Supporting Information

Pd-Catalyzed Efficient Synthesis of 3-Formylindole Derivatives with Diaziridinone

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Table of Contents

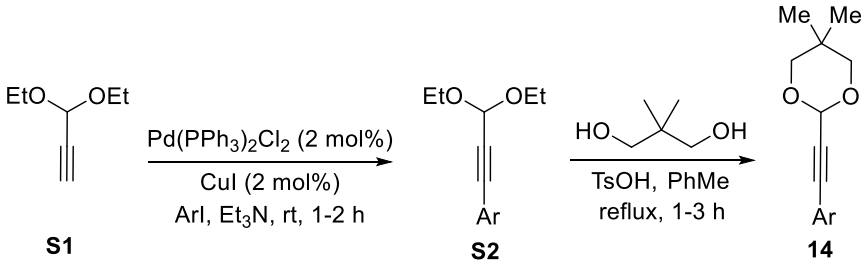
General Methods

All reactions were carried out in oven-dried glassware. All commercially available reagents were used without further purification unless otherwise noted. All dry solvents were purified with solvent purification system before use. Column chromatography was performed on silica gel (300-400 mesh). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz NMR spectrometer. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected. High resolution mass spectra (HRMS, ESI) were recorded using ion trap. Di-*t*-butyldiaziridinone was prepared according to the reported procedure.[1] Acetal alkynes **14** were prepared via Sonogashira coupling of commercially available 3,3-diethoxyprop-1-yne (**S1**) with aryl iodides[2] and subsequent transacetalization with 2,2-dimethylpropane-1,3-diol[3] (Scheme S-1).

1) Du, H.; Zhao, B.; Shi, Y. *Org. Synth.* **2009**, *86*, 315-324.

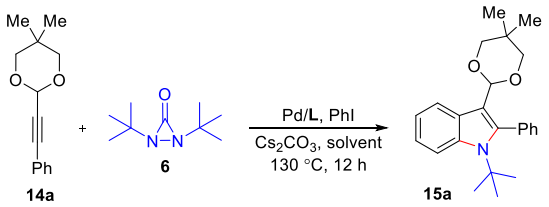
2) (a) Levi, L.; Boersch, C.; Gers, C. F.; Merkul, E.; Müller, T. J. J. *Molecules* **2011**, *16*, 9340-9356. (b) Pimpasri, C.; Luo, X.; Yang, S.; Díez-González, S. Adv. *Synth. Catal.* **2024**, *366*, 806-812.

3) Zlotskii, S. S.; Raskil'dina, G. Z.; Golovanov, A. A.; Bormotin, A. A.; Bekin, V. V. *Doklady Chem.* **2017**, *472*, 43-46.



Scheme S-1. Preparation of acetal alkynes **14**

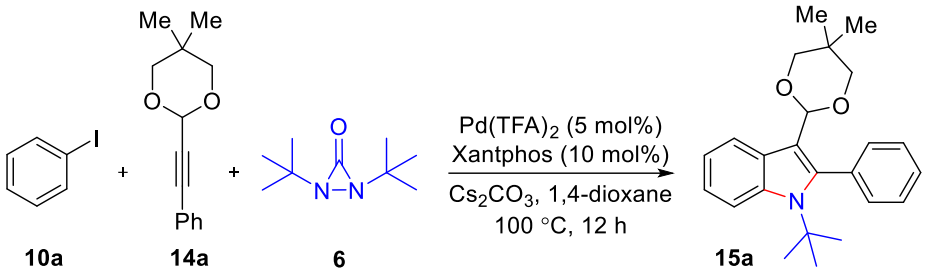
Table S-1. Studies of Reaction Conditions[a]



entry	[Pd]	ligands	Yields (%)[b]
1	$Pd(OAc)_2$	--	46
2	$Pd(OAc)_2$	PPh_3	59
3	$Pd(OAc)_2$	$(o\text{-tolyl})_3P$	53
4	$Pd(OAc)_2$	$(p\text{-tolyl})_3P$	46
5	$Pd(OAc)_2$	$(p\text{-MeOPh})_3P$	46
6	$Pd(OAc)_2$	$(p\text{-ClPh})_3P$	62
7	$Pd(OAc)_2$	$(p\text{-FPh})_3P$	57
8	$Pd(OAc)_2$	$CyPPh_2$	59
9	$Pd(OAc)_2$	Cy_2PPh	53
10	$Pd(OAc)_2$	Cy_3P	52
11	$Pd(OAc)_2$	dppm	56
12	$Pd(OAc)_2$	dppe	42
13	$Pd(OAc)_2$	dppp	41
14	$Pd(OAc)_2$	dppf	54
15	$Pd(OAc)_2$	DEPphos	47
16	$Pd(OAc)_2$	xantphos	63
17	$Pd(TFA)_2$	xantphos	65
18	$PdCl_2$	xantphos	trace
19	$PdBr_2$	xantphos	13
20	$Pd(CH_3CN)_4(BF_4)_2$	xantphos	37
21	$Pd(dba)_2$	xantphos	39
22	$Pd(TFA)_2$ (DMF)	xantphos	43
23	$Pd(TFA)_2$ (DMSO)	xantphos	50
24	$Pd(TFA)_2$ (CH_3CN)	xantphos	20
25	$Pd(TFA)_2$ (*p*-xylene)	xantphos	58
26	$Pd(TFA)_2$ (PhMe)	xantphos	52
27	$Pd(TFA)_2$ (hexane)	xantphos	42
28	$Pd(TFA)_2$ (DCE)	xantphos	trace
29	$Pd(TFA)_2$ (dioxane)	xantphos (100 °C)	49
30	$Pd(TFA)_2$ (dioxane)	xantphos (115 °C)	60
31	$Pd(TFA)_2$ (dioxane)	xantphos (145 °C)	52
32[c]	**$Pd(TFA)_2$ (dioxane)**	**xantphos** (100 °C)	**76**
33[c]	**$Pd(TFA)_2$ (dioxane)**	**$(p\text{-ClPh})_3P$** (115 °C)	**69**

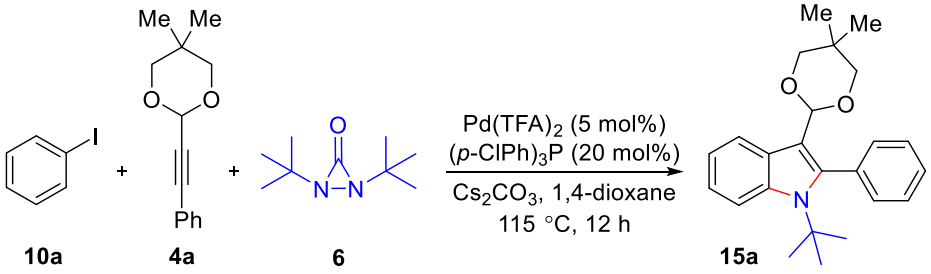
[a]All reactions were carried out with alkyne 14a (0.10 mmol), PhI (0.15 mmol), Pd (0.0050 mmol), ligand (0.010-0.020 mmol, Pd/P = 1/4), di-*t*-butyldiaziridinone (6) (0.15 mmol), and Cs_2CO_3 (0.20 mmol) in dioxane (1.0 mL) at 130 °C under N_2 for 12 h unless otherwise stated. [b]The yield was determined by ^1H NMR analysis of the crude reaction mixture with BnOMe as the internal standard. [c]With PhI (0.10 mmol) and 6 (0.13 mmol) in 1,4-dioxane (0.5 mL).

Representative procedure for 3-formylindole synthesis (Table 2, 15a) (Method A)



To an oven-dried 15 mL pressure tube equipped with magnetic bar, were added alkyne **14a** (0.1081 g, 0.50 mmol), $Pd(TFA)_2$ (0.0083 g, 0.025 mmol), xantphos (0.0289 g, 0.050 mmol), and Cs_2CO_3 (0.3258 g, 1.0 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with argon for three time, followed by addition of 1,4-dioxane (2.5 mL), PhI **10a** (0.1020 g, 0.50 mmol), and di-*t*-butyldiaziridinone (**6**) (0.1107 g, 0.65 mmol). The rubber septum was quickly replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (100 °C), stirred for 12 h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 60:1) to give **15a** as light yellow solid (0.1308 g, 72% yield).

Representative procedure for 3-formylindole synthesis (Table 2, 15a) (Method B)

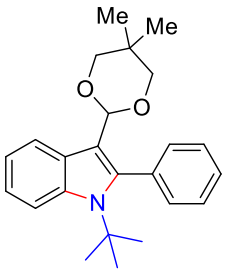


To an oven-dried 15 mL pressure tube equipped with magnetic bar, were added alkyne **14a** (0.1081 g, 0.50 mmol), $Pd(TFA)_2$ (0.0083 g, 0.025 mmol), $(p\text{-ClPh})_3P$ (0.0366 g, 0.10 mmol), and Cs_2CO_3 (0.3258 g, 1.0 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with argon for three time, followed by addition of 1,4-dioxane (2.5 mL), PhI **10a** (0.1020 g, 0.50 mmol), and di-*t*-butyldiaziridinone (**6**) (0.1107 g, 0.65 mmol). The rubber septum was quickly replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (115 °C), stirred for 12

h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (, eluent: petroleum ether/EtOAc = 60:1) to give **15a** as light yellow solid (0.1242 g, 68% yield).

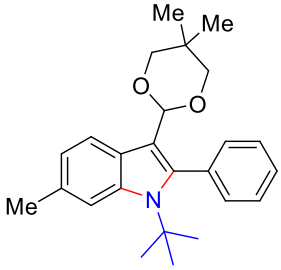
Characterization data of indoles 15

Table 2, 15a



Light yellow solid; 0.1308 g (72%, **Method A**); 0.1242 (68%, **Method B**); eluent: petroleum ether/EtOAc, 60:1; mp. 153.5-155.2 ^{o}C; IR (film) 1607, 1451 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.49-7.38 (m, 5H), 7.22-7.14 (m, 2H), 4.93 (s, 1H), 3.71 (d, J = 10.4 Hz, 2H), 3.39 (d, J = 11.2 Hz, 2H), 1.57 (s, 9H), 1.45 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 136.7, 135.7, 131.3, 128.1, 127.4, 126.5, 121.2, 121.16, 119.8, 114.9, 113.2, 99.9, 78.0, 59.1, 32.0, 30.1, 23.5, 22.0; HRMS (ESI) m/z: Calcd for $C_{24}H_{30}NO_2$ $[M+H]^+$: 364.2271; found: 364.2273.

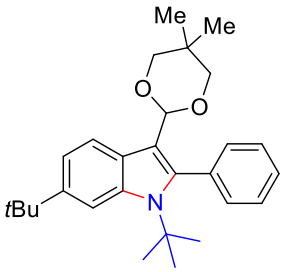
Table 2, 15b



Light yellow solid; 0.0962 g (51%, **Method B**); eluent: petroleum ether/EtOAc, 80:1; mp. 140.8-142.3 ^{o}C; IR (film) 1558, 1415, 1216, 1099 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 7.44-7.33 (m, 5H), 6.97 (d, J = 8.0 Hz, 1H), 4.87 (s, 1H), 3.67 (d, J = 11.2 Hz, 2H), 3.34 (d, J = 10.8 Hz, 2H), 2.49 (s, 3H), 1.53 (s, 9H), 1.40 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.3, 136.0, 131.4, 130.6, 128.0, 127.4, 124.4, 121.6, 120.8, 114.9, 113.2, 100.0, 78.0, 59.0, 32.1, 30.2, 23.6, 22.5, 22.0;

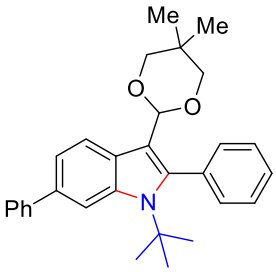
HRMS (ESI) m/z: Calcd for $C_{25}H_{32}NO_2$ $[M+H]^+$: 378.2428; found: 378.2429.

Table 2, 15c



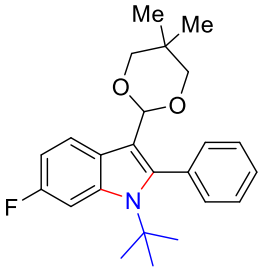
Light yellow solid; 0.0947 g (45%, **Method B**); eluent: petroleum ether/EtOAc, 90:1; mp. 199.1-201.4 °C; IR (film) 1558, 1485, 1108, 1095 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.65 (s, 1H), 7.42-7.35 (m, 5H), 7.23 (dd, J = 8.4, 1.6 Hz, 1H), 4.86 (s, 1H), 3.66 (d, J = 11.2 Hz, 2H), 3.34 (d, J = 10.8 Hz, 2H), 1.54 (s, 9H), 1.41 (s, 3H), 1.39 (s, 9H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.1, 137.0, 136.1, 131.4, 128.0, 127.4, 124.2, 120.4, 118.3, 113.1, 111.2, 99.9, 78.0, 58.9, 35.0, 32.1, 32.0, 30.2, 23.6, 22.1; HRMS (ESI) m/z: Calcd for $C_{28}H_{38}NO_2$ $[M+H]^+$: 420.2897; found: 420.2898.

Table 2, 15d



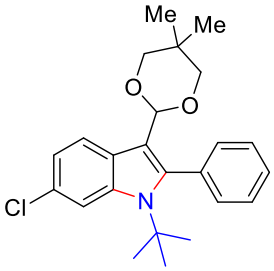
Light yellow solid; 0.1498 g (68%, **Method B**); eluent: petroleum ether/EtOAc, 80:1; mp. 204.6-206.4 °C; IR (film) 1600, 1475, 1099 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.88 (s, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.49-7.40 (m, 8H), 7.36-7.32 (m, 1H), 4.92 (s, 1H), 3.71 (d, J = 11.6 Hz, 2H), 3.38 (d, J = 11.2 Hz, 2H), 1.60 (s, 9H), 1.45 (s, 3H), 0.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.1, 137.3, 135.7, 134.7, 131.3, 128.8, 128.2, 127.7, 127.5, 126.5, 125.9, 121.3, 119.9, 113.8, 113.3, 99.8, 78.0, 59.3, 32.2, 30.2, 23.6, 22.0; HRMS (ESI) m/z: Calcd for $C_{30}H_{34}NO_2$ $[M+H]^+$: 440.2584; found: 440.2586.

Table 2, 15e



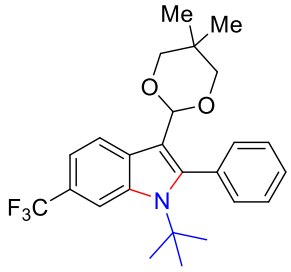
Light yellow solid; 0.0854 g (45%, **Method B**); eluent: petroleum ether/EtOAc, 80:1; mp. 160.1-161.3 ºC; IR (film) 1619，1562, 1485, 1096 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 8.8, 6.4 Hz, 1H), 7.46-7.36 (m, 6H), 6.95 (td, J = 9.2, 2.4 Hz, 1H), 4.90 (s, 1H), 3.70 (d, J = 11.6 Hz, 2H), 3.38 (d, J = 11.2 Hz, 2H), 1.53 (s, 9H), 1.42 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, J = 233.7 Hz), 139.9 (d, J = 3.5 Hz), 136.6 (d, J = 11.6 Hz), 135.3, 131.2, 128.3, 127.5, 122.9, 121.8 (d, J = 10.0 Hz), 113.2, 108.4 (d, J = 23.9 Hz), 101.3 (d, J = 27.5 Hz), 99.6, 78.0, 59.3, 31.8, 30.1, 23.5, 21.9; HRMS (ESI) m/z: Calcd for $C_{24}H_{29}FNO_2$ $[M+H]^+$: 382.2177; found: 382.2178.

Table 2, 15f



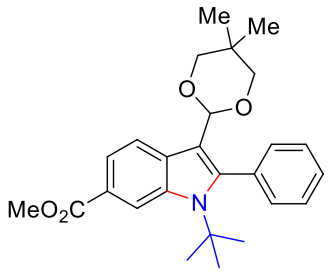
Light yellow solid; 0.0715 g (36%, **Method B**); eluent: petroleum ether/EtOAc, 80:1; mp. 108.6-110.2 ºC; IR (film) 1471, 1413, 1099, 1037 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 2.0 Hz, 1H), 7.44-7.37 (m, 5H), 7.12 (dd, J = 8.8, 2.0 Hz, 1H), 4.86 (s, 1H), 3.68 (d, J = 11.6 Hz, 2H), 3.35 (d, J = 12.0 Hz, 2H), 1.52 (s, 9H), 1.40 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 137.1, 135.2, 131.2, 128.4, 127.6, 127.1, 125.0, 122.0, 120.5, 114.7, 113.4, 99.6, 78.0, 59.5, 32.0, 30.2, 23.6, 22.0; HRMS (ESI) m/z: Calcd for $C_{24}H_{29}ClNO_2$ $[M+H]^+$: 398.1881; found: 398.1884.

Table 2, 15g



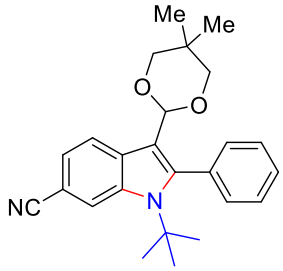
Light yellow solid; 0.1003 g (46%, **Method B**); eluent: petroleum ether/EtOAc, 60:1; mp. 106.6-108.4 ºC; IR (film) 1421, 1328, 1114, 1101 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.4 Hz, 1H), 7.97 (s, 1H), 7.47-7.39 (m, 6H), 4.90 (s, 1H), 3.70 (d, J = 11.6 Hz, 2H), 3.37 (d, J = 12.0 Hz, 2H), 1.57 (s, 9H), 1.42 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 135.6, 134.9, 131.1, 128.8, 128.6, 127.7, 125.6 (q, J = 270.0 Hz), 123.1 (q, J = 31.2 Hz), 121.6, 116.6 (q, J = 3.6 Hz), 113.7, 112.1 (q, J = 4.7 Hz), 99.5, 78.0, 59.8, 32.2, 30.2, 23.5, 22.0; HRMS (ESI) m/z: Calcd for $C_{25}H_{29}F_3NO_2$ $[M+H]^+$: 432.2145; found: 432.2147.

Table 2, 15h



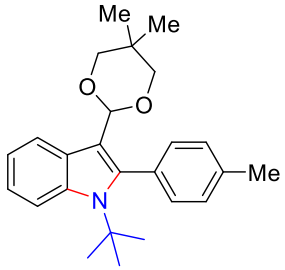
Light yellow solid; 0.0846 g (40%, **Method B**); eluent: petroleum ether/EtOAc, 45:1 to 35:1; mp. 187.9-189.1 ºC; IR (film) 1713, 1435, 1298, 1095 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.85 (dd, J = 8.4, 1.2 Hz, 1H), 7.46-7.39 (m, 5H), 4.89 (s, 1H), 3.95 (s, 3H), 3.69 (d, J = 11.6 Hz, 2H), 3.36 (d, J = 10.8 Hz, 2H), 1.58 (s, 9H), 1.41 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 142.8, 136.0, 135.0, 131.0, 130.1, 128.5, 127.6, 122.6, 120.9, 120.7, 117.2, 113.6, 99.5, 78.0, 59.8, 52.0, 32.2, 30.1, 23.5, 21.9; HRMS (ESI) m/z: Calcd for $C_{26}H_{32}NO_4$ $[M+H]^+$: 422.2326; found: 422.2331.

Table 2, 15i



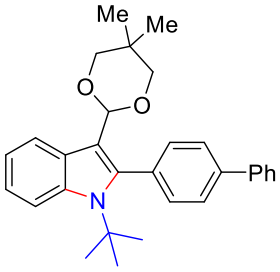
Light yellow solid; 0.1106 g (57%, **Method B**); eluent: petroleum ether/EtOAc, 60:1; mp. 213.5-215.3 ºC; IR (film) 2219, 1607, 1475, 1098 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 1H), 8.03 (s, 1H), 7.47-7.37 (m, 6H), 4.87 (s, 1H), 3.68 (d, J = 11.2 Hz, 2H), 3.35 (d, J = 11.2 Hz, 2H), 1.55 (s, 9H), 1.40 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 135.4, 134.4, 130.9, 129.7, 128.9, 127.8, 122.7, 122.1, 121.4, 119.6, 114.2, 103.7, 99.3, 78.0, 60.2, 32.2, 30.2, 23.5, 21.9; HRMS (ESI) m/z: Calcd for $C_{25}H_{29}N_2O_2$ $[M+H]^+$: 389.2224; found: 389.2223.

Table 2, 15j



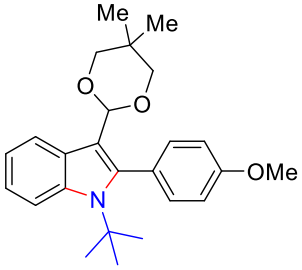
Light yellow solid; 0.1201 g (64%, **Method A**); eluent: petroleum ether/EtOAc, 60:1 to 50:1; mp. 165.7-167.1 ºC; IR (film) 1451, 1214, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 7.2, 2.0 Hz, 1H), 7.67 (dd, J = 7.2, 2.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.20-7.11 (m, 4H), 4.92 (s, 1H), 3.79 (d, J = 11.2 Hz, 2H), 3.38 (d, J = 10.8 Hz, 2H), 2.44 (s, 3H), 1.54 (s, 9H), 1.43 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 137.9, 136.8, 132.7, 131.1, 128.2, 126.5, 121.2, 121.1, 119.7, 114.9, 113.1, 100.0, 78.0, 59.1, 32.1, 30.2, 23.6, 22.0, 21.6; HRMS (ESI) m/z: Calcd for $C_{25}H_{32}NO_2$ $[M+H]^+$: 378.2428; found: 378.2434.

Table 2, 15k



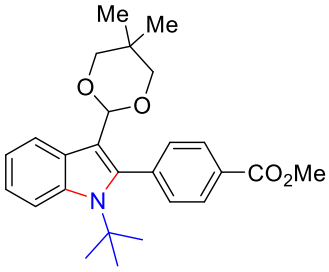
Light yellow solid; 0.1526 g (69%, **Method A**); eluent: petroleum ether/EtOAc, 60:1 to 50:1; mp. 187.4-188.3 ºC; IR (film) 1451, 1214, 1097 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21-8.13 (m, 1H), 7.75-7.68 (m, 3H), 7.65 (d, J = 8.4 Hz, 2H), 7.53-7.45 (m, 4H), 7.42-7.37 (m, 1H), 7.21-7.13 (m, 2H), 4.98 (s, 1H), 3.70 (d, J = 11.2 Hz, 2H), 3.40 (d, J = 11.2 Hz, 2H), 1.59 (s, 9H), 1.43 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.5, 139.1, 136.9, 134.8, 131.7, 129.0, 127.7, 127.1, 126.6, 126.0, 121.3, 121.26, 119.9, 114.9, 113.4, 99.9, 78.0, 59.2, 32.2, 30.2, 23.6, 22.0; HRMS (ESI) m/z: Calcd for $C_{30}H_{34}NO_2$ $[M+H]^+$: 440.2584; found: 440.2584.

Table 2, 15l



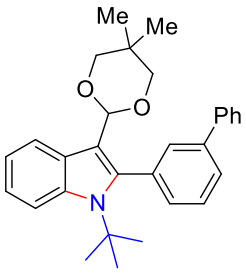
Light yellow solid; 0.1085 g (55%, **Method A**); eluent: petroleum ether/EtOAc, 40:1; mp. 159.2-160.4 ºC; IR (film) 1508, 1246, 1097 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, J = 7.2, 2.4 Hz, 1H), 7.70 (dd, J = 7.2, 2.0 Hz, 1H), 7.34 (d, J = 8.8 Hz, 2H), 7.22-7.12 (m, 2H), 6.93 (d, J = 8.4 Hz, 2H), 4.95 (s, 1H), 3.89 (s, 3H), 3.72 (d, J = 11.2 Hz, 2H), 3.41 (d, J = 10.8 Hz, 2H), 1.57 (s, 9H), 1.45 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 139.3, 136.7, 132.4, 127.8, 126.4, 121.1, 121.06, 119.7, 114.9, 113.3, 112.9, 100.0, 78.0, 59.0, 55.4, 32.1, 30.2, 23.6, 22.0; HRMS (ESI) m/z: Calcd for $C_{25}H_{32}NO_3$ $[M+H]^+$: 394.2377; found: 394.2378.

Table 2, 15m



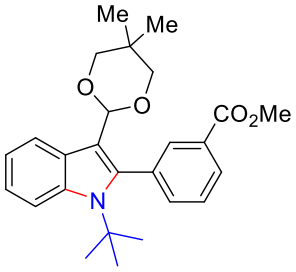
Light yellow solid; 0.1536 g (73%, **Method A**); eluent: petroleum ether/EtOAc, 45:1 to 35:1; mp. 171.3-172.4 ºC; IR (film) 1725, 1274, 1097 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 7.6, 2.0 Hz, 1H), 8.07 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.23-7.10 (m, 2H), 4.86 (s, 1H), 3.97 (s, 3H), 3.68 (d, J = 11.6 Hz, 2H), 3.34 (d, J = 10.8 Hz, 2H), 1.54 (s, 9H), 1.40 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 140.8, 138.0, 137.0, 131.3, 129.9, 128.7, 126.5, 121.6, 121.4, 120.1, 114.9, 113.6, 99.6, 78.0, 59.3, 52.4, 32.1, 30.2, 23.5, 22.0; HRMS (ESI) m/z: Calcd for $C_{26}H_{32}NO_4$ $[M+H]^+$: 422.2326; found: 422.2328.

Table 2, 15n



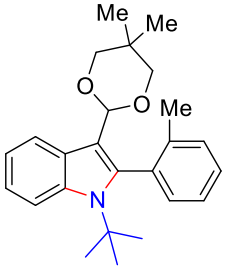
Light yellow solid; 0.1278 g (58%, **Method A**); eluent: petroleum ether/EtOAc, 80:1 to 70:1; mp. 105.7-106.9 ºC; IR (film) 1604, 1452, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 7.6 Hz, 1H), 7.74-7.65 (m, 5H), 7.51-7.45 (m, 3H), 7.44-7.36 (m, 2H), 7.23-7.14 (m, 2H), 4.99 (s, 1H), 3.72 (d, J = 10.8 Hz, 2H), 3.40 (d, J = 11.2 Hz, 2H), 1.59 (s, 9H), 1.44 (s, 3H), 0.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.1, 139.3, 136.8, 136.3, 130.2, 129.9, 129.0, 127.9, 127.7, 127.1, 126.8, 126.5, 121.3, 121.2, 119.9, 114.9, 113.3, 99.9, 78.0, 77.9, 59.2, 32.1, 30.2, 23.6, 22.0; HRMS (ESI) m/z: Calcd for $C_{30}H_{33}NO_2Na$ $[M+Na]^+$: 462.2404; found: 462.2402.

Table 2, 15o



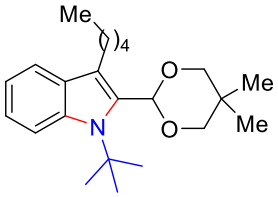
Light yellow solid; 0.1401 g (66%, **Method A**); eluent: petroleum ether/EtOAc, 50:1; mp. 180.6-182.4 ºC; IR (film) 1725, 1282, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20-8.17 (m, 3H), 7.69 (d, J = 7.6 Hz, 1H), 7.62 (dt, J = 7.6, 1.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.23-7.13 (m, 2H), 4.87 (s, 1H), 3.94 (s, 3H), 3.73-3.64 (m, 2H), 3.36 (d, J = 11.6 Hz, 1H), 3.34 (d, J = 11.2 Hz, 1H), 1.55 (s, 9H), 1.40 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 138.0, 136.8, 136.2, 135.5, 132.1, 129.5, 129.4, 127.6, 126.4, 121.5, 121.3, 120.0, 114.9, 113.7, 99.7, 77.9, 59.2, 52.4, 32.2, 30.1, 23.5, 22.0; HRMS (ESI) m/z: Calcd for $C_{26}H_{31}NO_4Na$ $[M+Na]^+$: 444.2145; found: 444.2145.

Table 2, 15p



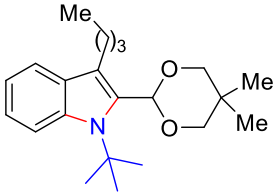
Light yellow solid; 0.1135 g (60%, **Method A**); eluent: petroleum ether/EtOAc, 80:1; mp. 145.5-147.0 ºC; IR (film) 1454, 1214, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.2 Hz, 1H), 7.69 (dd, J = 7.2, 2.0 Hz, 1H), 7.36-7.29 (m, 2H), 7.26-7.13 (m, 4H), 4.82 (s, 1H), 3.68 (d, J = 11.6 Hz, 2H), 3.34 (d, J = 10.8 Hz, 2H), 2.16 (s, 3H), 1.53 (s, 9H), 1.42 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.3, 136.6, 135.5, 131.7, 129.5, 128.6, 126.7, 125.0, 121.1, 121.0, 119.8, 114.8, 112.3, 99.8, 78.09, 78.05, 58.9, 31.3, 30.2, 23.6, 22.0, 20.4; HRMS (ESI) m/z: Calcd for $C_{25}H_{31}NO_2Na$ $[M+Na]^+$: 400.2247; found: 400.2247.

Table 2, 15q

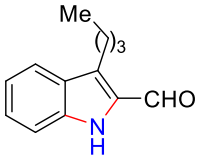


Light yellow solid; 0.0578 g (32%, **Method A**); eluent: petroleum ether/EtOAc, 100:1 to 90:1; mp. 48.6-50.3 ºC; IR (film) 1456, 1154, 1097 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.10 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.03 (ddd, J = 8.0, 7.2, 1.2 Hz, 1H), 6.03 (s, 1H), 3.83 (d, J = 11.6 Hz, 2H), 3.61 (d, J = 12.8 Hz, 2H), 3.12-3.03 (m, 2H), 1.86 (s, 9H), 1.74-1.66 (m, 2H), 1.48-1.37 (m, 4H), 1.40 (s, 3H), 0.93 (t, J = 6.8 Hz, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.9, 129.3, 121.7, 119.8, 119.6, 118.2, 114.7, 99.8, 78.8, 59.0, 32.83, 32.79, 31.1, 30.4, 25.3, 23.8, 22.8, 22.3, 14.3; HRMS (ESI) m/z: Calcd for $C_{23}H_{36}NO_2$ $[M+H]^+$: 358.2741; found: 358.2740.

Table 2, 15r



Light yellow oil; 0.0965 g (35%, **Method A**); eluent: petroleum ether/EtOAc, 100:1; IR (film) 1457, 1094, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.10 (ddd, J = 8.4, 6.8, 1.6 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H), 6.02 (s, 1H), 3.83 (d, J = 12.0 Hz, 2H), 3.61 (d, J = 10.8 Hz, 2H), 3.13-3.05 (m, 2H), 1.86 (s, 9H), 1.72-1.65 (m, 2H), 1.51-1.45 (m, 2H), 1.40 (s, 3H), 0.93 (t, J = 6.8 Hz, 3H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.9, 129.3, 121.7, 119.7, 119.66, 118.2, 114.6, 99.8, 78.8, 59.0, 33.7, 32.8, 30.3, 25.0, 23.8, 23.6, 22.3, 14.3; HRMS (ESI) m/z: Calcd for $C_{22}H_{34}NO_2$ $[M+H]^+$: 344.2584; found: 344.2587.



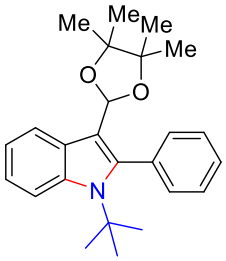
15r'

Yellow oil;[1] 0.0336 g (83% yield) [from the deprotection of **15r** with TFA/cyclohexane (v/v, 10:1) at 60 °C for 12 h]; eluent: petroleum ether/EtOAc, 8:1 to 5:1. ^1H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1H), 9.13 (br s, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.43-7.36 (m, 2H), 7.15 (ddd, J = 8.0, 6.4, 1.6 Hz, 1H), 3.10 (t, J = 7.6 Hz, 2H), 1.79-1.72 (m, 2H), 1.45-1.39 (m,

2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz,$CDCl_3$) δ 180.8, 137.8, 132.2, 130.4, 127.7, 127.6, 121.8, 120.5, 112.5, 34.3, 23.6, 22.8, 14.0.

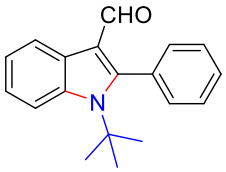
1) Ding, Y.; Shen, L.; Liang, K.; Xia, C. *J. Org. Chem.* **2022**, *87*, 16644-16654.

Table 2, 16



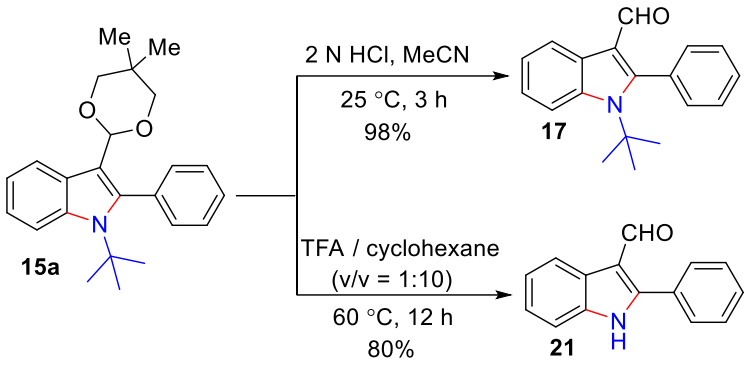
Light yellow solid; 0.0768 g (41%, **Method A**); eluent: petroleum ether/EtOAc, 60:1; mp. 106.4-107.2 ^{o}C; IR (film) 1450, 1153, 1091, 1055 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.44-7.40 (m, 2H), 7.39-7.33 (m, 3H), 7.19-7.09 (m, 2H), 5.49 (s, 1H), 1.54 (s, 9H), 1.39 (s, 6H), 1.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 137.1, 135.7, 131.4, 128.1, 127.3, 126.6, 121.0, 120.97, 119.6, 115.0, 110.9, 96.1, 81.6, 59.2, 32.1, 25.6, 23.0; HRMS (ESI) m/z: Calcd for $C_{25}H_{32}NO_2$ $[M+H]^+$: 378.2428; found: 378.2430.

Table 2, 17



Light yellow solid; 0.0835 g (60%, **Method A**, from alkyne **19**); 0.0966 (70%, **Method A**, from alkyne **20**); eluent: petroleum ether/EtOAc, 40:1 to 30:1; mp. 204.3-205.2 ^{o}C; IR (film) 1653, 1416, 1354 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.53-8.46 (m, 1H), 7.81-7.76 (m, 1H), 7.51-7.41 (m, 5H), 7.35-7.30 (m, 2H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 152.0, 136.7, 133.1, 131.1, 129.3, 127.7, 126.5, 123.1, 122.8, 122.2, 117.8, 115.4, 61.0, 32.0; HRMS (ESI) m/z: Calcd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539; found: 278.1549.

Synthetic transformations of indole 15a (Scheme 3)

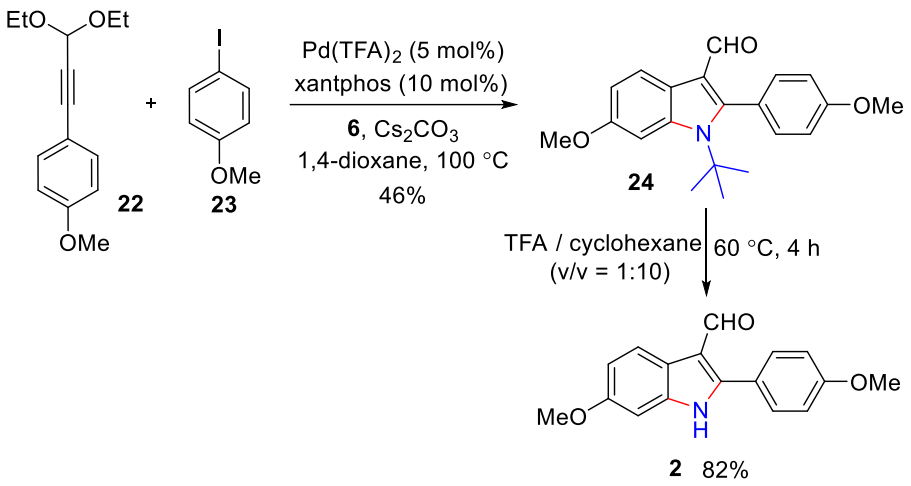


Indole 17. To a solution of **15a** (0.0727 g, 0.20 mmol) in MeCN (2 mL) was added 2N HCl (0.3 mL) at room temperature. The reaction mixture was stirred at room temperature for 3 h, quenched by slow addition of sat. $NaHCO_3$, extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure to give indole **17** as light yellow solid (0.0544 g, 98%) (essentially pure).

