Supporting Information

Facile Construction of *C,N*-Disulfonated 5-Amino Pyrazoles through Iodine-Catalyzed Cascade Reaction

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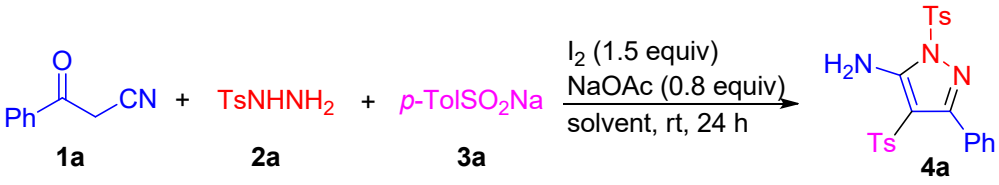
General Information

All commercially available reagents were used without further purification. Analytical TLC was performed on glass-backed plates pre-coated with silica gel, which were visualized by UV fluorescence (λmax = 254 nm). ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker 400 MHz spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz), using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 0 ppm (TMS). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.0 ppm) and were obtained with ^{1}H-decoupling. Data for ^{1}H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sep, septet; m, multiplet; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR are described in terms of chemical shift (δ in ppm). High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on X4 melting point apparatus and uncorrected.

Sulfonyl hydrazides[1] and *β*-ketonitriles [2] were prepared according to the reported procedures.

Table S1 Optimization of reaction solvent.[a)]

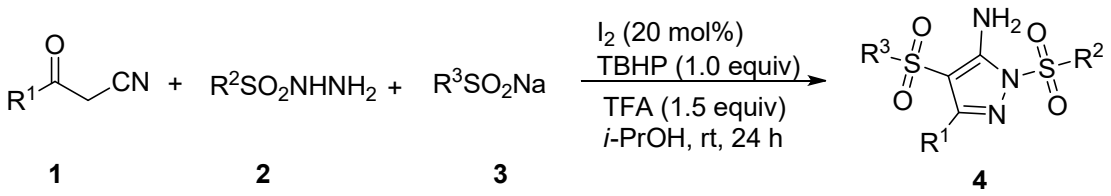


1a **2a** **3a** **4a**

Entry	Solvent	NMR yield of **4a** (%)	Recovery of **1a** (%)
1	EtOH	32	68
2	EA	27	41
3	toluene	30	19
4	DCM	23	46
5	DCE	23	55
6	DMSO	26	37
7	1,4-dioxane	29	58
8	THF	7	78
9	CH_3COOH	25	36
10	DMF	trace	26
11	*i*-PrOH	42	49
12	*i*-Pr$(CH_2)_2$OH	40	34
13	$(CF_3)_2$CHOH (HFIP)	5	31
14	*n*-BuOH	35	42
15	*t*-BuOH	42	48

[a)] General conditions: benzoylacetonitrile (**1a**) (0.5 mmol), (*p*-tolylsulfonyl)hydrazine (**2a**) (1.1 equiv), sodium 4-methylbenzenesulfinate (**3a**) (2.0 equiv), I_2 (1.5 equiv), and NaOAc (0.8 equiv) in 4.5 mL of solvent were stirred under air at rt for 24 h.

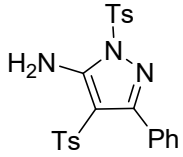
General procedure for the synthesis of pyrazoles 4



To a Schlenk tube (10 mL) were added *β*-ketonitrile (0.50 mmol), sulfonyl hydrazide (0.55 mmol), sodium sulfinate (1.0 mmol), I_2 (0.10 mmol), 4.5 mL of *i*-PrOH, TBHP (70% in water, 0.50 mmol), and trifluoroacetic acid (0.75 mmol) sequentially under air. Then the tube was sealed and the reaction mixture was stirred at room temperature for 22 h. It was then quenched (consumption of residual I_2) with saturated $Na_2S_2O_3$ solution, forming white precipitation. Filtration of the suspension gave crude product. Washing the crude product with water (15 mL), *i*-PrOH (5 mL), and petroleum ether (15 mL) sequentially afforded pure product **4**.

Synthesis and characterization of pyrazoles 4

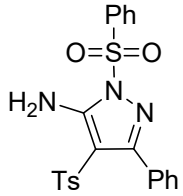
3-Phenyl-1,4-ditosyl-1*H*-pyrazol-5-amine (4a)



The title compound was obtained as a white solid (204.5 mg, 88%). Mp 179–180 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.44-7.39 (m, 2 H), 7.39-7.26 (m, 7 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.71 (s, 2 H), 2.44 (s, 3 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 151.2, 146.5, 143.9, 139.5, 133.5, 130.2, 130.0, 129.5, 129.3, 128.1, 127.8, 126.4, 100.3, 21.7, 21.4; **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{23}H_{22}N_3O_4S_2$: 468.1046; Found: 468.1053.

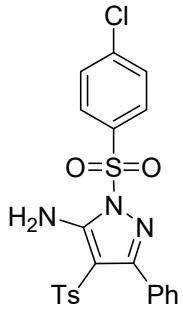
3-Phenyl-1-(phenylsulfonyl)-4-tosyl-1*H*-pyrazol-5-amine (4b)



The title compound was obtained as a white solid (178.2 mg, 79%). Mp 139–141 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.97 (m, 2 H), 7.70 (t, *J* = 7.6 Hz, 1 H), 7.61-7.53 (m, 2 H), 7.43-7.34 (m, 3 H), 7.34-7.27 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.73 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 151.3, 143.9, 139.4, 136.5, 135.1, 130.0, 129.6, 129.53, 129.49, 129.3, 128.0, 127.8, 126.4, 100.4, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{19}N_3O_4S_2Na$: 476.0709; Found: 476.0714.

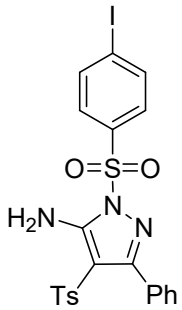
1-((4-Chlorophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4c)



The title compound was obtained as a white solid (189.4 mg, 78%). Mp 196–198 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.8 Hz, 2 H), 7.53 (d, *J* = 8.4 Hz, 2 H), 7.45-7.35 (m, 3 H), 7.35-7.27 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.72 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 151.3, 144.0, 142.0, 139.3, 134.8, 129.9, 129.8, 129.7, 129.53, 129.50, 129.3, 127.8, 126.5, 100.6, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{18}ClN_3O_4S_2Na$: 510.0319; Found: 510.0319.

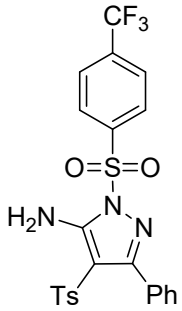
1-((4-Iodophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4d)



The title compound was obtained as a white solid (232.9 mg, 80%). Mp 198–200 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.45-7.36 (m, 3 H), 7.36-7.27 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.72 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 151.3, 144.0, 139.3, 138.9, 136.0, 129.8, 129.7, 129.5, 129.3, 129.2, 127.8, 126.5, 103.6, 100.6, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{18}IN_3O_4S_2Na$: 601.9676; Found: 601.9679.

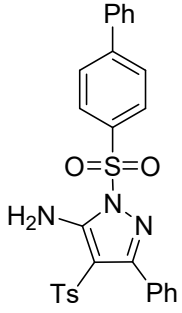
3-Phenyl-4-tosyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1H-pyrazol-5-amine (4e)



The title compound was obtained as a white solid (185.3 mg, 71%). Mp 172–174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.44-7.36 (m, 3 H), 7.34-7.27 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.74 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.0, 151.4, 144.1, 139.8, 139.2, 136.4 (q, *J* = 33.2 Hz), 129.8, 129.7, 129.5, 129.3, 128.7, 127.9, 126.7 (q, *J* = 3.7 Hz), 126.5, 122.8 (q, *J* = 271.7 Hz), 100.7, 21.4; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -63.4 (s, 3 F); **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{18}F_3N_3O_4S_2Na$: 544.0578; Found: 544.0580.

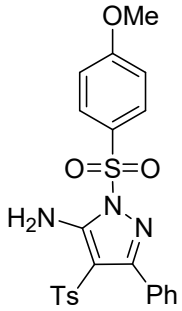
1-([1,1'-Biphenyl]-4-ylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4f)



The title compound was obtained as a white solid (217.1 mg, 83%). Mp 175–177 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.52-7.41 (m, 6 H), 7.36-7.27 (m, 4 H), 7.06 (*J* = 8.0 Hz, 2 H), 6.75 (s, 2 H), 2.31 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 151.3, 148.1, 143.9, 139.4, 138.7, 134.8, 130.0, 129.60, 129.56, 129.3, 129.1, 129.0, 128.6, 128.1, 127.8, 127.4, 126.5, 100.4, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{28}H_{23}N_3O_4S_2Na$: 552.1022; Found: 552.1027.

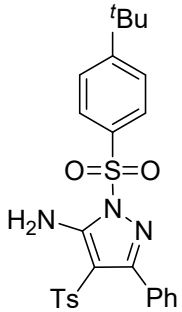
1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4g)



The title compound was obtained as a white solid (201.1 mg, 83%). Mp 183–185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2 H), 7.45-7.23 (m, 7 H), 7.05 (d, *J* = 8.0 Hz, 2 H), 6.99 (d, *J* = 9.2 Hz, 2 H), 6.70 (s, 2 H), 3.87 (s, 3 H), 2.31 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 164.9, 154.0, 151.0, 143.9, 139.5, 130.6, 130.1, 129.54, 129.50, 129.3, 127.8, 127.7, 126.4, 114.8, 100.2, 55.8, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{21}N_3O_5S_2Na$: 506.0815; Found: 506.0820.

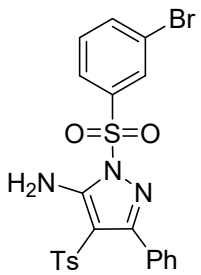
1-((4-(Tert-butyl)phenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4h)



The title compound was obtained as a white solid (195.2 mg, 77%). Mp 183–185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.45-7.41 (m, 2 H), 7.41-7.27 (m, 5 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 6.71 (s, 2 H), 2.32 (s, 3 H), 1.34 (s, 9 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 159.3, 154.0, 151.2, 143.9, 139.4, 133.4, 130.1, 129.5, 129.3, 127.9, 127.8, 126.6, 126.5, 100.3, 35.4, 30.9, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{26}H_{27}N_3O_4S_2Na$: 532.1335; Found: 532.1338.

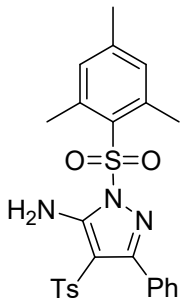
1-((3-Bromophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4i)



The title compound was obtained as a white solid (190.2 mg, 72%). Mp 189–191 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (t, *J* = 2.0 Hz, 1 H), 7.98-7.93 (m, 1 H), 7.84-7.79 (m, 1 H), 7.48-7.36 (m, 4 H), 7.34-7.27 (m, 4 H), 7.06 (d, *J* = 8.0 Hz, 2 H), 6.73 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.7, 151.3, 144.0, 139.2, 138.14, 138.10, 131.0, 130.7, 129.8, 129.7, 129.5, 129.3, 127.8, 126.7, 126.5, 123.3, 100.6, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{18}BrN_3O_4S_2Na$: 553.9814; Found: 553.9818.

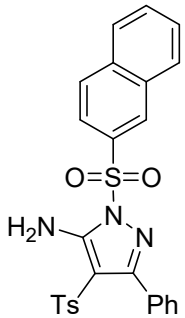
1-(Mesitylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4j)



The title compound was obtained as a white solid (189.5 mg, 77%). Mp 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2 H), 7.39-7.31 (m, 3 H), 7.30-7.23 (m, 2 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 6.96 (s, 2 H), 6.75 (s, 2 H), 2.64 (s, 6 H), 2.32 (s, 3 H), 2.29 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9, 151.2, 145.2, 143.7, 141.4, 139.8, 132.3, 131.2, 130.3, 129.5, 129.4, 129.3, 127.7, 126.3, 99.3, 22.8, 21.4, 21.1; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{25}H_{25}N_3O_4S_2Na$: 518.1179; Found: 518.1185.

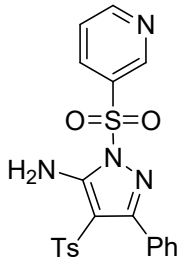
1-(Naphthalen-2-ylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4k)



The title compound was obtained as a white solid (210.0 mg, 83%). Mp 194–196 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1 H), 8.03-7.96 (m, 2 H), 7.96-7.90 (m, 2 H), 7.73-7.68 (m, 1 H), 7.67-7.62 (m, 1 H), 7.41-7.32 (m, 3 H), 7.31-7.25 (m, 4 H), 7.03 (d, *J* = 8.0 Hz, 2 H), 6.78 (s, 2 H), 2.30 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.3, 151.3, 143.9, 139.4, 135.8, 133.3, 131.8, 130.4, 130.1, 130.01, 129.99, 129.8, 129.5, 129.3, 128.04, 128.02, 127.8, 126.5, 122.1, 100.5, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_4S_2Na$: 526.0866; Found: 526.0873.

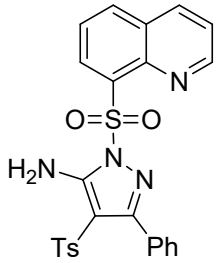
3-Phenyl-1-(pyridin-3-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4l)



The title compound was obtained as a white solid (149.2 mg, 65%). Mp 166–168 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (dd, *J* = 2.4, 0.8 Hz, 1 H), 8.91 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.30 (ddd, *J* = 8.0, 2.4, 1.6 Hz, 1 H), 7.52 (ddd, *J* = 8.4, 4.8, 0.8 Hz, 1 H), 7.45-7.37 (m, 3 H), 7.34-7.27 (m, 4 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 6.74 (s, 2 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 155.4, 155.0, 151.3, 148.6, 144.1, 139.2, 135.9, 133.5, 129.8, 129.7, 129.5, 129.3, 127.9, 126.5, 124.0, 100.7, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{21}H_{18}N_4O_4S_2Na$: 477.0662; Found: 477.0667.

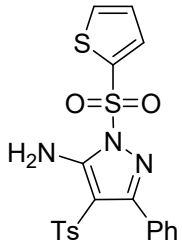
3-Phenyl-1-(quinolin-8-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4m)



The title compound was obtained as a white solid (198.6 mg, 79%). Mp 186–188 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 4.2, 1.8 Hz, 1 H), 8.63 (d, *J* = 7.6 Hz, 1 H), 8.23 (dd, *J* = 4.6, 1.8 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 8.63 (d, *J* = 7.8 Hz, 1 H), 7.53 (dd, *J* = 8.2, 4.2 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.31-7.23 (m, 3 H), 7.22-7.10 (m, 4 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 2.31 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.74, 153.67, 151.6, 143.64, 143.61, 140.0, 136.7, 135.7, 133.75, 133.69, 130.1, 129.5, 129.3, 129.2, 128.6, 127.6, 126.3, 125.5, 122.7, 99.4, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{25}H_{20}N_4O_4S_2Na$: 527.0818; Found: 527.0823.

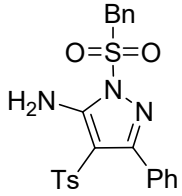
3-Phenyl-1-(thiophen-2-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4n)



The title compound was obtained as a yellow solid (188.9 mg, 82%). Mp 133–135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 4.0, 1.2 Hz, 1 H), 7.79 (dd, *J* = 5.0, 1.4 Hz, 1 H), 7.47-7.42 (m, 2 H), 7.42-7.36 (m, 1 H), 7.35-7.27 (m, 4 H), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1 H), 7.07 (d, *J* = 8.4 Hz, 2 H), 6.72 (s, 2 H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.6, 151.0, 144.0, 139.4, 136.1, 135.7, 135.6, 129.9, 129.7, 129.5, 129.3, 128.1, 127.8, 126.5, 100.4, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{20}H_{17}N_3O_4S_3Na$: 482.0273; Found: 482.0276.

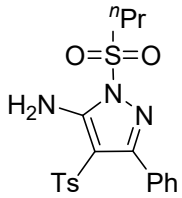
1-(Benzylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4o)



The title compound was obtained as a white solid (143.1 mg, 61%). Mp 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2 H), 7.48-7.41 (m, 2 H), 7.41-7.30 (m, 4 H), 7.29-7.26 (m, 2 H), 7.15 (dd, *J* = 8.0, 1.2 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 6.14 (s, 2 H), 4.69 (s, 2 H), 2.35 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.4, 152.5, 143.9, 139.5, 130.6, 130.0, 129.8, 129.5, 129.3, 129.1, 128.0, 126.5, 125.6, 99.7, 59.9, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{21}N_3O_4S_2Na$: 490.0866; Found: 490.0869.

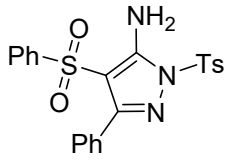
3-Phenyl-1-(propylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4p)



The title compound was obtained as a white solid (123.6 mg, 59%). Mp 157–159 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 2 H), 7.46-7.39 (m, 1 H), 7.38-7.30 (m, 4 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.63 (s, 2 H), 3.48 (t, *J* = 7.8 Hz, 2 H), 2.33 (s, 3 H), 1.91-1.77 (m, 2 H), 1.05 (t, *J* = 7.4 Hz, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 151.6, 144.0, 139.4, 129.9, 129.7, 129.5, 129.3, 127.9, 126.4, 100.1, 55.7, 21.4, 16.4, 12.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{19}H_{21}N_3O_4S_2Na$: 442.0866; Found: 442.0873.

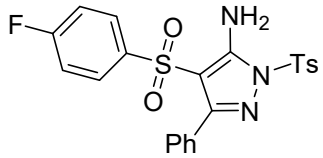
3-Phenyl-4-(phenylsulfonyl)-1-tosyl-1*H*-pyrazol-5-amine (4q)



The title compound was obtained as a white solid (183.2 mg, 81%). Mp 204–206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H), 7.47-7.33 (m, 8 H), 7.32-7.26 (m, 4 H), 6.73 (s, 2 H), 2.45 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.2, 151.3, 146.6, 142.3, 133.4, 133.0, 130.2, 130.0, 129.6, 129.5, 128.6, 128.1, 127.8, 126.4, 99.9, 21.7; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{19}N_3O_4S_2Na$: 476.0709; Found: 476.0715.

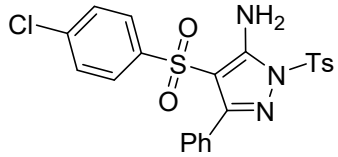
4-((4-Fluorophenyl)sulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4r)



The title compound was obtained as a white solid (180.9 mg, 77%). Mp 172–174 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.8 Hz, 2 H), 7.45-7.27 (m, 9 H), 6.96-6.87 (m, 2 H), 6.72 (s, 2 H), 2.44 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.1 (d, *J* = 254.1 Hz), 154.0, 151.2, 146.6, 138.3 (d, *J* = 2.5 Hz), 133.4, 130.2, 129.9, 129.7, 129.5, 129.3 (d, *J* = 9.6 Hz), 128.1, 127.9, 115.8 (d, *J* = 22.6 Hz), 99.9, 21.7; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -104.2−-104.4 (m, 1 F); **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{18}FN_3O_4S_2Na$: 494.0615; Found: 494.0616.

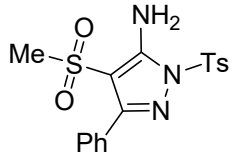
4-((4-Chlorophenyl)sulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4s)



The title compound was obtained as a white solid (177.3 mg, 73%). Mp 204–206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H), 7.46-7.27 (m, 9 H), 7.22 (dt, *J* = 8.8, 2.4 Hz, 2 H), 6.72 (s, 2 H), 2.44 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.9, 151.2, 146.7, 140.7, 139.5, 133.3, 130.2, 129.8, 129.7, 129.5, 128.9, 128.1, 127.9, 99.6, 21.7; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{22}H_{18}ClN_3O_4S_2Na$: 510.0319; Found: 510.0321.

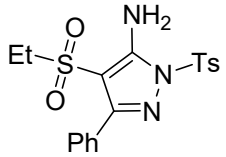
4-(Methylsulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4t)
(chloromatography)(PE/EA = 5/1 to 1/1)



The title compound was obtained as a white solid (102.2 mg, 52%). Mp 180–182 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2 H), 7.76 (dd, *J* = 7.4, 2.2 Hz, 2 H), 7.48-7.33 (m, 5 H), 6.59 (s, 2 H), 2.78 (s, 3 H), 2.45 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.1, 151.4, 146.6, 133.4, 130.2, 130.04, 129.99, 129.3, 128.4, 128.1, 99.0, 44.7, 21.7; **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{17}H_{18}N_3O_4S_2$: 392.0733; Found: 392.0735.

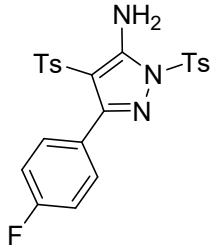
4-(Ethylsulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4u) (chloromatography)(PE/EA = 4/1 to 2/1)



The title compound was obtained as a white solid (103.0 mg, 51%). Mp 158–160 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.88 (m, 2 H), 7.77-7.72 (m, 2 H), 7.44-7.33 (m, 5 H), 6.59 (s, 2 H), 2.78 (q, *J* = 7.2 Hz, 2 H), 2.45 (s, 3 H), 1.09 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 153.5, 152.3, 146.6, 133.4, 130.15, 130.10, 129.9, 129.2, 128.3, 128.0, 96.4, 50.6, 21.7, 6.9; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{18}H_{19}N_3O_4S_2Na$: 428.0709; Found: 428.0712.

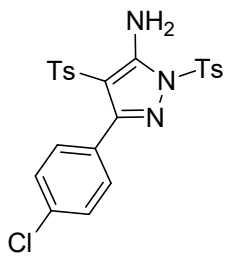
3-(4-Fluorophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4v)



The title compound was obtained as a white solid (191.8 mg, 80%). Mp 198–200 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.85 (m, 2 H), 7.48-7.40 (m, 2 H), 7.40-7.29 (m, 4 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 7.02-6.94 (m, 2 H), 6.71 (s, 2 H), 2.45 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 163.6 (d, *J* = 248.3 Hz), 153.1, 151.2, 146.6, 144.1, 139.4, 133.4, 131.6 (d, *J* = 8.5 Hz), 130.2, 129.4, 128.1, 126.4, 126.2 (d, *J* = 3.4 Hz), 114.9 (d, *J* = 21.6 Hz), 100.2, 21.8, 21.5; **^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.1−-111.2 (m, 1 F); **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{23}H_{21}FN_3O_4S_2$: 486.0952; Found: 486.0957.

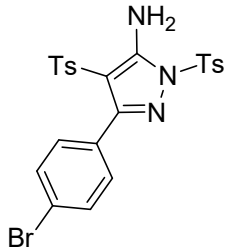
3-(4-Chlorophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4w)



The title compound was obtained as a white solid (192.4 mg, 76%). Mp 212–214 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2 H), 7.44-7.38 (m, 2 H), 7.36 (d, *J* = 8.4 Hz, 4 H), 7.30-7.26 (m, 2 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.71 (s, 2 H), 2.45 (s, 3 H), 2.34 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9, 151.3, 146.7, 144.1, 139.5, 135.8, 133.4, 130.9, 130.2, 129.4, 128.6, 128.12, 128.07, 126.3, 100.1, 21.8, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{20}ClN_3O_4S_2Na$: 524.0476; Found: 524.0479.

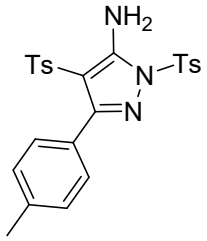
3-(4-Bromophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4x)



The title compound was obtained as a white solid (209.8 mg, 77%). Mp 223–225 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2 H), 7.46-7.40 (m, 2 H), 7.39-7.31 (m, 6 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.71 (s, 2 H), 2.45 (s, 3 H), 2.34 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.9, 151.3, 146.7, 144.1, 139.4, 133.3, 131.1, 131.0, 130.2, 129.4, 129.0, 128.1, 126.3, 124.2, 100.1, 21.7, 21.4; **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{23}H_{21}BrN_3O_4S_2$: 546.0151; Found: 546.0154.

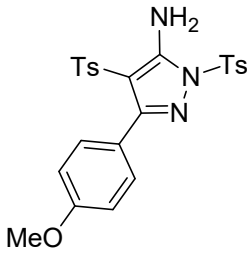
3-(*p*-Tolyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4y)



The title compound was obtained as a white solid (192.8 mg, 80%). Mp 159–161 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2 H), 7.41-7.29 (m, 6 H), 7.14-7.04 (m, 4 H), 6.70 (s, 2 H), 2.44 (s, 3 H), 2.35 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 154.1, 151.2, 146.4, 143.7, 139.6, 139.5, 133.4, 130.0, 129.3, 129.2, 128.4, 128.0, 127.1, 126.3, 100.0, 21.6, 21.3, 21.2; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{24}H_{23}N_3O_4S_2Na$: 504.1022; Found: 504.1028.

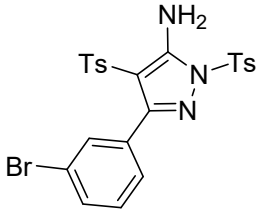
3-(4-Methoxyphenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4z)



The title compound was obtained as a white solid (139.1 mg, 56%). Mp 159–161 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2 H), 7.46-7.38 (m, 2 H), 7.38-7.29 (m, 4 H), 7.08 (d, *J* = 8.0 Hz, 2 H), 6.86-6.77 (m, 2 H), 6.70 (s, 2 H), 3.82 (s, 3 H), 2.44 (s, 3 H), 2.33 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 160.6, 153.8, 151.3, 146.4, 143.8, 139.6, 133.5, 130.9, 130.1, 129.3, 128.0, 126.3, 122.5, 113.2, 100.0, 55.2, 21.7, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{24}H_{23}N_3O_5S_2Na$: 520.0971; Found: 520.0972.

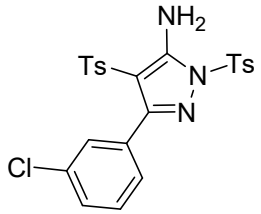
3-(3-Bromophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4aa)



The title compound was obtained as a white solid (222.6 mg, 82%). Mp 174–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.45-7.30 (m, 6 H), 7.22-7.07 (m, 3 H), 6.71 (s, 2 H), 2.46 (s, 3 H), 2.35 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.4, 151.2, 146.7, 144.2, 139.3, 133.3, 132.5, 132.1, 131.9, 130.2, 129.44, 129.36, 128.2, 128.1, 126.5, 121.7, 100.3, 21.8, 21.5; **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{23}H_{21}BrN_3O_4S_2$: 546.0151; Found: 546.0153.

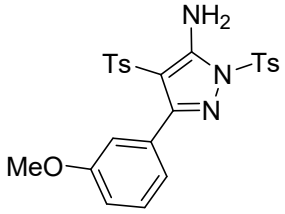
3-(3-Chlorophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4bb)



The title compound was obtained as a white solid (184.7 mg, 73%). Mp 169–171 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 2 H), 7.48-7.20 (m, 8 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.73 (s, 2 H), 2.45 (s, 3 H), 2.34 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 152.6, 151.2, 146.7, 144.2, 139.3, 133.7, 133.4, 131.7, 130.3, 139.6, 129.43, 129.35, 129.1, 128.1, 127.8, 126.5, 100.3, 21.8, 21.8; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{20}ClN_3O_4S_2Na$: 524.0476; Found: 524.0477.

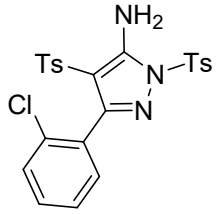
3-(3-Methoxyphenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4cc)



The title compound was obtained as a white solid (209.6 mg, 84%). Mp 94–96 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2 H), 7.39-7.31 (m, 4 H), 7.19 (t, *J* = 8.0 Hz, 1 H), 7.07 (d, *J* = 8.0 Hz, 2 H), 7.01-6.95 (m, 2 H), 6.91 (ddd, *J* = 8.4, 2.6, 1.0 Hz, 1 H), 6.71 (s, 2 H), 3.75 (s, 3 H), 2.45 (s, 3 H), 2.32 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 158.9, 153.9, 151.2, 146.5, 143.8, 139.4, 133.4, 131.2, 130.1, 129.2, 128.8, 128.1, 126.4, 121.9, 116.0, 114.4, 100.2, 55.2, 21.7, 21.4; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{24}H_{23}N_3O_5S_2Na$: 520.0971; Found: 520.0978.

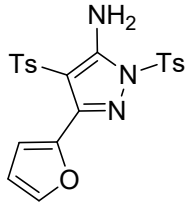
3-(2-Chlorophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4dd)



The title compound was obtained as a white solid (152.4 mg, 61%). Mp 163–165 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.30 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.27-7.23 (m, 3 H), 7.19 (td, *J* = 7.4, 1.6 Hz, 1 H), 7.13-7.03 (m, 3 H), 6.62 (s, 2 H), 2.45 (s, 3 H), 2.37 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.6, 150.6, 146.5, 144.0, 139.0, 134.4, 133.5, 131.8, 130.6, 130.1, 129.2, 129.0, 128.9, 128.0, 126.7, 125.8, 101.3, 21.7, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{23}H_{20}ClN_3O_4S_2Na$: 524.0476; Found: 524.0475.

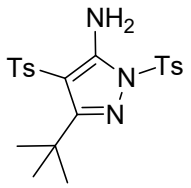
3-(Furan-2-yl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4ee)



The title compound was obtained as a white solid (165.9 mg, 72%). Mp 71–73 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.42 (d, *J* = 2.0 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 3.6 Hz, 1 H), 6.77 (s, 2 H), 6.39 (dd, *J* = 3.4, 1.8 Hz, 1 H), 2.43 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 151.6, 146.7, 144.1, 144.0, 143.9, 143.7, 139.6, 133.4, 130.2, 129.5, 128.1, 126.3, 113.7, 113.3, 98.0, 21.7, 21.5; **HRMS** (TOFMS) m/z $[M+Na]^+$ calcd for $C_{21}H_{19}N_3O_5S_2Na$: 480.0658; Found: 480.0662.

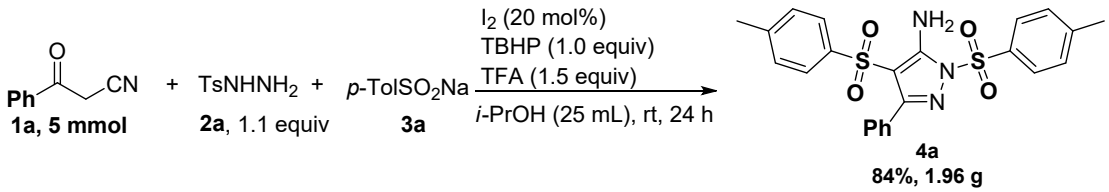
3-(tert-Butyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4ff)



The title compound was obtained as a white solid (85.9 mg, 38%). Mp 187–189 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 6.73 (s, 2 H), 2.50 (s, 3 H), 2.46 (s, 3 H), 2.40 (s, 3 H), 1.15 (s, 9 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 162.4, 153.5, 146.3, 143.6, 141.3, 133.5, 129.9, 129.5, 128.0, 125.6, 98.1, 34.6, 28.9, 21.7, 21.5; **HRMS** (TOFMS) m/z $[M+H]^+$ calcd for $C_{21}H_{26}N_3O_4S_2$: 448.1359; Found: 448.1362.

Gram-scale reaction



To a 50 mL round-bottom flask were added 3-oxo-3-phenylpropanenitrile (**1a**) (725.2 mg, 5.0 mmol), 4-methylbenzenesulfonohydrazide (**2a**) (1025.1 mg, 5.5 mmol), sodium 4-methylbenzenesulfinate (**3a**) (1778.2 mg, 10.0 mmol), I_2 (252.3 mg, 1.0 mmol), *i*-PrOH (25 mL), TBHP (70% in water) (648.8 mg, 5.0 mmol), and trifluoroacetic acid (TFA) (857.2 mg, 7.5 mmol) sequentially under air. The reaction mixture was then stirred at room temperature for 24 h. It was then quenched (consumption of residual I_2) with saturated $Na_2S_2O_3$ aqueous solution, forming white precipitation. Filtration of the suspension gave crude product. Washing the crude product with water (100 mL), *i*-PrOH (20 mL), and petroleum ether (100 mL) sequentially afforded pure product **4a** as a white solid (1.96 g, 84%).

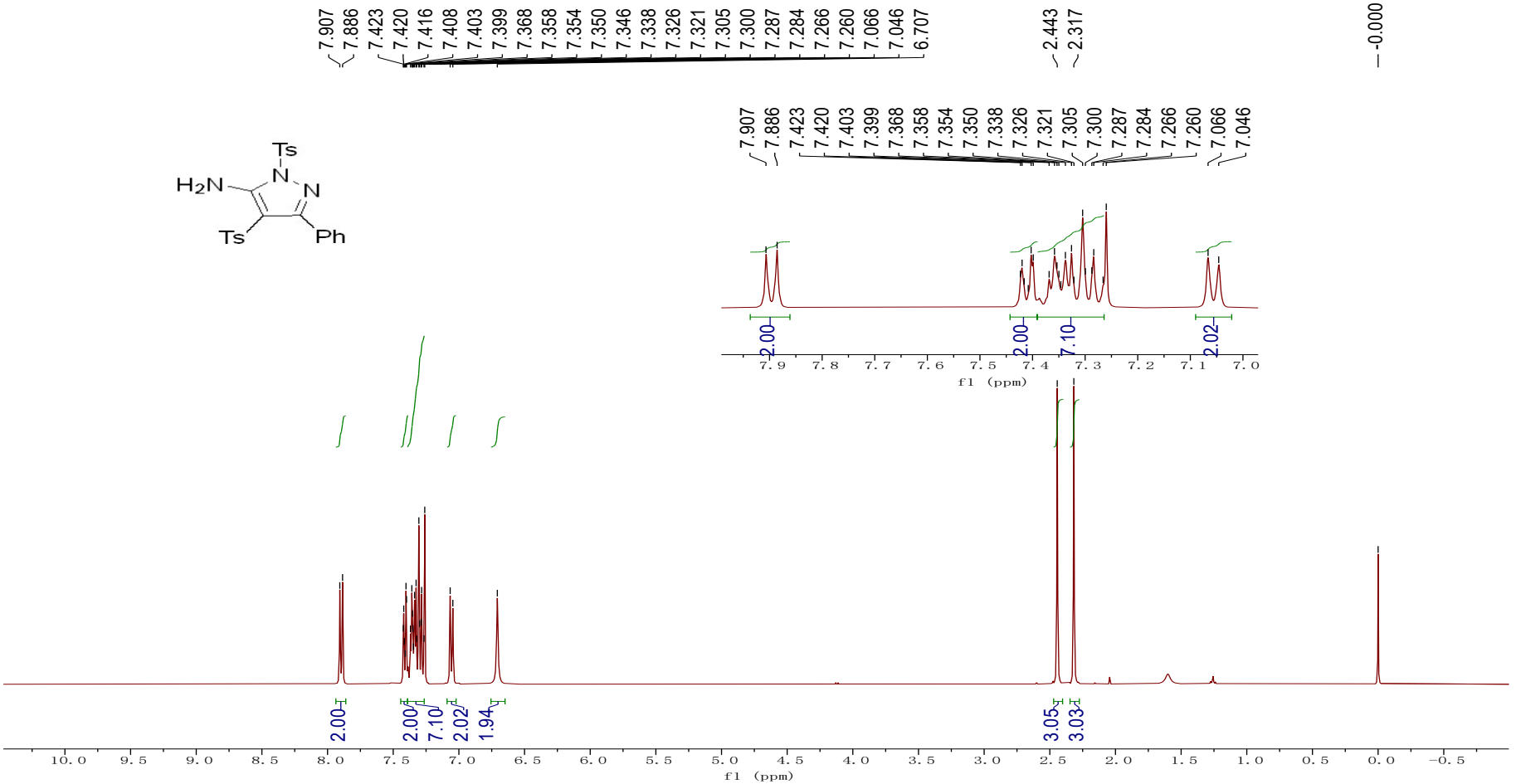
References

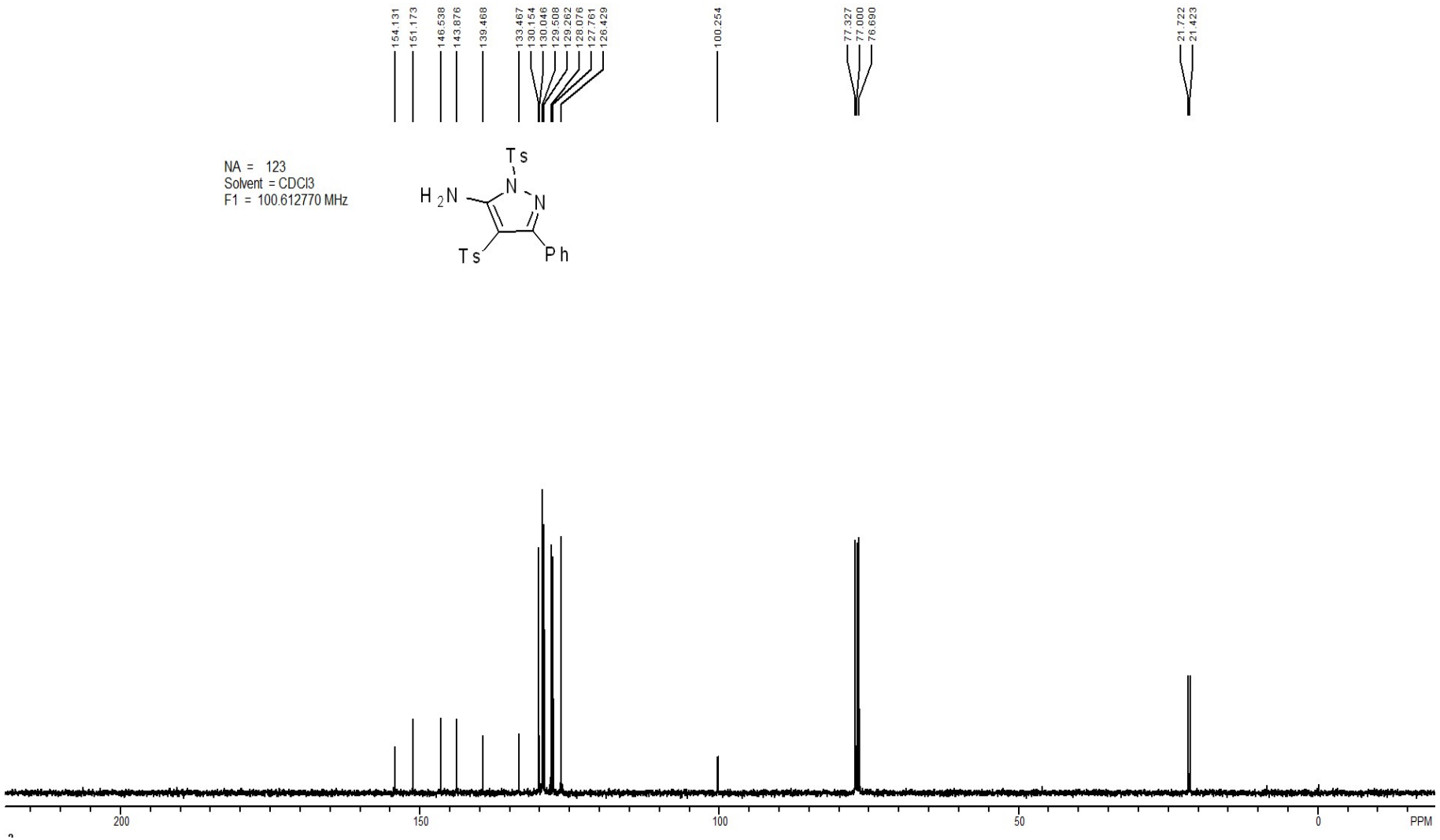
[1] F.-L. Yang, X.-T. Ma and S.-K. Tian, *Chem. Eur. J.* 2012, **18**, 1582–1585.

