

Supporting Information

**Ag(I)/PPh₃-catalyzed diastereoselective syntheses of spiro[indole-3,4'-
piperidine] derivatives via cycloisomerizations of tryptamine-ynamides**

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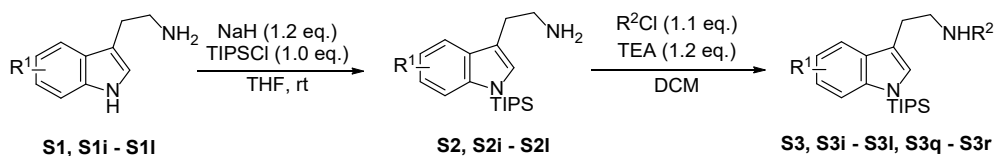
Contents

Part 1: General information	1
Part 2: General procedures and characteristic data for tryptamine derivatives S3, S3i-S3l and S3q-S3s.....	1
Part 3: General procedures and characteristic data for substrates 1, 1a-1s.....	6
Part 4: Table S1. Screening of reaction conditions ^a	18
Part 5: General procedures and characteristic data for products 2, 2a-2s.....	19
Part 6: General procedures and characteristic data for oxazolidinones S8a-S8d, S8l.....	30
Part 7: General procedures and characteristic data for substrates 3a-3n.....	35
Part 8: General procedures and characteristic data for products 4a-4n.....	44
Part 9: Gram-scale synthesis of spiro[indole-3,4'-piperidine].....	52
Part 10: Scheme S1. Derivatization of spiro[indole-3,4'-piperidine].....	52
Part 11: Procedures for derivatization and characteristic data for derivatives 5-8.....	53
Part 12: References.....	56
Part 13: X-ray crystal images	56
Part 14: Computational details.....	57
Part 15: NMR spectra data	65

Part 1: General information

Unless otherwise noted, all reactions were carried out under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Anhydrous tetrahydrofuran was distilled from sodium-benzophenone under a nitrogen atmosphere. Anhydrous dichloromethane and acetonitrile were distilled from calcium hydride under a nitrogen atmosphere. Anhydrous toluene was distilled from sodium under a nitrogen atmosphere. Anhydrous methanol was distilled from magnesium/iodine under a nitrogen atmosphere. TLC analysis of reaction mixtures was performed on Dynamic adsorbents silica gel F-254 TLC plates. Flash chromatography was carried out on Zeoprep 60 (200–300 mesh) silica gel. Alkaline silica gel was foregoing silica gel treated with 15% triethylamine in petroleum ether. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance-III 600 spectrometers and referenced to CDCl_3 , and $\text{DMSO}-d_6$. HR-ESI-MS was recorded on a Bruker micro-TOFQ-Q instrument. IR spectra were recorded on a Bruker IFS 55 spectrometer. Melting points were tested on Thomas Hoover capillary melting point apparatus.

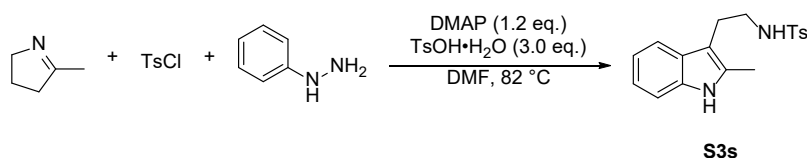
Part 2: General procedures and characteristic data for tryptamine derivatives S3, S3i-S3l and S3q-S3s



Tryptamines **S1** and **S1i-S1l** (10.0 mmol, 1.0 equiv.) were dissolved in THF (40 mL) and cooled in an ice bath. NaH (480.0 mg, 12.0 mmol, 1.2 equiv., 60% dispersion in mineral oil) was added portionwise and the mixture was stirred for 1 hour at room temperature. Then TIPSCl (1.928 g, 10.0 mmol, 1.0 equiv.) was added to the mixture dropwise in an ice bath and the resulting mixture was allowed to warm to room temperature gradually. When TLC analysis showed that the reaction was finished, the mixture was quenched with a saturated aqueous solution of NH_4Cl (20 mL) in an ice bath and extracted with ethyl acetate (40 mL) twice. Combined organic layers were washed with brine (60 mL) twice and dried over anhydrous Na_2SO_4 , filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further

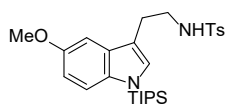
purification.

At 0 °C, to a stirred solution of the residue in DCM (40 mL) was added TEA (1.214 g, 12.0 mmol, 1.2 equiv.), followed by addition of sulfonyl chloride (0.615 mmol, 1.1 equiv.) in one portion. The mixture was allowed to warm to room temperature. When TLC showed that the reaction was finished, the mixture was quenched with a saturated aqueous solution of NH₄Cl (20 mL) in an ice bath and extracted with DCM (40 mL) twice. Combined organic layers were washed with brine (40 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel to afford tryptamine derivatives **S3**, **S3i-S3I** and **S3q-S3r**.



4-Methylbenzenesulfonyl chloride (TsCl) (2.478 g, 13.0 mmol, 1.2 equiv.) was added to a solution of 4-dimethylaminopyridine (DMAP) (1.588 g, 13.0 mmol, 1.2 equiv.) in DMF (10 mL) at 0 °C.^[s3] The reaction was stirred at room temperature for 15 min. A solution of the 5-methyl-3,4-dihydro-2*H*-pyrrole (897.8 mg, 10.8 mmol, 1.0 equiv.) in DMF (10 mL) was added and the reaction was stirred at room temperature for 3 h. *p*-Toluenesulfonic acid monohydrate (6.182 g, 32.5 mmol, 3.0 equiv.) was added at 0 °C under inert atmosphere. The reaction was then stirred at room temperature for 2 h. Phenylhydrazine (1.752 g, 16.2 mmol, 1.5 equiv.) was added and stirred for an addition 5 min at room temperature. The reaction was then heated to 82 °C for 20 h. The reaction was cooled down to room temperature. The residue was then dissolved in ethyl acetate and washed with brine and a saturated aqueous solution of NaHCO₃. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo* to give a crude solid, which was purified by a flash column chromatography on silica gel to afford tryptamine derivative **S3s**.

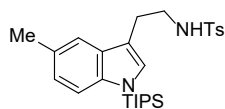
4-Methyl-*N*-(2-(1-(triisopropylsilyl)-1*H*-indol-3-yl)ethyl)benzenesulfonamide (S3)



S3j

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the tryptamine derivative **S3j** (3.647 g) as a light-yellow solid with a yield of 73%; Mp. 115.9-117.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 5.7 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.11 (s, 1H), 6.87 (d, *J* = 2.6 Hz, 1H), 6.72 (dd, *J* = 8.9, 2.6 Hz, 1H), 3.74 (s, 3H), 3.02 – 2.97 (m, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 1.65 (hept, *J* = 7.5 Hz, 3H), 1.04 (d, *J* = 7.4 Hz, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 153.4, 142.5, 137.8, 135.5, 131.1, 129.8, 129.6, 126.5, 114.3, 114.2, 110.9, 100.3, 55.2, 43.0, 25.2, 20.9, 17.9, 12.0; IR (thin film, cm⁻¹) 3281, 2946, 2867, 1597, 1464, 1407, 1320, 1268, 1161, 881, 802, 780; HRMS (ESI) *m/z* Calcd. for C₂₇H₄₁N₂O₃SSi [M+H]⁺: 501.2602, Found 501.2623.

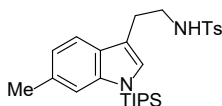
4-Methyl-N-(2-(5-methyl-1-(triisopropylsilyl)-1H-indol-3-yl)ethyl)benzenesulfonamide (S3k)



S3k

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the tryptamine derivative **S3k** (4.332 g) as a white solid with a yield of 86%; Mp. 119.6-121.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.71 – 7.68 (m, 2H), 7.66 (t, *J* = 5.7 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 7.09 (s, 1H), 6.89 (dd, *J* = 8.5, 1.8 Hz, 1H), 2.98 (dd, *J* = 8.1, 5.9 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.35 (d, *J* = 1.8 Hz, 3H), 2.34 (s, 3H), 1.65 (hept, *J* = 7.6 Hz, 3H), 1.04 (d, *J* = 7.5 Hz, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 142.5, 139.0, 137.8, 130.7, 129.6, 129.1, 127.8, 126.6, 122.9, 117.9, 113.8, 113.4, 43.1, 25.2, 21.0, 20.9, 17.9, 12.0; IR (thin film, cm⁻¹) 3312, 2946, 2867, 1597, 1461, 1405, 1340, 1307, 1159, 882, 809, 787; HRMS (ESI) *m/z* Calcd. for C₂₇H₄₁N₂O₂SSi [M+H]⁺: 485.2653, Found 485.2676.

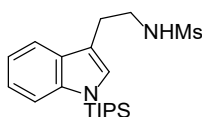
4-Methyl-N-(2-(6-methyl-1-(triisopropylsilyl)-1H-indol-3-yl)ethyl)benzenesulfonamide (S3l)



S3l

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the tryptamine derivative **S3l** (3.060 g) as a light-yellow solid with a yield of 63%; Mp. 114.7-116.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.70 – 7.65 (m, 3H), 7.36 – 7.33 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.23 (s, 1H), 7.06 (s, 1H), 6.85 (dd, *J* = 8.1, 1.3 Hz, 1H), 3.02 – 2.98 (m, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.37 (s, 3H), 2.35 (d, *J* = 2.3 Hz, 3H), 1.67 (hept, *J* = 7.6 Hz, 3H), 1.05 (d, *J* = 7.5 Hz, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 142.5, 141.2, 137.8, 130.3, 129.6, 128.4, 128.2, 126.5, 120.9, 117.9, 114.1, 113.5, 43.1, 25.3, 21.6, 20.9, 17.9, 12.1; IR (thin film, cm⁻¹) 3289, 2946, 2867, 1597, 1462, 1407, 1342, 1319, 1161, 882, 801, 693; HRMS (ESI) *m/z* Calcd. for C₂₇H₄₀N₂O₂SSiNa [M+Na]⁺: 507.2472, Found 507.2583.

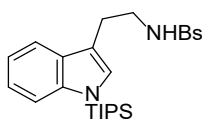
***N*-(2-(1-(Triisopropylsilyl)-1*H*-indol-3-yl)ethyl)methanesulfonamide (S3q)**



S3q

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the tryptamine derivative **S3q** (3.227 g) as a white solid with a yield of 82%; Mp. 97.8-98.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.54 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.25 (s, 1H), 7.14 – 7.09 (m, 2H), 7.08 – 7.04 (m, 1H), 3.27 – 3.22 (m, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.81 (s, 3H), 1.72 (hept, *J* = 7.5 Hz, 3H), 1.08 (d, *J* = 7.6 Hz, 18H); ¹³C NMR (150 MHz, CDCl₃) δ 141.6, 130.5, 129.6, 121.9, 119.8, 118.5, 114.3, 113.7, 43.5, 40.3, 26.4, 18.2, 12.9; IR (thin film, cm⁻¹) 3255, 2944, 2866, 1606, 1450, 1309, 1214, 1139, 980, 884, 738; HRMS (ESI) *m/z* Calcd. for C₂₀H₃₄N₂O₂SSiNa [M+Na]⁺: 417.2002, Found 417.2009.

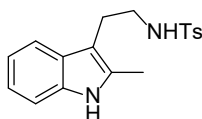
4-Bromo-*N*-(2-(1-(triisopropylsilyl)-1*H*-indol-3-yl)ethyl)benzenesulfonamide (S3r)



S3r

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the tryptamine derivative **S3r** (4.690 g) as a yellow solid with a yield of 88%; Mp. 119.3-121.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.89 (t, *J* = 5.7 Hz, 1H), 7.76 (dt, *J* = 8.5, 1.6 Hz, 2H), 7.73 – 7.71 (m, 2H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.15 (s, 1H), 7.10 – 7.07 (m, 1H), 7.02 (t, *J* = 7.4 Hz, 1H), 3.08 – 3.04 (m, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 1.68 (p, *J* = 7.6 Hz, 3H), 1.08 – 1.02 (m, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 140.7, 140.0, 132.2, 130.5, 129.0, 128.5, 126.1, 121.4, 119.2, 118.2, 114.2, 113.7, 43.0, 25.2, 17.9, 12.0; IR (thin film, cm⁻¹) 3309, 3949, 2867, 1575, 1451, 1405, 1346, 1322, 1164, 883, 740, 610; HRMS (ESI) *m/z* Calcd. for C₂₅H₃₅BrN₂O₂SSiNa [M+Na]⁺: 557.1264, Found 557.1275.

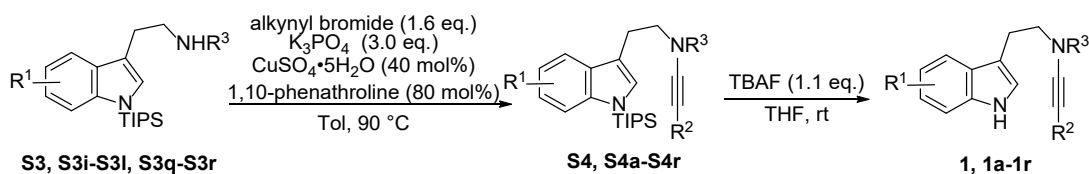
4-Methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (**S3s**)



S3s

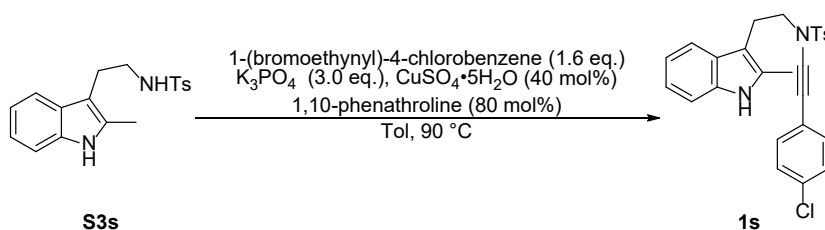
Purified by a flash column chromatography on silica gel with PE/EA (4:1) as an eluent to give the tryptamine derivative **S3s** (2.80 g) as a yellow solid with a yield of 78%; Mp. 115.2-116.9 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.88 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 4.39 (t, *J* = 6.3 Hz, 1H), 3.21 (q, *J* = 6.6 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.34 (s, 3H); IR (thin film, cm⁻¹) 3405, 3253, 1710, 1597, 1463, 1306, 1159, 742, 671, 550; HRMS (ESI) *m/z* Calcd. for C₁₈H₂₀N₂O₂SNa [M+Na]⁺: 351.1138, Found 351.1144.

Part 3: General procedures and characteristic data for substrates **1**, **1a-1s**



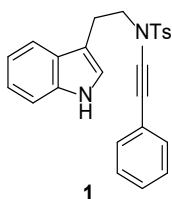
To a stirred solution of a tryptamine derivatives **S3**, **S3i-S3l** and **S3q-S3r** (2.0 mmol, 1.0 equiv.) and corresponding alkynyl bromide^[s1] (3.2 mmol, 1.6 equiv.) in toluene (20 mL) were added CuSO₄·5H₂O (199.7 mg, 0.8 mmol, 40 mol%), 1,10-phenanthroline (288.3 mg, 1.6 mmol, 80 mol%) and K₃PO₄ (1.274 g, 6.0 mmol, 3.0 equiv.) in sequence. The mixture was heated to 90 °C. After TLC analysis showed that the reaction was finished, the reaction was filtrated through a Celite pad, washed with ethyl acetate and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

At 0 °C, to a stirred solution of the residue in THF (20 mL) was added a solution of TBAF (2.2 mL, 2.2 mmol, 1.1 equiv.) in THF. The mixture was allowed to warm to room temperature. When TLC showed that the reaction was finished, the mixture was concentrated *in vacuo*. The residue was purified by a flash column chromatography on alkaline silica gel to afford substrates **1**, **1a-1r**.



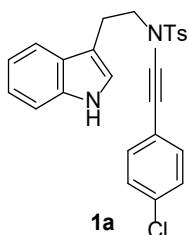
To a stirred solution of a tryptamine derivative **S3s** (1.905 g, 5.8 mmol, 1.0 equiv.) and 1-(bromoethynyl)-4-chlorobenzene (2.004 g, 9.3 mmol, 1.6 equiv.) in toluene (20 mL) were added CuSO₄·5H₂O (577.7 mg, 2.3 mmol, 40 mol%), 1,10-phenanthroline (834.0 mg, 4.6 mmol, 80 mol%) and K₃PO₄ (3.684 g, 17.4 mmol, 3.0 equiv.) in sequence. The mixture was heated to 90 °C. After TLC analysis showed that the reaction was finished, the reaction was filtrated through a Celite pad, washed with ethyl acetate and concentrated *in vacuo*. The residue was purified by a flash column chromatography on alkaline silica gel to afford substrate **1s**.

N-(2-(1H-Indol-3-yl)ethyl)-4-methyl-N-(phenylethynyl)benzenesulfonamide (1)^[s2]



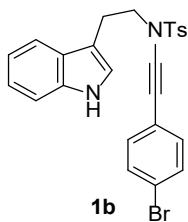
Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1** (767.7 mg) as a white solid with a yield of 93%; Mp. 135.1-136.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.88 (s, 1H), 7.77 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.31 (m, 6H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.00 – 6.97 (m, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 3.06 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.0, 136.2, 133.7, 130.9, 130.1, 128.7, 128.1, 127.3, 126.9, 123.5, 122.1, 121.0, 118.5, 117.9, 111.5, 109.6, 82.5, 70.5, 51.7, 23.7, 21.1; IR (thin film, cm⁻¹) 3446, 3051, 2936, 2974, 2229, 1596, 1454, 1350, 1164, 1091, 962, 905; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₃N₂O₂S [M+H]⁺: 415.1475, Found 415.1485.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-((4-chlorophenyl)ethynyl)-4-methylbenzenesulfonamide (**1a**)**



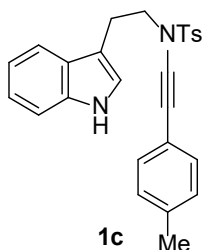
Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1a** (701.3 mg) as a white solid with a yield of 78%; Mp. 156.5-158.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.86 (s, 1H), 7.78 – 7.75 (m, 2H), 7.50 – 7.47 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.43 – 7.40 (m, 2H), 7.35 – 7.33 (m, 1H), 7.32 – 7.29 (m, 2H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.06 (m, 1H), 7.00 – 6.96 (m, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.1, 136.2, 133.7, 132.7, 132.5, 130.2, 128.8, 127.4, 126.9, 123.5, 121.1, 118.5, 118.0, 111.5, 109.6, 83.7, 69.6, 51.7, 23.8, 21.2; IR (thin film, cm⁻¹) 3396, 2924, 2238, 1631, 1596, 1491, 1366, 1165, 1117, 1089, 962, 830; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁ClN₂O₂SNa [M+Na]⁺: 471.0904, Found 471.0907.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-((4-bromophenyl)ethynyl)-4-methylbenzenesulfonamide (**1b**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1b** (740.1 mg) as a white solid with a yield of 75%; Mp. 157.9-159.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.87 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.53 (m, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.69 (t, *J* = 7.4 Hz, 2H), 3.05 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.1, 136.2, 133.7, 132.6, 131.7, 130.1, 127.3, 126.9, 123.5, 121.4, 121.2, 121.0, 118.5, 118.0, 111.5, 109.6, 83.8, 69.7, 51.6, 23.8, 21.1; IR (thin film, cm⁻¹) 3394, 2923, 2237, 1595, 1457, 1366, 1165, 1116, 1090, 961, 827, 747; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁BrN₂O₂SNa [M+Na]⁺: 515.0399, Found 515.0408.

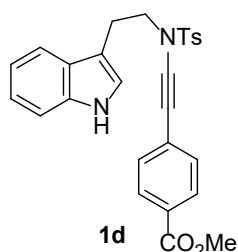
***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-methyl-*N*-(*p*-tolylethynyl)benzenesulfonamide (**1c**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1c** (582.0 mg) as a yellow solid with a yield of 68%; Mp. 120.3-121.8 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.88 (s, 1H), 7.76 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.44 (dd, *J* = 8.4, 2.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.19 – 7.15 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 3.67 (t, *J* = 7.4 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 2.40 (d, *J* = 2.6 Hz, 3H), 2.30 (d, *J* = 2.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.9, 137.9, 136.2, 133.7, 131.0, 130.1, 129.3, 127.3, 126.9, 123.5, 121.0, 119.0, 118.5, 117.9, 111.5, 109.6, 81.8, 70.5, 51.7, 23.7, 21.1, 21.0; IR (thin film, cm⁻¹) 3401, 2921, 2857, 2238, 1597, 1457, 1364,

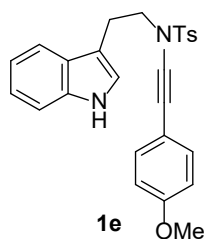
1164, 1090, 962, 818, 744; HRMS (ESI) m/z Calcd. for $C_{26}H_{24}N_2O_2SNa$ $[M+Na]^+$: 451.1451, Found 451.1455.

Methyl 4-(((*N*-(2-(1*H*-indol-3-yl)ethyl)-4-methylphenyl)sulfonamido)ethynyl)benzoate (1d**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1d** (403.6 mg) as a light-yellow solid with a yield of 43%; Mp. 99.7-101.3 °C; 1H NMR (600 MHz, $DMSO-d_6$) δ 10.86 (d, $J = 2.5$ Hz, 1H), 7.93 – 7.88 (m, 2H), 7.79 – 7.77 (m, 2H), 7.50 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.37 (m, 2H), 7.34 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.14 (d, $J = 2.4$ Hz, 1H), 7.10 – 7.07 (m, 1H), 7.01 – 6.97 (m, 1H), 3.85 (s, 3H), 3.74 (t, $J = 7.3$ Hz, 2H), 3.07 (t, $J = 7.3$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $DMSO-d_6$) δ 165.71, 145.16, 136.26, 133.66, 130.41, 130.17, 129.36, 128.24, 127.35, 127.29, 126.92, 123.57, 121.05, 118.50, 117.99, 111.53, 109.53, 86.09, 70.57, 52.24, 51.62, 23.87, 21.14; IR (thin film, cm^{-1}) 3398, 3058, 2950, 2230, 1719, 1602, 1364, 1276, 1166, 1118, 955, 860; HRMS (ESI) m/z Calcd. for $C_{27}H_{24}N_2O_4SNa$ $[M+Na]^+$: 495.1349, Found 495.1351.

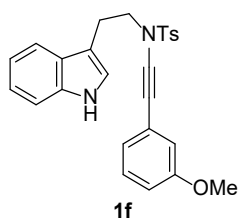
***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-((4-methoxyphenyl)ethynyl)-4-methylbenzenesulfonamide (**1e**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1e** (383.2 mg) as a light-yellow solid with a yield of 43%; Mp. 97.9-99.9 °C; 1H NMR (600 MHz, $DMSO-d_6$) δ 10.88 (d, $J = 2.6$ Hz, 1H), 7.75 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 7.9$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz,

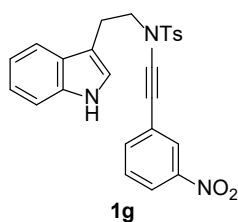
1H), 7.31 – 7.28 (m, 2H), 7.17 (d, $J = 2.4$ Hz, 1H), 7.08 (t, $J = 7.5$ Hz, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 6.94 – 6.91 (m, 2H), 3.77 (s, 3H), 3.65 (t, $J = 7.4$ Hz, 2H), 3.04 (t, $J = 7.5$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 159.3, 144.9, 136.3, 133.8, 133.1, 130.1, 127.3, 127.0, 123.5, 121.1, 118.5, 118.0, 114.4, 113.8, 111.5, 109.7, 80.9, 70.2, 55.3, 51.8, 23.7, 21.2; IR (thin film, cm^{-1}) 3396, 2924, 2240, 1603, 1511, 1457, 1361, 1245, 1163, 1090, 1029, 963; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 467.1400, Found 467.1402.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-((3-methoxyphenyl)ethynyl)-4-methylbenzenesulfonamide (1f)**



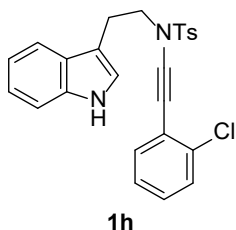
Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1f** (720.2 mg) as a light-yellow solid with a yield of 81%; Mp. 86.8-88.8 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 10.88 (s, 1H), 7.79 – 7.76 (m, 2H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 1H), 7.27 (t, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 2.4$ Hz, 1H), 7.10 – 7.07 (m, 1H), 6.99 (t, $J = 7.4$ Hz, 1H), 6.94 – 6.90 (m, 2H), 6.85 (dd, $J = 2.6, 1.5$ Hz, 1H), 3.76 (s, 3H), 3.69 (t, $J = 7.4$ Hz, 2H), 3.07 (t, $J = 7.4$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 159.2, 145.0, 136.2, 133.7, 130.1, 129.8, 127.4, 126.9, 123.5, 123.3, 123.2, 121.0, 118.5, 117.9, 115.6, 114.4, 111.5, 109.6, 82.4, 70.5, 55.2, 51.7, 23.7, 21.1; IR (thin film, cm^{-1}) 3397, 2925, 2868, 2238, 1596, 1580, 1458, 1363, 1168, 1090, 979, 889; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$: 467.1400, Found 467.1405.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-methyl-*N*-((3-nitrophenyl)ethynyl)benzenesulfonamide (1g)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1g** (827.1 mg) as a yellow solid with a yield of 90%; Mp. 115.4-117.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.87 (d, *J* = 2.7 Hz, 1H), 8.16 – 8.13 (m, 1H), 8.00 (t, *J* = 1.9 Hz, 1H), 7.82 – 7.79 (m, 2H), 7.67 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.64 – 7.61 (m, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.35 – 7.32 (m, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 7.09 – 7.06 (m, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 3.75 (t, *J* = 7.3 Hz, 2H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 147.85, 145.17, 136.64, 136.24, 133.69, 130.22, 130.17, 127.39, 126.93, 124.69, 123.91, 123.59, 122.45, 121.03, 118.46, 118.00, 111.50, 109.55, 85.05, 69.04, 51.63, 23.90, 21.14; IR (thin film, cm⁻¹) 3385, 3083, 2924, 2234, 1596, 1530, 1350, 1169, 1090, 1007, 881, 780; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁N₃O₄SNa [M+Na]⁺: 482.1145, Found 482.1140.

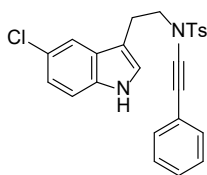
***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-((2-chlorophenyl)ethynyl)-4-methylbenzenesulfonamide (**1h**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1h** (688.7 mg) as a light-yellow solid with a yield of 77%; Mp. 114.8-116.8 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.88 (s, 1H), 7.81 – 7.78 (m, 2H), 7.52 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.40 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.17 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.00 – 6.97 (m, 1H), 3.73 (t, *J* = 7.4 Hz, 2H), 3.10 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 145.10, 136.23, 133.63, 133.58, 132.44, 130.09, 129.32, 129.25, 127.33, 127.29, 126.88, 123.49, 122.05, 121.04, 118.48, 117.91, 111.52, 109.49, 87.56, 68.04, 51.70, 23.60, 21.12; IR (thin film, cm⁻¹) 3341, 1590, 1462, 1417, 1310, 1172, 1088, 1051, 856, 778, 618; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁ClN₂O₂SNa [M+Na]⁺: 471.0904, Found 471.0912.

***N*-(2-(5-Chloro-1*H*-indol-3-yl)ethyl)-4-methyl-*N*-**

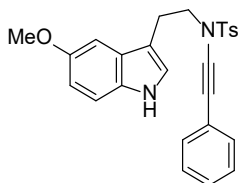
(phenylethynyl)benzenesulfonamide (1i)



1i

Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1i** (751.2 mg) as a light-yellow solid with a yield of 77%; Mp. 113.9-115.9 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 11.10 (s, 1H), 7.74 (dd, *J* = 8.5, 2.2 Hz, 2H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.43 – 7.39 (m, 2H), 7.38 – 7.32 (m, 6H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.07 (dd, *J* = 8.6, 2.1 Hz, 1H), 3.69 (t, *J* = 7.0 Hz, 2H), 3.05 (t, *J* = 7.0 Hz, 2H), 2.39 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.89, 134.66, 133.66, 130.90, 130.01, 128.63, 128.14, 128.06, 128.05, 127.25, 125.43, 123.22, 122.11, 120.95, 117.35, 112.99, 109.78, 82.48, 70.59, 51.62, 23.39, 21.12; IR (thin film, cm⁻¹) 3383, 3058, 2923, 2240, 1597, 1464, 1347, 1159, 1090, 966, 908, 789; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₂ClN₂O₂S [M+H]⁺: 449.1085, Found 449.1099.

***N*-(2-(5-Methoxy-1*H*-indol-3-yl)ethyl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (1j)**

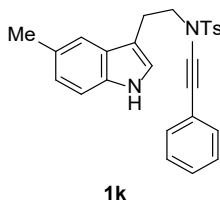


1j

Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1j** (522.8 mg) as a yellow oil with a yield of 59%; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.72 (d, *J* = 2.6 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.39 – 7.33 (m, 5H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.14 (d, *J* = 2.4 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.73 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.72 (s, 3H), 3.69 (t, *J* = 7.3 Hz, 2H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 153.1, 144.9, 133.7, 131.3, 130.9, 130.1, 128.7, 128.1, 127.3, 124.1, 122.1, 112.1, 111.2, 109.4, 99.8, 82.6, 70.5, 55.2, 51.7, 23.7, 21.1; IR (thin film, cm⁻¹) 3414, 2925, 2233, 1596, 1486, 1360, 1218, 1167, 1090, 962, 800, 755; HRMS (ESI) *m/z* Calcd. for

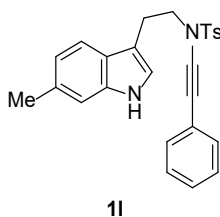
C₂₆H₂₄N₂O₃SNa [M+Na]⁺: 467.1400, Found 467.1404.

4-Methyl-N-(2-(5-methyl-1H-indol-3-yl)ethyl)-N-(phenylethynyl)benzenesulfonamide (1k)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1k** (616.2 mg) as a yellow solid with a yield of 72%; Mp. 108.6-110.6 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.76 (s, 1H), 7.80 – 7.76 (m, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.32 (m, 5H), 7.27 – 7.22 (m, 2H), 7.13 (d, *J* = 2.8 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 3.68 (t, *J* = 7.2 Hz, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.35 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.9, 134.6, 133.7, 130.9, 130.1, 128.7, 128.1, 127.3, 127.2, 126.9, 123.5, 122.6, 122.1, 117.5, 111.2, 109.1, 82.6, 70.6, 51.7, 23.6, 21.3, 21.1; IR (thin film, cm⁻¹) 3390, 2918, 2857, 2234, 1596, 1434, 1340, 1166, 1090, 960, 901, 791; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₄N₂O₂SNa [M+Na]⁺: 451.1451, Found 451.1473.

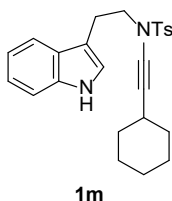
4-Methyl-N-(2-(6-methyl-1H-indol-3-yl)ethyl)-N-(phenylethynyl)benzenesulfonamide (1l)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1l** (606.8 mg) as a light-yellow solid with a yield of 71%; Mp. 126.3-128.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.72 (s, 1H), 7.76 (dd, *J* = 8.5, 2.7 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.38 – 7.30 (m, 6H), 7.13 (s, 1H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.82 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.67 (t, *J* = 7.3 Hz, 2H), 3.03 (t, *J* = 7.5 Hz, 2H), 2.40 (d, *J* = 3.3 Hz, 3H), 2.38 (d, *J* = 3.1 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 144.95, 136.69, 133.69, 130.89, 130.07, 130.04, 128.66, 128.05, 127.31, 124.89,

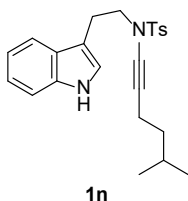
122.73, 122.12, 120.23, 117.66, 111.32, 109.43, 82.55, 70.48, 51.68, 23.79, 21.38, 21.12; IR (thin film, cm^{-1}) 3399, 3054, 2917, 2231, 1594, 1455, 1366, 1169, 1090, 969, 811, 756; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 451.1451, Found 451.1456.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-(cyclohexylethynyl)-4-methylbenzenesulfonamide (1m)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1m** (532.4 mg) as a light-yellow oil with a yield of 63 %; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.87 (s, 1H), 7.69 (d, $J = 8.1$ Hz, 2H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.14 (d, $J = 2.3$ Hz, 1H), 7.09 – 7.05 (m, 1H), 6.98 (t, $J = 7.4$ Hz, 1H), 3.50 (t, $J = 7.5$ Hz, 2H), 2.97 (t, $J = 7.5$ Hz, 2H), 2.57 – 2.51 (m, 1H), 2.40 (s, 3H), 1.71 – 1.66 (m, 2H), 1.62 – 1.55 (m, 2H), 1.46 – 1.21 (m, 6H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 144.6, 136.2, 133.6, 129.8, 127.3, 126.9, 123.3, 121.0, 118.4, 117.8, 111.5, 109.7, 74.0, 73.5, 51.6, 32.3, 27.8, 25.4, 23.9, 23.4, 21.1; IR (thin film, cm^{-1}) 3412, 2927, 2852, 2246, 1597, 1448, 1352, 1166, 1091, 892, 812, 742; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 443.1764, Found 443.1779.

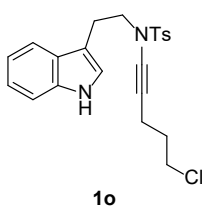
***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-methyl-*N*-(5-methylhex-1-yn-1-yl)benzenesulfonamide (1n)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1n** (546.6 mg) as a light-yellow oil with a yield of 67%; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.88 (s, 1H), 7.71 – 7.68 (m, 2H), 7.44 (dd, $J = 7.9$, 1.0 Hz, 1H), 7.42 (d, $J = 8.1$ Hz, 2H), 7.34 (dt, $J = 8.1$, 0.9 Hz, 1H), 7.15 (d, $J = 2.4$ Hz,

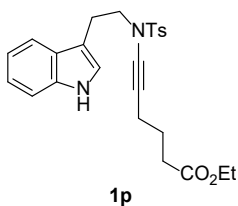
1H), 7.09 – 7.05 (m, 1H), 7.01 – 6.95 (m, 1H), 3.52 – 3.48 (m, 2H), 2.96 (t, $J = 7.6$ Hz, 2H), 2.40 (s, 3H), 2.28 (t, $J = 7.2$ Hz, 2H), 1.66 – 1.56 (m, 1H), 1.31 (q, $J = 7.1$ Hz, 2H), 0.86 (d, $J = 6.7$ Hz, 6H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 144.6, 136.2, 133.8, 129.9, 127.3, 126.9, 123.3, 121.0, 118.4, 117.8, 111.5, 109.7, 73.0, 70.2, 51.6, 37.3, 26.4, 23.4, 22.0, 21.1, 15.7; IR (thin film, cm^{-1}) 3412, 2926, 2342, 1631, 1458, 1384, 1354, 1272, 1167, 1092, 812, 742; HRMS (ESI) m/z Calcd. for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 431.1764, Found 431.1761.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-(5-chloropent-1-yn-1-yl)-4-methylbenzenesulfonamide (**1o**)^[2a]**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1o** (443.2 mg) as a light-yellow oil with a yield of 53%; ^1H NMR (600 MHz, DMSO- d_6) δ 10.89 (s, 1H), 7.72 – 7.69 (m, 2H), 7.46 – 7.44 (m, 1H), 7.43 – 7.41 (m, 2H), 7.35 (dd, $J = 8.1, 0.9$ Hz, 1H), 7.15 (d, $J = 2.4$ Hz, 1H), 7.09 – 7.06 (m, 1H), 7.00 – 6.97 (m, 1H), 3.64 (t, $J = 6.4$ Hz, 2H), 3.53 (t, $J = 7.5$ Hz, 2H), 2.96 (t, $J = 7.5$ Hz, 2H), 2.44 (t, $J = 6.8$ Hz, 2H), 2.40 (s, 3H), 1.85 (p, $J = 6.6$ Hz, 2H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 144.7, 136.2, 133.7, 129.9, 127.3, 126.9, 123.3, 121.0, 118.4, 117.9, 111.5, 109.7, 73.9, 68.7, 51.5, 44.0, 31.2, 23.5, 21.1, 15.3; IR (thin film, cm^{-1}) 3411, 2923, 2254, 1763, 1596, 1456, 1354, 1166, 1091, 1014, 813, 743; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 437.1061, Found 437.1070.

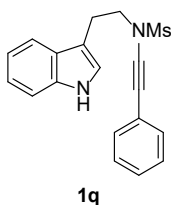
Ethyl 6-((*N*-(2-(1*H*-indol-3-yl)ethyl)-4-methylphenyl)sulfonamido)hex-5-ynoate (1p**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1p** (636.3 mg) as a light-yellow oil with a yield of 70%;

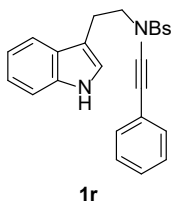
^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 10.88 (s, 1H), 7.72 – 7.69 (m, 2H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.34 (dd, $J = 8.2, 1.0$ Hz, 1H), 7.16 (d, $J = 2.4$ Hz, 1H), 7.09 – 7.06 (m, 1H), 7.00 – 6.96 (m, 1H), 4.06 (q, $J = 7.1$ Hz, 2H), 3.51 (dd, $J = 8.3, 6.9$ Hz, 2H), 2.96 (t, $J = 7.6$ Hz, 2H), 2.40 (s, 3H), 2.37 – 2.32 (m, 4H), 1.68 (p, $J = 7.2$ Hz, 2H), 1.18 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 172.5, 144.6, 136.2, 133.7, 129.9, 127.3, 126.9, 123.3, 121.0, 118.4, 117.9, 111.5, 109.7, 73.7, 69.5, 59.8, 51.5, 32.3, 23.9, 23.4, 21.1, 17.1, 14.1; IR (thin film, cm^{-1}) 3411, 3057, 2934, 2254, 1730, 1596, 1457, 1357, 1167, 1092, 814, 743; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{O}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 475.1662, Found 475.1662.

***N*-(2-(1*H*-Indol-3-yl)ethyl)-*N*-(phenylethynyl)methanesulfonamide (1q)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1q** (512.4 mg) as a light-yellow oil with a yield of 76%; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 10.93 (s, 1H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.41 – 7.33 (m, 6H), 7.28 (d, $J = 2.3$ Hz, 1H), 7.12 – 7.08 (m, 1H), 7.03 – 7.00 (m, 1H), 3.80 (t, $J = 7.4$ Hz, 2H), 3.18 (t, $J = 7.4$ Hz, 2H), 3.14 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$) δ 136.3, 131.1, 128.7, 128.1, 127.0, 123.6, 122.3, 121.1, 118.5, 118.1, 111.6, 109.9, 82.6, 70.3, 51.6, 38.0, 24.0; IR (thin film, cm^{-1}) 3417, 3056, 2928, 2236, 1598, 1457, 1354, 1161, 1116, 959, 745; HRMS (ESI) m/z Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 361.0981, Found 361.0989.

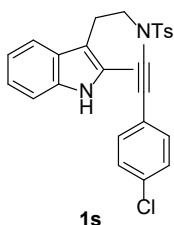
***N*-(2-(1*H*-Indol-3-yl)ethyl)-4-bromo-*N*-(phenylethynyl)benzenesulfonamide (1r)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **1r** (769.9 mg) as a light-yellow oil with a yield of 80%; Mp. 124.9-126.9 °C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$) δ 10.88 (s, 1H), 7.83 – 7.79 (m,

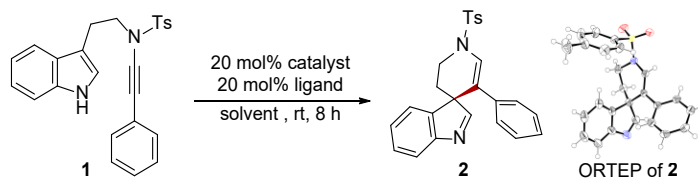
2H), 7.77 – 7.74 (m, 2H), 7.50 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.33 (m, 6H), 7.17 (d, $J = 2.4$ Hz, 1H), 7.10 – 7.07 (m, 1H), 7.00 – 6.97 (m, 1H), 3.75 (t, $J = 7.3$ Hz, 2H), 3.08 (t, $J = 7.3$ Hz, 2H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 136.2, 135.7, 132.7, 131.0, 129.1, 128.7, 128.4, 128.2, 126.9, 123.5, 121.9, 121.0, 118.5, 117.9, 111.5, 109.5, 81.9, 70.8, 51.8, 23.7; IR (thin film, cm^{-1}) 3411, 3055, 2914, 2235, 1571, 1460, 1374, 1168, 1068, 971, 818, 804; HRMS (ESI) m/z Calcd. for $\text{C}_{24}\text{H}_{19}\text{BrN}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 501.0243, Found 501.0251.

***N*-((4-Chlorophenyl)ethynyl)-4-methyl-*N*-(2-(2-methyl-1*H*-indol-3-yl)ethyl)benzenesulfonamide (**1s**)**



Purified by a flash column chromatography on alkaline silica gel with PE/EA (8:1) as an eluent to give the substrate **1s** (508.2 mg) as a light-yellow oil with a yield of 19%; ^1H NMR (600 MHz, CDCl_3) δ 7.77 (s, 1H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.28 (d, $J = 2.5$ Hz, 2H), 7.27 (d, $J = 2.5$ Hz, 2H), 7.25 (d, $J = 1.6$ Hz, 2H), 7.23 (d, $J = 1.9$ Hz, 1H), 7.15 – 7.11 (m, 1H), 7.08 (t, $J = 7.4$ Hz, 1H), 3.69 – 3.60 (m, 2H), 3.11 (t, $J = 7.7$ Hz, 2H), 2.43 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 144.7, 135.4, 134.9, 133.7, 132.5, 132.4, 129.8, 128.7, 128.4, 127.6, 121.6, 121.3, 119.6, 117.7, 110.4, 107.2, 83.7, 70.0, 52.0, 23.7, 21.8, 11.7; IR (thin film, cm^{-1}) 3410, 2922, 1625, 1462, 1362, 1167, 814, 707; HRMS (ESI) m/z Calcd. For $\text{C}_{26}\text{H}_{23}\text{ClN}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 485.1061, Found 485.1065.

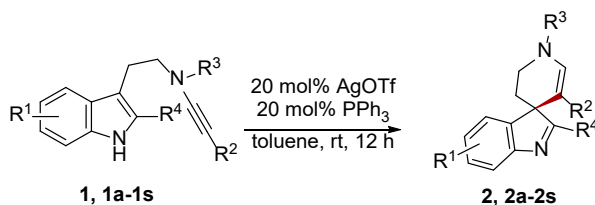
Part 4: Table S1. Screening of reaction conditions^a



entry	catalyst	ligand	solvent	yield (%)
1	AgBF ₄	PPh ₃	toluene	75
2	AgSbF ₆	PPh ₃	toluene	76
3	AgNTf ₂	PPh ₃	toluene	80
4	AgOTf	PPh ₃	toluene	81
5	AgOTf	PPh ₃	toluene	34 ^b
6	AgOTf	PPh ₃	toluene	45 ^c
7	AgOTf	PPh ₃	toluene	82 ^d
8	AgOTf	—	toluene	66
9	—	PPh ₃	toluene	0
10	AgOTf	PPh ₃	toluene	53 ^e
11	AgOTf	PPh ₃	THF	60
12	AgOTf	PPh ₃	DCM	66
13	AgOTf	PPh ₃	MeCN	53

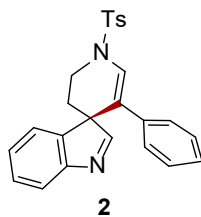
^aIsolated yields and the ORTEP of **2** is shown with 50% probability ellipsoids.; ^b5 mol% AgOTf and 5 mol% PPh₃ were used; ^c10 mol% AgOTf and 0 mol% PPh₃ were used; ^d30 mol% AgOTf and 30 mol% PPh₃ were used; ^e40 mol% PPh₃ were used.

Part 5: General procedures and characteristic data for products **2**, **2a-2s**



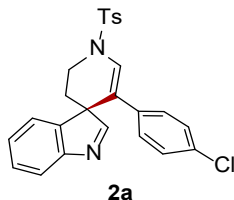
To a stirred solution of substrates **1**, **1a-1s** (1.0 mmol, 1.0 equiv.) in toluene (7 mL) was added a solution of AgOTf (51.4 mg, 0.2 mmol, 20 mol%) and PPh₃ (52.5 mg, 0.2 mmol, 20 mol%) in toluene (3 mL), which was stirred for 5-10 min before addition. The reaction mixture was stirred at room temperature. When TLC analysis showed that the reaction was finished, the solvent was concentrated *in vacuo* to give a residue, which was purified by a flash column chromatography on silica gel to afford products **2**, **2a-2s**.

5'-Phenyl-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (**2**)



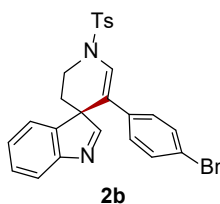
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2** (336.6 mg) as a yellow solid with a yield of 81%; Mp. 141.1-143.1 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.18 (s, 1H), 7.85 – 7.81 (m, 2H), 7.58 – 7.53 (m, 3H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.10 – 7.03 (m, 5H), 6.64 – 6.60 (m, 2H), 6.45 (dt, *J* = 7.3, 0.9 Hz, 1H), 3.89 – 3.82 (m, 1H), 3.41 – 3.33 (m, 1H), 2.48 (s, 3H), 2.18 – 2.10 (m, 1H), 1.39 – 1.32 (m, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 177.5, 154.7, 144.6, 142.9, 137.8, 133.0, 130.3, 128.4, 128.2, 127.2, 127.0, 126.2, 125.9, 125.5, 122.2, 121.2, 117.1, 57.6, 40.5, 28.0, 21.1; IR (thin film, cm⁻¹) 3426, 3070, 2922, 2875, 1638, 1595, 1556, 1443, 1361, 1169, 943; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₂N₂O₂SNa [M+Na]⁺: 437.1294, Found 437.1297.

5'-(4-Chlorophenyl)-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2a)



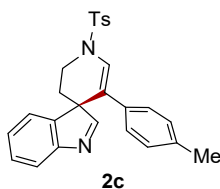
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2a** (383.4 mg) as a light-yellow solid with a yield of 85%; Mp. 169.3-171.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.20 (s, 1H), 7.85 – 7.82 (m, 2H), 7.55 (dd, *J* = 8.1, 2.4 Hz, 3H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.14 – 7.12 (m, 2H), 7.11 (s, 1H), 7.06 (td, *J* = 7.5, 1.1 Hz, 1H), 6.64 – 6.61 (m, 2H), 6.48 (d, *J* = 7.4 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.41 – 3.36 (m, 1H), 2.48 (s, 3H), 2.14 – 2.08 (m, 1H), 1.41 – 1.36 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.3, 154.7, 144.7, 142.6, 136.7, 133.1, 131.7, 130.3, 128.6, 128.2, 127.7, 127.2, 126.4, 126.2, 122.3, 121.3, 115.8, 57.5, 40.6, 28.0, 21.1; IR (thin film, cm⁻¹) 3436, 3064, 2923, 2854, 1630, 1594, 1489, 1354, 1172, 1088, 975; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁ClN₂O₂SNa [M+Na]⁺: 471.0904, Found 471.0923.

5'-(4-Bromophenyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2b)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2b** (434.2 mg) as a light-yellow solid with a yield of 88%; Mp. 183.1-185.0 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.20 (s, 1H), 7.85 – 7.82 (m, 2H), 7.57 – 7.54 (m, 3H), 7.32 (td, *J* = 7.7, 1.2 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.12 (d, *J* = 1.1 Hz, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.58 – 6.55 (m, 2H), 6.47 (d, *J* = 7.4 Hz, 1H), 3.85 – 3.80 (m, 1H), 3.42 – 3.34 (m, 1H), 2.48 (s, 3H), 2.13 – 2.08 (m, 1H), 1.41 – 1.36 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.3, 154.7, 144.7, 142.6, 137.0, 133.1, 131.1, 130.3, 128.6, 128.0, 127.3, 126.4, 126.2, 122.3, 121.3, 120.2, 115.8, 57.5, 40.6, 28.0, 21.1; IR (thin film, cm⁻¹) 3425, 3054, 2922, 1630, 1594, 1452, 1354, 1171, 1008, 945, 576; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁BrN₂O₂SNa [M+Na]⁺: 515.0399, Found 519.0390.

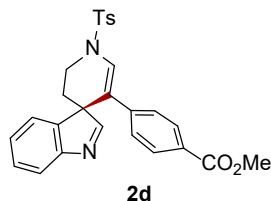
5'-(*p*-Tolyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2c)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2c** (382.2 mg) as a white solid with a yield of 89%; Mp. 174.3-176.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.16 (d, *J* = 1.6 Hz, 1H), 7.83 – 7.80 (m, 2H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.31 (td, *J* = 7.4, 1.3 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.86 (d, *J* = 7.9 Hz, 2H), 6.51 (d, *J* = 7.9 Hz, 2H), 6.43 (d, *J* = 7.4 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.39 – 3.31 (m, 1H), 2.48 (s, 3H), 2.15 – 2.09 (m, 4H), 1.37 – 1.32 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.6, 154.8, 144.6, 142.9, 136.4, 134.9, 133.0, 130.3, 128.8, 128.4, 127.2, 126.2, 125.8, 125.1, 122.3, 121.2, 117.3, 57.7, 40.5, 28.0, 21.1, 20.5; IR (thin film, cm⁻¹) 3428, 3065, 2921, 1630, 1595, 1552, 1450, 1363, 1170, 939, 818; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₄N₂O₂SNa

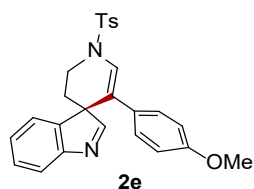
[M+Na]⁺: 451.1451, Found 451.1452.

Methyl 4-(1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridin]-5'-yl)benzoate (2d)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2d** (416.4 mg) as a white solid with a yield of 88%; Mp. 187.4–189.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.22 (s, 1H), 7.86 – 7.84 (m, 2H), 7.65 – 7.62 (m, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.25 (s, 1H), 7.06 (td, *J* = 7.5, 1.0 Hz, 1H), 6.76 – 6.74 (m, 2H), 6.49 (d, *J* = 7.4 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.45 – 3.39 (m, 1H), 2.48 (s, 3H), 2.15 – 2.09 (m, 1H), 1.44 – 1.40 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.3, 165.8, 154.7, 144.8, 142.7, 142.6, 133.1, 130.4, 129.1, 128.6, 127.9, 127.3, 127.0, 126.4, 125.9, 122.2, 121.3, 115.6, 57.4, 52.0, 40.6, 28.3, 21.1; IR (thin film, cm⁻¹) 3439, 2923, 2869, 1706, 1627, 1604, 1434, 1358, 1284, 1167, 1114, 979; HRMS (ESI) *m/z* Calcd. for C₂₇H₂₄N₂O₄SNa [M+Na]⁺: 495.1349, Found 495.1361.

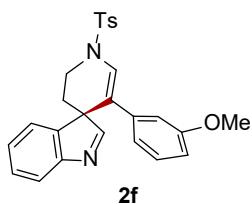
5'-(4-Methoxyphenyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2e)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2e** (325.2 mg) as a light-yellow solid with a yield of 73%; Mp. 61.1–63.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.16 (s, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.31 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.98 (s, 1H), 6.64 – 6.61 (m, 2H), 6.56 – 6.53 (m, 2H), 6.43 (d, *J* = 7.4 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.61 (s, 3H), 3.37 – 3.30 (m, 1H), 2.48 (s, 3H), 2.16 – 2.09 (m, 1H), 1.36 – 1.31 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.64, 158.36, 154.77, 144.55, 142.91, 132.99, 130.27, 130.09, 128.41, 127.22, 127.20, 126.20, 124.71, 122.25, 121.16, 117.11, 113.55, 57.79, 54.93, 40.49, 27.85, 21.10; IR

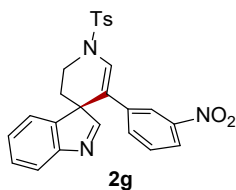
(thin film, cm^{-1}) 3418, 2923, 2853, 1631, 1607, 1642, 1511, 1362, 1245, 1168, 977, 943; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 445.1580, Found 445.1591.

5'-(3-Methoxyphenyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2f)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2f** (378.4 mg) as a white solid with a yield of 85%; Mp. 181.8-183.8 $^{\circ}\text{C}$; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.16 (s, 1H), 7.84 – 7.82 (m, 2H), 7.56 (d, $J = 7.9$ Hz, 3H), 7.33 (td, $J = 7.6, 1.2$ Hz, 1H), 7.11 (s, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 7.01 (t, $J = 8.0$ Hz, 1H), 6.66 (dd, $J = 8.3, 2.5$ Hz, 1H), 6.43 (d, $J = 7.4$ Hz, 1H), 6.32 – 6.29 (m, 1H), 6.00 (t, $J = 2.1$ Hz, 1H), 3.87 – 3.79 (m, 1H), 3.49 (s, 3H), 3.35 – 3.31 (m, 1H), 2.48 (s, 3H), 2.18 – 2.12 (m, 1H), 1.38 – 1.33 (m, 1H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 177.7, 158.8, 154.8, 144.7, 143.0, 139.1, 133.0, 130.3, 129.3, 128.5, 127.3, 126.3, 125.6, 122.3, 121.2, 118.2, 116.8, 112.4, 111.3, 57.6, 54.6, 40.5, 27.9, 21.1; IR (thin film, cm^{-1}) 3420, 3071, 2921, 1629, 1596, 1465, 1363, 1239, 1172, 981, 939; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 445.1580, Found 445.1600.

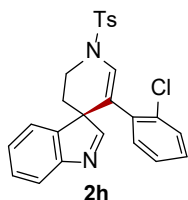
5'-(3-Nitrophenyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2g)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2g** (294.8 mg) as a white solid with a yield of 64%; Mp. 167.4-169.4 $^{\circ}\text{C}$; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.24 (s, 1H), 7.95 – 7.90 (m, 1H), 7.89 – 7.85 (m, 2H), 7.59 (d, $J = 7.7$ Hz, 1H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.38 (t, $J = 8.0$ Hz, 1H), 7.37 – 7.33 (m, 2H), 7.33 (s, 1H), 7.12 – 7.07 (m, 2H), 6.55 (d, $J = 7.4$ Hz, 1H), 3.88 – 3.83 (m, 1H), 3.46 – 3.40 (m, 1H), 2.48 (s, 3H), 2.19 – 2.13 (m, 1H), 1.50 – 1.46 (m, 1H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 177.2, 154.8, 147.5, 144.8, 142.3, 139.3, 133.1, 132.4, 130.3, 129.8, 128.8, 127.6, 127.3, 126.6, 122.3, 121.7, 121.4, 120.4, 114.4, 57.4,

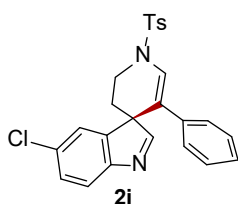
40.6, 28.0, 21.1; IR (thin film, cm^{-1}) 3420, 3065, 2923, 1647, 1450, 1525, 1349, 1090, 980, 944, 892; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{21}\text{N}_3\text{O}_4\text{SNa}$ $[\text{M}+\text{Na}]^+$: 482.1145, Found 482.1140.

5'-(2-Chlorophenyl)-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2h)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2h** (216.8 mg) as a white solid with a yield of 48%; Mp. 160.9-162.7 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.20 (s, 1H), 7.85 – 7.82 (m, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 7.6$ Hz, 1H), 7.31 (dd, $J = 8.1, 1.2$ Hz, 1H), 7.25 (td, $J = 7.6, 1.2$ Hz, 1H), 7.13 – 7.09 (m, 2H), 6.94 (td, $J = 7.5, 1.3$ Hz, 1H), 6.87 – 6.85 (m, 2H), 6.54 (dd, $J = 7.7, 1.7$ Hz, 1H), 3.89 – 3.84 (m, 1H), 3.61 – 3.56 (m, 1H), 2.49 (s, 3H), 2.06 – 2.00 (m, 1H), 1.59 – 1.54 (m, 1H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 175.76, 154.97, 144.59, 141.21, 135.29, 133.55, 132.62, 130.70, 130.23, 129.33, 129.28, 128.47, 128.14, 127.24, 126.26, 126.06, 122.92, 120.71, 113.71, 58.52, 40.78, 27.33, 21.12; IR (thin film, cm^{-1}) 3394, 3049, 2923, 2853, 1657, 1594, 1554, 1469, 1360, 1170, 934; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{21}\text{ClN}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 471.0904, Found 471.0901.

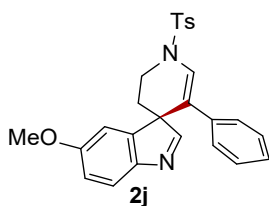
5-Chloro-5'-phenyl-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2i)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2i** (408.0 mg) as a white solid with a yield of 91%; Mp. 208.3-209.7 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.24 (s, 1H), 7.83 (d, $J = 8.1$ Hz, 2H), 7.56 (dd, $J = 8.3, 2.7$ Hz, 3H), 7.38 (dd, $J = 8.2, 2.1$ Hz, 1H), 7.13 – 7.07 (m, 4H), 6.64 – 6.61 (m, 2H), 6.31 (d, $J = 2.1$ Hz, 1H), 3.86 (dt, $J = 12.5, 4.5$ Hz, 1H), 3.27 – 3.21 (m,

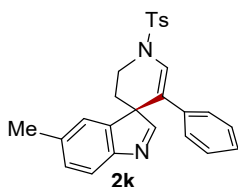
1H), 2.46 (s, 3H), 2.28 – 2.22 (m, 1H), 1.41 – 1.36 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 178.44, 153.47, 145.05, 144.85, 137.53, 132.52, 131.00, 130.38, 128.61, 128.36, 127.24, 127.20, 125.85, 125.80, 122.55, 122.47, 116.40, 58.05, 40.29, 27.55, 21.26; IR (thin film, cm⁻¹) 3441, 3065, 2928, 2868, 1632, 1595, 1448, 1360, 1332, 1168, 942; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₁ClN₂O₂SNa [M+Na]⁺: 471.0904, Found 471.0923.

5-Methoxy-5'-phenyl-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2j)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2j** (392.0 mg) as a white solid with a yield of 88%; Mp. 167.5-169.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.99 (s, 1H), 7.83 – 7.80 (m, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.10 – 7.06 (m, 4H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.65 – 6.63 (m, 2H), 5.98 (d, *J* = 2.5 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.58 (s, 3H), 3.33 – 3.27 (m, 1H), 2.44 (s, 3H), 2.22 – 2.16 (m, 1H), 1.36 – 1.32 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 175.3, 158.2, 148.2, 144.8, 144.7, 137.8, 132.7, 130.3, 128.3, 127.2, 127.1, 125.8, 125.5, 121.6, 117.2, 113.2, 108.6, 57.6, 55.4, 40.0, 28.0, 21.1; IR (thin film, cm⁻¹) 3423, 3065, 2920, 2878, 1632, 1591, 1466, 1364, 1171, 942, 775; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₄N₂O₃SNa [M+Na]⁺: 467.1400, Found 467.1410.

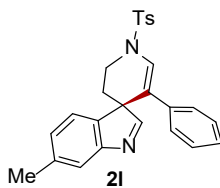
5-Methyl-5'-phenyl-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2k)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2k** (340.6 mg) as a white solid with a yield of 80%; Mp. 179.2-180.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.06 (d, *J* = 2.1 Hz, 1H), 7.83 (dd, *J* = 8.3, 2.0 Hz, 2H), 7.57 (dd, *J* = 8.4, 2.5 Hz, 2H), 7.44 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.15 – 7.12

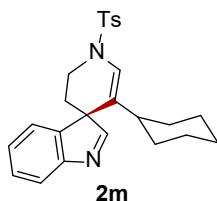
(m, 1H), 7.10 (s, 1H), 7.09 – 7.05 (m, 3H), 6.60 (dt, $J = 7.5, 1.7$ Hz, 2H), 6.07 (s, 1H), 3.91 – 3.86 (m, 1H), 3.22 (td, $J = 12.0, 3.3$ Hz, 1H), 2.46 (d, $J = 2.4$ Hz, 3H), 2.30 – 2.24 (m, 1H), 2.11 (d, $J = 2.1$ Hz, 3H), 1.24 (dt, $J = 14.6, 3.9$ Hz, 1H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 176.7, 152.5, 144.6, 143.3, 137.8, 135.6, 132.6, 130.4, 129.0, 128.3, 127.4, 127.1, 125.6, 125.1, 122.9, 120.9, 117.3, 57.2, 40.1, 27.8, 21.1, 20.9; IR (thin film, cm^{-1}) 3341, 3033, 2928, 2871, 1632, 1594, 1553, 1466, 1361, 1168, 943; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$: 451.1451, Found 451.1460.

6-Methyl-5'-phenyl-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2l)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2l** (361.6 mg) as a yellow solid with a yield of 84%; Mp. 138.4–140.4 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 8.13 (s, 1H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 7.36 (s, 1H), 7.09 – 7.05 (m, 4H), 6.85 (d, $J = 7.5$ Hz, 1H), 6.64 – 6.61 (m, 2H), 6.28 (d, $J = 7.5$ Hz, 1H), 3.34 – 3.29 (m, 1H), 2.48 (s, 3H), 2.31 (s, 3H), 2.16 – 2.10 (m, 1H), 1.32 – 1.27 (m, 1H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 177.72, 155.01, 144.60, 140.02, 138.02, 137.87, 132.95, 130.28, 128.21, 127.23, 127.03, 126.81, 125.84, 125.34, 121.84, 121.81, 117.41, 57.27, 40.48, 28.10, 21.11, 20.92; IR (thin film, cm^{-1}) 3427, 3053, 2921, 1633, 1596, 1443, 1363, 1170, 1023, 945, 814; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 429.1631, Found 429.1638.

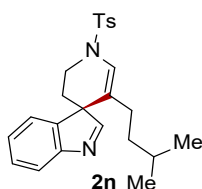
5'-Cyclohexyl-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2m)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2m** (370.0 mg) as a light-yellow solid with a yield of 88%; Mp. 169.7–171.2 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 8.12 (s, 1H), 7.77 – 7.74 (m, 2H), 7.57 – 7.53 (m, 3H), 7.32 (td, $J = 7.6, 1.2$ Hz, 1H), 7.07 (td, $J = 7.4, 1.0$ Hz, 1H), 6.74

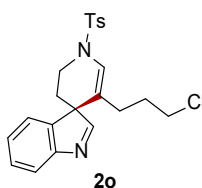
(s, 1H), 6.40 (d, $J = 7.4$ Hz, 1H), 3.69 – 3.64 (m, 1H), 3.30 – 3.25 (m, 1H), 2.48 (s, 3H), 1.90 – 1.84 (m, 1H), 1.60 – 1.54 (m, 1H), 1.54 – 1.50 (m, 1H), 1.47 – 1.40 (m, 2H), 1.29 – 1.22 (m, 1H), 1.06 – 0.96 (m, 4H), 0.91 – 0.82 (m, 1H), 0.79 – 0.71 (m, 1H), 0.71 – 0.62 (m, 1H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 177.0, 155.2, 144.3, 142.5, 133.0, 130.1, 128.3, 127.1, 126.0, 123.6, 123.1, 122.3, 120.9, 58.5, 40.8, 34.2, 33.7, 27.1, 26.3, 25.2, 21.1; IR (thin film, cm^{-1}) 3374, 2924, 2851, 1650, 1595, 1550, 1446, 1342, 1284, 1161, 942; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 421.1944, Found 421.1951.

5'-Isopentyl-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2n)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2n** (347.6 mg) as a light-yellow solid with a yield of 85%; Mp. 111.0-113.0 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 8.10 (s, 1H), 7.77 – 7.75 (m, 2H), 7.55 – 7.53 (m, 3H), 7.32 (td, $J = 7.6, 1.2$ Hz, 1H), 7.08 (td, $J = 7.5, 1.1$ Hz, 1H), 6.74 (d, $J = 1.2$ Hz, 1H), 6.50 – 6.47 (m, 1H), 3.69 – 3.64 (m, 1H), 3.40 – 3.35 (m, 1H), 2.47 (s, 3H), 1.90 – 1.85 (m, 1H), 1.49 – 1.40 (m, 2H), 1.39 – 1.33 (m, 1H), 1.09 (hept, $J = 6.6$ Hz, 1H), 0.75 – 0.69 (m, 1H), 0.69 – 0.64 (m, 1H), 0.63 (d, $J = 6.6$ Hz, 3H), 0.48 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 177.3, 155.1, 144.3, 142.2, 133.2, 130.1, 128.3, 127.1, 126.0, 123.2, 122.4, 120.9, 117.2, 58.0, 40.8, 36.9, 28.4, 27.2, 26.1, 21.9, 21.1; IR (thin film, cm^{-1}) 3423, 2956, 2928, 2867, 1653, 1596, 1545, 1457, 1344, 1328, 1156, 955; HRMS (ESI) m/z Calcd. for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 409.1944, Found 409.1953.

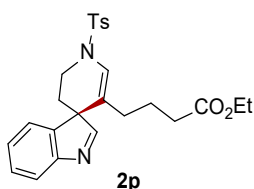
5'-(3-Chloropropyl)-1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2o)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent

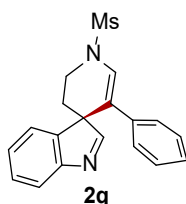
to give the substrate **2o** (349.0 mg) as a light-yellow oil with a yield of 84%; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.13 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 3H), 7.33 (td, *J* = 7.6, 1.2 Hz, 1H), 7.12 – 7.08 (m, 1H), 6.80 (s, 1H), 6.52 (d, *J* = 7.4 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.41 – 3.36 (m, 1H), 3.32 – 3.24 (m, 2H), 2.48 (s, 3H), 1.92 – 1.87 (m, 1H), 1.65 – 1.53 (m, 2H), 1.42 – 1.36 (m, 1H), 1.33 – 1.14 (m, 2H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.1, 155.1, 144.3, 142.1, 133.2, 130.1, 128.4, 127.1, 126.2, 124.0, 122.3, 121.0, 115.4, 58.0, 44.1, 40.8, 30.8, 27.9, 27.2, 21.1; IR (thin film, cm⁻¹) 3411, 2924, 1653, 1595, 1456, 1352, 1166, 1090, 940, 814, 745; HRMS (ESI) *m/z* Calcd. for C₂₂H₂₃ClN₂O₂SNa [M+Na]⁺: 437.1061, Found 437.1043.

Ethyl 4-(1'-tosyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridin]-5'-yl)butanoate (2p)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2p** (401.4 mg) as a light-yellow solid with a yield of 89%; Mp. 76.0-77.7 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.11 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 3H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.76 (s, 1H), 6.46 (d, *J* = 7.4 Hz, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.70 – 3.64 (m, 1H), 3.37 – 3.33 (m, 1H), 2.48 (s, 3H), 2.04 – 1.86 (m, 3H), 1.52 – 1.41 (m, 2H), 1.38 – 1.33 (m, 1H), 1.18 – 1.10 (m, 4H), 1.06 – 0.98 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.1, 172.3, 155.0, 144.3, 142.1, 133.1, 130.1, 128.3, 127.1, 126.0, 123.8, 122.2, 120.9, 116.1, 59.6, 57.9, 40.7, 32.2, 29.9, 27.2, 23.2, 21.1, 14.0; IR (thin film, cm⁻¹) 3430, 3039, 2937, 1730, 1450, 1360, 1231, 1170, 1021, 933, 759; HRMS (ESI) *m/z* Calcd. for C₂₅H₂₈N₂O₄SNa [M+Na]⁺: 475.1662, Found 475.1669.

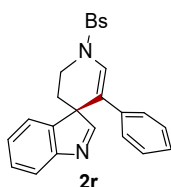
1'-Mesyl-5'-phenyl-2',3'-dihydro-1'*H*-spiro[indole-3,4'-pyridine] (2q)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent

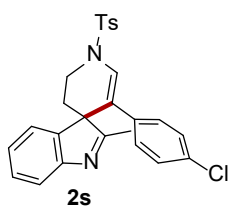
to give the substrate **2q** (251.4 mg) as a yellow solid with a yield of 74%; Mp. 141.5-143.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.36 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.27 (td, *J* = 7.4, 1.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.00 (s, 1H), 6.71 – 6.67 (m, 2H), 3.97 – 3.91 (m, 1H), 3.78 – 3.73 (m, 1H), 3.29 (s, 3H), 2.24 – 2.18 (m, 1H), 1.68 – 1.62 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.9, 154.9, 143.3, 138.2, 128.4, 128.1, 126.8, 126.5, 126.3, 125.9, 123.1, 121.1, 114.5, 57.9, 40.4, 37.7, 28.8; IR (thin film, cm⁻¹) 3428, 3073, 2925, 2861, 1634, 1544, 1440, 1349, 1241, 1154, 968, 793; HRMS (ESI) *m/z* Calcd. for C₁₉H₁₉N₂O₂S [M+H]⁺: 339.1162, Found 339.1157.

1'-Brosyl-5'-phenyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2r)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the substrate **2r** (454.0 mg) as a light-yellow solid with a yield of 95%; Mp. 185.5-187.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.21 (s, 1H), 8.00 – 7.95 (m, 2H), 7.90 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.33 (td, *J* = 7.7, 1.2 Hz, 1H), 7.11 – 7.04 (m, 5H), 6.66 – 6.62 (m, 2H), 6.56 (d, *J* = 7.4 Hz, 1H), 3.90 – 3.85 (m, 1H), 3.45 – 3.39 (m, 1H), 2.16 – 2.09 (m, 1H), 1.44 – 1.39 (m, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 177.4, 154.8, 142.7, 137.6, 135.2, 133.0, 129.1, 128.5, 128.2, 128.0, 127.1, 126.2, 126.0, 125.2, 122.2, 121.2, 117.7, 57.6, 40.7, 28.0; IR (thin film, cm⁻¹) 3425, 3051, 2927, 1629, 1572, 1462, 1388, 1359, 1293, 1170, 882; HRMS (ESI) *m/z* Calcd. for C₂₄H₂₀BrN₂O₂S [M+H]⁺: 479.0423, Found 479.0407.

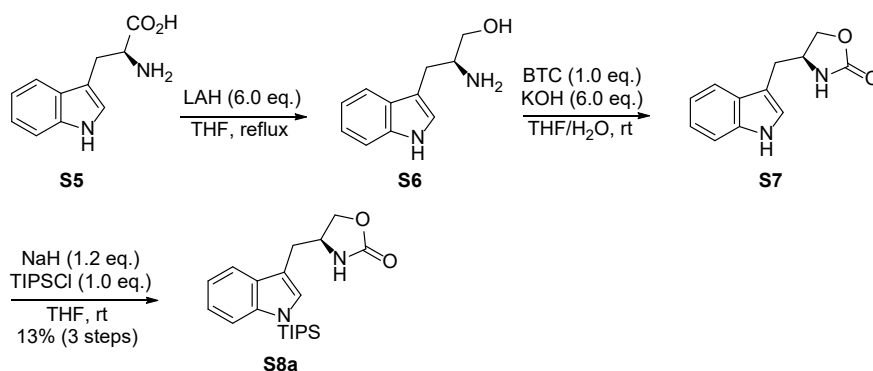
5'-(4-Chlorophenyl)-2-methyl-1'-tosyl-2',3'-dihydro-1'H-spiro[indole-3,4'-pyridine] (2s)



Purified by a flash column chromatography on silica gel with PE/EA (3:1) as an eluent to give the substrate **2s** (206.8 mg) as a light-yellow solid with a yield of 63%; Mp. 165.5-166.6 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.86 – 7.80 (m, 2H), 7.56 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.19 (d, *J* = 1.7 Hz, 1H), 7.17 – 7.13 (m, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.54 – 6.48 (m, 2H), 6.29 (d, *J* = 7.4 Hz, 1H), 3.92 (dt, *J* = 12.6, 3.8 Hz, 1H), 3.24 (td, *J* = 12.7, 3.6 Hz, 1H), 2.48 (s, 3H), 2.08 (td, *J* = 13.1, 12.7, 4.2 Hz, 1H), 1.78 (d, *J* = 1.8 Hz, 3H), 1.24 (q, *J* = 3.2 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 184.8, 154.1, 144.8, 144.1, 136.5, 132.6, 131.6, 131.4, 130.3, 128.6, 128.4, 127.3, 127.0, 126.4, 125.2, 122.0, 120.3, 116.2, 57.8, 29.3, 21.1, 16.1; IR (thin film, cm⁻¹) 3434, 2922, 1629, 1463, 1168, 1093, 833, 573; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₃ClN₂O₂SNa [M+Na]⁺:485.1061, Found 485.1067.

Part 6: General procedures and characteristic data for oxazolidinones **S8a-S8d**, **S8I**

Procedure for the synthesis of (*S*)-4-((1-(triisopropylsilyl)-1*H*-indol-3-yl)methyl)oxazolidin-2-one (**S8a**)



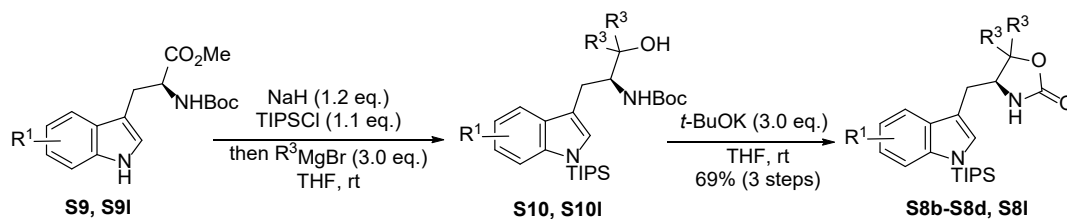
LiAlH₄ (5.575 g, 147 mmol, 6.0 equiv.) and *L*-tryptophan **S5** (5.000 g, 24.5 mmol, 1.0 equiv.) were suspended in THF (100 mL) under reflux until the reaction was finished. The mixture was cooled to 0 °C, followed by the treatment with water (5.6 mL), 10% NaOH aqueous solution (5.6 mL) and water (5.6 mL), extracted with Et₂O (100 mL) thrice. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtration and evaporation to afford a residue of crude *L*-tryptophanol **S6**.

The above residue was dissolved in THF (10 mL) and a solution of NaOH (28.242 g,

147 mmol, 6.0 equiv.) in water (100 mL) was added. At 0 °C, a solution of BTC (7.265 g, 24.5 mmol, 1.0 equiv.) in THF (25 mL) was slowly added to the above mixture. The reaction was then allowed to warm to room temperature and stirred until the reaction was finished. The mixture was diluted with water (100 mL), extracted with DCM (200 mL) thrice, the combined organic layers were washed with brine (300 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

The above residue was dissolved in THF (100 mL) and cooled in an ice bath. NaH (1.175 g, 29.4 mmol, 1.2 equiv., 60% dispersion in mineral oil) was added portionwise and the mixture was stirred for 1 hour at room temperature. Then TIPSCl (4.720 g, 24.5 mmol, 1.0 equiv.) was added to the mixture dropwise in an ice bath and allowed to warm to room temperature gradually. When TLC showed that the reaction was finished, the mixture was quenched with a saturated aqueous solution of NH₄Cl (20 mL) in an ice bath and extracted with ethyl acetate (400 mL) twice. The combined organic layers were washed with brine (600 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the oxazolidinone **S8a** (1.185 g) as a light-yellow solid with a yield of 13%; Mp. 123.0-124.7 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.80 (s, 1H), 7.56 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.28 (s, 1H), 7.12 – 7.09 (m, 1H), 7.07 – 7.04 (m, 1H), 4.24 (t, *J* = 8.3 Hz, 1H), 4.15 – 4.10 (m, 1H), 3.98 (dd, *J* = 8.3, 5.4 Hz, 1H), 2.97 (dd, *J* = 14.4, 4.6 Hz, 1H), 2.85 (dd, *J* = 14.5, 7.6 Hz, 1H), 1.73 (p, *J* = 7.5 Hz, 3H), 1.07 (dd, *J* = 7.5, 3.8 Hz, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 158.7, 140.7, 130.9, 130.0, 121.5, 119.3, 118.4, 113.7, 112.0, 68.3, 51.5, 30.0, 17.9, 12.0; IR (thin film, cm⁻¹) 3226, 3133, 2947, 2866, 1734, 1608, 1452, 1409, 1247, 1143, 960, 883; HRMS (ESI) *m/z* Calcd. for C₂₁H₃₂N₂O₂SiNa [M+Na]⁺: 395.2125, Found 395.2142.

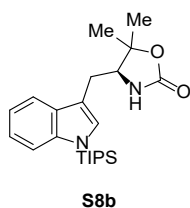
General procedures for the syntheses of oxazolidinones S8b-S8d, S8l



Methyl *L*-tryptophanate derivatives **S9**, **S9I** (10.0 mmol, 1.0 equiv.) were dissolved in THF (40 mL) and cooled in an ice bath. NaH (480.0 mg, 12.0 mmol, 1.2 equiv., 60% dispersion in mineral oil) was added portionwise and the mixture was stirred for 1 hour at room temperature. Then TIPSCl (2.121 g, 11.0 mmol, 1.1 equiv.) was added to the mixture dropwise in an ice bath and allowed to warm to room temperature gradually. When the reaction was finished, the solution was cooled with an ice-bath and the Grignard reagent (40.0 mmol, 4.0 equiv.) was added under nitrogen, then the solution was allowed to warm to room temperature. When the reaction was finished, the mixture was quenched with 2 M HCl (20 mL) in an ice bath and extracted with ethyl acetate (40 mL) twice. The combined organic layers were washed with brine (60 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

At 0 °C, to a stirred solution of the residue in THF (40 mL) was added *t*-BuOK (3.366 g, 30.0 mmol, 3.0 equiv.) in one portion, then the mixture was allowed to warm to room temperature. When the reaction was finished, the mixture was quenched with 2 M HCl (20 mL) in an ice bath and extracted with ethyl acetate (40 mL) twice. The combined organic layers were washed with brine (40 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel to afford oxazolidinones **S8b-S8d**, **S8I**.

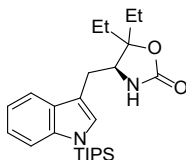
(*S*)-5,5-Dimethyl-4-((1-(triisopropylsilyl)-1*H*-indol-3-yl)methyl)oxazolidin-2-one (S8b)



Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent

to give the substrate **S8b** (2.764 g) as a white solid with a yield of 69%; Mp. 155.6-156.6 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.59 – 7.57 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.13 – 7.09 (m, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 3.95 (t, *J* = 7.2 Hz, 1H), 2.97 (dd, *J* = 14.7, 7.8 Hz, 1H), 2.87 (dd, *J* = 14.7, 6.5 Hz, 1H), 1.73 (hept, *J* = 7.5 Hz, 3H), 1.29 (s, 3H), 1.15 (s, 3H), 1.08 (dd, *J* = 7.5, 2.4 Hz, 18H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 157.5, 140.7, 130.4, 129.4, 121.5, 119.3, 118.5, 113.7, 113.1, 82.2, 60.5, 27.4, 26.0, 21.3, 17.9, 12.0; IR (thin film, cm⁻¹) 3435, 2925, 2866, 1748, 1631, 1451, 1142, 993, 884, 751, 516; HRMS (ESI) *m/z* Calcd. for C₂₃H₃₆N₂O₂SiNa [M+Na]⁺: 423.2438, Found 423.2441.

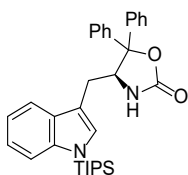
(S)-5,5-Diethyl-4-((1-(triisopropylsilyl)-1*H*-indol-3-yl)methyl)oxazolidin-2-one
(S8c)



S8c

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the substrate **S8c** (2.786 g) as a white solid with a yield of 65%; Mp. 177.1-177.4 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.55 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.54 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.13 – 7.09 (m, 1H), 7.08 – 7.05 (m, 1H), 3.99 (t, *J* = 6.9 Hz, 1H), 3.02 (dd, *J* = 14.7, 7.1 Hz, 1H), 2.84 (dd, *J* = 14.8, 6.7 Hz, 1H), 1.86 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.73 (hept, *J* = 7.5 Hz, 3H), 1.62 (dq, *J* = 14.5, 7.4 Hz, 1H), 1.57 (dq, *J* = 14.8, 7.3 Hz, 1H), 1.42 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.08 (t, *J* = 7.6 Hz, 18H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.68 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 157.4, 140.7, 130.5, 129.6, 121.5, 119.3, 118.4, 113.8, 113.3, 85.9, 58.1, 28.7, 26.2, 24.5, 17.9, 12.0, 7.6, 7.3; IR (thin film, cm⁻¹) 3434, 2924, 1744, 1451, 1385, 1144, 1002, 748, 655, 521; HRMS (ESI) *m/z* Calcd. for C₂₅H₄₀N₂O₂SiNa [M+Na]⁺: 451.2751, Found 451.2755.

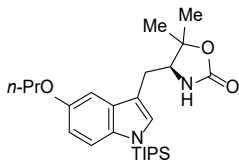
(S)-5,5-Diphenyl-4-((1-(triisopropylsilyl)-1*H*-indol-3-yl)methyl)oxazolidin-2-one
(S8d)



S8d

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the substrate **S8d** (2.834 g) as a white solid with a yield of 54%; Mp. 174.8-175.2 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 7.97 (s, 1H), 7.56 – 7.53 (m, 2H), 7.46 (d, J = 8.3 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.39 – 7.30 (m, 7H), 7.27 (t, J = 7.2 Hz, 1H), 7.11 – 7.07 (m, 1H), 7.02 (t, J = 7.4 Hz, 1H), 7.00 (s, 1H), 4.84 (dd, J = 8.3, 5.1 Hz, 1H), 2.67 (dd, J = 14.8, 4.9 Hz, 1H), 2.54 – 2.50 (m, 1H), 1.69 (hept, J = 7.5 Hz, 3H), 1.07 (t, J = 8.2 Hz, 18H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 156.7, 143.7, 140.6, 139.7, 130.8, 129.7, 128.4, 128.1, 128.0, 127.6, 126.3, 125.8, 121.3, 119.2, 118.3, 113.6, 112.4, 88.1, 59.9, 28.7, 18.0, 12.0; IR (thin film, cm^{-1}) 3436, 2948, 1754, 1450, 1296, 1145, 1016, 736, 698, 518; HRMS (ESI) m/z Calcd. for $\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$: 547.2751, Found 547.2756.

(S)-5,5-Dimethyl-4-((5-propoxy-1-(triisopropylsilyl)-1H-indol-3-yl)methyl)oxazolidin-2-one (S8I)

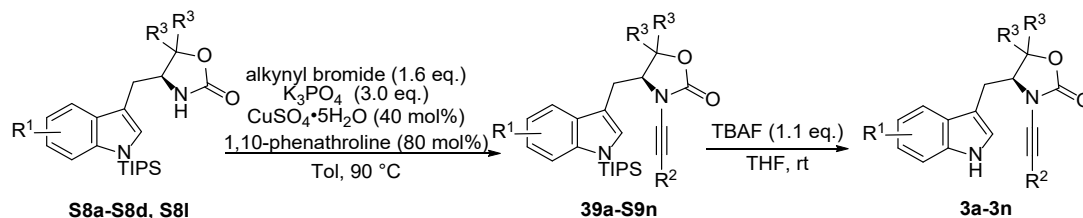


S8I

Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the substrate **S8I** (2.032 g) as a light-yellow oil with a yield of 44%; ^1H NMR (600 MHz, DMSO- d_6) δ 7.54 (s, 1H), 7.35 (d, J = 8.9 Hz, 1H), 7.20 (s, 1H), 7.05 (d, J = 2.6 Hz, 1H), 6.74 (dd, J = 8.9, 2.5 Hz, 1H), 3.98 – 3.90 (m, 3H), 2.92 (dd, J = 14.8, 8.0 Hz, 1H), 2.83 (dd, J = 14.6, 6.4 Hz, 1H), 1.77 – 1.71 (m, 2H), 1.71 – 1.65 (m, 3H), 1.29 (s, 3H), 1.14 (s, 3H), 1.06 (dd, J = 7.6, 2.1 Hz, 18H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 157.5, 152.9, 135.5, 131.1, 130.1, 114.2, 113.0, 111.4, 101.5, 82.2, 69.3, 60.3, 27.4, 26.0, 22.3, 21.3, 17.9, 11.9, 10.6; IR (thin film, cm^{-1}) 3435,

2924, 1749, 1631, 1467, 1385, 1210, 1018, 883, 652, 581; HRMS (ESI) m/z Calcd. for $C_{26}H_{42}N_2O_3SiNa$ $[M+Na]^+$: 481.2857, Found 481.2859.

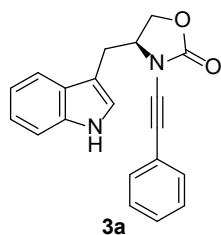
Part 7: General procedures and characteristic data for substrates 3a-3n



To a stirred solution of a tryptamine derivatives **S8a-S8d** and **S8l** (5.0 mmol, 1.0 equiv.) and corresponding alkynyl bromide^[S1] (8.0 mmol, 1.6 equiv.) in toluene (40 mL) were added $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (499.3 mg, 2.0 mmol, 40 mol%), 1,10-phenanthroline (720.8 mg, 4.0 mmol, 80 mol%) and K_3PO_4 (3.184 g, 15.0 mmol, 3.0 equiv.) in sequence. The mixture was heated to 90 °C. After finished, the reaction was filtrated through a Celite pad, washed with ethyl acetate and concentrated *in vacuo*. The residue was used directly for the next step without further purification.

At 0 °C, to a stirred solution of the residue in THF (40 mL) was added a solution of TBAF (5.5 mL, 5.5 mmol, 1.1 equiv.) in THF. The mixture was allowed to warm to room temperature. When the reaction was finished, the mixture was concentrated *in vacuo*. The residue was purified by a flash column chromatography on alkaline silica gel to afford substrates **3a-3m**.

(S)-4-((1H-Indol-3-yl)methyl)-3-(phenylethynyl)oxazolidin-2-one (**3a**)

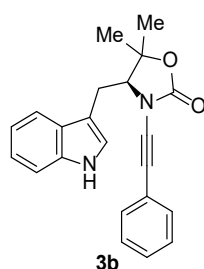


Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3a** (628.8 mg) as a light-yellow oil with a yield of 40%; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 11.02 (s, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.44 – 7.35 (m, 6H), 7.29 (d, $J = 2.4$ Hz, 1H), 7.12 – 7.09 (m, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 4.58 – 4.52 (m, 1H), 4.50 (t, $J = 8.4$ Hz, 1H), 4.20 (dd, $J = 8.3, 5.3$ Hz, 1H), 3.29 (dd, $J = 14.8, 4.1$ Hz, 1H), 3.17 (dd, $J = 14.7, 6.9$ Hz, 1H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 155.3,

136.2, 131.0, 128.7, 128.2, 127.5, 124.3, 122.0, 121.2, 118.7, 118.1, 111.5, 107.1, 79.6, 71.8, 68.2, 57.4, 27.0; IR (thin film, cm^{-1}) 3378, 3055, 2924, 2254, 1757, 1653, 1456, 1412, 1208, 1091, 1012, 743; HRMS (ESI) m/z Calcd. for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 317.1285, Found 317.1290; IR (thin film, cm^{-1}) 3412, 2923, 2254, 1752, 1631, 1410, 1208, 1090, 743, 423; HRMS (ESI) m/z Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 339.1104, Found 339.1117.

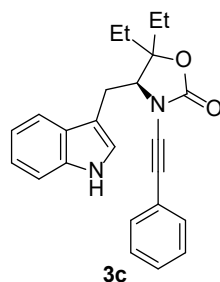
(S)-4-((1H-Indol-3-yl)methyl)-5,5-dimethyl-3-(phenylethynyl)oxazolidin-2-one

(3b)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3b** (819.2 mg) as a white solid with a yield of 48%; Mp. 152.7-153.5 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.99 (d, $J = 2.4$ Hz, 1H), 7.64 (d, $J = 7.9$ Hz, 1H), 7.37 (d, $J = 8.1$ Hz, 1H), 7.34 (d, $J = 2.4$ Hz, 1H), 7.32 – 7.28 (m, 3H), 7.17 – 7.13 (m, 2H), 7.12 – 7.09 (m, 1H), 7.04 – 7.01 (m, 1H), 4.43 (dd, $J = 7.9, 6.4$ Hz, 1H), 3.27 (dd, $J = 14.9, 6.4$ Hz, 1H), 3.19 (dd, $J = 14.9, 7.9$ Hz, 1H), 1.42 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 154.3, 136.2, 130.7, 128.5, 127.9, 126.9, 124.2, 122.1, 121.1, 118.6, 118.4, 111.6, 108.4, 84.0, 80.2, 71.4, 65.3, 27.1, 24.4, 21.4; IR (thin film, cm^{-1}) 3331, 2248, 1743, 1408, 1273, 1090, 742, 693, 618, 423; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 367.1417, Found 367.1436.

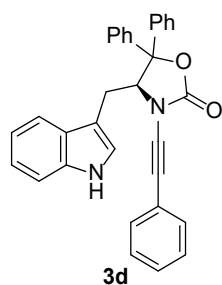
(S)-4-((1H-Indol-3-yl)methyl)-5,5-diethyl-3-(phenylethynyl)oxazolidin-2-one (3c)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3c** (1.042 g) as a white solid with a yield of 56%; Mp. 95.2-96.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.98 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.31 – 7.26 (m, 3H), 7.12 – 7.08 (m, 3H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.46 (t, *J* = 7.0 Hz, 1H), 3.30 – 3.22 (m, 2H), 1.95 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.78 – 1.69 (m, 2H), 1.51 (dq, *J* = 14.6, 7.3 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.77 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.4, 136.2, 130.7, 128.5, 127.9, 127.0, 124.2, 122.0, 121.1, 118.6, 118.2, 111.6, 108.7, 87.7, 80.1, 71.5, 63.4, 28.5, 24.6, 24.3, 7.6, 7.1; IR (thin film, cm⁻¹) 3407, 2974, 2245, 1753, 1414, 1236, 1091, 958, 748, 428; HRMS (ESI) *m/z* Calcd. for C₂₄H₂₄N₂O₂Na [M+Na]⁺: 395.1730, Found 395.1736.

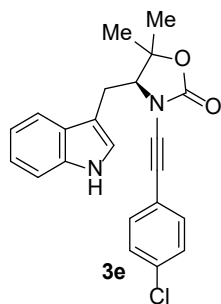
(S)-4-((1*H*-Indol-3-yl)methyl)-5,5-diphenyl-3-(phenylethynyl)oxazolidin-2-one

(3d)



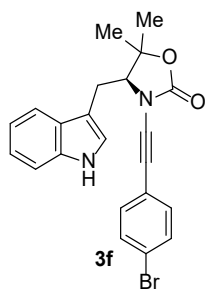
Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3d** (1.164 g) as a white solid with a yield of 50%; Mp. 169.5-170.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.91 (d, *J* = 2.6 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.41 (m, 4H), 7.40 – 7.30 (m, 3H), 7.24 – 7.21 (m, 1H), 7.21 – 7.16 (m, 2H), 7.11 – 7.06 (m, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 6.74 (dd, *J* = 6.7, 2.0 Hz, 2H), 5.42 (t, *J* = 6.8 Hz, 1H), 2.89 (d, *J* = 6.8 Hz, 2H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 153.6, 142.2, 138.0, 136.2, 130.7, 128.9, 128.7, 128.5, 128.2, 128.1, 127.9, 127.4, 125.9, 125.5, 124.9, 121.6, 120.9, 118.5, 118.4, 111.4, 107.8, 89.0, 79.5, 70.7, 65.4, 27.2; IR (thin film, cm⁻¹) 3424, 2923, 1748, 1629, 1461, 1385, 1120, 601; HRMS (ESI) *m/z* Calcd. for C₃₂H₂₅N₂O₂ [M+H]⁺: 469.1911, Found 469.1912.

(S)-4-((1*H*-Indol-3-yl)methyl)-3-((4-chlorophenyl)ethynyl)-5,5-dimethyloxazolidin-2-one (3e)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3e** (1.130 g) as a white solid with a yield of 60%; Mp. 145.2-145.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.97 (s, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.35 (m, 1H), 7.35 – 7.32 (m, 3H), 7.12 – 7.09 (m, 1H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 1H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.25 (dd, *J* = 14.5, 6.8 Hz, 1H), 3.18 (dd, *J* = 14.9, 7.5 Hz, 1H), 1.42 (s, 3H), 1.30 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.2, 136.2, 132.4, 132.3, 128.6, 127.0, 124.2, 121.1, 121.0, 118.6, 118.4, 111.6, 108.5, 84.1, 81.3, 70.4, 65.4, 27.0, 24.5, 21.4; IR (thin film, cm⁻¹) 3371, 2924, 1744, 1410, 1274, 1082, 832, 744, 527, 425; HRMS (ESI) *m/z* Calcd. for C₂₂H₁₉ClN₂O₂Na [M+Na]⁺: 401.1027, Found 401.1044.

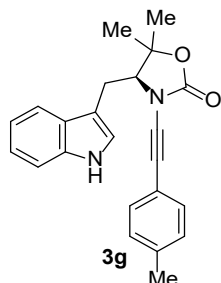
(S)-4-((1H-Indol-3-yl)methyl)-3-((4-bromophenyl)ethynyl)-5,5-dimethyloxazolidin-2-one (3f)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3f** (895.3 mg) as a white solid with a yield of 42%; Mp. 152.1-152.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.96 (d, *J* = 2.5 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.36 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.33 (d, *J* = 2.4 Hz, 1H), 7.12 – 7.09 (m, 1H), 7.04 – 7.00 (m, 1H), 6.99 (dd, *J* = 8.4, 1.6 Hz, 2H), 4.43 (t, *J* = 7.2 Hz, 1H), 3.25 (dd, *J* = 15.0, 6.9 Hz, 1H), 3.18 (dd, *J* = 14.9, 7.5 Hz, 1H), 1.43 (s, 3H), 1.30 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.2, 136.2, 132.4, 131.5, 127.0, 124.2, 121.4, 121.1, 121.0, 118.6, 118.4, 111.6, 108.5, 84.1, 81.5, 70.5, 65.3, 27.0, 24.5,

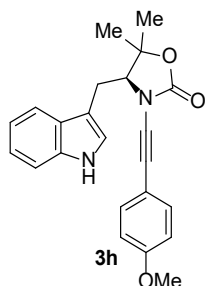
21.4; IR (thin film, cm^{-1}) 3370, 2924, 1741, 1408, 1274, 1087, 830, 743, 660, 527; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{19}\text{BrN}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 445.0522, Found 447.0526.

(S)-4-((1H-Indol-3-yl)methyl)-5,5-dimethyl-3-(p-tolylethynyl)oxazolidin-2-one (3g)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3g** (996.1 mg) as a white solid with a yield of 56%; Mp. 168.7-169.3 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.98 (s, 1H), 7.63 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 2.5$ Hz, 1H), 7.13 – 7.08 (m, 3H), 7.06 (dd, $J = 8.1, 1.8$ Hz, 2H), 7.02 (t, $J = 7.5$ Hz, 1H), 4.43 – 4.39 (m, 1H), 3.26 (dd, $J = 15.0, 6.2$ Hz, 1H), 3.18 (dd, $J = 15.0, 8.1$ Hz, 1H), 2.28 (s, 3H), 1.41 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 154.4, 137.6, 136.2, 130.8, 129.2, 126.9, 124.1, 121.1, 119.0, 118.6, 118.3, 111.6, 108.4, 83.9, 79.4, 71.4, 65.4, 27.1, 24.3, 21.4, 20.9; IR (thin film, cm^{-1}) 3314, 2251, 1743, 1413, 1275, 1087, 820, 740, 618, 523; HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 381.1573, Found 381.1590.

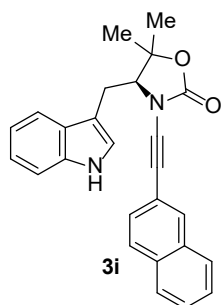
(S)-4-((1H-Indol-3-yl)methyl)-3-((4-methoxyphenyl)ethynyl)-5,5-dimethyloxazolidin-2-one (3h)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3h** (1.157 g) as a white solid with a yield of 62%; Mp. 152.4-152.9 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.98 (d, $J = 2.5$ Hz, 1H), 7.62 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.33 (d, $J = 2.4$ Hz, 1H), 7.18 – 7.15 (m, 2H), 7.10 (dd, $J = 8.2, 6.9$ Hz, 1H), 7.02 (t, $J = 7.4$ Hz, 1H), 6.89 – 6.86 (m, 2H), 4.39 (dd, J

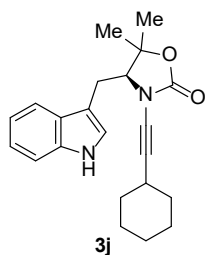
= 8.3, 6.0 Hz, 1H), 3.75 (s, 4H), 3.26 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.17 (dd, $J = 14.9, 8.3$ Hz, 1H), 1.40 (s, 3H), 1.26 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 159.1, 154.4, 136.2, 132.8, 126.9, 124.1, 121.1, 118.6, 118.3, 114.2, 113.8, 111.6, 108.4, 83.8, 78.5, 71.1, 65.4, 55.2, 27.1, 24.3, 21.4; IR (thin film, cm^{-1}) 3424, 2922, 1737, 1604, 1417, 1252, 1087, 838, 736, 617, 424; HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 397.1523, Found 397.1538.

(S)-4-((1H-Indol-3-yl)methyl)-5,5-dimethyl-3-(naphthalen-2-ylethynyl)oxazolidin-2-one (3i)



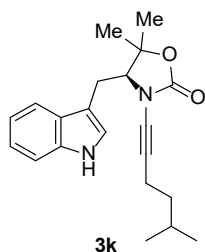
Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3i** (646.9 mg) as a white solid with a yield of 33%; Mp. 149.6-150.3 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 11.01 (s, 1H), 7.87 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.82 – 7.80 (m, 1H), 7.69 (d, $J = 7.9$ Hz, 1H), 7.60 (s, 1H), 7.54 – 7.48 (m, 2H), 7.40 (d, $J = 8.1$ Hz, 1H), 7.37 (d, $J = 2.6$ Hz, 1H), 7.17 – 7.11 (m, 2H), 7.05 (t, $J = 7.5$ Hz, 1H), 4.49 (td, $J = 7.2, 2.3$ Hz, 1H), 3.31 (dd, $J = 15.0, 7.0$ Hz, 1H), 3.23 (dd, $J = 14.9, 7.4$ Hz, 1H), 1.45 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 154.3, 136.3, 132.6, 131.9, 129.8, 128.0, 127.6, 127.6, 127.5, 127.0, 126.7, 126.6, 124.2, 121.2, 119.5, 118.6, 118.5, 111.6, 108.6, 84.1, 80.7, 71.8, 65.4, 27.0, 24.6, 21.4; IR (thin film, cm^{-1}) 3427, 2924, 1764, 1633, 1459, 1405, 1083, 831, 757, 598; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 417.1573, Found 417.1576.

(S)-4-((1H-Indol-3-yl)methyl)-3-(cyclohexylethynyl)-5,5-dimethyloxazolidin-2-one (3j)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3j** (839.4 mg) as a light-yellow oil with a yield of 48%; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.98 (s, 1H), 7.60 – 7.55 (m, 1H), 7.39 – 7.34 (m, 1H), 7.29 (s, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 6.98 (m, 1H), 4.25 – 4.19 (m, 1H), 3.21 (d, *J* = 14.7 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.47 – 2.41 (m, 1H), 1.70 – 1.62 (m, 2H), 1.62 – 1.54 (m, 2H), 1.42 (s, 1H), 1.34 (s, 3H), 1.31 – 1.20 (m, 6H), 1.16 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.7, 136.2, 126.9, 123.9, 121.1, 118.5, 118.2, 111.5, 108.3, 83.3, 75.2, 70.9, 65.2, 32.3, 28.0, 27.2, 25.3, 24.2, 23.9, 21.4; IR (thin film, cm⁻¹) 3426, 2923, 2853, 1631, 1461, 1384, 1105, 620; HRMS (ESI) *m/z* Calcd. for C₂₂H₂₆N₂O₂Na [M+Na]⁺: 373.1886, Found 373.1895.

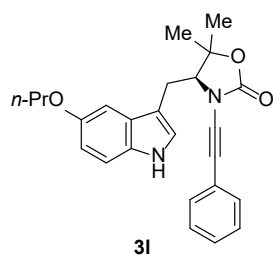
(S)-4-((1*H*-Indol-3-yl)methyl)-5,5-dimethyl-3-(5-methylhex-1-yn-1-yl)oxazolidin-2-one (3k)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (3:1) as an eluent to give the substrate **3k** (798.3 mg) as a white solid with a yield of 47%; Mp. 96.1-96.9 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.97 (s, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.03 – 6.99 (m, 1H), 4.21 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.19 (dd, *J* = 15.0, 4.9 Hz, 1H), 3.07 (dd, *J* = 14.9, 9.2 Hz, 1H), 2.22 (t, *J* = 7.3 Hz, 2H), 1.68 – 1.56 (m, *J* = 6.7 Hz, 1H), 1.33 (s, 3H), 1.26 (q, *J* = 7.2 Hz, 2H), 1.16 (s, 3H), 0.84 (d, *J* = 4.8 Hz, 3H), 0.83 (d, *J* = 4.7 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.78, 136.12, 126.84, 123.90, 121.10, 118.52, 118.15,

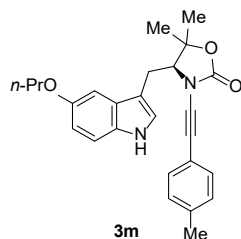
111.54, 108.31, 83.28, 71.46, 70.48, 65.13, 37.23, 27.20, 26.60, 23.88, 21.99, 21.97, 21.39, 15.70; IR (thin film, cm^{-1}) 3342, 2920, 1742, 1631, 1407, 1242, 1103, 737, 607, 429; HRMS (ESI) m/z Calcd. for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 361.1886, Found 361.1902.

