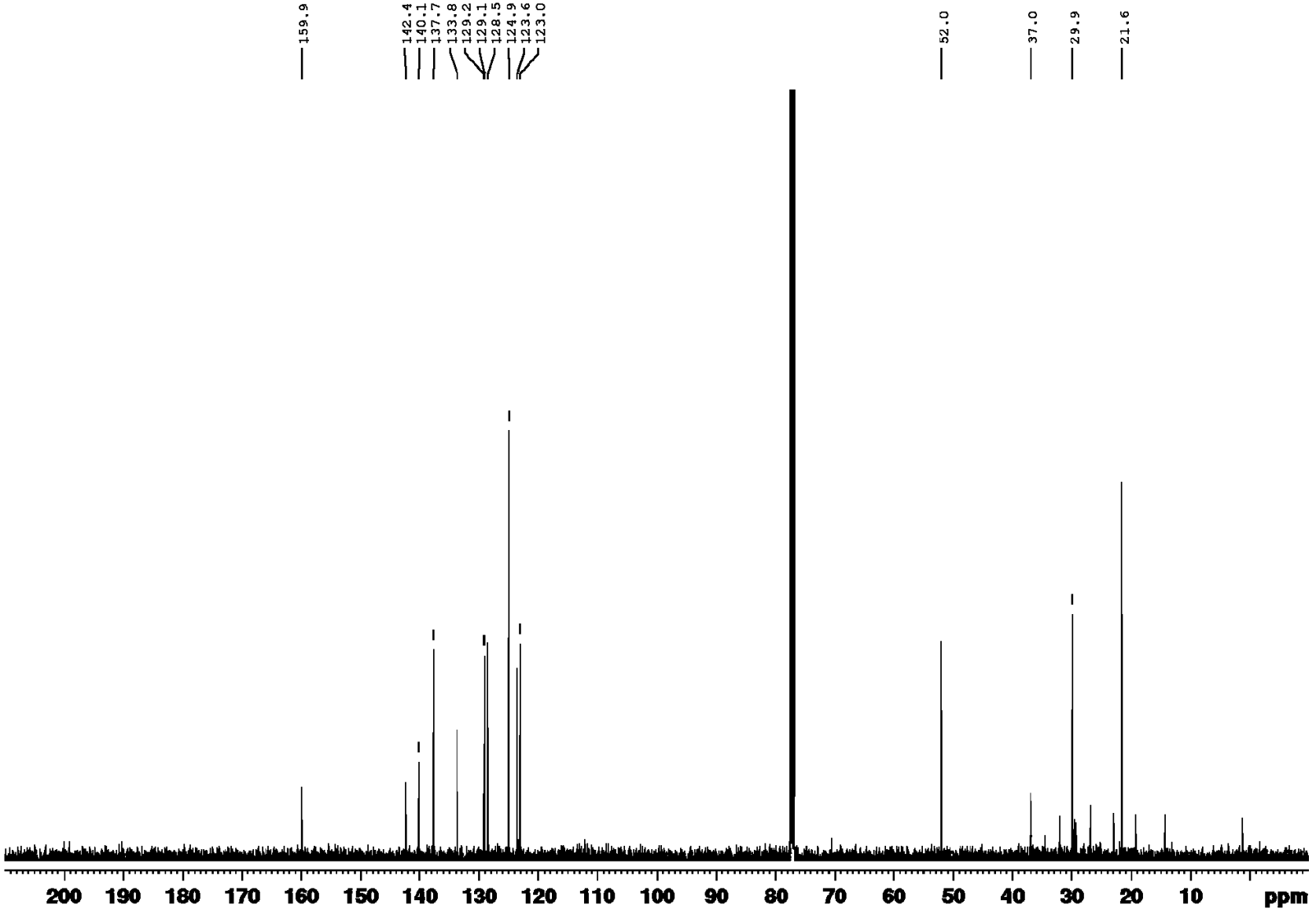


7-(3,5-Dimethylphenyl)-*N*,*N*-dimethylindoline-1-carboxamide (**2ah**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

