Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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AcOH-mediated dichloroimination of indoles using chloramine-B: A facile access to 2,3-functionalized indolines

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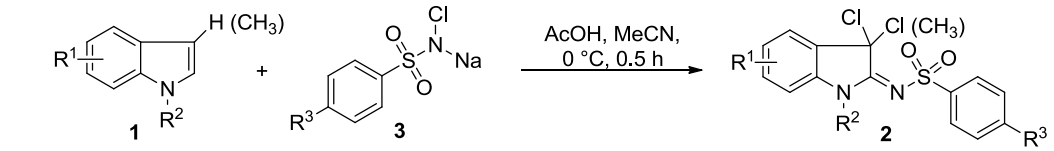
Electronic Supplementary Information

Content

Ⅰ. General information

All chemicals were purchased from commercial suppliers and used without further purification. ^{1}H-NMR and ^{13}C-NMR were recorded on an Agilent 400 MHz spectrometer using TMS as internal standard. Spin multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as brs (broad). Coupling constants (*J*) are given in hertz (Hz). High resolution mass spectra were obtained from Applied Biosystems (ABI) Q-Star Elite MALDI-TOF Mass Spectrometer. All experiments were monitored by thin layer chromatography (TLC).

Ⅱ. General procedure for AcOH-mediated dichloroimination of indoles using chloramine-B



R^1 = CH_3, CO_2Me, Br, Cl, F, OCH_3, CHO, CN, CF_3CONH
R^2 = CH_3, Bn, allyl

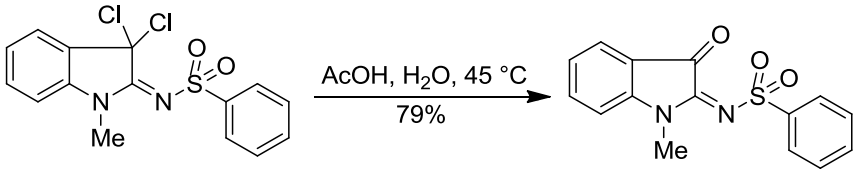
R^3 = H, CH_3

19 examples
up to 94% yield

To a stirred mixture of indoles **1** (1.0 mmol) and compound **3** (3.0 mmol) in CH_3CN (10 mL) at 0 ^{o}C, AcOH (5.0 mmol) was added. After addition, the reaction mixture was stirred for further 0.5 hour at the same temperature. The reaction mixture was filtered. The filtrate was concentrated in vacuo. Purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 3/1) afforded the desired product **2**.

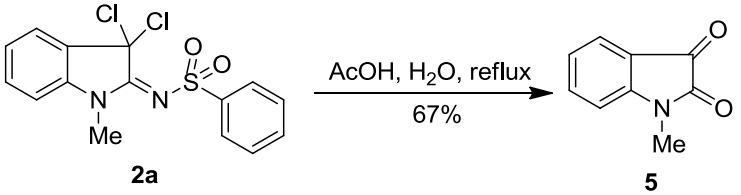
Ⅲ. Procedures for the transformation of indolines 2 to isatin analogs and 2-aminoindoles

1. Procedure for synthesis of 4



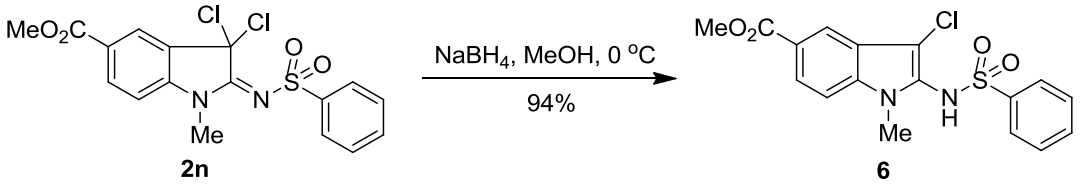
A mixture of **2a** (106.1 mg, 0.3 mmol) in AcOH/H_2O (9:1, 10 mL) was stirred in a round bottom flask at 45 ^{o}C for 6 hours. Removal of the solvent in vacuo and purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 5/1) afforded the desired product **4** as a brown solid (71.1 mg, 0.24 mmol, 79 %).

2. Procedure for synthesis of 5



A mixture of **2a** (106.1 mg, 0.3 mmol) in AcOH/H_2O (9:1, 10 mL) in a round bottom flask was refluxed for 4 hours. Removal of solvent in vacuo and purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 2/1) afforded the desired product **5** as a brown solid (32.4 mg, 0.20 mmol, 67 %).

3. Procedure for synthesis of 6

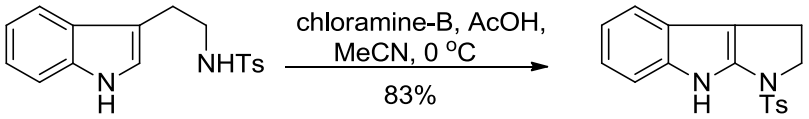


2n **6**

To a stirred solution of **2n** (123.6 mg, 0.3 mmol) in MeOH (10 mL) at 0 ℃, $NaBH_4$ (13.7 mg, 0.36 mmol) was added. The reaction mixture was stirred at 0 ℃ for 30 minutes and quenched with saturated aqueous NH_4Cl solution (5 mL). The resulted mixture was extracted by ethyl acetate (10 mL × 3). The combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated in vacuo. Purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 5/1) to afford the desired product **6** as a white solid (106.6 mg, 0.28 mmol, 94 %).

Ⅳ. Procedures for the syntheses of 8 and 9

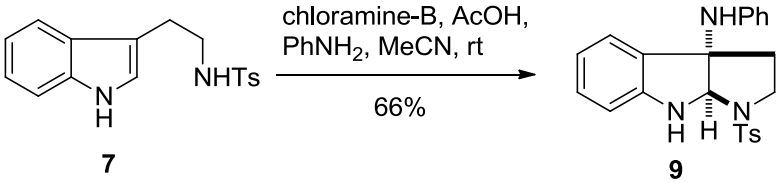
1. Synthesis of 8



7 **8**

To a stirred mixture of **7** (100.0 mg, 0.32 mmol) and chloramine-B (204.1 mg, 0.96 mmol) in CH_3CN (8 mL), AcOH (0.092 mL, 1.6 mmol) was added. The reaction mixture was stirred at 0 °C for further 1 hour. TLC monitoring indicated the substrate **7** was consumed completely. The reaction mixture was filtered. The filtrate was concentrated in vacuo. Purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 5/1) afforded the desired product **8** as a white solid (82.7 mg, 0.27 mmol, 83%).

2. Synthesis of 9

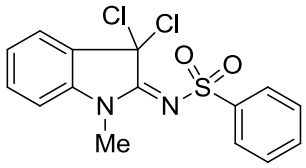


7 **9**

A mixture of **7** (62.6 mg, 0.20 mmol), aniline (0.073 mL, 0.80 mmol) and chloramine-B (85.2 mg, 0.4 mmol) in CH_3CN (3 mL) was cooled to 0 °C, followed by addition of AcOH (0.023 mL,

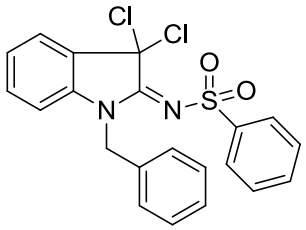
0.4 mmol). The reaction mixture was warming to room temperature and kept stirring for 4 hours. TLC monitoring indicated the substrate **7** was consumed completely. The reaction mixture was filtered. The filtrate was concentrated in vacuo. Purification of the resulted crude through a flash chromatography on silica gel with petroleum ether/ethyl acetate (v/v = 2/1) afforded the desired product **9** as a brown solid (53.5 mg, 0.13 mmol, 66%).

Ⅴ. Experimental data for the described substances



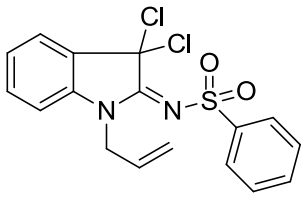
2a

(*E*)-*N*-(3,3-dichloro-1-methylindolin-2-ylidene)benzenesulfonamide (**2a**). yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.5 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.52-7.60 (m, 3H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.26-7.29 (m, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.92, 142.69, 140.08, 132.25, 131.92, 131.06, 128.72, 126.74, 125.37, 124.55, 110.00, 31.29. HRMS-ESI (m/z): calcd for $C_{15}H_{12}Cl_2N_2NaO_2S$ $[M+Na]^+$: 376.9894, found 376.9905.



2b

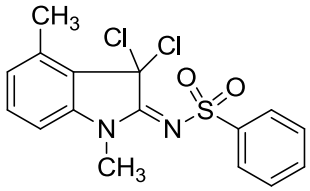
(*E*)-*N*-(1-benzyl-3,3-dichloroindolin-2-ylidene)benzenesulfonamide (**2b**). yellow solid, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.1 Hz, 2H), 7.68 (d, *J* = 6.9 Hz, 1H), 7.55-7.48 (m, 3H), 7.31-7.19 (m, 7H), 6.82 (d, *J* = 7.6 Hz, 1H), 5.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.59, 142.43, 138.45, 133.69, 132.29, 131.74, 131.47, 129.05, 128.73, 128.23, 127.19, 126.77, 125.27, 124.50, 110.69, 74.65, 46.57. HRMS-ESI (m/z): calcd for $C_{21}H_{16}Cl_2N_2NaO_2S$ $[M+Na]^+$: 453.0207, found 453.0220.



2c

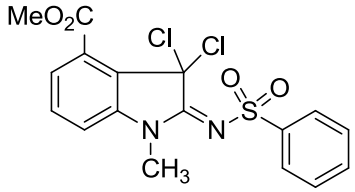
(*E*)-*N*-(1-allyl-3,3-dichloroindolin-2-ylidene)benzenesulfonamide (**2c**). brown solid, 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61-7.47 (m, 3H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.27-7.21 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.84 (td, *J* = 12.6, 10.9, 5.3 Hz, 1H), 5.24 (t, *J* = 13.7 Hz, 2H), 4.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.17, 142.66, 138.83, 132.20, 131.69, 131.35, 129.32, 128.67, 126.72, 125.20, 124.52, 118.93, 110.57, 75.37, 45.76. HRMS-ESI (m/z): calcd for $C_{17}H_{14}Cl_2N_2NaO_2S$ $[M+Na]^+$: 403.0051, found 403.0061.



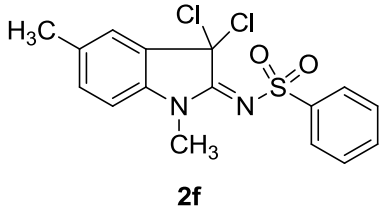
2d

(*E*)-*N*-(3,3-dichloro-1,4-dimethylindolin-2-ylidene)benzenesulfonamide (**2d**). yellow solid, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.2 Hz, 2H), 7.62-7.47 (m, 3H), 7.33 (t, *J* = 7.9 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.9 Hz, 1H), 3.59 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.76, 142.94, 140.57, 136.93, 132.14, 131.64, 128.68, 127.70, 127.32, 126.64, 107.63, 77.58, 31.58, 17.31. HRMS-ESI (m/z): calcd for $C_{16}H_{14}Cl_2N_2NaO_2S$ $[M+Na]^+$: 391.0051, found 391.0042.



2e

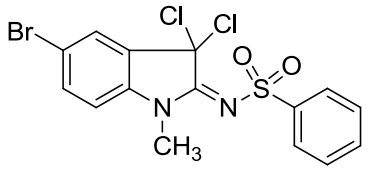
(*E*)-methyl3,3-dichloro-1-methyl-2-((phenylsulfonyl)imino)indoline-4-carboxylate (**2e**). yellow solid, 52% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.66-7.45 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H), 3.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.44, 161.16, 142.69, 141.71, 132.28, 132.10, 129.31, 128.73, 127.95, 127.27, 126.67, 114.01, 52.51, 32.06. HRMS-ESI (m/z): calcd for $C_{17}H_{14}Cl_2N_2NaO_4S$ $[M+Na]^+$: 434.9949, found 434.9943.



2f

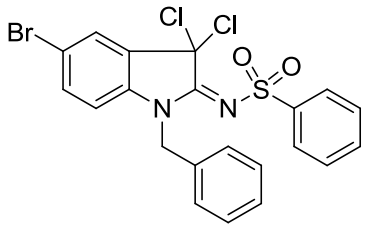
(*E*)-*N*-(3,3-dichloro-1,5-dimethylindolin-2-ylidene)benzenesulfonamide (**2f**). yellow solid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.6 Hz, 2H), 7.58-7.50 (m, 3H), 7.22 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz,

$CDCl_3$) δ 160.78, 157.87, 142.87, 133.24, 132.15, 131.97, 128.69, 126.63, 117.23, 110.97, 110.41, 56.01, 31.53. HRMS-ESI (m/z): calcd for $C_{16}H_{14}Cl_2N_2NaO_2S$ $[M+Na]^+$: 391.0051, found 391.0062.



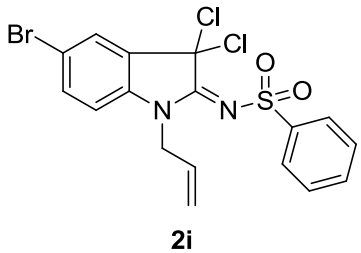
2g

(*E*)-*N*-(5-bromo-3,3-dichloro-1-methylindolin-2-ylidene)benzenesulfonamide (**2g**). yellow solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.78 (s, 1H), 7.63-7.49 (m, 4H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.30, 142.40, 139.11, 134.75, 132.66, 132.37, 128.74, 127.76, 126.76, 117.85, 111.43, 31.32. HRMS-ESI (m/z): calcd for $C_{15}H_{11}BrCl_2N_2NaO_2S$ $[M+Na]^+$: 454.8999, found 454.8997.



2h

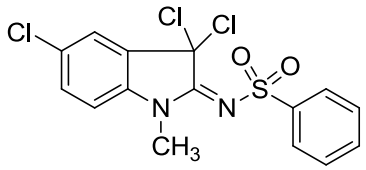
(*E*)-*N*-(1-benzyl-5-bromo-3,3-dichloroindolin-2-ylidene)benzenesulfonamide (**2h**). brown solid, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.79 (s, 1H), 7.59-7.53 (m, 1H), 7.48-7.45 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.27 (s, 3H), 7.16 (s, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.03 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.99, 142.26, 137.57, 134.60, 133.32, 133.06, 132.41, 129.12, 128.77, 128.37, 127.65, 127.13, 126.78, 117.72, 112.28, 73.88, 46.72. HRMS-ESI (m/z): calcd for $C_{21}H_{15}BrCl_2N_2NaO_2S$ $[M+Na]^+$: 530.9312, found 530.9306.



2i

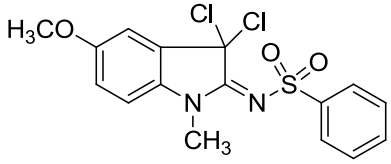
(*E*)-*N*-(1-allyl-5-bromo-3,3-dichloroindolin-2-ylidene)benzenesulfonamide (**2i**). yellow solid, 67% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 2H), 7.79 (d, *J* = 1.9 Hz, 1H), 7.61-7.44 (m, 4H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.81 (ddd, *J* = 22.4, 10.5, 5.3 Hz, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 4.52 (d, *J* = 5.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.59, 142.26,

137.78, 134.62, 132.88, 132.43, 128.93, 128.76, 127.70, 126.76, 119.13, 117.72, 112.15, 74.31, 45.75. HRMS-ESI (m/z): calcd for $C_{17}H_{13}BrCl_2N_2NaO_2S$ $[M+Na]^+$: 480.9156, found 480.9167.



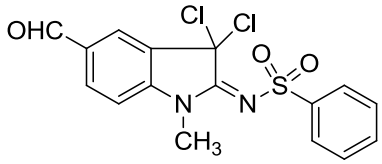
2j

(*E*)-*N*-(3,3,5-trichloro-1-methylindolin-2-ylidene)benzenesulfonamide (**2j**). brown solid, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.64 (s, 1H), 7.58-7.50 (m, 3H), 7.40 (d, *J* = 8.4, 1H), 6.88 (d, *J* = 6.9 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.38, 142.36, 138.57, 132.25, 131.86, 130.79, 128.70, 126.78, 124.87, 111.09, 75.60, 31.27. HRMS-ESI (m/z): calcd for $C_{15}H_{11}Cl_3N_2NaO_2S$ $[M+Na]^+$: 410.9505, found 410.9500.



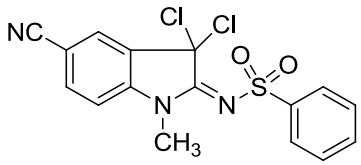
2k

(*E*)-*N*-(3,3-dichloro-5-methoxy-1-methylindolin-2-ylidene)benzenesulfonamide (**2k**). yellow solid, 59% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.6 Hz, 2H), 7.57-7.50 (m, 3H), 7.22 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 3.85 (s, 1H), 3.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.78, 157.87, 142.87, 133.24, 132.15, 131.97, 128.69, 126.63, 117.23, 110.97, 110.41, 56.01, 31.53. HRMS-ESI (m/z): calcd for $C_{16}H_{14}Cl_2N_2NaO_3S$ $[M+Na]^+$: 407.0000, found 406.9997.



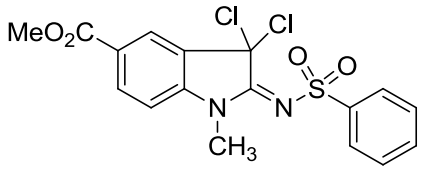
2l

(*E*)-*N*-(3,3-dichloro-5-formyl-1-methylindolin-2-ylidene)benzenesulfonamide (**2l**). yellow solid, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.20 (s, 1H), 8.09 (d, *J* = 7.9 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.63-7.53 (m, 3H), 7.10 (d, *J* = 8.2 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.68, 160.71, 144.68, 142.05, 134.63, 133.70, 132.60, 132.10, 128.83, 126.86, 125.33, 110.27, 74.63, 31.08. HRMS-ESI (m/z): calcd for $C_{16}H_{12}Cl_2N_2NaO_3S$ $[M+Na]^+$: 404.9843, found 404.9829.



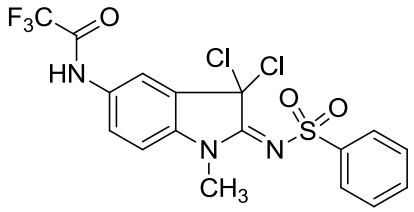
2m

(*E*)-*N*-(3,3-dichloro-5-cyano-1-methylindolin-2-ylidene)benzenesulfonamide (**2m**). yellow solid, 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.94 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.65-7.50 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.19, 143.37, 141.86, 136.47, 132.71, 132.14, 128.87, 128.10, 126.88, 117.60, 110.72, 108.63, 74.12, 31.05. HRMS-ESI (m/z): calcd for $C_{16}H_{11}Cl_2N_3NaO_2S$ $[M+Na]^+$: 401.9847, found 401.9835.



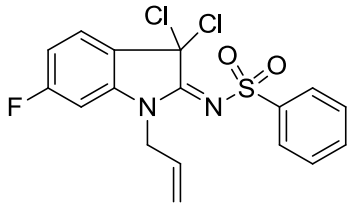
2n

(*E*)-methyl3,3-dichloro-1-methyl-2-((phenylsulfonyl)imino)indoline-5-carboxylate (**2n**). yellow solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 7.5 Hz, 2H), 7.62-7.52 (m, 3H), 7.00 (d, *J* = 8.4 Hz, 1H), 3.96 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (101 MHz, cdcl3) δ 165.50, 160.89, 143.51, 142.21, 134.01, 132.51, 131.20, 128.80, 127.28, 126.79, 125.87, 109.84, 75.06, 52.51, 31.10. HRMS-ESI (m/z): calcd for $C_{17}H_{14}Cl_2N_2NaO_4S$ $[M+Na]^+$: 434.9949, found 434.9956.



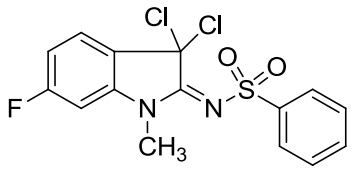
2o

(*E*)-*N*-(3,3-dichloro-1-methyl-2-((phenylsulfonyl)imino)indolin-5-yl)-2,2,2-trifluoroacetamide (**2o**). brown solid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.96 (s, 1H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.61-7.52 (m, 3H), 6.97 (d, *J* = 8.5 Hz, 1H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.59, 155.07 (q, *J* = 37.0 Hz), 143.00, 137.36, 134.35, 133.05, 130.88, 129.62, 126.56, 125.35, 117.28, 116.12(q, *J* = 287.0 HZ), 112.66, 76.54, 31.74. HRMS-ESI (m/z): calcd for $C_{17}H_{12}Cl_2F_3N_3NaO_3S$ $[M+Na]^+$: 487.9826, found 487.9804.



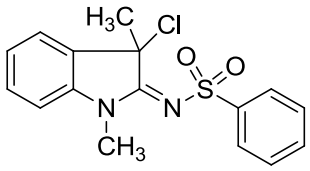
2p

(*E*)-N-(1-allyl-3,3-dichloro-6-fluoroindolin-2-ylidene)benzenesulfonamide (**2p**). yellow solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 8.5, 5.1 Hz, 1H), 7.61-7.49 (m, 3H), 6.92 (t, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 5.88-5.78 (m, 1H), 5.29 (d, *J* = 10.3 Hz, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 4.51 (d, *J* = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.64 (d, *J* = 250.0 Hz), 160.45, 142.31, 140.59 (d, *J* = 12.0 Hz), 132.41, 128.94, 128.74, 126.93 (d, *J* = 3.0 Hz), 126.75, 126.17(d, *J* = 11.0 Hz), 119.19, 111.81 (d, *J* = 24.0 Hz), 99.35 (d, *J* = 28.0 Hz), 74.51, 45.83.HRMS-ESI (m/z): calcd for $C_{17}H_{13}Cl_2FN_2NaO_2S$ $[M+Na]^+$: 420.9957, found 420.9937.



2q

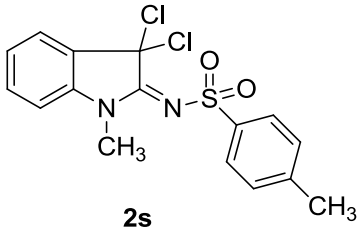
(*E*)-*N*-(3,3-dichloro-6-fluoro-1-methylindolin-2-ylidene)benzenesulfonamide (**2q**). yellow solid, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.0 Hz, 2H), 7.75-7.47 (m, 4H), 7.09-6.86 (m, 1H), 6.68 (d, *J* = 7.5 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.84 (d, *J* = 252.1 Hz), 161.16, 142.37, 141.88 (d, *J* = 11.7 Hz), 132.41, 128.77, 126.78, 126.68 (d, *J* = 3.0 Hz), 126.23 (d, *J* = 10.0 Hz), 111.86 (d, *J* = 23.0 Hz), 98.79 (d, *J* = 28.0 Hz), 75.57, 31.31. HRMS-ESI (m/z): calcd for $C_{15}H_{11}Cl_2FN_2NaO_2S$ $[M+Na]^+$: 394.9800, found 394.9791.



2r

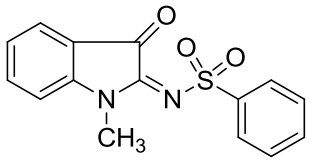
(*E*)-*N*-(3-chloro-1,3-dimethylindolin-2-ylidene)benzenesulfonamide (**2r**). yellow solid, 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.8 Hz, 2H), 7.62-7.43 (m, 4H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 3.47 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.06, 143.11, 141.05, 133.09, 132.01, 130.32, 128.67, 126.59, 124.84, 123.45,

109.80, 64.72, 30.43, 26.98. HRMS-ESI (m/z): calcd for $C_{16}H_{15}ClN_2NaO_2S$ $[M+Na]^+$: 357.0440, found 357.0423.



