Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Total Syntheses of (±)-Spiroindimicins B and C Enabled by a Late-Stage Schöllkopf-Magnus-Barton-Zard (SMBZ) Reaction

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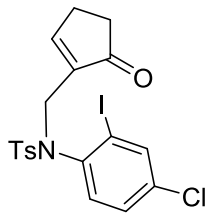
Table of Contents

1. Methods and Materials

General Information. Commercially available reagents were used throughout without purification unless otherwise stated. Anhydrous solvents were used as supplied. Diethyl ether, tetrahydrofuran and dichloromethane were dried using an LC Technology Solutions Inc. SP-1 solvent purification system under an atmosphere of dry nitrogen. Ether refers to diethyl ether. All reactions were routinely carried out in oven-dried glassware under a nitrogen or argon atmosphere unless otherwise stated. Analytical thin layer chromatography was performed using silica plates and compounds were visualized at 254 and/or 360 nm ultraviolet irradiation followed by staining with either alkaline permanganate or ethanolic vanillin solution. Infrared spectra were obtained using a Perkin Elmer spectrum One Fourier Transform Infrared spectrometer as thin films between sodium chloride plates. Absorption maxima are expressed in wavenumbers (cm-1). Melting points were recorded on an Electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded as indicated on either a spectrometer operating at 400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei or on a spectrometer operating at 500 MHz and 125 MHz for ^{1}H and ^{13}C nuclei, respectively. Chemical shifts are reported in parts per million (ppm) relative to the tetramethylsilane peak recorded as δ 0.00 ppm in $CDCl_3$/TMS solvent, or the residual chloroform (δ 7.26 ppm), DMSO (δ 2.50 ppm) or acetone (δ 2.05 ppm) peaks. The ^{13}C NMR values were referenced to the residual chloroform (δ 77.1 ppm), DMSO (δ 39.5 ppm) or acetone (δ 29.8 ppm) peaks. ^{13}C NMR values are reported as chemical shift δ, multiplicity and assignment. ^{1}H NMR shift values are reported as chemical shift δ, relative integral, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (*J* in Hz) and assignment. Assignments are made with the aid of DEPT 135, COSY, NOESY, HMBC and HSQC experiments. High resolution mass spectra were obtained by electrospray ionization in positive ion mode at a nominal accelerating voltage of 70 eV on a microTOF mass spectrometer.

2. Experimental Procedures

N-(4-Chloro-2-iodophenyl)-4-methyl-*N*-((5-oxocyclopent-1-en-1-yl)methyl)benzenesulfonamide (9)

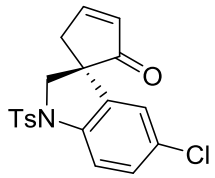


To a suspension of sodium hydride (60% dispersion in mineral oil, 734 mg, 18.4 mmol) in THF (30 mL) at 0 °C was added **10**[1] (3.74 g, 9.17 mmol), followed by tetra-*n*-butylammonium iodide (508 mg, 1.38 mmol) and the mixture was warmed to room temperature and stirred 30 min. The mixture was then cooled to 0 °C and solution of **11**[2] (2.41 g, 13.77 mmol) in THF (10 mL) was added, and the mixture was warmed to room temperature and stirred for 3 h. The mixture was then cooled to 0 °C and quenched by the slow addition of saturated ammonium chloride solution (50 mL), and was then warmed to room temperature and extracted with ethyl acetate (3 x 50 mL). The combined organic extracts were washed with brine (100 mL), then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel using hexanes:ethyl acetate (7:3) as the eluent to afford the *title compound* (3.73 g, 7.43 mmol, 81%) as colourless solid; mp 122-124 °C; ν_{max} (neat)/cm^{-1} 2915, 1709, 1466, 1348, 1291, 1160, 1086, 1029, 1014, 881, 759, 704, 662; δ_H (400 MHz, $CDCl_3$) 7.84-7.82 (2 H, m, CH + ArH), 7.61 (2 H, d, *J* = 8.4 Hz, 2 x ArH), 7.30 (2 H, d, *J* = 8.2 Hz, 2 x ArH), 7.23 (1 H, dd, *J* = 8.6 and 2.3 Hz, ArH), 6.88 (1 H, d, *J* = 8.5 Hz, ArH), 4.29 (2 H, dd, *J* = 93.6 and 14.7 Hz, CH_2), 2.59-2.57 (2 H, m, CH_2), 2.45 (3 H, s, Me), 2.32-2.28 (2 H, m, CH_2); δ_C (100 MHz, $CDCl_3$) 207.9 (C), 163.5 (CH), 144.4 (C), 140.6 (C), 140.4 (C), 139.9 (CH), 135.3 (C), 135.1 (C), 131.0 (CH), 129.8 (2 x CH), 129.1 (CH), 128.5 (2 x CH), 103.1 (C), 46.1 (CH_2), 34.4 (CH_2), 26.9 (CH_2), 21.8 (Me); HRMS (ESI, $[M + H]^+$) found 501.9738. $[C_{19}H_{17}{}^{35}ClINO_3S + H]^+$ requires 501.9735.

1 A. Nakhi, B. Prasad, U. Reddy, R. M. Rao, S. Sandra, R. Kapavarapu, D. Rambabu, G. R. Krishna, C. M. Reddy, K. Ravada, P. Misra, J. Iqbal, M. Pal, *Med. Chem. Commun.* **2011,** *2*, 1006.

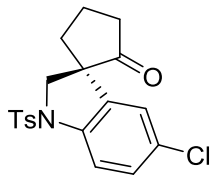
2 S. T. Handy, D. Omune, *Tetrahedron* **2007,** *63*, 1366.

(±)-5'-Chloro-1'-tosylspiro[cyclopent[3]ene-1,3'-indolin]-2-one (12)



To a degassed mixture of **9** (1.8 g, 3.59 mmol) in *N*-methyl-2-pyrrolidone (50 mL) was added tetra-*n*-butylammonium chloride hydrate (3.0 g, 17.6 mmol), sodium formate (537 mg, 7.90 mmol), palladium acetate (161 mg, 0.72 mmol), and silver nitrate (609 mg, 3.59 mmol), and the mixture stirred at room temperature for 3 h. The mixture was then poured onto saturated ammonium chloride (200 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were washed with brine (200 mL) and then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified flash chromatography on silica gel using hexanes:ethyl acetate (3:2) as the eluent to afford the *title compound* (1.25 g, 3.34 mmol, 93%) as yellow solid; mp 175-177 °C; ν_{max} (neat)/cm^{-1} 1713, 1588, 1473, 1354, 1161, 1091, 815, 662; δ_H (500 MHz, $CDCl_3$) 7.79 (1 H, dt, *J* = 5.9 and 2.7 Hz, CH), 7.69 (2 H, d, *J* = 8.4 Hz, 2 x ArH), 7.57 (1 H, d, *J* = 8.7 Hz, ArH), 7.28 (2 H, d, *J* = 8.1 Hz, 2 x ArH), 7.19 (1 H, dd, *J* = 8.8 and 2.3 Hz, ArH), 6.74 (1 H, d, *J* = 2.1 Hz, ArH), 6.29 (1 H, dt, *J* = 5.8 and 2.3 Hz, CH), 4.14 (1 H, d, *J* = 11.0 Hz, CH of CH_2), 3.92 (1 H, d, *J* = 11.0 Hz, CH of CH_2), 2.79-2.66 (2 H, m, CH_2), 2.40 (3 H, s, Me); δ_C (100 MHz, $CDCl_3$) 206.7 (C), 163.6 (CH), 144.8 (C), 140.9 (C), 136.8 (C), 133.6 (C), 133.1 (CH), 130.0 (2 x CH), 129.6 (C), 129.2 (CH), 127.6 (2 x CH), 122.5 (CH), 116.1 (CH), 59.3 (CH_2), 54.4 (C), 46.5 (CH_2), 21.7 (Me); HRMS (ESI, $[M + Na]^+$ found 396.0429. $[C_{19}H_{16}{}^{35}ClNO_3S + Na]^+$ requires 396.0432.

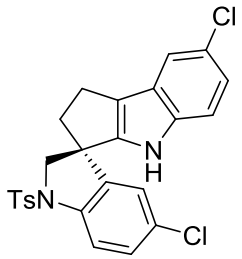
(±)-5'-Chloro-1'-tosylspiro[cyclopentane-1,3'-indolin]-2-one (8)



To a mixture of **12** (2.50 g, 6.69 mmol) in ethyl acetate (200 mL) was added 10% palladium on carbon (682 mg, 53% wetted) and hydrogen was bubbled through the heterogeneous mixture at room temperature for 1 h. The mixture was then filtered through a plug of Celite® and washed with ethyl acetate (100 mL) to afford the *title compound* (2.49 g, 6.64 mmol, 99%) as colourless solid; mp 123-126 °C; ν_{max} (neat)/cm^{-1} 2964, 1742, 1597, 1472, 1356, 1339, 1164, 822, 667; δ_H (400 MHz, $CDCl_3$) 7.67 (2 H, d, *J* = 8.4 Hz, 2 x ArH), 7.56 (1 H, d, *J* = 8.7 Hz, ArH), 7.27 (2 H, d, *J* = 7.1 Hz, 2 x ArH), 7.20 (1 H, dd, *J* = 8.6 and 2.1 Hz, ArH), 6.83 (1 H, d, *J* = 2.1 Hz, ArH), 3.99 (1 H, d, *J* = 10.5 Hz, CH

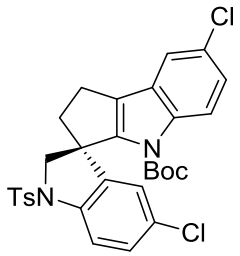
of CH_2), 3.82 (1 H, d, *J* = 10.5 Hz, CH of CH_2), 2.45-2.37 (2 H, m, CH_2), 2.39 (3 H, s, Me), 2.11-1.90 (4 H, m, 2 x CH_2); δ_C (100 MHz, $CDCl_3$) 216.6 (C), 144.8 (C), 140.9 (C), 136.6 (C), 133.6 (C), 130.0 (2 x CH), 129.3 (C), 129.1 (CH), 127.5 (2 x CH), 123.8 (CH), 115.9 (CH), 59.4 (CH_2), 57.3 (C), 38.4 (CH_2), 37.4 (CH_2), 21.7 (Me), 19.2 (CH_2); HRMS (ESI, $[M + Na]^+$) found 398.0586. $[C_{19}H_{18}{}^{35}ClNO_3S + Na]^+$ requires 398.0588.

(±)-5',7-Dichloro-1'-tosyl-2,4-dihydro-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline] (7)



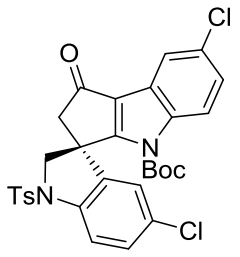
To a solution of **8** (550 mg, 1.46 mmol) in acetic acid (14 mL) was added 4-chloro-phenylhydrazine hydrochloride (341 mg, 1.90 mmol) and the mixture was heated to 110 °C for 40 h. The mixture was then cooled to room temperature and diluted with cyclohexane (20 mL) and concentrated *in vacuo*. The crude residue was taken up in ethyl acetate (40 mL) and washed with 10% aqueous hydrochloric acid (25 mL), followed by brine (25 mL) and finally saturated sodium bicarbonate (25 mL). The organic layer was then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel using hexanes-ethyl acetate (9:1) as the eluent to afford recovered **8** (107 mg, 0.28 mmol) and the *title compound* [530 mg, 1.10 mmol, 75%, (93% brsm)] as yellow solid; mp 224-227 °C; ν_{max} (neat)/cm^{-1} 3367, 1918, 2850, 1467, 1443, 1298, 1161, 1091, 1046, 821, 792, 665; δ_H (400 MHz, DMSO-*d*6) 11.10 (1 H, s, NH), 7.78 (2 H, d, *J* = 8.5 Hz, 2 x ArH), 7.57 (1 H, d, *J* = 8.8 Hz, ArH), 7.45-7.43 (3 H, m, 3 x ArH), 7.33 (1 H, dd, *J* = 8.7 and 2.3 Hz, ArH), 7.24 (1 H, d, *J* = 8.8 Hz, ArH), 7.03 (1 H, dd, *J* = 8.6 and 2.1 Hz, ArH), 6.83 (1 H, d, *J* = 2.2 Hz, ArH), 4.14 (1 H, d, *J* = 11.0 Hz, CH of CH_2), 4.04 (1 H, d, *J* = 11.0 Hz, CH of CH_2), 2.81-2.77 (2 H, m, CH_2), 2.48-2.42 (1 H, m, CH of CH_2), 2.39 (3 H, s, Me), 2.24-2.19 (1 H, m, CH of CH_2); δ_C (100 MHz, DMSO-*d*6) 145.6 (C), 144.7 (C), 139.9 (C), 139.8 (C), 139.5 (C), 132.9 (C), 130.1 (2 x CH), 128.5 (CH), 128.2 (C), 127.4 (2 x CH), 124.5 (C), 123.6 (CH), 123.5 (C), 120.7 (CH), 119.2 (C), 117.9 (CH), 115.6 (CH), 113.6 (CH), 60.4 (CH_2), 50.8 (C), 46.0 (CH_2), 22.5 (CH_2), 21.0 (Me); HRMS (ESI, $[M + Na]^+$) found 505.0496. $[C_{25}H_{20}{}^{35}Cl_2N_2O_2S + Na]^+$ requires 505.0515.

(±)-*tert*-Butyl 5',7-dichloro-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (13)



To a solution of **7** (1.28 g, 2.65 mmol) in THF (35 mL) was added di-*tert*-butyl dicarbonate (695 mg, 3.18 mmol) and 4-dimethylaminopyridine (4 mg, 0.13 mmol) and the solution was stirred at room temperature for 1 h. The mixture was then concentrated *in vacuo* and the crude residue was purified by flash chromatography on silica gel using hexanes-ethyl acetate (19:1 -> 9:1) as the eluent to afford the *title compound* (1.49 g, 2.55 mmol, 96%) as yellow solid; mp 83-85 °C; ν_{max} (neat)/cm^{-}1 2937, 1731, 1598, 1442, 1354, 1312, 1162, 1111, 810, 664; δ_H (400 MHz, acetone-*d*6) 8.07 (1 H, d, *J* = 9.0 Hz, ArH), 7.85 (2 H, d, *J* = 8.3 Hz, 2 x ArH), 7.62 (1 H, d, *J* = 8.6 Hz, ArH), 7.52 (1 H, d, *J* = 2.2 Hz, ArH), 7.43 (2 H, d, *J* = 8.3 Hz, 2 x ArH), 7.30 (1 H, dd, *J* = 9.1 and 2.2 Hz, ArH), 7.26 (1 H, dd, *J* = 8.6 and 2.2 Hz, ArH), 6.95 (1 H, d, *J* = 2.2 Hz, ArH), 4.33 (1 H, d, *J* = 10.3 Hz, CH of CH_2), 4.16 (1 H, d, *J* = 10.3 Hz, CH of CH_2), 2.91-2.79 (2 H, m, CH_2), 2.55-2.49 (1 H, m, CH of CH_2), 2.42 (3 H, s, Me), 2.35-2.28 (1 H, m, CH of CH_2), 1.21 (9 H, s, 3 x Me); δ_C (100 MHz, acetone-*d*6) 149.6 (C), 145.5 (C), 143.0 (C), 142.2 (C), 141.3 (C), 139.9 (C), 135.6 (C), 130.8 (2 x CH), 129.7 (C), 129.2 (C), 128.9 (C), 128.6 (CH), 128.4 (2 x CH), 127.9 (C), 124.9 (CH), 123.9 (CH), 119.6 (CH), 118.4 (CH), 116.1 (CH), 85.4 (C), 60.4 (CH_2), 55.0 (C), 48.6 (CH_2), 27.7 (3 x Me), 22.4 (CH_2), 21.5 (Me); HRMS (ESI, $[M + Na]^+$) found 605.1029. $[C_{30}H_{28}{}^{35}Cl_2N_2O_4S + Na]^+$ requires 605.1039.

(±)-*tert*-Butyl 5',7-dichloro-1-oxo-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (15)

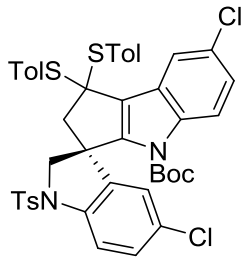


A dry flask was charged with **13** (1.49 g, 2.55 mmol), *N*-bromosuccinimide (476 mg, 2.68 mmol), azobisisobutyronitrile (21 mg, 0.13 mmol), and carbon tetrachloride (95 mL). The mixture was then heated to 65 °C for 2 h under irradiation from a desk lamp. The mixture was then cooled to room

temperature and filtered through cotton wool, and the filtrate was concentrated *in vacuo*. The residue was taken up in THF (30 mL) and treated with saturated sodium bicarbonate (10 mL) and stirred at room temperature for 1 h. The mixture was then diluted with ethyl acetate (100 mL), the aqueous phase was separated and the organic phase washed with brine (15 mL) then dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Impurities were removed by filtration through silica gel using hexanes-ethyl acetate (4:1) as the eluent to afford a diastereomeric mixture of alcohols as yellow oil.

The oil was immediately dissolved in dichloromethane (50 mL) and treated with manganese dioxide (11.0 g, 0.13 mol) and the suspension was stirred at room temperature for 20 h. The reaction mixture was then filtered through a plug of Celite® and the cake was washed with dichloromethane (40 mL) followed by ethyl acetate (40 mL). The filtrate was then concentrated in vacuo to afford the *title compound* (1.06 g, 1.77 mmol, 69% over 2 steps) as a yellow solid; mp 64-68 °C; ν_{max} (neat)/cm^{-1} 2923, 2852, 1748, 1705, 1474, 1443, 1397, 1353, 1293, 1257, 1163, 1133, 1092, 812, 665; δ_H (500 MHz, acetone-*d*6) 8.07 (1 H, d, *J* = 9.0 Hz, ArH), 7.84 (2 H, d, *J* = 8.2 Hz, 2 x ArH), 7.76 (1 H, s, ArH), 7.68 (1 H, d, *J* = 8.7 Hz, ArH), 7.44 (3 H, d, *J* = 7.9 Hz, 3 x ArH), 7.32 (1 H, dd, *J* = 8.6 and 1.6 Hz, ArH), 7.09 (1 H, d, *J* = 1.7 Hz, ArH), 4.78 (1 H, d, *J* = 10.9 Hz, CH of CH_2), 4.35 (1 H, d, *J* = 10.9 Hz, CH of CH_2), 2.98 (1 H, d, *J* = 18.0 Hz, CH of CH_2), 2.72 (1 H, d, *J* = 18.0 Hz, CH of CH_2), 2.43 (3 H, s, Me), 1.36 (9 H, s, 3 x Me); δ_C (125 MHz, acetone-*d*6) 192.9 (C), 164.7 (C), 148.7 (C) 145.7 (C), 141.8 (C), 140.7 (C), 139.1 (C), 135.4 (C), 130.9 (2 x CH), 130.6 (C), 129.6 (C), 129.3 (CH), 128.4 (2 x CH), 127.3 (C), 126.9 (CH), 123.5 (CH), 123.4 (C), 120.5 (CH), 119.0 (CH), 116.6 (CH), 87.6 (C), 61.6 (CH_2), 60.2 (CH_2), 50.9 (C), 27.7 (3 x Me), 21.5 (Me). HRMS (ESI, $[M + Na]^+$) found 619.0838. $[C_{30}H_{26}{}^{35}Cl_2N_2O_5S + Na]^+$ requires 619.0832.

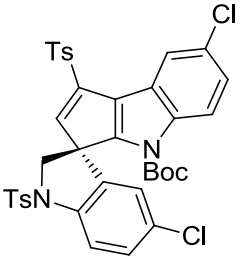
(±)-*tert*-Butyl 5',7-dichloro-1,1-bis(*p*-tolylthio)-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (17)



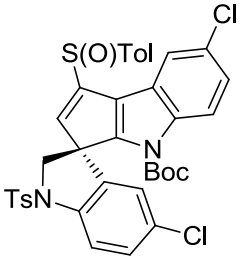
To a solution of **15** (1.06 g, 1.77 mmol) in THF (20 mL) at room temperature was added titanium tetrachloride (1 M in dichloromethane, 5.32 mL, 5.32 mmol), followed by a solution of 4-methylbenzenethiol (815 mg, 6.56 mmol) and triethylamine (2.47 mL, 17.7 mmol) in THF (15 mL) and the reaction mixture stirred at room temperature for 2 h. The mixture was then poured onto

saturated sodium bicarbonate (200 mL) and extracted with ethyl acetate (3 x 100 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography on silica gel using hexanes-ethyl acetate (9:1) as the eluent to afford the *title compound* (1.15 g, 1.39 mmol, 78%) as yellow oil; ν_{max} (neat)/cm^{-1} 2924, 1739, 1597, 1474, 1443, 1351, 1299, 1164, 1141, 1121, 1092, 807, 664; δ_H (500 MHz, acetone-*d*6) 8.03 (1 H, d, *J* = 9.0 Hz, ArH), 7.75 (2 H, d, *J* = 8.3 Hz, 2 x ArH), 7.53 (1 H, d, *J* = 8.7 Hz, ArH), 7.45 (2 H, d, *J* = 8.2 Hz, 2 x ArH), 7.34-7.31 (3 H, m, 3 x ArH), 7.21 (1 H, d, *J* = 2.2 Hz, ArH), 7.20-7.17 (3 H, m, 3 x ArH), 7.05-7.00 (4 H, m, 4 x ArH), 5.54 (1 H, d, *J* = 2.1 Hz, ArH), 4.17 (1 H, d, *J* = 10.7 Hz, CH of CH_2), 3.80 (1 H, d, *J* = 10.7 Hz, CH of CH_2), 2.57 (2 H, s, CH_2), 2.45 (3 H, s, Me), 2.40 (3 H, s, Me), 2.30 (3 H, s, Me), 1.22 (9 H, s, 3 x Me); δ_H (400 MHz, $CDCl_3$) 7.92 (1 H, d, *J* = 9.0 Hz, ArH), 7.71 (2 H, d, *J* = 8.1 Hz, 2 x ArH), 7.50 (1 H, d, *J* = 8.5 Hz, ArH), 7.31-7.28 (4 H, m, 4 x ArH), 7.21 (1 H, dd, *J* = 9.1 and 2.3 Hz, ArH), 7.09-7.06 (4 H, m, 4 x ArH), 6.93 (4 H, s, 4 x ArH), 5.41 (1 H, d, *J* = 2.1 Hz, ArH), 4.12 (1 H, d, *J* = 10.7 Hz, CH of CH_2), 3.95 (1 H, d, *J* = 10.7 Hz, CH of CH_2), 2.46 (2 H, q, *J* = 14.7 Hz, CH_2), 2.44 (3 H, s, Me), 2.40 (3 H, s, Me), 2.29 (3 H, s, Me), 1.20 (9 H, s, 3 x Me); δ_C (100 MHz, $CDCl_3$) 148.4 (C), 144.5 (C), 141.8 (C), 140.9 (C), 140.3 (C), 140.1 (C), 139.7 (C), 138.5 (C), 137.7 (2 x CH), 136.9 (2 x CH), 134.9 (C), 130.6 (C), 130.00 (2 x CH), 129.98 (2 x CH), 129.9 (2 x CH), 129.1 (C), 128.9 (C), 128.6 (C), 128.2 (CH), 127.9 (C), 127.5 (2 x CH), 125.2 (C), 125.0 (CH), 122.4 (CH), 119.9 (CH), 117.2 (CH), 115.4 (CH), 85.5 (C), 64.3 (C), 60.1 (CH_2), 59.9 (CH_2), 53.1 (C), 27.7 (3 x Me), 21.8 (Me), 21.5 (2 x Me); HRMS (ESI, $[M + Na]^+$) found 849.1402. $[C_{44}H_{40}{}^{35}Cl_2N_2O_4S_3 + Na]^+$ requires 849.1419.

(±)-*tert*-Butyl 5',7-dichloro-1,1'-ditosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (16) and (±)-*tert*-butyl 5',7-dichloro-1-(p-tolylsulfinyl)-1'-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (18)



16



18

To a solution of thioketal **17** (1.15 g, 1.38 mmol) in dichloromethane (130 mL) at 0 °C was added finely ground potassium carbonate (1.28 g, 9.26 mmol) and 77% *m*-chloroperoxybenzoic acid (0.53 g, 3.20 mmol) and the mixture stirred for 2 h at 0 °C, and then at room temperature 14 h. The mixture was then heated to reflux for 2 h, before cooling to 0 °C for the addition of 77% *m*-

chloroperoxybenzoic acid (0.35 g, 2.13 mmol). The mixture stirred at 0 °C for 1 h, and was then warmed to room temperature and stirred for 2 h, and finally heated to reflux for 4 h. The mixture was then cooled, and a saturated solution of sodium bicarbonate (100 mL) was added and the reaction mixture was vigorously stirred for 10 min. The organic phase was then separated, and the aqueous phase extracted with dichloromethane (2 x 70 mL). The combined organic extracts were then dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography on deactivated silica gel using hexanes-ethyl acetate (9:1 -> 4:1) as the eluent afforded sulfoxide **18** and sulfone **16**.

18 (0.31 g, 0.44 mmol, 31%) as an orange solid; mp 90-95 °C. A mixture of inseparable diastereomers (5:3); ν_{max} (neat)/cm^{-1} 2973, 1737, 1597, 1474, 1439, 1358, 1305, 1252, 1155, 1090, 1069, 1047, 808, 666; δ_H (500 MHz, $CDCl_3$) 7.95 (2 H, d, *J* = 9 Hz, 2 x ArH_{maj}), 7.77-7.70 (8 H, m, 4 x ArH_{maj} + 4 x ArH_{min}), 7.59 (1 H, d, *J* = 2.1 Hz, ArH_{min}), 7.57-7.55 (4 H, m, 2 x ArH_{maj} + 2 x ArH_{min}), 7.49 (2 H, d, *J* = 8.3 Hz, 2 x ArH), 7.37-7.20 (9 H, m, 5 x ArH_{maj} + 4 x ArH_{min}), 6.45 (1 H, d, *J* = 2 Hz, ArH_{maj}), 6.28 (1 H, d, *J* = 2.3 Hz, ArH_{min}), 5.75 (1 H, s, CH_{maj}), 5.72 (1 H, s, CH_{min}), 4.80 (1 H, d, *J* = 10.9 Hz, CH of CH_{2min}), 4.78 (1 H, d, *J* = 10.7 Hz, CH of CH_{2maj}), 4.16 (1 H, d, *J* = 10.9 Hz, CH of CH_{2min}), 4.05 (1 H, d, *J* = 10.8 Hz, CH of CH_{2maj}), 2.45 (3 H, s, Me_{min}), 2.44 (3 H, s, Me_{maj}), 2.38 (3 H, s, Me_{maj}), 2.36 (3 H, s, Me_{min}), 1.30 (18 H, s, 3 x Me_{maj} + 3 x Me_{min}), $_{maj}$ = major diastereomer, $_{min}$ = minor diastereomer; δ_C (125 MHz, $CDCl_3$) $_{min}$ + $_{maj}$, 148.4 (C), 146.6 (C), 146.5 (C), 145.14 (C), 145.11 (C), 142.8 (C), 142.7 (C), 142.4 (C), 142.1 (C), 142.0 (C), 141.8 (C), 140.4 (CH), 140.3 (CH), 139.3 (C), 139.2 (C), 138.18 (C), 138.15 (C), 134.2 (C), 134.1 (C), 131.7 (C), 131.6 (C), 130.4 (2 x CH), 130.3 (2 x CH), 130.2 (CH), 130.13 (2 x CH), 130.09 (2 x CH), 129.6 (C), 129.4 (C), 129.3 (C), 129.2 (CH), 129.1 (CH), 127.4 (4 x CH), 125.4 (2 x CH), 125.1 (CH), 125.02 (CH), 125.96 (C), 122.80 (C), 122.77 (C), 122.4 (CH), 122.1 (CH), 121.4 (CH), 121.2 (2 x CH), 117.2 (CH), 117.1 (CH), 117.0 (CH), 85.9 (2 x C), 58.7 (2 x C), 53.6 (CH_2), 53.5 (CH_2), 27.7 (6 x Me), 21.7 (2 x Me), 21.42 (Me), 21.37 (Me), 3 x C and 1 x CH not observed; HRMS (ESI, $[M + H]^+$) found 719.1216. $[C_{37}H_{32}{}^{35}Cl_2N_2O_5S_2 + H]^+$ requires 719.1202.

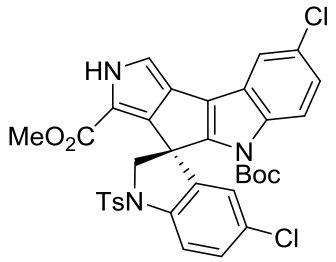
16 (0.39 g, 0.53 mmol, 39%) as an orange solid; mp 95-102 °C; ν_{max} (neat)/cm^{-1} 2975, 1737, 1471, 1439, 1360, 1304, 1153, 1092, 1069, 811, 664; δ_H (500 MHz, acetone-*d*6) 8.14 (1 H, d, *J* = 9.2 Hz, ArH), 7.97 (1 H, d, *J* = 1.9 Hz, ArH), 7.89 (2 H, d, *J* = 8.3, 2 x ArH), 7.84 (2 H, d, *J* = 8.3 Hz, 2 x ArH), 7.75 (1 H, d, *J* = 8.7, ArH), 7.51 (4 H, t, *J* = 9.0 Hz, 4 x ArH), 7.40-7.36 (2 H, m, 2 x ArH), 6.66 (1 H, d, *J* = 2.1 Hz, ArH), 5.87 (1 H, s, CH), 4.91 (1 H, d, *J* = 11.4 Hz, CH of CH_2), 4.22 (1 H, d, *J* = 11.4 Hz, CH of CH_2), 2.49 (3 H, s, Me), 2.43 (3 H, s, Me), 1.32 (9 H, s, 3 x Me); δ_C (125 MHz, acetone-*d*6) 149.3 (C), 148.0 (C), 146.6 (C), 146.1 (C), 146.0 (CH), 143.6 (C), 143.3 (C), 139.8 (C), 139.5 (C), 138.3 (C), 135.0 (C), 132.3 (C), 131.23 (2 x CH), 131.15 (2 x CH), 130.1 (CH), 130.0 (C), 129.7 (C), 128.5 (2 x CH), 128.3 (2 x CH), 125.7 (CH), 123.7 (C), 123.6 (CH), 120.5 (CH), 118.7

(CH), 118.2 (CH), 86.8 (C), 59.9 (C), 54.1 (CH_2), 27.8 (3 x Me), 21.7 (Me), 21.5 (Me); HRMS (ESI, $[M + Na]^+$) found 757.0968. $[C_{37}H_{32}{}^{35}Cl_2N_2O_6S_2 + Na]^+$ requires 757.0971.

Synthesis of sulfone **16** from sulfoxide **18**:

To a solution of **18** (19 mg, 26.4 µmol) in dichloromethane (0.3 mL) at 0 °C was added finely ground potassium carbonate (5.5 mg, 39.8 µmol) followed by a solution of 77% *m*-chloroperoxybenzoic acid (6.5 mg, 29.0 µmol) in dichloromethane (0.2 mL), and the reaction mixture was warmed to room temperature and stirred for 3 h. The mixture was quenched by the addition of saturated sodium bicarbonate (5 mL) and extracted with dichloromethane (3 x 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification by flash chromatography on deactivated silica gel using hexanes-ethyl acetate (9:1 -> 4:1) as the eluent afforded the sulfone **16** as orange solid (13.6 mg, 18.5 µmol, 70%); spectroscopic data was consistent with that reported above.

(±)-5'-*tert*-Butyl 3'-methyl 5,8'-dichloro-1-tosylspiro[indoline-3,4'-pyrrolo[3',4':3,4]cyclopenta[1,2-*b*]indole]-3',5'(2'*H*)-dicarboxylate (19)

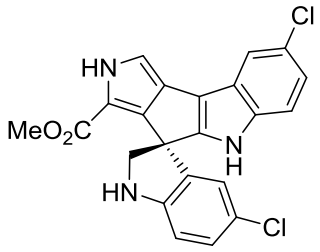


From sulfone (16): To a solution of potassium *tert*-butoxide (1 M in THF, 1.04 mL, 1.04 mmol) in THF (2 mL) at 0 °C was added methyl isocyanoacetate (0.09 mL, 1.03 mmol) and the mixture was stirred for 15 min. A solution of sulfone **16** (187 mg, 0.26 mmol) in THF (1 mL) was then added, and the reaction mixture was warmed to room temperature and stirred for 15 min. The reaction mixture was then quenched by the addition of saturated ammonium chloride (20 mL), and poured onto additional saturated ammonium chloride (50 mL) and extracted with ethyl acetate (3 x 75 mL). The combined organic extracts were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude solid was then triturated with diethyl ether, and the mother liquor was removed by cannula and the remaining colourless solid was dried under vacuum to afford the *title compound* (110 mg, 0.16 mmol, 62%); mp 198-200 °C; ν_{max} (neat)/cm^{-1} 3299, 2980, 1737, 1686, 1598, 1475, 1438, 1347, 1251, 1160, 1141, 1127, 811, 755, 663; δ_H ($CDCl_3$, 500 MHz) 8.91 (1 H, br s, NH), 7.93 (2 H, d, *J* = 8.6 Hz, 2 x ArH), 7.76 (1 H, d, *J* = 8.5 Hz, ArH), 7.62 (1 H, d, *J* = 2.2 Hz,

ArH), 7.53 (1 H, d, *J* = 8.6 Hz, ArH), 7.29 (2 H, d, *J* = 8.5 Hz, 2 x ArH), 7.24 (1 H, dd, *J* = 9.0 and 2.0 Hz, ArH), 7.09 (1 H, dd, *J* = 8.7 and 2.0 Hz, ArH), 6.95 (1 H, d, *J* = 2.9 Hz, ArH), 6.32 (1 H, d, *J* = 2.2 Hz, ArH), 4.76 (1 H, d, *J* = 9.6 Hz, CH of CH_2), 4.57 (1 H, d, *J* = 9.6 Hz, CH of CH_2), 3.78 (3 H, s, Me), 2.40 (3 H, s, Me), 1.27 (9 H, s, 3 x Me); δ_C ($CDCl_3$, 125 MHz) 161.1 (C), 150.2 (C), 148.4 (C), 143.7 (C), 143.6 (C), 143.3 (C), 137.2 (C), 136.3 (C), 133.8 (C), 129.7 (2 x CH), 129.0 (C), 128.2 (CH), 127.5 (2 x CH), 126.7 (C), 124.5 (CH), 123.8 (C), 122.8 (CH), 122.7 (C), 121.3 (C), 119.7 (CH), 117.4 (CH), 117.0 (C), 112.4 (CH), 111.1 (CH), 84.7 (C), 57.1 (CH_2), 53.3 (C), 51.7 (Me), 27.7 (3 x Me), 21.7 (Me); HRMS (ESI, $[M + Na]^+$) found 700.1030. $[C_{34}H_{29}{}^{35}Cl_2N_3O_6S + Na]^+$ requires 700.1046.

From sulfoxide (18): To a solution of potassium *tert*-butoxide (1 M in THF, 0.1 mL, 0.1 mmol) in THF (0.25 mL) at 0 °C was added methyl isocyanoacetate (9 µL, 0.1 mmol) and the mixture was stirred for 15 min. A solution of sulfoxide **18** (20 mg, 0.03 mmol) in THF (0.25 mL) was then added, and the reaction mixture was warmed to room temperature and stirred for 18 h. The reaction mixture was then quenched by the addition of saturated ammonium chloride (5 mL), and extracted with ethyl acetate (3 x 5 mL). The combined organic extracts were washed with brine (100 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel using hexanes-ethyl acetate (9:1 -> 4:1) afforded the title compound (5.8 mg, 8.55 µmol, 31%) as colourless solid. Spectroscopic data was consistent with the above.

(±)-Spiroindimicin C (3)



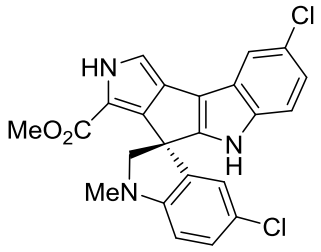
To a solution of **19** (30 mg, 44.2 µmol) in THF (2.5 mL) at -78 °C was added dropwise a freshly prepared* ~0.37 M solution of sodium naphthalenide in THF until a green-yellow colour persisted (after ~0.6 mL). The reaction was then quenched by the addition of saturated ammonium chloride (2 mL) and warmed to room temperature. The whole was poured onto saturated ammonium chloride (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residual naphthalene was then removed by filtration

through a short plug of deactivated silica gel using hexanes-ethyl acetate (1:1) as the eluent, to afford the intermediate indoline as yellow oil.

