SUPPORTING INFORMATION FOR:

Palladium-Catalyzed Synthesis of Indoles via Ammonia Cross-Coupling-Alkyne Cyclization

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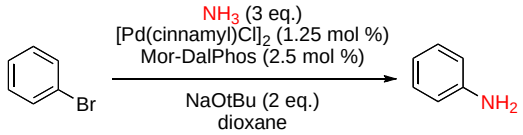
Contents:

General Considerations:

Unless otherwise noted, all reactions were setup inside a dinitrogen-filled inert atmosphere glovebox and worked up in air using benchtop procedures. 1,4-Dioxane (Aldrich) was dried over Na/benzophenone followed by distillation under an atmosphere of dinitrogen. Toluene was deoxygenated by sparging with dinitrogen followed by passage through an mBraun double column solvent purification system packed with alumina and copper-Q5 reactant. $[Pd(cinnamyl)Cl]_2$[S1] was prepared according to a literature procedure and Josiphos CyPF*t*Bu was purchased from Strem Chemicals or provided by Solvias. Each of the 2-alkynylbromoarene substrates were prepared by using literature synthetic protocols involving Sonogashira reactions of aryl iodides (for **1a-j,p**)[S2] or bromides (for **1k-o,q**)[S3] with appropriate terminal alkyne precursors. All other chemicals were obtained from commercial sources in high purity. Ammonia cross-coupling reactions were best conducted with fresh bottles (<2 weeks after opening) of 0.5 M NH_3 in 1,4-dioxane. All methylamine cross-coupling reactions were conducted with 2.0 M $MeNH_2$ in THF, and all hydrazine reactions were conducted with 98% $N_2H_4 \cdot H_2O$. Column chromatography was carried out using Silicycle SiliaFlash 60 with particle size 40-63 μm (230-400 mesh). Gas chromatography data were obtained on a Shimadzu GC-2014 equipped with a SGE BP-5 30 m, 0.25 mm I.D. column. Conversions and yields based on gas chromatography data were corrected by calibration with internal standards of dodecane and product identity was confirmed on the basis of ^{1}H NMR and/or by comparison with authentic samples. ^{1}H and ^{13}C NMR characterization data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1 and 125.8 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$. NMR data were acquired with the technical assistance of Dr. Michael Lumsden (NMR-3, Dalhousie University), while mass spectrometric data were acquired by Mr. Xiao Feng (Mass Spectrometry Laboratory, Dalhousie University). Chemical shifts of common trace ^{1}H NMR impurities ($CDCl_3$, ppm): H_2O, 1.56; DMSO, 2.50; 1,4-dioxane, 3.71; EtOAc, 1.26, 2.05, 4.12; CH_2Cl_2, 5.30; $CHCl_3$, 7.26.

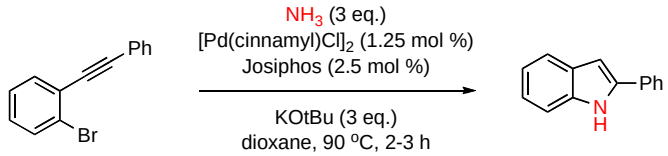
Table S1. Test reactions of Mor-DalPhos/Pd-catalyzed cross-coupling of ammonia with bromobenzene that demonstrate alkyne inhibition.[a]



entry	additive	time (h)	temp	GC yield[b]
1	none	0.75	110 °C	78%
2	20 mol% Ph—≡—Ph	0.75	110 °C	50%
3	none	2	65 °C	82%
4	20 mol% Ph—≡—Ph	2	65 °C	--[c]

[a]Standard reaction conditions: 0.1 mmol scale, [Pd]/L=1:1, NH_3=0.3 mmol, NaO*t*Bu (0.2 mmol) in 1,4-dioxane (1.6 mL). Yields based on calibrated GC data relative to dodecane as an internal standard. [b] >99% conversion of PhBr based on GC analysis. [c] <5% conversion of PhBr.

Table S2. Conditions screen of Pd-catalyzed synthesis of indoles from ammonia.[a]

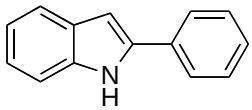


Entry	Variation from standard conditions	Conv. [%][b]	GC Yield [%][b]
1	none	>99	89
2	NaO*t*Bu instead of KO*t*Bu	>99	<5 (89)[c]
3	KOH instead of KO*t*Bu	61	<5
4	Cs_2CO_3 instead of KOtBu	54	-
5	toluene istead of 1,4-dioxane	>99	62
6	Pd:L ratio 1:2 instead of 1:1	>99	89
7	0.5 mol% $[Pd(cinnamyl)Cl]_2$	>99	56
8	ArCl instead of ArBr	<5	-
9	ArOTs instead of ArBr	>99	-[d]
10	Pd_2dba_3 instead of $[Pd(cinnamyl)Cl]_2$	>99	73
11	$Pd[P(o\text{-tolyl})_3]_2$ instead of $[Pd(cinnamyl)Cl]_2$	>99	83
12	0.08 M of ArBr instead of 0.0625 M	>99	89

[a]Standard reaction conditions: 0.1 mmol scale, [Pd]/L=1:1, NH_3=0.3 mmol and KO*t*Bu=0.3 mmmol, 90 °C,in 1,4-dioxane (0.0625 M in substrate). [b]Conversions of ArBr and yields of indole are based on calibrated GC data using dodecane as an internal standard. [c]Isolated yield of 2-(phenyethynyl)aniline at 18 h reaction time. [d]Full consumption of ArOTs; only corresponding phenol observed.

Representative protocol-I: Tandem reaction of ammonia with *o*-alkynylaryl bromides to form NH-indoles:

From a stock solution in 1,4-dioxane, 3.2 mg (0.00625 mmol, 1.25 mol%) of $[Pd(cinnamyl)Cl]_2$ was added to a vial containing the Josiphos ligand CyPF-*t*-Bu (6.9 mg, 0.0125 mmol, 2.50 mol%). The mixture was diluted to 2.000 mL with additional 1,4-dioxane and then stirred for 2 minutes. To this solution was added KO*t*Bu (168 mg, 1.5 mmol), the mixture was stirred briefly and 1-bromo-2-(phenylethynyl)benzene (128.6 mg, 0.5 mmol) was added in 3 x 1 mL portions of 1,4-dioxane. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox, followed by the addition of NH_3 as a 0.5 M solution in 1,4-dioxane (3.000 mL, 1.5 mmol). The solution was heated at 90 ^oC and the reaction progress was monitored by use of TLC or GC methods. After complete consumption of the aryl bromide (3 h), the reaction was cooled, diluted with EtOAc (40 mL) and washed with water (60 mL) followed by 1:1 water/brine (60 mL). The organic fractions were dried with Na_2SO_4, filtered and silica powder (0.5-1.0 g) was added to the crude material. The solvent was removed from the silica-product mixture and the compound was purified by column chromatography with 5% EtOAc/hexanes to afford 2-phenyl-1*H*-indole as a yellow solid in 84% yield (81 mg, 0.42 mmol).

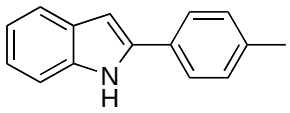


(2a) 2-phenyl-1*H*-indole.[S4]

^1H NMR ($CDCl_3$): δ 8.33 (br s, 1H), 7.68-7.64 (m, 3H), 7.47-7.44 (m, 2H), 7.41 (m, 1H), 7.34 (m, 1H), 7.21 (m, 1H), 7.14 (m, 1H), 6.85 (dd, J = 1.0, 2.2 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 137.8, 136.8, 132.3, 129.2, 129.0, 127.7, 125.1, 122.3, 120.7, 120.3, 110.9, 100.0.

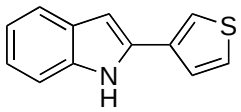
Tandem reaction set-up in air of ammonia with 1-bromo-2-(phenylethynyl)benzene to form 2-phenyl-1*H*-indole (2a). Without the use of the glovebox, a vial containing $[Pd(cinnamyl)Cl]_2$ (3.2 mg, 0.00625 mmol, 1.25 mol%), Josiphos ligand CyPF-*t*-Bu (6.9 mg, 0.0125 mmol, 2.50 mol%) and KO*t*Bu (168 mg, 1.5 mmol) was sealed with a PTFE septum cap and evacuated/backfilled with dinitrogen gas four times. To the vial was added 2.000 mL

of 1,4-dioxane and the resulting mixture was stirred for two minutes. To this solution was added a mixture of 1-bromo-2-(phenylethynyl)benzene (128.6 mg, 0.5 mmol) and dodecane (0.114 mL, 0.500 mmol) in 3 x 1 mL portions of 1,4-dioxane. NH_3 as a 0.5 M solution in 1,4-dioxane (3.000 mL, 1.5 mmol) was then added, the resulting solution was heated at 90 ^oC and the reaction progress was monitored by use of TLC or GC methods. After complete consumption of the aryl bromide (3 h), analysis of the crude reaction mixture gave **2a** in 84% GC yield relative to the dodecane internal standard.



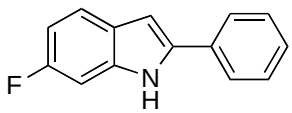
(2b) 2-(4-methylphenyl)-1*H*-indole.[S5] The representative protocol-I was followed to afford the product as a yellow solid in 89% yield (92 mg, 0.44 mmol).

^1H NMR ($CDCl_3$): δ 8.29 (br s, 1H), 7.63 (m, 1H), 7.58-56 (m, 2H), 7.40 (m, 1H), 7.27-7.25 (m, 2H), 7.19 (m, 1H), 7.13 (m, 1H), 6.80 (dd, J = 0.9, 2.1 Hz, 1H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 138.0, 137.6, 136.6, 129.7, 129.5, 129.3, 125.0, 122.1, 120.5, 120.2, 110.8, 99.4, 21.2.



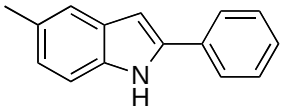
(2c) 2-(3-thienyl)-1*H*-indole.[S6] The representative protocol-I was followed to afford the product as a beige solid in 85% yield (85 mg, 0.43 mmol).

^1H NMR ($CDCl_3$): δ 8.22 (br s, 1H), 7.62 (m, 1H), 7.43-7.41 (m, 3H), 7.39 (m, 1H), 7.20 (m, 1H), 7.13 (m, 1H), 6.71 (dd, J = 0.9, 2.1 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 136.4, 134.1, 134.0, 129.0, 126.7, 125.7, 122.3, 120.6, 120.3, 119.1, 110.7, 99.9.

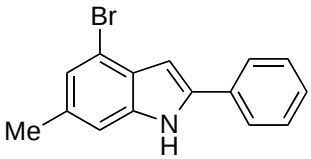


(2d) 6-fluoro-2-phenyl-1*H*-indole. The representative protocol-I was followed to afford the product as a yellow solid in 69% yield (73 mg, 0.35 mmol).

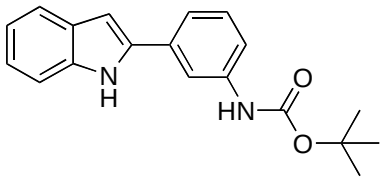
^{1}H NMR (CD_3OD): δ 7.66-7.64 (m, 2H), 7.37 (dd, J = 5.4, 8.7 Hz, 1H), 7.33-7.29 (m, 2H), 7.18 (m, 1H), 6.97 (dd, J = 2.3, 9.8 Hz, 1H), 6.70-6.66 (m, 2H). The N-H proton is not visible due to exchange with the deuterated solvent; ^{13}C{^{1}H} NMR (CD_3OD): 161.4 (d, J_{CF} = 236.3 Hz), 140.2, 138.9 (d, J_{CF} = 13.4 Hz), 134.1, 130.1, 128.5, 127.4, 126.1, 122.1 (d, J_{CF} = 10.1 Hz), 109.0 (d, J_{CF} = 24.9 Hz), 99.8, 98.1 (d, J_{CF} = 26.1 Hz). HRMS (ESI/[M+H]$^+$) calcd. for $C_{14}H_{11}FN$: 212.0870. Found: 212.0877.



(2e) 5-methyl-2-phenyl-1*H*-indole.[S7] The representative protocol-I was followed using 2.5 mol% [Pd(cinnamyl)Cl]$_2$ (6.5 mg, 0.0125 mmol) and 5 mol% JosiPhos (13.9 mg, 0.025 mmol) to afford the product as a yellow solid in 80% yield (84 mg, 0.40 mmol).
^{1}H NMR ($CDCl_3$): δ 8.24 (br s, 1H), 7.67-7.65 (m, 2H), 7.46-7.41 (m, 3H), 7.33-7.29 (m, 2H), 7.02 (dd, J = 1.3, 8.3 Hz, 1H), 6.76 (dd, J = 0.9, 2.2 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.9, 135.1, 132.5, 129.5, 129.5, 129.0, 127.6, 125.0, 124.0, 120.3, 110.5, 99.5, 21.5.

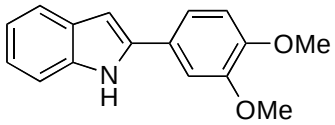


(2f) 4-bromo-6-methyl-2-phenyl-1*H*-indole. The representative protocol-I was followed using 10% EtOAc/hexanes for column chromatography to afford the product as a beige solid in 66% yield (94 mg, 0.33 mmol).
^{1}H NMR ($CDCl_3$): δ 8.32 (br s, 1H), 7.67-7.64 (m, 2H), 7.47-7.43 (m, 2H), 7.34 (m, 1H), 7.13 (dd, J = 0.5, 1.1 Hz, 1H), 7.12 (m, 1H), 6.82 (dd, J = 0.9, 3.2 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 137.8, 137.2, 133.5, 131.9, 129.1, 127.9, 127.9, 125.1, 124.7, 114.1, 110.1, 99.9, 21.5. HRMS (ESI/[M+H]$^+$) calcd. for $C_{15}H_{13}BrN$: 286.0226. Found: 286.0223.



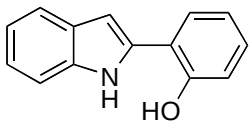
(2g) *tert*-butyl-3-(1*H*-indol-2-yl)phenylcarbamate. The representative protocol-I was followed using 3.5 equiv. of KO*t*Bu (196.4 mg, 1.75 mmol) and 10% EtOAc/hexanes for column chromatography to afford the product as a beige solid in 63% yield (97 mg, 0.31 mmol).

^{1}H NMR ($CDCl_3$): δ 8.44 (br s, 1H), 7.90 (br s, 1H), 7.62 (dd, J = 0.8, 7.9 Hz, 1H), 7.39 (dd, J = 0.9, 8.1 Hz, 1H), 7.88-7.32 (m, 2H), 7.19 (m, 1H), 7.14-7.10 (m, 2H), 6.83 (dd, J = 0.9, 2.1 Hz, 1H), 6.57 (br s, 1H), 1.56 (s, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.8, 139.0, 137.6, 136.8, 133.2, 129.5, 129.1, 122.3, 120.6, 120.1, 120.0, 117.5, 114.8, 111.0, 100.1, 80.8, 28.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{21}N_2O_2$: 309.1598. Found: 309.1602.



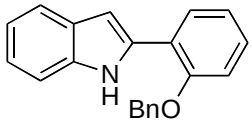
(2h) 2-(3,4-dimethoxyphenyl)-1*H*-indole.[S8] The representative protocol-I was followed using 20% EtOAc/hexanes for column chromatography to afford the product as a beige solid in 88% yield (111 mg, 0.44 mmol).

^{1}H NMR (CD_3OD): δ 7.50 (m, 1H), 7.39 (d, J = 2.1 Hz, 1H), 7.37-7.35 (m, 2H), 7.06 (m, 1H), 7.01-6.96 (m, 2H), 6.70 (d, J = 0.8 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 3H). The N-H proton is not visible due to exchange with the deuterated solvent; ^{13}C{^{1}H} NMR (CD_3OD): δ 150.9, 150.2, 139.6, 138.9, 130.9, 127.8, 122.5, 121.0, 120.5, 119.2, 113.4, 112.0, 110.4, 99.0, 56.7, 56.7.

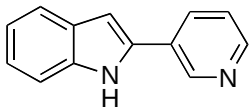


(2i) 2-(2-hydroxyphenyl)-1*H*-indole.[S9] The representative protocol-I was followed using the

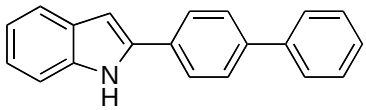
TBS-protected substrate as starting material and 10% EtOAc/hexanes for column chromatography to afford the product as a yellow solid in 49% yield (51 mg, 0.24 mmol). ^{1}H NMR ($CDCl_3$): δ 9.24 (br s, 1H), 7.70 (dd, *J* =1.6, 7.8 Hz, 1H), 7.66 (m, 1H), 7.42 (m, 1H), 7.23-7.20 (m, 2H), 7.15 (m, 1H), 7.04 (m, 1H), 6.92 (dd, *J* = 1.0, 8.1 Hz, 1H), 6.87 (dd, *J* = 0.9, 2.2 Hz, 1H), 5.62 (br s, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.9, 136.4, 134.8, 128.9, 128.3, 128.3, 122.2, 121.5, 120.4, 120.1, 119.1, 116.5, 111.0, 100.1.



(2j) 2-(2-(benzyloxy)phenyl)-1H-indole. The representative protocol-I was followed using 5-20% EtOAc/hexanes for column chromatography to enable the isolation of the product as a yellow solid in 53% combined yield (80 mg, 0.27 mmol). **2i** was also isolated from the reaction as a light brown solid in 34% yield (36 mg, 0.17 mmol).
^{1}H NMR ($CDCl_3$): δ 9.76 (br s, 1H), 7.90 (dd, *J* = 1.5, 7.7 Hz, 1H), 7.64 (m, 1H), 7.53-7.51 (m, 2H), 7.49-7.42 (m, 3H), 7.29 (m, 1H), 7.19 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.16-7.08 (m, 4H), 6.94 (dd, *J* = 0.8, 2.2 Hz, 1H), 5.24 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.9, 136.3, 136.0, 135.8, 128.9, 128.6, 128.5, 128.3, 127.9, 127.7, 121.9, 121.7, 121.0, 120.2, 119.7, 113.5, 110.8, 99.7, 71.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{21}H_{18}NO$: 300.1383. Found 300.1377.

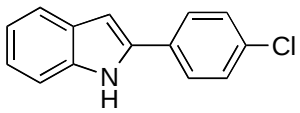


(2k) 2-(3-pyridyl)-1*H*-indole.[S10] The representative protocol-I was followed using 2.5 mol% $[Pd(cinnamyl)Cl]_2$ (6.5 mg, 0.0125 mmol) and 5 mol% JosiPhos (13.9 mg, 0.025 mmol) with heating for 4 h. The crude material was purified using column chromatography employing 50% EtOAc/hexanes to afford the product as a beige solid in 61% yield (59 mg, 0.30 mmol). ^{1}H NMR (CD_3OD): δ 8.97 (d, *J* = 1.8 Hz, 1H), 8.42 (dd, *J* = 1.3, 4.8 Hz, 1H), 8.19 (m, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.47 (ddd, *J* = 0.6, 4.8, 8.0 Hz, 1H), 7.41 (dd, *J* = 0.8, 8.2 Hz, 1H), 7.16-7.12 (m, 1H), 7.02 (m, 1H), 6.93 (d, *J* = 0.7 Hz, 1H). The N-H proton is not visible due to exchange with the deuterated solvent; ^{13}C{^{1}H} NMR (CD_3OD): δ 148.4, 146.8, 139.4, 135.4, 134.3, 131.1, 130.5, 125.6, 123.7, 121.7, 121.0, 112.4, 101.6.



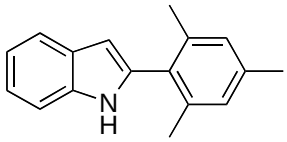
(2l) 2-(4-biphenyl)-1*H*-indole. The representative protocol-I was followed to obtain the crude material, which was washed with dichloromethane (50 mL) to afford the pure product as a light brown solid in 78% yield (105 mg, 0.39 mmol).

^{1}H NMR ($(CD_3)_2SO$): δ 11.59 (br s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.82-7.70 (m, 4H), 7.55-7.36 (m, 5H), 7.12 (m, 1H), 7.01 (m, 1H), 6.96 (s, 1H); ^{13}C{^{1}H} NMR ($(CD_3)_2SO$): δ 139.5, 138.8, 137.2, 131.3, 129.0, 128.7, 127.5, 127.1, 126.4, 125.5, 121.6, 120.0, 119.4, 111.3, 98.9. HRMS (ESI/$[M+H]^+$) calcd. for $C_{20}H_{16}N$: 270.1277. Found 270.1272.



(2m) 2-(4-chlorophenyl)-1*H*-indole.[S4] The representative protocol-I was followed using 2.5 mol% $[Pd(cinnamyl)Cl]_2$ (6.5 mg, 0.0125 mmol) and 5 mol% Josiphos (13.9 mg, 0.025 mmol) to afford the product as a yellow solid in 84% yield (96 mg, 0.42 mmol).

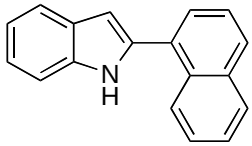
^{1}H NMR ($CDCl_3$): δ 8.28 (br s, 1H), 7.63 (d, J = 7.9 Hz, 1H), 7.60-7.57 (m, 2H), 7.43-7.40 (m, 3H), 7.22 (m, 1H), 7.14 (m, 1H), 6.82 (m, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 136.9, 136.7, 133.4, 130.9, 129.2, 129.1, 126.3, 122.7, 120.7, 120.5, 110.9, 100.4.



(2n) 2-mesityl-1H-indole. The representative protocol-I was followed using 6.0 equiv. of KO*t*Bu (336.6 mg, 3.00 mmol) at 110 ^{o}C for 60 h. The crude product was purified using 2% EtOAc/hexanes for column chromatography to afford the product as a yellow solid, which was initially washed followed by recrystallization using hexanes to give the pure product as a white solid in 75% combined yield (88 mg, 0.37 mmol).

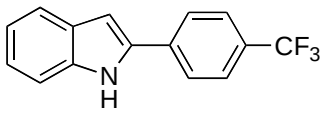
^{1}H NMR ($CDCl_3$): δ 7.86 (br s, 1H), 7.68 (m, 1H), 7.41 (ddd, J = 0.9, 1.8, 8.0 Hz, 1H), 7.22 (m, 1H), 7.17 (m, 1H), 7.00 (d, J = 0.6 Hz, 2H), 6.41 (dd, J = 0.9, 2.2 Hz, 1H), 2.38 (s, 3H),

2.18 (s, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 138.2, 138.2, 136.2, 135.9, 130.0, 128.8, 128.1, 121.4, 120.3, 119.7, 110.6, 102.6, 21.1, 20.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{18}N$: 236.1434. Found 236.1433.



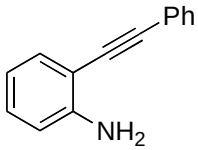
(2o) 2-(1-naphthenyl)-1*H*-indole.[S11] The representative protocol-I was followed using 2% EtOAc/hexanes for column chromatography to afford the product as an orange solid in 74% yield (90 mg, 0.37 mmol).

^{1}H NMR ($CDCl_3$): δ 8.34 (m, 1H), 8.30 (br s, 1H), 7.94 (m, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.73 (m, 1H), 7.65 (dd, J = 1.2, 7.1 Hz, 1H), 7.57-7.51 (m, 3H), 7.46 (dd, J = 0.8, 8.0 Hz, 1H), 7.27 (m, 1H), 7.21 (m, 1H), 6.82 (dd, J = 0.9, 2.1 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 136.7, 136.3, 133.9, 131.5, 131.1, 128.8, 128.6, 128.5, 127.2, 126.7, 126.2, 125.7, 125.3, 122.2, 120.6, 120.2, 110.8, 103.7.



(2p) 2-(4-(trifluoromethyl)phenyl)-1H-indole. The representative protocol-I was followed using 2.5 mol% $[Pd(cinnamyl)Cl]_2$ (6.5 mg, 0.0125 mmol) and 5 mol% JosiPhos (13.9 mg, 0.025 mmol) with heating overnight. The crude material was purified using column chromatography employing 5% EtOAc/hexanes to afford the product as an off-white solid in 31% yield (41 mg, 0.16 mmol).

^{1}H NMR (CD_3OD): δ 7.95 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.56 (d, J = 8.0 Hz, 1H), 7.41 (dd, J = 0.8, 8.2 Hz, 1H), 7.14 (m, 1H), 7.03 (m, 1H), 6.94 (s, 1H). The N-H proton is not visible due to exchange with the deuterated solvent; $^{13}C\{^{1}H\}$ NMR (CD_3OD): δ 139.4, 138.1, 137.6, 130.5, 129.8 (q, J_{CF} = 32.4 Hz), 126.9 (d, J_{CF} = 3.6 Hz), 126.5, 126.0 (q, J_{CF} = 270.8 Hz), 123.7, 121.8, 121.0, 112.5, 101.8. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{11}F_3N$: 262.0838. Found 262.0839.

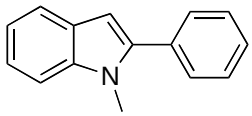


(2a') 2-(phenylethynyl)aniline.[S12] The representative protocol-I was followed using 2.0 eq. NaO*t*Bu (96.1 mg, 1.0 mmol) in place of KO*t*Bu to afford the product as a yellow solid in 89% yield (86 mg, 0.45 mmol).

^{1}H NMR ($CDCl_3$): δ 7.56-7.54 (m, 2H), 7.40-7.33 (m, 4H), 7.16 (m, 1H), 6.76-6.73 (m, 2H), 4.29 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 147.7, 132.1, 131.4, 129.7, 128.3, 128.2, 123.3, 117.9, 114.3, 107.9, 94.7, 85.9.

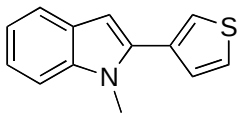
Representative protocol-II: Tandem reaction of methylamine with *o*-alkynylaryl bromides to form NMe-indoles:

From a stock solution in toluene, 3.2 mg (0.00625 mmol, 1.25 mol%) of $[Pd(cinnamyl)Cl]_2$ was added to a vial containing Josiphos ligand CyPF*t*Bu (6.9 mg, 0.0125 mmol, 2.50 mol%) in 5.200 ml toluene followed by stirring for 2 minutes. To this solution was added KO*t*Bu (168.3 mg, 1.5 mmol). The mixture was stirred briefly and 1-bromo-2-(phenylethynyl)benzene (128.6 mg, 0.500 mmol) was added in portions using a total amount of 1.250 mL of toluene. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox, followed by the addition of NH_2CH_3 as a 2.0 M solution in tetrahydrofuran (0.300 mL, 0.6 mmol). The solution was heated to 90 °C and the reaction progress was monitored using by TLC or GC methods. After complete consumption of the aryl bromide (16-24 h), the reaction was cooled, diluted with EtOAc (40 mL) and washed with water (70 mL) followed by 1:1 water/brine (70 mL). The organic fractions were dried with Na_2SO_4, filtered and silica powder (0.5-1.0 g) was added to the crude material. The solvent was removed from the product-silica mixture and the compound was purified by column chromatography with hexanes to afford 1-methyl-2-phenyl-1*H*-indole as a yellow solid in 88% yield (91 mg, 0.44 mmol).



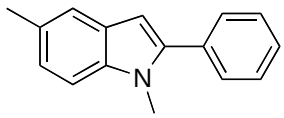
(3a) 1-methyl-2-phenyl-1*H*-indole.[S13]

^{1}H NMR ($CDCl_3$): δ 7.70-7.68 (m, 1H), 7.57-7.55 (m, 2H), 7.53-7.49 (m, 2H), 7.44 (m, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.30 (m, 1H), 7.20 (m, 1H), 6.62 (s, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.9, 138.7, 133.2, 129.7, 128.8, 128.3, 128.2, 122.0, 120.8, 120.2, 109.9, 102.0, 31.5.



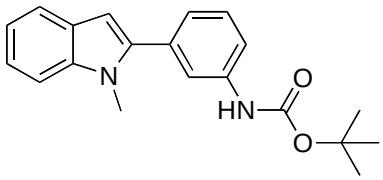
(3b) 1-methyl-2-(thiophen-3-yl)-1*H*-indole. The representative protocol-II was followed using column chromatography employing 0-2% EtOAc/hexaness to afford the product as a yellow solid in 86% yield (92 mg, 0.43 mmol).

^{1}H NMR ($CDCl_3$): δ 7.66 (m, 1H), 7.46 (m, 1H), 7.42 (dd, *J* = 1.5, 3.0 Hz, 1H), 7.38 (m, 1H), 7.32 (dd, *J* = 1.5, 5.0 Hz, 1H), 7.27 (m, 1H), 7.18 (m, 1H), 6.63 (d, *J* = 0.5 Hz, 1H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.4, 136.7, 133.7, 128.8, 128.1, 126.2, 123.5, 122.0, 120.7, 120.2, 109.8, 101.8, 31.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{13}H_{12}NS$: 214.0685. Found: 214.0686.



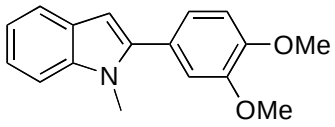
(3c) 1,5-Dimethyl-2-phenyl-1*H*-indole.[S14] The representative protocol-II was followed using 2.5 mol% $[Pd(cinnamyl)Cl]_2$ (6.5 mg, 0.0125 mmol), 5 mol% JosiPhos (13.9 mg, 0.025 mmol) and 0-5% EtOAc/hexanes for column chromatography to afford the product as a yellow solid in 78% yield (86 mg, 0.39 mmol).

^{1}H NMR ($CDCl_3$): δ 7.54-7.51 (m, 2H), 7.49-7.46 (m, 2H), 7.44 (m, 1H), 7.40 (m, 1H), 7.27 (m, 1H), 7.09 (dd, *J* = 1.5, 8.5 Hz, 1H), 6.51 (d *J* = 0.7 Hz, 1H), 3.74 (s, 3H), 2.49 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.0, 137.2, 133.3, 129.6, 129.4, 128.8, 128.5, 128.1, 123.6, 120.4, 109.6, 101.5, 31.6, 21.8.



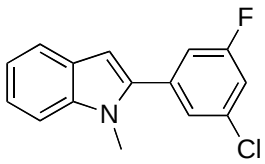
(3d) *tert*-butyl-3-(1-methyl-1*H*-indol-2-yl)phenylcarbamate. The representative protocol-II was followed using 4.0 eq. of KO*t*Bu (224.4 mg, 2.00 mmol) and 10% EtOAc/hexanes for column chromatography to afford the product as a yellow solid in 67% yield (108 mg, 0.34 mmol).

^{1}H NMR ($CDCl_3$): δ 7.64 (m, 1H), 7.54 (br s, 1H), 7.40-7.36 (m, 3H), 7.26 (m, 1H),7.20-7.15 (m, 2H), 6.59 (br s, 1H), 6.57 (s, 1H), 3.76 (s, 3H), 1.55 (s, 9H); ^{13}C{1H} NMR ($CDCl_3$): δ 153.0, 141.5, 138.9, 138.7, 133.9, 129.4, 128.2, 124.3, 122.0, 120.8, 120.2, 119.8, 188.3, 109.9, 102.1, 81.1, 31.6, 28.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{20}H_{23}N_2O_2$: 323.1754. Found: 323.1767.



(3e) 2-(3,4-dimethoxyphenyl)-1-methyl-1*H*-indole. The representative protocol-II was followed using 6.0 eq. of KO*t*Bu (224.4 mg, 2.00 mmol), heating overnight at 110 ^{o}C and 20% EtOAc/hexanes for column chromatography to afford the product as a light brown solid in 76% yield (101 mg, 0.38 mmol).

^{1}H NMR ($CDCl_3$): δ 7.64 (d, J = 8.0 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.25 (m, 1H), 7.16 (m, 1H), 7.08-7.04 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.54 (s, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.75 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 149.3, 149.1, 141.8, 138.5, 128.2, 125.8, 122.2, 121.8, 120.6, 120.2, 113.0, 111.4, 109.9, 101.4, 56.3, 56.3, 31.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{17}H_{18}NO_2$: 268.1332. Found: 268.1353.

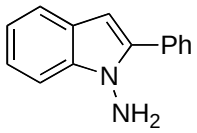


(3f) 2-(3-chloro-5-fluorophenyl)-1-methyl-1*H*-indole. The representative protocol-II was

followed using 4.0 eq. Cs_2CO_3 (651.6 mg, 2.00 mmol) with heating overnight. A solution of 3.0 eq. KO*t*Bu (168.3 mg, 1.5 mmol) in toluene was then added to the reaction mixture followed by heating overnight. The crude material was purified using column chromatography employing hexanes to afford the product as a yellow oil in 52% yield (68 mg, 0.26 mmol).

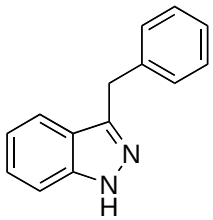
^{1}H NMR ($CDCl_3$): δ 7.65 (m, 1H), 7.38 (m, 1H), 7.32-7.28 (m, 2H), 7.18 (m, 1H), 7.15-7.12 (m, 2H), 6.61 (d, J = 0.5 Hz, 1H), 3.77 (s, 3H); ^{13}C DEPTQ-135 NMR ($CDCl_3$): δ 162.8 (d, J_{CF} = 250.0 Hz), 139.0, 136.2 (d, J_{CF} = 8.8 Hz), 135.5 (d, J_{CF} = 11.3 Hz), 128.0, 125.5, 125.4, 122.8, 121.2, 120.6, 115.8 (d, J_{CF} = 23.9 Hz), 114.9 (d, J_{CF} = 22.7 Hz), 110.1, 103.3, 31.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{12}ClFN$: 260.0637. Found: 260.0636.

Representative protocol-III: Tandem reaction of hydrazine monohydrate with *o*-alkynylaryl bromides: From a stock solution in 1,4-dioxane, 6.5 mg (0.0125 mmol, 2.50 mol%) of $[Pd(cinnamyl)Cl]_2$ was added to a vial containing Josiphos ligand CyPF*t*Bu (13.8 mg, 0.0250 mmol, 5.0 mol%). The mixture was diluted to 2.000 mL with additional 1,4-dioxane and then was stirred for 2 minutes. To this solution was added KO*t*Bu (168 mg, 1.5 mmol), the mixture was stirred briefly and 1-bromo-2-(phenylethynyl)benzene was added in 3 x 1 mL portions of 1,4-dioxane. The vial was sealed with a cap containing a PTFE septum and removed from the glovebox, followed by the addition of $N_2H_4 \cdot H_2O$ (0.0500 mL, 1.0 mmol). The solution was heated at 90 ^{o}C and the reaction progress was monitored by use of TLC methods. After complete consumption of the aryl bromide (1 h), the reaction was cooled, diluted with EtOAc (40 mL) and washed with water (70 mL) followed by 1:1 water/brine (70 mL). The organic fractions were dried with Na_2SO_4, filtered and silica powder (0.5-1.0 g) was added to the crude material. The solvent was removed and the compound was purified by column chromatography with 10-30% EtOAc/hexanes to afford 2-phenyl-1*H*-indol-1-amine (**4a**) as a beige solid in 56% yield (58 mg, 0.28 mmol) and 2-phenyl-1*H*-indazole (**4a'**) in 31% yield (32 mg, 0.15 mmol) also as a beige solid.



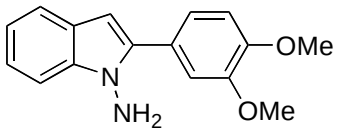
(4a) 2-phenyl-1*H*-indol-1-amine.

^{1}H NMR ($CDCl_3$): δ 7.71-7.69 (m, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.50-7.47 (m, 3H), 7.40 (m, 1H), 7.28 (m, 1H), 7.17 (m, 1H), 6.57 (s, 1H), 4.50 (br s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.0, 138.6, 131.9, 129.2, 128.4, 127.8, 125.6, 122.1, 120.5, 120.3, 108.9, 99.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{13}N_2$: 209.1073. Found: 209.1062.



(4a') 3-benzyl-1*H*-indazole.

