Electronic Supplementary Material (ESI) for RSC Advances.

$K_2S_2O_8$/Arenesulfinate: an Unprecedented Thiolating System Enabling Selective Sulfenylation of Indoles under Metal-Free Conditions**

Honghua Rao, Ping Wang, Jianchun Wang, Zhongfeng Li, Xinzhan Sun and Shengli Cao*

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General experimental procedure

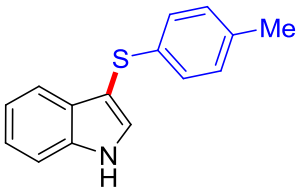
All reactions were carried out under a nitrogen atmosphere unless otherwise stated. All chemicals were directed used as purchased from Alfa-Aesar, Aladdin Industrial Corporation, and Energy Chemical Company. Analytical thin-layer chromatography (TLC) and preparative thin layer chromatography (PTLC) were performed using silica gel 60 HF254 pre-coated plates (0.4-0.6 mm). The developed chromatography was analyzed by UV lamp (254 nm) as visualization methods. Flash column chromatography was performed with silica gel 60 (230–400 mesh). Nuclear magnetic resonance (NMR) spectra were recorded on Varian-600 spectrometer (^{1}H 600 MHz, ^{13}C 150 MHz). Chemical shifts for ^{1}H-NMR spectra are reported in parts per million (ppm) with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm, DMSO: 2.50 ppm). Chemical shifts for ^{13}C-NMR spectra are reported in parts per million (ppm) with the solvent as the internal standard ($CDCl_3$: 77.0 ppm; DMSO: 40.00 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, td = triplet of doublets, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

General procedure for selective sulfenylation of indoles to 3-arylthioindoles 3a-q

An oven-dried reaction vessel was charged with indoles (0.20 mmol, 1.0 equiv.), sodium arenesulfinate ($ArSO_2Na$, 0.30 mmol, 1.5 equiv.), and $K_2S_2O_8$ (0.20 mmol, 1.0 equiv.; 54.1 mg). After the reaction vessel was purged with nitrogen for 3-4 times, acetonitrile/distilled water (1.0 mL, *v/v* ratio 10:1) were added by syringe sequentially under nitrogen, then the sealed reaction vessel was placed into an oil bath, and stirred at 100 ^{o}C for 24 h. The resulting mixture was cooled to room temperature, extracted with EtOAc (20 mL x 3), washed with brine (10 mL) and dried over anhydrous Na_2SO_4. The above solution was evaporated under vacuum, and the residue was purified by silica gel column with petroleum ether/ethyl acetate as the eluent to give

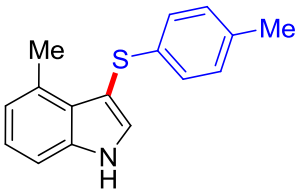
the analytically 3-arylthioindole products **3a-q**.

The spectroscopic data of 3-arylthioindoles 3a-q



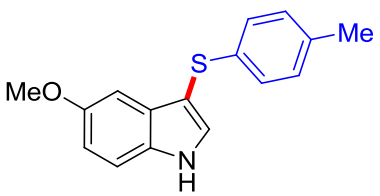
3a

3-*p*-Tolylthioindole (3a).[1] Eluent: ethyl acetate/petroleum ether 1:20. Yield 89% (42.9 mg from 23.6 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.39 (s, br, 1 H), 7.63 (d, J = 7.92 Hz, 1 H), 7.47 (d, J = 2.34 Hz, 1 H), 7.43 (d, J = 8.16 Hz, 1 H), 7.26 (td, J = 7.62, 0.78 Hz, 1 H), 7.17 (t, J = 7.50 Hz, 1 H), 7.04 (d, J = 8.22 Hz, 2 H), 6.98 (d, J = 8.10 Hz, 2 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 136.5, 135.5, 134.6, 130.4, 129.5, 129.1, 126.2, 123.0, 120.8, 119.7, 111.5, 103.5, 20.9. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{14}NS$: 240.0847; found 240.0842.



3b

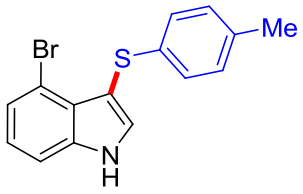
4-Methyl-3-*p*-tolylthioindole (3b).[1] Eluent: ethyl acetate/petroleum ether 1:25. Yield 80% (40.8 mg from 26.4 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.41 (s, br, 1 H), 7.42 (d, J = 2.58 Hz, 1 H), 7.28-7.26 (m, 1 H), 7.14 (t, J = 7.65 Hz, 1 H), 7.00 (d, J = 8.58 Hz, 2 H), 6.98 (d, J = 8.46 Hz, 2 H), 6.89 (d, J = 7.14 Hz, 1 H), 2.66 (s, 3 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.9, 137.0, 134.2, 132.1, 131.7, 129.5, 127.0, 125.4, 123.0, 122.4, 109.4, 102.8, 20.8, 18.6. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{16}NS$: 254.1003; found 254.0997.



3c

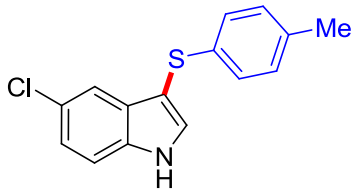
5-Methoxy-3-*p*-tolylthioindole (3c).[2] Eluent: ethyl acetate/petroleum ether 1:20.

Yield 85% (46.4 mg from 29.8 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.35 (s, br, 1 H), 7.42 (d, J = 2.64 Hz, 1 H), 7.31 (d, J = 8.76 Hz, 1 H), 7.06 (d, J = 2.40 Hz, 1 H), 7.03 (d, J = 8.28 Hz, 2 H), 6.99 (d, J = 8.04 Hz, 2 H), 6.91 (dd, J = 8.82, 2.46 Hz, 1 H), 3.79 (s, 3 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 155.1, 135.6, 134.5, 131.3, 131.1, 130.0, 129.5, 126.0, 113.5, 112.4, 102.8, 100.8, 55.8, 20.8. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{16}NOS$: 270.0953; found 270.0944.



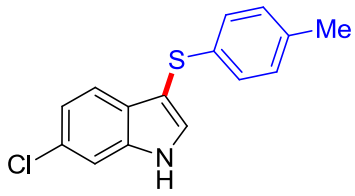
3d

4-Bromo-3-*p*-tolylthioindole (3d).[3] Eluent: ethyl acetate/petroleum ether 1:20. Yield 69% (44.0 mg from 39.3 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.57 (s, br, 1 H), 7.46 (d, J = 2.58 Hz, 1 H), 7.36 (d, J = 8.16 Hz, 1 H), 7.33 (d, J = 7.62 Hz, 1 H), 7.07 (t, J = 7.89 Hz, 1 H), 7.03-7.00 (m, 4 H), 2.27 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.6, 137.3, 134.5, 132.9, 129.5, 126.3, 126.2, 125.7, 123.8, 114.6, 111.1, 104.3, 20.9. HR-ESI-MS: $[M+Na]^+$ *m/z* cald. for $C_{15}H_{12}BrNSNa$: 339.9772; found 339.9765.



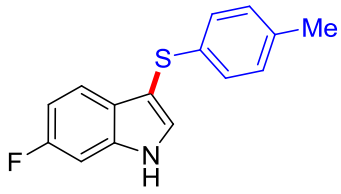
3e

5-Chloro-3-*p*-tolylthioindole (3e).[1] Eluent: ethyl acetate/petroleum ether 1:20. Yield 71% (39.9 mg from 31.1 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.49 (s, br, 1 H), 7.59 (d, J = 1.92 Hz, 1 H), 7.48 (d, J = 2.58 Hz, 1 H), 7.33 (d, J = 8.58 Hz, 1 H), 7.20 (dd, J = 8.64, 1.98 Hz, 1 H), 7.02 (d, J = 8.46 Hz, 2 H), 6.99 (d, J = 8.40 Hz, 2 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 134.9, 134.8, 131.7, 130.4, 129.9, 129.6, 126.8, 126.3, 123.4, 119.2, 112.6, 103.5, 20.9. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{13}ClNS$: 274.0457; found 274.0456.



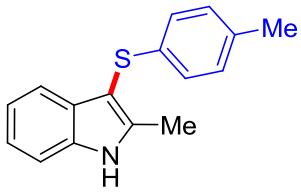
3f

6-Chloro-3-*p*-tolylthioindole (3f).[3] Eluent: ethyl acetate/petroleum ether 1:20. Yield 73% (40.6 mg from 30.8 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.39 (s, br, 1 H), 7.50 (d, J = 8.46 Hz, 1 H), 7.45 (d, J = 2.52 Hz, 1 H), 7.41 (d, J = 1.32 Hz, 1 H), 7.12 (dd, J = 8.46, 1.68 Hz, 1 H), 7.02 (d, J = 8.22 Hz, 2 H), 6.99 (d, J = 8.22 Hz, 2 H), 6.98 (d, J = 8.34 Hz, 2 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 136.8, 134.9, 130.9, 129.9, 129.5, 129.0, 127.7, 126.4, 121.6, 120.6, 111.5, 104.1, 20.9. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{13}ClNS$: 274.0457; found 274.0452.



3g

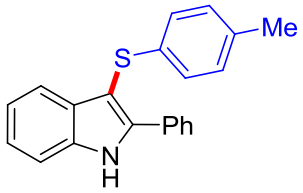
6-Fluoro-3-*p*-tolylthioindole (3g).[4] Eluent: ethyl acetate/petroleum ether 1:40. Yield 78% (39.7 mg from 26.7 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.45 (s, br, 1 H), 7.50 (dd, J = 3.36, 8.70 Hz, 1 H), 7.10 (dd, J = 7.14, 2.22 Hz, 1 H), 7.03 (d, J = 8.22 Hz, 2 H), 6.99 (d, J = 8.10 Hz, 2 H), 6.91 (td, J = 9.15, 2.22 Hz, 1 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 160.4 (d, J = 237.8 Hz), 136.4 (d, J = 12.5 Hz), 135.1, 134.8, 130.6 (d, J = 3.3 Hz), 129.5, 126.4, 125.5, 124.9, 120.6 (d, J = 10.1 Hz), 109.6 (d, J = 24.5 Hz), 103.9, 97.9 (d, J = 26.3 Hz), 20.8. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{13}FNS$: 258.0753; found 258.0749.



3h

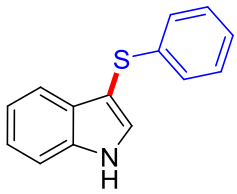
2-Methyl-3-*p*-tolylthioindole (3h).[5] Eluent: ethyl acetate/petroleum ether 1:25. Yield 91% (48.2 mg from 27.4 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.20 (s, br, 1 H), 7.57 (d, J = 7.86 Hz, 1 H), 7.33 (d, J = 8.04 Hz, 1 H), 7.20 (td, J =

7.58, 1.14 Hz, 1 H), 7.14 (td, J = 7.47, 0.96 Hz, 1 H), 6.98 (s, 4 H), 2.51 (s, 3 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 140.9, 135.7, 135.4, 134.3, 130.3, 129.5, 125.8, 122.1, 120.6, 119.0, 110.6, 99.8, 20.8, 12.1. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{16}NS$: 254.1003; found 254.0997.



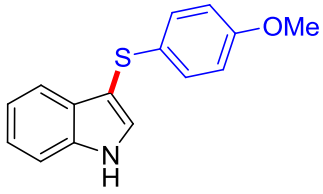
3i

2-Phenyl-3-*p*-tolylthioindole (3i).[6] Eluent: ethyl acetate/petroleum ether 1:30. Yield 74% (46.8 mg from 38.7 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.57 (s, br, 1 H), 7.78 (dt, J = 7.50, 1.44 Hz, 2 H), 7.65 (d, J = 7.86 Hz, 1 H), 7.44 (d, J = 7.53 Hz, 3 H), 7.39 (tt, J = 7.38, 2.10 Hz, 1 H), 7.28 (td, J = 7.62, 1.08 Hz, 1 H), 7.17 (t, J = 7.50 Hz, 1 H), 7.02 (d, J = 8.34 Hz, 2 H), 6.98 (d, J = 8.10 Hz, 2 H), 2.26 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 141.8, 135.8, 135.6, 134.3, 131.5, 131.2, 129.6, 128.7, 128.6, 128.1, 125.7, 123.3, 121.1, 120.0, 111.1, 99.9. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{21}H_{18}NS$: 316.1160; found 316.1153.



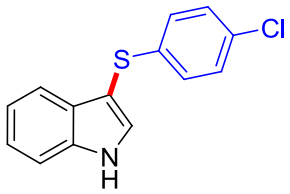
3j

3-Phenylthioindole (3j).[1] Eluent: ethyl acetate/petroleum ether 1:20. Yield 83% (38.4 mg from 24.2 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.42 (s, br, 1 H), 7.62 (d, J = 7.92 Hz, 1 H), 7.49 (d, J = 2.58 Hz, 1 H), 7.44 (d, J = 8.22 Hz, 1 H), 7.27 (t, J = 7.14 Hz, 1 H), 7.18-7.15 (m, 3 H), 7.11 (dd, J = 7.14, 1.32 Hz, 2 H), 7.06 (t, J = 7.23 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 139.2, 136.5, 130.7, 129.1, 128.7, 125.8, 124.8, 123.0, 119.7, 111.6, 102.8. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{14}H_{12}NS$: 226.0690; found 226.0683.



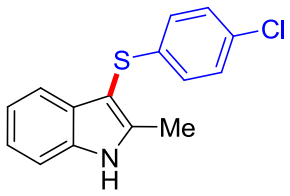
3k

3-(4-Methoxypehnylthio)indole (3k).[3] Eluent: ethyl acetate/petroleum ether 1:20. Yield 87% (45.2 mg from 23.8 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.26 (s, br, 1 H), 7.57 (d, J = 7.92 Hz, 1 H), 7.35 (d, J = 2.34 Hz, 1 H), 7.32 (d, J = 8.10 Hz, 1 H), 7.18 (t, J = 7.53 Hz, 1 H), 7.11-7.06 (m, 3 H), 6.67 (d, J = 8.76 Hz, 2 H), 3.66 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 157.8, 136.4, 130.1, 129.5, 129.0, 128.5, 122.9, 120.8, 119.6, 114.5, 111.5, 104.5, 55.3. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{14}NOS$: 256.0796; found 256.0791.



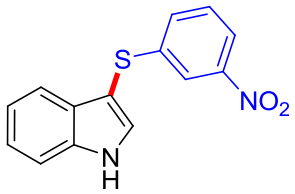
3l

3-(4-Chlorophenylthio)indole (3l).[1] Eluent: ethyl acetate/petroleum ether 1:20. Yield 87% (45.3 mg from 23.5 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.47 (s, br, 1 H), 7.58 (d, J = 7.92 Hz, 1 H), 7.49 (d, J = 2.58 Hz, 1 H), 7.45 (d, J = 8.16 Hz, 1 H), 7.28 (t, J = 7.59 Hz, 1 H), 7.18 (t, J = 7.50 Hz, 1 H), 7.12 (d, J = 8.58 Hz, 2 H), 7.02 (d, J = 8.64 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.8, 136.5, 130.7, 130.5, 128.8, 128.7, 127.1, 123.2, 121.0, 119.5, 111.7, 102.4. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{14}H_{11}ClNS$: 260.0301; found 260.0293.



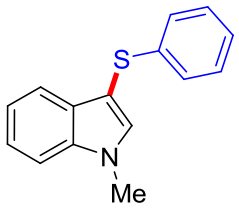
3m

2-Methyl-3-(4-chlorophenylthio)indole (3m).[7] Eluent: ethyl acetate/petroleum ether 1:20. Yield 88% (50.4 mg from 27.4 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.64 (s, br, 1 H), 7.94 (s, 1 H), 7.88 (d, J = 7.92 Hz, 1 H), 7.57 (d, J = 7.86 Hz, 1 H), 7.54 (d, J = 1.98 Hz, 1 H), 7.48 (d, J = 8.16 Hz, 1 H), 7.37 (d, J = 7.80 Hz, 1 H), 7.32-7.28 (m, 2 H), 7.20 (t, J = 7.44, 1 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 148.6, 142.6, 136.6, 131.3, 129.3, 128.5, 123.4, 121.3, 120.2, 119.6, 119.1, 112.0, 100.7. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{13}ClNS$: 274.0457; found 274.0450.



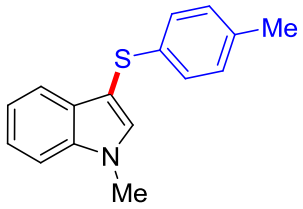
3n

3-(3-nitrophenylthio)indole (3n).[3] Eluent: ethyl acetate/petroleum ether 1:10. Yield 89% (48.9 mg from 23.7 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 8.30 (s, br, 1 H), 7.52 (d, J = 7.86 Hz, 1 H), 7.35 (d, J = 8.10 Hz, 1 H), 7.21 (td, J = 7.59, 1.02 Hz, 1 H), 7.14 (t, J = 7.44 Hz, 1 H), 7.11 (d, J = 8.58 Hz, 2 H), 6.96 (d, J = 8.64 Hz, 2 H), 2.51 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 141.2, 138.0, 135.4, 130.2, 130.0, 128.7, 126.7, 122.3, 120.8, 118.8, 110.7, 98.9, 29.7. HR-ESI-MS: $[M+Na]^+$ *m/z* cald. for $C_{14}H_{10}N_2O_2SNa$: 293.0361; found 293.0357.



3o

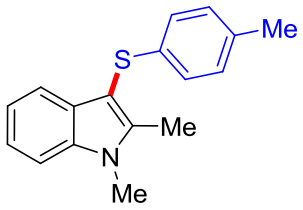
***N*-Methyl-3-phenylthioindole (2o)**.[1] Eluent: ethyl acetate/petroleum ether 1:40. Yield 79% (39.9 mg from 27.6 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.62 (d, J = 7.92 Hz, 1 H), 7.40 (d, J = 8.28 Hz, 1 H), 7.34 (s, 1 H), 7.31 (t, J = 7.62 Hz, 1 H), 7.19-7.15 (m, 3 H), 7.11 (d, J = 7.26 Hz, 2 H), 7.05 (t, J = 7.20 Hz, 1 H), 3.85 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 139.7, 137.5, 135.0, 129.8, 128.6, 125.7, 124.6, 122.5, 120.5, 119.7, 109.7, 100.5, 33.1. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{14}NS$: 240.0847; found 240.0842.



3p

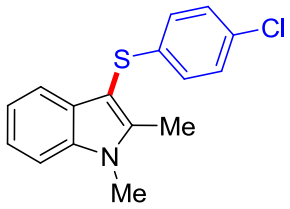
***N*-Methyl-3-*p*-tolylthioindole (3p)**.[7] Eluent: ethyl acetate/petroleum ether 1:40. Yield 80% (40.7 mg from 26.3 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.63 (d, J = 7.92 Hz, 1 H), 7.38 (d, J = 8.22 Hz, 1 H), 7.33 (s, 1 H), 7.30 (t, J = 7.62 Hz, 1 H), 7.17 (t, J = 7.47 Hz, 1 H), 7.03 (d, J = 8.22 Hz, 2 H), 6.98 (d, J = 8.04 Hz, 2

H), 3.84 (s, 3 H), 2.25 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 137.5, 135.9, 134.8, 134.5, 129.8, 129.4, 126.1, 122.5, 120.4, 119.8, 109.6, 101.2, 33.1, 20.8. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{16}NS$: 254.1003; found 254.0997.



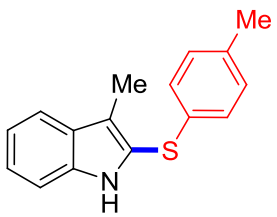
3q

1,2-Dimethyl-3-*p*-tolylthioindole (3q).[4] Eluent: ethyl acetate/petroleum ether 1:50. Yield 91% (50.1 mg from 29.9 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.60 (d, J = 7.86 Hz, 1 H), 7.34 (d, J = 8.22 Hz, 1 H), 7.24 (td, J = 7.62, 1.08 Hz, 1 H), 7.14 (td, J = 7.44, 0.78 Hz, 1 H), 6.98-6.95 (m, 4 H), 3.76 (s, 3 H), 2.53 (s, 3 H), 2.25 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 142.7, 137.0, 136.1, 134.1, 129.8, 129.4, 125.6, 121.7, 120.4, 119.0, 108.9, 98.6, 30.3, 20.8, 10.9. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{17}H_{18}NS$: 268.1160; found 268.1153.



3r

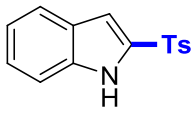
1,2-Dimethyl-3-(4-chlorophenylthio)indole (3r).[4] Eluent: ethyl acetate/petroleum ether 1:50. Yield 88% (50.8 mg from 29.1 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.59 (d, J = 7.86 Hz, 1 H), 7.35 (d, J = 8.16 Hz, 1 H), 7.25 (t, J = 7.83 Hz, 1 H), 7.15 (t, J = 7.44 Hz, 1 H), 7.10 (dd, J = 8.58, 1.74 Hz, 2 H), 6.94 (d, J = 8.58 Hz, 2 H), 3.77 (s, 3 H), 2.51 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 142.9, 138.4, 137.1, 130.1, 129.5, 128.7, 126.6, 121.9, 120.6, 118.8, 109.1, 97.6, 30.4, 10.8. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{15}ClNS$: 288.0614; found 288.0608.



3s

3-Methyl-2-*p*-Tolylthioindole (3s).[3] Eluent: ethyl acetate/petroleum ether 1:20. Yield 34% (17.3 mg from 26.2 mg starting material). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 7.96 (s, br, 1 H), 7.60 (d, J = 7.98 Hz, 1 H), 7.29 (d, J = 8.04 Hz, 1 H), 7.24 (t, J = 8.25 Hz, 1 H), 7.15 (t, J = 7.47 Hz, 1 H), 7.04 (d, J = 8.16 Hz, 2 H), 7.00 (d, J = 8.10 Hz, 2 H), 2.41 (s, 3 H), 2.29 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 135.7, 134.8, 132.2, 128.8, 127.5, 126.1, 122.3, 121.2, 118.5, 118.30, 118.27, 109.7, 19.9, 8.4. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{16}H_{16}NS$: 254.1003; found 254.0997.