The indoline was then dissolved in dichloromethane (1.7 mL) and cooled to 0 °C, whereupon aluminium trichloride (9.9 mg, 71.6 µmol) was added in one portion. The solution was then warmed to room temperature and stirred for 30 min. A further portion of aluminium trichloride (5 mg, 36.1 µmol) was added, and the mixture stirred for 5 min and was then quenched by the addition of saturated ammonium chloride (2 mL) and stirred vigorously for 20 min. The mixture was poured onto saturated ammonium chloride (20 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried ($MgSO_4$) filtered and concentrated *in vacuo*. The crude residue was purified by flash chromatography on deactivated silica gel using hexanes-ethyl acetate (2:3) as the eluent to afford the *title compound* (12.6 mg, 29.7 µmol, 67% over 2 steps) as colourless solid; mp 260 °C (decomp); ν_{max} (neat)/cm^{-1} 3444, 3295, 2944, 1704, 1572, 1547, 1475, 1455, 1437, 1287, 1201, 806, 882; δ_H see Table S1 p. S62; δ_C see Table S2 p. S63; HRMS (ESI, $[M + H]^+$) found 424.0605. $[C_{22}H_{15}{}^{35}Cl_2N_3O_2 + H]^+$ requires 424.0614.

**A stock solution of sodium naphthalenide in THF was prepared by dissolving naphthalene (512 mg, 3.99 mmol) in THF (10 mL), to which sodium metal (85 mg, 3.70 mmol) was added in small pieces with vigorous stirring for 30 min until the mixture had formed a homogeneous dark green solution.*

(±)-Spiroindimicin B (2)

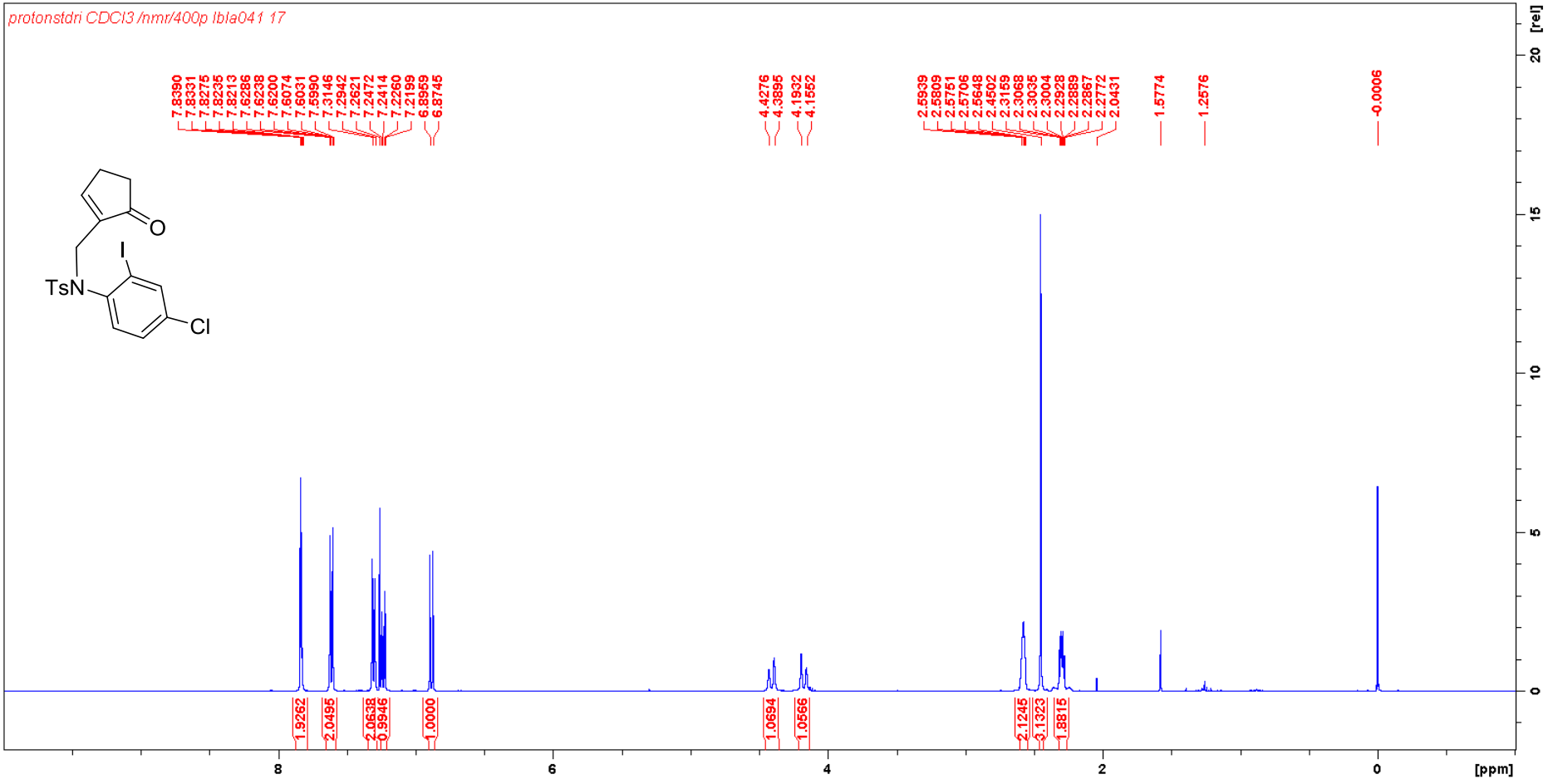


To a solution of **3** (5.6 mg, 13.2 µmol) in methanol (0.3 mL) was added 37% aqueous formaldehyde (2 drops), sodium cyanoborohydride (3 mg, 47.7 µmol), and acetic acid (2 drops) and the mixture stirred at room temperature for 15 min. The mixture was then diluted with ethyl acetate (6 mL), and the whole was poured onto a saturated solution of sodium bicarbonate (20 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were then dried ($MgSO_4$) filtered and concentrated *in vacuo*. The crude residue was purified by preparative TLC using hexanes-ethyl acetate (7:3) as the eluent to afford the *title compound* (5.3 mg, 12.1 µmol, 92%) as colourless solid; mp 120-130 °C; ν_{max} (neat)/cm^{-1} 3297, 2924, 2853, 1687, 1602, 1487, 1441, 1309, 1282, 1196, 1123,

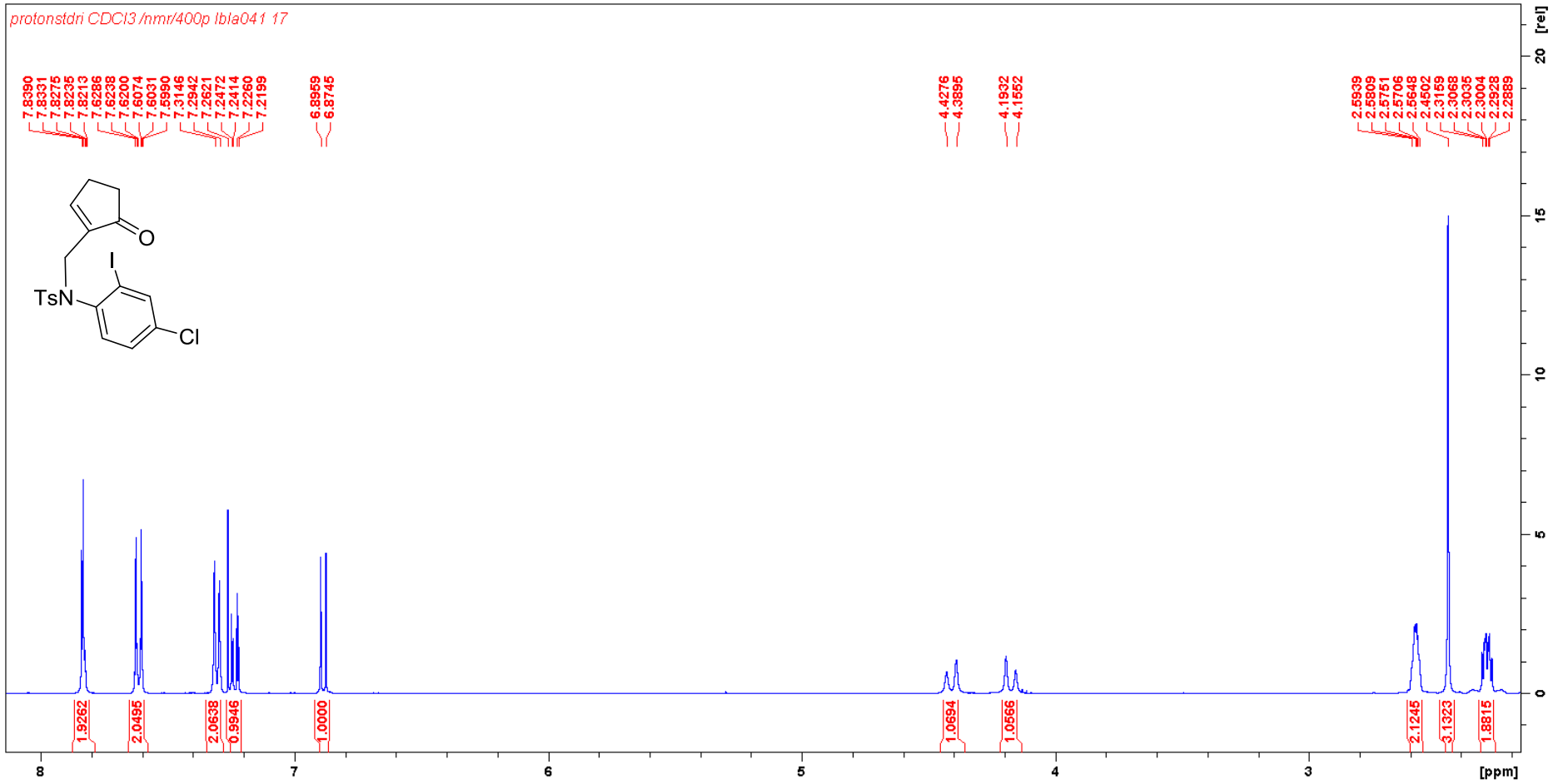
1069, 799, 719; δ_H see Table S3 p. S67, and Table S5 p. S69 ; δ_C see Table S4 p. S68, and Table S6 p. S70; HRMS (ESI, $[M + Na]^+$) found 460.0582. $[C_{23}H_{17}{}^{35}Cl_2N_3O_2 + Na]^+$ requires 460.0590.

3. NMR Spectra

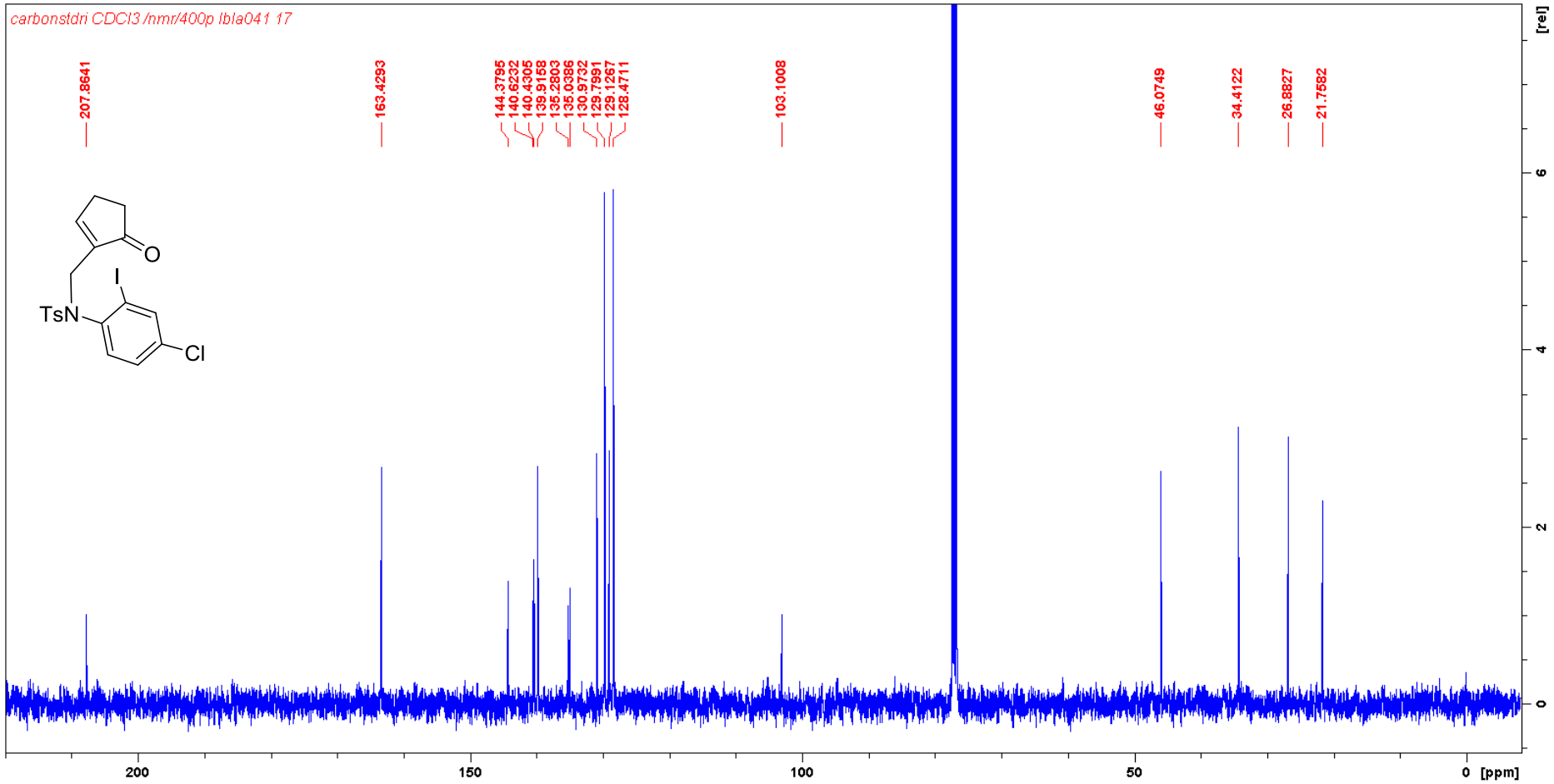
***N*-(4-Chloro-2-iodophenyl)-4-methyl-*N*-((5-oxocyclopent-1-en-1-yl)methyl)benzenesulfonamide (9) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)**



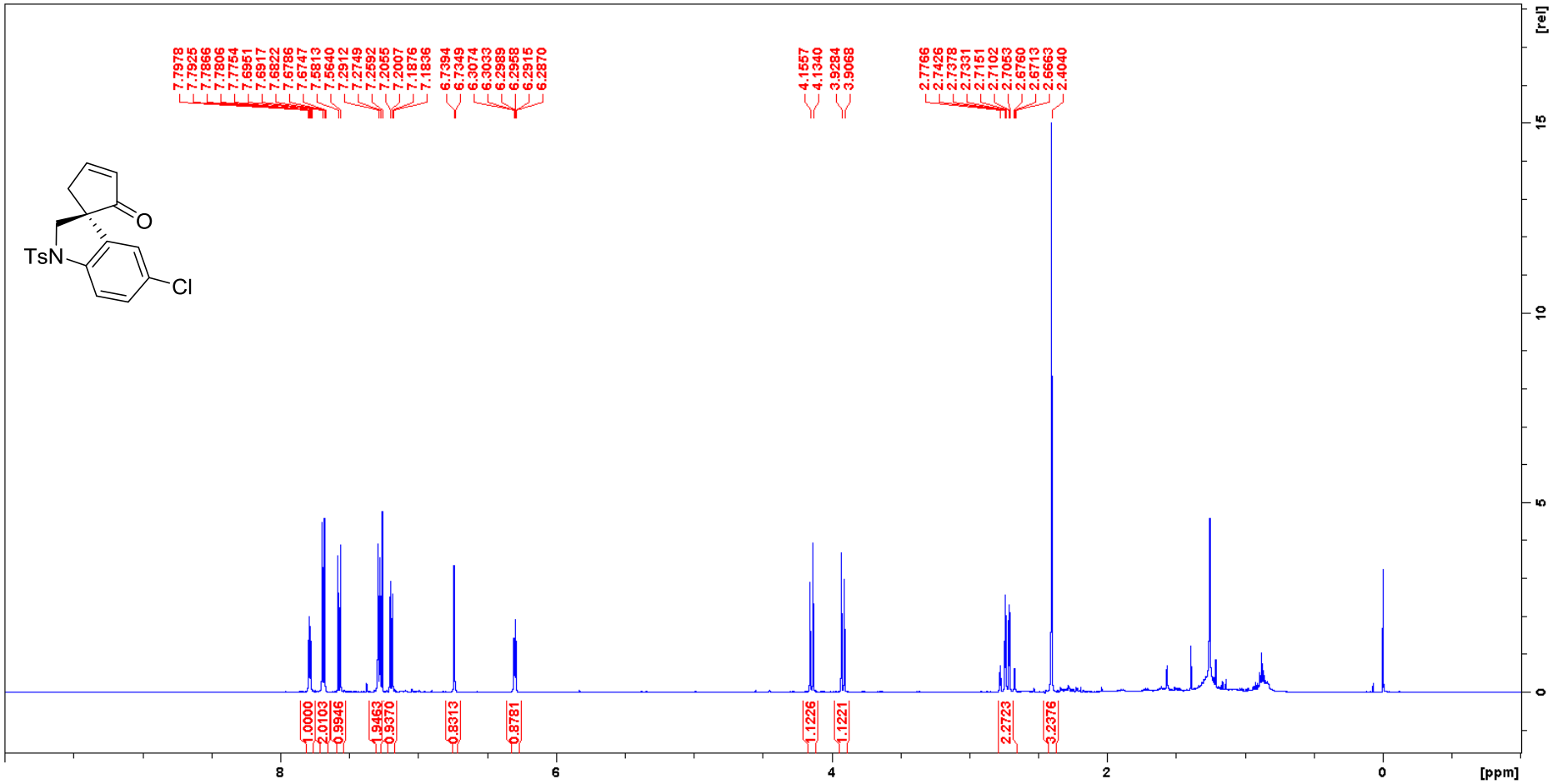
***N*-(4-Chloro-2-iodophenyl)-4-methyl-*N*-((5-oxocyclopent-1-en-1-yl)methyl)benzenesulfonamide (9) ^{1}H NMR spectrum zoom in ($CDCl_3$, 400 MHz)**



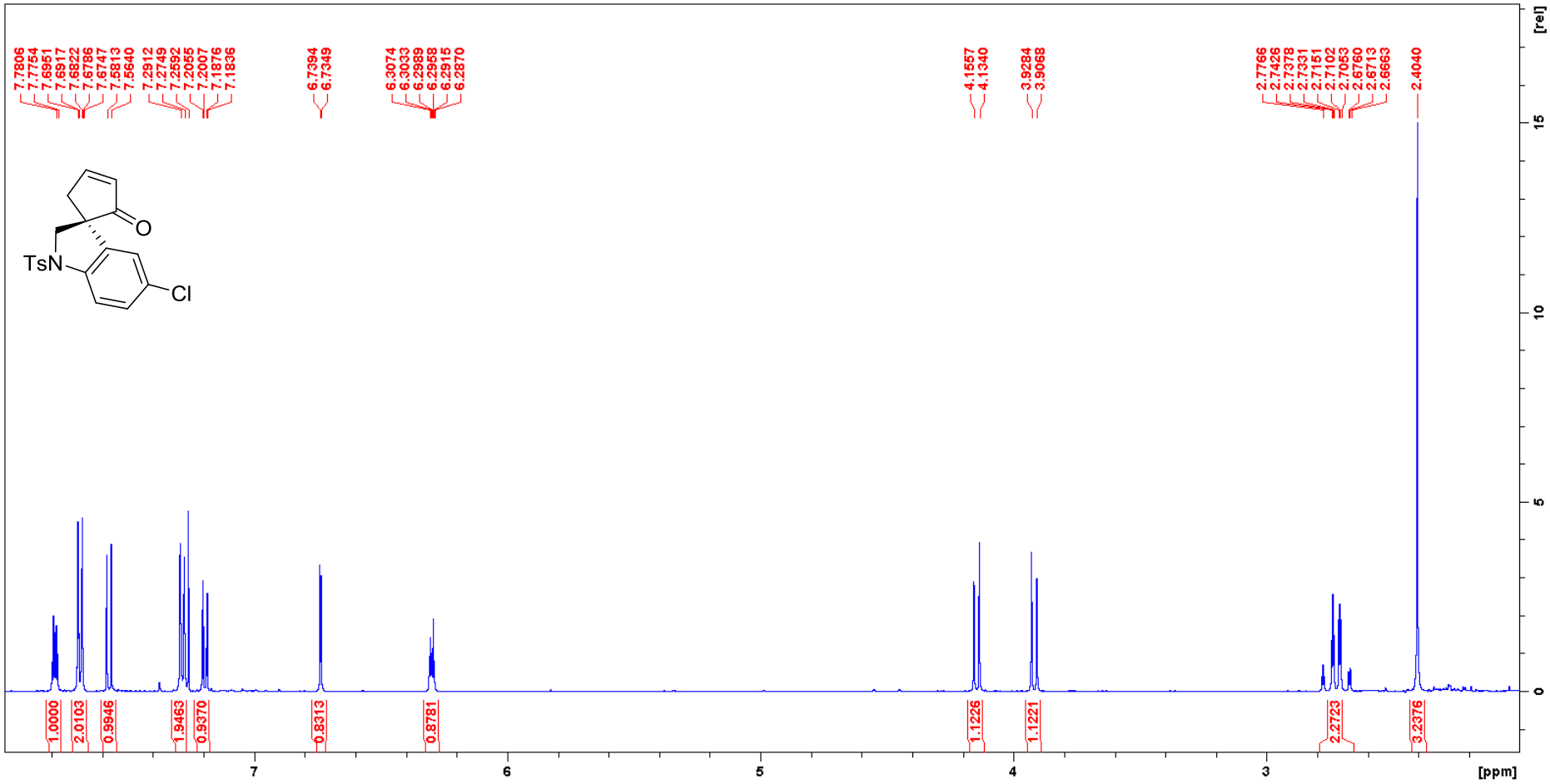
***N*-(4-Chloro-2-iodophenyl)-4-methyl-*N*-((5-oxocyclopent-1-en-1-yl)methyl)benzenesulfonamide (9) ^{13}C NMR spectrum ($CDCl_3$, 100 MHz)**



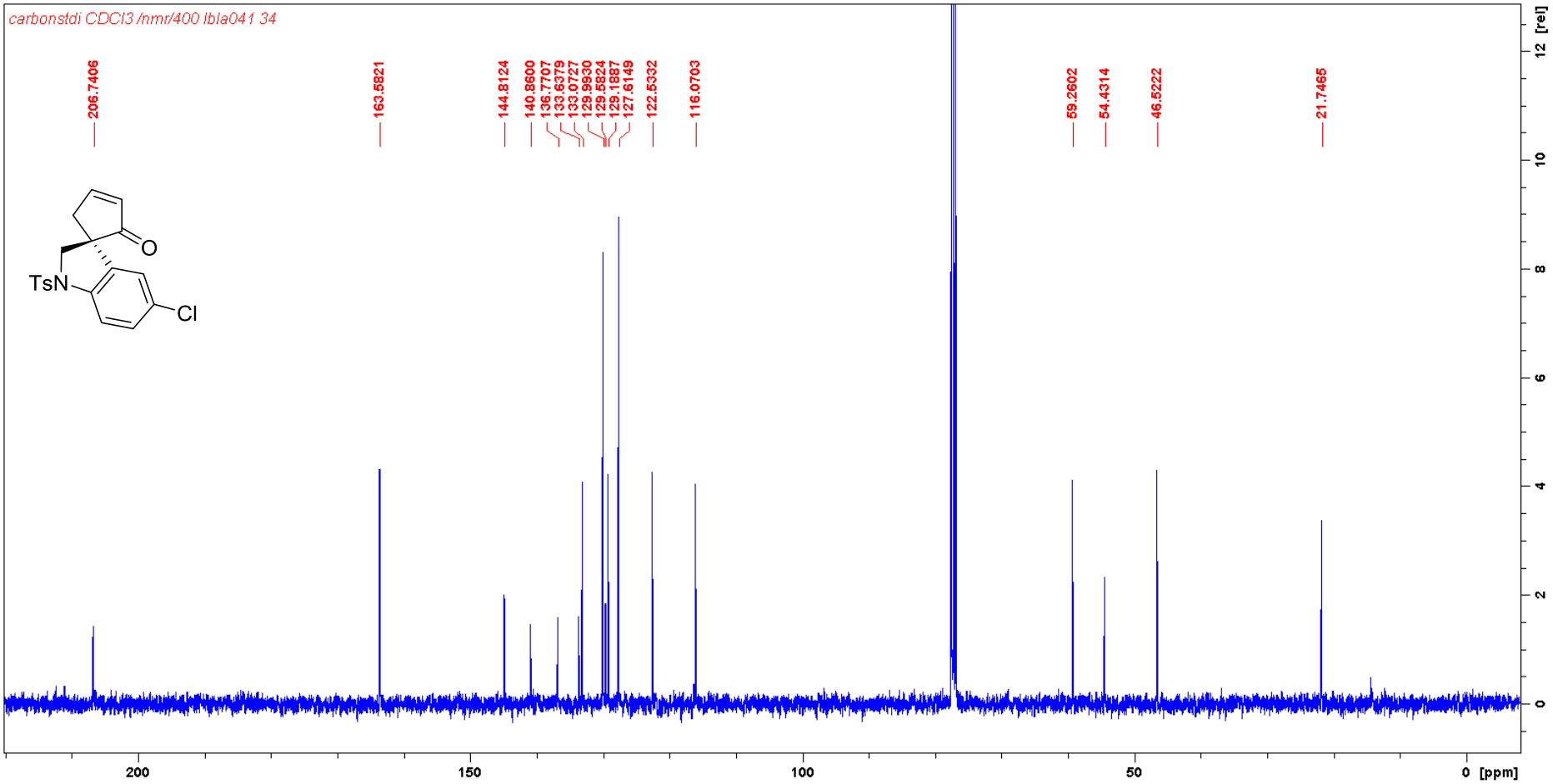
(±)-5'-Chloro-1'-tosylspiro[cyclopent[3]ene-1,3'-indolin]-2-one (12) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



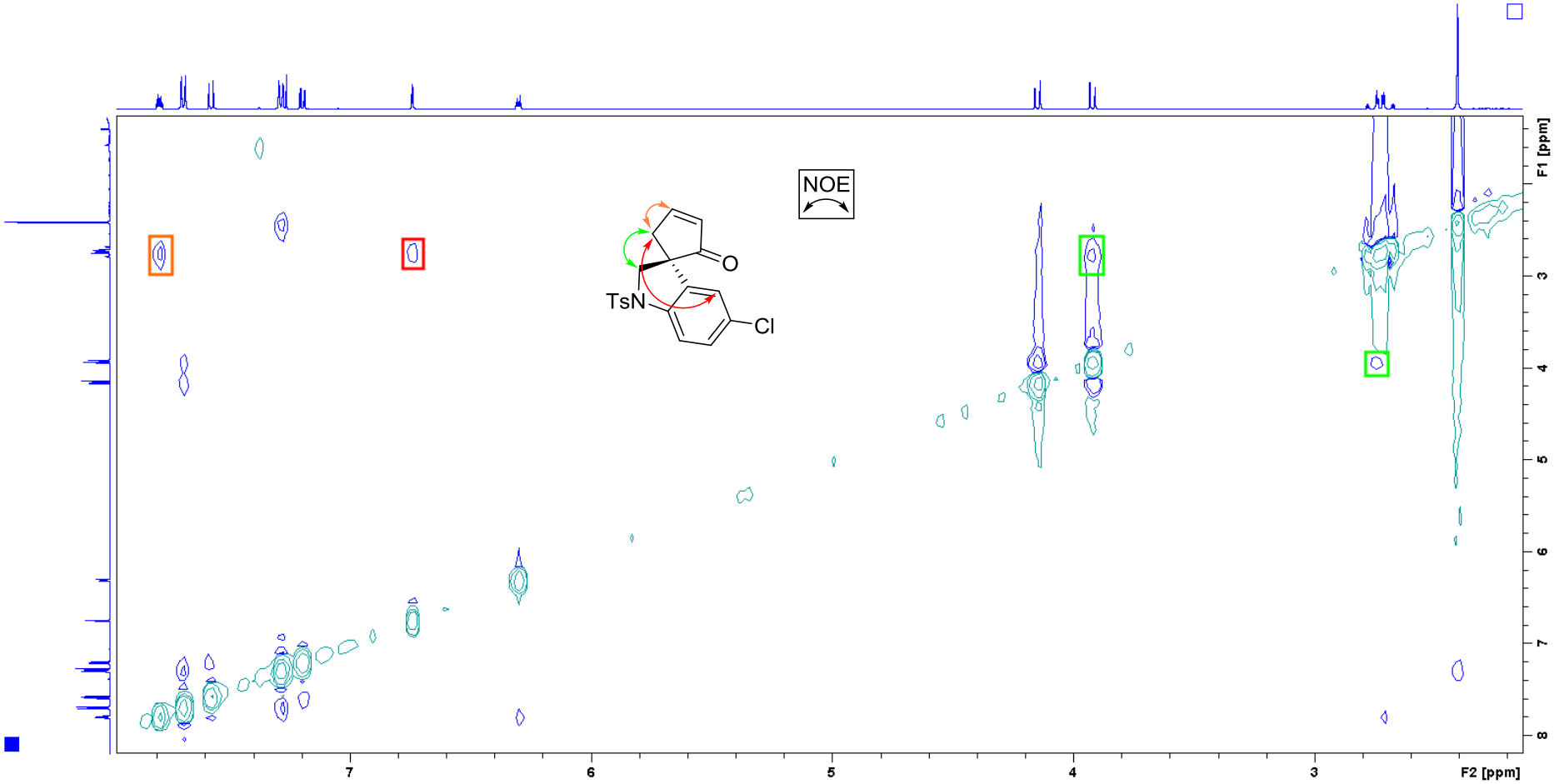
(±)-5'-Chloro-1'-tosylspiro[cyclopent[3]ene-1,3'-indolin]-2-one (12) ^{1}H NMR spectrum zoom in ($CDCl_3$, 500 MHz)



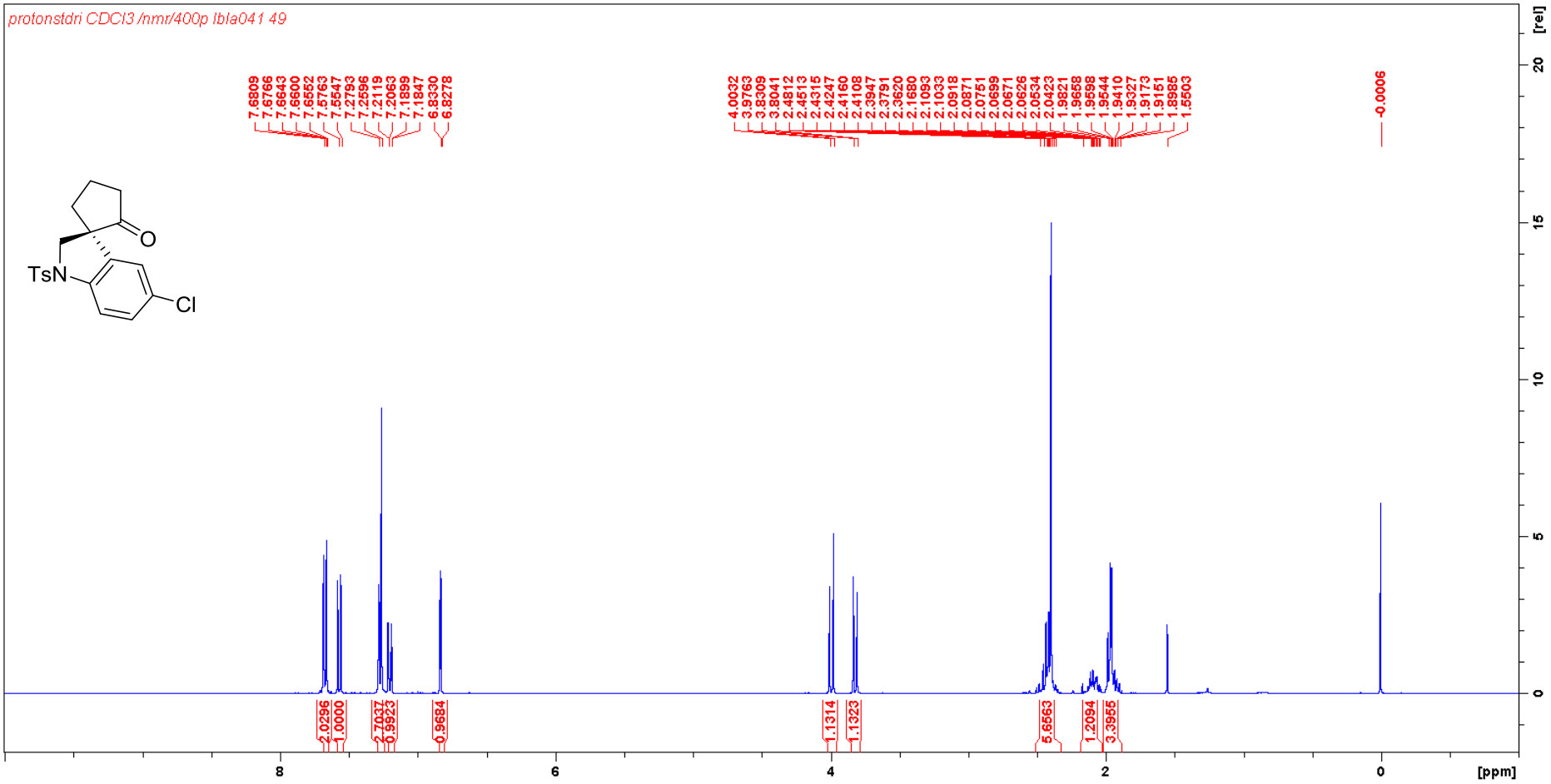
(±)-5'-Chloro-1'-tosylspiro[cyclopent[3]ene-1,3'-indolin]-2-one (12) ^{13}C NMR spectrum ($CDCl_3$, 100 MHz)



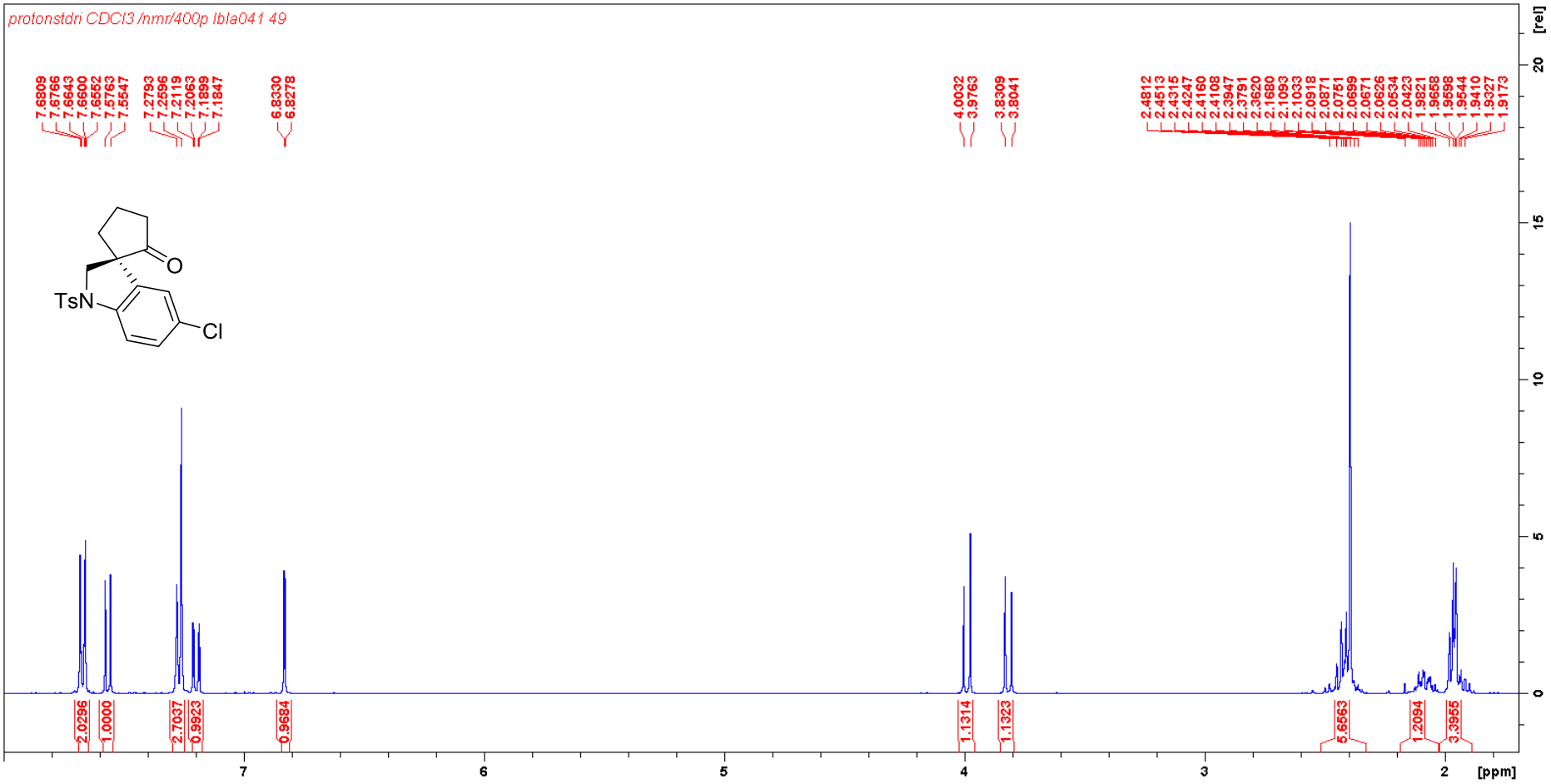
(±)-5'-Chloro-1'-tosylspiro[cyclopent[3]ene-1,3'-indolin]-2-one (12) NOESY spectrum, with key correlations annotated



