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Supporting Information

Zinc-Promoted Cyclization of Tosylhydrazones and 2-(Dimethylamino)malononitrile: an Efficient Strategy for the Synthesis of Substituted 1-Tosyl-1*H*-pyrazoles

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content

1. General information……S2

2. General experimental procedures……S2

3. Characterization of substrates and products……S2-S17

4. General procedures for the synthetic transformation of products……..... S17-S18

5. References……S18-S19

6. ^{1}H NMR and ^{13}C NMR spectra for products……S20-S79

1. General Information

All reactions under standard conditions were carried out under argon, dry atmosphere and monitored by thin-layer chromatography (TLC) on gel F254 plates. All products were purified through silica gel chromatography (200~300 mesh). Column chromatography was carried out with light petroleum ether (b p. 60~90 °C), ethyl acetate and dichloromethane as eluent. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ or DMSO on 400 MHz instruments and spectral data were reported in ppm. High-resolution mass spectral analysis (HRMS) data were measured on the Apex II by means of the ESI technique. Melting point was measured with SGW-X4B instrument. All the chemicals were used as obtained from vendors.

2. General experimental procedure

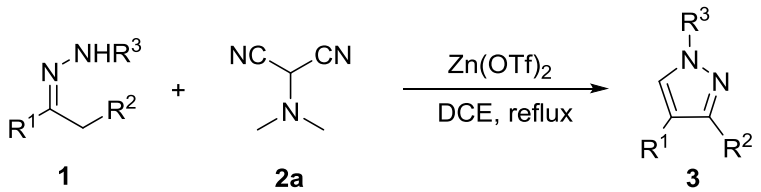
2.1 General Procedure for Preparation of Hydrazones 1a – 1aa.

To an oven dried round-bottom flask previously equipped with a magnetic stir bar, was charged with hydrazide (5 mmol) in dry methanol (10 mL) at 60 °C, the ketone (5 mmol) was added drop wise. After the completion of reaction the product was began to precipitate. The crude product was filtered, washed with petroleum ether: ethyl acetate (10:1) and dried to afford the corresponding pure hydrazones. The reaction provides the hydrazone derivatives **1a-1aa** in about 85−98% yields.

2.2 General experimental procedure A for products 2a.

Substrates **2a**, were prepared using the strategy developed by us.[1]

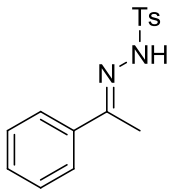
2.3 General experimental procedure B for products 3a-3aa.



To a stirred solution of hydrazones **1** (50 mg) in DCE (2.0 mL) was added 2-(dimethylamino)malononitrile **2a** (1.5 equiv), $Zn(OTf)_2$ (0.5 equiv). The reaction mixture was heated to reflux for 36 h. The completion of reaction was monitored by TLC chromatography. After completion, the reaction mixture was cooled to room temperature and filtrated through a pad of silica gel. The filtration was concentrated under reduced pressure to get the crude product. The obtained crude product was then purified using column chromatography to afford pure pyrazoles derivatives **3a-3aa**. Caution: The reaction should be handled with care in a fume hood as HCN will be released from the reaction mixture.

3. Characterization substrates of products.

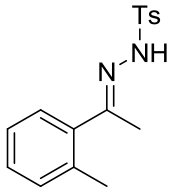
3.1 Characterization of substrates 1a–1aa.



1a

(*E*)-4-methyl-*N'*-(1-phenylethylidene)benzenesulfonohydrazide (1a)[2]

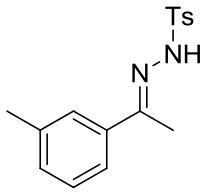
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.50 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.63–7.60 (m, 2H), 7.42–7.36 (m, 5H), 2.36 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.23, 143.42, 137.48, 136.31, 129.54, 129.45, 128.44, 127.66, 126.03, 21.09, 14.36.



1b

(*E*)-4-methyl-*N'*-(1-(o-tolyl)ethylidene)benzenesulfonohydrazide (1b)[3]

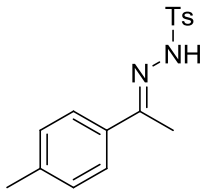
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.49 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.23–7.13 (m, 4H), 2.36 (s, 3H), 2.15 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.00, 143.30, 138.87, 136.57, 135.20, 130.69, 129.50, 128.32, 127.84, 127.61, 125.71, 21.08, 19.90, 18.28.



1c

(*E*)-4-methyl-*N'*-(1-(m-tolyl)ethylidene)benzenesulfonohydrazide (1c)[4]

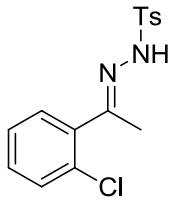
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.53 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.44–7.36 (m, 4H), 7.25–7.14 (m, 2H), 2.31 (s, 3H), 2.28 (s, 3H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.35, 143.40, 137.58, 137.54, 136.44, 130.08, 129.50, 128.31, 127.74, 126.69, 123.28, 21.13, 21.06, 14.46.



1d

(*E*)-4-methyl-*N'*-(1-(p-tolyl)ethylidene)benzenesulfonohydrazide (1d)[2]

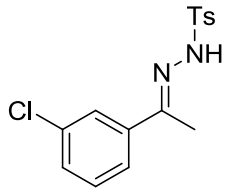
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.44 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.34 (s, 3H), 2.28 (s, 3H), 2.15 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.27, 143.36, 139.07, 136.36, 134.75, 129.49, 129.00, 127.68, 125.97, 21.07, 20.85, 14.28.



1e

(*E*)-*N'*-(1-(2-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1e)[4]

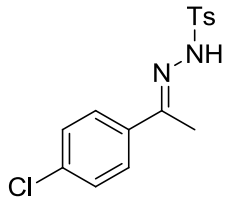
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.39–7.24 (m, 5H), 7.17–7.16 (m, 1H), 2.29 (s, 3H), 2.21 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.89, 143.36, 138.40, 136.49, 131.14, 130.23, 130.01, 129.76, 129.50, 127.58, 127.20, 21.06, 18.55.



1f

(*E*)-*N'*-(1-(3-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1f)[5]

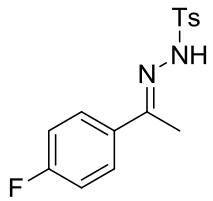
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.70 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.61–7.56 (m, 2H), 7.41–7.37 (m, 4H), 2.33 (s, 3H), 2.18 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 139.60, 143.54, 139.59, 136.25, 133.36, 130.30, 129.57, 129.15, 127.63, 125.71, 124.69, 21.06, 14.33.



1g

(*E*)-*N'*-(1-(4-chlorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1g)[3]

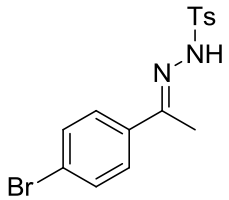
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.39–7.35 (m, 4H), 2.30 (s, 3H), 2.18 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.92, 143.46, 136.35, 136.29, 134.26, 129.56, 128.44, 127.75, 127.71, 21.06, 14.24.



1h

(*E*)-*N'*-(1-(4-fluorophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1h)[2]

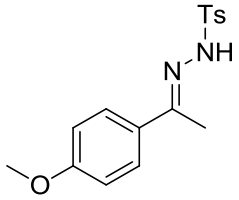
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.57 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.69–7.66 (m, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.19–7.15 (t, *J* = 8.9 Hz, 2H), 2.32 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.85 (d, *J* = 245 Hz), 152.20, 143.35, 136.26, 133.89 (d, *J* = 2 Hz), 129.46, 128.18 (d, *J* = 8 Hz), 127.61, 115.22 (d, *J* = 21 Hz), 20.96, 14.29.



1i

(*E*)-*N'*-(1-(4-bromophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1i)[3]

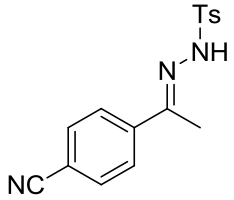
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.61 (s, 1H), 7.94–7.83 (m, 2H), 7.56 (s, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.92, 143.38, 136.55, 136.13, 131.30, 129.48, 127.94, 127.53, 122.84, 20.99, 14.10.



1j

(*E*)-*N'*-(1-(4-methoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1j)[2]

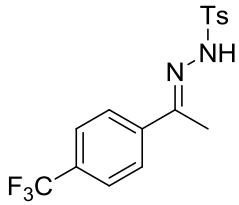
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.89–6.93 (m, 2H), 3.75 (s, 3H), 2.34 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 160.38, 153.25, 143.34, 136.39, 129.94, 129.49, 127.71, 127.54, 113.78, 55.27, 21.08, 14.23.



1K

(*E*)-*N'*-(1-(4-cyanophenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1k)[2]**:**

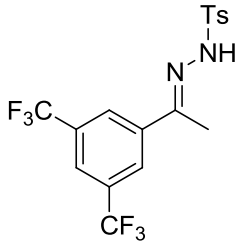
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 7.86–7.75 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H), 2.19 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.98, 143.52, 141.54, 136.11, 132.29, 129.55, 127.55, 126.62, 118.61, 111.58, 20.98, 14.09.



1l

(*E*)-4-methyl-*N'*-(1-(4-(trifluoromethyl)phenyl)ethylidene)benzenesulfonohydrazide (1l)[2]**:**

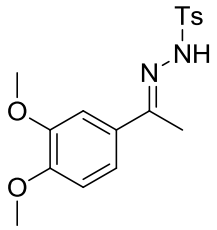
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 2.23 (s, 3H);**^{13}C NMR** (100 MHz, DMSO-d_6) δ 151.44, 143.56, 141.33, 136.36, 129.60, 129.54 (q, *J* = 32 Hz), 127.75, 126.73, 125.30 (q, *J* = 4 Hz), 124.23 (q, *J* = 271 Hz), 21.00, 14.31.



1m

(*E*)-*N'*-(1-(3,5-bis(trifluoromethyl)phenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1m)[5]

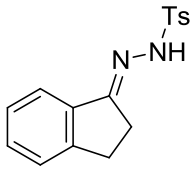
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 8.12 (s, 2H), 8.05 (s, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 2.33 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.11, 143.74, 139.96, 135.90, 130.48 (q, J = 33 Hz), 129.48, 127.61, 126.36, 123.18 (q, J = 271 Hz), 122.53, 20.95, 14.23.



1n

(*E*)-*N'*-(1-(3,4-dimethoxyphenyl)ethylidene)-4-methylbenzenesulfonohydrazide (1n)[6]

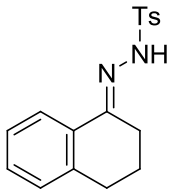
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.35 (s, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.18–7.15 (m, 2H), 6.90 (d, J = 8.4 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H),2.34 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.29, 150.17, 148.39, 143.36, 136.15, 129.97, 129.33, 127.83, 119.29, 110.95, 108.70, 55.46, 55.26, 20.97, 14.06.



1o

(*E*)-*N'*-(2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonohydrazide (1o)[7]

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.6 Hz, 1H), 7.39–7.30 (m, 4H), 7.25–7.21 (m, 1H), 2.99–2.96 (m, 2H), 2.76–2.73 (m, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.18, 148.61, 143.28, 137.21, 136.42, 130.73, 129.48, 127.65, 126.98, 125.80, 121.11, 28.01, 27.38, 21.06.

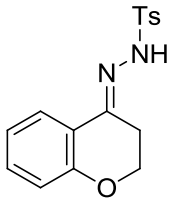


1p

(*E*)-*N'*-(3,4-dihydronaphthalen-1(2H)-ylidene)-4-methylbenzenesulfonohydrazide (1p)[2]**:**

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 7.92–7.85 (m, 3H), 7.36 (d, J = 8.0 Hz, 2H), 7.23–7.15 (m, 2H), 7.08 (d, J = 7.6 Hz, 1H), 2.64–2.57 (m, 4H), 2.29 (s, 3H), 1.72 (p, J = 6.0 Hz, 2H);

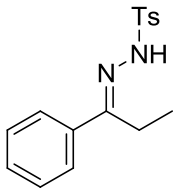
^{13}C NMR (100 MHz, DMSO-d_6) δ 152.94, 143.36, 139.87, 136.50, 131.72, 129.49, 129.34, 128.64, 127.79, 126.30, 124.23, 28.88, 26.10, 21.34, 21.05.



1q

(*E*)-*N'*-(chroman-4-ylidene)-4-methylbenzenesulfonohydrazide (1q)[8]

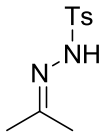
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.60 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.27–7.23 (m, 1H), 6.95–6.85 (m, 2H), 4.18 (t, *J* = 6.4 Hz, 2H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.78, 147.74, 143.40, 136.08, 131.32, 129.46, 127.62, 124.17, 121.22, 119.66, 117.44, 64.48, 25.57, 21.00.



1r

(*E*)-4-methyl-*N'*-(1-phenylpropylidene)benzenesulfonohydrazide (1r)[8]

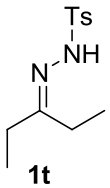
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.71 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.64–7.61 (m, 2H), 7.38–7.32 (m, 5H), 2.72 (q, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.00 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.20, 143.33, 136.47, 136.37, 129.52, 129.32, 128.49, 127.62, 126.19, 21.03, 20.05, 10.52.



1s

4-methyl-*N'*-(propan-2-ylidene)benzenesulfonohydrazide (1s)[9]

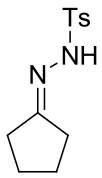
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 156.67, 143.06, 136.59, 129.36, 127.62, 24.79, 21.00, 17.62.



1t

4-methyl-*N'*-(pentan-3-ylidene)benzenesulfonohydrazide (1t)[9]

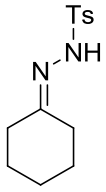
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.27 (s, 3H), 2.22 (q, *J* = 7.6 Hz, 2H), 2.07 (q, *J* = 7.6 Hz, 2H), 0.93 (t, *J* = 7.6 Hz, 3H), 0.88(t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 163.47, 142.89, 136.39, 129.14, 127.58, 28.40, 22.65, 20.93, 10.24, 9.42.



1u

***N'*-cyclopentylidene-4-methylbenzenesulfonohydrazide (1u)**[4]

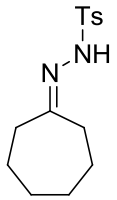
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.23 (t, *J* = 7.2 Hz, 2H), 2.16 (t, *J* = 7.2 Hz, 2H), 1.71–1.64 (m, 2H), 1.62–1.55 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 168.29, 143.12, 136.63, 129.48, 127.57, 32.91, 28.67, 24.50, 24.36, 21.08.



1v

***N'*-cyclohexylidene-4-methylbenzenesulfonohydrazide (1v)**[10]

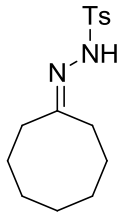
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.15 (s, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 2H), 2.07 (s, 2H), 1.48 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 162.30, 143.03, 136.52, 129.40, 127.58, 34.72, 27.44, 26.78, 25.56, 24.92, 21.08.



1w

***N'*-cycloheptylidene-4-methylbenzenesulfonohydrazide (1w)**[10]

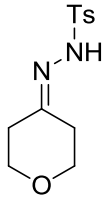
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 2.34–2.33 (m, 2H), 2.25–2.23 (m, 2H), 1.60–1.55 (m, 2H), 1.46–1.42 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 164.58, 143.02, 136.59, 129.37, 127.58, 36.38, 30.69, 29.86, 29.83, 27.08, 23.87, 21.06.



1x

***N'*-cyclooctylidene-4-methylbenzenesulfonohydrazide (1x)**[10]

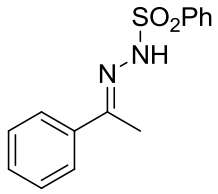
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 5H), 2.12 (s, 2H), 1.64 (s, 2H), 1.64 (s, 2H), 1.35 (s, 4H), 1.23 (s, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 164.17, 142.80, 136.68, 129.18, 127.44, 35.45, 27.88, 26.61, 26.31, 25.03, 24.62, 22.92, 20.93.



1y

***N'*-(dihydro-2H-pyran-4(3H)-ylidene)-4-methylbenzenesulfonohydrazide (1y)**[9]

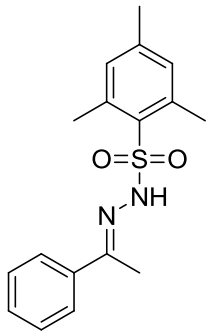
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.62–3.58 (m, 4H), 2.13 (t, *J* = 5.6 Hz, 2H), 2.02 (s, 3H), 1.90 (t, *J* = 5.6 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 157.54, 143.22, 136.52, 129.47, 127.70, 67.66, 66.01, 35.04, 29.27, 21.06.



1z

(*E*)-*N'*-(1-phenylethylidene)benzenesulfonohydrazide (1z)[2]**:**

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.70 (s, 1H), 8.06–8.03 (m, 2H), 7.66–7.60 (m, 5H), 7.36–7.33 (m, 3H), 2.23 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 153.52, 139.22, 137.41, 132.94, 129.41, 129.02, 128.36, 127.64, 126.01, 14.39.

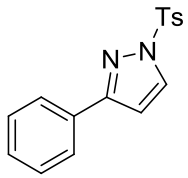


1aa

(*E*)-2,4,6-trimethyl-*N'*-(1-phenylethylidene)benzenesulfonohydrazide (1aa)[11]

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.70 (s, 1H), 7.56–7.55 (m, 2H), 7.34–7.31 (m, 3H), 6.98 (s, 2H), 2.68 (s, 6H), 2.19 (s, 3H). 2.18 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 150.92, 142.15, 139.47, 137.66; 133.49, 131.50, 129.08, 128.27, 125.75, 22.84, 20.36, 14.11.

3.2 Characterization of products 3a-3aa.

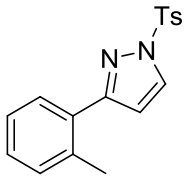


3a

3-phenyl-1-tosyl-1H-pyrazole (3a)[12]

3a (47 mg) was obtained through the general procedure B in 92% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.83–7.80 (m, 2H), 7.41–7.34 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 3H);**^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.77, 145.64, 134.03, 132.43, 131.30, 129.84 , 129.05, 128.51, 127.95, 126.26, 106.40, 21.51.

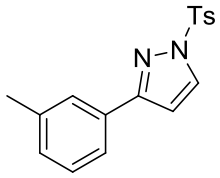


3b

3-(o-tolyl)-1-tosyl-1H-pyrazole (3b)

3b (41 mg) was obtained through the general procedure B in 80% yield as a white solid.

mp 80–84°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.8 Hz, 1H), 7.94–7.92 (m, 2H), 7.47–7.45 (m, 1H), 7.32–7.30 (m, 2H), 7.27–7.18 (m, 3H), 6.55 (d, *J* = 2.8 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.40, 145.64, 136.47, 134.15, 131.48, 131.14, 130.92, 129.84, 129.34 , 128.70, 128.09,125.75, 109.22, 21.64, 21.13; **HRMS** (ESI) calcd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$: 313.1005, found 313.1006.

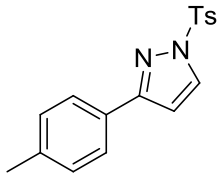


3c

3-(m-tolyl)-1-tosyl-1H-pyrazole (3c)

3c (40 mg) was obtained through the general procedure B in 78% yield as a white solid.

mp 109–111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.8 Hz, 1H), 7.94–7.92 (m, 2H), 7.67–7.66 (m, 1H), 7.60–7.57 (m, 1H), 7.31–7.26 (m, 3H), 7.18–7.15 (m, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 2.38 (s, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.97, 145.60, 138.22, 134.12, 132.41, 131.20, 129.87, 129.86, 128.42, 127.94, 126.87, 123.46, 106.54, 21.55, 21.25; **HRMS** (ESI) calcd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$： 313.1005, found 313.1006.

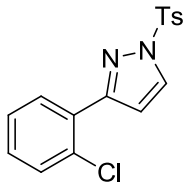


3d

3-(p-tolyl)-1-tosyl-1H-pyrazole (3d)[13]

3d (37.7 mg) was obtained through the general procedure B in 73% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 2.8 Hz, 1H), 7.94–7.91 (m, 2H), 7.71–7.69 (m, 2H), 7.32–7.29 (m, 2H), 7.20–7.18 (m, 2H), 6.66 (d, *J* = 2.8 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.96, 145.58, 139.15, 134.22, 132.43, 129.89, 129.27, 128.60, 128.04, 126.26, 106.38, 21.63, 21.29.

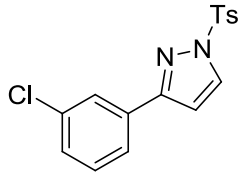


3e

3-(2-chlorophenyl)-1-tosyl-1H-pyrazole (3e)

3e (44.3 mg) was obtained through the general procedure in 86% yield as a white solid.

mp 100–103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14–8.13(m, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.76–7.73 (m, 1H), 7.40–7.36 (m, 1H), 7.31–7.25 (m, 4H), 6.91–6.90 (m, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.66, 145.79, 133.89, 132.41, 131.33, 130.96, 130.41, 130.12, 129.94, 129.90, 128.03, 126.79, 110.06, 21.57; **HRMS** (ESI) calcd for $C_{16}H_{13}ClN_2O_2S$ $[M+H]^+$: 333.0459, found 333.0460.

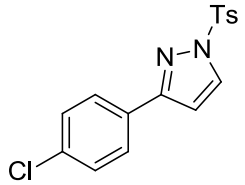


3f

3-(3-chlorophenyl)-1-tosyl-1H-pyrazole (3f)

3f (41.8 mg) was obtained through the general procedure B in 81% yield as a white solid.

mp 108–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.8 Hz, 1H), 7.94–7.92 (m, 2H), 7.81–7.80 (m, 1H), 7.66–7.63 (m, 1H), 7.32–7.29 (m, 4H), 6.67 (d, *J* = 2.8 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 155.36, 145.88, 134.55, 133.84, 133.13, 132.57, 129.97, 129.83, 129.02, 128.07, 126.27, 124.43, 106.34, 21.61; **HRMS** (ESI) calcd for $C_{16}H_{13}ClN_2O_2S$ $[M+H]^+$: 333.0459, found 333.0460.

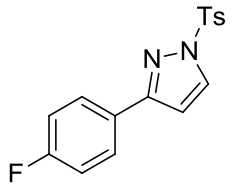


3g

3-(4-chlorophenyl)-1-tosyl-1H-pyrazole (3g)

3g (42.8 mg) was obtained through the general procedure B in 83% yield as a white solid.

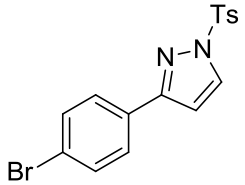
mp 115–118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.8 Hz, 1H), 7.94–7.92 (m, 2H), 7.74–7.72 (m, 2H), 7.36–7.31 (m, 4H), 7.66 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.69, 145.84, 135.00, 134.01, 132.59, 129.98, 129.95, 128.80, 128.12, 127.62, 106.25, 21.66; **HRMS** (ESI) calcd for $C_{16}H_{13}ClN_2O_2S$ $[M+H]^+$: 333.0459, found 333.0460.



3h

3-(4-fluorophenyl)-1-tosyl-1H-pyrazole (3h)

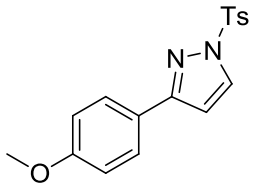
3h (43.9 mg) was obtained through the general procedure B in 85% yield as a white solid.
mp 100–104 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.8 Hz, 1H), 7.93–7.91 (m, 2H), 7.79–7.74 (m, 2H), 7.30–7.28 (m, 2H), 7.07–7.01 (m, 2H), 6.64 (d, *J* = 2.8 Hz, 1H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.16 (d, *J* = 247 Hz), 155.78, 145.74, 133.92, 132.54, 129.88, 128.10 (d, *J* = 8 Hz), 127.95, 127.56 (d, *J* = 3 Hz), 115.47 (d, *J* = 21 Hz), 106.19, 21.50; **HRMS** (ESI) calcd for $C_{16}H_{13}FN_2O_2S$ $[M+H]^+$: 317.0755, found 317.0757.



3i

3-(4-bromophenyl)-1-tosyl-1H-pyrazole (3i)[14]

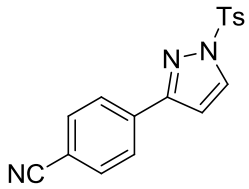
3i (44. 7mg) was obtained through the general procedure B in 87% yield as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.8 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.68–7.65 (m, 2H), 7.51–7.49 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.73, 145.86, 133.99, 132.60, 131.76, 130.39, 129.99, 128.14, 127.89, 123.28, 106.24, 21.68.



3j

3-(4-methoxyphenyl)-1-tosyl-1H-pyrazole (3j)[15]

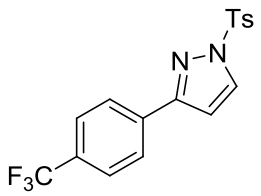
3j (46.9 mg) was obtained through the general procedure B in 91% yield as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09–8.08 (m, 1H), 7.92–7.90 (m, 2H), 7.75–7.72 (m, 2H), 7.29–7.27 (m, 2H), 6.91–6.88 (m, 2H), 6.63–6.62 (m, 1H), 3.80 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.30, 156.66, 145.53, 134.13, 132.43, 129.82, 127.91, 127.65, 123.97, 113.88, 106.15, 55.17, 21.54.



3k

4-(1-tosyl-1H-pyrazol-3-yl)benzonitrile (3k)

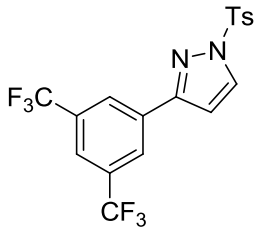
3k (28.4 mg) was obtained through the general procedure B in 55% yield as a white solid. mp 166–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.8 Hz, 1H), 7.95–7.88 (m, 4H), 7.67–7.64 (m, 2H), 7.35–7.32 (m, 2H), 6.74 (d, *J* = 2.8 Hz, 1H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.64, 146.14, 135.69, 133.64, 132.76, 132.38, 130.05, 128.19, 126.77, 118.54, 112.36, 106.47, 21.66; **HRMS** (ESI) calcd for $C_{17}H_{13}N_3O_2S$ $[M+H]^+$: 324.0801, found 324.0799.



3l

1-tosyl-3-(4-(trifluoromethyl)phenyl)-1H-pyrazole (3l)

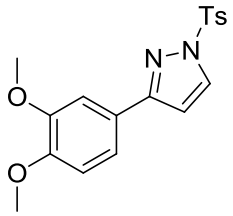
3l (44.2 mg) was obtained through the general procedure B in 86% yield as a white solid. mp 145–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.4 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 2.4 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.18, 146.01, 134.79, 133.79, 132.68, 130.66 (q, *J* = 323 Hz), 129.96, 128.06, 126.49, 125.43 (q, *J* = 4 Hz), 123.91 (q, *J* = 271 Hz), 106.48, 21.47; **HRMS** (ESI) calcd for $C_{17}H_{13}F_3N_2O_2S$ $[M+H]^+$: 367.0723, found 367.0726.



3m

3-(3,5-bis(trifluoromethyl)phenyl)-1-tosyl-1H-pyrazole (3m)

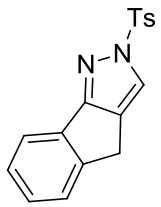
3m (32.3 mg) was obtained through the general procedure B in 63% yield as a white solid.
mp 93–96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.22 (m, 3H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.82 (s, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 2.8 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.71, 146.31, 133.70, 133.61, 133.06, 131.96 (q, *J* = 333 Hz), 130.08, 128.20, 126.23, 123.08 (q, *J* = 272 Hz), 122.32 (q, *J* = 3 Hz), 122.28 (q, *J* = 4 Hz), 106.27, 21.46; **HRMS** (ESI) calcd for $C_{18}H_{12}F_6N_2O_2S$ $[M+H]^+$: 435.0596, found 435.0598.



3n

3-(3,4-dimethoxyphenyl)-1-tosyl-1H-pyrazole (3n)

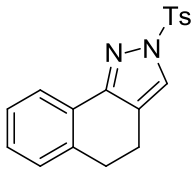
3n (35.5 mg) was obtained through the general procedure B in 69% yield as a white solid. mp 134–137 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 2.8 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.39–7.28 (m, 4H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 2.8 Hz, 1H), 3.93 (s, 3H), 3.89 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.82, 149.96, 149.06, 145.59, 134.24, 132.56, 129.90, 128.00 , 124.36, 119.34, 110.84, 109.19, 106.36, 56.02, 55.86, 21.64; **HRMS** (ESI) calcd for $C_{18}H_{18}N_2O_4S$ $[M+H]^+$: 359.1060, found 359.1066.



3o

2-tosyl-2,4-dihydroindeno[1,2-c]pyrazole (3o)

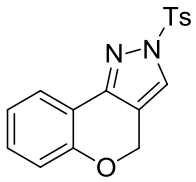
3o (35.1 mg) was obtained through the general procedure B in 68% yield as a white solid. mp 131–135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92–7.89 (m, 3H), 7.84–7.82 (m, 1H), 7.45–7.42 (m, 1H), 7.35–7.30 (m, 2H), 7.28–7.26 (m, 2H), 3.64 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.76, 148.84, 145.33, 134.56, 132.42, 129.83, 128.81, 127.74, 127.29, 126.90, 125.90, 125.25, 121.85, 28.24, 21.56; **HRMS** (ESI) calcd for $C_{17}H_{14}N_2O_2S$ $[M+H]^+$: 311.0849, found 311.0852.



3p

2-tosyl-4,5-dihydro-2H-benzo[g]indazole (3p)

3p (27.8 mg) was obtained through the general procedure B in 54% yield as a white solid. mp 109–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99–7.92 (m, 3H), 7.87–7.86 (m, 1H), 7.32–7.27 (m, 4H), 7.24–7.21 (m, 1H), 2.92–2.89 (m, 2H), 2.78 (t, *J* = 7.2 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.16, 145.31, 137.54, 134.49, 129.82, 129.12, 128.35, 127.84, 127.83, 127.27, 126.86, 123.72, 120.22, 28.79, 21.59, 18.98; **HRMS** (ESI) calcd for $C_{18}H_{16}N_2O_2S$ $[M+H]^+$: 325.1005, found 325.1006.

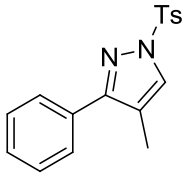


3q

2-tosyl-2,4-dihydrochromeno[4,3-c]pyrazole (3q)[16]

3q (34.0 mg) was obtained through the general procedure B in 66% yield as a white solid.

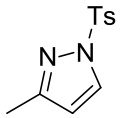
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.90 (m, 2H), 7.86–7.82 (m, 2H), 7.32–7.30 (m, 2H), 7.27–7.23 (m, 1H), 7.02–6.98 (m, 1H), 6.94–6.92 (m, 1H), 5.20 (d, *J* = 1.2 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.91, 149.38, 145.76, 134.13, 131.10, 129.98, 128.02, 125.65, 123.79, 122.08, 117.43,116.52, 115.63, 62.60, 21.68; **HRMS** (ESI) calcd for $C_{17}H_{14}N_2O_3S$ $[M+H]^+$: 327.0798, found 327.0799.



3r

4-methyl-3-phenyl-1-tosyl-1H-pyrazole (3r)

3r (16.5 mg) was obtained through the general procedure B in 32% yield as a white solid. mp 113–115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93–7.91 (m, 3H), 7.66–7.63 (m, 2H), 7.42–7.36 (m, 3H), 7.32–7.29 (m, 2H), 2.40 (s, 3H), 2.20 (d, *J* = 0.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.27, 145.41, 134.27, 131.92; 130.64, 129.81, 128.56, 128.31, 127.87, 127.82, 118.03, 21.56, 10.06; **HRMS** (ESI) calcd for $C_{17}H_{16}N_2O_2S$ $[M+H]^+$: 313.1005, found 313.1010.

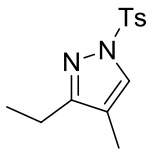


3s

3-methyl-1-tosyl-1H-pyrazole (3s)[12]

3s (14.6 mg) was obtained through the general procedure B in 28% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.96 (m, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.30–7.28 (m, 2H), 6.17 (d, *J* = 2.8 Hz, 1H), 2.39 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.27, 145.45, 134.28, 131.92, 129.86, 127.85, 109.51, 21.60, 13.88.

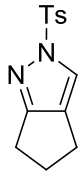


3t

3-ethyl-4-methyl-1-tosyl-1H-pyrazole (3t)[17]

3t (18.2 mg) was obtained through the general procedure in 35% yield as a white solid.

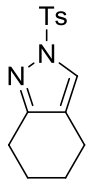
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.80 (m, 2H), 7.71 (s, 1H), 7.28–7.25 (m, 2H), 2.53 (q, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.96 (s, 3H), 1.14 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.26, 145.04, 134.61, 129.69, 129.64; 127.63, 118.44, 21.54, 20.09, 12.42, 8.25.



