

"Palladium-Catalyzed Tsuji–Trost-Type Reaction of 3-Indolylmethylacetates with O, and S Soft Nucleophiles"

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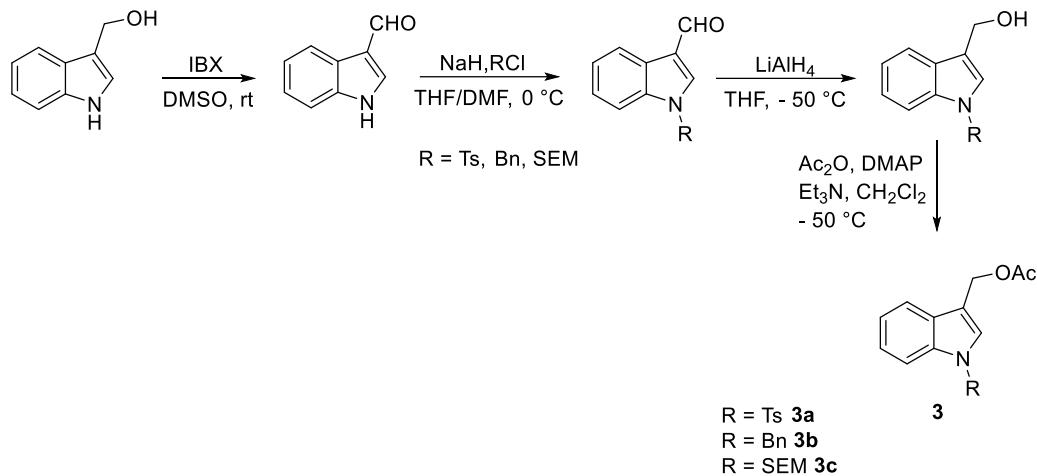
1. GENERAL INFORMATION

1.1. Reagents and methods

All of the commercially available reagents, catalysts, bases and solvents were used as purchased, without further purification. Starting materials and reaction products were purified by flash chromatography using SiO₂ as stationary phase, eluting with *n*-hexane/ethyl acetate. ¹H NMR (400.13 MHz), ¹³C NMR (100.6 MHz), and ¹⁹F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer. Mass spectra were determined with a Shimadzu QP2010 Gas Chromatograph Mass spectrometer (EI ion source) or with a Shimadzu QP2010-Plus Gas Chromatograph Mass spectrometer (CI ion source/ NCI ionsource, DI). HRMS were recorded with an Orbitrap Exactive Mass spectrometer with ESI source. Melting points were determined with a Büchi B-545 apparatus and are uncorrected.

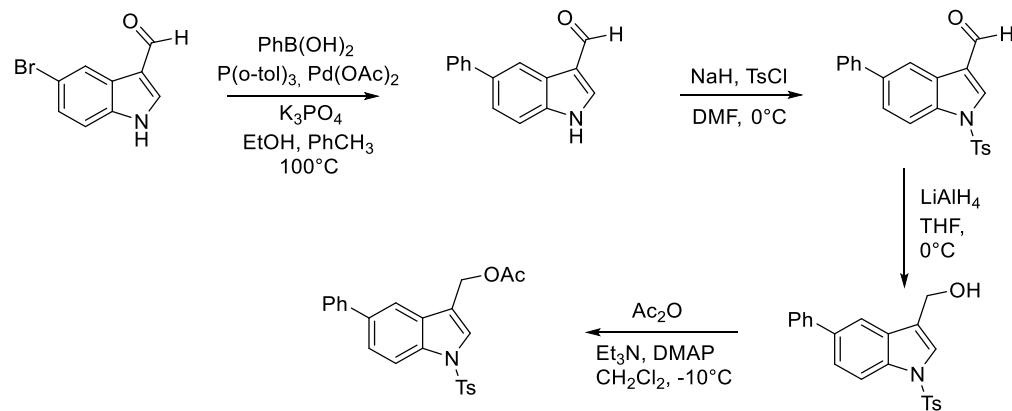
2. SYNTHETIC PROCEDURES FOR STARTING MATERIALS

Starting materials **3a-3d** and **3f-3g** were prepared according to literature procedures^{1,2,3} through the four-step sequence of reactions depicted in the following scheme.



2.1 Typical procedure for the preparation of the 5-phenyl(1-tosyl-1*H*-indol-3-yl)methyl acetate **3e**:

Starting materials **3e** was prepared through the four-step sequence of reactions depicted in the following scheme.



2.2.1 Typical procedure for the preparation of the 5-phenyl-1*H*-indole-3-carbaldehyde:

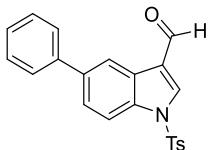
In a 100 ml two-necked round bottom flask equipped with a stirring bar P(o-tol)₃ (0.220 g, 0.725 mmol, 0.10 equiv.) and Pd(OAc)₂ (0.081 g, 0.363 mmol, 0.05 equiv.) were dissolved in ethanol (10 ml) and toluene (5 ml) under inert atmosphere. Then, 5-bromo-1*H*-indole-3-carbaldehyde (1.62 g, 7.250 mmol, 1.00 equiv.), phenylboronic acid (1.75 g, 14.50 mmol, 2.00 equiv.) and K₃PO₄ (3.07 g, 14.50 mmol, 2.00 equiv) were added to the mixture. The reaction was allowed to stir until disappearance of the starting material (monitored by HPLC), then toluene and ethanol were removed under reduced pressure. The residue was diluted with Et₂O, washed with a KHSO₄ solution (10% w/w) and brine (2x). The organic layer was dried over Na₂SO₄, filtered and concentrated under reduced pressure, then the crude was purified by flash chromatography (silica gel, *n*-hexane/AcOEt 85/15 v/v, R_f = 0.22) to afford 1.55 g of 5-phenyl-1*H*-indole-3-carbaldehyde in 95% yield.



5-phenyl-1H-indole-3-carbaldehyde: known compound; 95% yield; orange solid; mp: 255-257 °C; lit.⁴ mp: 257-258 °C; R_f = 0.21 (*n*-hexane/AcOEt, 75:25); IR (neat): 3330, 2360, 1732, 1582, 1082, 812 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-*d*₆): δ 11.7 (s, 1H), 9.43 (s, 1H), 7.81 - 7.76 (m, 2H), 7.13 - 7.11 (m, 2H), 7.08 - 7.00 (m, 2H), 6.95 - 6.91 (m, 2H) 6.82 - 6.78 (m, 1H); ¹³C NMR (100.6 MHz) (DMSO-*d*₆): δ 185.1 (CH), 141.2 (C), 139.1 (CH), 136.6 (C), 134.8 (C), 128.9 (CH), 126.9 (CH), 126.8 (CH), 124.8 (C), 122.8 (CH), 118.8 (CH), 118.4 (C), 112.9 (CH); HRMS: *m/z* [M + H]⁺ calcd for C₁₅H₁₁NO: 221.0800; found: 221.0801.

2.2.2 Typical procedure for the preparation of ethyl 5-phenyl-1-tosyl-1*H*-indole-3-carbaldehyde:

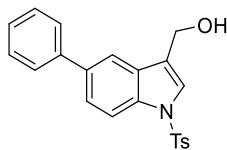
To a stirred solution of NaH (60% dispersion in mineral oil, 0.33 g, 8.27 mmol, 1.2 equiv.) in dry THF (5 mL) *5-phenyl-1H-indole-3-carbaldehyde* (1.52 g, 6.89 mmol, 1.0 equiv.), dissolved in anhydrous DMSO (7.5 mL), was added dropwise at 0°C under argon. The reaction mixture was warmed to room temperature, stirred for 5 minutes and, after cooling to 0°C, a solution of TsCl (1.45 g, 7.58 mmol, 1.1 equiv.) in anhydrous THF (25 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature again and stirred for 5h. After the consumption of the substrate (TLC, *n*-hexane/AcOEt, 80:20), the reaction was quenched with the addition of H₂O, diluted with Et₂O, washed with a solution of KHSO₄ (10% w/w), a saturated solution of NaHCO₃, and brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by chromatography on SiO₂ (25-40 μm), eluting with 85/15 (v/v) *n*-hexane/AcOEt mixture (R_f = 0.23) to obtain 1.87 g (73% yield) of 1-tosyl-1*H*-indole-3-carbaldehyde.



5-phenyl-1-tosyl-1H-indole-3-carbaldehyde: 73% yield; white solid; mp: 204-206 °C; R_f = 0.23 (*n*-hexane/AcOEt 85:15); IR (neat): 3123, 2830, 1676, 1495, 1230, 972 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 10.12 (s, 1H), 8.48 (d, *J* = 1.4 Hz, 1H), 8.25 (s, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.67 - 7.60 (m, 3H), 7.46 - 7.42 (m, 2H), 7.35 (tt, *J*₁ = 7.3 Hz, *J*₂ = 1.6 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 2H), 2.38 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 185.6 (CH), 146.4 (C), 140.8 (C), 138.8 (C), 136.8 (CH), 134.7 (C), 134.5 (C), 130.5 (CH), 128.9 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.0 (CH), 122.6 (C), 121.1 (CH), 113.6 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₂₂H₁₇NNaO₃S: [M+Na]⁺ 398.0827, Found: 398.0829.

2.2.3 Typical procedure for the preparation of the 5-phenyl(1-tosyl-1*H*-indol-3-yl)methanol:

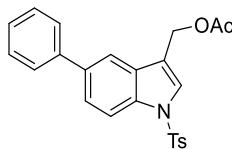
A flame-dried three-necked round bottom flask, equipped with a magnetic stirring bar, was charged with 1-tosyl-1*H*-indole-3-carbaldehyde (1.87 g, 4.98 mmol, 1.0 equiv.) dissolved in anhydrous THF (20 mL) under argon. The resulting solution was cooled to -50 °C before adding dropwise a solution of LiAlH₄ in THF (2 M, 1.50 mL, 2.99 mmol, 0.6 equiv.) and was stirred for 15 minutes. After consuming the starting material (TLC, *n*-hexane/AcOEt, 70/30), the reaction was quenched by slow addition of an 80% aqueous MeOH solution at 0 °C. The resulting mixture was extracted with Et₂O, washed with a solution of NaHSO₄ (10% w/w), brine, and the organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure at 30°C. The resulting crude product was used in the next step without further purification (1.63 g, 87% yield)



5-phenyl(1-tosyl-1H-indol-3-yl)methanol: 87% yield; yellow solid; mp: 93-95 °C; R_f = 0.20 (*n*-hexane/AcOEt 70:30); IR (neat): 2981, 1676, 1453, 1230, 1032, 816 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 8.04 (d, *J* = 8.6 Hz, 1H), 7.83 - 7.77 (m, 3H), 8.62 - 7.54 (m, 4H), 7.45 - 7.41 (m, 2H), 7.35 - 7.32 (m, 1H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.85 (s, 3H), 2.34 (s, 3H), 1.68 (s, 1H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 145.2 (C), 141.3 (C), 137.0 (C), 135.3 (C), 134.9 (C), 130.1 (CH), 128.9 (CH) overlapping, 127.5 (CH), 127.2 (CH), 127.0 (CH), 124.7 (CH), 124.5 (CH), 122.6 (C), 118.5 (CH), 114.5 (CH), 57.3 (CH₂), 21.7 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₂₂H₁₉KNO₃S: [M+K]⁺ 416.0723, Found: 416.0718.

2.2.4 Typical procedure for the preparation of the 5 phenyl(1-tosyl-1H-indol-3-yl)methyl acetate 3e:

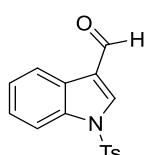
To a stirred solution of 5-phenyl(1-tosyl-1H-indol-3-yl)methanol (1.63 g, 4.33 mmol, 1.0 equiv.) in CH₂Cl₂ (10 mL) DMAP (0.052 g, 0.43 mmol, 0.1 equiv.), triethylamine (0.933 mL, 6.50 mmol, 1.5 equiv.) and acetic anhydride (0.61 mL, 6.50 mmol, 1.5 equiv.) were added at -50 °C and the resulting reaction mixture was stirred for 15 minutes. After the consumption of substrate (TLC, *n*-hexane/AcOEt, 85:15), the reaction was diluted with Et₂O, washed with a saturated NaHCO₃ solution, and with brine. The combined organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting compound **3e** was used in the next step without further purification (1.63 g, 90% yield).



5 phenyl(1-tosyl-1H-indol-3-yl)methyl acetate 3e: 90% yield; pale pink solid; mp: 112-114 °C; R_f = 0.22 (*n*-hexane/AcOEt 85:15); IR (neat): 3679, 2980, 1732, 1455, 1214, 1003, 885 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 8.03 (d, *J* = 8.6 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 1.2 Hz, 1H), 7.65 (s, 1H), 7.61 - 7.56 (m, 3H), 7.46 - 7.42 (m, 2H), 7.36 - 7.33 (m, 1H), 7.25 (d, *J* = 8.3 Hz, 2H), 5.27 (s, 2H), 2.35 (s, 3H), 2.08 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 145.3 (C), 141.2 (C), 137.1 (C), 135.3 (C), 134.6 (C), 130.1 (CH), 128.9 (CH), 127.5 (CH), 127.3 (CH), 127.1 (CH), 126.4 (CH), 124.8 (CH), 118.2 (CH), 117.6 (C), 114.0 (CH), 57.9 (CH₂), 21.7 (CH₃), 21.1 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₂₄H₂₁KNO₄S: [M+K]⁺ 458.0828, Found: 458.0830.

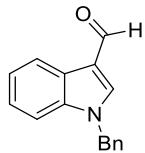
4. CHARACTERIZATION DATA OF STARTING MATERIAL

4.1. Characterization data of substituted 1-tosyl-1*H*-indole-3-carbaldehydes:



1-tosyl-1H-indole-3-carbaldehyde: known compound; 95% yield; pink solid; mp: 138-140 °C; lit.¹ mp: 138-140 °C; R_f = 0.21 (*n*-hexane/AcOEt, 75:25); IR (neat): 2981, 1663, 1396, 1161, 780 cm⁻¹; ¹H NMR (400.13 MHz)

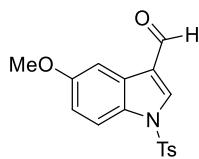
(CDCl₃): δ 10.09 (s, 1H), 8.26 - 8.24 (m, 1H), 8.23 (s, 1H), 7.96 - 7.94 (m, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.41 (td, J₁ = 7.3 Hz, J₂ = 1.36 Hz, 1H), 7.36 (td, J₁ = 7.3 Hz, J₂ = 1.4 Hz, 1H), 7.29 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 185.3 (CH), 146.2 (C), 136.24 (C), 136.21 (CH), 135.2 (C), 134.3 (C), 130.3 (CH), 127.2 (CH), 126.3 (CH), 125.1 (CH), 122.6 (CH), 122.3 (C), 113.3 (CH), 21.7 (CH₃); HRMS: m/z [M + Na]⁺ calcd for C₁₆H₁₃NO₃SnA: 322.0508; found: 322.0509.



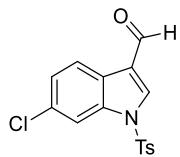
1-benzyl-1H-indole-3-carbaldehyde: known compound; 95% yield; yellow solid; mp: 101-103 °C lit.¹, mp: 101-103 °C; R_f = 0.27 (n-hexane/AcOEt, 75:25); IR (neat): 3460, 3278, 2933, 1649, 1353, 1018 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 9.94 (s, 1H), 8.27 - 8.25 (m, 1H), 7.64 (s, 1H), 7.30 - 7.22 (m, 6H), 7.11 (d, J = 7.3 Hz, 2H), 5.29 (s, 2H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 184.7 (CH), 138.6 (C), 137.5 (C), 135.4 (C), 129.1 (CH), 128.4 (CH), 127.3 (CH), 125.5 (C), 124.2 (CH), 123.1 (CH), 122.2 (CH), 118.5 (C), 110.4 (CH), 50.9 (CH₂).



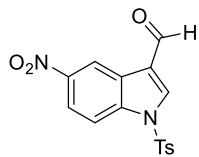
1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indole-3-carbaldehyde: known compound;¹ 97% yield; yellow oil; R_f = 0.22 (n-hexane/AcOEt, 85:15); IR (neat): 2953, 2892, 1660, 1081, 744 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 10.04 (s, 1H), 8.32 - 8.30 (m, 1H), 7.79 (s, 1H), 7.54 - 7.52 (m, 1H), 7.39 - 7.32 (m, 2H), 5.53 (s, 3H), 3.51 (t, J = 8.0 Hz, 2H), 0.91 (t, J = 8.0 Hz, 2H), -0.05 (s, 9H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 185.1 (CH), 138.3 (CH), 137.3 (C), 125.7 (C), 124.5 (CH), 123.5 (CH), 122.2 (CH), 119.0 (C), 110.8 (CH), 76.6 (CH₂), 66.7 (CH₂), 17.8 (CH₂), -1.33 (CH₃).



5-methoxy-1-tosyl-1H-indole-3-carbaldehyde: known compound; quantitative yield; white solid; mp: 103-105 °C lit.³ mp: 128-130 °C; IR (neat): 3662, 2830, 1678, 1251, 1094, 848 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-d₆): δ 10.1 (s, 1H), 8.82 (s, 1H), 7.98 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 9.1 Hz, 1H), 7.58 (d, J = 2.5 Hz, 1H), 7.44 (d, J = 8.2 Hz, 2H), 7.05 (dd, J₁ = 9.1 Hz, J₂ = 2.6 Hz, 1H), 3.78 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100.6 MHz) (DMSO-d₆): δ 187.2 (CH), 157.7 (C), 146.9 (C), 139.4 (CH), 133.8 (C), 131.0 (CH), 129.3 (C), 127.7 (CH), 127.4 (C), 121.9 (C), 115.6 (CH), 114.6 (CH), 104.3 (CH), 21.5 (CH₃); HRMS: m/z [M + Na]⁺ calcd for C₁₇H₁₅NO₄SnA: 352.0614; found: 352.0614.

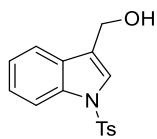


6-chloro-1-tosyl-1H-indole-3-carbaldehyde: known compound; 96% yield; orange solid; mp: 149-151 °C lit.³; mp: 149-151 °C; IR (neat): 2914, 1698, 1420, 1223, 1045 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 10.0 (s, 1H), 8.20 (s, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 1.7 Hz, 1H), 7.84 (d, J = 8.5 Hz, 2H), 7.34 - 7.32 (m, 3H), 2.40 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 185.1 (CH), 146.6 (C), 136.5 (CH), 135.7 (C), 134.2 (C), 132.5 (C), 130.6 (CH), 127.4 (CH), 125.9 (CH), 124.9 (C), 123.6 (CH), 122.1 (C), 113.6 (CH), 21.8 (CH₃); HRMS: m/z [M + H]⁺ calcd for C₁₆H₁₃ClNO₃S: 334.0299; found: 334.0295.

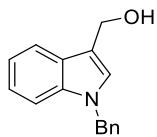


5-nitro-1-tosyl-1H-indole-3-carbaldehyde: known compound; 90% yield; orange solid; mp: 165-167 °C; lit.² mp: 165-167 °C; R_f = 0.17 (n-hexane/AcOEt, 75:25); IR (neat): 3052, 2830, 1736, 1255, 984 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-d₆): δ 10.11 (s, 1H), 9.13 (s, 1H), 8.87 (s, 1H), 8.30 (dd, J₁ = 9.3 Hz, J₂ = 2.2 Hz, 1H), 8.21 (d, J = 9.3 Hz, 1H), 8.08 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 2.36 (s, 3H); ¹³C NMR (100.6 MHz) (DMSO-d₆): δ 187.2 (CH), 147.7 (C), 145.3 (C), 141.3 (CH), 137.6 (C), 133.3 (C), 131.3 (CH), 128.0 (CH), 121.83 (CH), 121.79 (C), 118.0 (CH), 114.7 (CH), 21.6 (CH₃); HRMS: m/z (MALDI-TOF) positive ion, calculated for C₁₆H₁₂N₂NaO₅S: [M+Na]⁺ 367.0365, Found: 367.0367.

4.2. Characterization data of substituted (1-tosyl-1*H*-indol-3-yl)methanols:



(1-tosyl-1H-indol-3-yl)methanol: known compound; 98% yield; pink solid; mp: 104-105 °C; lit.¹ mp: 104-105 °C; R_f = 0.24 (n-hexane/AcOEt, 70:30); ¹H NMR (400.13 MHz) (CDCl₃): δ 7.92 (d, J = 8.3 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.47 (s, 1H), 7.26 (dt, J₁ = 8.2 Hz, J₂ = 1.0 Hz, 1H), 7.20 - 7.13 (m, 3H), 4.75 (s, 2H), 2.26 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 145.1 (C), 135.6 (C), 135.4 (C), 130.0 (CH), 129.6 (C), 127.0 (CH), 125.1 (CH), 123.9 (CH), 123.4 (CH), 122.4 (C), 120.0 (CH), 113.9 (CH), 57.3 (CH₂), 21.7 (CH₃); HRMS: m/z [M + Na]⁺ calcd for C₁₆H₁₅NO₃Na: 324.0665; found: 324.0663

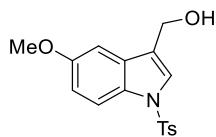


(1-benzyl-1H-indol-3-yl)methanol: known compound; 97% yield; yellow solid; mp: 87-89 °C; lit.¹ mp: 87-89 °C; R_f = 0.28 (n-hexane/AcOEt, 70:30); ¹H NMR (400.13 MHz) (CDCl₃): δ 77.78 (d, J = 7.6 Hz, 1H), 7.35 - 7.29 (m, 4H), 7.24 (td, J₁ = 7.6 Hz, J₂ = 1.1 Hz, 1H), 7.20 - 7.15 (m, 4H), 5.32 (s, 2H), 4.91 (d, J = 4.1 Hz, 2H), 1.55 (bs, 1H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 137.2 (C), 136.9 (C), 128.8 (CH), 127.7 (CH), 127.2 (C), 127.0 (CH),

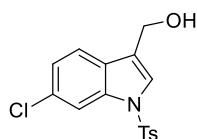
126.9 (CH), 122.3 (CH), 119.7 (CH), 119.2 (CH), 115.4 (C), 109.9 (CH), 57.3 (CH₂), 50.0 (CH₂); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₁₆H₁₅KNO: [M+K]⁺ 276.0791, Found: 276.0790.



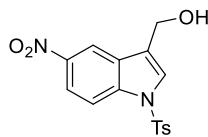
*(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methanol*: known compound¹; 98% yield; yellow oil; R_f = 0.23 (*n*-hexane/AcOEt, 85:15); ¹H NMR (400.13 MHz) (DMSO-d₆): δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.57 (s, 2H), 4.92 (t, *J* = 5.1 Hz, 1H), 4.71 (d, *J* = 5.1 Hz, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 0.89 (t, *J* = 8.0 Hz, 2H), 0.00 (s, 9H); ¹³C NMR (100.6 MHz) (DMSO-d₆): δ 137.4 (C), 128.4 (C), 127.7 (CH), 122.4 (CH), 120.14 (CH), 120.11 (CH), 117.3 (C), 111.0 (CH), 75.5 (CH₂), 65.7 (CH₂), 56.1 (CH₂), 18.1 (CH₂), -0.50 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₁₅H₂₃KNO₂Si: [M+K]⁺ 316.1135, Found: 316.1140.



*(5-methoxy-1-tosyl-1*H*-indol-3-yl)methanol*: known compound; quantitative yield; brown solid; mp: 122-124 °C; lit.³ mp: 112-124; IR (neat): 3636, 2364, 1710, 1434, 1078 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.48 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 2.4 Hz, 1H), 6.94 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.5 Hz, 1H), 4.77 (s, 2H), 3.81 (s, 3H), 2.33 (s, 3H); ¹H NMR (100.6 MHz) (CDCl₃): δ 156.6 (C), 145.0 (C), 135.3 (C), 130.6 (C), 130.2 (C), 130.0 (CH), 126.9 (CH), 124.7 (CH), 122.4 (C), 114.8 (CH), 114.3 (CH), 102.3 (CH), 57.3 (CH₂), 55.8 (CH₃), 21.7 (CH₃); HRMS: *m/z* [M + Na]⁺ calcd for C₁₇H₁₇NO₄SNa : 354.0770; found: 354.0771.

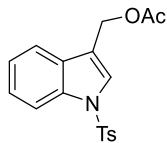


*(6-chloro-1-tosyl-1*H*-indol-3-yl)methanol*: known compound; quantitative yield; pink solid; mp: 123-125 °C; lit.³ mp: 123-125 °C; IR (neat): 3357, 2871, 1725, 1169, 1084, 908 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 7.93 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.45 - 7.43 (m, 2H), 7.19 - 7.13 (m, 3H), 4.71 (s, 2H), 2.28 (s, 3H), 1.65 (s, 1H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 145.5 (C), 135.9 (C), 135.1 (C), 131.2 (C), 130.2 (CH), 128.0 (C), 127.0 (CH), 124.3 (CH), 124.1 (CH), 122.2 (q), 120.9 (CH), 114.0 (CH), 57.1 (CH₂), 21.7 (CH₃); HRMS: *m/z* [M - H]⁻ calcd for C₁₆H₁₃Cl NO₃S: 334.0310; found: 334.0304.

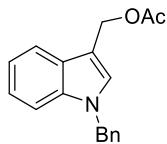


(5-nitro-1-tosyl-1H-indol-3-yl)methanol: known compound; 98% yield; yellow solid; mp: 120-122°C; lit² mp: 120-122°C; R_f = 0.17 (*n*-hexane/AcOEt, 65:35); IR (neat): 3014, 1731, 1143, 1064 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-*d*₆): δ 8.60 (d, *J* = 2.2 Hz, 1H), 8.23 (dd, *J*₁ = 9.2 Hz, *J*₂ = 2.2 Hz, 1H), 8.16 (d, *J* = 9.2 Hz, 1H), 7.95 - 7.92 (m, 3H), 7.42 (d, *J* = 8.1 Hz, 2H), 4.68 (d, *J* = 0.7 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (100.6 MHz) (DMSO-*d*₆): δ 146.7 (C), 143.9 (C), 138.0 (C), 134.2 (C), 131.0 (CH), 130.0 (C), 127.3 (CH), 126.9 (CH), 125.0 (C), 120.4 (CH), 117.4 (CH), 114.3 (CH), 55.1 (CH₂), 21.5 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₁₆H₁₂N₂NaO₅S: [M+Na]⁺ 367.0365, Found: 367.0367.

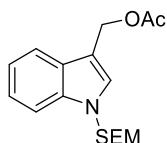
4.3. Characterization data of (1-tosyl-1*H*-indol-3-yl)methyl acetates **3a-3d and 3f-3g**:



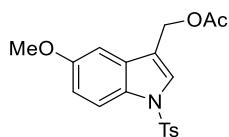
*(1-tosyl-1H-indol-3-yl)methyl acetate **3a**:* known compound; 98% yield; pale pink solid; mp: 138-140°C; lit.¹ mp: 138-140 °C; R_f = 0.20 (*n*-hexane/AcOEt, 85:15); IR (neat): 2982, 1662, 1538, 1368, 1099, 968 cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.55 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.27 (td, *J*₁ = 8.3 Hz, *J*₂ = 1 Hz, 1H), 7.21-7.15 (m, 3H); 5.16 (s, 2H), 2.27 (s, 3H), 2.00 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 171.0 (C), 145.2 (C), 135.34 (C), 135.28 (C), 130.1 (CH), 129.6 (C), 127.1 (CH), 125.8 (CH), 125.2 (CH), 123.6 (CH), 119.8 (CH), 117.4 (C), 113.8 (CH), 57.9 (CH₂), 21.7 (CH₃), 21.1(CH₃); HRMS: *m/z* [M + Na]⁺ calcd for C₁₈H₁₇NO₄SNa: 366.0770; found: 366.0768.



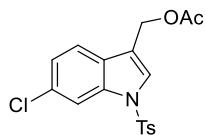
*(1-benzyl-1H-indol-3-yl)methyl acetate **3b**:* known compound;¹ 98% yield; orange oil; R_f = 0.24 (*n*-hexane/AcOEt, 75:25); IR (neat): 3032, 2933, 1730, 1468, 1226, 943cm⁻¹; ¹H NMR (400.13 MHz) (CDCl₃): δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.15 (m, 4H), 7.12 - 7.09 (m, 3H), 7.07 - 7.01 (m, 2H), 5.23 (s, 2H), 5.16 (s, 2H), 1.95 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 171.4 (C), 137.1 (q), 136.8 (C), 129.0 (CH), 128.9 (CH), 127.8 (CH), 127.7 (C), 127.0 (CH), 122.4 (CH), 120.1 (CH), 119.3 (CH), 110.3 (C), 110.0 (CH), 58.6 (CH₂), 50.2 (CH₂), 21.3 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₁₈H₁₇KNO₂: [M+K]⁺ 318.0896, Found: 318.0898.



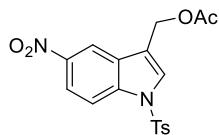
*(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl acetate **3c**:* known compound;¹ yellow oil; 98% yield ; R_f = 0.18 (*n*-hexane/ACOEt, 85:15); IR (neat): 2954, 1735, 1245, 1077, 833 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-*d*₆): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.65 - 7.63 (m, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 5.62 (s, 2H), 5.33 (s, 2H), 3.53 (t, *J* = 8.0 Hz, 2H), 2.09 (s, 3H), 0.90 (t, *J* = 8.0 Hz, 2H), 0.00 (s, 9H); ¹³C NMR (100.6 MHz) (DMSO-*d*₆): δ 171.3 (C), 137.2 (C), 130.6 (CH), 128.4 (C), 122.9 (CH), 120.9 (CH), 119.8 (CH), 111.4 (CH), 111.0 (C), 75.6 (CH₂), 65.8 (CH₂), 58.6 (CH₂), 21.7 (CH₃), 18.0 (CH₂), -0.50 (CH₃); HRMS: *m/z* (MALDI-TOF) positive ion, calculated for C₁₇H₂₅KNO₃Si: [M+K]⁺ 358.1241, Found: 358.1244.



*(5-methoxy-1-tosyl-1*H*-indol-3-yl)methyl acetate **3d**:* known compound; quantitative yield; brown solid; mp: 163-165 °C; lit.³ mp: 163-165 °C; IR (neat): 3553, 2365, 1785, 1529, 1168, 1014 cm⁻¹; ¹H NMR (400.16 MHz) (DMSO-*d*₆): δ 7.84 - 7.81 (m, 4H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 1H), 6.98 (dd, *J*₁ = 9.0 Hz, *J*₂ = 2.4 Hz, 1H), 5.18 (s, 2H), 3.77 (s, 3H), 2.31 (s, 3H), 2.04 (s, 3H); ¹³C NMR (100.6 MHz) (DMSO-*d*₆): δ 170.9 (C), 156.6 (C), 146.0 (C), 134.5 (C), 130.9 (C), 130.7 (CH), 129.4 (C), 127.4 (CH), 127.1 (CH), 118.2 (C), 114.6 (CH), 114.4 (CH), 103.2 (CH), 57.7 (CH₂), 55.9 (CH₃), 21.5 (CH₃), 21.1 (CH₃); HRMS: *m/z* [M + Na]⁺ calcd for C₁₉H₁₉NO₄SNa: 396.0876; found: 396.0871.



*(6-chloro-1-tosyl-1*H*-indol-3-yl)methyl acetate **3f**:* known compound; 95% yield (1.36 mmol scale, 0.51 g); yellow solid; mp: 104-106 °C; lit.³ mp: 104-106 °C; IR (neat): 2965, 2364, 1877, 1593, 1104, 950 cm⁻¹; ¹H NMR (400 MHz) (CDCl₃): δ 7.92 (d, *J* = 1.5 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.52 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.16 (dd, *J*₁ = 8.4 Hz, *J*₂ = 1.8 Hz, 1H) 5.12 (s, 2H), 2.29 (s, 3H), 2.00 (s, 3H); ¹³C NMR (100.6 MHz) (CDCl₃): δ 170.9 (C), 145.6 (C), 135.6 (C), 135.0 (C), 131.3 (C), 130.3 (CH), 128.1 (C), 127.0 (CH), 126.3 (CH), 124.3 (CH), 120.7 (CH), 117.3 (C), 114.0 (CH), 57.6 (CH₂), 21.7 (CH₃), 21.0 (CH₃); HRMS: *m/z* [M + Na]⁺ calcd for C₁₈H₁₆ClNO₄SNa: 400.0381; found: 400.0382.



*(5-nitro-1-tosyl-1*H*-indol-3-yl)methyl acetate **3g**:* known compound; 73% yield (6.22 mmol scale, 1.76 g); yellow solid; mp: 163-165°C; lit.² mp: 163-165°C; R_f = 0.25 (*n*-hexane/AcOEt, 65:35); IR (neat): 2952, 2790, 1710, 1247, 1078 cm⁻¹; ¹H NMR (400.13 MHz) (DMSO-*d*₆): δ 8.76 (d, *J* = 2.1 Hz, 1H), 8.40 (dd, *J*₁ = 9.2 Hz, *J*₂ = 2.1 Hz, 1H), 8.35 (s, 1H), 8.33 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 5.45 (s, 2H), 2.49 (s, 3H), 2.20 (s, 3H); ¹³C NMR (100.6 MHz) (DMSO-*d*₆): δ 170.8 (C), 146.9 (C), 144.2 (C), 137.6 (C), 134.0 (C), 131.0 (CH), 129.8 (CH), 129.6 (C), 127.5 (CH), 120.6 (CH), 118.8 (C), 117.1 (CH), 114.4 (CH), 57.2 (CH₂),

21.5 (CH_3), 21.1 (CH_3). HRMS: m/z (MALDI-TOF) positive ion, calculated for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_6\text{S}$: $[\text{M}+\text{H}]^+$ 389.0807, Found: 389.0810.

5. REFERENCES

¹ Arcadi, A.; Calcaterra, A.; Chiarini, M.; Fabrizi, G.; Fochetti, A.; Goggiamani, A.; Iazzetti, A.; Marrone, F.; Marsicano, V.; Serraiocco, A., Synthesis of Indole/Benzofuran-Containing Diarylmethanes through Palladium-Catalyzed Reaction of Indolylmethyl or Benzofuranyl methyl Acetates with Boronic Acids. *Synthesis* **2021**, 54 (03), 741-753. DOI: 10.1055/s-0041-1737275.

² Arcadi, A.; Aschi, M.; Chiarini, M.; Fabrizi, G.; Fochetti, A.; Goggiamani, A.; Iavarone, F.; Iazzetti, A.; Serraiocco, A.; Zoppoli, R. *ACS Omega* **2024** 9 (26), 28450-28462. DOI: 10.1021/acsomega.4c02409.

³ Arcadi, A.; Berden, G.; Ciogli, A.; Corinti, D.; Crestoni, M. E.; De Angelis, M.; Fabrizi, G.; Goggiamani, A.; Iazzetti, A.; Marrone, F.; Marsicano, V.; Oomens, J.; Serraiocco, A. Reactivity of Indolylmethylacetates with N, O, and S Soft Nucleophiles: Evidence of 2-Alkylideneindolenines and 3-Alkylideneindoleninium Generation by ESI-MS and IRMPD Spectroscopy. *European Journal of Organic Chemistry* **2022**, 2022 (43), e202201166.

<https://doi.org/10.1002/ejoc.202201166>

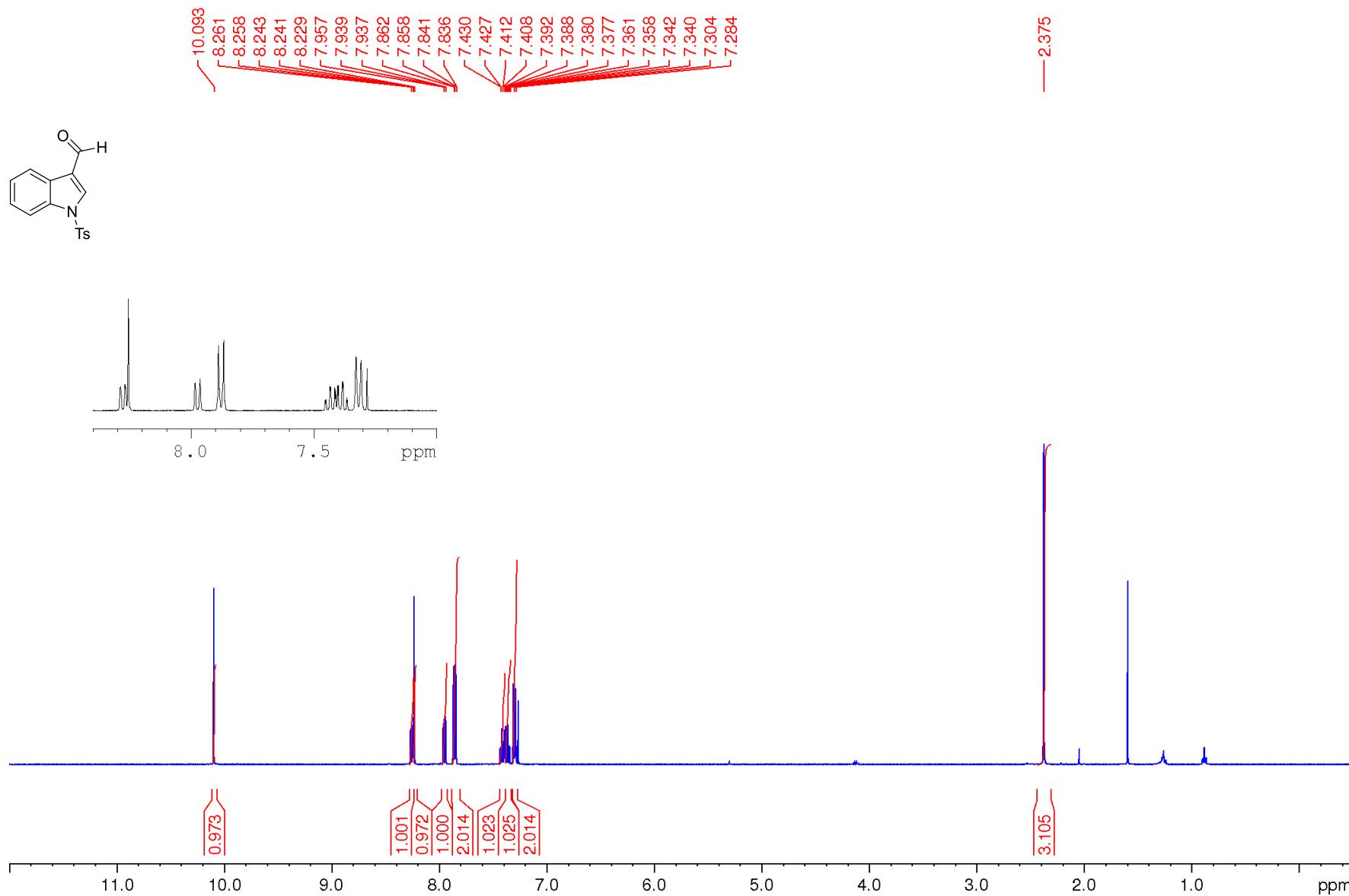
⁴ Moseley, J. D.; Murray, P. M.; Turp, E. R.; Tyler, S. N. G.; Burn, R. T., A mild robust generic protocol for the Suzuki reaction using an air stable catalyst. *Tetrahedron* **2012**, 68 (30), 6010-6017.

<https://doi.org/10.1016/j.tet.2012.05.030>

6. COPIES OF NMR SPECTRA

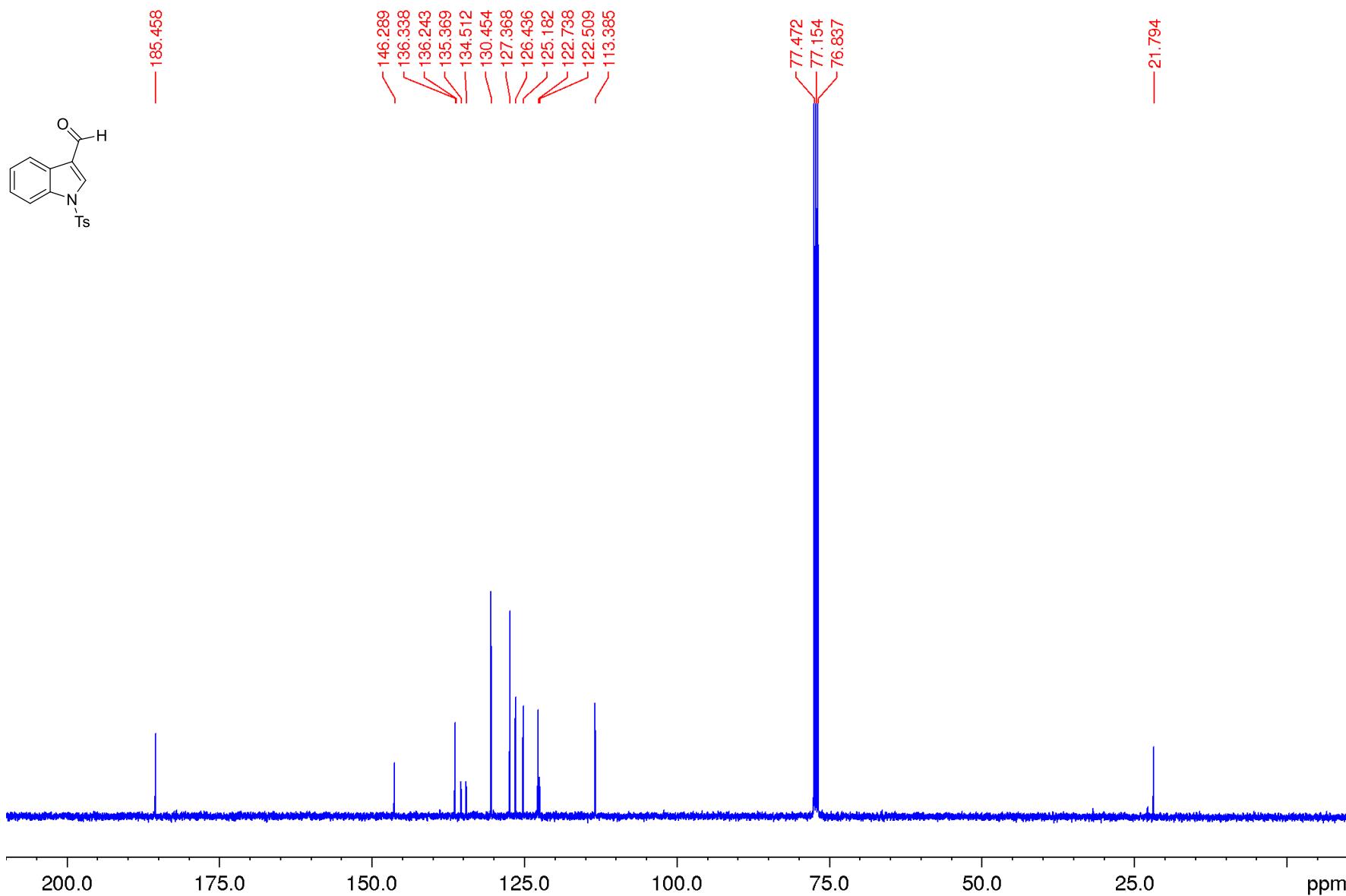
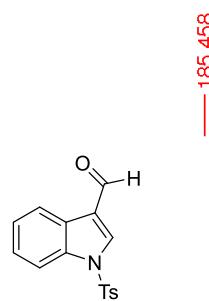
1-tosyl-1H-indole-3-carbaldehyde

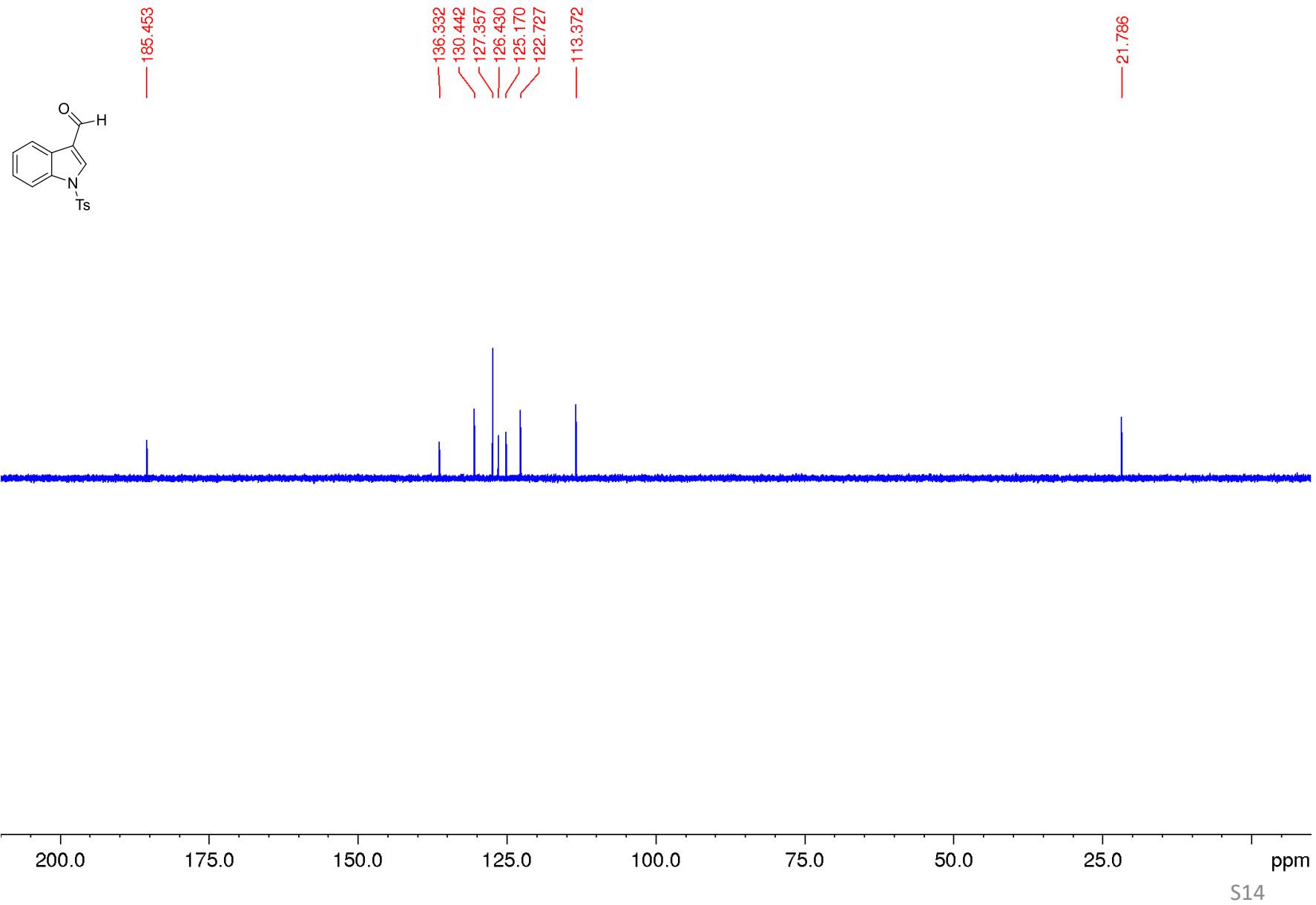
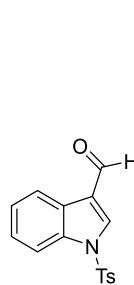
^1H NMR-spectrum (400.13 MHz) (CDCl_3)



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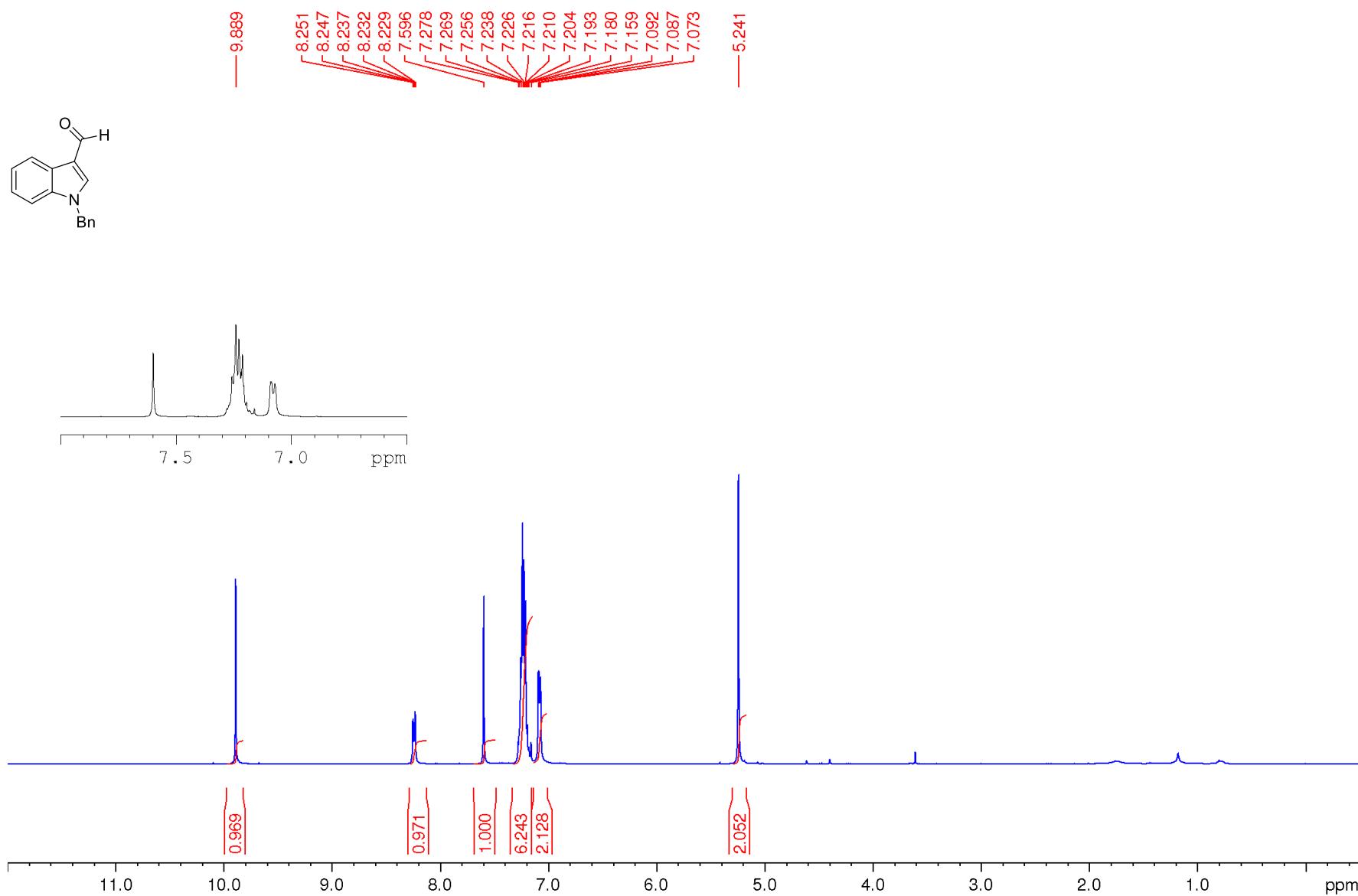
^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)





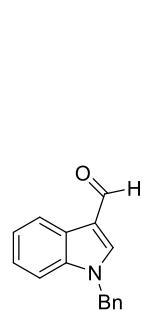
1-tosyl-1H-indole-3-carbaldehyde

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



1-tosyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)

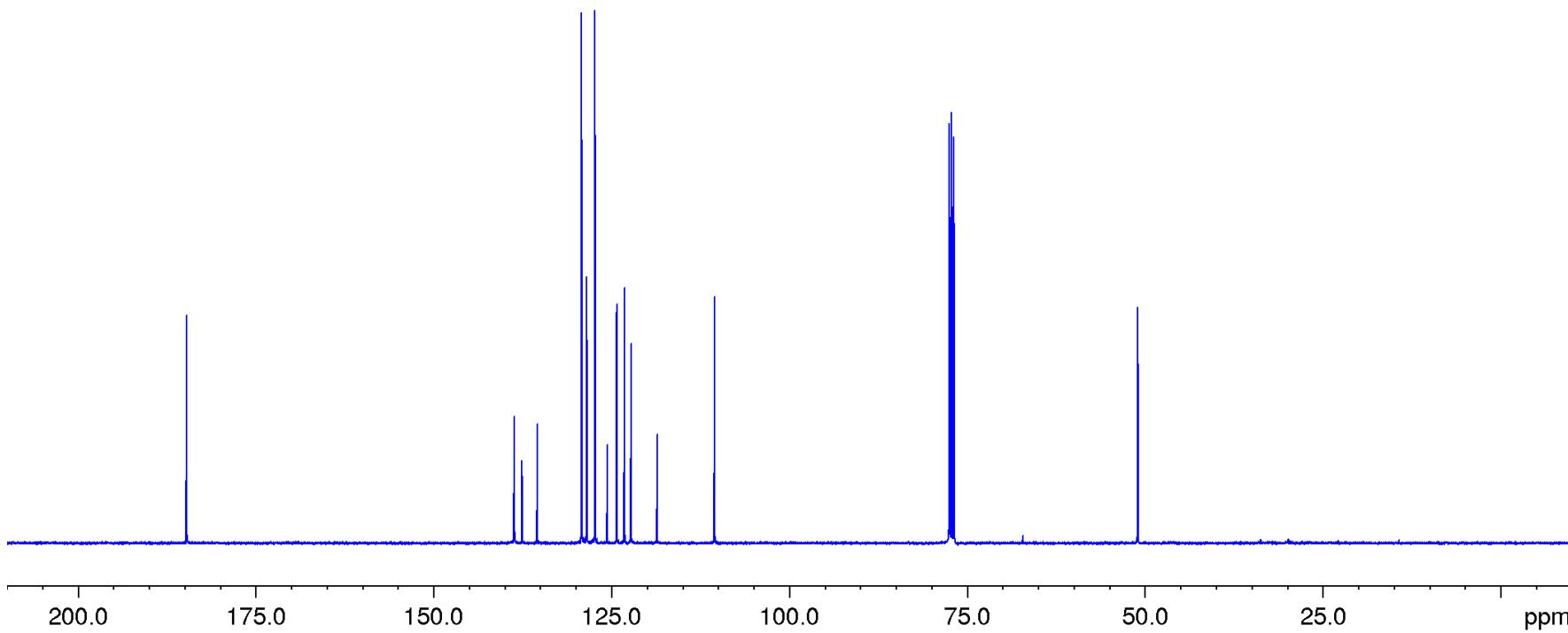


184.723

138.657
137.554
135.409
129.204
128.475
127.313
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124.248
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118.566
110.489

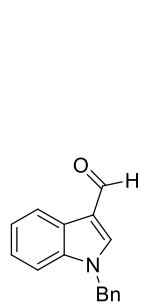
77.477
77.159
76.841

50.995



1-tosyl-1H-indole-3-carbaldehyde

DEPT 135 NMR-spectrum (CDCl_3)

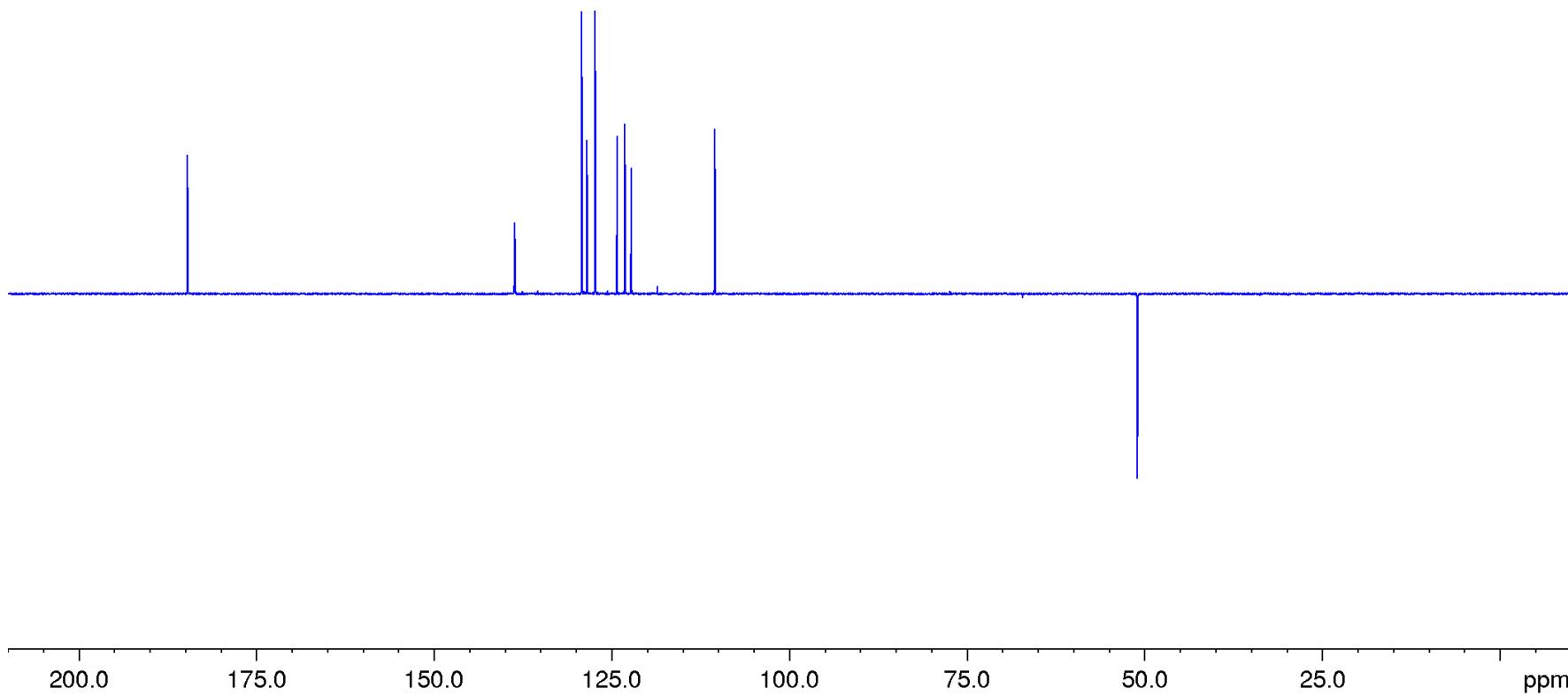


— 184.709

— 138.644
— 129.190
— 128.461
— 127.300
— 124.234
— 123.143
— 122.227

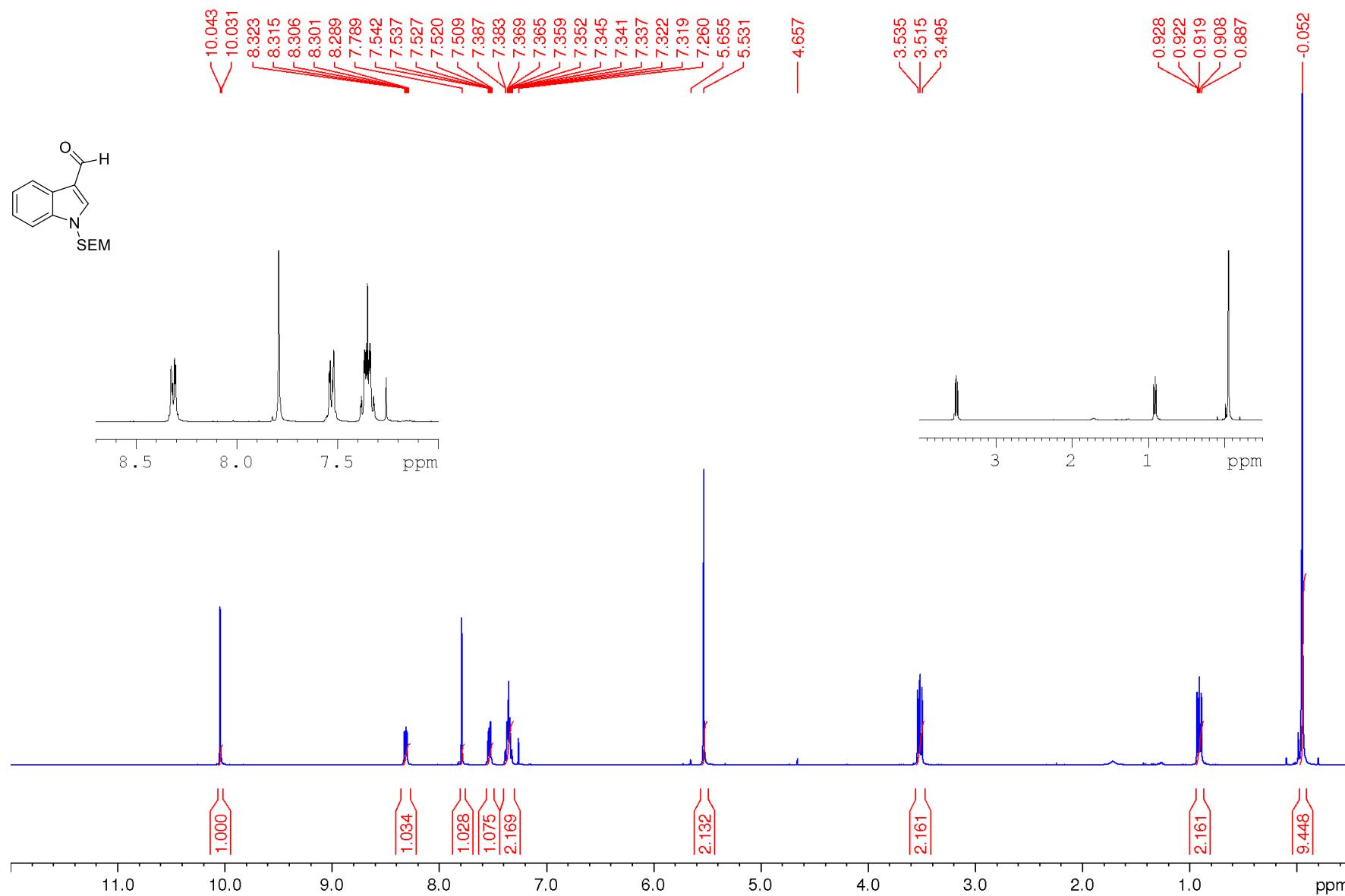
— 110.475

— 50.981



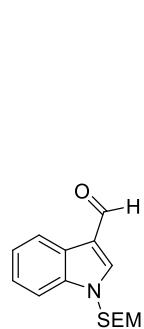
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^1H NMR-spectrum (400.13 MHz) (CDCl_3)



1-tosyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



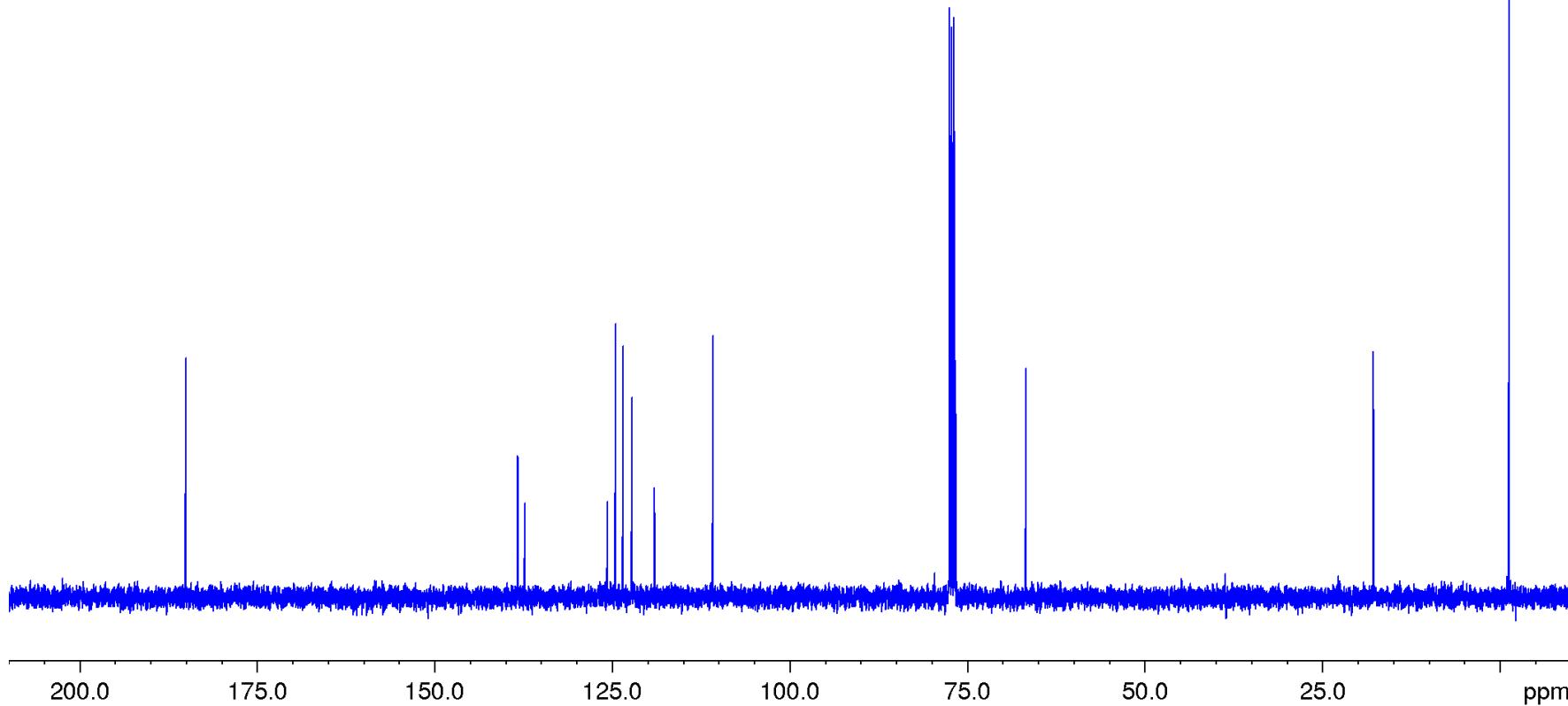
— 185.074

— 138.281
— 137.331
— 125.679
— 124.554
— 123.474
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— 77.475
— 77.157
— 76.840
— 76.628
— 66.731

— 17.810

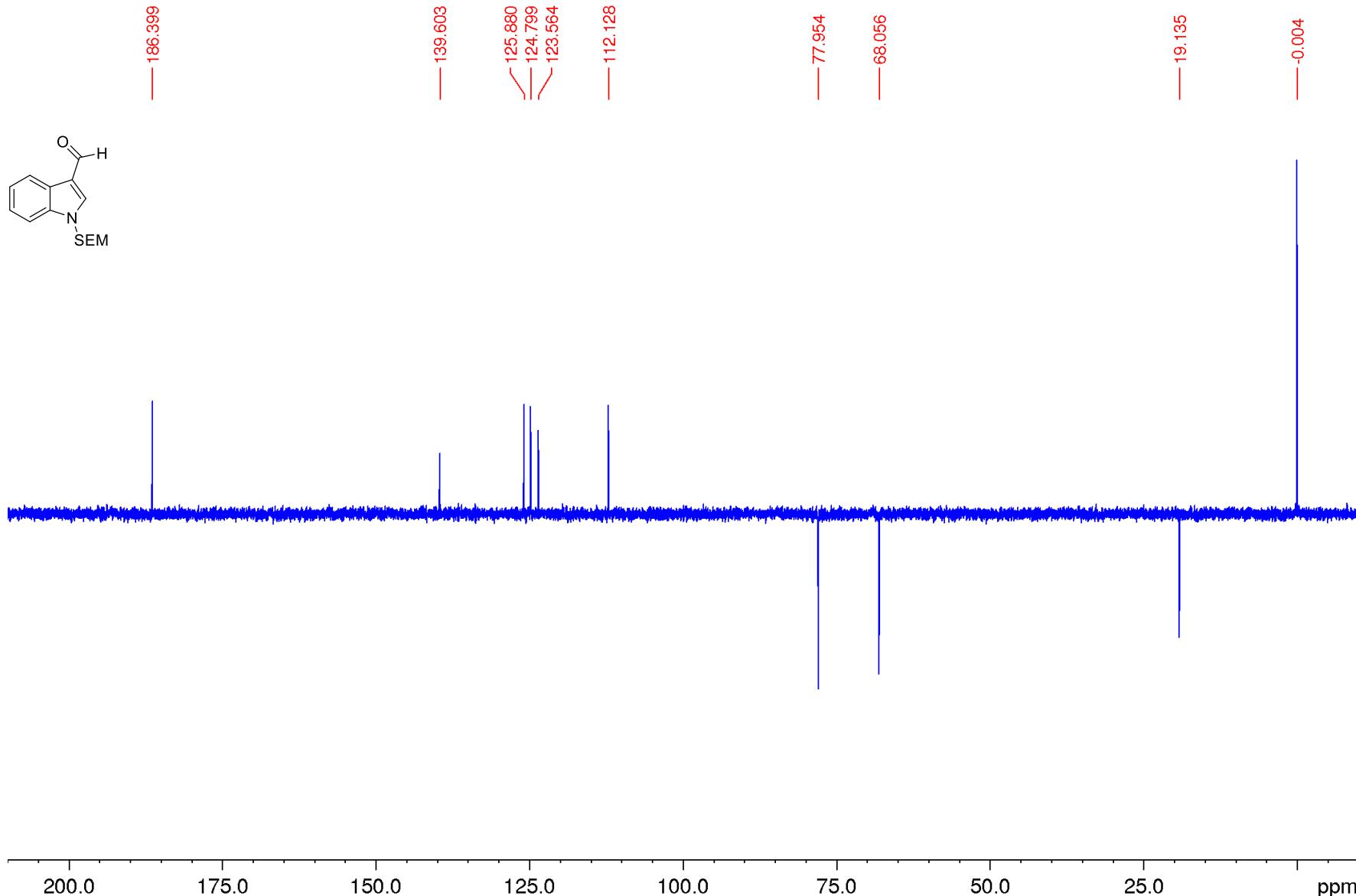
— -1.329



200.0 175.0 150.0 125.0 100.0 75.0 50.0 25.0 ppm

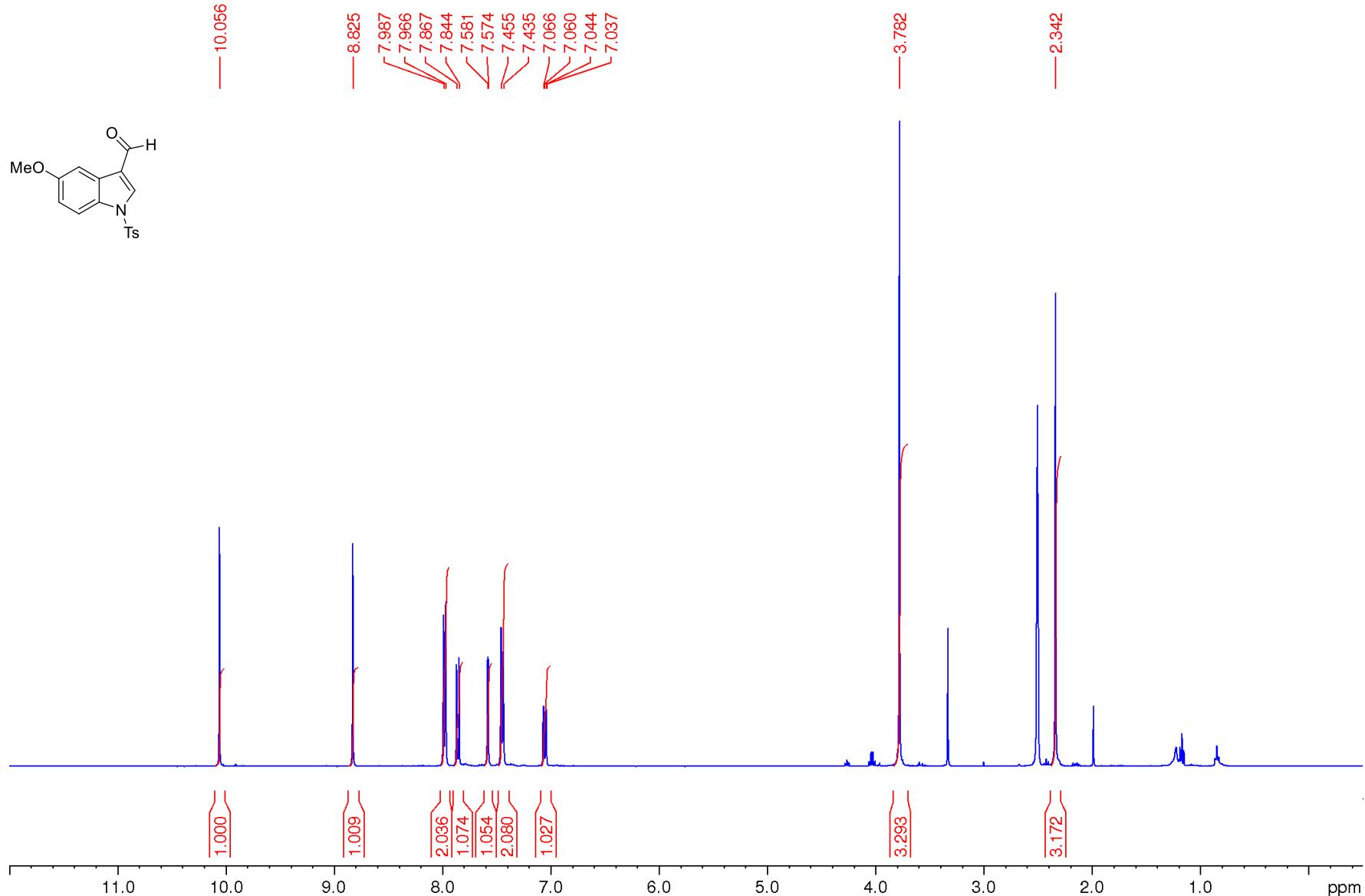
1-tosyl-1H-indole-3-carbaldehyde

DEPT 135 NMR-spectrum (CDCl_3)