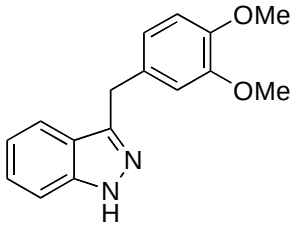
^{1}H NMR ($CDCl_3$): δ 10.43 (br s, 1H), 7.55 (dt, *J* = 1.0, 8.2 Hz, 1H), 7.41 (dt, *J* = 0.9, 8.4 Hz, 1H), 7.36-7.33 (m, 3H), 7.31-7.28 (m, 2H), 7.22 (m, 1H), 7.09 (m, 1H), 4.39 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.9, 141.3, 138.9, 128.8, 128.5, 126.8, 126.3, 122.1, 120.5, 120.4, 109.8, 33.7. HRMS (ESI/$[M+H]^+$) calcd. for $C_{14}H_{13}N_2$: 209.1073. Found: 209.1070.



(4b) 2-(3,4-dimethoxyphenyl)-1*H*-indol-1-amine. The representative protocol-III was followed using 35-40% EtOAc/hexanes for column chromatography to afford **4b** as a beige solid in 61% yield (82 mg, 0.31 mmol) and **4b'** as a beige solid in 10% yield (14 mg, 0.052 mmol). An accurate ^{1}H NMR yield was obtained of the crude product mixture relative to 1,3,5-trimethoxybenzene (61% and 17%, respectively).

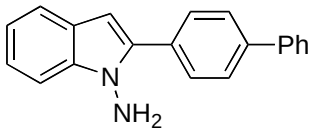
^{1}H NMR ($CDCl_3$): δ 7.60 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.26 (m, 3H), 7.16 (m, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.52 (d, *J* = 0.7 Hz, 1H), 4.58 (s, 2H), 3.94 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.9, 148.7, 140.8, 138.3, 125.6, 124.5, 121.8, 121.7, 120.3,

112.5, 111.0, 108.7, 98.9, 55.9, 55.9. HRMS (ESI/$[M+H]^+$) calcd. for $C_{16}H_{17}N_2O_2$: 269.1285. Found: 269.1299.



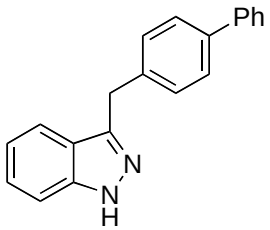
(4b') 3-(3,4-dimethoxybenzyl)-1*H*-indazole.

^{1}H NMR ($CDCl_3$): δ 10.22 (br s, 1H), 7.55 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.34 (m, 1H), 7.08 (m, 1H), 6.89-6.85 (m, 2H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.31 (s, 2H), 3.84 (s, 3H), 3.80 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.9, 147.5, 146.2, 141.3, 131.5, 126.7, 122.0, 120.7, 120.5, 120.4, 112.0, 111.1, 109.7, 55.8, 55.8, 33.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{16}H_{17}N_2O_2$: 269.1285. Found: 269.1308.



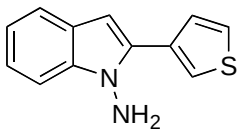
(4c) 2-(biphenyl-4-yl)-1*H*-indol-1-amine. The representative protocol-III was followed using 5-40% EtOAc/hexanes for column chatography to afford **4c** as a beige solid in 56% yield (79 mg, 0.29 mmol) and **4c'** as a beige solid in 34% yield (48 mg, 0.17 mmol).

^{1}H NMR ($(CD_3)_2SO$): δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.78-7.74 (m, 4H), 7.55 (t, *J* = 8.0 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.40 (m, 1H), 7.20 (m, 1H), 7.06 (m, 1H), 6.63 (s, 1H), 5.92 (s, 2H); ^{13}C{^{1}H} NMR ($(CD_3)_2SO$): δ 139.7, 139.7, 138.9, 138.7, 131.2, 129.4, 129.0, 127.5, 126.6, 126.4, 125.0, 121.3, 119.9, 119.6, 110.0, 98.2. HRMS (ESI/$[M+H]^+$) calcd. for $C_{20}H_{17}N_2$: 285.1386. Found: 285.1376.

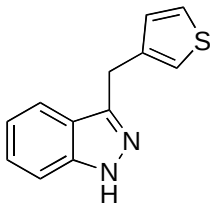


(4c') 3-(biphenyl-4-ylmethyl)-1*H*-indazole.

^{1}H NMR ($CDCl_3$): δ 9.89 (br s, 1H), 7.60 (m, 1H), 7.57-7.55 (m, 2H), 7.54-7.52 (m, 2H), 7.45-7.39 (m, 5H), 7.36 (m, 1H), 7.32 (m, 1H), 7.11 (m, 1H), 4.40 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 146.0, 141.3, 140.9, 139.3, 138.0, 129.2, 128.7, 127.3, 127.1, 127.0, 126.8, 122.1, 120.5, 120.5, 109.7, 33.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{20}H_{17}N_2$: 285.1386. Found: 285.1380.



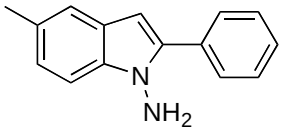
(4d) 2-(thiophen-3-yl)-1H-indol-1-amine. The representative protocol-III was followed using 20-25% EtOAc/hexanes for column chromatography to afford **4d** as a beige solid in 65% yield (70 mg, 0.33 mmol) and **4d'** as a beige solid in 23% yield (25 mg, 0.12 mmol). ^{1}H NMR ($CDCl_3$): δ 7.93, (dd, J = 3.0, 1.2 Hz, 1H), 7.60 (dt, J = 7.9, 1.2 Hz, 1H), 7.52 (dd, J = 5.1, 1.3 Hz, 1H), 7.41-7.38 (m, 2H), 7.26 (m, 1H), 7.16 (m, 1H), 6.60 (d, J = 0.8 Hz, 1H), 4.62 (s, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 138.3, 136.0, 132.3, 128.0, 125.7, 125.2, 122.8, 122.0, 120.5, 120.3, 108.3, 98.5. HRMS (ESI/$[M+H]^+$) calcd. for $C_{12}H_{11}N_2S$: 215.0637. Found: 215.0644.



(4d') 3-(thiophen-3-ylmethyl)-1*H*-indazole.

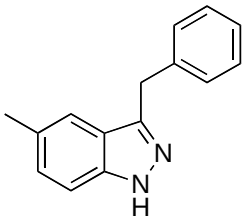
^{1}H NMR ($CDCl_3$): δ 10.34 (br s, 1H), 7.57 (dt, J = 7.6, 0.9 Hz, 1H), 7.42 (m, 1H), 7.36 (m, 1H), 7.25 (dd, J = 5.1, 3.1 Hz, 1H), 7.10 (m, 1H), 7.07 (m, 1H), 7.03 (dd, J = 5.0, 3.1 Hz,

1H), 4.39 (s, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 145.5, 141.3, 139.1, 128.5, 126.8, 125.7, 122.0, 121.5, 120.5, 120.4, 109.8, 28.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{12}H_{11}N_2S$: 215.0637. Found: 215.0636.



(4e) 5-methyl-2-phenyl-1*H*-indol-1-amine. The representative protocol-III was followed using 20-25% EtOAc/hexanes for column chromatography to afford **4e** as a beige solid in 34% yield (38 mg, 0.17 mmol) and **4e'** as a beige solid in 33% yield (37 mg, 0.17 mmol). An accurate ^{1}H NMR yield was obtained of the crude product mixture relative to 1,3,5-trimethoxybenzene, both resulting in 36% yield.

^{1}H NMR ($CDCl_3$): δ 7.71-7.69 (m, 2H), 7.48 (t, J = 7.3 Hz, 2H), 7.41-7.38 (m, 3H), 7.36 (d, J = 8.3 Hz, 1H), 7.11 (dd, J = 8.3, 1.0 Hz, 1H), 6.49 (s, 2H), 2.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 141.0, 137.1, 132.0, 129.6, 129.1, 128.3, 127.7, 125.9, 123.7, 120.2, 108.6, 99.2, 21.4. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{15}N_2$: 223.1230. Found: 223.1235.



(4e') 3-benzyl-5-methyl-1*H*-indazole.

^{1}H NMR ($CDCl_3$): δ 10.28 (br s, 1H), 7.34-7.28 (m, 6H), 7.21 (m, 1H), 7.18 (dd, J = 8.5, 1.2 Hz, 1H), 4.36 (s, 2H), 2.41 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): 145.1, 140.0, 139.1, 129.7, 128.8, 128.7, 128.5, 126.2, 122.4, 119.4, 109.5, 33.6, 21.3. HRMS (ESI/$[M+H]^+$) calcd. for $C_{15}H_{15}N_2$: 223.1230. Found: 223.1236.

Supporting Information References:

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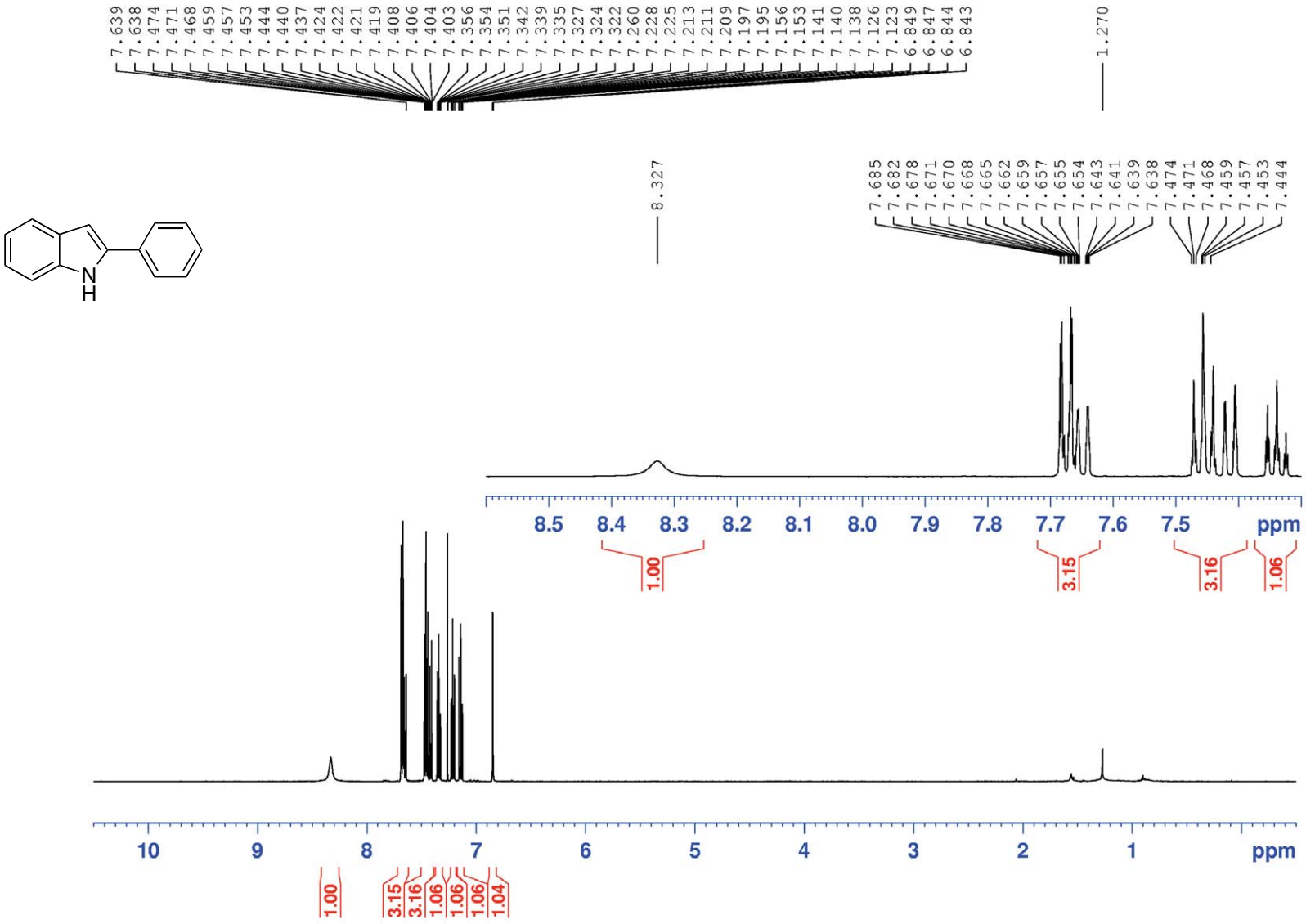
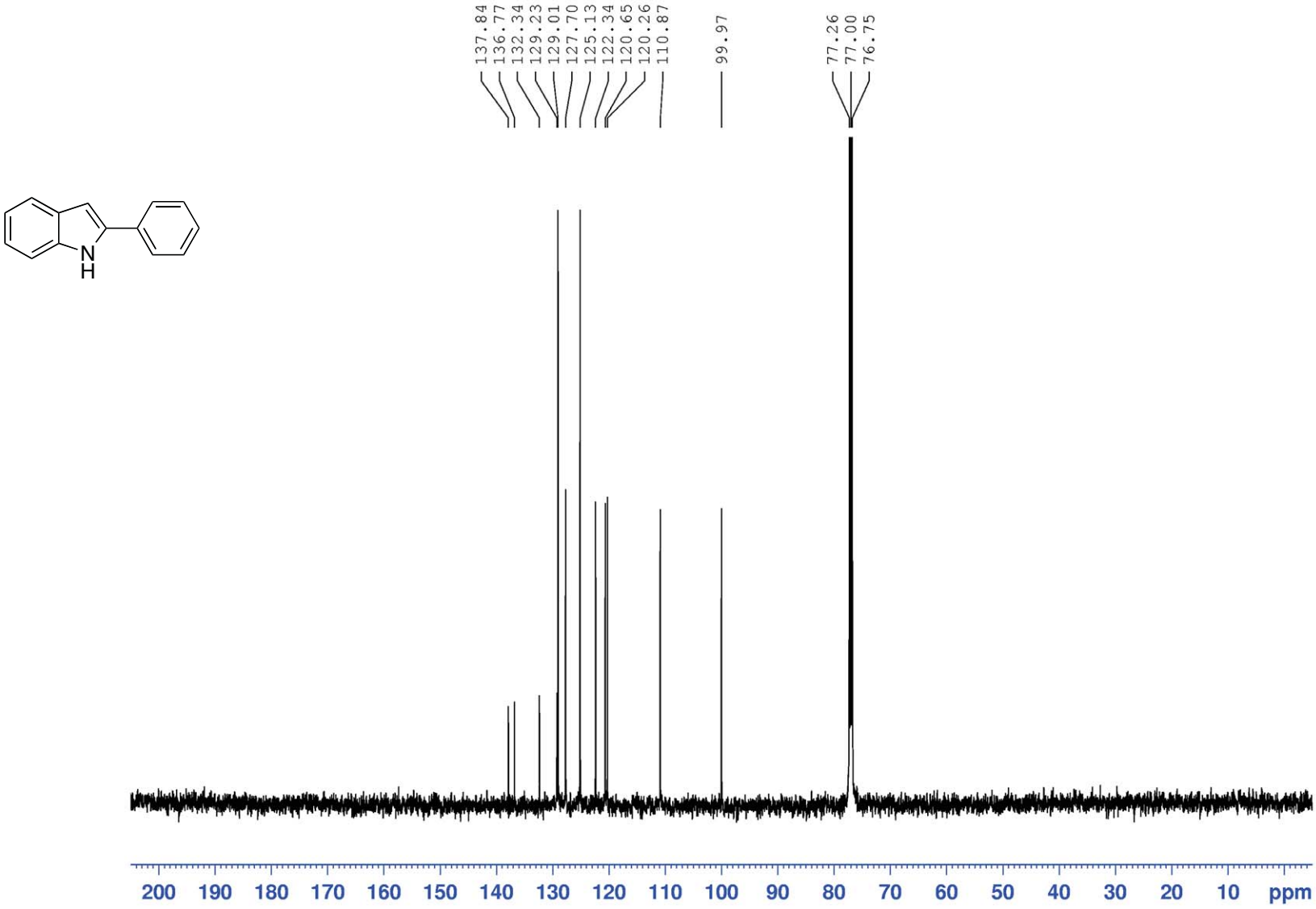
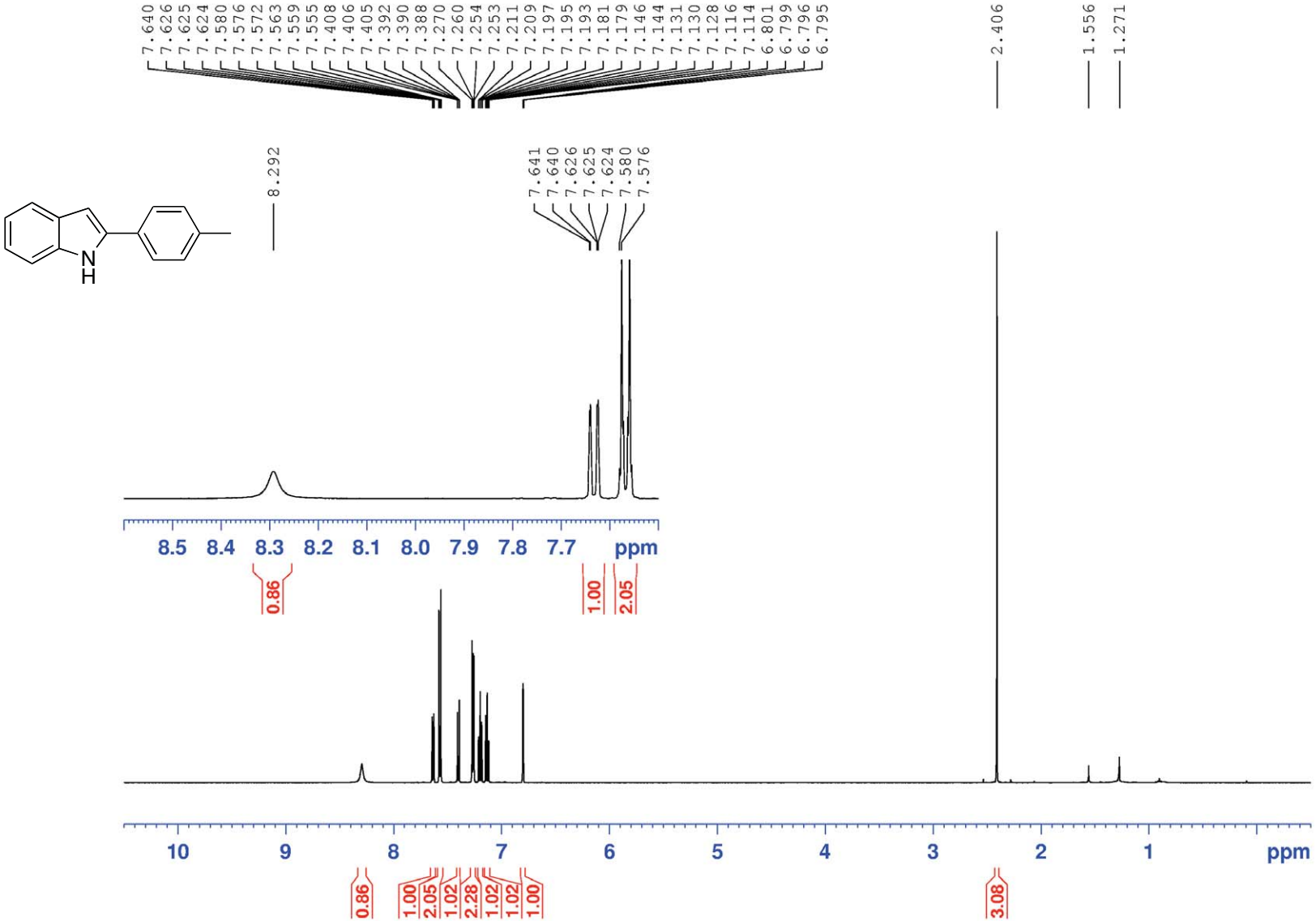
^{1}H NMR of **2a** ($CDCl_3$, 500 MHz, 300 K)



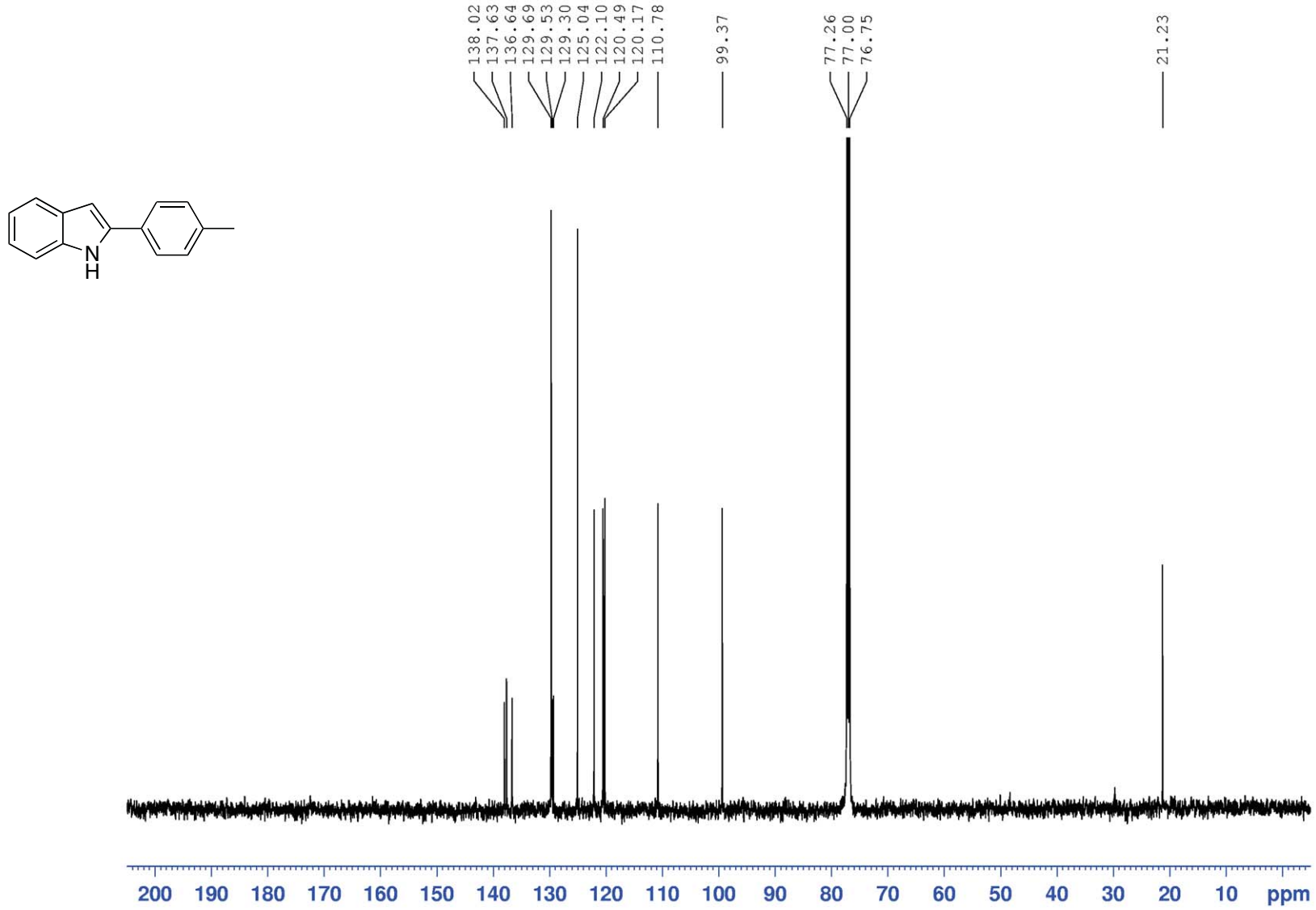
^{13}C NMR of **2a** ($CDCl_3$, 126 MHz, 300 K)



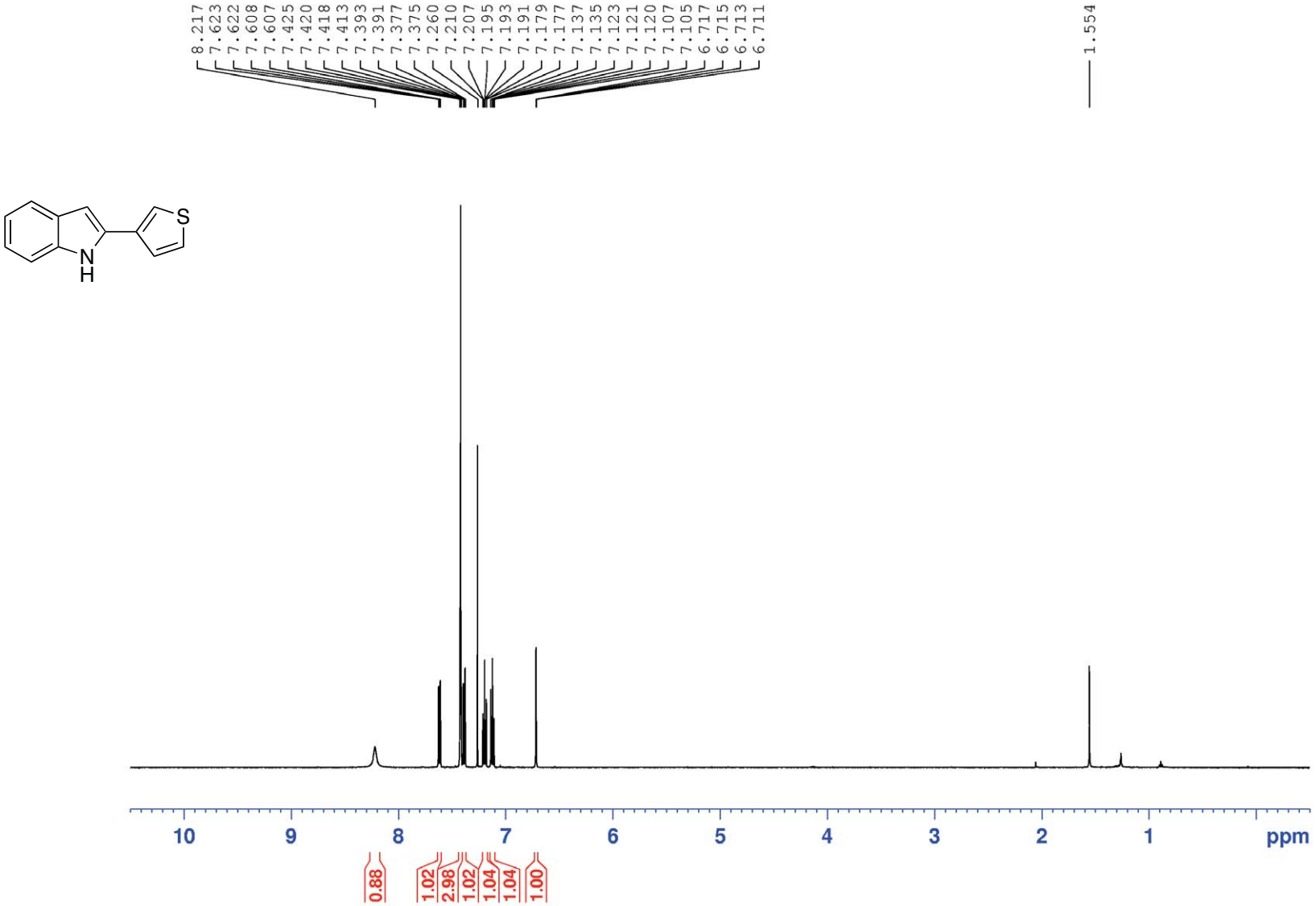
^{1}H NMR of **2b** ($CDCl_3$, 500 MHz, 300 K)



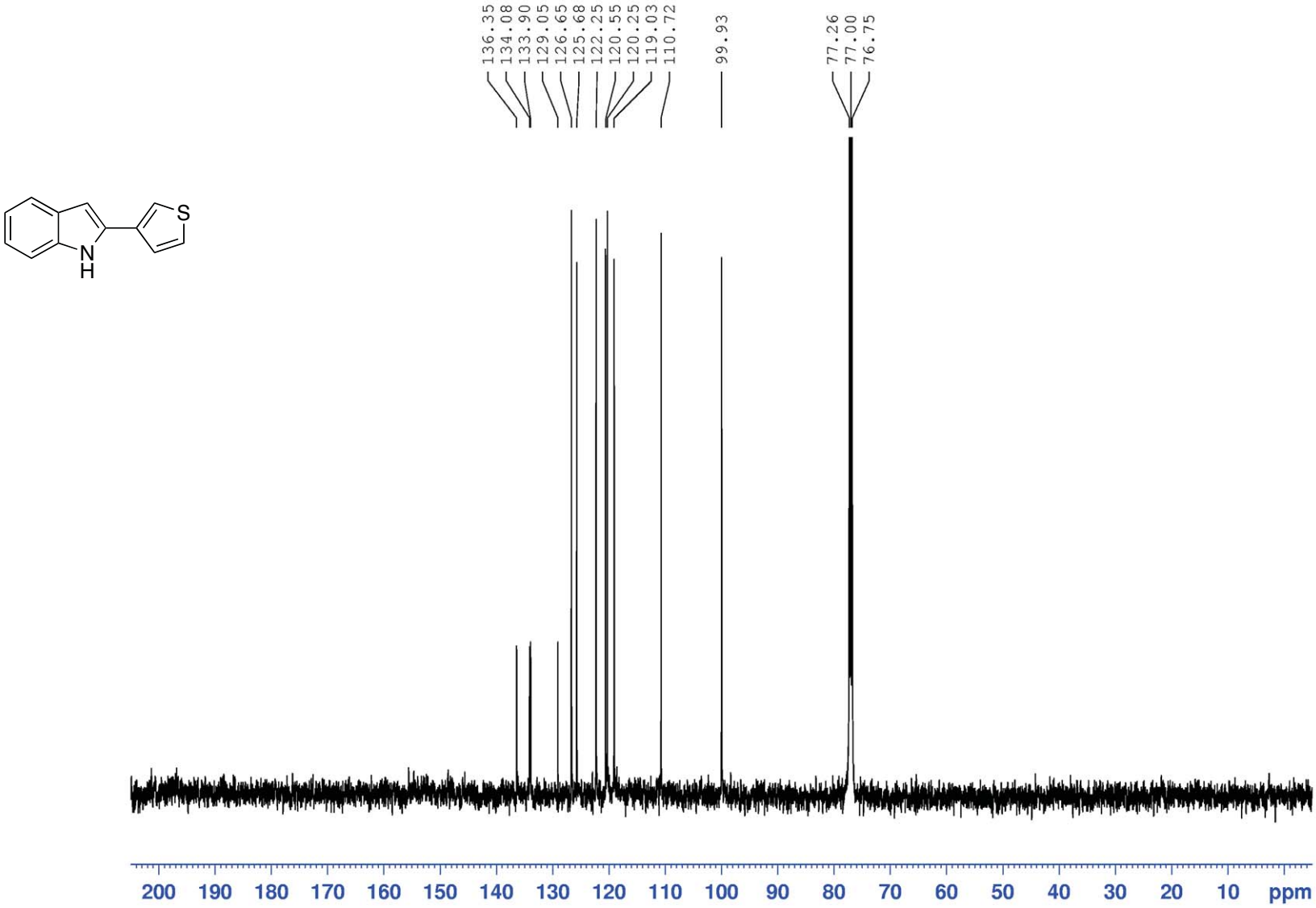
^{13}C NMR of **2b** ($CDCl_3$, 126 MHz, 300 K)



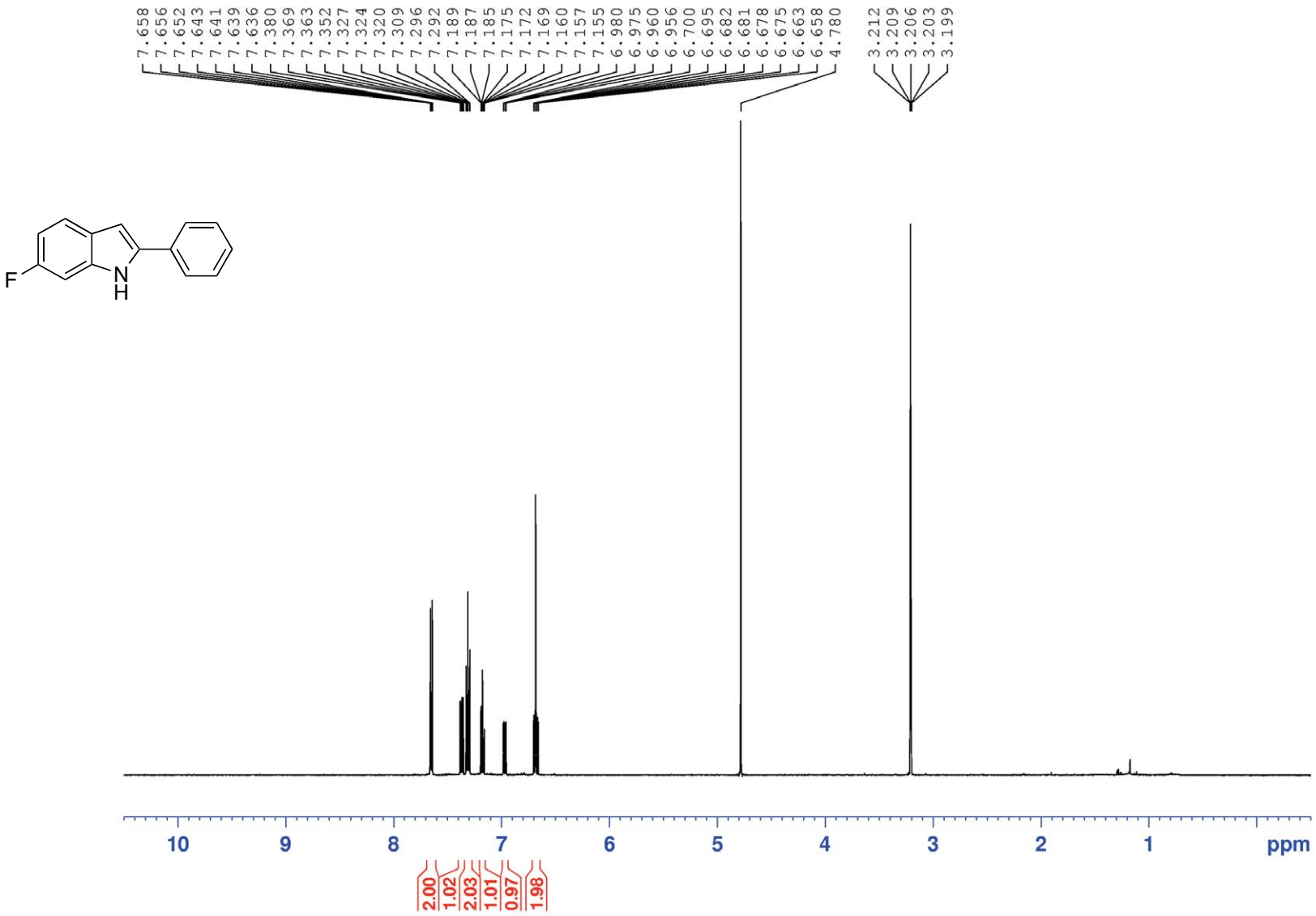
^{1}H NMR of **2c** ($CDCl_3$, 500 MHz, 300 K)



