Facile, Catalyst free Cascade Synthesis of Sulfonyl Guanidines via Carbodiimide Coupling with amines

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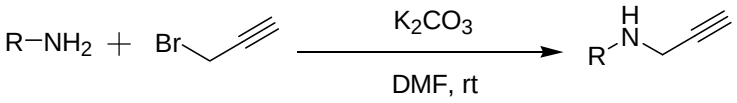
1. **General Information:**

All the reactions were carried out in open atmosphere using flame-dried glassware. Distilled analytical grade solvents were used. The starting materials *N*,*N*-dibromoarylsulfonamides were synthesized according to the literature procedures.[1] ^{1}H and ^{13}C spectra were recorded on a Bruker Ultrashield 300 MHz spectrometer. Chemical shifts are given in δ units relative to the tetramethylsilane (TMS) signal as an internal reference in $CDCl_3$. ^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); m (multiplet); br (broad). IR spectra were recorded in IR Affinity-1 (SHIMADZU) spectrometer. Mass spectra were recorded on Q-TOF ESI-MS instrument (model HAB 273) and Bruker MaXis 10138 Q-TOF ESI instrument. Chromatographic purification was performed using flash column chromatography over a manually packed column containing silica gel (230-400 mesh). Melting points were measured in Relitech melting point apparatus. Single crystal X-ray diffraction data was collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Data integration was done using SAINT. Intensities for absorption were corrected using SADABS. Structure solution and refinement were carried out using Bruker SHELXTL. The hydrogen atoms were refined isotropically, and all the other atoms were refined anisotropically. N−H hydrogen was located from difference electron density maps, and C−H hydrogens were fixed using the HFIX command in SHELXTL. Molecular graphics were prepared using Mercury version 1.4.1 (free version).

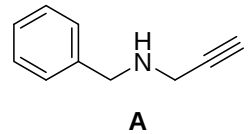
2. **General procedure for synthesis of *N*-propargyl amines:**[2]



To a solution of amine (10 mmol, 1.0 eqiuv) in DMF (15 mL), K_2CO_3 (5 mmol, 0.5 equiv) was added and stirred for 5 min at room temperature. Then a solution of propargyl bromide (2.5 mmol, 0.25 equiv) in DMF (5 mL) was added dropwise to the reaction mixture. The resulting mixture was stirred overnight at room temperature. After completion of the reaction, the mixture was diluted with ethyl acetate (20 mL) and washed with brine. The aqueous layer was extracted using ethyl acetate, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The

residue was purified by flash column chromatography on silica gel using petroleum ether-ethyl acetate (8:2) as eluent to afford *N*-propargyl amine.

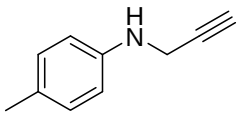
Benzyl-prop-2-ynyl-amine (A):



A

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35-7.29 (m, 5H), 3.89 (s, 2H), 3.43 (d, J = 2.4 Hz, 1H), 2.28 (t, J = 2. Hz, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 139.1, 128.34, 128.33, 127.0, 81.9, 71.5, 52.1, 37.1.

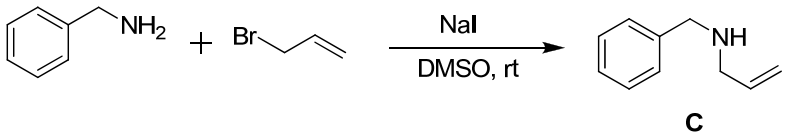
Prop-2-ynyl-*p*-tolylamine (B):



B

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.06 (d, J = 7.8 Hz, 2H), 6.64 (d, J = 8.1 Hz, 2H), 3.93 (s, 2H), 3.77 (s, 1H), 2.28 (s, 3H), 2.22 (s, 1H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 144.4, 129.6, 127.8, 113.6, 81.6, 71.1, 33.8, 20.3.

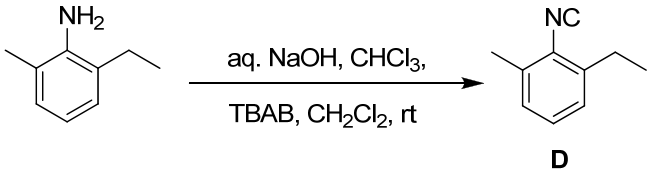
3. **General procedure for synthesis of *N*-allyl benzylamine (C):**[3]



C

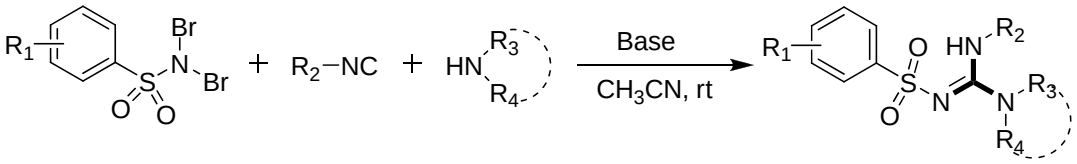
To a stirred solution of benzylamine (26.1 mmol, 2.05 equiv) and NaI (0.125 mmol, 0.01 equiv) in DMSO (20 mL), allyl bromide (12.7 mmol, 1.0 equiv) was added dropwise at 0 ^oC. The reaction was stirred for 18 h at room temperature. 1M aqueous $NaHCO_3$ (30 mL) was added to the reaction mixture and the aqueous layer was extracted using diethyl ether. The combined organic layer was washed with saturated brine solution, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using petroleum ether-ethyl acetate (7:3) as eluent to afford *N*-allyl benzylamine (**C**) as yellow oil. **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.34-7.27 (m, 5H), 6.01-5.87 (m, 1H), 5.23-5.11 (m, 2H), 3.80 (s, 2H), 3.28 (d, J = 5.7 Hz, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 140.0, 136.5, 128.2, 128.0, 126.8, 115.9, 53.1, 51.6.

4. **General procedure for synthesis of 2-ethyl-6-methyl isocyanobenzene (D):**[4]



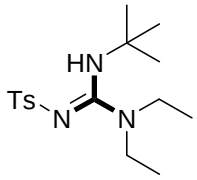
To a solution of 2-ethyl-6-methyl aniline (22 mmol, 1 equiv) in CH_2Cl_2 (100 mL), 50 wt% of aqueous NaOH (50 mL), TBAB (1 mol%) and $CHCl_3$ (33 mmol, 1.5 equiv) was added and stirred at room temperature for 6 h. After completion of the reaction, the mixture was diluted with 200 mL of water and the organic layer was separated. The organic layer was further washed twice with 100 mL of water and once with 100 mL saturated NaCl solution. The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography using petroleum ether-dichloromethane (4:1) as eluent to afford 2-ethyl-6-methyl isocyanobenzene (**D**) as pale yellow liquid. **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.25-7.20 (m, 1H), 7.10 (d, J = 7.5 Hz, 2H), 2.78 (q, J = 7.5 Hz, 2H), 2.43 (s, 3H), 1.27 (t, J = 7.5 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 167.5, 140.4, 134.9, 128.7, 127.6, 126.0, 25.6, 18.8, 13.7.