Indole 21. To an oven-dried 15 mL pressure tube equipped with magnetic bar, was added indole **15a** (0.0727 g, 0.20 mmol). The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of cyclohexane (2.0 mL) and TFA (0.2 mL). The rubber septum was replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (60 ^oC) overnight, cooled down to room temperature, quenched with sat. $NaHCO_3$, extracted with EtOAc, washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc, 5:1 to 3:1) to give indole **21** as a brown solid (0.0354 g, 80% yield). mp. 213.7-214.6 ^oC; IR (film) cm^{-1} 1625, 1455, 1373, 1081; ^1H NMR (400 MHz, DMSO-d6) δ 12.43 (br s, 1H), 9.97 (s, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.82-7.75 (m, 2H), 7.64-7.55 (m, 3H), 7.52 (d, J = 8.4 Hz, 1H), 7.30 (td, J = 7.2, 1.2 Hz, 1H), 7.25 (td, J = 7.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d6) δ 185.6, 149.2, 136.0, 129.93, 129.88, 129.82, 129.0, 125.8, 123.8, 122.5, 121.1, 113.5, 112.1. HRMS (ESI) m/z: Calcd for $C_{15}H_{11}NONa$ $[M+Na]^+$: 244.0733; found: 244.0734.

1) Yuan, Y.; Guo, X.; Zhang, X.; Li, B.; Huang, Q. *Org. Chem. Front.* **2020**, *7*, 3146-3159.

Synthesis of bioactive indoles (Scheme 4)

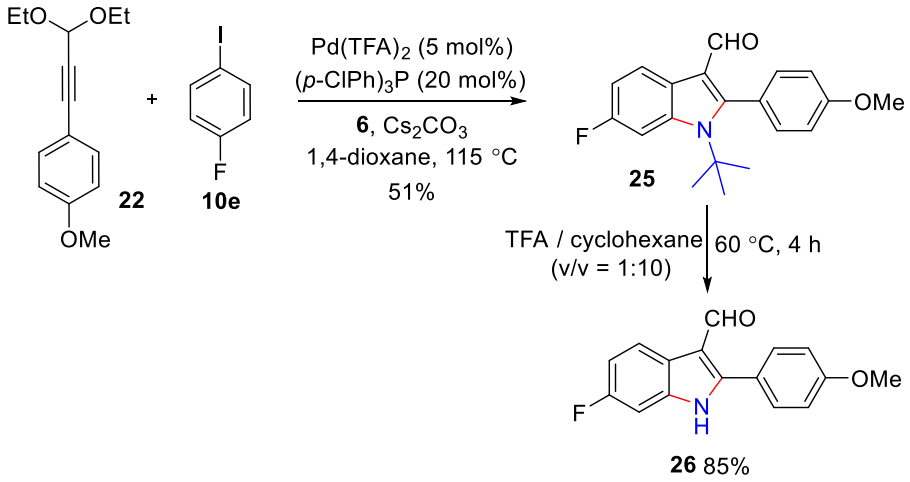


Indole 24. To an oven-dried 15 mL pressure tube equipped with magnetic bar, were added 4-iodoanisole **23** (0.0940 g, 0.40 mmol), $Pd(TFA)_2$ (0.0066 g, 0.020 mmol), xantphos (0.0230 g, 0.040 mmol), and Cs_2CO_3 (0.2607 g, 0.80 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of 1,4-dioxane (2.0 mL), alkyne **22** (0.0937 g, 0.40 mmol), and di-*t*-butyldiaziridinone (**6**) (0.088 g, 0.52 mmol). The rubber septum was replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (100 ^oC), stirred for 12 h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 45:1 to 30:1) to give indole **24** as light yellow solid (0.0615 g, 46% yield). mp. 208.4-209.2 ^oC; IR (film) 1651, 1495, 1355, 1252, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.35 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 2.0 Hz, 1H), 6.98 (dd, J = 8.8, 2.4 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 160.3, 156.3, 151.8, 137.6, 132.3, 125.1, 122.5, 120.7, 117.8, 113.1, 110.6, 101.0, 60.6, 56.1, 55.5, 31.8. HRMS (ESI) m/z: Calcd for $C_{21}H_{23}NO_3Na$ $[M+Na]^+$: 360.1570; found: 360.1570.

Indole 2. To an oven-dried 15 mL pressure tube equipped with magnetic bar, was added indole **24** (0.0675 g, 0.20 mmol). The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of cyclohexane (2.0 mL) and TFA (0.2 mL). The rubber septum was replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (60 ^oC), stirred for 4 h, cooled to room temperature, quenched by sat. $NaHCO_3$, extracted with EtOAc, washed with brine, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent:

petroleum ether/EtOAc = 4:1 to 2:1) to give **2** as brown solid (0.0461 g, 82% yield). mp. 217.4-218.3 °C; IR (film) cm^{-1} 1614, 1575, 1461, 1371, 1157; ^1H NMR (400 MHz, DMSO-d6) δ 12.1 (br s, 1H), 9.88 (s, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.97 (s, 1H), 6.86 (dd, J = 8.8, 2.0 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 185.5, 160.6, 157.0, 148.8, 137.0, 131.2, 122.3, 121.8, 120.0, 114.6, 113.3, 111.9, 95.3, 55.5, 55.4.

Wang, J.; Sun, X.; Hu, D.; Shi, Y. *Org. Lett.* **2021**, *23*, 7561-7565.

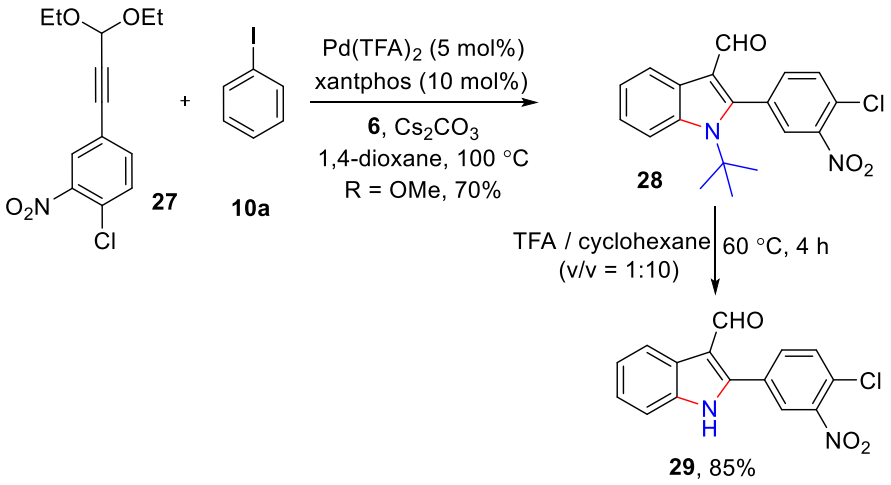


Indole 25. To an oven-dried 15 mL pressure tube equipped with magnetic bar, were added $Pd(TFA)_2$ (0.0083 g, 0.025 mmol), $(p\text{-ClPh})_3P$ (0.0366 g, 0.10 mmol), and Cs_2CO_3 (0.3258 g, 1.0 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of 1,4-dioxane (2.5 mL), alkyne **22** (0.1172 g, 0.50 mmol), 4-iodoanisole **10e** (0.111 g, 0.50 mmol), and di-*t*-butyldiaziridinone (**6**) (0.1107 g, 0.65 mmol). The rubber septum was replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (115 °C), stirred for 12 h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent: petroleum ether/EtOAc = 40:1 to 5:1) to give indole **25** as light yellow solid (0.0826 g, 51% yield). mp. 210.6-211.5 °C; IR (film) 1655, 1611, 1491, 1354, 1253 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.40 (dd, J = 8.4, 6.0 Hz, 1H), 7.44 (dd, J = 11.2, 2.4 Hz, 1H), 7.35 (d, J = 8.8 Hz, 2H), 7.07 (td, J = 9.2, 2.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 160.4, 159.6 (d, J = 237.2 Hz), 152.6 (d, J = 2.7 Hz), 136.8 (d, J = 11.4 Hz), 132.3, 124.6, 122.9 (d, J = 9.8 Hz), 122.8, 117.7, 113.2, 110.1 (d, J = 23.4 Hz), 102.2 (d, J = 27.8

Hz), 61.0, 55.5, 31.8. HRMS (ESI) m/z: Calcd for $C_{20}H_{21}FNO_2$ $[M+H]^+$: 326.1551; found: 326.1552.

Indole 26 was obtained from **25** in a manner similar to indole **2** from **24.** Brown solid (0.0458 g, 85% yield);[1] eluent: CH_2Cl_2/MeOH = 10:1. mp. 234.5-235.3 °C; IR (film) cm^{-1} 1615, 1593, 1370, 1261, 1137; ^1H NMR (400 MHz, DMSO-d6) δ 12.4 (br s, 1H), 9.94 (s, 1H), 8.18 (dd, J = 8.8, 5.6 Hz, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.25 (dd, J = 9.6, 2.0 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 10.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d6) δ 185.5, 160.7, 159.7 (d, J = 236.1 Hz), 150.0 (d, J = 2.4 Hz), 136.1 (d, J = 12.5 Hz), 131.3, 122.6, 122.2 (d, J = 9.7 Hz), 121.8, 114.5, 112.9, 110.5 (d, J = 23.5 Hz), 98.3 (d, J = 25.6 Hz), 55.4. HRMS (ESI) m/z: Calcd for $C_{16}H_{13}FNO_2$ $[M+H]^+$: 270.0925; found: 270.0924.

1) Gastpar, R.; Goldbrunner, M.; Marko, D.; Angerer, E. V. *J. Med. Chem.* **1998**, *41*, 4965-4972.



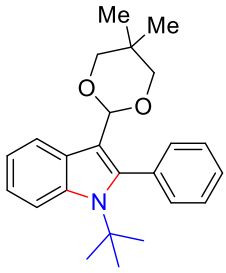
Indole 28. To an oven-dried 15 mL pressure tube equipped with magnetic bar, were added alkyne **27** (0.227 g, 0.80 mmol), $Pd(TFA)_2$ (0.0133 g, 0.040 mmol), xantphos (0.0463 g, 0.080 mmol), and Cs_2CO_3 (0.5213 g, 1.6 mmol), successively. The tube was fitted with rubber septum, evacuated under high vacuum, and refilled with N_2 for three time, followed by addition of 1,4-dioxane (4.0 mL), PhI (0.1632 g, 0.80 mmol), and di-*t*-butyldiaziridinone (**6**) (0.1771 g, 1.04 mmol). The rubber septum was replaced with Teflon-coated screw cap. The reaction mixture was placed in a pre-heated oil bath (100 °C), stirred for 12 h, cooled to room temperature, diluted with EtOAc, filtered over a plug of silica gel, washed with EtOAc, concentrated under reduced pressure, and purified by flash chromatography (silica gel, eluent:

petroleum ether/EtOAc = 25:1 to 10:1) to give indole **28** as light yellow solid (0.1986 g, 70% yield). mp. 216.9-217.7 ºC; IR (film) 1654, 1541, 1352, 1208 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 8.50-8.43 (m, 1H), 8.01 (d, *J* = 2.0 Hz, 1H), 7.81-7.76 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.64 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.39-7.33 (m, 2H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 147.1, 146.3, 136.9, 135.2, 133.5, 131.4, 128.4, 127.6, 126.2, 124.0, 123.3, 122.3, 118.3, 115.5, 61.4, 32.3. HRMS (ESI) m/z: Calcd for $C_{19}H_{18}ClN_2O_3$ $[M+H]^+$: 357.1001 ; found: 357.1001.

Indole 29 was obtained from **28** in a manner similar to indole **2** from **24**. Brown solid (0.0512 g, 85% yield); mp. 253.1-253.9 ºC; IR (film) cm^{-1} 1744, 1626, 1450, 1369, 1243, 1048; ^{1}H NMR (400 MHz, DMSO-d6) δ 12.7 (br s, 1H), 10.00 (s, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 8.23 (d, *J* = 8.0 Hz, 1H), 8.13 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d6) δ 185.5, 147.9, 144.4, 136.1, 134.8, 132.2, 130.2, 126.3, 126.1, 125.7, 124.3, 122.8, 121.2, 114.2, 112.3. HRMS (ESI) m/z: Calcd for $C_{15}H_{10}ClN_2O_3$ $[M+H]^+$: 301.0375; found: 301.0375.

The X-ray structure of compound **15a**

Compound **15a** (0.010 g) was dissolved in EtOAc (3 mL) and the solvent was allowed to slowly evaporated at room temperature to give a yellow crystal suitable for X-ray diffraction analysis. The intensity data was collected on a D8 VENTURE instrument. The data were outlined below.



(CCDC: 2368262)

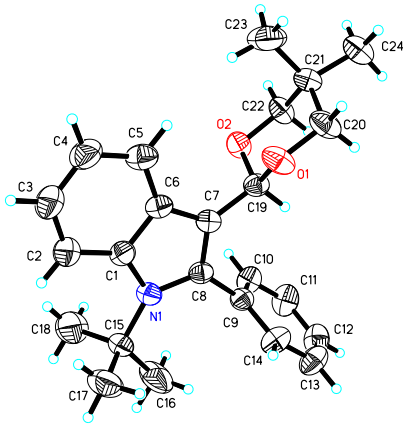


Figure S-1. Ortep diagram of compound **15a** (the thermal ellipsoids are drawn at the 30% probability level).

Table S-2. Crystal data and structure refinement for **15a**.

Identification code	**15a**	
Empirical formula	C24 H29 N O2	
Formula weight	363.48	
Temperature	293 K	
Wavelength	1.54178 Å	
Crystal system	Tetragonal	
Space group	I 41/a	
Unit cell dimensions	a = 31.5114(3) Å	a= 90°.
	b = 31.5114(3) Å	b= 90°.
	c = 9.2754(2) Å	g = 90°.
Volume	9210.2(3) $Å^3$	
Z	16	
Density (calculated)	1.049 Mg/m^3	
Absorption coefficient	0.514 mm^{-1}	
F(000)	3136	
Crystal size	0.16 x 0.14 x 0.11 mm^3	
Theta range for data collection	2.804 to 70.112°.	
Index ranges	-33<=h<=37, -38<=k<=33, -11<=l<=10	
Reflections collected	51855	
Independent reflections	4338 [R(int) = 0.1971]	
Completeness to theta = 67.679°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.3813	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4338 / 0 / 249	
Goodness-of-fit on F^2	1.167	
Final R indices [I>2sigma(I)]	R1 = 0.0743, wR2 = 0.1870	
R indices (all data)	R1 = 0.1206, wR2 = 0.2147	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.138 and -0.183 $e.Å^{-3}$	

Table S-3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **15a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3442(1)	7516(1)	4800(2)	81(1)
O(2)	4019(1)	7495(1)	6340(2)	68(1)
N(1)	3039(1)	6895(1)	9000(2)	61(1)
C(1)	3152(1)	6582(1)	7997(3)	64(1)
C(2)	3095(1)	6142(1)	8009(4)	85(1)
C(3)	3246(1)	5915(1)	6857(5)	104(1)
C(4)	3450(1)	6099(1)	5716(4)	97(1)
C(5)	3505(1)	6531(1)	5682(3)	79(1)
C(6)	3360(1)	6777(1)	6827(3)	62(1)
C(7)	3369(1)	7219(1)	7130(3)	60(1)
C(8)	3178(1)	7285(1)	8436(3)	56(1)
C(9)	3128(1)	7709(1)	9092(2)	57(1)
C(10)	3482(1)	7913(1)	9649(3)	73(1)
C(11)	3451(1)	8318(1)	10193(4)	93(1)
C(12)	3069(1)	8524(1)	10190(3)	88(1)
C(13)	2720(1)	8334(1)	9618(3)	90(1)
C(14)	2751(1)	7930(1)	9065(3)	78(1)
C(15)	2850(1)	6794(1)	10441(3)	71(1)
C(16)	2776(2)	7180(1)	11355(4)	141(2)
C(17)	2415(1)	6595(1)	10193(4)	117(1)
C(18)	3149(1)	6501(1)	11241(4)	122(1)
C(19)	3577(1)	7550(1)	6234(3)	61(1)
C(20)	3639(1)	7833(1)	3923(3)	86(1)
C(21)	4121(1)	7794(1)	3951(3)	68(1)
C(22)	4243(1)	7806(1)	5513(3)	73(1)
C(23)	4264(1)	7380(1)	3262(5)	125(2)
C(24)	4321(1)	8173(1)	3172(3)	93(1)

Table S-4. Bond lengths [Å] and angles [°] for **15a**.

O(1)-C(19)	1.400(3)
O(1)-C(20)	1.430(3)
O(2)-C(19)	1.409(3)
O(2)-C(22)	1.432(3)
N(1)-C(1)	1.402(3)
N(1)-C(8)	1.407(3)
N(1)-C(15)	1.497(3)
C(1)-C(2)	1.397(4)
C(1)-C(6)	1.408(4)
C(2)-H(2)	0.9300
C(2)-C(3)	1.372(4)
C(3)-H(3)	0.9300
C(3)-C(4)	1.369(5)
C(4)-H(4)	0.9300
C(4)-C(5)	1.373(4)
C(5)-H(5)	0.9300
C(5)-C(6)	1.392(3)
C(6)-C(7)	1.421(3)
C(7)-C(8)	1.369(3)
C(7)-C(19)	1.485(3)
C(8)-C(9)	1.477(3)
C(9)-C(10)	1.388(3)
C(9)-C(14)	1.378(4)
C(10)-H(10)	0.9300
C(10)-C(11)	1.373(4)
C(11)-H(11)	0.9300
C(11)-C(12)	1.368(4)
C(12)-H(12)	0.9300
C(12)-C(13)	1.360(4)
C(13)-H(13)	0.9300
C(13)-C(14)	1.377(4)
C(14)-H(14)	0.9300
C(15)-C(16)	1.499(4)
C(15)-C(17)	1.524(4)
C(15)-C(18)	1.516(4)
C(16)-H(16A)	0.9600

C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(19)-H(19)	0.9800
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(20)-C(21)	1.524(4)
C(21)-C(22)	1.500(4)
C(21)-C(23)	1.521(4)
C(21)-C(24)	1.531(4)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(19)-O(1)-C(20)	110.8(2)
C(19)-O(2)-C(22)	111.51(19)
C(1)-N(1)-C(8)	106.77(19)
C(1)-N(1)-C(15)	123.0(2)
C(8)-N(1)-C(15)	129.9(2)
N(1)-C(1)-C(6)	108.8(2)
C(2)-C(1)-N(1)	131.3(3)
C(2)-C(1)-C(6)	119.9(2)
C(1)-C(2)-H(2)	121.1
C(3)-C(2)-C(1)	117.9(3)
C(3)-C(2)-H(2)	121.1
C(2)-C(3)-H(3)	118.6
C(4)-C(3)-C(2)	122.9(3)
C(4)-C(3)-H(3)	118.6
C(3)-C(4)-H(4)	120.0

C(3)-C(4)-C(5)	119.9(3)
C(5)-C(4)-H(4)	120.0
C(4)-C(5)-H(5)	120.2
C(4)-C(5)-C(6)	119.5(3)
C(6)-C(5)-H(5)	120.2
C(1)-C(6)-C(7)	106.6(2)
C(5)-C(6)-C(1)	119.9(3)
C(5)-C(6)-C(7)	133.5(3)
C(6)-C(7)-C(19)	126.0(2)
C(8)-C(7)-C(6)	108.3(2)
C(8)-C(7)-C(19)	125.6(2)
N(1)-C(8)-C(9)	127.2(2)
C(7)-C(8)-N(1)	109.5(2)
C(7)-C(8)-C(9)	123.3(2)
C(10)-C(9)-C(8)	119.2(2)
C(14)-C(9)-C(8)	122.8(2)
C(14)-C(9)-C(10)	117.8(2)
C(9)-C(10)-H(10)	119.7
C(11)-C(10)-C(9)	120.6(3)
C(11)-C(10)-H(10)	119.7
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-C(10)	120.2(3)
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-H(12)	119.9
C(13)-C(12)-C(11)	120.2(3)
C(13)-C(12)-H(12)	119.9
C(12)-C(13)-H(13)	120.2
C(12)-C(13)-C(14)	119.6(3)
C(14)-C(13)-H(13)	120.2
C(9)-C(14)-H(14)	119.3
C(13)-C(14)-C(9)	121.5(3)
C(13)-C(14)-H(14)	119.3
N(1)-C(15)-C(16)	113.3(2)
N(1)-C(15)-C(17)	108.1(2)
N(1)-C(15)-C(18)	108.6(2)
C(16)-C(15)-C(17)	106.3(3)
C(16)-C(15)-C(18)	108.3(3)
C(18)-C(15)-C(17)	112.4(3)

C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(15)-C(18)-H(18A)	109.5
C(15)-C(18)-H(18B)	109.5
C(15)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
O(1)-C(19)-O(2)	110.9(2)
O(1)-C(19)-C(7)	110.1(2)
O(1)-C(19)-H(19)	109.2
O(2)-C(19)-C(7)	108.1(2)
O(2)-C(19)-H(19)	109.2
C(7)-C(19)-H(19)	109.2
O(1)-C(20)-H(20A)	109.3
O(1)-C(20)-H(20B)	109.3
O(1)-C(20)-C(21)	111.6(2)
H(20A)-C(20)-H(20B)	108.0
C(21)-C(20)-H(20A)	109.3
C(21)-C(20)-H(20B)	109.3
C(20)-C(21)-C(24)	109.8(2)
C(22)-C(21)-C(20)	105.6(2)
C(22)-C(21)-C(23)	110.6(3)
C(22)-C(21)-C(24)	109.3(2)
C(23)-C(21)-C(20)	110.9(3)
C(23)-C(21)-C(24)	110.5(3)
O(2)-C(22)-C(21)	112.0(2)
O(2)-C(22)-H(22A)	109.2

O(2)-C(22)-H(22B)	109.2
C(21)-C(22)-H(22A)	109.2
C(21)-C(22)-H(22B)	109.2
H(22A)-C(22)-H(22B)	107.9
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S-5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **15a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	68(1)	120(2)	54(1)	7(1)	-6(1)	-22(1)
O(2)	56(1)	77(1)	72(1)	14(1)	-6(1)	-7(1)
N(1)	61(1)	65(1)	58(1)	0(1)	7(1)	-2(1)
C(1)	59(2)	62(2)	71(2)	-6(1)	2(1)	2(1)
C(2)	89(2)	65(2)	101(2)	-1(2)	14(2)	-2(2)
C(3)	117(3)	63(2)	130(3)	-15(2)	17(2)	4(2)
C(4)	105(3)	82(2)	105(3)	-27(2)	19(2)	3(2)
C(5)	75(2)	85(2)	77(2)	-21(2)	11(1)	-2(2)
C(6)	56(2)	67(2)	62(2)	-10(1)	3(1)	1(1)
C(7)	56(2)	66(2)	57(2)	-2(1)	4(1)	-2(1)
C(8)	52(1)	64(2)	52(1)	-3(1)	1(1)	0(1)
C(9)	61(2)	64(2)	46(1)	-2(1)	0(1)	4(1)
C(10)	71(2)	68(2)	80(2)	-8(1)	-14(1)	1(1)
C(11)	100(2)	76(2)	102(3)	-17(2)	-25(2)	-10(2)
C(12)	120(3)	68(2)	78(2)	-12(2)	-13(2)	6(2)
C(13)	96(2)	86(2)	88(2)	-21(2)	-10(2)	28(2)
C(14)	69(2)	86(2)	79(2)	-21(2)	-11(1)	12(2)
C(15)	70(2)	76(2)	66(2)	13(1)	14(1)	0(1)
C(16)	231(5)	108(3)	84(3)	-8(2)	75(3)	-17(3)
C(17)	79(2)	139(3)	132(3)	24(3)	29(2)	-12(2)
C(18)	121(3)	156(4)	90(3)	41(2)	2(2)	26(3)
C(19)	61(2)	71(2)	52(2)	-5(1)	-1(1)	3(1)
C(20)	77(2)	125(3)	55(2)	21(2)	-2(1)	-12(2)
C(21)	62(2)	82(2)	61(2)	-3(1)	8(1)	-9(1)
C(22)	69(2)	83(2)	67(2)	17(1)	-4(1)	-16(1)
C(23)	132(3)	112(3)	132(3)	-35(2)	65(3)	-11(2)
C(24)	93(2)	108(3)	76(2)	16(2)	9(2)	-21(2)

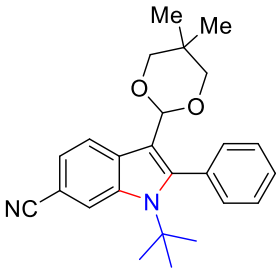
Table S-6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **15a**.

	x	y	z	U(eq)
H(2)	2960	6008	8775	102
H(3)	3207	5622	6851	124
H(4)	3551	5932	4964	117
H(5)	3639	6659	4900	95
H(10)	3743	7775	9654	87
H(11)	3690	8451	10564	111
H(12)	3048	8795	10580	106
H(13)	2461	8477	9601	108
H(14)	2512	7803	8665	93
H(16A)	3041	7320	11532	211
H(16B)	2651	7096	12255	211
H(16C)	2587	7370	10862	211
H(17A)	2245	6781	9614	175
H(17B)	2278	6549	11104	175
H(17C)	2449	6328	9704	175
H(18A)	3210	6258	10653	183
H(18B)	3019	6410	12124	183
H(18C)	3408	6649	11454	183
H(19)	3500	7831	6606	73
H(20A)	3558	8112	4267	103
H(20B)	3540	7804	2938	103
H(22A)	4546	7756	5601	88
H(22B)	4183	8086	5899	88
H(23A)	4568	7374	3213	188
H(23B)	4148	7359	2307	188
H(23C)	4165	7146	3832	188
H(24A)	4225	8432	3611	139
H(24B)	4238	8170	2176	139
H(24C)	4624	8156	3240	139

Table S-7. Torsion angles [°] for **15a**.

The X-ray structure of compound **15i**

Compound **15i** (0.010 g) was dissolved in petroleum ether/EtOAc (3 mL, 3:1) and the solvent was allowed to slowly evaporated at room temperature to give a yellow crystal suitable for X-ray diffraction analysis. The intensity data was collected on a D8 VENTURE instrument. The data were outlined below.



(CCDC: 2368365)

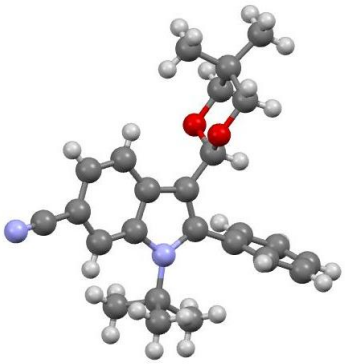


Figure S-2. Ortep diagram of compound **15i** (the thermal ellipsoids are drawn at the 30% probability level).

Table S-8. Crystal data and structure refinement for **15i**.

Identification code	**15i**
Empirical formula	$C_{25}H_{28}N_2O_2$
Formula weight	388.49
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	9.734
b/Å	10.474(4)
c/Å	11.936(4)
α/°	78.427(5)
β/°	66.163(9)
γ/°	81.294(9)
Volume/Å^3	1087.2(6)
Z	2
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.075
F(000)	416.0
Crystal size/mm^3	0.22 × 0.2 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.59 to 50.238
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	3842
Independent reflections	3842 [R_{int} = 0, R_{sigma} = 0.1841]
Data/restraints/parameters	3842/0/267
Goodness-of-fit on F^2	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.1043, wR_2 = 0.2641
Final R indexes [all data]	R_1 = 0.2168, wR_2 = 0.3097
Largest diff. peak/hole / e Å^{-3}	0.29/-0.31

Table S-9. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **15i**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	1219(6)	4633(5)	7566(4)	58.7(14)
C2	-445(6)	4406(6)	8217(5)	77.4(17)
C3	2080(6)	4061(6)	8409(5)	74.0(16)
C4	1381(7)	6089(5)	7240(5)	83.5(18)
C5	2506(5)	4431(4)	5189(4)	49.2(12)
C6	3050(5)	3420(4)	4515(4)	50.6(12)
C7	2732(5)	2231(5)	5365(4)	52.6(13)
C8	1968(5)	2571(4)	6554(4)	50.8(12)
C9	1382(6)	1622(5)	7585(5)	59.9(14)
C10	1585(6)	341(5)	7390(5)	63.9(14)
C11	2425(7)	-27(5)	6226(5)	71.9(16)
C12	2976(6)	905(5)	5220(5)	66.0(15)
C13	890(8)	-636(6)	8418(6)	78.5(18)
C14	2530(5)	5840(4)	4639(4)	50.4(12)
C15	1269(6)	6541(5)	4523(5)	68.0(15)
C16	1304(7)	7839(5)	4002(6)	74.7(17)
C17	2604(7)	8436(5)	3572(5)	68.3(15)
C18	3875(7)	7766(5)	3665(5)	69.7(16)
C19	3843(6)	6455(5)	4194(5)	63.3(14)
C20	3723(6)	3524(5)	3139(4)	55.7(13)
C21	3426(6)	2892(6)	1479(5)	69.7(15)
C22	5069(6)	2389(5)	947(4)	58.7(14)
C23	5901(6)	3137(5)	1409(5)	66.1(15)
C24	5661(7)	2683(6)	-469(5)	85.8(19)
C25	5288(8)	921(5)	1350(5)	87.5(19)
N1	341(7)	-1427(5)	9232(5)	101.6(19)
N2	1866(4)	3938(3)	6449(3)	51.3(10)
O1	2864(4)	2819(3)	2792(3)	67.0(10)
O2	5229(4)	3030(3)	2737(3)	61.0(10)

Table S-10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **15i**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	64(3)	55(3)	51(3)	-18(2)	-11(3)	-8(2)
C2	60(4)	90(4)	70(4)	-33(3)	-4(3)	-1(3)
C3	83(4)	93(4)	63(3)	-25(3)	-37(3)	-11(3)
C4	118(5)	65(4)	62(4)	-26(3)	-18(3)	-18(3)
C5	48(3)	54(3)	45(3)	-10(2)	-15(2)	-10(2)
C6	55(3)	54(3)	42(3)	-8(2)	-15(2)	-10(2)
C7	53(3)	61(3)	46(3)	-18(2)	-16(2)	-5(2)
C8	52(3)	50(3)	50(3)	-11(2)	-19(2)	-1(2)
C9	66(3)	63(3)	50(3)	-12(3)	-23(3)	-1(3)
C10	83(4)	55(3)	51(3)	-7(3)	-23(3)	-7(3)
C11	96(4)	49(3)	59(4)	-9(3)	-19(3)	-1(3)
C12	83(4)	54(3)	52(3)	-17(3)	-15(3)	1(3)
C13	111(5)	56(4)	60(4)	-10(3)	-28(4)	5(3)
C14	54(3)	51(3)	49(3)	-16(2)	-20(2)	-7(3)
C15	67(4)	56(3)	93(4)	-8(3)	-44(3)	-7(3)
C16	72(4)	60(4)	105(5)	-6(3)	-49(4)	-7(3)
C17	82(4)	54(3)	72(4)	-3(3)	-32(3)	-16(3)
C18	64(4)	68(4)	75(4)	3(3)	-26(3)	-21(3)
C19	54(3)	64(4)	70(4)	-7(3)	-21(3)	-12(3)
C20	58(3)	58(3)	55(3)	-12(2)	-23(3)	-8(3)
C21	66(4)	96(4)	49(3)	-24(3)	-20(3)	-5(3)
C22	71(4)	57(3)	43(3)	-12(2)	-14(3)	-9(3)
C23	58(3)	78(4)	52(3)	-16(3)	-8(3)	-7(3)
C24	96(5)	98(4)	51(3)	-19(3)	-9(3)	-17(4)
C25	117(5)	68(4)	69(4)	-21(3)	-24(4)	-3(3)
N1	152(5)	66(3)	61(3)	-9(3)	-15(3)	-9(3)
N2	52(3)	53(3)	47(2)	-12.9(19)	-14(2)	-4.2(19)
O1	57(2)	91(3)	52(2)	-18.5(18)	-14.8(17)	-16.1(19)
O2	52(2)	76(2)	53(2)	-18.5(17)	-15.1(17)	-4.0(18)

Table S-11. Bond Lengths for **15i**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.520(7)	C11	C12	1.360(7)
C1	C3	1.537(7)	C13	N1	1.144(7)
C1	C4	1.512(7)	C14	C15	1.374(7)
C1	N2	1.509(6)	C14	C19	1.376(7)
C5	C6	1.371(6)	C15	C16	1.376(7)
C5	C14	1.489(6)	C16	C17	1.358(7)
C5	N2	1.394(5)	C17	C18	1.361(7)
C6	C7	1.425(6)	C18	C19	1.390(7)
C6	C20	1.490(6)	C20	O1	1.417(6)
C7	C8	1.402(6)	C20	O2	1.395(6)
C7	C12	1.407(6)	C21	C22	1.515(7)
C8	C9	1.393(6)	C21	O1	1.426(6)
C8	N2	1.403(6)	C22	C23	1.517(7)
C9	C10	1.379(7)	C22	C24	1.530(7)
C10	C11	1.396(7)	C22	C25	1.526(7)
C10	C13	1.430(8)	C23	O2	1.437(6)

Table S-12. Bond Angles for **15i**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C3	111.5(4)	C15	C14	C5	121.3(4)
C4	C1	C2	108.8(4)	C15	C14	C19	118.5(5)
C4	C1	C3	107.7(4)	C19	C14	C5	120.2(4)
N2	C1	C2	107.9(4)	C14	C15	C16	121.0(5)
N2	C1	C3	107.8(4)	C17	C16	C15	119.9(5)
N2	C1	C4	113.2(4)	C16	C17	C18	120.5(5)
C6	C5	C14	124.4(4)	C17	C18	C19	119.7(5)
C6	C5	N2	109.7(4)	C14	C19	C18	120.4(5)
N2	C5	C14	125.8(4)	O1	C20	C6	107.8(4)
C5	C6	C7	107.6(4)	O2	C20	C6	110.4(4)
C5	C6	C20	126.8(4)	O2	C20	O1	111.1(4)
C7	C6	C20	125.3(4)	O1	C21	C22	112.0(4)
C8	C7	C6	107.0(4)	C21	C22	C23	106.4(4)
C8	C7	C12	119.4(5)	C21	C22	C24	109.1(4)
C12	C7	C6	133.5(4)	C21	C22	C25	111.7(5)
C7	C8	N2	108.3(4)	C23	C22	C24	109.5(4)
C9	C8	C7	121.0(4)	C23	C22	C25	110.7(5)
C9	C8	N2	130.6(4)	C25	C22	C24	109.3(4)
C10	C9	C8	117.6(5)	O2	C23	C22	110.8(4)
C9	C10	C11	122.3(5)	C5	N2	C1	130.4(4)
C9	C10	C13	118.5(5)	C5	N2	C8	107.2(4)
C11	C10	C13	119.2(5)	C8	N2	C1	122.3(4)
C12	C11	C10	119.8(5)	C20	O1	C21	111.1(4)
C11	C12	C7	119.8(5)	C20	O2	C23	111.1(4)
N1	C13	C10	179.3(7)				

Table S-13. Torsion Angles for **15i**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C1	N2	C5	116.9(5)	C10	C11	C12	C7	1.8(8)
C2	C1	N2	C8	-66.0(6)	C12	C7	C8	C9	-3.2(7)
C3	C1	N2	C5	-122.6(5)	C12	C7	C8	N2	-179.8(4)
C3	C1	N2	C8	54.5(6)	C13	C10	C11	C12	174.0(5)
C4	C1	N2	C5	-3.5(7)	C14	C5	C6	C7	-176.0(4)
C4	C1	N2	C8	173.5(4)	C14	C5	C6	C20	-1.3(8)
C5	C6	C7	C8	0.9(5)	C14	C5	N2	C1	-8.0(7)
C5	C6	C7	C12	177.9(5)	C14	C5	N2	C8	174.6(4)
C5	C6	C20	O1	-122.0(5)	C14	C15	C16	C17	1.3(9)
C5	C6	C20	O2	116.5(5)	C15	C14	C19	C18	1.4(7)
C5	C14	C15	C16	-179.3(5)	C15	C16	C17	C18	-0.8(9)
C5	C14	C19	C18	179.2(4)	C16	C17	C18	C19	0.6(8)
C6	C5	C14	C15	99.9(6)	C17	C18	C19	C14	-0.9(8)
C6	C5	C14	C19	-77.8(6)	C19	C14	C15	C16	-1.6(8)
C6	C5	N2	C1	175.2(4)	C20	C6	C7	C8	-174.0(4)
C6	C5	N2	C8	-2.2(5)	C20	C6	C7	C12	3.1(9)
C6	C7	C8	C9	174.3(4)	C21	C22	C23	O2	54.0(5)
C6	C7	C8	N2	-2.2(5)	C22	C21	O1	C20	57.3(6)
C6	C7	C12	C11	-174.6(5)	C22	C23	O2	C20	-59.6(5)
C6	C20	O1	C21	179.0(4)	C24	C22	C23	O2	171.8(4)
C6	C20	O2	C23	-179.3(4)	C25	C22	C23	O2	-67.6(5)
C7	C6	C20	O1	51.9(6)	N2	C5	C6	C7	0.8(5)
C7	C6	C20	O2	-69.7(6)	N2	C5	C6	C20	175.6(4)
C7	C8	C9	C10	0.1(7)	N2	C5	C14	C15	-76.5(6)
C7	C8	N2	C1	-174.9(4)	N2	C5	C14	C19	105.8(6)
C7	C8	N2	C5	2.7(5)	N2	C8	C9	C10	175.8(5)
C8	C7	C12	C11	2.2(8)	O1	C20	O2	C23	61.2(5)
C8	C9	C10	C11	4.0(8)	O1	C21	C22	C23	-53.5(6)
C8	C9	C10	C13	-175.0(5)	O1	C21	C22	C24	-171.6(4)
C9	C8	N2	C1	9.0(8)	O1	C21	C22	C25	67.4(6)
C9	C8	N2	C5	-173.4(5)	O2	C20	O1	C21	-59.9(5)
C9	C10	C11	C12	-5.1(9)					

Table S-14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **15i**.