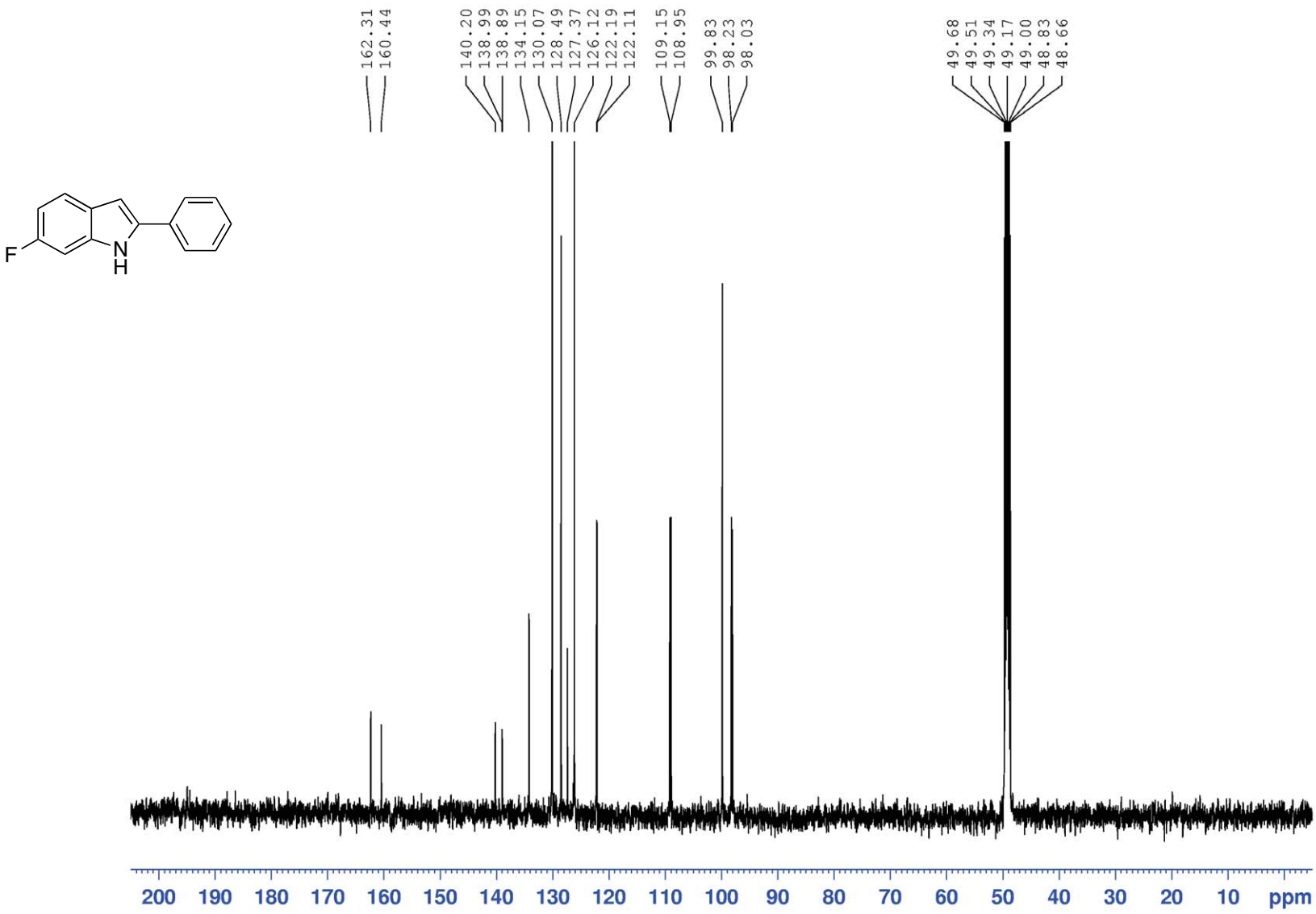
^{13}C NMR of **2c** ($CDCl_3$, 126 MHz, 300 K)



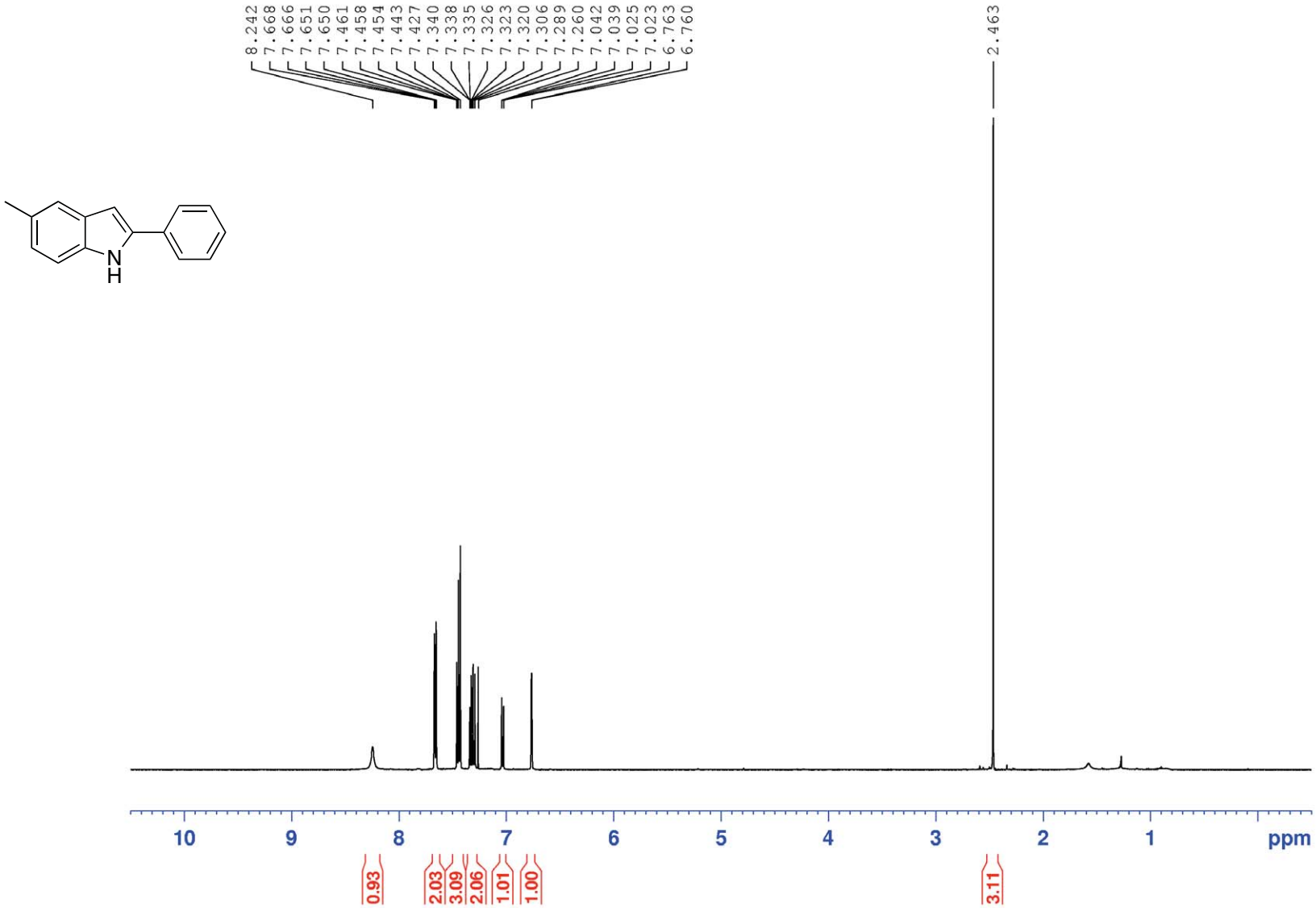
^{1}H NMR of **2d** (CD_3OD, 500 MHz, 300 K)



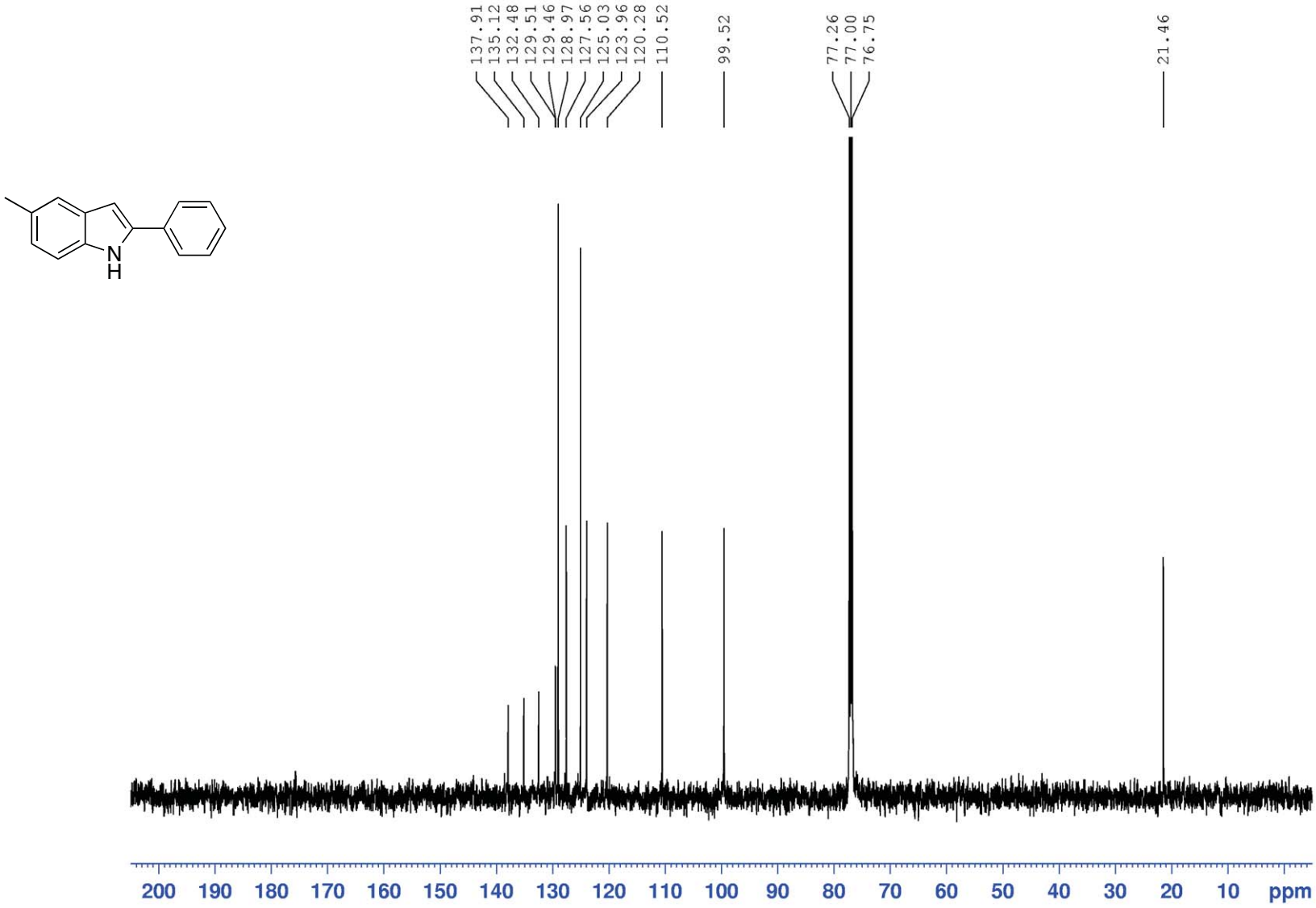
^{13}C NMR of **2d** (CD_3OD, 126 MHz, 300 K)



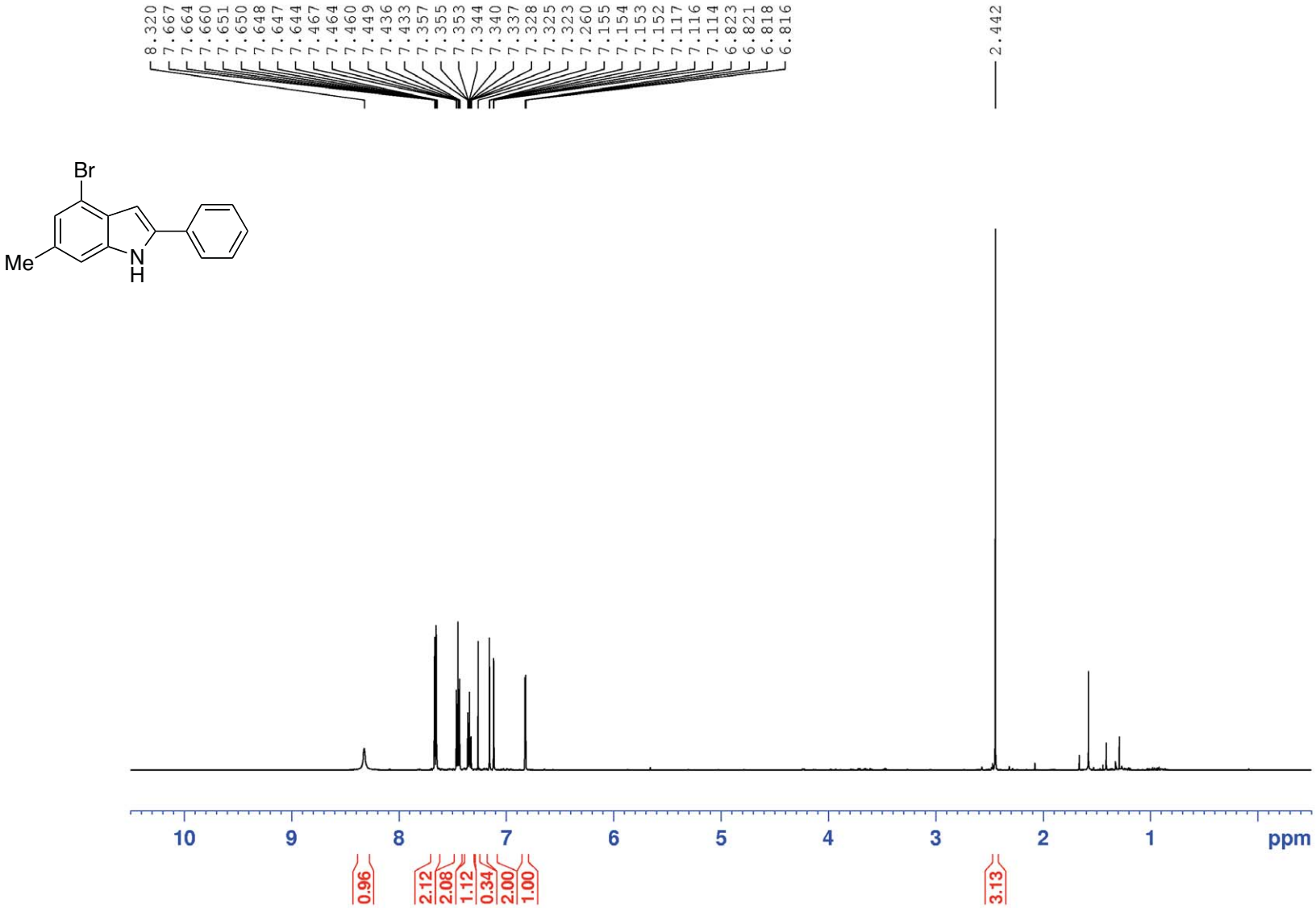
^{1}H NMR of **2e** ($CDCl_3$, 500 MHz, 300 K)



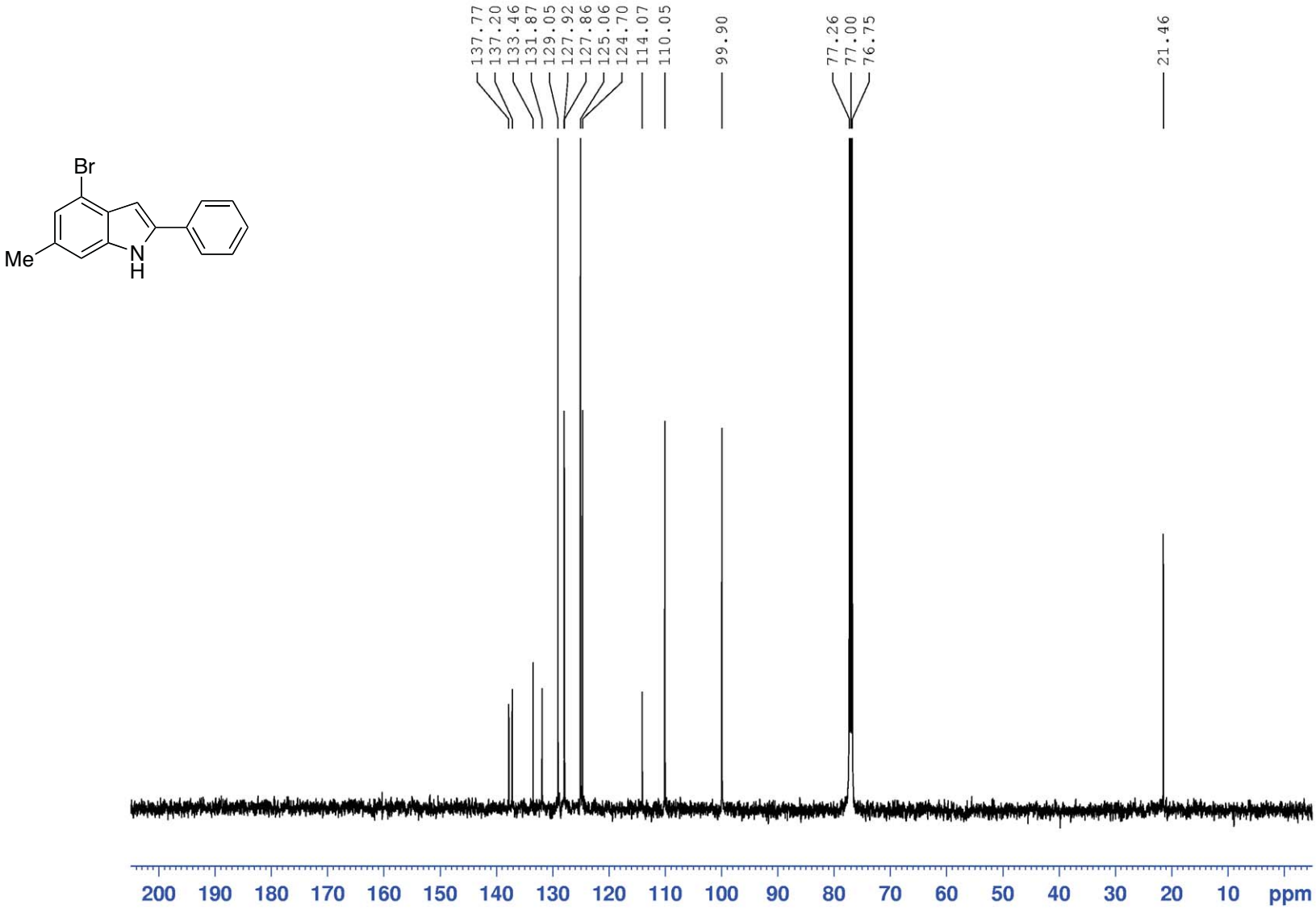
^{13}C NMR of **2e** ($CDCl_3$, 126 MHz, 300 K)



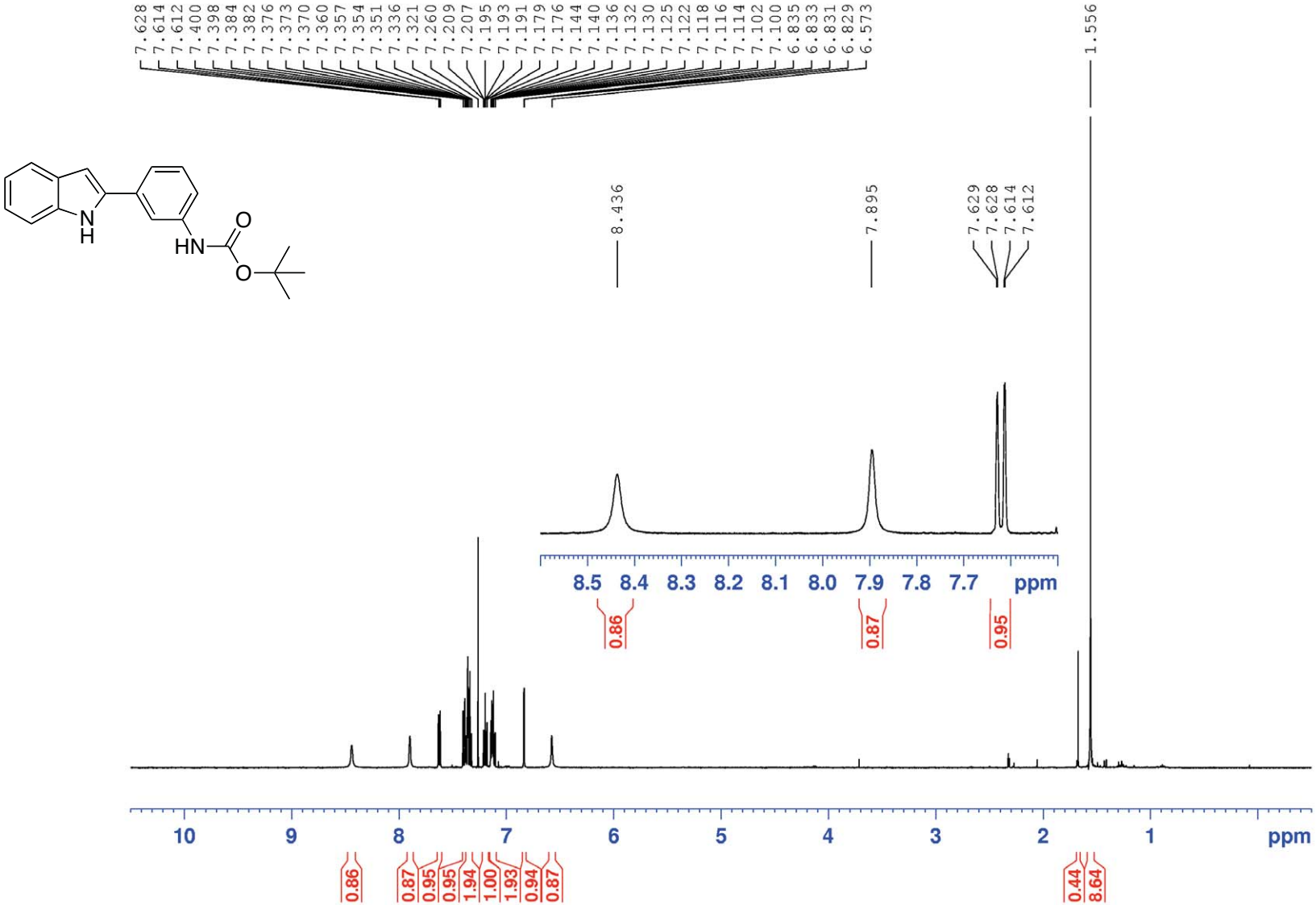
^{1}H NMR of **2f** ($CDCl_3$, 500 MHz, 300 K)



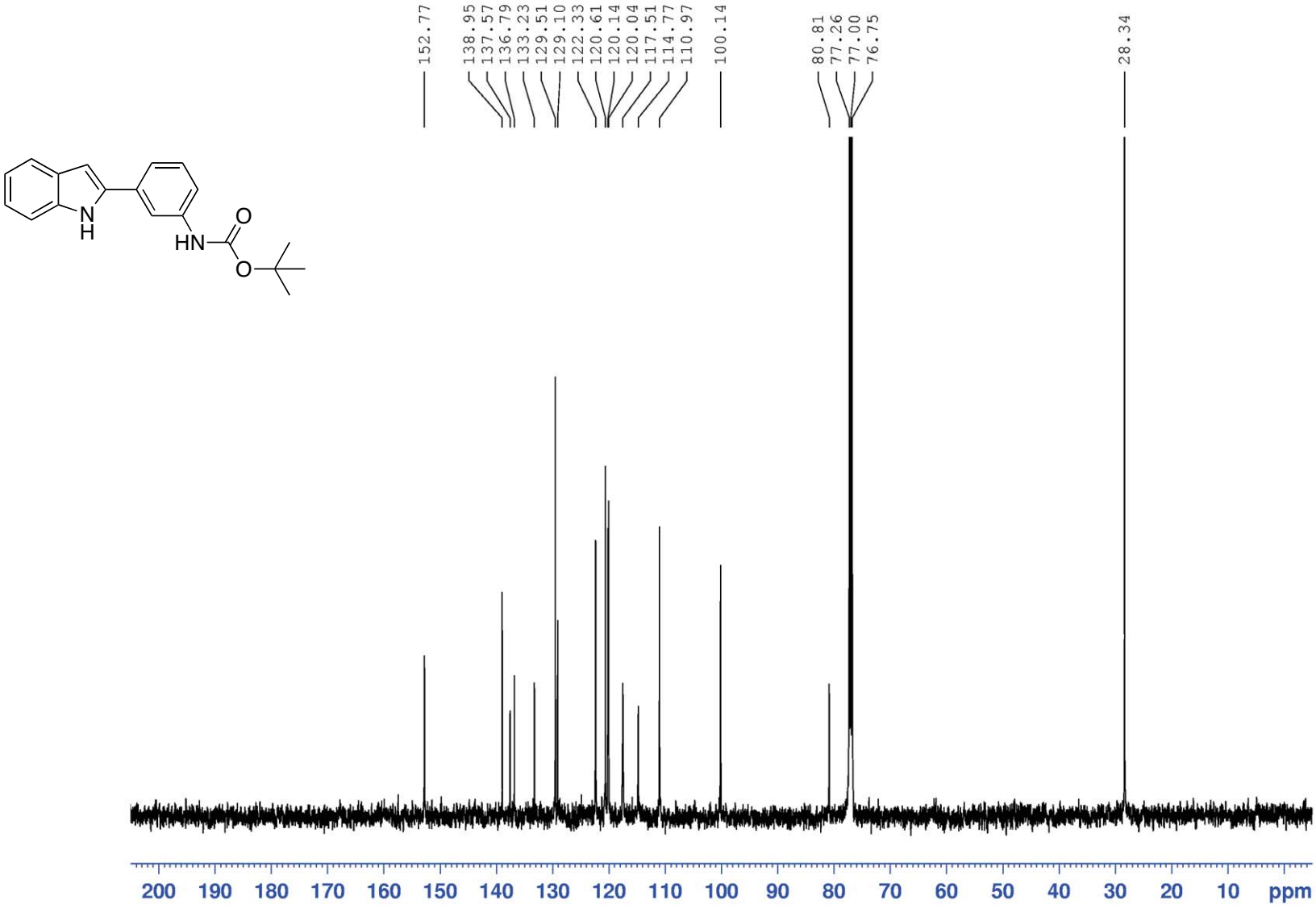
^{13}C NMR of **2f** ($CDCl_3$, 126 MHz, 300 K)



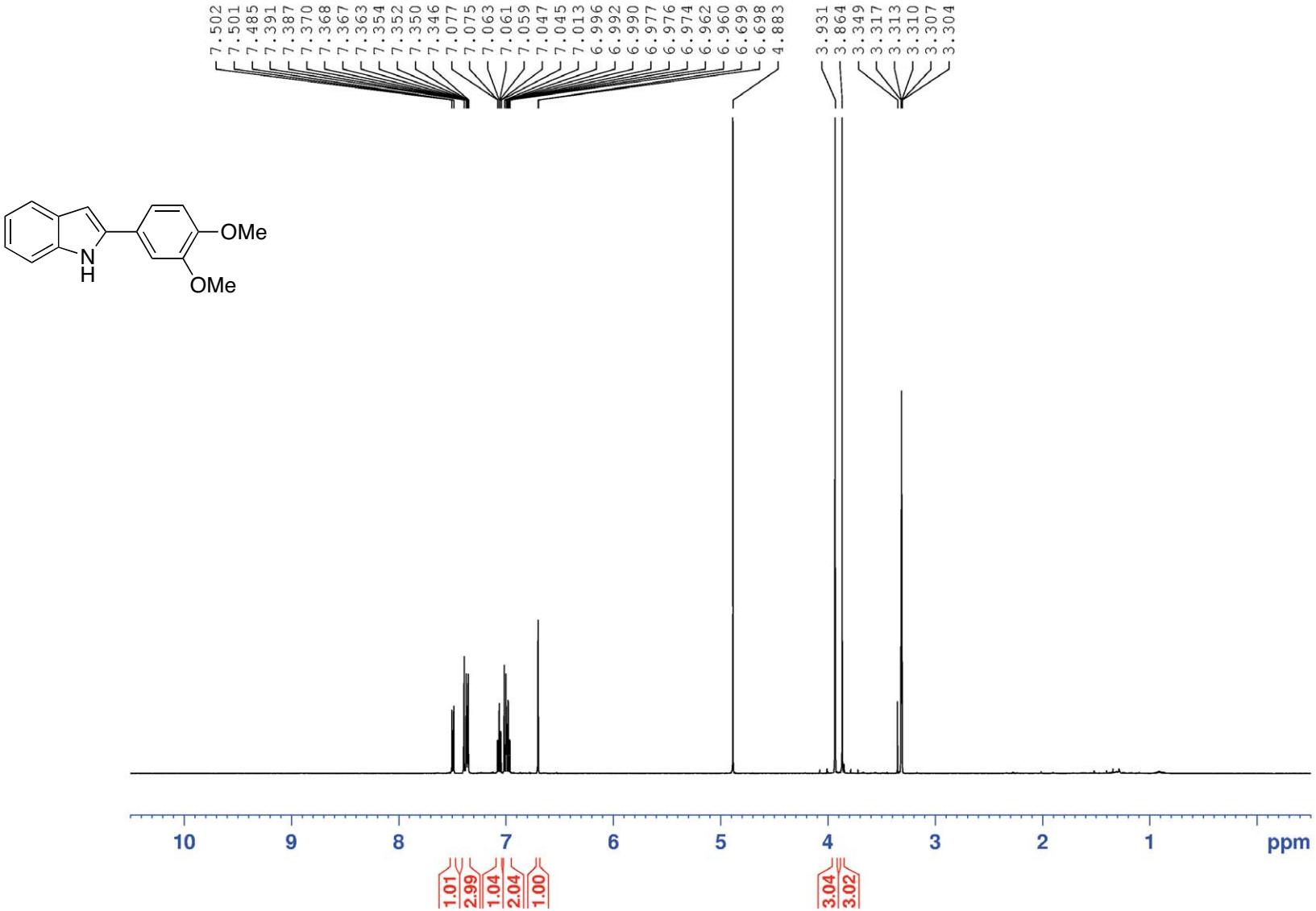
^{1}H NMR of **2g** ($CDCl_3$, 500 MHz, 300 K)



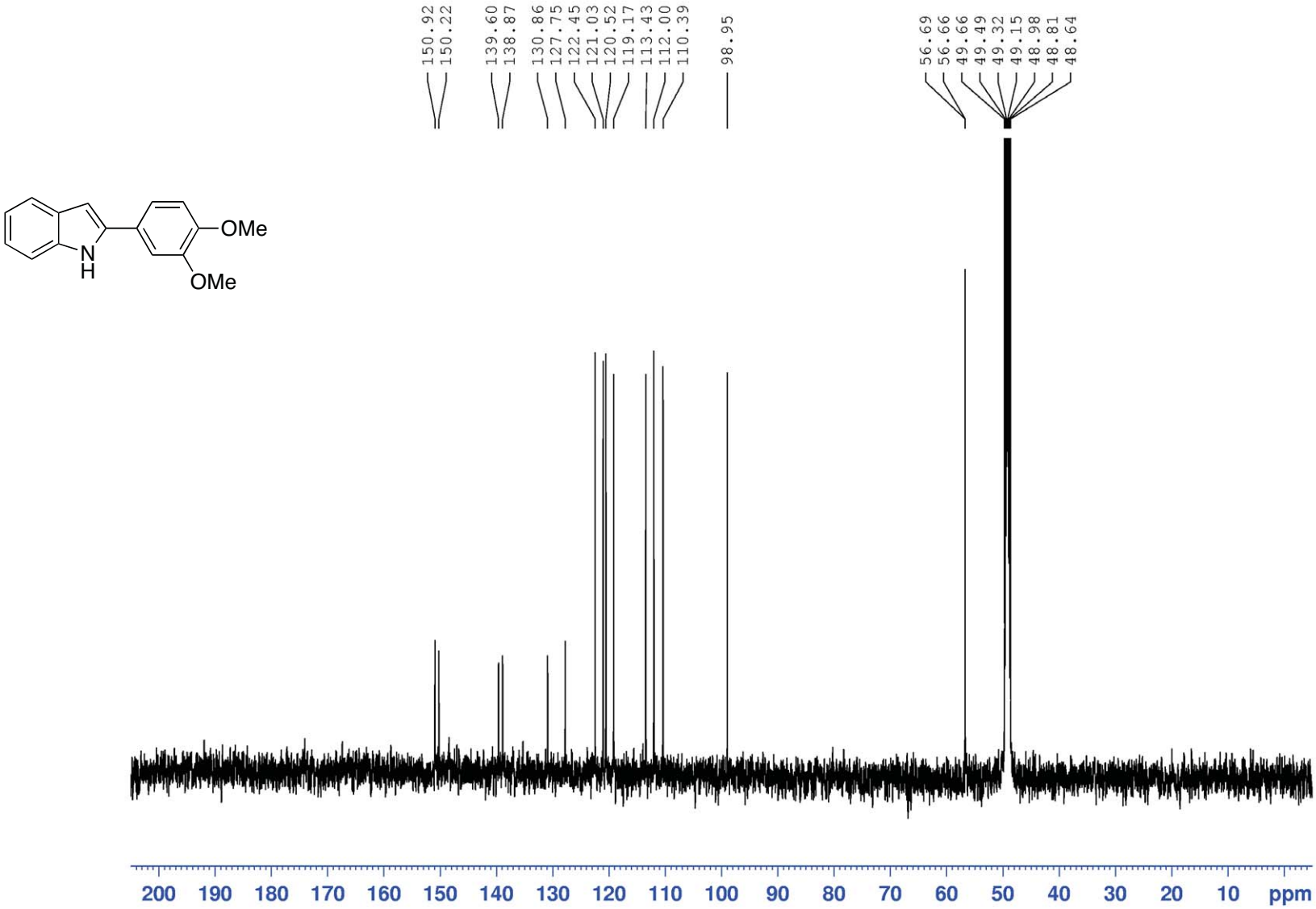
^{13}C NMR of **2g** ($CDCl_3$, 126 MHz, 300 K)



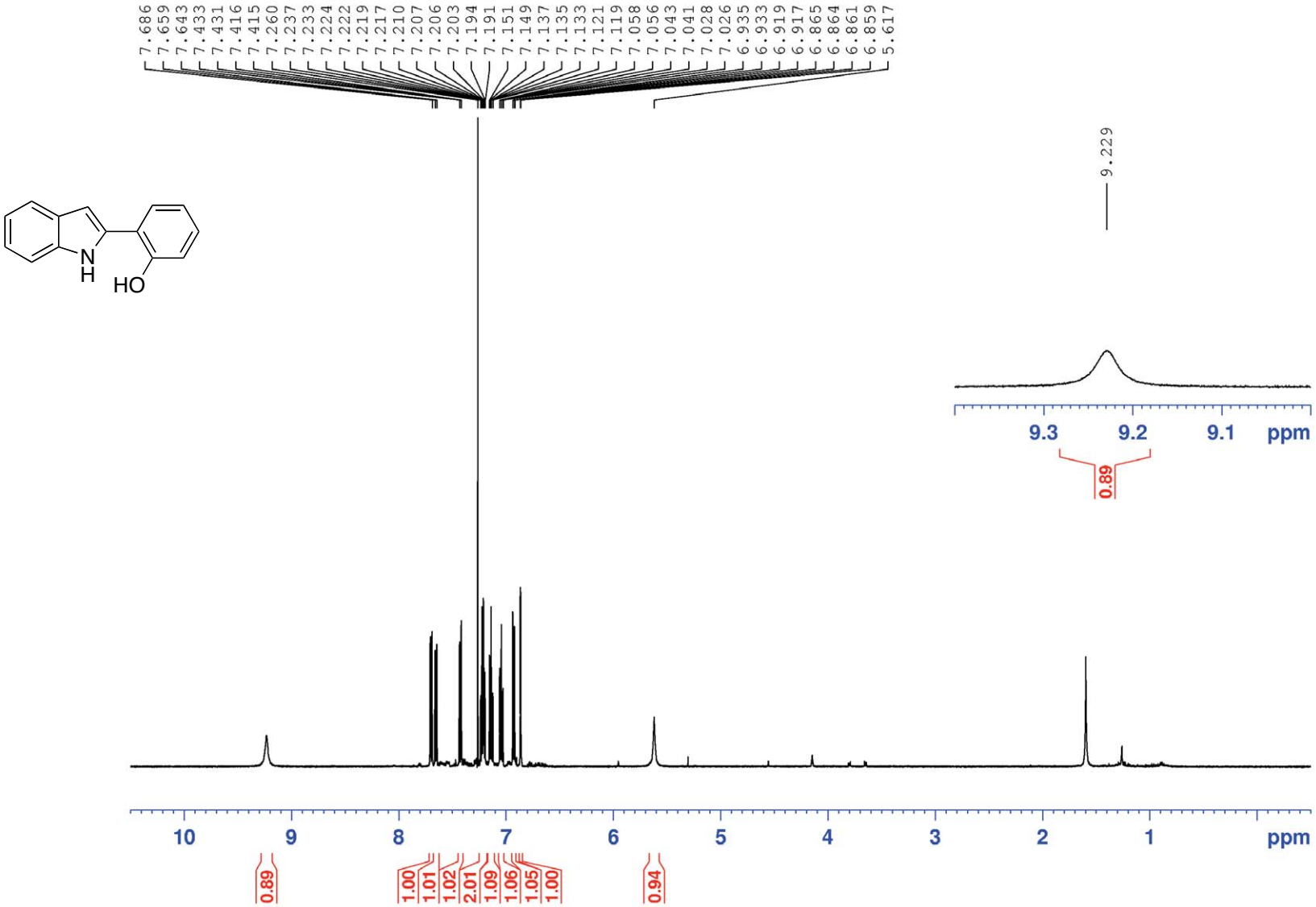
^{1}H NMR of **2h** (CD_3OD, 500 MHz, 300 K)