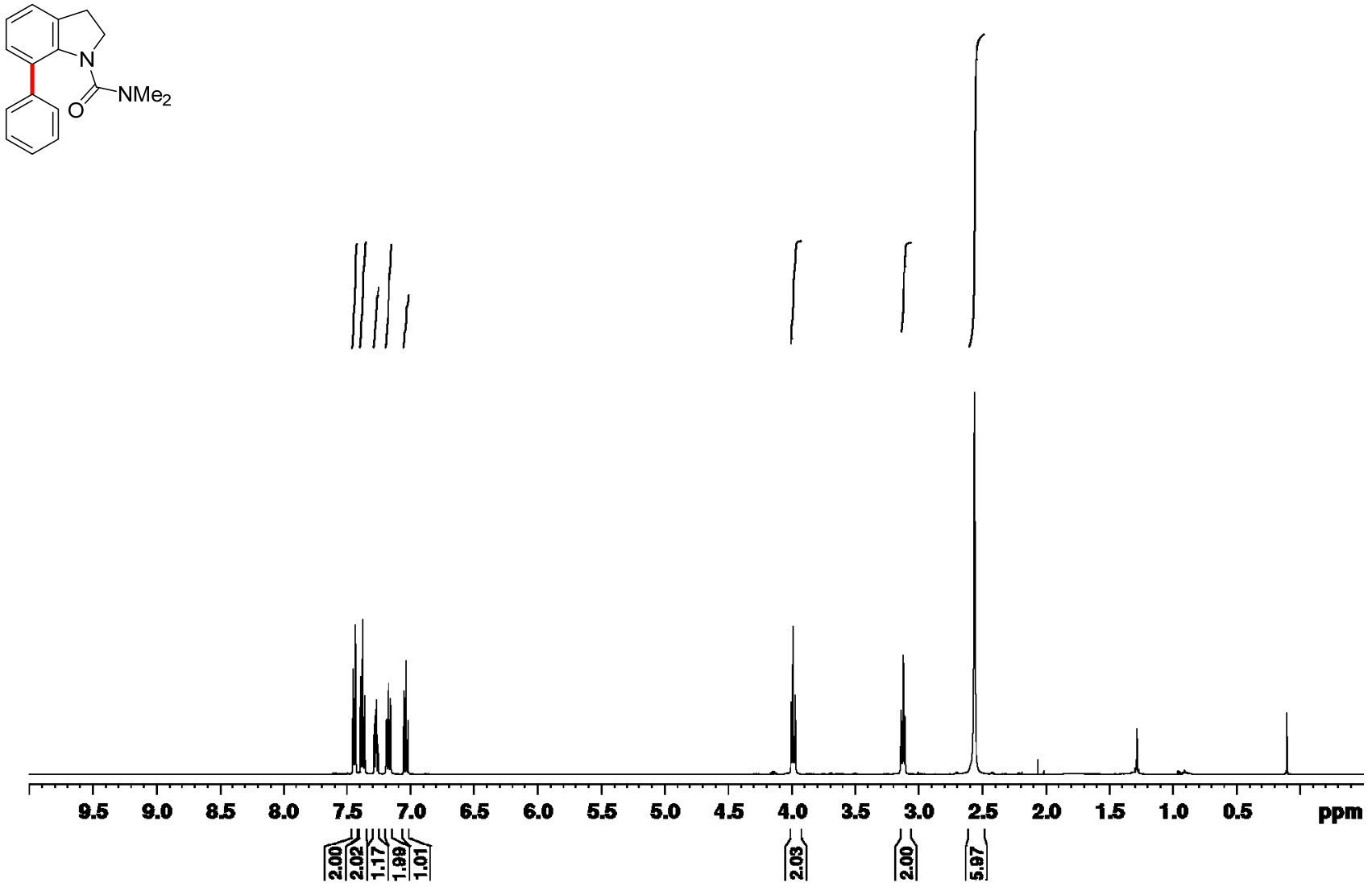


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

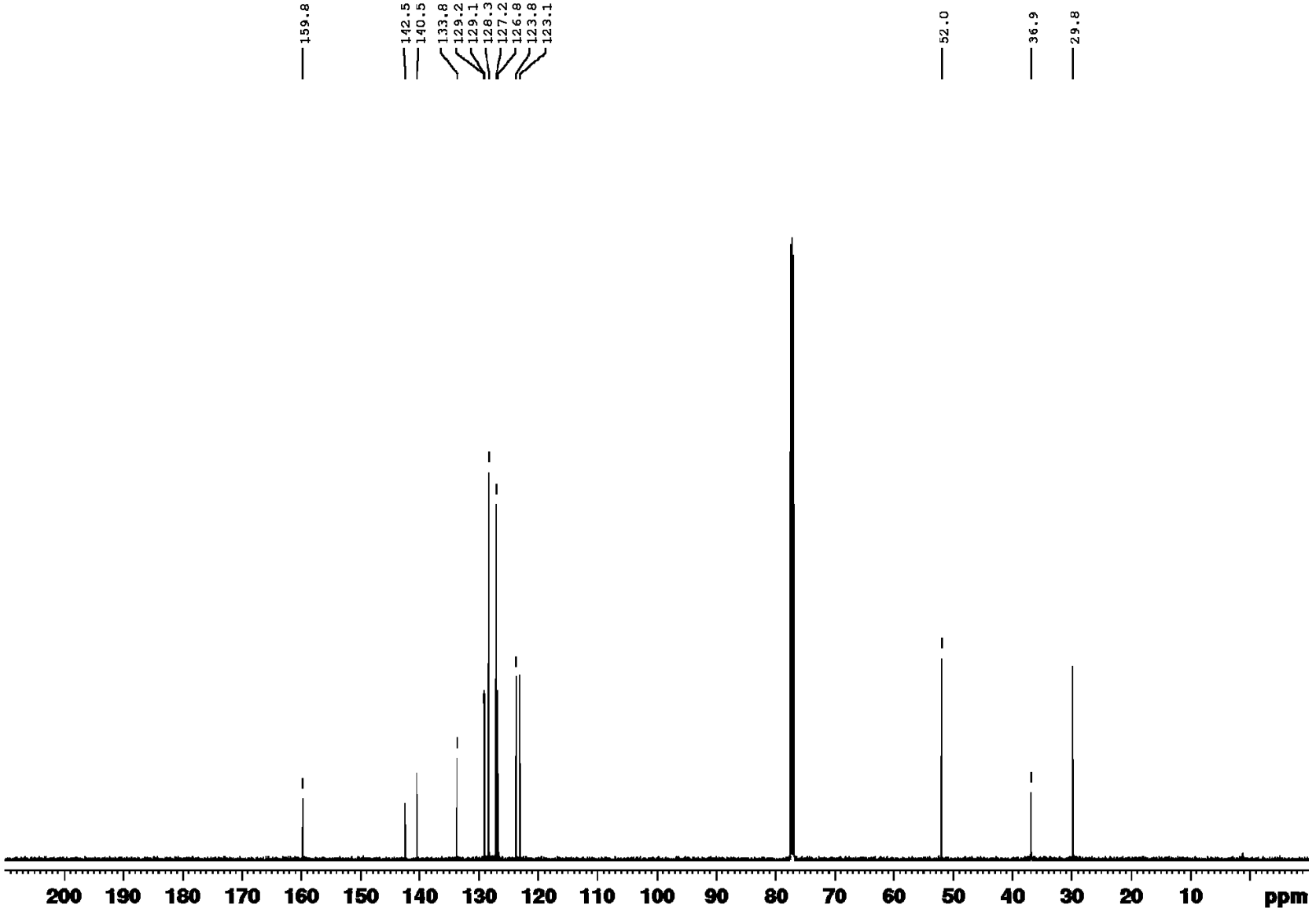


***N*,*N*-Dimethyl-7-phenylindoline-1-carboxamide (2ak)**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

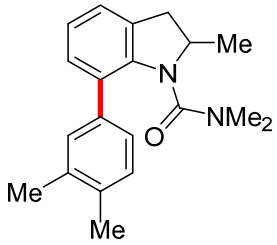


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

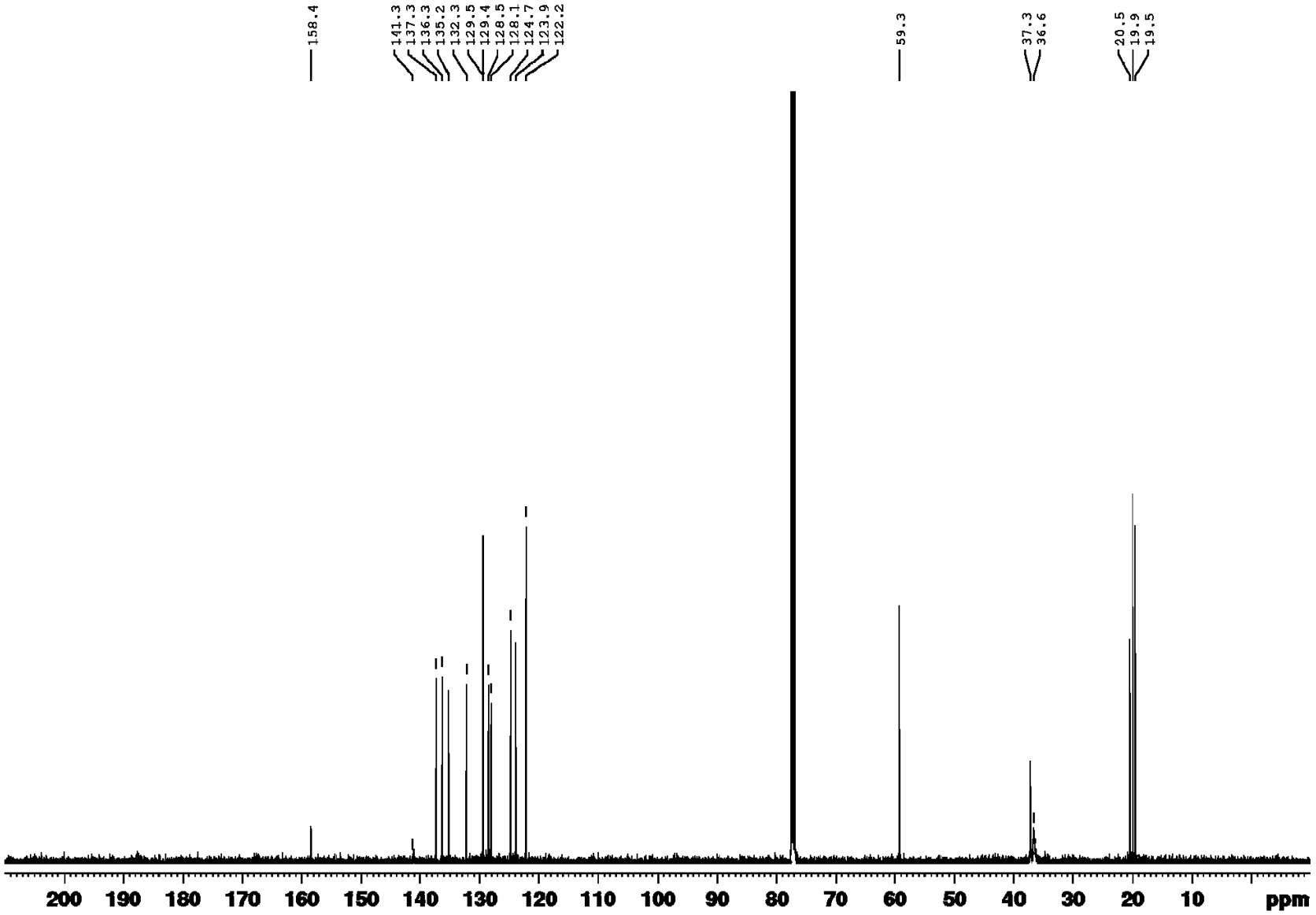