Atom	*x*	*y*	*z*	U(eq)
H2A	-559	3484	8460	116
H2B	-947	4757	7662	116
H2C	-881	4831	8938	116
H3A	1666	4466	9142	111
H3B	3125	4222	7974	111
H3C	1988	3136	8637	111
H4A	913	6463	6665	125
H4B	2430	6245	6869	125
H4C	902	6485	7978	125
H9	872	1844	8375	72
H11	2607	-906	6139	86
H12	3512	666	4439	79
H15	380	6133	4800	82
H16	437	8307	3944	90
H17	2627	9311	3212	82
H18	4760	8182	3376	84
H19	4714	5991	4247	76
H20	3666	4445	2770	67
H21A	3314	3793	1105	84
H21B	2834	2381	1271	84
H23A	6947	2794	1154	79
H23B	5875	4051	1043	79
H24A	5105	2237	-759	129
H24B	6709	2387	-811	129
H24C	5539	3607	-727	129
H25A	4983	741	2235	131
H25B	6331	629	962	131
H25C	4688	470	1109	131

NMR Spectra

^{1}H NMR Spectrum of **15a** ($CDCl_3$, 400 MHz)

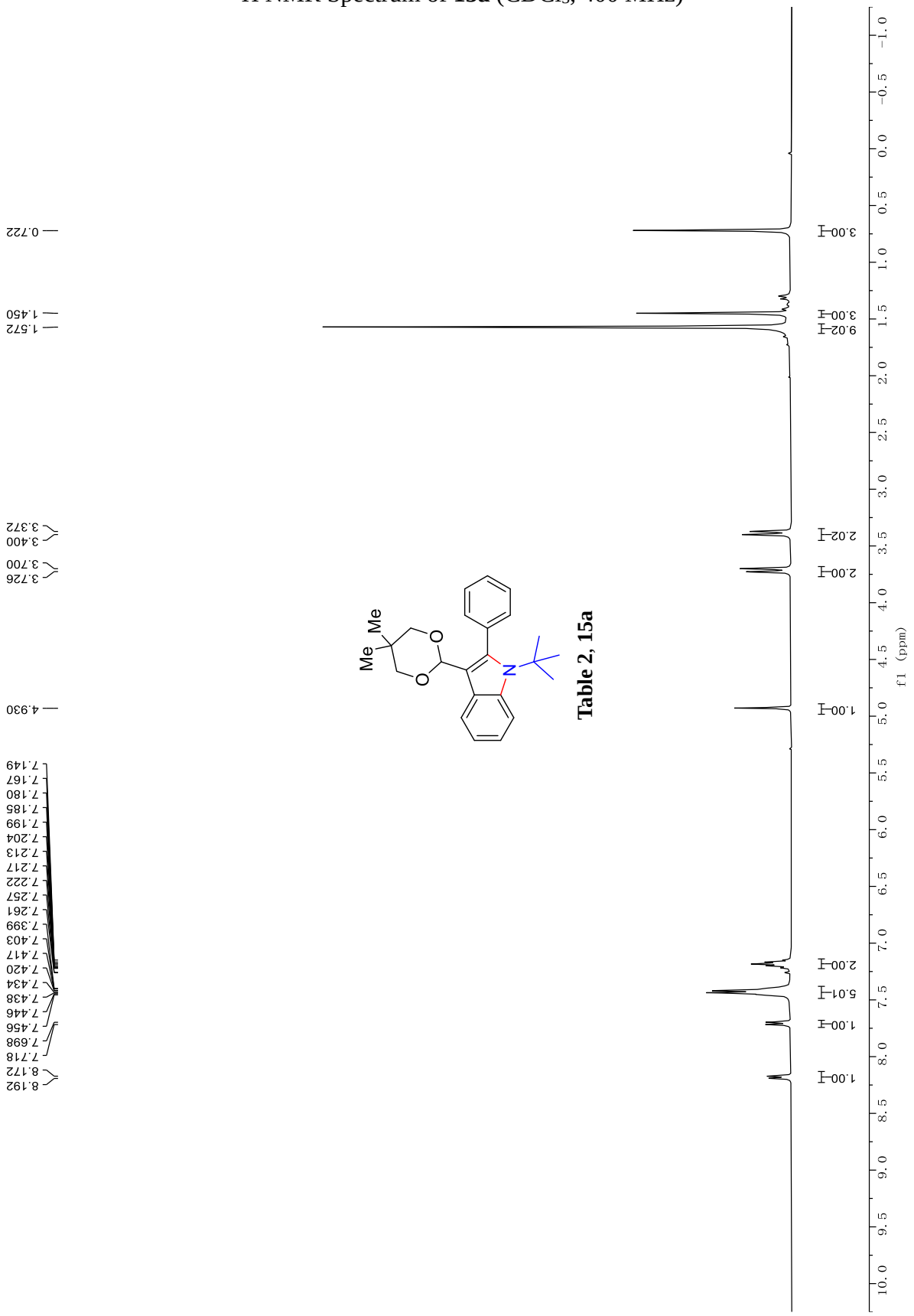
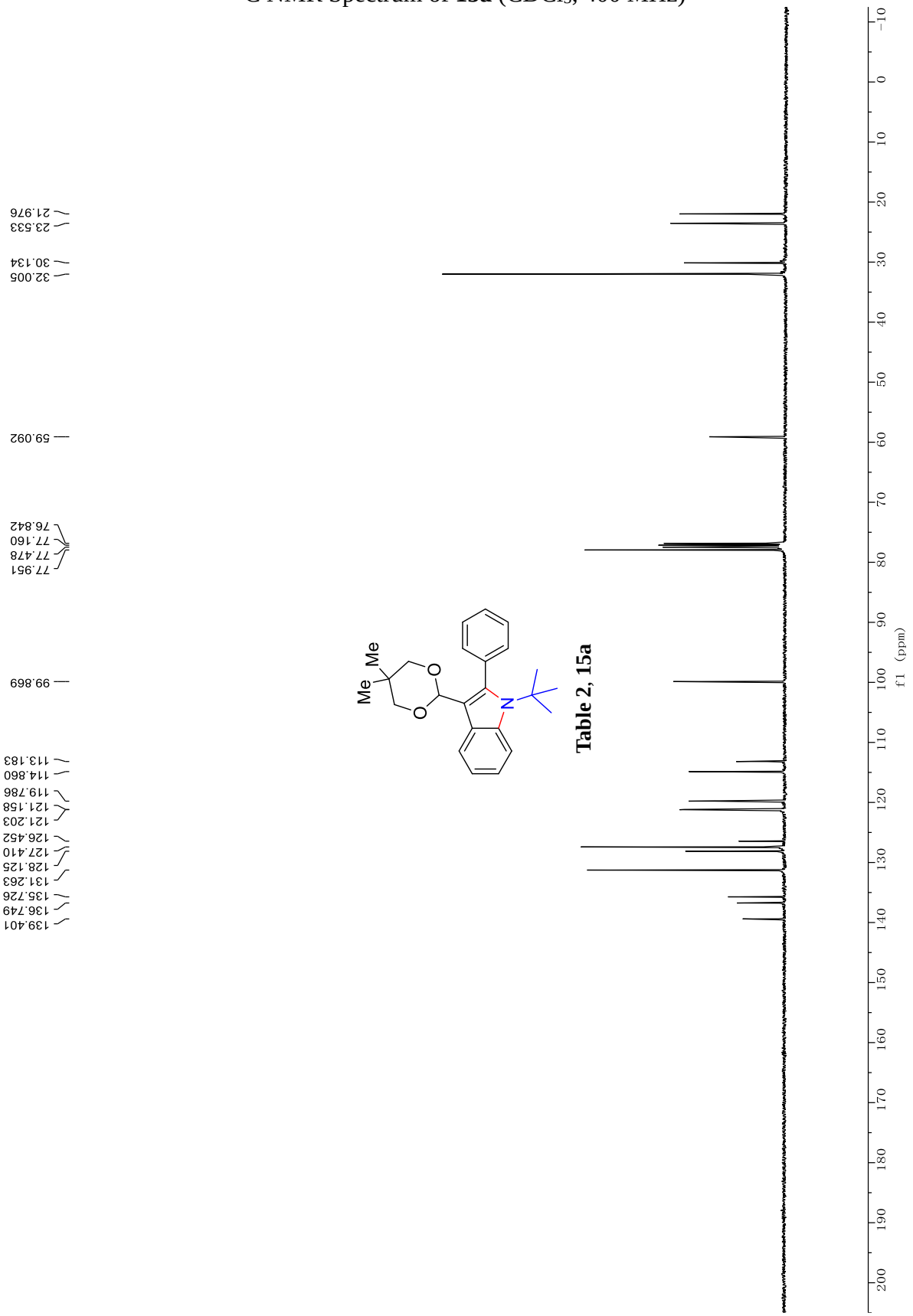
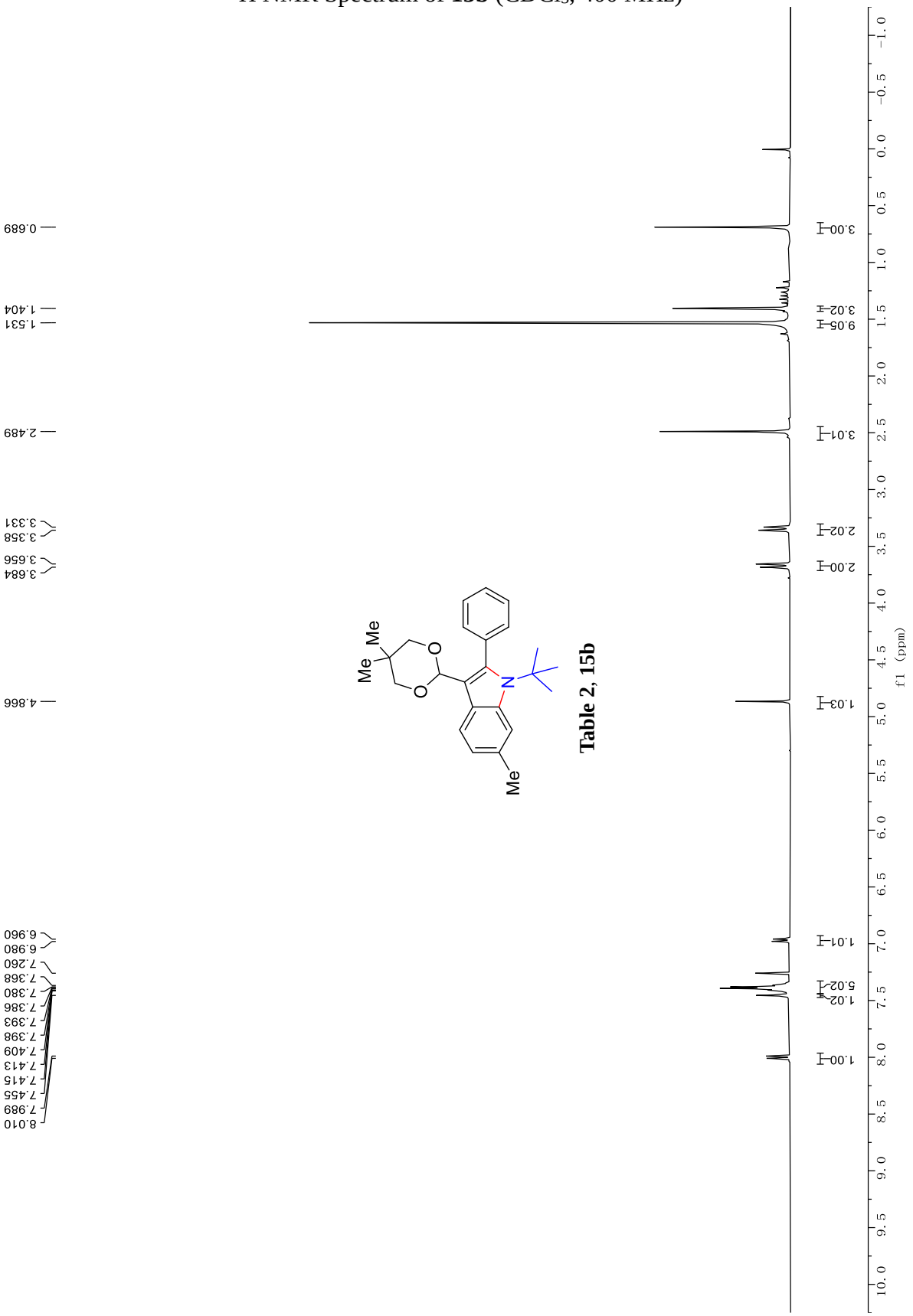


Table 2, 15a

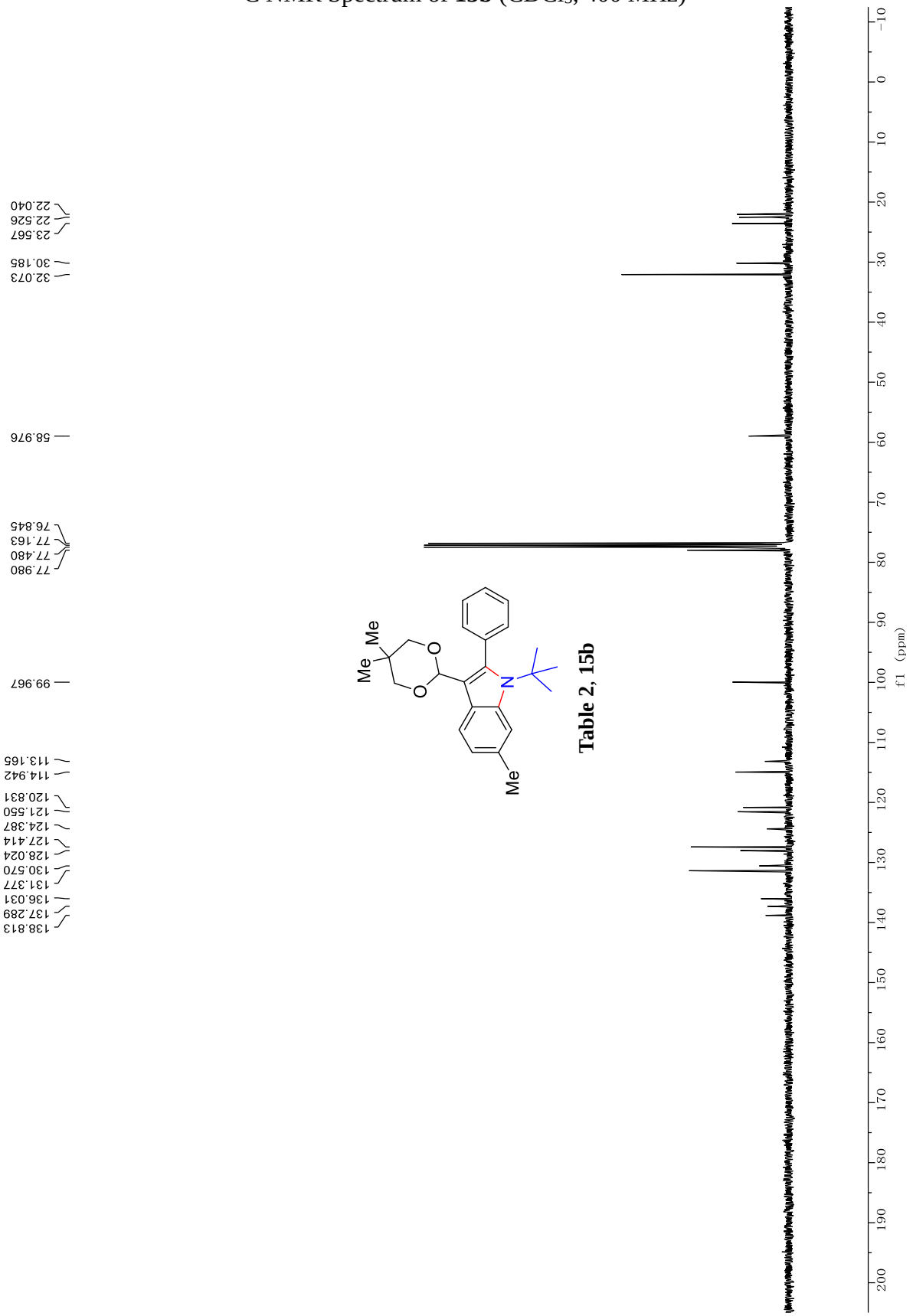
^{13}C NMR Spectrum of **15a** ($CDCl_3$, 400 MHz)



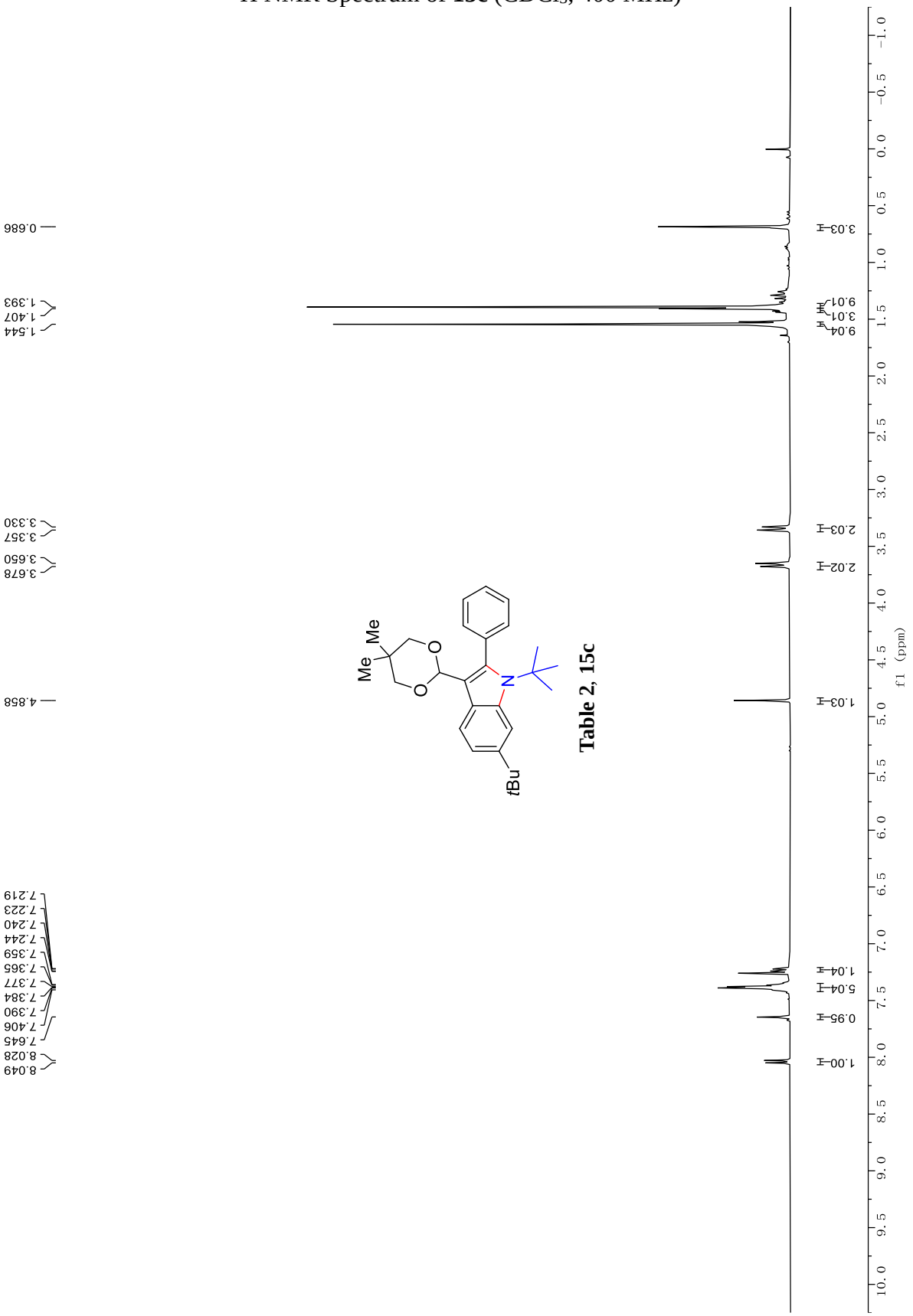
^{1}H NMR Spectrum of **15b** ($CDCl_3$, 400 MHz)



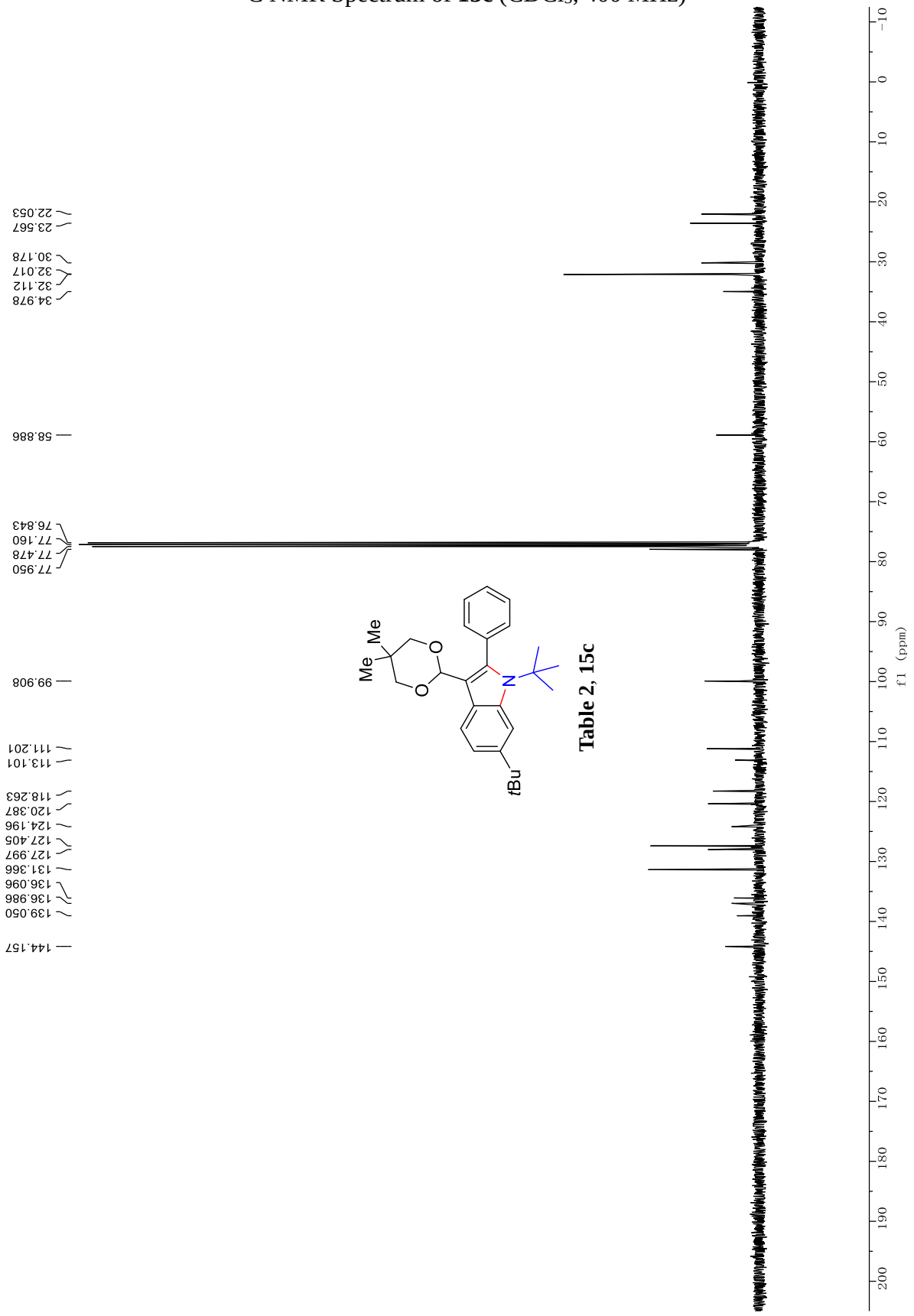
^{13}C NMR Spectrum of **15b** ($CDCl_3$, 400 MHz)



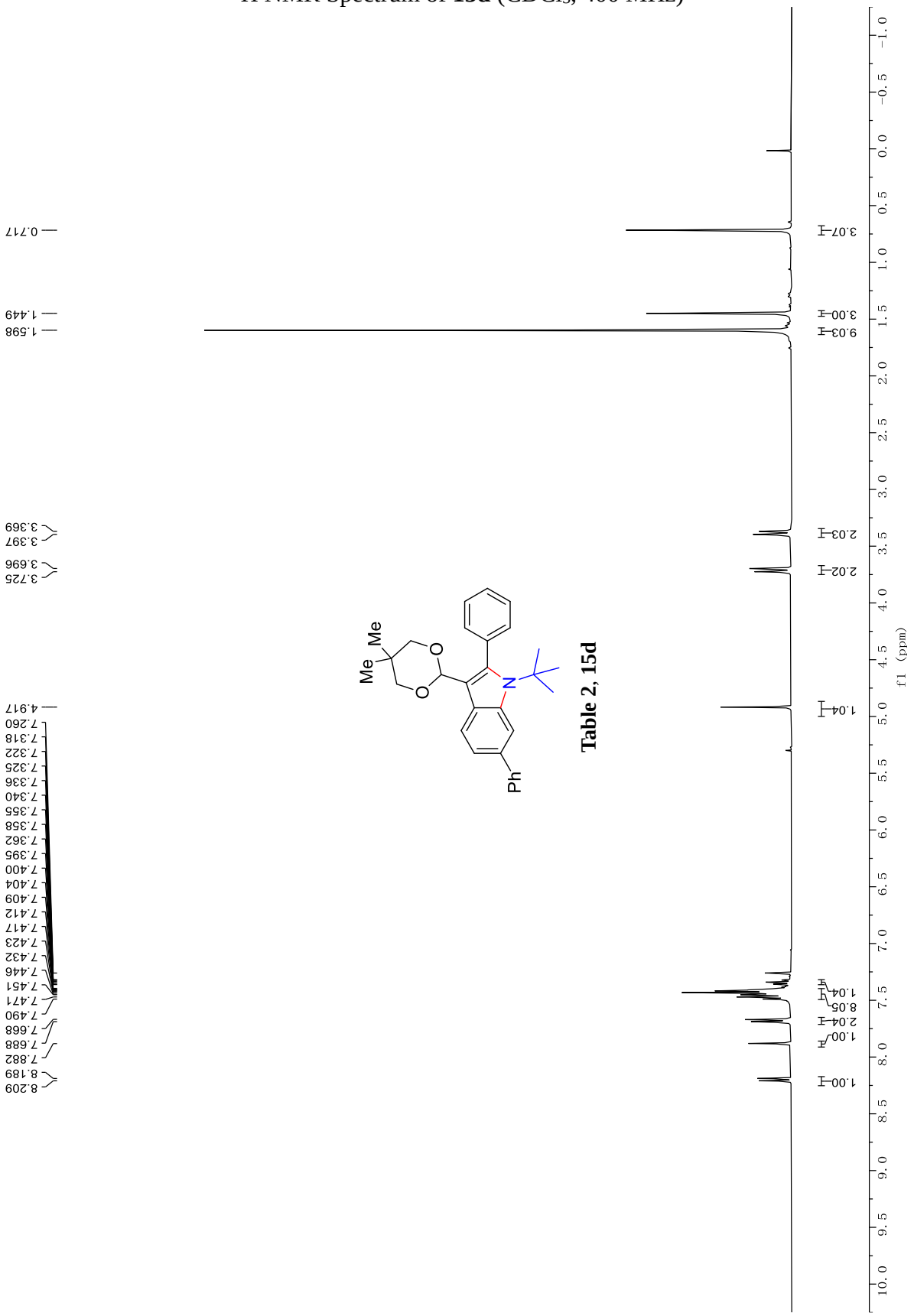
^{1}H NMR Spectrum of **15c** ($CDCl_3$, 400 MHz)



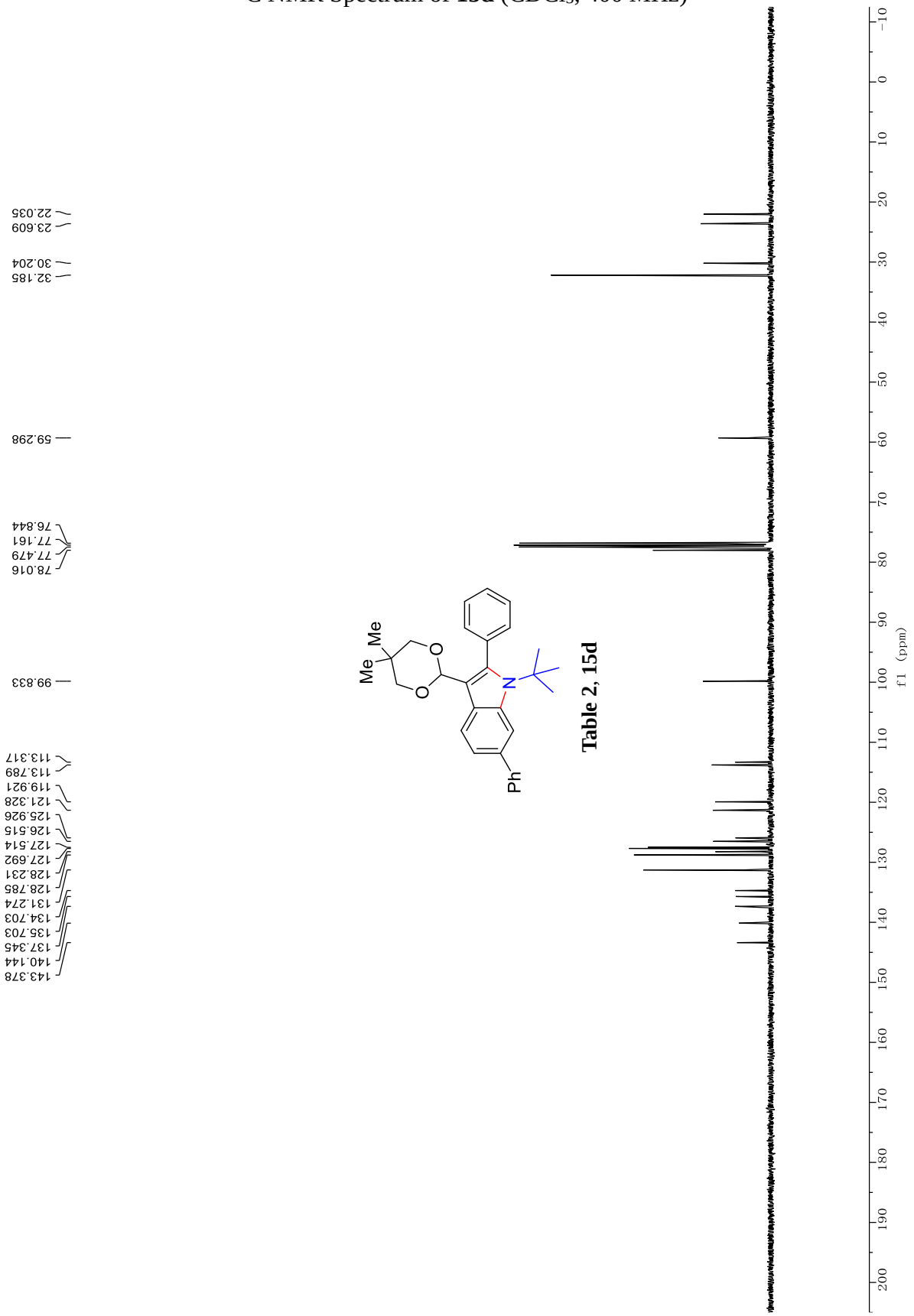
^{13}C NMR Spectrum of **15c** ($CDCl_3$, 400 MHz)



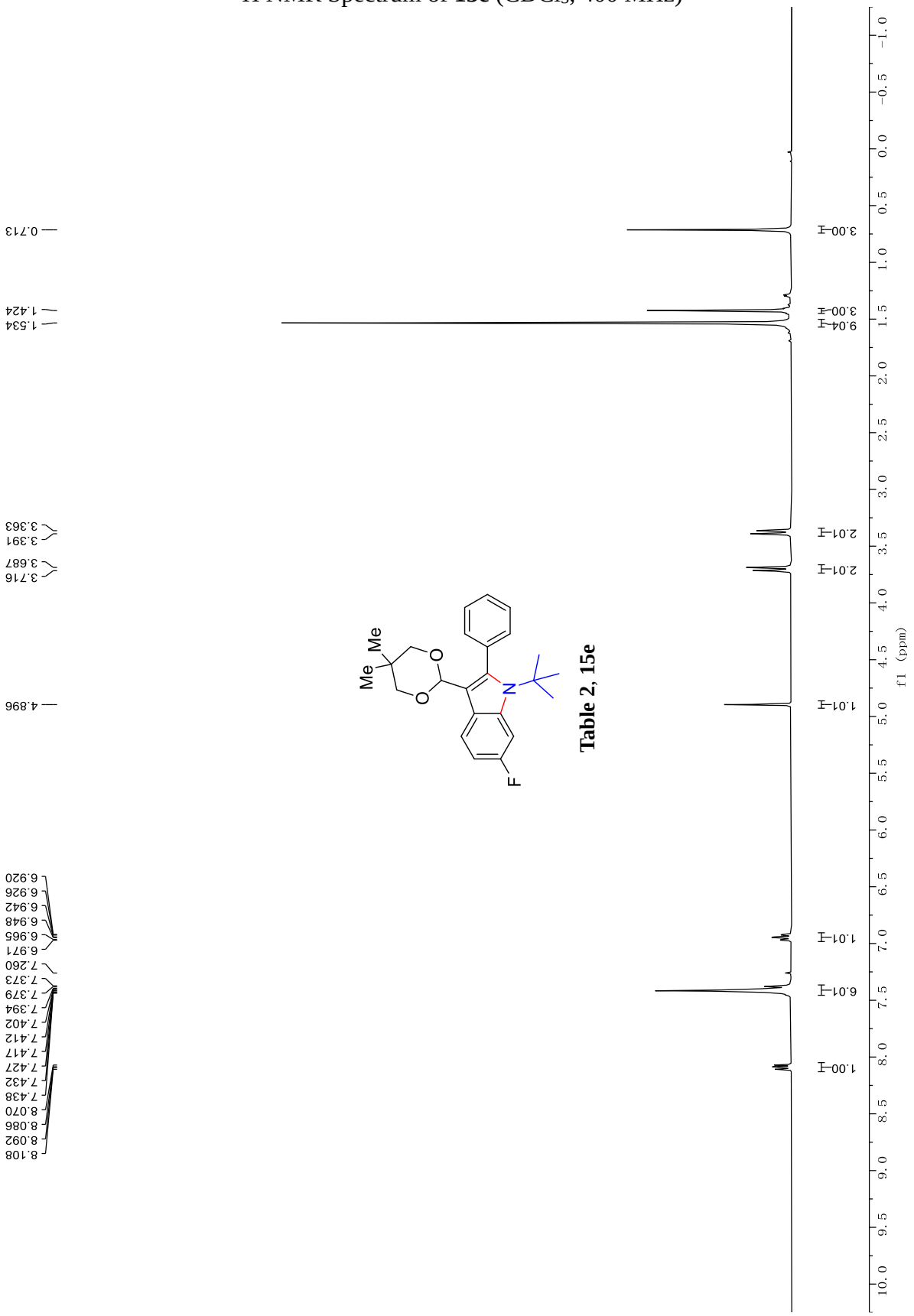
^{1}H NMR Spectrum of **15d** ($CDCl_3$, 400 MHz)