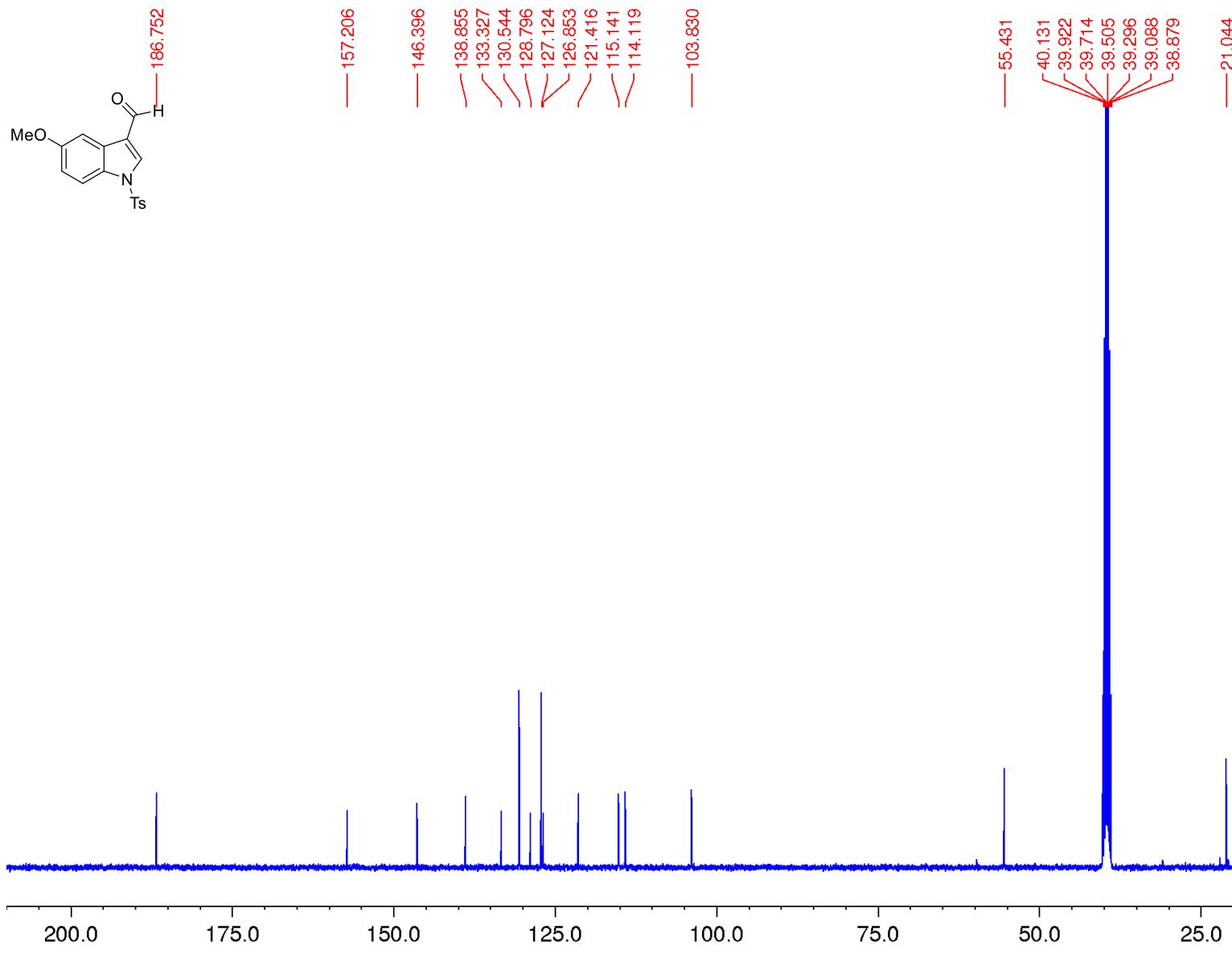
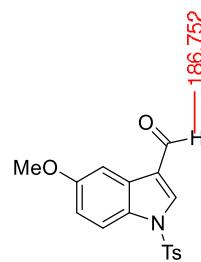
5-methoxy-1-tosyl-1H-indole-3-carbaldehyde

^1H NMR-spectrum (400.13 MHz) (DMSO- d_6)



5-methoxy-1-tosyl-1H-indole-3-carbaldehyde

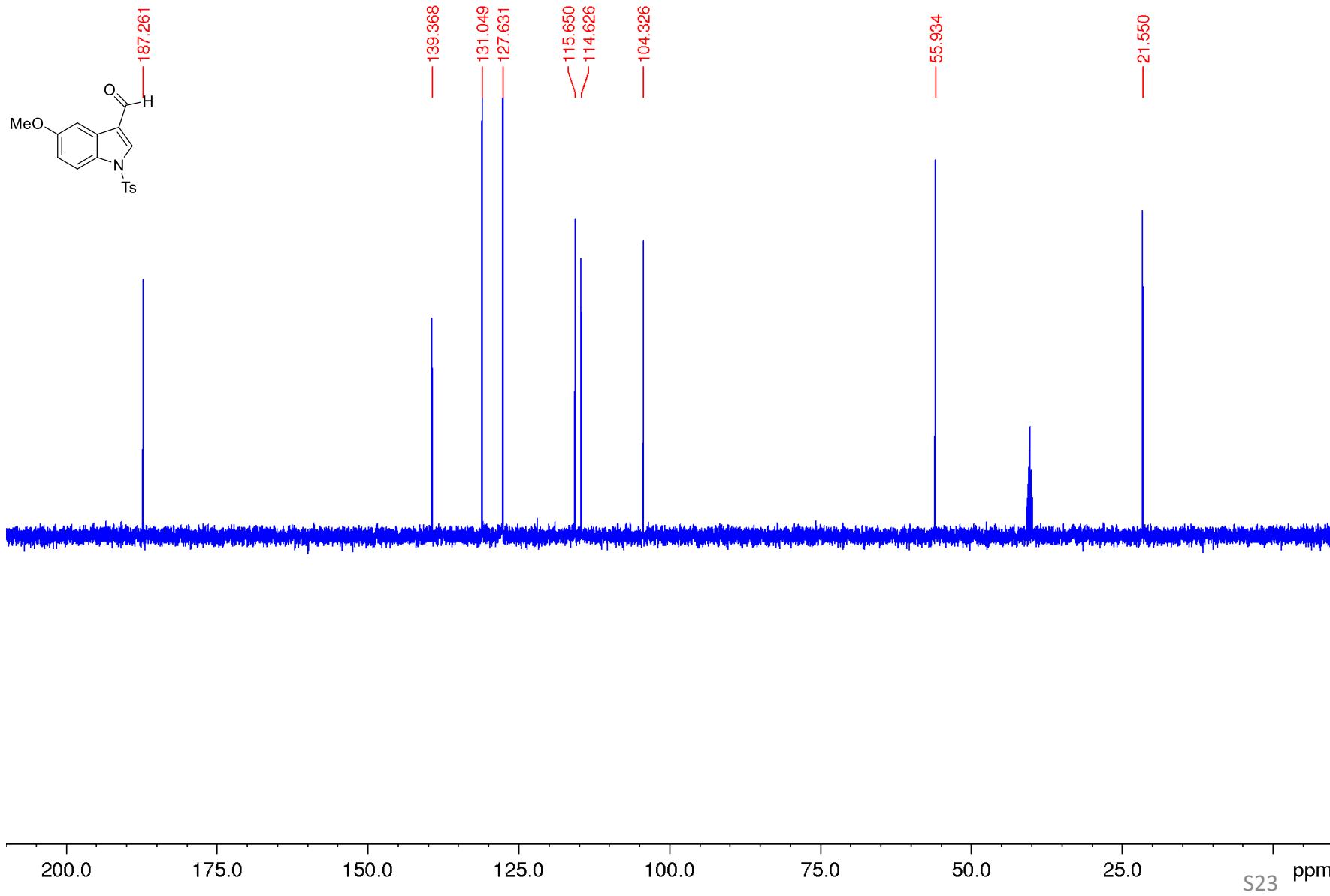
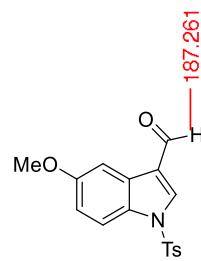
^{13}C NMR-spectrum (100.6 MHz) (DMSO- d_6)

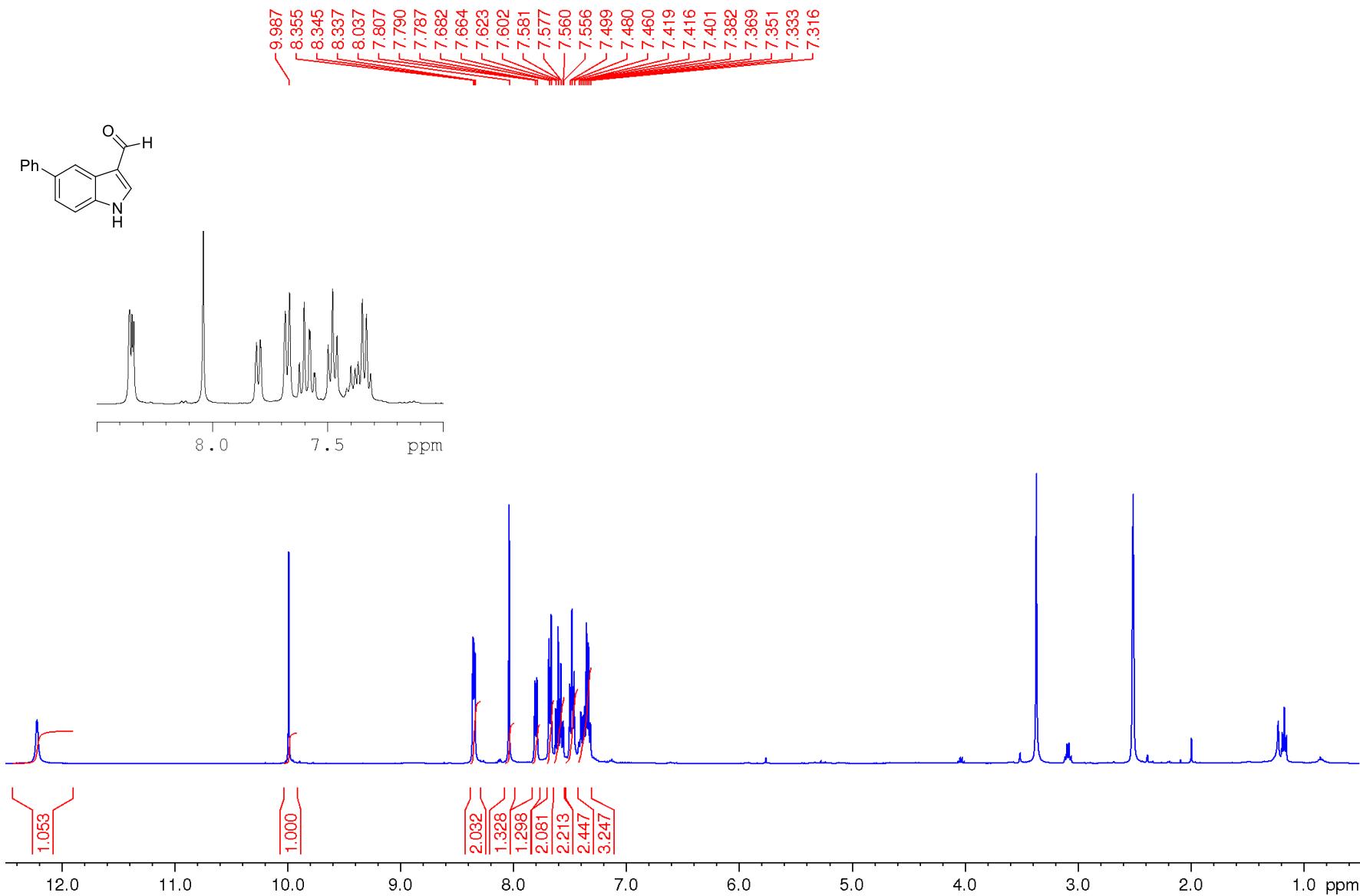


S22 ppm

5-methoxy-1-tosyl-1H-indole-3-carbaldehyde

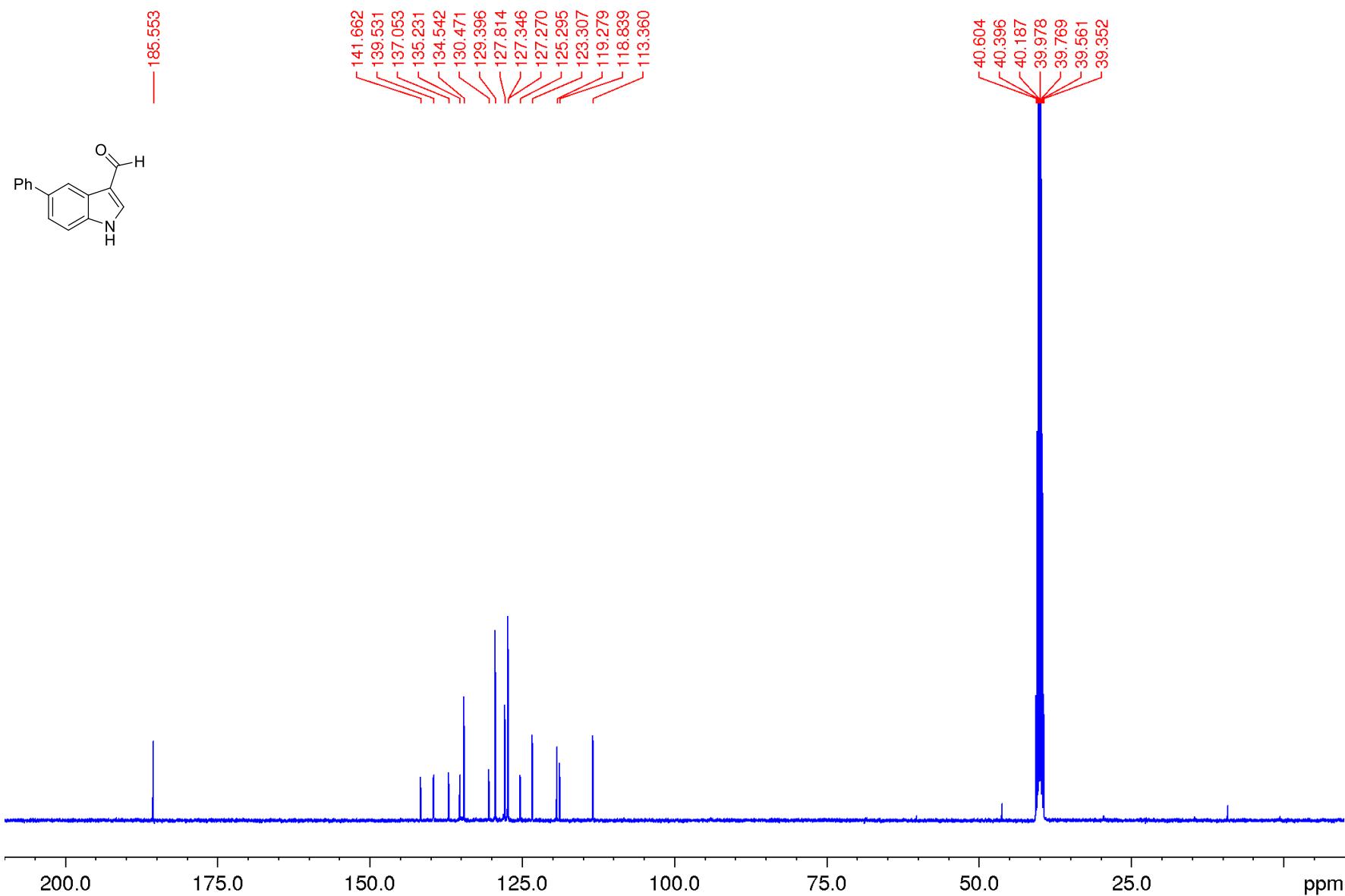
DEPT 135 NMR-spectrum (DMSO-*d*₆)





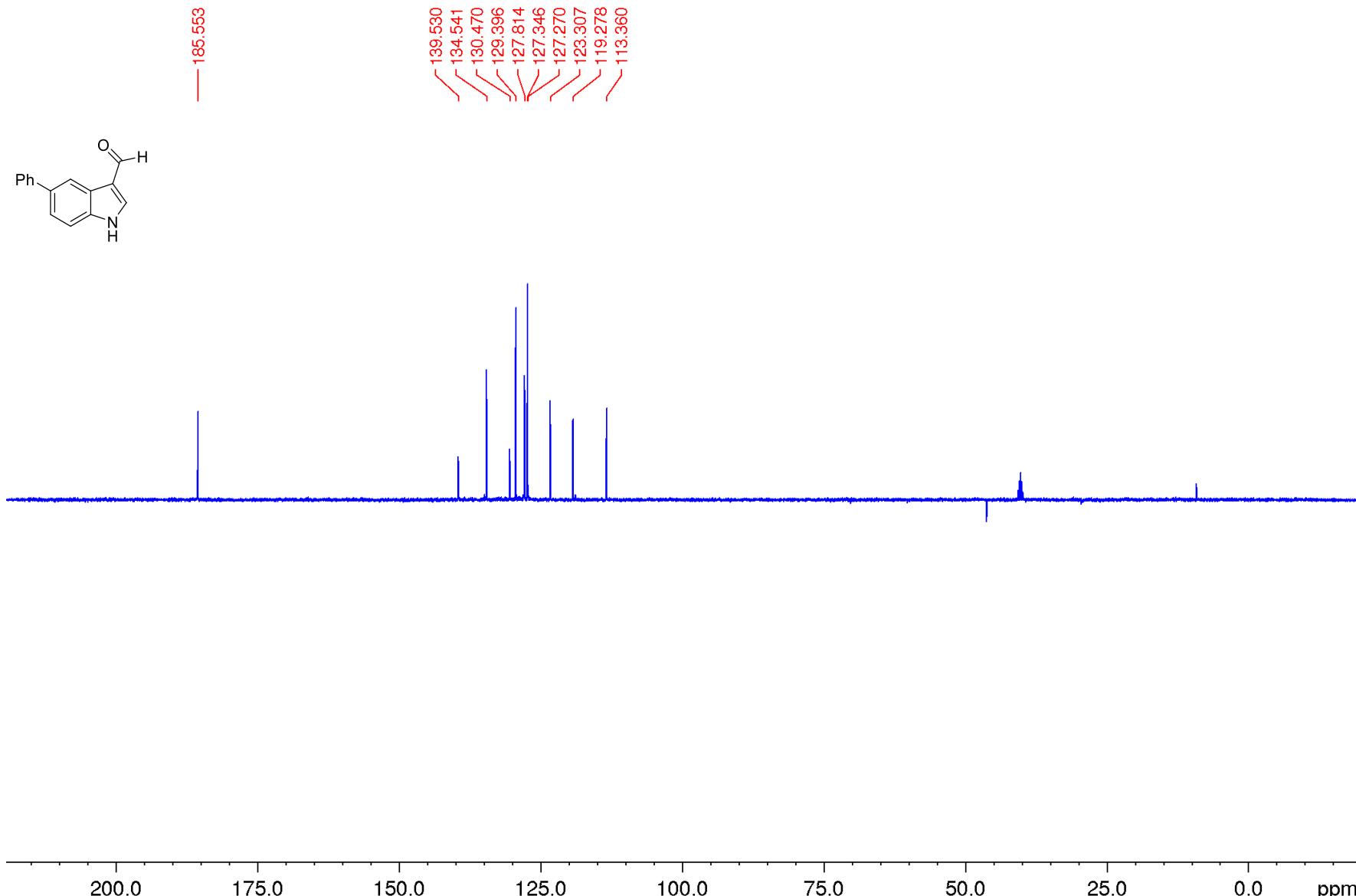
5-phenyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (DMSO- d_6)



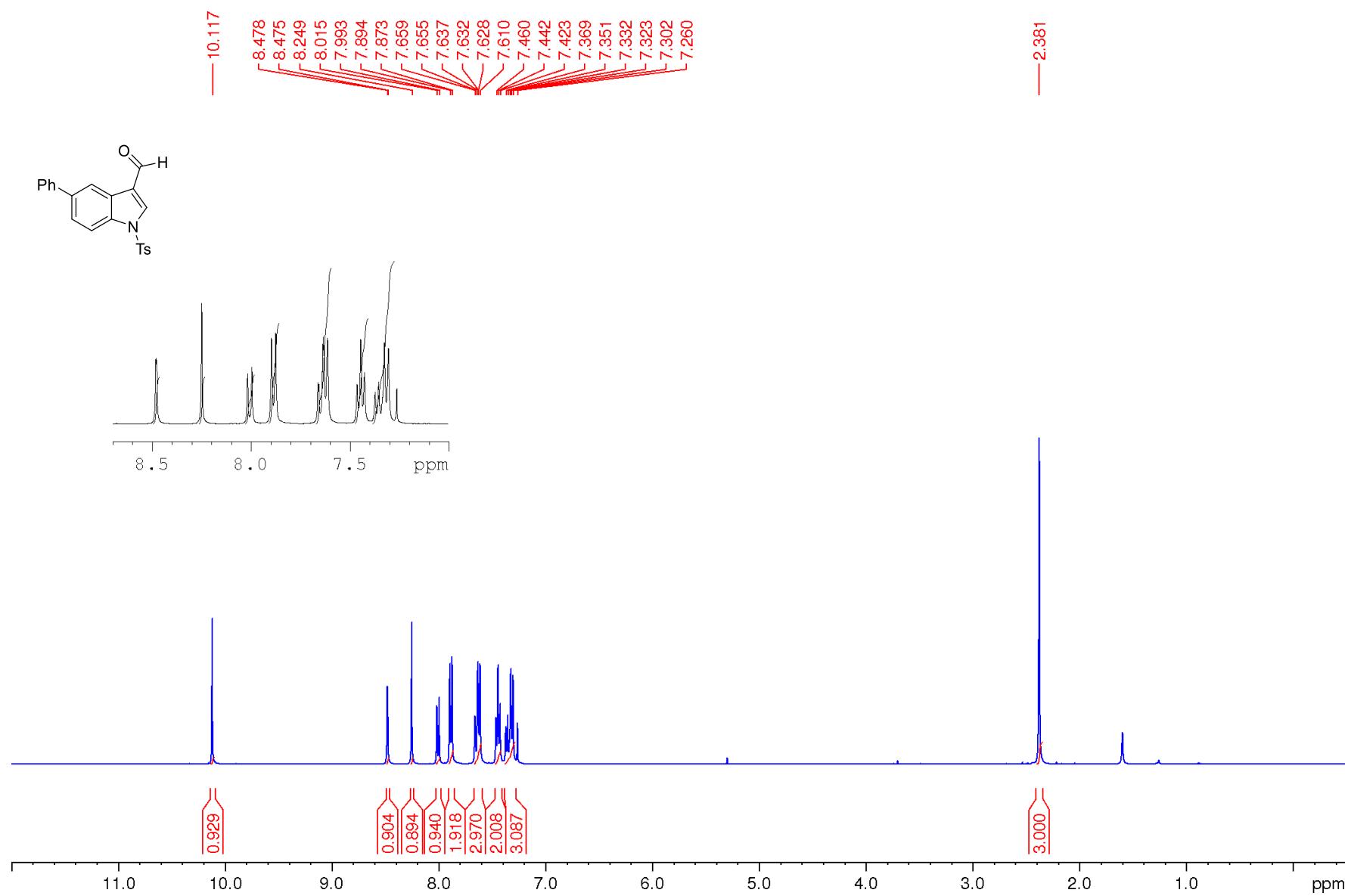
5-phenyl-1H-indole-3-carbaldehyde

DEPT 135 NMR-spectrum (DMSO-*d*₆)



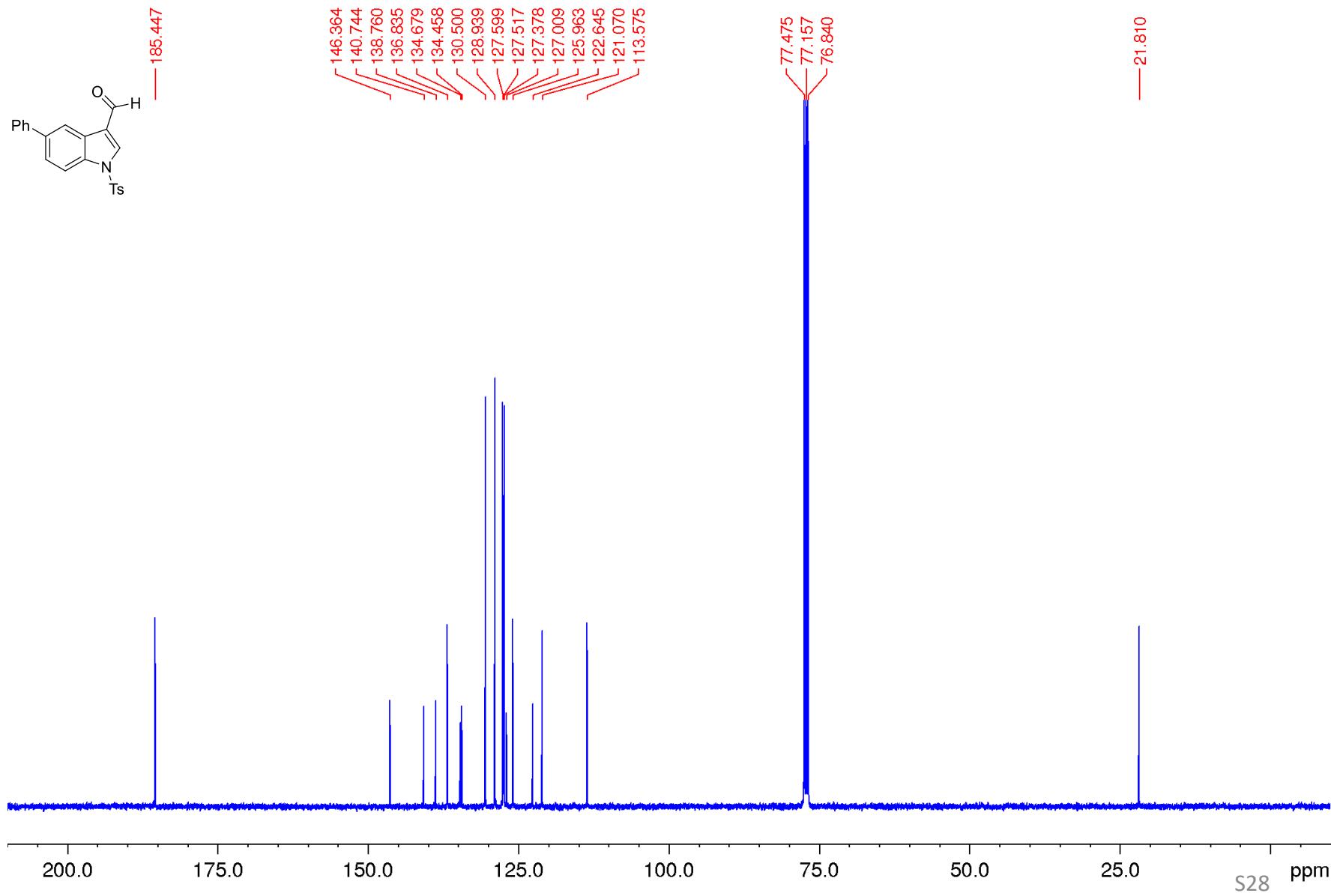
5-phenyl-1-tosyl-1H-indole-3-carbaldehyde

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



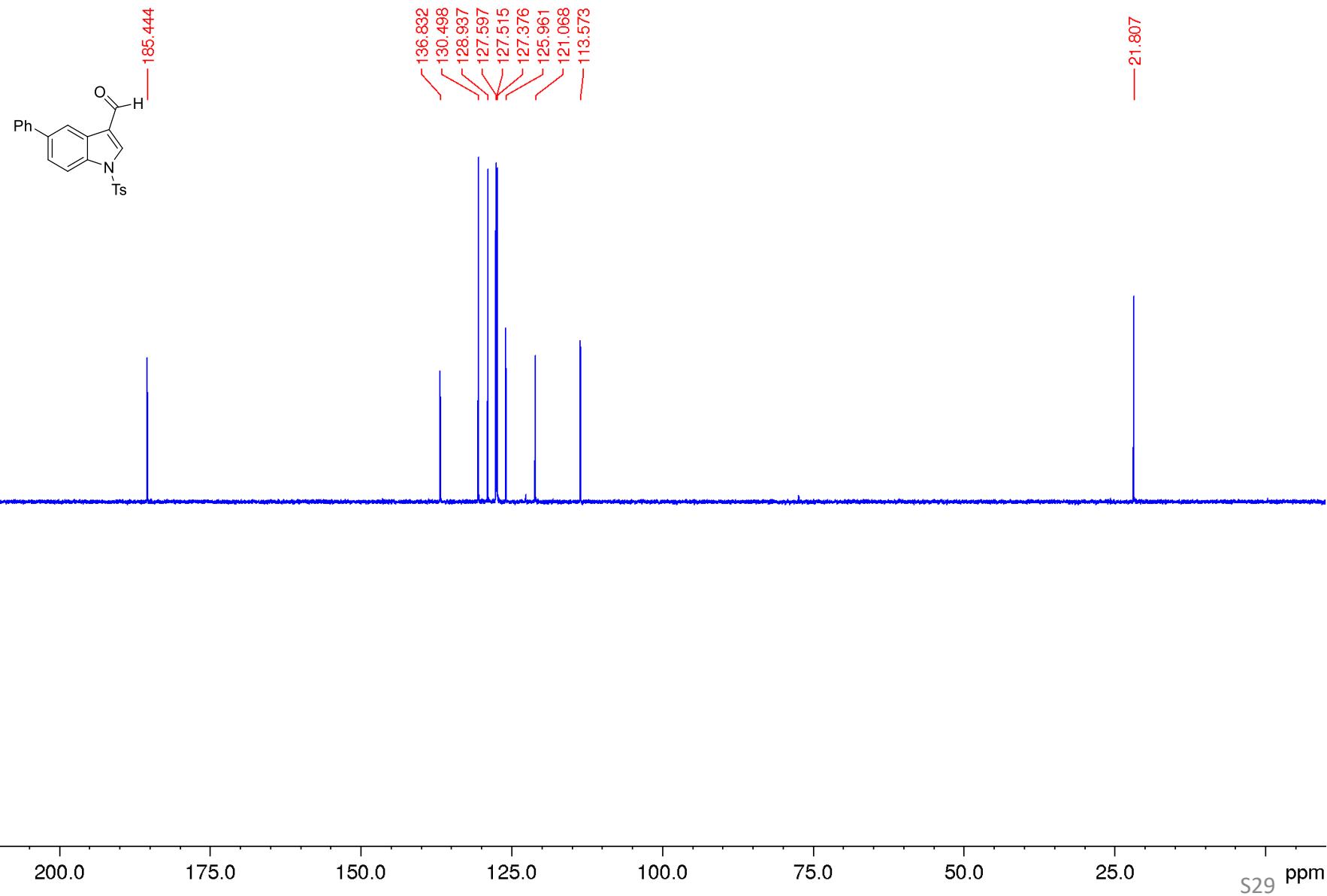
5-phenyl-1-tosyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



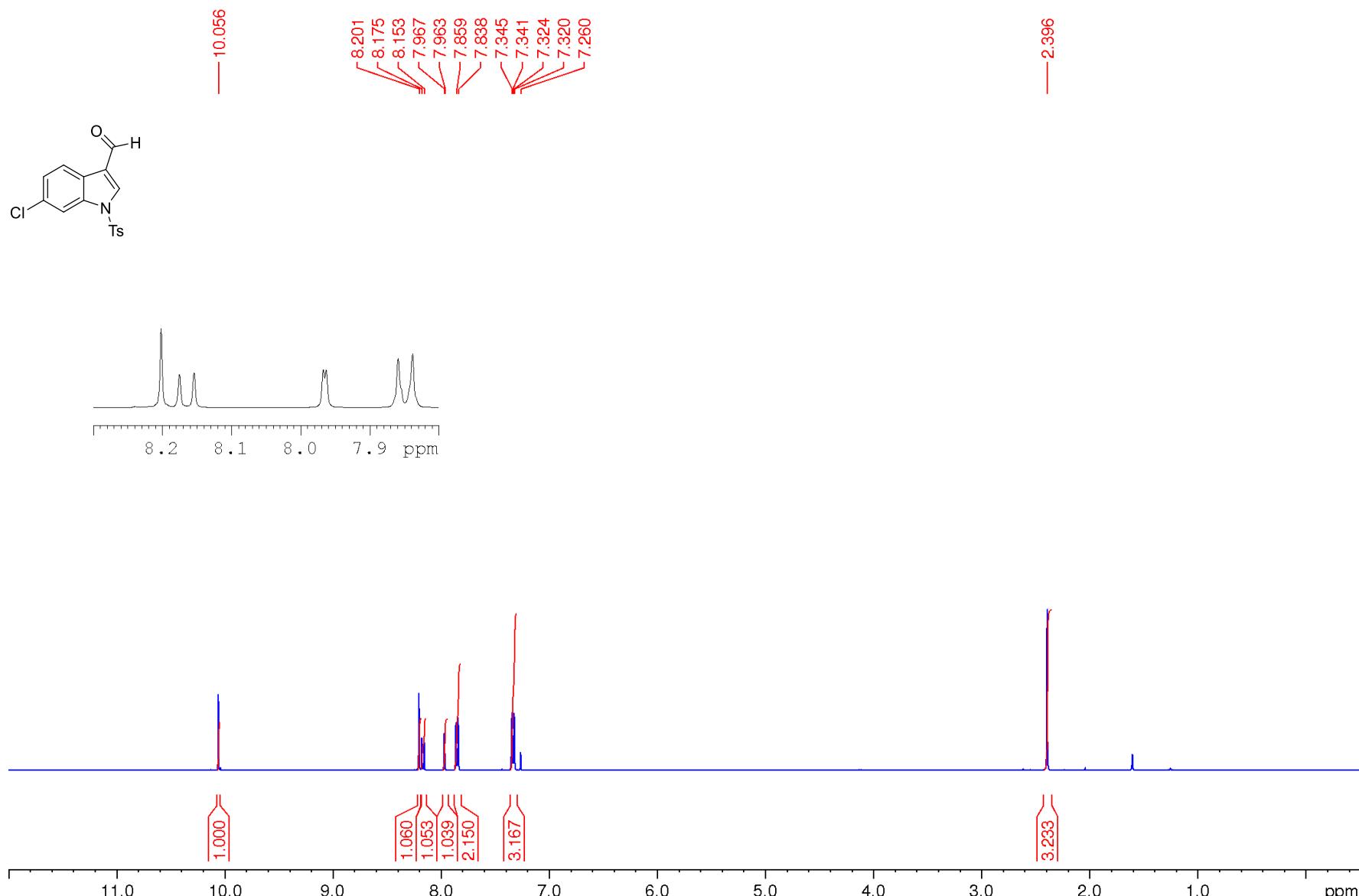
5-phenyl-1-tosyl-1H-indole-3-carbaldehyde

DEPT 135 NMR-spectrum (CDCl_3)



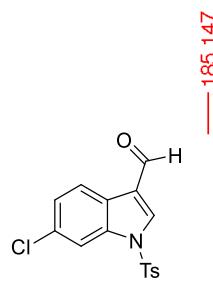
6-chloro-1-tosyl-1H-indole-3-carbaldehyde

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



6-chloro-1-tosyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)

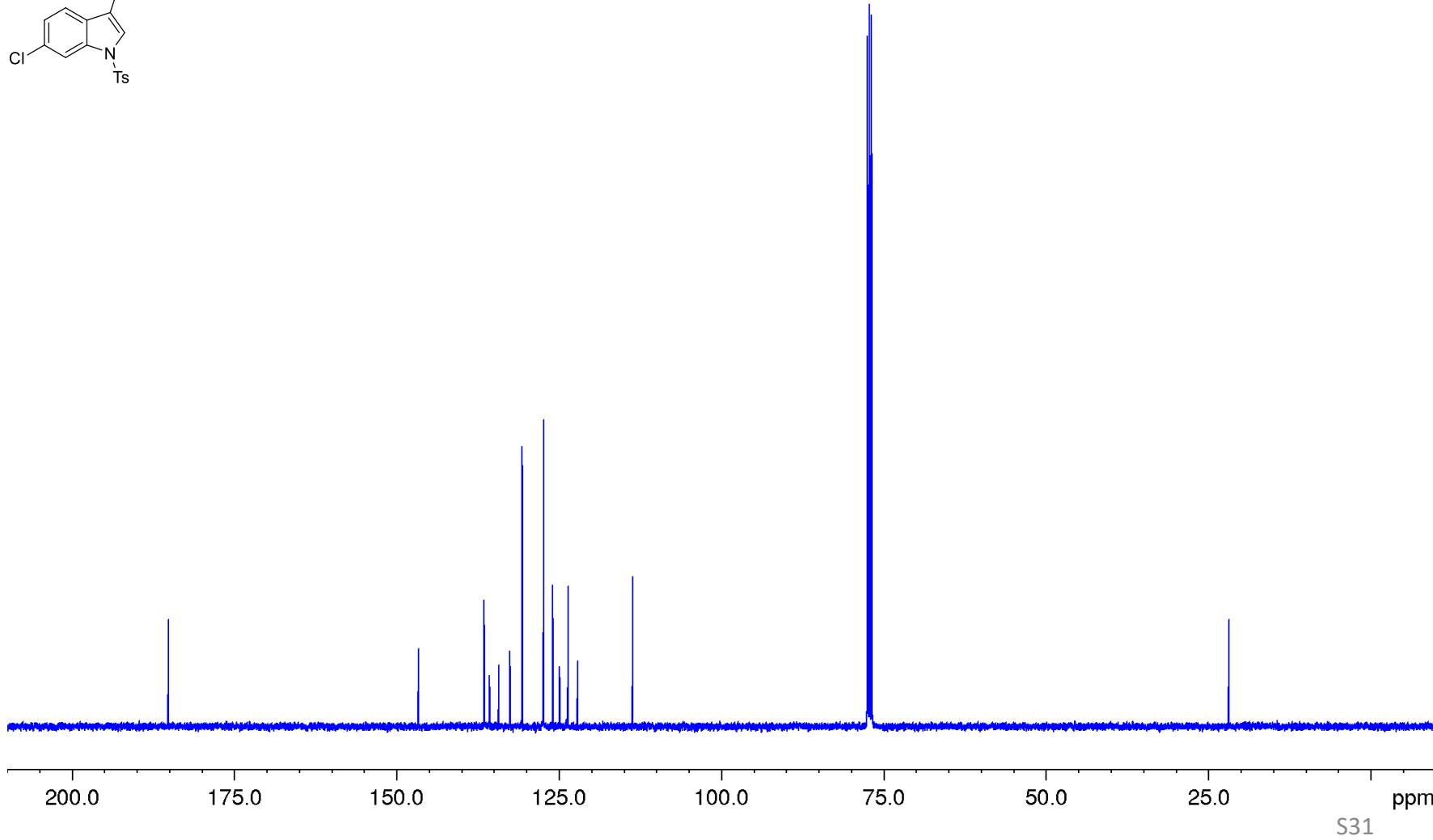


— 185.147

146.643
136.508
135.682
134.233
132.527
130.637
127.364
125.949
124.884
123.574
122.145
113.636

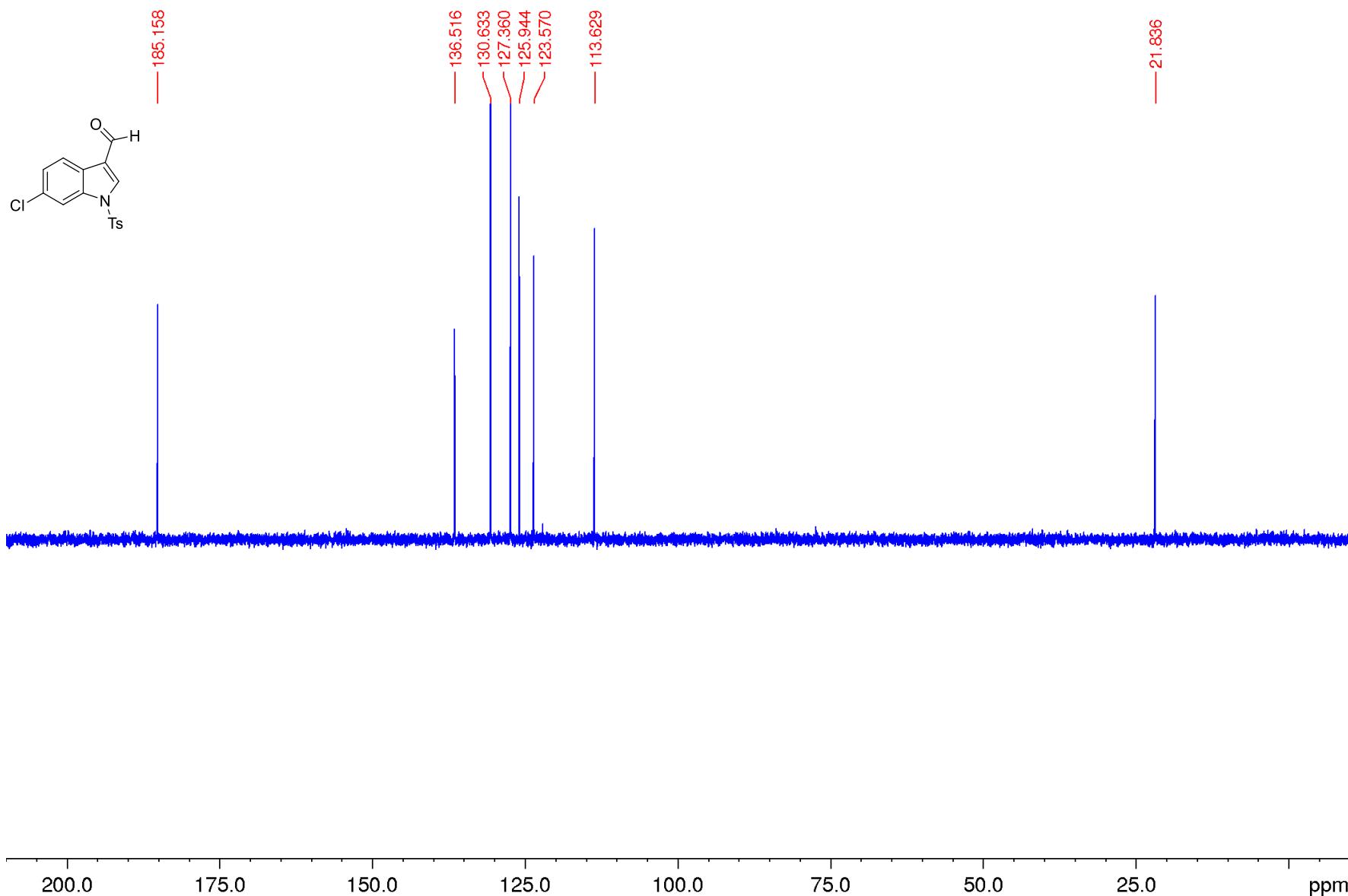
77.472
77.155
76.837

— 21.837



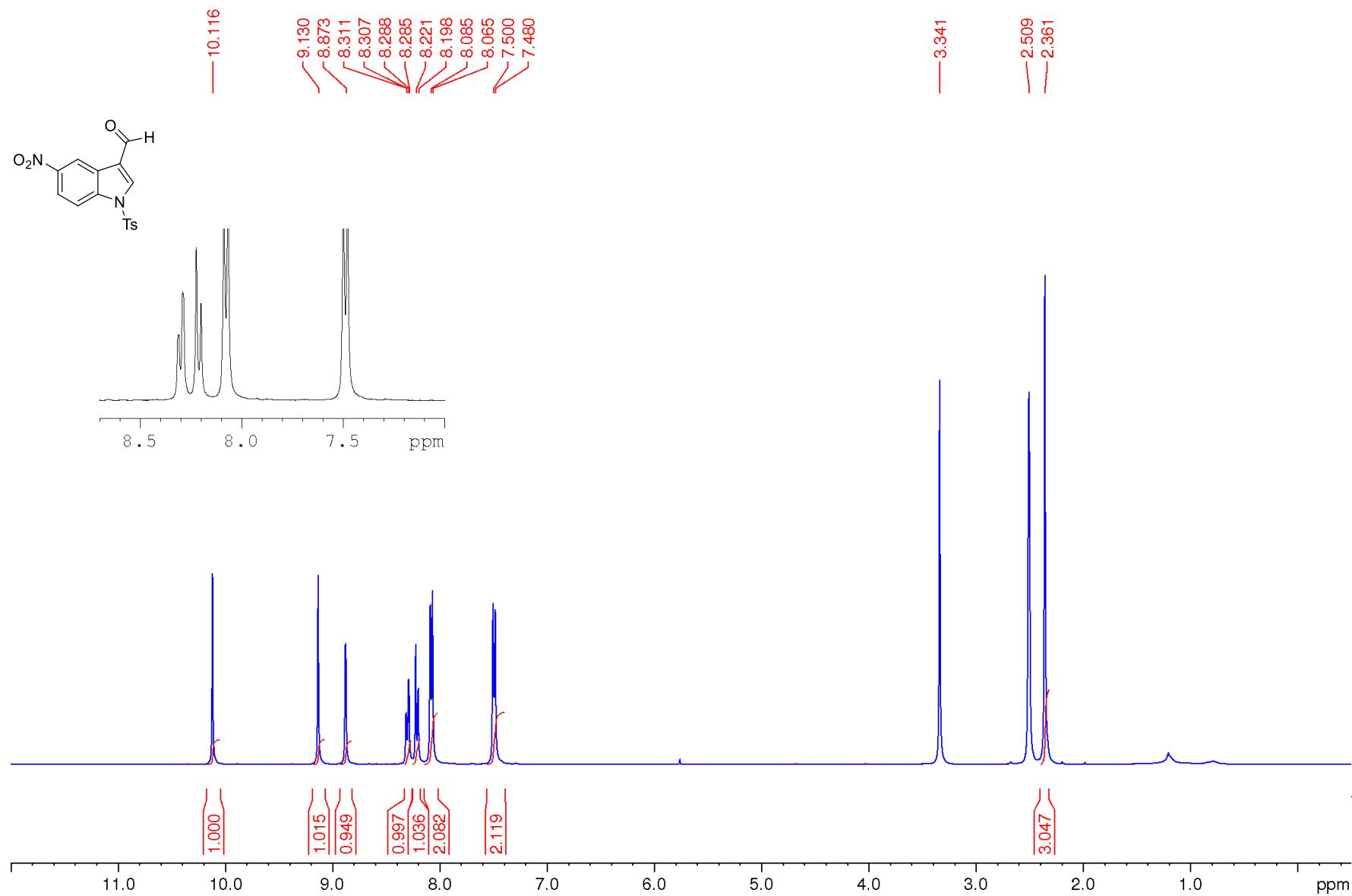
6-chloro-1-tosyl-1H-indole-3-carbaldehyde

DEPT 135 NMR-spectrum (CDCl_3)



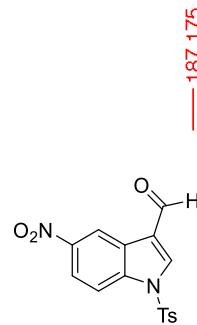
5-nitro-1-tosyl-1H-indole-3-carbaldehyde

^1H NMR-spectrum (400.13 MHz) (DMSO- d_6)



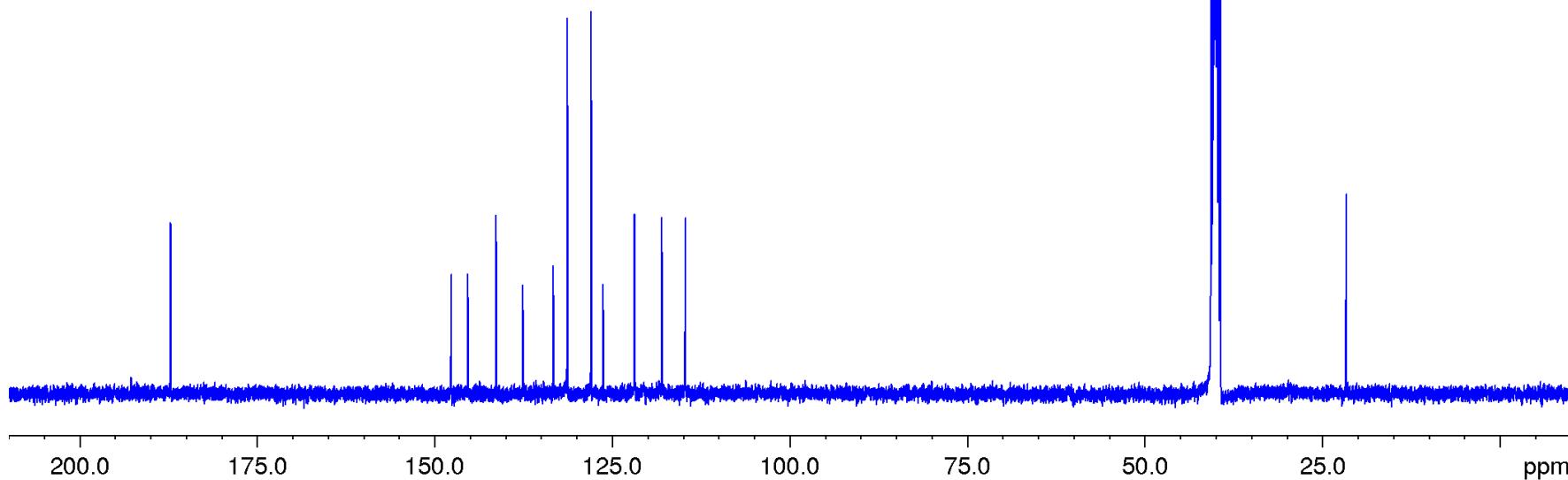
5-nitro-1-tosyl-1H-indole-3-carbaldehyde

^{13}C NMR-spectrum (100.6 MHz) (DMSO- d_6)



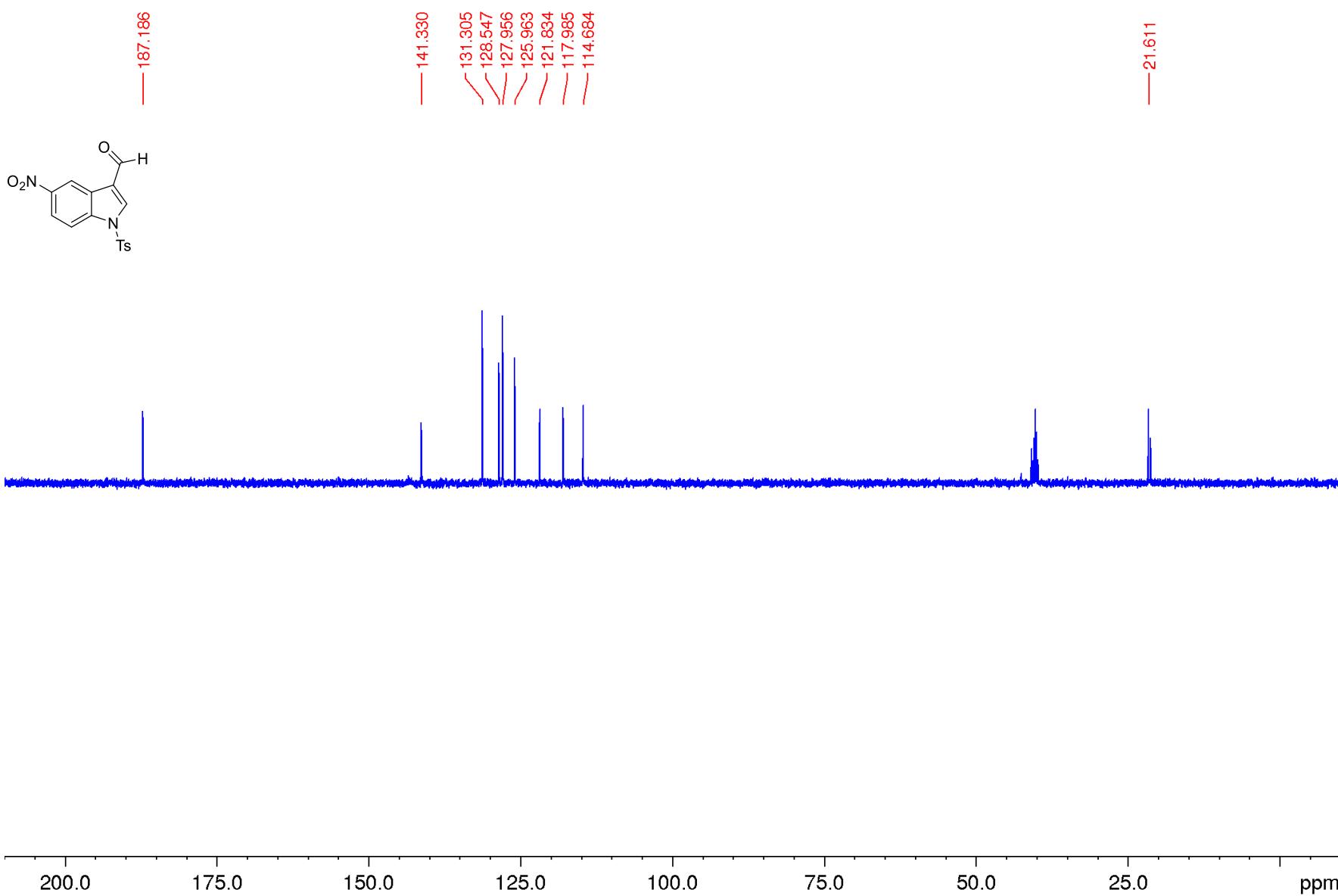
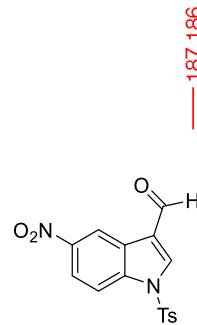
187.175
147.660
145.312
141.326
137.583
133.295
131.311
127.989
126.275
121.887
121.783
117.992
114.684

40.616
40.407
40.198
39.989
39.781
39.572
39.364
21.618



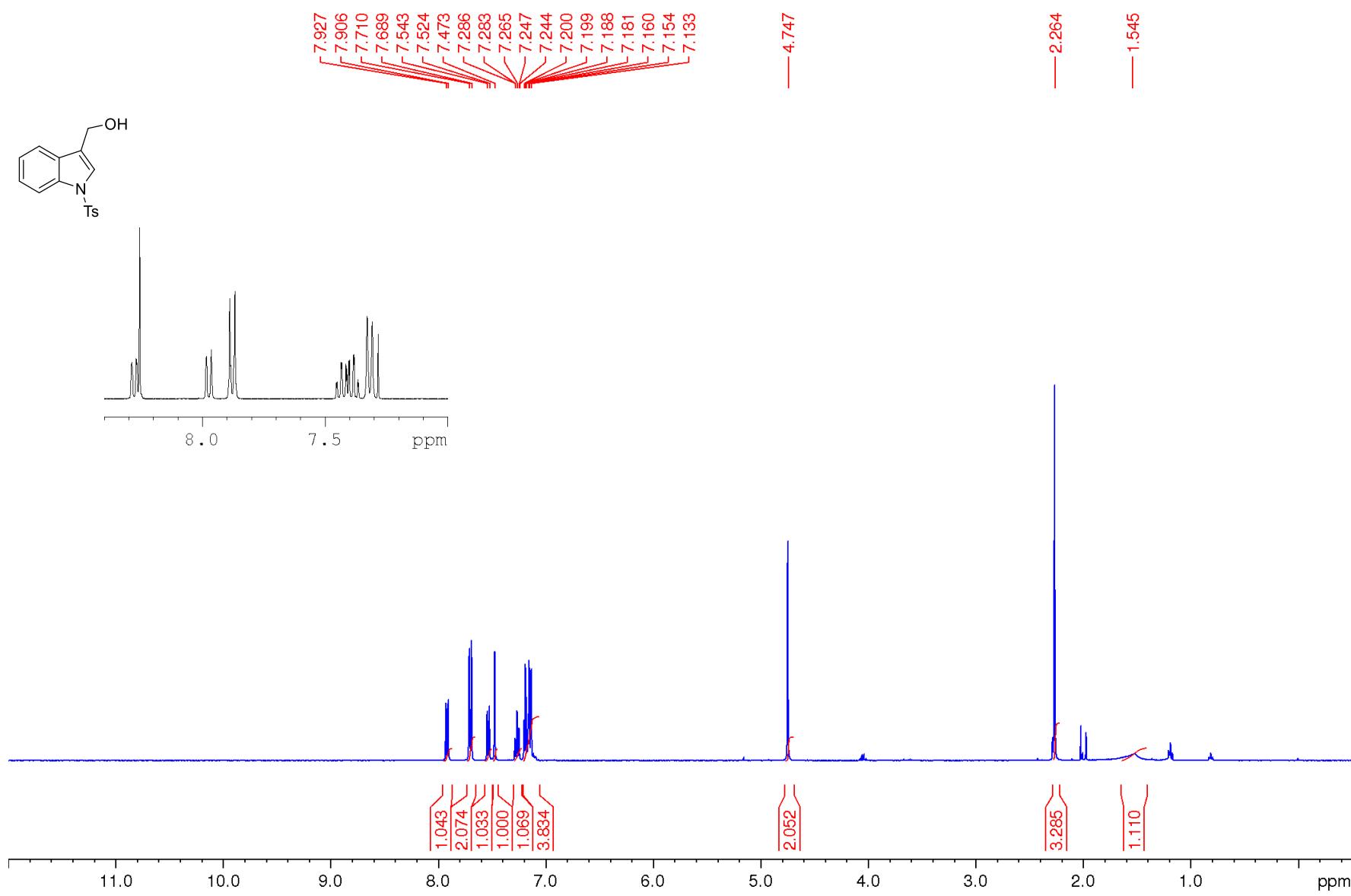
5-nitro-1-tosyl-1H-indole-3-carbaldehyde

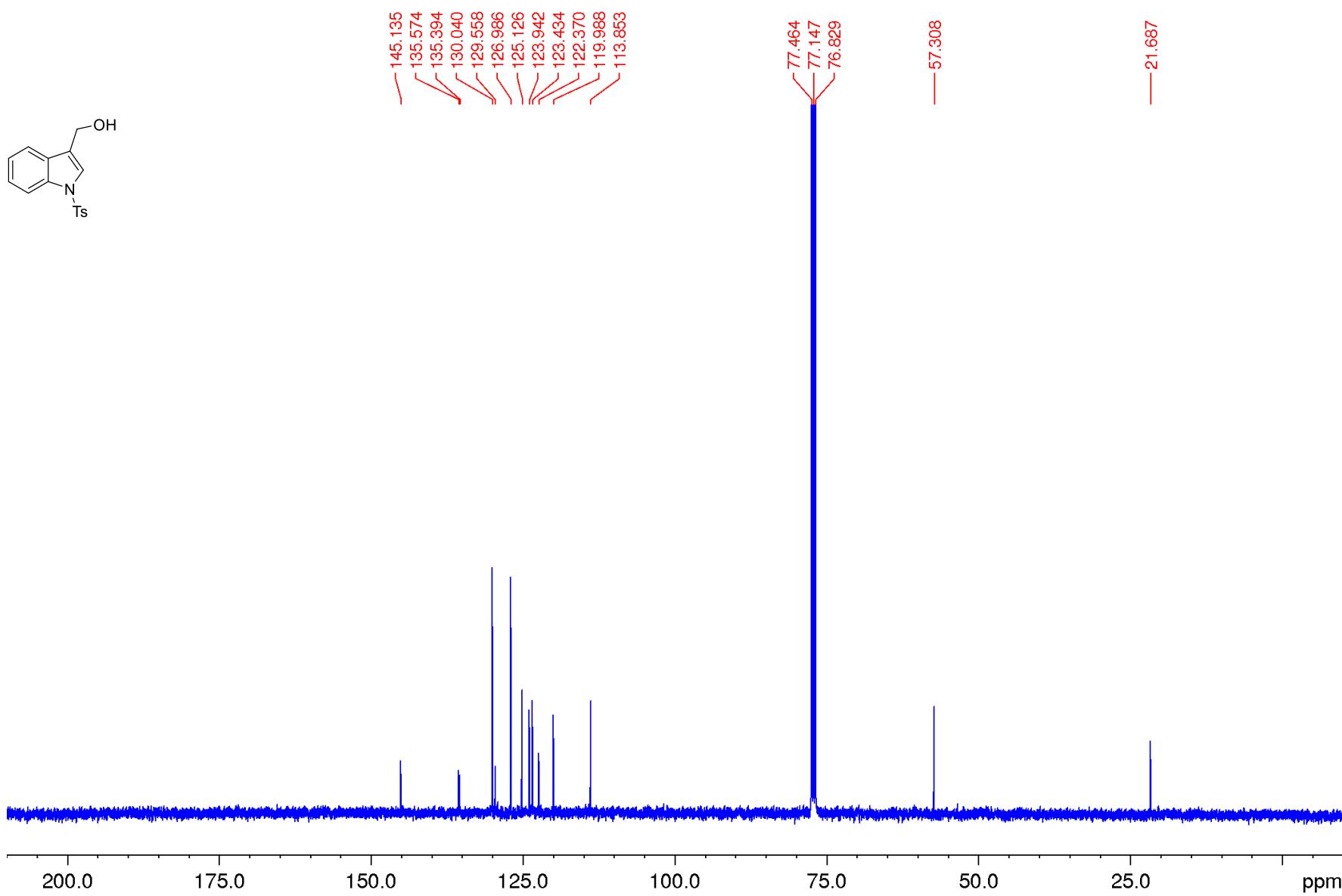
DEPT 135 NMR-spectrum (DMSO-*d*₆)

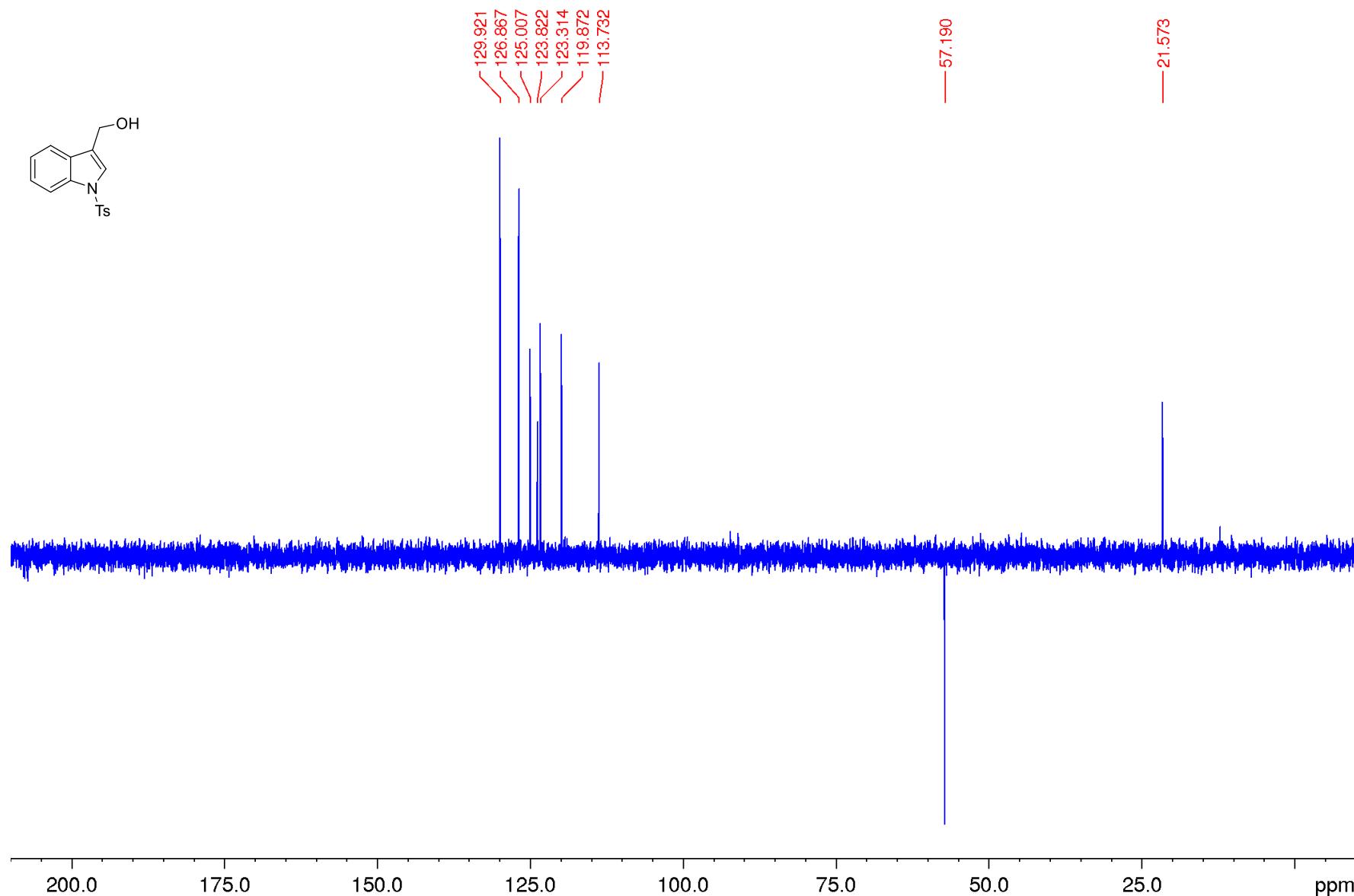


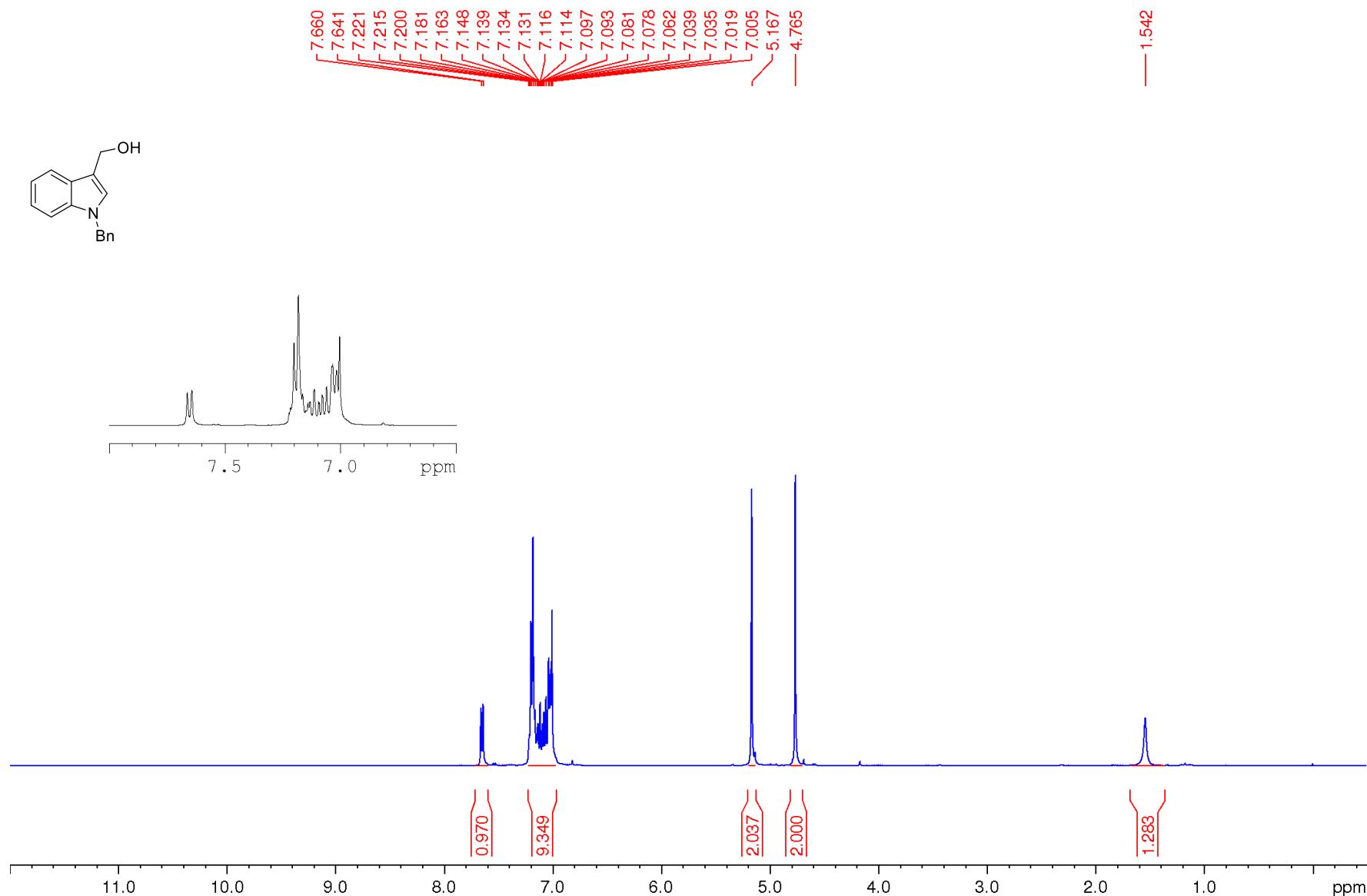
(1-tosyl-1H-indol-3-yl)methanol

^1H NMR-spectrum (400.13 MHz) (CDCl_3)

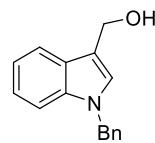




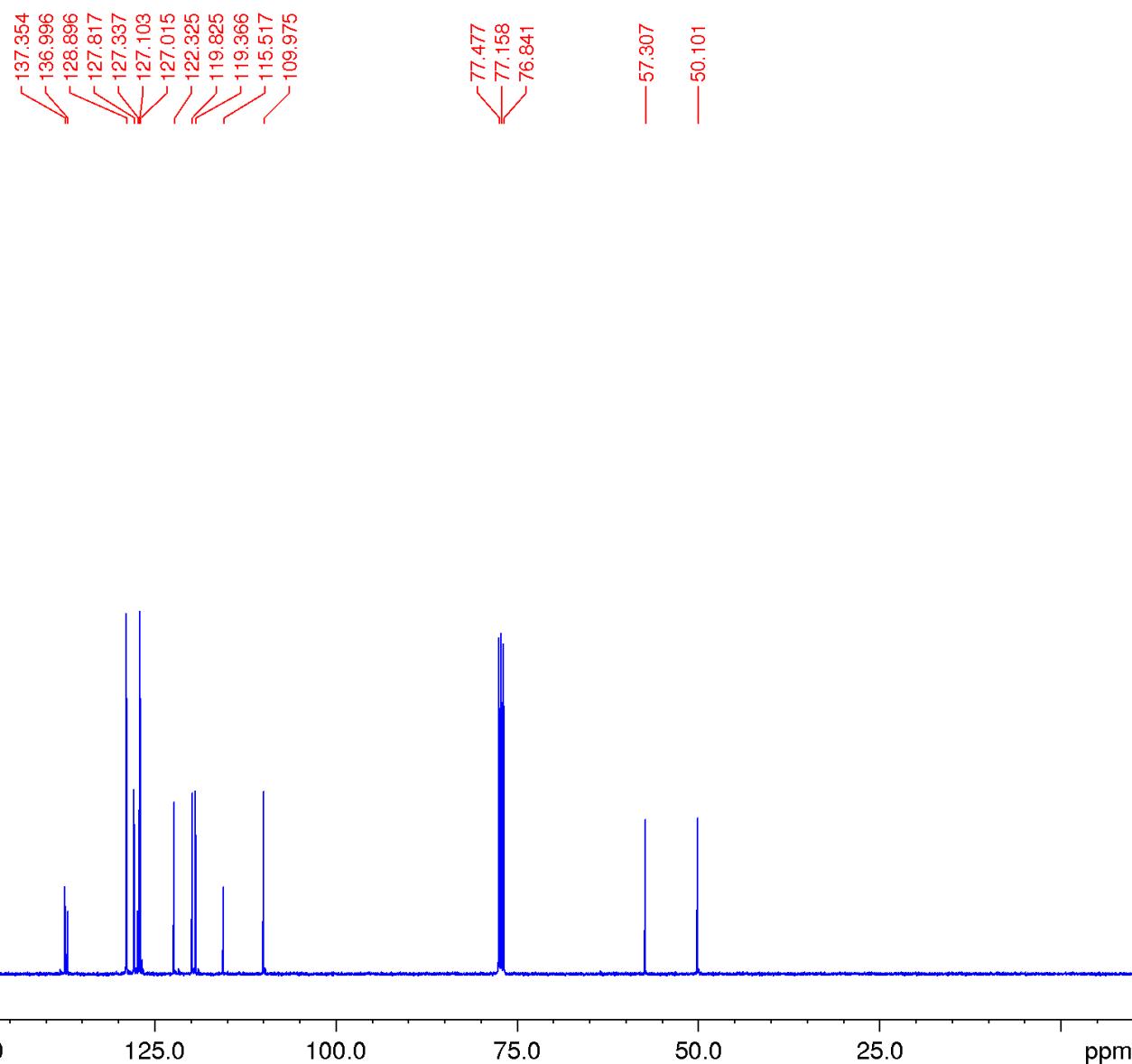


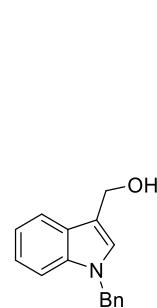


(1-tosyl-1H-indol-3-yl)methanol



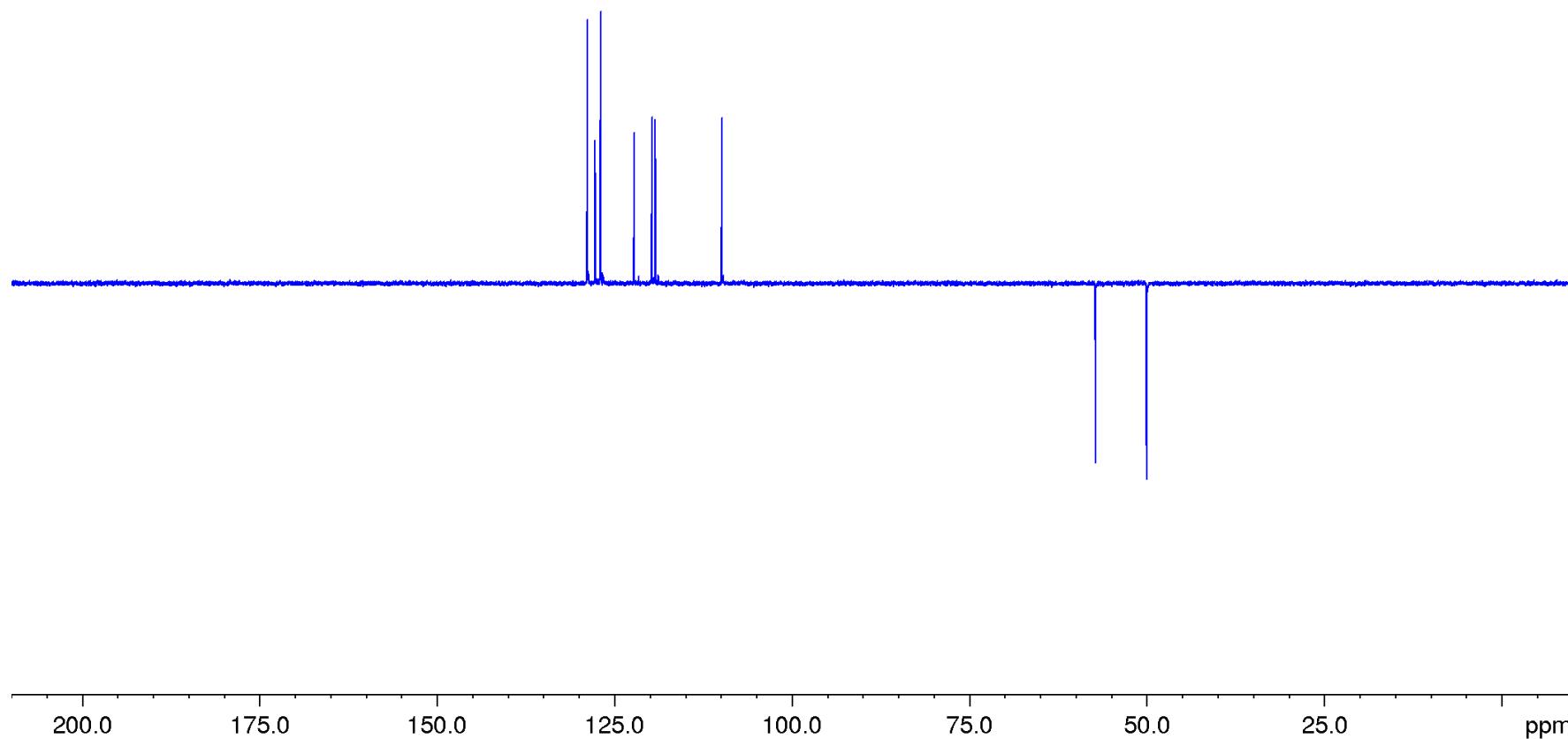
^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)