The spectroscopic data of 2-*p*-tosylindole 4



4

Eluent: ethyl acetate/petroleum ether 1:10. Yield 29% ^{1}H NMR ($CDCl_3$, 600 MHz, ppm) δ 9.31 (s, br, 1 H), 7.90 (d, J = 7.98 Hz, 2 H), 7.66 (d, J = 8.10 Hz, 1 H), 7.42 (d, J = 8.34 Hz, 1 H), 7.32 (t, J = 7.65 Hz, 1 H), 7.28 (d, J = 7.98 Hz, 2 H), 7.19-7.15 (m, 2 H), 2.38 (s, 3 H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm) δ 144.5, 138.5, 137.1, 134.4, 130.0, 127.3, 127.0, 125.9, 122.6, 121.5, 112.3, 108.8, 21.6. HR-ESI-MS: $[M+H]^+$ *m/z* cald. for $C_{15}H_{14}NO_2S$: 272.0745; found 272.0742.

Reference

[1] F. Xiao, H. Xie, S. Liu, G.-J. Deng, *Adv. Synth. Catal.* 2014, **356**, 364.

[2] Ch. D. Prasad, S. Kumar, Moh. Sattar, A. Adhikary, S. Kumar, *Org. Biomol. Chem.* 2013, **11**, 8036.

[3] F. Yang, S.-K. Tian, *Angew. Chem. Int. Ed.* 2013, **52**, 4929.

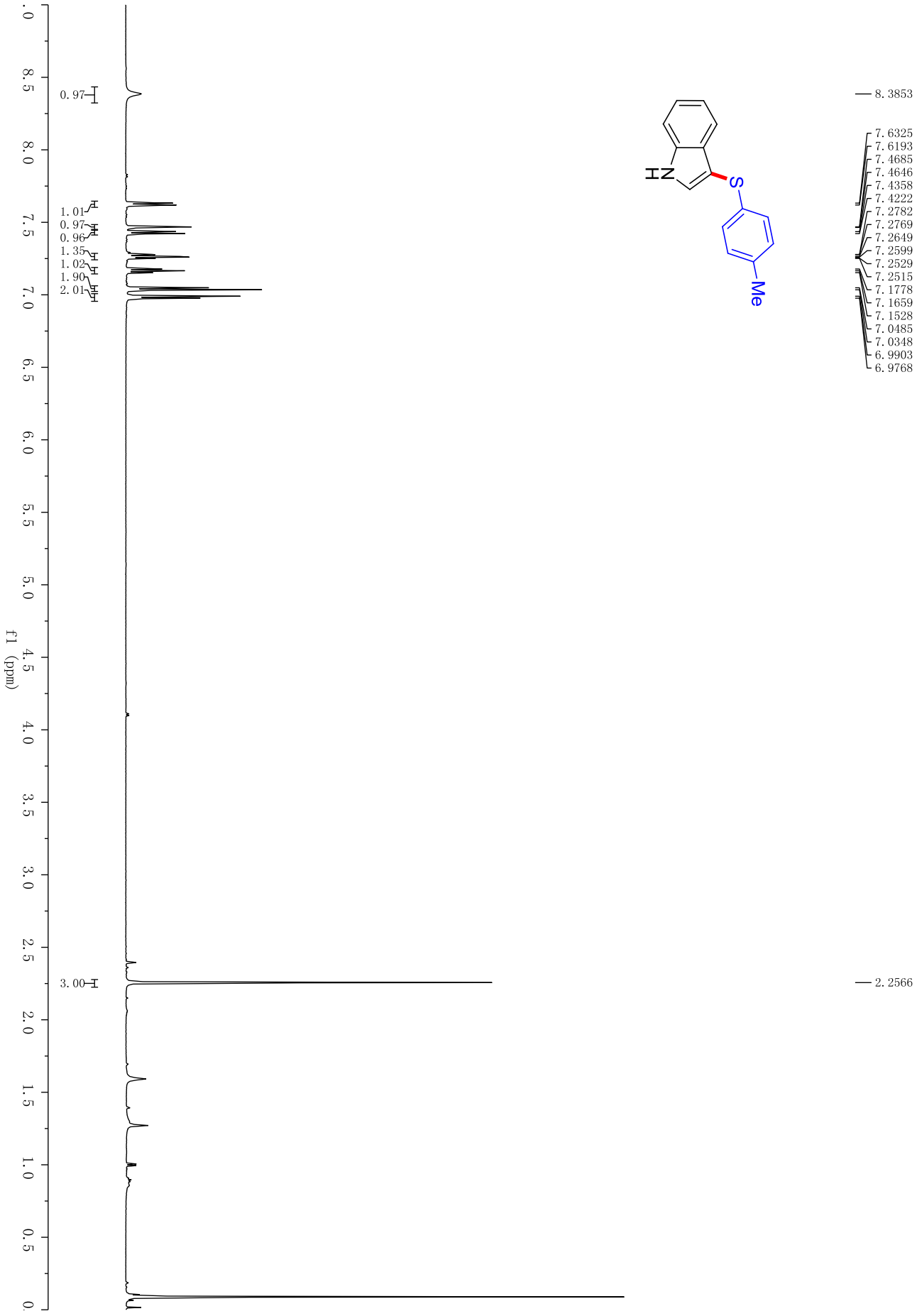
[4] M. Chen, Z. Huang, Q. Zheng, *Chem. Commun.* 2012, **48**, 11686.

[5] W. Ge, Y. Wei, *Green Chem.* 2012, **14**, 2066.

[6] Y. Guo, R. Tang, J.-H. Li, P. Zhong, X. Zhang, *Adv. Synth. Catal.* 2009, **351**, 2615.

[7] D. Huang, J. Chen, W. Dan, J. Ding, M. Liu, H. Wu, *Adv. Synth. Catal.* 2012, **354**, 2123..