5. **General procedure for synthesis of sulfonyl guanidines and characterization:**



To a solution of isocyanide (0.5 mmol, 1.0 equiv) and amine (0.5 mmol, 1.0 equiv) in CH_3CN (4 mL), *N,N*-dibromoarylsulfonamide (0.5 mmol, 1.0 equiv) and base (2-3 equiv) was added and stirred at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was pass through a short pad of celite and the washed with ethyl acetate. The solvent was concentrated under reduced pressure and further purified by flash column chromatography using petroleum ether-ethyl acetate as eluent to afford the desired product.

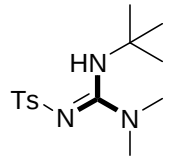
***N*-(*tert*-Butylamino-diethylamino-methylene)-4-methylbenzenesulfonamide (4a):**



4a

Following the general procedure, compound **4a** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (84%, 136.5 mg); mp 110-112 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 7.2 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 5.25 (s, 1H), 3.46 (q, J = 7.2 Hz, 4H), 2.37 (s, 3H), 1.18- 1.14 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.5, 141.9, 141.1, 128.8, 125.8, 54.0, 44.0, 29.8, 21.3, 12.8; **IR (KBr, cm^{-1})**: ν 3307, 2972, 2362, 1566, 1508, 1454, 1253, 1138, 1068, 862, 754, 711; **HRMS m/z (ESI)** calculated for $C_{16}H_{28}N_3O_2S$ $(M+H)^+$ 326.1896 found 326.1896.

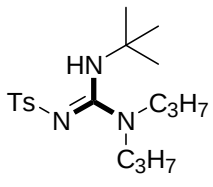
***N*-(*tert*-Butylamino-dimethylamino-methylene)-4-methylbenzenesulfonamide (4b):**



4b

Following the general procedure, compound **4b** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and dimethylamine (34 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (82%, 121.7 mg); mp 152-154 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 4.92 (s, 1H), 3.06 (s, 6H), 2.38 (s, 3H), 1.15 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.3, 142.1, 141.1, 128.8, 125.8, 53.6, 40.4, 29.6, 21.3; **IR (KBr, cm^{-1})**: ν 3311, 2959, 2354, 1560, 1510, 1457, 1242, 1119, 1075, 860, 733; **HRMS m/z (ESI)** calculated for $C_{14}H_{24}N_3O_2S$ $(M+H)^+$ 298.1583 found 298.1580.

***N*-(*tert*-Butylamino-dipropylamino-methylene)-4-methylbenzenesulfonamide (4c):**

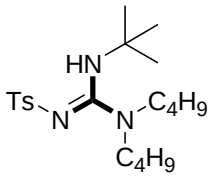


4c

Following the general procedure, compound **4c** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and di-n-propylamine (68 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (84%, 148.2 mg); mp 138-140 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.77 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 5.26 (s, 1H), 3.34 (t, J = 7.5 Hz, 4H), 2.36 (s, 3H), 1.62-1.52 (m, 4H), 1.19 (s, 9H), 0.87 (t, J = 7.2 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.0, 141.9, 141.1, 128.8, 125.8, 54.1, 51.7, 29.8, 21.3, 20.9, 11.2; **IR (KBr, cm^{-1})**: ν 3302, 2951,

2364, 1565, 1506, 1455, 1250, 1102, 1071, 857, 728; **HRMS m/z (ESI)** calculated for $C_{18}H_{32}N_3O_2S$ $(M+H)^+$ 354.2209 found 354.2225.

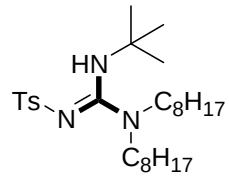
***N*-(*tert*-Butylamino-dibutylamino-methylene)-4-methylbenzenesulfonamide (4d):**



4d

Following the general procedure, compound **4d** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and di-n-butylamine (84 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (87%, 165.7 mg); mp 110-112 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.36 (s, 1H), 3.37 (t, J = 7.2 Hz, 4H), 2.37 (s, 3H), 1.55-1.48 (m, 4H), 1.32-1.21 (m, 13H), 0.89 (t, J = 7.2 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.2, 141.9, 141.2, 128.8, 125.9, 54.4, 49.7, 30.0, 29.7, 21.3, 20.0, 13.7; **IR (KBr, cm^{-1})**: ν 3332, 2964, 2362, 1566, 1508, 1458, 1255, 1136, 1074, 883, 719; **HRMS m/z (ESI)** calculated for $C_{20}H_{36}N_3O_2S$ $(M+H)^+$ 382.2522 found 382.2528.

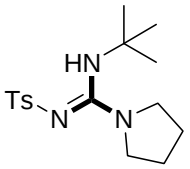
***N*-(*tert*-Butylamino-dioctylamino-methylene)-4-methylbenzenesulfonamide (4e):**



4e

Following the general procedure, compound **4e** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and di-n-octylamine (151 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Colorless oil (83%, 204.5 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.74 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.36 (s, 1H), 3.32 (t, J = 6.9 Hz, 4H), 2.33 (s, 3H), 1.47 (s, br, 4H), 1.33-1.17 (m, 29H), 0.84 (t, J = 6 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.0, 141.9, 141.0, 128.7, 125.8, 54.2, 49.9, 31.6, 29.8, 29.1, 29.0, 27.5, 26.6, 22.4, 21.2, 13.9; **IR (KBr, cm^{-1})**: ν 3320, 2948, 2367, 1558, 1514, 1447, 1236, 1108, 1069, 880, 751; **HRMS m/z (ESI)** calculated for $C_{28}H_{52}N_3O_2S$ $(M+H)^+$ 494.3774 found 494.3774.

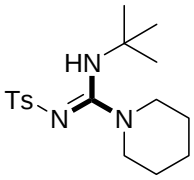
***N*-(*tert*-Butylamino-pyrrolidin-1-yl-methylene)-4-methylbenzenesulfonamide (4f):**



4f

Following the general procedure, compound **4f** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and pyrrolidine (41 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (76%, 122.7 mg); mp 141-143 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.76 (d, J = 7.5 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 4.53 (s, 1H), 3.59 (s, br, 4H), 2.34 (s, 3H), 1.90 (s, br, 4H), 1.10 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.5, 142.8, 140.5, 128.6, 125.5, 52.6, 49.6, 29.3, 25.3, 21.2; **IR (KBr, cm^{-1})**: ν 3341, 2965, 2362, 1577, 1515, 1433, 1271, 1129, 1071, 866, 707; **HRMS m/z (ESI)** calculated for $C_{16}H_{26}N_3O_2S$ $(M+H)^+$ 324.1740 found 324.1744.

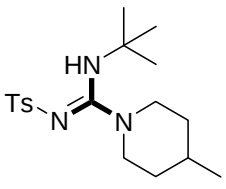
***N*-(*tert*-Butylamino-piperidin-1-yl-methylene)-4-methylbenzenesulfonamide (4g):**



4g

Following the general procedure, compound **4g** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and piperidine (49 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (83%, 139.8 mg); mp 115-117 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.17 (s, 1H), 3.44 (s, br, 4H), 2.37 (s, 3H), 1.63 (s, br, 6H), 1.16 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.9, 141.8, 141.2, 128.8, 125.9, 54.0, 50.0, 29.8, 25.4, 24.2, 21.3; **IR (KBr, cm^{-1})**: ν 3332, 2958, 2358, 1571, 1512, 1436, 1257, 1132, 1076, 879, 744; **HRMS m/z (ESI)** calculated for $C_{17}H_{28}N_3O_2S$ $(M+H)^+$ 338.1896 found 338.1907.

