Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Rhodium Catalyzed C-H Olefination of *N*-Benzoylsulfonamide with Internal Alkene

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1. General Procedures

All reactions were maintained under an argon atmosphere unless otherwise stated. Anhydrous solvents (THF, DME, benzene) were freshly distilled from sodium benzophenone ketyl or from CaH_2 (CH_2Cl_2, toluene) under argon. Commercially available reagents were used without further purification. Flash chromatography (FC) was performed using E. Merck silica gel 60 (240–400 mesh). Thin layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on spectrometers at operating frequencies of 400/500 MHz (^{1}H) or 100/125 MHz (^{13}C) as indicated in the individual spectrum. Chemical shifts (δ) are given in ppm relative to residual solvent (usually chloroform δ = 7.26 for ^{1}H NMR or δ = 77.3 for proton decoupled ^{13}C NMR) and coupling constants (*J*) in Hz. Multiplicity is tabulated as s for singlet, d for doublet, t for triplet, q for quadruplet, and m for multiplet. Low resolution LC/MS spectra were obtained with an Agilent 1200 series API-LC/MSD spectrometer. High resolution mass spectral analyses were kindly provided by Professor Kasem Nithipatikom at the Medical College of Wisconsin Mass Spectroscopy Facility or at the Mass Spectrometry & Proteomic Facility, University of Notre Dame.

2. Survey of Catalysts

Entry	Condition (solvent: Toluene, 130^{o}C, 24 h)	Yield (%)
1	10 mol% $Pd(OAc)_2$ + 2 equiv $Cu(OAc)_2{\cdot}H_2O$	0
2	10 mol% $Pd(OAc)_2$ + 1.5 equiv Ag_2CO_3	0
3	10 mol% $Pd(OAc)_2$ + 1.5 equiv BQ	0
4	10 mol% $Pd(OAc)_2$ + 10 mol% dbpy + 2 equiv $Cu(OAc)_2{\cdot}H_2O$	0
5	10 mol% $Pd(TFA)_2$ + 2 equiv $Cu(OAc)_2{\cdot}H_2O$	0
6	10 mol% $PdCl_2$ + 2 equiv $Cu(OAc)_2{\cdot}H_2O$	0
7	4 mol% $[RhCl_2Cp^*]_2$ + 2 equiv $Cu(OAc)_2{\cdot}H_2O$	82

8	4 mol% $[RhCl_2Cp^*]_2$ + 2 equiv $Cu(OAc)_2 \cdot H_2O$, DCE instead of Toluene	80
9	4 mol% $[RhCl_2Cp^*]_2$ + 2 equiv $Cu(OAc)_2 \cdot H_2O$, THF instead of Toluene	72
10	4 mol% $[RhCl_2Cp^*]_2$ + 2 equiv $Cu(OAc)_2 \cdot H_2O$, DMF instead of Toluene	35

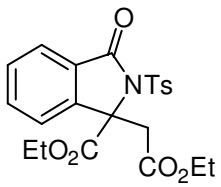
3. Representative Experiments

Annulation with diethyl fumarate

N-Benzoylsulfonamide **4a** (27.5 mg, 0.1 mmol), $[RhCl_2Cp^*]_2$ (2.4 mg, 0.004 mmol) and $Cu(OAc)_2 \cdot H_2O$ (42.0 mg, 0.21 mmol) were loaded in a dry vial which was subjected to evacuation/flushing with dry argon three times. Anhydrous toluene (0.8 mL) solution of diethyl fumarate **5a** (20.6 mg, 0.12 mmol) was syringed into the mixture which was then stirred at 130 °C for 24 h or until the starting material had been consumed as determined by TLC. Upon cooling to room temperature, all volatiles were evaporated and the residue was purified by preparative TLC (eluent: ethyl acetate/hexane 1:2) to give isoindolinone **6a** in 82% yield.

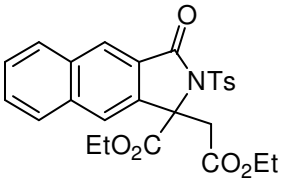
4. New Compounds Characterization

Compound **6a**



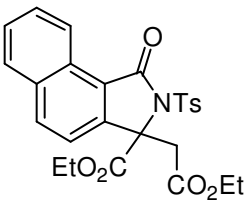
White solid. ^{1}H NMR (500 MHz) δ 0.79 (t, *J* = 7.0 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 2.42 (s, 3H), 3.52-3.64 (m, 2H), 3.71 (d, *J* = 17.5 Hz, 1H), 3.94 (d, *J* = 17.5 Hz, 1H), 4.16-4.24 (m, 1H), 4.28-4.36 (m, 1H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.51 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.63 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.7, 14.0, 21.9, 38.5, 60.8, 63.5, 70.5, 121.3, 125.1, 129.2, 129.4, 129.9, 130.1, 134.4, 136.1, 143.7, 145.4, 166.6, 167.9, 168.6. FT-IR (CH_2Cl_2) 2982, 1738, 1468, 1366, 1248, 1169, 1123, 1089, 1028, 693, 664 cm^{-1}. HRMS calcd for $C_{22}H_{24}NO_7S$ $[M+H]^+$ 446.1268, found 446.1252.

Compound **6b**



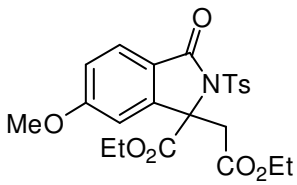
White solid. ^{1}H NMR (400 MHz) δ 0.74 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.41 (s, 3H), 3.51 (q, *J* = 7.2, 2H), 3.82 (d, *J* = 18.0 Hz, 1H), 4.01 (d, *J* = 18.0 Hz, 1H), 4.14-4.20 (m, 1H), 4.30-4.38 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.57 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.62 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.84 (s, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 2H), 8.36 (s, 1H); ^{13}C NMR (100 MHz) δ 13.7, 14.0, 21.9, 39.1, 60.8, 63.5, 70.2, 120.5, 126.3, 127.4, 127.6, 128.7, 129.1, 129.2, 129.5, 130.1, 133.6, 136.1, 136.2, 138.3, 145.4, 166.6, 168.1, 169.1. FT-IR (CH_2Cl_2) 2983, 1736, 1365, 1252, 1180, 1163, 1130, 1086, 1027, 764, 664 cm^{-1}. HRMS calcd for $C_{26}H_{26}NO_7S$ $[M+H]^+$ 496.1424, found 496.1421.

Compound **6c**



White solid. ^{1}H NMR (400 MHz) δ 0.68 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 3.46-3.56 (m, 2H), 3.79 (d, *J* = 17.2 Hz, 1H), 3.99 (d, *J* = 17.2 Hz, 1H), 4.14-4.22 (m, 1H), 4.30-4.38 (m, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.60 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.68 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 9.05 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz) δ 13.6, 14.0, 21.9, 38.3, 60.7, 63.6, 70.0, 117.6, 124.0, 124.1, 127.8, 128.7, 129.2, 129.3, 129.4, 129.5, 133.8, 135.7, 136.3, 144.4, 145.3, 167.5, 167.9, 168.6. FT-IR (CH_2Cl_2) 2983, 1729, 1364, 1247, 1190, 1167, 1133, 1090, 1028, 815, 765, 660 cm^{-1}. HRMS calcd for $C_{26}H_{26}NO_7S$ $[M+H]^+$ 496.1424, found 496.1411.

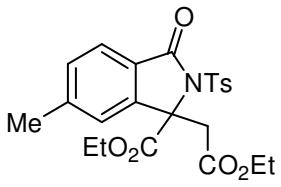
Compound **6d**



White solid. ^{1}H NMR (400 MHz) δ 0.80 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 3.54-3.62 (m, 2H), 3.66 (d, *J* = 17.6 Hz, 1H), 3.86 (s, 3H), 3.92 (d, *J* = 17.6 Hz, 1H), 4.14-4.22 (m, 1H), 4.30-4.38 (m, 1H), 6.86 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 2.0, 8.8 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 2H); ^{13}C

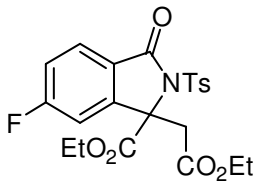
NMR (100 MHz) δ 13.7, 14.0, 21.9, 38.7, 56.1, 60.8, 63.5, 70.0, 105.8, 116.9, 122.2, 126.8, 129.1, 129.4, 136.3, 145.2, 146.1, 164.9, 166.2, 167.9, 168.7. FT-IR (CH_2Cl_2) 2982, 1738, 1604, 1495, 1362, 1343, 1291, 1254, 1168, 1126, 1085, 1026, 855, 659 cm^{-1}. HRMS calcd for $C_{23}H_{26}NO_8S$ $[M+H]^+$ 476.1374, found 476.1376.

Compound **6e**



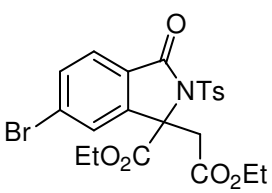
White solid. ^1H NMR (400 MHz) δ 0.77 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 2.43 (s, 3H), 3.52-3.62 (m, 2H), 3.66 (d, *J* = 17.6 Hz, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 4.12-4.22 (m, 1H), 4.28-4.36 (m, 1H), 7.20 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.7, 14.0, 21.9, 22.4, 38.5, 60.7, 63.4, 70.2, 121.6, 125.0, 127.4, 129.2, 129.4, 131.2, 136.2, 144.0, 145.3, 145.7, 166.6, 168.0, 168.8. FT-IR (CH_2Cl_2) 2983, 1737, 1613, 1598, 1364, 1284, 1250, 1169, 1133, 1088, 1027, 853, 808, 704, 666 cm^{-1}. HRMS calcd for $C_{23}H_{26}NO_7S$ $[M+H]^+$ 460.1424, found 460.1413.

Compound **6f**



White solid. ^1H NMR (400 MHz) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 3.63 (q, *J* = 7.2 Hz, 2H), 3.65 (d, *J* = 17.6 Hz, 1H), 3.94 (d, *J* = 17.6 Hz, 1H), 4.18-4.26 (m, 1H), 4.30-4.38 (m, 1H), 7.12 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.20 (ddd, *J* = 2.0, 8.4, 8.8 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.82 (dd, *J* = 4.8, 8.4 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.8, 14.0, 21.9, 38.4, 60.9, 63.7, 70.1, 109.0 (d, $J_{C\text{-}F}$ = 25.0 Hz), 118.1 (d, $J_{C\text{-}F}$ = 23.4 Hz), 126.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 127.5 (d, $J_{C\text{-}F}$ = 9.9 Hz), 129.2, 129.5, 135.9, 145.5, 146.3 (d, $J_{C\text{-}F}$ = 10.0 Hz), 165.2, 166.8 (d, $J_{C\text{-}F}$ = 267 Hz), 167.7, 167.8. FT-IR (CH_2Cl_2) 2983, 1736, 1606, 1488, 1365, 1287, 1250, 1170, 1124, 1084, 1027, 853, 814, 655 2cm^{-1}. HRMS calcd for $C_{22}H_{23}FNO_7S$ $[M+H]^+$ 464.1174, found 464.1158.

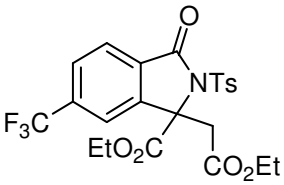
Compound **6g**



White solid. ^1H NMR (400 MHz) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 3.63 (q, *J* = 7.2 Hz, 2H), 3.65 (d, *J* = 17.6

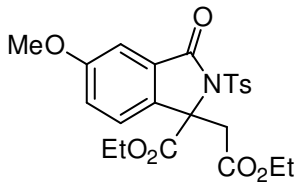
Hz, 1H), 3.93 (d, *J* = 17.6 Hz, 1H), 4.16-4.26 (m, 1H), 4.32-4.42 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.59 (s, 1H), 7.66 (dd, *J* = 8.0, 16.8 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.8, 14.0, 21.9, 38.3, 61.0, 63.8, 70.0, 124.7, 126.4, 129.0, 129.1, 129.2, 129.5, 133.6, 135.8, 145.3, 145.6, 165.7, 167.7, 168.1. FT-IR (CH_2Cl_2) 2983, 1737, 1605, 1593, 1367, 1278, 1247, 1170, 1131, 1090, 1028, 839, 664 cm^{-1}. HRMS calcd for $C_{22}H_{23}BrNO_7S$ $[M+H]^+$ 524.0373, found 524.0378.

Compound **6h**



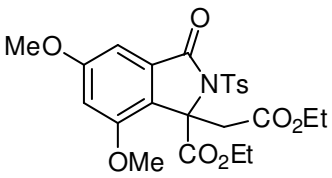
White solid. ^{1}H NMR (400 MHz) δ 0.87 (t, *J* = 7.2 Hz, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 3.63 (q, *J* = 7.2 Hz, 2H), 3.72 (d, *J* = 17.6 Hz, 1H), 3.98 (d, *J* = 17.6 Hz, 1H), 4.18-4.28 (m, 1H), 4.34-4.42 (m, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.69 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.8, 14.0, 21.9, 38.2, 61.0, 63.9, 70.6, 118.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.3 (q, $J_{C\text{-}F}$ = 272 Hz), 125.8, 127.3 (q, $J_{C\text{-}F}$ = 3.5 Hz), 129.2, 129.5, 133.3, 135.6, 136.0 (q, $J_{C\text{-}F}$ = 32.9 Hz), 144.2, 145.8, 165.3, 167.7, 167.9. FT-IR (CH_2Cl_2) 2986, 1739, 1369, 1329, 1259, 1171, 1133, 1099, 1028, 846, 696, 659 cm^{-1}. HRMS calcd for $C_{23}H_{23}F_3NO_7S$ $[M+H]^+$ 514.1142, found 514.1158.

Compound **6i**



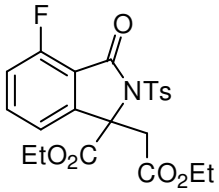
White solid. ^{1}H NMR (400 MHz) δ 0.81 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 2.40 (s, 3H), 3.55-3.65 (m, 2H), 3.64 (d, *J* = 17.2 Hz, 1H), 3.80 (s, 3H), 3.87 (d, *J* = 17.2 Hz, 1H), 4.14-4.22 (m, 1H), 4.26-4.34 (m, 1H), 7.14 (dd, *J* = 2.4, 8.4 Hz, 1H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 8.08 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.8, 14.0, 21.9, 38.3, 56.0, 60.7, 63.4, 70.2, 107.6, 122.4, 122.7, 129.2, 129.4, 131.3, 135.8, 136.0, 145.3, 161.3, 166.6, 168.0, 168.7. FT-IR (CH_2Cl_2) 2983, 1736, 1494, 1365, 1289, 1251, 1169, 1129, 1091, 1028, 664 cm^{-1}. HRMS calcd for $C_{23}H_{26}NO_8S$ $[M+H]^+$ 476.1374, found 476.1382.

Compound **6j**



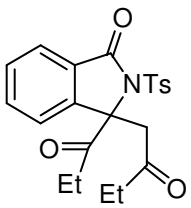
Colorless oil. ^{1}H NMR (400 MHz) δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 3.57-3.65 (m, 2H), 3.79 (d, *J* = 17.2 Hz, 1H), 3.81 (s, 3H), 3.83 (s, 3H), 3.90 (d, *J* = 17.2 Hz, 1H), 4.16-4.24 (m, 1H), 4.26-4.34 (m, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.8, 14.1, 21.9, 36.0, 56.0, 56.1, 60.5, 62.9, 69.3, 98.7, 105.1, 124.3, 129.1, 129.4, 132.5, 136.1, 145.3, 155.1, 162.9, 166.7, 167.8, 168.6. FT-IR (CH_2Cl_2) 2982, 1741, 1625, 1598, 1503, 1459, 1356, 1323, 1244, 1169, 1151, 1090, 1068, 1031, 827, 664 cm^{-1}. HRMS calcd for $C_{24}H_{28}NO_9S$ $[M+H]^+$ 506.1479, found 506.1458.

Compound **6k**



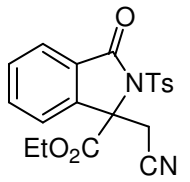
Off-white solid. ^{1}H NMR (400 MHz) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 3.56-3.68 (m, 2H), 3.67 (d, *J* = 17.6 Hz, 1H), 3.94 (d, *J* = 17.6 Hz, 1H), 4.16-4.26 (m, 1H), 4.30-4.38 (m, 1H), 7.14 (dd, *J* = 8.4, 8.4 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.61 (ddd, *J* = 4.8, 7.6, 8.0 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 13.7, 14.0, 21.9, 38.6, 60.9, 63.7, 70.1, 117.2 (d, $J_{C\text{-}F}$ = 4.2 Hz), 117.4 (d, $J_{C\text{-}F}$ = 18.8 Hz), 129.3, 129.5, 135.7, 136.4 (d, $J_{C\text{-}F}$ = 7.9 Hz), 145.6, 145.9 (d, $J_{C\text{-}F}$ = 2.3 Hz), 159.4 (d, $J_{C\text{-}F}$ = 274 Hz), 163.3 (d, $J_{C\text{-}F}$ = 2.6 Hz), 167.8, 168.2. FT-IR (CH_2Cl_2) 2984, 1740, 1622, 1483, 1367, 1256, 1236, 1196, 1171, 1122, 1090, 1073, 1035, 814, 691, 664 cm^{-1}. HRMS calcd for $C_{22}H_{23}FNO_7S$ $[M+H]^+$ 464.1174, found 464.1186.