[2] G. Zhang, Y. Wang, J. Xu, J. Sun, F. Sun, Y. Zhang, C. Zhang and Y. Du, *Chem. Sci.* 2020, **11**, 947-953.

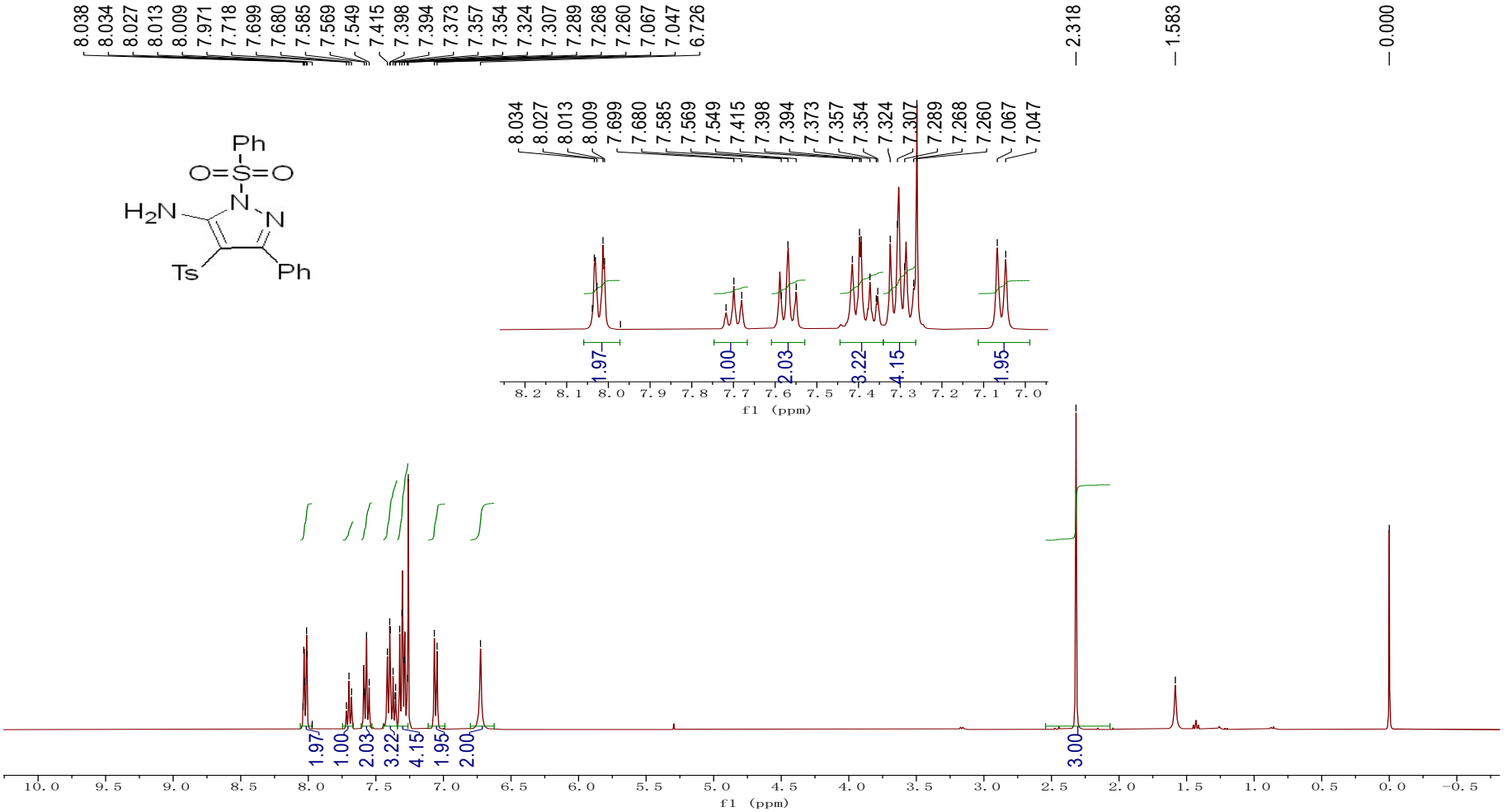
^{1}H NMR and ^{13}C NMR spectra of pyrazoles 4

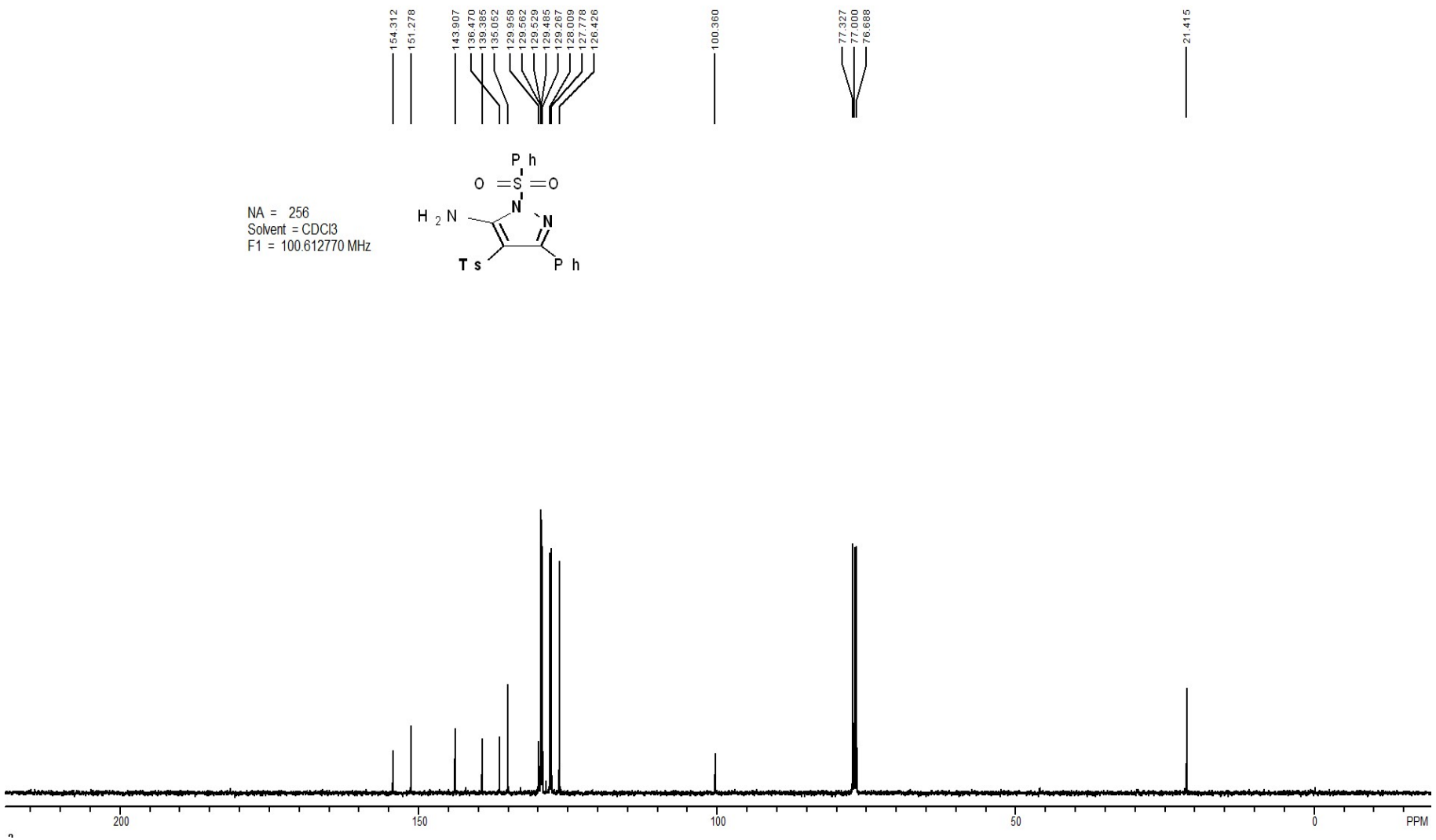
3-Phenyl-1, 4-ditosyl-1*H*-pyrazol-5-amine (4a)



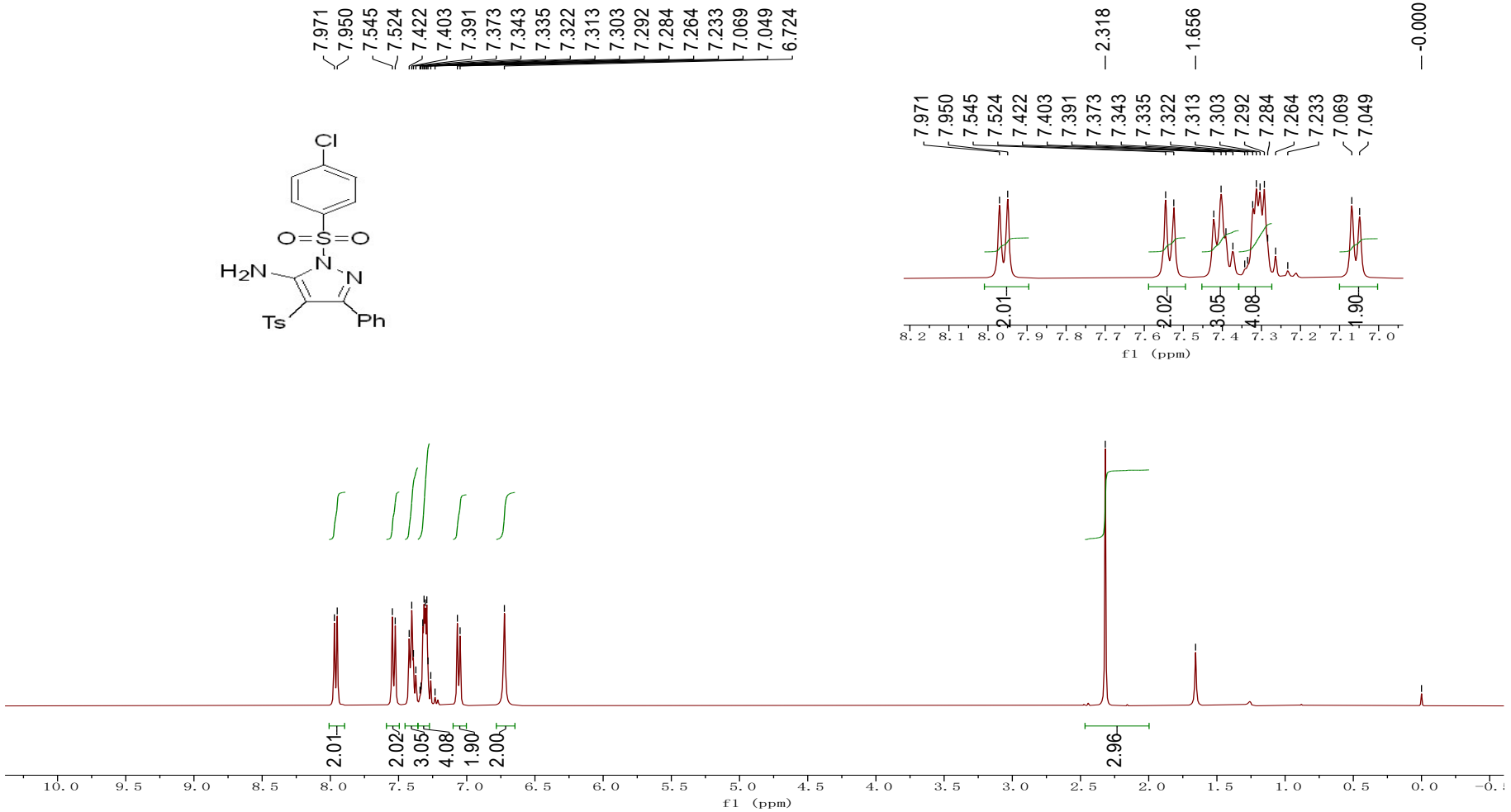

154.131
151.173
146.538
143.876
139.468
133.467
130.154
130.046
129.508
129.262
128.076
127.761
126.429
100.254
77.327
77.000
76.690
21.722
21.423
NA = 123
Solvent = CDCl3
F1 = 100.612770 MHz
Ts
N
H2N
N
Ts
Ph
200
150
100
50
0
PPM

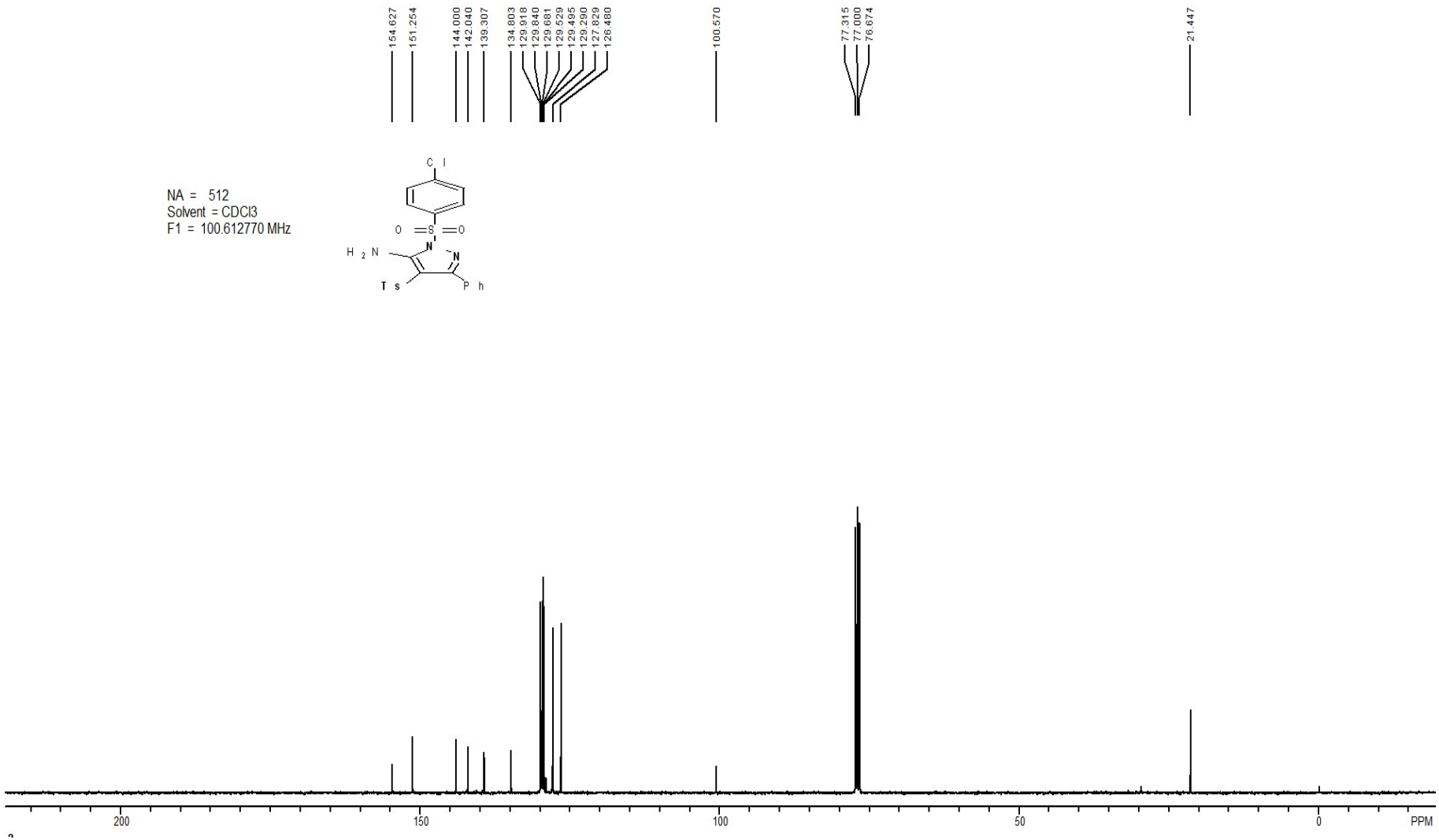
3-Phenyl-1-(phenylsulfonyl)-4-tosyl-1*H*-pyrazol-5-amine (4b)



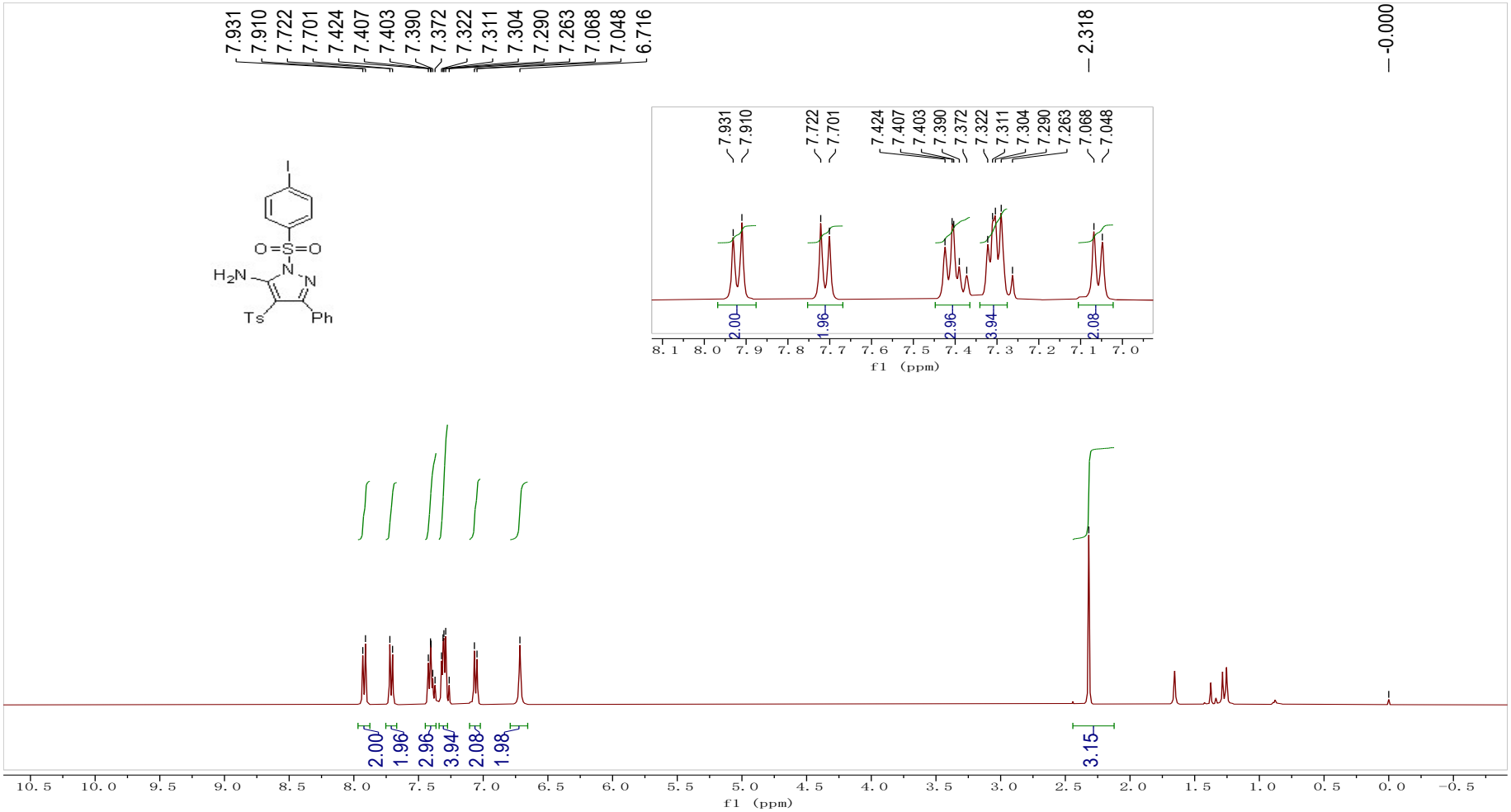

154.312
151.278
143.907
136.470
139.385
135.052
129.958
129.562
129.529
129.485
129.267
128.009
127.778
126.426
100.360
77.327
77.000
76.688
21.415
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
Ph
O =S =O
N
H2N
N
Ts
Ph
200
150
100
50
0
PPM

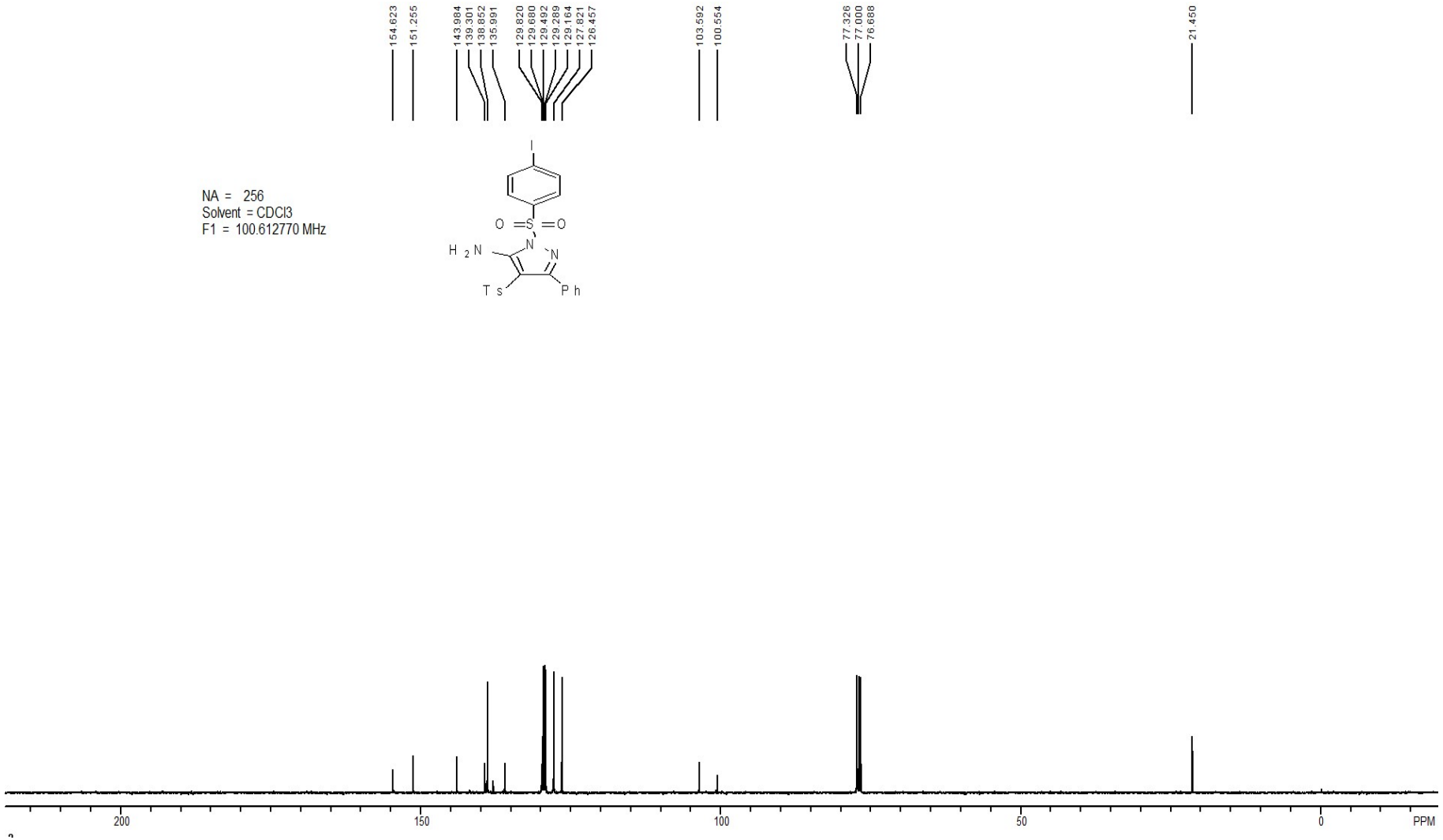
1-((4-Chlorophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4c)



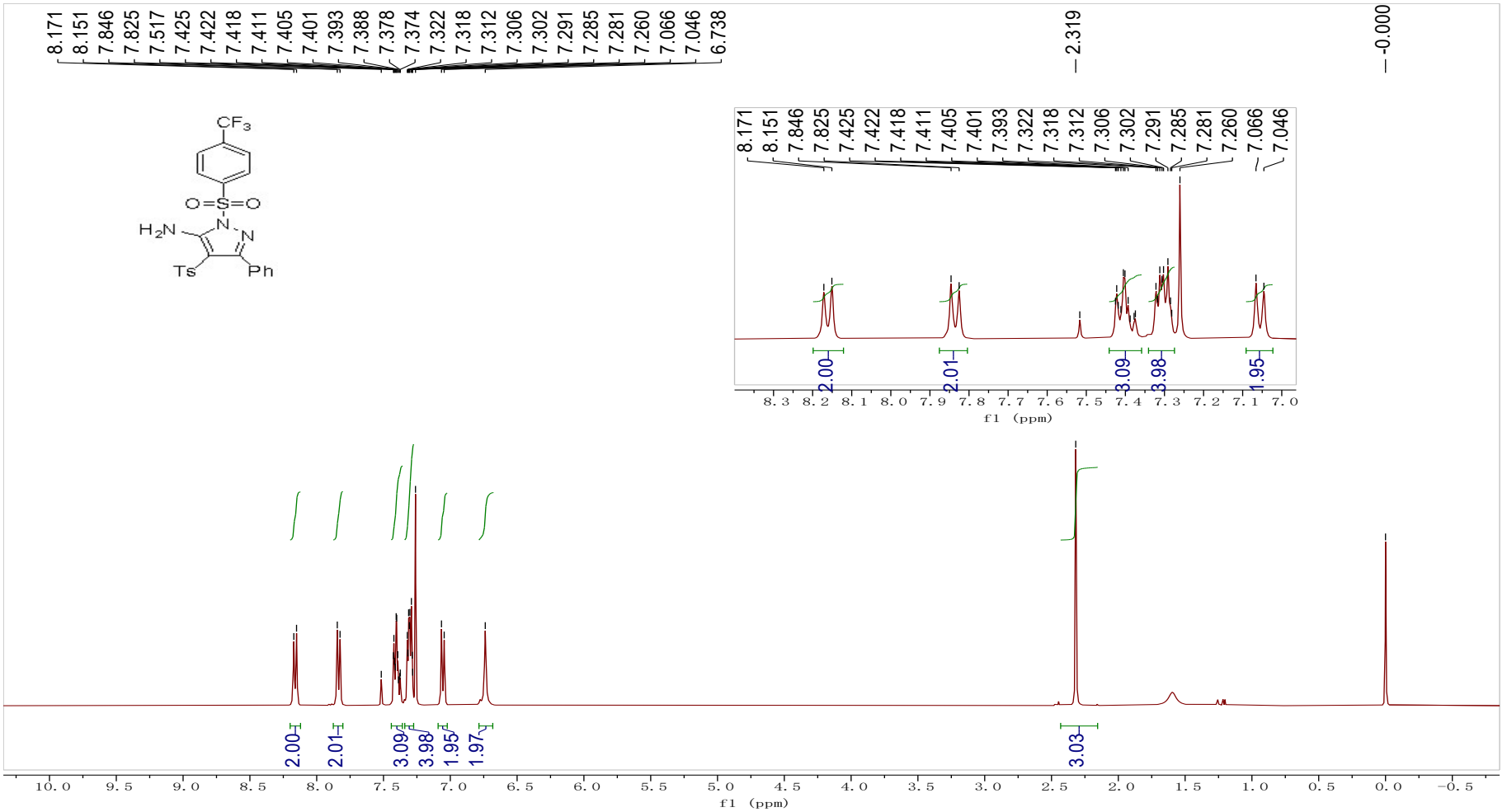

154.627
151.254
144.000
142.040
139.307
134.803
129.918
129.840
129.681
129.529
129.495
129.290
127.829
126.480
100.570
77.315
77.000
76.674
21.447
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
Cl
O
S
O
H2N
N
N
Ts
Ph
200
150
100
50
0
PPM

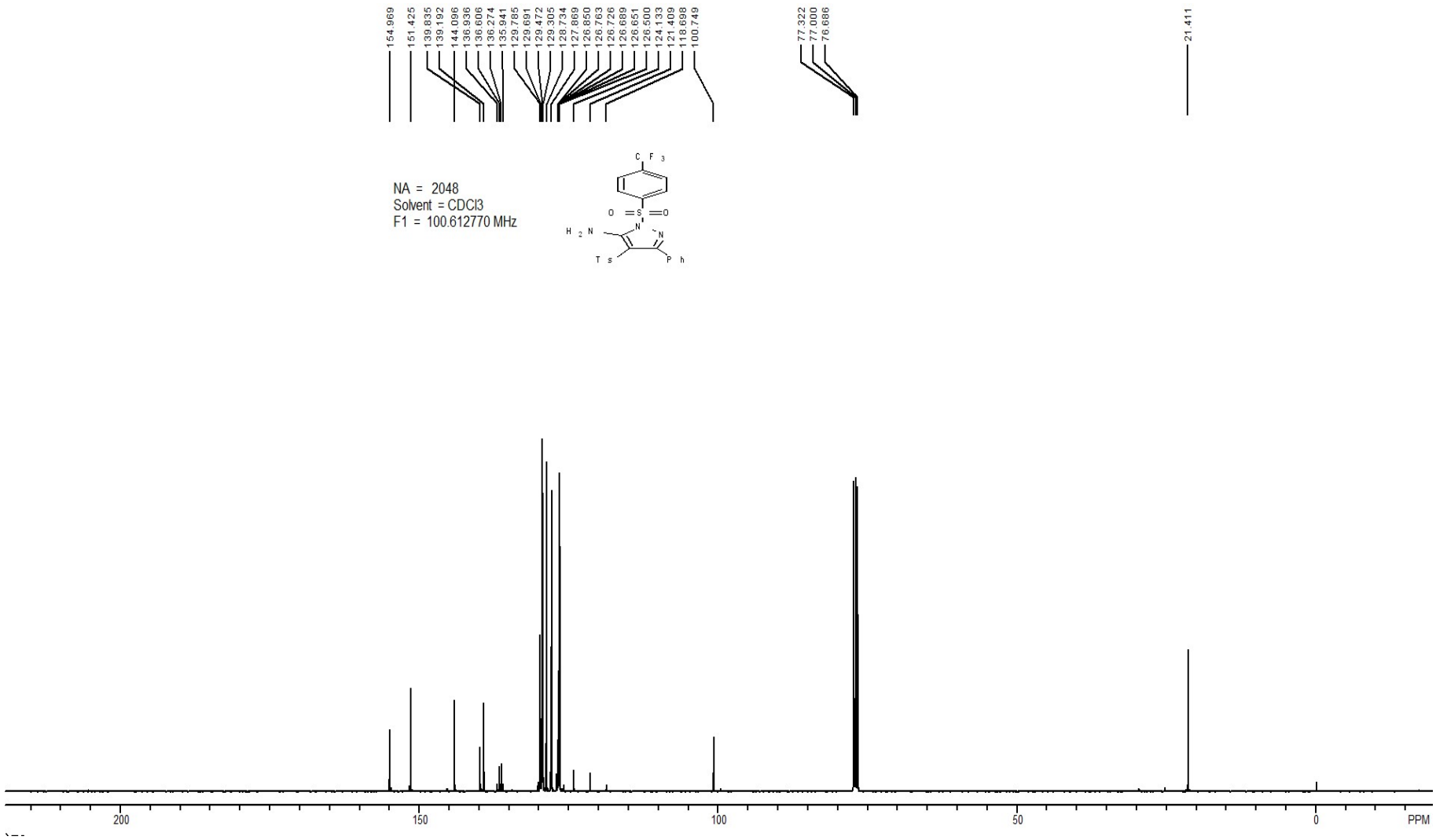
1-((4-Iodophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4d)