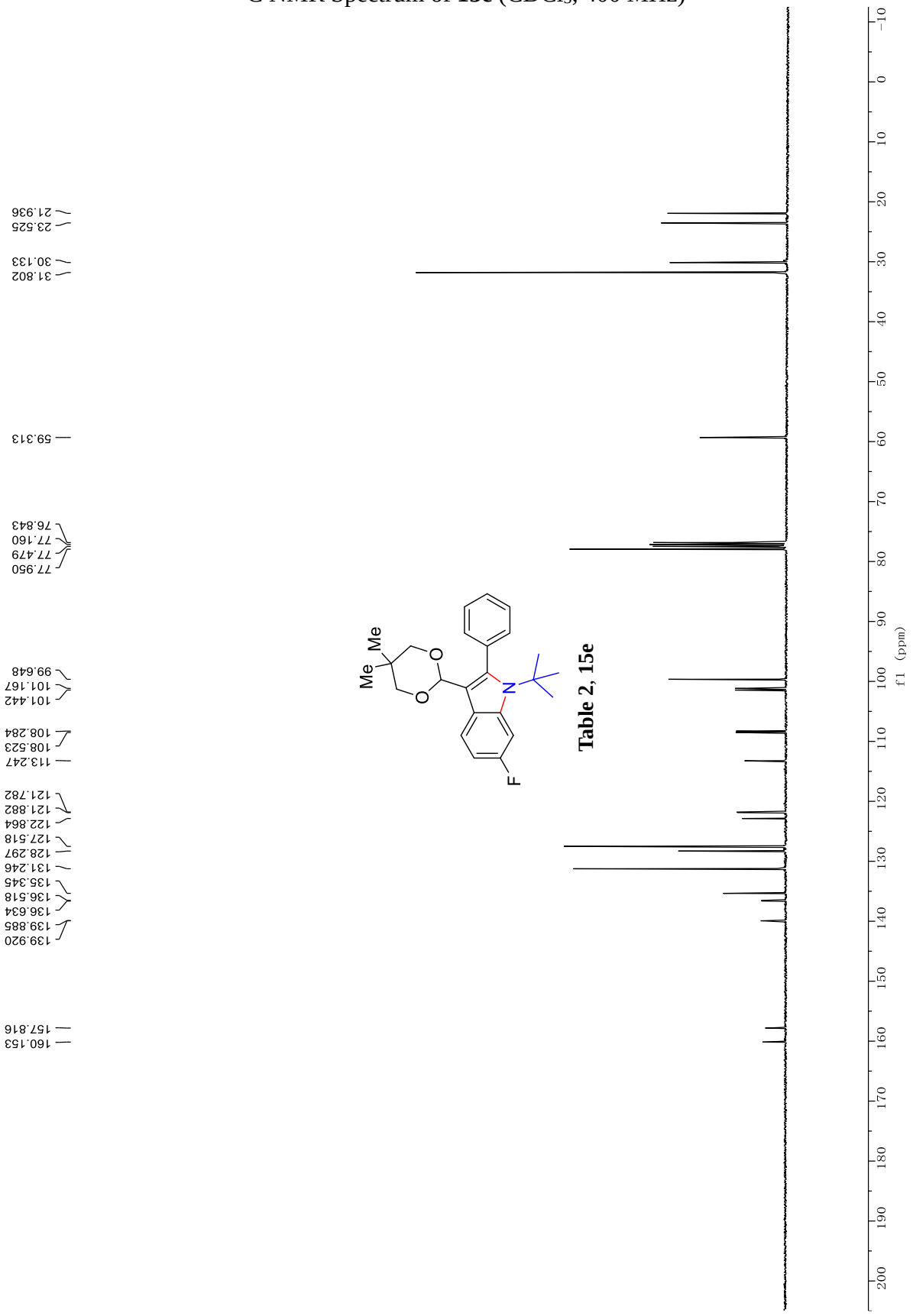
^{13}C NMR Spectrum of **15d** ($CDCl_3$, 400 MHz)



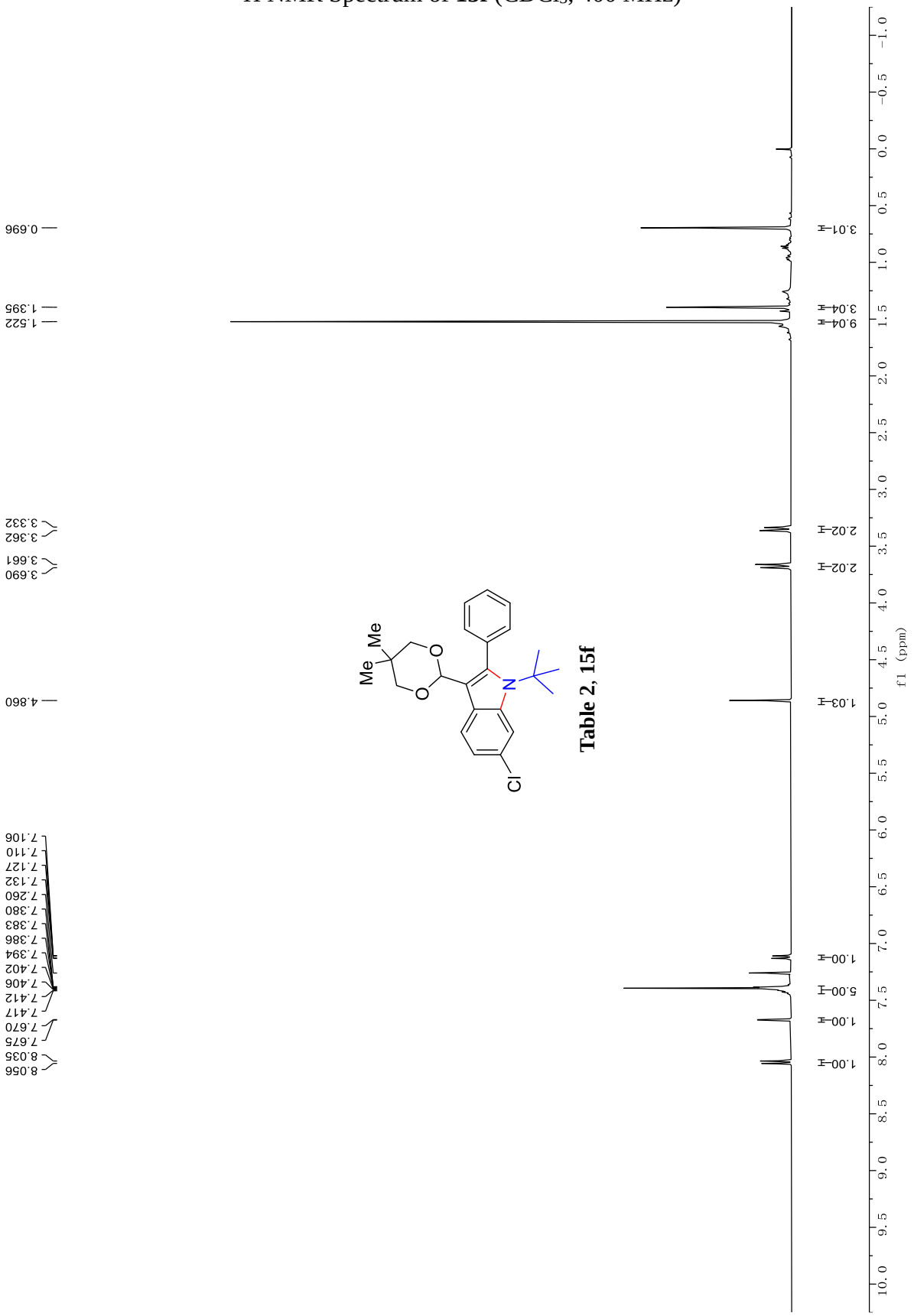
^{1}H NMR Spectrum of **15e** ($CDCl_3$, 400 MHz)



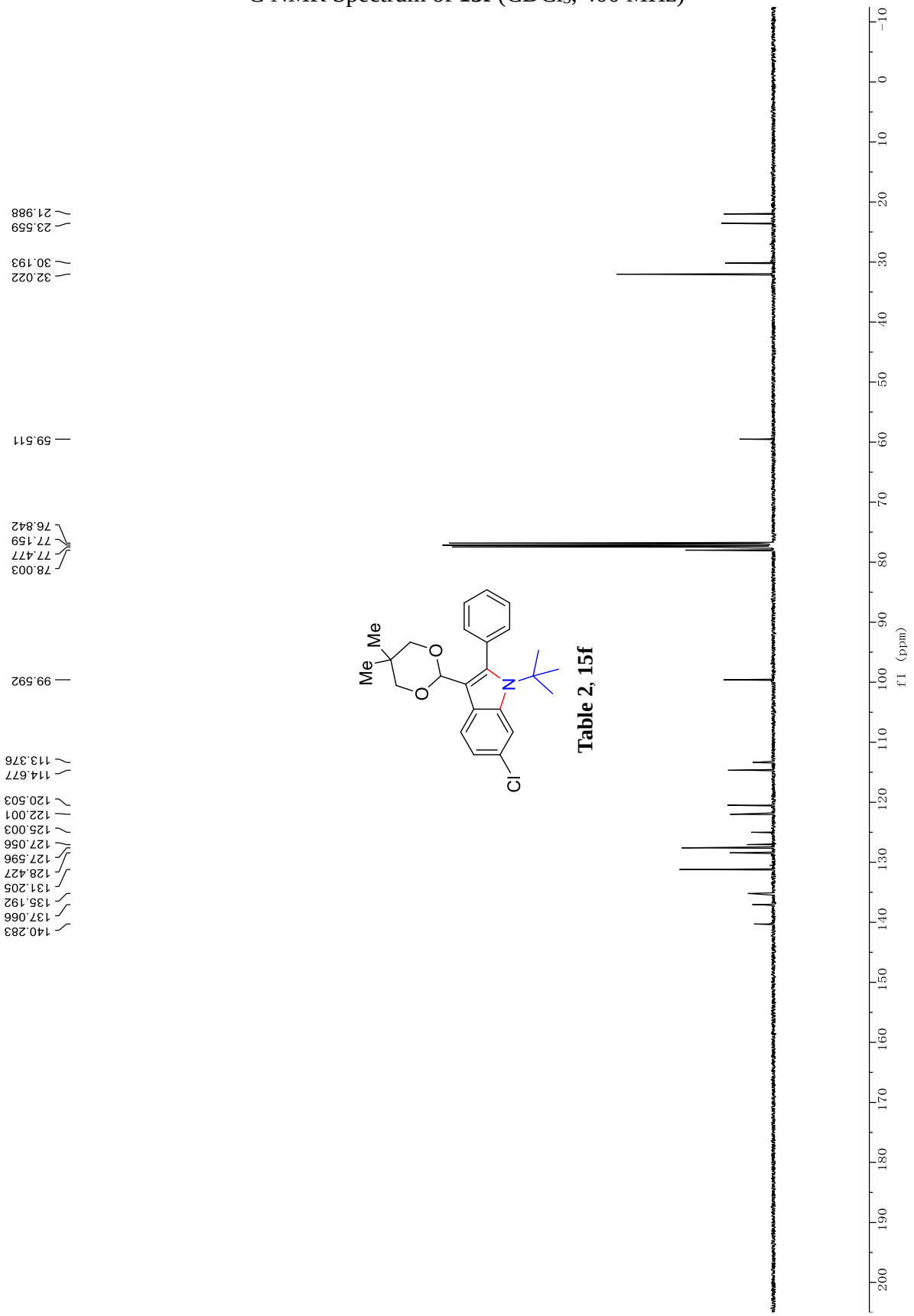
^{13}C NMR Spectrum of **15e** ($CDCl_3$, 400 MHz)



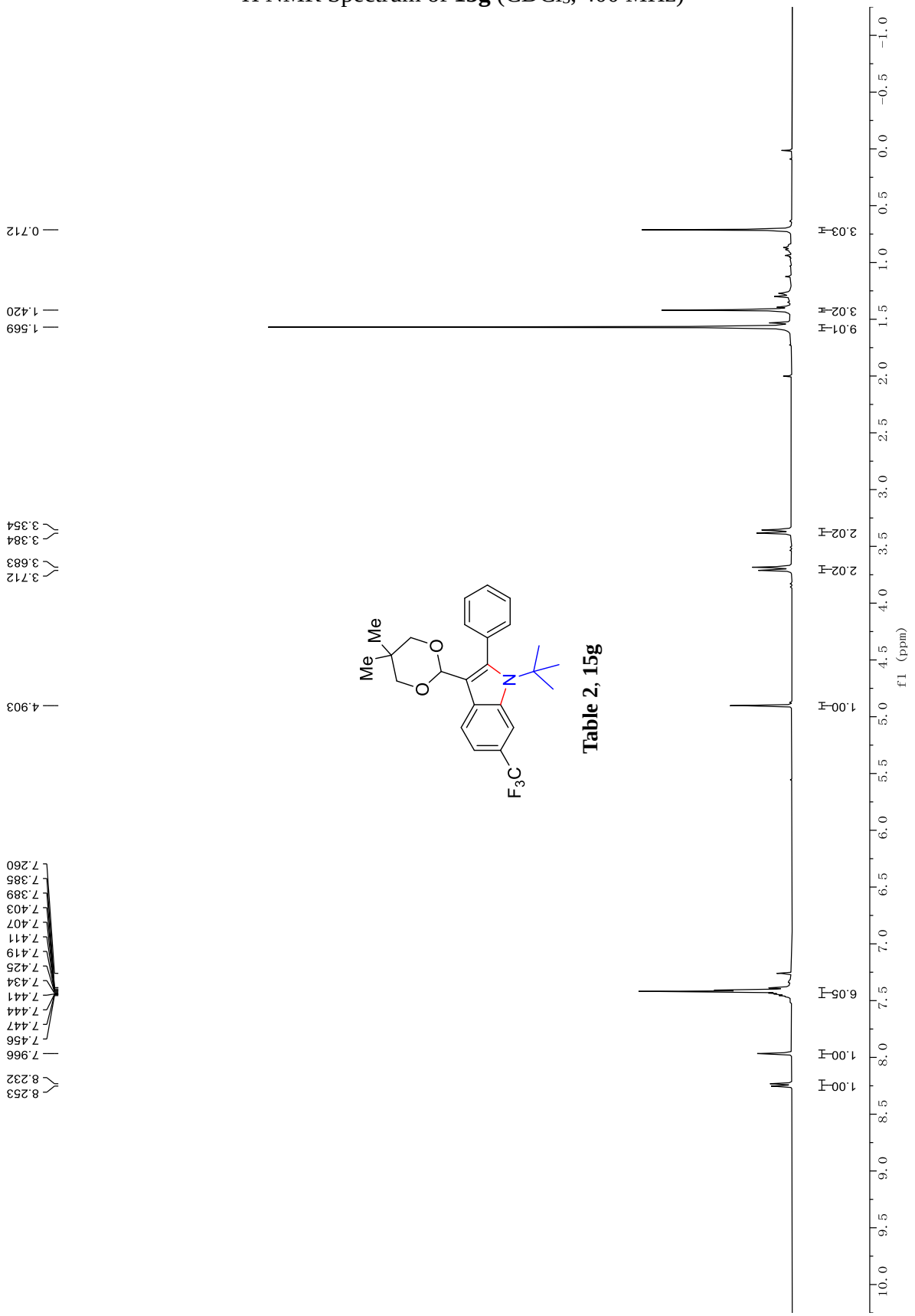
^{1}H NMR Spectrum of **15f** ($CDCl_3$, 400 MHz)



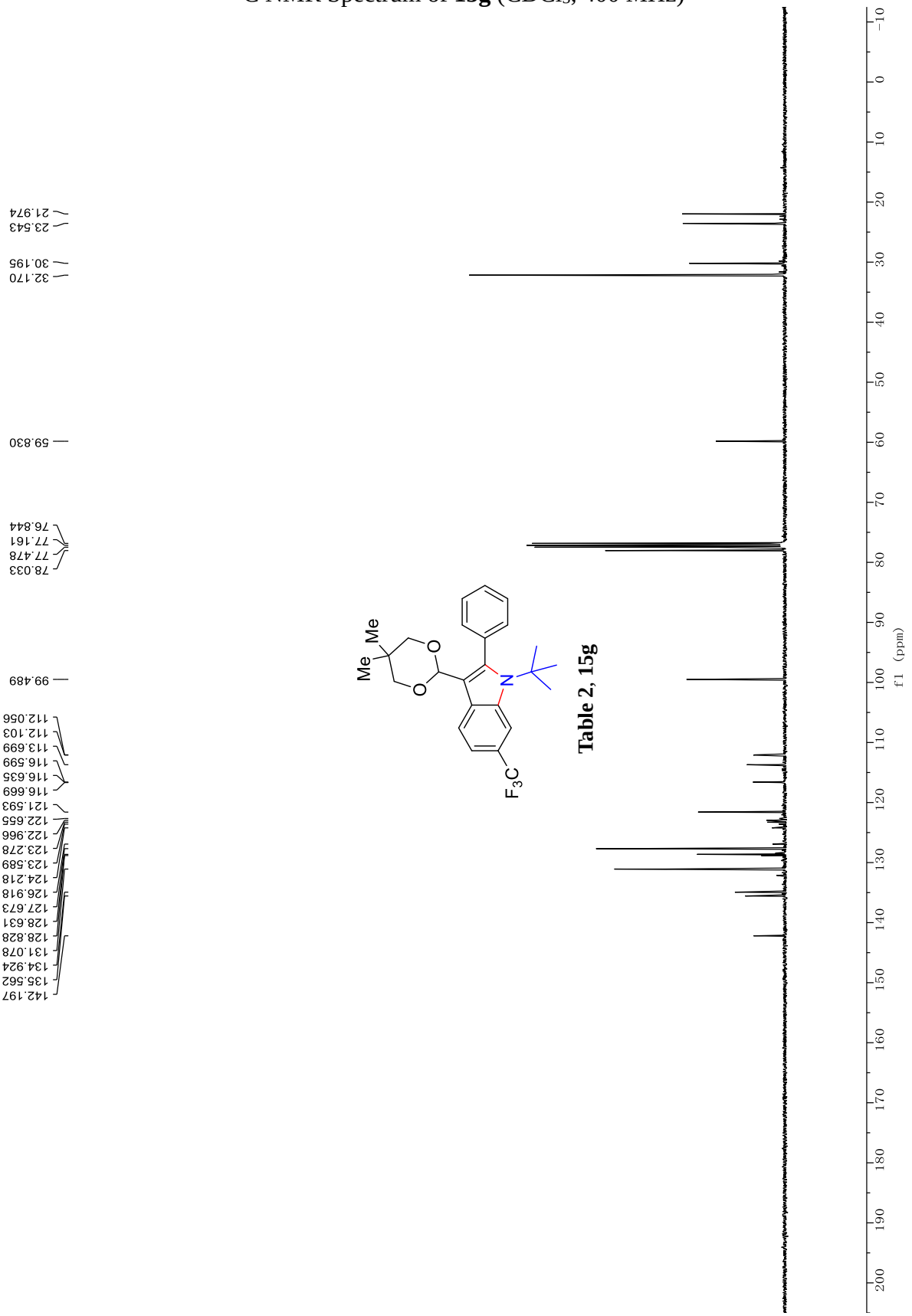
^{13}C NMR Spectrum of **15f** ($CDCl_3$, 400 MHz)



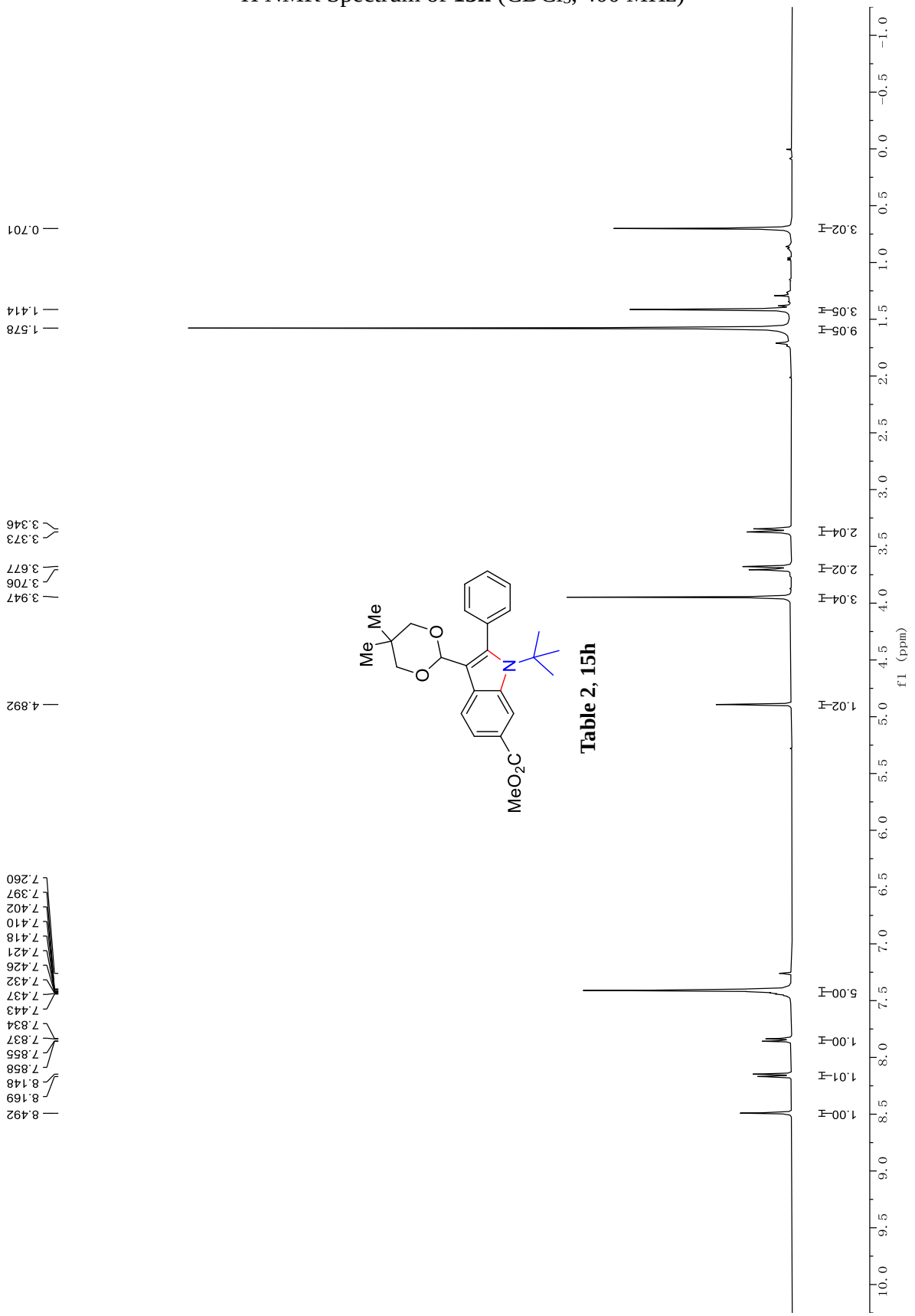
^{1}H NMR Spectrum of **15g** ($CDCl_3$, 400 MHz)



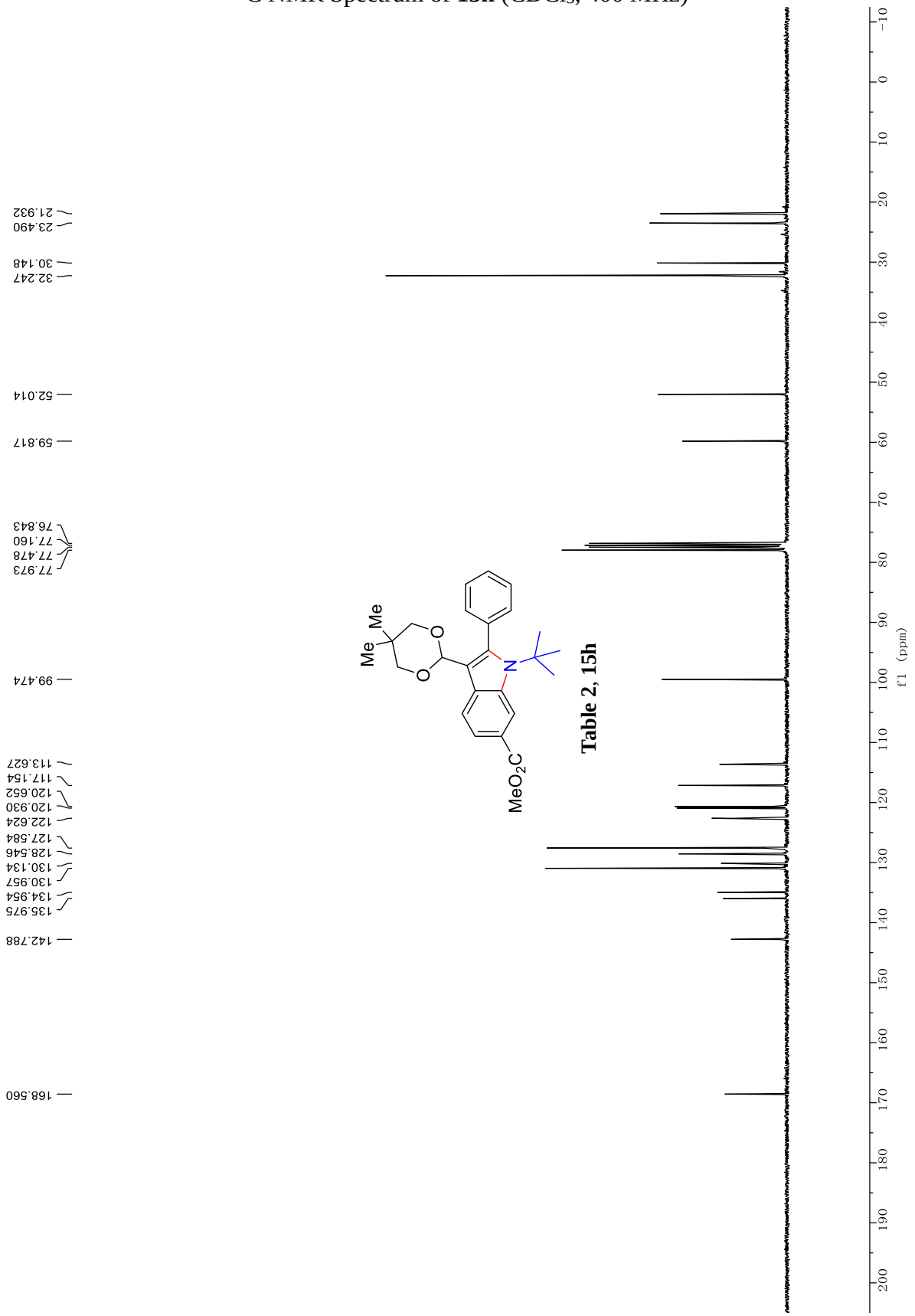
^{13}C NMR Spectrum of **15g** ($CDCl_3$, 400 MHz)



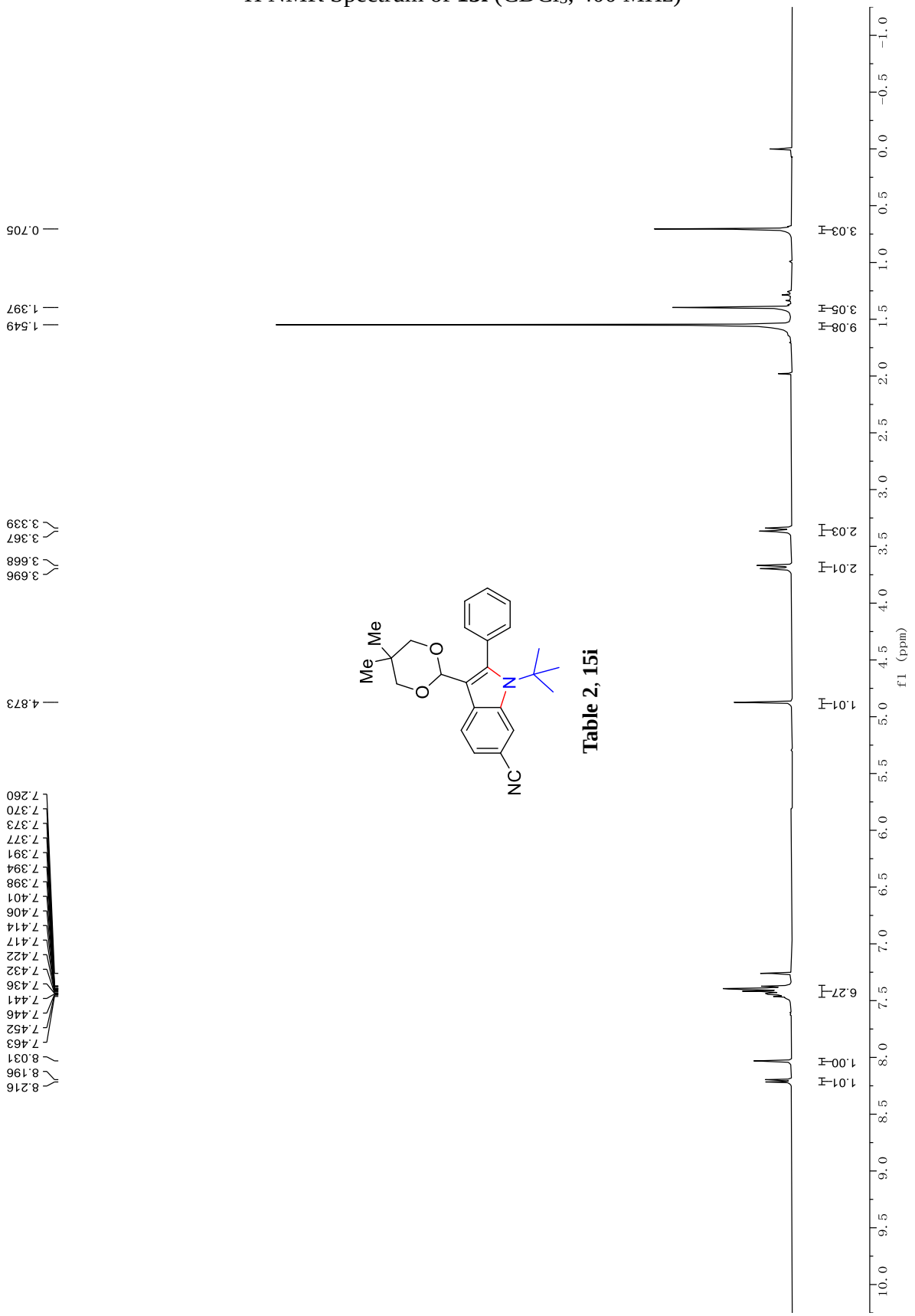
^{1}H NMR Spectrum of **15h** ($CDCl_3$, 400 MHz)



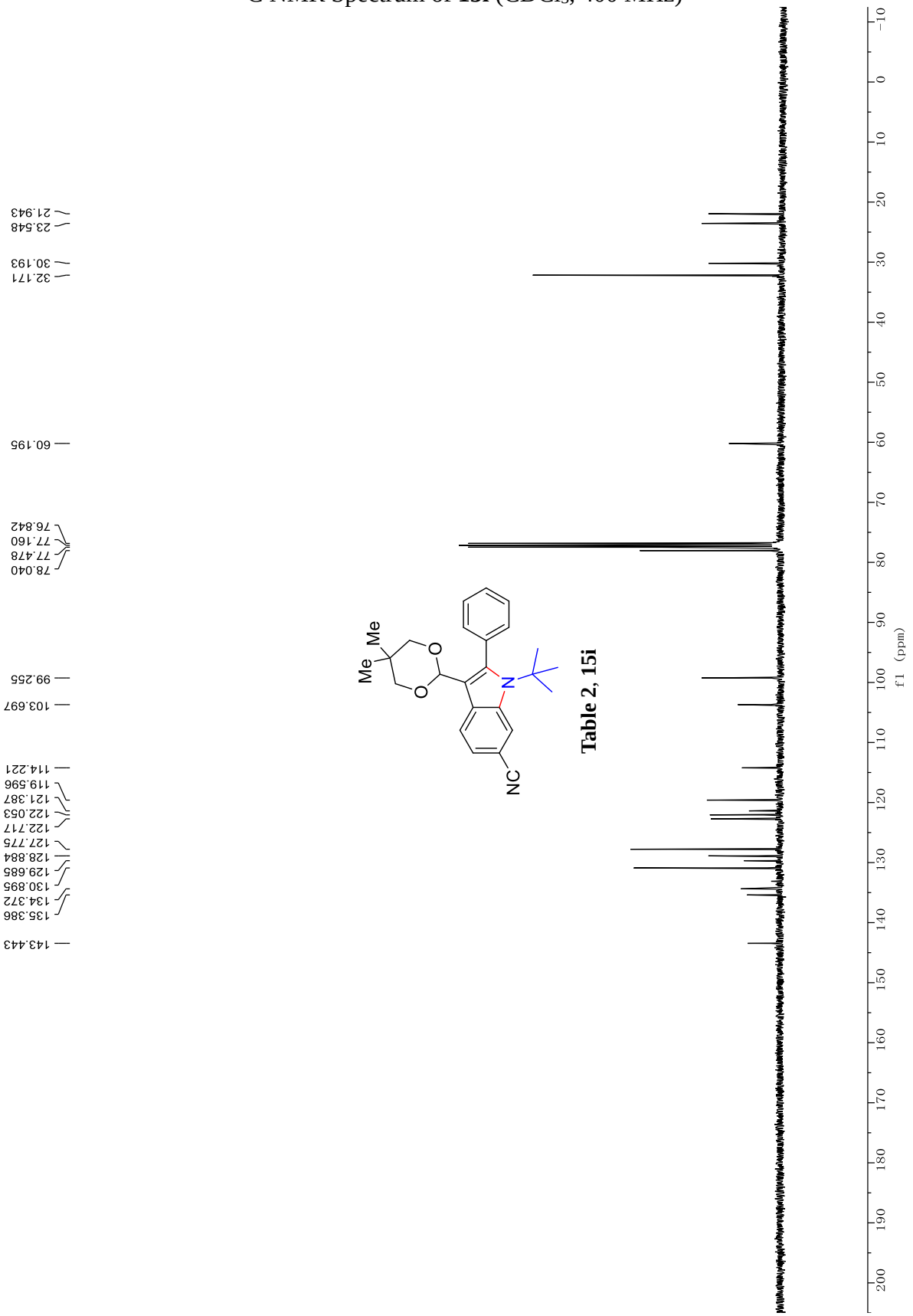
^{13}C NMR Spectrum of **15h** ($CDCl_3$, 400 MHz)