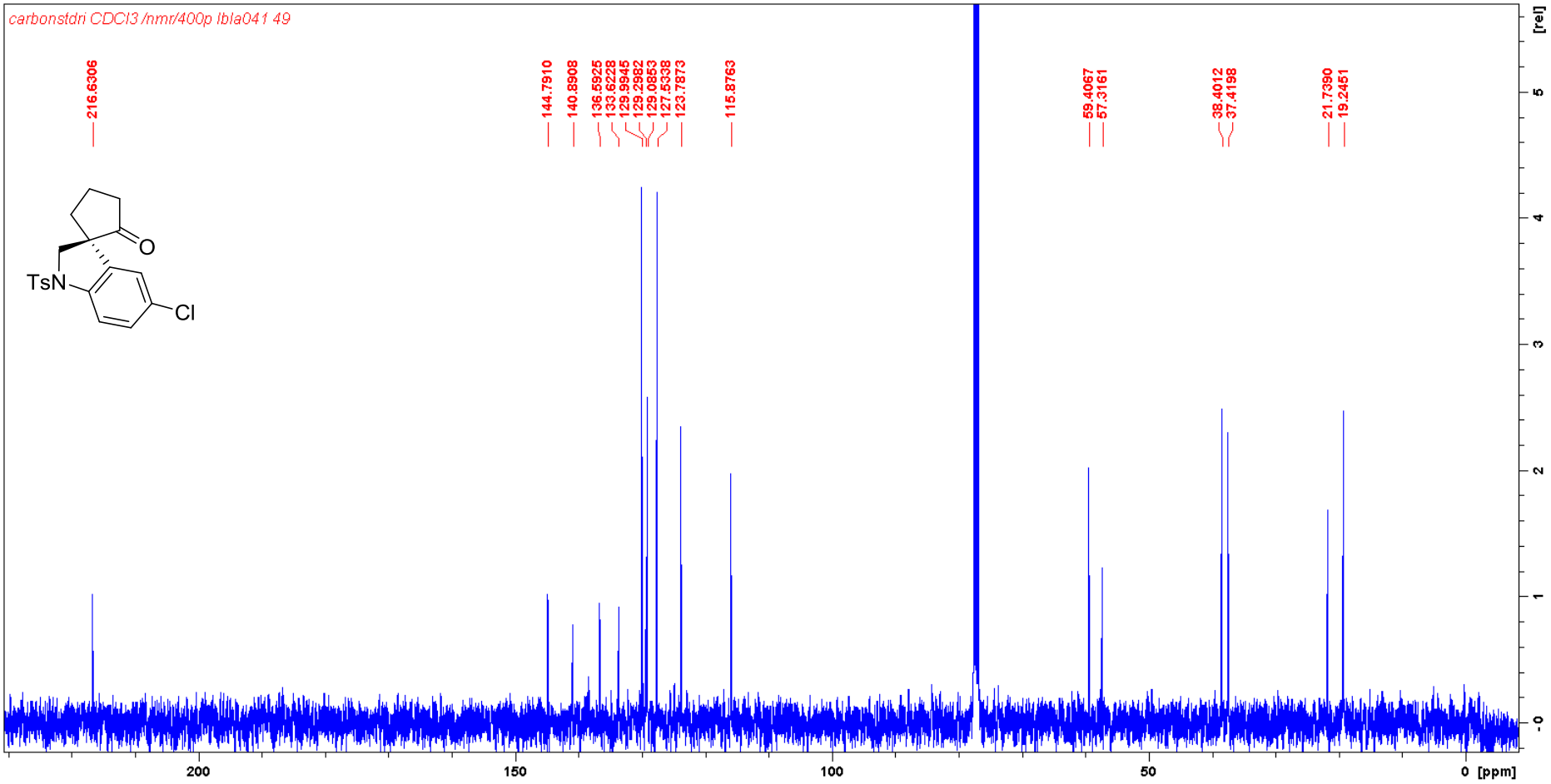
(±)-5'-Chloro-1'-tosylspiro[cyclopentane-1,3'-indolin]-2-one (8) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)



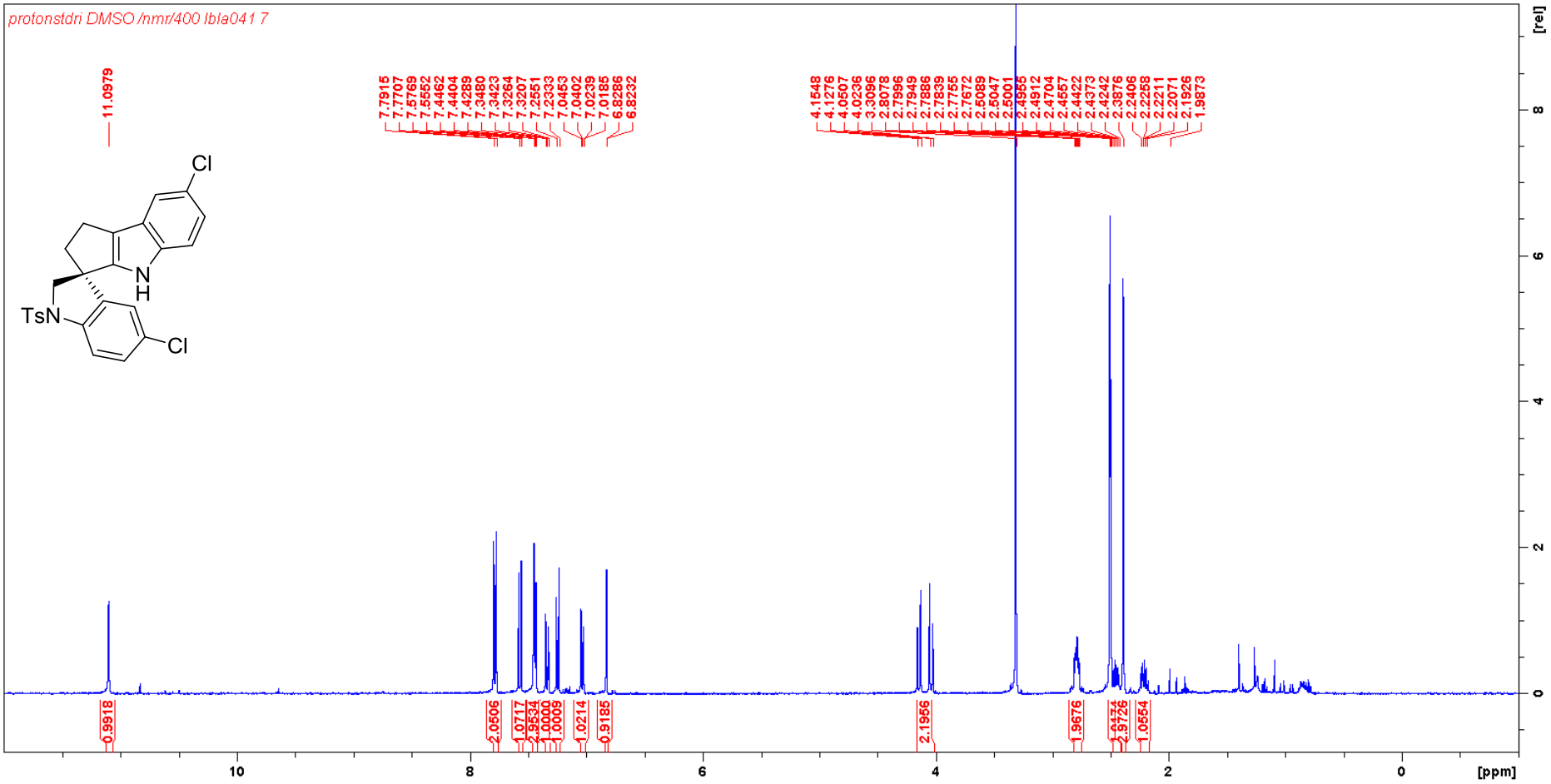
(±)-5'-Chloro-1'-tosylspiro[cyclopentane-1,3'-indolin]-2-one (8) ^{1}H NMR spectrum zoom in ($CDCl_3$, 400 MHz)



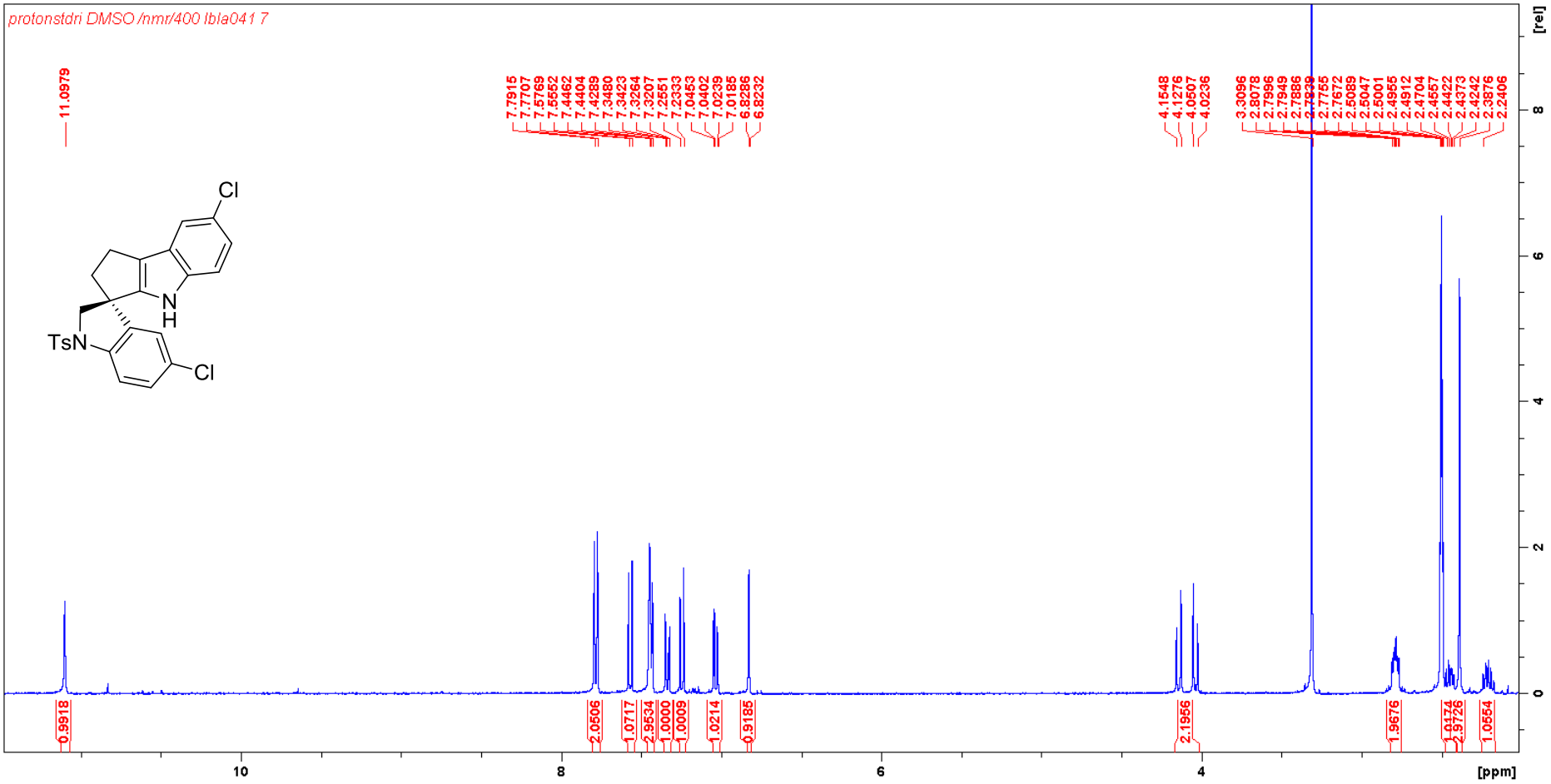
(±)-5'-Chloro-1'-tosylspiro[cyclopentane-1,3'-indolin]-2-one (8) ^{13}C NMR spectrum zoom in ($CDCl_3$, 400 MHz)



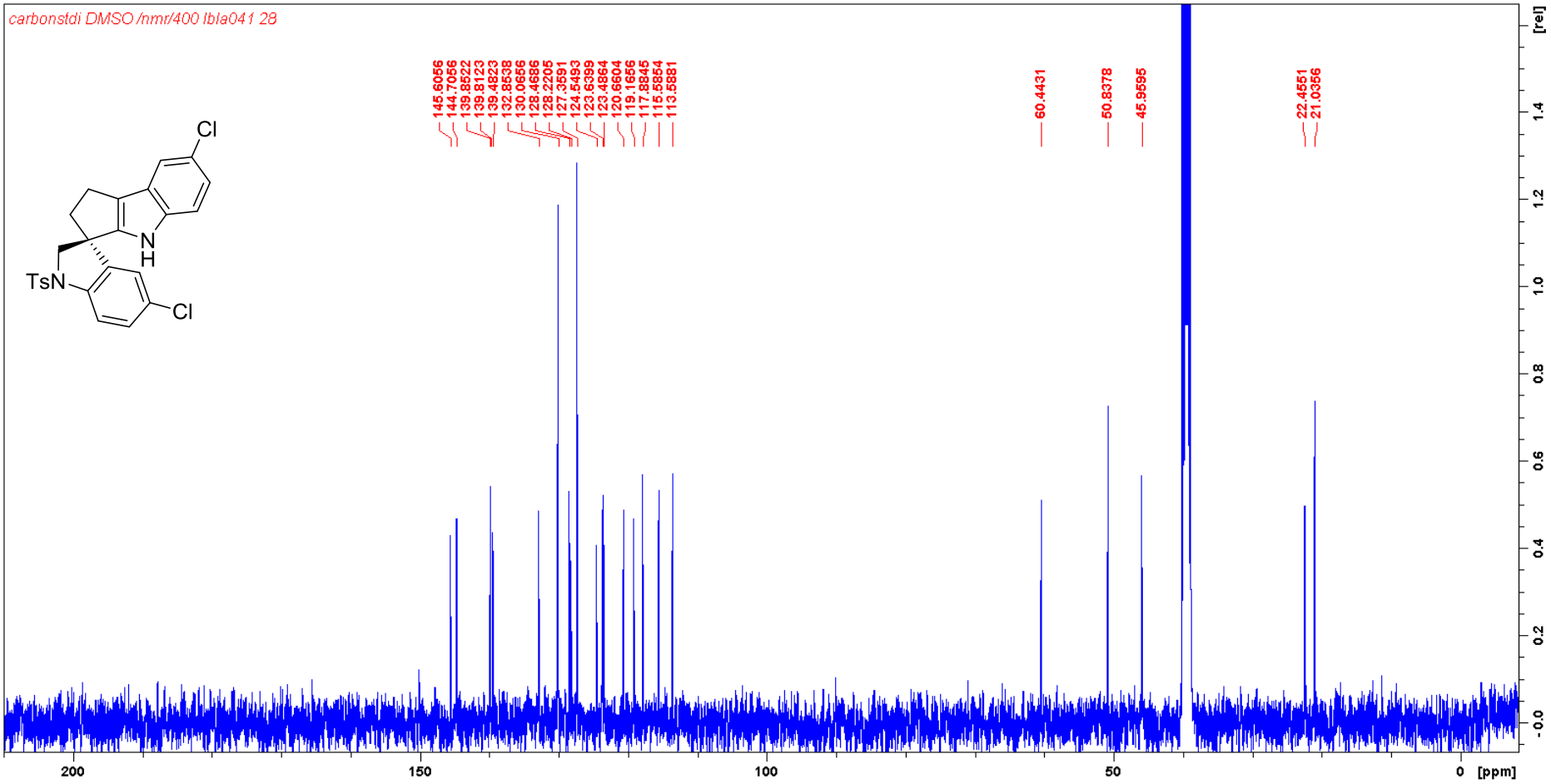
(±)-5',7-Dichloro-1'-tosyl-2,4-dihydro-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline] (7) ^{1}H NMR spectrum (DMSO-d$_6$, 400 MHz)



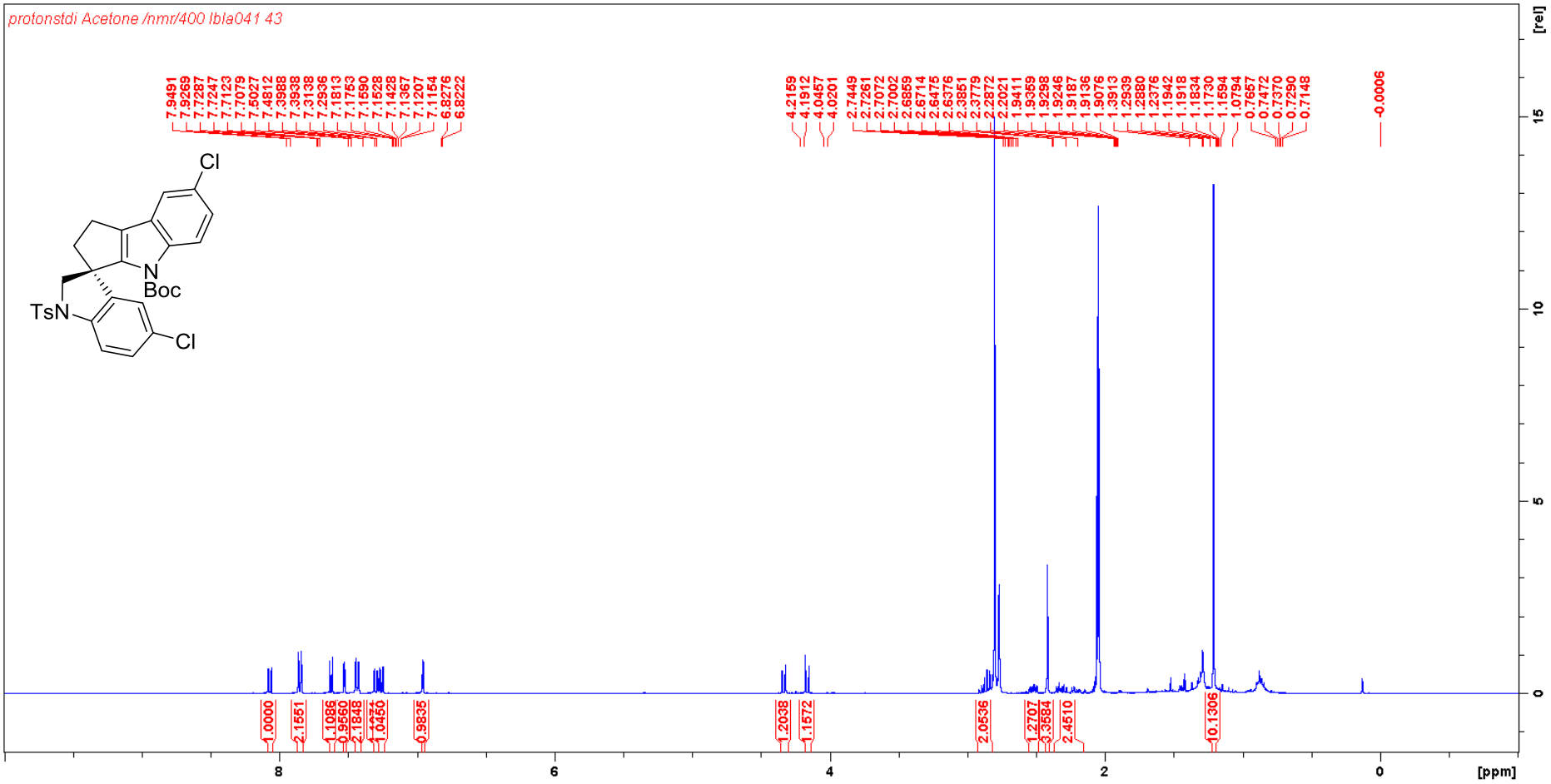
(±)-5',7-Dichloro-1'-tosyl-2,4-dihydro-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline] (7) ^{1}H NMR spectrum zoom in (DMSO-d$_6$, 400 MHz)



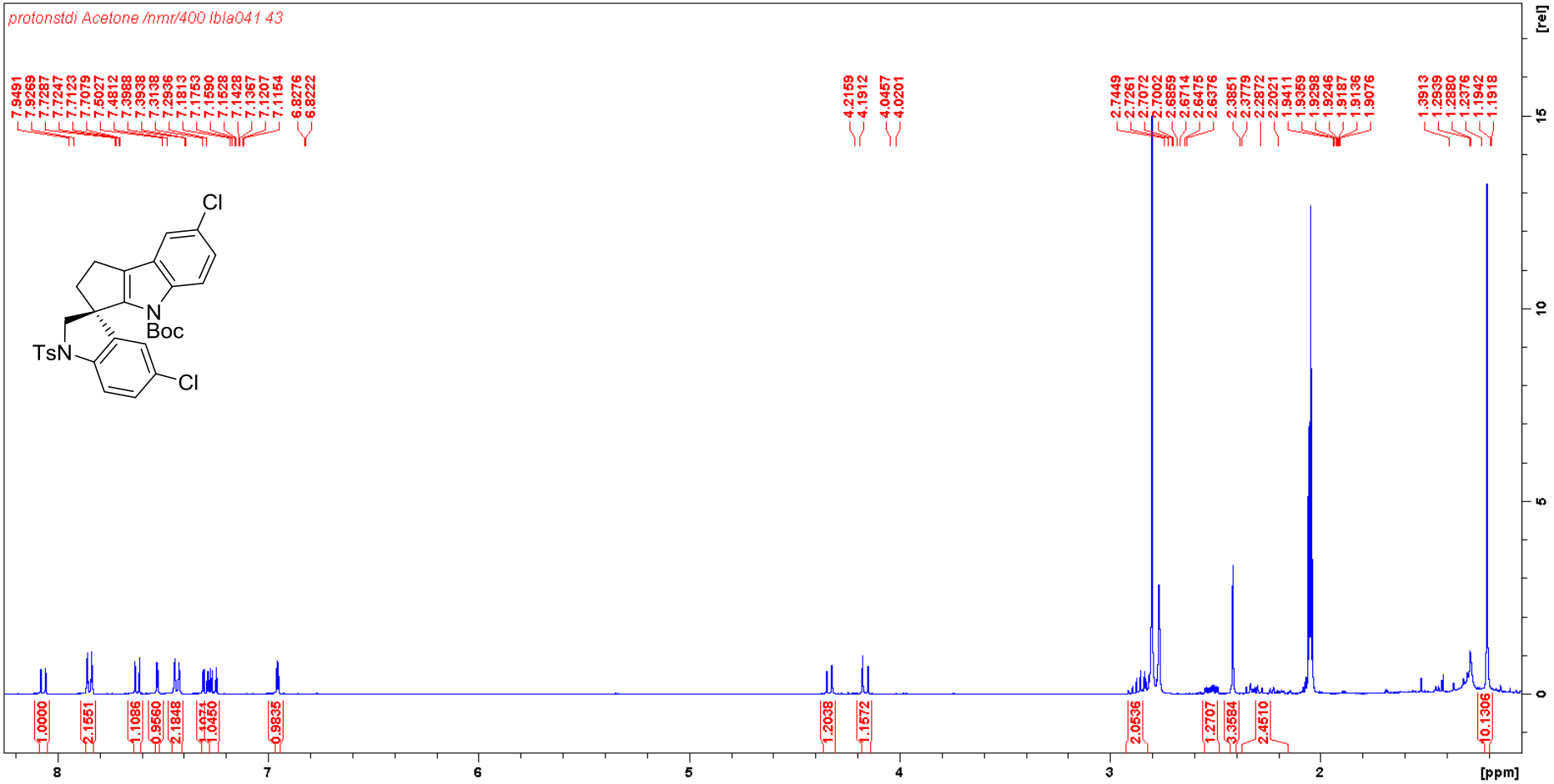
(±)-5',7-Dichloro-1'-tosyl-2,4-dihydro-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline] (7) ^{13}C NMR spectrum (DMSO-d$_6$, 100 MHz)



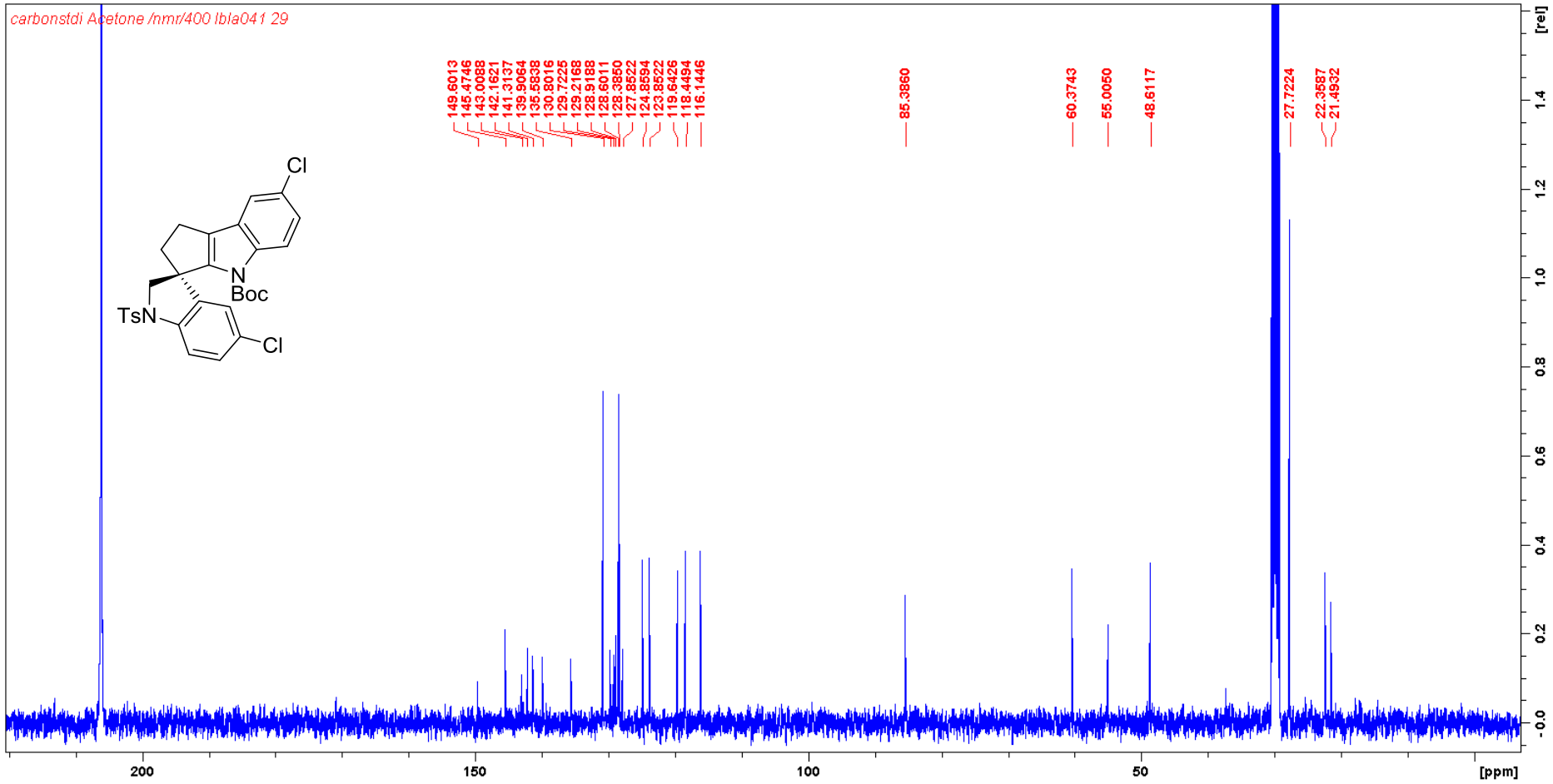
(±)-*tert*-Butyl 5',7-dichloro-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (13) ^{1}H NMR spectrum (acetone-d_6, 400 MHz)



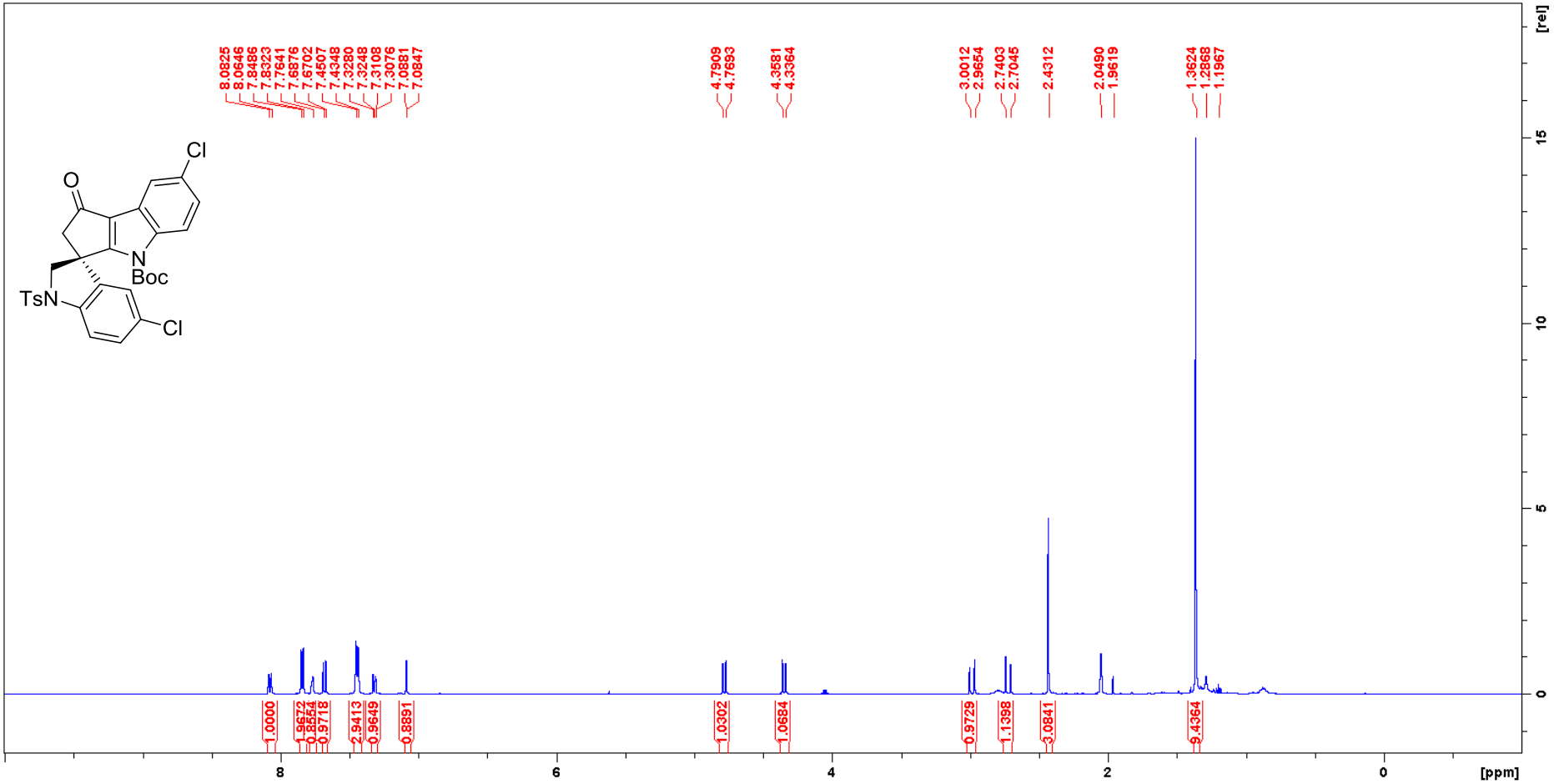
(±)-*tert*-Butyl 5',7-dichloro-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (13) ^{1}H NMR spectrum zoom in (acetone-d$_6$, 400 MHz)



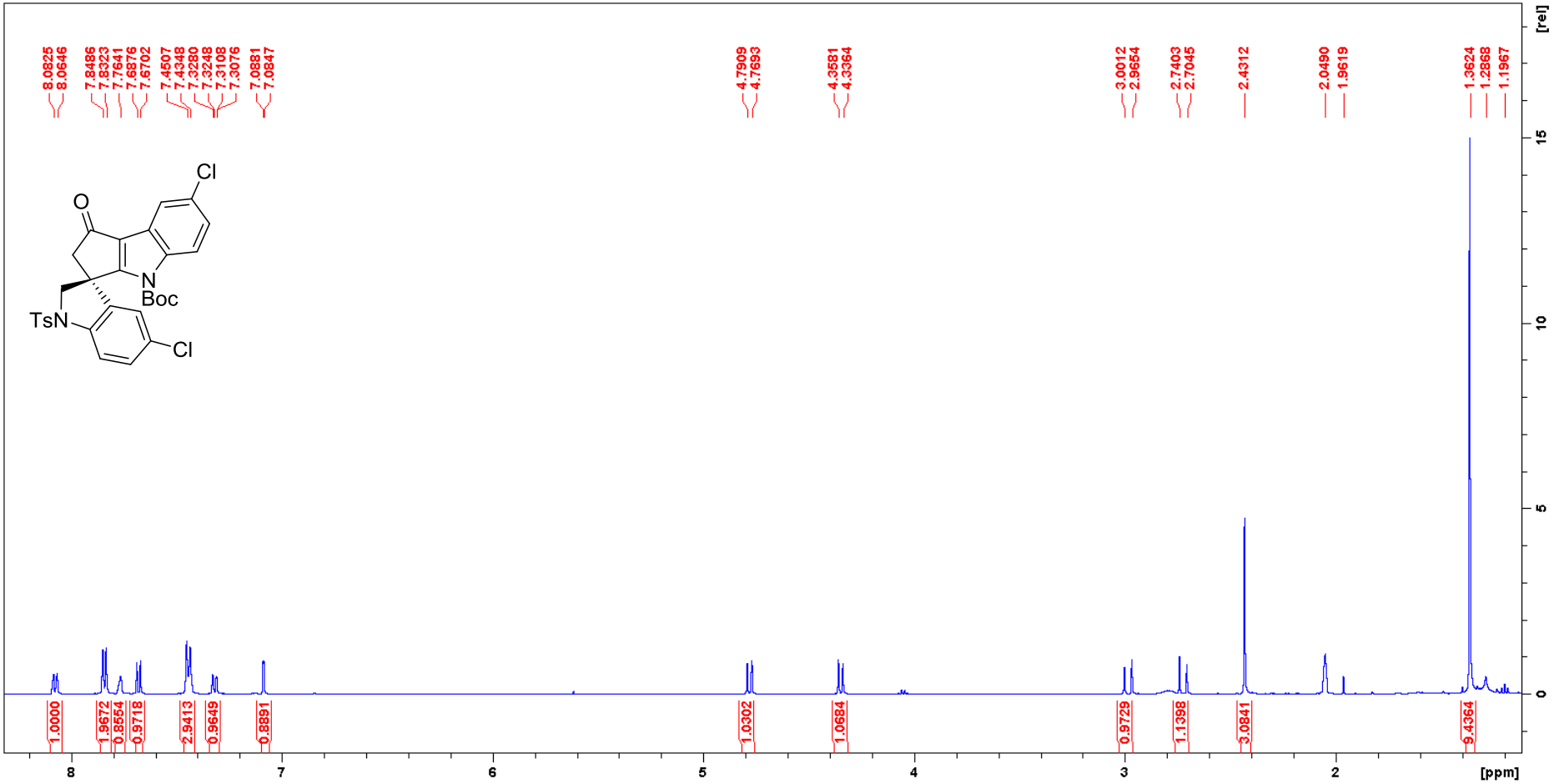
(±)-*tert*-Butyl 5',7-dichloro-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (13) ^{13}C NMR spectrum (acetone-d_6, 100 MHz)