7-(3,4-Dimethylphenyl)-*N*,*N*,2-trimethylindoline-1-carboxamide (**12aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

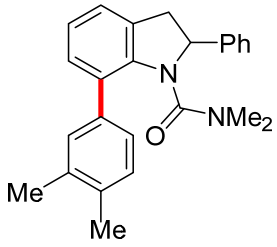


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

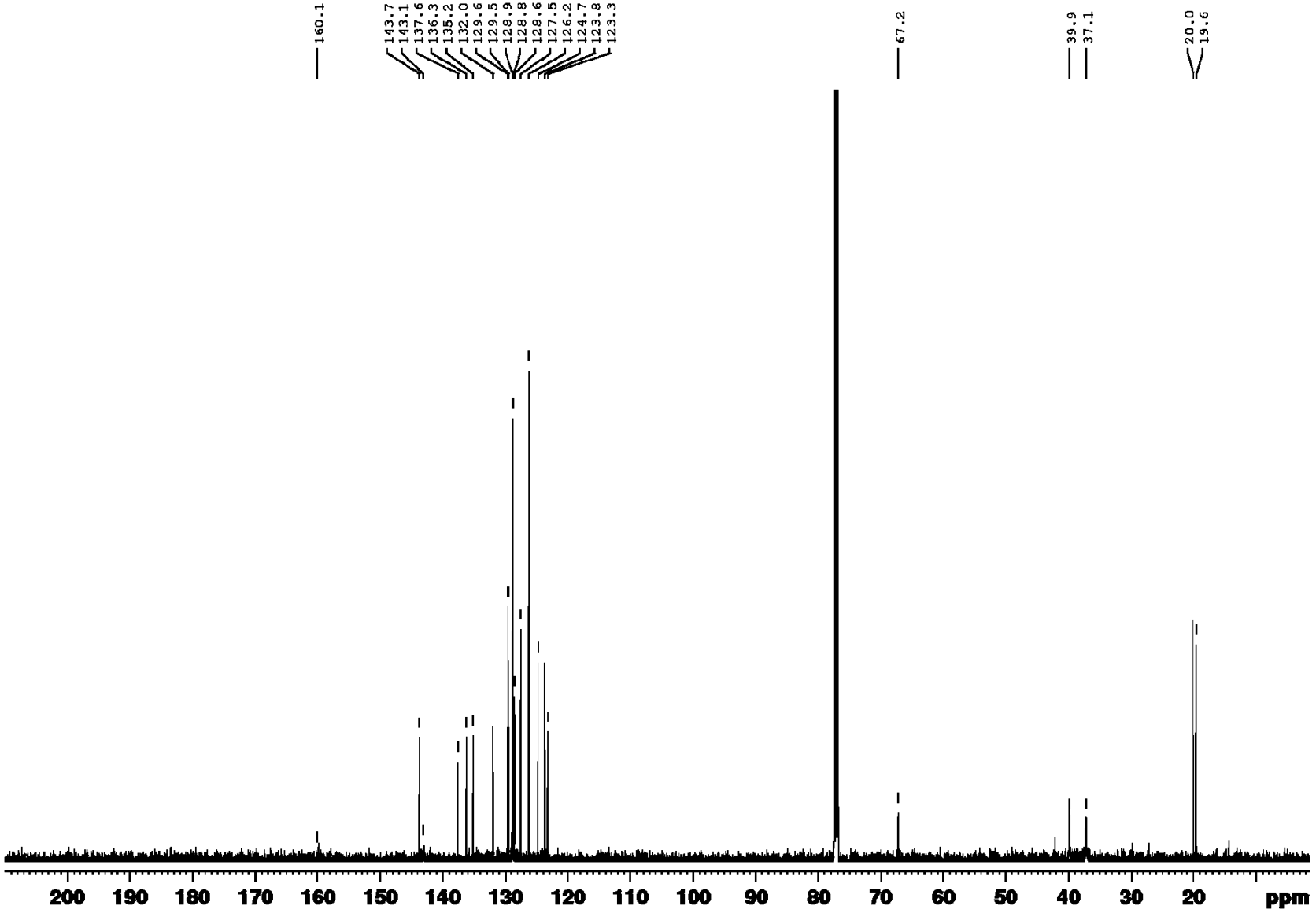


7-(3,4-Dimethylphenyl)-*N*,*N*-dimethyl-2-phenylindoline-1-carboxamide (**13aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