Copies of the ^{1}H- and ^{13}C-NMR spectra for 3-arylthioindoles 3a-q and 4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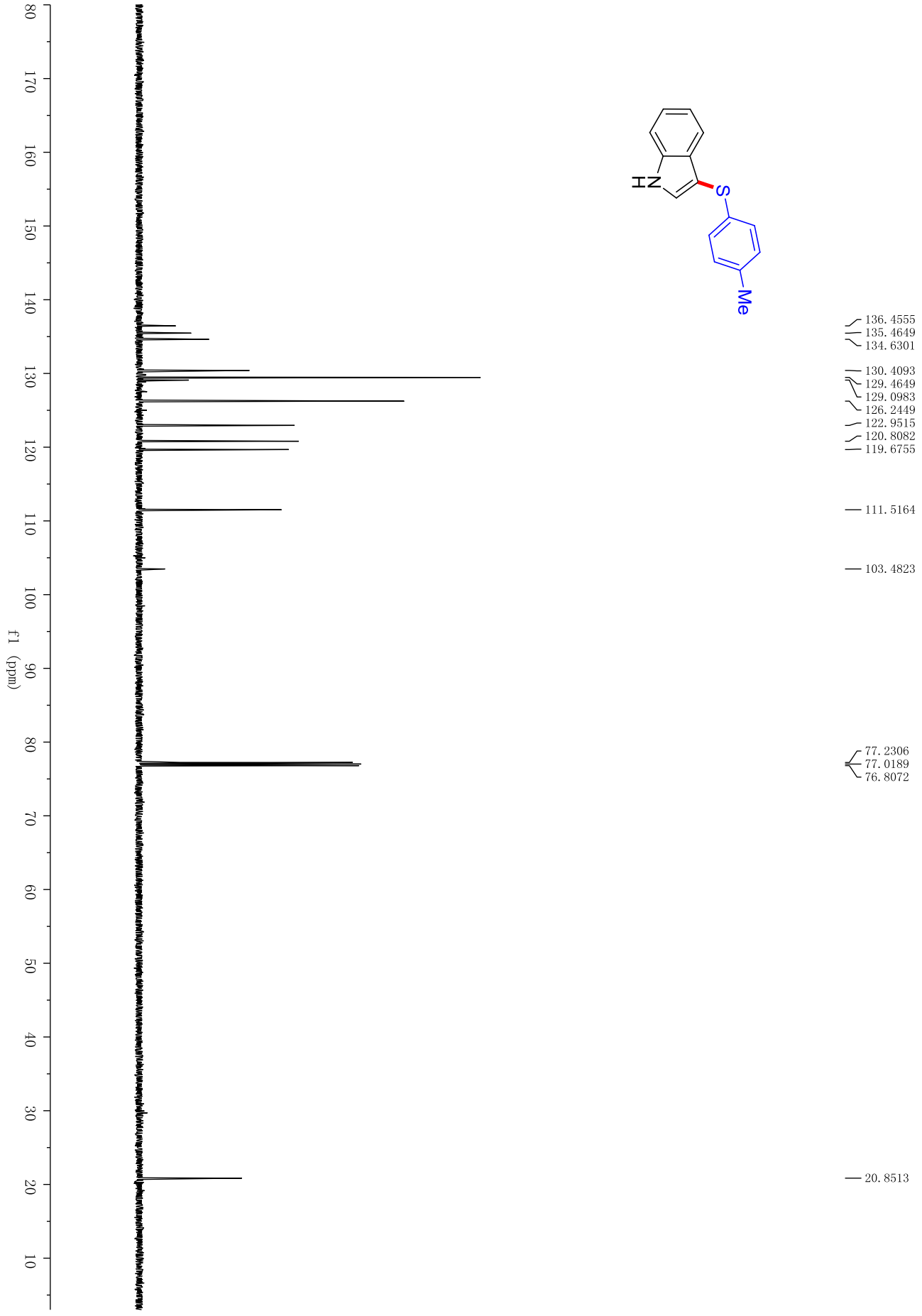
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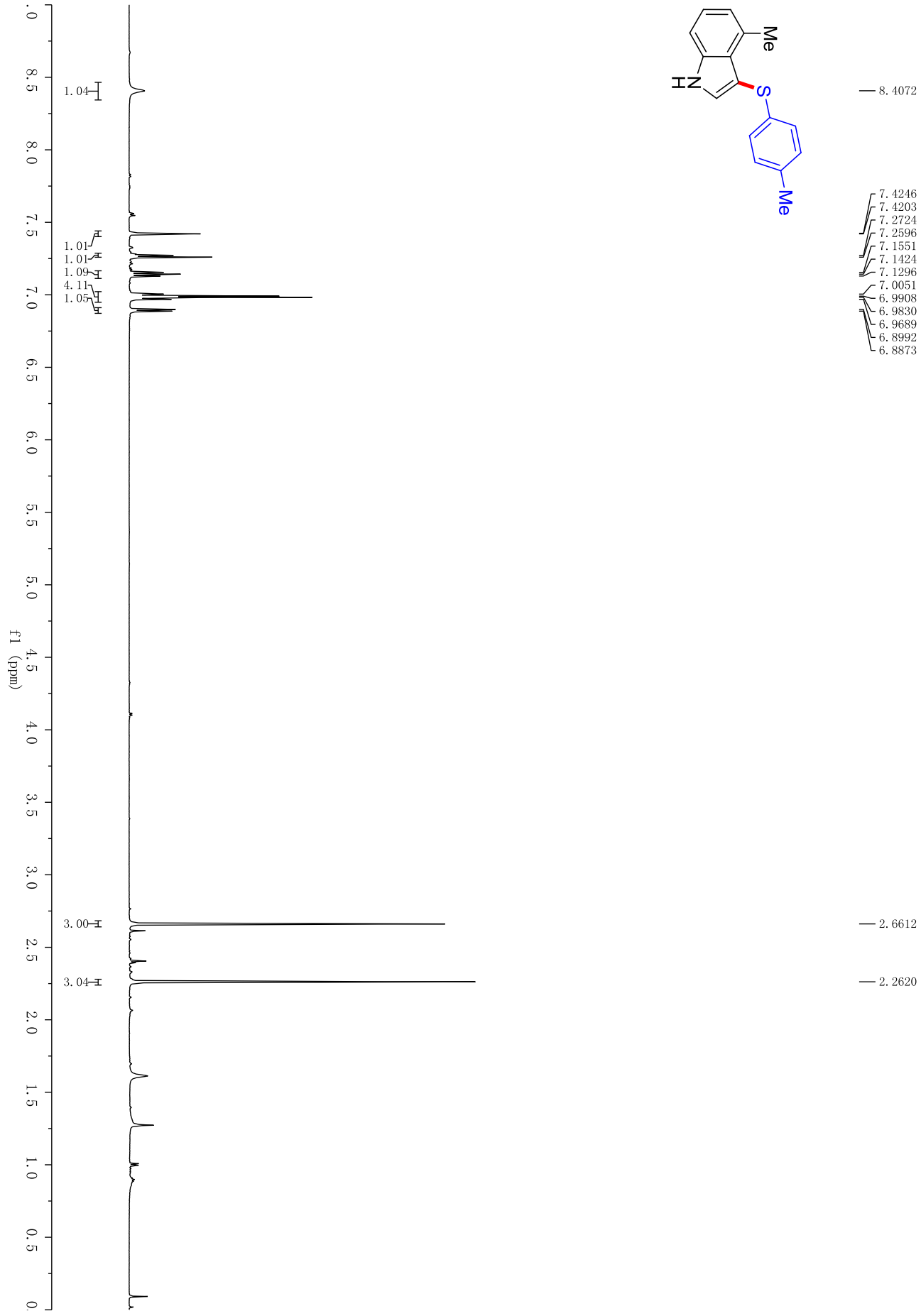
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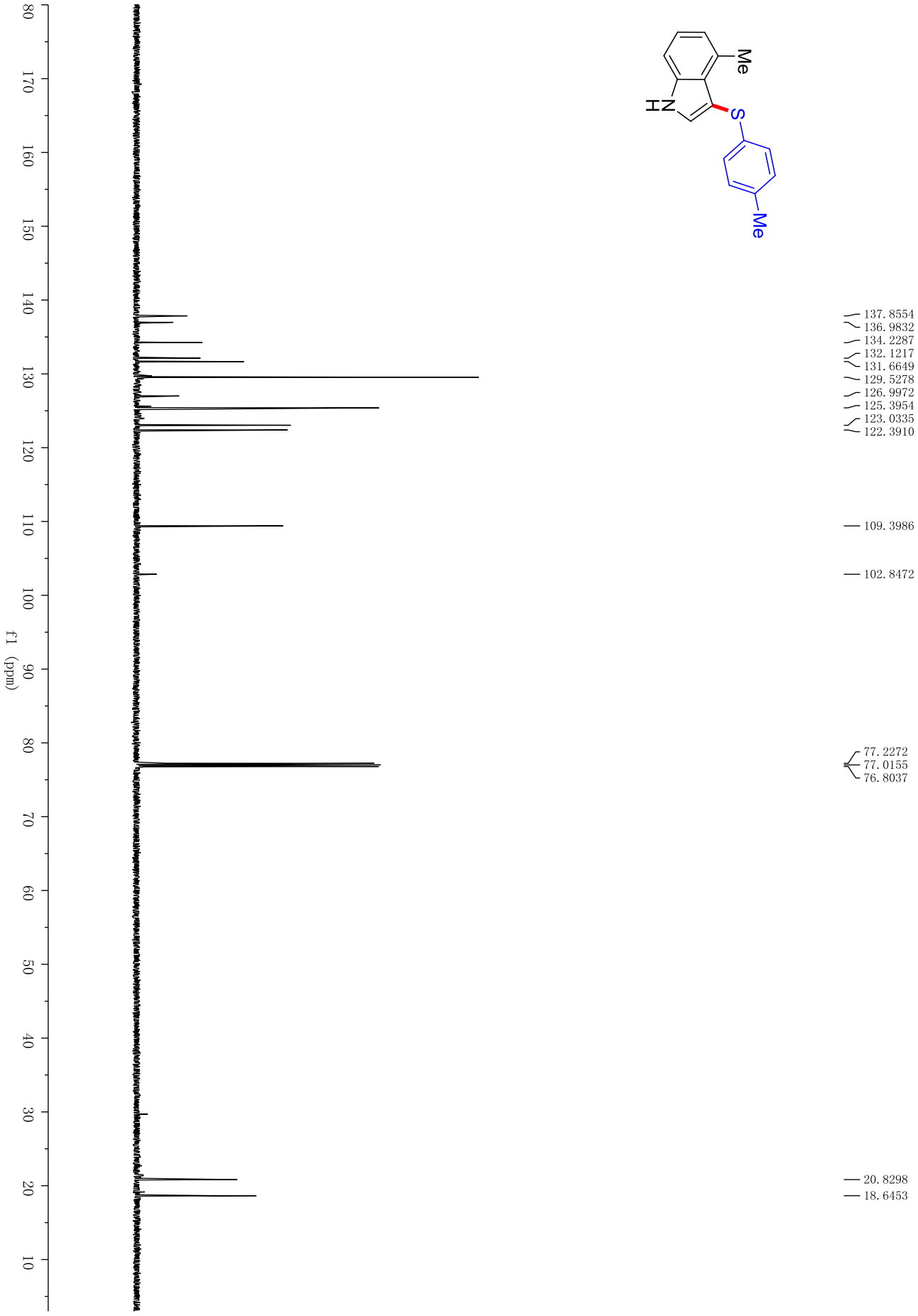
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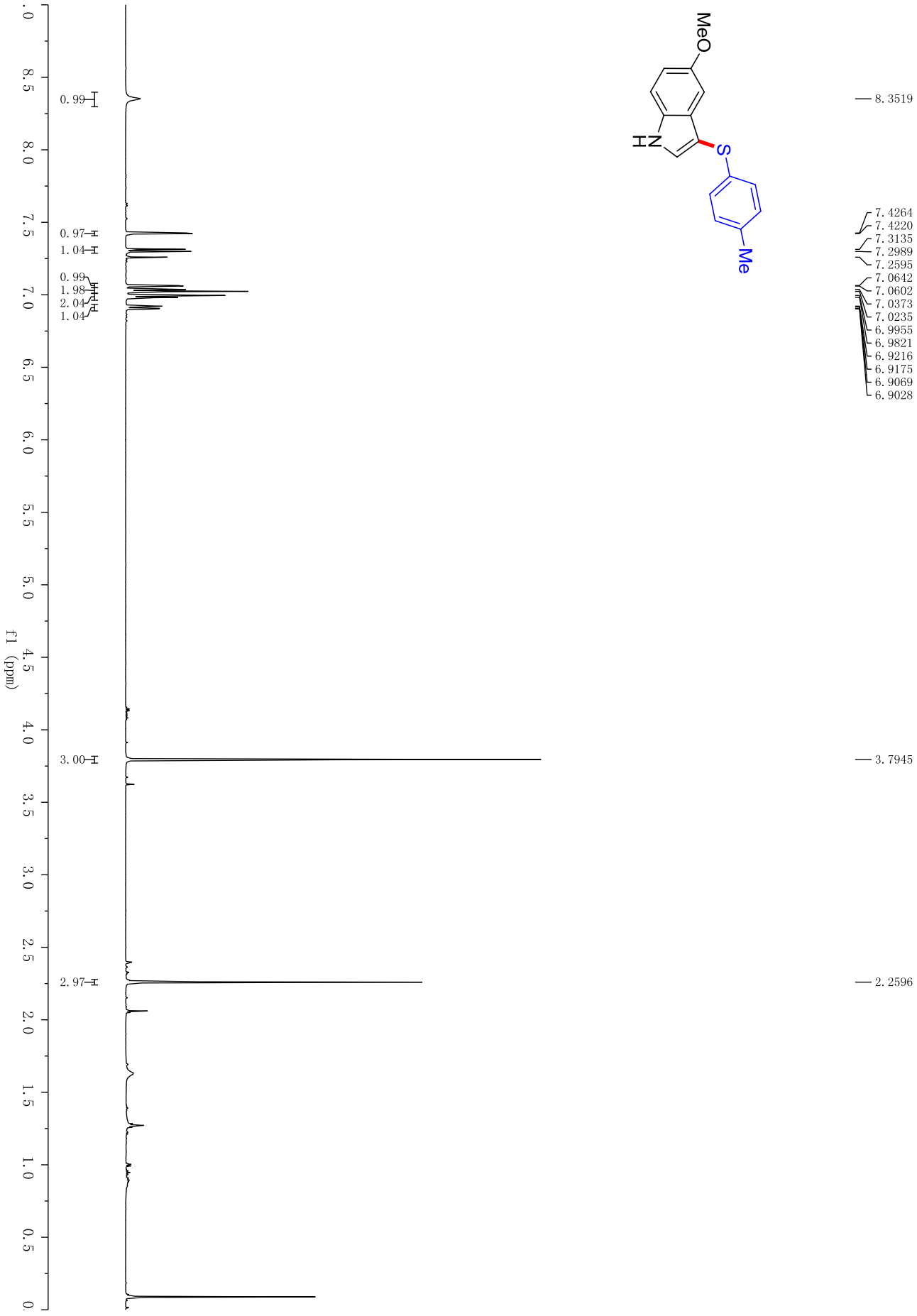
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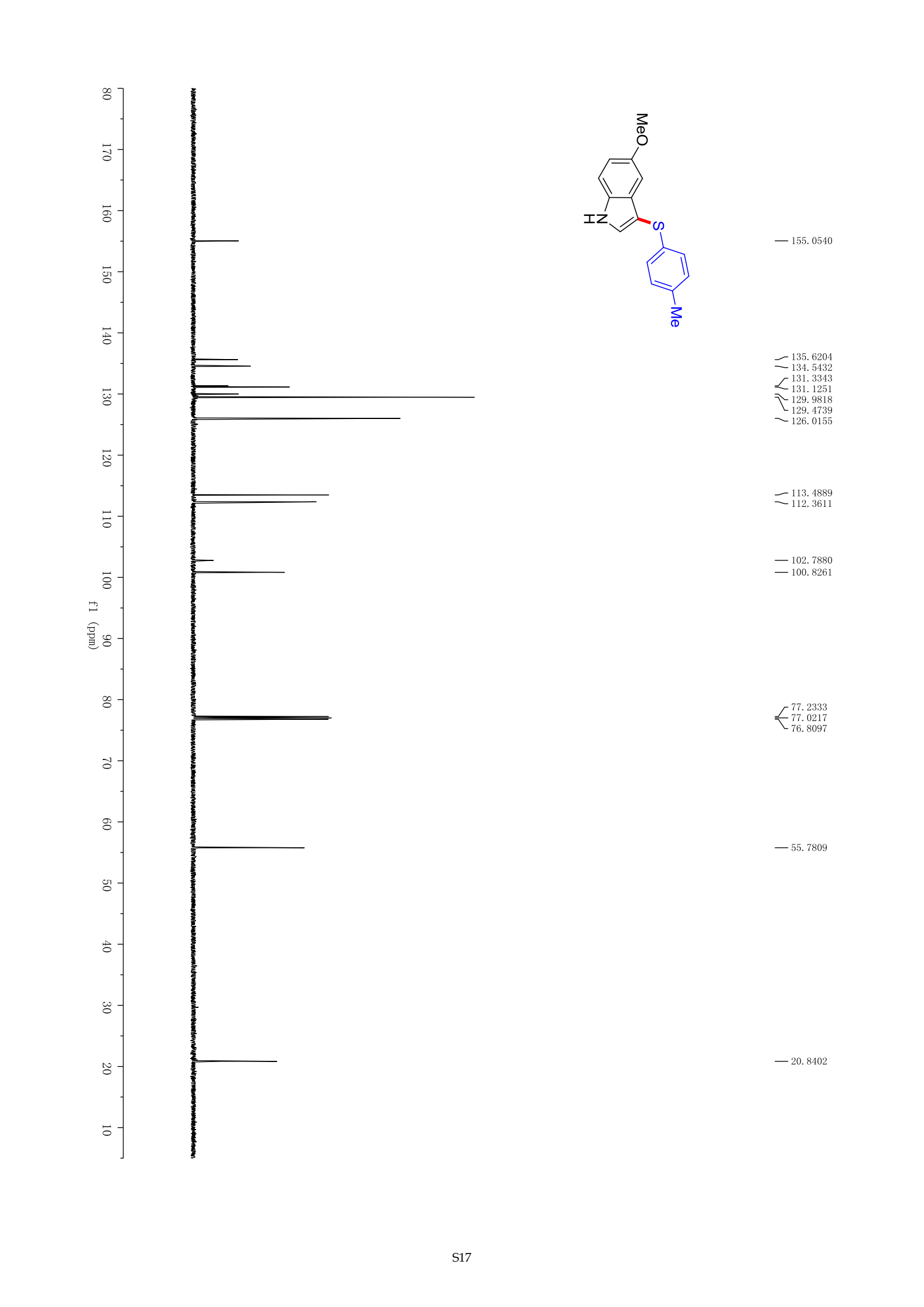
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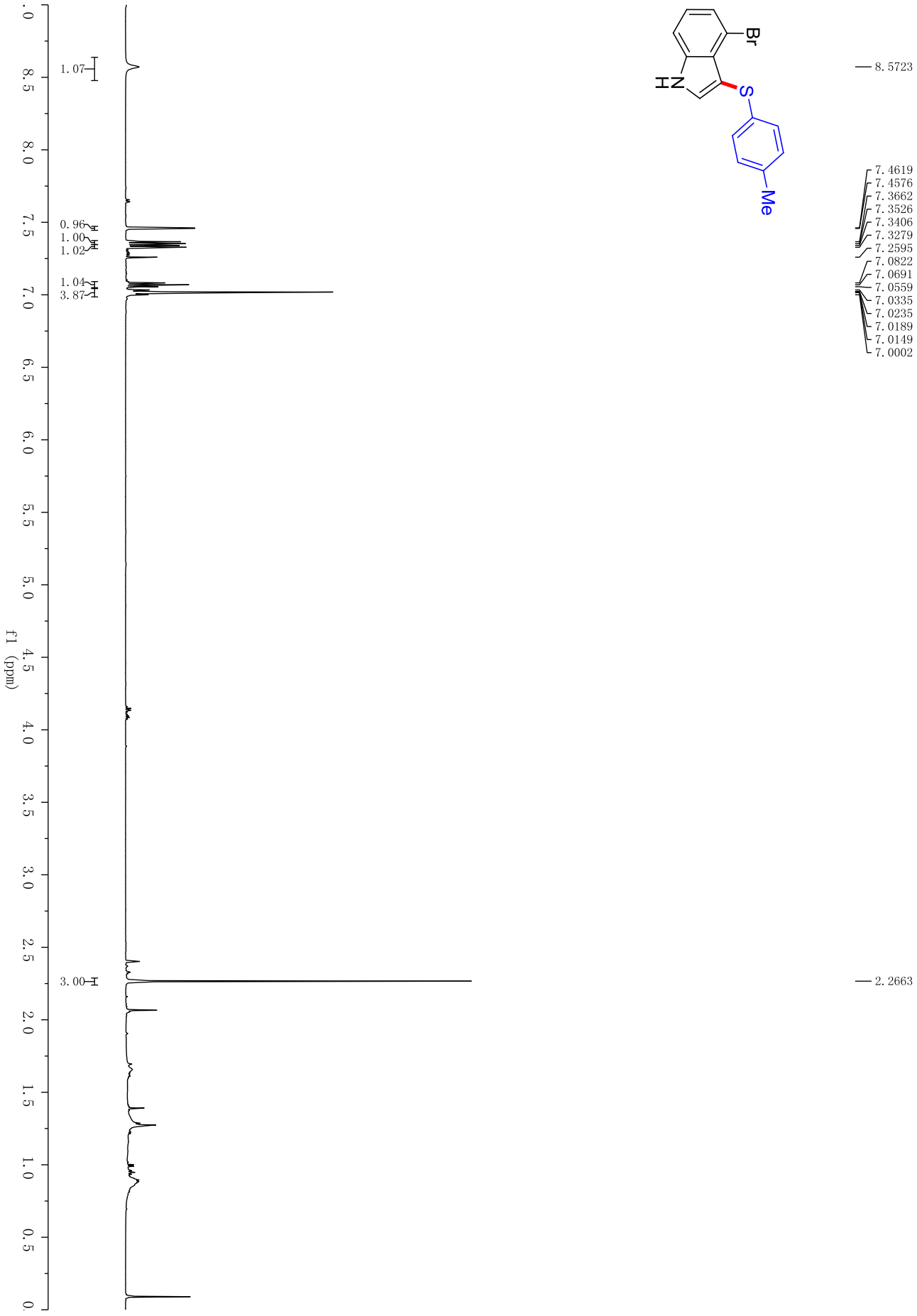
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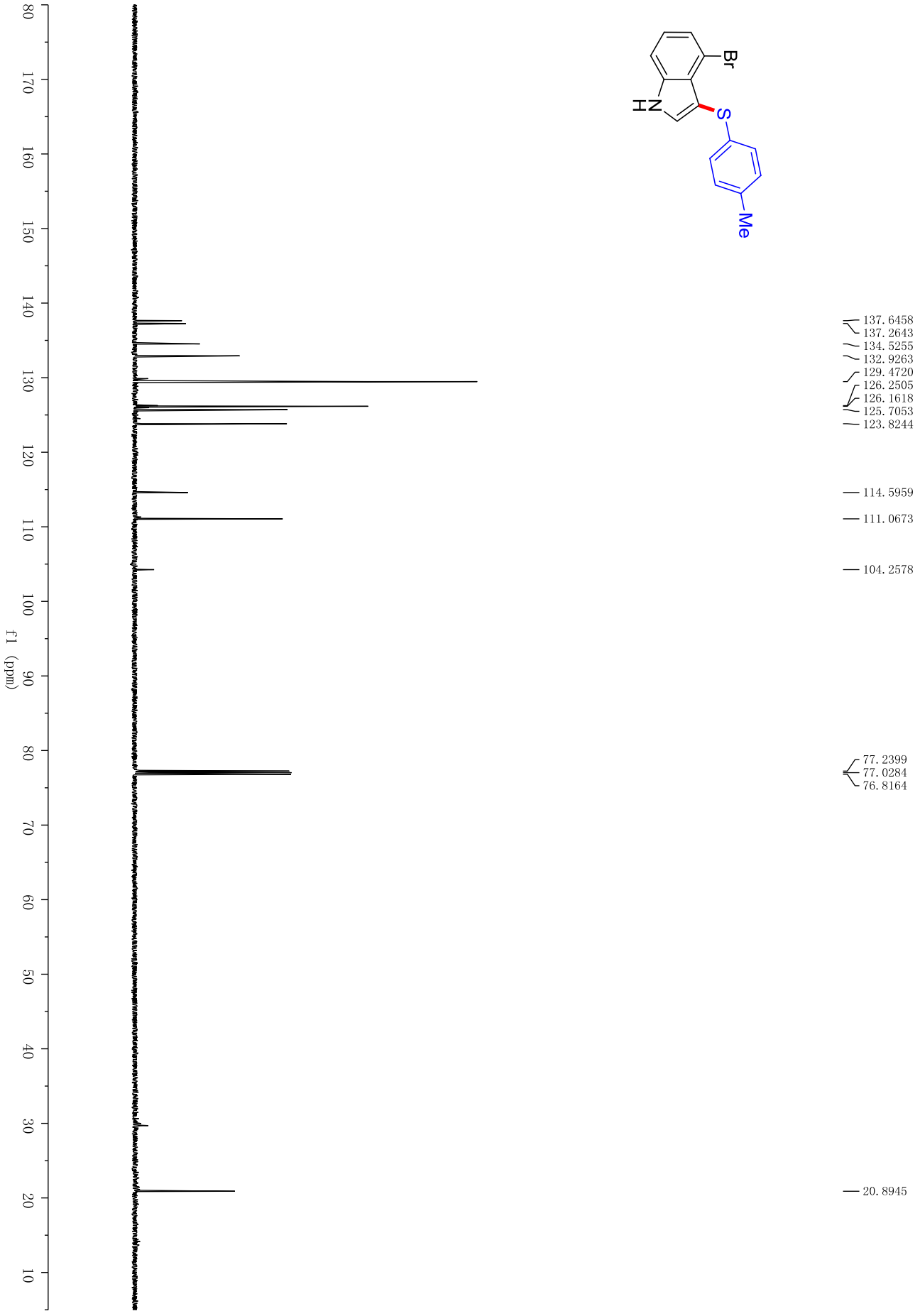
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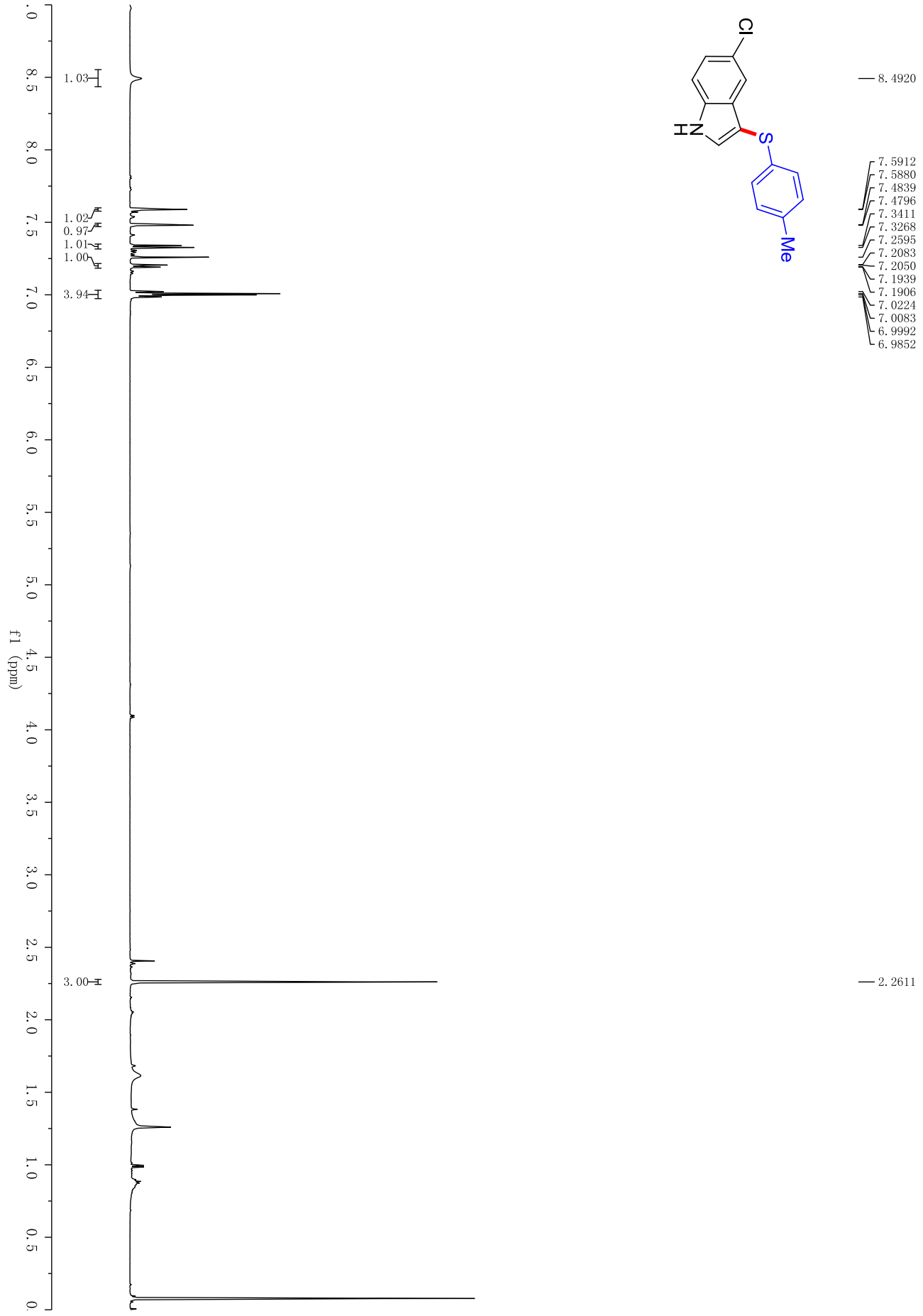