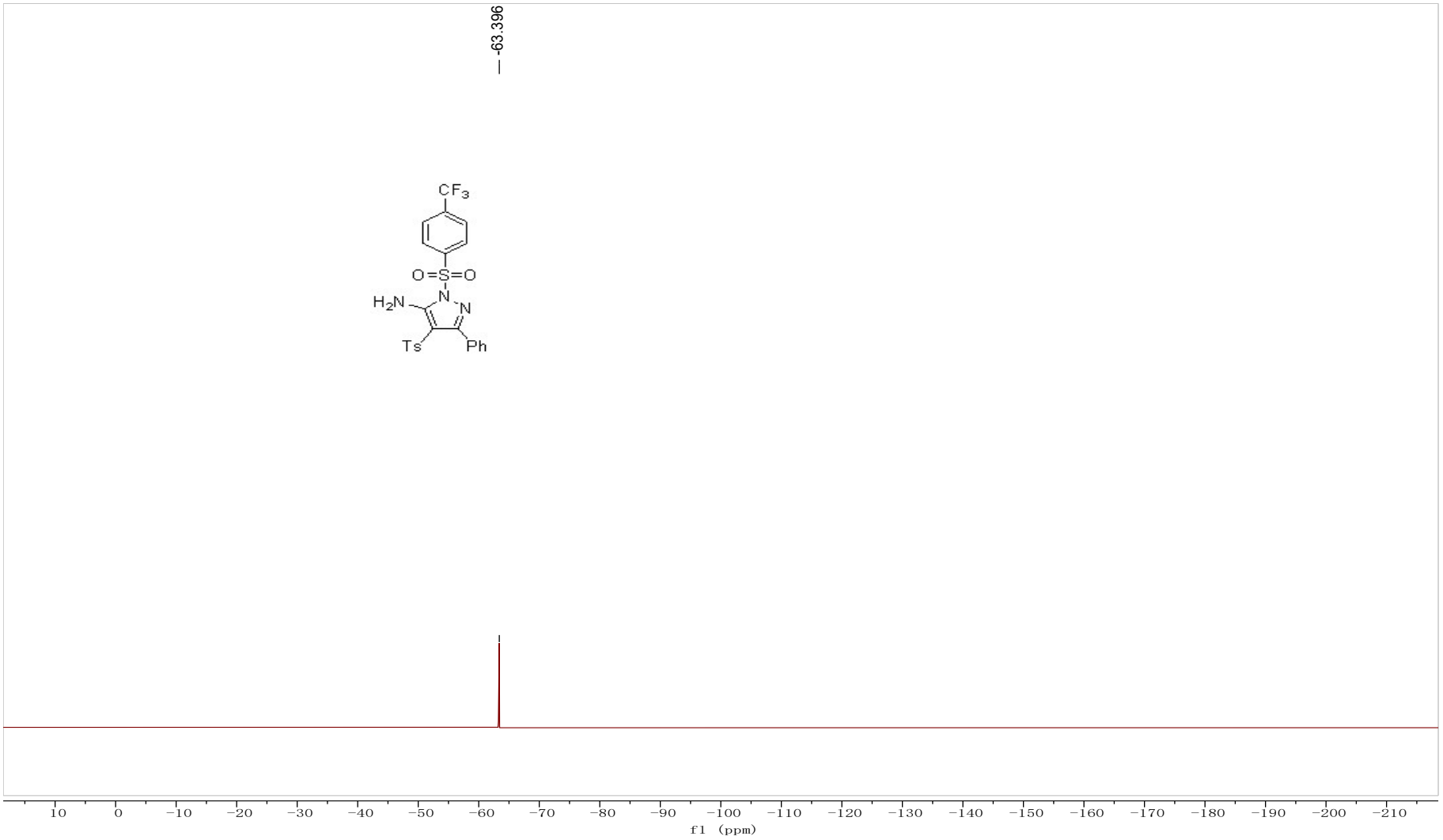



154.623
151.255
143.984
139.301
138.852
135.991
129.820
129.680
129.492
129.289
129.164
127.821
126.457
103.592
100.554
77.326
77.000
76.688
21.450
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
I
O =S= O
N
N
H 2 N
T s
P h
200
150
100
50
0
PPM

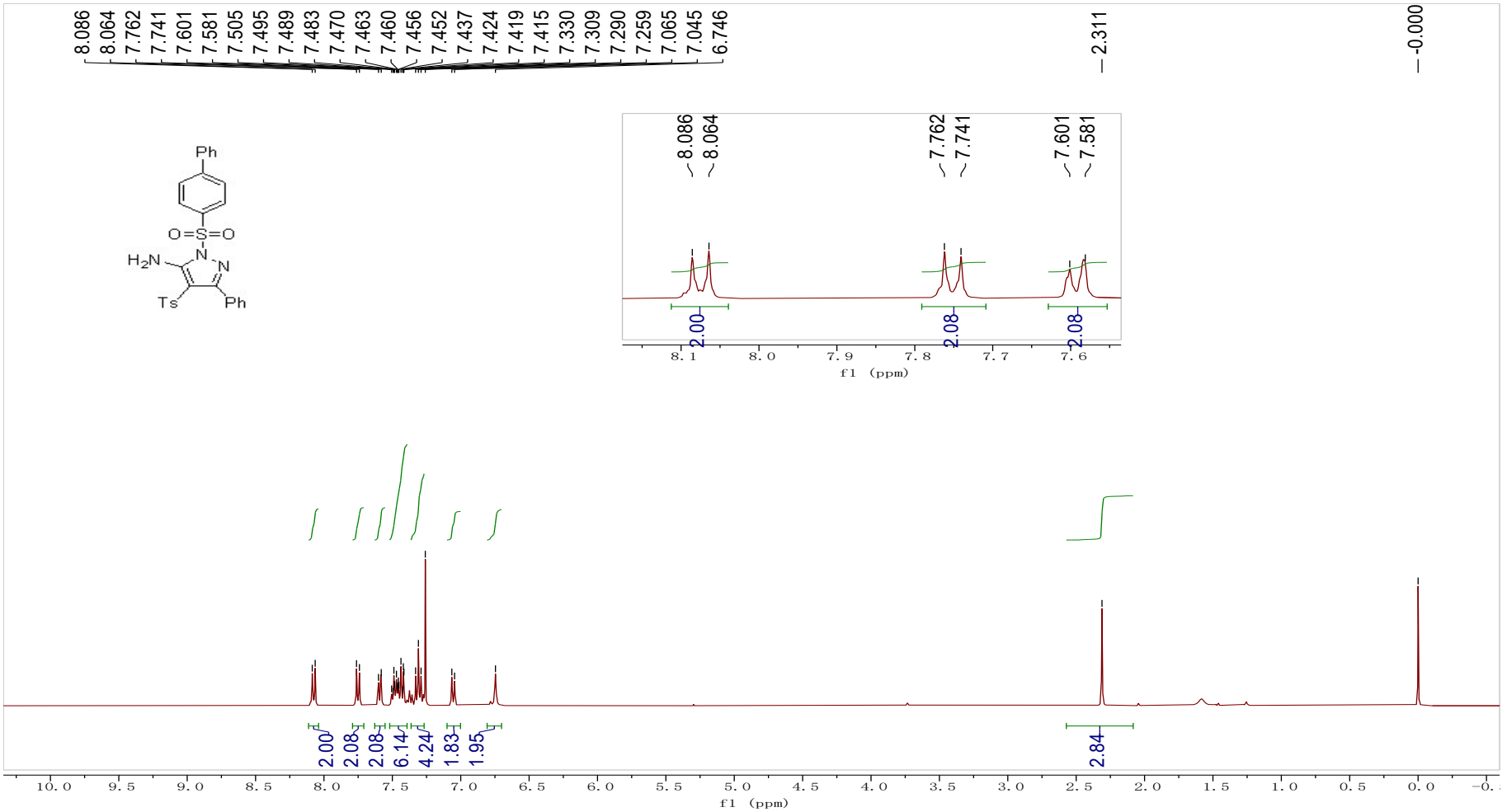
3-Phenyl-4-tosyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-1H-pyrazol-5-amine (4e)

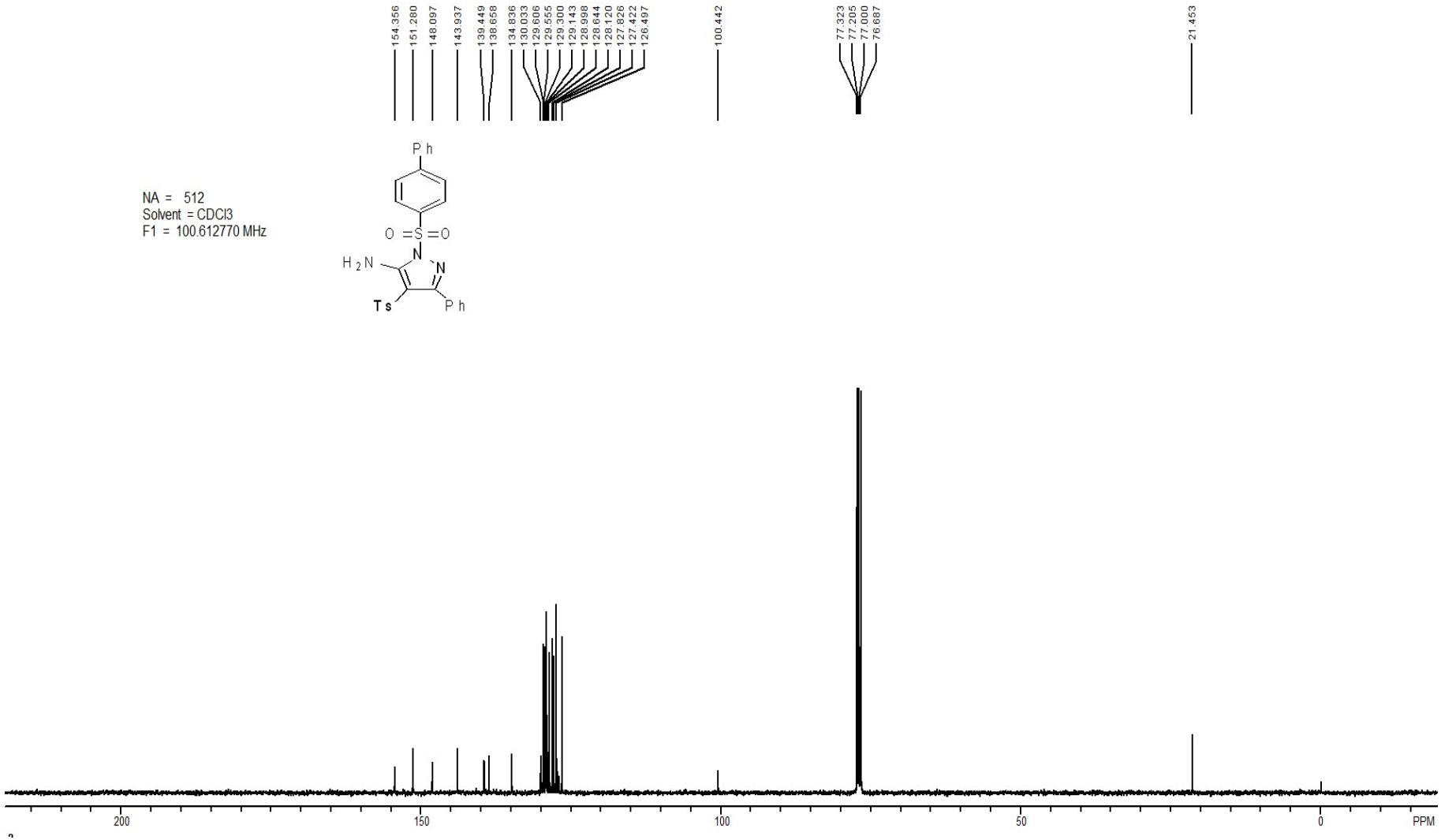



154.969
151.425
139.835
139.192
144.096
136.936
136.606
136.274
135.941
129.785
129.691
129.472
129.305
128.734
127.869
126.850
126.763
126.726
126.689
126.651
126.500
124.133
121.409
118.698
100.749
77.322
77.000
76.686
21.411
NA = 2048
Solvent = CDCl3
F1 = 100.612770 MHz
200
150
100
50
0
PPM

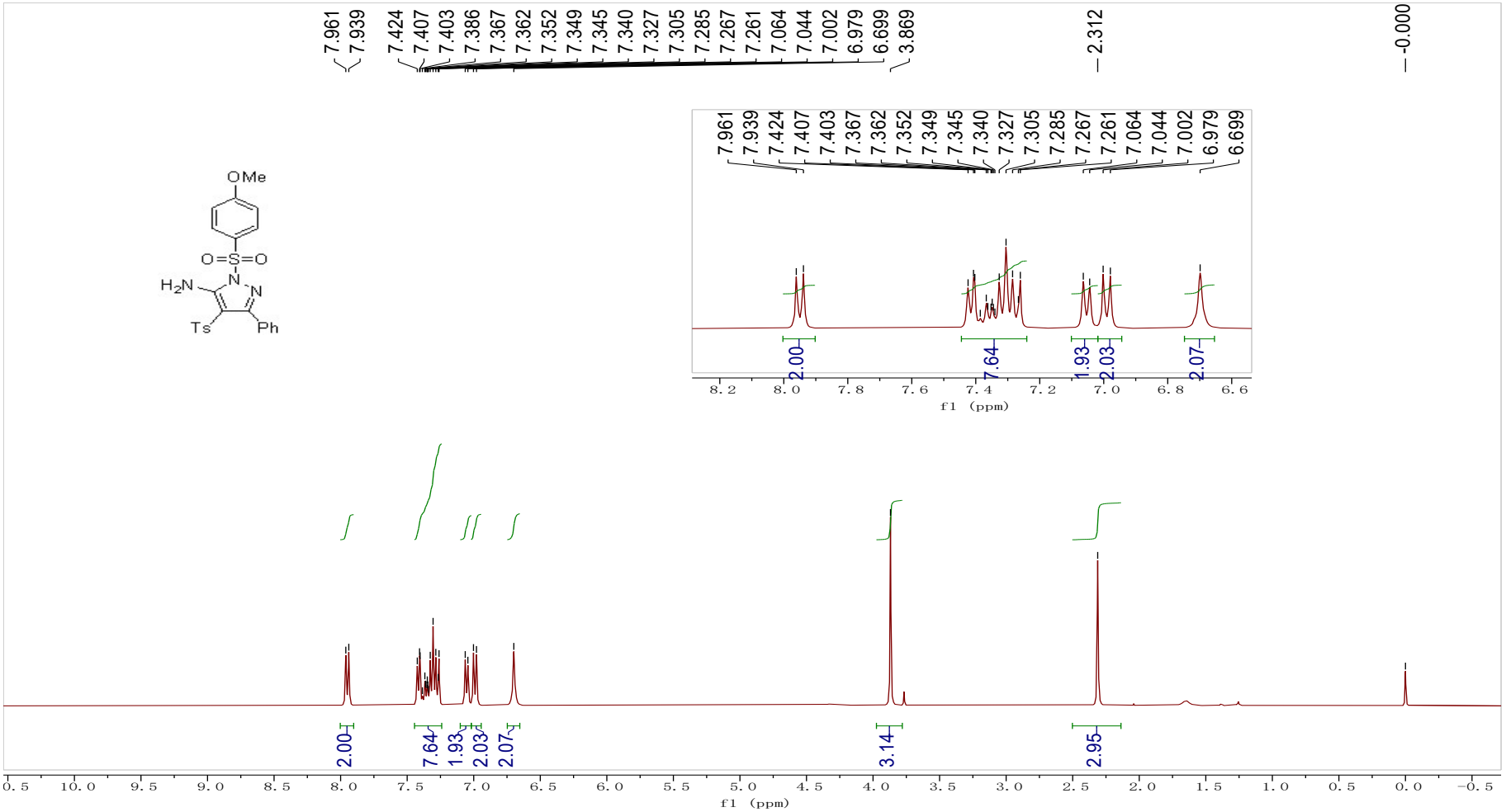

-63.396
CF3
O=S=O
N
N
H2N
Ts
Ph
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

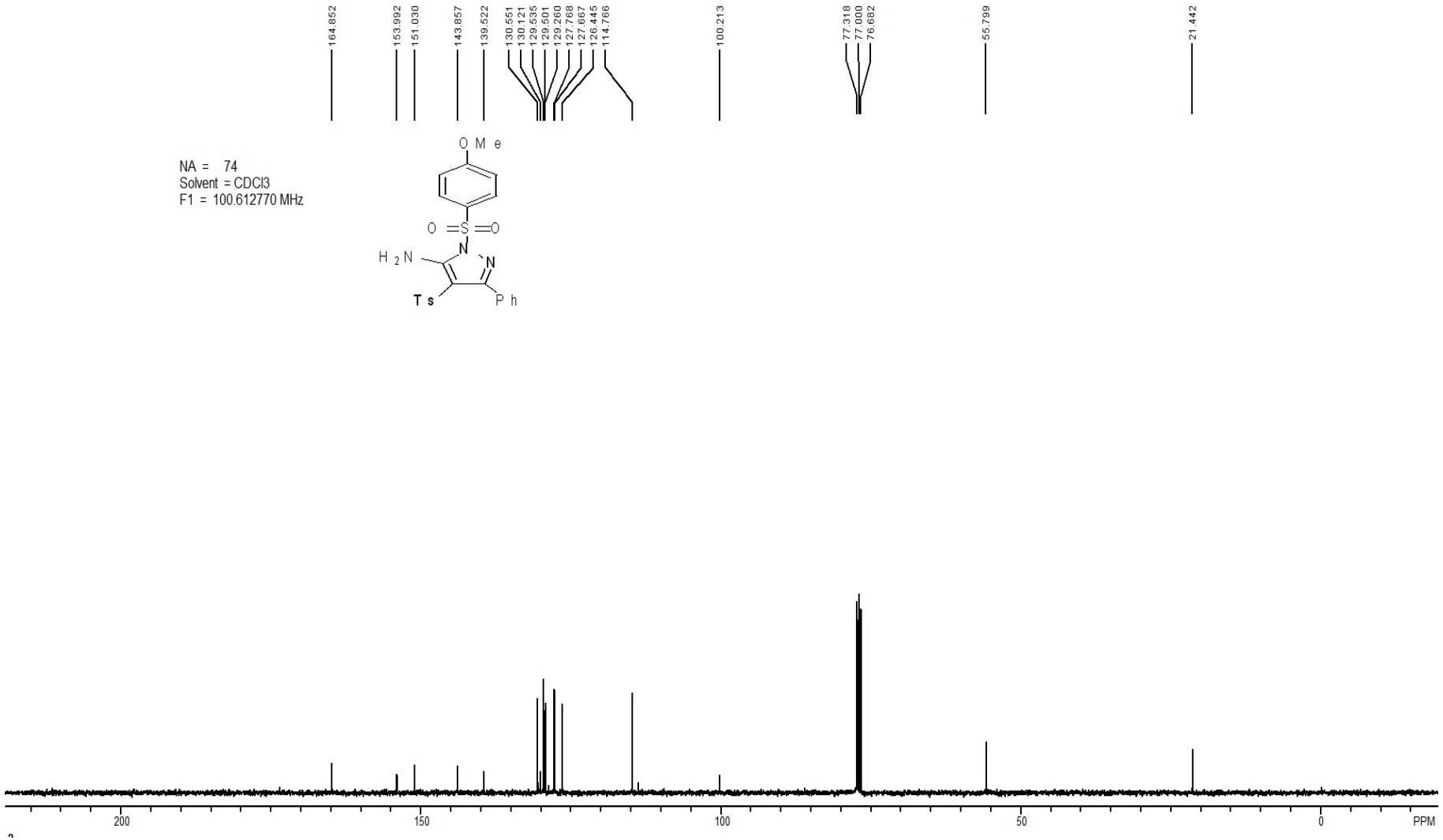
1-([1,1'-Biphenyl]-4-ylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4f)



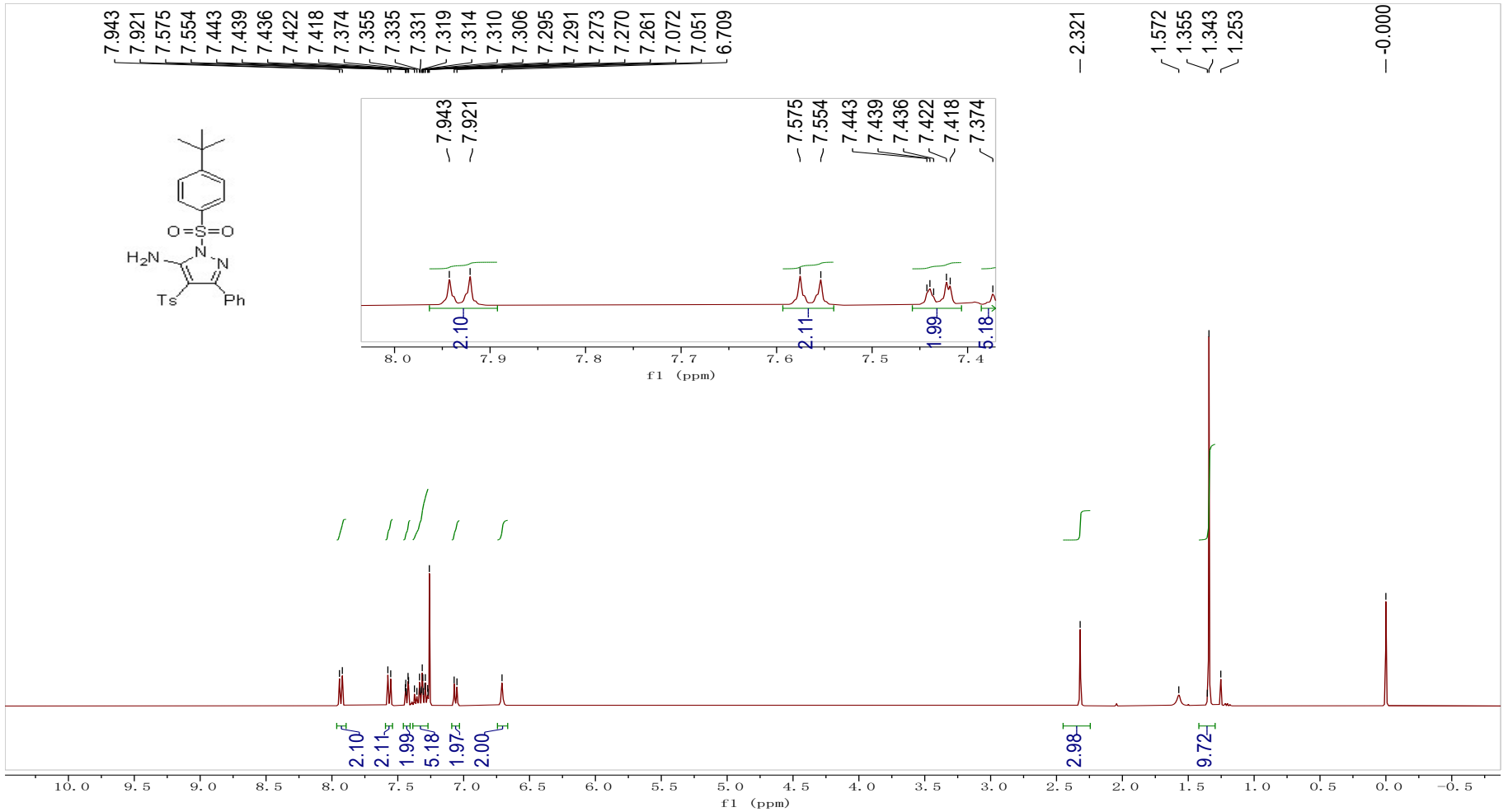

154.356
151.280
148.097
143.937
139.449
138.658
134.836
130.033
129.606
129.555
129.300
129.143
128.998
128.644
128.120
127.826
127.422
126.497
100.442
77.323
77.205
77.000
76.687
21.453
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
Ph
O =S=O
N
H2N
N
Ts
Ph
200
150
100
50
0
PPM

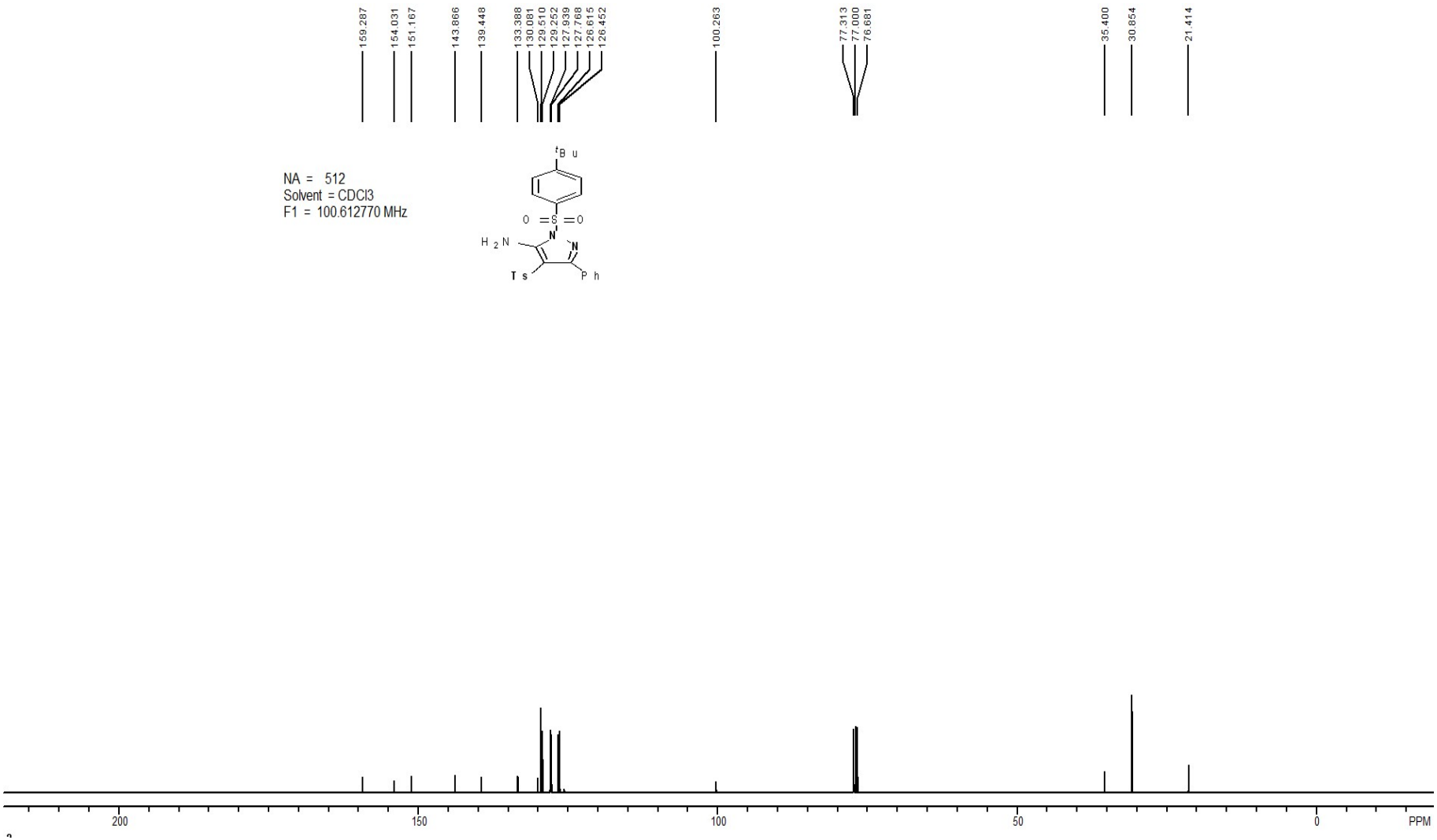
1-((4-Methoxyphenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4g)



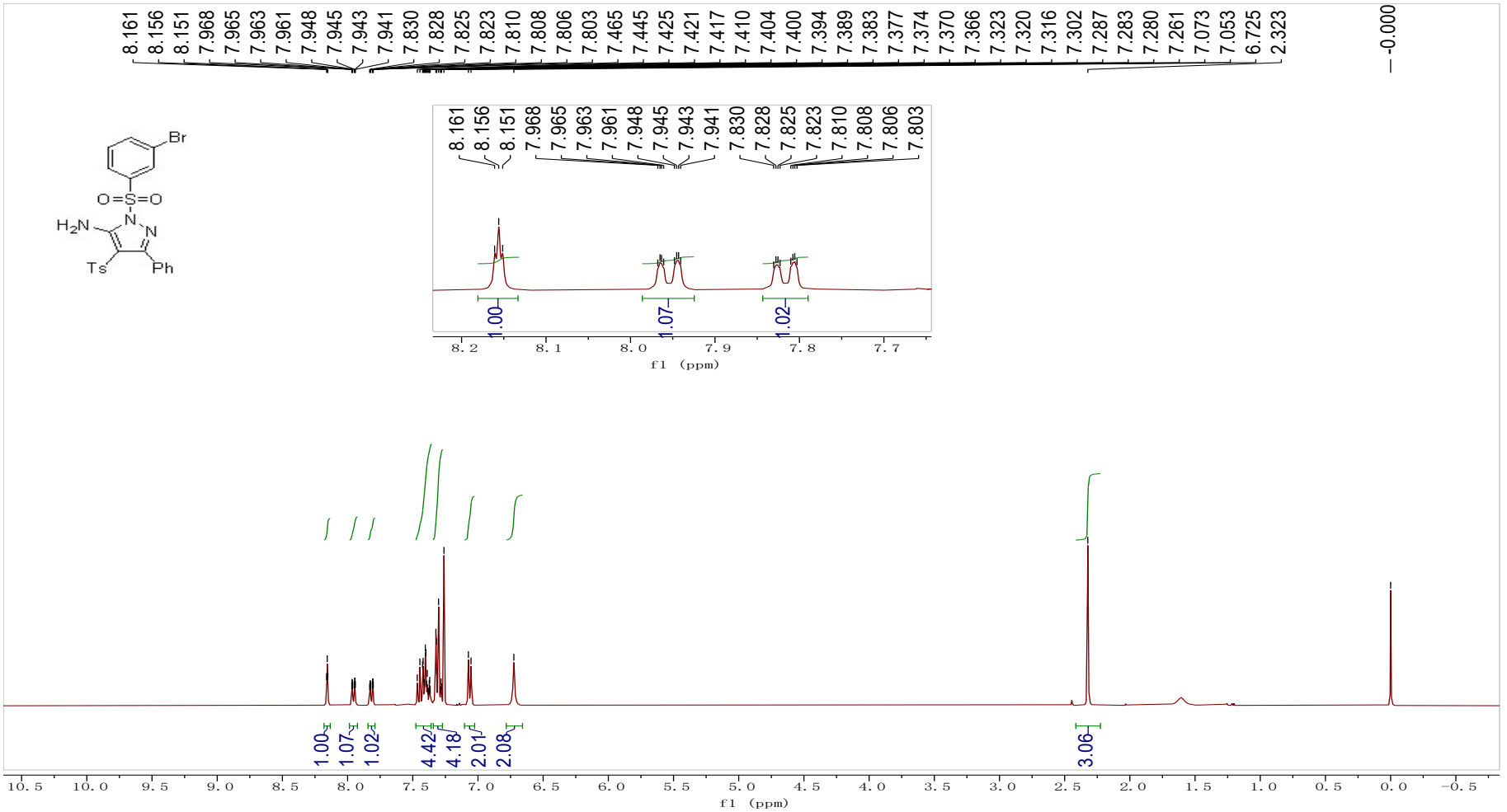

164.852
153.992
151.030
143.857
139.522
130.551
130.121
129.535
129.501
129.260
127.768
127.667
126.445
114.766
100.213
77.318
77.000
76.682
55.799
21.442
NA = 74
Solvent = CDCl3
F1 = 100.612770 MHz
O Me
O =S= O
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

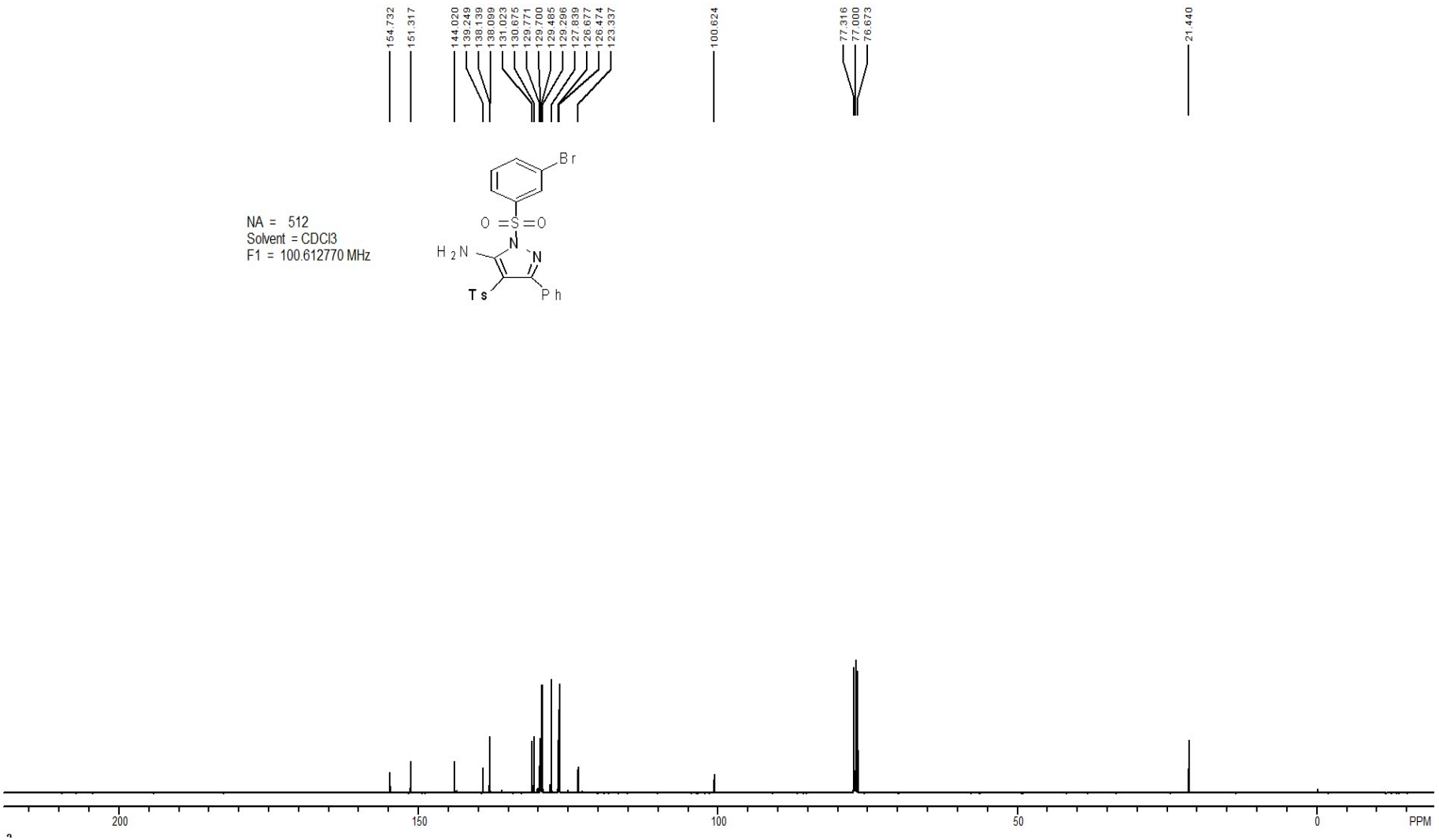
1-((4-(Tert-butyl)phenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4h)



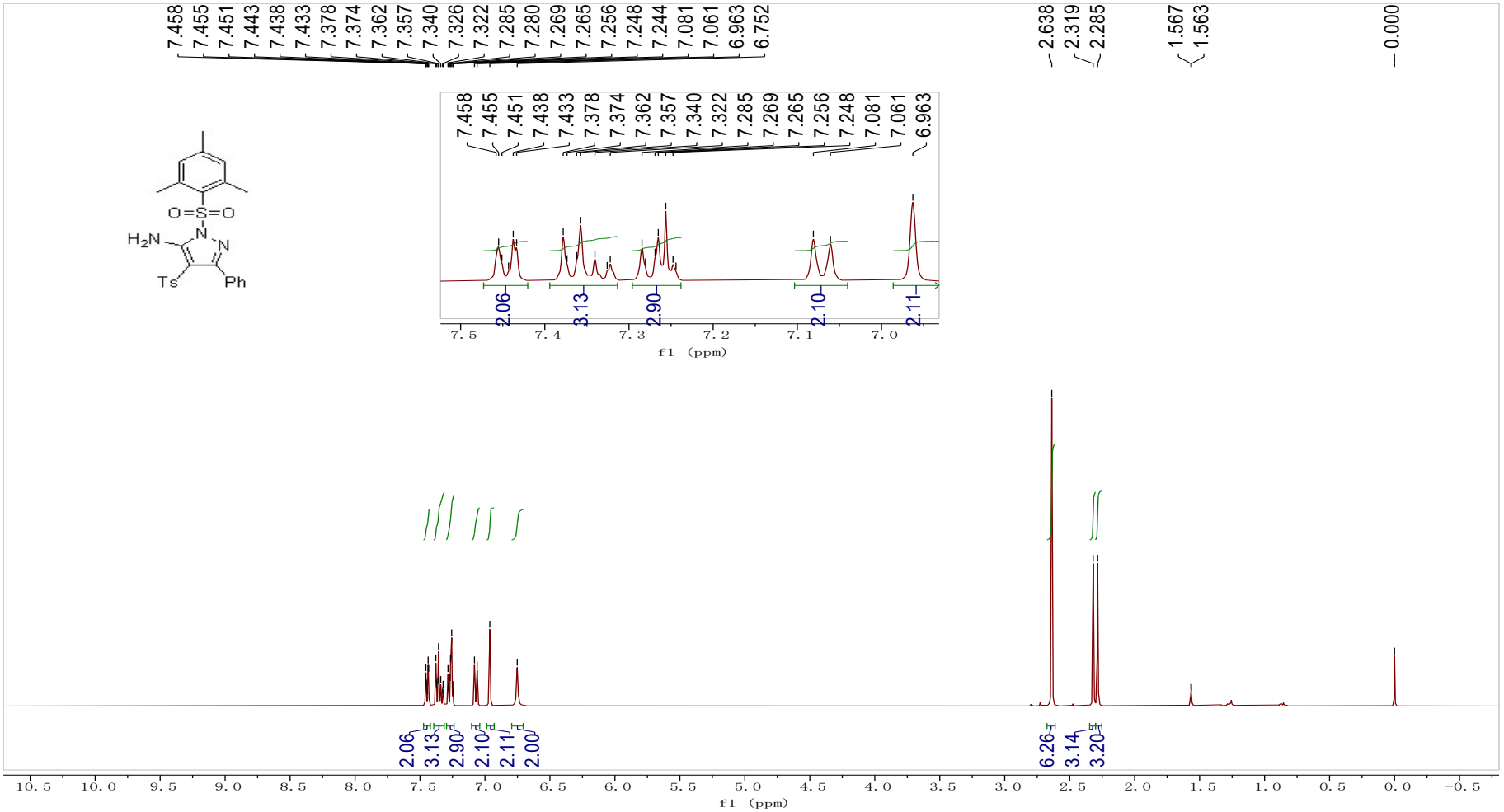

159.287
154.031
151.167
143.866
139.448
133.388
130.081
129.510
129.252
127.939
127.768
126.615
126.452
100.263
77.313
77.000
76.681
35.400
30.854
21.414
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
tBu
O
S
O
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