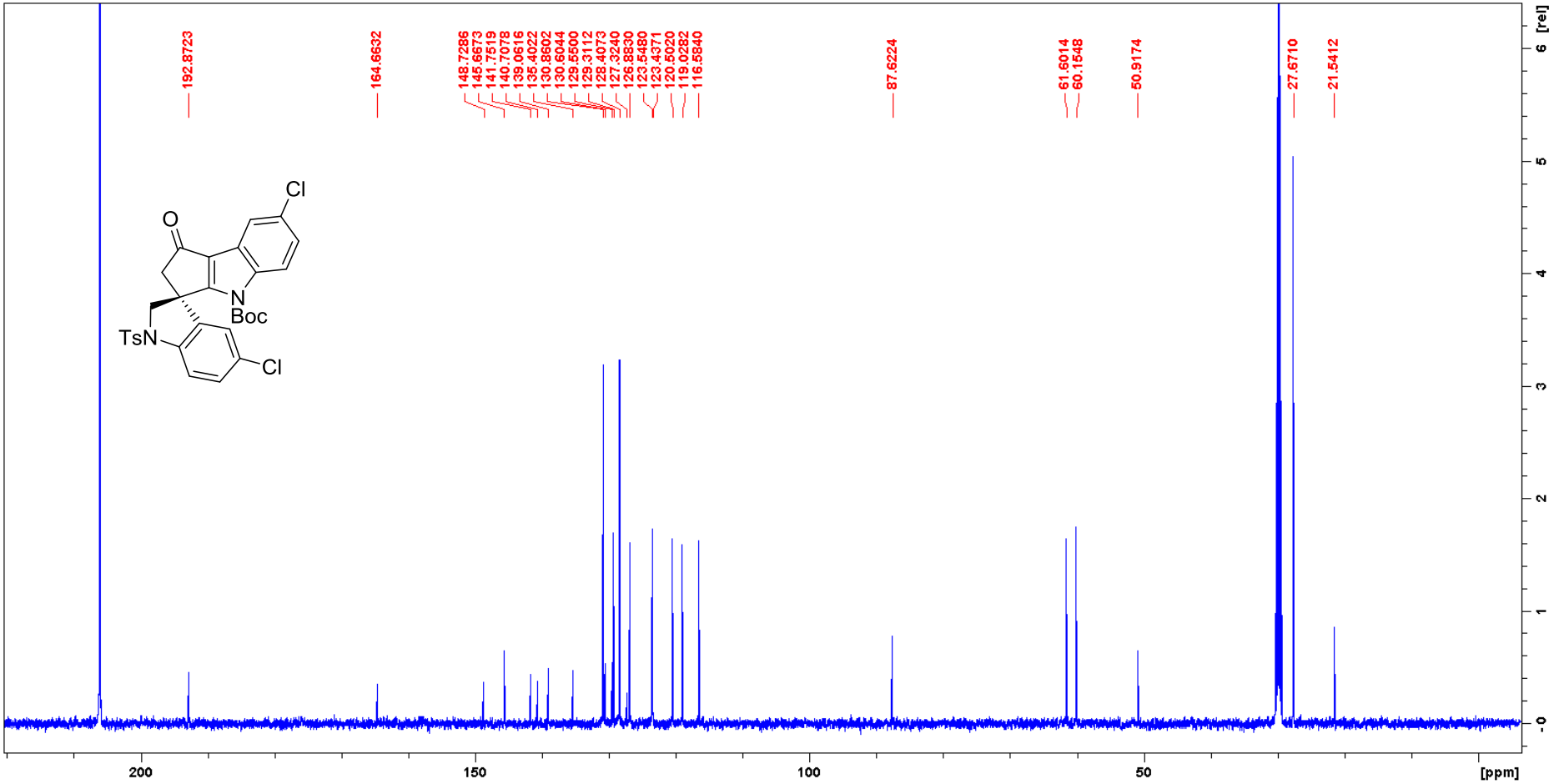
(±)-*tert*-Butyl 5',7-dichloro-1-oxo-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (15) ^{1}H NMR spectrum (acetone-d_6, 500 MHz)



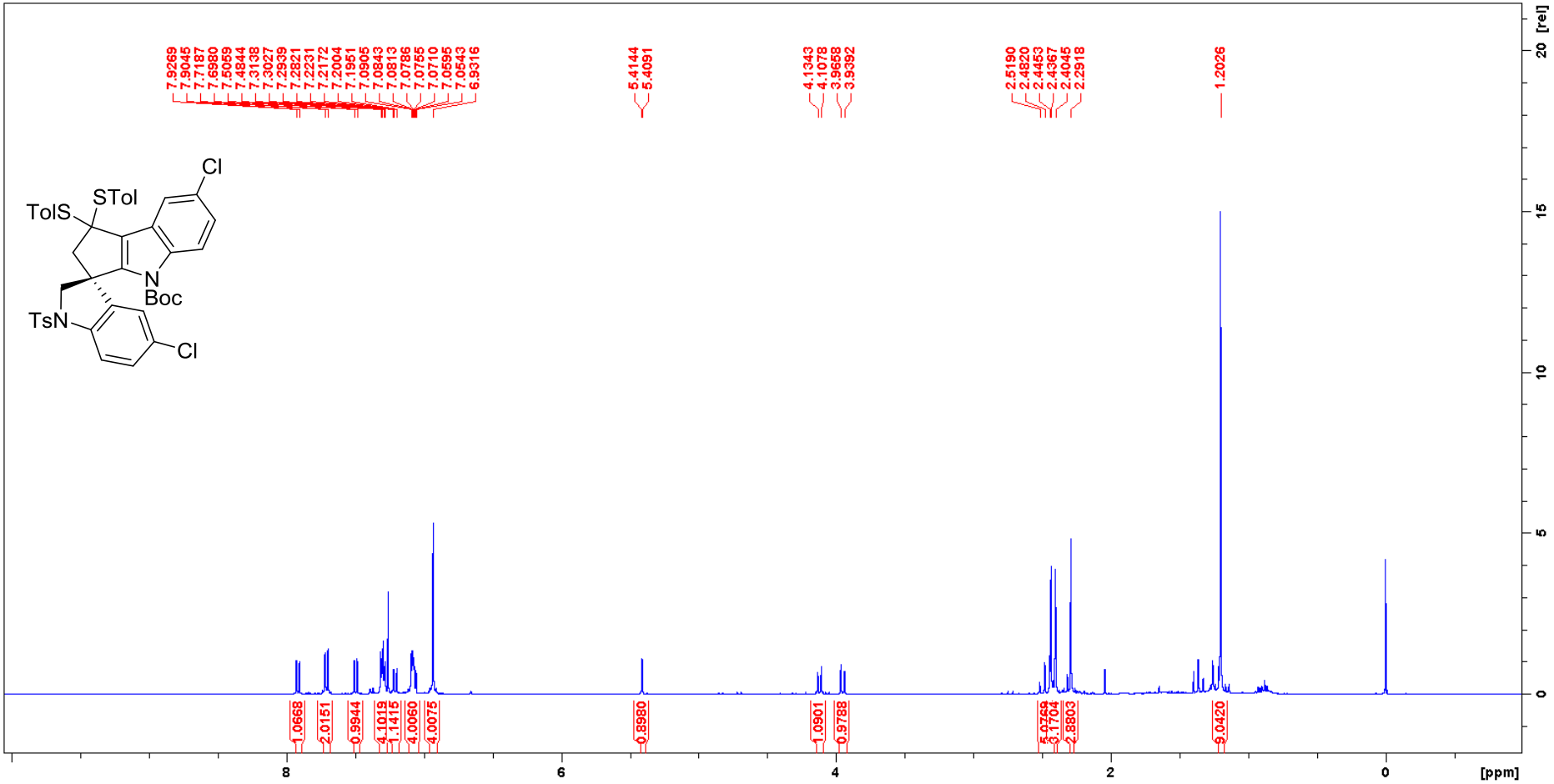
(±)-*tert*-Butyl 5',7-dichloro-1-oxo-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (15) ^{1}H NMR spectrum zoom in (acetone-d$_6$, 500 MHz)



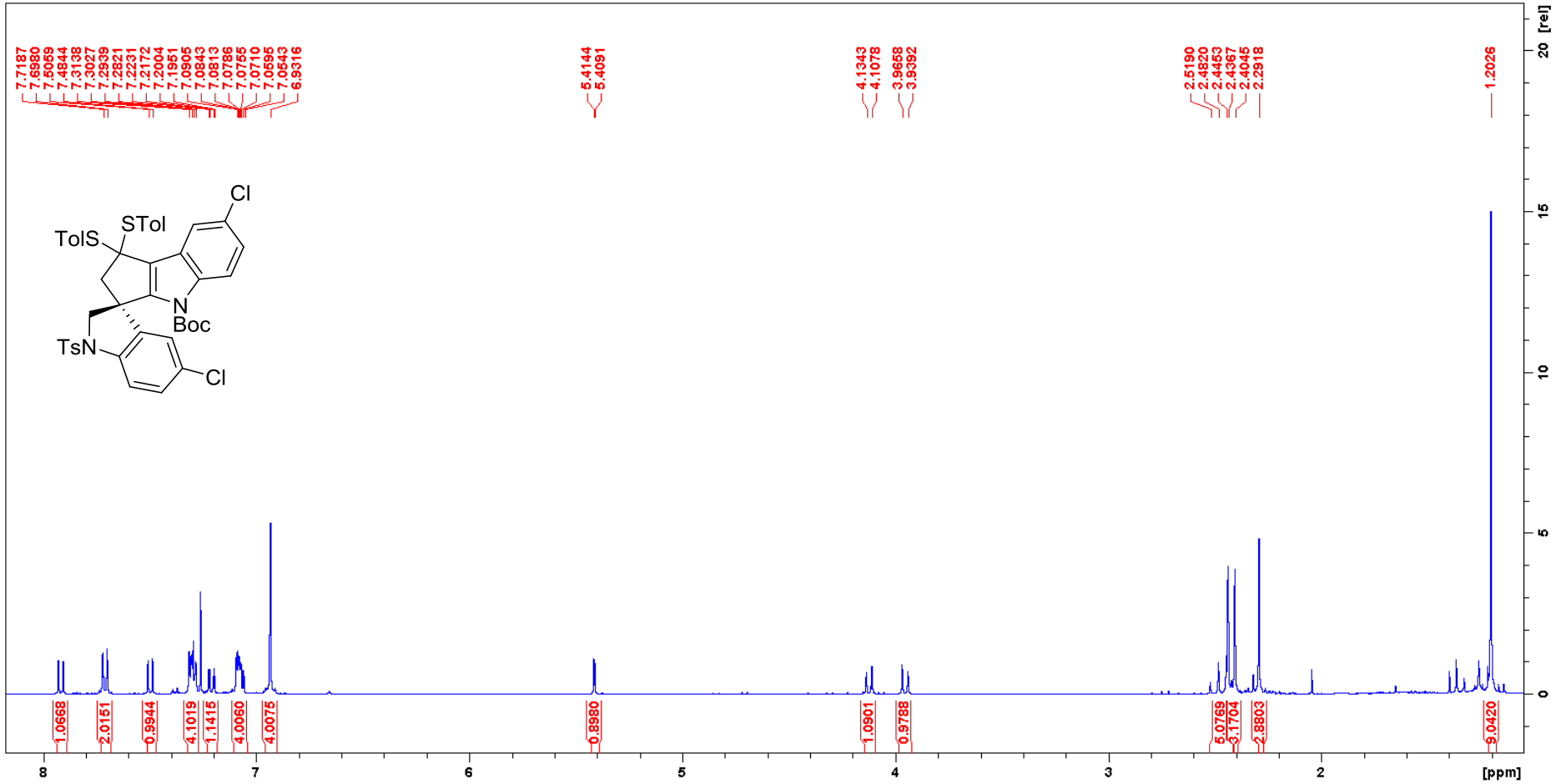
(±)-*tert*-Butyl 5',7-dichloro-1-oxo-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (15) ^{13}C NMR spectrum (acetone-d$_6$, 125 MHz)



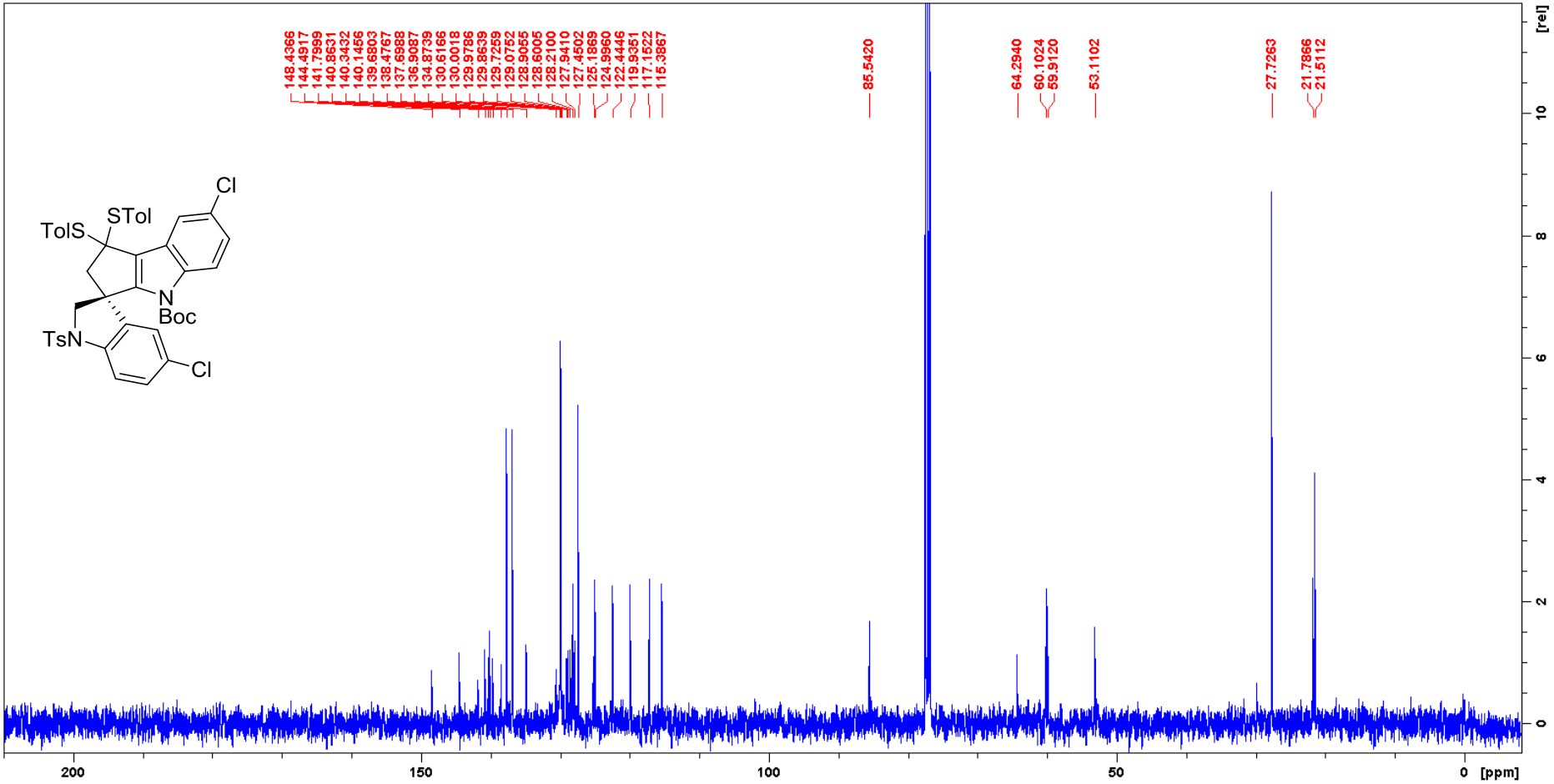
(±)-*tert*-Butyl 5',7-dichloro-1,1-bis(*p*-tolylthio)-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (17) ^{1}H NMR spectrum ($CDCl_3$, 400 MHz)



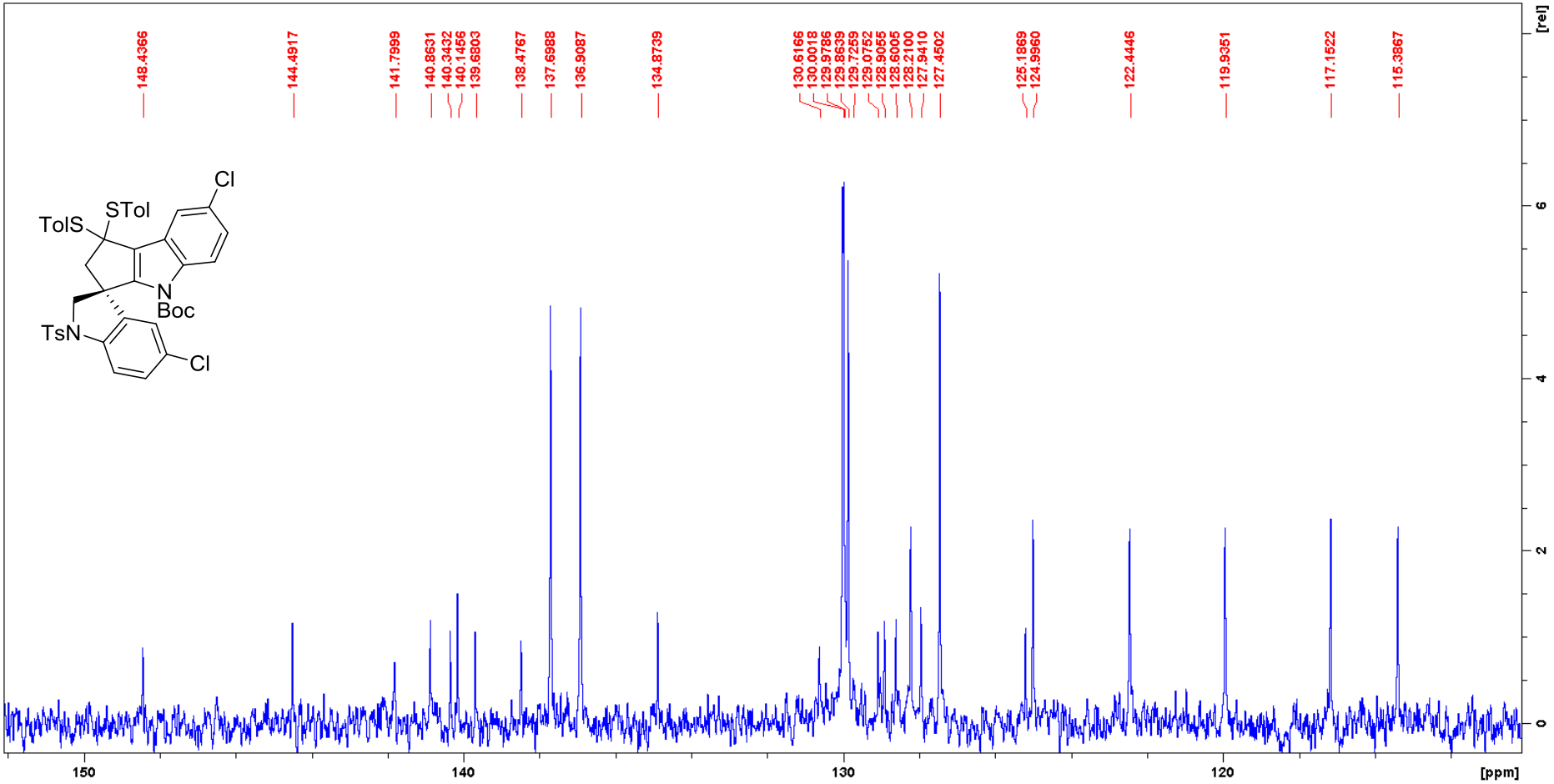
(±)-*tert*-Butyl 5',7-dichloro-1,1-bis(*p*-tolylthio)-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (17) ^{1}H NMR spectrum zoom in ($CDCl_3$, 400 MHz)



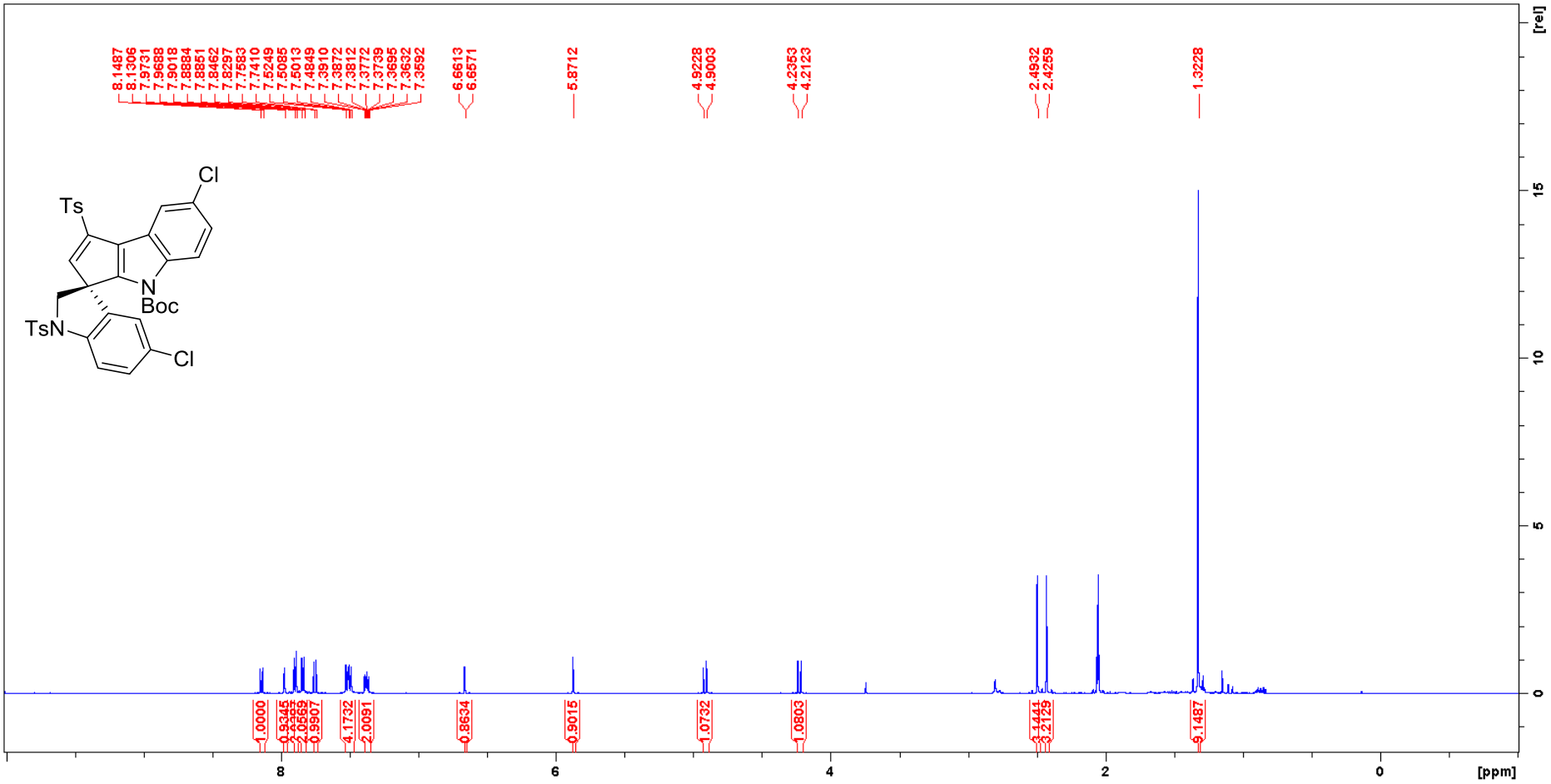
(±)-*tert*-Butyl 5',7-dichloro-1,1-bis(*p*-tolylthio)-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (17) ^{13}C NMR spectrum ($CDCl_3$, 100 MHz)



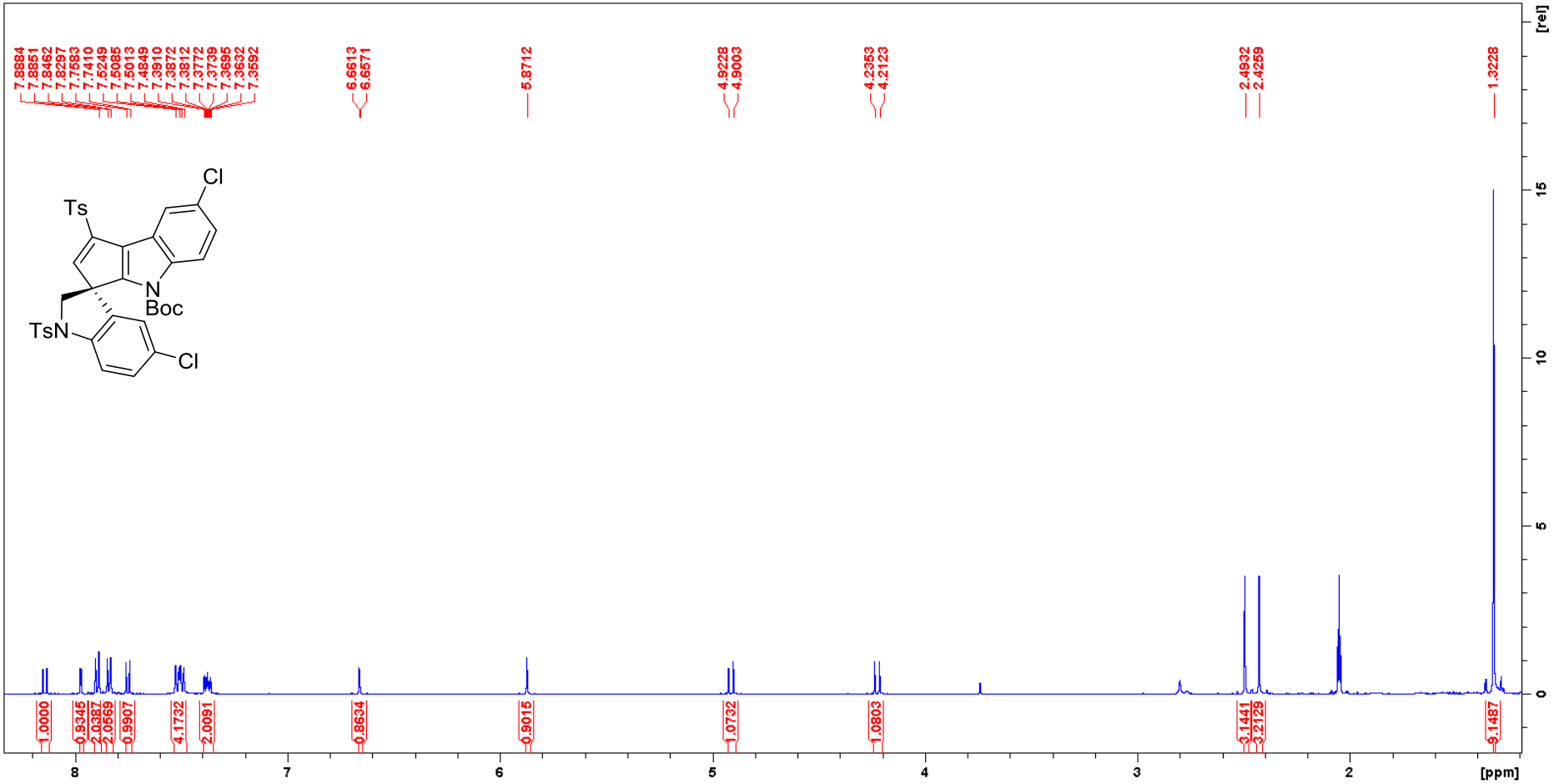
(±)-*tert*-Butyl 5',7-dichloro-1,1-bis(*p*-tolylthio)-1'-tosyl-1*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4(2*H*)-carboxylate (17) ^{13}C NMR spectrum zoom in ($CDCl_3$, 100 MHz)



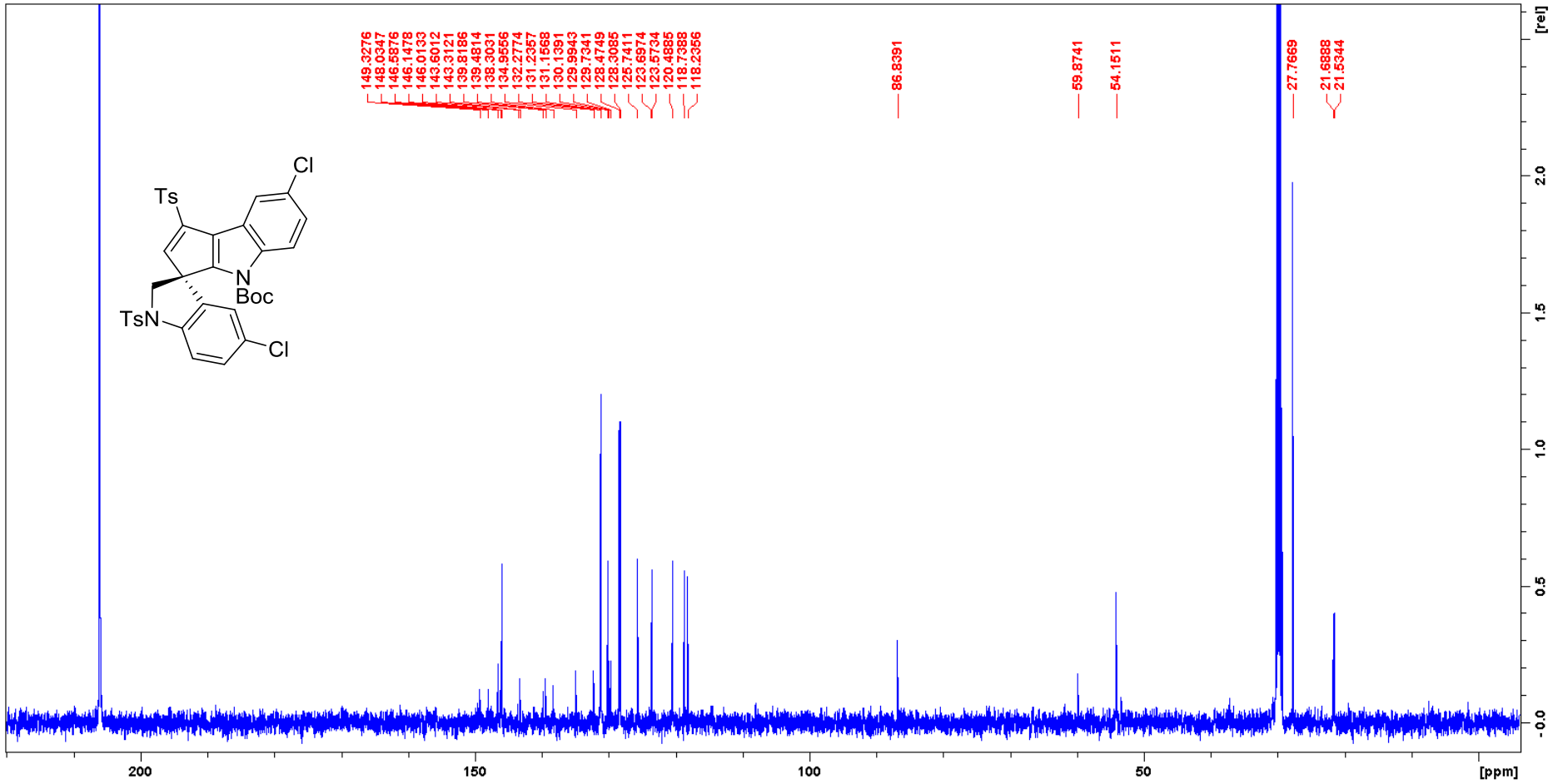
(±)-*tert*-Butyl 5',7-dichloro-1,1'-ditosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (16) ^{1}H NMR spectrum (acetone-d_6, 500 MHz)



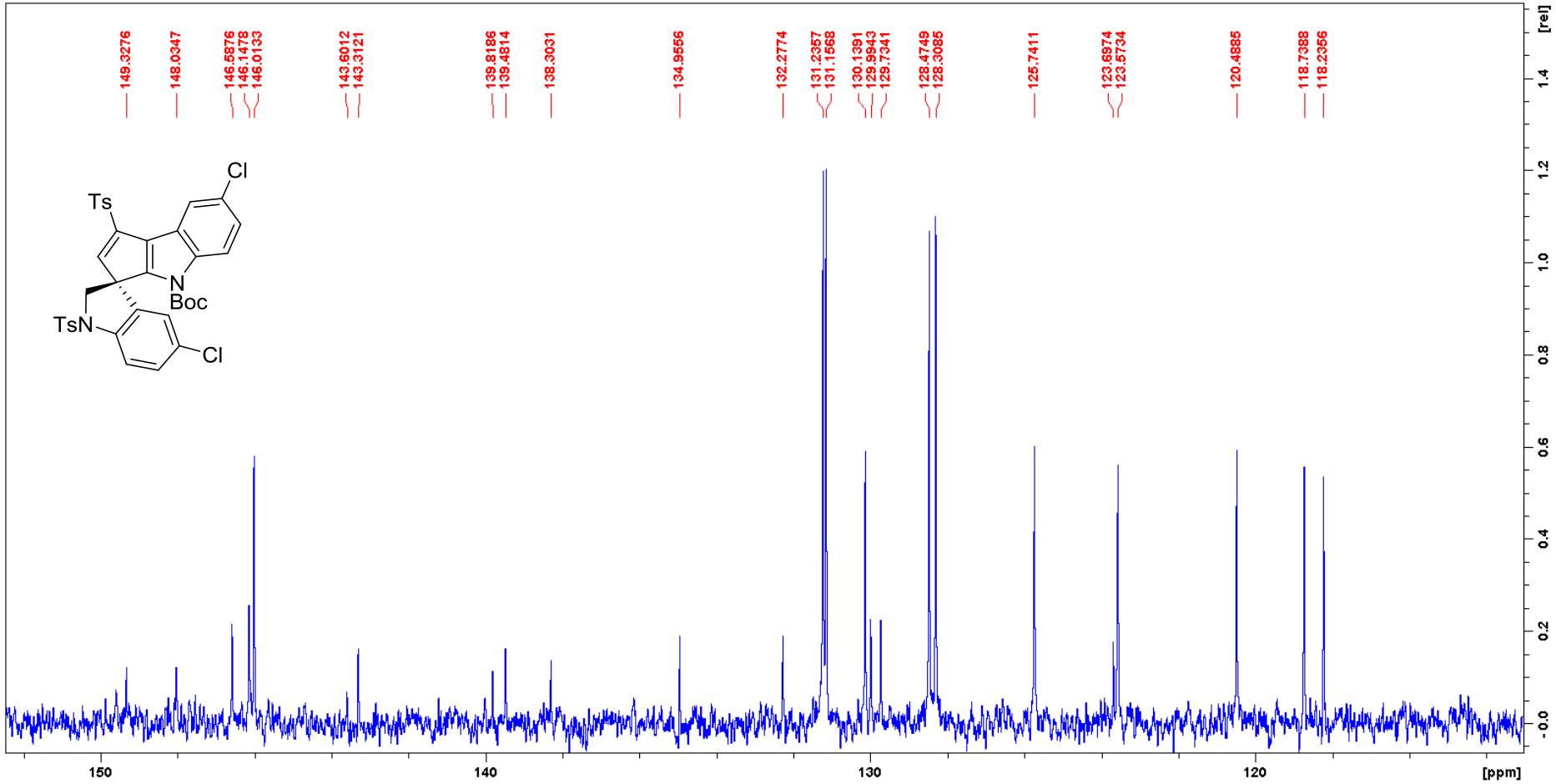
(±)-*tert*-Butyl 5',7-dichloro-1,1'-ditosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (16) ^{1}H NMR spectrum zoom in (acetone-d_6, 500 MHz)