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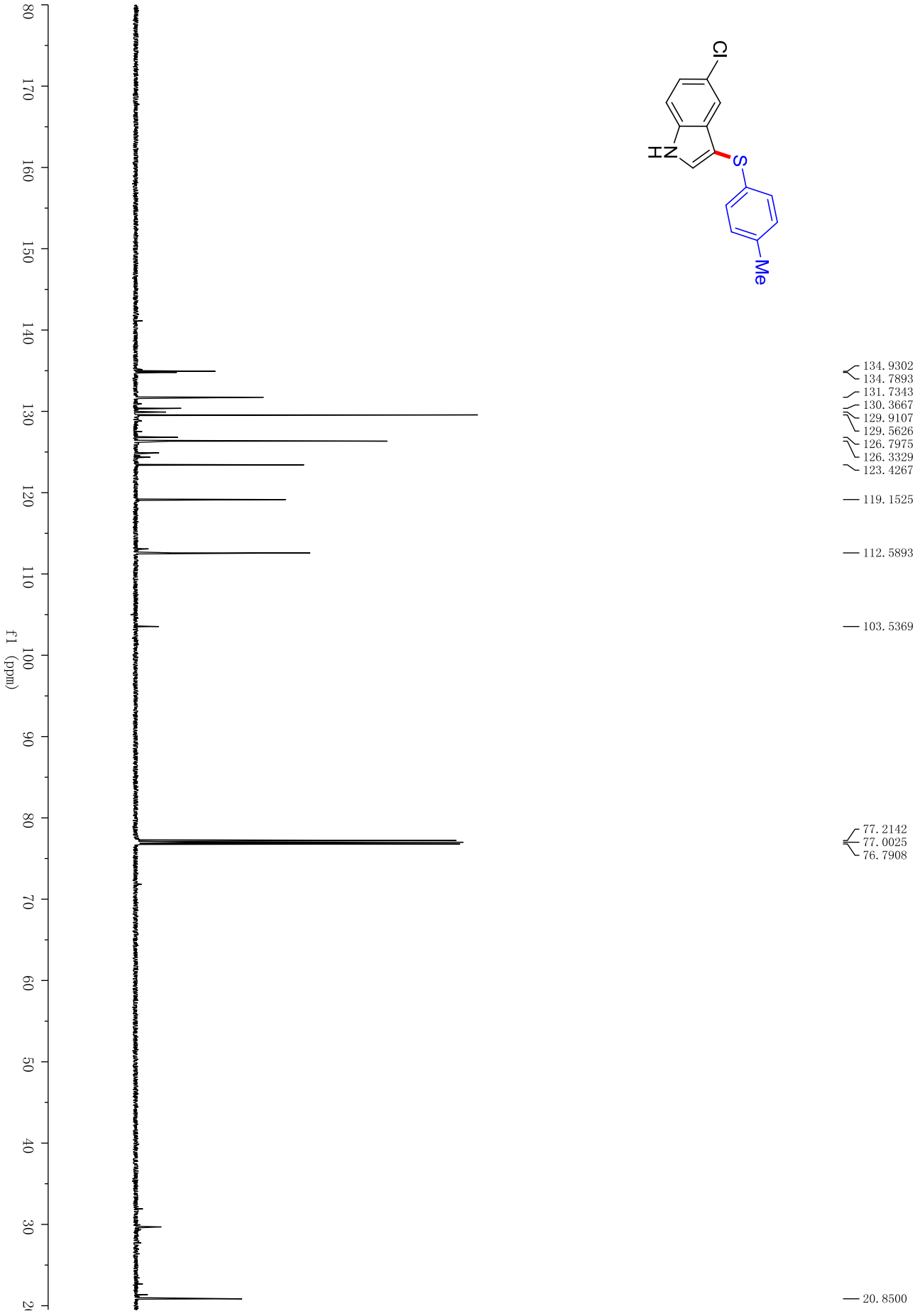
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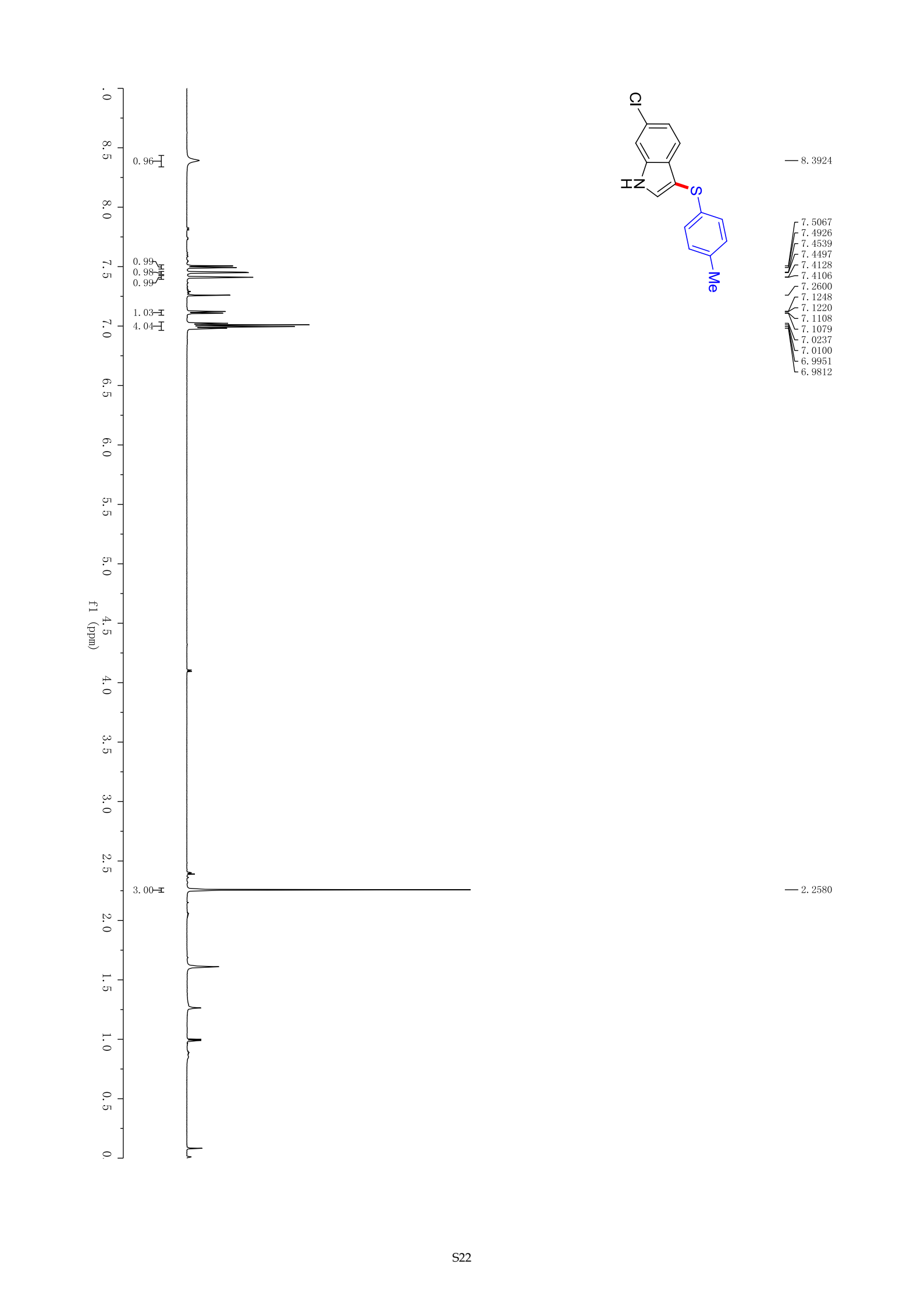
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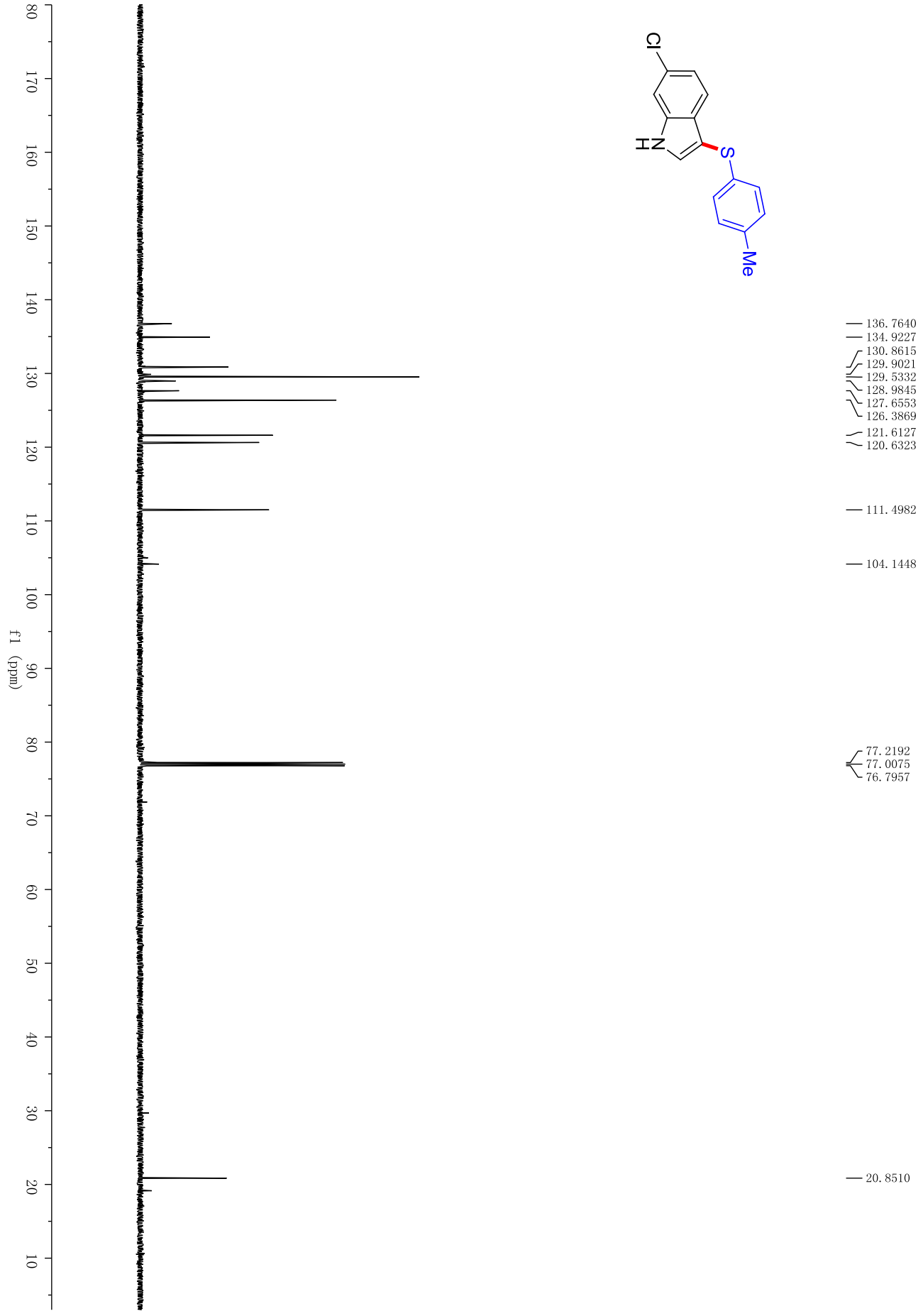
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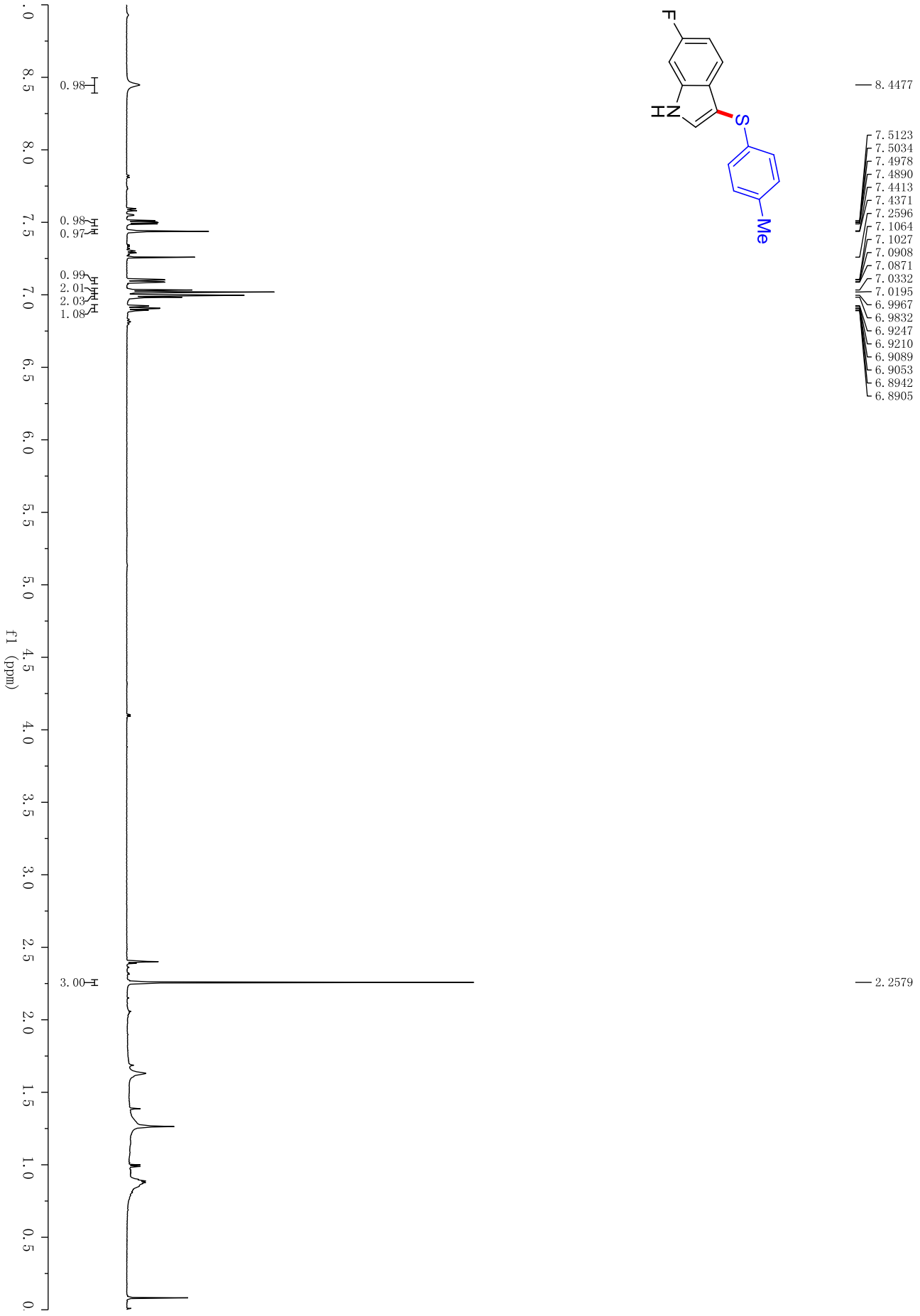
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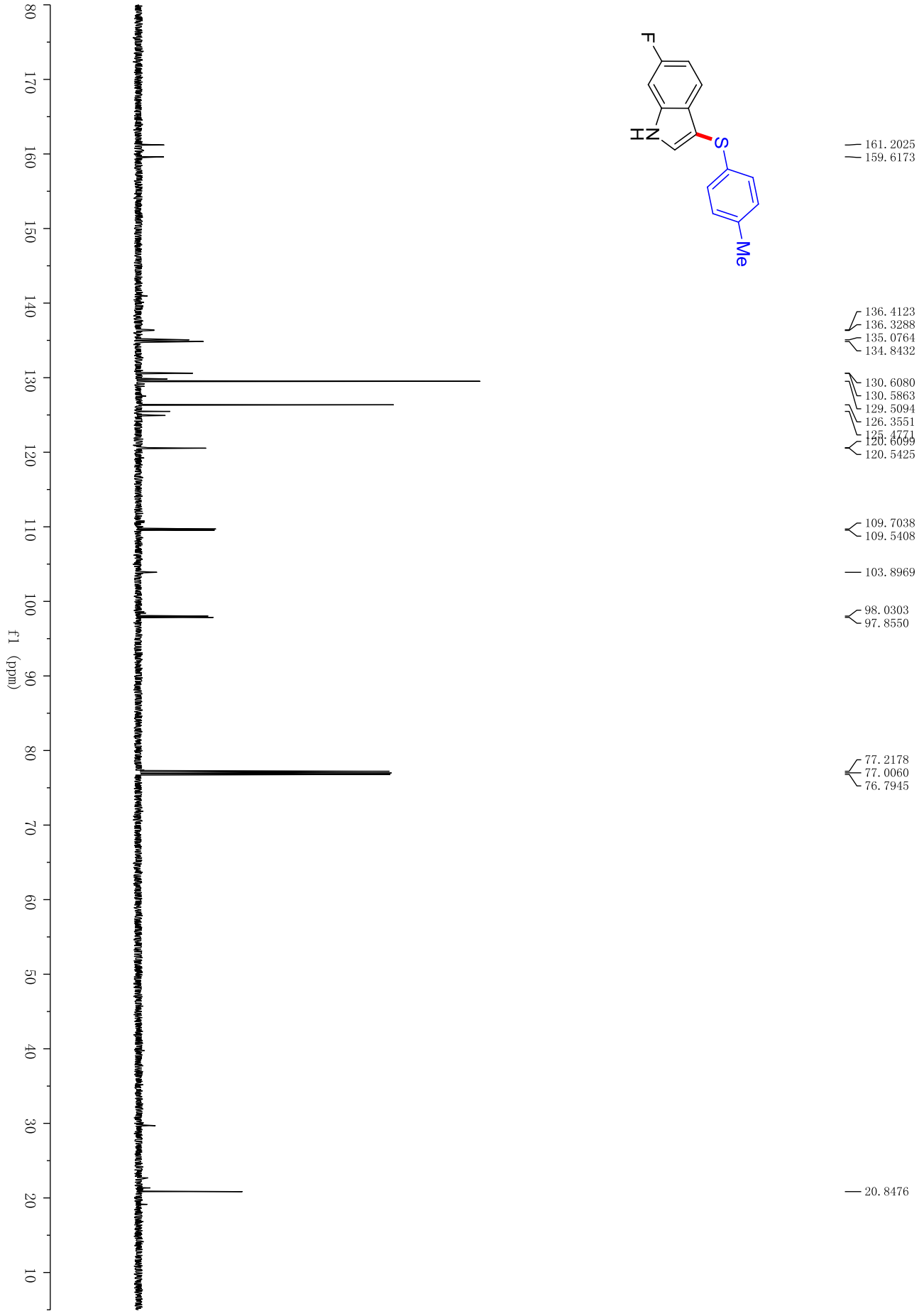
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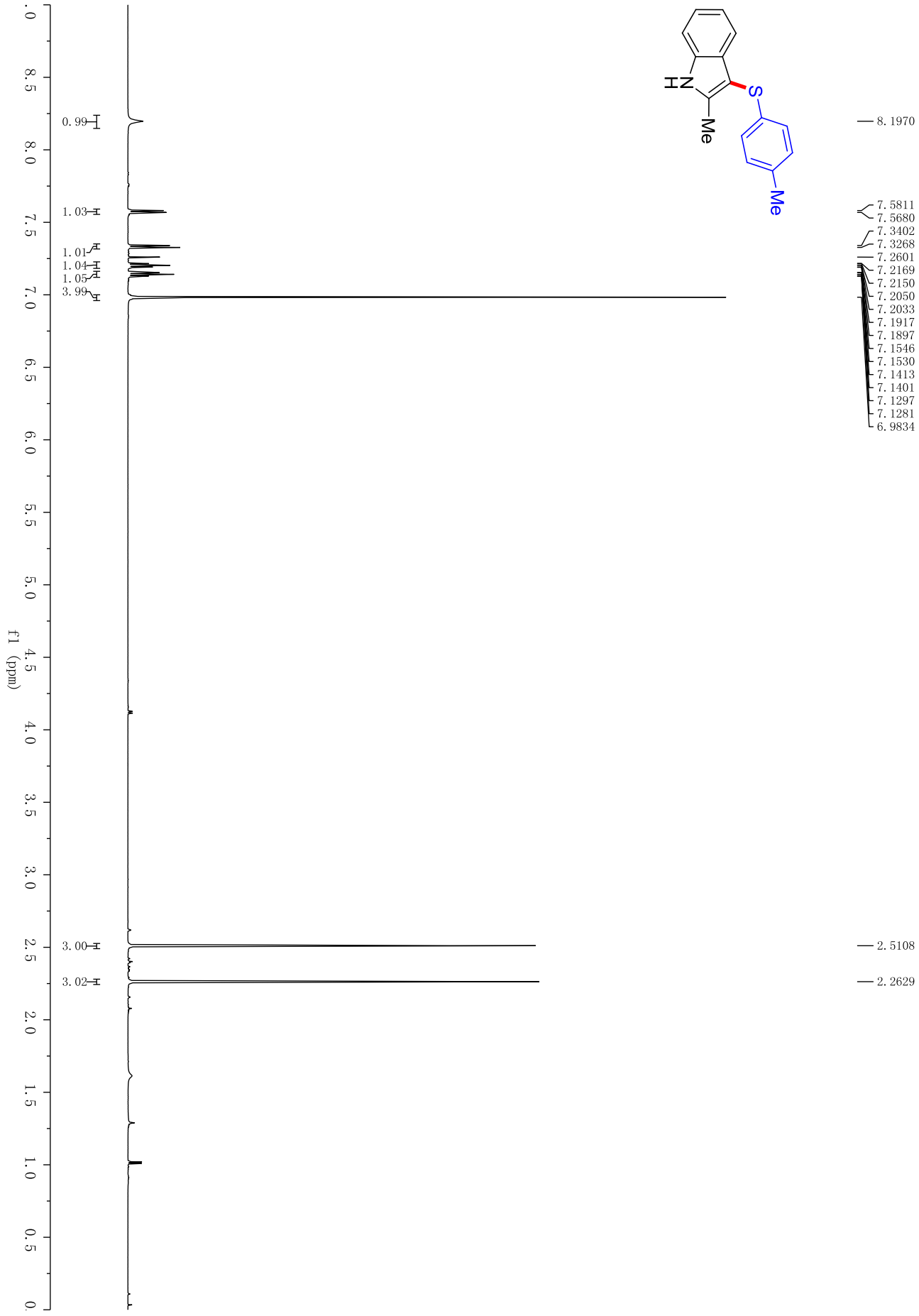
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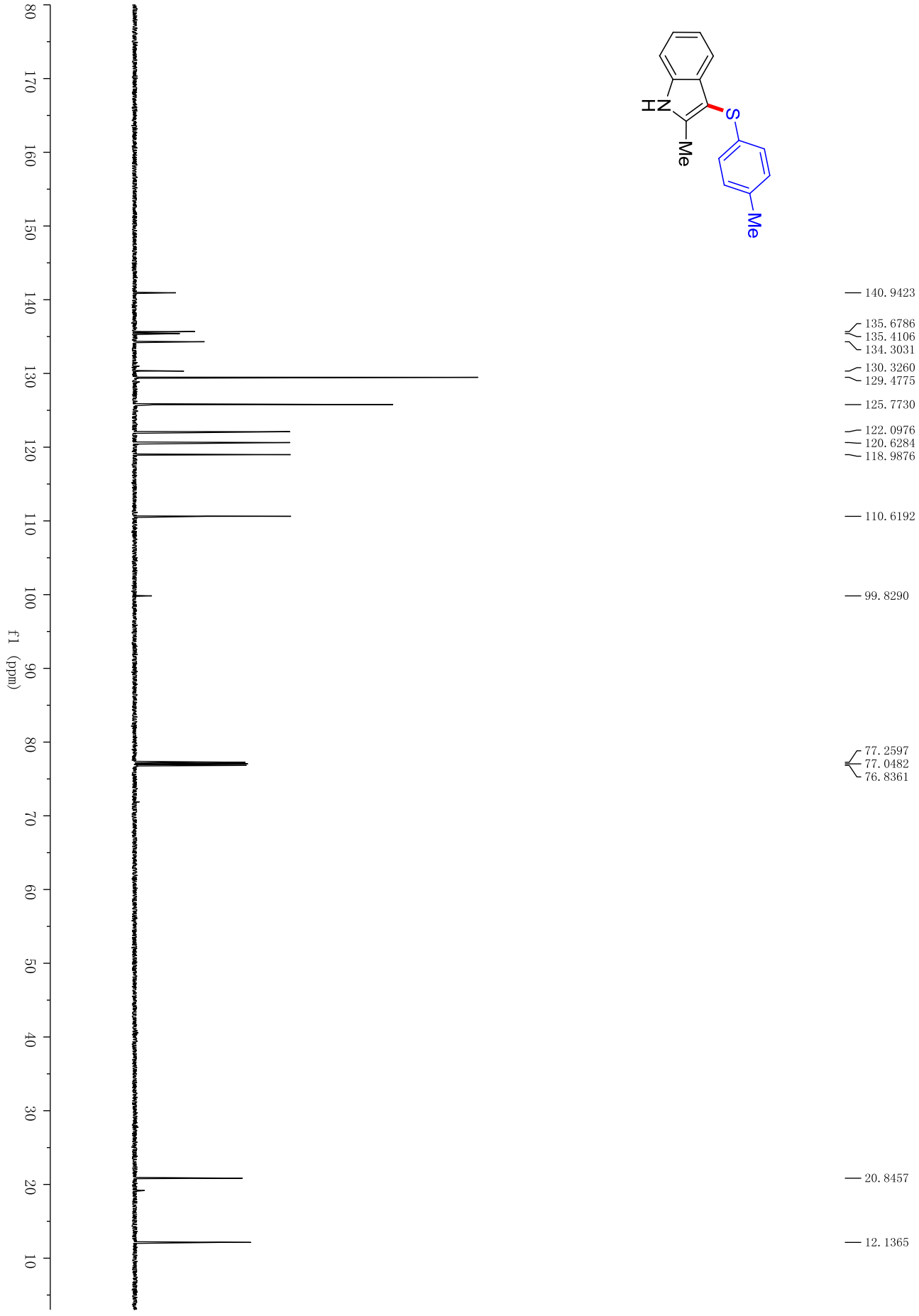
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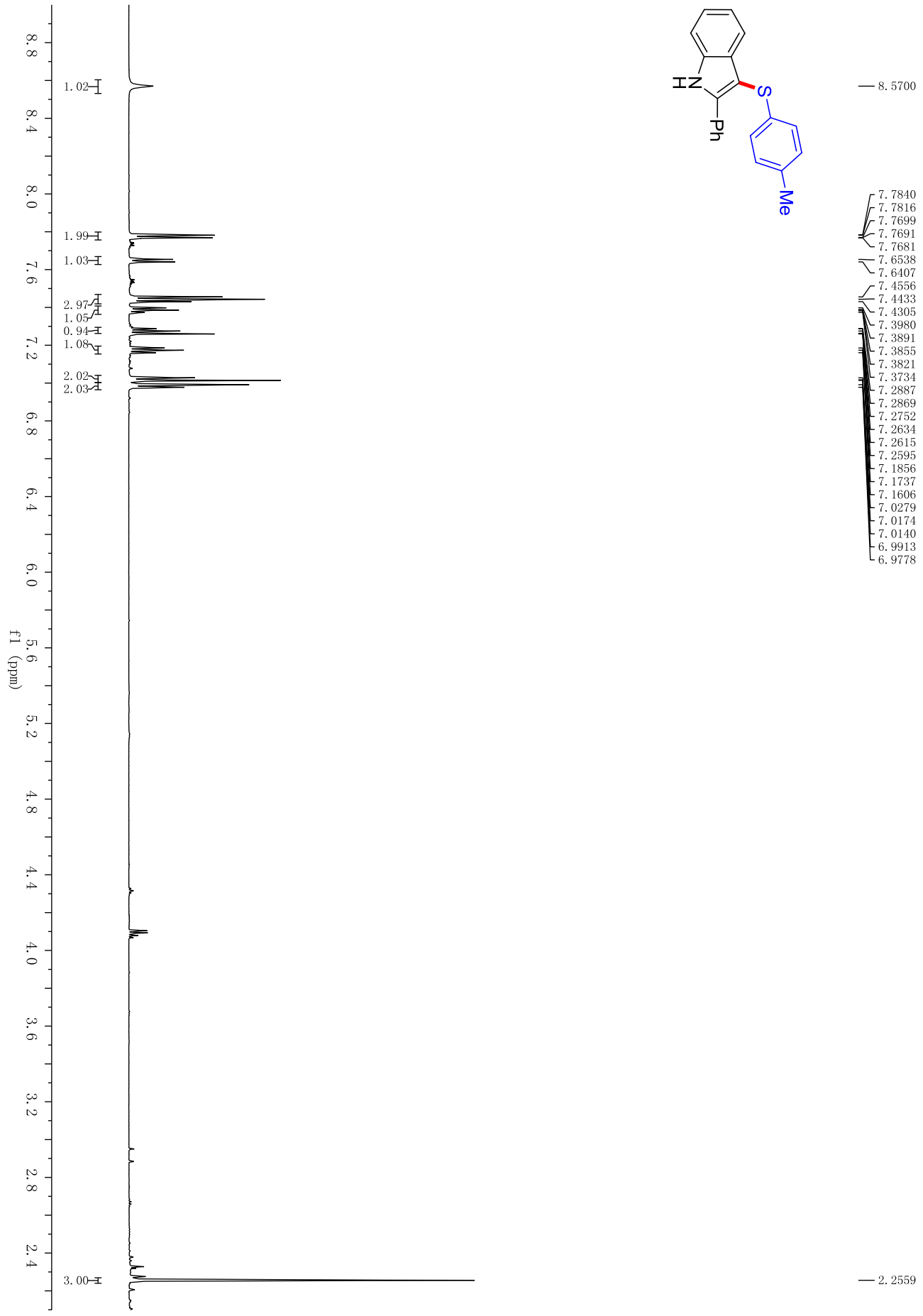
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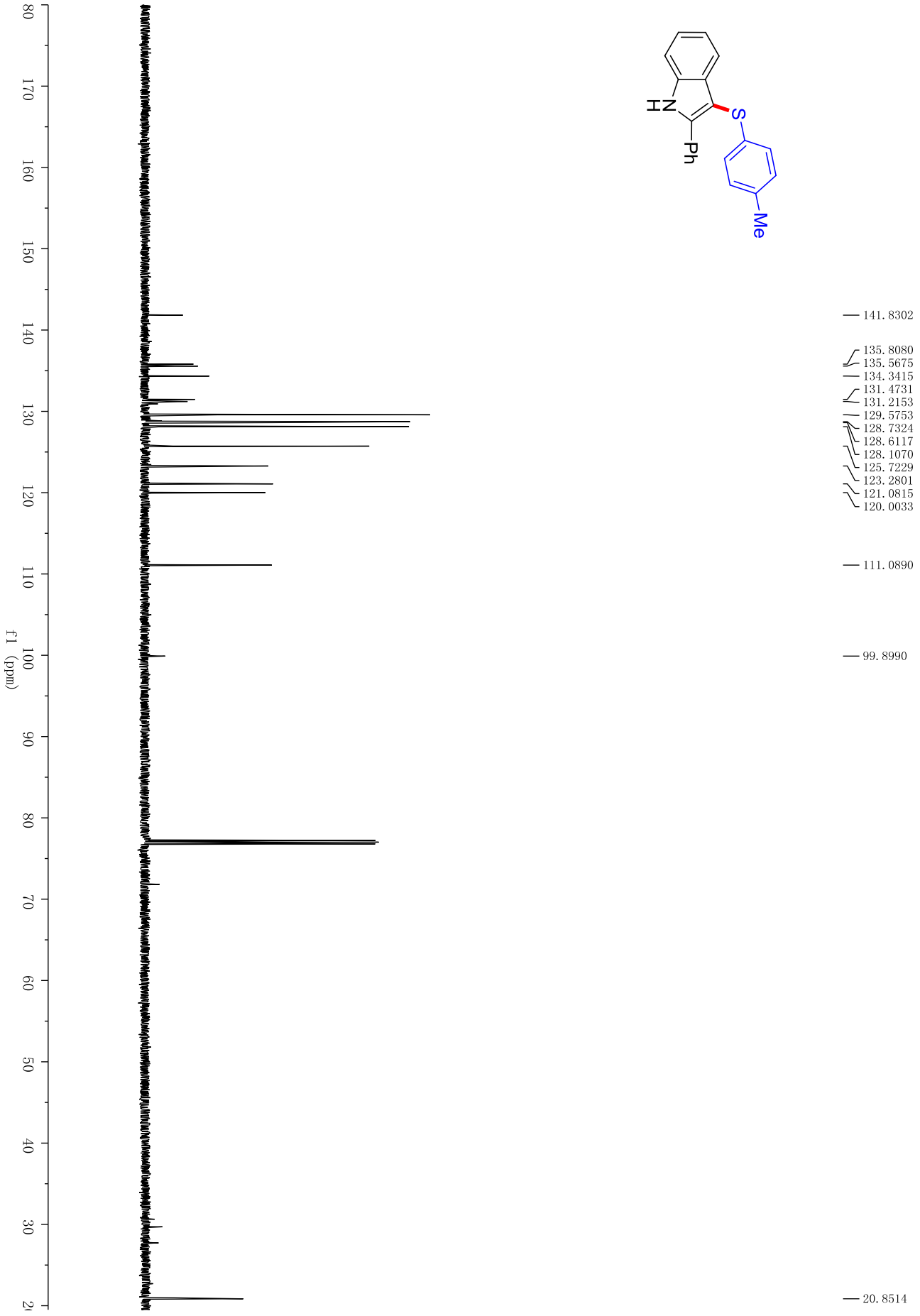