Compound **6l**



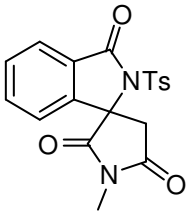
White solid. ^{1}H NMR (400 MHz) δ 0.57 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 2.06-2.16 (m, 3H), 2.41 (s, 3H), 2.80-2.92 (m, 1H), 3.70 (d, *J* = 19.2 Hz, 1H), 3.78 (d, *J* = 19.2 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.51 (dd, *J* = 7.2, 7.6 Hz, 1H), 7.58 (dd, *J* = 7.2, 7.6 Hz, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 6.9, 8.5, 21.9, 28.6, 36.3, 42.5, 75.4, 121.1, 125.6, 128.3, 129.8, 130.0, 130.6, 134.6, 135.8, 143.1, 145.7, 167.0, 205.3, 205.6. FT-IR (CH_2Cl_2) 1745, 1716, 1357, 1169, 1123, 1087, 1057, 822, 702, 658 cm^{-1}. HRMS calcd for $C_{22}H_{24}NO_5S$ $[M+H]^+$ 414.1370, found 414.1368.

Compound **6m**



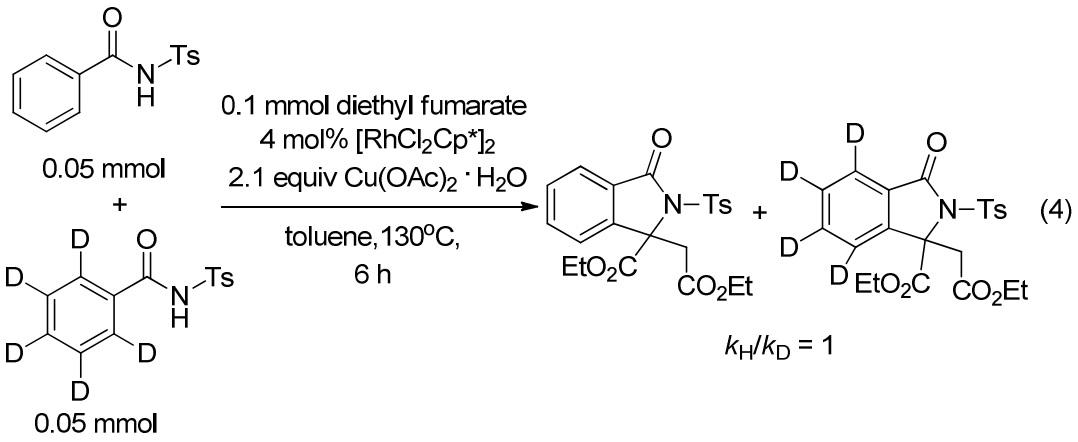
Colorless oil. ^{1}H NMR (400 MHz) δ 1.25 (t, *J* = 7.2 Hz, 3H), 2.43 (s, 3H), 3.78 (d, *J* = 17.6 Hz, 1H), 3.90 (d, *J* = 17.6 Hz, 1H), 4.16-4.24 (m, 1H), 4.32-4.40 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.73 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 14.0, 22.0, 26.2, 64.1, 69.5, 114.7, 121.5, 126.0, 129.1, 129.2, 129.8, 131.3, 135.2, 135.3, 141.9, 146.2, 165.5, 167.3. FT-IR (CH_2Cl_2) 2987, 1743, 1598, 1468, 1365, 1294, 1267, 1169, 1128, 1088, 815, 748, 698, 666 cm^{-1}. HRMS calcd for $C_{20}H_{19}N_2O_5S$ $[M+H]^+$ 399.1009, found 399.1009.

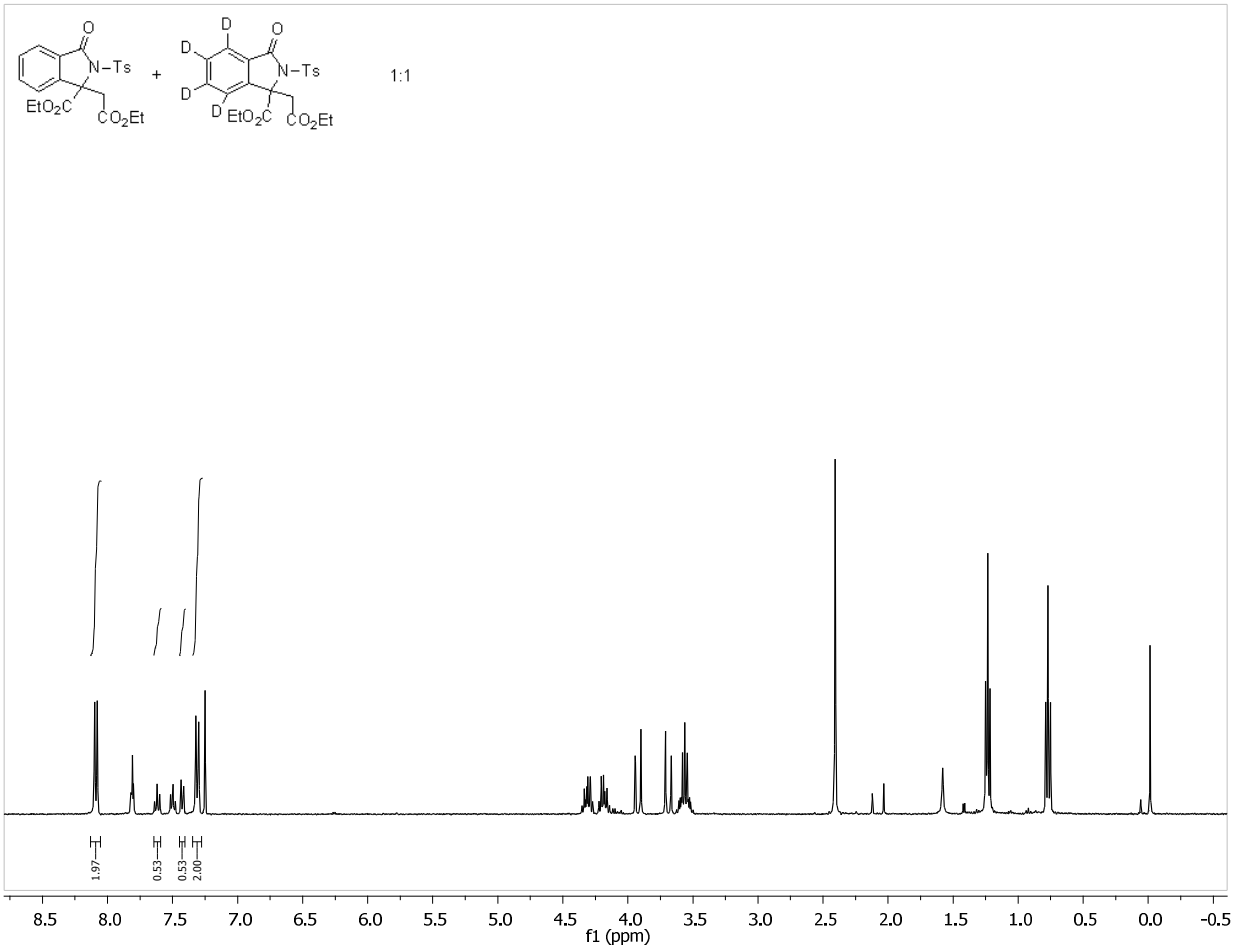
Compound **6n**

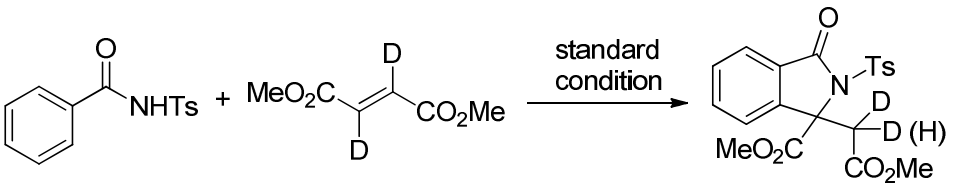


Colorless oil. ^{1}H NMR (400 MHz) δ 2.44 (s, 3H), 3.21 (d, *J* = 14.4 Hz, 1H), 3.27 (s, 3H), 3.89 (d, *J* = 14.4 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.68 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) δ 22.0, 26.3, 41.6, 69.3, 120.5, 125.8, 128.6, 129.6, 129.7, 130.7, 134.8, 135.4, 144.6, 146.3, 165.4, 172.9, 173.4. FT-IR (CH_2Cl_2) 1791, 1738, 1715, 1597, 1436, 1382, 1359, 1286, 1263, 1168, 1123, 1091, 1059, 702, 665 cm^{-1}. HRMS calcd for $C_{19}H_{17}N_2O_5S$ $[M+H]^+$ 385.0853, found 385.0827.

5. Deuterium Experiments

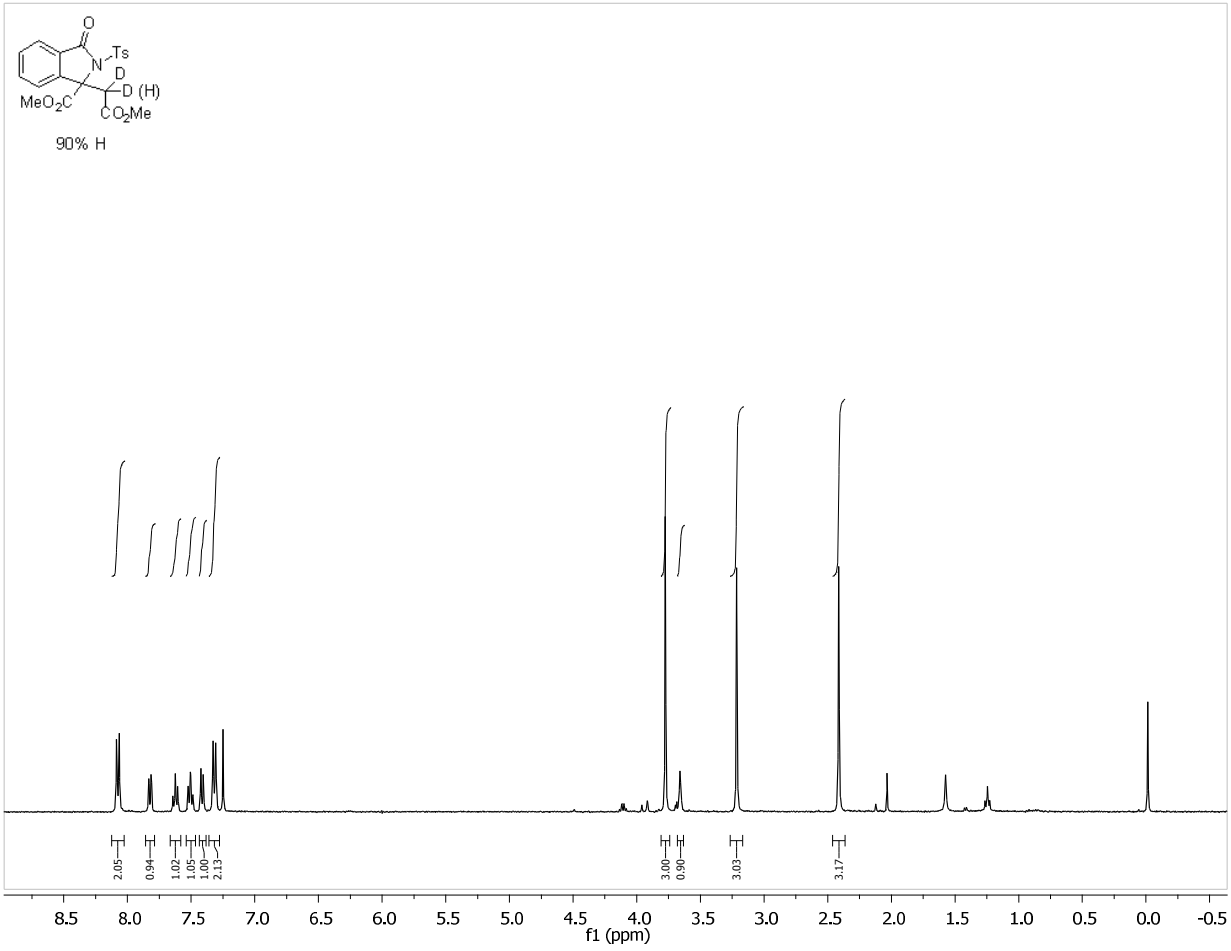

0.05 mmol
+
0.05 mmol
0.1 mmol diethyl fumarate
4 mol% [RhCl2Cp*]2
2.1 equiv Cu(OAc)2 · H2O
toluene, 130°C,
6 h
+
(4)
kH/kD = 1


1:1
1.97
0.53
0.53
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

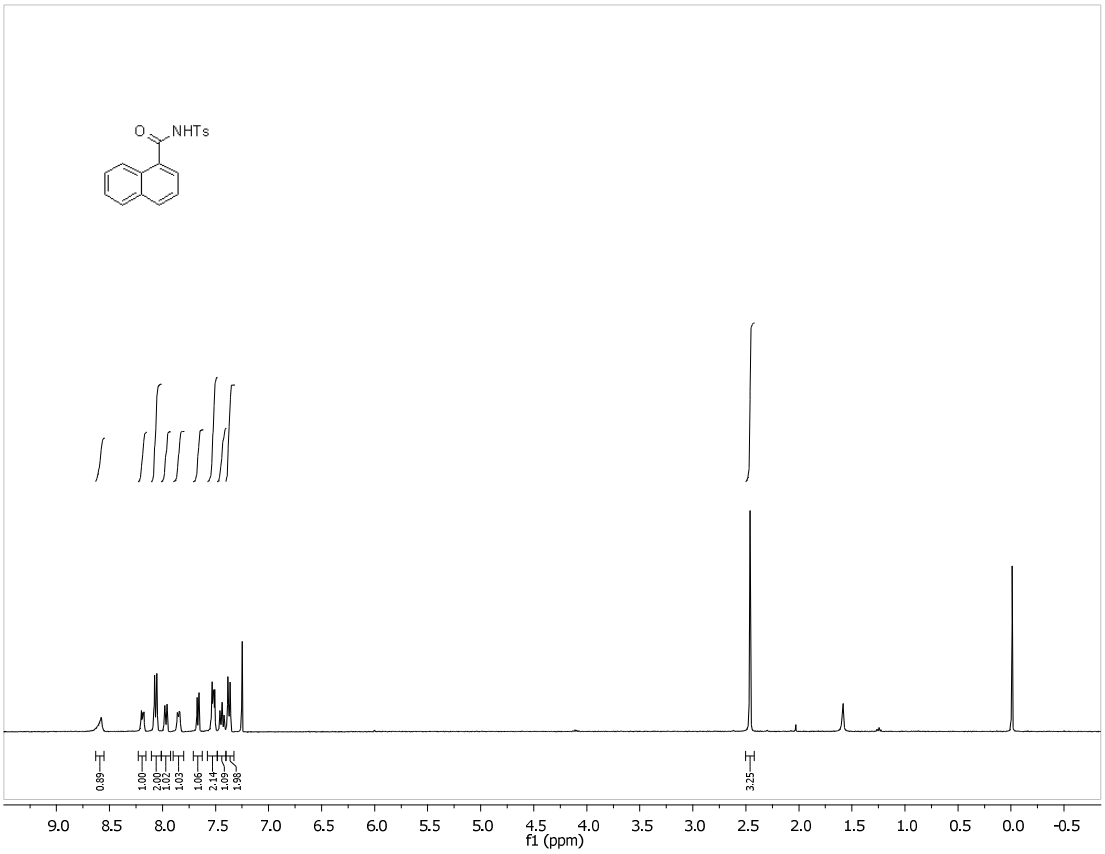


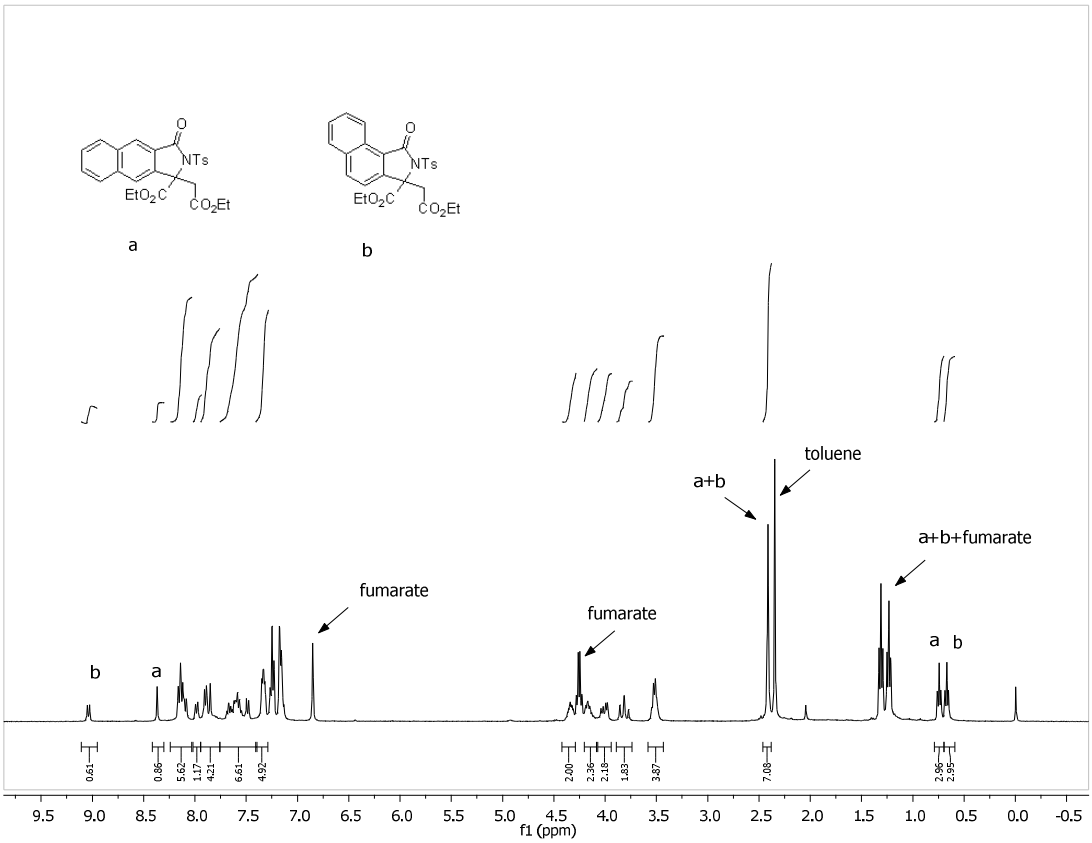
(5)