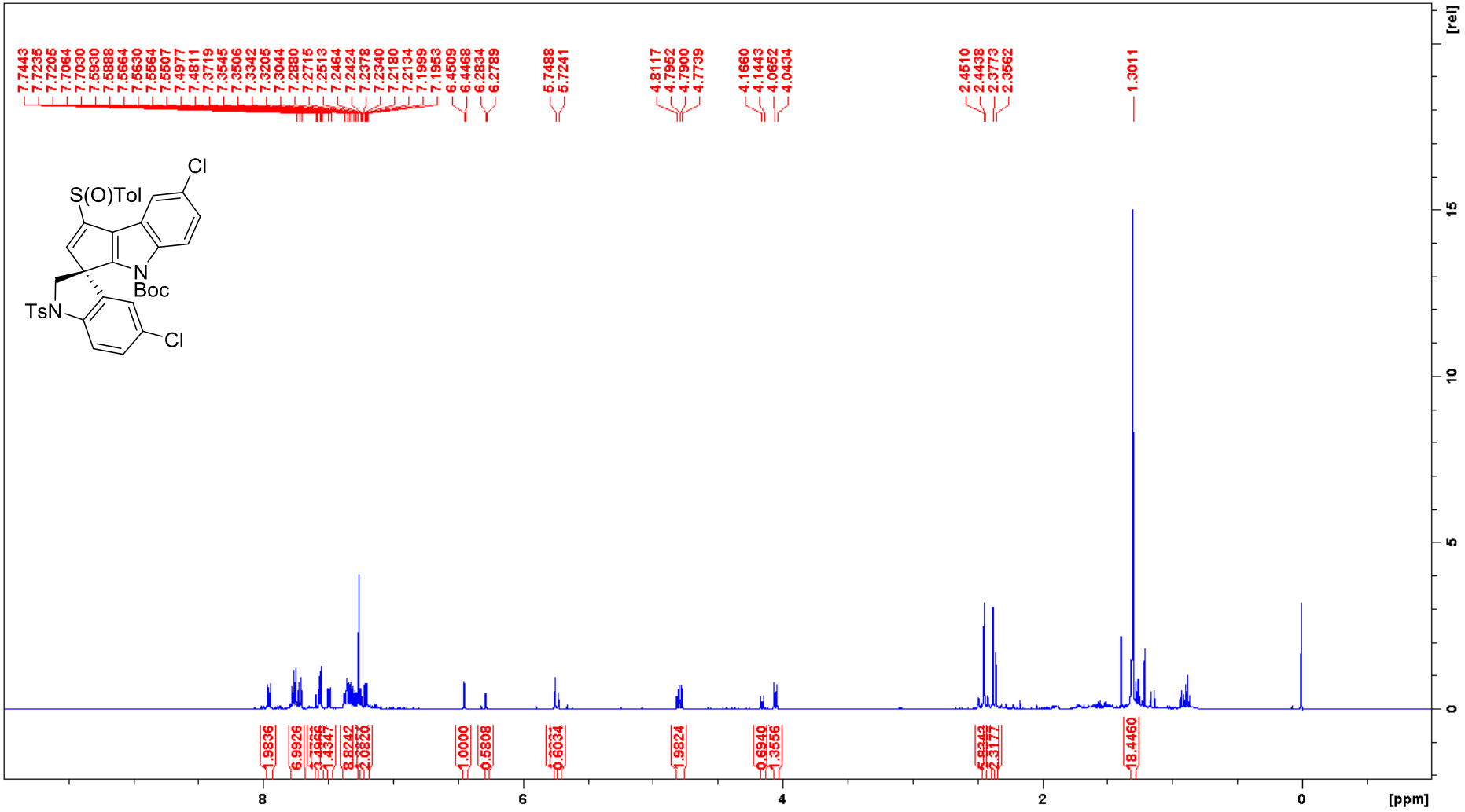
(±)-*tert*-Butyl 5',7-dichloro-1,1'-ditosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (16) ^{13}C NMR spectrum (acetone-d_6, 125 MHz)



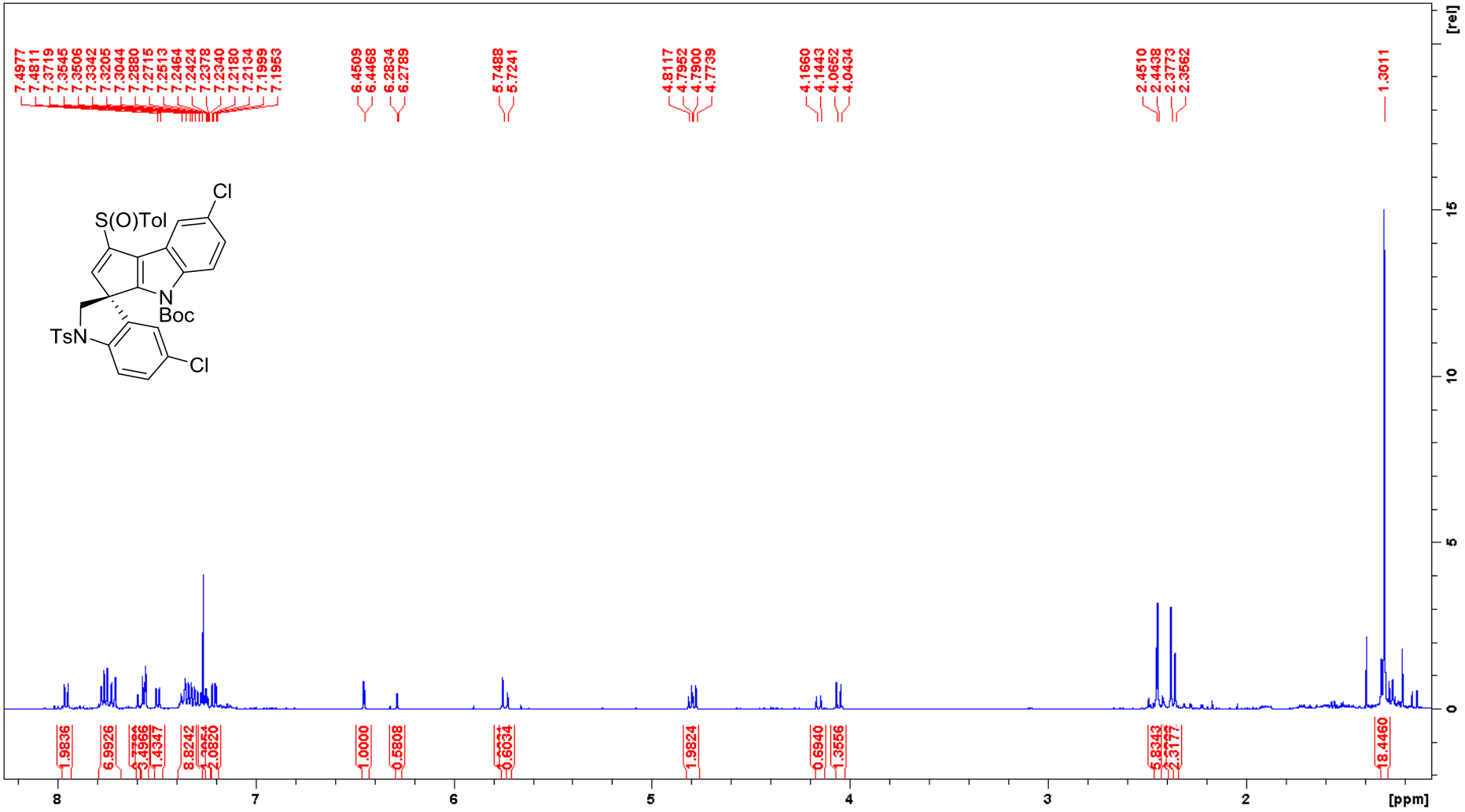
(±)-*tert*-Butyl 5',7-dichloro-1,1'-ditosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (16) ^{13}C NMR spectrum zoom in (acetone-d_6, 125 MHz)



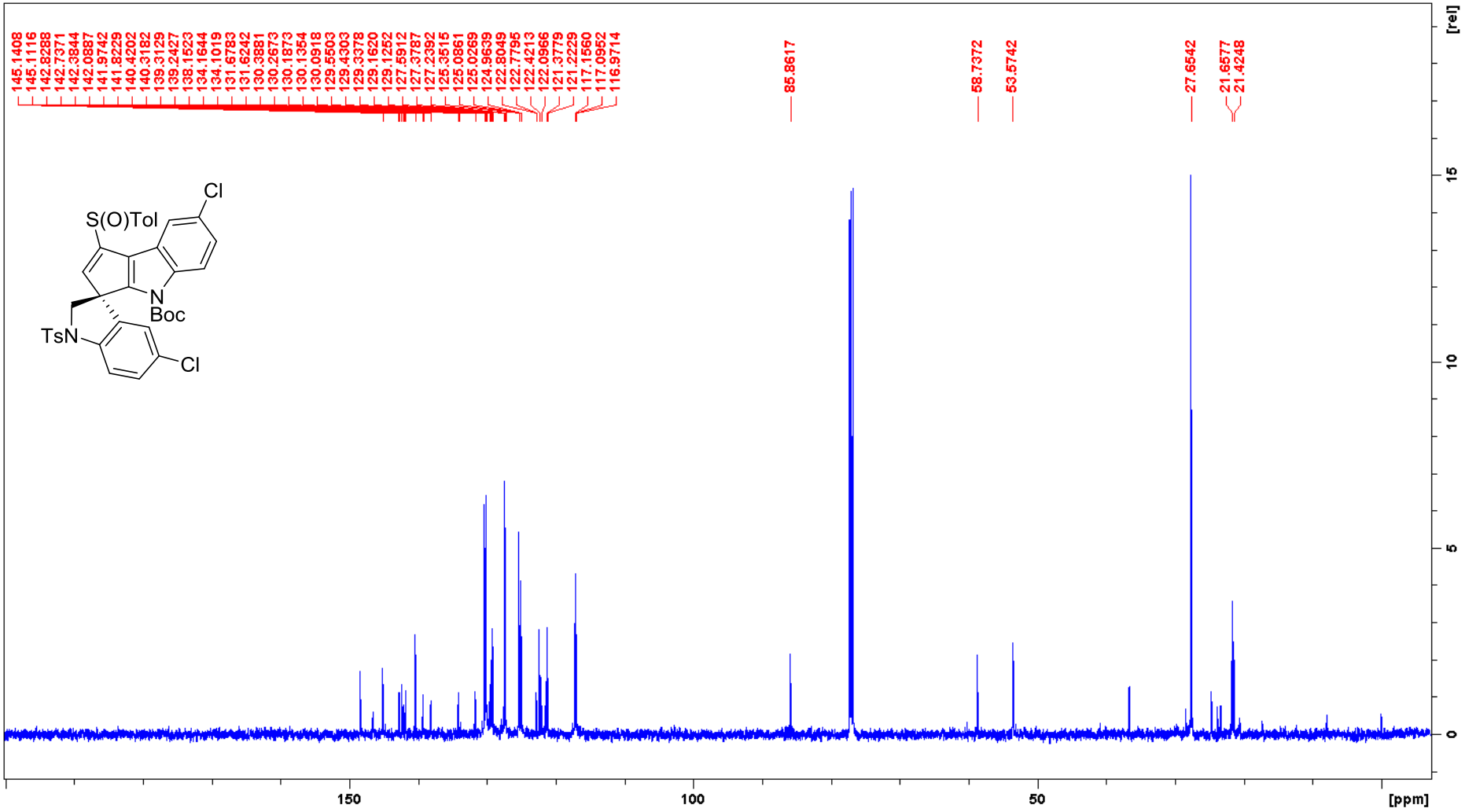
(±)-*tert*-butyl 5',7-dichloro-1-(p-tolylsulfinyl)-1'-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (18) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



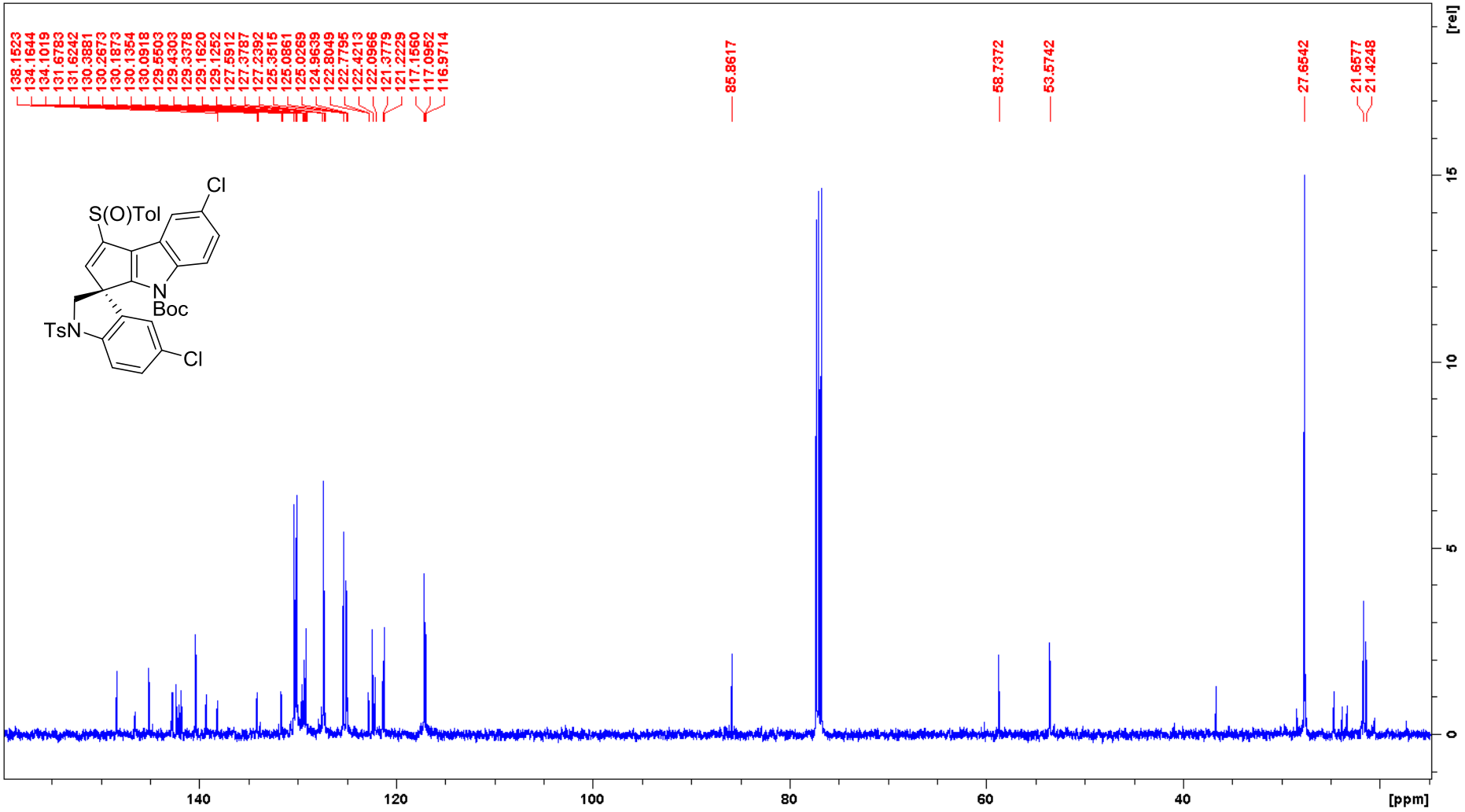
(±)-*tert*-butyl 5',7-dichloro-1-(p-tolylsulfinyl)-1'-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (18) ^{1}H NMR spectrum zoom-in ($CDCl_3$, 500 MHz)



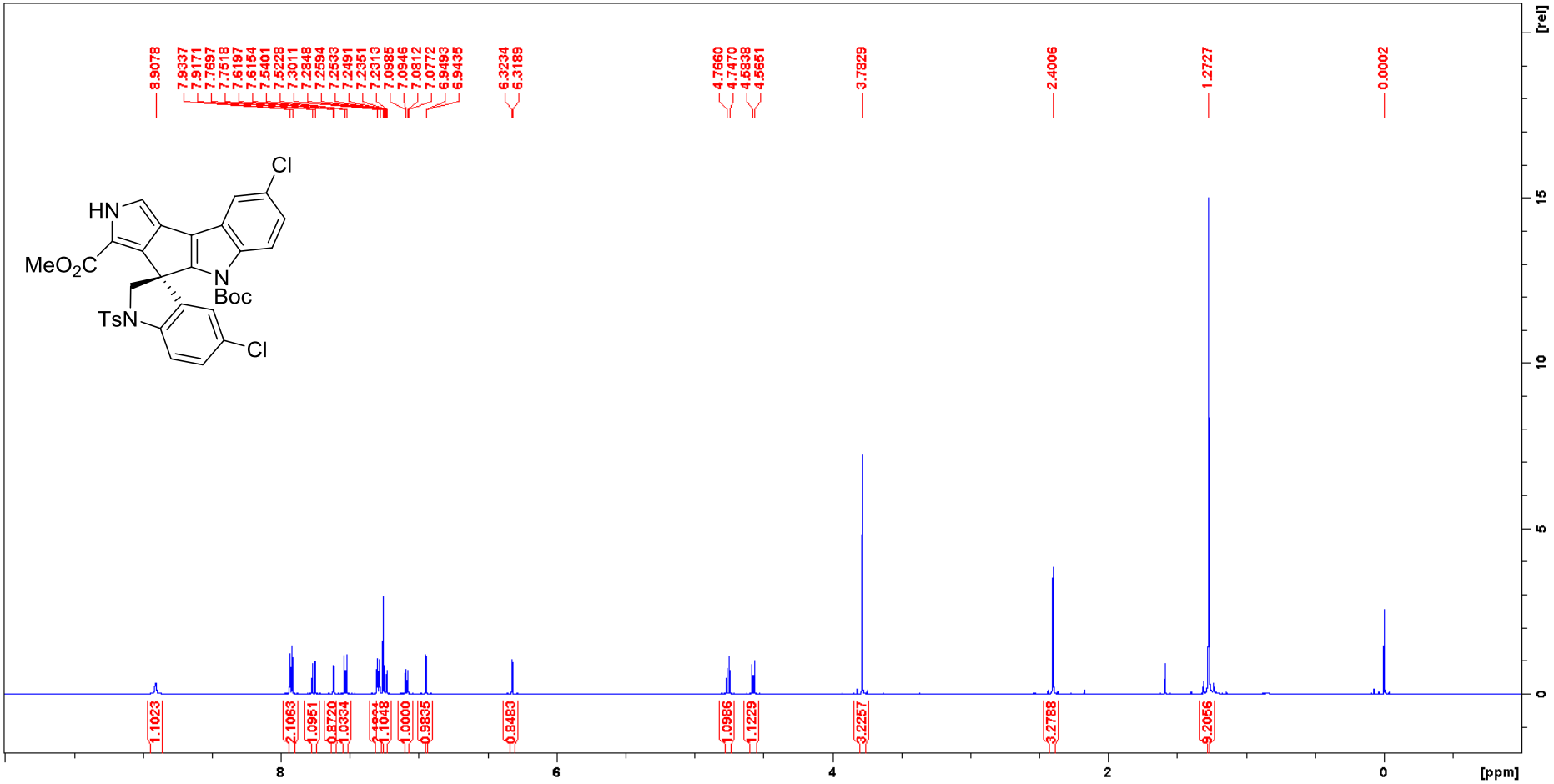
(±)-*tert*-butyl 5',7-dichloro-1-(p-tolylsulfinyl)-1'-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (18) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz)



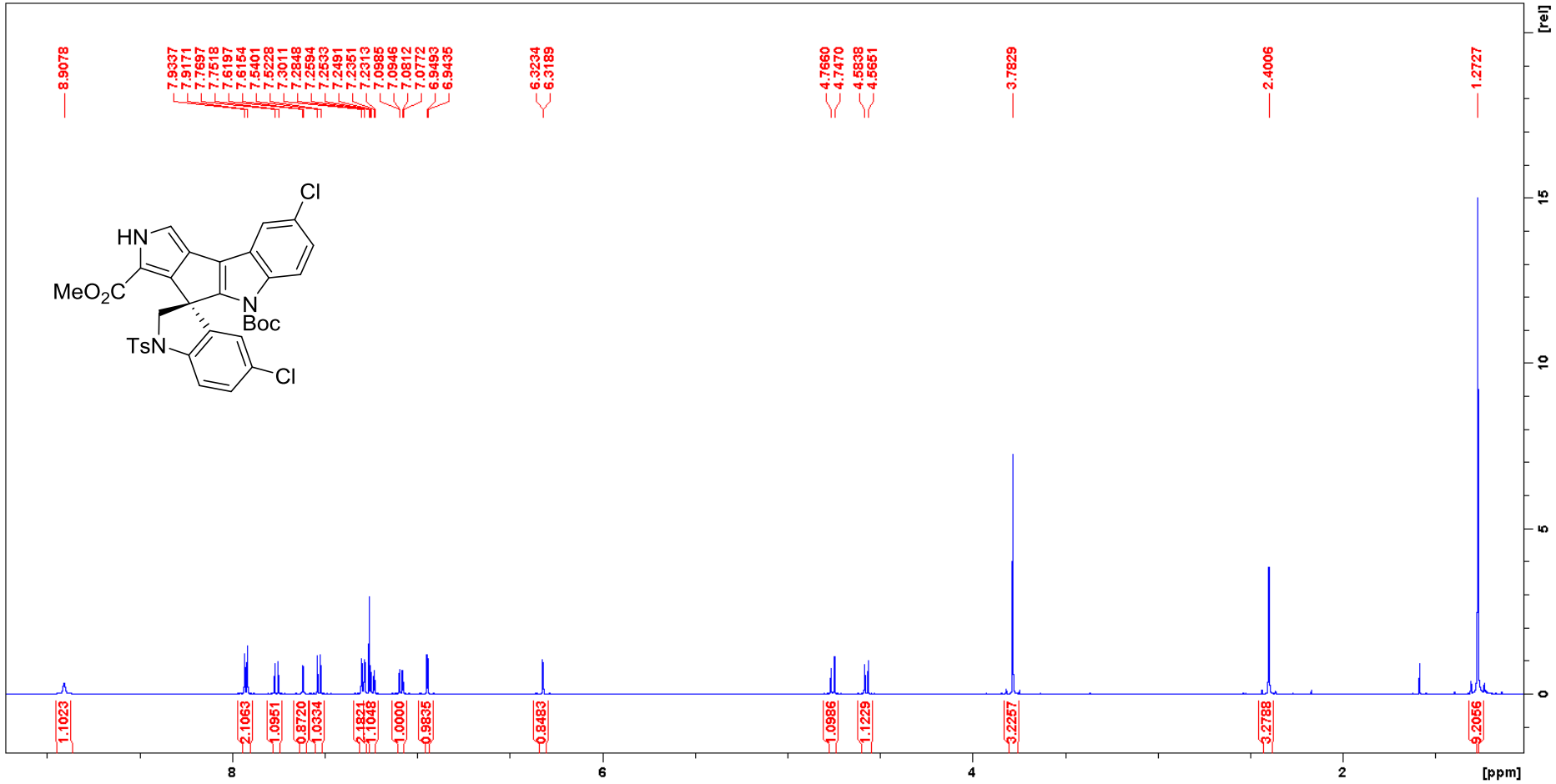
(±)-*tert*-butyl 5',7-dichloro-1-(p-tolylsulfinyl)-1'-tosyl-4*H*-spiro[cyclopenta[*b*]indole-3,3'-indoline]-4-carboxylate (18) ^{13}C NMR spectrum zoom-in ($CDCl_3$, 125 MHz)



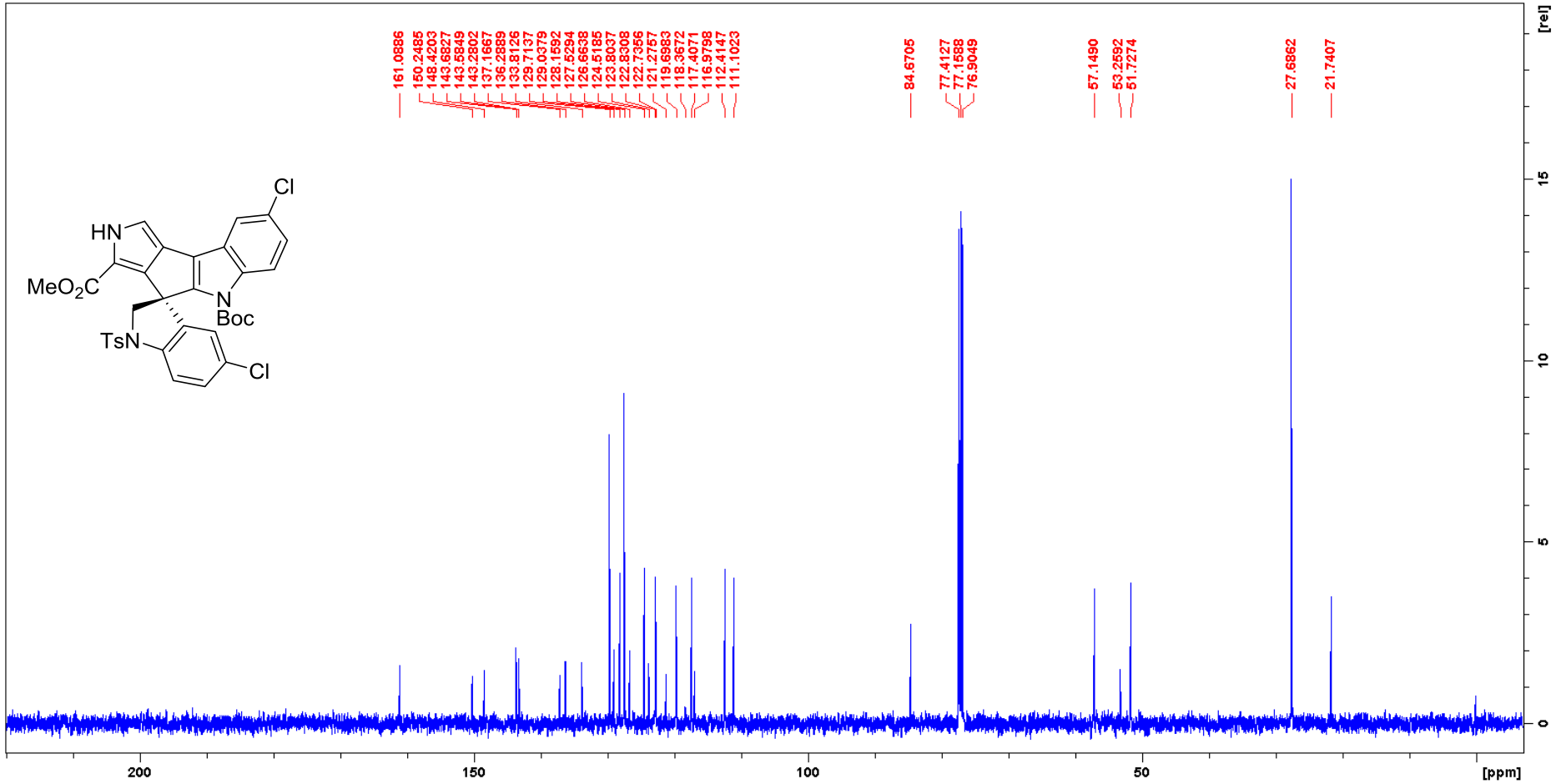
(±)-5'-*tert*-Butyl 3'-methyl 5,8'-dichloro-1-tosylspiro[indoline-3,4'-pyrrolo[3',4':3,4]cyclopenta[1,2-*b*]indole]-3',5'(2'*H*)-dicarboxylate (19) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



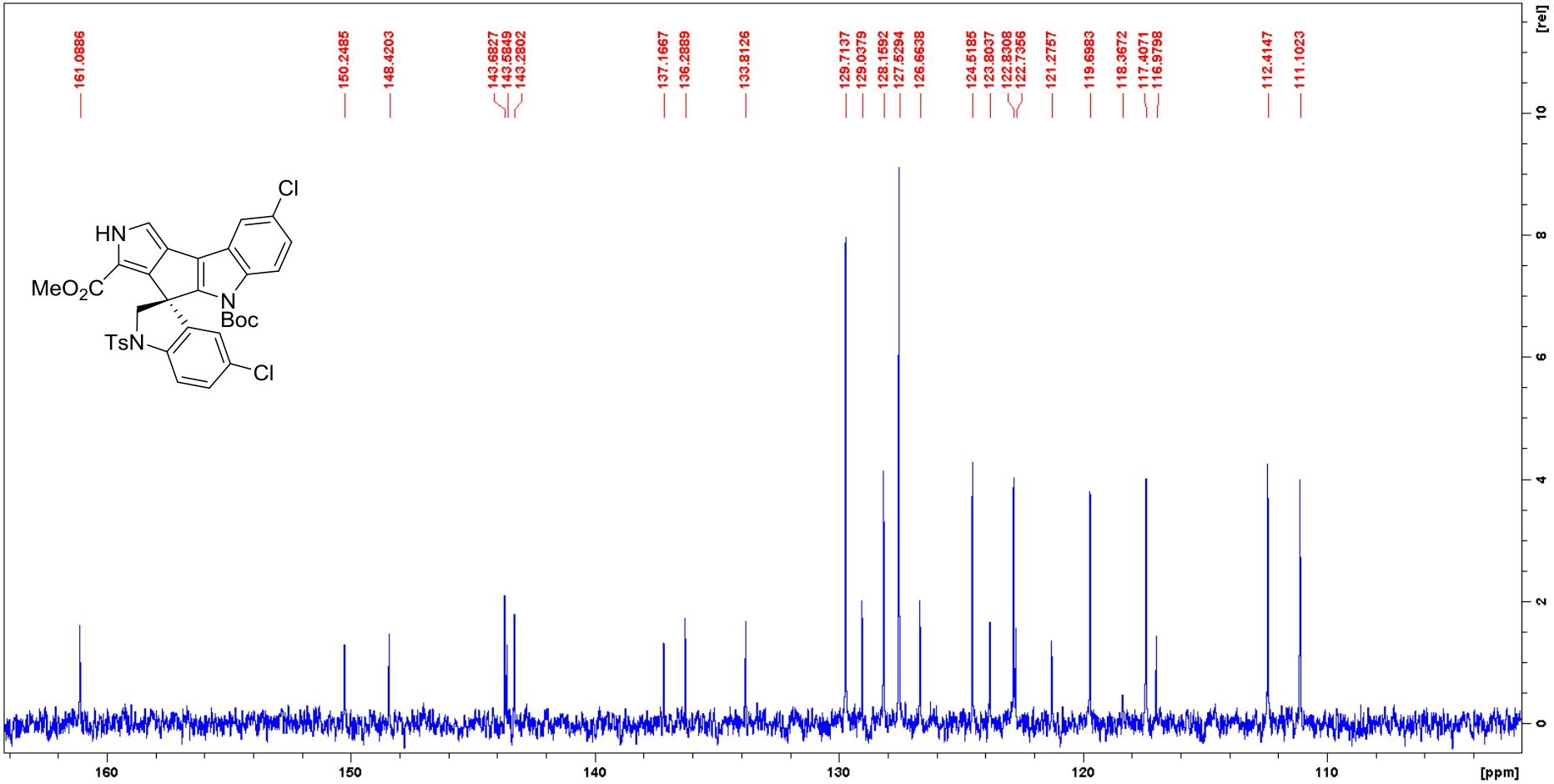
(±)-5'-*tert*-Butyl 3'-methyl 5,8'-dichloro-1-tosylspiro[indoline-3,4'-pyrrolo[3',4':3,4]cyclopenta[1,2-*b*]indole]-3',5'(2'*H*)-dicarboxylate (19) ^{1}H NMR spectrum zoom in ($CDCl_3$, 500 MHz)



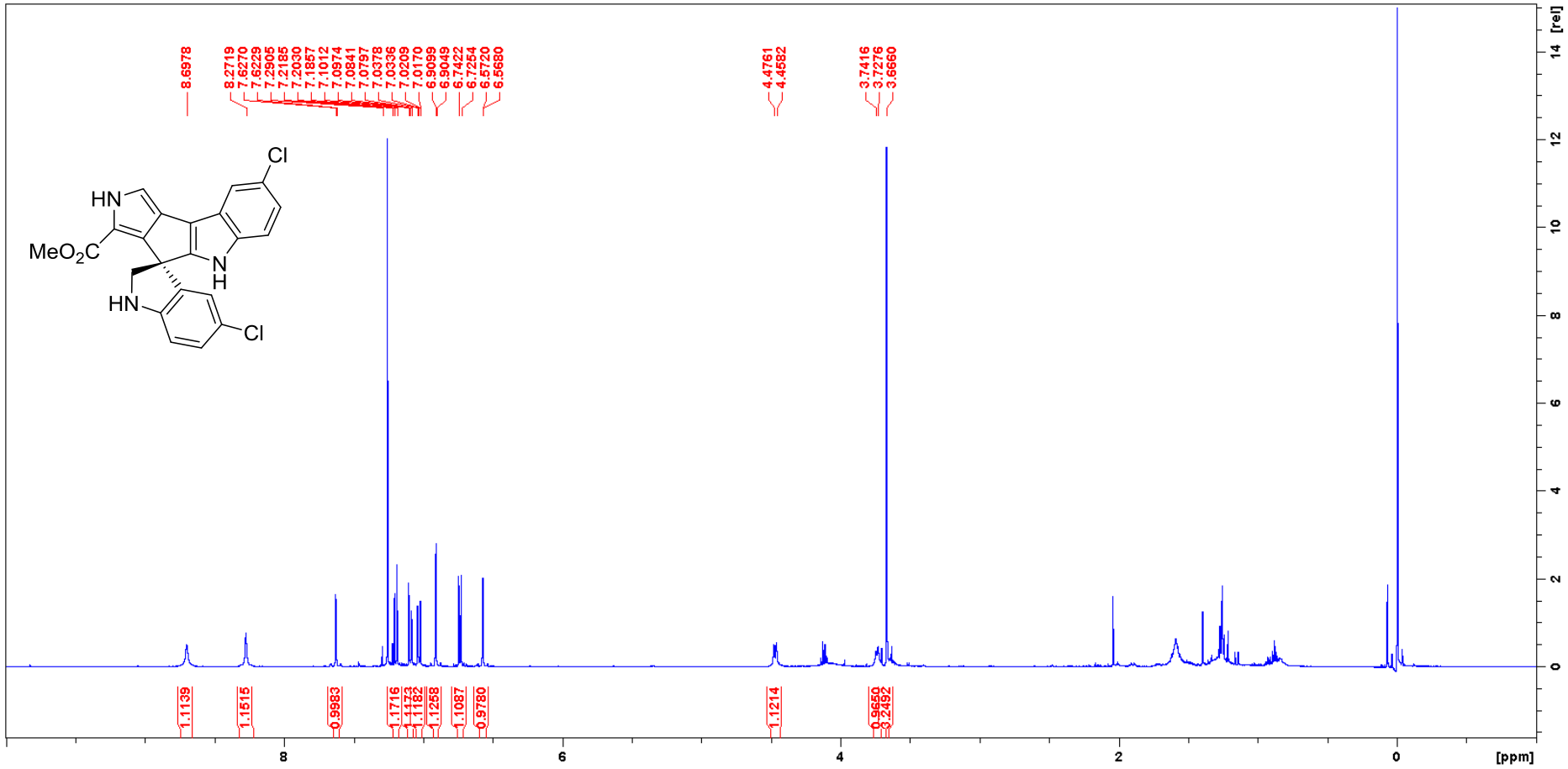
(±)-5'-*tert*-Butyl 3'-methyl 5,8'-dichloro-1-tosylspiro[indoline-3,4'-pyrrolo[3',4':3,4]cyclopenta[1,2-*b*]indole]-3',5'(2'*H*)-dicarboxylate (19) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz)