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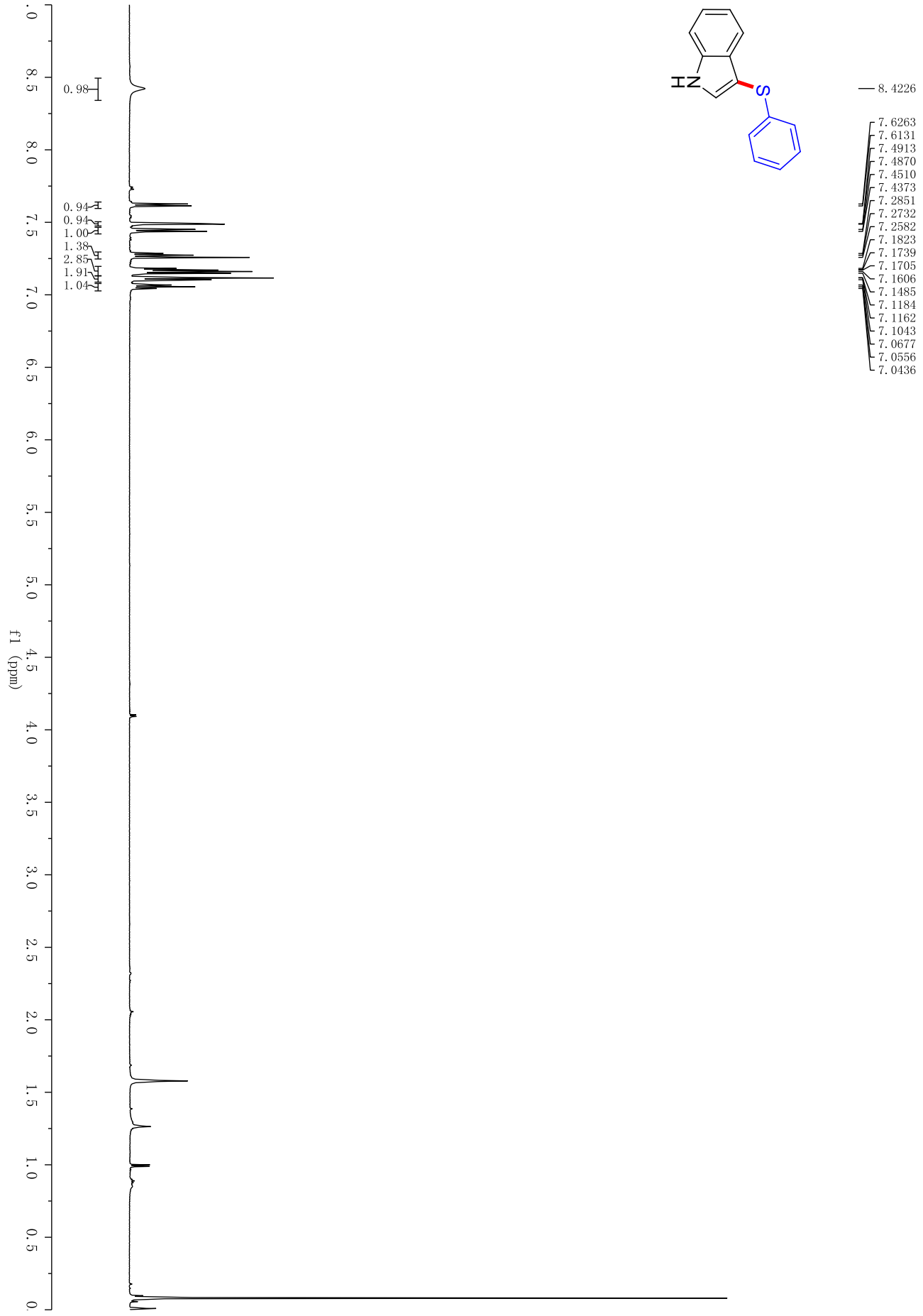
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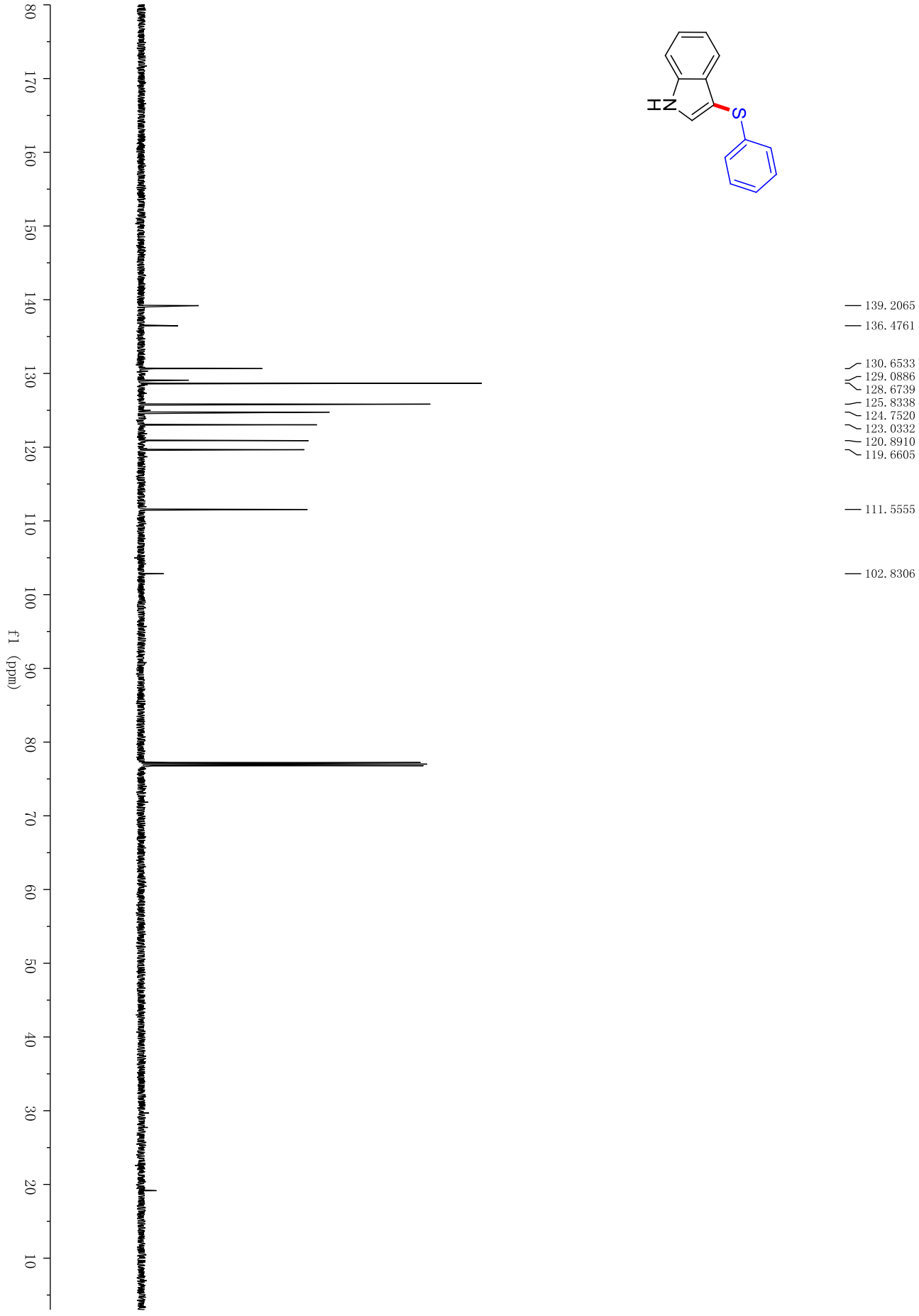
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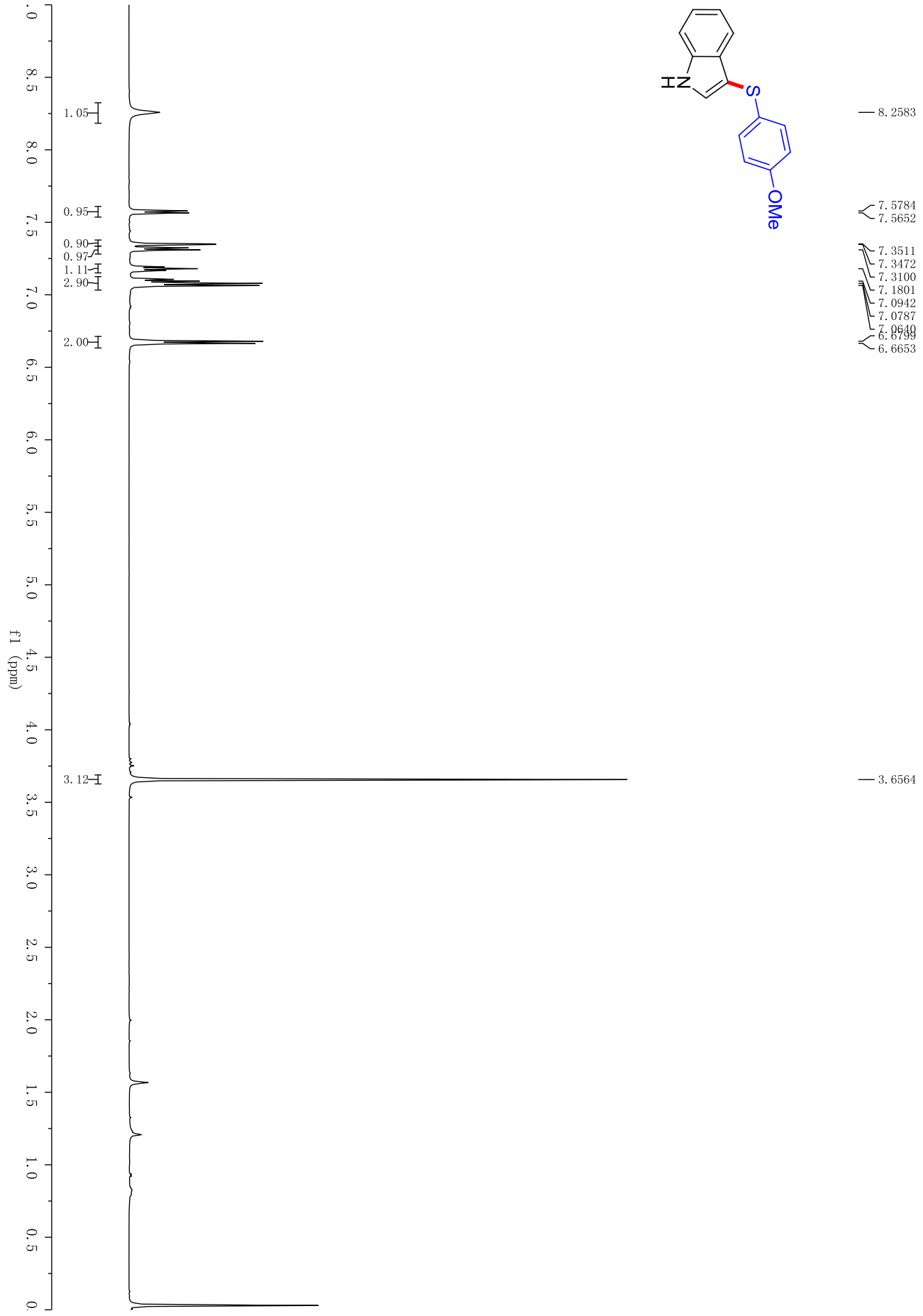
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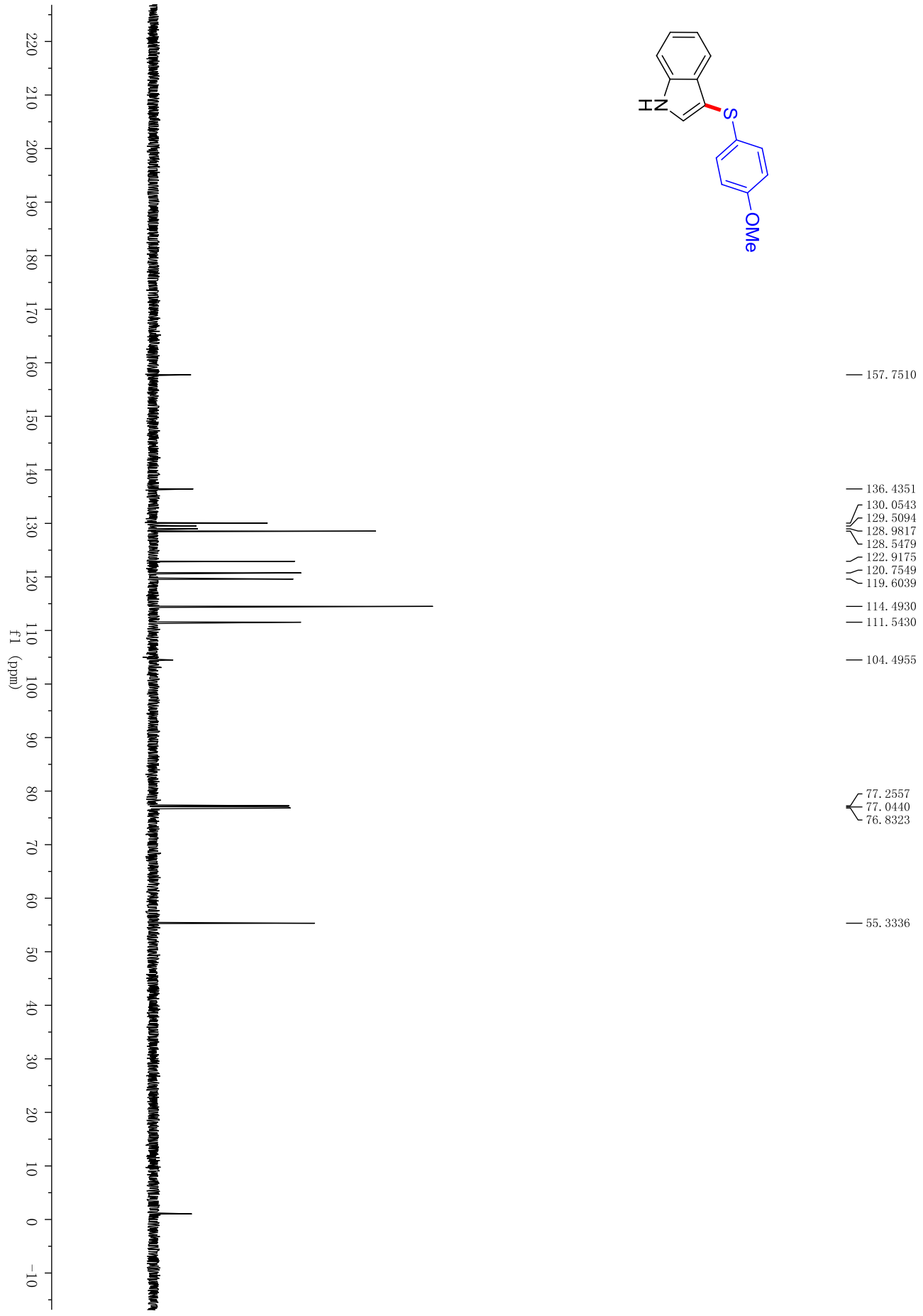
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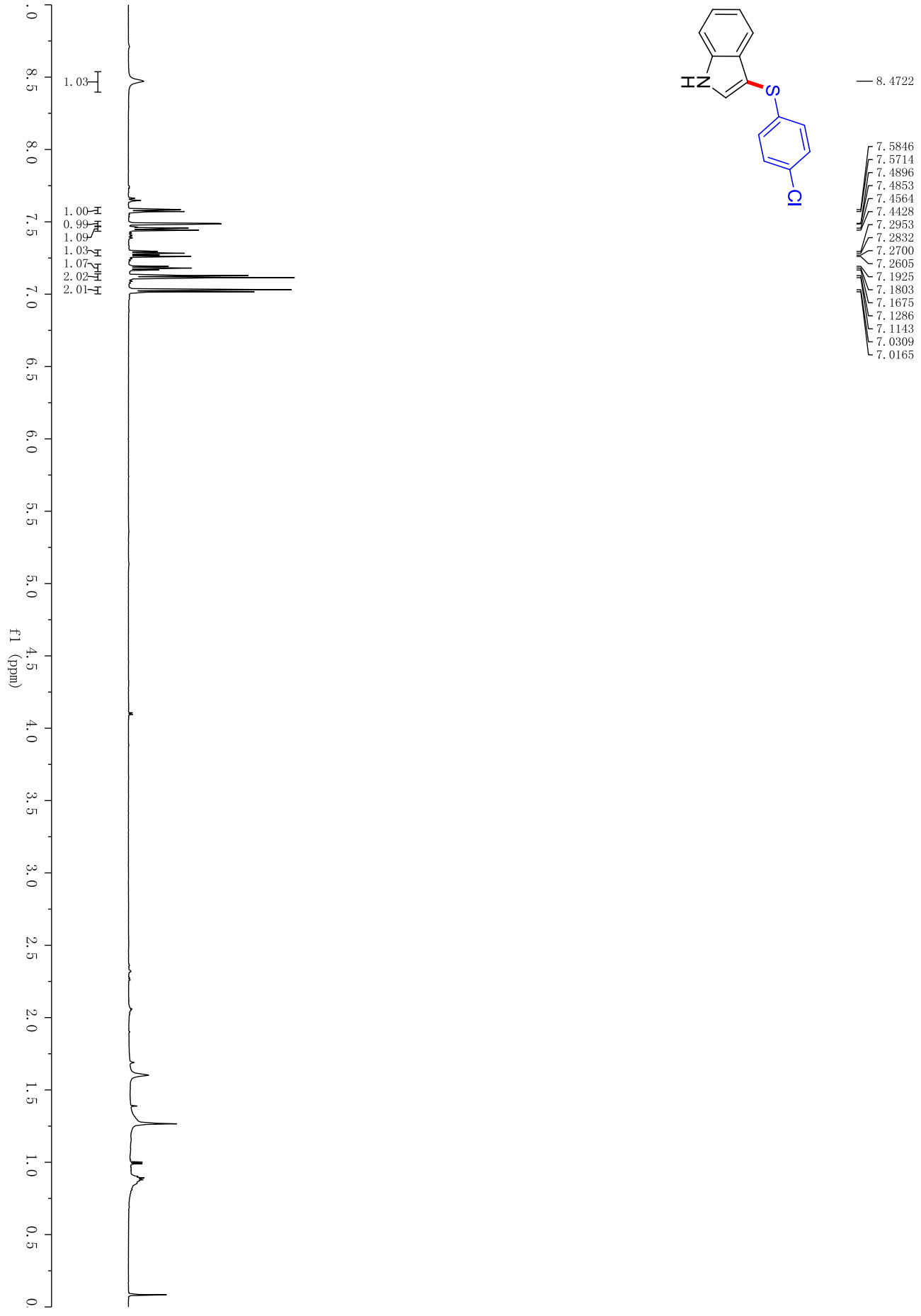
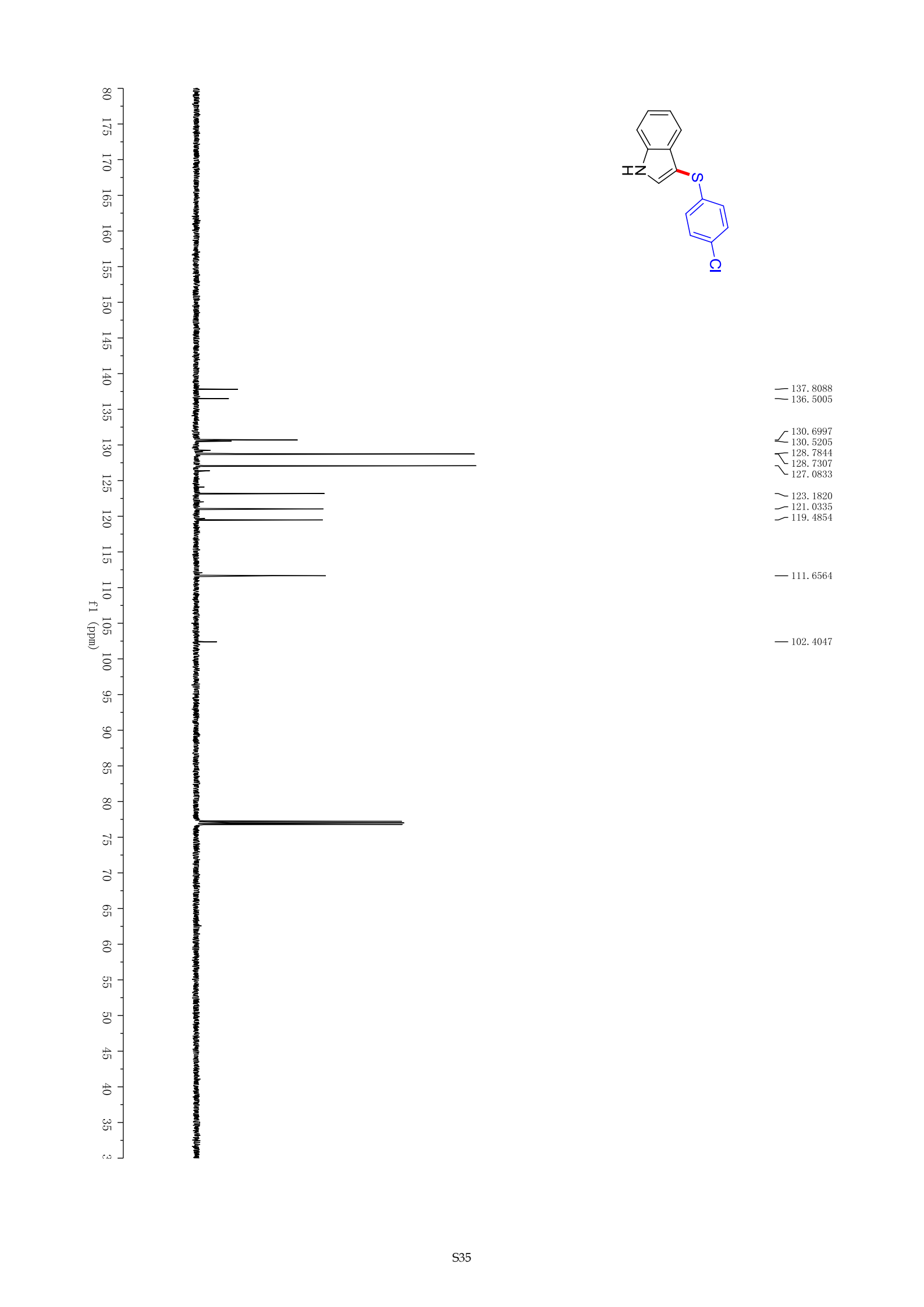
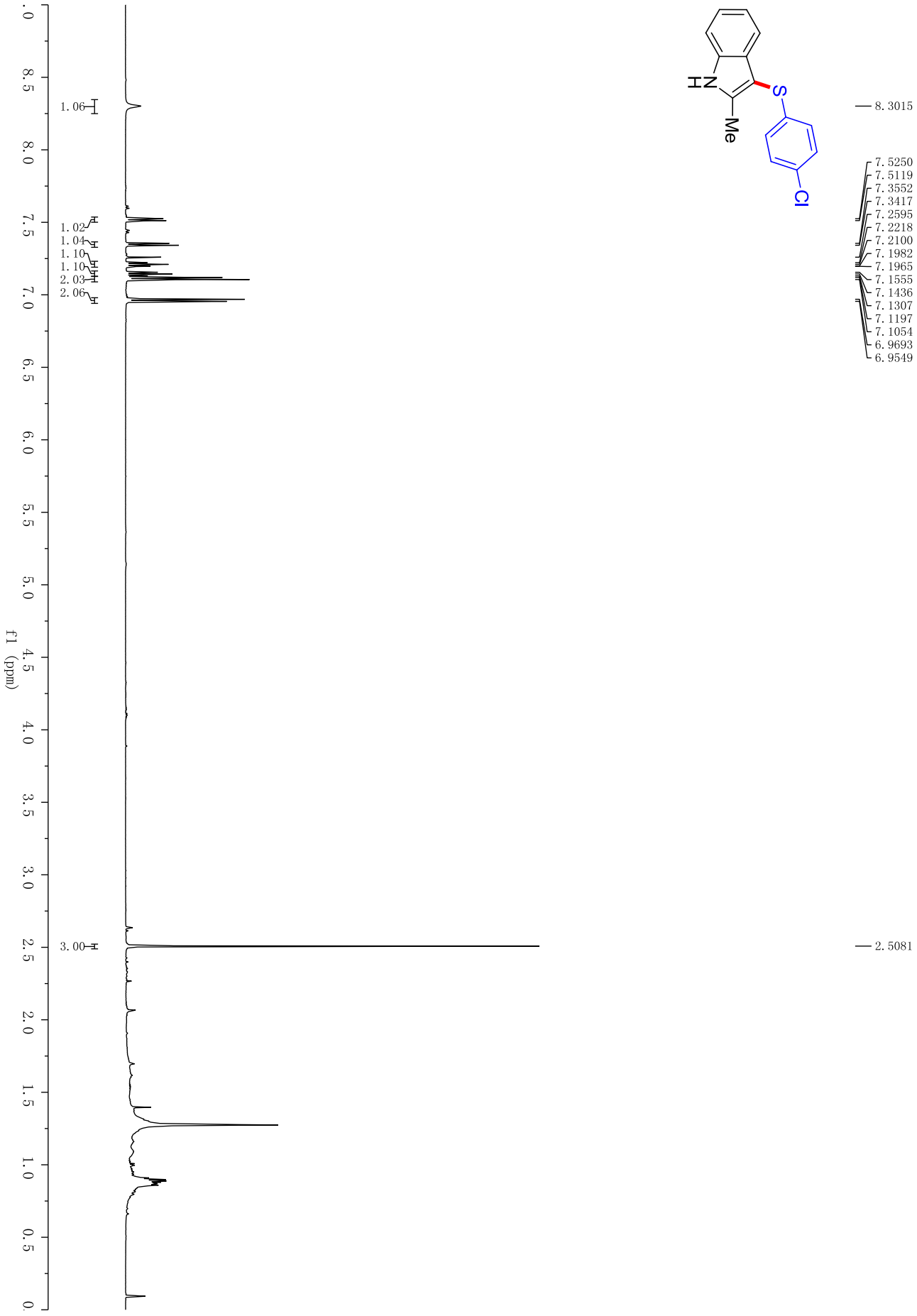
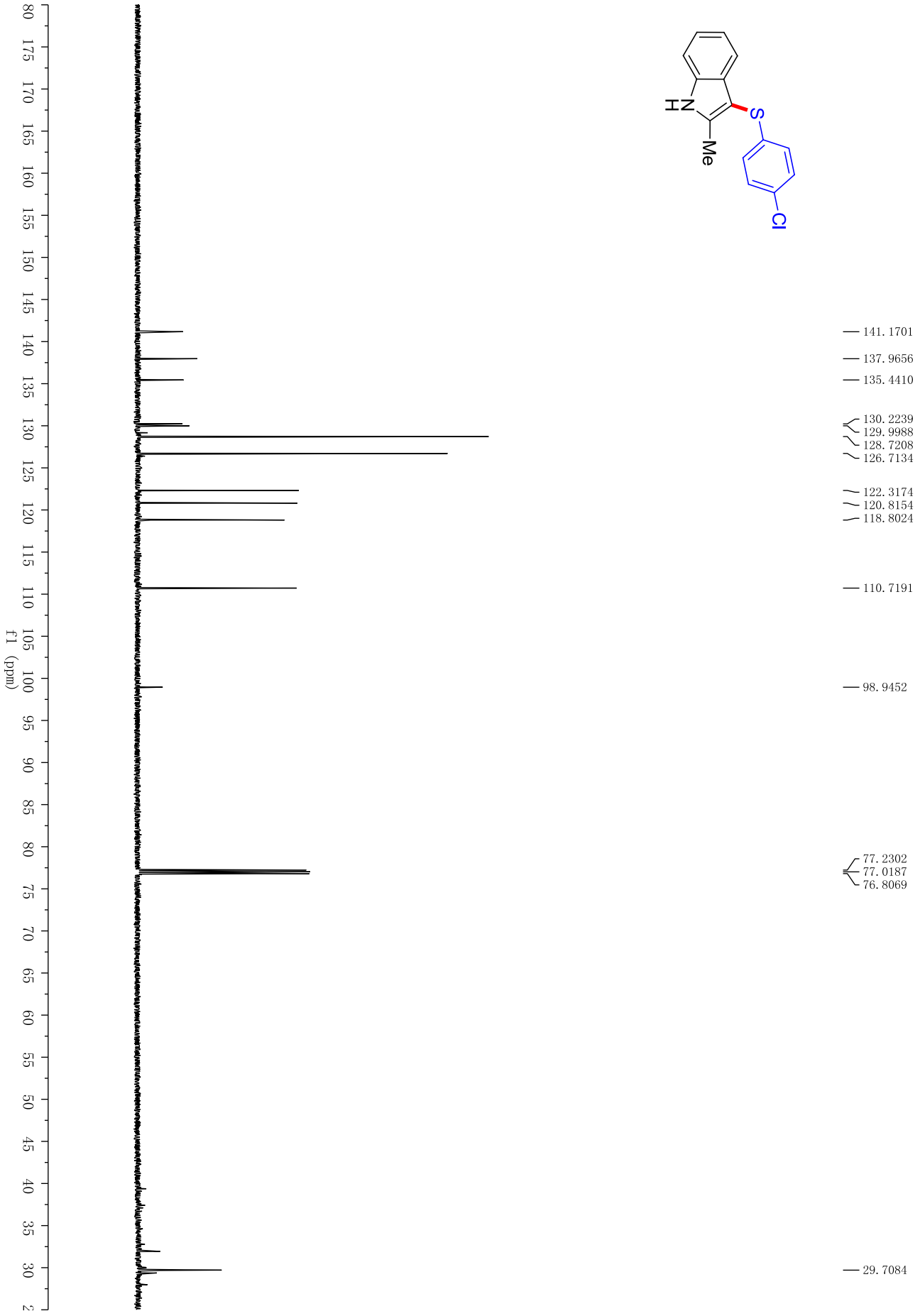
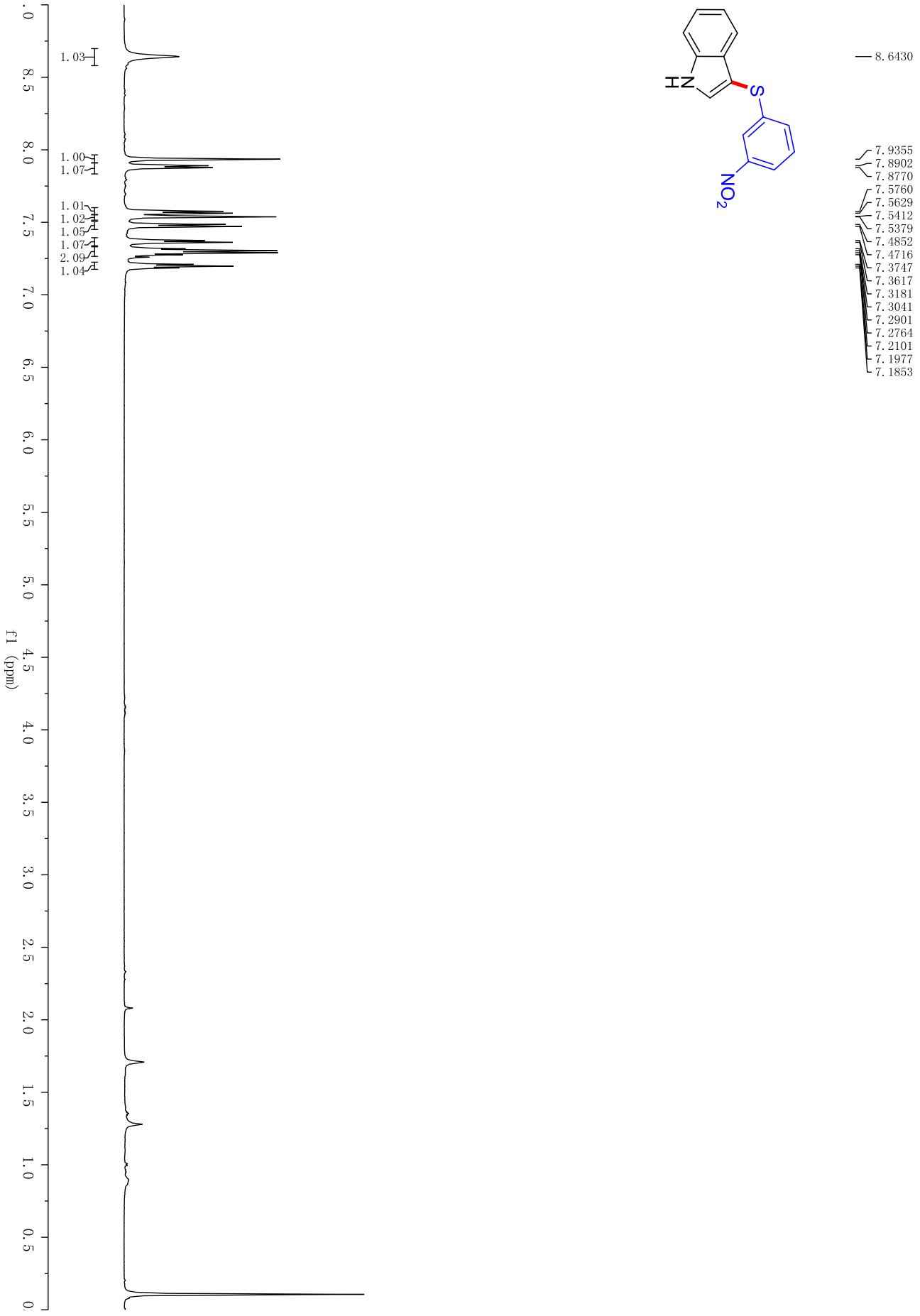
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
HN
S
OMe
157.7510
136.4351
130.0543
129.5094
128.9817
128.5479
122.9175
120.7549
119.6039
114.4930
111.5430
104.4955
77.2557
77.0440
76.8323
55.3336