(S)-5,5-Dimethyl-3-(phenylethynyl)-4-((5-propoxy-1H-indol-3-yl)methyl)oxazolidin-2-one (3l)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (4:1) as an eluent to give the substrate **3l** (658.3 mg) as a yellow solid with a yield of 60%; Mp. 90.7-91.2 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.80 (d, $J = 2.5$ Hz, 1H), 7.32 – 7.30 (m, 3H), 7.28 (d, $J = 2.5$ Hz, 1H), 7.24 (d, $J = 8.7$ Hz, 1H), 7.20 – 7.18 (m, 2H), 7.11 (d, $J = 2.4$ Hz, 1H), 6.74 (dd, $J = 8.7, 2.4$ Hz, 1H), 4.41 (dd, $J = 8.1, 6.1$ Hz, 1H), 3.92 – 3.86 (m, 2H), 3.23 (dd, $J = 15.0, 6.0$ Hz, 1H), 3.15 (dd, $J = 14.9, 8.2$ Hz, 1H), 1.70 (h, $J = 7.1$ Hz, 2H), 1.42 (s, 3H), 1.29 (s, 3H), 0.96 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 154.68, 152.88, 131.71, 131.10, 128.91, 128.31, 127.70, 125.05, 122.45, 112.50, 112.04, 108.52, 101.65, 84.43, 80.62, 71.80, 69.80, 65.68, 27.47, 24.65, 22.66, 21.80, 10.93; IR (thin film, cm^{-1}) 3424, 2924, 1752, 1627, 1406, 1273, 1085, 754, 691, 618; HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{26}\text{N}_2\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 425.1836, Found 425.1863.

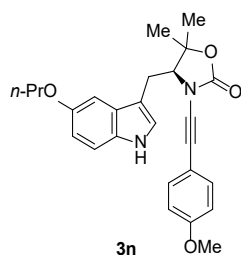
(S)-5,5-Dimethyl-4-((5-propoxy-1H-indol-3-yl)methyl)-3-(p-tolylolethynyl)oxazolidin-2-one (3m)



Purified by a flash column chromatography on alkaline silica gel with PE/EA (5:1) as an eluent to give the substrate **3m** (601.2 mg) as a yellow solid with a yield of 66%;

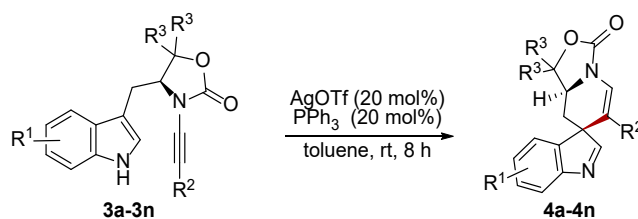
Mp. 90.8-91.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.80 – 10.78 (m, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.14 – 7.09 (m, 5H), 6.74 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.38 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.92 – 3.85 (m, 2H), 3.21 (dd, *J* = 15.0, 5.9 Hz, 1H), 3.14 (dd, *J* = 14.9, 8.3 Hz, 1H), 2.28 (s, 3H), 1.70 (p, *J* = 7.1 Hz, 2H), 1.41 (s, 3H), 1.27 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.72, 152.88, 131.69, 131.21, 129.54, 127.68, 125.02, 119.35, 112.50, 112.05, 108.52, 101.60, 84.33, 79.87, 71.78, 69.79, 65.70, 27.51, 24.60, 22.67, 21.80, 21.30, 10.92; IR (thin film, cm⁻¹) 3412, 2924, 2253, 1753, 1408, 1273, 1084, 816, 615, 429; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₉N₂O₃ [M+H]⁺: 417.2173, Found 417.2276.

(*S*)-3-((4-Methoxyphenyl)ethynyl)-5,5-dimethyl-4-((5-propoxy-1*H*-indol-3-yl)methyl)oxazolidin-2-one (3n**)**



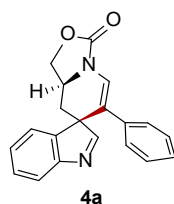
Purified by a flash column chromatography on alkaline silica gel with PE/EA (4:1) as an eluent to give the substrate **3n** (540.3 mg) as a yellow solid with a yield of 59%; Mp. 115.2-116.2 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.79 (d, *J* = 2.5 Hz, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.21 – 7.19 (m, 2H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.90 – 6.87 (m, 2H), 6.73 (dd, *J* = 8.7, 2.4 Hz, 1H), 4.36 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.88 (qt, *J* = 9.3, 6.5 Hz, 2H), 3.75 (s, 3H), 3.21 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.13 (dd, *J* = 15.0, 8.5 Hz, 1H), 1.70 (h, *J* = 7.1 Hz, 2H), 1.40 (s, 3H), 1.26 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 159.53, 154.79, 152.88, 133.20, 131.67, 127.68, 124.98, 114.57, 114.17, 112.51, 112.07, 108.52, 101.55, 84.23, 78.96, 71.51, 69.77, 65.77, 55.58, 27.56, 24.54, 22.66, 21.82, 10.93; IR (thin film, cm⁻¹) 3432, 2924, 1628, 1461, 1248, 1083, 835, 614; HRMS (ESI) *m/z* Calcd. for C₂₆H₂₈N₂O₄Na [M+Na]⁺: 455.1941, Found 455.1946.

Part 8: General procedures and characteristic data for products 4a-4n



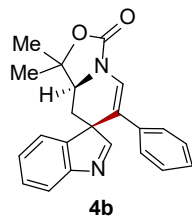
To a stirred solution of substrates **3a-3n** (1.0 mmol, 1.0 equiv.) in toluene (7 mL) was added a solution of AgOTf (51.4 mg, 0.2 mmol, 20 mol%) and PPh₃ (52.5 mg, 0.2 mmol, 20 mol%) in toluene (3 mL), which was stirred for 5-10 min before addition. The reaction mixture was stirred at room temperature until the TLC analysis showed that the starting material was consumed completely. The solvent was concentrated *in vacuo* to give a residue, which was purified by a flash column chromatography on silica gel to afford products **4a-4n**.

(3*R*,8*a'**S*)-6'-Phenyl-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (**4a**)



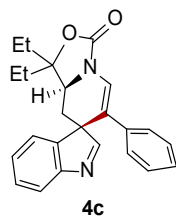
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4a** (256.9 mg) as a yellow solid with a yield of 81%; Mp. 219.3-221.3 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.64 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 4.9 Hz, 4H), 6.75 (dd, *J* = 6.6, 3.0 Hz, 2H), 4.70 (t, *J* = 8.2 Hz, 1H), 4.66 – 4.60 (m, 1H), 4.09 (t, *J* = 8.9 Hz, 1H), 2.33 (t, *J* = 12.5 Hz, 1H), 1.74 (dd, *J* = 13.1, 3.0 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.2, 155.1, 153.6, 142.1, 137.5, 128.1, 127.9, 126.8, 126.5, 126.2, 123.3, 122.8, 121.0, 116.2, 68.8, 59.4, 51.0, 33.9; IR (thin film, cm⁻¹) 3450, 3059, 2924, 1743, 1652, 1550, 1428, 1321, 1232, 1093, 978, 868; HRMS (ESI) *m/z* Calcd. for C₂₀H₁₇N₂O₂ [M+H]⁺: 317.1285, Found 317.1283.

(3*R*,8*a'**S*)-1',1'-Dimethyl-6'-phenyl-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (**4b**)



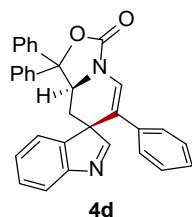
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4b** (316.2 mg) as a white solid with a yield of 92%; Mp. 162.3–164.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.67 (s, 1H), 7.56 – 7.53 (m, 1H), 7.25 (t, *J* = 7.1 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H), 7.03 – 6.98 (m, 3H), 6.77 – 6.73 (m, 2H), 4.35 (dd, *J* = 12.7, 2.9 Hz, 1H), 2.23 (t, *J* = 12.8 Hz, 1H), 1.73 (dd, *J* = 13.0, 2.9 Hz, 1H), 1.53 (s, 3H), 1.30 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.5, 155.1, 152.4, 142.3, 137.5, 128.1, 127.9, 126.7, 126.5, 126.1, 123.6, 123.0, 120.9, 115.4, 83.1, 59.7, 59.0, 30.6, 26.1, 21.7; IR (thin film, cm⁻¹) 3434, 2924, 1757, 1640, 1409, 1265, 1082, 967, 749, 604; HRMS (ESI) *m/z* Calcd. for C₂₂H₂₁N₂O₂ [M+H]⁺: 345.1598, Found 345.1605.

(3*R*,8*a'S*)-1',1'-Diethyl-6'-phenyl-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4c)**



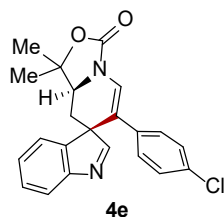
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4c** (305.8 mg) as a white solid with a yield of 82%; Mp. 174.9–175.8 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.74 (s, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.24 (t, *J* = 7.1 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.04 – 6.98 (m, 4H), 6.76 – 6.73 (m, 2H), 4.43 (dd, *J* = 12.8, 2.8 Hz, 1H), 2.34 (t, *J* = 12.9 Hz, 1H), 1.90 – 1.79 (m, 2H), 1.79 – 1.72 (m, 1H), 1.63 – 1.56 (m, 2H), 0.93 – 0.85 (m, 6H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.4, 155.1, 152.4, 142.2, 137.5, 128.1, 127.9, 126.7, 126.5, 126.1, 123.6, 123.1, 120.9, 115.6, 86.8, 59.8, 57.6, 31.1, 28.1, 24.4, 7.4, 7.0; IR (thin film, cm⁻¹) 3430, 2924, 1735, 1404, 1236, 1095, 927, 758, 696, 601; HRMS (ESI) *m/z* Calcd. for C₂₄H₂₅N₂O₂ [M+H]⁺: 373.1911, Found 373.1916.

(3*R*,8*a*'*S*)-1',1',6'-Triphenyl-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4d)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4d** (382.8 mg) as a white solid with a yield of 82%; Mp. 198.2–200.0 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.89 (s, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.51 – 7.45 (m, 4H), 7.43 – 7.40 (m, 1H), 7.37 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.21 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.10 (s, 1H), 7.02 – 6.97 (m, 4H), 6.82 (dt, *J* = 7.4, 0.9 Hz, 1H), 6.74 – 6.71 (m, 2H), 5.39 (dd, *J* = 12.5, 2.7 Hz, 1H), 2.01 (dd, *J* = 13.4, 2.8 Hz, 1H), 1.34 (t, *J* = 13.0 Hz, 1H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.21, 155.21, 152.23, 141.78, 140.85, 138.44, 137.01, 128.69, 128.60, 128.56, 128.34, 128.19, 127.93, 126.87, 126.64, 126.15, 126.13, 125.82, 123.36, 122.45, 121.09, 116.42, 87.56, 59.86, 59.02, 33.57; IR (thin film, cm⁻¹) 3437, 1758, 1405, 1253, 978, 753, 701, 628; HRMS (ESI) *m/z* Calcd. for C₃₂H₂₅N₂O₂ [M+H]⁺: 469.1911, Found 469.1916.

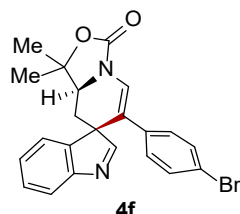
(3*R*,8*a*'*S*)-6'-(4-Chlorophenyl)-1',1'-dimethyl-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4e)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4e** (344.8 mg) as a white solid with a yield of 91%; Mp. 179.6–180.9 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.66 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.24 (m, 2H), 7.14 (td, *J* = 7.4, 1.0 Hz, 1H), 7.09 – 7.05 (m, 3H), 6.76 – 6.73 (m, 2H), 4.35 (dd, *J* = 12.7, 2.9 Hz, 1H), 2.22 (t, *J* = 12.9 Hz, 1H), 1.73 (dd, *J* = 13.0, 3.0 Hz, 1H), 1.53 (s, 3H), 1.29 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.4, 155.1, 152.3,

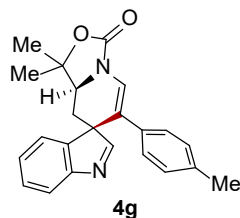
142.0, 136.5, 131.2, 128.2, 127.9, 126.6, 124.2, 123.1, 121.0, 114.0, 83.2, 59.6, 59.0, 30.4, 26.1, 21.7; IR (thin film, cm^{-1}) 3452, 1757, 1638, 1414, 1275, 1081, 830, 750, 499; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{20}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 379.1208, Found 379.1207.

(3*R*,8*a'S*)-6'-(4-Bromophenyl)-1',1'-dimethyl-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4f)**



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4f** (394.5 mg) as a white solid with a yield of 93%; Mp. 165.2–166.9 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.66 (s, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.18 (m, 2H), 7.14 (td, $J = 7.5, 1.0$ Hz, 1H), 7.08 (s, 1H), 6.70 – 6.66 (m, 2H), 4.34 (dd, $J = 12.7, 2.9$ Hz, 1H), 2.22 (t, $J = 12.9$ Hz, 1H), 1.73 (dd, $J = 13.0, 2.9$ Hz, 1H), 1.52 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, $\text{DMSO}-d_6$) δ 176.5, 155.2, 152.4, 142.1, 137.0, 131.0, 128.4, 126.8, 124.3, 123.2, 121.2, 119.9, 114.2, 83.3, 59.6, 59.1, 30.5, 26.2, 21.8; IR (thin film, cm^{-1}) 3438, 1743, 1638, 1412, 1085, 828, 771, 497; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{20}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 423.0703, Found 423.0709.

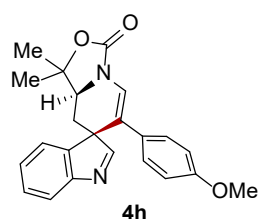
(3*R*,8*a'S*)-1',1'-Dimethyl-6'-(*p*-tolyl)-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4g)**



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4g** (310.8 mg) as a white solid with a yield of 87%; Mp. 195.6–197.1 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 8.64 (s, 1H), 7.55 – 7.52 (m, 1H), 7.28 – 7.23 (m, 2H), 7.15 – 7.11 (m, 1H), 6.98 (s, 1H), 6.81 (d, $J = 7.9$ Hz, 2H), 6.63 (d, $J = 8.1$ Hz, 2H), 4.33 (dd, $J = 12.7, 2.9$ Hz, 1H), 2.21 (t, $J = 12.8$ Hz, 1H), 2.09 (s, 3H),

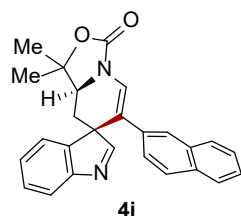
1.71 (dd, $J = 13.0, 2.9$ Hz, 1H), 1.52 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 176.5, 155.1, 152.4, 142.4, 135.8, 134.7, 128.6, 128.1, 126.5, 126.0, 123.2, 123.1, 120.9, 115.4, 83.0, 59.7, 59.0, 30.6, 26.1, 21.7, 20.5; IR (thin film, cm^{-1}) 3432, 2924, 1765, 1631, 1400, 1086, 957, 750, 598; HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 359.1754, Found 359.1759.

(3*R*,8*a'S*)-6'-(4-Methoxyphenyl)-1',1'-dimethyl-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4h)**



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4h** (352.0 mg) as a white solid with a yield of 94%; Mp. 155.5-157.1 $^{\circ}\text{C}$; ^1H NMR (600 MHz, DMSO- d_6) δ 8.63 (s, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.29 – 7.24 (m, 2H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.94 (s, 1H), 6.68 – 6.65 (m, 2H), 6.59 – 6.55 (m, 2H), 4.32 (dd, $J = 12.7, 2.9$ Hz, 1H), 3.59 (s, 3H), 2.21 (t, $J = 12.9$ Hz, 1H), 1.71 (dd, $J = 13.0, 2.9$ Hz, 1H), 1.52 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 176.5, 158.0, 155.1, 152.4, 142.4, 129.8, 128.1, 127.5, 126.5, 123.1, 122.9, 120.9, 115.3, 113.3, 82.9, 59.9, 59.0, 54.8, 30.5, 26.2, 21.7; IR (thin film, cm^{-1}) 3438, 1771, 1636, 1401, 1244, 1086, 845, 774, 524; HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 375.1703, Found 375.1708.

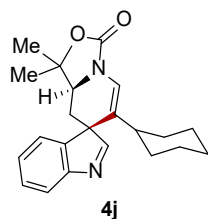
(3*R*,8*a'S*)-1',1'-Dimethyl-6'-(naphthalen-2-yl)-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4i)**



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4i** (316.4 mg) as a white solid with a yield of 80%; Mp. 197.8-198.4 $^{\circ}\text{C}$; ^1H NMR (600 MHz, DMSO- d_6) δ 8.76 (s, 1H), 7.69 (dd, $J = 7.2, 1.8$ Hz, 1H),

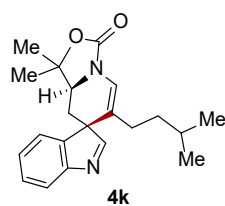
7.63 (dd, $J = 7.3, 1.9$ Hz, 1H), 7.56 (d, $J = 7.7$ Hz, 1H), 7.52 (d, $J = 8.6$ Hz, 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.32 (m, 1H), 7.26 (d, $J = 7.4$ Hz, 1H), 7.23 – 7.20 (m, 2H), 7.07 (td, $J = 7.5, 1.0$ Hz, 1H), 6.82 (dd, $J = 8.6, 1.9$ Hz, 1H), 4.40 (dd, $J = 12.7, 3.0$ Hz, 1H), 2.27 (t, $J = 12.9$ Hz, 1H), 1.77 (dd, $J = 13.1, 3.0$ Hz, 1H), 1.55 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 176.70, 155.19, 152.40, 142.36, 135.24, 132.60, 131.63, 128.14, 127.58, 127.28, 127.19, 126.56, 126.15, 125.71, 124.52, 124.46, 124.10, 123.08, 120.99, 115.11, 83.20, 59.74, 59.08, 30.65, 26.10, 21.69; IR (thin film, cm^{-1}) 3433, 2924, 1745, 1629, 1409, 1080, 739, 609; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 395.1754, Found 395.1759.

(3*R*,8*a*'*S*)-6'-Cyclohexyl-1',1'-dimethyl-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4j)



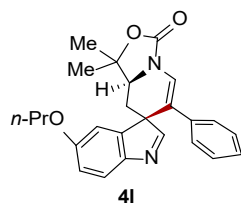
Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4j** (303.8 mg) as a white solid with a yield of 87%; Mp. 138.4–140.3 °C; ^1H NMR (600 MHz, DMSO- d_6) δ 8.33 (s, 1H), 7.62 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 7.4$ Hz, 1H), 7.42 – 7.38 (m, 1H), 7.30 (t, $J = 7.4$ Hz, 1H), 6.76 (s, 1H), 4.15 (dd, $J = 12.7, 2.8$ Hz, 1H), 2.12 (t, $J = 12.8$ Hz, 1H), 1.64 (dd, $J = 13.0, 2.8$ Hz, 1H), 1.54 – 1.45 (m, 5H), 1.44 – 1.37 (m, 2H), 1.31 (d, $J = 12.3$ Hz, 1H), 1.24 (s, 3H), 1.20 – 1.09 (m, 1H), 1.04 – 0.91 (m, 2H), 0.74 – 0.61 (m, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 176.07, 155.79, 152.32, 141.79, 128.39, 126.35, 123.00, 120.87, 120.86, 120.67, 82.36, 60.51, 58.76, 37.72, 35.15, 32.52, 29.64, 26.41, 26.35, 26.30, 25.18, 21.74; IR (thin film, cm^{-1}) 3436, 2931, 1757, 1411, 1275, 1082, 916, 758; HRMS (ESI) m/z Calcd. for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 373.1886, Found 373.1990.

(3*R*,8*a*'*S*)-6'-Isopentyl-1',1'-dimethyl-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4k)



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4k** (292.1 mg) as a white solid with a yield of 86%; Mp. 117.4–118.5 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.35 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.43 (m, 1H), 7.41 – 7.38 (m, 1H), 7.33 – 7.29 (m, 1H), 6.75 (d, *J* = 1.3 Hz, 1H), 4.21 (dd, *J* = 12.7, 2.9 Hz, 1H), 2.11 (t, *J* = 12.8 Hz, 1H), 1.65 (dd, *J* = 12.9, 2.9 Hz, 1H), 1.49 – 1.42 (m, 4H), 1.29 – 1.16 (m, 5H), 0.92 – 0.85 (m, 1H), 0.83 – 0.76 (m, 1H), 0.60 (d, *J* = 6.7 Hz, 3H), 0.57 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 176.24, 155.67, 152.25, 141.56, 128.37, 126.38, 123.17, 120.99, 120.96, 114.53, 82.46, 60.06, 58.76, 36.77, 29.31, 27.37, 26.61, 26.26, 22.30, 21.73, 21.70; IR (thin film, cm⁻¹) 3436, 2931, 1758, 1661, 1382, 1078, 985, 895, 754, 591; HRMS (ESI) *m/z* Calcd. for C₂₁H₂₆N₂O₂ [M+Na]⁺: 361.1886, Found 361.1897.

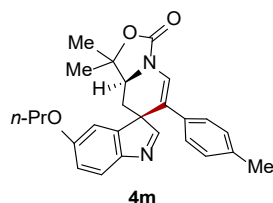
(3*R*,8*a*'*S*)-1',1'-Dimethyl-6'-phenyl-5-propoxy-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4l)



Purified by a flash column chromatography on silica gel with PE/EA (5:1) as an eluent to give the product **4l** (501.9 mg) as a white solid with a yield of 93%; Mp. 151.1–152.6 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.49 (s, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.04 – 7.01 (m, 4H), 6.85 (d, *J* = 2.5 Hz, 1H), 6.75 – 6.78 (m, 3H), 4.31 (dd, *J* = 12.7, 2.9 Hz, 1H), 3.84 (dt, *J* = 9.5, 6.6 Hz, 1H), 3.75 (dt, *J* = 9.5, 6.6 Hz, 1H), 2.23 (t, *J* = 12.8 Hz, 1H), 1.69 (dd, *J* = 13.0, 2.9 Hz, 1H), 1.61 (h, *J* = 7.1 Hz, 2H), 1.52 (s, 3H), 1.30 (s, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 174.62, 158.04, 152.76, 148.90, 138.01, 128.37, 127.06, 126.43, 123.79, 121.72, 116.06, 114.19, 109.95, 83.45, 69.63, 60.09, 59.39, 31.27, 26.54, 22.27, 22.11, 10.69; IR (thin film, cm⁻¹) 3426, 2926,

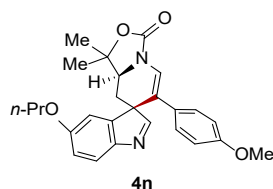
1739, 1637, 1410, 1234, 984, 755, 692; HRMS (ESI) m/z Calcd. for $C_{25}H_{26}N_2O_3Na$ $[M+Na]^+$: 425.1836, Found 425.1839.

(3*R*,8*a'S*)-1',1'-Dimethyl-5-propoxy-6'-(*p*-tolyl)-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4*m*)**



Purified by a flash column chromatography on silica gel with PE/EA (6:1) as an eluent to give the product **4m** (475.6 mg) as a white solid with a yield of 96%; Mp. 160.2–161.2 °C; 1H NMR (600 MHz, $DMSO-d_6$) δ 8.47 (d, $J = 1.4$ Hz, 1H), 7.43 – 7.40 (m, 1H), 6.97 (d, $J = 1.2$ Hz, 1H), 6.86 – 6.82 (m, 3H), 6.77 (dt, $J = 8.9, 1.9$ Hz, 1H), 6.66 (d, $J = 7.7$ Hz, 2H), 4.29 (dd, $J = 12.5, 2.9$ Hz, 1H), 3.87 – 3.82 (m, 1H), 3.78 – 3.73 (m, 1H), 2.22 (t, $J = 12.9$ Hz, 1H), 2.11 (s, 3H), 1.67 (dd, $J = 13.1, 2.8$ Hz, 1H), 1.61 (p, $J = 7.1$ Hz, 2H), 1.52 (s, 3H), 1.29 (s, 3H), 0.92 – 0.88 (m, 3H); ^{13}C NMR (150 MHz, $DMSO-d_6$) δ 174.65, 158.03, 152.74, 148.92, 144.63, 136.18, 135.12, 128.98, 126.32, 123.36, 121.71, 116.05, 114.14, 109.97, 83.37, 69.63, 60.13, 59.39, 31.33, 26.56, 22.29, 22.10, 20.85, 10.69; IR (thin film, cm^{-1}) 3441, 1752, 1414, 1275, 1087, 981, 816, 750; HRMS (ESI) m/z Calcd. for $C_{26}H_{28}N_2O_3Na$ $[M+Na]^+$: 439.1992, Found 439.1996.

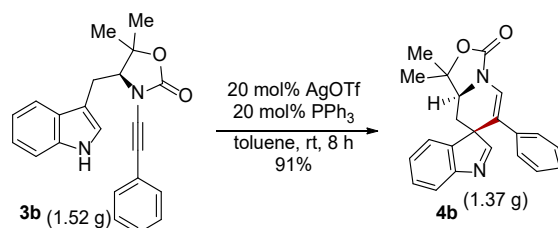
(3*R*,8*a'S*)-6'-(4-Methoxyphenyl)-1',1'-dimethyl-5-propoxy-8',8*a'*-dihydro-1'*H*,3'*H*-spiro[indole-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (4*n*)**



Purified by a flash column chromatography on silica gel with PE/EA (2:1) as an eluent to give the product **4n** (424.8 mg) as a white solid with a yield of 97%; Mp. 131.7–133.2 °C; 1H NMR (600 MHz, $DMSO-d_6$) δ 8.46 (s, 1H), 7.41 (d, $J = 8.4$ Hz, 1H), 6.92 (s, 1H), 6.88 (d, $J = 2.5$ Hz, 1H), 6.77 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.71 – 6.69 (m, 2H), 6.61 – 6.58 (m, 2H), 4.28 (dd, $J = 12.7, 2.9$ Hz, 1H), 3.86 (dt, $J = 9.5, 6.6$ Hz, 1H), 3.77

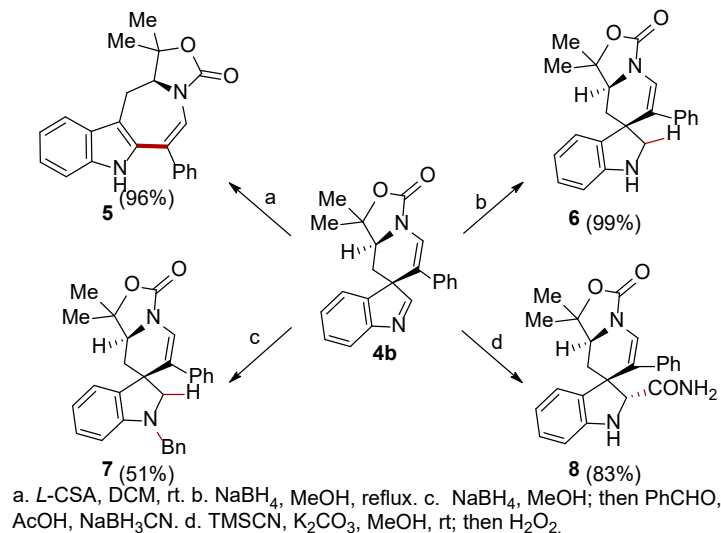
(dt, $J = 9.5, 6.6$ Hz, 1H), 3.60 (s, 3H), 2.22 (t, $J = 12.8$ Hz, 1H), 1.67 (dd, $J = 12.9, 2.8$ Hz, 1H), 1.62 (p, $J = 7.1$ Hz, 2H), 1.52 (s, 3H), 1.29 (s, 3H), 0.91 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 174.59, 158.34, 158.04, 152.73, 148.92, 144.63, 130.29, 127.74, 123.02, 121.71, 115.89, 114.17, 113.71, 109.99, 83.30, 69.65, 60.26, 59.39, 55.20, 31.24, 26.58, 22.30, 22.11, 10.70; IR (thin film, cm^{-1}) 3440, 1751, 1608, 1420, 1248, 1089, 982, 836, 748, 598; HRMS (ESI) m/z Calcd. for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_4\text{Na}$ $[\text{M}+\text{Na}]^+$: 455.1941, Found 455.1949.

Part 9: Gram-scale synthesis of spiro[indole-3,4'-piperidine]



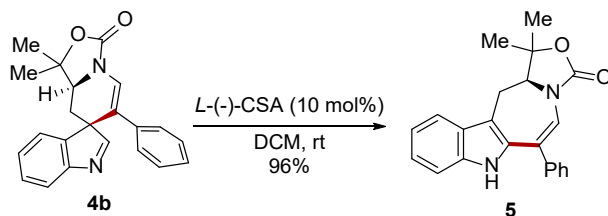
To a stirred solution of substrate **3b** (4.4 mmol, 1.52 g, 1.0 equiv.) in toluene (21 mL) was added a solution of AgOTf (226.8 mg, 0.9 mmol, 20 mol%) and PPh₃ (231.5 mg, 0.9 mmol, 20 mol%) in toluene (9 mL), which was stirred for 10 min before addition. The reaction mixture was stirred at room temperature until the TLC analysis showed that the starting material was consumed completely. The solvent was concentrated *in vacuo* to give a residue, which was purified by a flash column chromatography on silica gel using PE/EA (2:1) as an eluent to afford products **4b** (1.37 g) as a white solid with a yield of 91%.

Part 10: Scheme S1. Derivatization of spiro[indole-3,4'-piperidine]



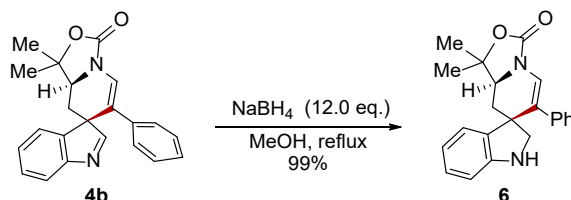
Part 11: Procedures for derivatization and characteristic data for derivatives 5-8

Procedure for the synthesis of (*S*)-1,1-dimethyl-6-phenyl-1,7,12,12a-tetrahydro-3*H*-oxazolo[3',4':1,7]azepino[4,5-*b*]indol-3-one (**5**)



To a stirred solution of product **4b** (200.0 mg, 0.581 mmol, 1.0 equiv.) in DCM (10 mL) was added *L*-CSA (13.5 mg, 0.0581 mmol, 10 mol%) in an ice bath, then the mixture was stirred at room temperature. When the reaction was finished, it was quenched with triethylamine and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel with PE/EA (8:1) as an eluent to give the product **5** (192.4 mg) as a white solid with a yield of 96%; Mp. 179.9-180.1 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.20 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.44 – 7.40 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.05 – 7.01 (m, 1H), 7.01 – 6.98 (m, 1H), 6.70 (d, *J* = 1.5 Hz, 1H), 3.94 (d, *J* = 9.6 Hz, 1H), 3.64 (d, *J* = 15.2 Hz, 1H), 2.88 (dd, *J* = 15.3, 9.8 Hz, 1H), 1.55 (s, 3H), 1.50 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 154.1, 139.0, 135.8, 131.2, 128.9, 128.8, 127.8, 127.5, 122.9, 121.4, 118.7, 117.6, 114.0, 111.6, 110.4, 81.6, 64.9, 26.8, 25.3, 22.4; IR (thin film, cm⁻¹) 3449, 2923, 1742, 1396, 1093, 145, 563, 442; HRMS (ESI) *m/z* Calcd. for C₂₂H₂₀N₂O₂Na [M+Na]⁺: 367.1417, Found 367.1416.

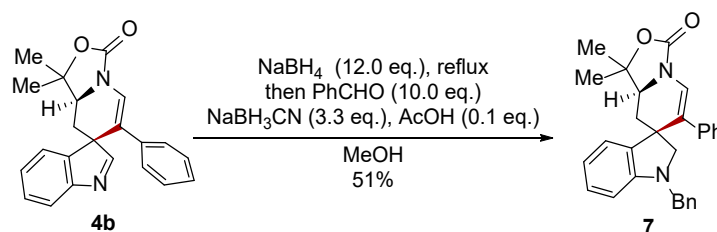
Procedure for the synthesis of (*3R,8a'S*)-1',1'-dimethyl-6'-phenyl-8',8a'-dihydro-1'*H,3'H*-spiro[indoline-3,7'-oxazolo[3,4-*a*]pyridin]-3'-one (**6**)



NaBH₄ (263.6 mg, 6.97 mmol, 12.0 equiv.) and product **4b** (200.0 mg, 0.581 mmol, 1.0 eq.) were suspended in MeOH (20 mL) under reflux until the reaction was finished. The mixture was cooled in an ice bath, followed by the treatment with 2 M HCl (15

mL). The methanol was removed out *in vacuo*. Then the solution was extracted with ethyl acetate (10 mL) thrice. The combined organic layers were washed with brine (15 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was used directly for the next step without further purification. The residue was purified by a flash column chromatography on silica gel with PE/EA (3:1) as an eluent to give the product **6** (200.0 mg) as a white solid with a yield of 99%; Mp. 191.0-191.4 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.20 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 7.08 – 7.05 (m, 1H), 6.87 – 6.83 (m, 2H), 6.72 – 6.69 (m, 1H), 6.49 – 6.46 (m, 1H), 6.41 – 6.38 (m, 1H), 5.72 (t, *J* = 2.1 Hz, 1H), 3.95 (dd, *J* = 12.6, 2.9 Hz, 1H), 3.78 – 3.74 (m, 1H), 3.44 (dd, *J* = 10.3, 1.6 Hz, 1H), 2.15 (dd, *J* = 12.8, 2.9 Hz, 1H), 1.70 (t, *J* = 12.7 Hz, 1H), 1.53 (s, 3H), 1.27 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 152.50, 151.78, 138.46, 133.16, 127.82, 127.62, 127.58, 126.15, 123.79, 122.25, 120.44, 117.01, 108.81, 82.72, 58.84, 57.23, 48.29, 35.95, 26.02, 22.00; IR (thin film, cm⁻¹) 3382, 1744, 1634, 1408, 1267, 1079, 751, 603; HRMS (ESI) *m/z* Calcd. for C₂₂H₂₂N₂O₂Na [M+Na]⁺: 369.1573, Found 369.1578.

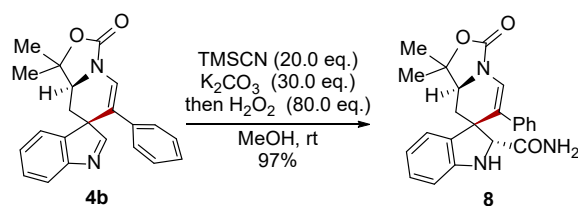
Procedure for the synthesis of (8a'S)-1-benzyl-1',1'-dimethyl-6'-phenyl-8',8a'-dihydro-1'H,3'H-spiro[indoline-3,7'-oxazolo[3,4-a]pyridin]-3'-one (7)



Product **4b** (100.0 mg, 0.290 mmol, 1.0 eq.) and NaBH₄ (129.4 mg, 3.484 mmol, 12.0 eq.) were suspended in MeOH (10 mL) under reflux for 12 h. To the above solution PhCHO (306.3 mg, 2.904 mmol, 10.0 equiv.) and AcOH (1.65 mL, 0,029 mmol, 0.1 equiv.) were added, followed by the addition of NaBH₃CN (59.9 mg, 0.958 mmol) portionwise over 30 minutes at room temperature. The resulting mixture was stirred at the same temperature for 1 hour. After cooling to 0 °C, the reaction was quenched with H₂O, and the mixture was basified with solid NaOH. The resulting mixture was extracted with Et₂O thrice. The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The

residue was purified by a flash column chromatography on silica gel using PE/EA (10:1) as an eluent to afford **7** (64.6 mg, 1.93 mmol) as a white solid with a yield of 51%; Mp. 158.4-159.0 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.31 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.27 – 7.25 (m, 1H), 7.23 (d, *J* = 6.9 Hz, 2H), 7.02 – 7.08 (m, 3H), 6.98 (dt, *J* = 6.7, 1.7 Hz, 2H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.77 (s, 1H), 6.76 (s, 2H), 6.56 (d, *J* = 7.9 Hz, 1H), 6.45 – 6.43 (m, 1H), 4.52 (d, *J* = 15.4 Hz, 1H), 4.22 (d, *J* = 15.4 Hz, 1H), 3.90 (dd, *J* = 12.6, 2.8 Hz, 1H), 3.67 (d, *J* = 10.0 Hz, 1H), 3.39 (s, 1H), 2.17 (dd, *J* = 12.8, 2.9 Hz, 1H), 1.81 (t, *J* = 12.7 Hz, 1H), 1.51 (s, 3H), 1.28 (s, 3H); ¹³C NMR (150 MHz, DMSO-*d*₆) δ 152.81, 151.68, 138.55, 138.31, 128.76, 128.33, 128.19, 128.11, 128.06, 127.46, 124.23, 122.46, 120.78, 117.32, 107.15, 83.02, 64.91, 57.64, 51.21, 47.20, 36.51, 26.43, 22.37; IR (thin film, cm⁻¹) 3450, 2921, 1743, 1637, 1493, 1084, 752, 701; HRMS (ESI) *m/z* Calcd. for C₂₉H₂₈N₂O₂Na [M+Na]⁺: 459.2043, Found 459.2046.

Procedure for the synthesis of (2*R*,3*R*,8*a*'*S*)-1',1'-dimethyl-3'-oxo-6'-phenyl-8',8*a*'-dihydro-1'*H*,3'*H*-spiro[indoline-3,7'-oxazolo[3,4-*a*]pyridine]-2-carboxamide (8**)**



To a solution of product **4b** (134 mg, 0.68 mmol) in MeOH (20 mL) was added TMSCN (1.152 g, 11.6 mmol, 20.0 equiv.) and K₂CO₃ (2.322 g, 17.4 mmol, 30.0 equiv.) in sequence in an ice-bath. Then the mixture was allowed to stir at room temperature. When the reaction was finished, the solution was cooled with an ice-bath and a solution of H₂O₂ (5.858 g, 46.5 mmol, 30% in water, 80.0 equiv.) was added and then the solution was allowed to warm to room temperature for 18 h. The mixture was quenched with water (20 mL) and methanol was removed out *in vacuo*. Then the solution was extracted with ethyl acetate (30 mL) thrice. Combined organic layers were washed with brine (45 mL) twice and dried over anhydrous Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by a flash column chromatography on silica gel with PE/EA (2:1) to EA as an eluent to give the product **8** (187.7 mg) as a white solid with a yield of 83%; Mp. 223.1-223.4 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.60 (d, *J* = 2.5

Hz, 1H), 7.55 (d, $J = 2.5$ Hz, 1H), 7.18 – 7.12 (m, 5H), 7.07 (dd, $J = 7.4, 1.3$ Hz, 1H), 6.98 (td, $J = 7.5, 1.2$ Hz, 1H), 6.74 (s, 1H), 6.69 – 6.66 (m, 1H), 6.53 (d, $J = 7.8$ Hz, 1H), 6.05 (d, $J = 3.6$ Hz, 1H), 4.17 (d, $J = 3.5$ Hz, 1H), 3.85 (dd, $J = 12.8, 2.7$ Hz, 1H), 2.58 (dd, $J = 13.7, 2.8$ Hz, 1H), 1.60 (t, $J = 13.2$ Hz, 1H), 1.44 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (150 MHz, DMSO- d_6) δ 172.7, 152.5, 149.8, 138.6, 133.5, 129.9, 128.0, 127.7, 126.7, 123.8, 122.2, 121.9, 118.7, 109.8, 82.4, 68.4, 57.3, 51.2, 33.5, 26.4, 21.6; IR (thin film, cm^{-1}) 3419, 1738, 1684, 1414, 1268, 758, 625, 462; HRMS (ESI) m/z Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_3\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 412.1632, Found 412.1637.

Part 12: References

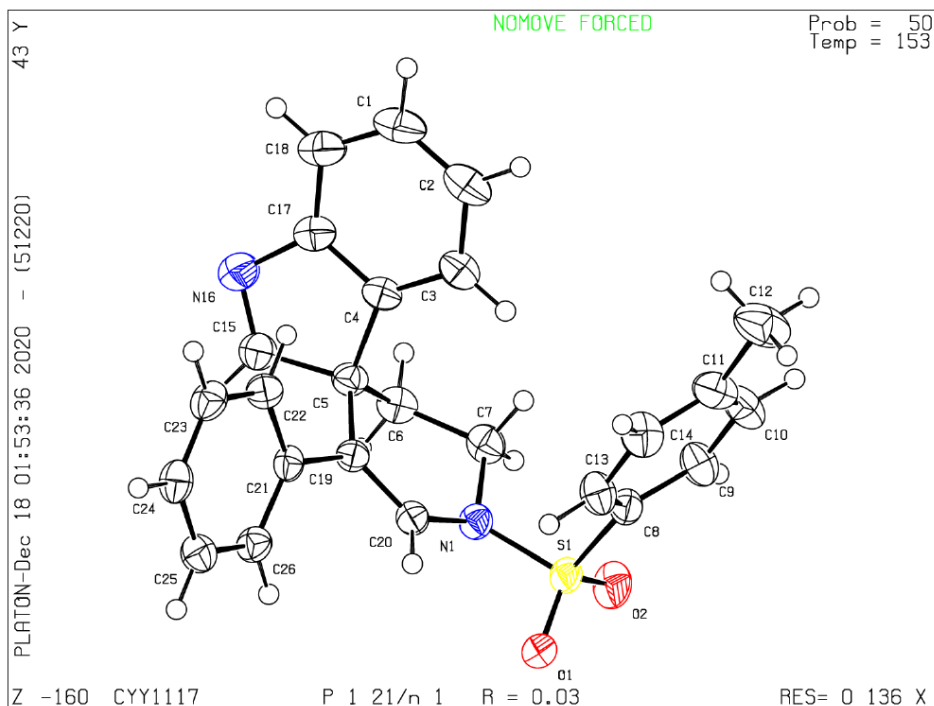
[s1] (a) K. Tanaka, T. Kobayashi, H. Mori and S. Katsumura, *J. Org. Chem.*, 2004, **69**, 5906; (b) S. Nicolai, R. Sedigh-Zadeh and J. Waser, *J. Org. Chem.*, 2013, **78**, 3783; (c) L. Zhu, Y. Yu, Z. Mao and X. Huang, *Org. Lett.*, 2015, **17**, 30; (d) B. Pigulski, A. Arendt, D. N. Tomilin, L. N. Sobenina, B. A. Trofimov and S. J. Szafert, *Org. Chem.*, 2016, **81**, 9188; (e) Y. Shen, B. Huang, J. Zheng, C. Lin, Y. Liu and S. Cui, *Org. Lett.*, 2017, **19**, 1744; (f) Z. Zeng, H. Jin, J. Xie, B. Tian, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Org. Lett.*, 2017, **19**, 1020; (g) G. Jiang, C. Zhu, J. Li, W. Wu and H. Jiang, *Adv. Synth. Catal.*, 2017, **359**, 1208.

[s2] (a) X. Zhang, Y. Zhang, J. Huang, R. Hsung, K. Kurtz, J. Oppenheimer, M. Petersen, I. Sagamanova, L. Shen, and Mi. Tracey, *J. Org. Chem.*, 2006, **71**, 4170; (b) Y. Pang, G. Liang, F. Xie, H. Hu, C. Du, X. Zhang, M. Cheng, B. Lin and Y. Liu, *Org. Biomol. Chem.*, 2019, **17**, 2247.

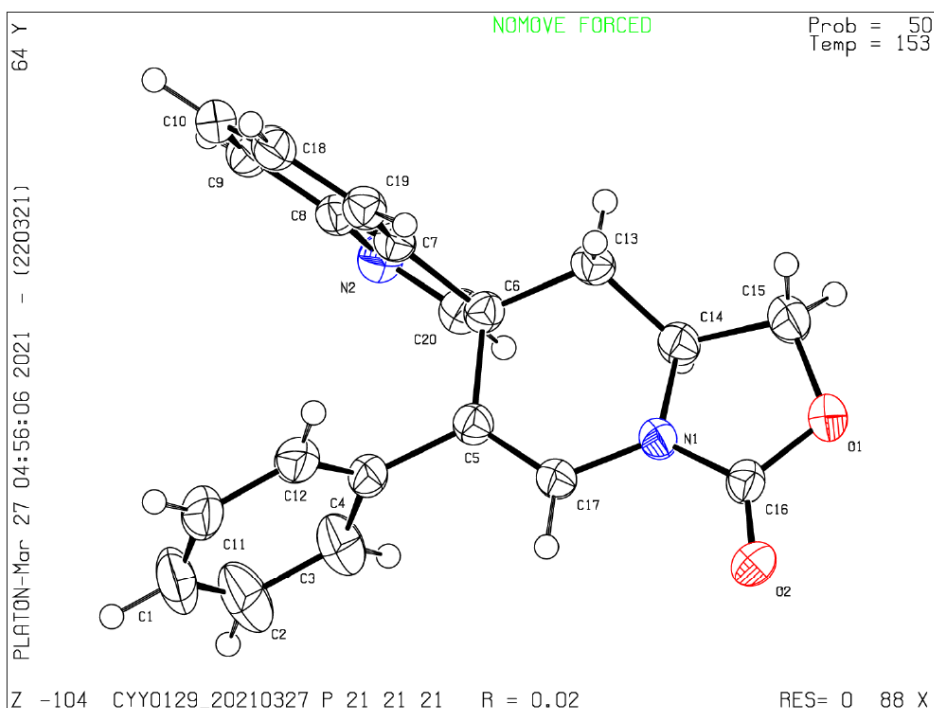
[s3] S. J. Yeo, Y. Liu and X. Wang, *Tetrahedron.*, 2012, **68**, 813.

Part 13: X-ray crystal images

CCDC 2092996 contain the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



CCDC 2092997 contain the supplementary crystallographic data for compound **4a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.



Part 14: Computational details

14.1 Complete reference for Gaussian 09

Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,

M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

14.2. Computational methods

All of the DFT calculations in this study were performed using the GAUSSIAN 09 series of programs. DFT method B3LYP with a standard 6-31G + (d,p) basis set (LANL2DZ basis set for Ag) was used for the geometry optimizations and the single point energies. The energies presented in this paper are the B3LYP calculated Gibbs free energies in gas phase.

14.3. Optimized geometries for all the calculated compounds

Ph₃P

Energy: -1036.1213600

Number of Imaginary Frequencies: 0

C	0.41135	-1.61948	-0.40355
P	-0.00061	0.00087	-1.20893
C	1.19709	1.16669	-0.40309
C	1.96137	0.86327	0.73460
C	2.86304	1.79596	1.25677
C	3.01074	3.04768	0.65420
C	2.25762	3.36073	-0.48153
C	1.36772	2.42369	-1.01019
C	-1.60918	0.45369	-0.40259
C	-1.72951	1.26337	0.73793
C	-2.98860	1.57644	1.25978
C	-4.14590	1.08072	0.65422
C	-4.03944	0.27583	-0.48413

C	-2.78253	-0.02465	-1.01259
C	1.41495	-2.39478	-1.01126
C	1.78299	-3.63355	-0.48266
C	1.13645	-4.12978	0.65349
C	0.12572	-3.37714	1.25651
C	-0.23272	-2.13030	0.73443
H	1.85735	-0.10471	1.21455
H	3.44825	1.54249	2.13659
H	3.71166	3.77086	1.06135
H	2.37119	4.32825	-0.96256
H	0.80076	2.66864	-1.90519
H	-0.83962	1.65553	1.22020
H	-3.06252	2.20705	2.14163
H	-5.12303	1.32500	1.06115
H	-4.93377	-0.10772	-0.96730
H	-2.71032	-0.63498	-1.90964
H	1.90973	-2.02572	-1.90648
H	2.56435	-4.21505	-0.96405
H	1.41351	-5.09807	1.06055
H	-0.38580	-3.75784	2.13640
H	-1.01949	-1.55705	1.21466

3b-1'

Energy: -1255.601518

Number of Imaginary Frequencies: 0

N	-2.18418	2.95659	-1.81558
C	-2.88936	1.93771	-1.21156
C	-2.41301	1.72562	0.06523
C	-2.92610	0.78715	1.12918
C	-2.53116	-0.71740	1.09799
N	-1.26703	-1.04798	0.38679
C	-0.06809	-0.46783	0.56604
C	-1.24613	3.45359	-0.93265
C	-1.36397	2.70214	0.26852
C	-0.53846	3.03928	1.35931
C	0.36631	4.08670	1.22511
C	0.47436	4.80848	0.01466
C	-0.32874	4.50230	-1.07970
H	-3.70227	1.46410	-1.74142
H	-2.59088	1.17825	2.09427
H	-4.02083	0.82183	1.17790
H	-0.60846	2.50077	2.30058
H	0.99495	4.36395	2.06608
H	1.18335	5.62784	-0.05658

H	-0.25808	5.06846	-2.00402
H	-2.36959	3.31862	-2.73852
Ag	1.78640	-2.32694	-0.61362
C	-3.51139	-1.72103	0.41226
C	-4.25297	-1.20441	-0.81693
H	-4.78518	-2.03492	-1.28765
H	-4.98923	-0.44632	-0.53636
H	-3.56377	-0.77757	-1.54873
C	-4.44547	-2.38636	1.41280
H	-5.06152	-3.14151	0.91814
H	-3.88499	-2.86607	2.21976
H	-5.11285	-1.63696	1.85118
O	-2.58583	-2.77480	-0.09242
C	-1.35040	-2.31529	-0.17956
O	-0.42677	-2.95503	-0.68704
C	1.09720	-0.11320	0.61830
C	2.48920	0.23337	0.55328
C	2.92153	1.46764	0.03275
C	3.45582	-0.73218	0.94550
C	4.28673	1.71775	-0.10803
H	2.18753	2.21303	-0.25407
C	4.82047	-0.47733	0.76887
H	3.13707	-1.62119	1.49169
C	5.23518	0.74782	0.24183
H	4.61455	2.67391	-0.50426
H	5.55176	-1.21938	1.07388
H	6.29351	0.95433	0.11784
H	-2.40598	-1.04405	2.13818

3b-1

Energy: -2291.761261

Number of Imaginary Frequencies: 0

N	3.41487	-1.22357	2.76938
C	4.02824	-1.29767	1.53378
C	4.23229	-0.02919	1.03173
C	4.89581	0.41698	-0.24921
C	4.46445	-0.24107	-1.58122
N	3.00005	-0.46243	-1.65206
C	2.07107	0.51589	-1.64353
C	3.21711	0.09976	3.10648
C	3.71604	0.88325	2.02981
C	3.64116	2.28720	2.12439
C	3.08436	2.85994	3.26252
C	2.59772	2.05870	4.32002

C	2.65619	0.66980	4.25704
H	4.25653	-2.26515	1.11189
H	4.70052	1.48827	-0.36232
H	5.98869	0.33339	-0.18515
H	4.02396	2.92195	1.32984
H	3.03505	3.94124	3.34983
H	2.18658	2.53581	5.20486
H	2.29460	0.05407	5.07590
H	3.18821	-2.01771	3.34789
Ag	-0.26389	-1.05312	-0.77141
P	-2.50216	-0.63636	0.11022
C	-2.55182	0.71055	1.35444
C	-1.42619	0.92619	2.16622
C	-3.69397	1.50742	1.53550
C	-1.44693	1.91081	3.15587
H	-0.52842	0.32837	2.02913
C	-3.70962	2.49558	2.52343
H	-4.56674	1.36429	0.90590
C	-2.58971	2.69637	3.33570
H	-0.56796	2.06651	3.77395
H	-4.59714	3.10709	2.65645
H	-2.60597	3.46506	4.10273
C	-3.15155	-2.13711	0.94601
C	-3.94173	-2.06328	2.10413
C	-2.85616	-3.39539	0.39408
C	-4.43468	-3.23153	2.69225
H	-4.17050	-1.10200	2.55263
C	-3.35966	-4.55892	0.97804
H	-2.23412	-3.47097	-0.49471
C	-4.14852	-4.47828	2.12993
H	-5.04206	-3.16443	3.58992
H	-3.12872	-5.52507	0.53964
H	-4.53341	-5.38362	2.58960
C	-3.73603	-0.18634	-1.17299
C	-3.42233	0.85324	-2.06627
C	-4.96778	-0.84759	-1.28968
C	-4.33608	1.23410	-3.04900
H	-2.47037	1.37321	-1.99344
C	-5.87593	-0.46751	-2.28326
H	-5.22256	-1.65696	-0.61354
C	-5.56405	0.57258	-3.16104
H	-4.08727	2.04215	-3.73031
H	-6.82588	-0.98682	-2.36728
H	-6.27121	0.86520	-3.93134

C	4.95469	-1.68335	-1.92384
C	6.19142	-2.17193	-1.18611
H	6.36676	-3.22443	-1.42490
H	7.06656	-1.60367	-1.51575
H	6.10462	-2.06950	-0.10363
C	5.09366	-1.87297	-3.43616
H	5.25199	-2.92899	-3.66958
H	4.19999	-1.52997	-3.96647
H	5.95249	-1.30437	-3.80660
O	3.80639	-2.52471	-1.49067
C	2.69734	-1.79165	-1.45875
O	1.57599	-2.26883	-1.28256
C	1.35137	1.49859	-1.68169
C	0.51674	2.65897	-1.75430
C	0.21644	3.39831	-0.59170
C	0.01671	3.09443	-2.99970
C	-0.56840	4.54732	-0.67824
H	0.60627	3.06888	0.36604
C	-0.76767	4.24448	-3.07527
H	0.25568	2.53125	-3.89649
C	-1.06158	4.97192	-1.91652
H	-0.79313	5.11352	0.22041
H	-1.14266	4.57850	-4.03806
H	-1.66954	5.86949	-1.97957
H	4.75623	0.42634	-2.39730

3b-2'

Energy: -1255.602165

Number of Imaginary Frequencies: 0

N	1.91962	-1.00475	2.07836
C	0.69010	-0.98720	1.57586
C	0.71173	-1.33458	0.12688
C	-0.34026	-2.35510	-0.36667
C	-1.69087	-1.70319	-0.67357
N	-1.87353	-0.42954	0.05415
C	-0.93250	0.57837	-0.02140
C	0.38708	0.19246	-0.11930
C	1.48221	1.18819	-0.29801
C	2.25524	1.20486	-1.47175
C	3.24172	2.17387	-1.66274
C	3.47763	3.14168	-0.68115
C	2.71778	3.13758	0.49143
C	1.72880	2.16801	0.68002
C	2.85681	-1.46981	1.11905

C	2.15758	-1.72705	-0.06817
C	2.84203	-2.25348	-1.15837
C	4.21817	-2.48803	-1.03523
C	4.89750	-2.20075	0.15659
C	4.22142	-1.68212	1.26667
H	-0.17929	-0.76453	2.17819
H	0.03677	-2.82883	-1.27702
H	-0.42699	-3.14302	0.38690
H	-1.71209	-1.45452	-1.74401
H	2.07025	0.46834	-2.24779
H	3.82073	2.17836	-2.58138
H	4.24508	3.89486	-0.83141
H	2.89364	3.88667	1.25808
H	1.13724	2.17308	1.59238
H	2.33364	-2.47186	-2.09289
H	4.76797	-2.89660	-1.87694
H	5.96369	-2.39062	0.22507
H	4.74184	-1.46913	2.19505
H	2.16843	-0.66421	2.99974
Ag	-1.77120	2.57881	0.03887
C	-3.00822	-2.44779	-0.32388
C	-2.96937	-3.27759	0.95907
H	-3.99032	-3.55440	1.23360
H	-2.39776	-4.19939	0.81617
H	-2.53560	-2.71848	1.79415
C	-3.57660	-3.23152	-1.49953
H	-2.90569	-4.05655	-1.76200
H	-4.55042	-3.65474	-1.24020
H	-3.70200	-2.58934	-2.37556
O	-3.92432	-1.31453	-0.06855
C	-3.25229	-0.18472	0.19403
O	-3.76934	0.86935	0.50060

3b-2

Energy: -2291.747703

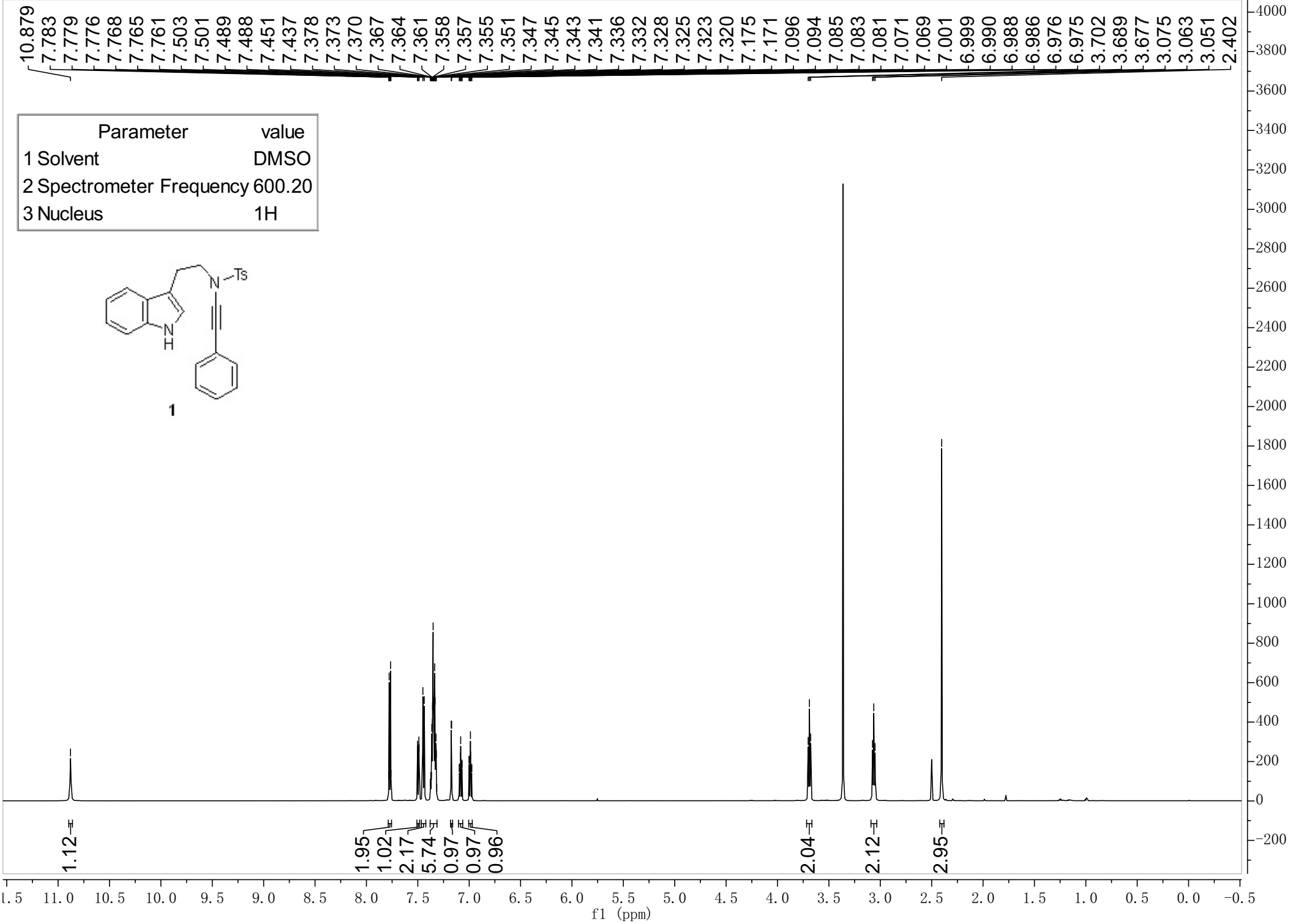
Number of Imaginary Frequencies: 0

N	3.89305	-1.23675	-2.10303
C	3.33955	-0.07220	-1.57110
C	4.04639	0.23894	-0.29011
C	4.46954	1.67478	0.03153
C	3.31755	2.51036	0.57885
N	1.99470	2.10860	0.02497
C	1.54013	0.84674	-0.05524
C	2.54353	-0.18113	-0.11795

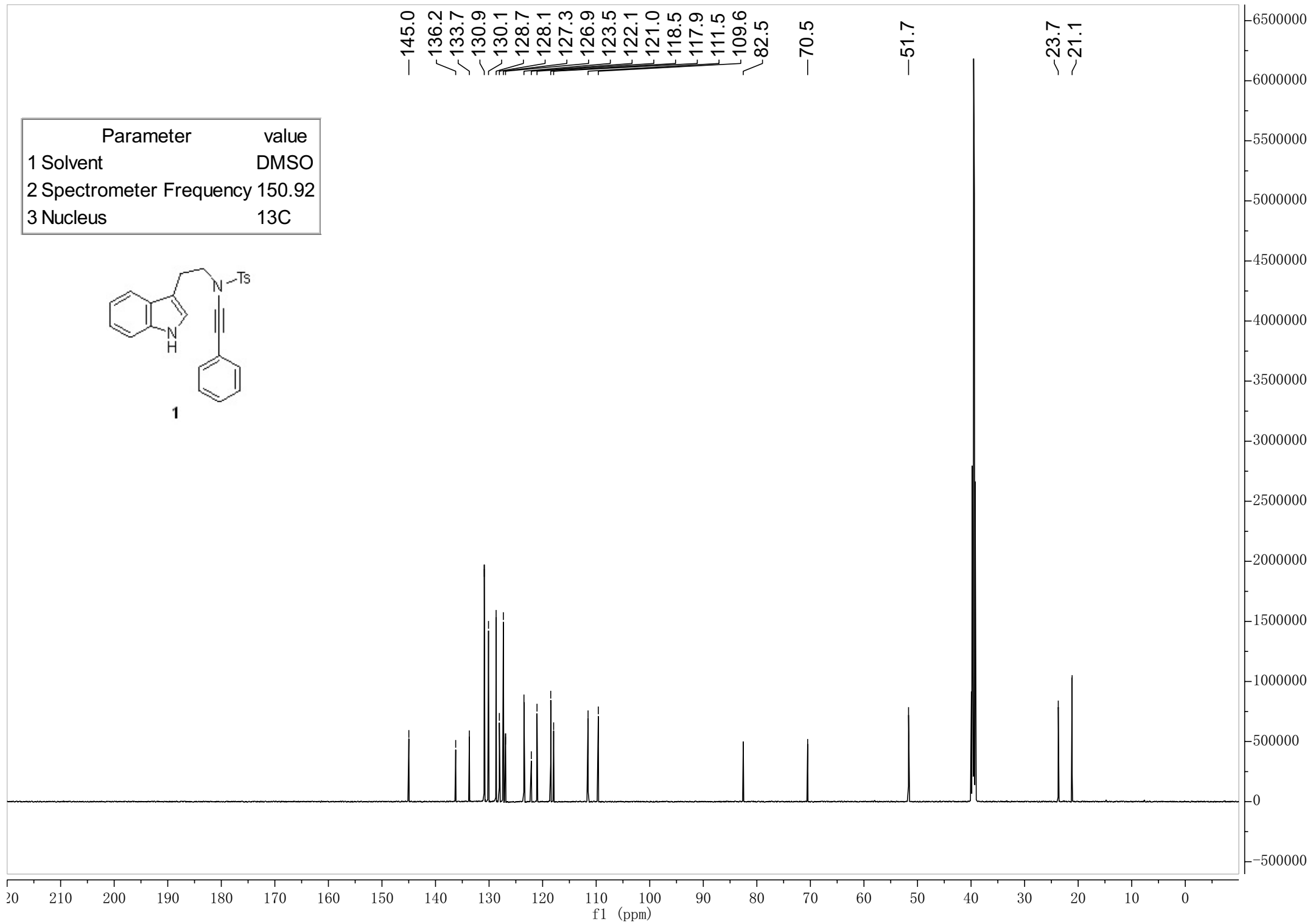
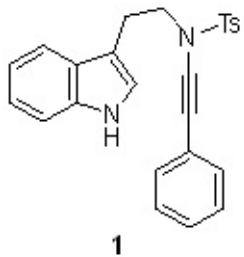
C	2.14189	-1.55885	0.33058
C	2.52466	-2.03402	1.59312
C	2.10809	-3.29152	2.03574
C	1.30101	-4.09119	1.22072
C	0.90968	-3.62555	-0.03771
C	1.33068	-2.36798	-0.47911
C	4.86859	-1.75368	-1.24221
C	5.04182	-0.87113	-0.15973
C	6.01680	-1.12850	0.80000
C	6.79521	-2.28566	0.67686
C	6.59119	-3.16939	-0.39258
C	5.62201	-2.91970	-1.36929
H	2.93701	0.67283	-2.24825
H	5.26829	1.65559	0.77912
H	4.89495	2.11696	-0.87380
H	3.24526	2.33689	1.66083
H	3.15445	-1.42052	2.23066
H	2.41515	-3.64645	3.01506
H	0.98155	-5.07103	1.56307
H	0.28075	-4.23911	-0.67618
H	1.01827	-2.01016	-1.45697
H	6.17039	-0.45573	1.63953
H	7.55832	-2.50379	1.41682
H	7.20187	-4.06362	-0.47026
H	5.47665	-3.60236	-2.20076
H	3.44920	-1.78209	-2.82758
C	3.31144	4.04144	0.33627
C	3.86298	4.48855	-1.01684
H	3.59733	5.53584	-1.18107
H	4.95345	4.40739	-1.04182
H	3.44875	3.90006	-1.84162
C	3.91188	4.82708	1.49422
H	4.98011	4.60420	1.58522
H	3.80249	5.90112	1.32361
H	3.41948	4.57471	2.43746
O	1.85966	4.33404	0.31751
C	1.12840	3.24930	0.05080
O	-0.06331	3.23872	-0.13054
Ag	-0.61715	0.47184	-0.11185
P	-3.01637	-0.09744	-0.04805
C	-3.50791	-1.42059	-1.22867
C	-4.27756	-2.52965	-0.84848
C	-3.09629	-1.29692	-2.56726
C	-4.63247	-3.49694	-1.79487

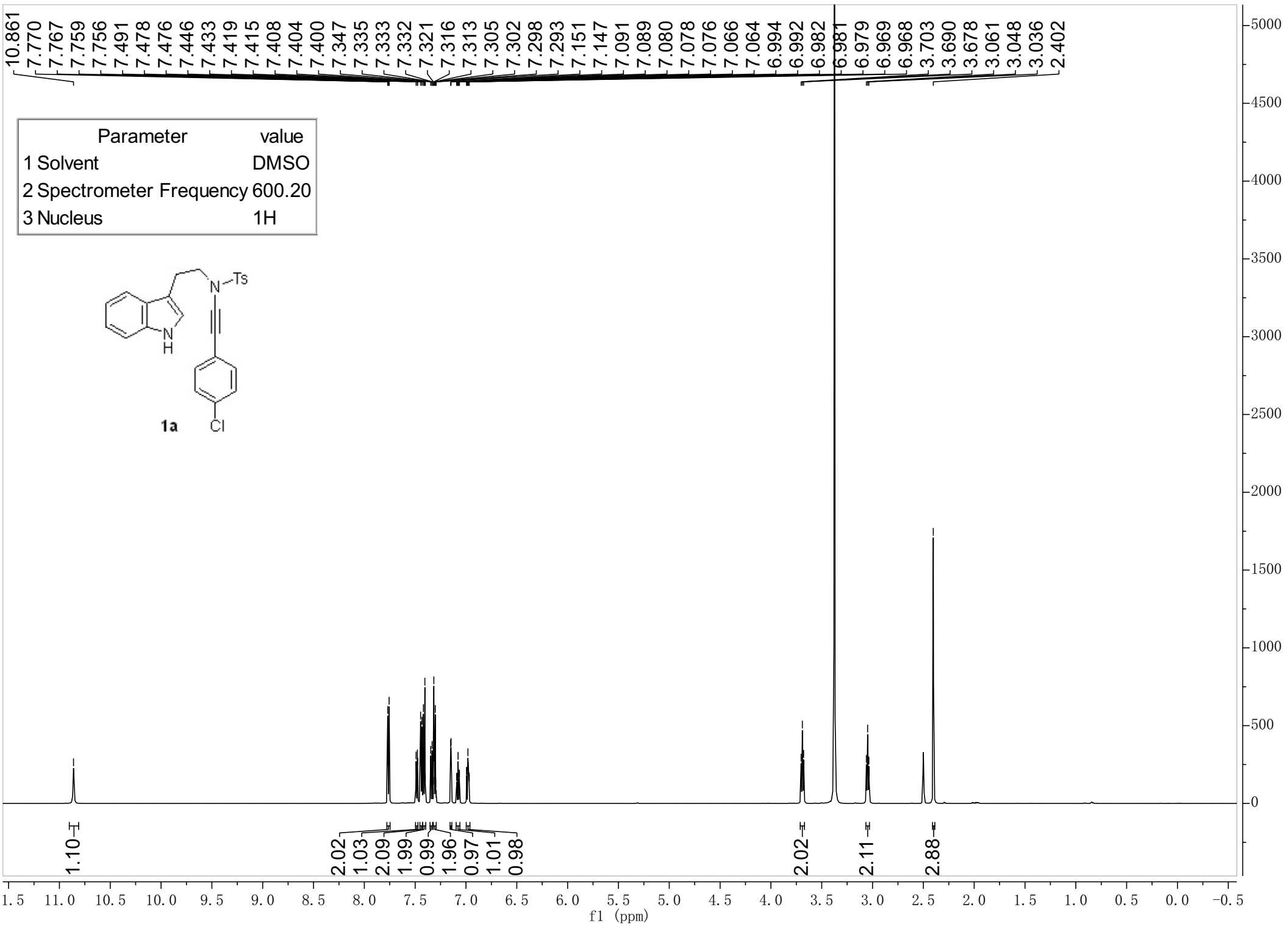
H	-4.60062	-2.64484	0.18110
C	-3.46069	-2.25807	-3.51054
H	-2.49967	-0.44207	-2.87717
C	-4.22826	-3.36281	-3.12484
H	-5.22955	-4.35122	-1.48956
H	-3.14543	-2.14669	-4.54391
H	-4.50886	-4.11314	-3.85799
C	-4.12579	1.31482	-0.42145
C	-3.64869	2.62226	-0.23123
C	-5.43898	1.11894	-0.88307
C	-4.48138	3.71661	-0.48029
H	-2.62747	2.79344	0.09746
C	-6.26497	2.21612	-1.13441
H	-5.81536	0.11495	-1.05480
C	-5.78876	3.51538	-0.93030
H	-4.10226	4.72328	-0.33227
H	-7.27772	2.05593	-1.49226
H	-6.43261	4.36692	-1.12965
C	-3.48570	-0.71484	1.61888
C	-2.63822	-1.64933	2.24098
C	-4.63596	-0.27761	2.29274
C	-2.94978	-2.15285	3.50450
H	-1.73426	-1.98722	1.73953
C	-4.93804	-0.77651	3.56391
H	-5.29433	0.45399	1.83614
C	-4.10039	-1.71571	4.16950
H	-2.29098	-2.87835	3.97247
H	-5.82889	-0.42811	4.07803
H	-4.33828	-2.10140	5.15636

Part 15: NMR spectra data

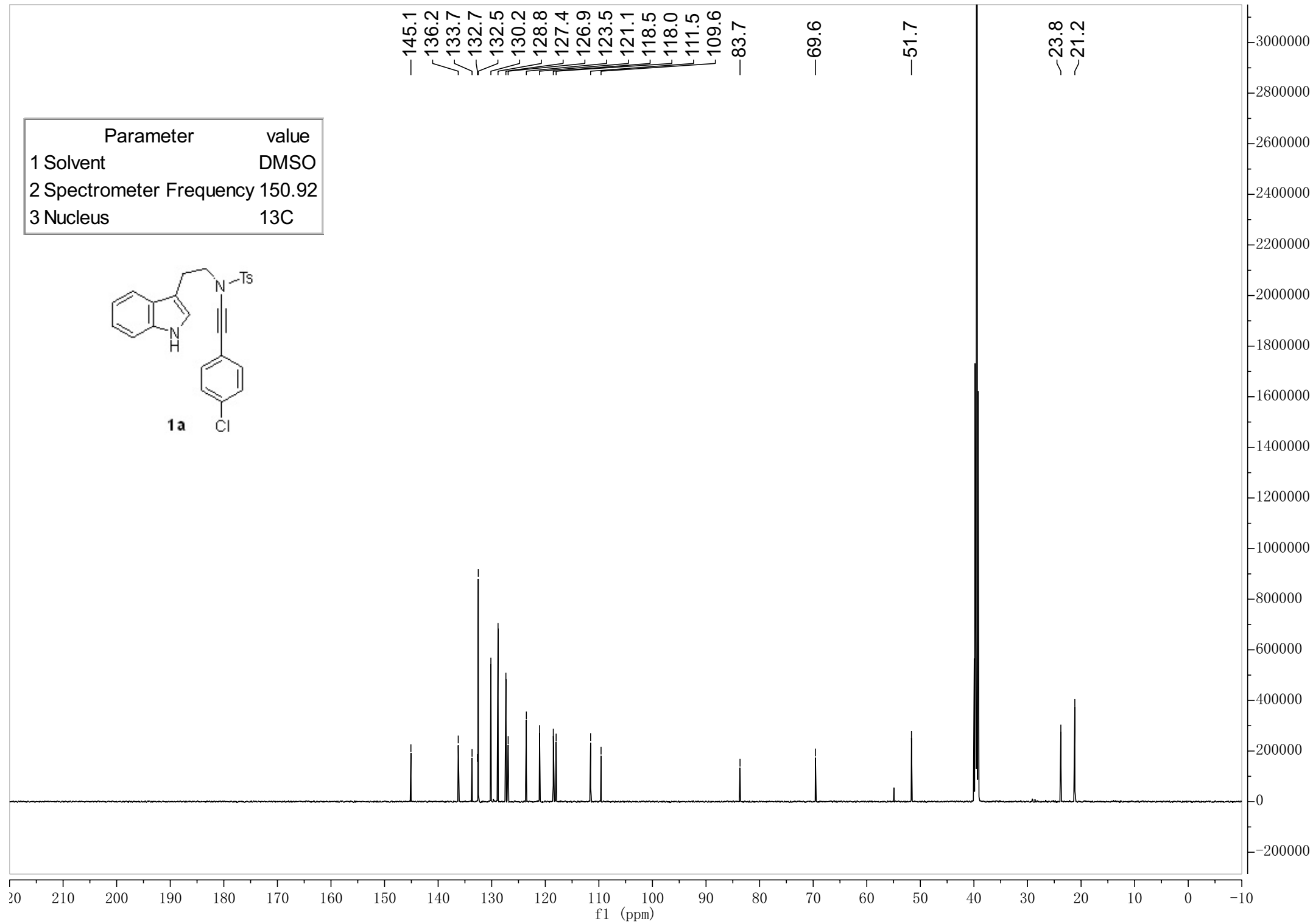
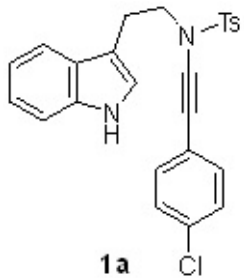


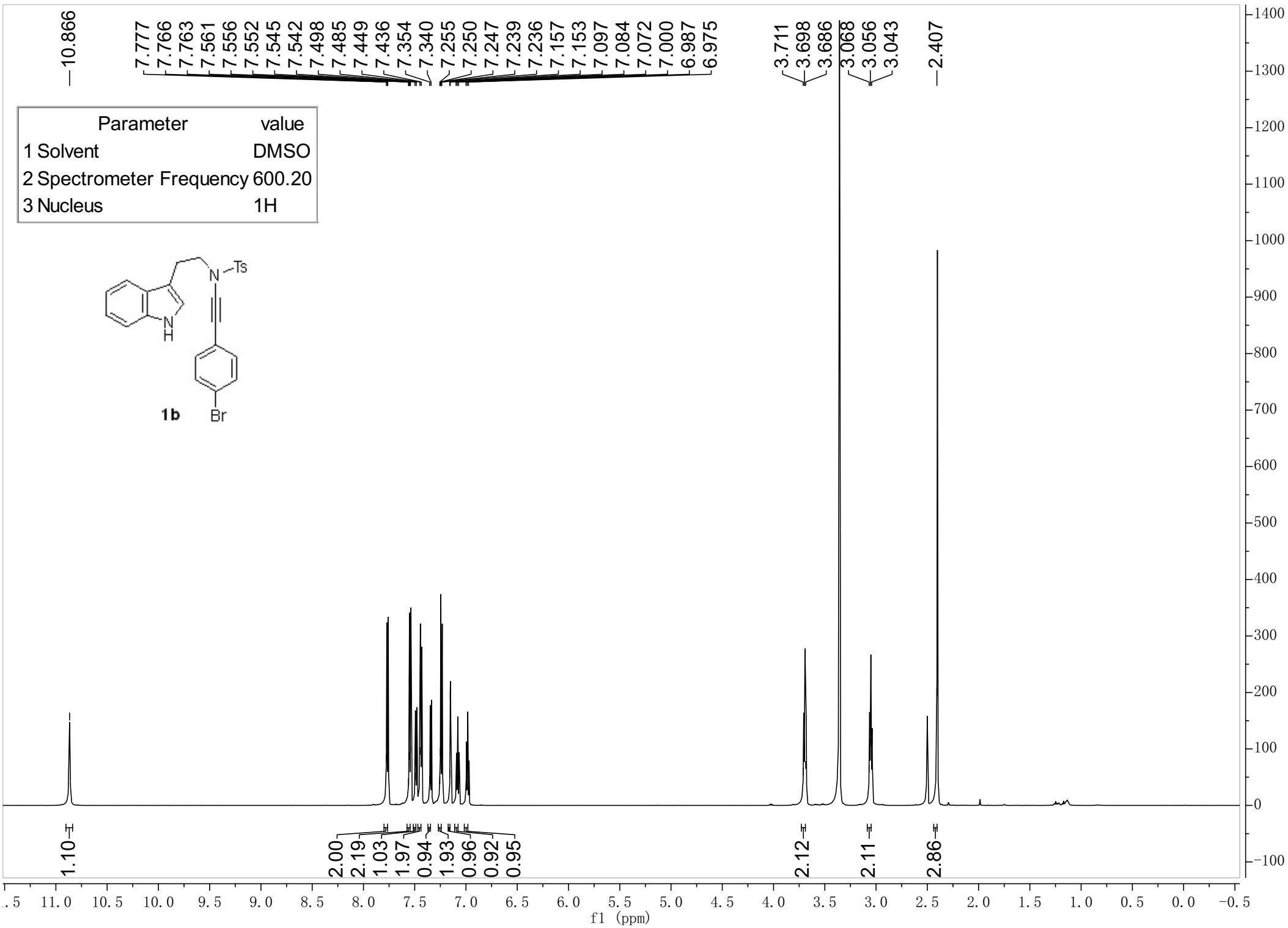
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



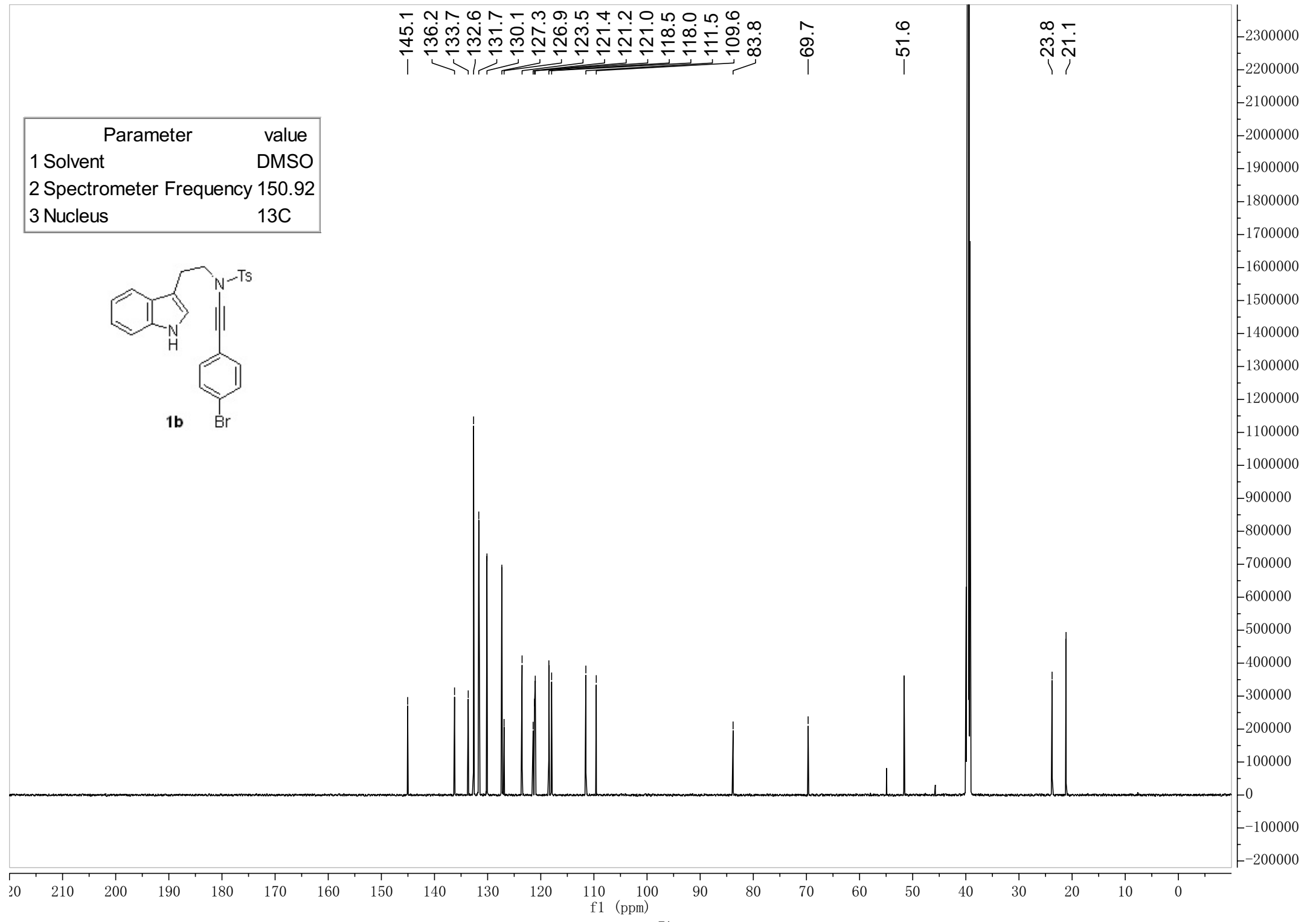
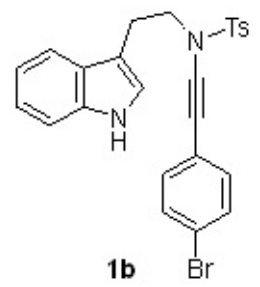


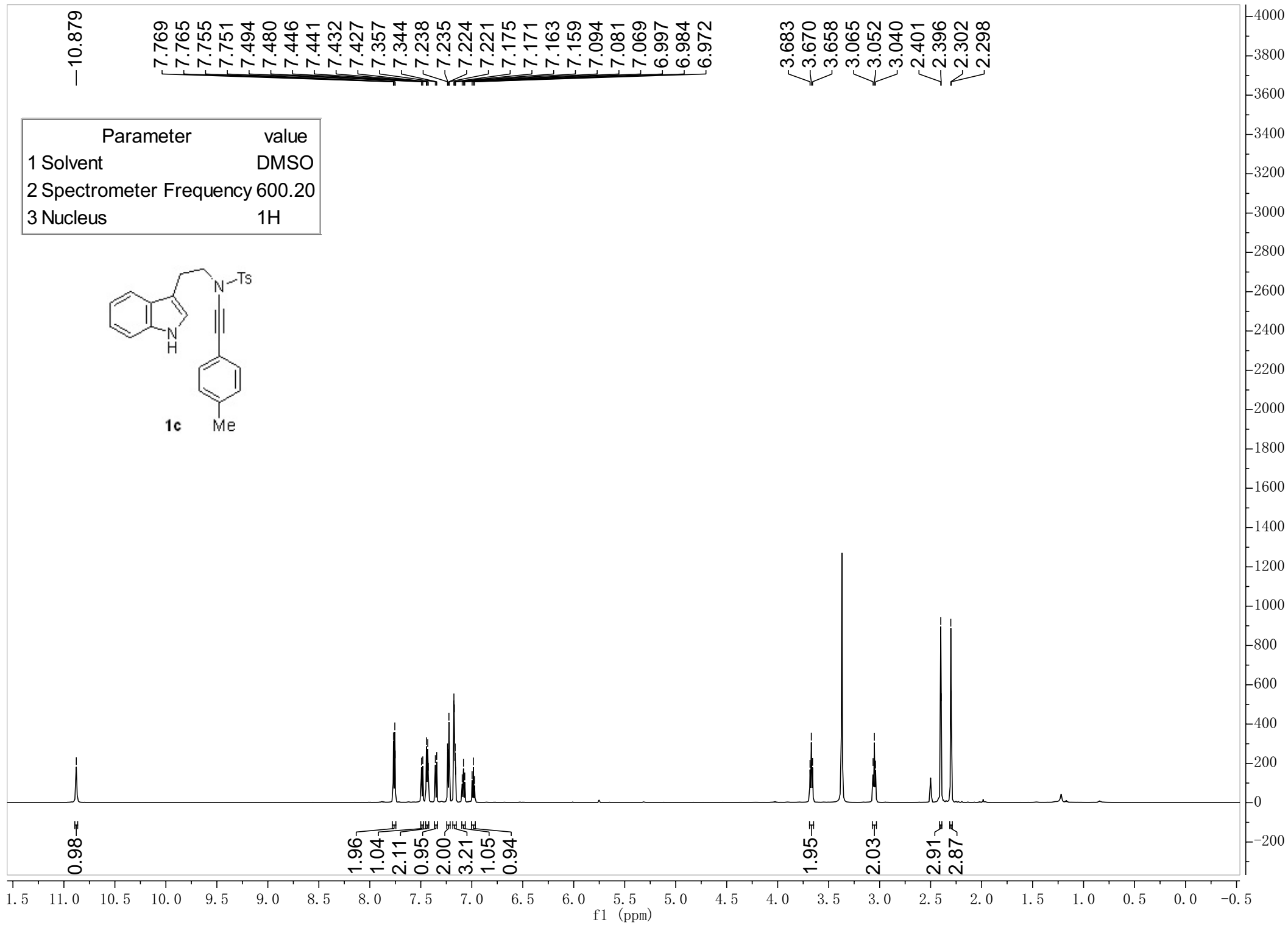
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



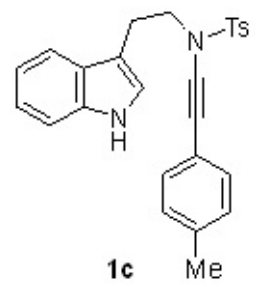


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



144.9
137.9
136.2
133.7
131.0
130.1
129.3
127.3
126.9
123.5
121.0
119.0
118.5
117.9
111.5
109.6

—81.8

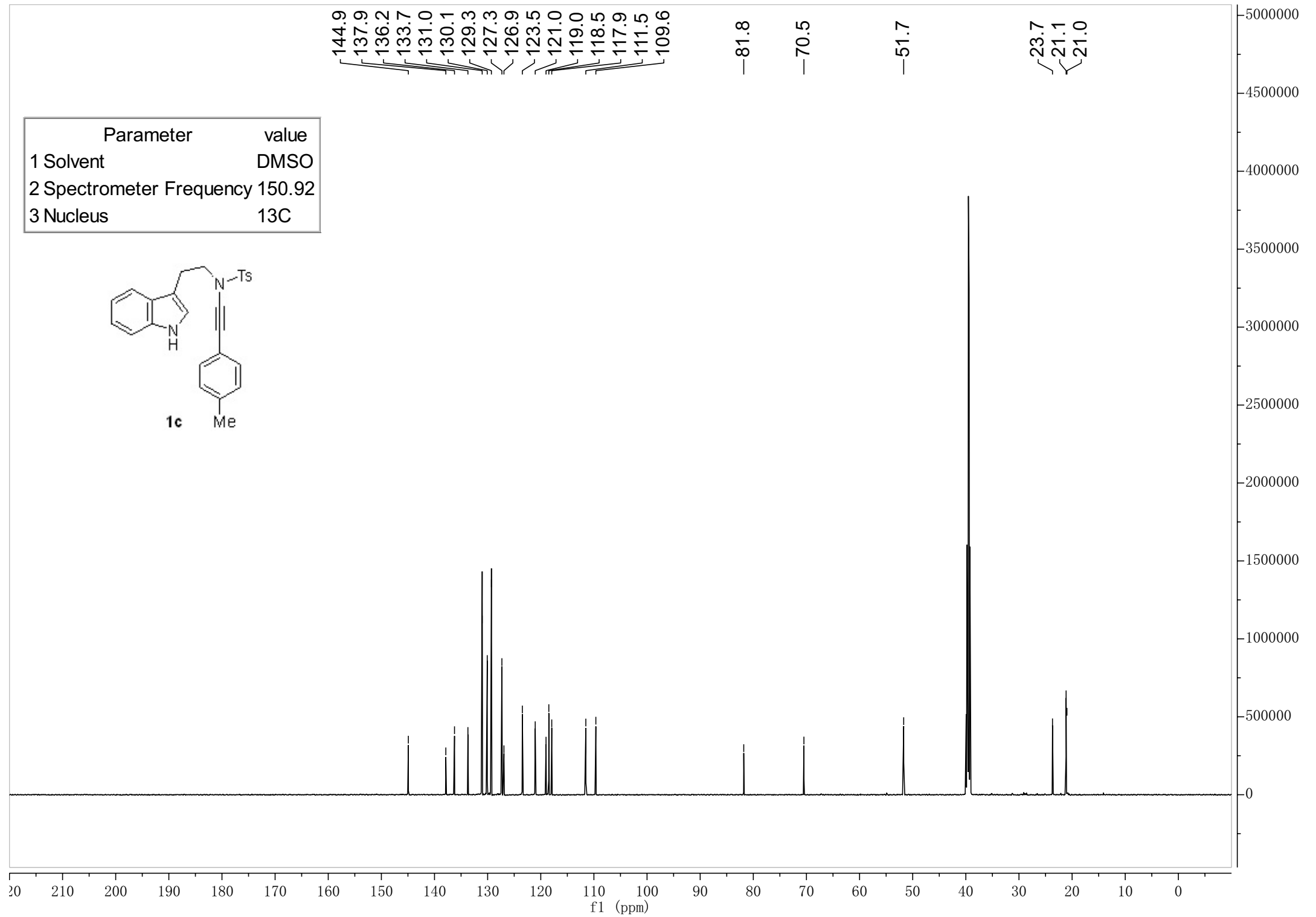
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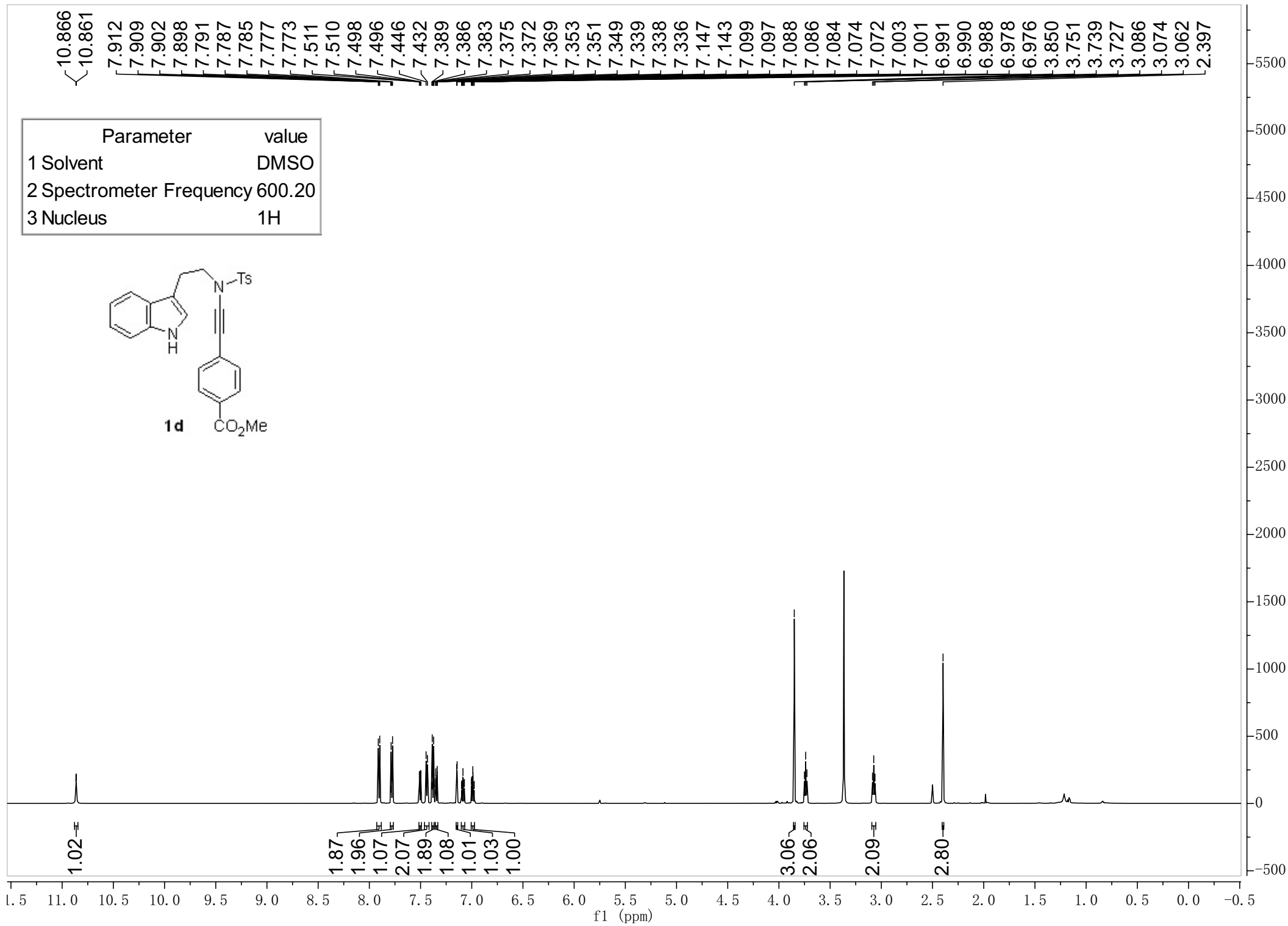
—51.7

23.7

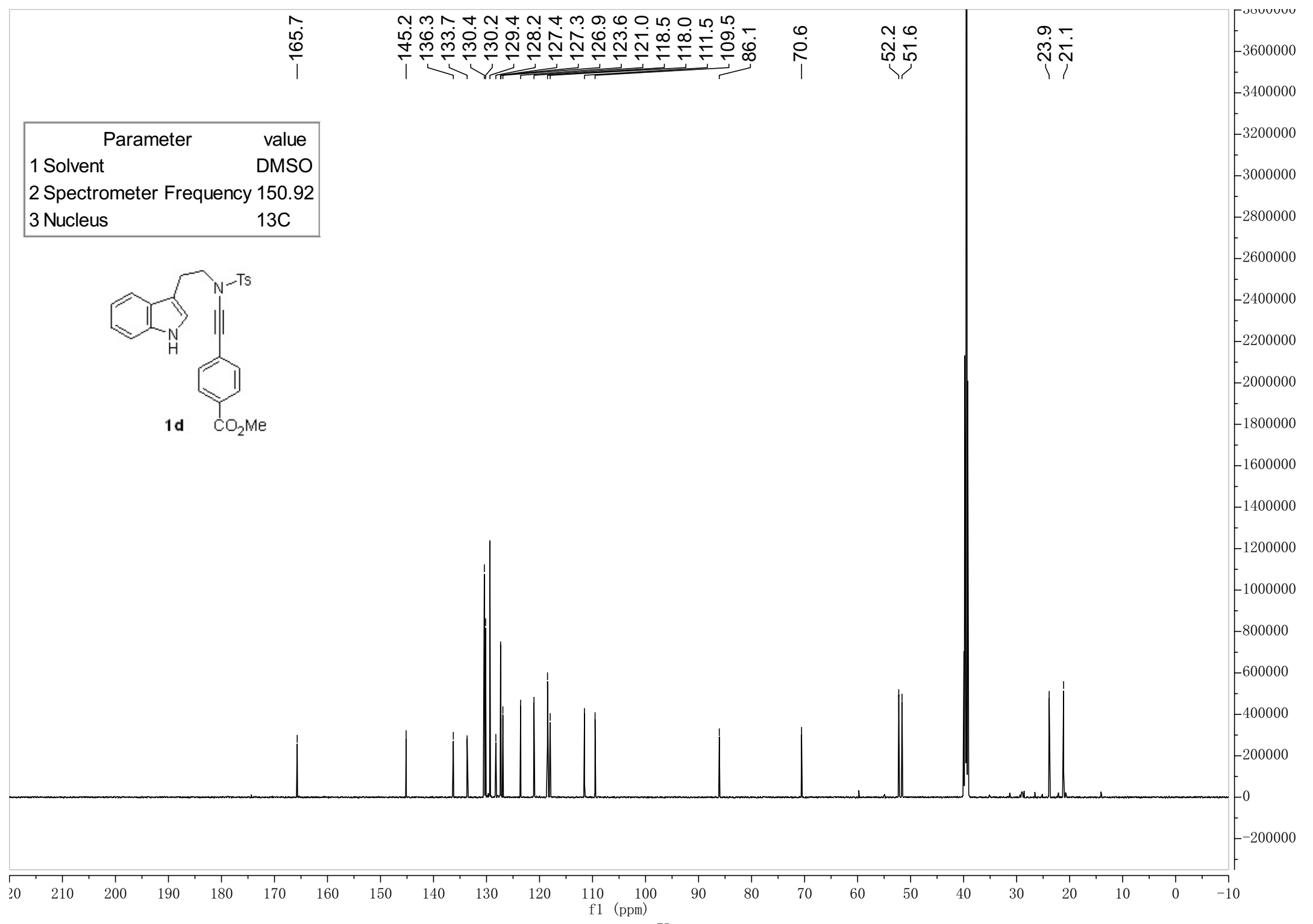
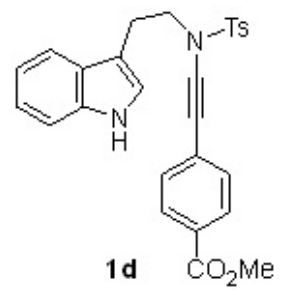
21.1

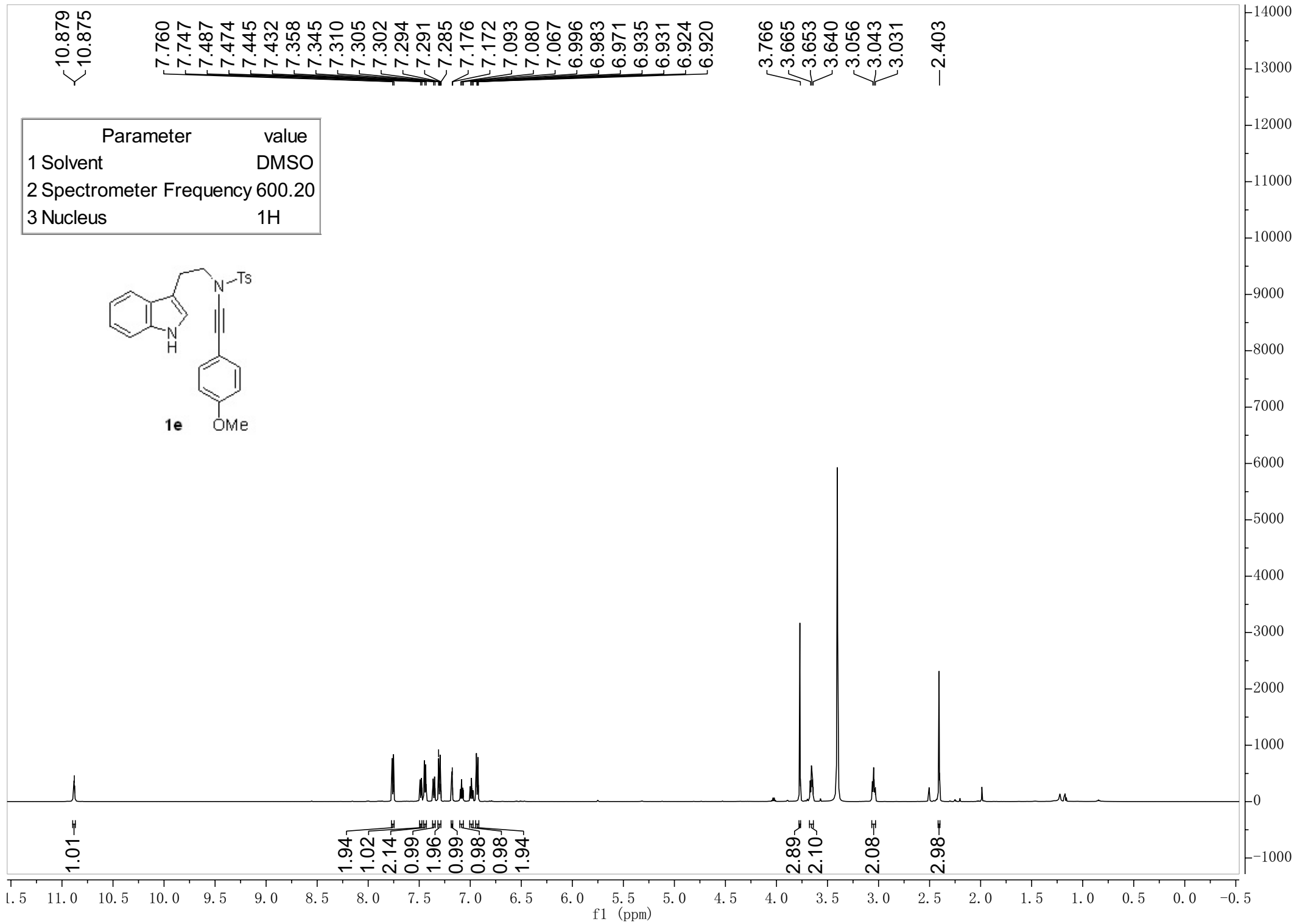
21.0





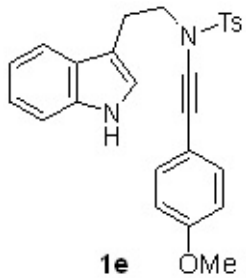
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