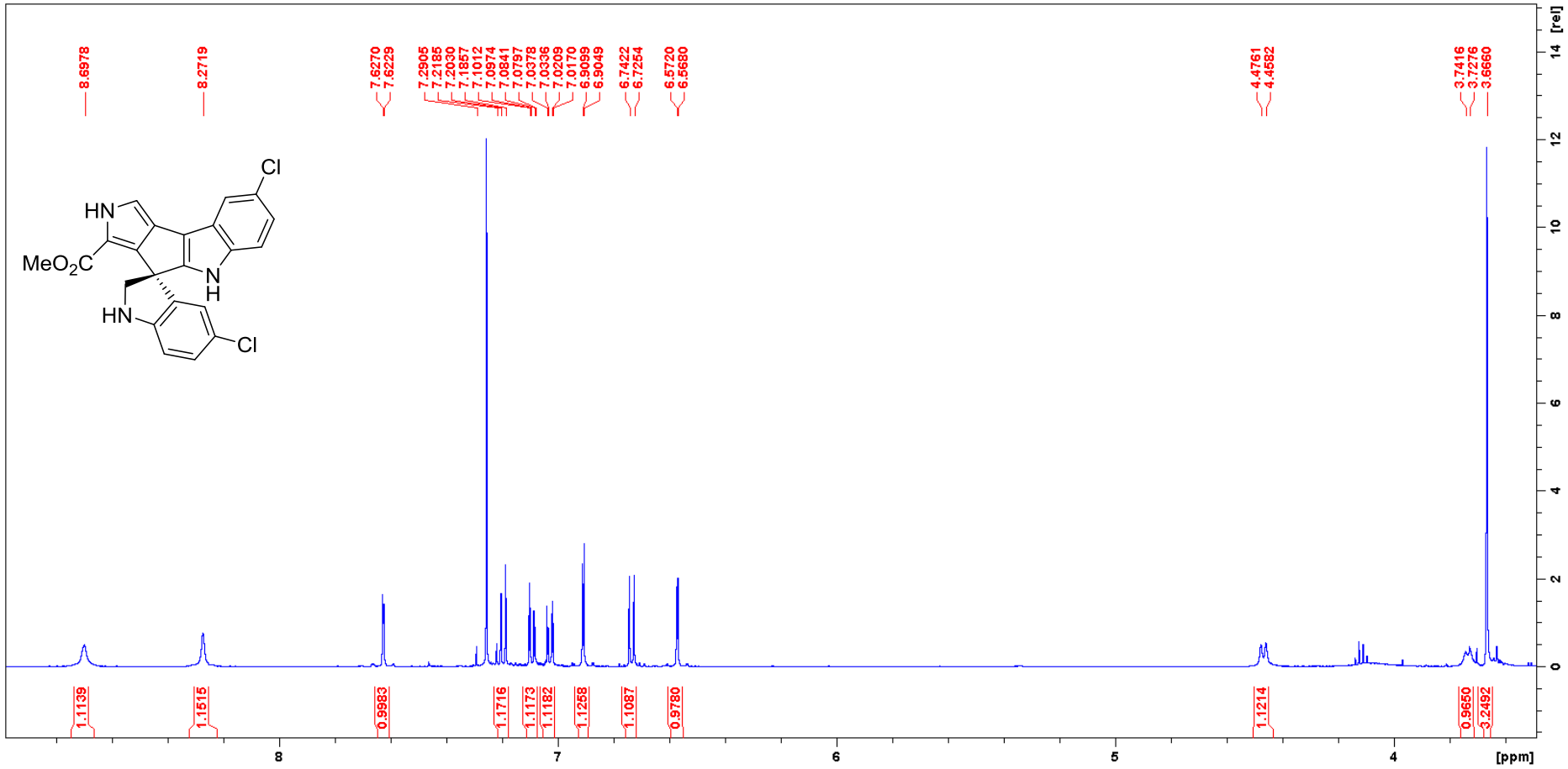
(±)-5'-*tert*-Butyl 3'-methyl 5,8'-dichloro-1-tosylspiro[indoline-3,4'-pyrrolo[3',4':3,4]cyclopenta[1,2-*b*]indole]-3',5'(2'*H*)-dicarboxylate (19) ^{13}C NMR spectrum zoom in ($CDCl_3$, 125 MHz)



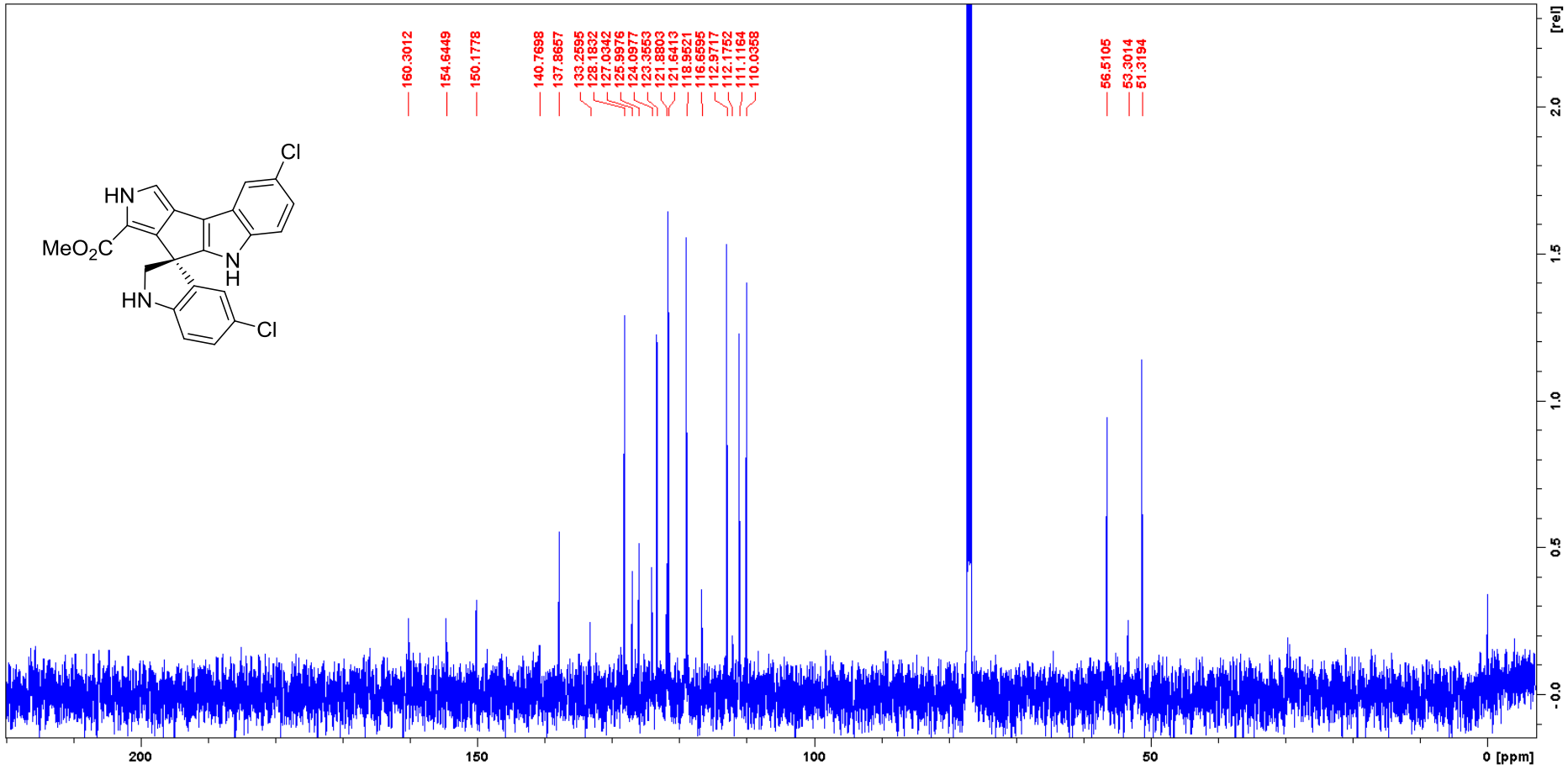
Synthetic (±)-spiroindimicin C (3) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



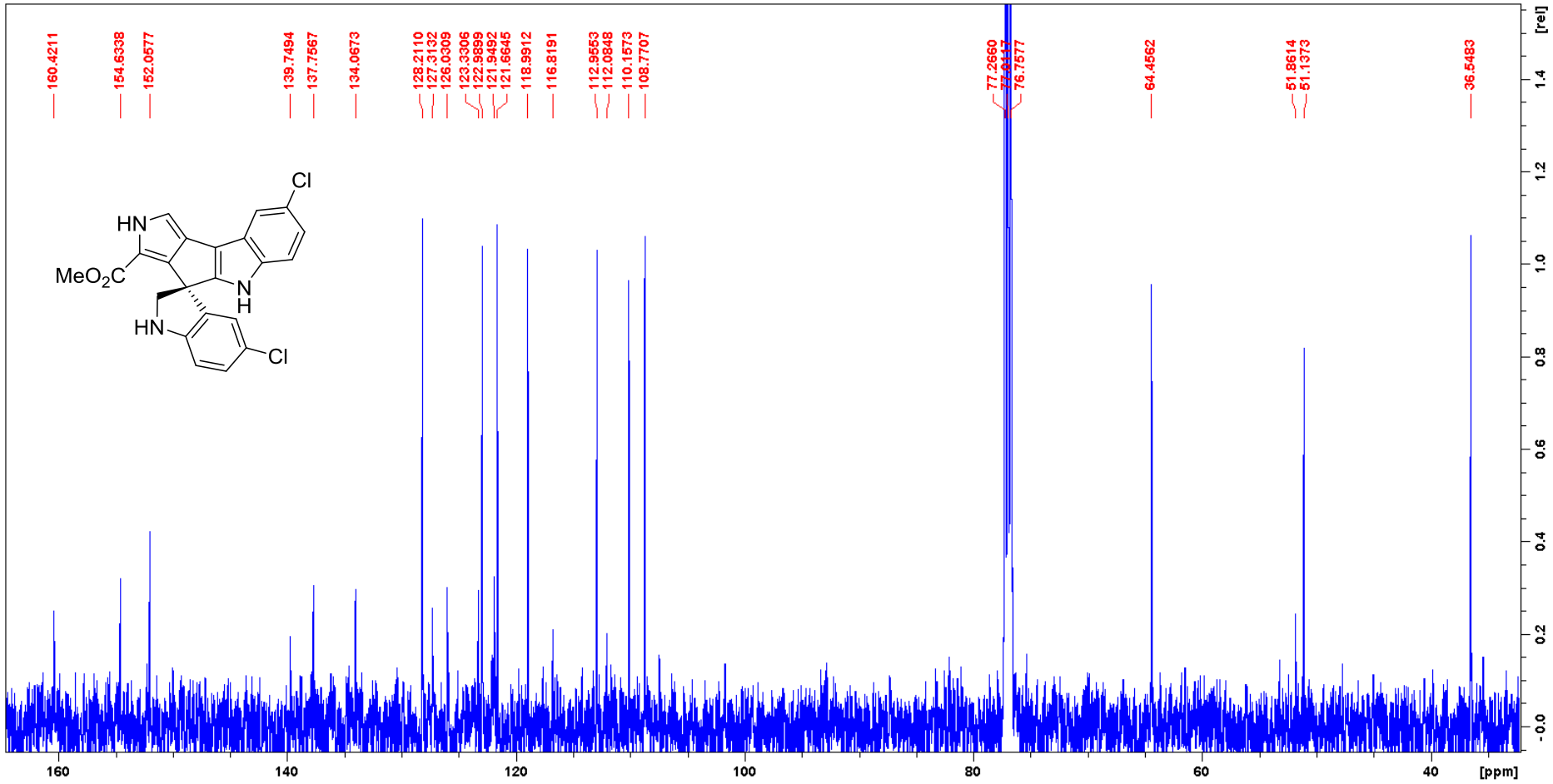
Synthetic (±)-spiroindimicin C (3) ^{1}H NMR spectrum zoom in ($CDCl_3$, 500 MHz)



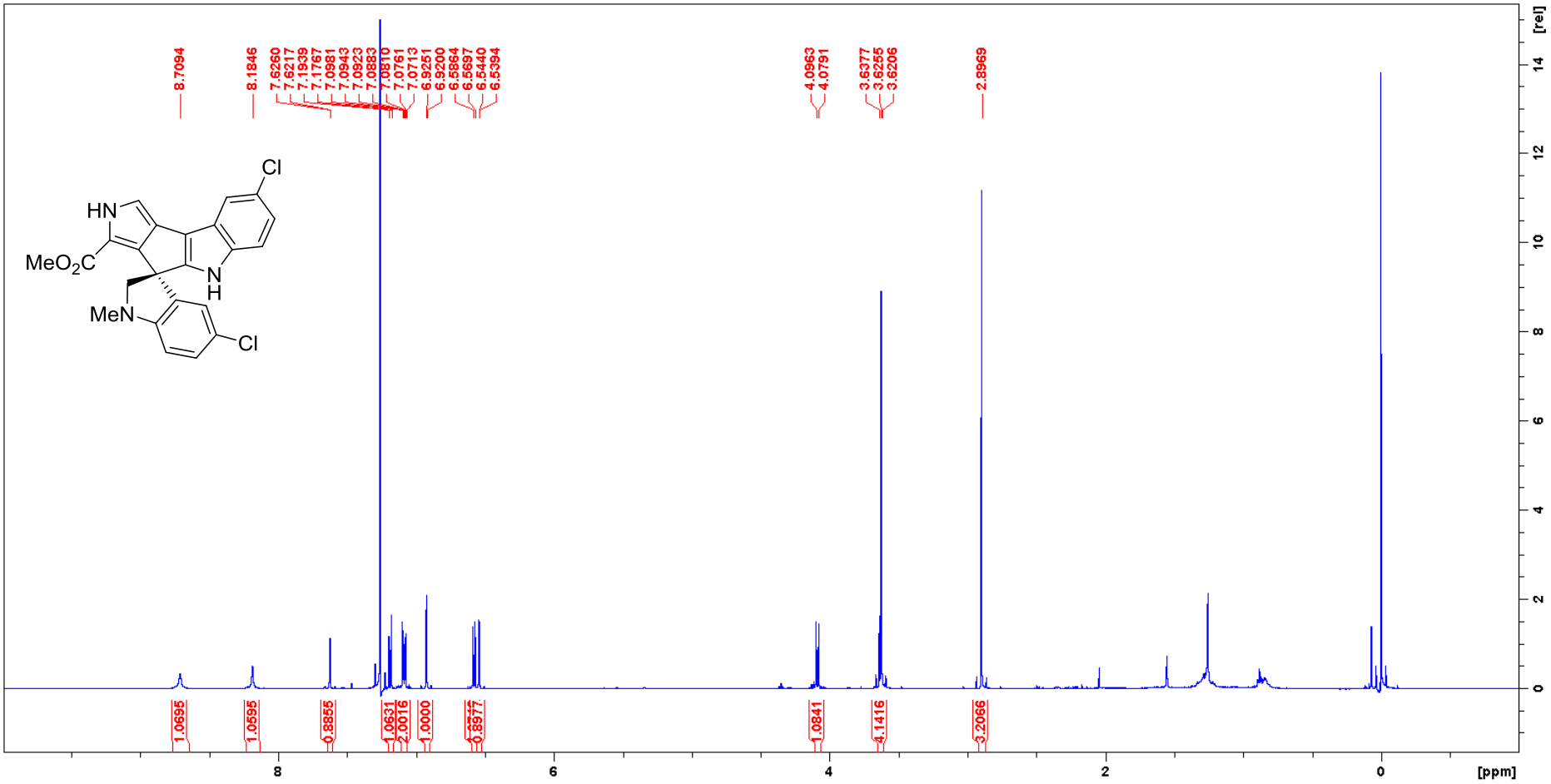
Synthetic (±)-spiroindimicin C (3) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz)



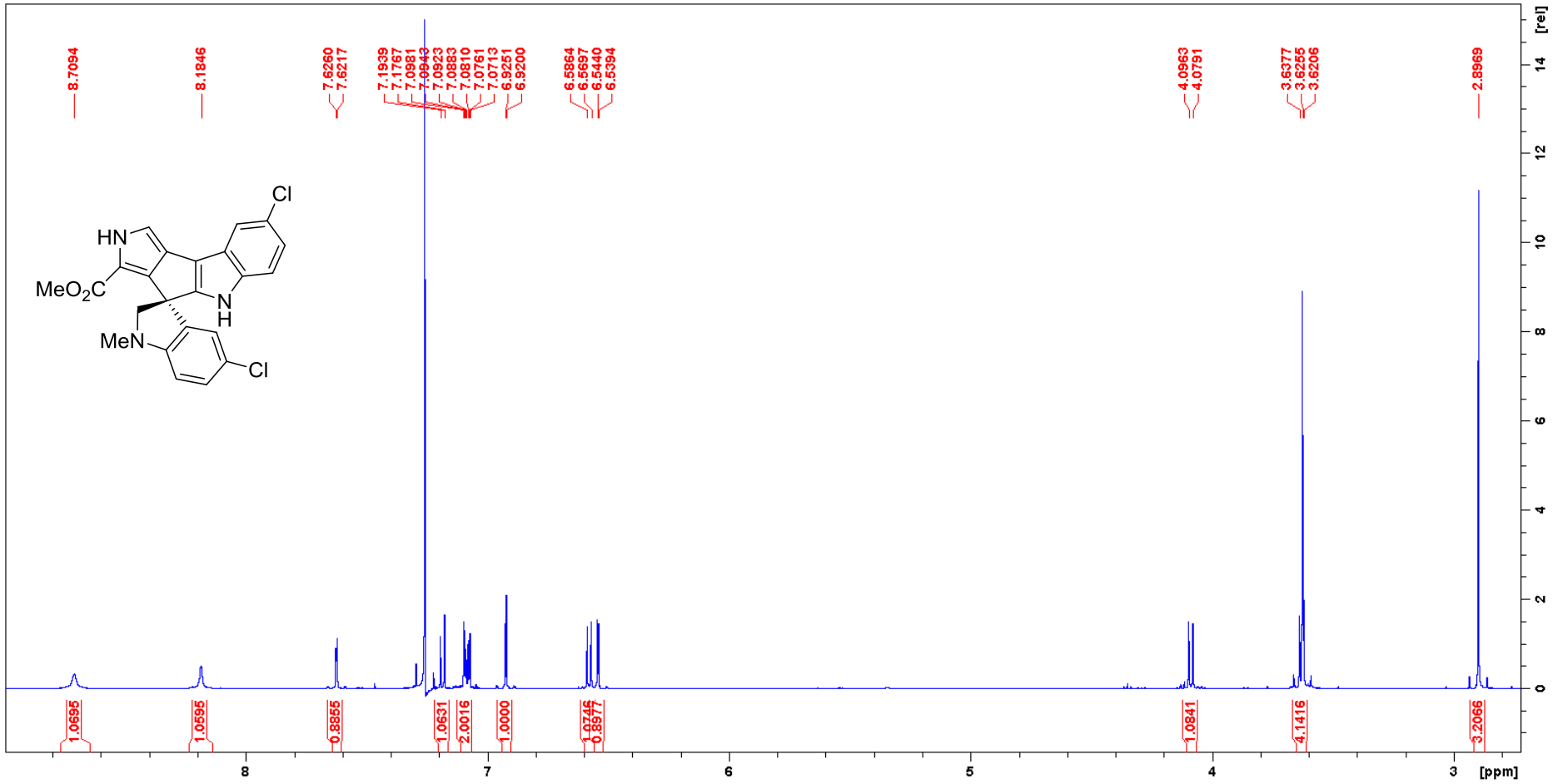
Synthetic (±)-spiroindimicin C (3) ^{13}C NMR spectrum zoom in ($CDCl_3$, 125 MHz)



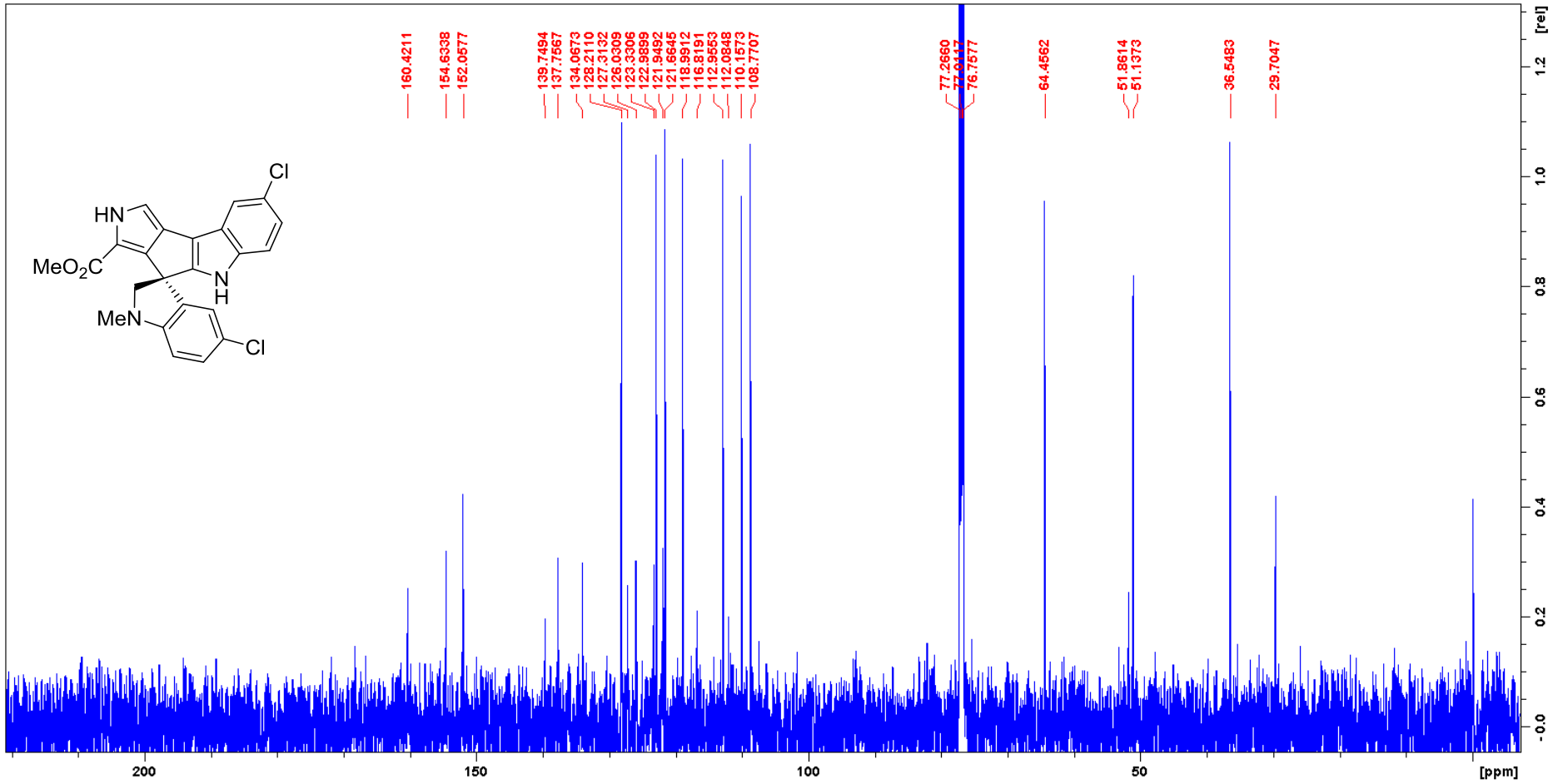
Synthetic (±)-spiroindimicin B (2) ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



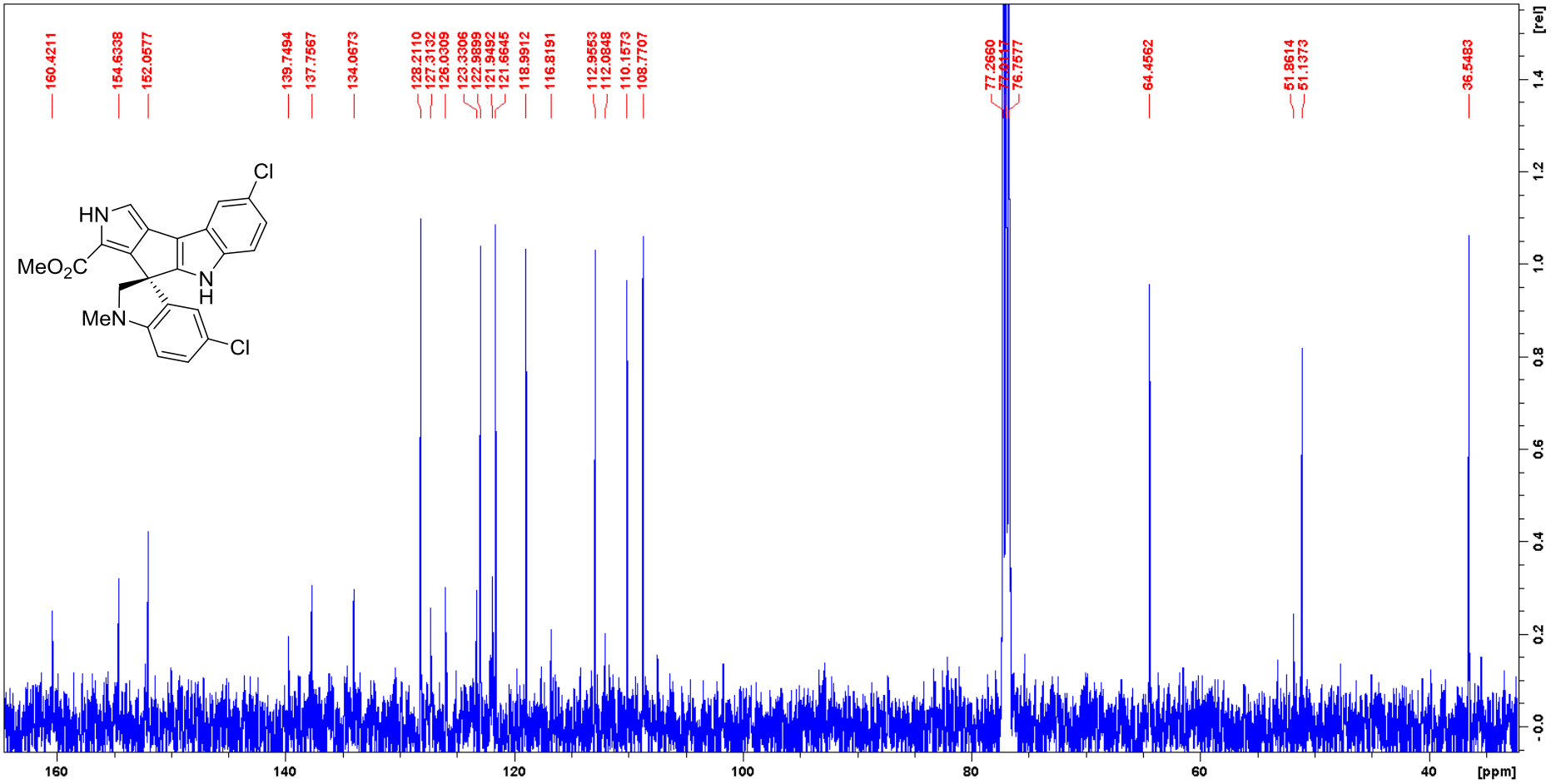
Synthetic (±)-spiroindimicin B (2) ^{1}H NMR spectrum zoom in ($CDCl_3$, 500 MHz)



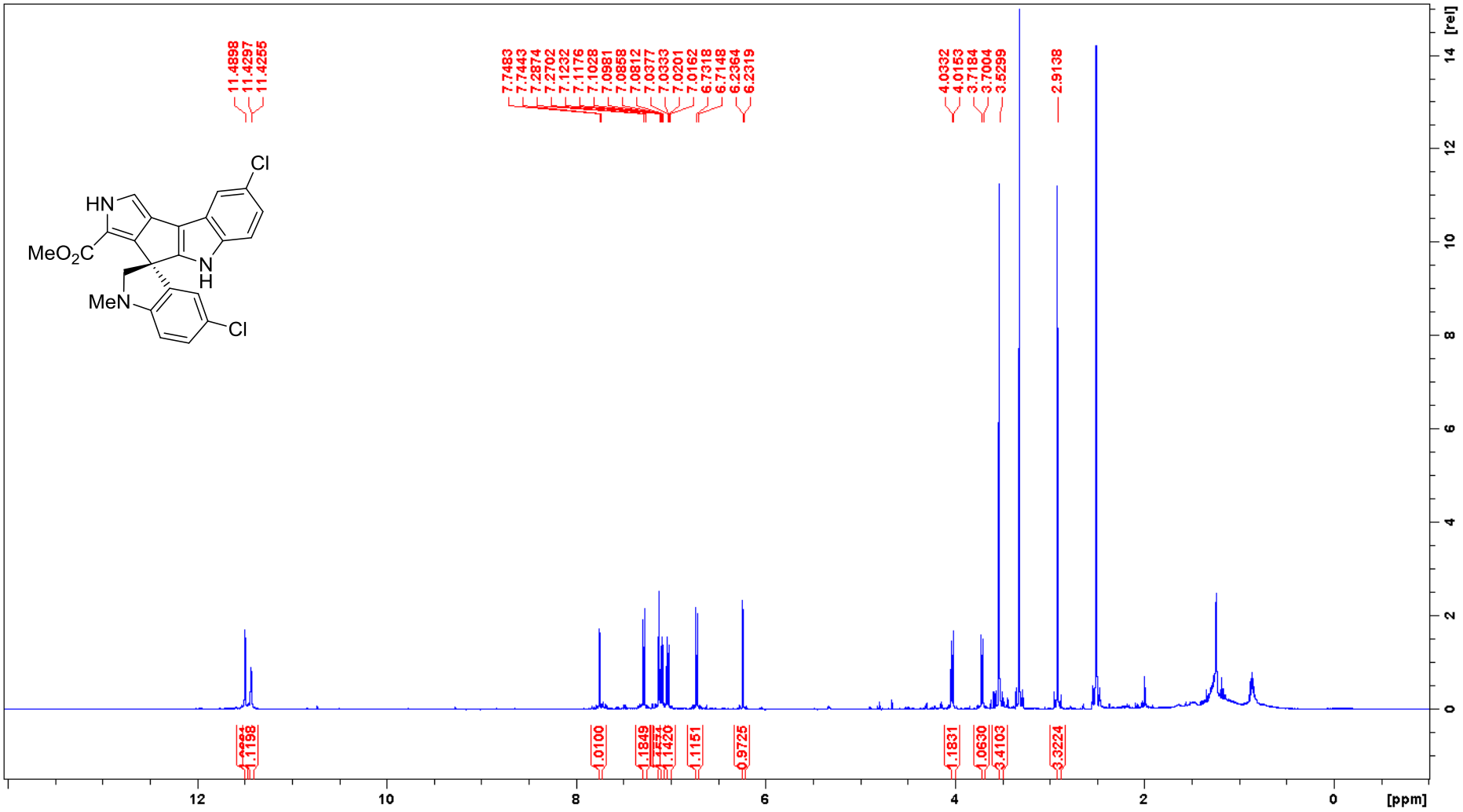
Synthetic (±)-spiroindimicin B (2) ^{13}C NMR spectrum ($CDCl_3$, 125 MHz)



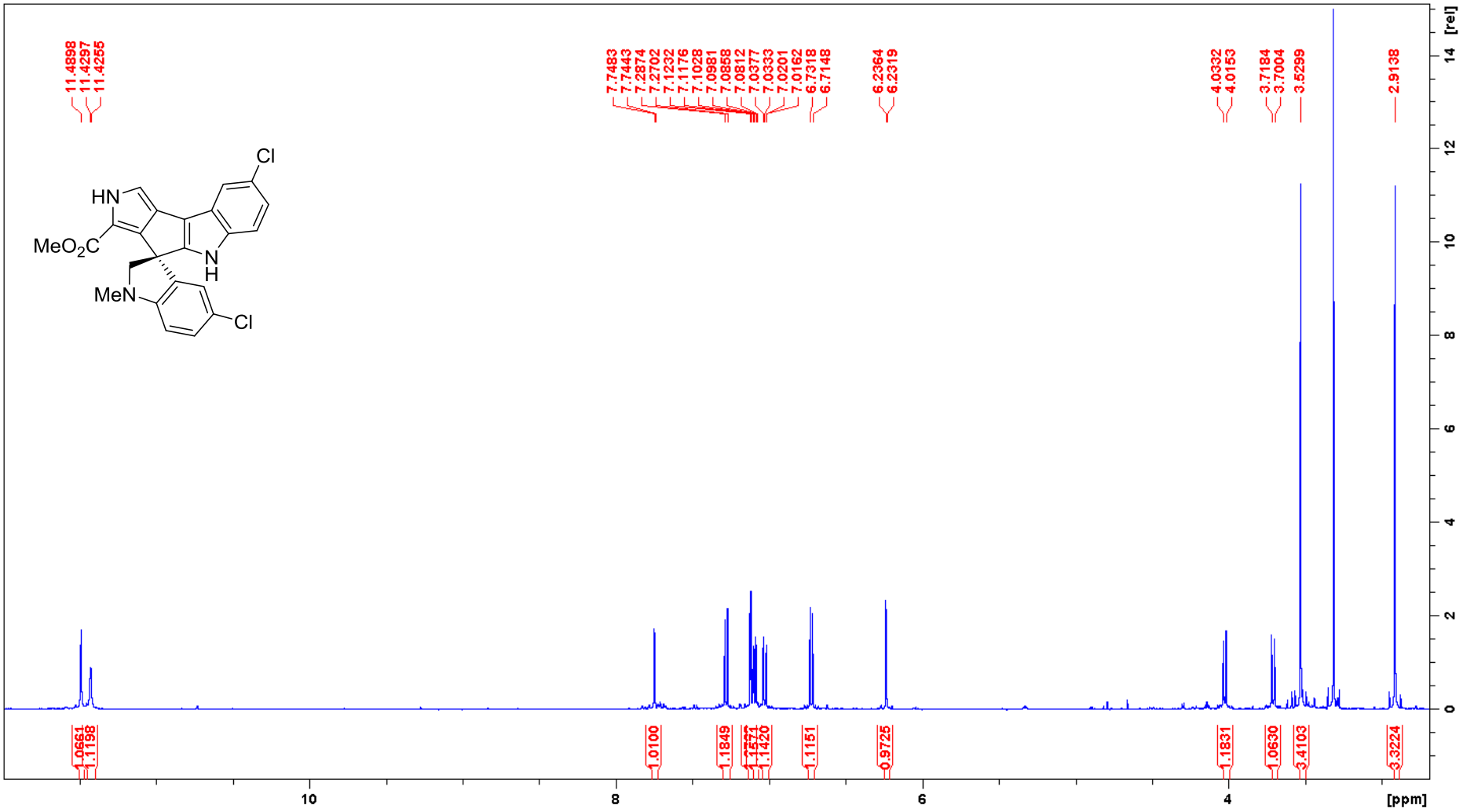
Synthetic (±)-spiroindimicin B (2) ^{13}C NMR spectrum zoom in ($CDCl_3$, 125 MHz)



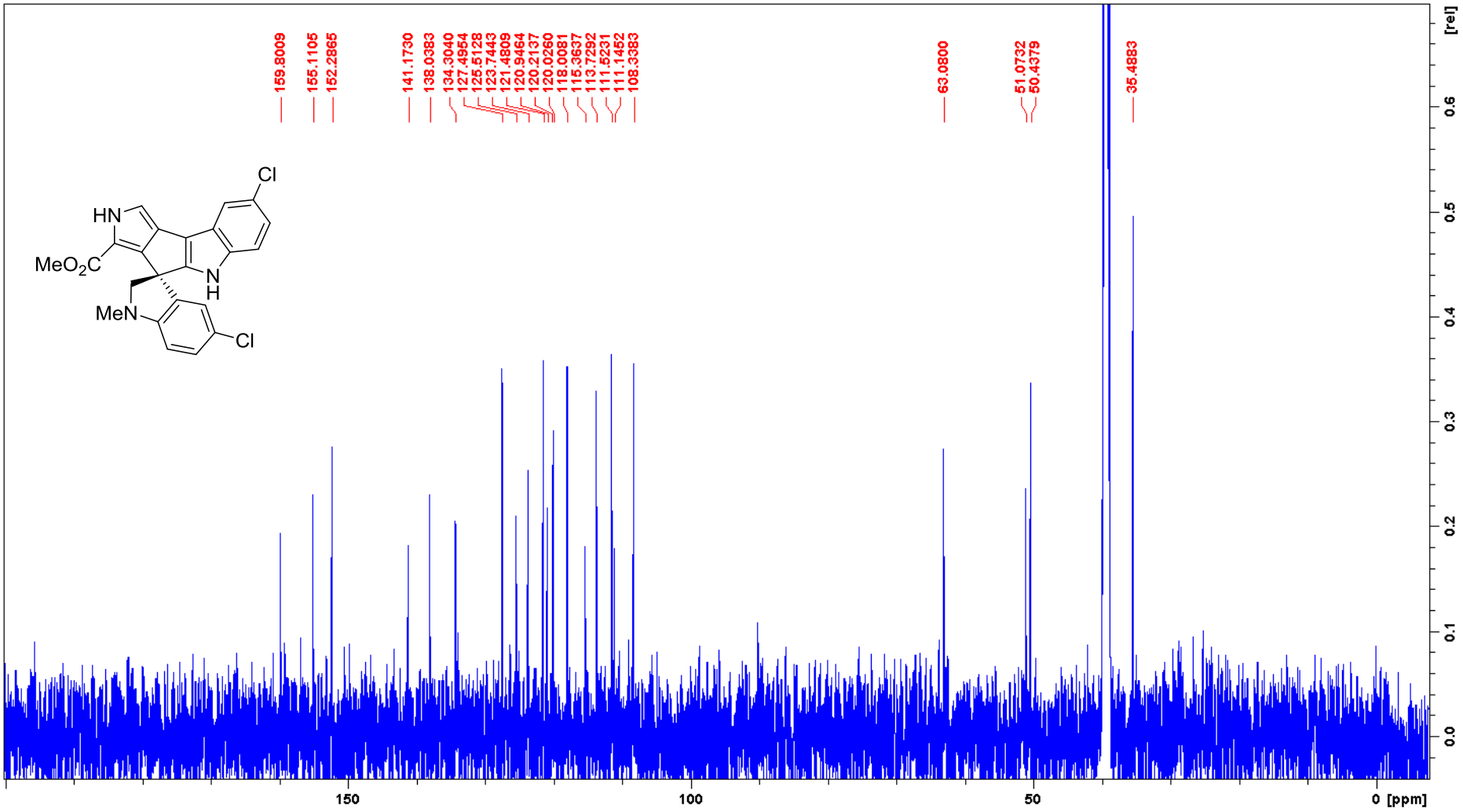
Synthetic (±)-spiroindimicin B (2) ^{1}H NMR spectrum (DMSO-d_6, 500 MHz)