128.802
127.723
127.009
126.921
122.231
119.752
119.272
109.881

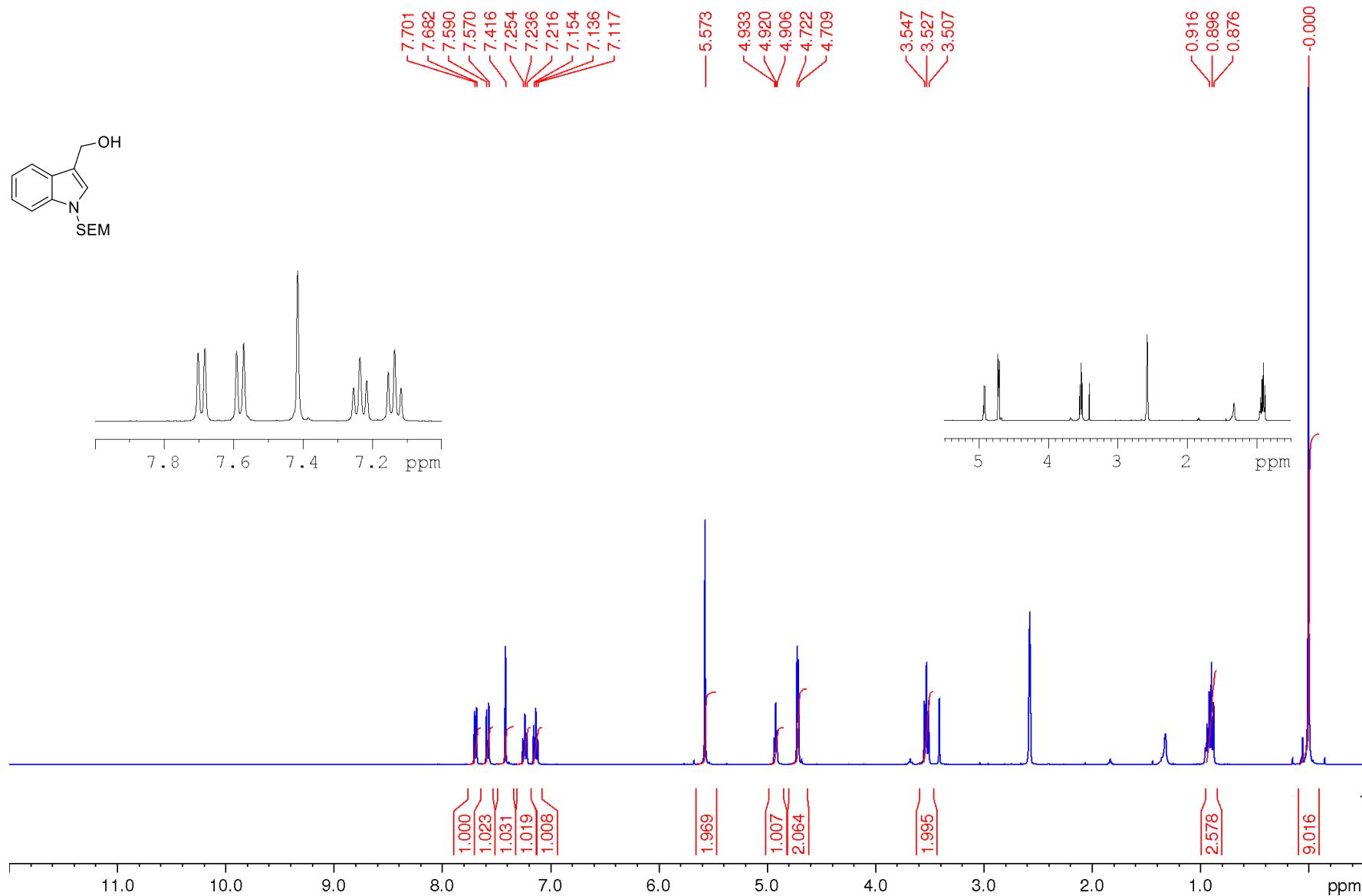
57.212
50.007

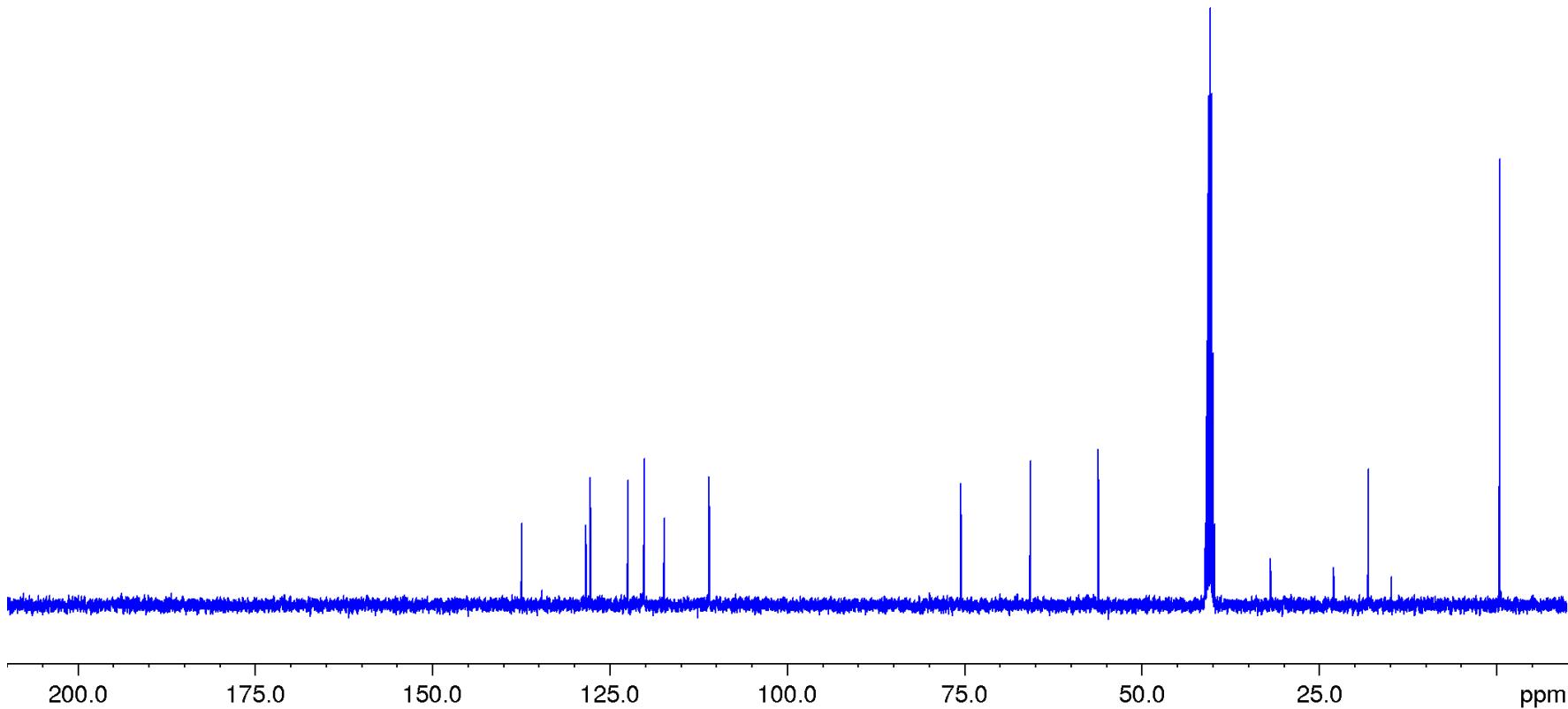


(1-tosyl-1H-indol-3-yl)methanol



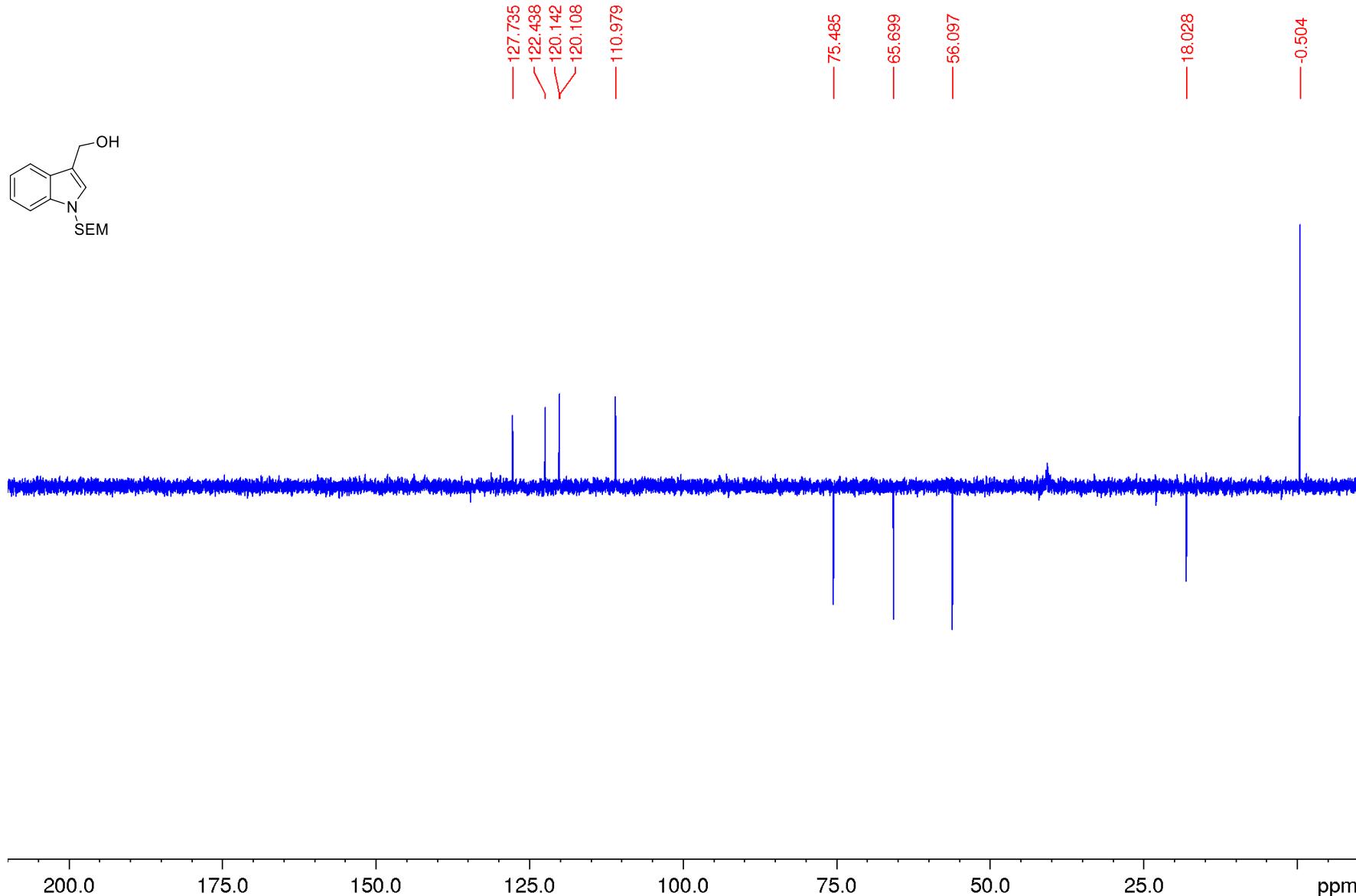
^1H NMR-spectrum (400.13 MHz) (DMSO- d_6)





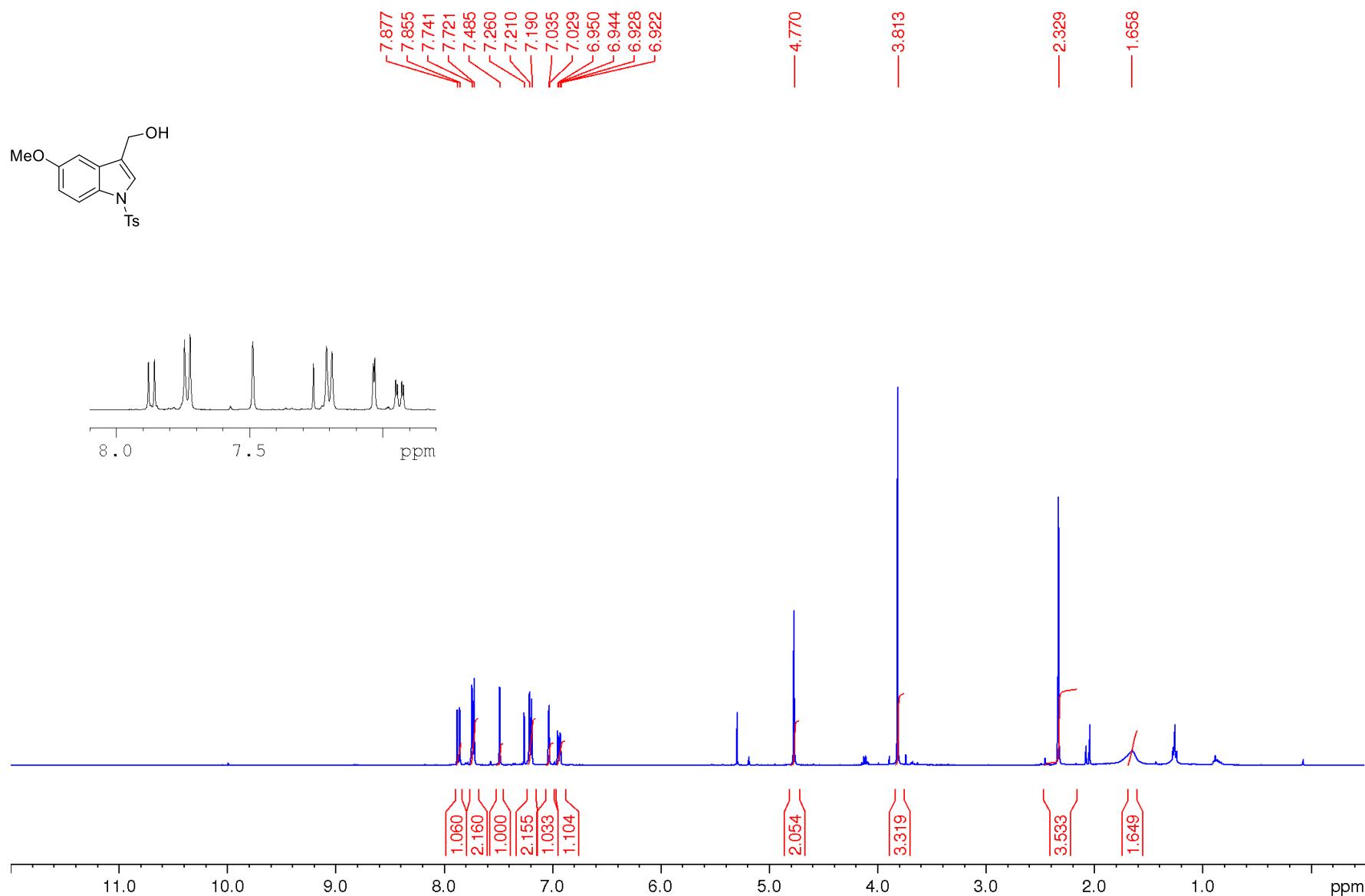
(1-tosyl-1H-indol-3-yl)methanol

DEPT 135 NMR-spectrum (CDCl_3)



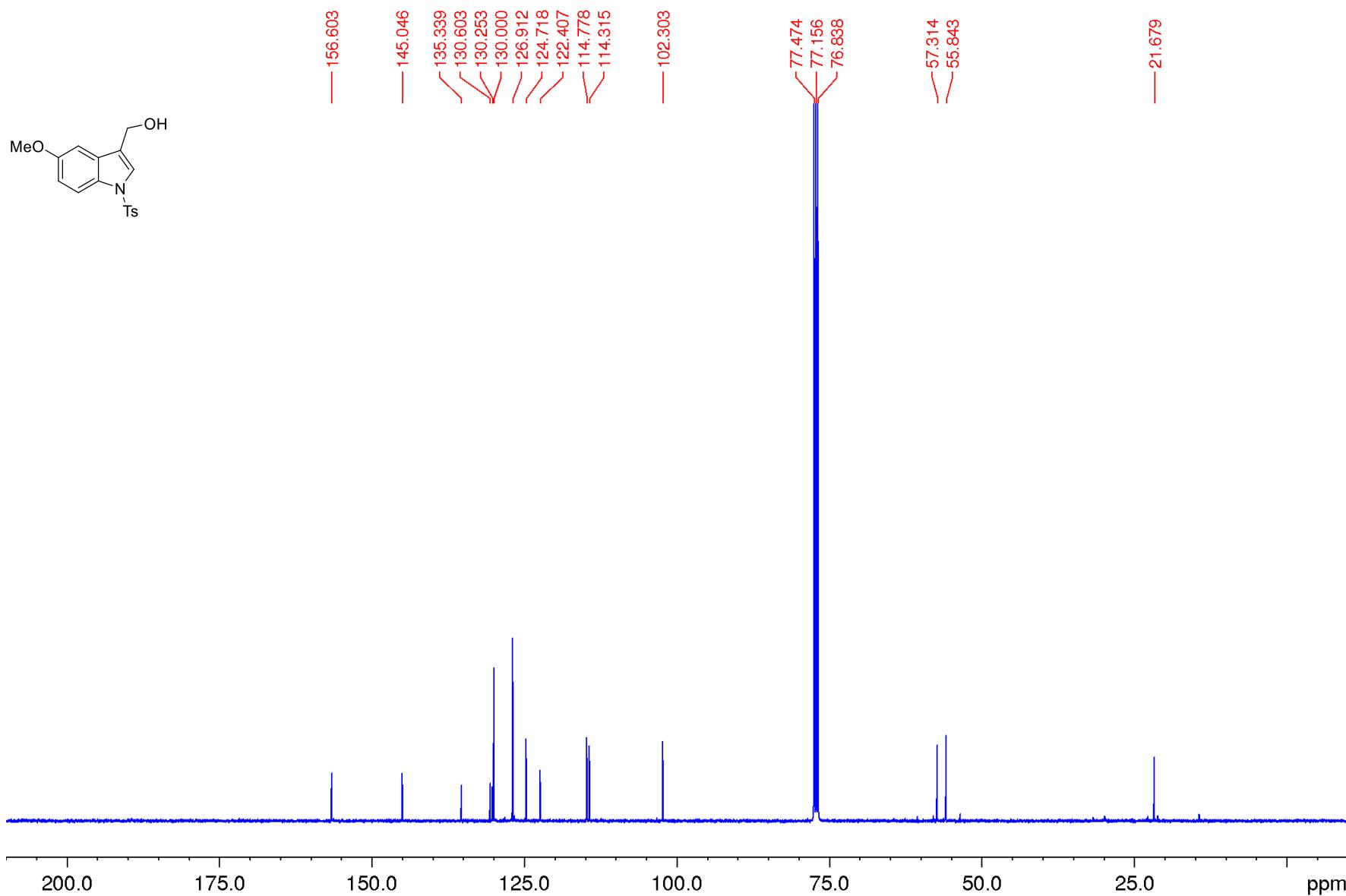
(5-methoxy-1-tosyl-1H-indol-3-yl)methanol

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



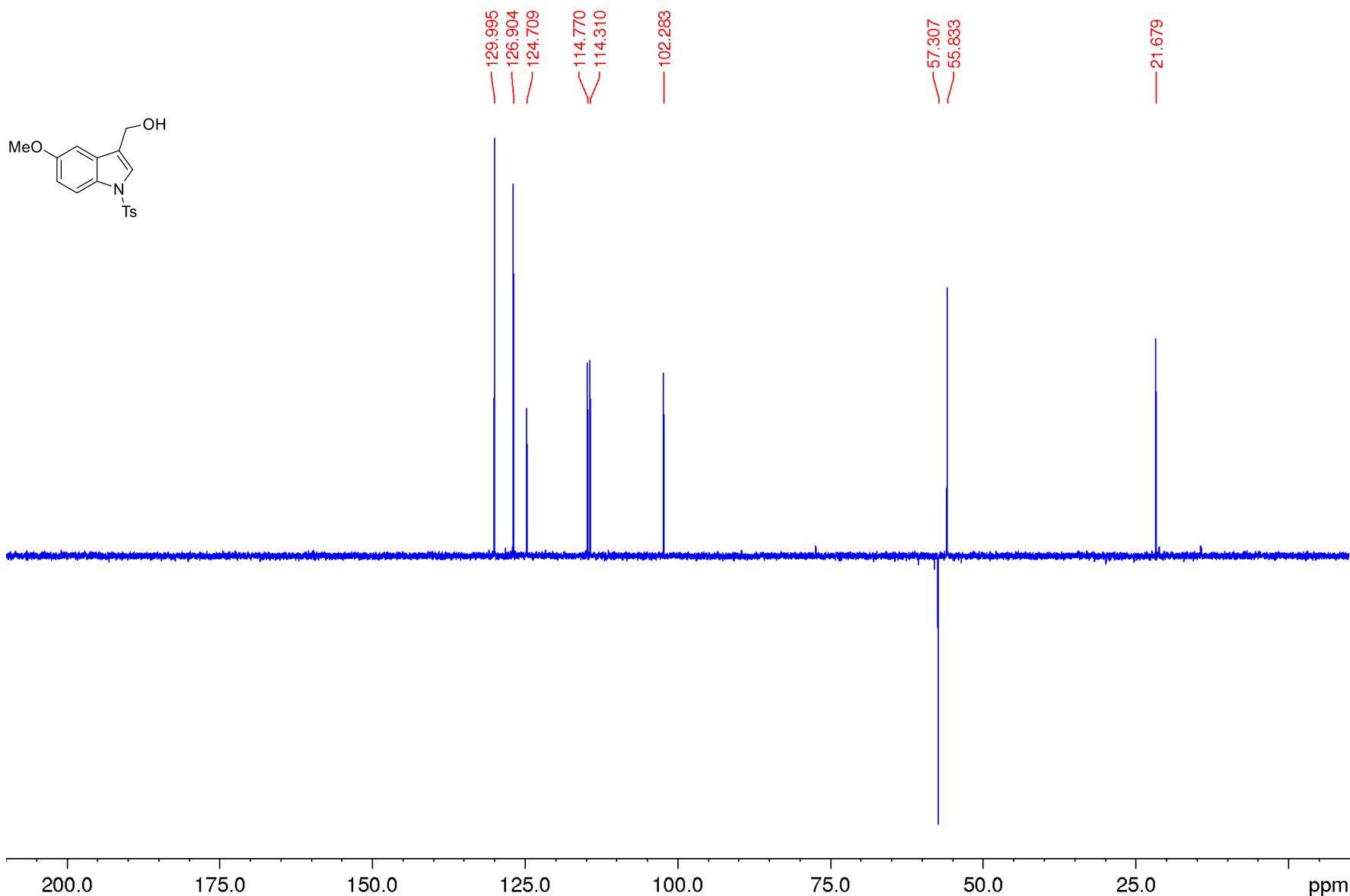
(5-methoxy-1-tosyl-1H-indol-3-yl)methanol

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



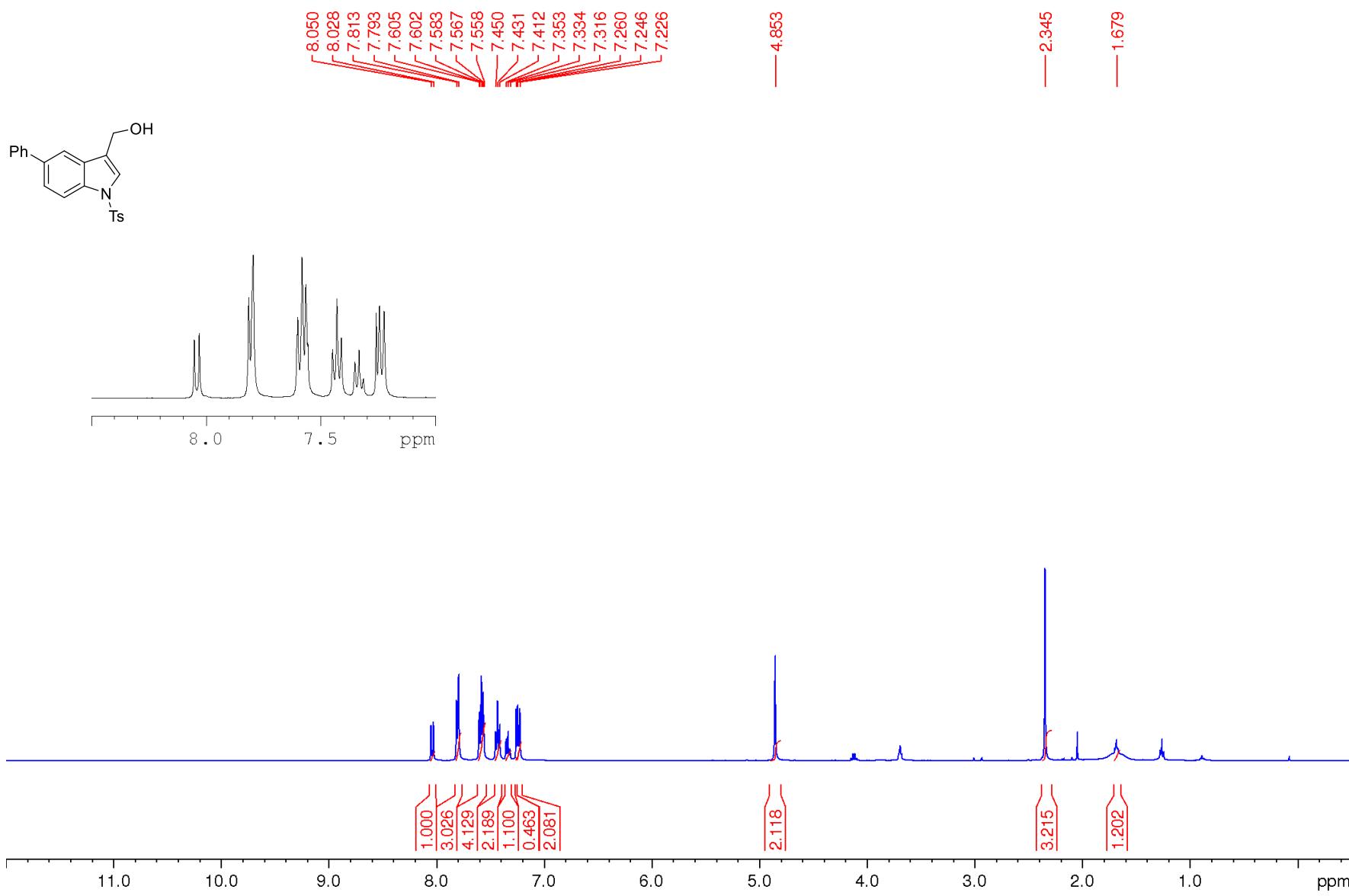
(5-methoxy-1-tosyl-1H-indol-3-yl)methanol

DEPT 135 NMR-spectrum (CDCl_3)

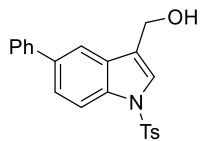


(5-phenyl-1-tosyl-1H-indol-3-yl)methanol

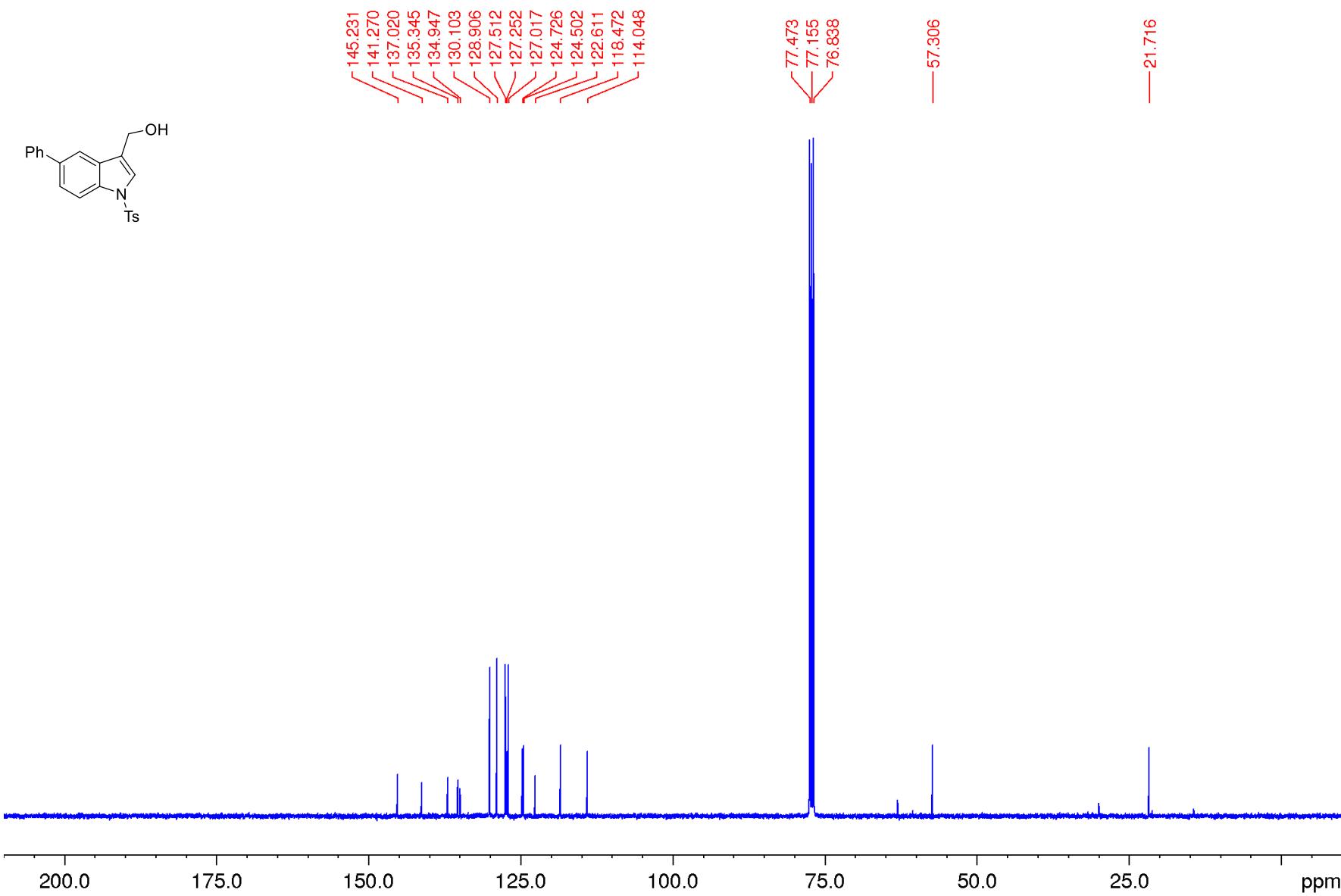
^1H NMR-spectrum (400.13 MHz) (CDCl_3)



((5-phenyl-1-tosyl-1H-indol-3-yl)methanol

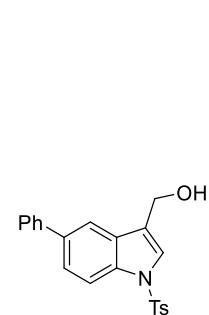


^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



(5-phenyl-1-tosyl-1H-indol-3-yl)methanol

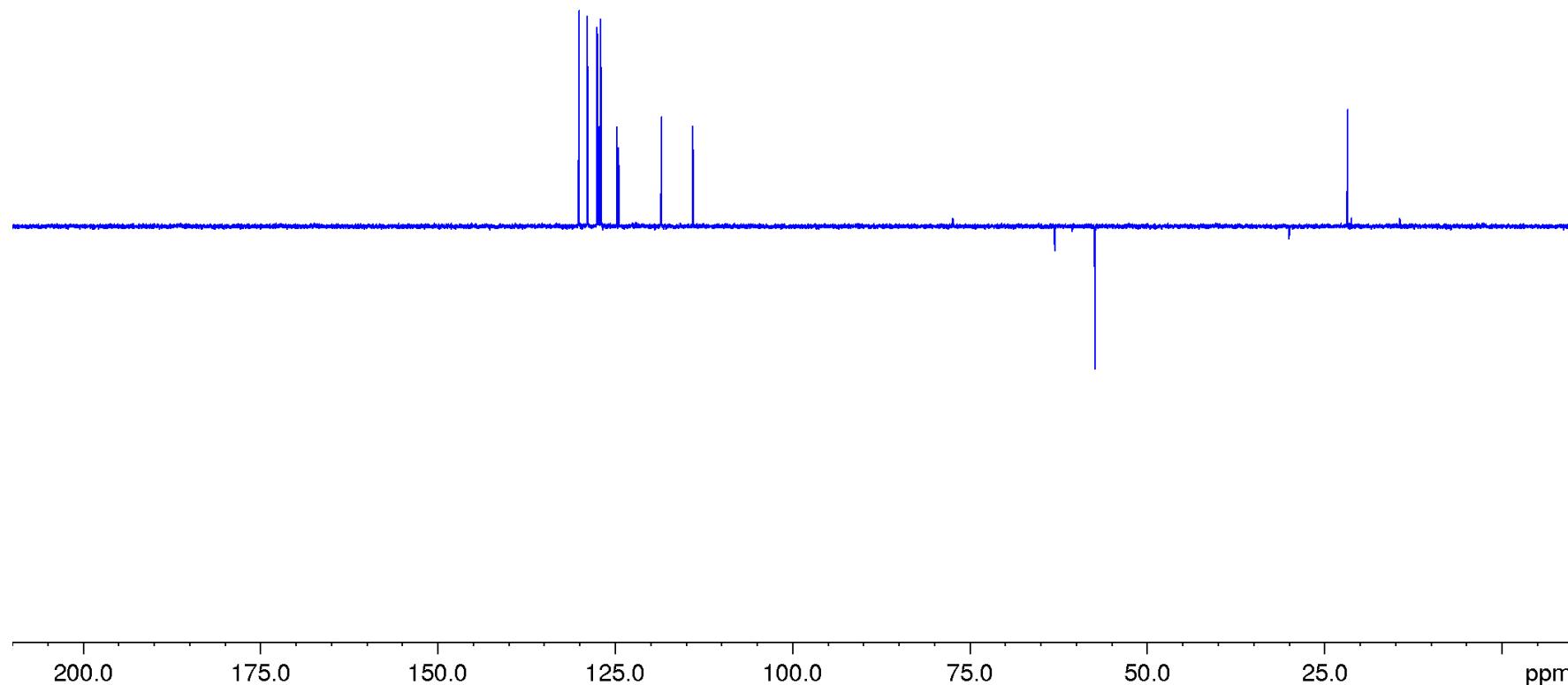
DEPT 135 NMR-spectrum (CDCl_3)



130.091
128.894
127.500
127.240
127.006
124.714
124.491
118.461
114.037

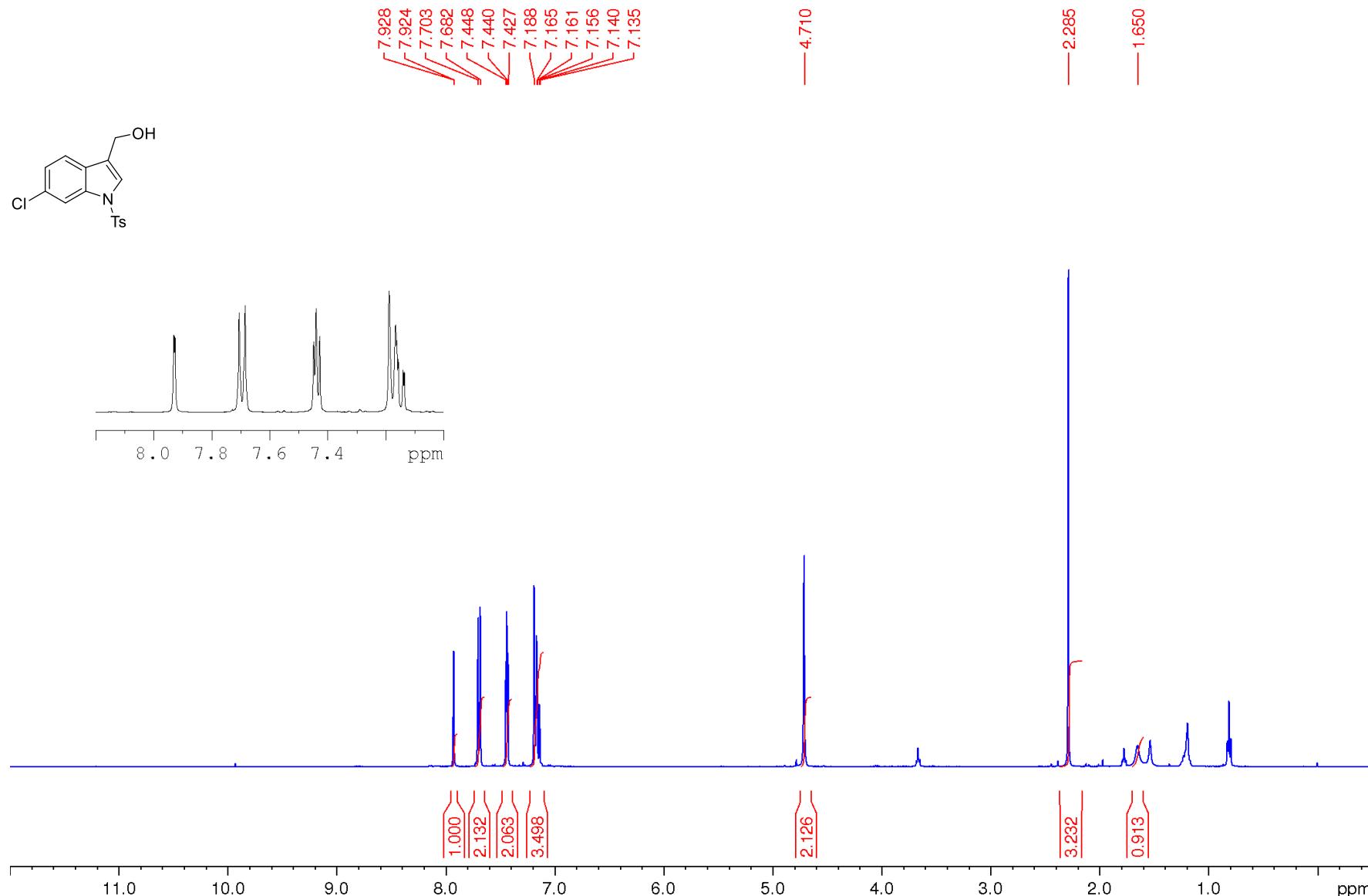
— 57.295

— 21.706



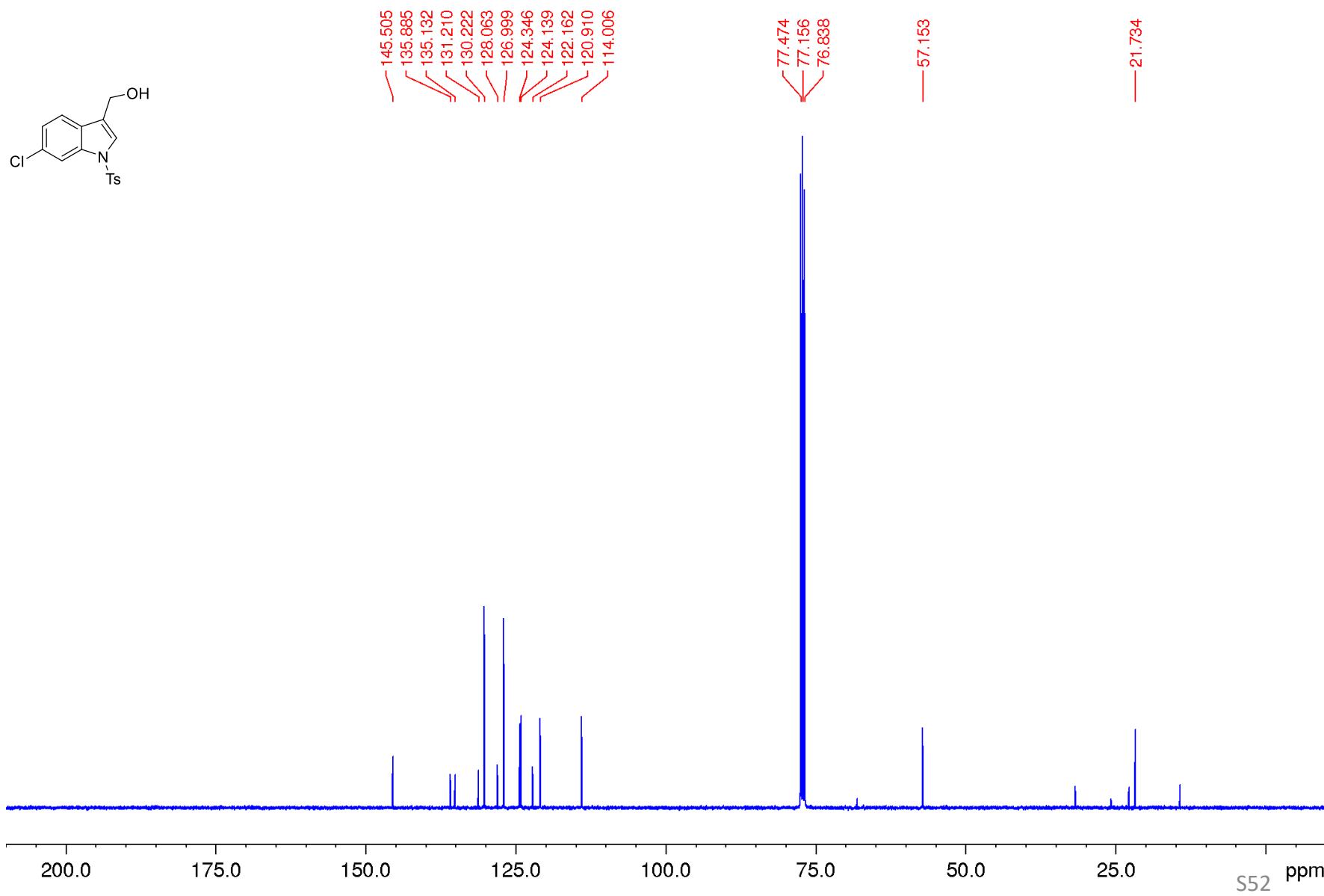
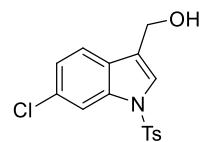
(6-chloro-1-tosyl-1H-indol-3-yl)methanol

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



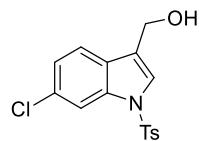
(6-chloro-1-tosyl-1H-indol-3-yl)methanol

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



(6-chloro-1-tosyl-1H-indol-3-yl)methanol

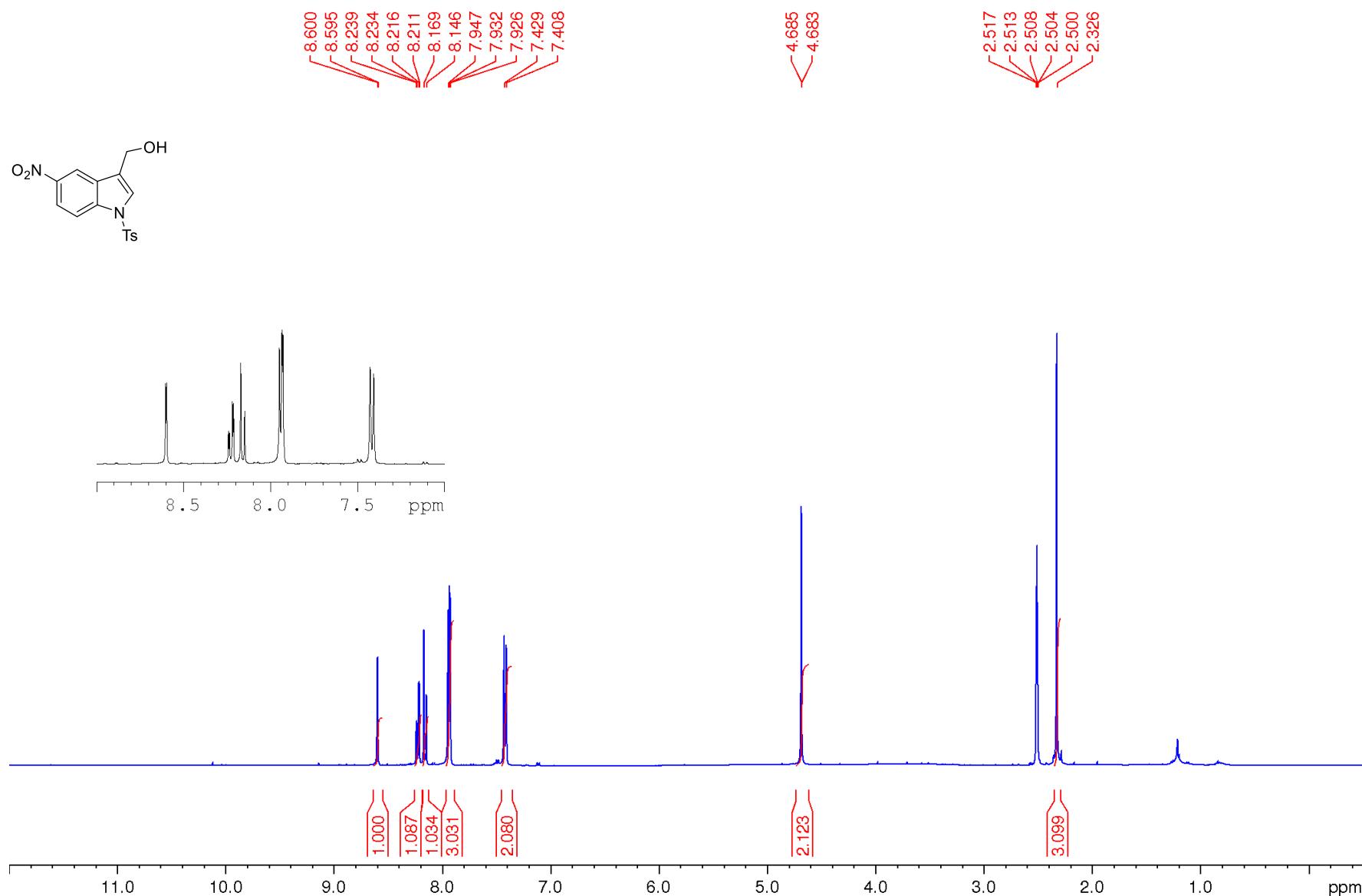
DEPT 135 NMR-spectrum (CDCl_3)

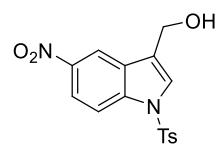


200.0 175.0 150.0 125.0 100.0 75.0 50.0 25.0 S53 ppm

(5-nitro-1-tosyl-1H-indol-3-yl)methanol

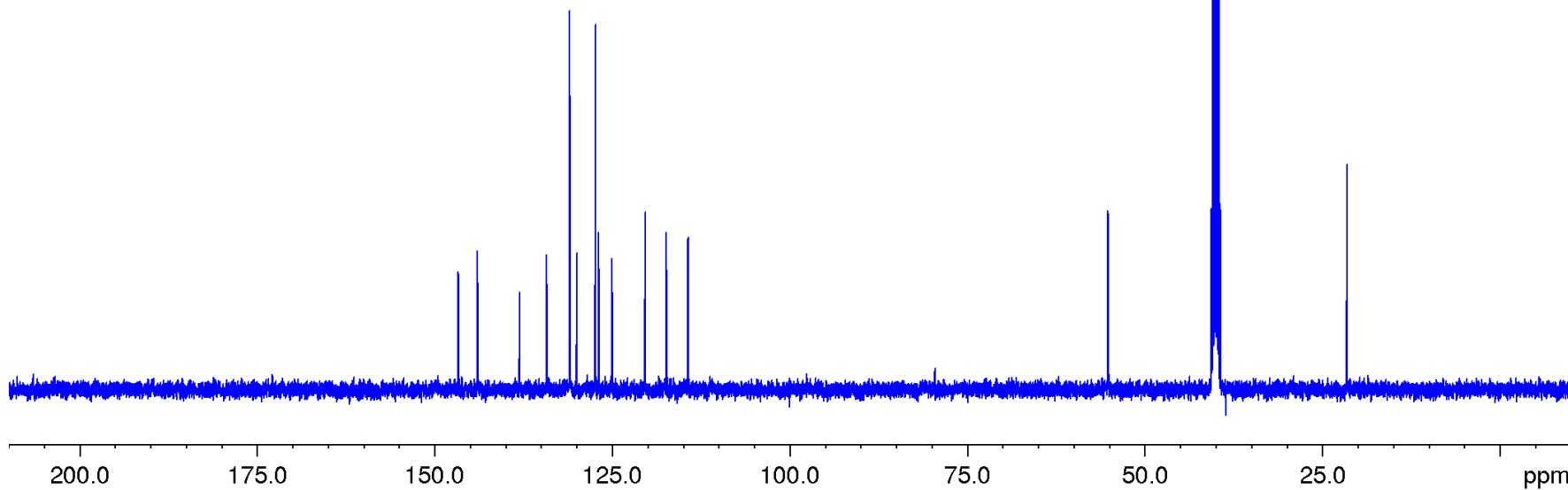
^1H NMR-spectrum (400.13 MHz) (DMSO- d_6)

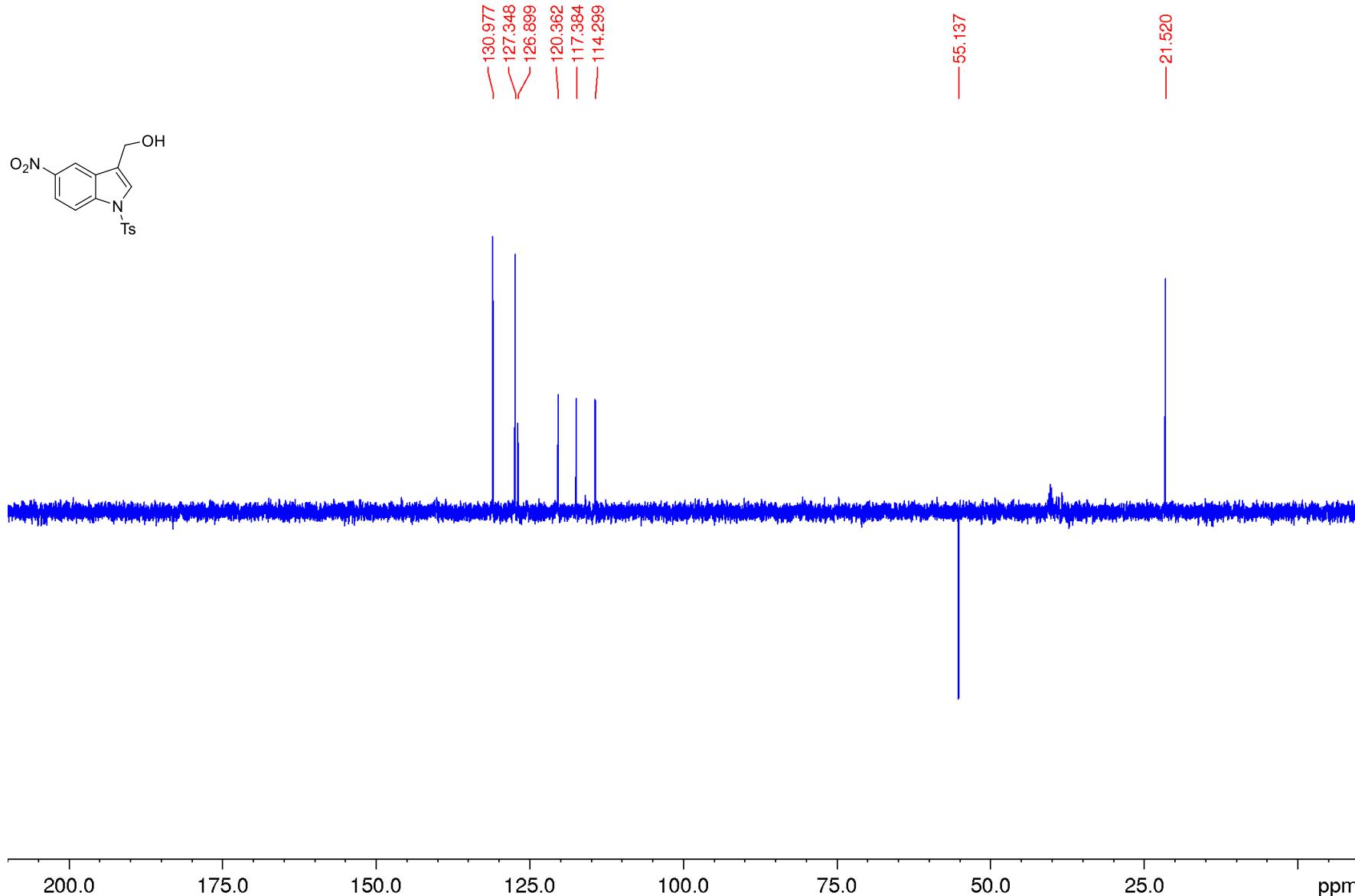
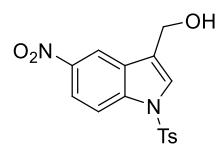




146.668
143.949
138.002
134.209
130.977
129.992
127.348
125.008
120.361
117.384
114.298

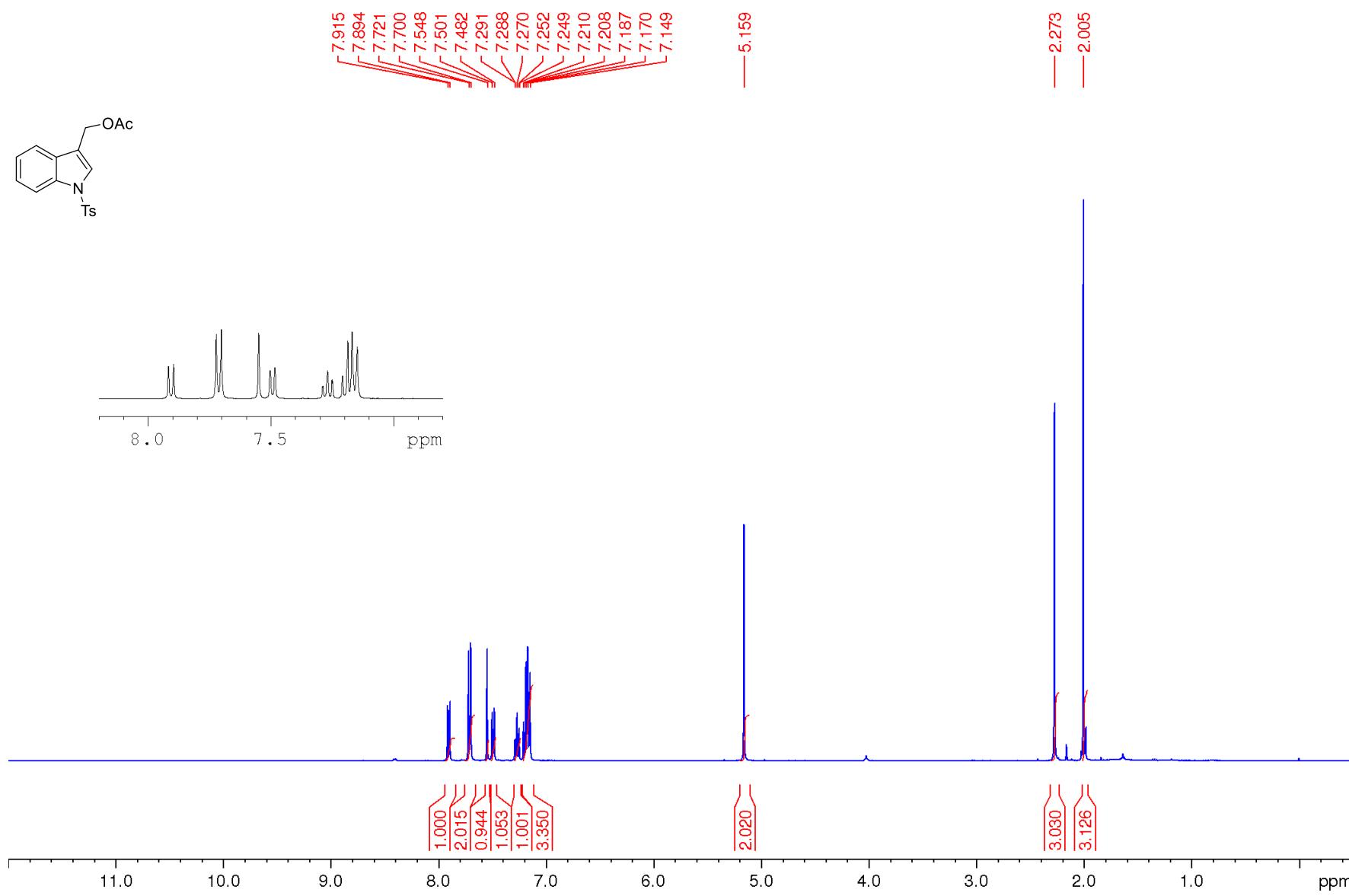
55.138
40.585
40.376
40.167
39.959
39.750
39.542
39.333
21.520





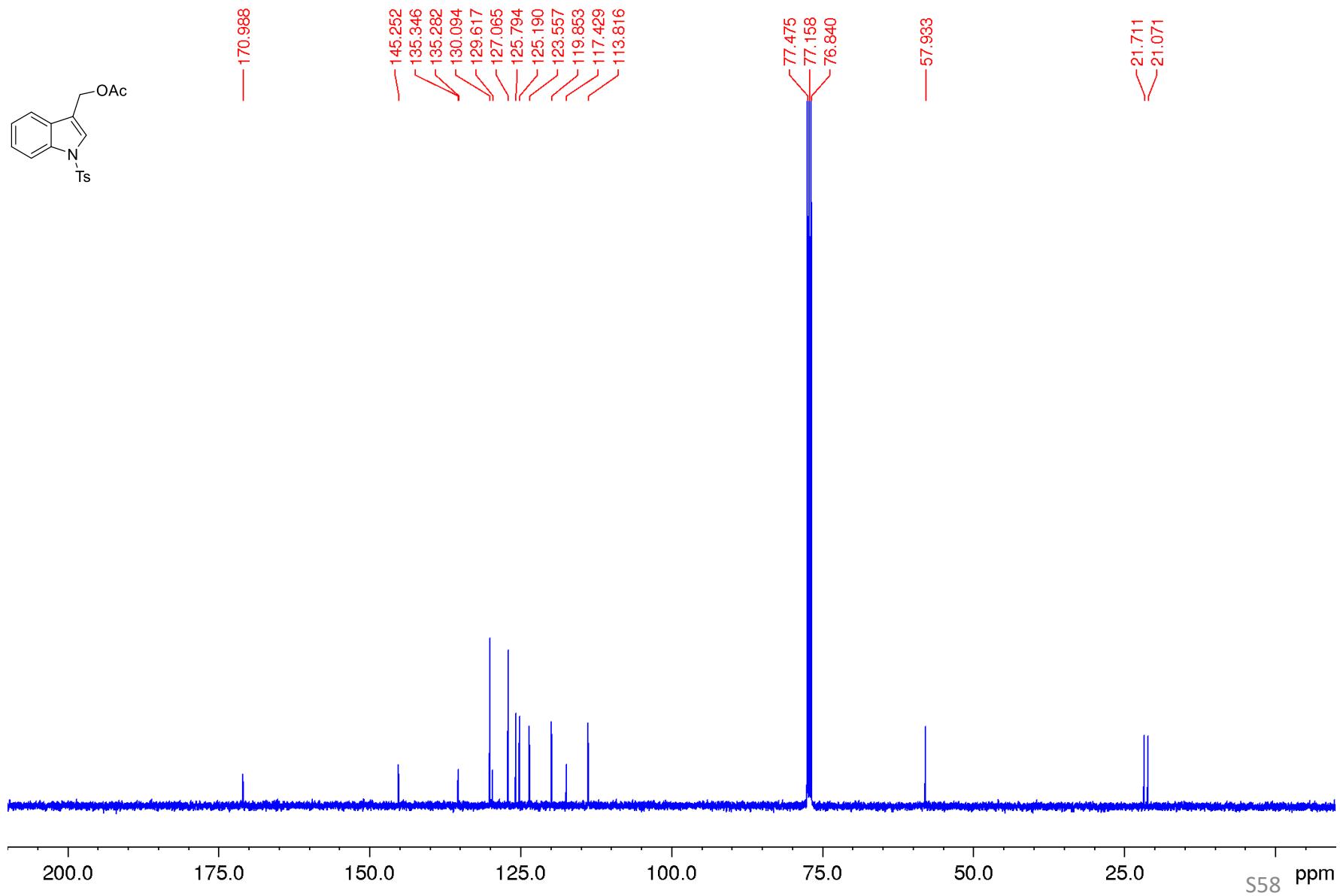
(1-tosyl-1*H*-indol-3-yl)methyl acetate **3a**

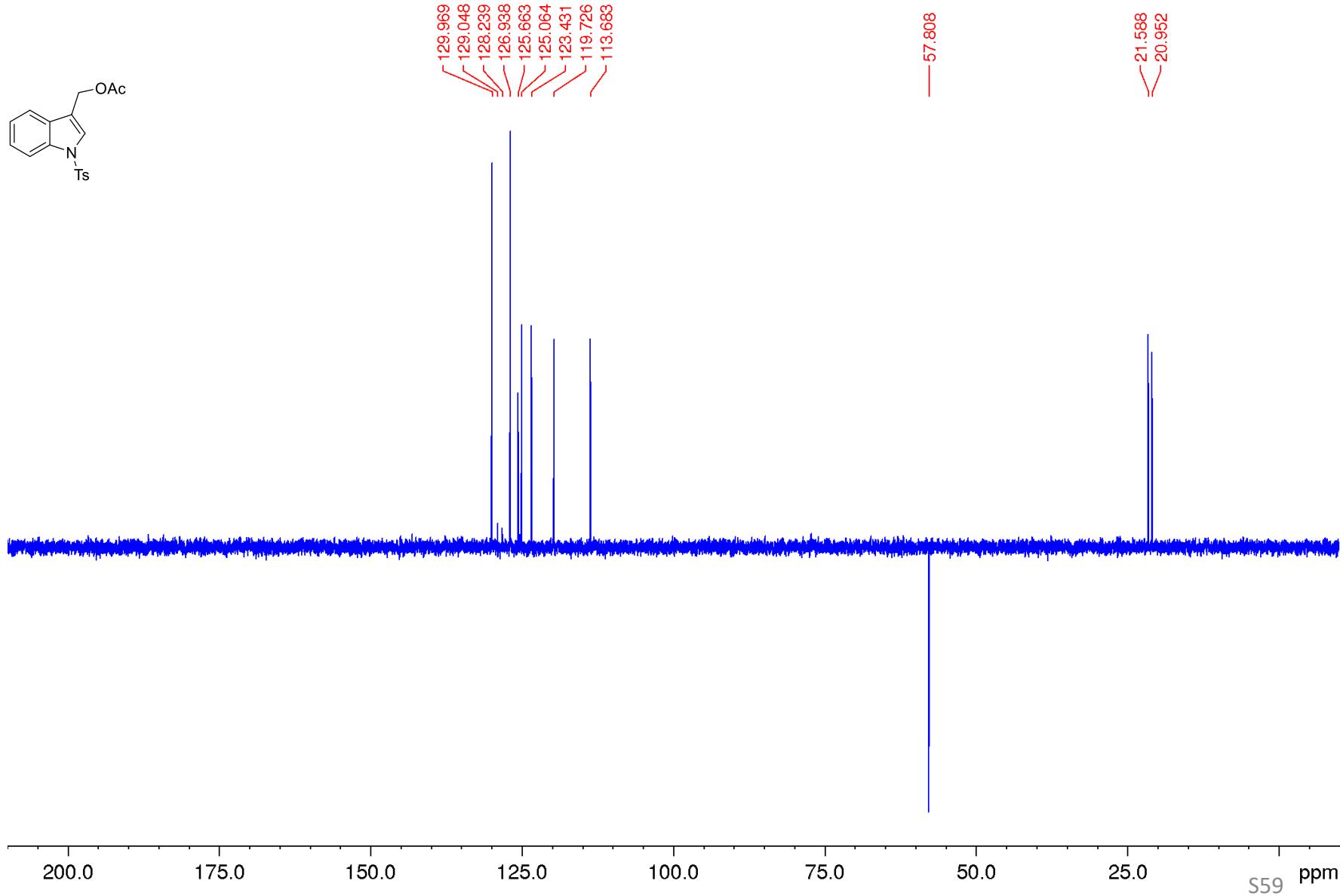
¹H NMR-spectrum (400.13 MHz) (CDCl_3)

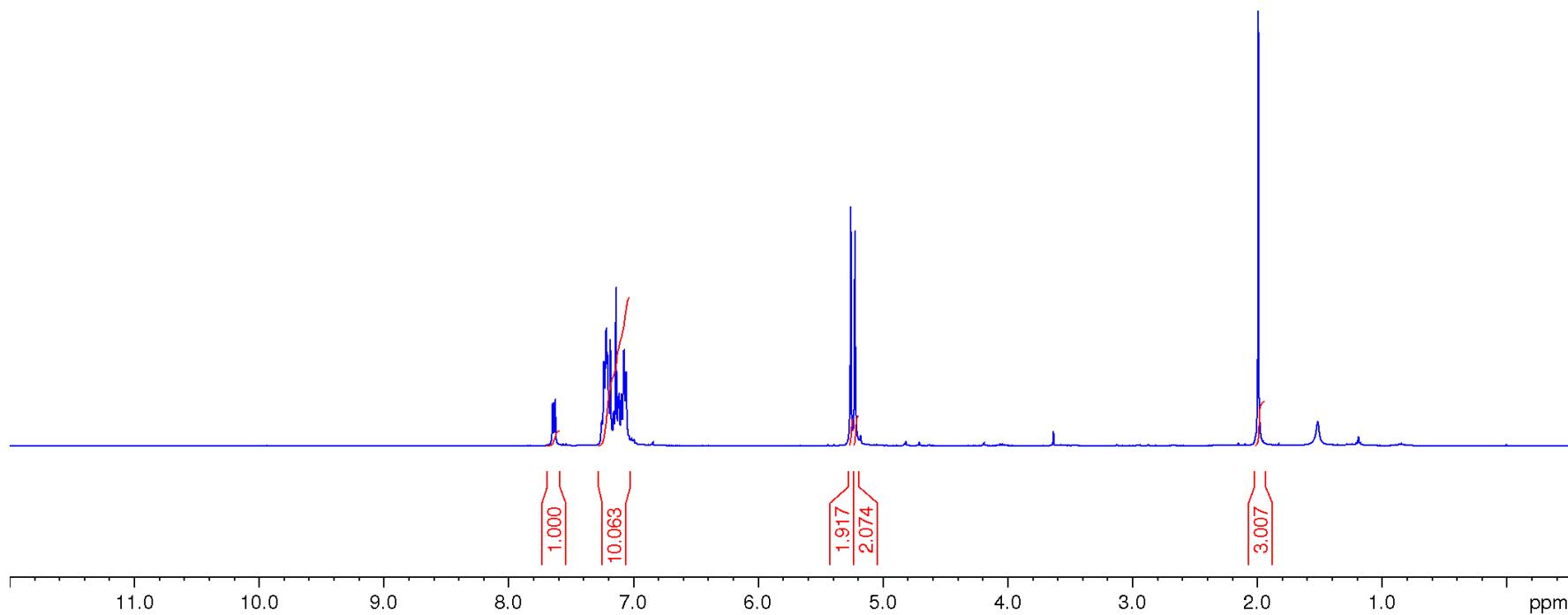
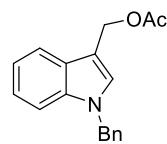


(1-tosyl-1*H*-indol-3-yl)methyl acetate **3a**

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)

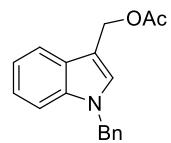






(1-benzyl-1H-indol-3-yl)methyl acetate 3b

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



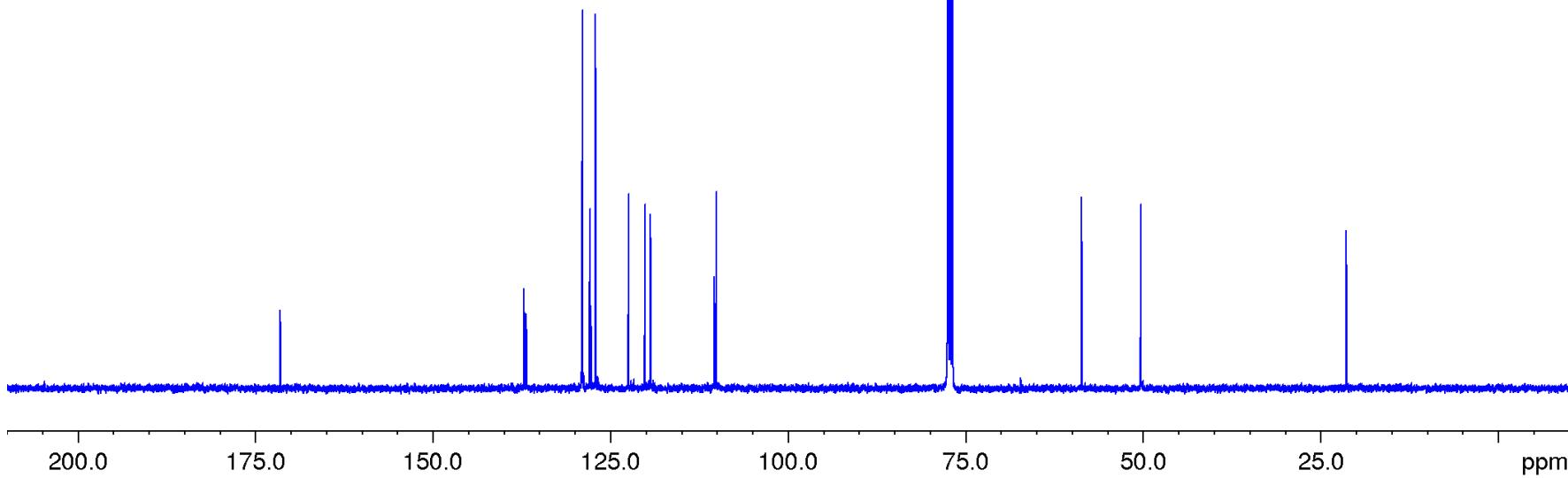
137.163
136.834
129.029
128.959
127.907
127.763
127.080
122.450
120.125
119.338
110.374
110.098