4a (0.10 mmol) **7** (0.12 mmol) **8** 90% H

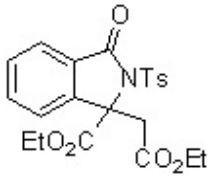


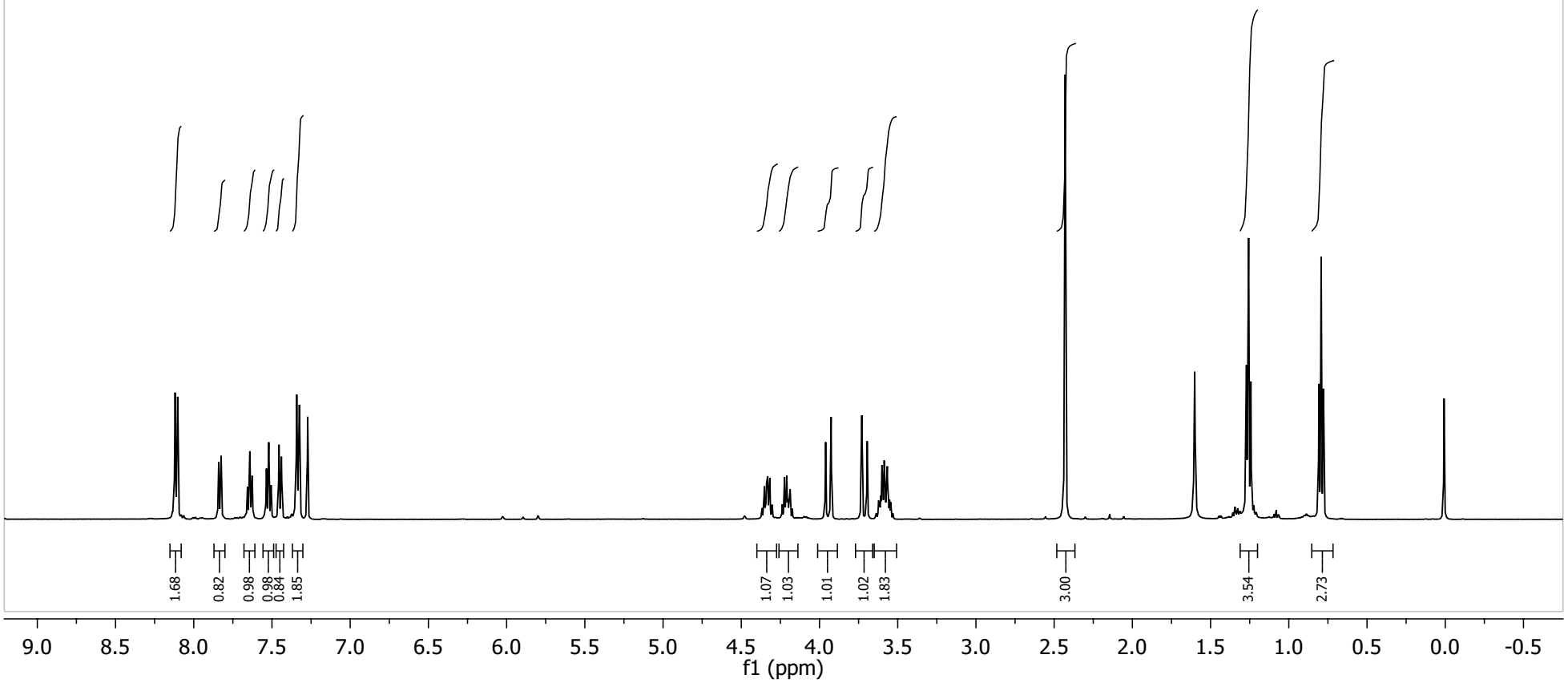
6. Table 1 entry 3 (HNMR spectra of crude reaction and starting material)

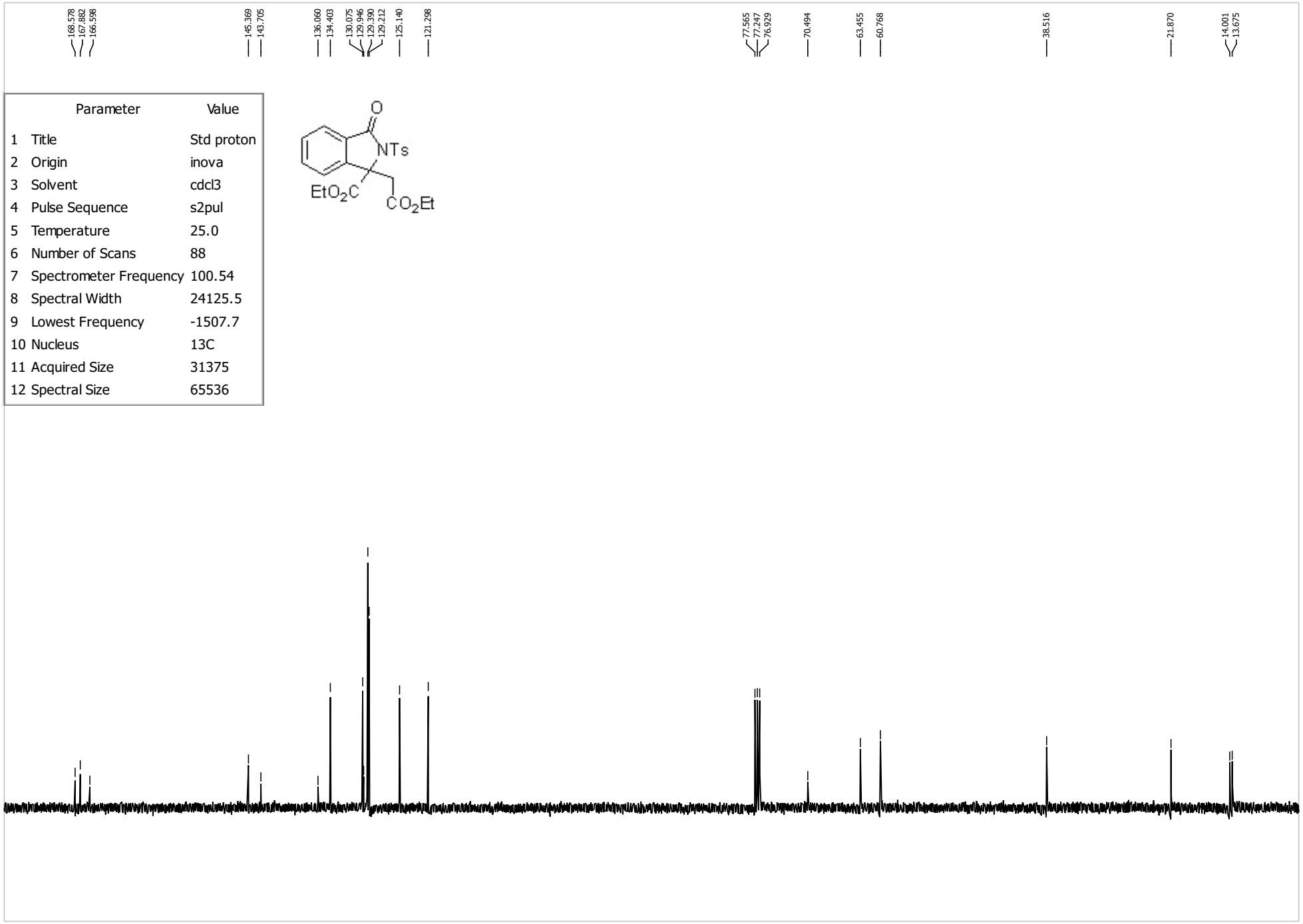

O
NHTs
0.89
1.00
2.00
1.02
1.03
1.06
2.14
1.09
1.98
3.25
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


O
NTs
EtO2C
CO2Et
a
b
toluene
a+b
a+b+fumarate
fumarate
fumarate
a b
b
a
0.61
0.86
5.62
1.17
4.21
6.61
4.92
2.00
2.36
2.18
1.83
3.87
7.08
2.96
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

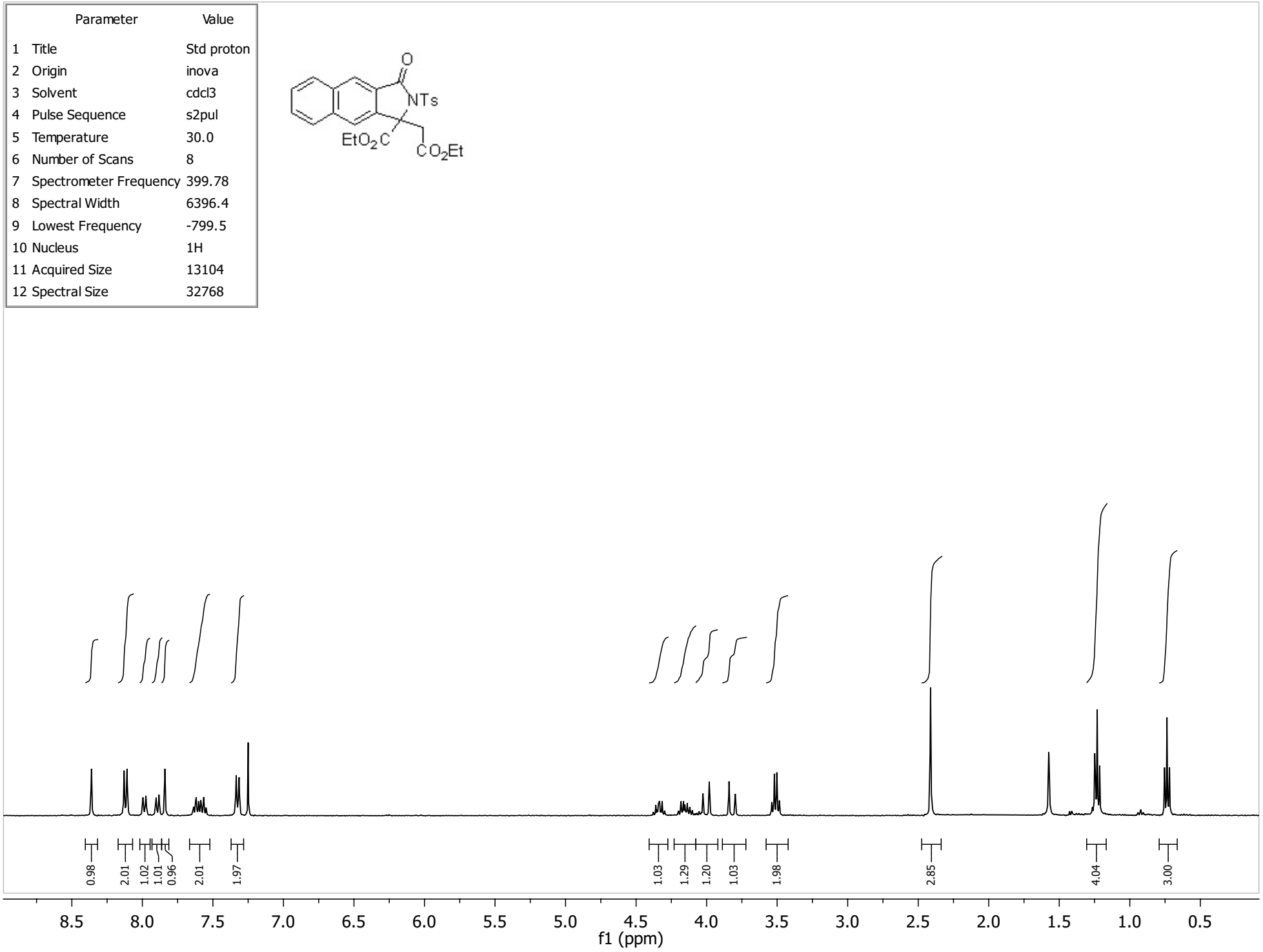
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	16
7	Spectrometer Frequency	499.78
8	Spectral Width	8000.0
9	Lowest Frequency	-1001.4
10	Nucleus	1H
11	Acquired Size	16389
12	Spectral Size	65536

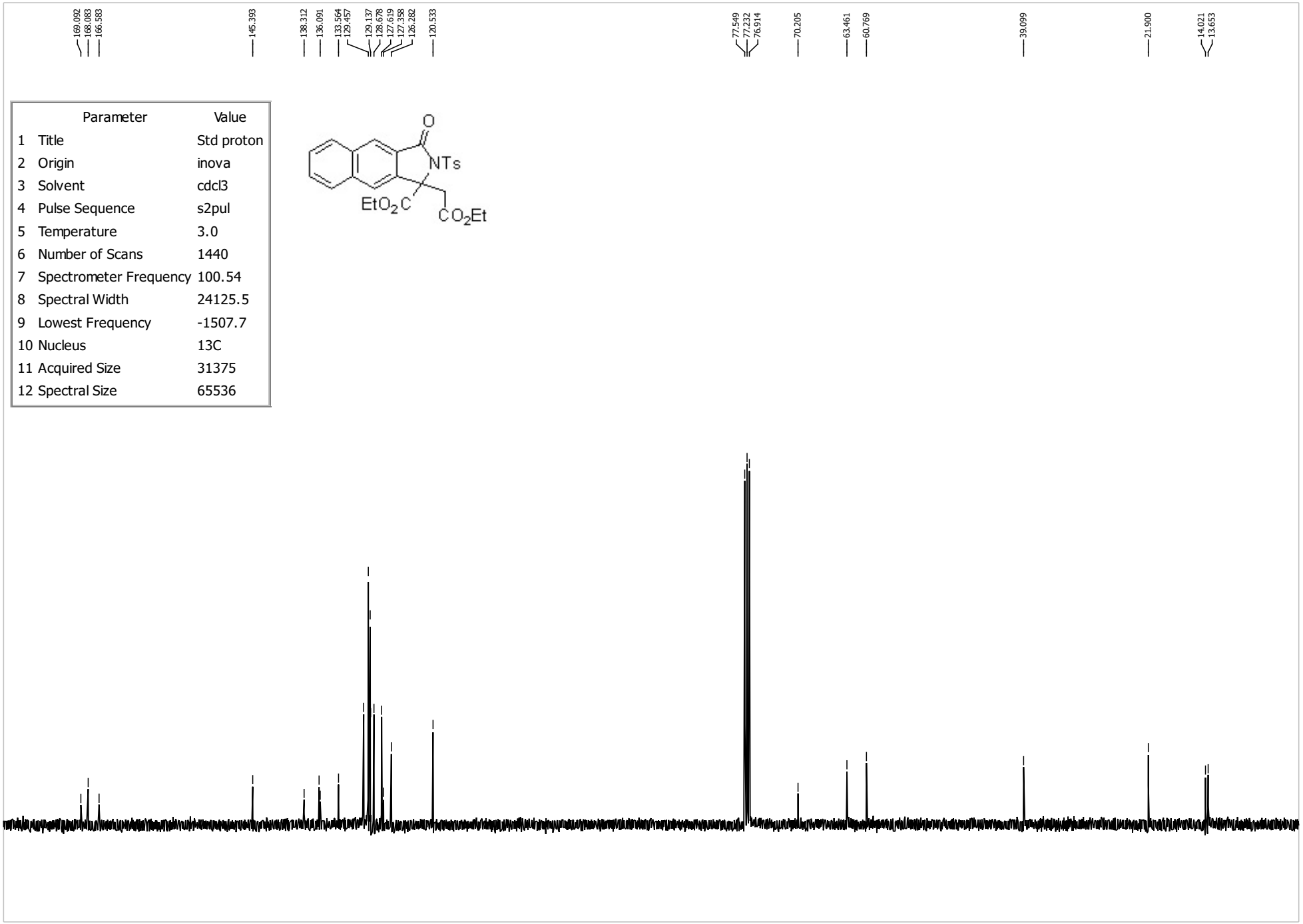





168.578
167.882
166.598
145.369
143.705
136.060
134.403
130.075
129.946
129.390
129.212
125.140
121.298
77.565
77.247
76.929
70.494
63.455
60.768
38.516
21.870
14.001
13.675
O
NTs
EtO2C
CO2Et
Parameter Value
1 Title Std proton
2 Origin inova
3 Solvent cdcl3
4 Pulse Sequence s2pul
5 Temperature 25.0
6 Number of Scans 88
7 Spectrometer Frequency 100.54
8 Spectral Width 24125.5
9 Lowest Frequency -1507.7
10 Nucleus 13C
11 Acquired Size 31375
12 Spectral Size 65536
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

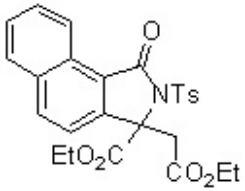
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