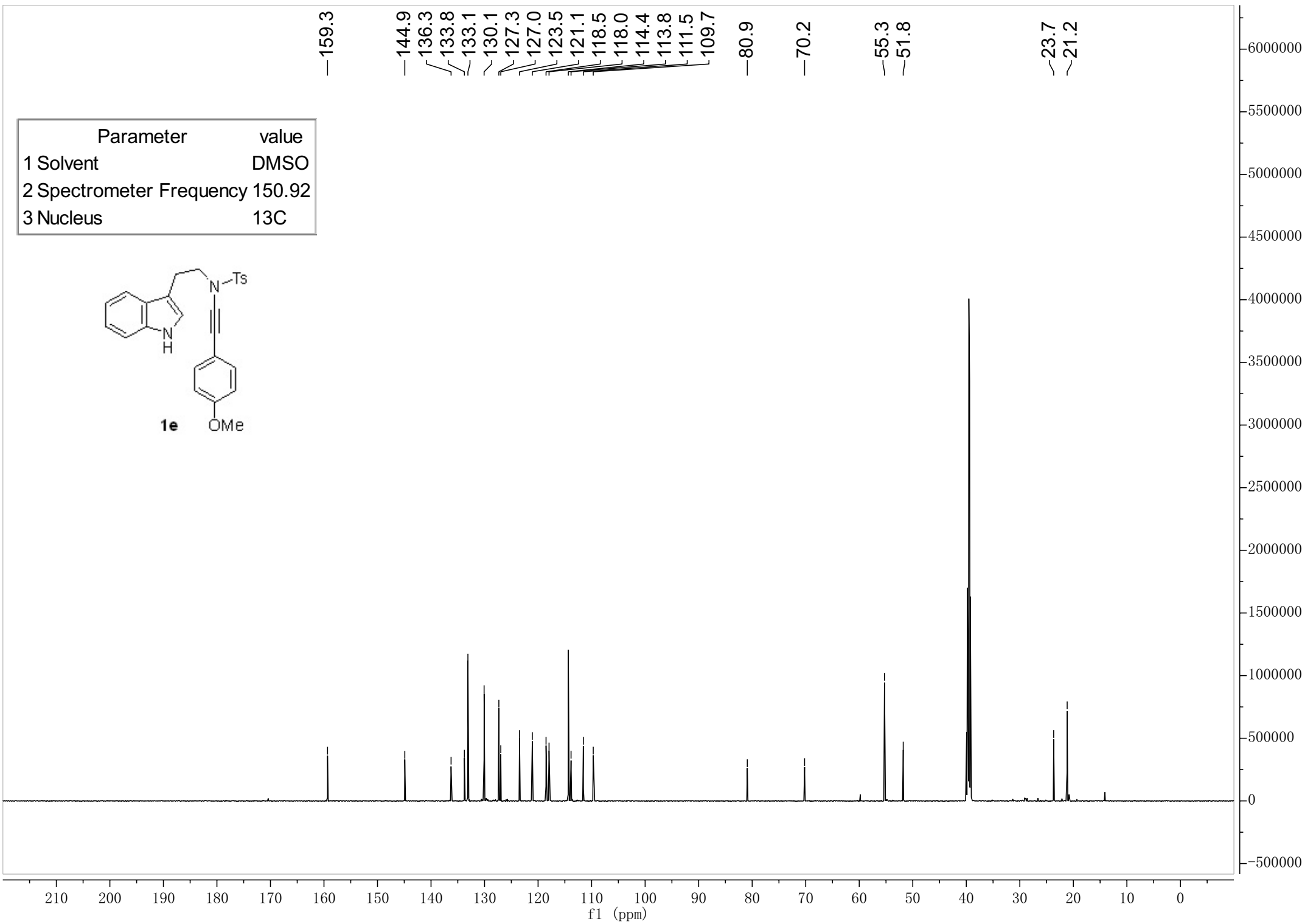


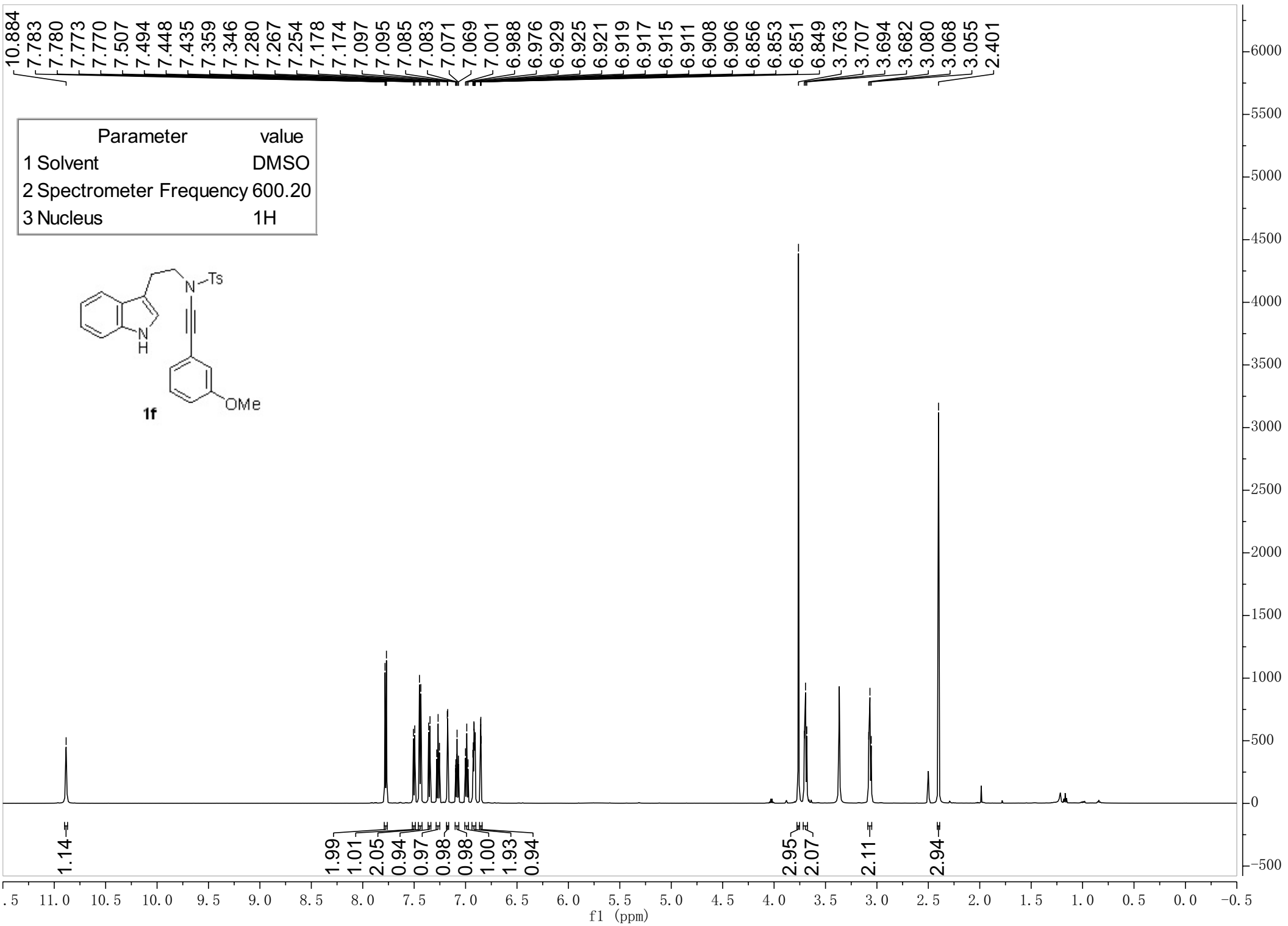
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

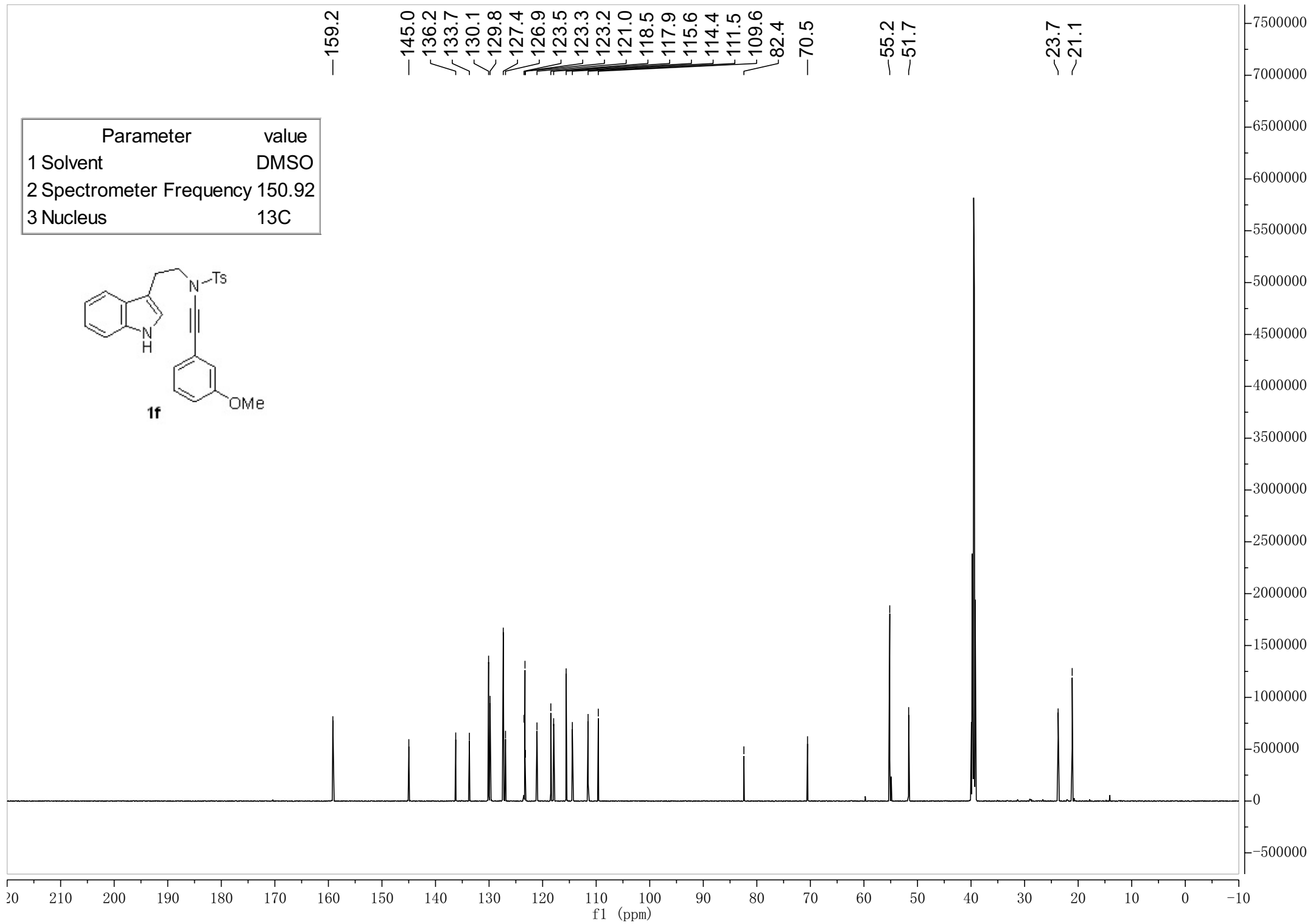
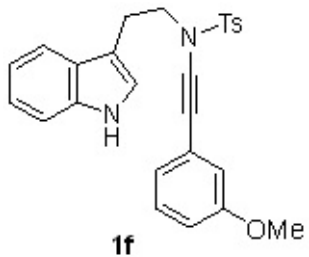


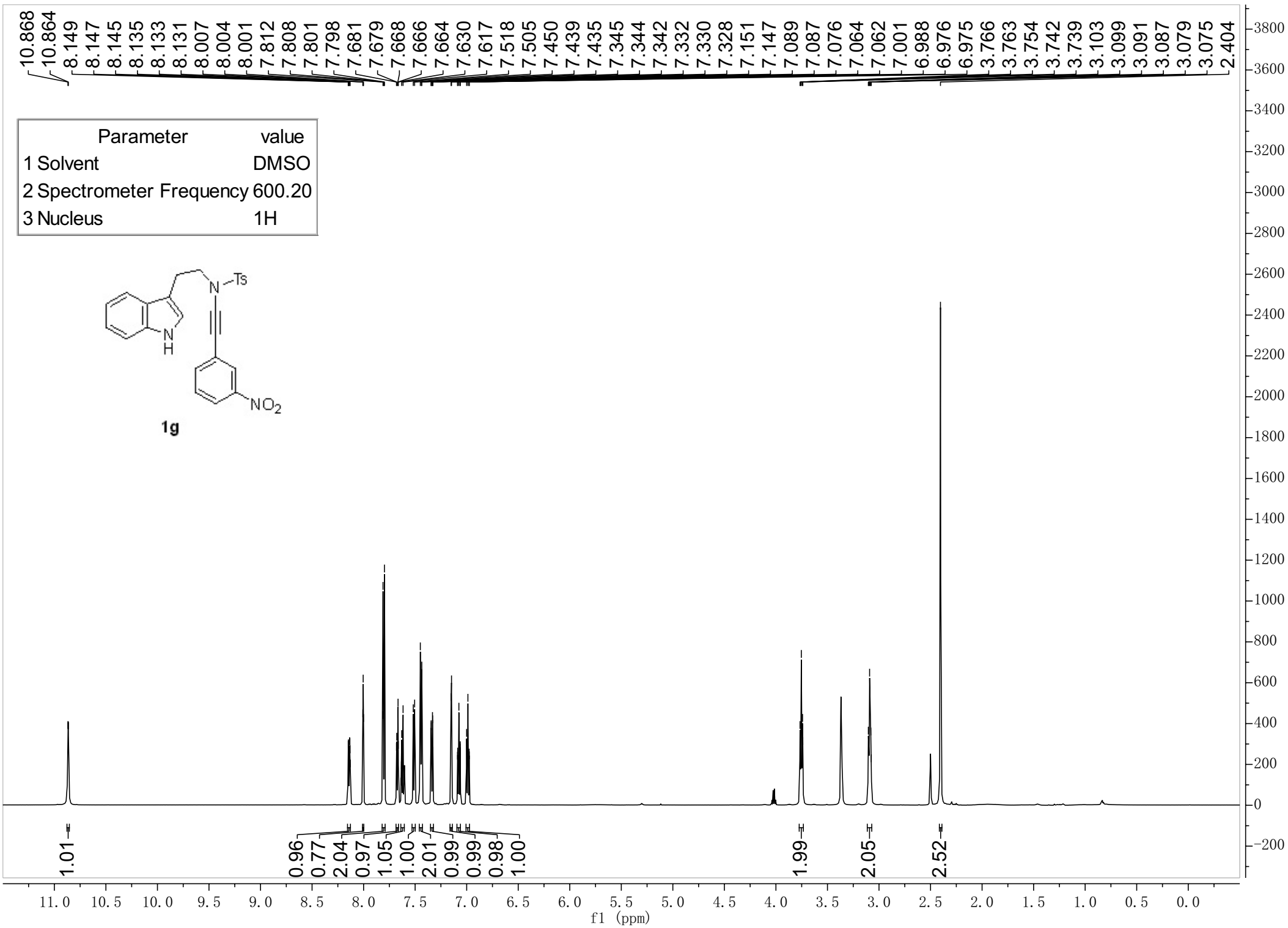
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 — 144.9
 — 136.3
 / 133.8
 \ 133.1
 / 130.1
 \ 127.3
 / 127.0
 \ 123.5
 / 121.1
 \ 118.5
 / 118.0
 \ 114.4
 / 113.8
 \ 111.5
 / 109.7
 — 80.9
 — 70.2
 — 55.3
 — 51.8
 ~ 23.7
 ~ 21.2



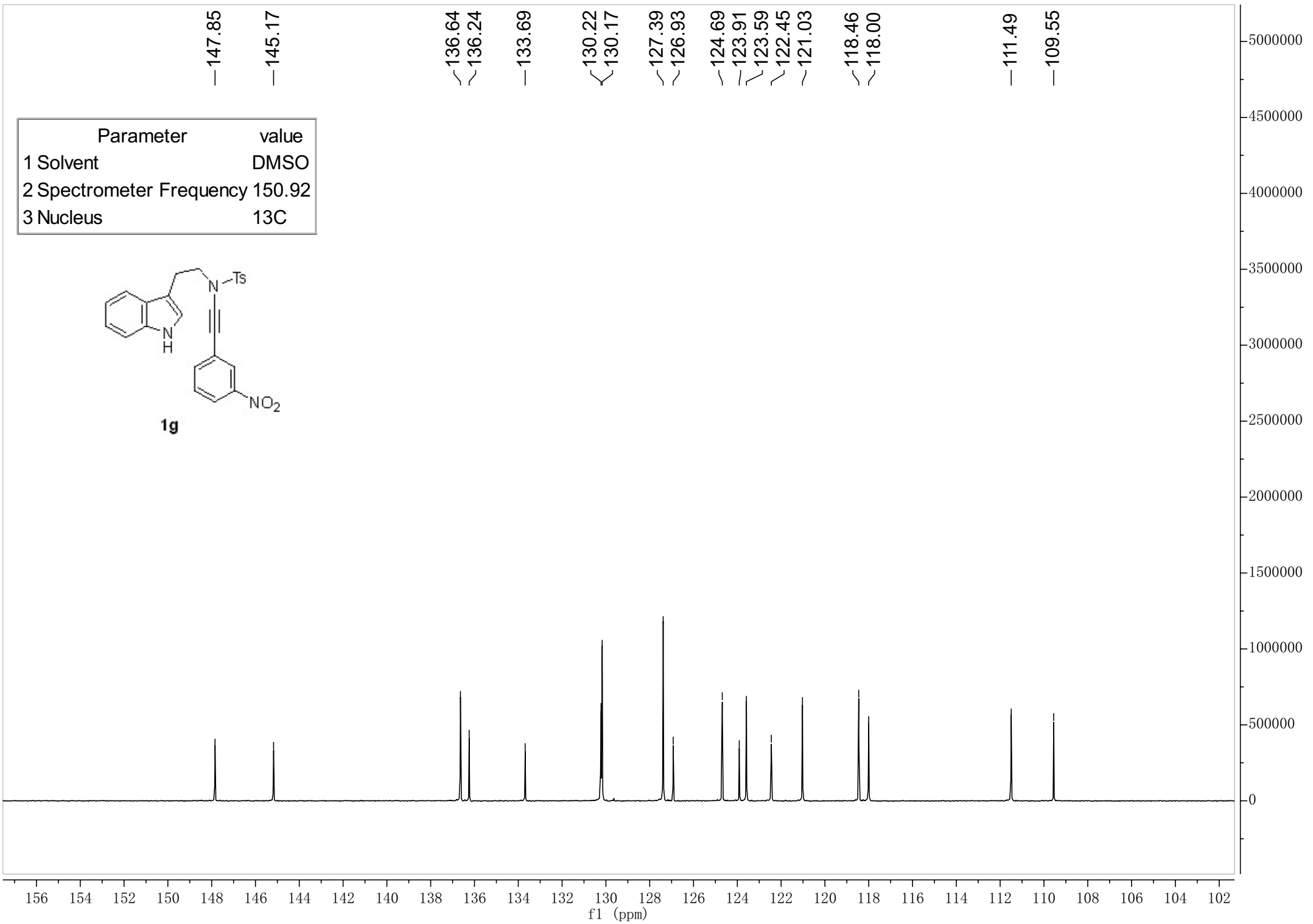
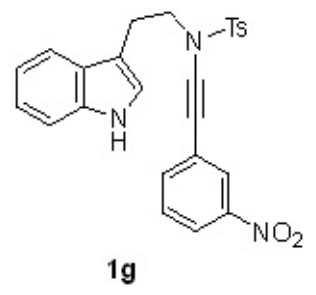


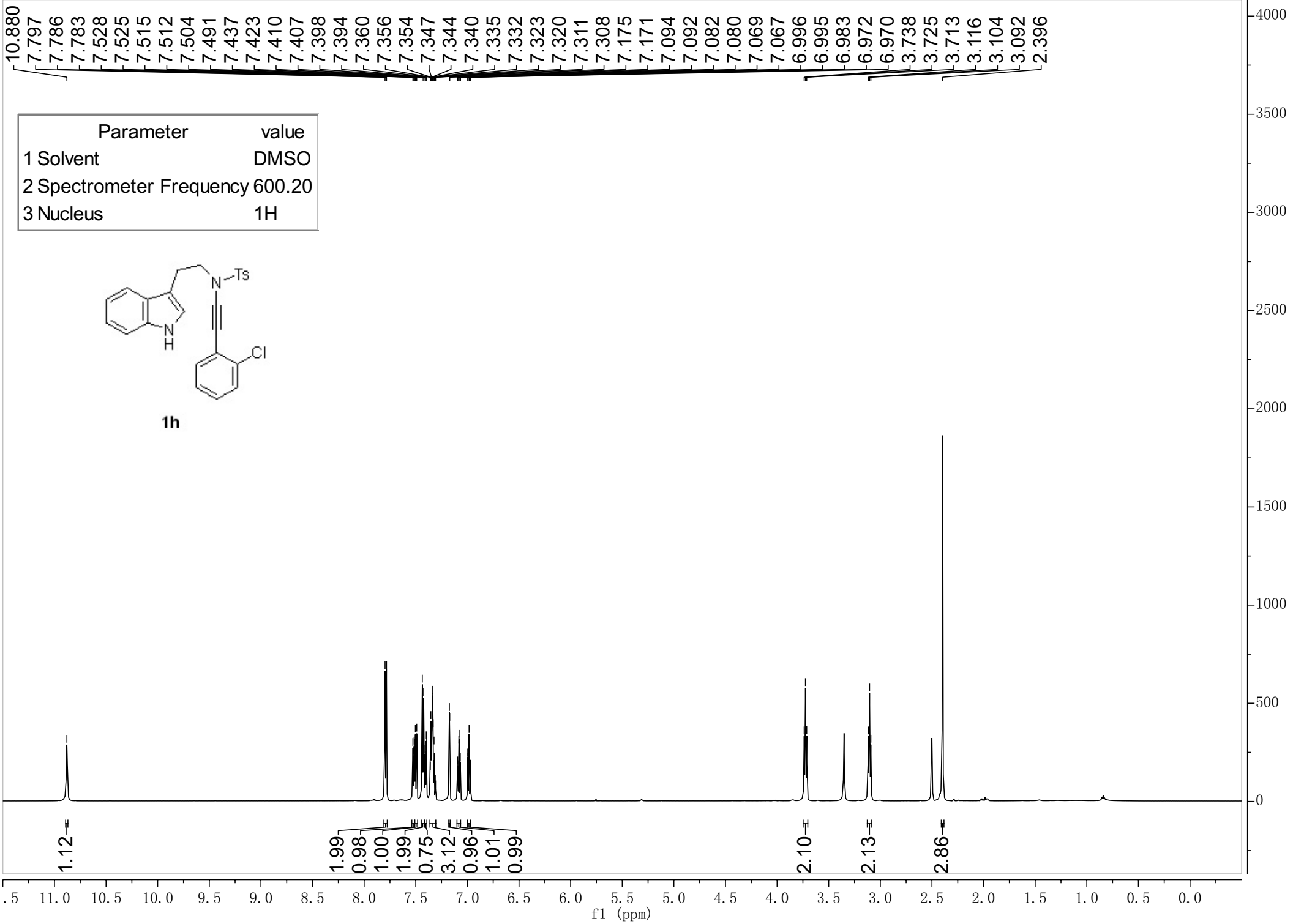
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C





145.10
 136.23
 133.63
 133.58
 132.44
 130.09
 129.32
 129.25
 127.33
 127.29
 126.88
 123.49
 122.05
 121.04
 118.48
 117.91
 111.52
 109.49
 —87.56

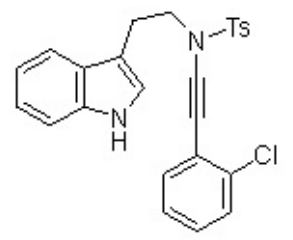
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—51.70

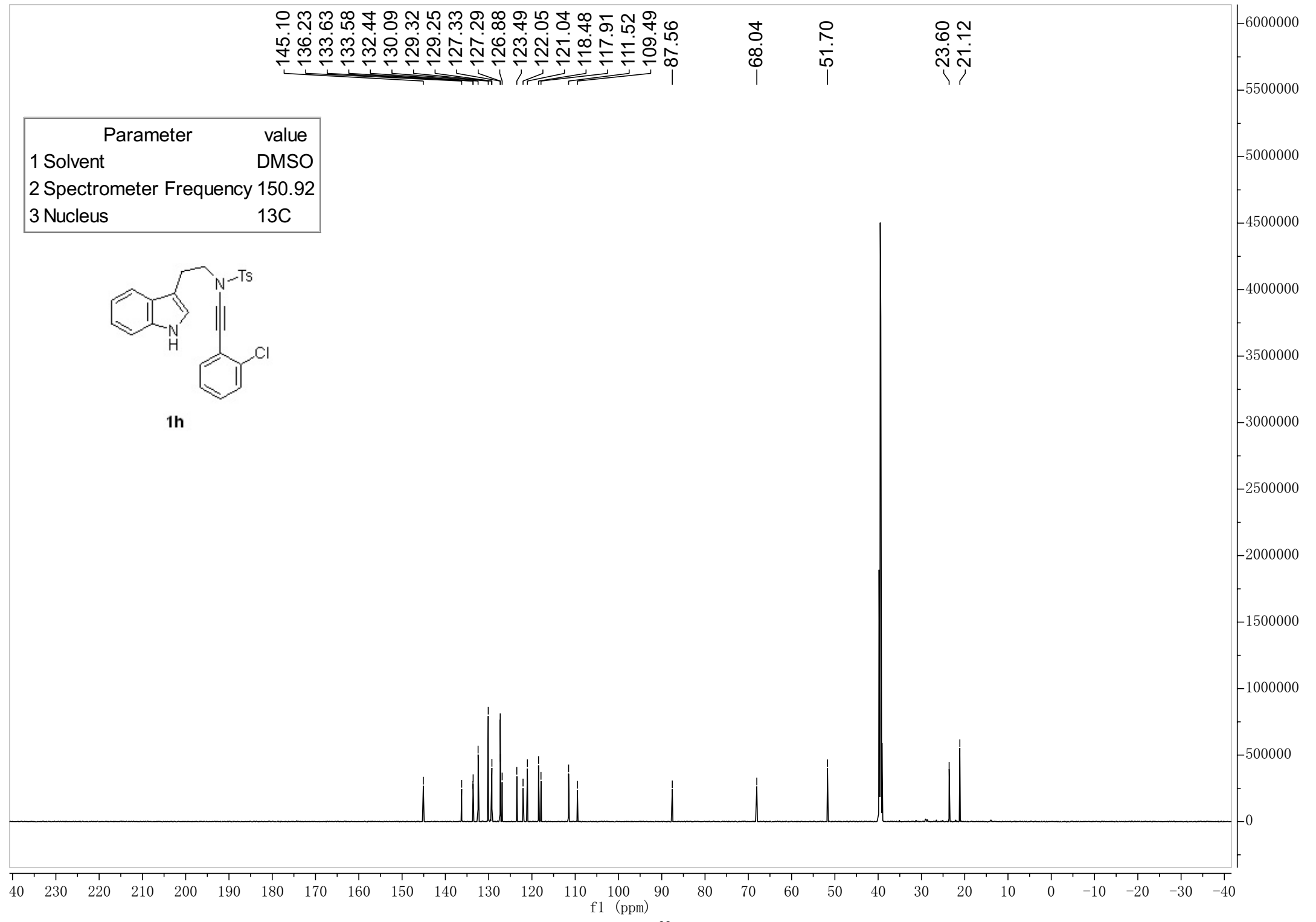
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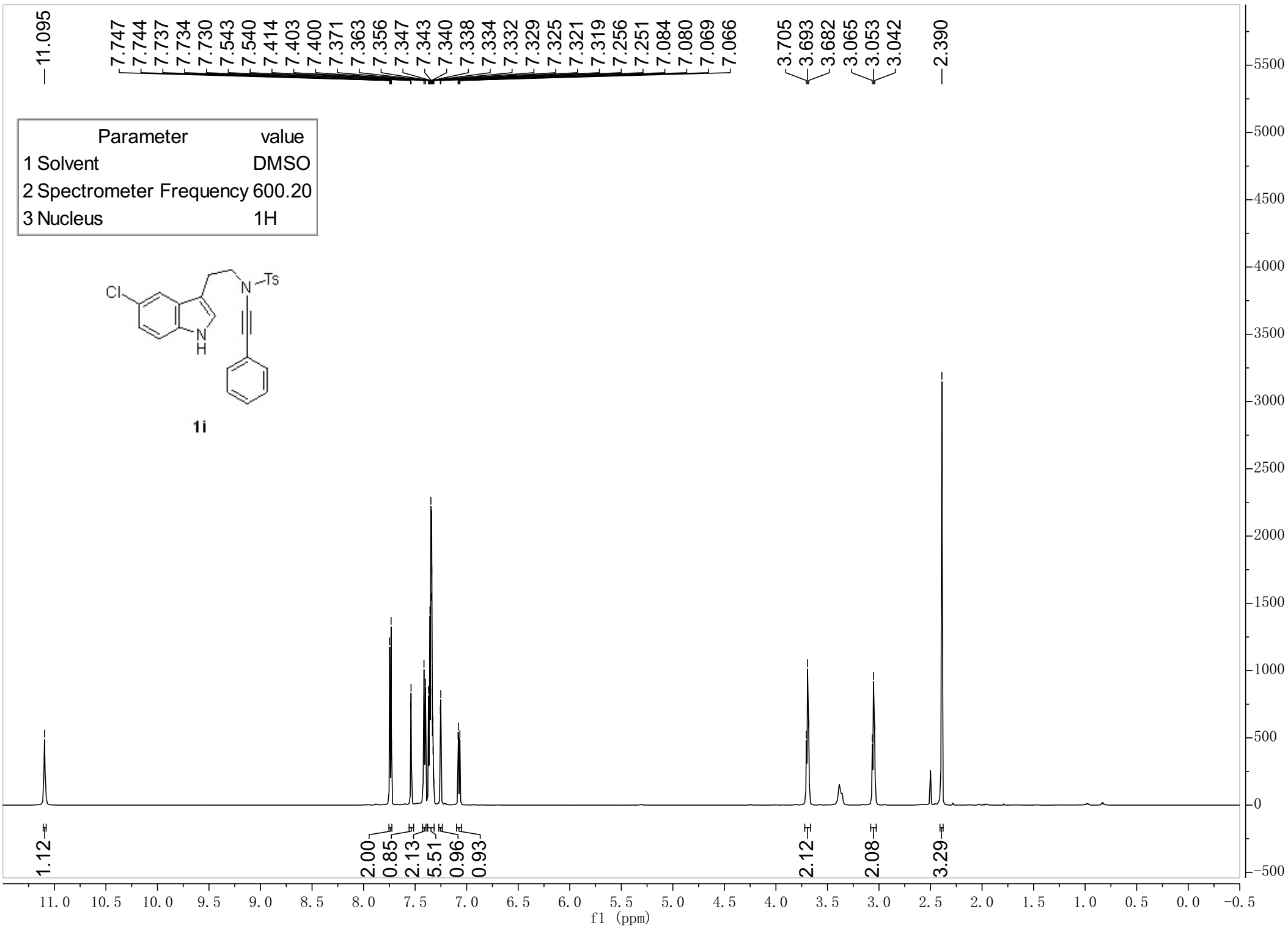
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Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

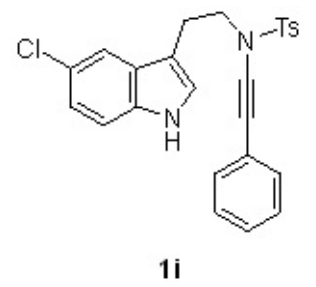


1h

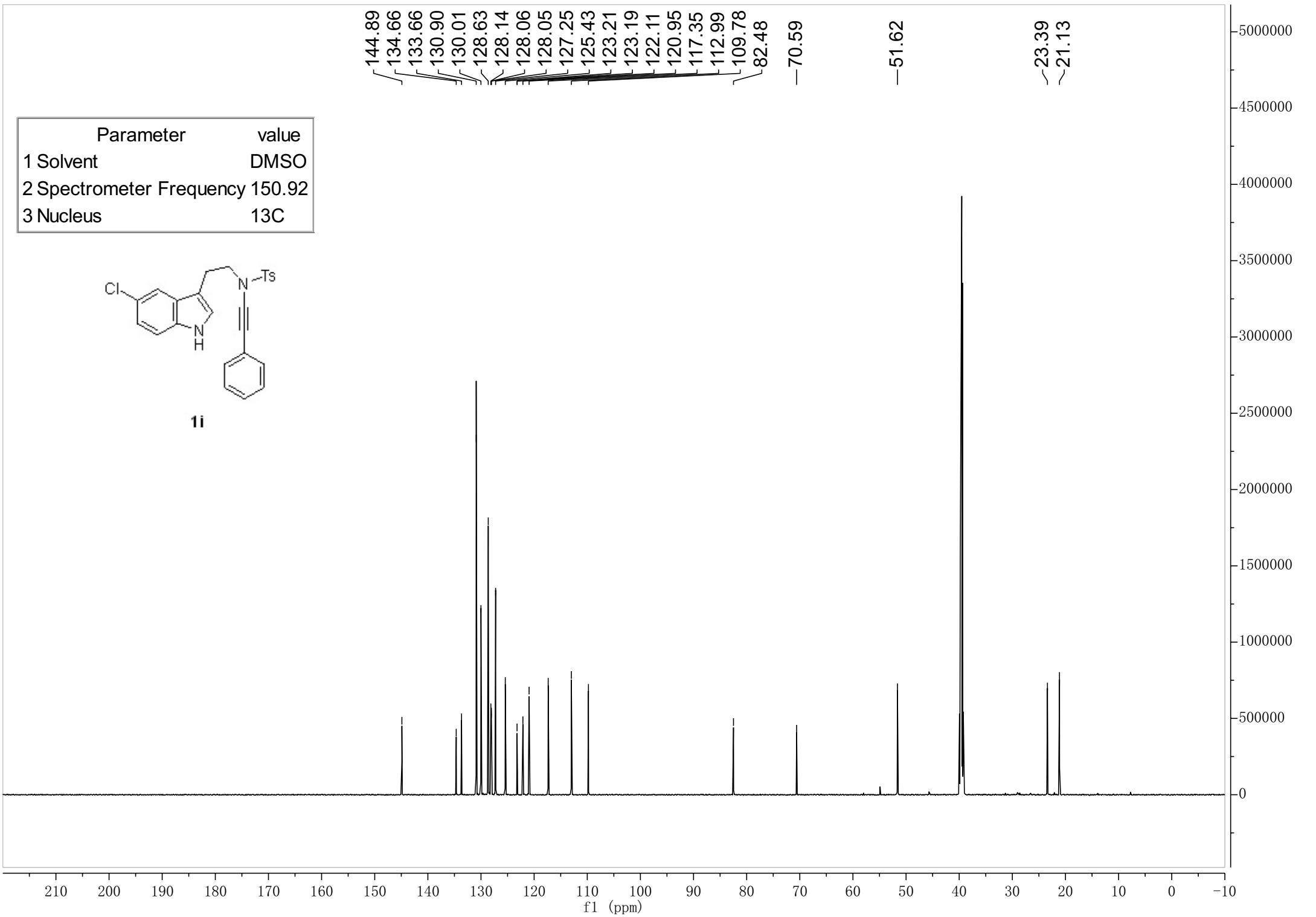




Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

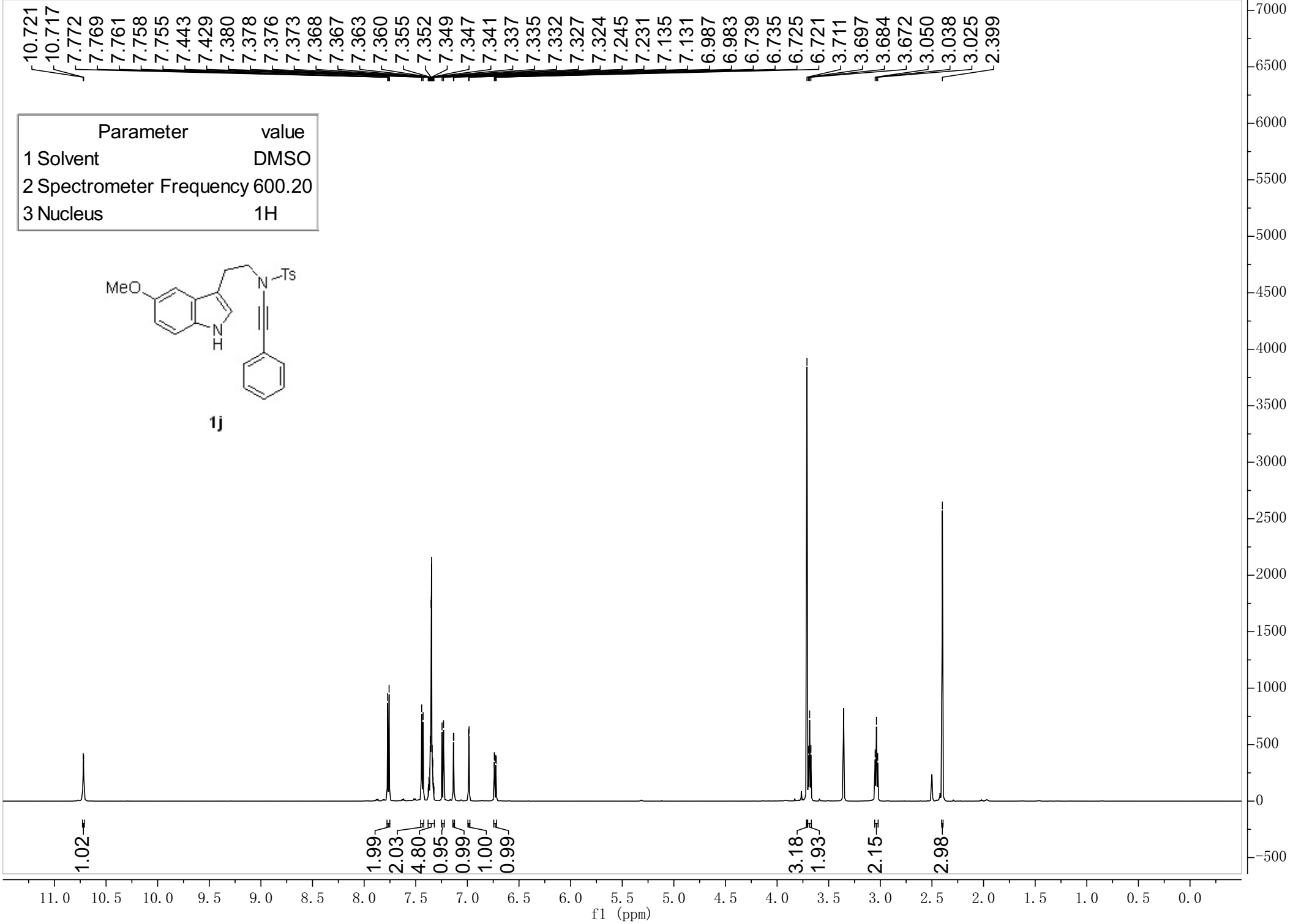
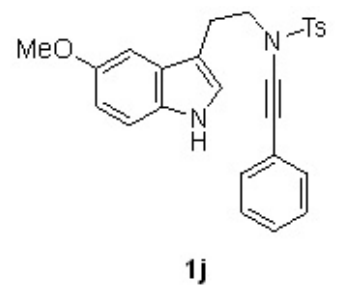


144.89
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 133.66
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 130.01
 128.63
 128.14
 128.06
 128.05
 127.25
 125.43
 123.21
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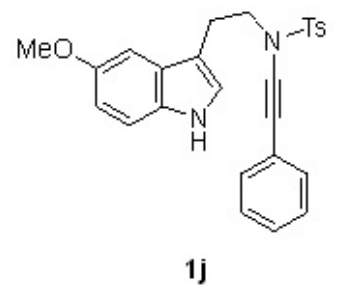


10.721
10.717
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7.758
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7.380
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7.376
7.373
7.368
7.367
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7.245
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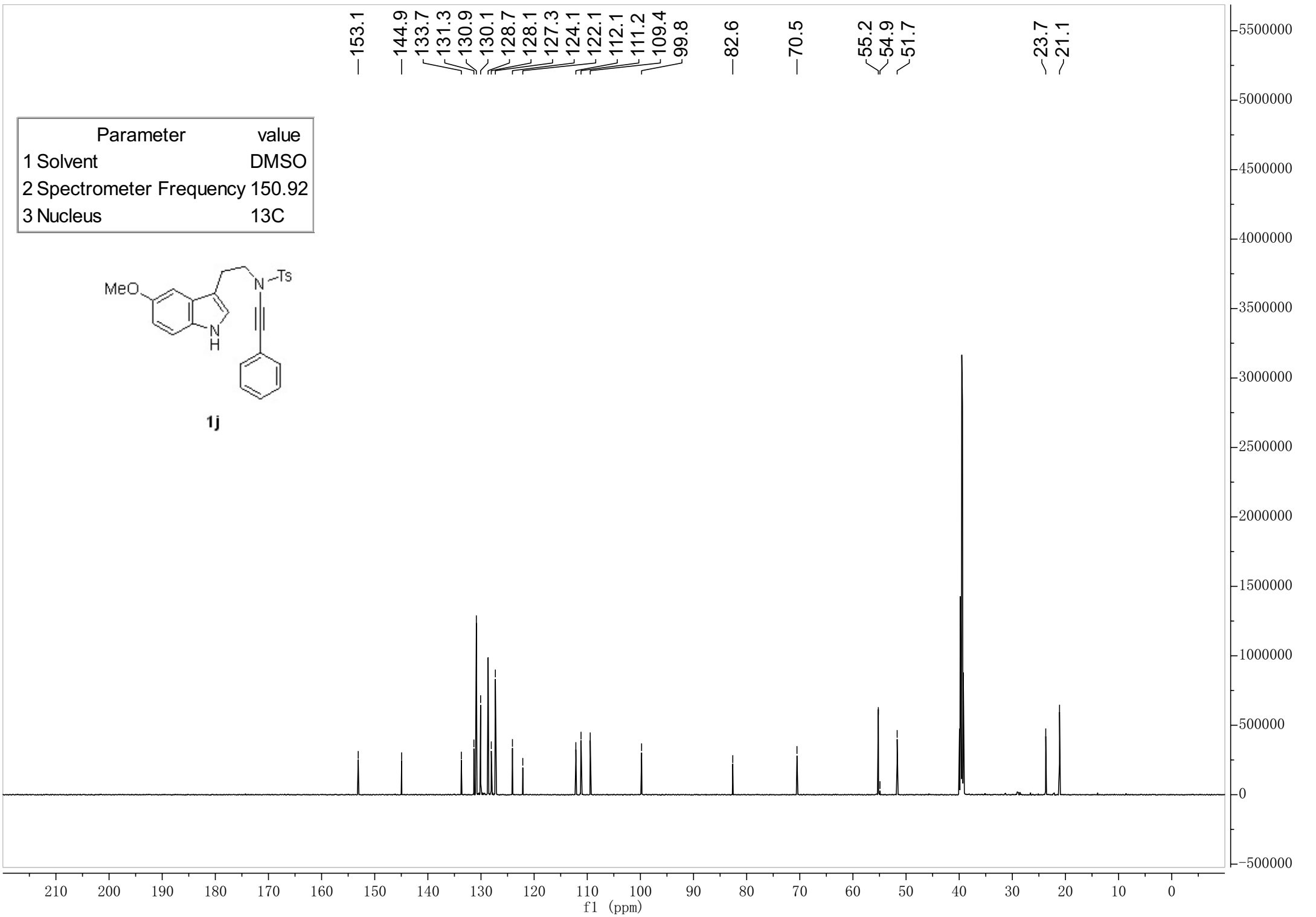
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

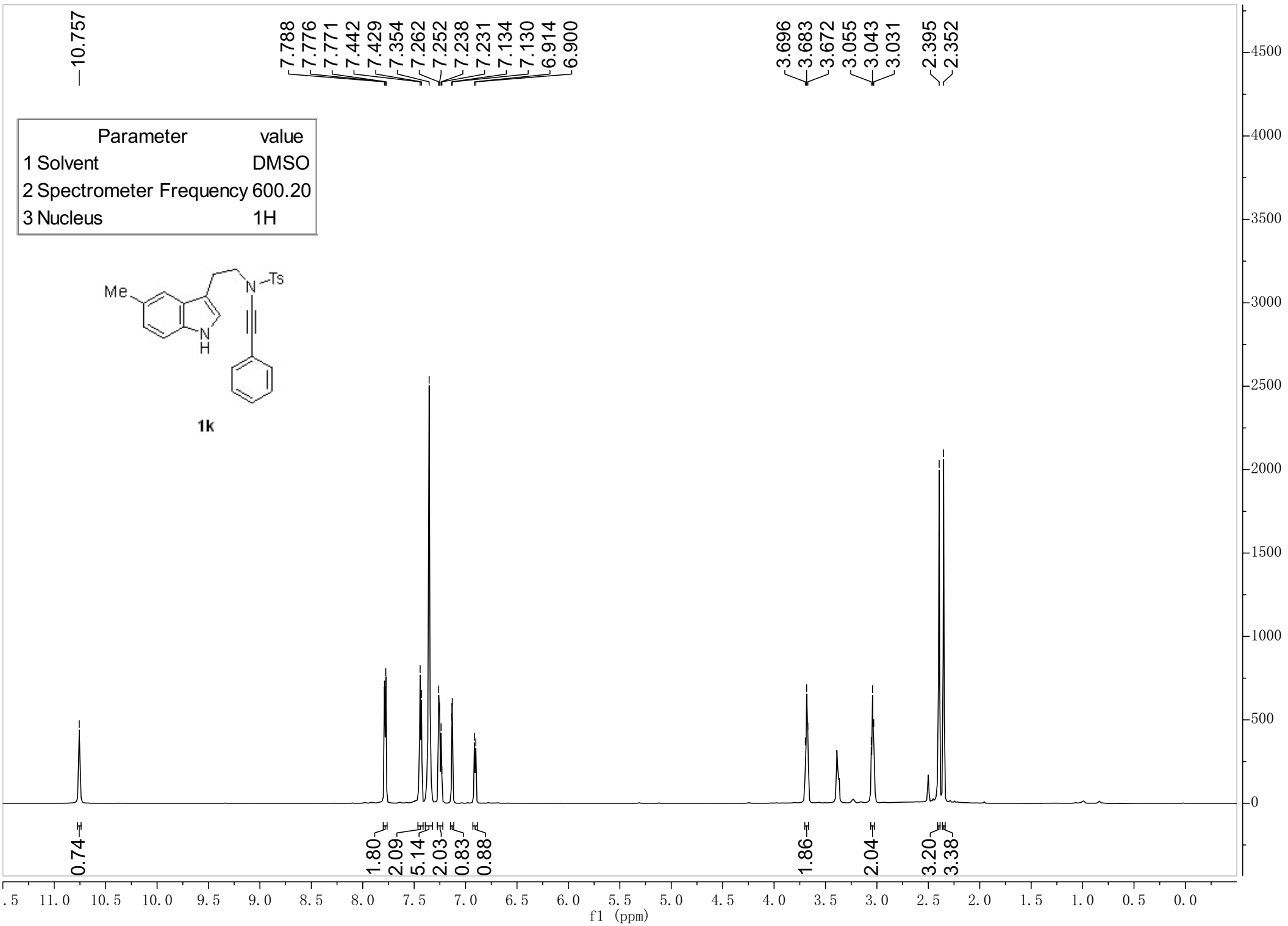


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

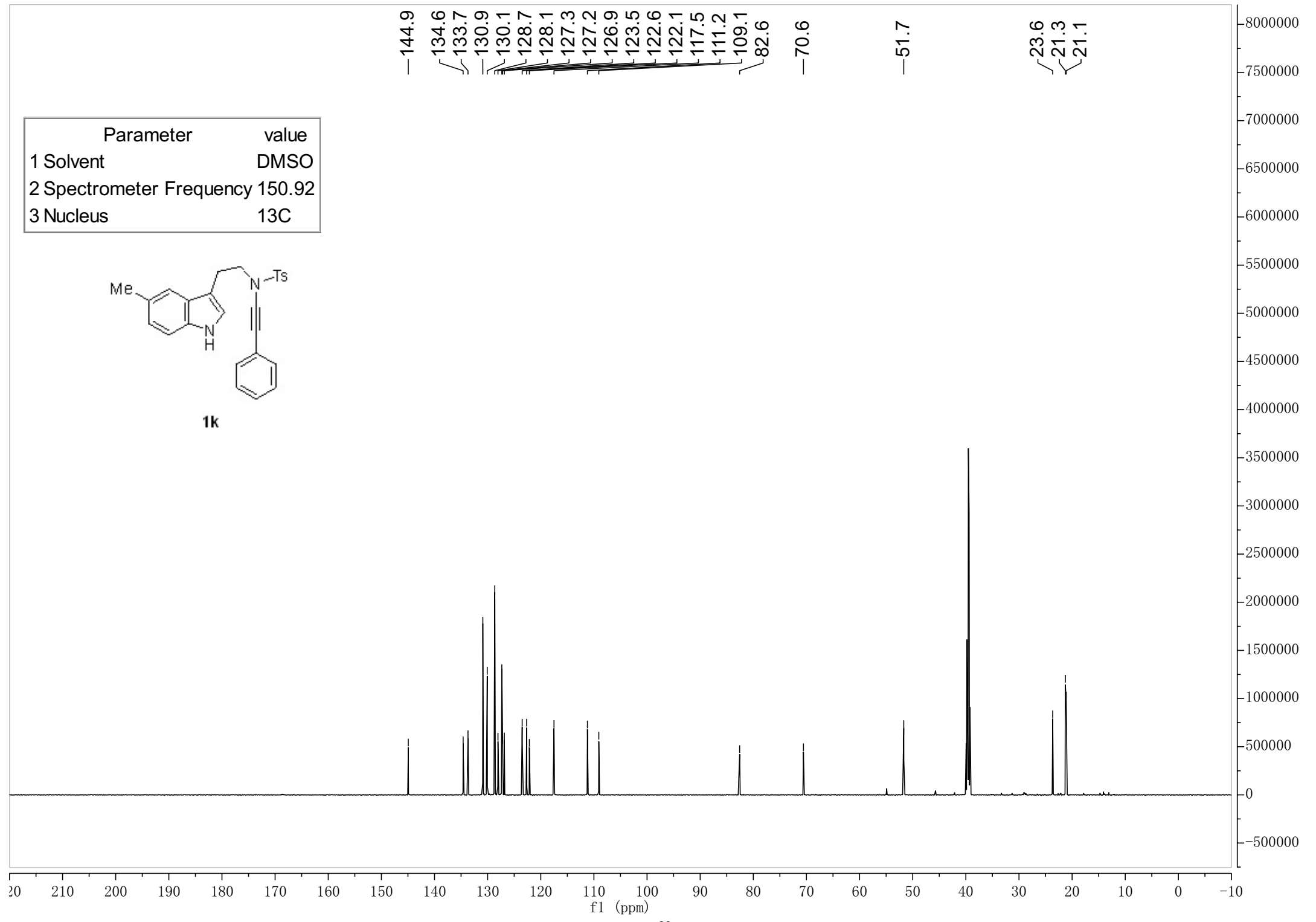
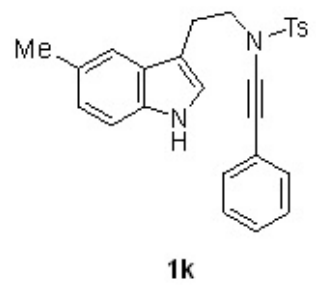


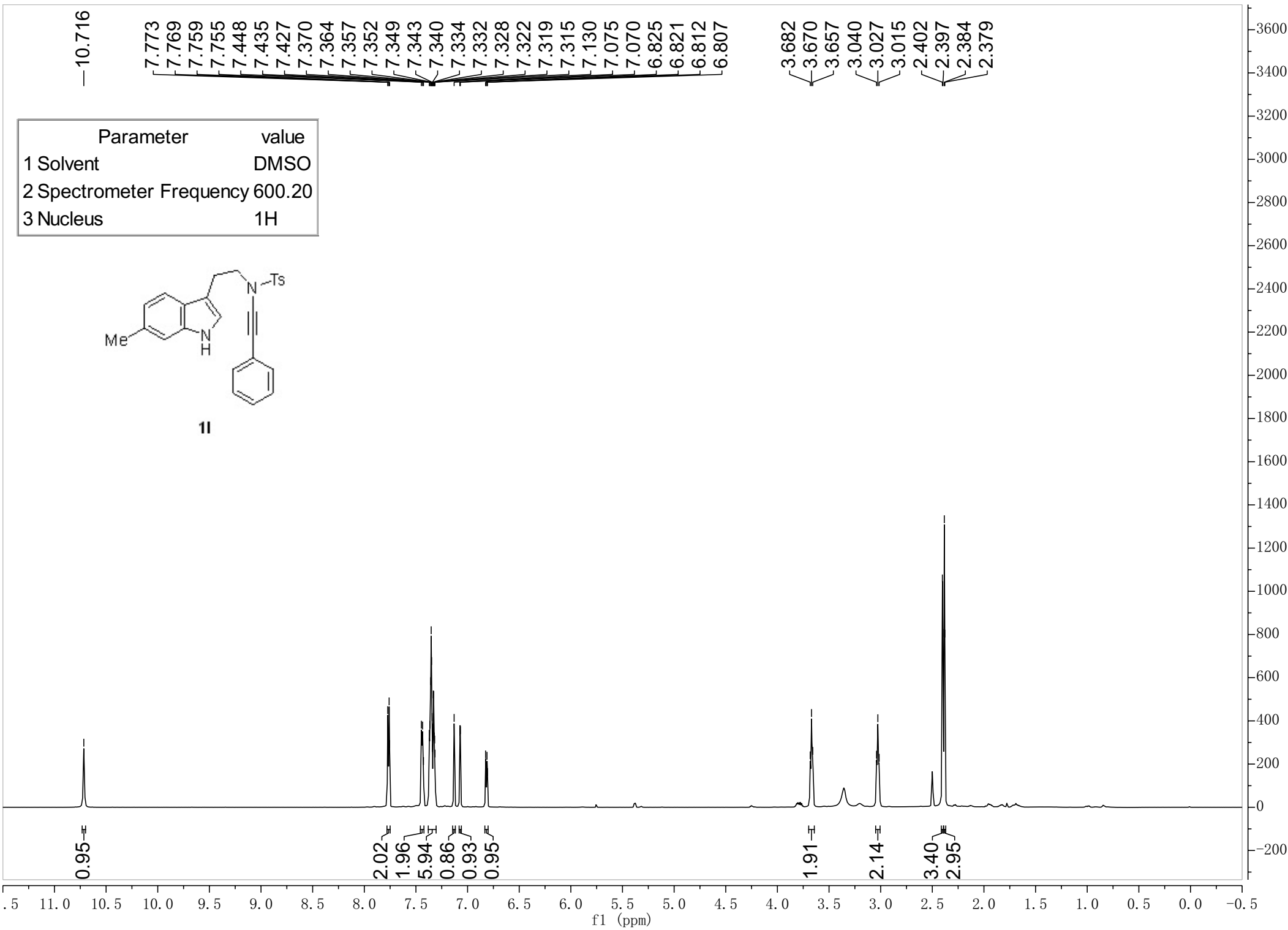
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 { 133.7
 { 131.3
 { 130.9
 { 130.1
 { 128.7
 { 128.1
 { 127.3
 { 124.1
 { 122.1
 { 112.1
 { 111.2
 { 109.4
 { 99.8
 —82.6
 —70.5
 { 55.2
 { 54.9
 { 51.7
 ~23.7
 ~21.1



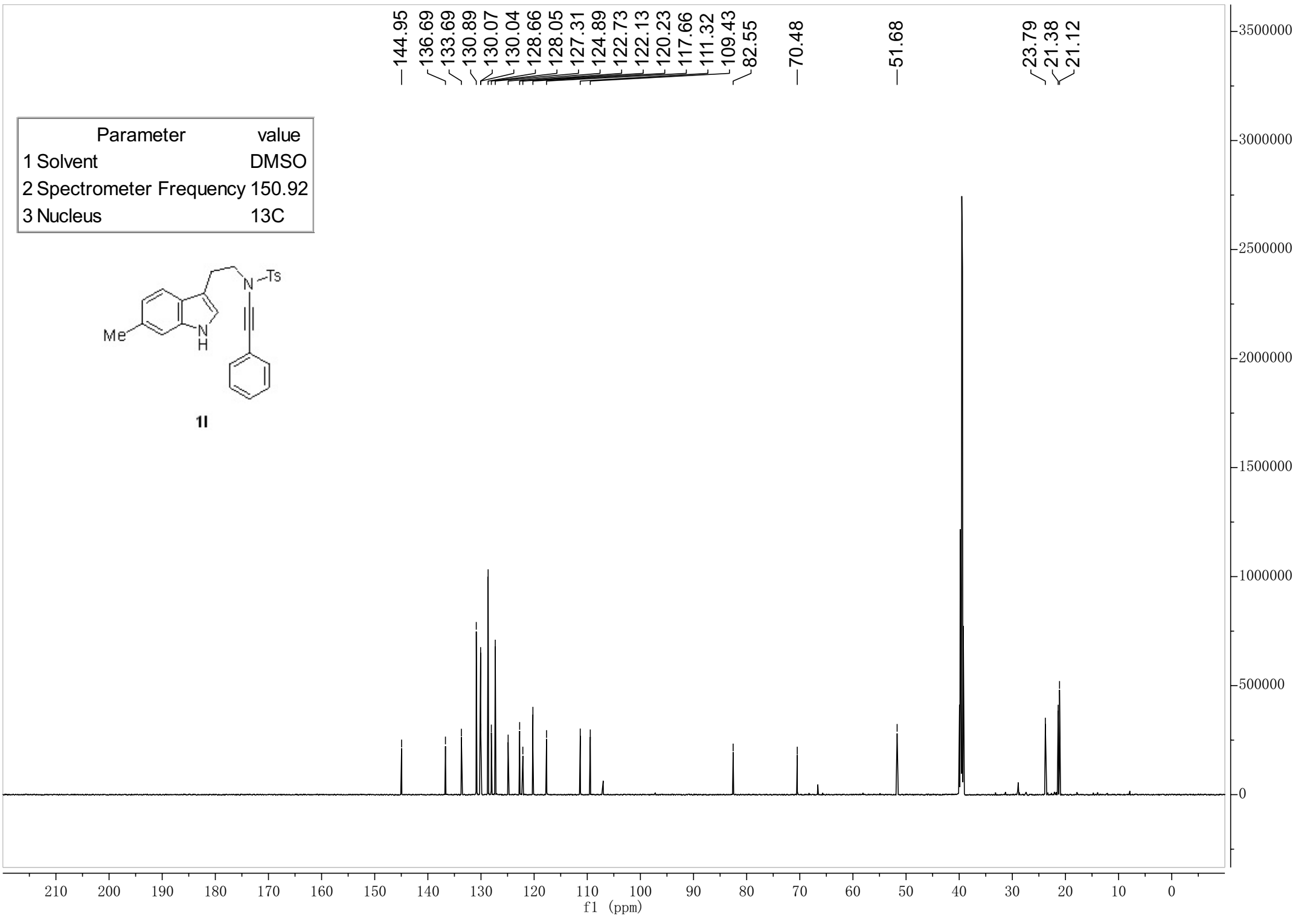
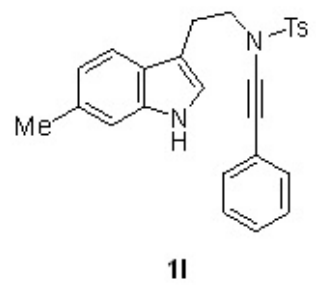


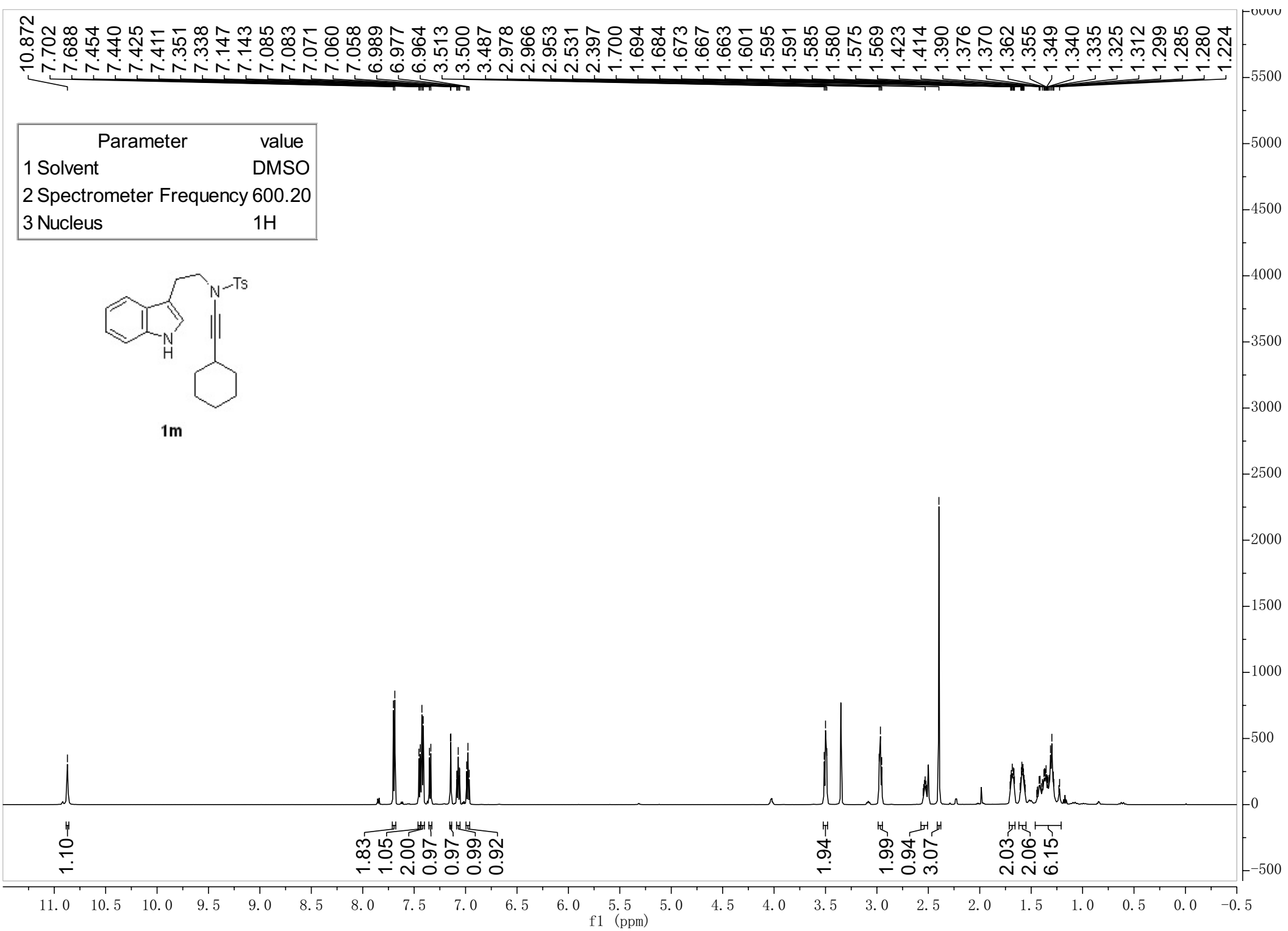
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

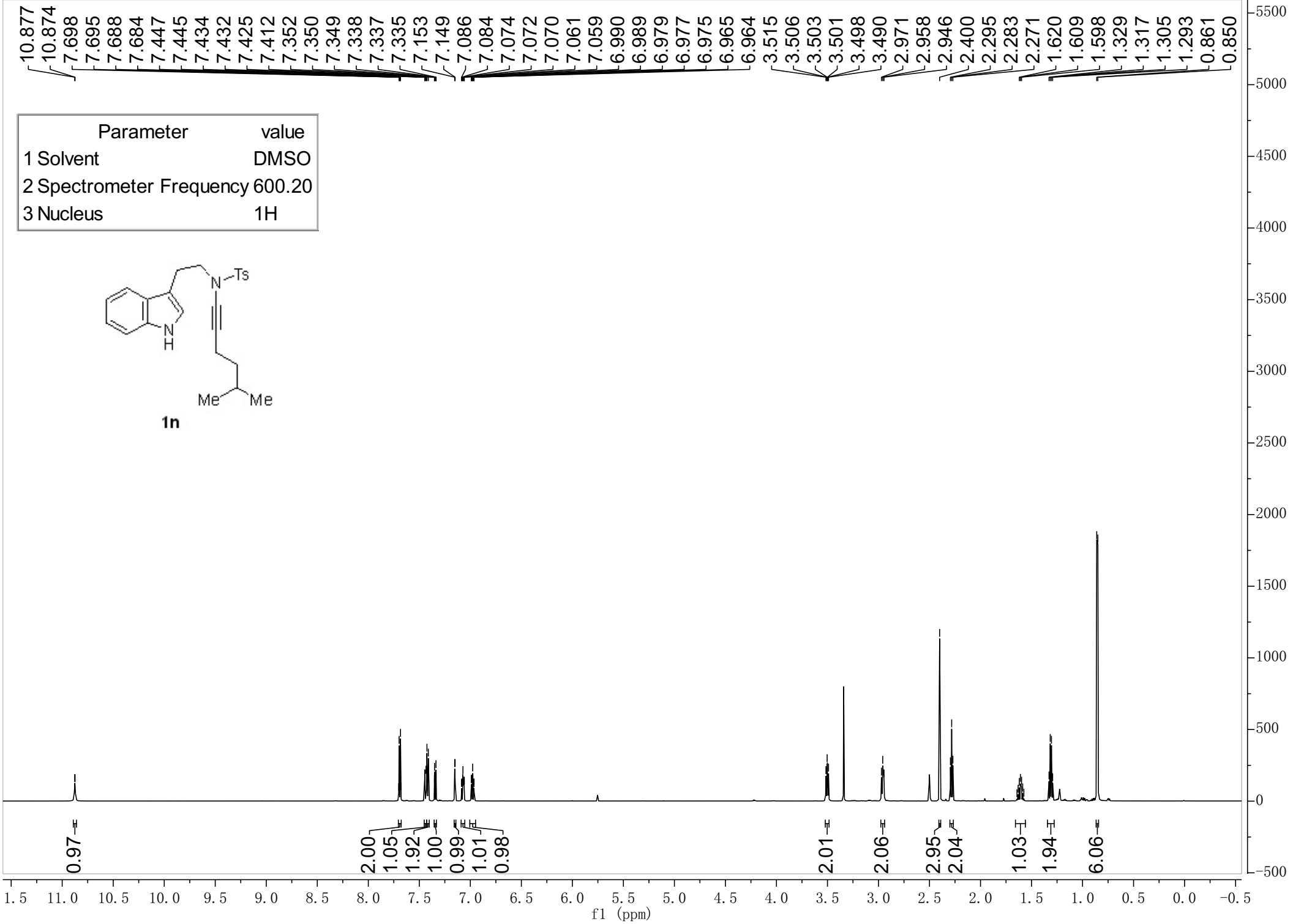




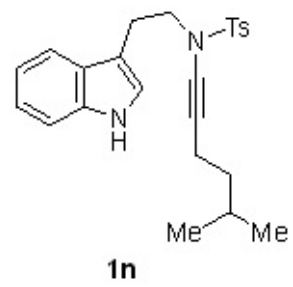
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C







Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



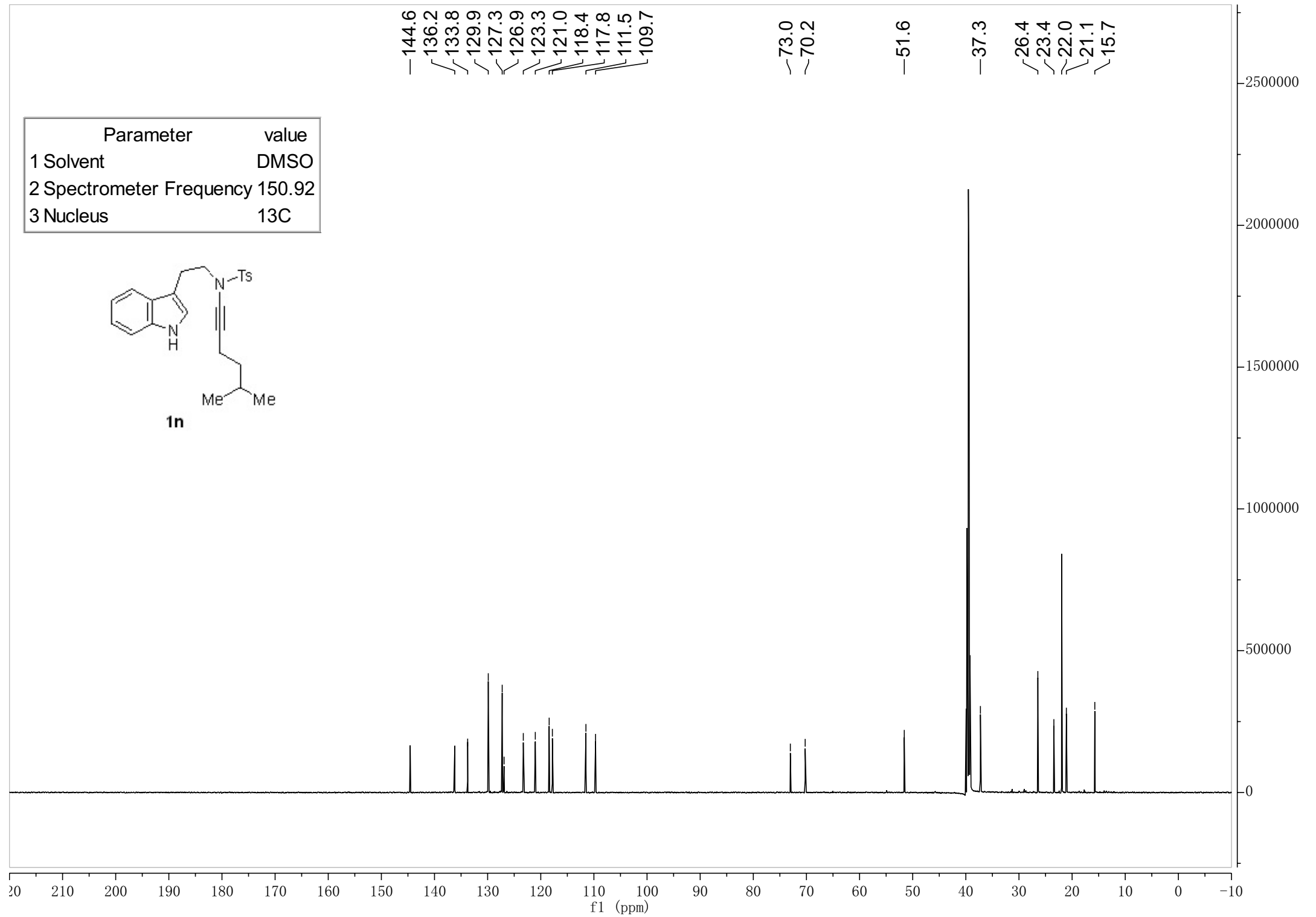
— 144.6
 / 136.2
 / 133.8
 / 129.9
 / 127.3
 / 126.9
 / 123.3
 / 121.0
 / 118.4
 / 117.8
 / 111.5
 / 109.7

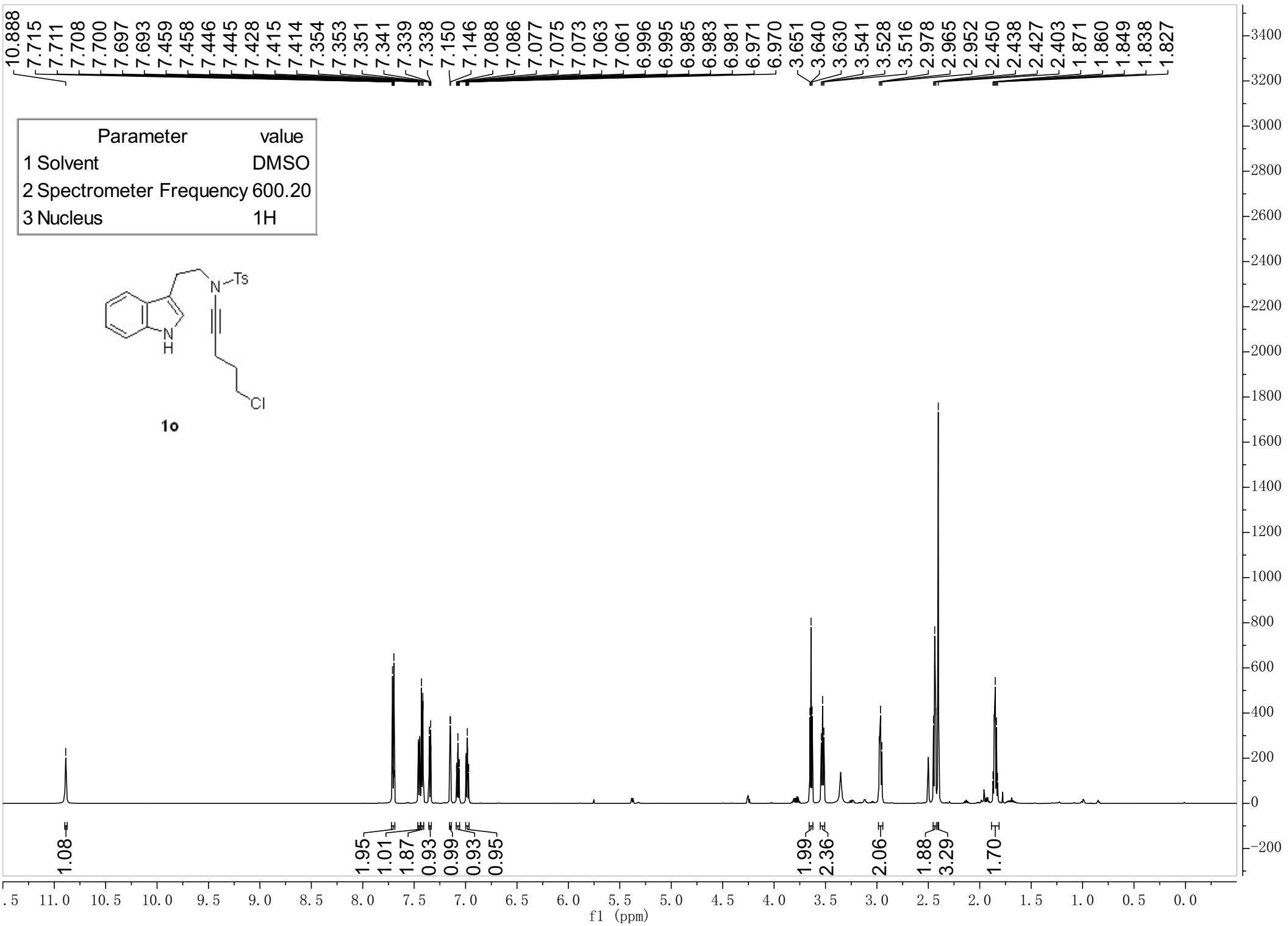
~ 73.0
 ~ 70.2

— 51.6

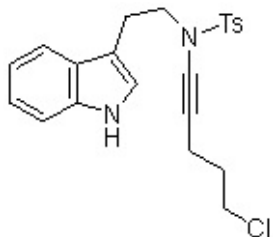
— 37.3

/ 26.4
 / 23.4
 / 22.0
 / 21.1
 / 15.7

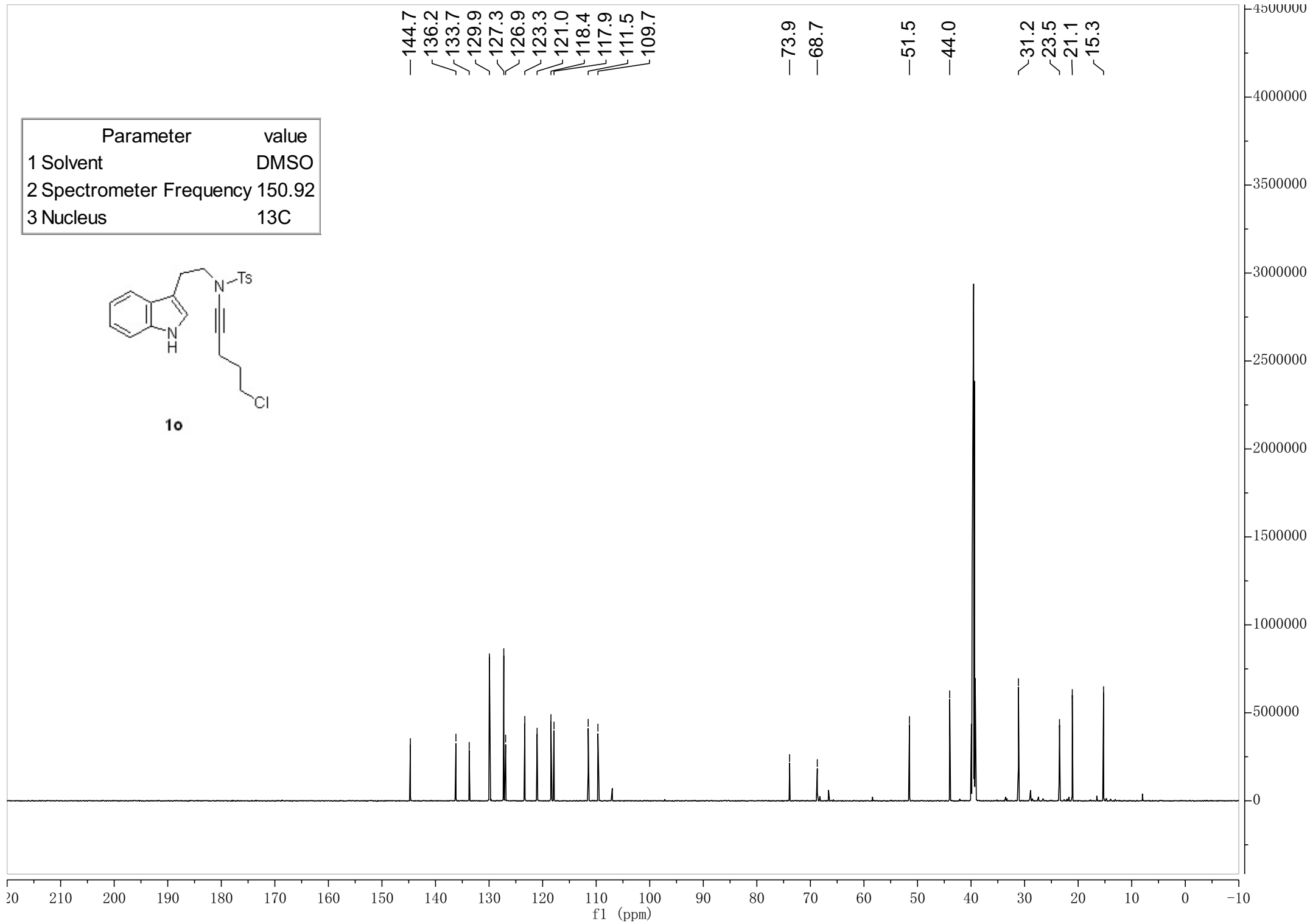


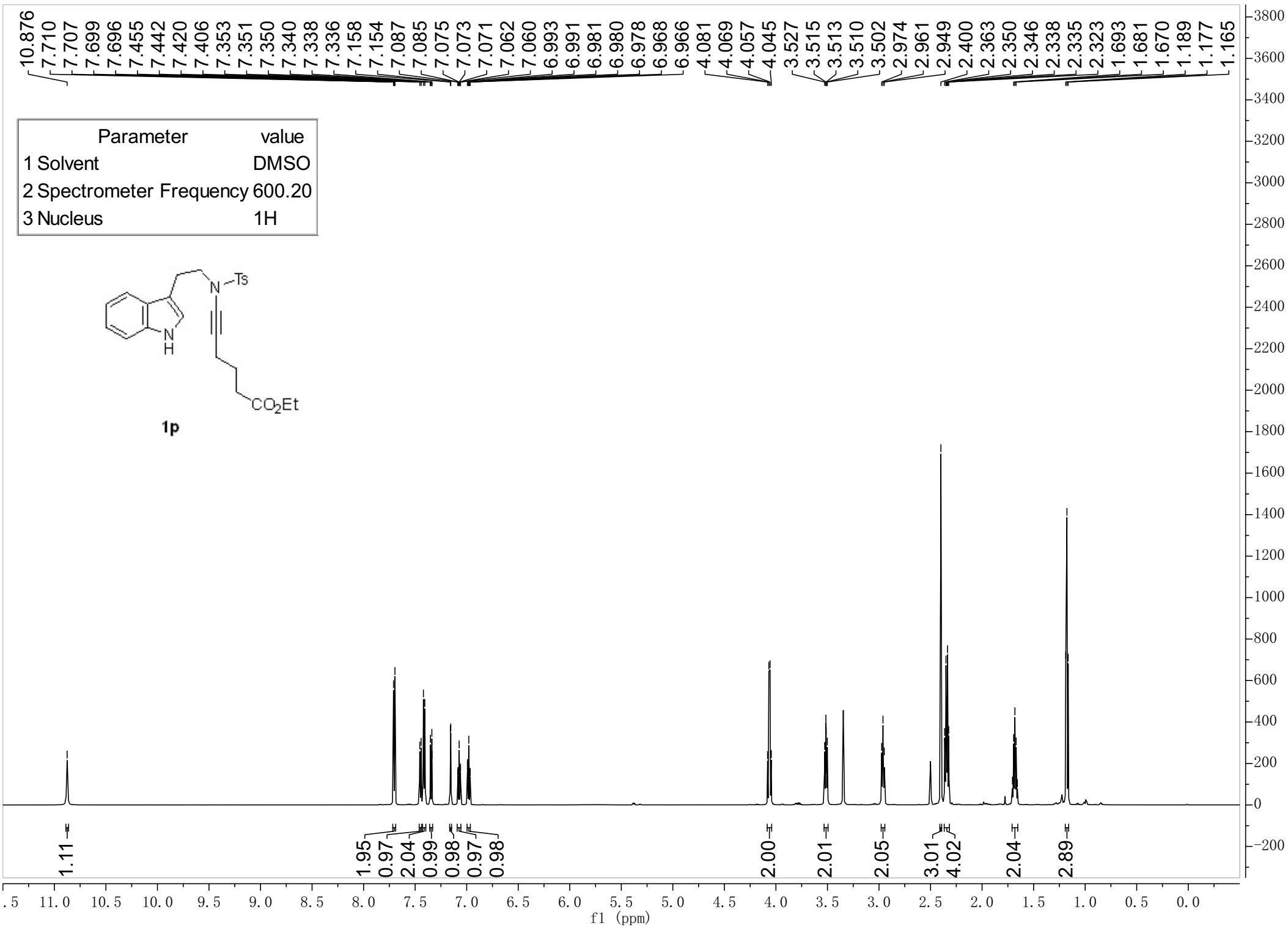


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

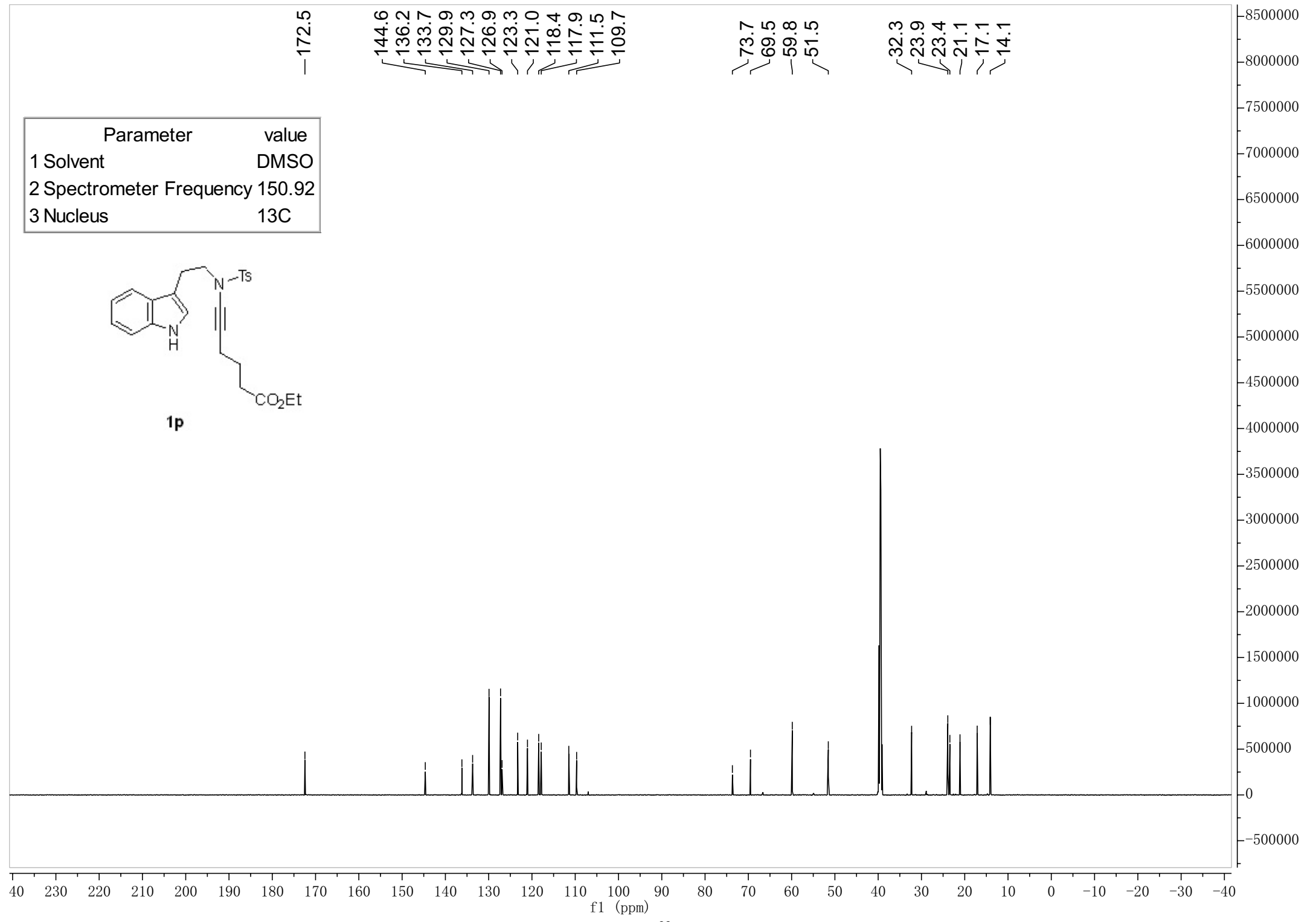
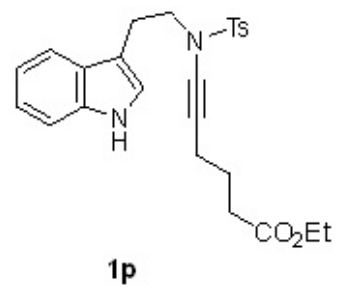


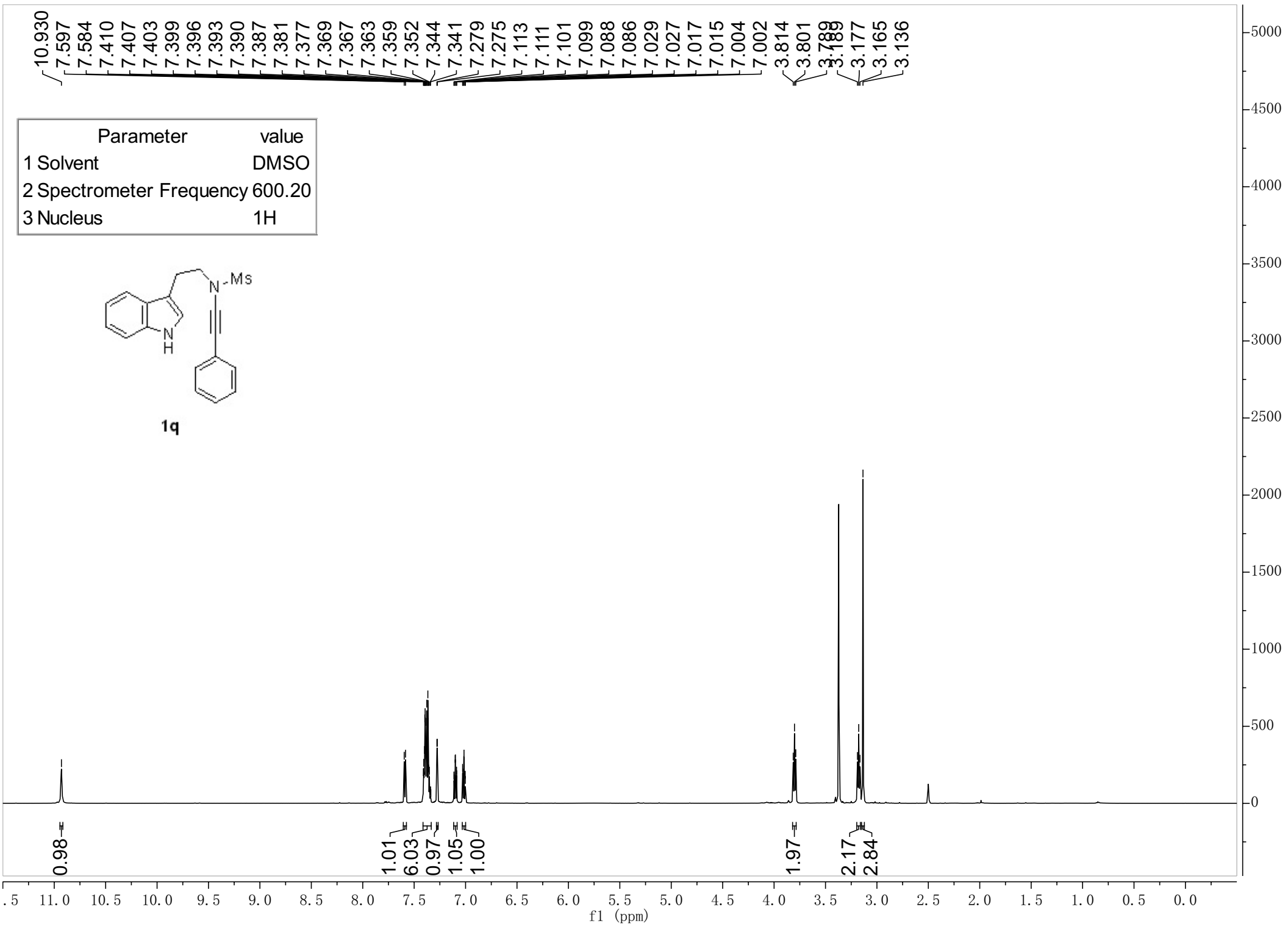
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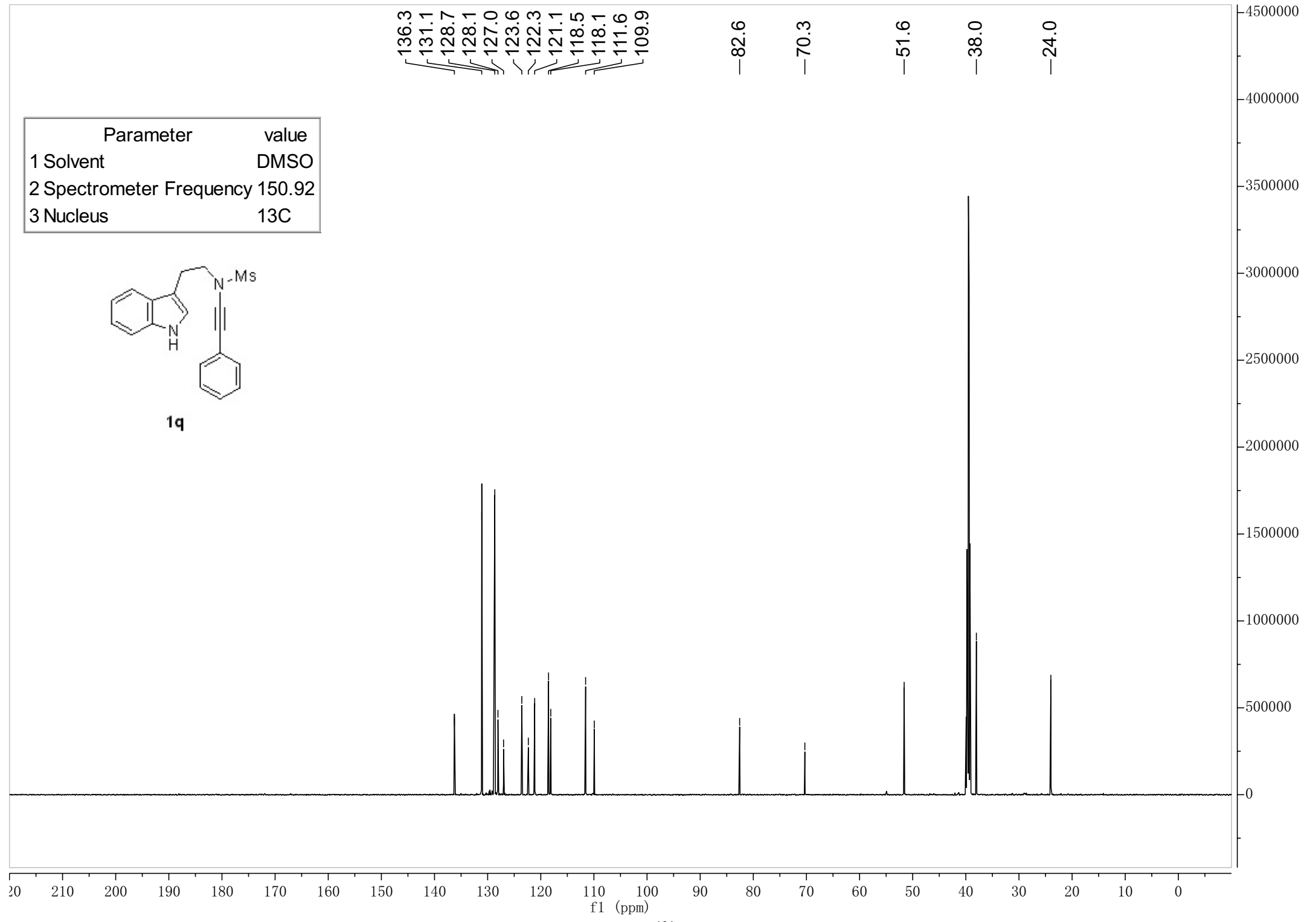
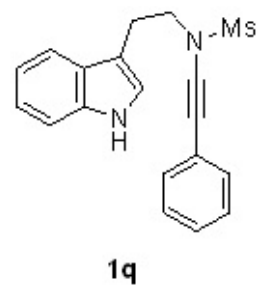


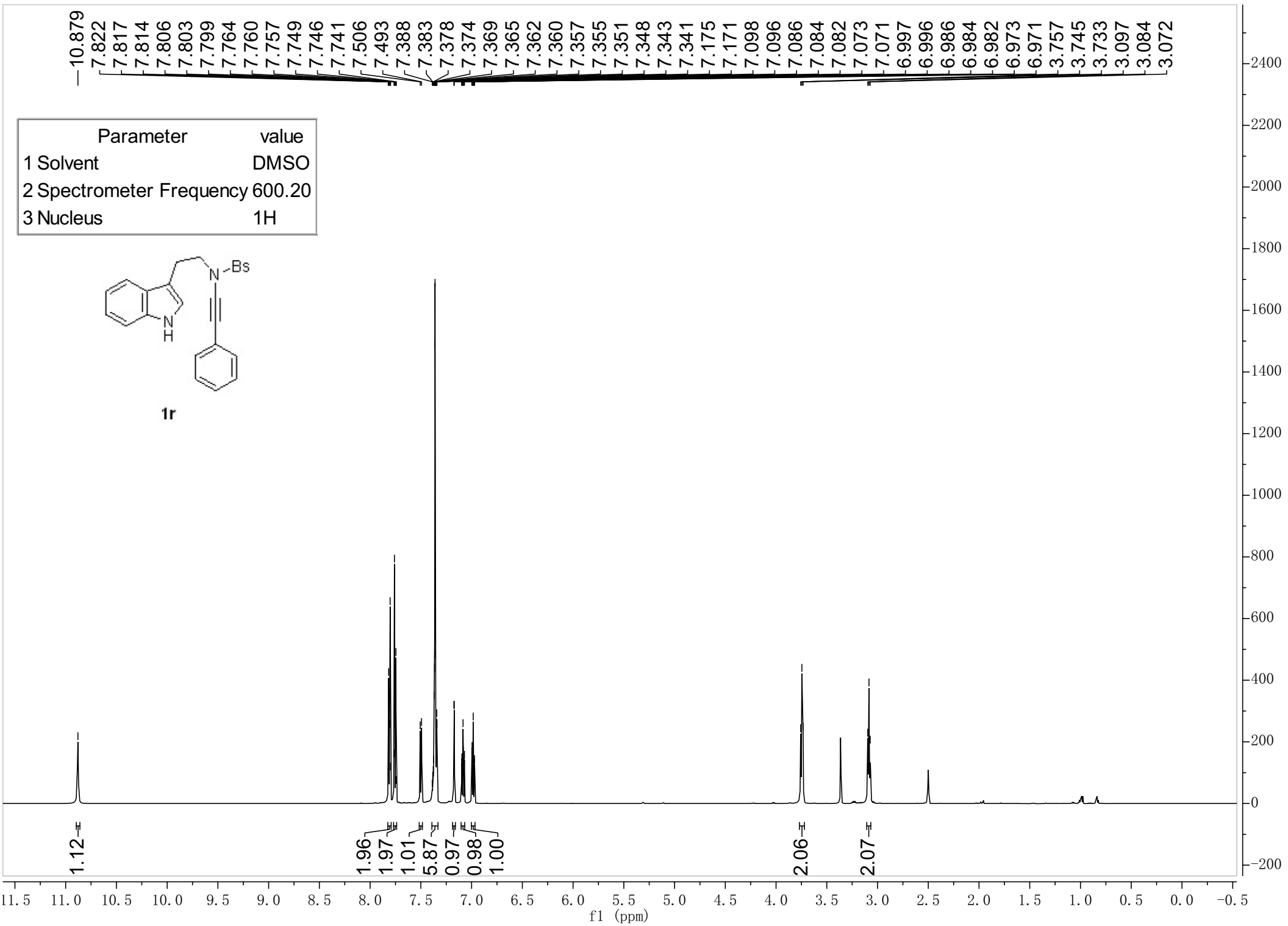
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



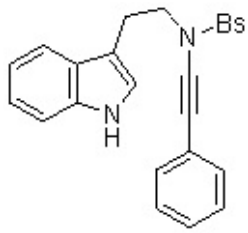


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



1r

136.2
135.7
132.7
131.0
129.1
128.7
128.4
128.2
126.9
123.5
121.9
121.0
118.5
117.9
111.5
109.5

—81.9

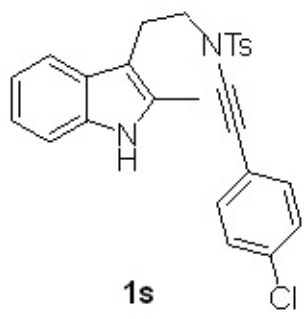
—70.8

—51.8

—23.7

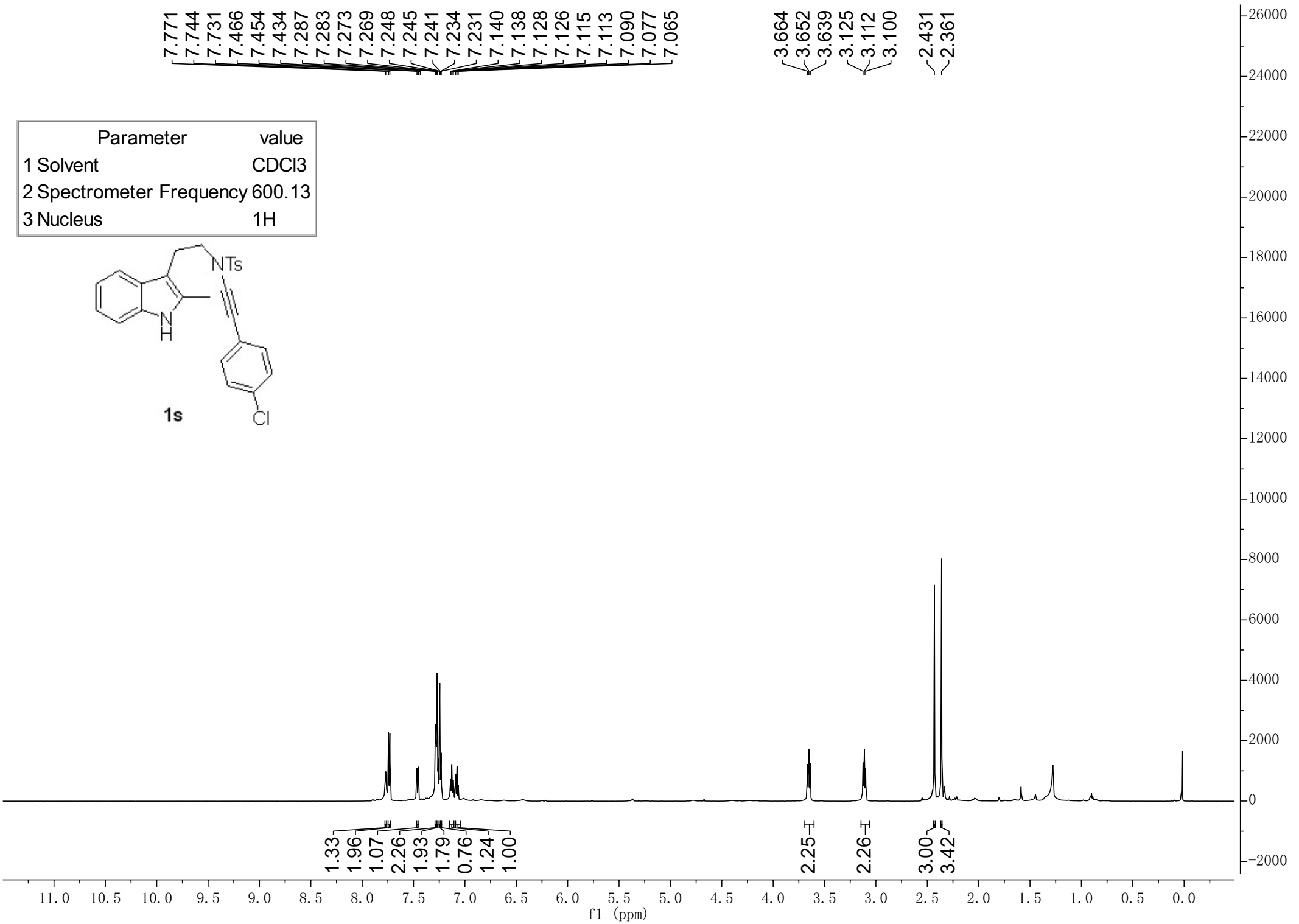
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	600.13
3 Nucleus	1H

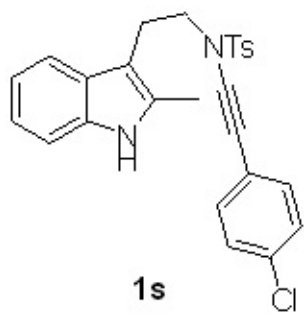


7.771
7.744
7.731
7.466
7.454
7.434
7.287
7.283
7.273
7.269
7.248
7.245
7.241
7.234
7.231
7.140
7.138
7.128
7.126
7.115
7.113
7.090
7.077
7.065