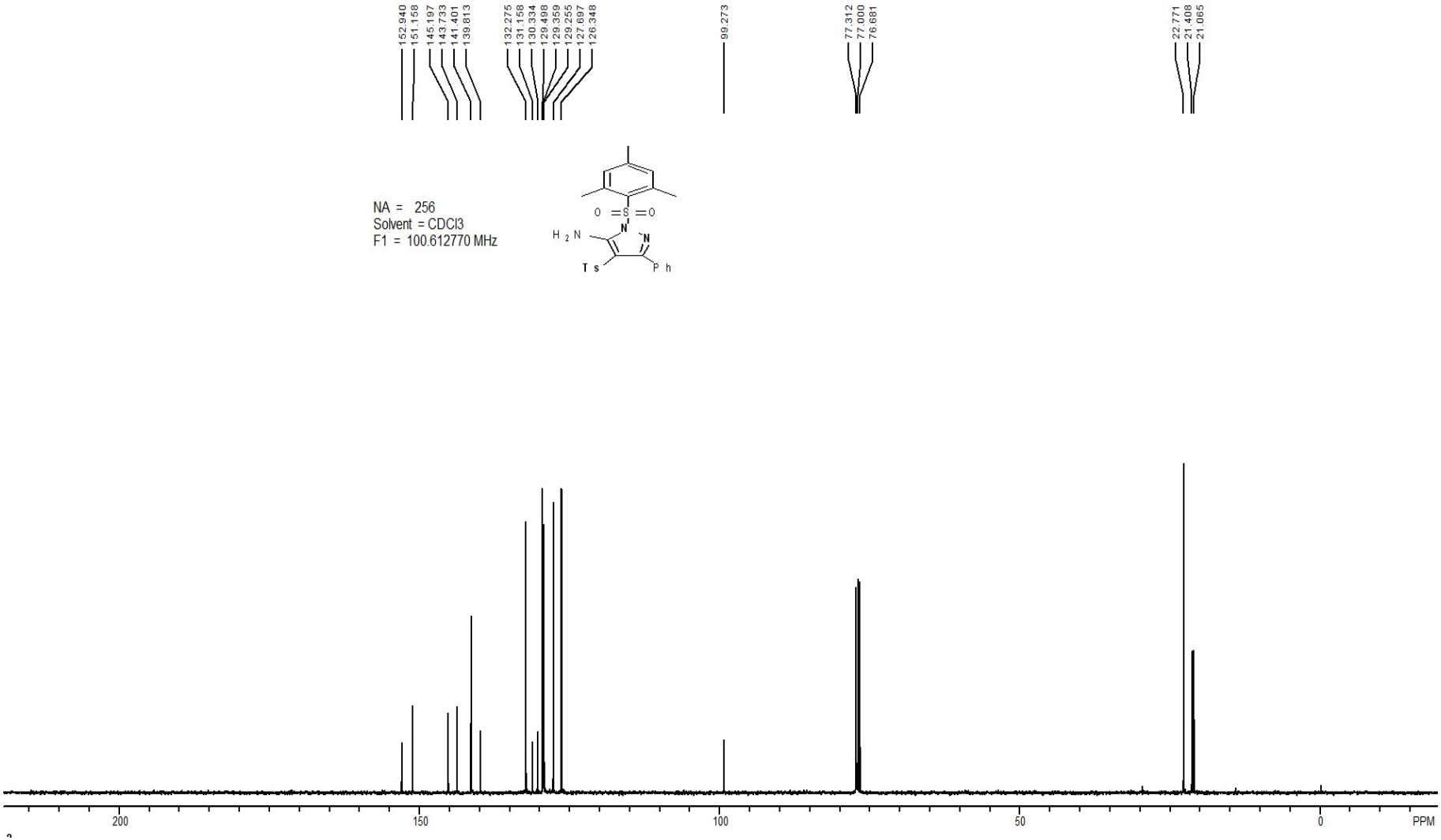
1-((3-Bromophenyl)sulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4i)



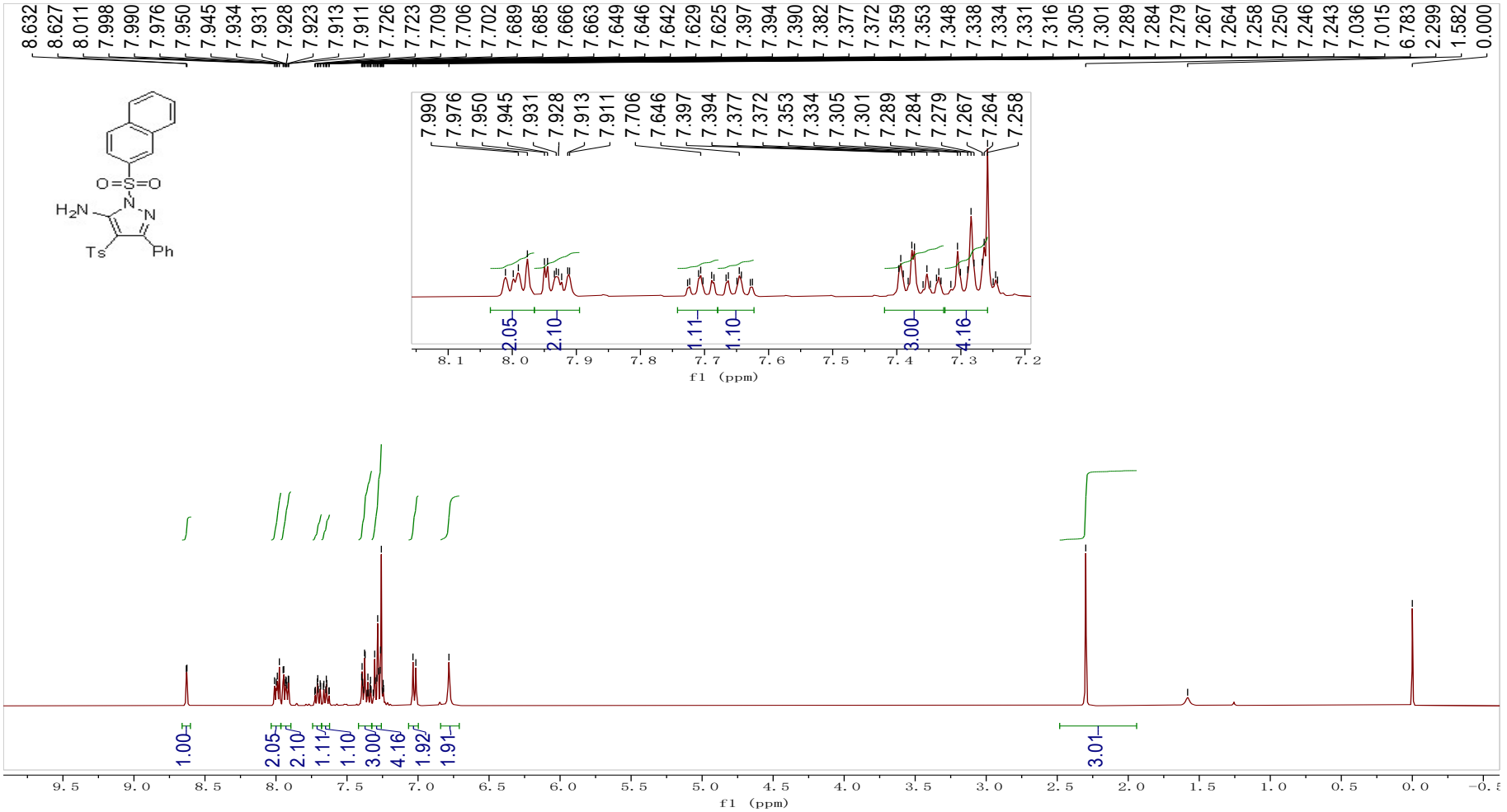

154.732
151.317
144.020
139.249
138.139
138.099
131.023
130.675
129.771
129.700
129.485
129.296
127.839
126.677
126.474
123.337
100.624
77.316
77.000
76.673
21.440
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
Br
O=S=O
N
H2N
N
Ts
Ph
200
150
100
50
0
PPM

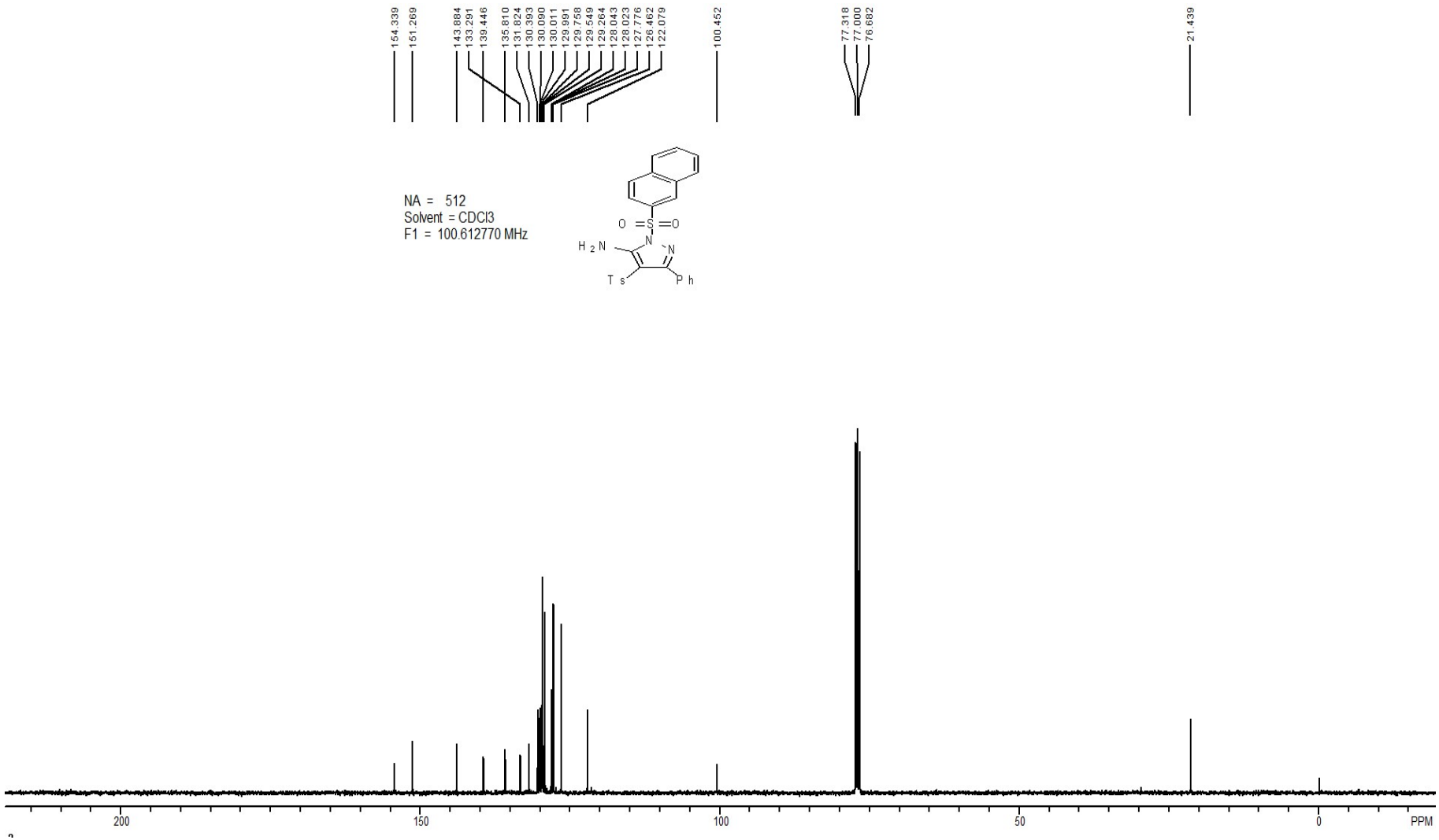
1-(Mesitylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4j)



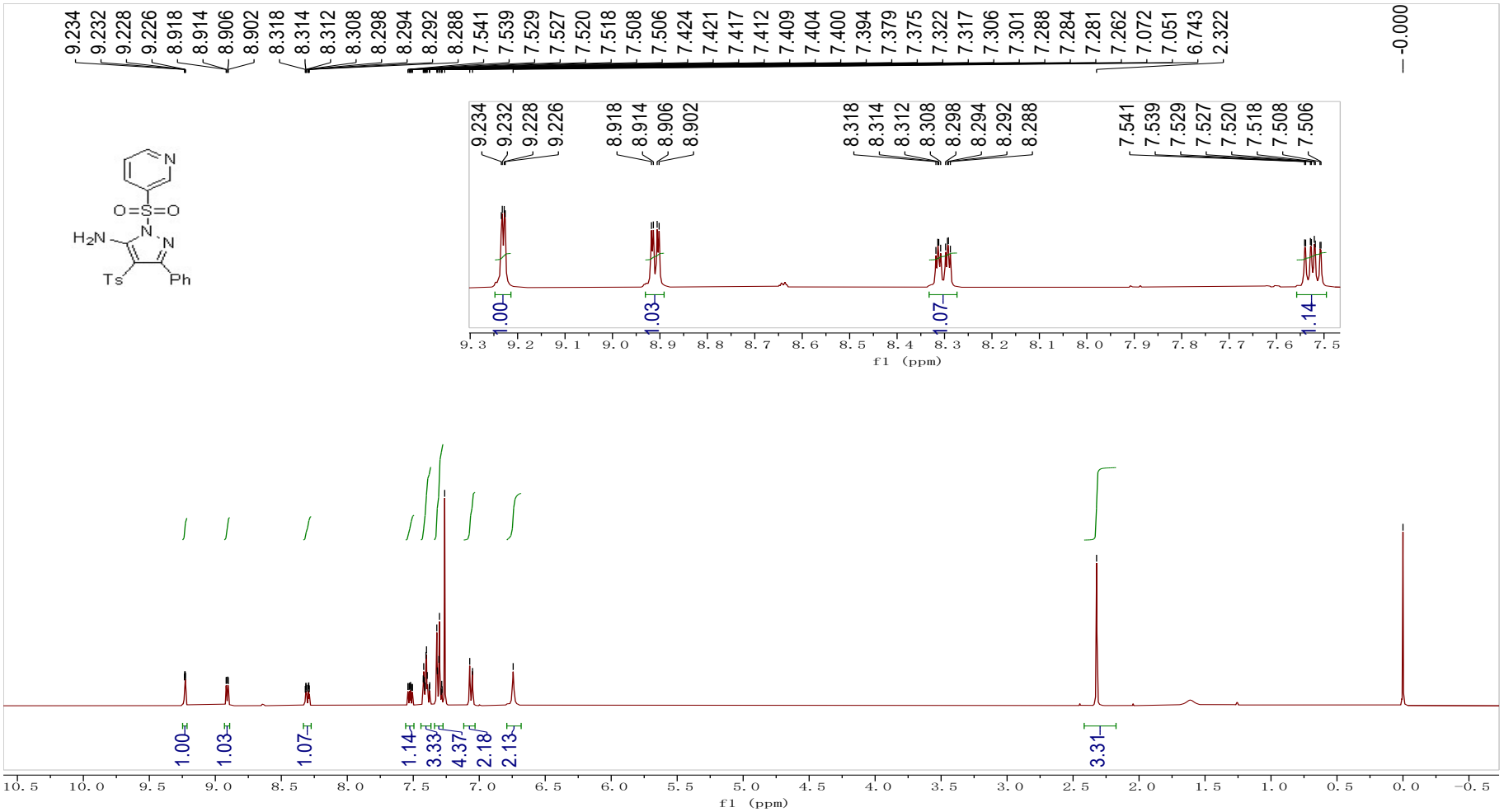

152.940
151.158
145.197
143.733
141.401
139.813
132.275
131.158
130.334
129.498
129.359
129.255
127.697
126.348
99.273
77.312
77.000
76.681
22.771
21.408
21.065
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
O =S= O
H2N
N
N
Ts
Ph
200
150
100
50
0
PPM

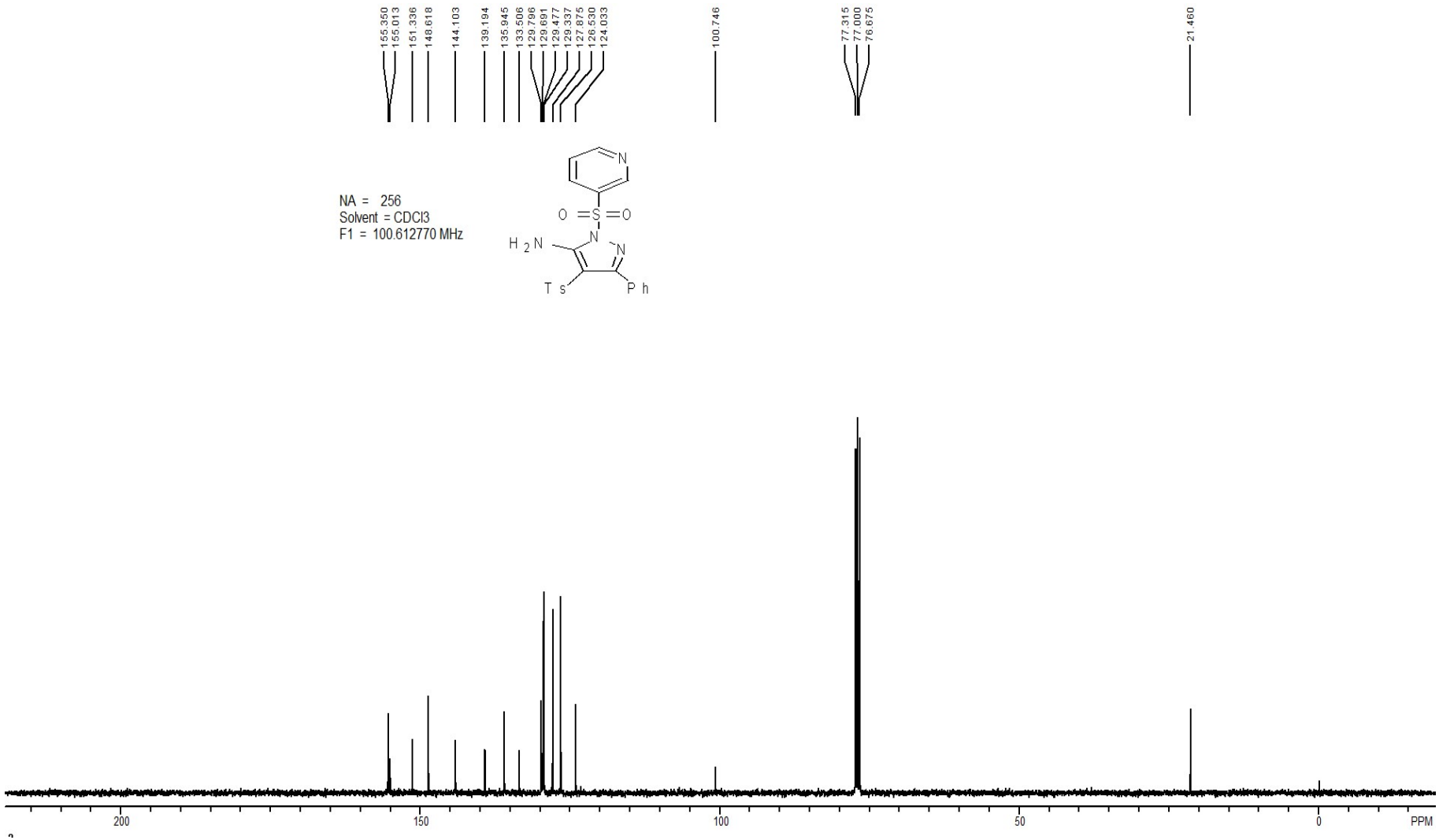
1-(Naphthalen-2-ylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4k)



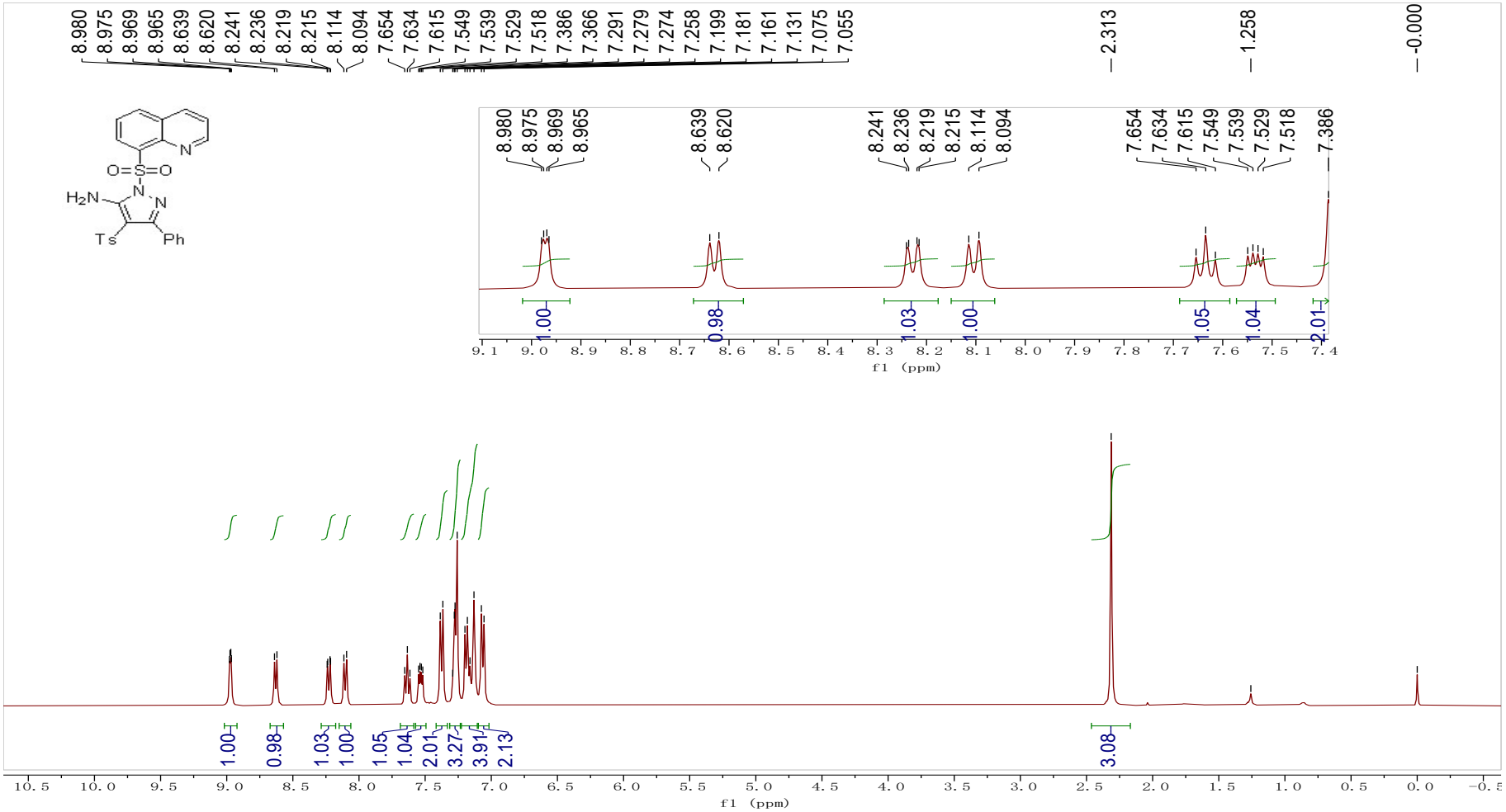

154.339
151.269
143.884
133.291
139.446
135.810
131.824
130.393
130.090
130.011
129.991
129.758
129.549
129.264
128.043
128.023
127.776
126.462
122.079
100.452
77.318
77.000
76.682
21.439
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
O
S
O
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

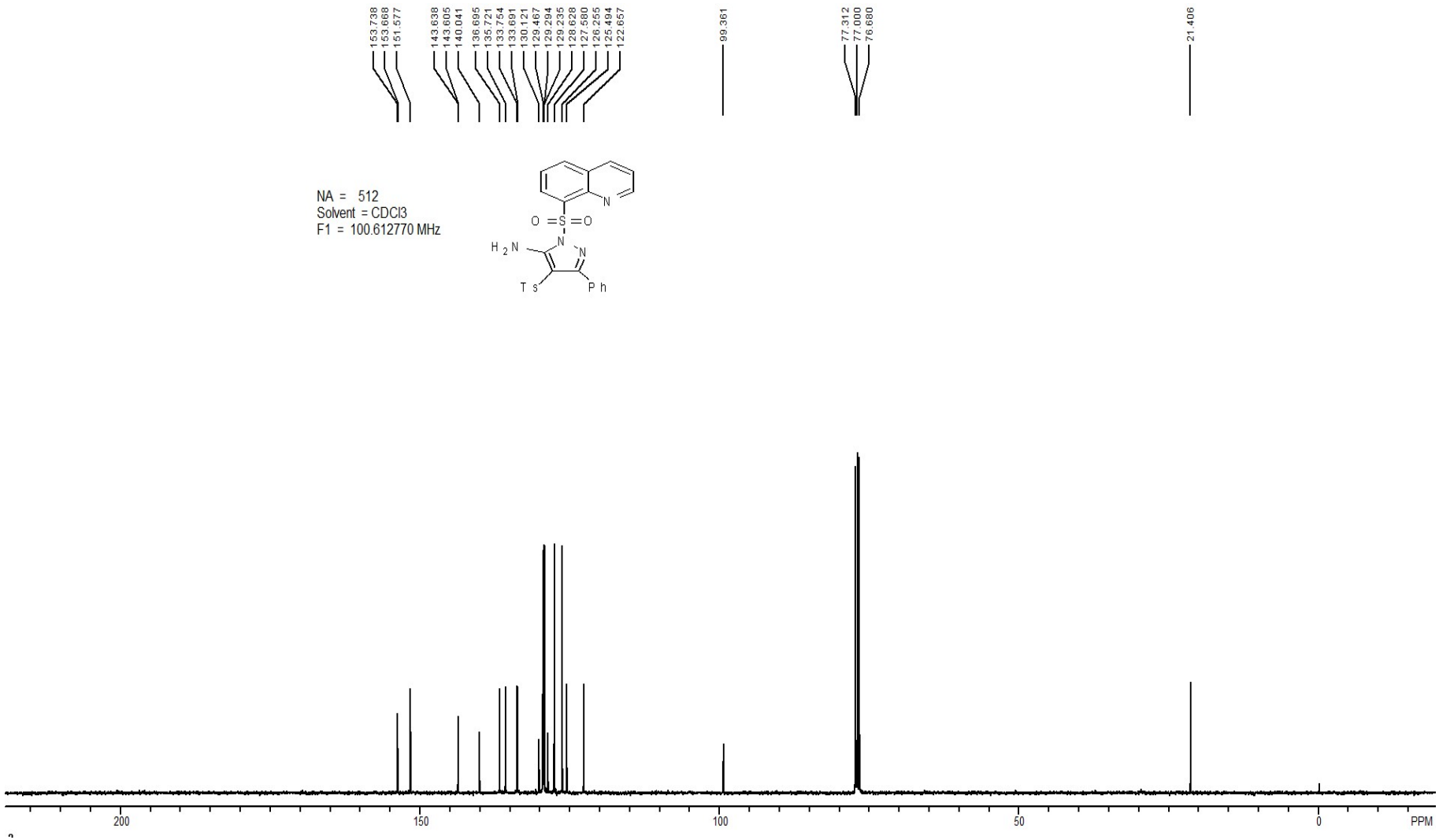
3-Phenyl-1-(pyridin-3-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4l)



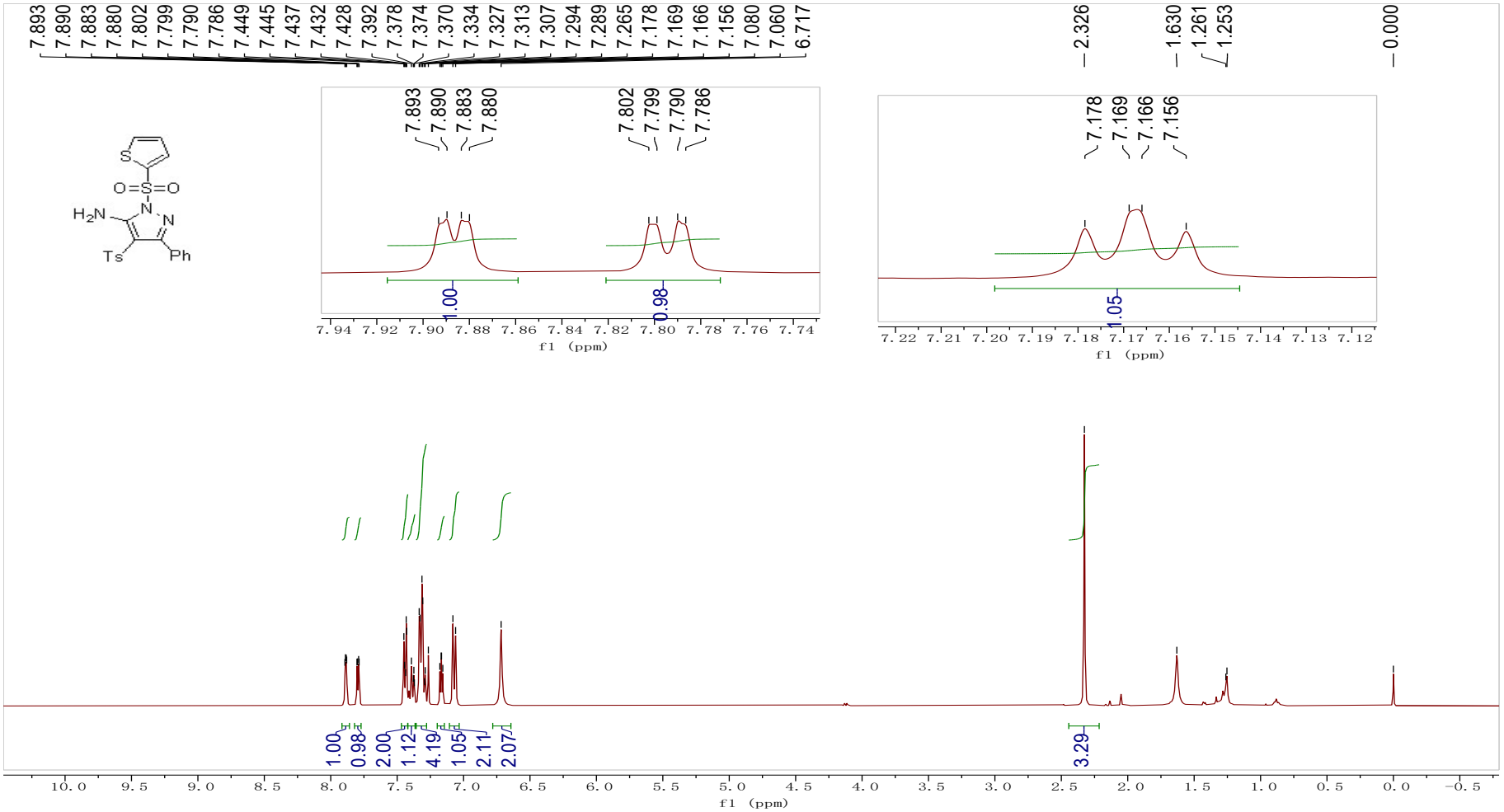

155.350
155.013
151.336
148.618
144.103
139.194
135.945
133.506
129.796
129.691
129.477
129.337
127.875
126.530
124.033
100.746
77.315
77.000
76.875
21.460
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
O =S =O
N
H 2N
N
N
T s
P h
200
150
100
50
0
PPM

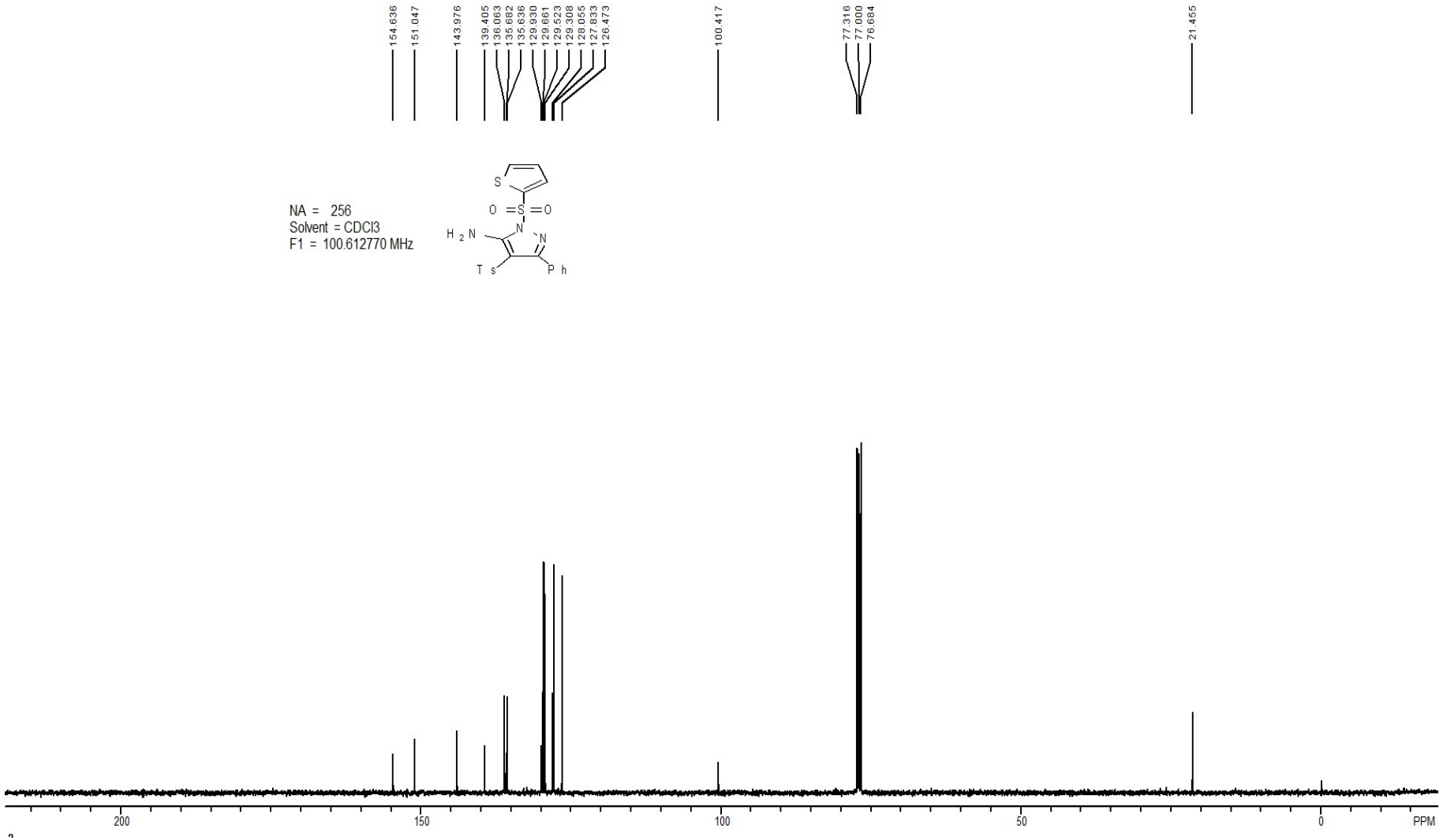
3-Phenyl-1-(quinolin-8-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4m)