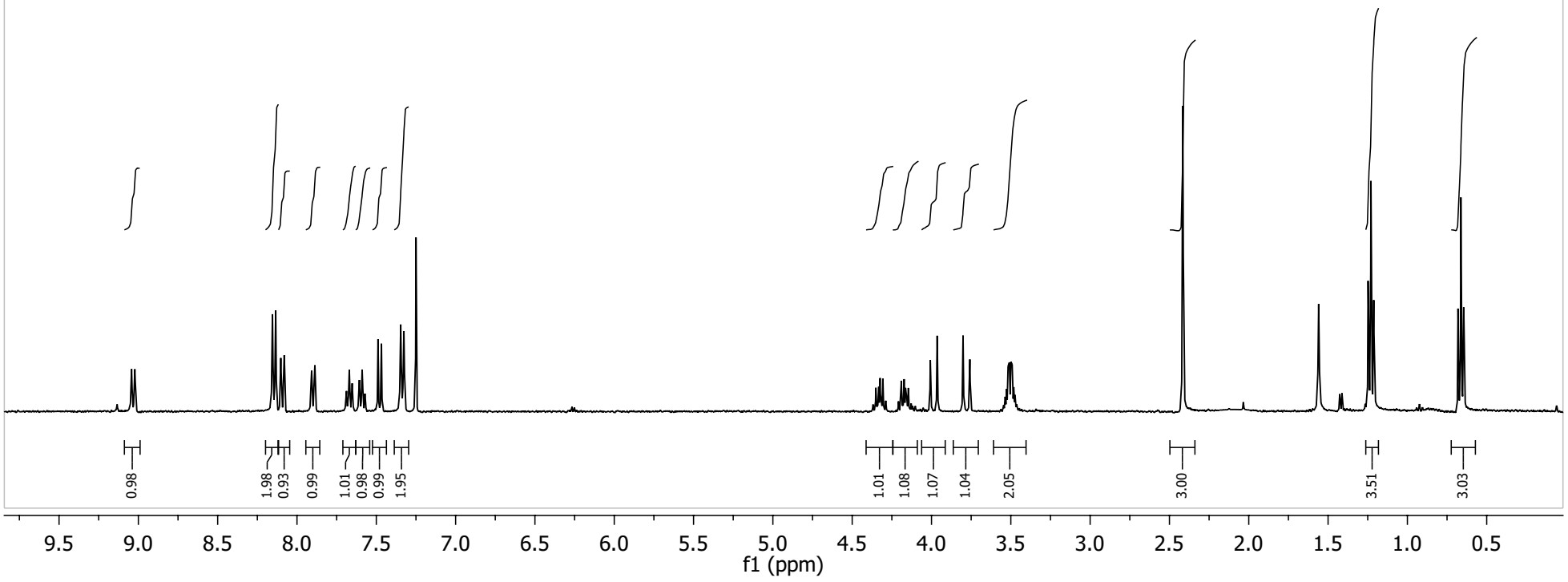


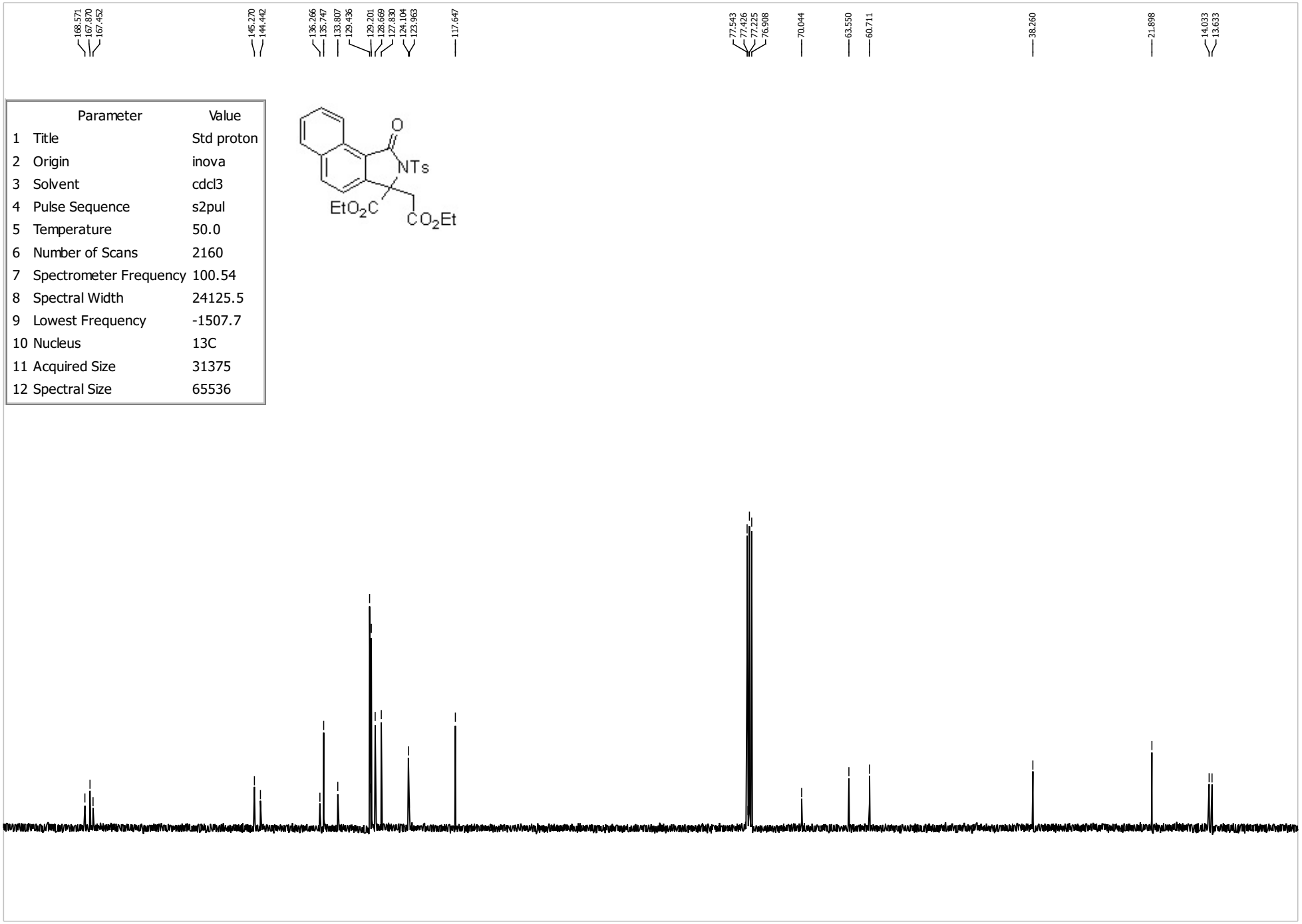


	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	3.0
6	Number of Scans	1440
7	Spectrometer Frequency	100.54
8	Spectral Width	24125.5
9	Lowest Frequency	-1507.7
10	Nucleus	13C
11	Acquired Size	31375
12	Spectral Size	65536

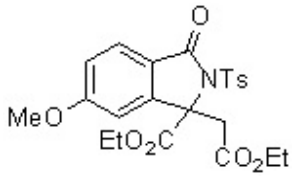
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

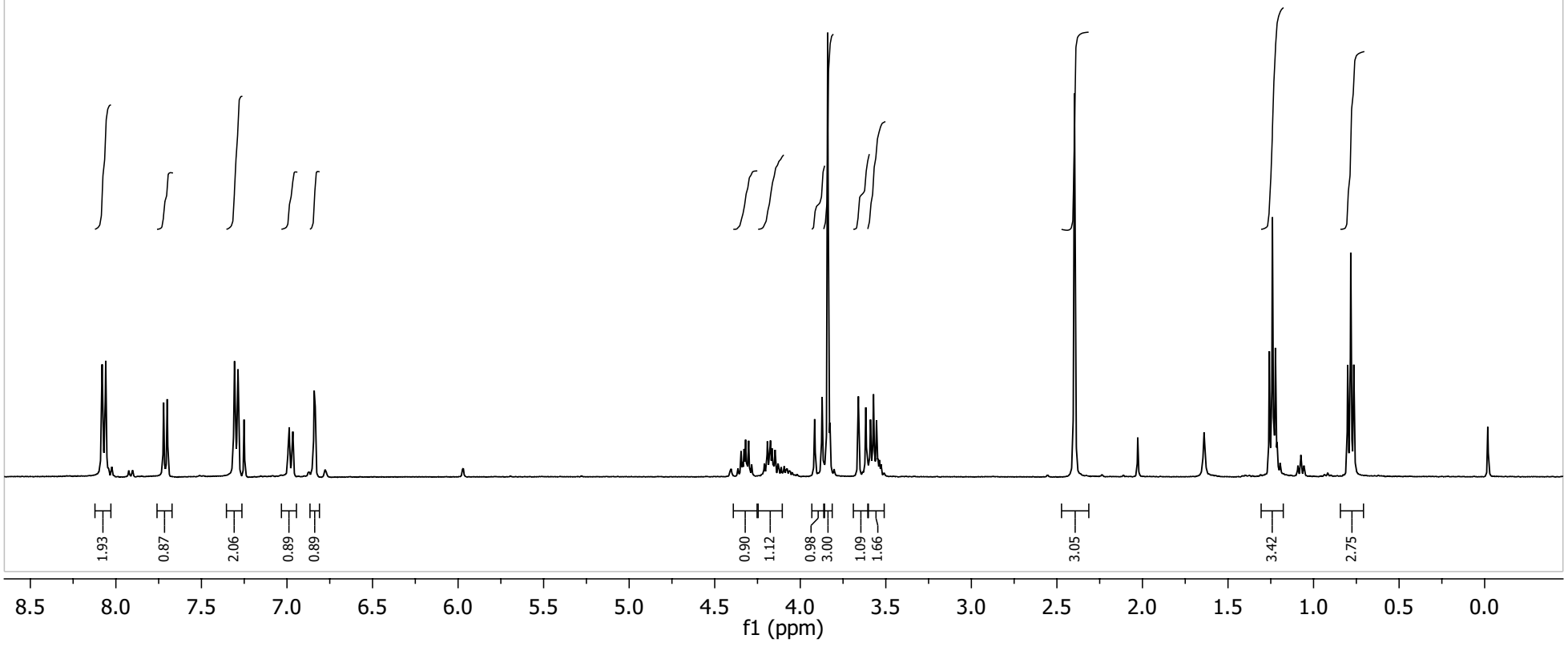


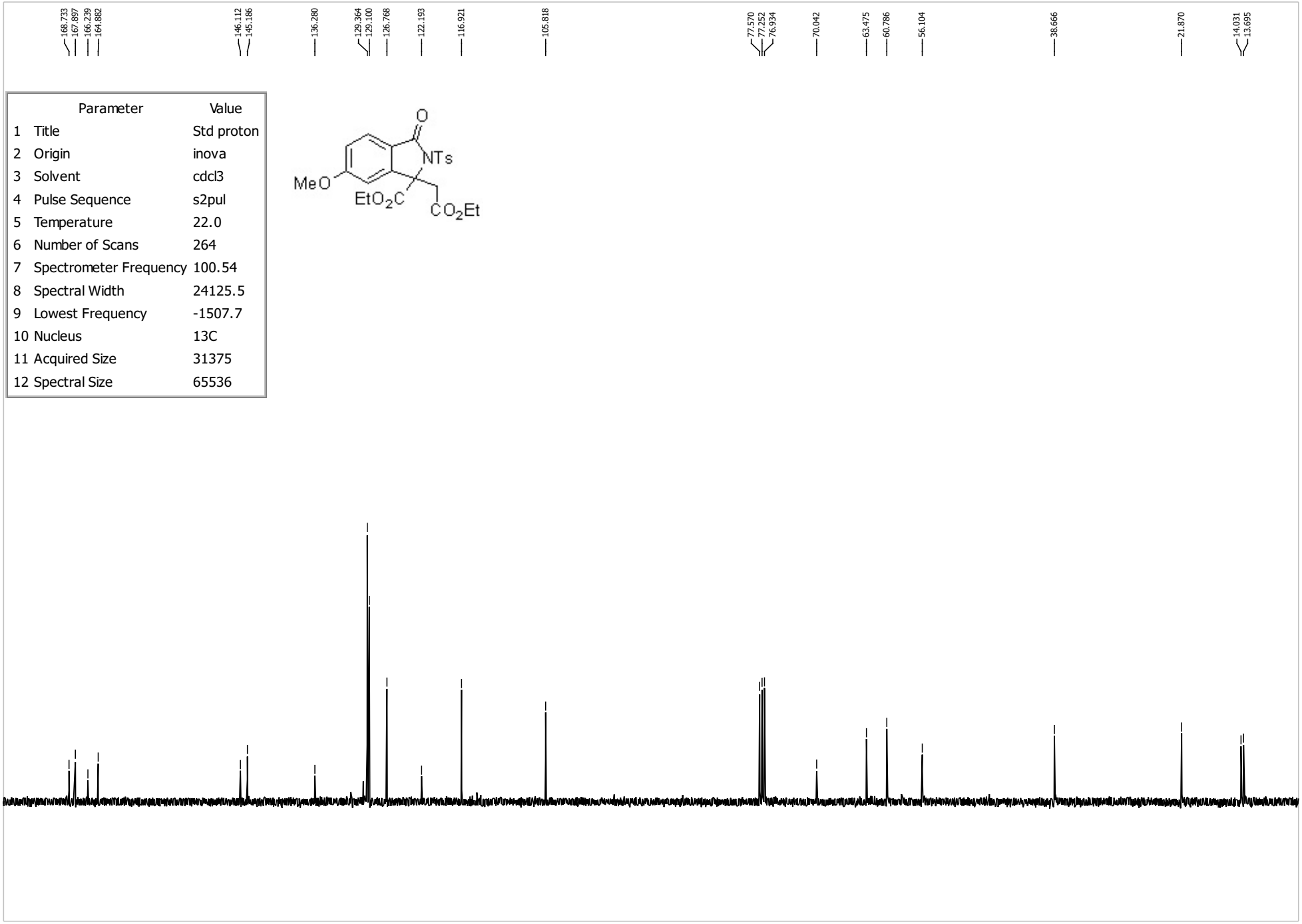



168.571
167.870
167.452
145.270
144.442
136.266
135.747
133.807
129.436
129.201
128.669
127.830
124.104
123.963
117.647
77.543
77.426
77.225
76.908
70.044
63.550
60.711
38.260
21.898
14.033
13.633
Parameter Value
1 Title Std proton
2 Origin inova
3 Solvent cdcl3
4 Pulse Sequence s2pul
5 Temperature 50.0
6 Number of Scans 2160
7 Spectrometer Frequency 100.54
8 Spectral Width 24125.5
9 Lowest Frequency -1507.7
10 Nucleus 13C
11 Acquired Size 31375
12 Spectral Size 65536
O
NTs
EtO2C
CO2Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

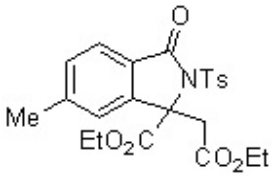
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	22.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