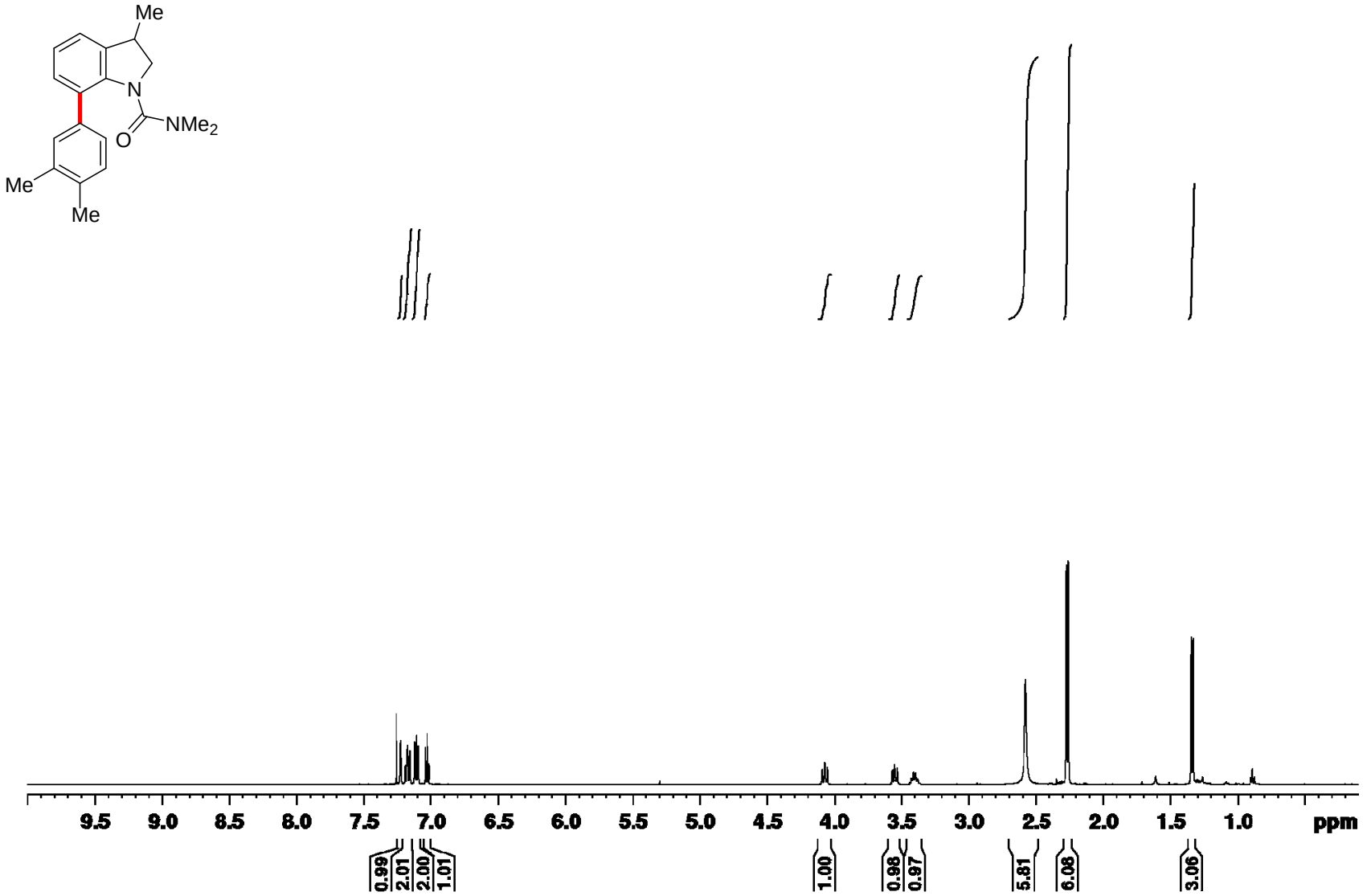


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

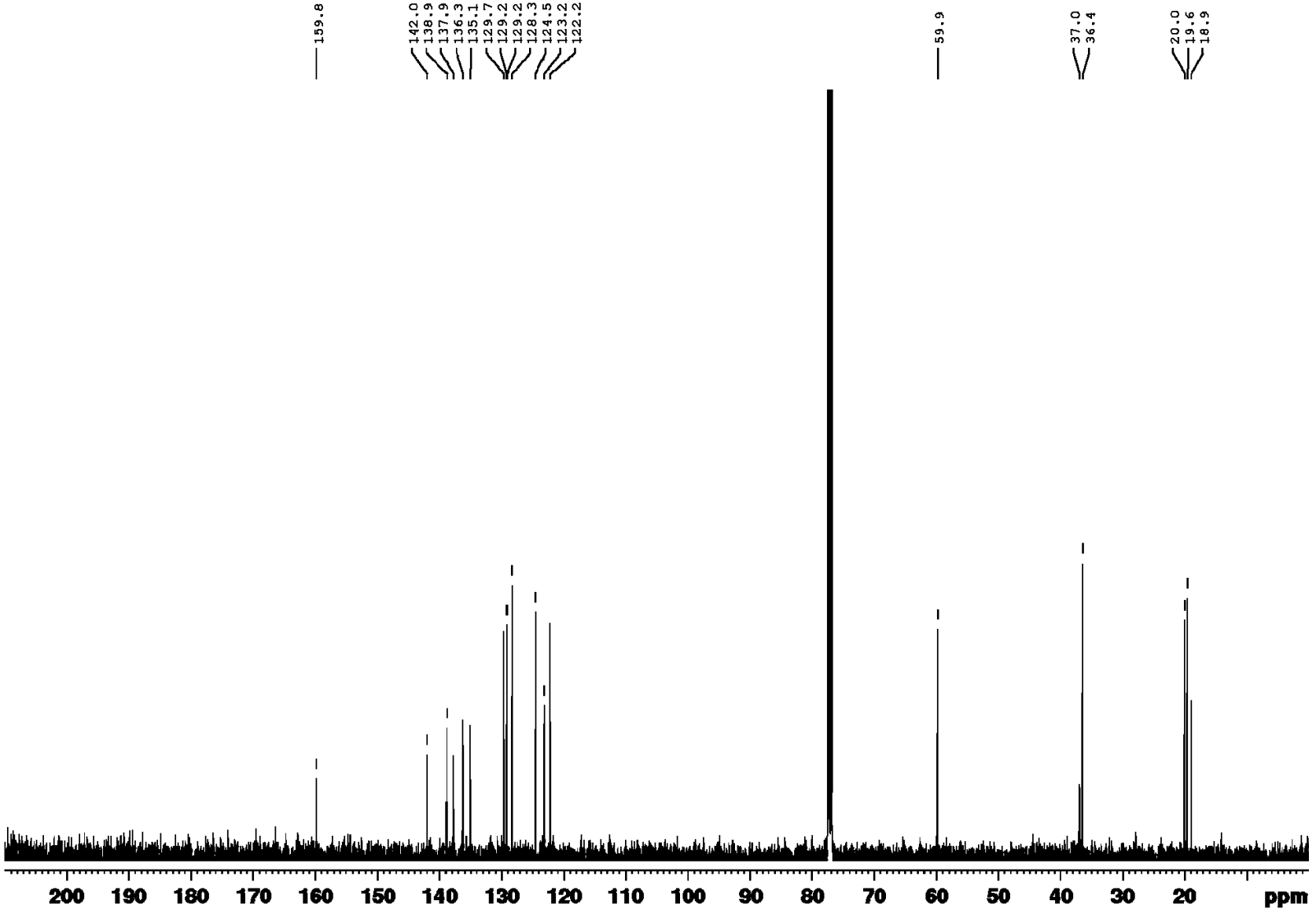


7-(3,4-Dimethylphenyl)-*N*,*N*,3-trimethylindoline-1-carboxamide (**14aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