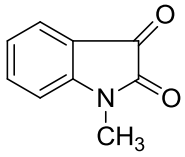
2s

(*E*)-*N*-(3,3-dichloro-1-methylindolin-2-ylidene)-4-methylbenzenesulfonamide (**2s**). yellow solid, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26 (m, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 3.57 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.46, 143.34, 140.32, 140.22, 132.93, 130.51, 130.02, 126.62, 126.03, 124.57, 111.98, 77.00, 31.66, 21.46. HRMS-ESI (m/z): calcd for $C_{16}H_{14}Cl_2N_2NaO_2S$ $[M+Na]^+$: 391.0051, found 391.0057.



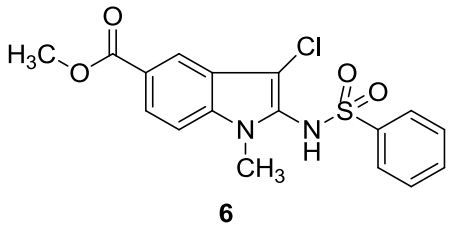
4

(*E*)-*N*-(1-methyl-3-oxoindolin-2-ylidene)benzenesulfonamide (**4**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.58-7.48 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.98, 151.44, 151.19, 142.56, 137.94, 132.23, 128.53, 126.93, 126.36, 124.55, 118.20, 110.40, 28.46. HRMS-ESI (m/z): calcd for $C_{15}H_{13}N_2O_3S[M+H]^+$: 301.0647, found 301.0641.



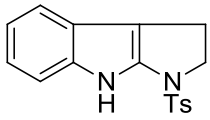
5

1-Methylindoline-2,3-dione (**5**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.36, 158.21, 151.43, 138.43, 125.27, 123.84, 117.39, 109.95, 26.21. Spectral data was in agreement with that reported in the literature.[1]



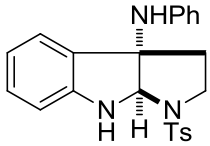
6

Methyl 3-chloro-1-methyl-2-(phenylsulfonamido)-1*H*-indole-5-carboxylate (**6**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.71 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.68, 138.49, 136.25, 133.68, 129.23, 127.69, 127.47, 124.68, 122.90, 122.47, 121.46, 109.92, 103.18, 52.09, 30.48. HRMS-ESI (m/z): calcd for $C_{17}H_{16}ClN_2O_4S$ $[M+H]^+$: 379.0519, found 379.0548.



8

1-Tosyl-1,2,3,8-tetrahydropyrrolo[2,3-*b*]indole (**8**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (brs, 1H), 7.58 (d, *J* = 6.6 Hz, 2H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.28-7.21 (m, 3H), 7.14-7.07 (m, 2H), 4.12 (t, *J* = 7.8 Hz, 2H), 2.80 (t, *J* = 6.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.64, 141.43, 137.97, 131.72, 129.90, 127.70, 124.07, 120.50, 117.60, 111.81, 109.99, 104.10, 55.69, 23.25, 21.60. HRMS-ESI (m/z): calcd for $C_{17}H_{17}N_2O_2S$ $[M+H]^+$: 313.1011, found 313.1005.



9

N-phenyl-1-tosyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-*b*]indol-3a-amine (**9**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.18-7.13 (m, 2H), 6.98 (t, *J* = 7.5 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.70-6.65 (m, 2H), 6.23 (d, *J* = 8.4 Hz, 2H), 5.65 (s, 1H), 4.92 (s, 1H), 3.80 (br s, 1H), 3.55-3.47 (m, 1H), 3.35-3.28 (m, 1H), 2.47-2.36 (m, 4H), 2.32-2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.73, 144.56, 143.70, 135.55, 129.91, 129.79, 129.52, 129.08, 127.20, 123.28, 119.50, 118.34, 114.84, 109.84, 79.10, 73.39, 46.02, 37.79, 21.56. HRMS-ESI (m/z): calcd for $C_{23}H_{23}N_3NaO_2S$ $[M+Na]^+$: 428.1409, found 428.1403.

Ⅵ. X-ray Crystallographic Data of 2i

Colorless crystals of **2i** suitable for X-ray analysis were obtained by recrystallization from Et_2O /hexane.

Datablock: dj816_0m

Bond precision: C-C = 0.0127 A Wavelength=0.71073

Cell: a=8.9358(18) b=9.326(2) c=12.002(3)

alpha=106.670(3) beta=101.817(4) gamma=93.100(4)

Temperature: 296 K

Calculated Reported

Volume	931.0(4)	931.0(4)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C17H13BrCl2N2O2S	?
Sum formula	C17H13BrCl2N2O2S	C17H13BrCl2N2O2S
Mr	460.16	460.16
Dx,g cm-3	1.641	1.641
Z	2	2
Mu (mm-1)	2.620	2.620
F000	460.0	460.0
F000’	460.41	
h,k,lmax	10,11,14	10,11,14
Nref	3280	3254
Tmin,Tmax	0.630,0.730	0.650,0.744
Tmin’	0.618	

Correction method= MULTI-SCAN

Data completeness= 0.992 Theta(max)= 25.000

R(reflections)= 0.0770(2472) wR2(reflections)= 0.2417(3254)

S = 1.045 Npar= 226

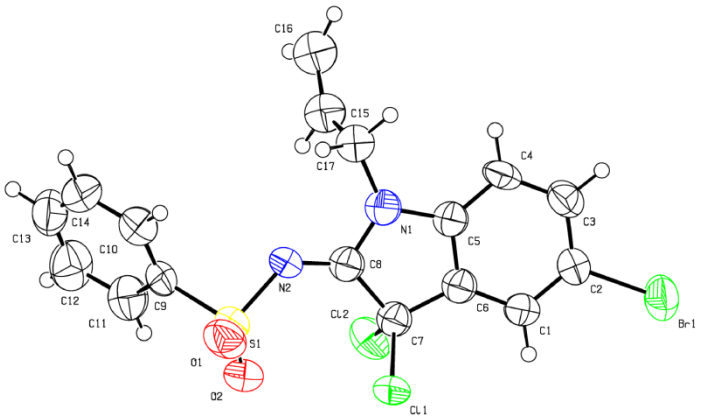
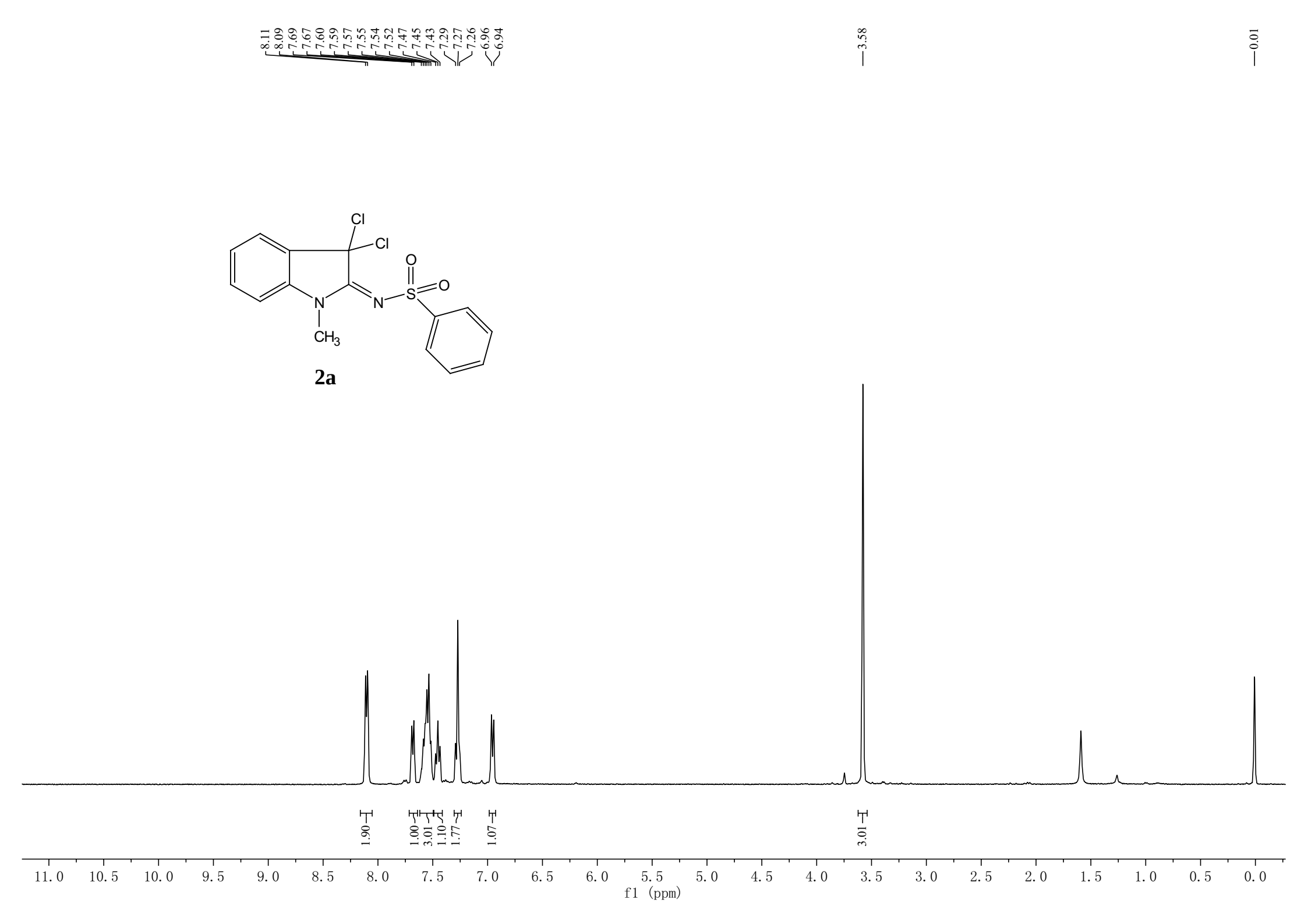


Figure 1. The crystal structure of 2i.

Ⅶ. References

1. Esmaeili, A.; Darbanian, M. *Tetrahedron*, 2003, **59**, 5545.

Ⅷ. Spectral copies of ^{1}H- and ^{13}C-NMR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7.43
7.29
7.27
7.26
6.96
6.94
3.58
0.01
Cl
Cl
O
O
N
N
S
CH3
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1.00
3.01
1.10
1.77
1.07
3.01
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
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5.5
5.0
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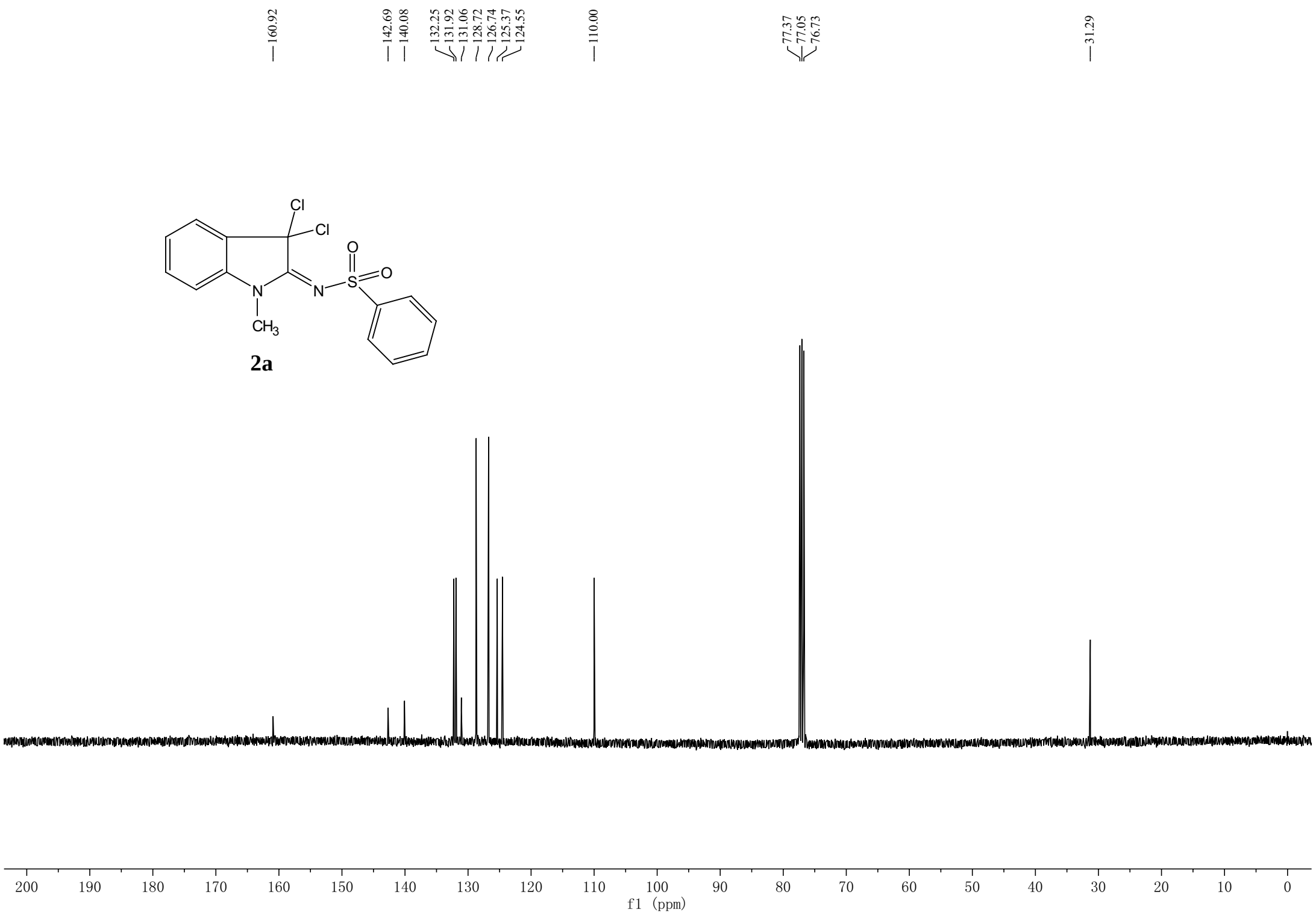
0.0
f1 (ppm)

2a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110.00
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77.05
76.73
31.29
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Cl
O
O
S
N
N
CH3
2a
200
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180
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110
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50
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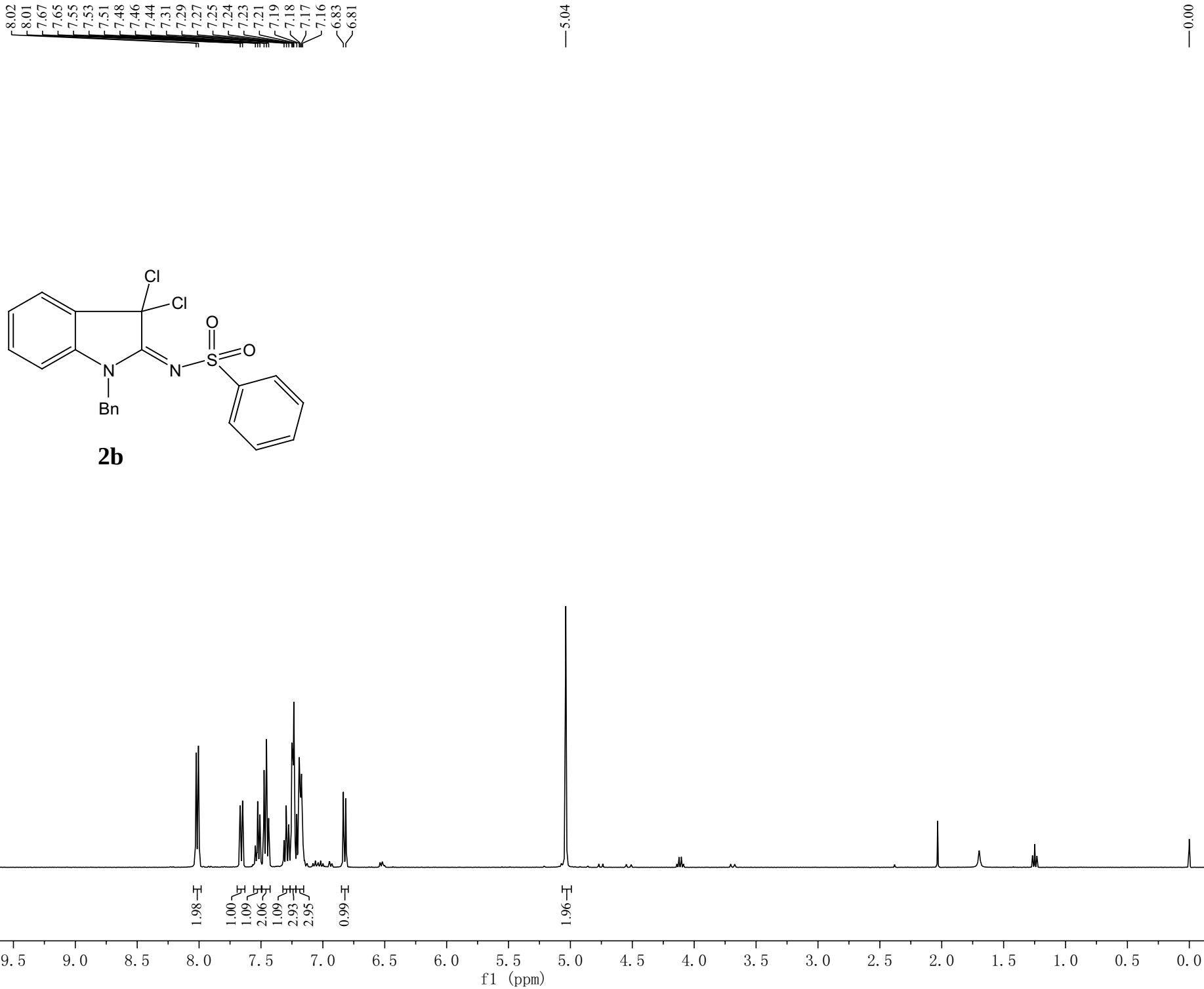
f1 (ppm)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Cl
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S
O
N
N
Bn
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1.00
1.09
2.06
1.09
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2.0
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0.5
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f1 (ppm)

2b

160.59
142.43
138.45
133.69
132.29
131.74
131.47
129.05
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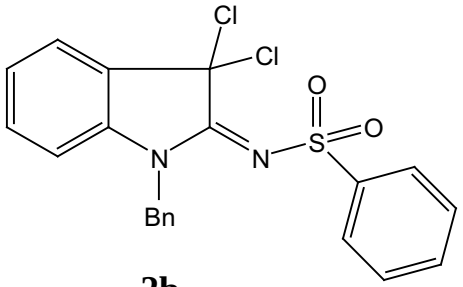
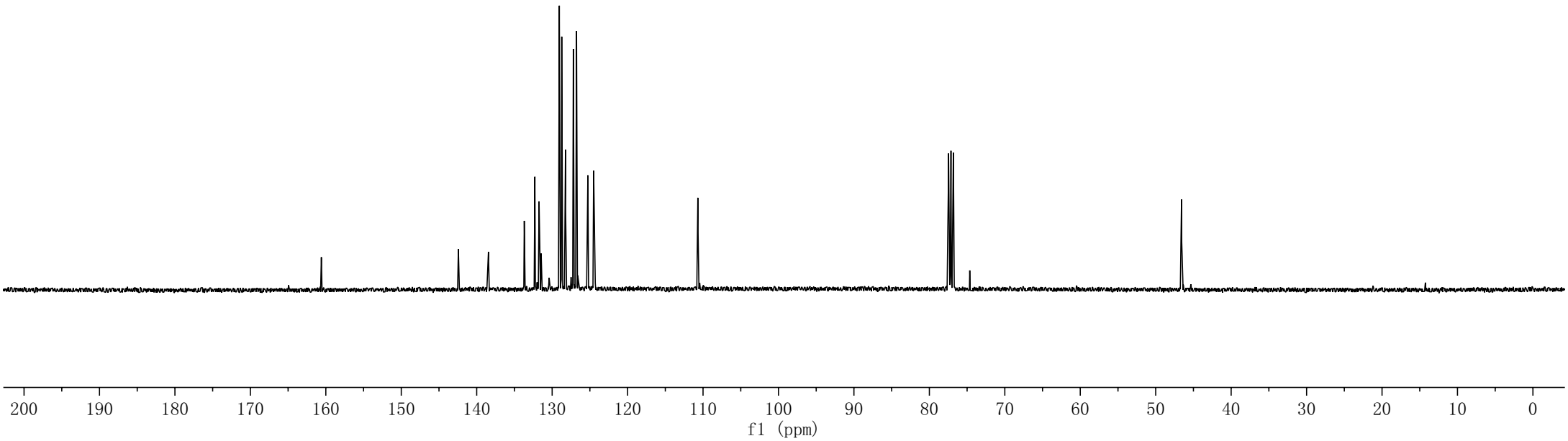


2b

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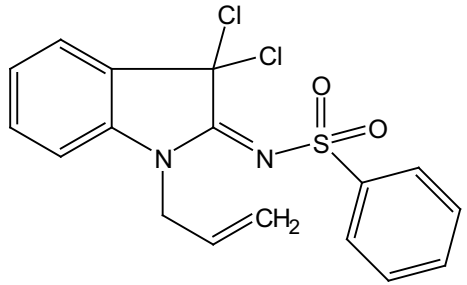
Cl
Cl
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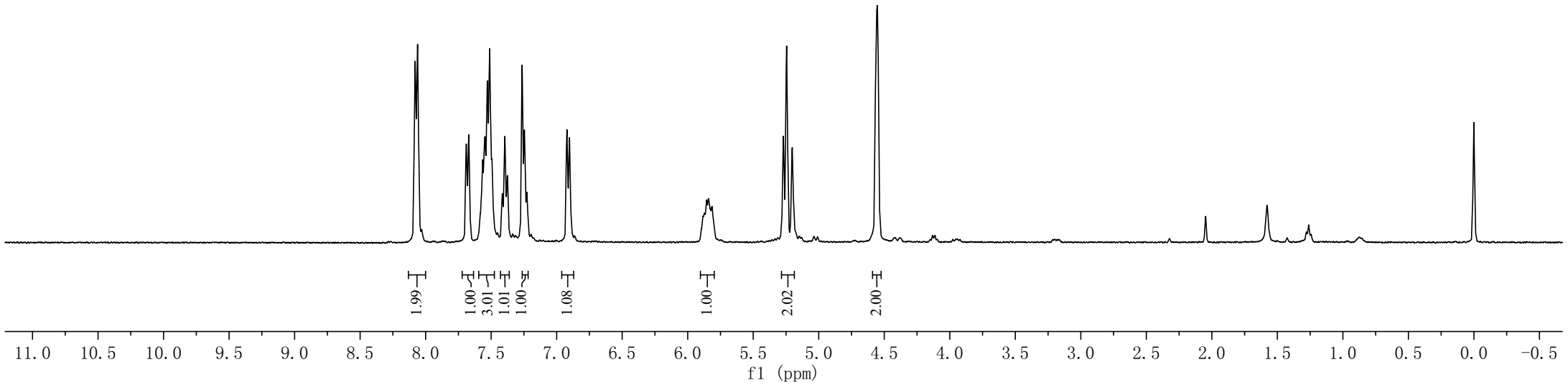
S
O
N
N
CH2