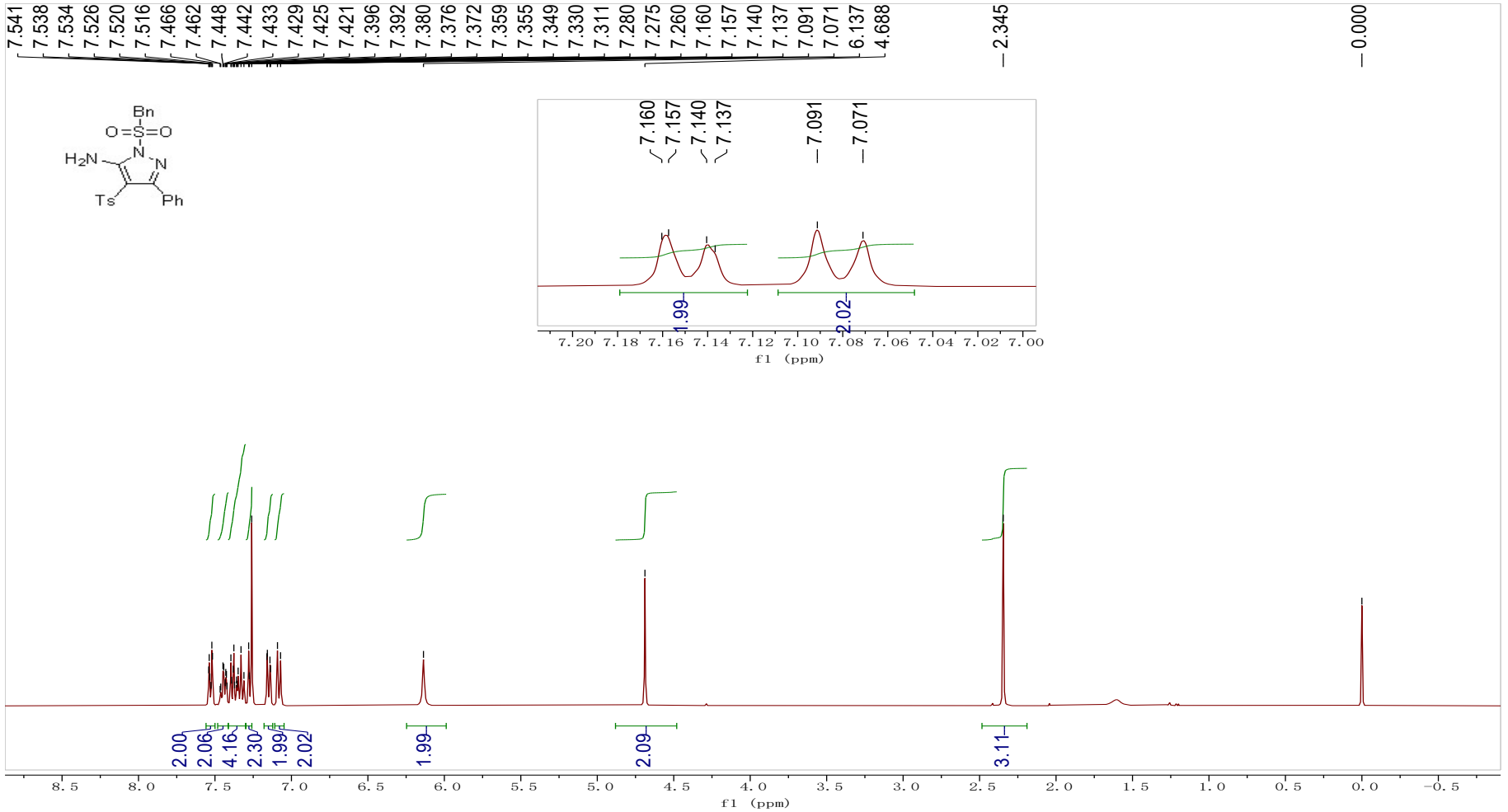

153.738
153.668
151.577
143.638
143.605
140.041
136.695
135.721
133.754
133.691
130.121
129.467
129.294
129.235
128.628
127.580
126.255
125.494
122.657
99.361
77.312
77.000
76.680
21.406
NA = 512
Solvent = CDCl3
F1 = 100.612770 MHz
O
S
O
N
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

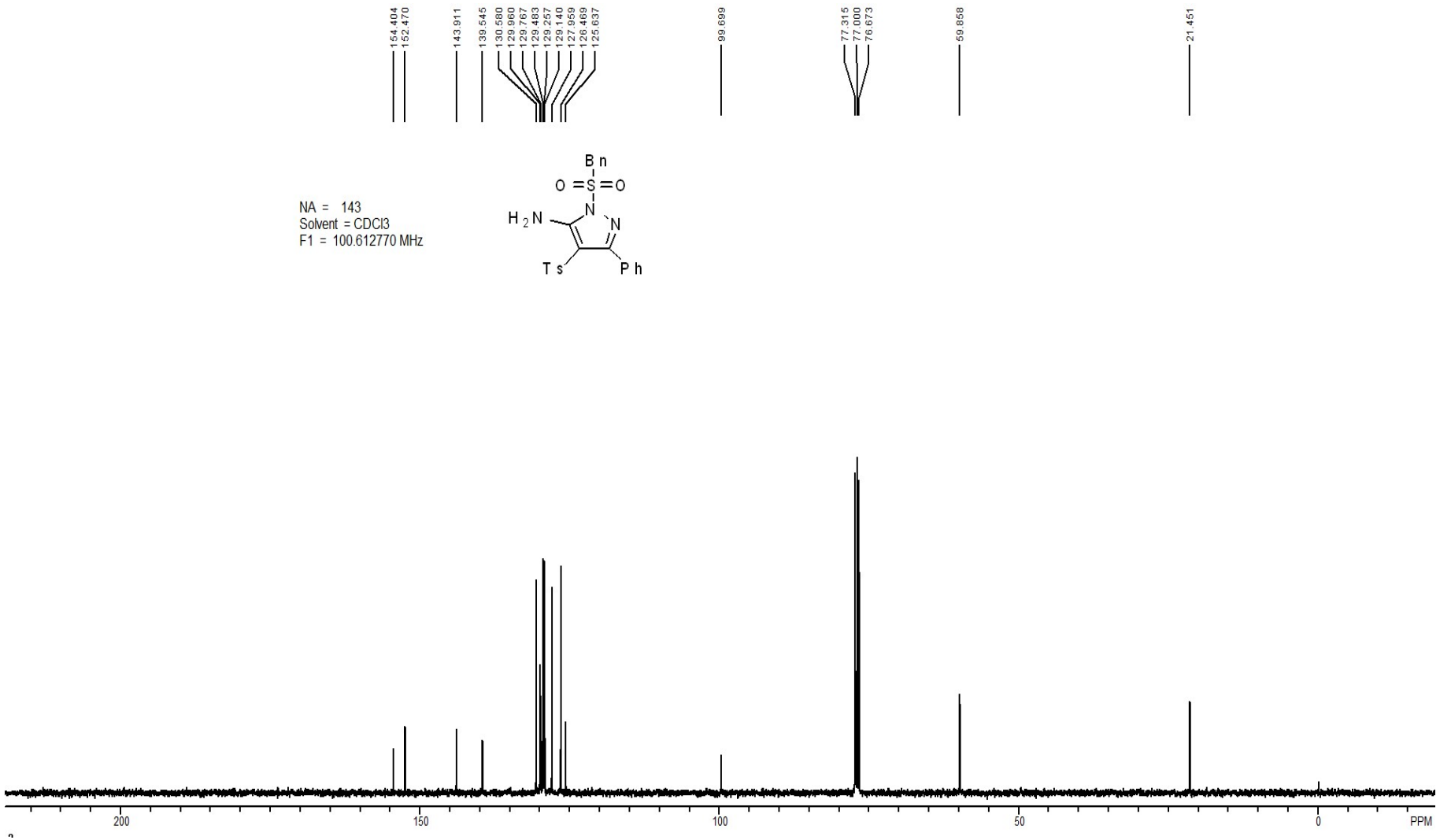
3-Phenyl-1-(thiophen-2-ylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4n)



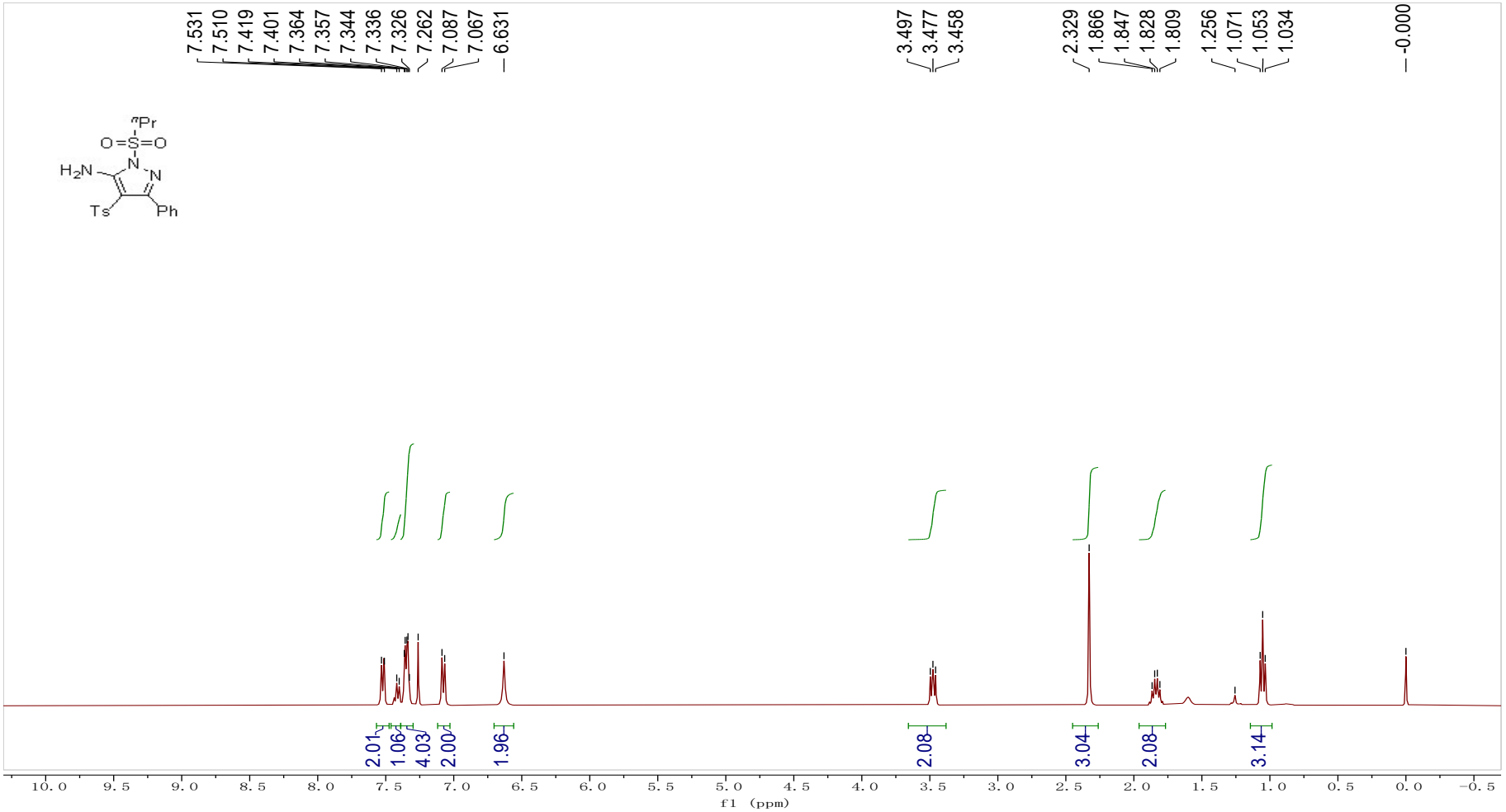

154.636
151.047
143.976
139.405
136.063
135.682
135.636
129.930
129.661
129.523
129.308
128.055
127.933
126.473
100.417
77.316
77.000
76.684
21.455
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
S
O =S =O
N
N
H 2 N
T s
P h
200
150
100
50
0
PPM

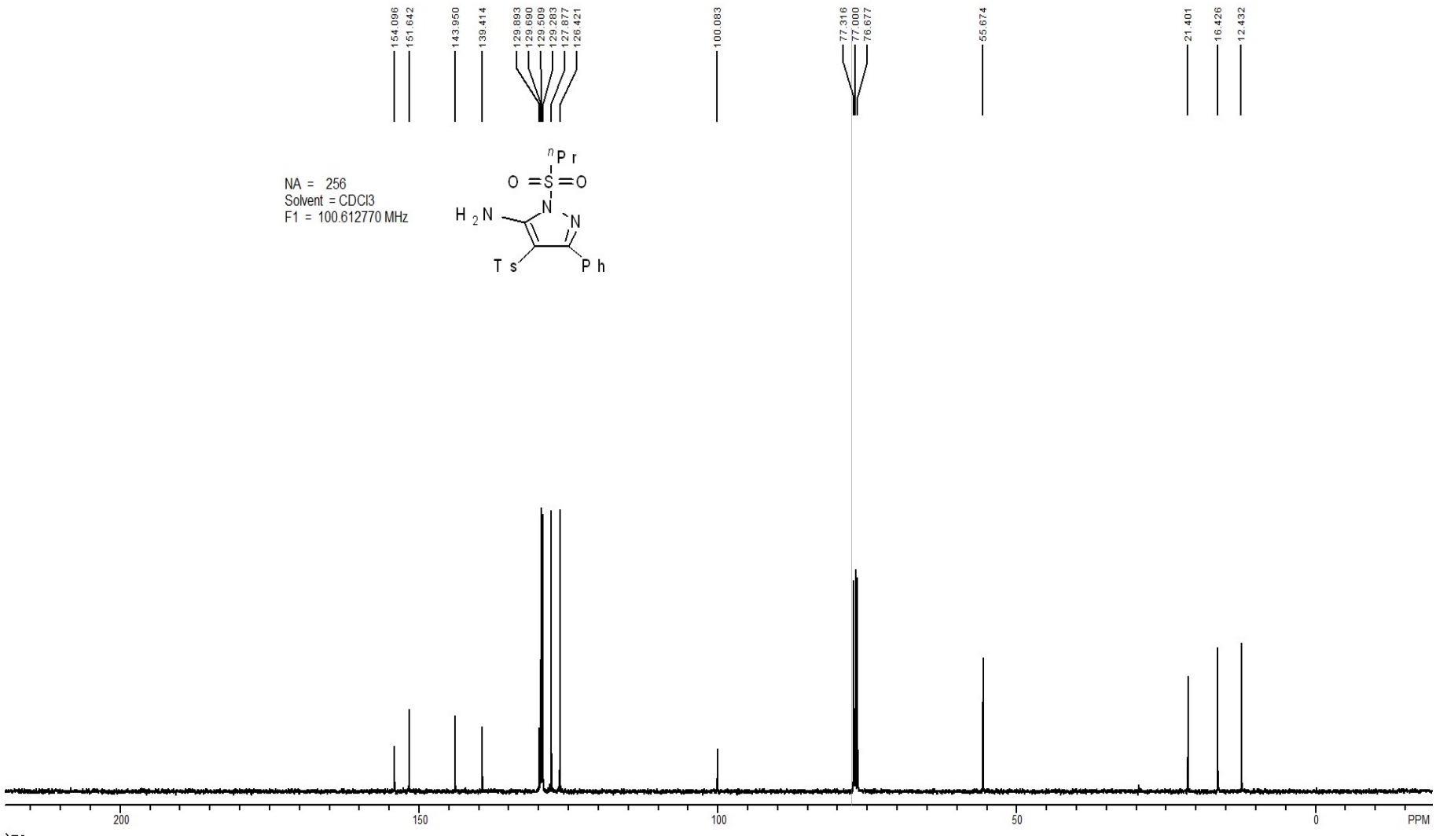
1-(Benzylsulfonyl)-3-phenyl-4-tosyl-1H-pyrazol-5-amine (4o)



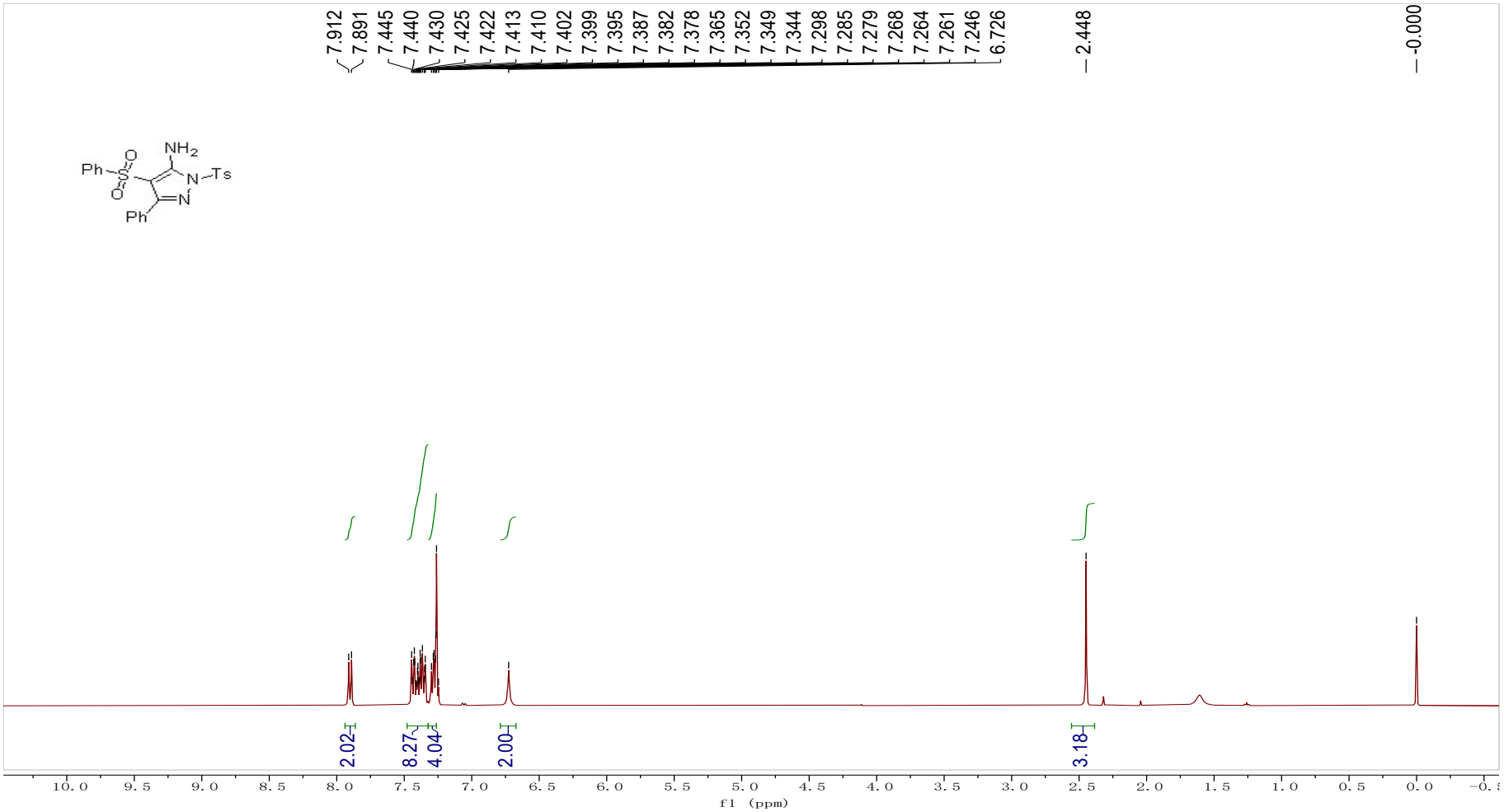

154.404
152.470
143.911
139.545
130.580
129.960
129.767
129.483
129.257
129.140
127.959
126.469
125.637
99.699
77.315
77.000
76.673
59.858
21.451
NA = 143
Solvent = CDCl3
F1 = 100.612770 MHz
Bn
O=S=O
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

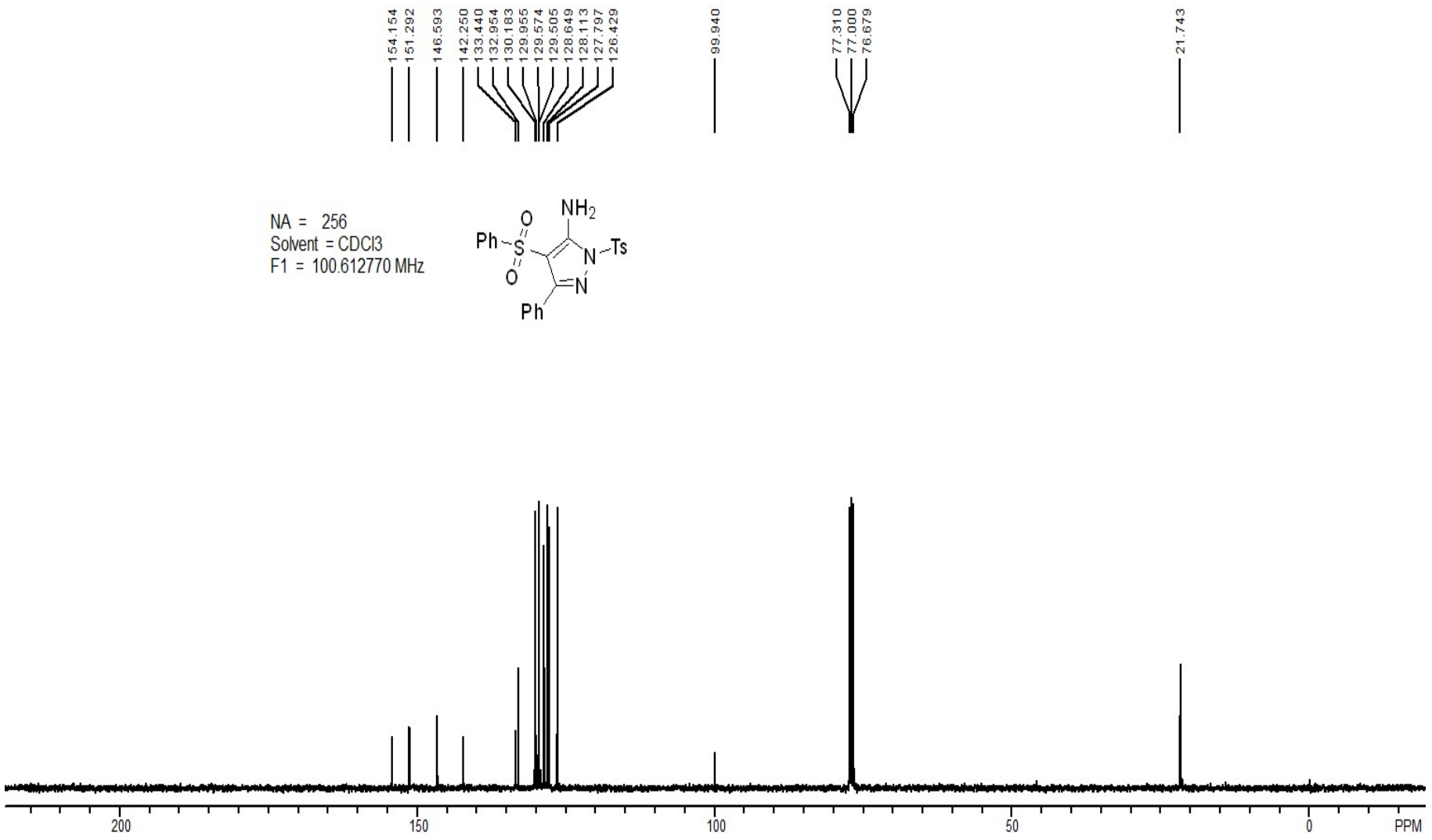
3-Phenyl-1-(propylsulfonyl)-4-tosyl-1H-pyrazol-5-amine (4p)



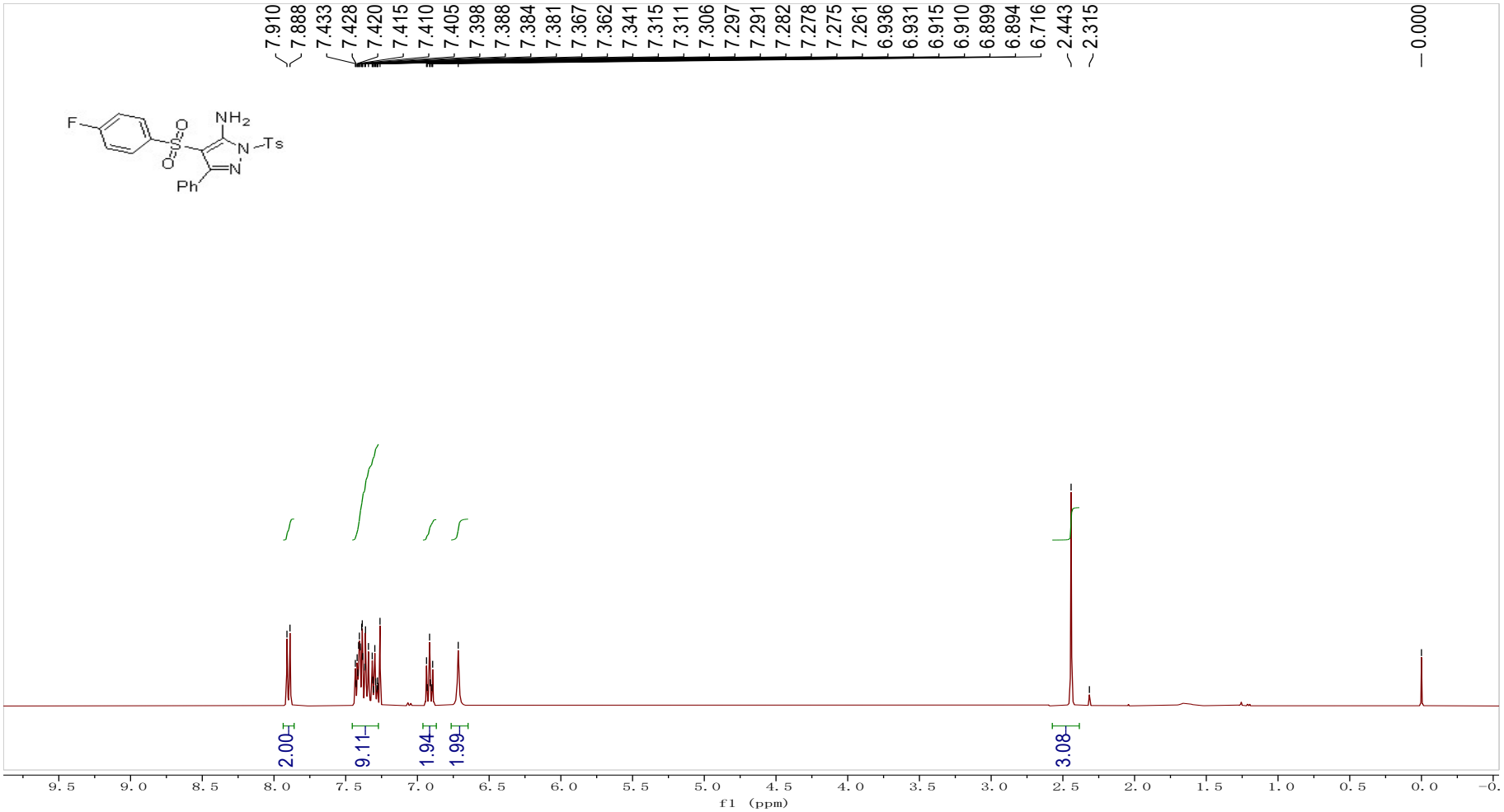

154.096
151.642
143.950
139.414
129.893
129.690
129.509
129.283
127.877
126.421
100.083
77.316
77.000
76.677
55.674
21.401
16.426
12.432
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
nPr
O=S=O
N
N
H2N
Ts
Ph
200
150
100
50
0
PPM

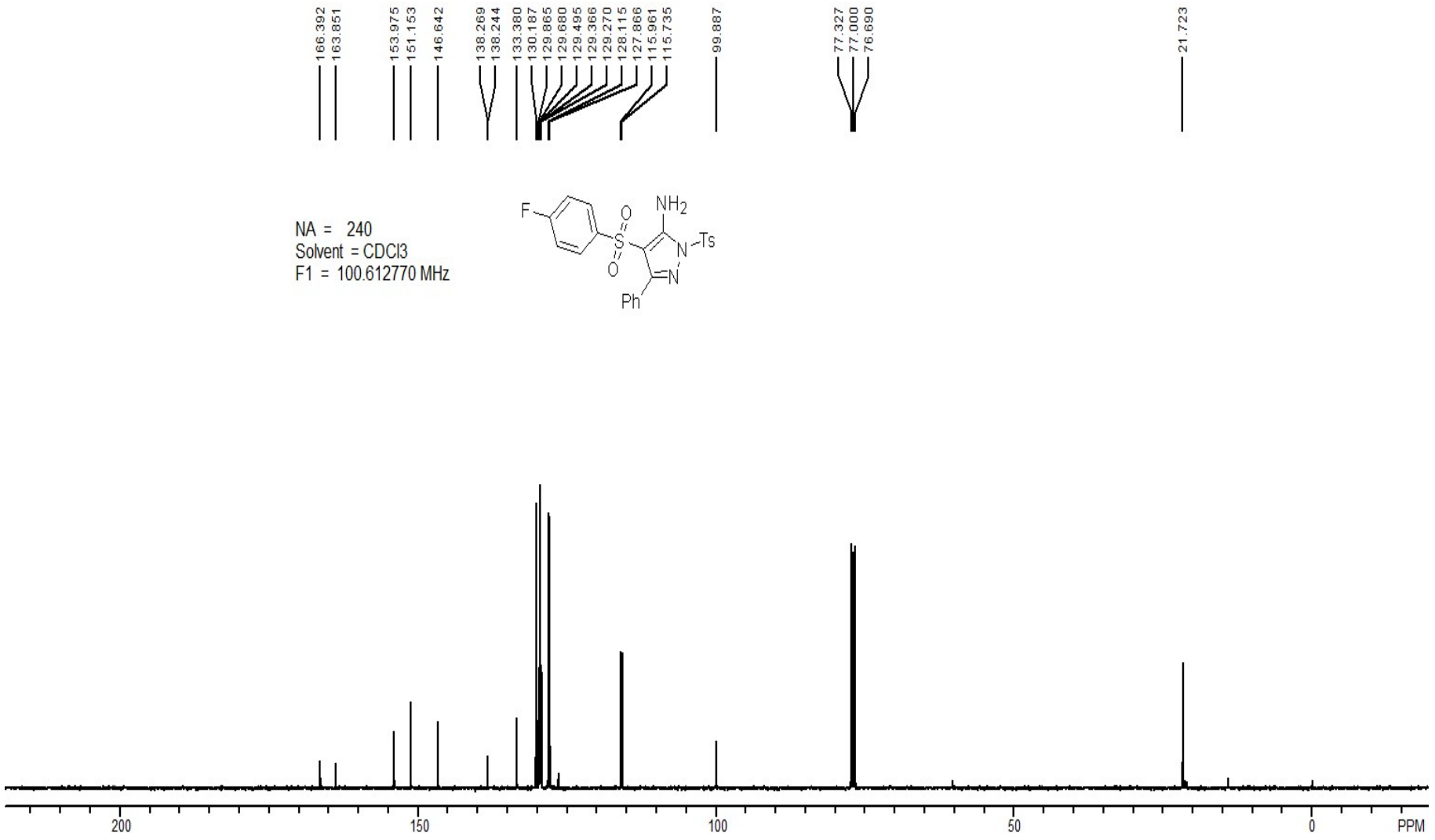
3-Phenyl-4-(phenylsulfonyl)-1-tosyl-1*H*-pyrazol-5-amine (4q)

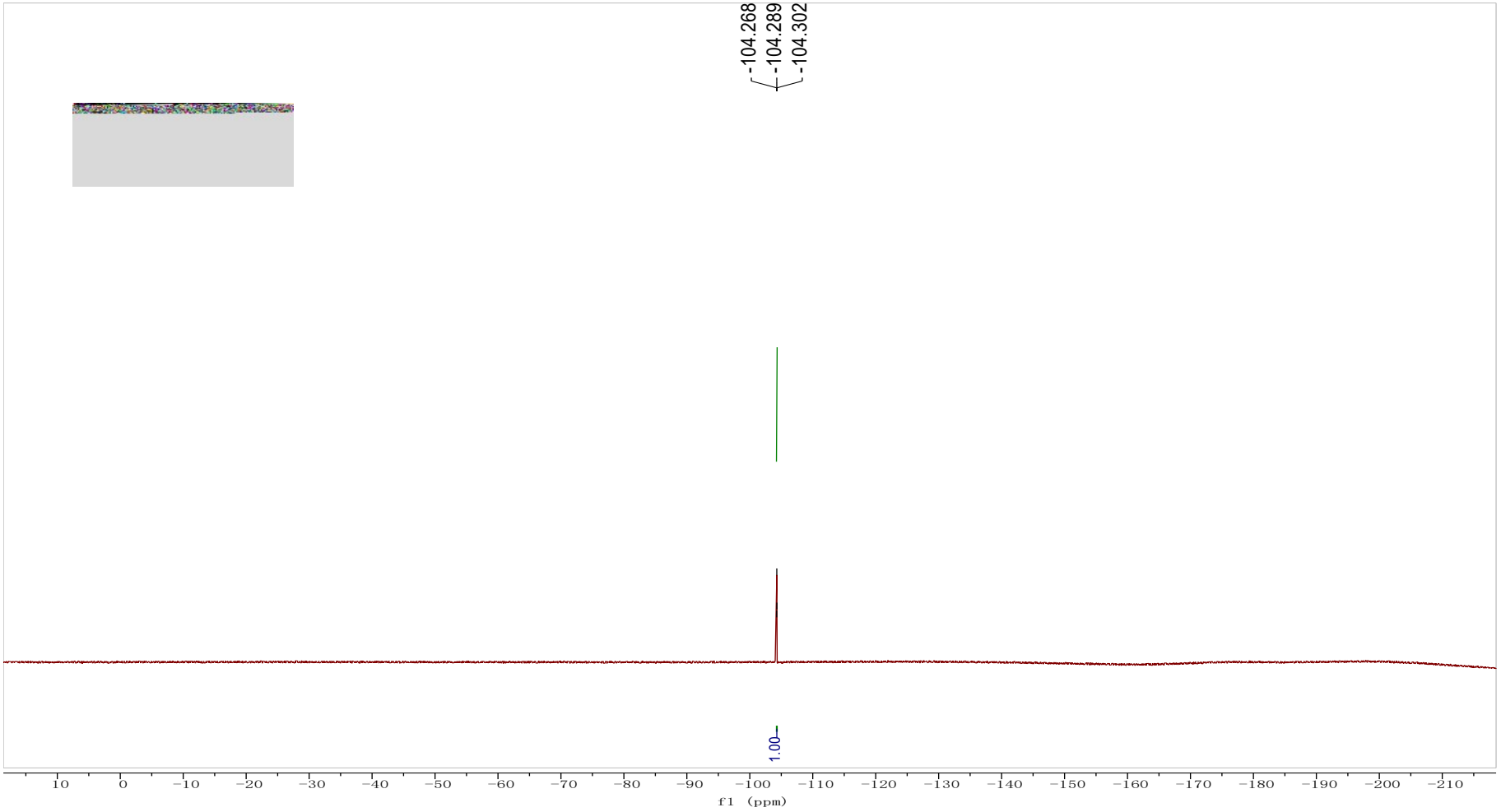



154.154
151.292
146.593
142.250
133.440
132.954
130.183
129.955
129.574
129.505
128.649
128.113
127.797
126.429
99.940
77.310
77.000
76.679
21.743
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
O
Ph
S
O
N
Ts
N
Ph
200
150
100
50
0
PPM