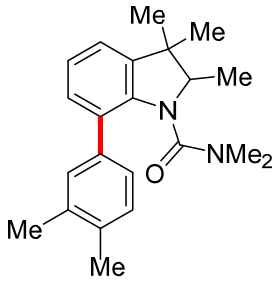


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

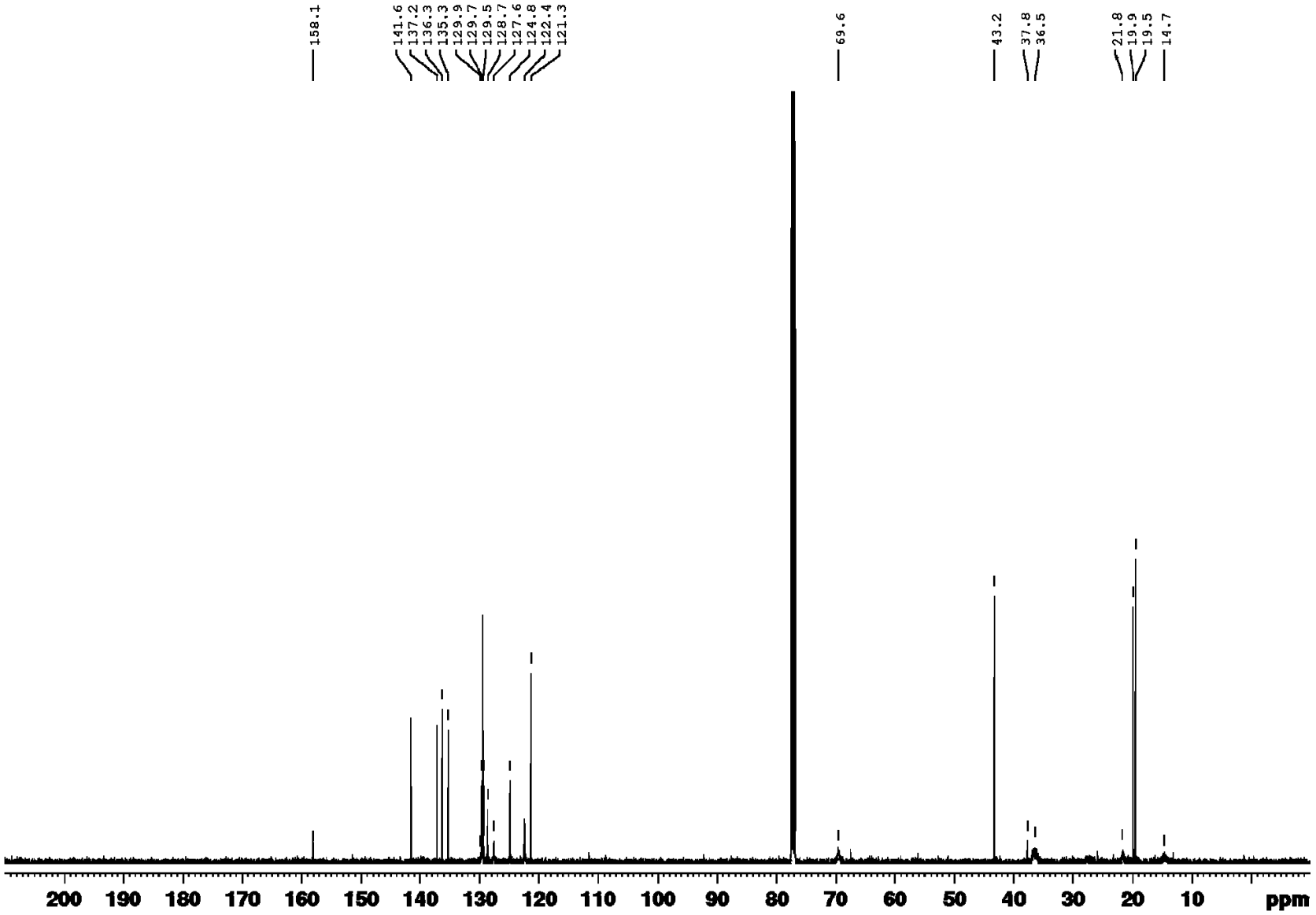


7-(3,4-Dimethylphenyl)-*N*,*N*,2,3,3-pentamethylindoline-1-carboxamide (**15aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