3u

2-tosyl-2,4,5,6-tetrahydrocyclopenta[c]pyrazole (3u)

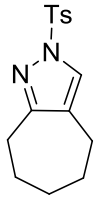
3u (41.6 mg) was obtained through the general procedure B in 80% yield as a white solid. mp 120–124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.64 (s, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 2.67–2.58 (m, 4H), 2.40 (s, 3H), 2.37–2.30 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.19, 145.16, 134.69, 129.83; 128.88, 127.79, 124.27, 29.52, 24.41, 22.48, 21.62; **HRMS** (ESI) calcd for $C_{13}H_{14}N_2O_2S$ $[M+H]^+$: 263.0849, found 263.0852.



3v

2-tosyl-4,5,6,7-tetrahydro-2H-indazole (3v)

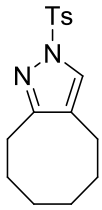
3v (29.1 mg) was obtained through the general procedure B in 56% yield as a white solid. mp 131–135 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.55 (t, *J* = 6.4 Hz, 2H), 2.43 (t, *J* = 6.4 Hz, 2H), 2.29 (s, 3H), 1.67–1.54 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.11, 145.00, 134.23, 129.56, 127.43, 127.25, 119.85, 23.31, 22.38, 21.30, 20.04; **HRMS** (ESI) calcd for $C_{14}H_{16}N_2O_2S$ $[M+H]^+$: 277.1005, found 277.1006.



3w

2-tosyl-2,4,5,6,7,8-hexahydrocyclohepta[c]pyrazole (3w)

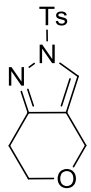
3w (41.4 mg) was obtained through the general procedure B in 80% yield as a white solid. mp 105–108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.69 (s, 1H), 7.30–7.28 (m, 2H), 2.72–2.69 (m, 2H), 2.50–2.47 (m, 2H), 2.40 (s, 3H), 1.79–1.73 (m, 2H), 1.62–1.55 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.20, 145.10, 134.68, 129.79, 128.49, 127.75, 125.52, 32.00, 29.70, 28.83, 27.12, 25.09, 21.61; **HRMS** (ESI) calcd for $C_{15}H_{18}N_2O_2S$ $[M+H]^+$: 291.1162, found 291.1163.



3x

2-tosyl-4,5,6,7,8,9-hexahydro-2H-cycloocta[c]pyrazole (3x)

3x (37.2 mg) was obtained through the general procedure B in 72% yield as a white solid. mp 93–95 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.68 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 2.66–2.63 (m, 2H), 2.47 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H), 1.61–1.53 (m, 4H), 1.33–1.32 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.71, 145.00, 134.52, 129.66, 128.71, 127.47, 124.09, 30.50, 29.23, 25.42; 25.26, 25.04, 21.81, 21.48; **HRMS** (ESI) calcd for $C_{16}H_{20}N_2O_2S$ $[M+H]^+$: 305.1318, found 305.1320.

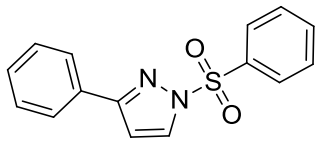


3y

2-tosyl-2,4,6,7-tetrahydropyrano[4,3-c]pyrazole(3y)

3y (29.1 mg) was obtained through the general procedure B in 56% yield as a white solid.

mp 106–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.78 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 2H), 3.88 (t, *J* = 5.6 Hz, 2H), 2.78 (t, *J* = 5.6 Hz, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.68, 145.61, 134.26, 129.96, 127.95, 125.22, 117.90, 64.88, 62.68, 24.39, 21.67; **HRMS** (ESI) calcd for $C_{13}H_{14}N_2O_3S$ $[M+H]^+$: 279.0798, found 279.0801.

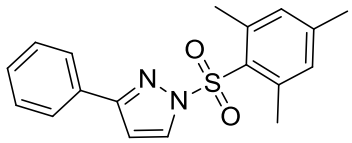


3z

3-phenyl-1-(phenylsulfonyl)-1H-pyrazole (3z)[18]

3z (43.5 mg) was obtained through the general procedure B in 84% yield as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.8 Hz, 1H), 8.08–8.05 (m, 2H), 7.83–7.80 (m, 2H), 7.64–7.59 (m, 1H), 7.54–7.50 (m, 2H), 7.42–7.36 (m, 3H), 6.72 (d, *J* = 2.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.00, 137.11, 134.38, 132.59, 131.26, 129.26, 129.18, 128.59, 127.95, 126.33, 106.62.

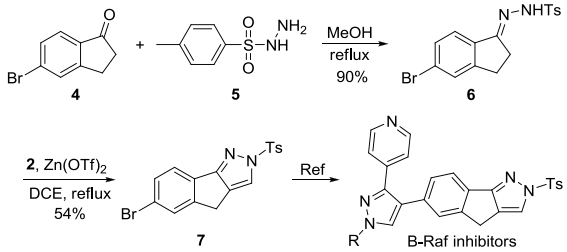


3aa

1-(mesitylsulfonyl)-3-phenyl-1H-pyrazole (3aa)

3aa (39.2 mg) was obtained through the general procedure B in 76% yield as a white solid. mp 140–142°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 2.8 Hz, 1H), 7.81–7.78 (m, 2H), 7.40–7.32 (m, 3H), 6.97 (s, 2H), 6.70 (d, *J* = 2.8 Hz, 1H), 2.76 (s, 6H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.74, 144.53, 141.18, 132.22, 131.77, 131.76, 131.54, 131.15, 128.89, 128.51, 126.10, 23.06, 23.04, 20.97; **HRMS** (ESI) calcd for $C_{18}H_{18}N_2O_2S$ $[M+H]^+$: 327.1162, found 3327.1163.

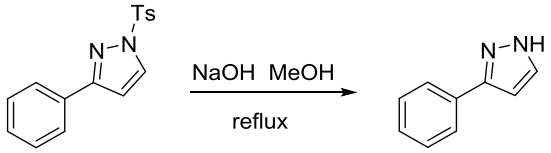
4 General procedures for the synthetic transformation of products.



To a stirred solution of p-Toluenesulfonylhydrazide **5** (44 mg, 0.24 mmol) in methanol (2.0 mL) was added 5-Bromo-1-indanone **4** (31 µl, 0.24 mmol) and allowed to stir the reaction mixture at 60°C. The completion of the reaction was monitored by TLC chromatography. After the completion of reaction, the reaction mixture was cooled and concentrated under reduced pressure to get the crude compound. The obtained crude was then purified using column chromatography to afford pure **6** (81 mg) in 90% yield as a white solid. mp 222–225°C; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.46 (s, 1H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.44–7.37 (m, 4H), 3.01–2.98 (m, 2H), 2.75–2.72 (m,

2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6) δ 160.87, 150.95, 143.35, 136.50, 136.19, 130.11, 129.51, 128.80, 127.57, 123.98, 122.69, 27.83, 27.40, 21.05; **HRMS** (ESI) calcd for $C_{16}H_{15}BrN_2O_2S$ $[M+H]^+$: 379.0113, found 379.0113.

To a stirred solution of (E)-N'-(5-bromo-2,3-dihydro-1H-inden-1-ylidene)-4-methylbenzenesulfonohydrazide **6** (0.13 mmol, 50 mg) in DCE (2.0 mL) was added 2-(dimethylamino)malononitrile **2a** (0.20 mmol, 21.6 mg), $Zn(OTf)_2$ (0.5 equiv, 24 mg); The reaction mixture was was heated to reflux for 36 h. The completion of reaction was monitored by TLC chromatography. After completion, the reaction mixture was cooled to room temperature and filtration. The filter liquor concentrated under reduced pressure to get the crude compound. The obtained crude was then purified using column chromatography to afford pure pyrazoles derivatives **7**[19] (27.7 mg) in 54% yield as a brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 5.2 Hz, 2H), 7.89 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 3.61 (s, 2H), 2.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.40, 150.58, 145.50, 134.24, 131.36, 130.40, 129.84, 129.05, 127.73, 126.42, 125.30, 122.77, 122.73, 28.14, 21.53.



3a 8

To a 25 ml sealed tube was charged with **3a** (100 mg, 0.50 mmol), sodium hydroxide (40 mg, 1.01 mmol) and MeOH (2.0 mL). The resulting solution was heated to reflux and stirred overnight. The solvent was removed under reduced pressure.Then the residue was purified by flash column chromatography on silica gel to afford the title compound **8**[20] (54 mg, 75% yield) as a white oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.44–7.34 (m, 3H), 6.63 (d, *J* = 2.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.06, 133.22, 132.15, 128.69, 127.92, 125.88, 102.54.