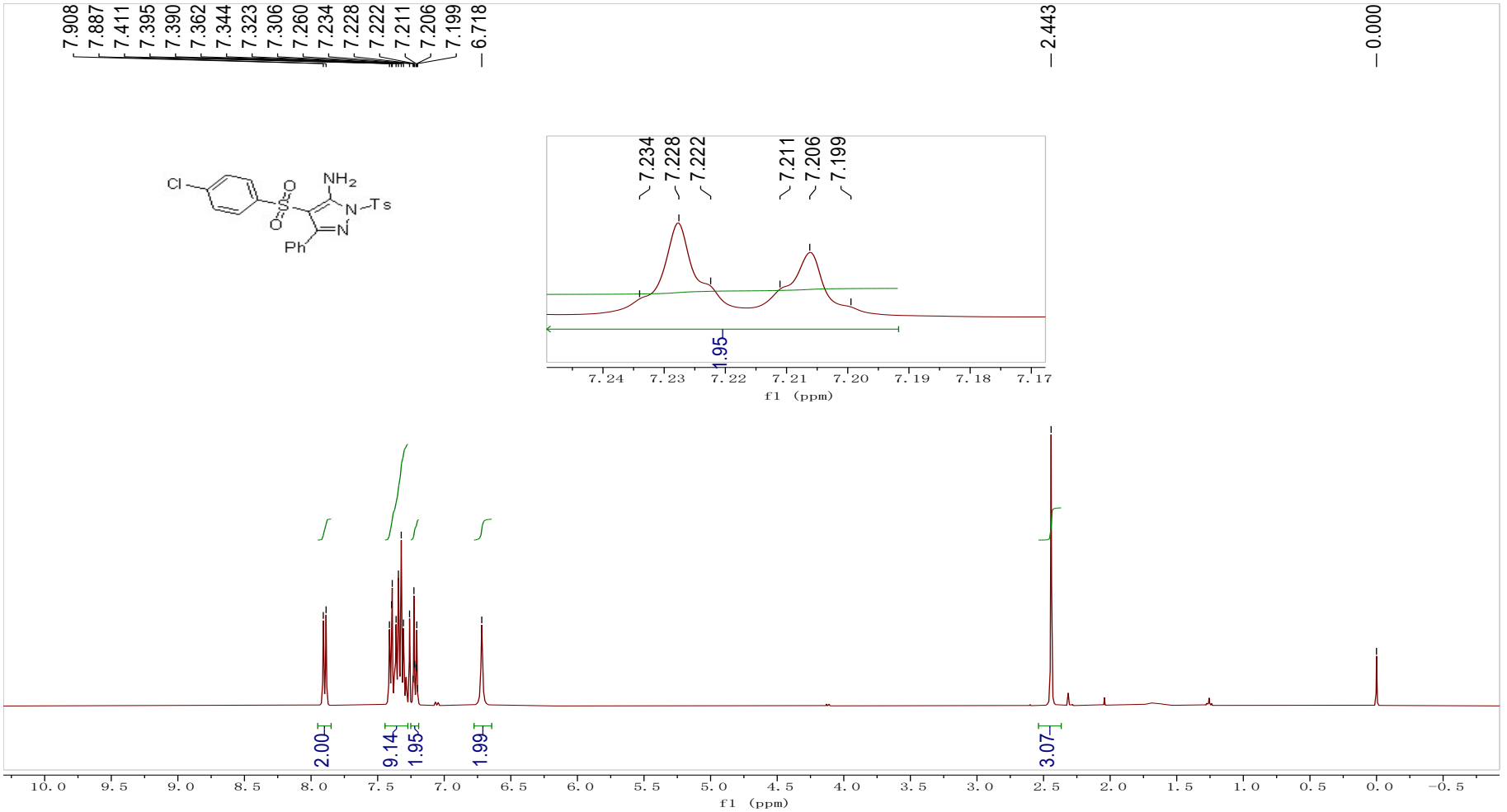
4-((4-Fluorophenyl)sulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4r)

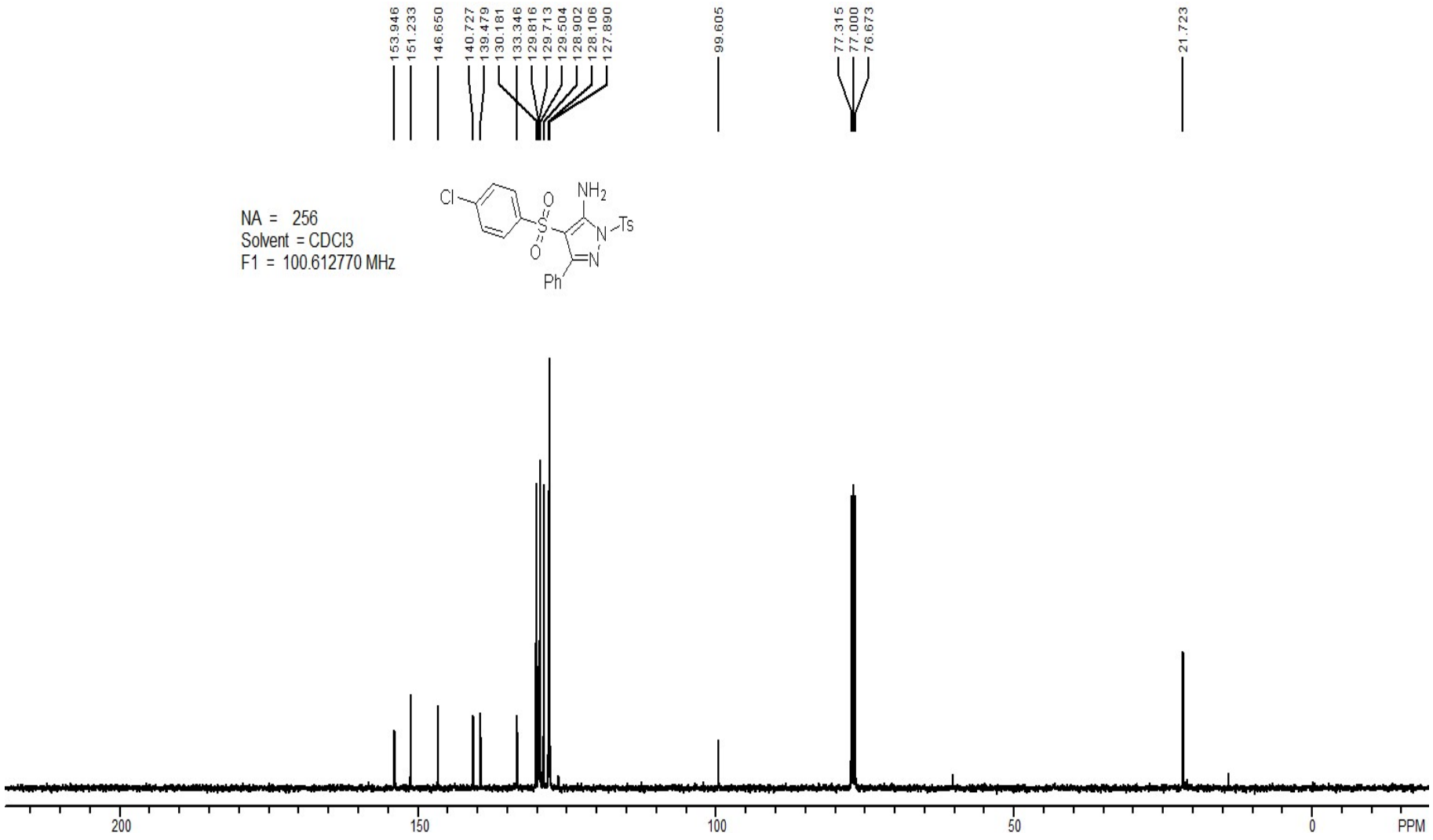



166.392
163.851
153.975
151.153
146.642
138.269
138.244
133.380
130.187
129.865
129.680
129.495
129.366
129.270
128.115
127.866
115.961
115.735
99.887
77.327
77.000
76.690
21.723
NA = 240
Solvent = CDCl3
F1 = 100.612770 MHz
F
O
S
O
NH2
N
Ts
N
Ph
200
150
100
50
0
PPM

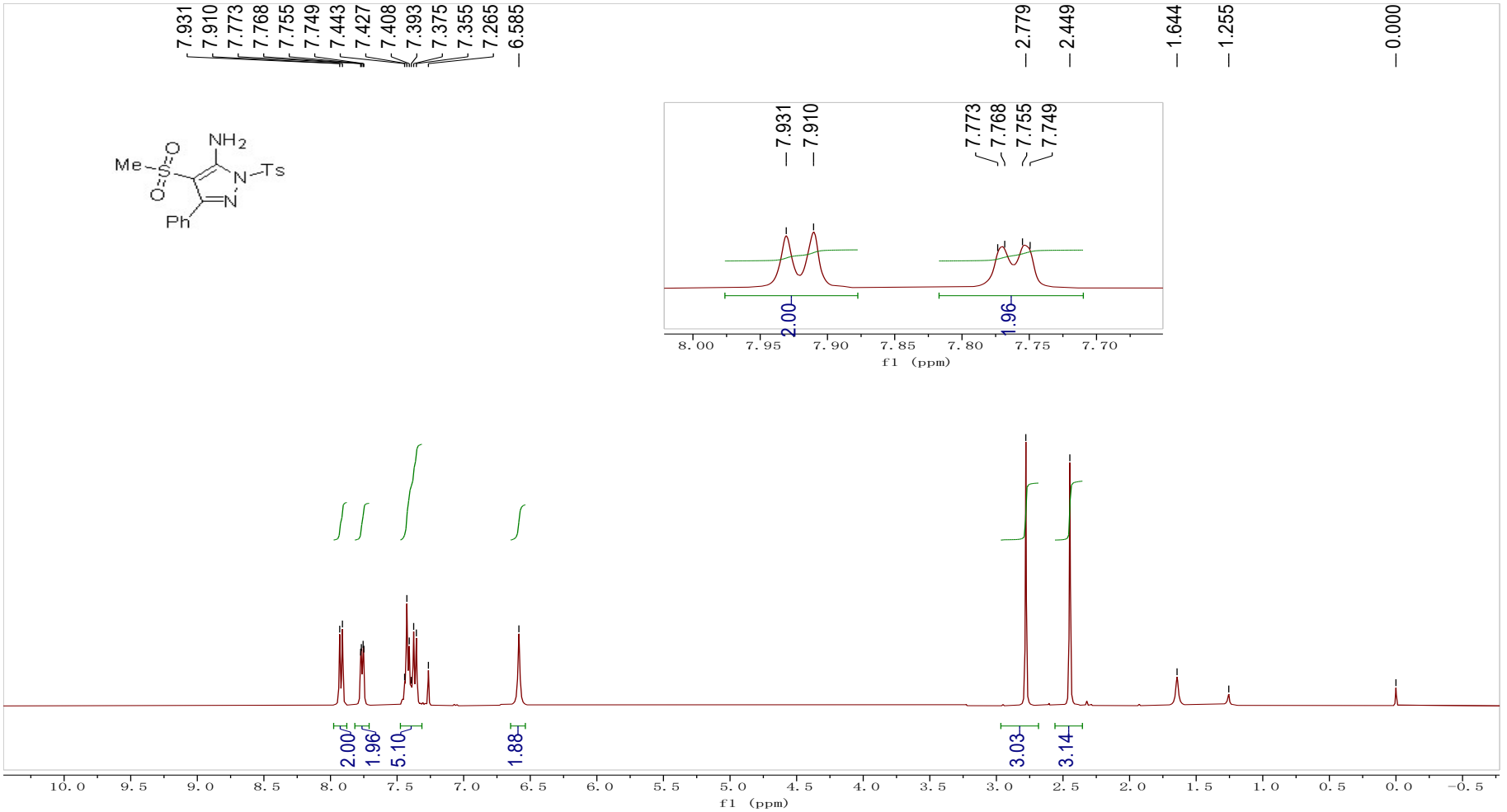

-104.268
-104.289
-104.302
1.00
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

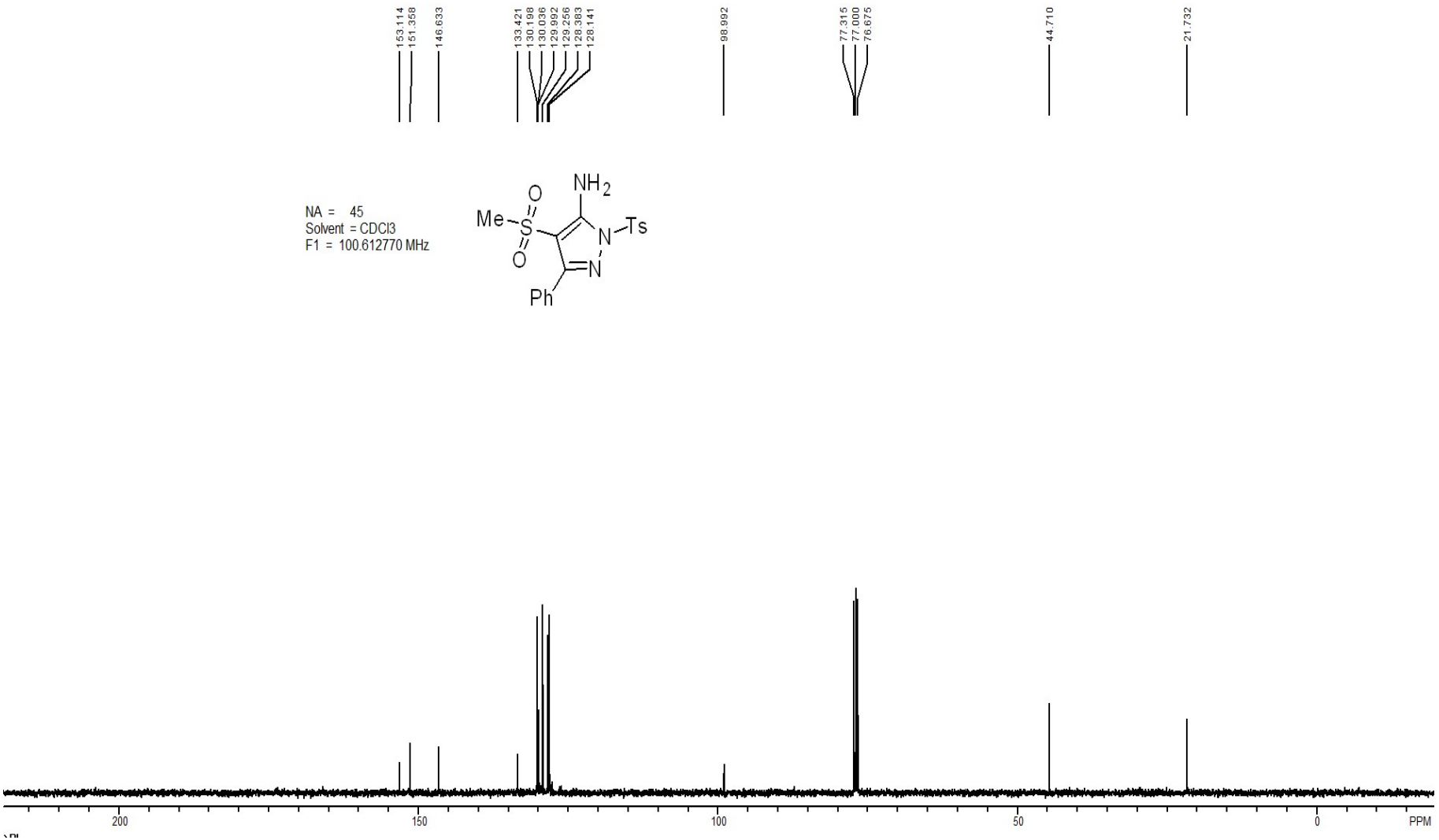
4-((4-Chlorophenyl)sulfonyl)-3-phenyl-1-tosyl-1*H*-pyrazol-5-amine (4s)



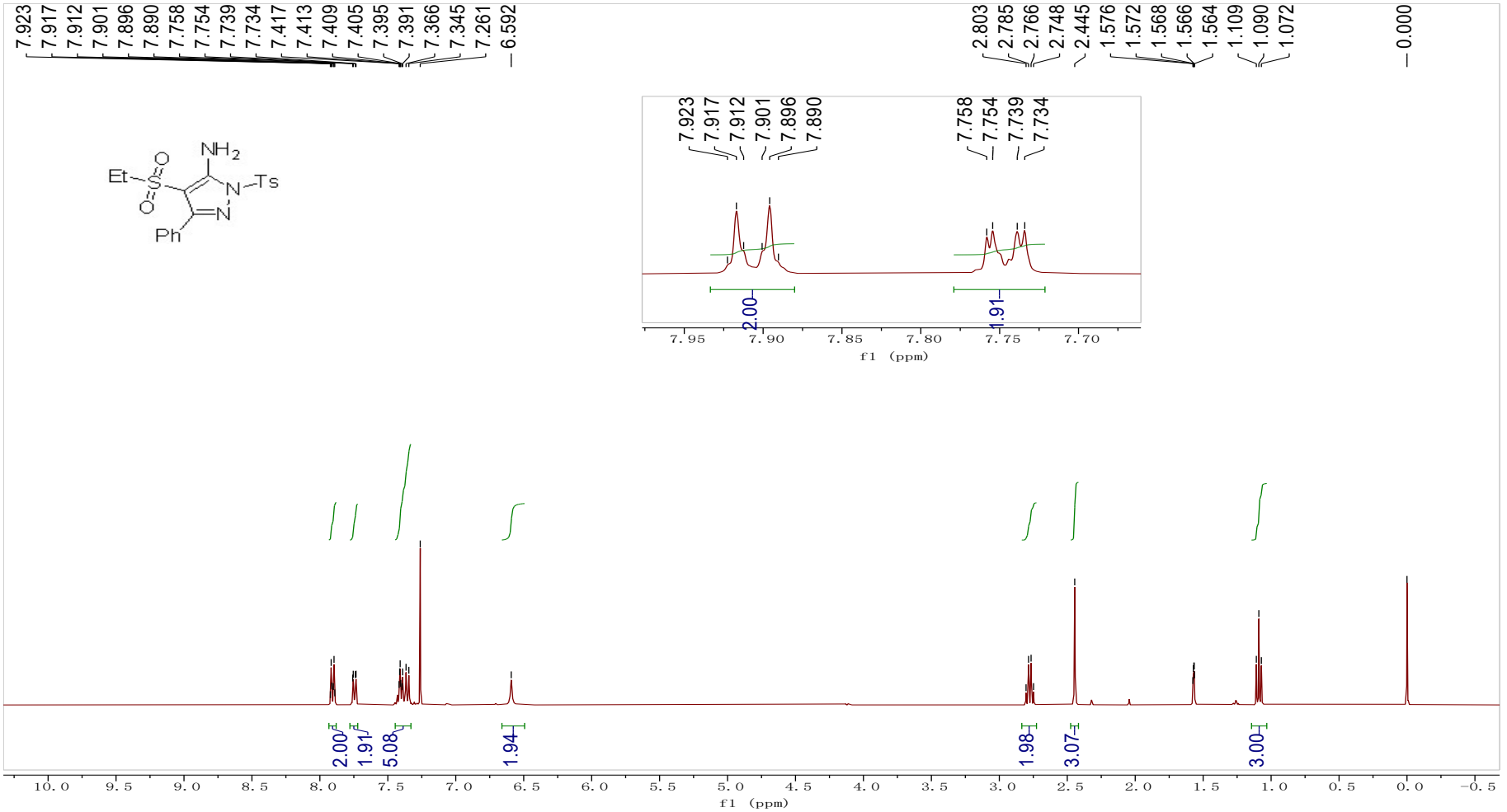

153.946
151.233
146.650
140.727
139.479
130.181
133.346
129.816
129.713
129.504
128.902
128.106
127.890
99.605
77.315
77.000
76.673
21.723
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
Cl
NH2
Ts
Ph
200
150
100
50
0
PPM

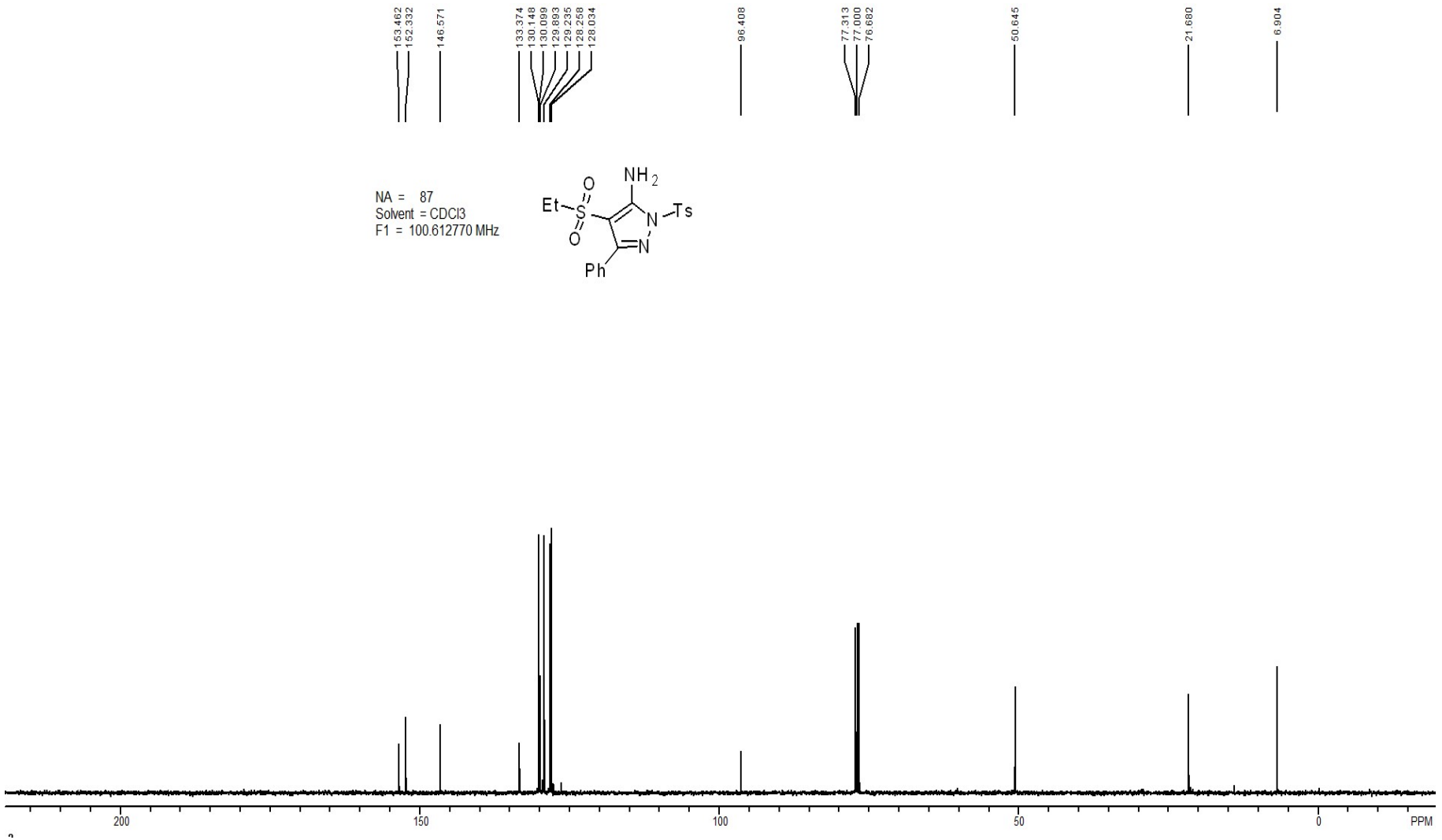
4-(Methylsulfonyl)-3-phenyl-1-tosyl-1H-pyrazol-5-amine (4t)



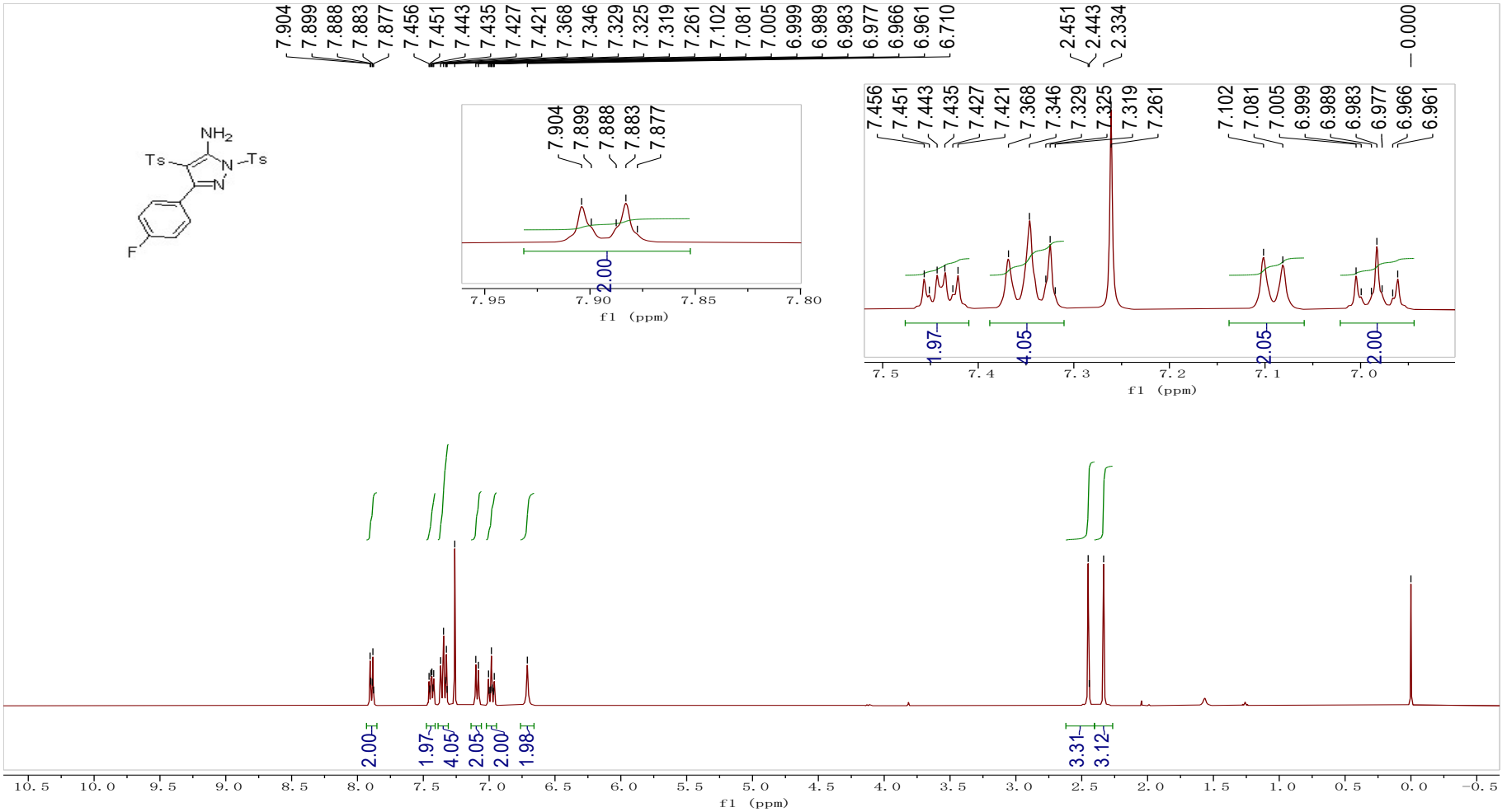

153.114
151.358
146.633
133.421
130.198
130.036
129.992
129.256
128.383
128.141
98.992
77.315
77.000
76.675
44.710
21.732
NA = 45
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
O
Me
S
O
N
Ts
N
Ph
200
150
100
50
0
PPM

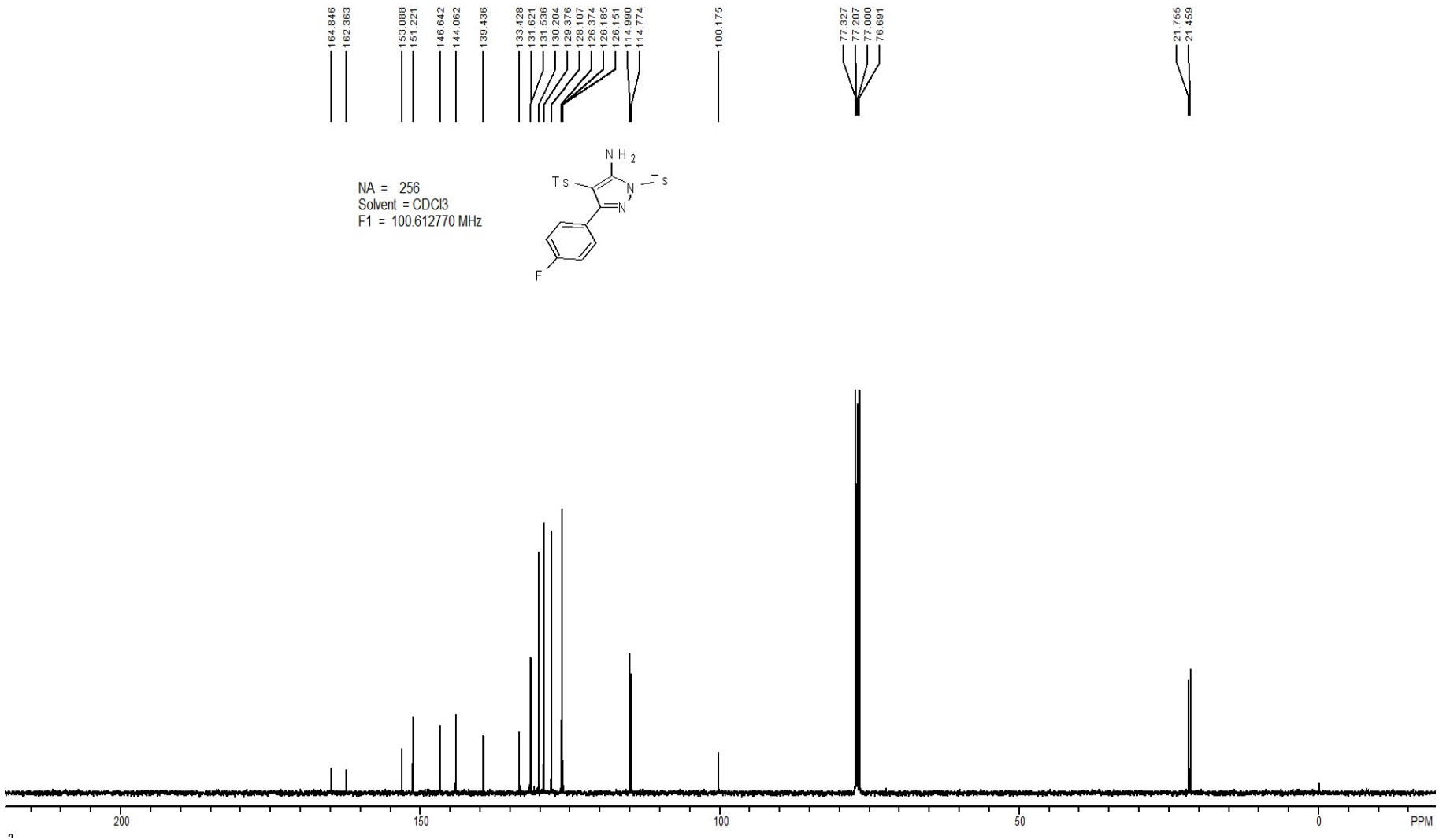
4-(Ethylsulfonyl)-3-phenyl-1-tosyl-1H-pyrazol-5-amine (4u)

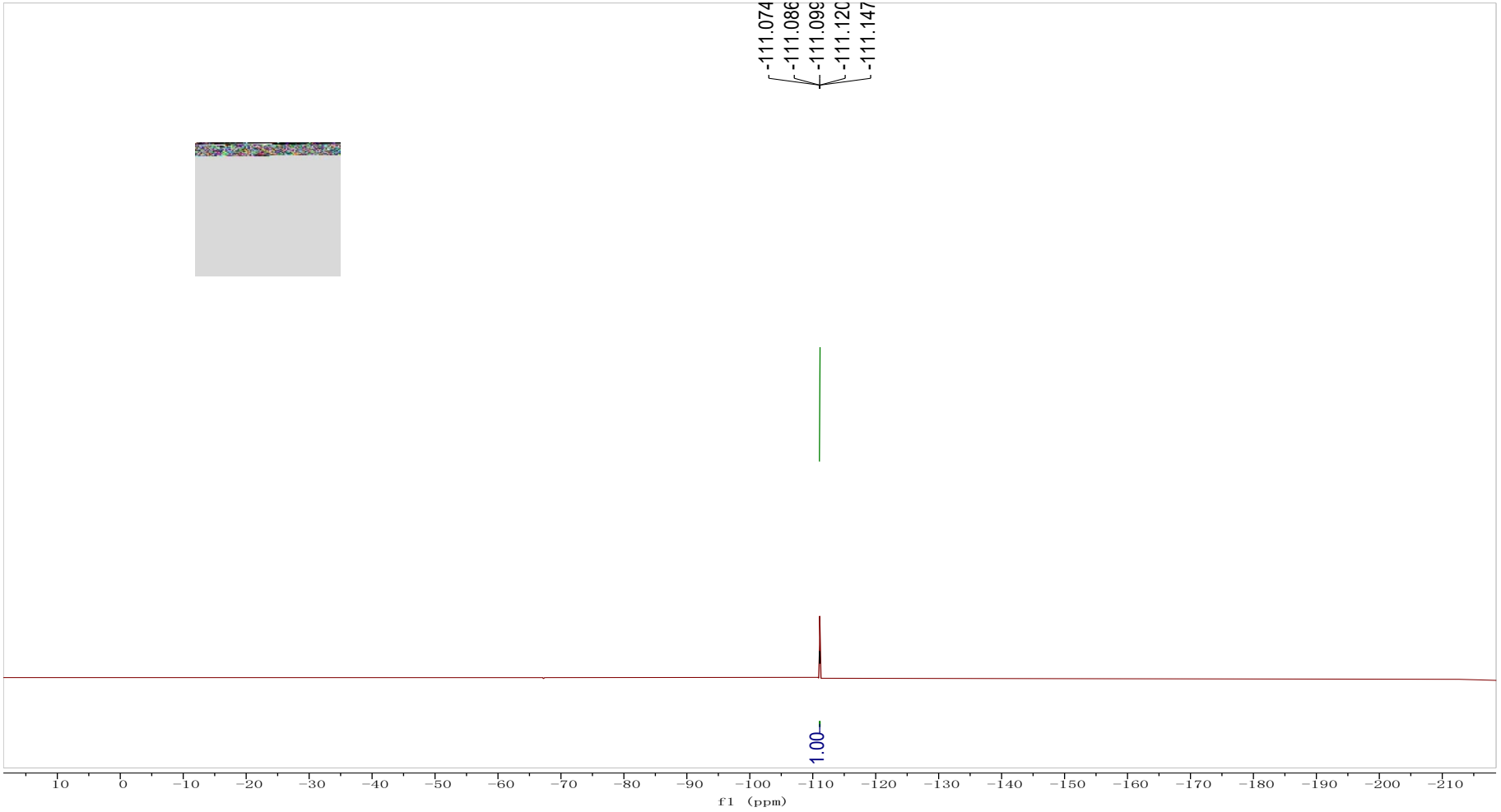



153.462
152.332
146.571
133.374
130.148
130.099
129.893
129.235
128.258
128.034
96.408
77.313
77.000
76.682
50.645
21.680
6.904
NA = 87
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Et
S
O
O
N
Ts
N
Ph
200
150
100
50
0
PPM