77.473
77.155
76.837

58.629

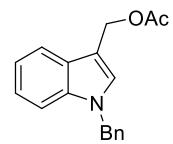
50.279

21.339



(1-benzyl-1H-indol-3-yl)methyl acetate 3b

DEPT 135 NMR-spectrum (CDCl_3)

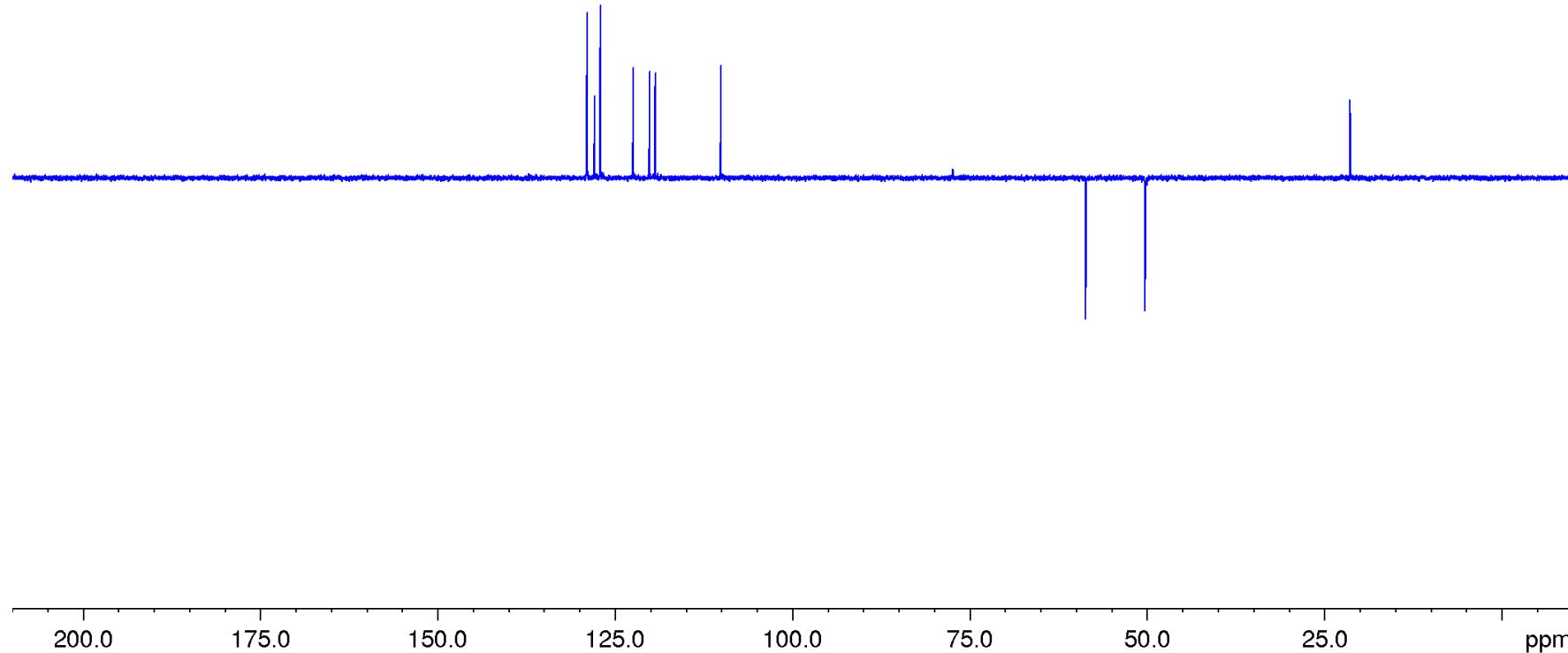


129.016
128.946
127.893
127.067
122.437
120.112
119.325
110.085

58.616

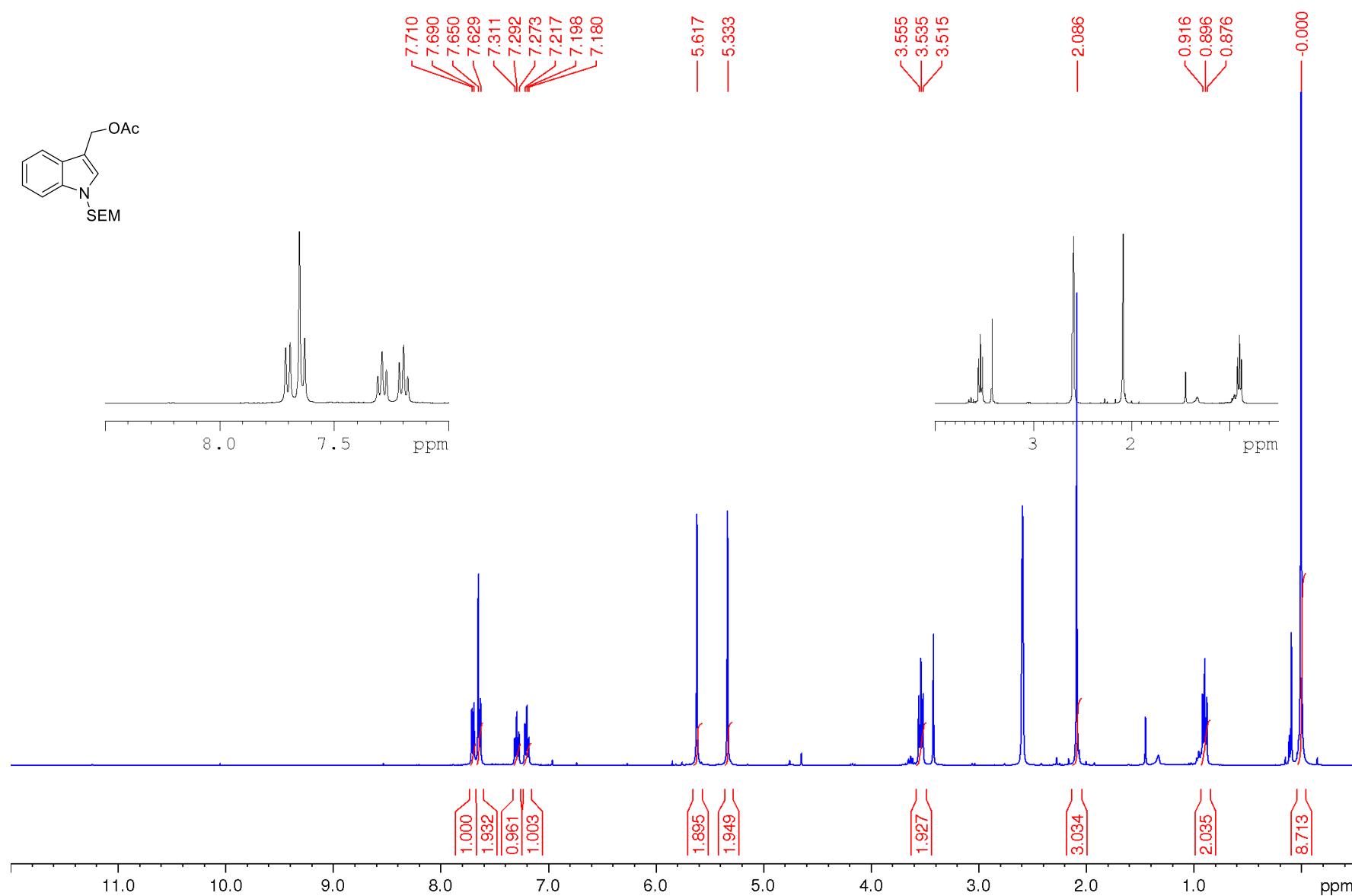
50.266

21.327



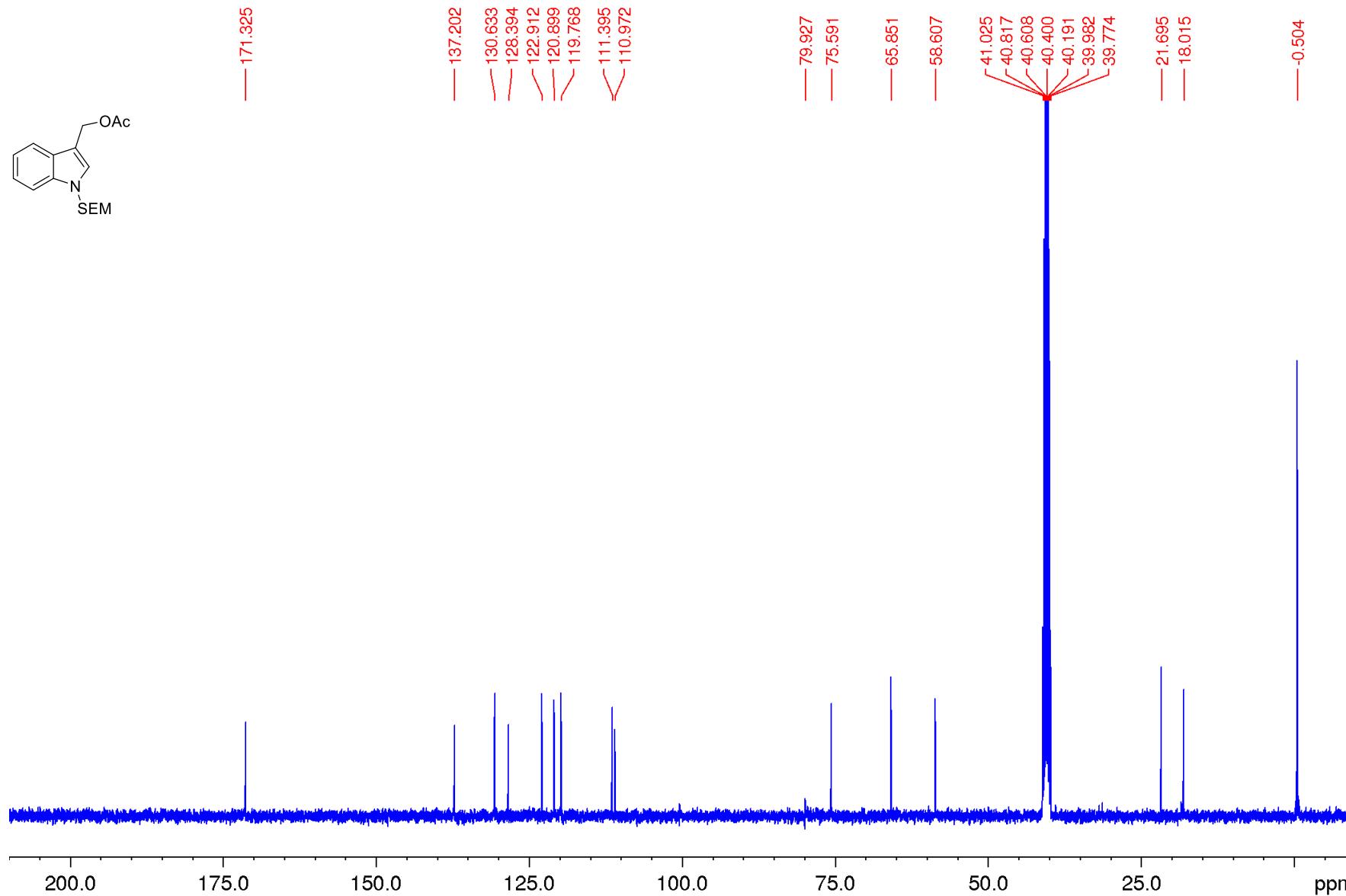
(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl acetate **3c**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



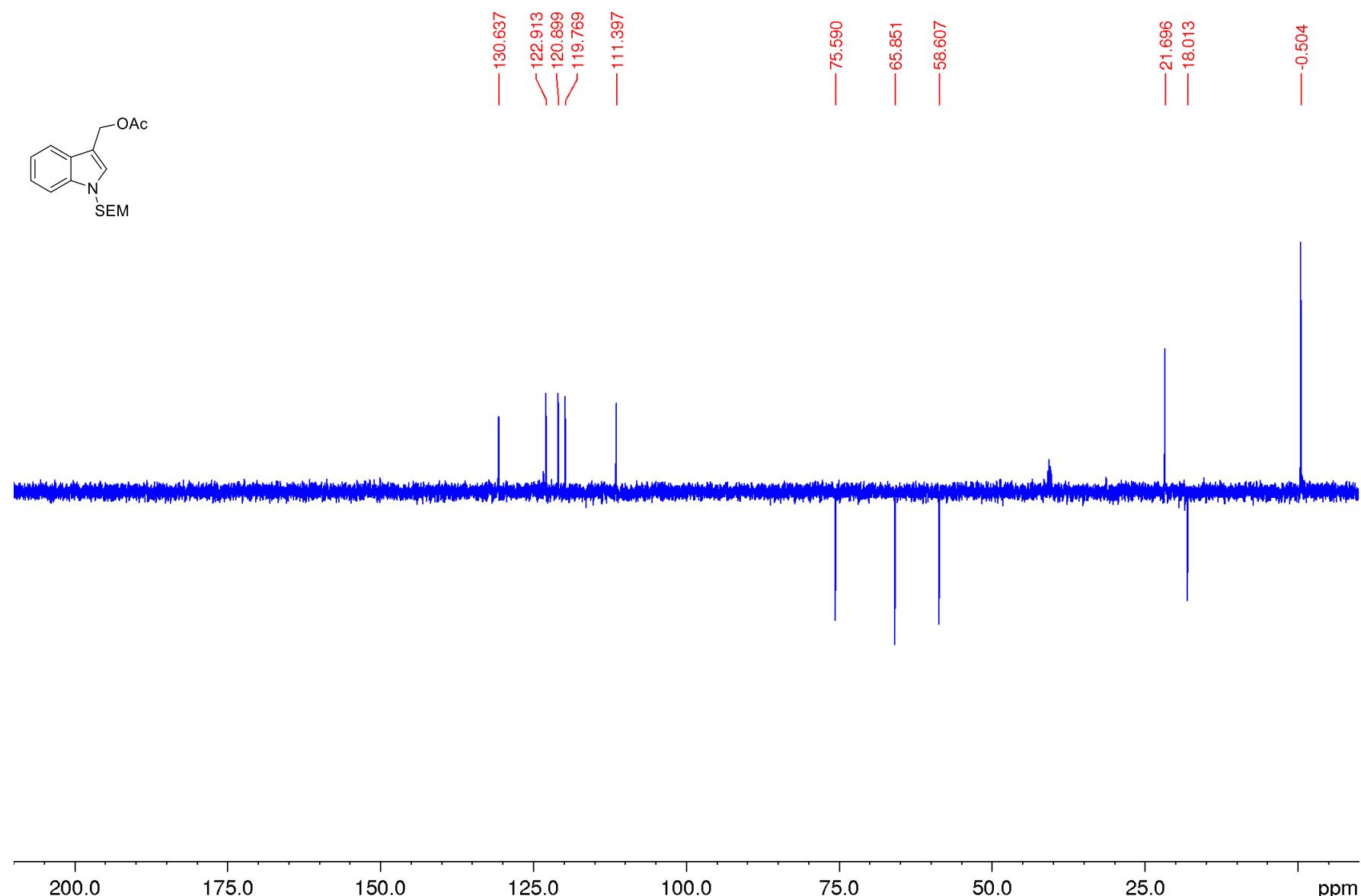
(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl acetate **3c**

¹³C NMR-spectrum (100.6 MHz) (DMSO-*d*₆)



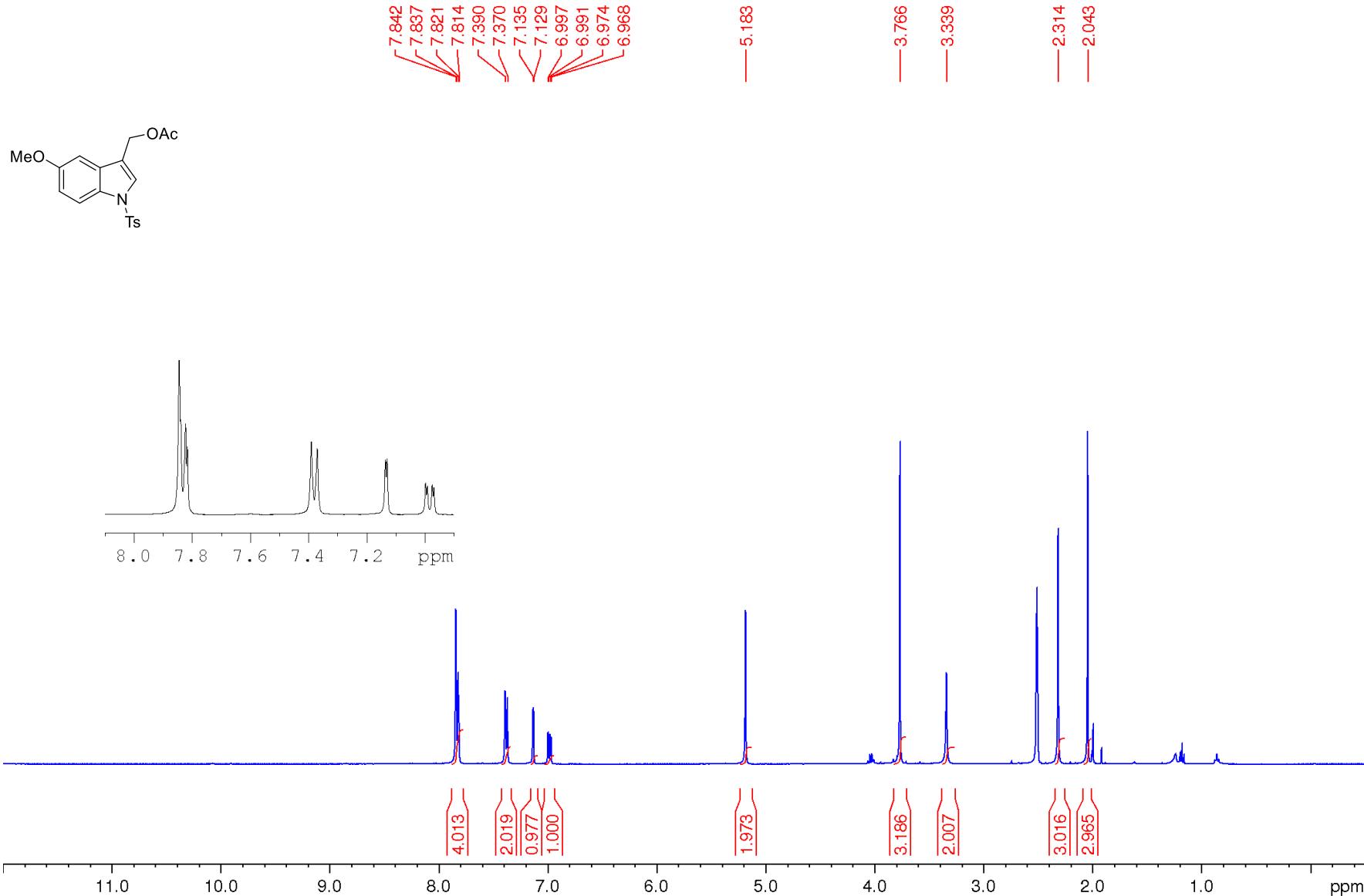
*(1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl acetate **3c***

DEPT 135 NMR-spectrum (DMSO-*d*₆)



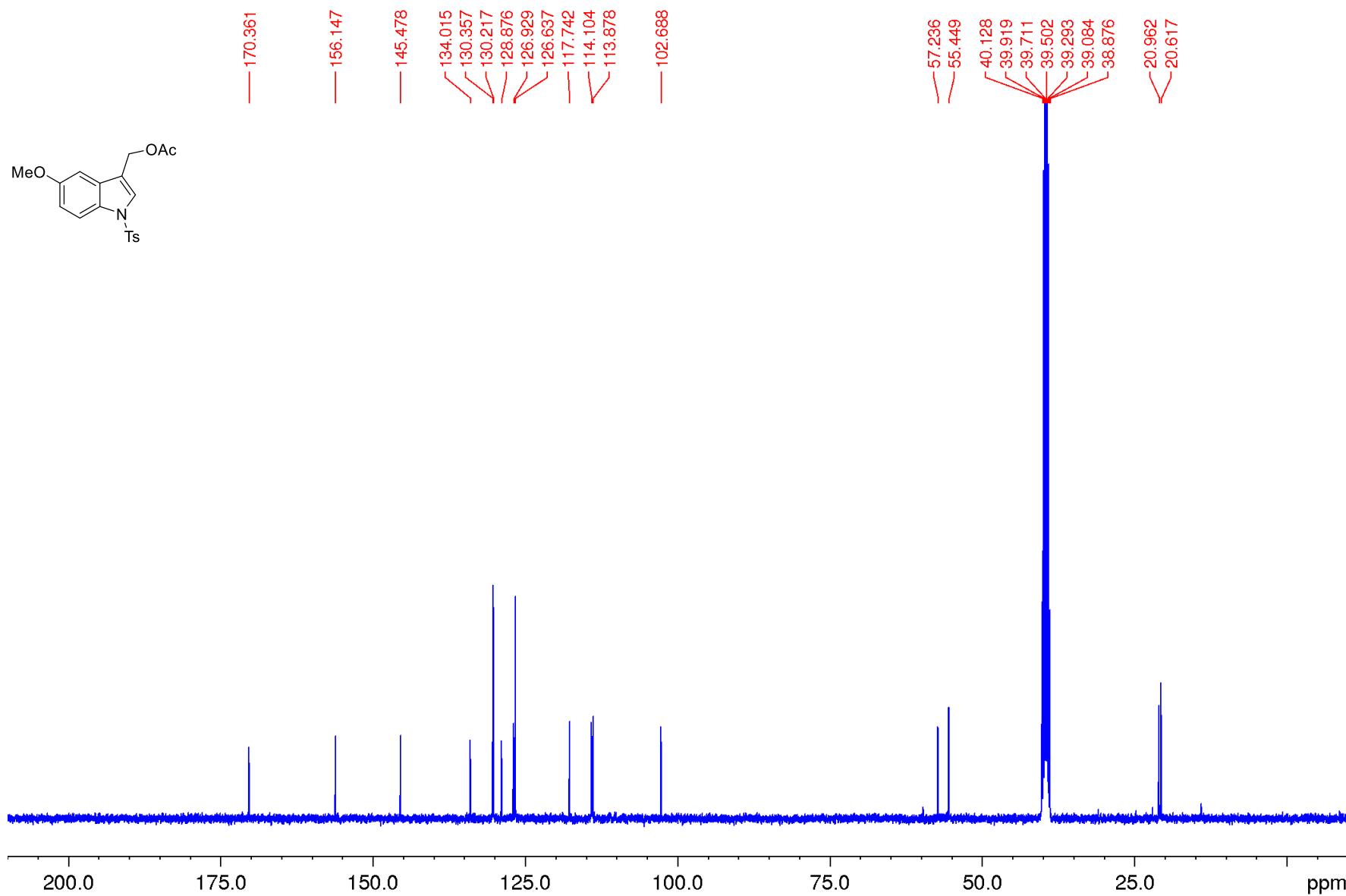
(5-methoxy-1-tosyl-1H-indol-3-yl)methyl acetate 3d

^1H NMR-spectrum (400.13 MHz) (DMSO- d_6)



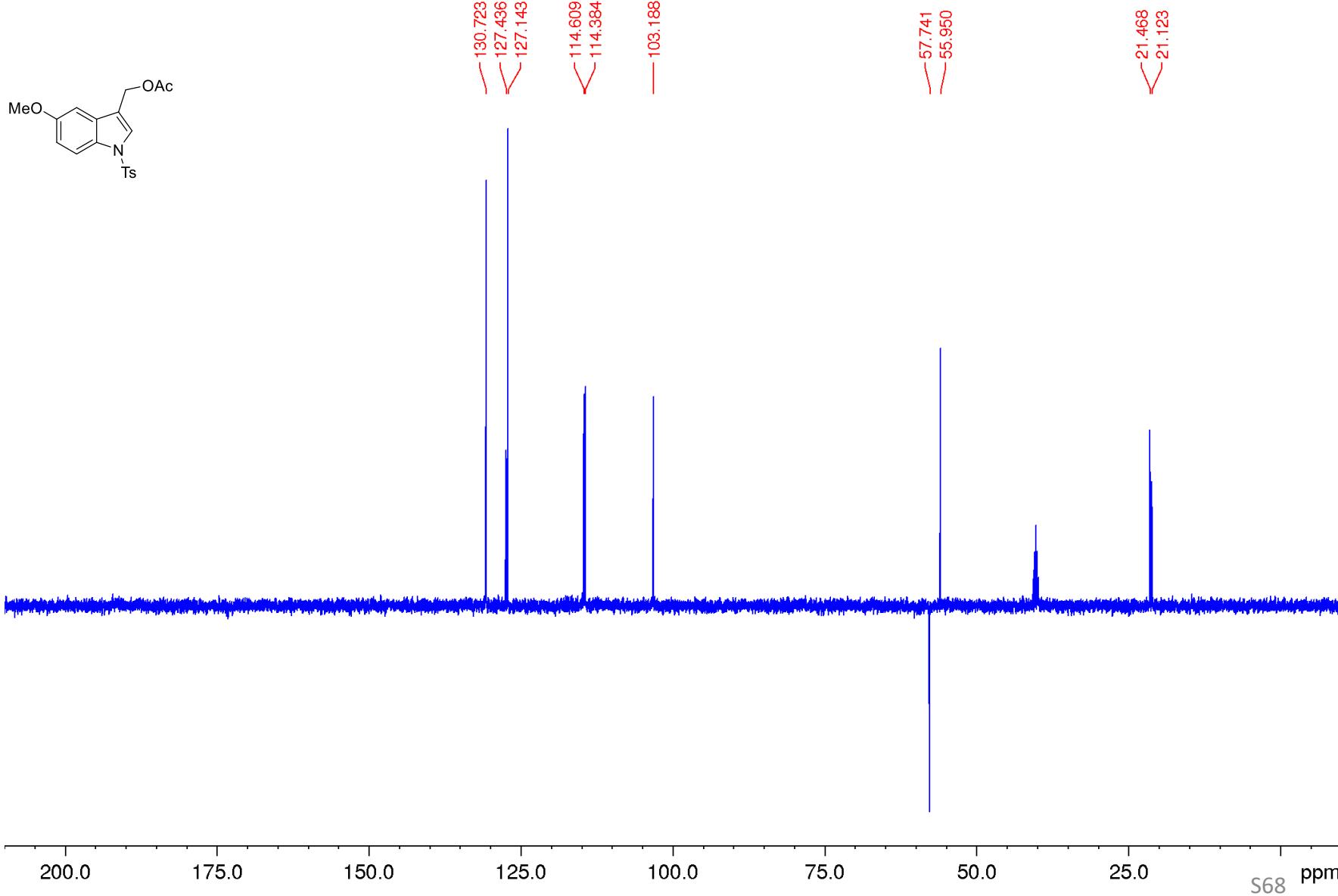
(5-methoxy-1-tosyl-1H-indol-3-yl)methyl acetate 3d

^{13}C NMR-spectrum (100.6 MHz) (DMSO- d_6)



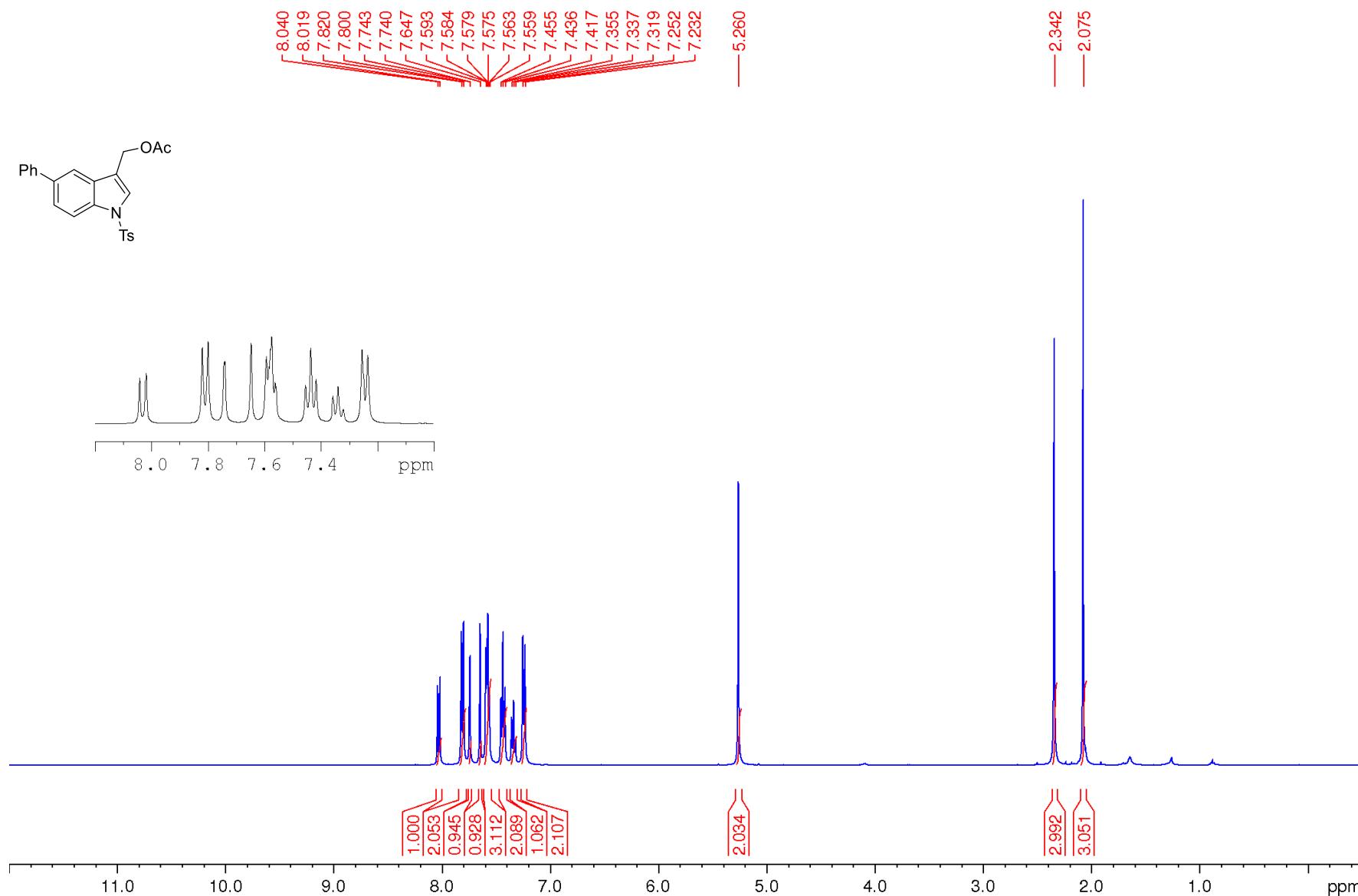
(5-methoxy-1-tosyl-1H-indol-3-yl)methyl acetate 3d

DEPT 135 NMR-spectrum (DMSO-*d*₆)



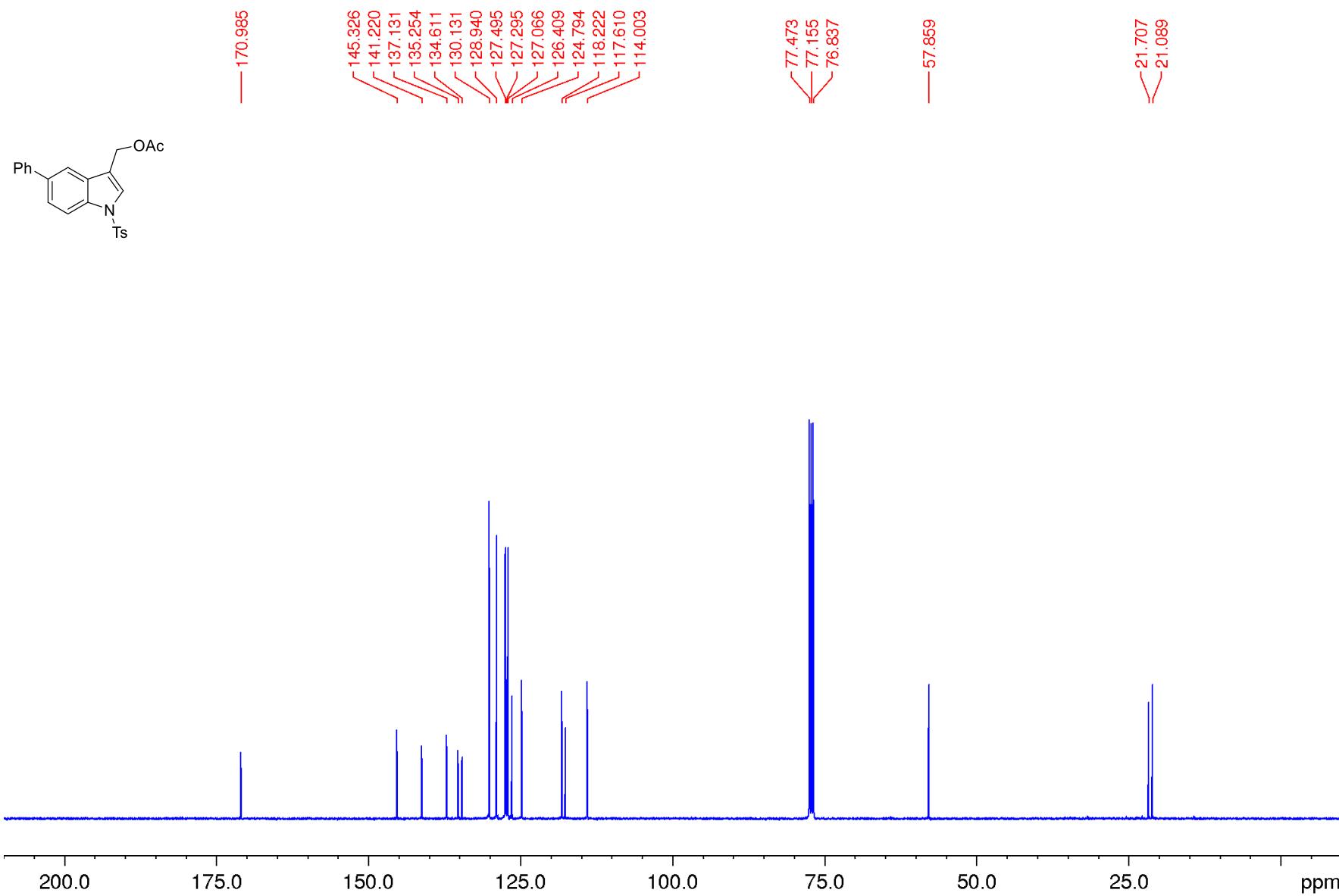
(5-phenyl-1-tosyl-1H-indol-3-yl)methyl acetate **3e**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



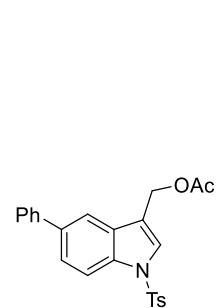
(5-phenyl-1-tosyl-1H-indol-3-yl)methyl acetate 3e

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



(5-phenyl-1-tosyl-1H-indol-3-yl)methyl acetate 3e

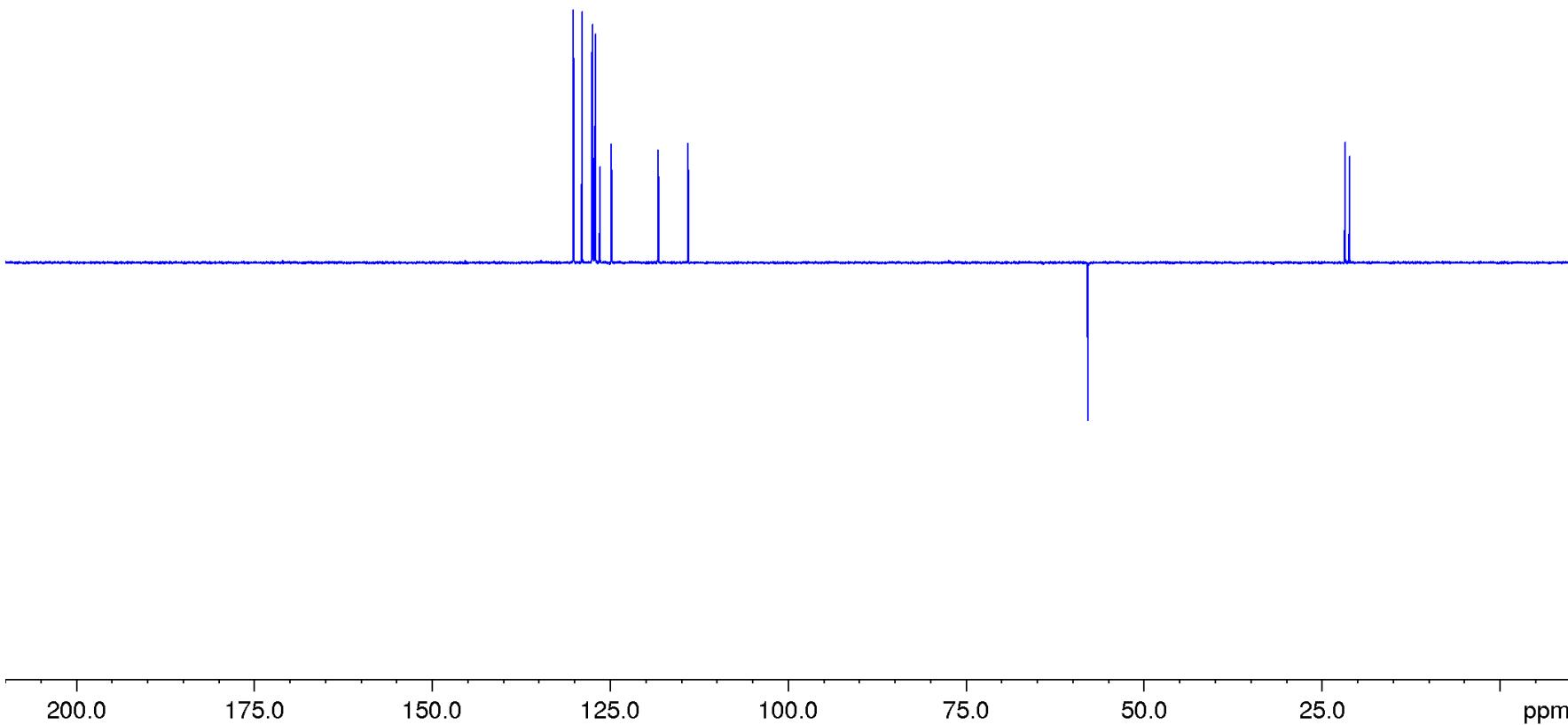
DEPT 135 NMR-spectrum (CDCl_3)



130.126
128.937
127.496
127.294
127.069
126.415
124.794
118.222
114.013

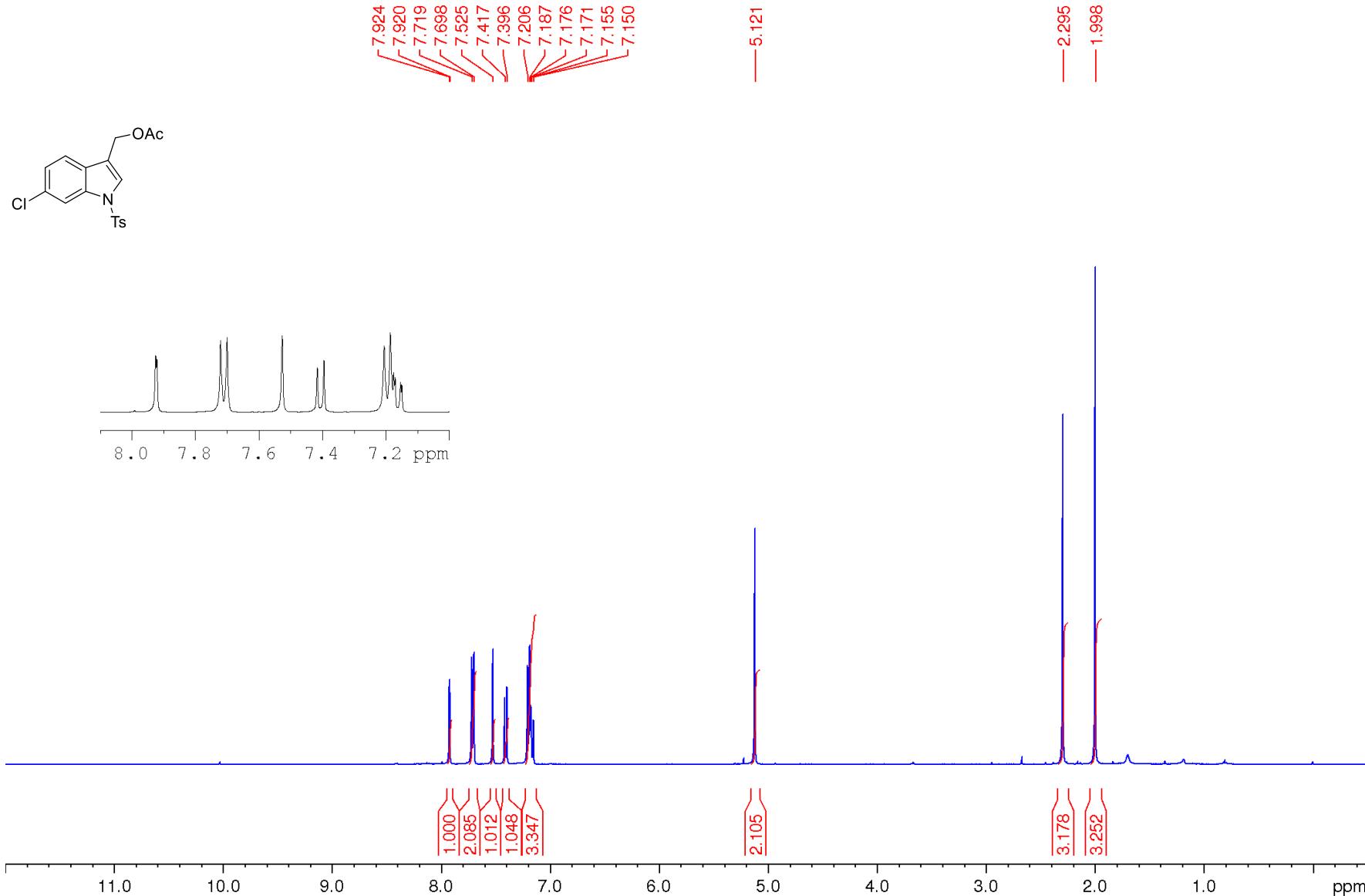
57.855

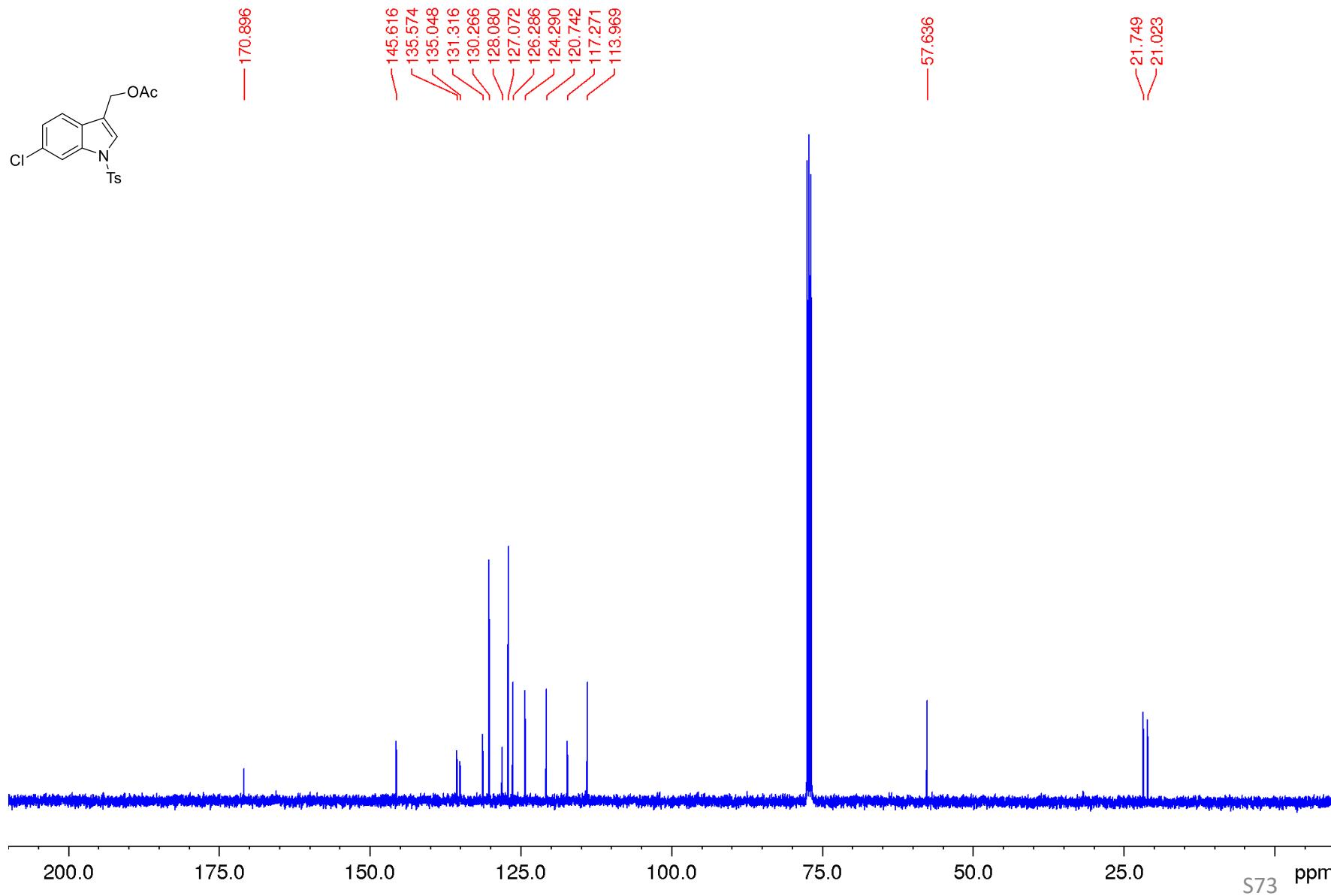
21.696
21.071

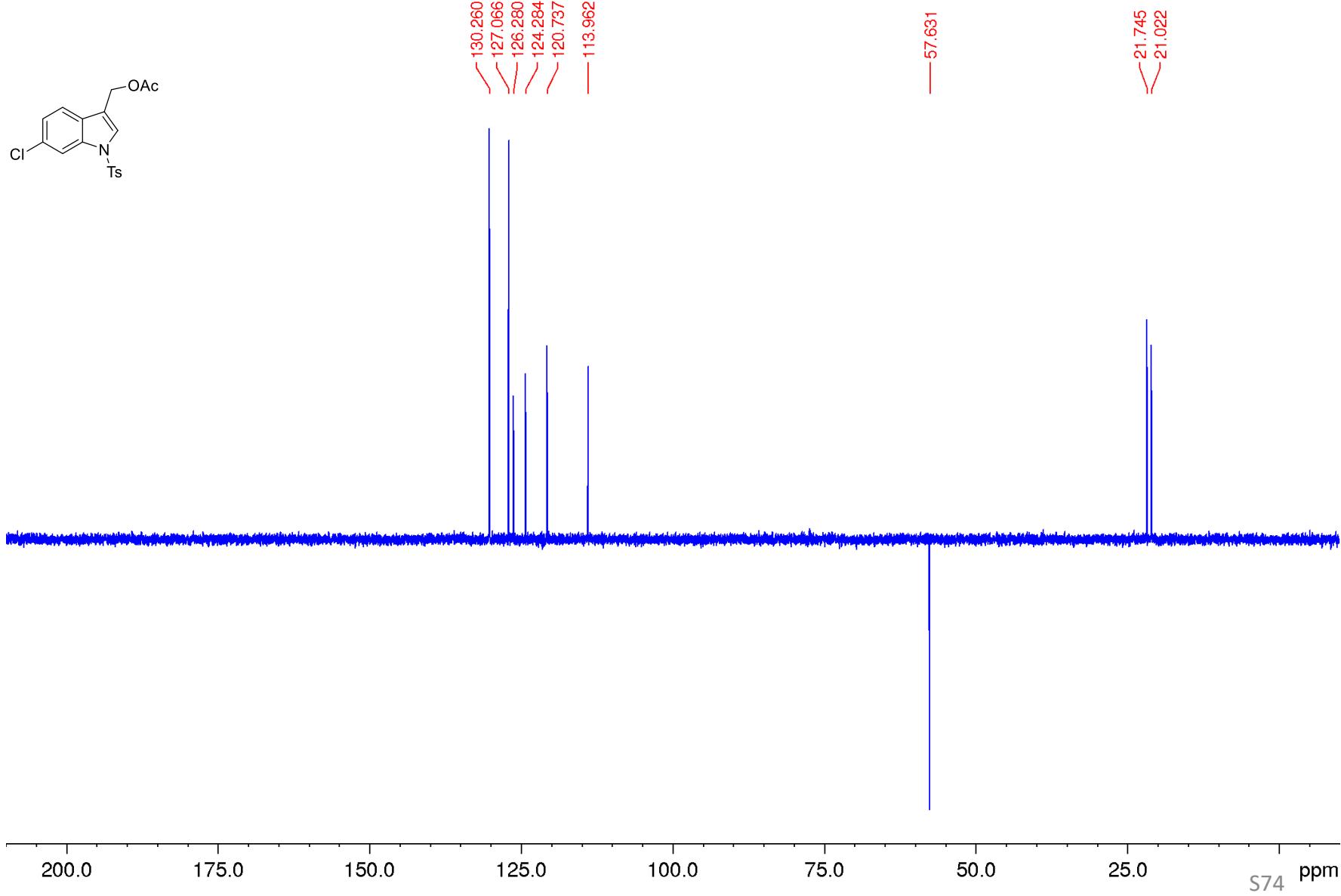
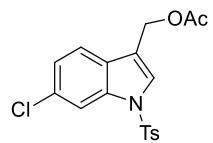


(6-chloro-1-tosyl-1H-indol-3-yl)methyl acetate 3f

^1H NMR-spectrum (400.13 MHz) (CDCl_3)

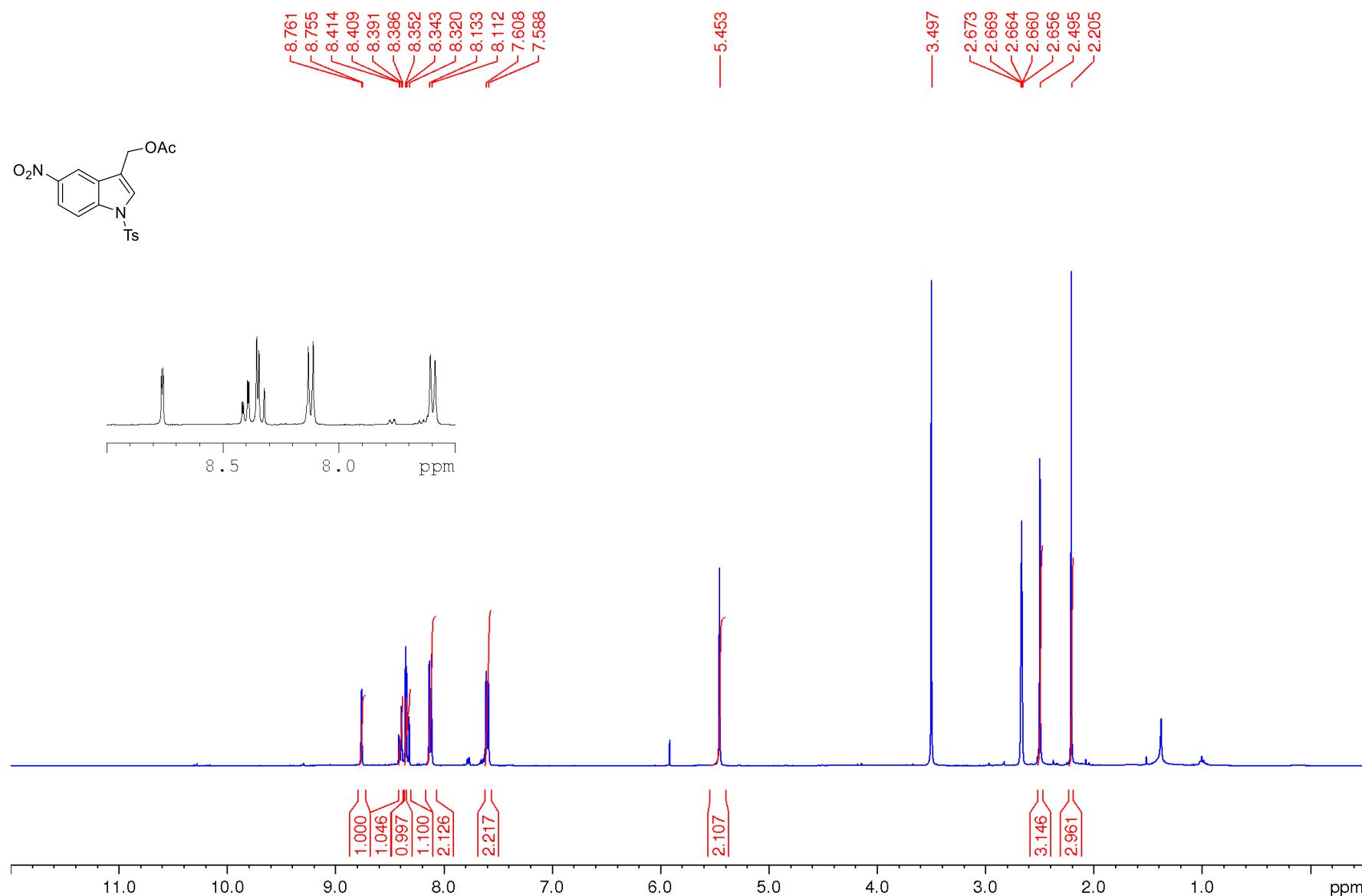






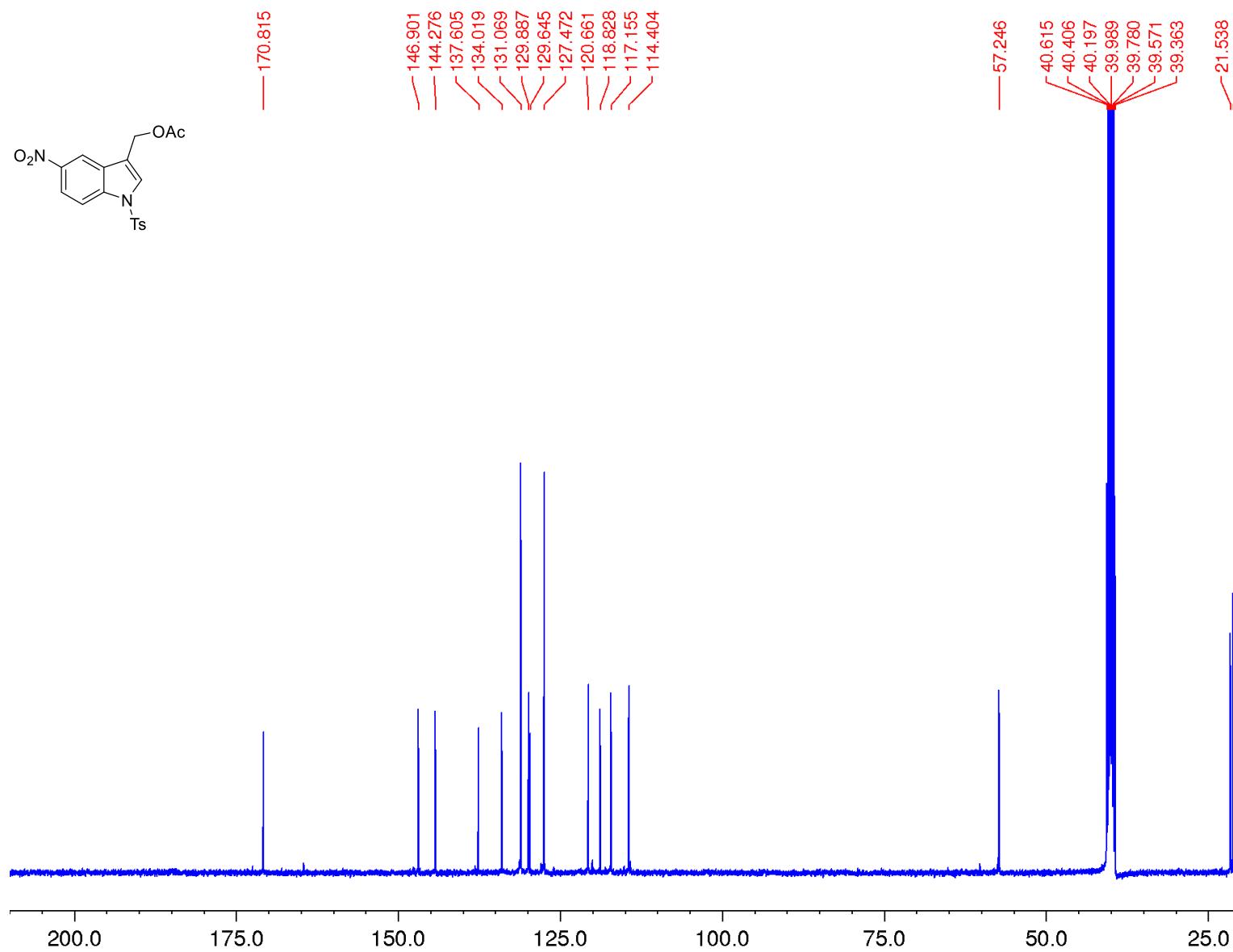
(5-nitro-1-tosyl-1*H*-indol-3-yl)methyl acetate **3g**

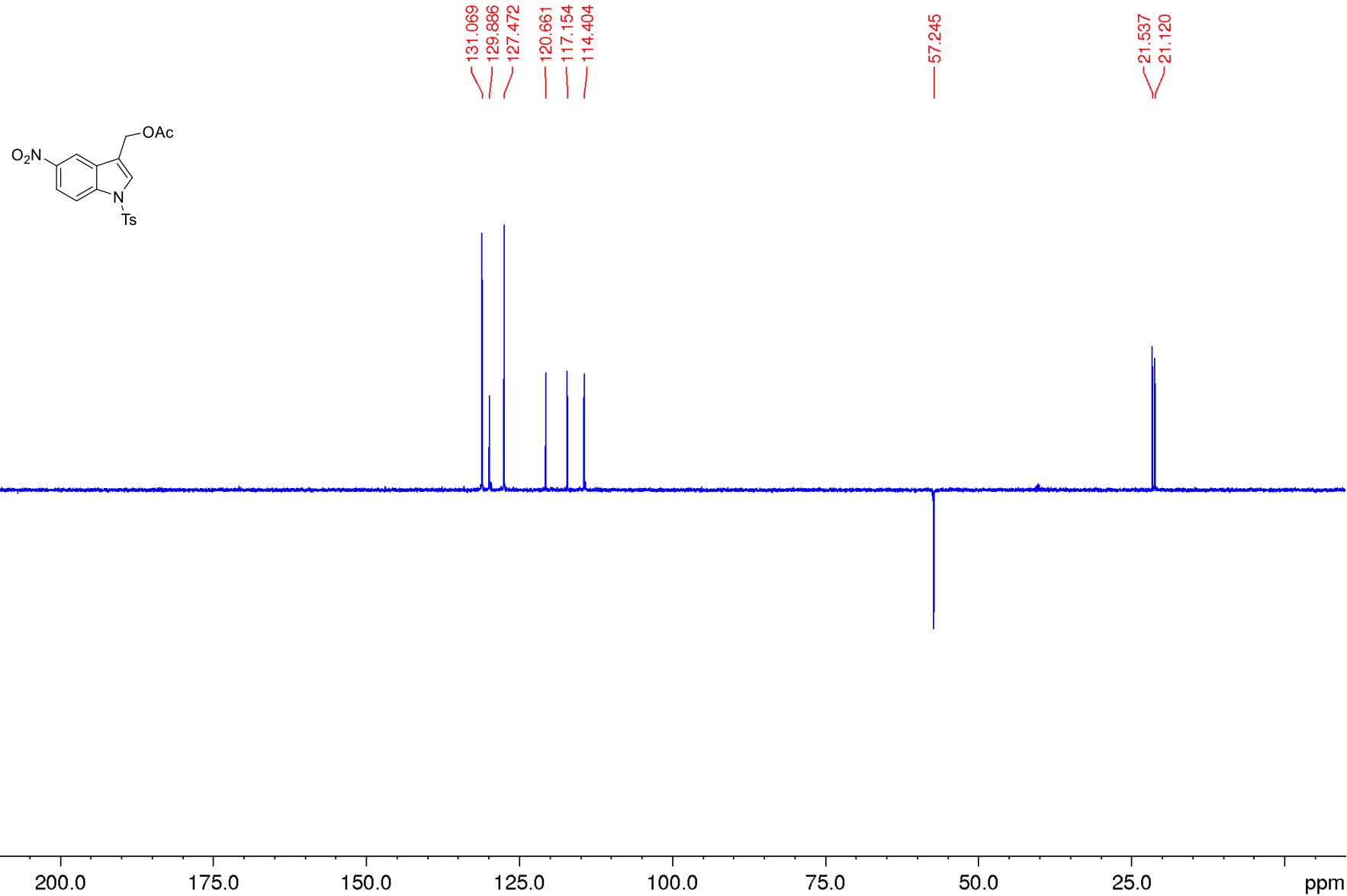
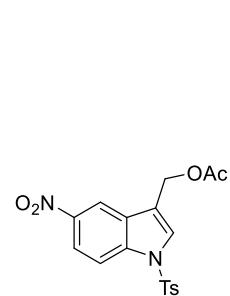
¹H NMR-spectrum (400.13 MHz) (DMSO-*d*₆)



(5-nitro-1-tosyl-1*H*-indol-3-yl)methyl acetate **3g**

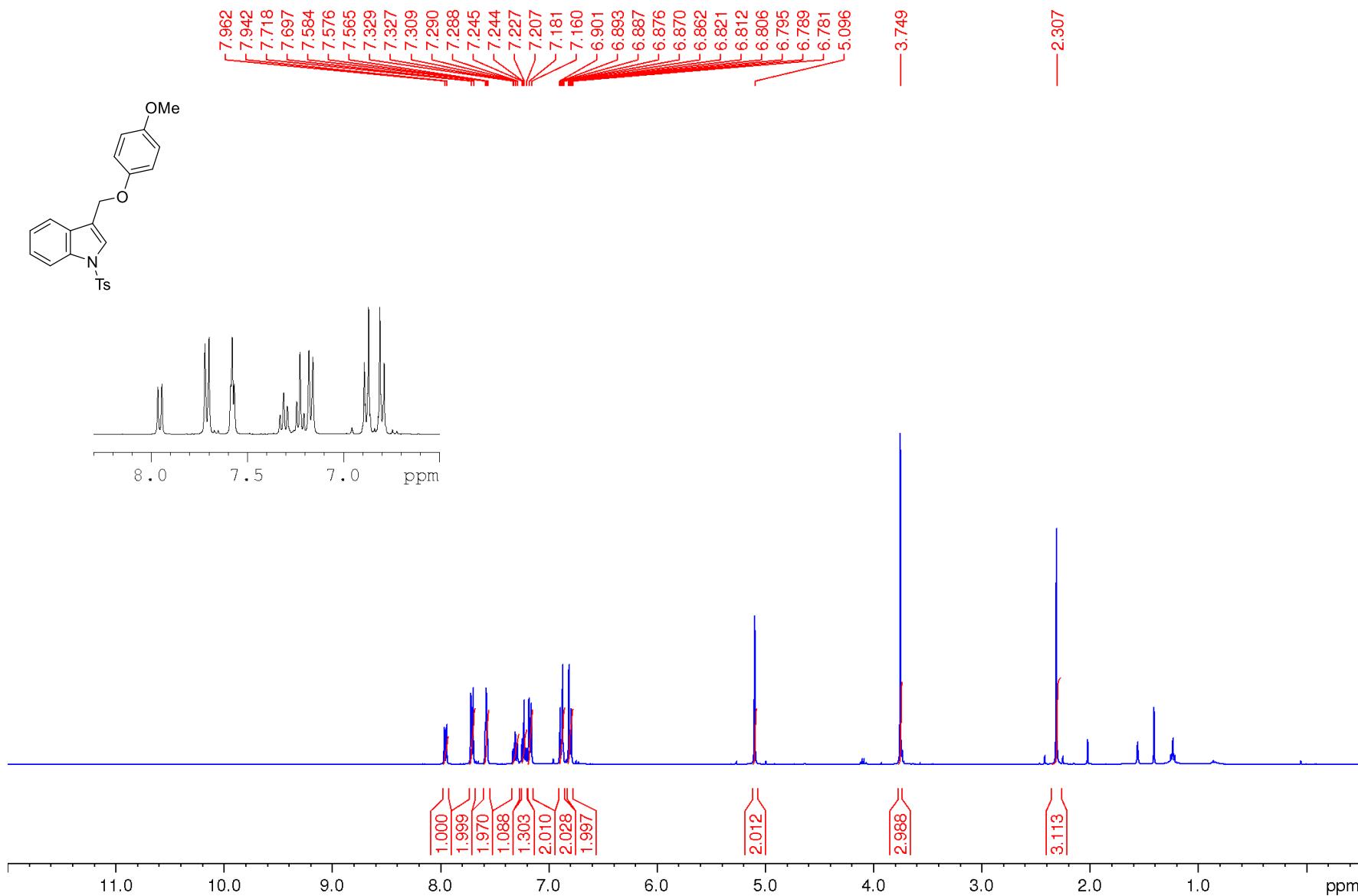
¹³C NMR-spectrum (100.6 MHz) (DMSO-*d*₆)





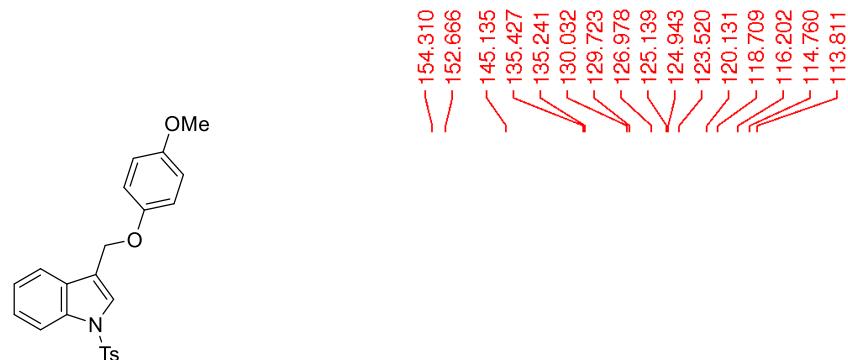
3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4aa

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



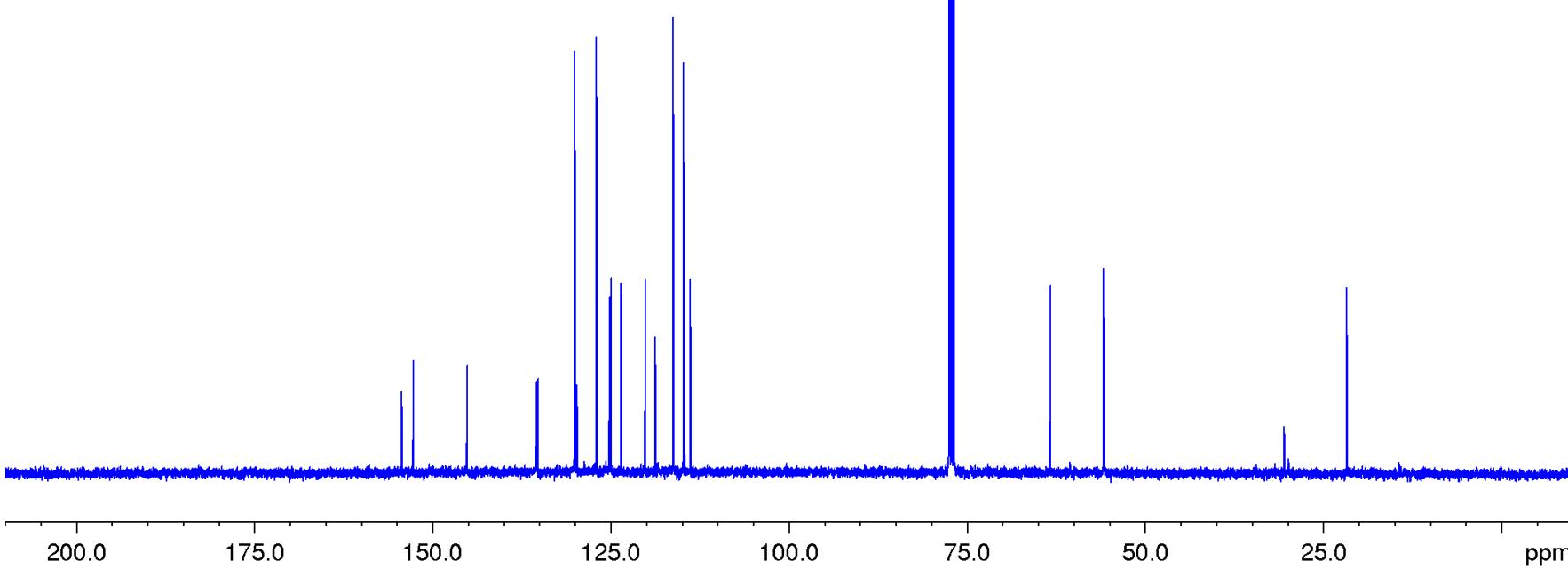
3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4aa

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



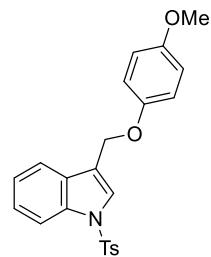
154.310
152.666
145.135
135.427
135.241
130.032
129.723
126.978
125.139
124.943
123.520
120.131
118.709
116.202
114.760
113.811

77.474
77.156
76.839
63.279
55.828
21.698



3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4aa

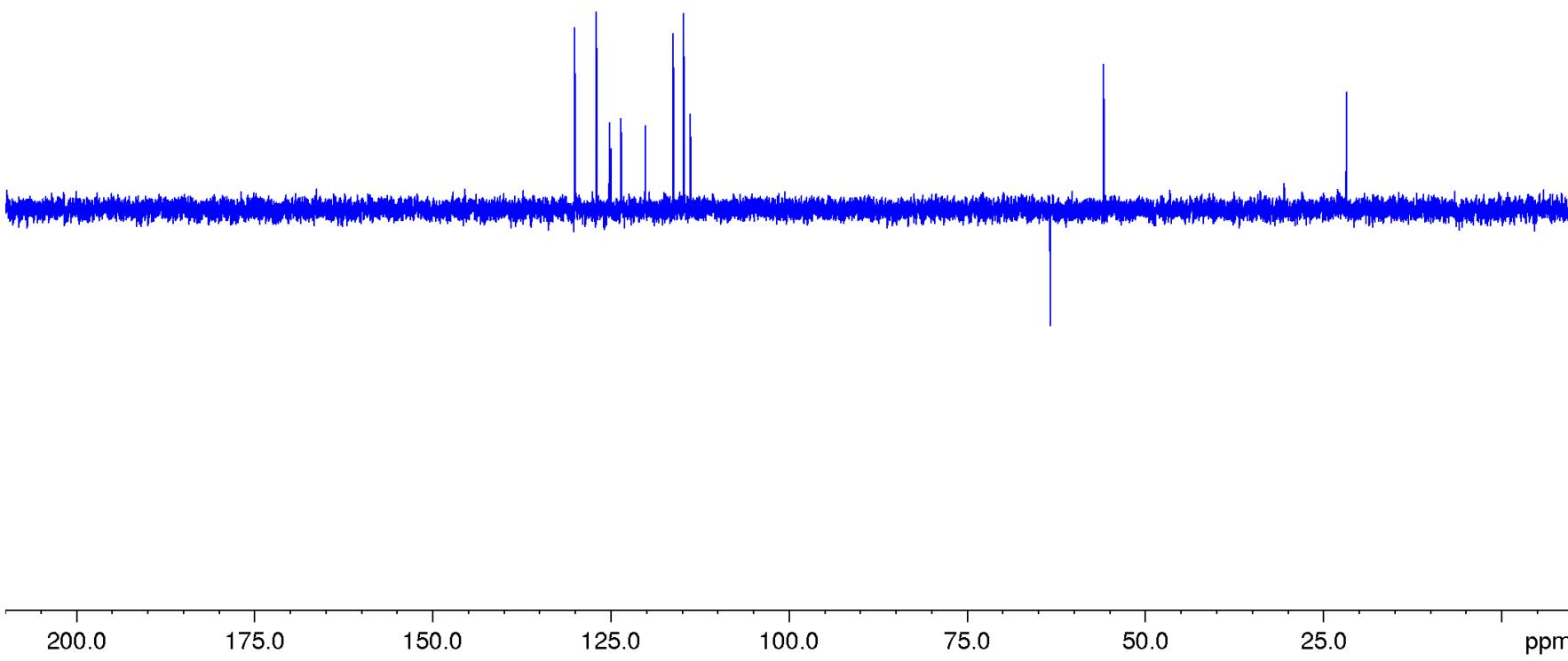
DEPT 135 NMR-spectrum (CDCl_3)