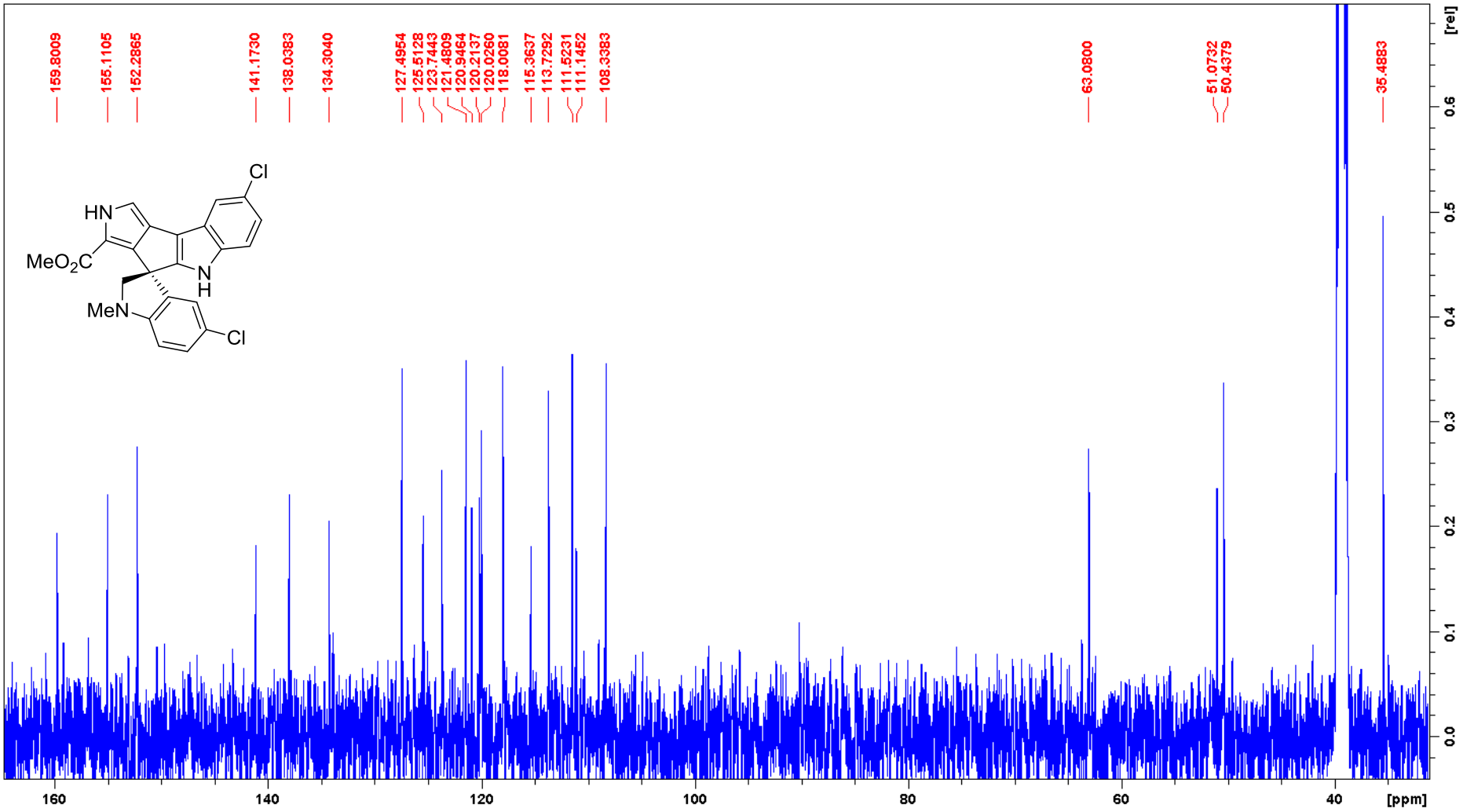
Synthetic (±)-spiroindimicin B (2) ^{1}H NMR spectrum zoom in (DMSO-d_6, 500 MHz)



Synthetic (±)-spiroindimicin B (2) ^{13}C NMR spectrum (DMSO-d_6, 125 MHz)



Synthetic (±)-spiroindimicin B (2) ^{13}C NMR spectrum zoom in (DMSO-d_6, 125 MHz)



4. Comparison of Natural vs. Synthetic Spiroindimicin C

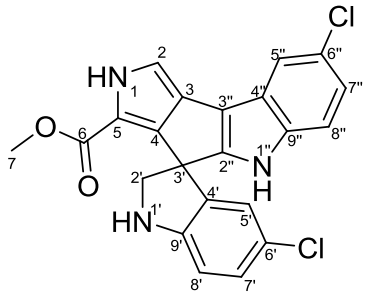


Table S1. ^{1}H NMR Chemical Shifts in $CDCl_3$ of natural[1] vs. synthetic spiroindimicin C (**3**)

No.	δ_H (Literature, 500 MHz)[1]	δ_H (Synthetic, 500 MHz)	Difference (ppm)
1	8.78 s	8.70 s	-0.08
2	6.91 d (2.5)	6.91 d (2.5)	0
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	3.66 s	3.67 s	+0.01
1'	-	-	-
2'	3.76 d (9.0)	3.73 d (9.0)	-0.03
	4.45 d (9.0)	4.47 d (9.0)	+0.02
3'	-	-	-
4'	-	-	-
5'	6.57 d (2.0)	6.57 d (2.0)	0
6'	-	-	-
7'	7.04 dd (8.5, 2.0)	7.03 dd (8.4, 2.1)	-0.01
8'	6.76 d (8.5)	6.73 d (8.4)	-0.03
9'	-	-	-
1''	8.55 (s)	8.27 s	-0.28
2''	-	-	-
3''	-	-	-
4''	-	-	-
5''	7.63 d (2.0)	7.62 d (2.0)	-0.01
6''	-	-	-
7''	7.09 dd (8.8, 2.0)	7.09 dd (8.7, 2.1)	0
8''	7.19 d (8.8)	7.19 d (8.7)	0
9''	-	-	-

1 W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.

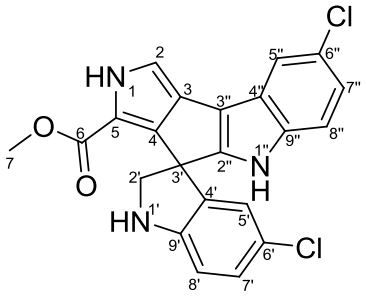
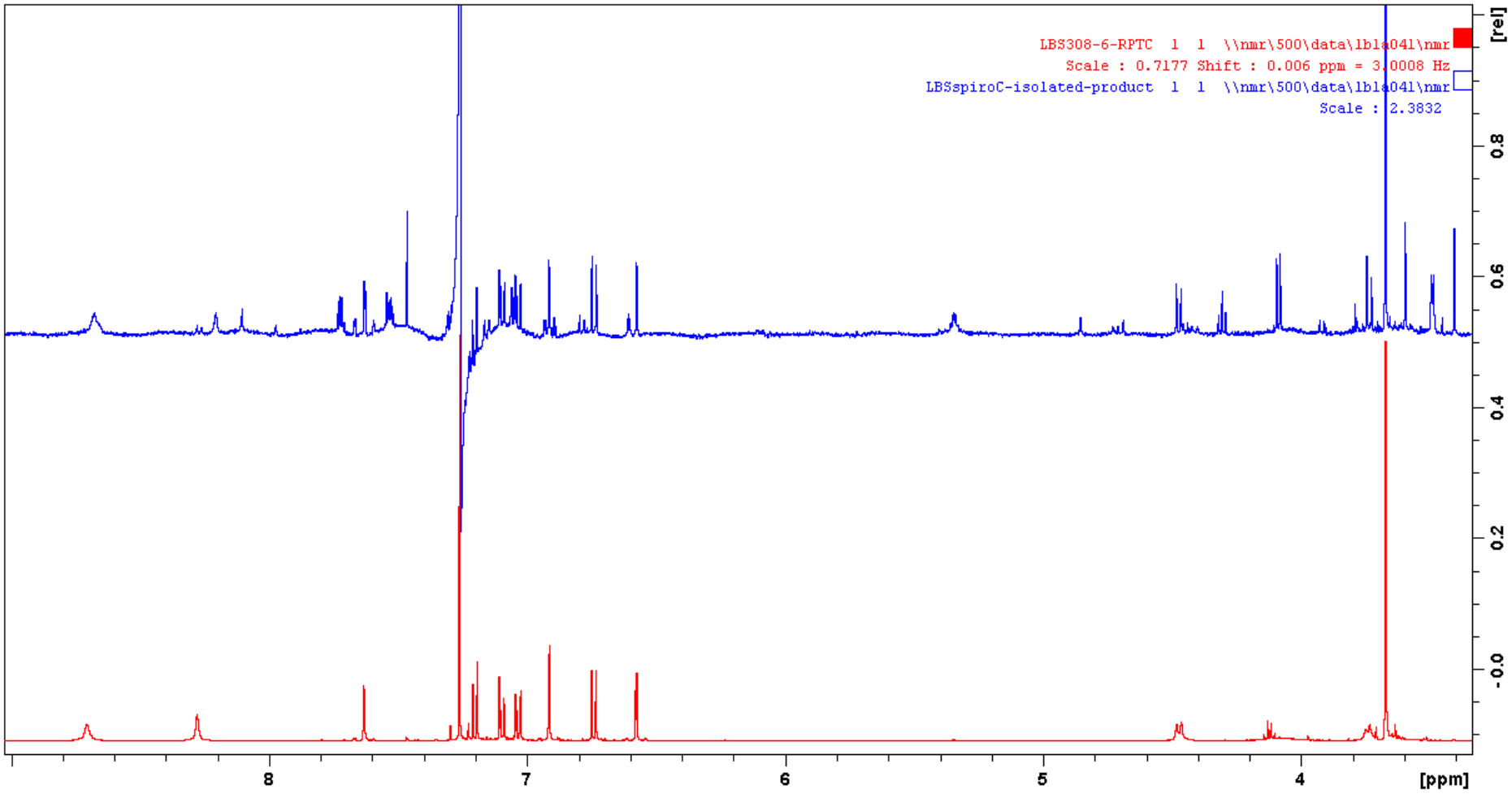


Table S2. ^{13}C NMR Chemical Shifts in $CDCl_3$ of natural[1] vs. synthetic spiroindimicin C (**3**)

	δ_C (Literature, 125 MHz)[1]	**δ_C (Synthetic, 125 MHz)**	**Difference**
2	110.1 CH	110.0 CH	-0.1
3	127.0 C	127.0 C	0
4	141.0 C	140.8 C	-0.2
5	116.7 C	116.7 C	0
6	160.4 C	160.3 C	-0.1
7	51.4 CH_3	51.3 CH_3	-0.1
2'	56.3 CH_2	56.5 CH_2	+0.2
3'	53.3 C	53.3 C	0
4'	133.6 C	133.3 C	-0.3
5'	123.4 CH	123.4 CH	0
6'	124.7 C	124.1 C	-0.6
7'	128.3 CH	128.2 CH	-0.1
8'	111.6 CH	111.1 CH	-0.5
9'	149.7 C	150.2 C	+0.5
2''	154.5 C	154.6 C	+0.1
3''	112.3 C	112.2 C	-0.1
4''	121.8 C	121.9 C	+0.1
5''	118.9 CH	119.0 CH	+0.1
6''	126.0 C	126.0 C	0
7''	121.6 CH	121.6 CH	0
8''	113.1 CH	113.0 CH	-0.1
9''	137.8 C	137.9 C	+0.1

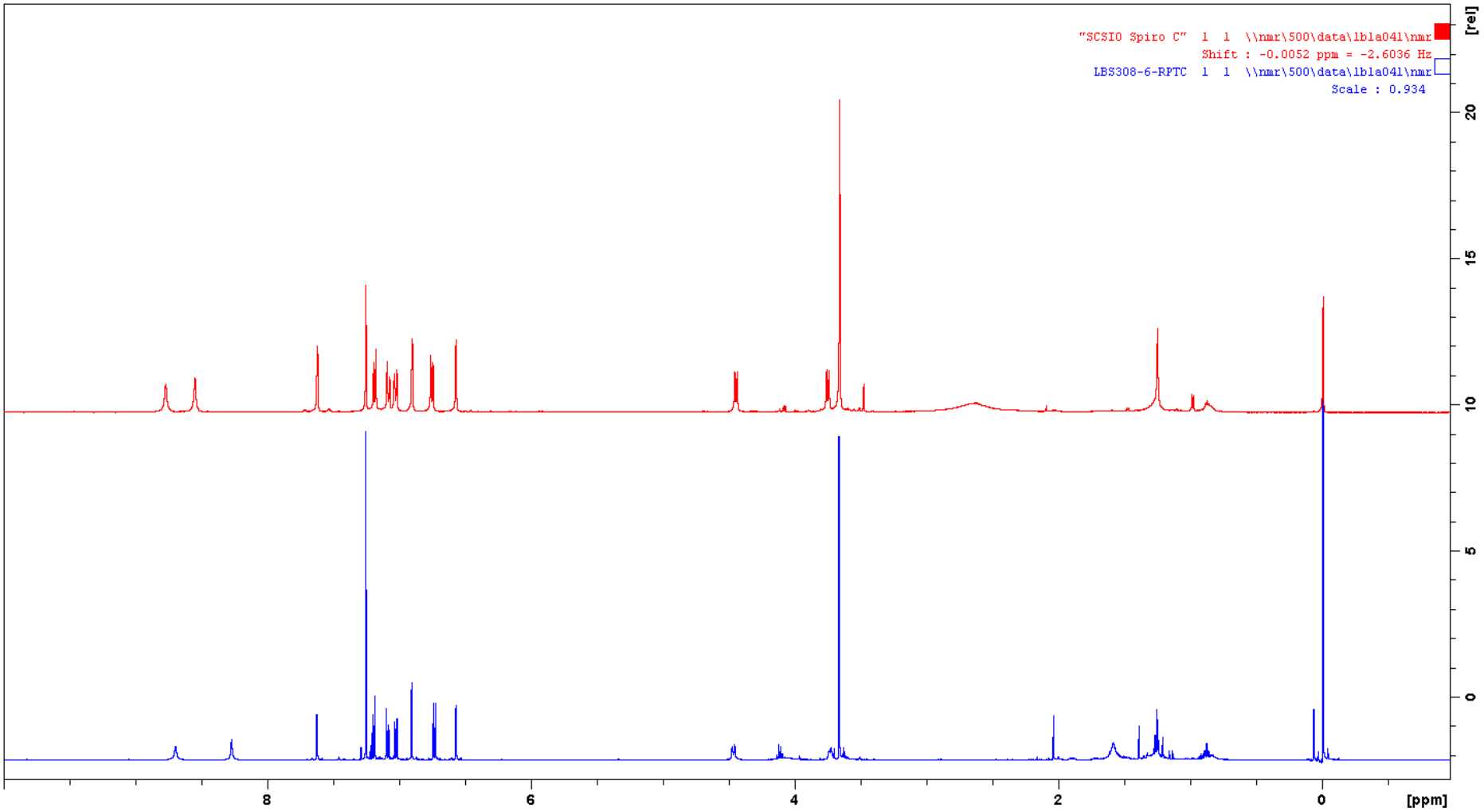
1 W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.

Natural spiroindimicin C[a] (upper spectrum) vs. synthetic spiroindimicin C (lower spectrum) ^{1}H NMR overlay ($CDCl_3$, 500 MHz)



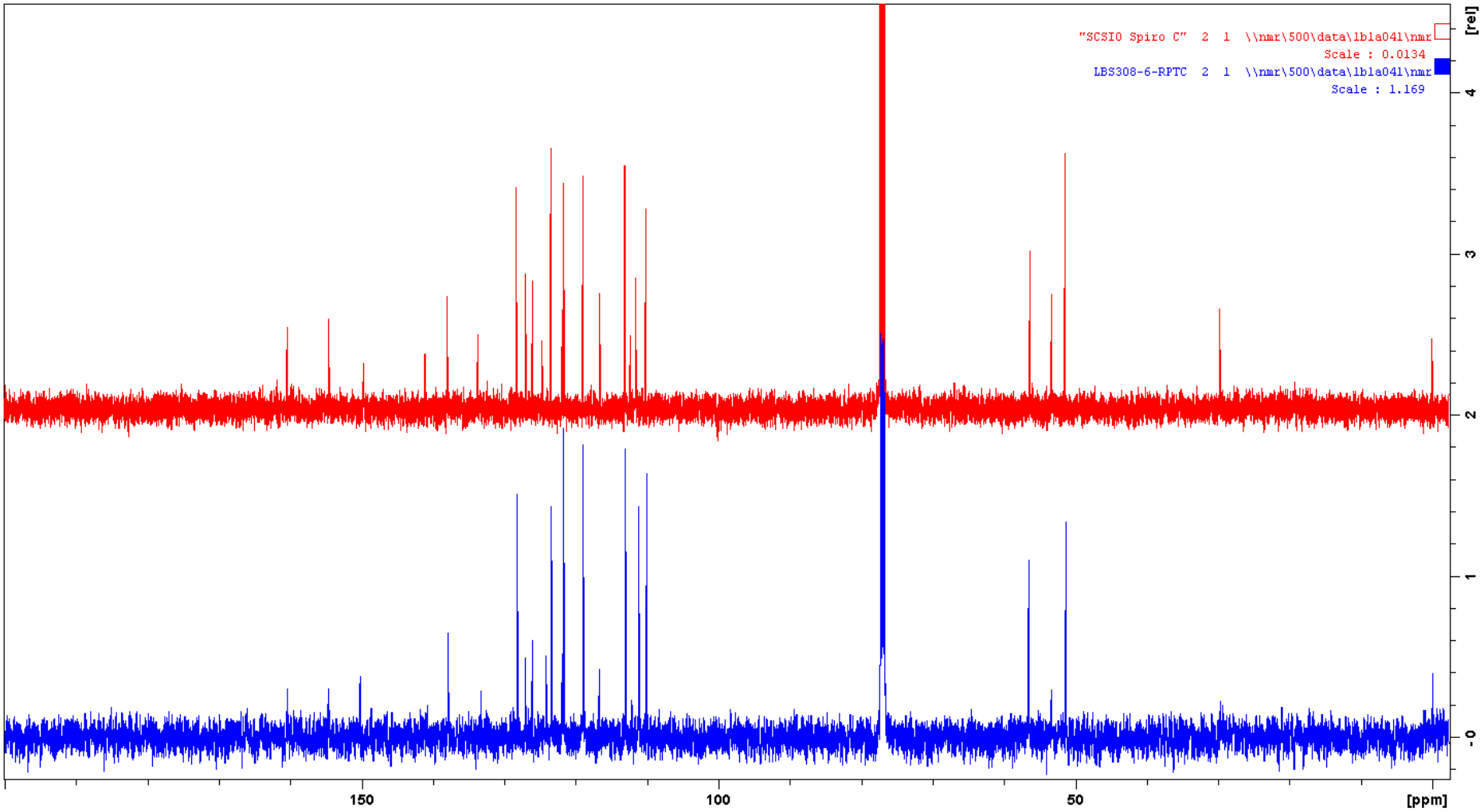
a An authentic sample of spiroindimicin C (~0.4mg, impure), kindly provided by Prof. Changsheng Zhang (SCSIO), which was not subjected to further purification upon its arrival at our laboratory

Natural spiroindimicin C[a] (upper spectrum) vs. synthetic spiroindimicin C (lower spectrum) ^{1}H NMR overlay ($CDCl_3$, 500 MHz)



a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

Natural spiroindimicin C[a] (upper spectrum) vs. synthetic spiroindimicin C (lower spectrum) ^{13}C NMR overlay ($CDCl_3$, 125 MHz)



a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

5. Comparison of Natural vs. Synthetic Spiroindimicin B

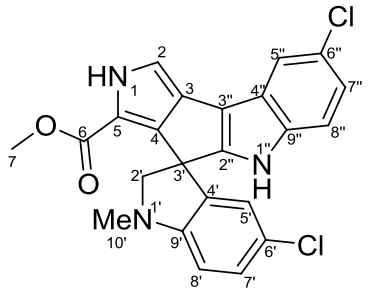


Table S3. ^{1}H NMR Chemical Shifts in $CDCl_3$ of natural[a,b] vs. synthetic spiroindimicin B (**2**)

No.	δ_H (Literature, 500MHz)[a] (ppm)	δ_H (Natural, 500MHz)[b] (ppm)	δ_H (Synthetic, 500MHz) (ppm)	Difference[d] (ppm)
1	8.88 br s	8.72 br s	8.71 br s	-0.16 / -0.01
2	6.91 d (3.0)	6.92 d (2.5)	6.92 d (2.7)	+0.01 / 0
3	-	-	-	-
4	-	-	-	-
5	-	-	-	-
6	-	-	-	-
7	3.61 s	3.62 s[c]	3.62 s[c]	+0.01 / 0
2'	3.64 d (8.5)	3.63 d (7.5)[c]	3.63 d (8.6)[c]	-0.01 / 0
	4.07 d (8.5)	4.09 d (8.6)	4.09 d (8.6)	+0.02 / 0
3'	-	-	-	-
4'	-	-	-	-
5'	6.54 d (2.0)	6.54 d (2.0)	6.54 d (2.1)	0 / 0
6'	-	-	-	-
7'	7.07 dd (2.0, 8.5)	7.09 dd (2.2, 8.7)[c]	7.09 dd (2.3, 8.4)[c]	+0.02 / 0
8'	6.57 d (8.5)	6.58 d (8.4)	6.58 d (8.4)	+0.01 / 0
9'	-	-	-	-
10'	2.88 s	2.90 s	2.90 s	+0.01 / 0
1''	8.45 br s	8.23 br s	8.18 br s	-0.27 / - 0.05
2''	-	-	-	-
3''	-	-	-	-
4''	-	-	-	-
5''	7.62 d (1.5)	7.62 d (1.9)	7.62 d (2.2)	0 / 0
6''	-	-	-	-
7''	7.06 dd (1.5, 9.0)	7.08 dd (2.2, 8.4)[c]	7.08 dd (2.3, 8.4)[c]	+0.02 / 0
8''	7.15 d (9.0)	7.19 d (8.6)	7.19 d (8.3)	+0.04 / 0
9''	-	-	-	-

a W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.
b An authentic sample of spiroindimicin B kindly provided by Prof. Changsheng Zhang (SCSIO).
c Overlapping peaks.
d ("Literature" – "Synthetic") / ("Natural" – "Synthetic").

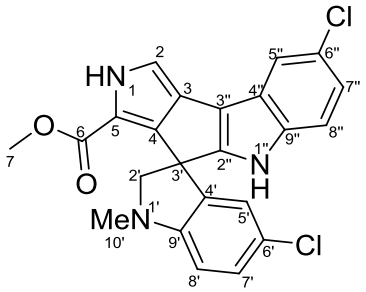


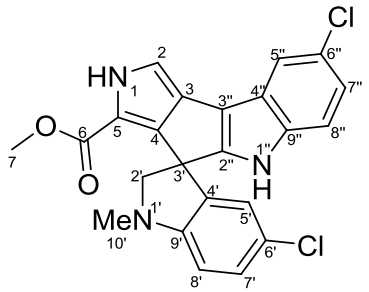
Table S4. ^{13}C NMR Chemical Shifts in $CDCl_3$ of natural[a,b] vs. synthetic spiroindimicin B (**2**)

No.	δ_H (Literature, 125 MHz)[a] (ppm)	δ_H (Natural, 125 MHz)[b] (ppm)	δ_H (Synthetic, 125 MHz) (ppm)	Difference[c] (ppm)
2	110.3 CH	110.2 CH	110.2 CH	-0.1 / 0
3	127.2 C	127.3 C	127.3 C	+0.1 / 0
4	140.1 C	139.8 C	ND	-
5	116.7 C	116.8 C	116.8 C	+0.1 / 0
6	160.5 C	160.4 C	160.4 C	-0.1 / 0
7	51.1 CH_3	51.1 CH_3	51.1 CH_3	0 / 0
2'	64.3 CH_2	64.4 CH_2	64.4 CH_2	+0.1 / 0
3'	51.8 C	51.9 C	51.8 C	0 / -0.1
4'	134.2 C	134.1 C	134.1 C	-0.1 / 0
5'	123.1 CH	123.0 CH	123.0 CH	-0.1 / 0
6'	123.5 C	123.4 C	123.4 C	-0.1 / 0
7'	128.2 CH	128.2 CH	128.2 CH	0 / 0
8'	108.9 CH	108.8 CH	108.8 CH	-0.1 / 0
9'	151.9 C	152.0 C	152.0 C	+0.1 / 0
10'	36.6 CH_3	36.6 CH_3	36.5 CH_3	-0.1 / -0.1
2''	154.5 C	154.6 C	154.6 C	+0.1 / 0
3''	112.1 C	112.1 C	ND	-
4''	121.8 C	121.9 C	121.9 C	+0.1 / 0
5''	118.9 CH	119.0 CH	118.9 CH	+0.1 / -0.1
6''	125.9 C	126.0 C	126.0 C	+0.1 / 0
7''	121.5 CH	121.6 CH	121.6 CH	+0.1 / 0
8''	113.1 CH	113.0 CH	112.9 CH	-0.2 / -0.1
9''	137.8 C	137.8 C	137.7 C	-0.1 / -0.1

ND = not detected

a W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.
b An authentic sample of spiroindimicin B kindly provided by Prof. Changsheng Zhang (SCSIO).
c ("Literature" – "Synthetic") / ("Natural" – "Synthetic").

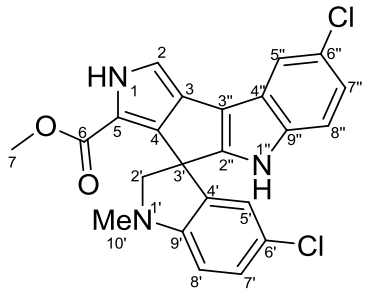
Table S5. ^{1}H NMR Chemical Shifts in DMSO-d_6 of natural[1] vs. synthetic spiroindimicin B (**2**)



No.	δ_H (Literature, 500MHz)[1] (ppm)	δ_H (Synthetic, 500MHz) (ppm)	Difference (ppm)
1	11.43 d (2.0)	11.43 d (1.8)	0
2	7.12 d (3.0)	7.12 d (2.9)	0
3	-	-	-
4	-	-	-
5	-	-	-
6	-	-	-
7	3.53 s	3.53 s	0
2'	3.71 d (9.0)	3.71 d (9.0)	0
	4.03 d (9.0)	4.03 d (8.9)	0
3'	-	-	-
4'	-	-	-
5'	6.24 d (2.0)	6.23 d (2.2)	-0.01
6'	-	-	-
7'	7.10 dd (2.5, 8.5)	7.09 dd (2.3, 8.4)	-0.01
8'	6.72 d (8.5)	6.72 d (8.2)	0
9'	-	-	-
10'	2.91 s	2.91 s	0
1''	11.49 s	11.49 s	0
2''	-	-	-
3''	-	-	-
4''	-	-	-
5''	7.75 d (1.5)	7.75 d (1.9)	0
6''	-	-	-
7''	7.04 dd (2.5, 9.0)	7.03 dd (2.2, 8.6)	-0.01
8''	7.29 d (8.5)	7.28 d (8.6)	-0.01
9''	-	-	-

1 W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.

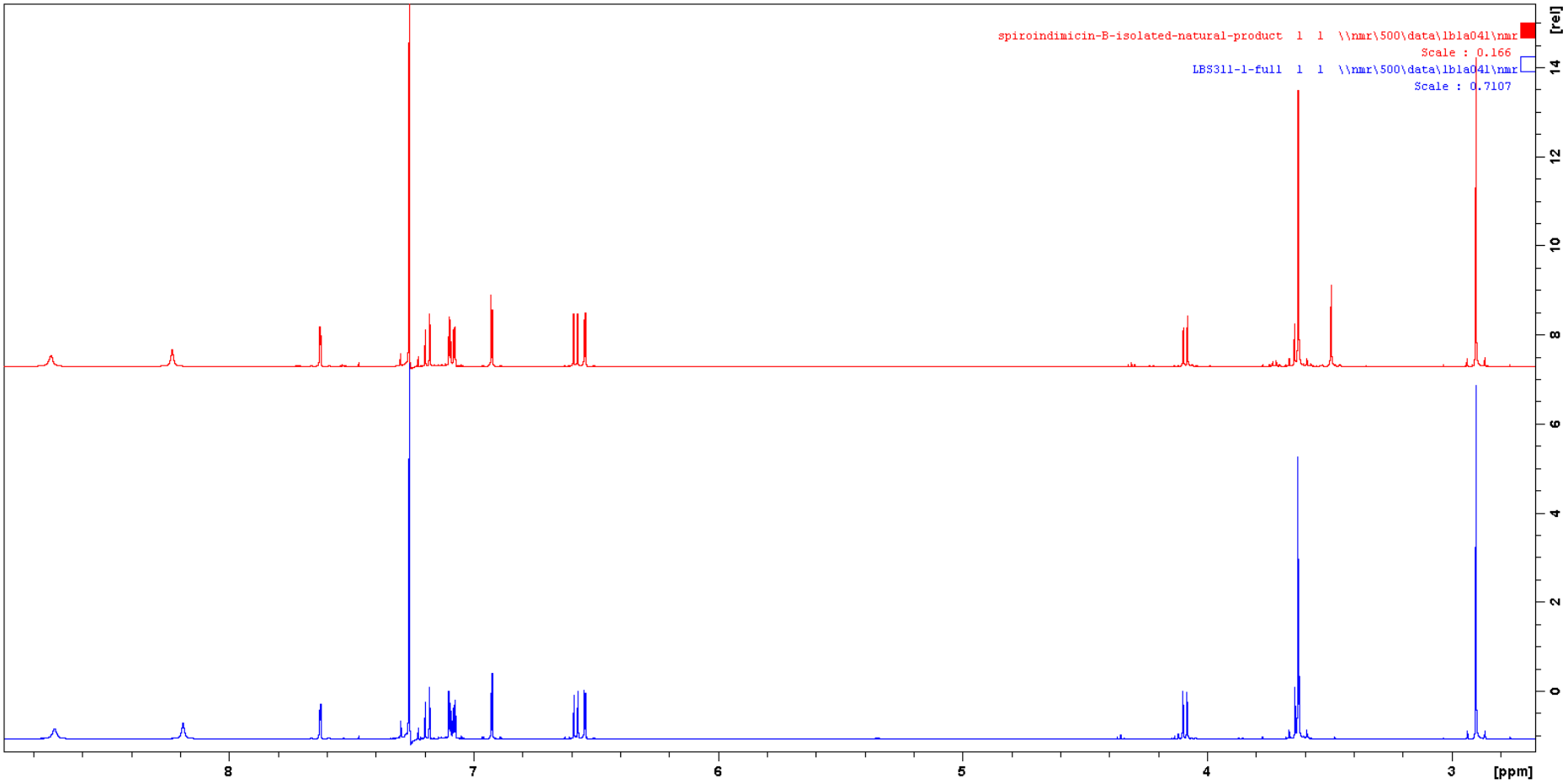
Table S6. ^{13}C NMR Chemical Shifts in DMSO-d_6 of natural[1] vs. synthetic spiroindimicin B (**2**)



No.	δ_C (Literature, 125MHz)[1] (ppm)	δ_C (Synthetic, 125MHz) (ppm)	Difference (ppm)
2	111.5 CH	111.5 CH	0
3	125.5 C	125.5 C	0
4	141.3 C	141.2 C	-0.1
5	115.4 C	115.4 C	0
6	159.8 C	159.8 C	0
7	50.4 CH_3	50.4 CH_3	0
2'	63.1 CH_2	63.1 CH_2	0
3'	51.1 C	51.1 C	0
4'	134.3 C	134.3 C	0
5'	121.5 CH	121.5 CH	0
6'	120.2 C	120.2 C	0
7'	127.5 CH	127.5 CH	0
8'	108.2 CH	108.3 CH	+0.1
9'	152.3 C	152.3 C	0
10'	35.5 CH_3	35.5 CH_3	0
2''	155.2 C	155.1 C	-0.1
3''	111.2 C	111.1 C	-0.1
4''	121.0 C	120.9 C	-0.1
5''	113.8 CH	113.7 CH	-0.1
6''	123.8 C	123.7 C	-0.1
7''	120.1 CH	120.0 CH	-0.1
8''	118.0 CH	118.0 CH	0
9''	138.1 C	138.0 C	-0.1

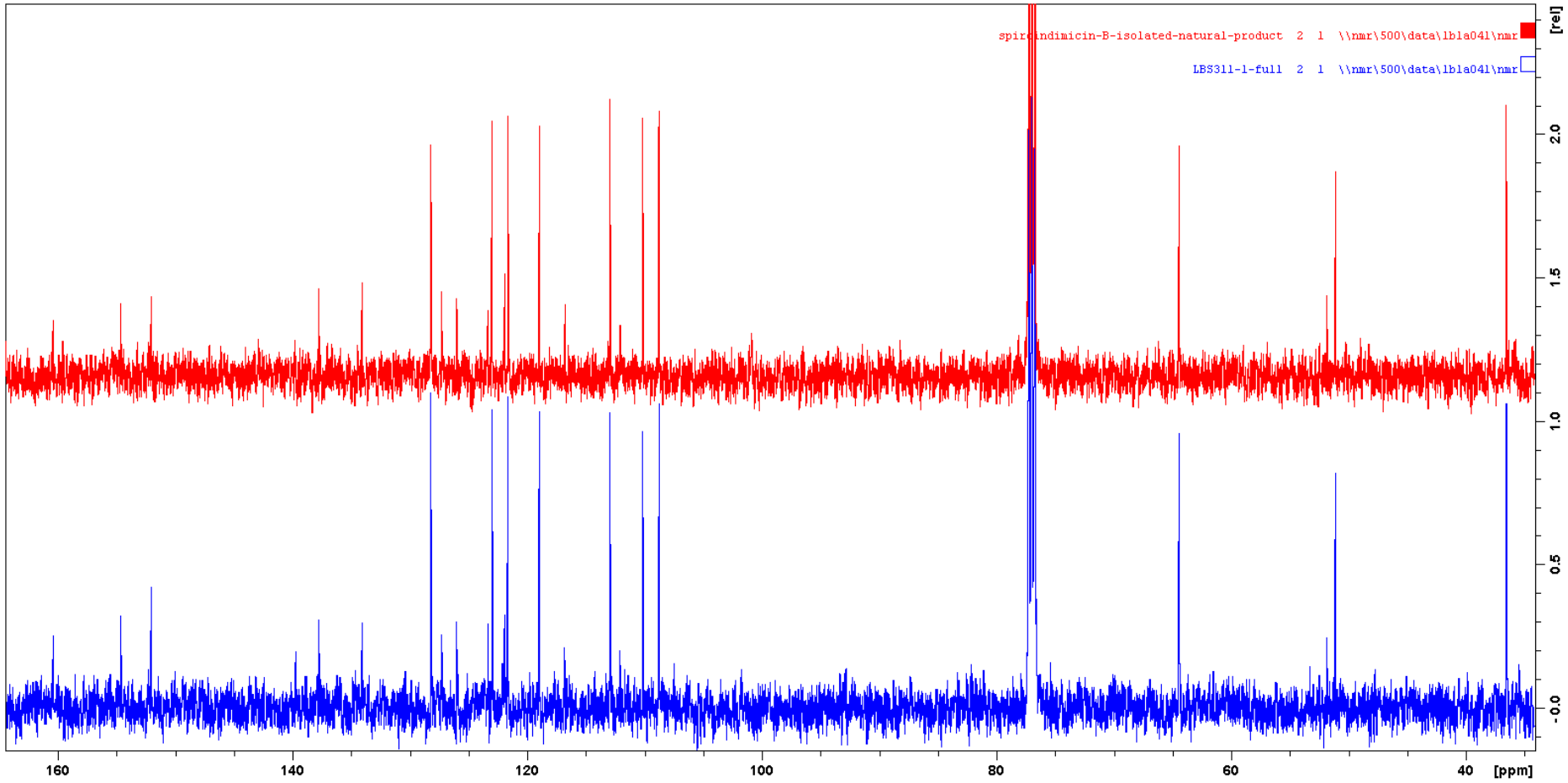
1 W. Zhang, et. al., *Org. Lett.* **2012,** *14*, 3364.