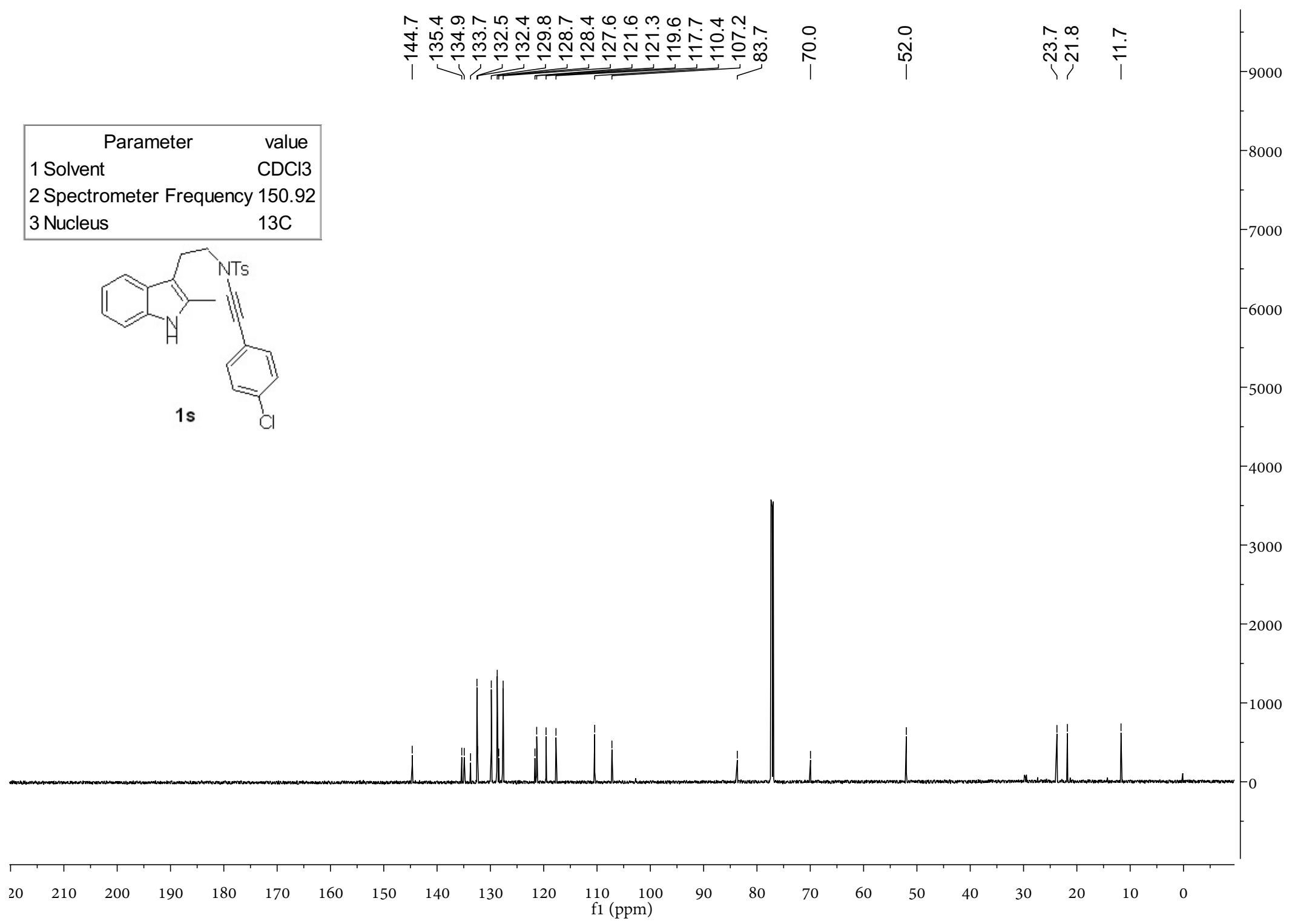
3.664
3.652
3.639
3.125
3.112
3.100
2.431
2.361

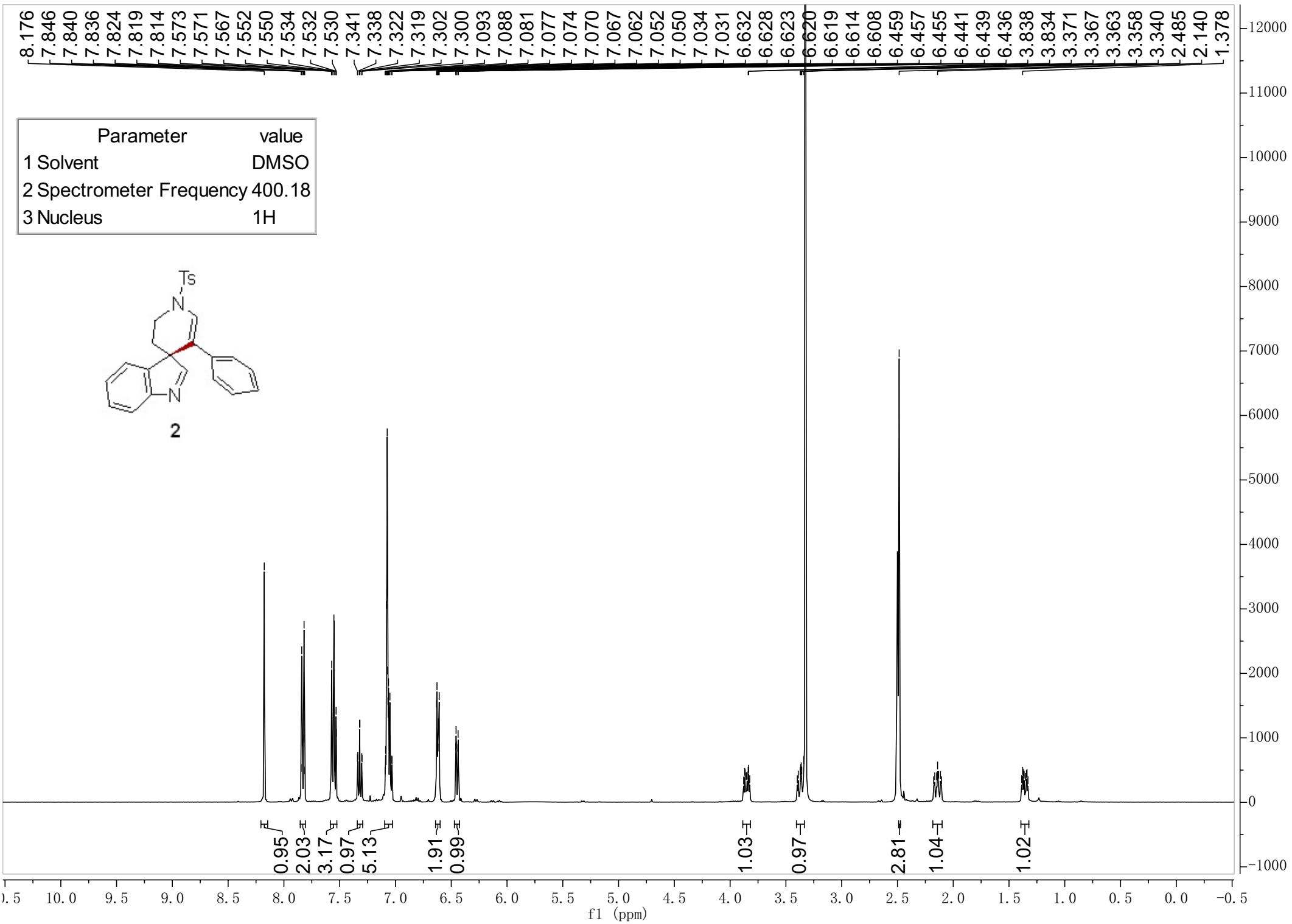


Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	150.92
3 Nucleus	13C

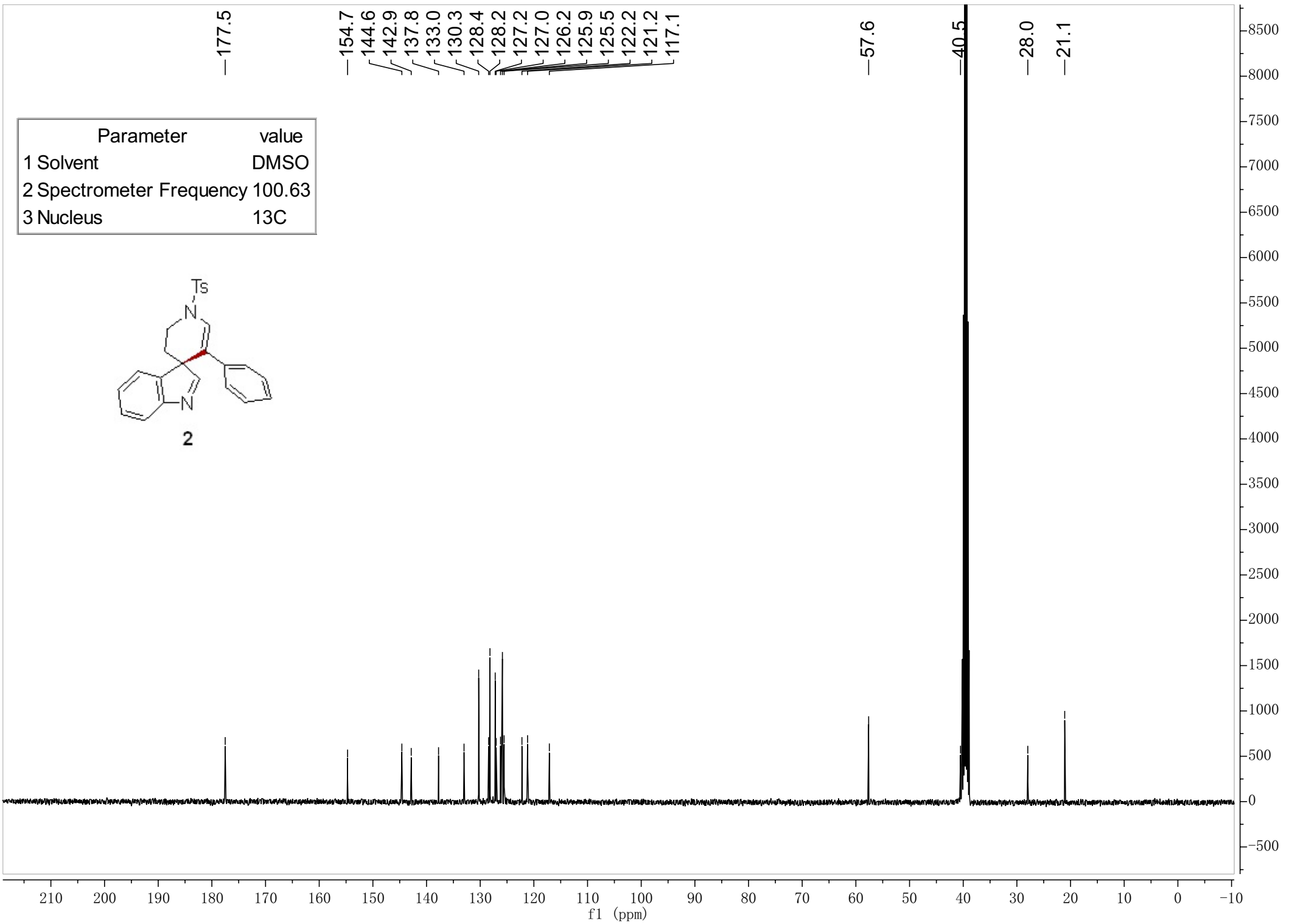
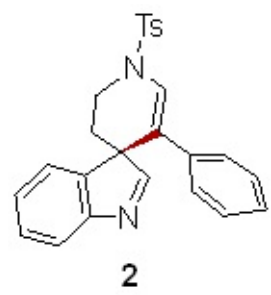


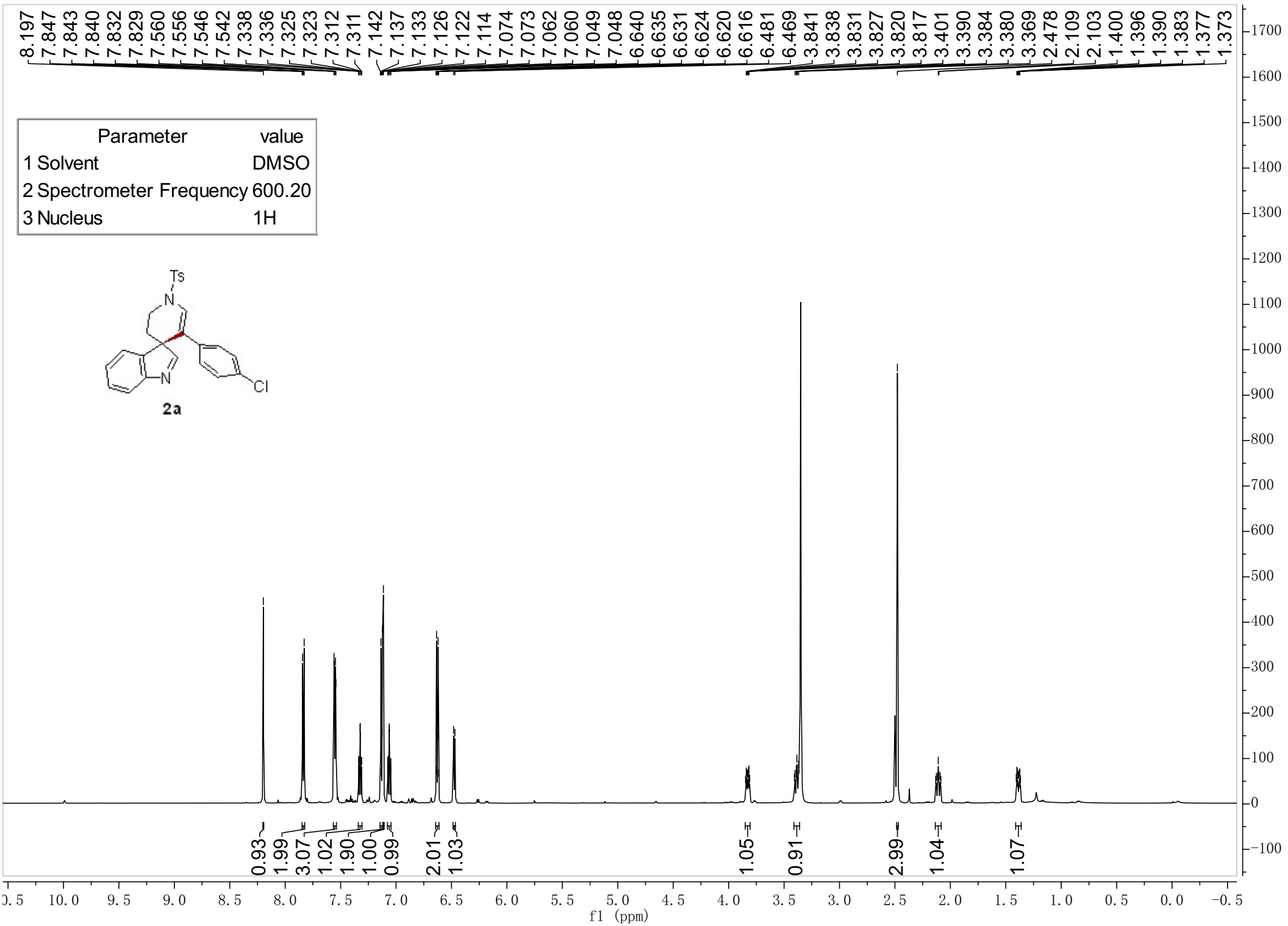
- 144.7
- 135.4
- 134.9
- 133.7
- 132.5
- 132.4
- 129.8
- 128.7
- 128.4
- 127.6
- 121.6
- 121.3
- 119.6
- 117.7
- 110.4
- 107.2
- 83.7
- 70.0
- 52.0
- 23.7
- 21.8
- 11.7



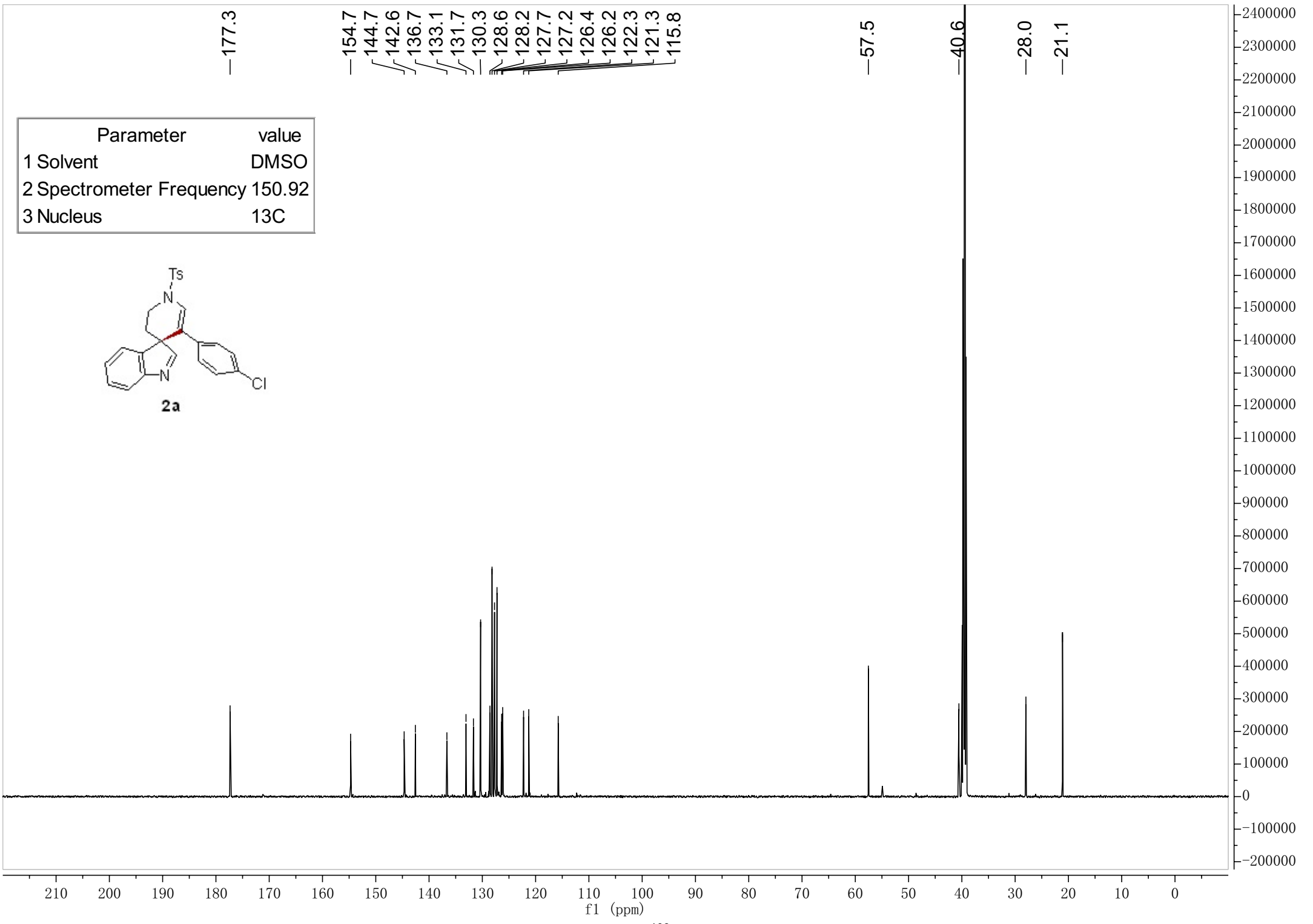
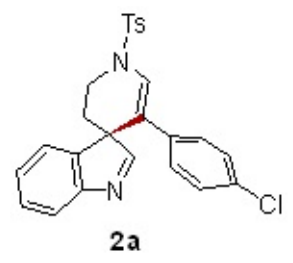


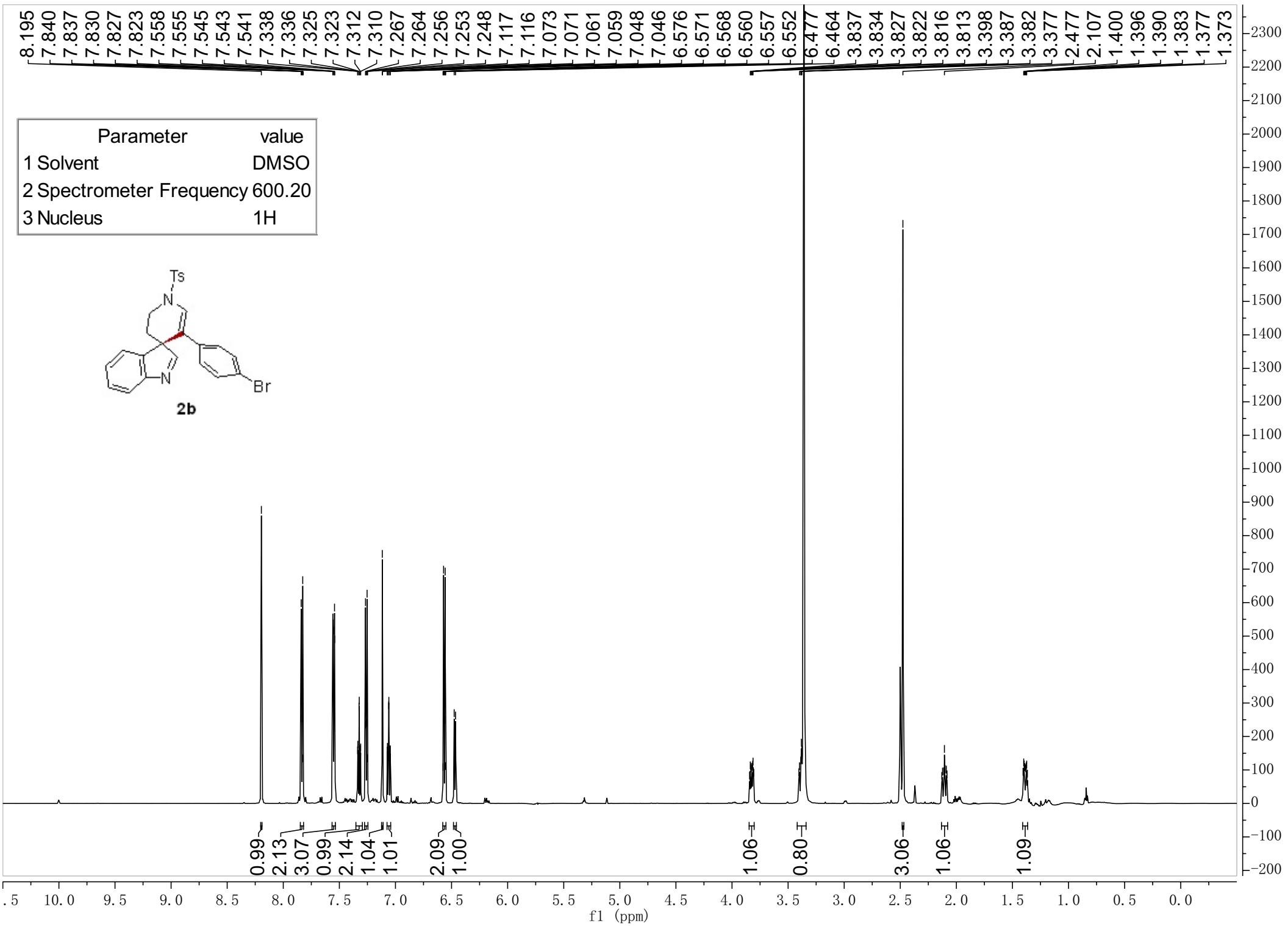
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	100.63
3 Nucleus	13C

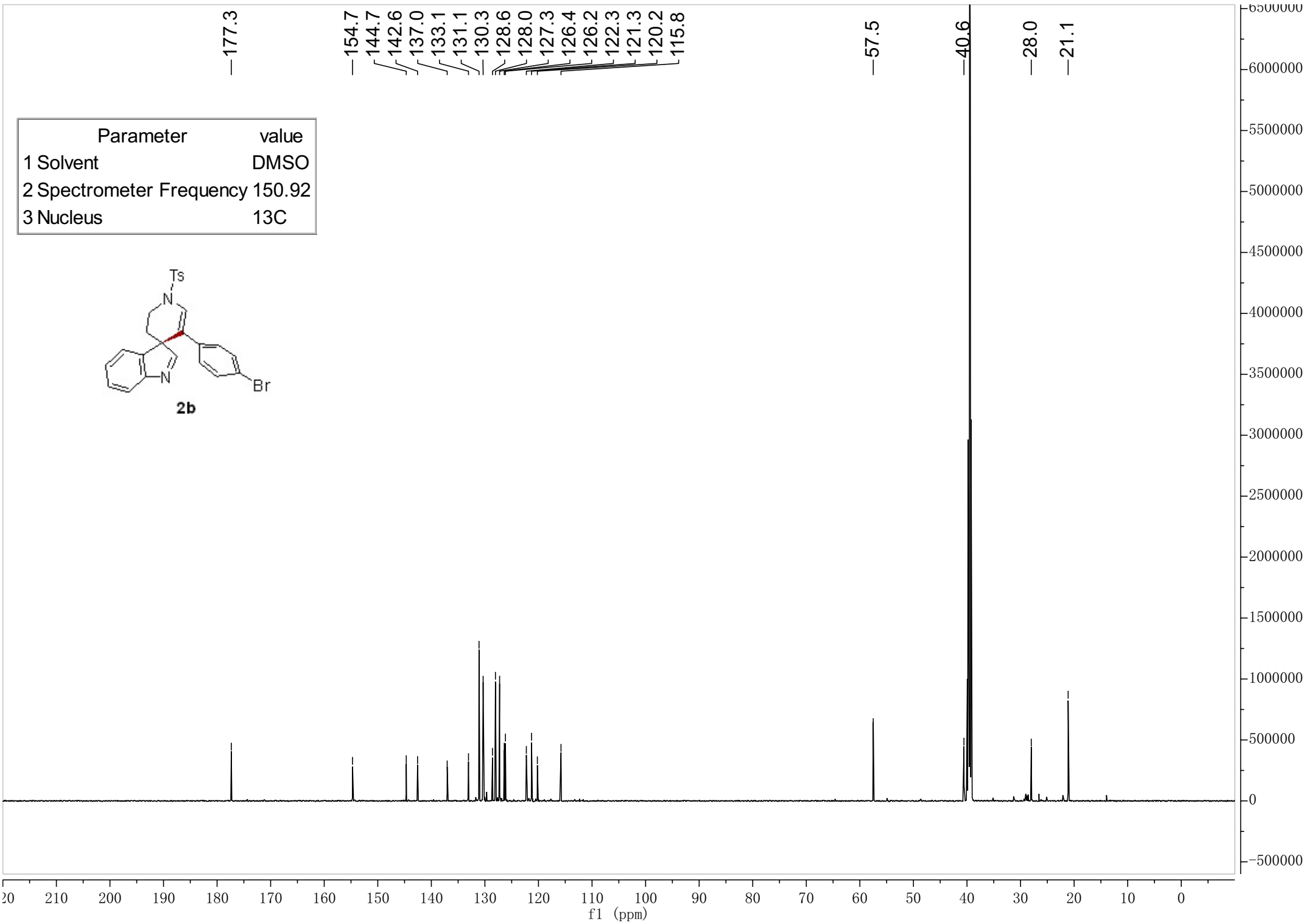


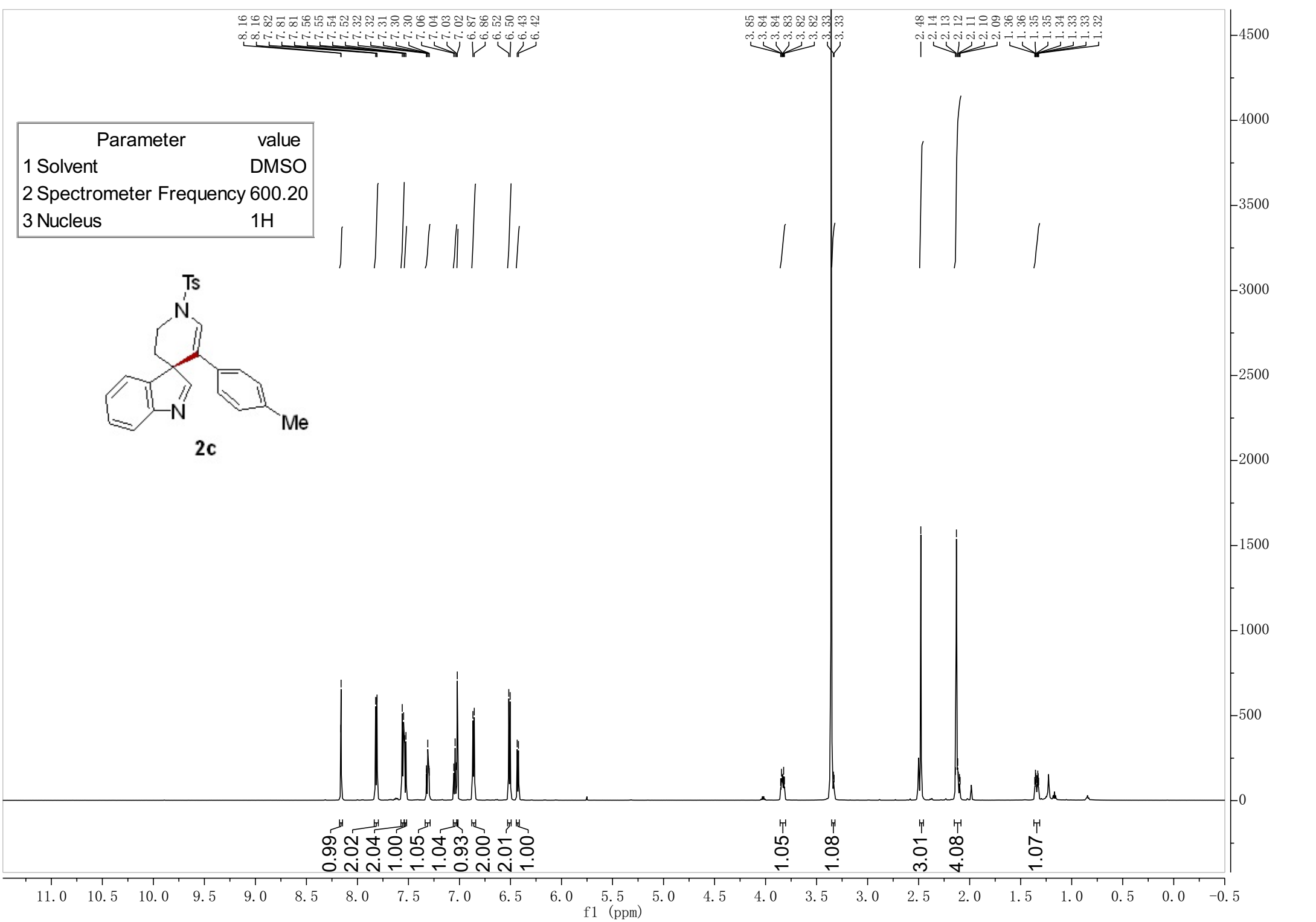


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

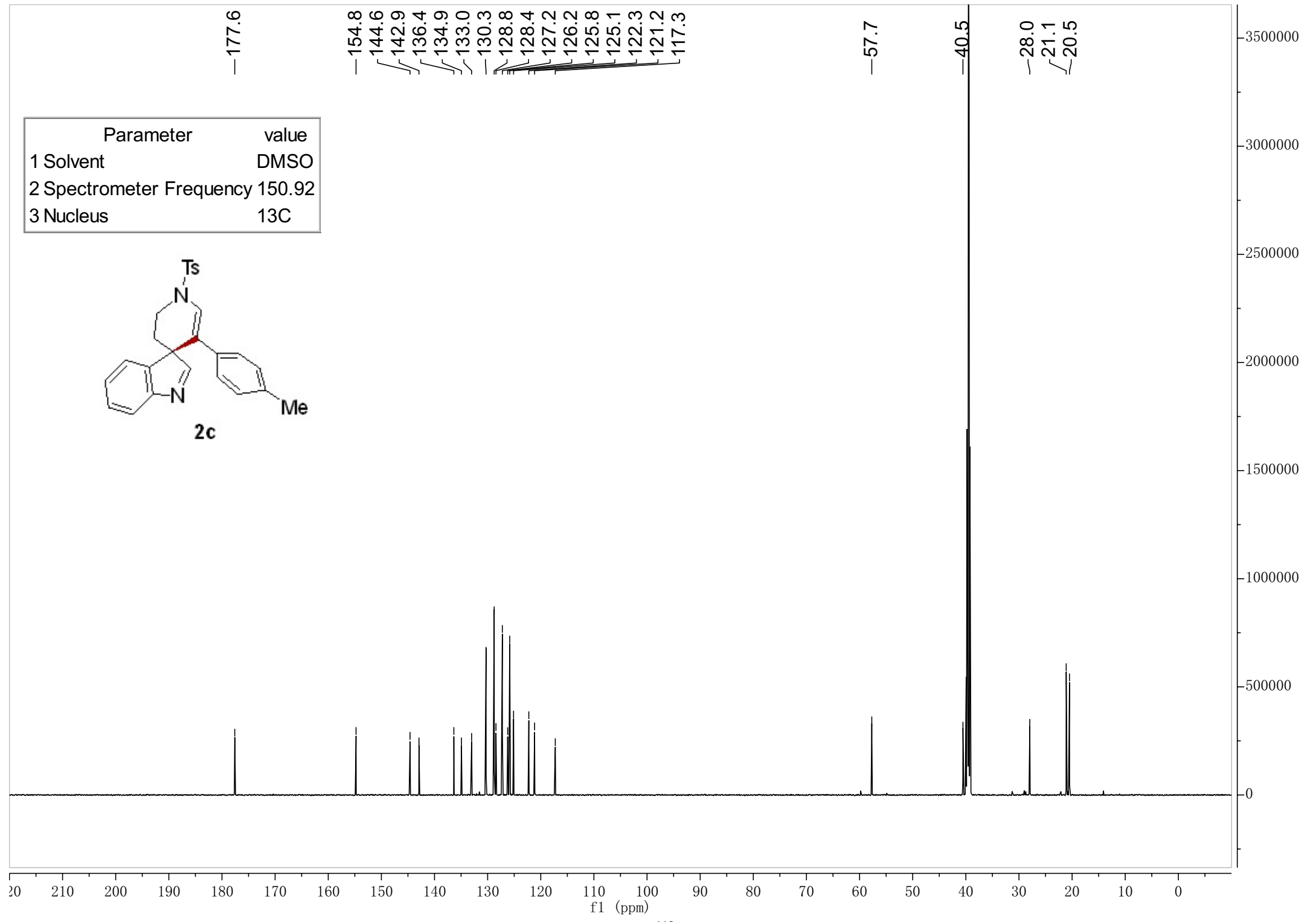
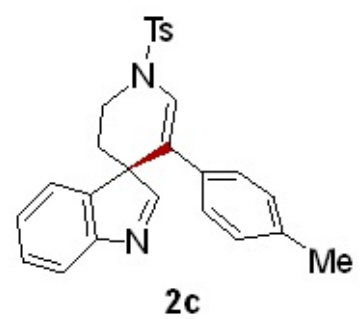


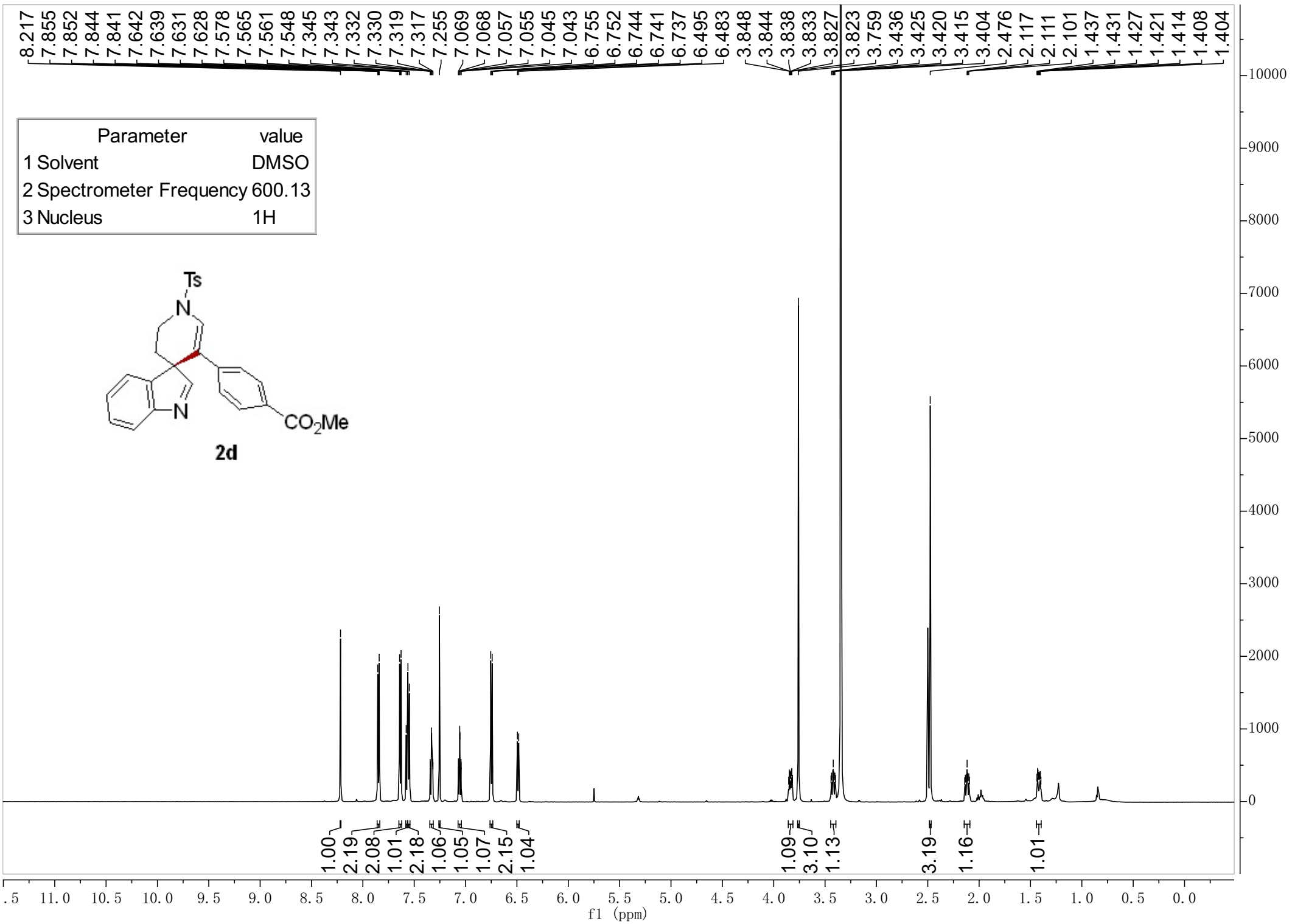




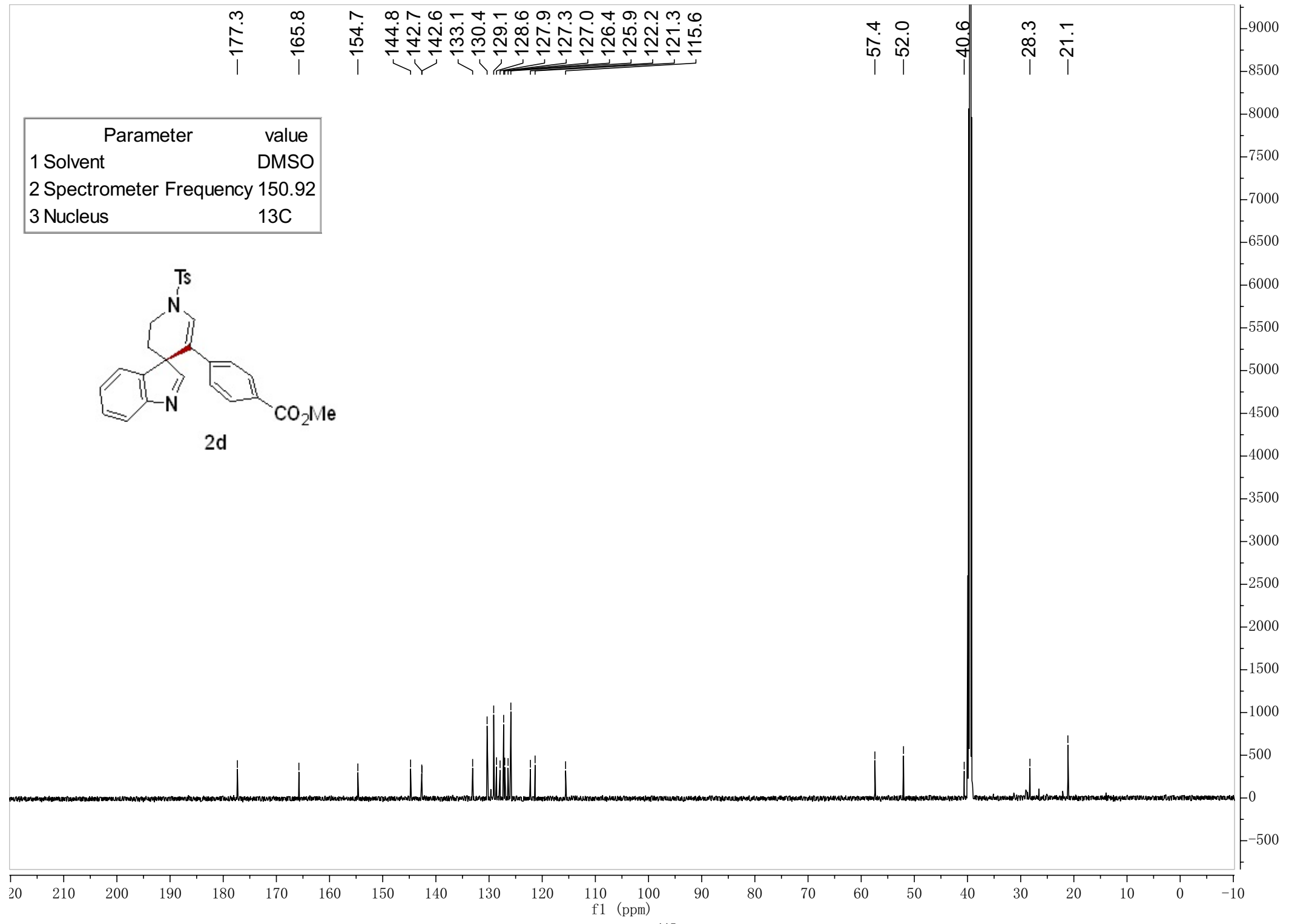
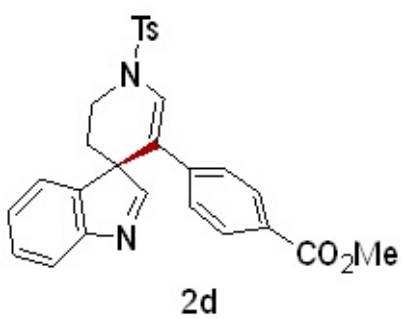


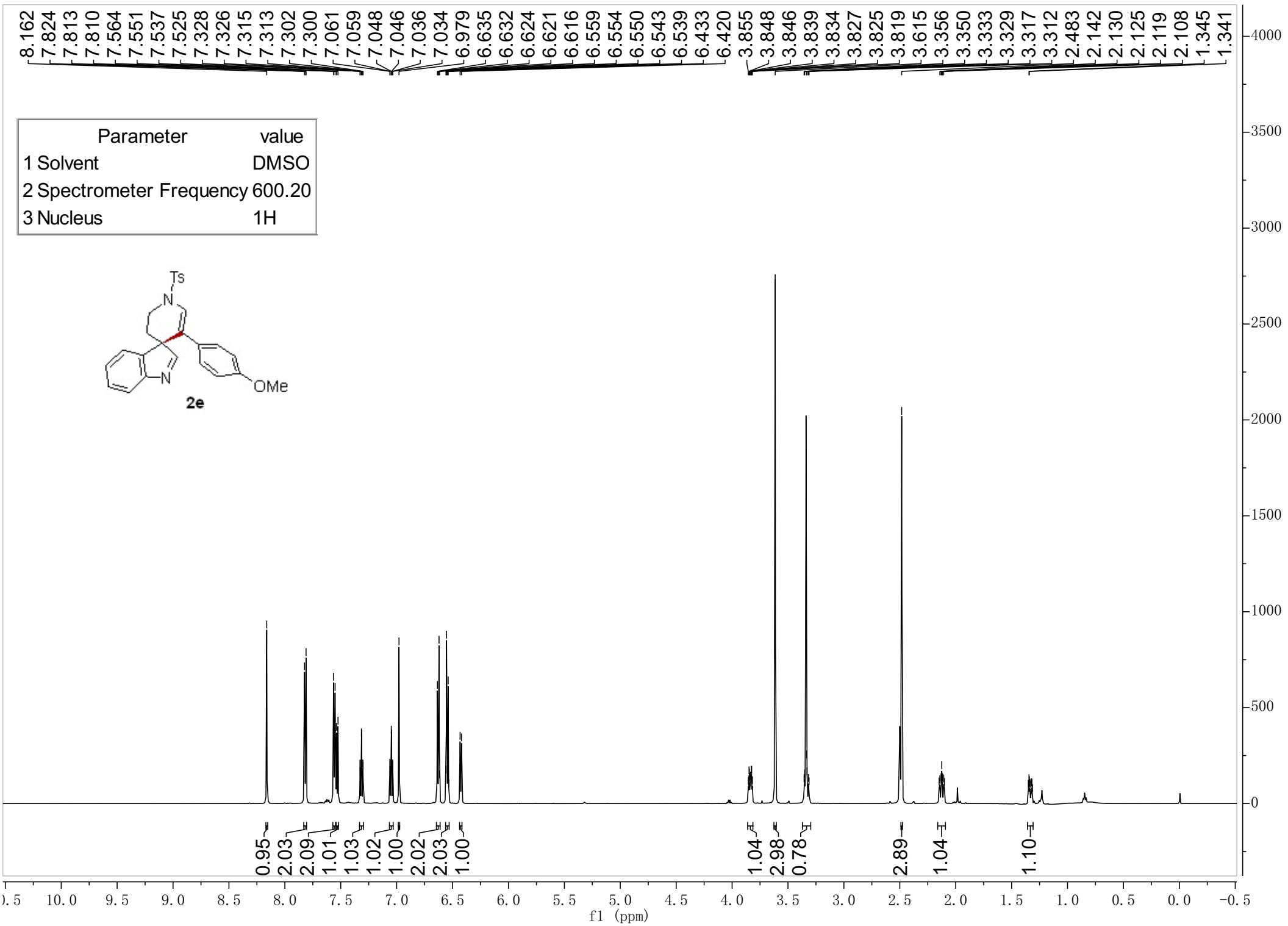
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



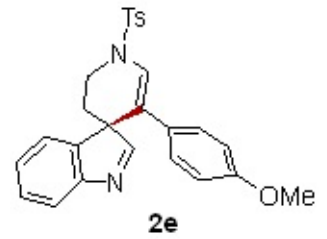


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C

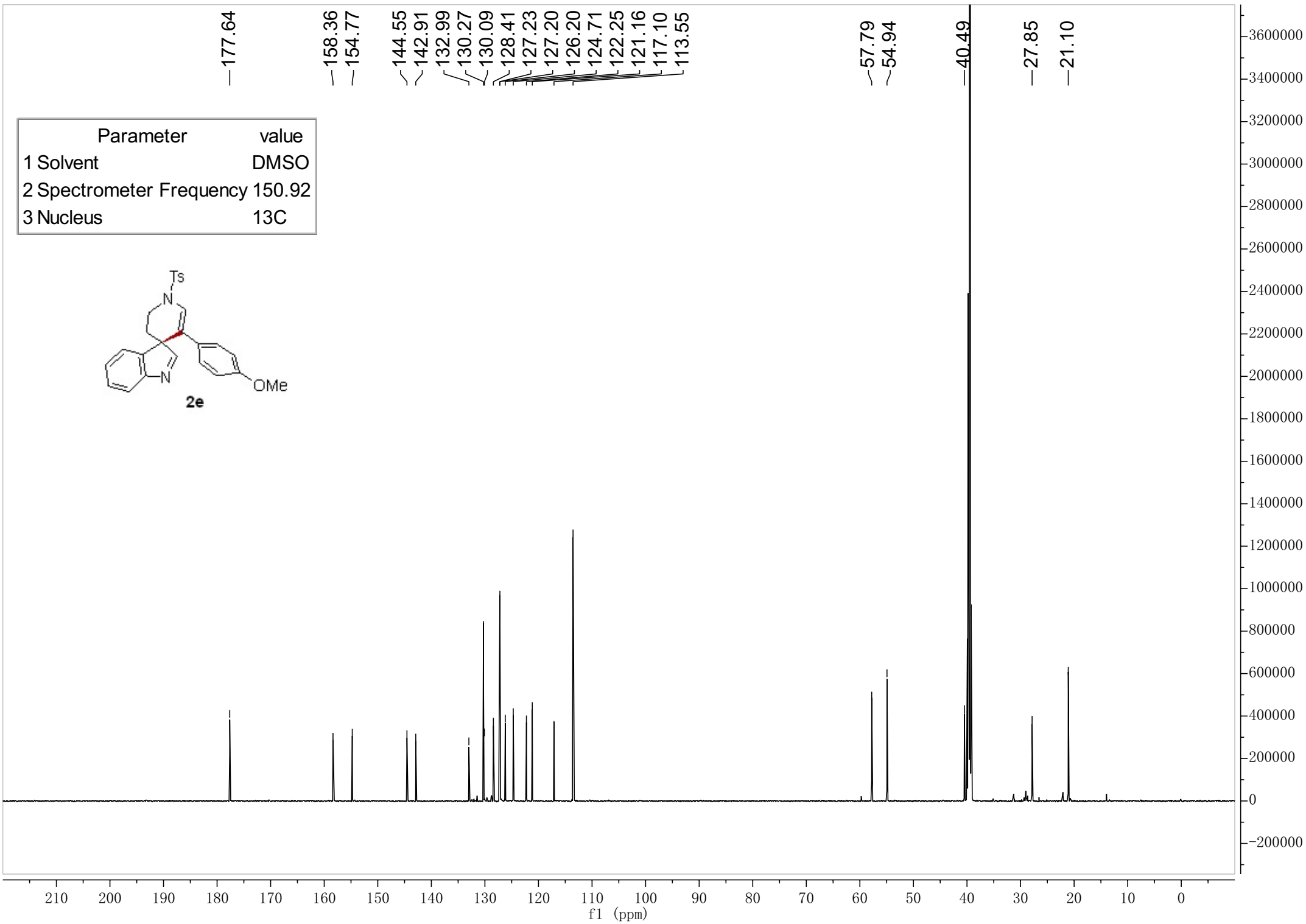
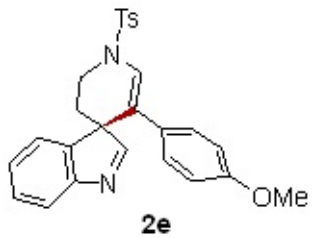


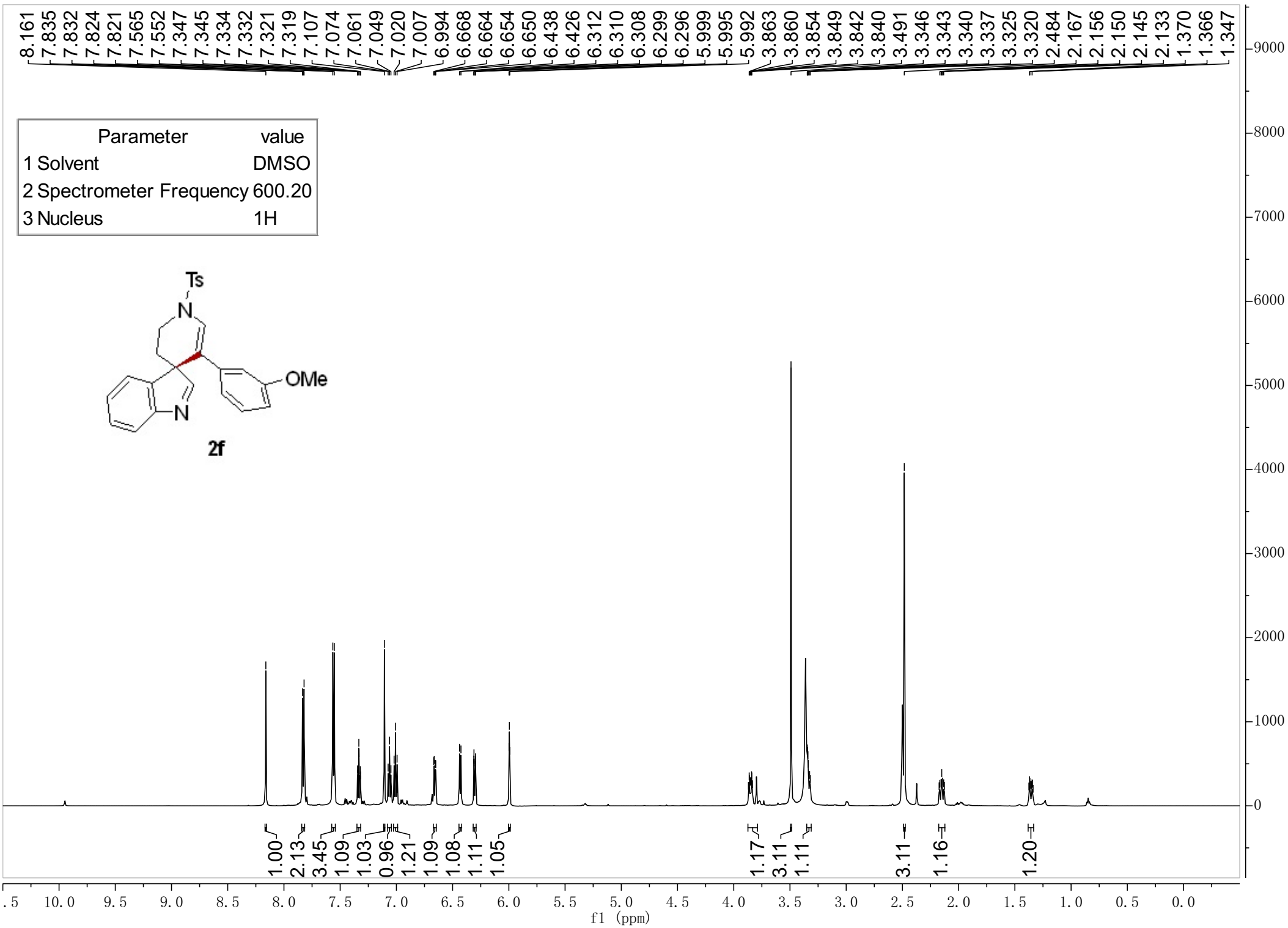


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

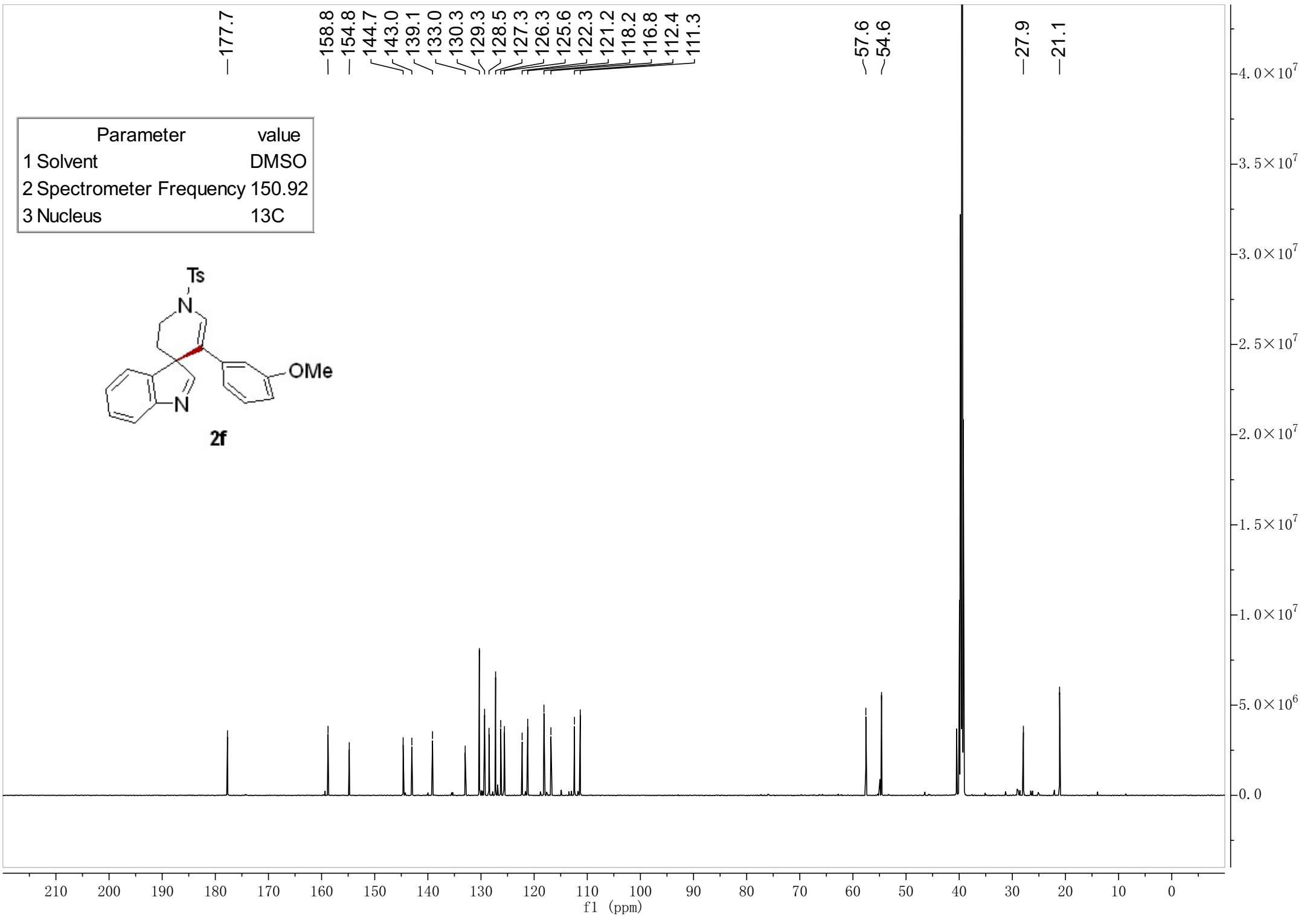
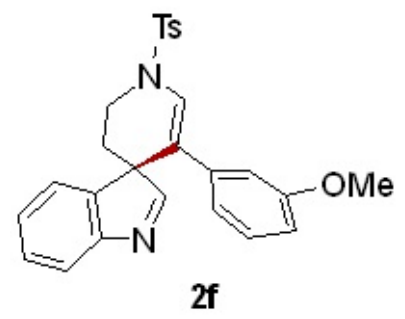


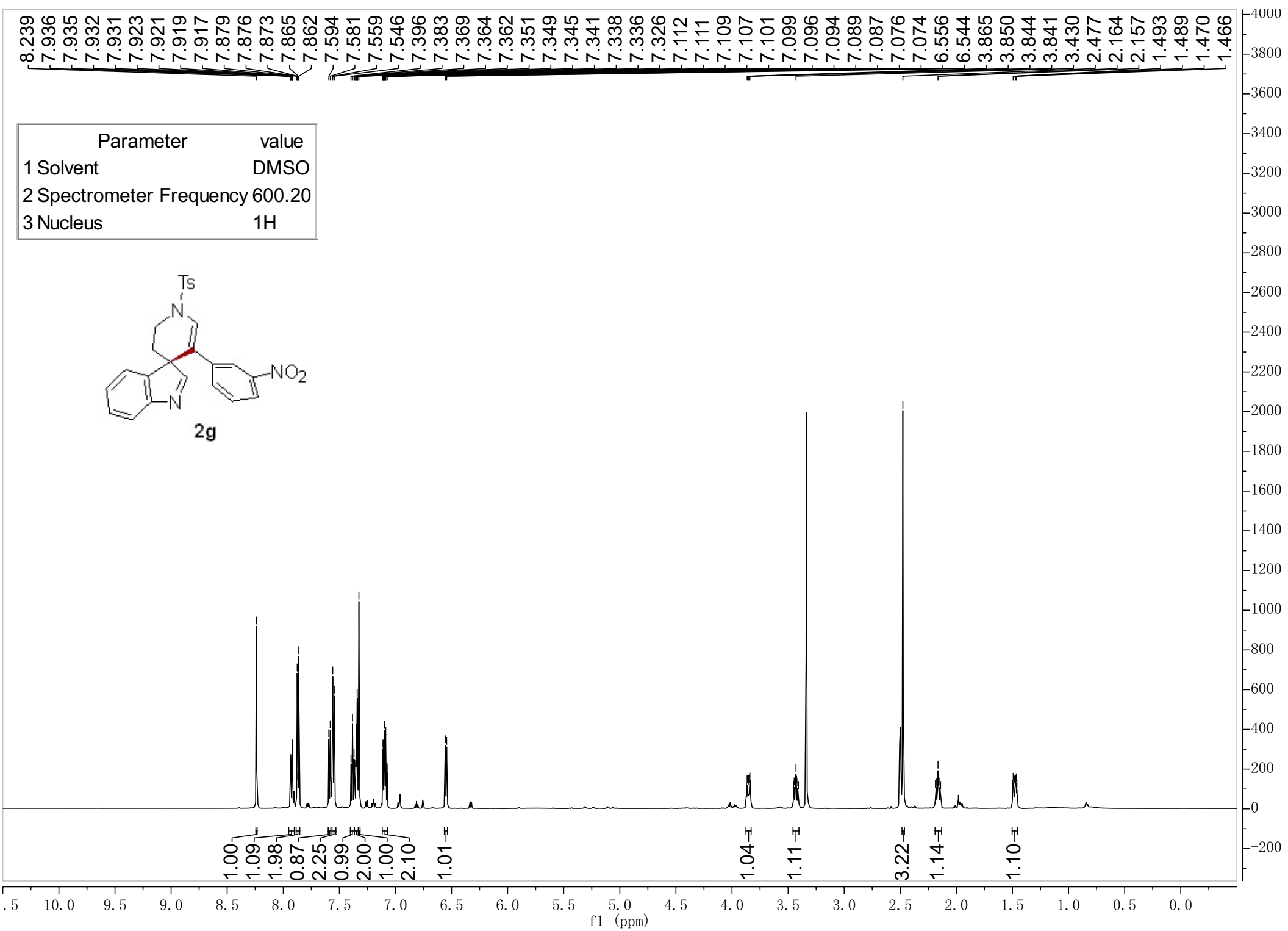
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



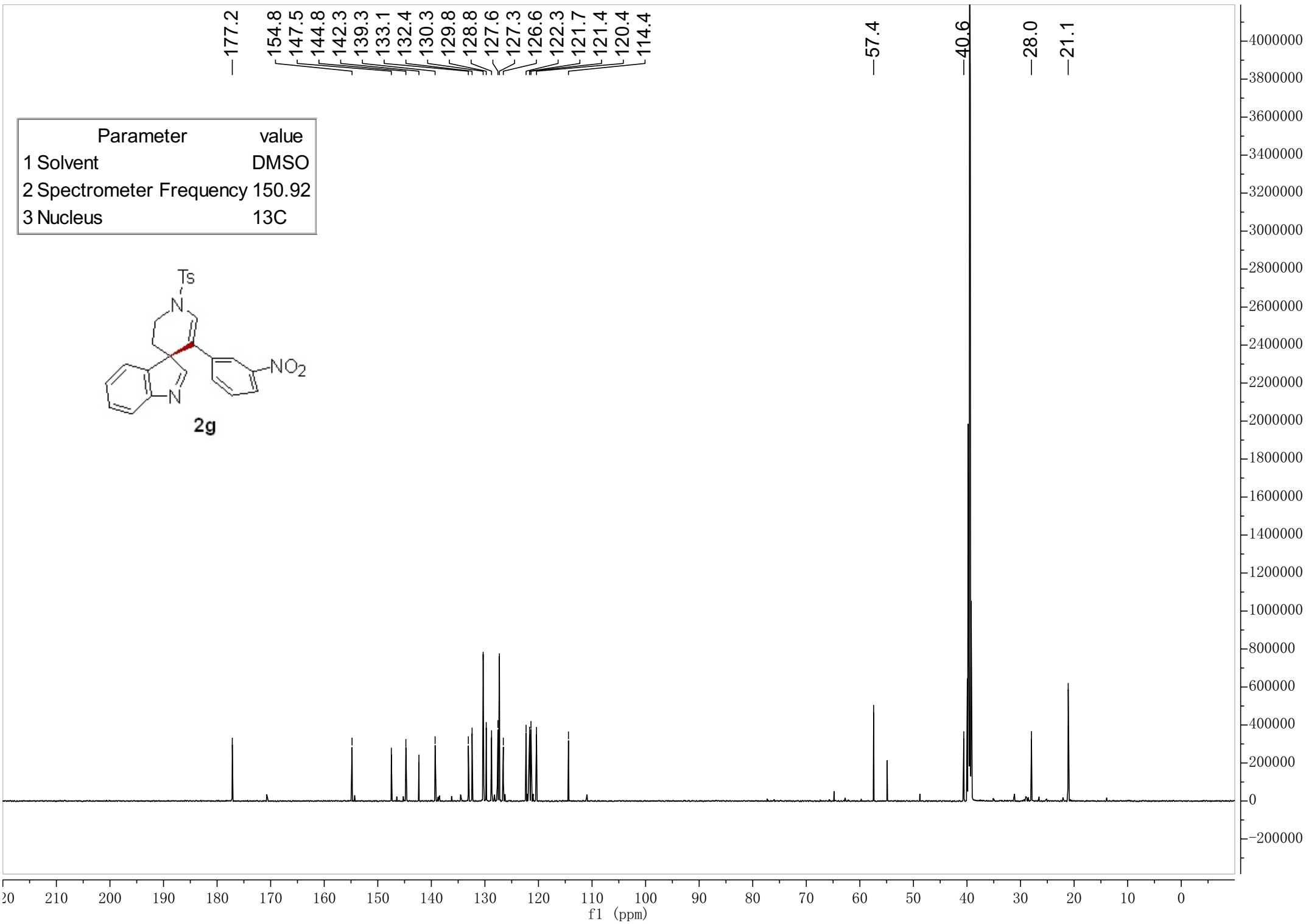


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

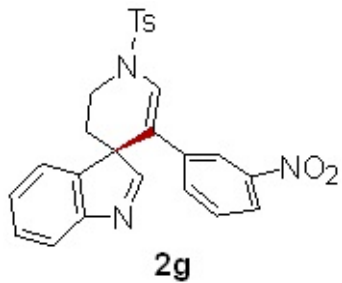


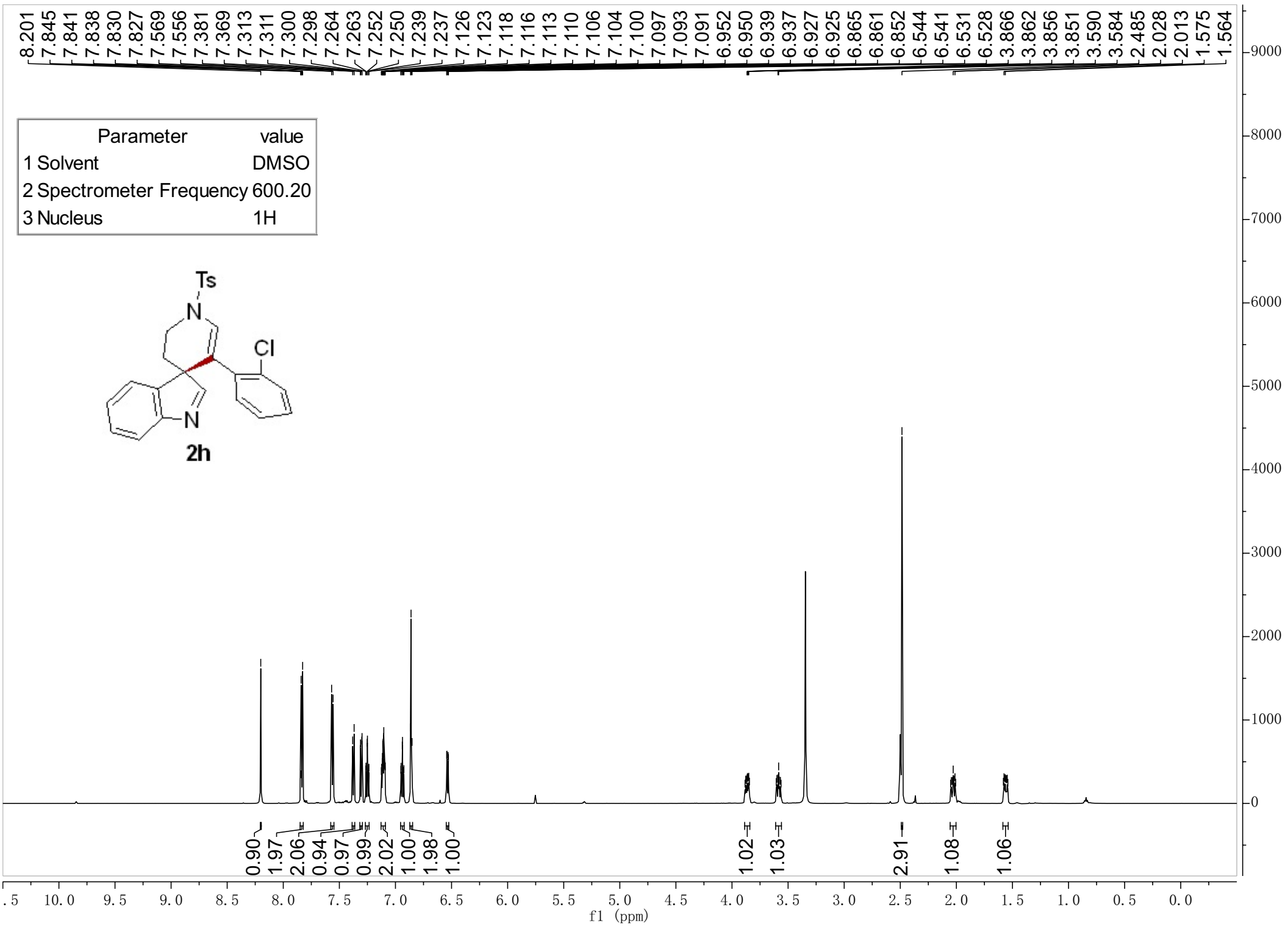


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

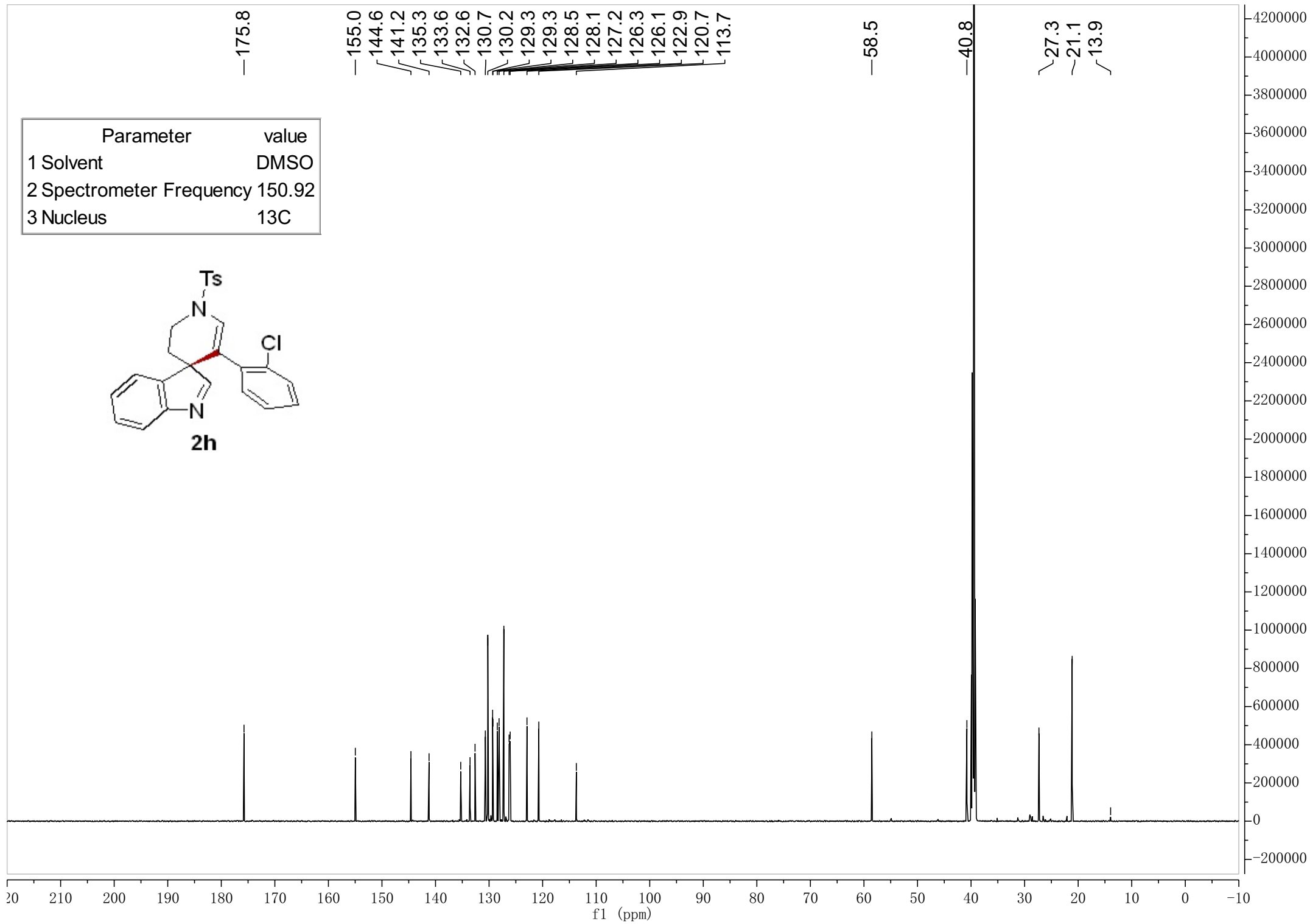
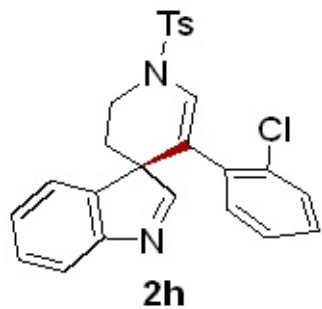


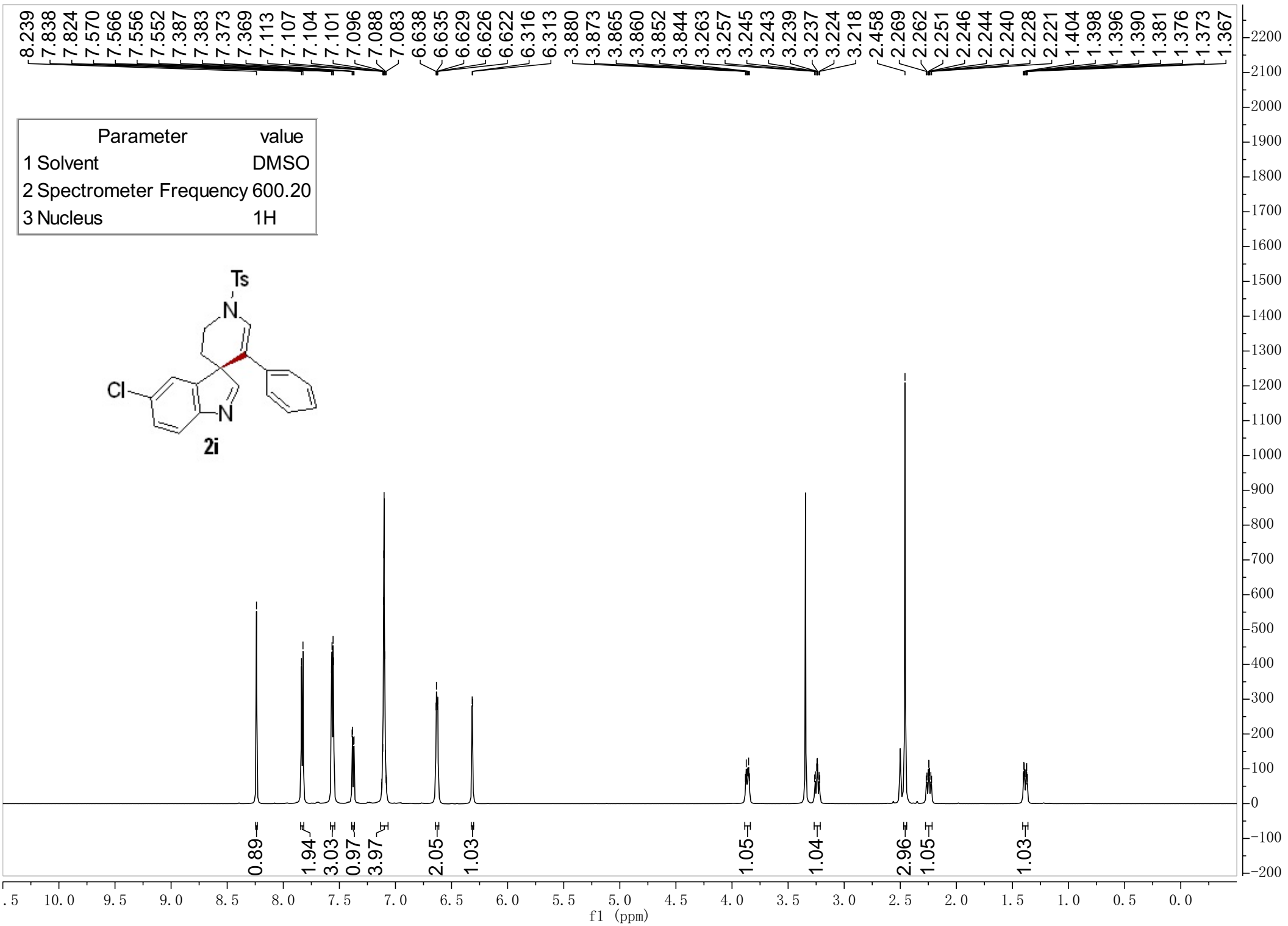
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

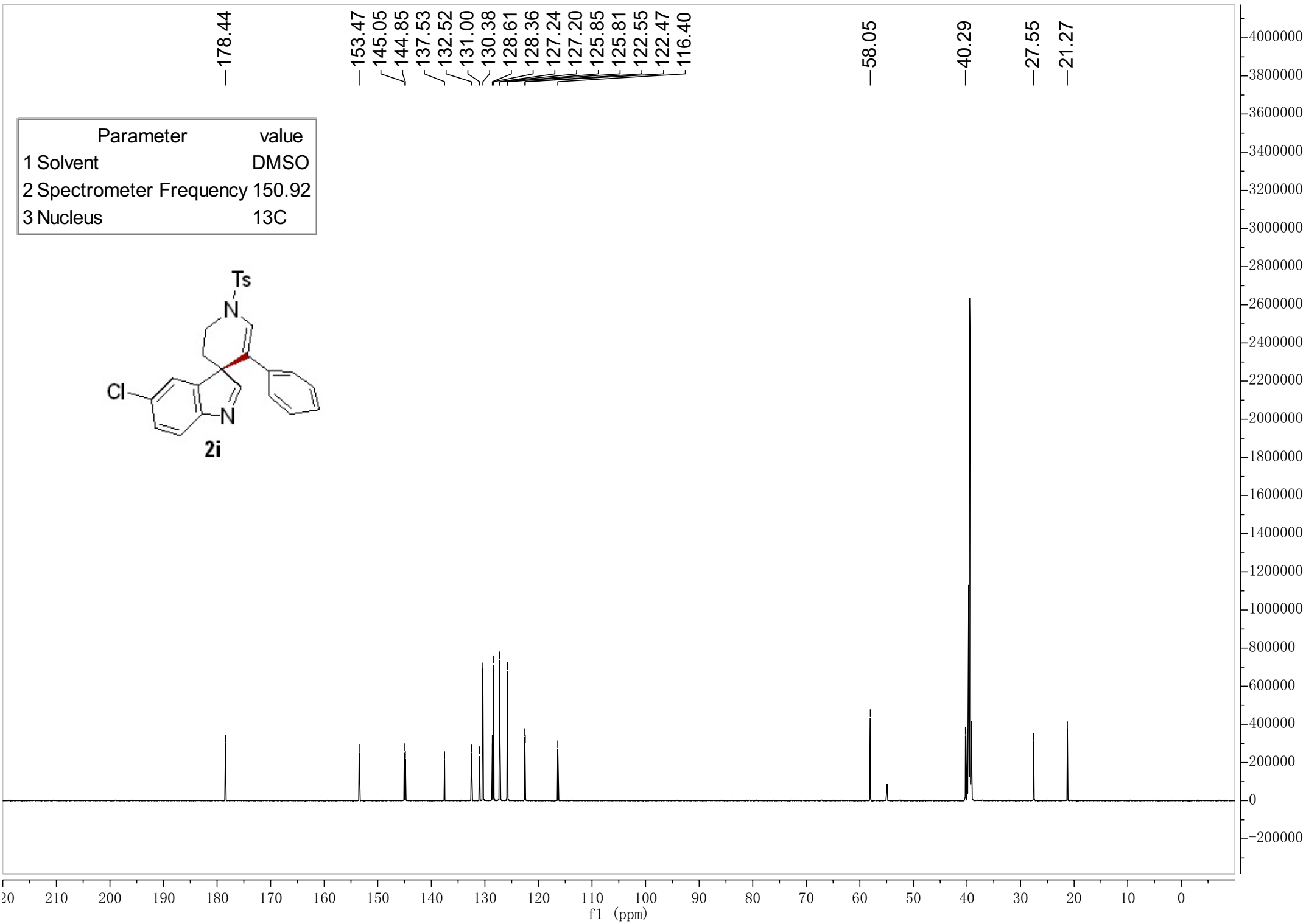


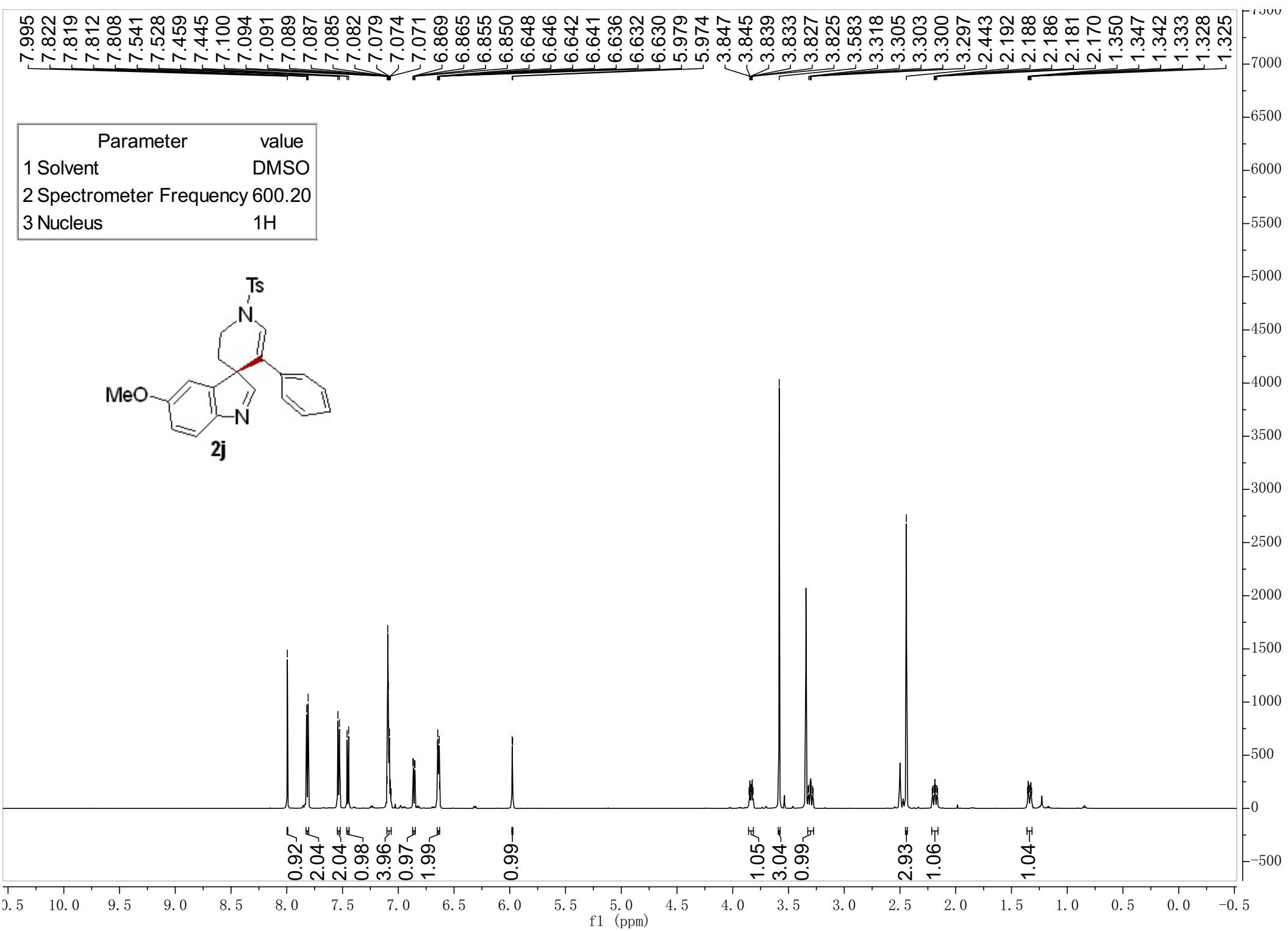


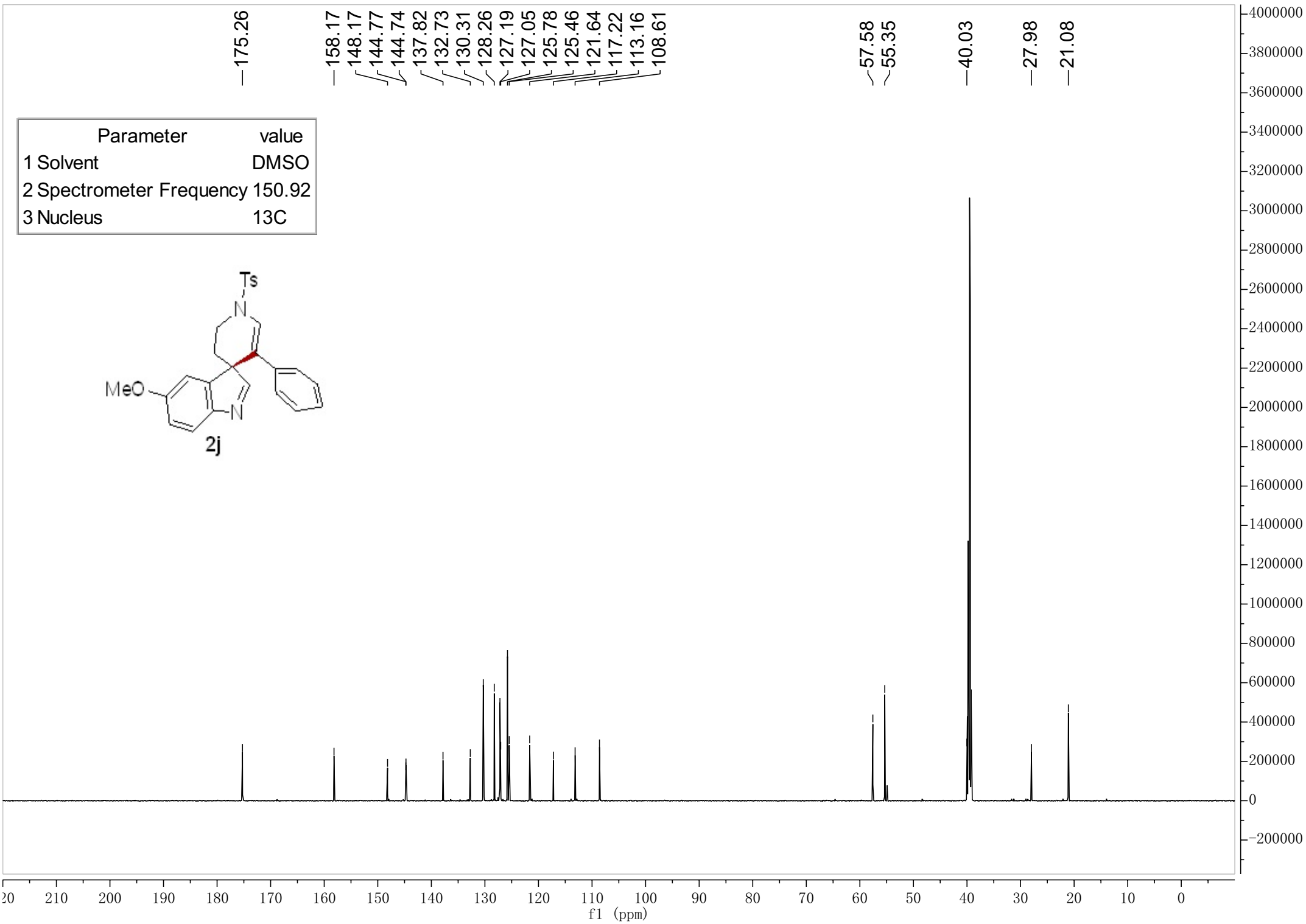
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

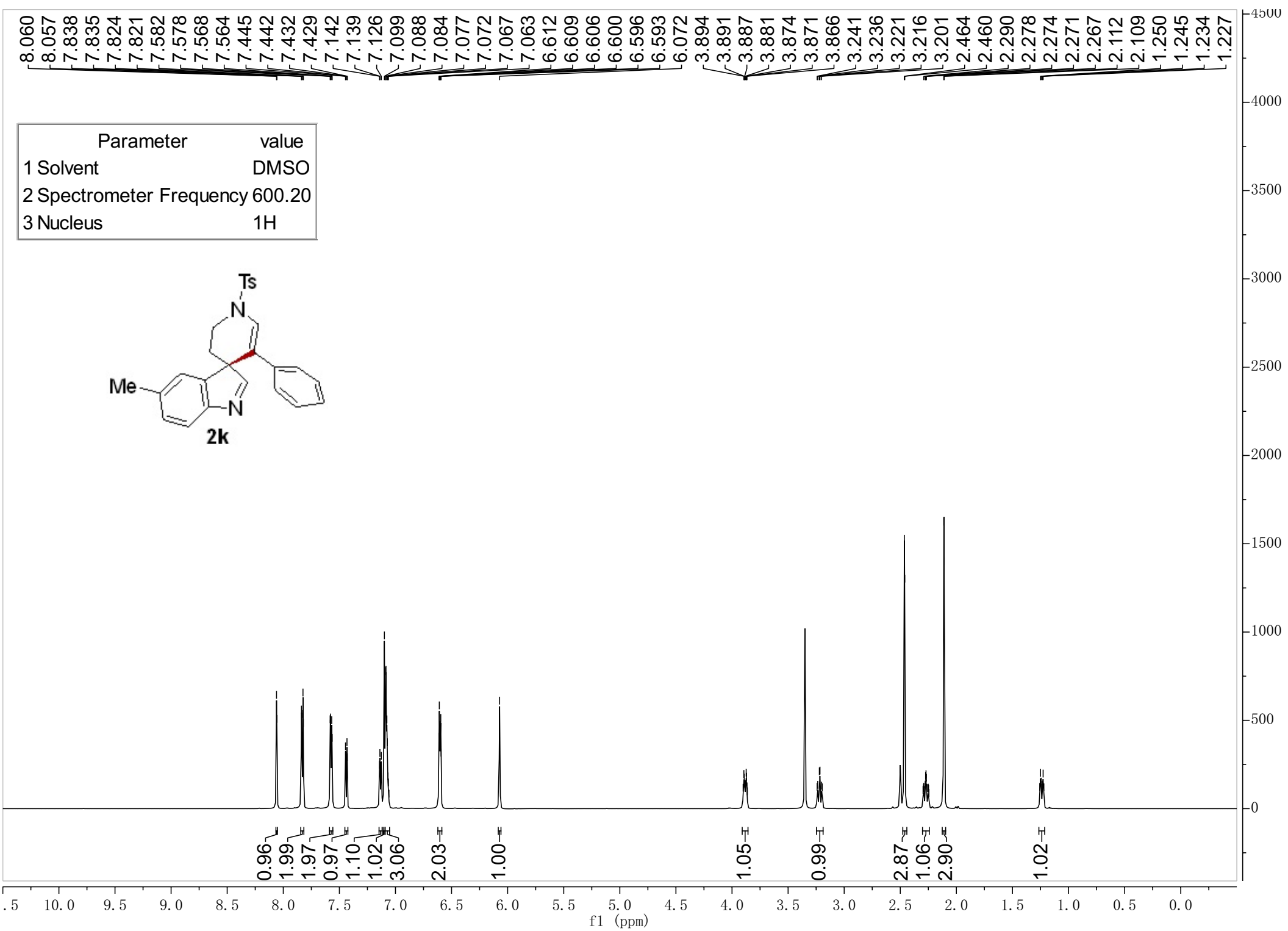




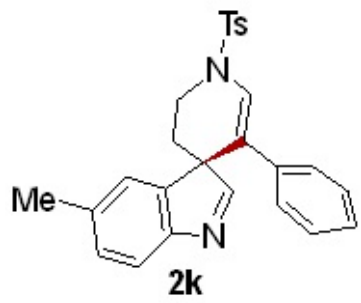






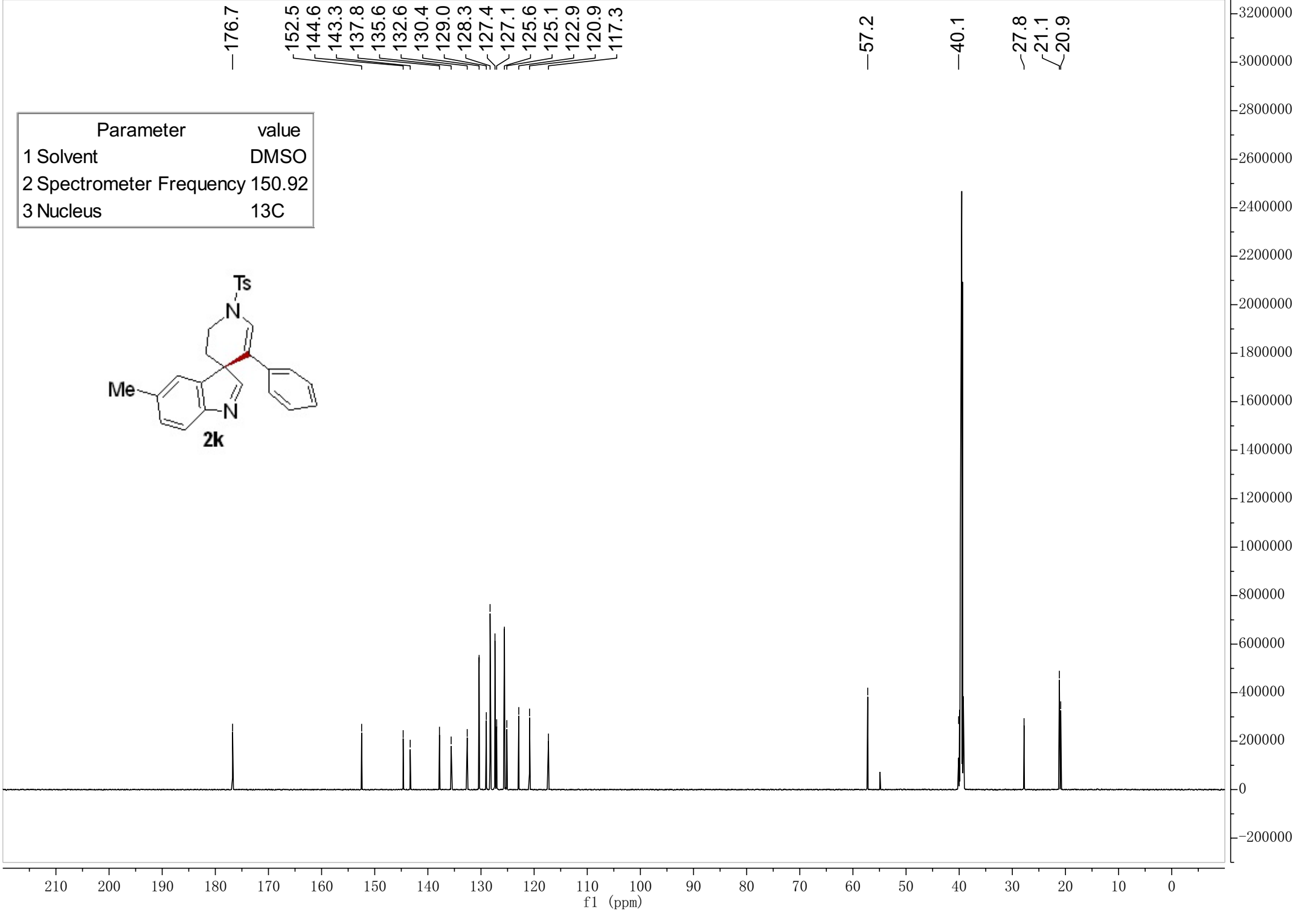


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



176.7
 152.5
 144.6
 143.3
 137.8
 135.6
 132.6
 130.4
 129.0
 128.3
 127.4
 127.1
 125.6
 125.1
 122.9
 120.9
 117.3

57.2
 40.1
 27.8
 21.1
 20.9

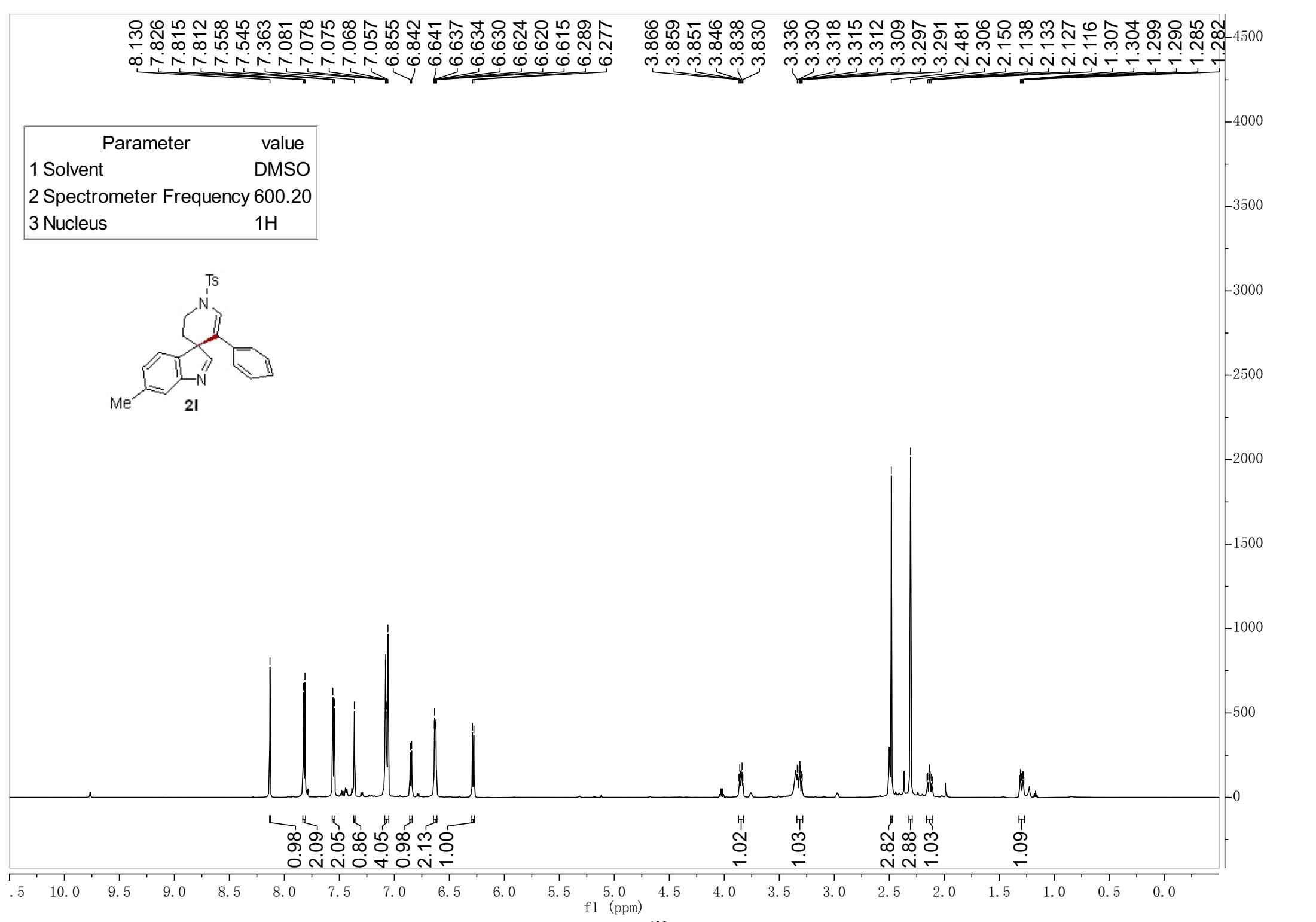
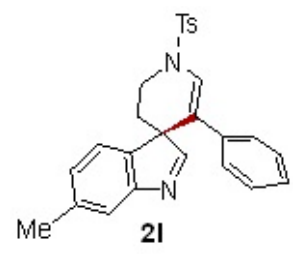