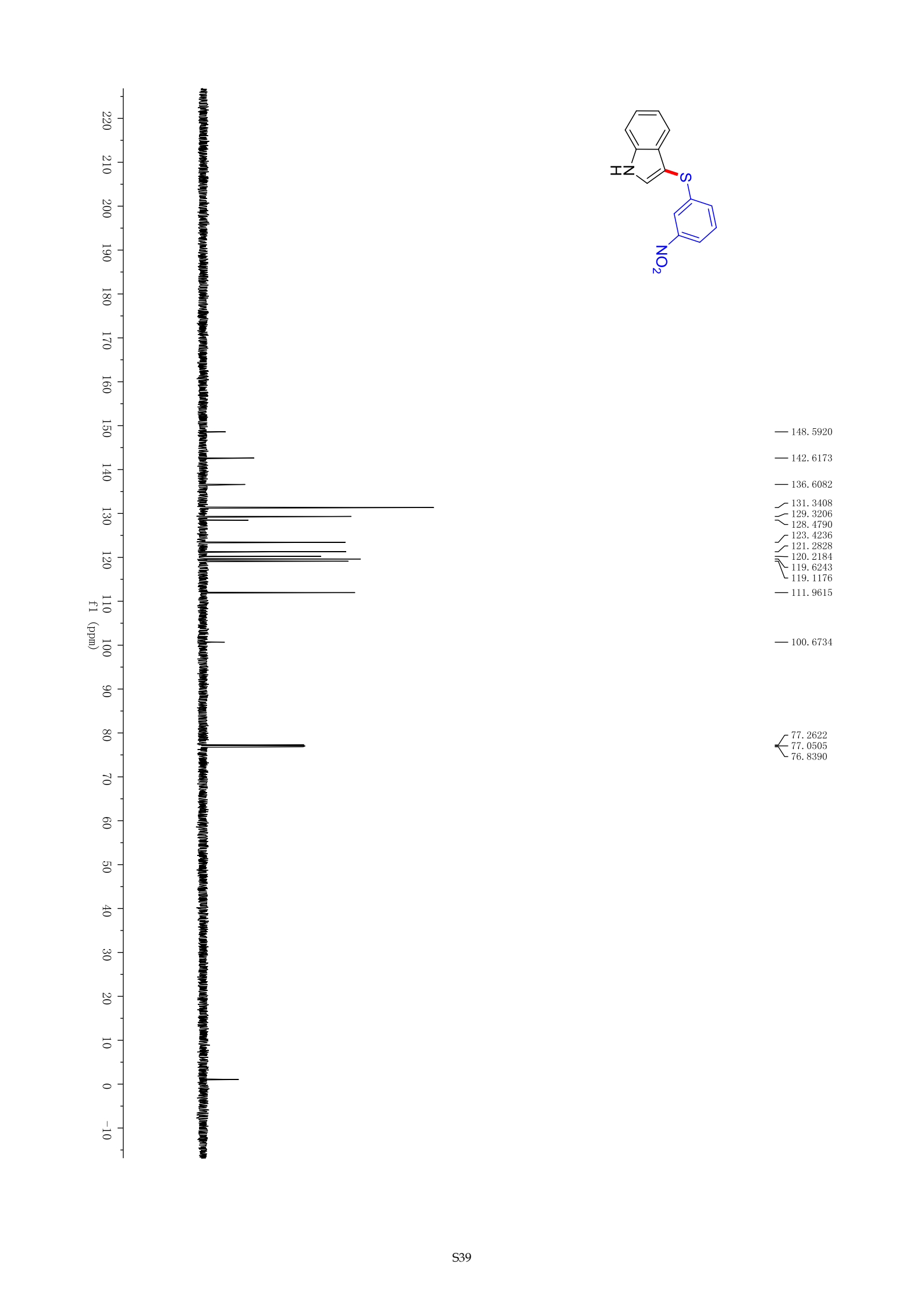

1.03
1.00
0.99
1.09
1.03
1.07
2.02
2.01
f1 (ppm)
8.4722
7.5846
7.5714
7.4896
7.4853
7.4564
7.4428
7.2953
7.2832
7.2700
7.2605
7.1925
7.1803
7.1675
7.1286
7.1143
7.0309
7.0165

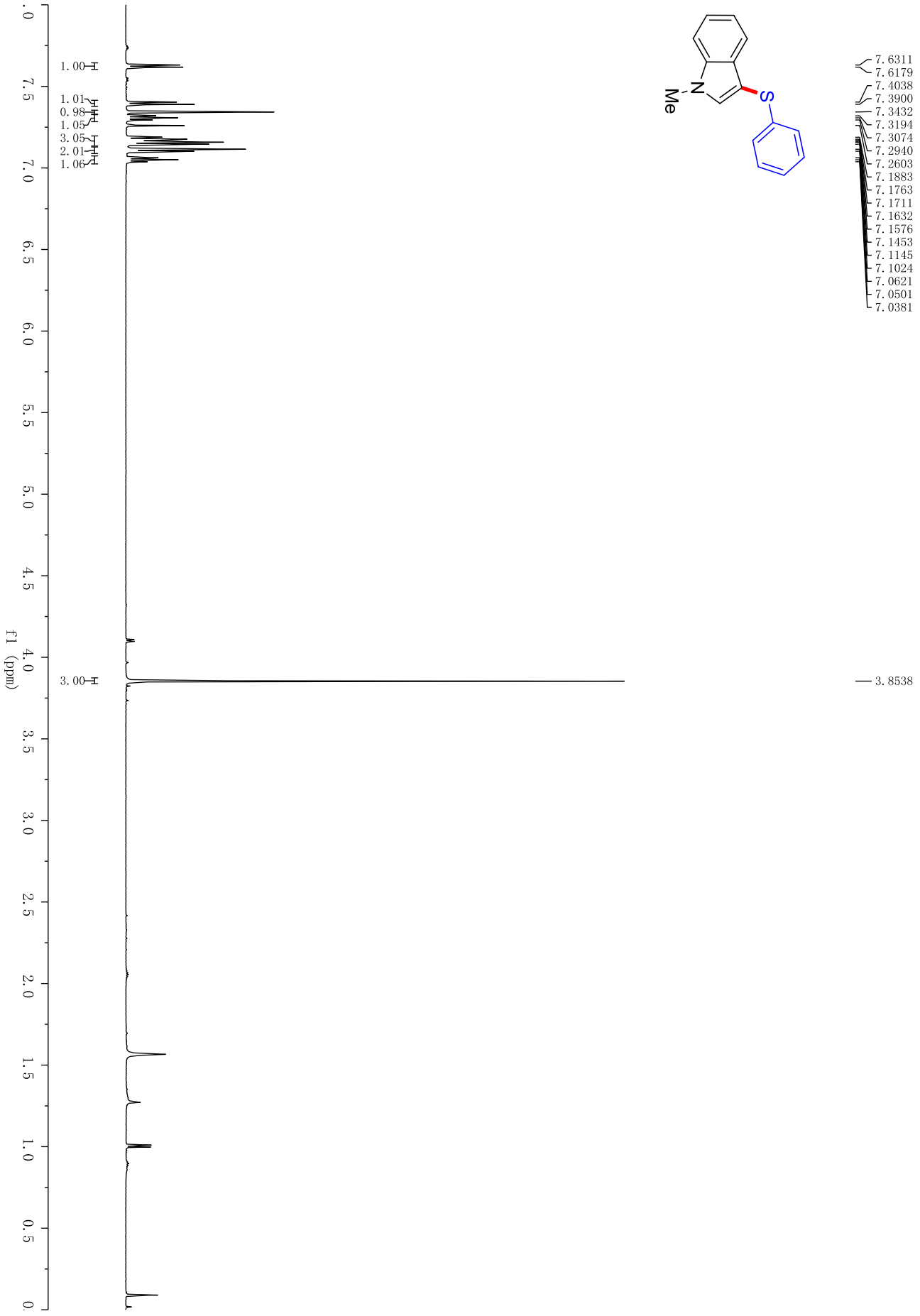

137.8088
136.5005
130.6997
130.5205
128.7844
128.7307
127.0833
123.1820
121.0335
119.4854
111.6564
102.4047
f1 (ppm)