130.035
126.980
125.141
124.944
123.523
120.133
116.202
114.760
113.813

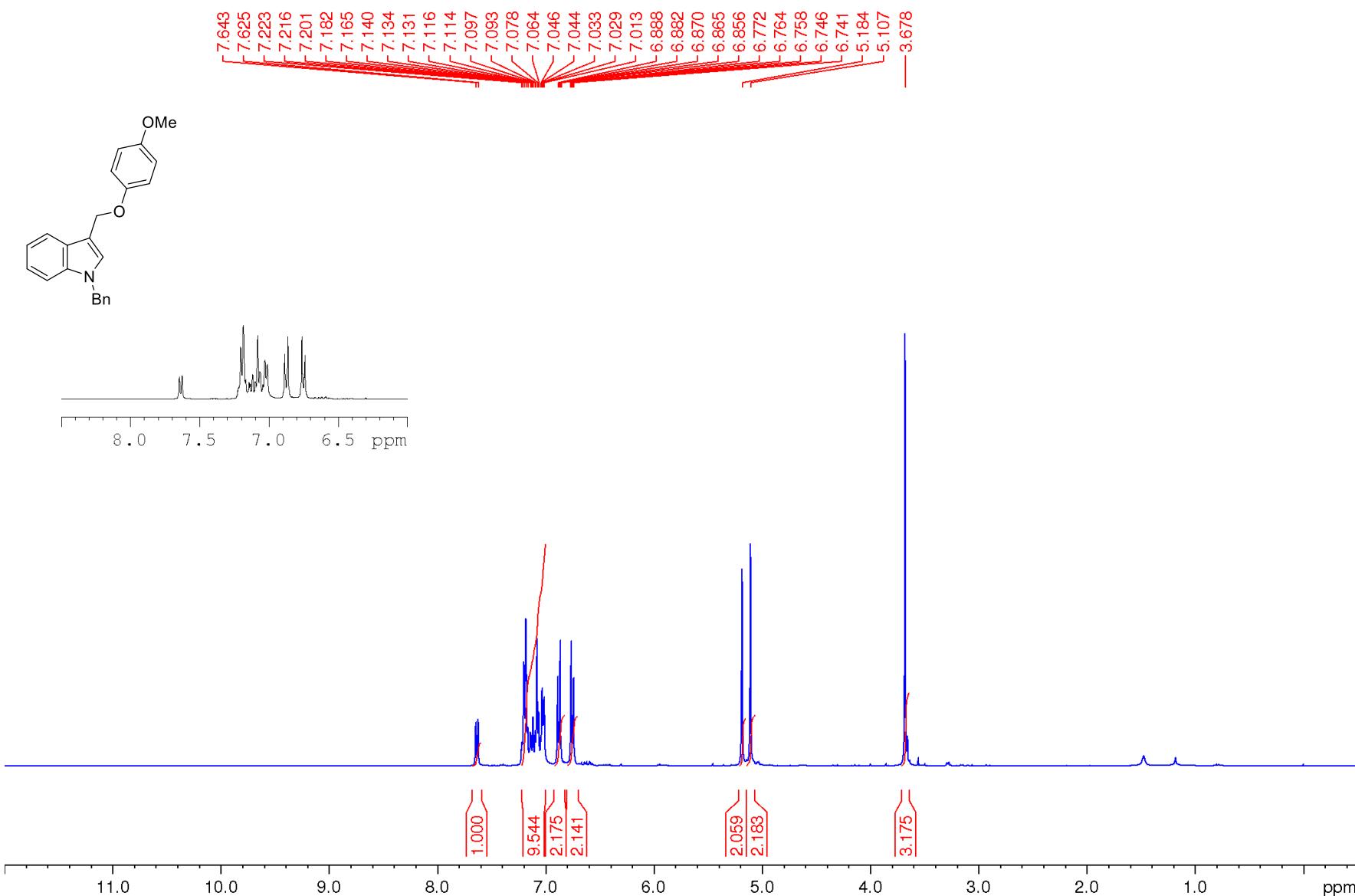
— 63.278
— 55.830

— 21.701



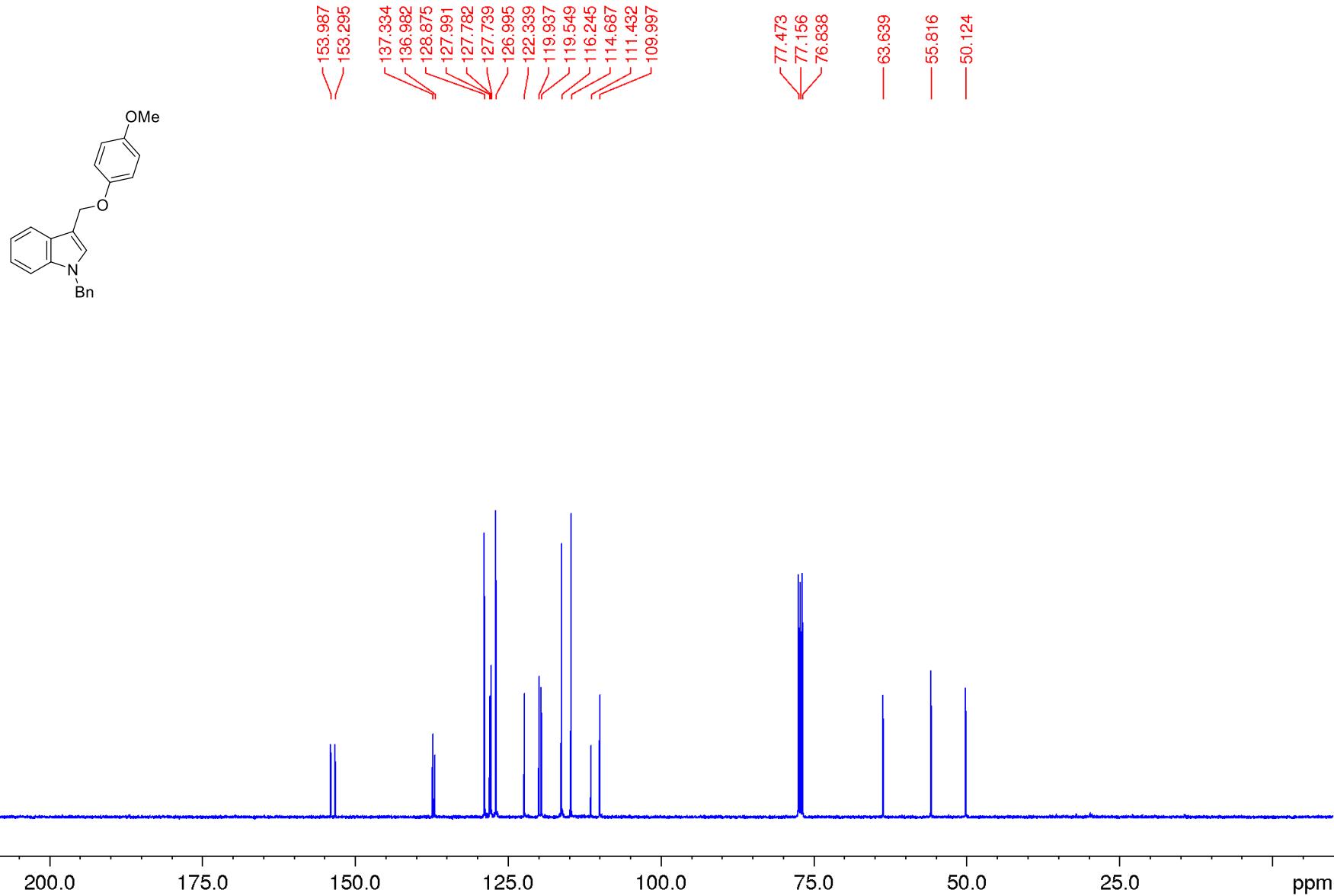
1-benzyl-3-((4-methoxyphenoxy)methyl)-1H-indole 4ba

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



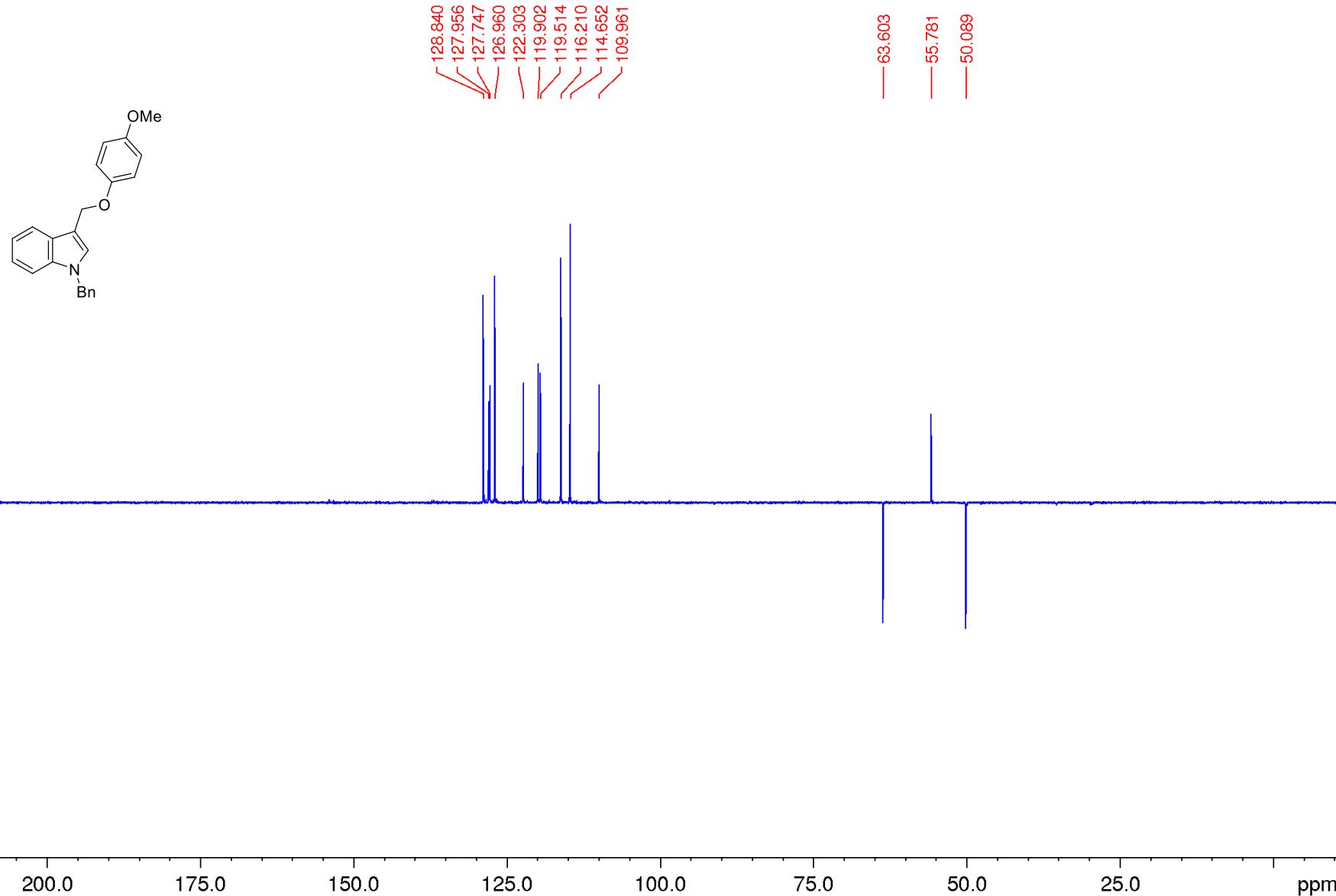
1-benzyl-3-((4-methoxyphenoxy)methyl)-1H-indole 4ba

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



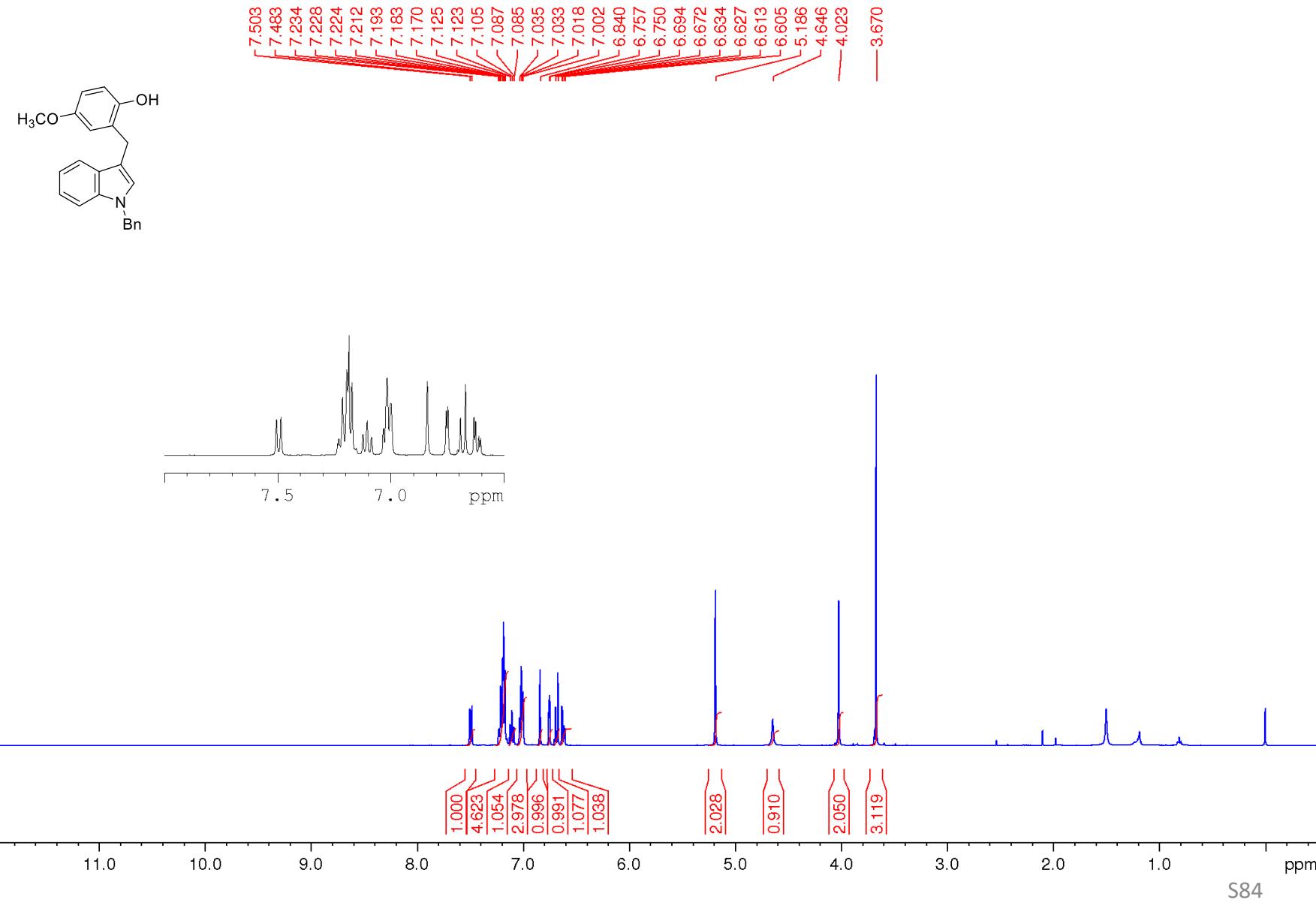


DEPT 135 NMR-spectrum (CDCl_3)



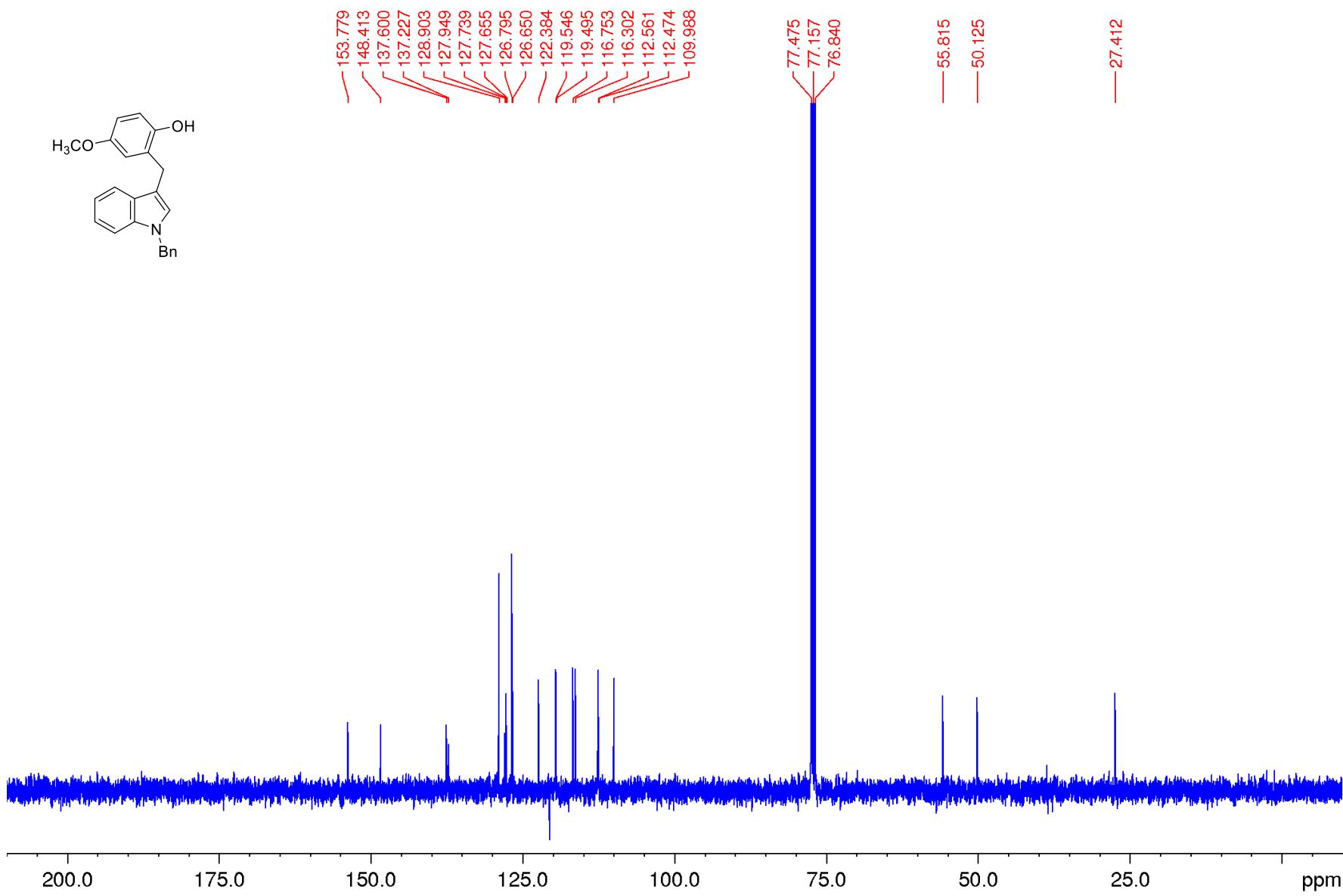
*2-((1-benzyl-1*H*-indol-3-yl)methyl)-4-methoxyphenol 7ba*

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



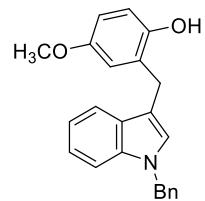
*2-((1-benzyl-1*H*-indol-3-yl)methyl)-4-methoxyphenol 7ba*

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



*2-((1-benzyl-1*H*-indol-3-yl)methyl)-4-methoxyphenol 7ba*

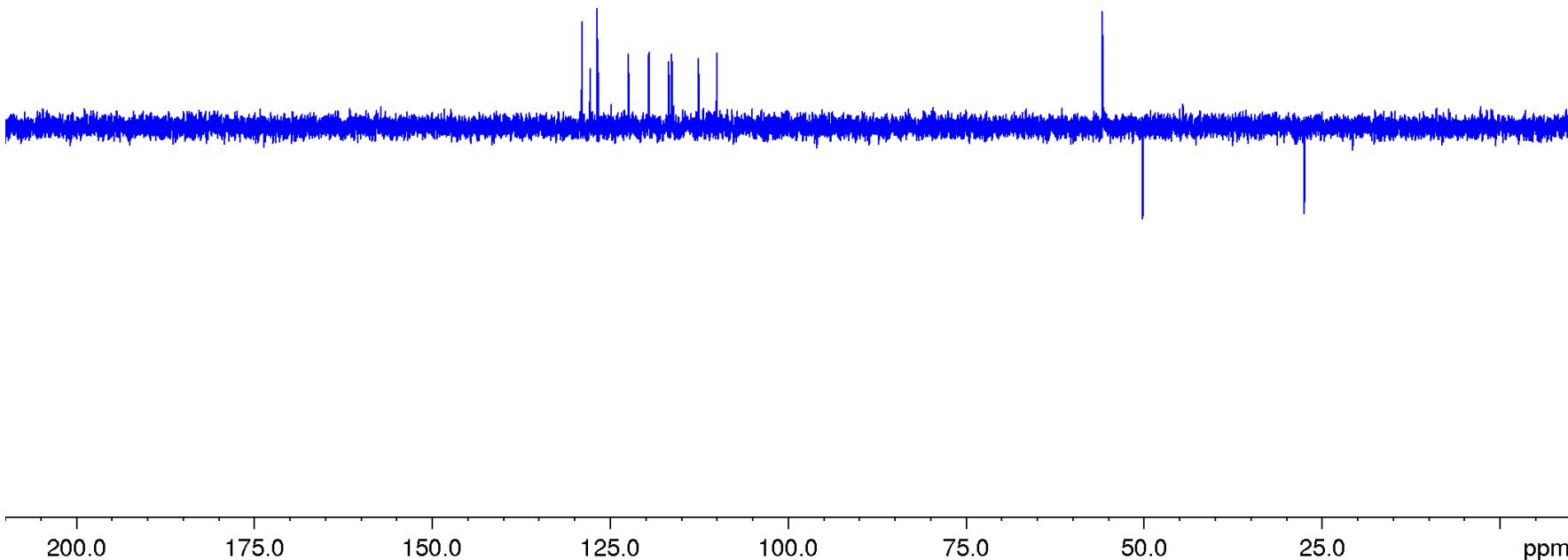
DEPT 135 NMR-spectrum (CDCl_3)



128.894
127.728
126.787
126.642
122.376
119.537
119.488
116.744
116.294
112.553
109.980

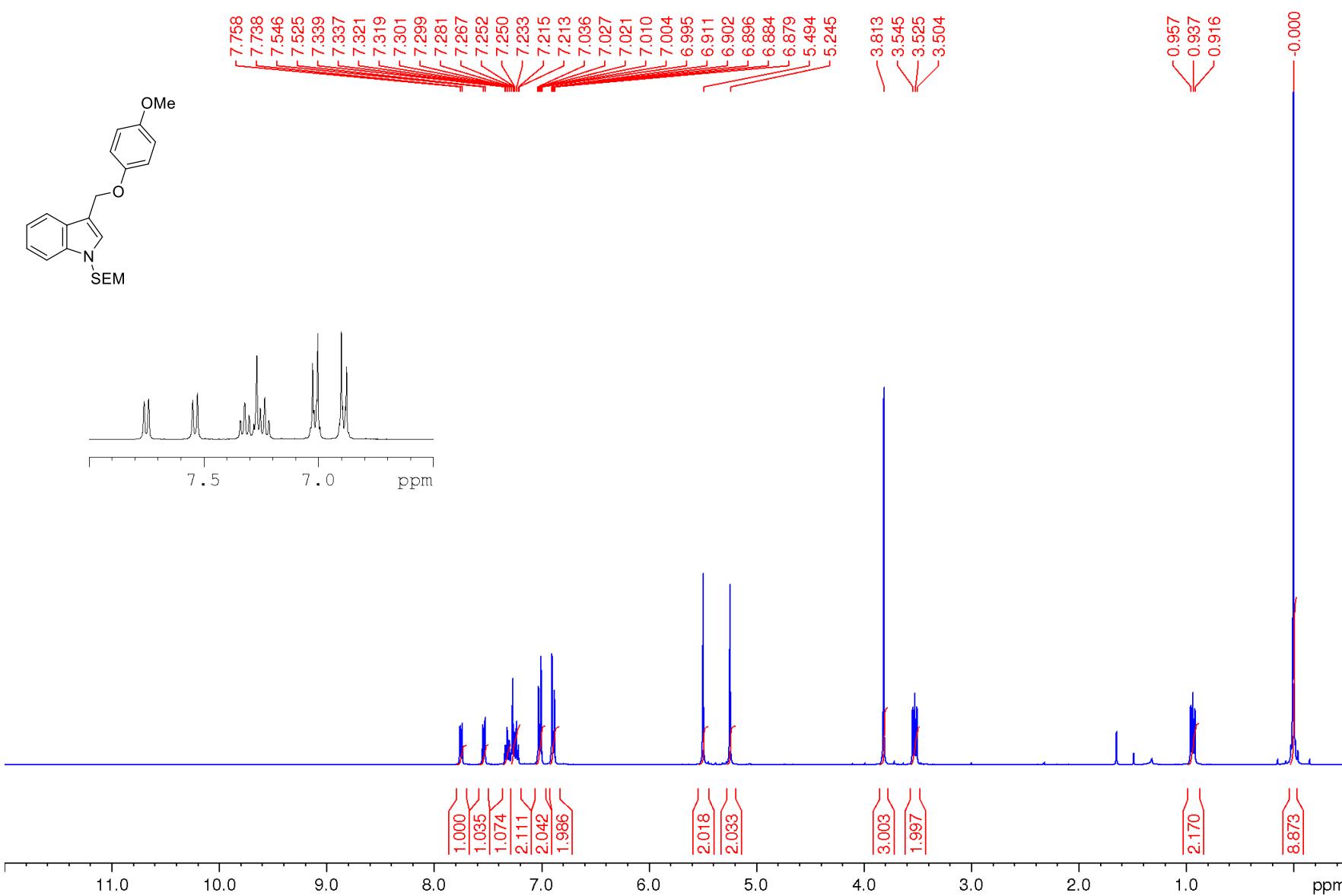
55.807
50.116

-27.403

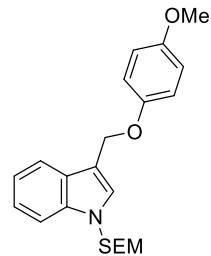


3-((4-methoxyphenoxy)methyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indole **4ca**

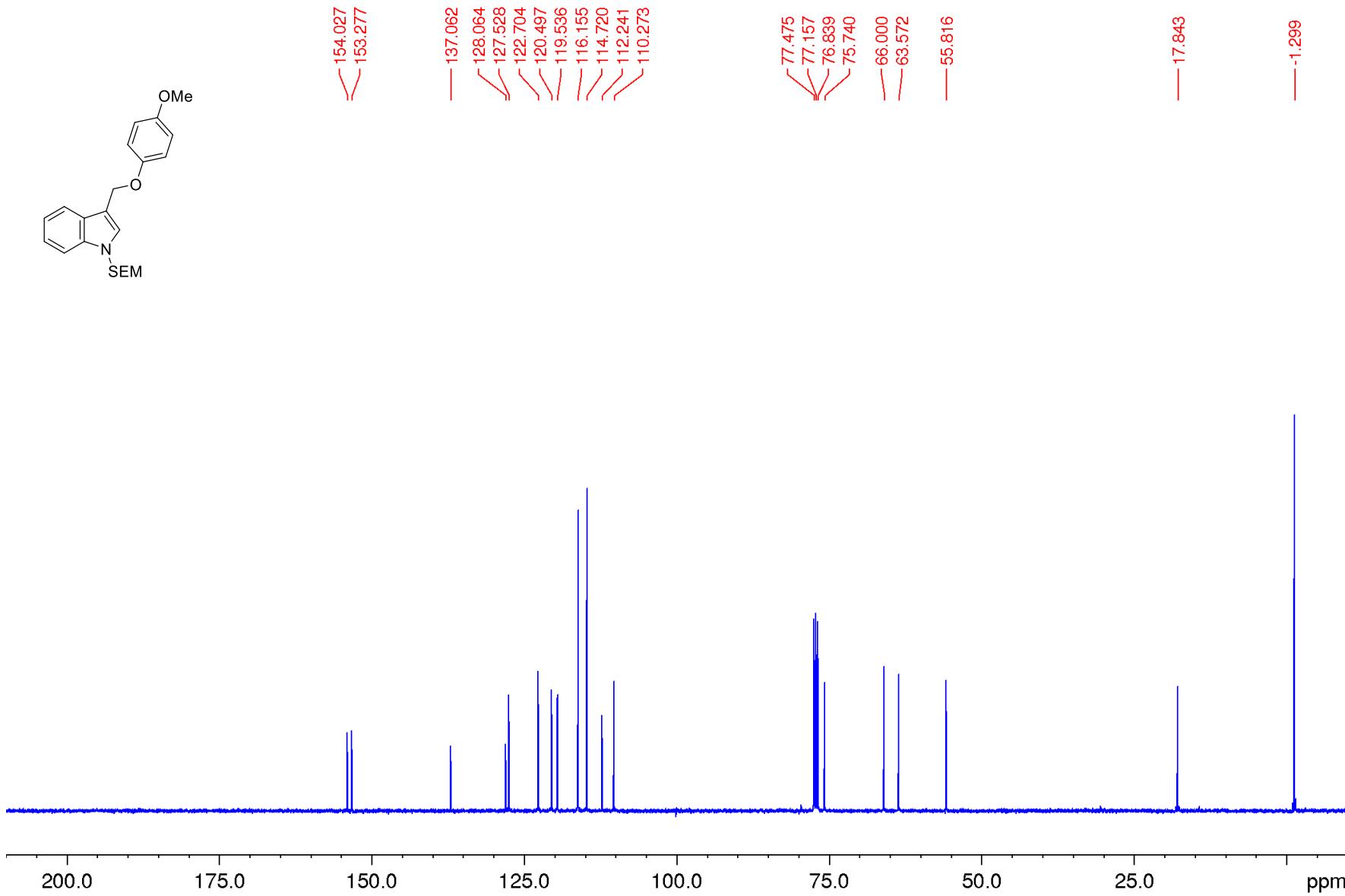
¹H NMR-spectrum (400.13 MHz) (CDCl_3)



3-((4-methoxyphenoxy)methyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indole 4ca

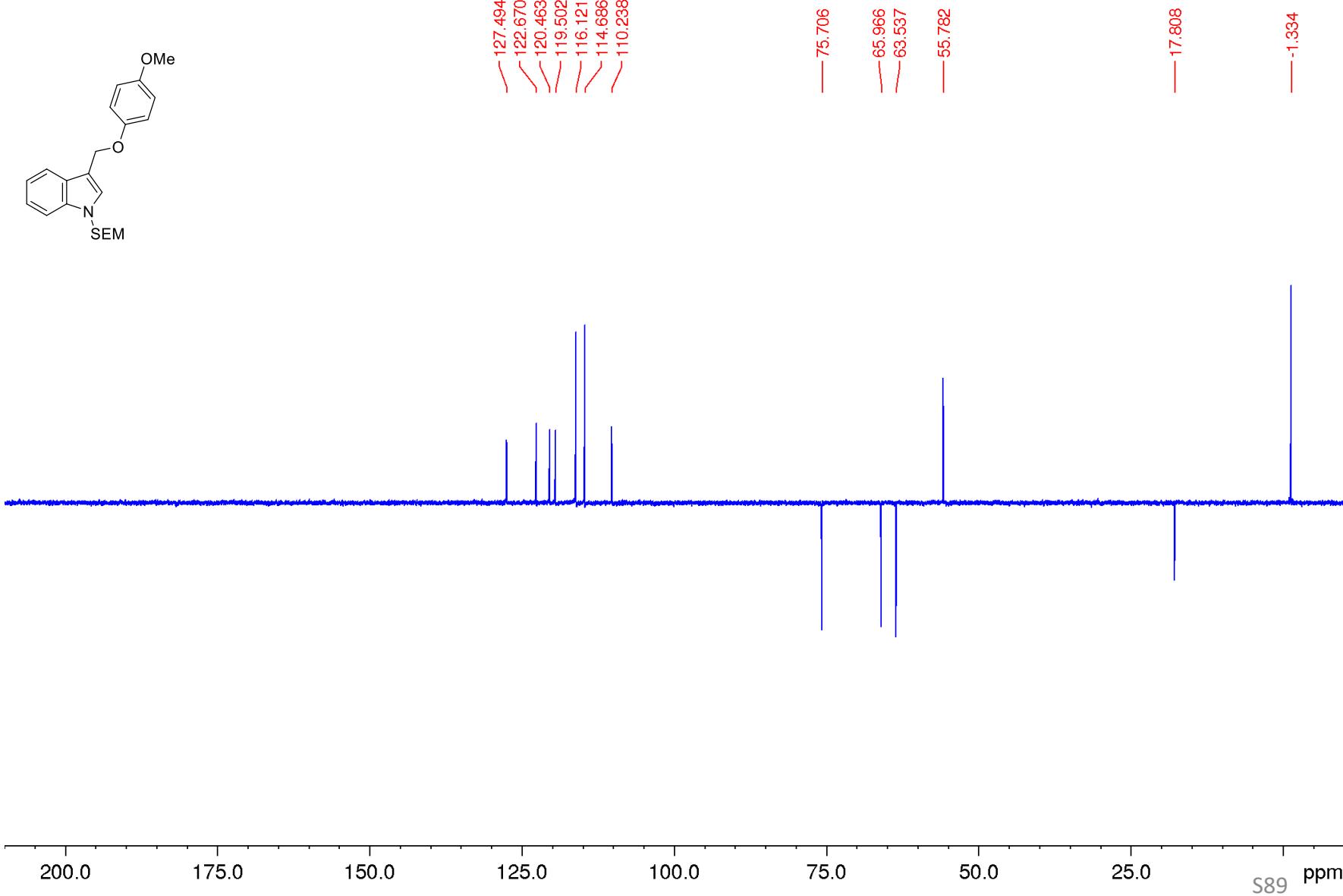
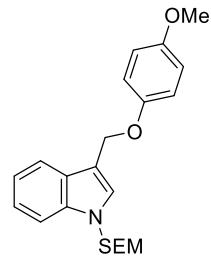


^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



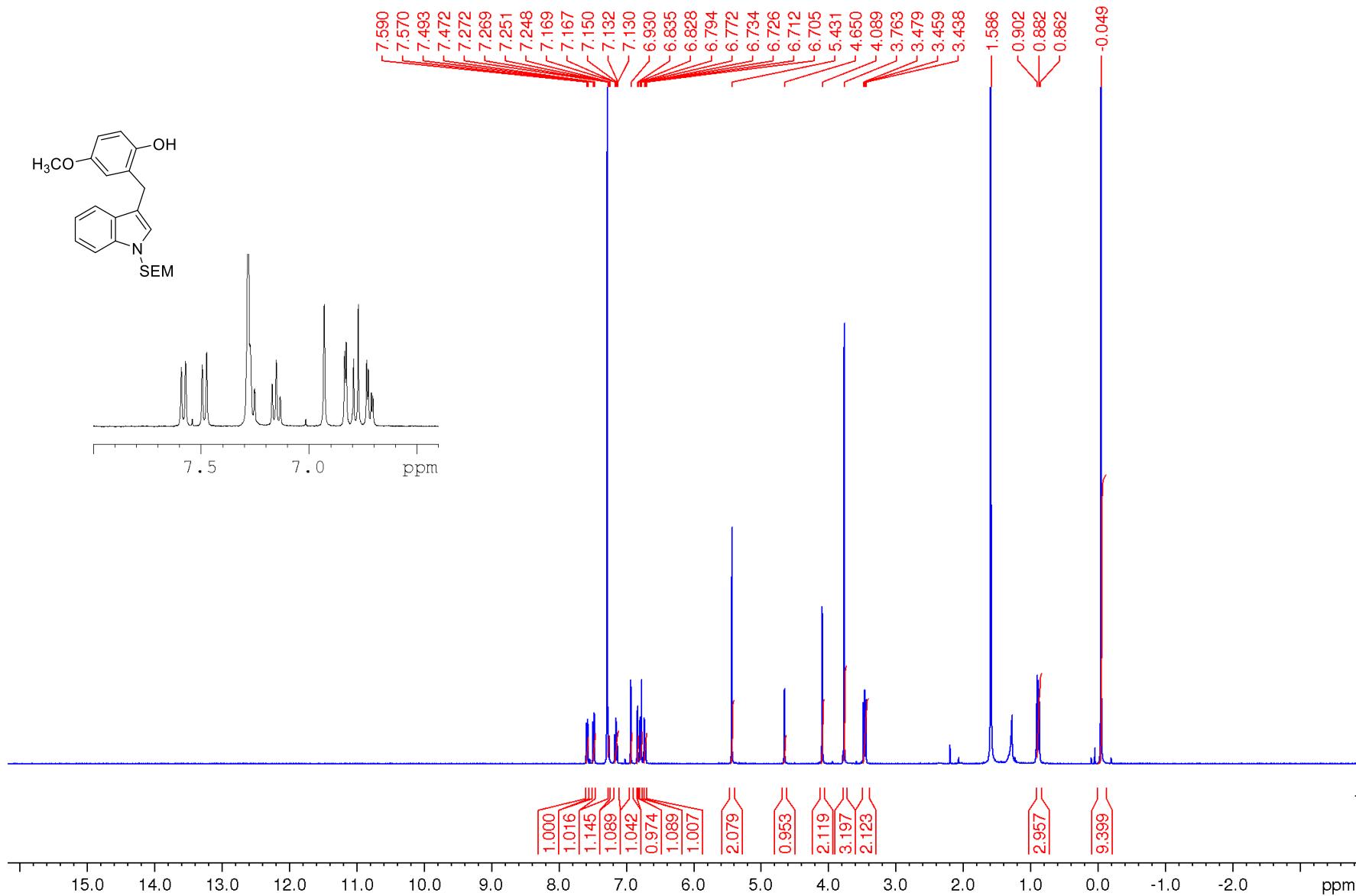
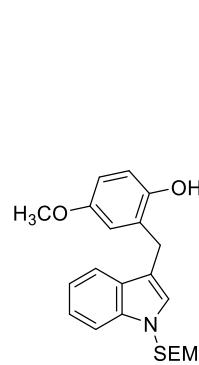
3-((4-methoxyphenoxy)methyl)-1-((2-(trimethylsilyl)ethoxy)methyl)-1H-indole **4ca**

DEPT 135 NMR-spectrum (CDCl_3)

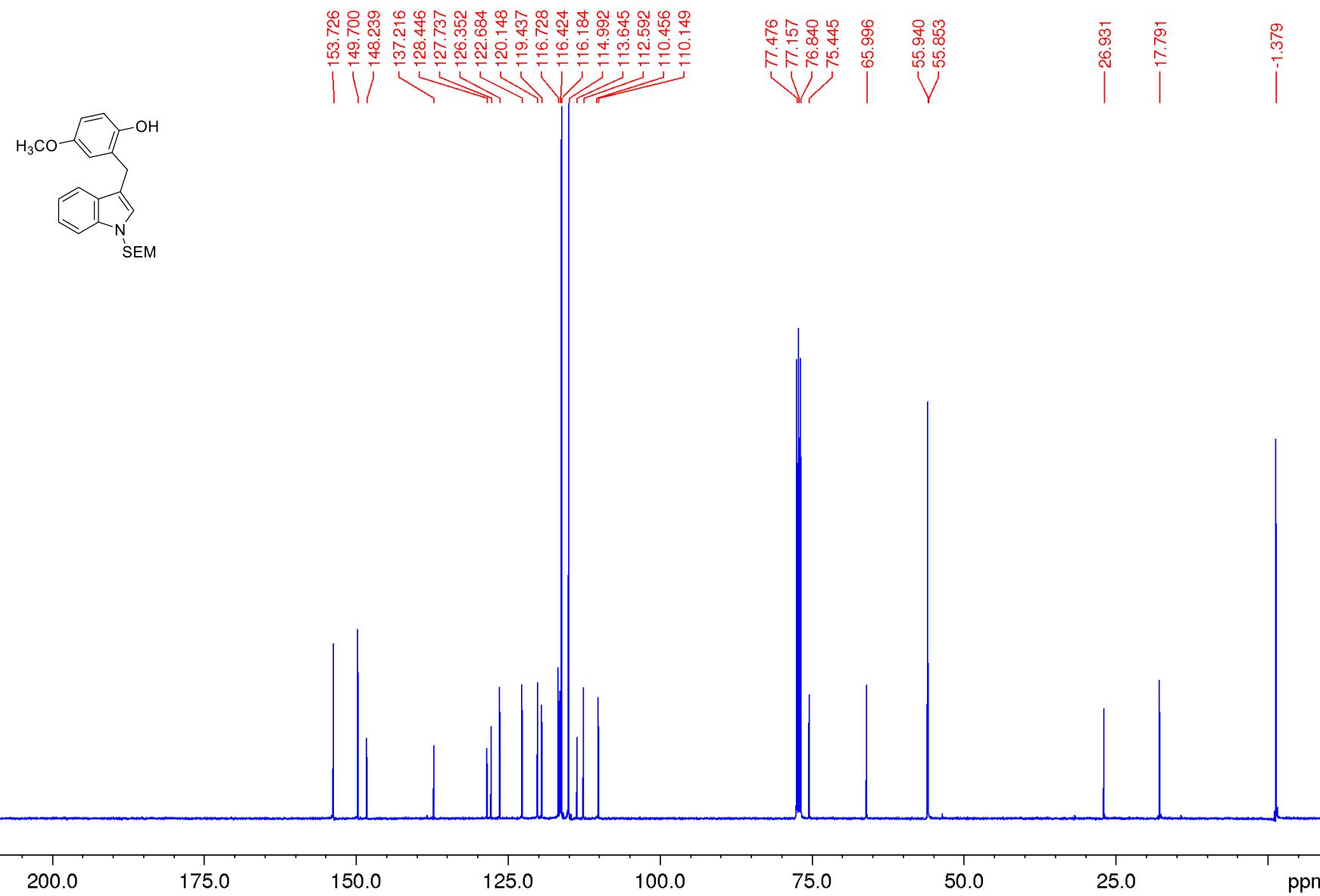


*4-methoxy-2-((1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl)phenol 7ca*

¹H NMR-spectrum (400.13 MHz) (CDCl₃)

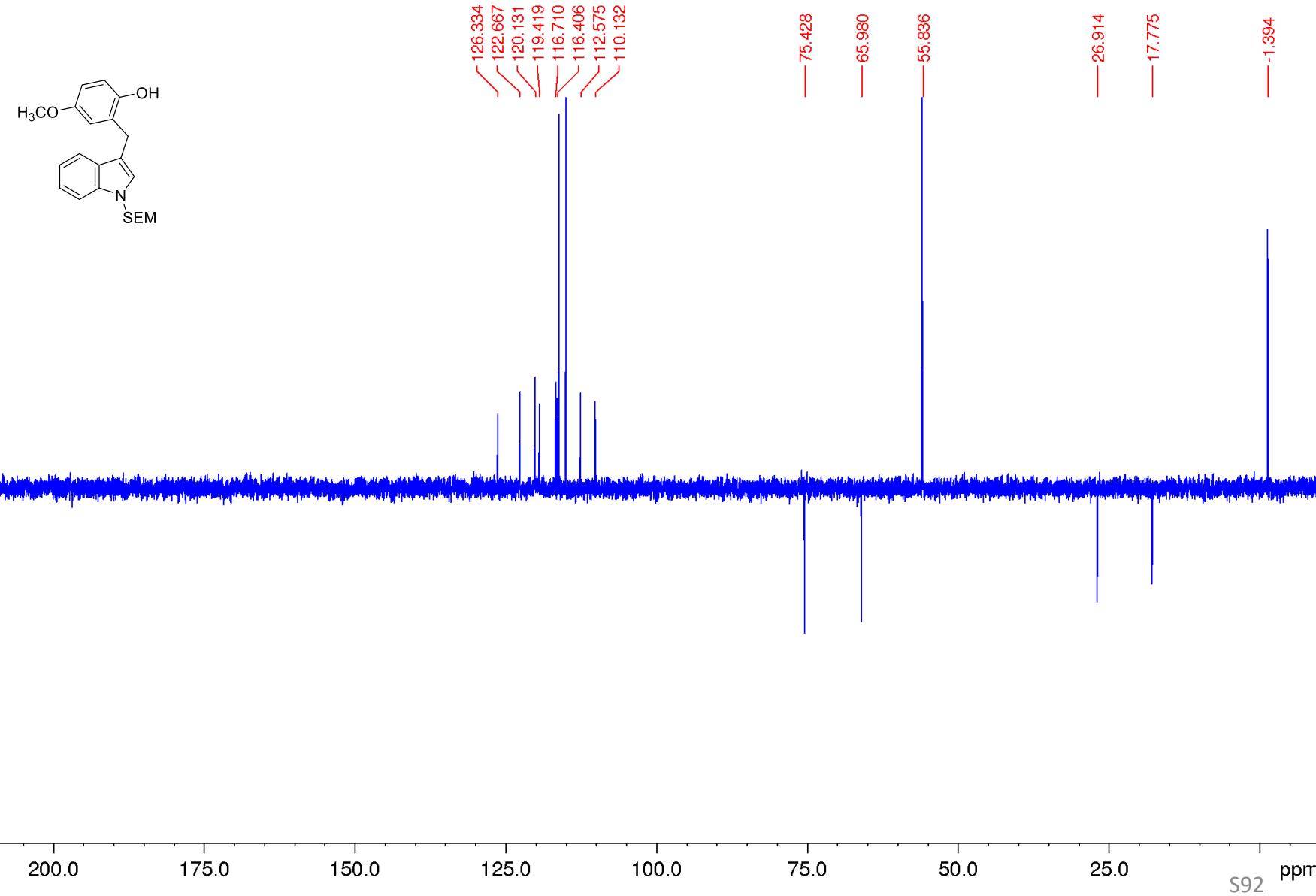


*4-methoxy-2-((1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-*y*l)methyl)phenol 7ca*



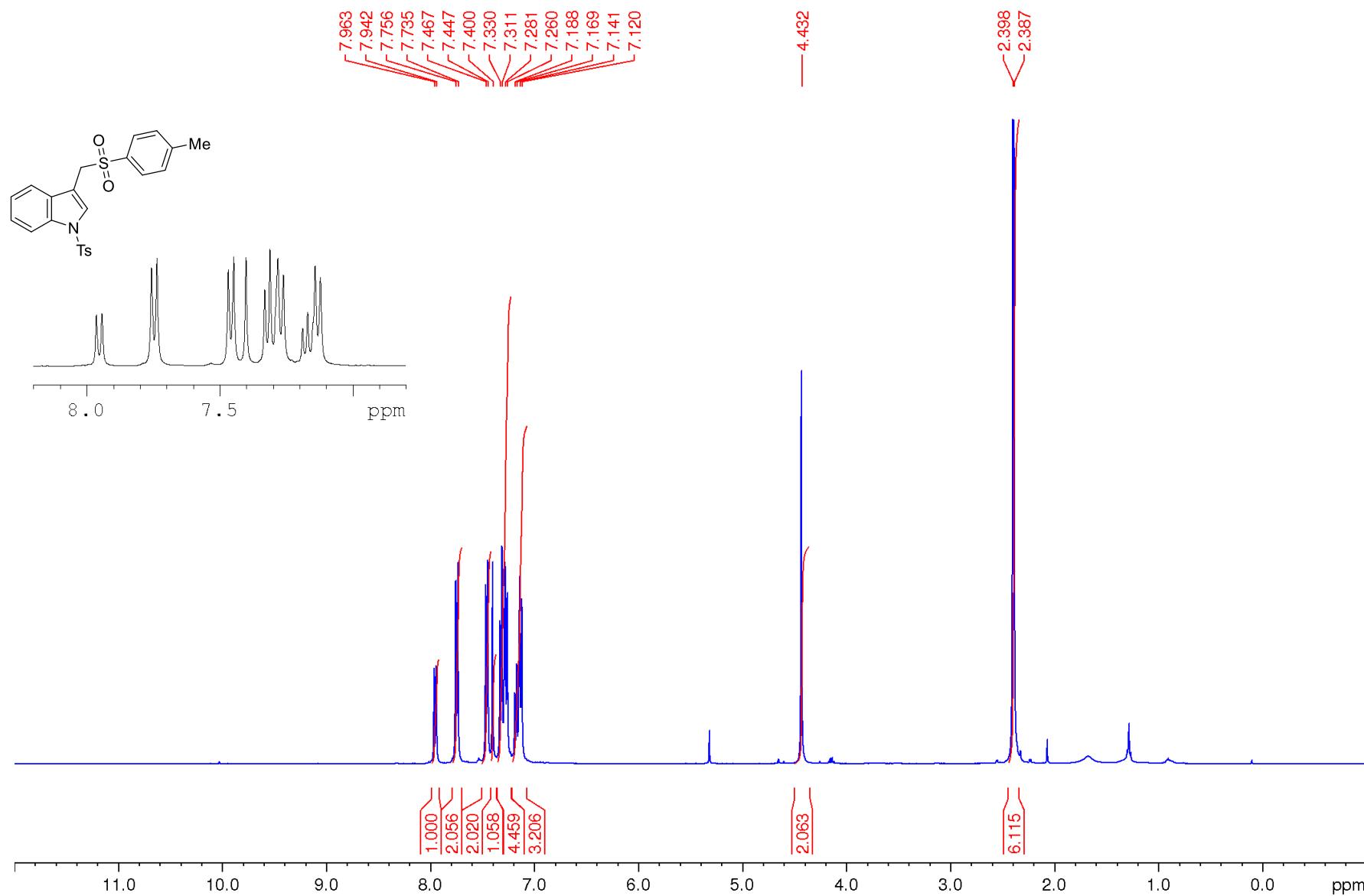
*4-methoxy-2-((1-((2-(trimethylsilyl)ethoxy)methyl)-1*H*-indol-3-yl)methyl)phenol 7ca*

DEPT 135 NMR-spectrum (CDCl_3)



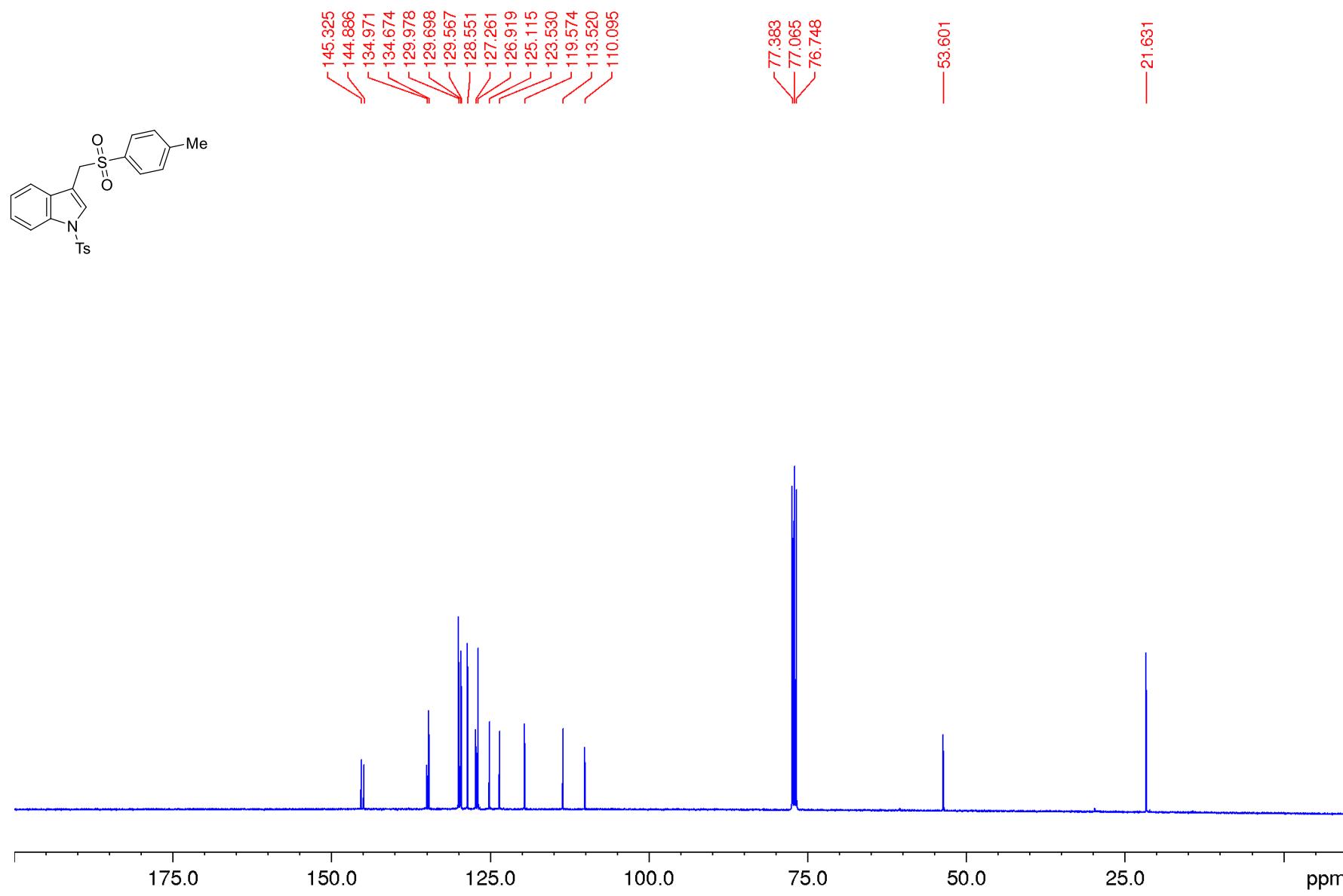
1-tosyl-3-(tosylmethyl)-1*H*-indole **9aa**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



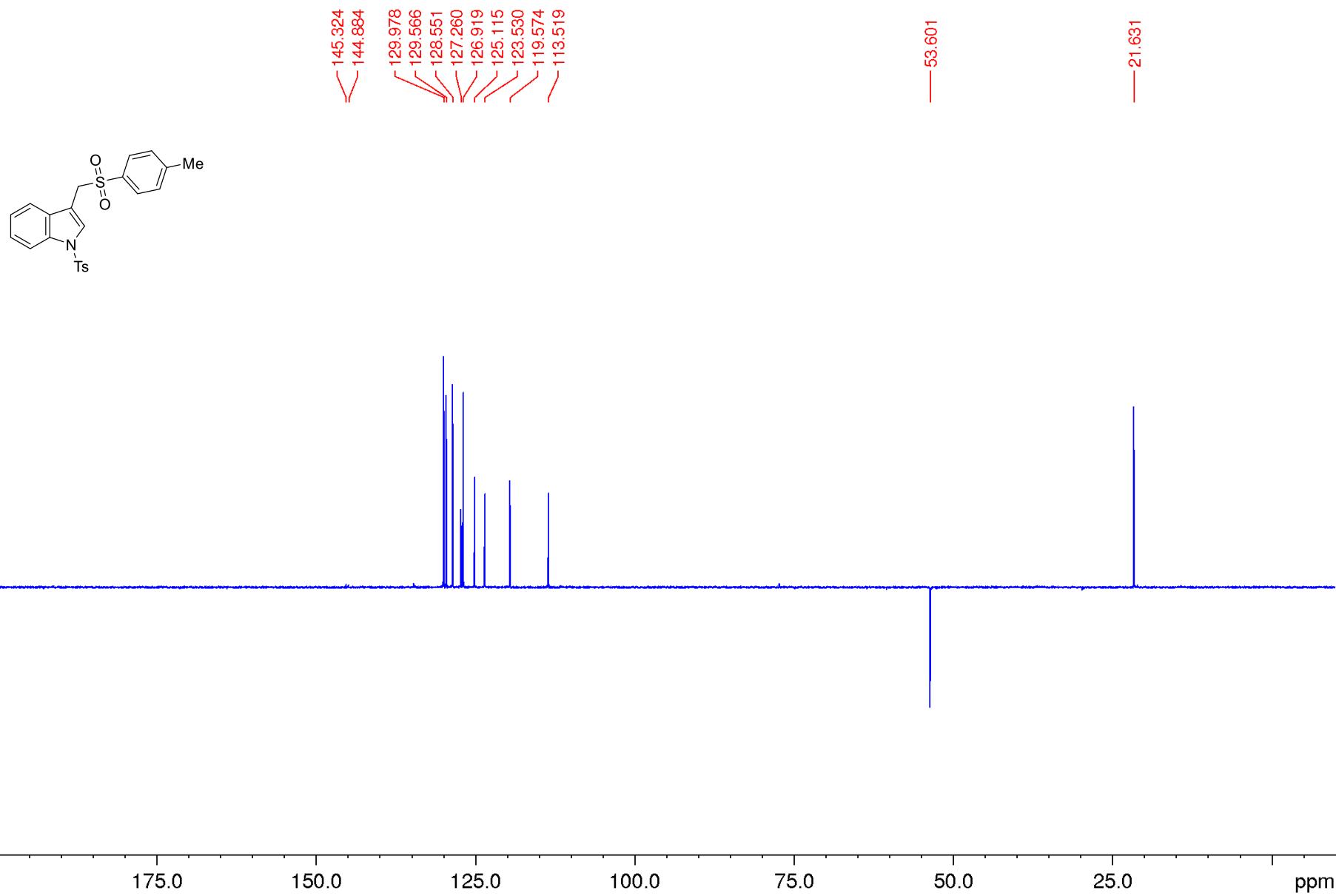
1-tosyl-3-(tosylmethyl)-1*H*-indole **9aa**

¹³C NMR-spectrum (100.6 MHz) (CDCl_3)



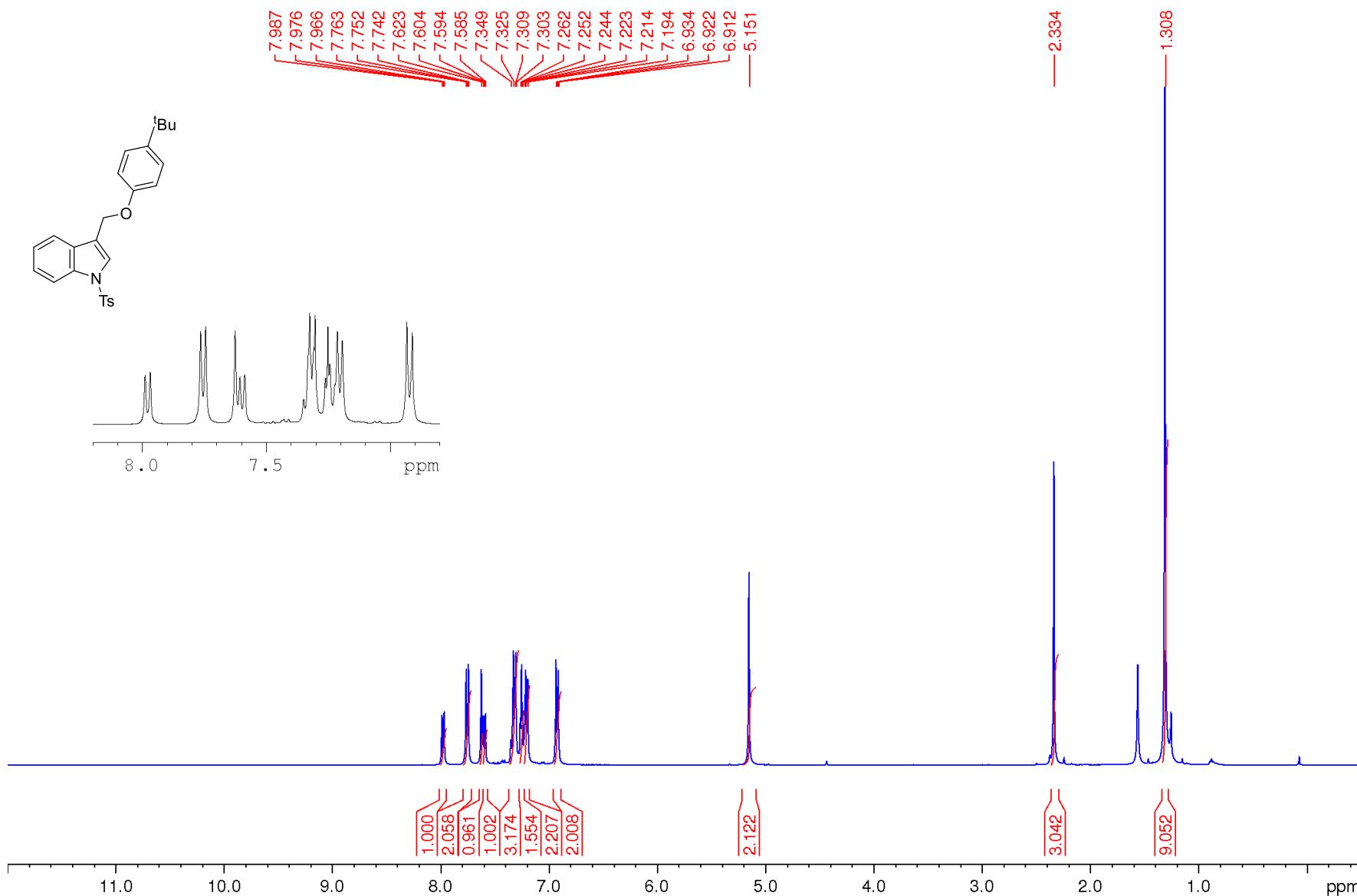
1-tosyl-3-(tosylmethyl)-1*H*-indole **9aa**

DEPT 135 NMR-spectrum (CDCl_3)



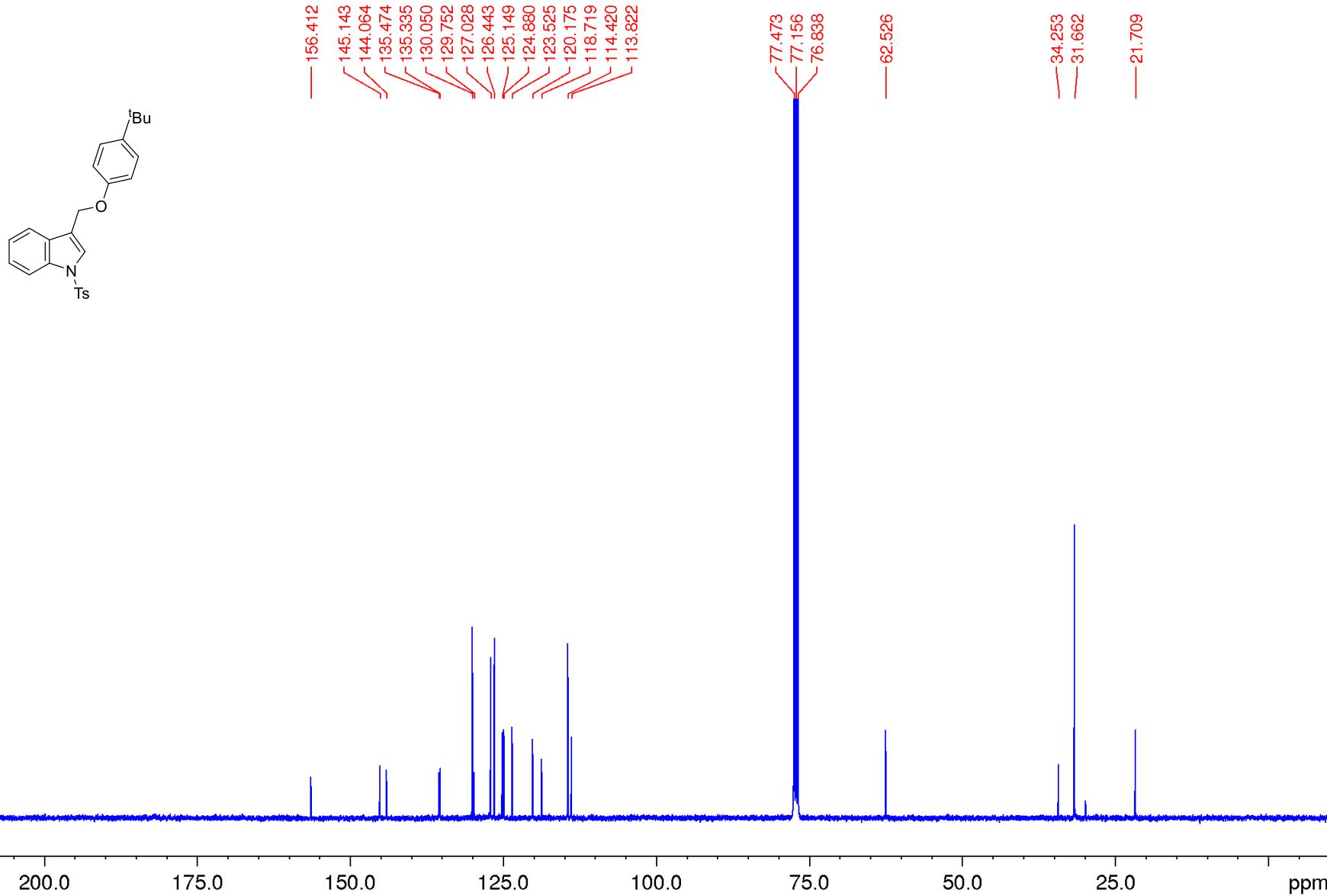
3-((4-(tert-butyl)phenoxy)methyl)-1-tosyl-1H-indole 4ab

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



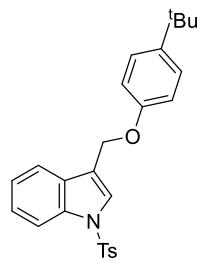
3-((4-(tert-butyl)phenoxy)methyl)-1-tosyl-1H-indole 4ab

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



3-((4-(tert-butyl)phenoxy)methyl)-1-tosyl-1H-indole 4ab

DEPT 135 NMR-spectrum (CDCl_3)

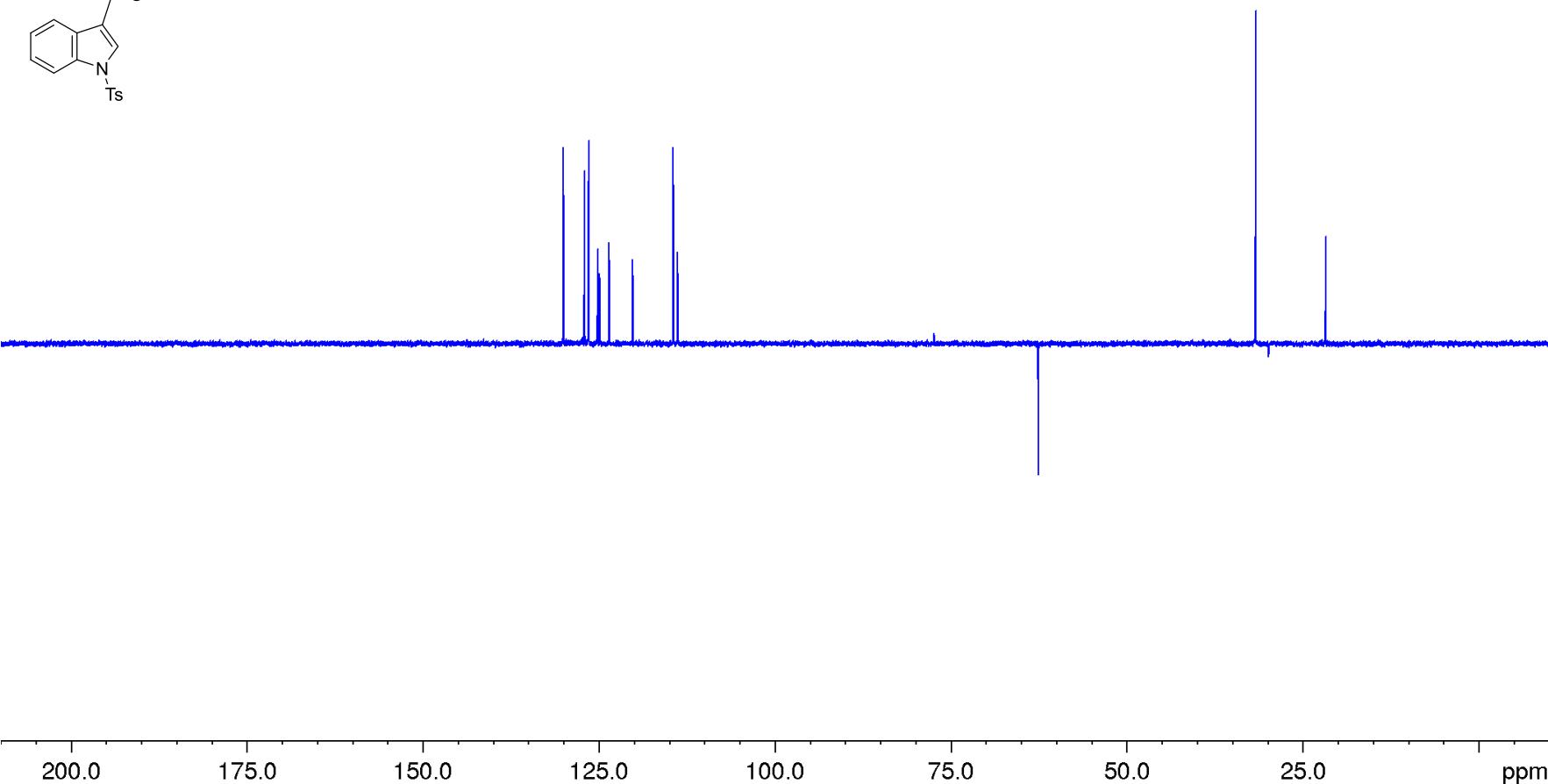


130.048
127.025
126.440
125.147
124.877
123.522
120.173
114.417
113.819

62.524

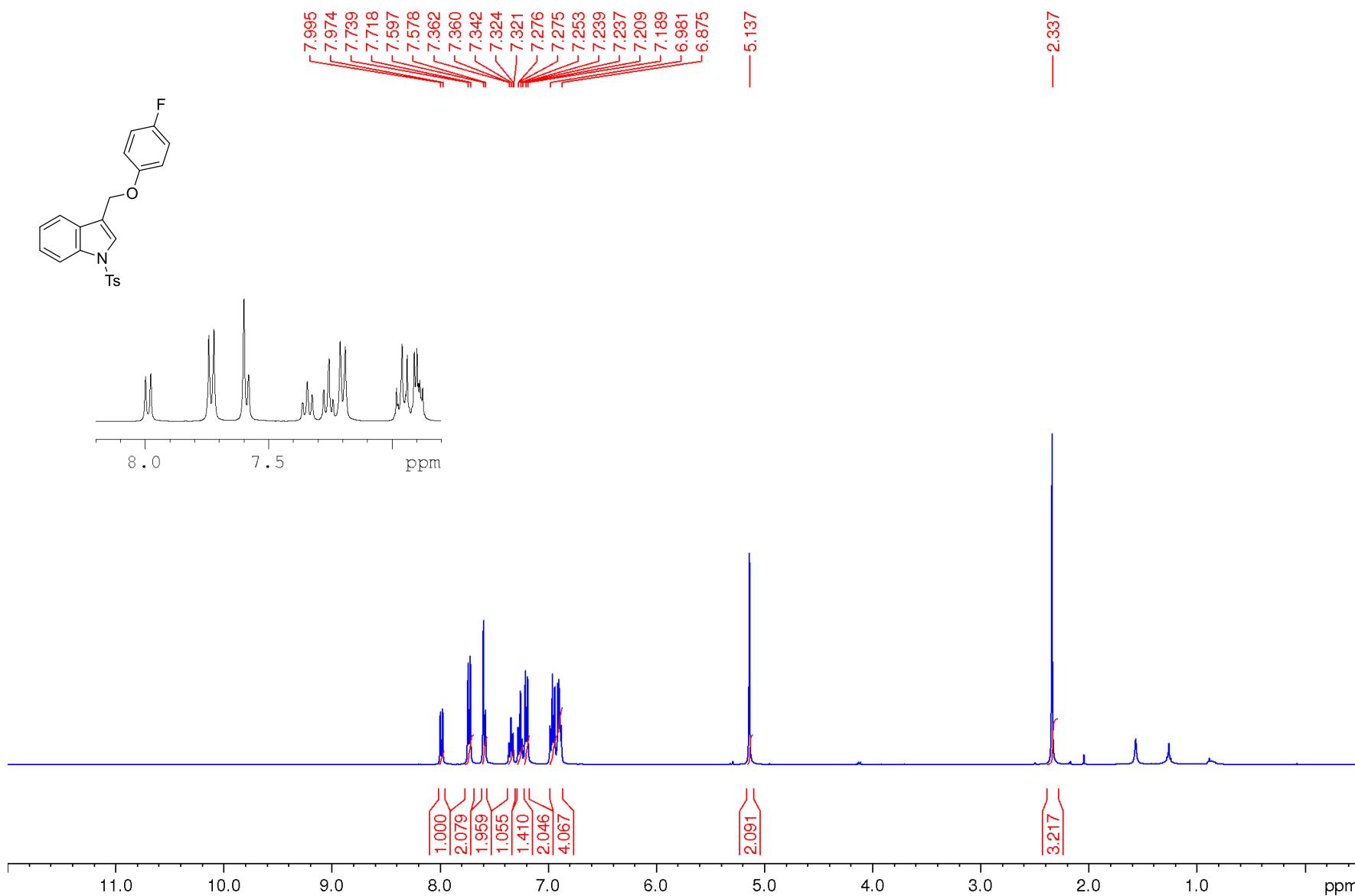
31.660

21.707

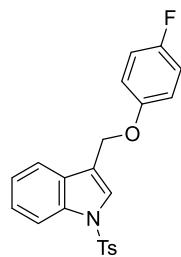


3-((4-fluorophenoxy)methyl)-1-tosyl-1H-indole 4ac

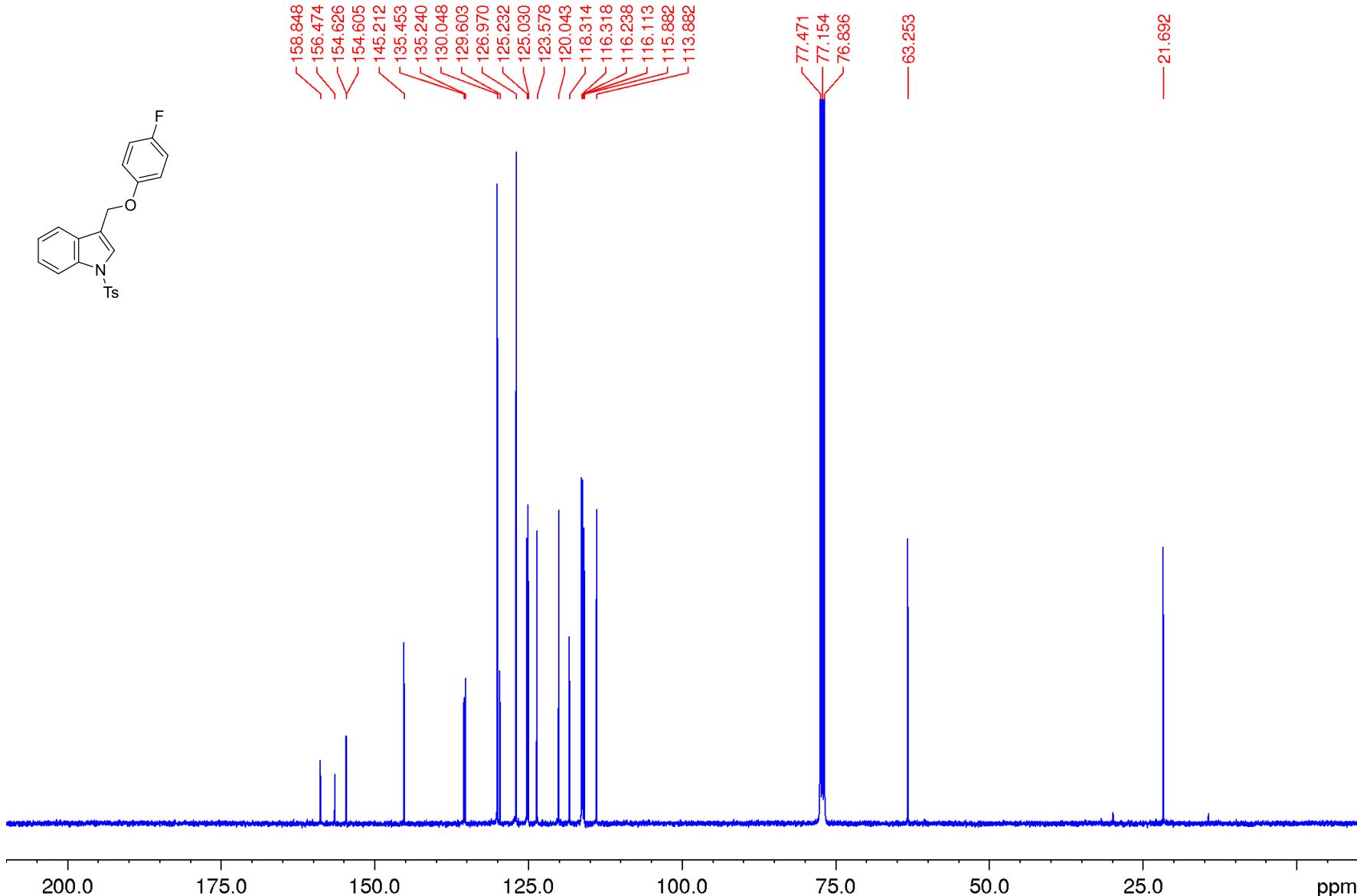
^1H NMR-spectrum (400.13 MHz) (CDCl_3)