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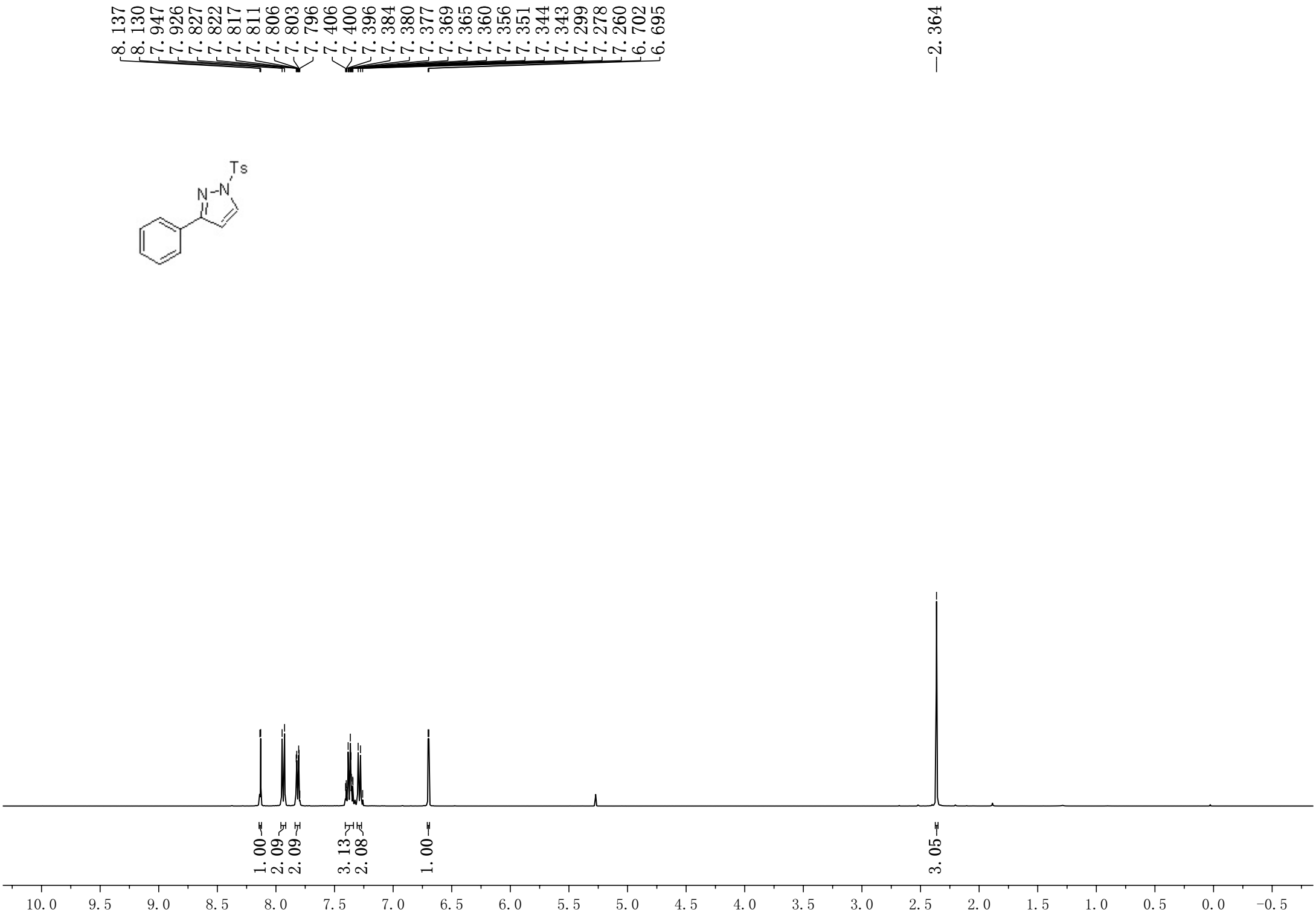
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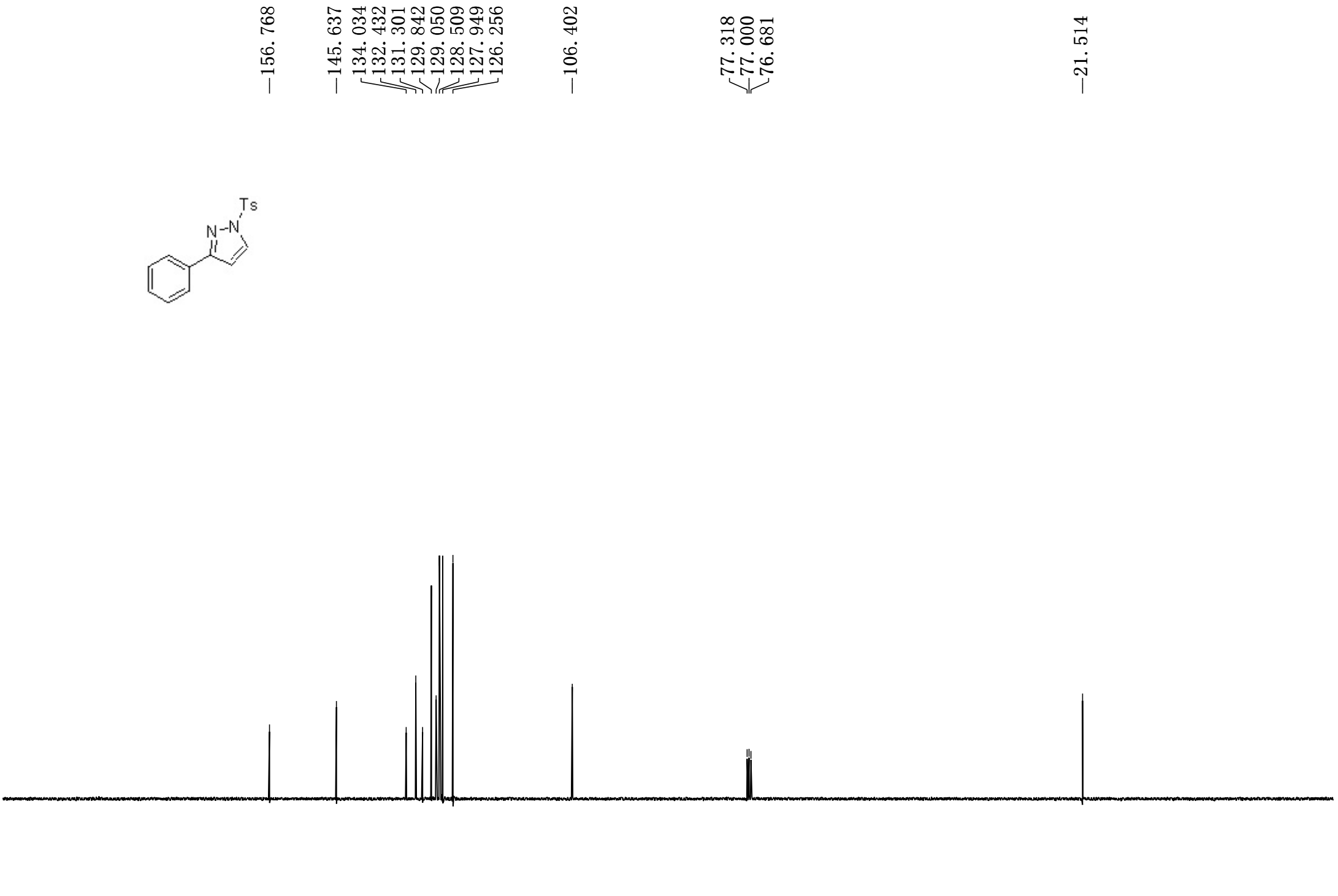
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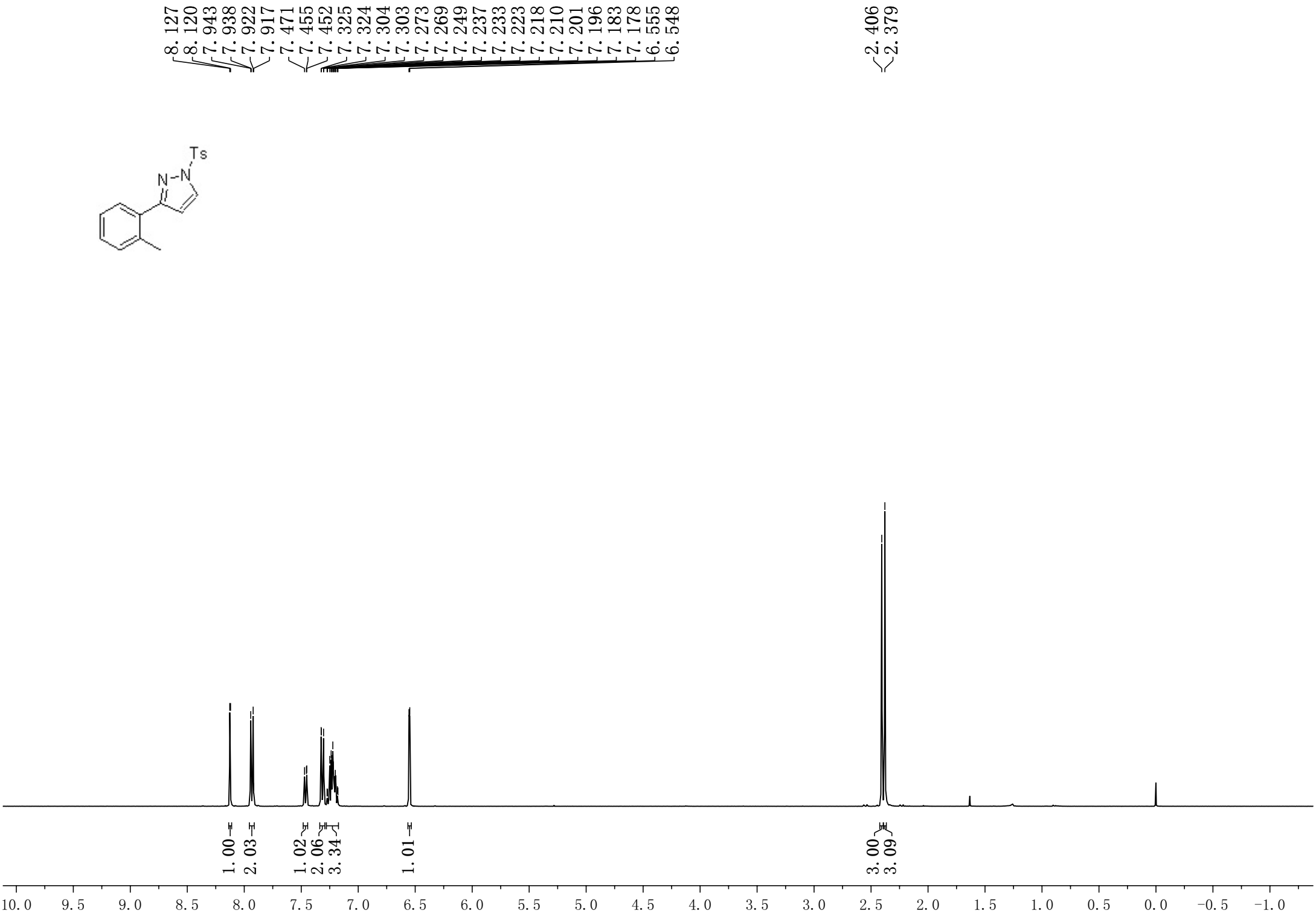
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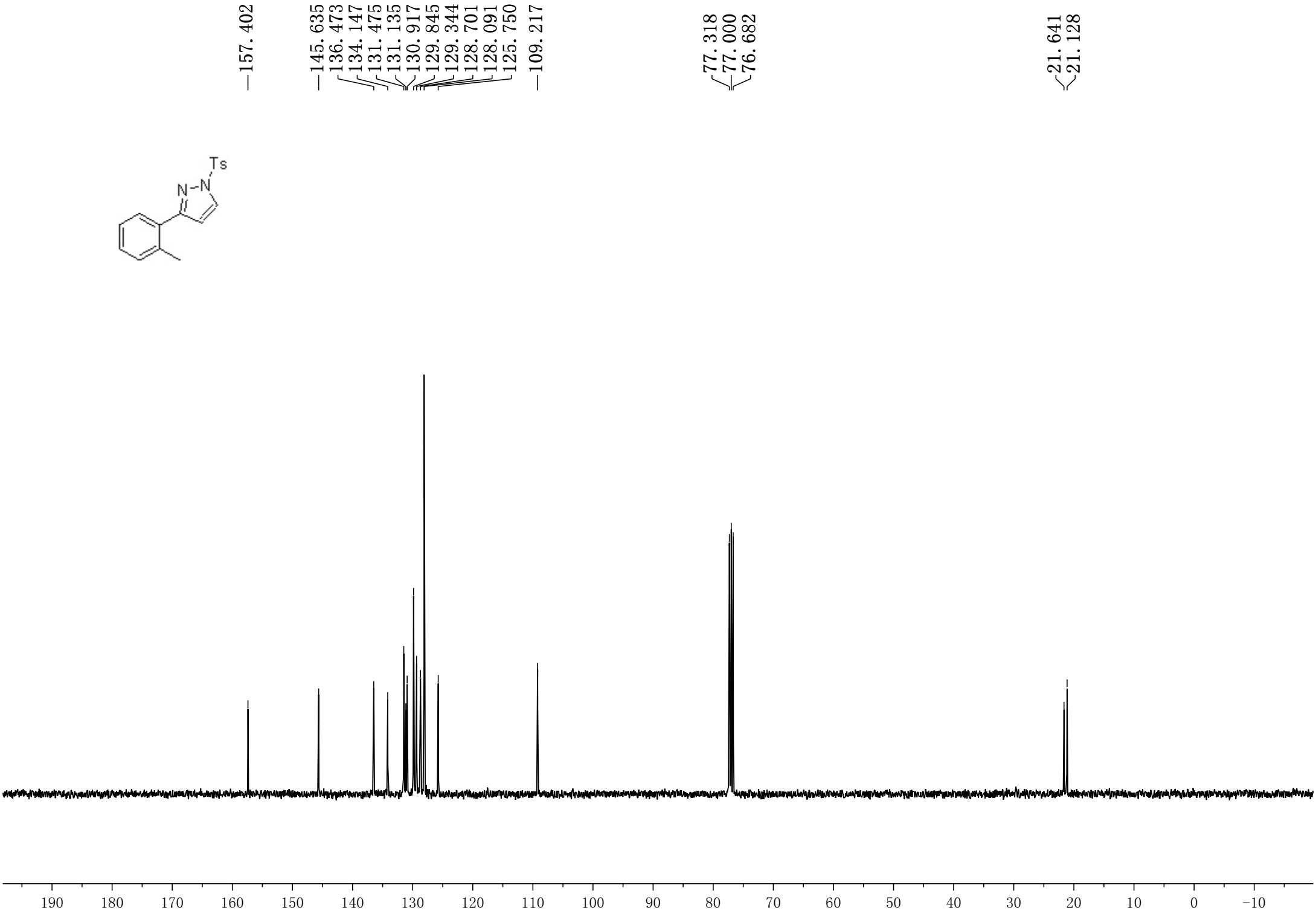
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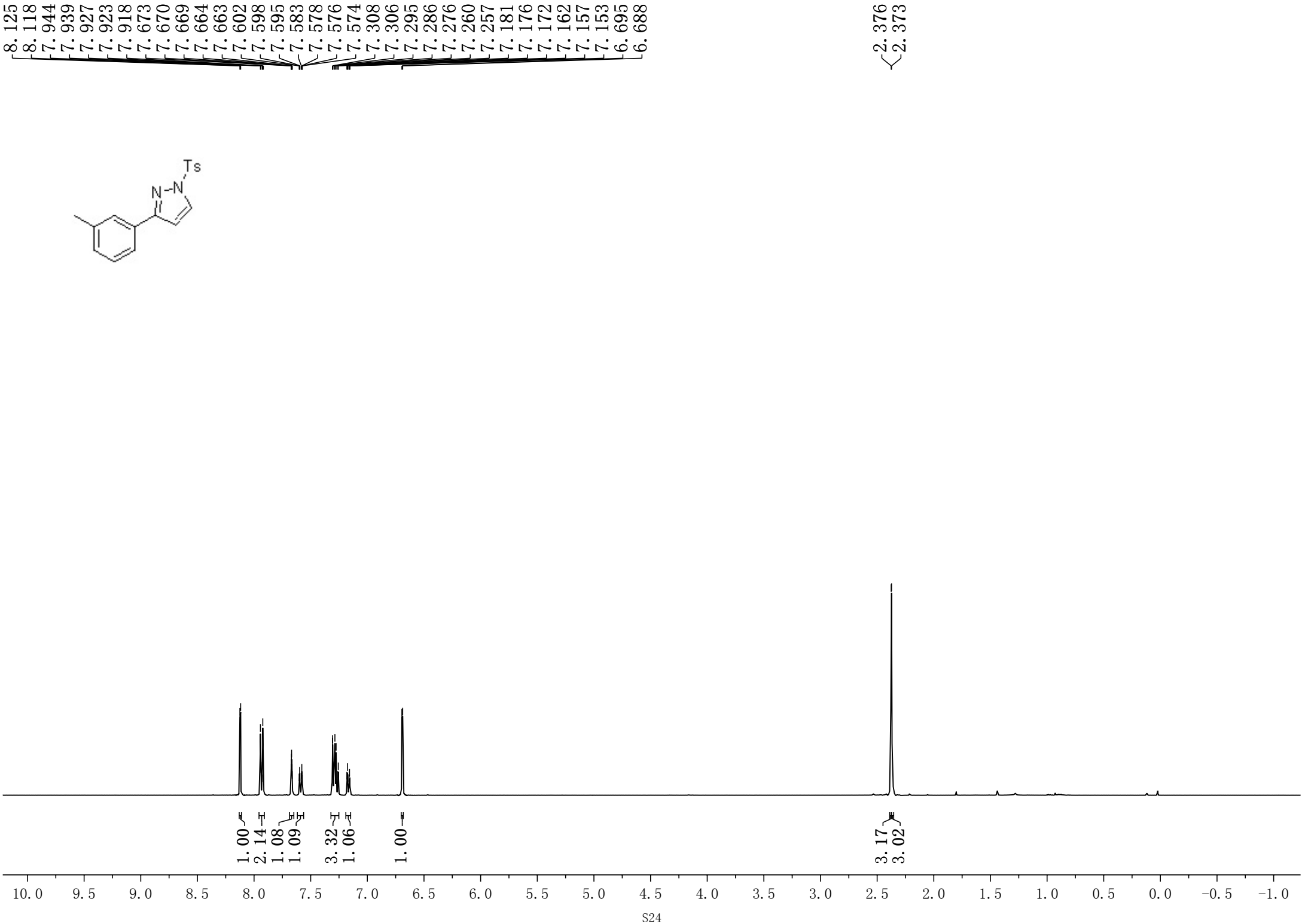
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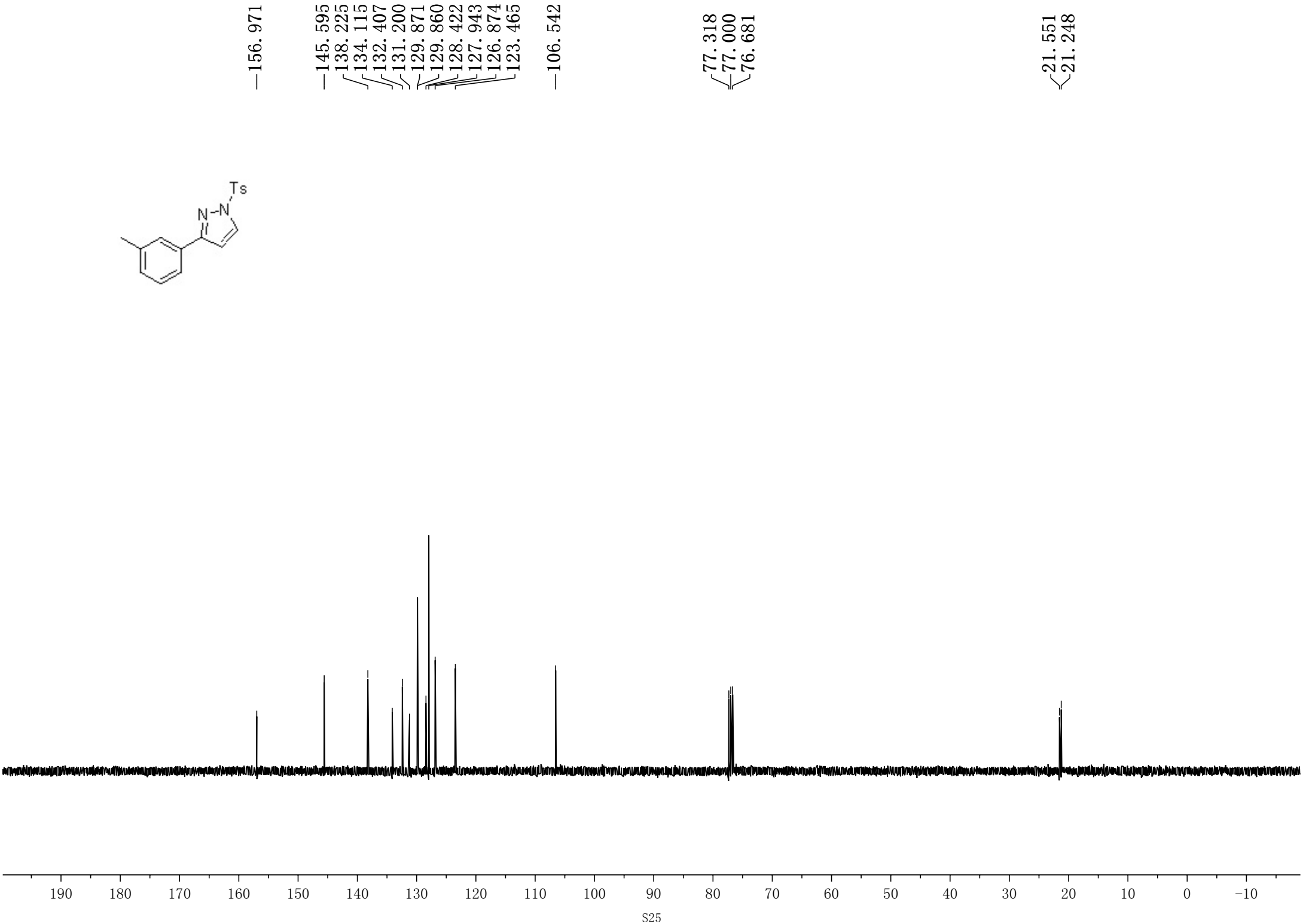
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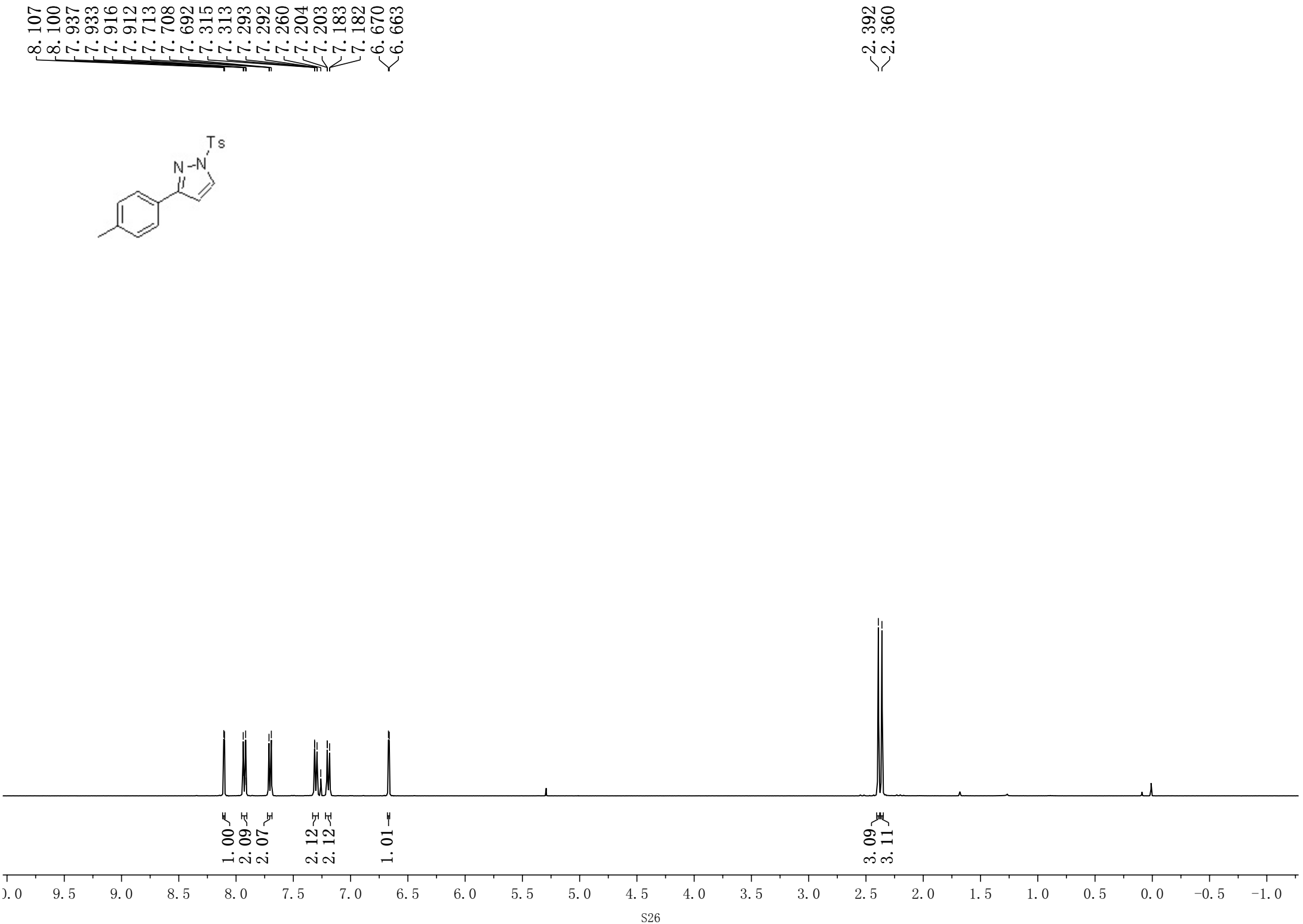
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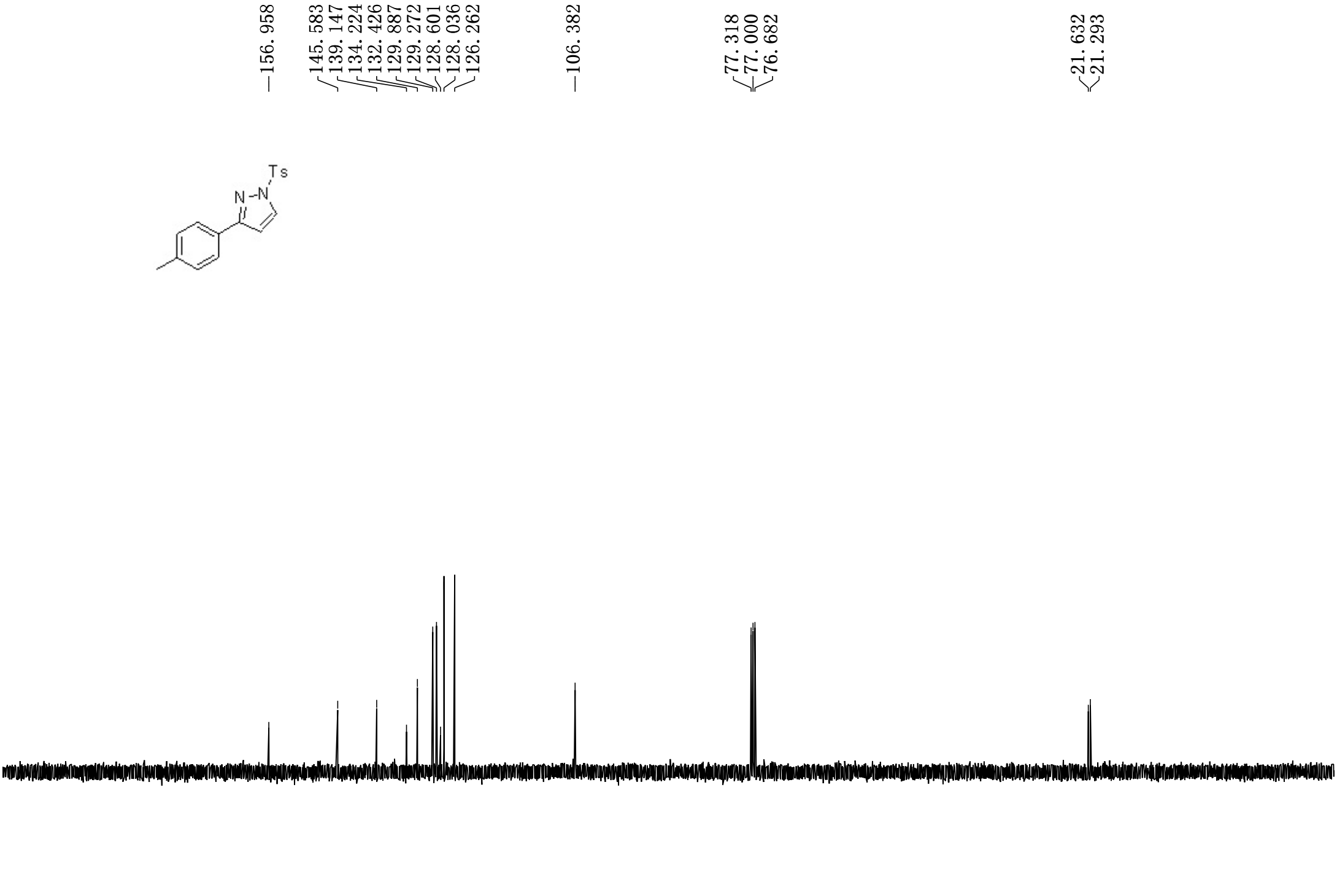
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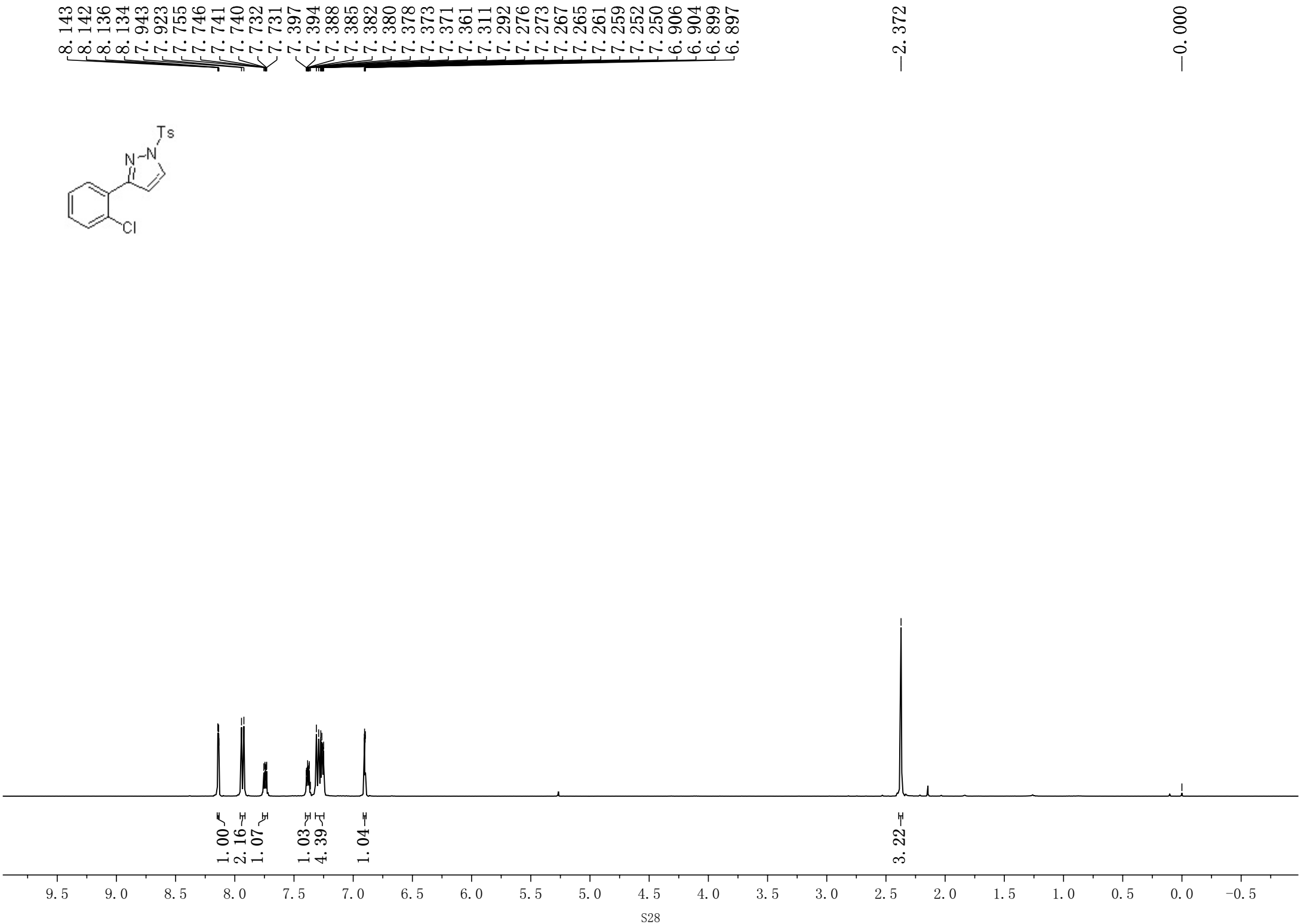
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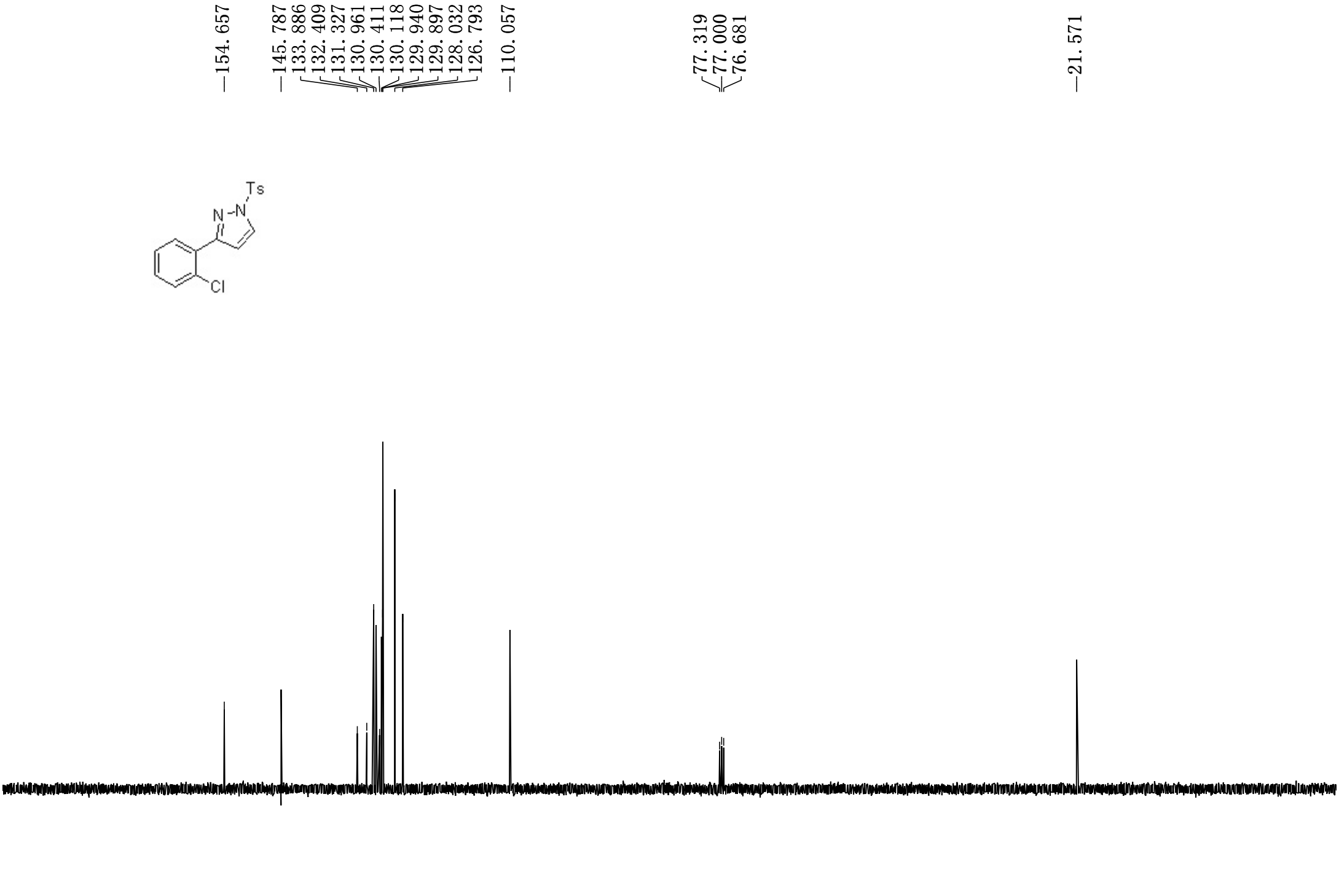