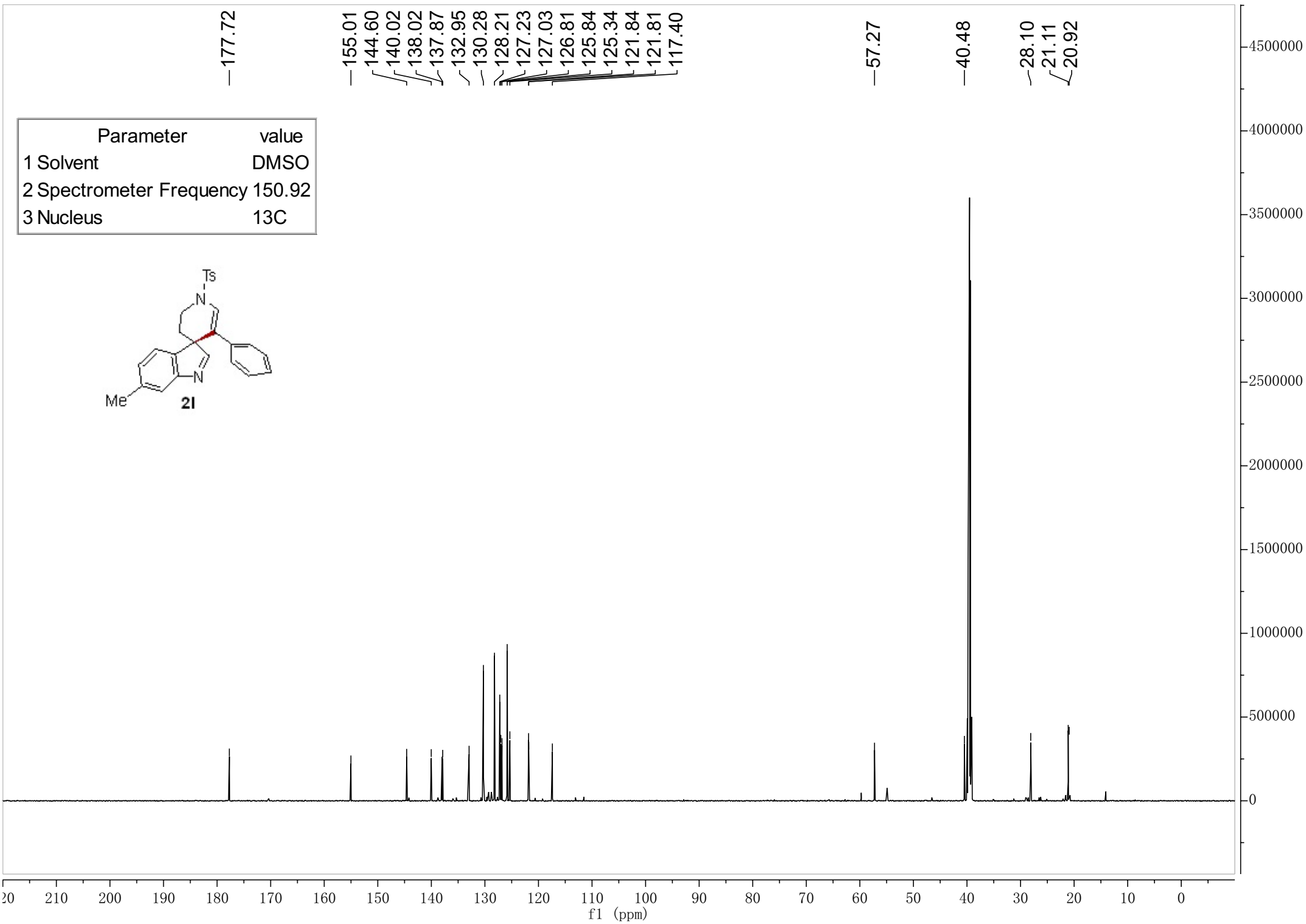
8.130
7.826
7.815
7.812
7.558
7.545
7.363
7.081
7.078
7.075
7.068
7.057
6.855
6.842
6.641
6.637
6.634
6.630
6.624
6.620
6.615
6.289
6.277

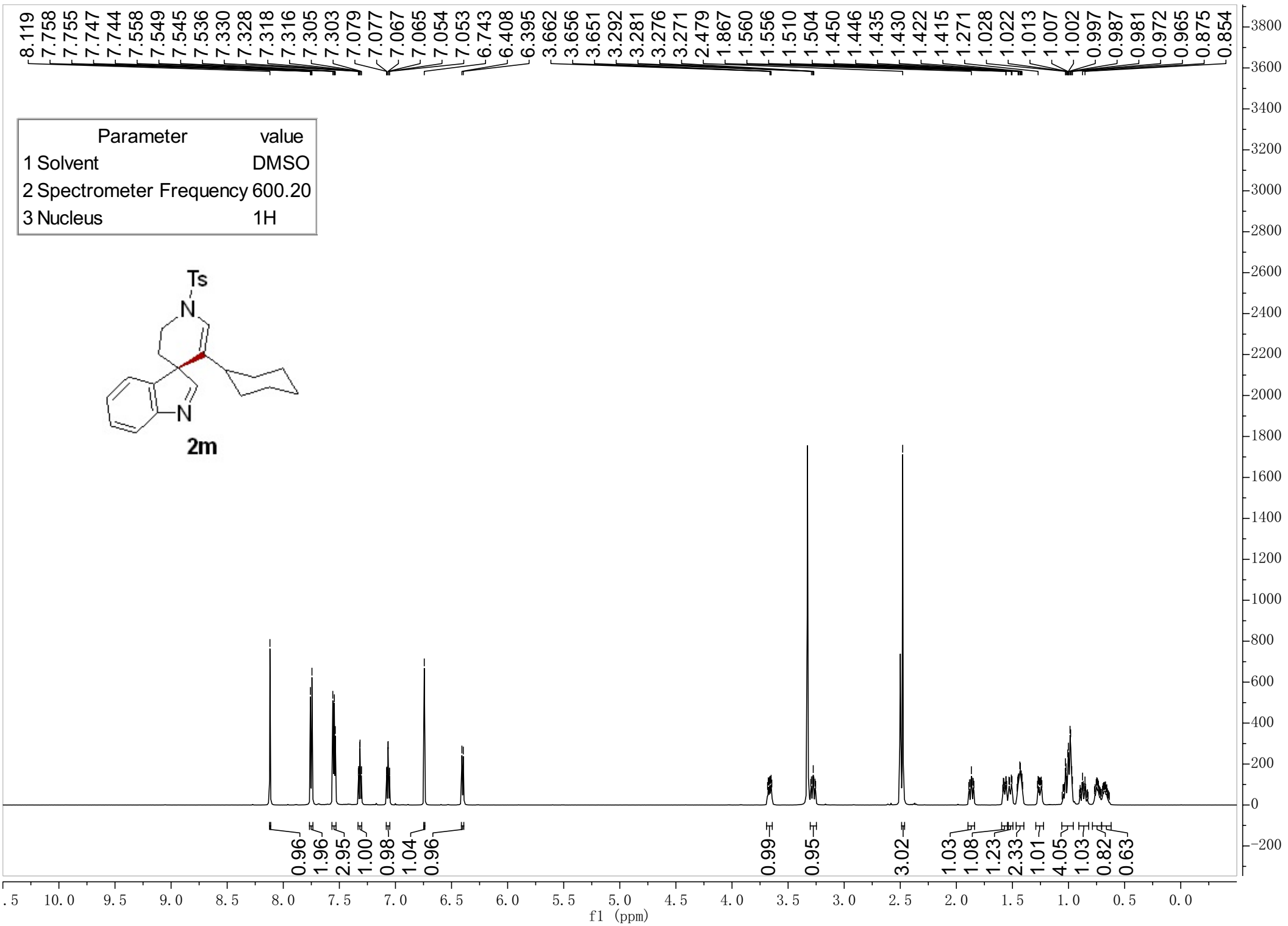
3.866
3.859
3.851
3.846
3.838
3.830

3.336
3.330
3.318
3.315
3.312
3.309
3.297
3.291
2.481
2.306
2.150
2.138
2.133
2.127
2.116
1.307
1.304
1.299
1.290
1.285
1.282

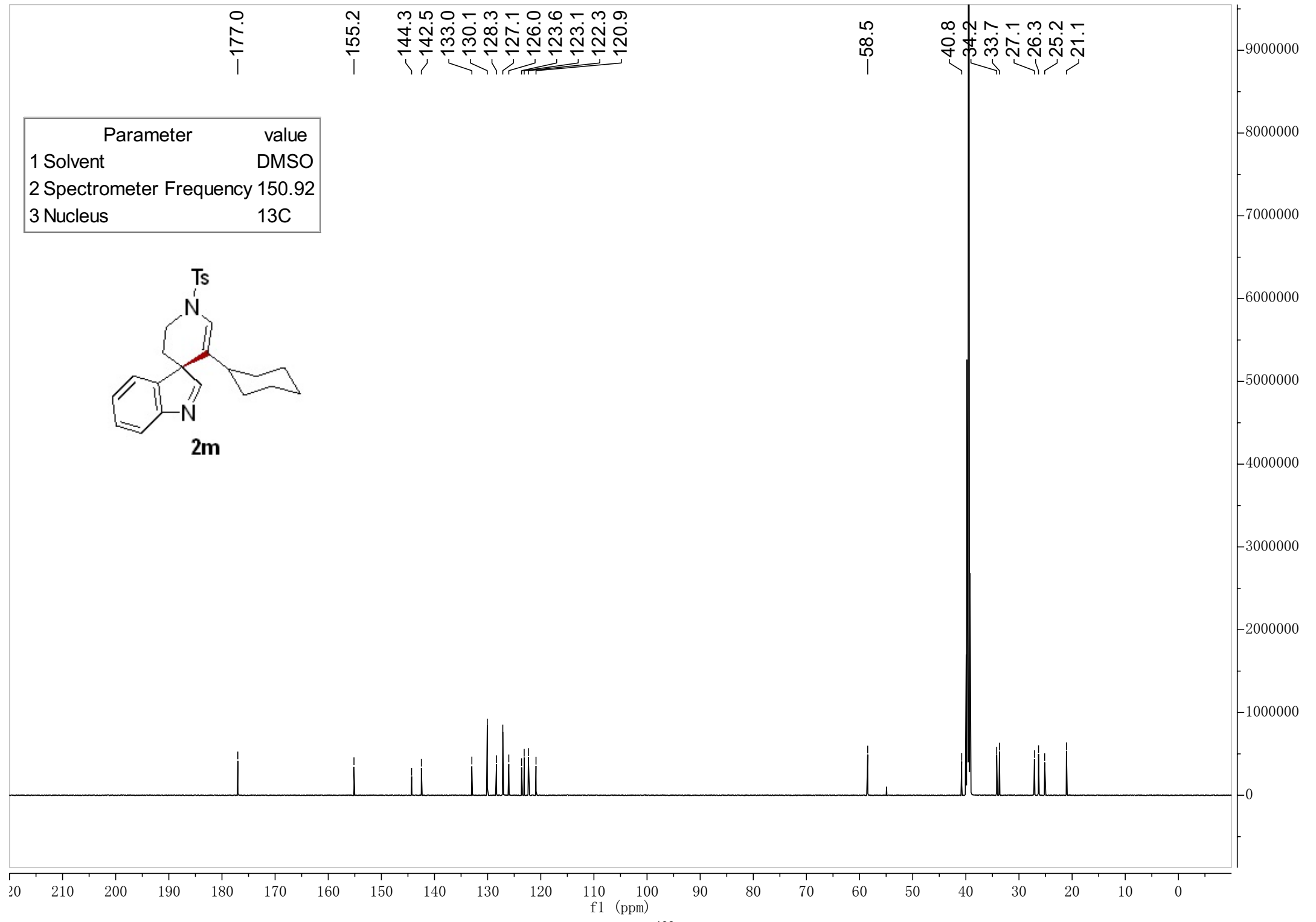
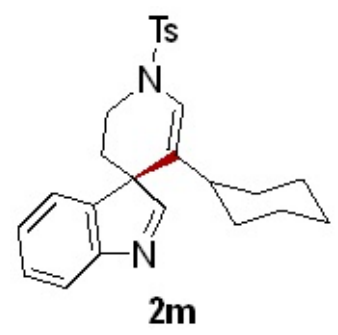
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

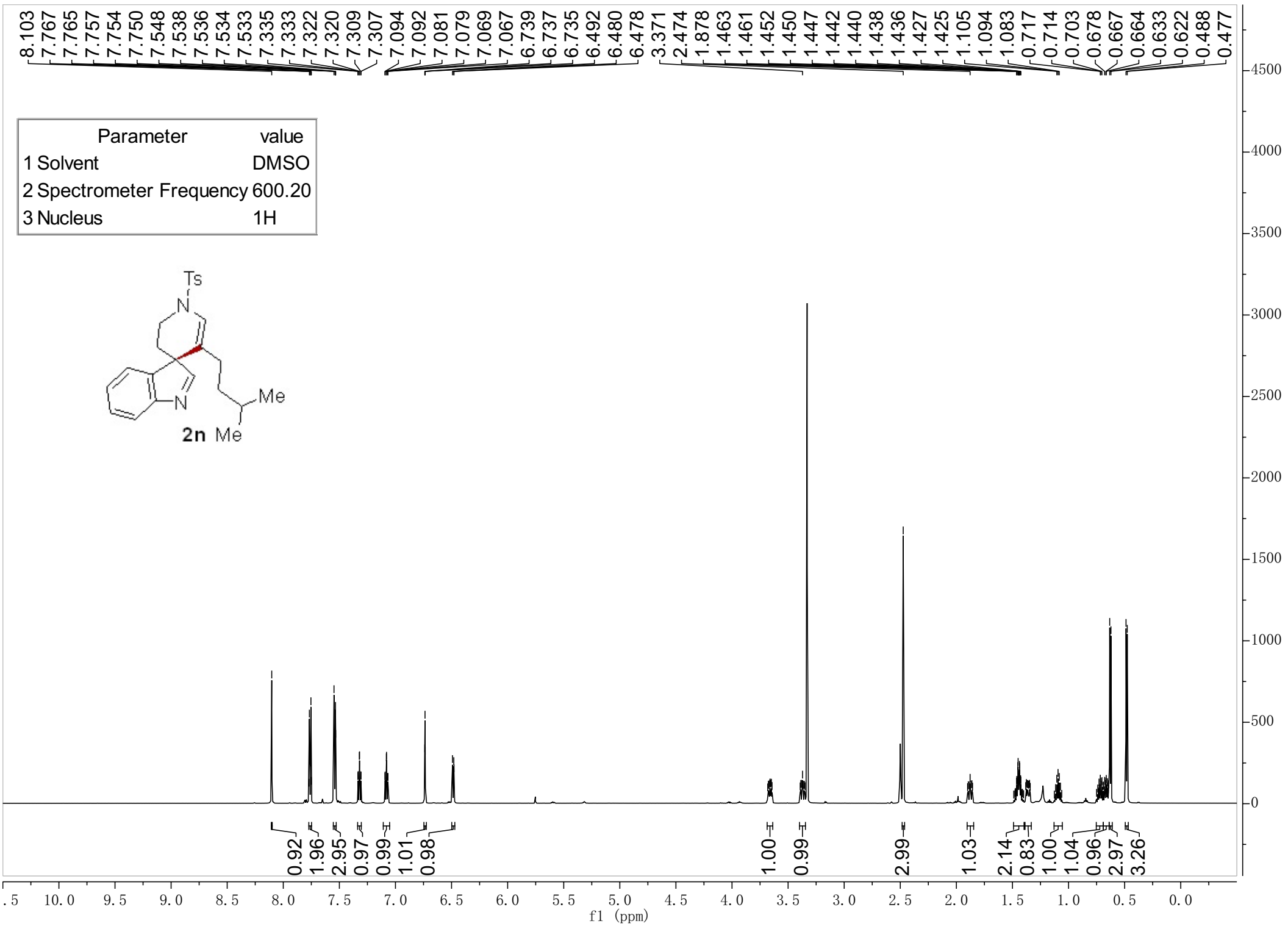




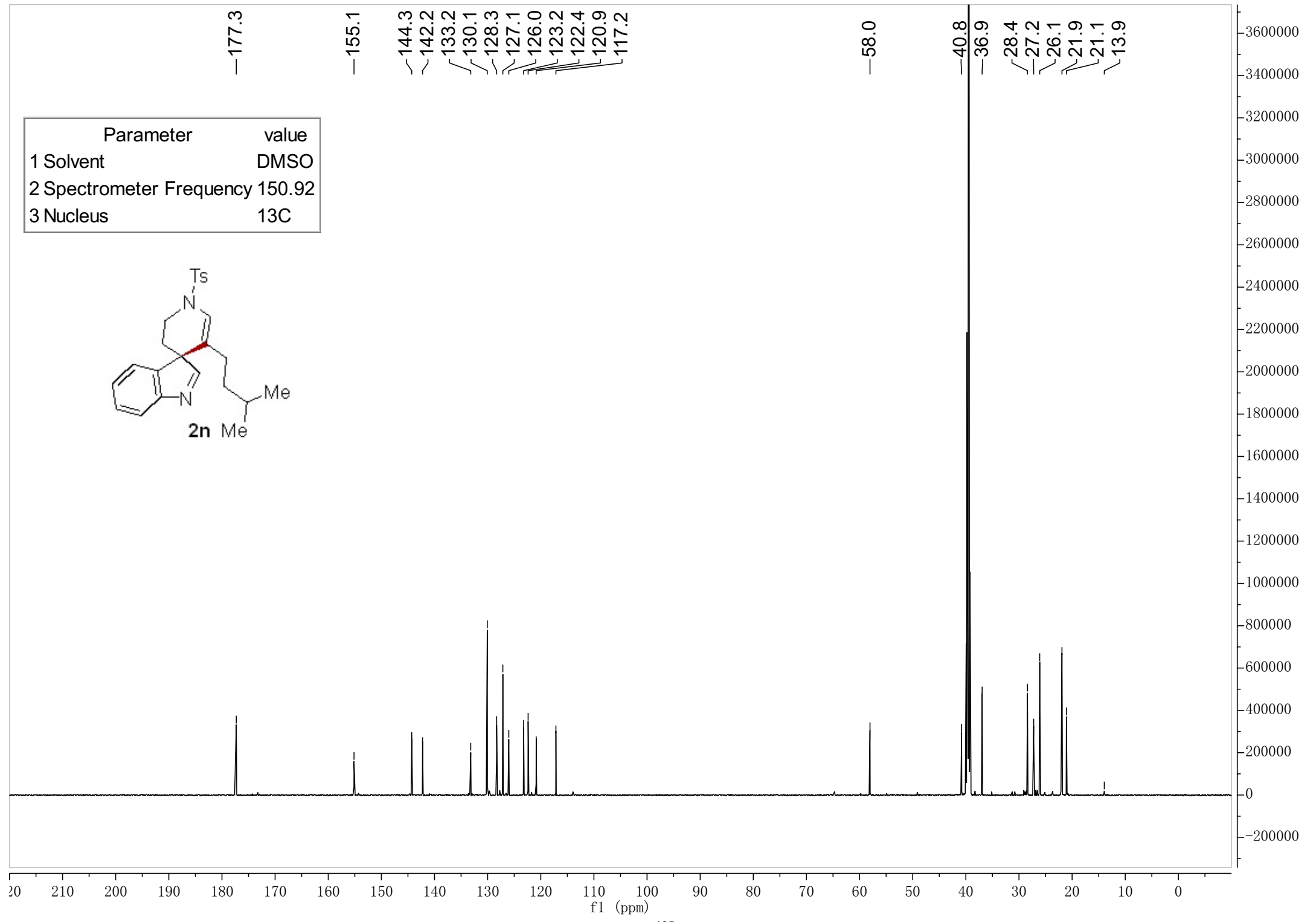
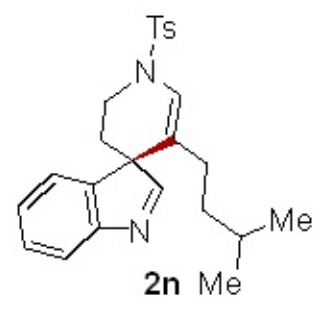


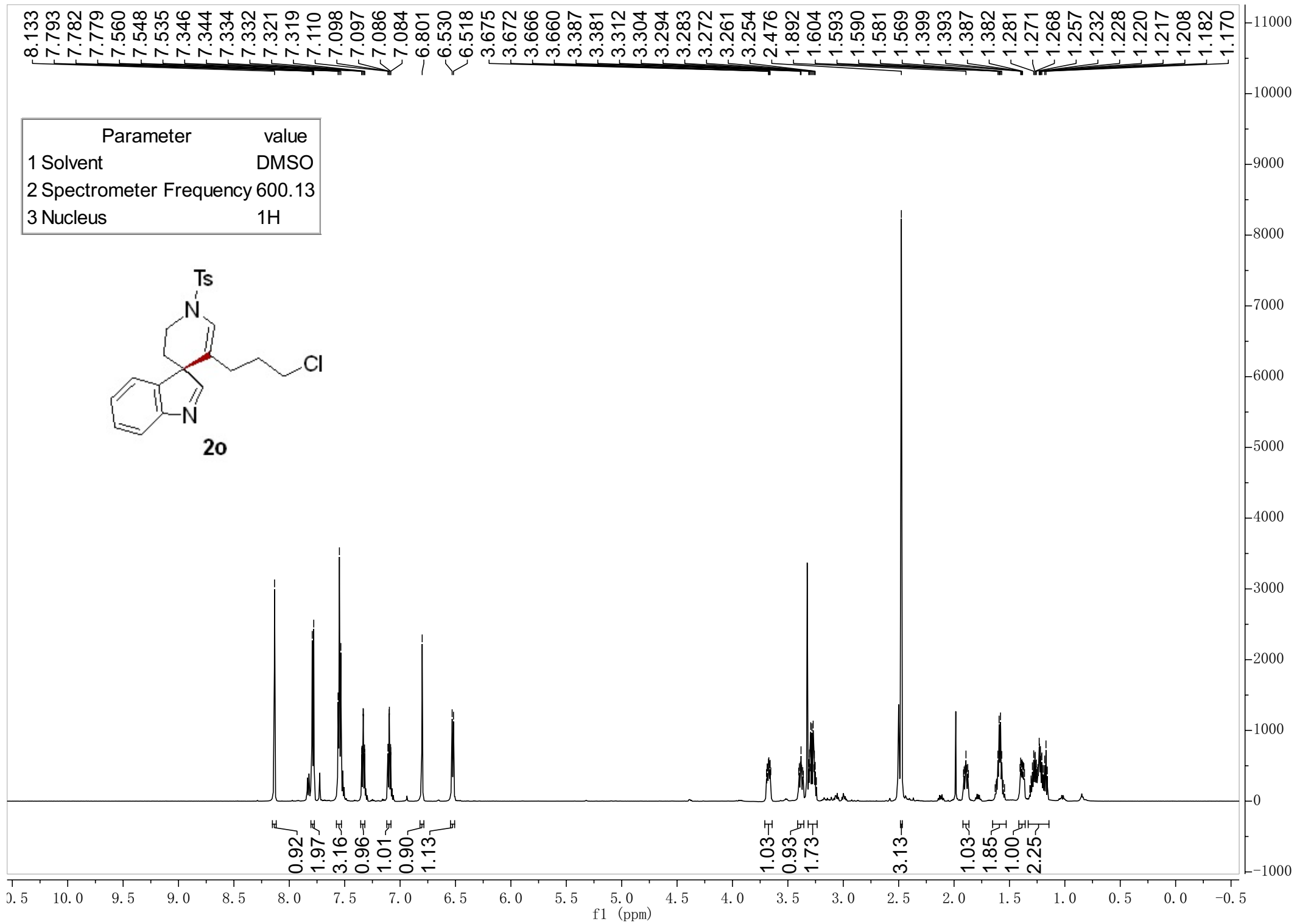
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



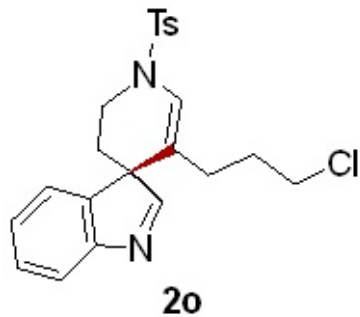


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

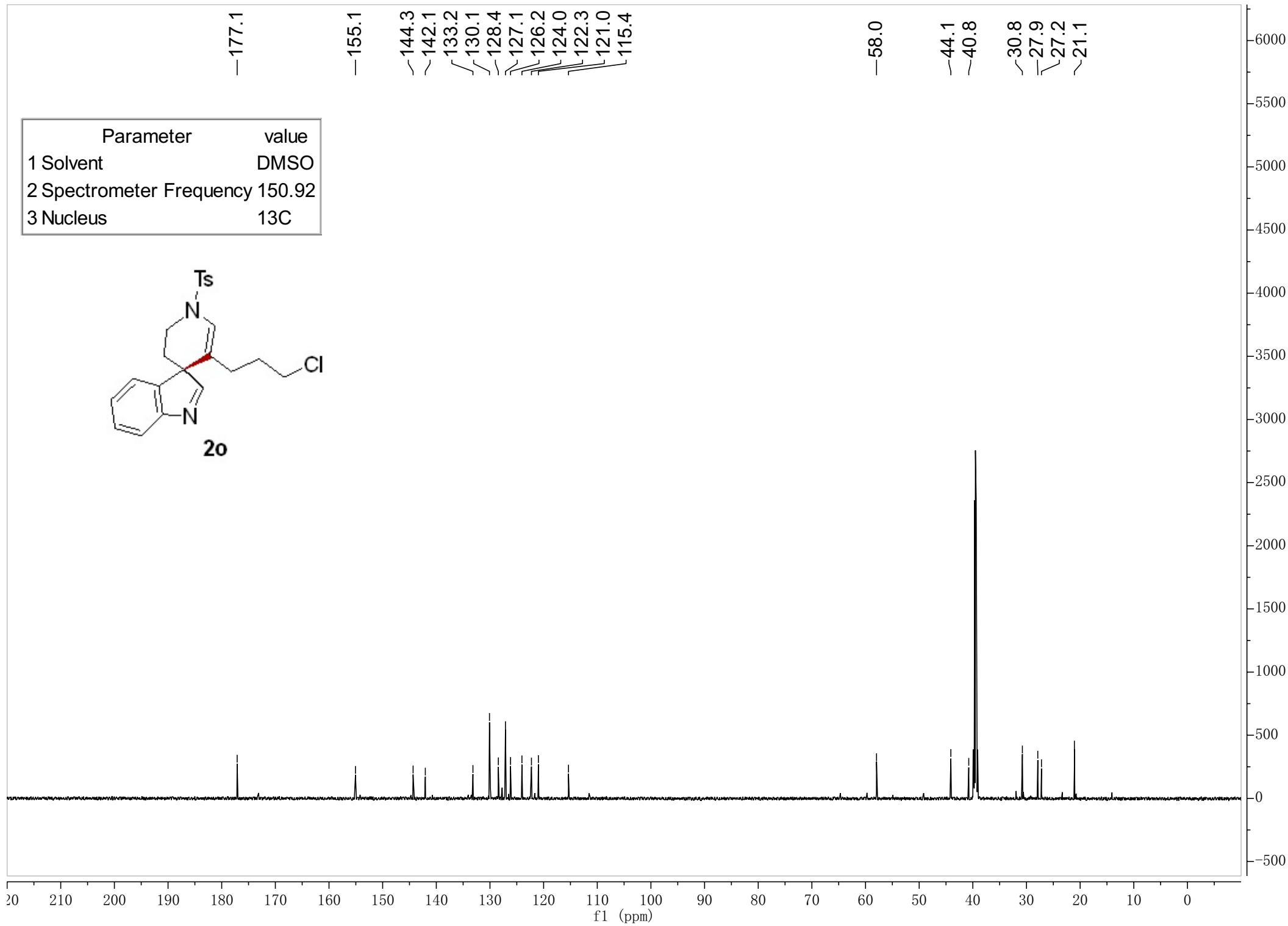


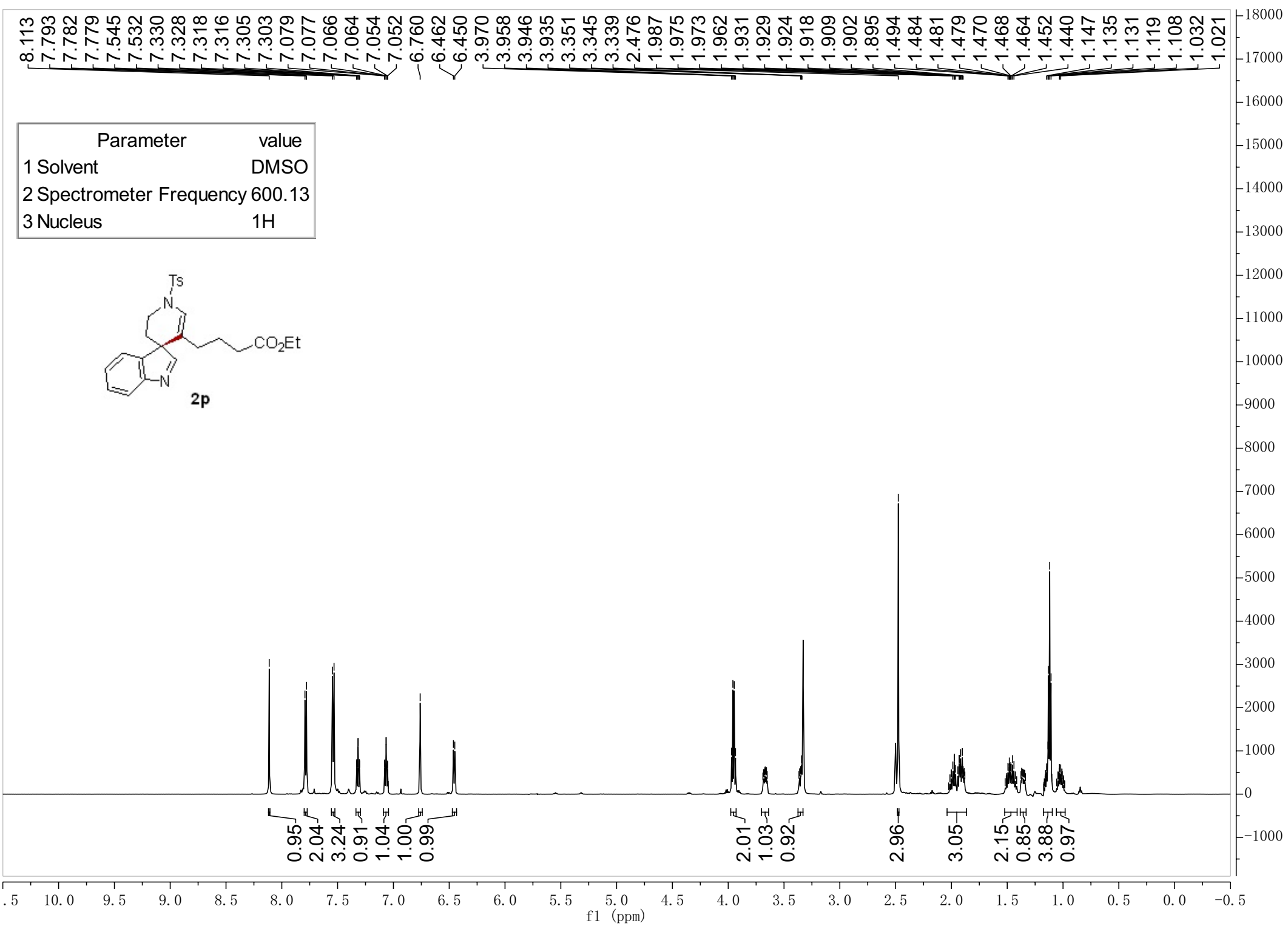


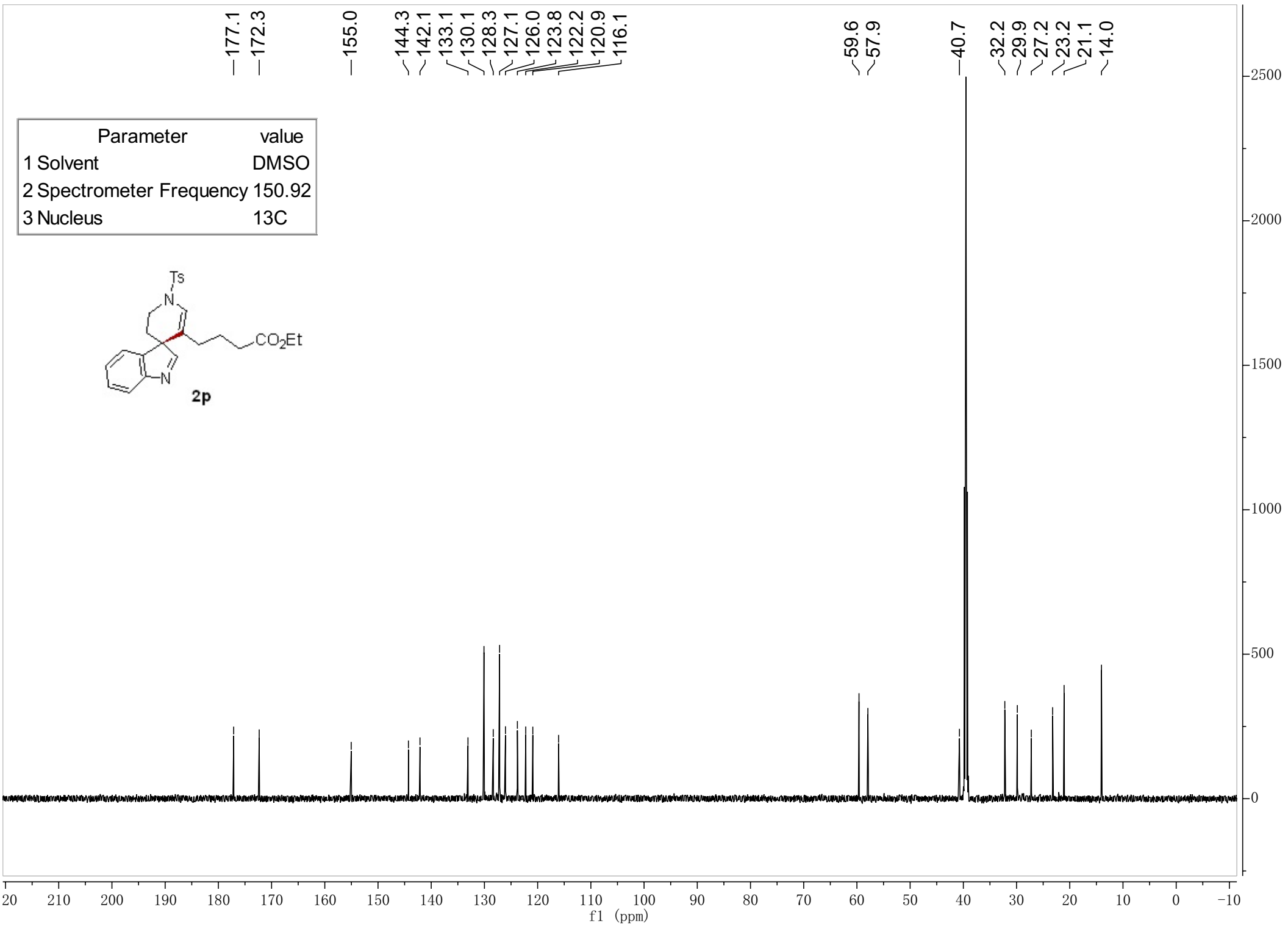
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



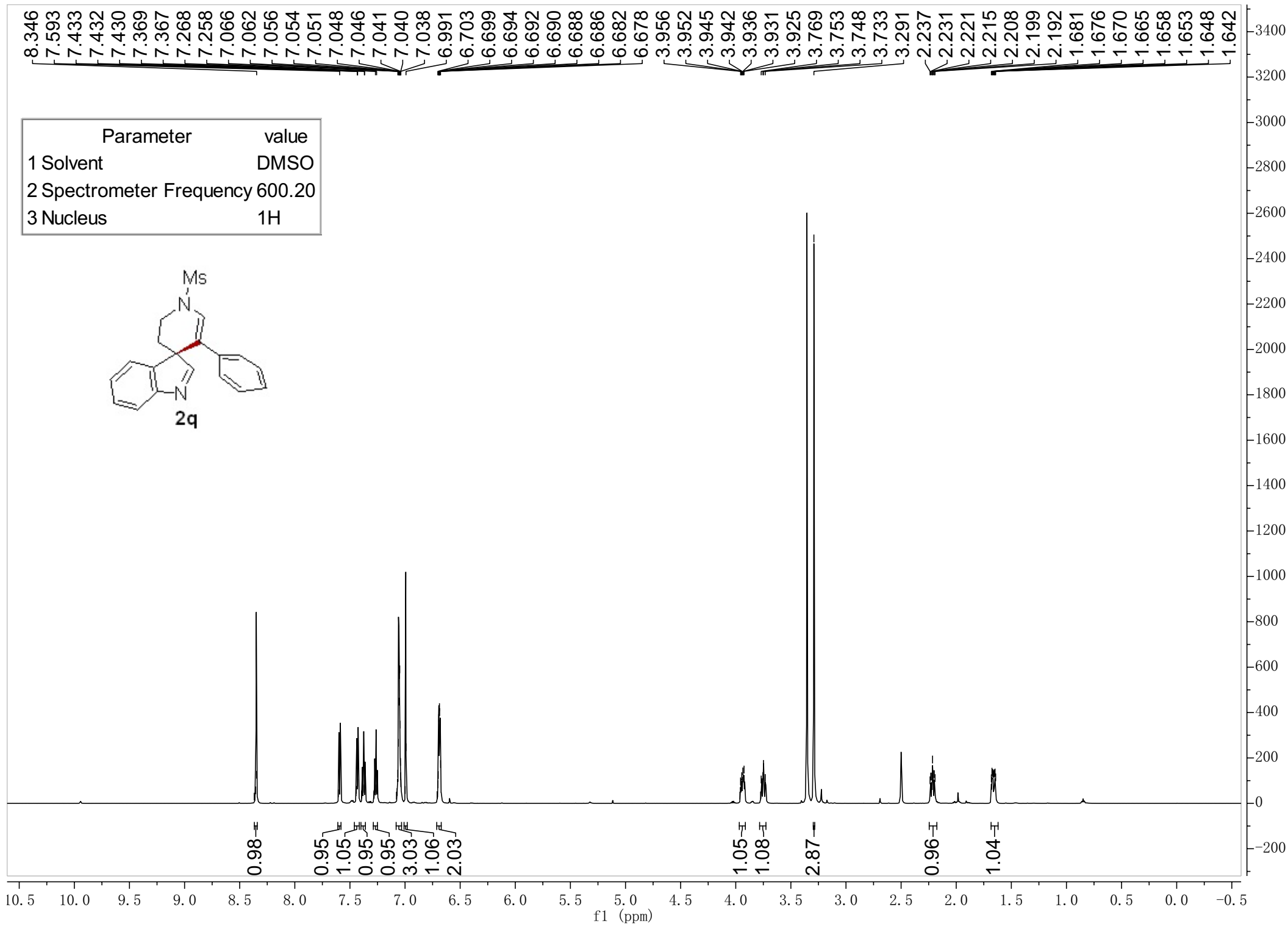
— 177.1
 — 155.1
 ~ 144.3
 ~ 142.1
 / 133.2
 / 130.1
 / 128.4
 / 127.1
 / 126.2
 / 124.0
 / 122.3
 / 121.0
 / 115.4
 — 58.0
 ~ 44.1
 ~ 40.8
 / 30.8
 ~ 27.9
 / 27.2
 ~ 21.1



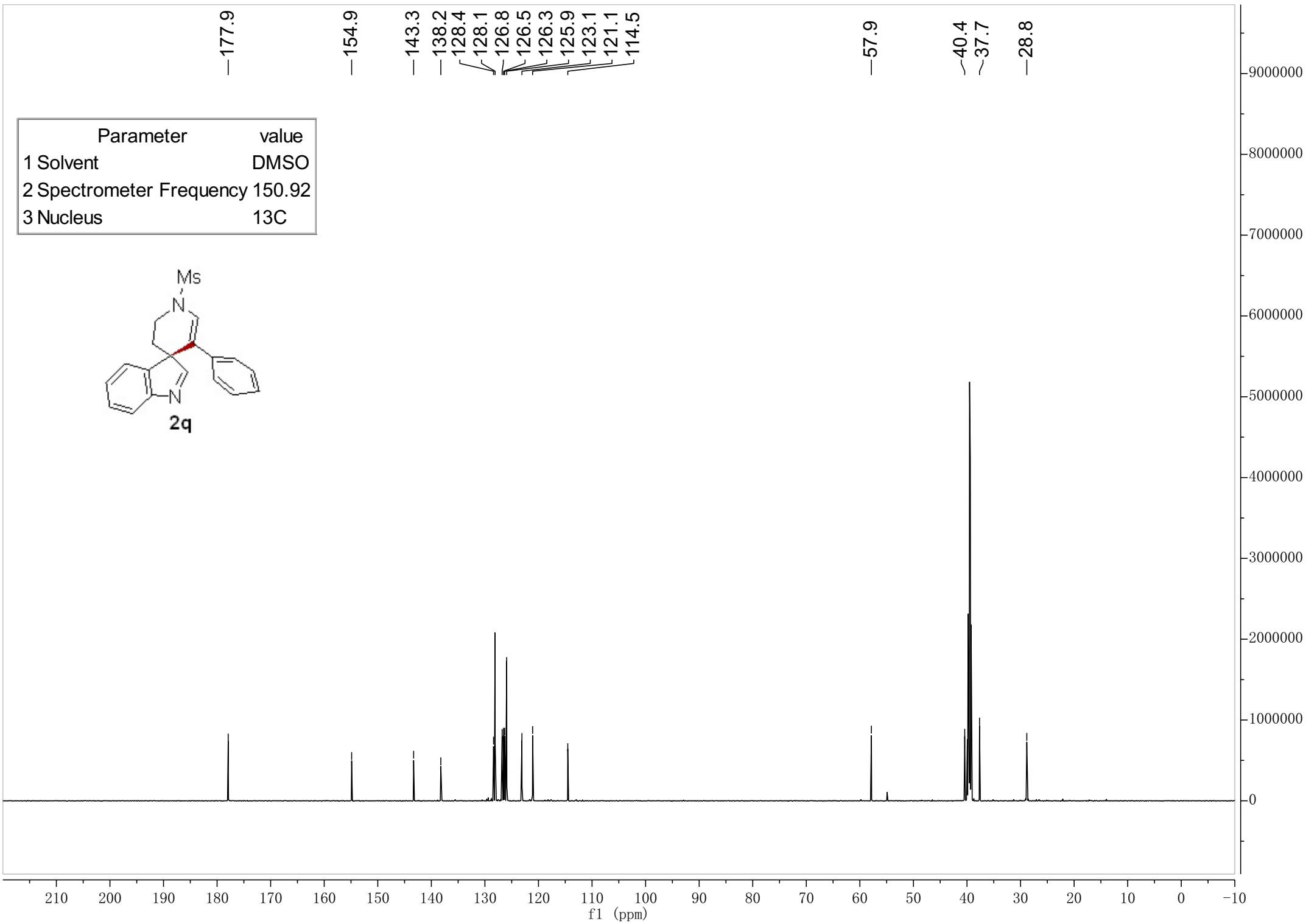
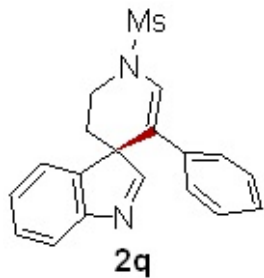


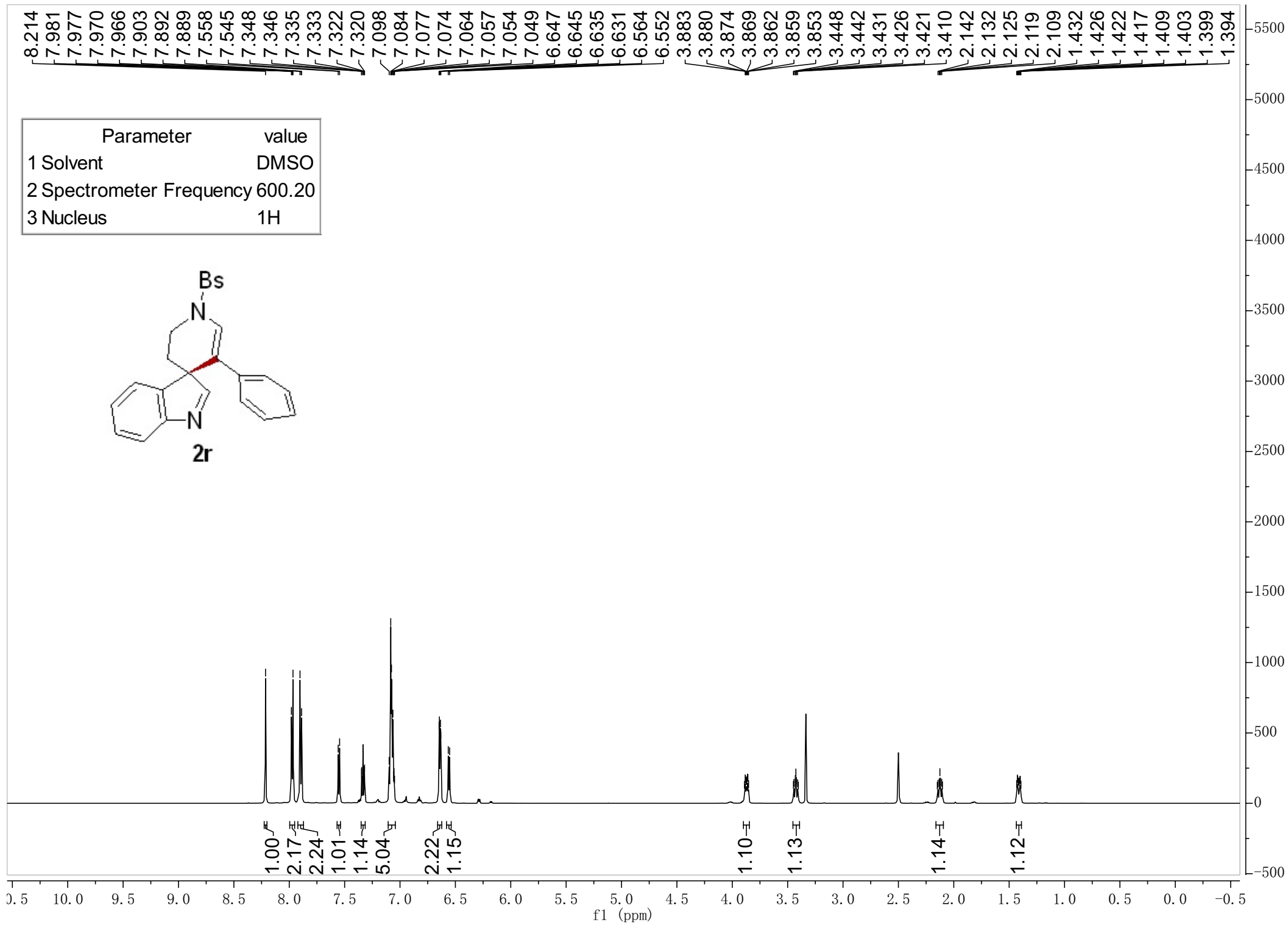


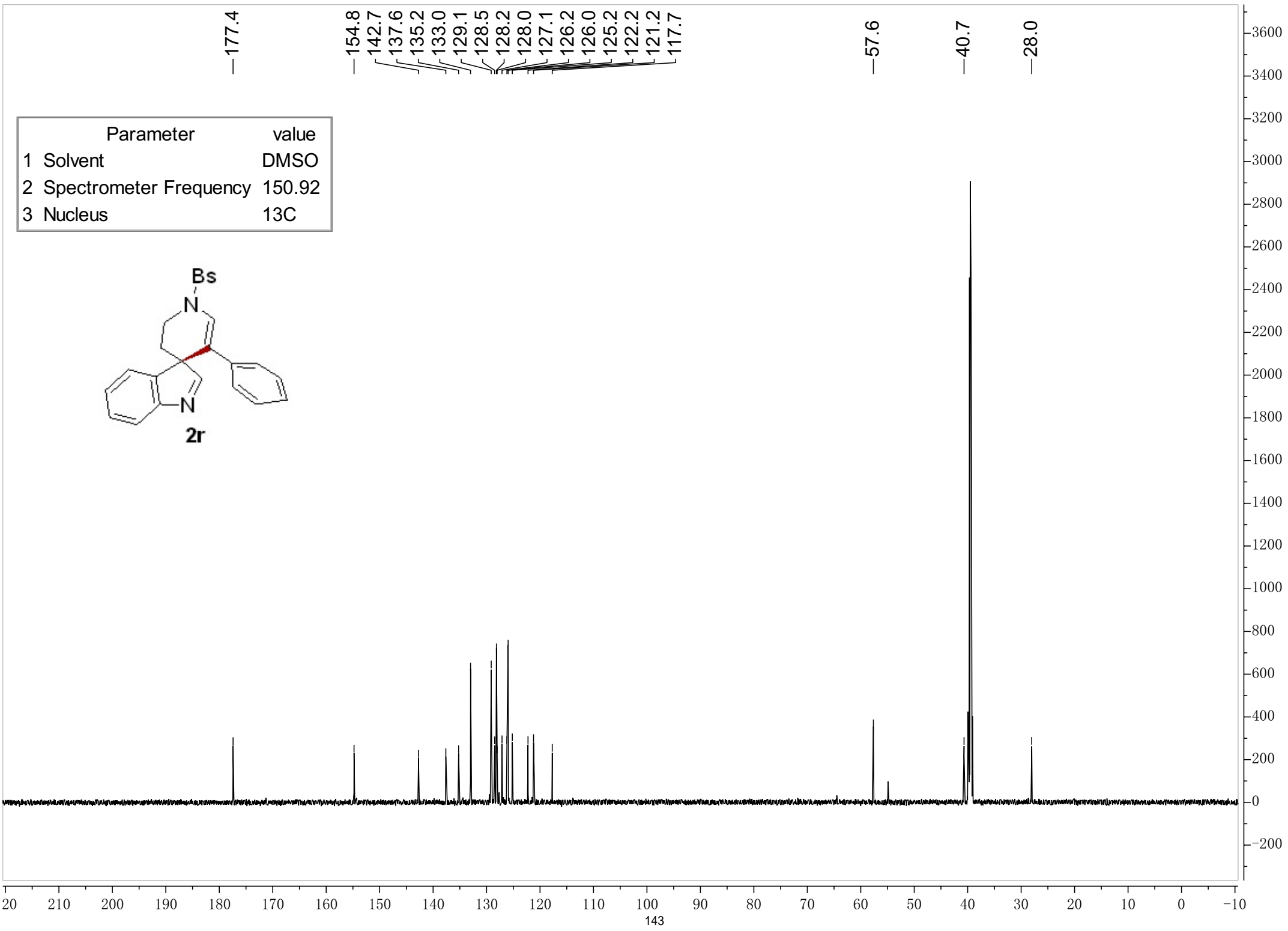
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C





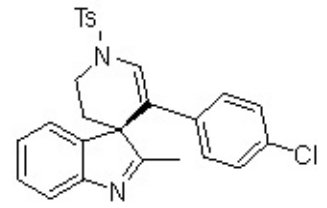


7.840
7.837
7.826
7.823
7.565
7.552
7.489
7.476
7.350
7.338
7.336
7.325
7.323
7.192
7.189
7.166
7.163
7.152
7.148
6.994
6.982
6.969
6.953
6.520
6.508
6.505
6.298
6.286

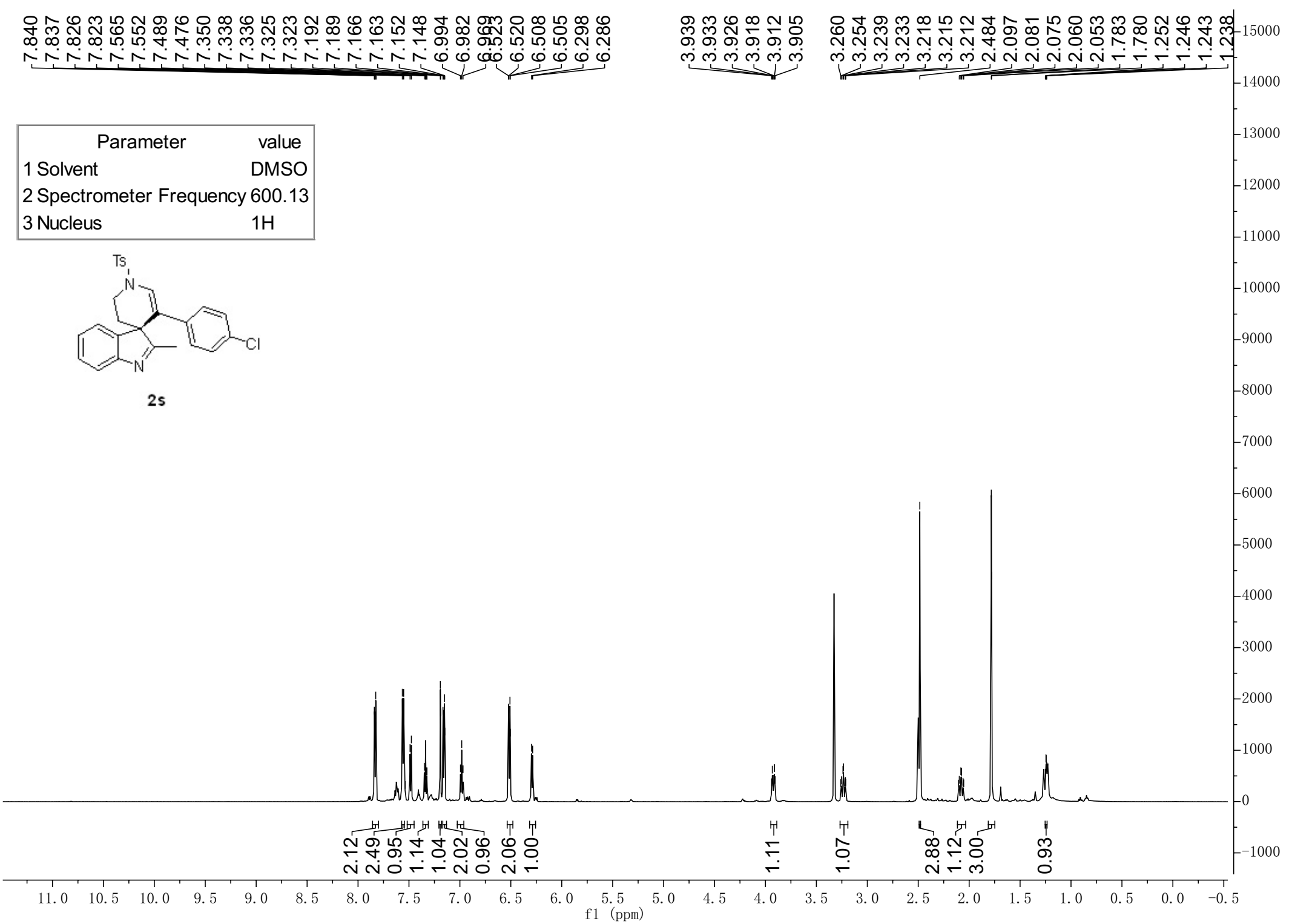
3.939
3.933
3.926
3.918
3.912
3.905

3.260
3.254
3.239
3.233
3.218
3.215
3.212
2.484
2.097
2.081
2.075
2.060
2.053
1.783
1.780
1.252
1.246
1.243
1.238

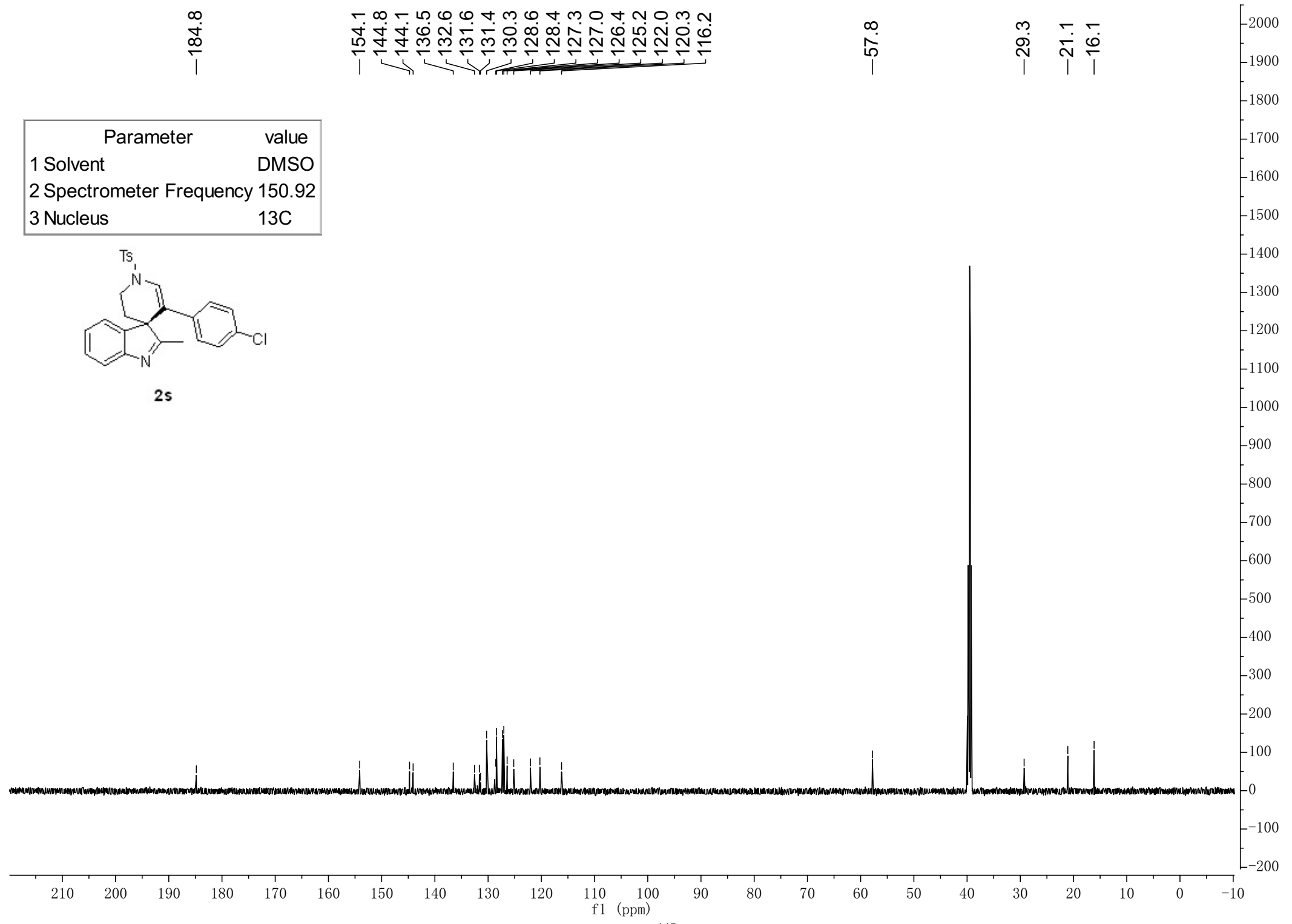
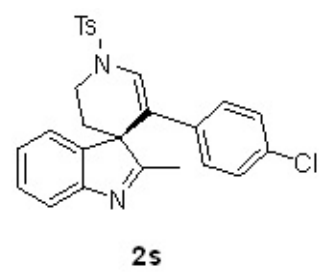
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.13
3 Nucleus	1H

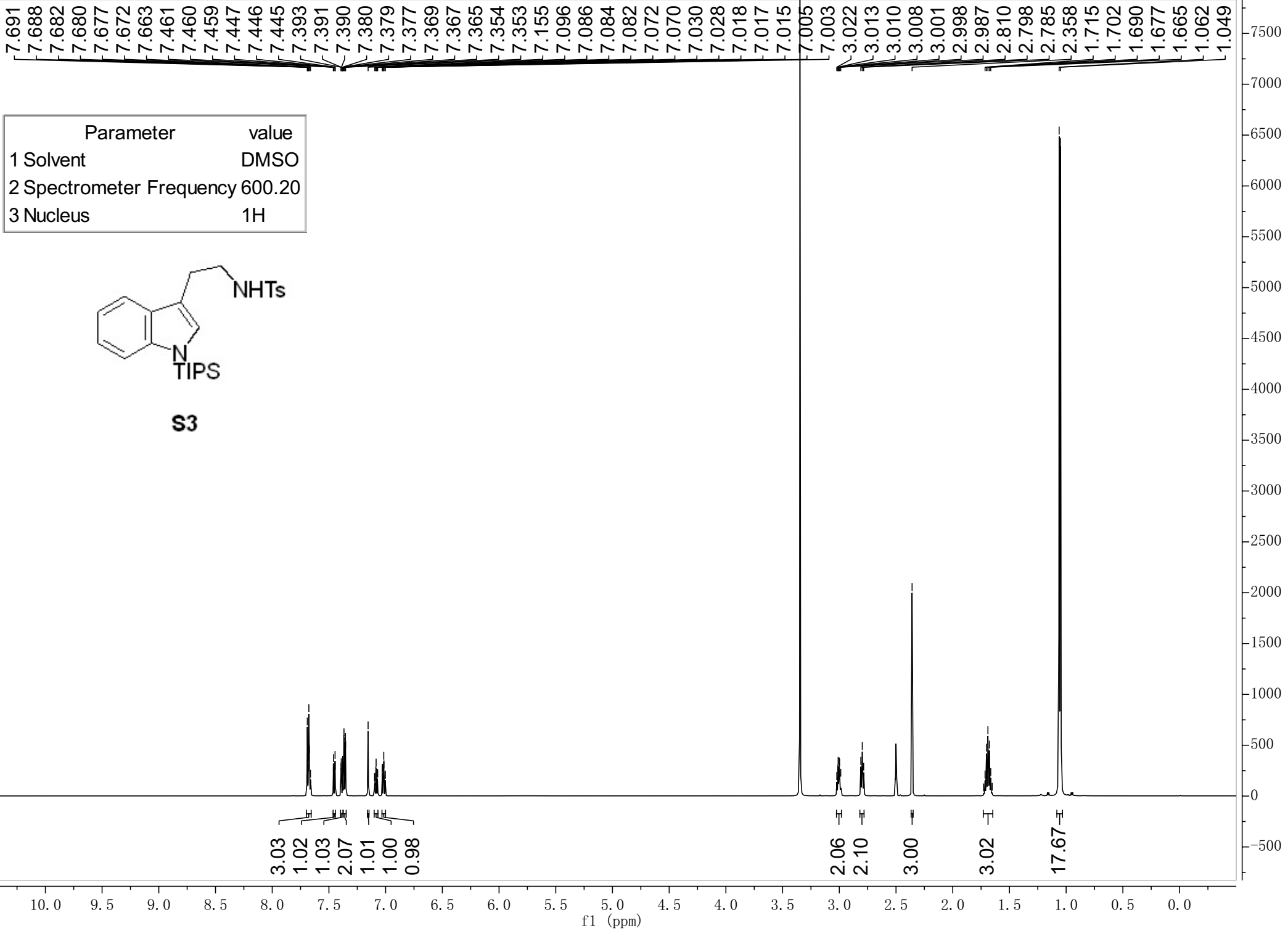


25

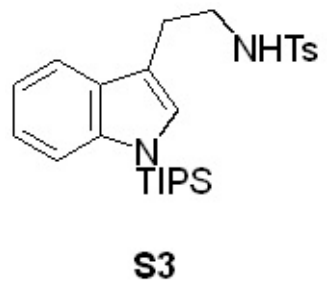


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



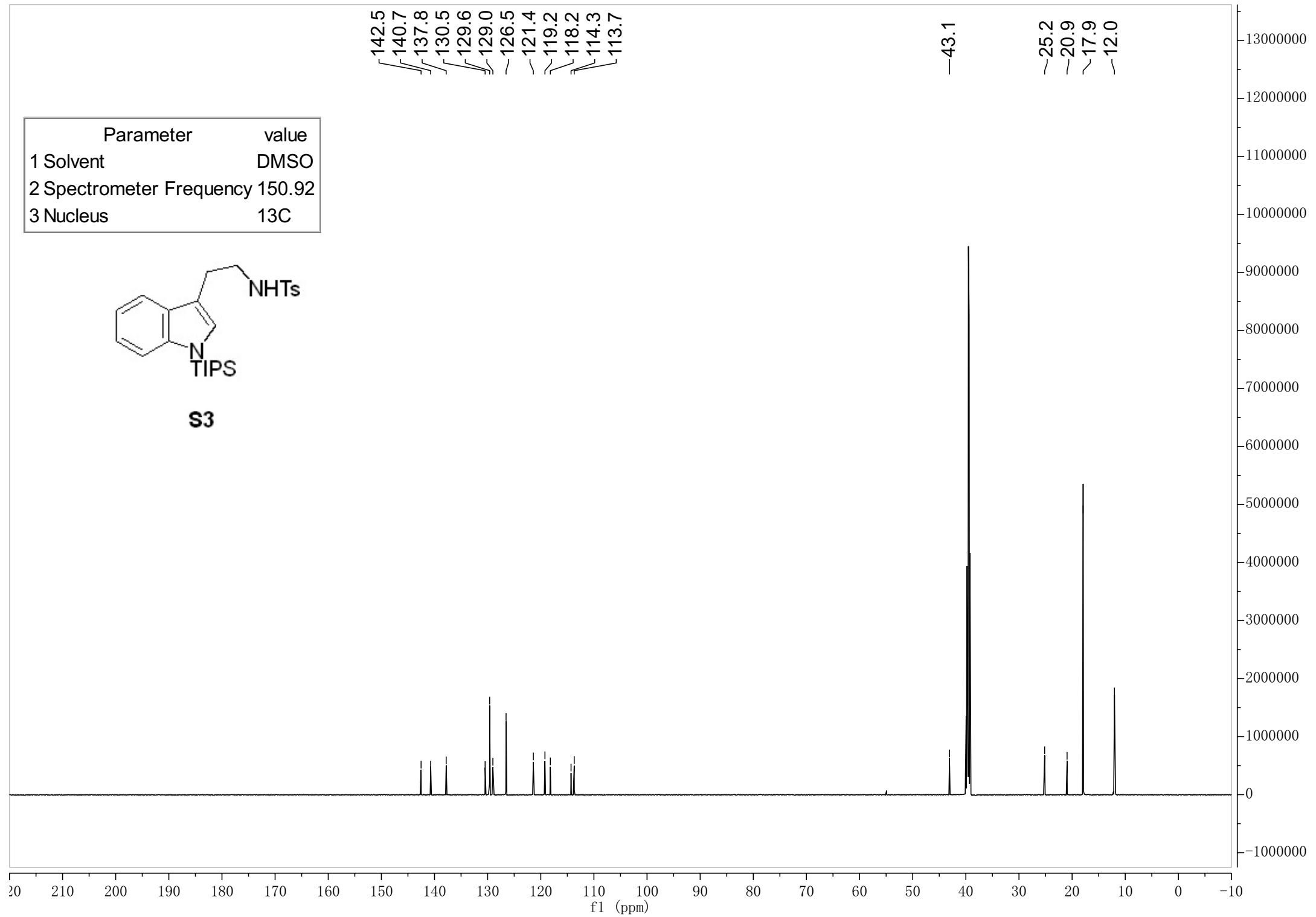


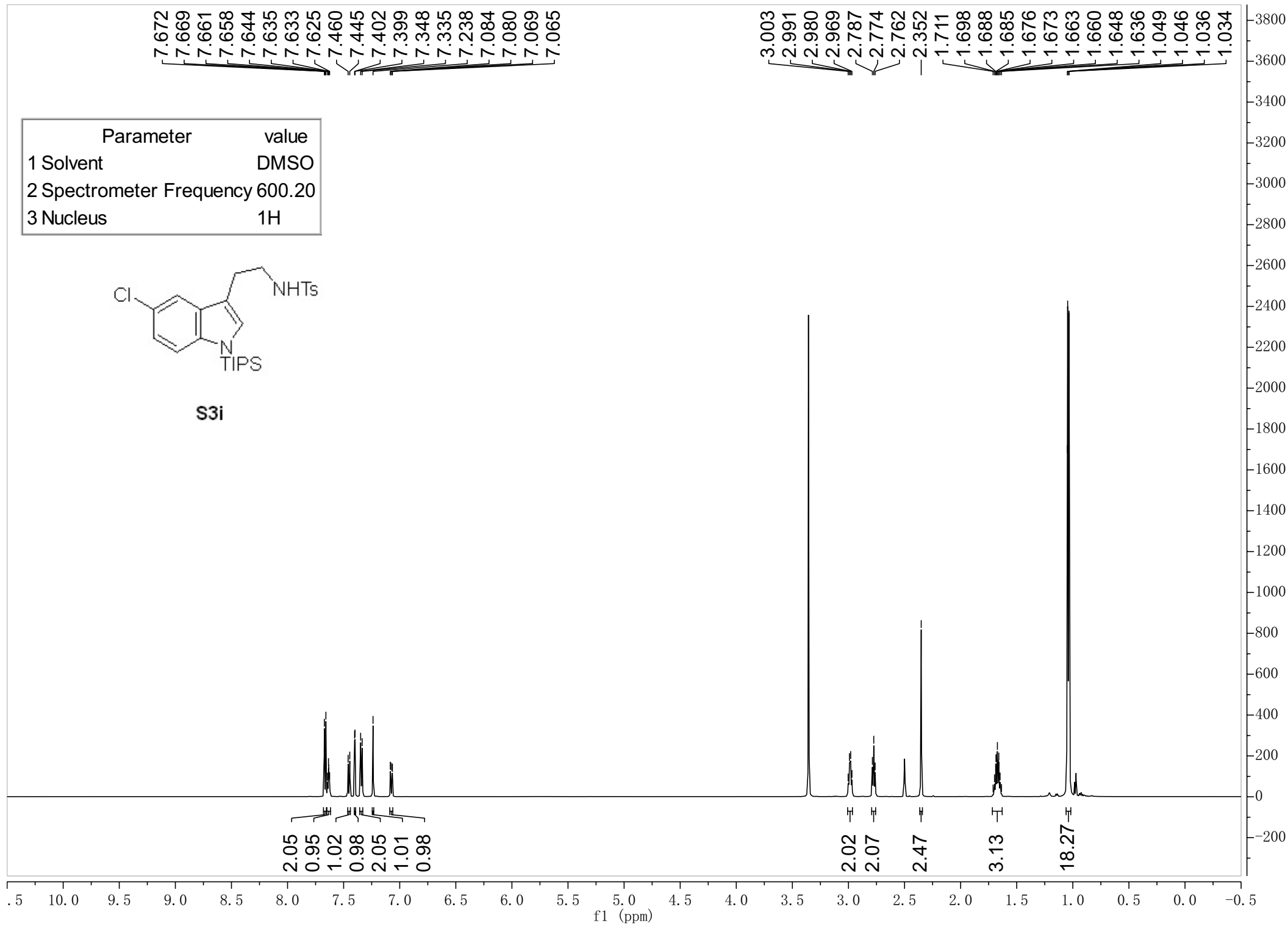
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



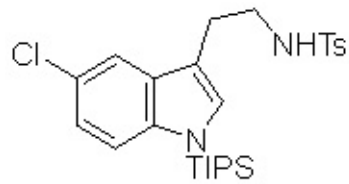
142.5
140.7
137.8
130.5
129.6
129.0
~126.5
~121.4
119.2
118.2
114.3
113.7

—43.1
~25.2
~20.9
~17.9
~12.0





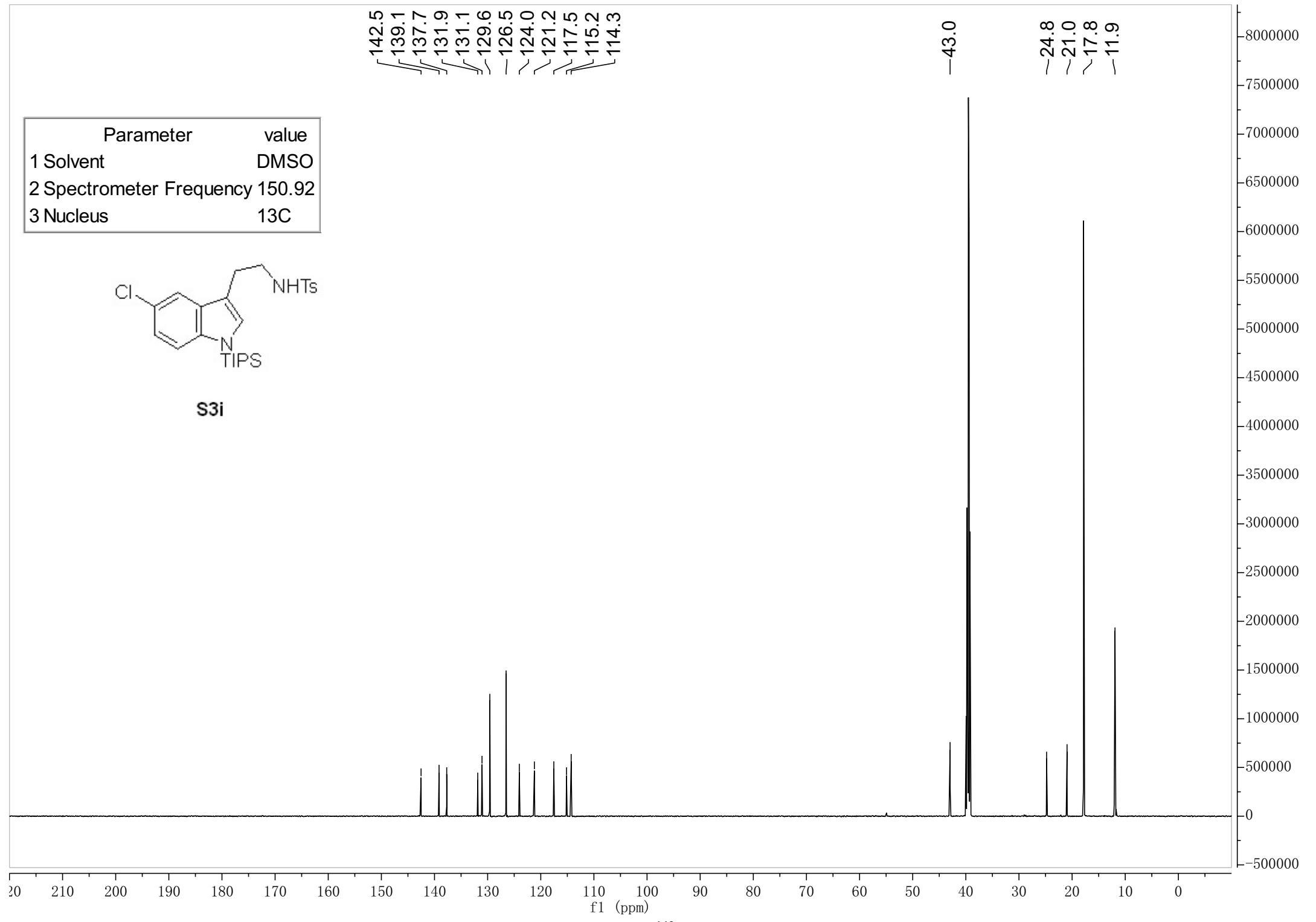
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

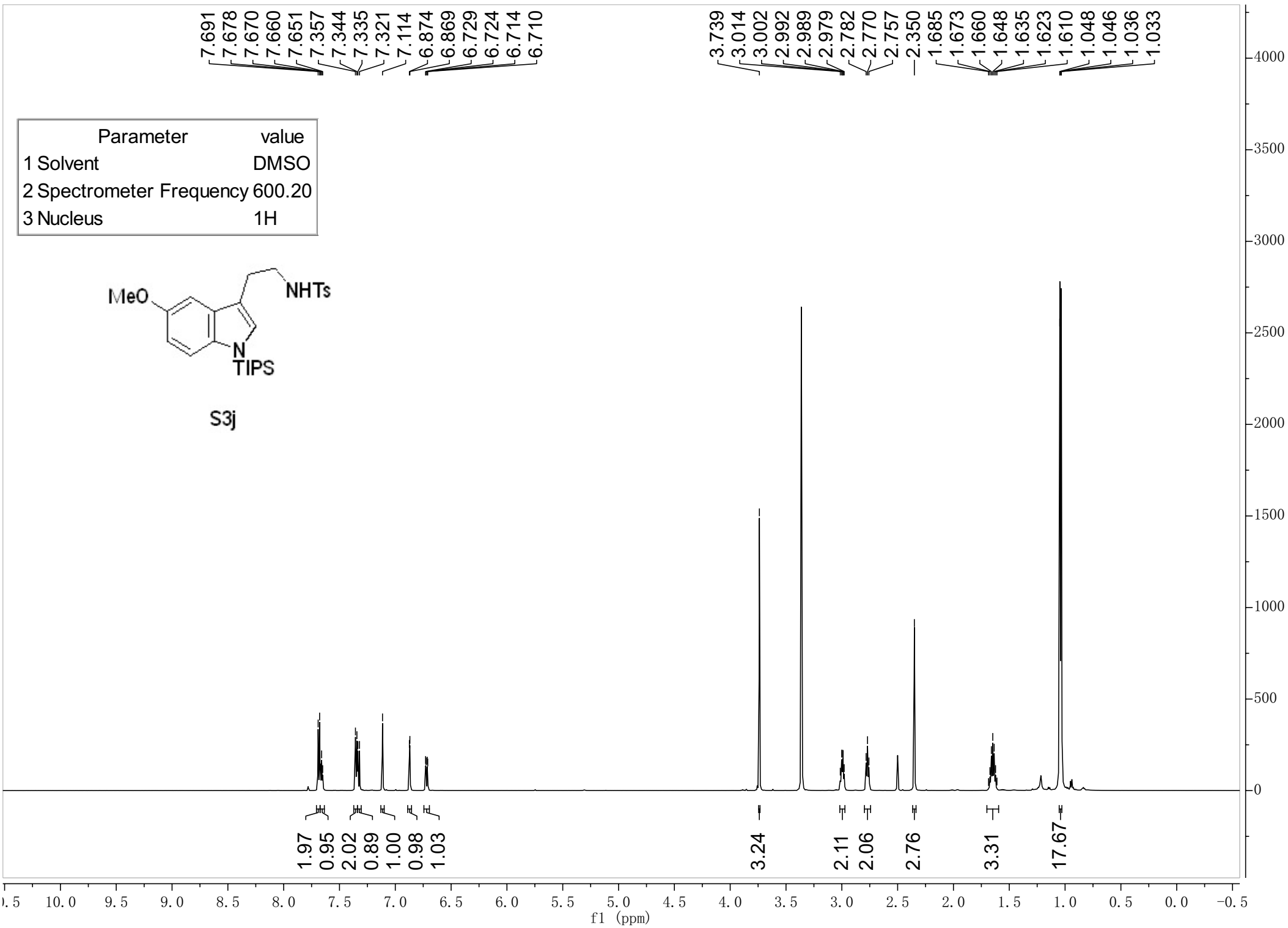


S3i

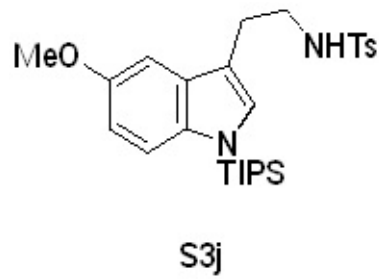
142.5
139.1
137.7
131.9
131.1
129.6
126.5
124.0
121.2
117.5
115.2
114.3

43.0
24.8
21.0
17.8
11.9



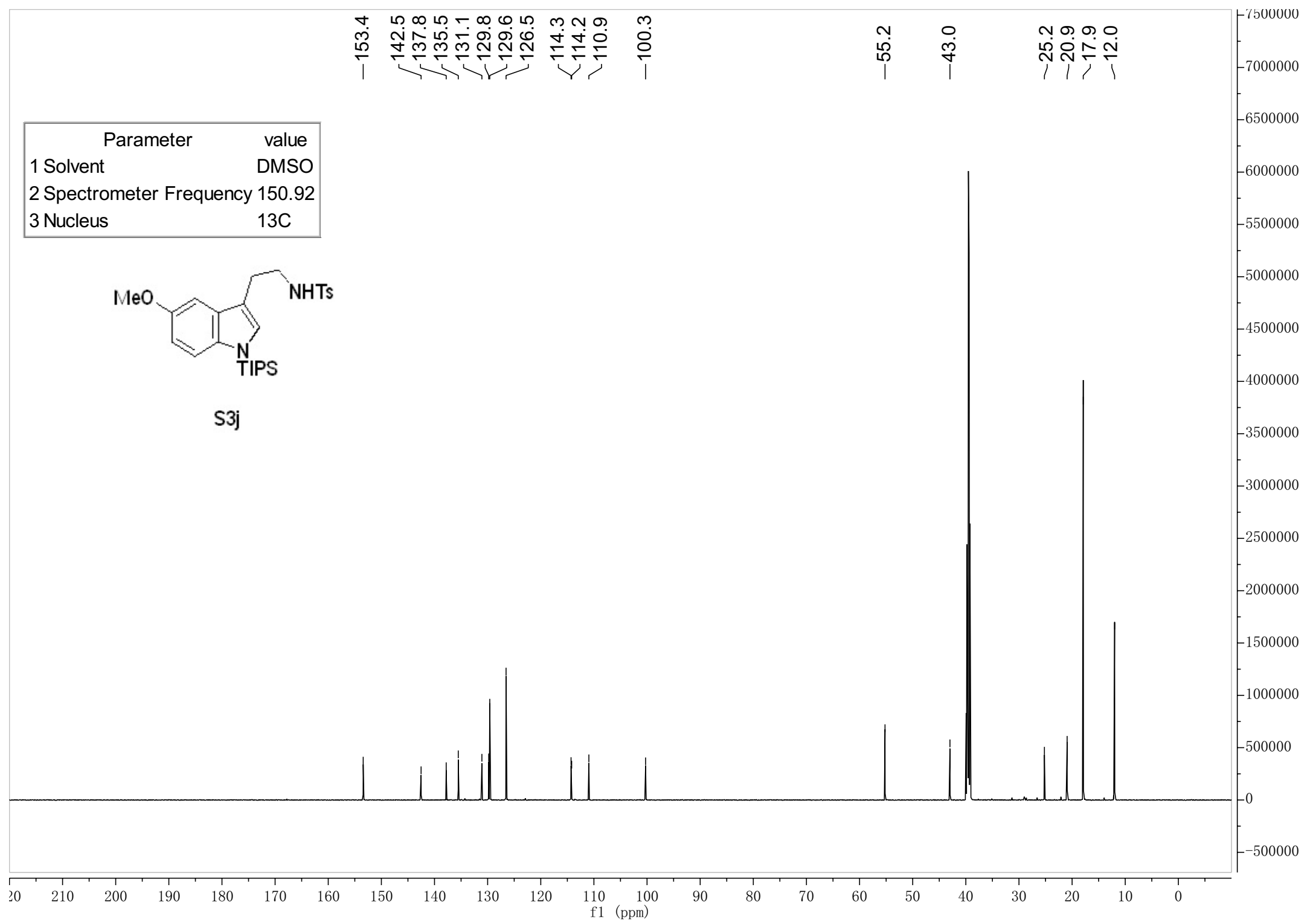


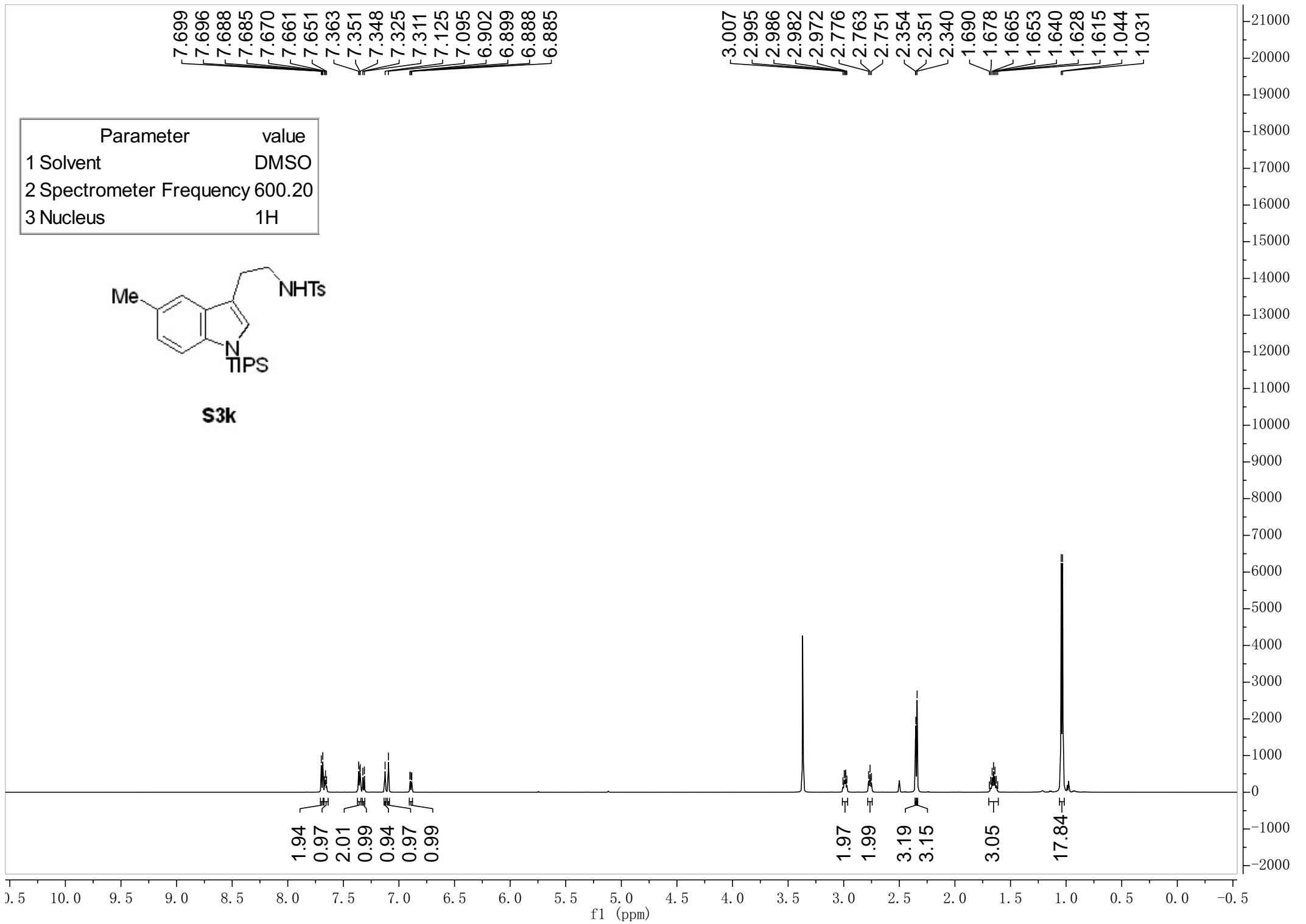
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



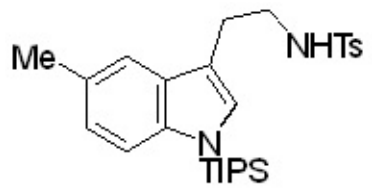
— 153.4
 / 142.5
 / 137.8
 / 135.5
 / 131.1
 / 129.8
 / 129.6
 / 126.5
 / 114.3
 / 114.2
 / 110.9
 — 100.3

— 55.2
 — 43.0
 ~ 25.2
 ~ 20.9
 ~ 17.9
 ~ 12.0





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

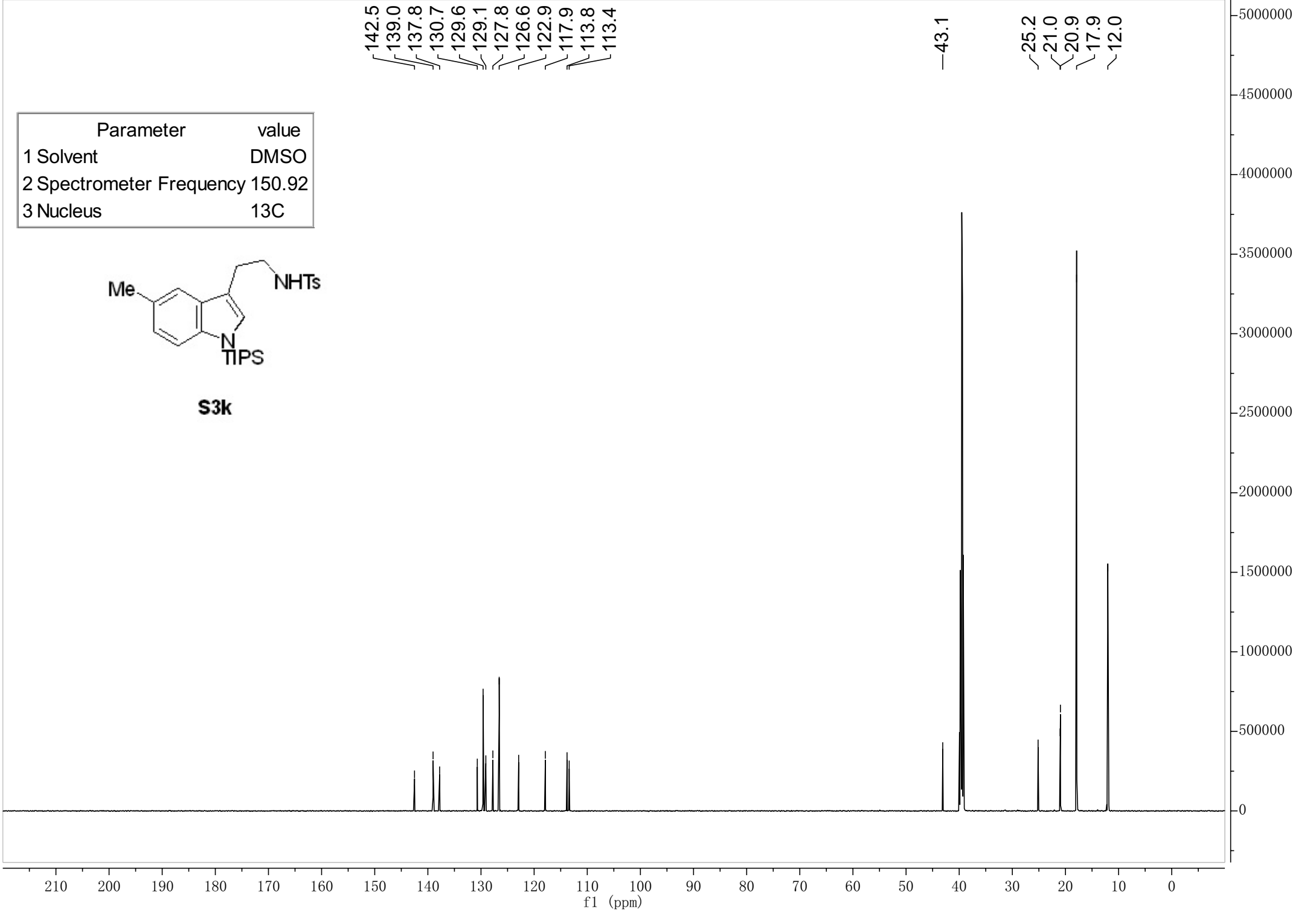


S3k

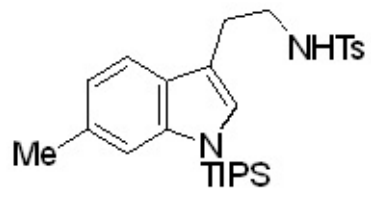
142.5
139.0
137.8
130.7
129.6
129.1
127.8
126.6
122.9
117.9
113.8
113.4

43.1

25.2
21.0
20.9
17.9
12.0



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H



S31

7.693
7.679
7.666
7.663
7.657
7.653
7.355
7.351
7.340
7.337
7.266
7.253
7.228
7.058
6.859
6.857
6.845
6.843

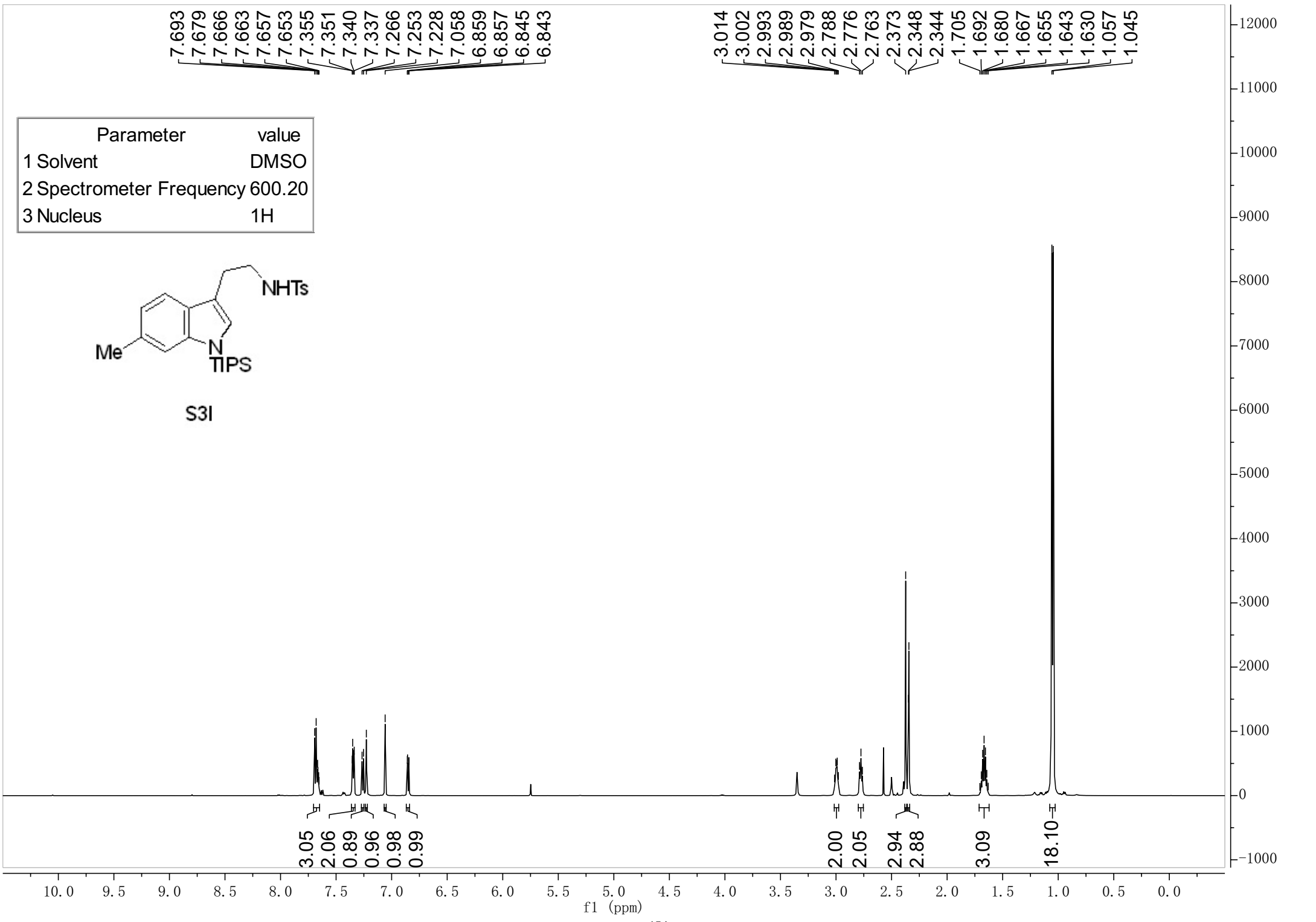
3.014
3.002
2.993
2.989
2.979
2.788
2.776
2.763
2.373
2.348
2.344
1.705
1.692
1.680
1.667
1.655
1.643
1.630
1.057
1.045