***N*-[*tert*-Butylamino-(4-methyl-piperidin-1-yl)-methylene]-4-methylbenzenesulfonamide (4h):**

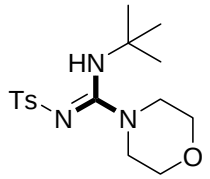


4h

Following the general procedure, compound **4h** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 4-methylpiperidine (59 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Yellow oil (80%, 140.4 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.75 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 5.16 (s, 1H), 3.92 (d, J = 13.2 Hz, 2H), 2.92 (t, J = 12.6 Hz,

2H), 2.34 (s, 3H), 1.65-1.54 (m, 3H), 1.32-1.20 (m, 2H), 1.13 (s, 9H), 0.92 (d, J = 6 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.6, 141.7, 141.1, 128.8, 125.8, 53.8, 49.3, 33.5, 30.8, 29.7, 21.4, 21.3; **IR (KBr, cm^{-1})**: ν 3330, 2953, 2365, 1576, 1511, 1440, 1241, 1137, 1080, 881, 739; **HRMS m/z (ESI)** calculated for $C_{18}H_{30}N_3O_2S$ $(M+H)^+$ 352.2053 found 352.2058.

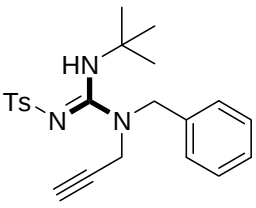
***N*-(*tert*-Butylamino-morpholin-4-yl-methylene)-4-methylbenzenesulfonamide (4i):**



4i

Following the general procedure, compound **4i** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and morpholine (43 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (82%, 138.9 mg); mp 159-161 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.77 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 5.20 (s, 1H), 3.77 (t, J = 4.8 Hz, 4H), 3.49 (t, J = 4.8 Hz, 4H), 2.38 (s, 3H), 1.17 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.6, 141.5, 141.3, 129.0, 125.9, 66.2, 54.1, 49.2, 29.7, 21.4; **IR (KBr, cm^{-1})**: ν 3410, 2970, 2358, 1570, 1517, 1450, 1274, 1138, 1078, 883, 705; **HRMS m/z (ESI)** calculated for $C_{16}H_{26}N_3O_3S$ $(M+H)^+$ 340.1689 found 340.1701.

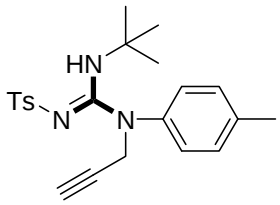
***N*-[(Benzyl-prop-2-ynyl-amino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (4j):**



4j

Following the general procedure, compound **4j** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *N*-propargyl benzylamine (73 mg) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (71%, 140.9 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, J = 7.8 Hz, 2H), 7.37-7.29 (m, 5H), 7.23 (d, J = 8.1 Hz, 2H), 5.54 (s, 1H), 4.69 (s, 2H), 4.14 (d, J = 2.4 Hz, 2H), 2.39 (s, 3H), 2.33-2.31 (m, 1H), 1.15 (s, 9 H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.6, 141.5, 141.3, 135.3, 128.9, 128.6, 128.5, 127.9, 125.9, 54.4, 54.0, 39.9, 29.5, 21.3; **IR (KBr, cm^{-1})**: ν 3353, 2924, 2374, 2067, 1593, 1413, 1382, 1267, 1078, 754; **HRMS m/z (ESI)** calculated for $C_{22}H_{28}N_3O_2S$ $(M+H)^+$ 398.1896 found 398.1894.

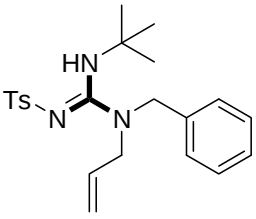
***N*-(*tert*-Butylamino-(prop-2-ynyl-*p*-tolyl-amino)-methylene]-4-methylbenzenesulfonamide (4k):**



4k

Following the general procedure, compound **4k** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *N*-propargyl-*p*-tolylamine (73 mg) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (69%, 136.9 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.83 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 7.14 (s, br, 4H), 5.95 (s, 1H), 4.57 (s, 2H), 2.38 (s, 3H), 2.22 (s, 1H), 0.95 (s, 9 H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.9, 141.7, 141.3, 140.8, 136.7, 130.1, 128.9, 126.2, 125.4, 79.0, 73.2, 54.5, 43.1, 29.3, 21.3, 20.9; **IR (KBr, cm^{-1})**: ν 3339, 2941, 2362, 2066, 1581, 1377, 1254, 1073, 749; **HRMS m/z (ESI)** calculated for $C_{22}H_{28}N_3O_2S$ $(M+H)^+$ 398.1896 found 398.1903.

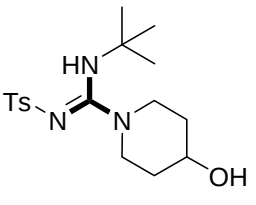
***N*-[(Allyl-benzyl-amino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (4l):**



4l

Following the general procedure, compound **4l** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *N*-allyl benzylamine (74 mg) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Pale yellow oil (65%, 129.6 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.80 (d, J = 8.4 Hz, 2H), 7.34-7.28 (m, 5H), 7.22 (d, J = 8.1 Hz, 2H), 5.85-5.72 (m, 1H), 5.21 (d, J = 8.7 Hz, 1H), 5.13 (d, J = 13.8 Hz, 1H), 4.62 (s, 2H), 4.05 (d, J = 6.3 Hz, 2H), 2.38 (s, 3H) 1.05 (s, 9 H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.8, 142.0, 141.0, 136.1, 133.4, 128.8, 128.6, 127.9, 127.7, 125.8, 119.4, 53.9, 53.68, 53.60, 29.3, 21.3; **IR (KBr, cm^{-1})**: ν 3327, 2929, 2381, 1644, 1505, 1389, 1251, 1070, 737; **HRMS m/z (ESI)** calculated for $C_{22}H_{30}N_3O_2S$ $(M+H)^+$ 400.2053 found 400.2041.

***N*-[*tert*-Butylamino-(4-hydroxy-piperidin-1-yl)-methylene]-4-methylbenzenesulfonamide (4m):**

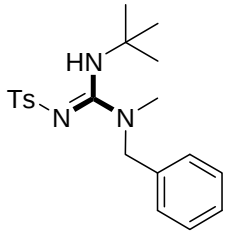


4m

Following the general procedure, compound **4m** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 4-hydroxypiperidine (51 mg) in presence of K_2CO_3 (2 equiv., 138 mg).

Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 1:1). Yellow oil (72%, 127.0 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.77 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 5.24 (s, 1H), 3.95-3.93 (m, 1H), 3.80-3.74 (m, 2H), 3.30-3.23 (m, 2H), 2.38 (s, 3H), 1.99-1.96 (m, 3H), 1.70-1.63 (m, 2H), 1.17 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.8, 141.5, 141.4, 128.9, 125.9, 66.7, 54.2, 46.1, 33.5, 29.8, 21.4; **IR (KBr, cm^{-1})**: v 3445, 3327, 2944, 2360, 1587, 1448, 1259, 1053, 855, 756; **HRMS m/z (ESI)** calculated for $C_{17}H_{28}N_3O_3S$ $(M+H)^+$ 354.1845 found 354.1853.

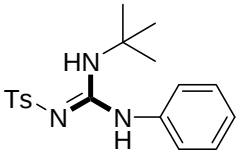
***N*-[(Benzyl-methyl-amino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (4n):**



4n

Following the general procedure, compound **4n** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *N*-methyl benzylamine (64 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (79%, 147.3 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, J = 8.1 Hz, 2H), 7.36-7.29 (m, 3H), 7.24-7.19 (m, 4H), 5.03 (s, 1H), 4.58 (s, 2H), 3.04 (s, 3H), 2.36 (s, 3H), 1.08 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.3, 142.0, 141.1, 135.6, 128.8, 127.7, 127.4, 125.7, 56.0, 53.6, 39.3, 29.5, 21.3; **IR (KBr, cm^{-1})**: v 3352, 2968, 2360, 1570, 1510, 1440, 1263, 1136, 1091, 887, 743; **HRMS m/z (ESI)** calculated for $C_{20}H_{28}N_3O_2S$ $(M+H)^+$ 374.1896 found 374.1897.

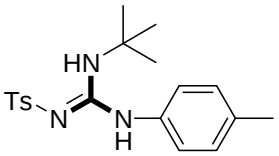
***N*-(*tert*-Butylamino-phenylamino-methylene)-4-methylbenzenesulfonamide (4o)**:[5]



4o

Following the general procedure, compound **4o** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and aniline (46 µL) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (47%, 81.0 mg); mp 93-95 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.87 (s, 1H), 7.82 (t, J = 6.9 Hz, 2H), 7.40 (t, J = 7.8 Hz, 2H), 7.30-7.24 (m, 3H), 7.11 (d, J = 7.5 Hz, 2H), 4.68 (s, 1H), 2.40 (s, 3H), 1.29 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.8, 141.8, 140.8, 135.7, 130.1, 129.1, 127.2, 125.8, 125.5, 52.5, 29.1, 21.4; **IR (KBr, cm^{-1})**: v 3315, 3009, 2971, 2368, 1634, 1444, 1237, 1054, 766.

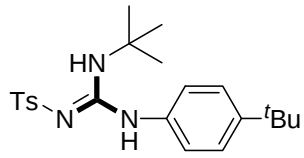
***N*-(*tert*-Butylamino-*p*-tolylamino-methylene)-4-methylbenzenesulfonamide (4p):**[6]



4p

Following the general procedure, compound **4p** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *p*-toluidine (54 mg) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (54%, 96.9 mg); mp 129-131 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.77 (s, 1H), 7.83 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 4.62 (s, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.28 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 153.2, 141.7, 140.9, 137.4, 132.8, 130.6, 129.0, 125.8, 125.7, 52.4, 29.1, 21.4, 20.9; **IR (KBr, cm^{-1})**: ν 3345, 2983, 2365, 1622, 1439, 1248, 1055, 844, 751.

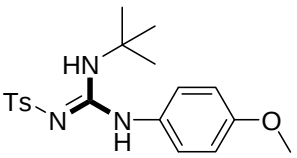
***N*-[*tert*-Butylamino-(4-*tert*-butyl-phenylamino)-methylene]-4-methylbenzenesulfonamide (4q):**[6]



4q

Following the general procedure, compound **4q** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 4-*t*-butylaniline (80 µL) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless oil (57%, 114.2 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.80 (s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 4.71 (s, 1H), 2.40 (s, 3H), 1.31-1.30 (m, 18H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.9, 150.3, 141.6, 140.9, 132.8, 128.9, 126.8, 125.8, 125.0, 52.3, 34.4, 31.1, 29.1, 21.3; **IR (KBr, cm^{-1})**: ν 3331, 2976, 2380, 1655, 1428, 1211, 1063, 851, 755.

***N*-[(*tert*-Butylamino-(4-methoxy-phenylamino)-methylene]-4-methylbenzenesulfonamide (4r):**[6]

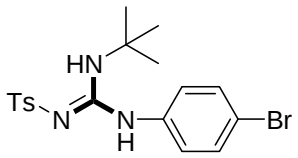


4r

Following the general procedure, compound **4r** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and *p*-anisidine (57 mg) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (52%, 97.5 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.70 (s, 1H), 7.83 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.5 Hz, 2H), 7.04 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 4.47

(s, 1H), 3.81 (s, 3H), 2.41 (s, 3H), 1.27 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.8, 153.6, 141.7, 141.0, 129.0, 128.0, 127.8, 125.8, 115.2, 55.4, 52.4, 29.2, 21.4; **IR (KBr, cm^{-1})**: ν 3357, 2994, 2366, 1635, 1441, 1230, 1054, 749.

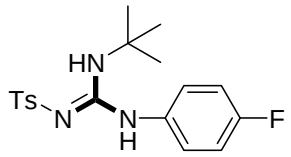
***N*-[(4-Bromo-phenylamino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (4s)**:[6]



4s

Following the general procedure, compound **4s** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 4-bromoaniline (86 mg) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (43%, 91.1 mg); mp 98-100 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.80 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 4.63 (s, 1H), 2.40 (s, 3H), 1.30 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.4, 141.9, 140.6, 134.8, 133.2, 129.1, 127.1, 125.8, 120.6, 52.7, 29.1, 21.4; **IR (KBr, cm^{-1})**: ν 3337, 2985, 2369, 1640, 1422, 1238, 1031, 842, 750.

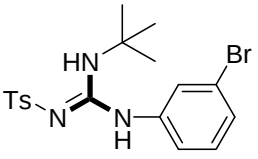
***N*-[(*tert*-Butylamino-(4-fluoro-phenylamino)-methylene]-4-methylbenzenesulfonamide (4t)**:[6]



4t

Following the general procedure, compound **4t** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 4-fluoroaniline (47 µL) in presence of KF (2 equiv., 58 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (46%, 83.4 mg); mp 90-92 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.76 (s, 1H), 7.81 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.15-7.05 (m, 4H), 4.50 (s, 1H), 2.39 (s, 3H), 1.27 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 161.3 (J_{CF} = 247.1 Hz), 153.0, 141.8, 140.7, 131.44, 131.40, 129.0 (J_{CF} = 3.3 Hz), 128.0 (J_{CF} = 8.7 Hz), 125.7, 116.9 (J_{CF} = 22.4 Hz), 52.5, 29.0, 21.3; **IR (KBr, cm^{-1})**: ν 3319, 2990, 2372, 1636, 1438, 1221, 1023, 757.