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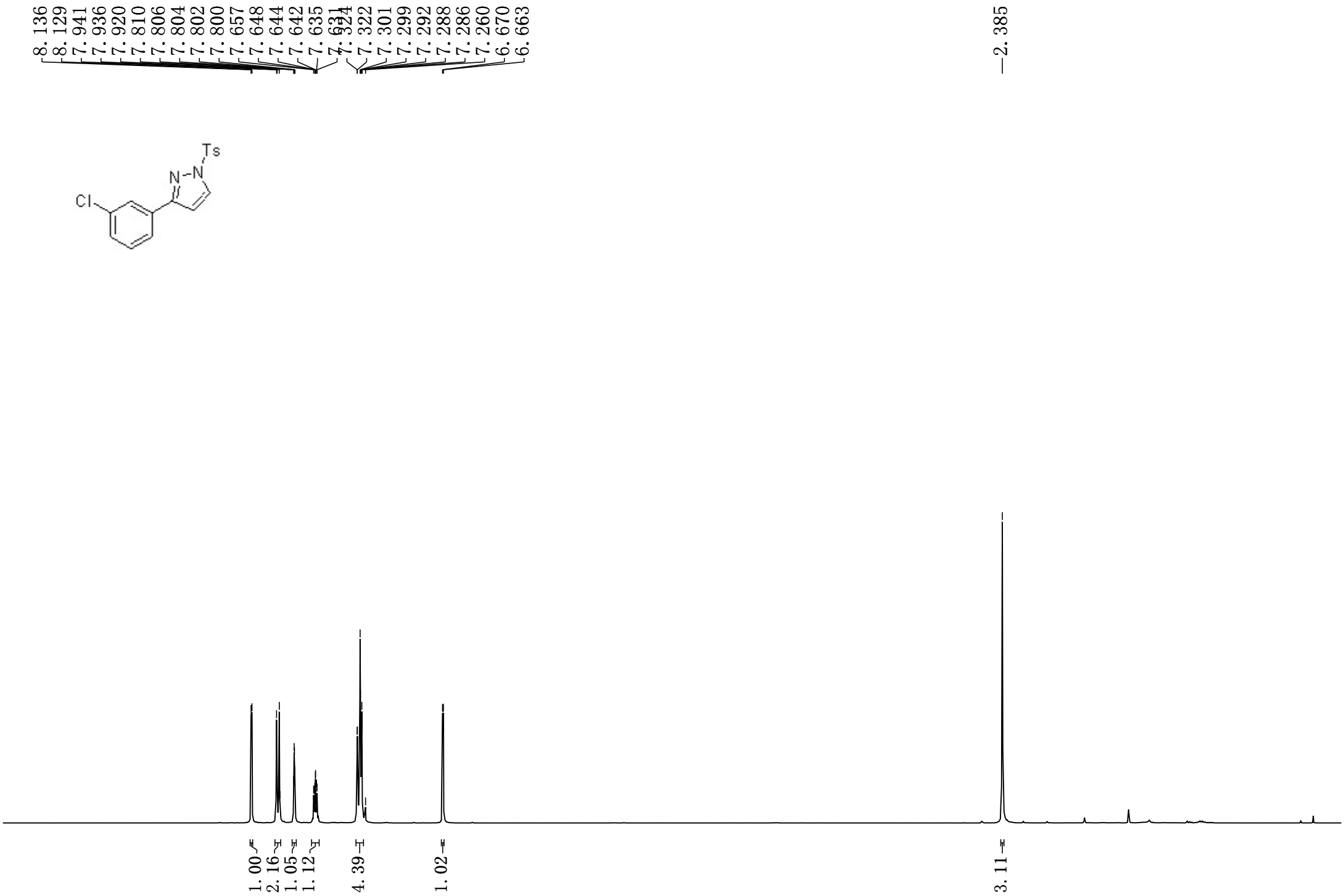
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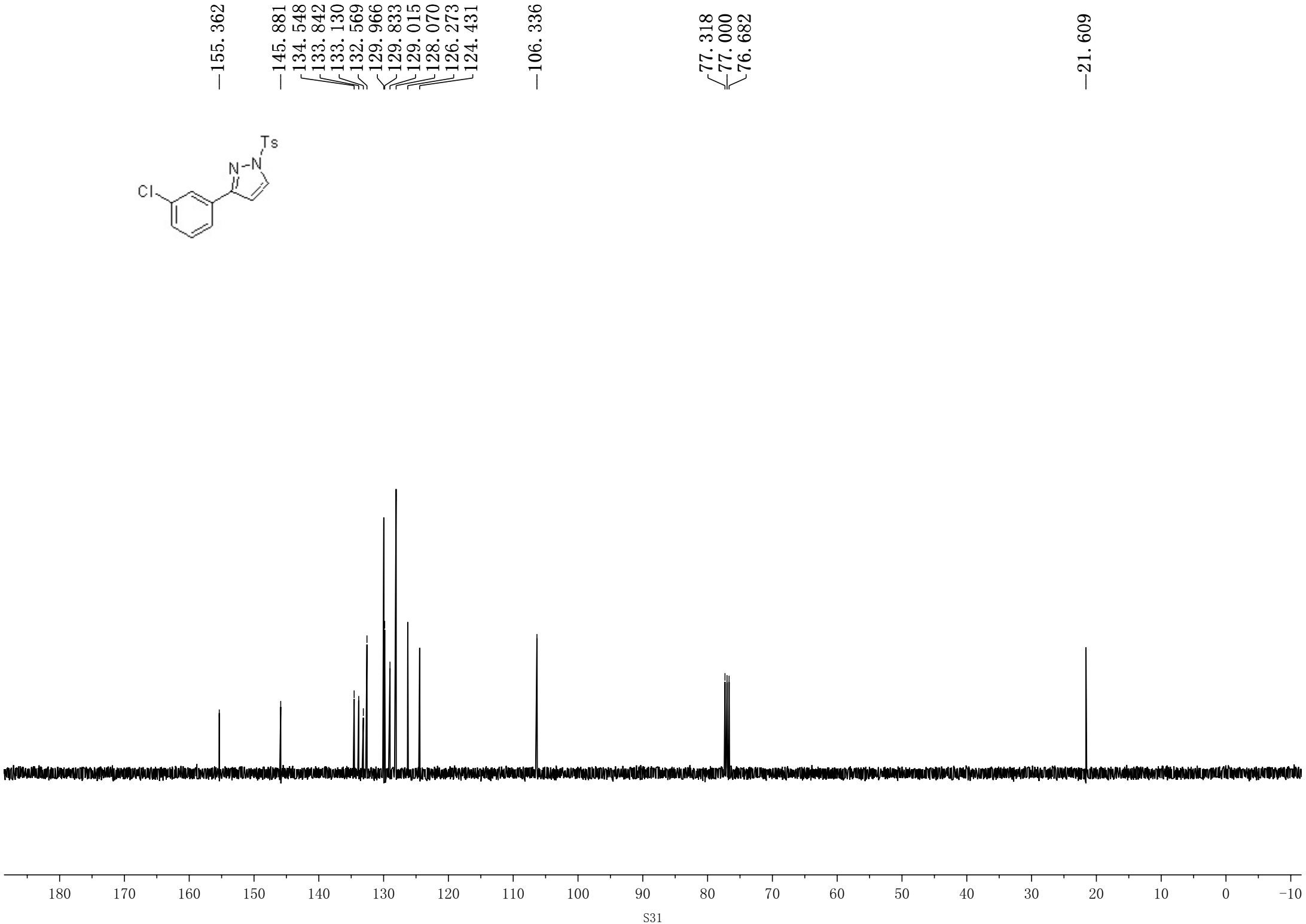
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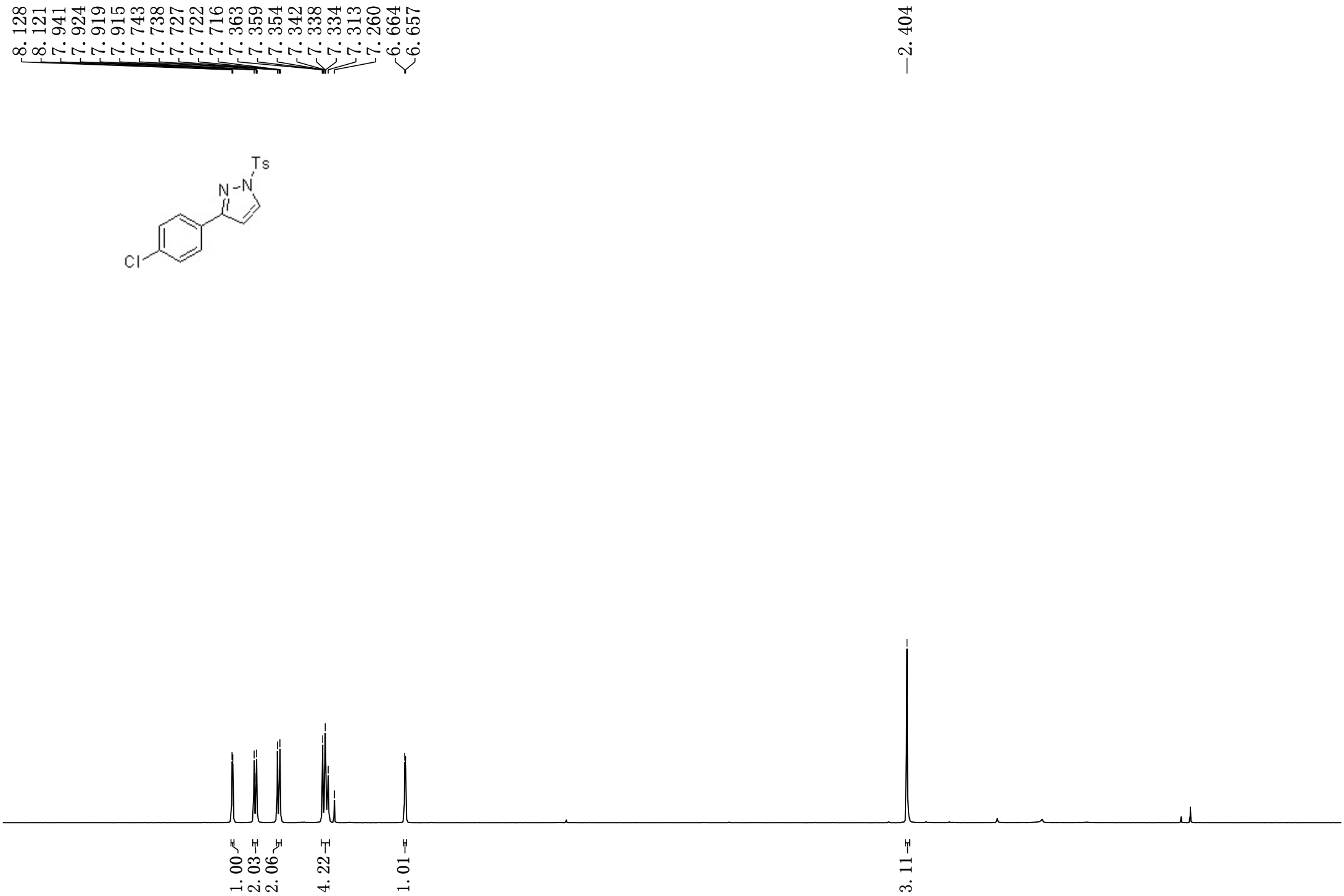
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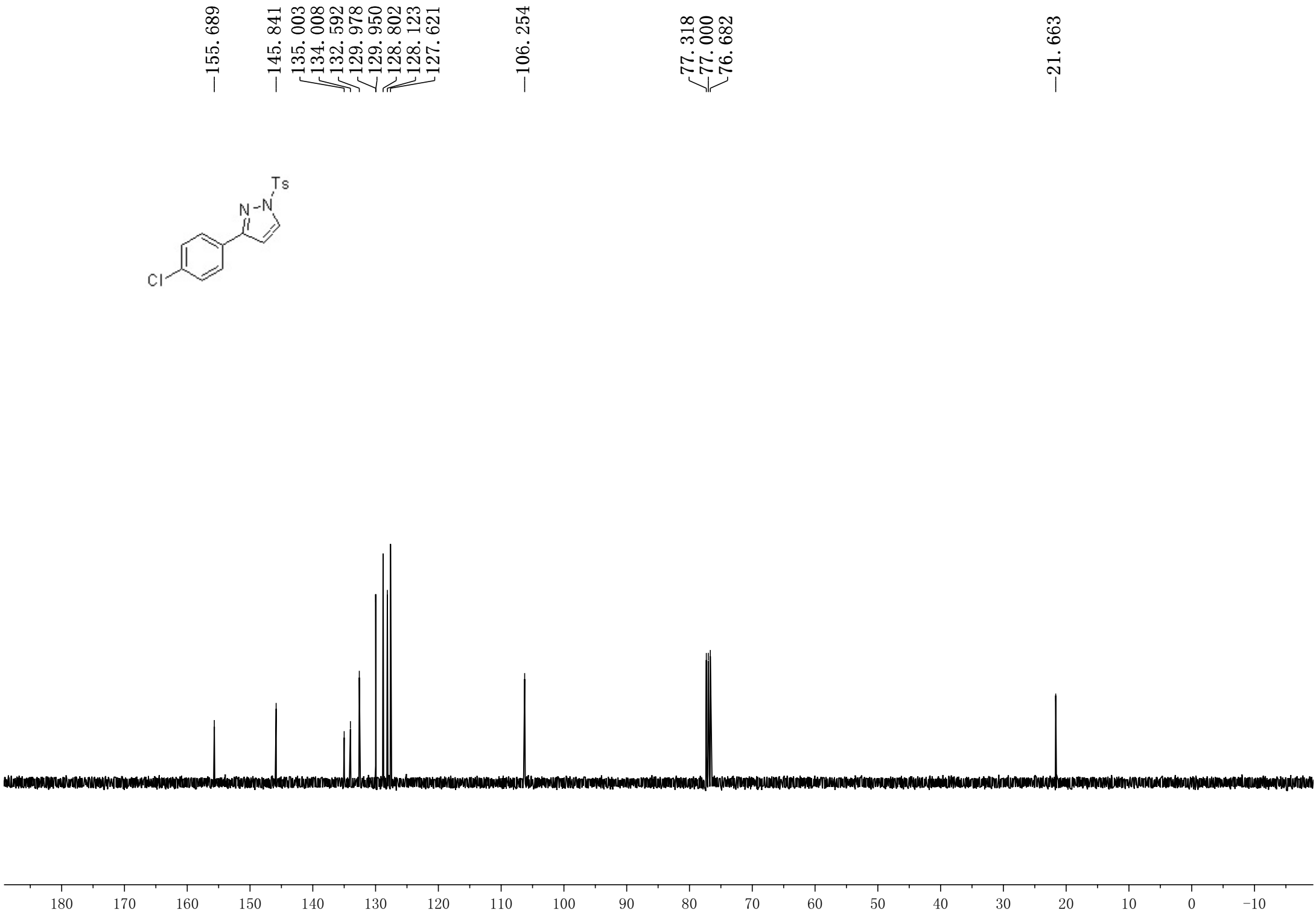
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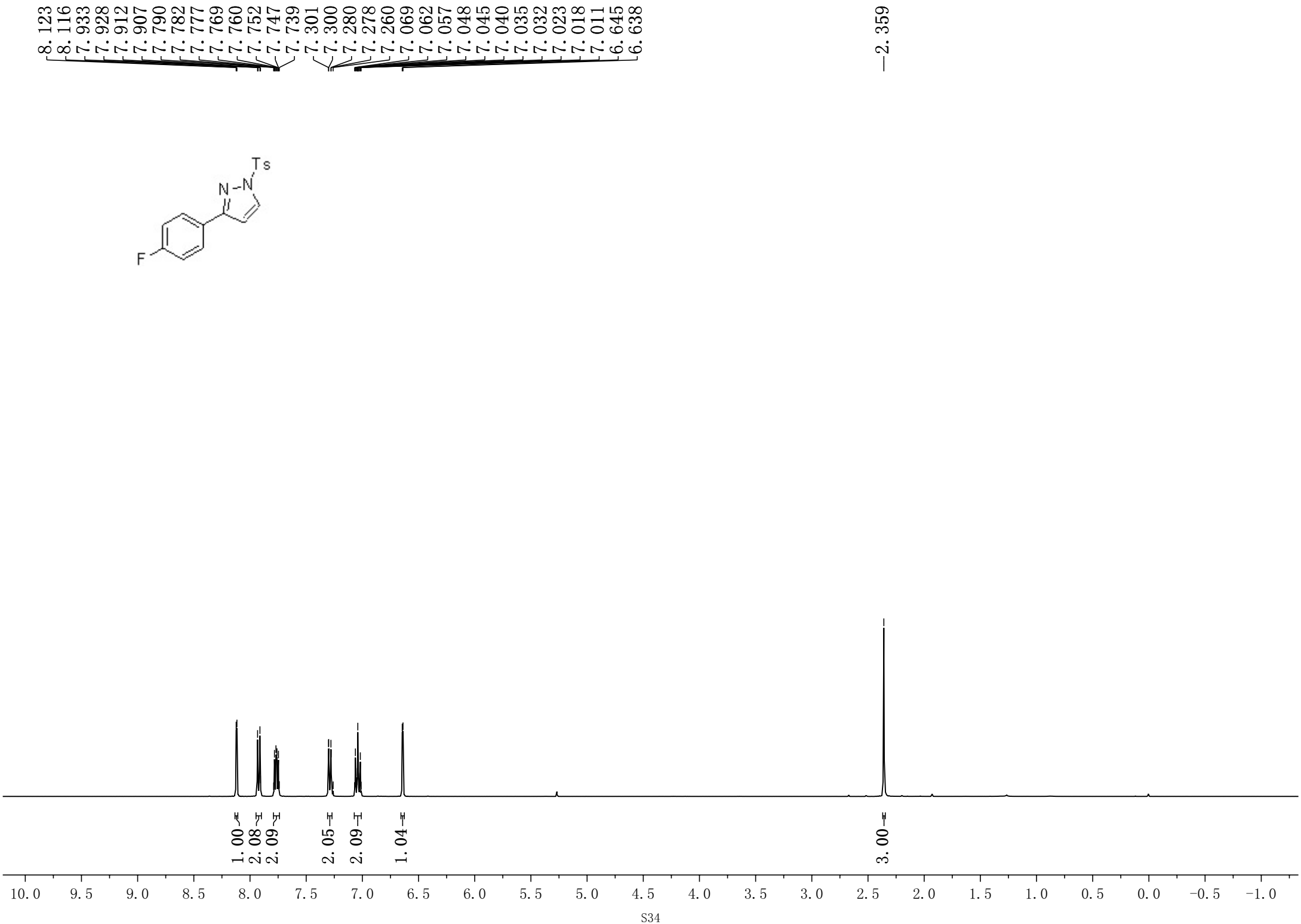
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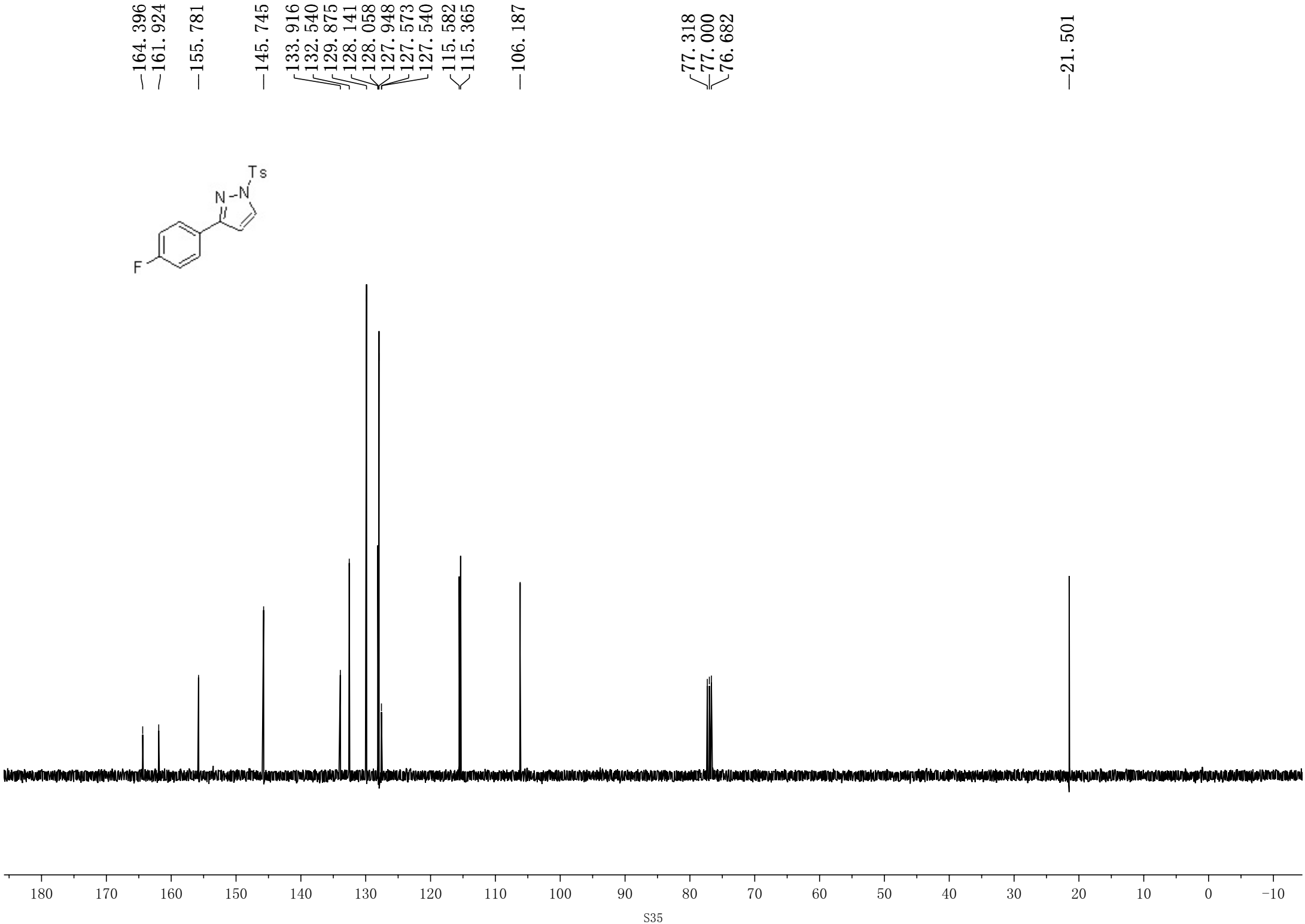
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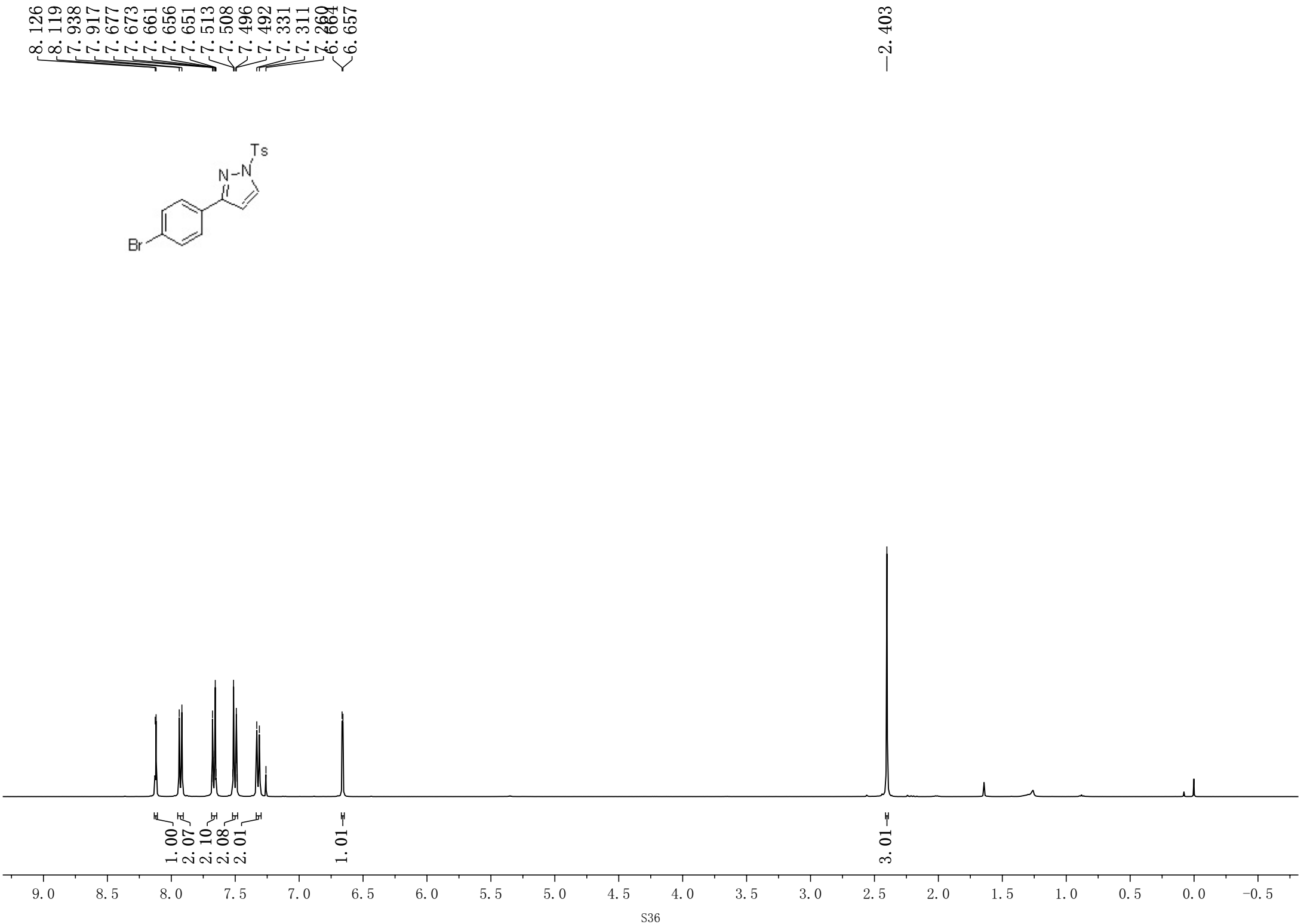
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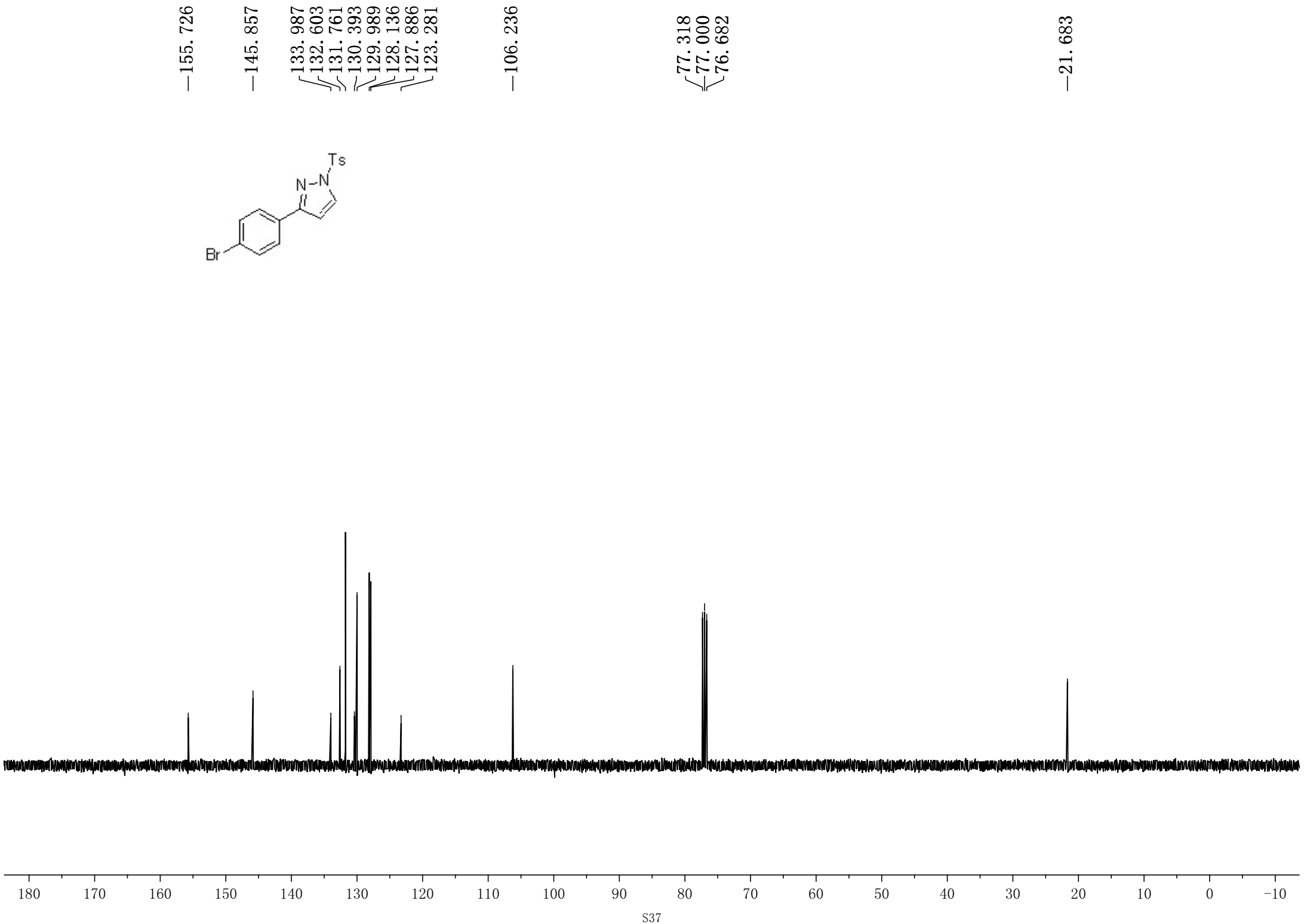
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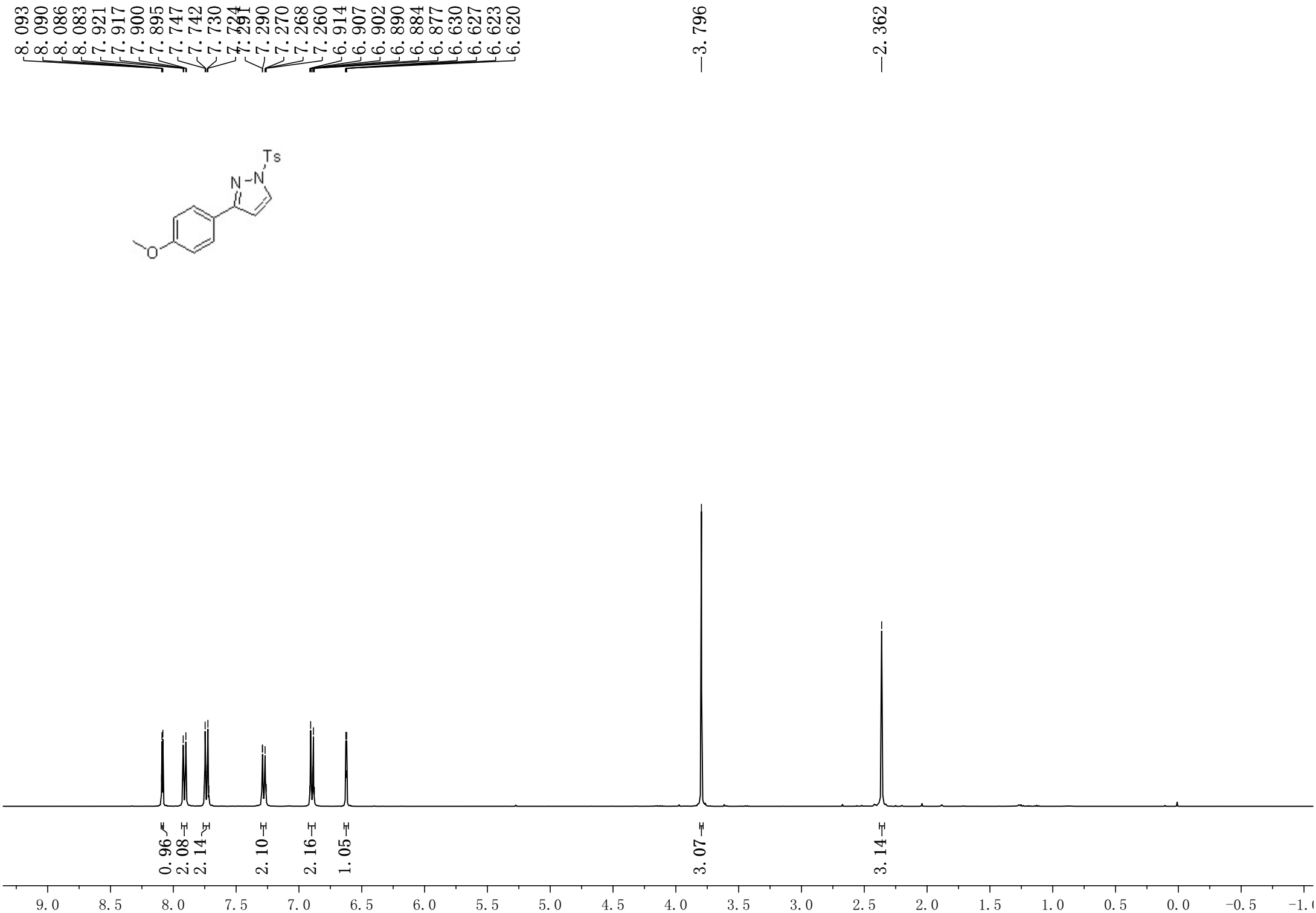
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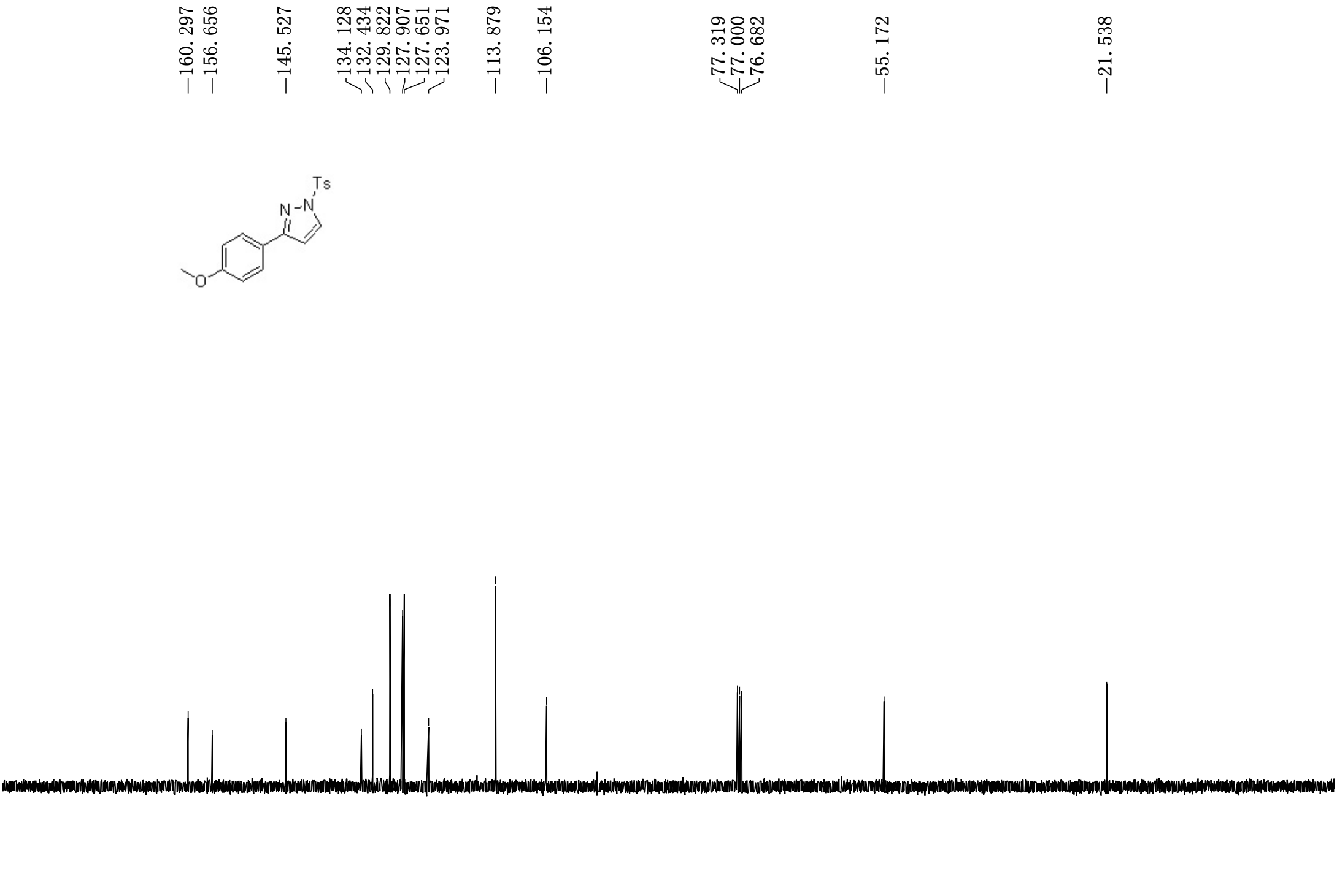