3-((4-fluorophenoxy)methyl)-1-tosyl-1H-indole 4ac

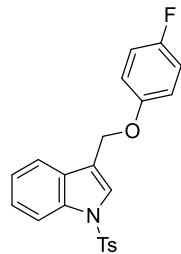


^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



3-((4-fluorophenoxy)methyl)-1-tosyl-1H-indole 4ac

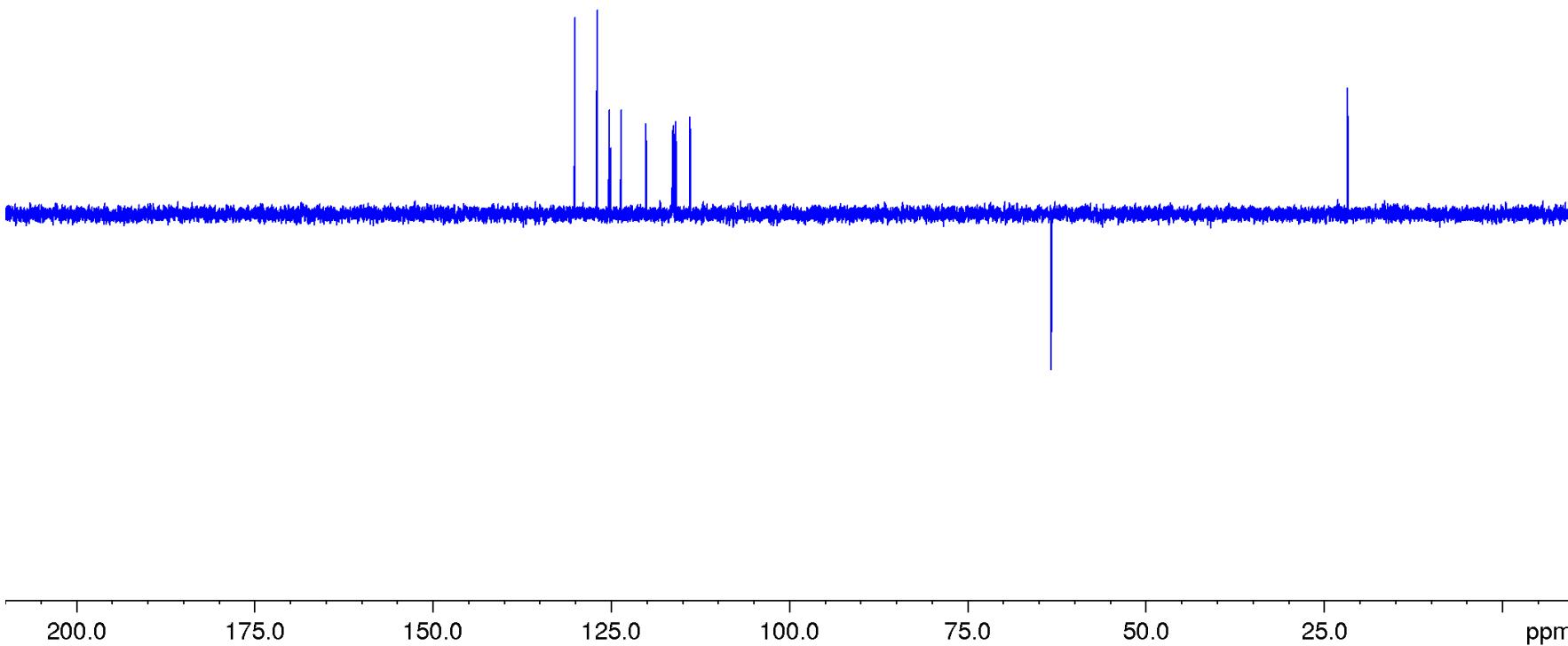
DEPT 135 NMR-spectrum (CDCl_3)



130.050
126.964
125.237
125.042
123.589
120.065
116.330
116.252
116.110
115.881
113.884

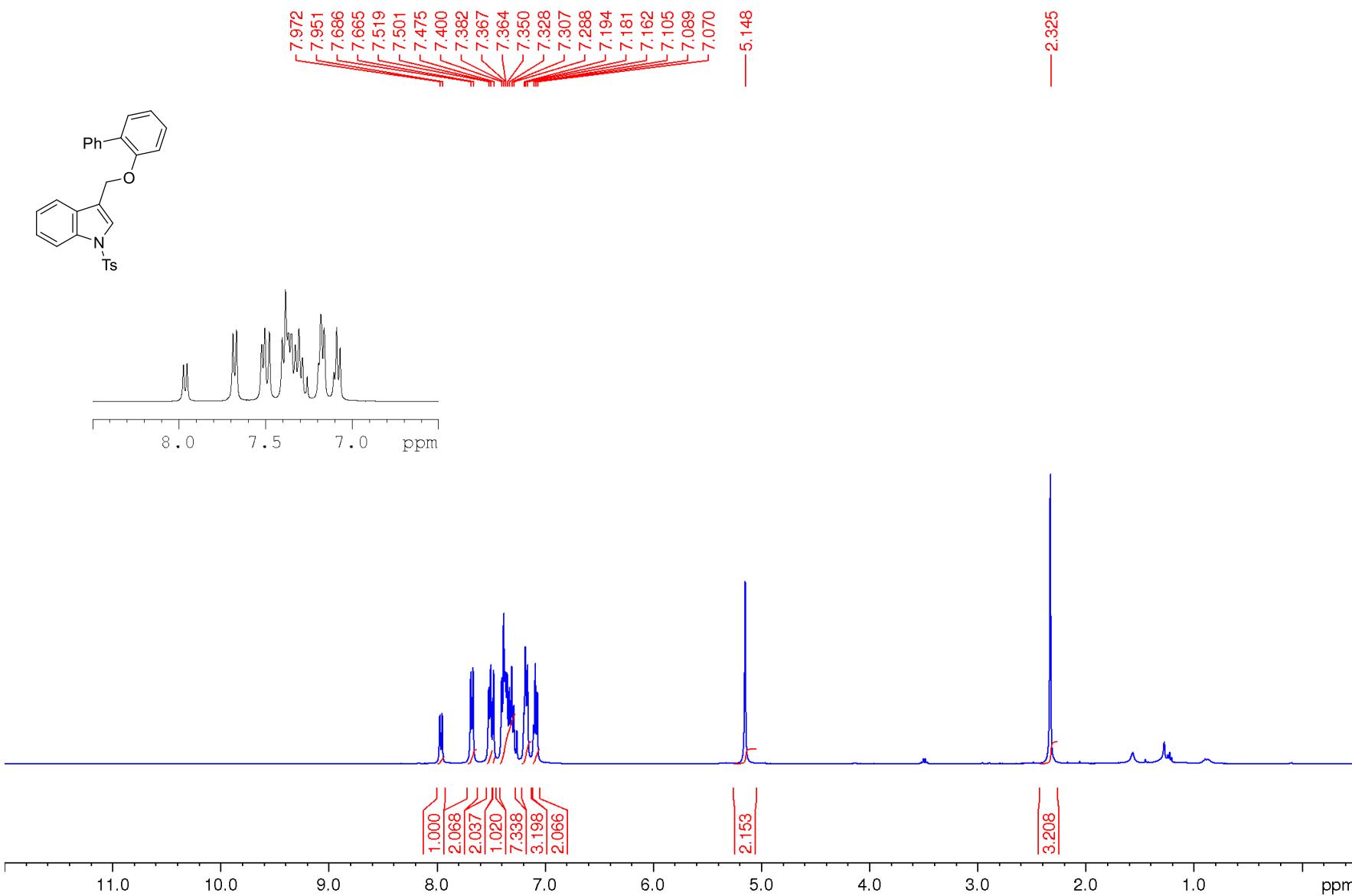
63.246

21.675



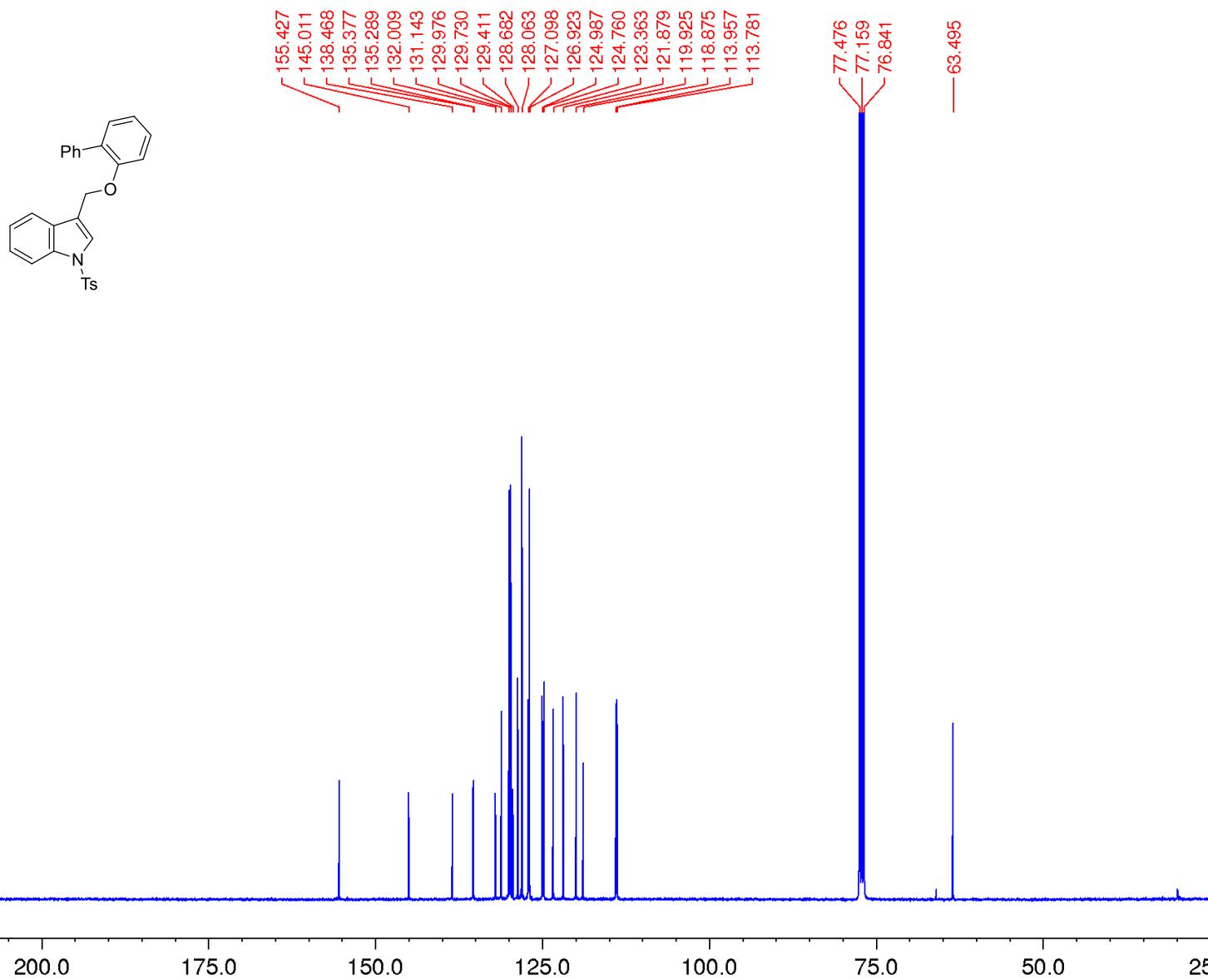
3-(([1,1'-biphenyl]-2-yloxy)methyl)-1-tosyl-1H-indole **4ad**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



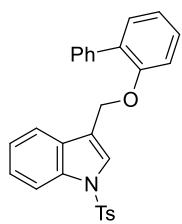
3-(([1,1'-biphenyl]-2-yloxy)methyl)-1-tosyl-1H-indole 4ad

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



3-(([1,1'-biphenyl]-2-yloxy)methyl)-1-tosyl-1H-indole 4ad

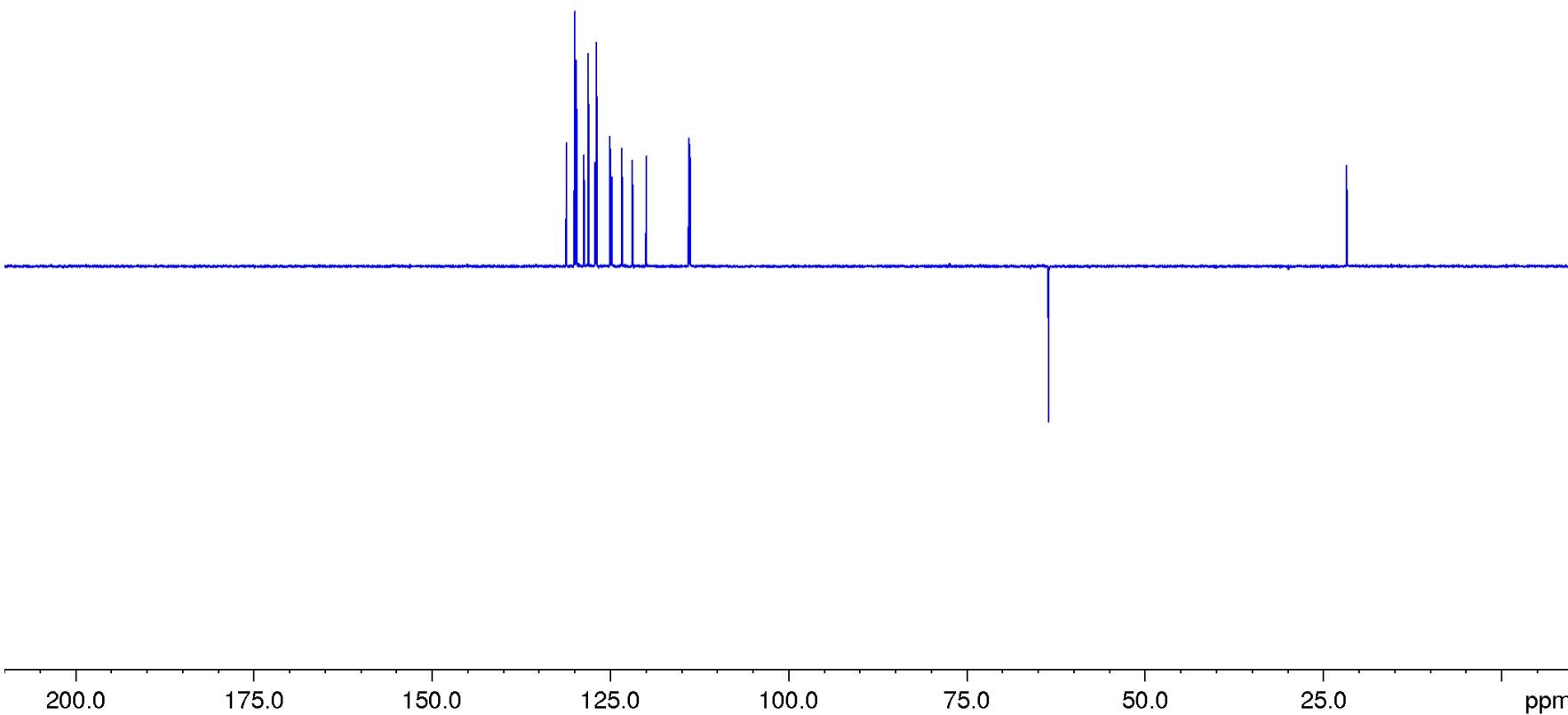
DEPT 135 NMR-spectrum (CDCl_3)

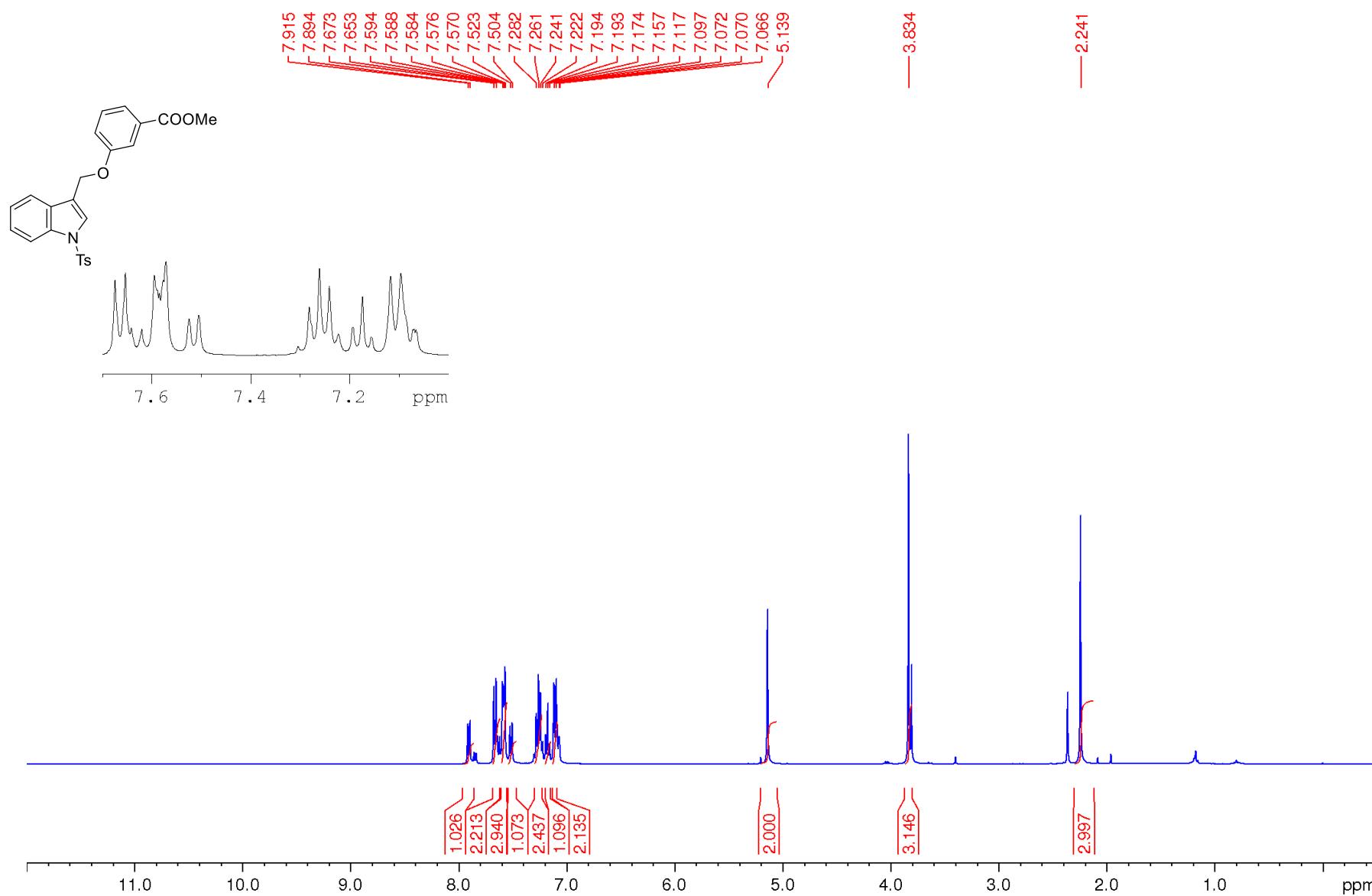


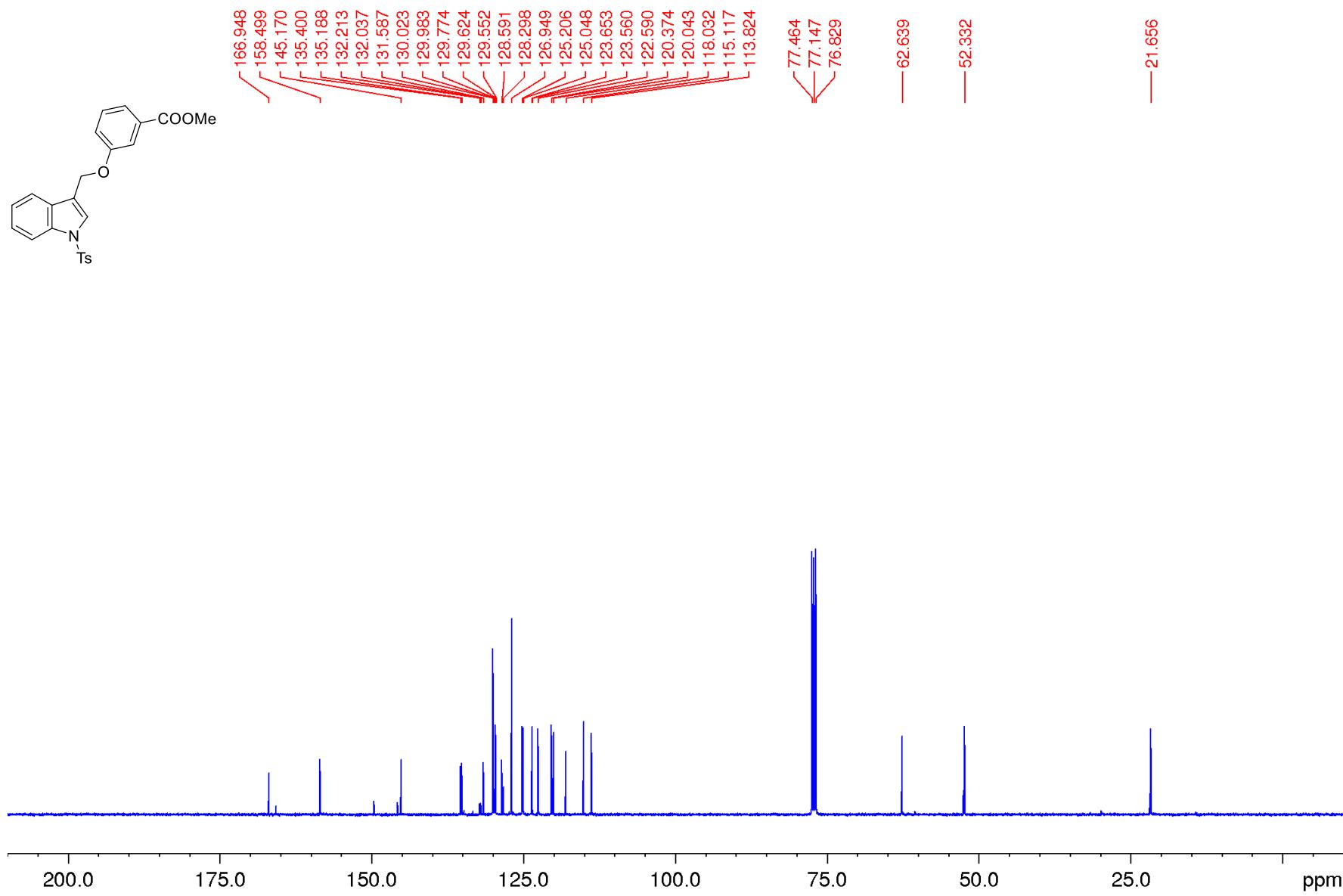
131.136
129.969
129.723
128.676
128.056
127.090
126.916
124.981
124.754
123.356
121.871
119.919
113.951
113.775

— 63.488

— 21.681

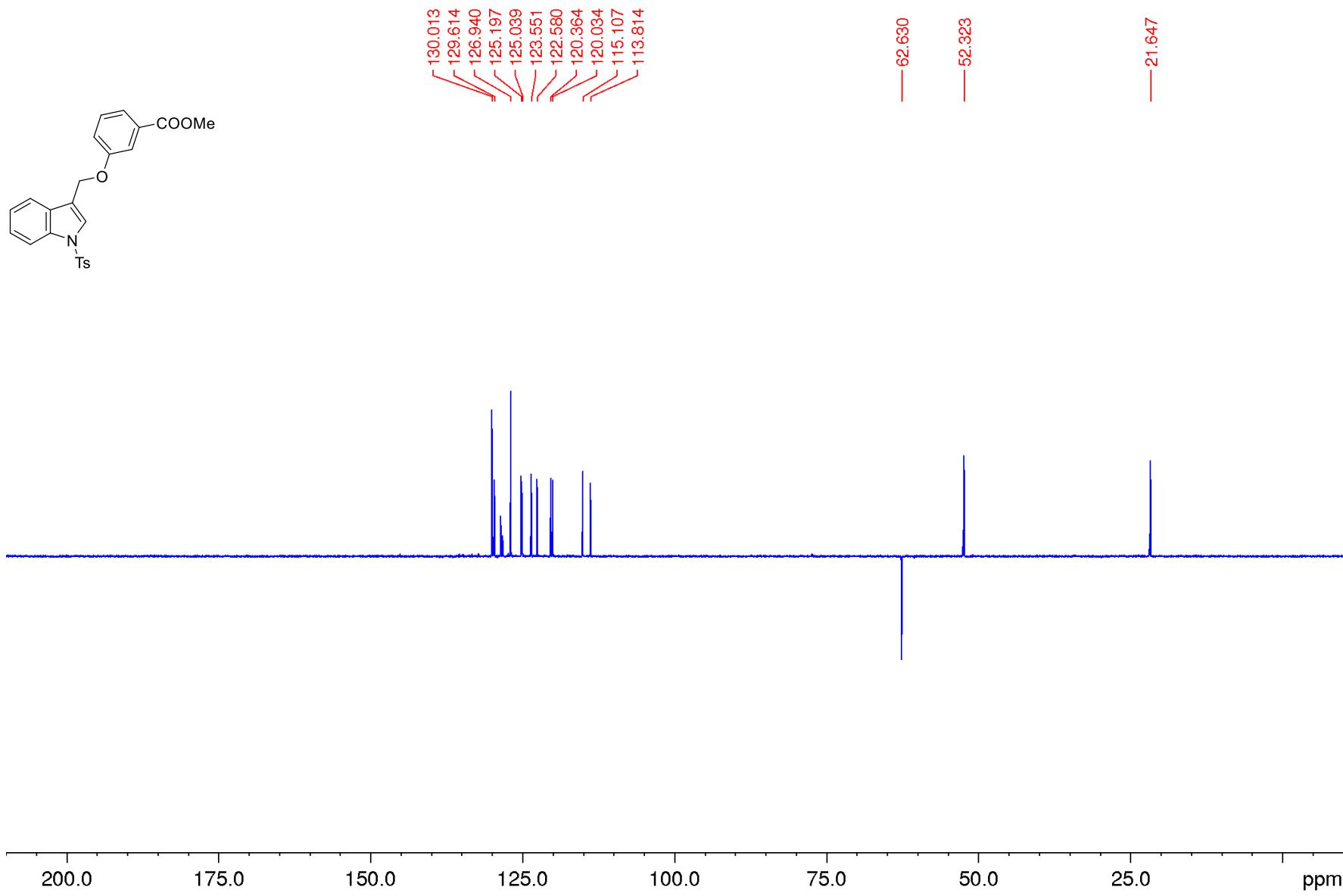






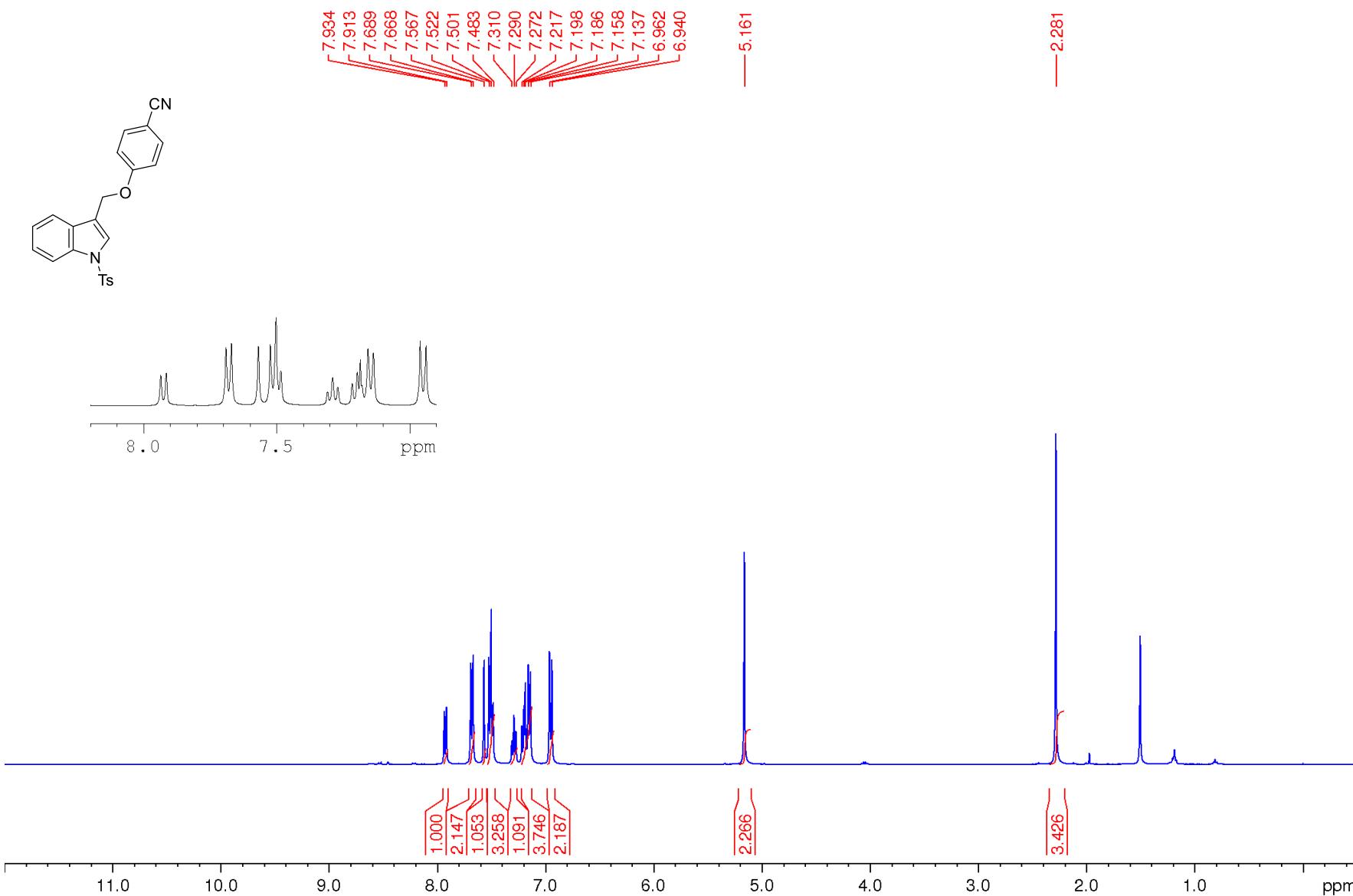
methyl 3-((1-tosyl-1H-indol-3-yl)methoxy)benzoate 4ae

DEPT 135 NMR-spectrum (CDCl_3)



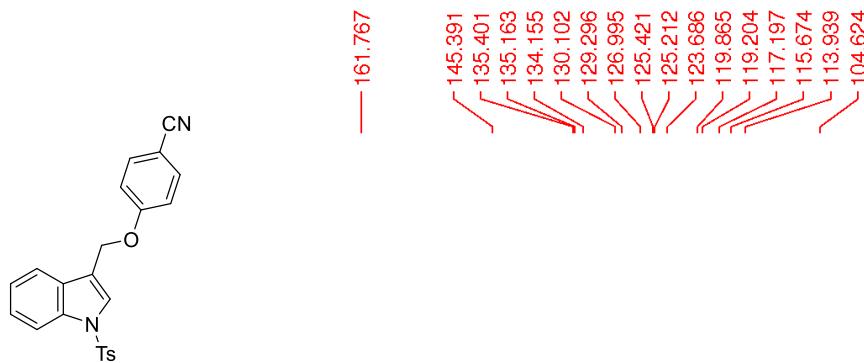
4-((1-tosyl-1H-indol-3-yl)methoxy)benzonitrile 4af

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



4-((1-tosyl-1H-indol-3-yl)methoxy)benzonitrile 4af

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



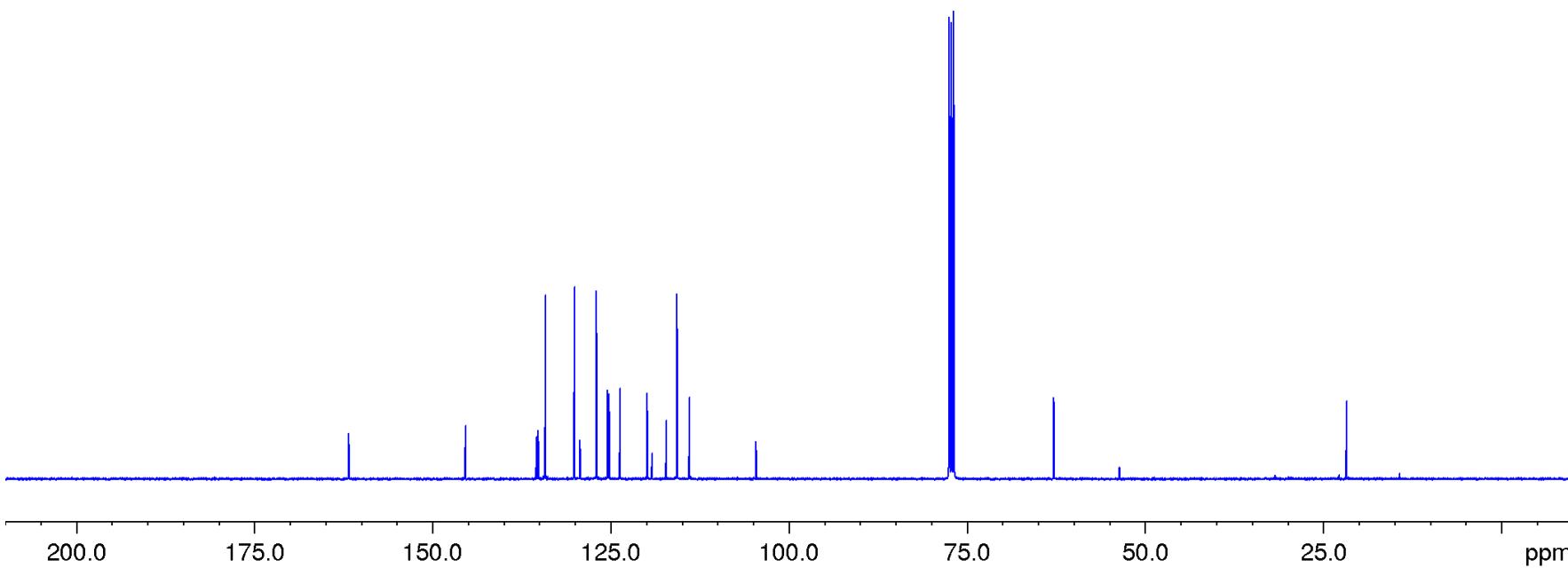
— 161.767

146.391
135.401
135.163
134.155
130.102
129.296
126.995
125.421
125.212
123.686
119.865
119.204
117.197
115.674
113.939
104.624

77.174
77.157
76.839

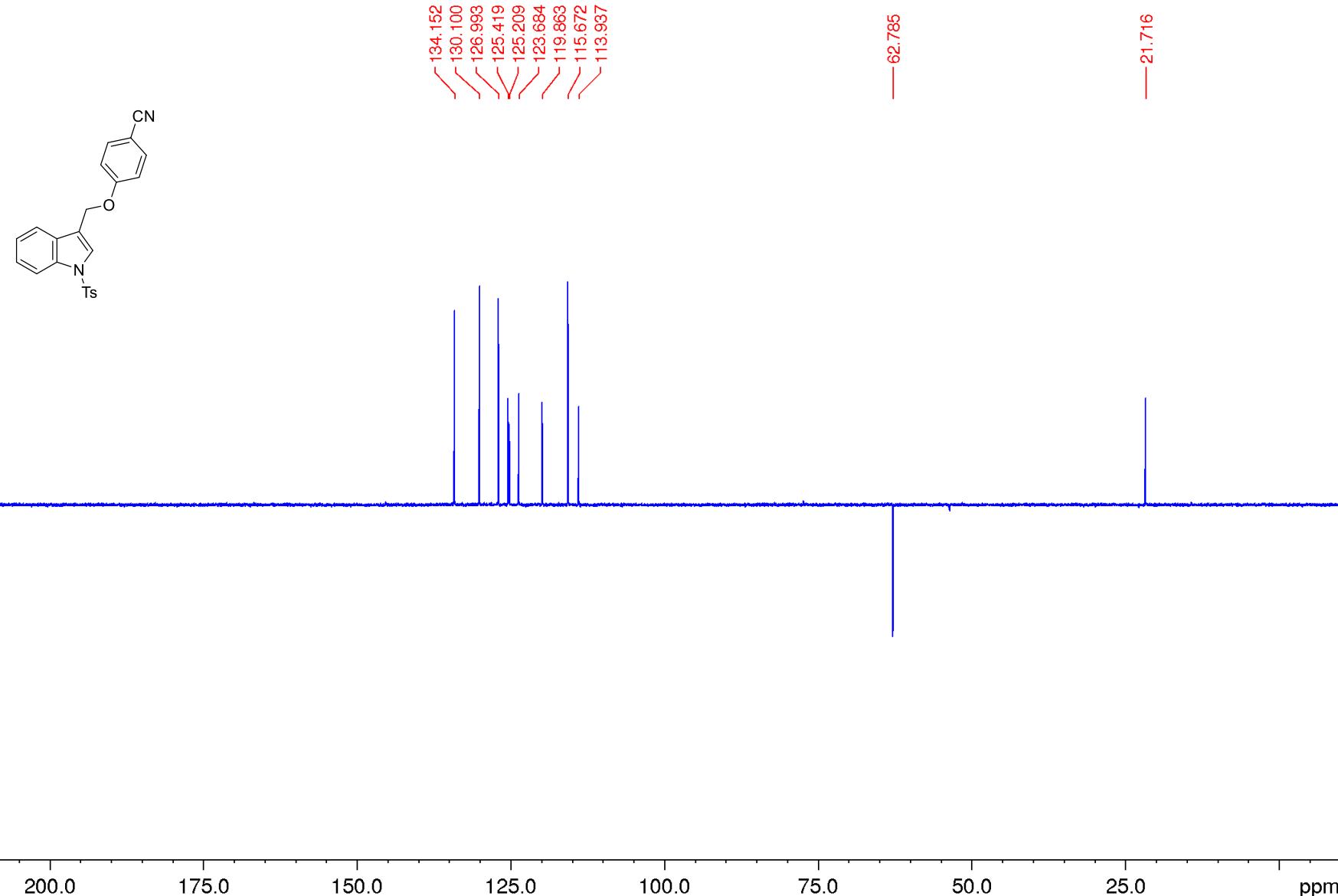
— 62.788

— 21.719



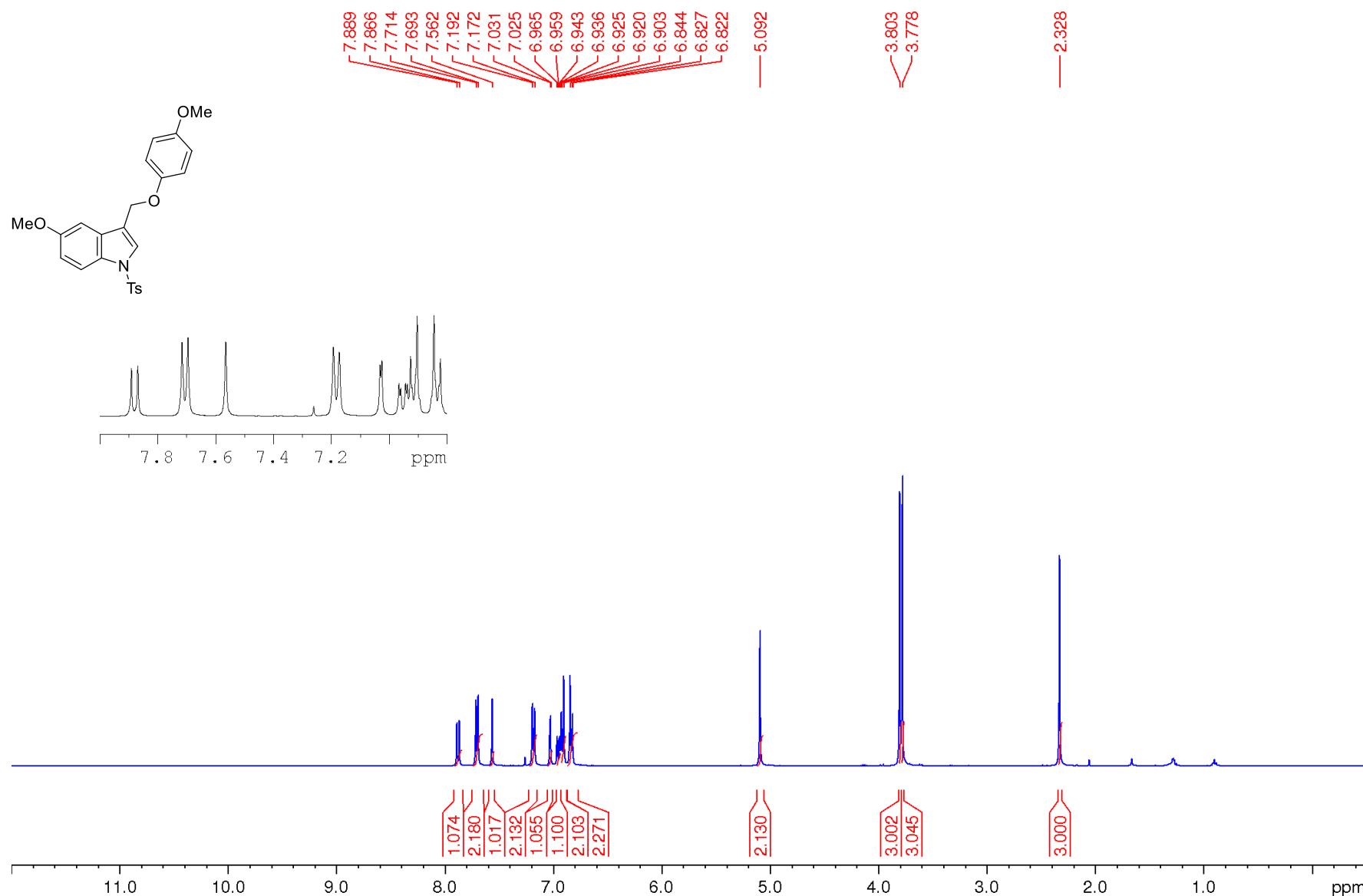
4-((1-tosyl-1H-indol-3-yl)methoxy)benzonitrile 4af

DEPT 135 NMR-spectrum (CDCl_3)



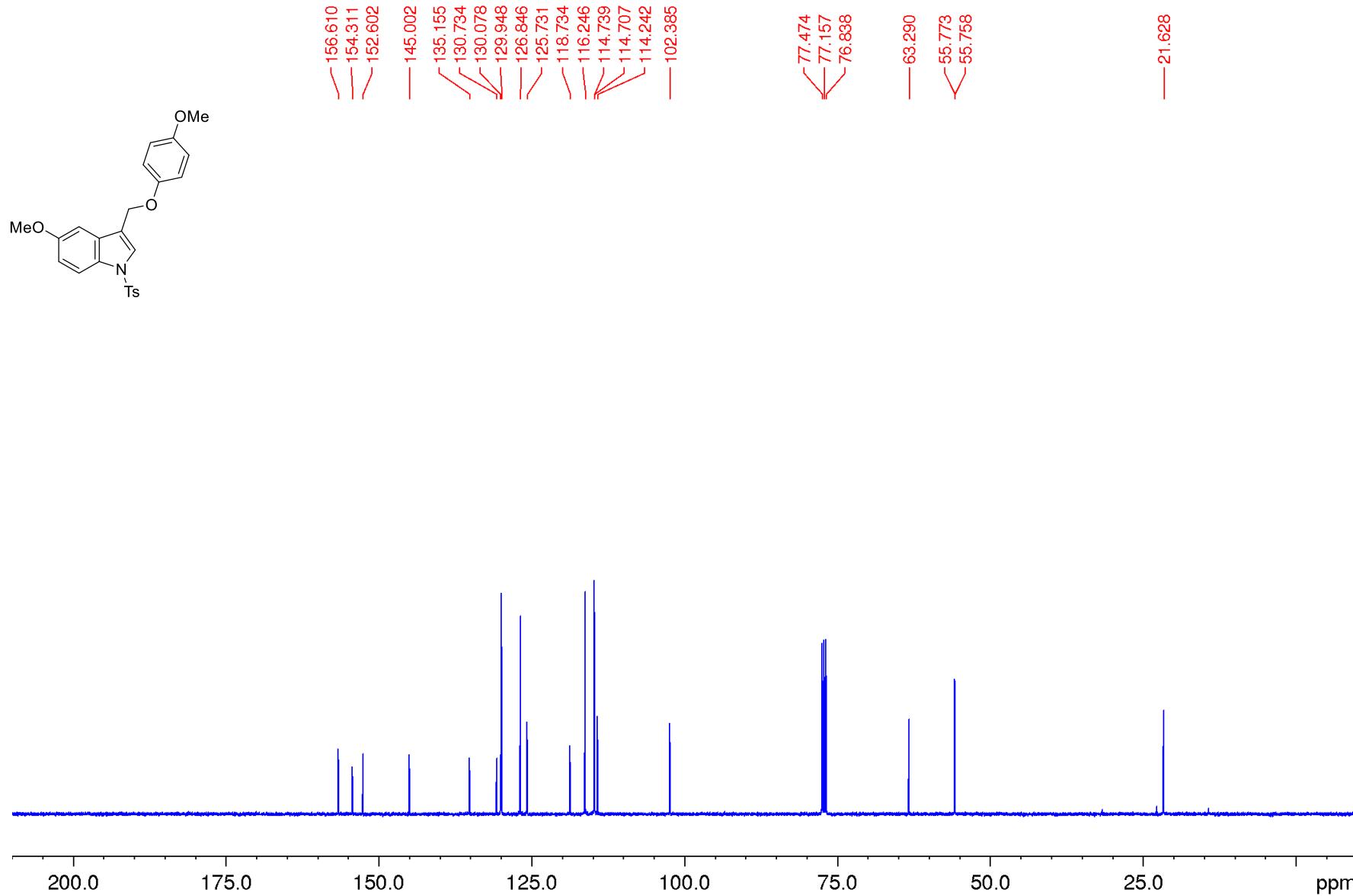
5-methoxy-3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4da

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



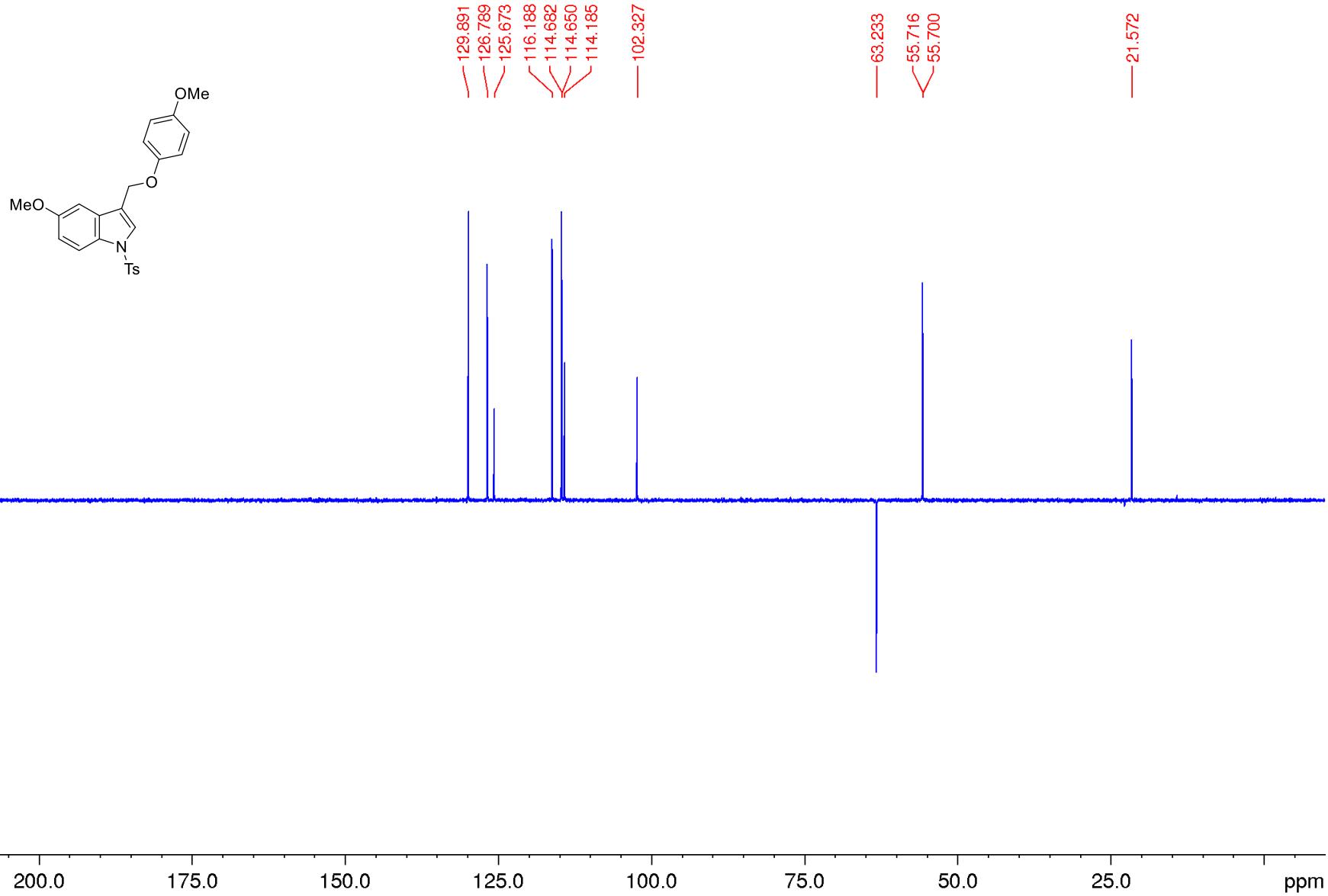
5-methoxy-3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4da

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



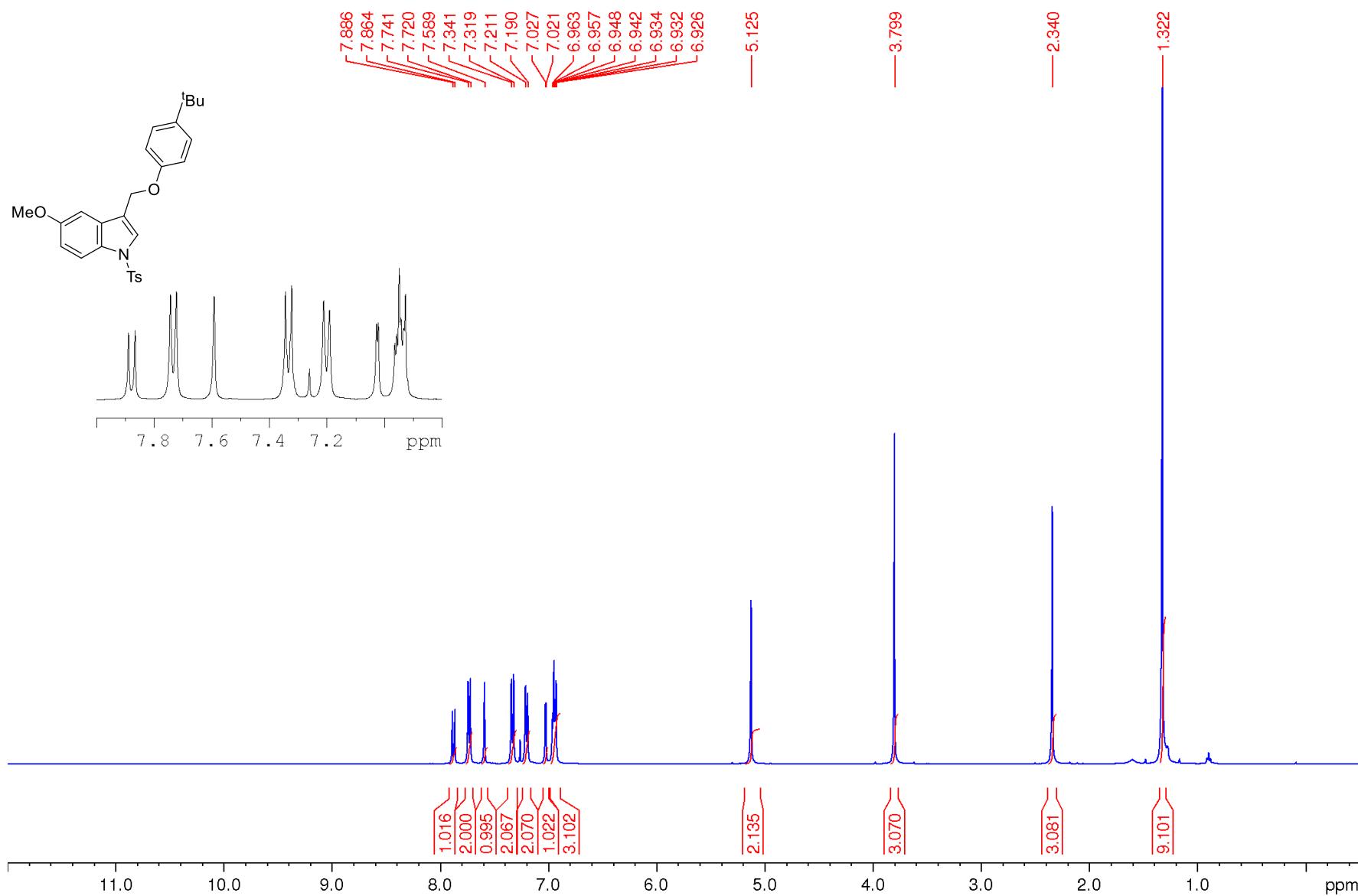
5-methoxy-3-((4-methoxyphenoxy)methyl)-1-tosyl-1H-indole 4da

DEPT 135 NMR-spectrum (CDCl_3)



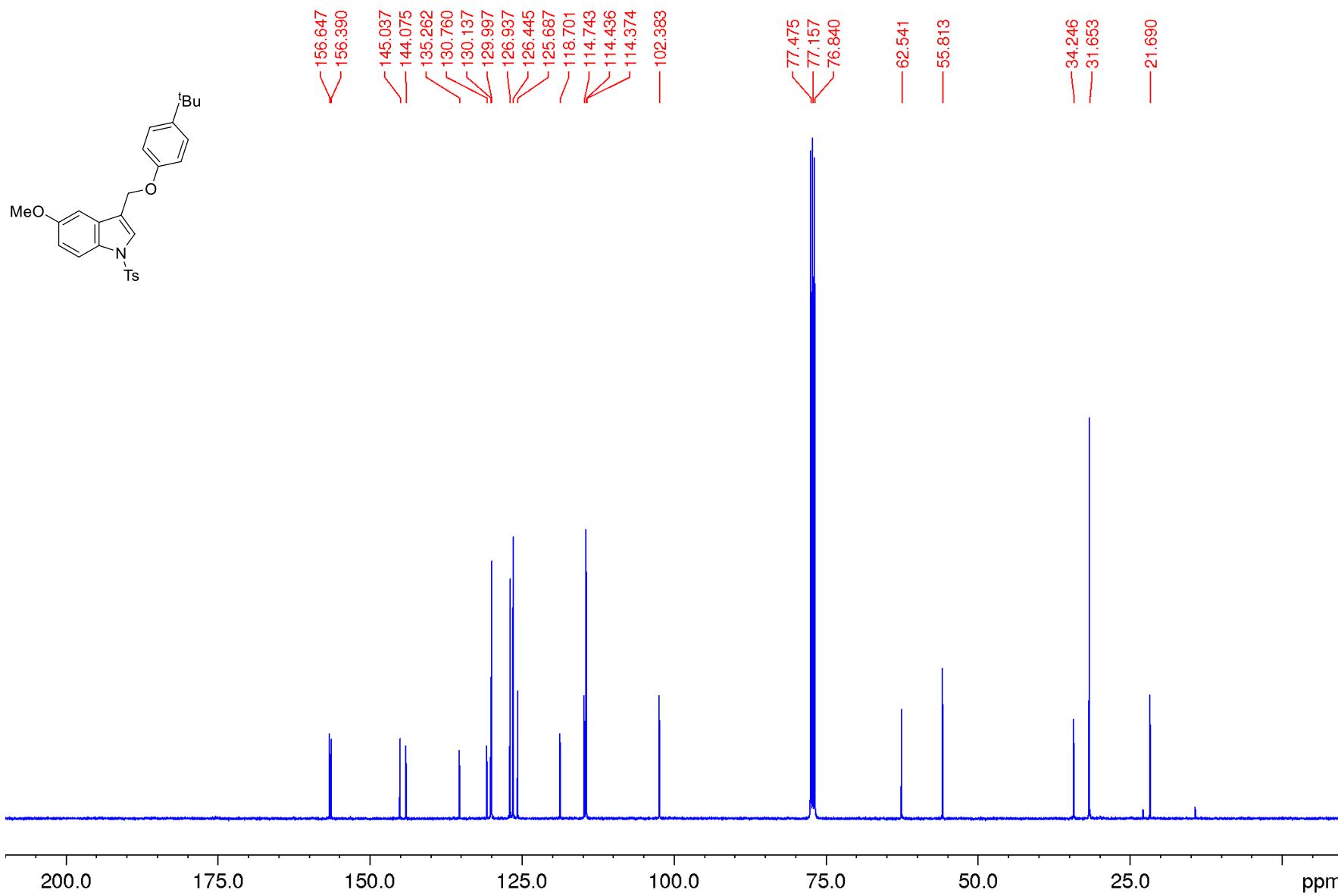
3-((4-(tert-butyl)phenoxy)methyl)-5-methoxy-1-tosyl-1H-indole 4db

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



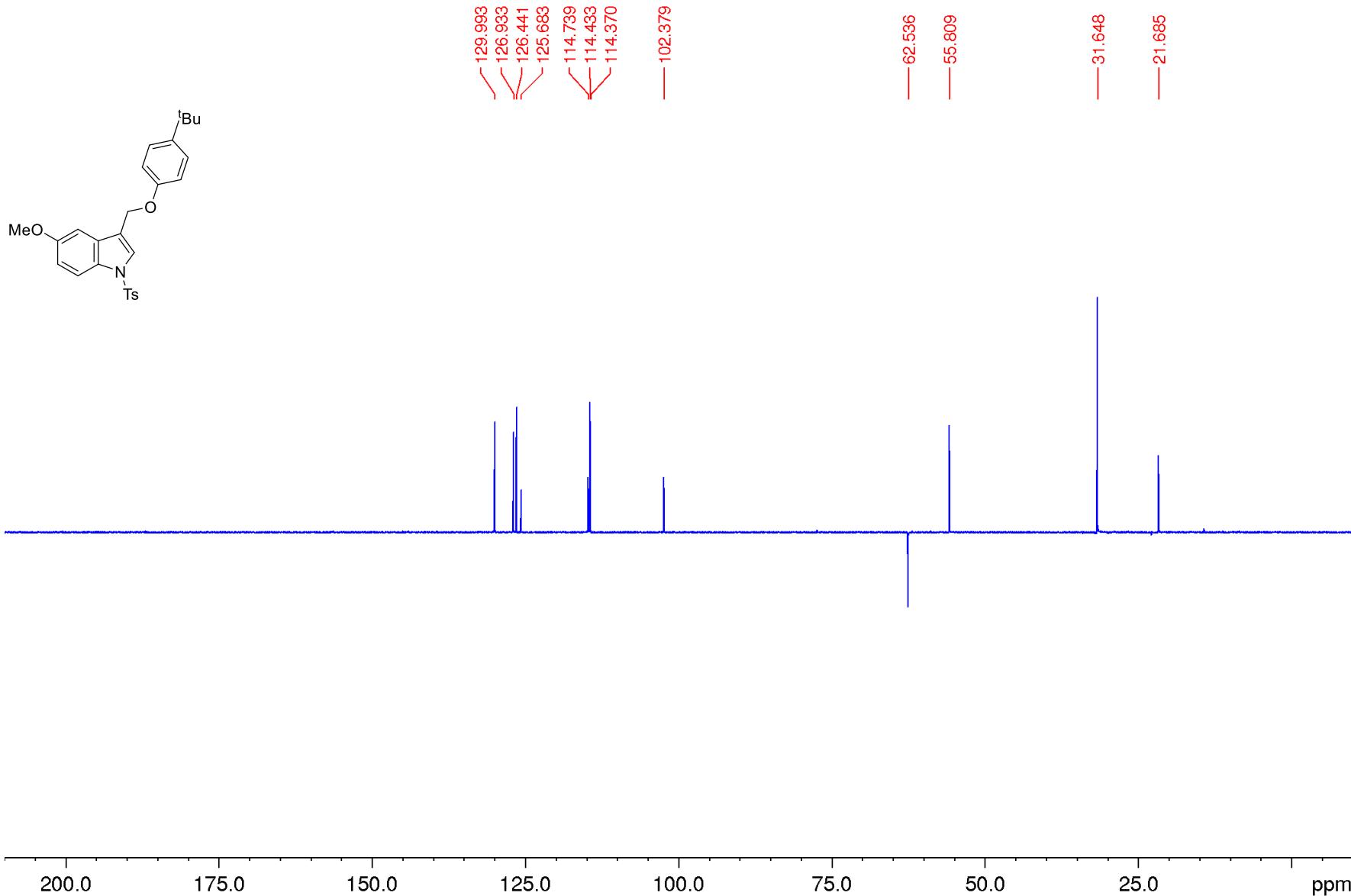
3-((4-(tert-butyl)phenoxy)methyl)-5-methoxy-1-tosyl-1H-indole 4db

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



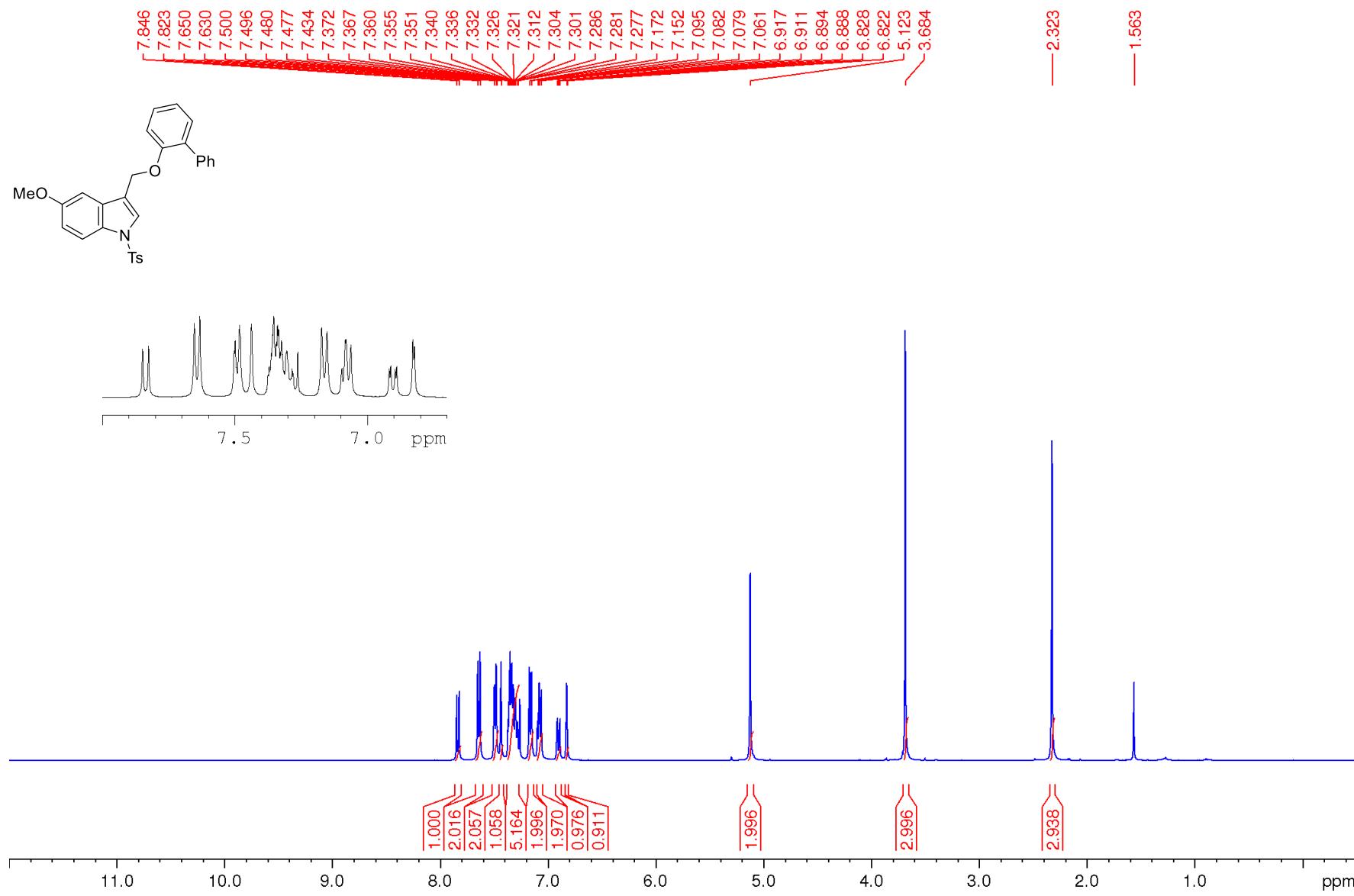
3-((4-(tert-butyl)phenoxy)methyl)-5-methoxy-1-tosyl-1H-indole 4db

DEPT 135 NMR-spectrum (CDCl_3)



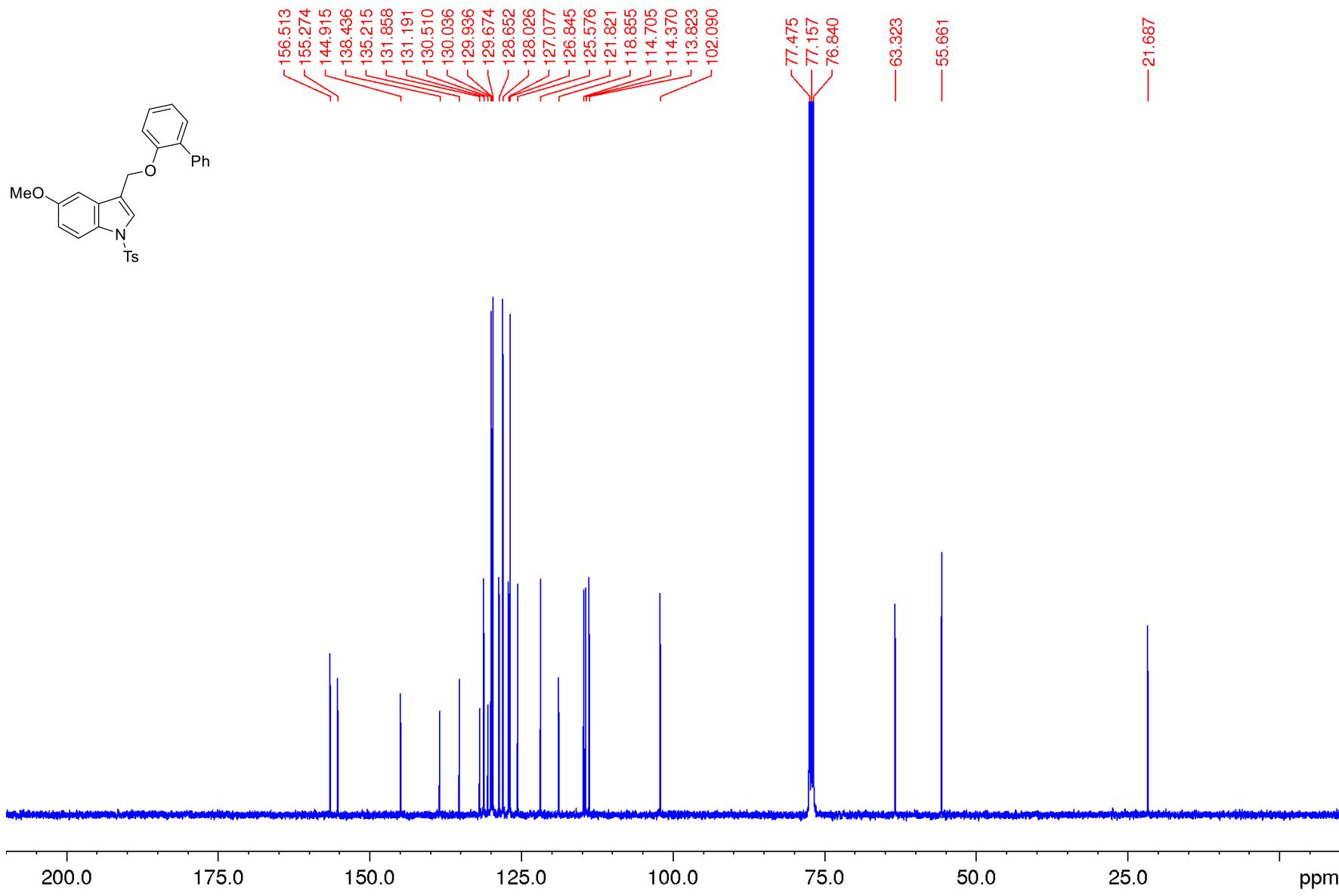
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-methoxy-1-tosyl-1H-indole 4dc