2c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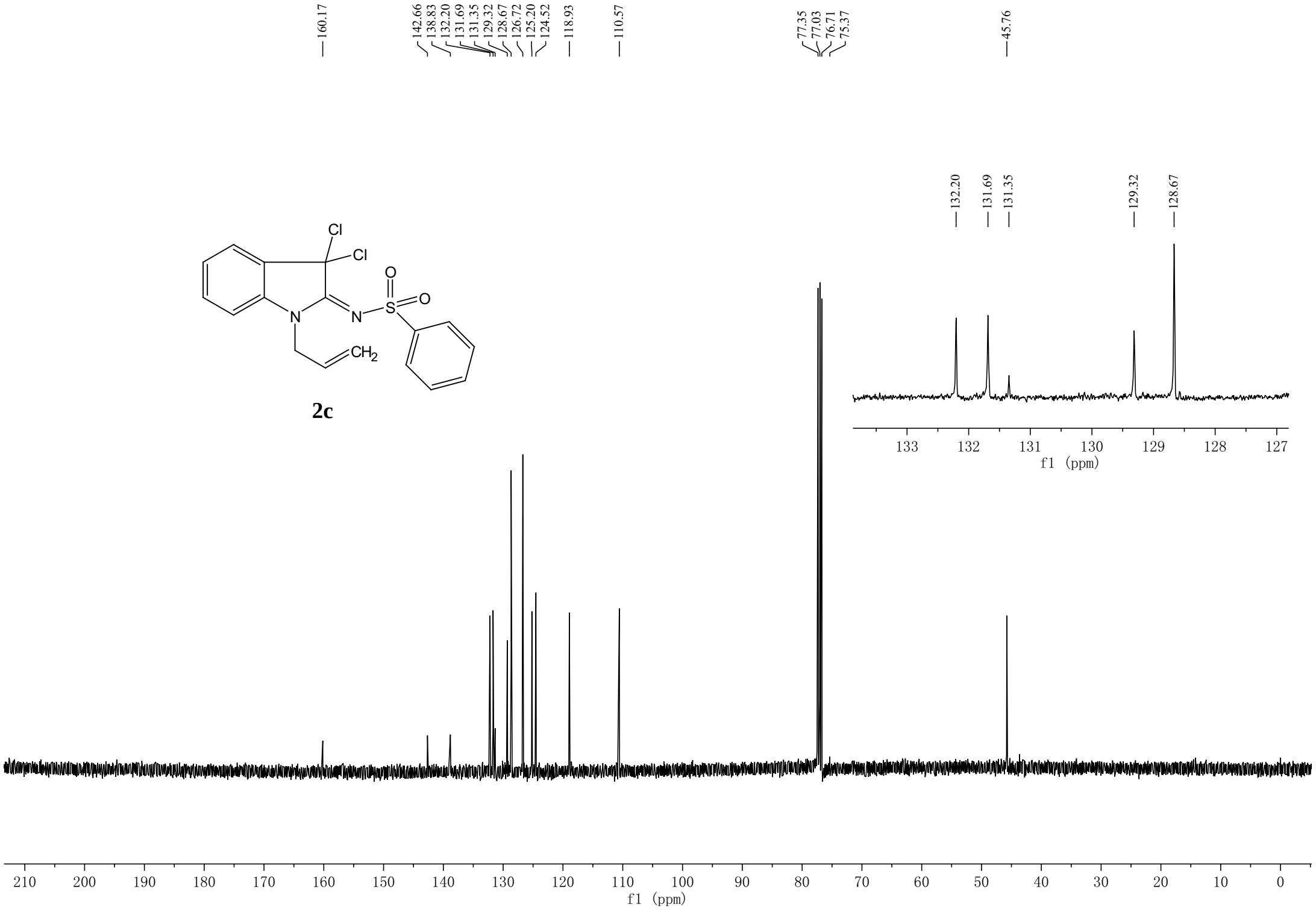
f1 (ppm)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75.37
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Cl
Cl
O
O
N
N
S
CH2
2c
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131.69
131.35
129.32
128.67
133
132
131
130
129
128
127
f1 (ppm)
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200
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180
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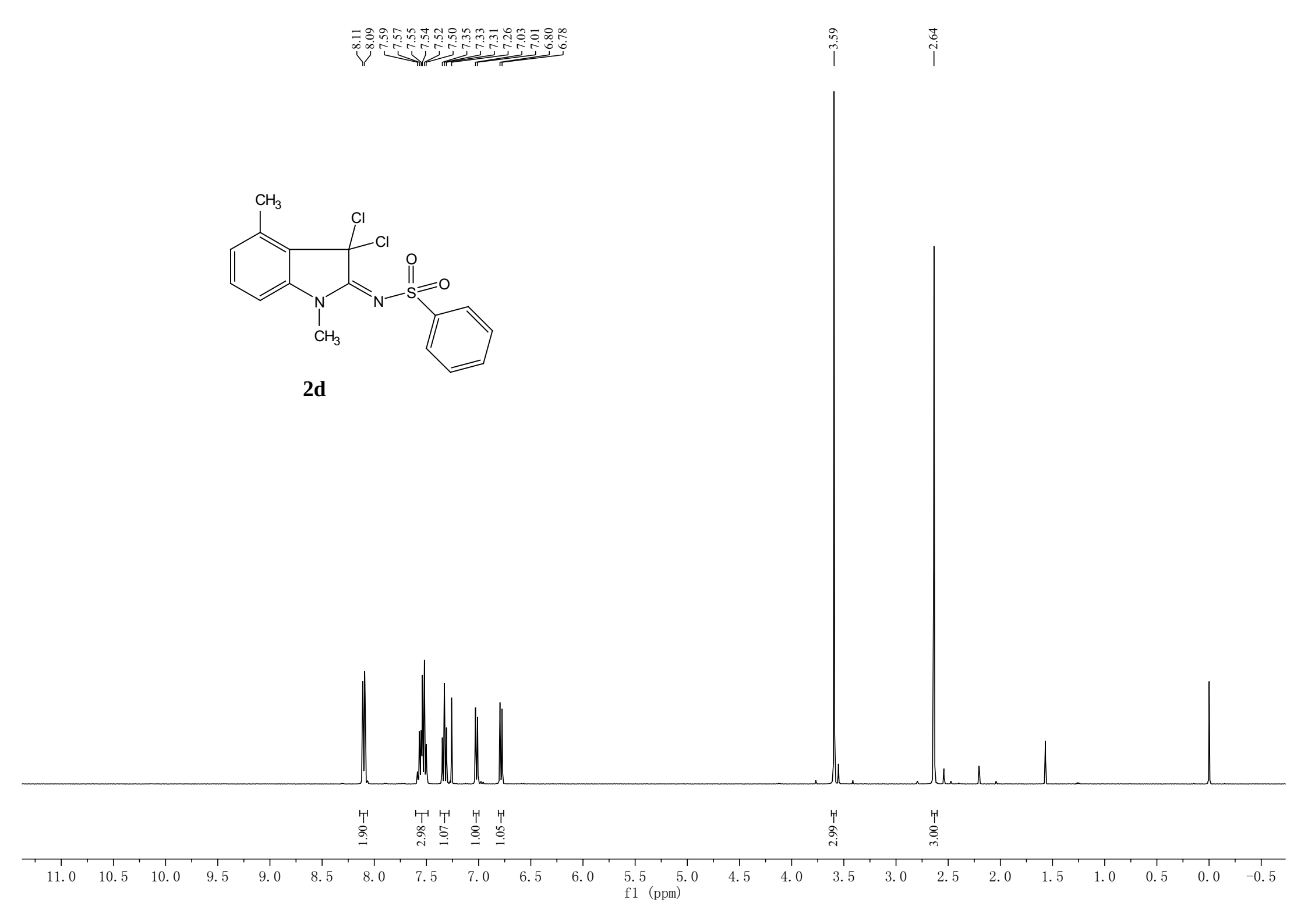
f1 (ppm)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3.59
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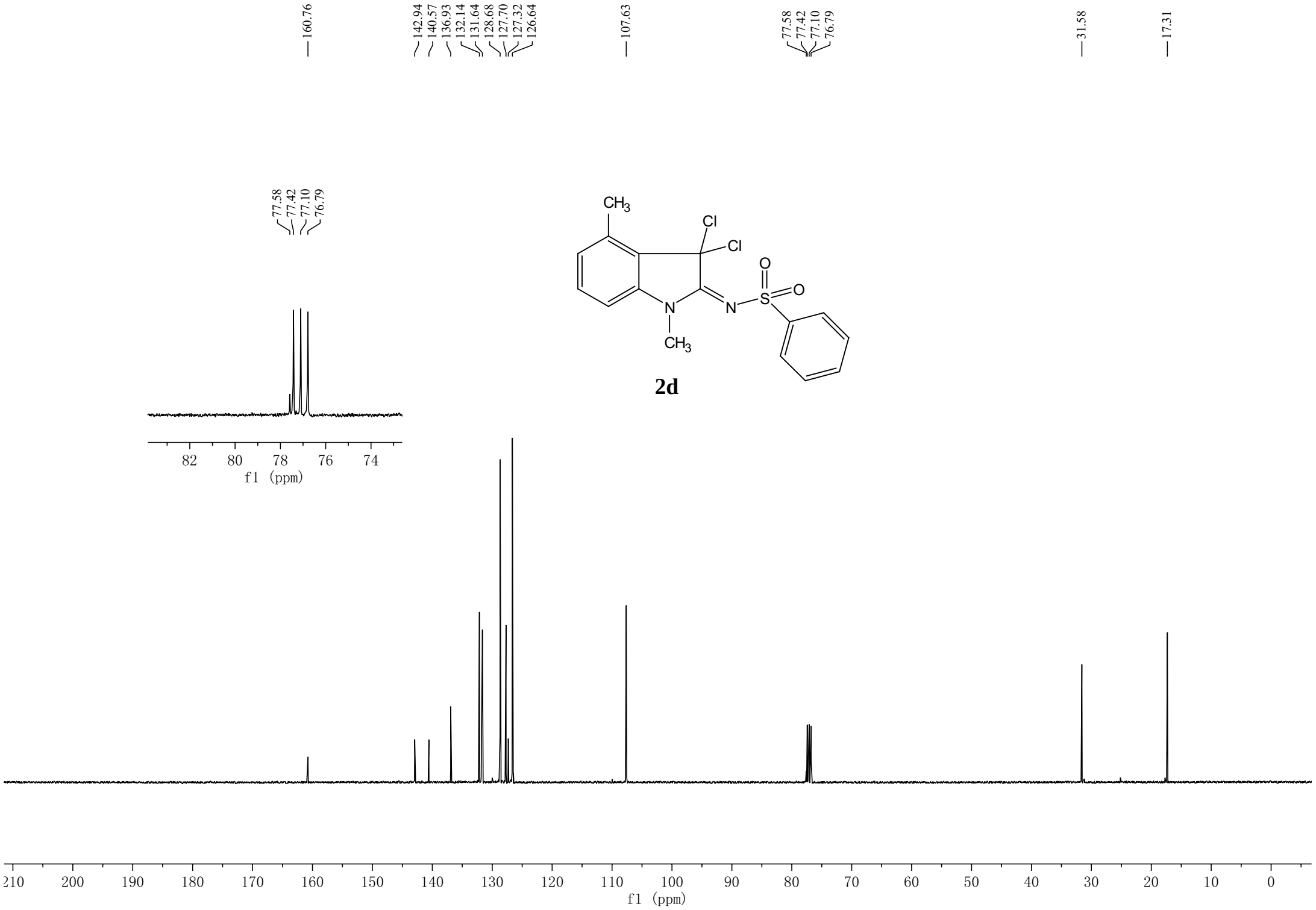
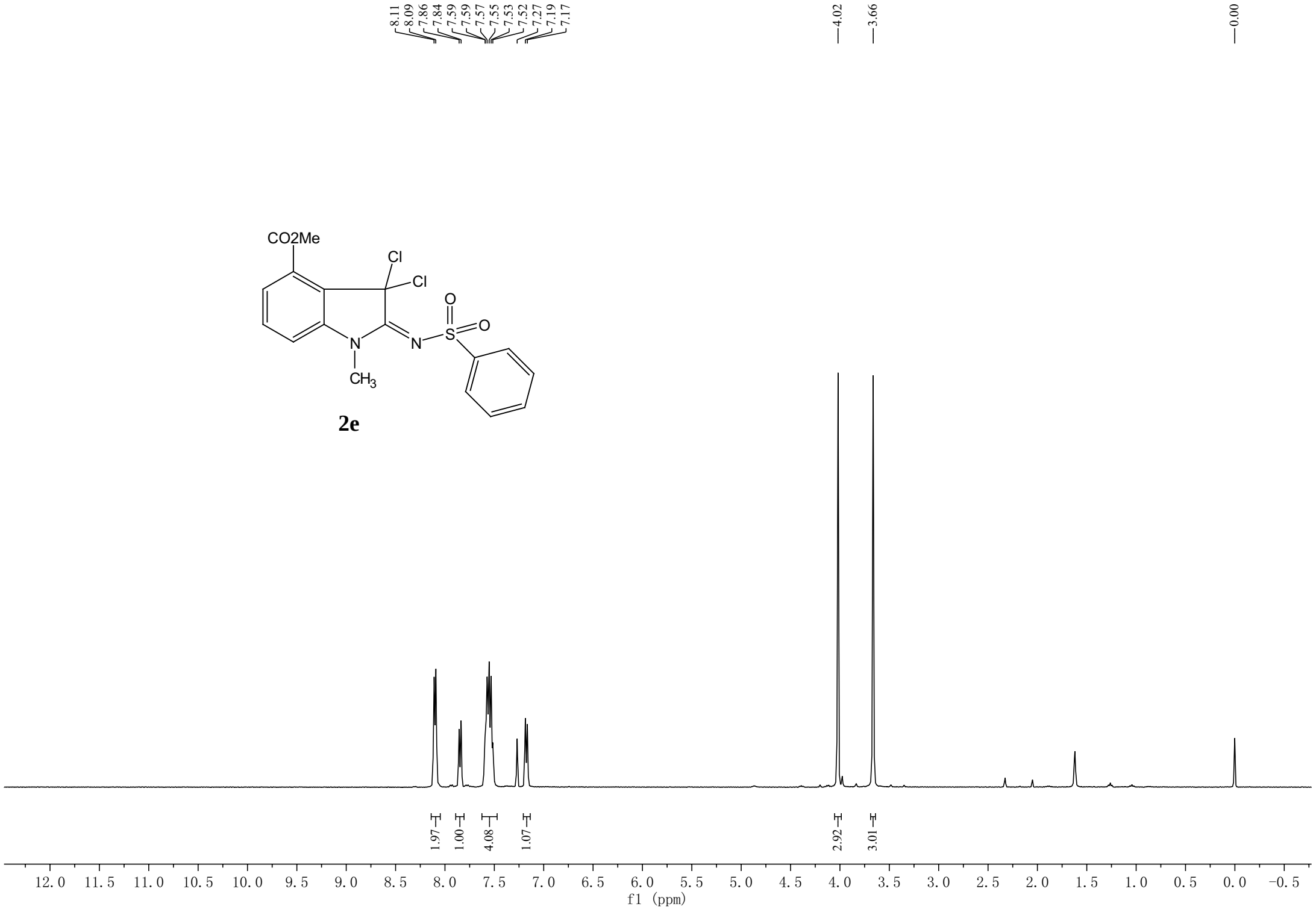
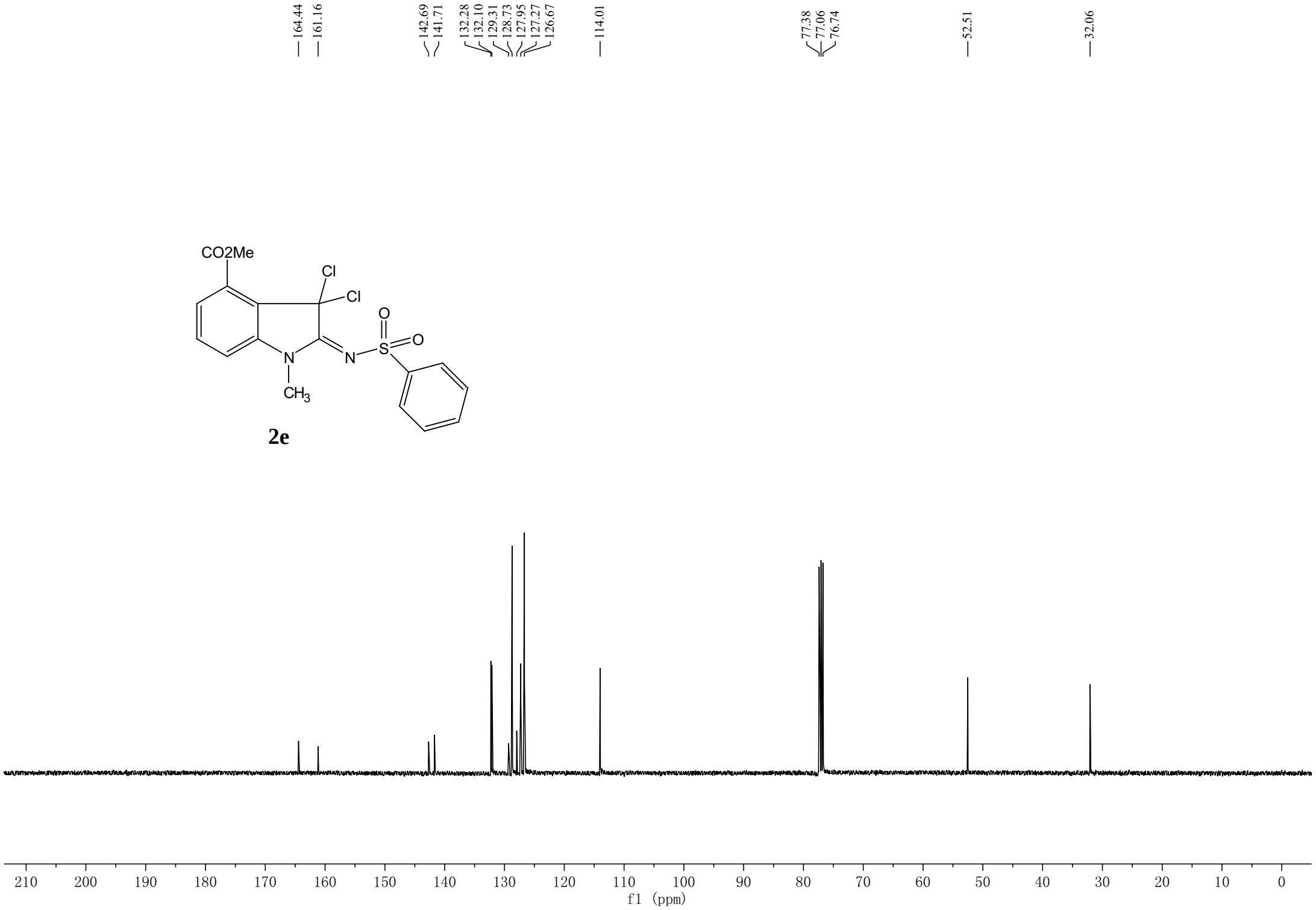
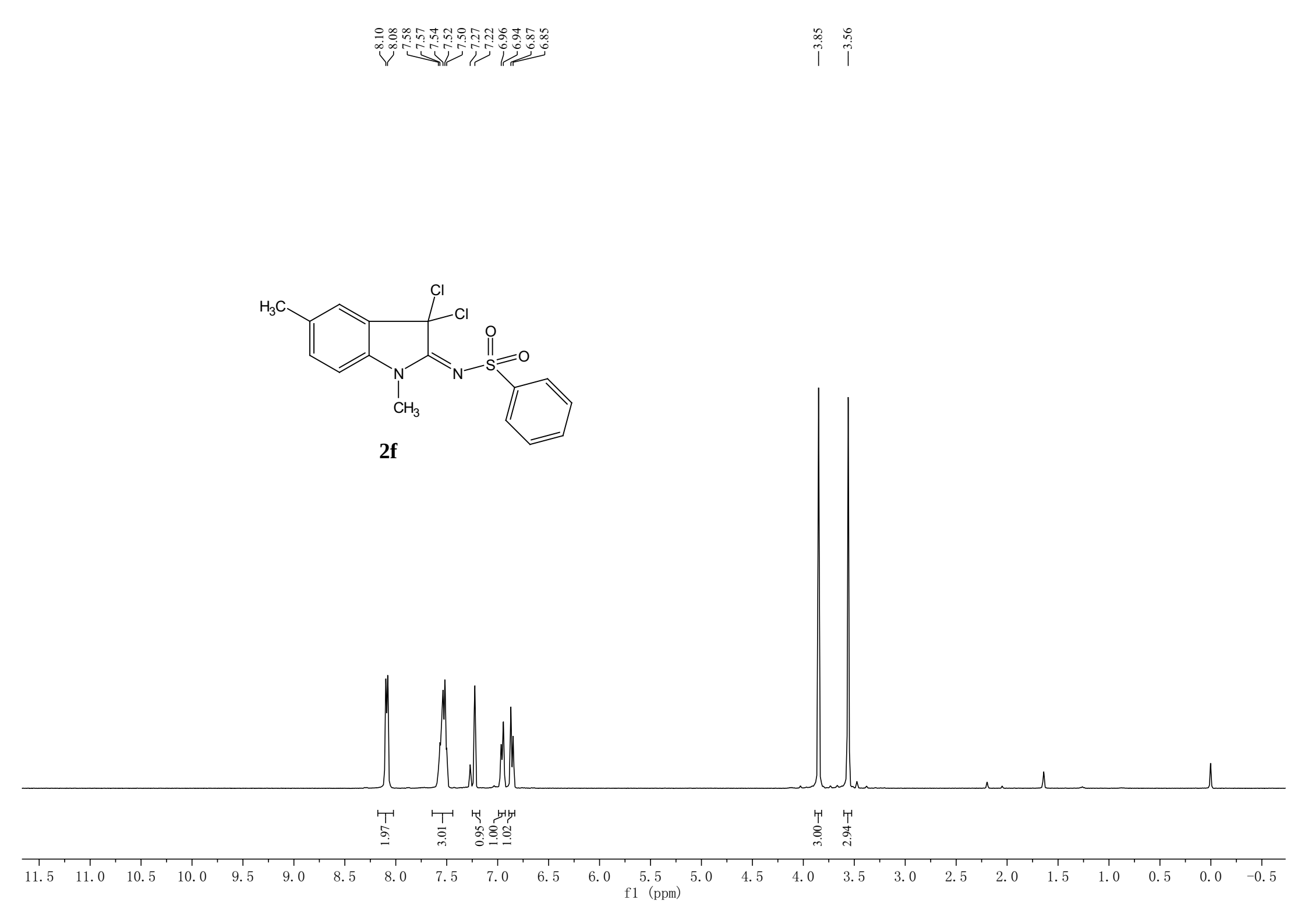
CH3
1.90
2.98
1.07
1.00
1.05
2.99
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