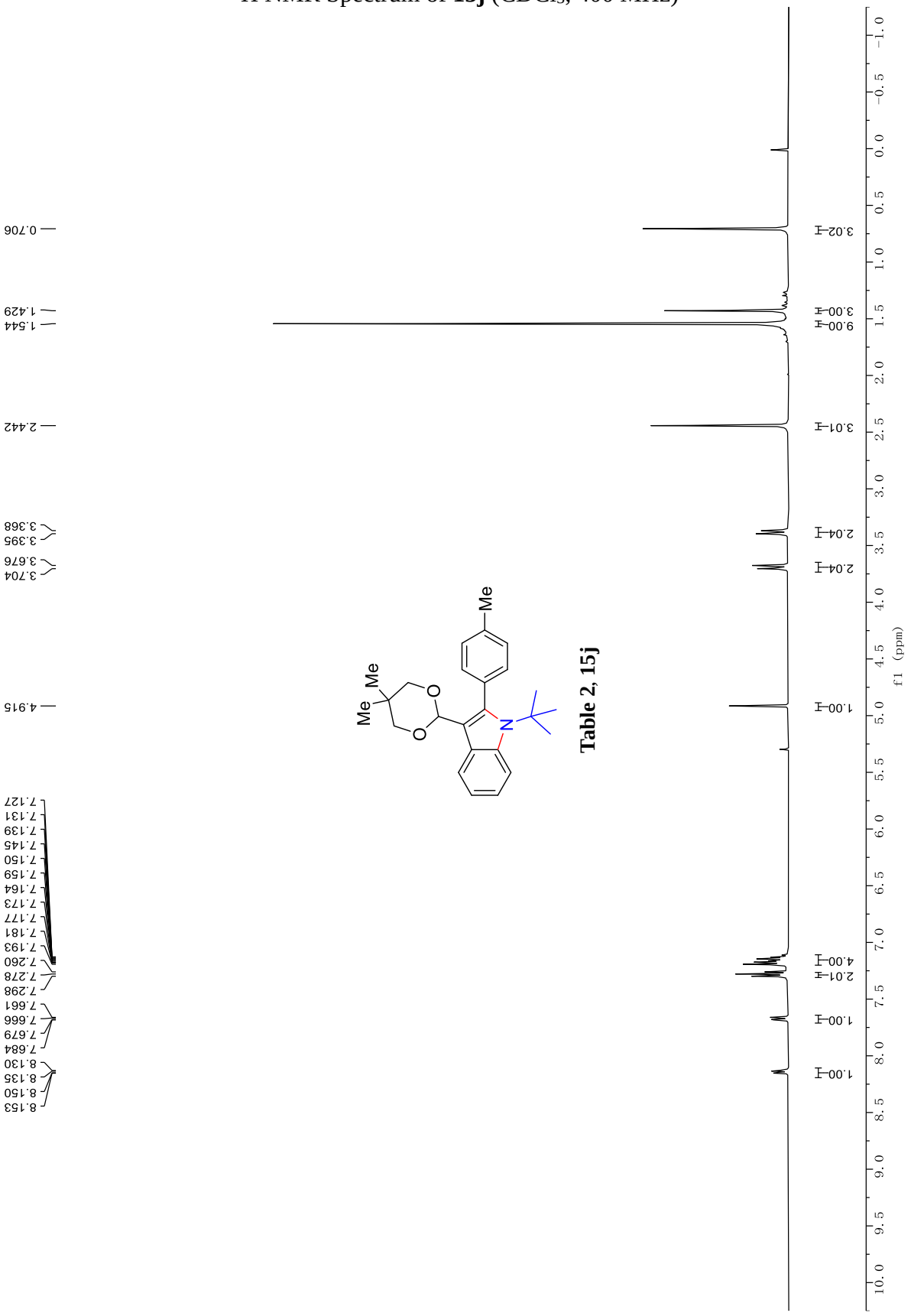
^{1}H NMR Spectrum of **15i** ($CDCl_3$, 400 MHz)



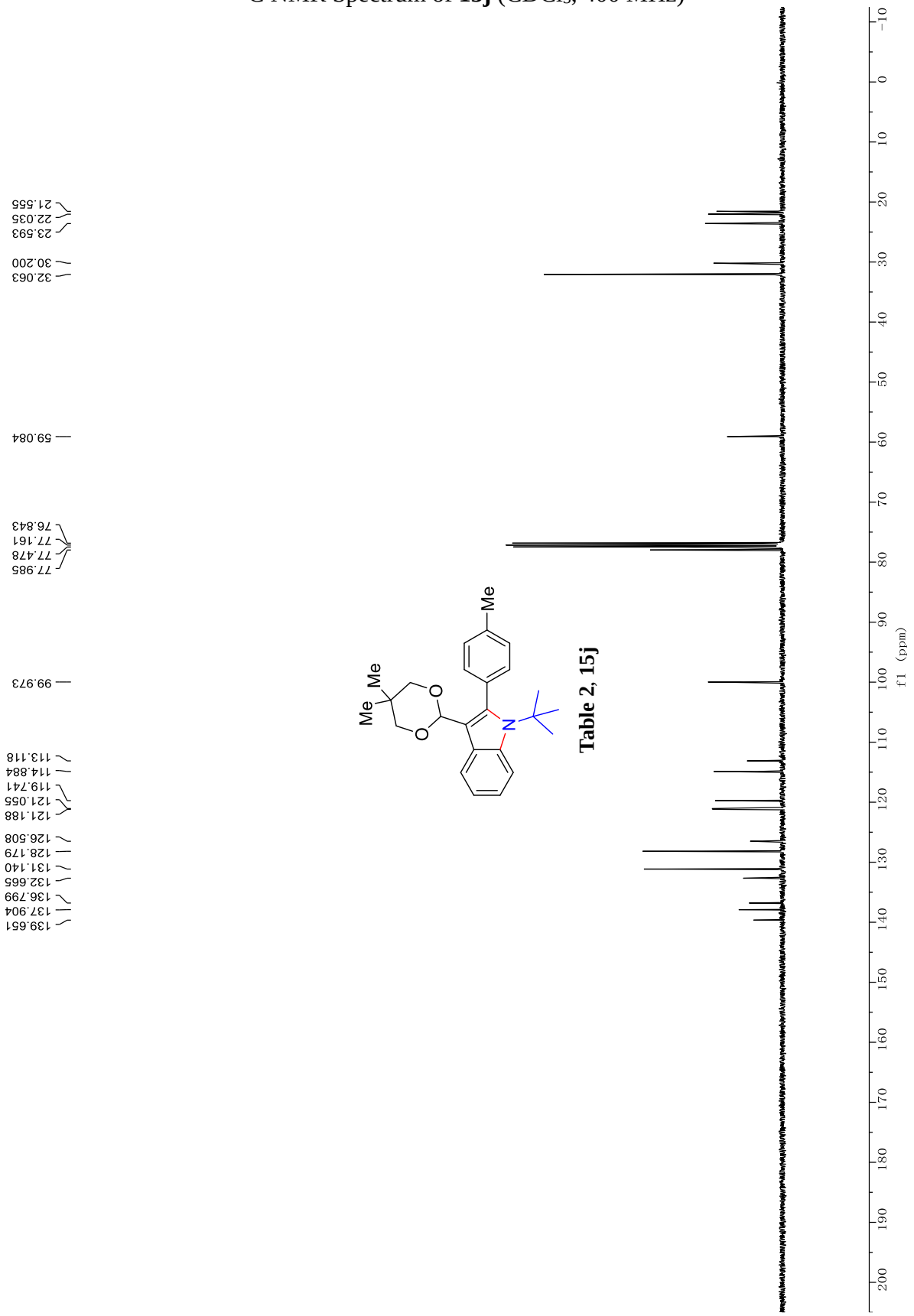
^{13}C NMR Spectrum of **15i** ($CDCl_3$, 400 MHz)



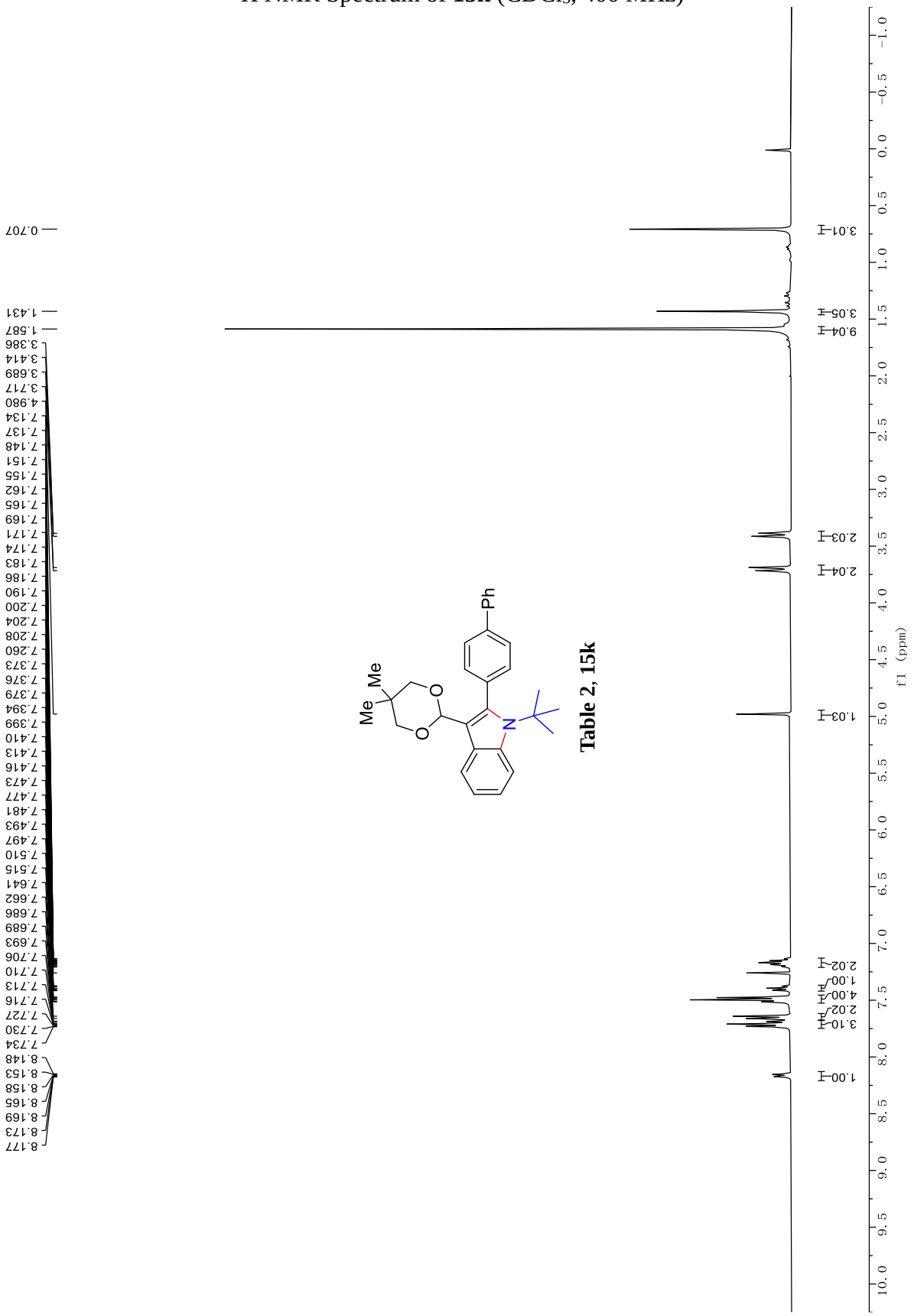
^{1}H NMR Spectrum of **15j** ($CDCl_3$, 400 MHz)



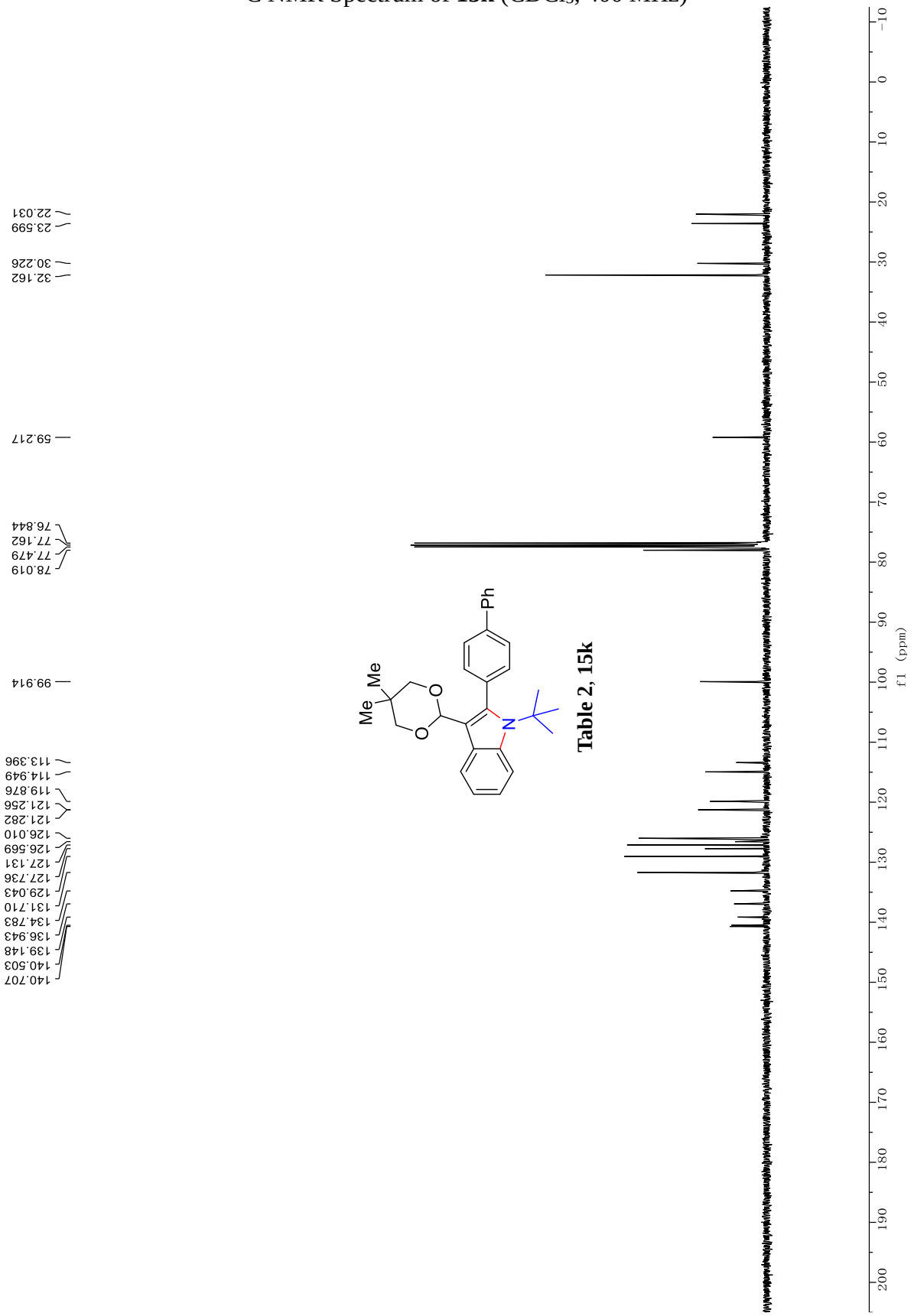
^{13}C NMR Spectrum of **15j** ($CDCl_3$, 400 MHz)



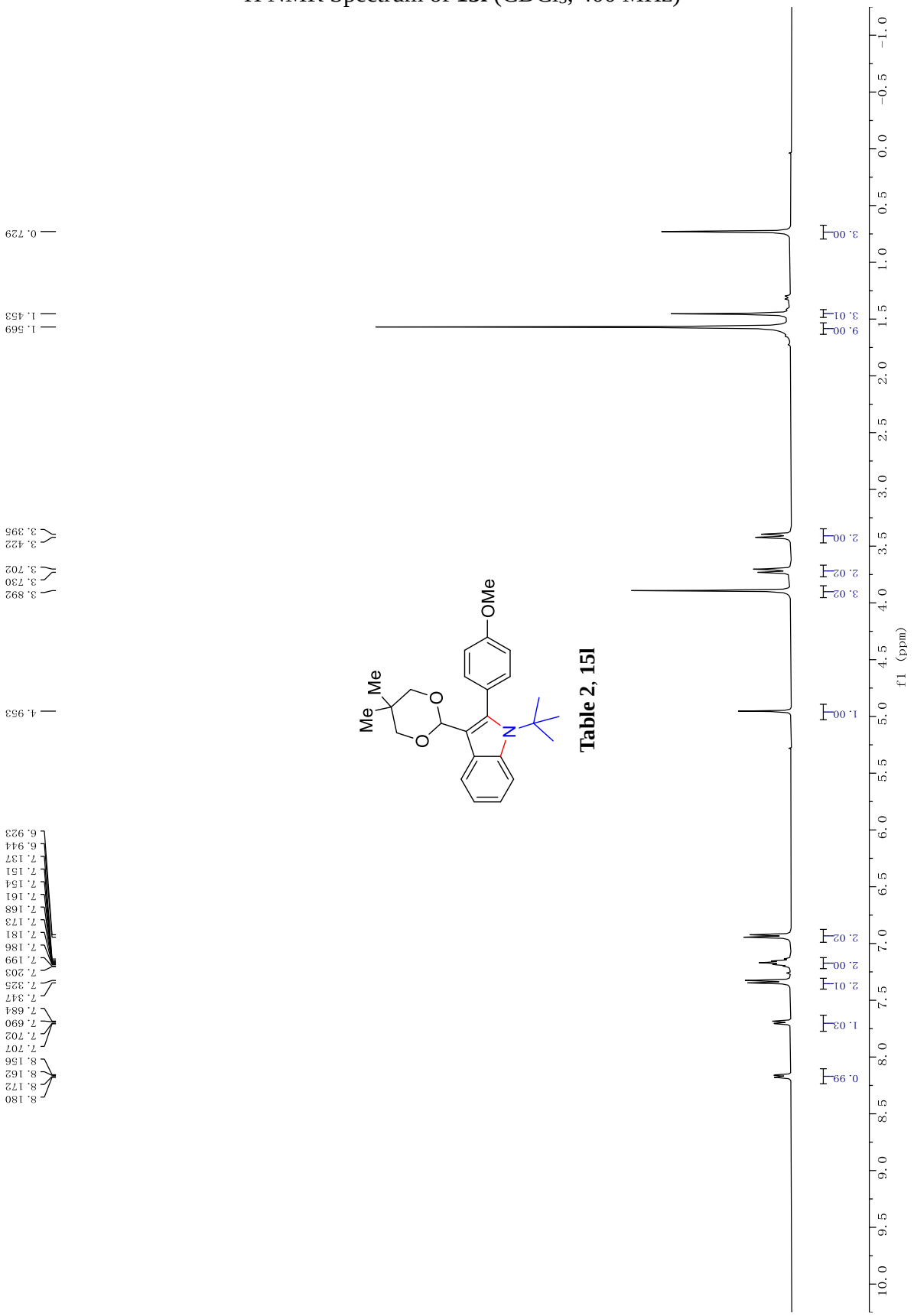
^{1}H NMR Spectrum of **15k** ($CDCl_3$, 400 MHz)



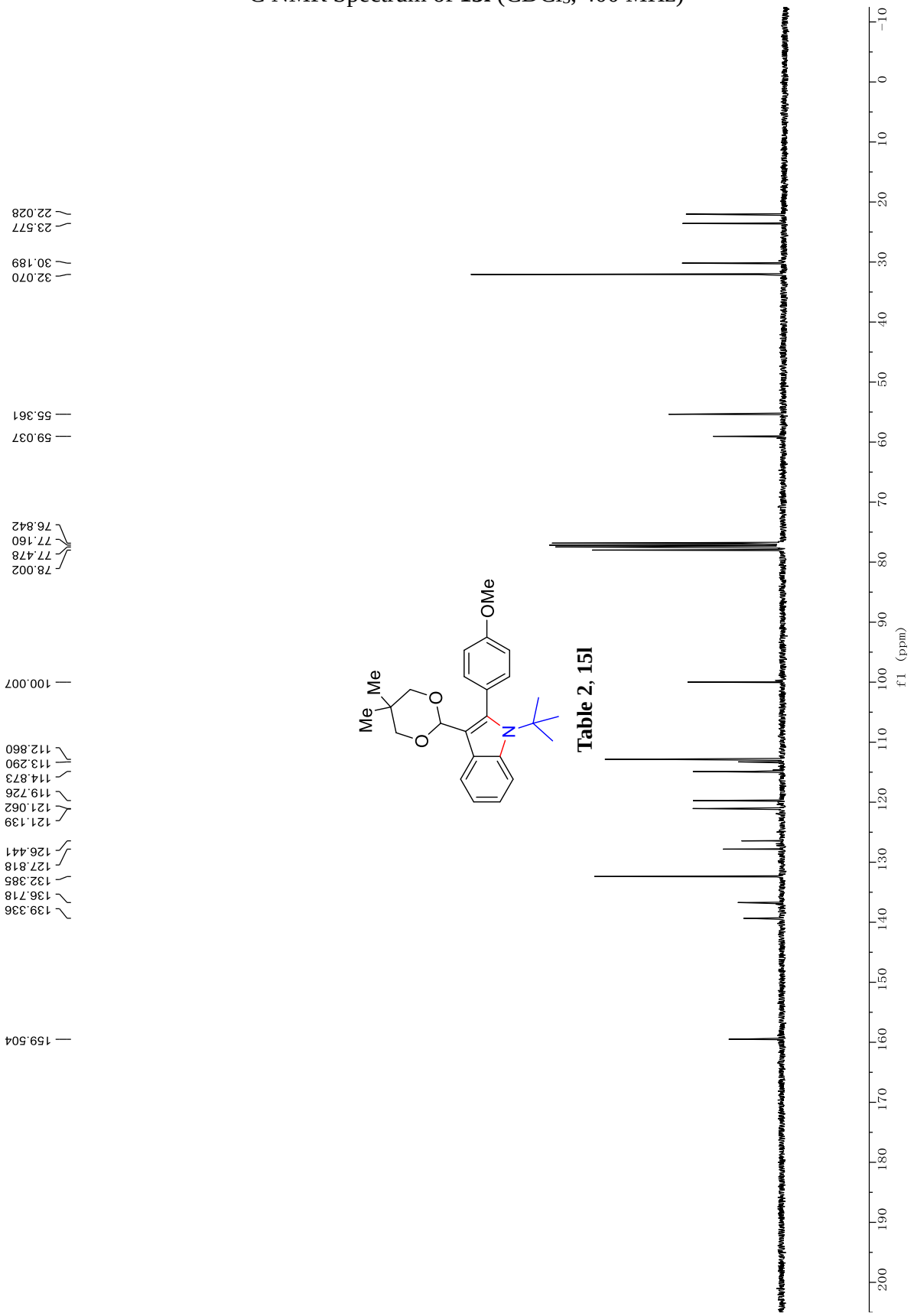
^{13}C NMR Spectrum of **15k** ($CDCl_3$, 400 MHz)



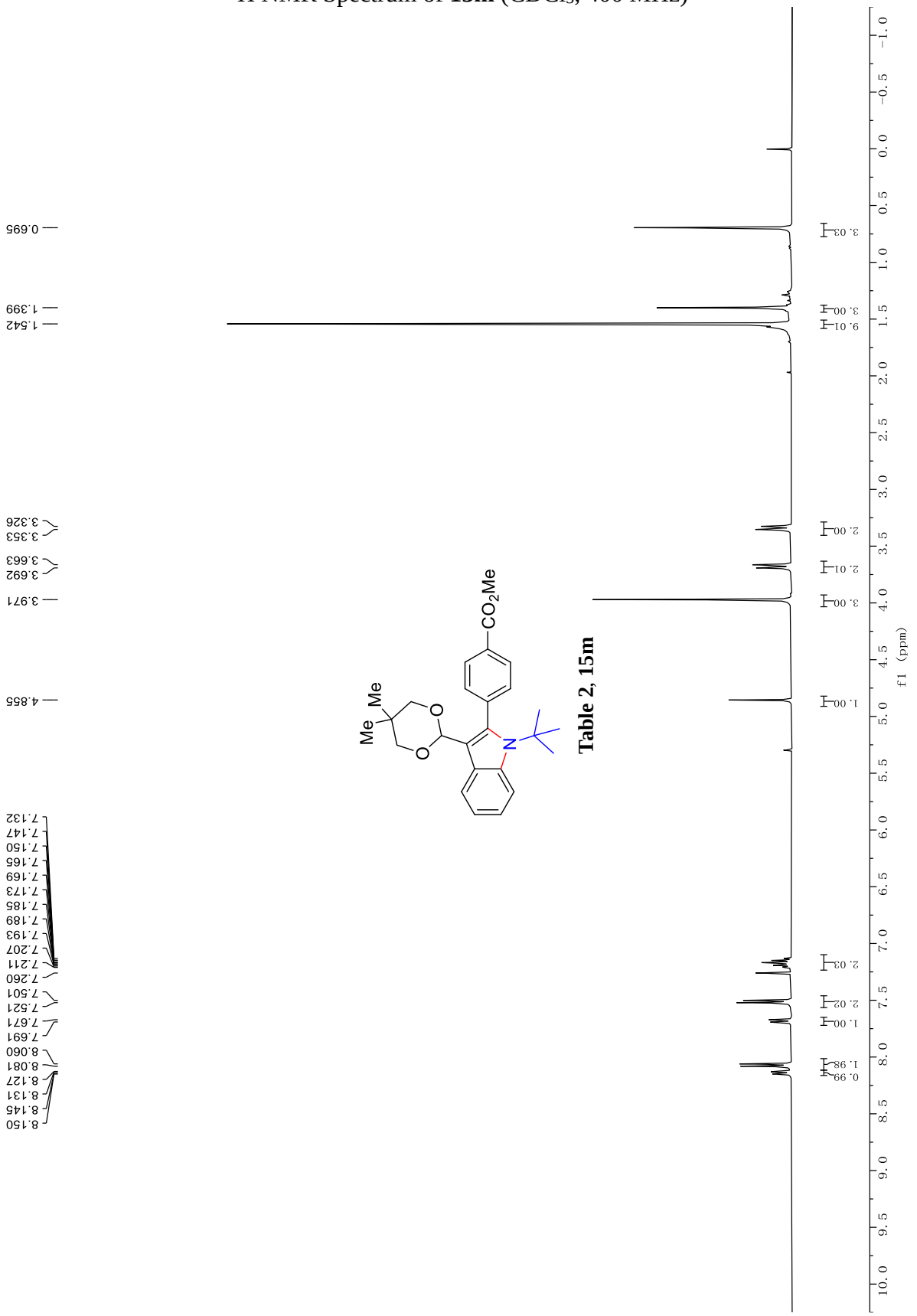
^{1}H NMR Spectrum of **15l** ($CDCl_3$, 400 MHz)



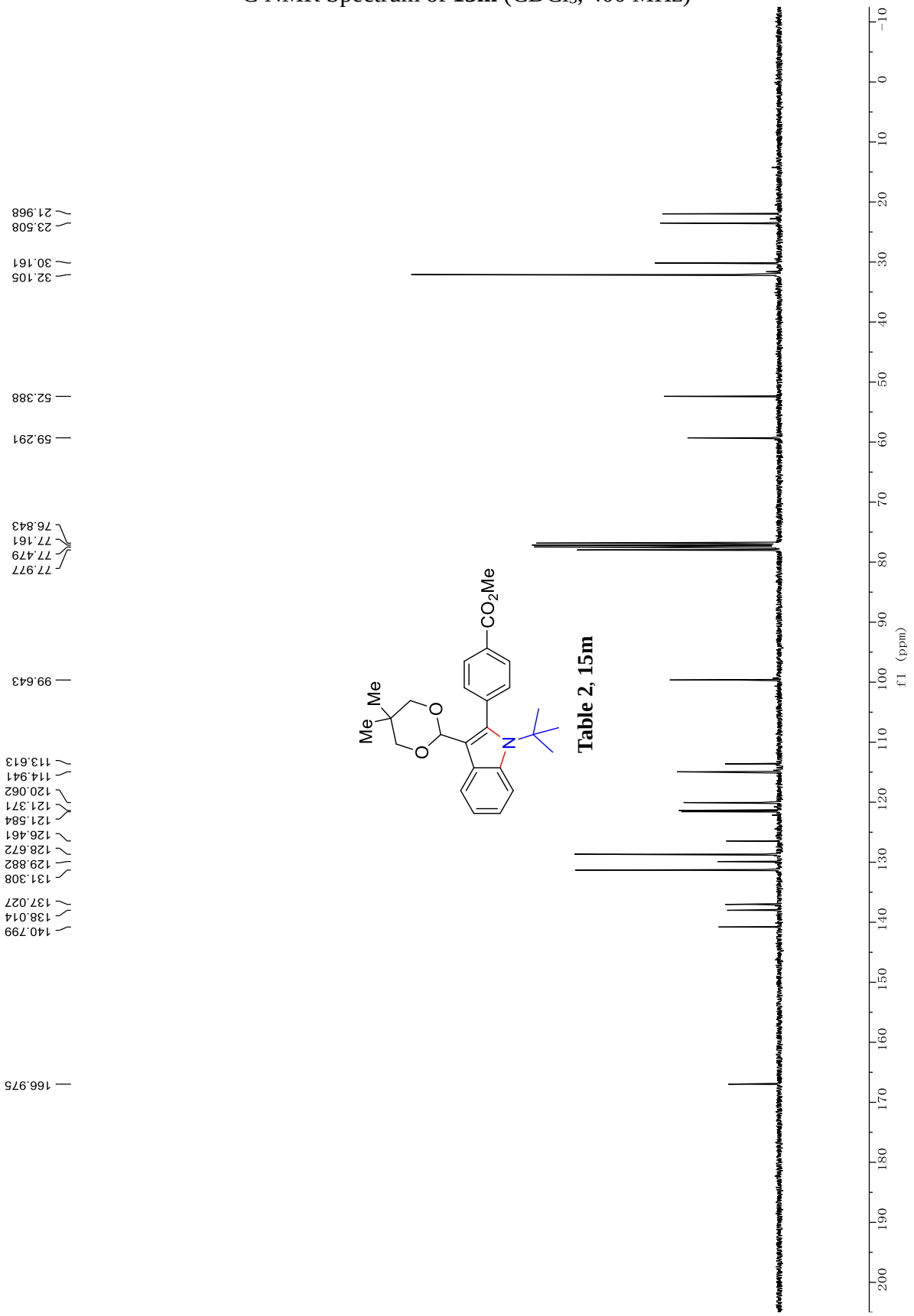
^{13}C NMR Spectrum of **15l** ($CDCl_3$, 400 MHz)



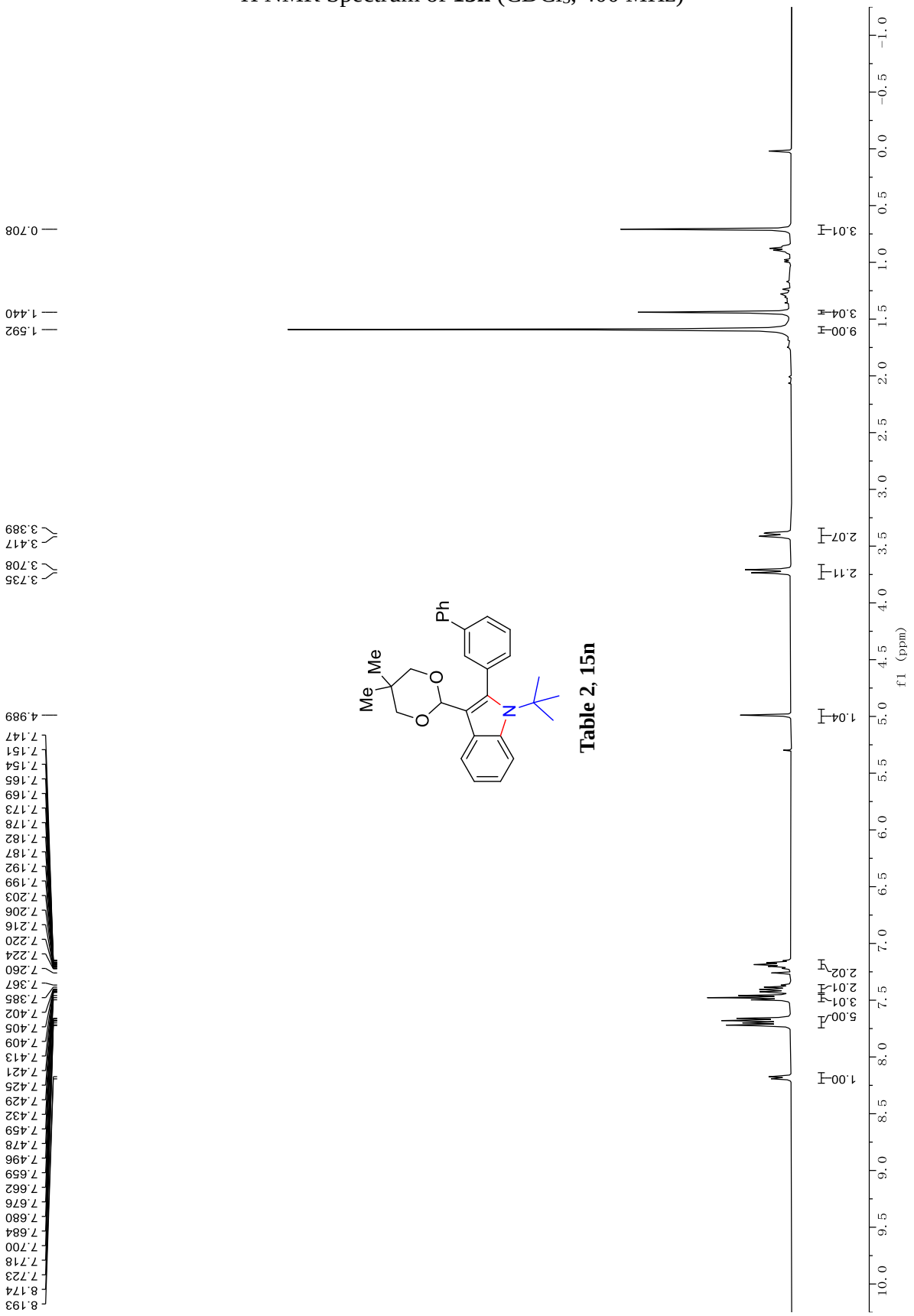
^{1}H NMR Spectrum of **15m** ($CDCl_3$, 400 MHz)



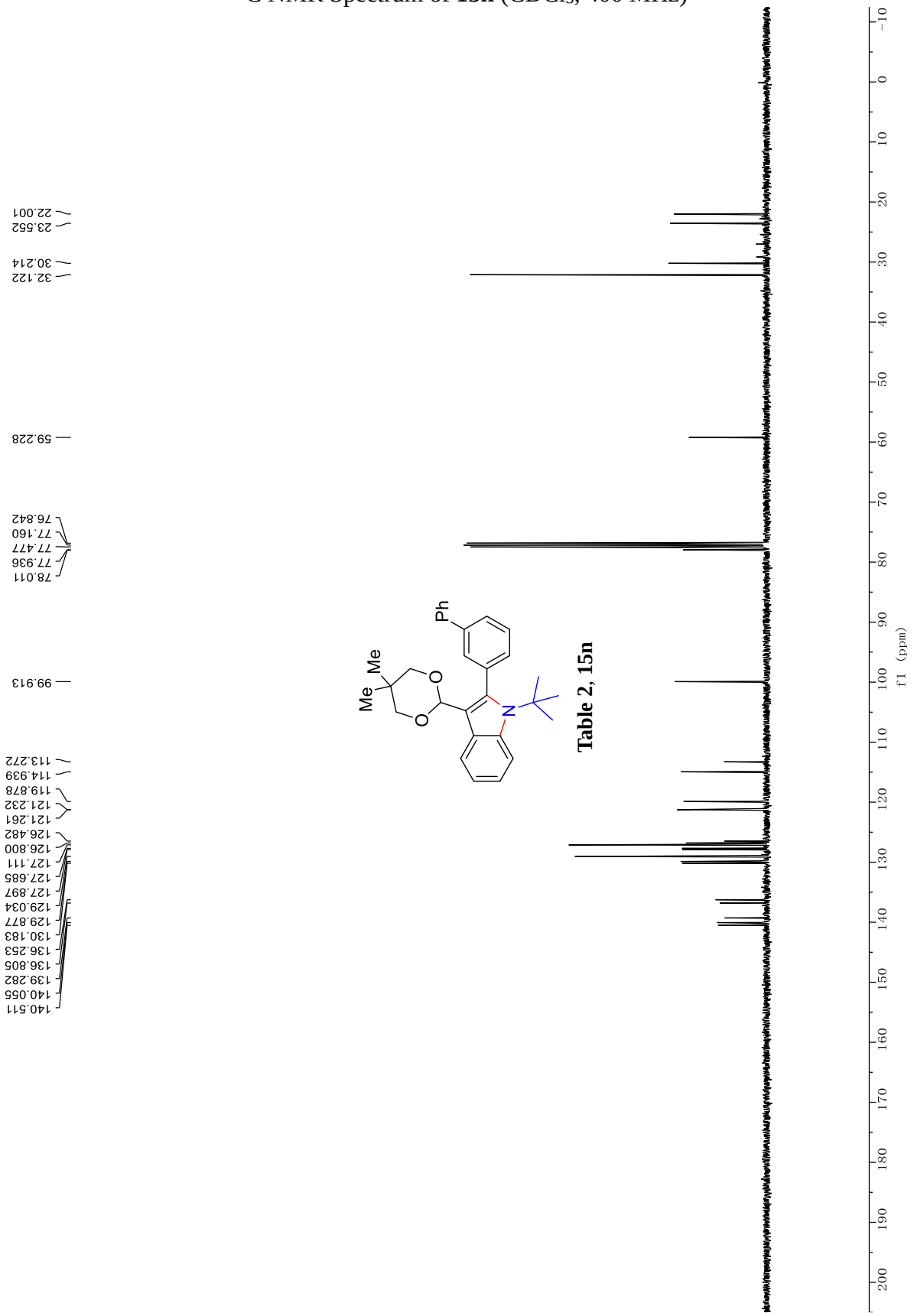
^{13}C NMR Spectrum of **15m** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **15n** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **15n** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **15o** ($CDCl_3$, 400 MHz)