3.05
2.06
0.89
0.96
0.98
0.99

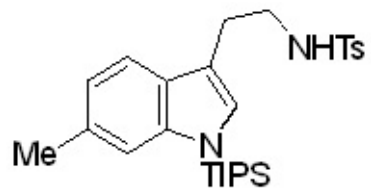
2.00
2.05
2.94
2.88

3.09

18.10



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

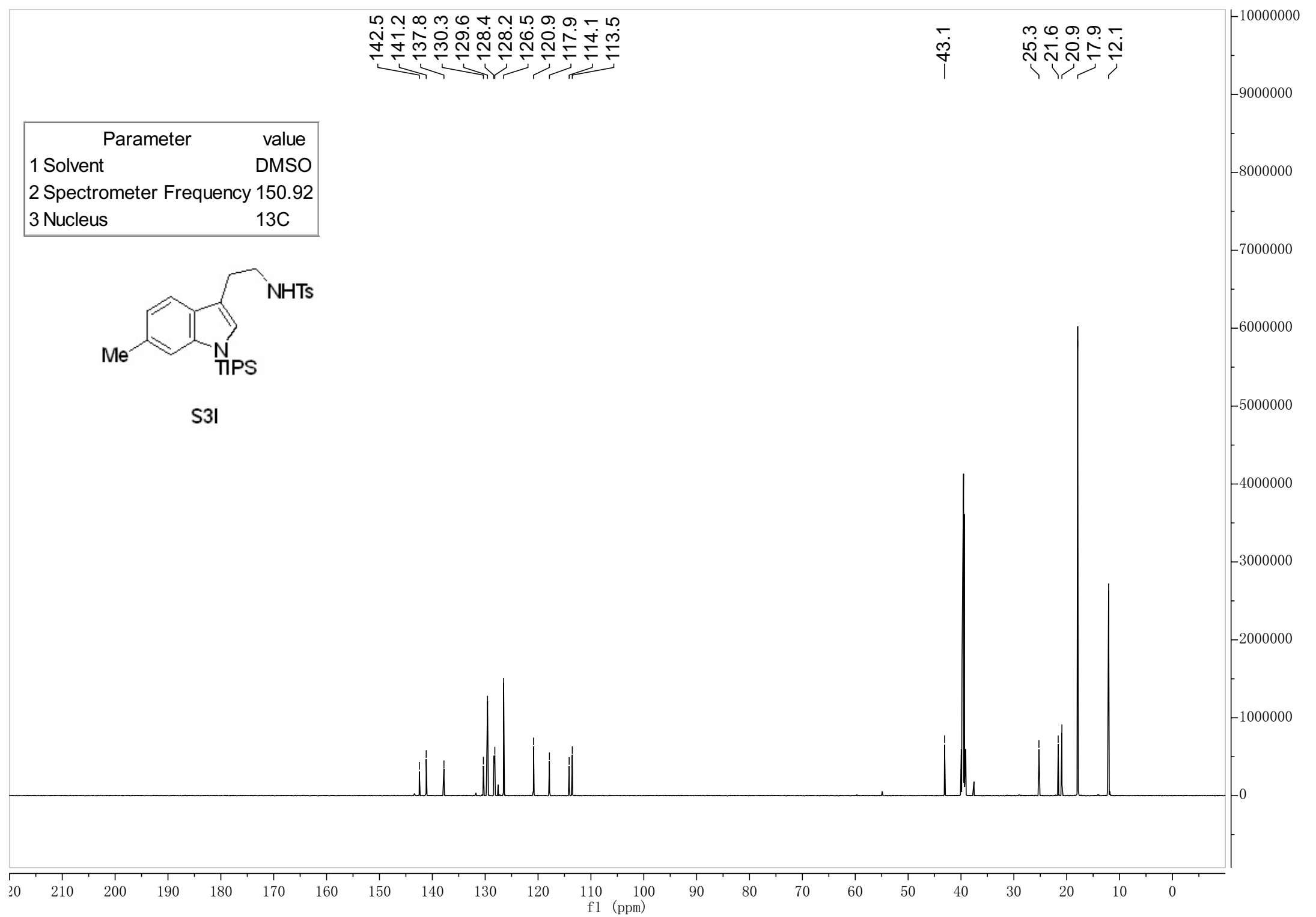


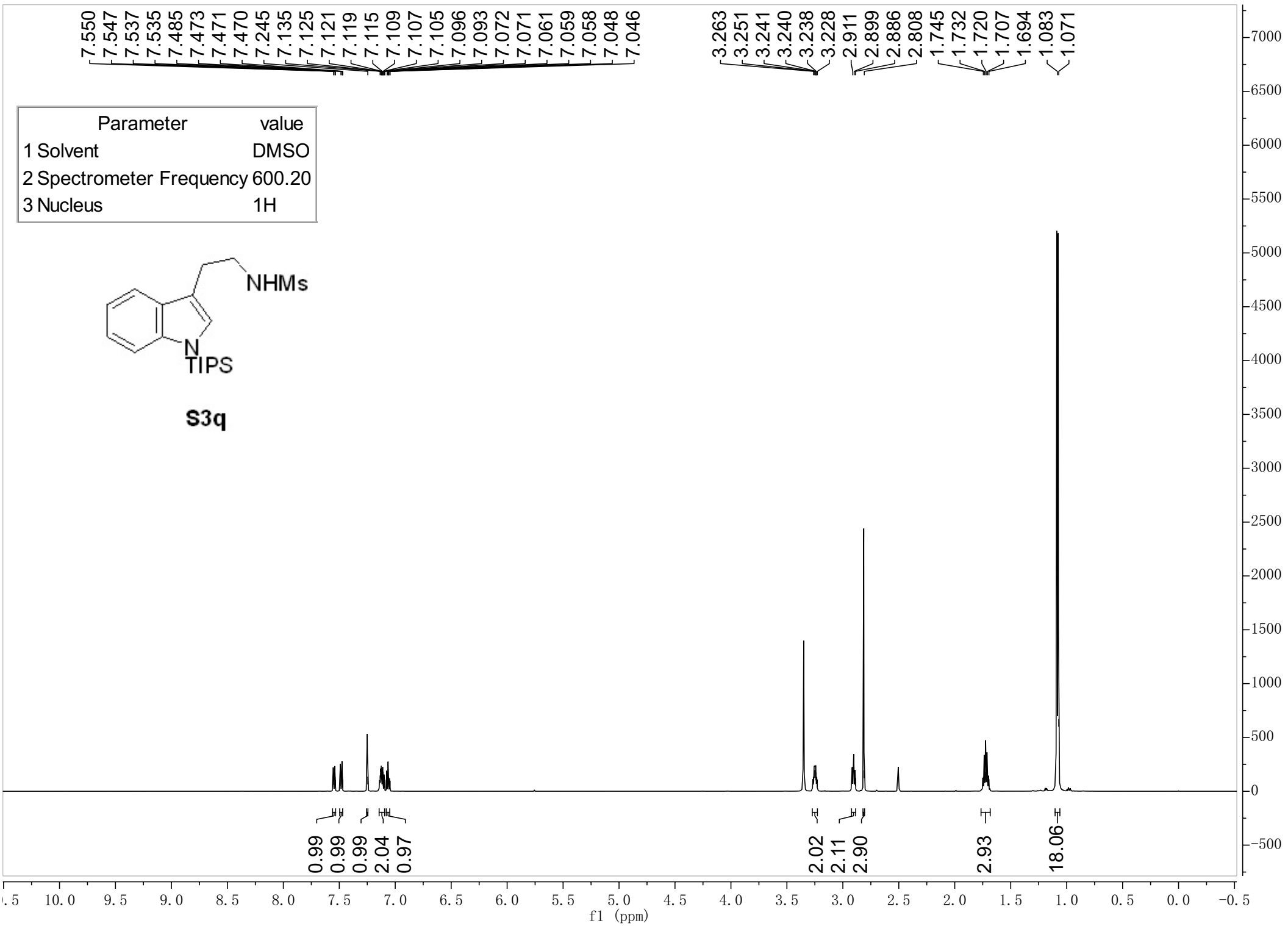
S3I

142.5
141.2
137.8
130.3
129.6
128.4
128.2
126.5
120.9
117.9
114.1
113.5

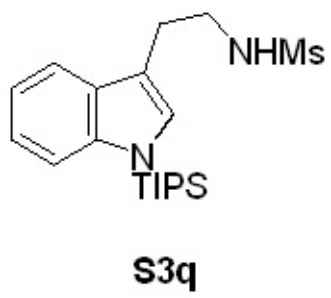
43.1

25.3
21.6
20.9
17.9
12.1



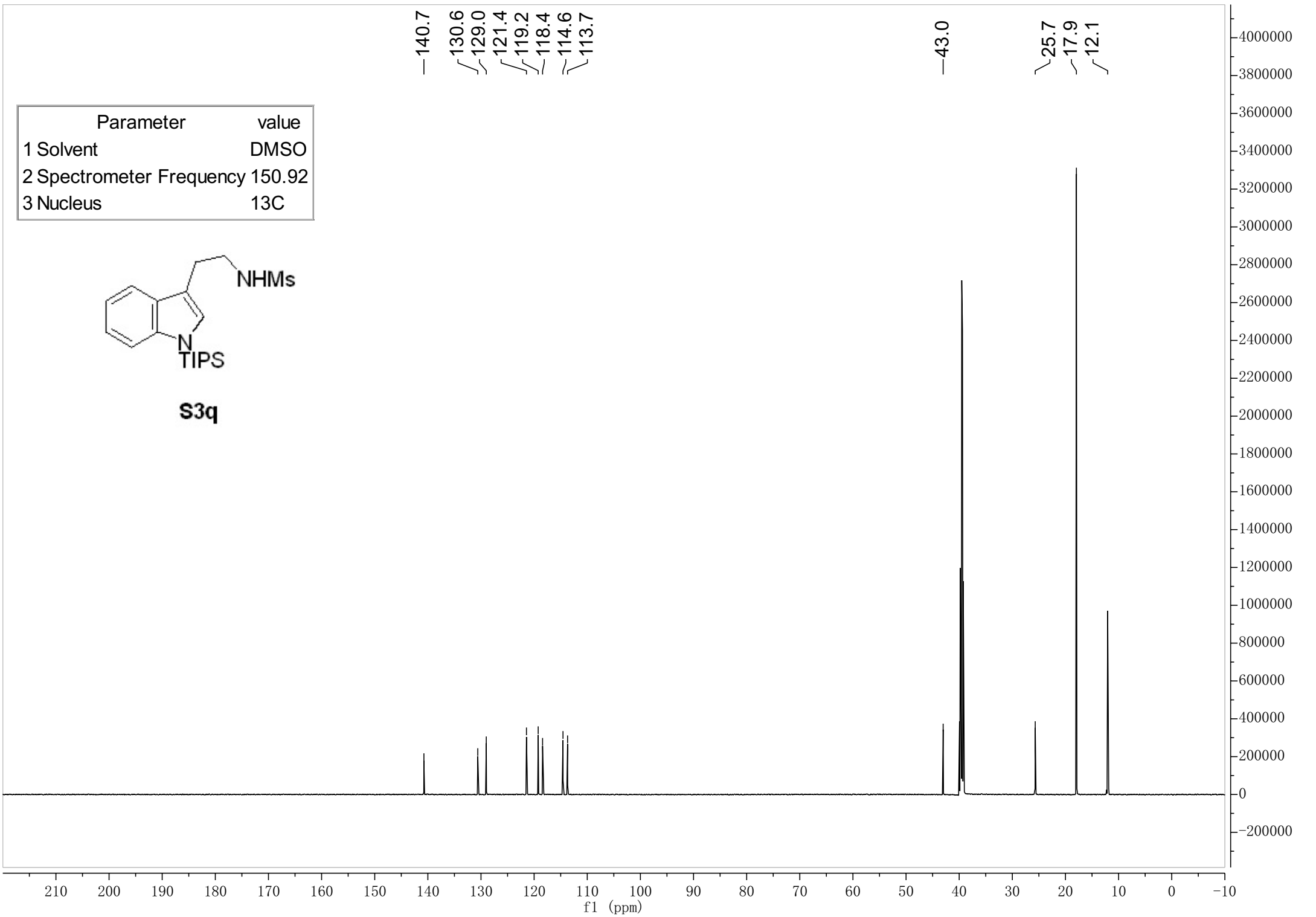


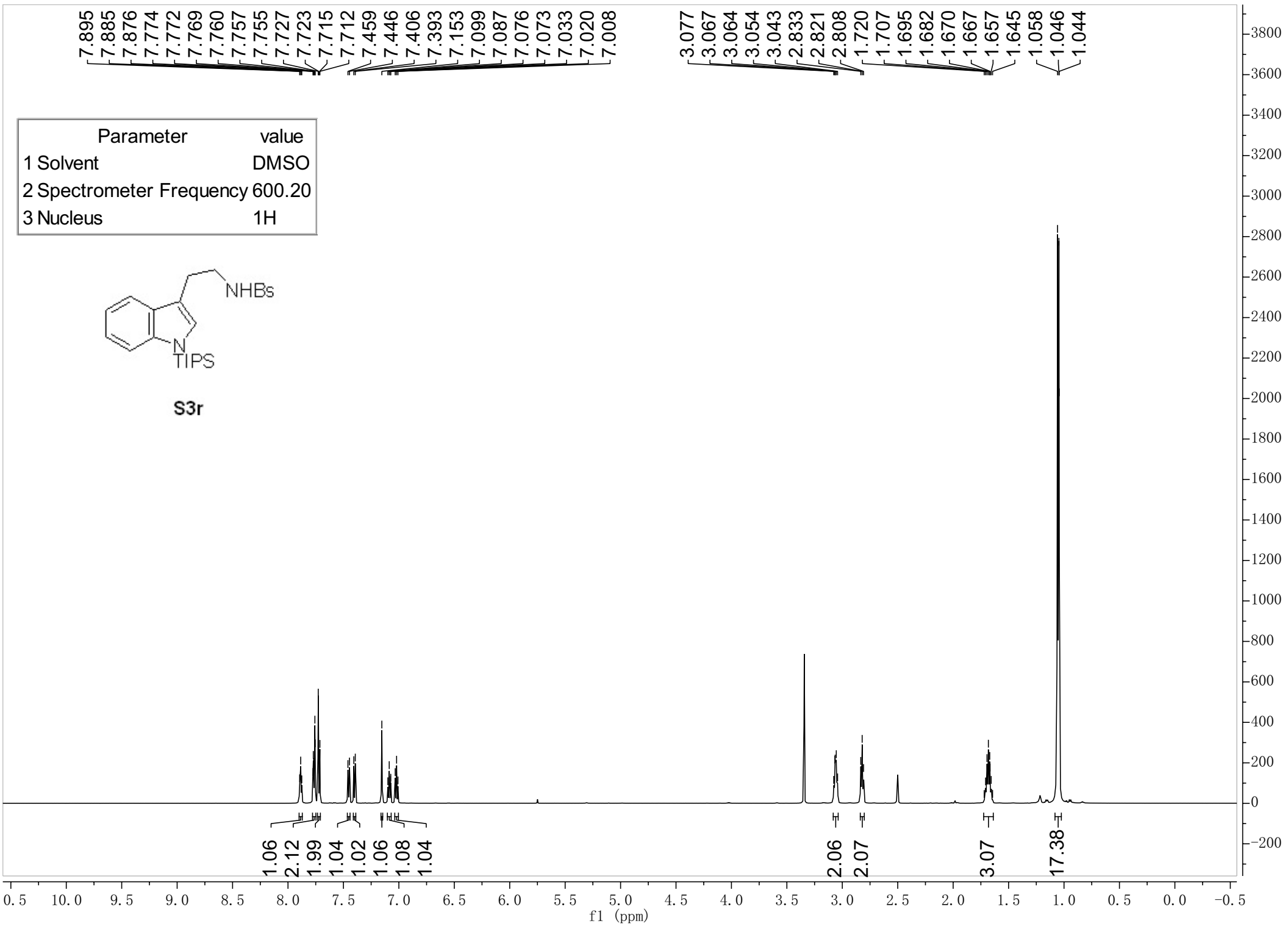
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



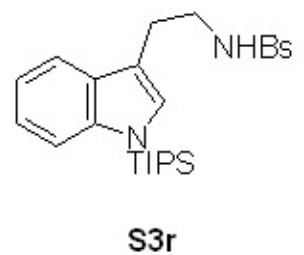
140.7
130.6
129.0
121.4
119.2
118.4
114.6
113.7

43.0
25.7
17.9
12.1

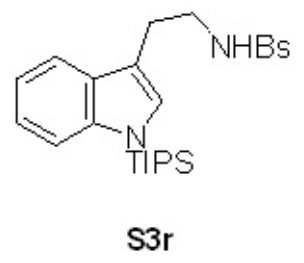




Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	¹ H



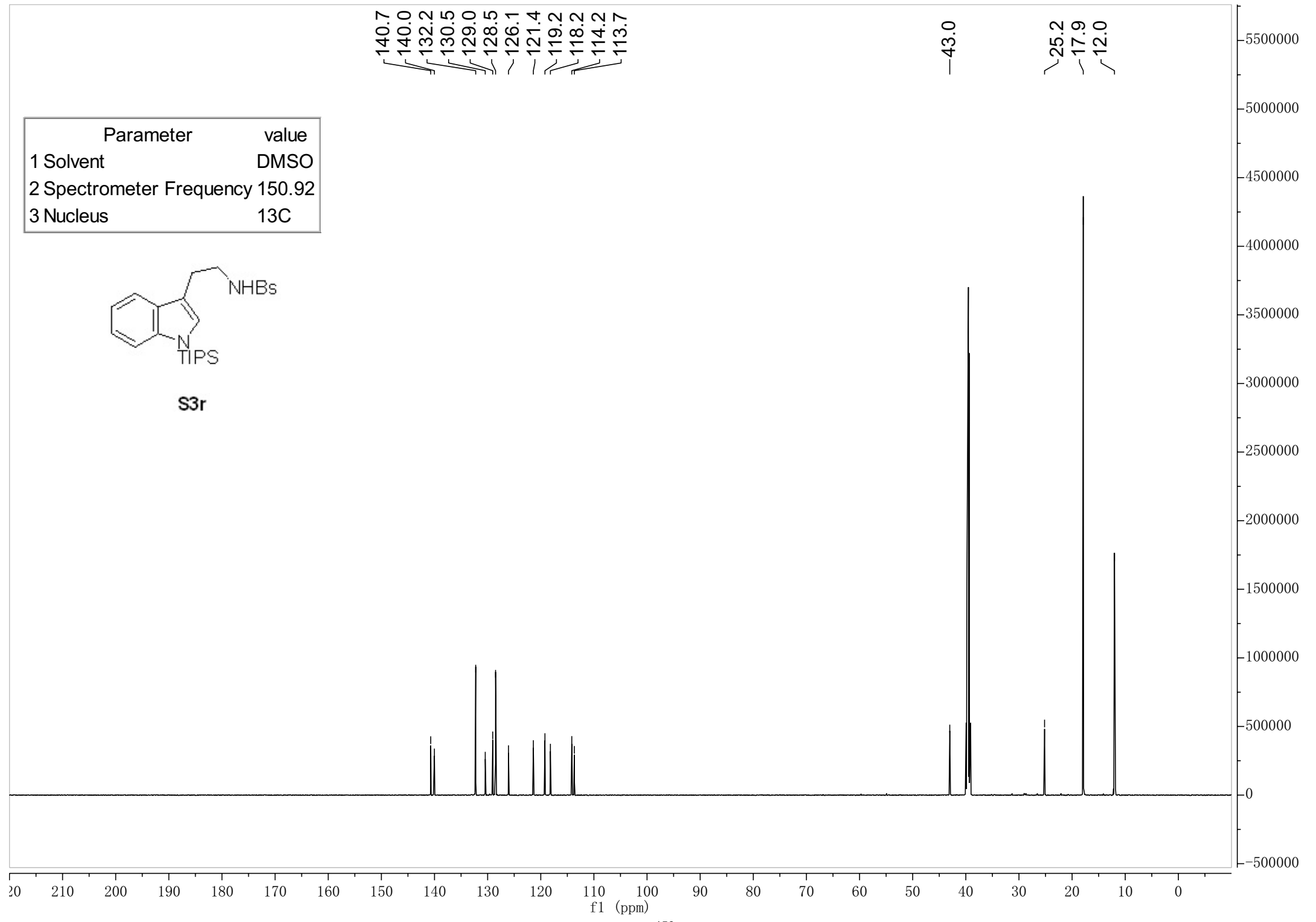
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



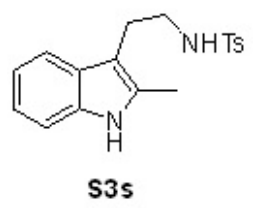
140.7
140.0
132.2
130.5
129.0
128.5
126.1
121.4
119.2
118.2
114.2
113.7

43.0

25.2
17.9
12.0

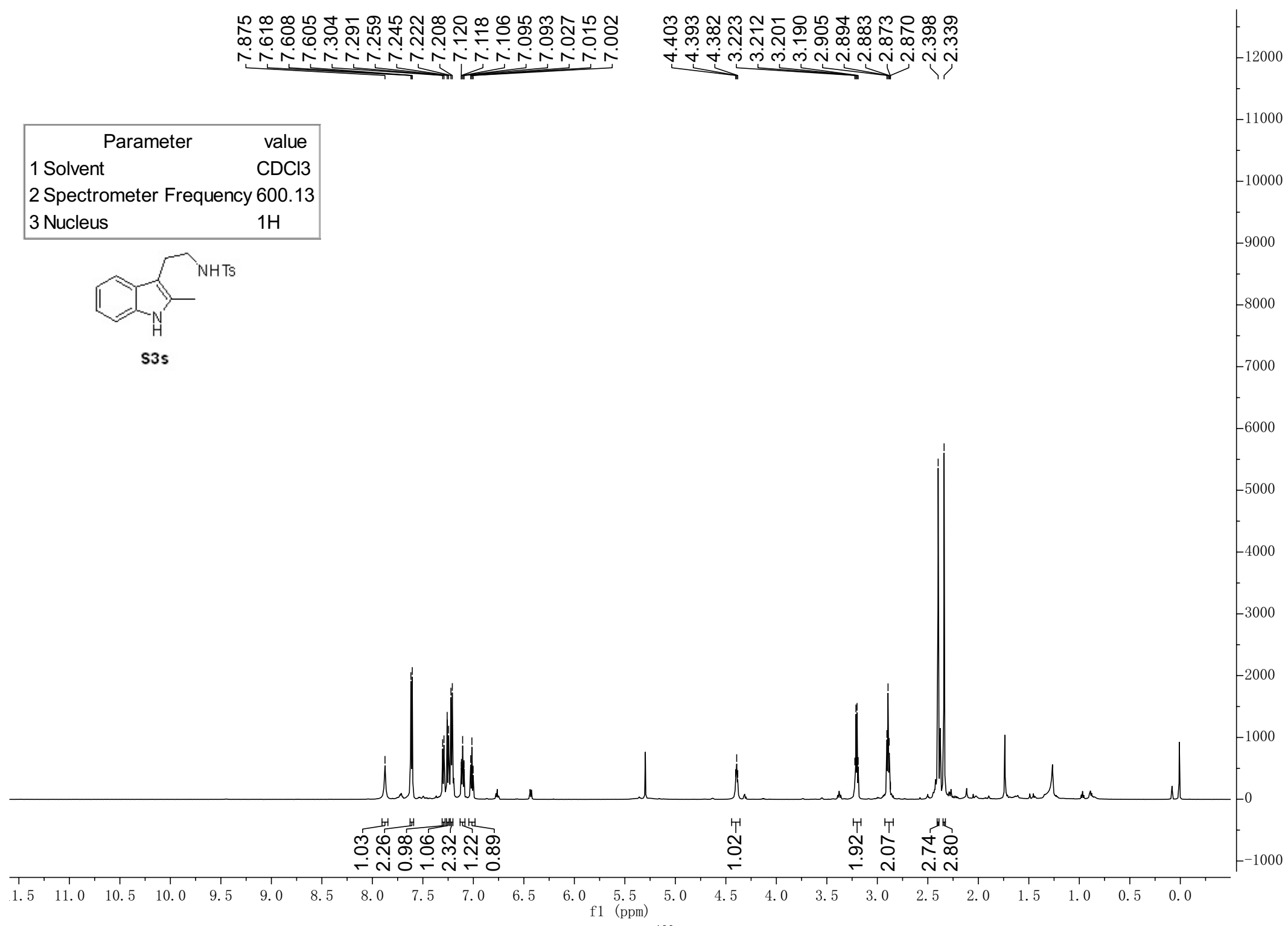


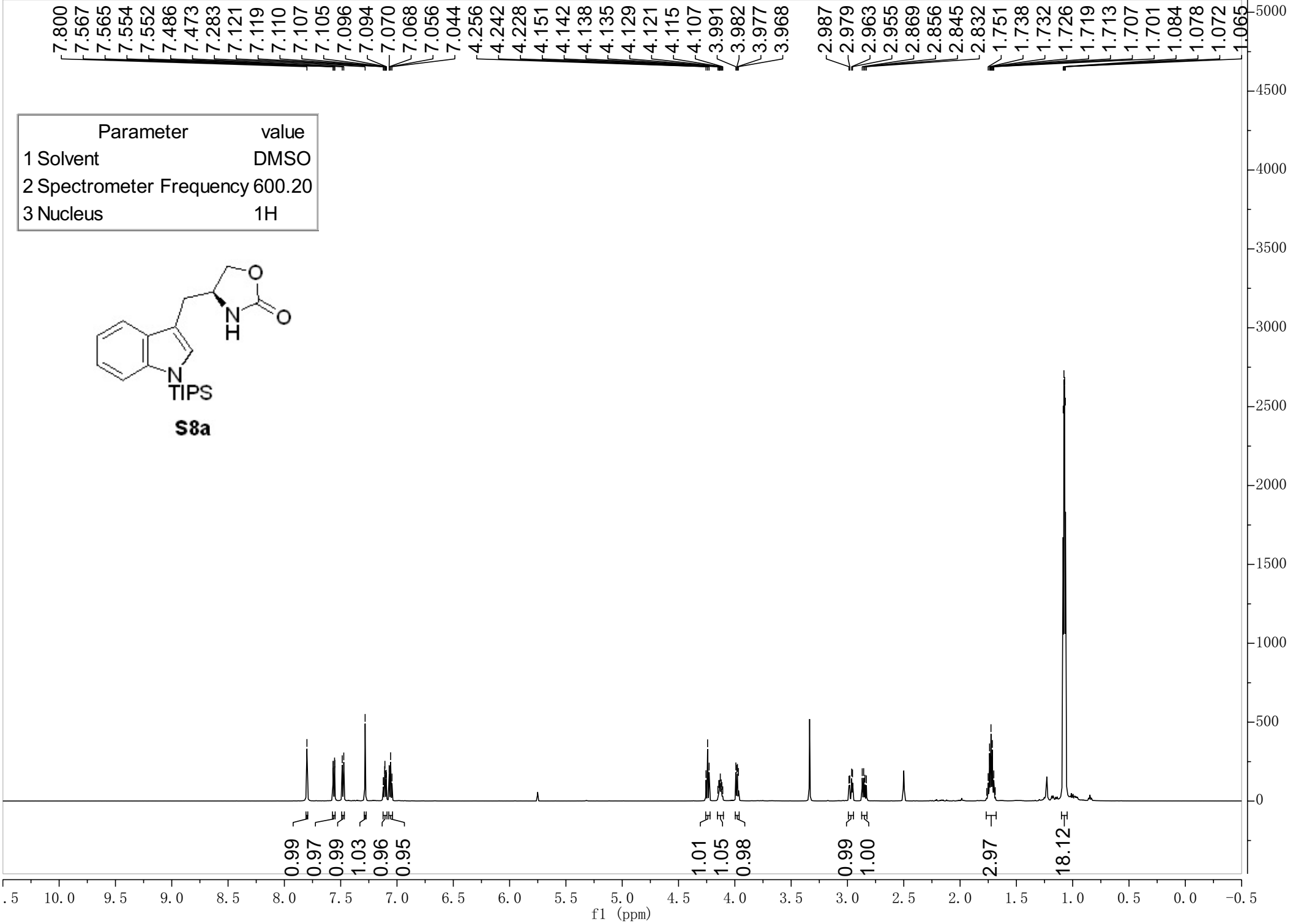
Parameter	value
1 Solvent	CDCl3
2 Spectrometer Frequency	600.13
3 Nucleus	1H



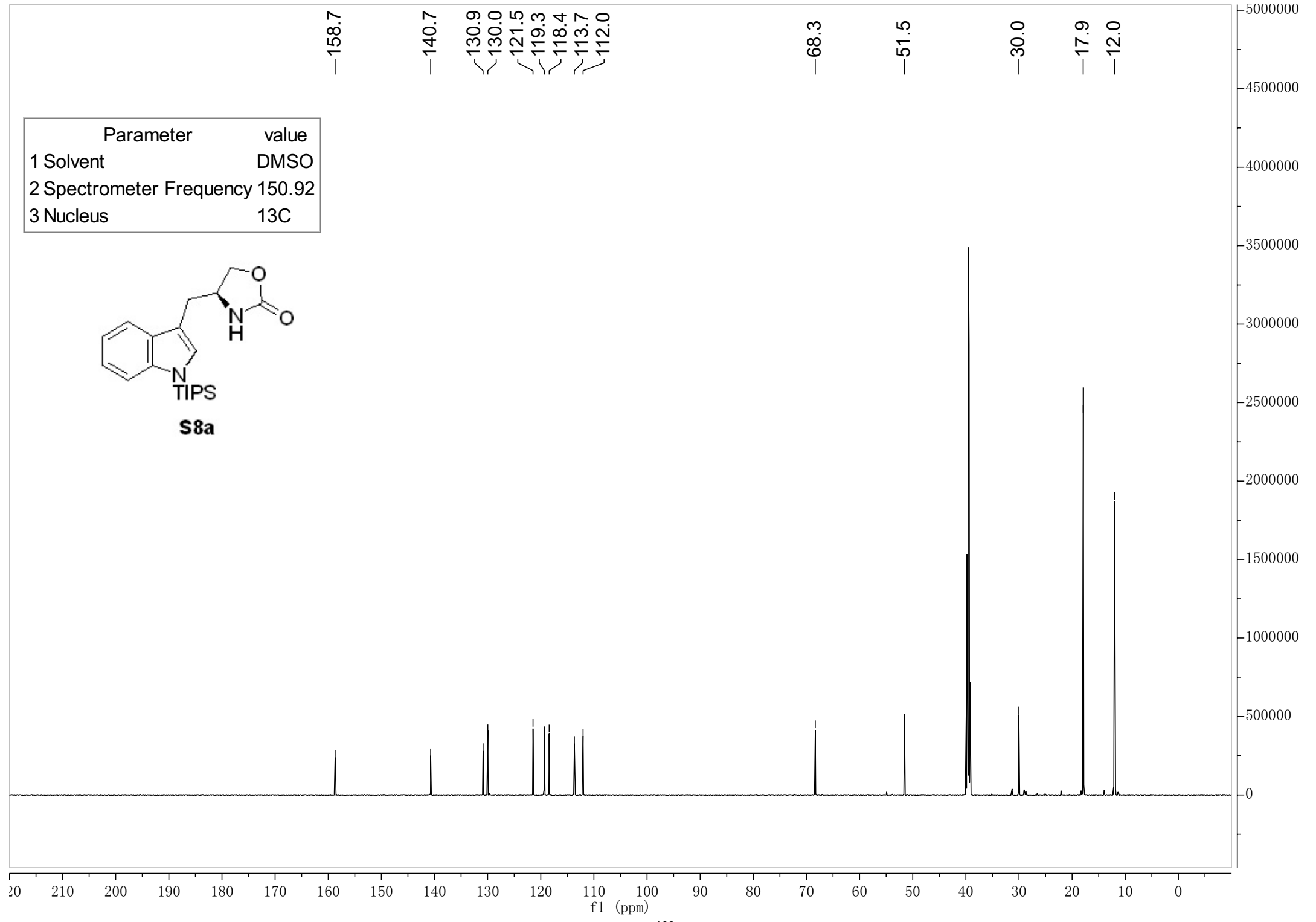
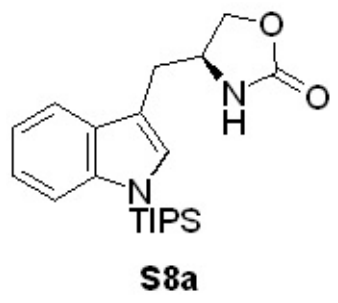
7.875
7.618
7.608
7.605
7.304
7.291
7.259
7.245
7.222
7.208
7.120
7.118
7.106
7.095
7.093
7.027
7.015
7.002

4.403
4.393
4.382
3.223
3.212
3.201
3.190
2.905
2.894
2.883
2.873
2.870
2.398
2.339





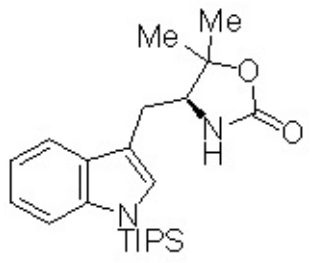
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



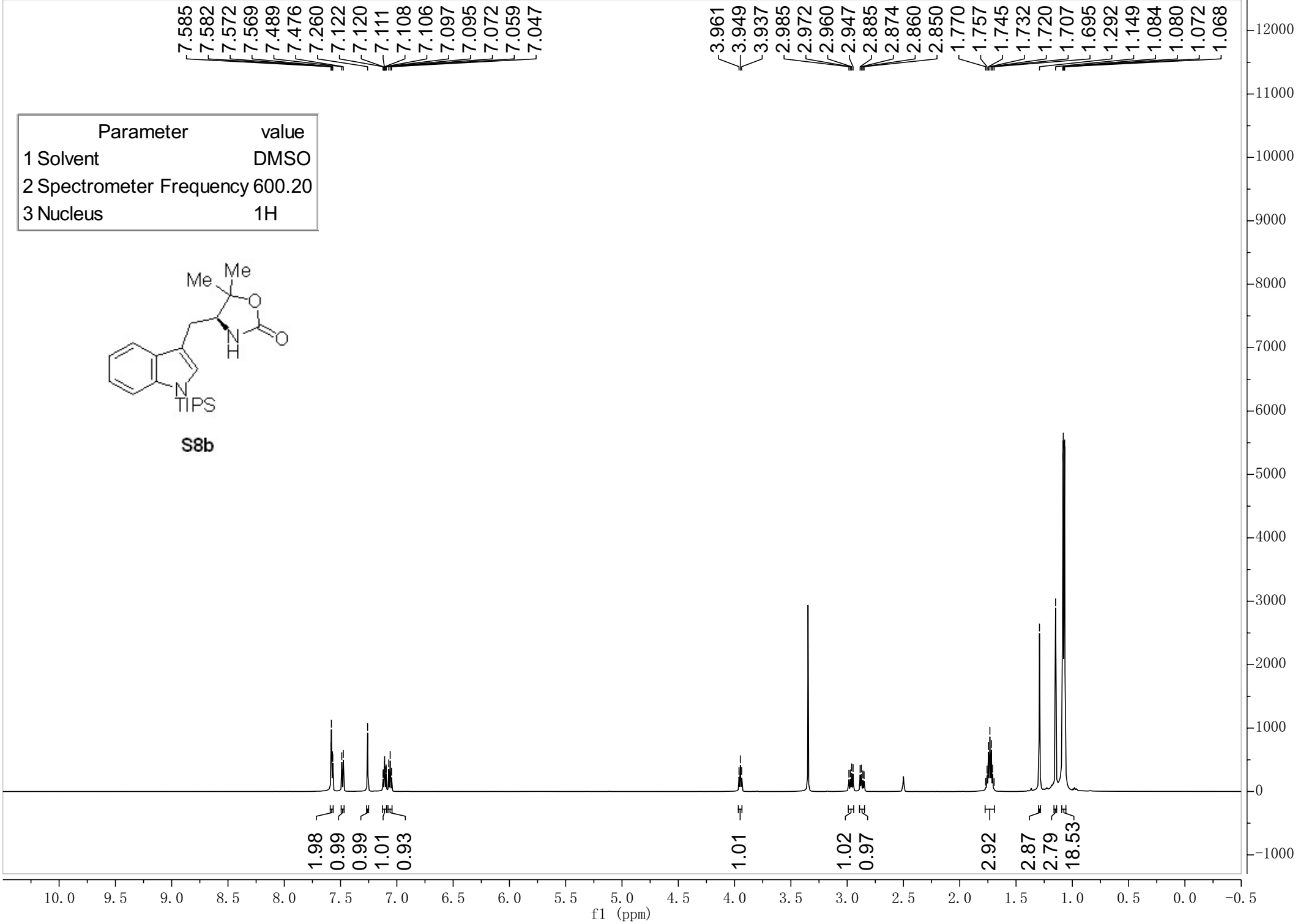
7.585
7.582
7.572
7.569
7.489
7.476
7.260
7.122
7.120
7.111
7.108
7.106
7.097
7.095
7.072
7.059
7.047

3.961
3.949
3.937
2.985
2.972
2.960
2.947
2.885
2.874
2.860
2.850
1.770
1.757
1.745
1.732
1.720
1.707
1.695
1.292
1.149
1.084
1.080
1.072
1.068

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H



S8b



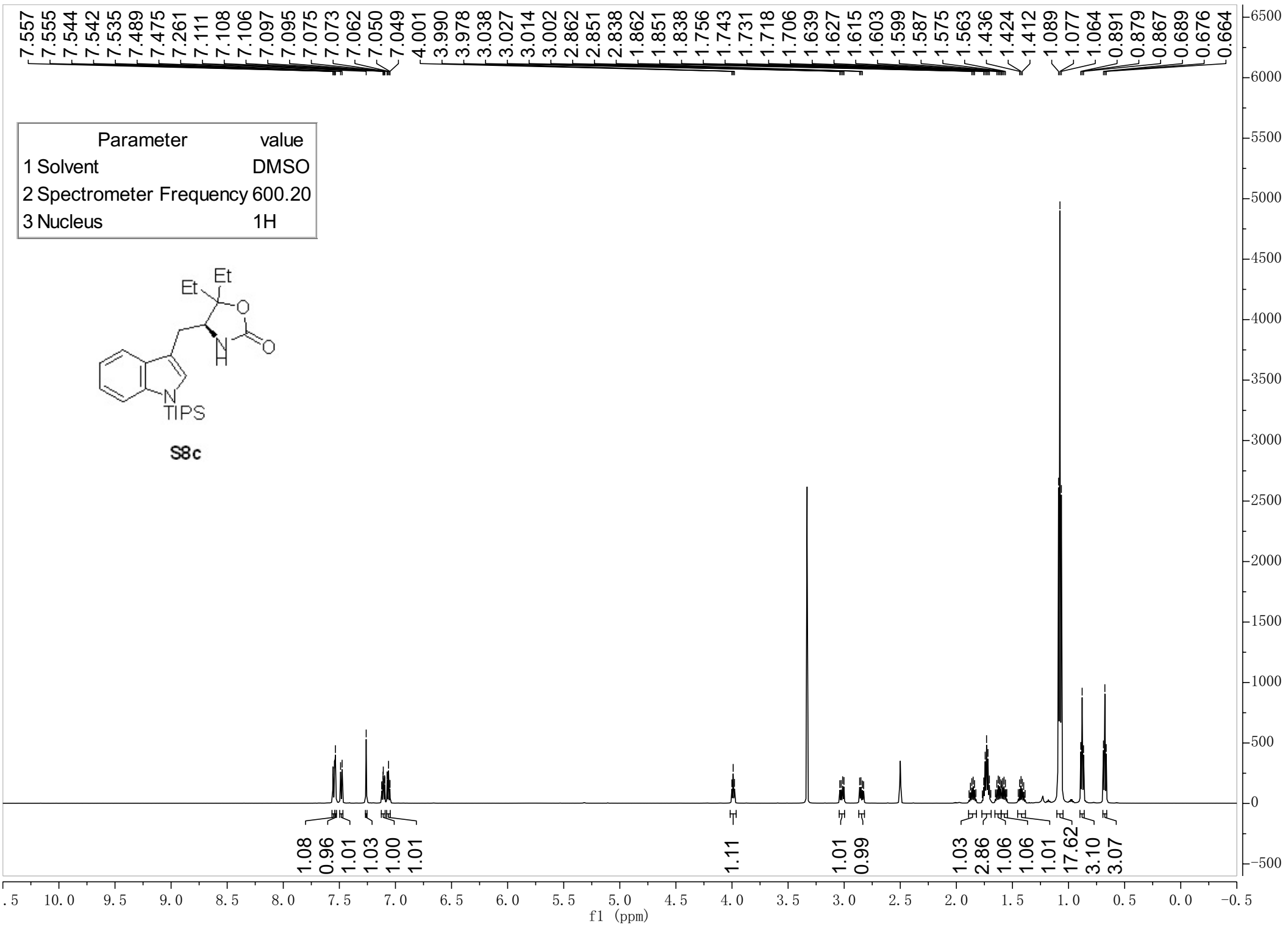
1.98
0.99
0.99
1.01
0.93

1.01

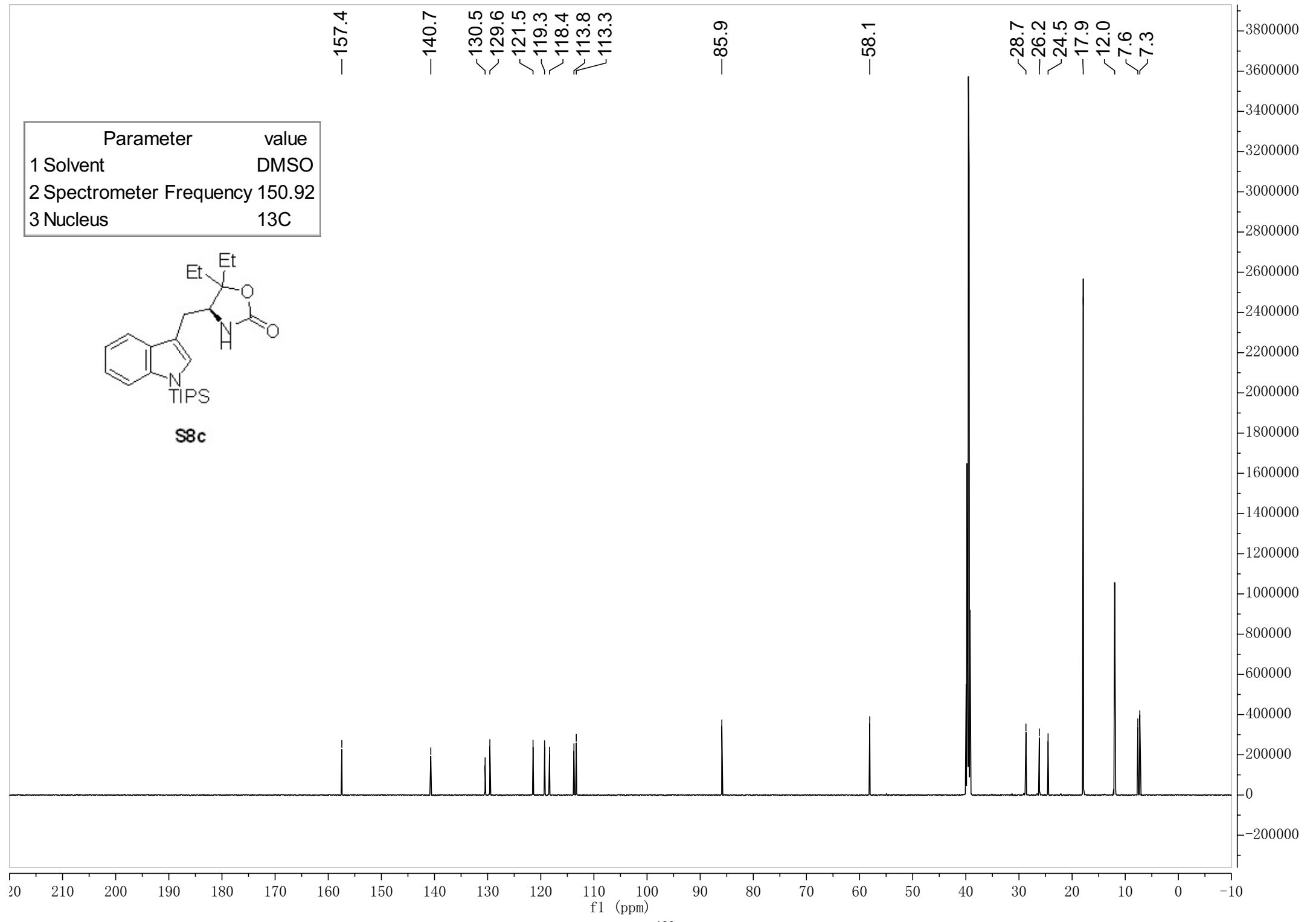
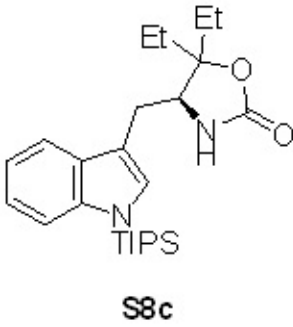
1.02
0.97

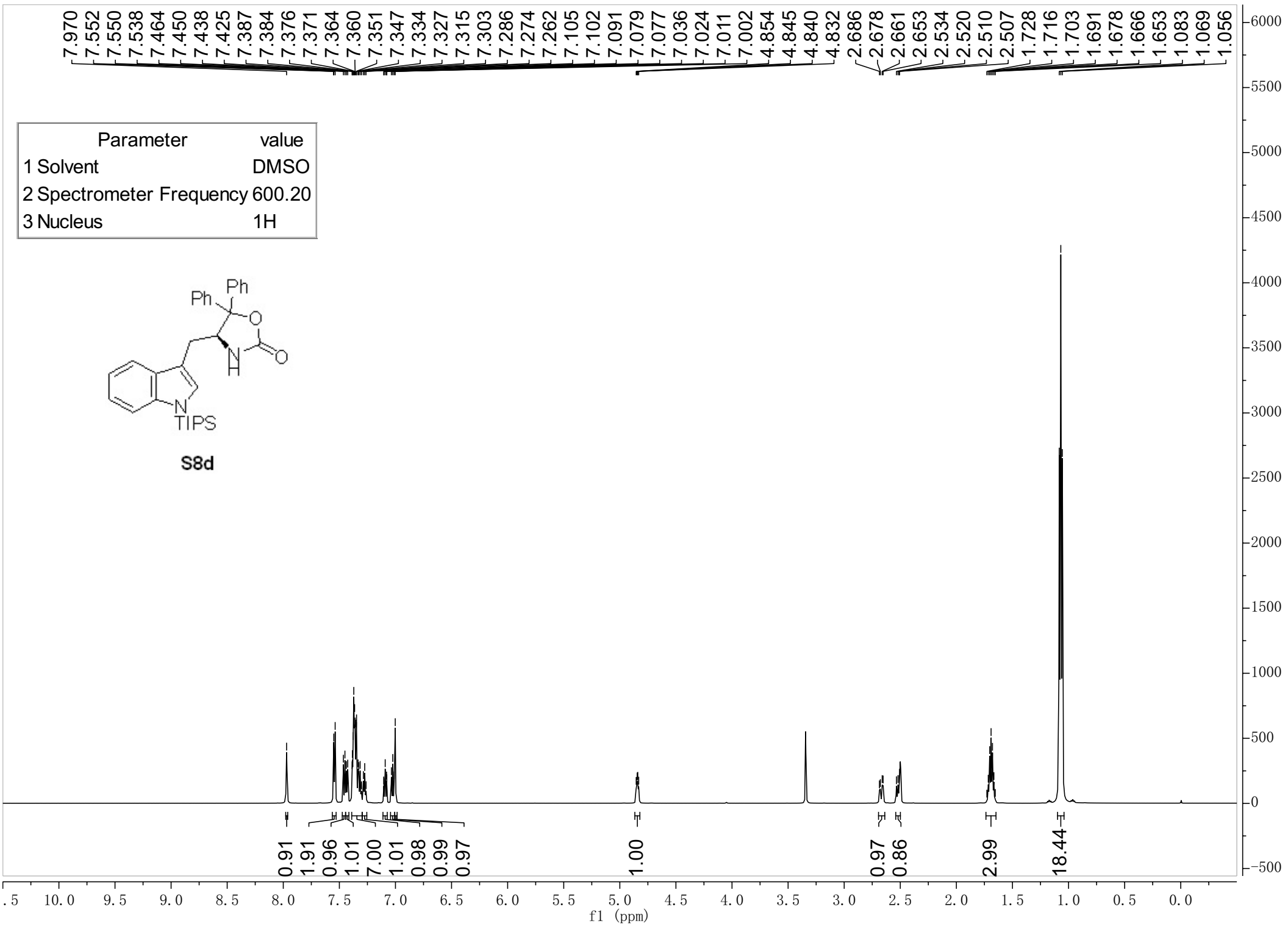
2.92

2.87
2.79
18.53

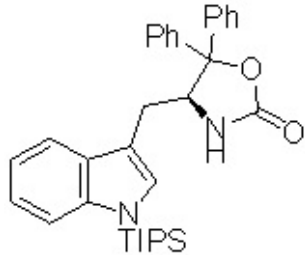


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



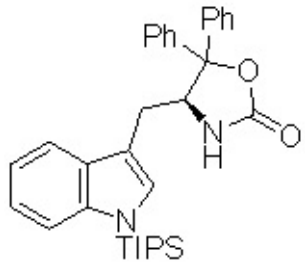


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	¹ H

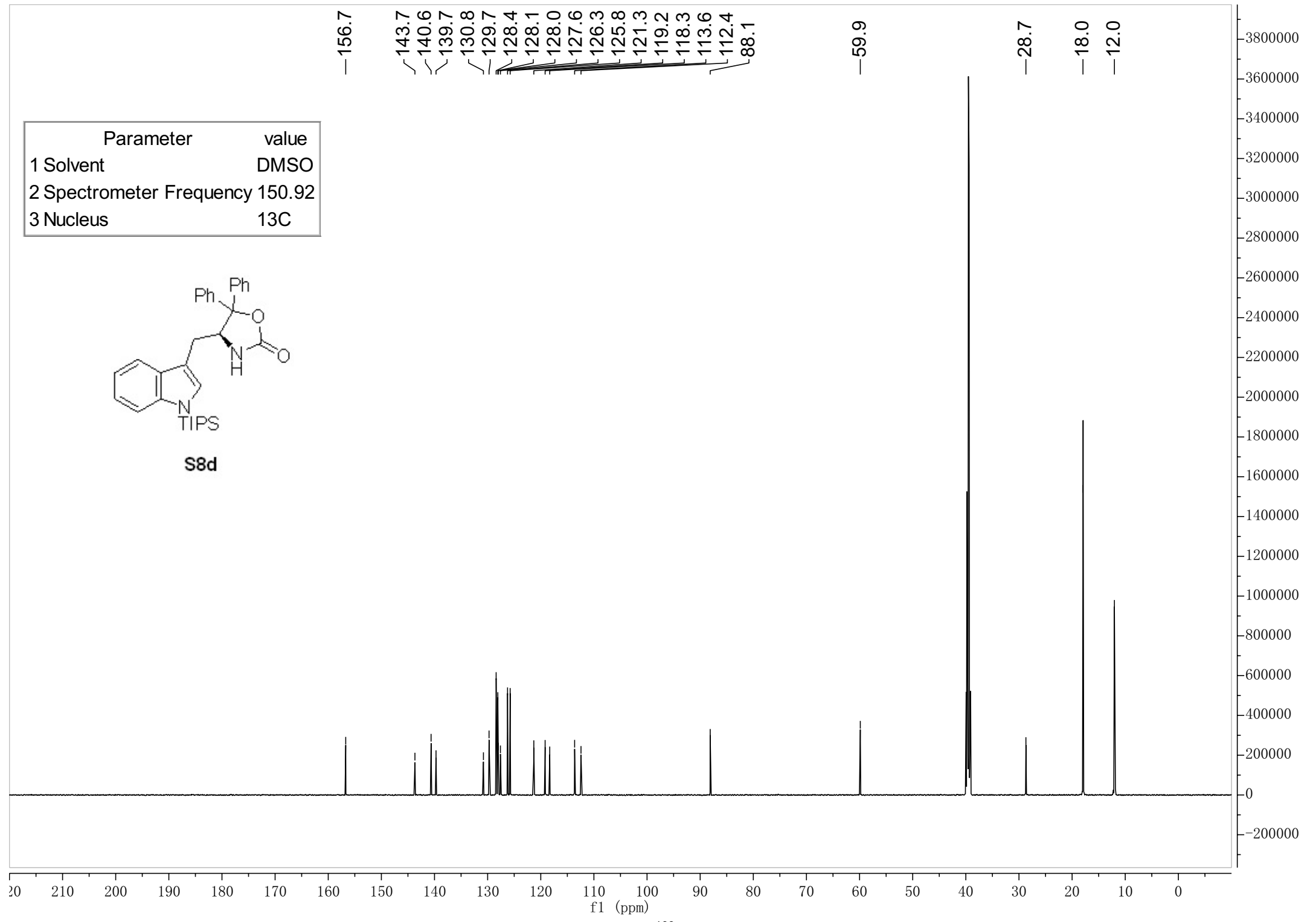


S8d

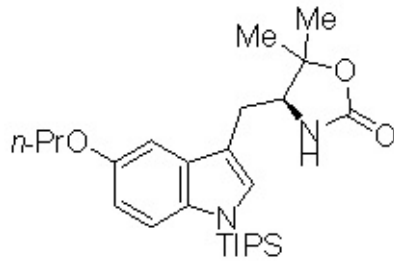
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



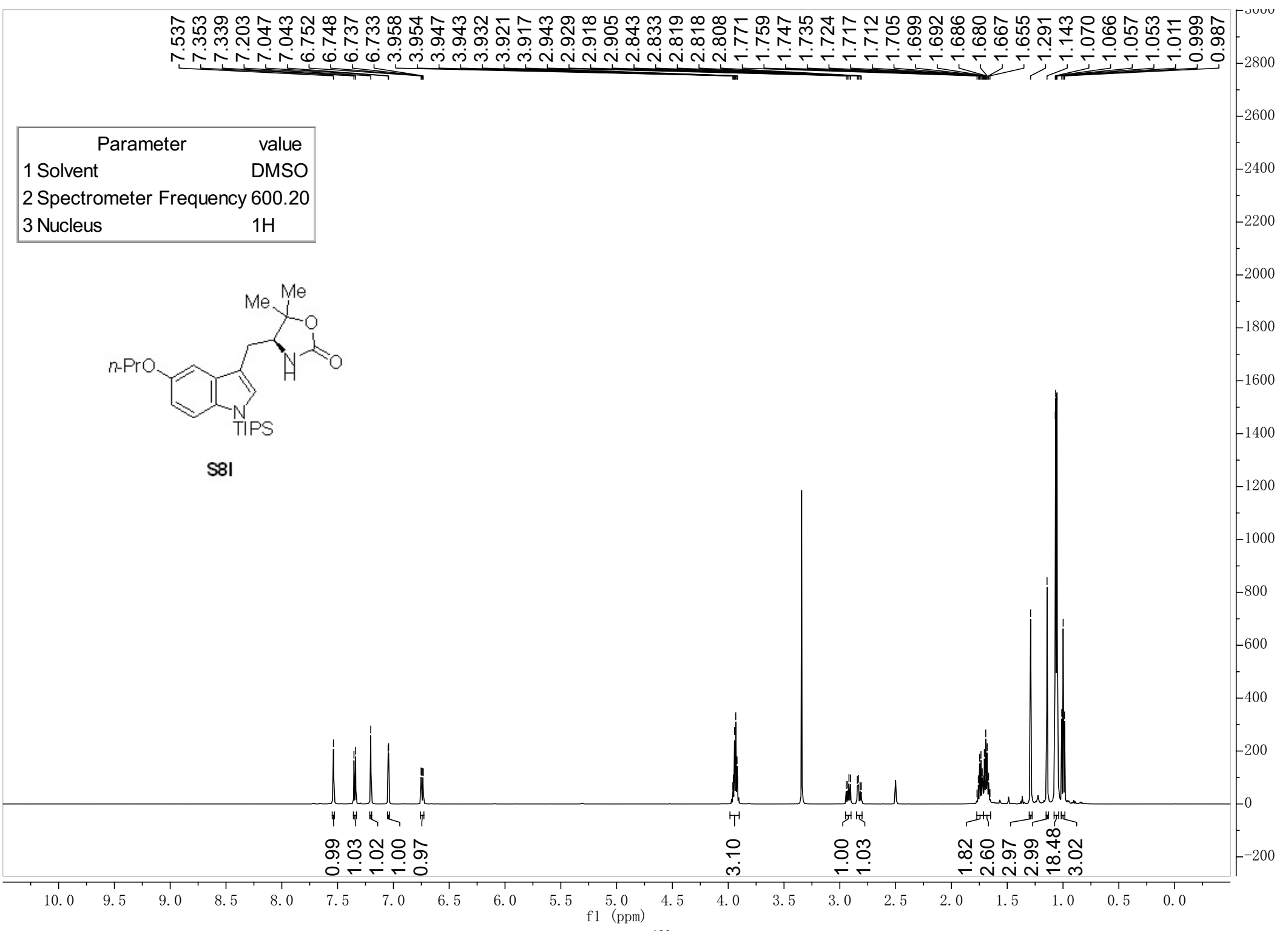
S8d



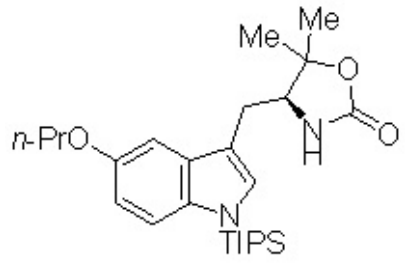
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	¹ H



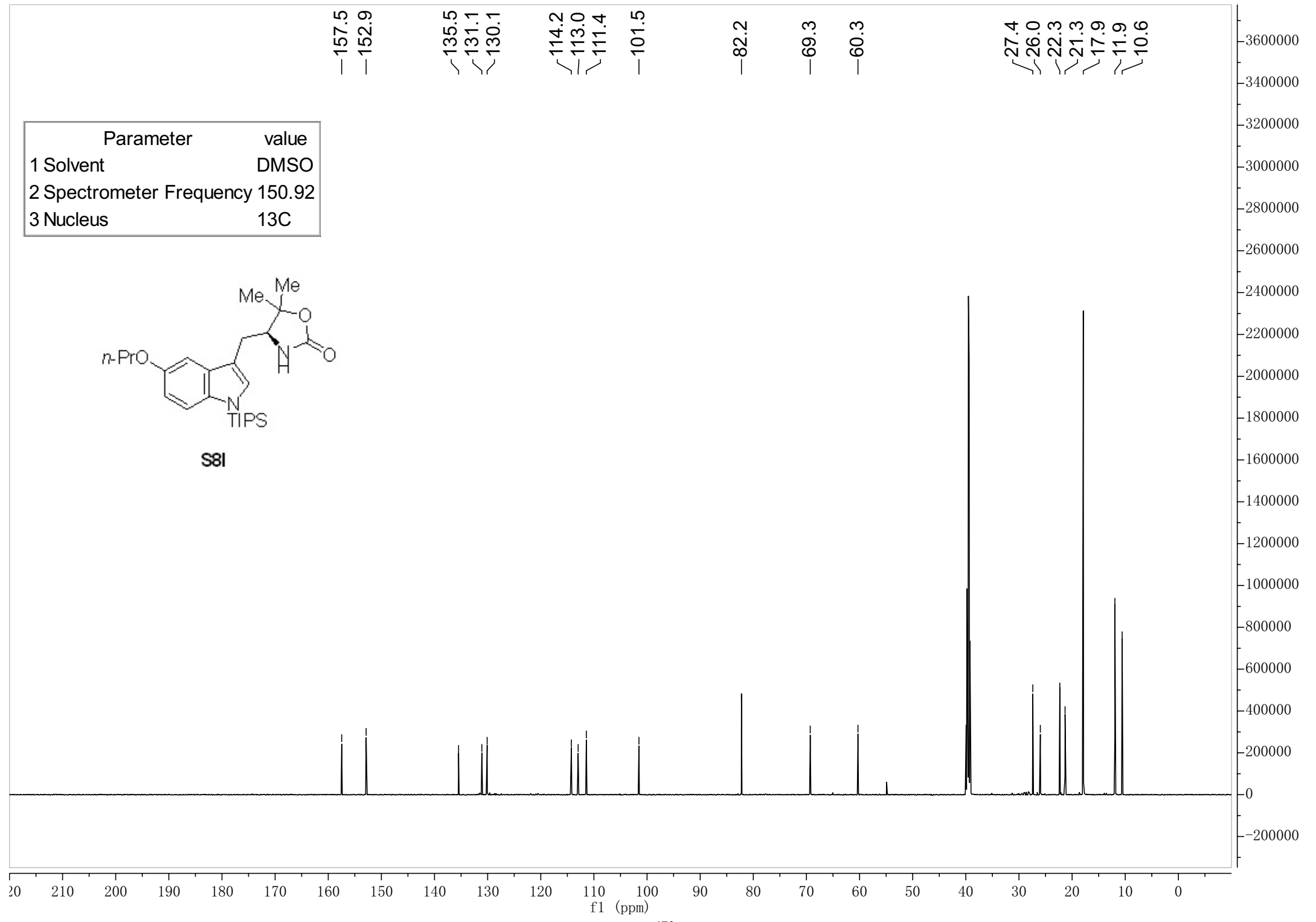
S81

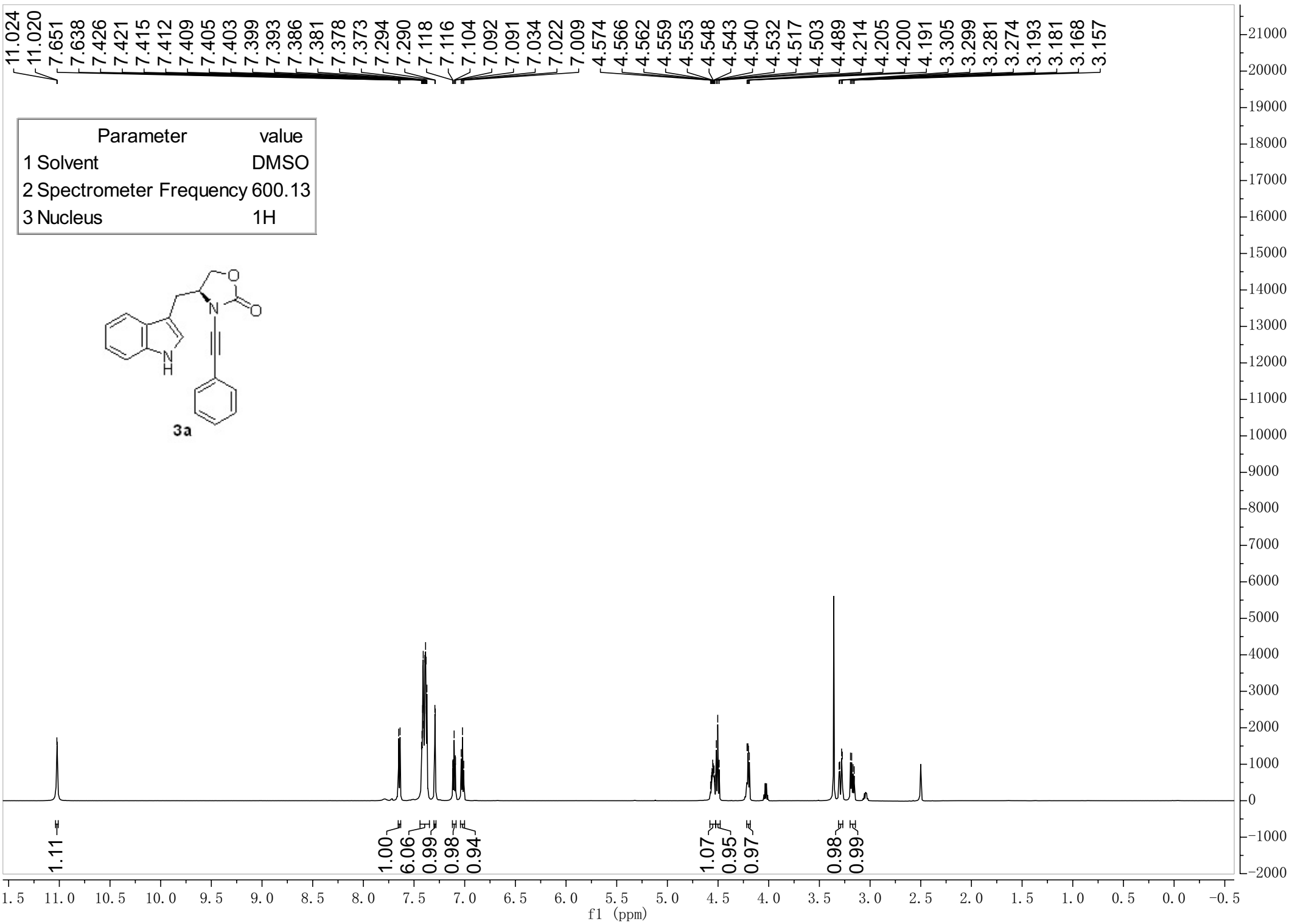


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



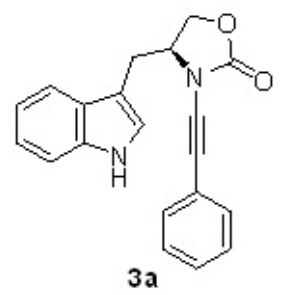
S8I



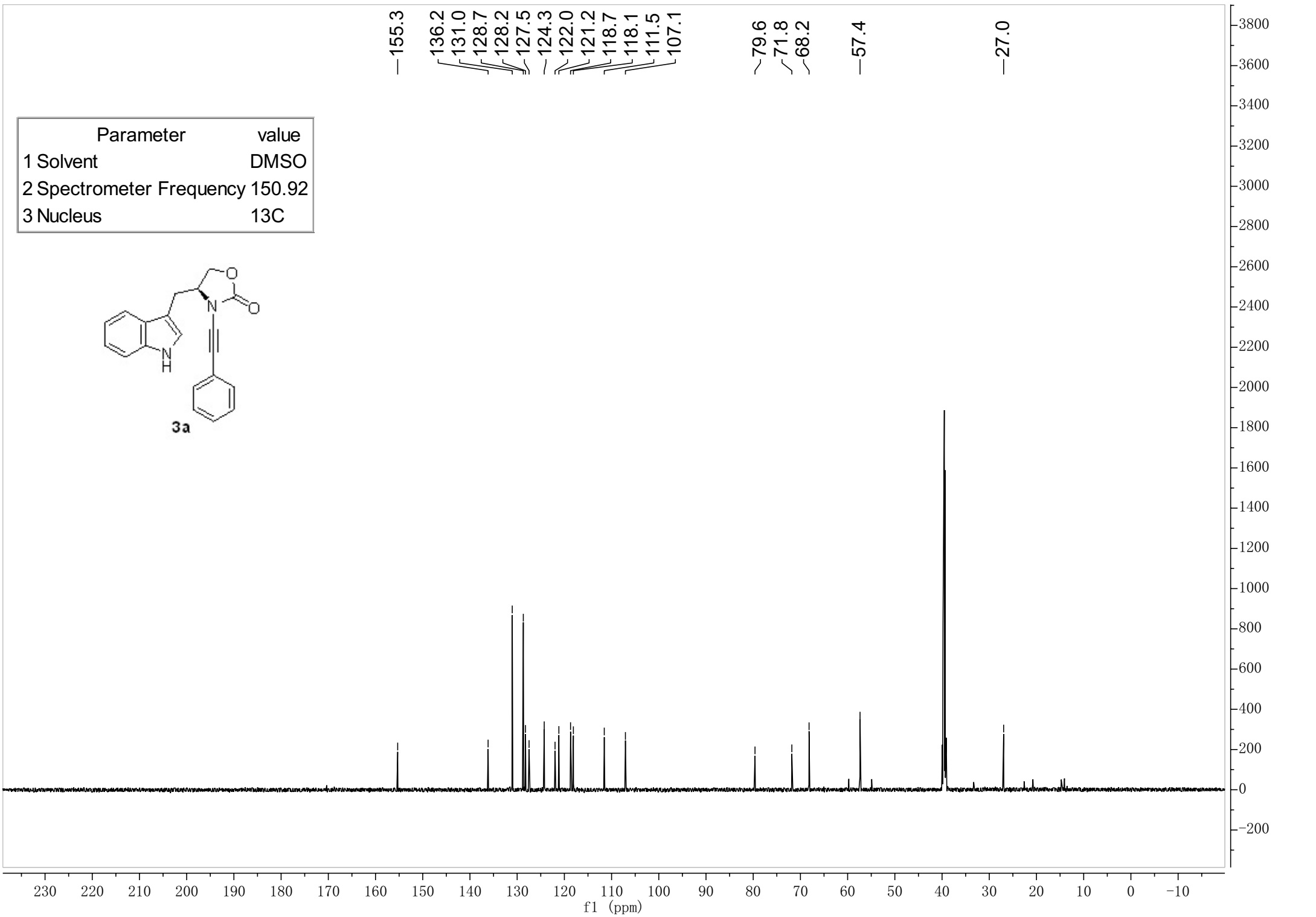


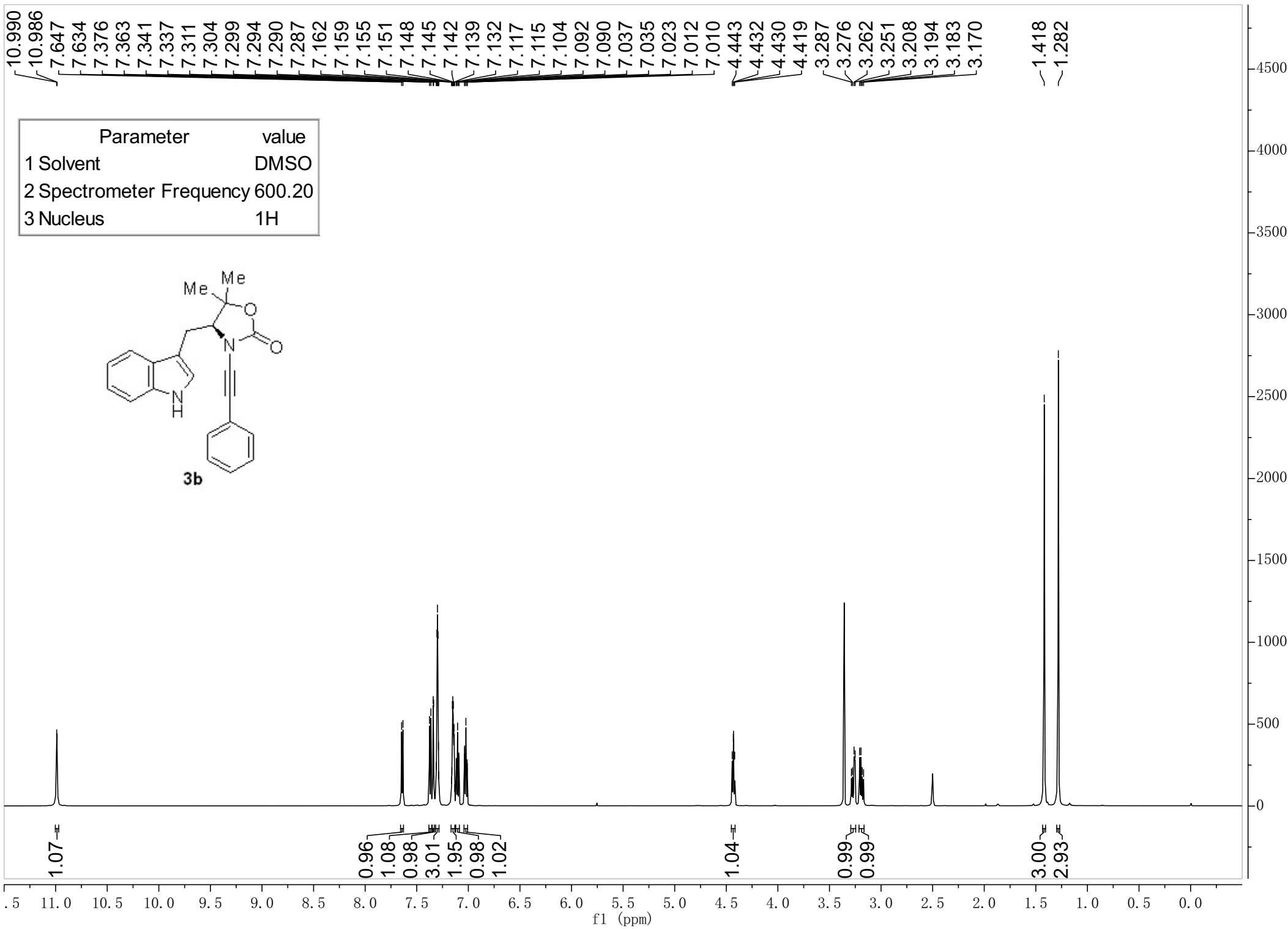
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.13
3 Nucleus	1H

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

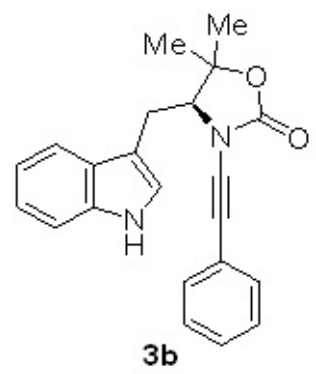


—155.3
 136.2
 131.0
 128.7
 128.2
 127.5
 124.3
 122.0
 121.2
 118.7
 118.1
 111.5
 107.1
 79.6
 71.8
 68.2
 —57.4
 —27.0

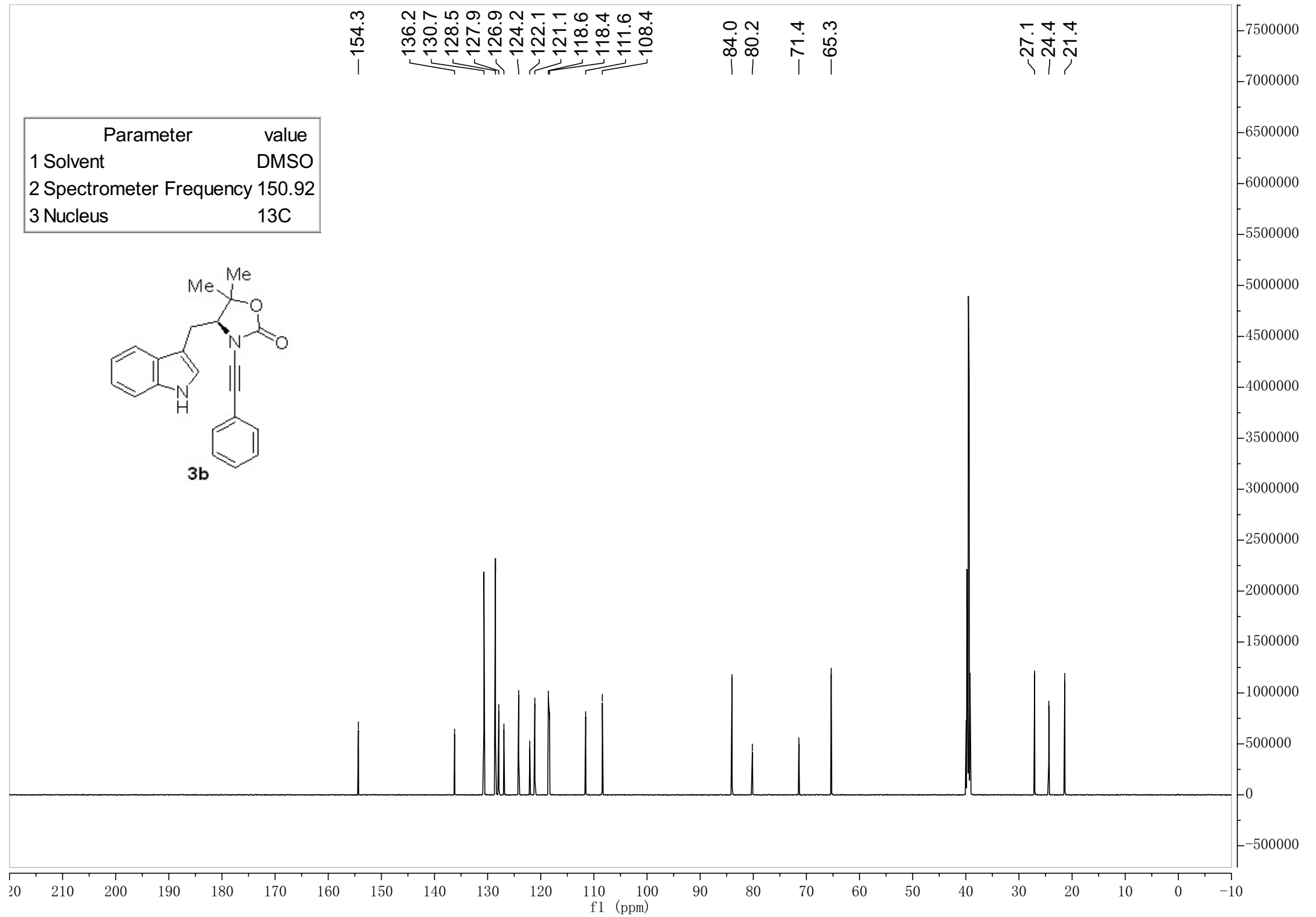


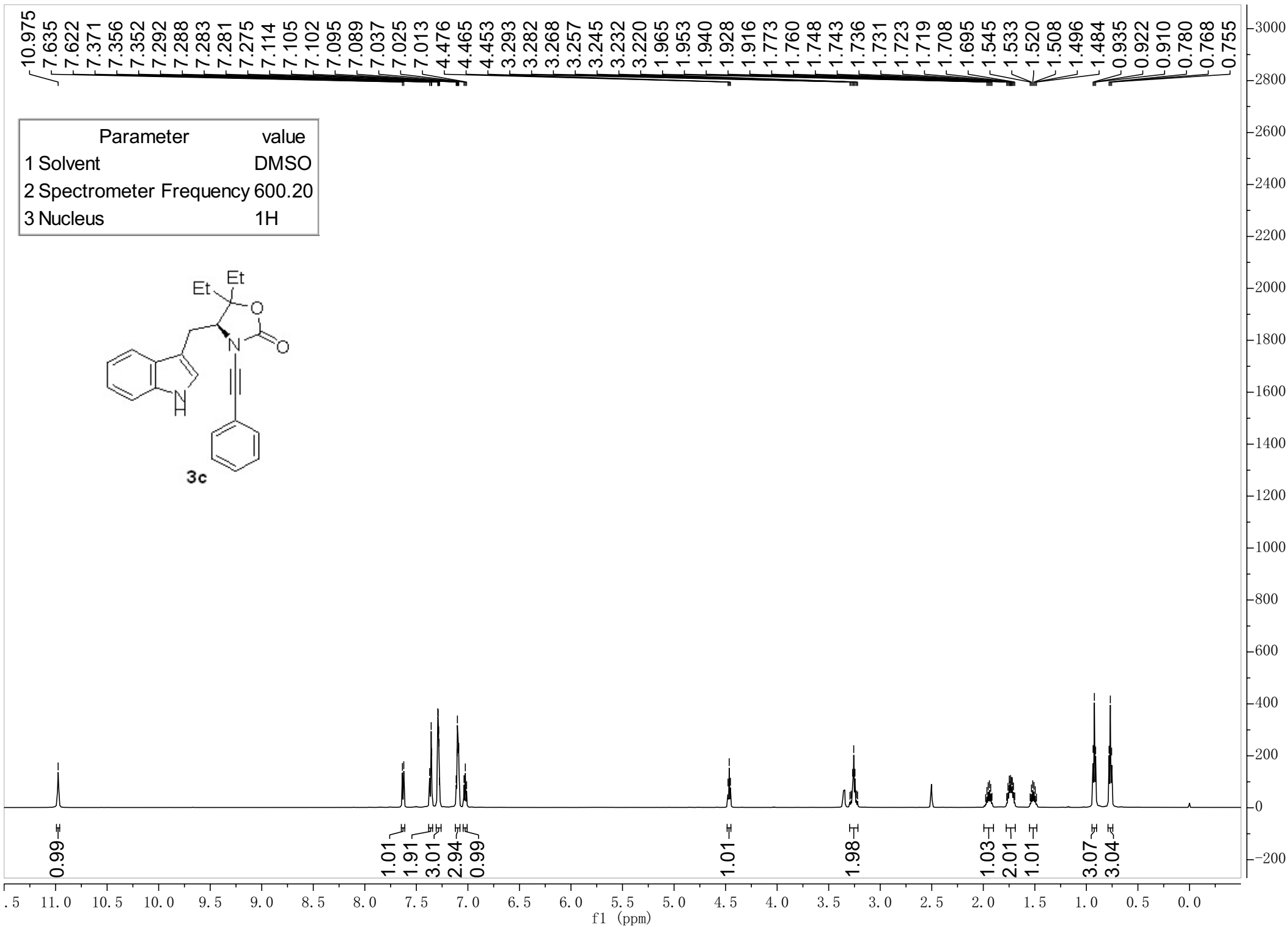


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C

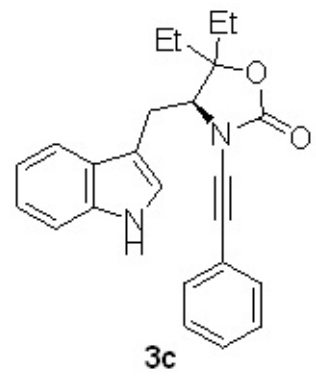


- 154.3
- 136.2
- 130.7
- 128.5
- 127.9
- 126.9
- 124.2
- 122.1
- 121.1
- 118.6
- 118.4
- 111.6
- 108.4
- 84.0
- 80.2
- 71.4
- 65.3
- ~ 27.1
- ~ 24.4
- ~ 21.4

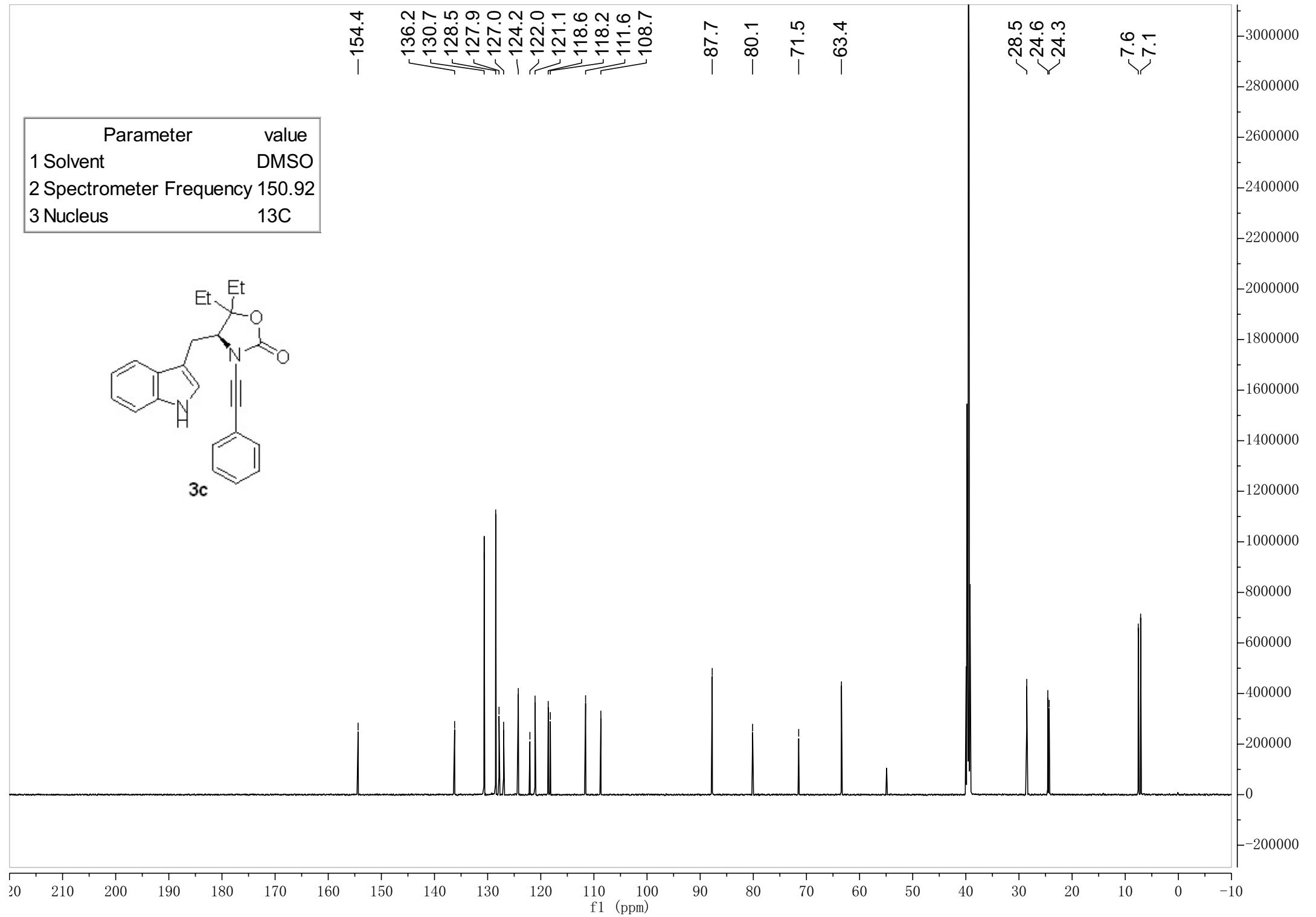


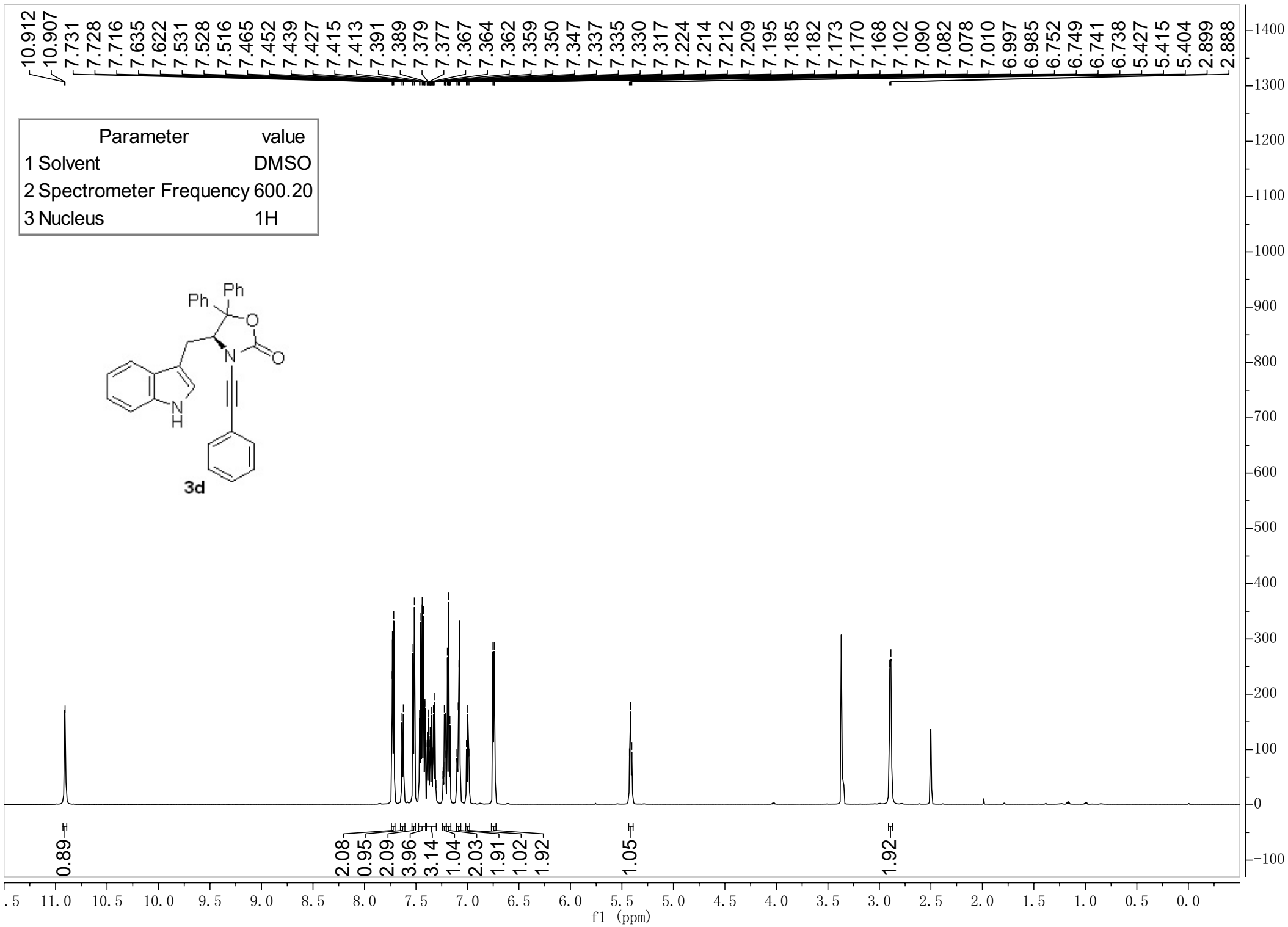


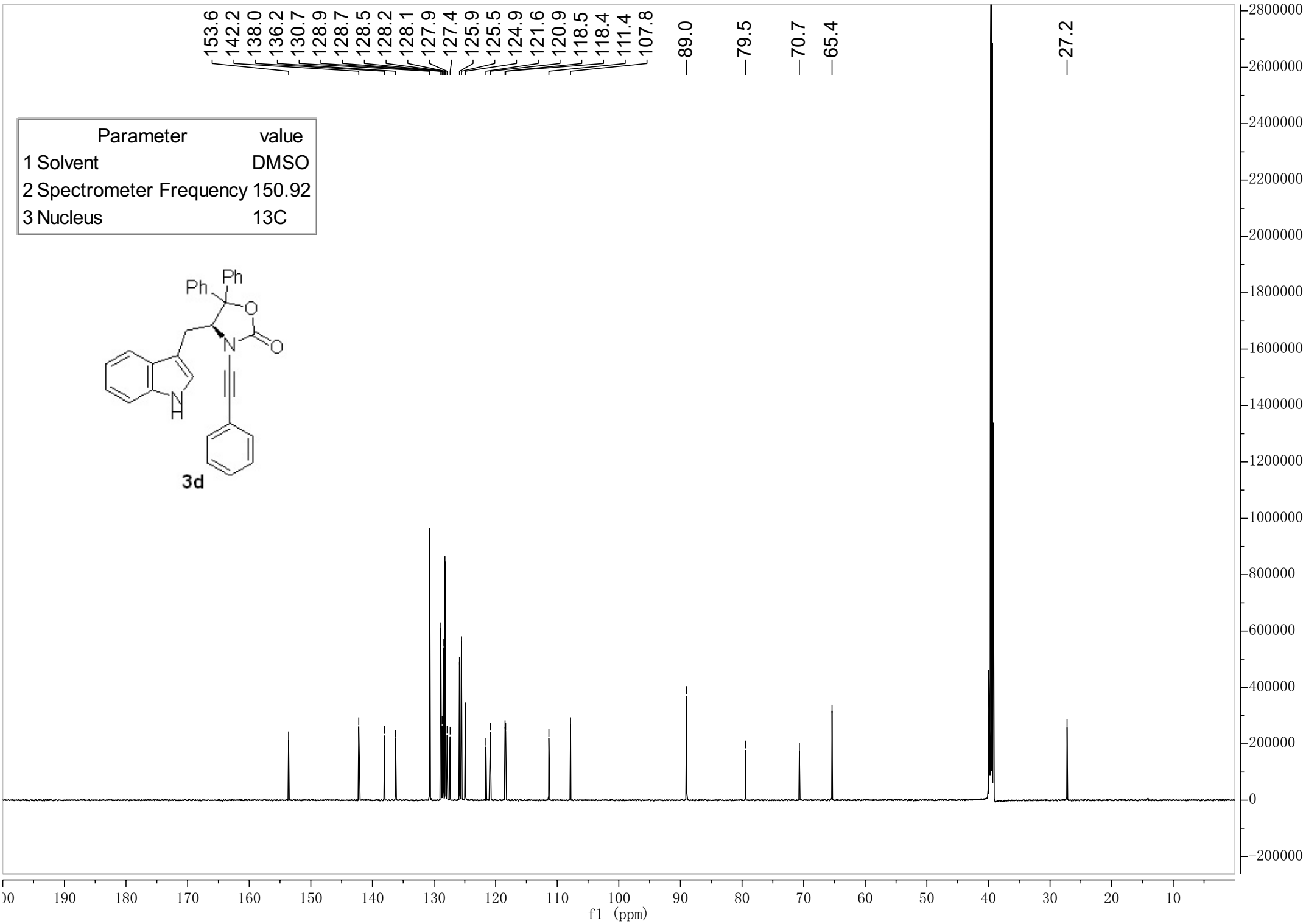
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

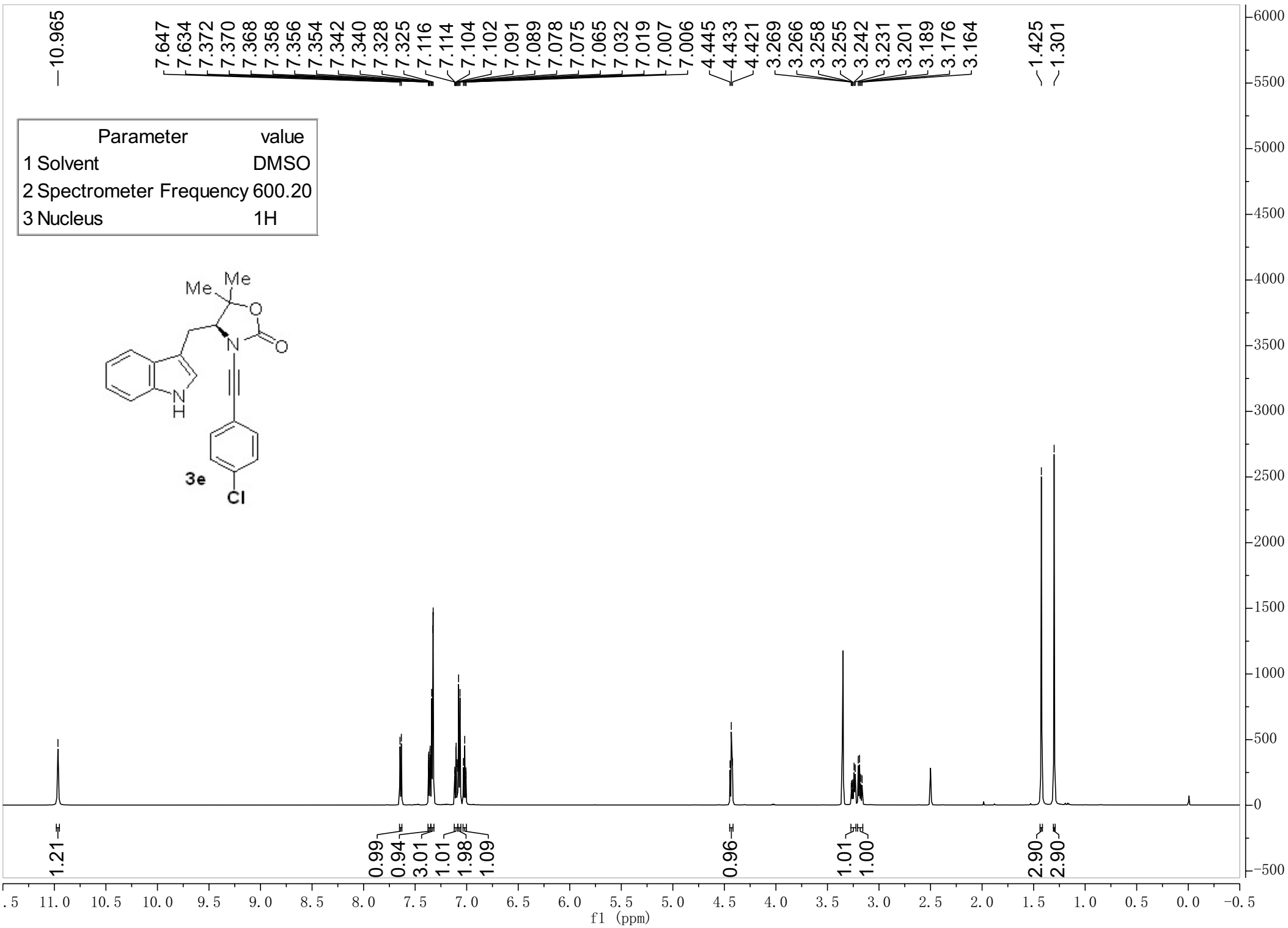


—154.4
 136.2
 130.7
 128.5
 127.9
 127.0
 —124.2
 122.0
 121.1
 118.6
 118.2
 111.6
 108.7
 —87.7
 —80.1
 —71.5
 —63.4
 28.5
 24.6
 24.3
 7.6
 7.1

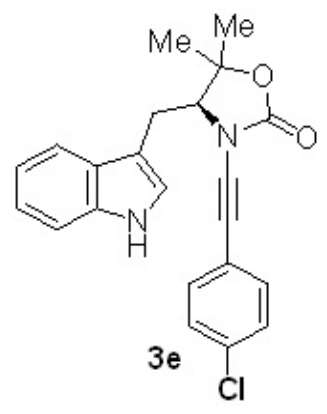




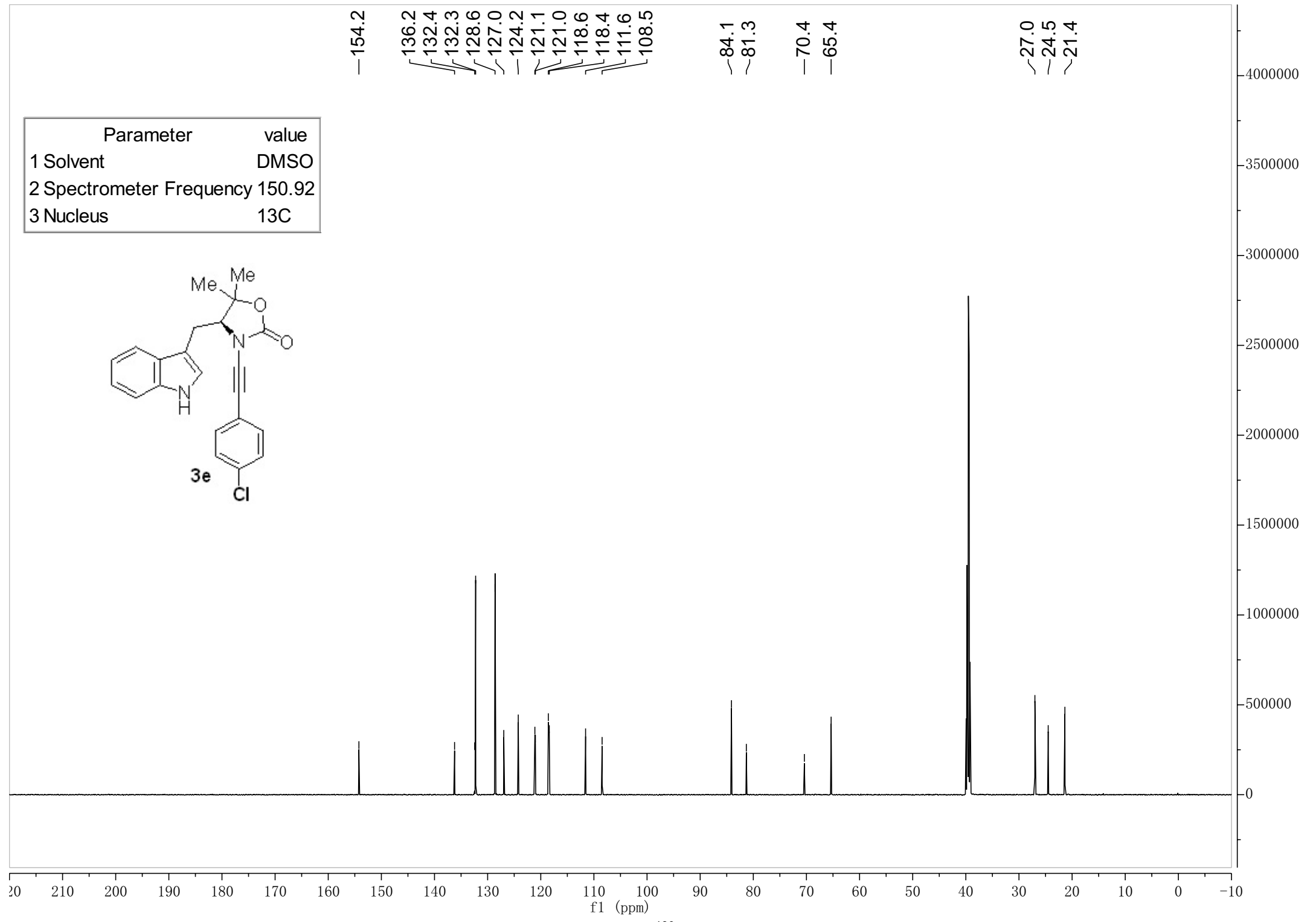


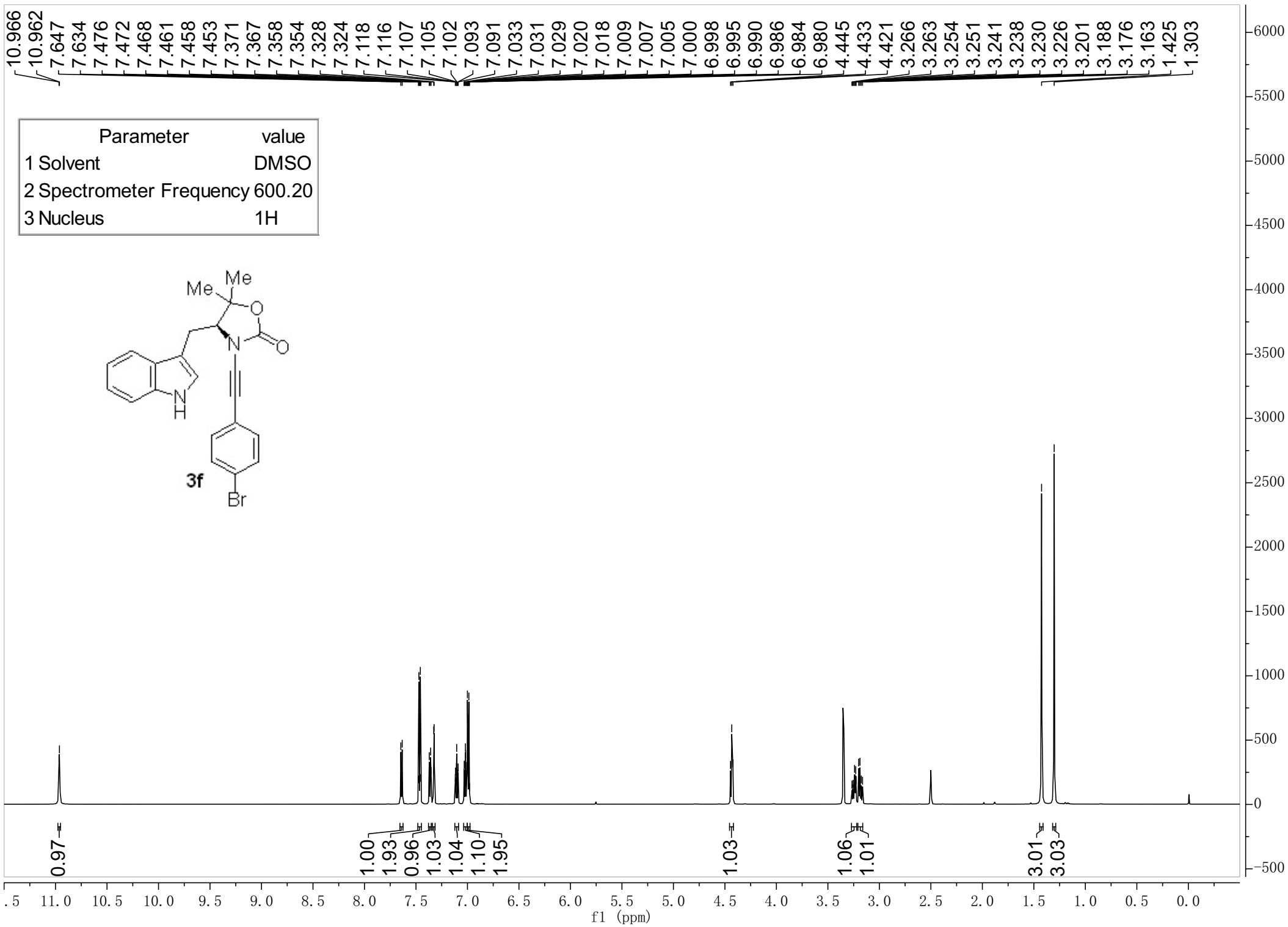


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



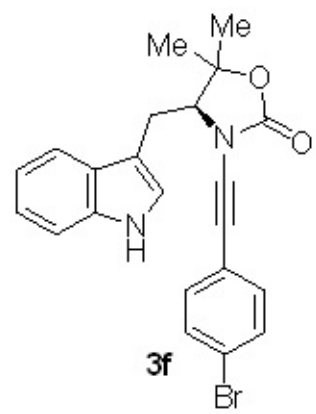
— 154.2
 136.2
 132.4
 132.3
 128.6
 127.0
 — 124.2
 121.1
 121.0
 118.6
 118.4
 111.6
 108.5
 ~ 84.1
 ~ 81.3
 — 70.4
 — 65.4
 ~ 27.0
 ~ 24.5
 ~ 21.4



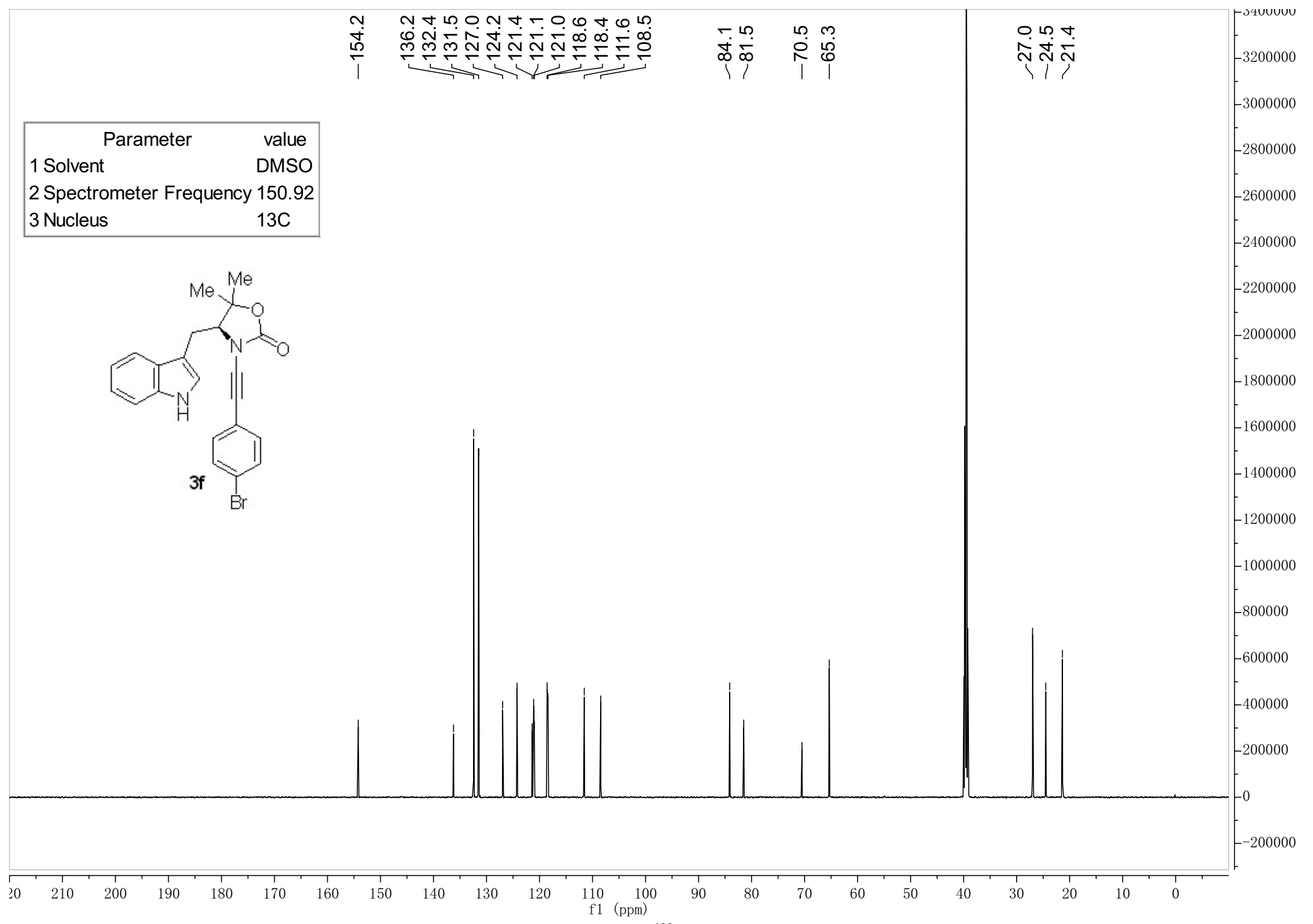


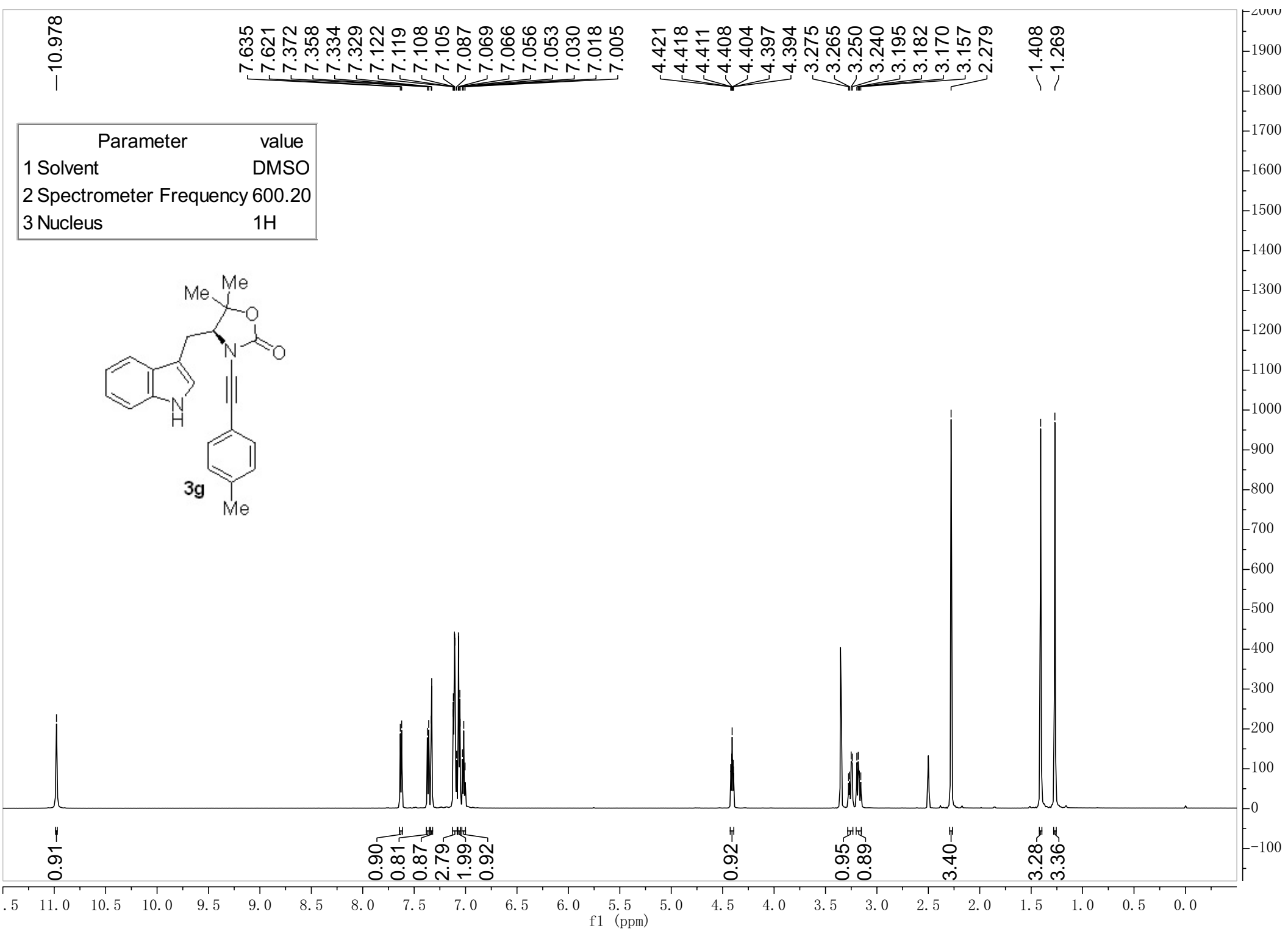
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