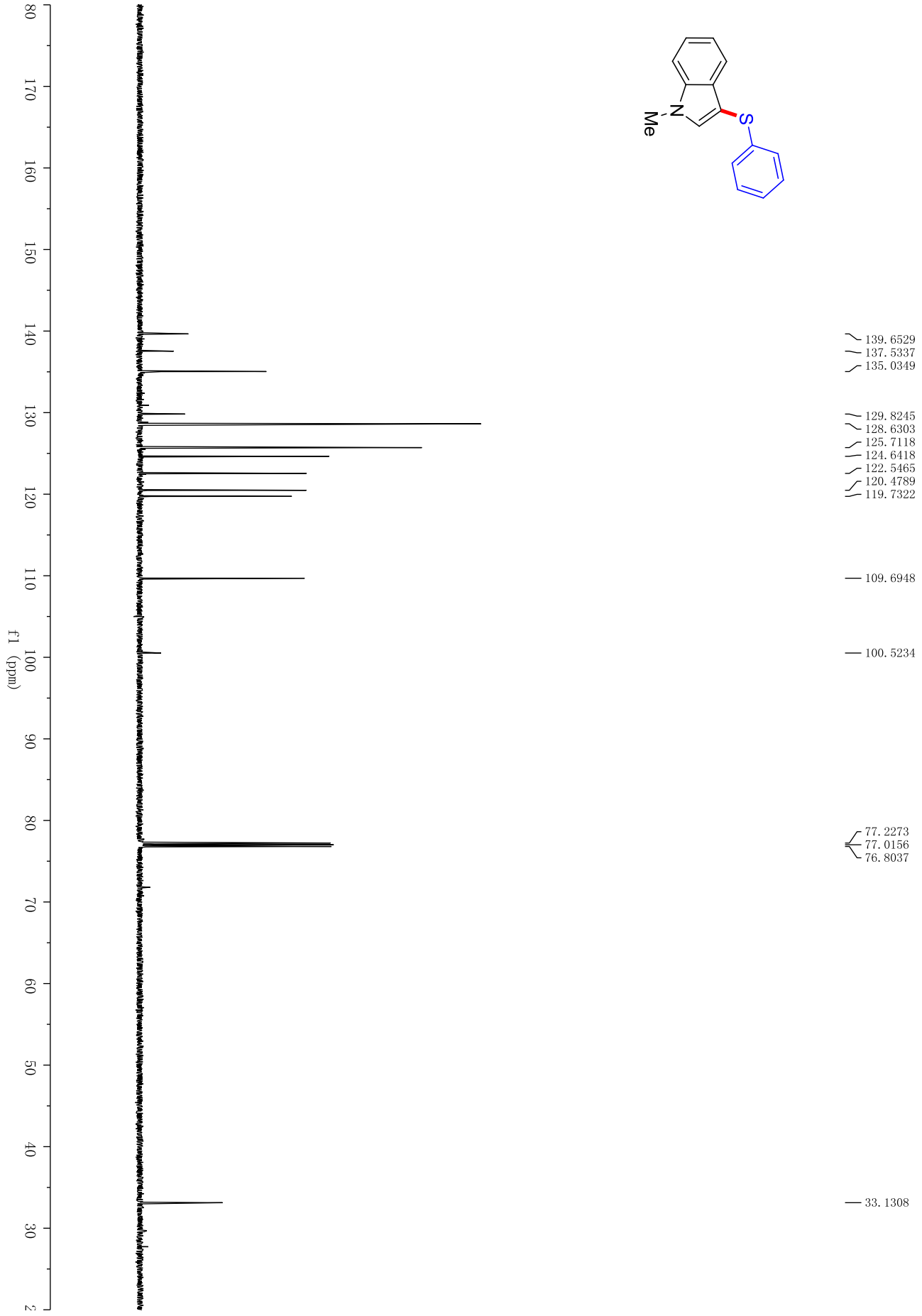

f1 (ppm)
1.06
1.02
1.04
1.10
1.10
2.03
2.06
3.00
8.3015
7.5250
7.5119
7.3552
7.3417
7.2595
7.2218
7.2100
7.1982
7.1965
7.1555
7.1436
7.1307
7.1197
7.1054
6.9693
6.9549
2.5081
N
H
Me
S
Cl

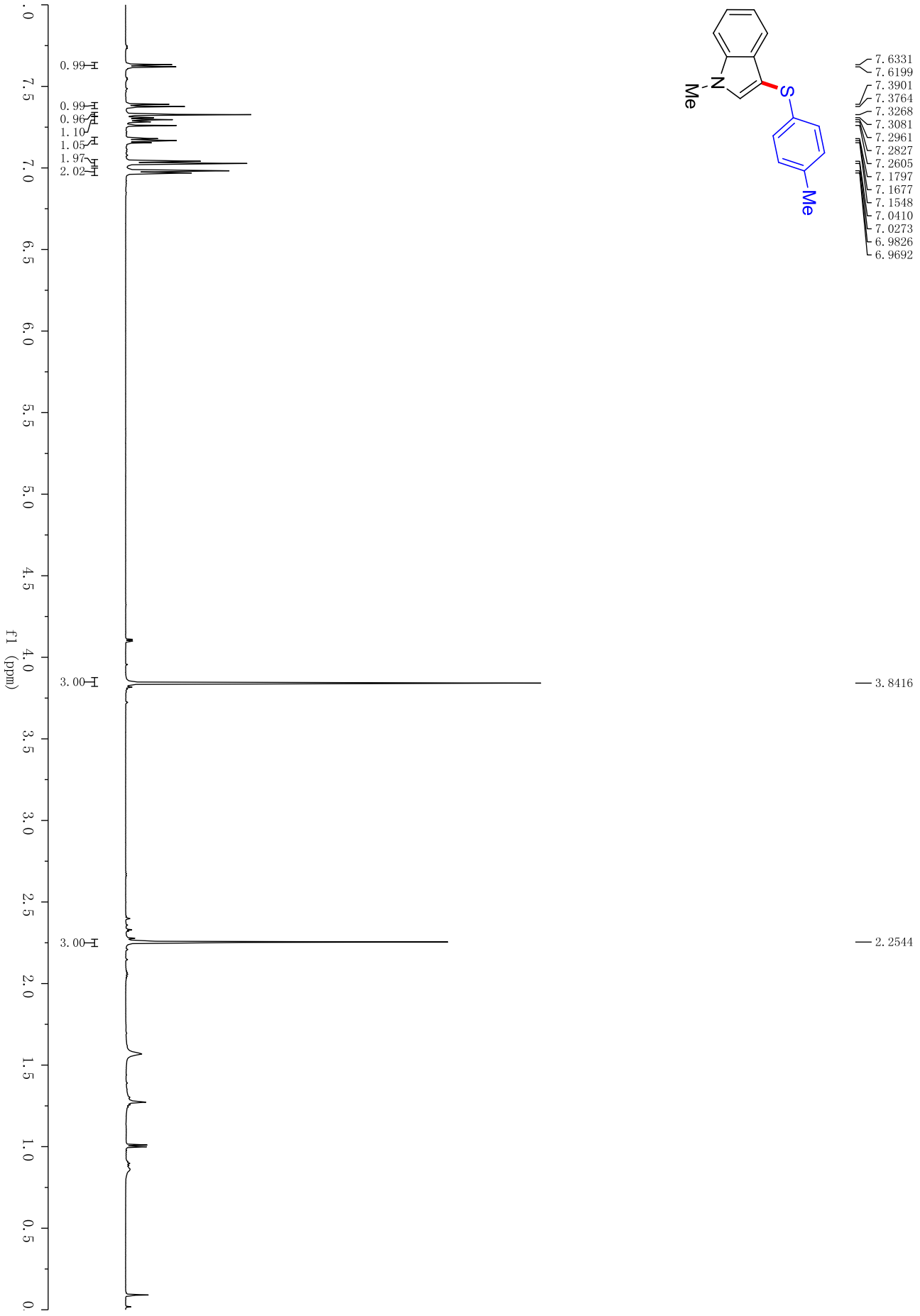

141.1701
137.9656
135.4410
130.2239
129.9988
128.7208
126.7134
122.3174
120.8154
118.8024
110.7191
98.9452
77.2302
77.0187
76.8069
29.7084
f1 (ppm)
N
H
Me
S
Cl

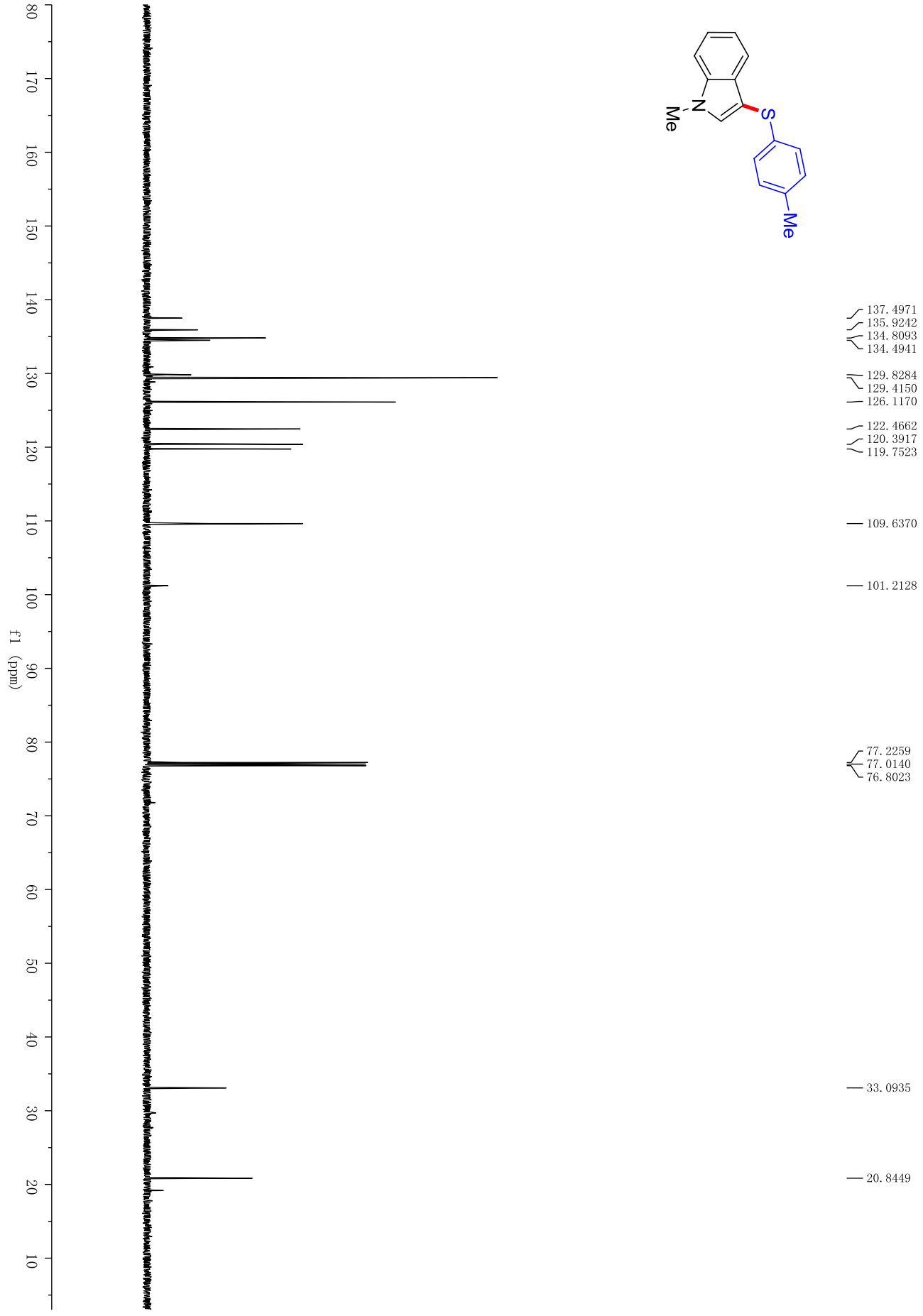

1.03
1.00
1.07
1.01
1.02
1.05
1.07
2.09
1.04
f1 (ppm)
8.6430
7.9355
7.8902
7.8770
7.5760
7.5629
7.5412
7.5379
7.4852
7.4716
7.3747
7.3617
7.3181
7.3041
7.2901
7.2764
7.2101
7.1977
7.1853

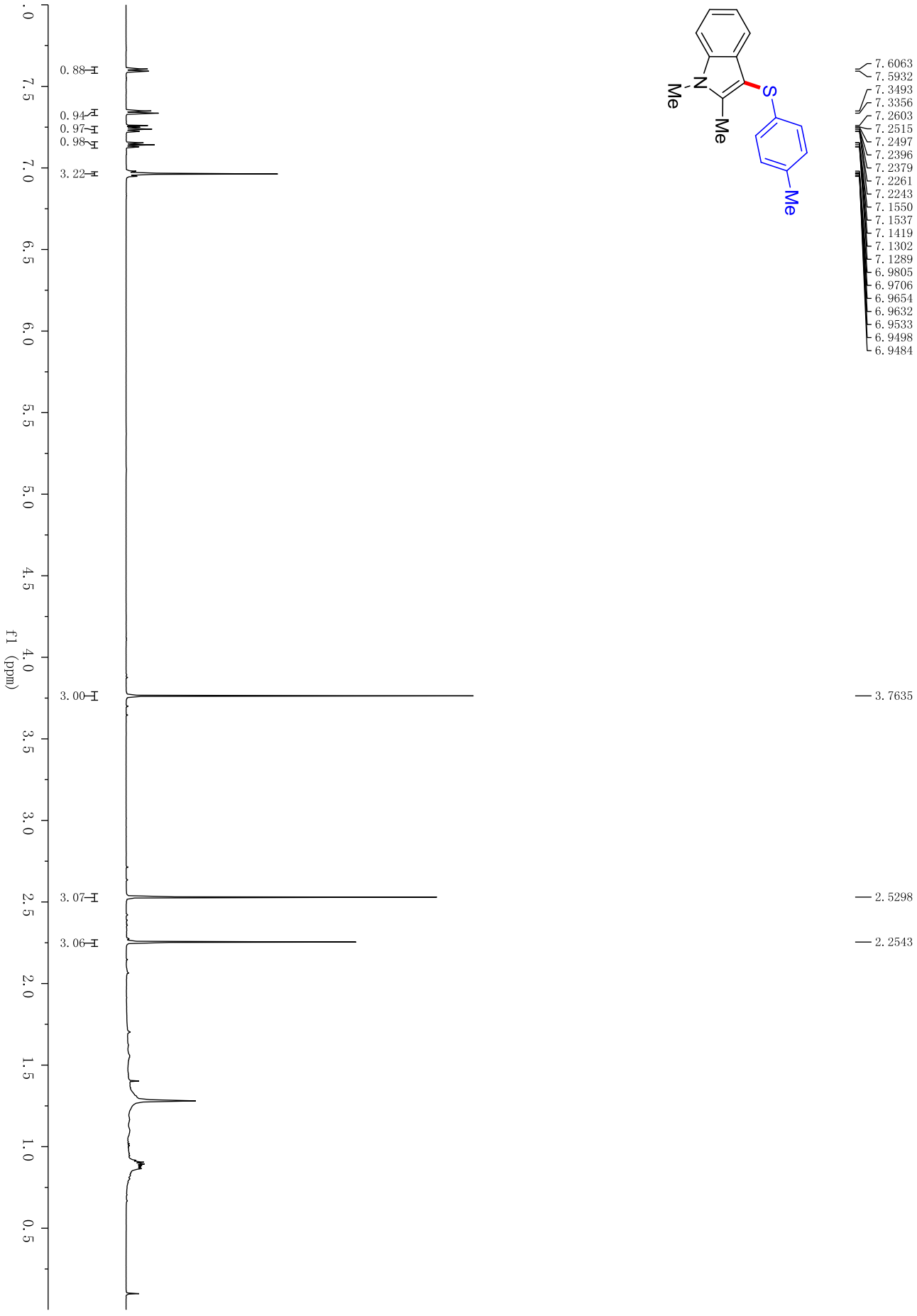

148.5920
142.6173
136.6082
131.3408
129.3206
128.4790
123.4236
121.2828
120.2184
119.6243
119.1176
111.9615
100.6734
77.2622
77.0505
76.8390
f1 (ppm)

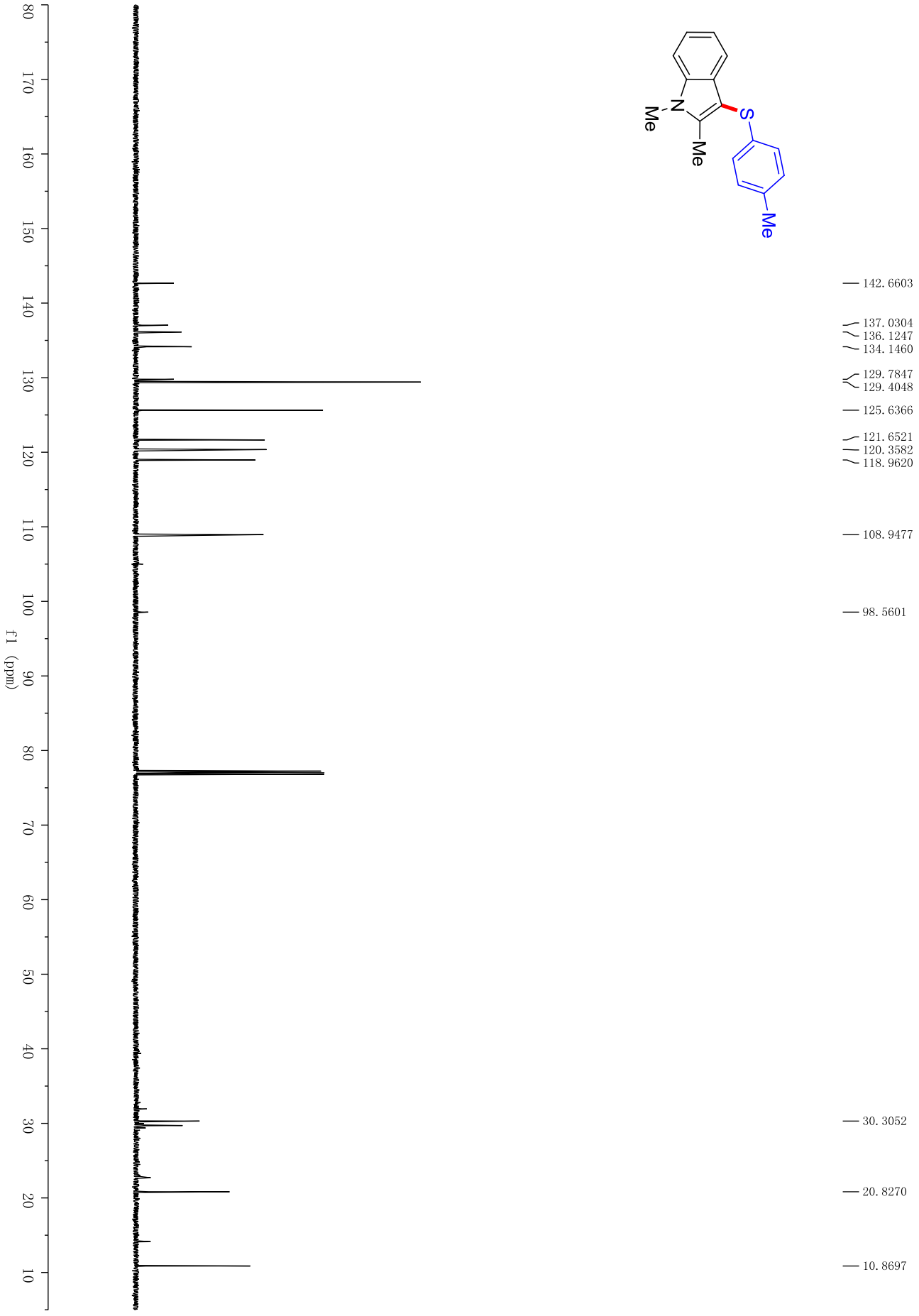

1.00
1.01
0.98
1.05
3.05
2.01
1.06
3.00
Me
N
S
7.6311
7.6179
7.4038
7.3900
7.3432
7.3194
7.3074
7.2940
7.2603
7.1883
7.1763
7.1711
7.1632
7.1576
7.1453
7.1145
7.1024
7.0621
7.0501
7.0381
3.8538
f1 (ppm)

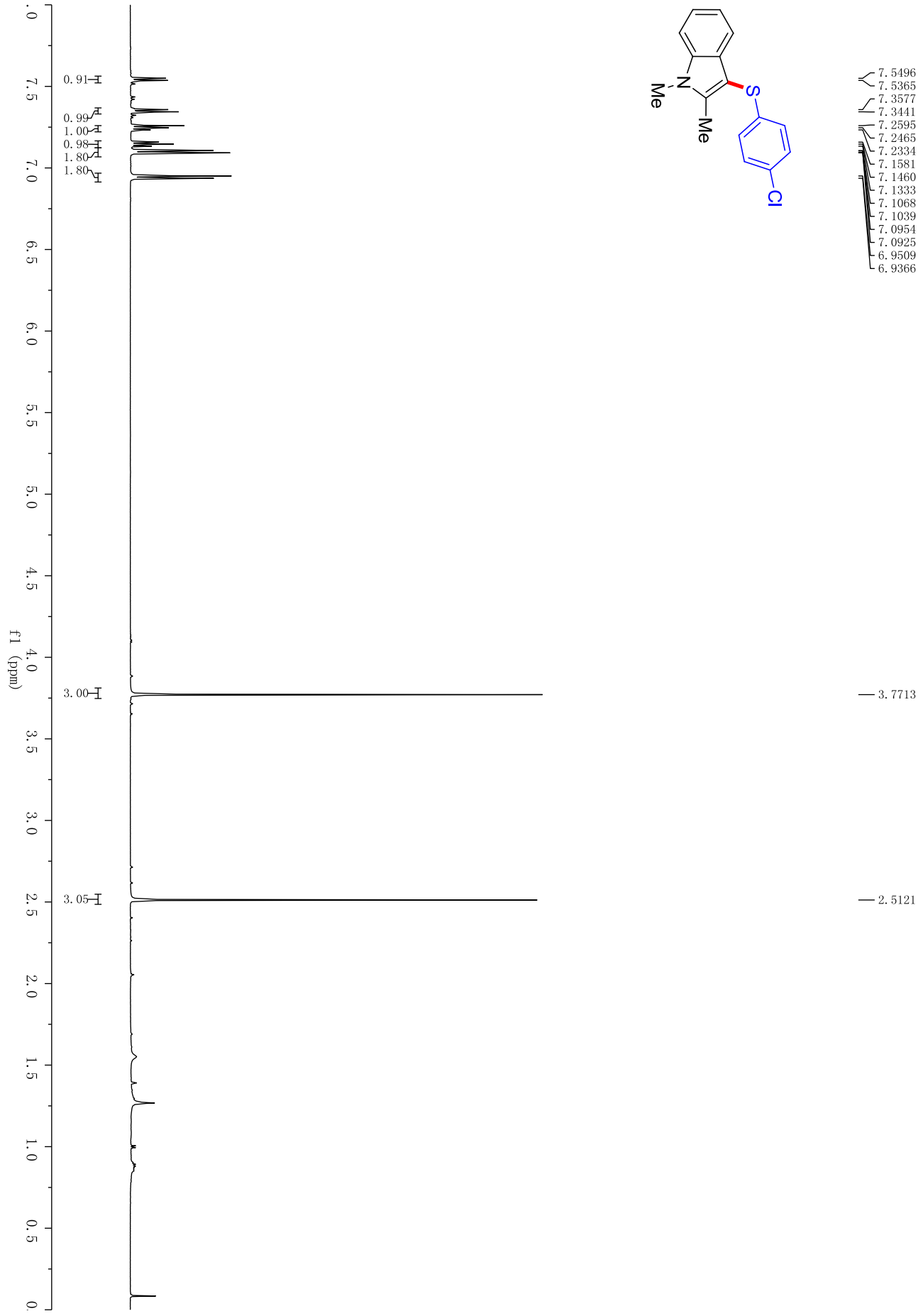

139.6529
137.5337
135.0349
129.8245
128.6303
125.7118
124.6418
122.5465
120.4789
119.7322
109.6948
100.5234
77.2273
77.0156
76.8037
33.1308
f1 (ppm)
Me
N
S