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{1}H NMR overlay ($CDCl_3$, 500 MHz)



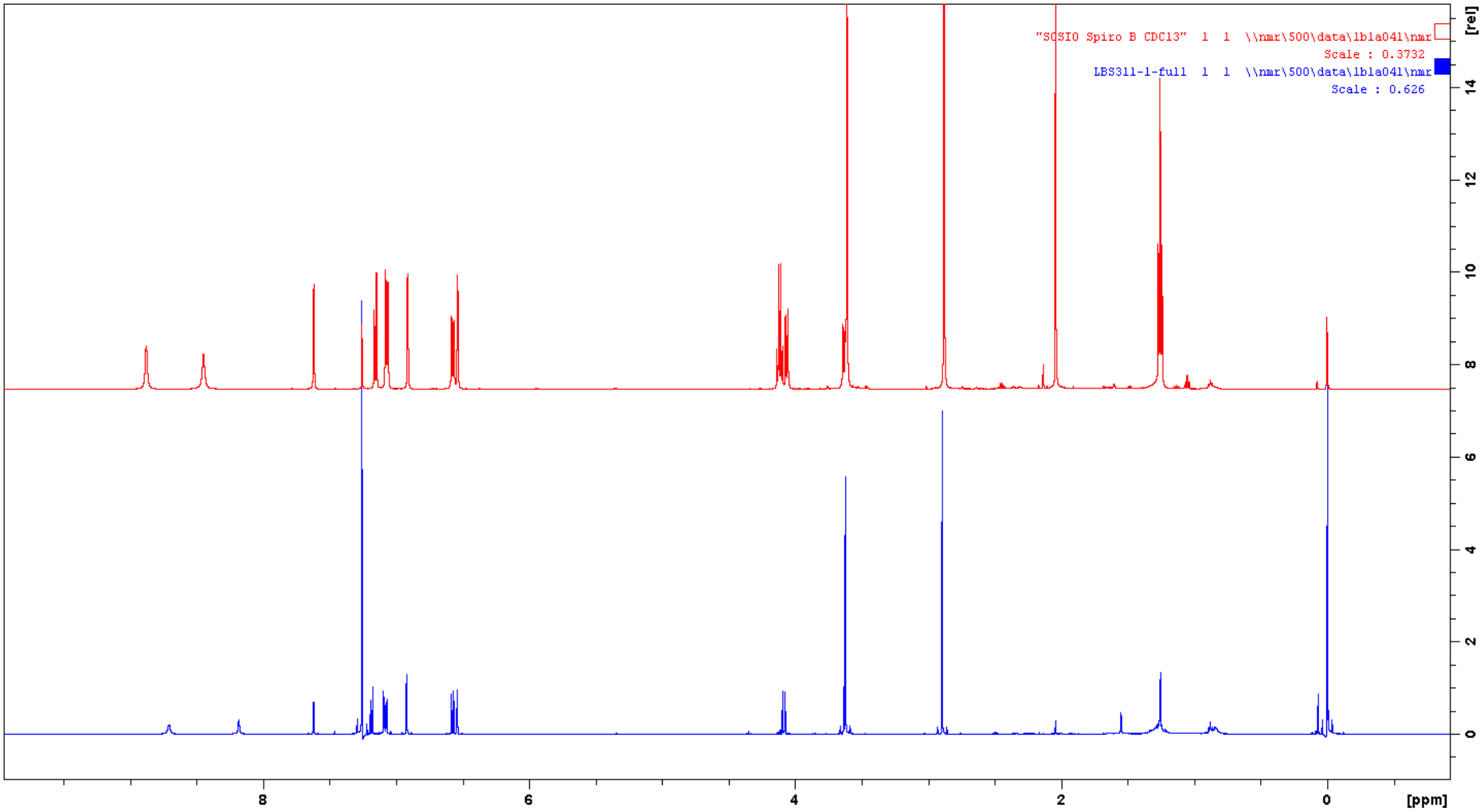
a An authentic sample of spiroindimicin B, kindly provided by Prof. Changsheng Zhang (SCSIO) which was not subjected to further purification upon its arrival at our laboratory

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{13}C NMR overlay ($CDCl_3$, 125 MHz)



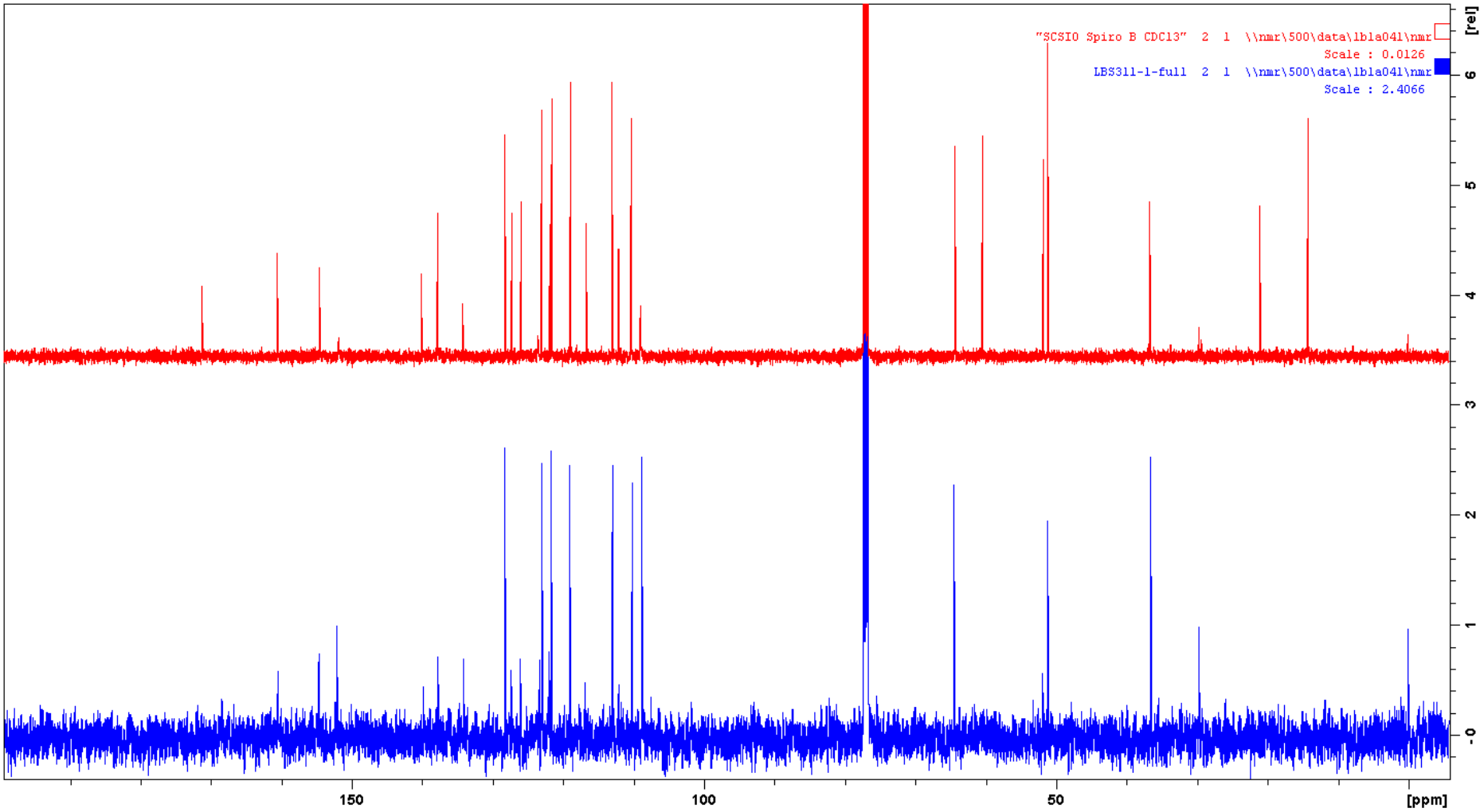
a An authentic sample of spiroindimicin B, kindly provided by Prof. Changsheng Zhang (SCSIO) which was not subjected to further purification upon its arrival at our laboratory

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{1}H NMR overlay ($CDCl_3$, 500 MHz)



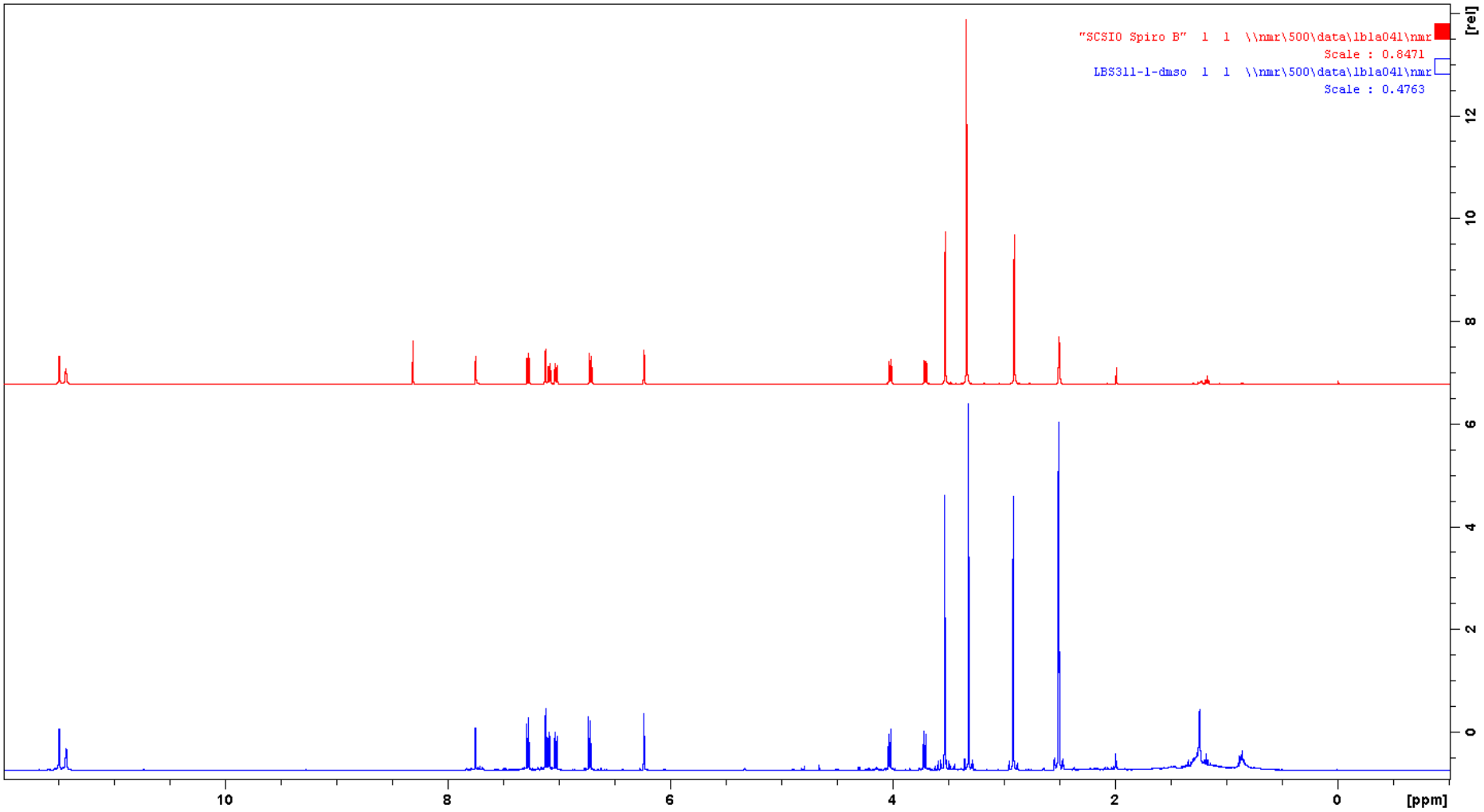
a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{13}C NMR overlay ($CDCl_3$, 125 MHz)



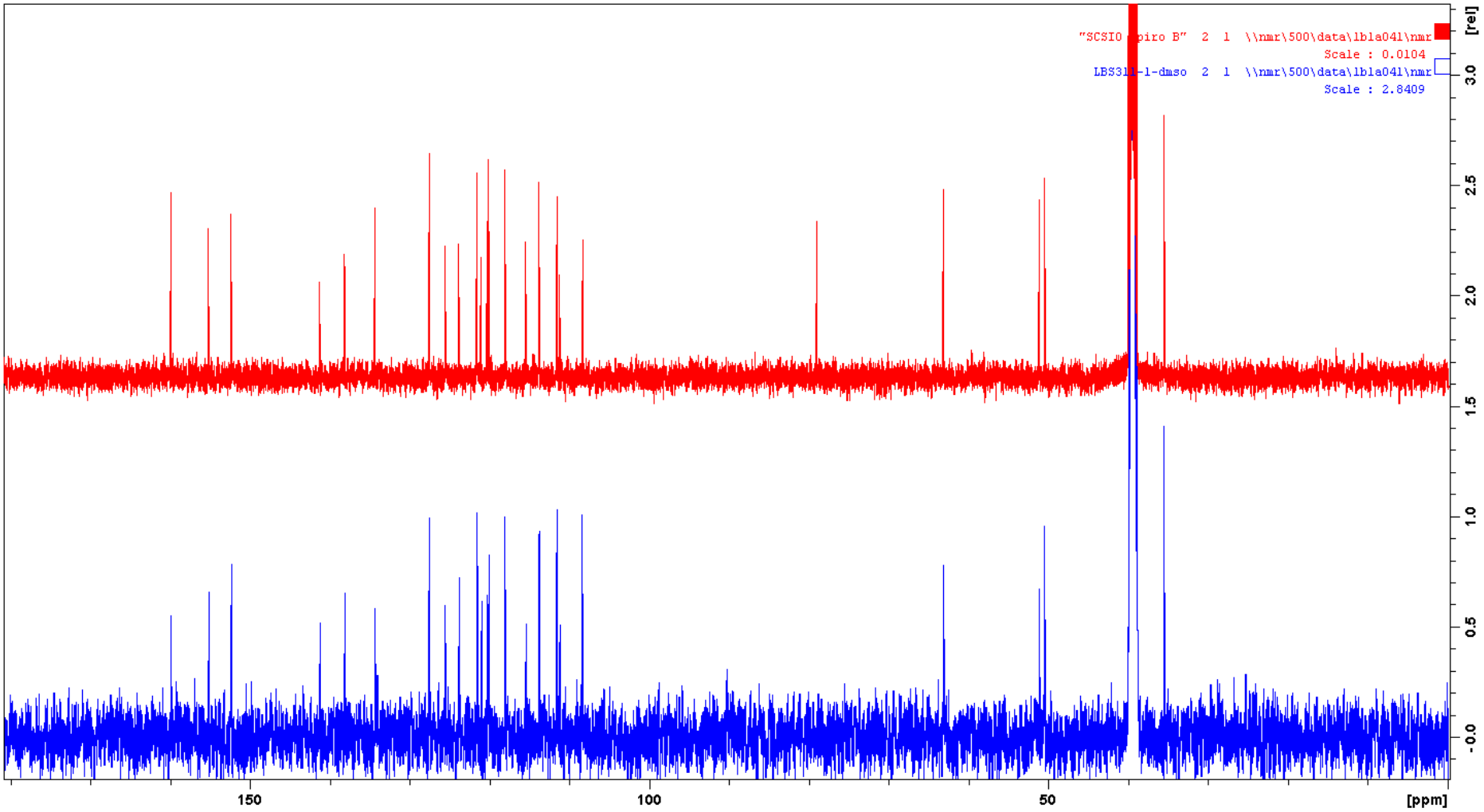
a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{1}H NMR overlay (DMSO-d_6, 500 MHz)



a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

Natural spiroindimicin B[a] (upper spectrum) vs. synthetic spiroindimicin B (lower spectrum) ^{13}C NMR overlay (DMSO-d_6, 125 MHz)



a Original NMR data recorded and kindly provided to us by Prof. Changsheng Zhang and co-workers (SCSIO)

6. Single Crystal X-ray Diffraction Data for 19

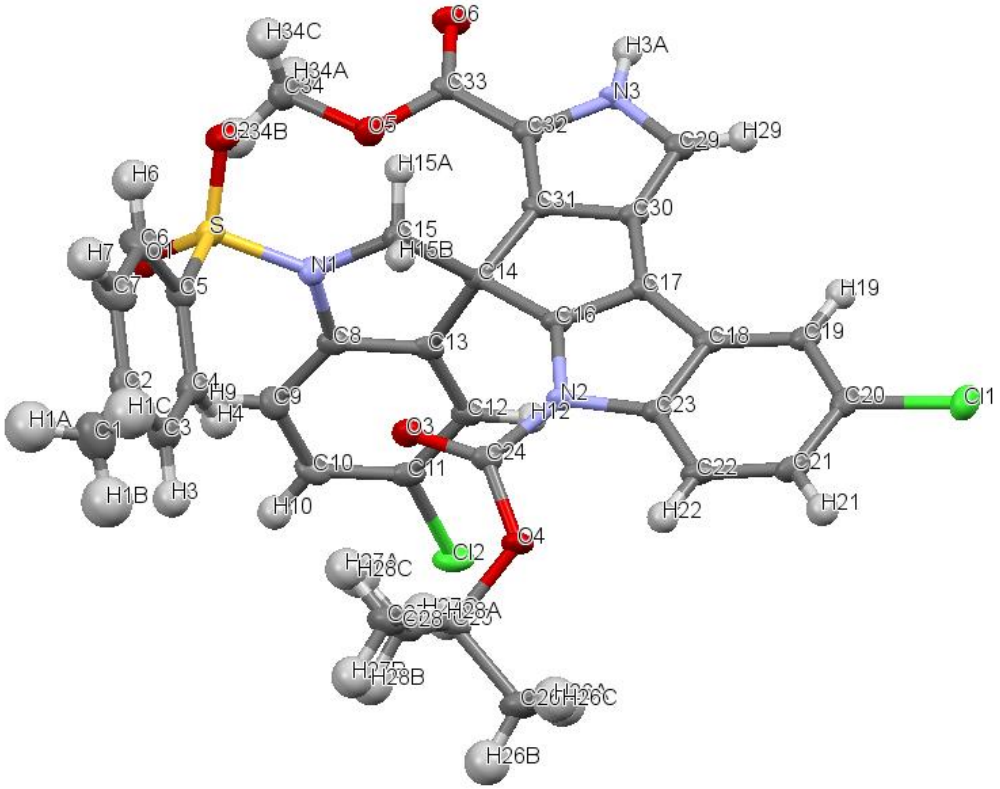


Table 1. Crystal data and structure refinement for lbs305a_0m.

Identification code	lbs305a_0m
Empirical formula	C34 H29 Cl2 N3 O6 S
Formula weight	678.56
Temperature	372(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P-1
Unit cell dimensions	a = 9.468(5) A alpha = 73.289(5) deg. b = 12.672(5) A beta = 72.517(5) deg. c = 14.441(5) A gamma = 76.408(5) deg.
Volume	1561.7(12) A^3
Z, Calculated density	2, 1.443 Mg/m^3
Absorption coefficient	0.327 mm^-1
F(000)	704
Crystal size	0.34 x 0.10 x 0.10 mm
Theta range for data collection	2.41 to 27.83 deg.
Limiting indices	-12<=h<=12, -16<=k<=16, -18<=l<=18
Reflections collected / unique	33016 / 7370 [R(int) = 0.0820]
Completeness to theta = 27.83	99.1 %
Max. and min. transmission	0.9681 and 0.8970
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7370 / 0 / 420
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R1 = 0.0506, wR2 = 0.1183
R indices (all data)	R1 = 0.0893, wR2 = 0.1329
Largest diff. peak and hole	0.598 and -0.430 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for lbs305a_0m. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	6057(4)	2590(3)	-719(2)	39(1)
C(2)	7371(3)	2513(2)	-299(2)	27(1)
C(3)	7410(3)	3306(2)	178(2)	26(1)
C(4)	8624(3)	3231(2)	569(2)	24(1)
C(5)	9796(3)	2359(2)	471(2)	21(1)
C(6)	9774(4)	1556(2)	-13(2)	33(1)
C(7)	8559(4)	1641(3)	-389(2)	35(1)
C(8)	10525(3)	3544(2)	2285(2)	17(1)
C(9)	10646(3)	4608(2)	1680(2)	23(1)
C(10)	10301(3)	5495(2)	2135(2)	22(1)
C(11)	9879(3)	5308(2)	3165(2)	19(1)
C(12)	9754(3)	4247(2)	3773(2)	18(1)
C(13)	10076(3)	3365(2)	3313(2)	15(1)
C(14)	9929(3)	2144(2)	3807(2)	15(1)

C(15)	10221(3)	1637(2)	2889(2)	16(1)
C(16)	8445(3)	1994(2)	4577(2)	15(1)
C(17)	8543(3)	1495(2)	5531(2)	15(1)
C(18)	7051(3)	1504(2)	6172(2)	16(1)
C(19)	6456(3)	1089(2)	7189(2)	18(1)
C(20)	4906(3)	1251(2)	7545(2)	19(1)
C(21)	3950(3)	1791(2)	6928(2)	20(1)
C(22)	4513(3)	2212(2)	5920(2)	18(1)
C(23)	6067(3)	2077(2)	5548(2)	16(1)
C(24)	6496(3)	3126(2)	3722(2)	17(1)
C(25)	4666(3)	4793(2)	3305(2)	21(1)
C(26)	3328(3)	5334(2)	4007(2)	31(1)
C(27)	4179(3)	4468(2)	2529(2)	26(1)
C(28)	5886(3)	5509(2)	2860(2)	28(1)
C(29)	11170(3)	669(2)	6067(2)	17(1)
C(30)	10141(3)	1198(2)	5510(2)	15(1)
C(31)	10960(3)	1544(2)	4506(2)	16(1)
C(32)	12474(3)	1191(2)	4471(2)	16(1)
C(33)	13828(3)	1255(2)	3673(2)	18(1)
C(34)	14796(3)	1907(2)	1932(2)	26(1)
N(1)	10760(2)	2517(2)	2011(2)	18(1)
N(2)	6933(2)	2391(2)	4557(2)	15(1)
N(3)	12563(2)	664(2)	5436(2)	17(1)
O(1)	12198(2)	3146(2)	276(1)	26(1)
O(2)	12108(2)	1125(2)	1028(1)	28(1)
O(3)	7256(2)	3154(2)	2886(1)	21(1)
O(4)	5190(2)	3761(2)	4017(1)	22(1)
O(5)	13521(2)	1799(2)	2795(1)	21(1)
O(6)	15100(2)	880(2)	3775(1)	25(1)
S	11386(1)	2267(1)	901(1)	19(1)
Cl(1)	4106(1)	780(1)	8821(1)	26(1)
Cl(2)	9478(1)	6451(1)	3708(1)	25(1)

Table 3. Bond lengths [A] and angles [deg] for lbs305a_0m.

C(1)-C(2)	1.513(4)
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600
C(2)-C(7)	1.383(4)
C(2)-C(3)	1.384(4)
C(3)-C(4)	1.398(4)
C(3)-H(3)	0.9300
C(4)-C(5)	1.376(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.397(4)
C(5)-S	1.761(3)
C(6)-C(7)	1.384(4)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(8)-C(13)	1.382(3)
C(8)-C(9)	1.388(4)
C(8)-N(1)	1.417(3)
C(9)-C(10)	1.388(4)
C(9)-H(9)	0.9300
C(10)-C(11)	1.383(4)
C(10)-H(10)	0.9300
C(11)-C(12)	1.388(4)
C(11)-Cl(2)	1.753(3)
C(12)-C(13)	1.389(3)
C(12)-H(12)	0.9300
C(13)-C(14)	1.527(3)
C(14)-C(16)	1.520(3)
C(14)-C(31)	1.532(3)
C(14)-C(15)	1.560(3)
C(15)-N(1)	1.475(3)
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(16)-C(17)	1.363(3)
C(16)-N(2)	1.407(3)
C(17)-C(18)	1.437(3)
C(17)-C(30)	1.463(3)
C(18)-C(19)	1.395(3)
C(18)-C(23)	1.421(3)
C(19)-C(20)	1.387(4)
C(19)-H(19)	0.9300
C(20)-C(21)	1.388(4)
C(20)-Cl(1)	1.751(3)
C(21)-C(22)	1.382(4)
C(21)-H(21)	0.9300
C(22)-C(23)	1.394(3)
C(22)-H(22)	0.9300
C(23)-N(2)	1.414(3)
C(24)-O(3)	1.201(3)
C(24)-O(4)	1.331(3)
C(24)-N(2)	1.402(3)
C(25)-O(4)	1.498(3)

C(25)-C(28)	1.511(4)
C(25)-C(27)	1.517(4)
C(25)-C(26)	1.524(4)
C(26)-H(26A)	0.9600
C(26)-H(26B)	0.9600
C(26)-H(26C)	0.9600
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-N(3)	1.359(3)
C(29)-C(30)	1.377(3)
C(29)-H(29)	0.9300
C(30)-C(31)	1.420(3)
C(31)-C(32)	1.388(3)
C(32)-N(3)	1.381(3)
C(32)-C(33)	1.443(4)
C(33)-O(6)	1.223(3)
C(33)-O(5)	1.339(3)
C(34)-O(5)	1.450(3)
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
N(1)-S	1.629(2)
N(3)-H(3A)	0.8600
O(1)-S	1.4324(19)
O(2)-S	1.433(2)

C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(7)-C(2)-C(3)	119.0(2)
C(7)-C(2)-C(1)	120.0(3)
C(3)-C(2)-C(1)	121.0(3)
C(2)-C(3)-C(4)	120.9(3)
C(2)-C(3)-H(3)	119.6
C(4)-C(3)-H(3)	119.6
C(5)-C(4)-C(3)	119.3(3)
C(5)-C(4)-H(4)	120.3
C(3)-C(4)-H(4)	120.3
C(4)-C(5)-C(6)	120.3(2)
C(4)-C(5)-S	120.8(2)
C(6)-C(5)-S	118.8(2)
C(7)-C(6)-C(5)	119.5(3)
C(7)-C(6)-H(6)	120.3
C(5)-C(6)-H(6)	120.3
C(6)-C(7)-C(2)	120.9(3)
C(6)-C(7)-H(7)	119.5
C(2)-C(7)-H(7)	119.5
C(13)-C(8)-C(9)	121.3(2)

C(13)-C(8)-N(1)	109.3(2)
C(9)-C(8)-N(1)	129.3(2)
C(10)-C(9)-C(8)	118.3(2)
C(10)-C(9)-H(9)	120.9
C(8)-C(9)-H(9)	120.9
C(11)-C(10)-C(9)	120.2(2)
C(11)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	121.8(2)
C(10)-C(11)-Cl(2)	118.6(2)
C(12)-C(11)-Cl(2)	119.6(2)
C(11)-C(12)-C(13)	117.7(2)
C(11)-C(12)-H(12)	121.2
C(13)-C(12)-H(12)	121.2
C(8)-C(13)-C(12)	120.7(2)
C(8)-C(13)-C(14)	111.5(2)
C(12)-C(13)-C(14)	127.7(2)
C(16)-C(14)-C(13)	113.27(19)
C(16)-C(14)-C(31)	97.36(19)
C(13)-C(14)-C(31)	115.10(18)
C(16)-C(14)-C(15)	115.48(18)
C(13)-C(14)-C(15)	102.16(19)
C(31)-C(14)-C(15)	114.18(19)
N(1)-C(15)-C(14)	105.17(19)
N(1)-C(15)-H(15A)	110.7
C(14)-C(15)-H(15A)	110.7
N(1)-C(15)-H(15B)	110.7
C(14)-C(15)-H(15B)	110.7
H(15A)-C(15)-H(15B)	108.8
C(17)-C(16)-N(2)	110.0(2)
C(17)-C(16)-C(14)	115.6(2)
N(2)-C(16)-C(14)	133.8(2)
C(16)-C(17)-C(18)	108.6(2)
C(16)-C(17)-C(30)	107.1(2)
C(18)-C(17)-C(30)	144.2(2)
C(19)-C(18)-C(23)	119.5(2)
C(19)-C(18)-C(17)	134.6(2)
C(23)-C(18)-C(17)	105.9(2)
C(20)-C(19)-C(18)	117.8(2)
C(20)-C(19)-H(19)	121.1
C(18)-C(19)-H(19)	121.1
C(21)-C(20)-C(19)	122.4(2)
C(21)-C(20)-Cl(1)	118.1(2)
C(19)-C(20)-Cl(1)	119.5(2)
C(22)-C(21)-C(20)	120.8(2)
C(22)-C(21)-H(21)	119.6
C(20)-C(21)-H(21)	119.6
C(21)-C(22)-C(23)	117.8(2)
C(21)-C(22)-H(22)	121.1
C(23)-C(22)-H(22)	121.1
C(22)-C(23)-N(2)	129.6(2)
C(22)-C(23)-C(18)	121.6(2)
N(2)-C(23)-C(18)	108.7(2)
O(3)-C(24)-O(4)	128.0(2)
O(3)-C(24)-N(2)	122.3(2)

O(4)-C(24)-N(2)	109.7(2)
O(4)-C(25)-C(28)	109.4(2)
O(4)-C(25)-C(27)	109.5(2)
C(28)-C(25)-C(27)	113.5(2)
O(4)-C(25)-C(26)	100.9(2)
C(28)-C(25)-C(26)	111.5(2)
C(27)-C(25)-C(26)	111.3(2)
C(25)-C(26)-H(26A)	109.5
C(25)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(25)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(25)-C(27)-H(27A)	109.5
C(25)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(25)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(25)-C(28)-H(28A)	109.5
C(25)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(25)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
N(3)-C(29)-C(30)	107.9(2)
N(3)-C(29)-H(29)	126.0
C(30)-C(29)-H(29)	126.0
C(29)-C(30)-C(31)	107.3(2)
C(29)-C(30)-C(17)	145.0(2)
C(31)-C(30)-C(17)	107.5(2)
C(32)-C(31)-C(30)	107.7(2)
C(32)-C(31)-C(14)	140.0(2)
C(30)-C(31)-C(14)	112.2(2)
N(3)-C(32)-C(31)	106.5(2)
N(3)-C(32)-C(33)	119.8(2)
C(31)-C(32)-C(33)	133.7(2)
O(6)-C(33)-O(5)	123.6(2)
O(6)-C(33)-C(32)	125.2(2)
O(5)-C(33)-C(32)	111.2(2)
O(5)-C(34)-H(34A)	109.5
O(5)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
O(5)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(8)-N(1)-C(15)	110.50(19)
C(8)-N(1)-S	128.54(17)
C(15)-N(1)-S	120.77(16)
C(24)-N(2)-C(16)	123.0(2)
C(24)-N(2)-C(23)	129.3(2)
C(16)-N(2)-C(23)	106.70(19)
C(29)-N(3)-C(32)	110.55(19)
C(29)-N(3)-H(3A)	124.7
C(32)-N(3)-H(3A)	124.7

C(24)-O(4)-C(25)	119.9(2)
C(33)-O(5)-C(34)	116.35(19)
O(1)-S-O(2)	120.48(12)
O(1)-S-N(1)	107.12(11)
O(2)-S-N(1)	106.67(11)
O(1)-S-C(5)	108.61(12)
O(2)-S-C(5)	106.75(12)
N(1)-S-C(5)	106.42(12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for lbs305a_0m.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	36(2)	52(2)	36(2)	-3(2)	-16(2)	-19(2)
C(2)	26(2)	32(2)	23(1)	1(1)	-8(1)	-16(1)
C(3)	18(1)	32(2)	26(1)	-4(1)	-5(1)	-3(1)
C(4)	24(1)	26(2)	24(1)	-7(1)	-4(1)	-6(1)
C(5)	20(1)	21(1)	21(1)	-2(1)	-7(1)	-5(1)
C(6)	42(2)	21(2)	42(2)	-9(1)	-22(2)	0(1)
C(7)	46(2)	28(2)	43(2)	-8(1)	-25(2)	-10(1)
C(8)	11(1)	17(1)	24(1)	-5(1)	-6(1)	-2(1)
C(9)	22(1)	22(1)	23(1)	-2(1)	-5(1)	-8(1)
C(10)	22(1)	14(1)	30(2)	-1(1)	-10(1)	-5(1)
C(11)	12(1)	17(1)	30(1)	-8(1)	-8(1)	0(1)
C(12)	13(1)	18(1)	24(1)	-6(1)	-8(1)	1(1)
C(13)	9(1)	15(1)	23(1)	-3(1)	-8(1)	-2(1)
C(14)	11(1)	14(1)	21(1)	-5(1)	-6(1)	0(1)
C(15)	13(1)	16(1)	20(1)	-5(1)	-4(1)	-2(1)
C(16)	11(1)	13(1)	22(1)	-4(1)	-6(1)	-1(1)
C(17)	12(1)	14(1)	21(1)	-5(1)	-4(1)	-1(1)
C(18)	12(1)	14(1)	24(1)	-7(1)	-6(1)	-1(1)
C(19)	15(1)	15(1)	25(1)	-8(1)	-5(1)	-1(1)
C(20)	19(1)	18(1)	20(1)	-7(1)	0(1)	-6(1)
C(21)	11(1)	21(1)	30(1)	-10(1)	-1(1)	-3(1)
C(22)	13(1)	16(1)	27(1)	-8(1)	-8(1)	2(1)
C(23)	13(1)	14(1)	21(1)	-6(1)	-4(1)	-1(1)
C(24)	12(1)	15(1)	24(1)	-4(1)	-7(1)	-2(1)
C(25)	20(1)	12(1)	30(2)	-2(1)	-14(1)	2(1)
C(26)	23(2)	27(2)	41(2)	-12(1)	-10(1)	6(1)
C(27)	23(2)	23(2)	37(2)	-8(1)	-15(1)	1(1)
C(28)	25(2)	22(2)	40(2)	-2(1)	-16(1)	-3(1)
C(29)	14(1)	16(1)	22(1)	-2(1)	-6(1)	-3(1)
C(30)	11(1)	13(1)	22(1)	-5(1)	-5(1)	-1(1)
C(31)	15(1)	11(1)	22(1)	-4(1)	-9(1)	0(1)
C(32)	14(1)	14(1)	22(1)	-4(1)	-6(1)	-2(1)
C(33)	15(1)	13(1)	27(1)	-3(1)	-8(1)	-1(1)
C(34)	22(1)	27(2)	25(1)	-6(1)	0(1)	-7(1)

N(1)	18(1)	17(1)	18(1)	-4(1)	-4(1)	-5(1)
N(2)	9(1)	16(1)	21(1)	-4(1)	-6(1)	0(1)
N(3)	10(1)	17(1)	24(1)	-2(1)	-8(1)	0(1)
O(1)	20(1)	37(1)	22(1)	-6(1)	-1(1)	-12(1)
O(2)	29(1)	27(1)	26(1)	-10(1)	-8(1)	7(1)
O(3)	15(1)	25(1)	21(1)	-5(1)	-7(1)	1(1)
O(4)	15(1)	20(1)	25(1)	-4(1)	-6(1)	6(1)
O(5)	13(1)	26(1)	21(1)	-3(1)	-4(1)	-2(1)
O(6)	11(1)	27(1)	35(1)	-2(1)	-7(1)	-1(1)
S	15(1)	23(1)	20(1)	-7(1)	-5(1)	-1(1)
Cl(1)	22(1)	30(1)	22(1)	-7(1)	2(1)	-7(1)
Cl(2)	23(1)	17(1)	39(1)	-12(1)	-13(1)	2(1)