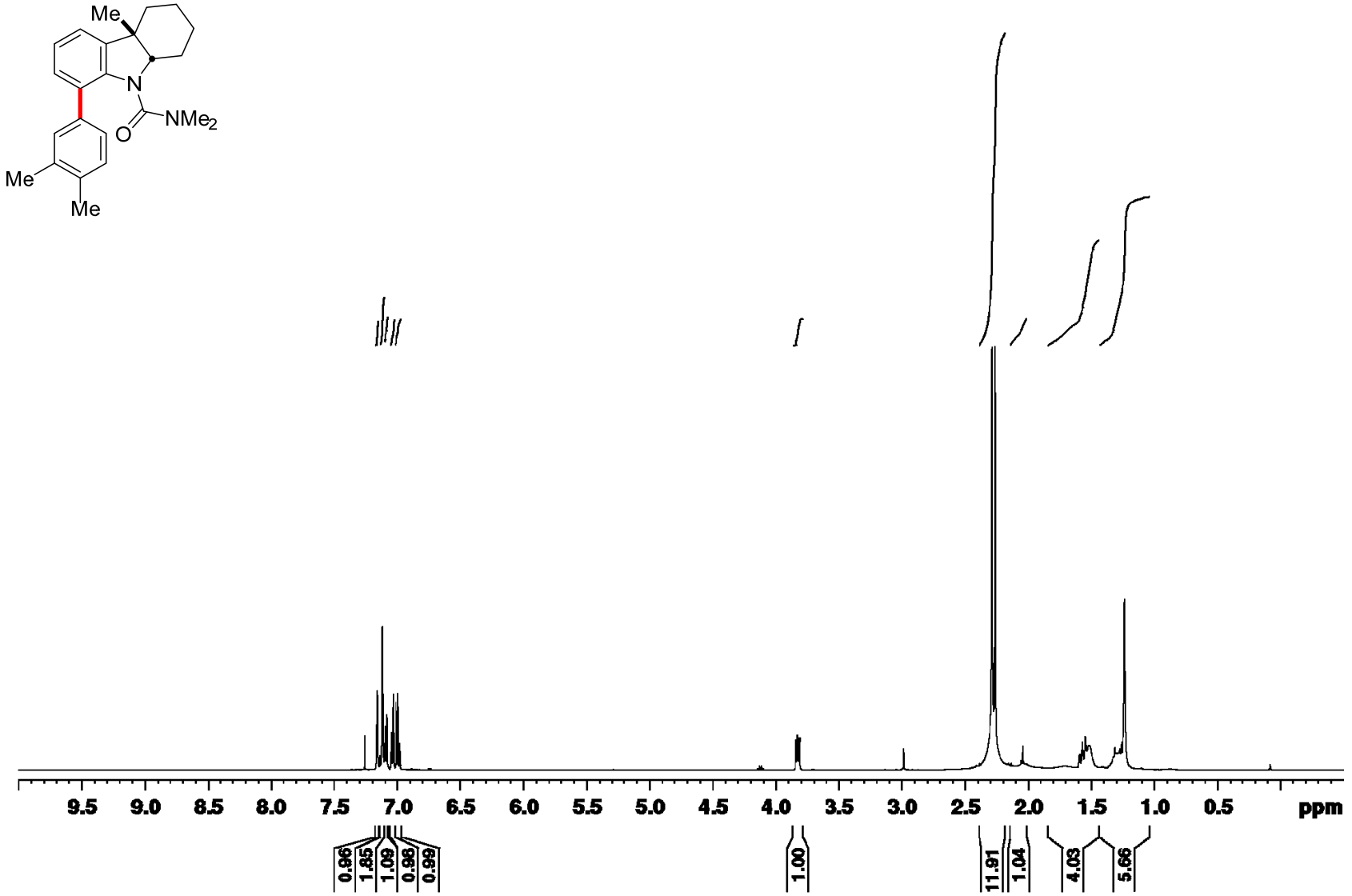


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

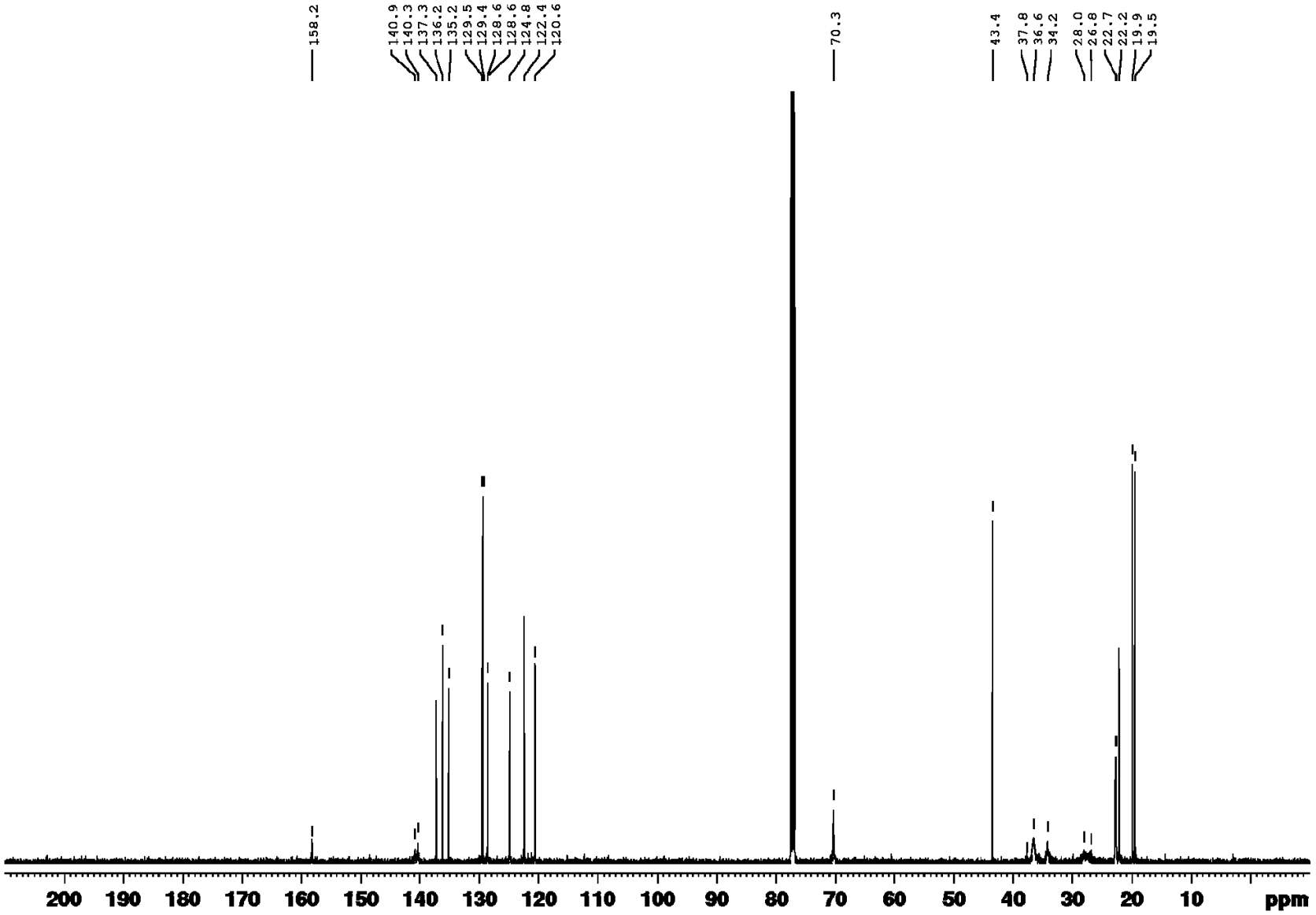


***cis*-8-(3,4-Dimethylphenyl)-*N*,*N*,4a-trimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide (16aa)**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