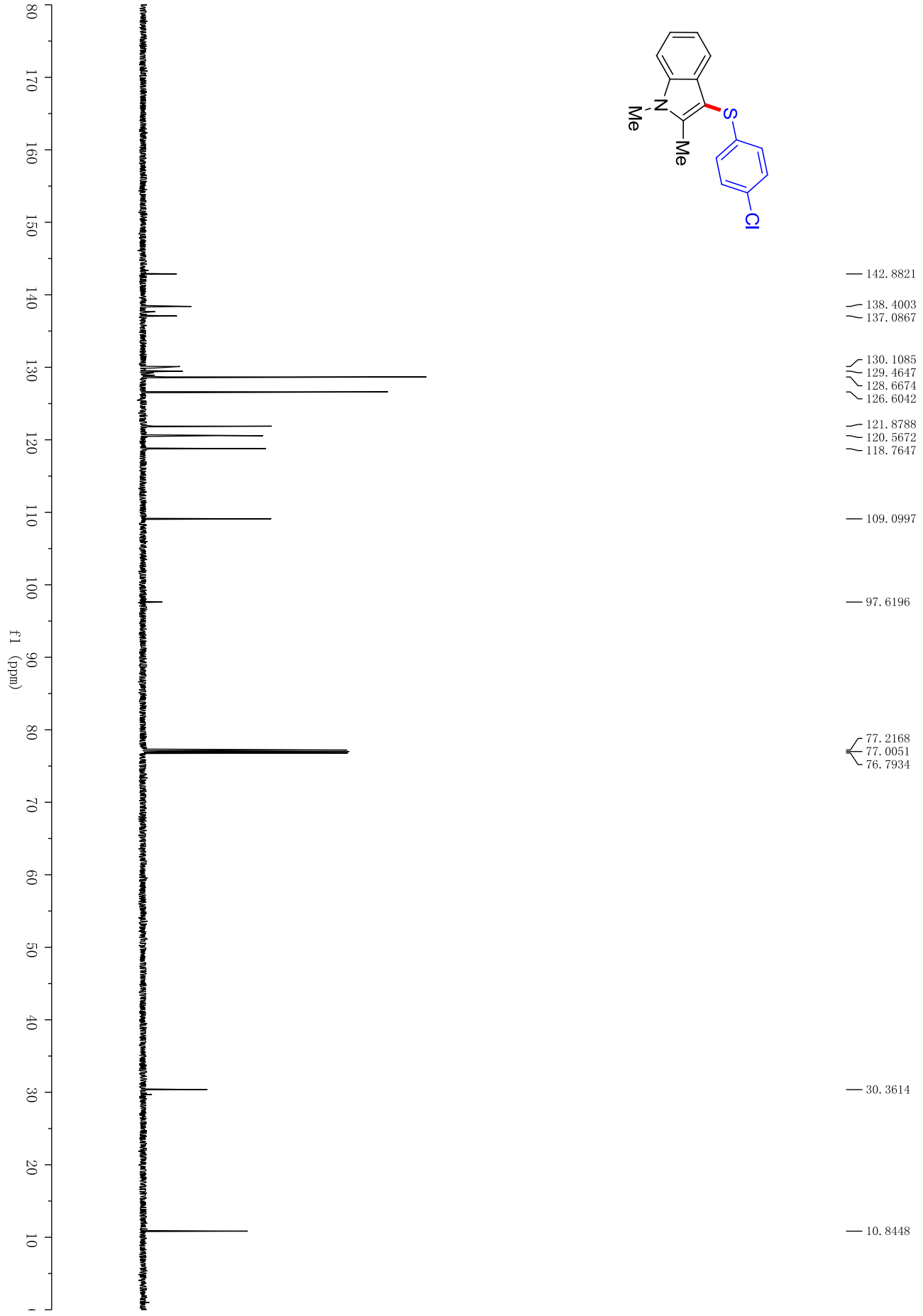

0.99
0.99
0.96
1.10
1.05
1.97
2.02
3.00
3.00
f1 (ppm)
7.6331
7.6199
7.3901
7.3764
7.3268
7.3081
7.2961
7.2827
7.2605
7.1797
7.1677
7.1548
7.0410
7.0273
6.9826
6.9692
3.8416
2.2544
N
Me
S
Me

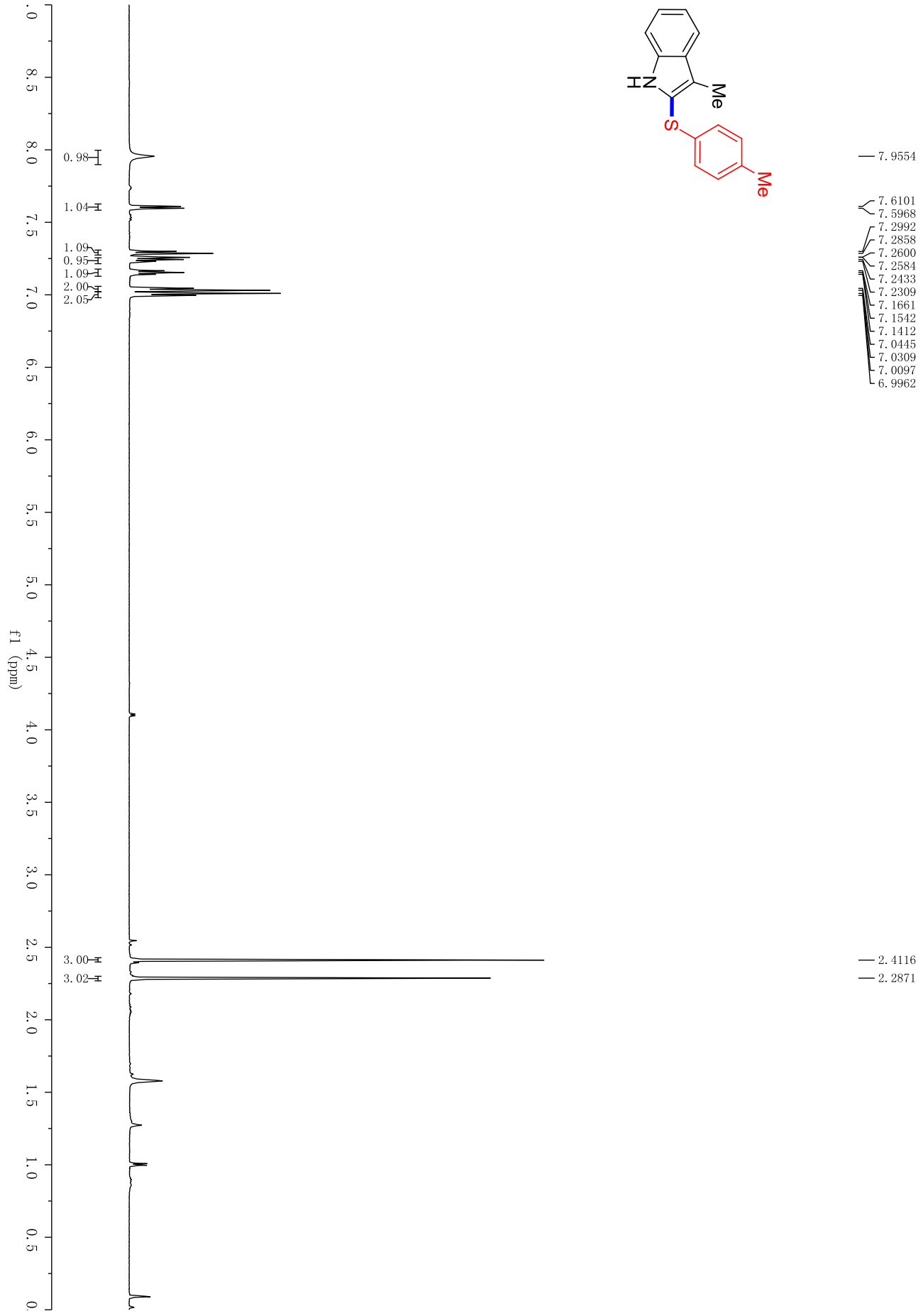

137.4971
135.9242
134.8093
134.4941
129.8284
129.4150
126.1170
122.4662
120.3917
119.7523
109.6370
101.2128
77.2259
77.0140
76.8023
33.0935
20.8449
f1 (ppm)
Me
N
S
Me

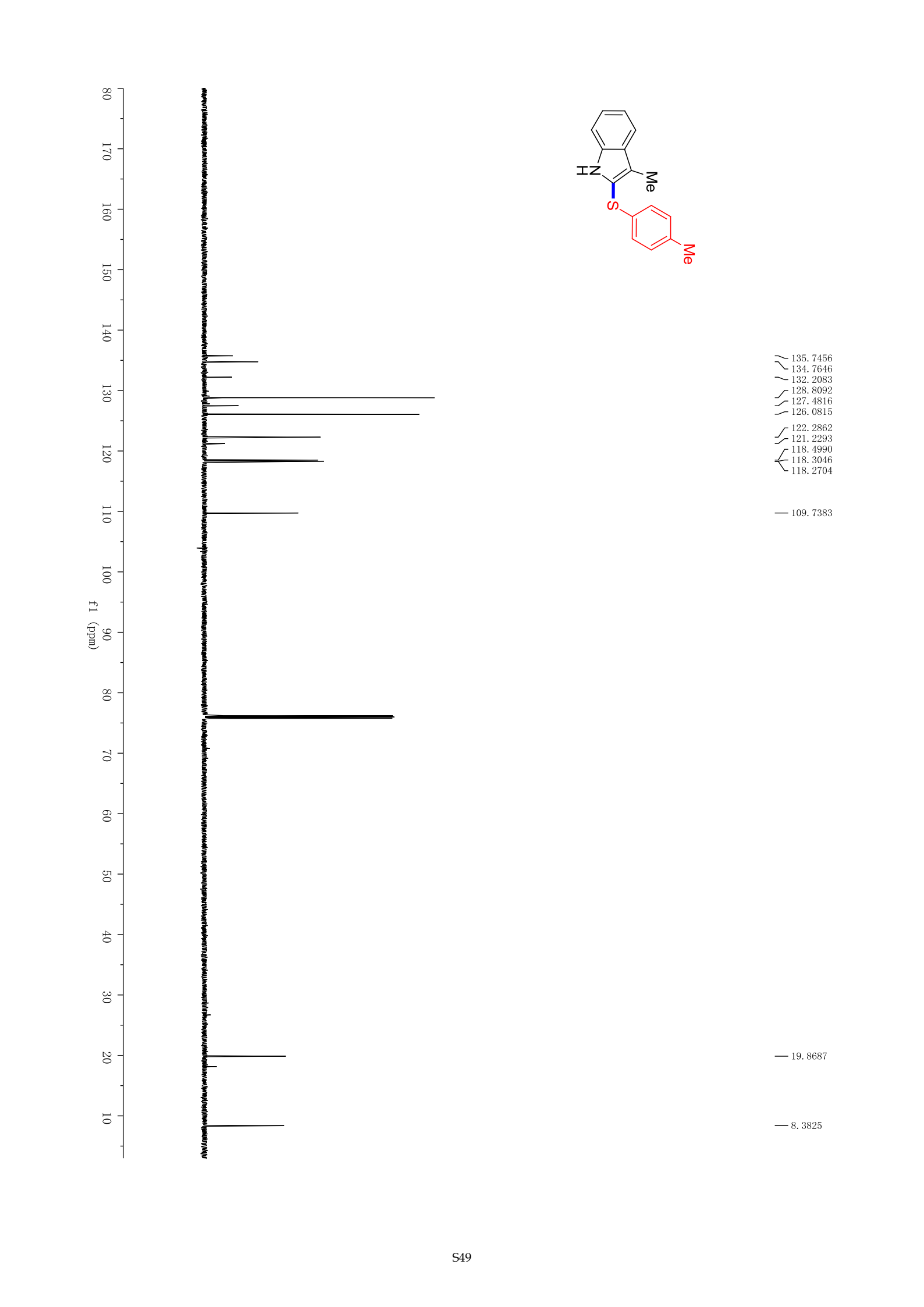

0.88
0.94
0.97
0.98
3.22
3.00
3.07
3.06
f1 (ppm)
7.6063
7.5932
7.3493
7.3356
7.2603
7.2515
7.2497
7.2396
7.2379
7.2261
7.2243
7.1550
7.1537
7.1419
7.1302
7.1289
6.9805
6.9706
6.9654
6.9632
6.9533
6.9498
6.9484
3.7635
2.5298
2.2543
N
Me
Me
S
Me

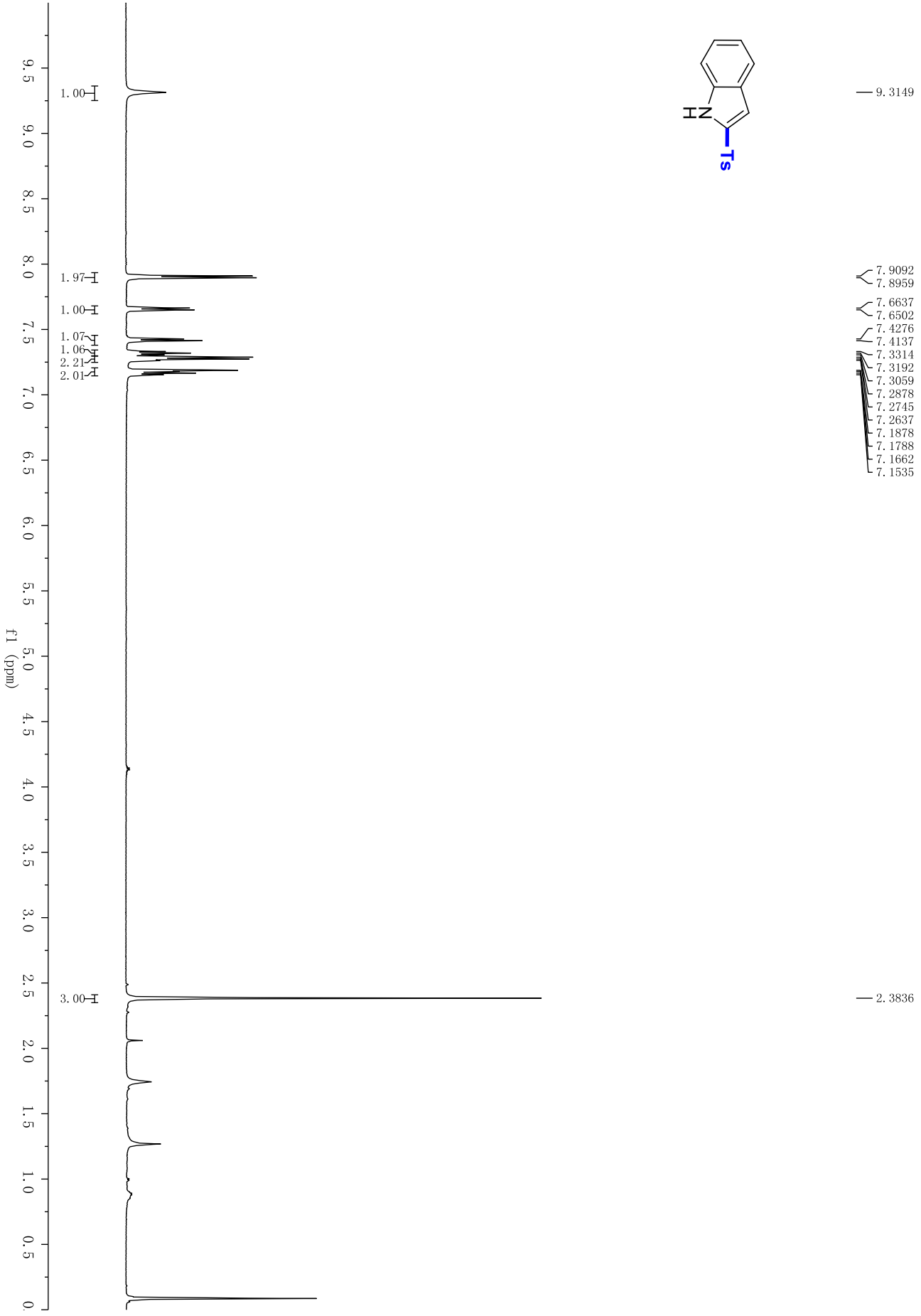

f1 (ppm)
142.6603
137.0304
136.1247
134.1460
129.7847
129.4048
125.6366
121.6521
120.3582
118.9620
108.9477
98.5601
30.3052
20.8270
10.8697
N
Me
Me
S
Me

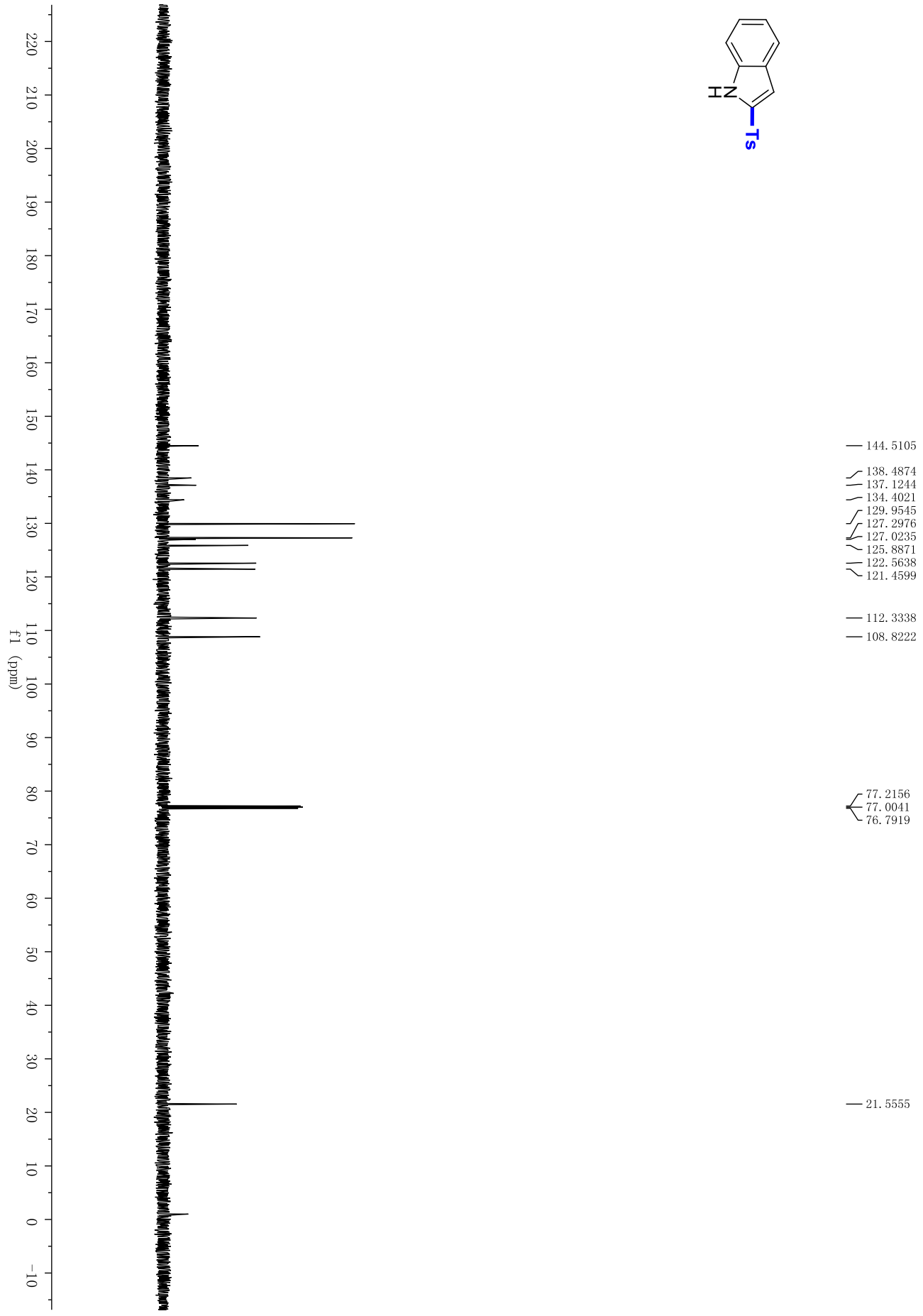

f1 (ppm)
0.91
0.99
1.00
0.98
1.80
1.80
3.00
3.05
N
Me
Me
S
Cl
7.5496
7.5365
7.3577
7.3441
7.2595
7.2465
7.2334
7.1581
7.1460
7.1333
7.1068
7.1039
7.0954
7.0925
6.9509
6.9366
3.7713
2.5121


142.8821
138.4003
137.0867
130.1085
129.4647
128.6674
126.6042
121.8788
120.5672
118.7647
109.0997
97.6196
77.2168
77.0051
76.7934
30.3614
10.8448
f1 (ppm)
N
Me
Me
S
Cl


f1 (ppm)
0.98
1.04
1.09
0.95
1.09
2.00
2.05
3.00
3.02
7.9554
7.6101
7.5968
7.2992
7.2858
7.2600
7.2584
7.2433
7.2309
7.1661
7.1542
7.1412
7.0445
7.0309
7.0097
6.9962
2.4116
2.2871
HN
Me
S
Me


135.7456
134.7646
132.2083
128.8092
127.4816
126.0815
122.2862
121.2293
118.4990
118.3046
118.2704
109.7383
19.8687
8.3825
f1 (ppm)
Me
S
Me
H
N


1.00
1.97
1.00
1.07
1.06
2.21
2.01
3.00
f1 (ppm)
9.3149
7.9092
7.8959
7.6637
7.6502
7.4276
7.4137
7.3314
7.3192
7.3059
7.2878
7.2745
7.2637
7.1878
7.1788
7.1662
7.1535
2.3836
HN
Ts


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)
N
H
Ts
144.5105
138.4874
137.1244
134.4021
129.9545
127.2976
127.0235
125.8871
122.5638
121.4599
112.3338
108.8222
77.2156
77.0041
76.7919
21.5555