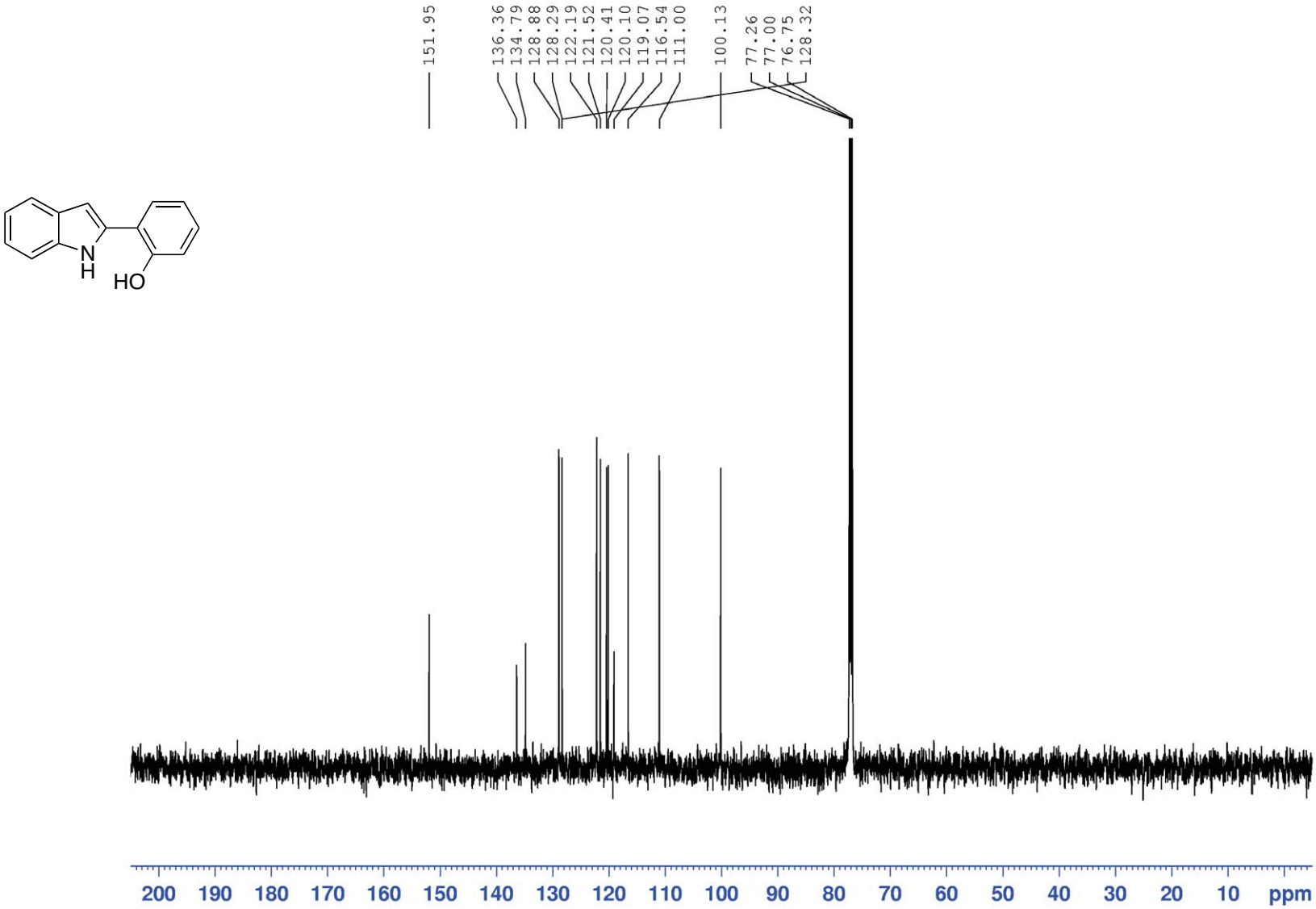
^{13}C NMR of **2h** (CD_3OD, 126 MHz, 300 K)



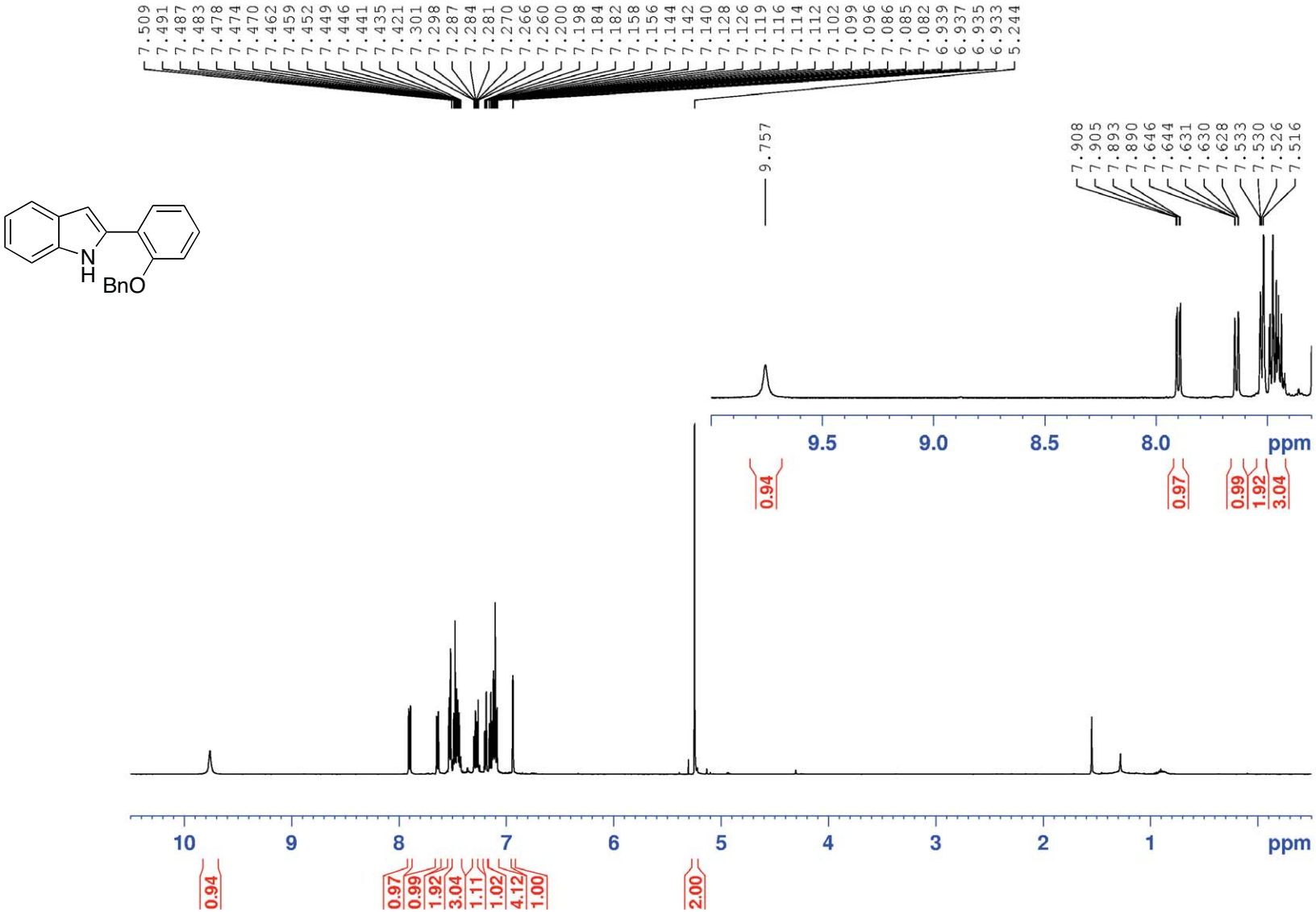
^{1}H NMR of **2i** ($CDCl_3$, 500 MHz, 300 K)



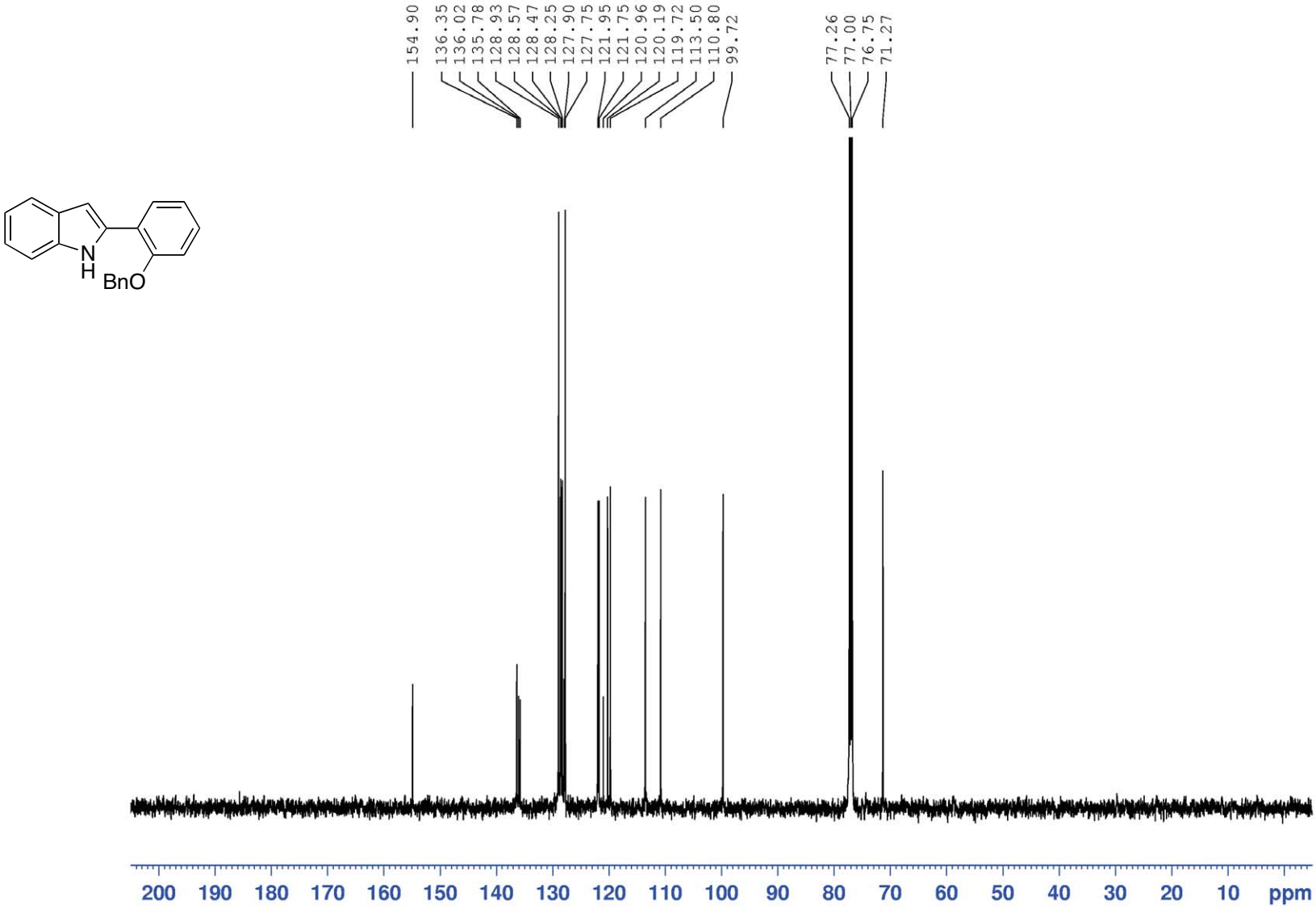
^{13}C NMR of **2i** ($CDCl_3$, 126 MHz, 300 K)



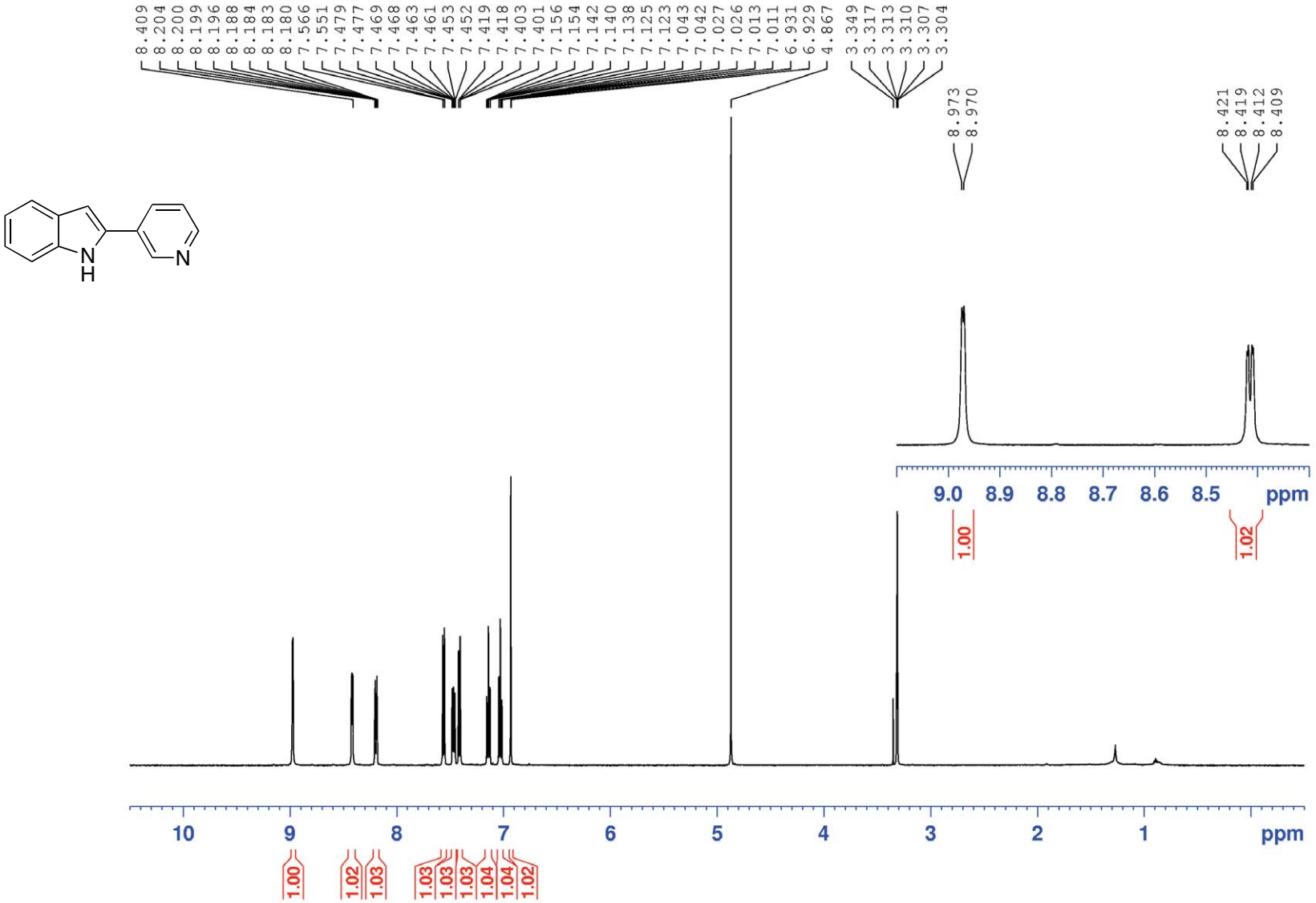
^{1}H NMR of **2j** ($CDCl_3$, 500 MHz, 300 K)



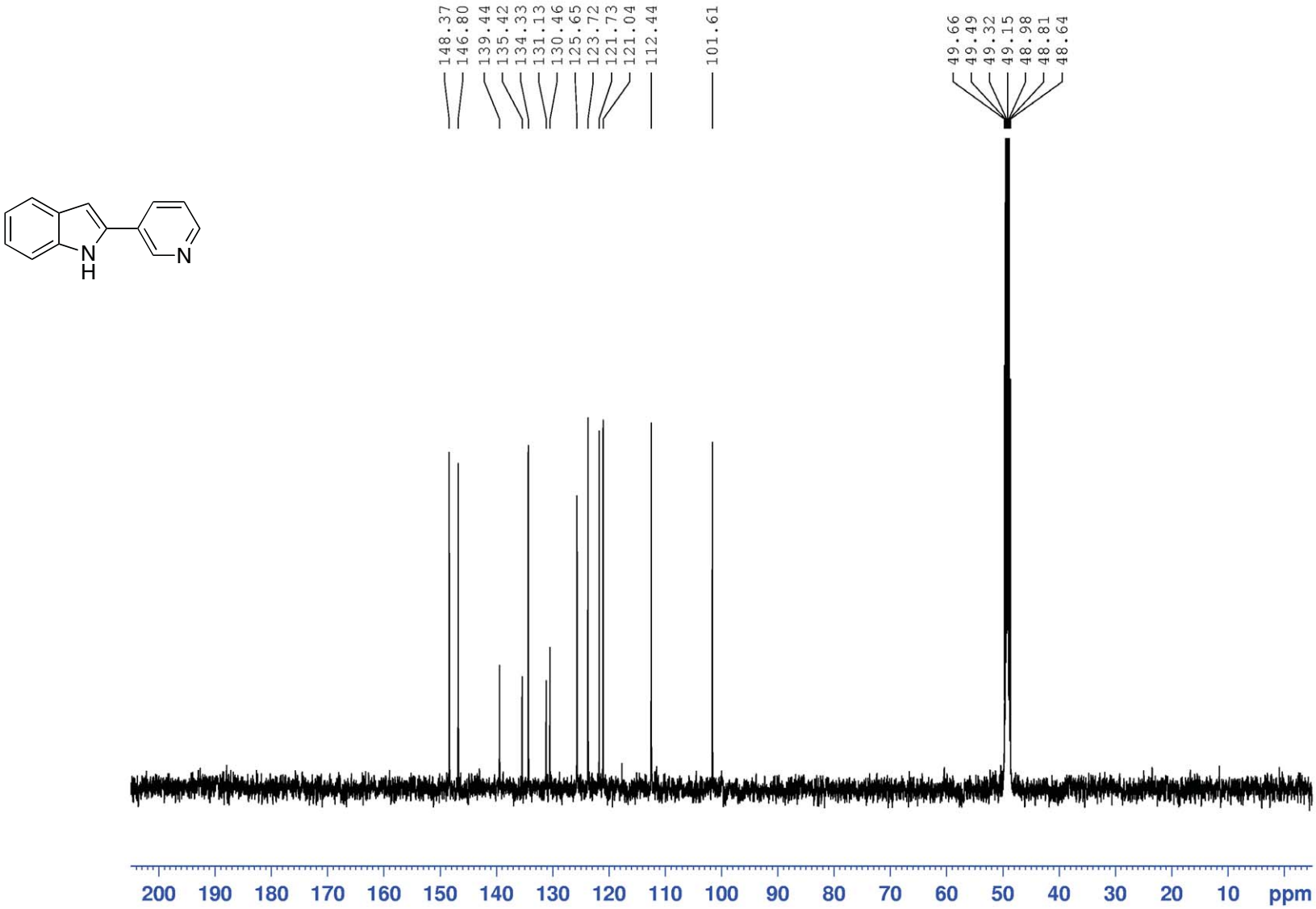
^{13}C NMR of **2j** ($CDCl_3$, 126 MHz, 300 K)



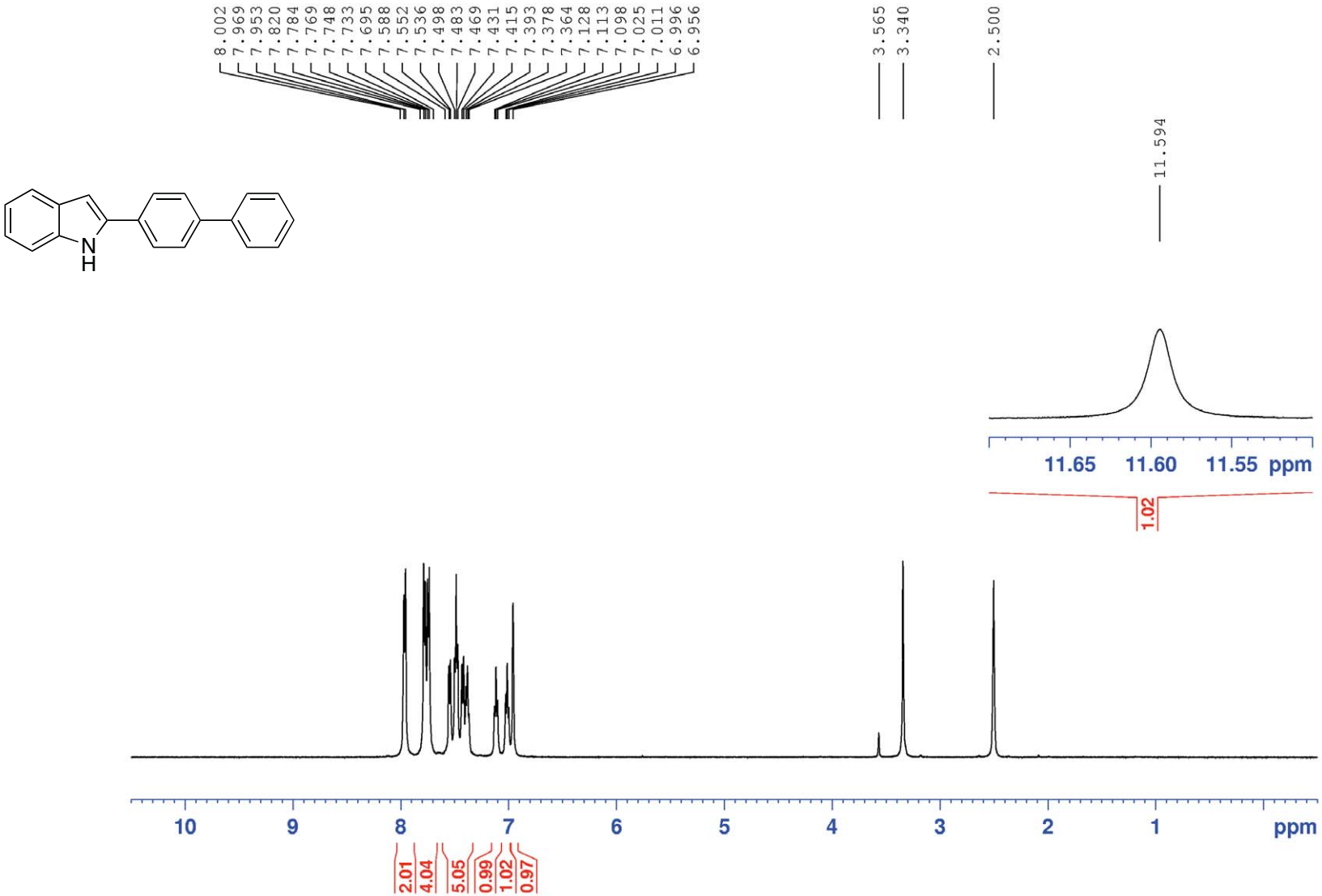
^{1}H NMR of **2k** (CD_3OD, 500 MHz, 300 K)



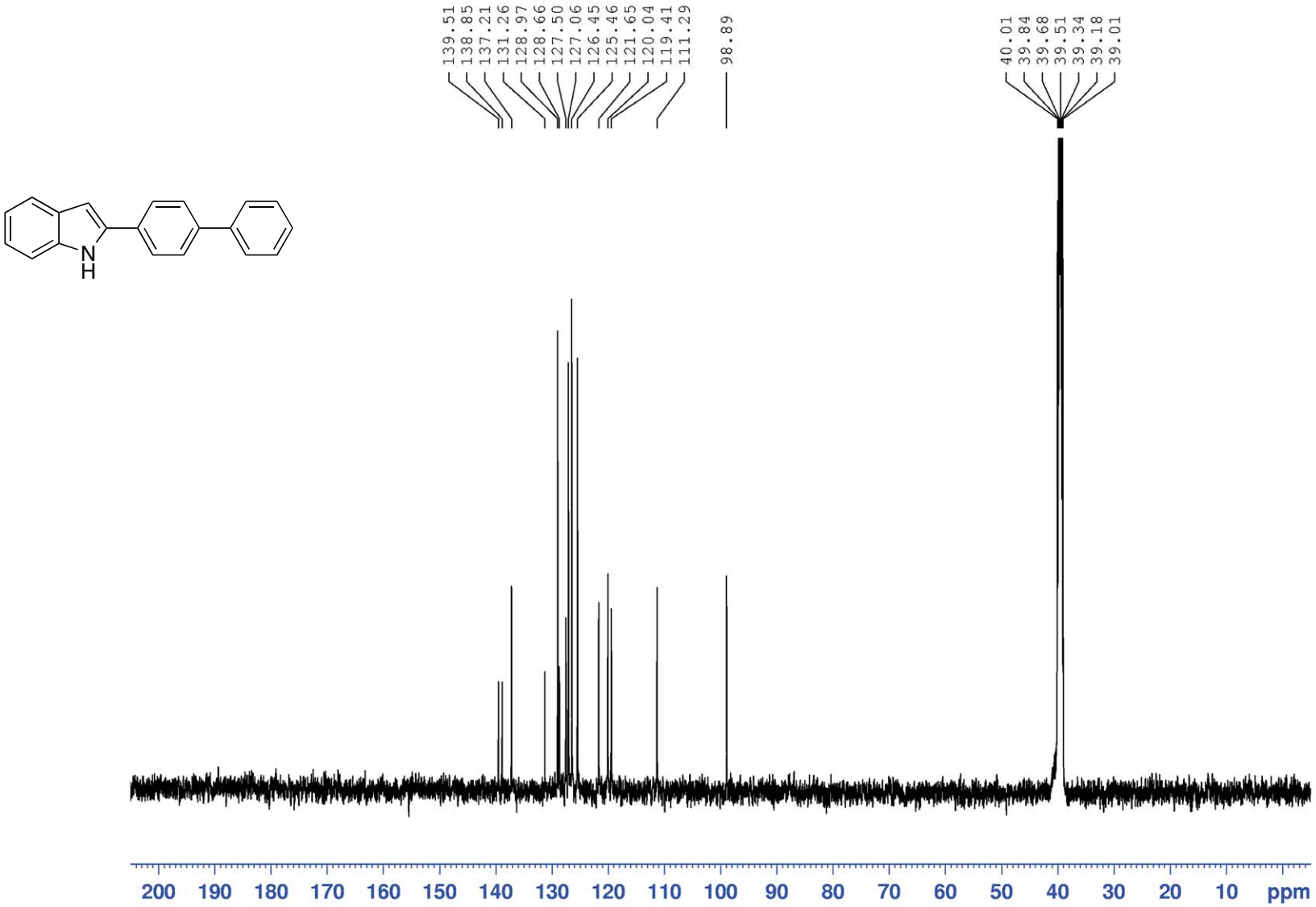
^{13}C NMR of **2k** (CD_3OD, 126 MHz, 300 K)



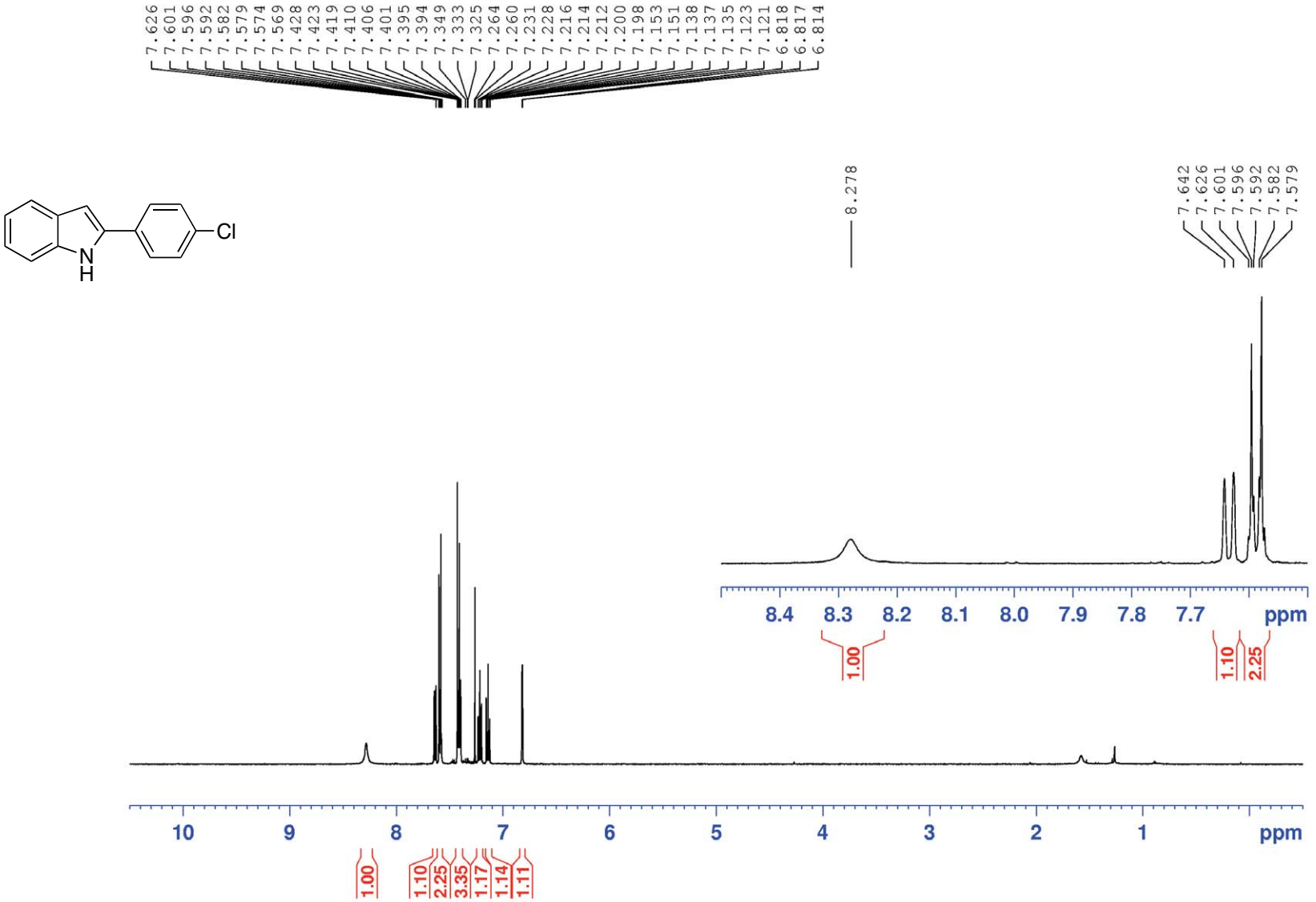
^{1}H NMR of **2l** (DMSO-d_6, 500 MHz, 300 K)



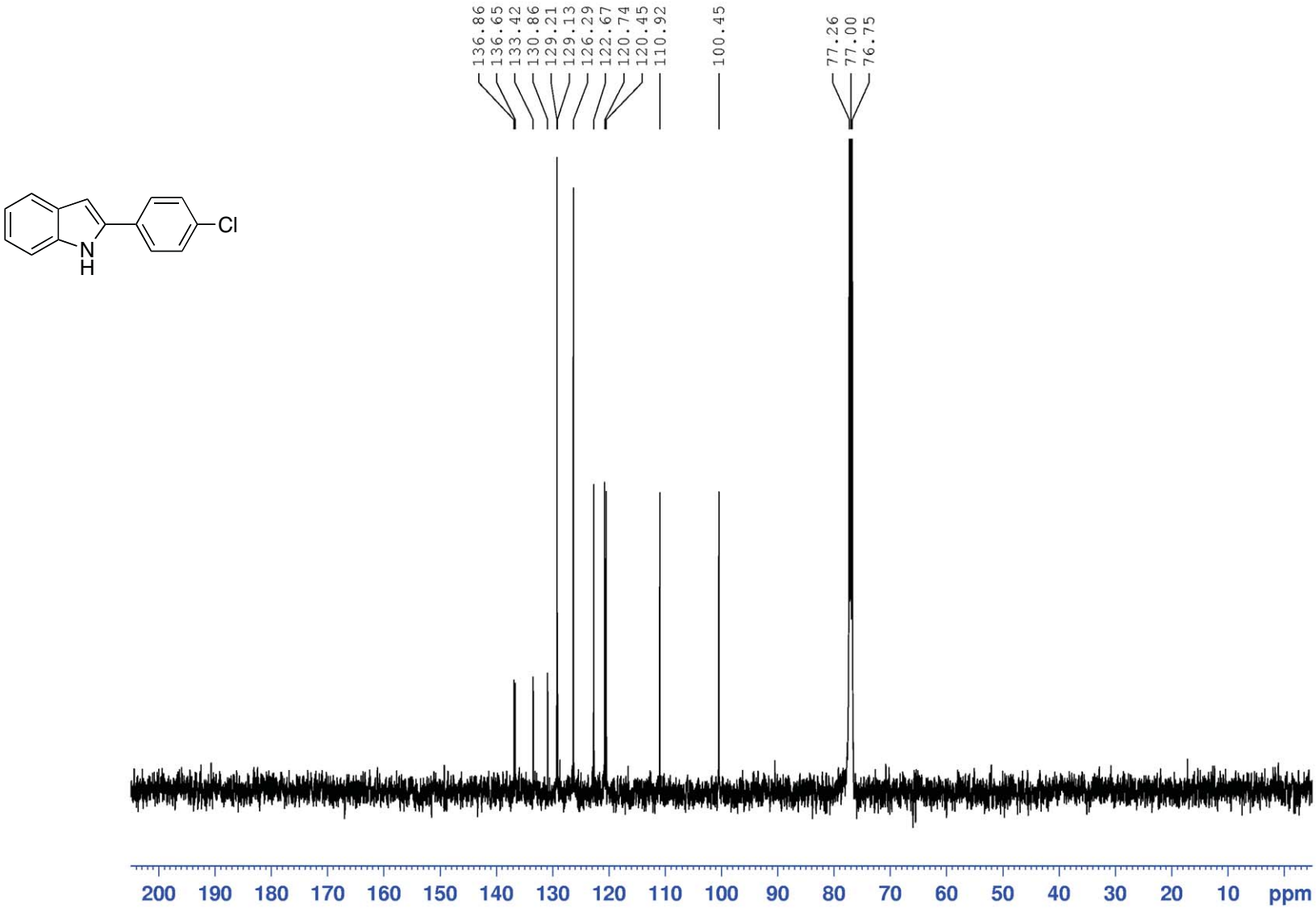
^{13}C NMR of **2l** (DMSO-d_6, 126 MHz, 300 K)