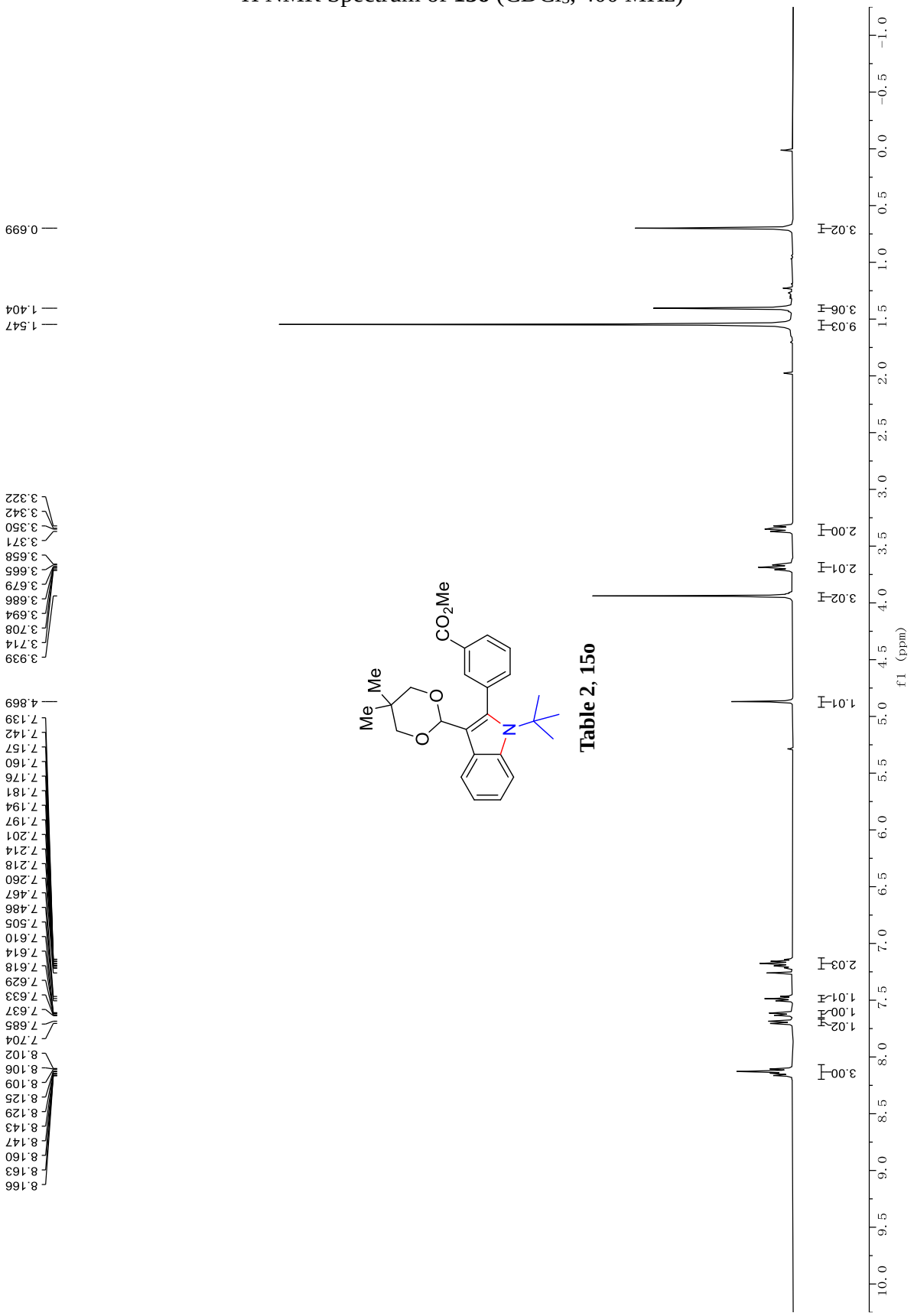
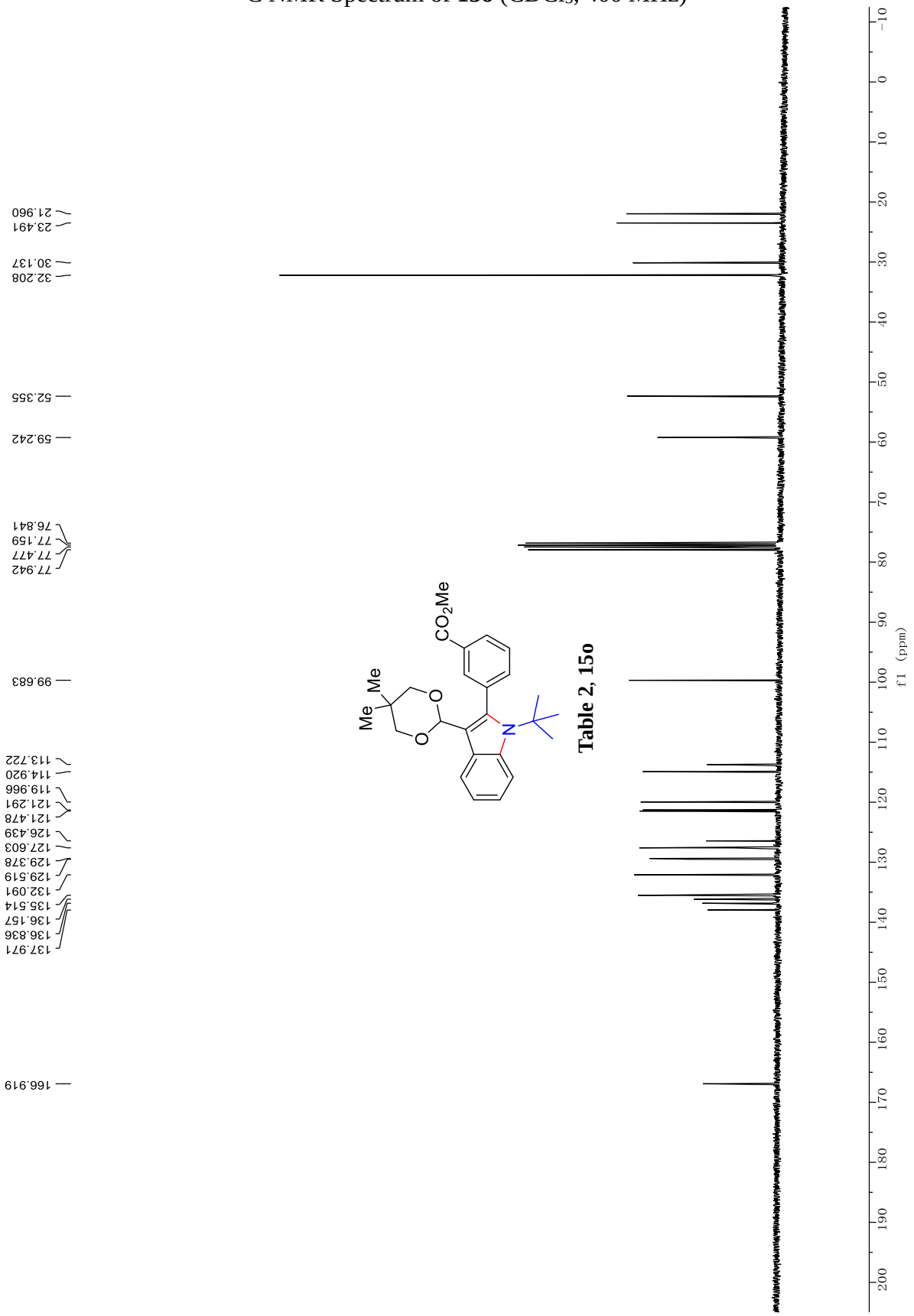
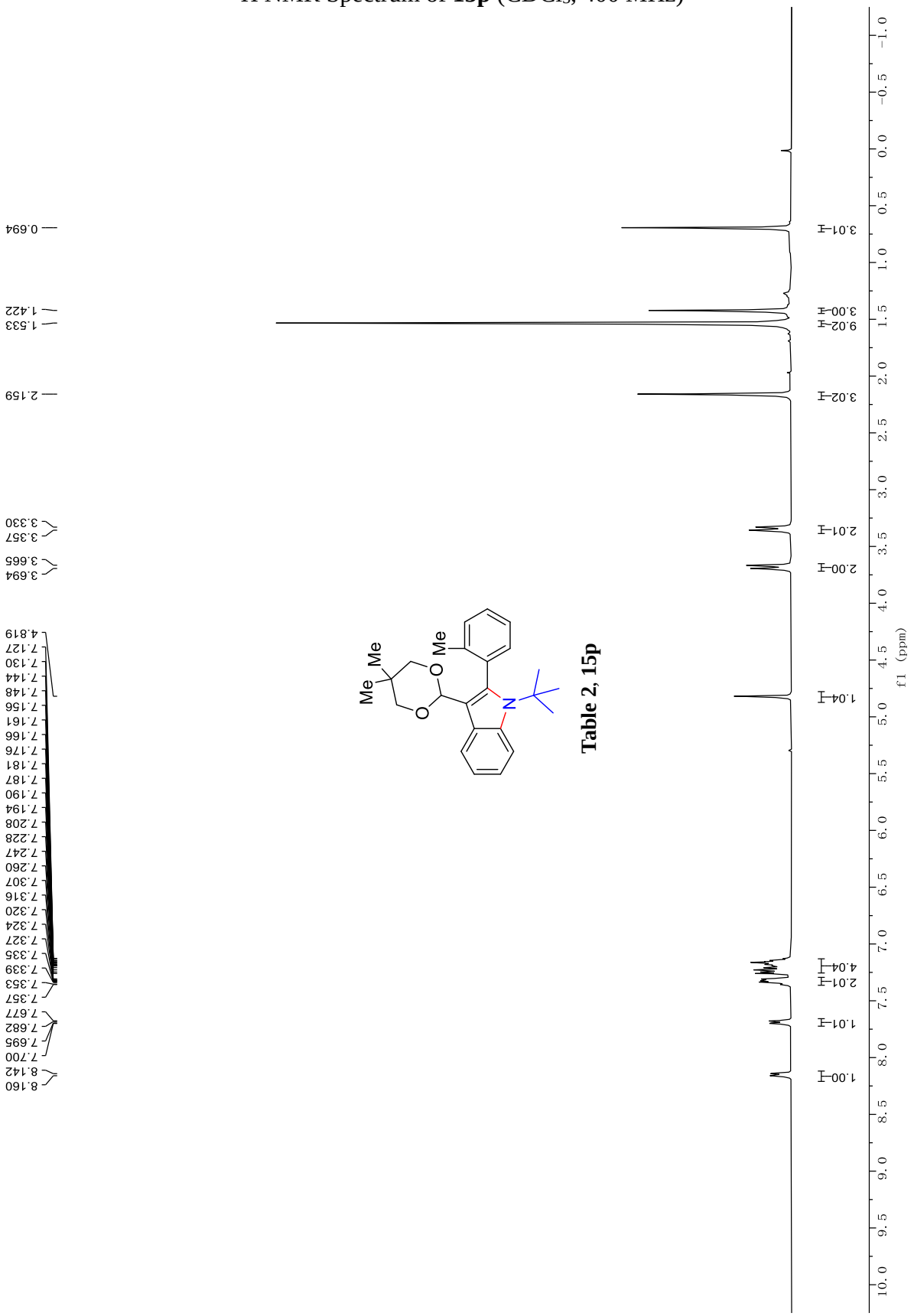


Table 2, 15o

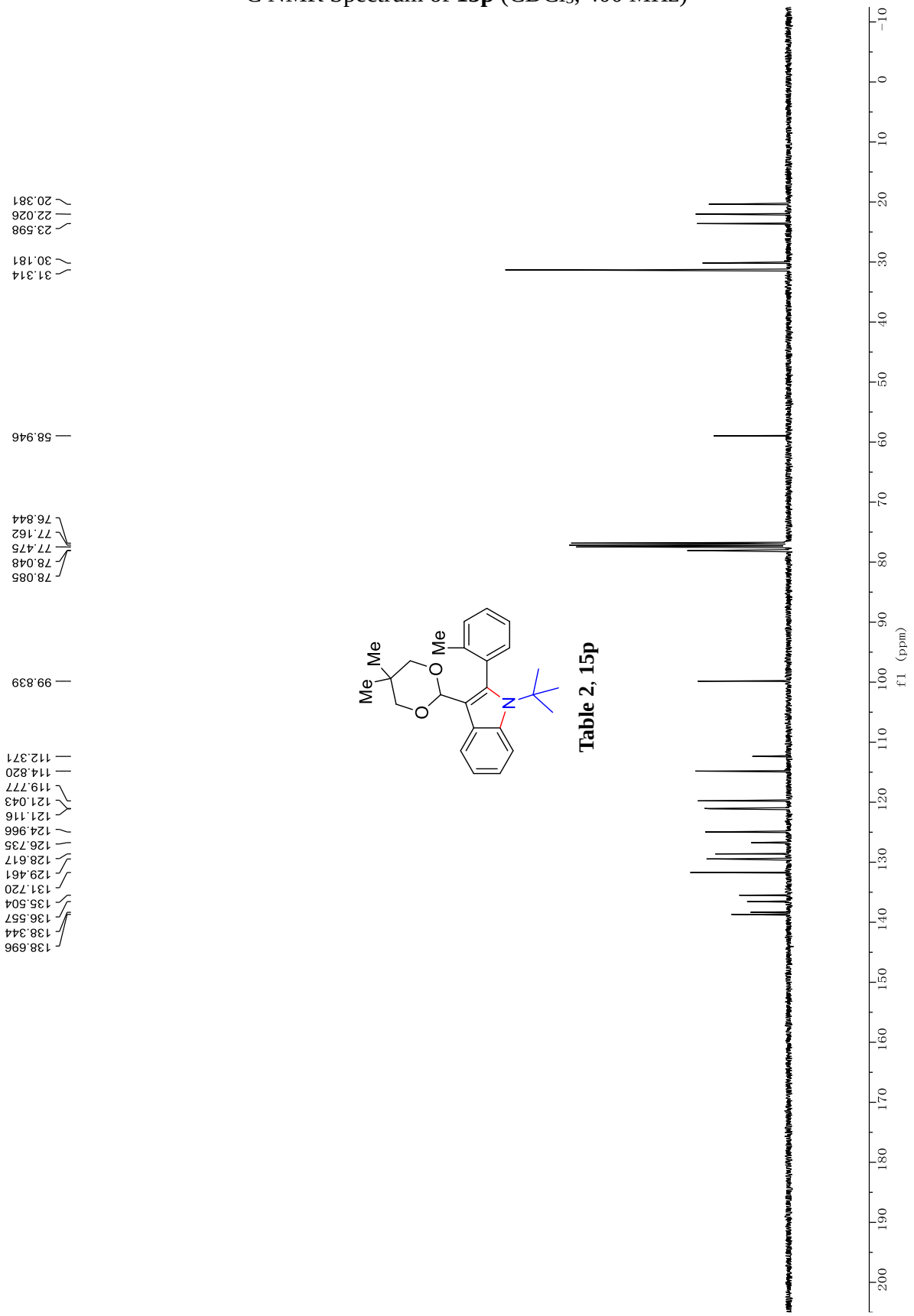
^{13}C NMR Spectrum of **15o** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **15p** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **15p** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **15q** ($CDCl_3$, 400 MHz)

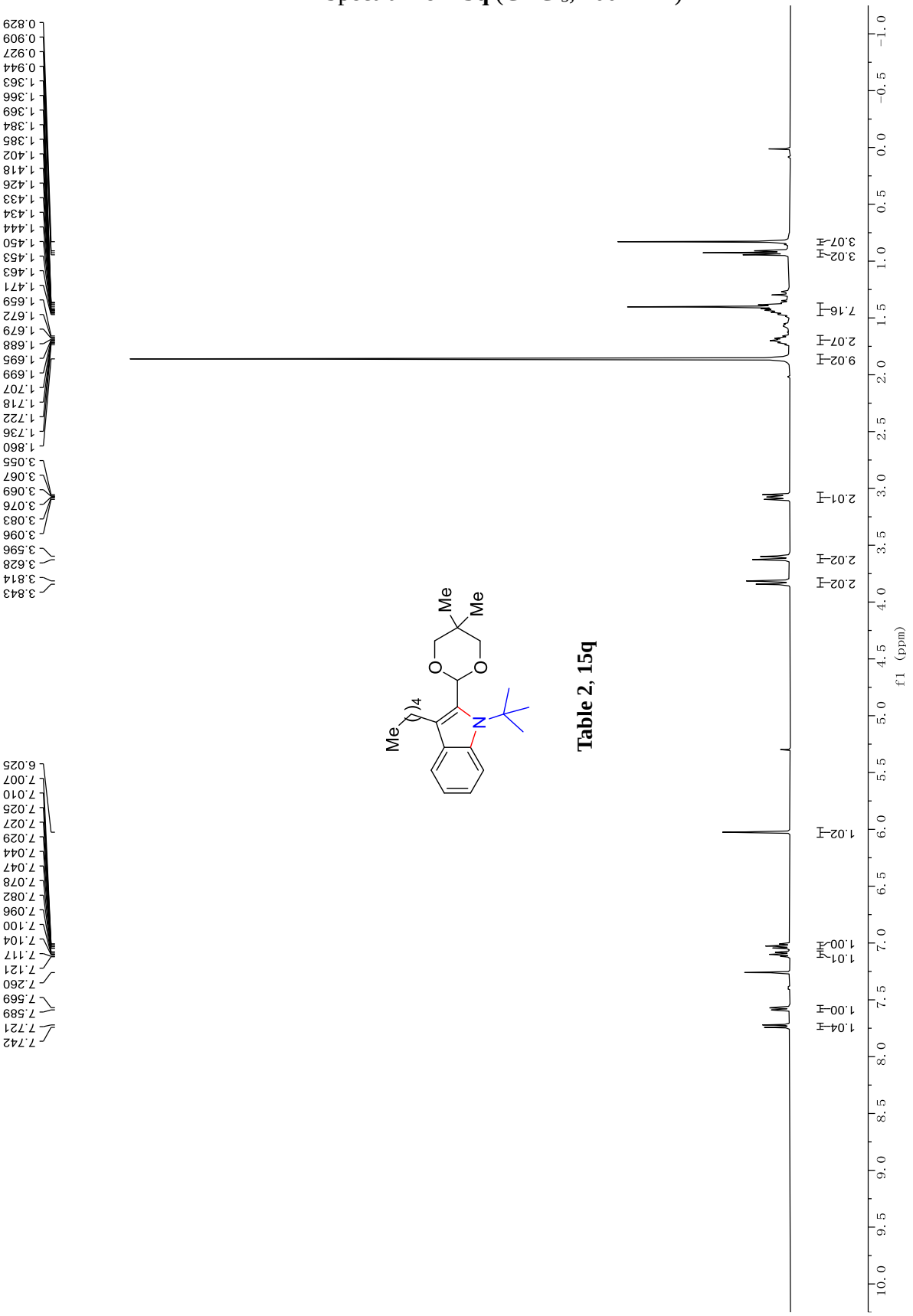
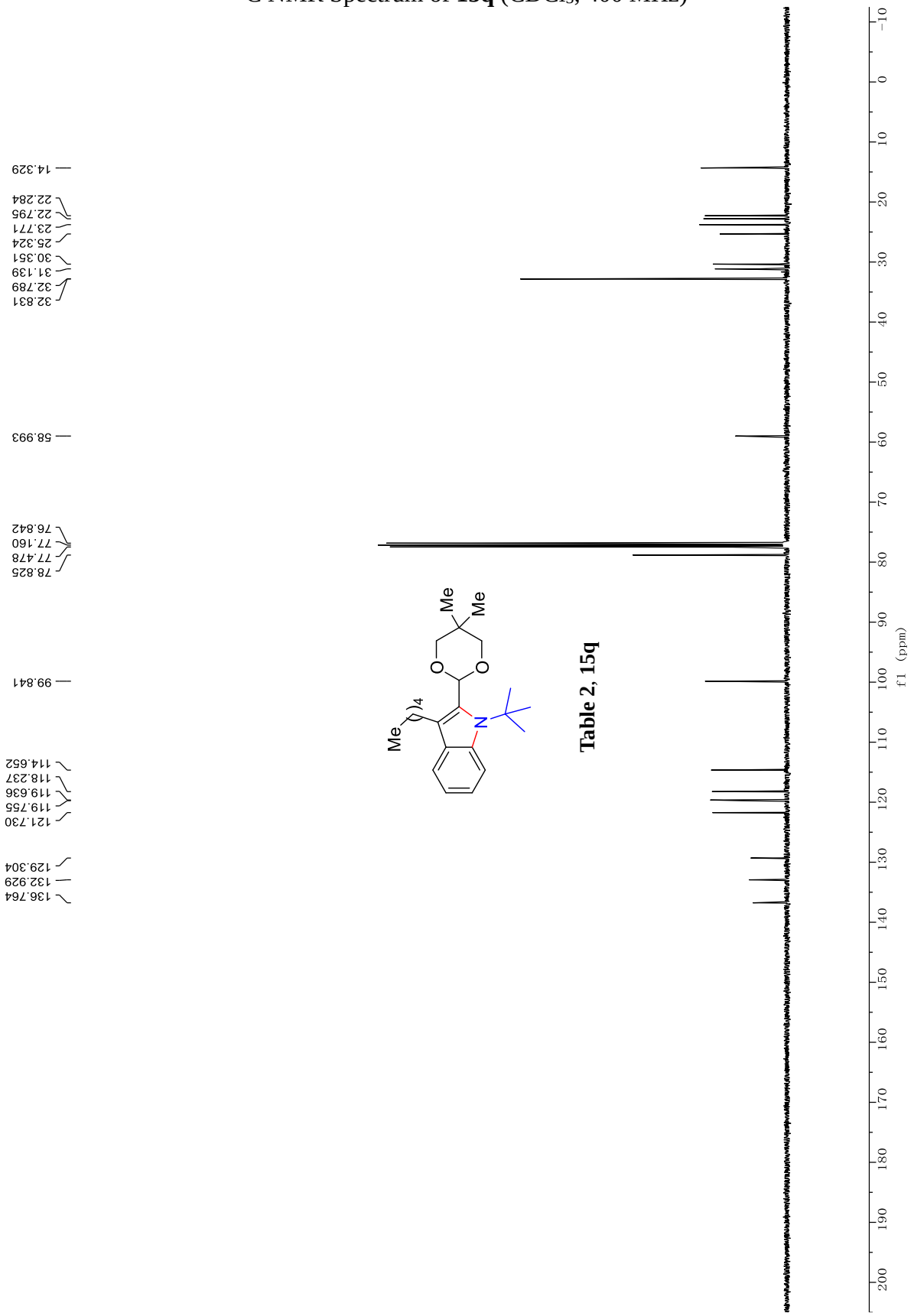
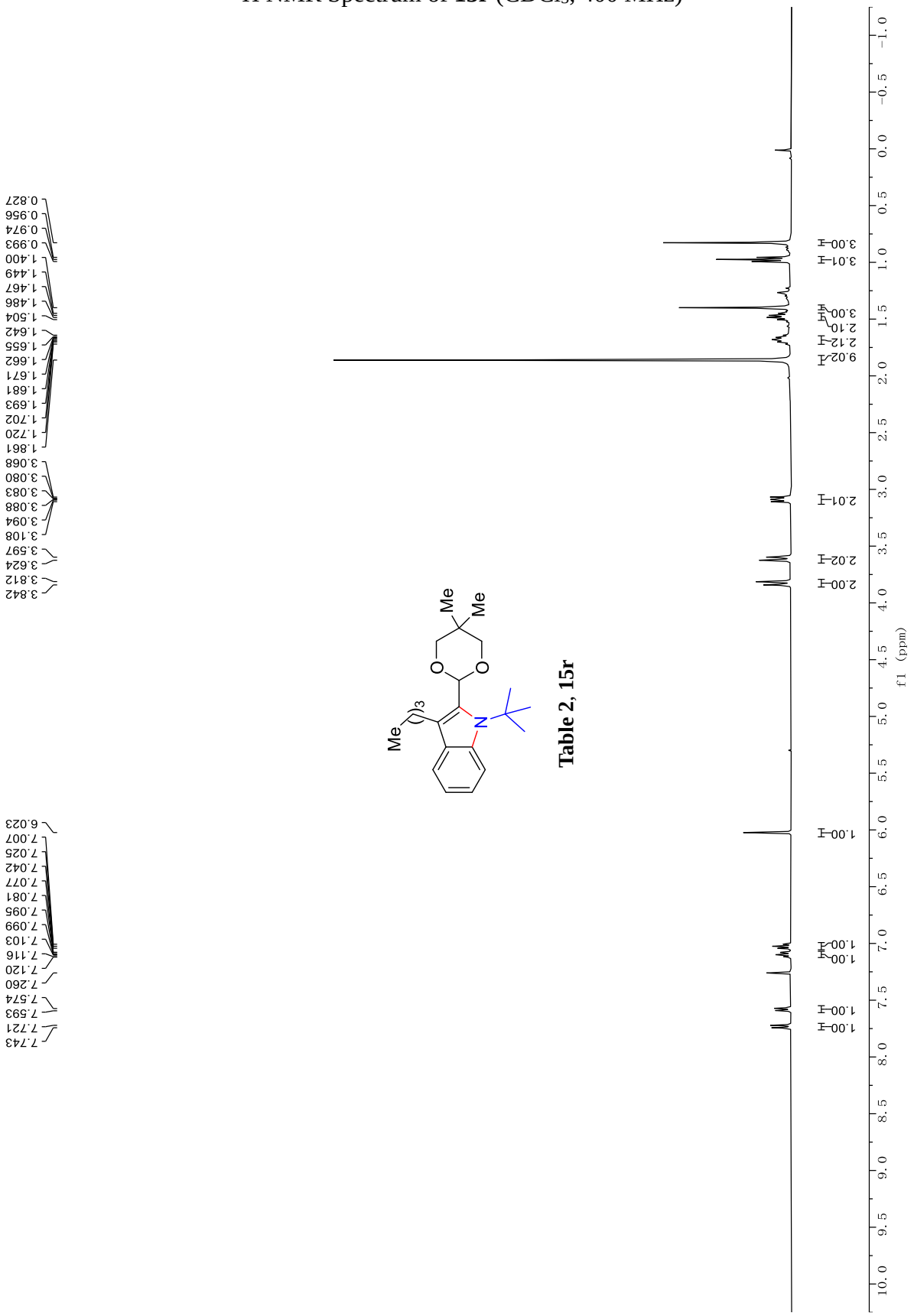


Table 2, 15q

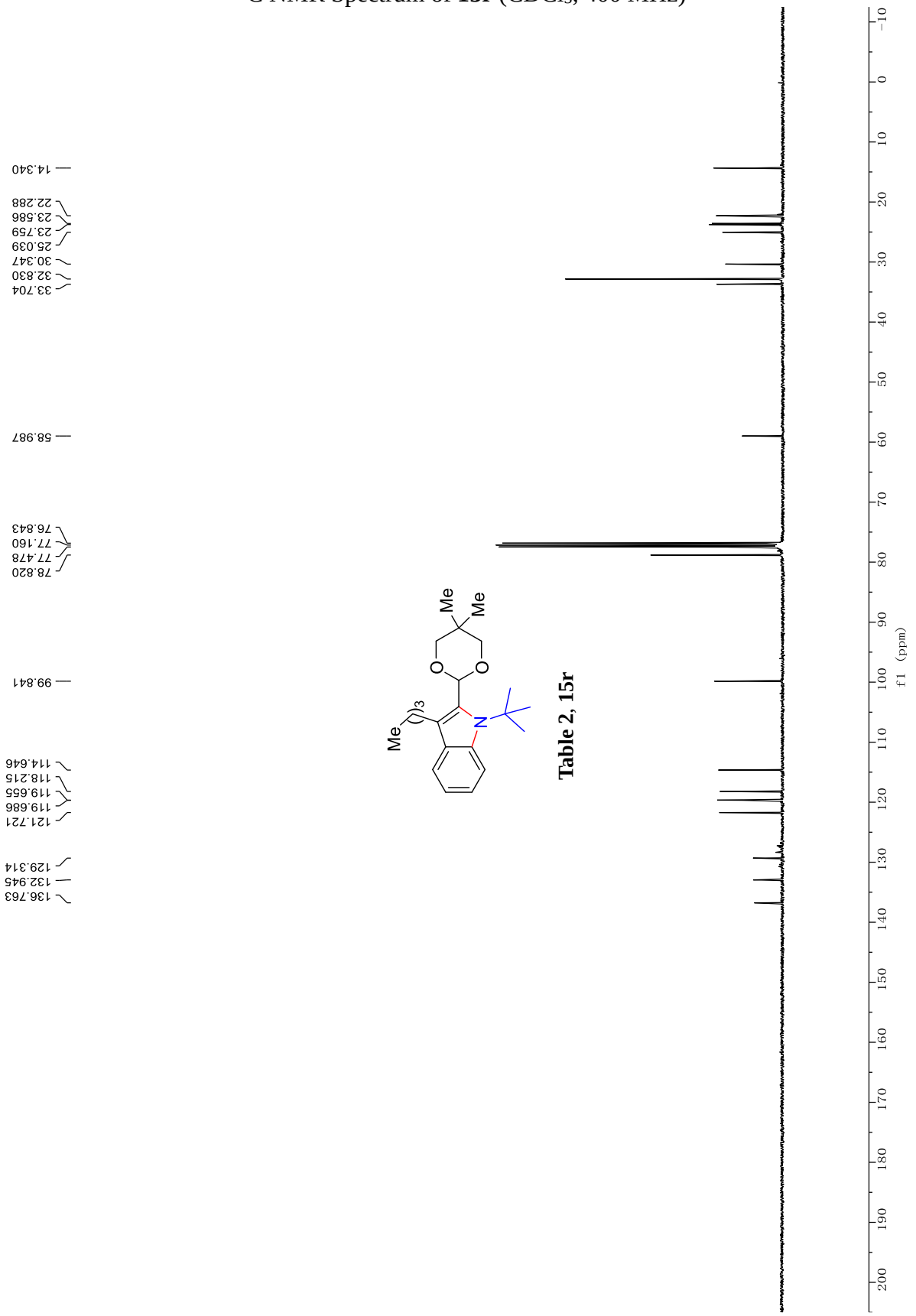
^{13}C NMR Spectrum of **15q** ($CDCl_3$, 400 MHz)



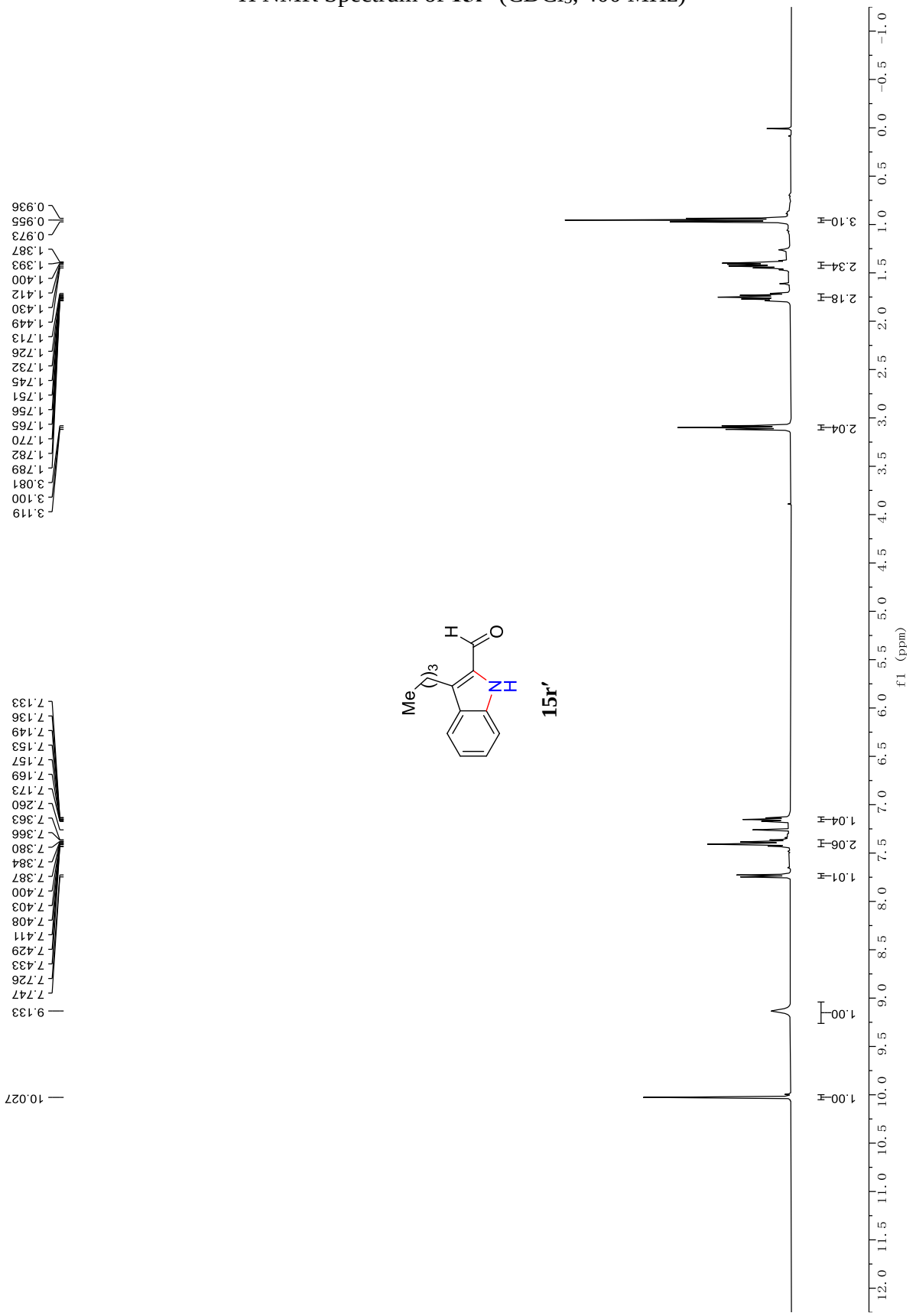
^{1}H NMR Spectrum of **15r** ($CDCl_3$, 400 MHz)