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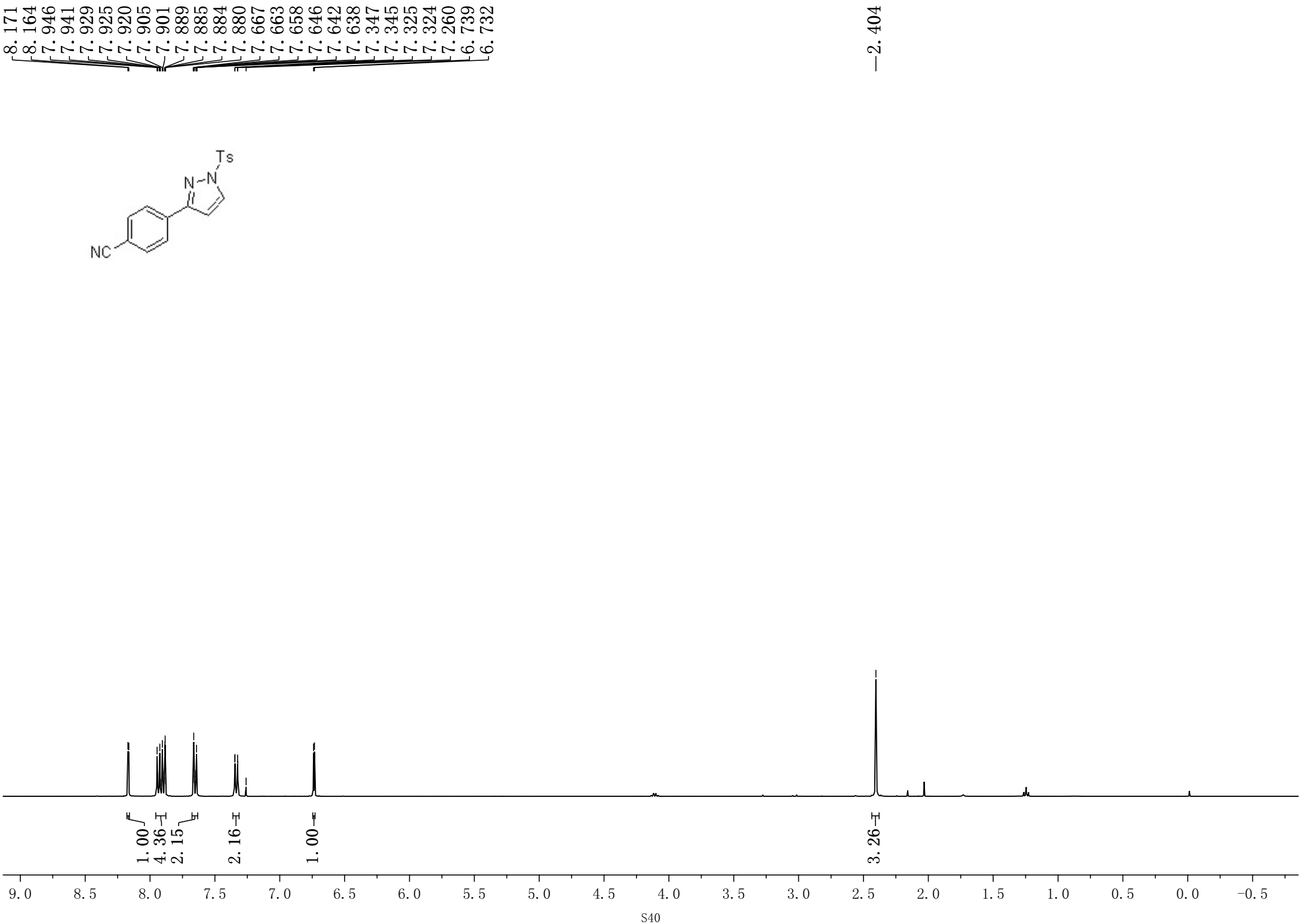
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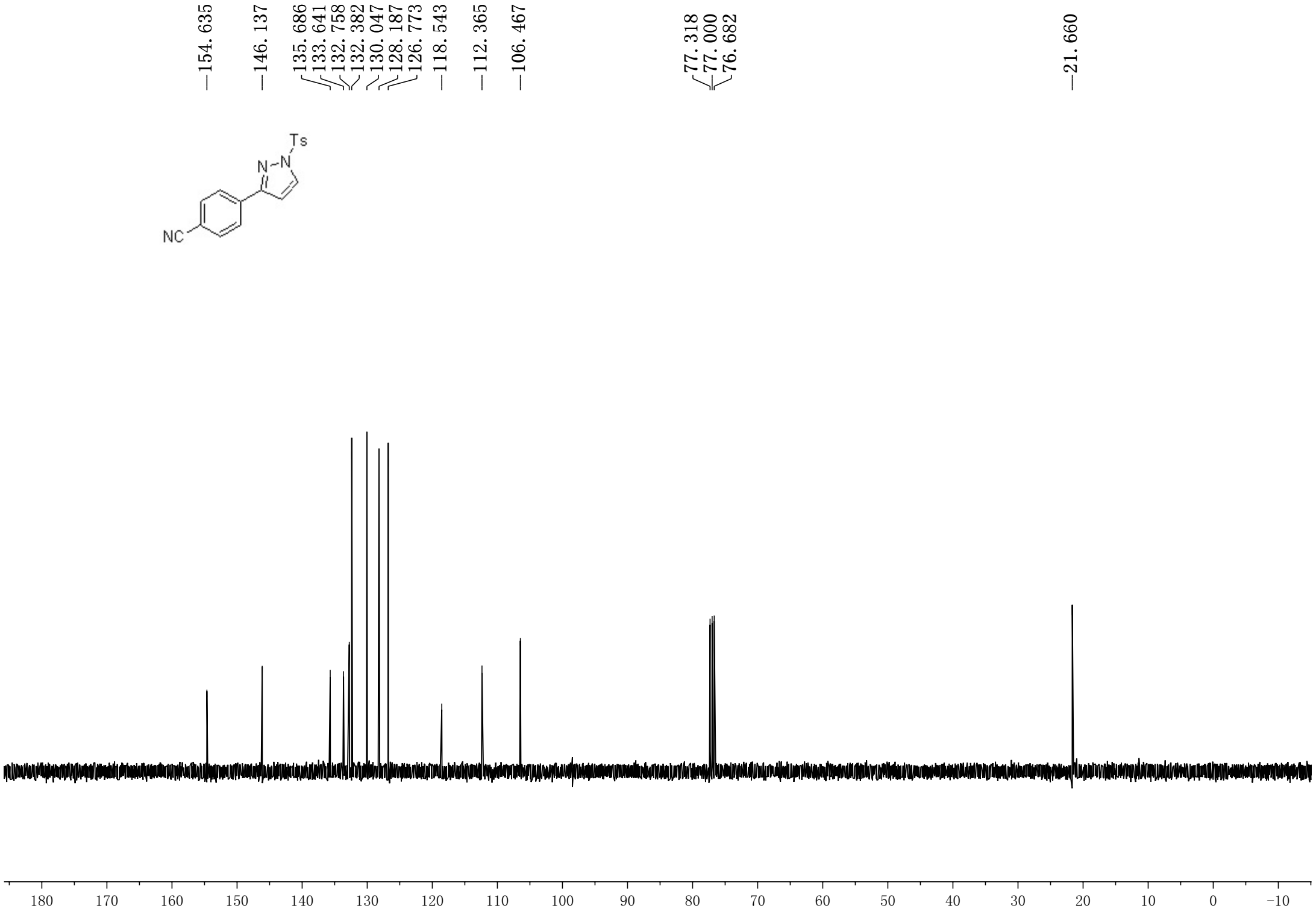
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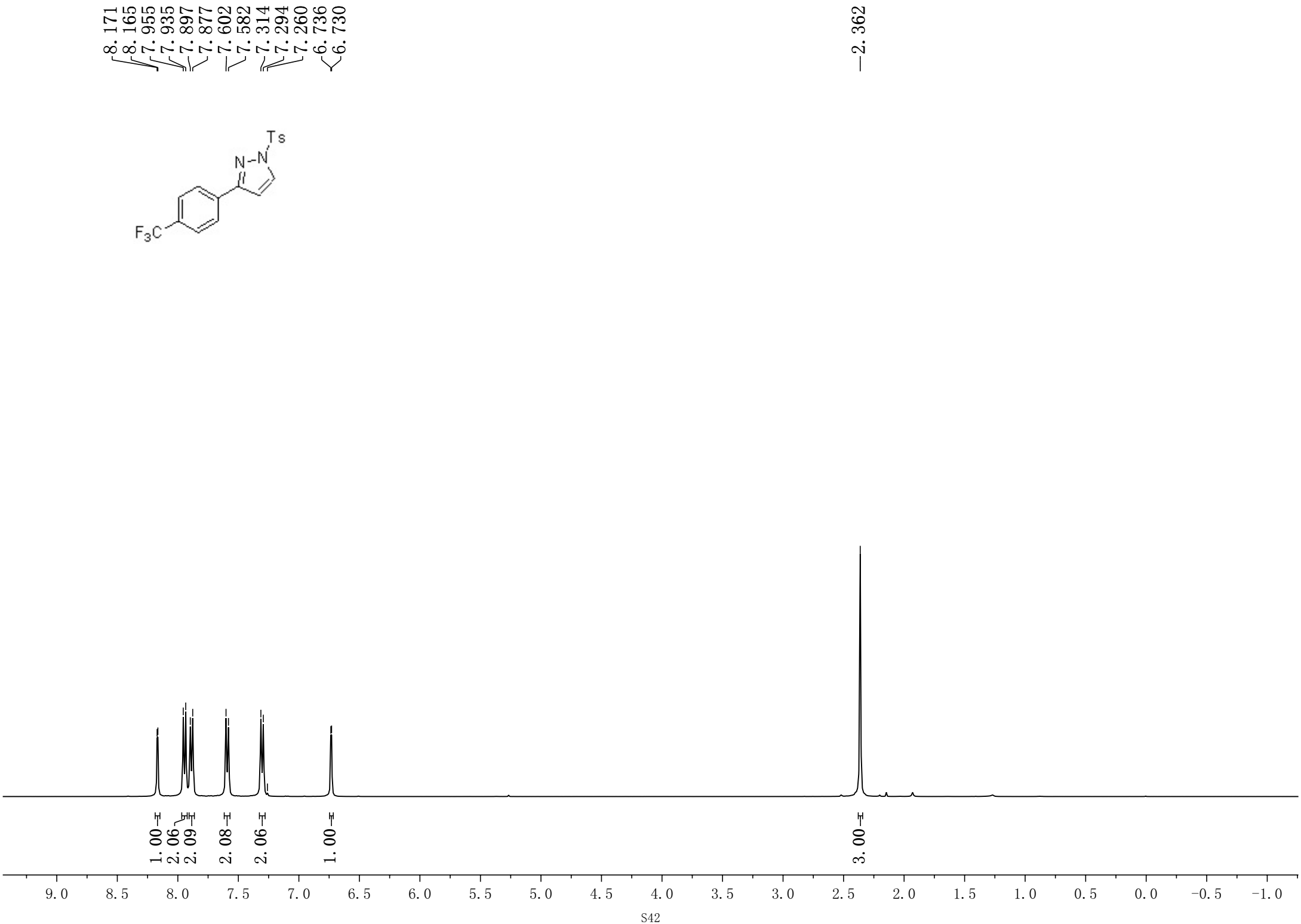
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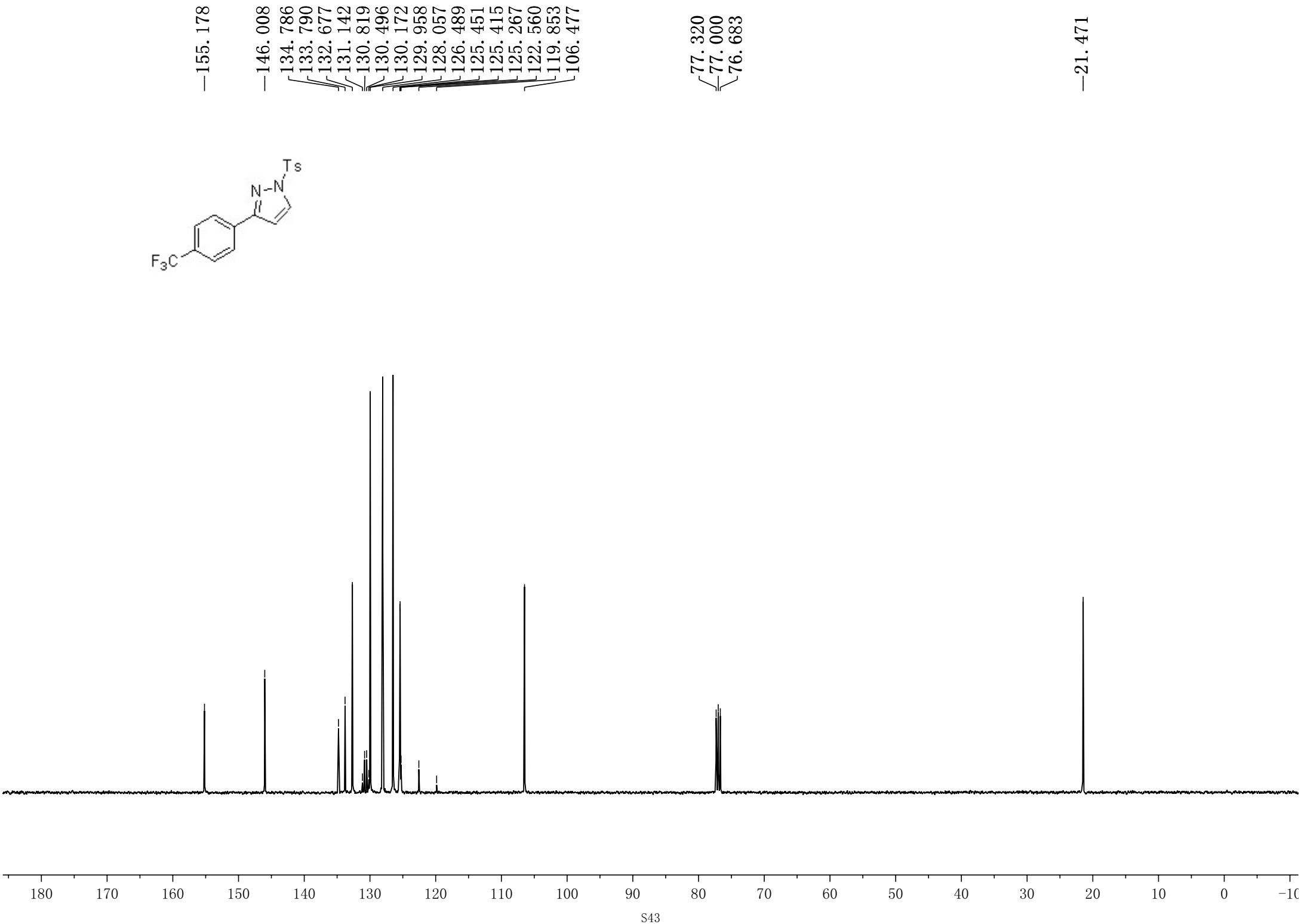
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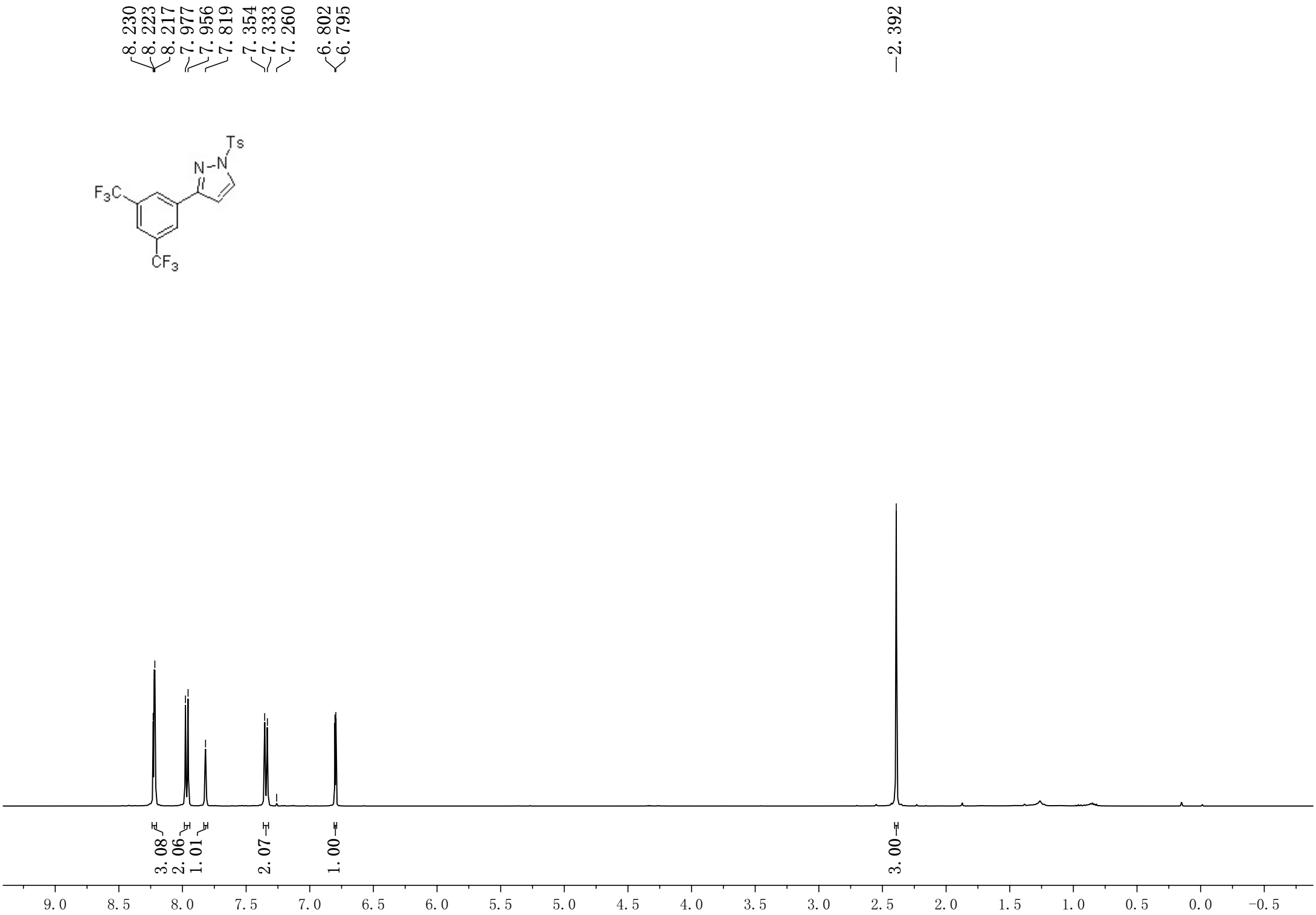
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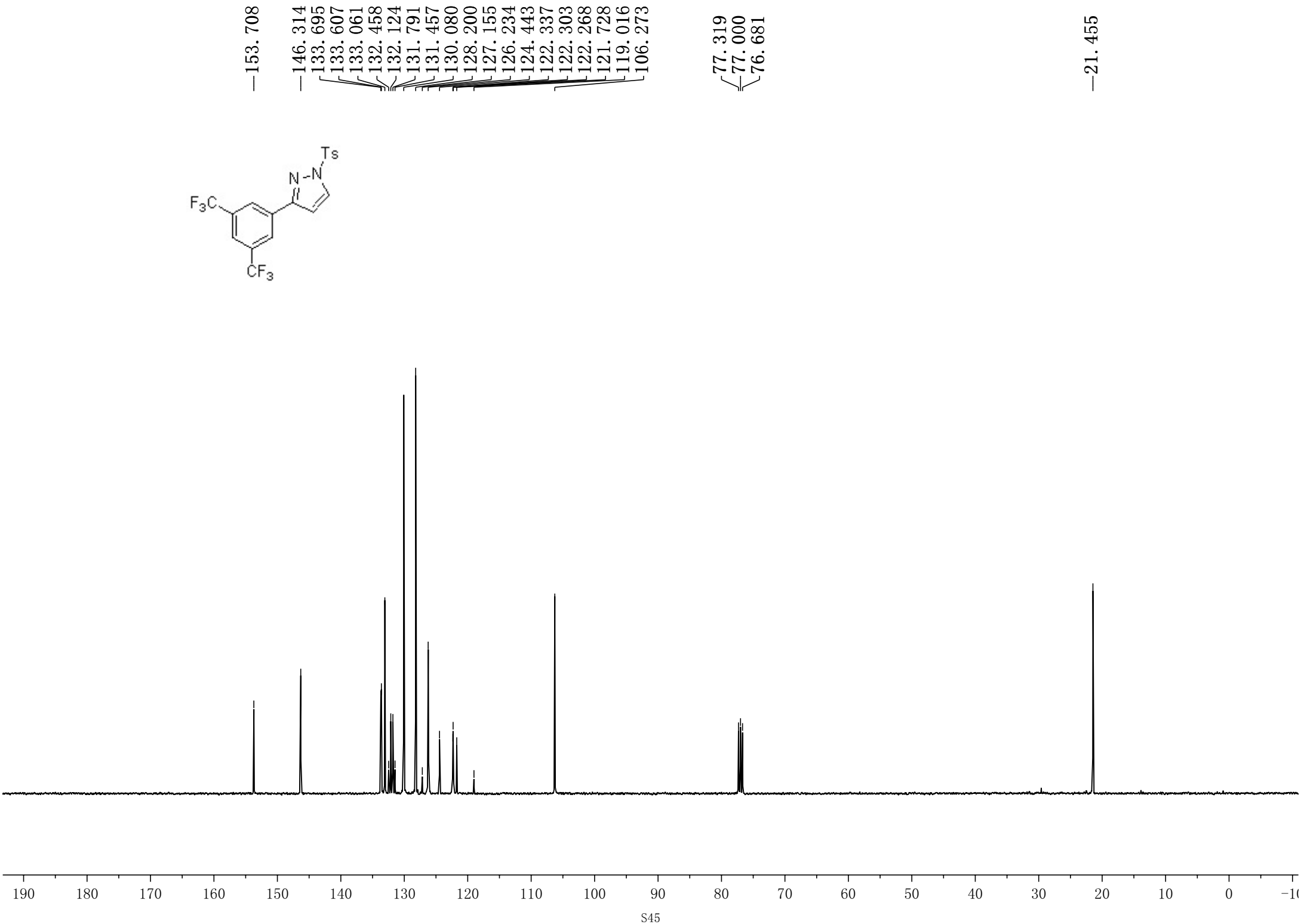
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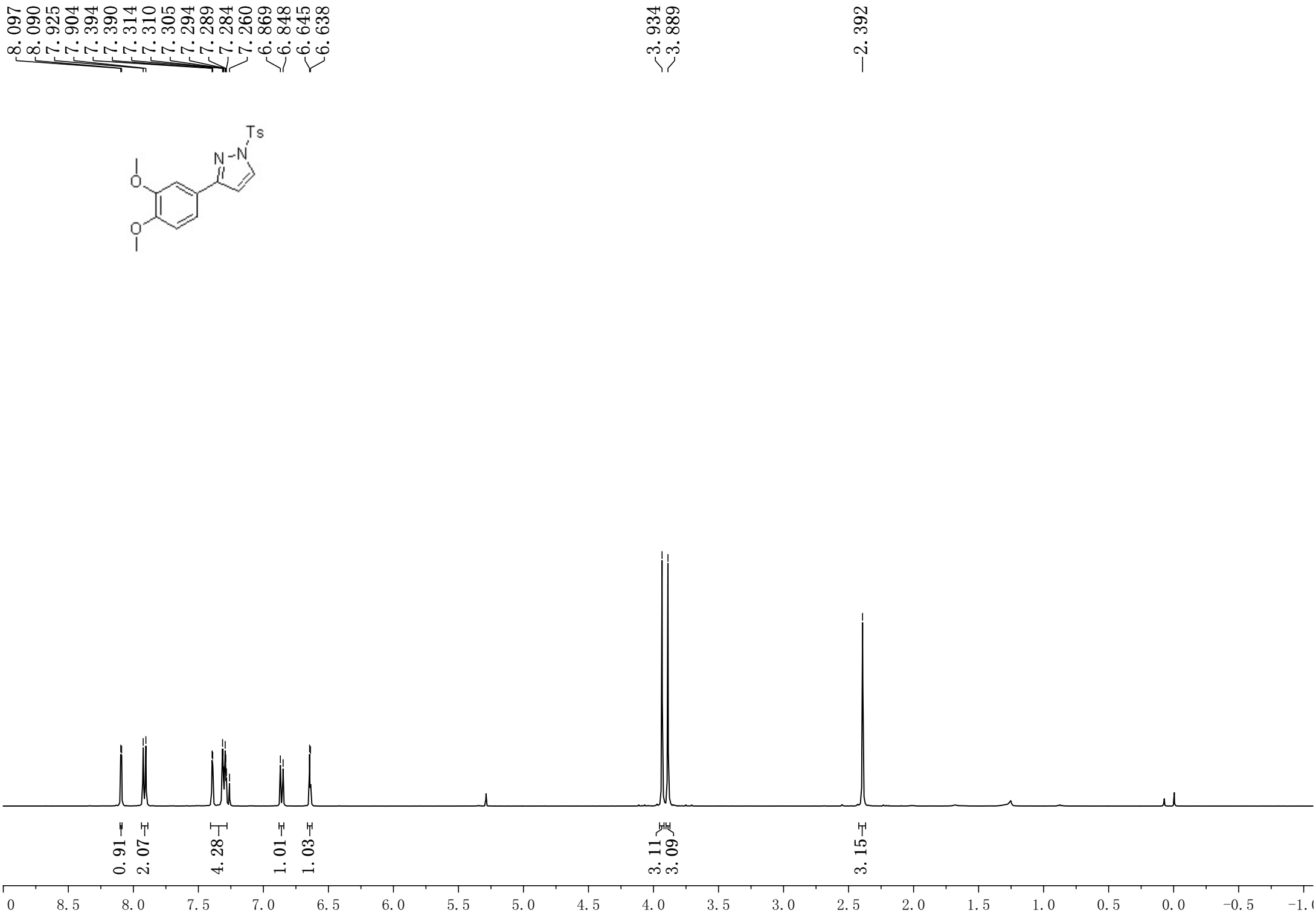
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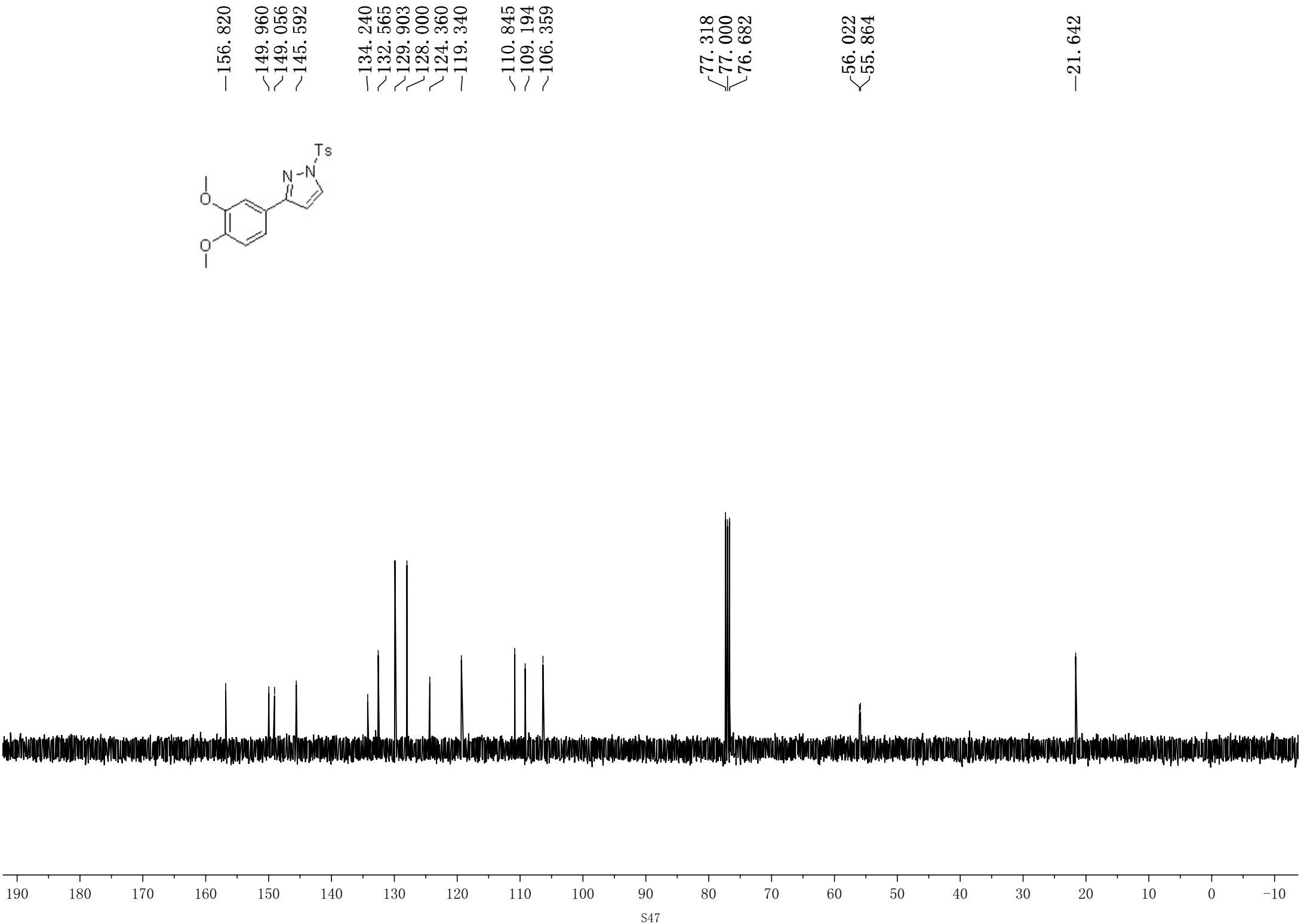
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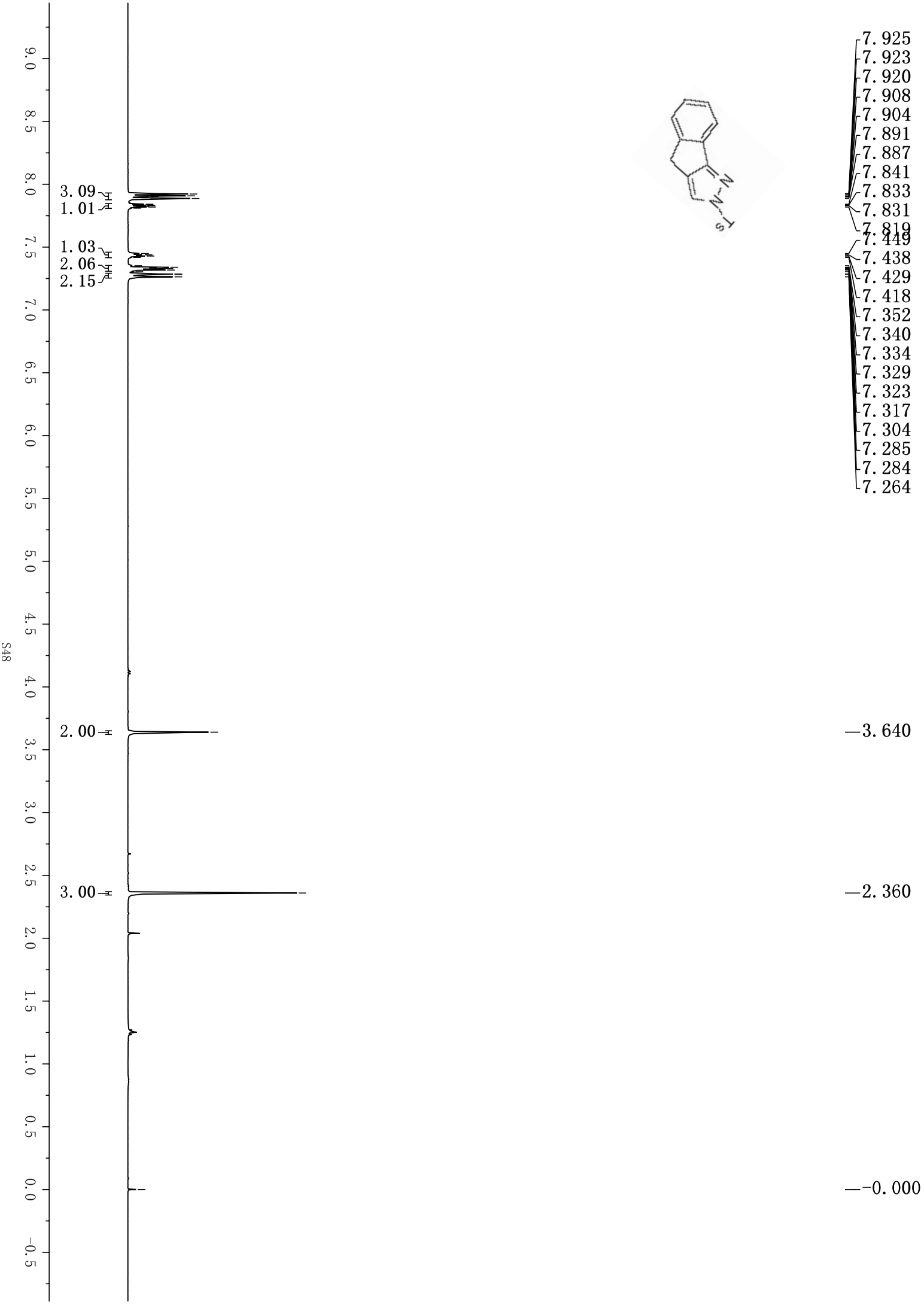
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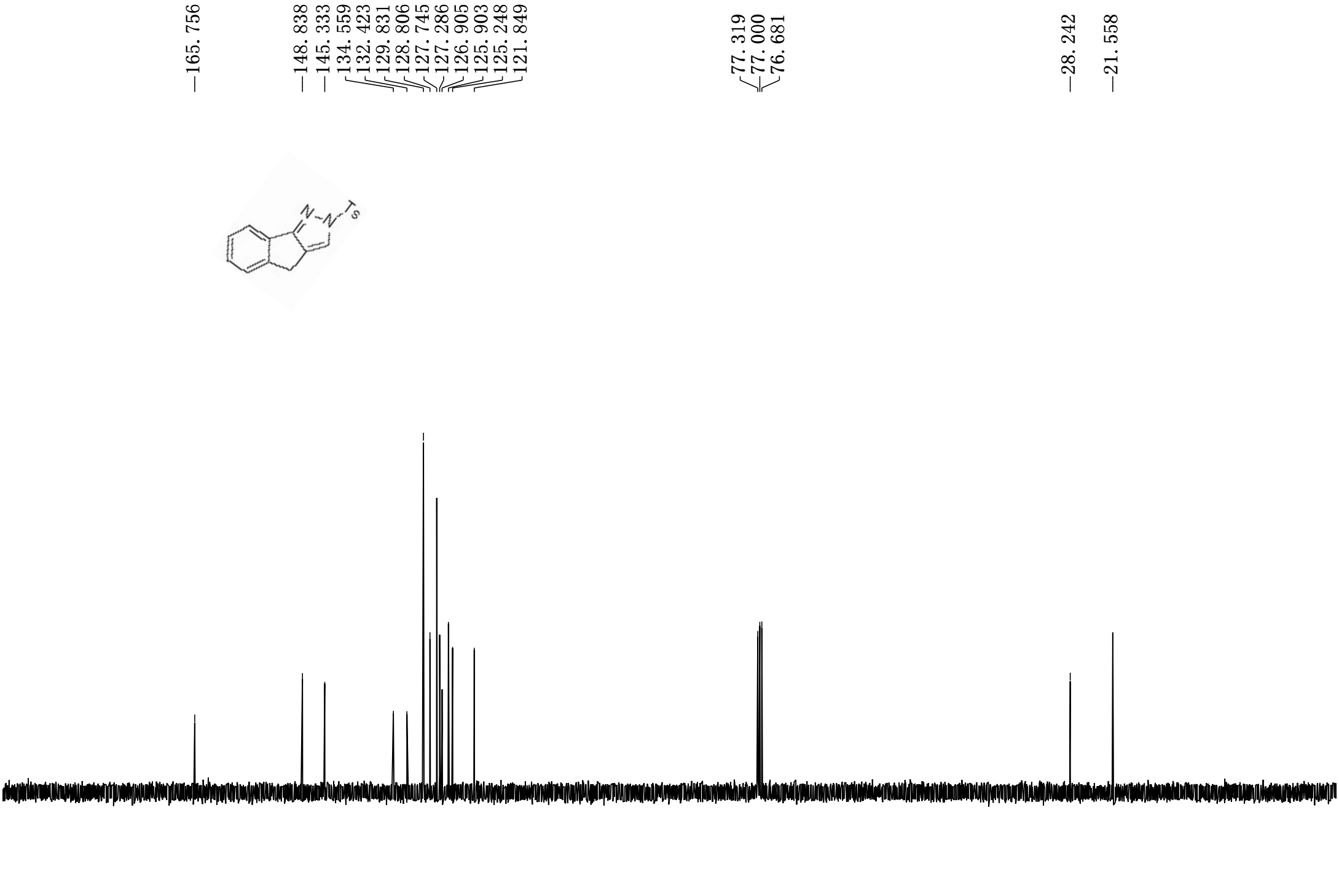