***N*-[(3-Bromo-phenylamino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (4u)**:

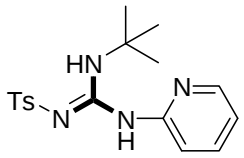


4u

Following the general procedure, compound **4u** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 3-bromoaniline (54 µL) in presence of KF (2 equiv., 58 mg). Purified

by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Semi solid (42%, 89.0 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 8.86 (s, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 6.9 Hz, 1H), 7.29-7.25 (m, 4H), 7.07 (d, J = 7.5 Hz, 1H), 4.71 (s, 1H), 2.41 (s, 3H), 1.31 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 152.2, 141.9, 140.5, 137.1, 131.1, 130.0, 129.1, 128.2, 125.7, 123.7, 123.3, 52.7, 29.0, 21.3; **IR (KBr, cm^{-1})**: ν 3331, 2983, 2376, 1621, 1444, 1219, 1042, 831, 745; **HRMS m/z (ESI)** calculated for $C_{18}H_{23}BrN_3O_2S$ $(M+H)^+$ 424.0688 found 424.0693.

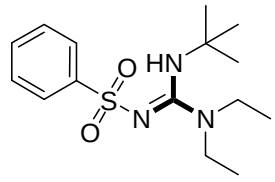
***N*-[*tert*-Butylamino-(pyridine-2-ylamino)-methylene]-4-methylbenzenesulfonamide (4v)**:



4v

Following the general procedure, compound **4v** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and 2-aminopyridine (47 mg) in presence of KF (3 equiv., 87 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Semi solid (22%, 38.0 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 10.51 (s, 1H), 10.11 (s, 1H), 8.16 (d, J = 4.2 Hz, 1H), 7.81 (d, J = 8.4 Hz, 2H), 7.66 (t, J = 6.9 Hz, 1H), 7.24 (d, J = 9 Hz, 2H), 6.97 (t, J = 5.4 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 2.38 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 152.5, 150.8, 145.7, 141.7, 141.2, 138.7, 129.1, 125.6, 118.0, 113.1, 52.3, 29.0, 21.4; **IR (KBr, cm^{-1})**: ν 3342, 2977, 2371, 1645, 1381, 1223, 1051, 847, 752; **HRMS m/z (ESI)** calculated for $C_{17}H_{23}N_4O_2S$ $(M+H)^+$ 347.1536 found 347.1545.

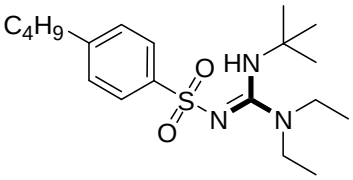
***N*-(*tert*-Butylamino-diethylamino-methylene)-benzenesulfonamide (5a):**



5a

Following the general procedure, compound **5a** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (158 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (82%, 127.5 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.81 (d, J = 7.5 Hz, 2H), 7.36-7.35 (m, 3H), 5.17 (s, 1H), 3.39 (q, J = 7.2 Hz, 4H), 1.10-1.05 (m, 15H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 156.7, 144.6, 130.6, 128.0, 125.5, 53.5, 43.8, 29.4, 12.5**; IR (KBr, cm^{-1})**: ν 3325, 2993, 2365, 1621, 1586, 1435, 1236, 1134, 1048, 734; **HRMS m/z (ESI)** calculated for $C_{15}H_{26}N_3O_2S$ $(M+H)^+$ 312.1740 found 312.1755.

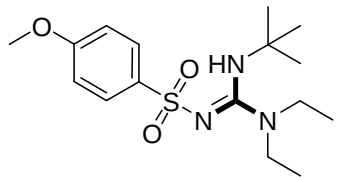
4-Butyl-*N*-(*tert*-butylamino-diethylamino-methylene)-benzenesulfonamide (5b):



5b

Following the general procedure, compound **5b** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-4-butylbenzenesulfonamide (186 mg) and diethylamine (52 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Pale yellow oil (84%, 154.1 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 5.25 (s, 1H), 3.45 (q, J = 6.6 Hz, 4H), 2.61 (t, J = 7.5 Hz, 2H), 1.59-1.56 (m, 2H), 1.34-1.29 (m, 3H), 1.23-1.12 (m, 14H), 0.89 (t, J = 7.2 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.5, 146.0, 142.0, 128.2, 125.8, 54.0, 43.9, 35.3, 33.2, 29.7, 22.0, 13.8, 12.7; **IR (KBr, cm^{-1})**: ν 3317, 2974, 2362, 1581, 1505, 1422, 1245, 1154, 1030, 810, 716; **HRMS m/z (ESI)** calculated for $C_{19}H_{34}N_3O_2S$ $(M+H)^+$ 368.2366 found 368.2363.

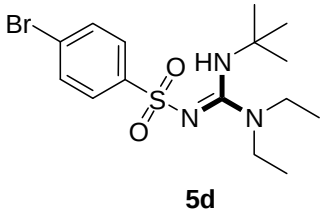
***N*-(*tert*-Butylamino-diethylamino-methylene)-4-methoxybenzenesulfonamide (5c):**



5c

Following the general procedure, compound **5c** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-4-methoxybenzenesulfonamide (173 mg) and diethylamine (52 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 3:2). Colorless semi solid (81%, 138.1 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.85 (d, J = 9 Hz, 2H), 6.91 (d, J = 9 Hz, 2H), 5.25 (s, 1H), 3.84 (s, 3H), 3.47 (q, J = 7.2 Hz, 4H), 1.25-1.15 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 161.3, 157.3, 137.0, 127.7, 113.2, 55.3, 53.9, 43.9, 29.7, 12.7; **IR (KBr, cm^{-1})**: ν 3326, 2980, 2368, 1651, 1577, 1434, 1228, 1147, 757; **HRMS m/z (ESI)** calculated for $C_{16}H_{28}N_3O_3S$ $(M+H)^+$ 342.1845 found 342.1845.

4-Bromo-*N*-(*tert*-butylamino-diethylamino-methylene)-benzenesulfonamide (5d):

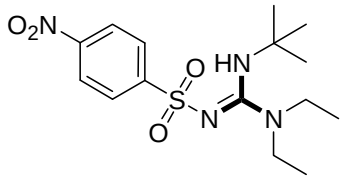


5d

Following the general procedure, compound **5d** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-4-bromobenzenesulfonamide (197 mg) and diethylamine (52 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (81%, 157.9 mg); mp

102-104 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.74 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 5.02 (s, 1H), 3.44 (q, J = 7.2 Hz, 4H), 1.17-1.14 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.5, 144.0, 131.3, 127.4, 125.1, 53.6, 43.9, 29.5, 12.7; **IR (KBr, cm^{-1})**: ν 3345, 2970, 2359, 1584, 1446, 1268, 1109, 1056, 854, 742; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}BrN_3O_2S$ $(M+H)^+$ 390.0845 found 390.0843.

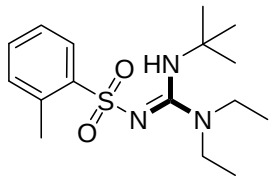
***N*-(*tert*-Butylamino-diethylamino-methylene)-4-nitrobenzenesulfonamide (5e):**



5e

Following the general procedure, compound **5e** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzenesulfonamide (180 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 1:1). Yellow solid (79%, 140.6 mg); mp 108-110 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.27 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 9 Hz, 2H), 4.87 (s, 1H), 3.49 (q, J = 6.9 Hz, 4H), 1.20 (t, J = 7.2 Hz, 6H), 1.13 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.9, 150.6, 148.6, 126.9, 123.6, 53.4, 44.0, 29.4, 12.7; **IR (KBr, cm^{-1})**: ν 3359, 2961, 2363, 1644, 1599, 1469, 1363, 1282, 1087, 878, 756; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}N_4O_4S$ $(M+H)^+$ 357.1591 found 357.1600.