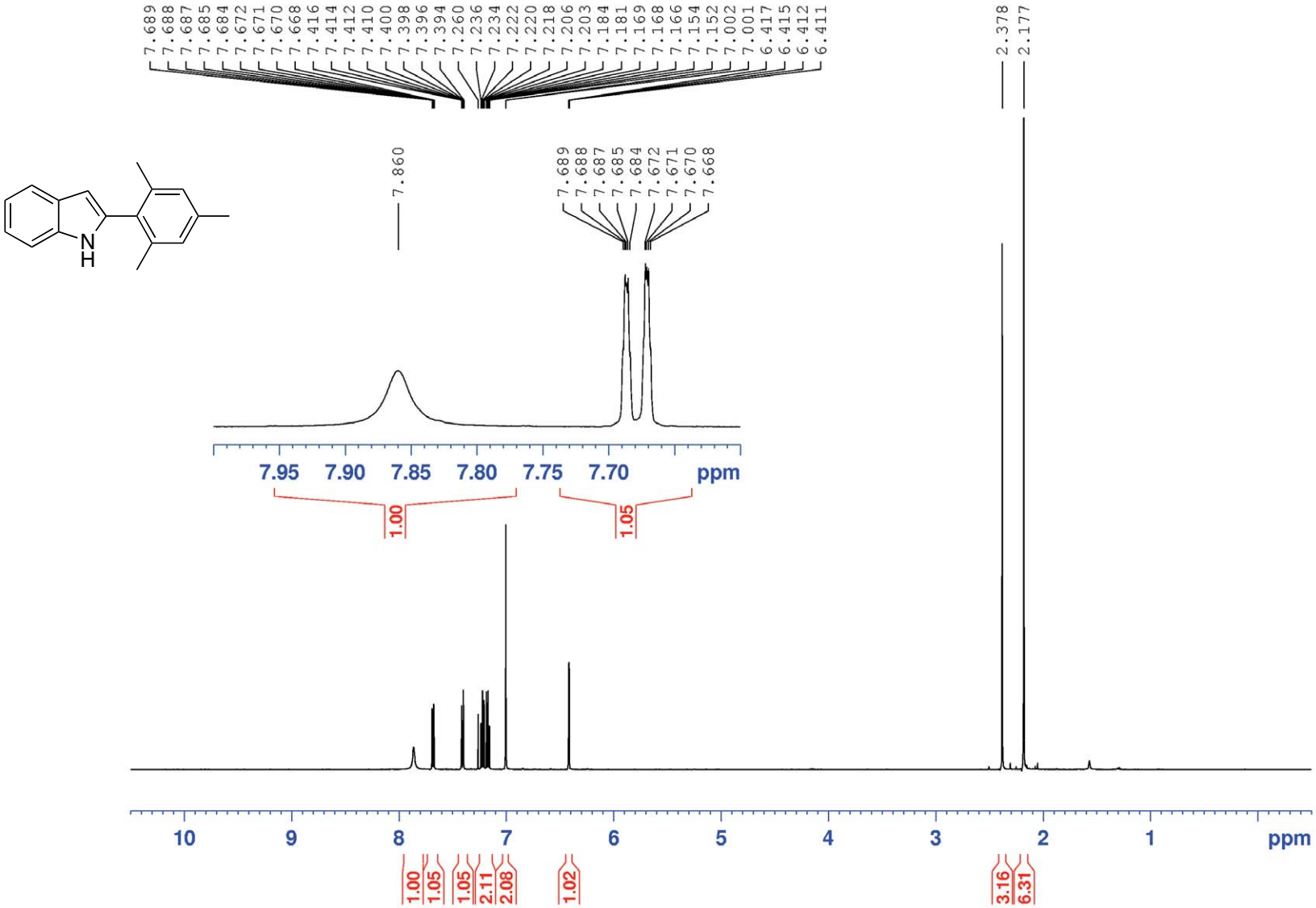
^{1}H NMR of **2m** ($CDCl_3$, 500 MHz, 300 K)



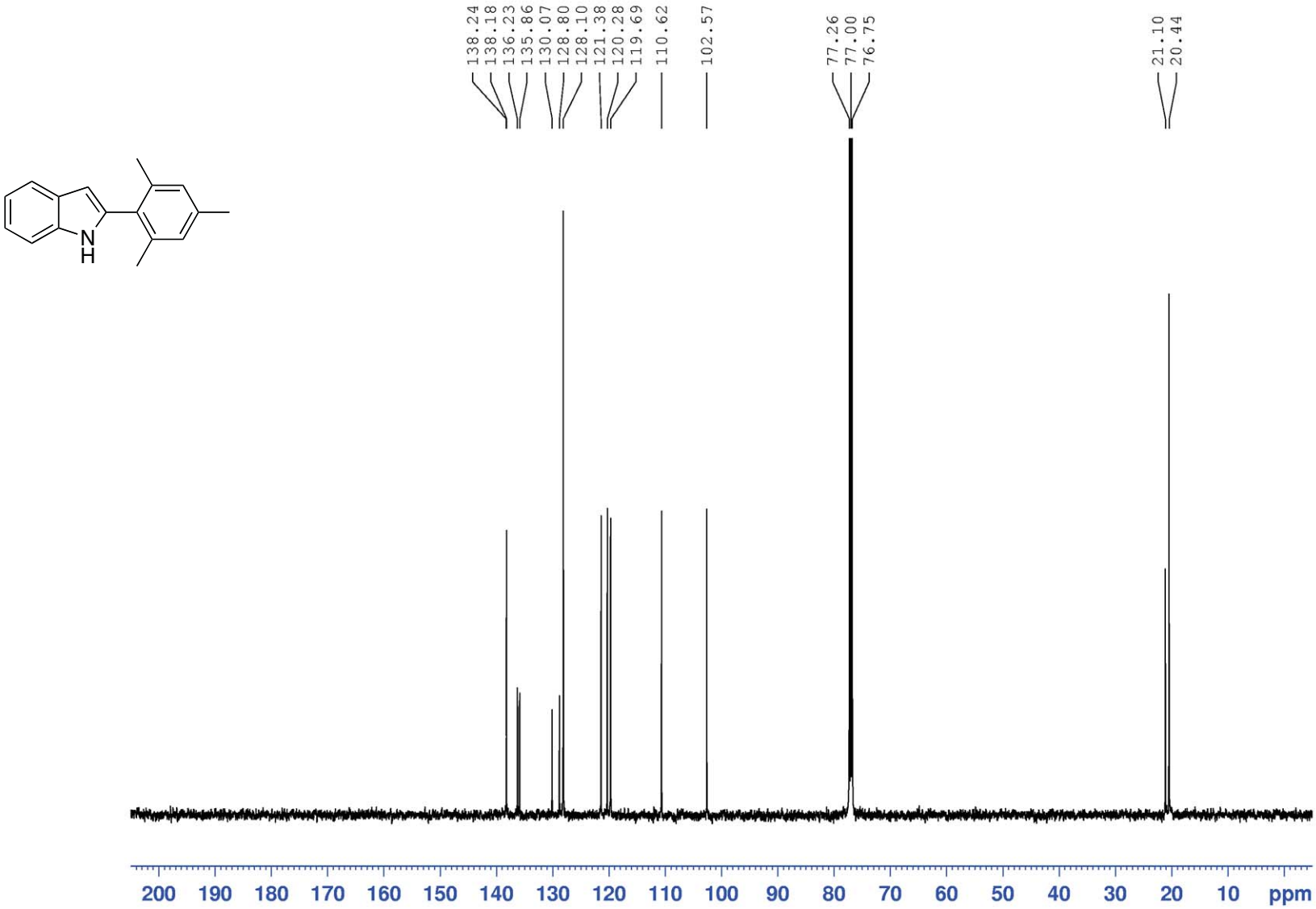
^{13}C NMR of **2m** ($CDCl_3$, 126 MHz, 300 K)



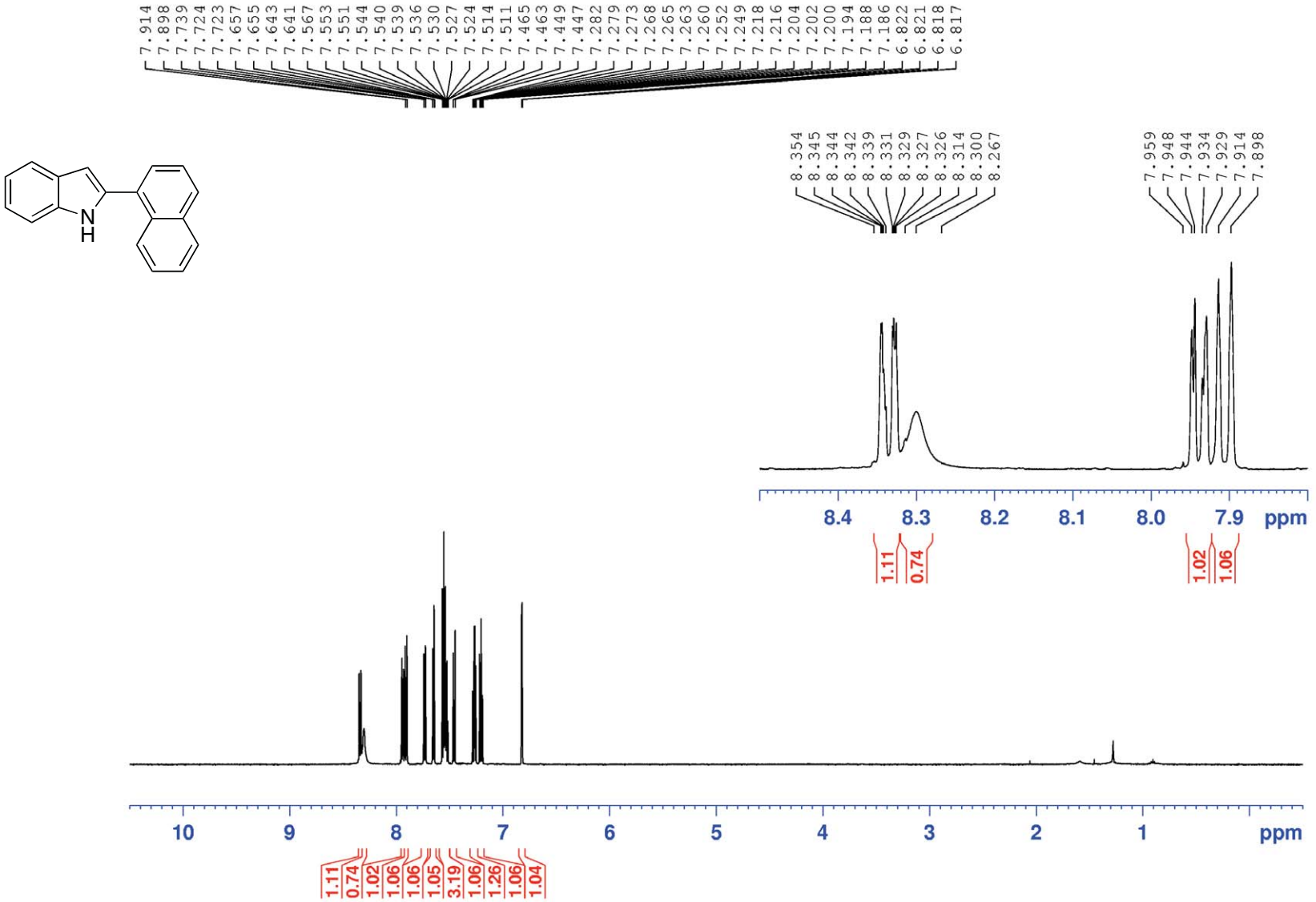
^{1}H NMR of **2n** ($CDCl_3$, 500 MHz, 300 K)



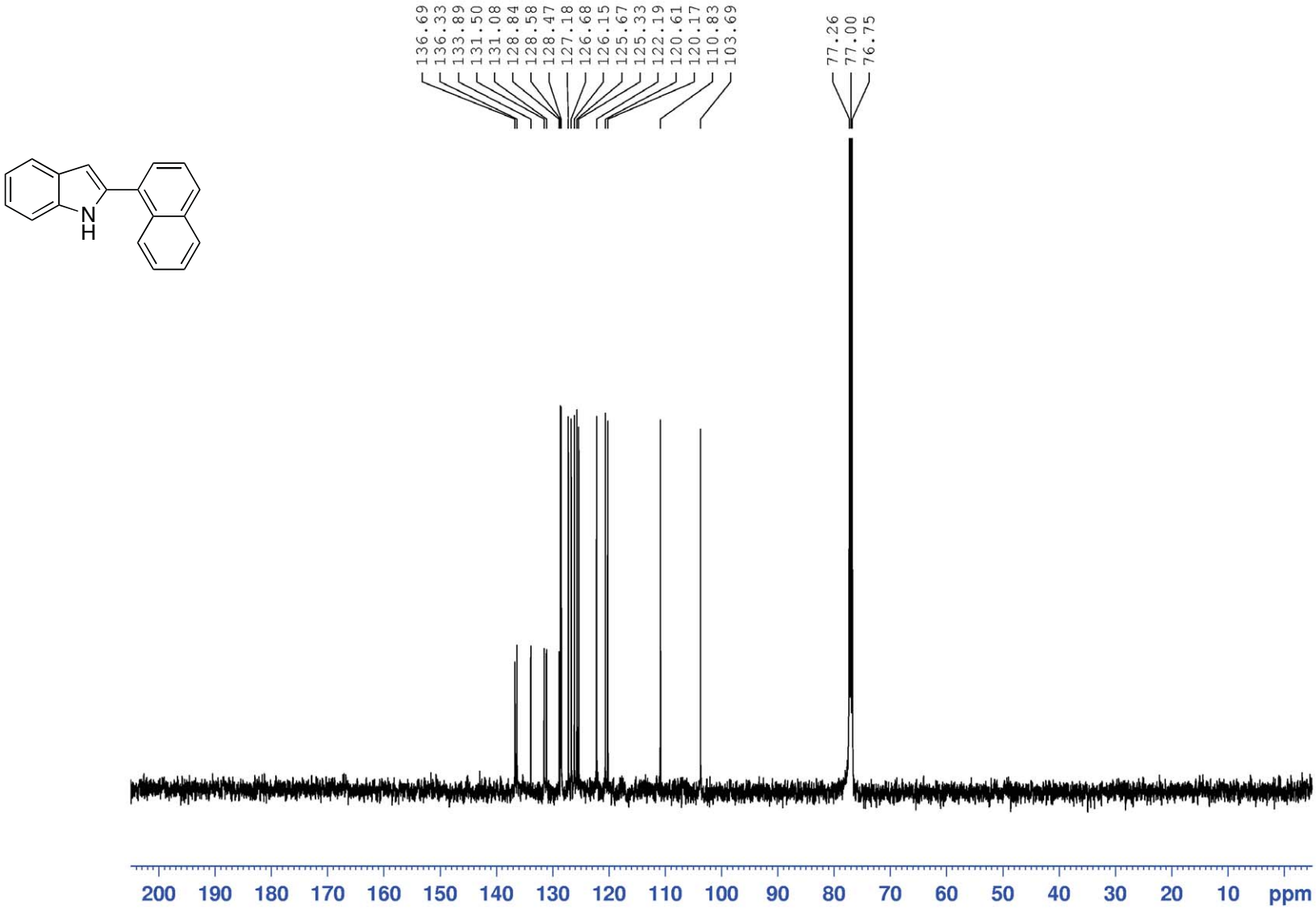
^{13}C NMR of **2n** ($CDCl_3$, 126 MHz, 300 K)



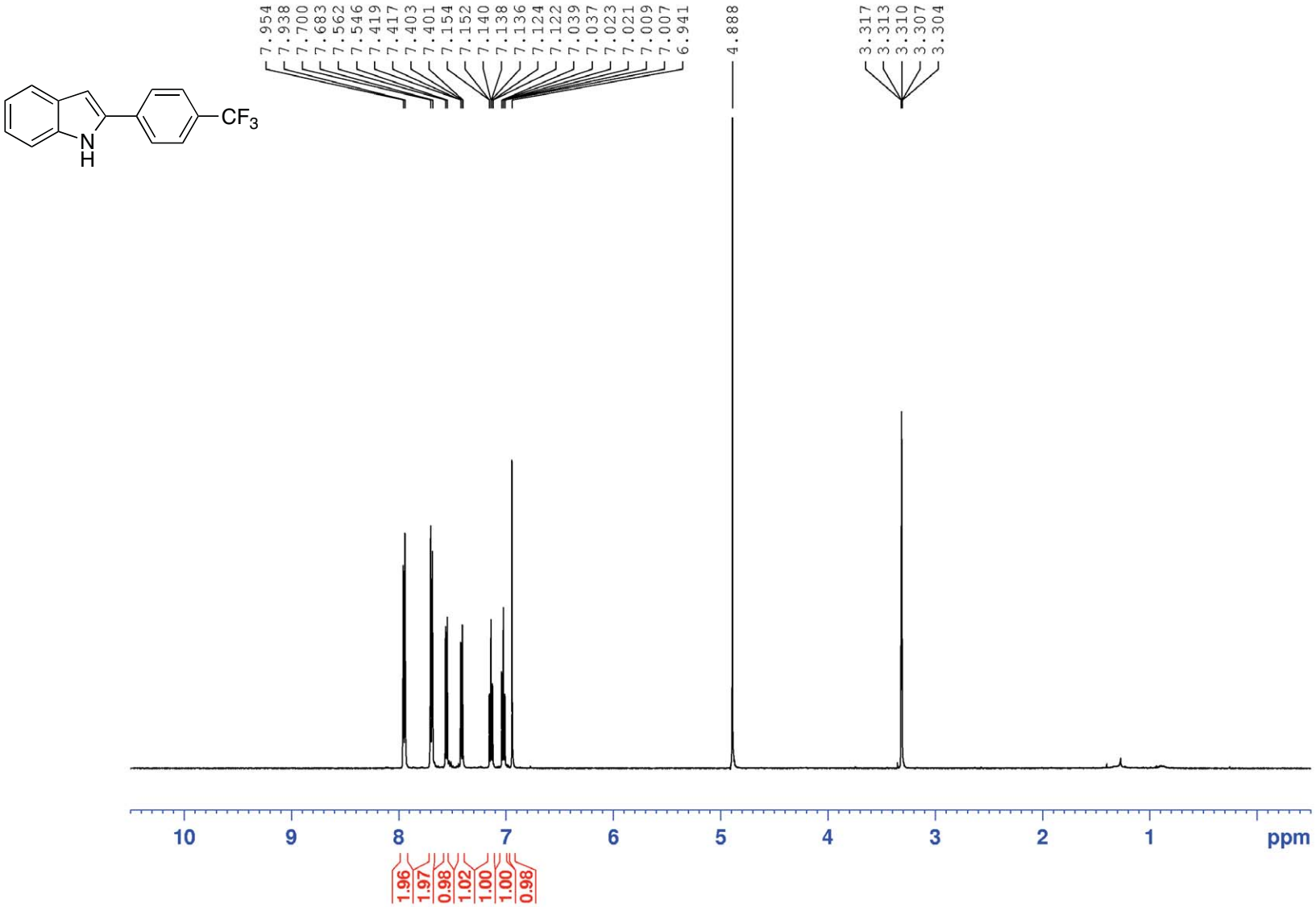
^{1}H NMR of **2o** ($CDCl_3$, 500 MHz, 300 K)



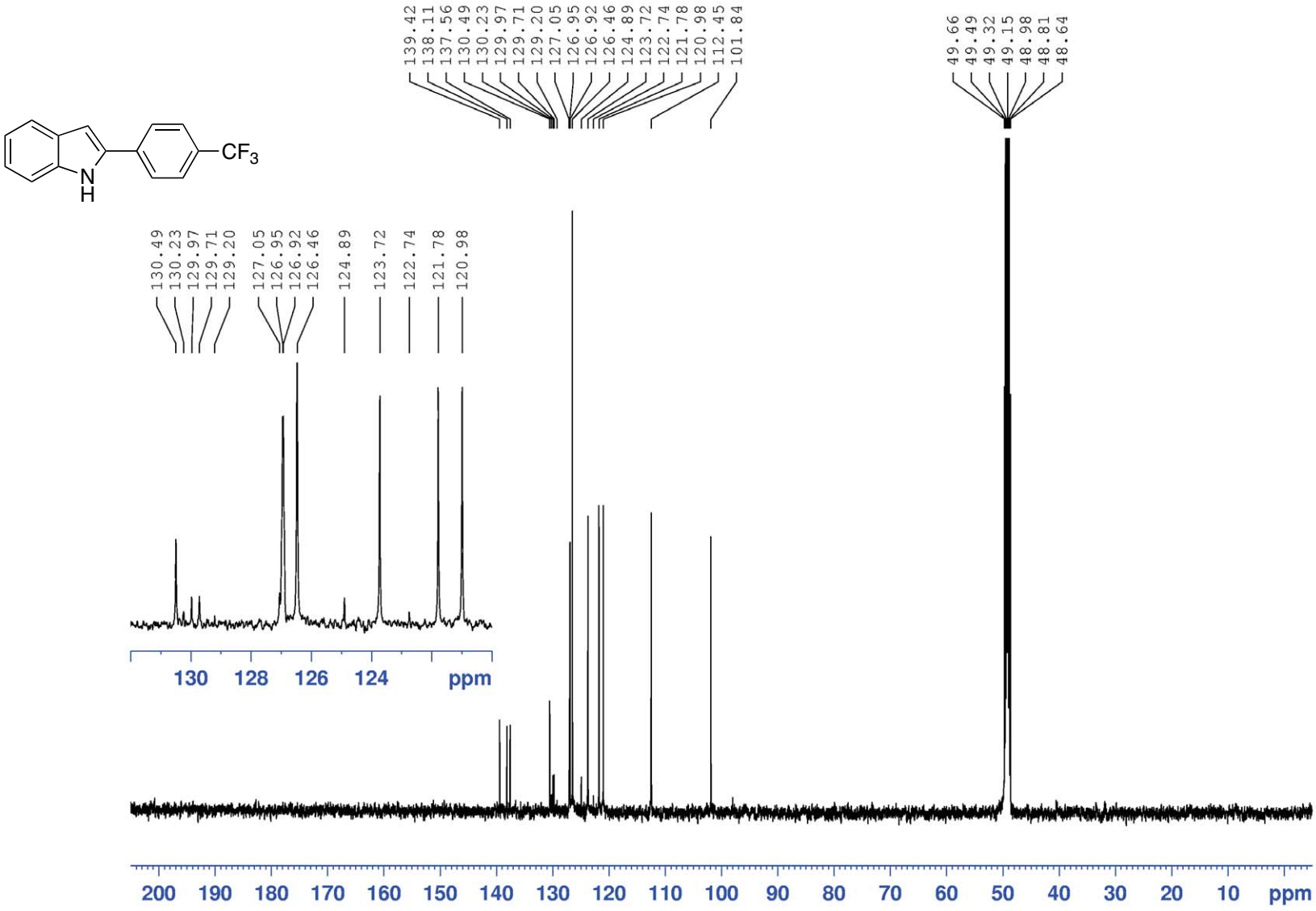
^{13}C NMR of **2o** ($CDCl_3$, 126 MHz, 300 K)



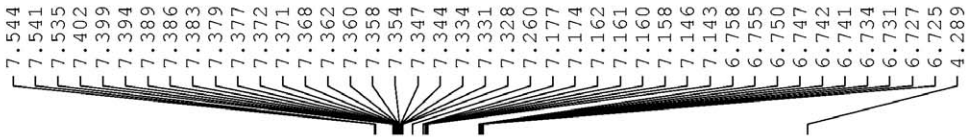
^{1}H NMR of **2p** (CD_3OD, 500 MHz, 300 K)

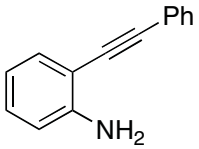


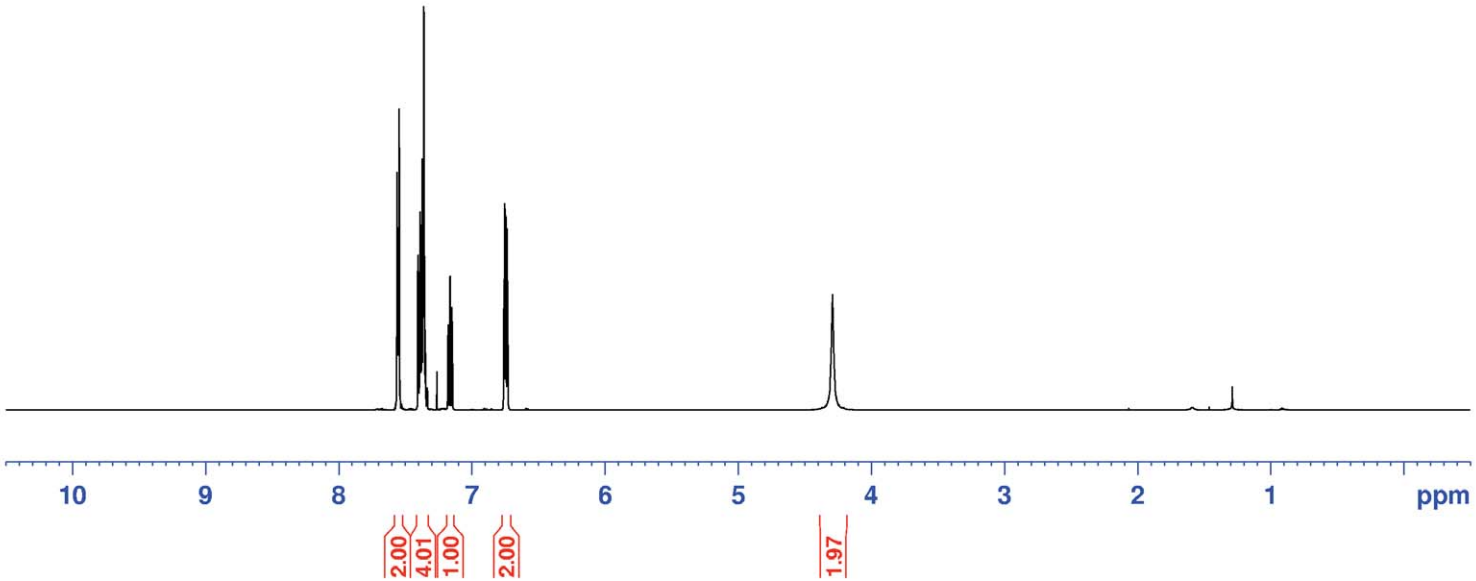
^{13}C NMR of **2p** (CD_3OD, 126 MHz, 300 K)



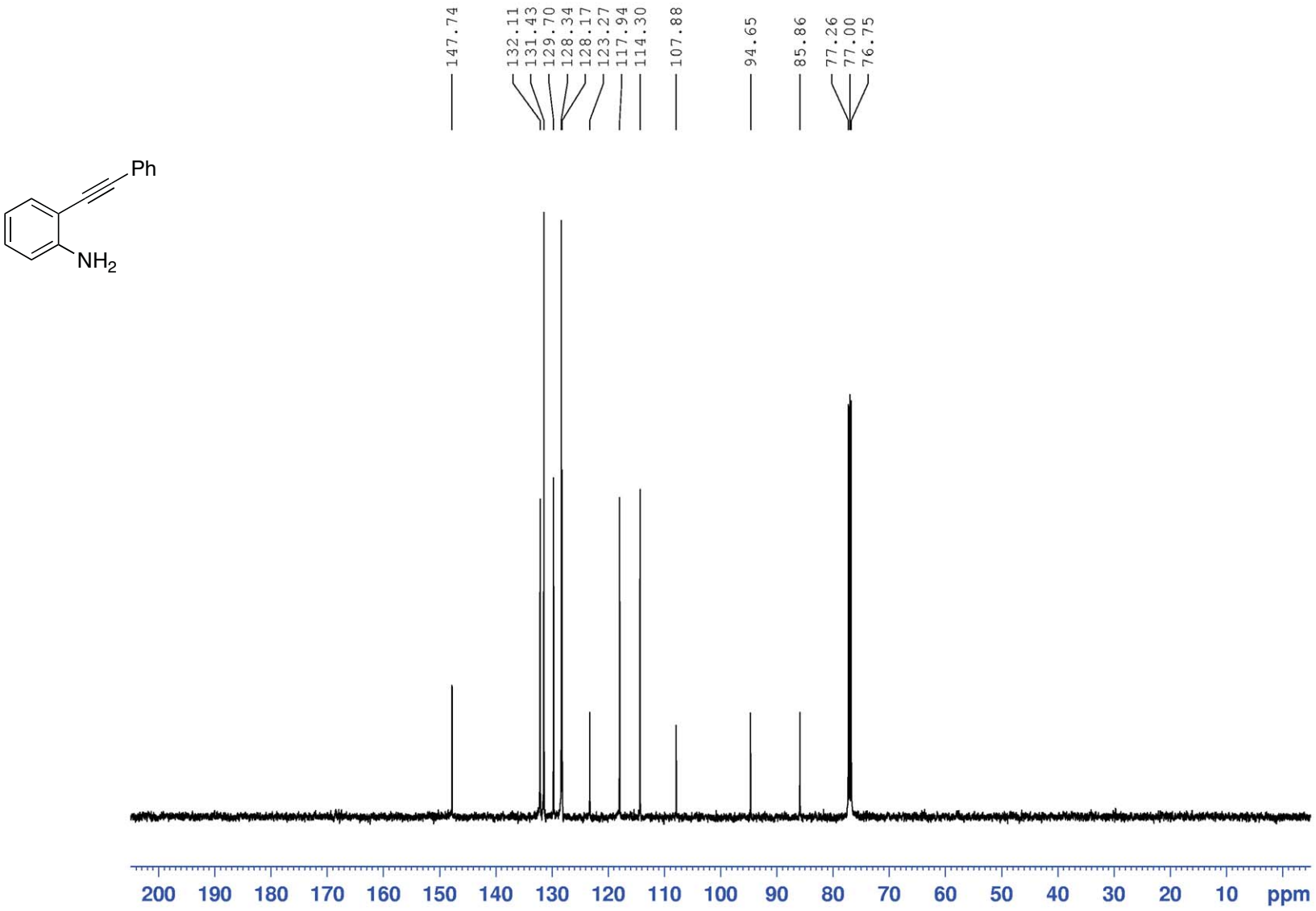
^{1}H NMR of **2a'** ($CDCl_3$, 500 MHz, 300 K)



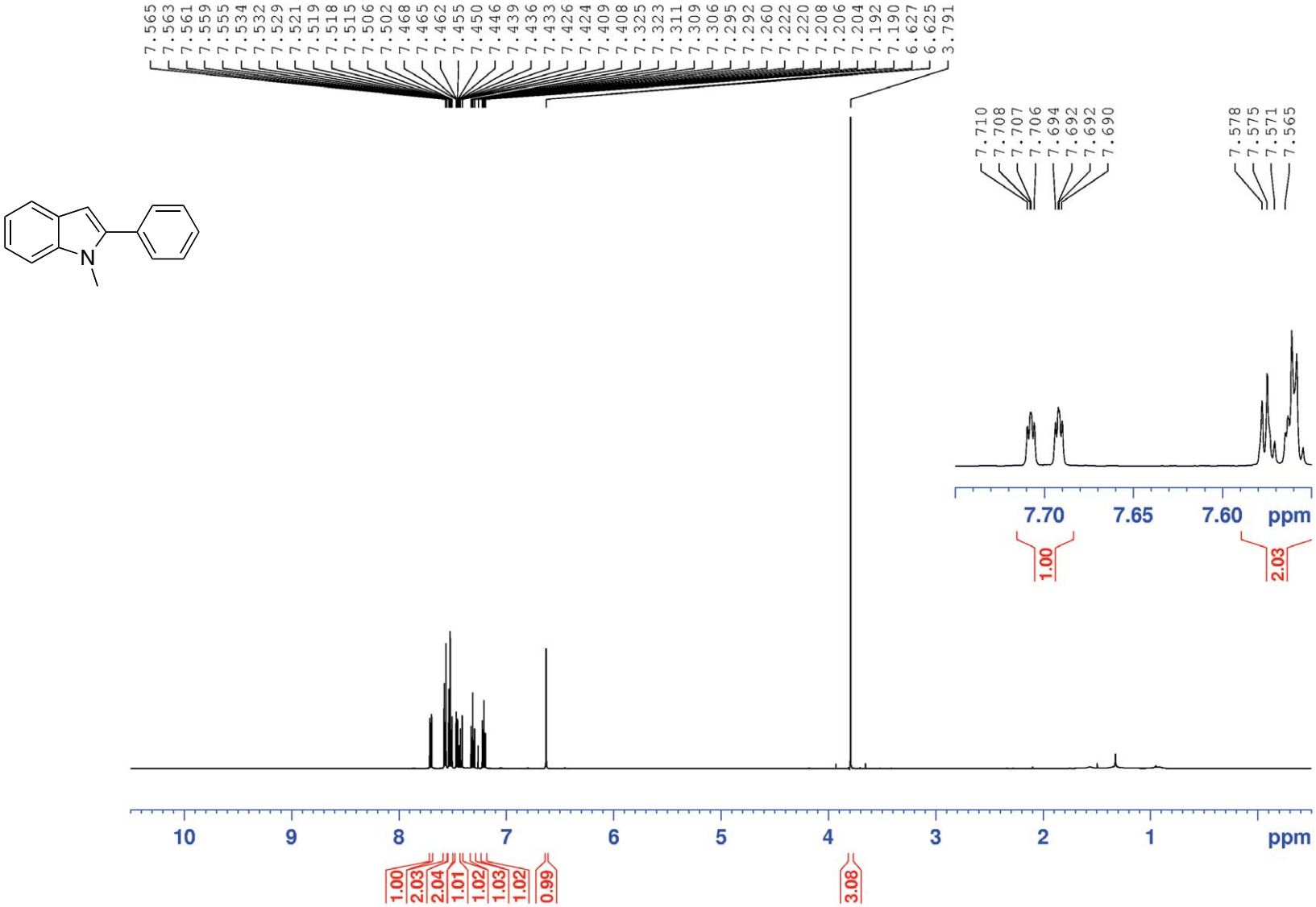




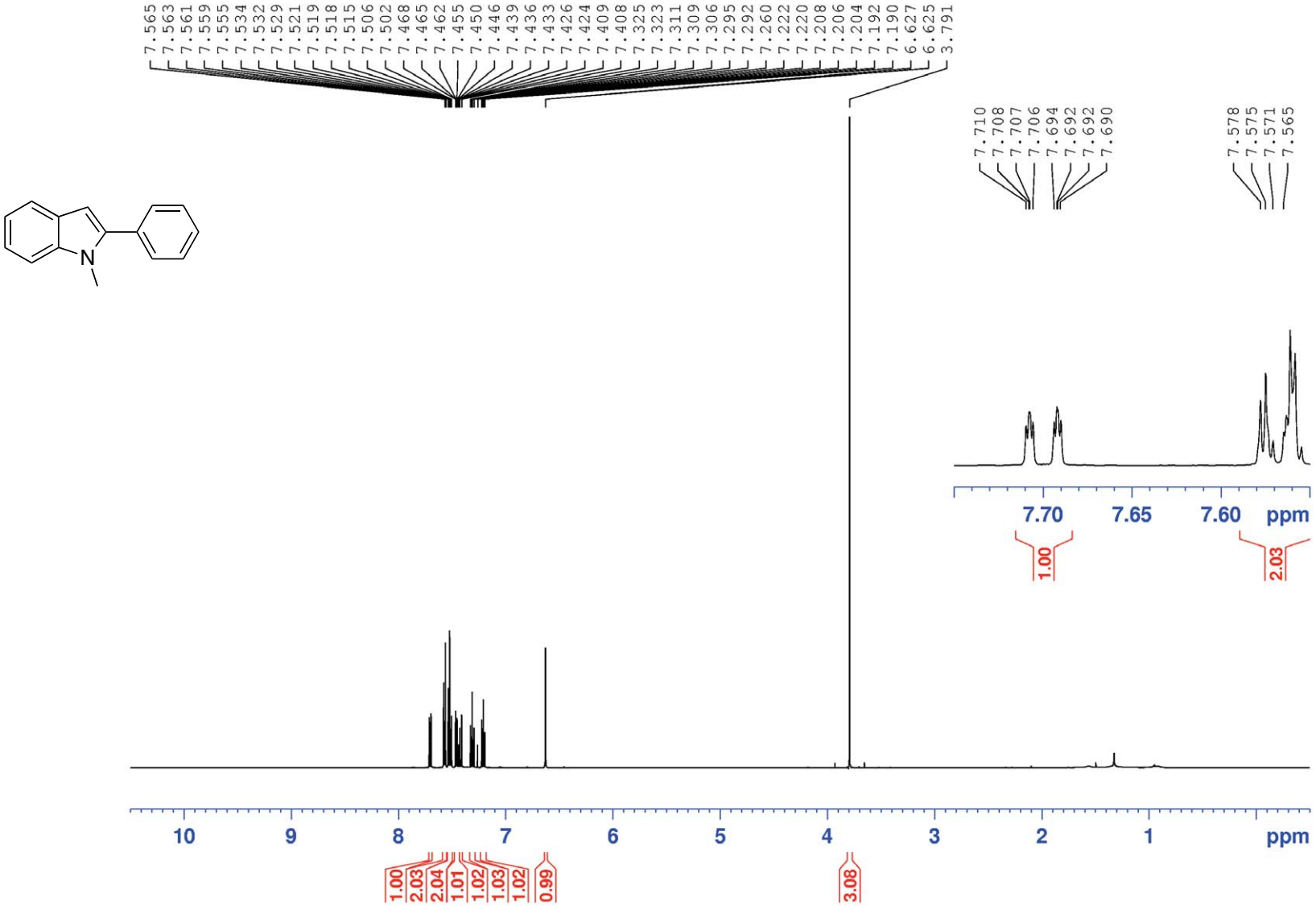
^{13}C NMR of **2a'** ($CDCl_3$, 126 MHz, 300 K)