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



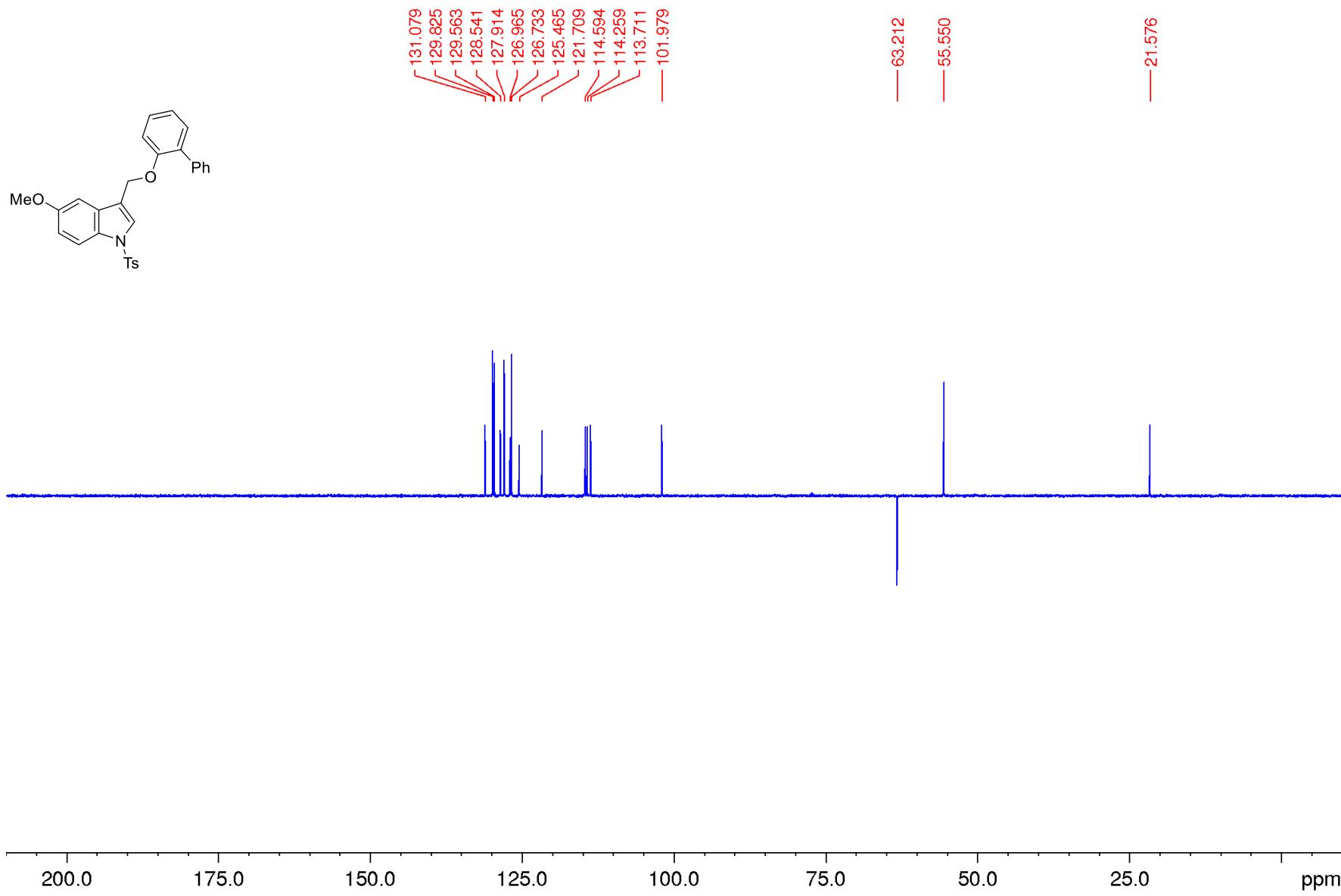
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-methoxy-1-tosyl-1H-indole 4dc

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



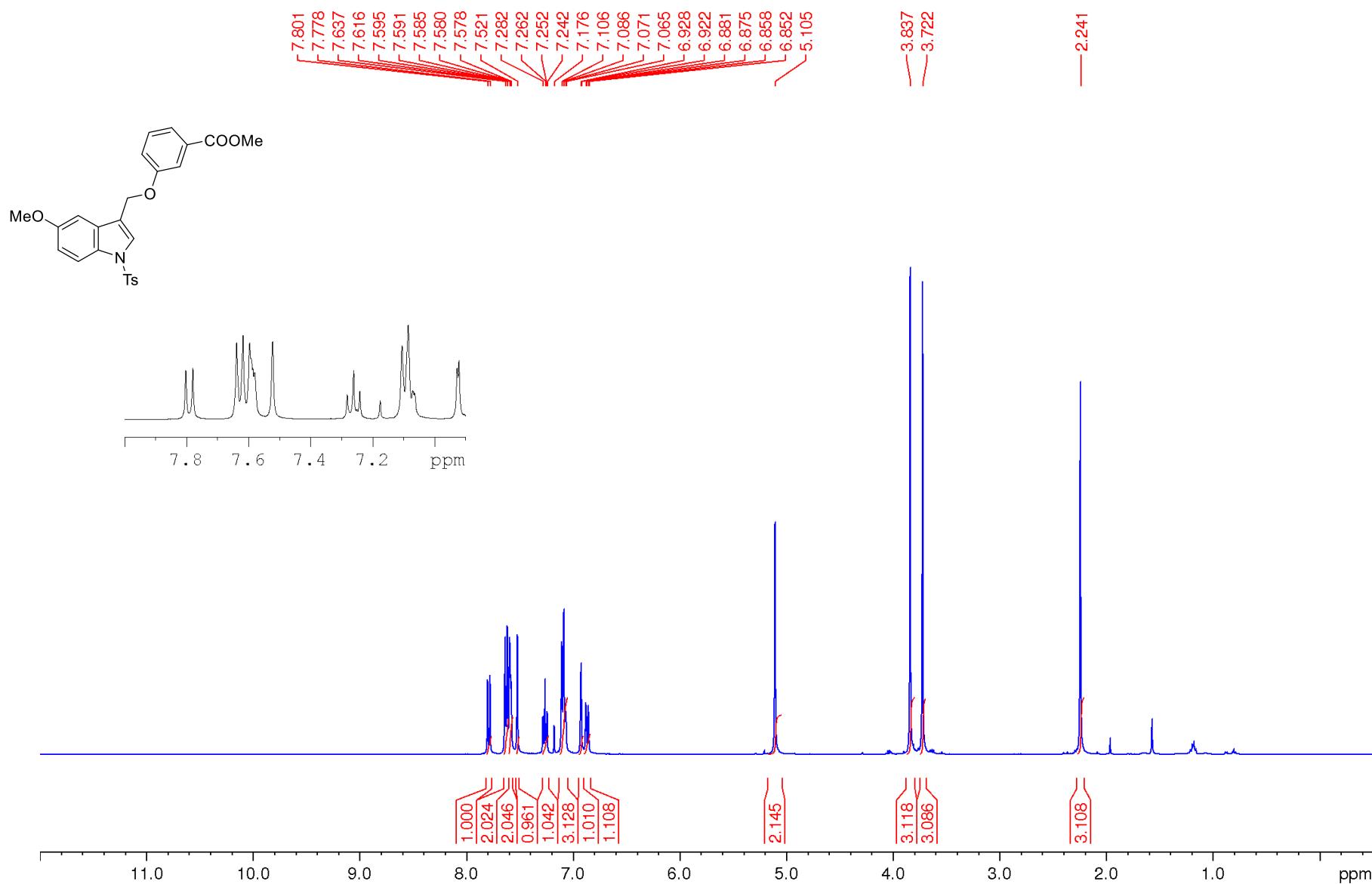
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-methoxy-1-tosyl-1H-indole 4dc

DEPT 135 NMR-spectrum (CDCl_3)



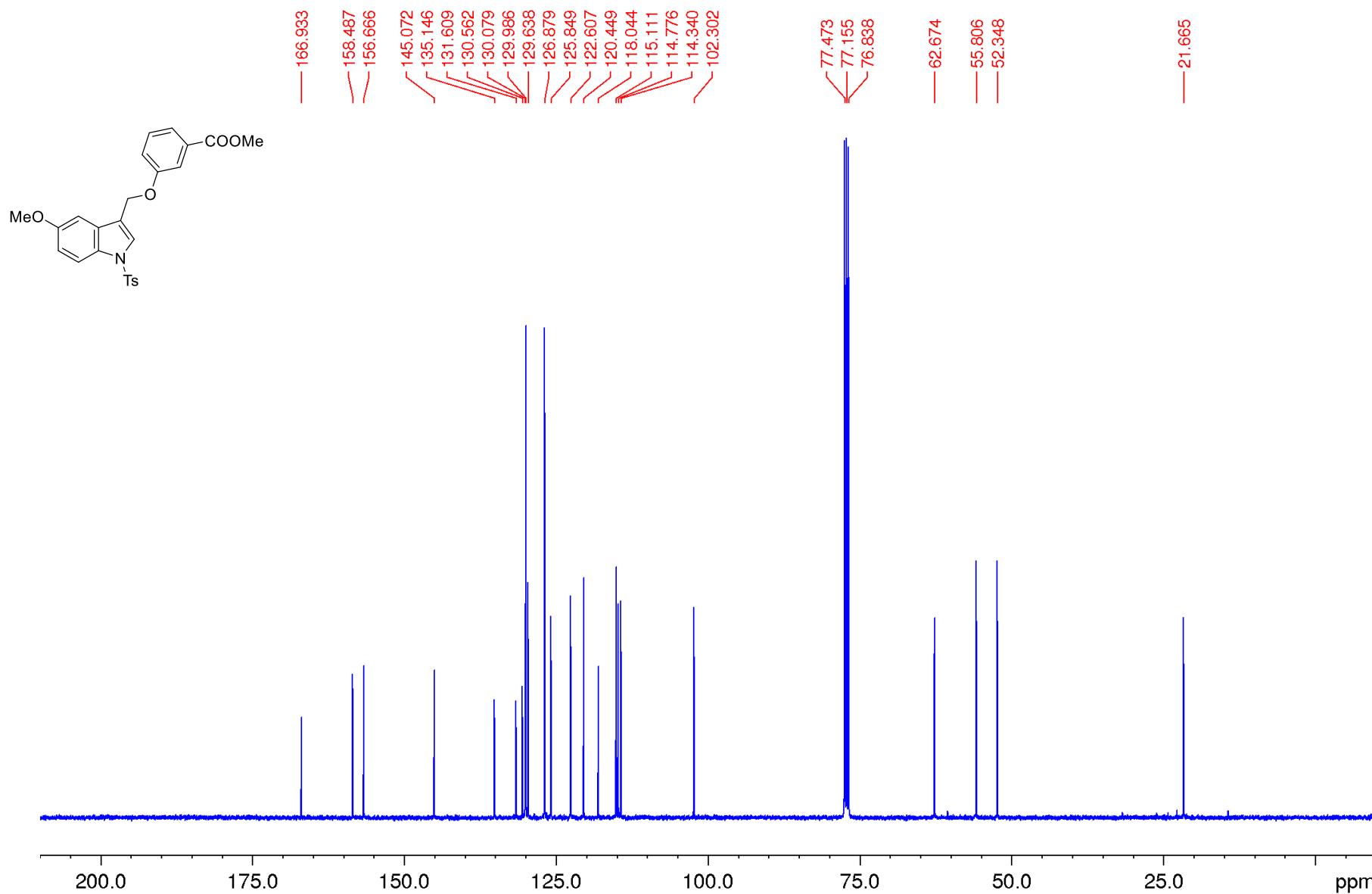
methyl 3-((5-methoxy-1-tosyl-1H-indol-3-yl)methoxy)benzoate 4de

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



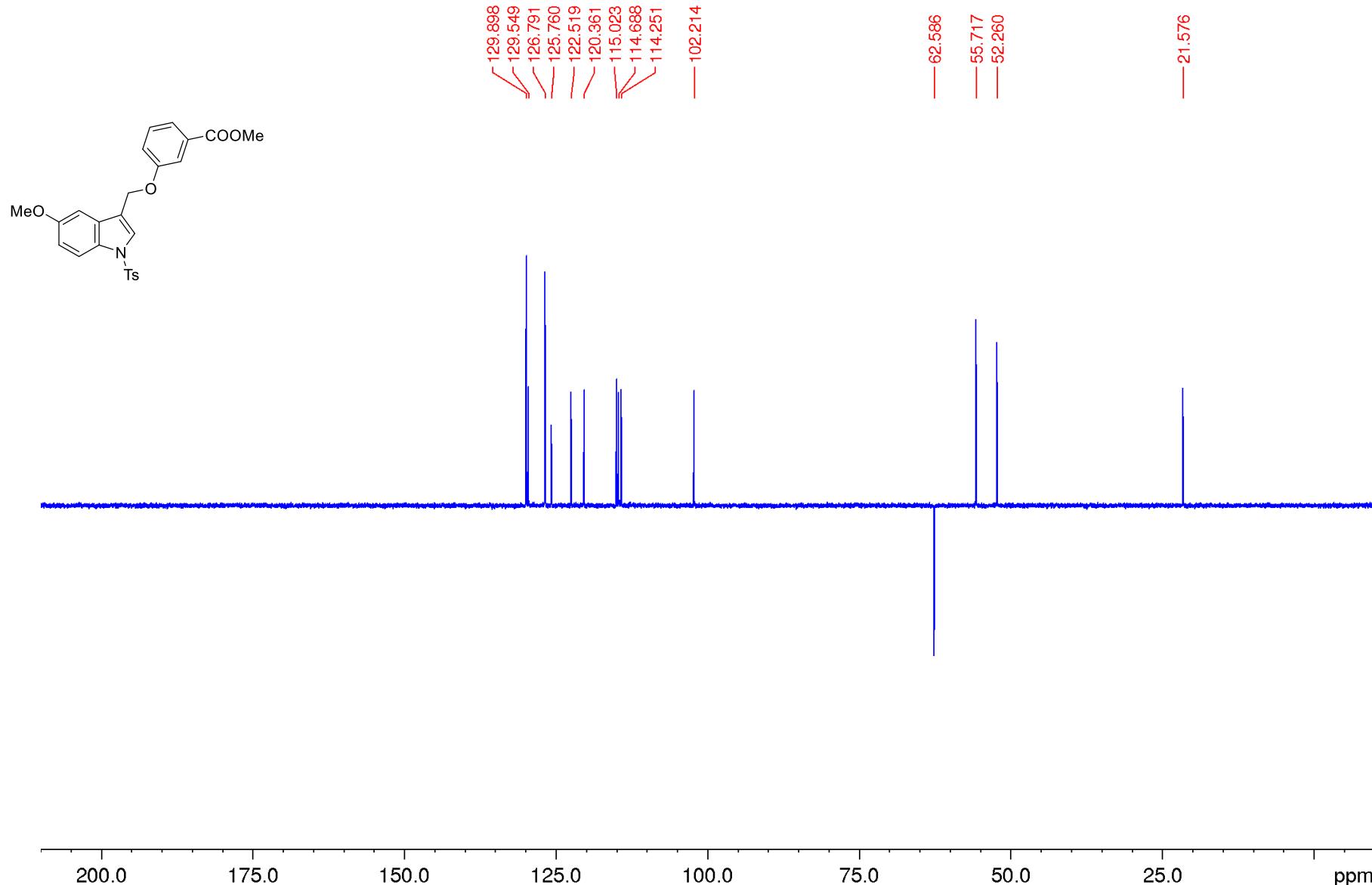
methyl 3-((5-methoxy-1-tosyl-1H-indol-3-yl)methoxy)benzoate 4de

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



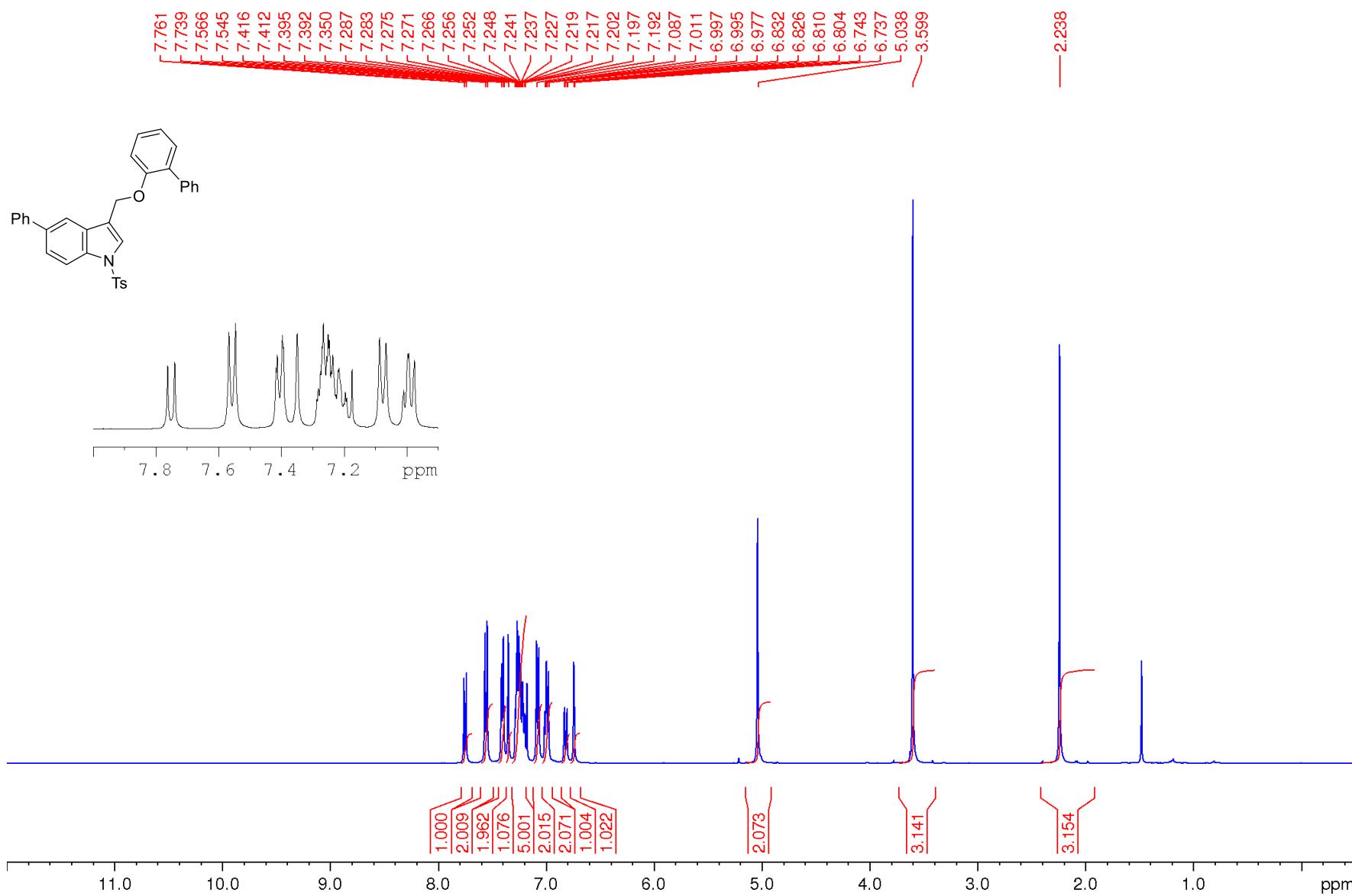
methyl 3-((5-methoxy-1-tosyl-1H-indol-3-yl)methoxy)benzoate 4de

DEPT 135 NMR-spectrum (CDCl_3)



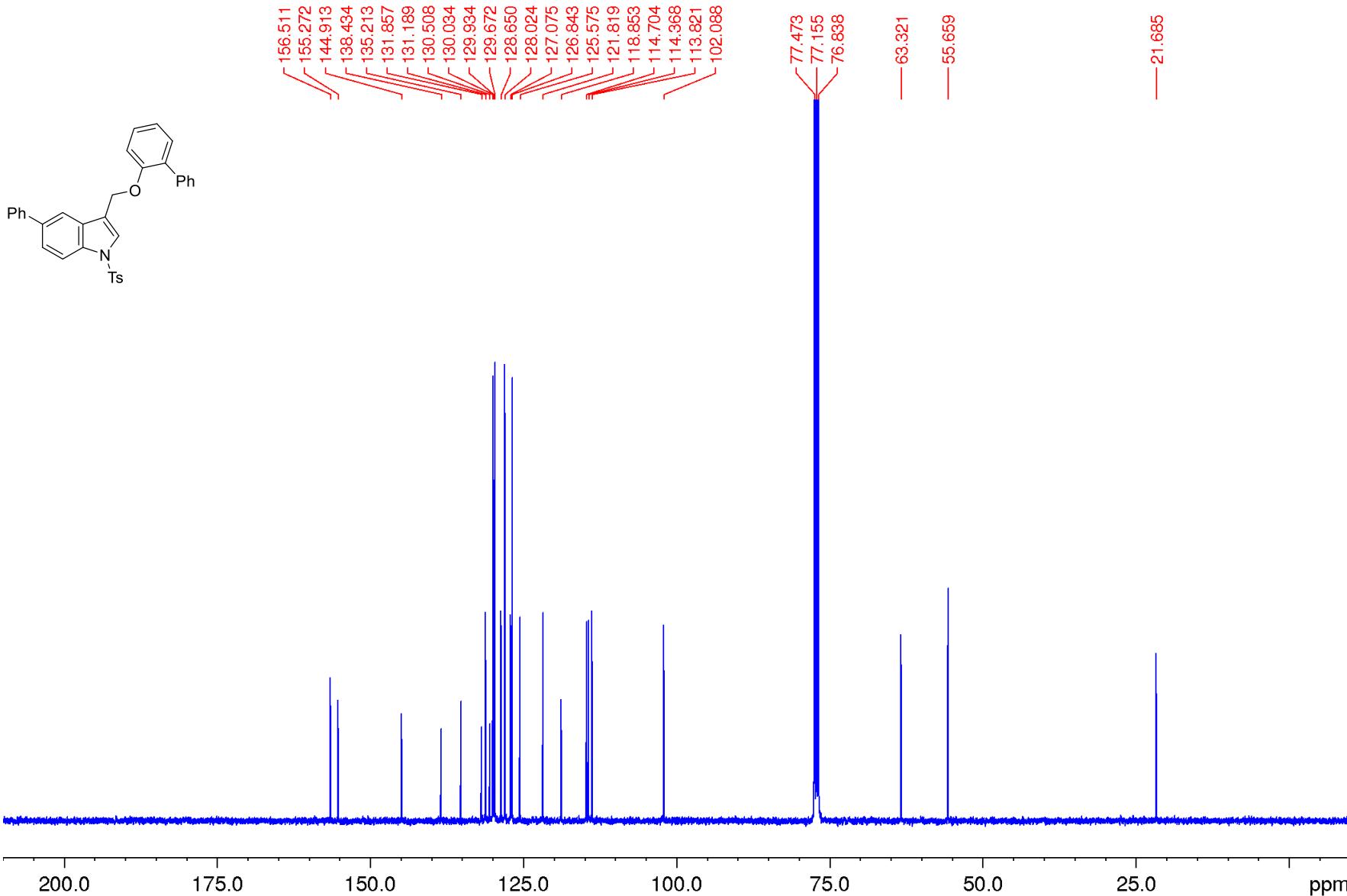
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-phenyl-1-tosyl-1H-indole 4ed

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



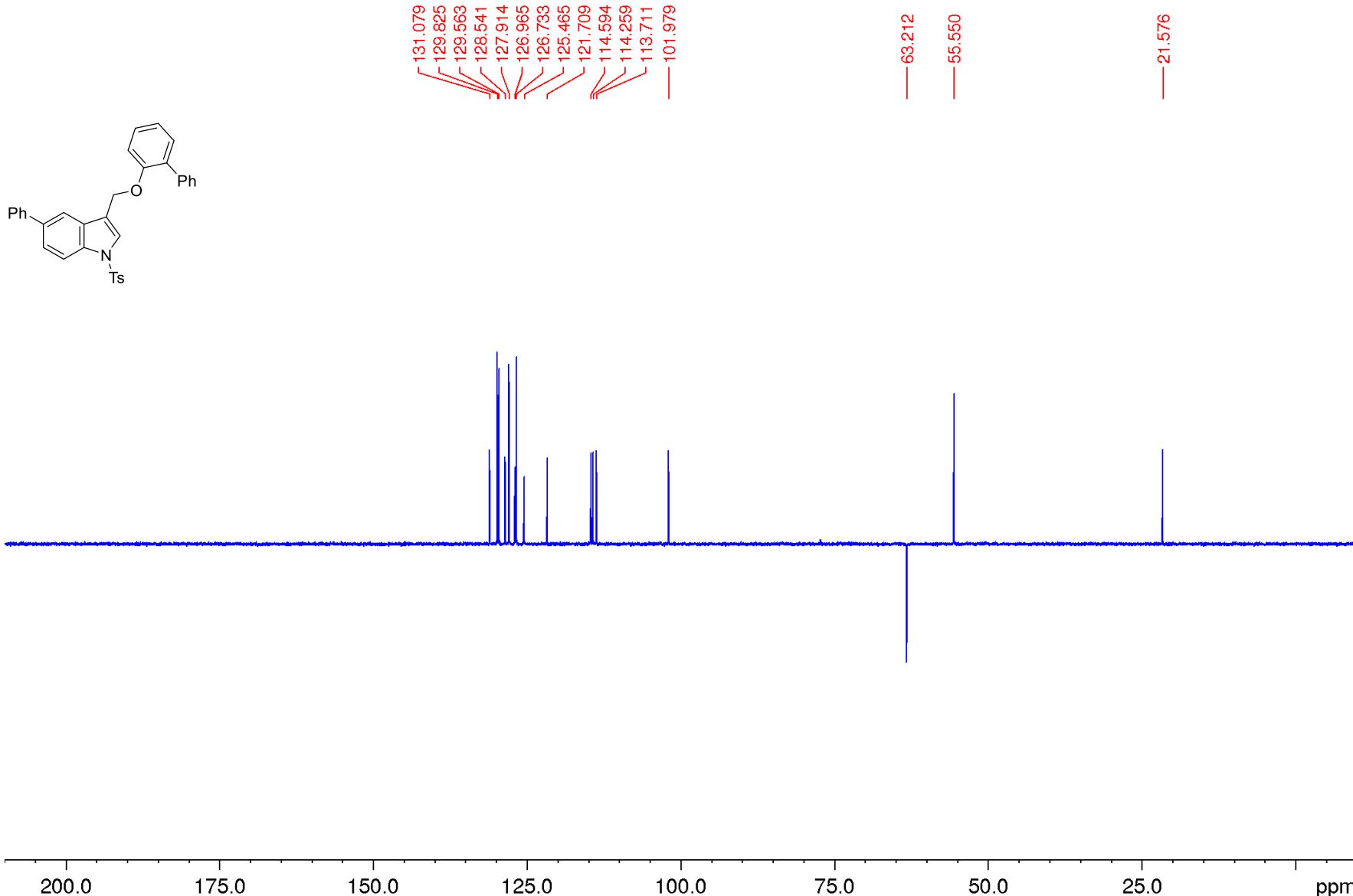
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-phenyl-1-tosyl-1H-indole 4ed

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



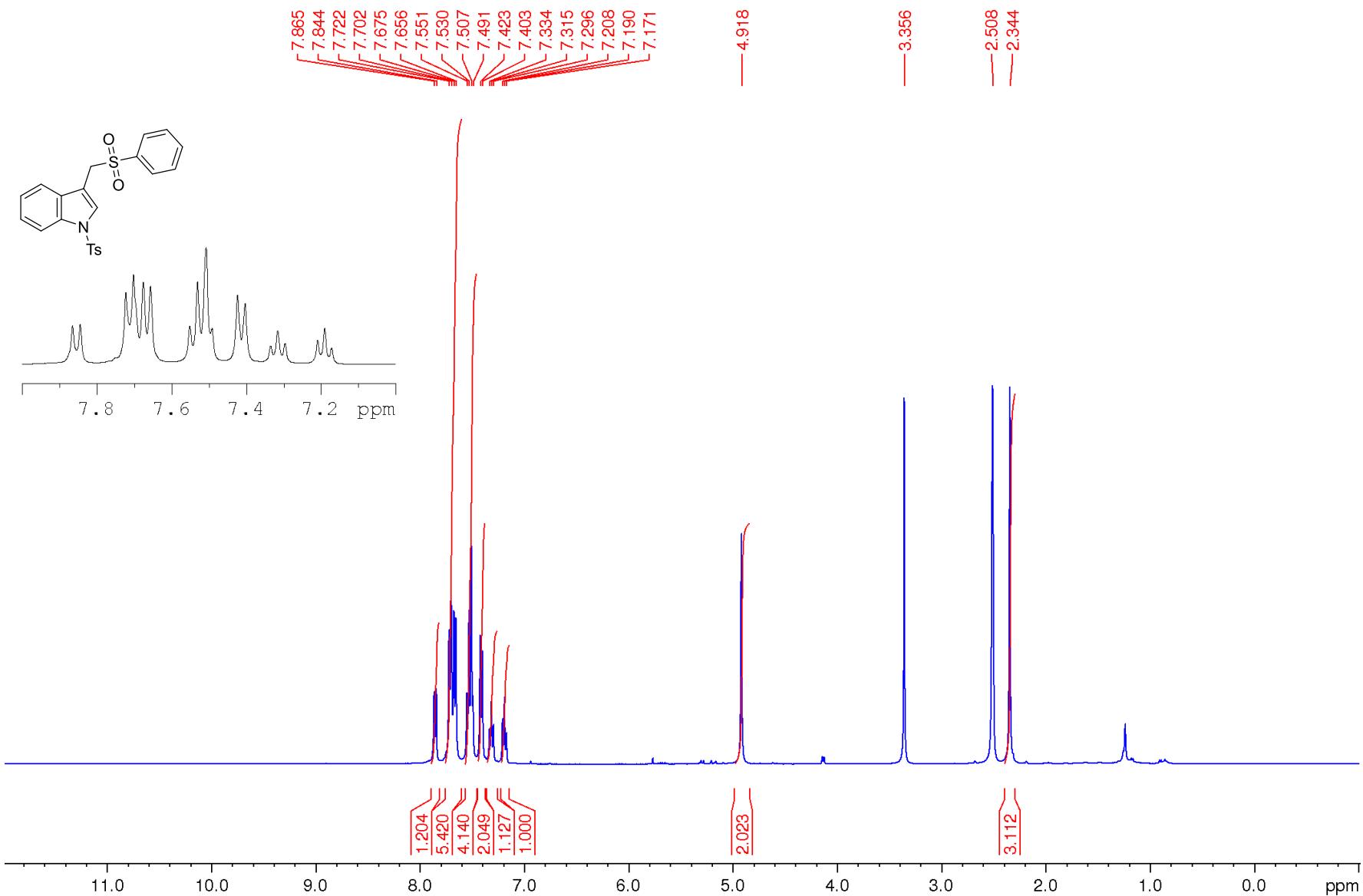
3-(([1,1'-biphenyl]-2-yloxy)methyl)-5-phenyl-1-tosyl-1H-indole 4ed

DEPT 135 NMR-spectrum (CDCl_3)



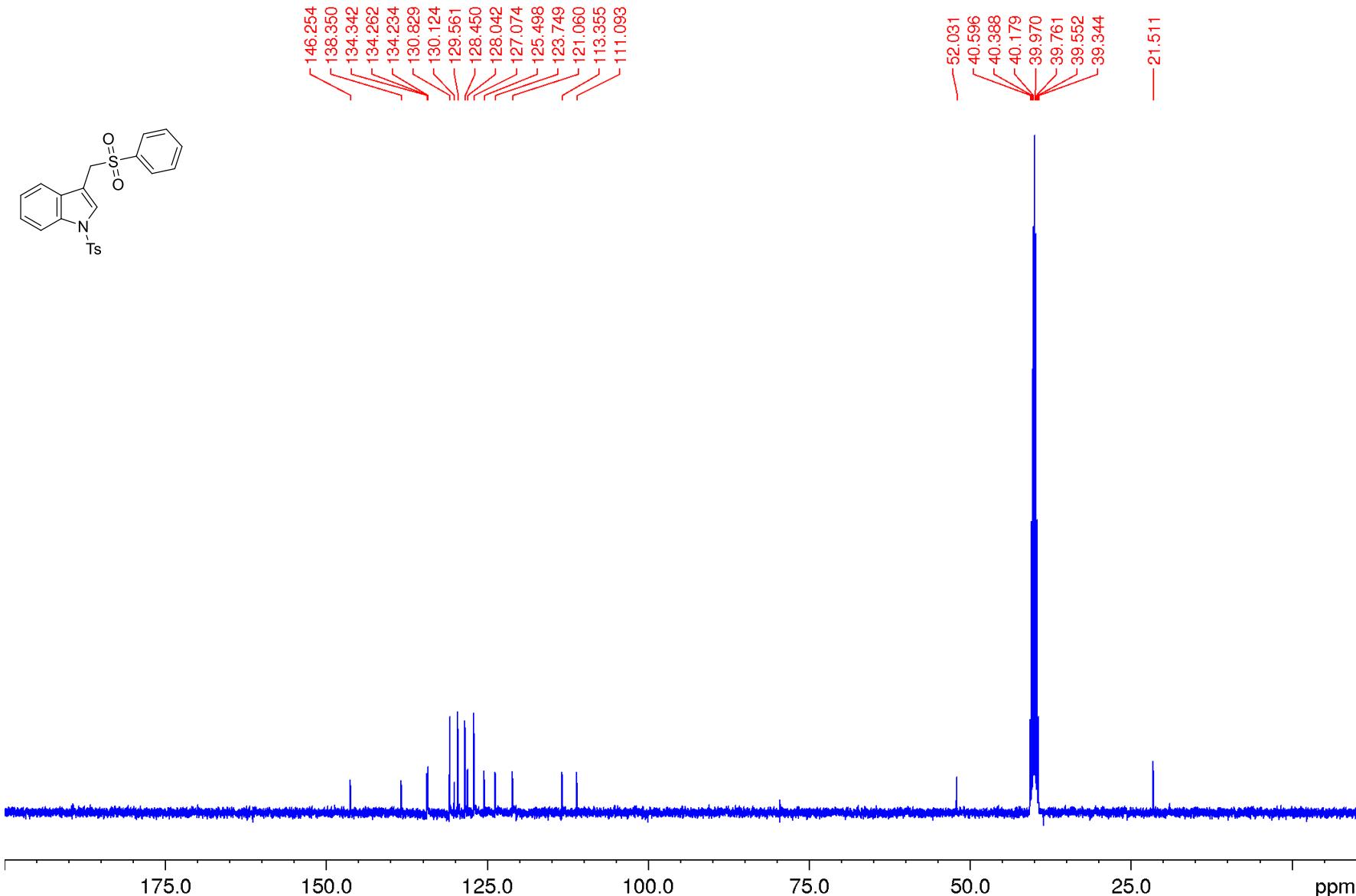
3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9ab**

¹H NMR-spectrum (400.13 MHz) (DMSO-*d*₆)



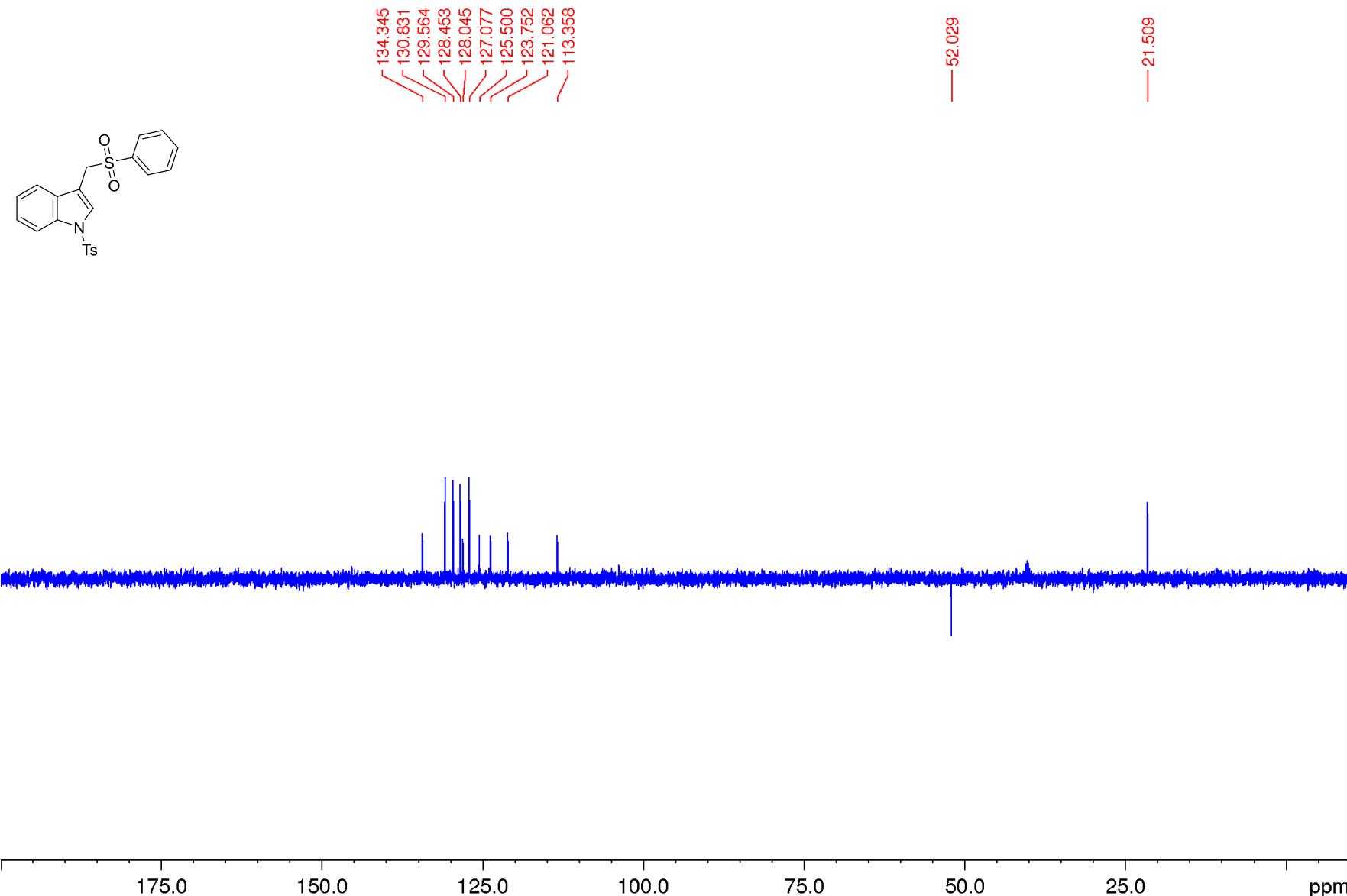
3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9ab**

¹³C NMR-spectrum (100.6 MHz) (DMSO-*d*₆)



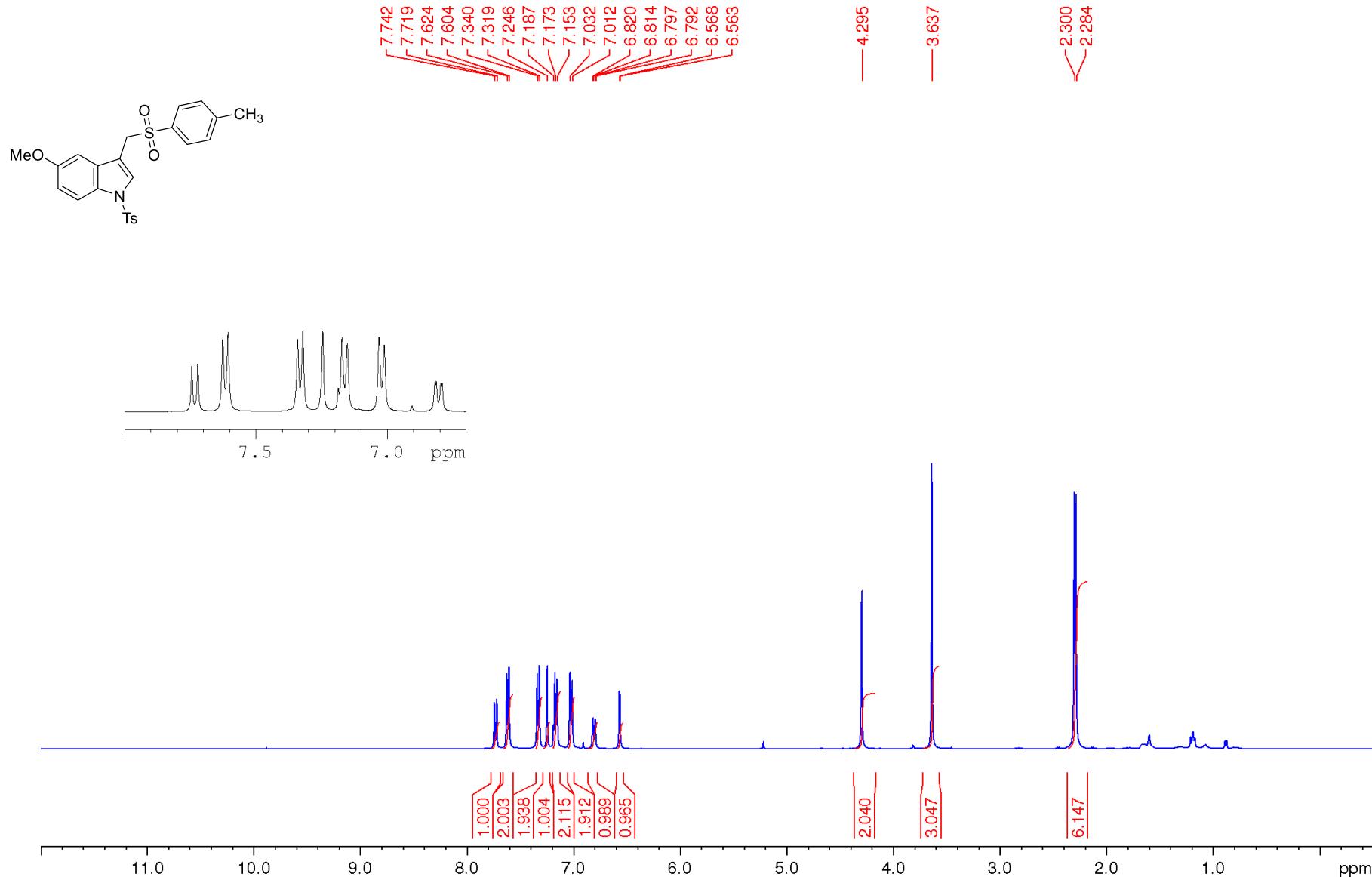
3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9ab**

DEPT 135 NMR-spectrum ((DMSO-*d*₆))



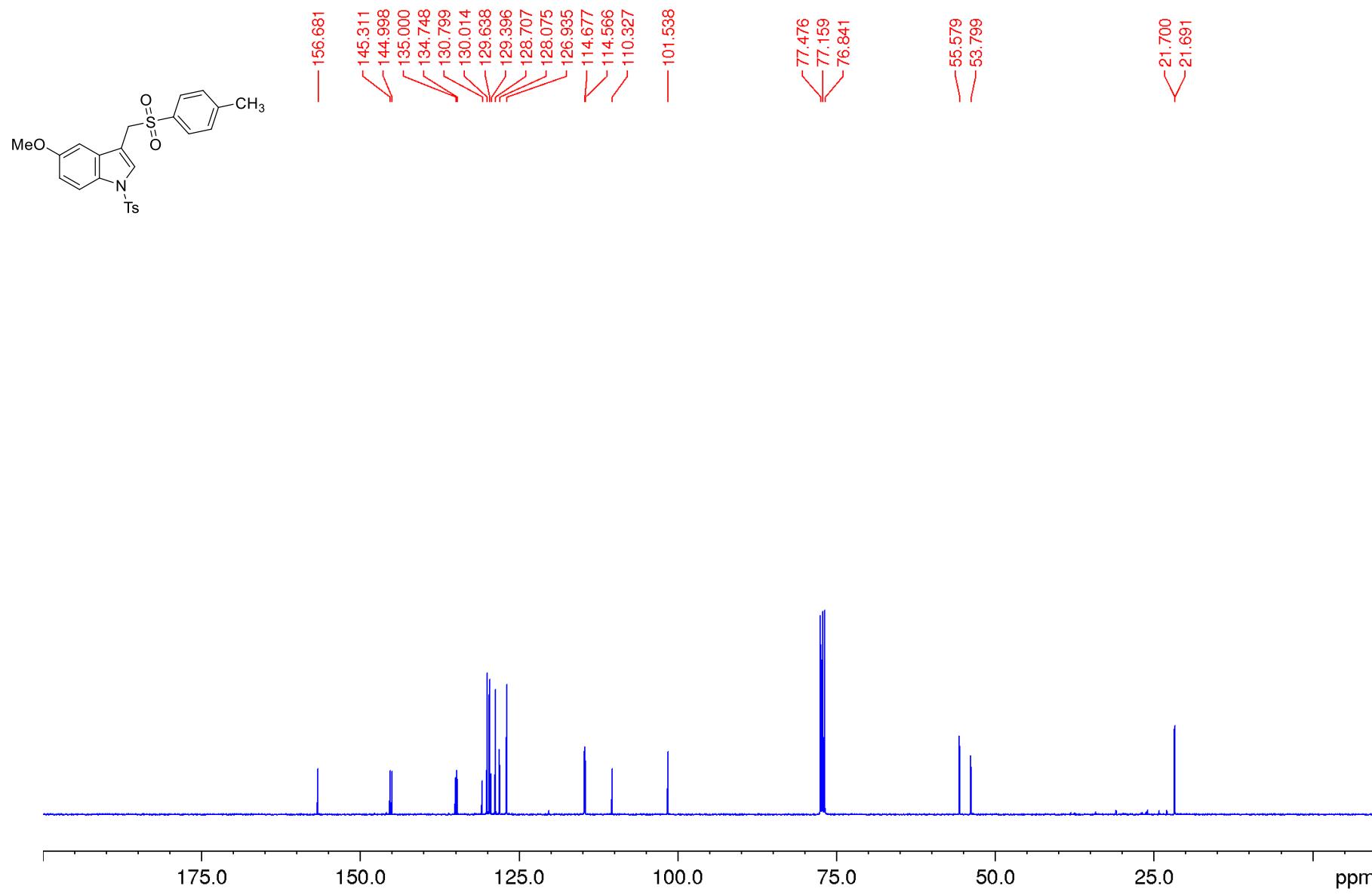
5-methoxy-1-tosyl-3-(tosylmethyl)-1*H*-indole **9da**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



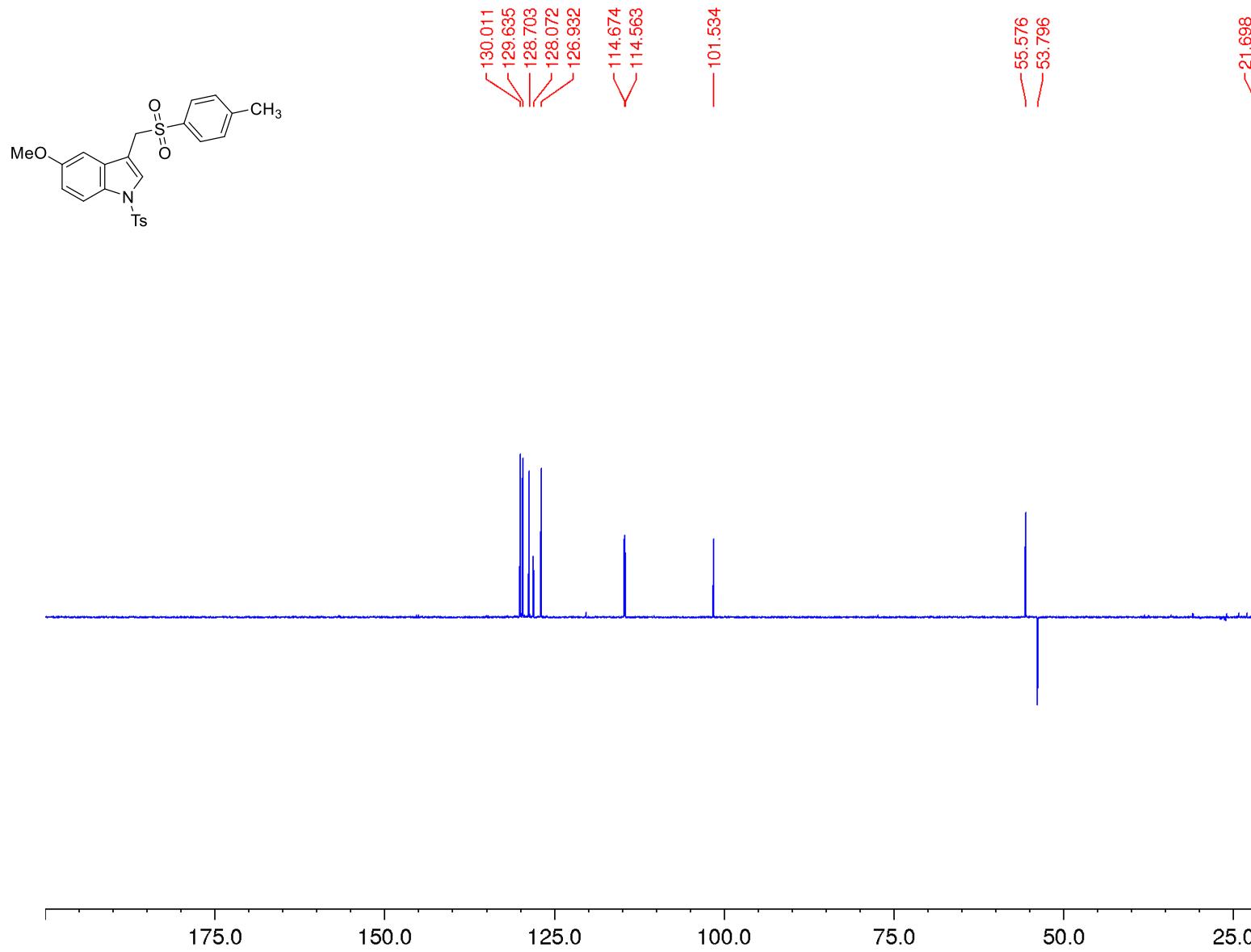
5-methoxy-1-tosyl-3-(tosylmethyl)-1*H*-indole **9da**

¹³C NMR-spectrum (100.6 MHz) (CDCl_3)



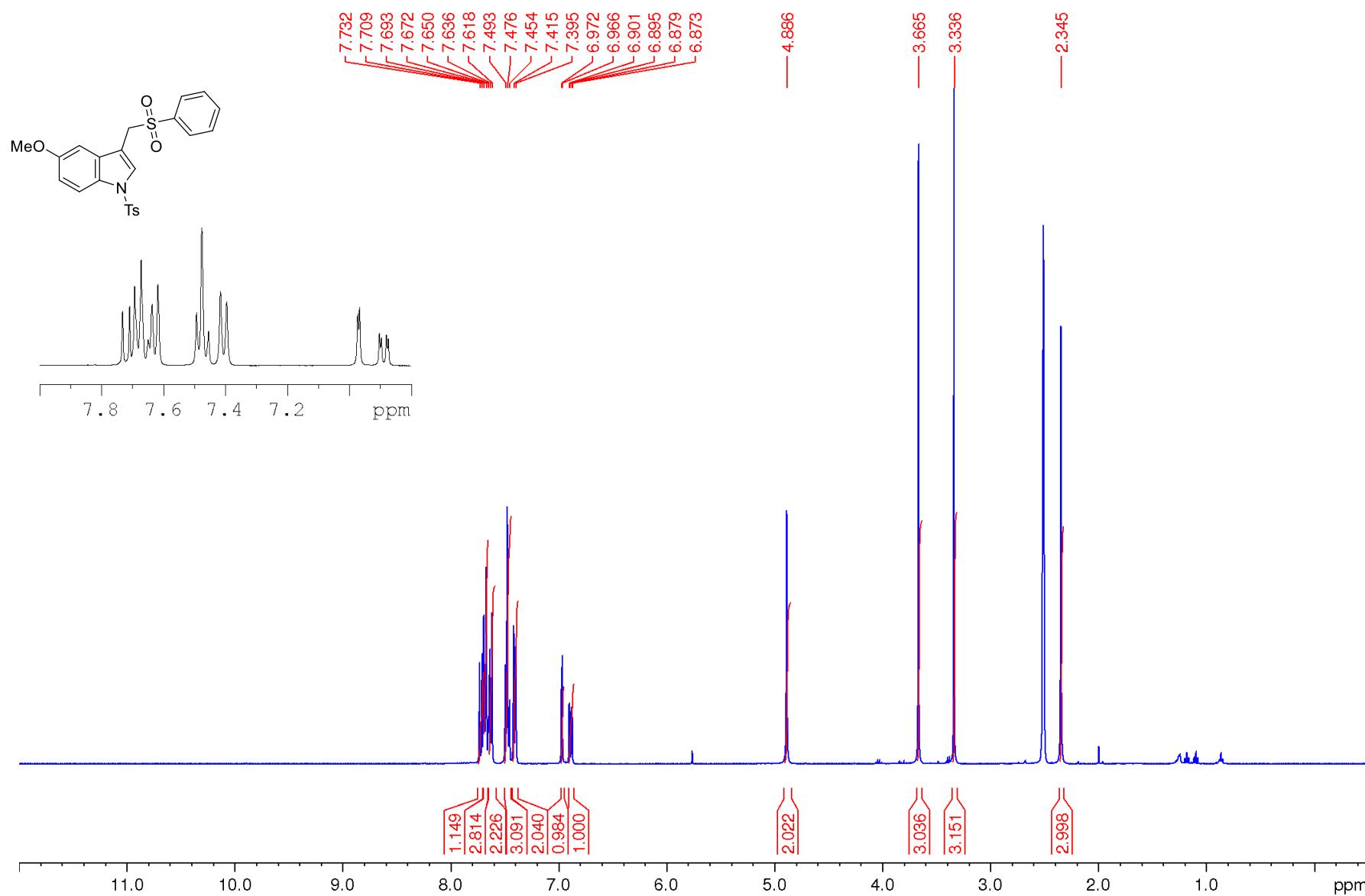
5-methoxy-1-tosyl-3-(tosylmethyl)-1*H*-indole **9da**

DEPT 135 NMR-spectrum (CDCl_3)

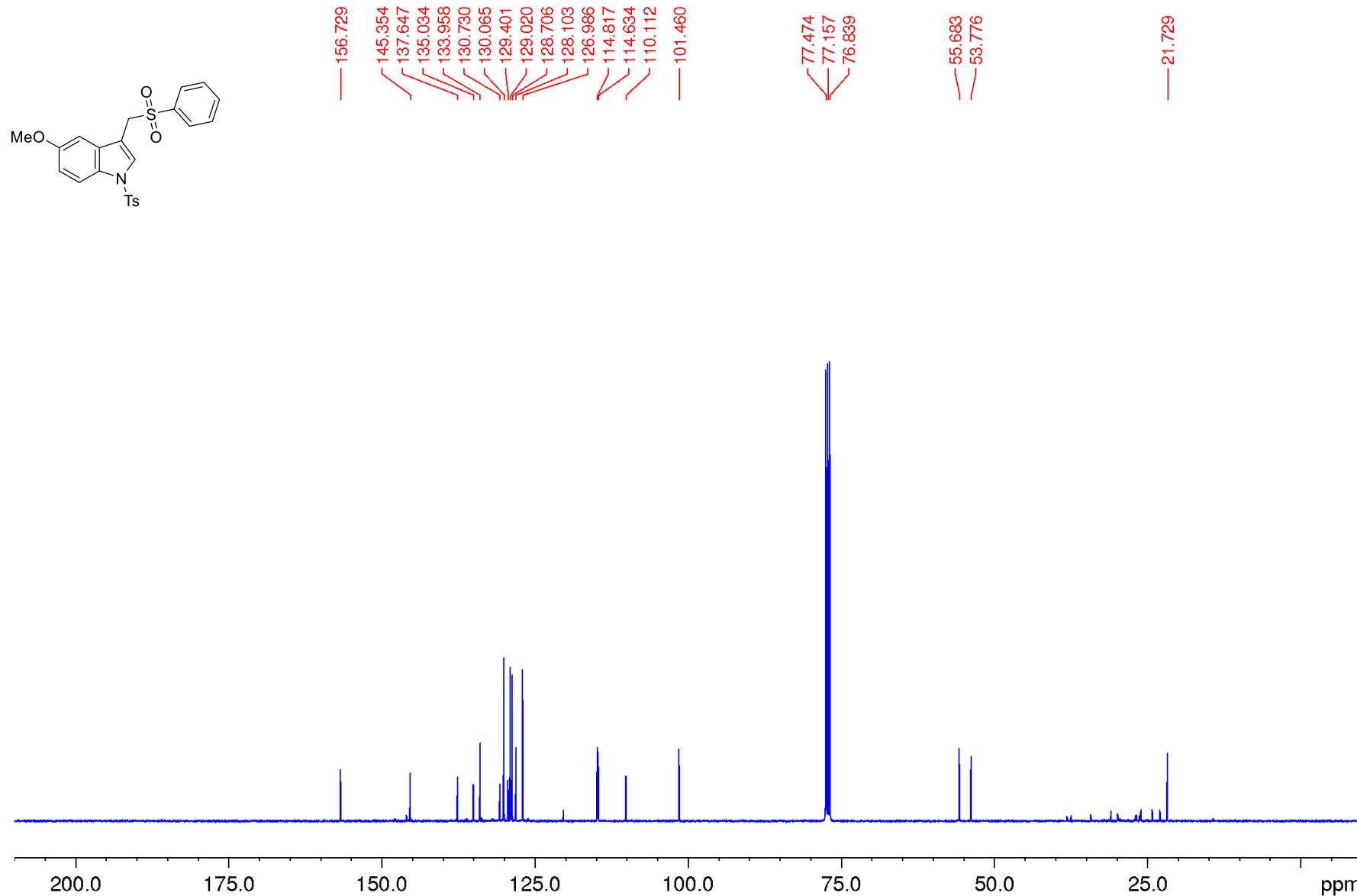


5-methoxy-3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9db**

¹H NMR-spectrum (400.13 MHz) (CDCl_3)

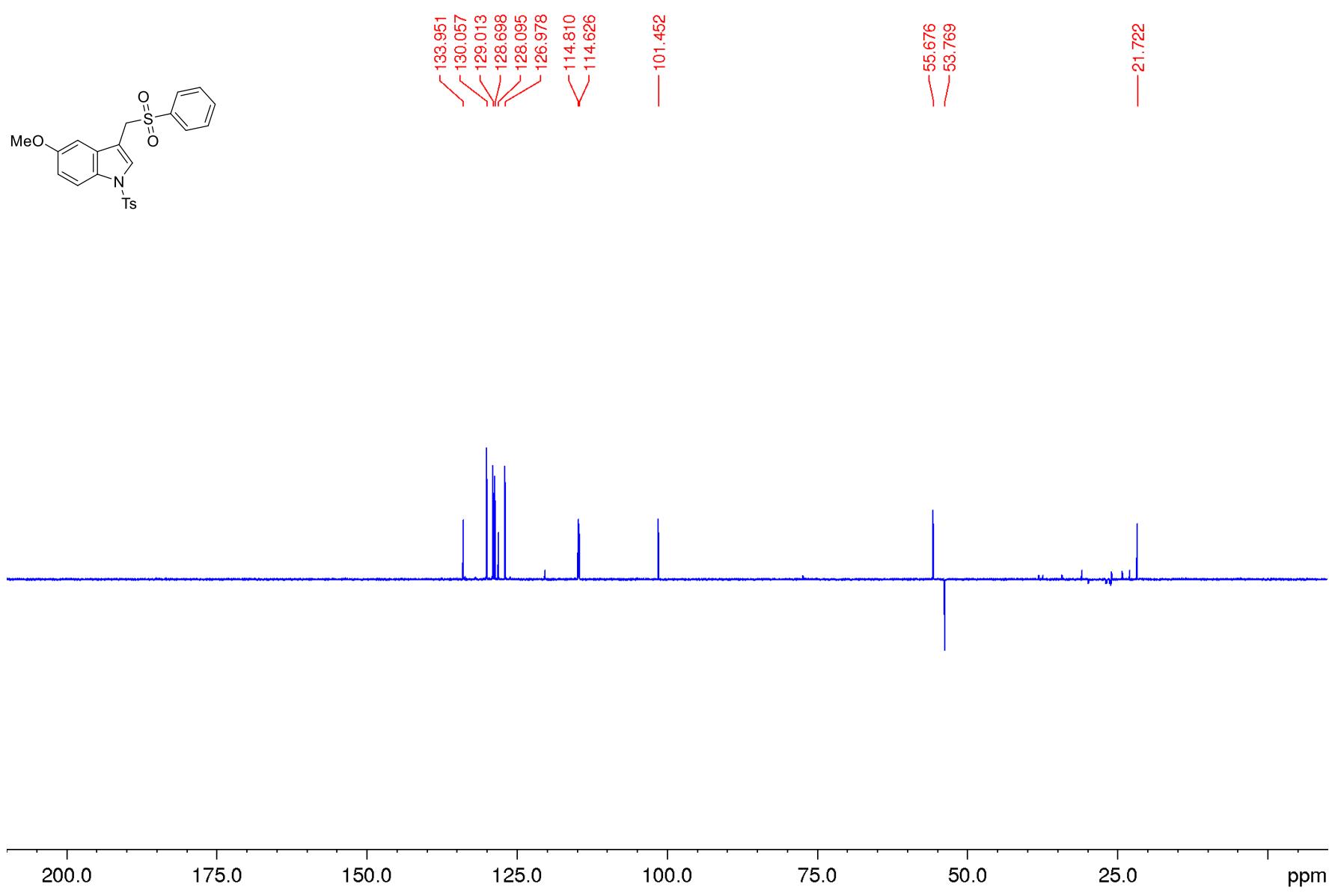


5-methoxy-3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9db**



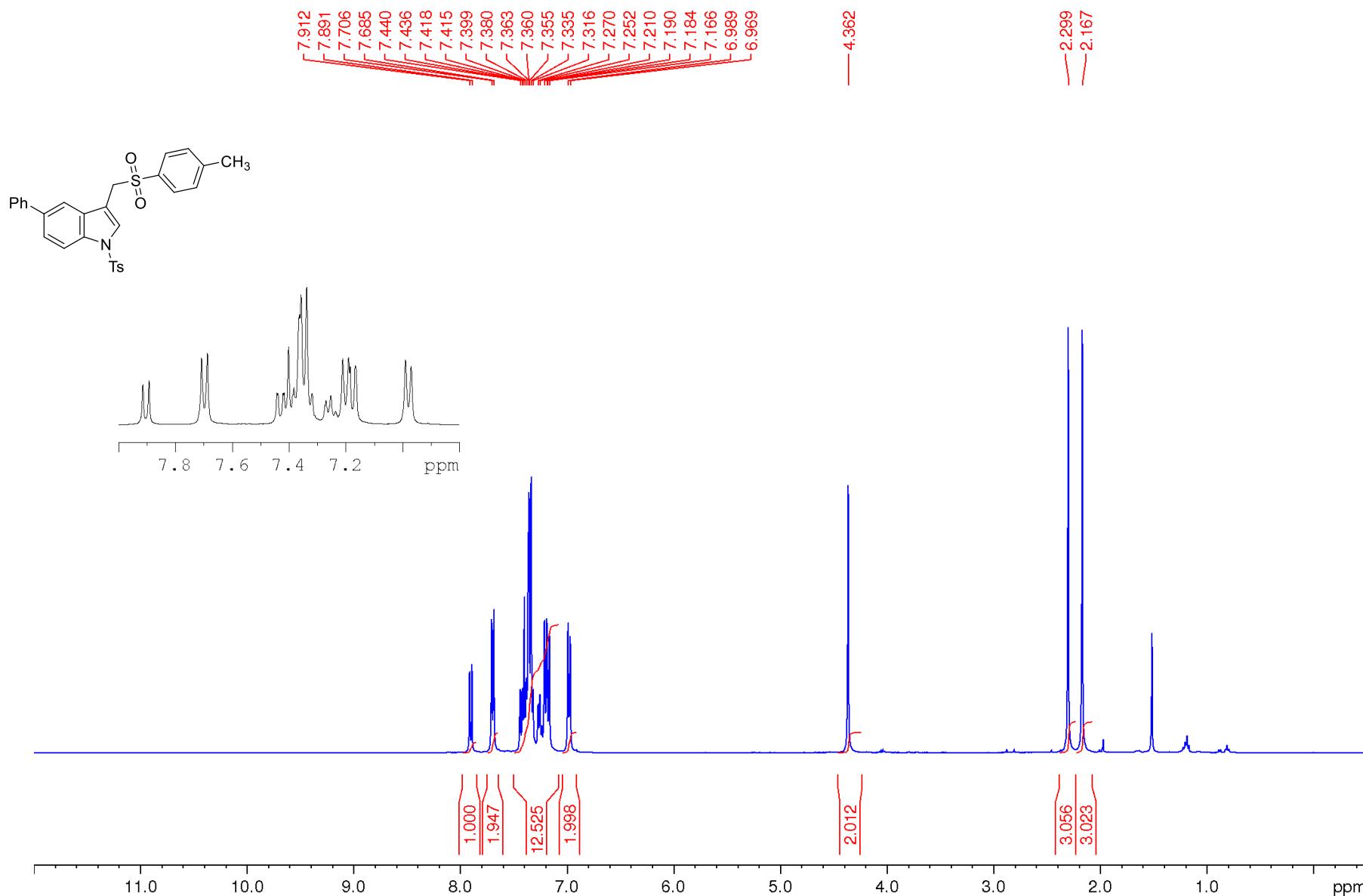
5-methoxy-3-((phenylsulfonyl)methyl)-1-tosyl-1*H*-indole **9db**

DEPT 135 NMR-spectrum (CDCl_3)

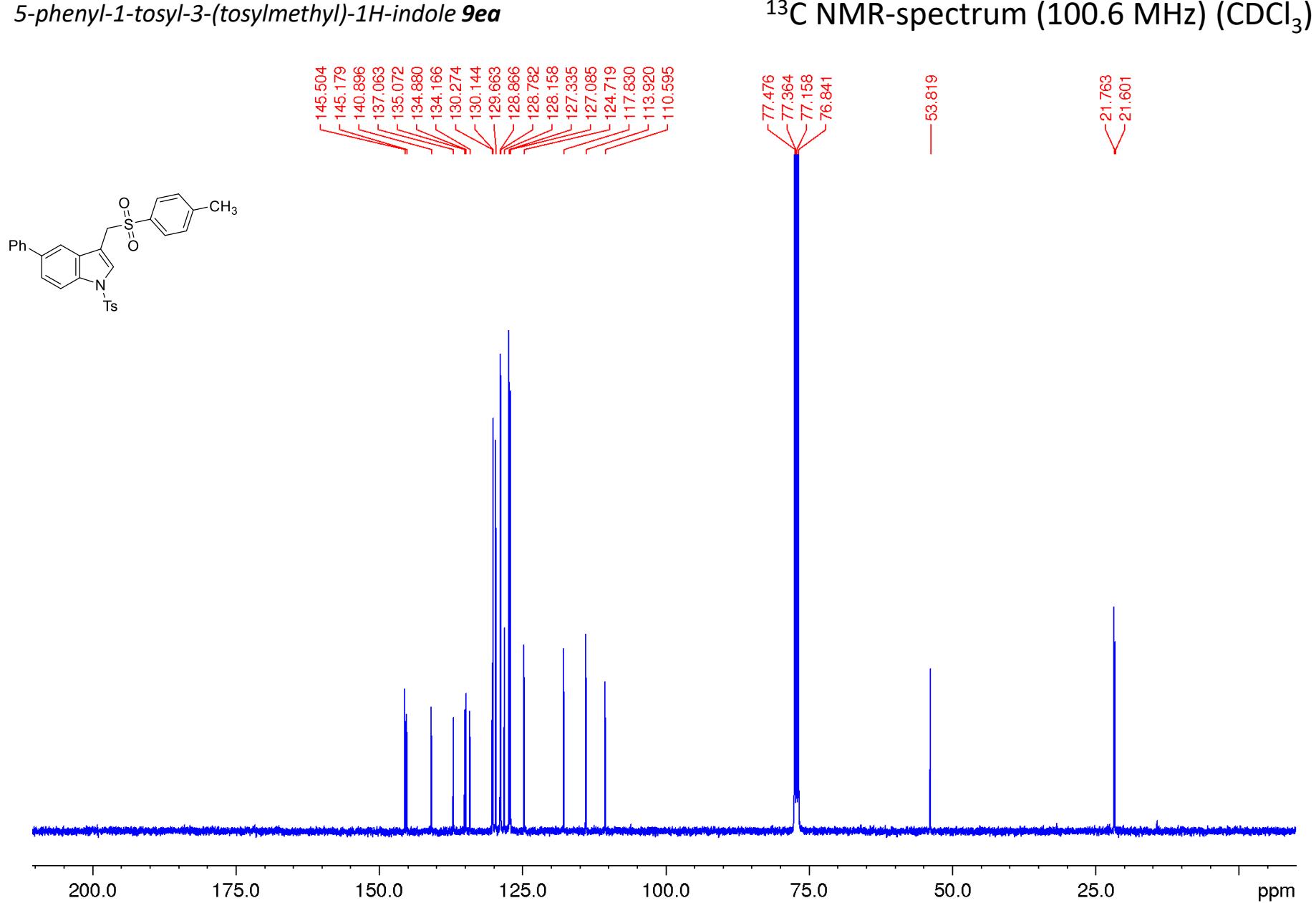


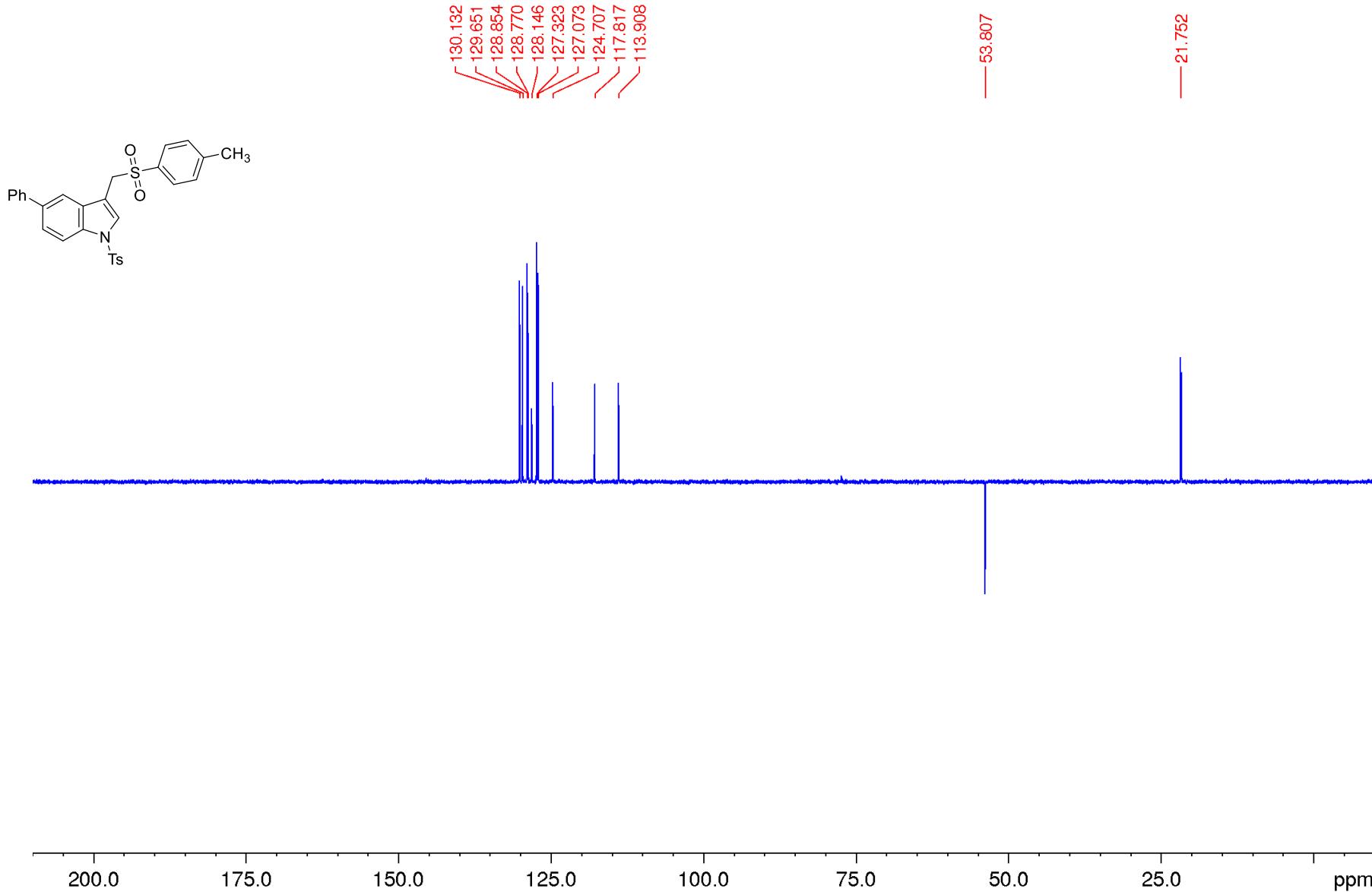
5-phenyl-1-tosyl-3-(tosylmethyl)-1H-indole 9ea