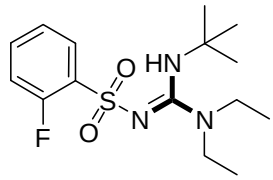
***N*-(*tert*-Butylamino-diethylamino-methylene)-2-methylbenzenesulfonamide (5f):**



5f

Following the general procedure, compound **5f** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*o*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (83%, 134.8 mg); mp 85-87 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.94 (d, J = 7.8 Hz, 1H), 7.32-7.29 (m, 1H), 7.25-7.20 (m, 2H), 5.22 (s, 1H), 3.45 (q, J = 7.2 Hz, 4H), 2.73 (s, 3H) 1.31-1.13 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.6, 142.7, 136.6, 131.7, 130.9, 126.6, 125.2, 53.9, 43.9, 29.8, 20.4, 12.8; **IR (KBr, cm^{-1})**: ν 3315, 2978, 2370, 1560, 1507, 1423, 1228, 1178, 1016, 844, 748; **HRMS m/z (ESI)** calculated for $C_{16}H_{28}N_3O_2S$ $(M+H)^+$ 326.1896 found 326.1891.

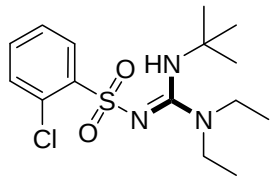
***N*-(*tert*-Butylamino-diethylamino-methylene)-2-fluorobenzenesulfonamide (5g):**



5g

Following the general procedure, compound **5g** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-fluorobenzenesulfonamide (167 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (74%, 121.7 mg); mp 80-82 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.89-7.86 (m, 1H), 7.43-7.41 (m, 1H), 7.18-7.09 (m, 2H), 5.13 (s, 1H), 3.47 (q, J = 7.2 Hz, 4H), 1.18-1.14 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.7 (J_{CF} = 252.6 Hz), 156.9, 132.9 (J_{CF} = 8.25 Hz), 132.5 (J_{CF} = 14.7 Hz), 128.2, 123.4, 116.5 (J_{CF} = 21.9 Hz), 53.8, 43.9, 29.6, 12.7; **IR (KBr, cm^{-1})**: ν 3320, 2972, 2358, 1627, 1568, 1421, 1254, 1056, 852, 757; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}FN_3O_2S$ $(M+H)^+$ 330.1646 found 330.1655.

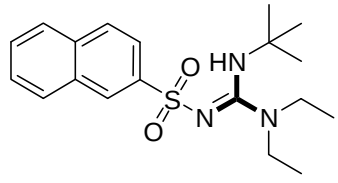
***N*-(*tert*-Butylamino-diethylamino-methylene)-2-chlorobenzenesulfonamide (5h):**



5h

Following the general procedure, compound **5h** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-chlorobenzenesulfonamide (175 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (77%, 132.8 mg); mp 107-109 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.08-8.05 (m, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.36-7.29 (m, 2H), 5.10 (s, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.23-1.15 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.2, 141.8, 131.78, 131.71, 131.3, 128.7, 126.2, 53.9, 43.9, 29.7, 12.7; **IR (KBr, cm^{-1})**: ν 3329, 2977, 2363, 1577, 1503, 1454, 1238, 808, 743; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}ClN_3O_2S$ $(M+H)^+$ 346.1350 found 346.1365.

***N*-(*tert*-Butylamino-diethylamino-methylene)-2-naphthylsulfonamide (5i):**

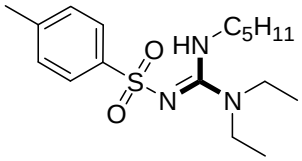


5i

Following the general procedure, compound **5i** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-naphthalenesulfonamide (183 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (80%, 144.4

mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.43 (s, 1H), 7.95-7.88 (m, 4H), 7.57-7.54 (m, 2H), 5.16 (s, 1H), 3.50 (q, J = 7.2 Hz, 4H), 1.22-1.17 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.1, 141.7, 133.9, 132.0, 129.0, 128.4, 127.6, 126.7, 125.5, 122.7, 53.9, 44.0, 29.7, 12.7; **IR (KBr, cm^{-1})**: ν 3345, 2985, 2360, 1572, 1440, 1224, 1058, 826, 759; **HRMS m/z (ESI)** calculated for $C_{19}H_{28}N_3O_2S$ $(M+H)^+$ 362.1896 found 362.1901.

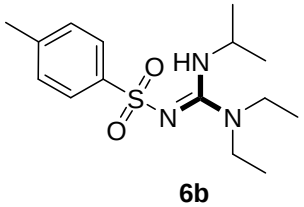
***N*-(Diethylamino-pentylamino-methylene)-4-methylbenzenesulfonamide (6a):**



6a

Following the general procedure, compound **6a** was prepared from 1-pentyl isocyanide (67 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (83%, 140.6 mg); mp 67-69 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.75 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 6.62 (s, 1H), 3.26 (q, J = 7.2 Hz, 4H), 3.05 (q, J = 5.4 Hz, 2H), 2.37 (s, 3H), 1.44-1.43 (m, 2H), 1.24 (s, br, 4H), 1.11-1.06 (m, 6H), 0.85 (t, J = 6.3 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 159.8, 141.5, 141.2, 129.0, 125.9, 46.1, 43.1, 29.9, 28.6, 22.1, 21.3, 13.8, 13.0; **IR (KBr, cm^{-1})**: ν 3332, 2931, 2362, 1577, 1502, 1429, 1253, 1138, 1085, 871, 810, 709; **HRMS m/z (ESI)** calculated for $C_{17}H_{30}N_3O_2S$ $(M+H)^+$ 340.2053 found 340.2041.

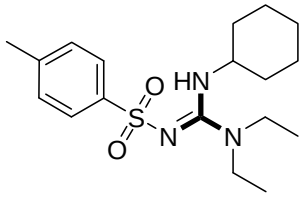
***N*-(Diethylamino-isopropylamino-methylene)-4-methylbenzenesulfonamide (6b):**



6b

Following the general procedure, compound **6b** was prepared from isopropyl isocyanide (47 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (79%, 122.8 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.73 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 6.36 (d, J = 8.7 Hz, 1H), 3.57-3.50 (m, 1H), 3.25 (q, J = 7.2 Hz, 4H), 2.33 (s, 3H), 1.07-1.01 (m, 12H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.8, 141.4, 141.2, 128.8, 125.9, 47.4, 43.2, 23.1, 21.2, 12.8; **IR (KBr, cm^{-1})**: ν 3321, 2960, 2358, 1561, 1443, 1218, 1071, 858, 702; **HRMS m/z (ESI)** calculated for $C_{15}H_{26}N_3O_2S$ $(M+H)^+$ 312.1740 found 312.1729.