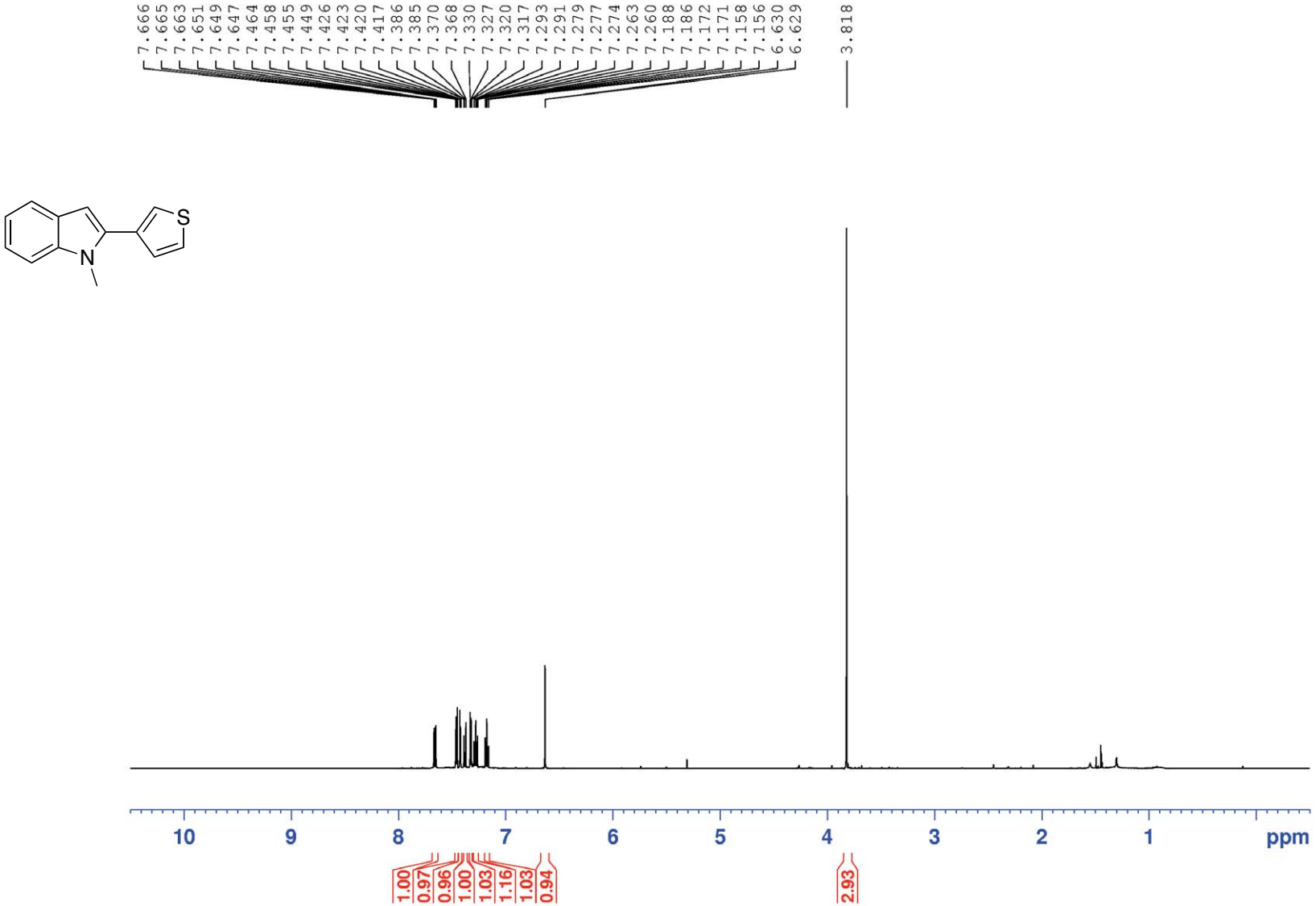
^{1}H NMR of **3a** ($CDCl_3$, 500 MHz, 300 K)



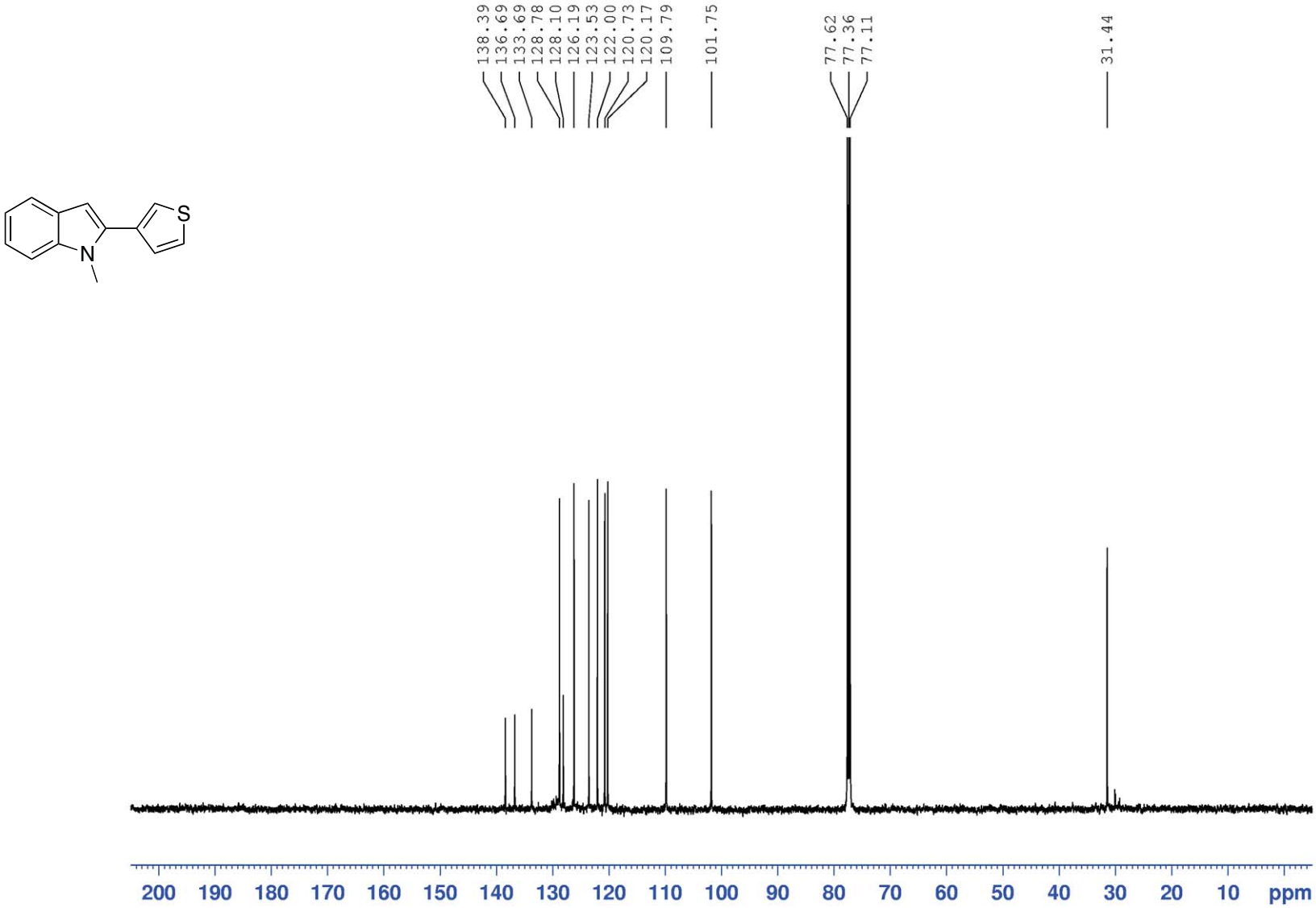
^{13}C NMR of **3a** ($CDCl_3$, 126 MHz, 300 K)



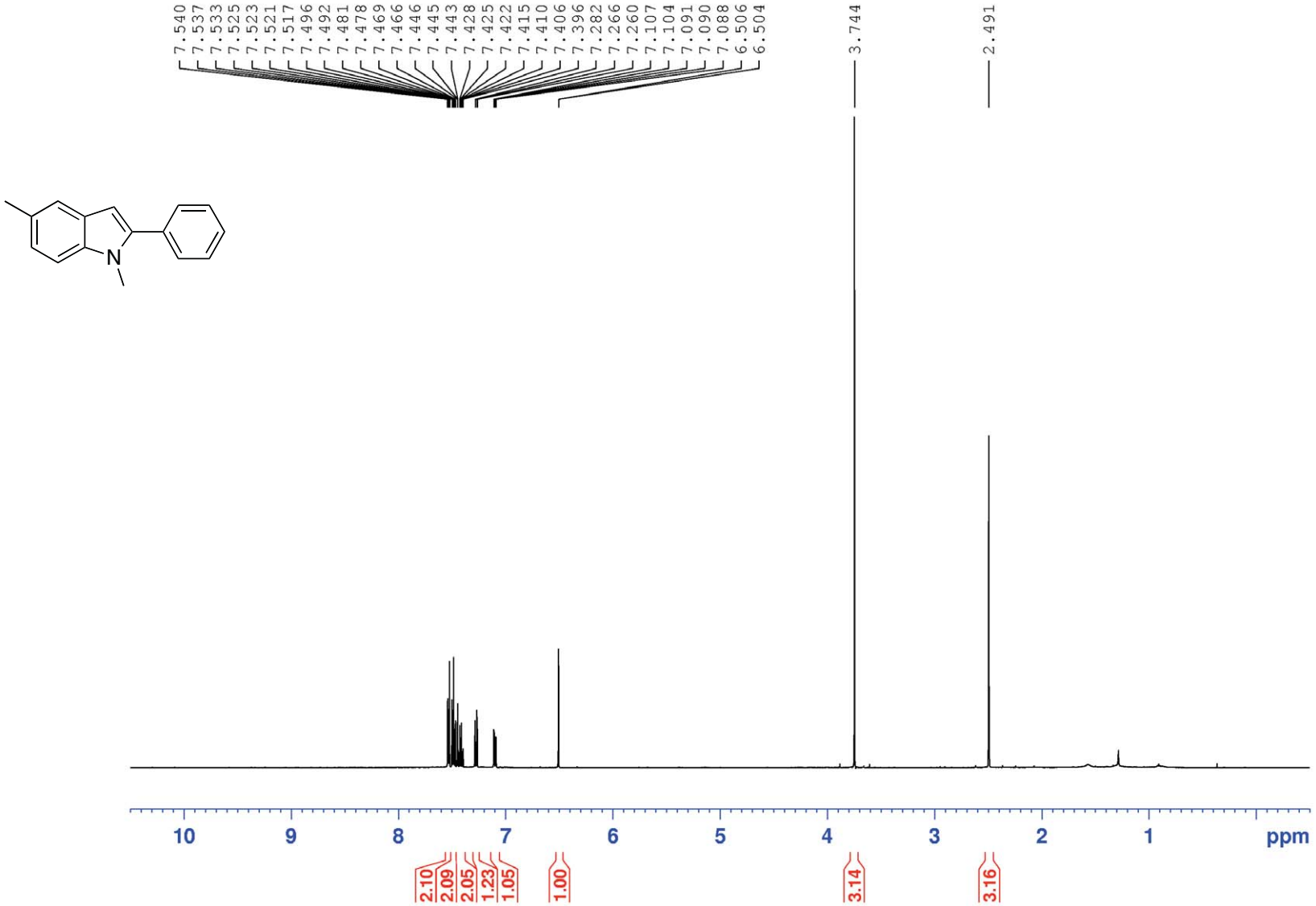
^{1}H NMR of **3b** ($CDCl_3$, 500 MHz, 300 K)



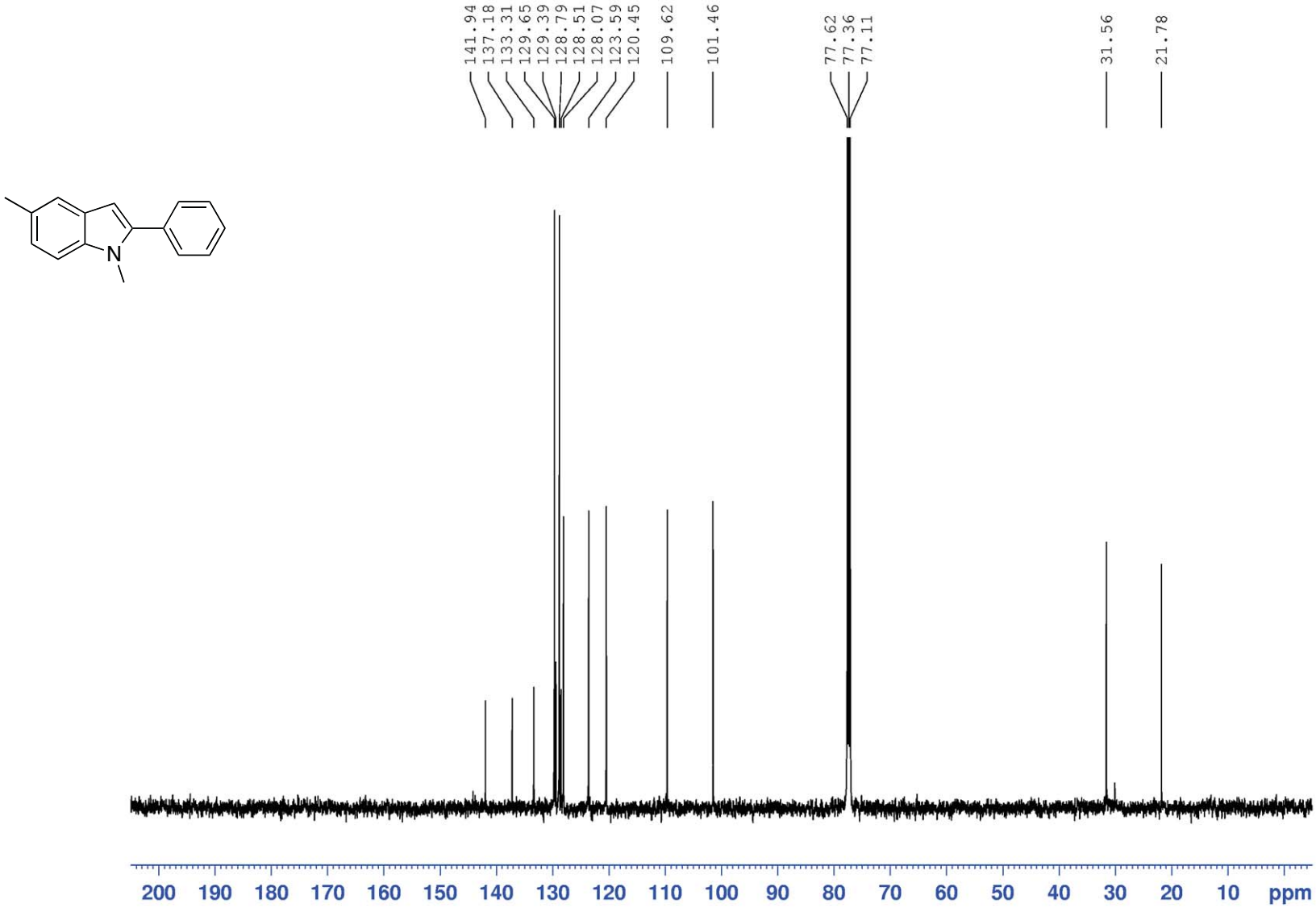
^{13}C NMR of **3b** ($CDCl_3$, 126 MHz, 300 K)



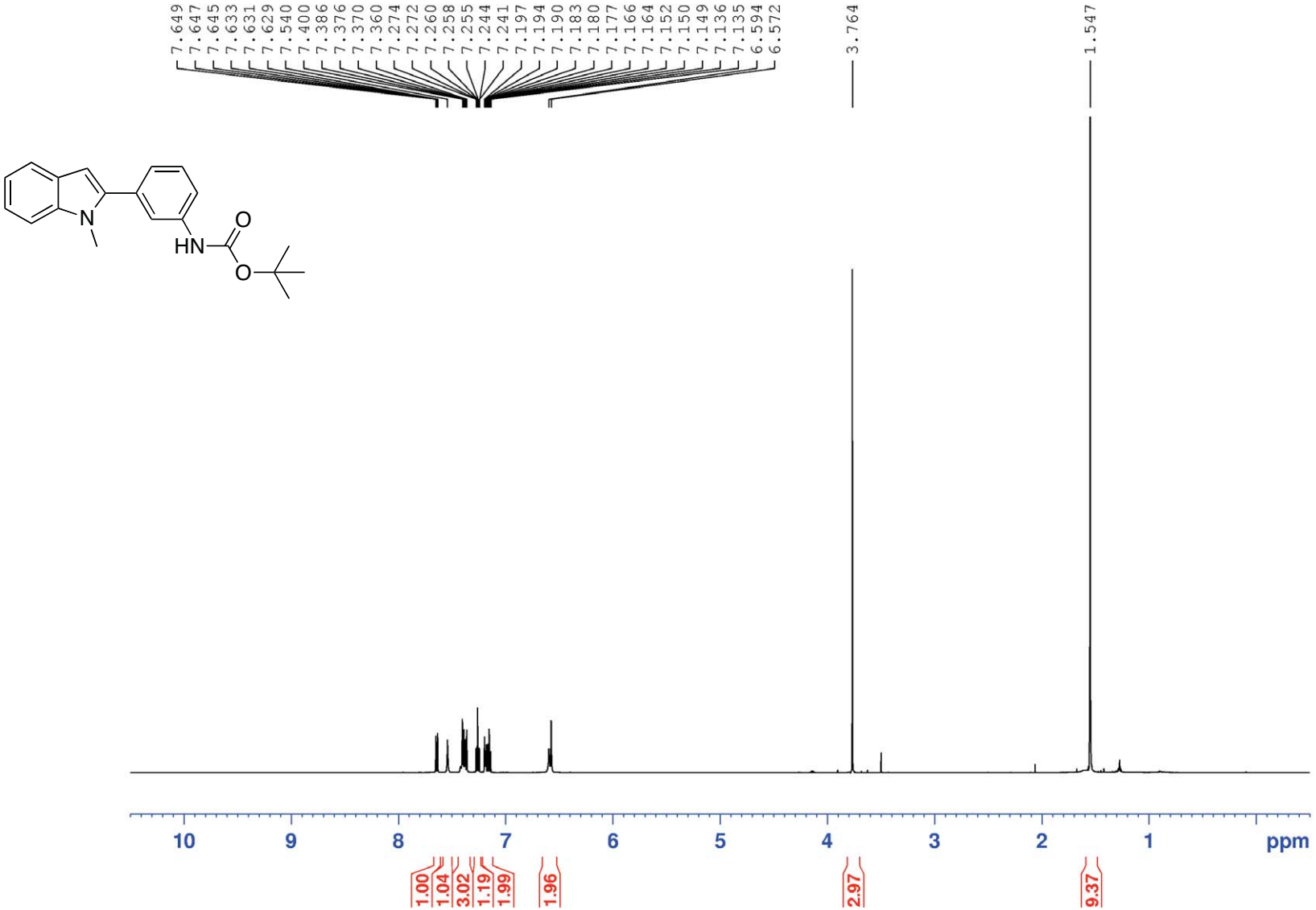
^{1}H NMR of **3c** ($CDCl_3$, 500 MHz, 300 K)



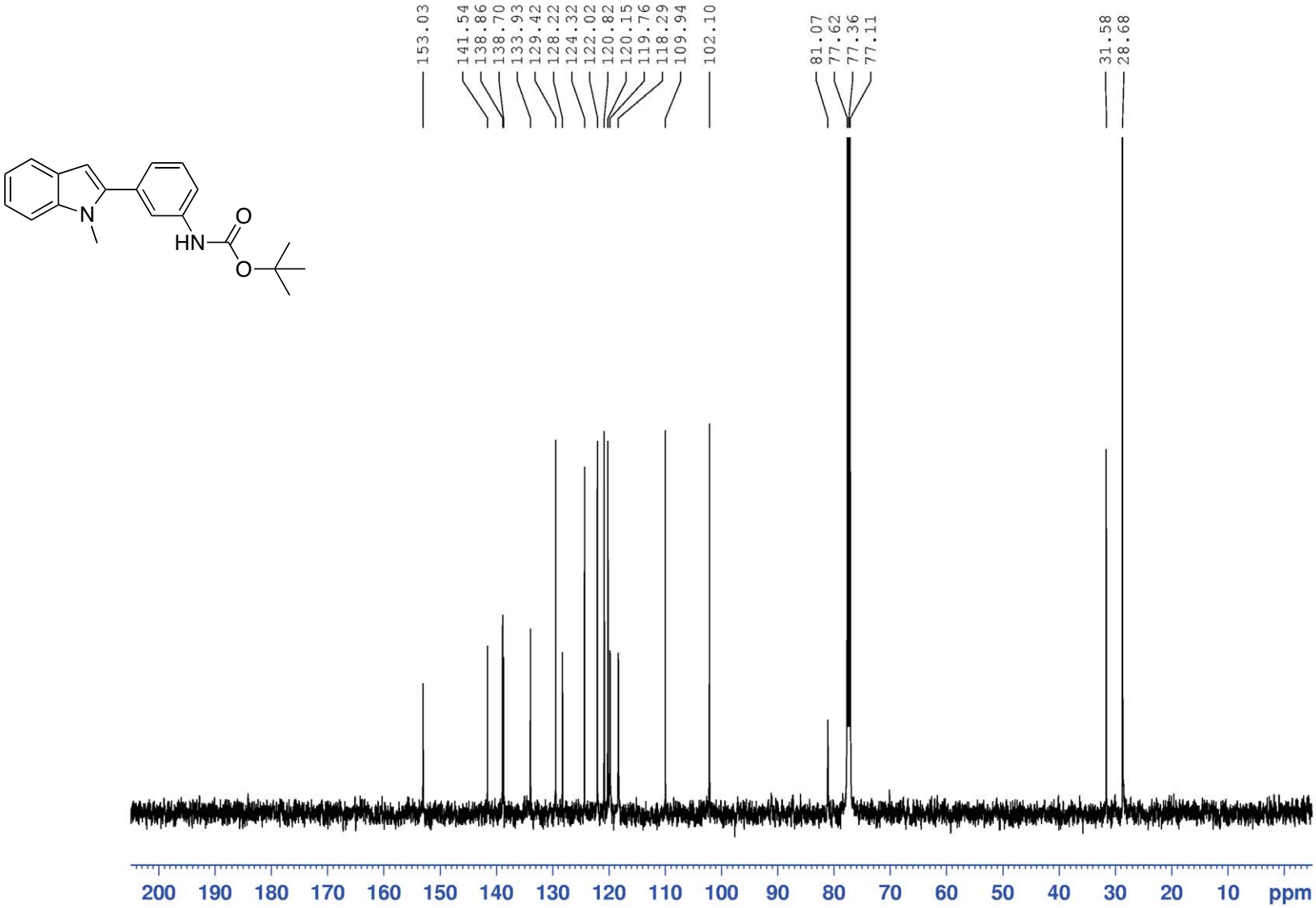
^{13}C NMR of **3c** ($CDCl_3$, 126 MHz, 300 K)



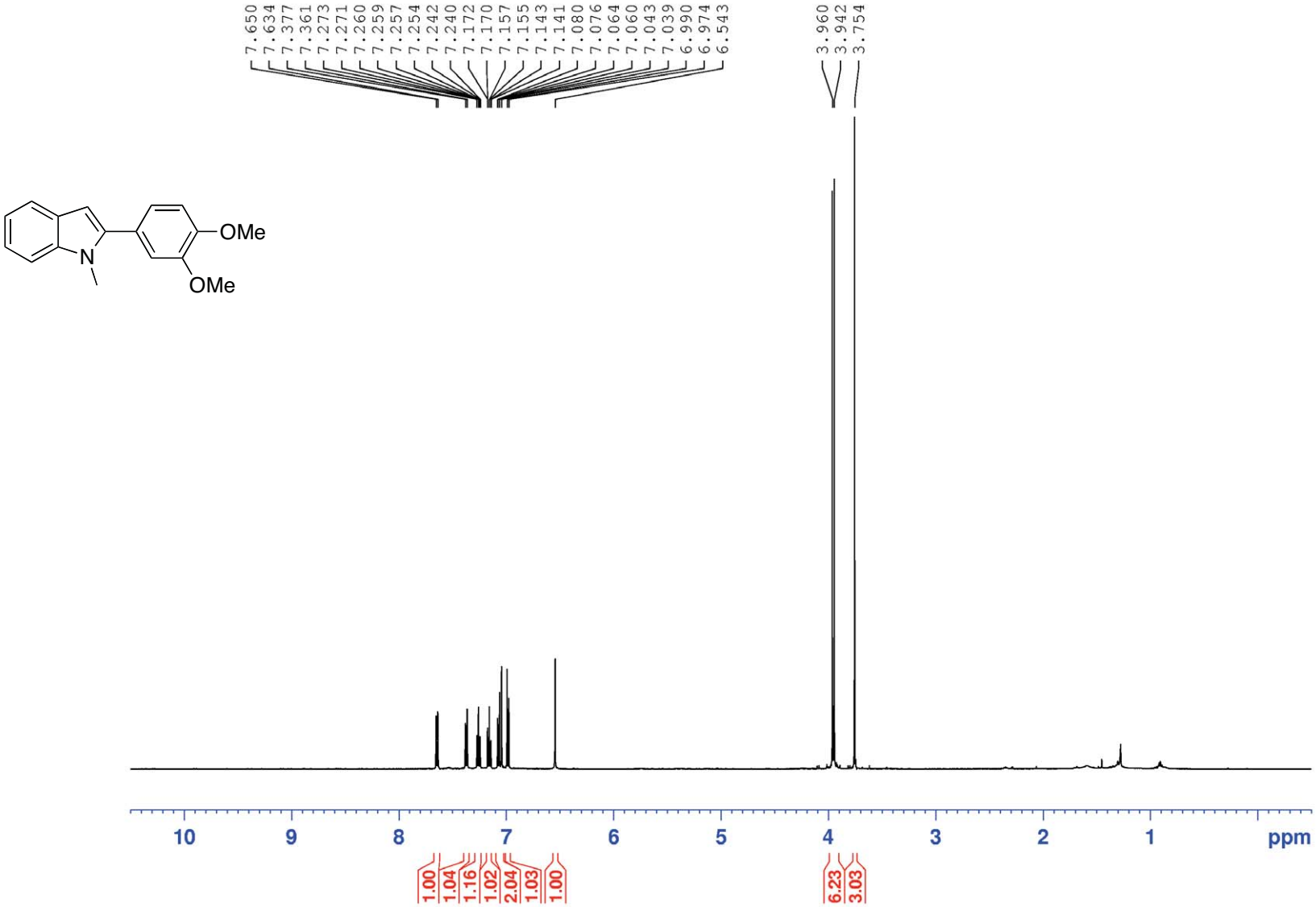
^{1}H NMR of **3d** ($CDCl_3$, 500 MHz, 300 K)



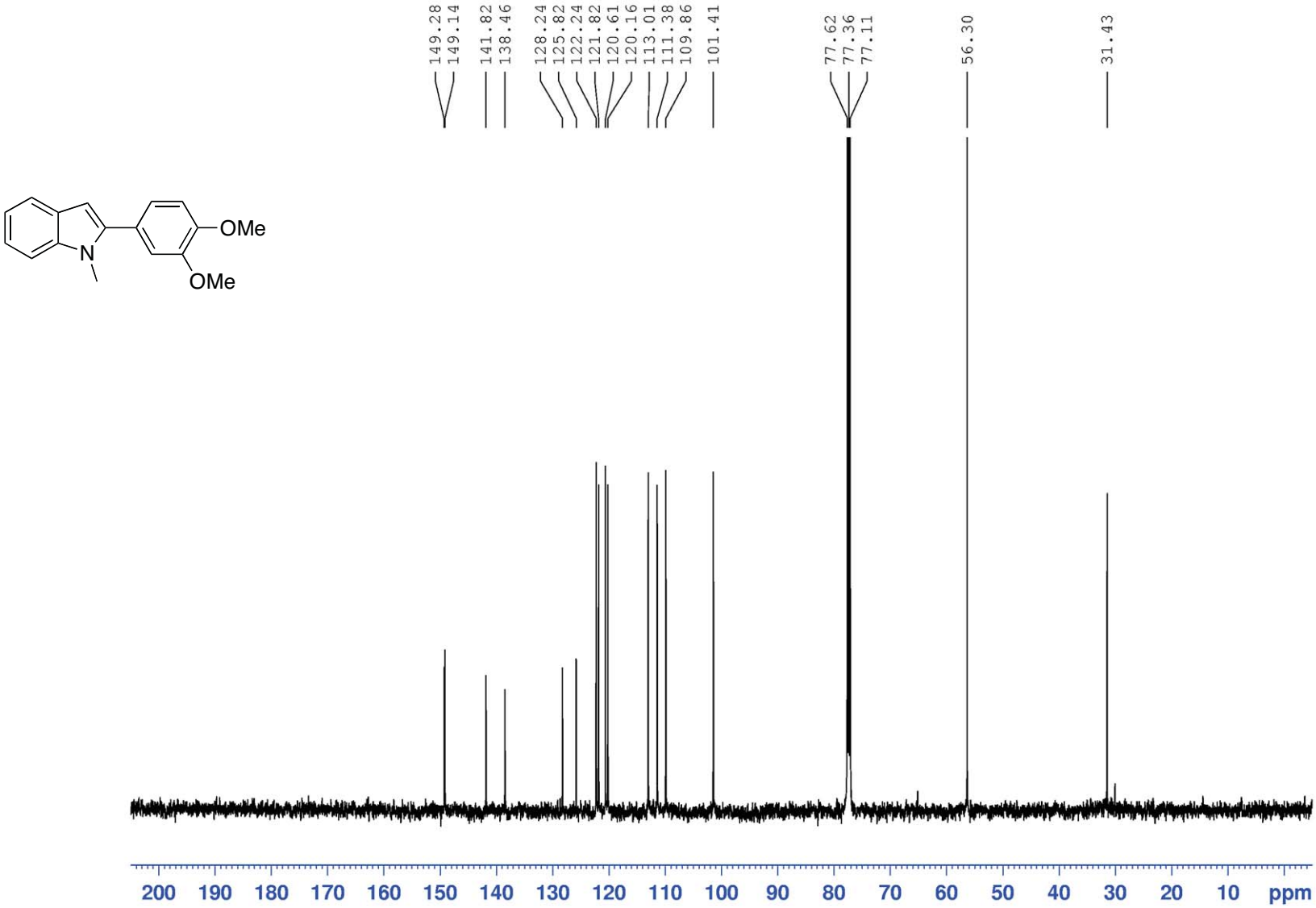
^{13}C NMR of **3d** ($CDCl_3$, 126 MHz, 300 K)



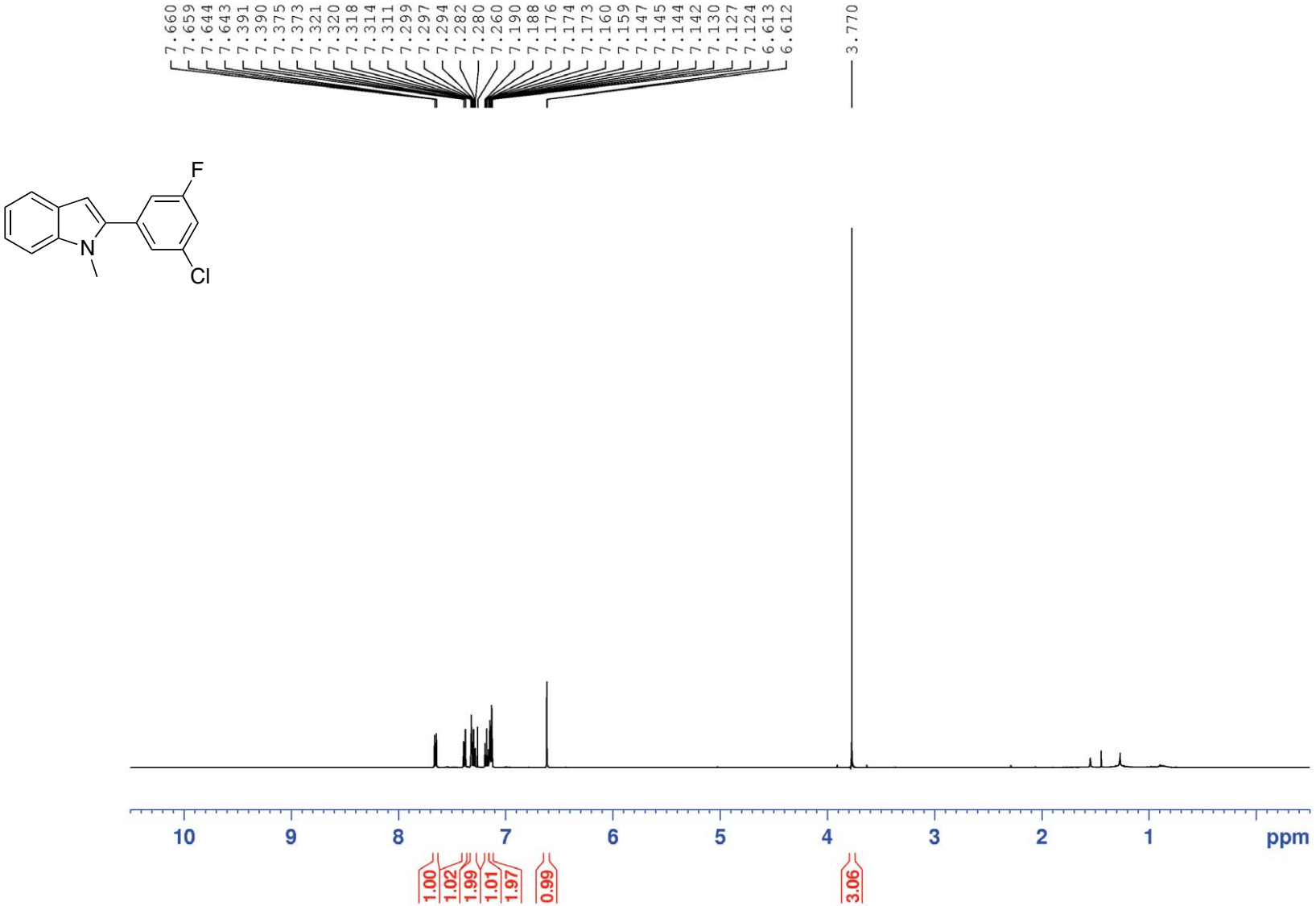
^{1}H NMR of **3e** ($CDCl_3$, 500 MHz, 300 K)



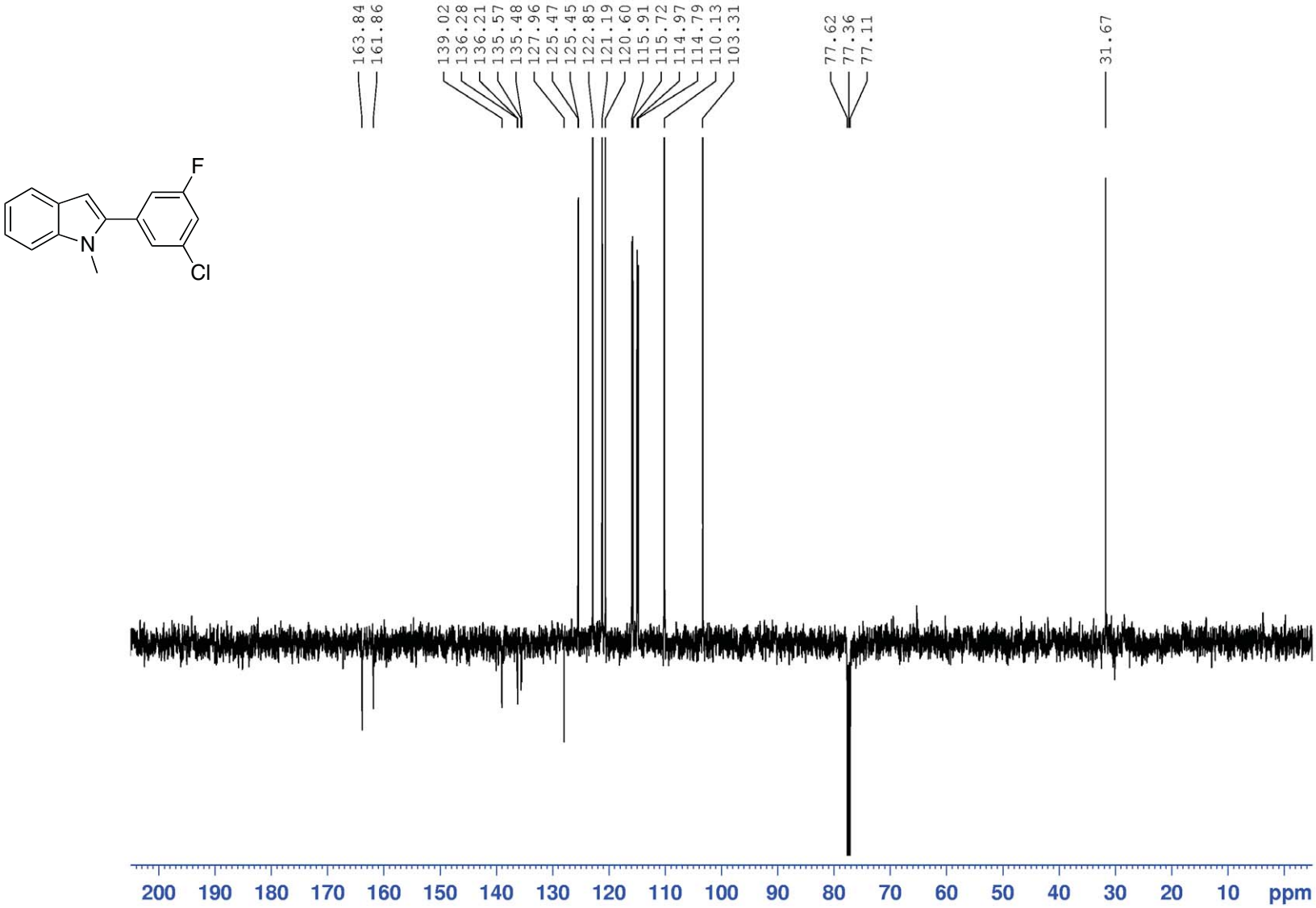
^{13}C NMR of **3e** ($CDCl_3$, 126 MHz, 300 K)