2d

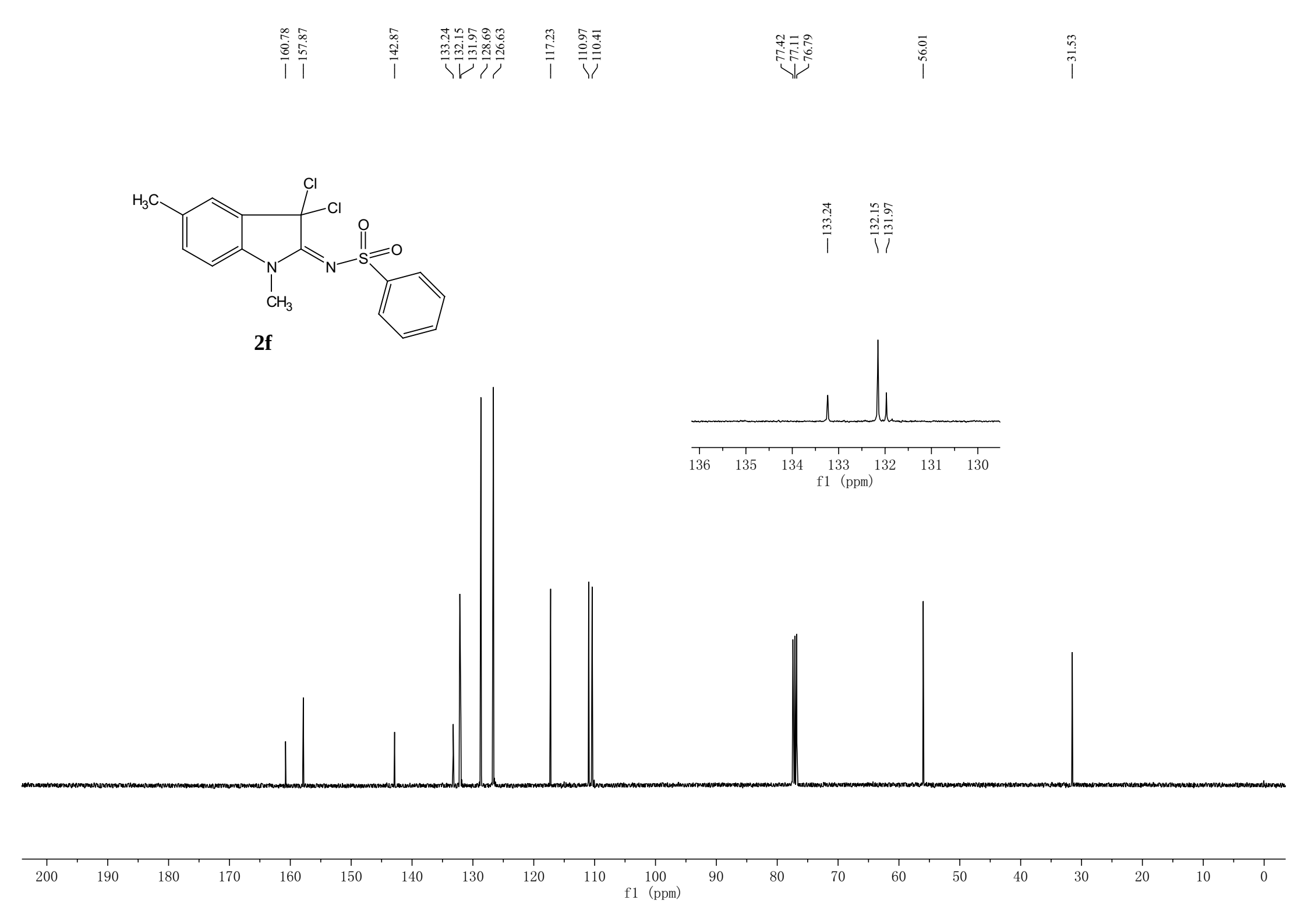

160.76
142.94
140.57
136.93
132.14
131.64
128.68
127.70
127.32
126.64
107.63
77.58
77.42
77.10
76.79
31.58
17.31
77.58
77.42
77.10
76.79
82
80
78
76
74
f1 (ppm)
CH3
Cl
Cl
O
O
S
N
N
CH3
2d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

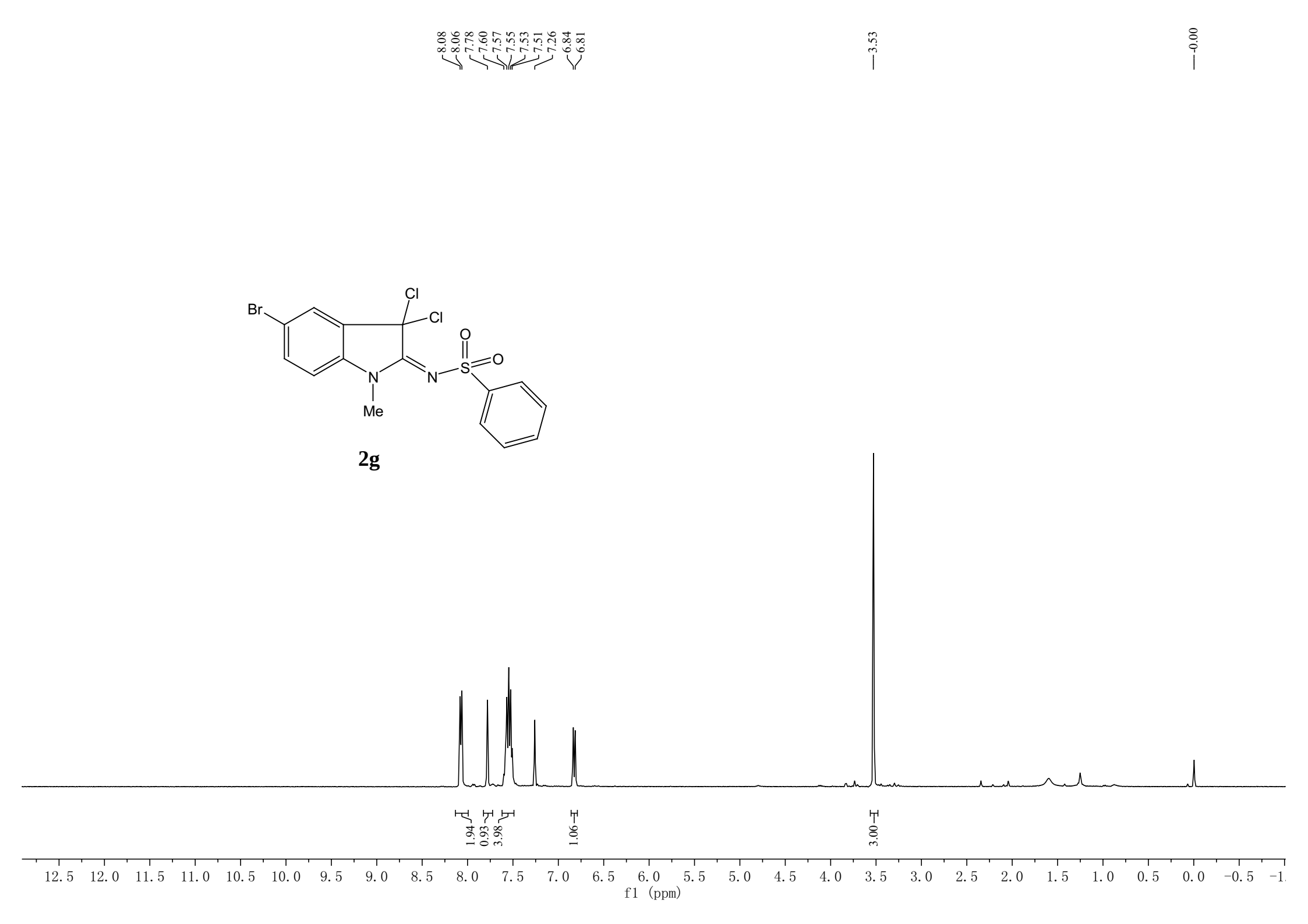

8.11
8.09
7.86
7.84
7.59
7.59
7.57
7.55
7.53
7.52
7.27
7.19
7.17
4.02
3.66
0.00
CO2Me
Cl
Cl
O
O
S
N
N
CH3
2e
1.97
1.00
4.08
1.07
2.92
3.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

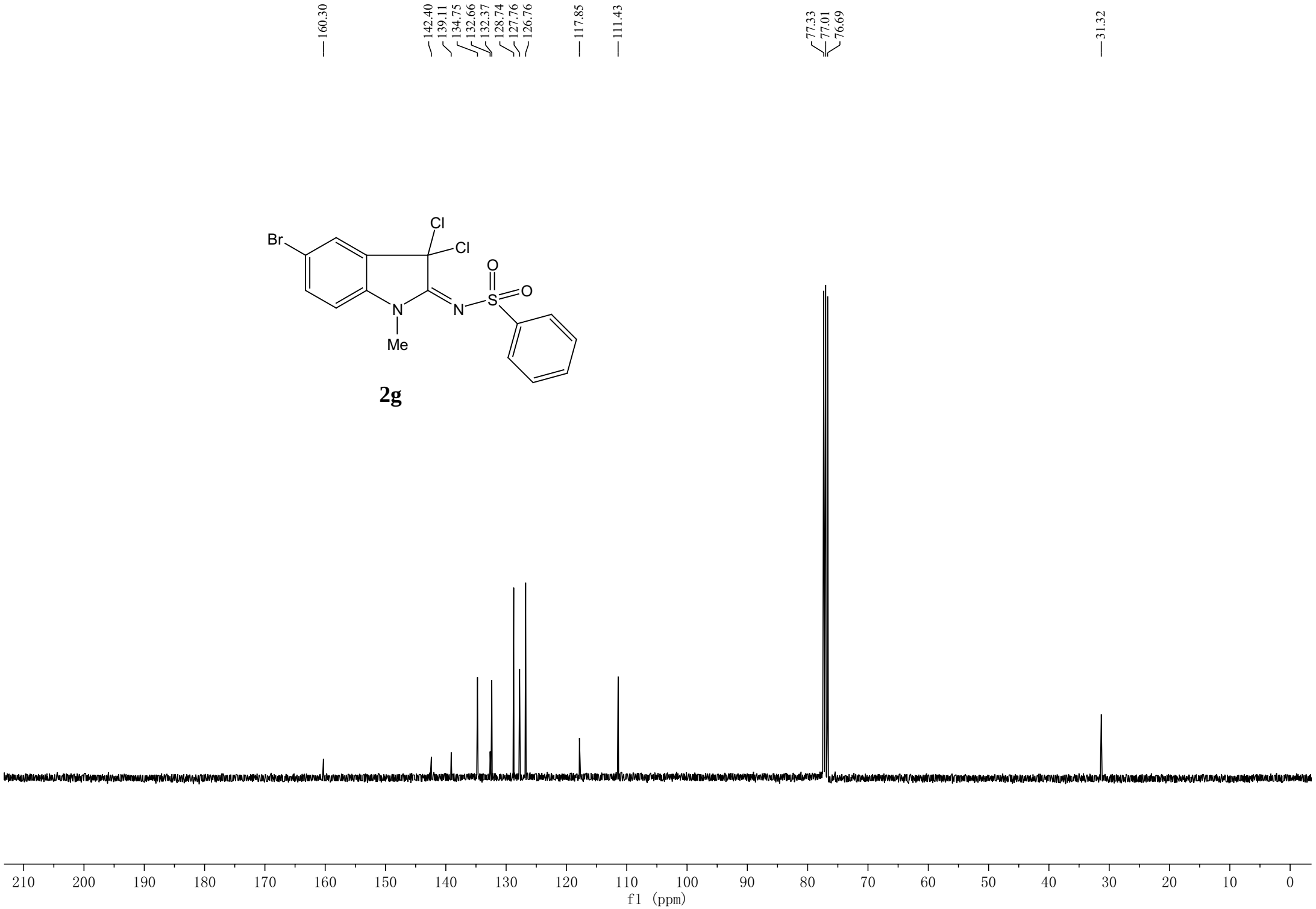

164.44
161.16
142.69
141.71
132.28
132.10
129.31
128.73
127.95
127.27
126.67
114.01
77.38
77.06
76.74
52.51
32.06
CO2Me
Cl
Cl
O
O
N
S
N
CH3
2e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

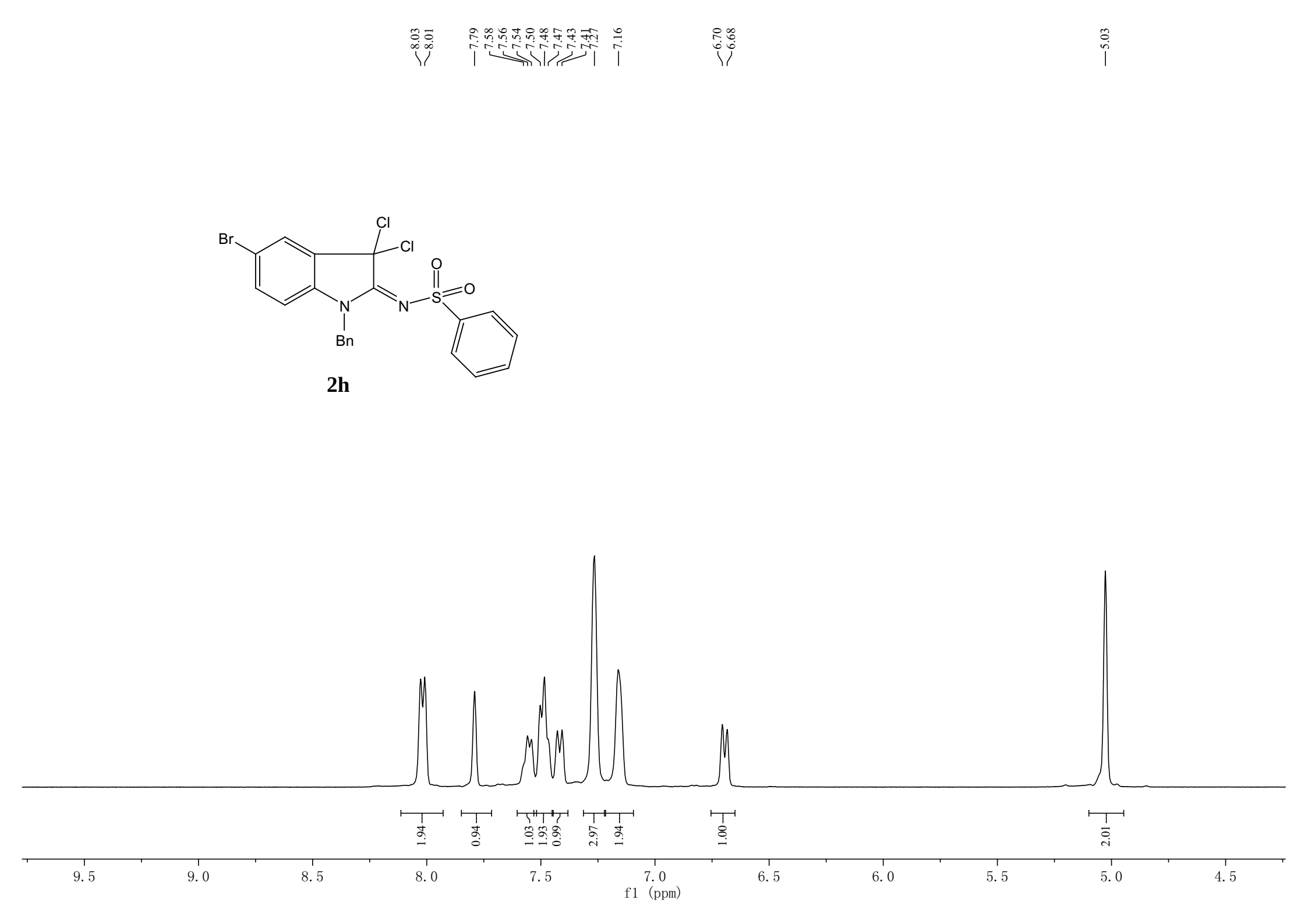

8.10
8.08
7.58
7.57
7.54
7.52
7.50
7.27
7.22
6.96
6.94
6.87
6.85
3.85
3.56
Cl
Cl
H3C
O
O
S
N
N
CH3
1.97
3.01
0.95
1.00
1.02
3.00
2.94
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

2f

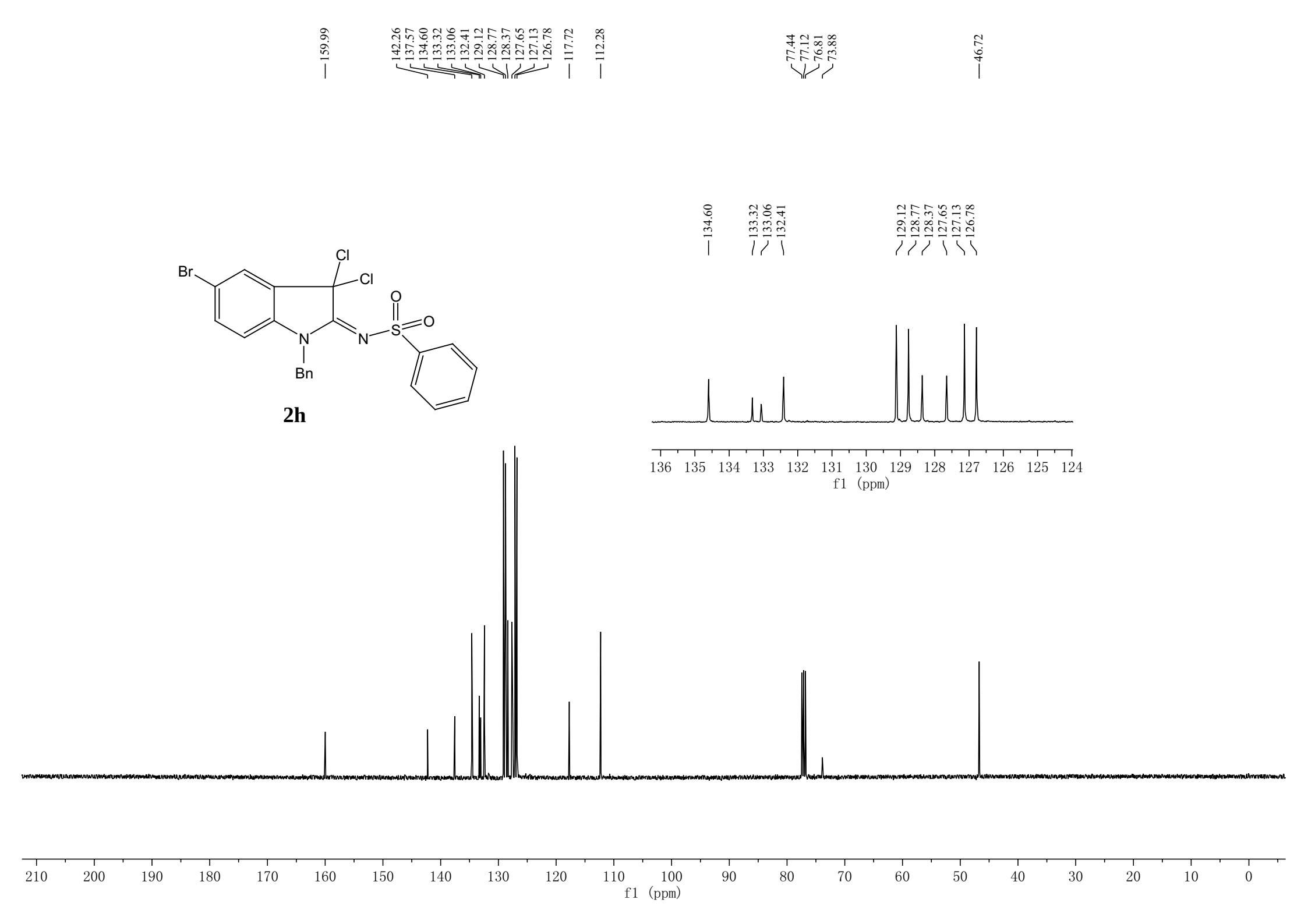

160.78
157.87
142.87
133.24
132.15
131.97
128.69
126.63
117.23
110.97
110.41
77.42
77.11
76.79
56.01
31.53
Cl
Cl
H3C
O
O
N
N
S
CH3
2f
133.24
132.15
131.97
136
135
134
133
132
131
130
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.08
8.06
7.78
7.60
7.57
7.55
7.53
7.51
7.26
6.84
6.81
3.53
0.00
Br
Cl
Cl
O
O
S
N
N
Me
2g
1.94
0.93
3.98
1.06
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

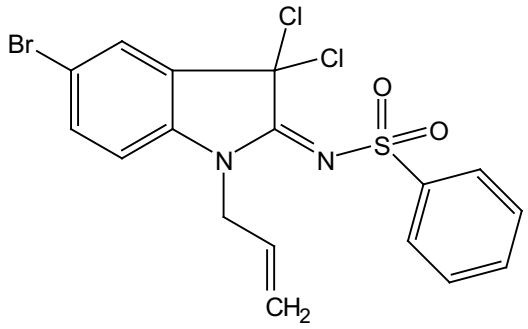

160.30
142.40
139.11
134.75
132.66
132.37
128.74
127.76
126.76
117.85
111.43
77.33
77.01
76.69
31.32
Br
Cl
Cl
O
O
S
N
N
Me
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.03
8.01
7.79
7.58
7.56
7.54
7.50
7.48
7.47
7.43
7.41
7.27
7.16
6.70
6.68
5.03
Cl
Cl
Br
O
O
S
N
N
Bn
1.94
0.94
1.03
1.93
0.99
2.97
1.94
1.00
2.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)

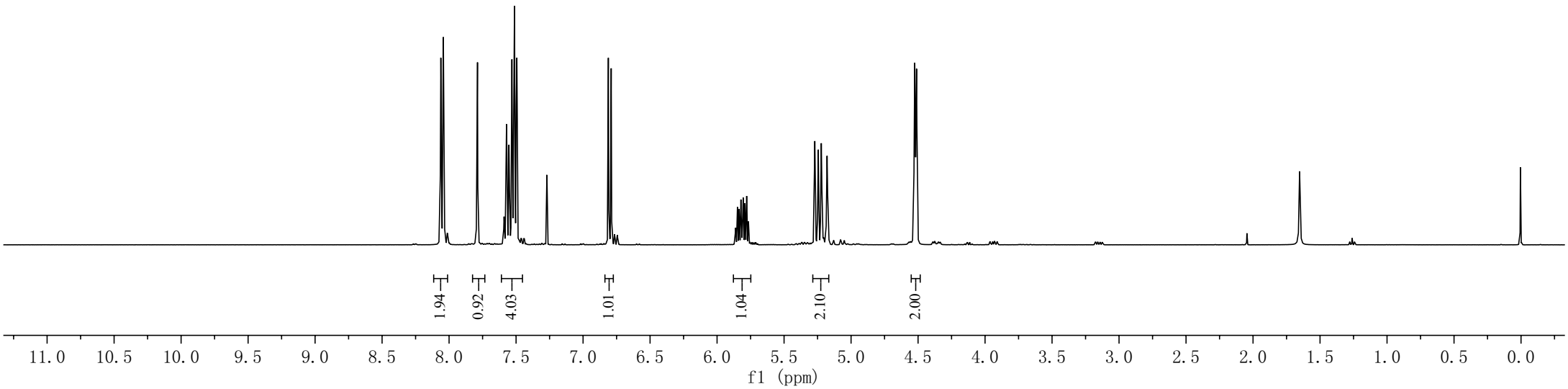
2h

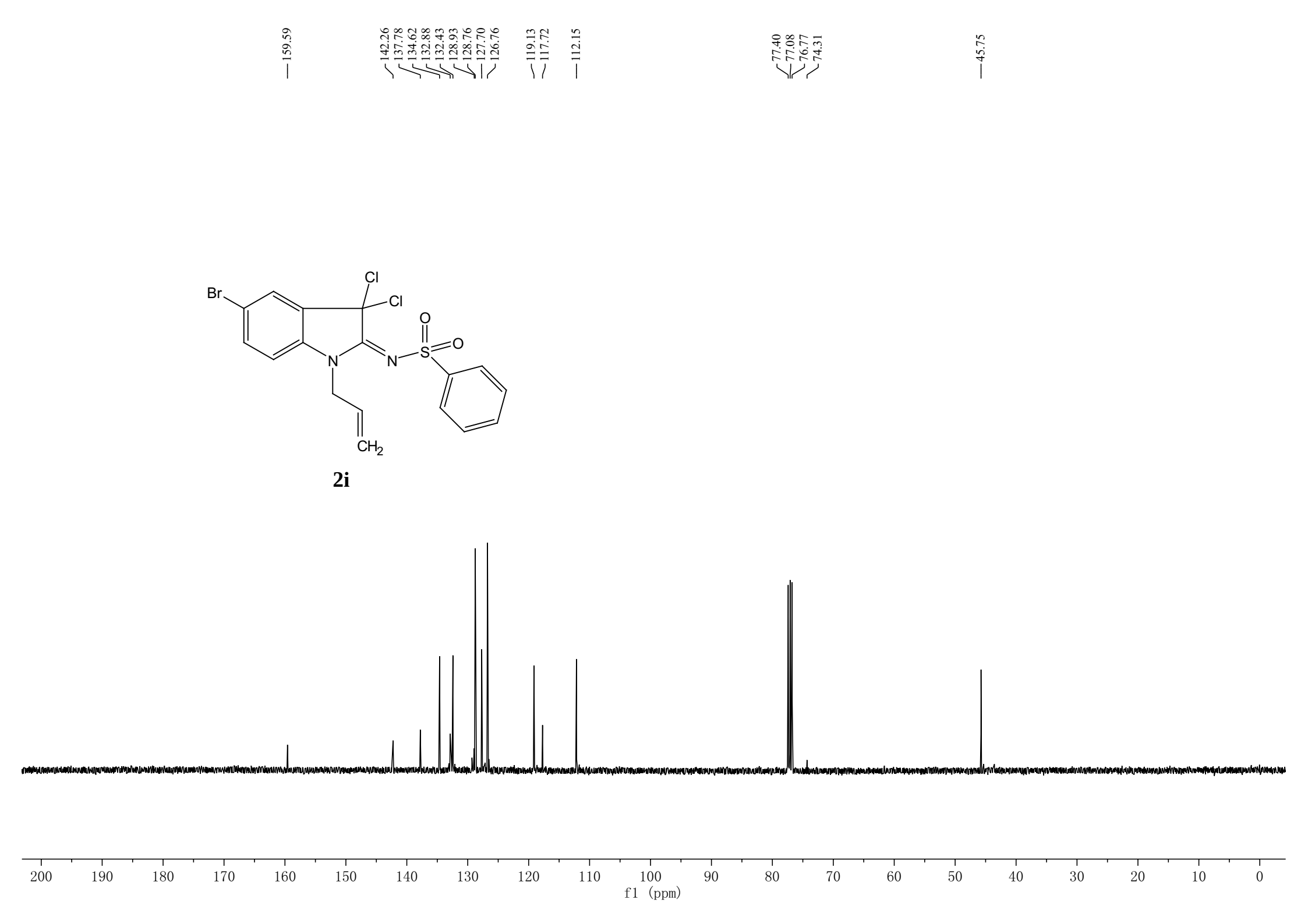

159.99
142.26
137.57
134.60
133.32
133.06
132.41
129.12
128.77
128.37
127.65
127.13
126.78
117.72
112.28
77.44
77.12
76.81
73.88
46.72
Br
Cl
Cl
O
O
S
N
N
Bn
2h
134.60
133.32
133.06
132.41
129.12
128.77
128.37
127.65
127.13
126.78
136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.06
8.04
7.79
7.79
7.59
7.58
7.57
7.57
7.55
7.53
7.51
7.49
7.27
5.86
5.85
5.84
5.82
5.81
5.79
5.78
5.77
5.27
5.24
5.22
5.18
4.52
4.51
0.00