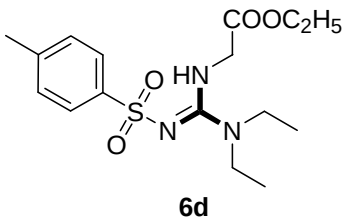
***N*-(Cyclohexylamino-diethylamino-methylene)-4-methylbenzenesulfonamide (6c):**



6c

Following the general procedure, compound **6c** was prepared from cyclohexyl isocyanide (62 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 3:2). Colorless semi solid (80%, 140.4 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.75 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.45 (d, J = 9 Hz, 1H), 3.27 (q, J = 7.2 Hz, 4H), 3.14-3.11 (m, 1H), 2.35 (s, 3H), 1.78-1.66 (m, 4H), 1.56-1.54 (m, 1H), 1.22-1.05 (m, 11H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 158.8, 141.5, 141.2, 128.9, 125.9, 54.6, 43.5, 33.5, 25.0, 24.8, 21.3, 12.8; **IR (KBr, cm^{-1})**: ν 3309, 2972, 2365, 1568, 1451, 1232, 1068, 855, 749; **HRMS m/z (ESI)** calculated for $C_{18}H_{30}N_3O_2S$ $(M+H)^+$ 352.2053 found 352.2055.

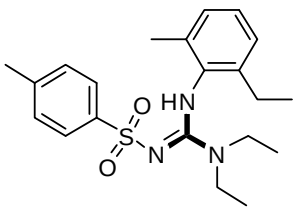
{[Diethylamino-(toluene-4-sulfonylimino)-methyl]-amino}-acetic acid ethyl ester (6d):



6d

Following the general procedure, compound **6d** was prepared from ethyl isocyanoacetate (55 µL), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 2:3). Semi solid (70%, 124.2 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.78 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.26 (s, 1H), 4.24-4.16 (m, 4H), 3.27 (q, J = 7.2 Hz, 4H), 2.36 (s, 3H), 1,26 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 6H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 169.9, 156.4, 142.2, 141.2, 128.9, 125.6, 61.8, 46.7, 43.3, 21.3, 14.0, 12.9; **IR (KBr, cm^{-1})**: ν 3332, 2981, 2357, 1761, 1589, 1455, 1248, 1057, 841, 751, 713; **HRMS m/z (ESI)** calculated for $C_{16}H_{26}N_3O_4S$ $(M+H)^+$ 356.1638 found 356.1638.

***N*-[Diethylamino-(2-ethyl-6-methyl-phenylamino)-methylene]-4-methylbenzenesulfonamide (6e):**

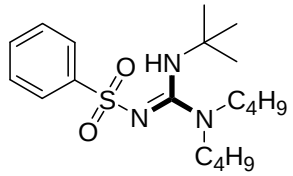


6e

Following the general procedure, compound **6e** was prepared from 2-ethyl-6-methyl isocyanobenzene (194 mg), *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) and diethylamine (52 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Brown oil (76%, 147.0 mg);

^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (s, 1H), 7.83 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.11 (t, J = 7.5 Hz, 2H), 7.01-6.99 (m, 1H), 3.08 (s, br, 4H), 2.49-2.39 (m, 5H), 1.93 (s, 3H), 1.13 (t, J = 7.5 Hz, 3H), 0.87-0.85 (m, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.0, 141.9, 140.6, 139.4, 135.6, 134.0, 129.0, 128.8, 127.0, 126.6, 126.4, 42.9, 24.3, 21.4, 18.4, 13.9, 12.5; **IR (KBr, cm^{-1})**: v 3318, 2977, 2361, 1655, 1606, 1366, 1257, 1081, 736; **HRMS m/z (ESI)** calculated for $C_{21}H_{30}N_3O_2S$ $(M+H)^+$ 388.2053 found 388.2057.

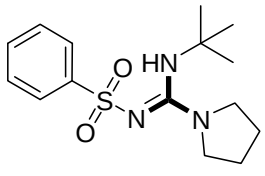
***N*-(*tert*-Butylamino-dibutylamino-methylene)-benzenesulfonamide (6f):**



6f

Following the general procedure, compound **6f** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (158 mg) and di-n-butylamine (84 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). Colorless semi solid (79%, 144.9 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.88-7.85 (m, 2H), 7.40-7.38 (m, 3H), 5.28 (s, 1H), 3.34 (t, J = 7.2 Hz, 4H), 1.52-1.45 (m, 4H), 1.29-1.21 (m, 4H), 1.16 (s, 9H), 0.86 (t, J = 7.5 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.8, 144.7, 130.7, 128.1, 125.7, 54.0, 49.6, 29.7, 29.6, 19.8, 13.6; **IR (KBr, cm^{-1})**: v 3341, 2967, 2360, 1580, 1443, 1237, 1124, 1060, 711; **HRMS m/z (ESI)** calculated for $C_{19}H_{34}N_3O_2S$ $(M+H)^+$ 368.2366 found 368.2368

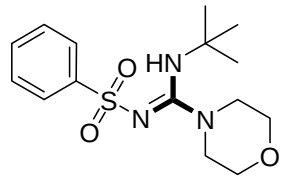
***N*-(*tert*-Butylamino-pyrrolidin-1-yl-methylene)-benzenesulfonamide (6g):**



6g

Following the general procedure, compound **6g** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (158 mg) and pyrrolidine (41 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 3:2). Pale yellow solid (73%, 112.7 mg); mp 150-152 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.91-7.88 (m, 2H), 7.41-7.39 (m, 3H), 4.50 (s, 1H), 3.60 (t, J = 6 Hz, 4H), 1.96-1.89 (m, 4H), 1.09 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.4, 145.5, 130.3, 128.1, 125.5, 52.6, 49.6, 29.2, 25.3; **IR (KBr, cm^{-1})**: v 3337, 2972, 2358, 1562, 1451, 1257, 1138, 1059, 851, 747 711; **HRMS m/z (ESI)** calculated for $C_{15}H_{24}N_3O_2S$ $(M+H)^+$ 310.1583 found 310.1575.

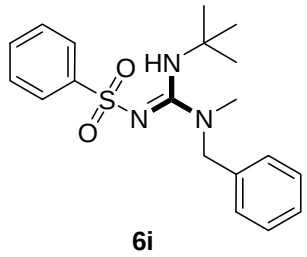
***N*-(*tert*-Butylamino-morpholin-4-yl-methylene)-benzenesulfonamide (6h):**



6h

Following the general procedure, compound **6h** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromobenzenesulfonamide (158 mg) and morpholine (43 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 3:2). White solid (81%, 131.6 mg); mp 173-175 °C; **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.91-7.88 (m, 2H), 7.46-7.42 (m, 3H), 5.12 (s, 1H), 3.78 (t, J = 4.8 Hz, 4H), 3.51 (t, J = 4.8 Hz, 4H), 1.16 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 157.4, 144.2, 131.1, 128.4, 125.8, 66.2, 54.0, 49.2, 29.6; **IR (KBr, cm^{-1})**: ν 3392, 2981, 2377, 1581, 1437, 1246, 1117, 1063, 869, 719; **HRMS m/z (ESI)** calculated for $C_{15}H_{24}N_3O_3S$ $(M+H)^+$ 326.1532 found 326.1534.