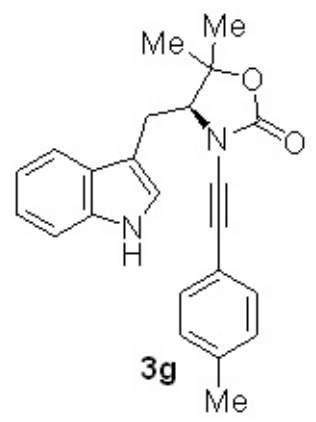


— 154.2
 { 136.2
 { 132.4
 { 131.5
 { 127.0
 { 124.2
 { 121.4
 { 121.1
 { 121.0
 { 118.6
 { 118.4
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 { 108.5
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 ~ 81.5
 — 70.5
 — 65.3
 ~ 27.0
 ~ 24.5
 ~ 21.4

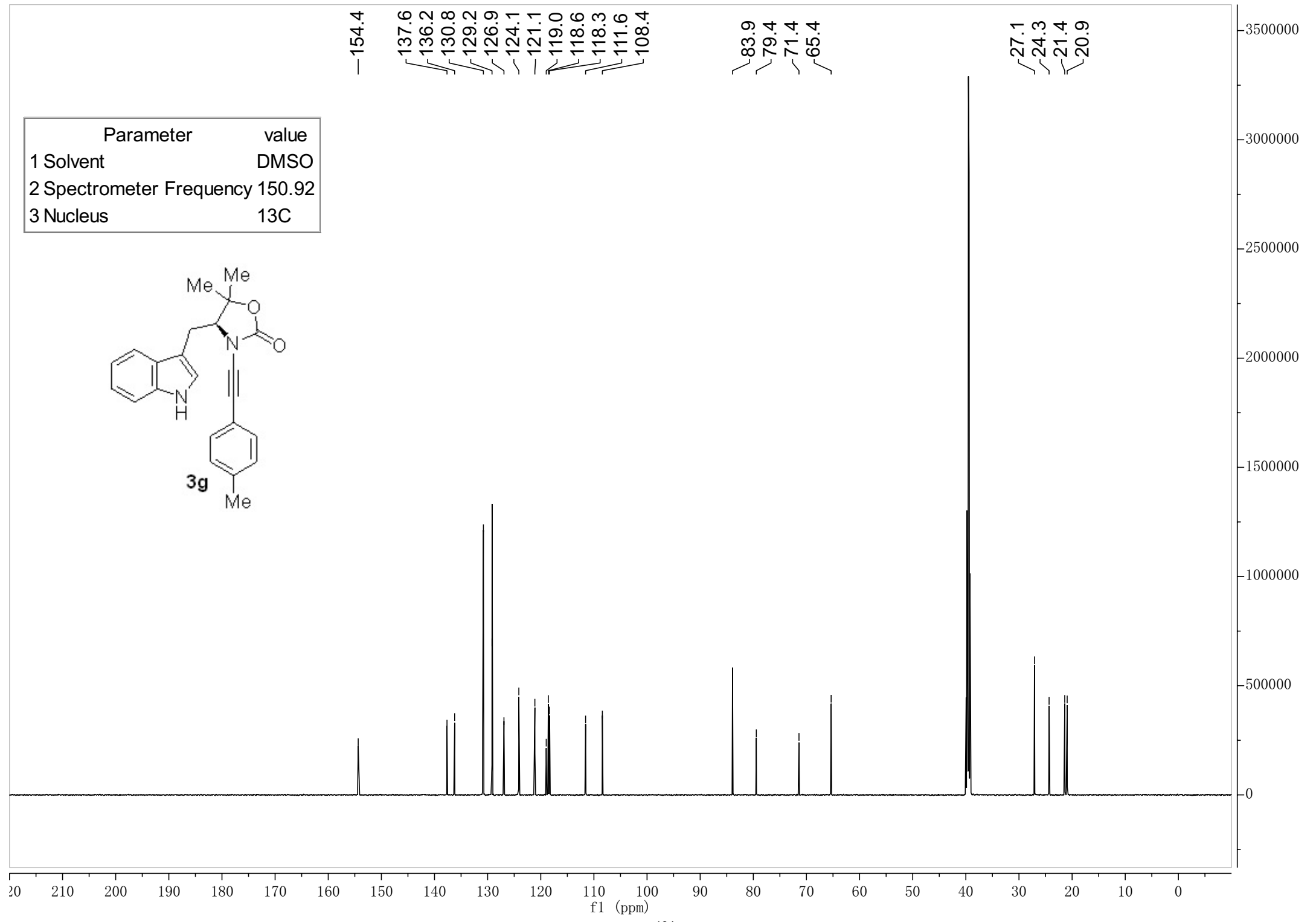


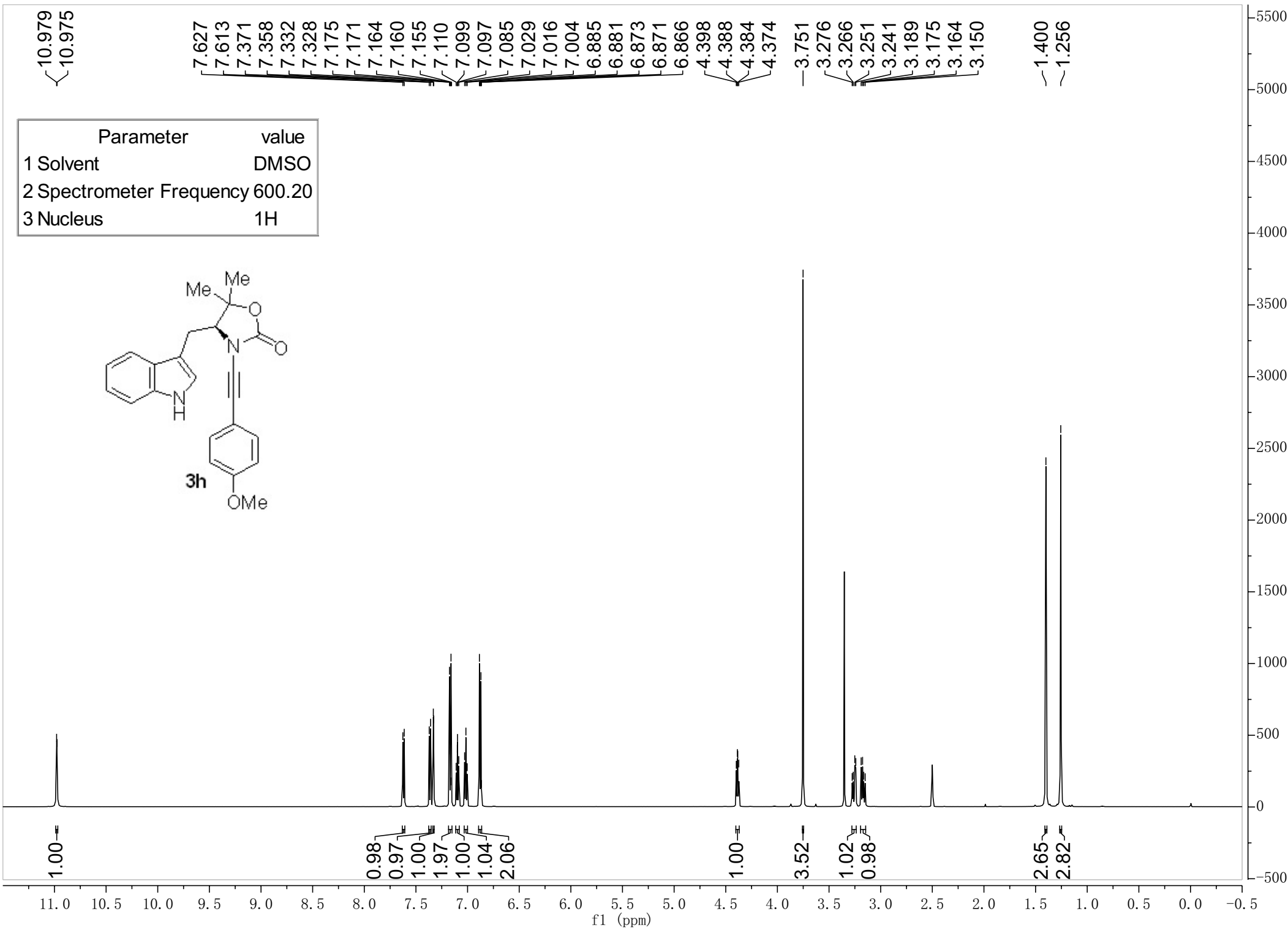


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



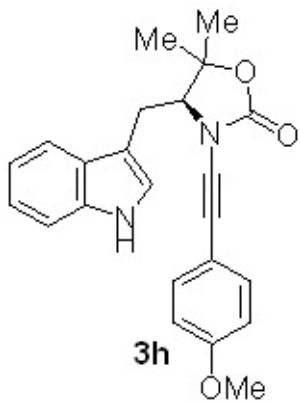
- 154.4
- 137.6
- 136.2
- 130.8
- 129.2
- 126.9
- 124.1
- 121.1
- 119.0
- 118.6
- 118.3
- 111.6
- 108.4
- 83.9
- 79.4
- 71.4
- 65.4
- 27.1
- 24.3
- 21.4
- 20.9





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

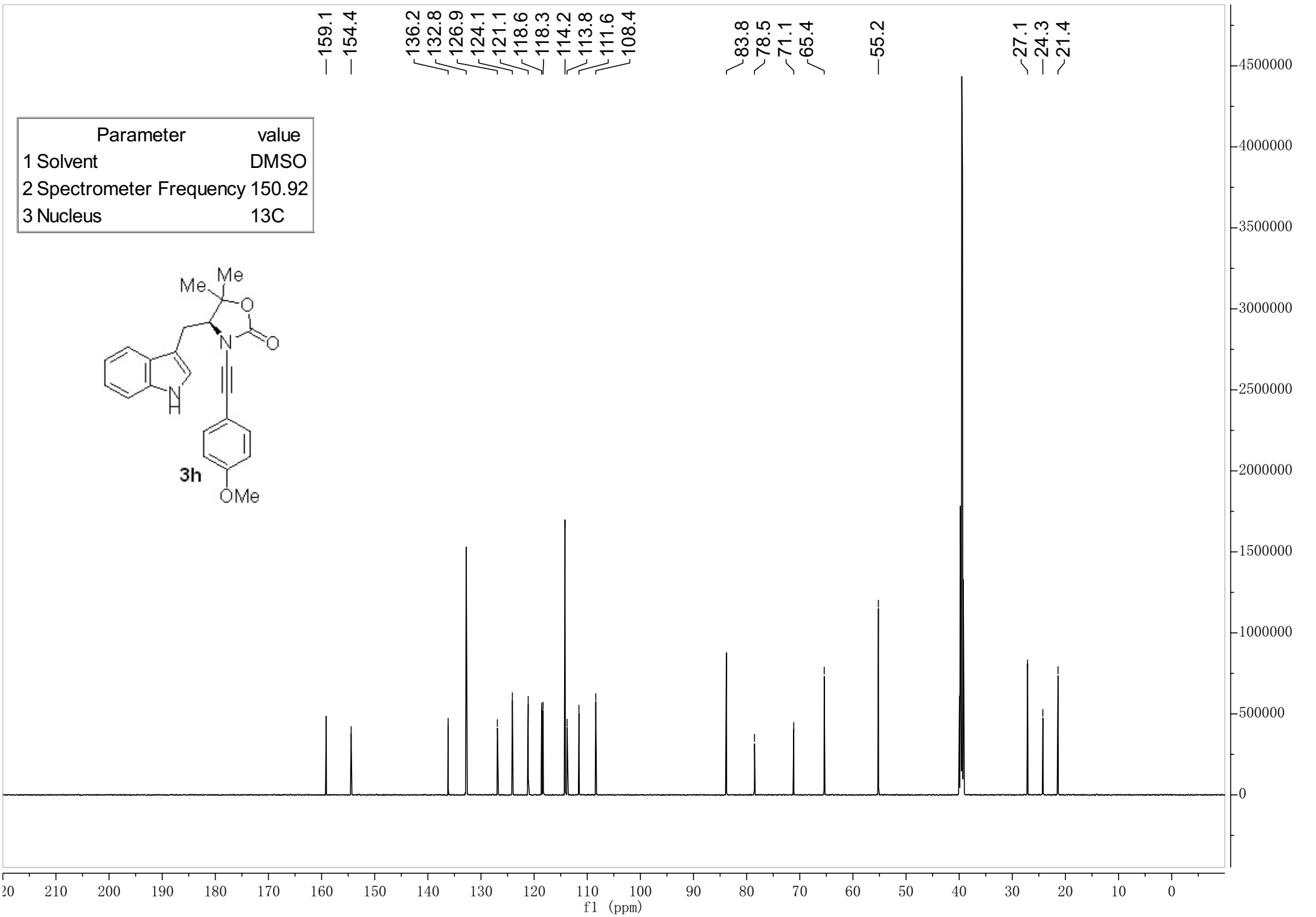
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

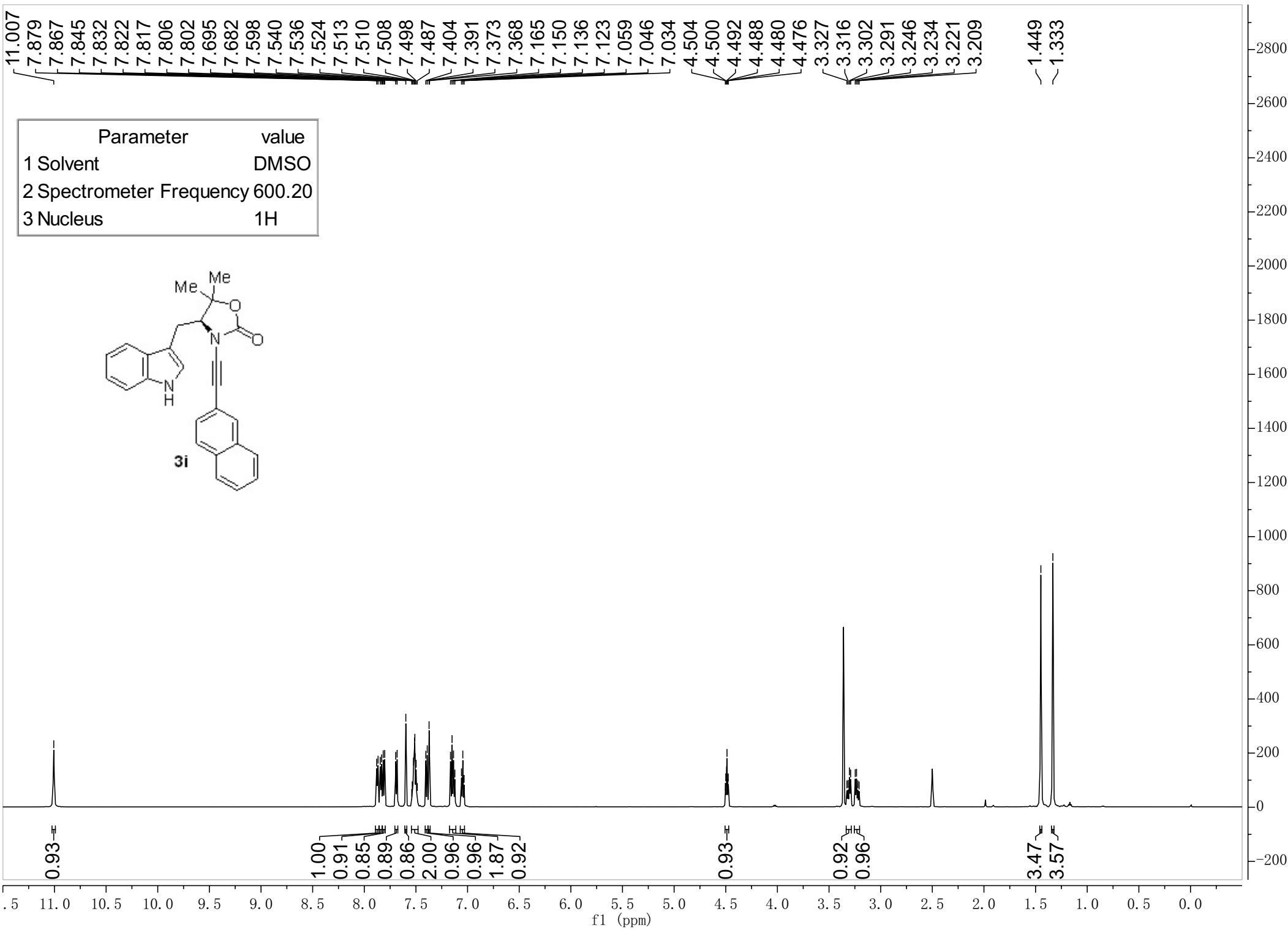


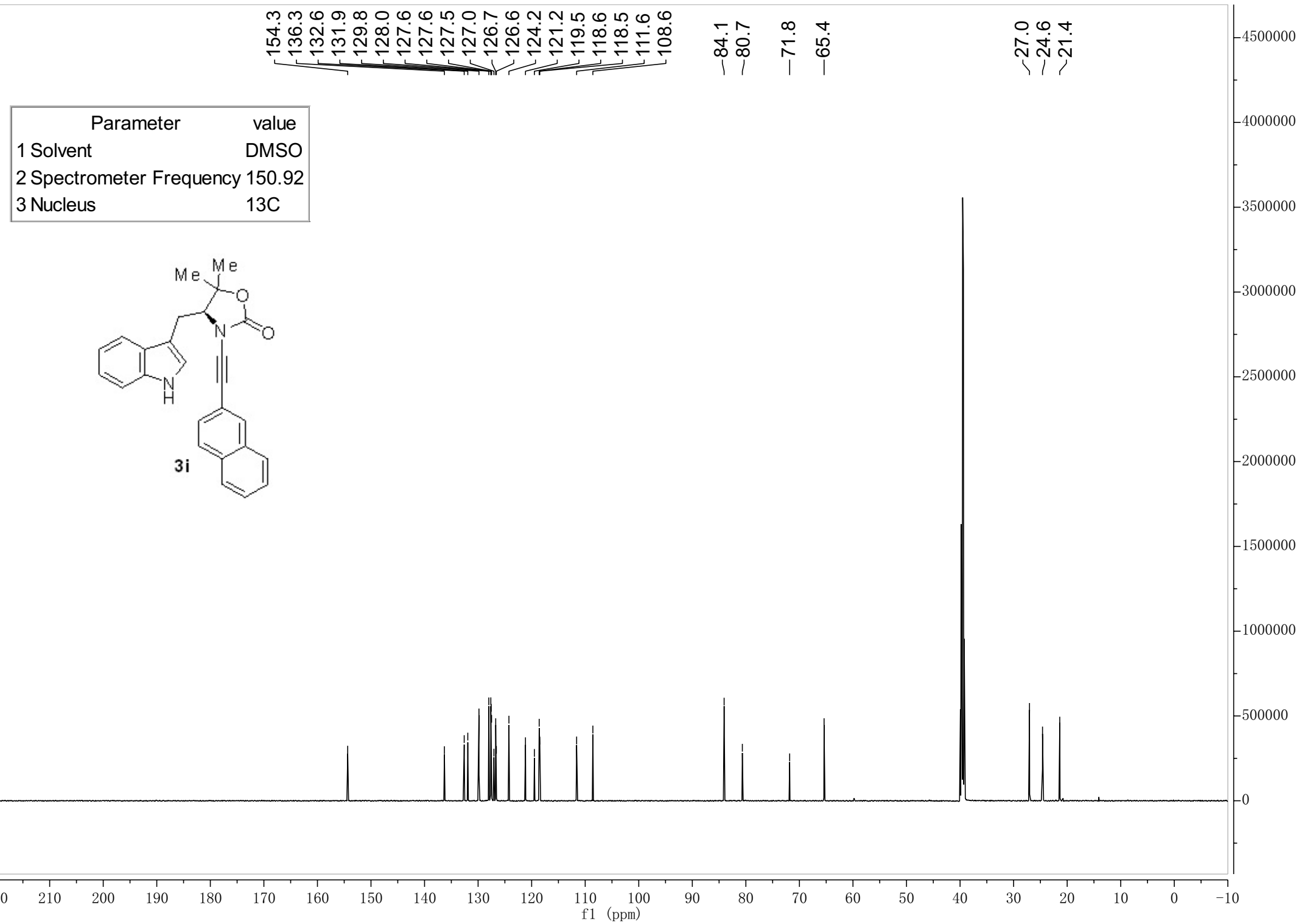
— 159.1
 — 154.4
 / 136.2
 / 132.8
 / 126.9
 / 124.1
 / 121.1
 / 118.6
 / 118.3
 / 114.2
 / 113.8
 / 111.6
 / 108.4

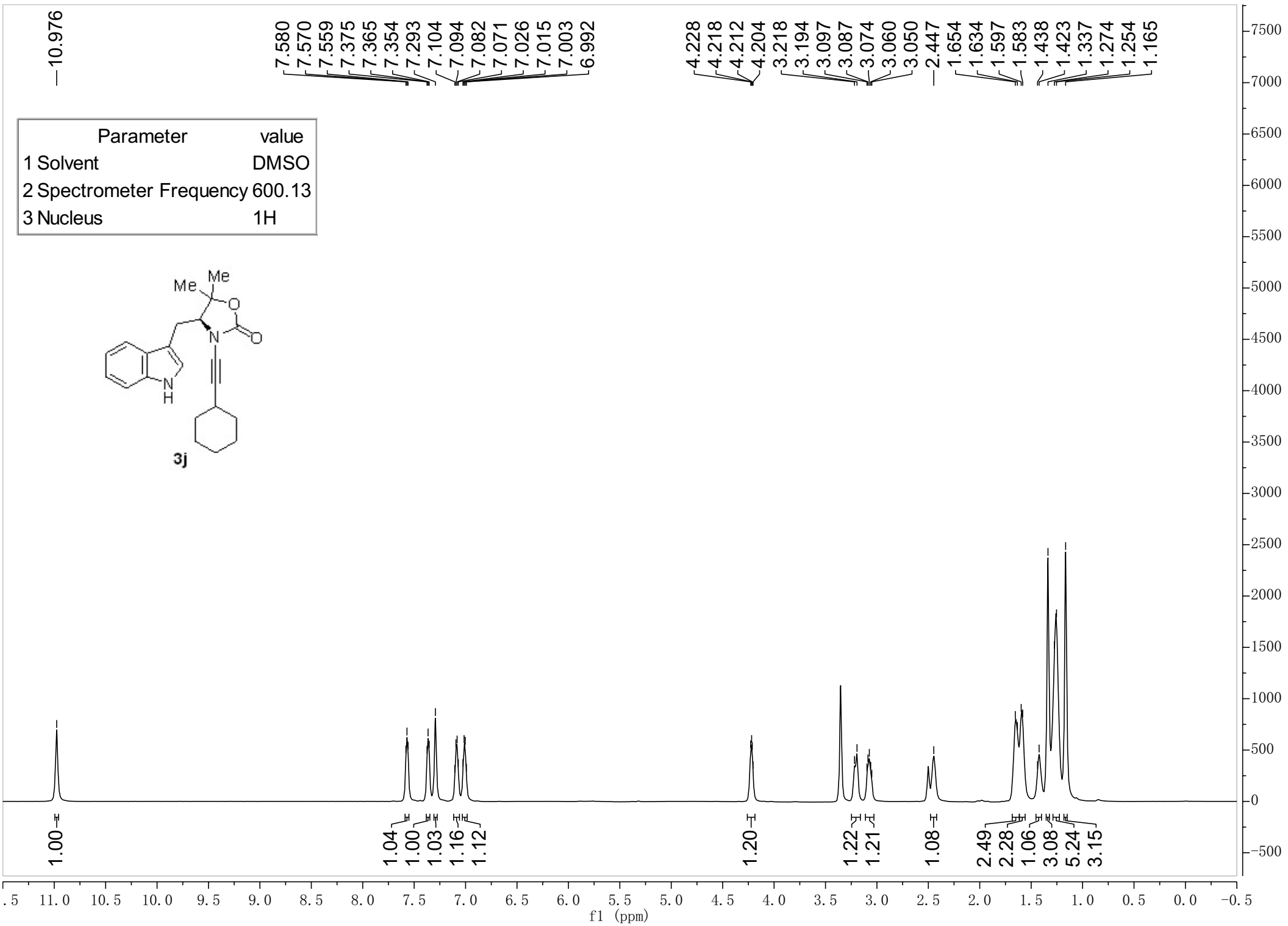
/ 83.8
 / 78.5
 / 71.1
 / 65.4
 — 55.2

/ 27.1
 — 24.3
 / 21.4



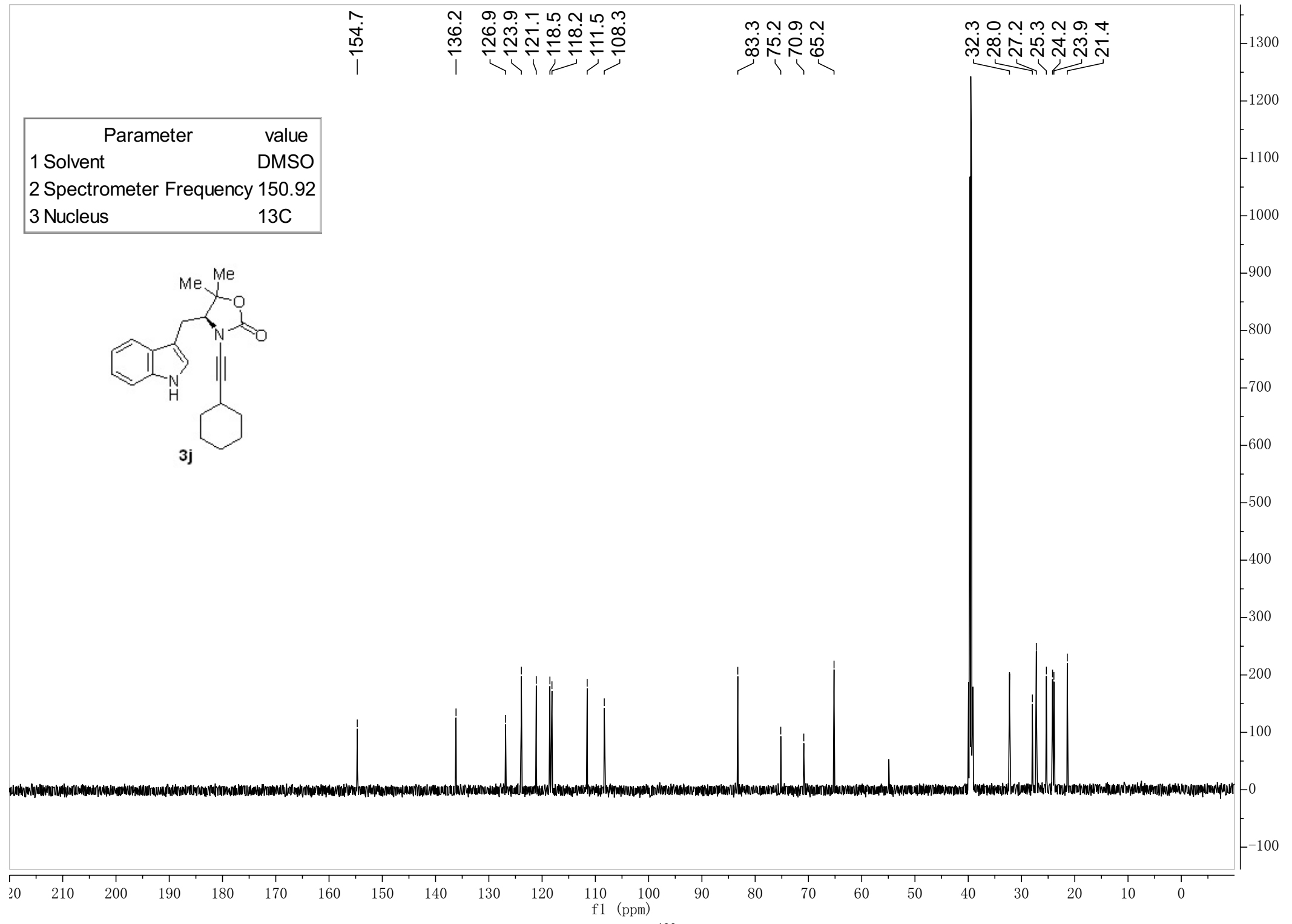
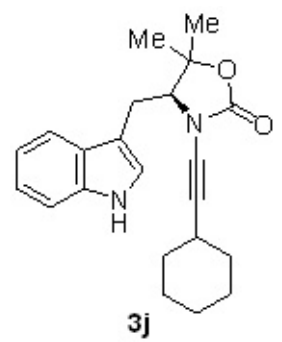


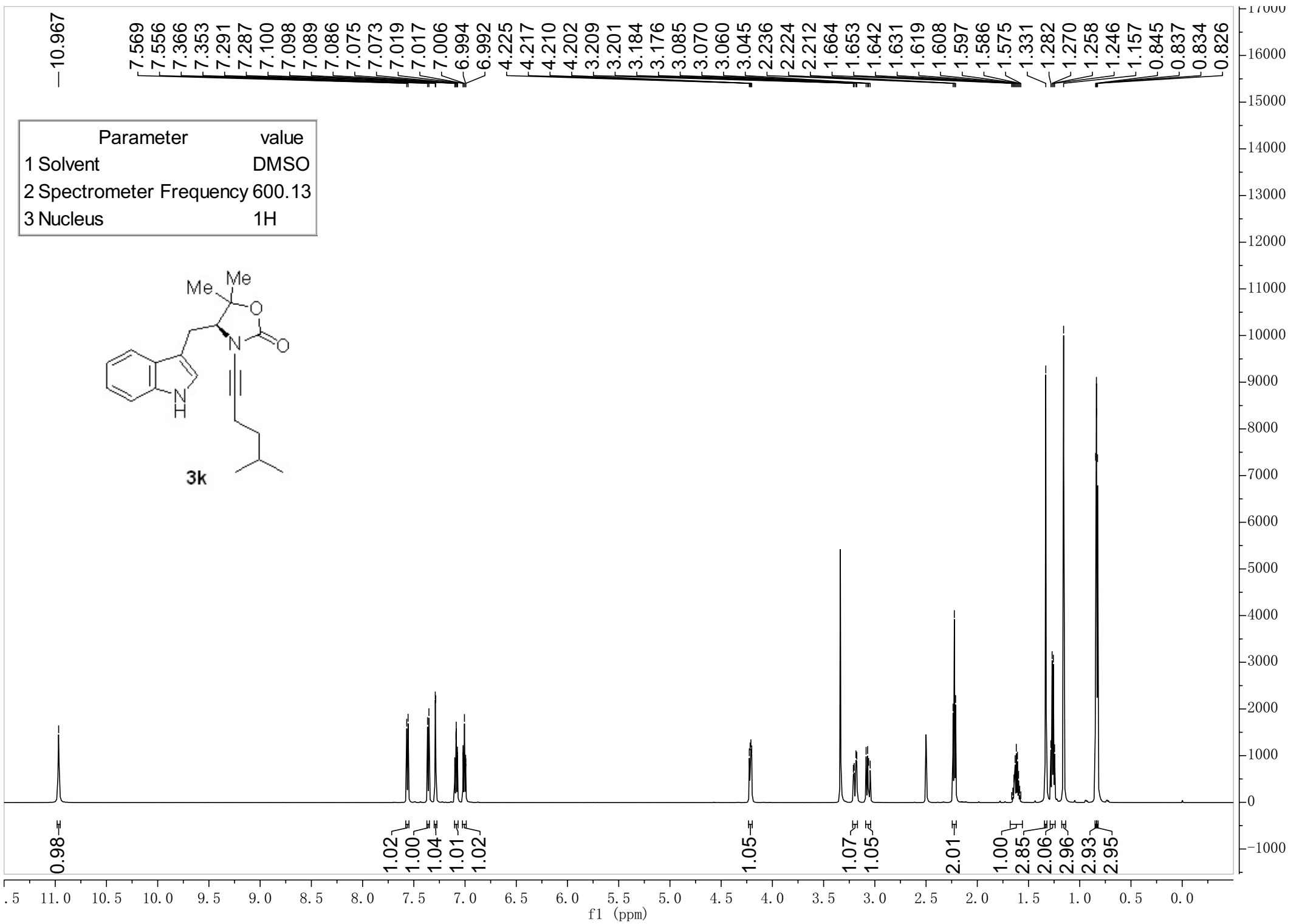




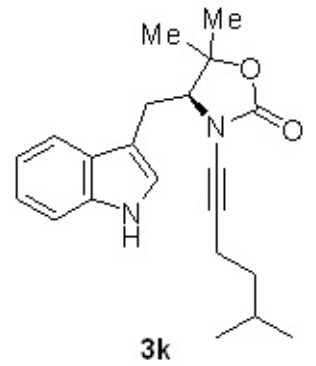
Parameter	value
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2 Spectrometer Frequency	600.13
3 Nucleus	1H

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

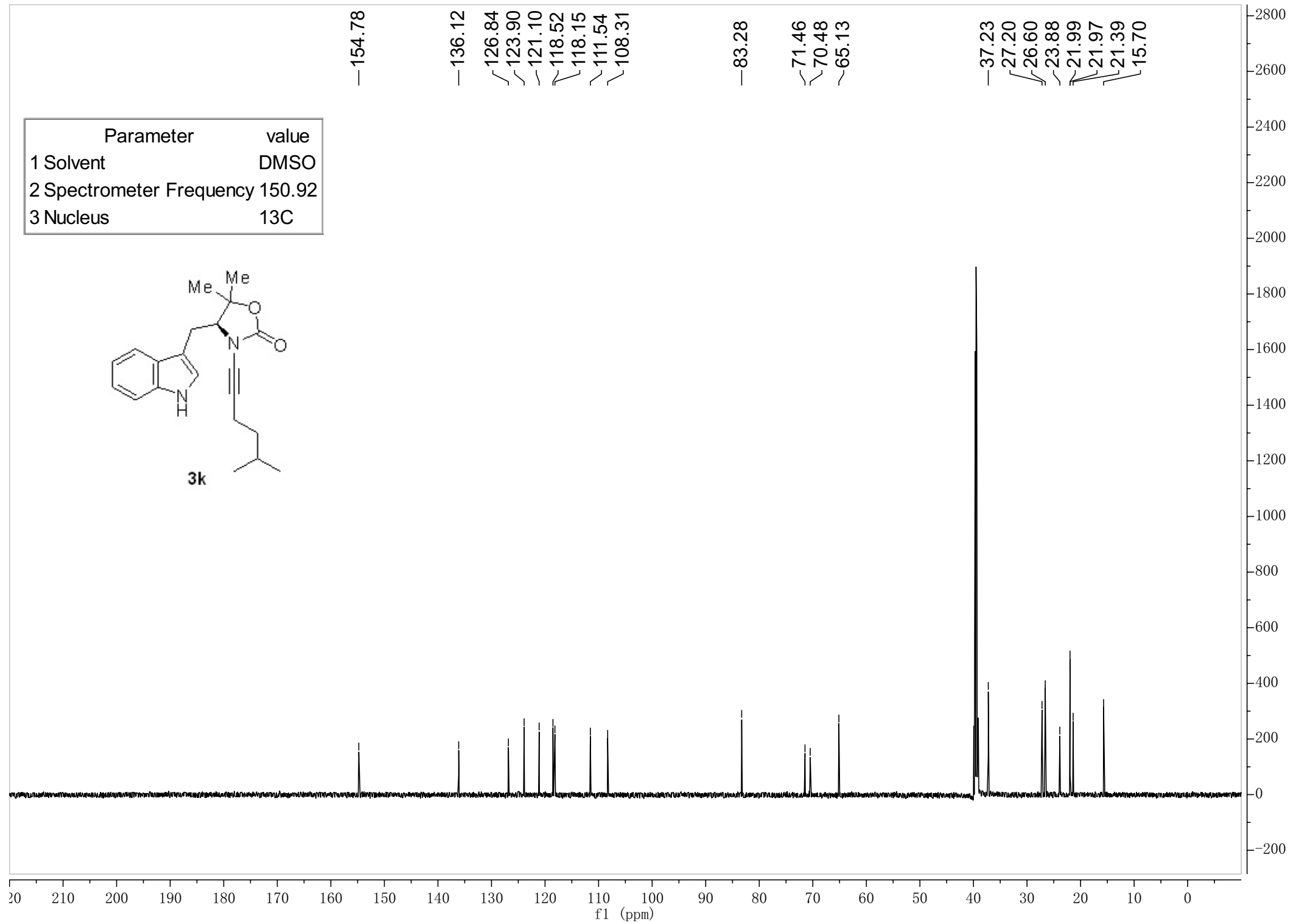


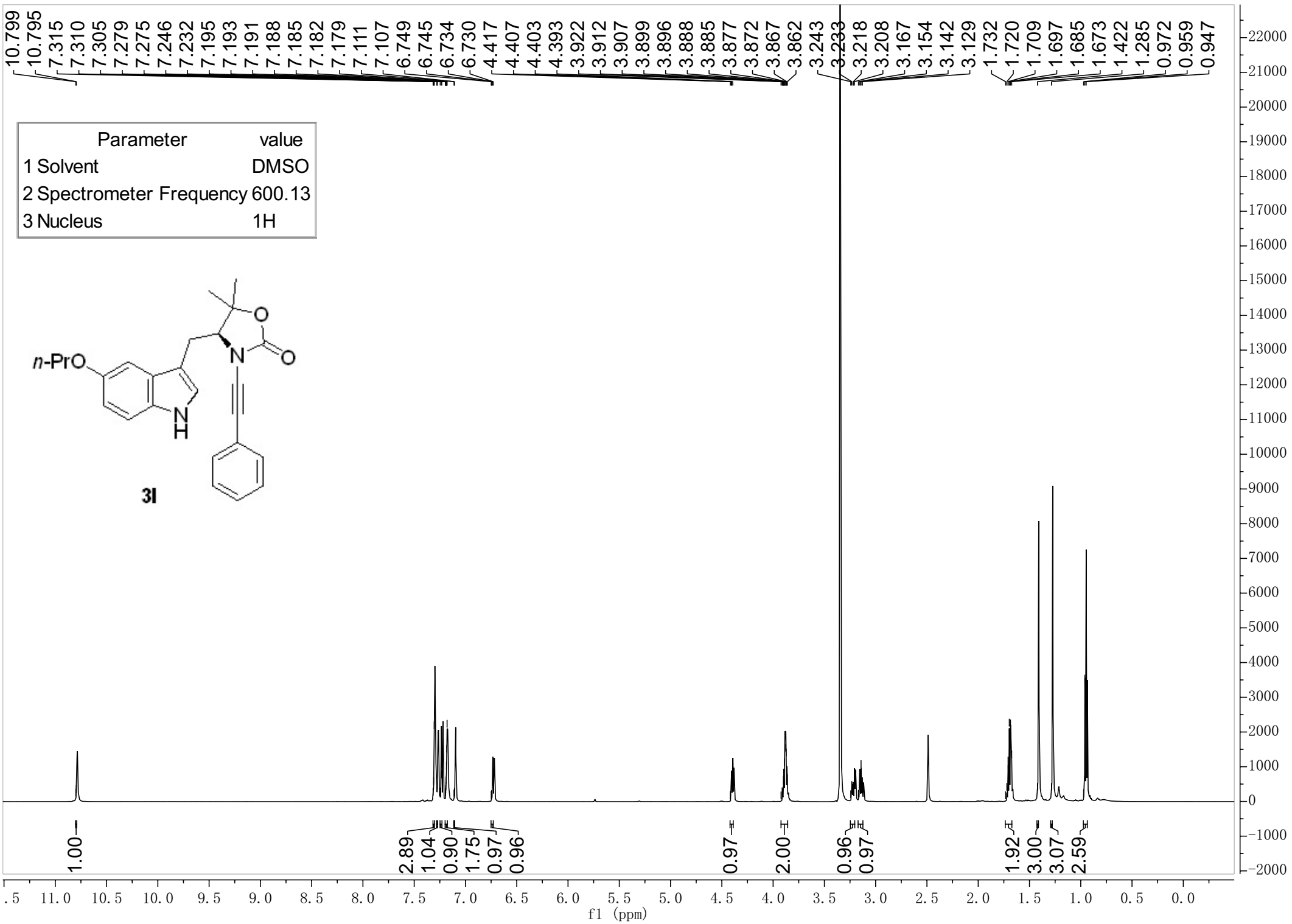


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

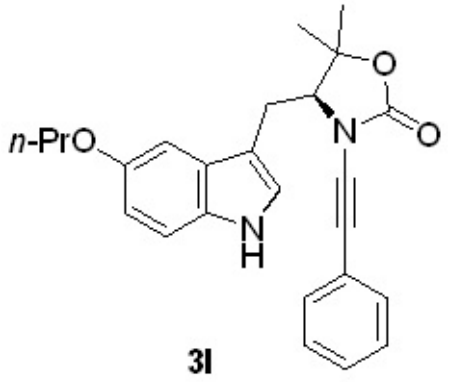


- 154.78
- 136.12
- ↘ 126.84
- ↘ 123.90
- ↘ 121.10
- ↘ 118.52
- ↘ 118.15
- ↘ 111.54
- ↘ 108.31
- 83.28
- ↘ 71.46
- ↘ 70.48
- ↘ 65.13
- 37.23
- ↘ 27.20
- ↘ 26.60
- ↘ 23.88
- ↘ 21.99
- ↘ 21.97
- ↘ 21.39
- ↘ 15.70

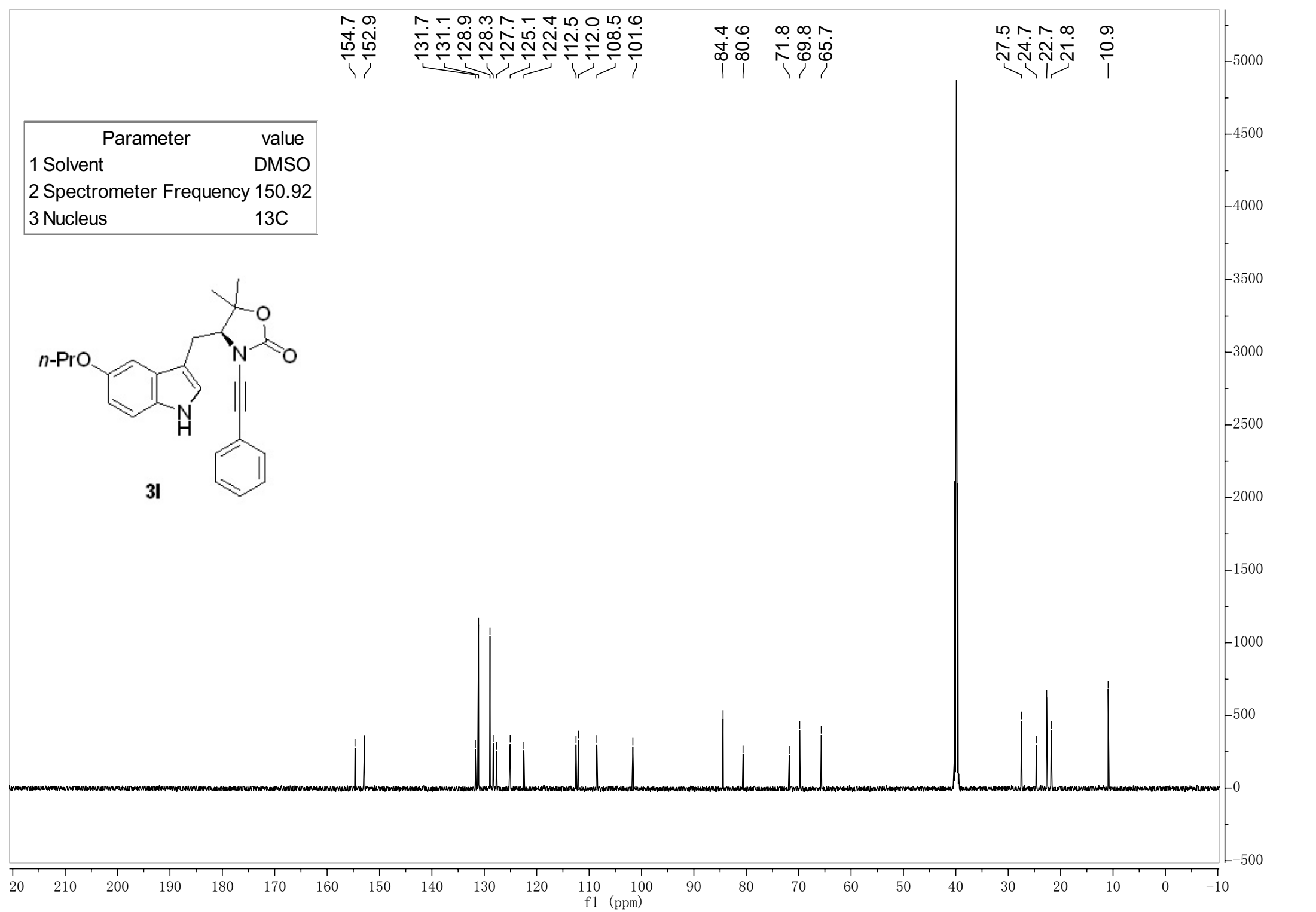


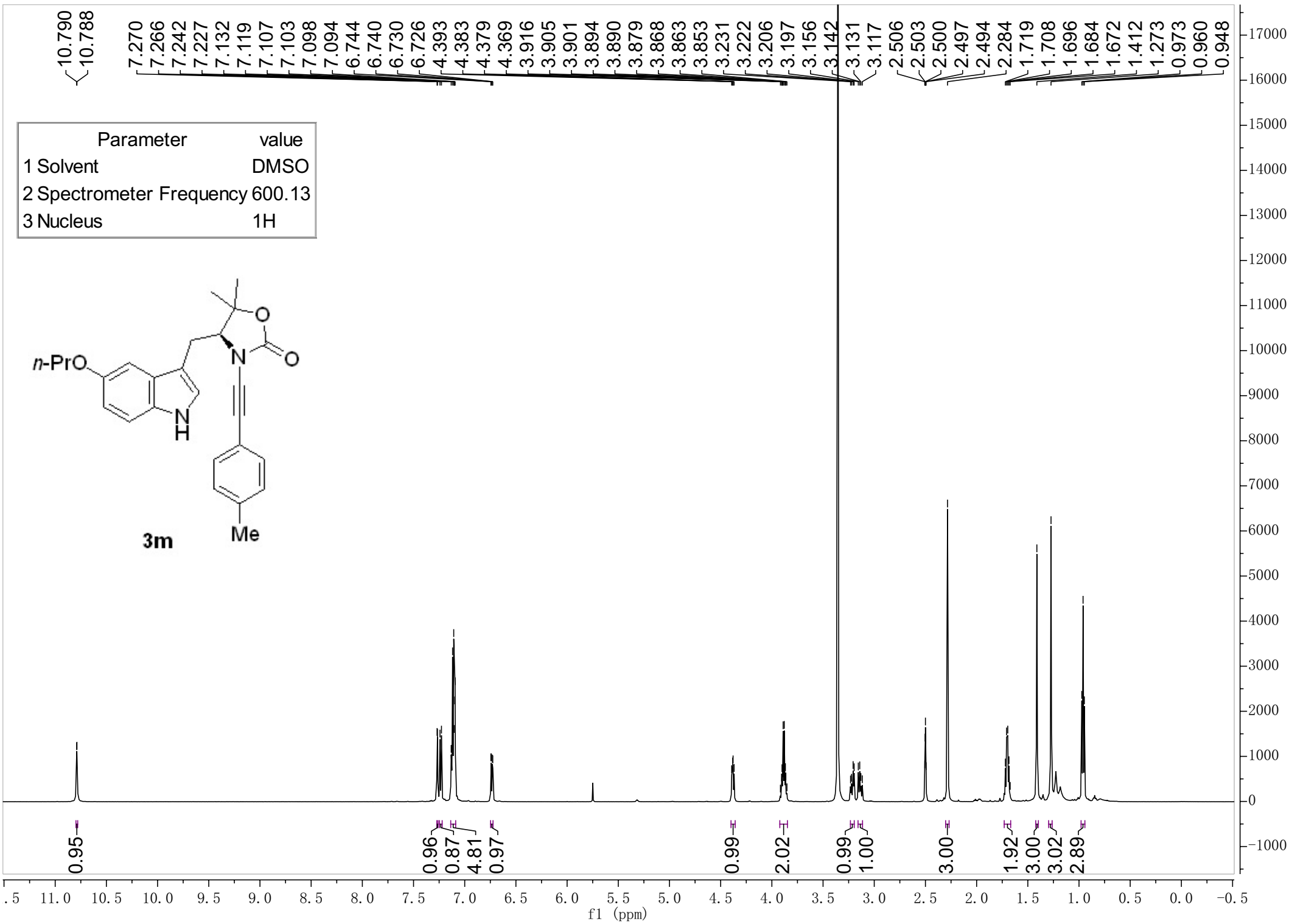


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

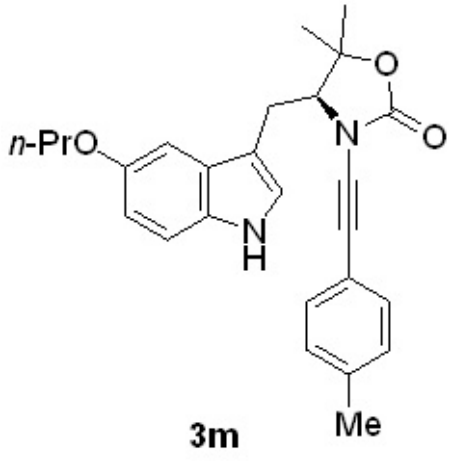


- ~154.7
- ~152.9
- 131.7
- 131.1
- 128.9
- 128.3
- 127.7
- 125.1
- 122.4
- 112.5
- 112.0
- 108.5
- 101.6
- 84.4
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- 71.8
- 69.8
- 65.7
- 27.5
- 24.7
- 22.7
- 21.8
- 10.9

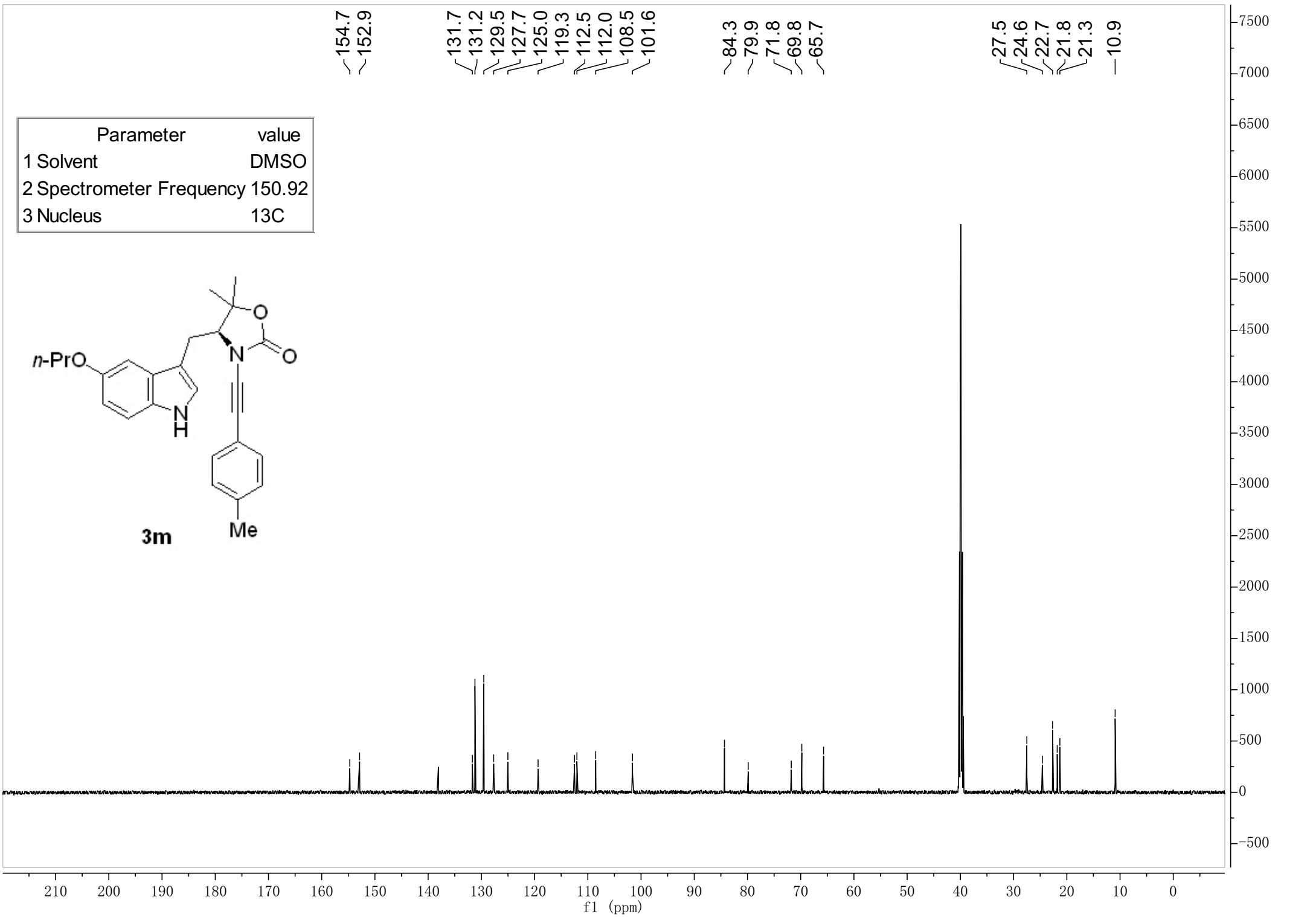


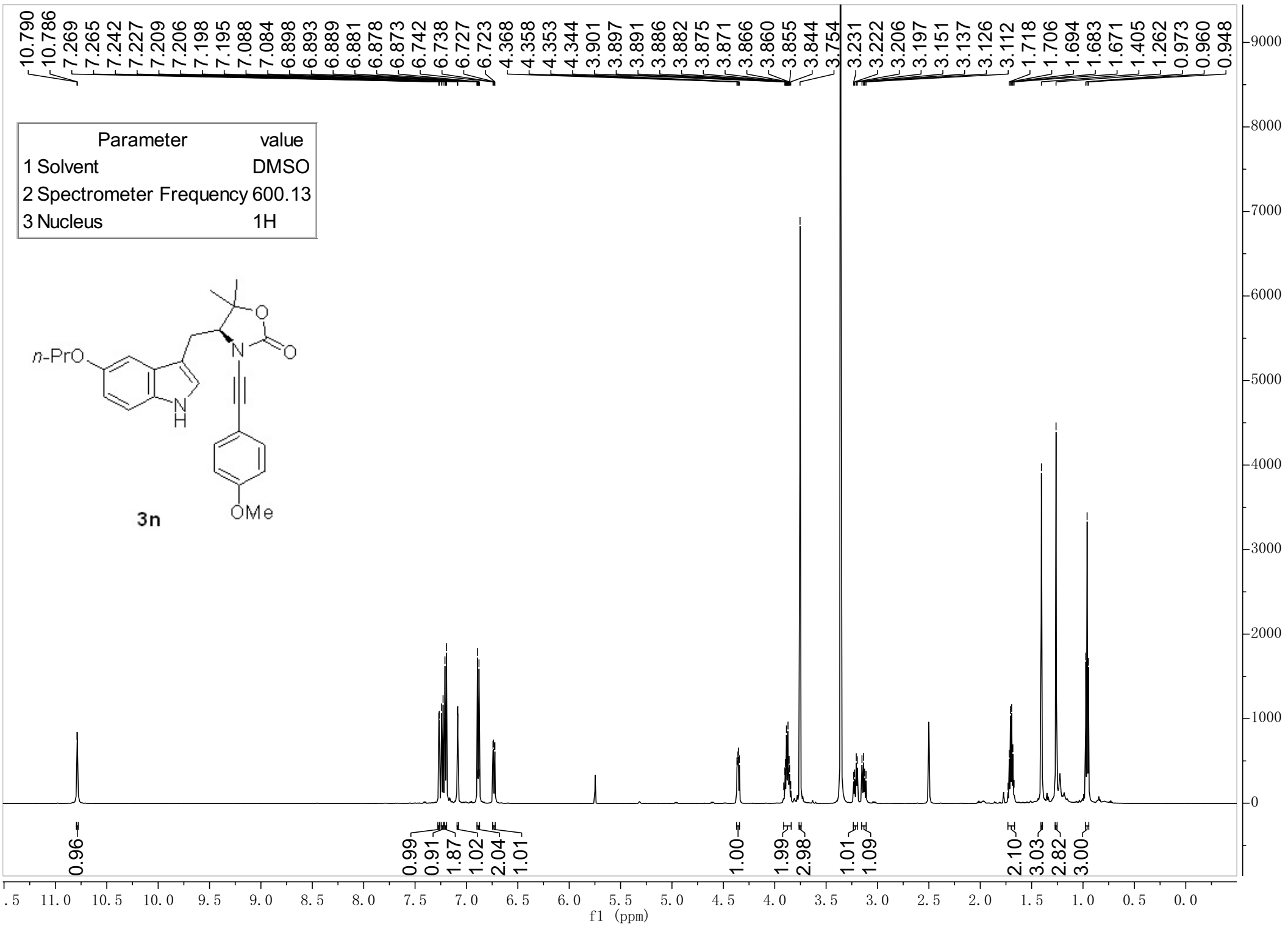


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C

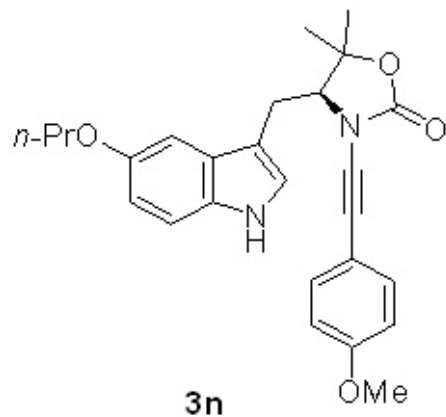


- ~154.7
- ~152.9
- ~131.7
- ~131.2
- ~129.5
- ~127.7
- ~125.0
- ~119.3
- ~112.5
- ~112.0
- ~108.5
- ~101.6
- ~84.3
- ~79.9
- ~71.8
- ~69.8
- ~65.7
- ~27.5
- ~24.6
- ~22.7
- ~21.8
- ~21.3
- 10.9

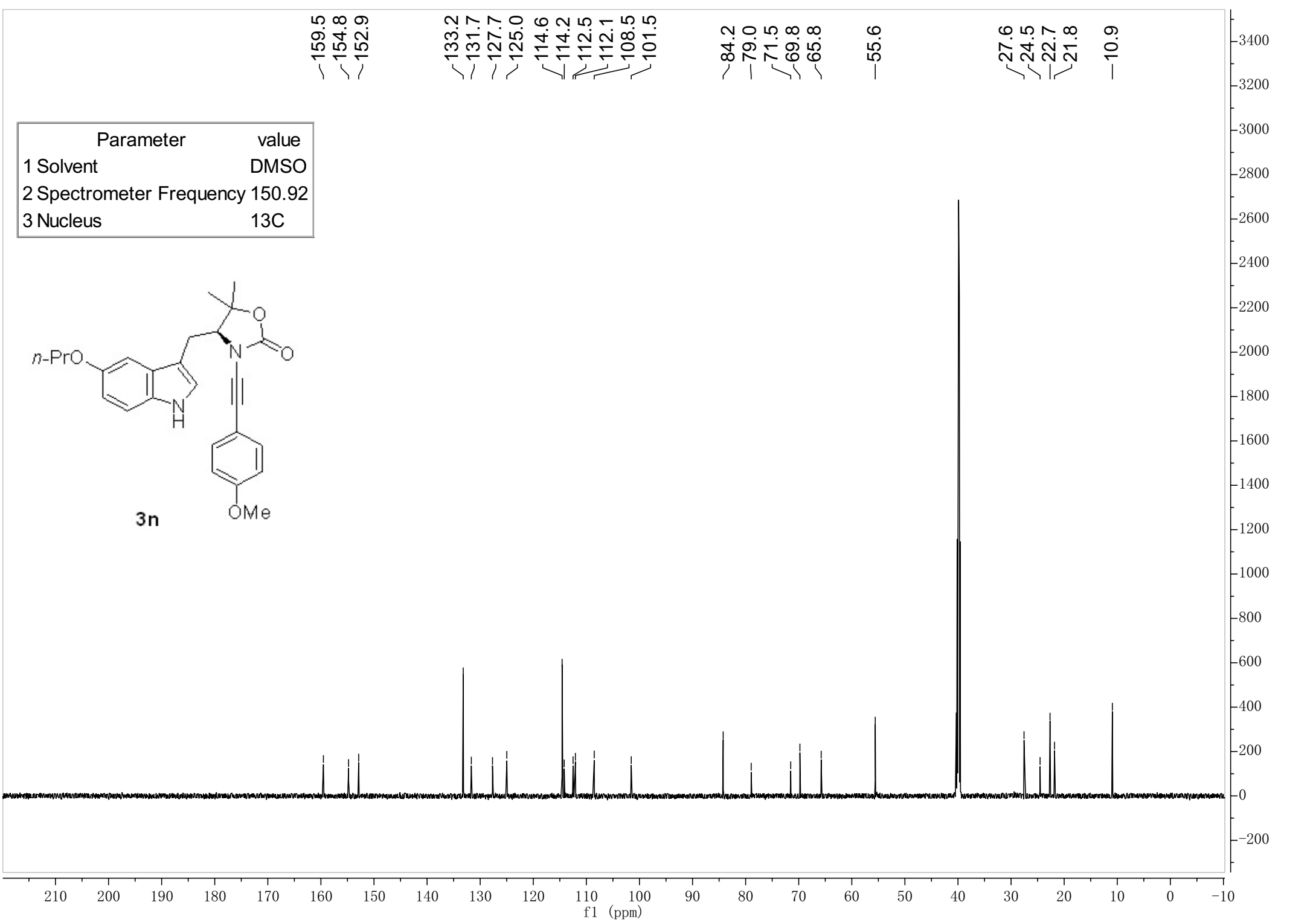




Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



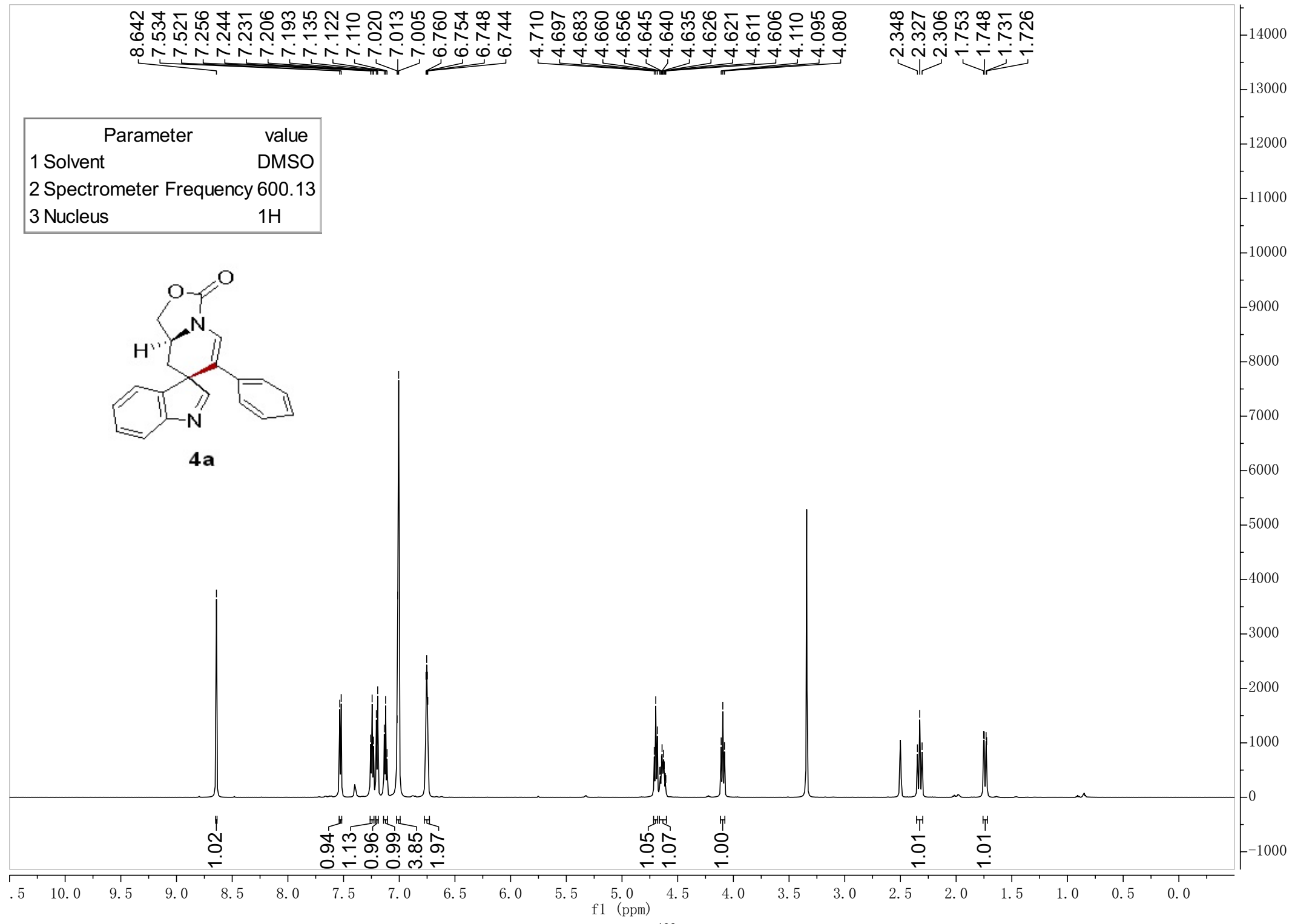
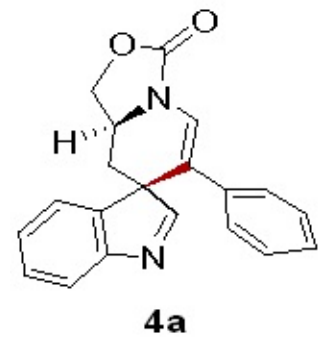
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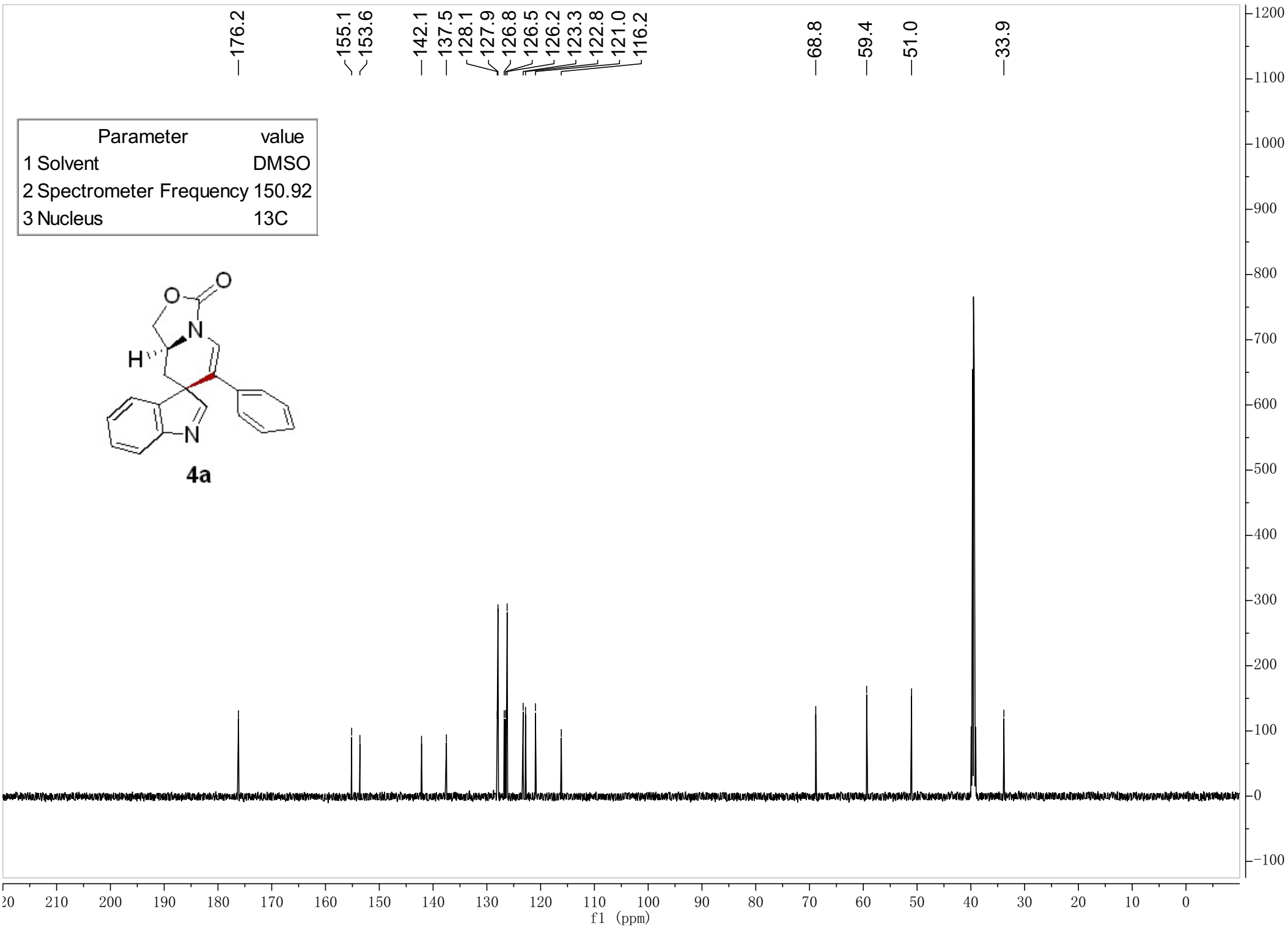


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7.521
7.256
7.244
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7.206
7.193
7.135
7.122
7.110
7.020
7.013
7.005
6.760
6.754
6.748
6.744
4.710
4.697
4.683
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4.606
4.110
4.095
4.080

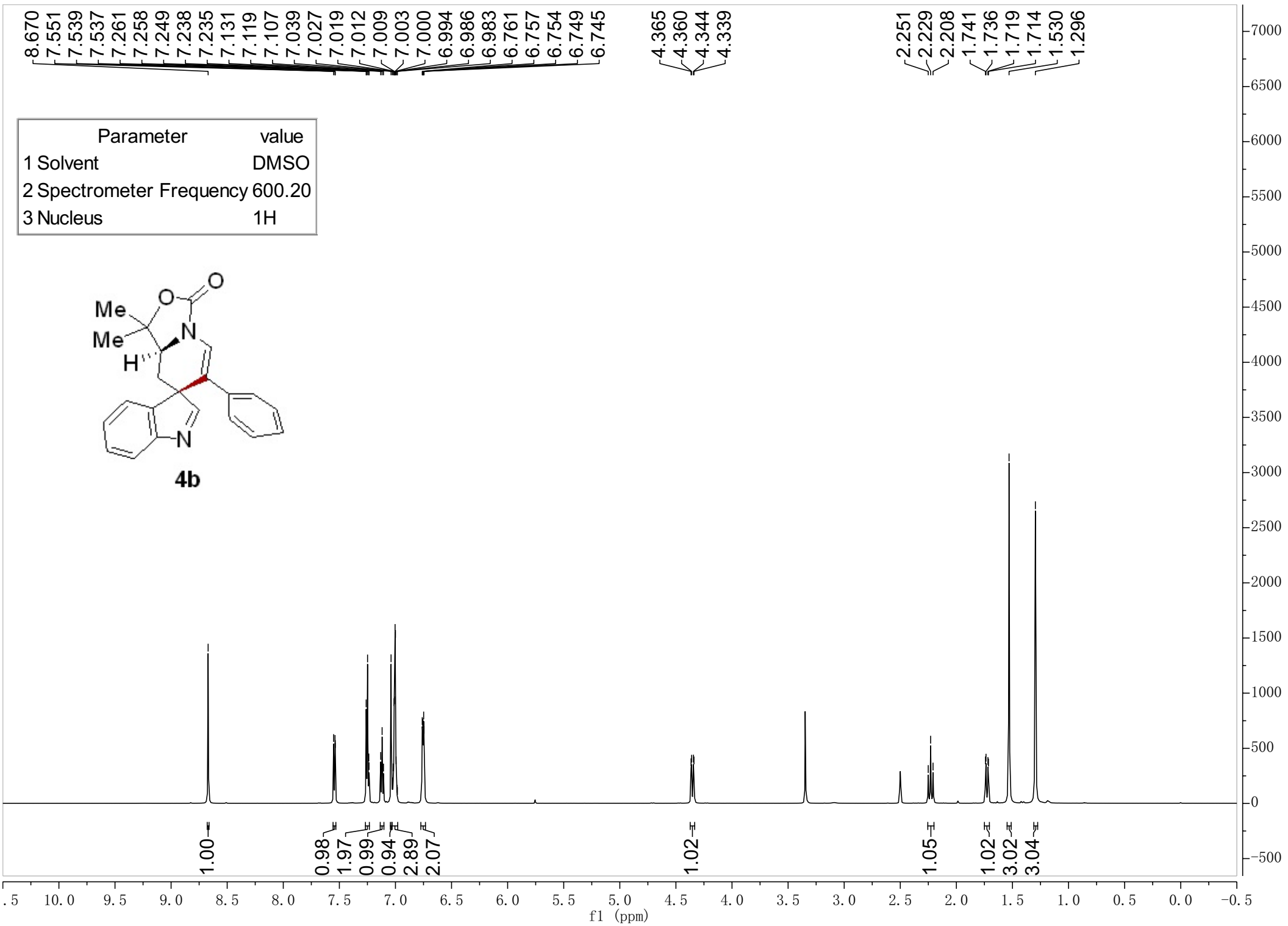
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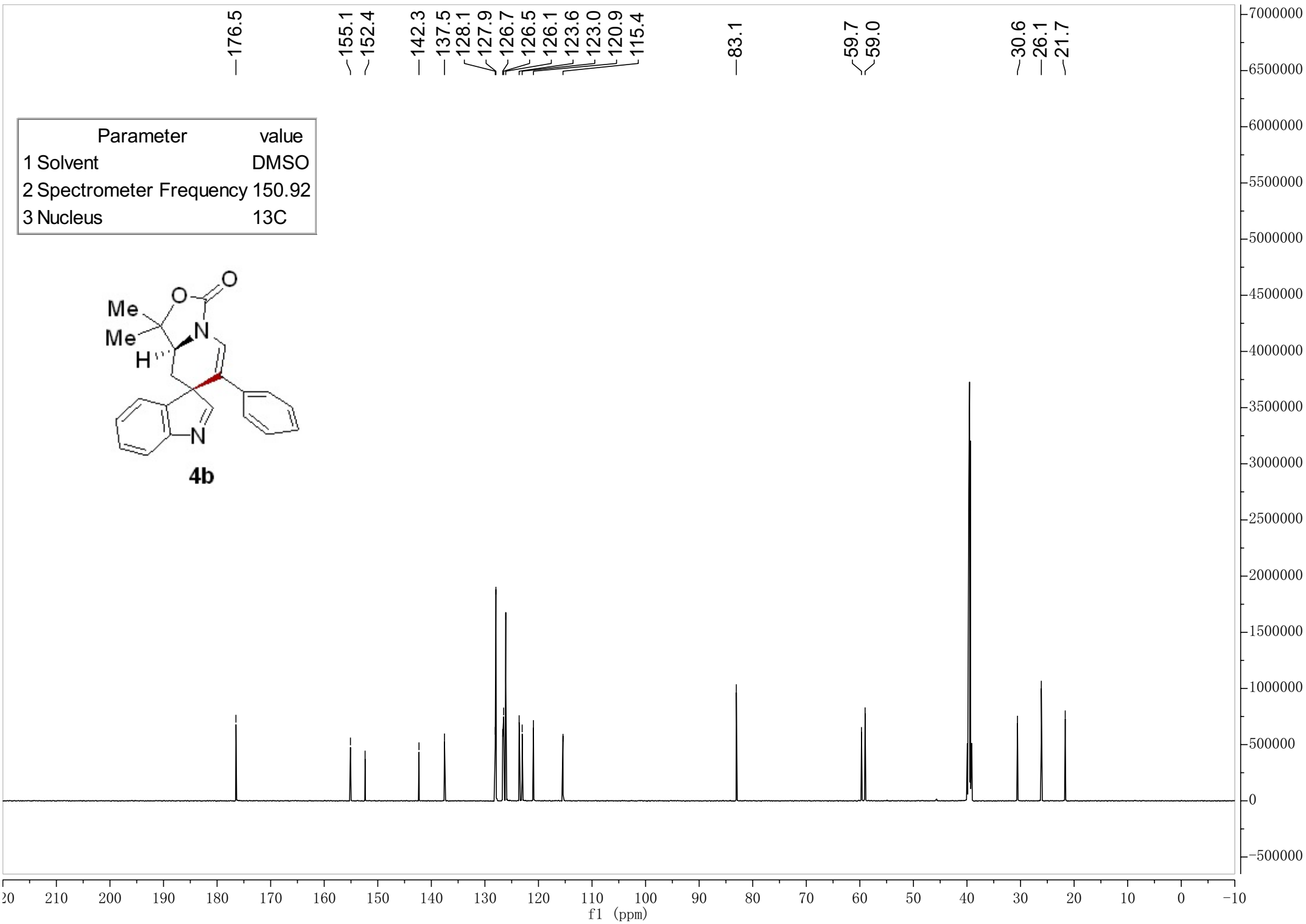
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.13
3 Nucleus	1H





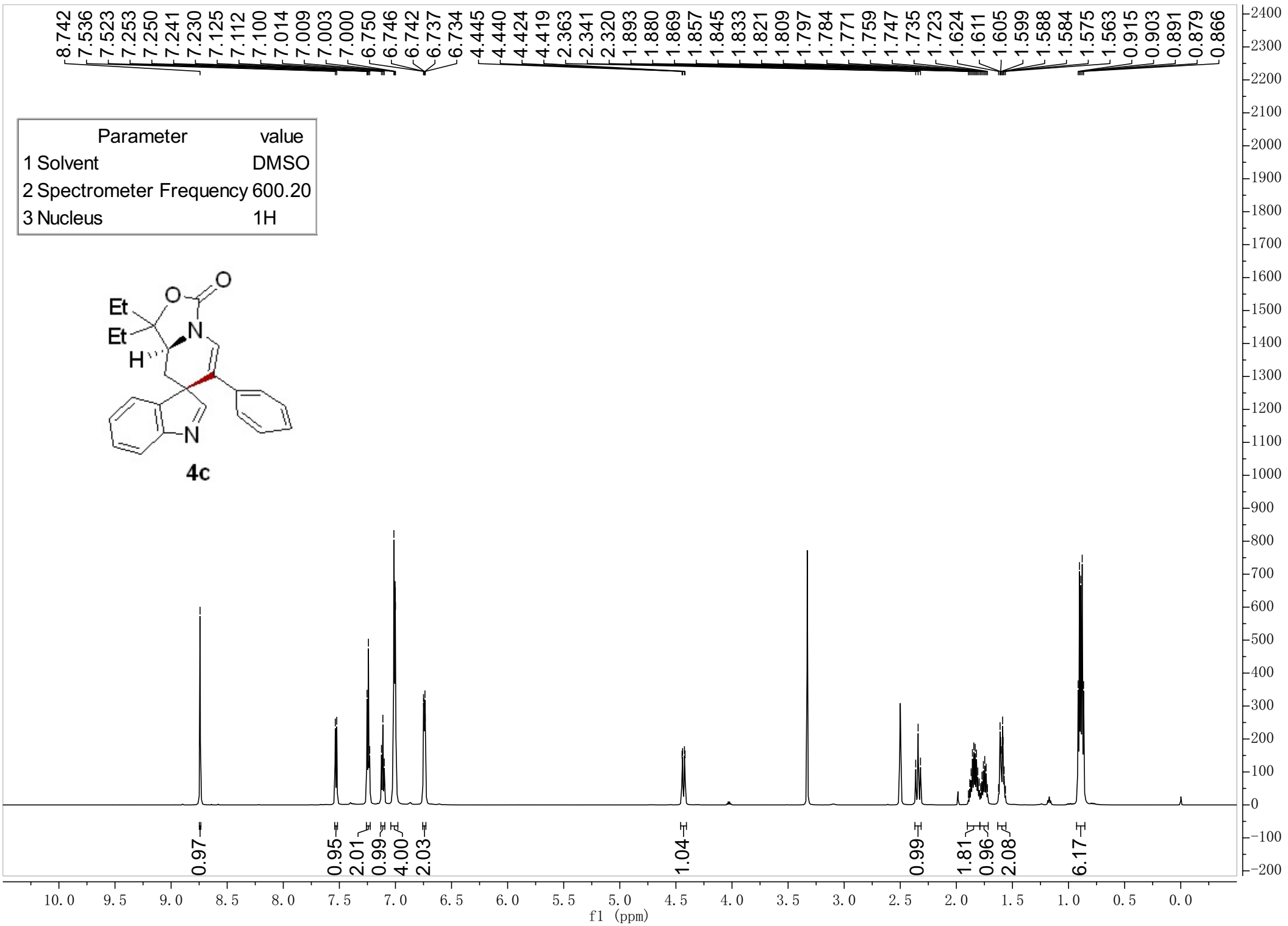
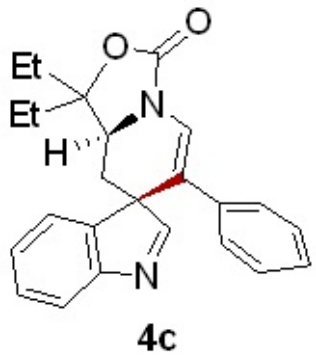
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



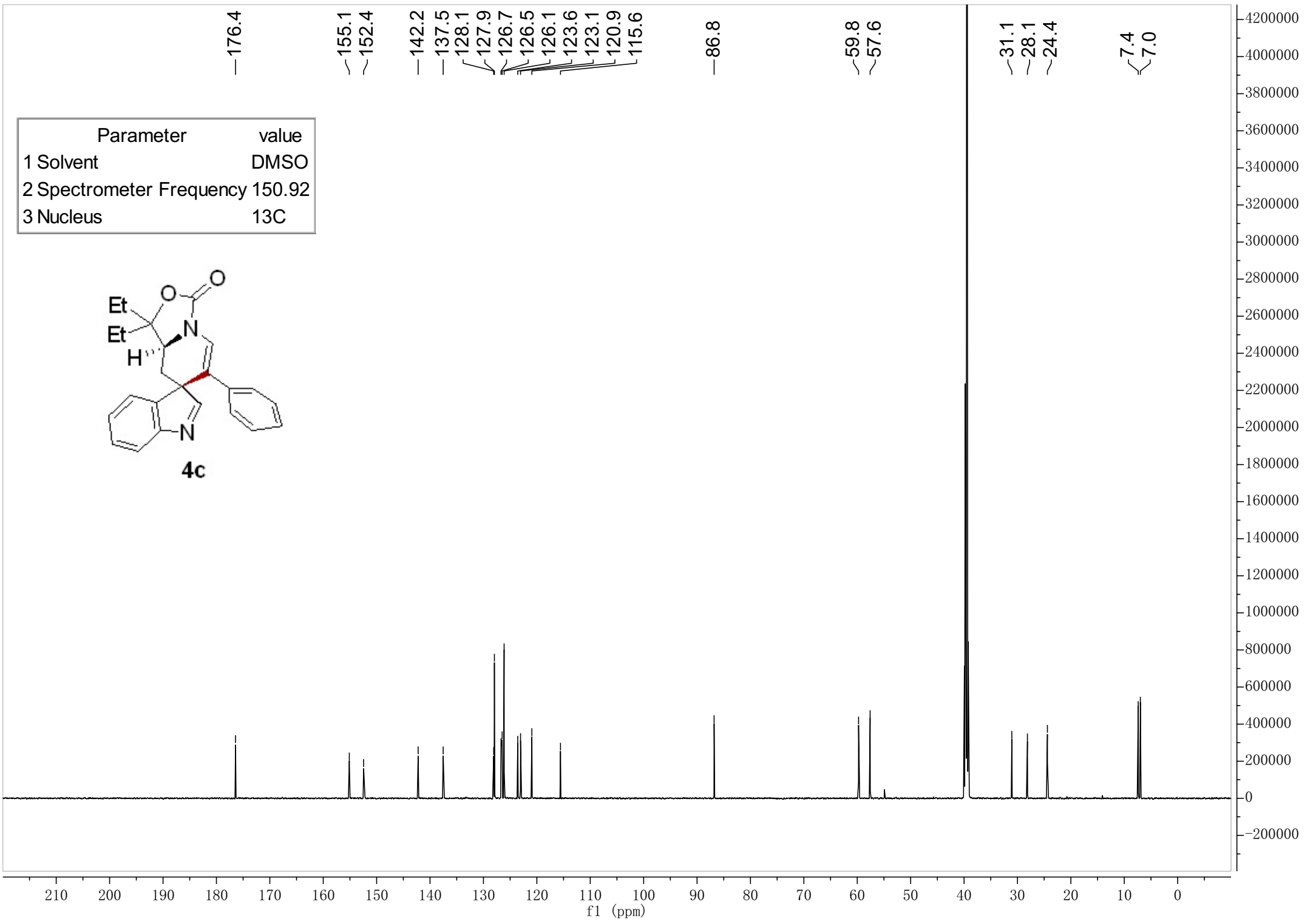
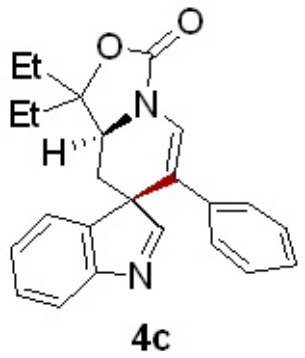


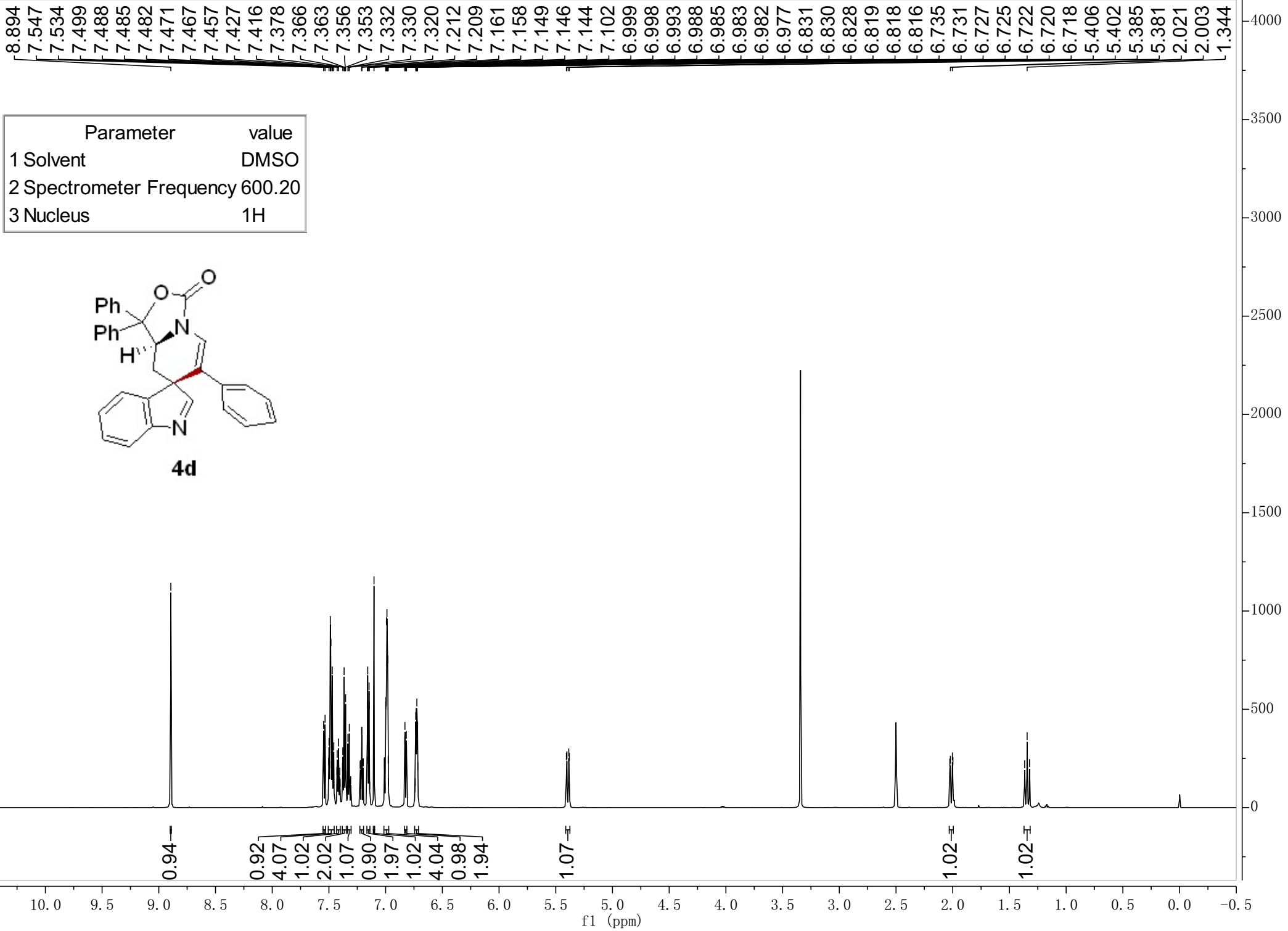
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

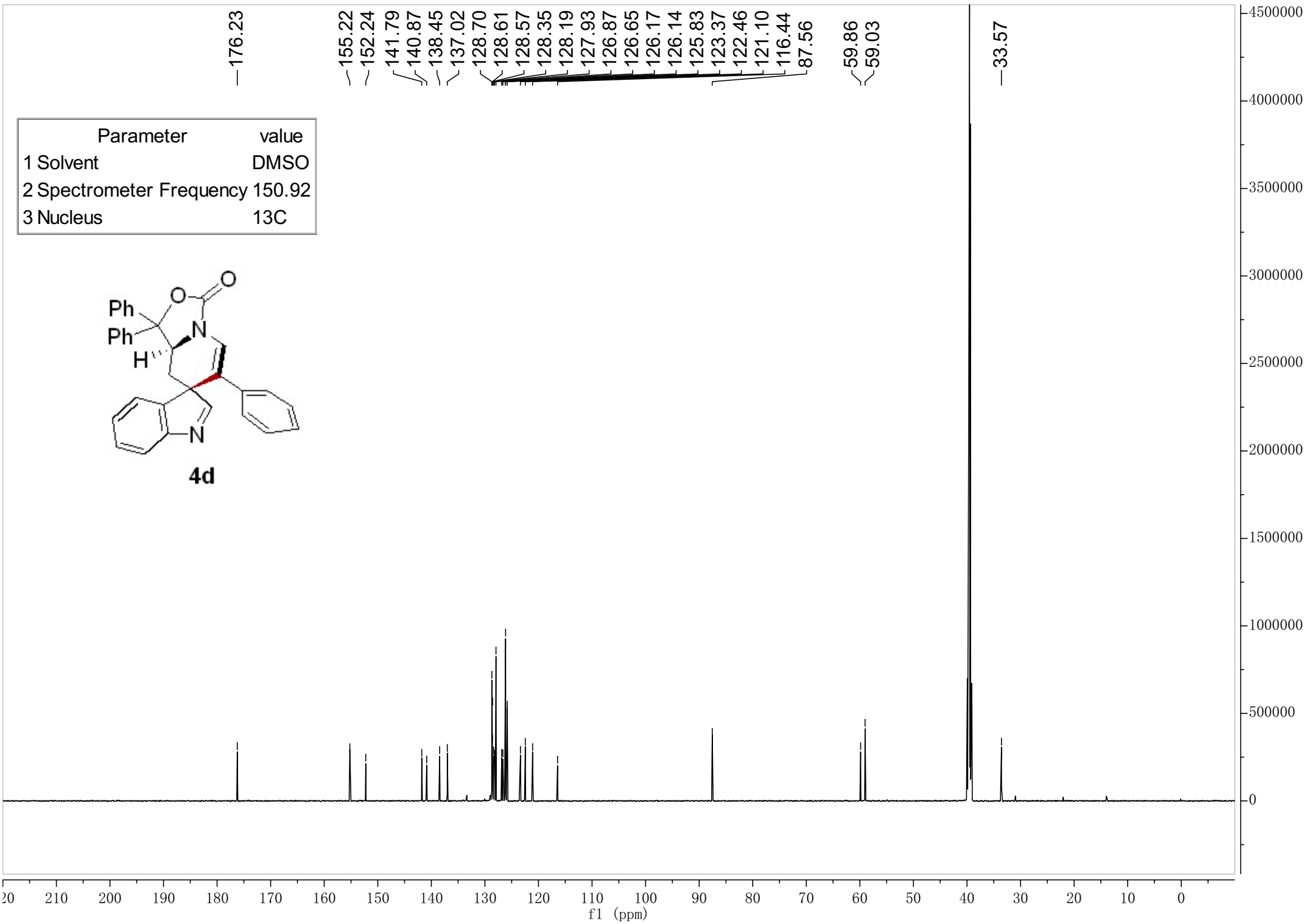
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

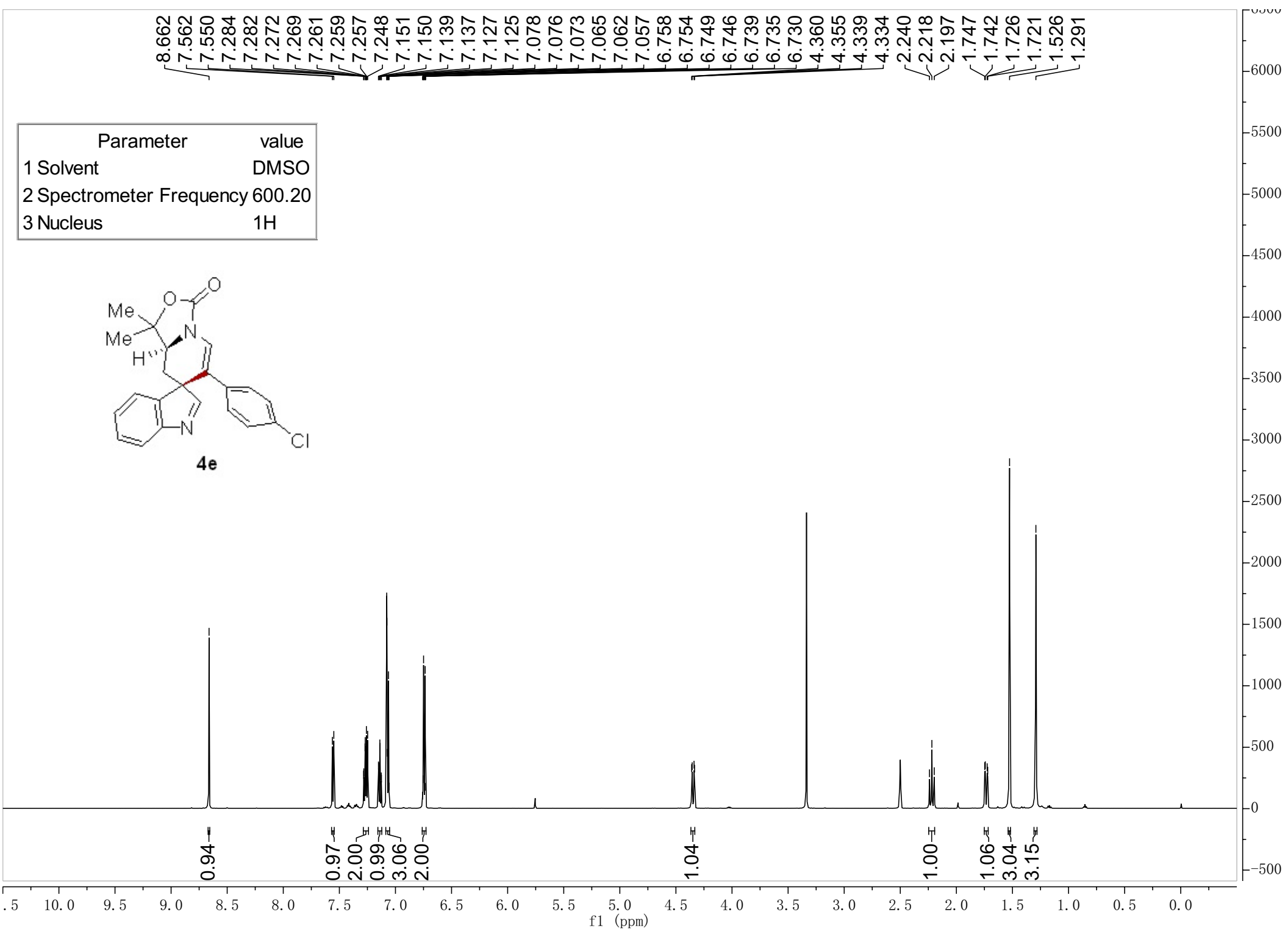
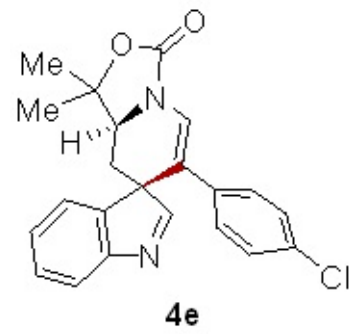




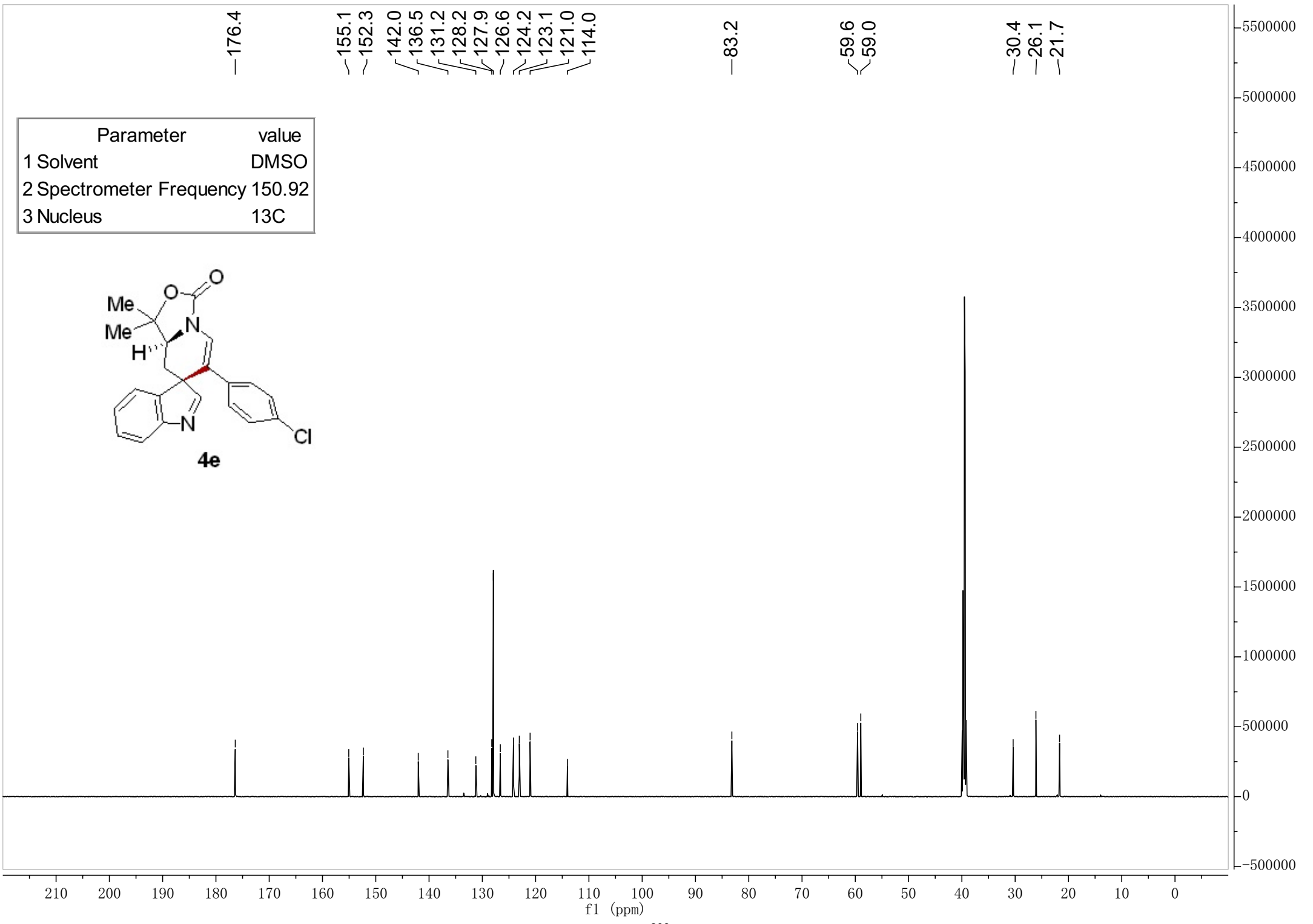
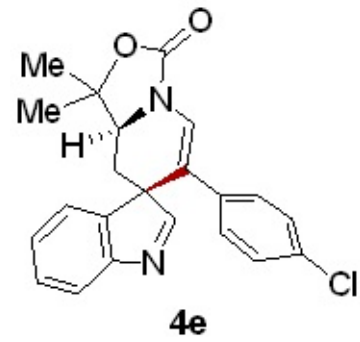