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



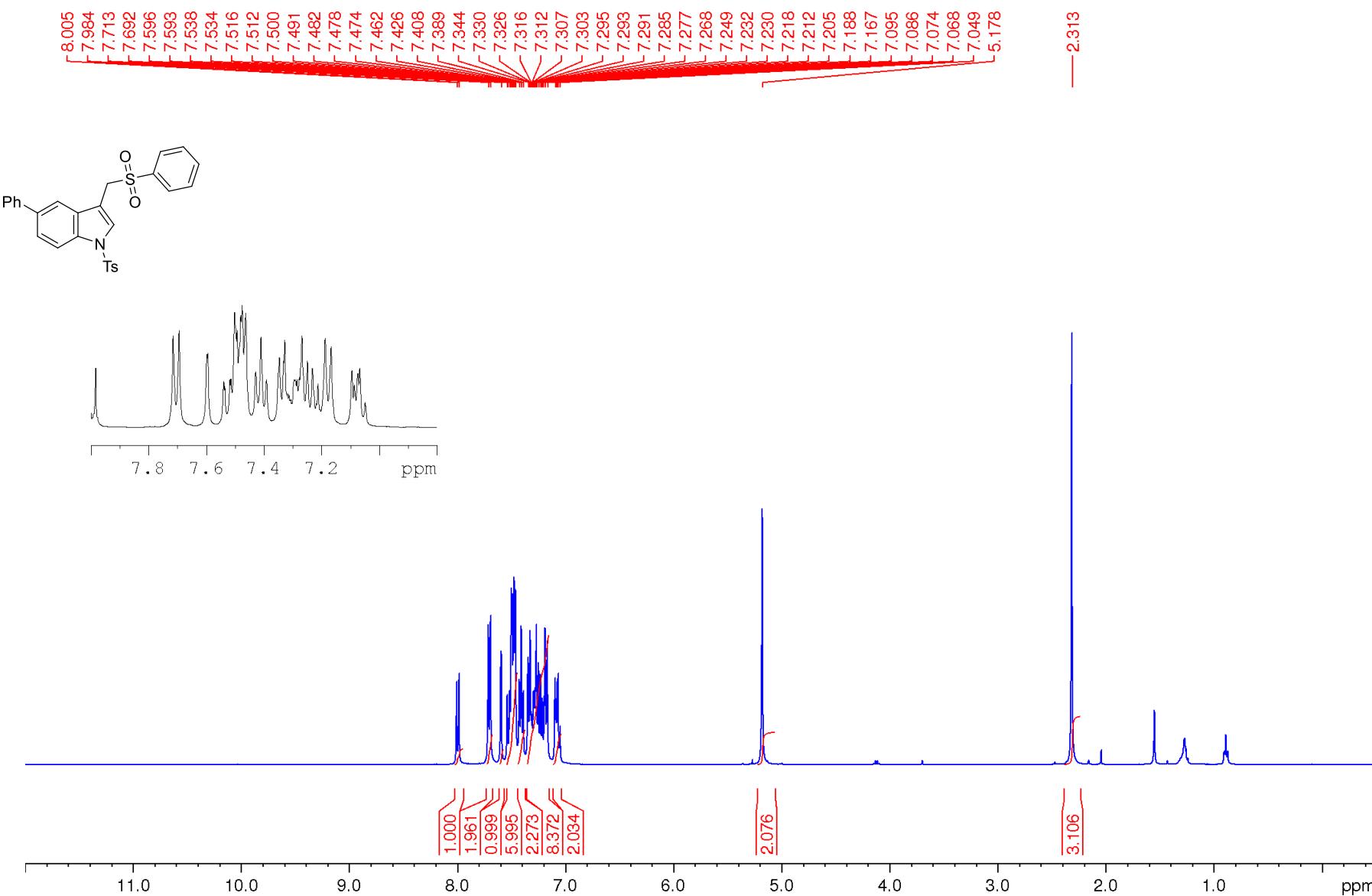
5-phenyl-1-tosyl-3-(tosylmethyl)-1H-indole 9ea



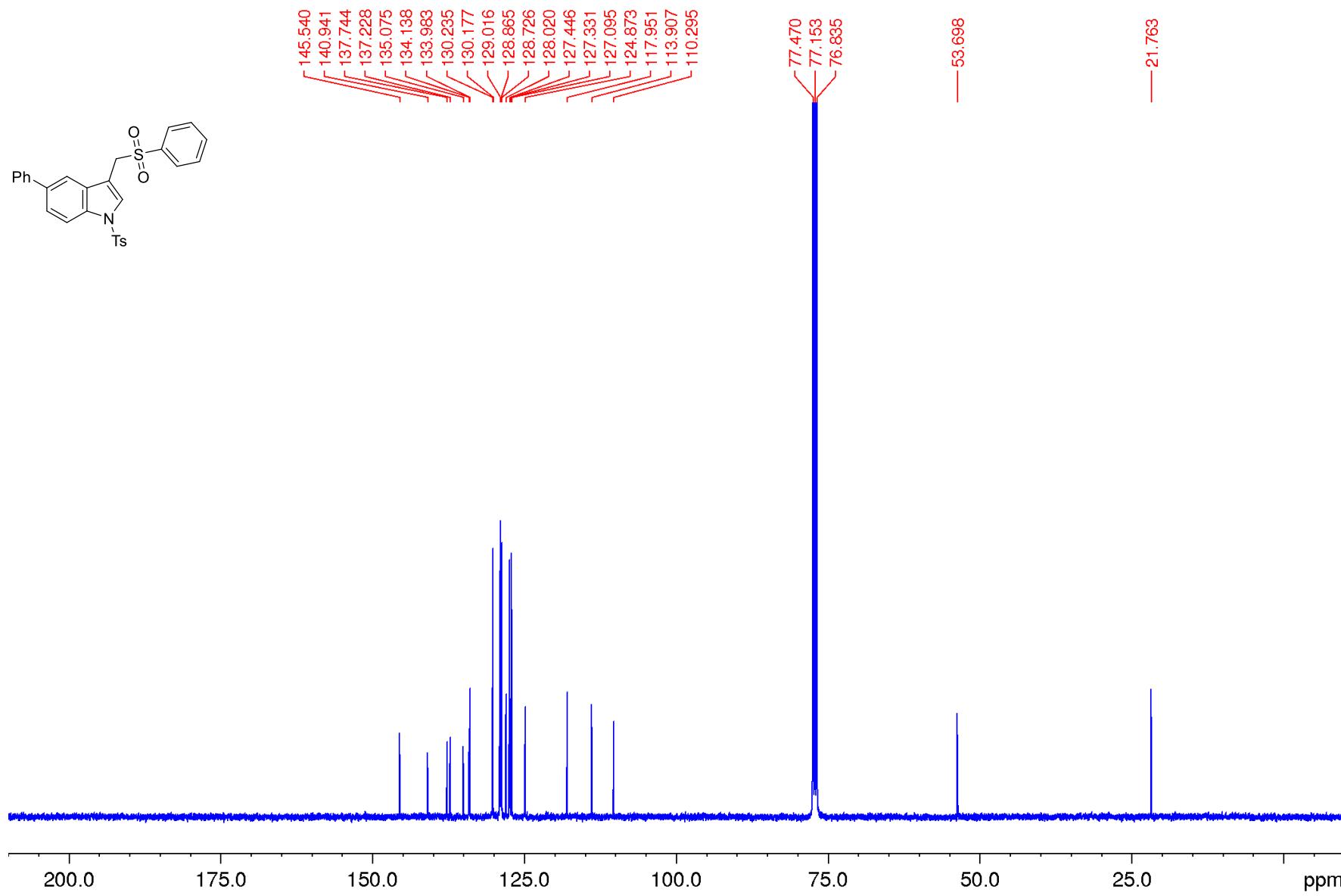


5-phenyl-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9eb

^1H NMR-spectrum (400.13 MHz) (CDCl_3)

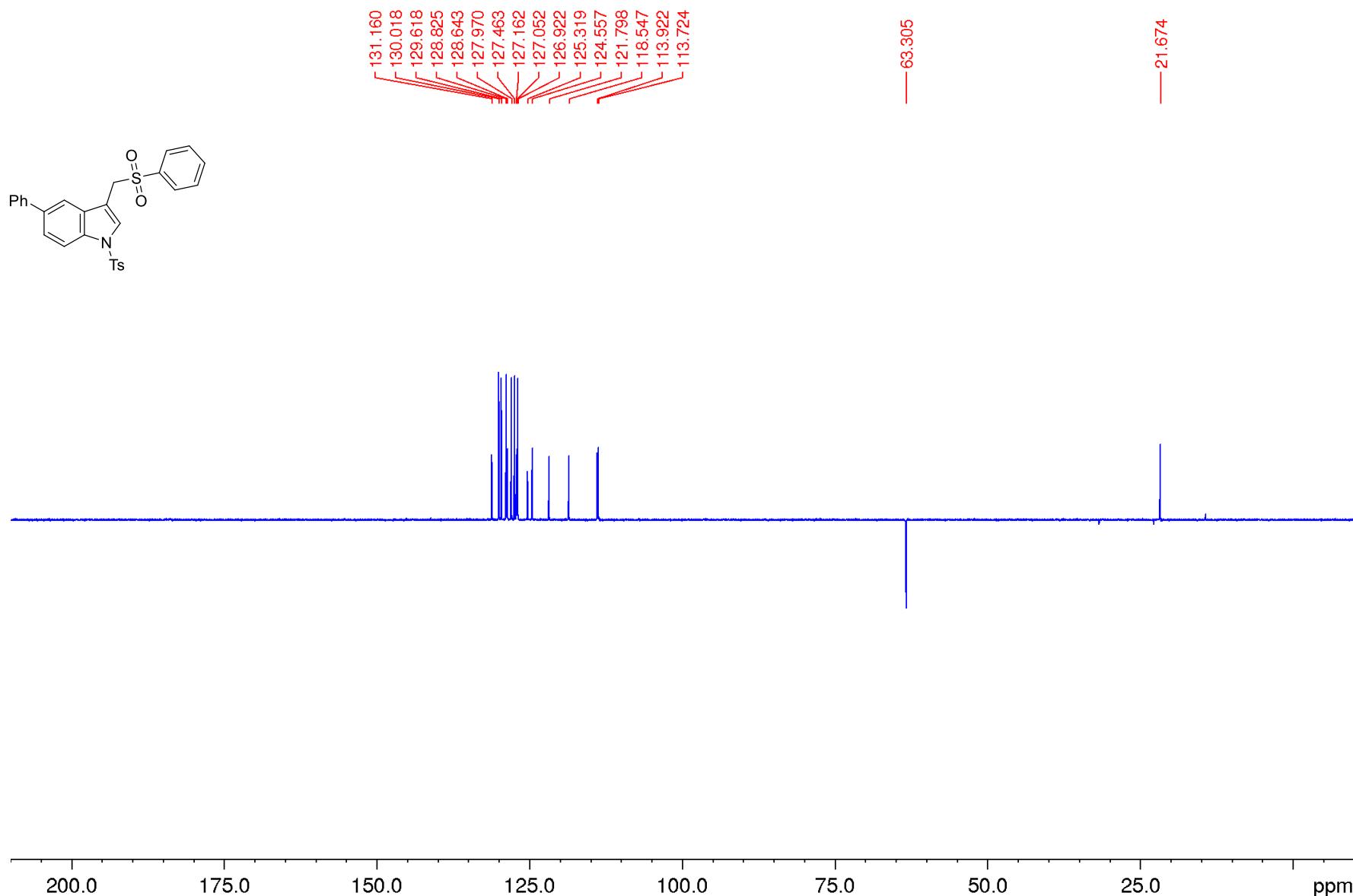


5-phenyl-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9eb



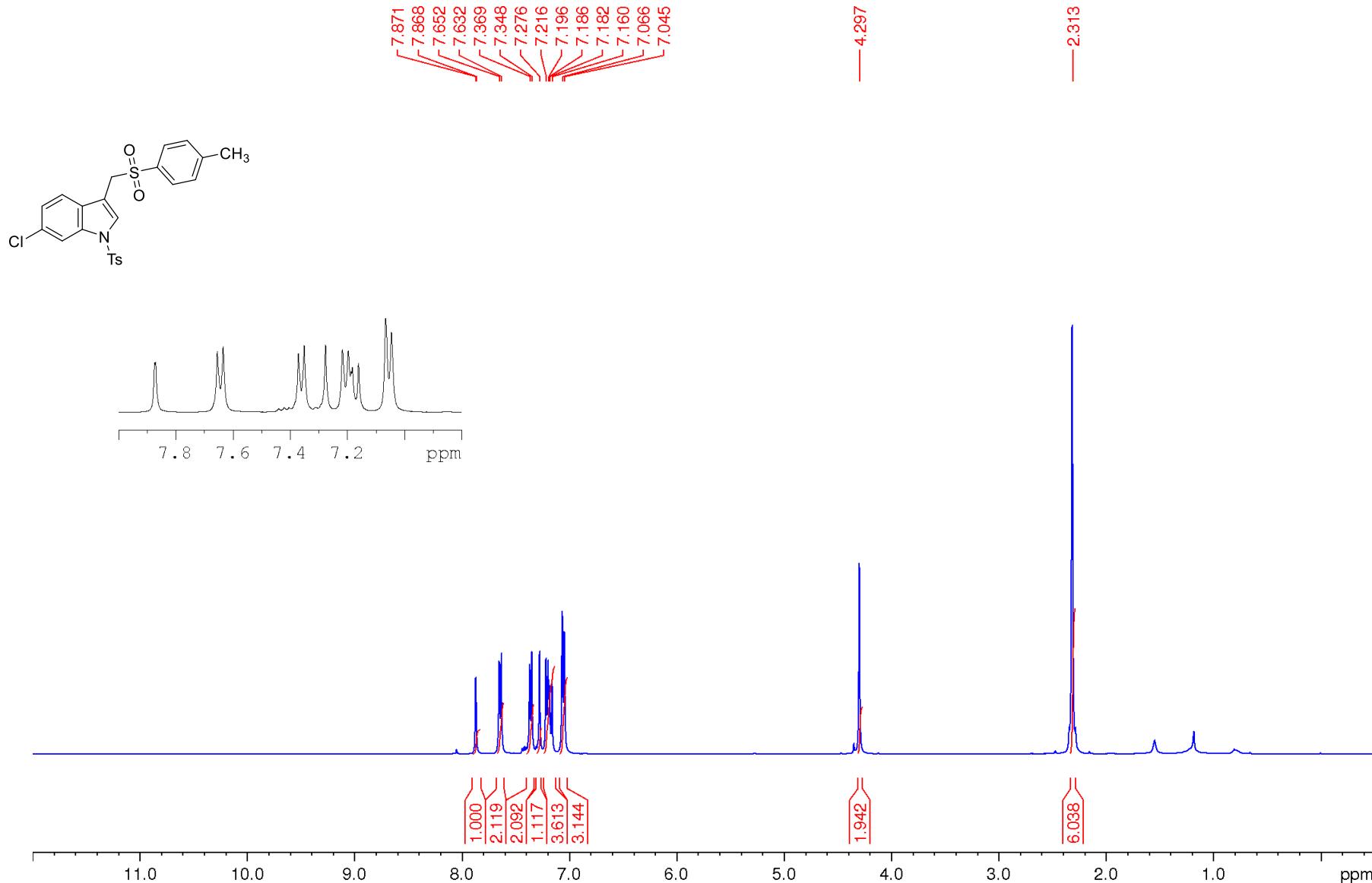
5-phenyl-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9eb

DEPT 135 NMR-spectrum (CDCl_3)



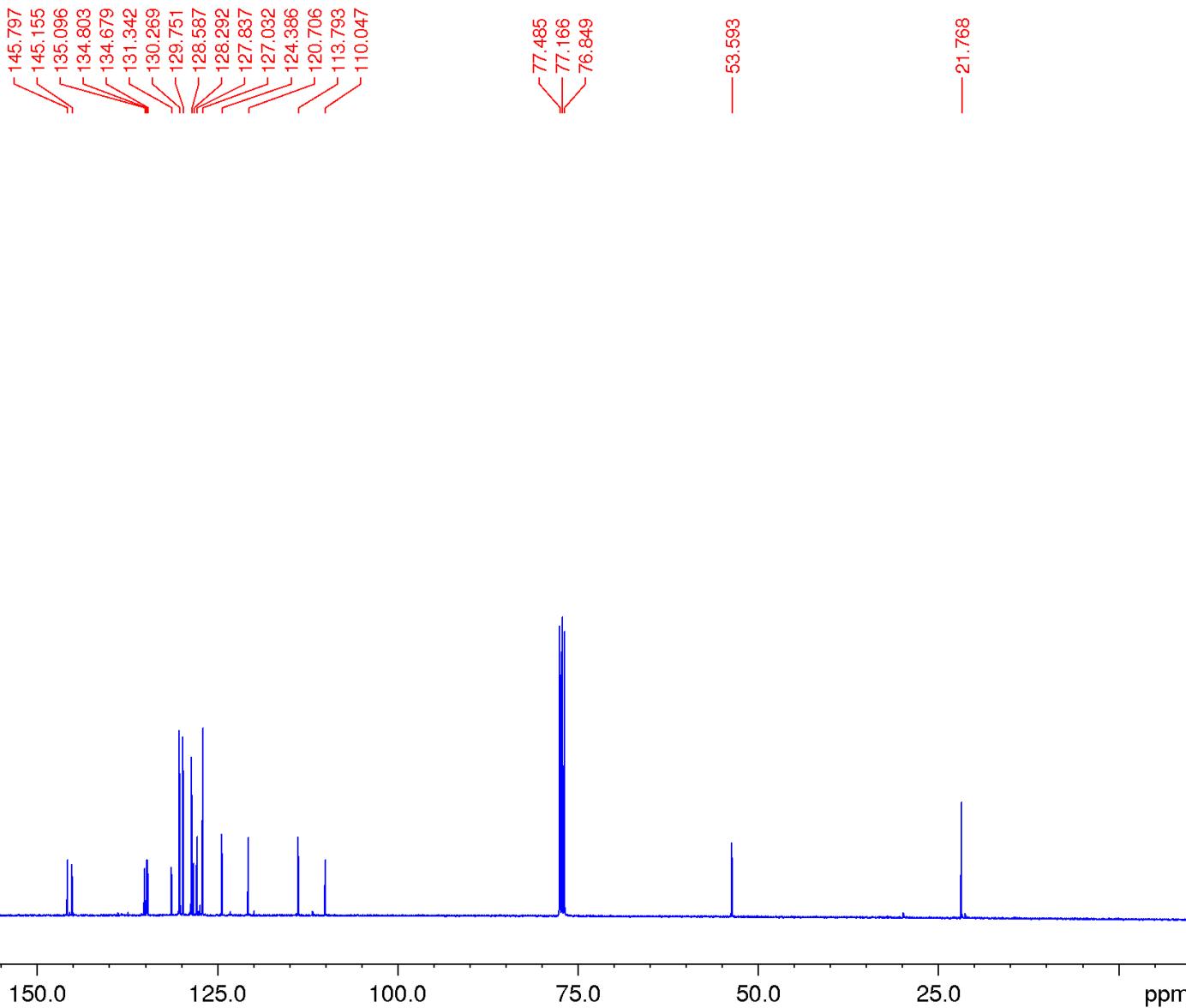
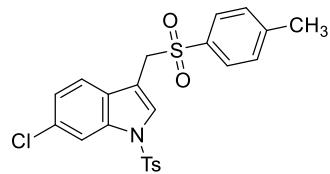
6-chloro-1-tosyl-3-(tosylmethyl)-1H-indole 9fa

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



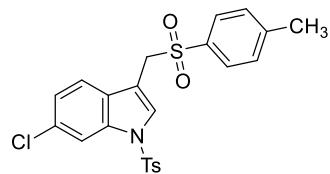
6-chloro-1-tosyl-3-(tosylmethyl)-1H-indole 9fa

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



6-chloro-1-tosyl-3-(tosylmethyl)-1H-indole 9fa

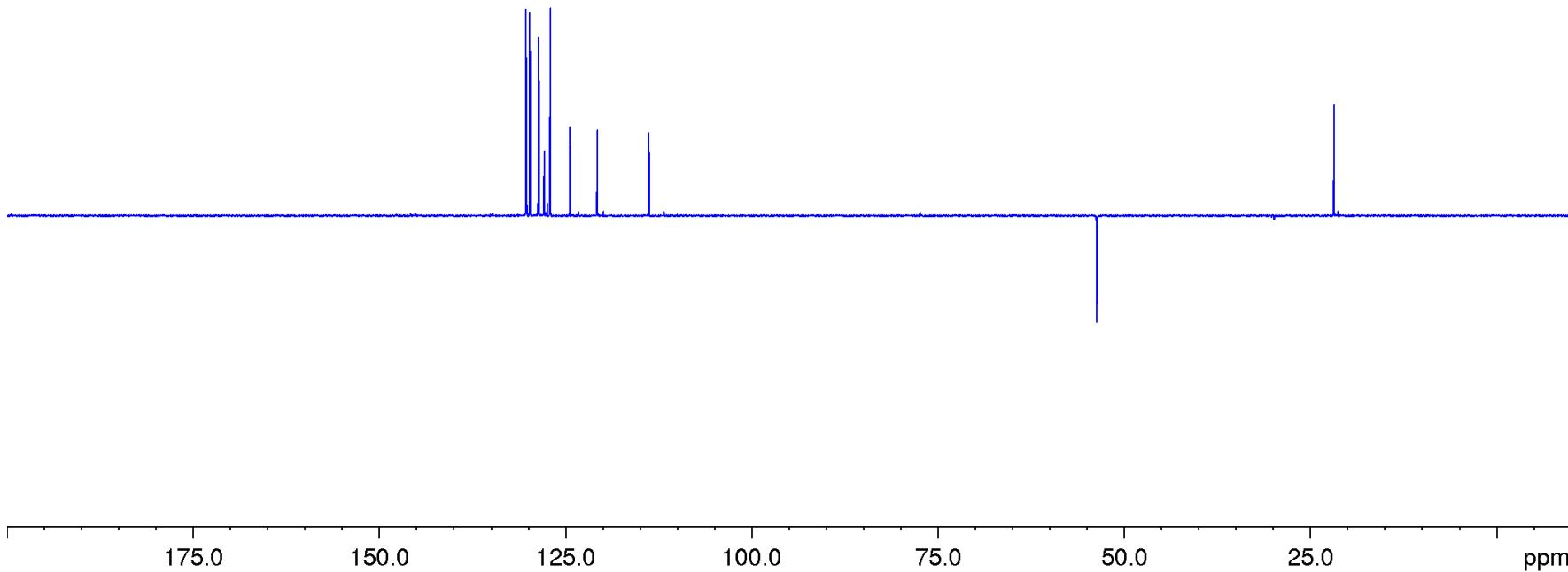
DEPT 135 NMR-spectrum (CDCl_3)



130.265
129.747
128.582
127.833
127.028
124.382
120.702
113.788

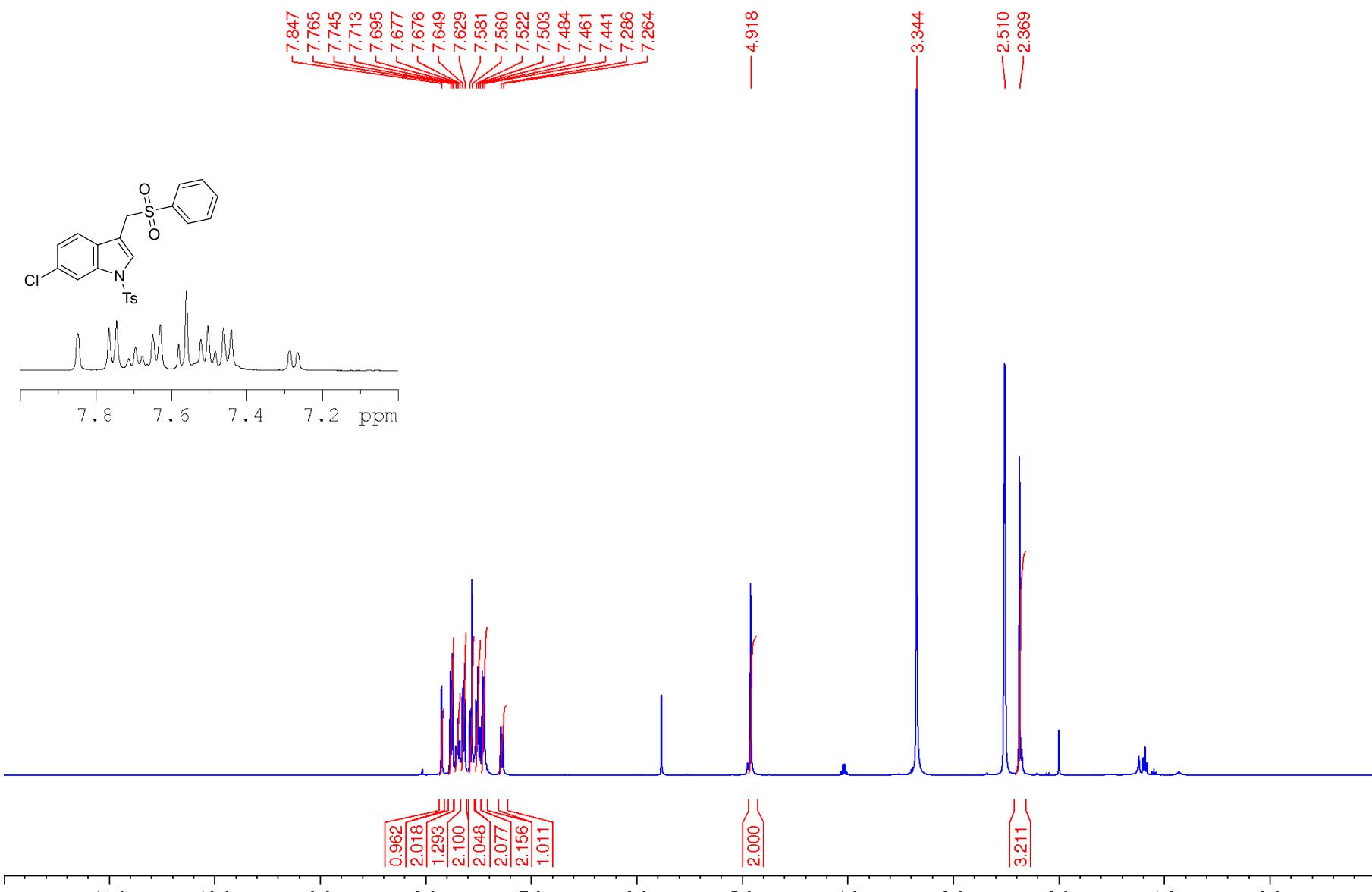
53.589

21.765



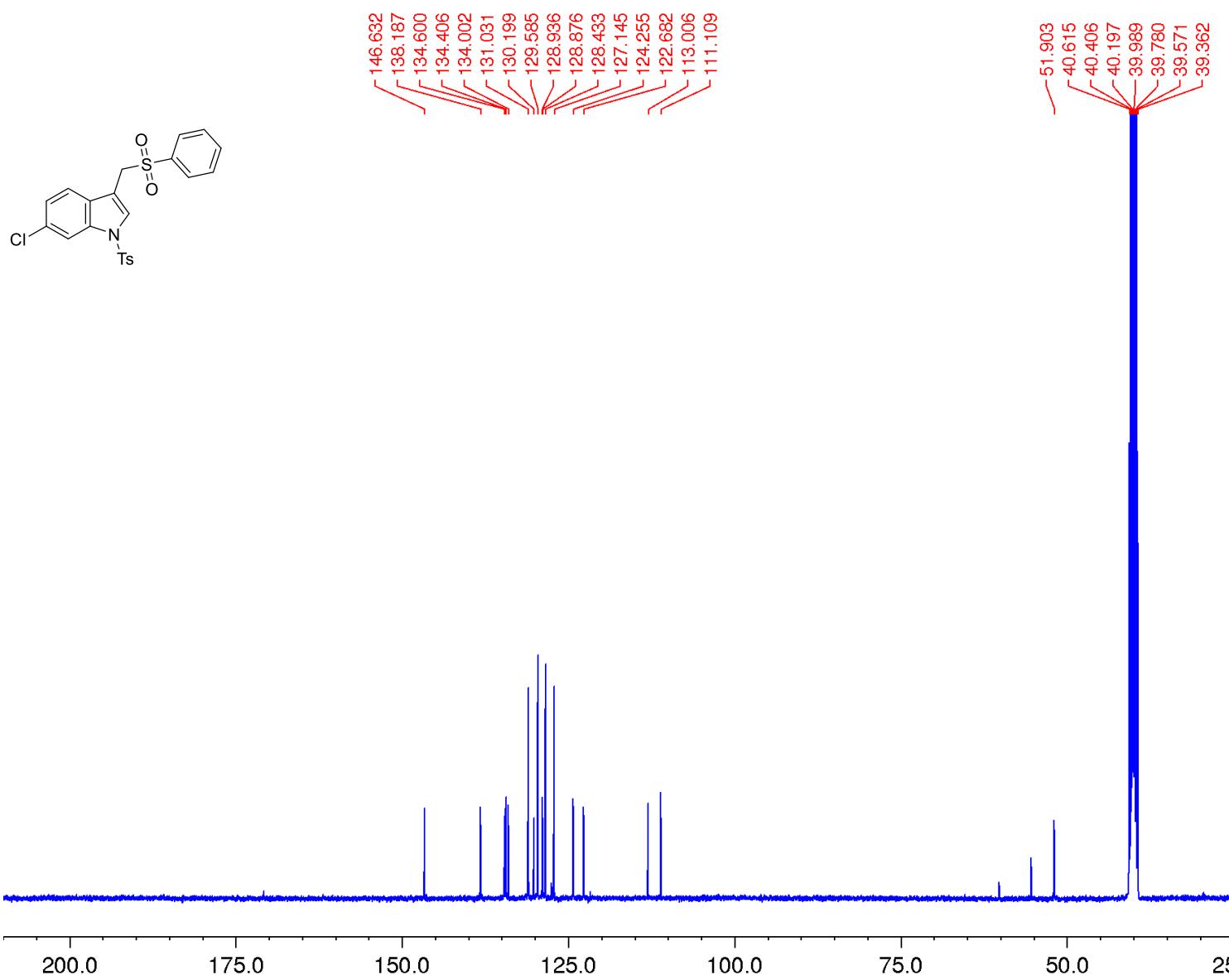
6-chloro-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9fb

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



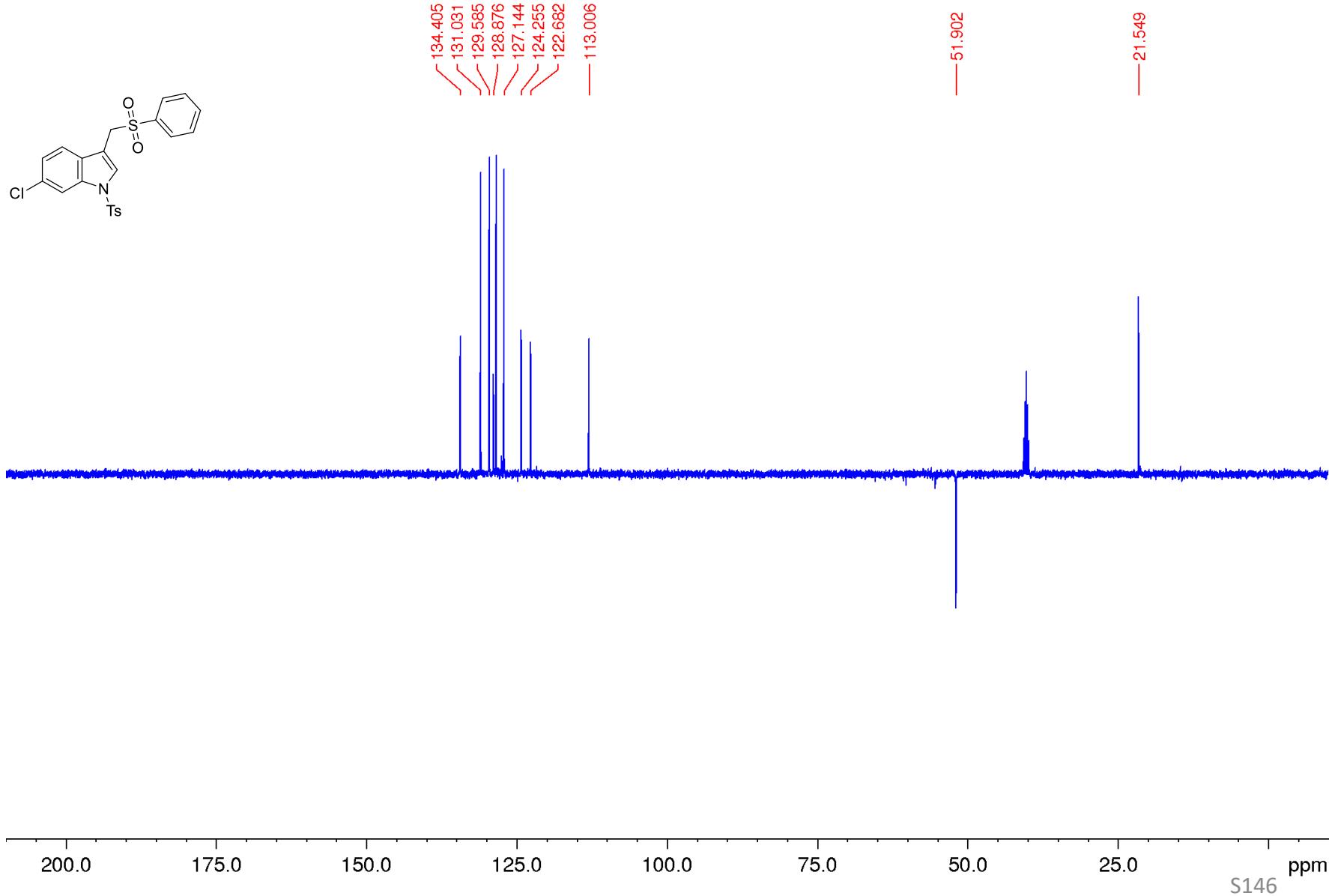
6-chloro-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9fb

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



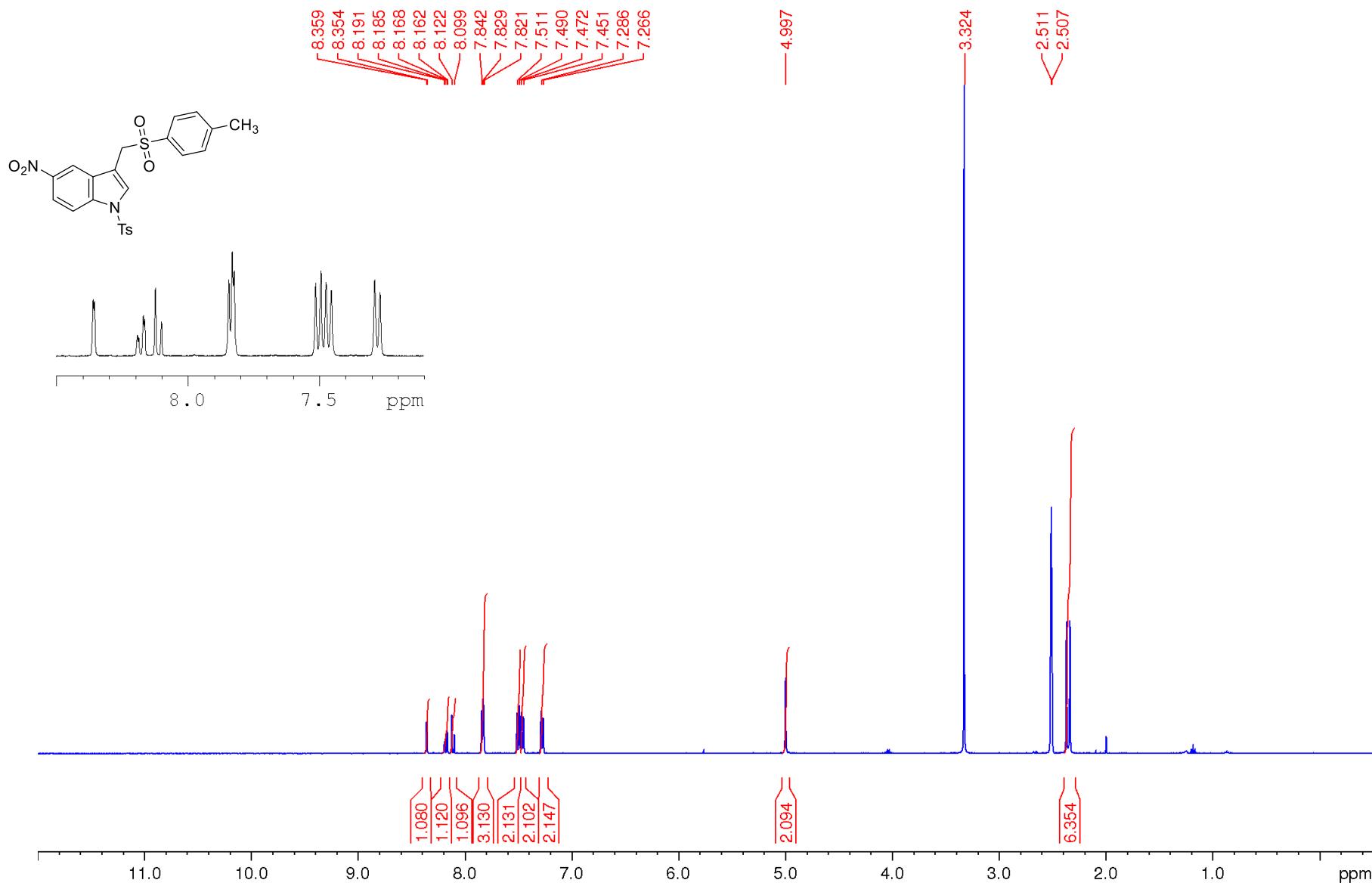
6-chloro-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9fb

DEPT 135 NMR-spectrum (CDCl_3)



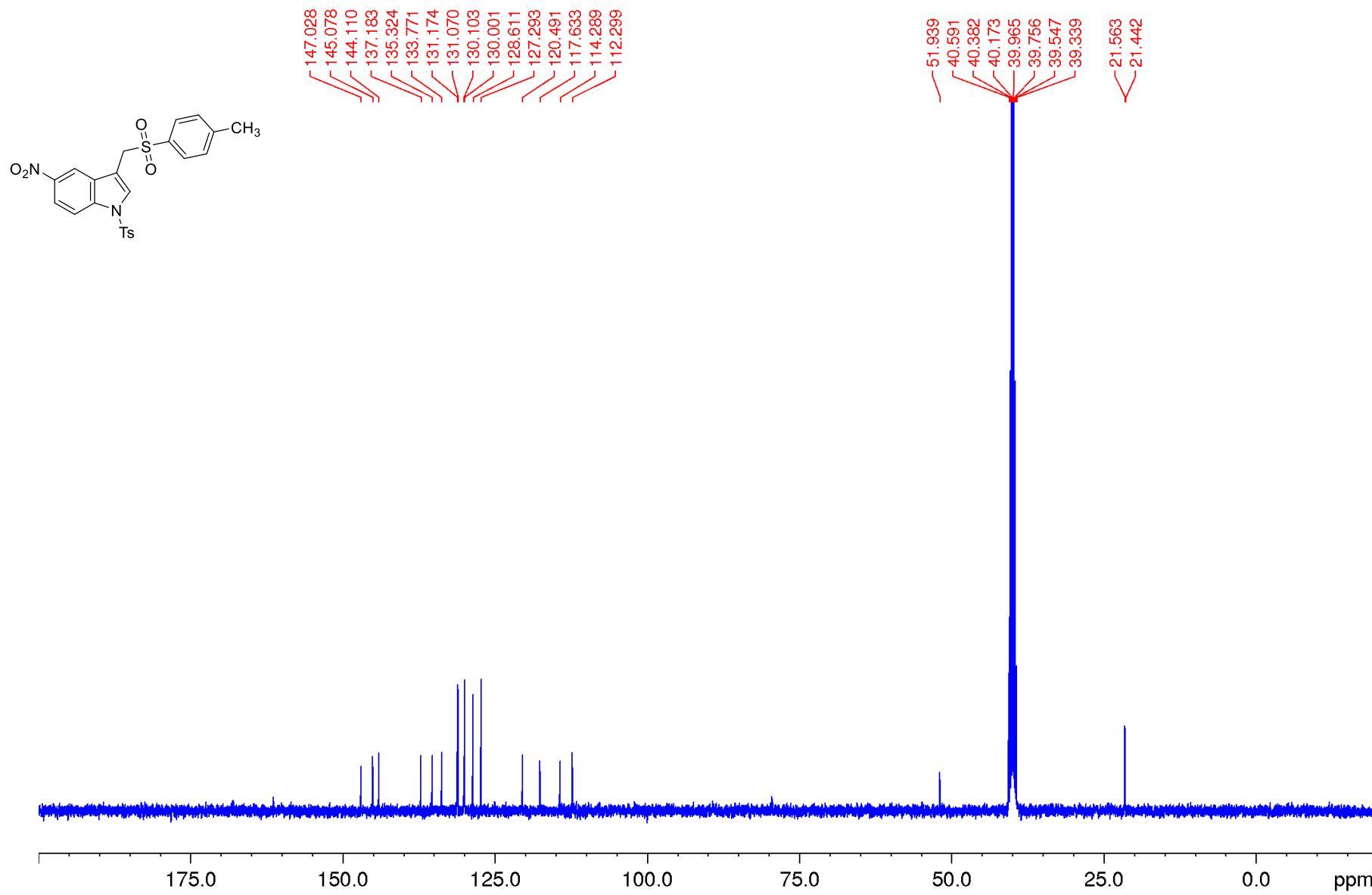
5-nitro-1-tosyl-3-(tosylmethyl)-1H-indole 9ga

^1H NMR-spectrum (400.13 MHz) (CDCl_3)



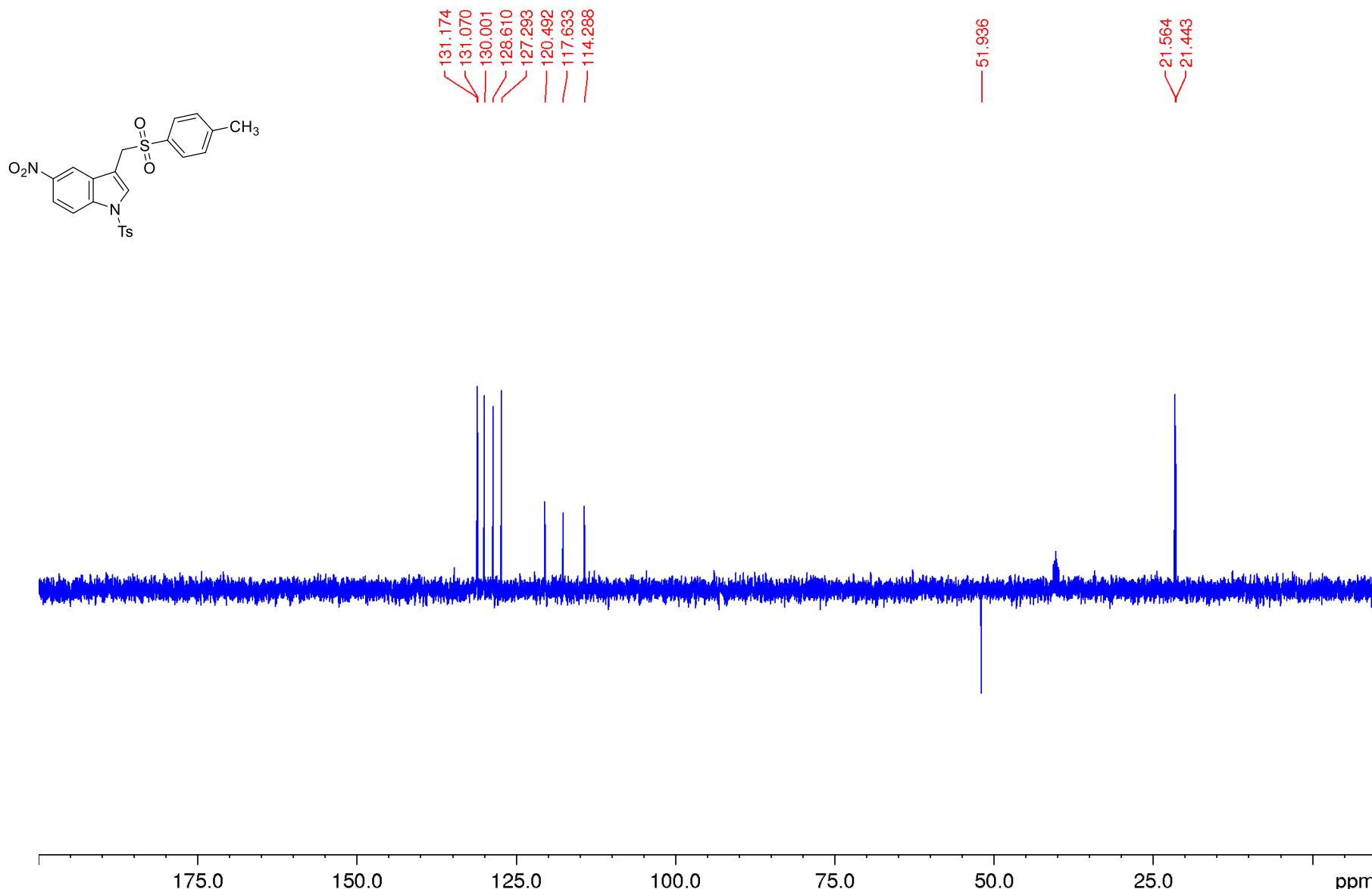
5-nitro-1-tosyl-3-(tosylmethyl)-1H-indole 9ga

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



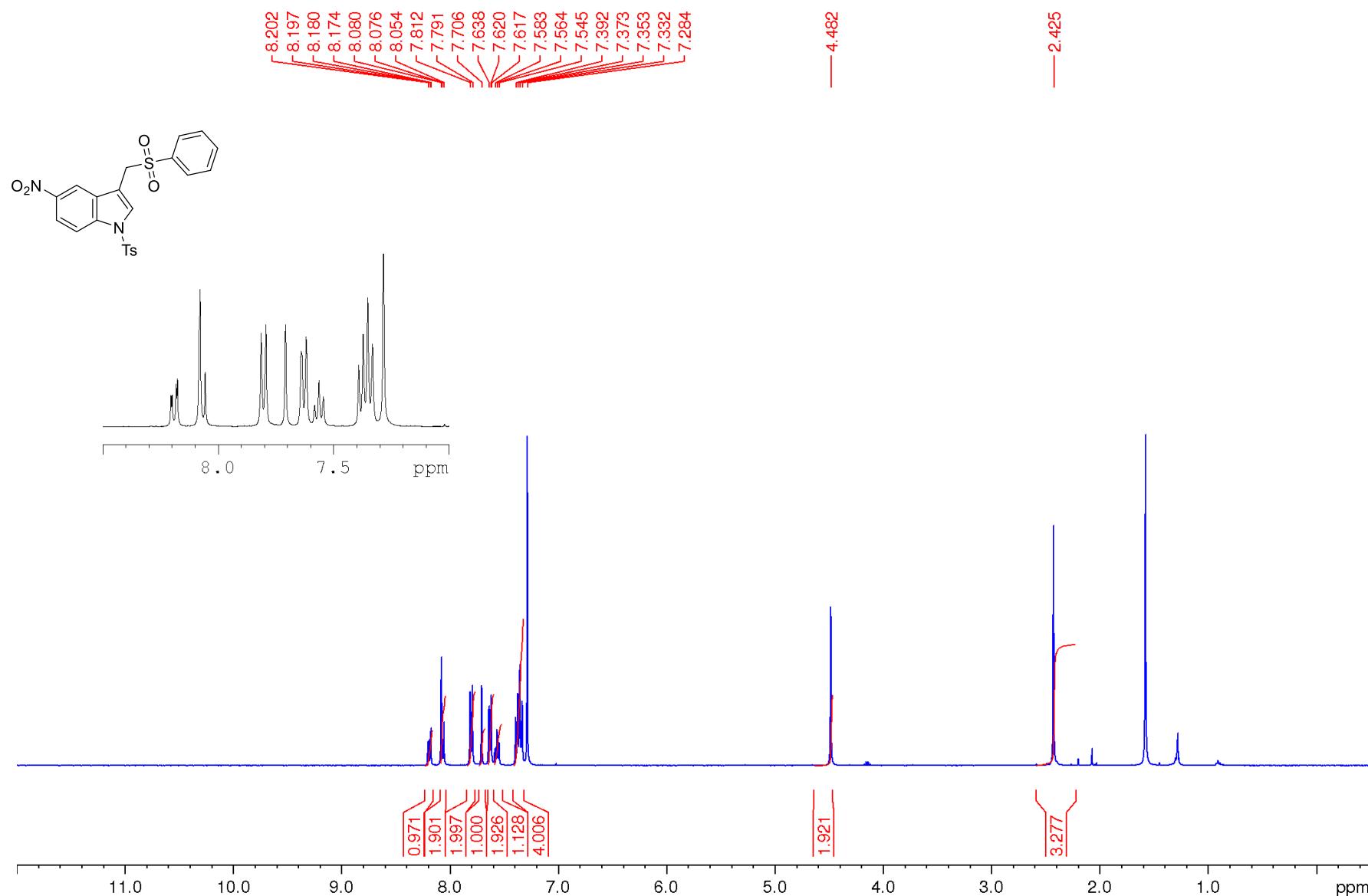
5-nitro-1-tosyl-3-(tosylmethyl)-1H-indole 9ga

DEPT 135 NMR-spectrum (CDCl_3)



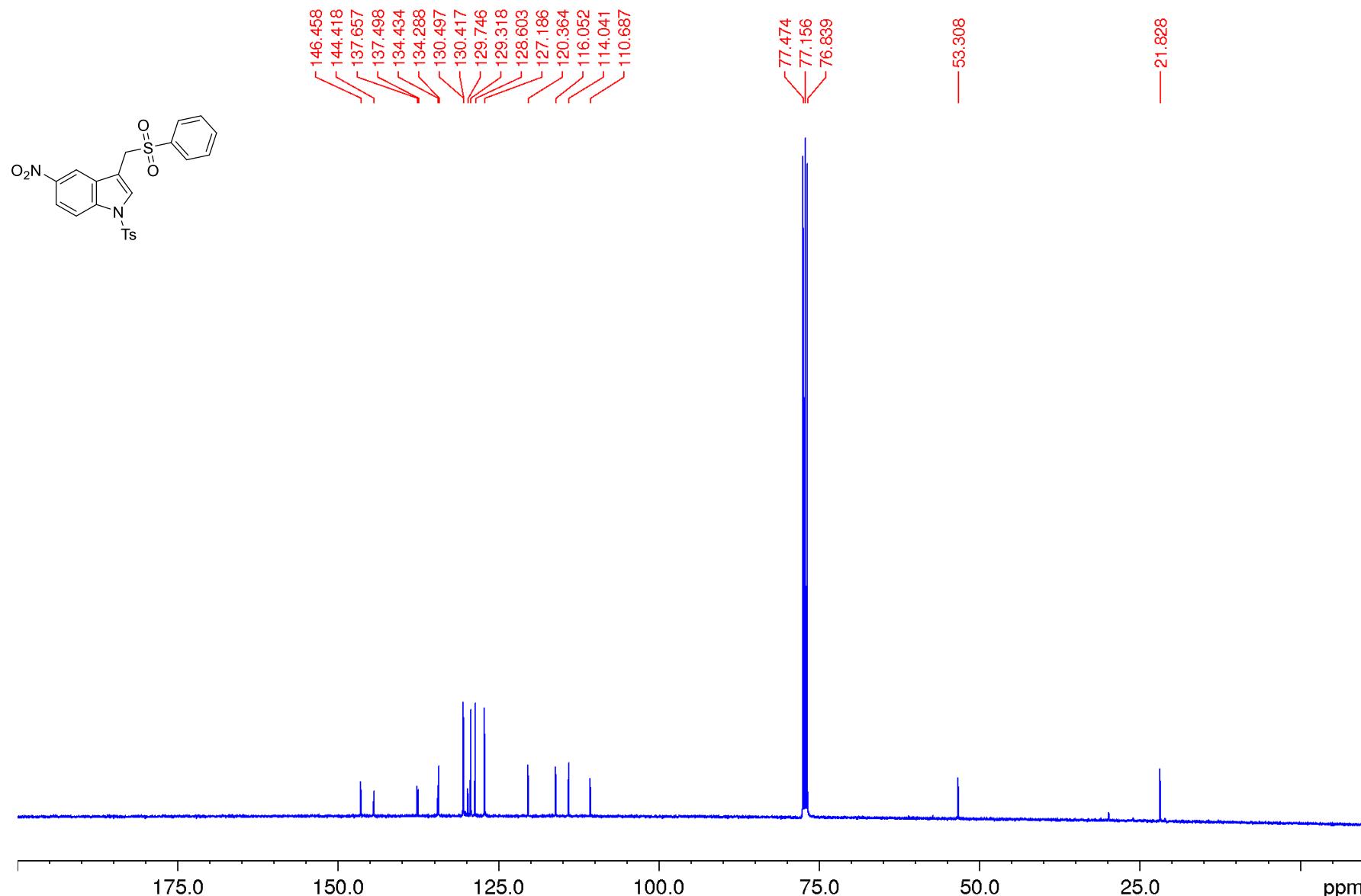
5-nitro-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9gb

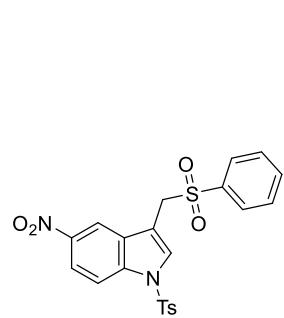
^1H NMR-spectrum (400.13 MHz) (CDCl_3)



5-nitro-3-((phenylsulfonyl)methyl)-1-tosyl-1H-indole 9gb

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)

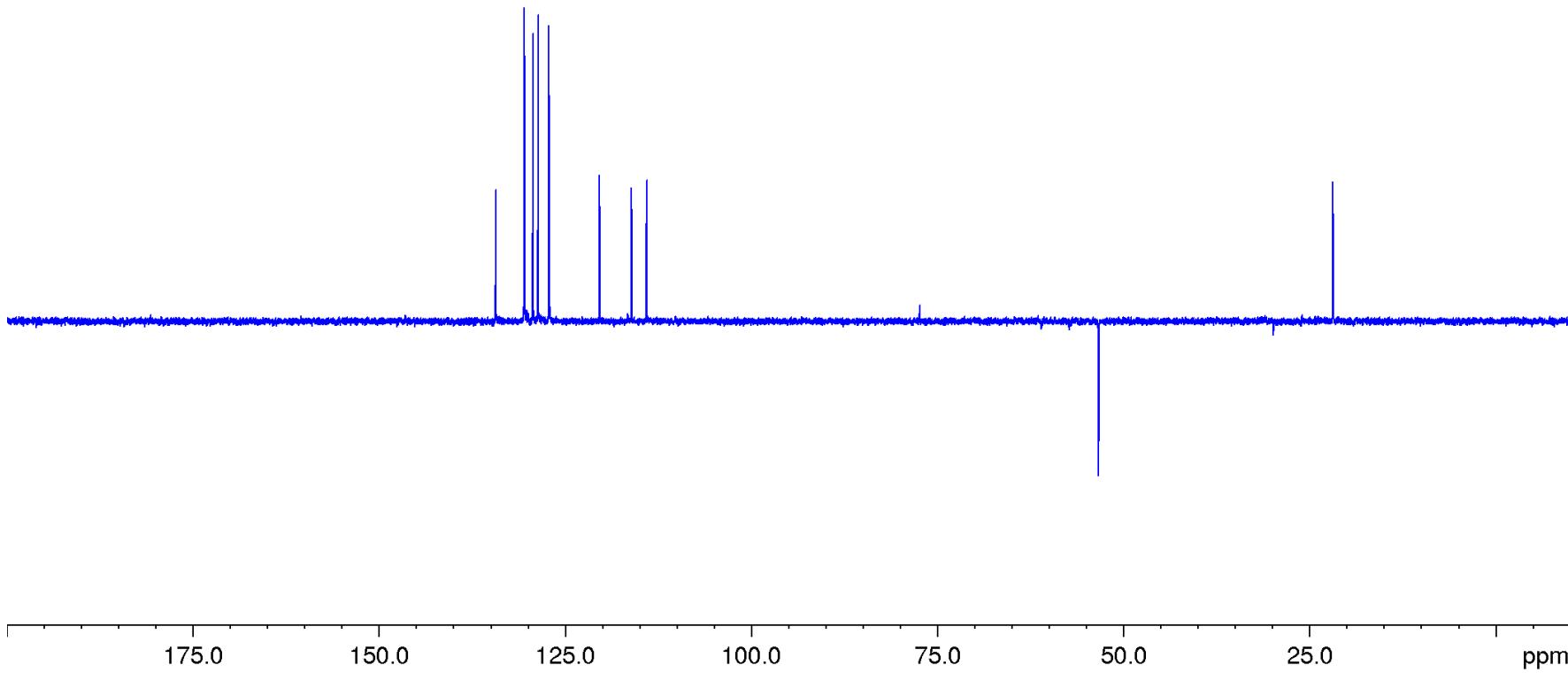




134.286
130.495
129.316
128.601
127.184
120.362
116.051
114.039

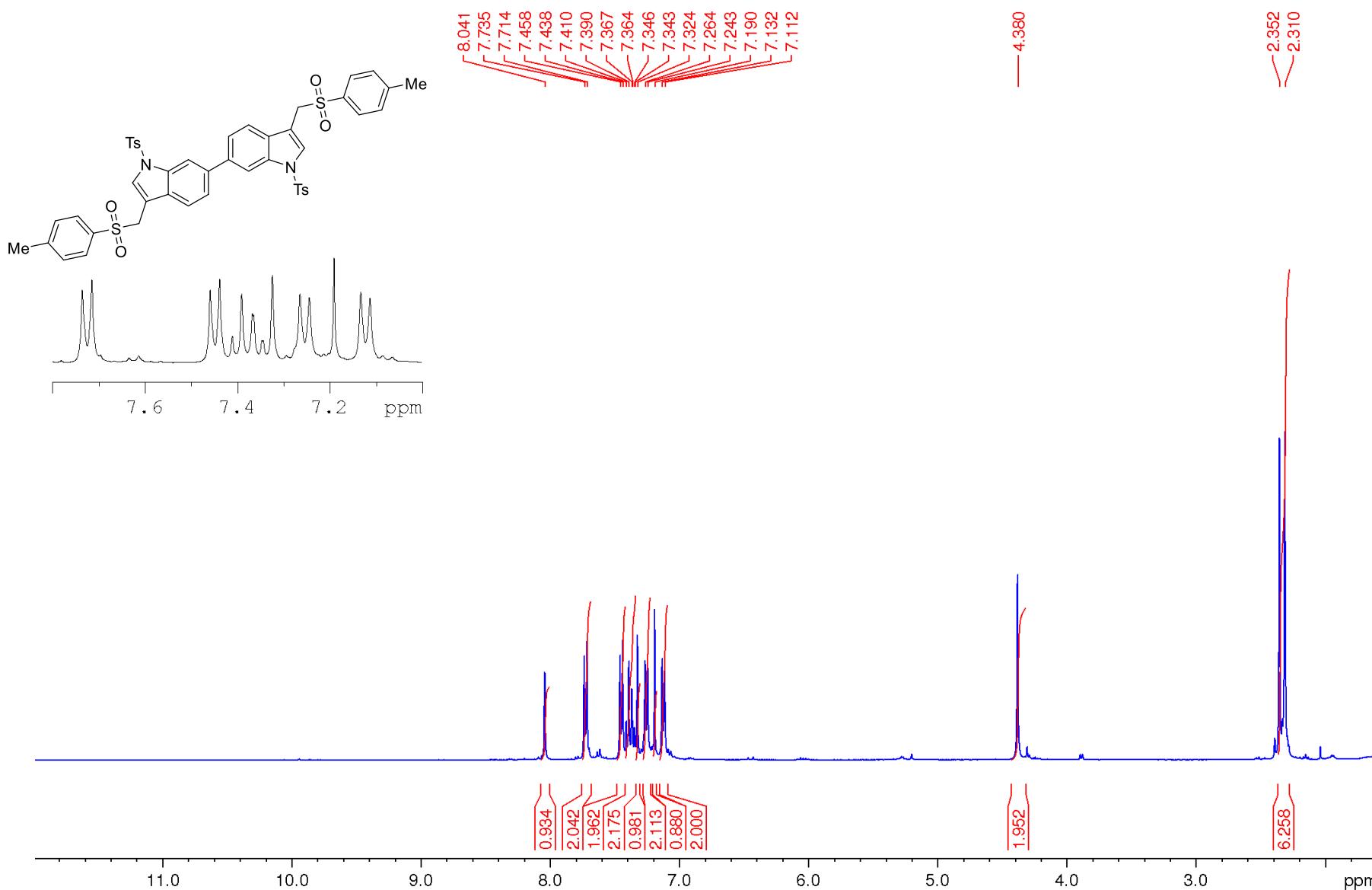
53.306

21.827



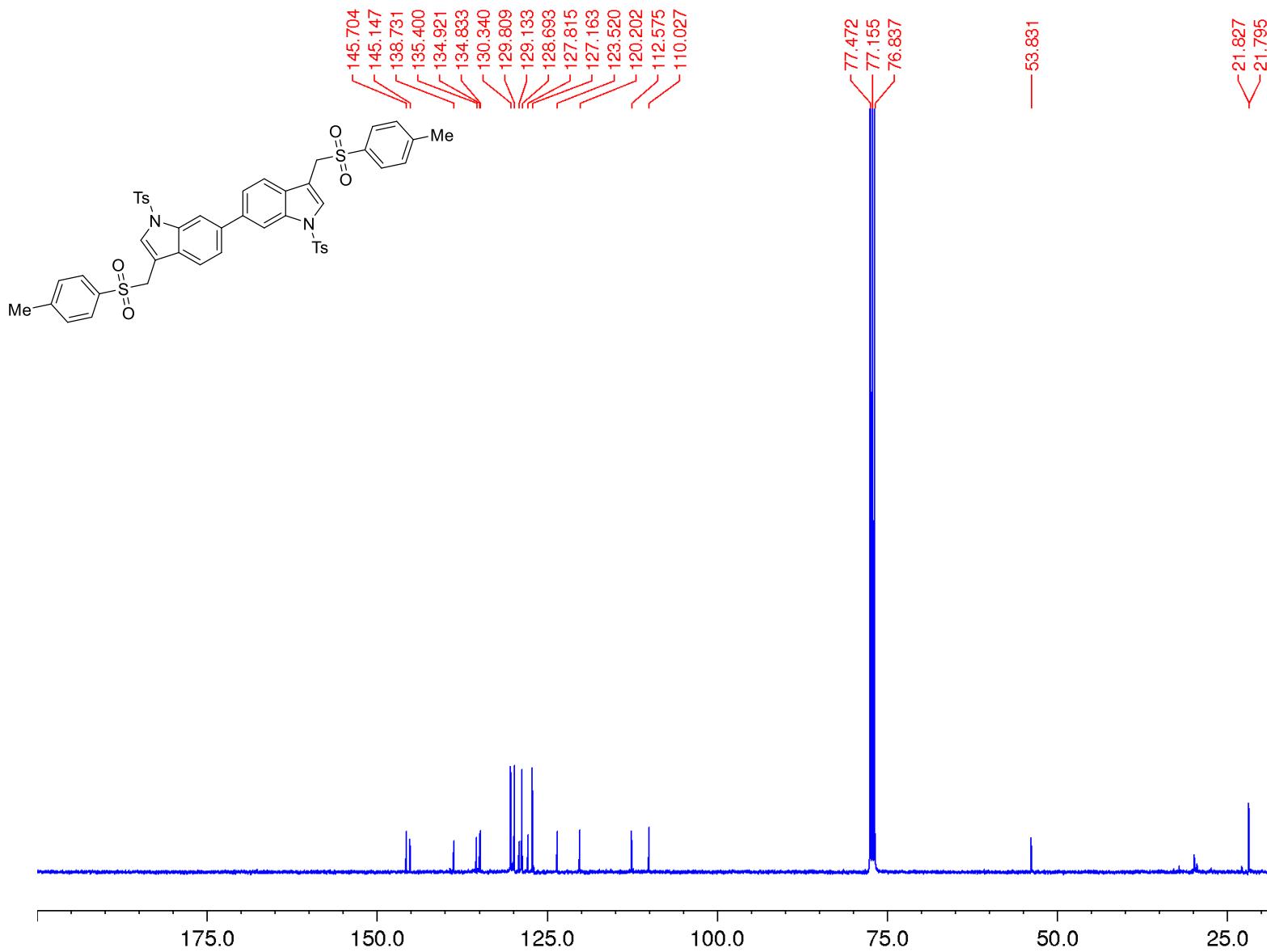
*1,1'-ditosyl-3,3'-bis(tosylmethyl)-1*H*,1*H*-6,6'-biindole 13a*

¹H NMR-spectrum (400.13 MHz) (CDCl_3)



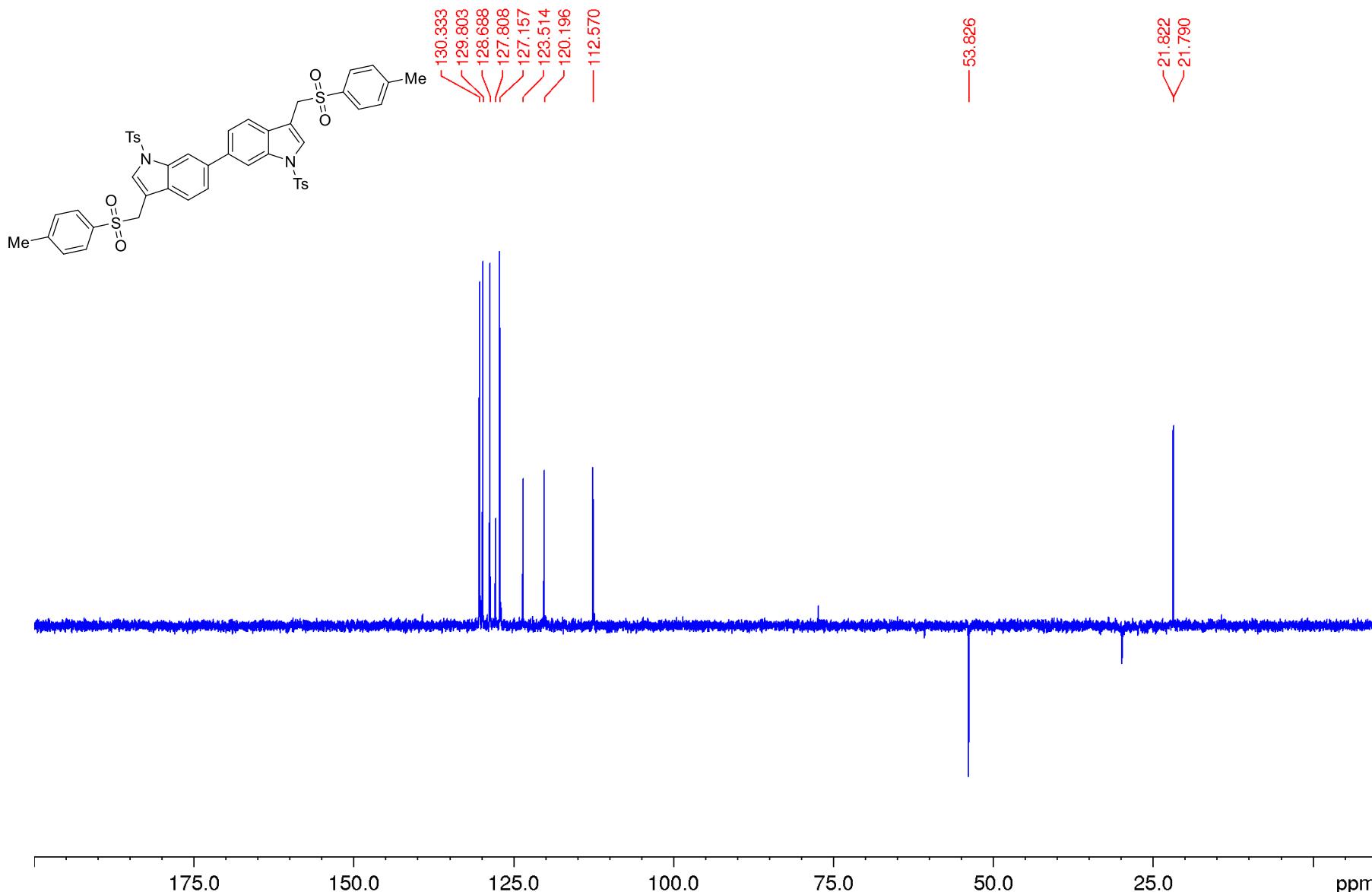
*1,1'-ditosyl-3,3'-bis(tosylmethyl)-1*H*,1*H*-6,6'-biindole 13a*

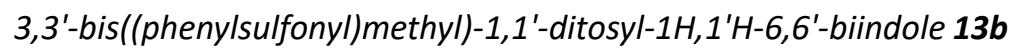
^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)



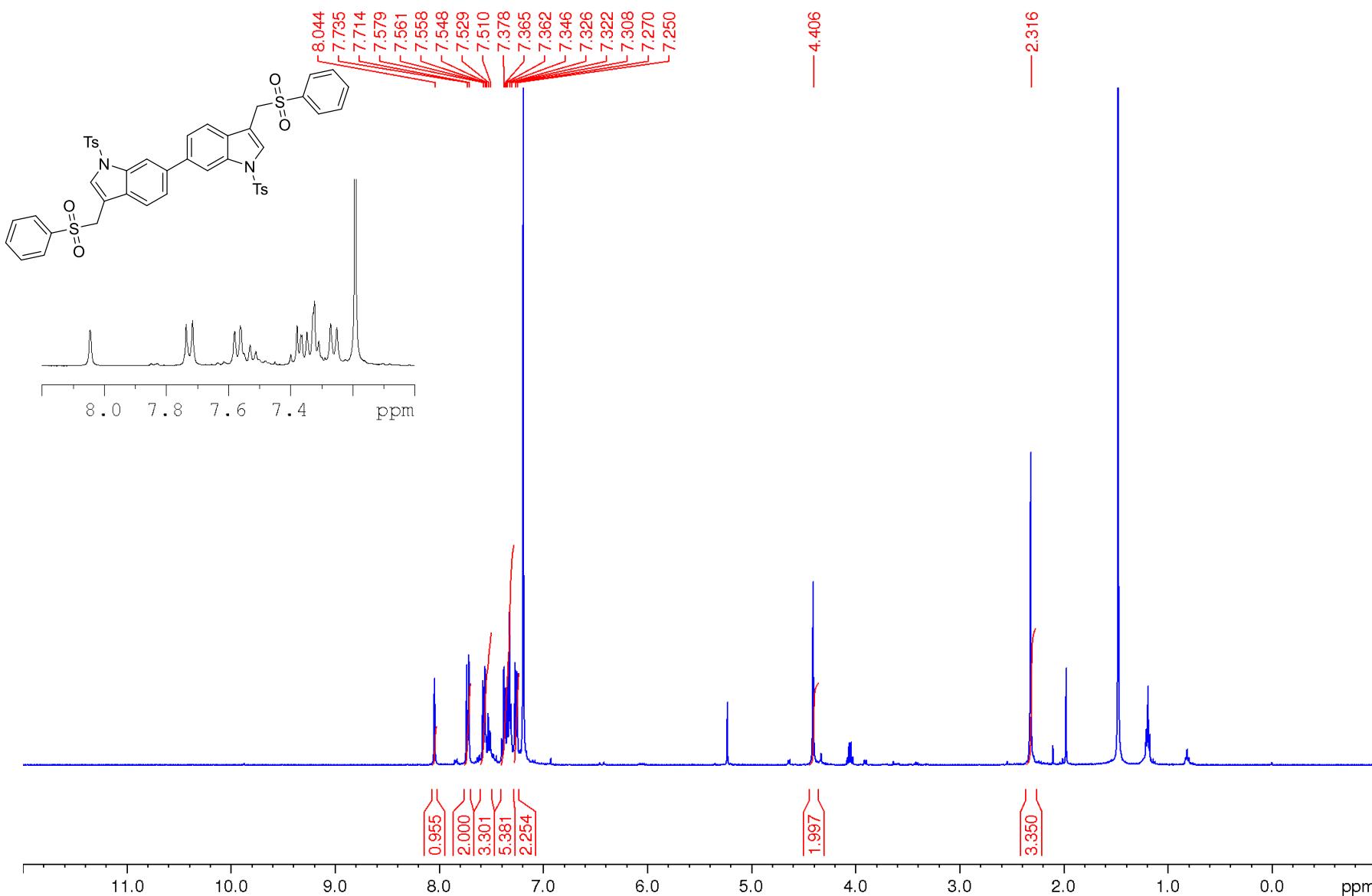
*1,1'-ditosyl-3,3'-bis(tosylmethyl)-1*H*,1*H*-6,6'-biindole 13a*

DEPT 135 NMR-spectrum (CDCl_3)





^1H NMR-spectrum (400.13 MHz) (CDCl_3)



3,3'-bis((phenylsulfonyl)methyl)-1,1'-ditosyl-1H,1'H-6,6'-biindole 13b

^{13}C NMR-spectrum (100.6 MHz) (CDCl_3)