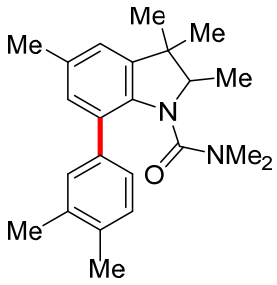


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

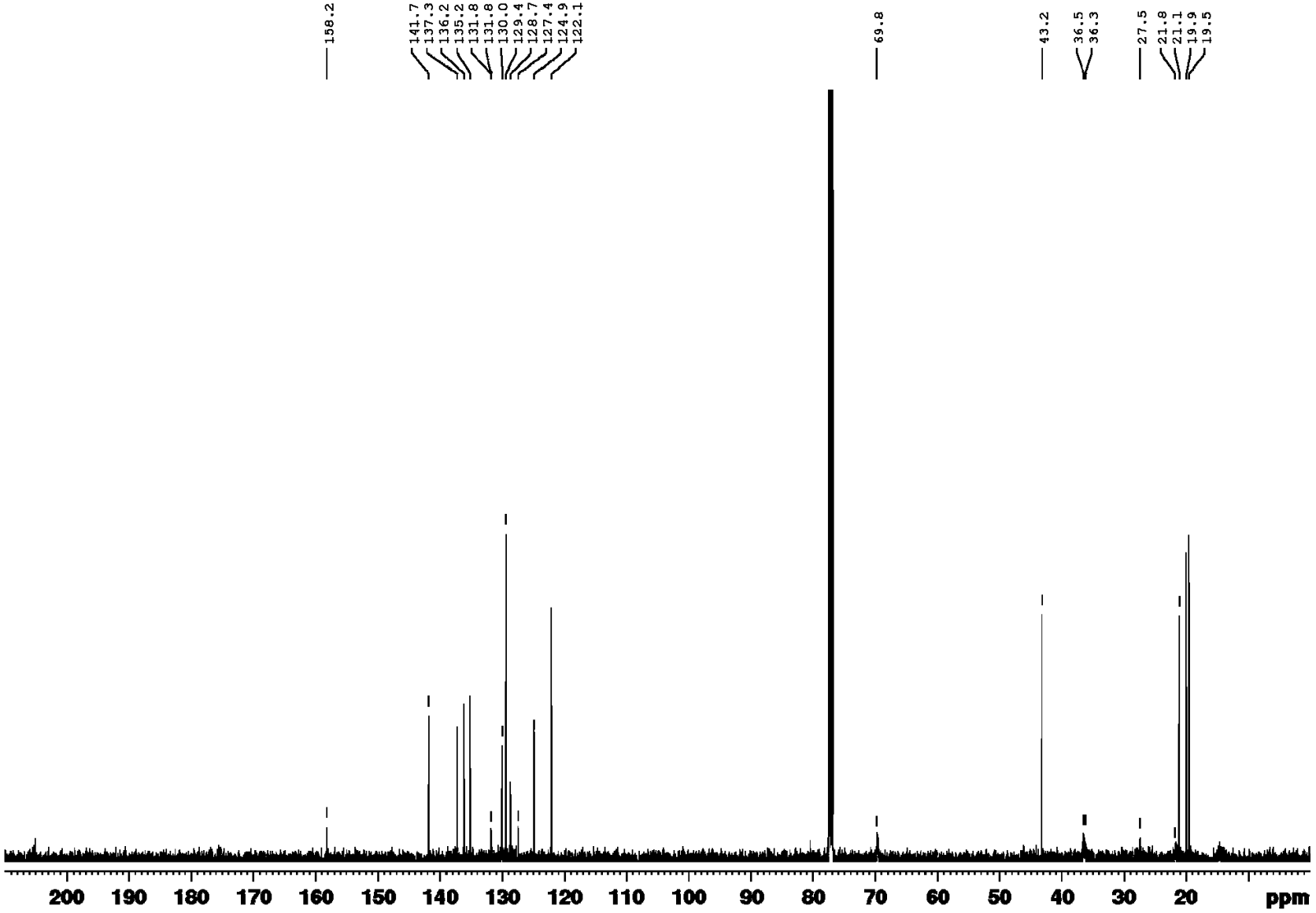


7-(3,4-Dimethylphenyl)-*N*,*N*,2,3,3,5-hexamethylindoline-1-carboxamide (**17aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