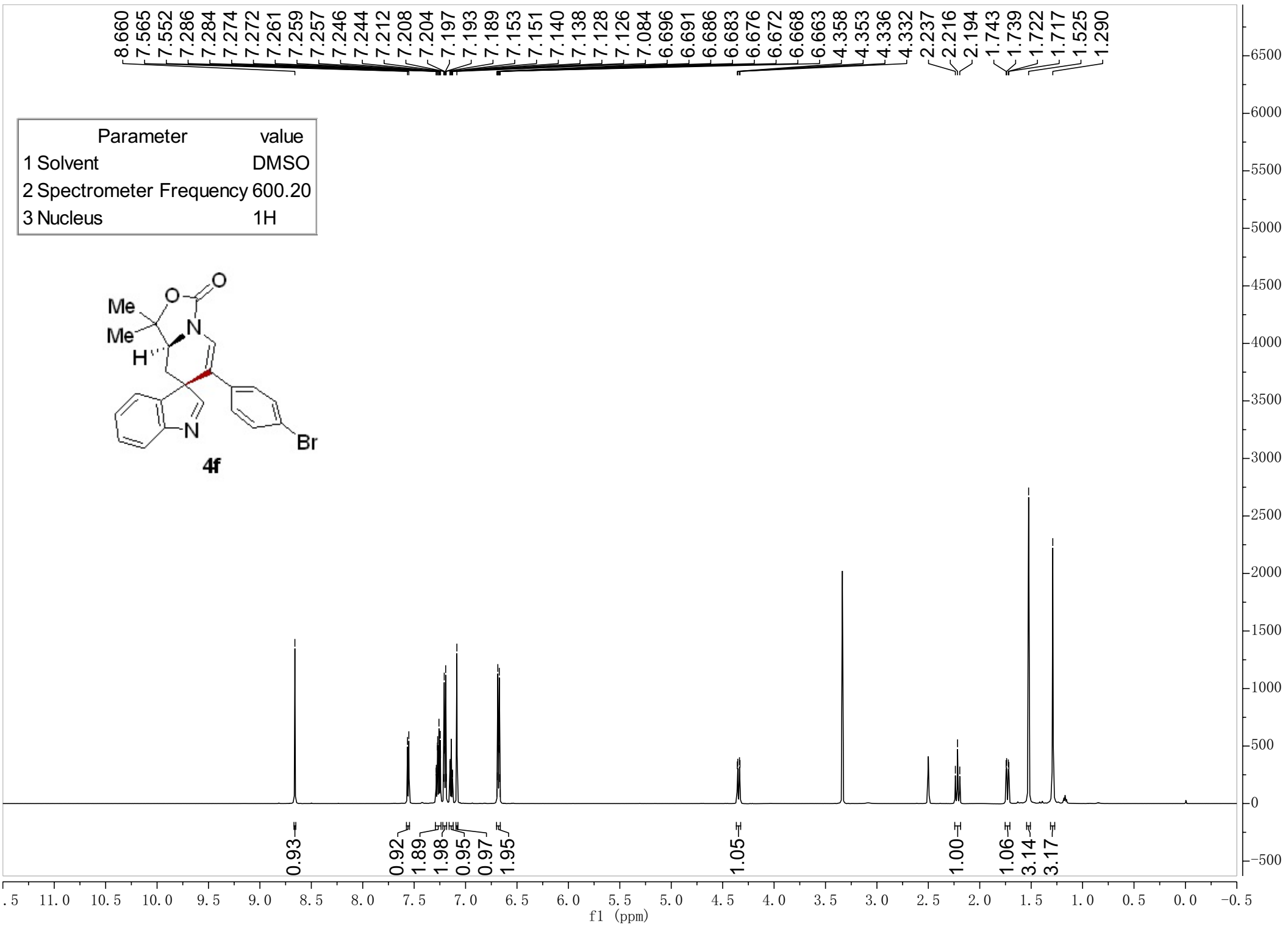
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7.137
7.127
7.125
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7.076
7.073
7.065
7.062
7.057
6.758
6.754
6.749
6.746
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4.334
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2.197
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1.721
1.526
1.291

Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

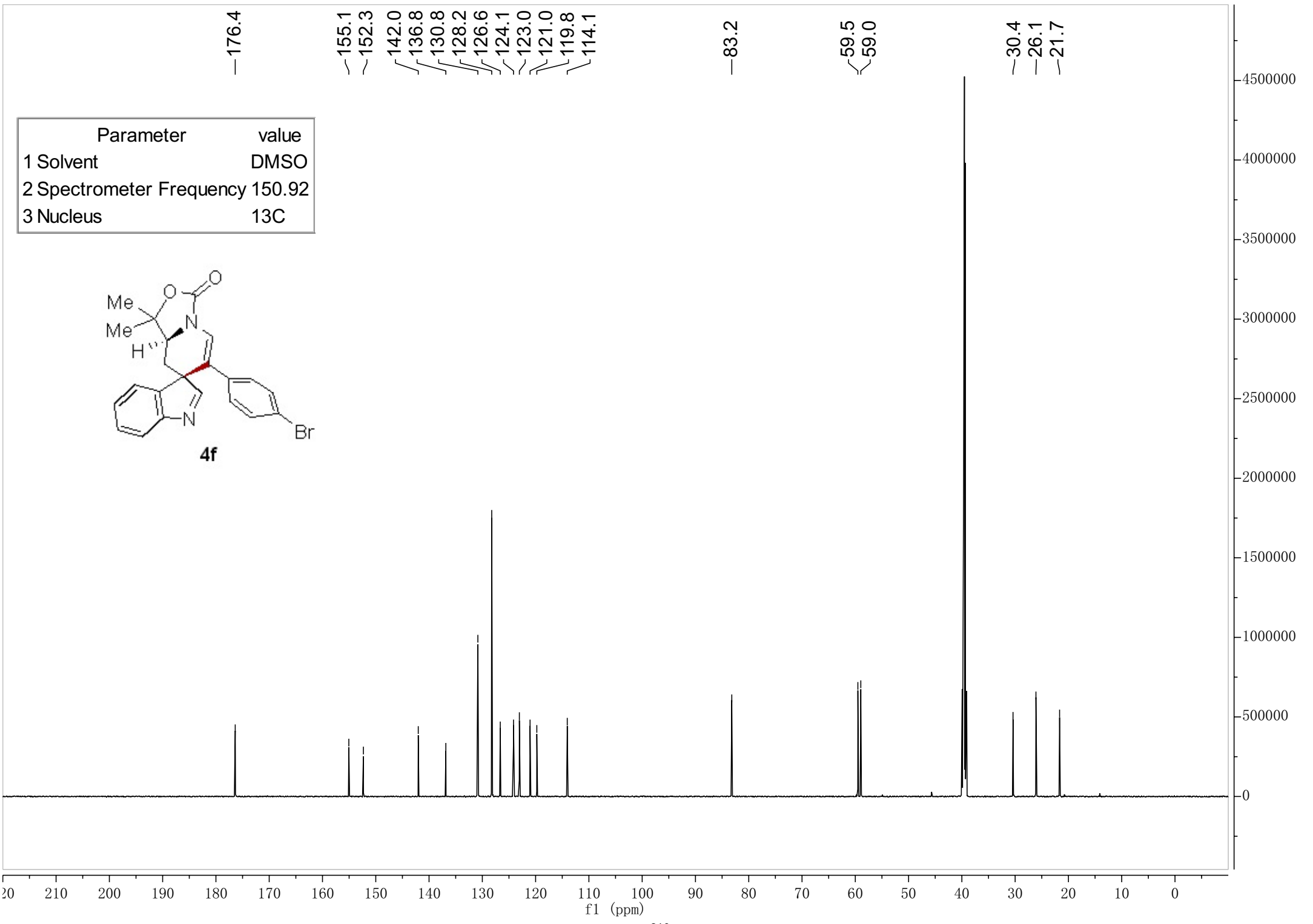
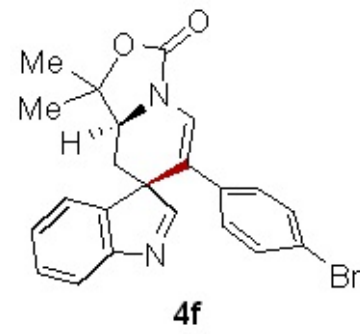


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

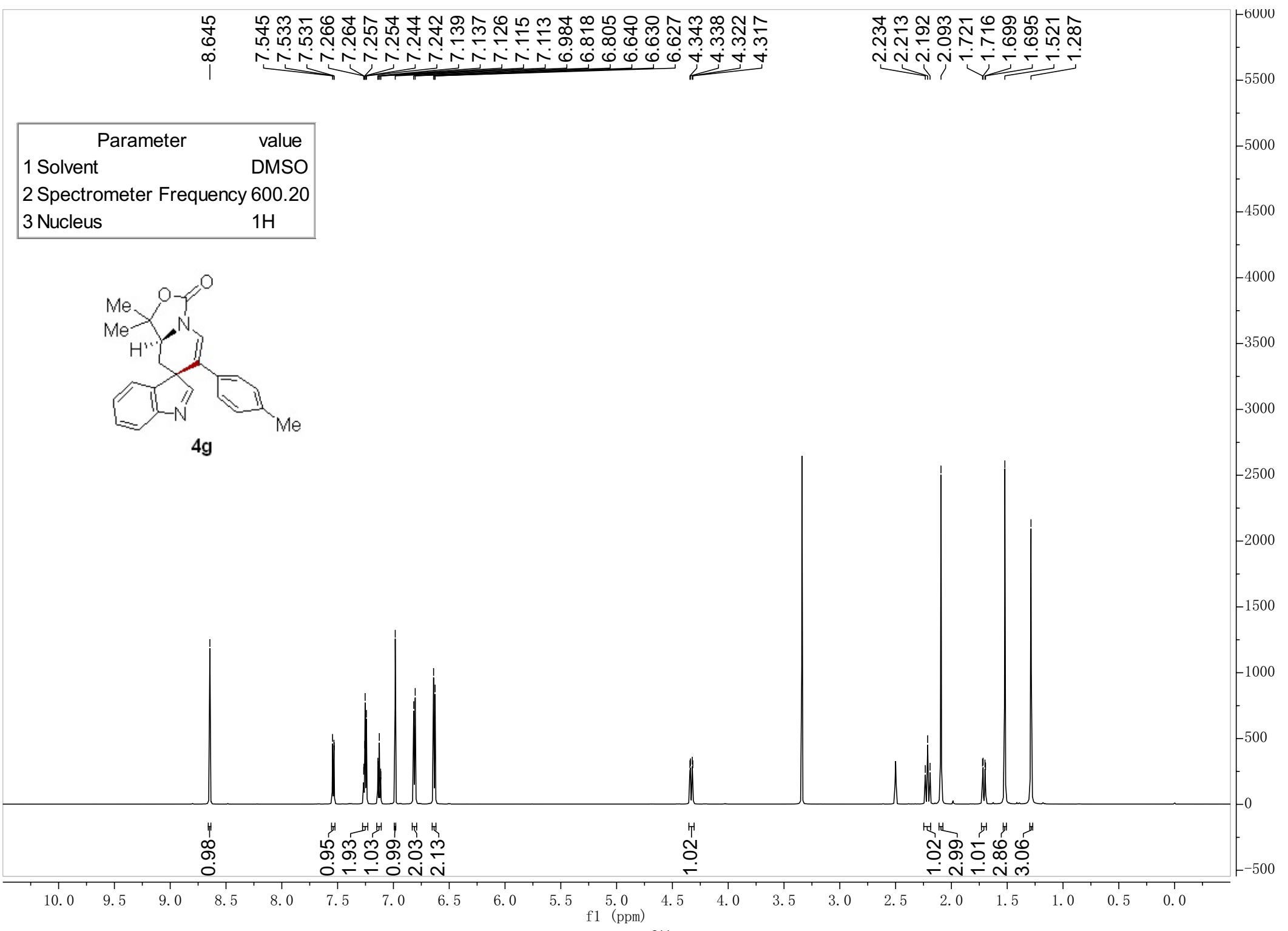
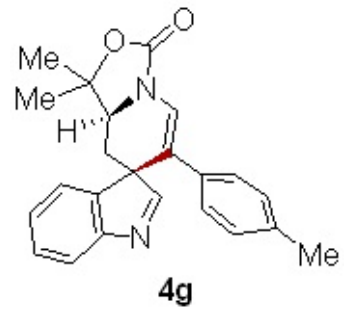




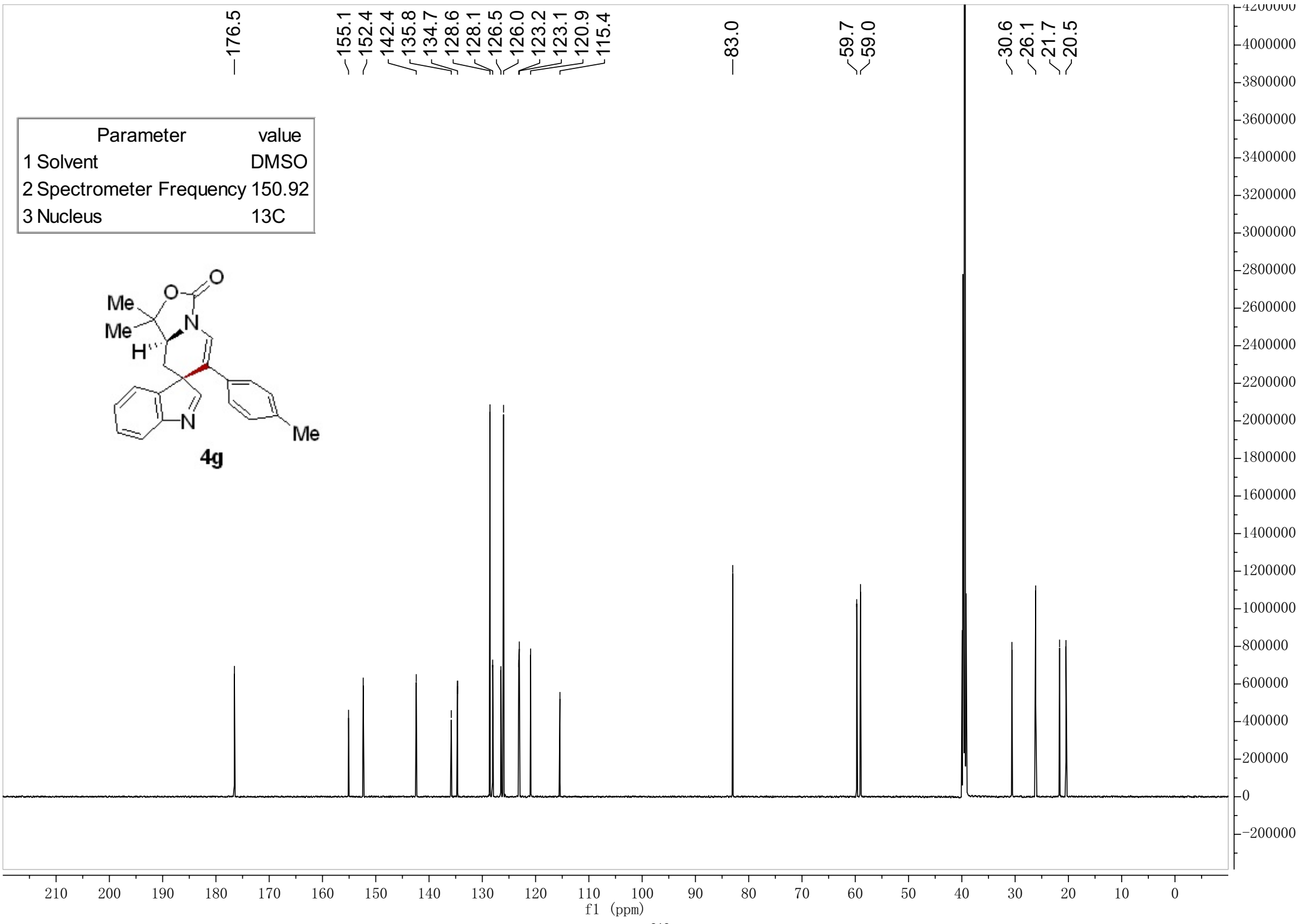
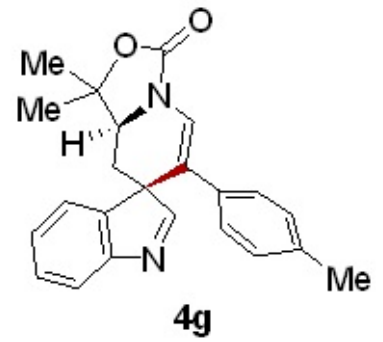
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

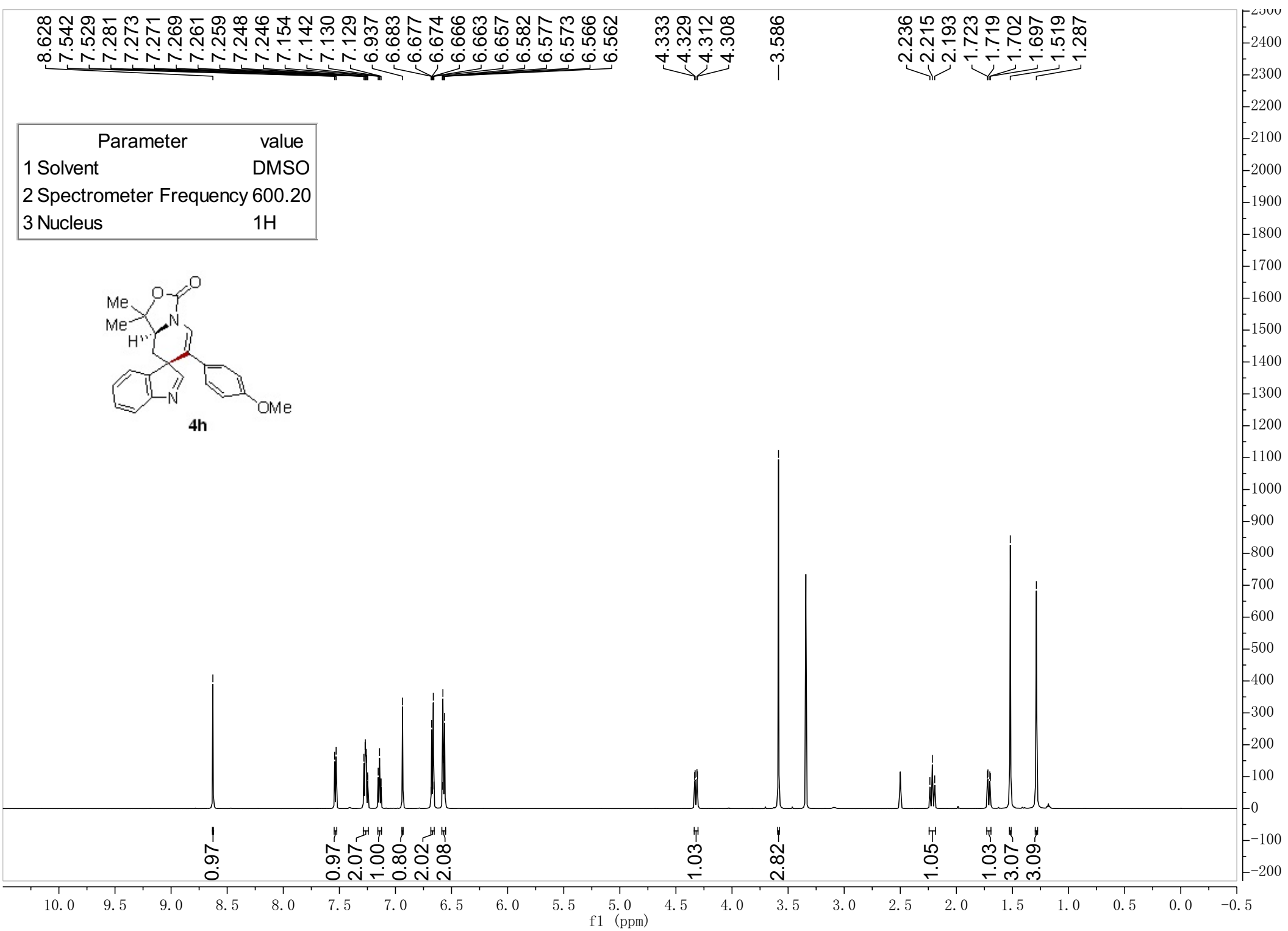


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H



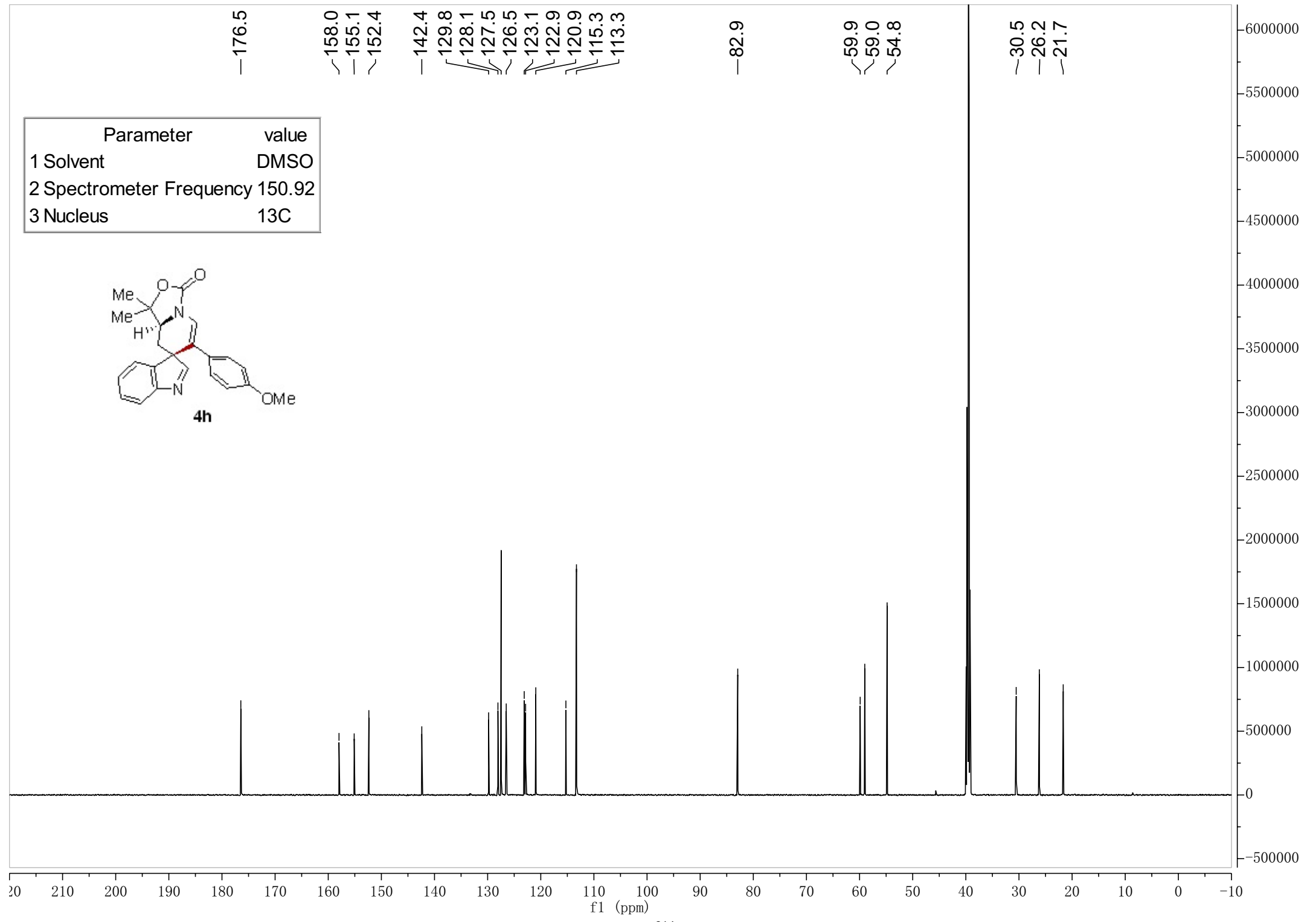
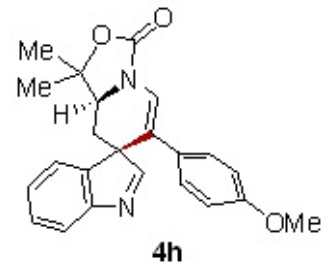
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

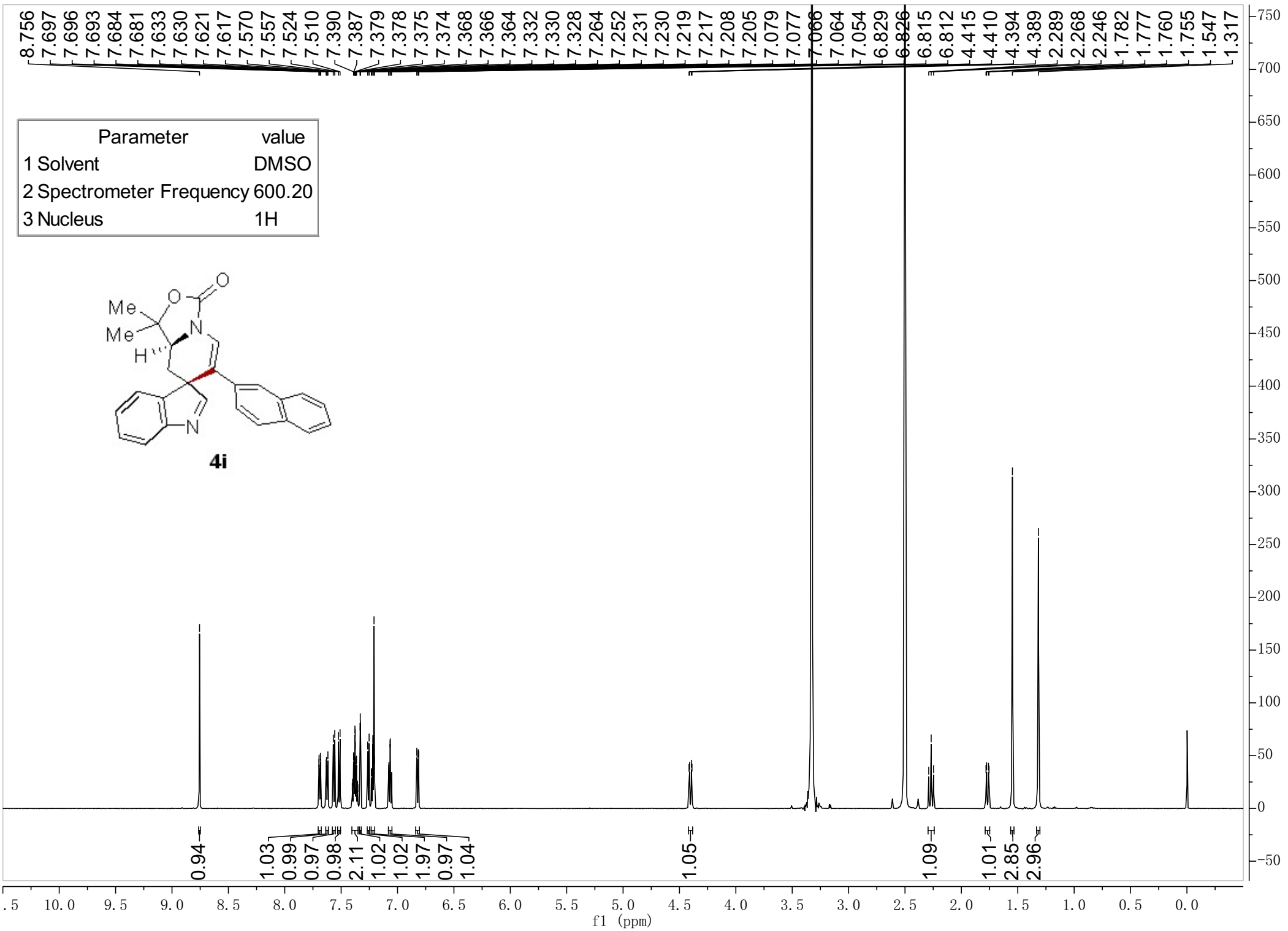




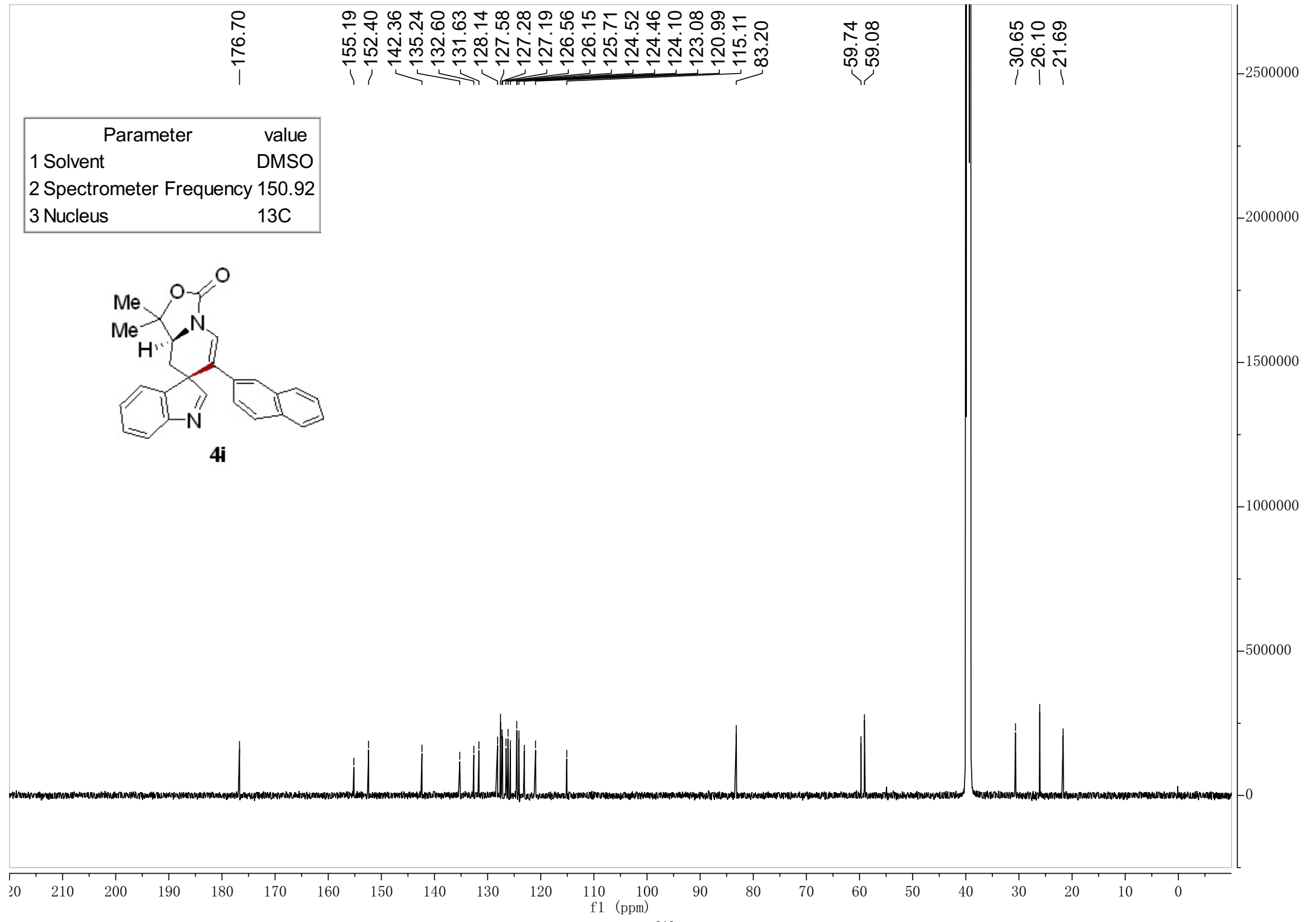
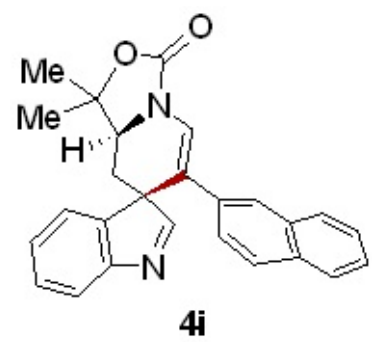
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	1H

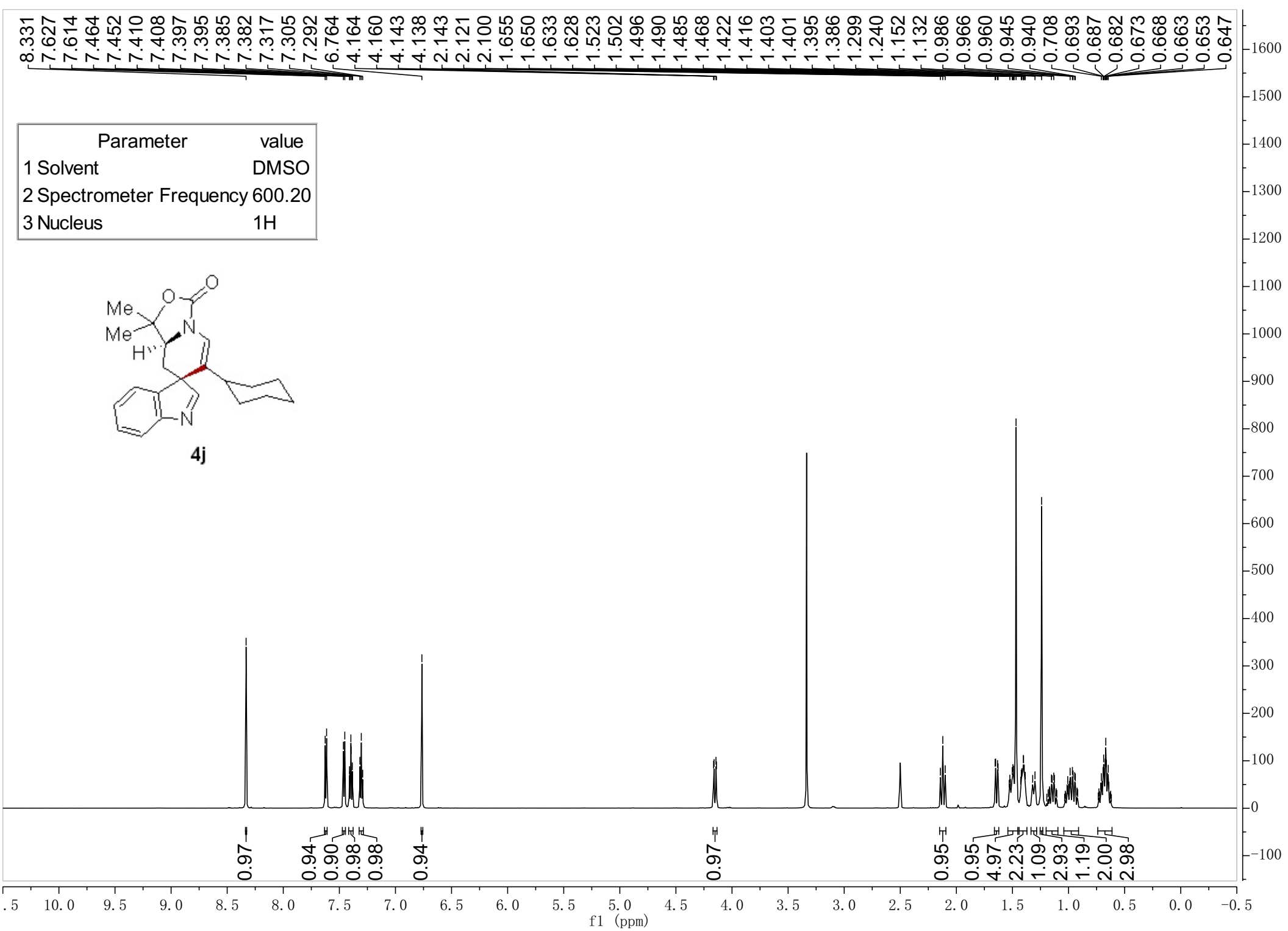
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

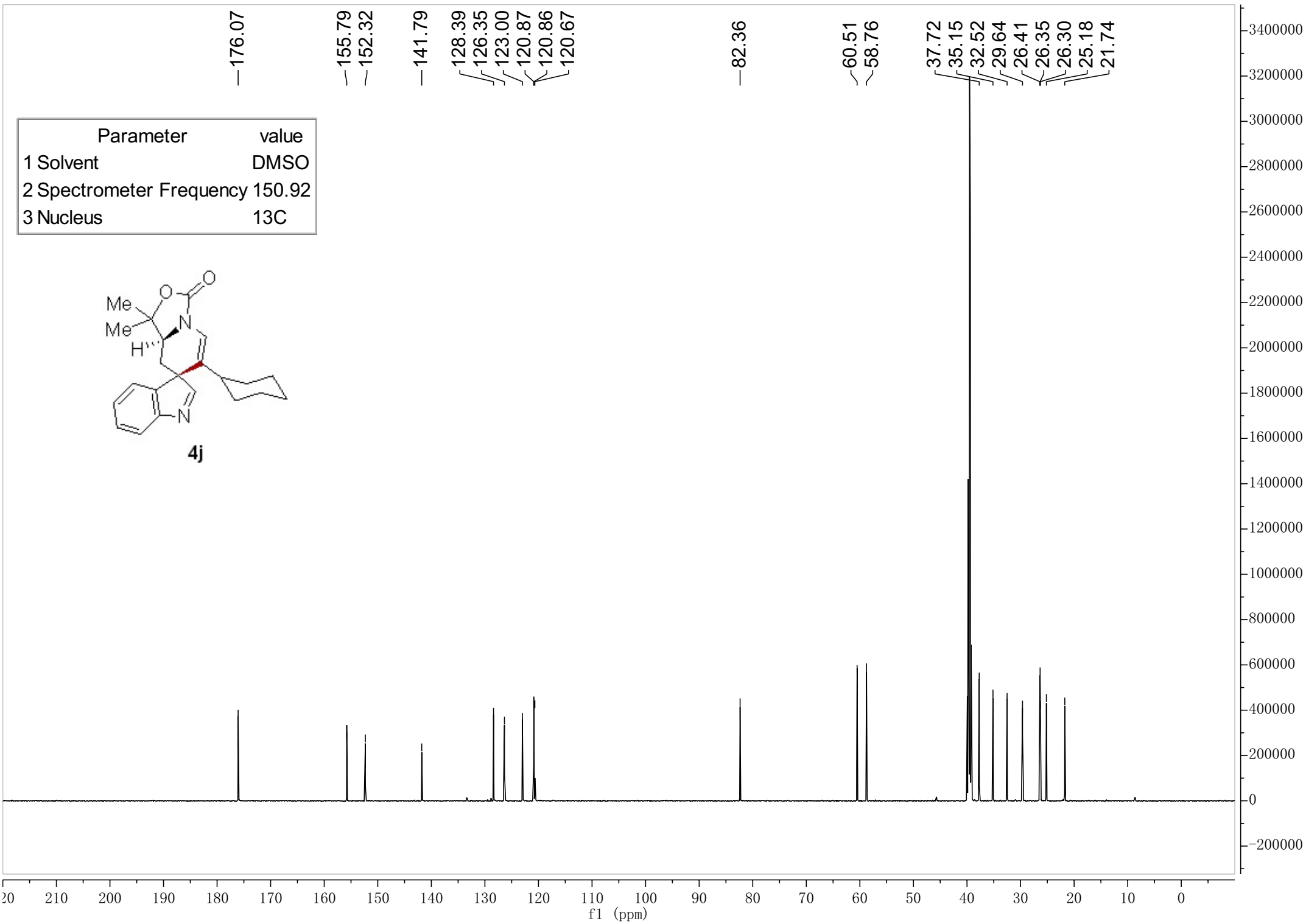




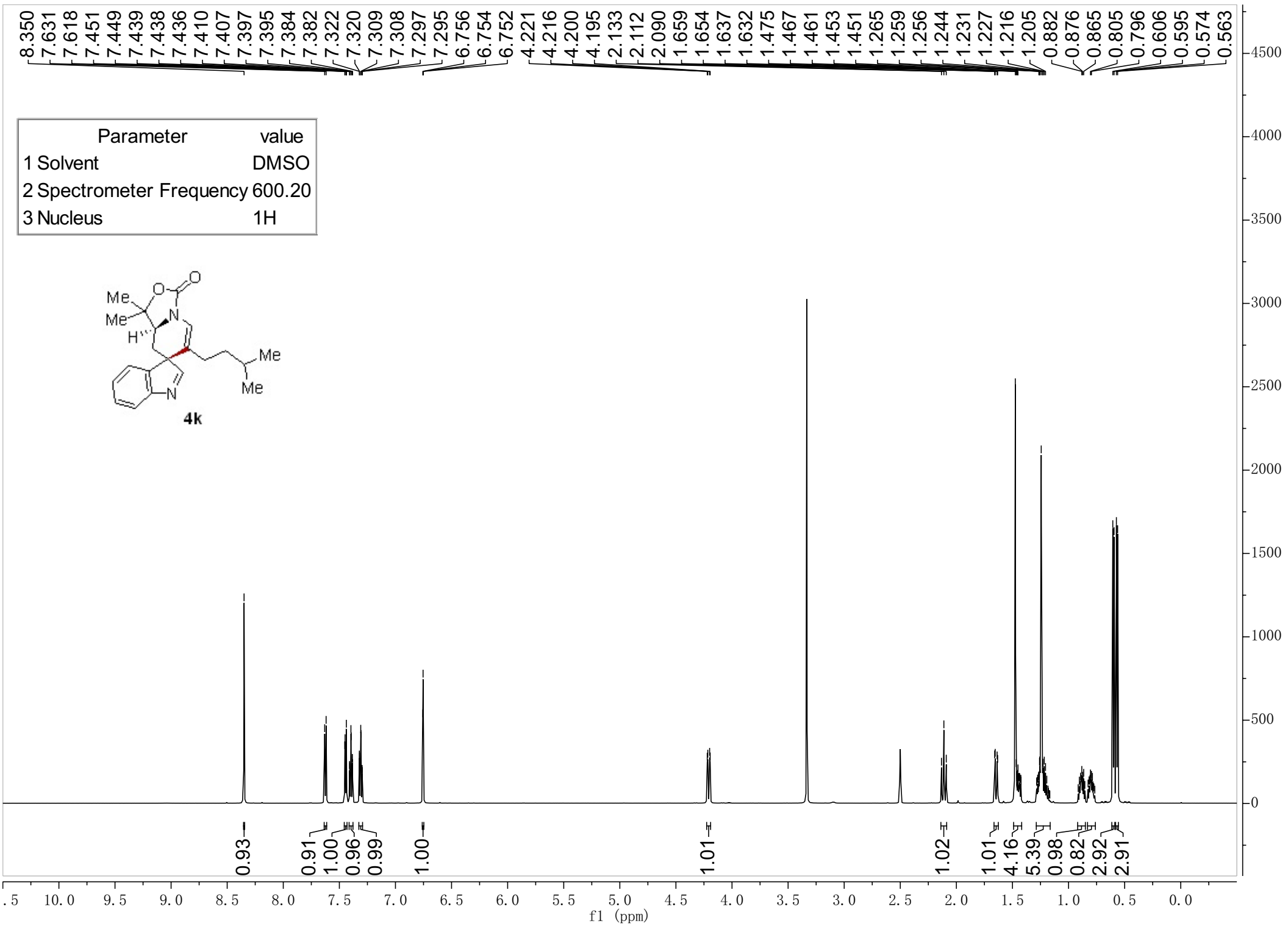
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



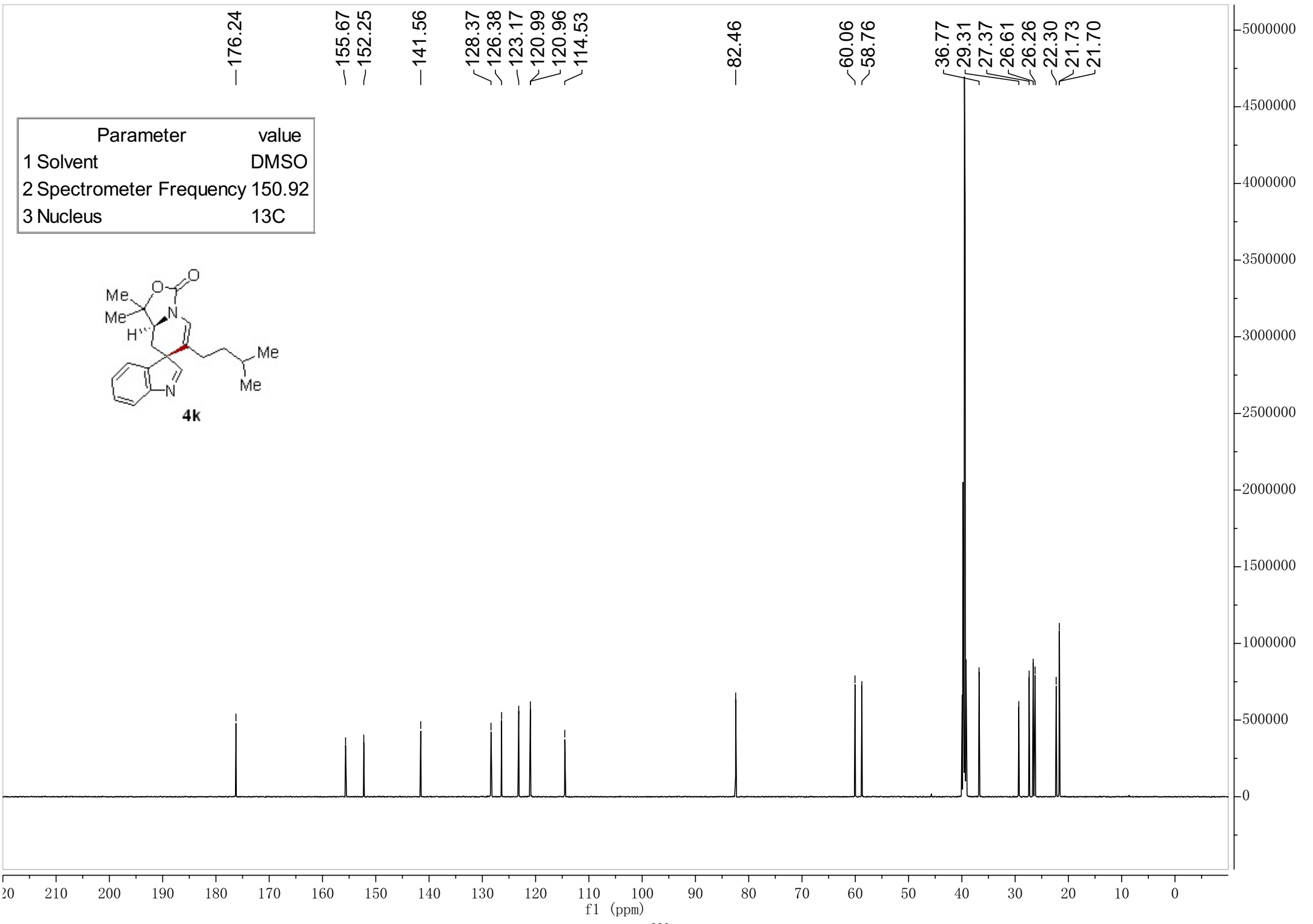
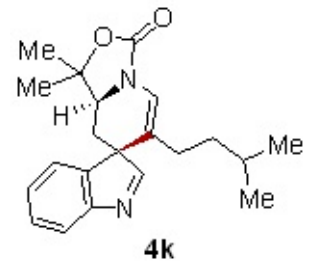


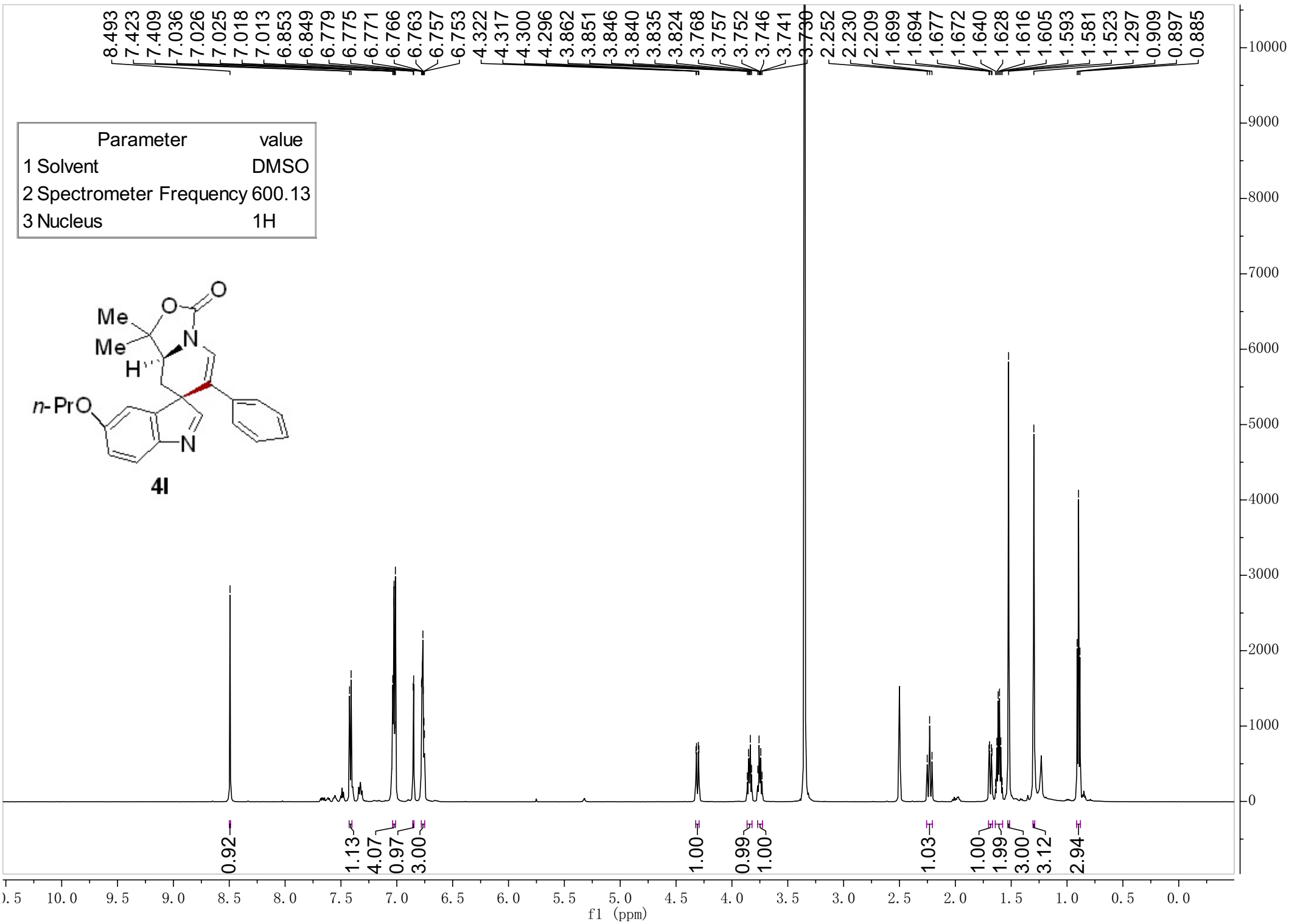


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

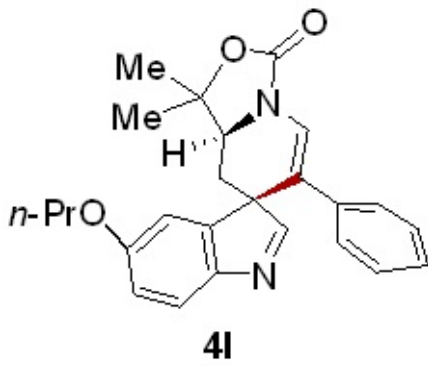


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

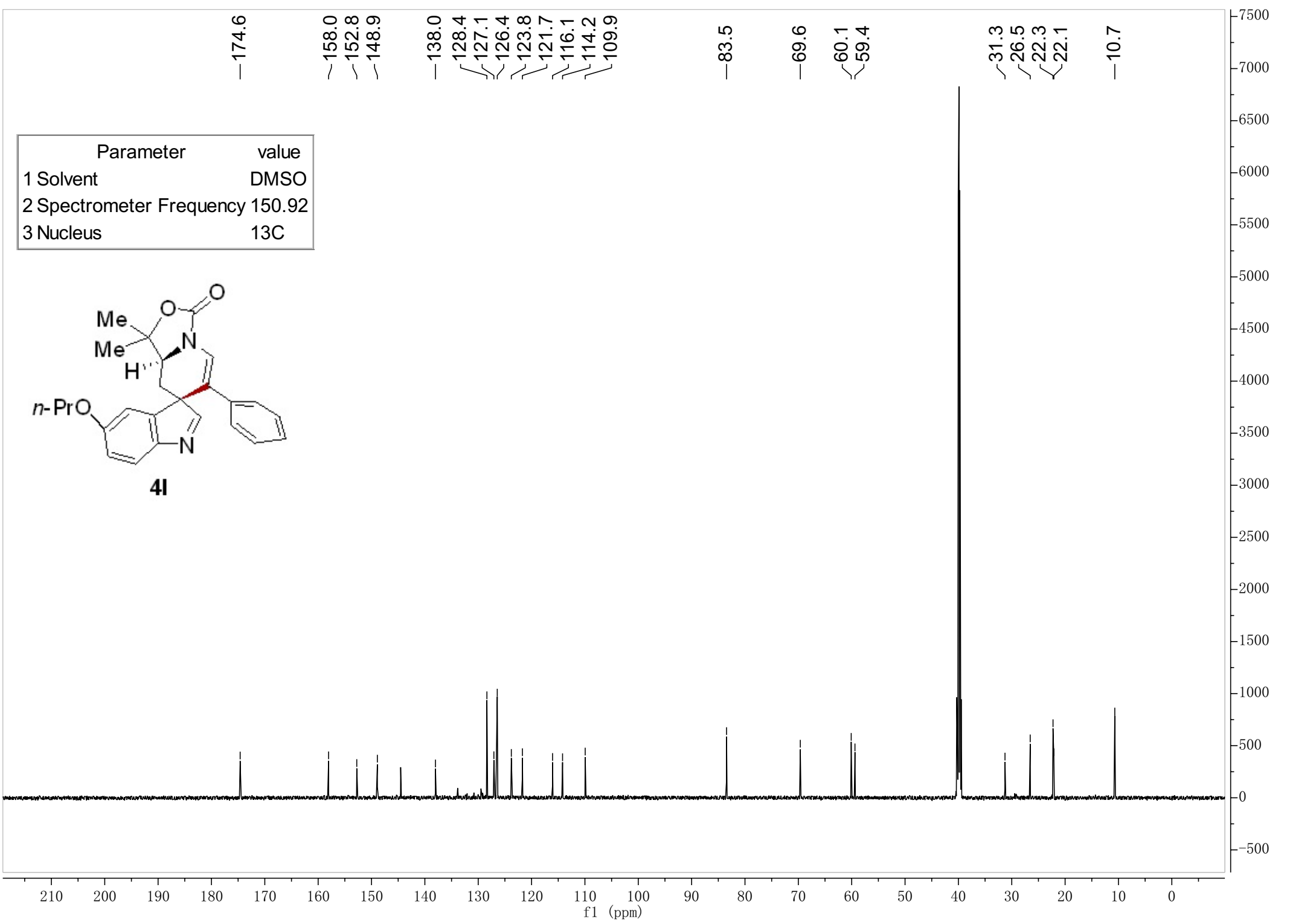


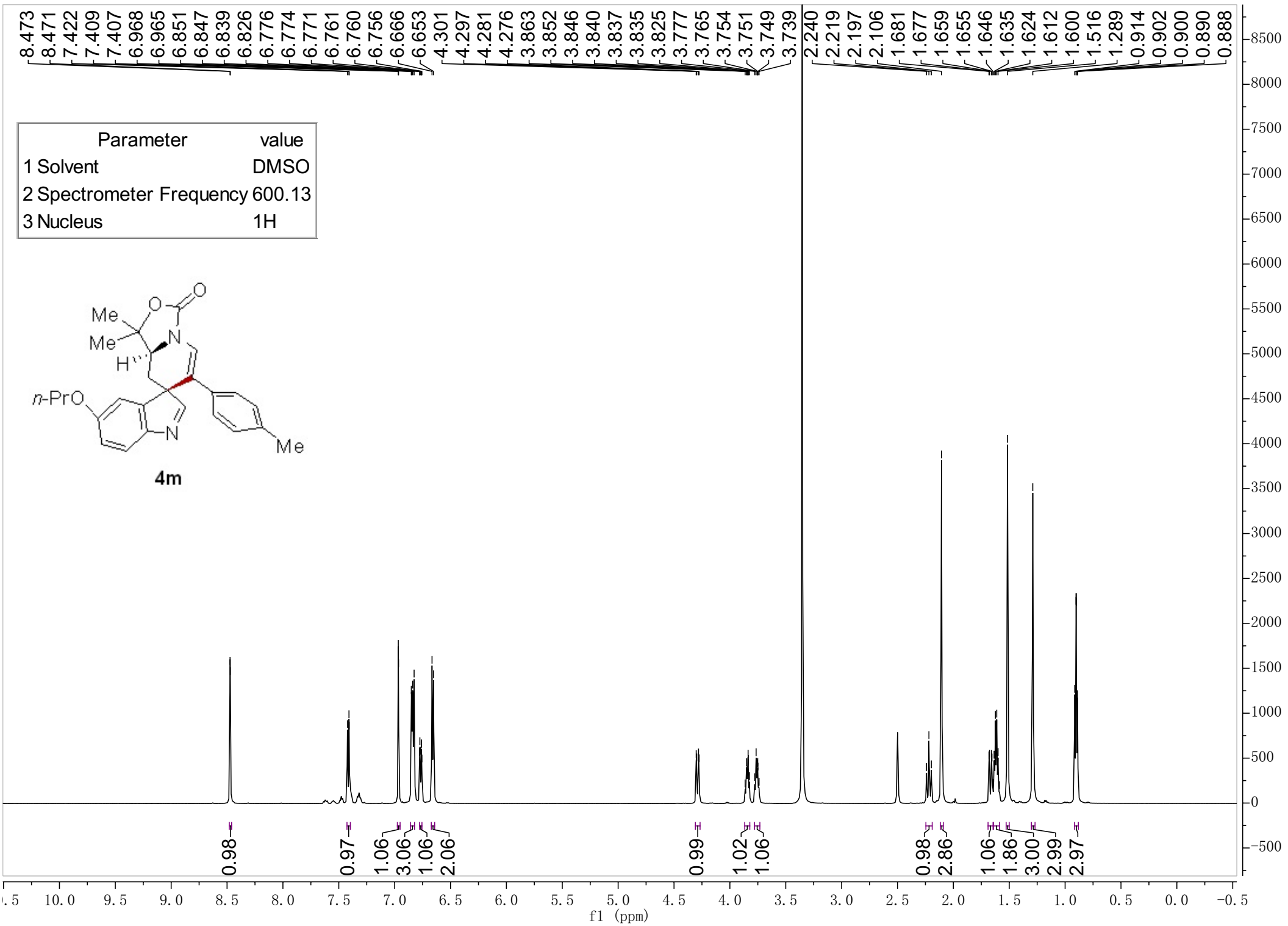


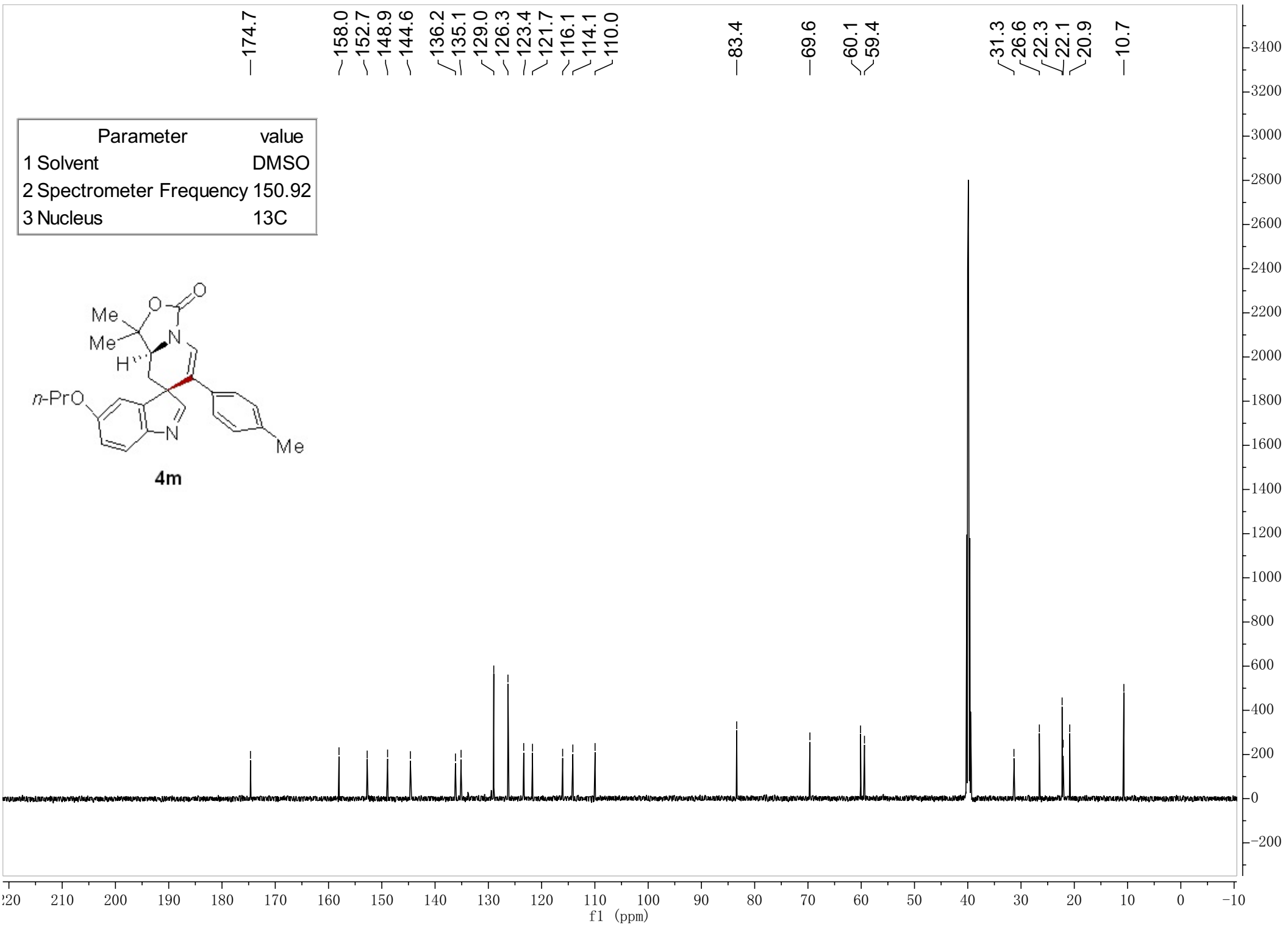
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

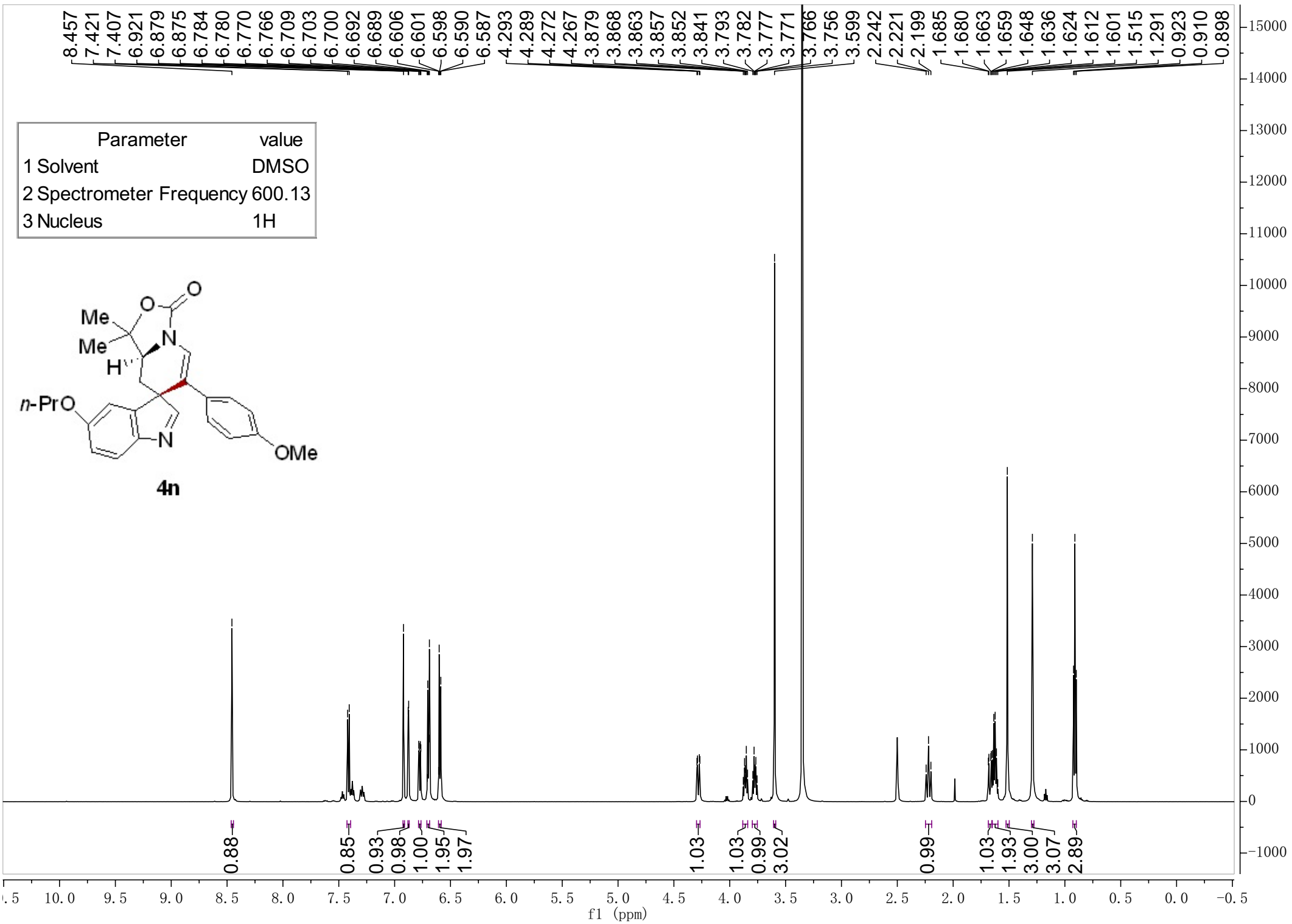


— 174.6
 ~ 158.0
 ~ 152.8
 ~ 148.9
 — 138.0
 / 128.4
 / 127.1
 / 126.4
 / 123.8
 / 121.7
 / 116.1
 / 114.2
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 / 60.1
 / 59.4
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 / 26.5
 / 22.3
 / 22.1
 — 10.7

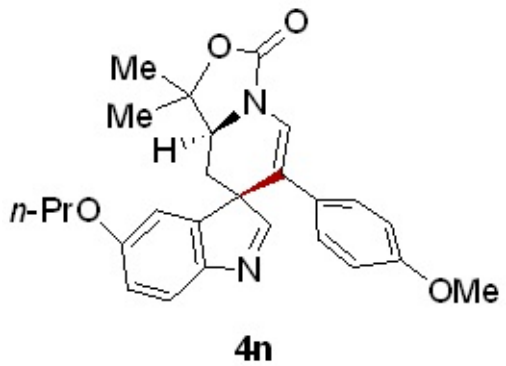




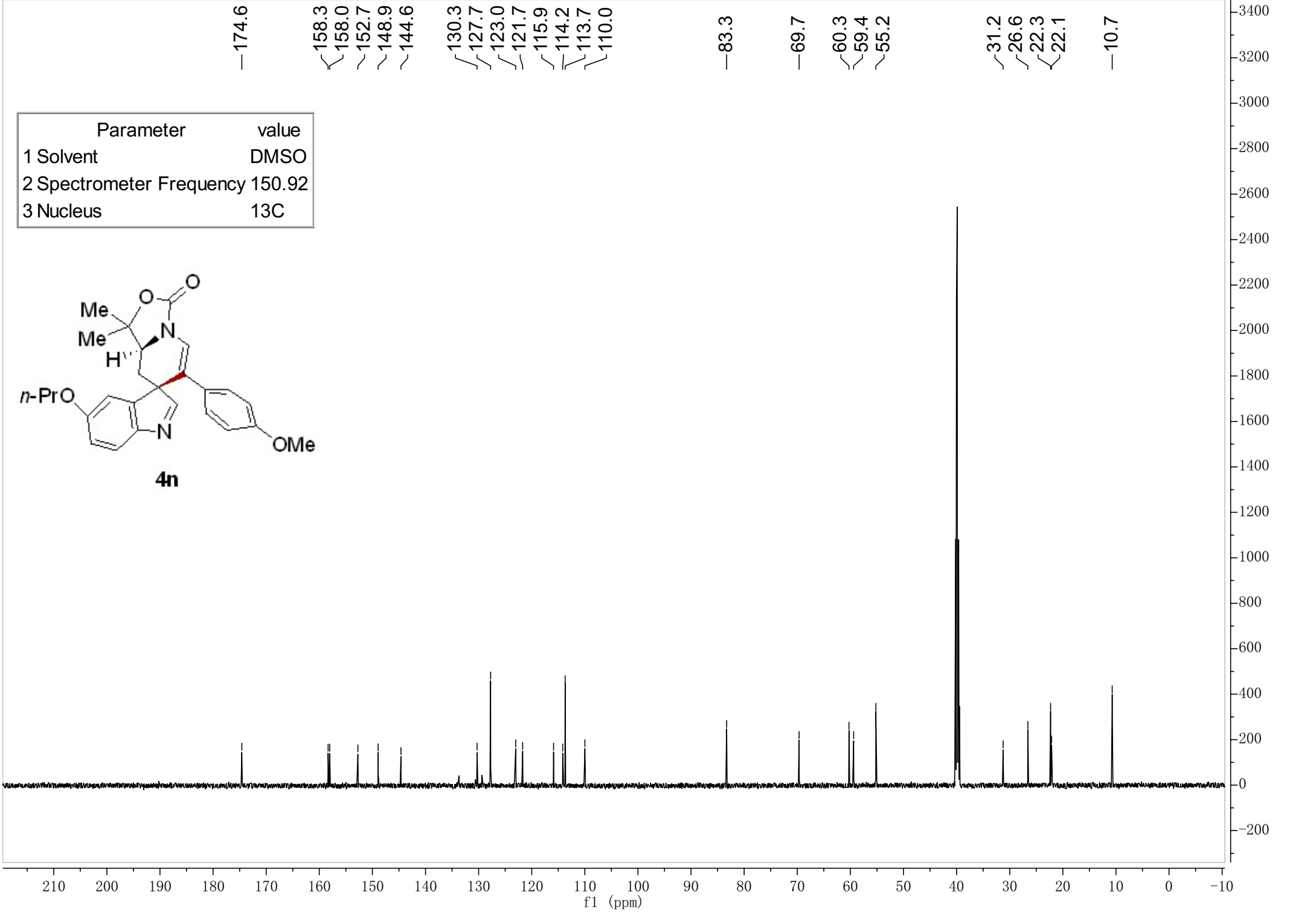


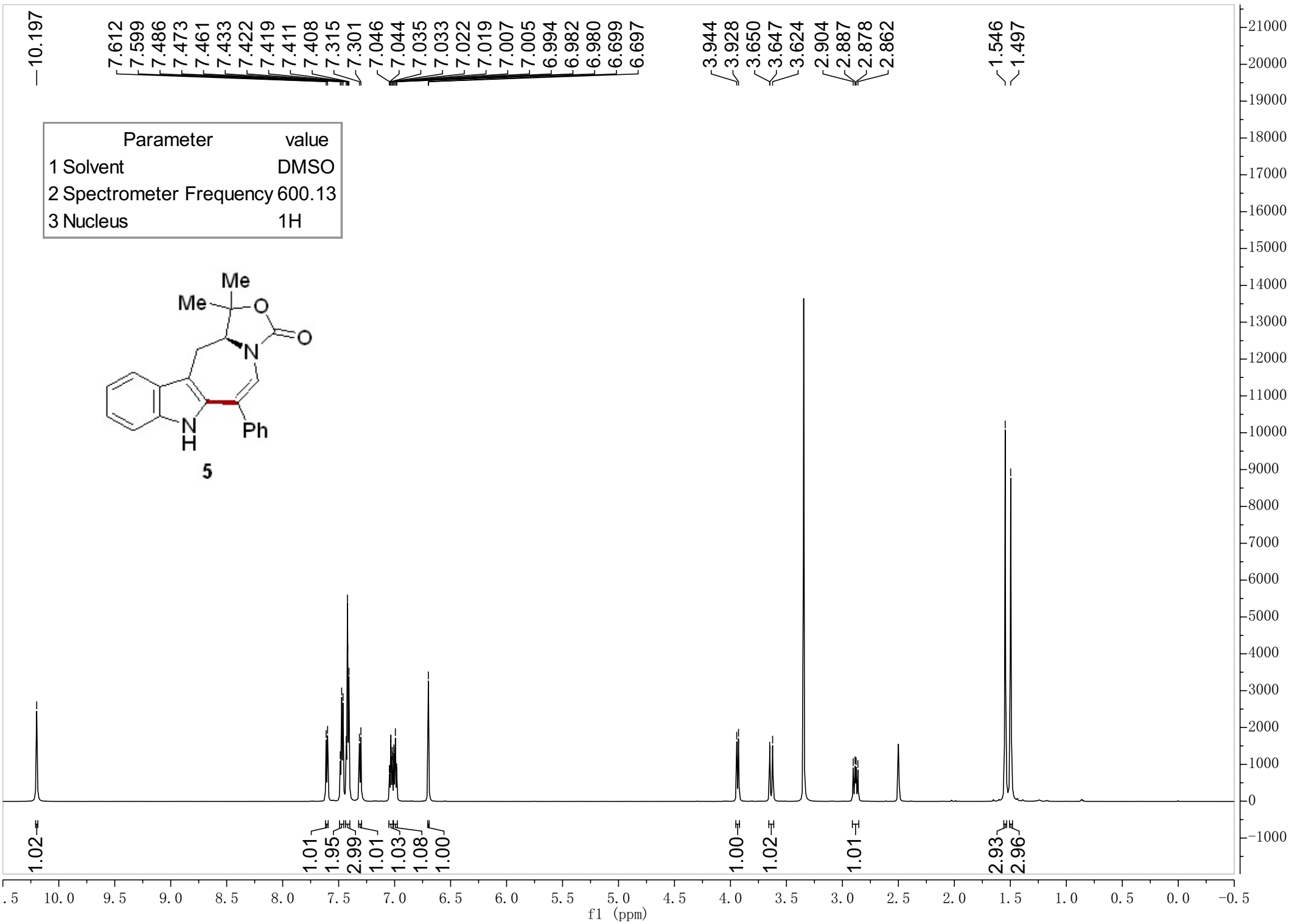


Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C

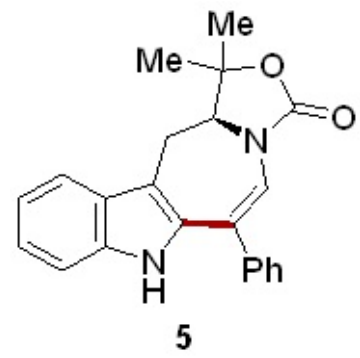


— 174.6
 { 158.3
 { 158.0
 ~ 152.7
 ~ 148.9
 ~ 144.6
 / 130.3
 / 127.7
 / 123.0
 / 121.7
 / 115.9
 / 114.2
 / 113.7
 / 110.0
 — 83.3
 — 69.7
 { 60.3
 { 59.4
 ~ 55.2
 / 31.2
 / 26.6
 { 22.3
 { 22.1
 — 10.7





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C

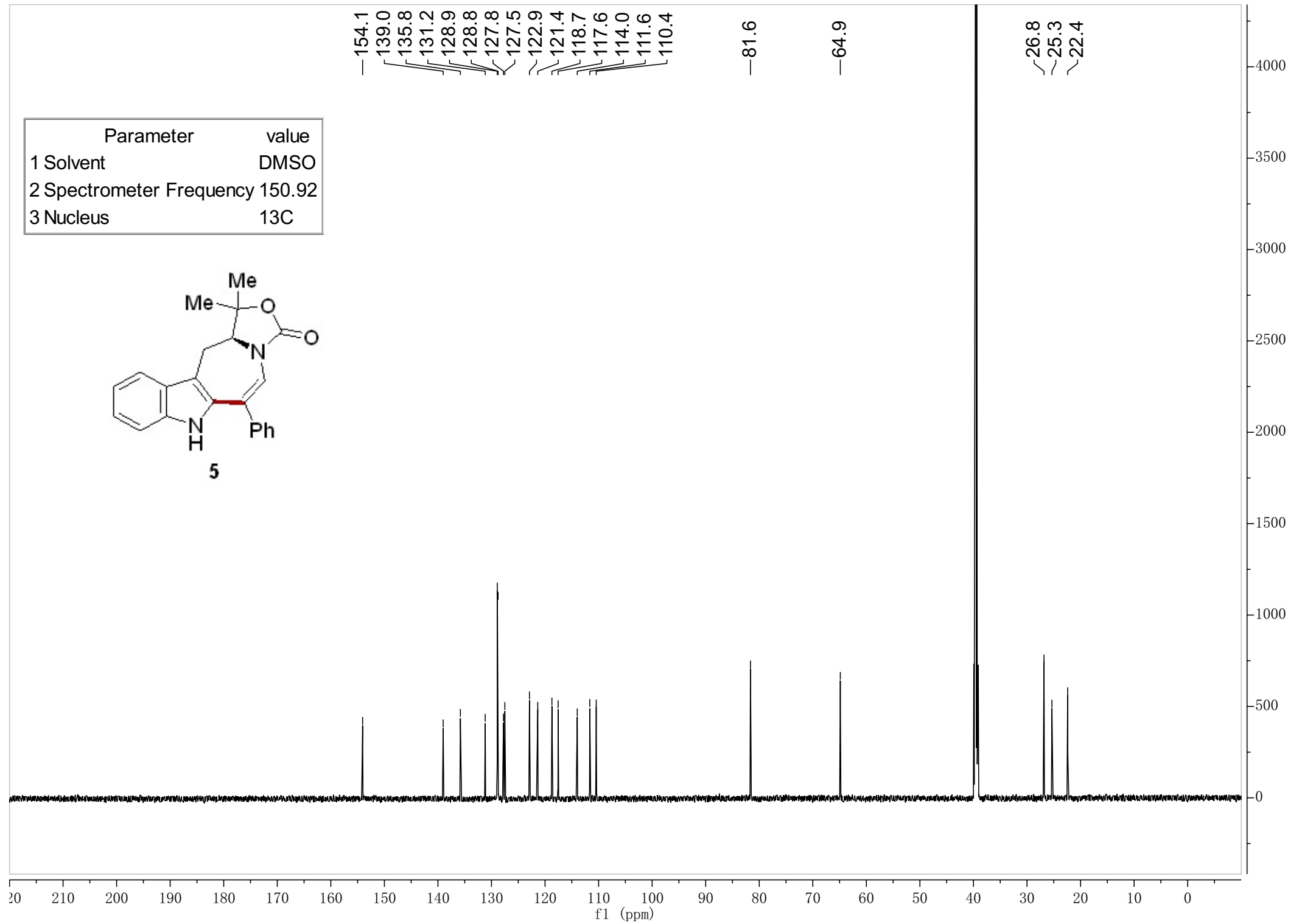


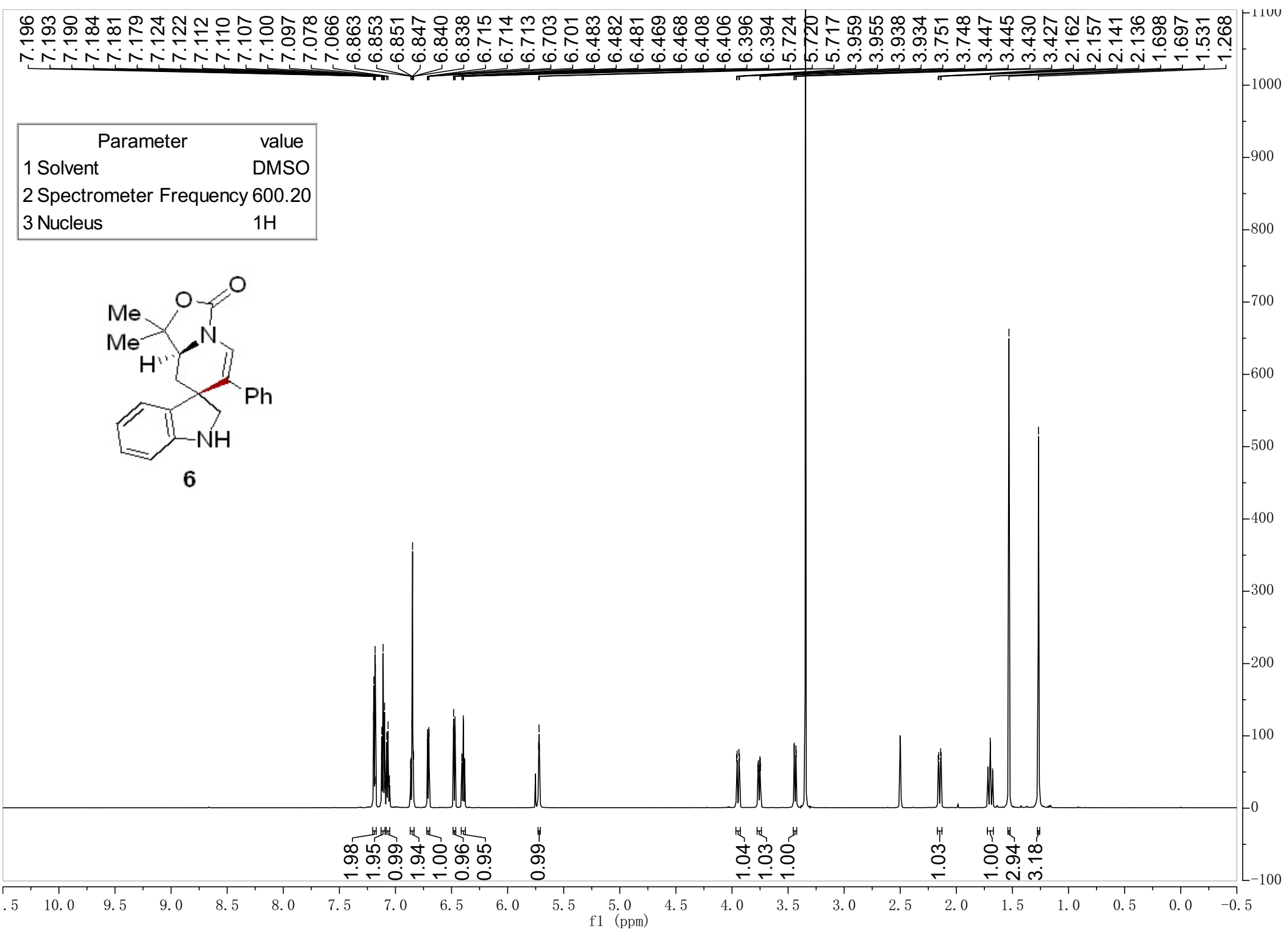
— 154.1
 — 139.0
 — 135.8
 — 131.2
 — 128.9
 — 128.8
 — 127.8
 — 127.5
 — 122.9
 — 121.4
 — 118.7
 — 117.6
 — 114.0
 — 111.6
 — 110.4

— 81.6

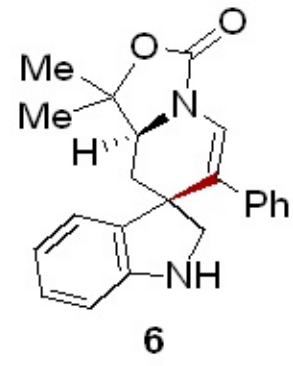
— 64.9

— 26.8
 — 25.3
 — 22.4





Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



152.50
151.78
138.46
133.16
127.82
127.62
127.58
126.15
123.79
122.25
120.44
117.01
108.81

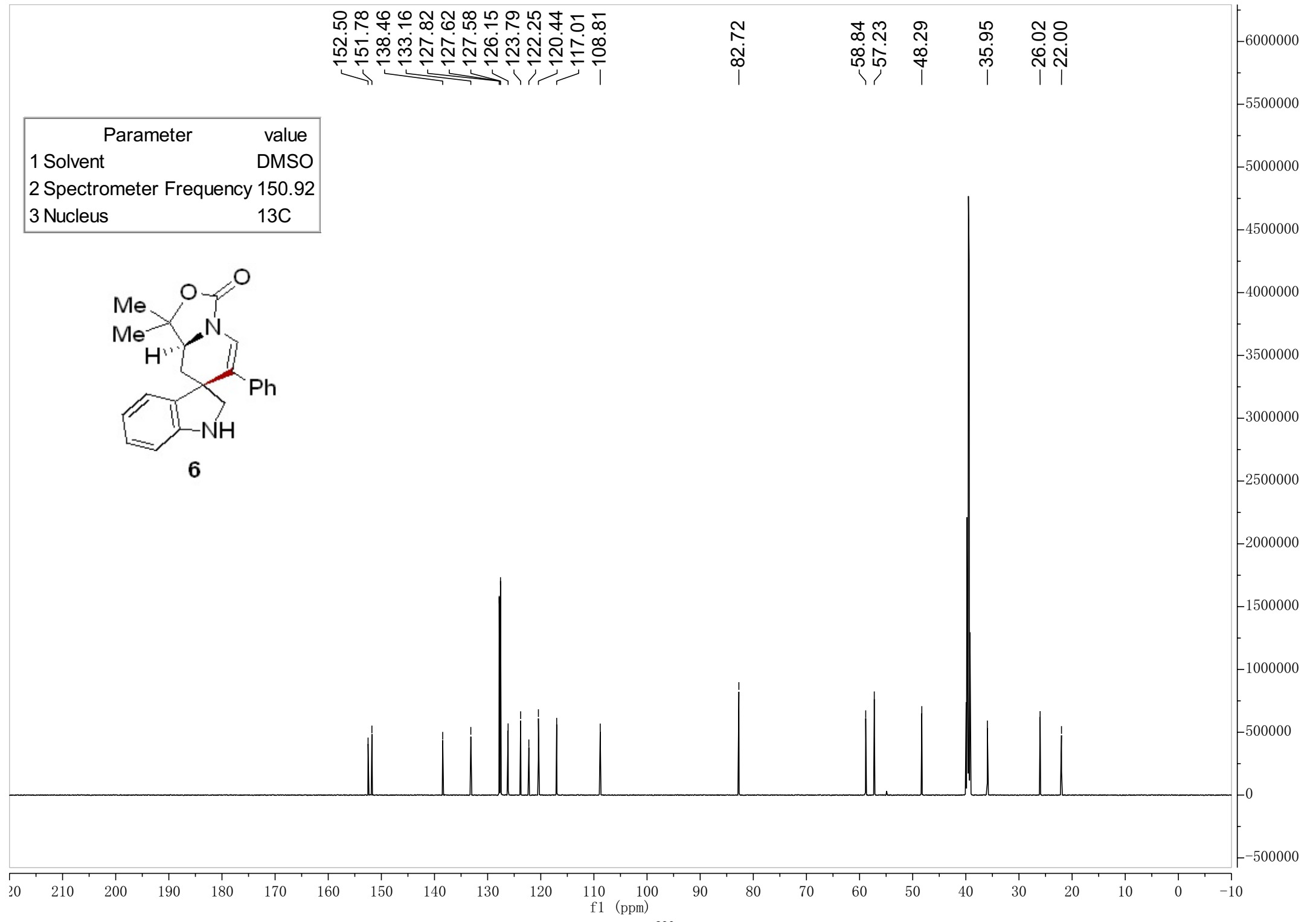
82.72

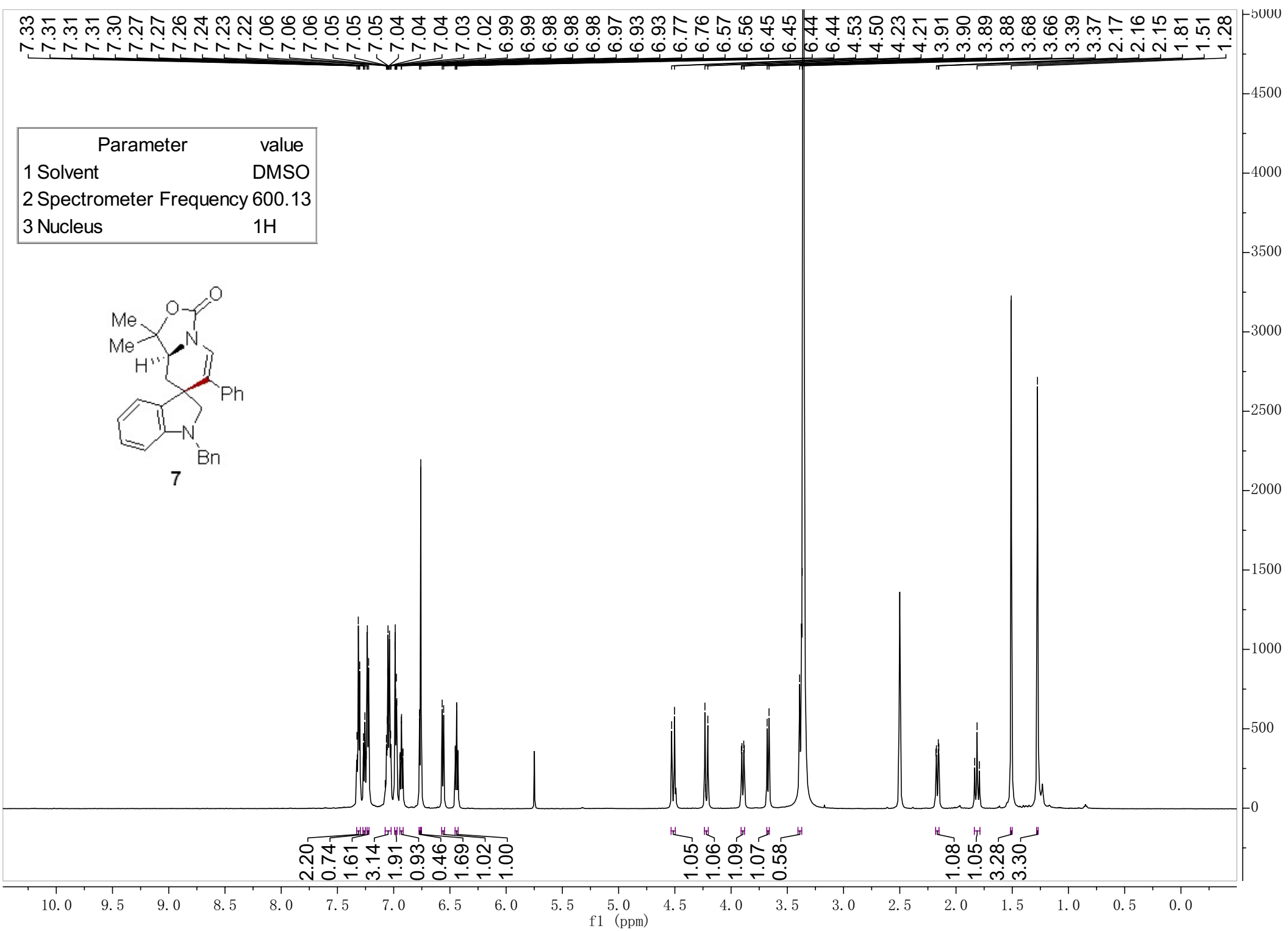
58.84
57.23

48.29

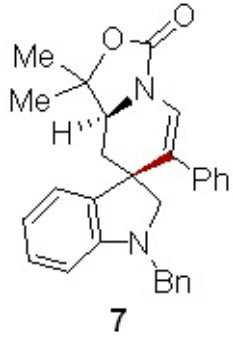
35.95

26.02
22.00

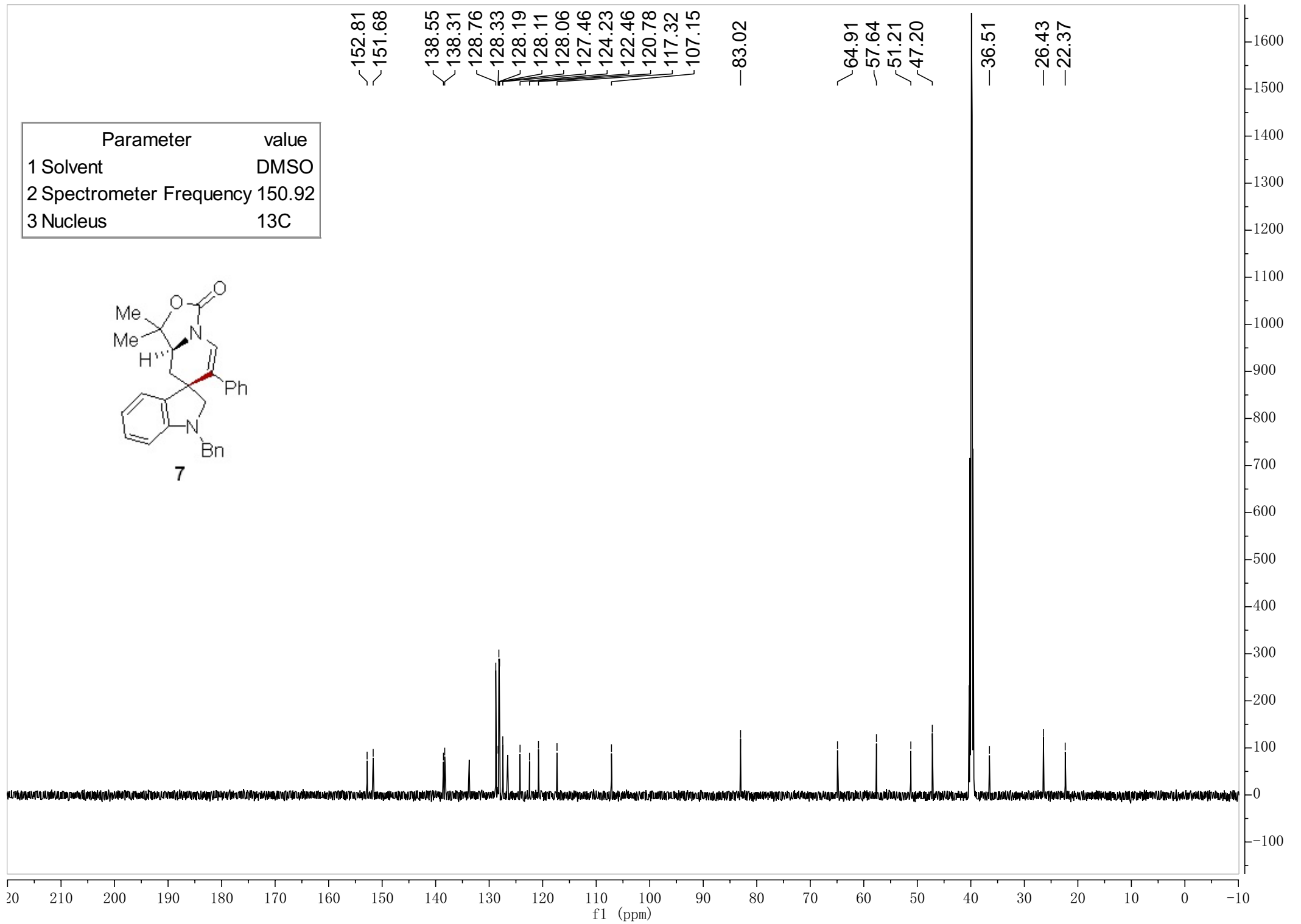




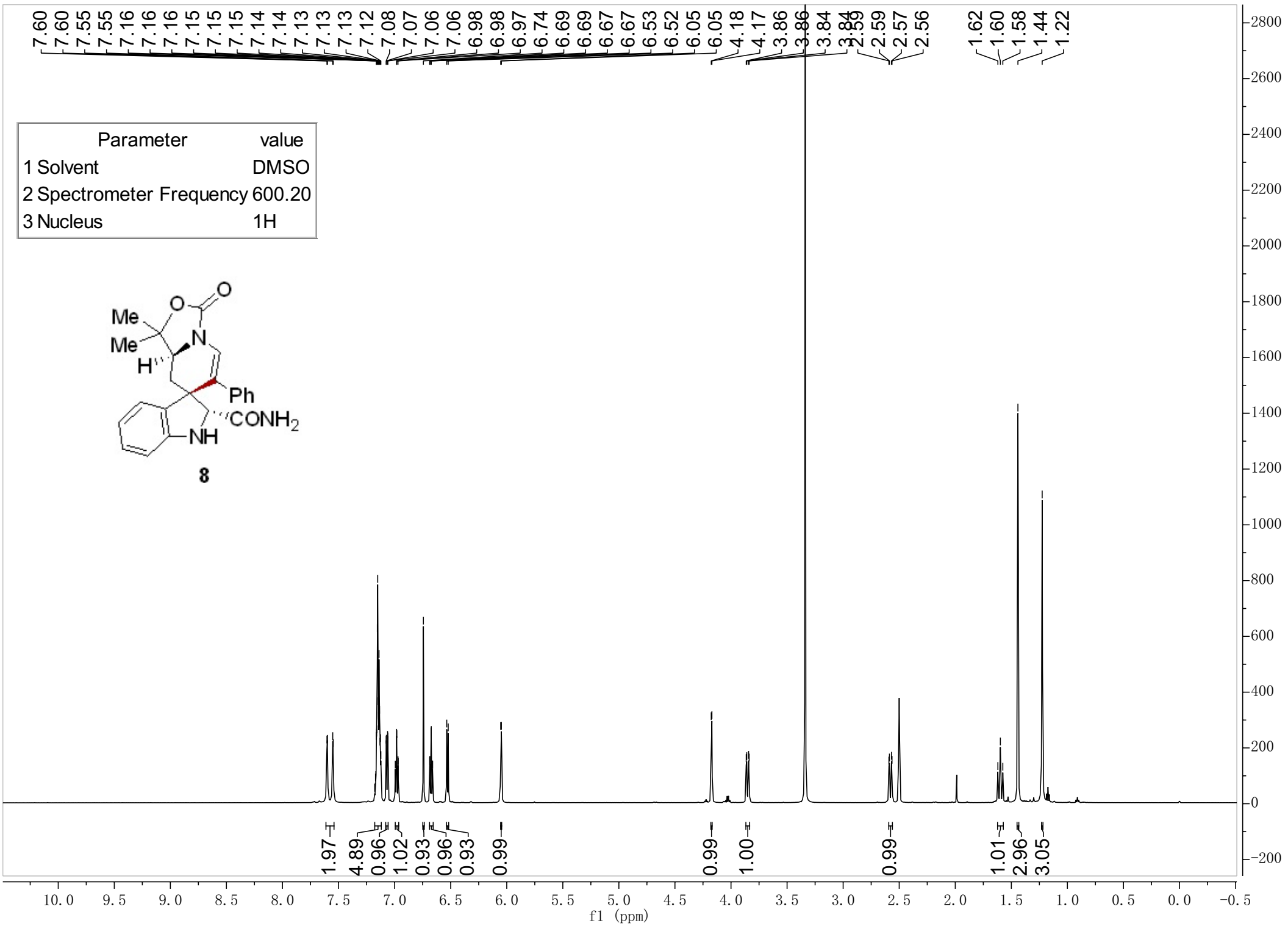
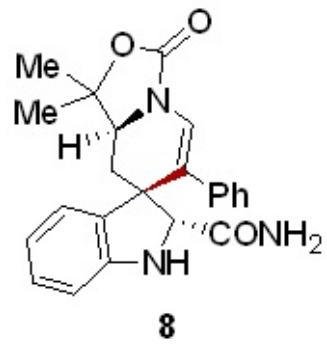
Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	13C



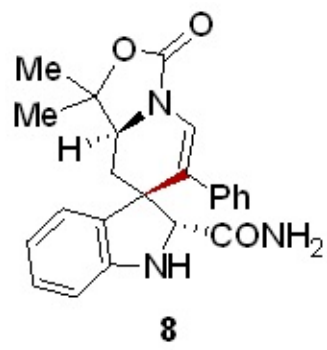
152.81
151.68
138.55
138.31
128.76
128.33
128.19
128.11
128.06
127.46
124.23
122.46
120.78
117.32
107.15
83.02
64.91
57.64
51.21
47.20
36.51
26.43
22.37



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	600.20
3 Nucleus	¹ H



Parameter	value
1 Solvent	DMSO
2 Spectrometer Frequency	150.92
3 Nucleus	¹³ C



- 173.19
- 152.96
- 150.29
- 139.02
- 133.96
- 130.35
- 128.50
- 128.22
- 127.18
- 124.23
- 122.67
- 122.36
- 119.14
- 110.26
- 82.88
- 68.85
- 57.78
- 51.70
- 33.97
- 26.85
- 22.03