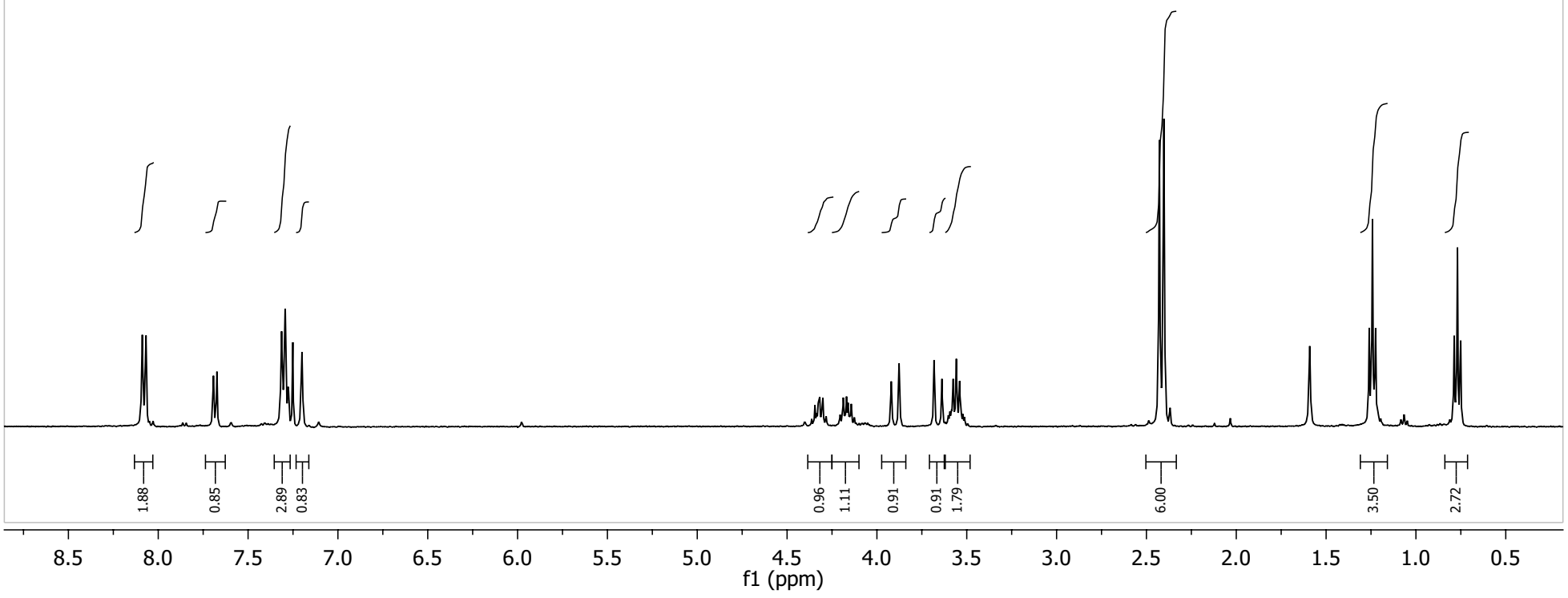


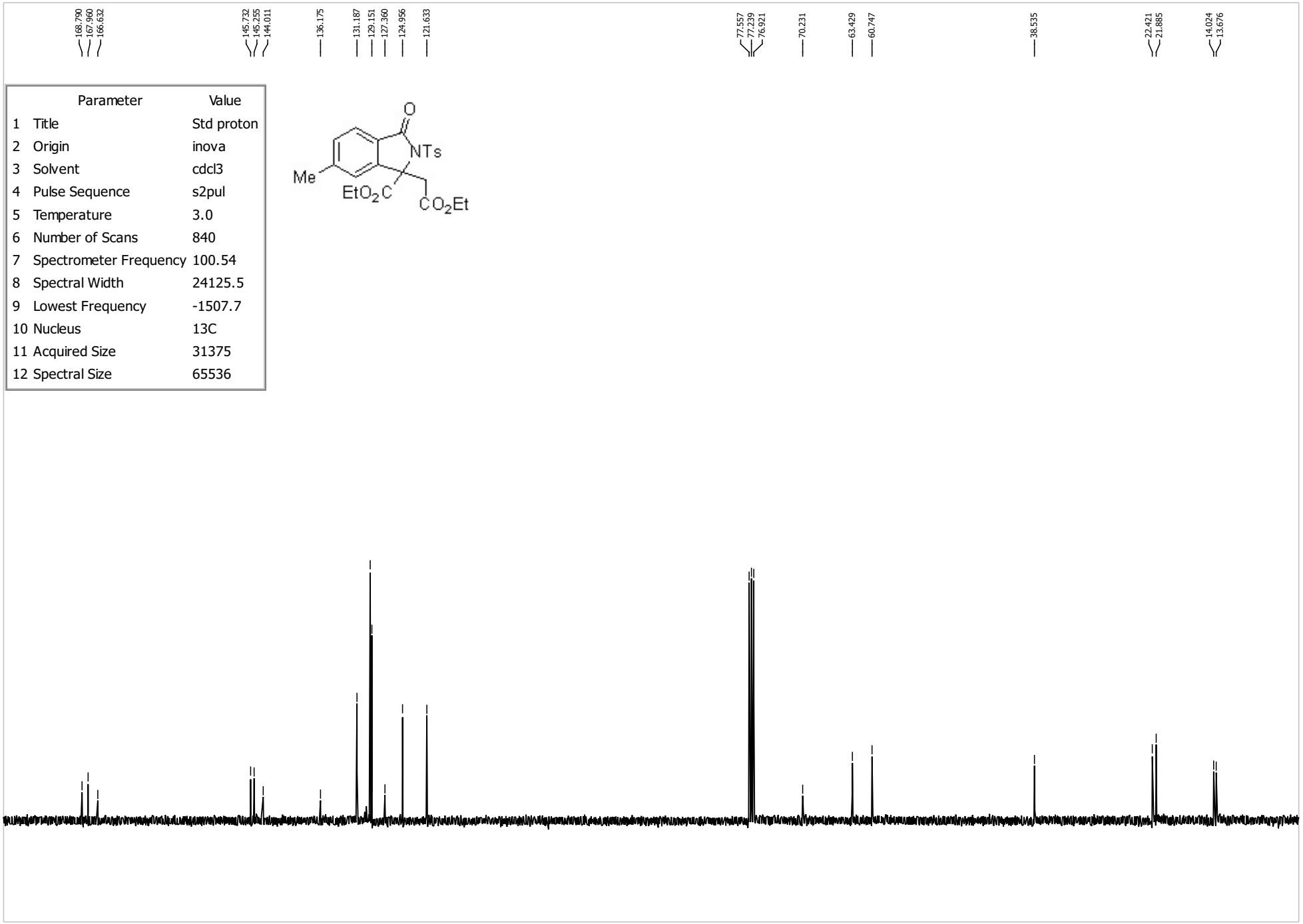



168.733
167.897
166.239
164.882
146.112
145.186
136.280
129.364
129.100
126.768
122.193
116.921
105.818
77.570
77.252
76.934
70.042
63.475
60.786
56.104
38.666
21.870
14.031
13.695
Parameter Value
1 Title Std proton
2 Origin inova
3 Solvent cdcl3
4 Pulse Sequence s2pul
5 Temperature 22.0
6 Number of Scans 264
7 Spectrometer Frequency 100.54
8 Spectral Width 24125.5
9 Lowest Frequency -1507.7
10 Nucleus 13C
11 Acquired Size 31375
12 Spectral Size 65536
O
NTs
MeO
EtO2C
CO2Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

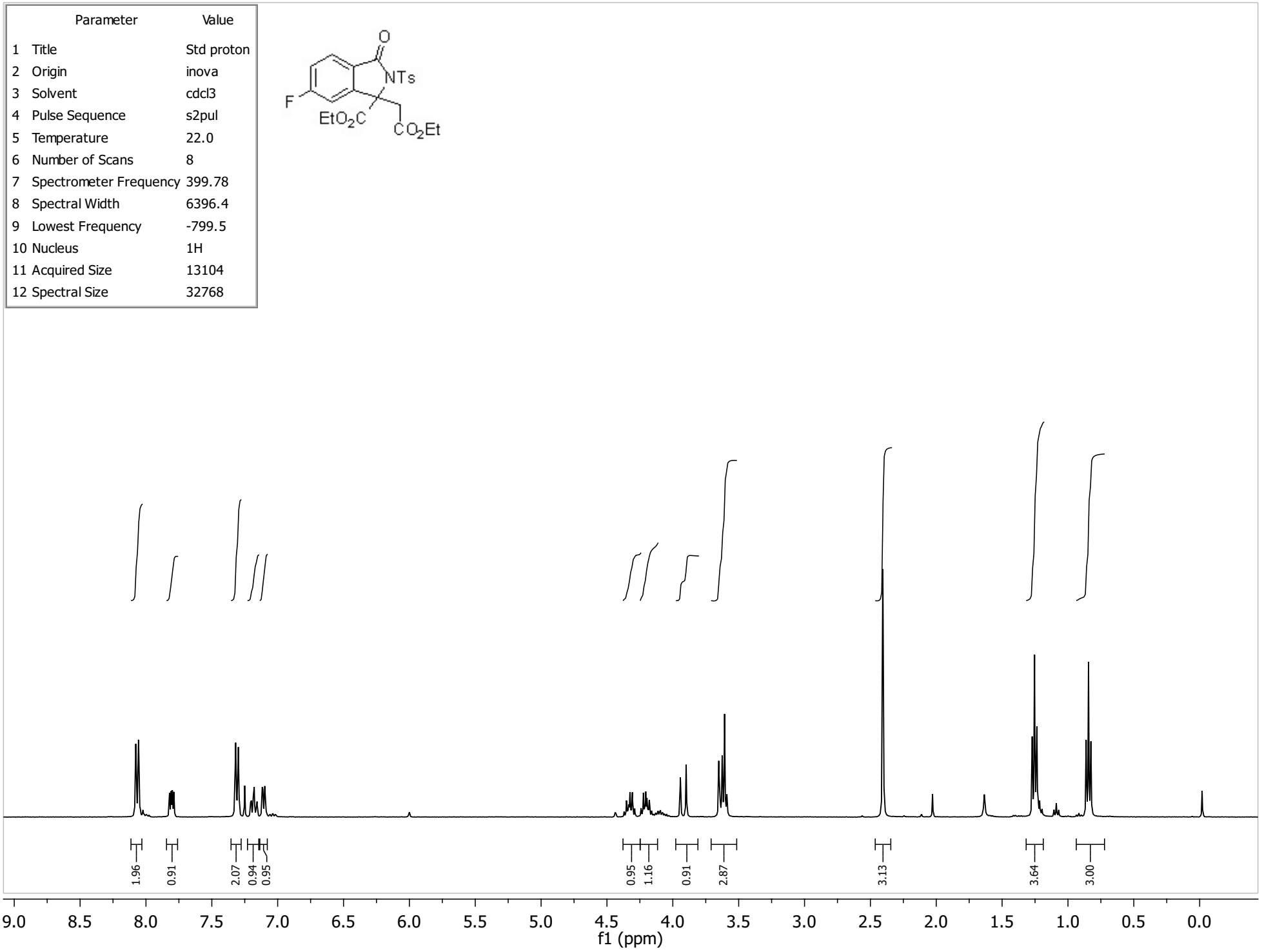
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

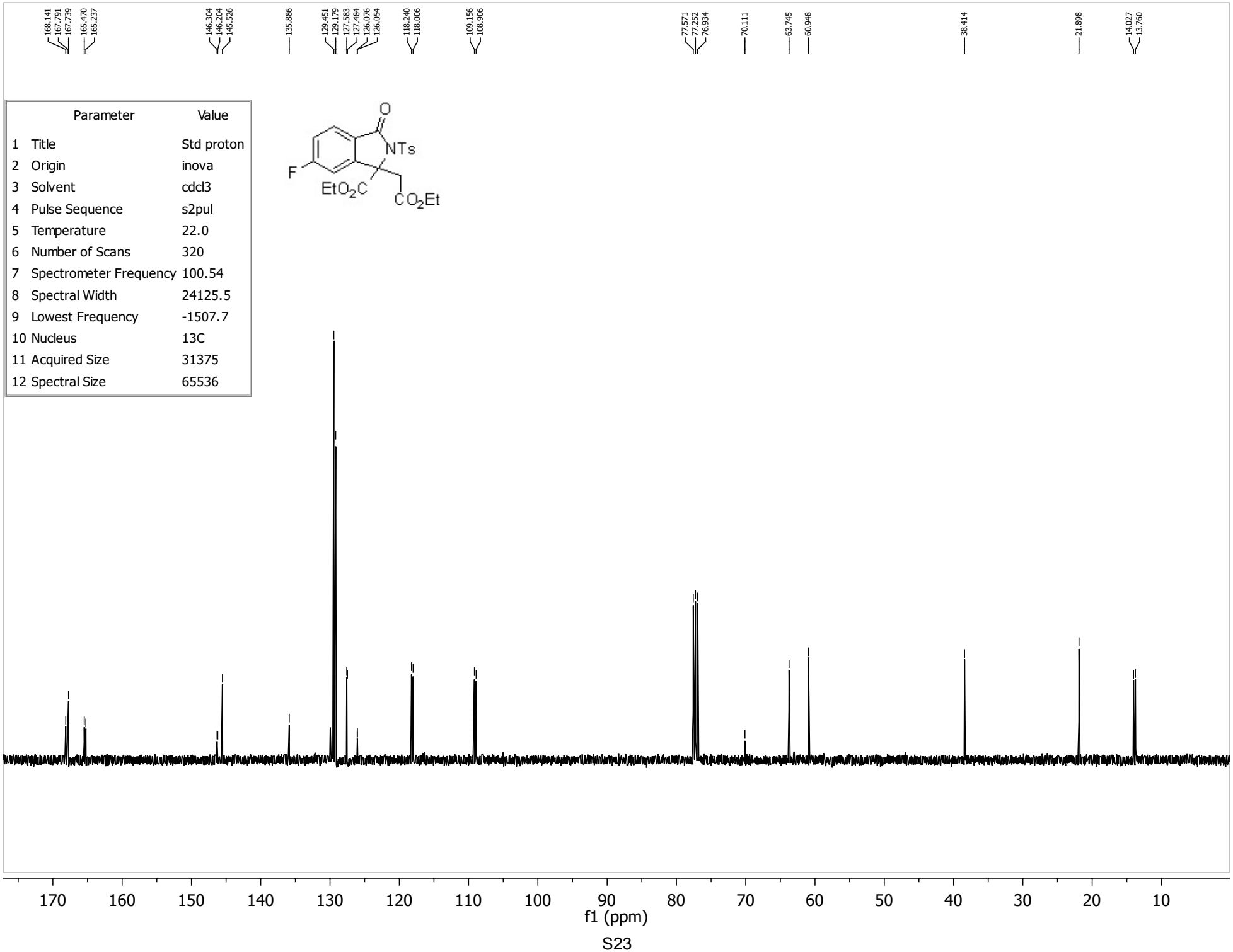




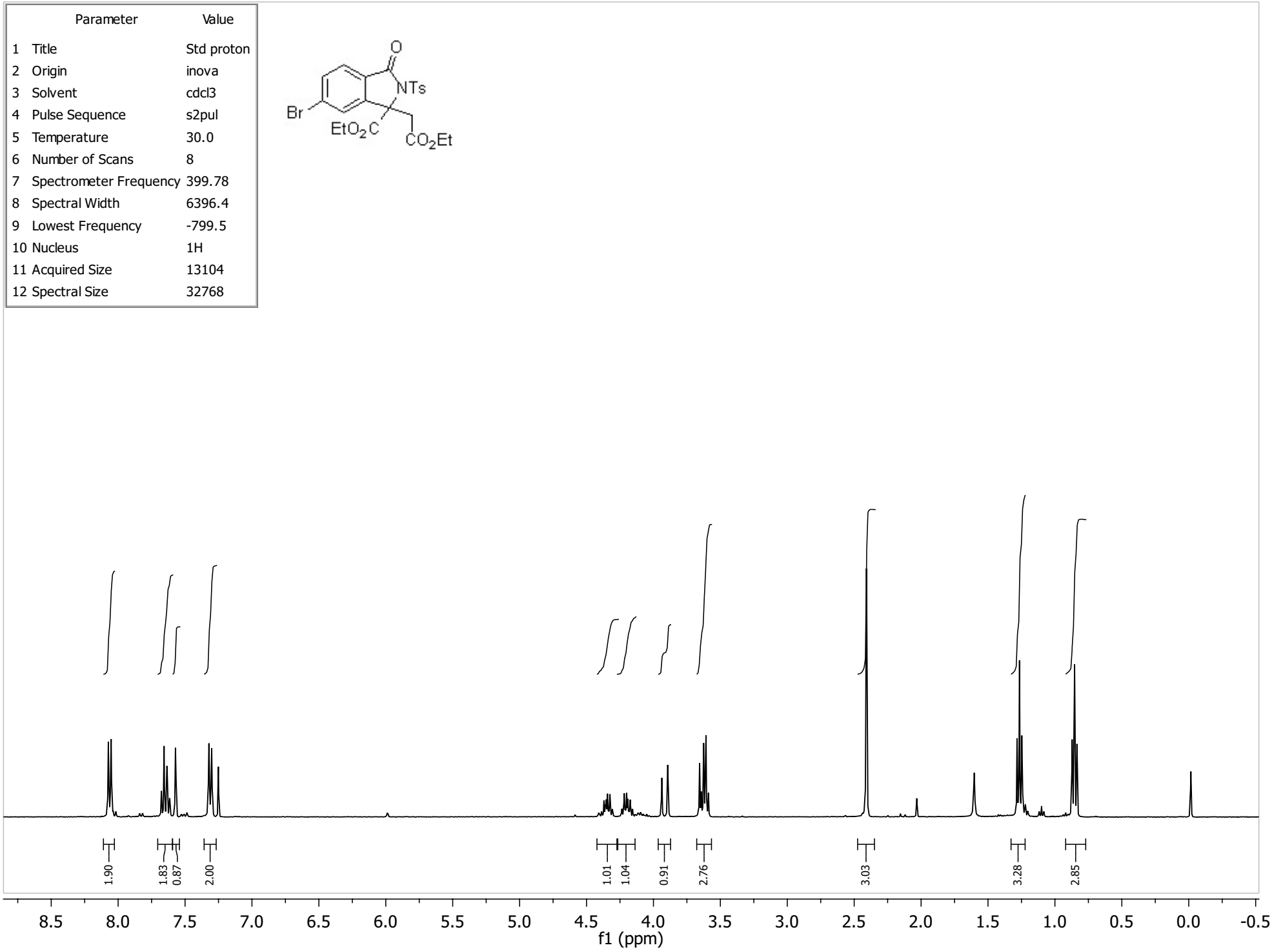


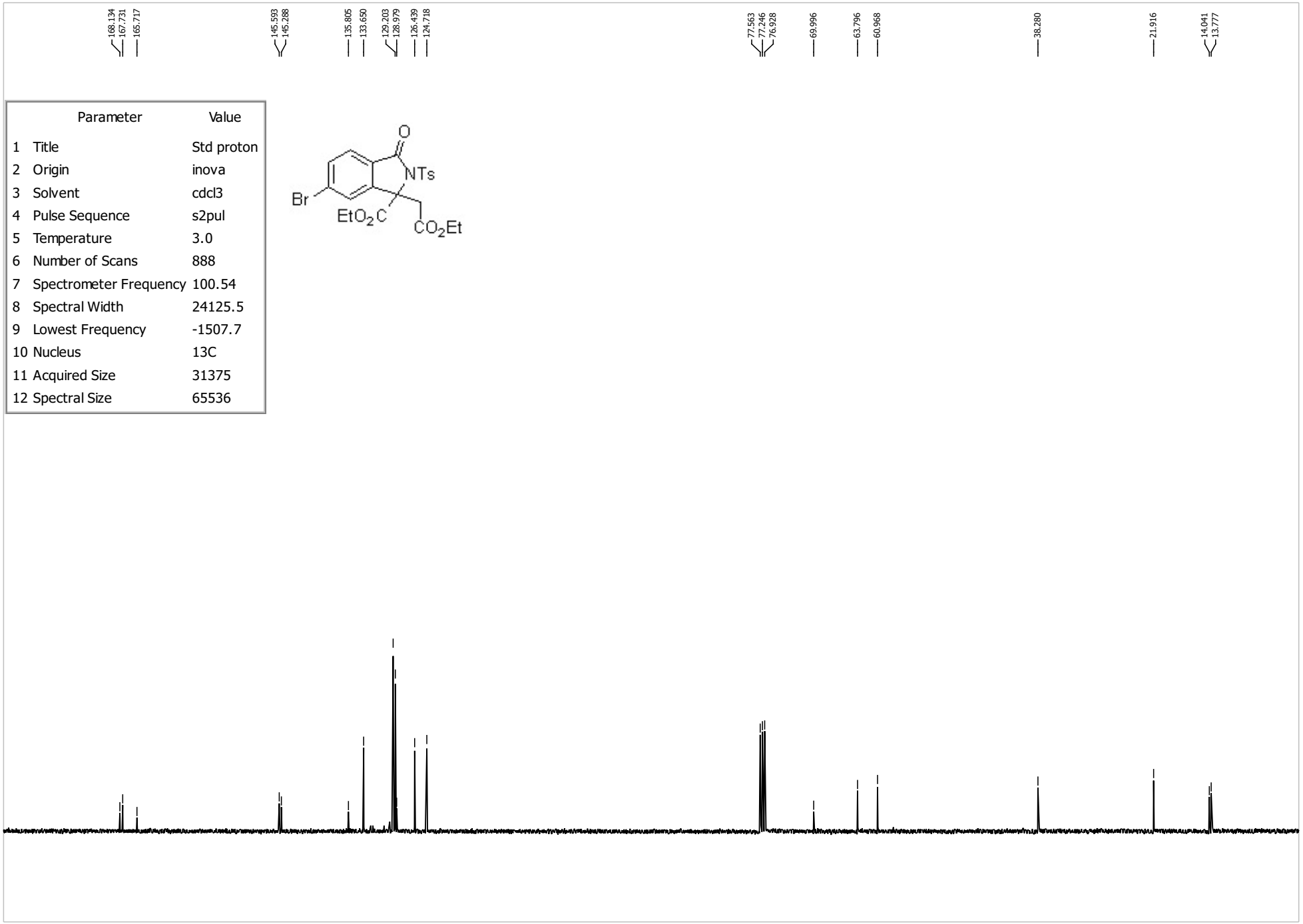
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	22.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768