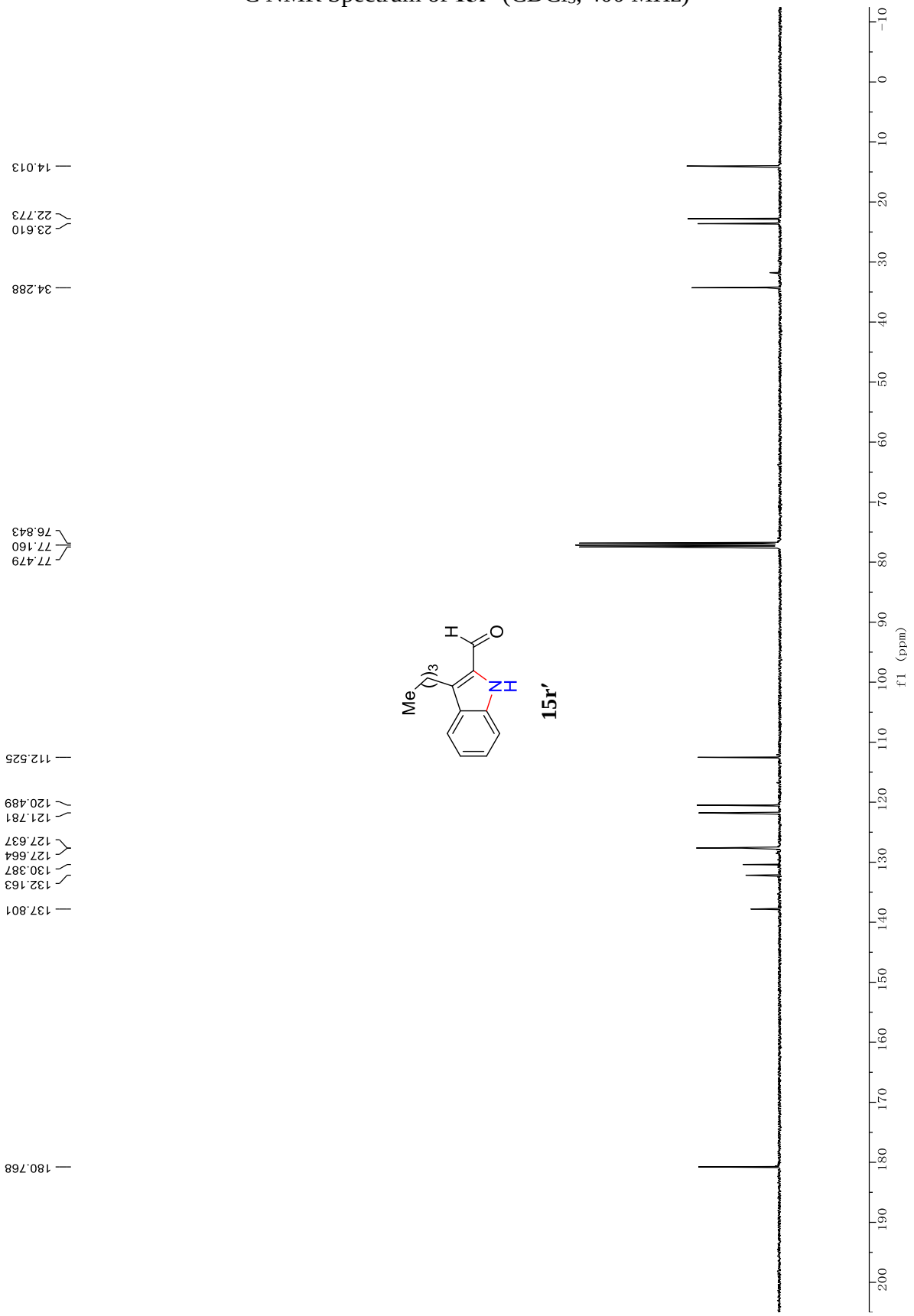
^{13}C NMR Spectrum of **15r** ($CDCl_3$, 400 MHz)



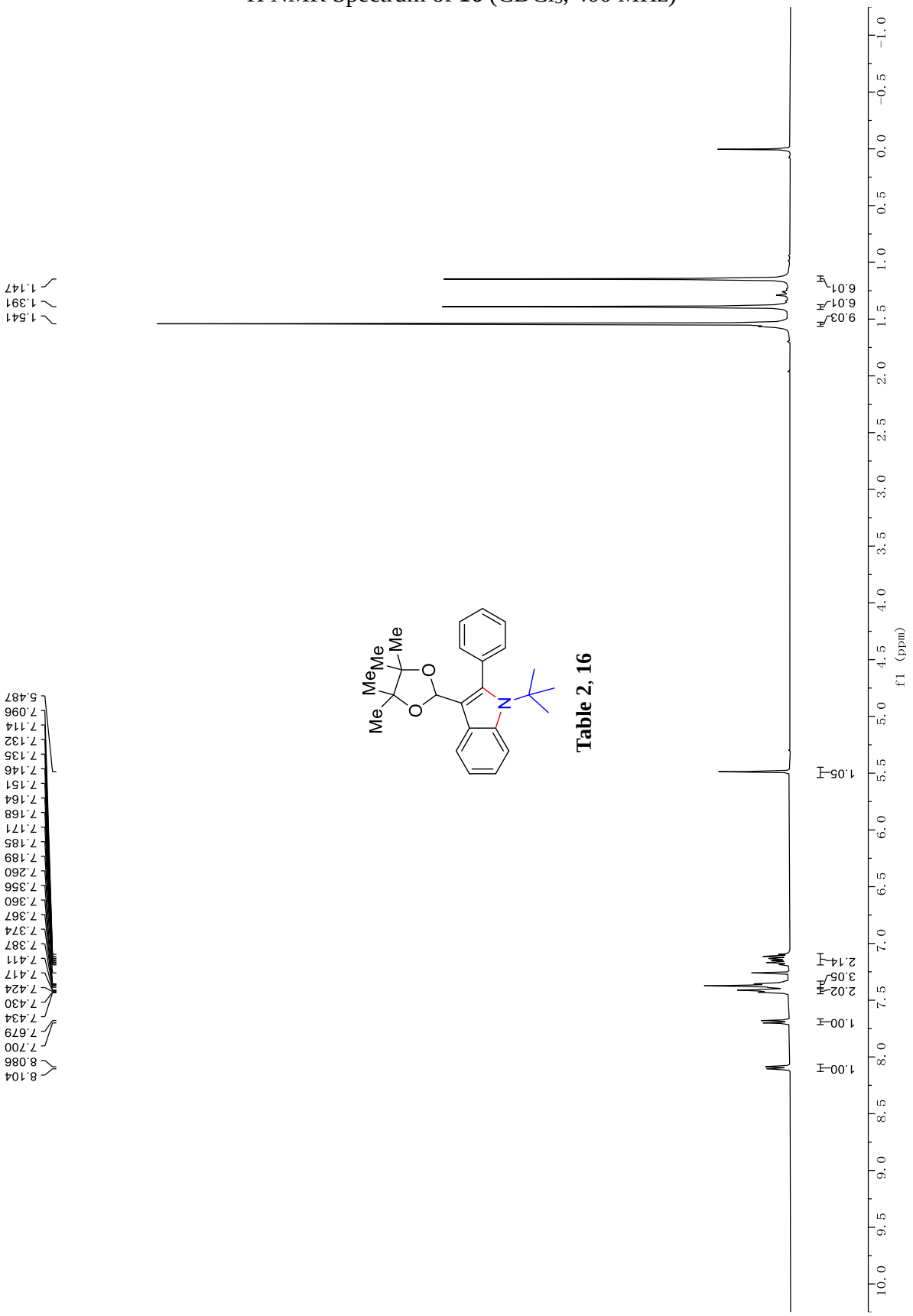
^{1}H NMR Spectrum of **15r′** ($CDCl_3$, 400 MHz)



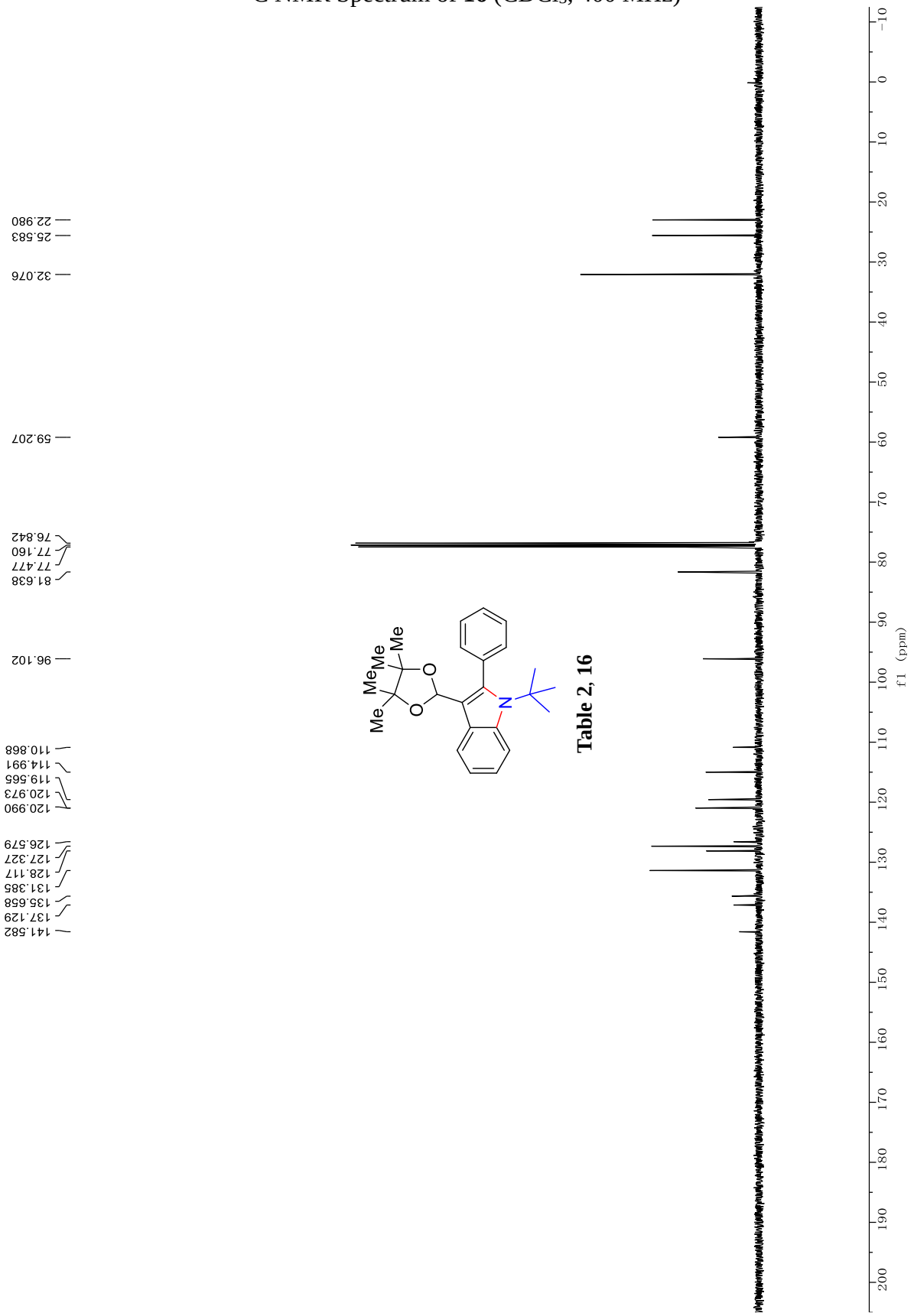
^{13}C NMR Spectrum of **15r′** ($CDCl_3$, 400 MHz)



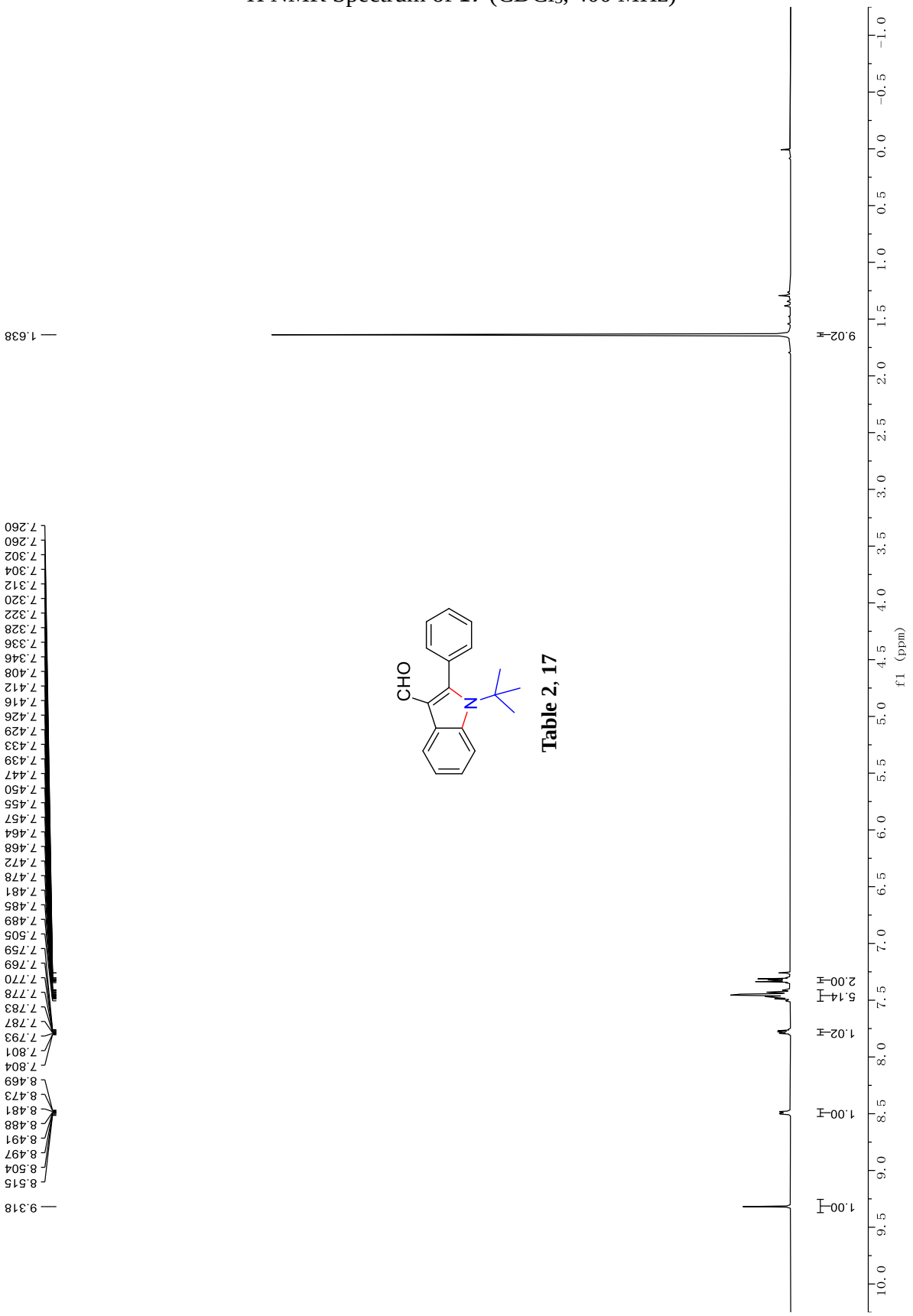
^{1}H NMR Spectrum of **16** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **16** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **17** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **17** ($CDCl_3$, 400 MHz)

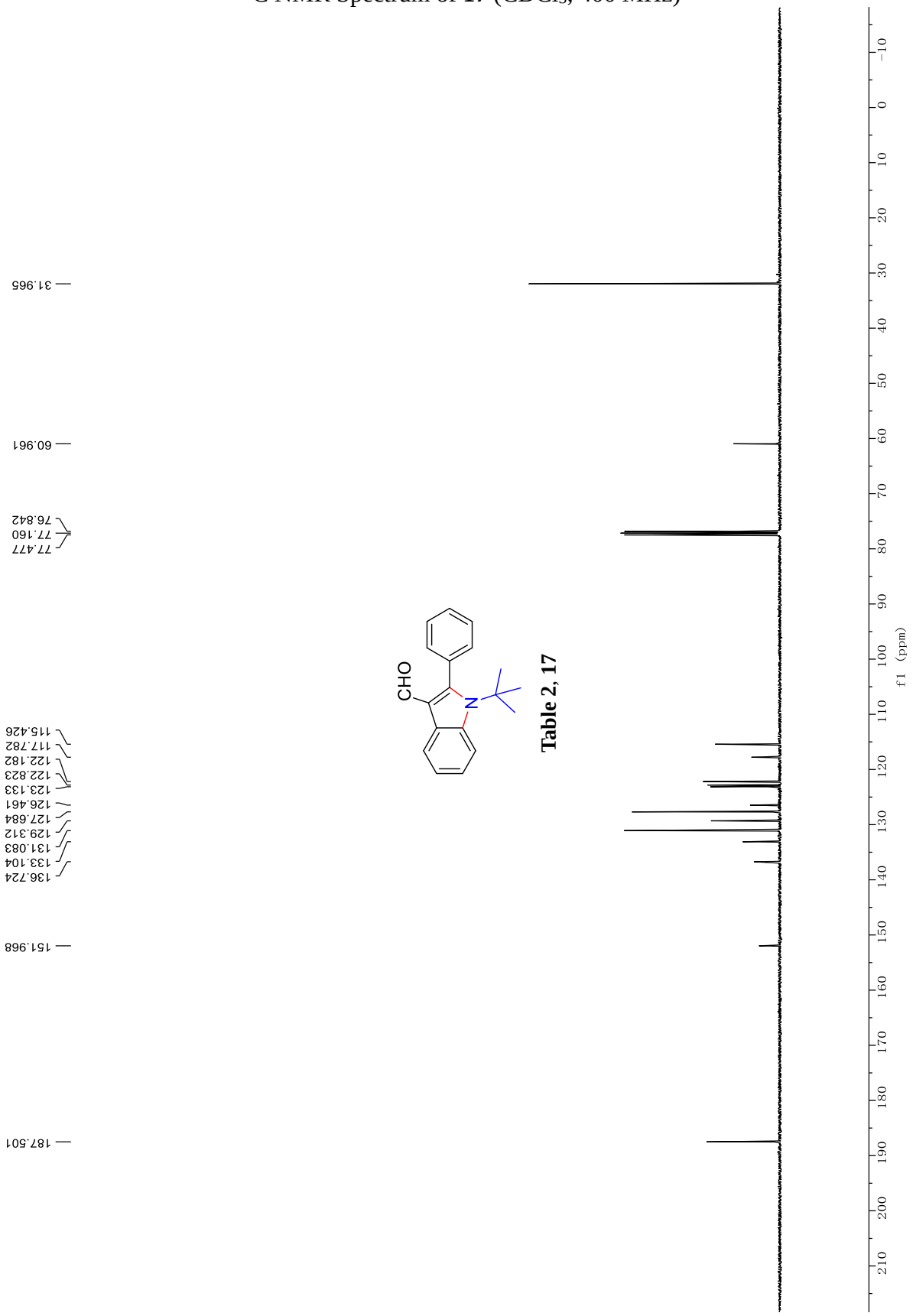
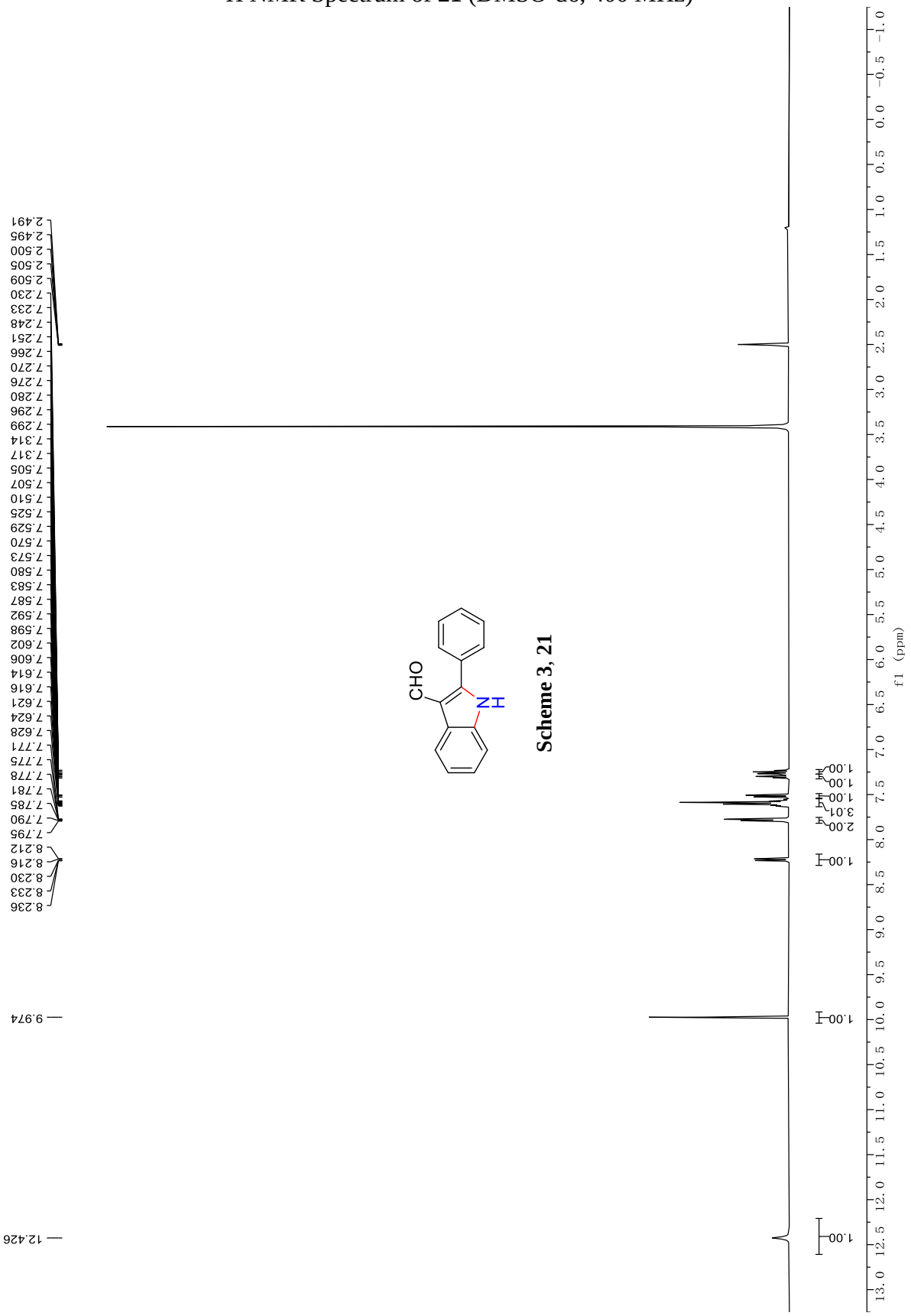
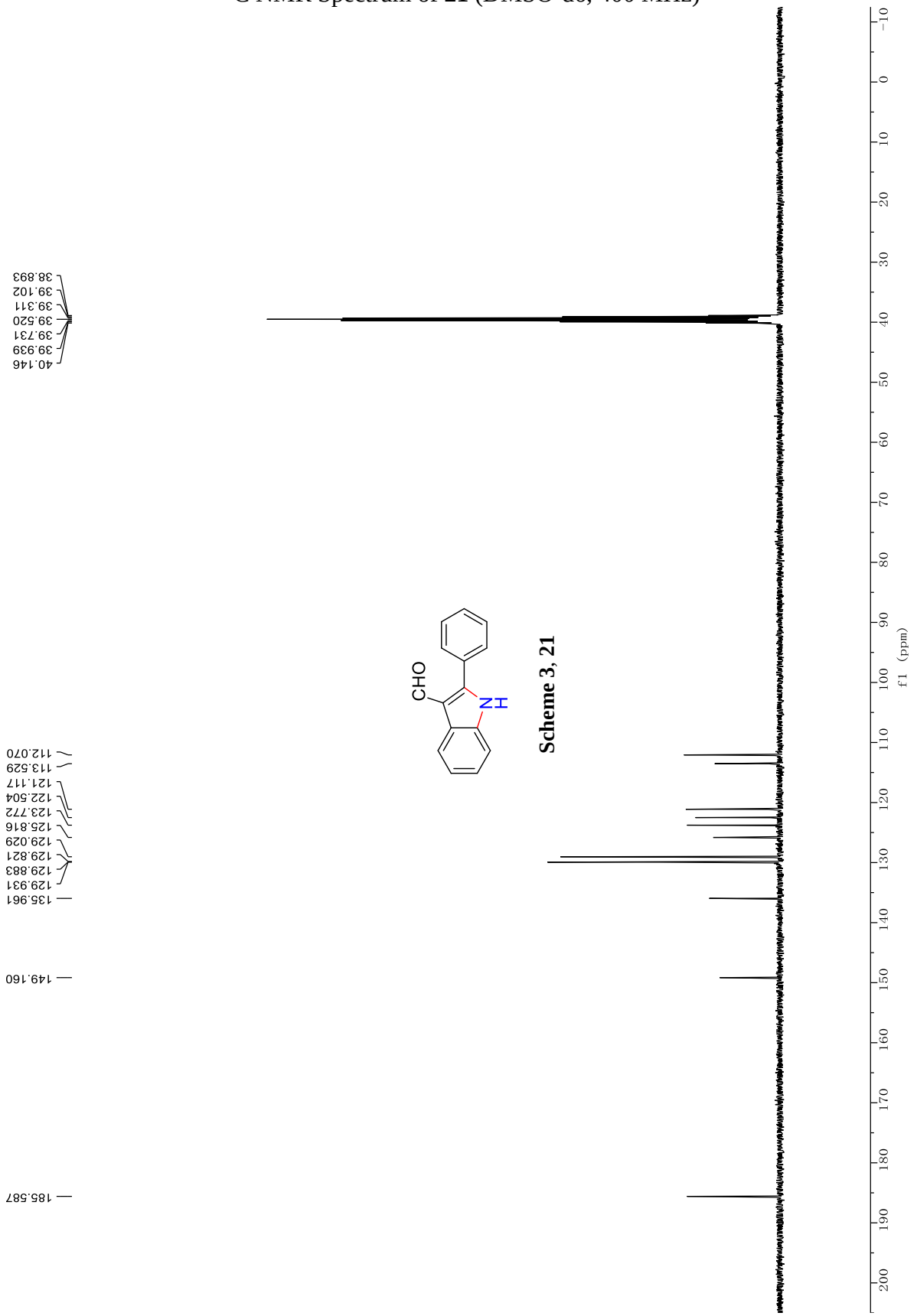


Table 2, 17

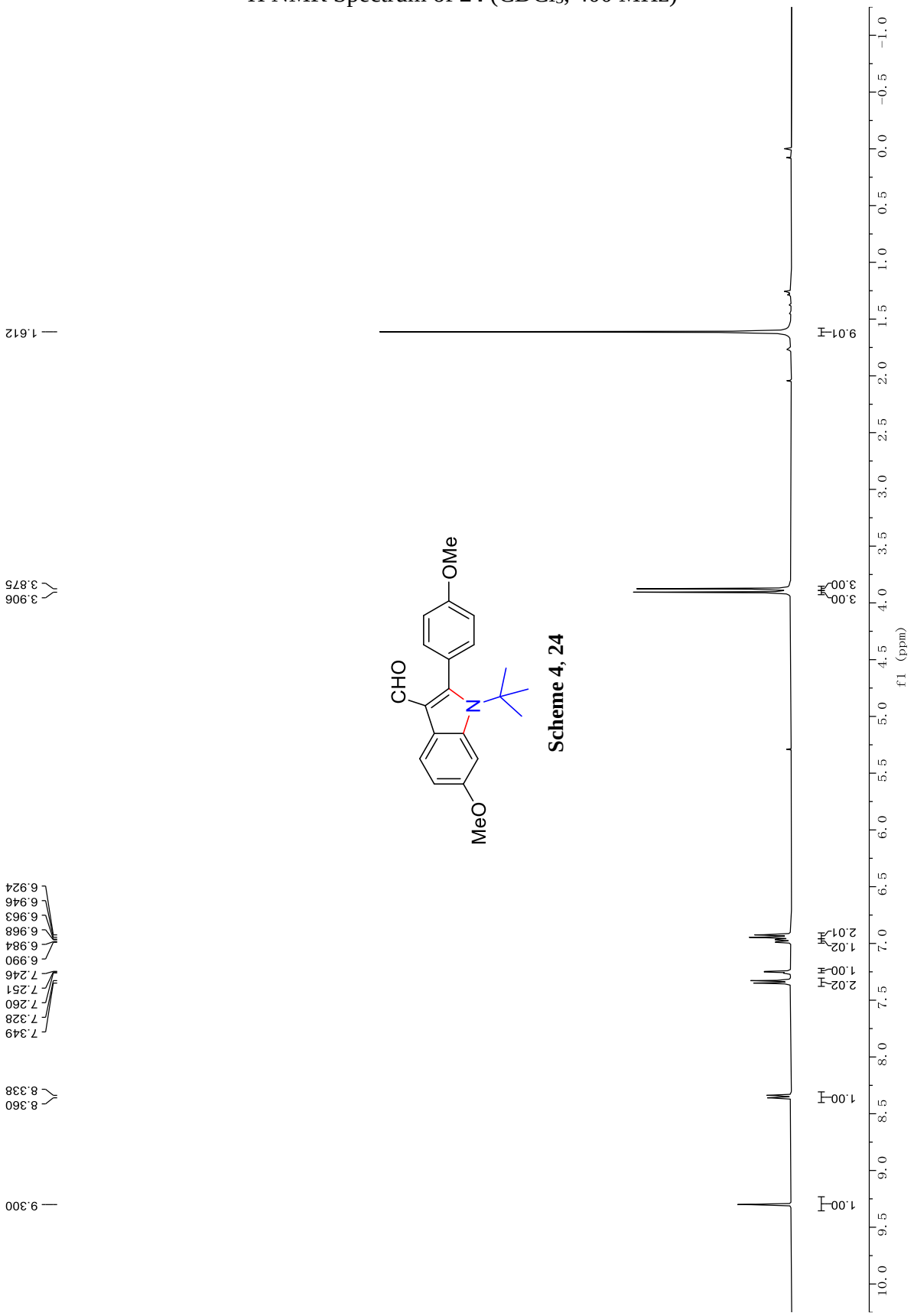
^{1}H NMR Spectrum of **21** (DMSO-d6, 400 MHz)



^{13}C NMR Spectrum of **21** (DMSO-d6, 400 MHz)

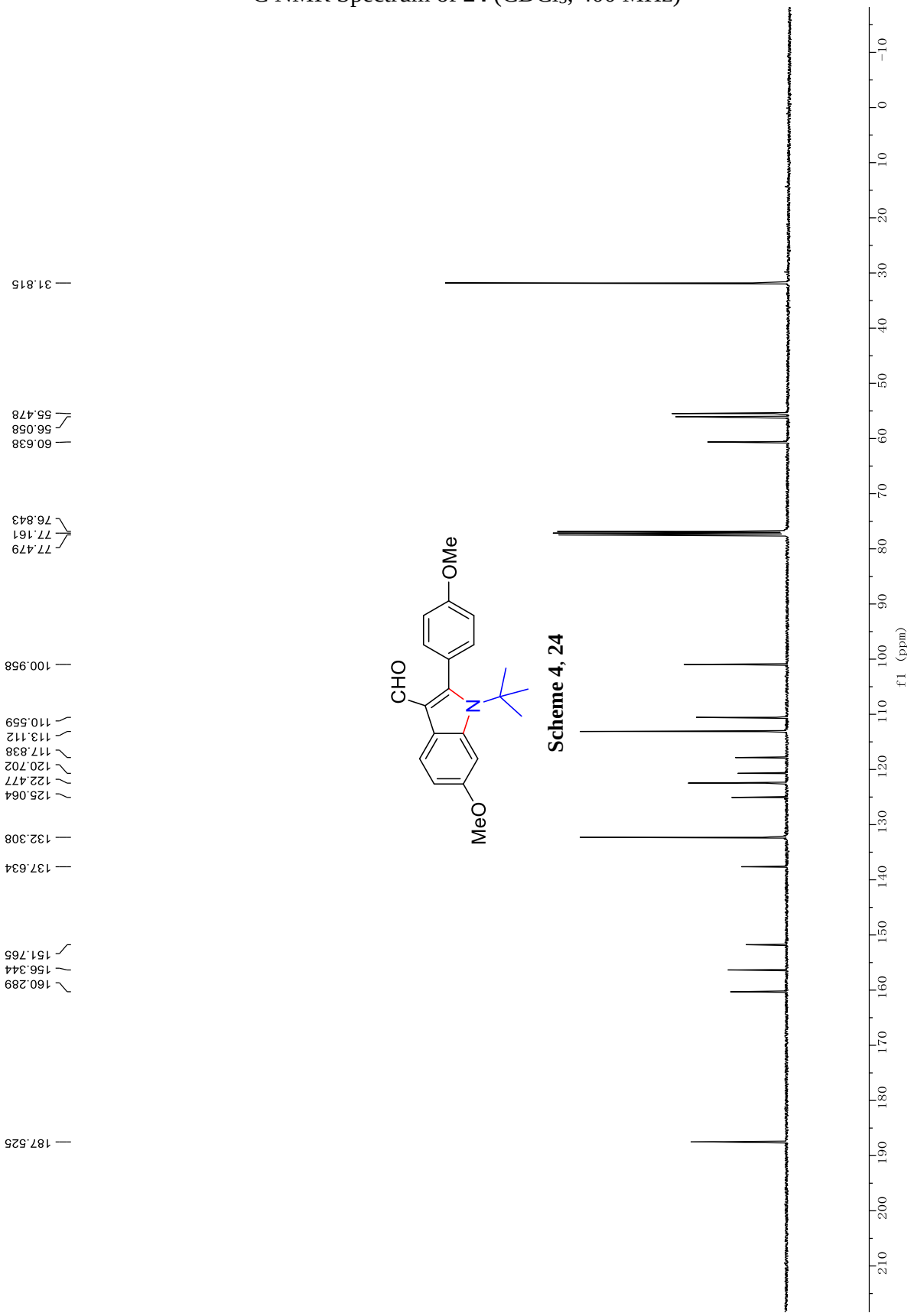


^{1}H NMR Spectrum of **24** ($CDCl_3$, 400 MHz)

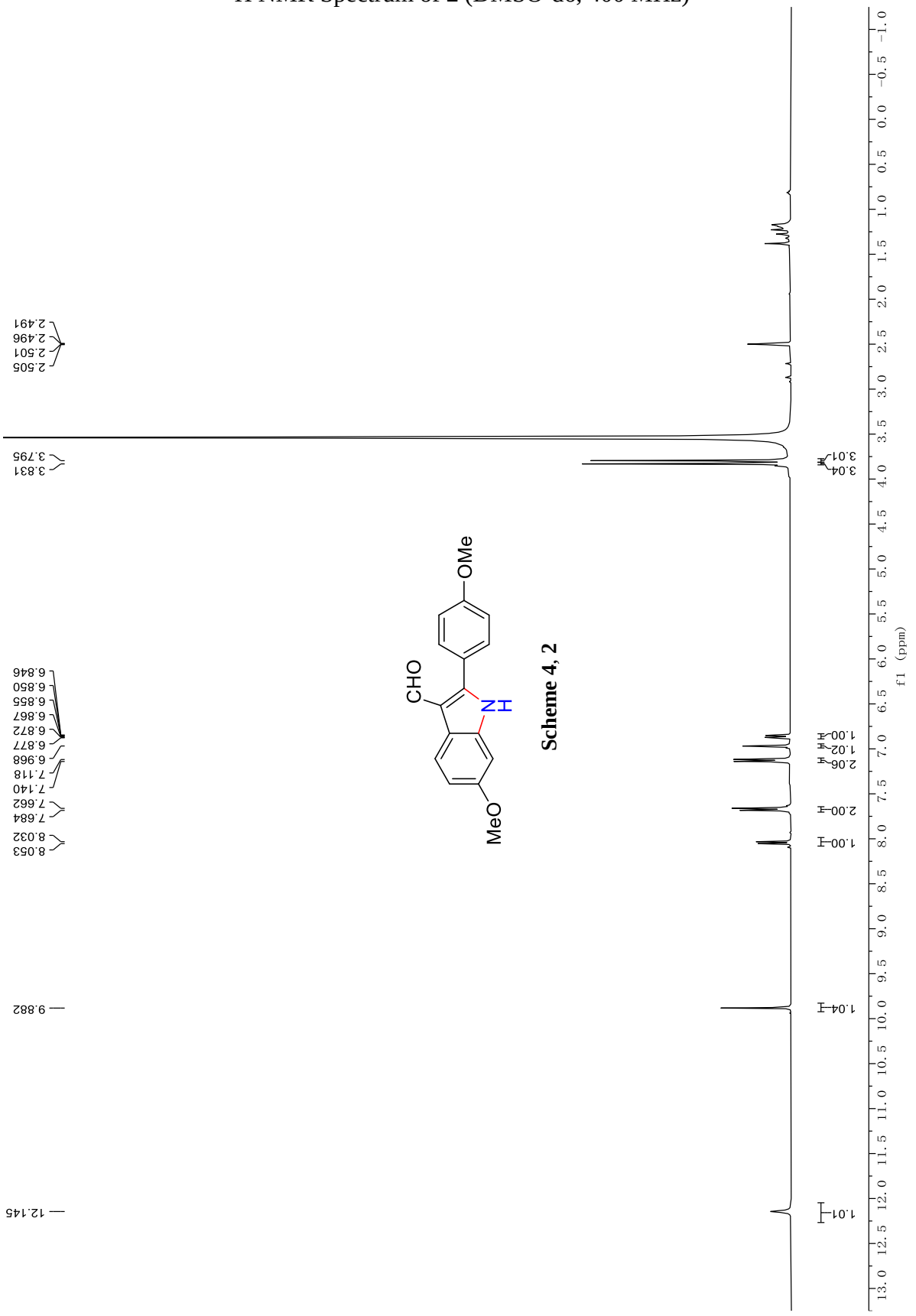


Scheme 4, 24

^{13}C NMR Spectrum of **24** ($CDCl_3$, 400 MHz)