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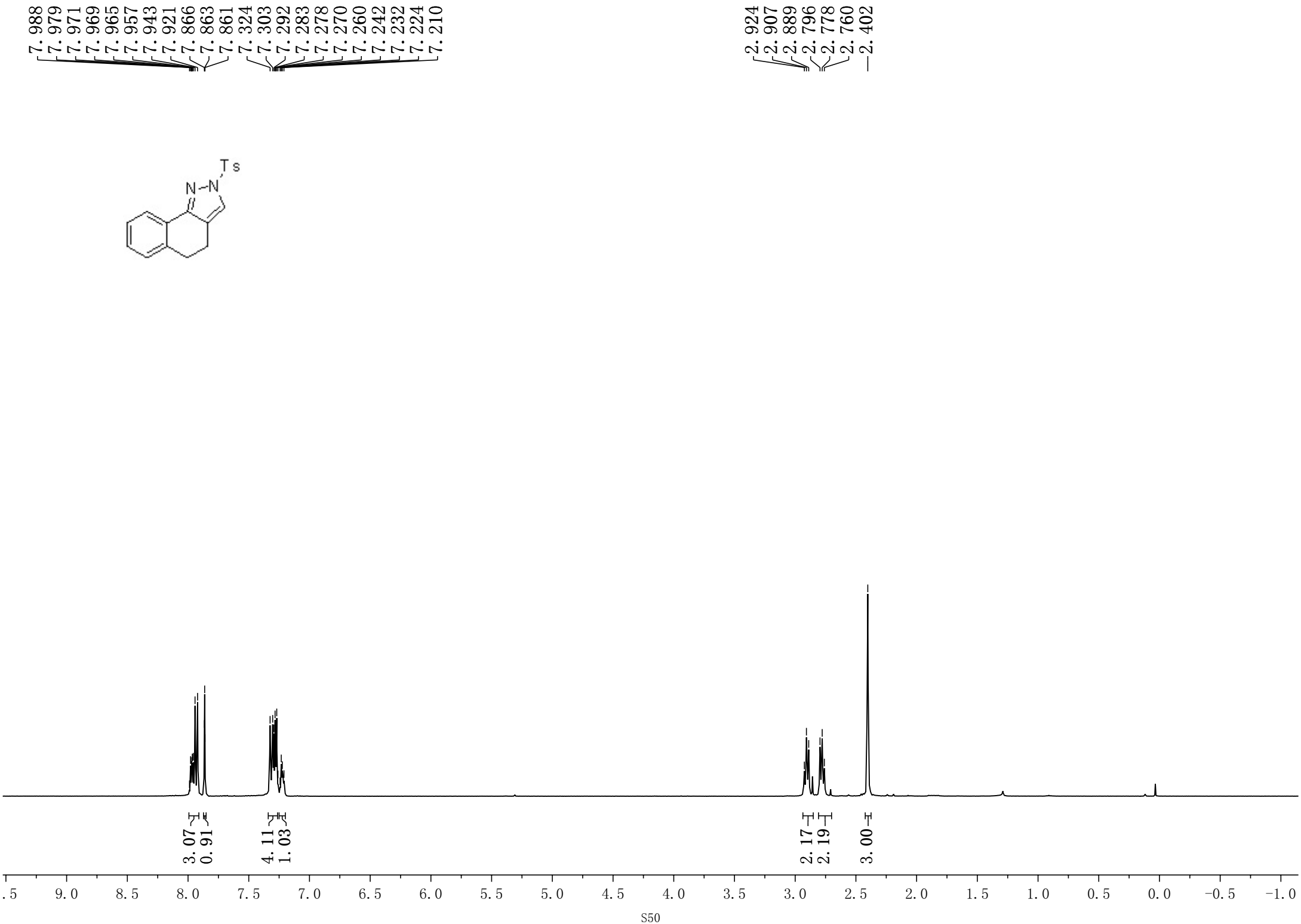
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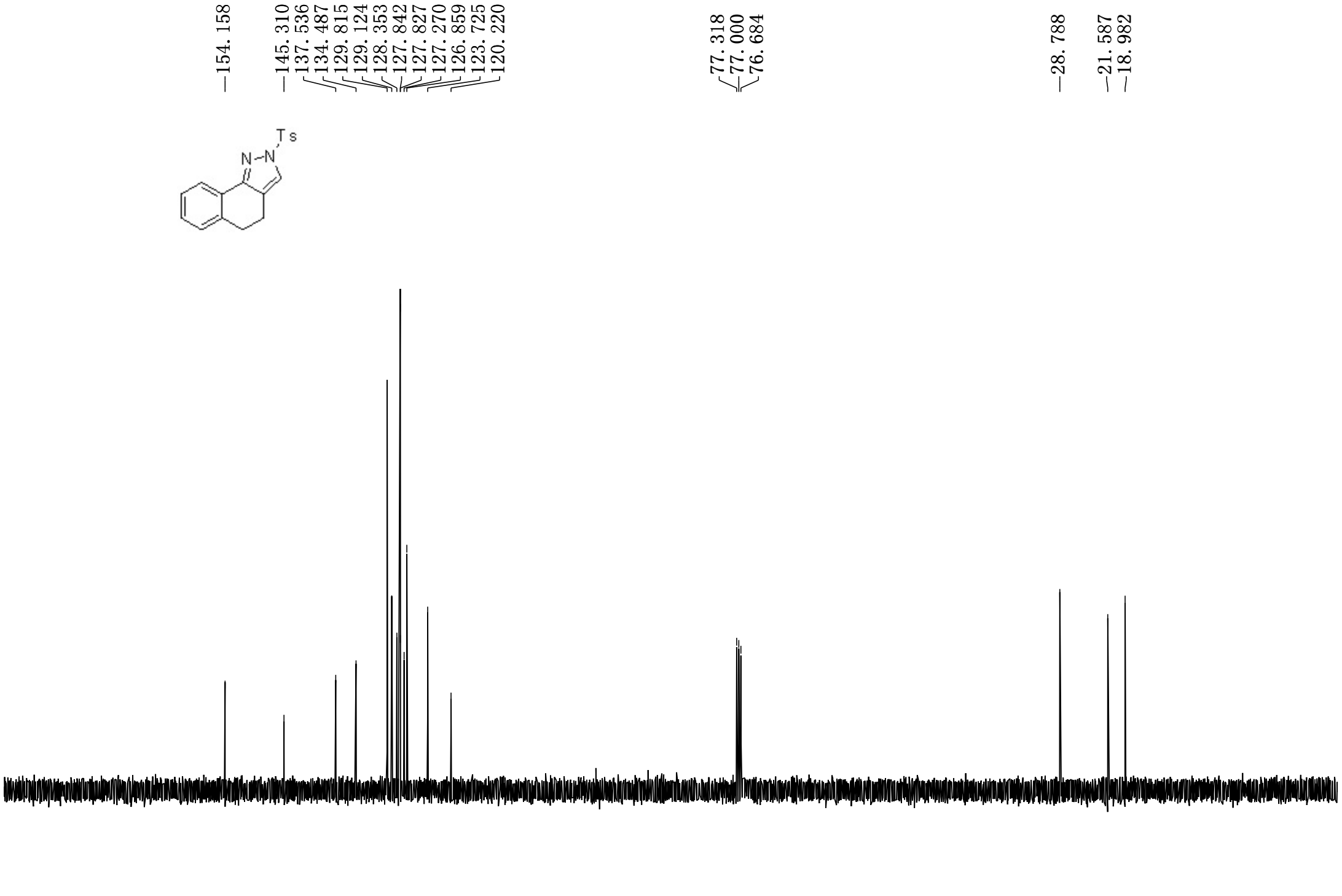
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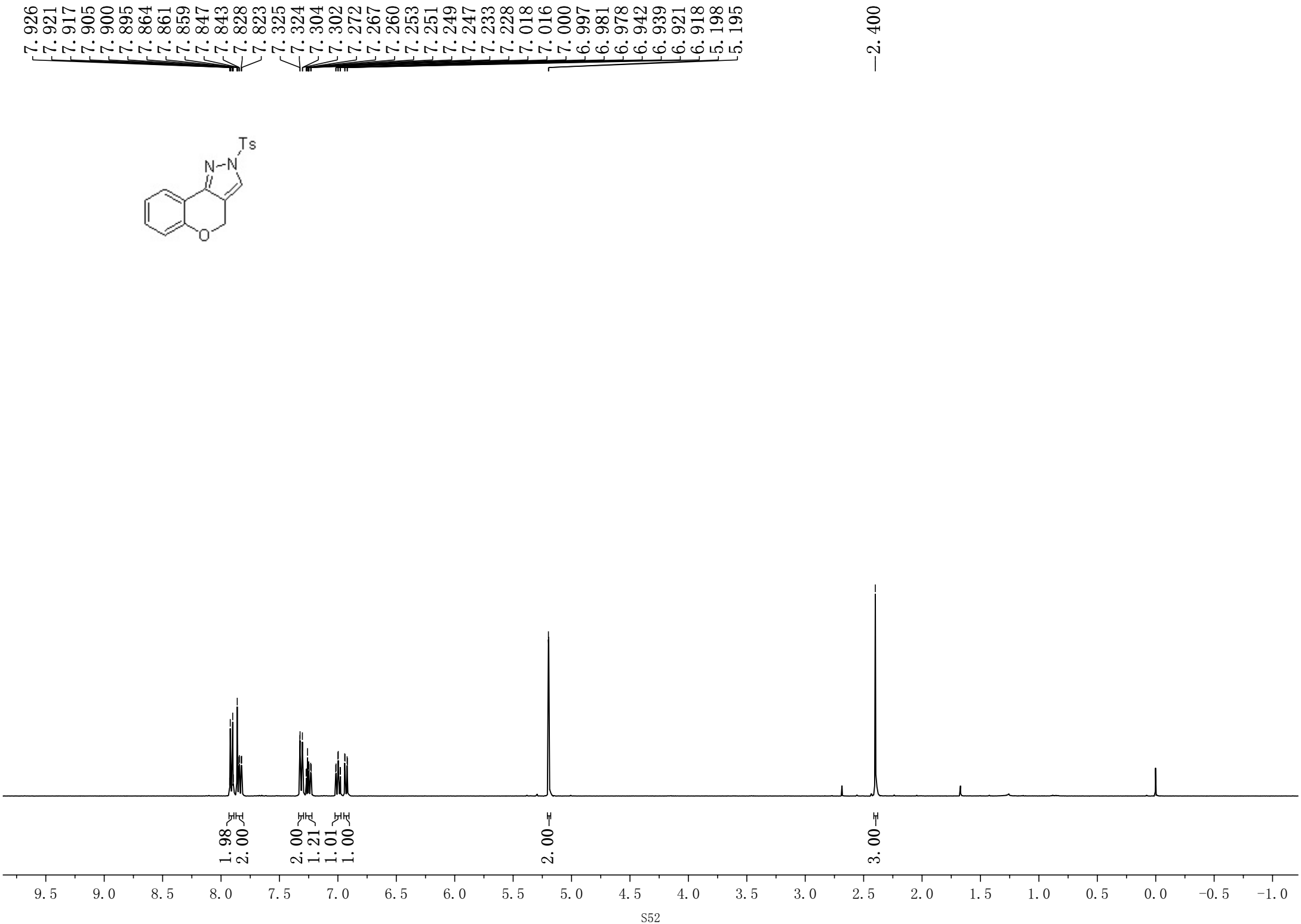
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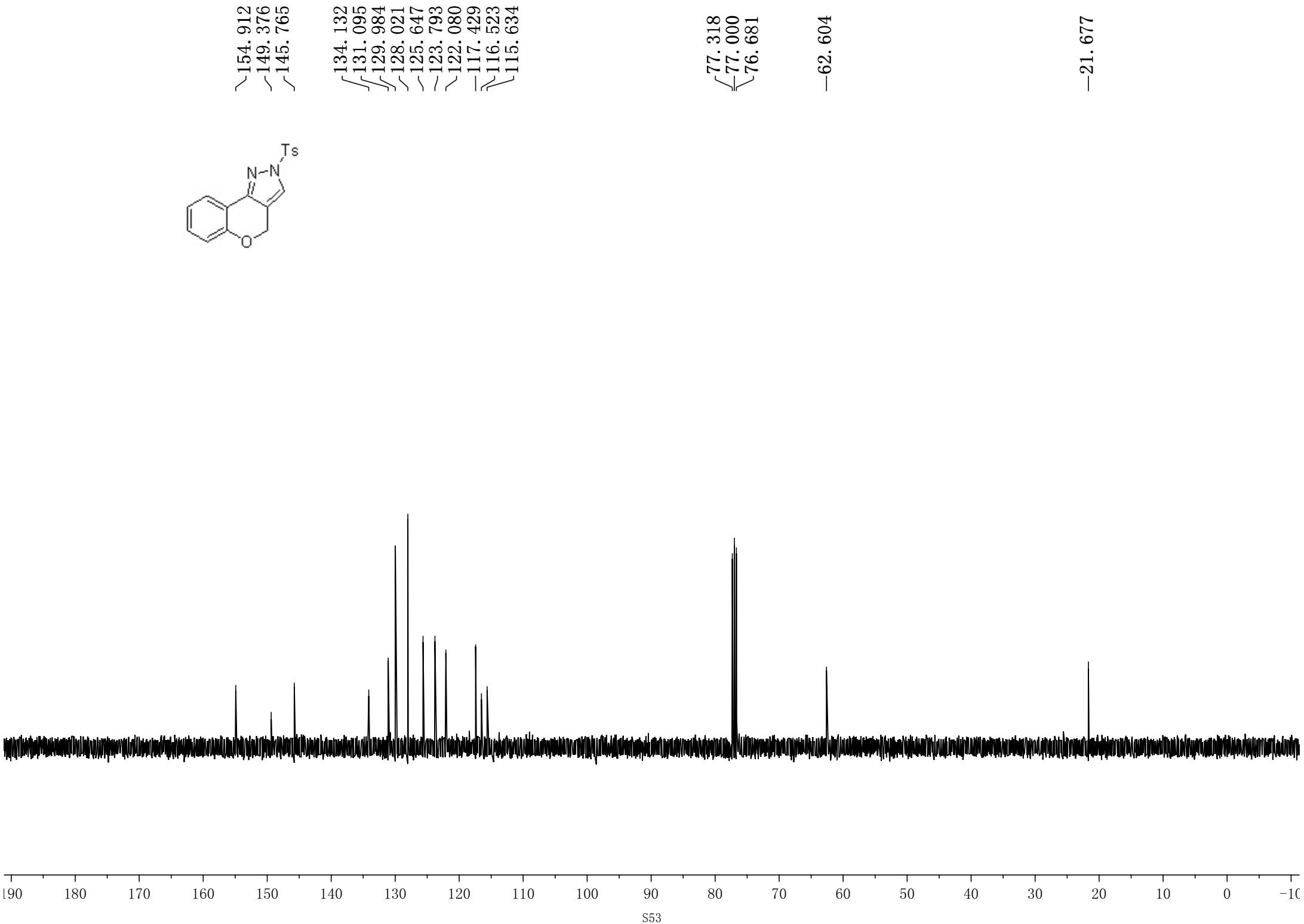
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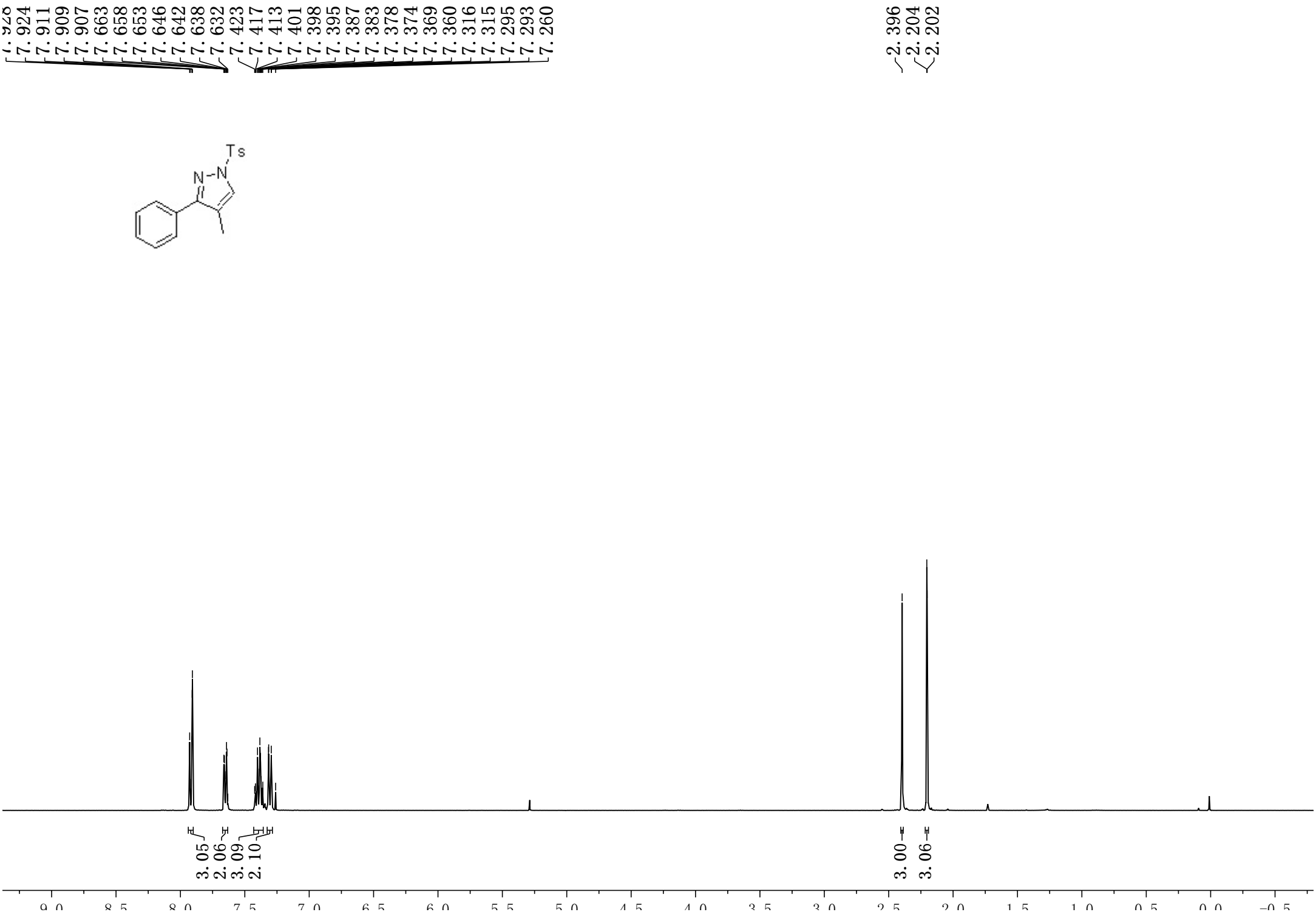
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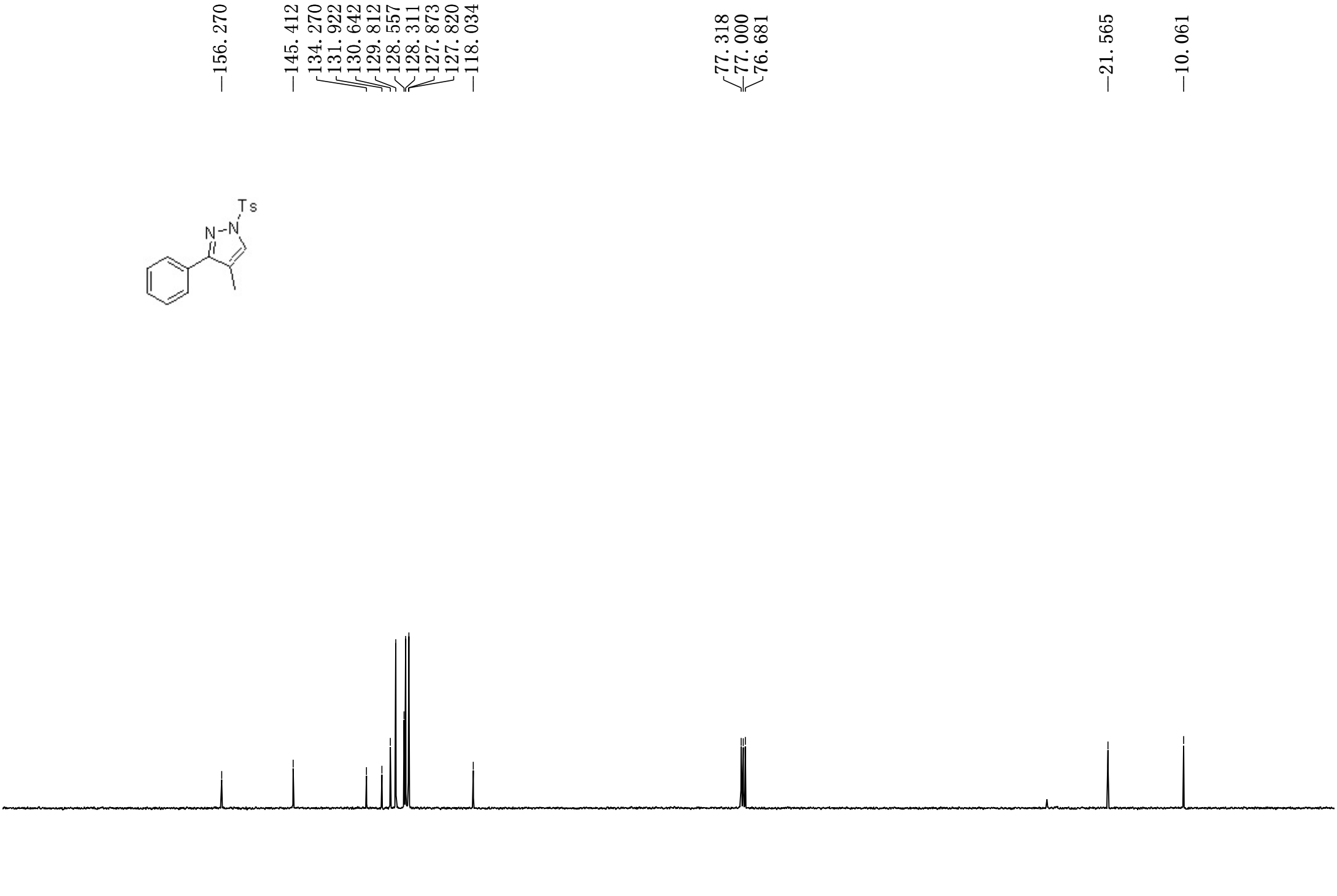
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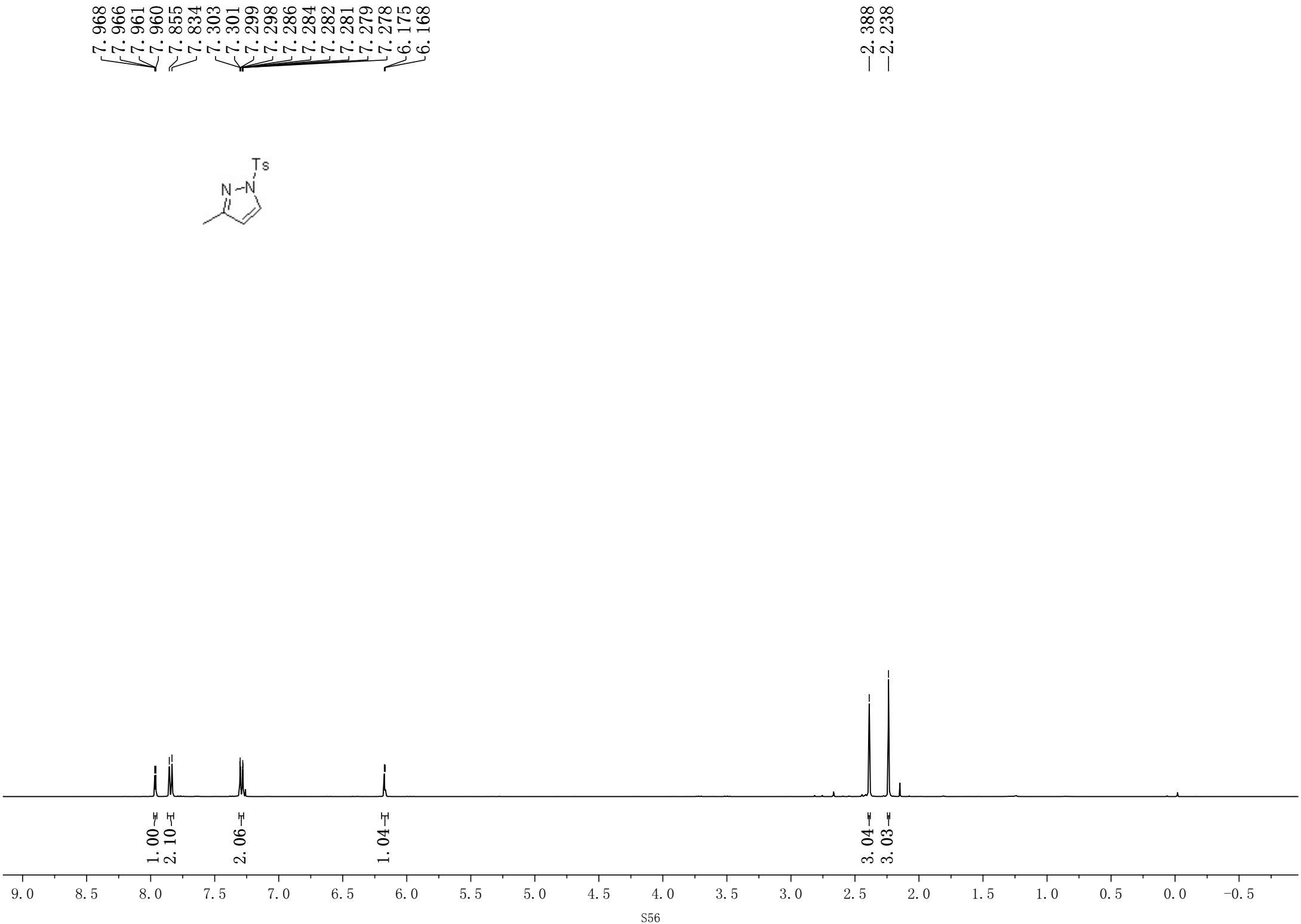
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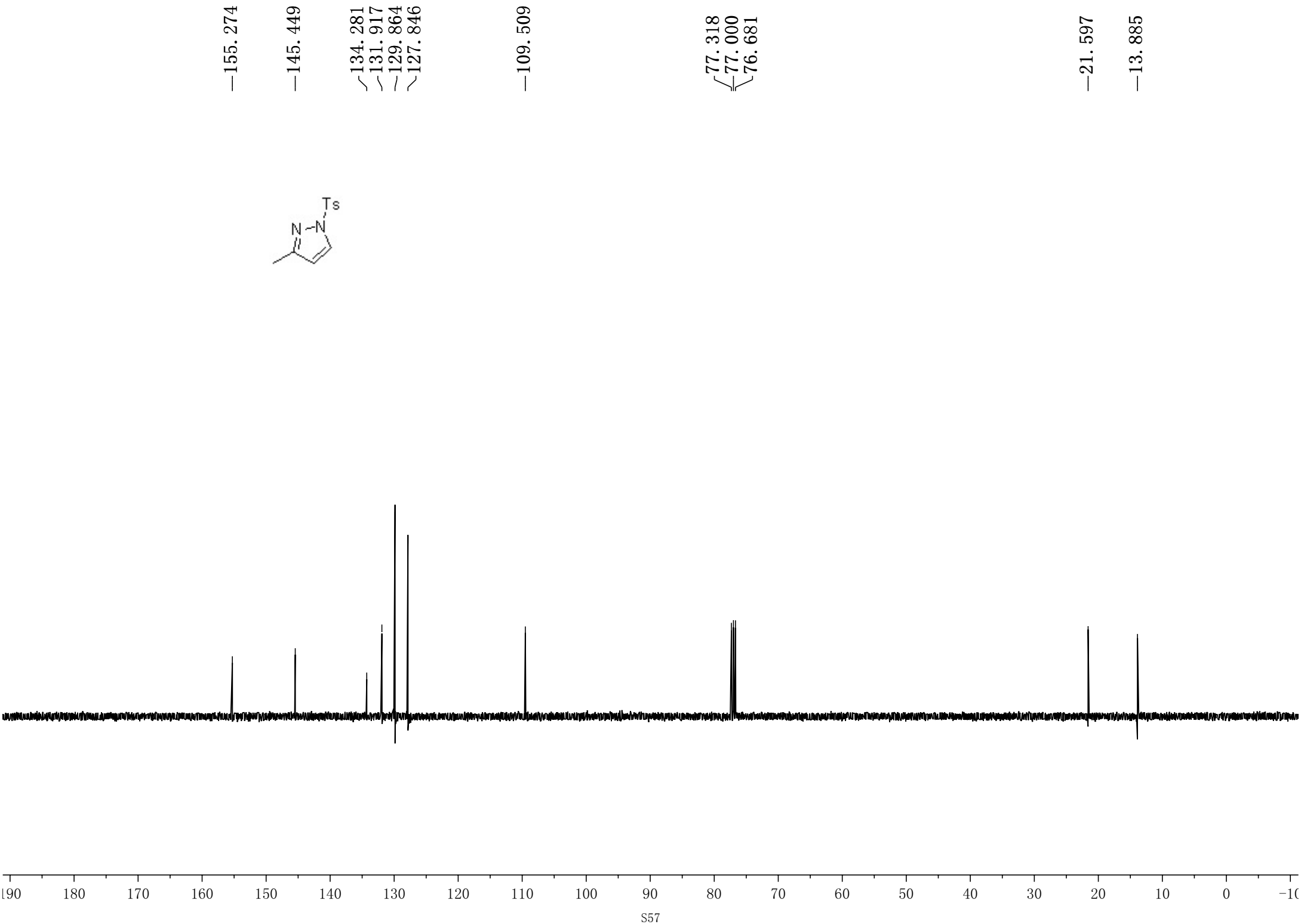
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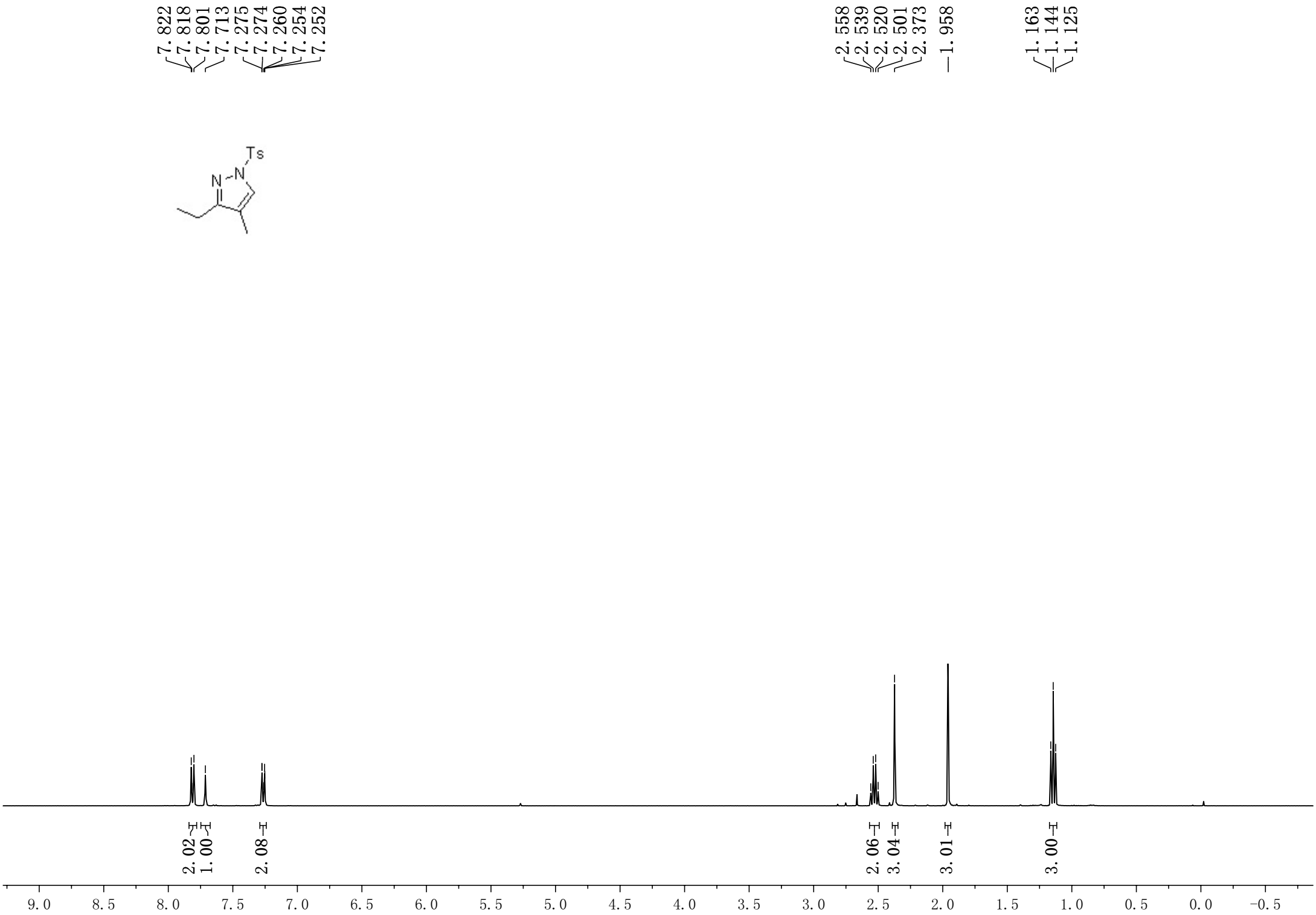
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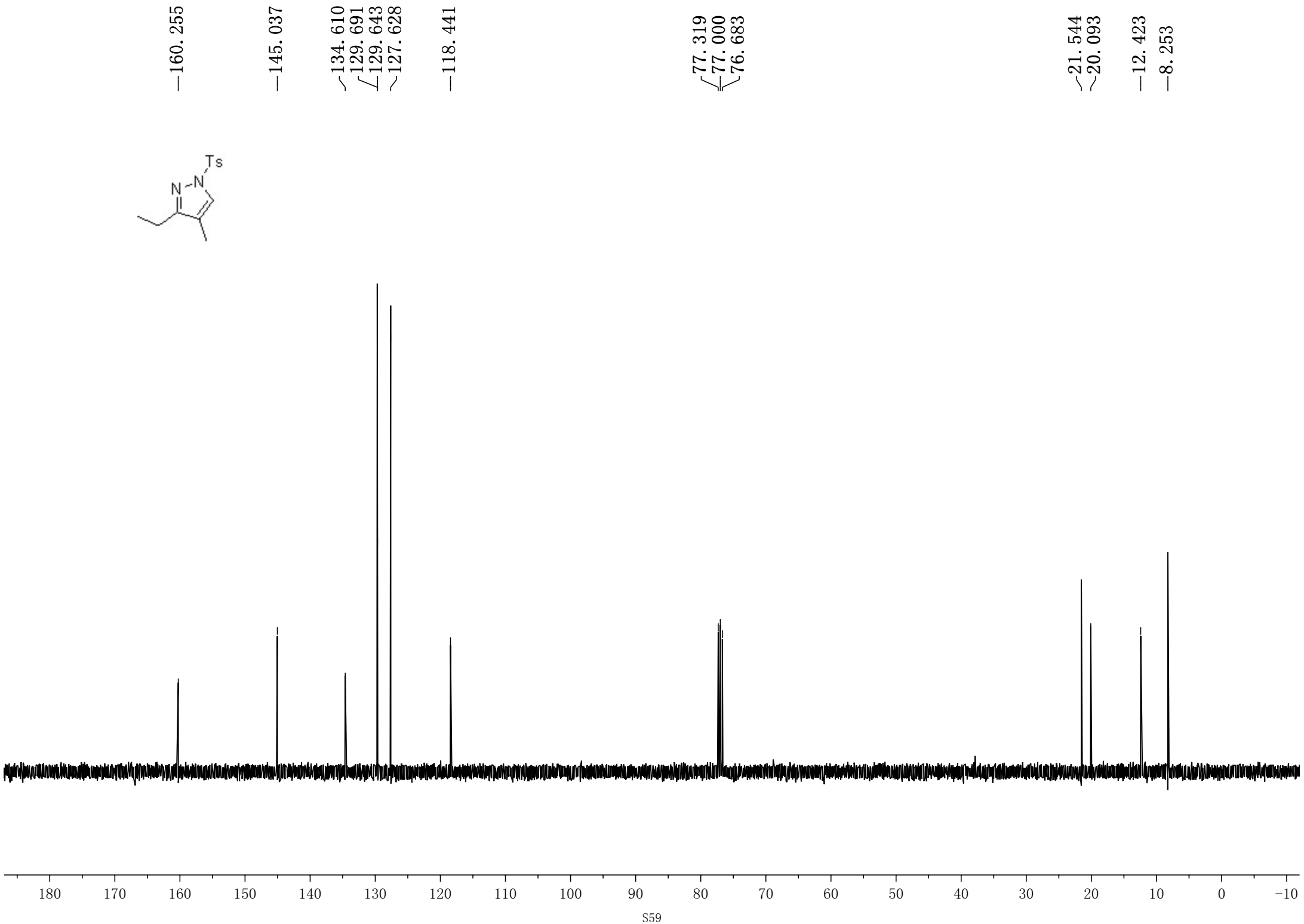