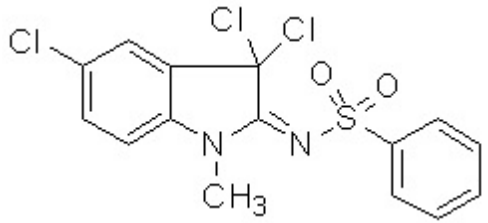

Cl
Br
Cl
O
S
O
N
N
CH2

2i


1.94
0.92
4.03
1.01
1.04
2.10
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

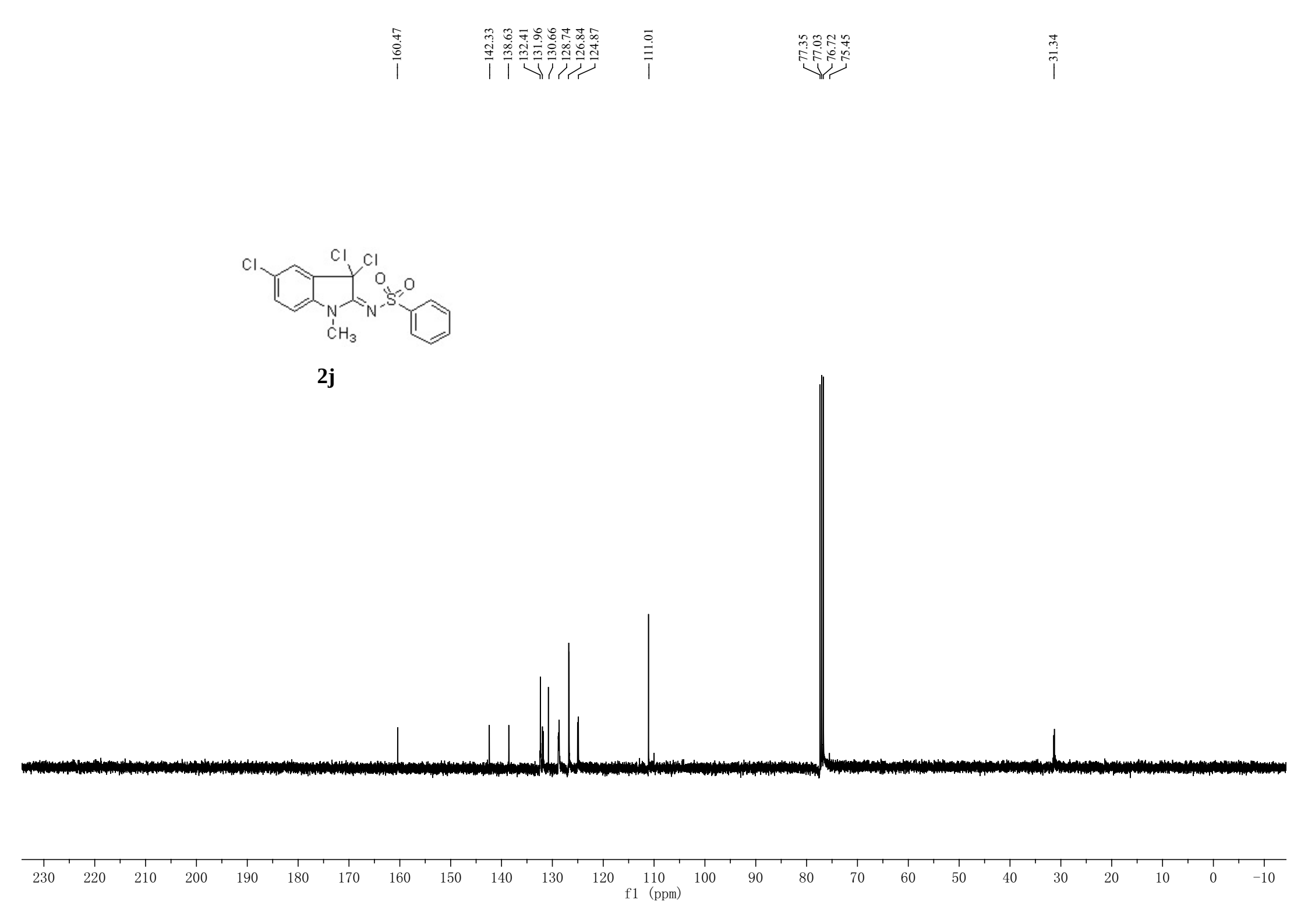

159.59
142.26
137.78
134.62
132.88
132.43
128.93
128.76
127.70
126.76
119.13
117.72
112.15
77.40
77.08
76.77
74.31
45.75
Br
Cl
Cl
O
O
S
N
N
CH2
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

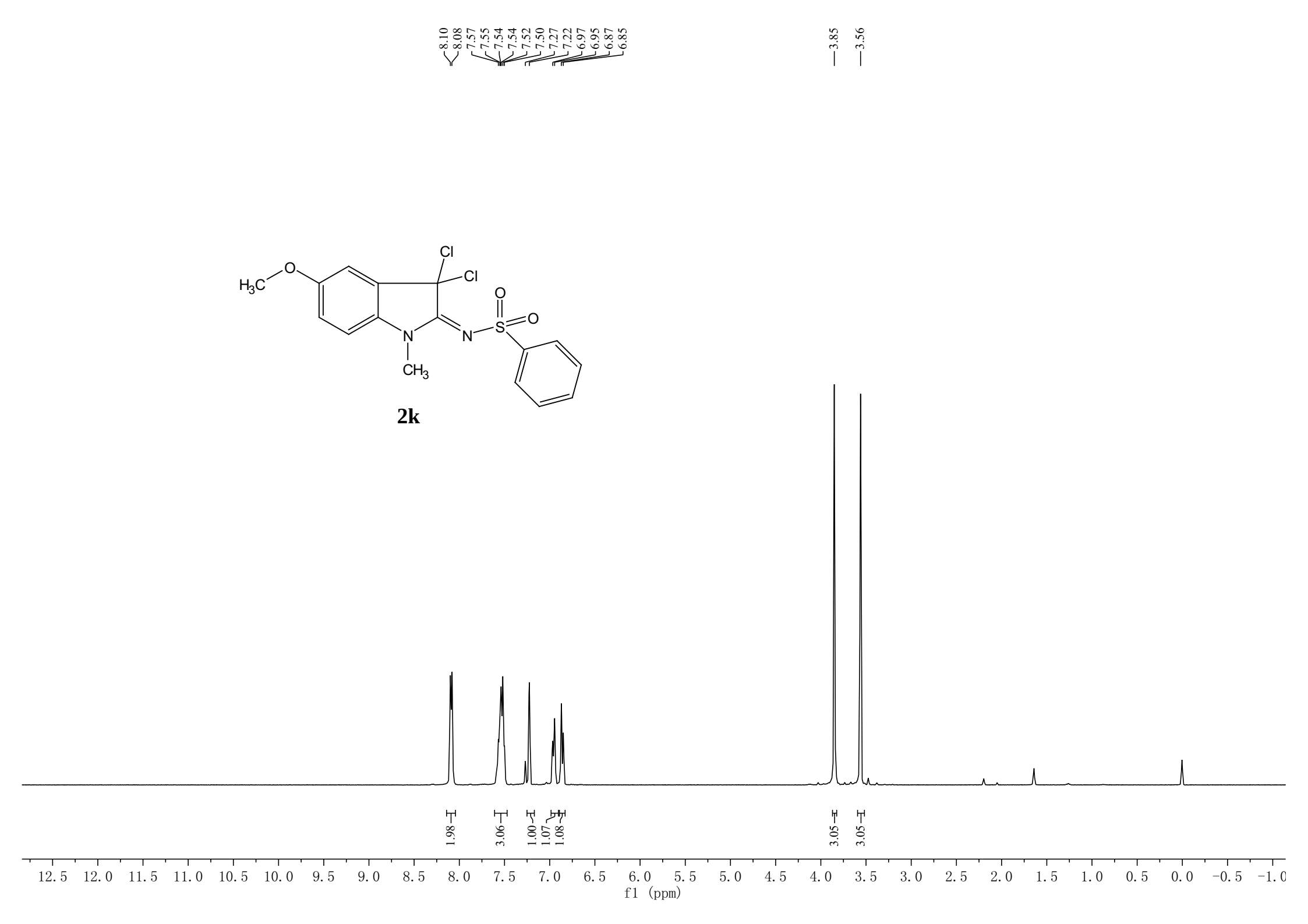
2i


Cl
Cl
Cl
O
O
S
N
N
CH3

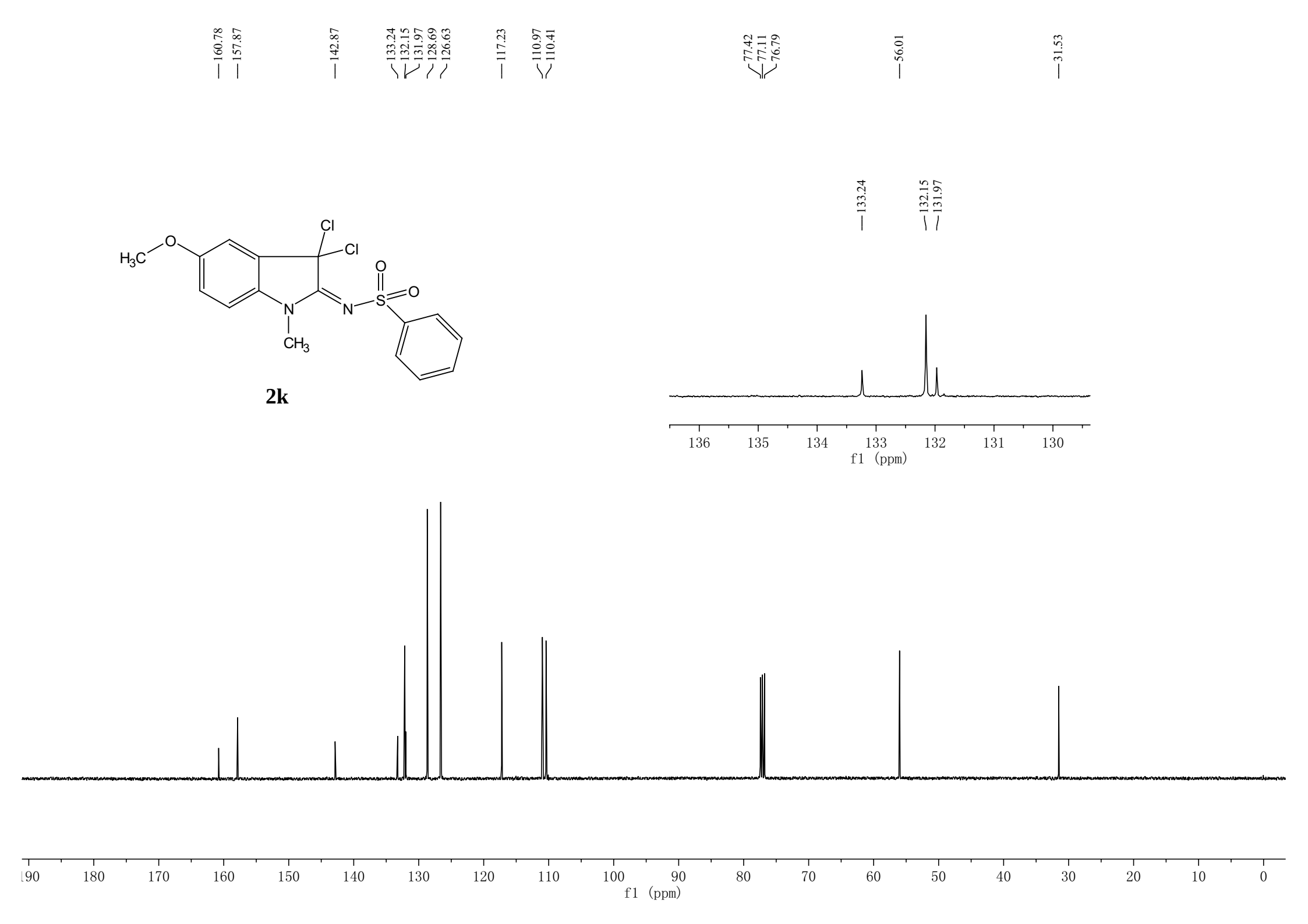
2j

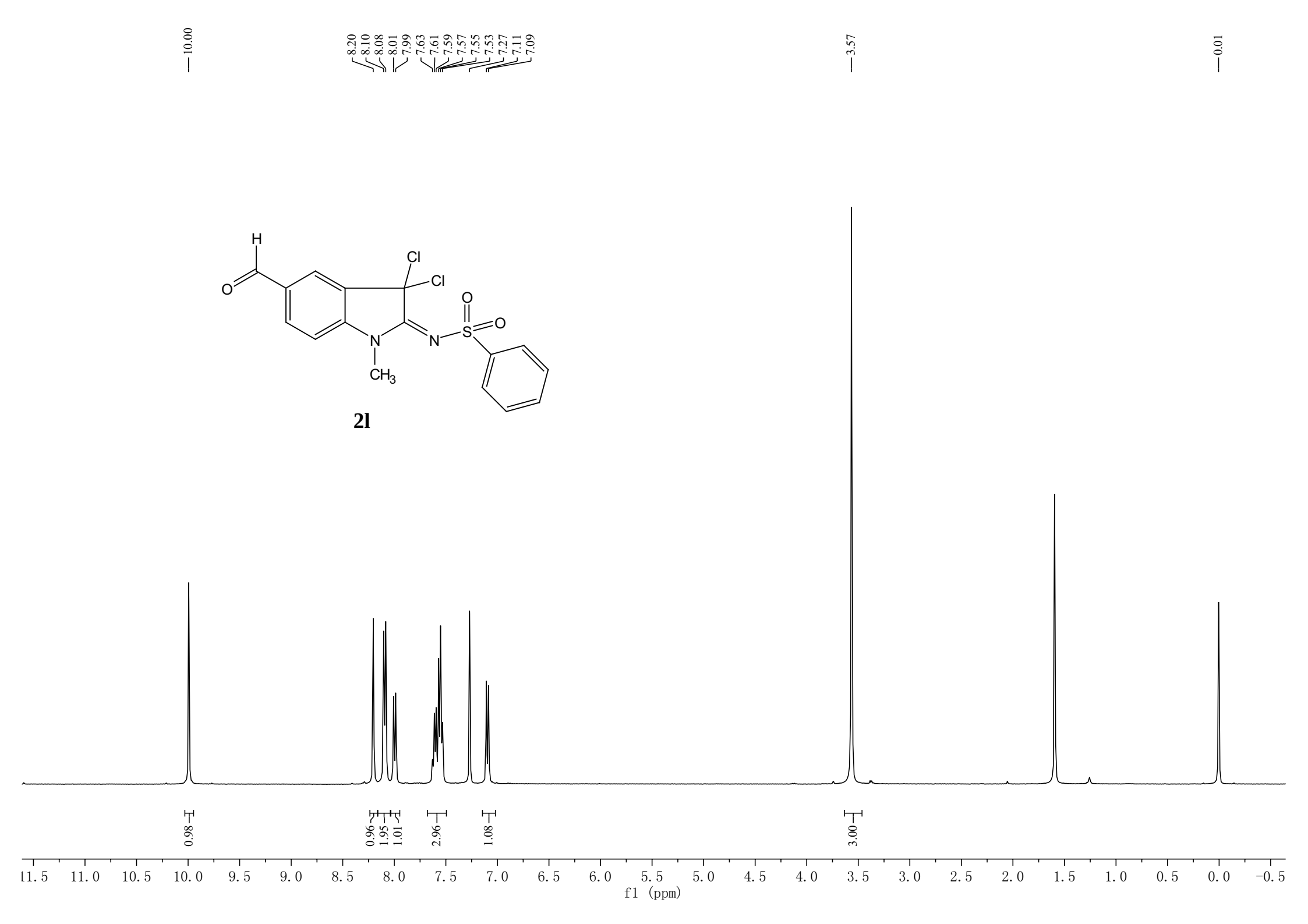
8.08
8.06
7.64
7.54
7.50
7.39
7.26
6.89
6.87
3.52
0.00
1.94
1.00
2.99
1.00
1.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


160.47
142.33
138.63
132.41
131.96
130.66
128.74
126.84
124.87
111.01
77.35
77.03
76.72
75.45
31.34
Cl
Cl
Cl
O
O
S
N
N
CH3
2j
230
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)

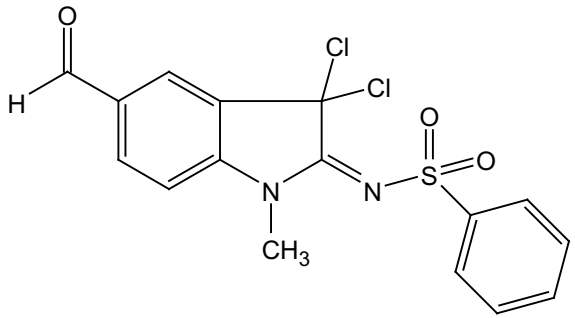

8.10
8.08
7.57
7.55
7.54
7.54
7.52
7.50
7.27
7.22
6.97
6.95
6.87
6.85
3.85
3.56
Cl
Cl
O
H3C
O
O
S
N
N
CH3
1.98
3.06
1.00
1.07
1.08
3.05
3.05
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

2k

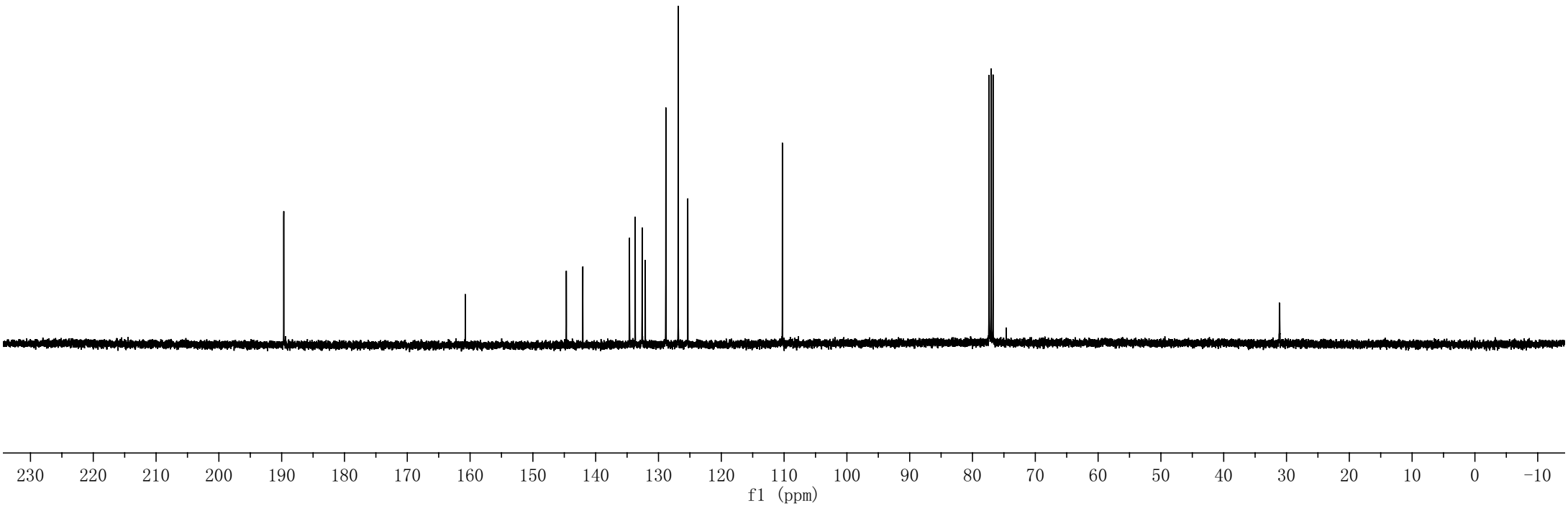

160.78
157.87
142.87
133.24
132.15
131.97
128.69
126.63
117.23
110.97
110.41
77.42
77.11
76.79
56.01
31.53
Cl
Cl
O
H3C
O
O
S
N
N
CH3
2k
133.24
132.15
131.97
136
135
134
133
132
131
130
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

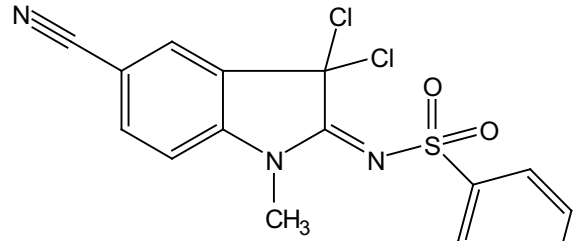

10.00
8.20
8.10
8.08
8.01
7.99
7.63
7.61
7.59
7.57
7.55
7.53
7.27
7.11
7.09
3.57
0.01
H
O
Cl
Cl
O
S
O
N
N
CH3
21
0.98
0.96
1.95
1.01
2.96
1.08
3.00
f1 (ppm)

189.68
160.71
144.68
142.05
133.70
132.60
132.10
128.83
126.86
125.33
110.27
77.37
77.05
76.73
74.63
31.08