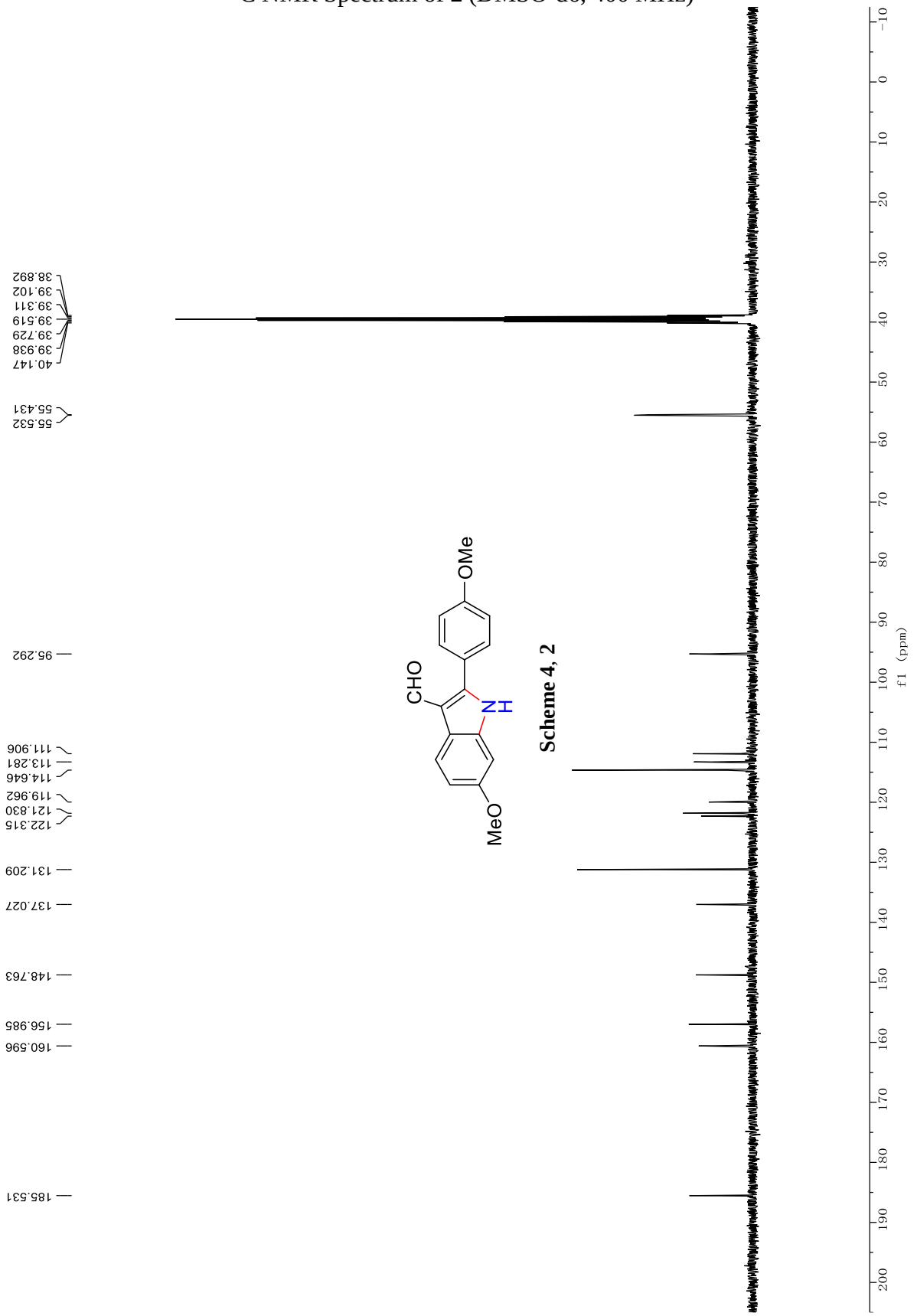


^{1}H NMR Spectrum of **2** (DMSO-d6, 400 MHz)



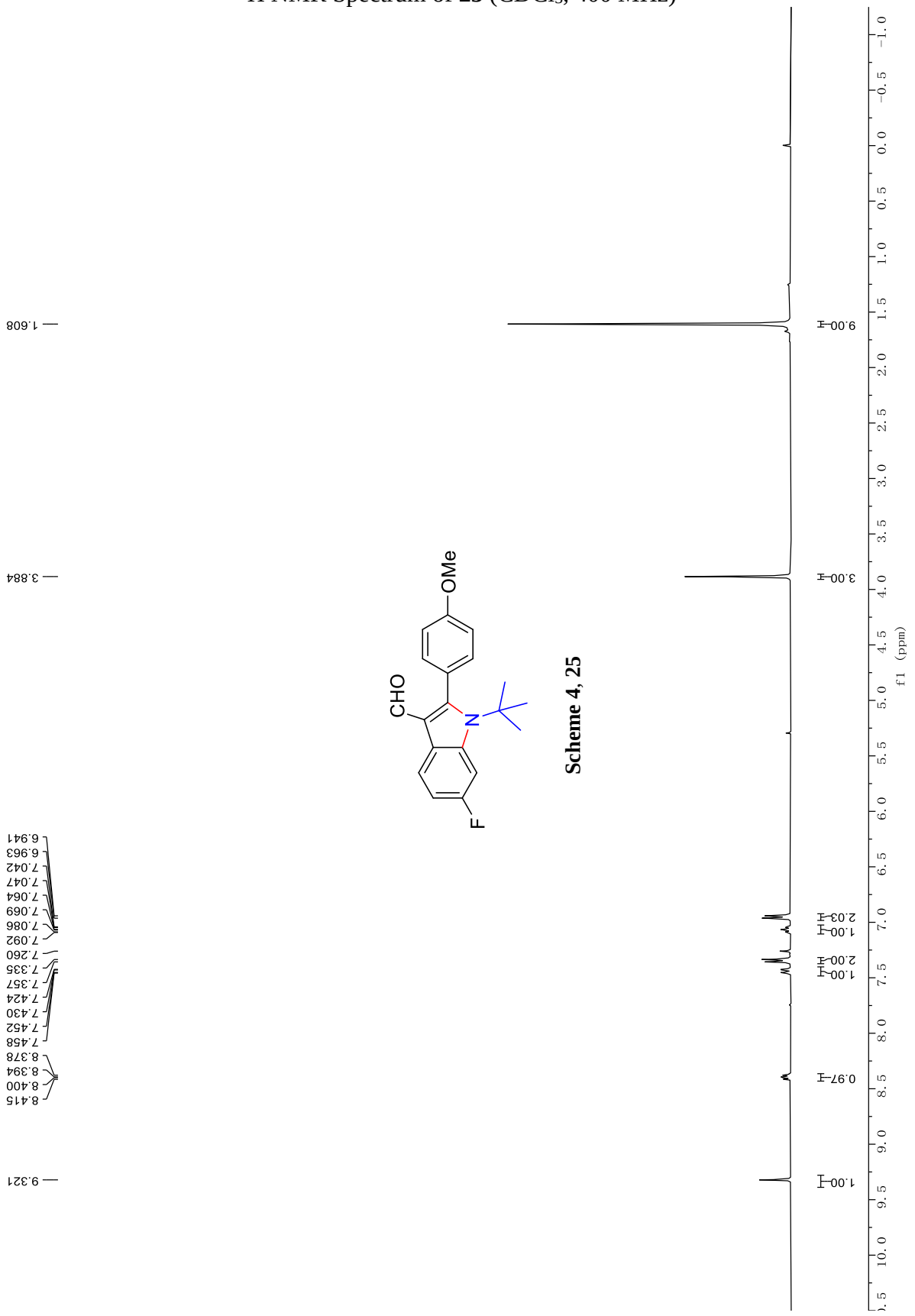
Scheme 4, 2

^{13}C NMR Spectrum of **2** (DMSO-d6, 400 MHz)



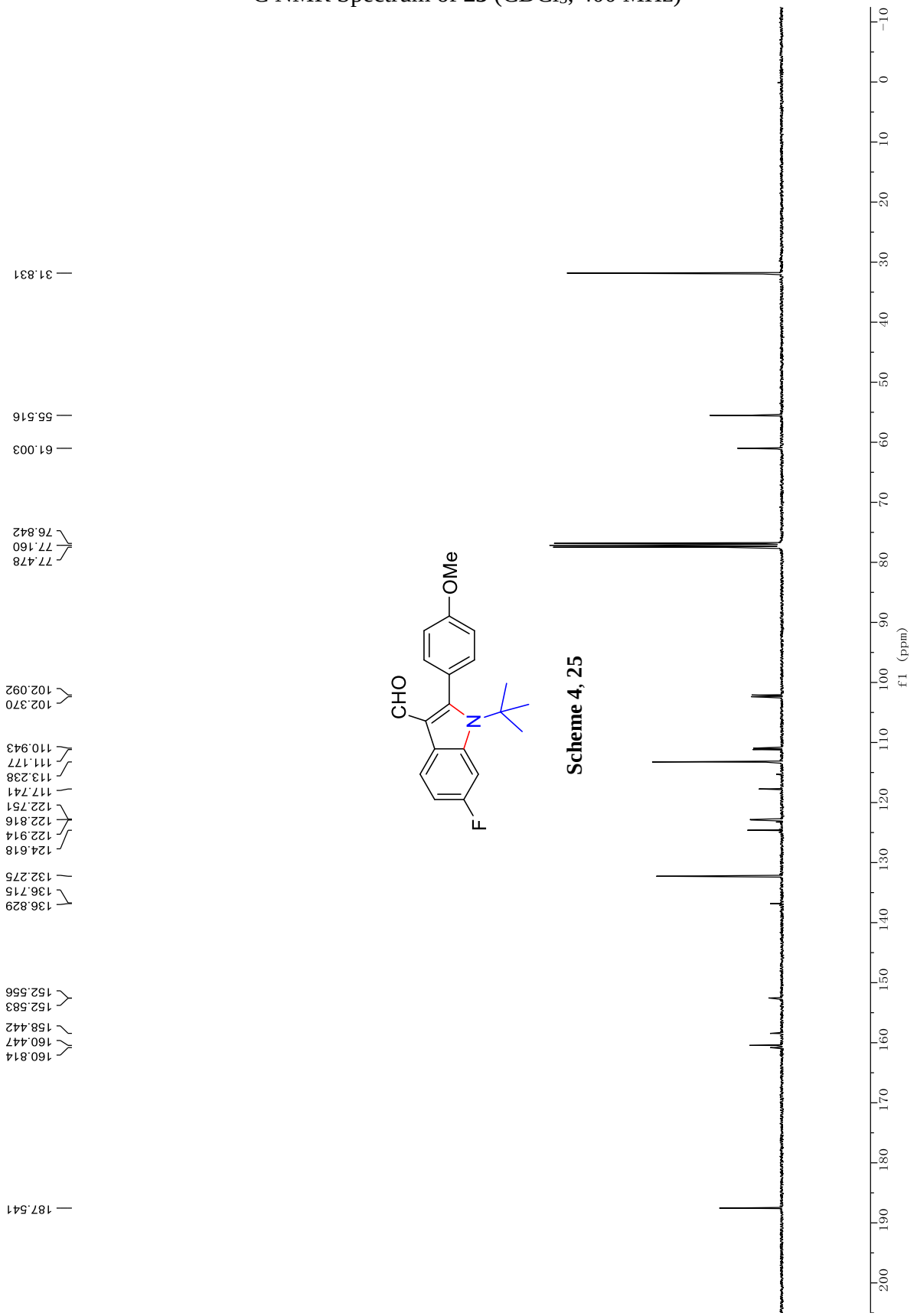
Scheme 4, 2

^{1}H NMR Spectrum of **25** ($CDCl_3$, 400 MHz)

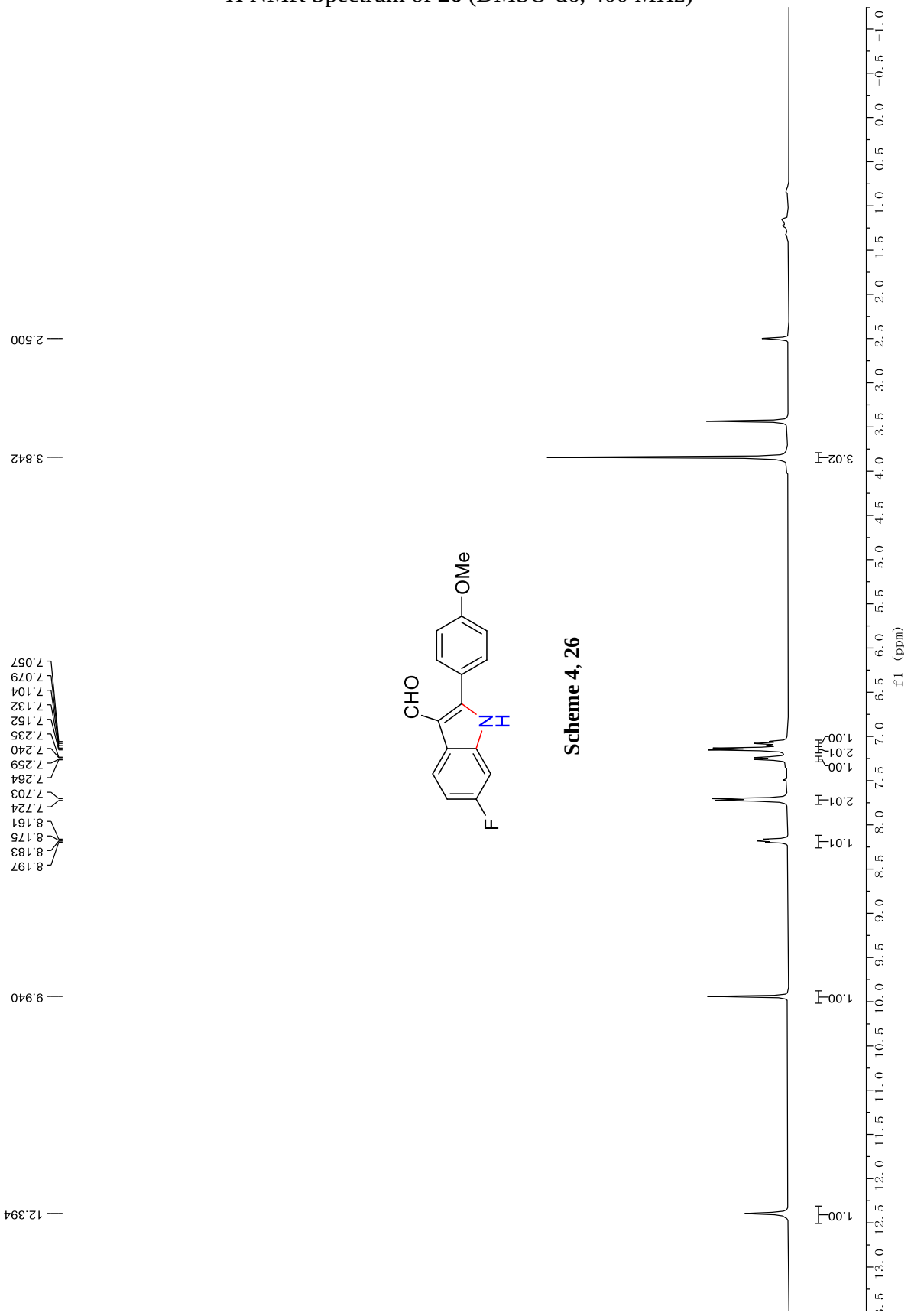


Scheme 4, 25

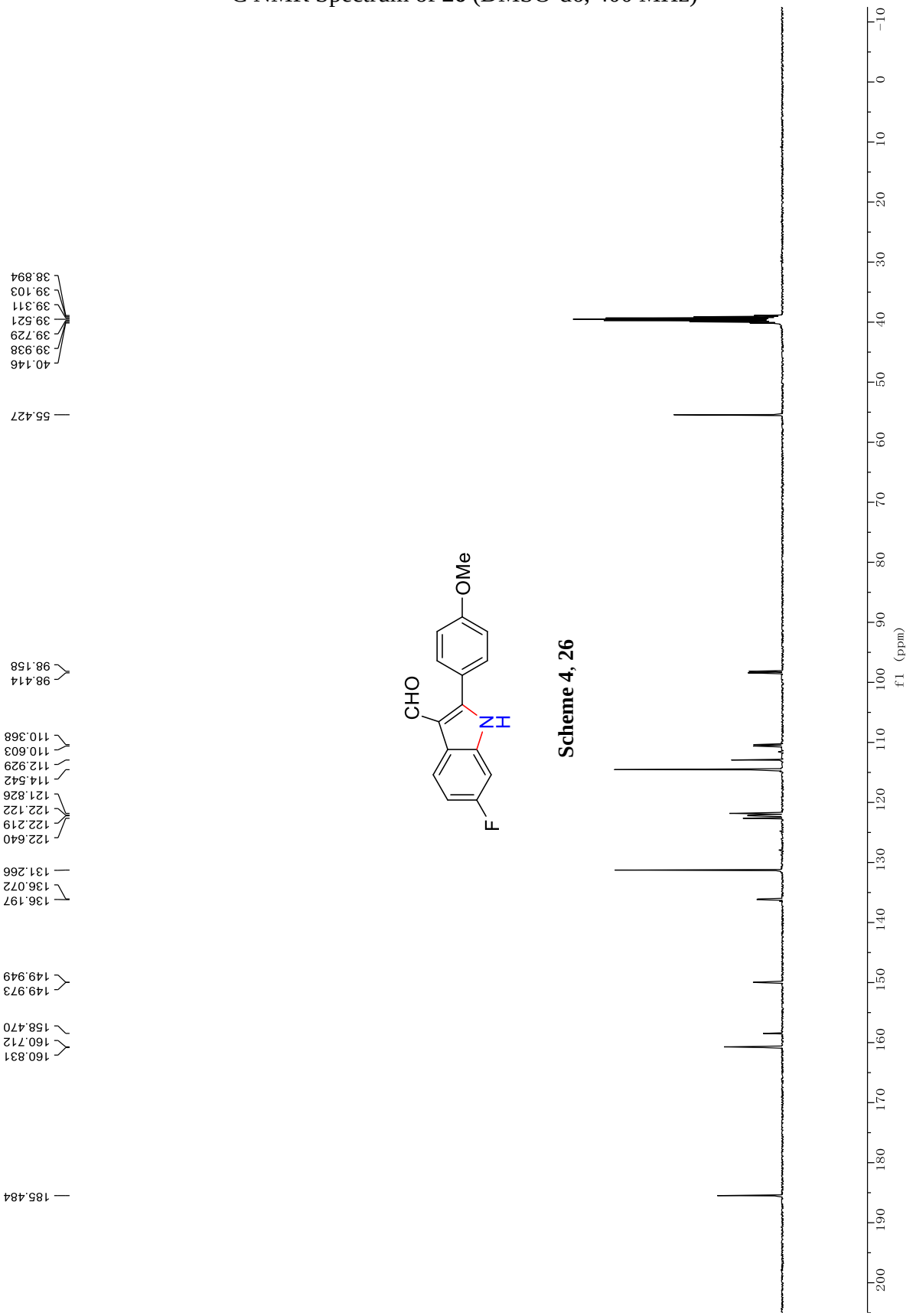
^{13}C NMR Spectrum of **25** ($CDCl_3$, 400 MHz)



^{1}H NMR Spectrum of **26** (DMSO-d6, 400 MHz)

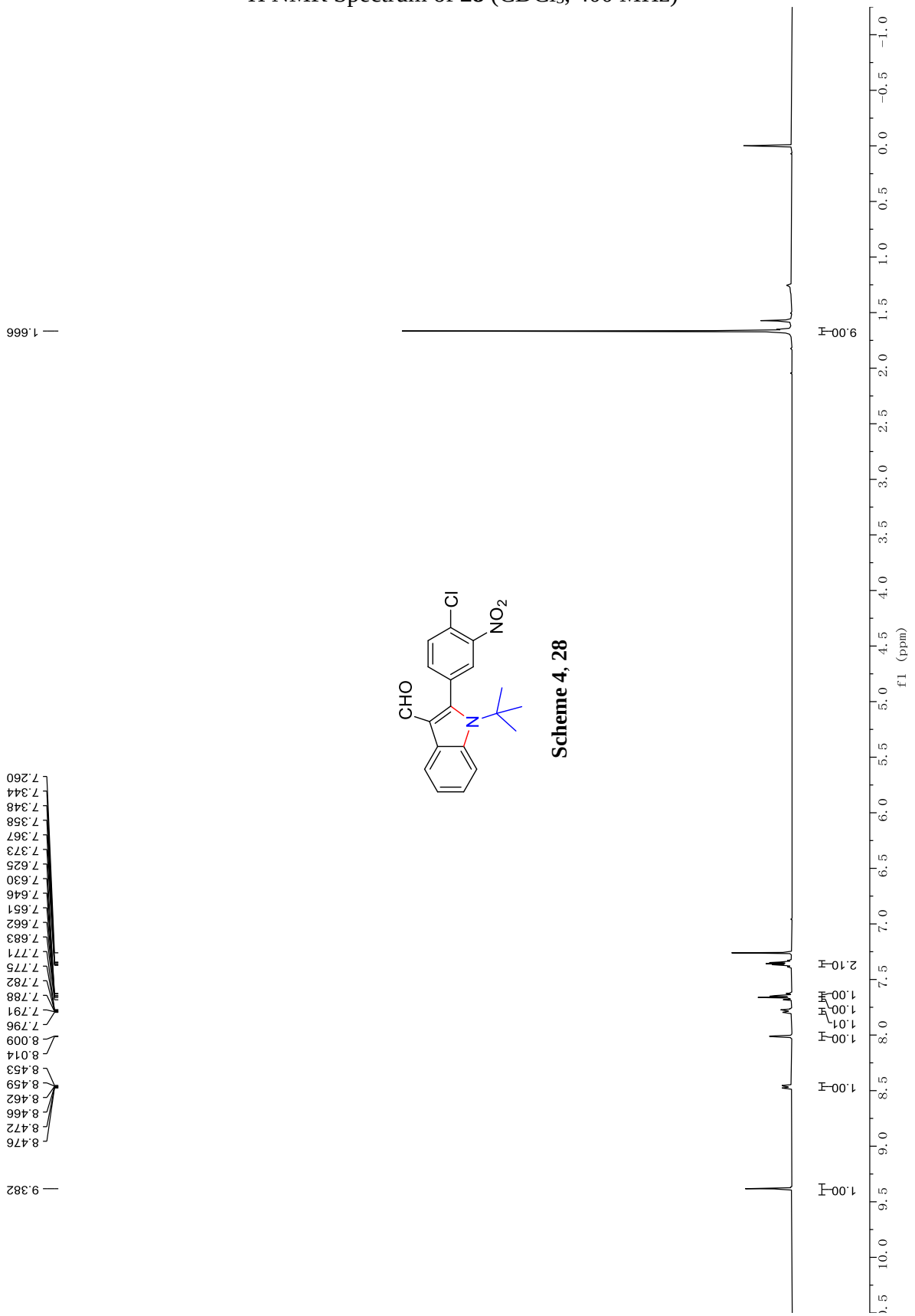


^{13}C NMR Spectrum of **26** (DMSO-d6, 400 MHz)



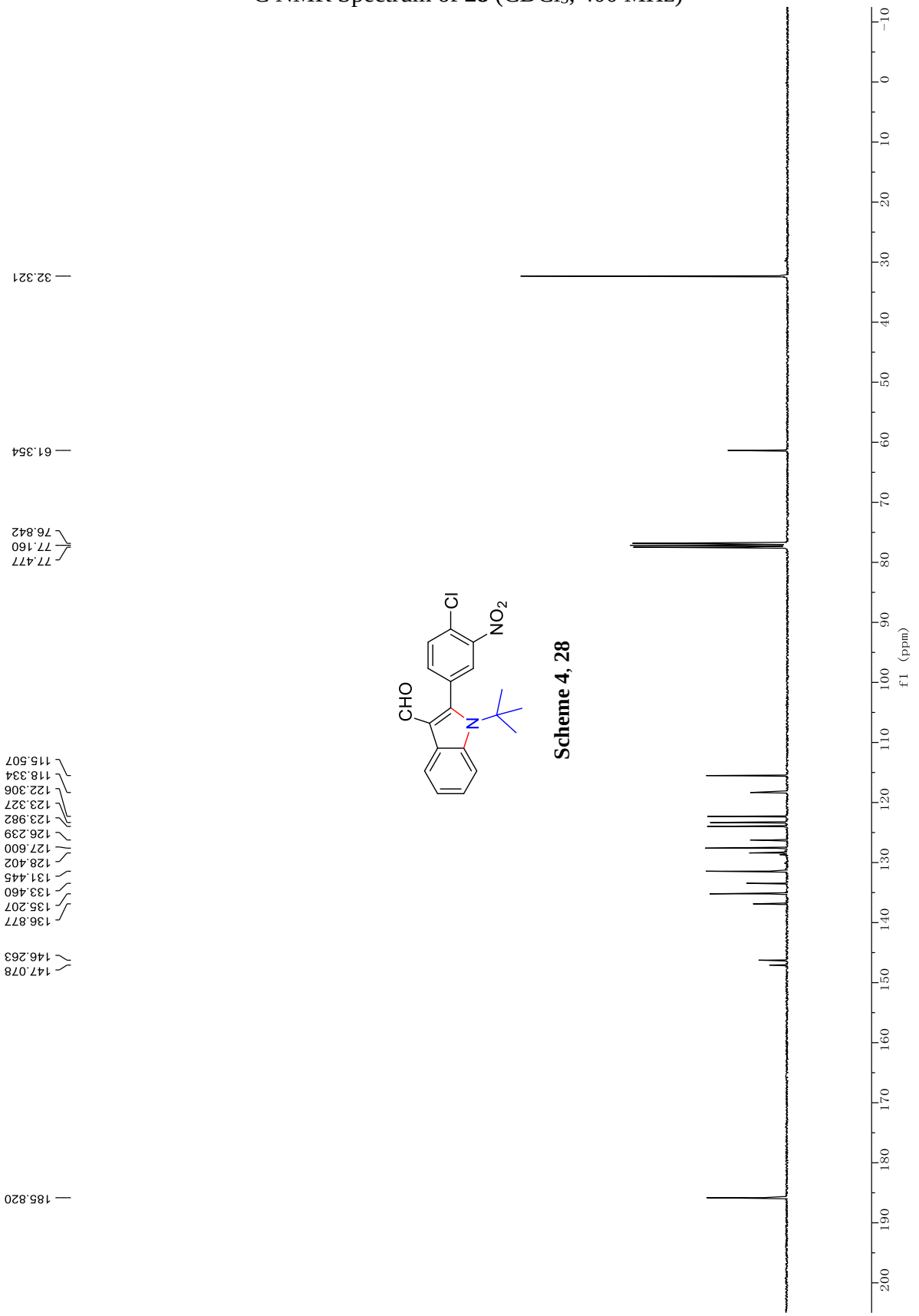
Scheme 4, 26

^{1}H NMR Spectrum of **28** ($CDCl_3$, 400 MHz)



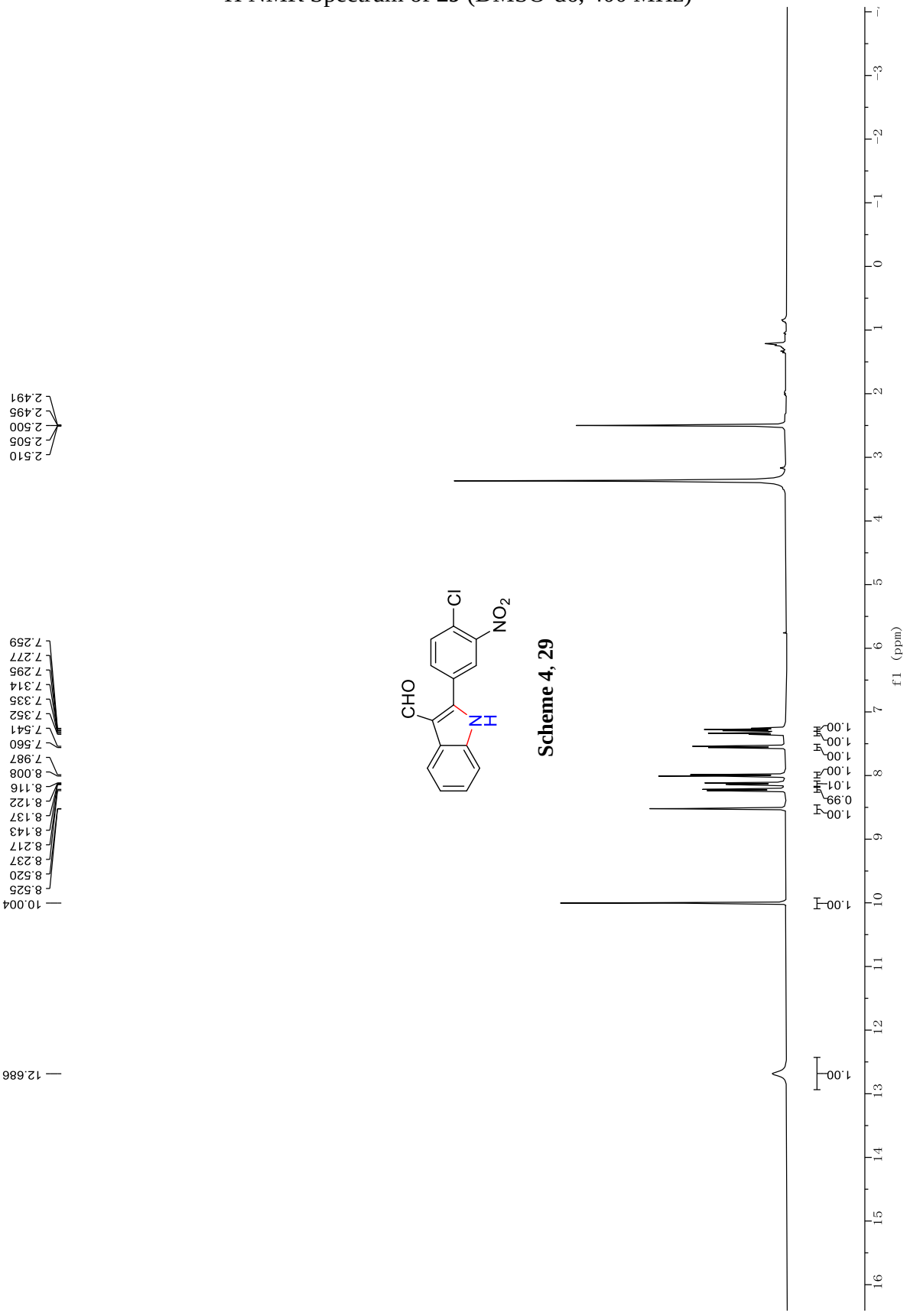
Scheme 4, 28

^{13}C NMR Spectrum of **28** ($CDCl_3$, 400 MHz)

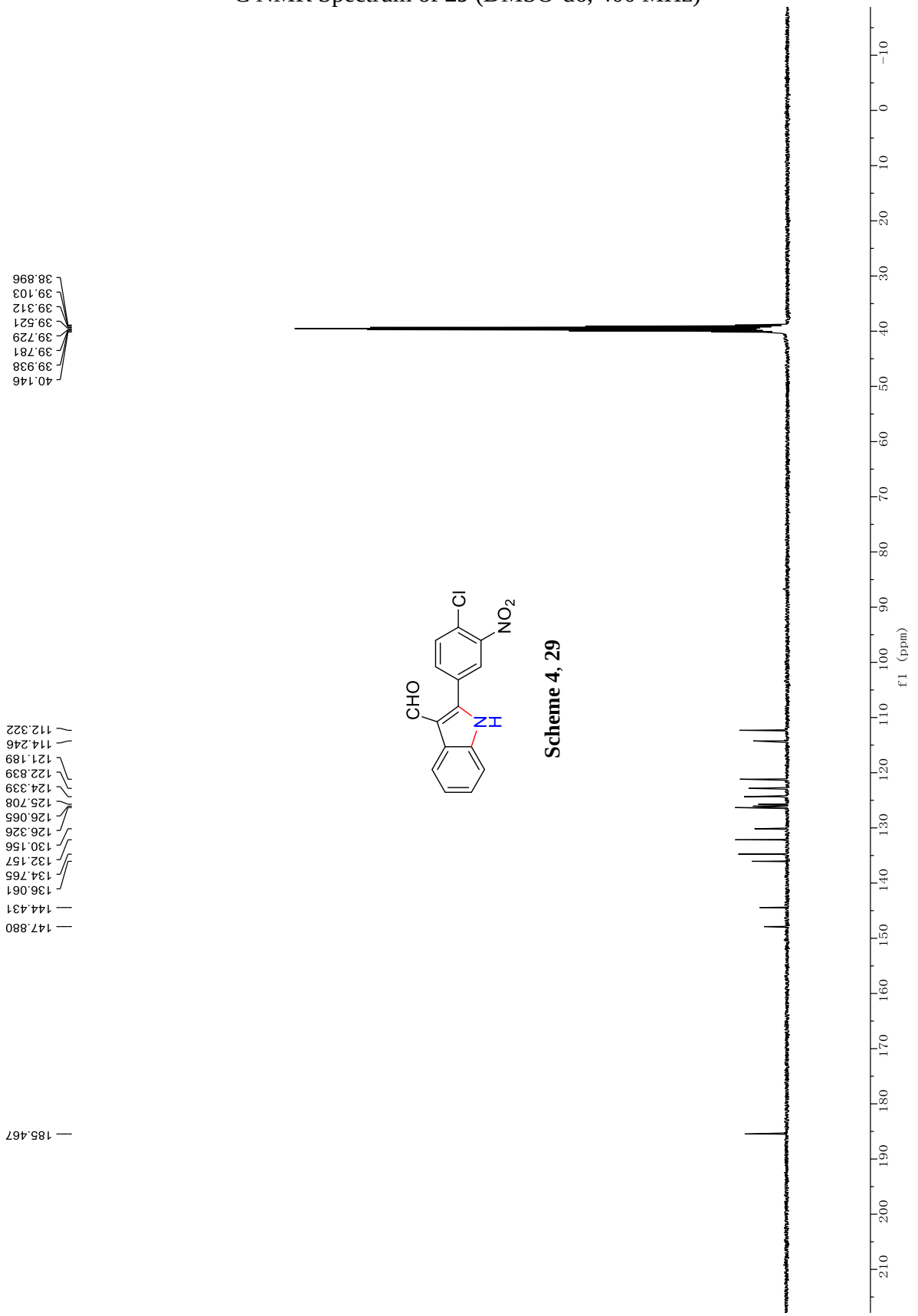


Scheme 4, 28

^{1}H NMR Spectrum of **29** (DMSO-d6, 400 MHz)



^{13}C NMR Spectrum of **29** (DMSO-d6, 400 MHz)



Scheme 4, 29