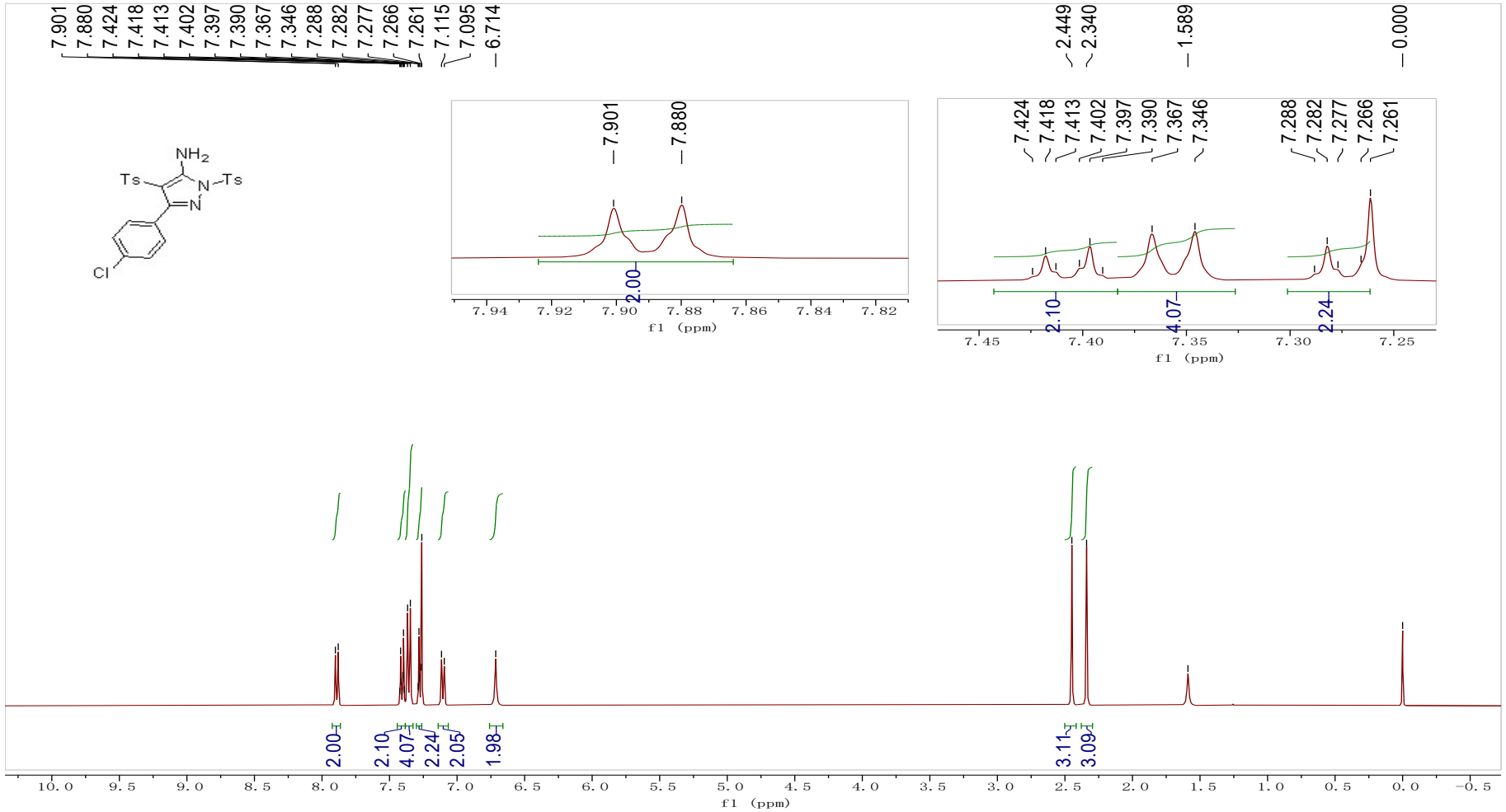
3-(4-Fluorophenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4v)

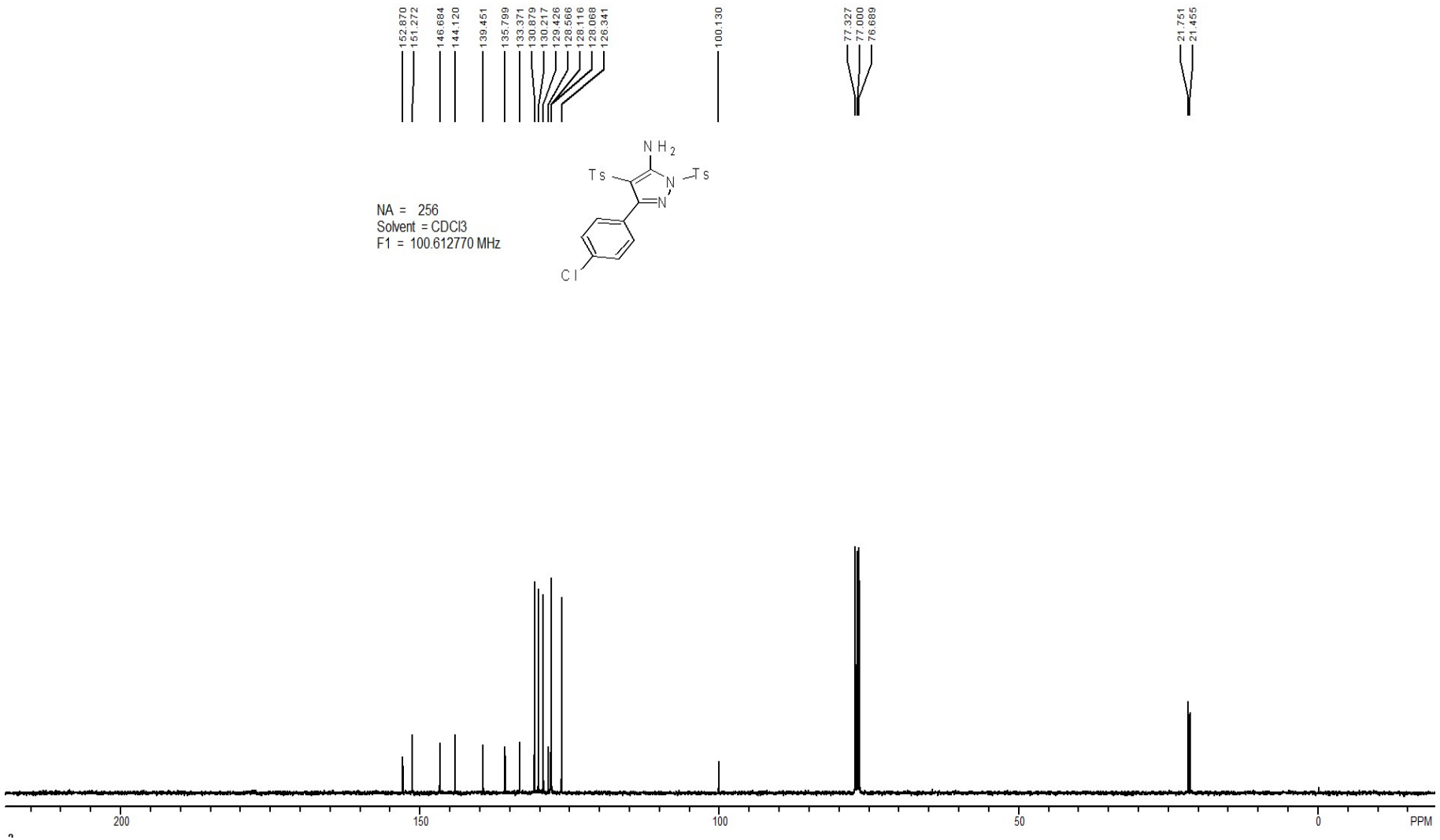



164.846
162.363
153.088
151.221
146.642
144.062
139.436
133.428
131.621
131.536
130.204
129.376
128.107
126.374
126.185
126.151
114.990
114.774
100.175
77.327
77.207
77.000
76.691
21.755
21.459
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
F
200
150
100
50
0
PPM

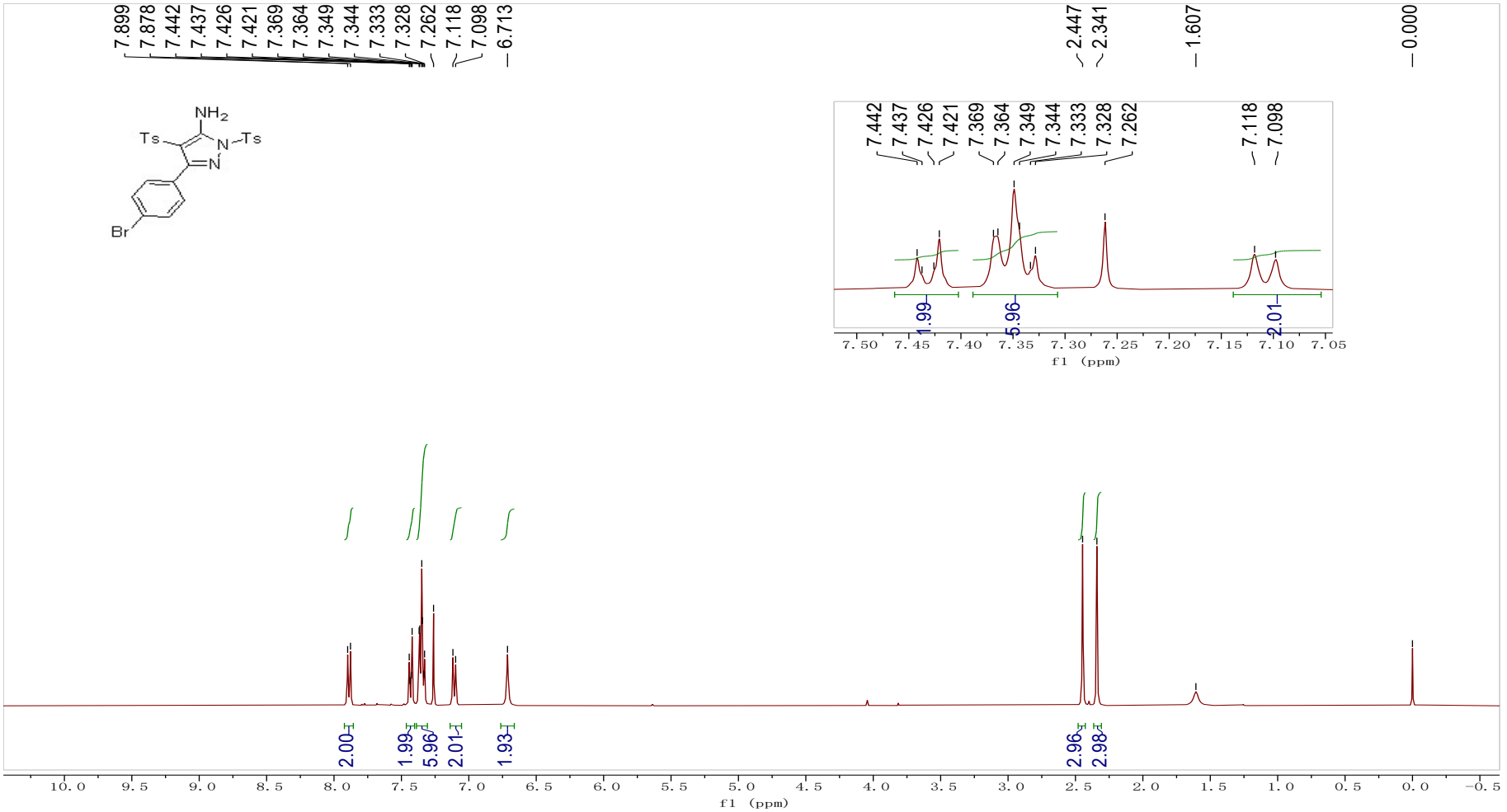

-111.074
-111.086
-111.099
-111.120
-111.147
1.00
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

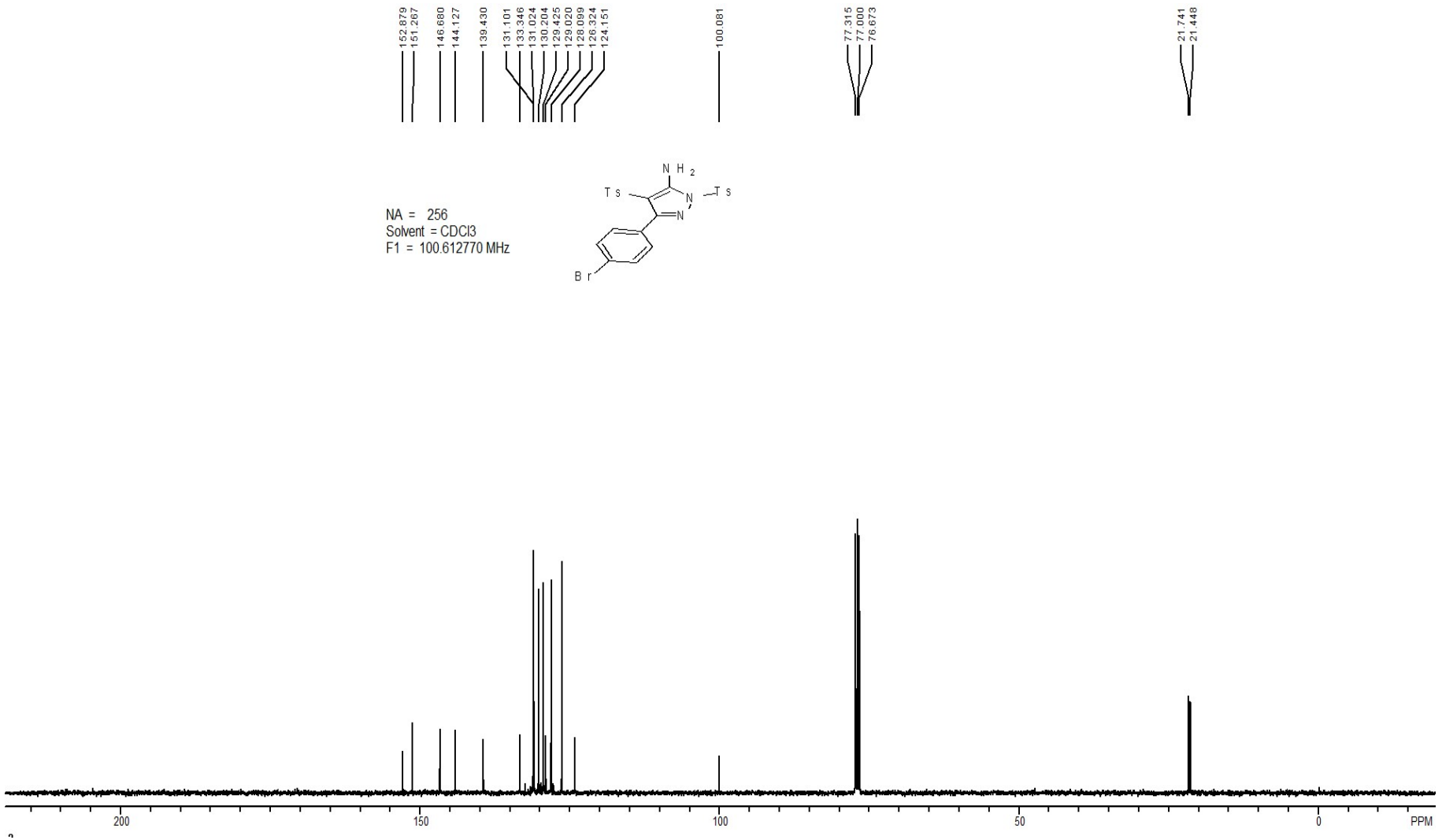
3-(4-Chlorophenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4w)



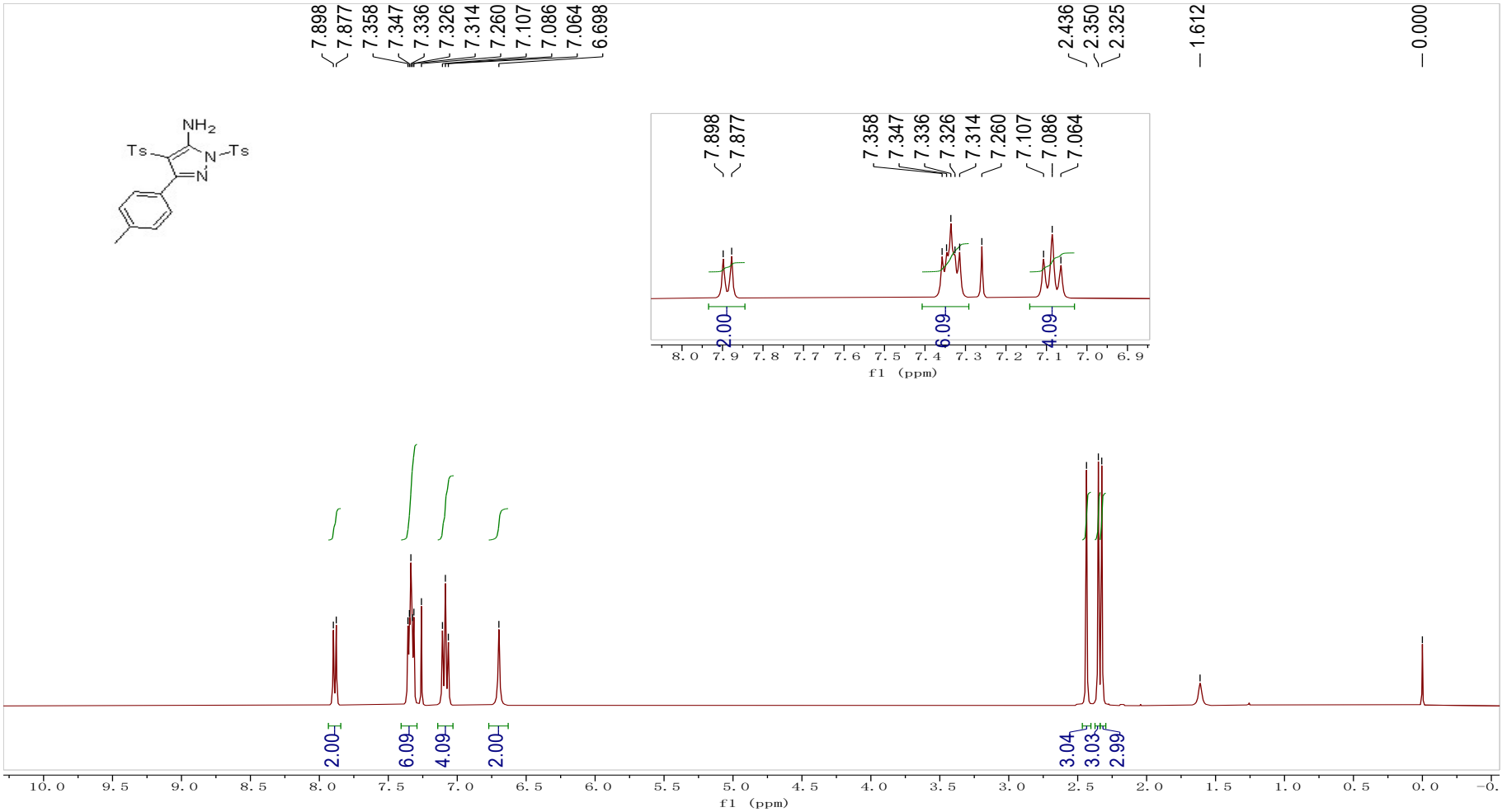

152.870
151.272
146.684
144.120
139.451
135.799
133.371
130.879
130.217
129.426
128.566
128.116
128.068
126.341
100.130
77.327
77.000
76.689
21.751
21.455
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
Cl
200
150
100
50
0
PPM

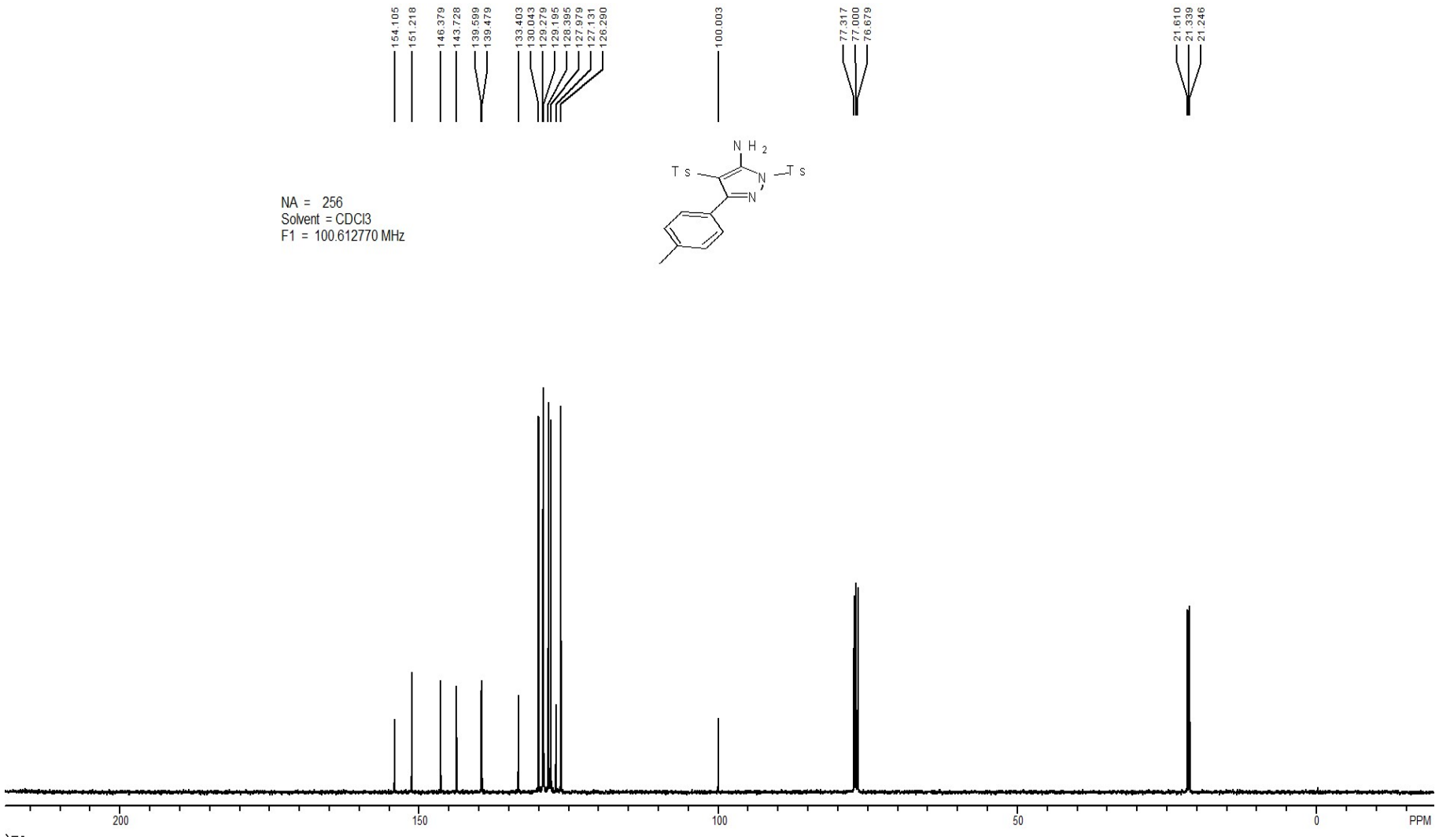
3-(4-Bromophenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4x)



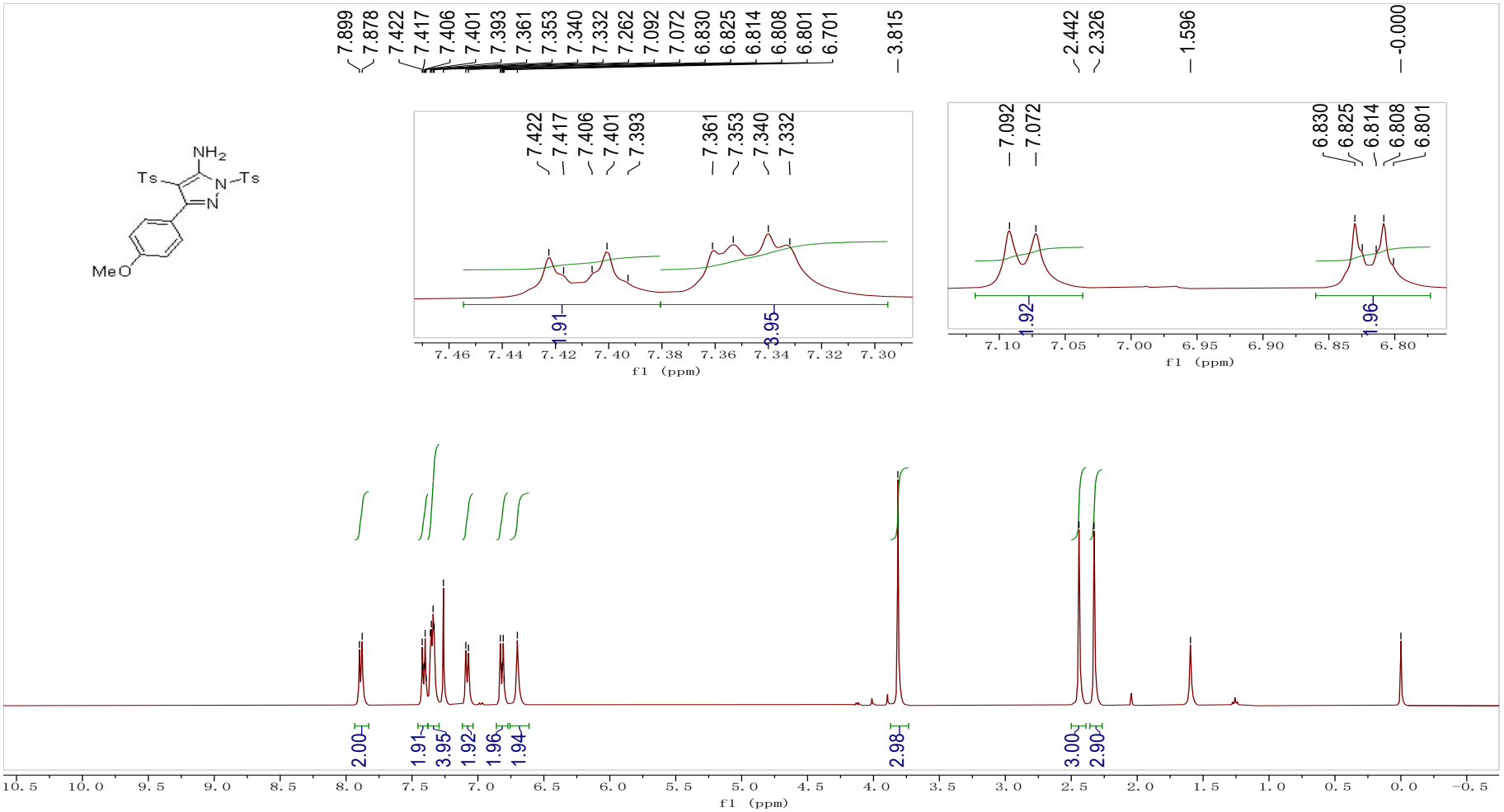

152.879
151.267
146.680
144.127
139.430
131.101
133.346
131.024
130.204
129.425
129.020
128.099
126.324
124.151
100.081
77.315
77.000
76.673
21.741
21.448
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
N
N
Ts
Br
200
150
100
50
0
PPM

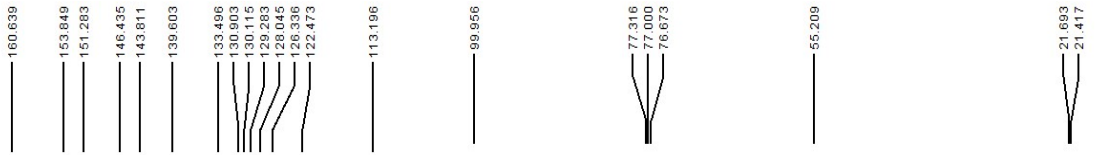
3-(*p*-Tolyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4y)



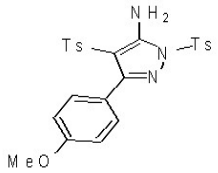

154.105
151.218
146.379
143.728
139.599
139.479
133.403
130.043
129.279
129.195
128.395
127.979
127.131
126.290
100.003
77.317
77.000
76.879
21.610
21.339
21.246
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
200
150
100
50
0
PPM

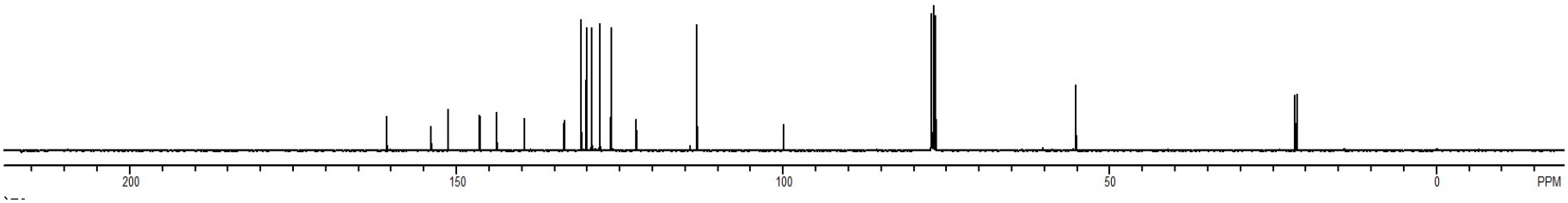
3-(4-Methoxyphenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4z)



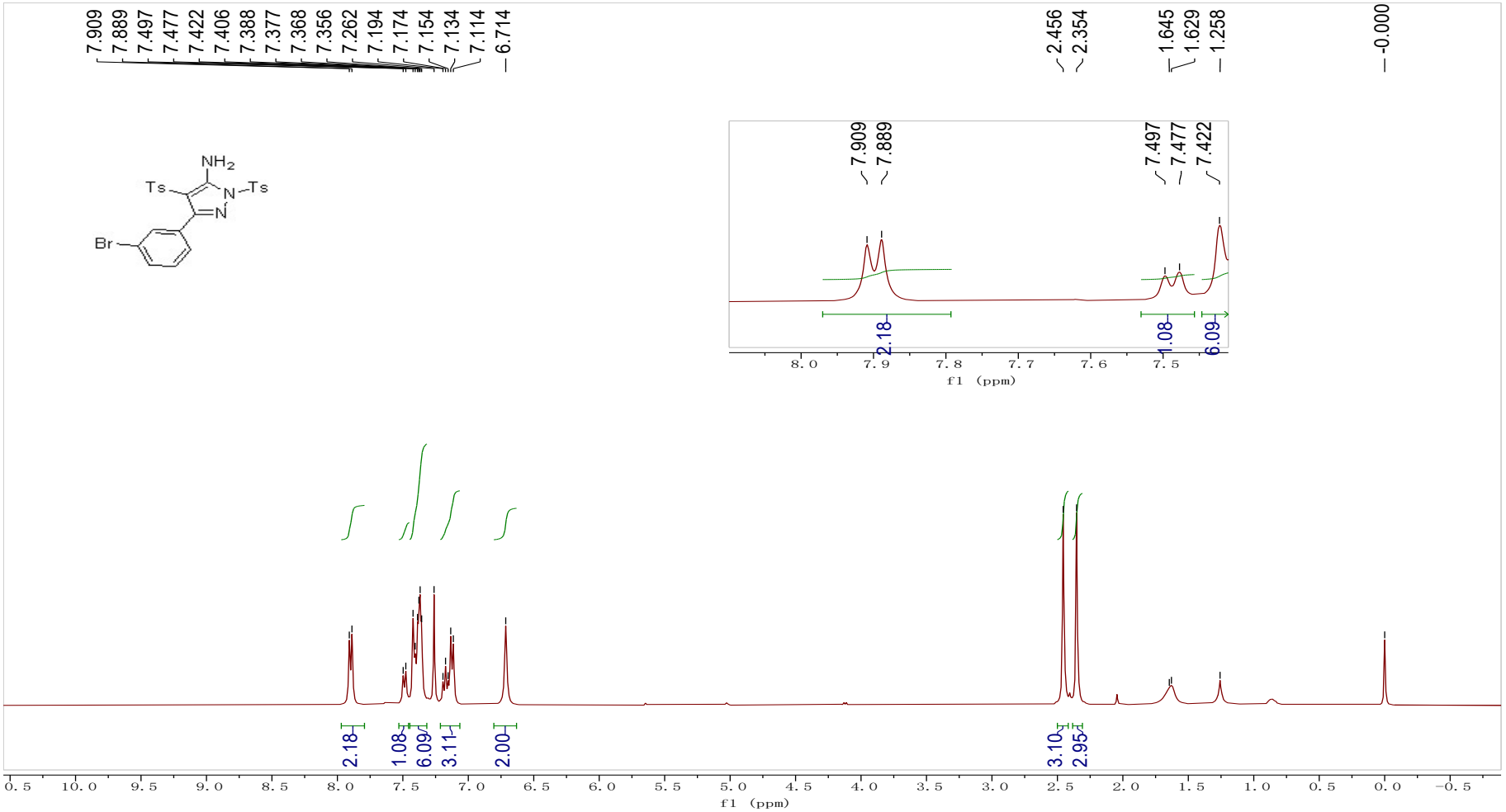


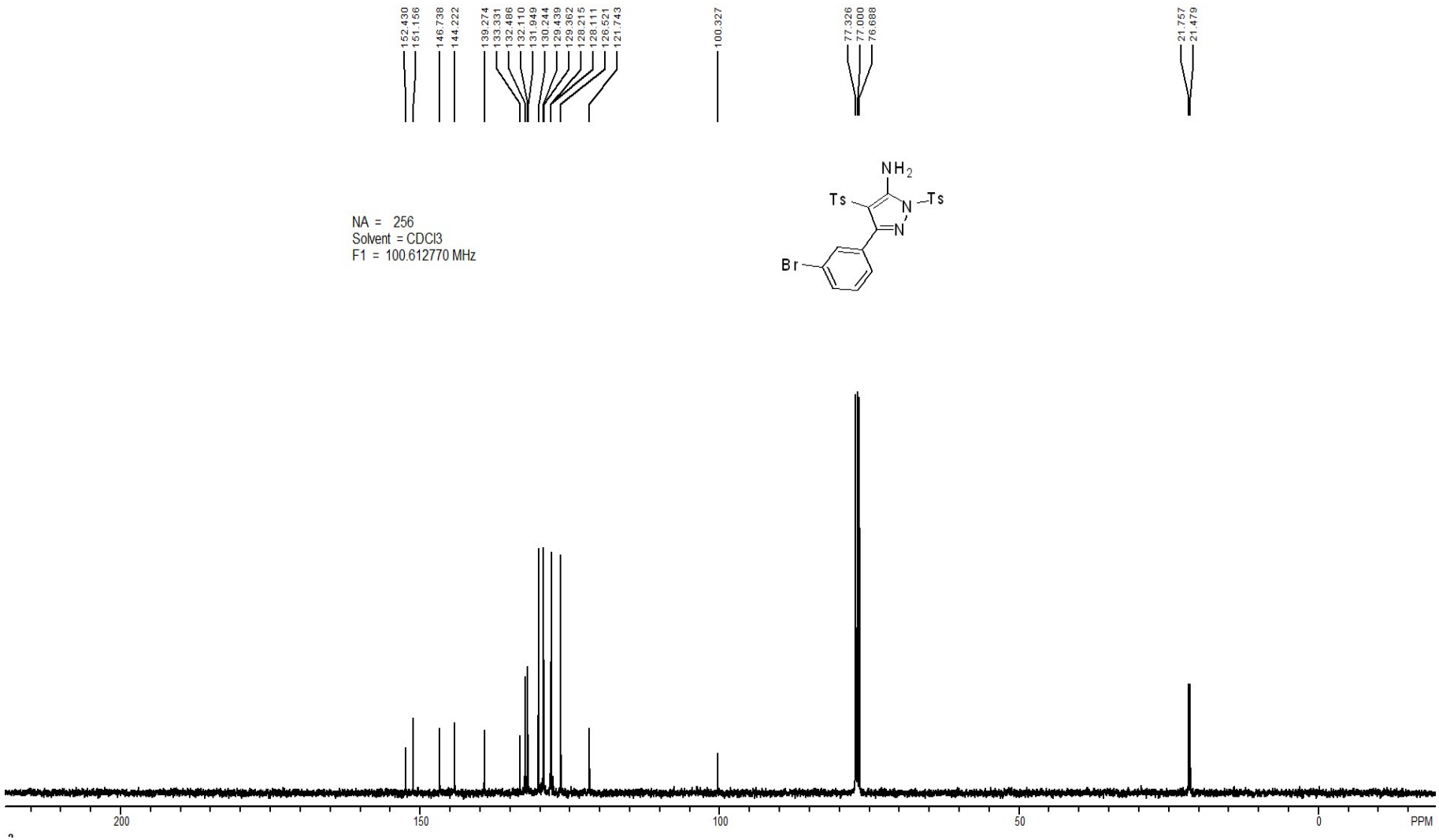
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz