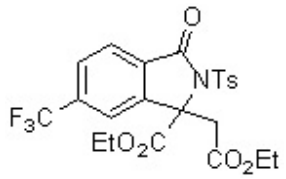


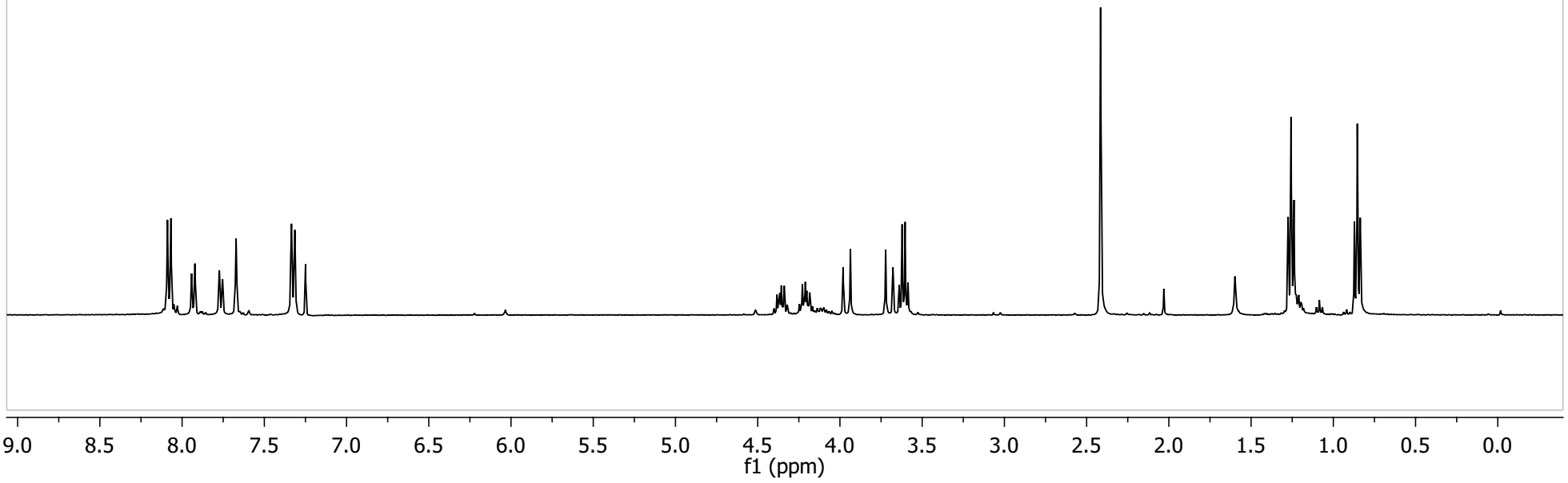
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

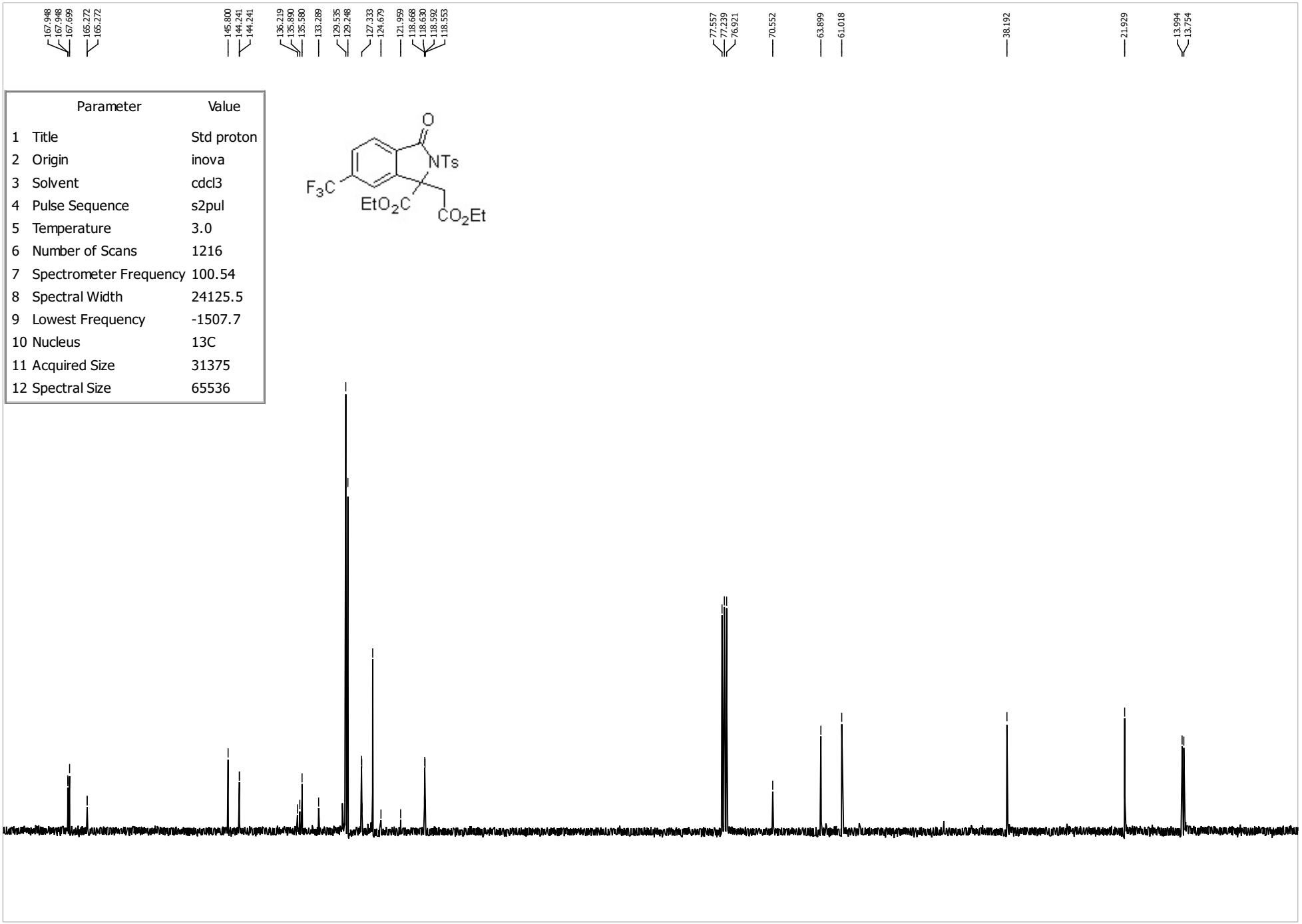




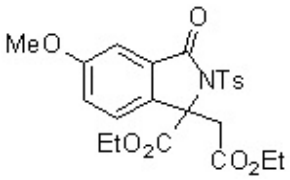
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

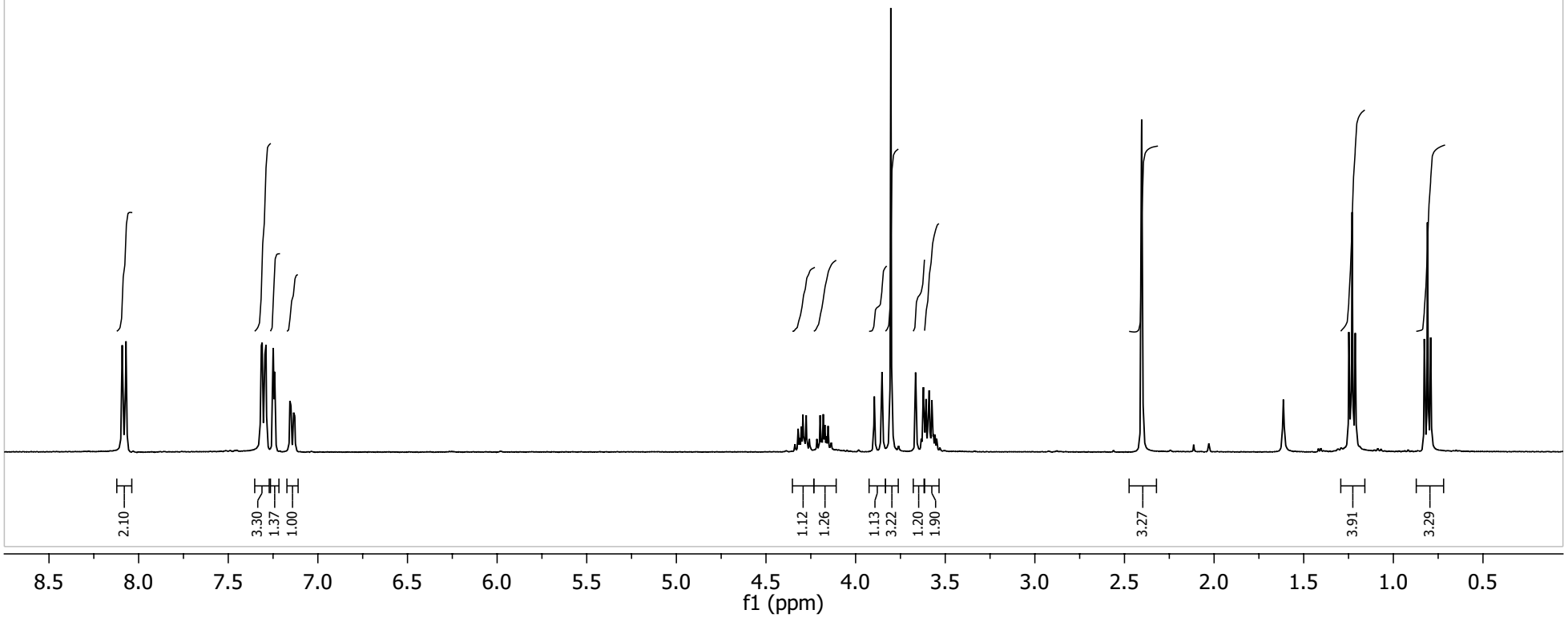


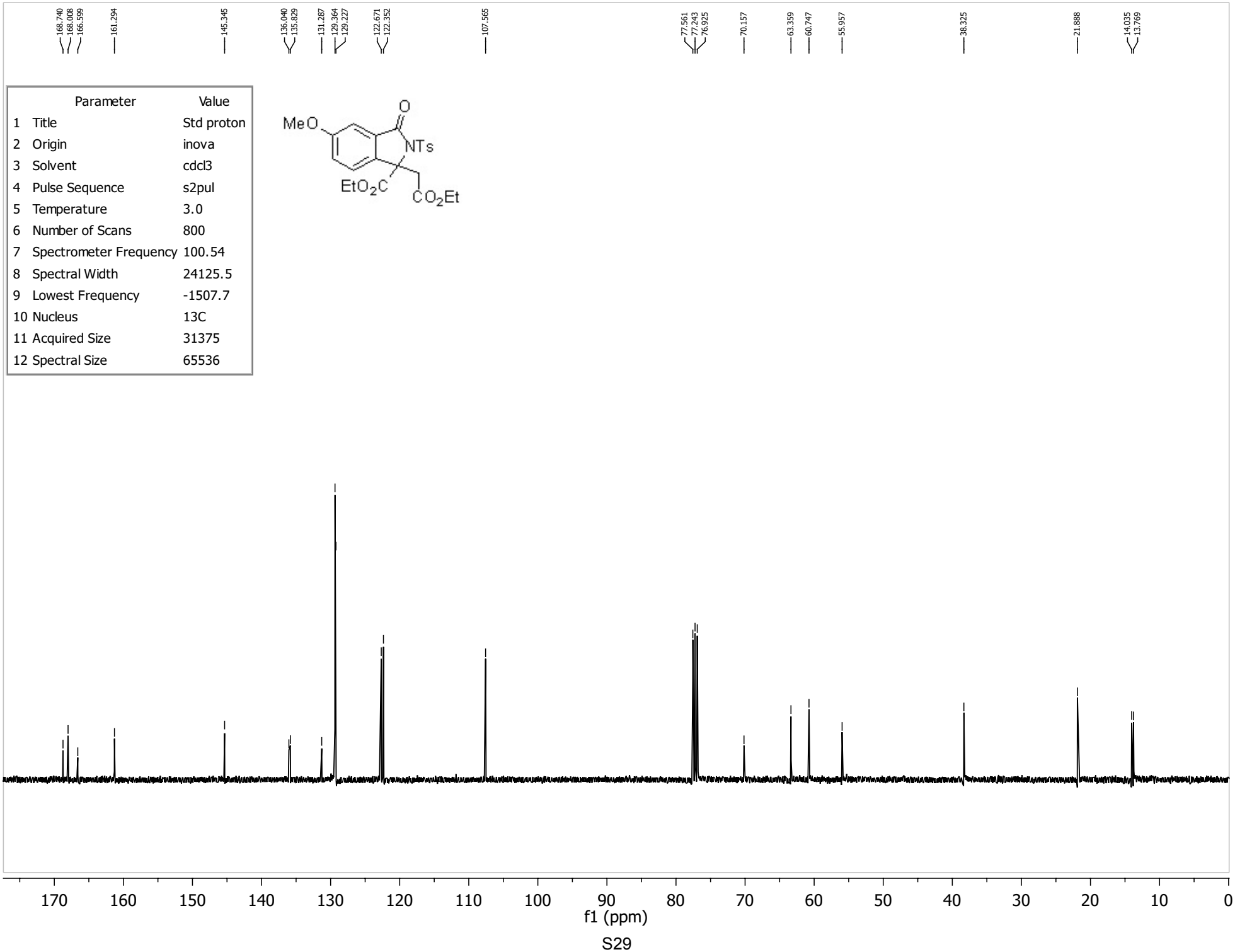




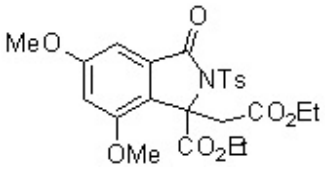
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