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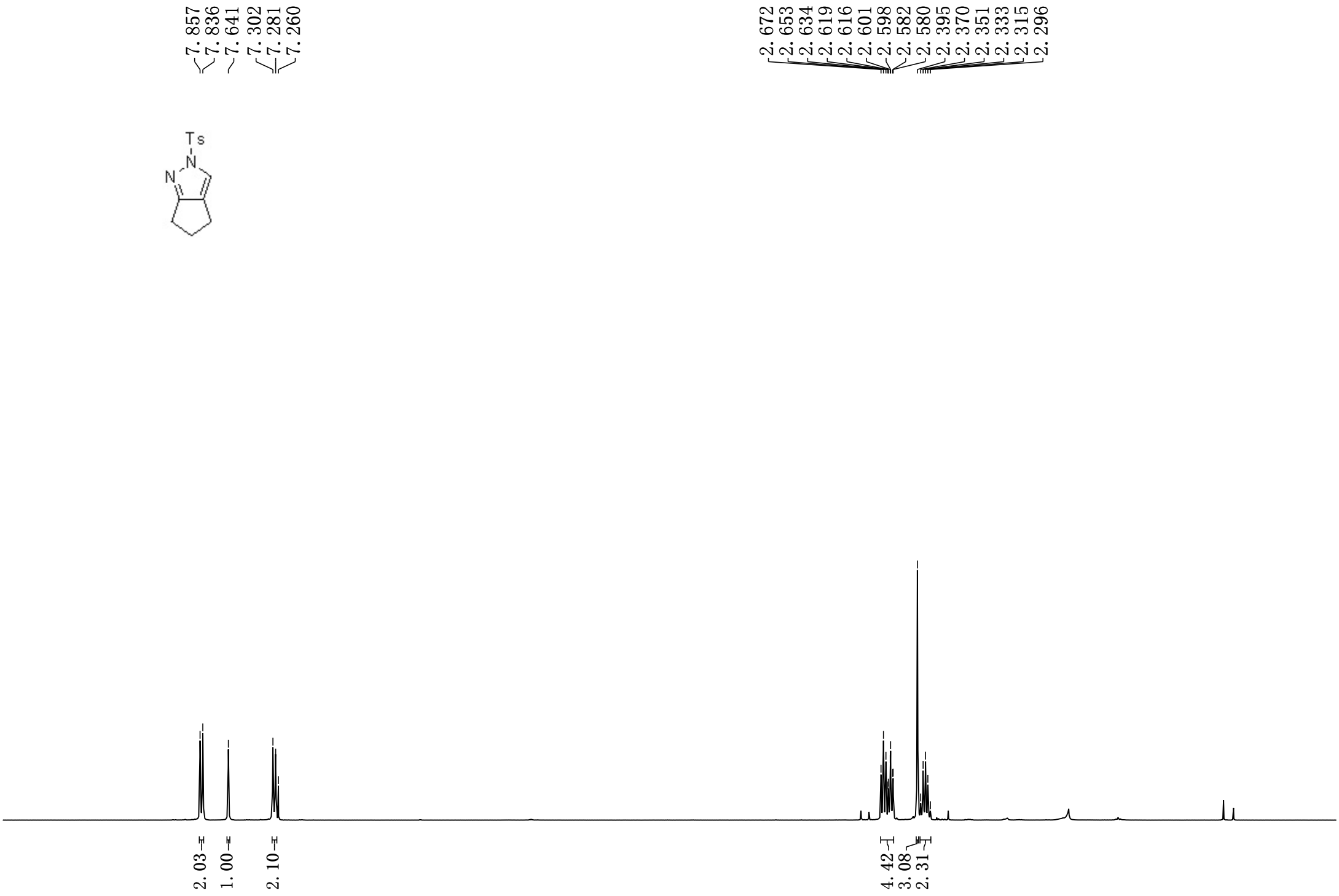
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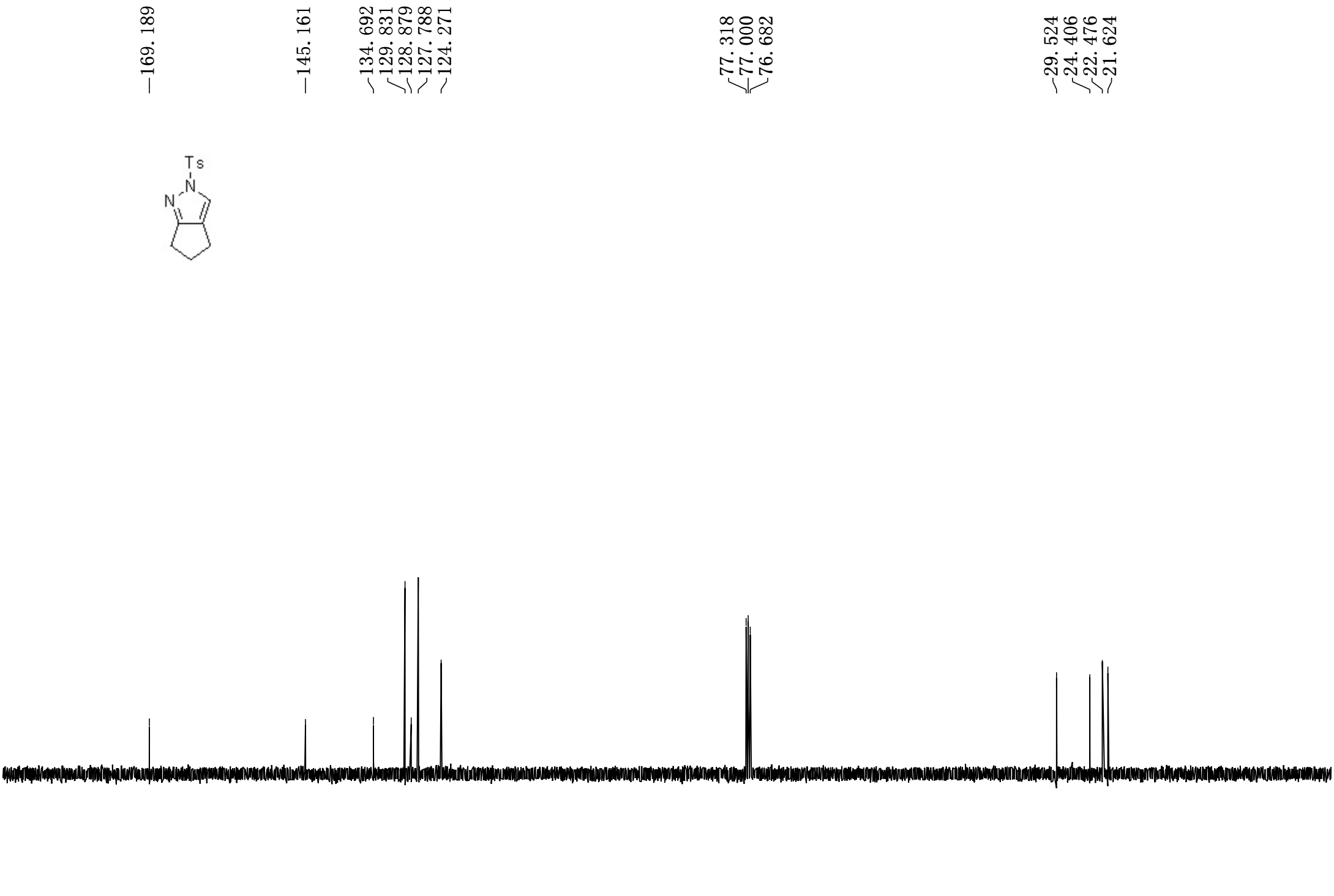
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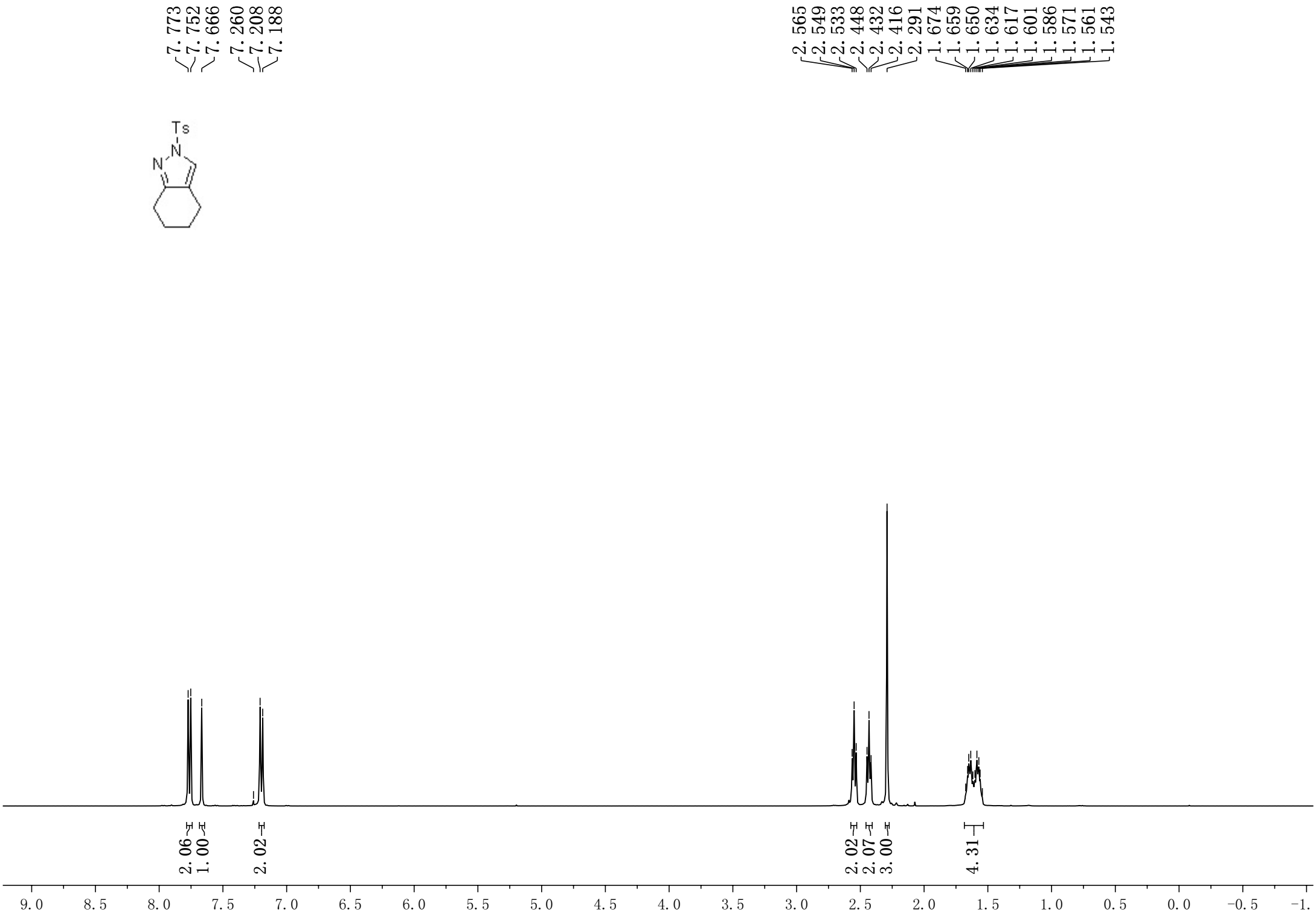
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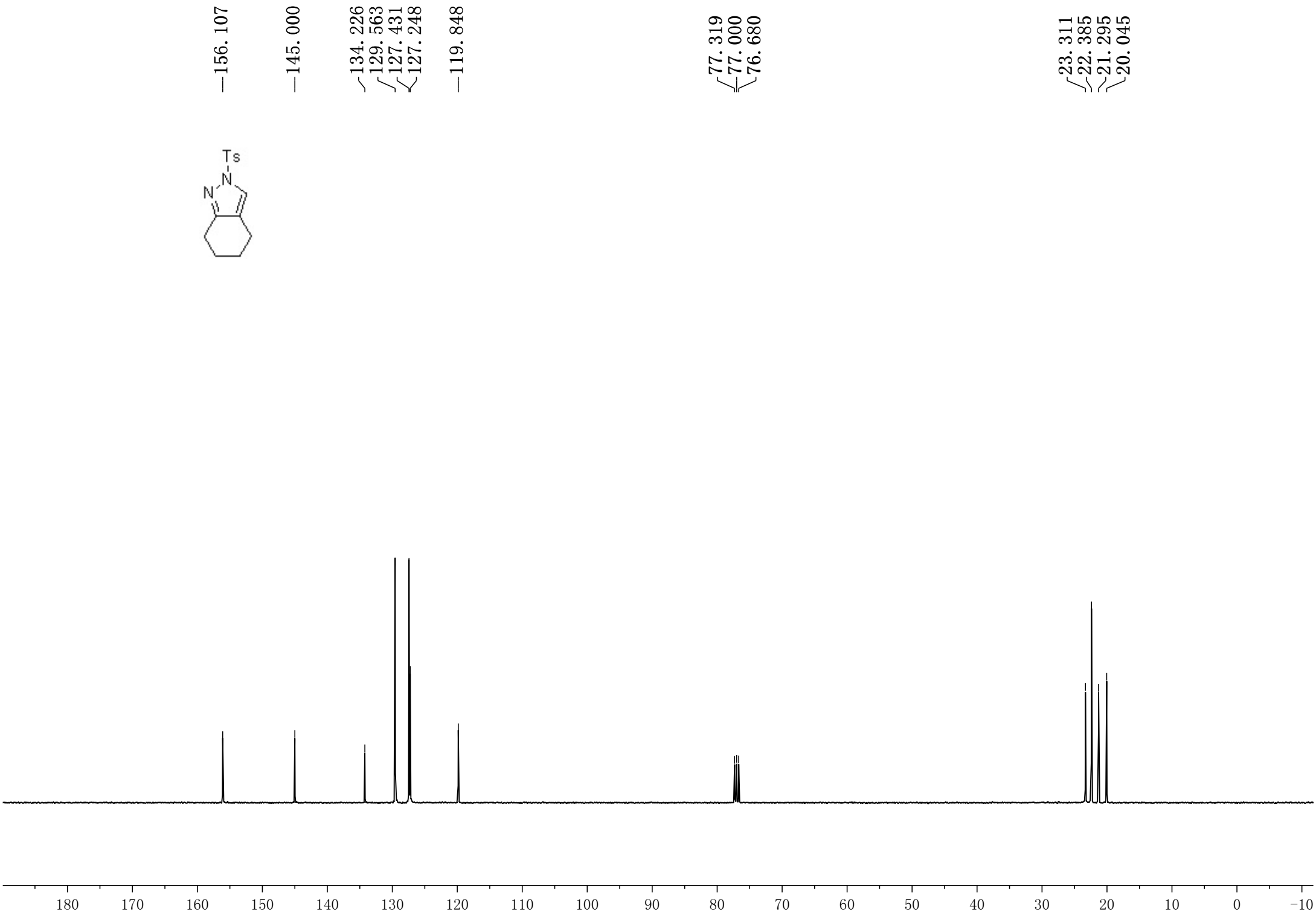
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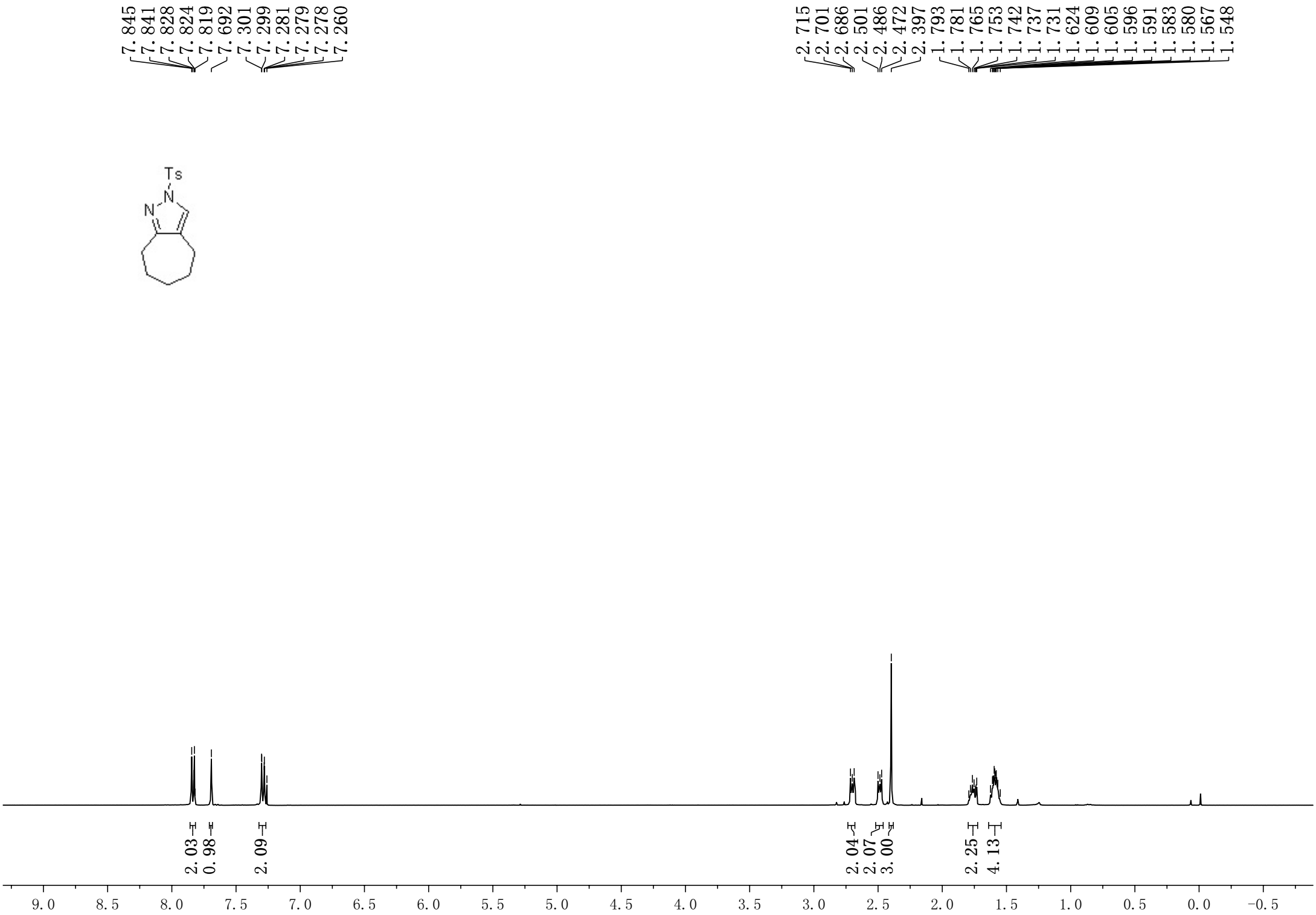
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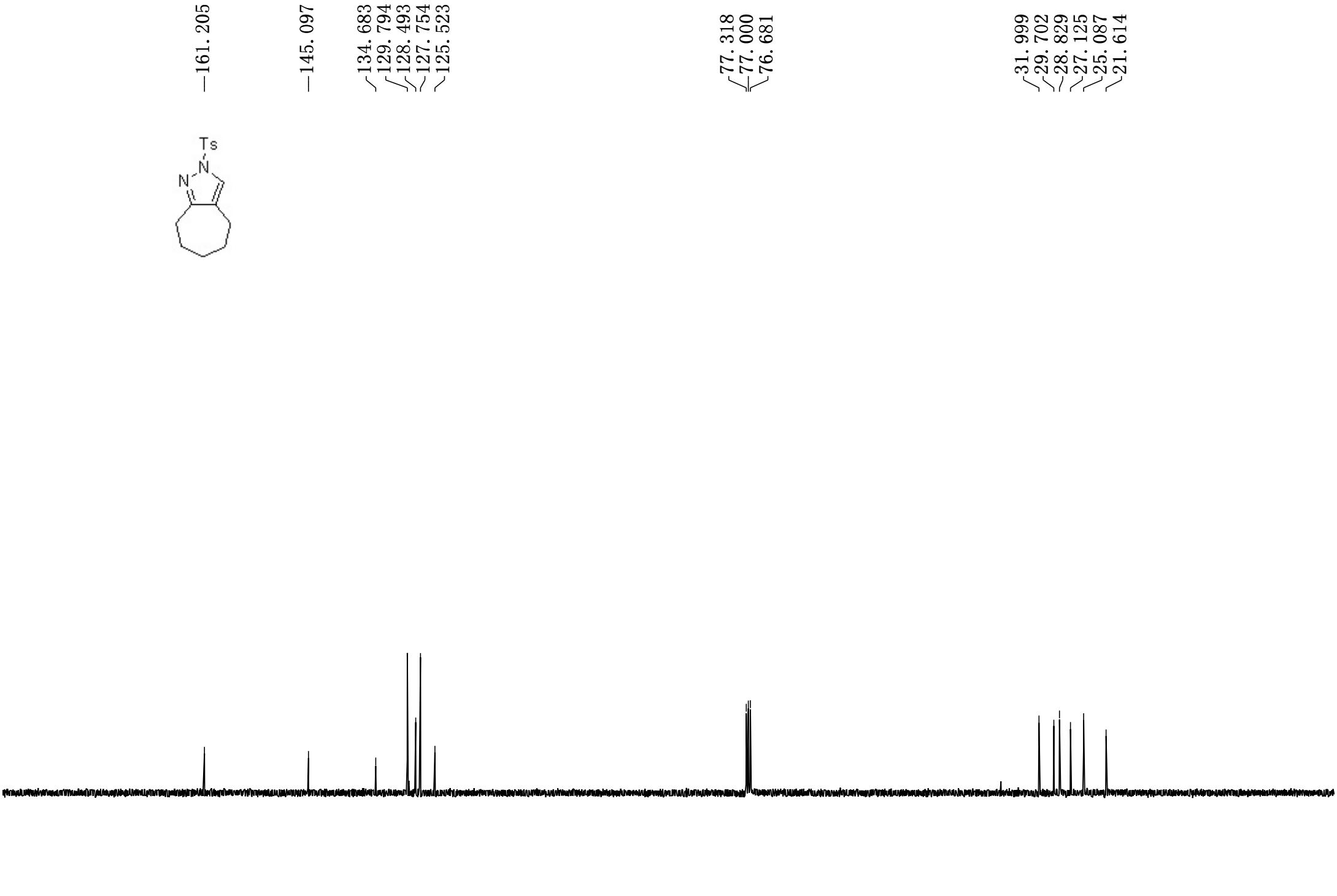
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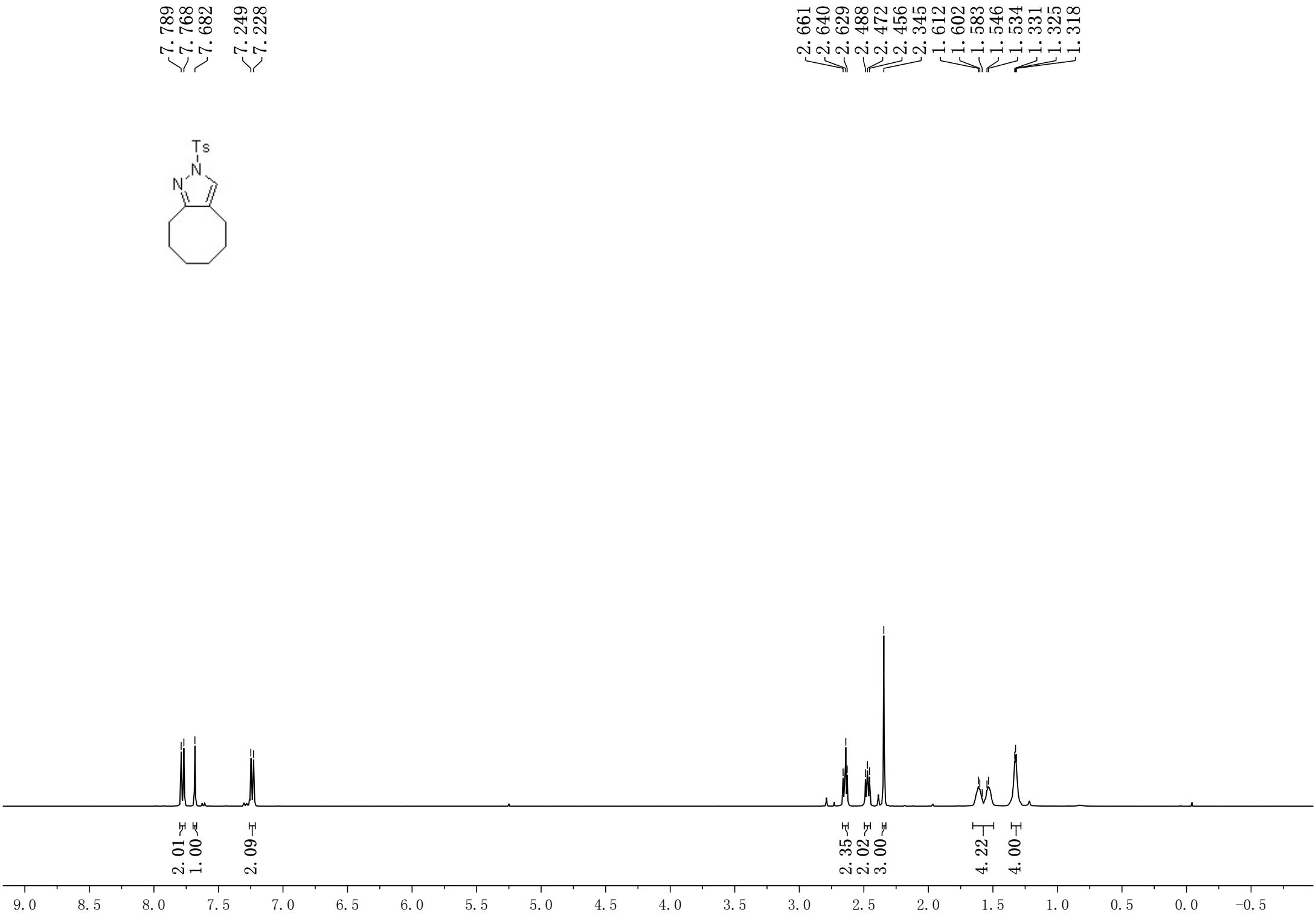
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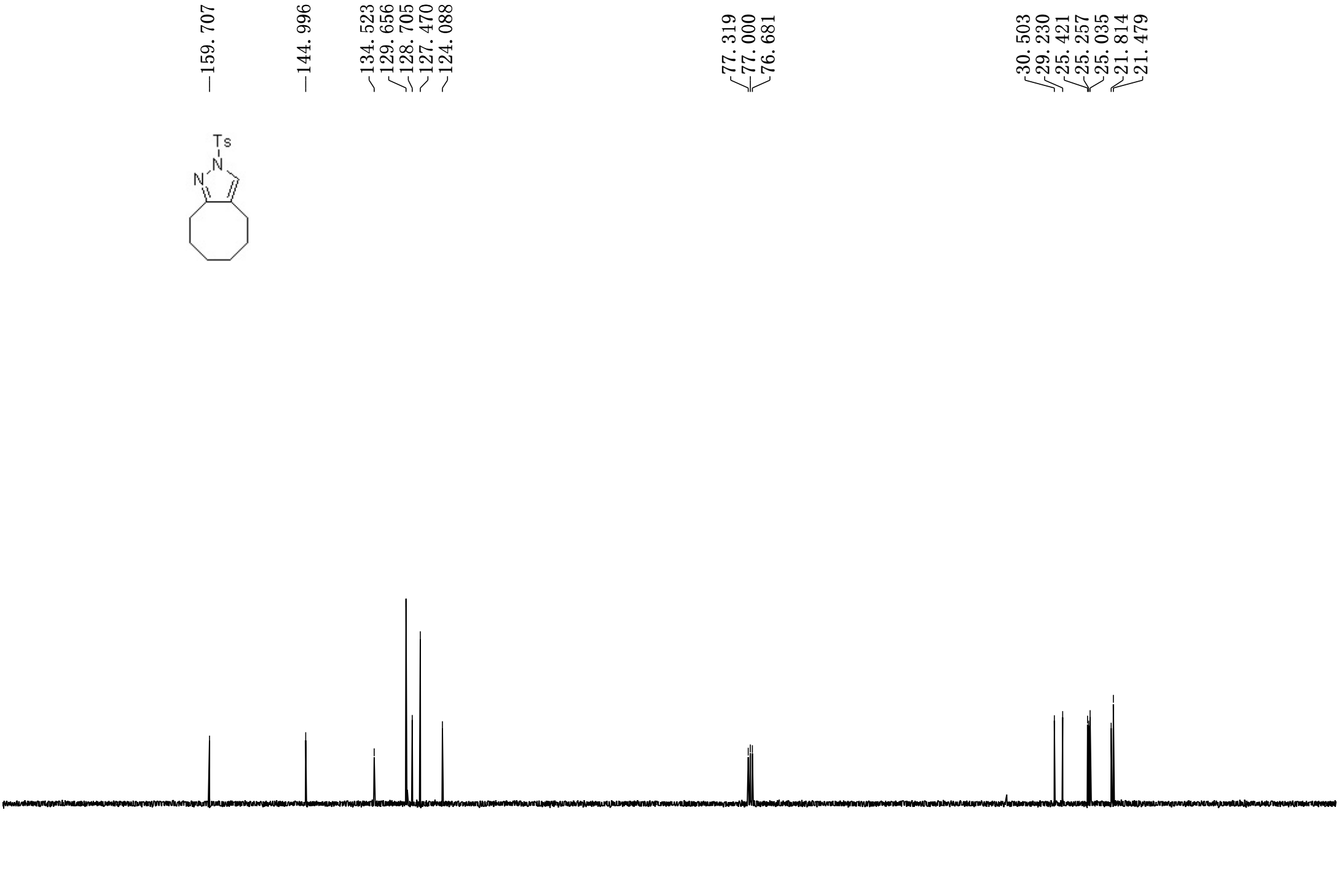
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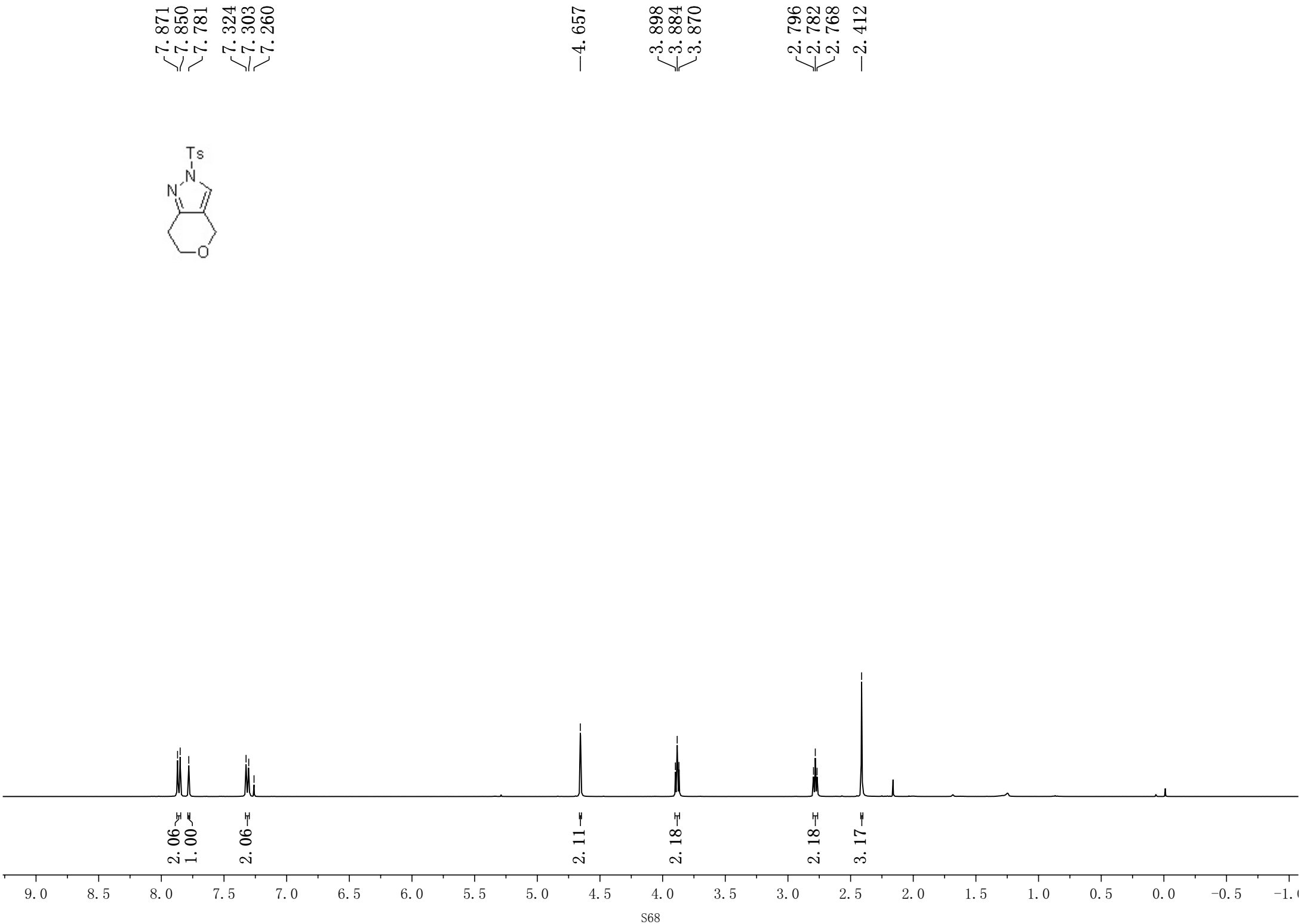
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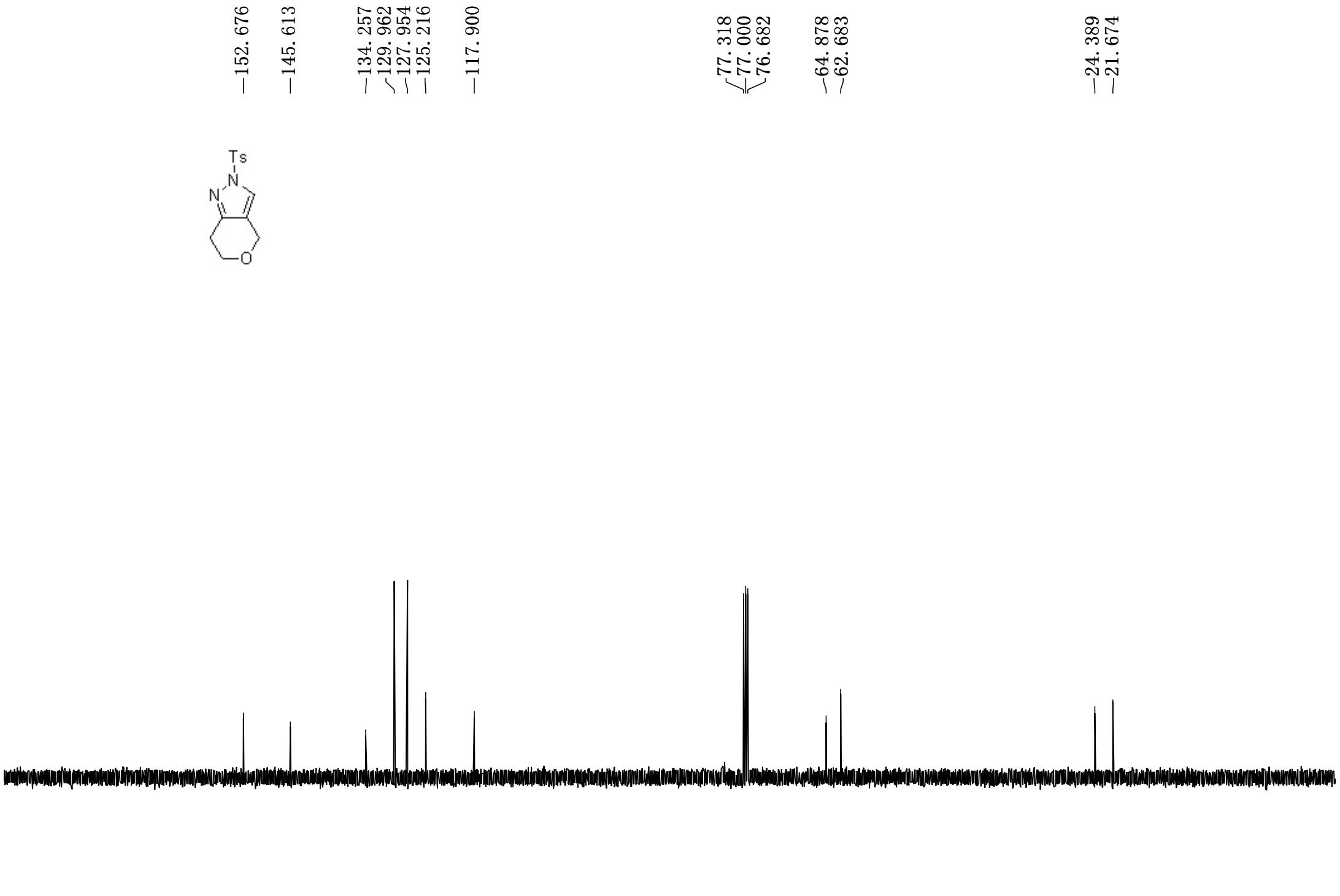