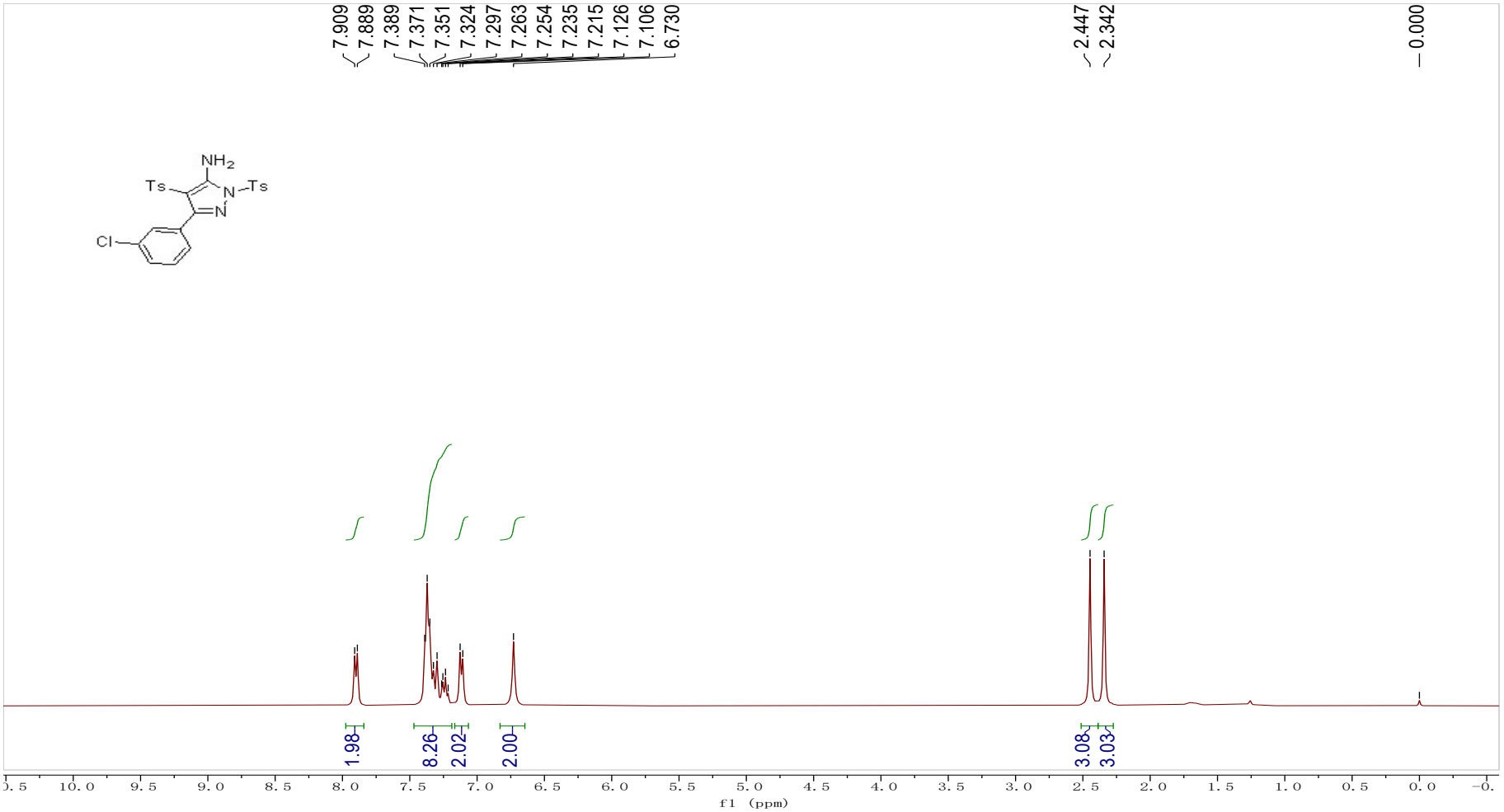


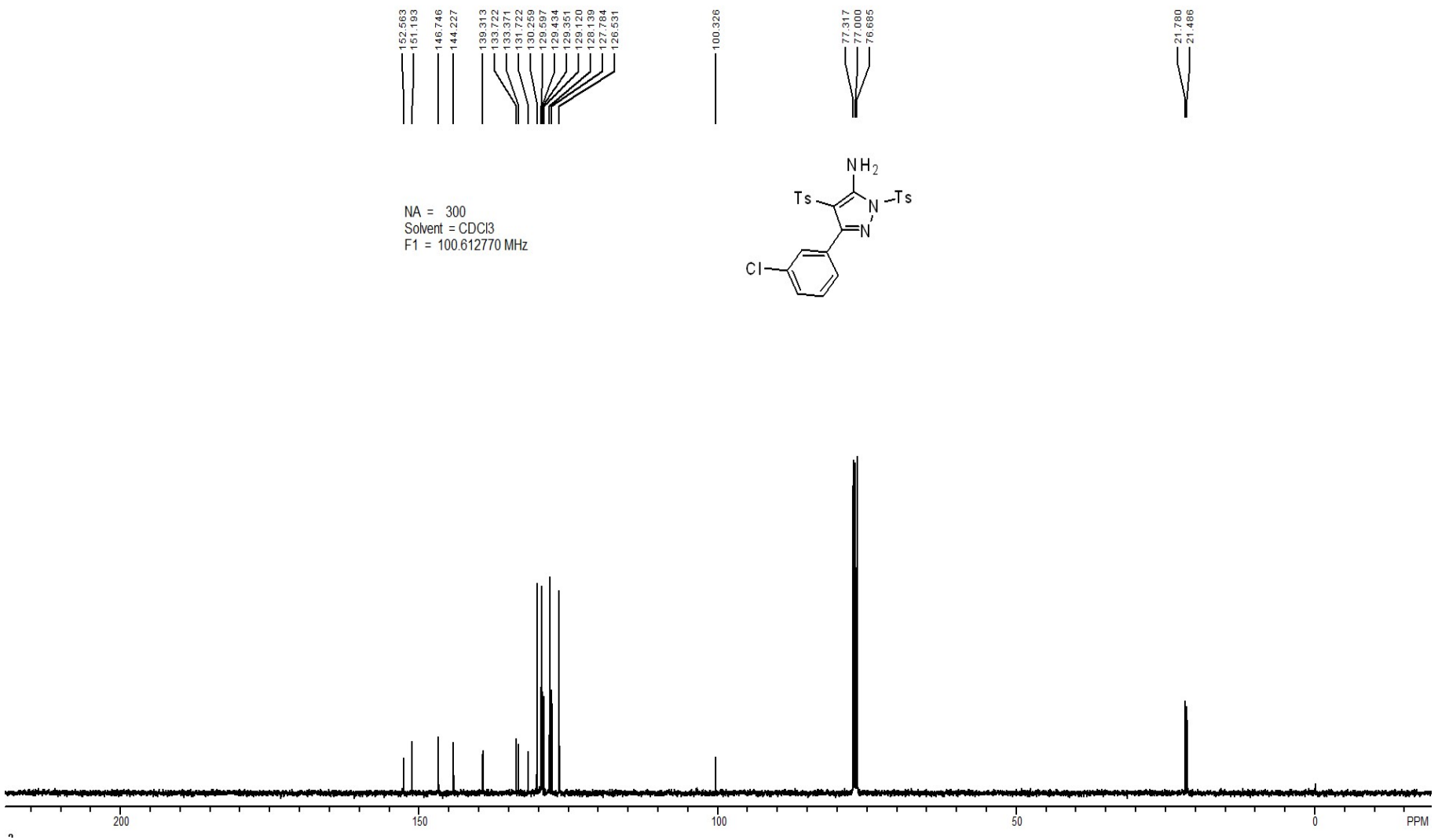
3-(3-Bromophenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4aa)



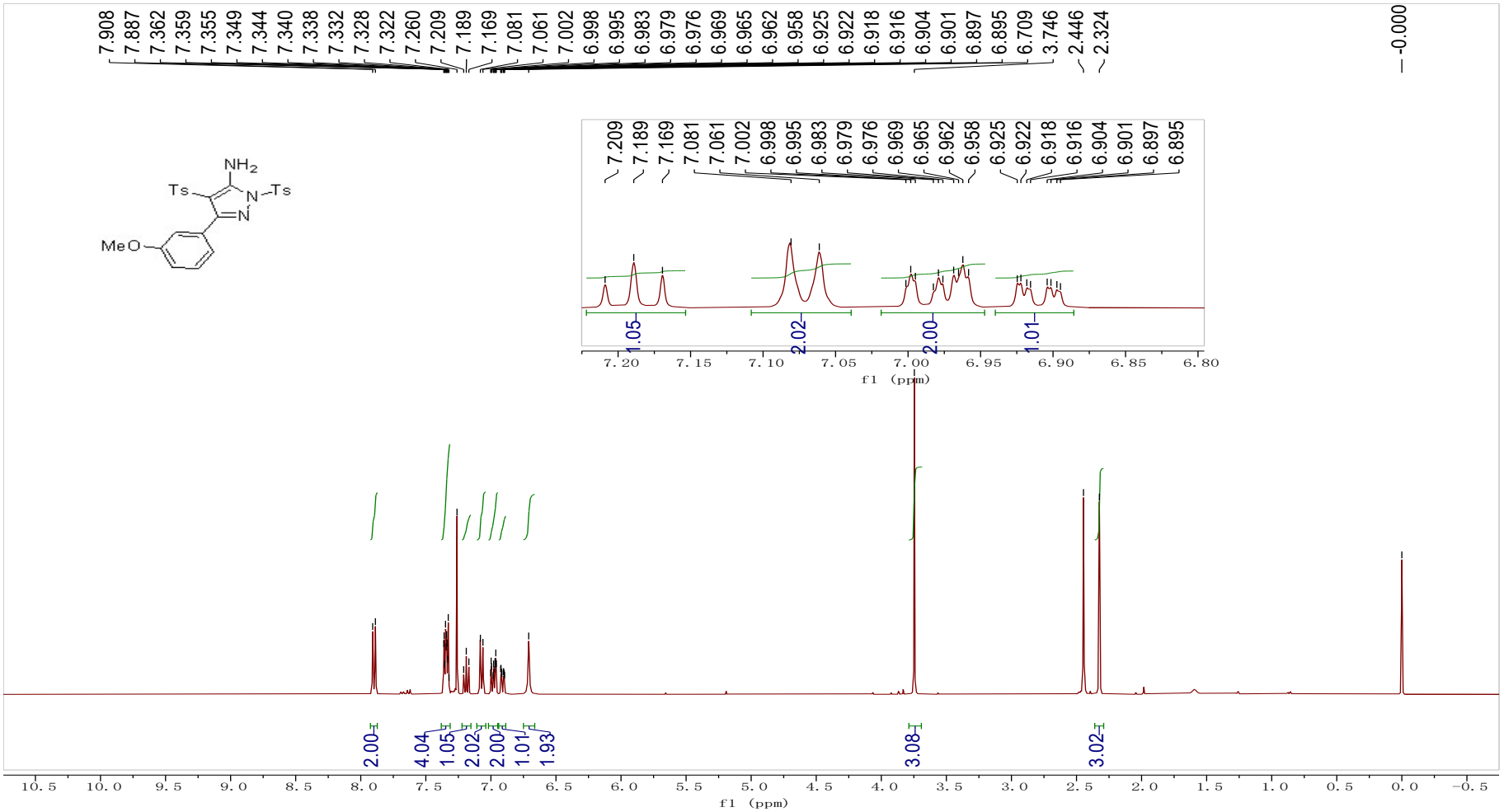

152.430
151.156
146.738
144.222
139.274
133.331
132.486
132.110
131.949
130.244
129.439
129.362
128.215
128.111
126.521
121.743
100.327
77.326
77.000
76.688
21.757
21.479
NA = 256
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
Br
200
150
100
50
0
PPM

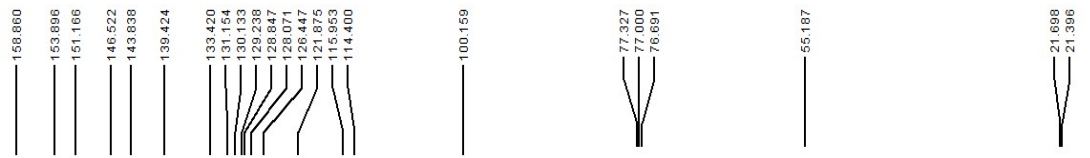
3-(3-Chlorophenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4bb)



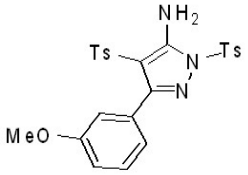

152.563
151.193
146.746
144.227
139.313
133.722
133.371
131.722
130.259
129.597
129.434
129.351
129.120
128.139
127.784
126.531
100.326
77.317
77.000
76.685
21.780
21.486
NA = 300
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
Cl
200
150
100
50
0
PPM

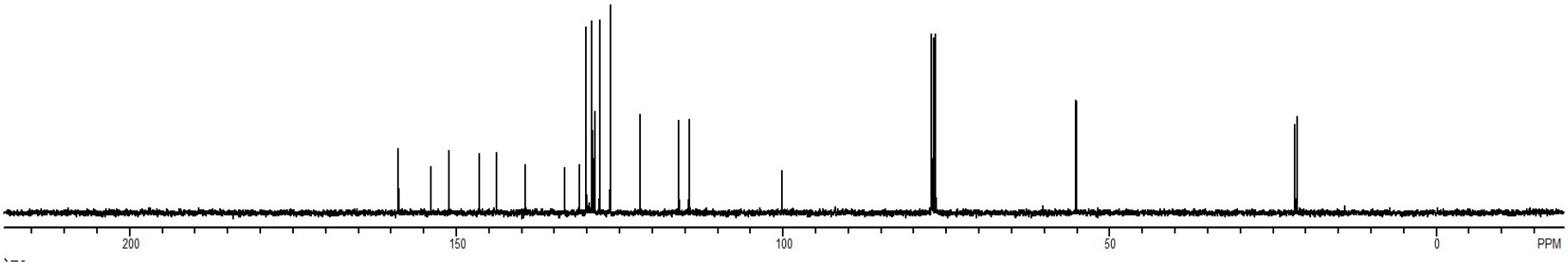
3-(3-Methoxyphenyl)-1,4-ditosyl-1H-pyrazol-5-amine (4cc)



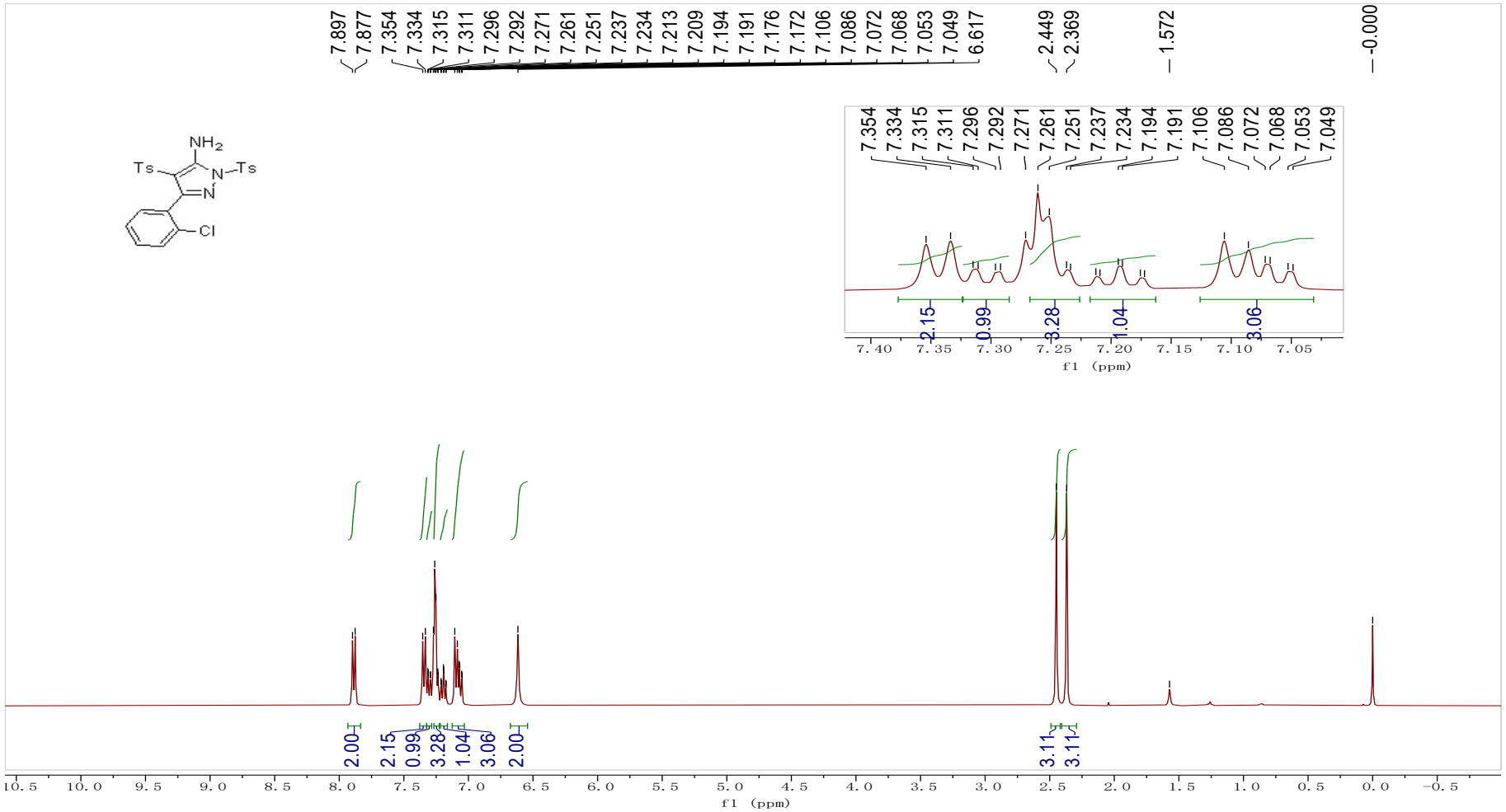


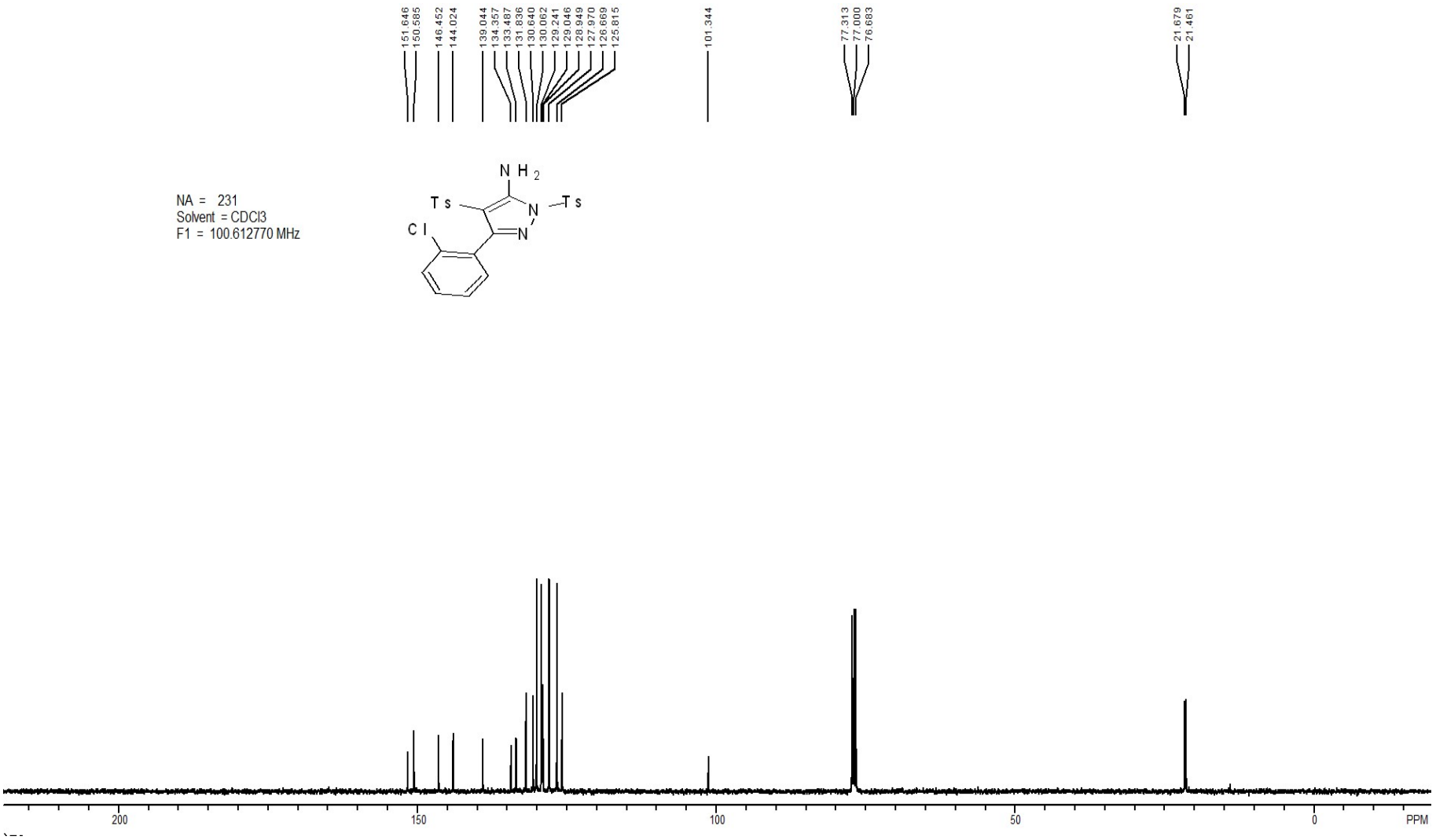
NA = 36
Solvent = CDCl3
F1 = 100.612770 MHz



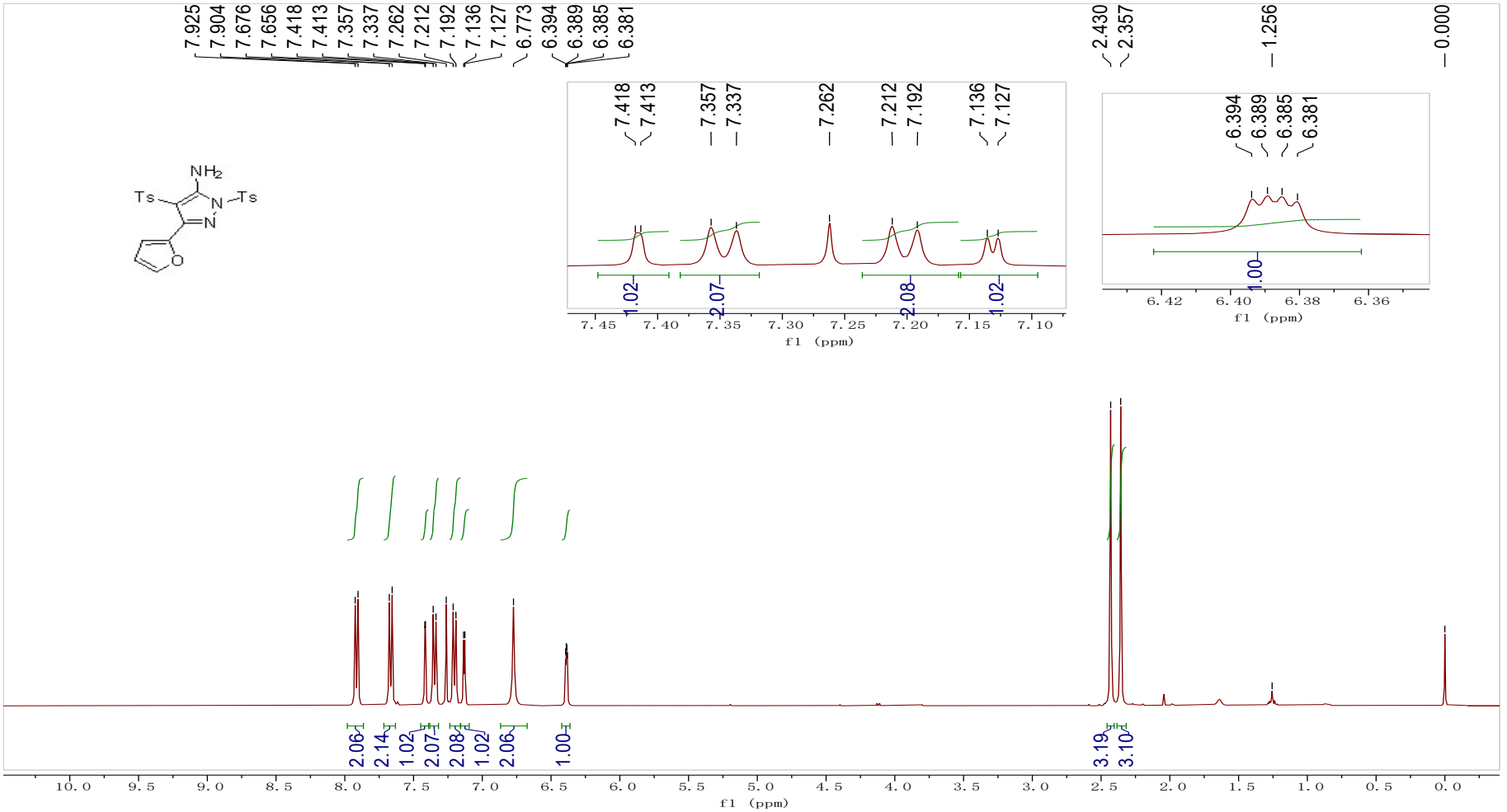


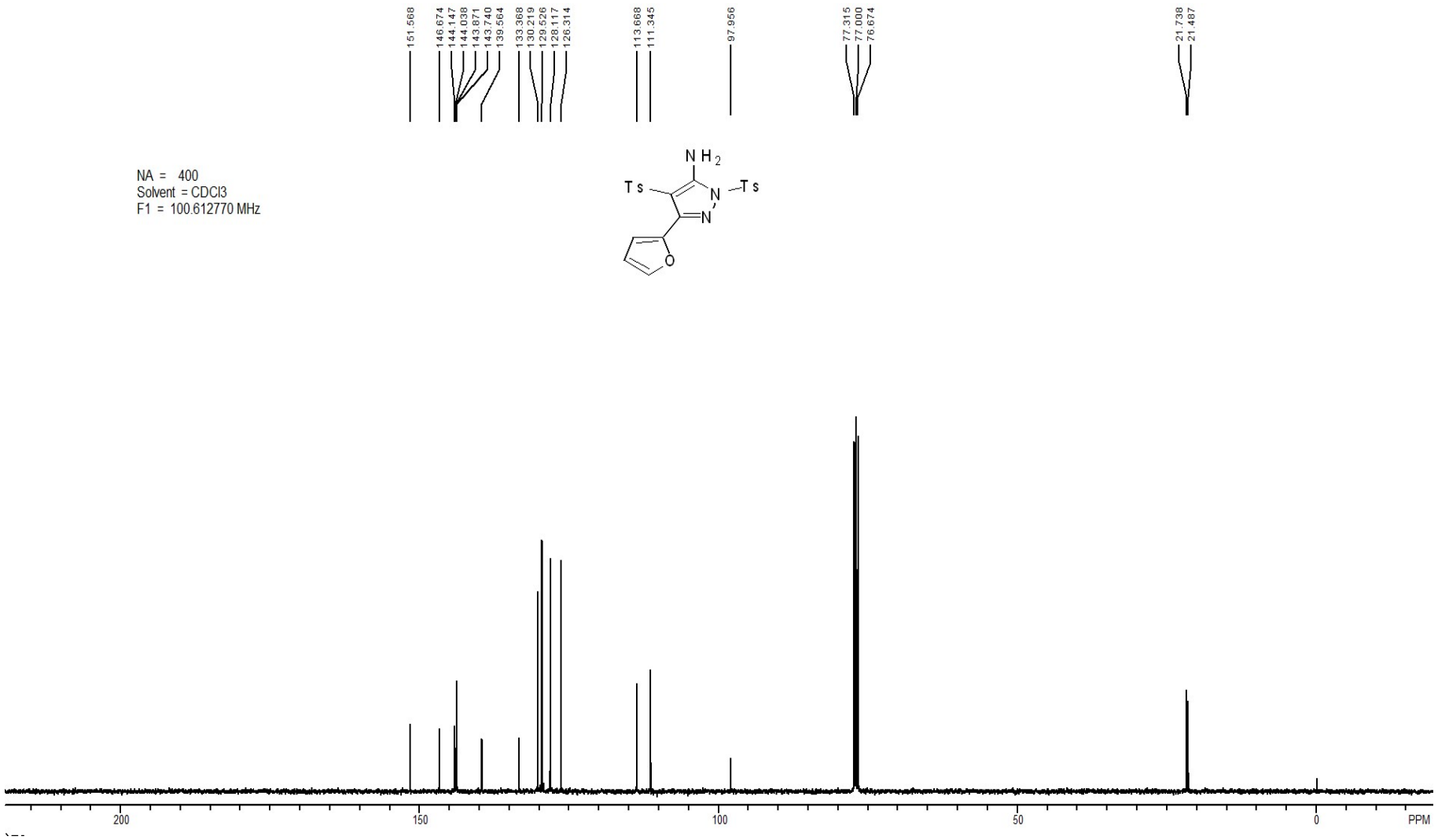
3-(2-Chlorophenyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4dd)



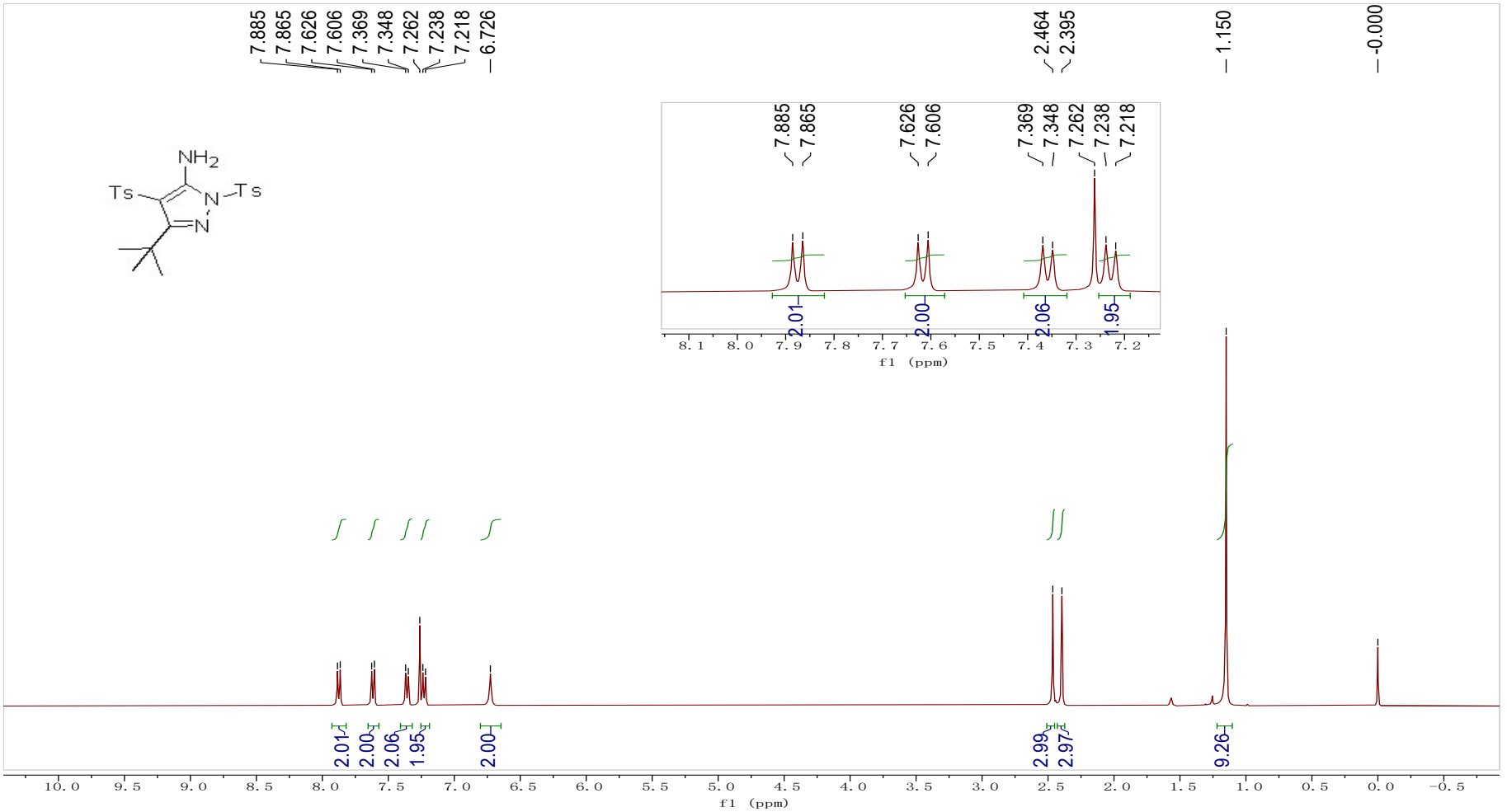

151.646
150.585
146.452
144.024
139.044
134.357
133.487
131.836
130.640
130.062
129.241
129.046
128.949
127.970
126.669
125.815
101.344
77.313
77.000
76.683
21.679
21.461
NA = 231
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
Cl
200
150
100
50
0
PPM

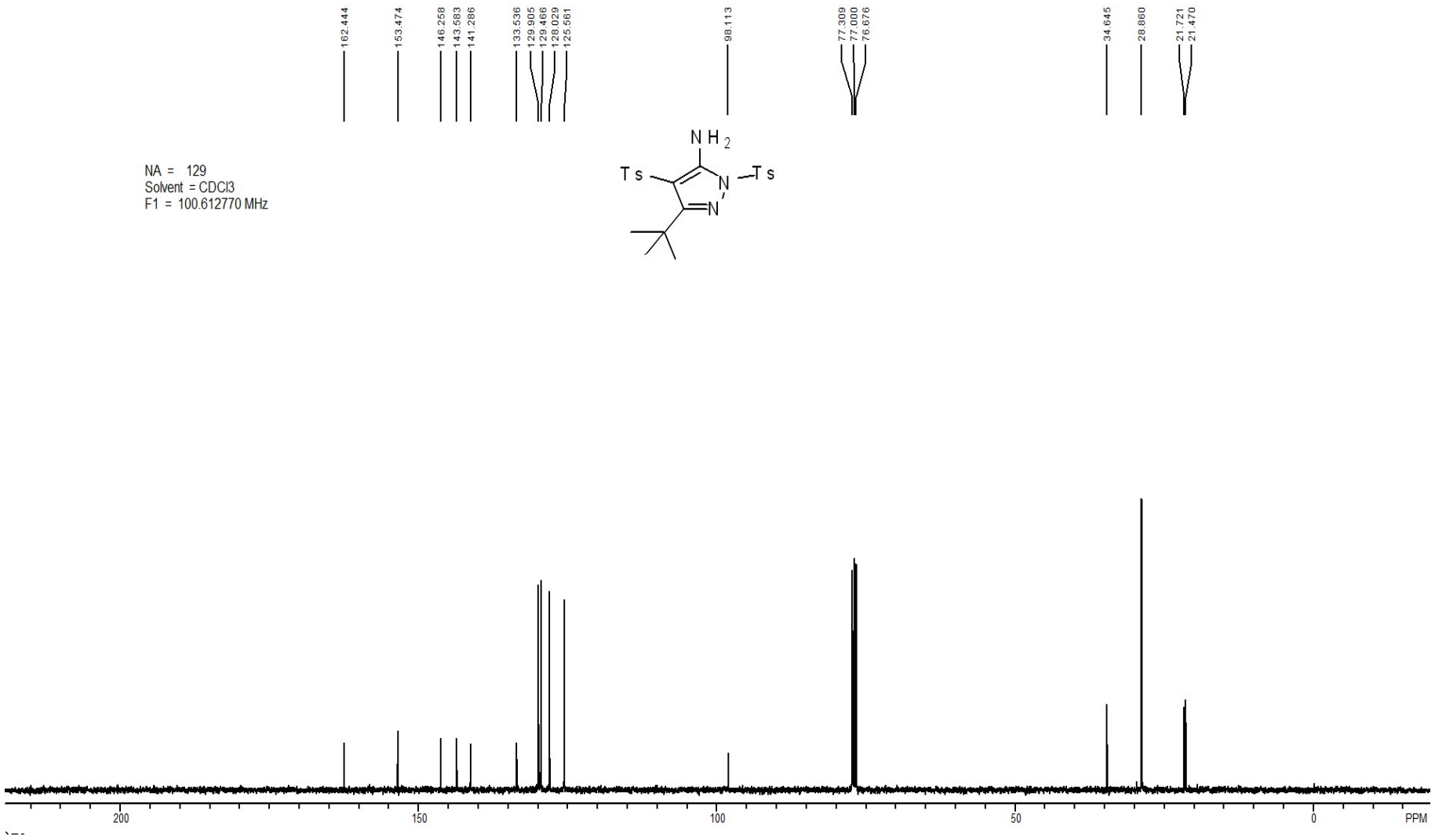
3-(Furan-2-yl)-1,4-ditosyl-1H-pyrazol-5-amine (4ee)




151.568
146.674
144.147
144.038
143.871
143.740
139.564
133.368
130.219
129.526
128.117
126.314
113.668
111.345
97.956
77.315
77.000
76.674
21.738
21.487
NA = 400
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
N
N
Ts
O
200
150
100
50
0
PPM

3-(tert-Butyl)-1,4-ditosyl-1*H*-pyrazol-5-amine (4ff)




162.444
153.474
146.258
143.583
141.286
133.536
129.905
129.466
128.029
125.561
98.113
77.309
77.000
76.676
34.645
28.860
21.721
21.470
NA = 129
Solvent = CDCl3
F1 = 100.612770 MHz
NH2
Ts
Ts
N
N
200
150
100
50
0
PPM