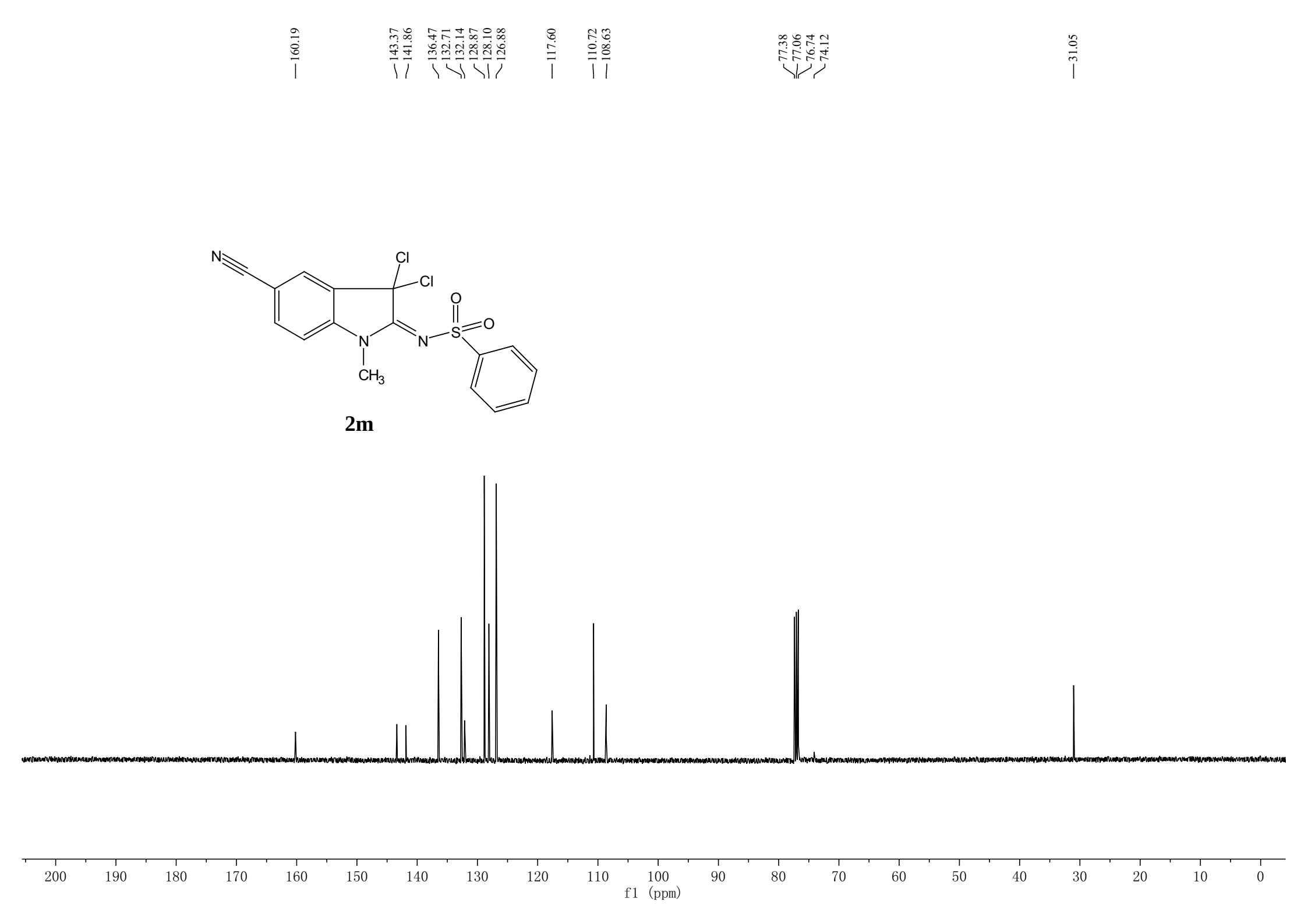
2l

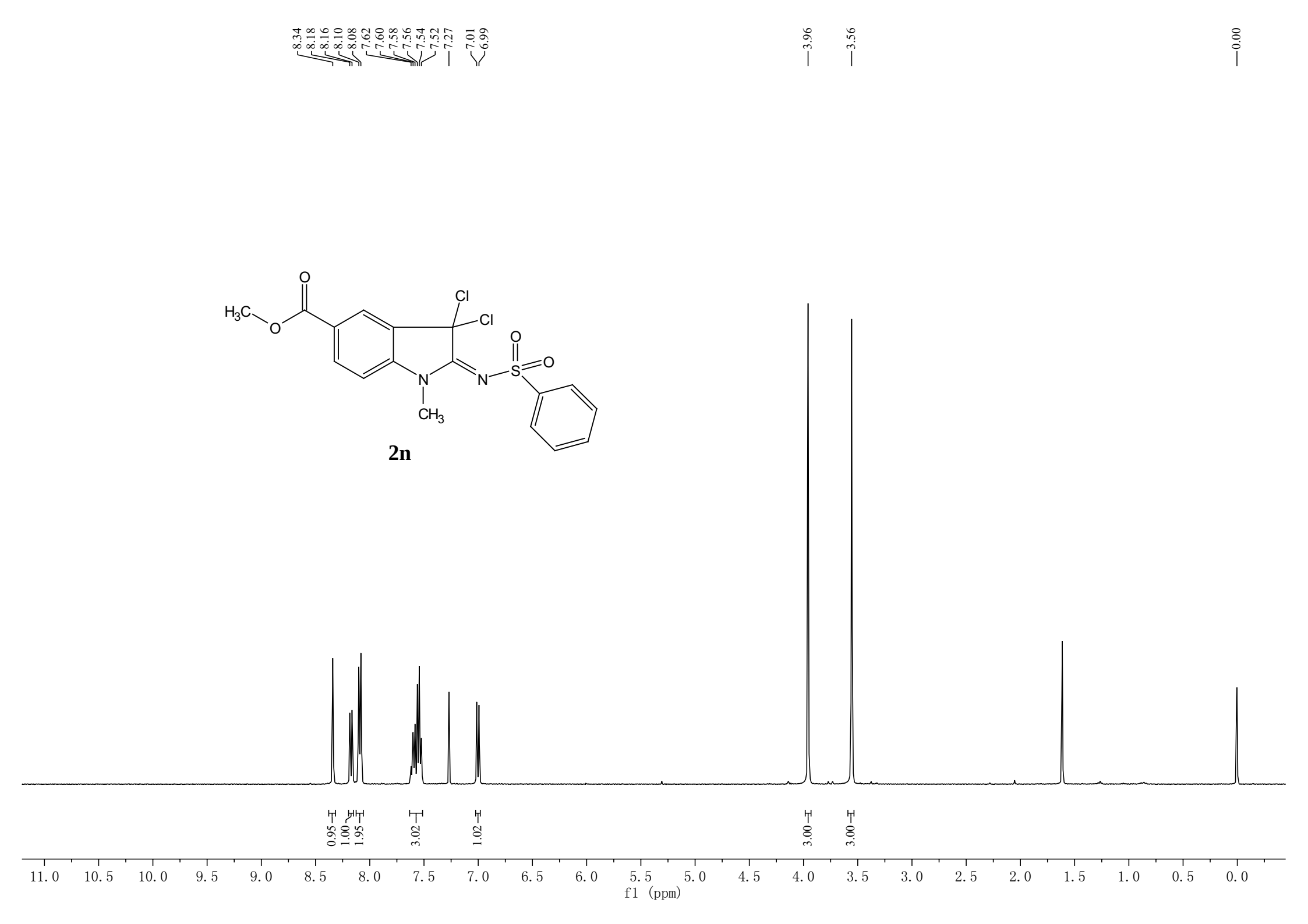


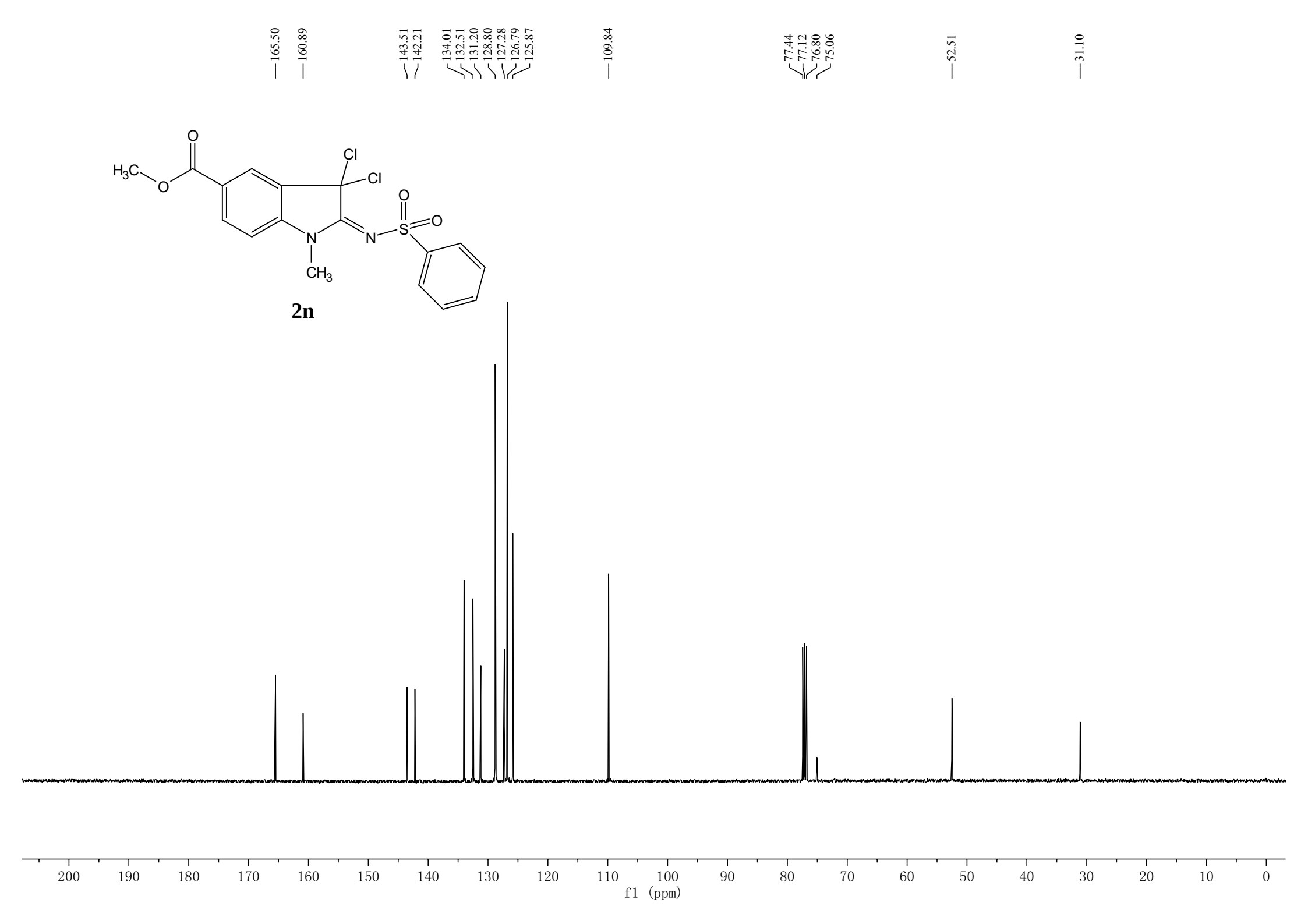

N
Cl
Cl
O
S
O
N
N
CH3

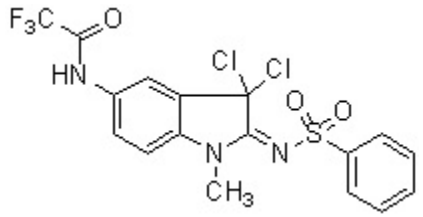
2m

8.09
8.07
7.94
7.77
7.77
7.76
7.75
7.75
7.74
7.64
7.64
7.63
7.62
7.60
7.60
7.60
7.57
7.55
7.53
7.27
7.06
7.04
3.54
0.00
1.92
0.92
1.00
3.11
1.07
3.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


160.19
143.37
141.86
136.47
132.71
132.14
128.87
128.10
126.88
117.60
110.72
108.63
77.38
77.06
76.74
74.12
31.05
N
Cl
Cl
O
O
S
N
N
CH3
2m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

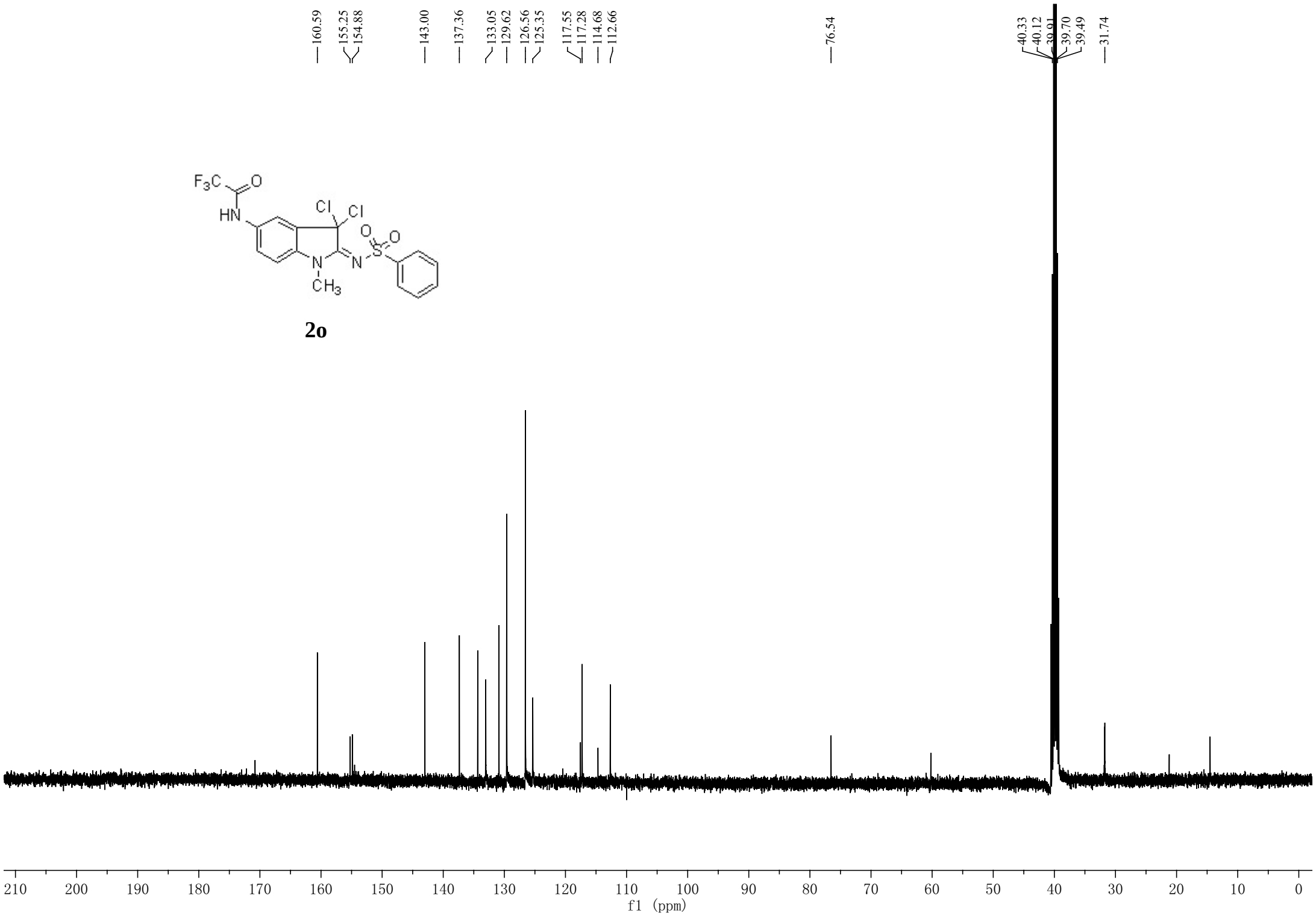

8.34
8.18
8.16
8.10
8.08
7.62
7.60
7.58
7.56
7.54
7.52
7.27
7.01
6.99
3.96
3.56
0.00
O
H3C
O
Cl
Cl
O
S
O
N
N
CH3
2n
0.95
1.00
1.95
3.02
1.02
3.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.50
160.89
143.51
142.21
134.01
132.51
131.20
128.80
127.28
126.79
125.87
109.84
77.44
77.12
76.80
75.06
52.51
31.10
O
H3C
O
Cl
Cl
O
S
O
N
N
CH3
2n
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

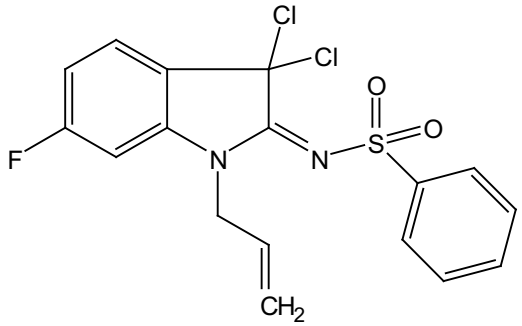

F3C
O
HN
Cl
Cl
O
O
S
N
N
CH3

2o

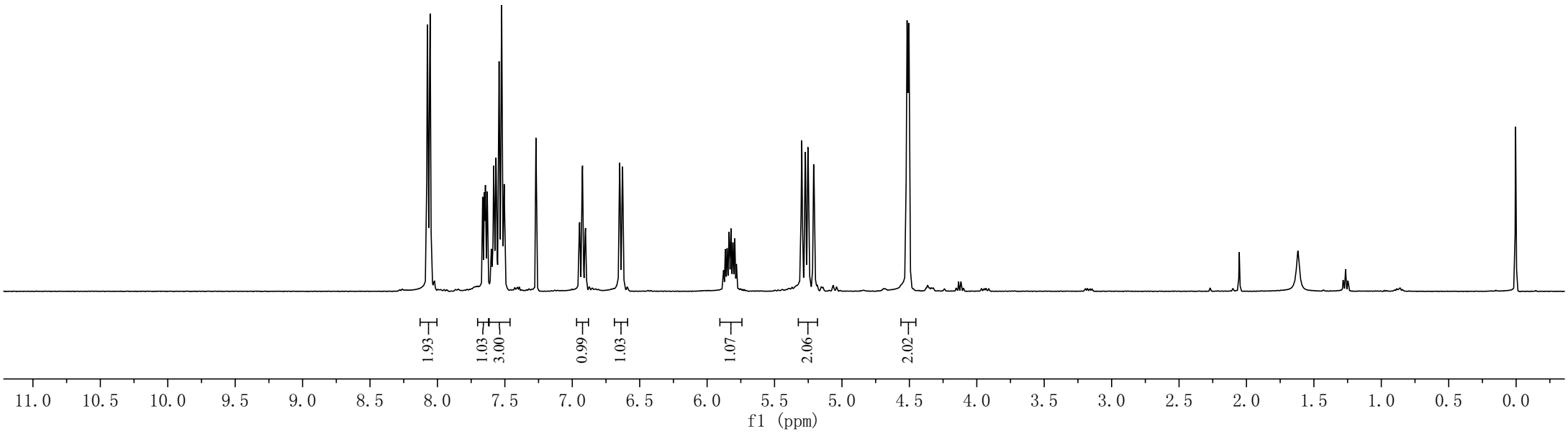
8.17
8.10
8.07
7.96
7.60
7.52
7.27
6.98
6.96
3.56
0.01
0.99
1.97
0.98
1.00
2.98
0.97
2.99
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

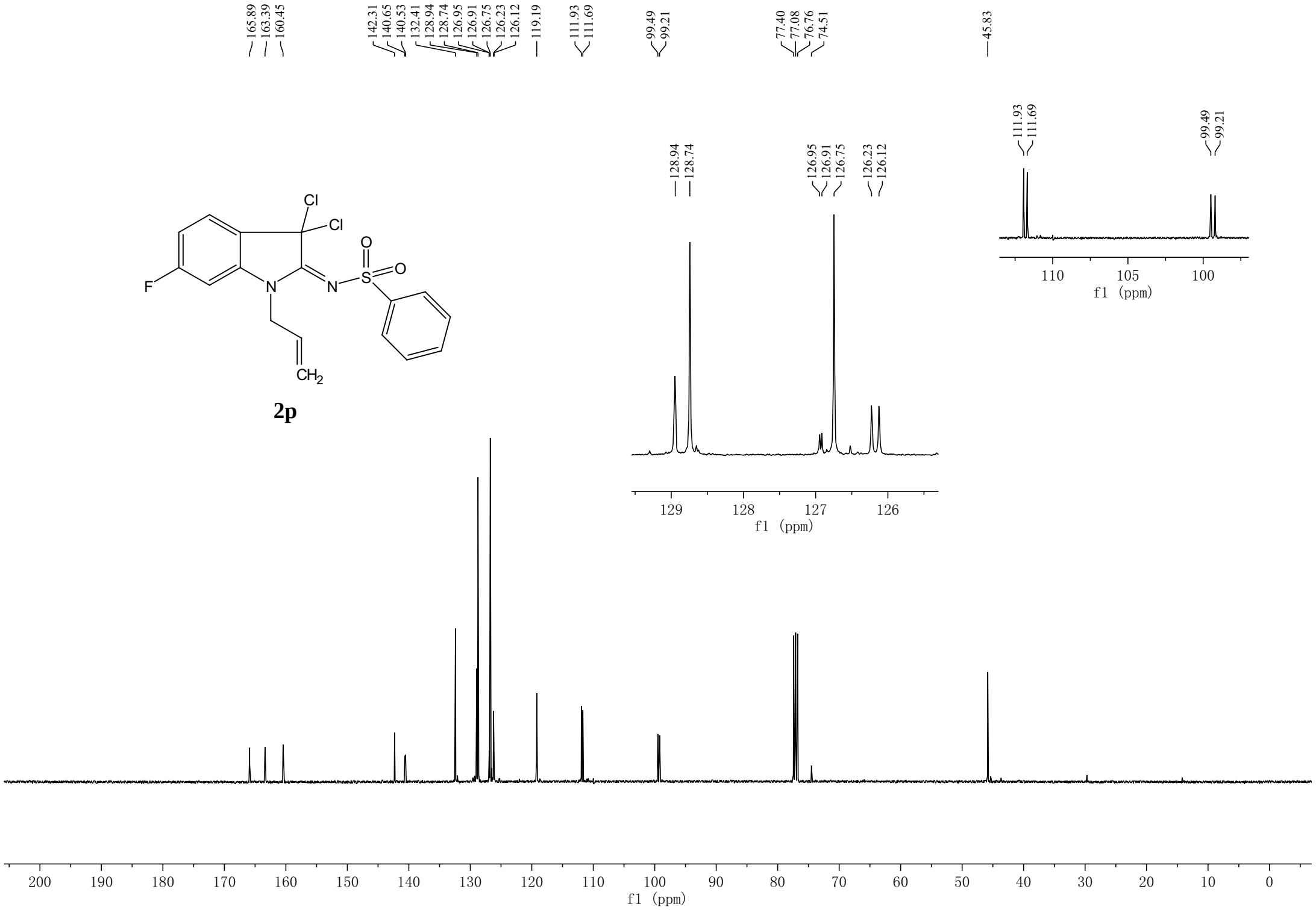

160.59
155.25
154.88
143.00
137.36
133.05
129.62
126.56
125.35
117.55
117.28
114.68
112.66
76.54
40.33
40.12
39.91
39.70
39.49
31.74
F3C
O
HN
Cl
Cl
O
O
S
N
N
CH3
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