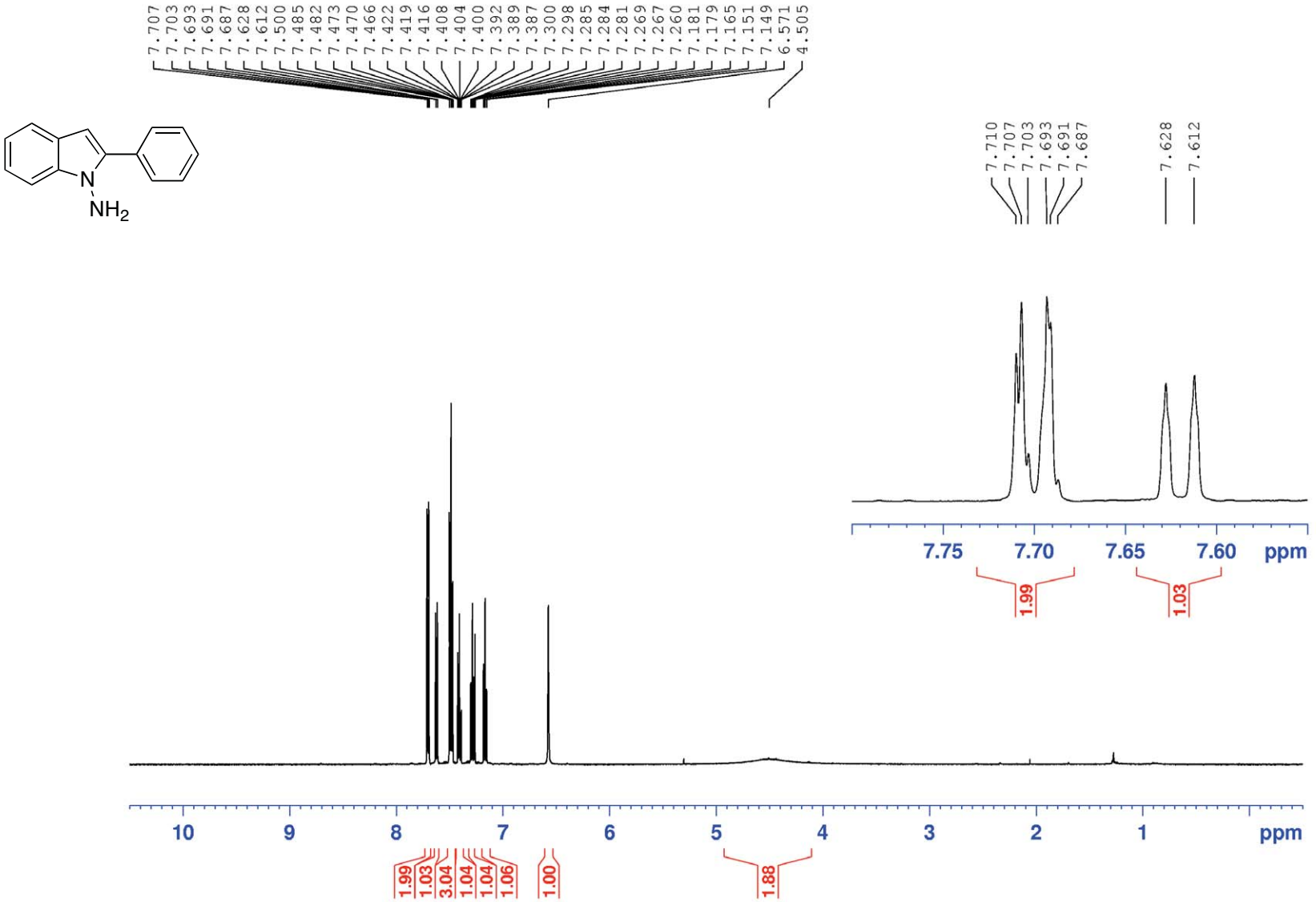
^{1}H NMR of **3f** ($CDCl_3$, 500 MHz, 300 K)



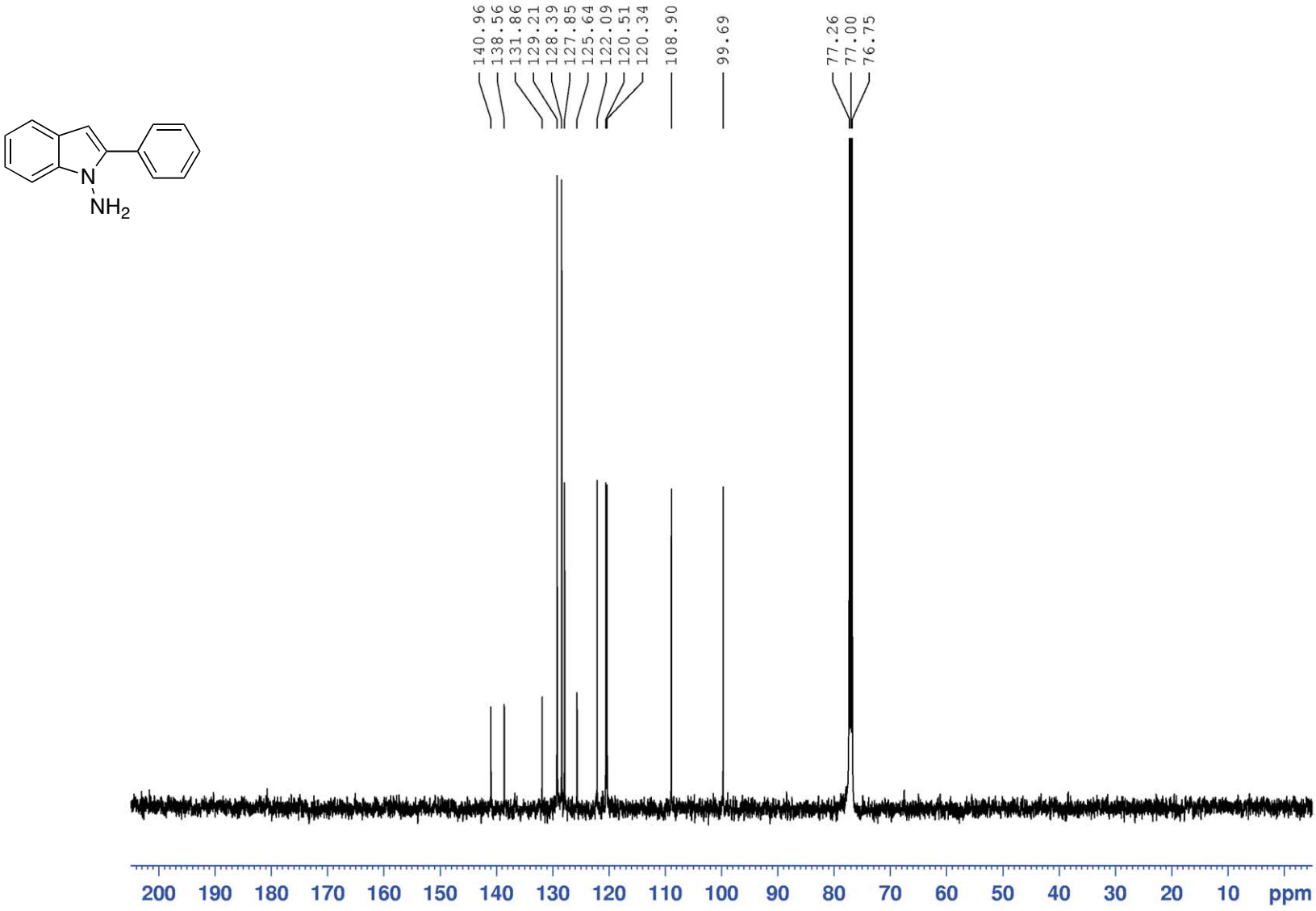
^{13}C DEPT-135-Q NMR of **3f** ($CDCl_3$, 126 MHz, 300 K)



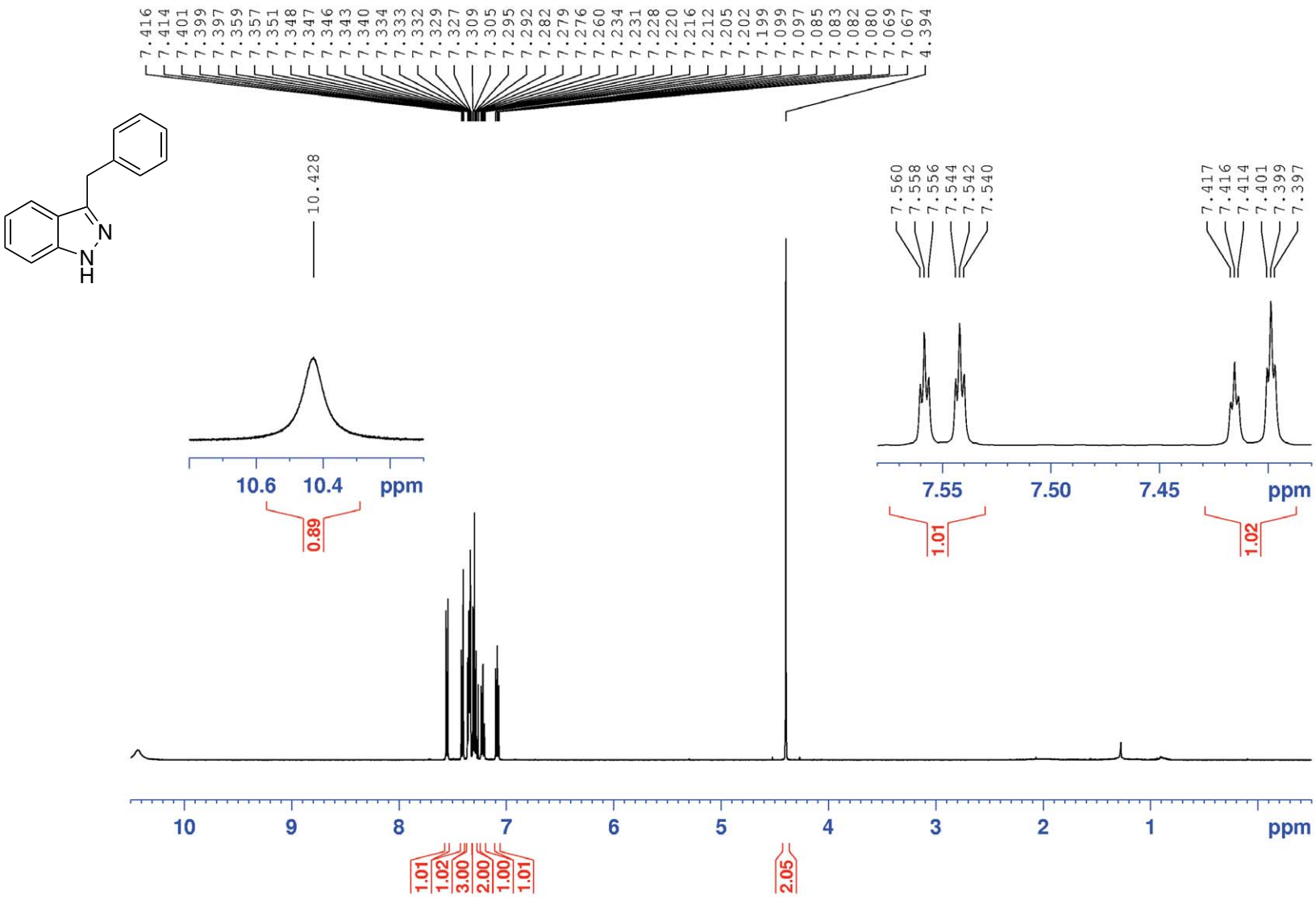
^{1}H NMR of **4a** ($CDCl_3$, 500 MHz, 300 K)



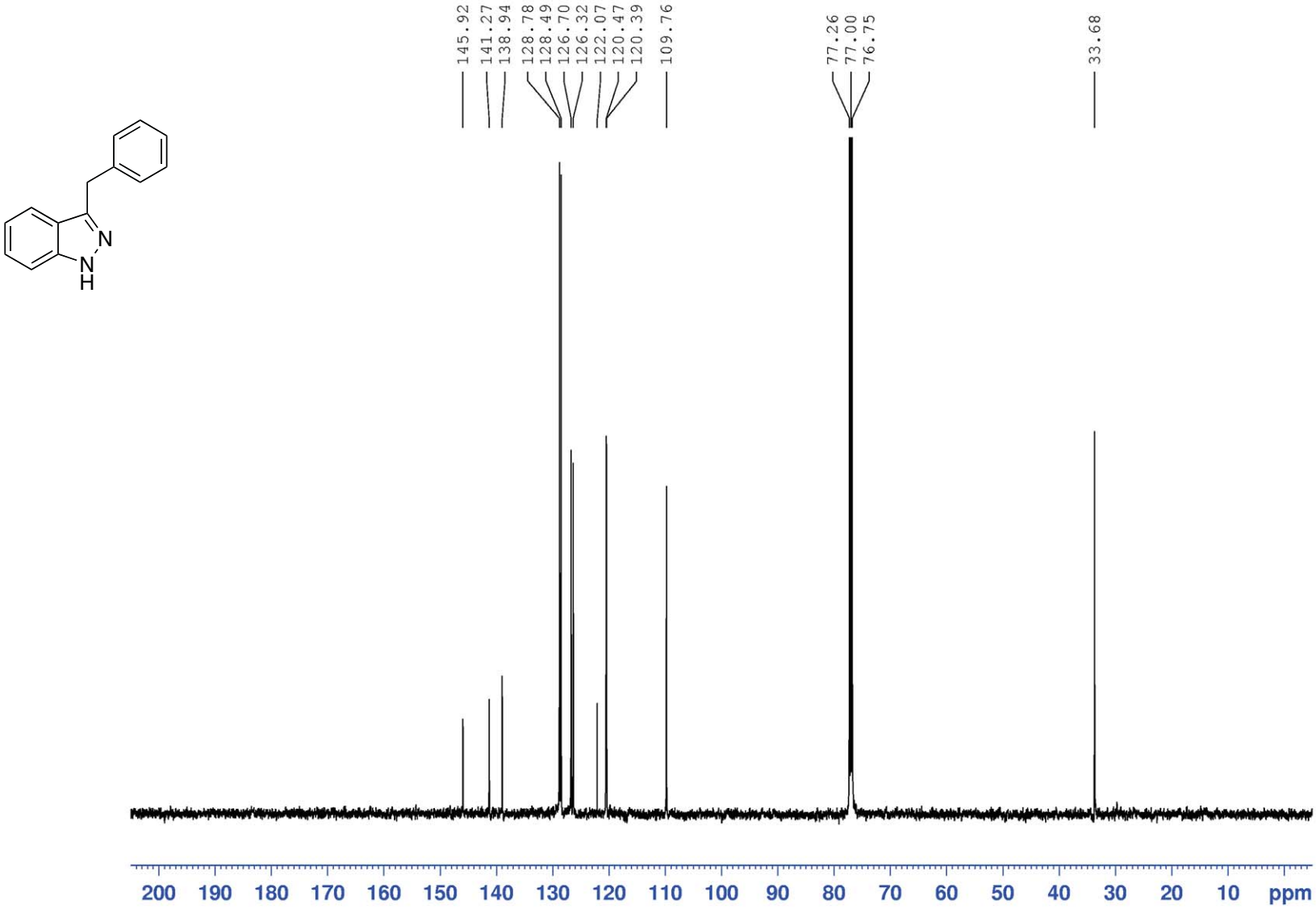
^{13}C NMR of **4a** ($CDCl_3$, 126 MHz, 300 K)



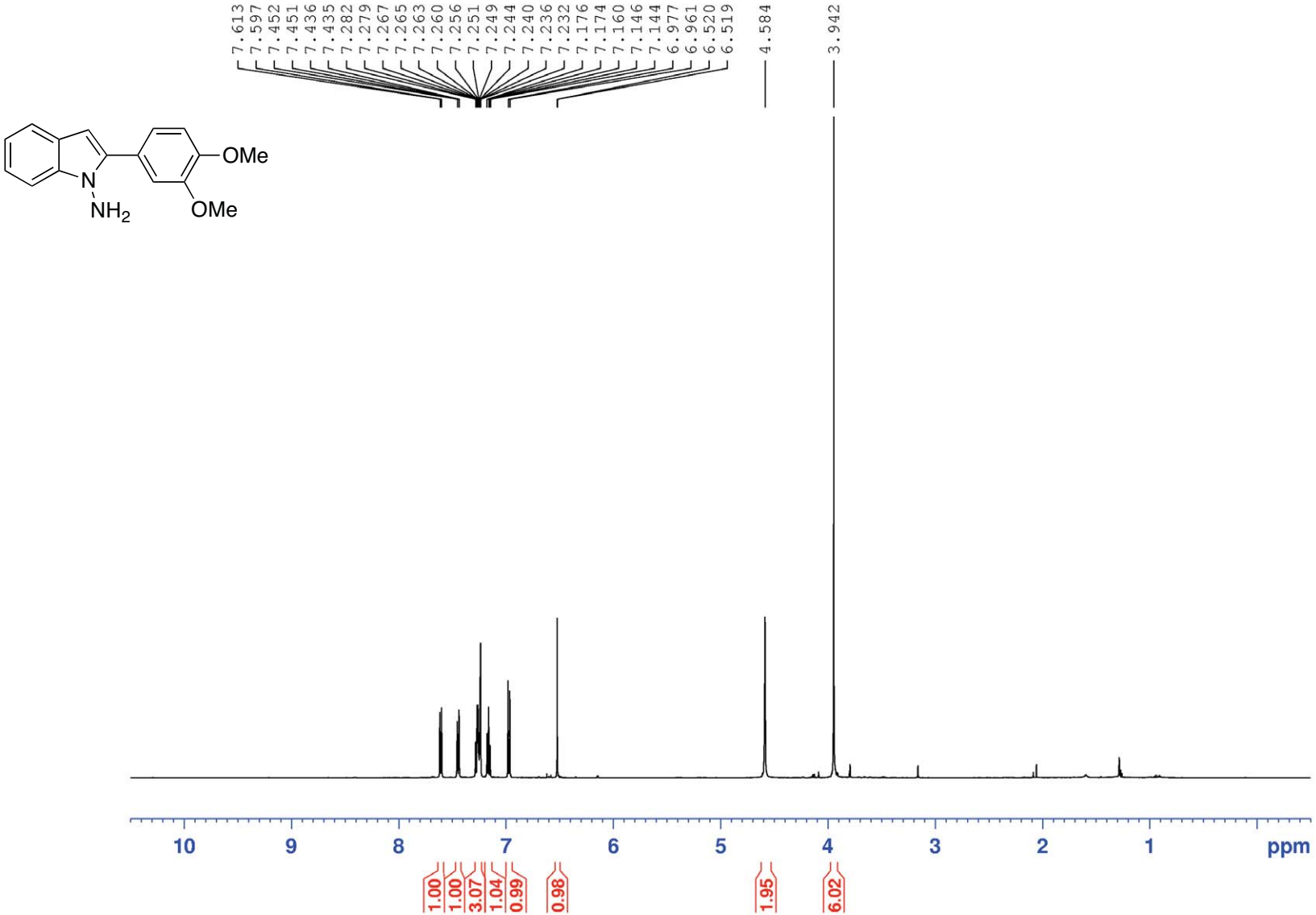
^{1}H NMR of **4a'** ($CDCl_3$, 500 MHz, 300 K)



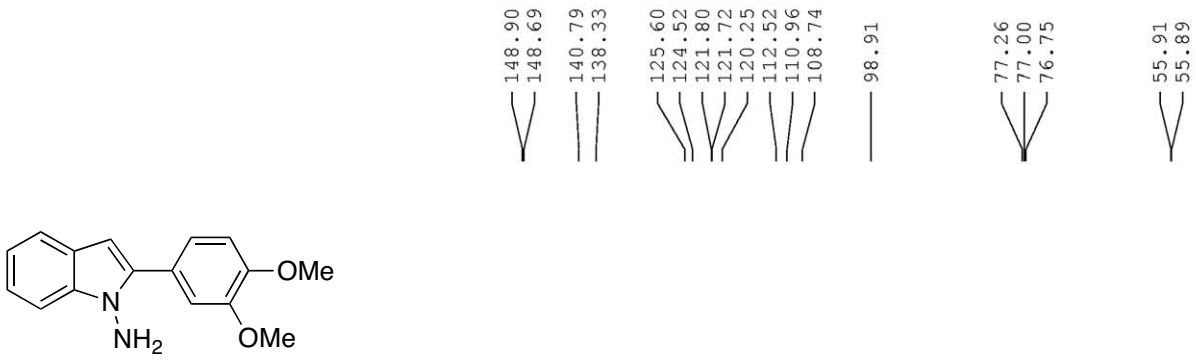
^{13}C NMR of **4a'** ($CDCl_3$, 126 MHz, 300 K)

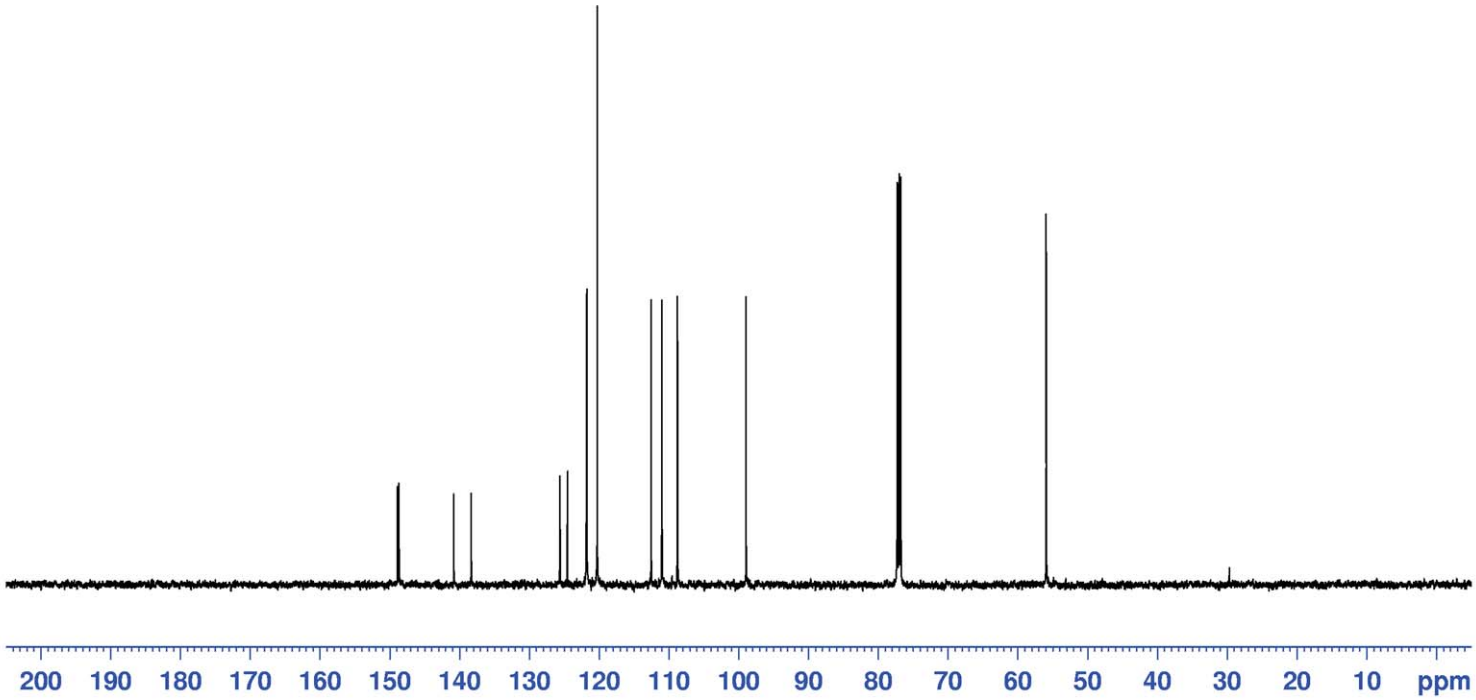


^{1}H NMR of **4b** ($CDCl_3$, 500 MHz, 300 K)

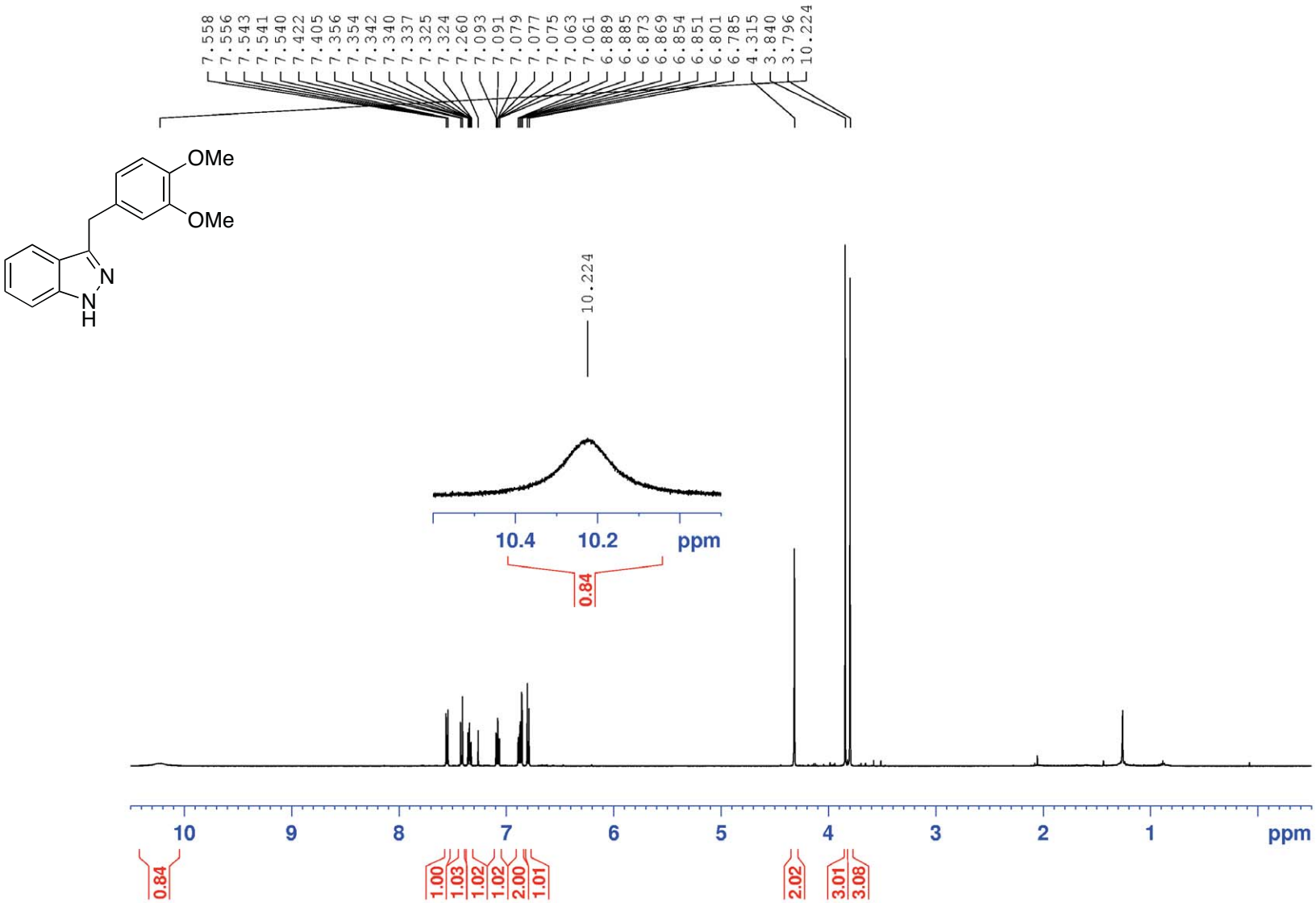


^{13}C NMR of **4b** ($CDCl_3$, 126 MHz, 300 K)

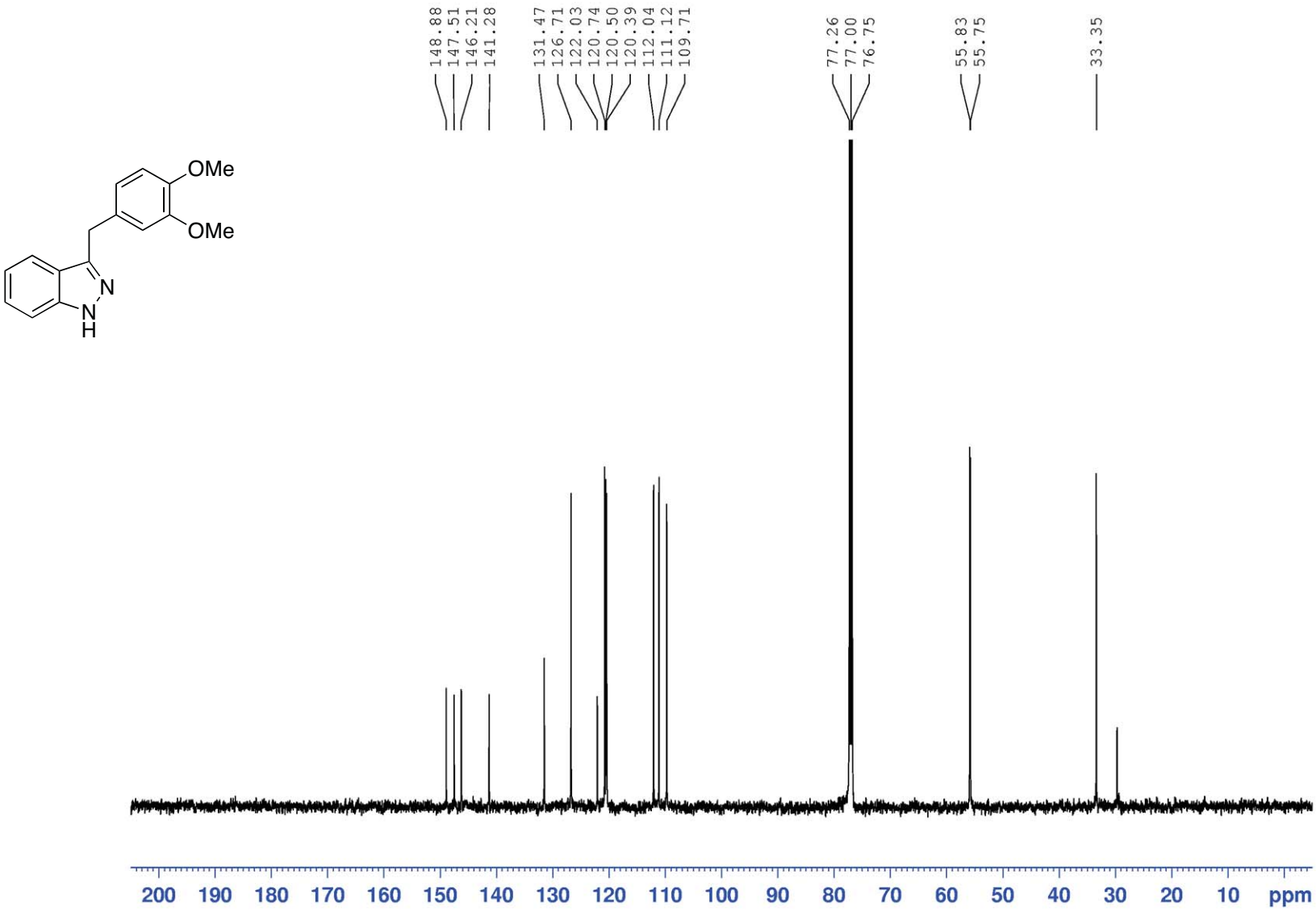




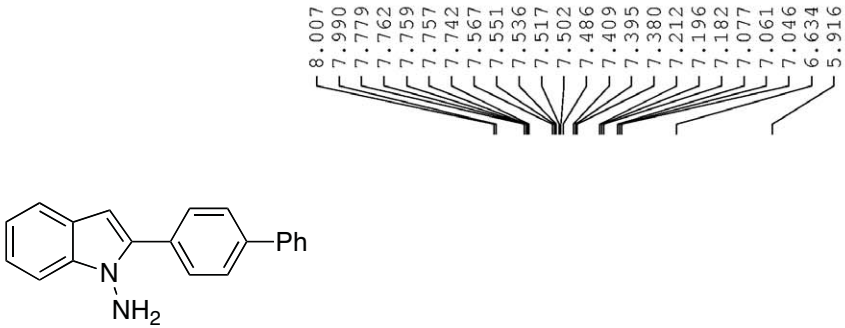
^{1}H NMR of **4b'** ($CDCl_3$, 500 MHz, 300 K)



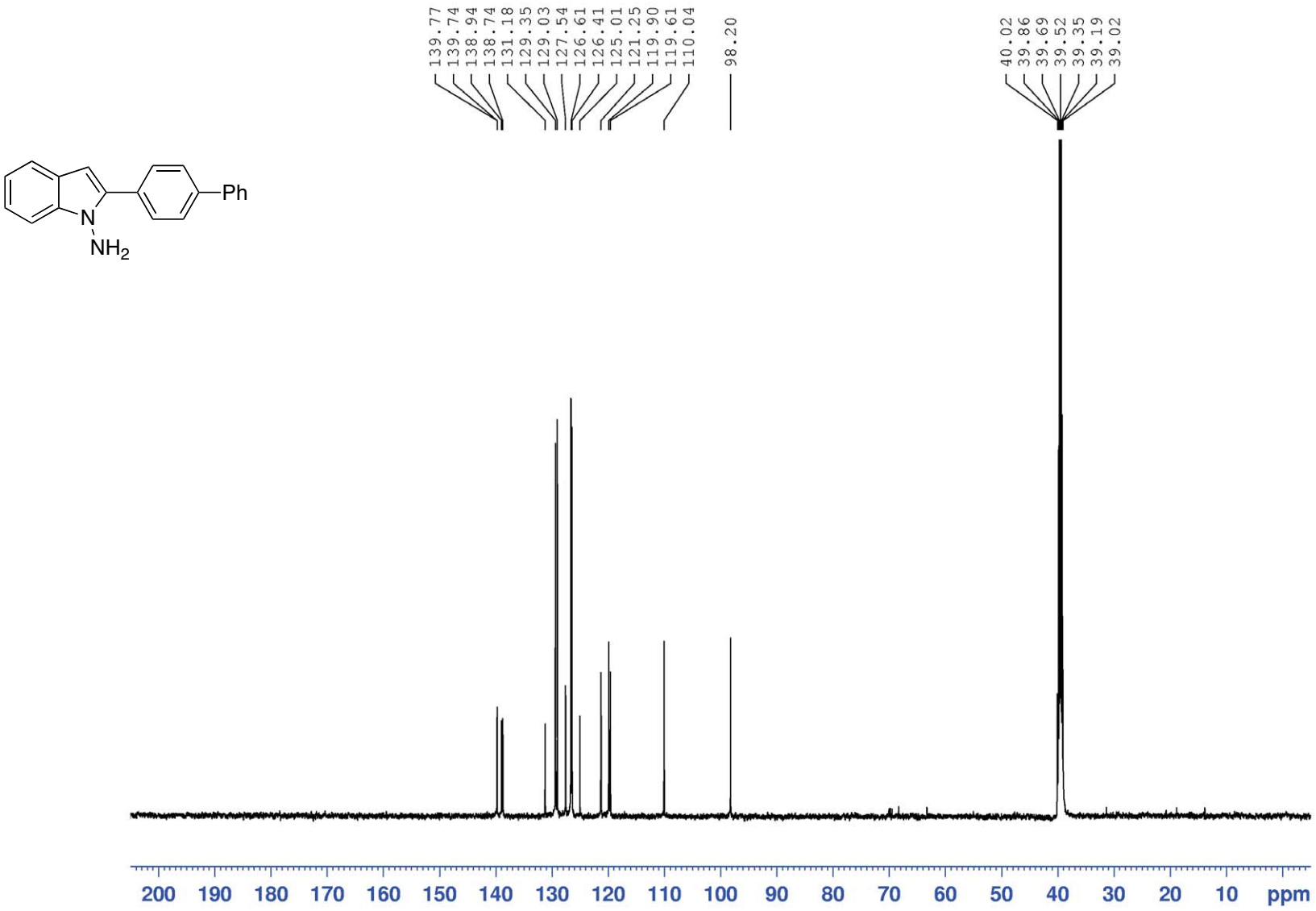
^{13}C NMR of **4b'** ($CDCl_3$, 126 MHz, 300 K)