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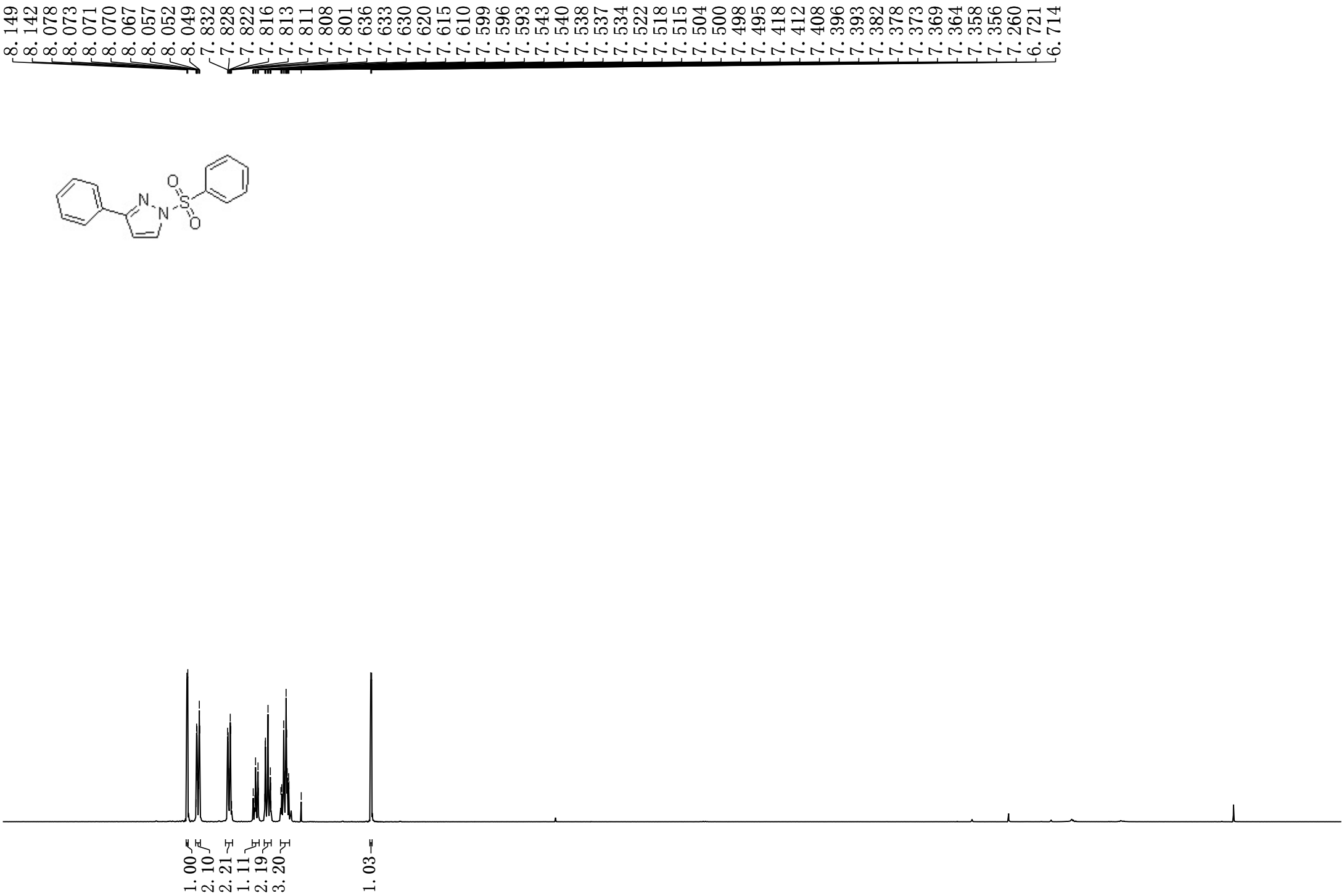
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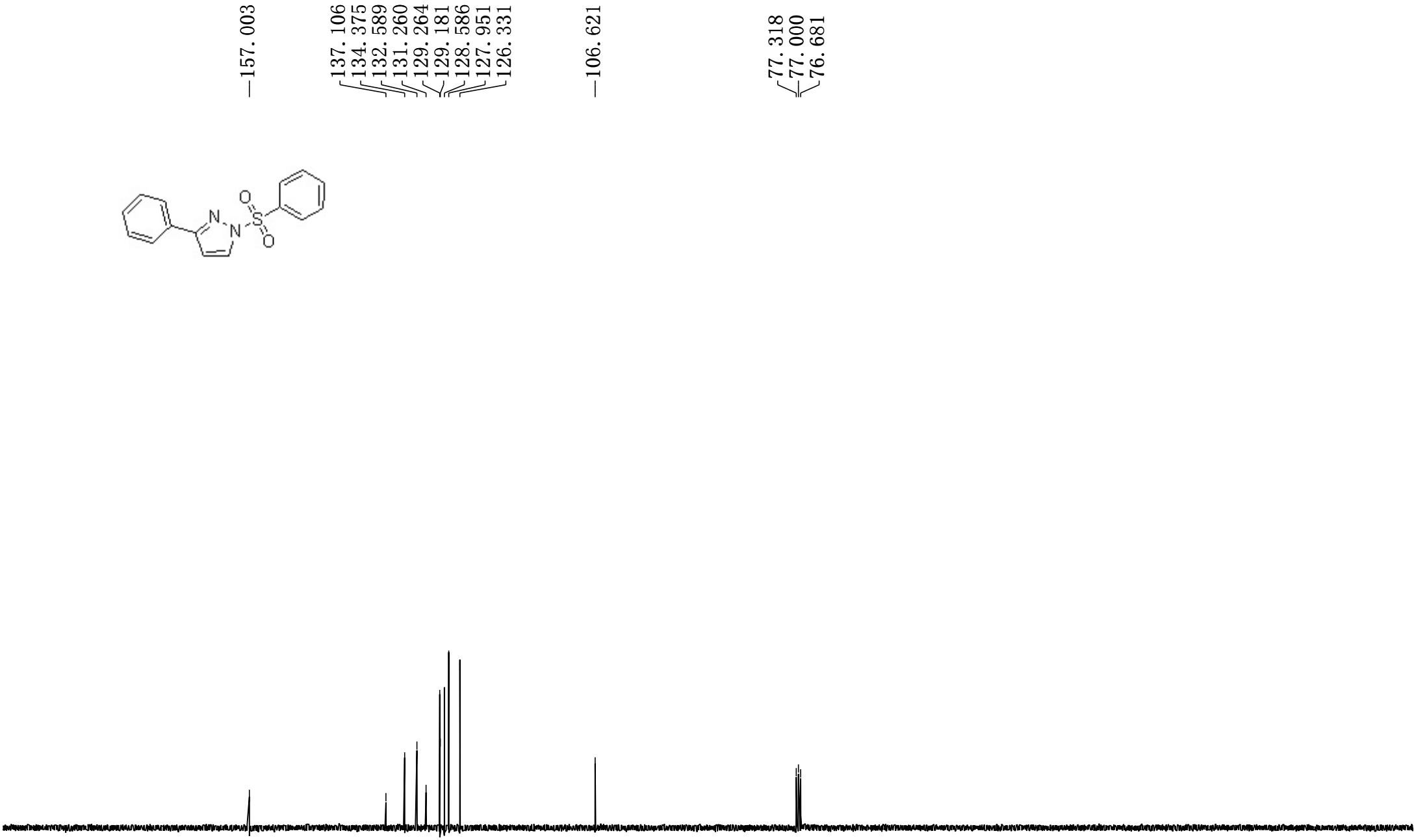
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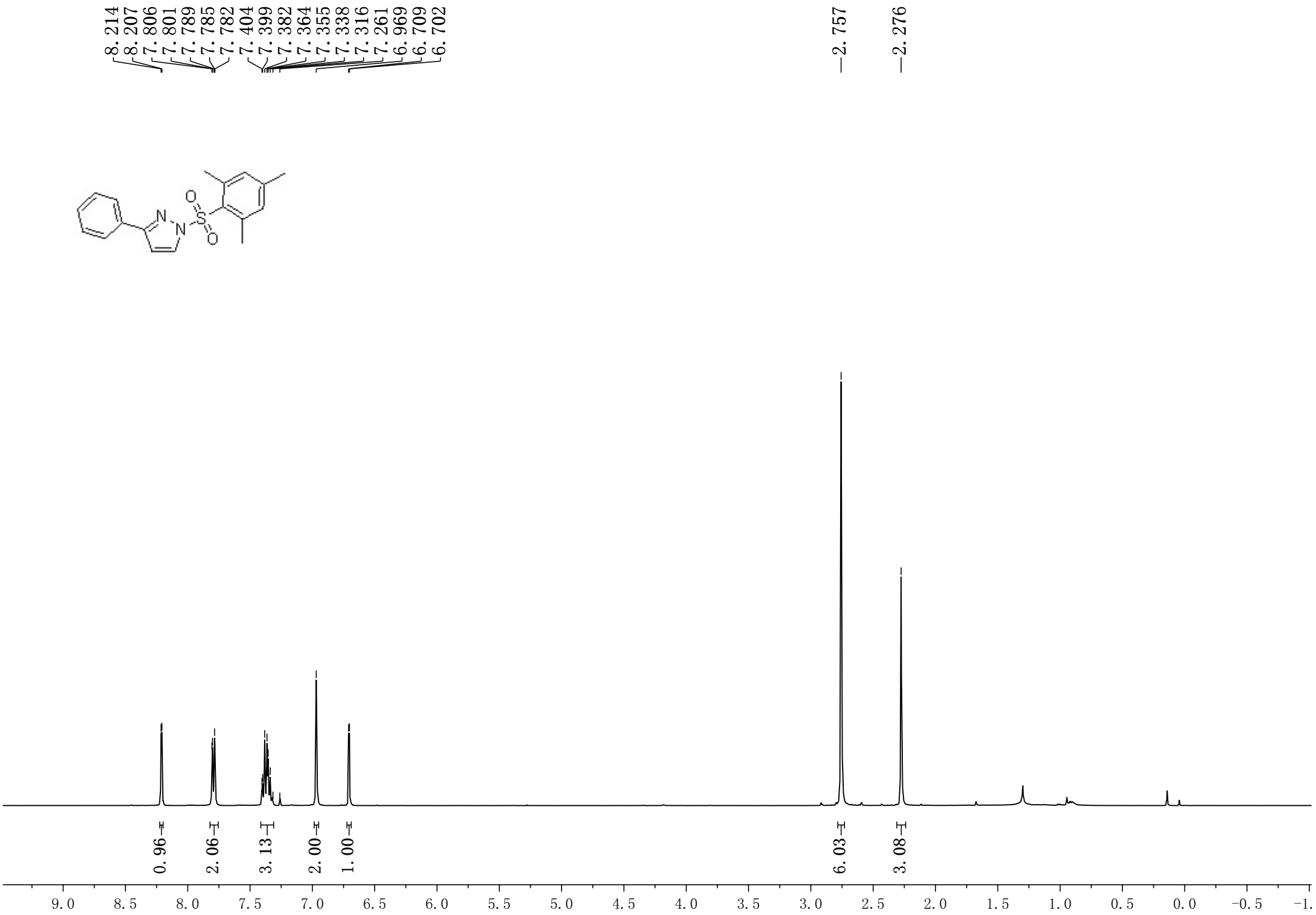
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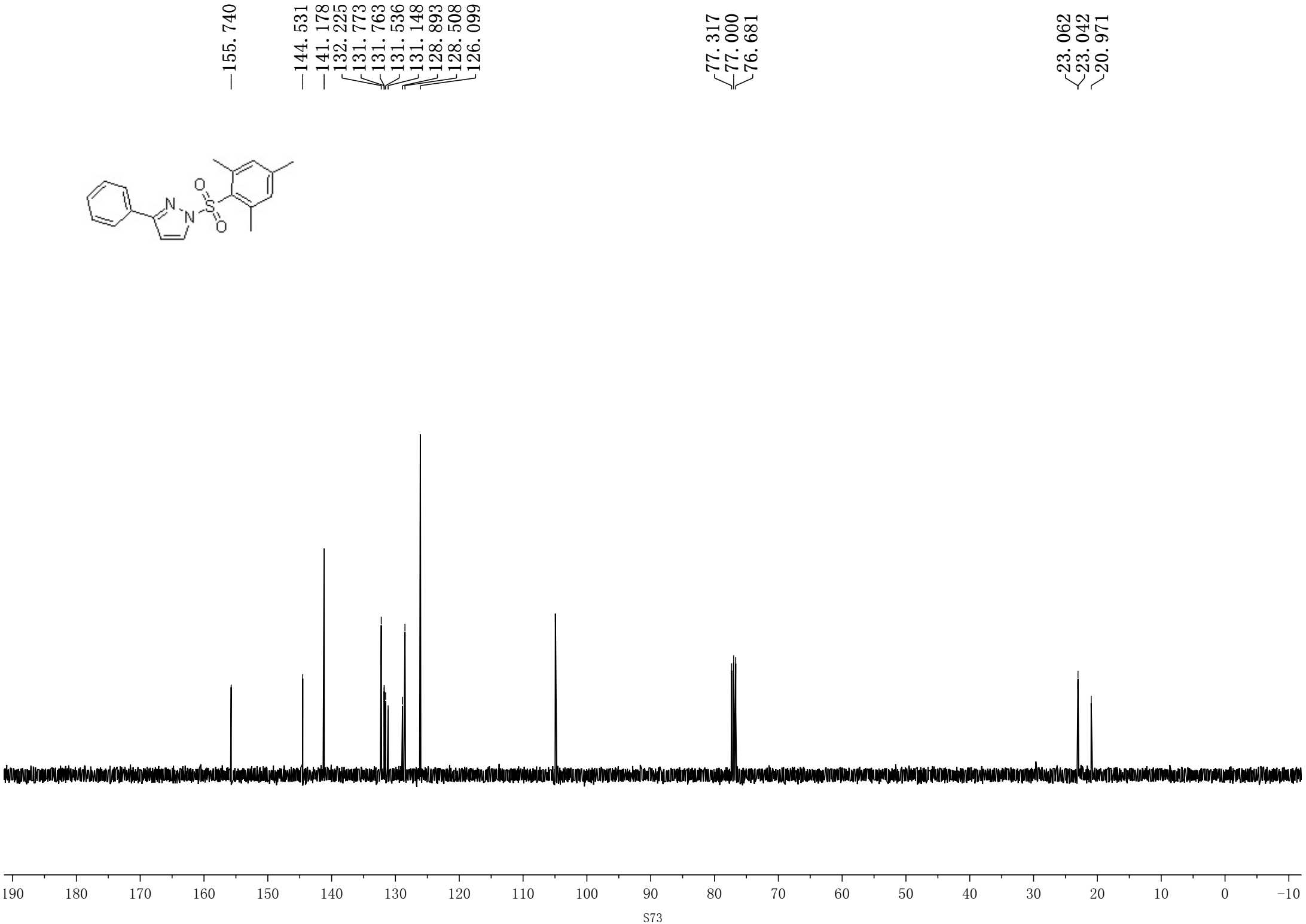
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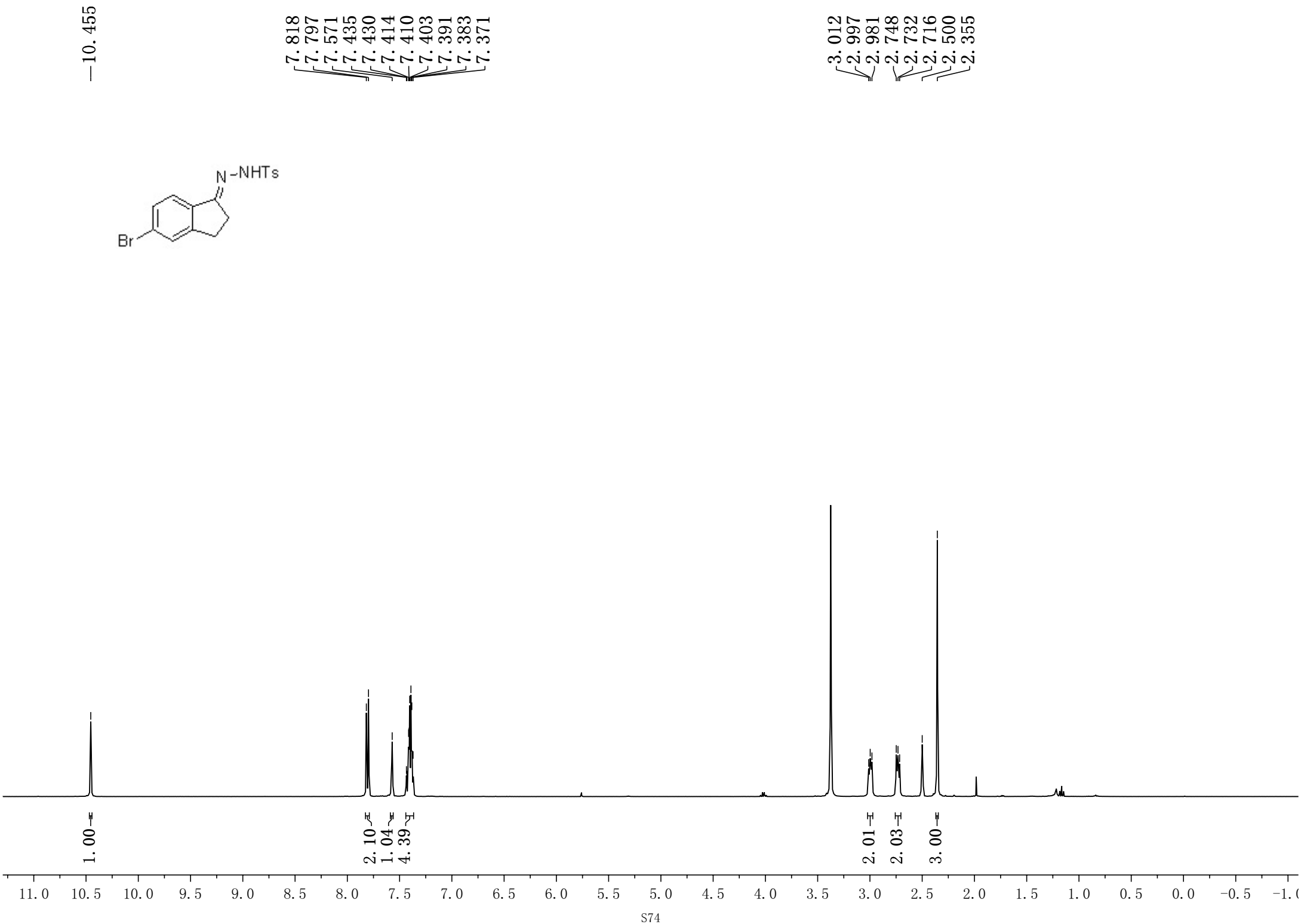
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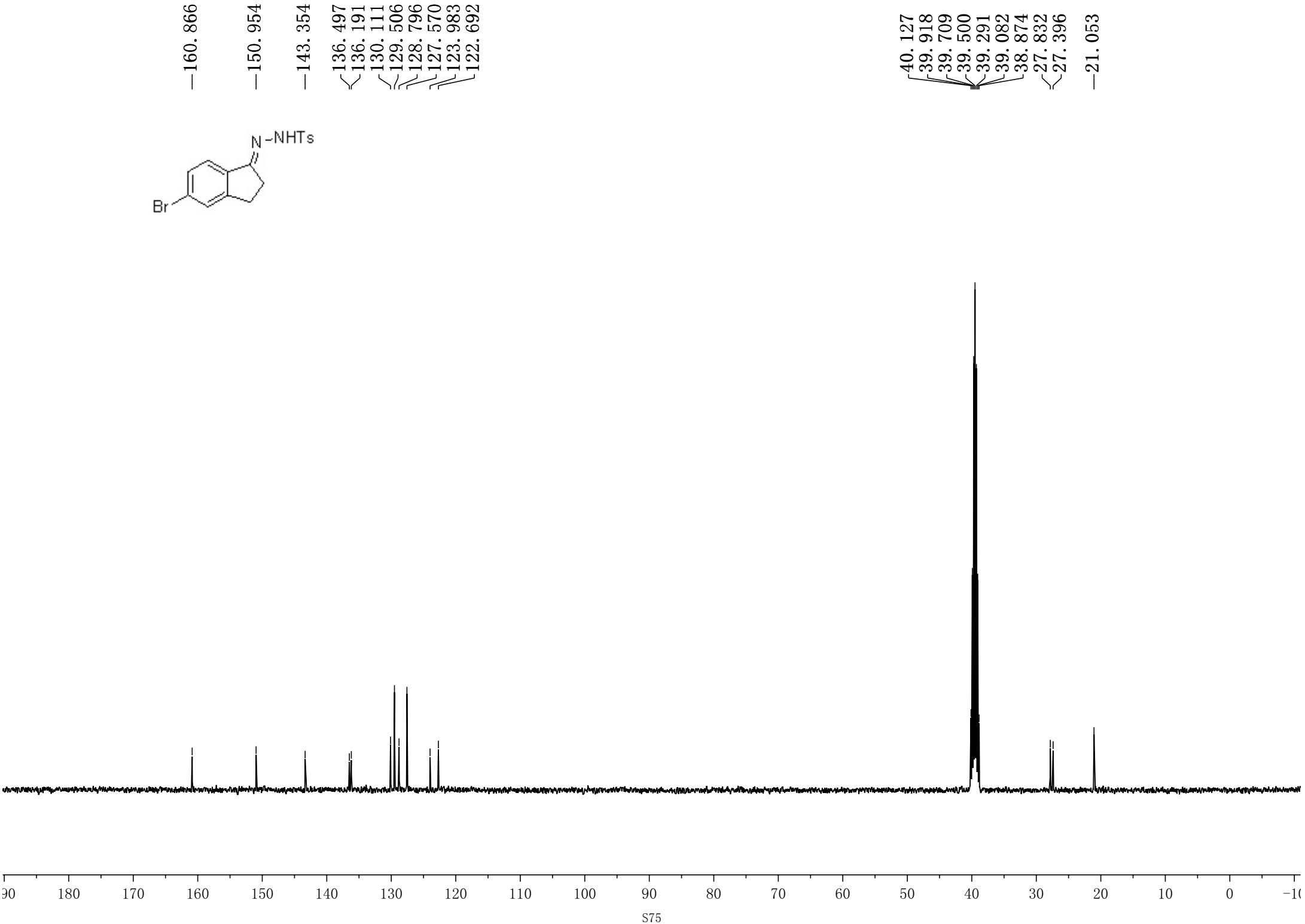
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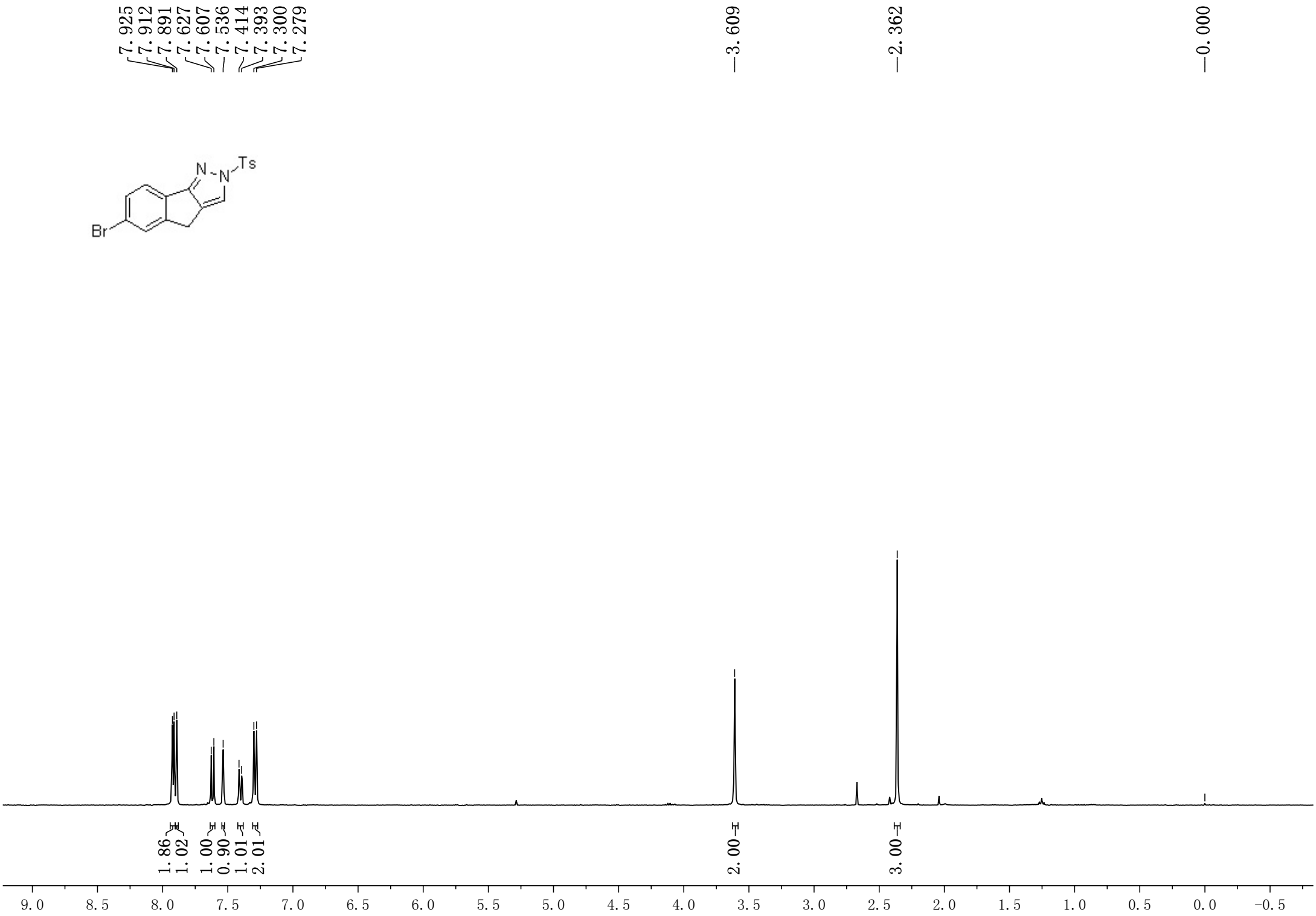
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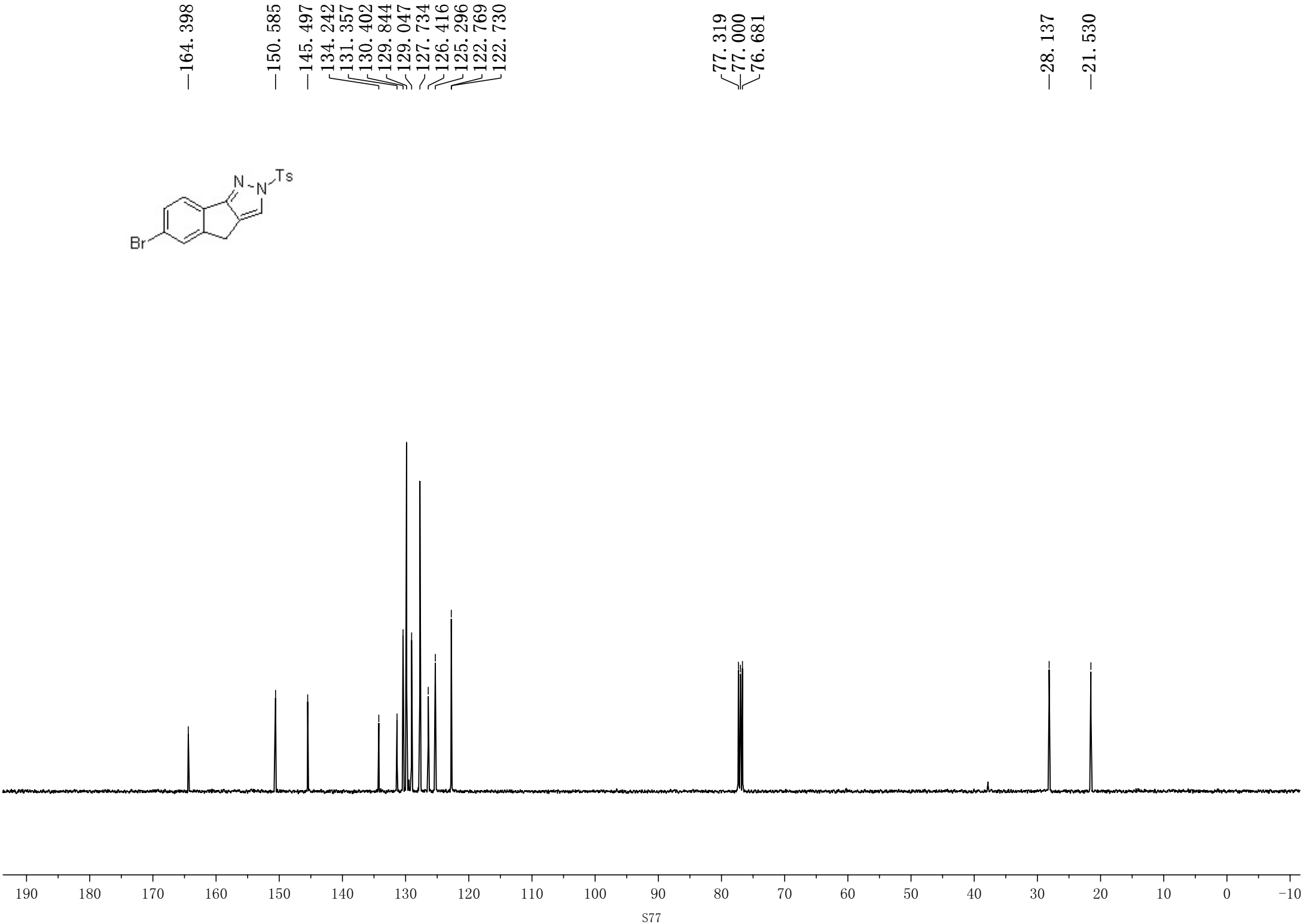
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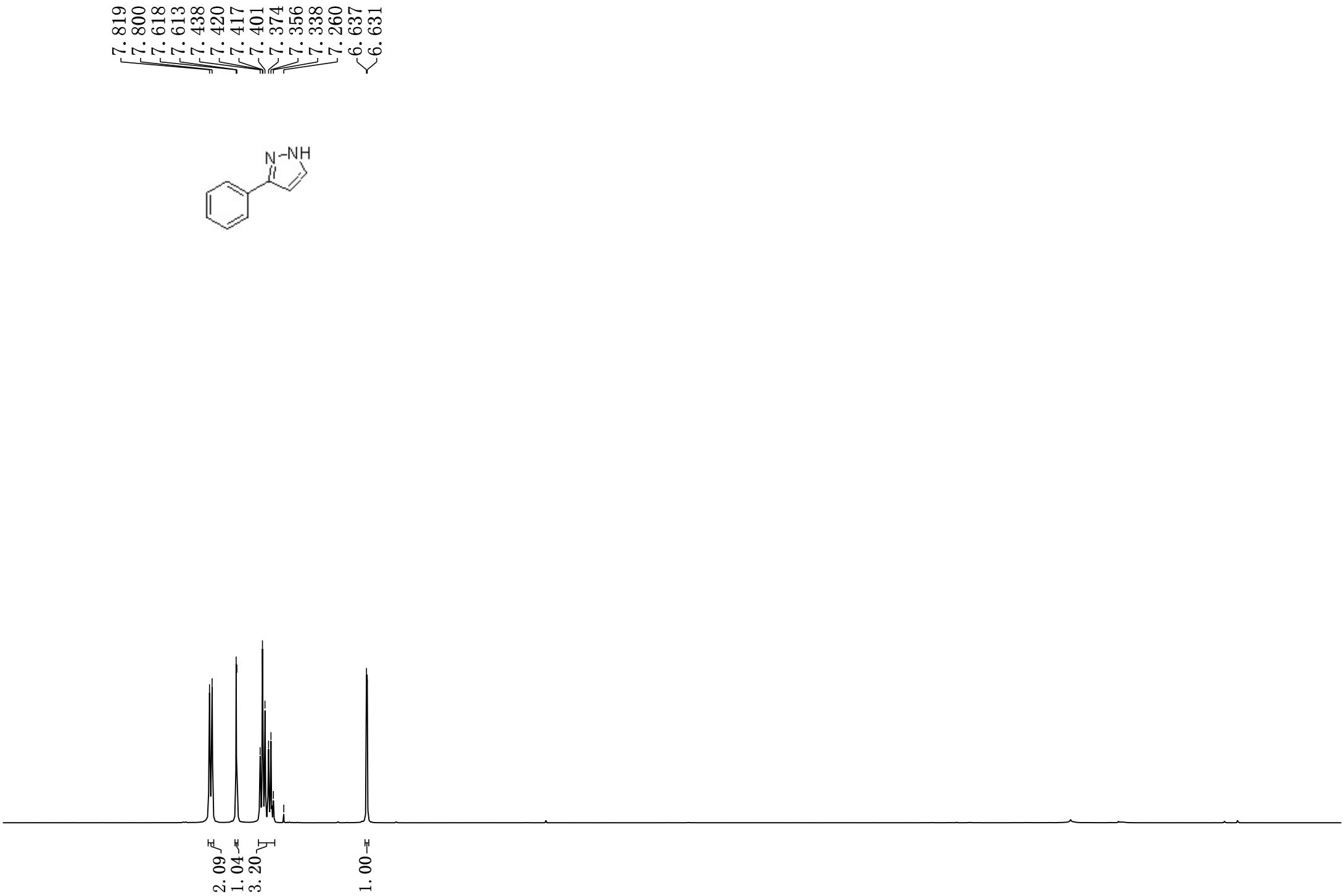
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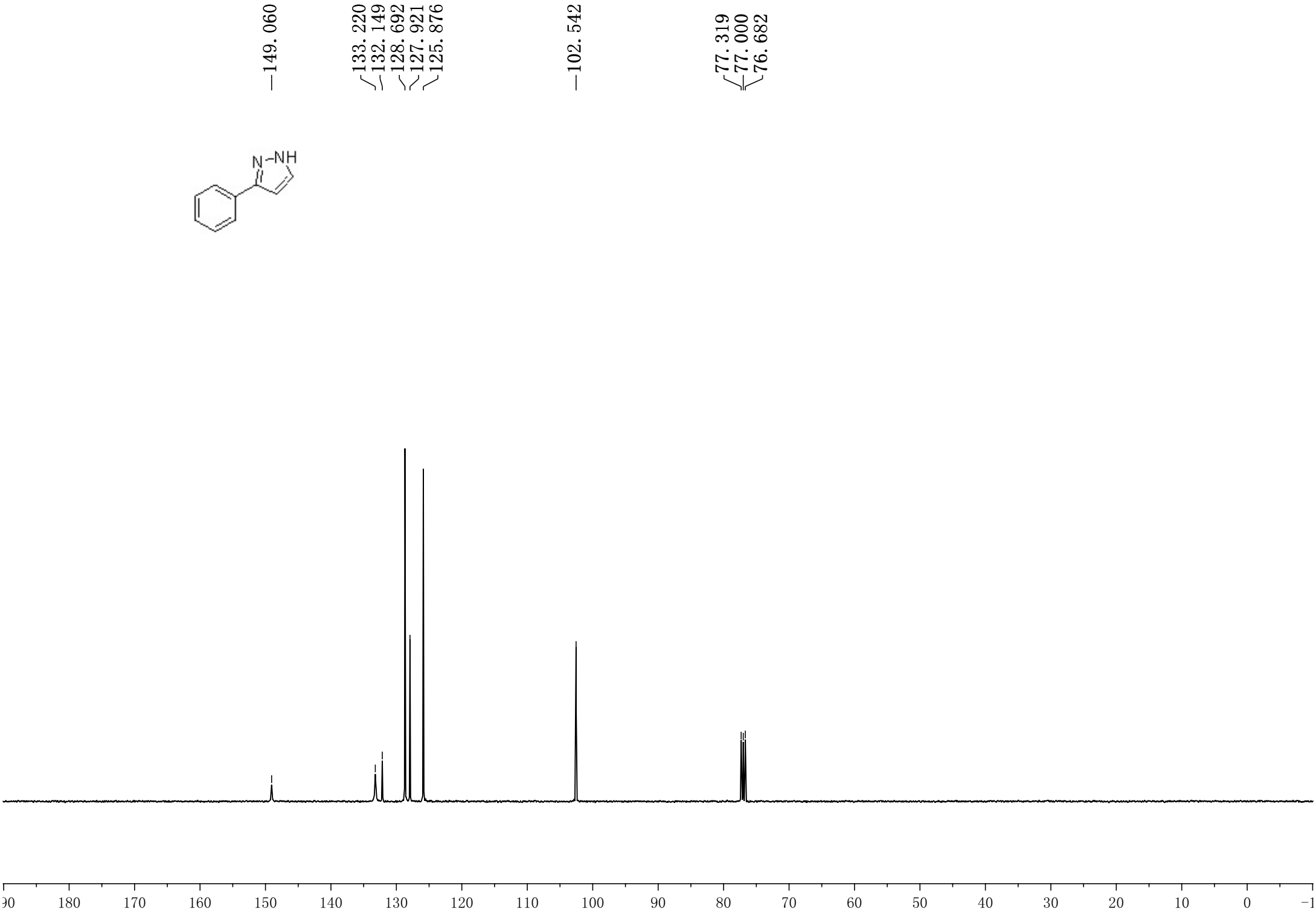
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