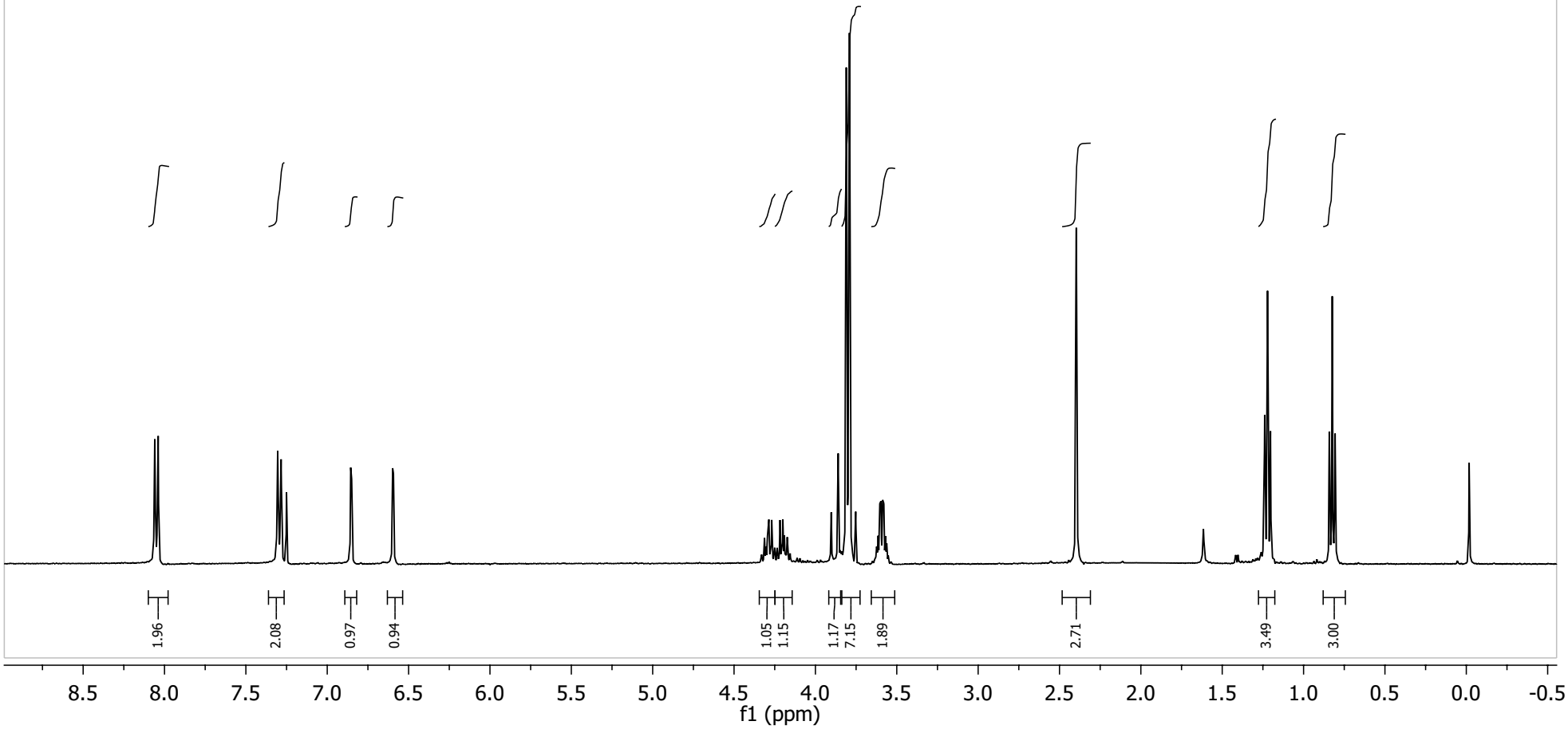


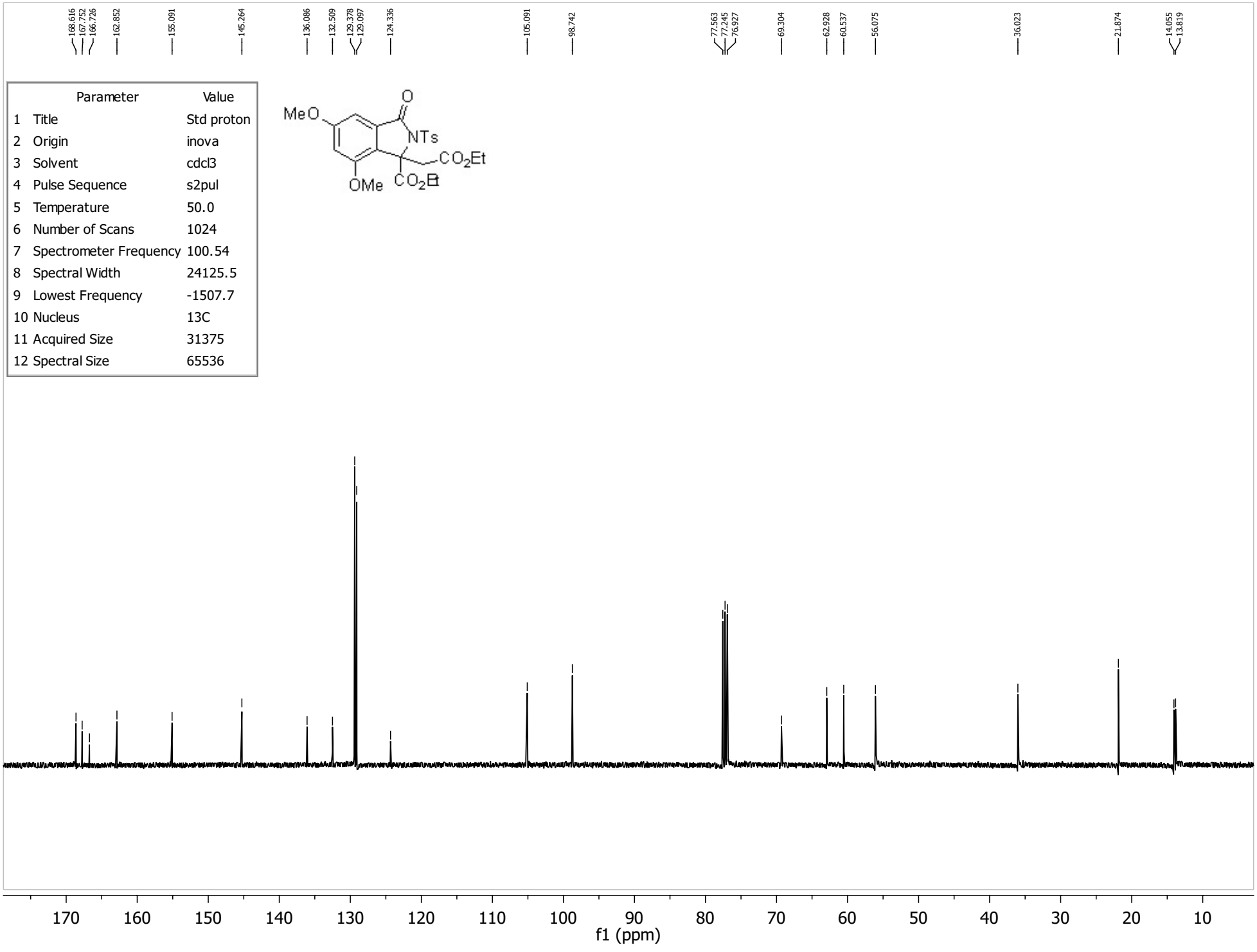




	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

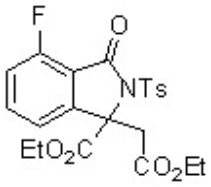


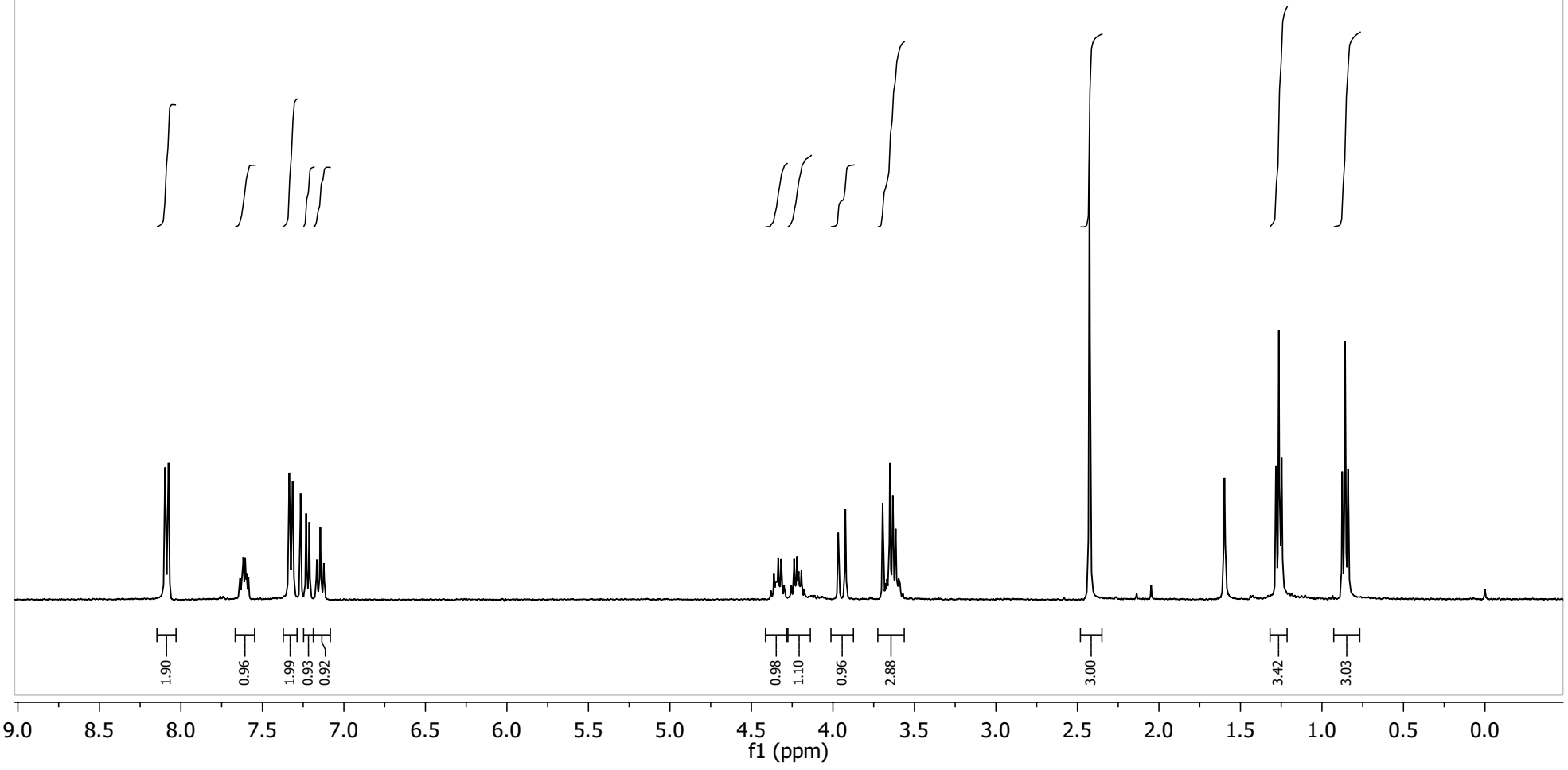


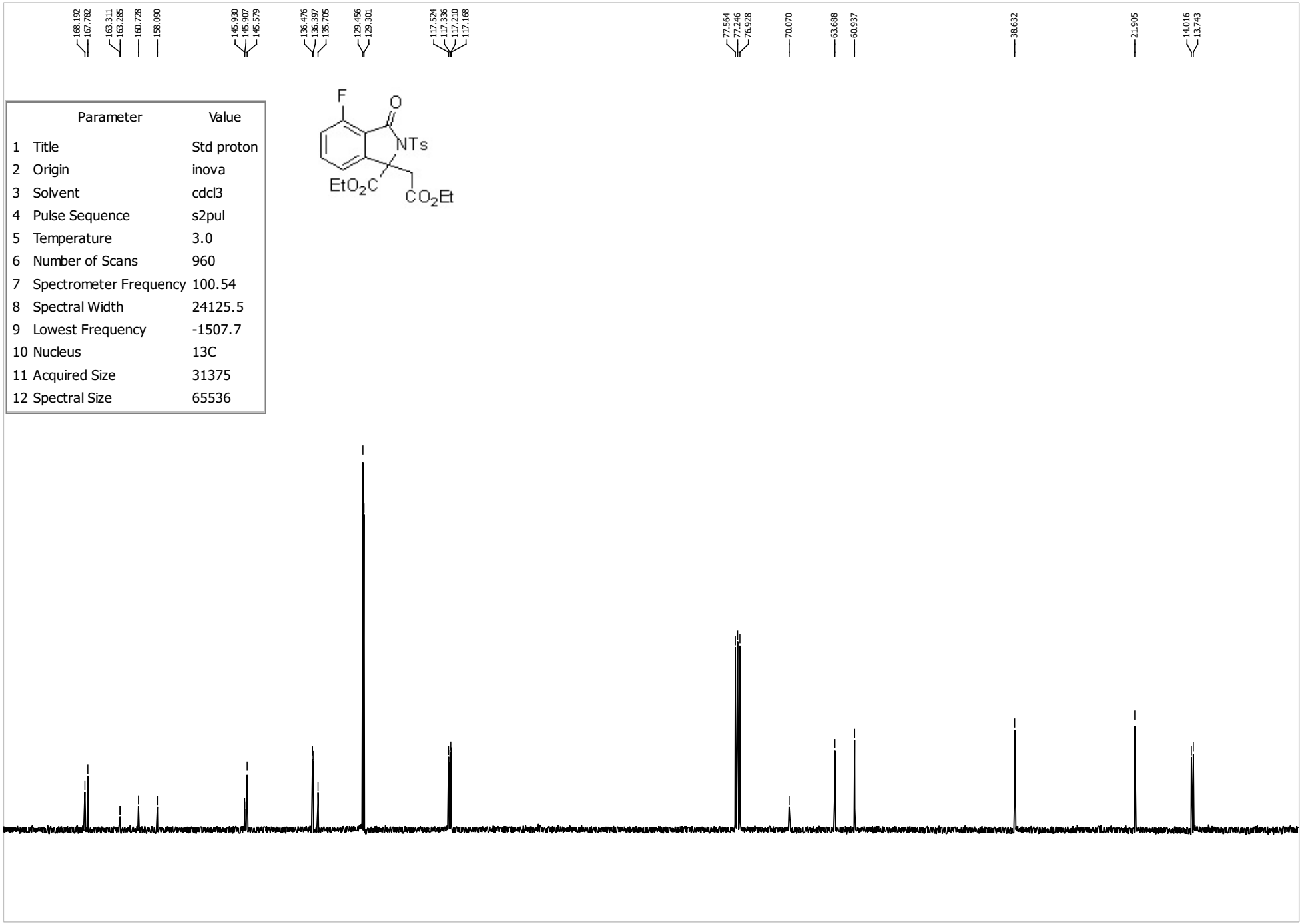


	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	1024
7	Spectrometer Frequency	100.54
8	Spectral Width	24125.5
9	Lowest Frequency	-1507.7
10	Nucleus	13C
11	Acquired Size	31375
12	Spectral Size	65536

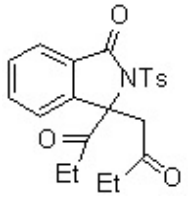
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	30.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-793.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