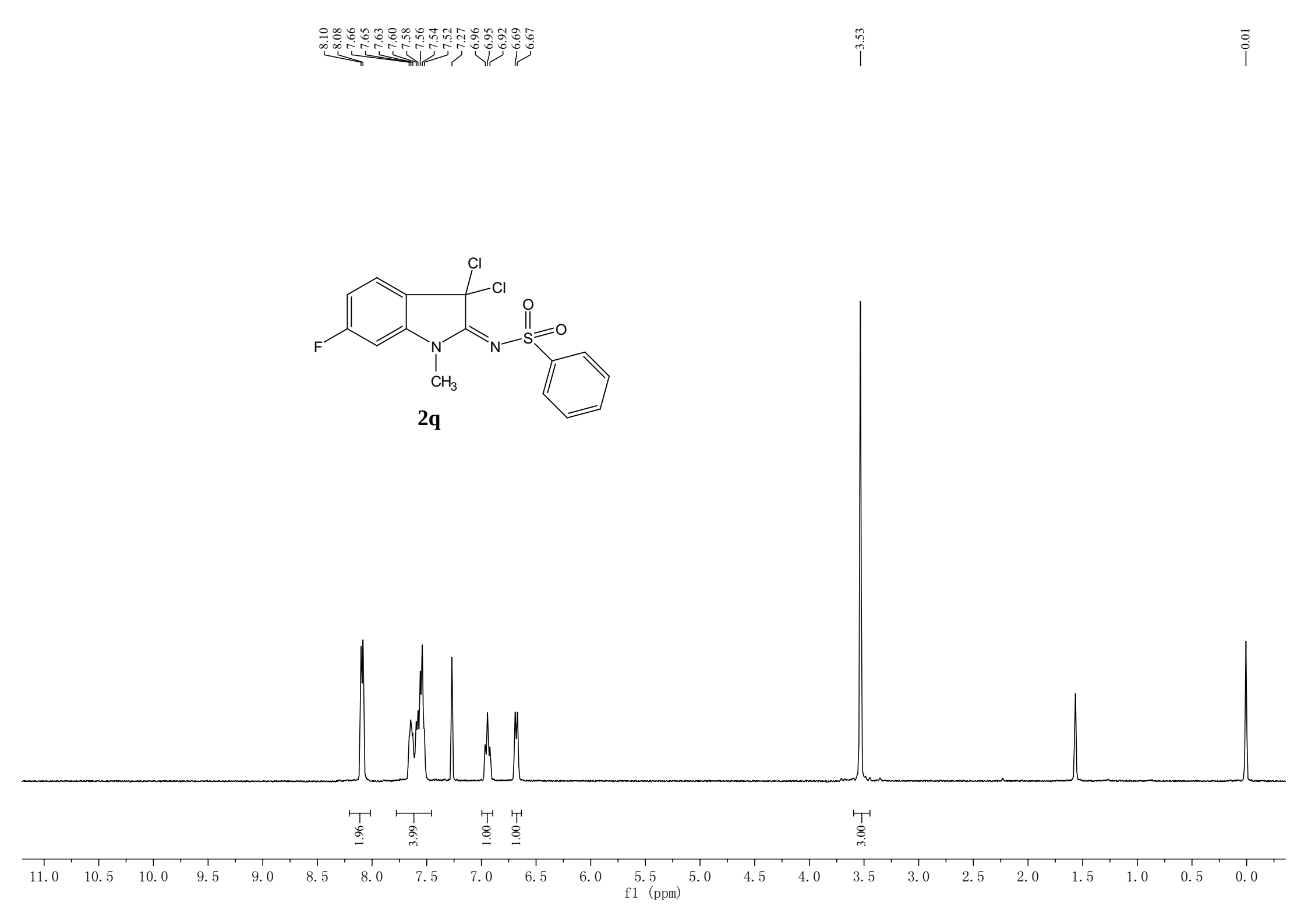

8.07
8.05
7.66
7.65
7.64
7.63
7.60
7.58
7.56
7.54
7.52
7.51
7.27
6.95
6.92
6.90
6.65
6.63
5.88
5.86
5.85
5.84
5.82
5.81
5.80
5.78
5.30
5.27
5.25
5.21
4.52
4.50
0.00

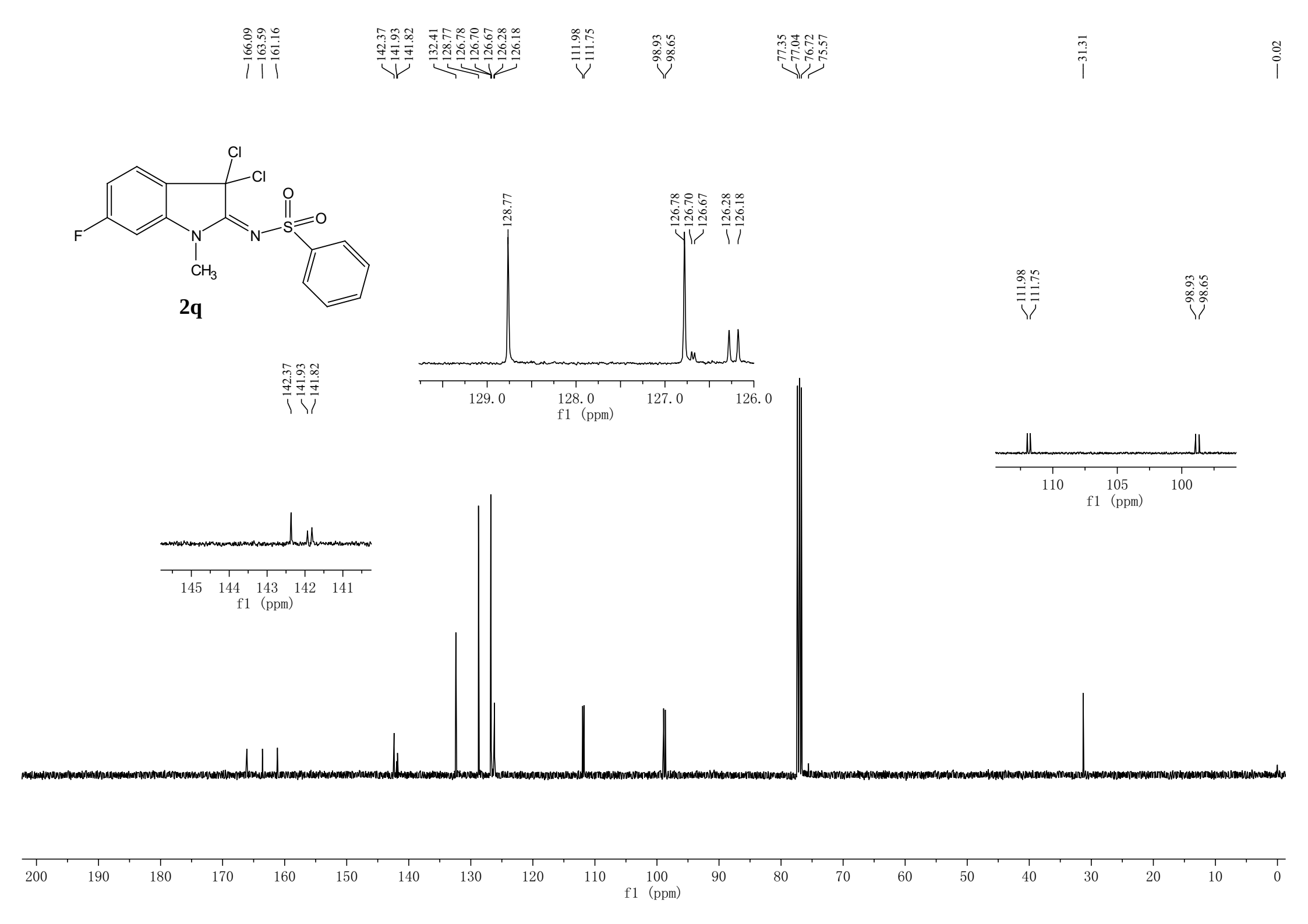

Cl
Cl
O
O
F
N
N
S
CH2

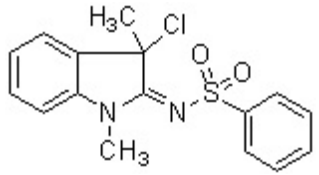
2p


1.93
1.03
3.00
0.99
1.03
1.07
2.06
2.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.89
163.39
160.45
142.31
140.65
140.53
132.41
128.94
128.74
126.95
126.91
126.75
126.23
126.12
119.19
111.93
111.69
99.49
99.21
77.40
77.08
76.76
74.51
45.83
Cl
Cl
O
O
S
F
N
N
CH2
2p
f1 (ppm)

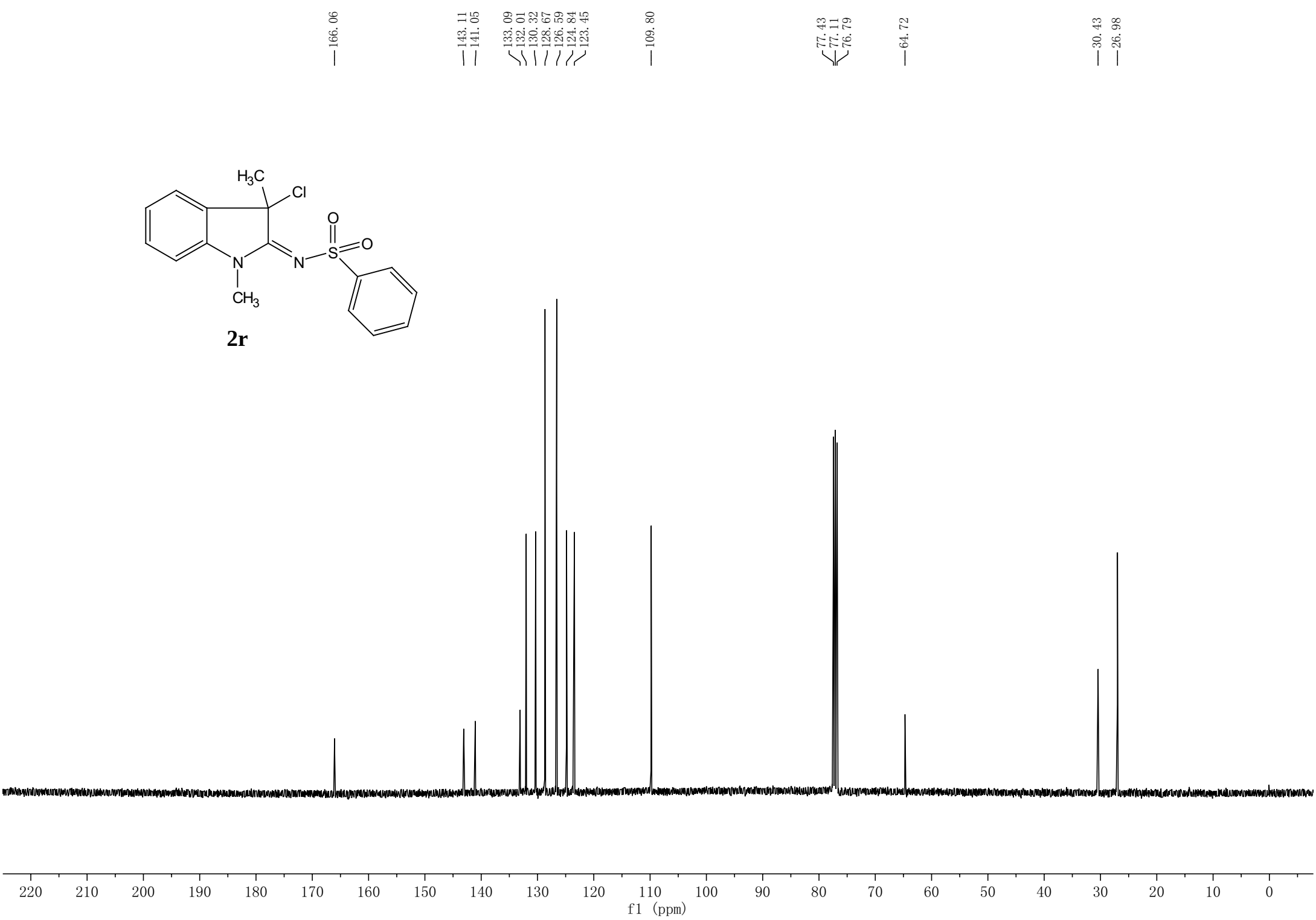

8.10
8.08
7.66
7.65
7.63
7.60
7.58
7.56
7.54
7.52
7.27
6.96
6.95
6.92
6.69
6.67
3.53
0.01
Cl
Cl
O
O
S
N
N
F
CH3
2q
1.96
3.99
1.00
1.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

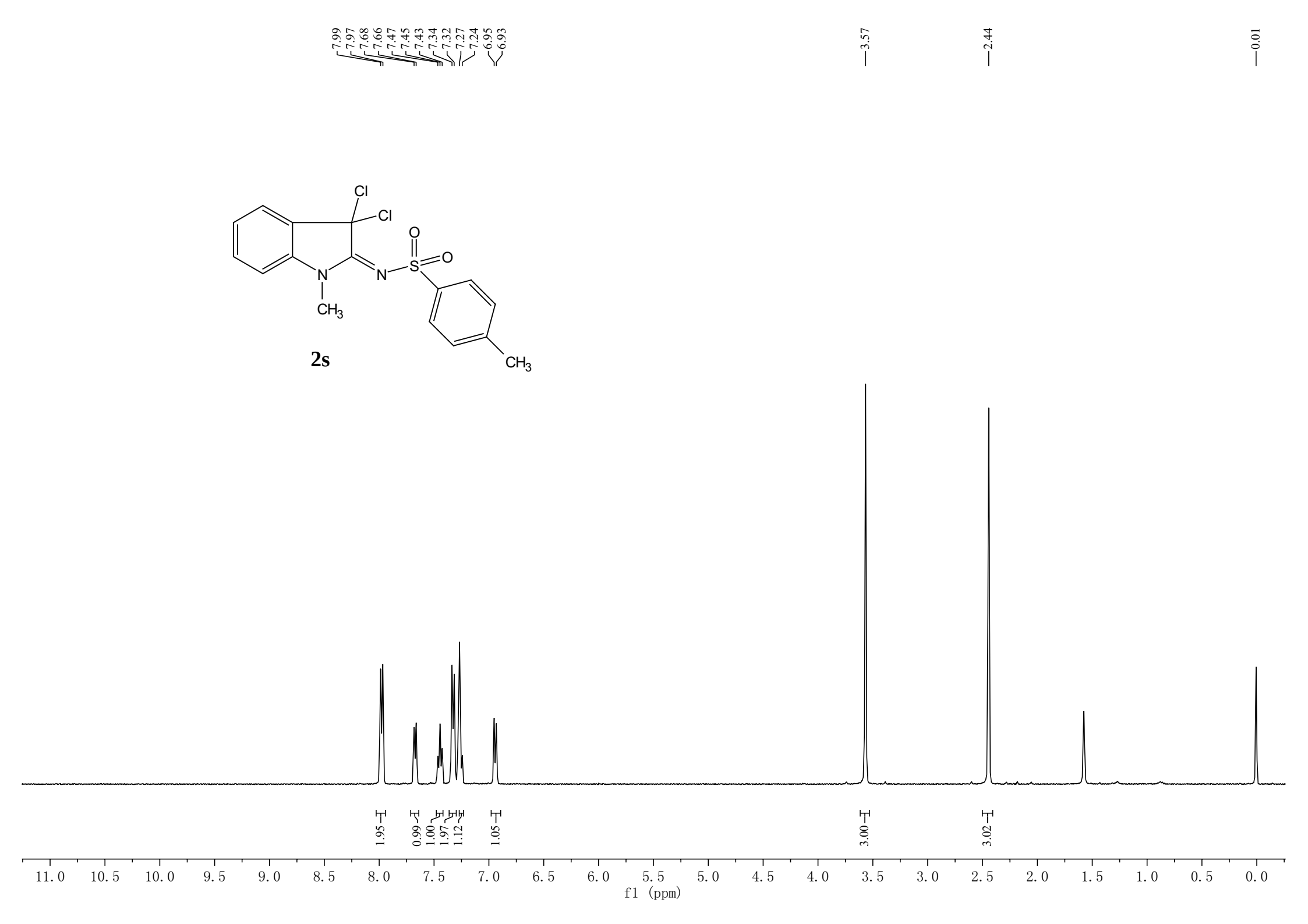

166.09
163.59
161.16
142.37
141.93
141.82
132.41
128.77
126.78
126.70
126.67
126.28
126.18
111.98
111.75
98.93
98.65
77.35
77.04
76.72
75.57
31.31
0.02
Cl
Cl
O
S
O
F
N
N
CH3
2q
128.77
126.78
126.70
126.67
126.28
126.18
129.0
128.0
127.0
126.0
f1 (ppm)
111.98
111.75
98.93
98.65
110
105
100
f1 (ppm)
142.37
141.93
141.82
145
144
143
142
141
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

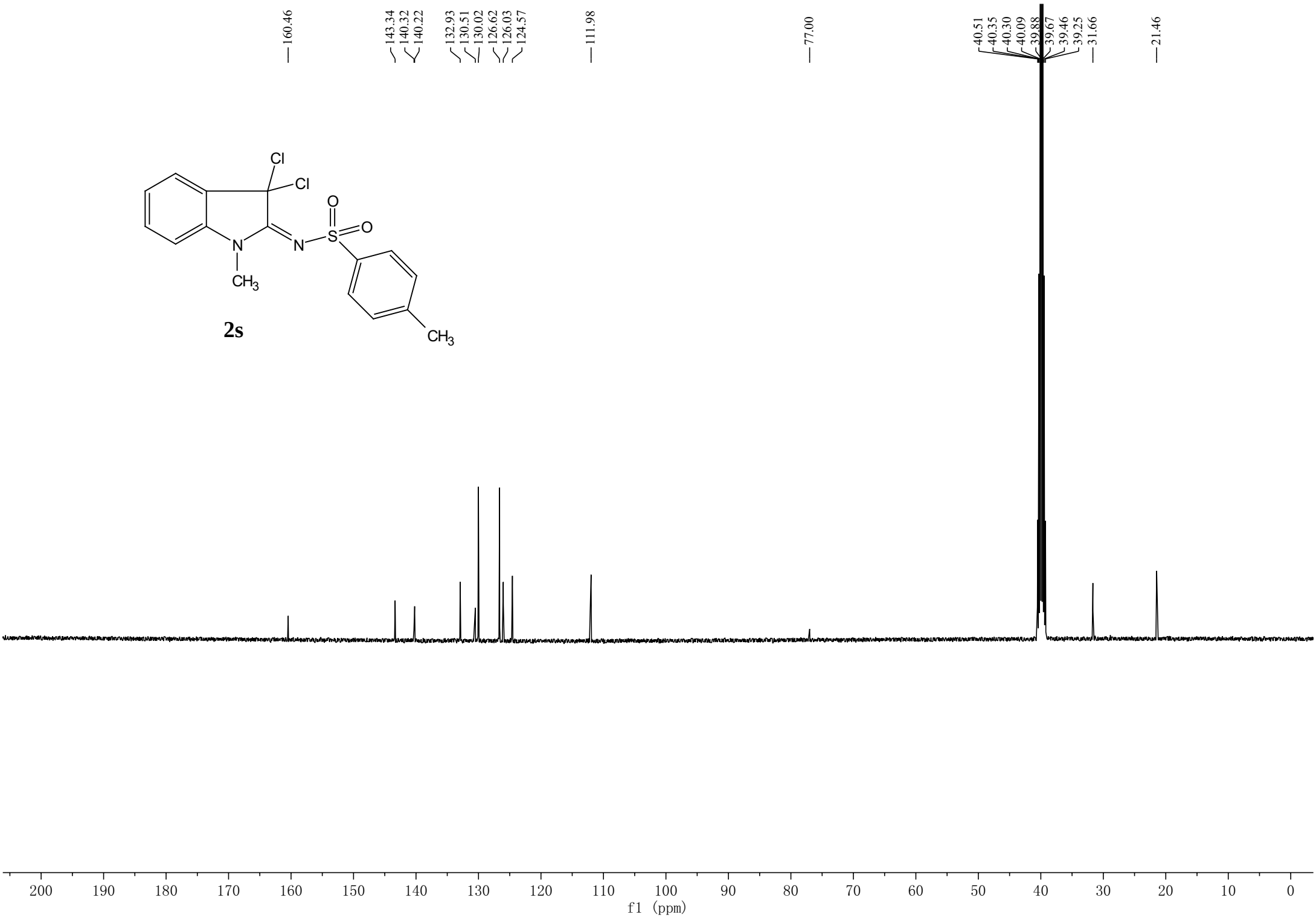


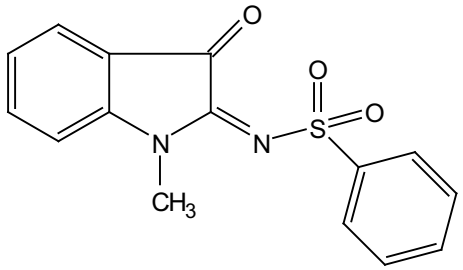
2r

8.08
8.06
7.53
7.40
7.36
7.23
7.19
6.95
6.93
3.47
2.23
-0.01
1.87
3.94
1.01
1.11
1.03
3.00
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


166.06
143.11
141.05
133.09
132.01
130.32
128.67
126.59
124.84
123.45
109.80
77.43
77.11
76.79
64.72
30.43
26.98
H3C
Cl
O
O
S
N
N
CH3
2r
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

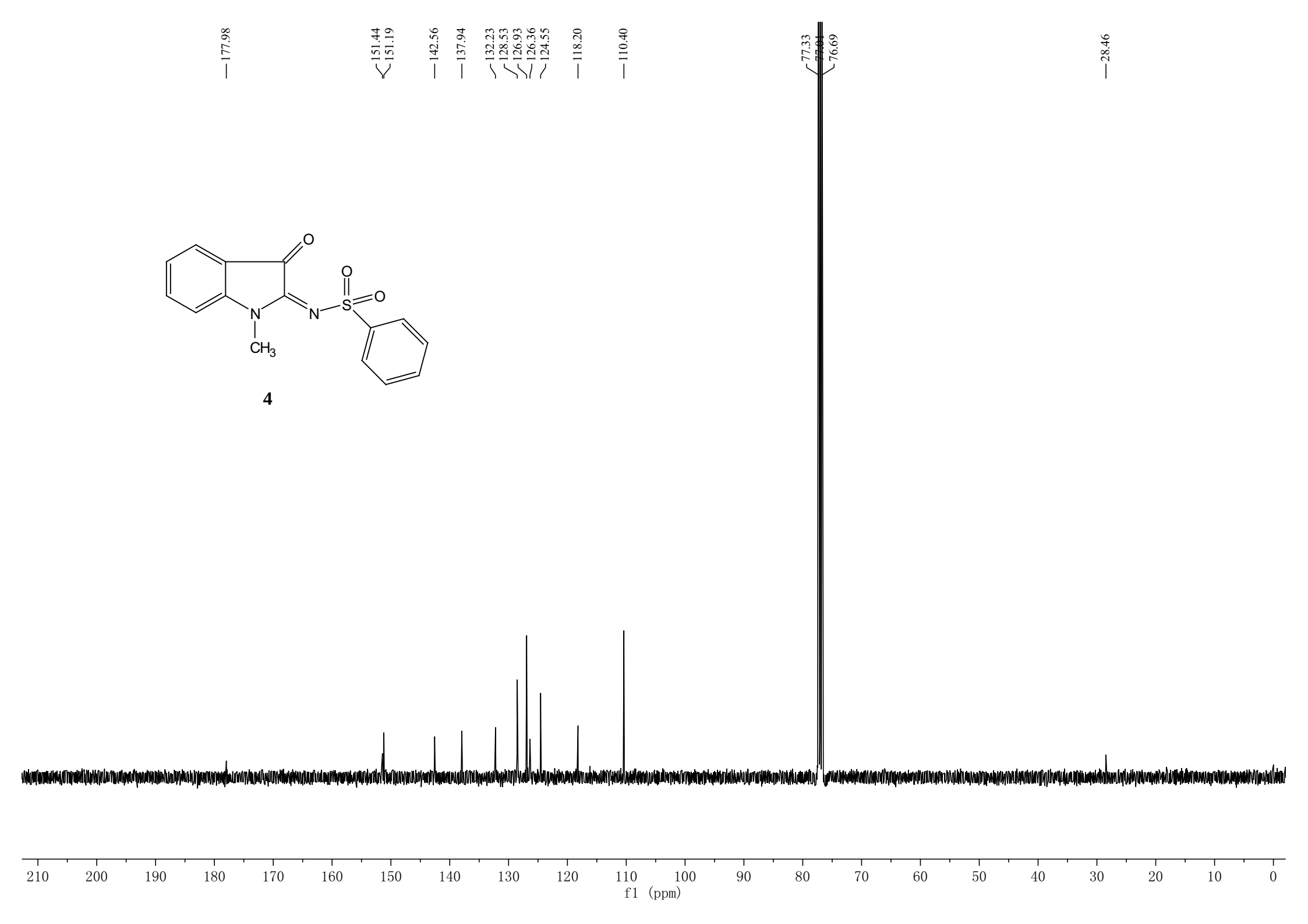

7.99
7.97
7.68
7.66
7.47
7.45
7.43
7.34
7.32
7.27
7.24
6.95
6.93
3.57
2.44
0.01
Cl
Cl
O
O
N
N
S
CH3
CH3
2s
1.95
0.99
1.00
1.97
1.12
1.05
3.00
3.02
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