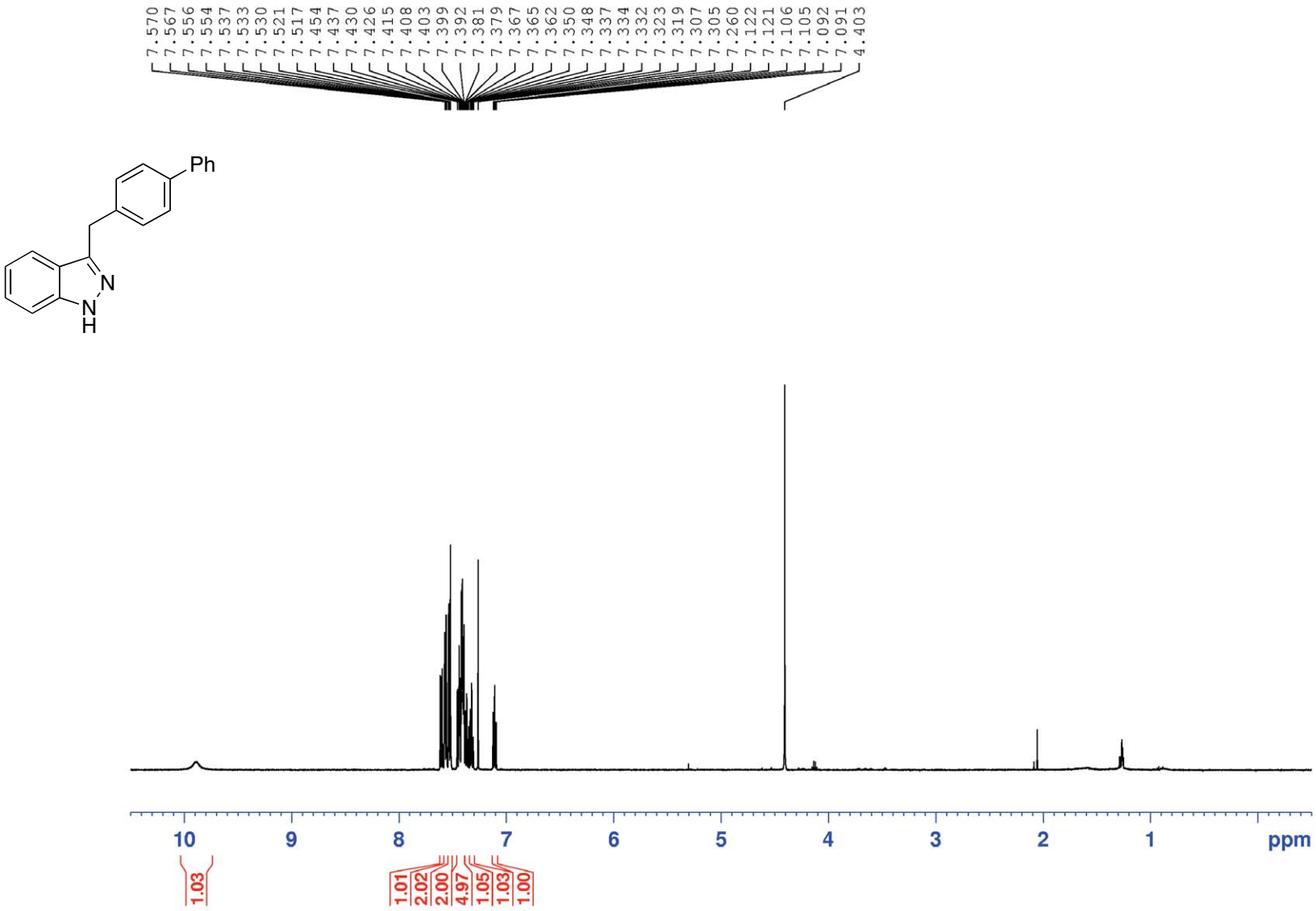
^{1}H NMR of **4c** (DMSO-d_6, 500 MHz, 300 K)



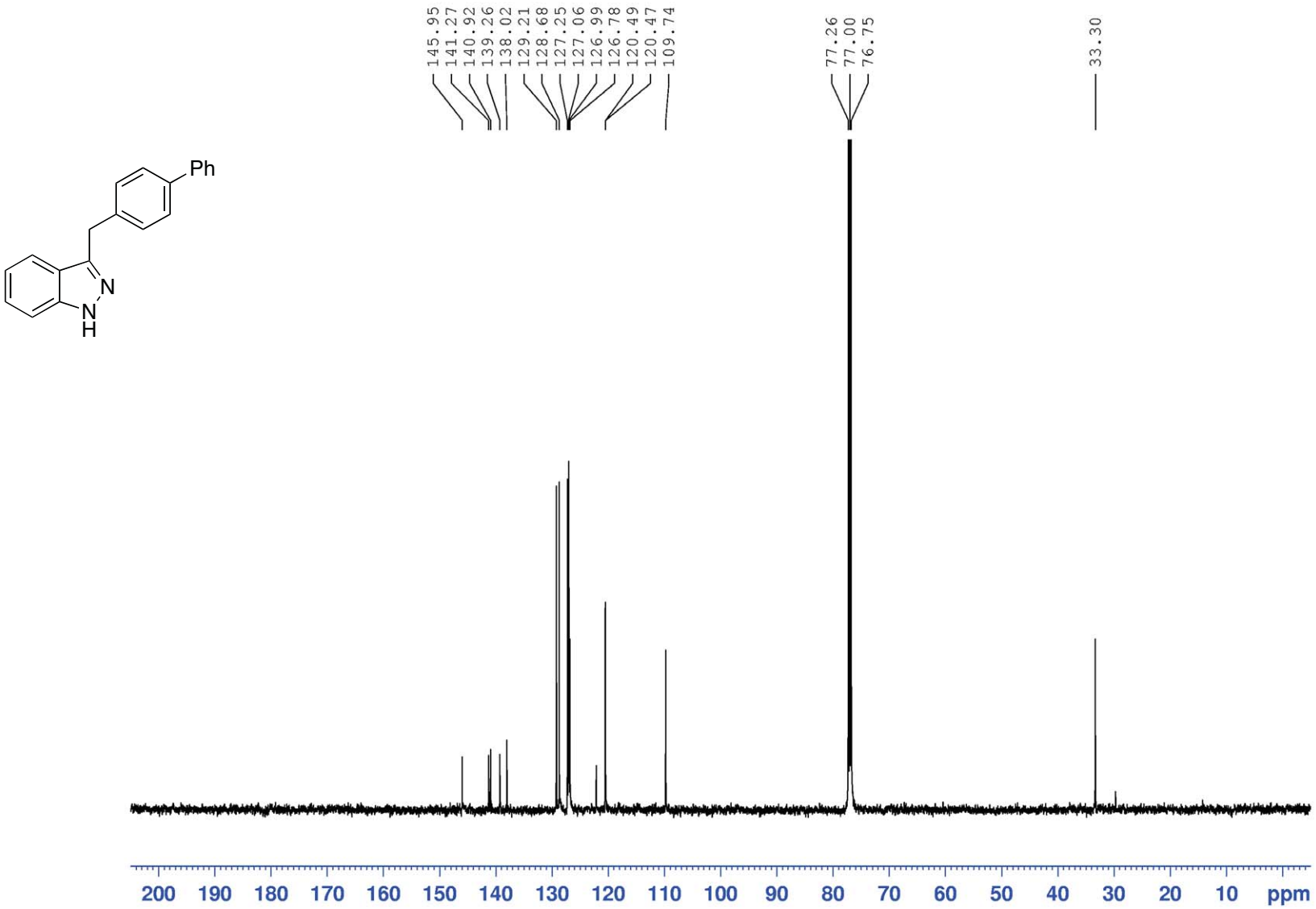
^{13}C NMR of **4c** (DMSO-d_6, 126 MHz, 300 K)



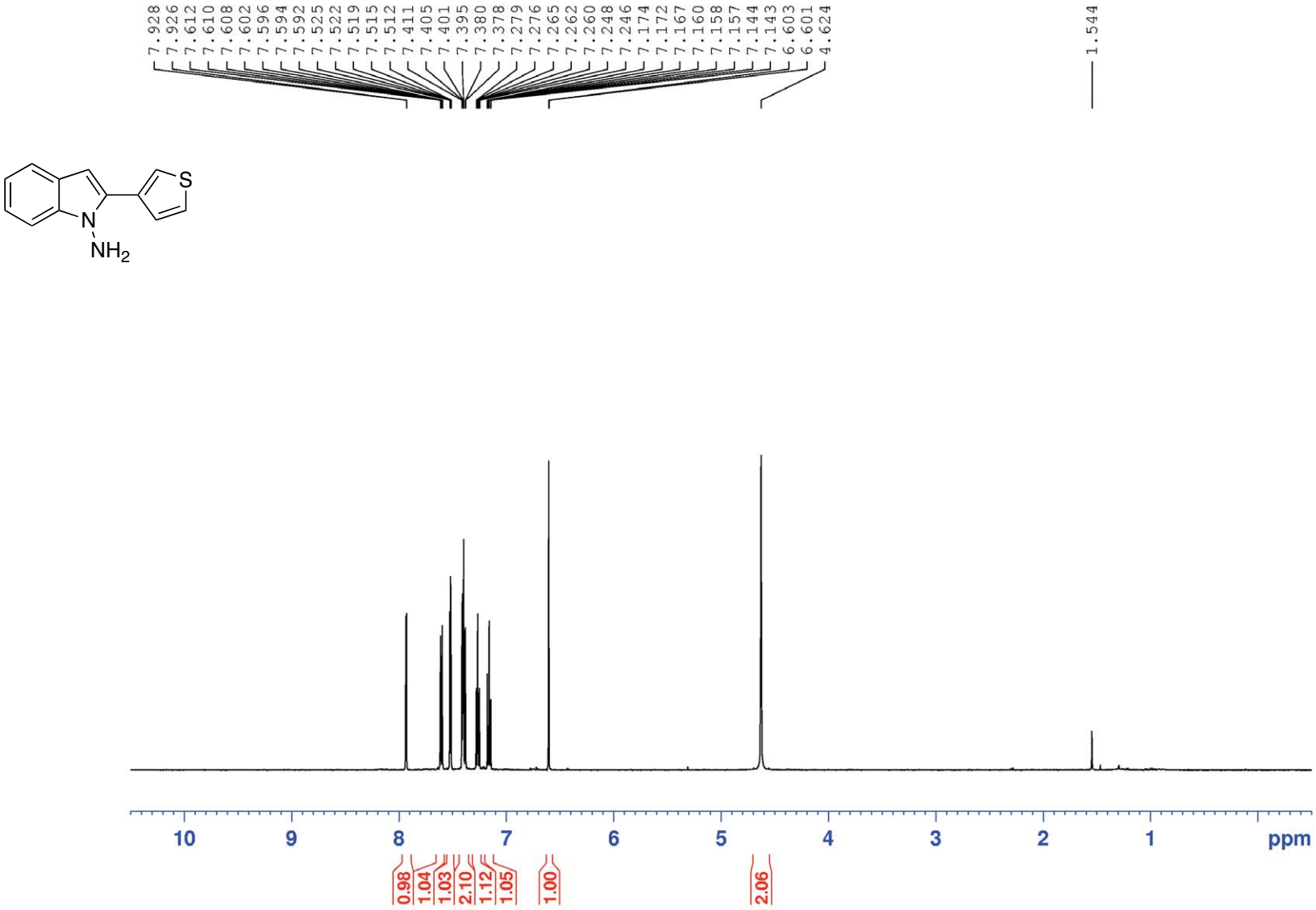
^{1}H NMR of **4c'** ($CDCl_3$, 500 MHz, 300 K)



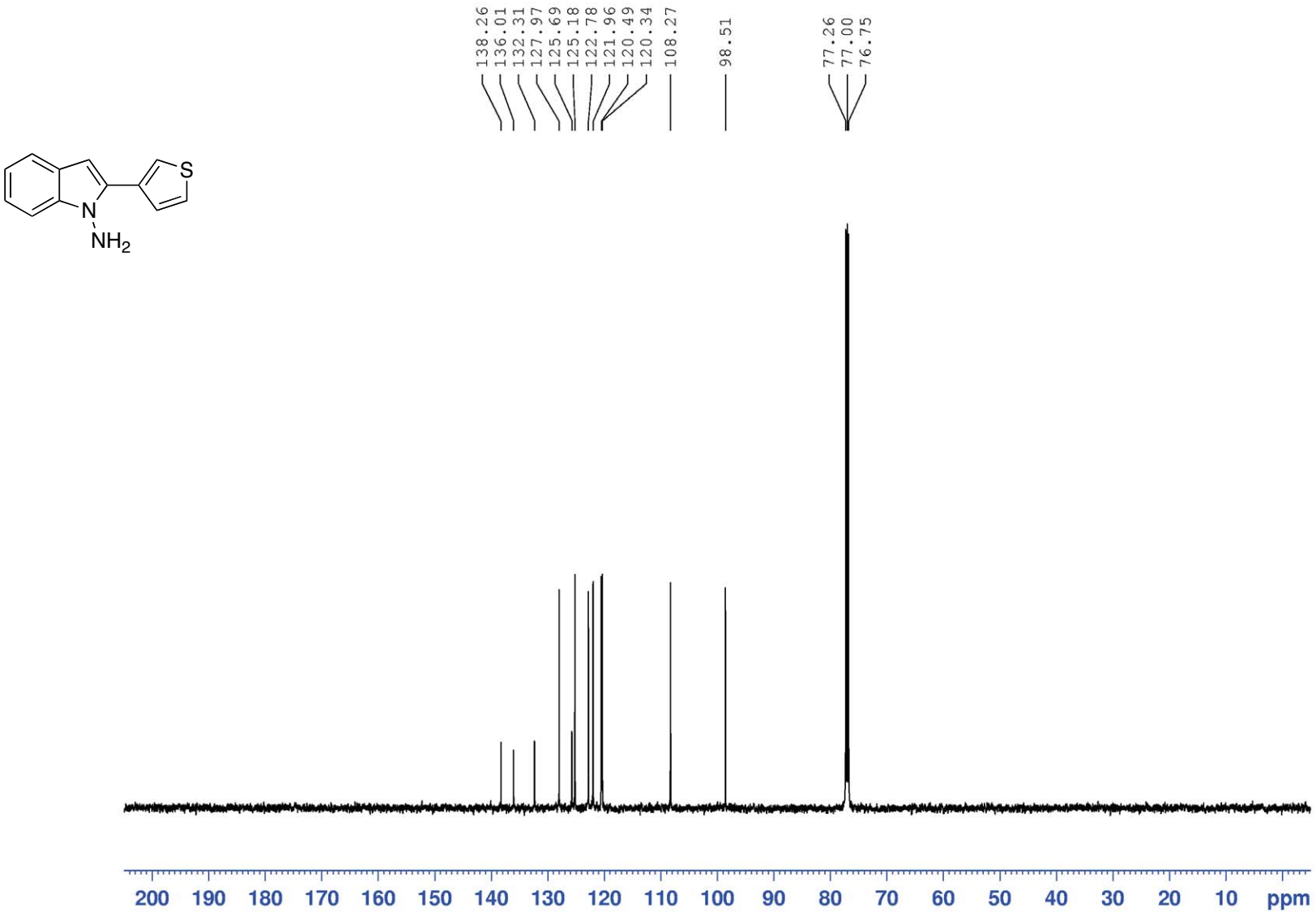
^{13}C NMR of **4c'** ($CDCl_3$, 126 MHz, 300 K)



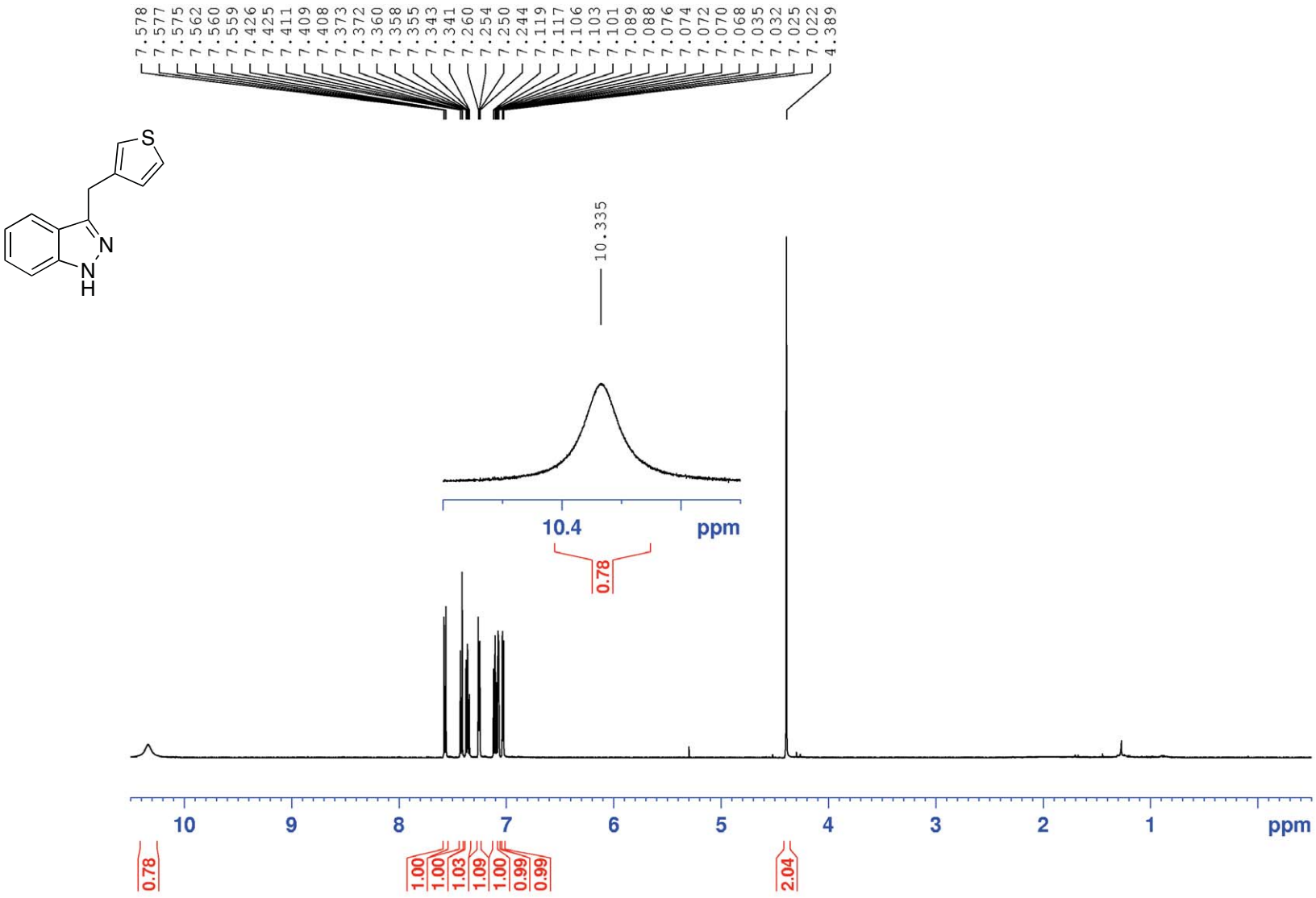
^{1}H NMR of **4d** ($CDCl_3$, 500 MHz, 300 K)



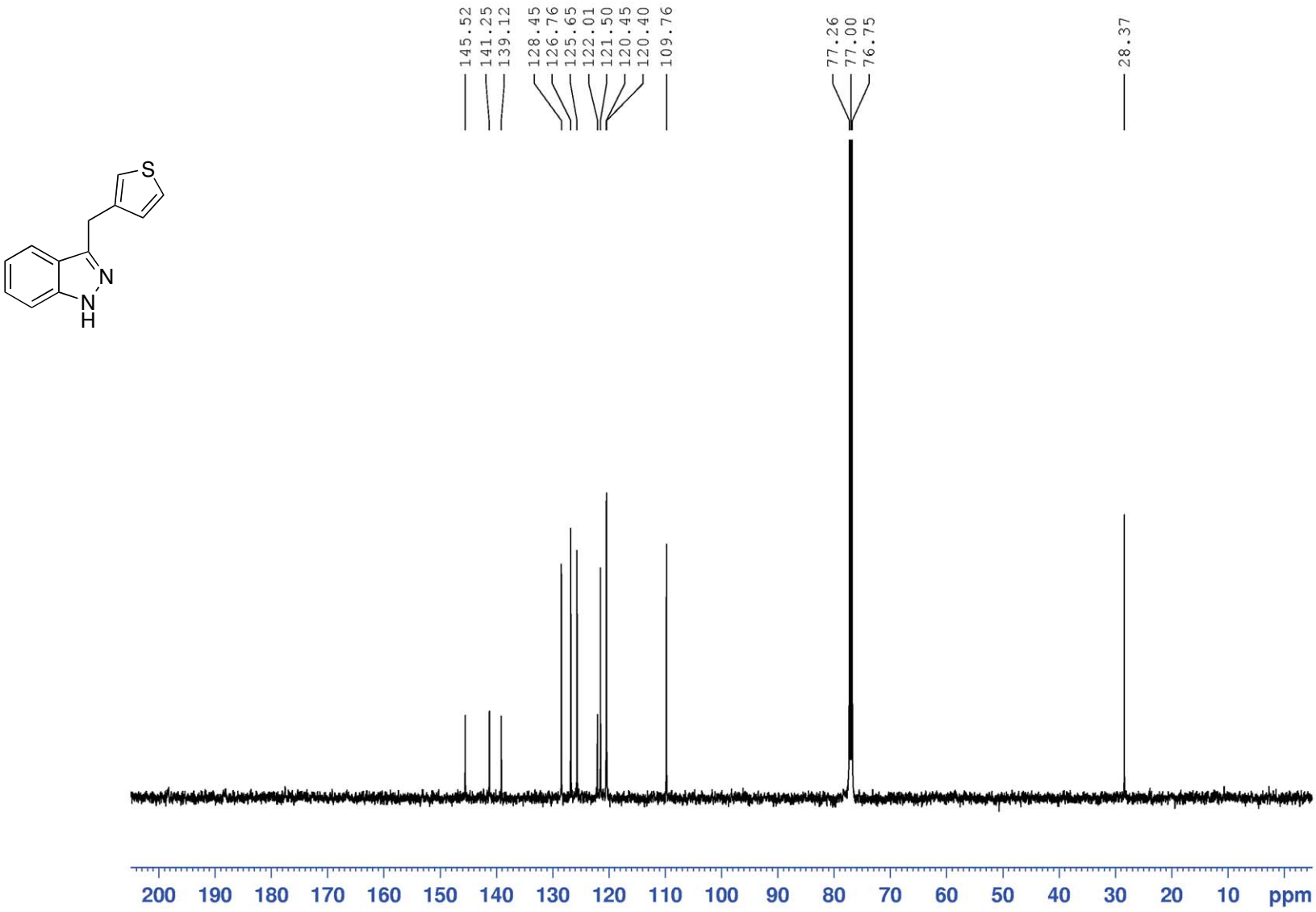
^{13}C NMR of **4d** ($CDCl_3$, 126 MHz, 300 K)



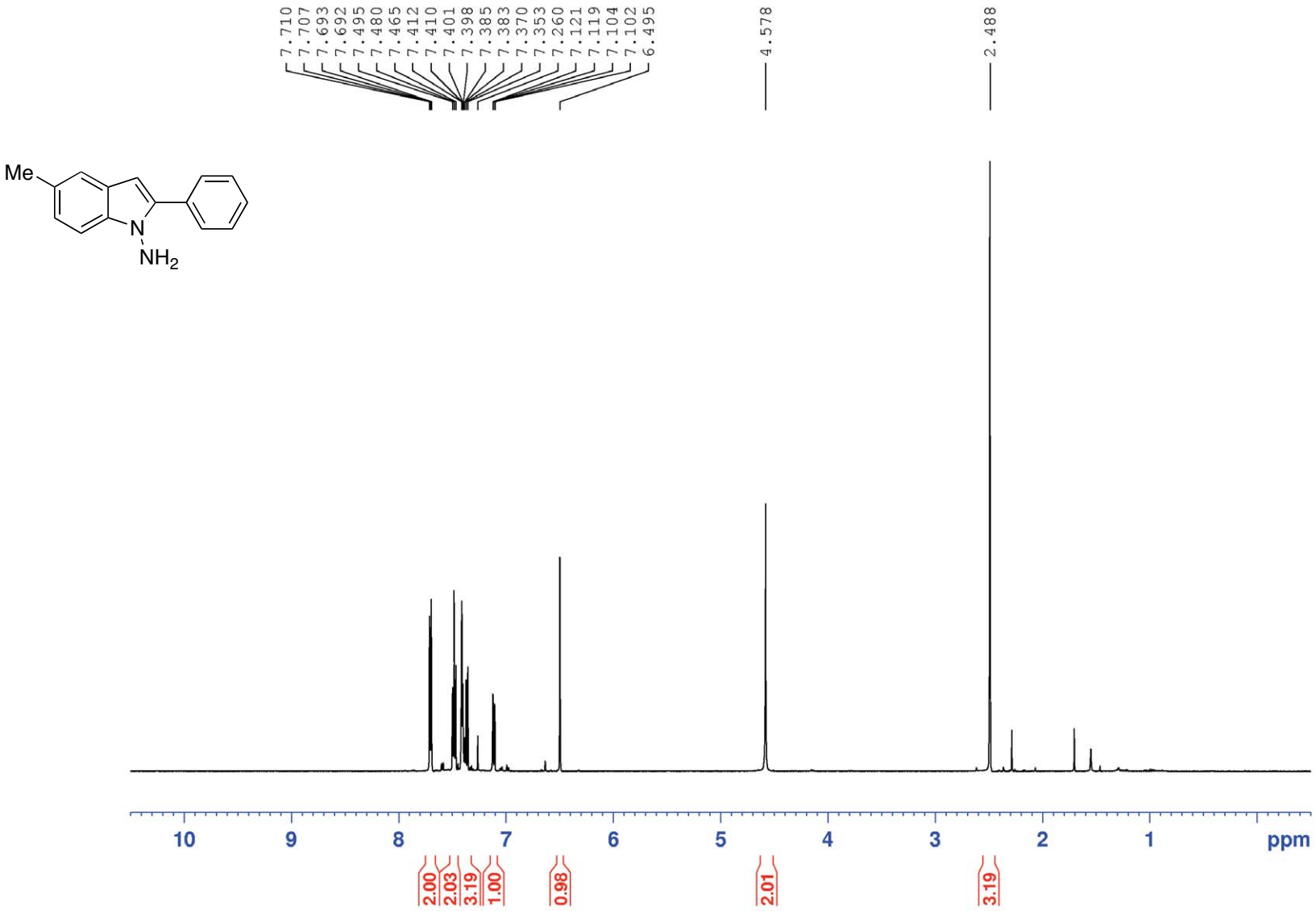
^{1}H NMR of **4d'** ($CDCl_3$, 500 MHz, 300 K)



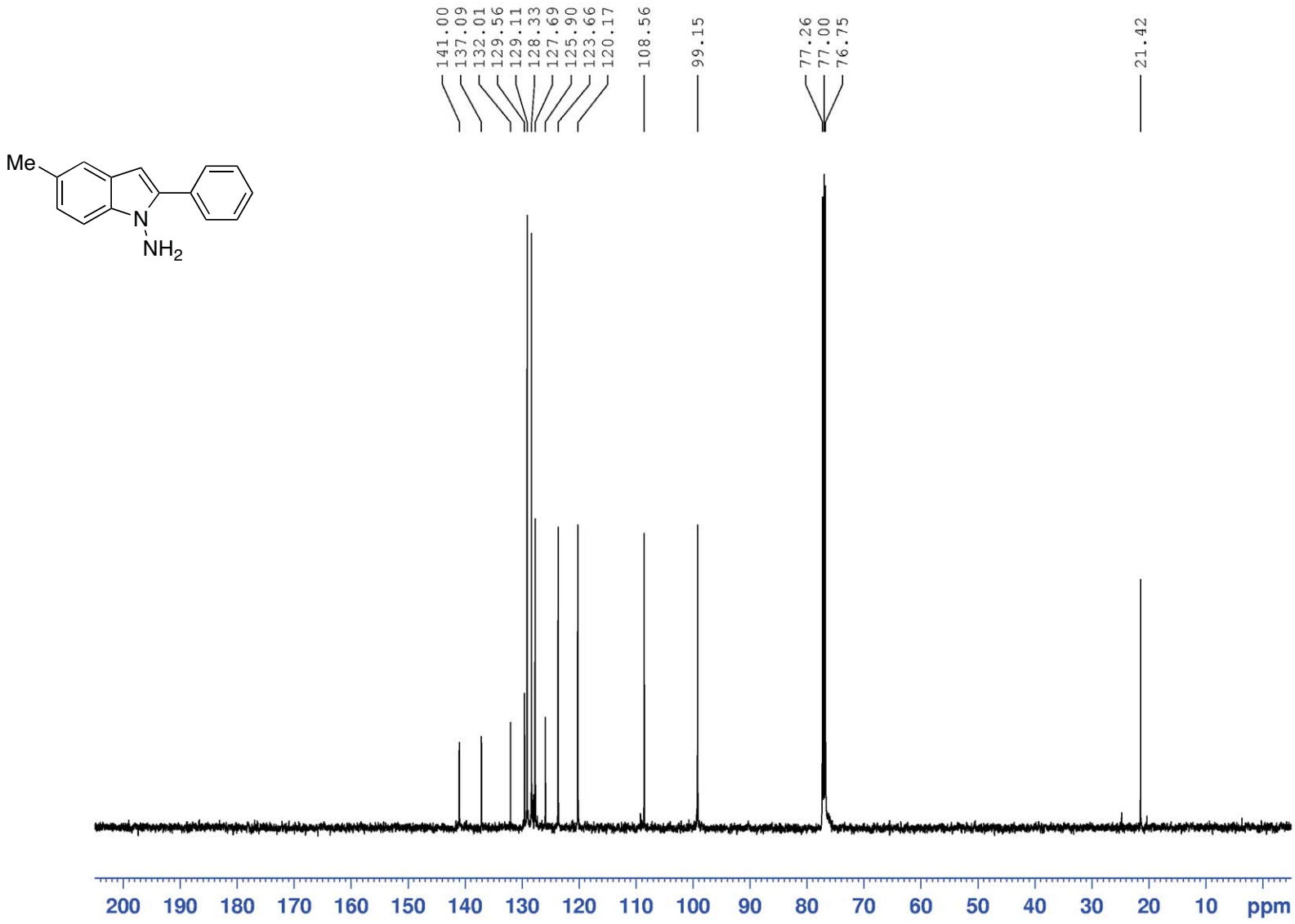
^{13}C NMR of **4d'** ($CDCl_3$, 126 MHz, 300 K)



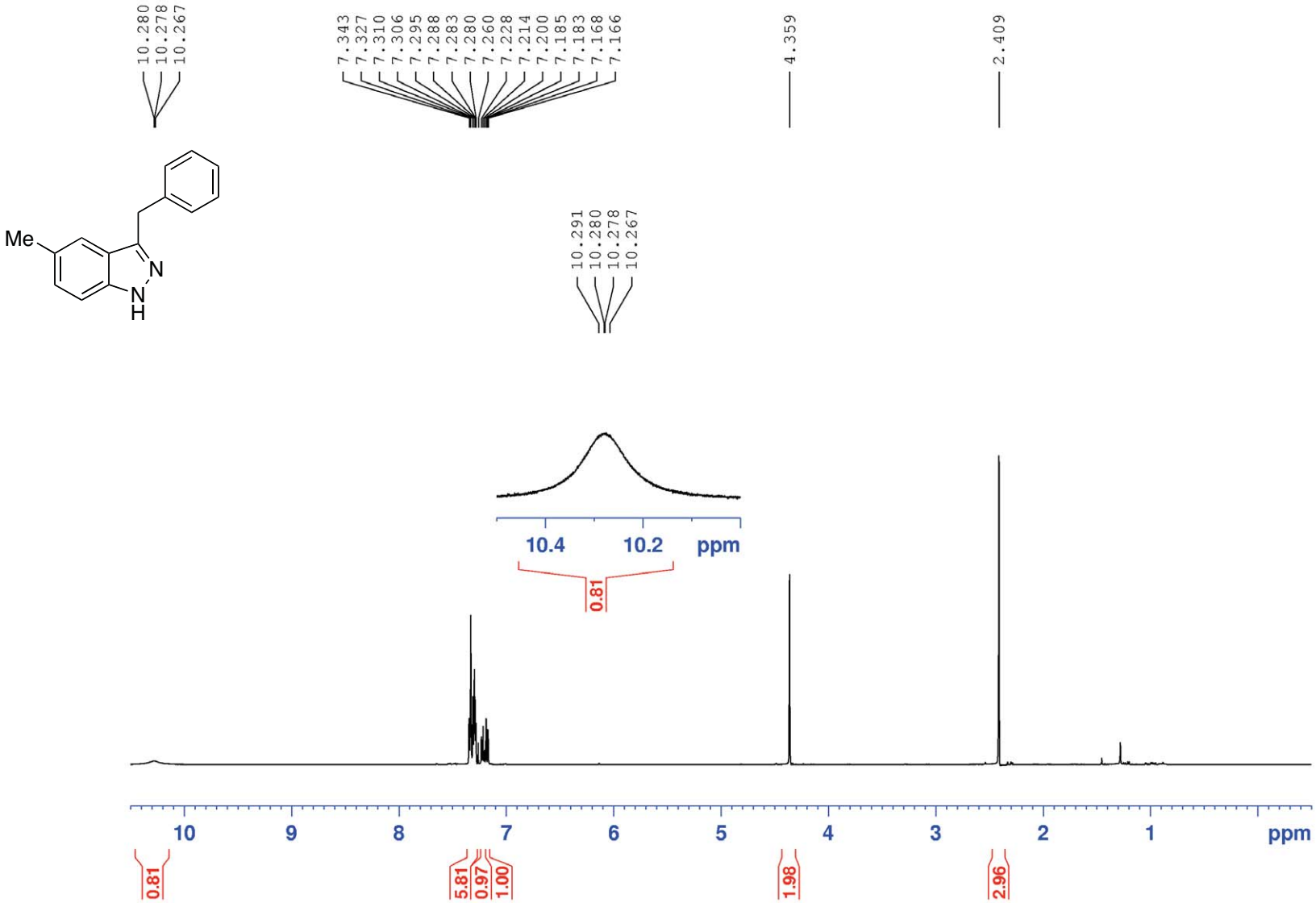
^{1}H NMR of **4e** ($CDCl_3$, 500 MHz, 300 K)



^{13}C NMR of **4e** ($CDCl_3$, 126 MHz, 300 K)



^{1}H NMR of **4e'** ($CDCl_3$, 500 MHz, 300 K)



^{13}C NMR of **4e'** ($CDCl_3$, 126 MHz, 300 K)