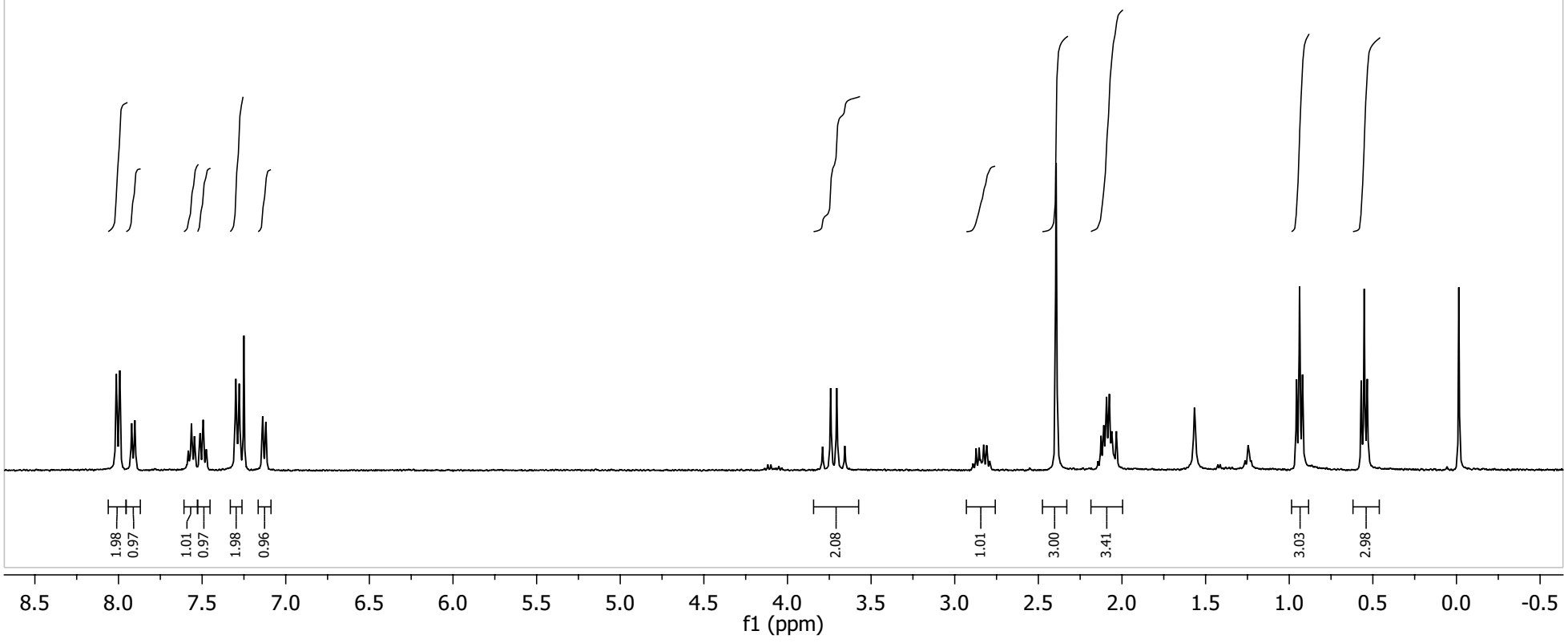


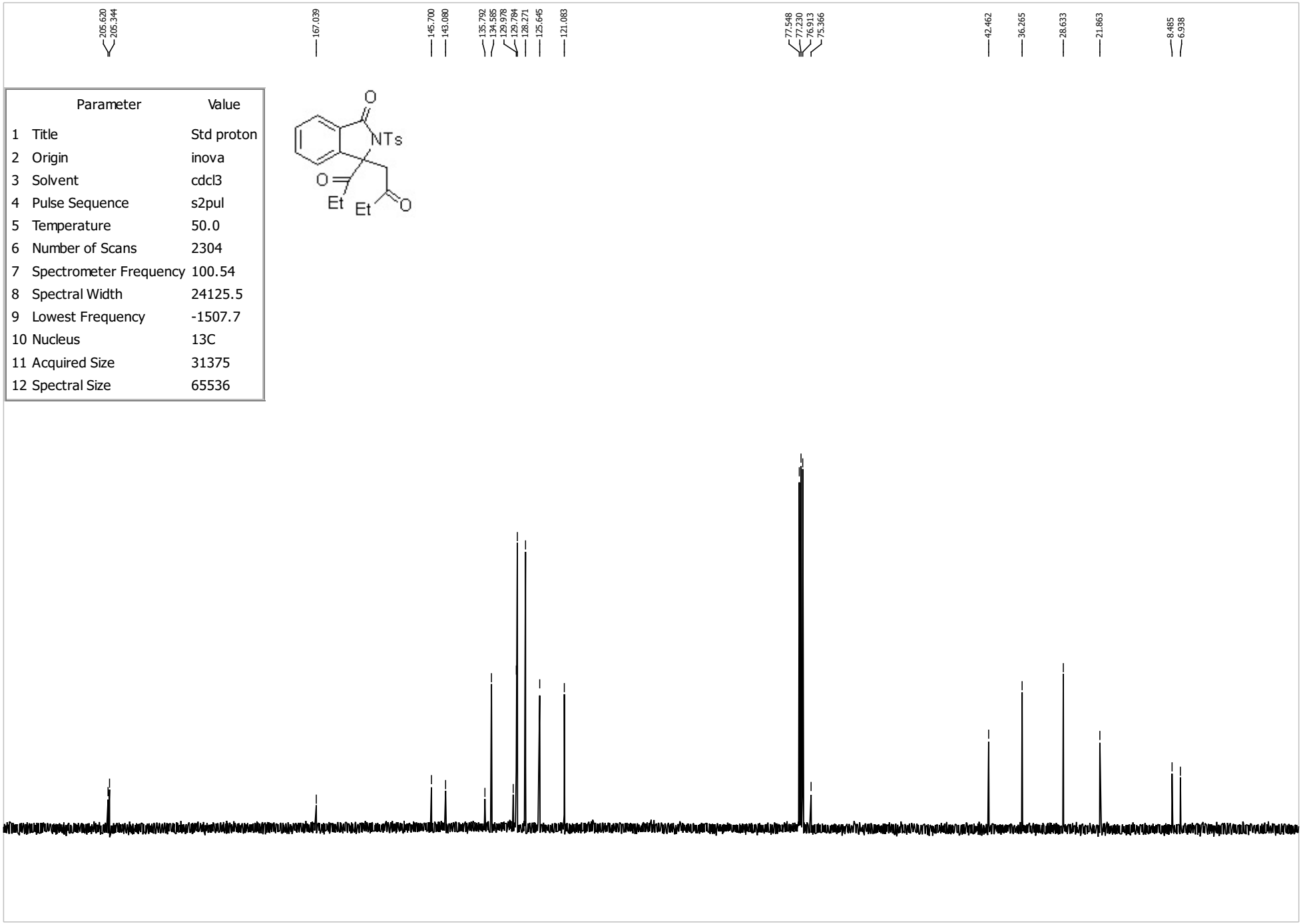




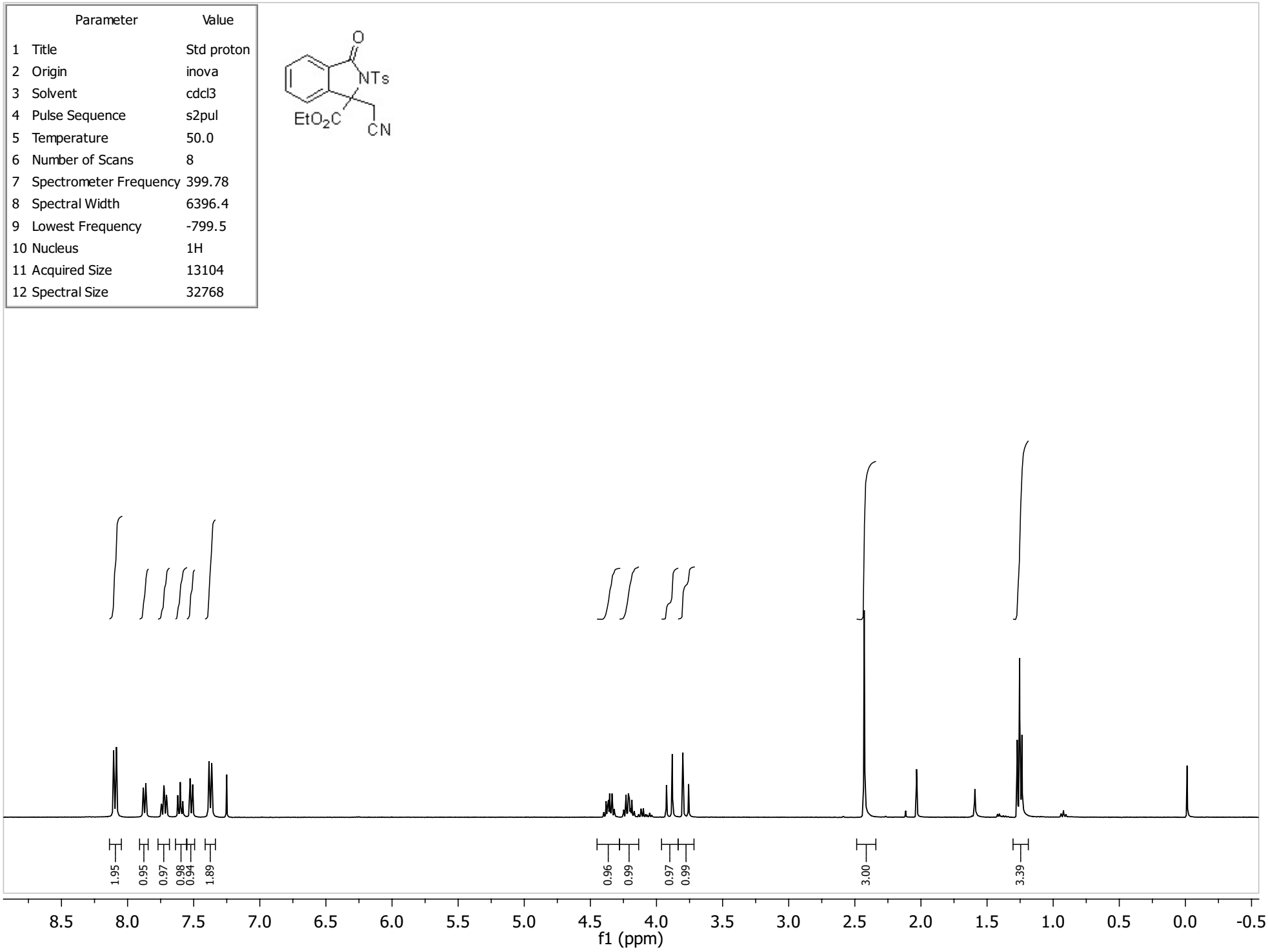
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	16
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

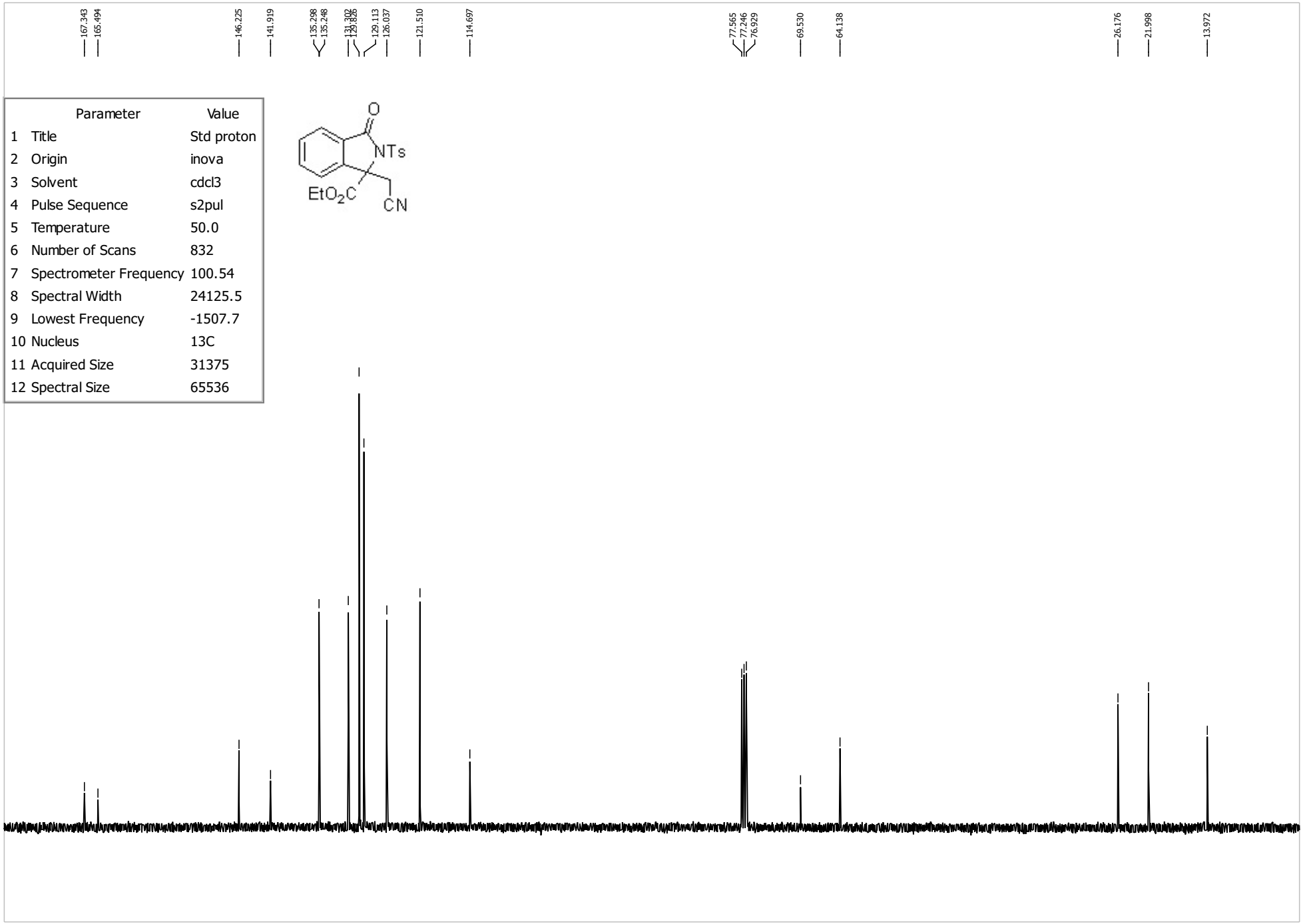




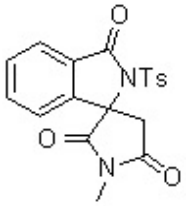


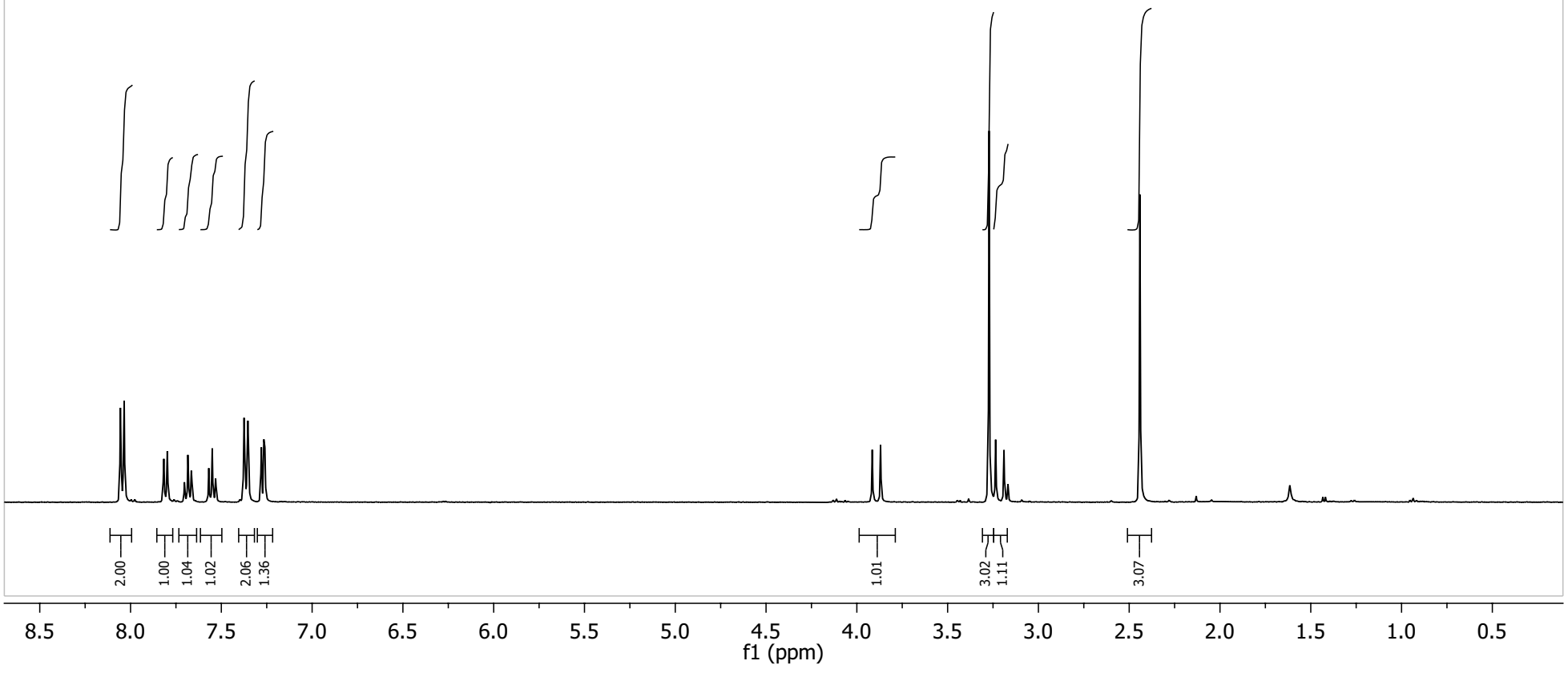
	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-799.5
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768

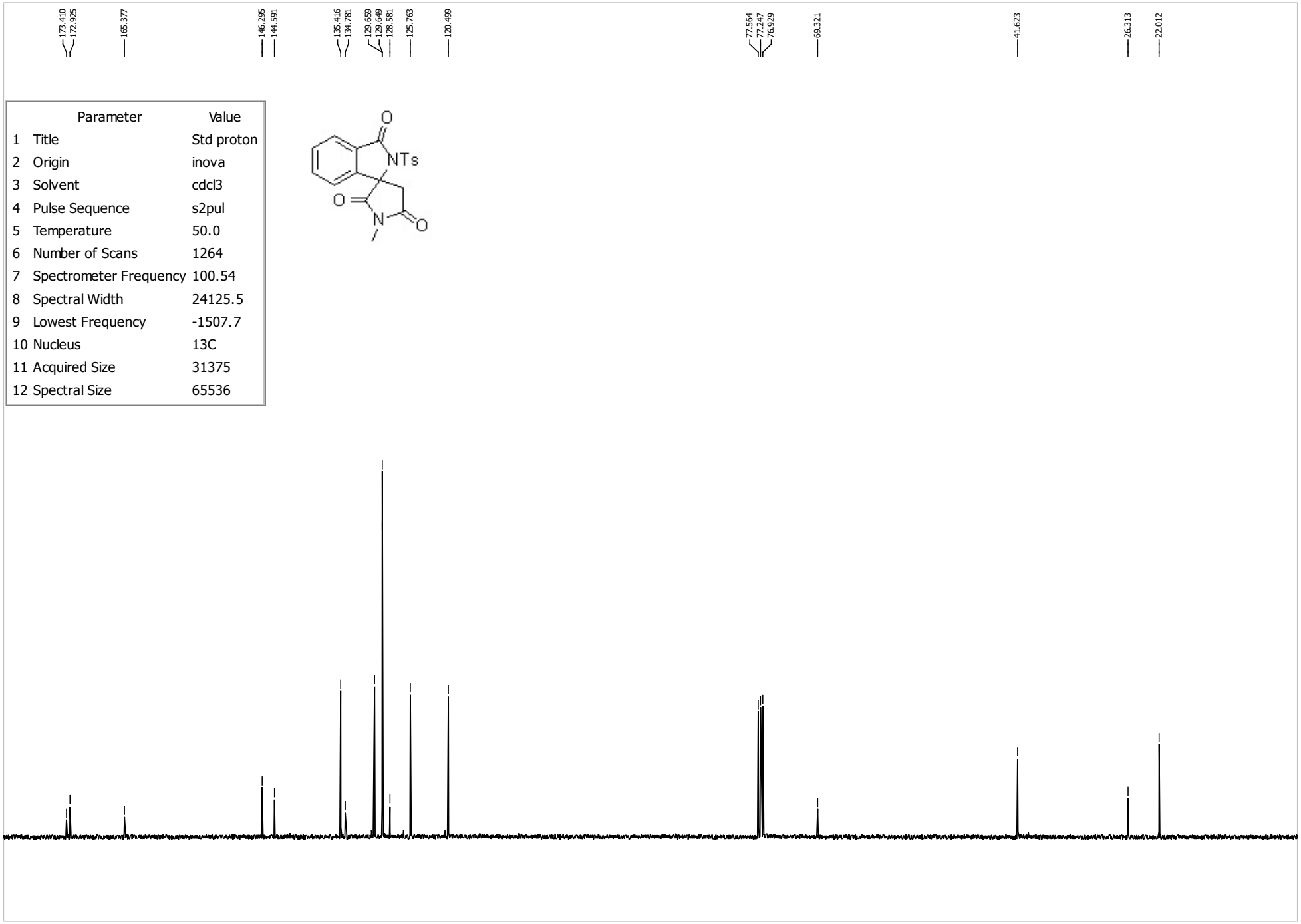




	Parameter	Value
1	Title	Std proton
2	Origin	inova
3	Solvent	cdcl3
4	Pulse Sequence	s2pul
5	Temperature	50.0
6	Number of Scans	8
7	Spectrometer Frequency	399.78
8	Spectral Width	6396.4
9	Lowest Frequency	-793.1
10	Nucleus	1H
11	Acquired Size	13104
12	Spectral Size	32768



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172.925
165.377
146.295
144.591
135.416
134.781
129.659
129.649
128.581
125.763
120.499
77.564
77.247
76.929
69.321
41.623
26.313
22.012
Parameter Value
1 Title Std proton
2 Origin inova
3 Solvent cdcl3
4 Pulse Sequence s2pul
5 Temperature 50.0
6 Number of Scans 1264
7 Spectrometer Frequency 100.54
8 Spectral Width 24125.5
9 Lowest Frequency -1507.7
10 Nucleus 13C
11 Acquired Size 31375
12 Spectral Size 65536
NTs
O
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)