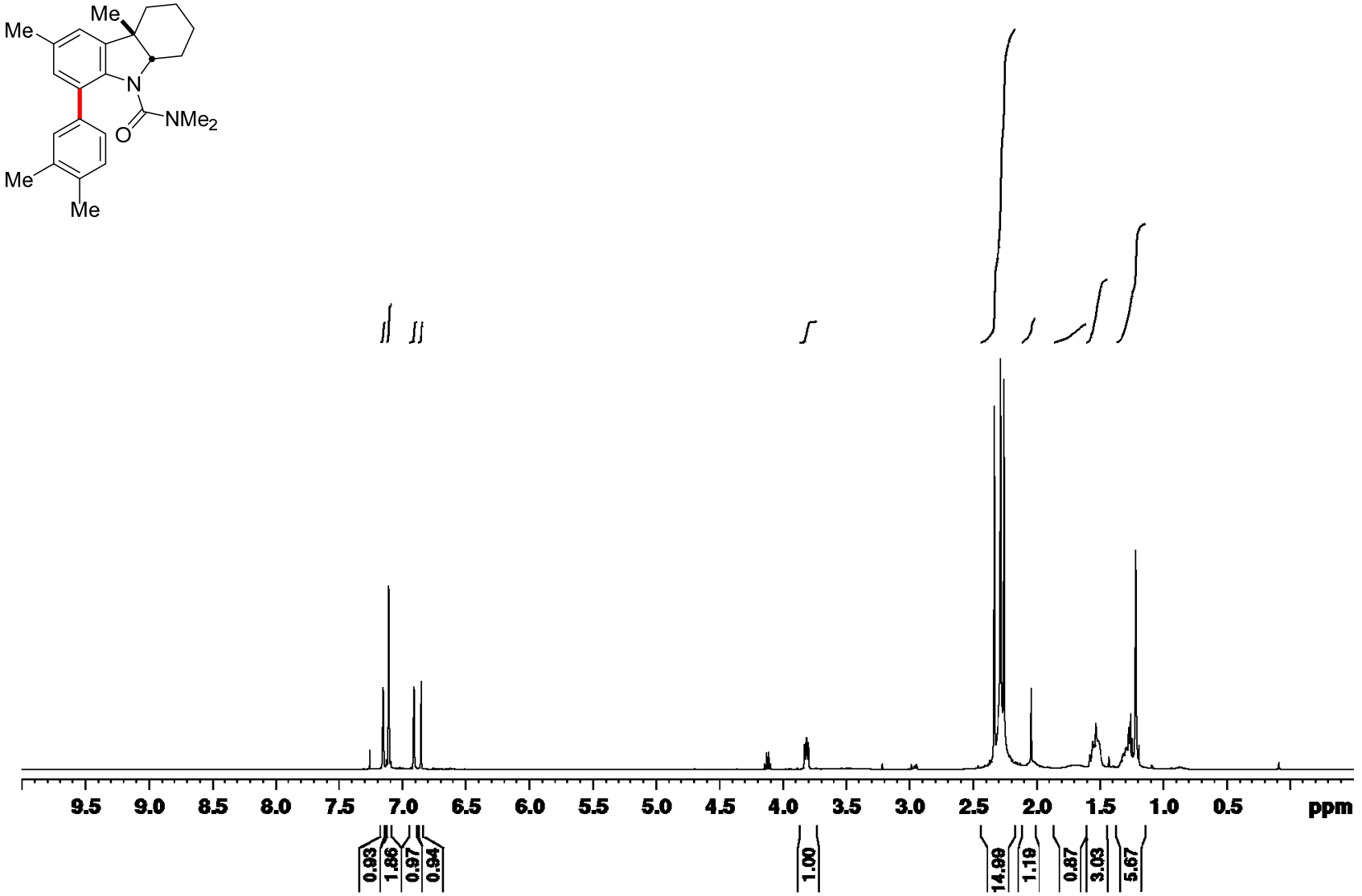


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):

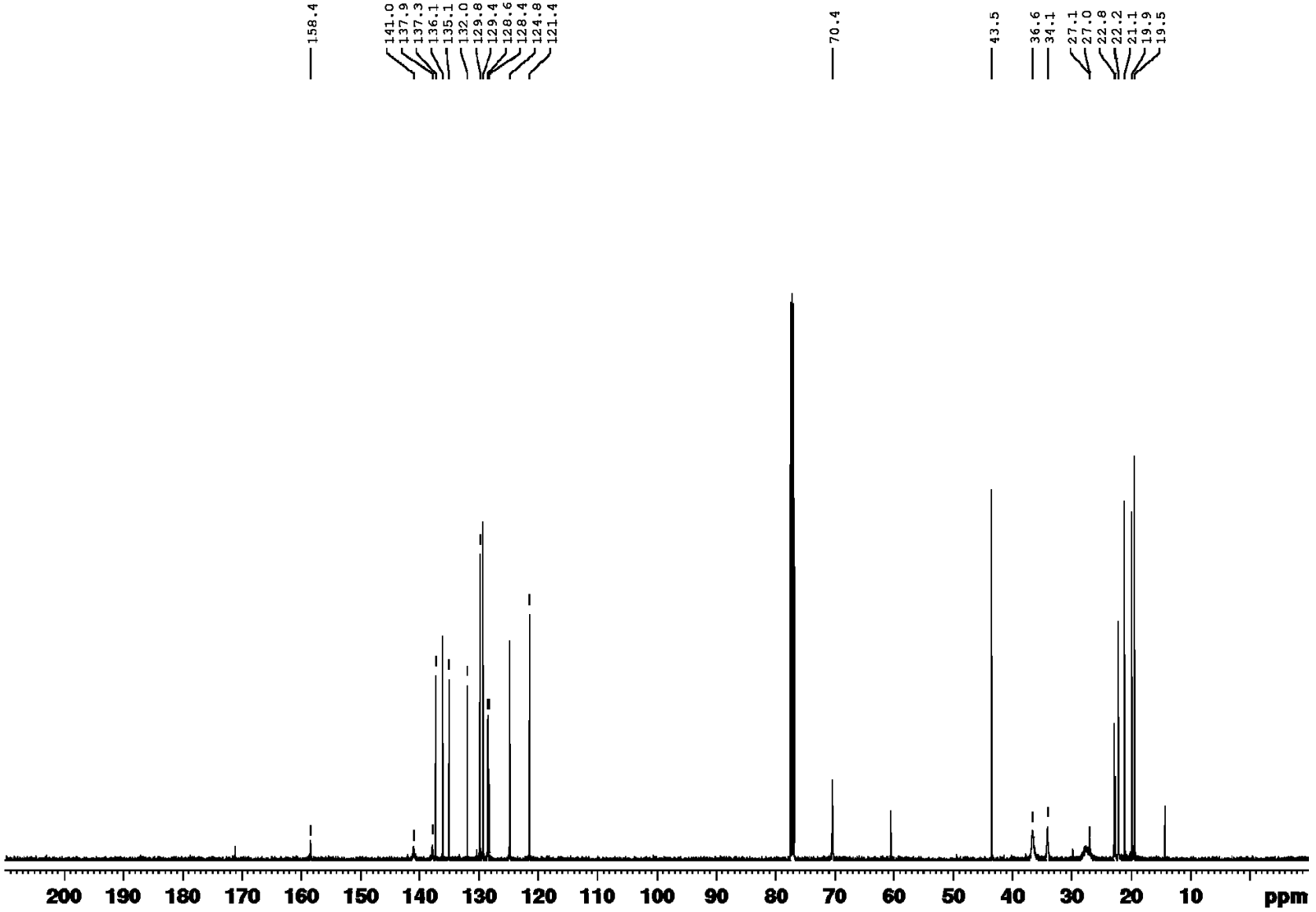


***cis*-8-(3,4-Dimethylphenyl)-*N*,*N*,4a,6-tetramethyl-1,2,3,4,4a,9a-hexahydro-9*H*-carbazole-9-carboxamide (18aa)**

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):

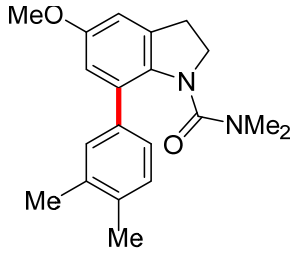


^{13}C NMR (126 MHz, $CDCl_3$, 298 K):



7-(3,4-Dimethylphenyl)-5-methoxy-*N*,*N*-dimethylindoline-1-carboxamide (**19aa**)

^{1}H NMR (500 MHz, $CDCl_3$, 298 K):



^{13}C NMR (126 MHz, $CDCl_3$, 298 K):