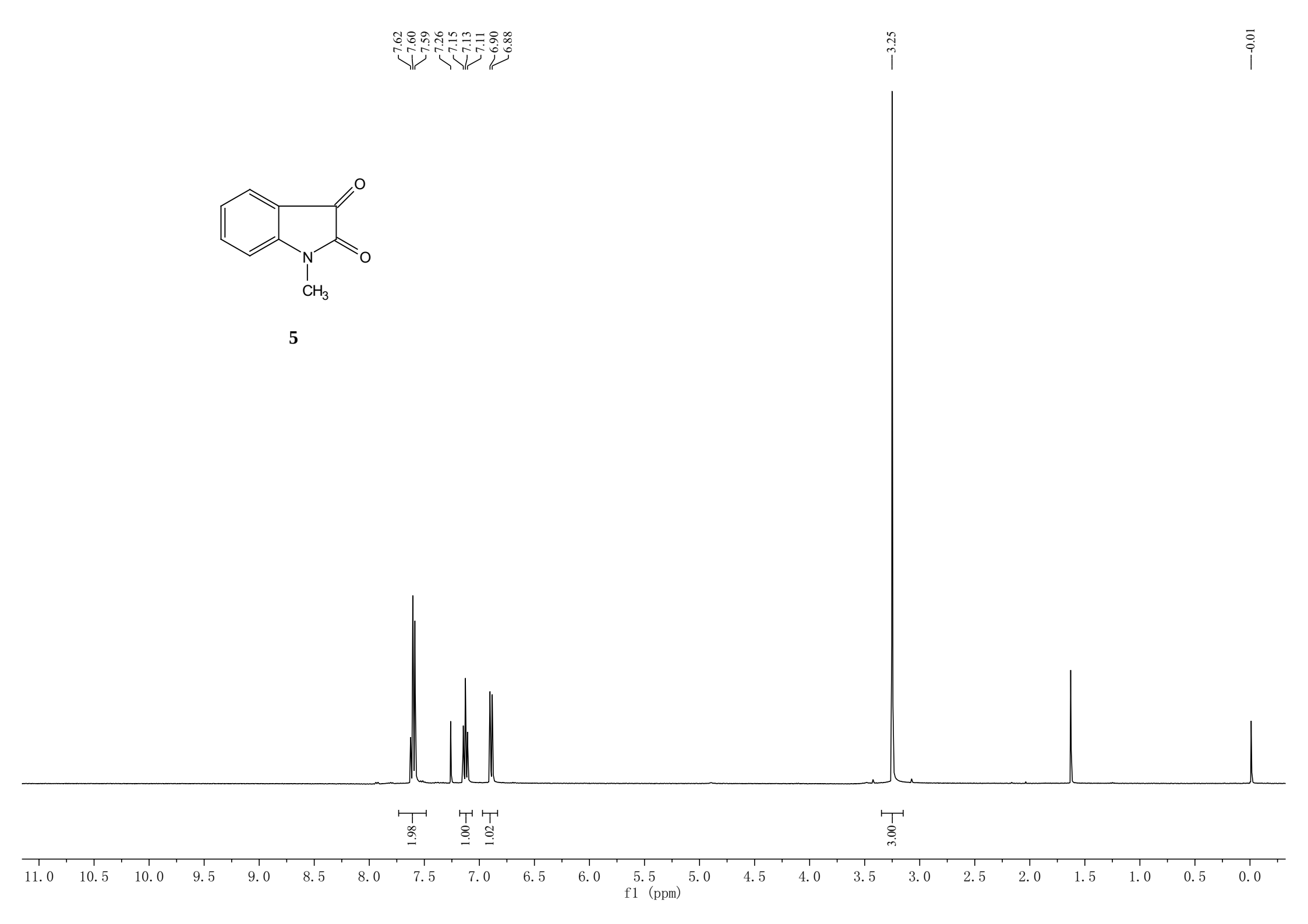

160.46
143.34
140.32
140.22
132.93
130.51
130.02
126.62
126.03
124.57
111.98
77.00
40.51
40.35
40.30
40.09
39.88
39.67
39.46
39.25
31.66
21.46
Cl
Cl
O
O
S
N
N
CH3
CH3
2s
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
O
N
N
S
CH3

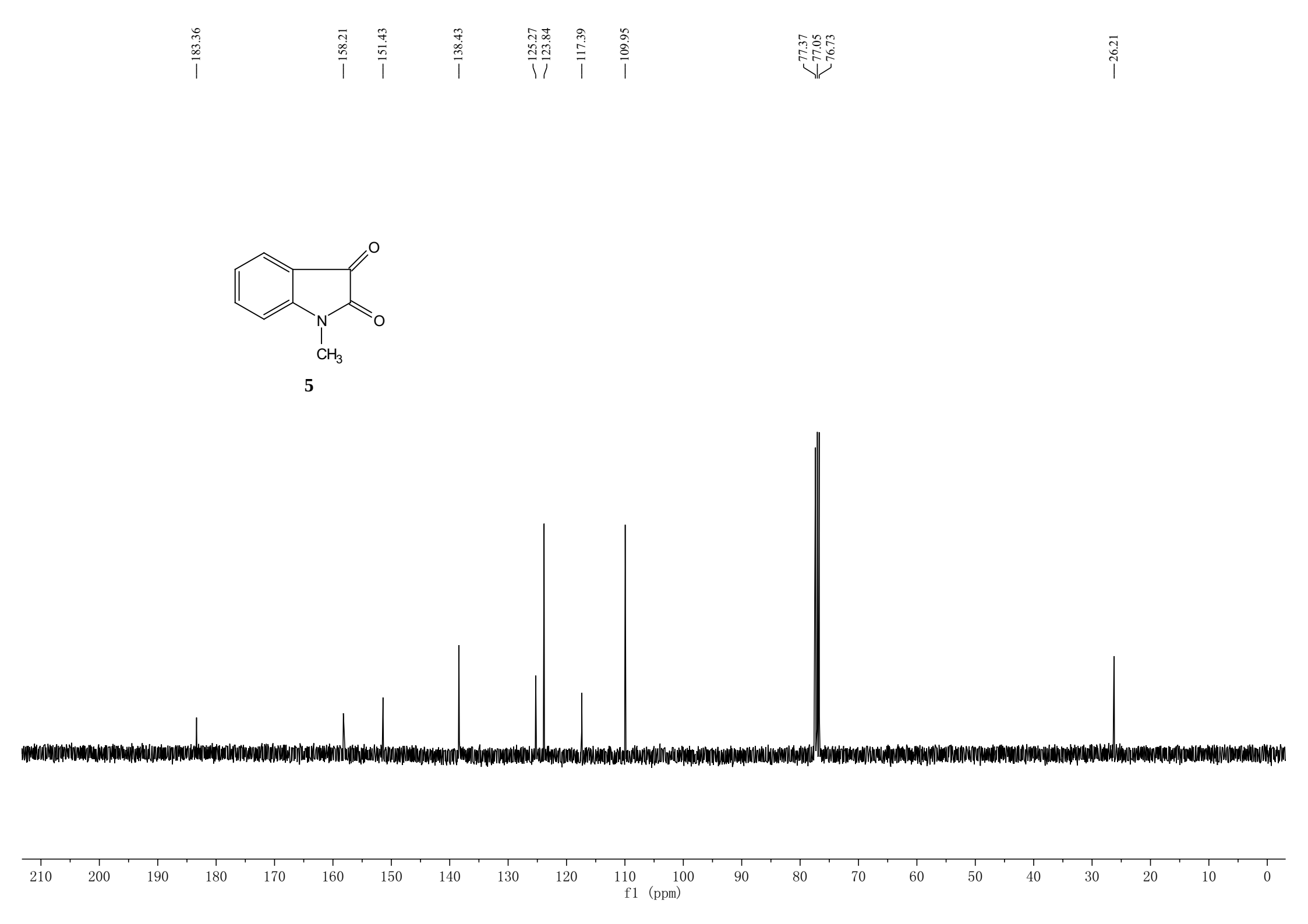
4

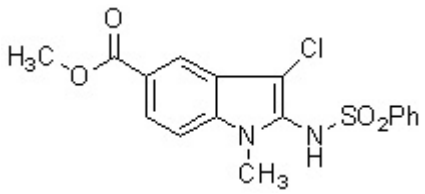
8.08
8.06
7.69
7.67
7.63
7.61
7.59
7.57
7.55
7.54
7.52
7.50
7.27
7.19
7.17
7.15
6.97
6.95
3.33
0.01
1.98
4.95
0.99
0.98
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


177.98
151.44
151.19
142.56
137.94
132.23
128.53
126.93
126.36
124.55
118.20
110.40
77.33
77.01
76.69
28.46
O
O
O
N
N
S
CH3
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.62
7.60
7.59
7.26
7.15
7.13
7.11
6.90
6.88
3.25
-0.01
O
O
N
CH3
1.98
1.00
1.02
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

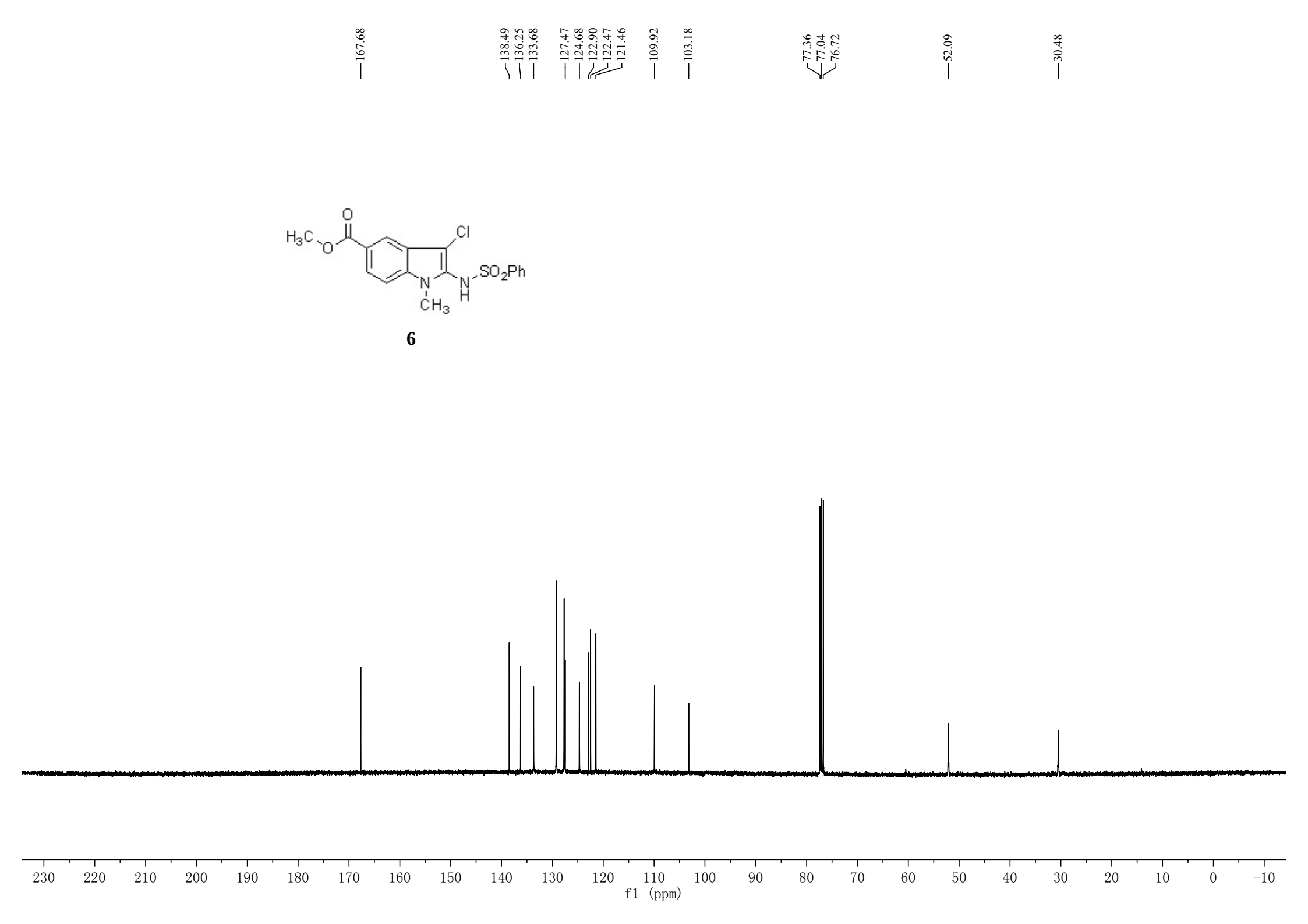
5


183.36
158.21
151.43
138.43
125.27
123.84
117.39
109.95
77.37
77.05
76.73
26.21
O
O
N
CH3
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H3C
O
Cl
N
CH3
N
H
SO2Ph

6

8.21
7.98
7.62
7.47
7.45
7.37
7.35
7.27
6.71
3.94
3.88
0.01
0.96
1.04
1.95
1.04
2.02
1.03
1.02
3.07
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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138.49
136.25
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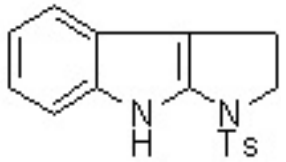
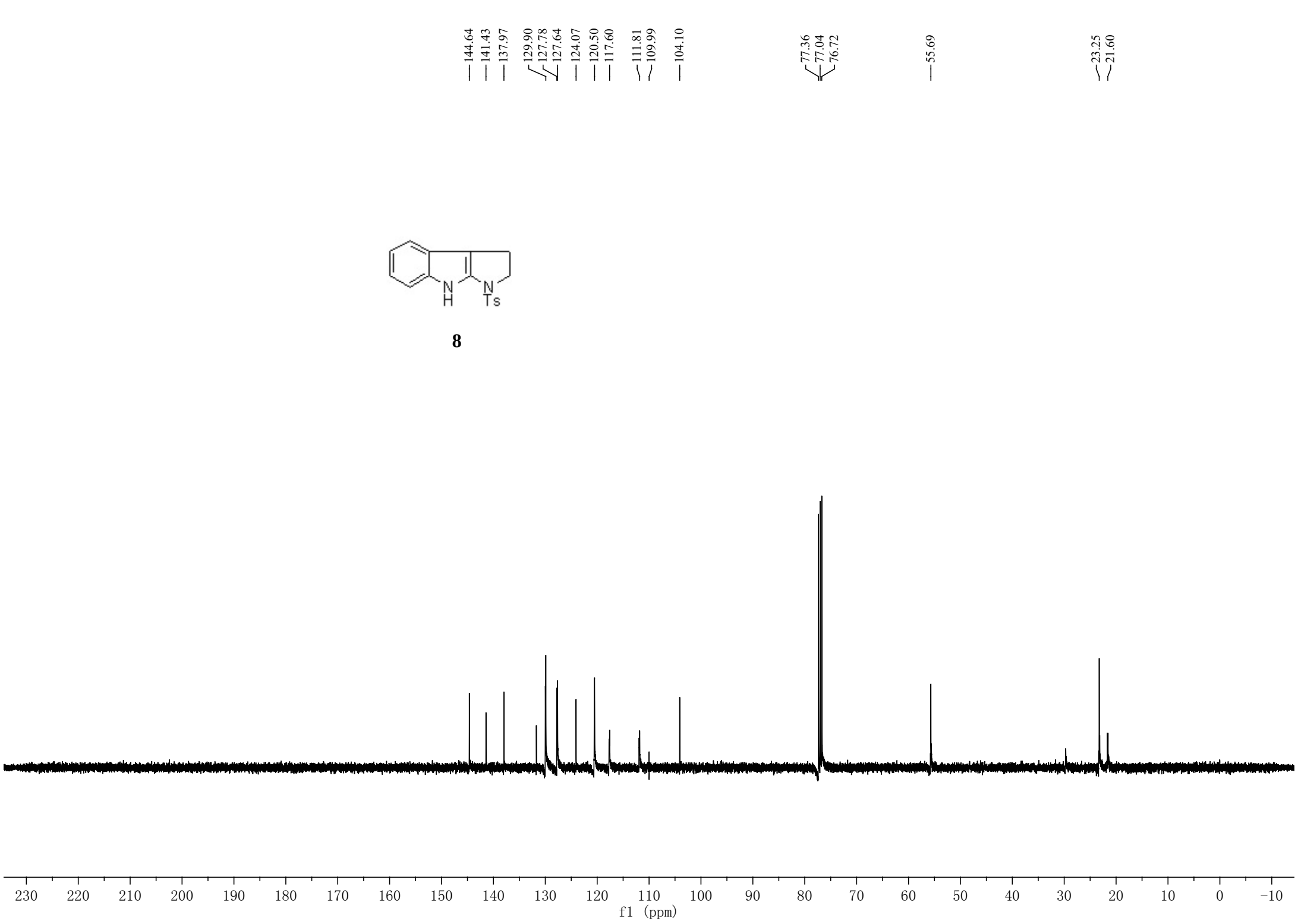
127.47
124.68
122.90
122.47
121.46
109.92
103.18
77.36
77.04
76.72
52.09
30.48
O
H3C
O
Cl
SO2Ph
N
H
N
CH3
6
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
H
N
Ts

8

8.73
7.59
7.57
7.36
7.34
7.28
7.26
7.23
7.21
7.14
7.12
7.10
7.09
7.07
4.14
4.12
4.11
2.82
2.80
2.78
2.37
0.00
0.96
2.01
1.00
3.19
2.06
2.01
2.04
3.09
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


144.64
141.43
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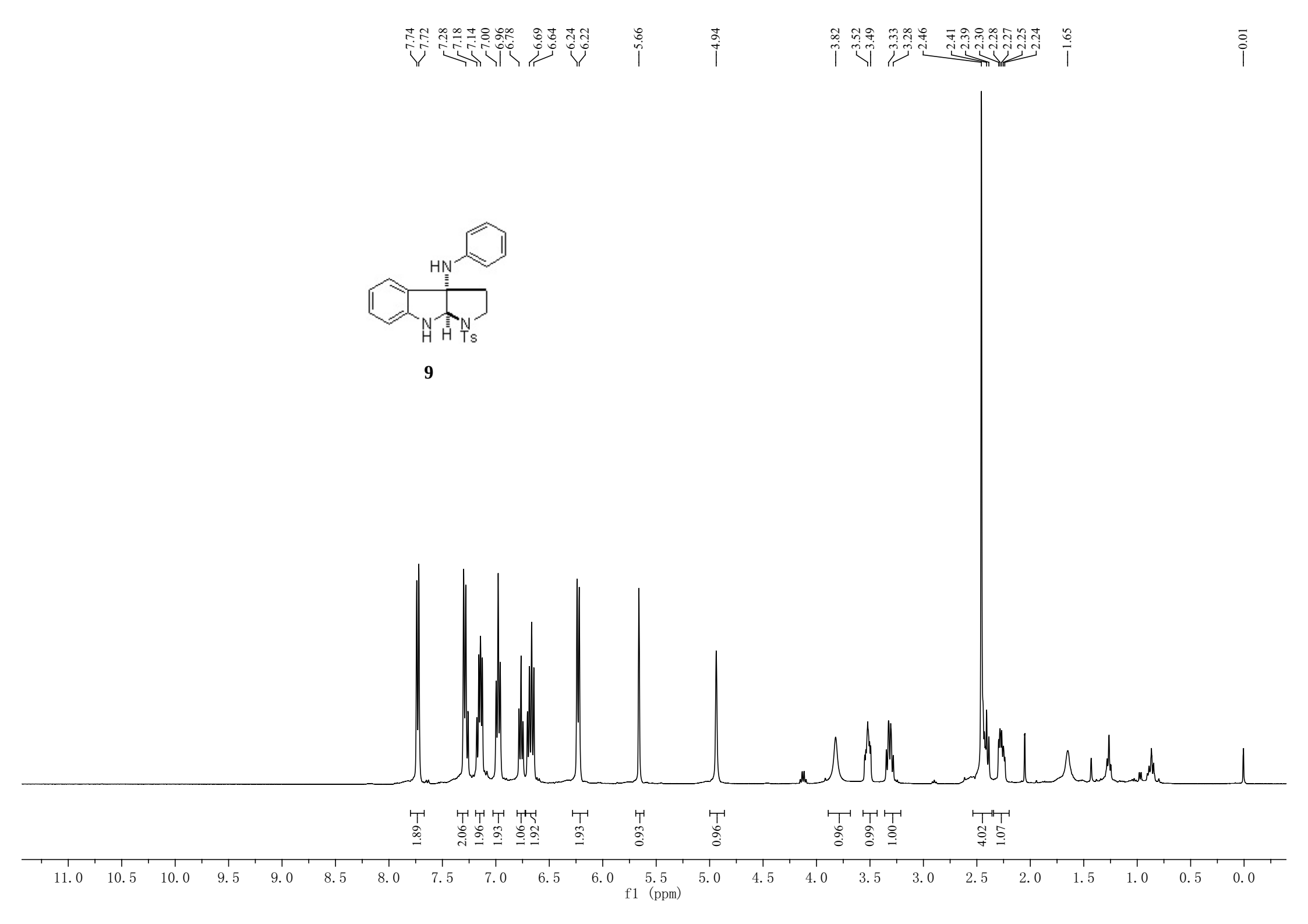
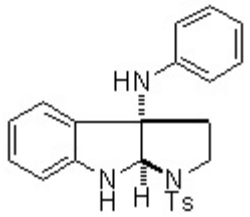
129.90
127.78
127.64
124.07
120.50
117.60
111.81
109.99
104.10
77.36
77.04
76.72
55.69
23.25
21.60
N
H
N
Ts
8
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.74
7.72
7.28
7.18
7.14
7.00
6.96
6.78
6.69
6.64
6.24
6.22
5.66
4.94
3.82
3.52
3.49
3.33
3.28
2.46
2.41
2.39
2.30
2.28
2.27
2.25
2.24
1.65
0.01
HN
N
H
H
N
Ts
1.89
2.06
1.96
1.93
1.06
1.92
1.93
0.93
0.96
0.96
0.99
1.00
4.02
1.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

9

148.73
144.56
143.70
135.55
129.91
127.20
123.28
118.34
114.84
109.84
79.10
77.37
77.06
76.74
73.39
46.02
37.79
21.56



9