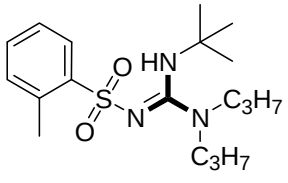
***N*-[(Benzyl-methyl-amino)-*tert*-butylamino-methylene]-benzenesulfonamide (6i):**



6i

Following the general procedure, compound **6i** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromobenzenesulfonamide (158 mg) and *N*-methyl benzylamine (64 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Semi solid (77%, 138.2 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.92-7.89 (m, 2H), 7.43-7.41 (m, 3H), 7.33-7.31 (m, 3H), 7.24-7.21 (m, 2H), 4.99 (s, 1H), 4.58 (s, 2H), 3.06 (s, 3H), 1.05 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 157.1, 144.7, 135.4, 130.8, 128.8, 128.2, 127.8, 127.3, 125.7, 56.0, 53.5, 39.3, 29.3; **IR (KBr, cm^{-1})**: ν 3339, 2971, 2368, 1588, 1502, 1426, 1151, 1079, 755; **HRMS m/z (ESI)** calculated for $C_{19}H_{26}N_3O_2S$ $(M+H)^+$ 360.1740 found 360.1743.

***N*-(*tert*-Butylamino-dipropylamino-methylene)-2-methylbenzenesulfonamide (6j):**

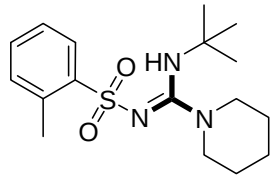


6j

Following the general procedure, compound **6j** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*o*-toluenesulfonamide (165 mg) and di-n-propylamine (68 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 4:1). White solid (82%, 144.7 mg); mp 123-125 °C; **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.93 (d, J = 7.5 Hz, 1H), 7.32-7.18 (m, 3H), 5.28 (s, 1H), 3.31 (t, J = 7.5

Hz, 4H), 2.71 (s, 3H), 1.60-1.50 (m, 4H), 1.17 (s, 9H), 0.84 (t, J = 7.2 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.1, 142.6, 136.6, 131.7, 130.8, 126.7, 125.1, 54.0, 51.6, 29.8, 20.8, 20.3, 11.1; **IR (KBr, cm^{-1})**: v 3317, 2962, 2358, 1561, 1453, 1248, 1112, 1075, 862, 744; **HRMS m/z (ESI)** calculated for $C_{18}H_{32}N_3O_2S$ $(M+H)^+$ 354.2209 found 354.2208.

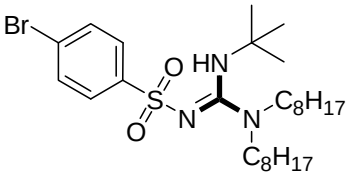
***N*-(*tert*-Butylamino-piperidin-1-yl-methylene)-2-methylbenzenesulfonamide (6k):**



6k

Following the general procedure, compound **6k** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-*o*-toluenesulfonamide (158 mg) and piperidine (49 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). White solid (78%, 131.4 mg); mp 119-121 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.94 (d, J = 8.1 Hz, 1H), 7.31 (d, J = 6.3 Hz, 1H), 7.25-7.20 (m, 2H), 5.17 (s, 1H), 3.42 (s, br, 4H), 2.73 (s, 3H), 1.61 (s, br, 6H), 1.14 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.0, 142.5, 136.6, 131.8, 130.9, 126.8, 125.2, 53.9, 50.0, 29.8, 25.3, 24.2, 20.4; **IR (KBr, cm^{-1})**: v 3329, 2977, 2364, 1582, 1522, 1424, 1255, 1134, 1080, 867, 751; **HRMS m/z (ESI)** calculated for $C_{17}H_{28}N_3O_2S$ $(M+H)^+$ 338.1896 found 338.1903.

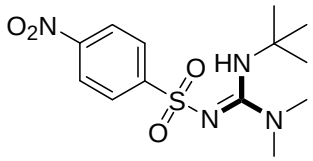
4-Bromo-*N*-(*tert*-butylamino-dioctylamino-methylene)-benzenesulfonamide (6l):



6l

Following the general procedure, compound **6l** was prepared from *tert*-butyl isocyanide (57 μL), *N,N*-dibromo-4-bromobenzenesulfonamide (197 mg) and di-n-octylamine (151 μL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Pale yellow oil (77%, 214.8 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.73 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 5.11 (s, 1H), 3.32 (t, J = 7.2 Hz, 4H), 1.49 (s, br, 4H), 1.21-1.16 (m, 30H), 0.84 (t, J = 6.9 Hz, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.1, 144.0, 131.3, 127.4, 125.1, 53.8, 49.9, 31.6, 29.7, 29.1, 29.0, 27.5, 26.6, 22.4, 13.9; **IR (KBr, cm^{-1})**: v 3330, 2968, 2362, 1576, 1451, 1257, 1117, 1061, 850, 745, 709; **HRMS m/z (ESI)** calculated for $C_{27}H_{49}BrN_3O_2S$ $(M+H)^+$ 558.2723 found 558.2720.

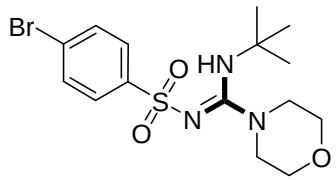
***N*-(*tert*-Butylamino-dimethylamino-methylene)-4-nitrobenzenesulfonamide (6m):**



6m

Following the general procedure, compound **6m** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzenesulfonamide (180 mg) and dimethylamine (34 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 1:1). White solid (73%, 119.7 mg); mp 164-166 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.29 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 4.60 (s, 1H), 3.13 (s, 6H), 1.12 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.2, 150.6, 148.7, 127.0, 123.7, 53.2, 40.4, 29.4; **IR (KBr, cm^{-1})**: ν 3340, 2972, 2362, 1587, 1510, 1446, 1269, 1143, 1068, 852, 690; **HRMS m/z (ESI)** calculated for $C_{13}H_{21}N_4O_4S$ $(M+H)^+$ 329.1278 found 329.1279.

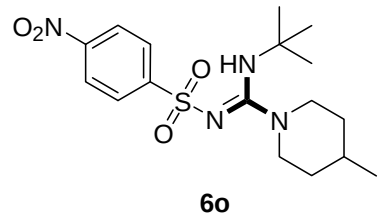
4-Bromo-*N*-(*tert*-butylamino-morpholin-4-yl-methylene)-benzenesulfonamide (6n):



6n

Following the general procedure, compound **6n** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-bromobenzenesulfonamide (197 mg) and morpholine (43 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow solid (78%, 157.5 mg); mp 126-128 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.74 (d, J = 9 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 5.00 (s, 1H), 3.76 (t, J = 4.8 Hz, 4H), 3.48 (t, J = 4.8 Hz, 4H), 1.13 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.7, 143.4, 131.5, 127.4, 125.5, 66.1, 53.7, 49.1, 29.4; **IR (KBr, cm^{-1})**: ν 3373, 2981, 2369, 1581, 1444, 1265, 1142, 1069, 878, 751, 709; **HRMS m/z (ESI)** calculated for $C_{15}H_{23}BrN_3O_3S$ $(M+H)^+$ 404.0638 found 404.0639.

***N*-[*tert*-Butylamino-(4-methyl-piperidin-1-yl)-methylene]-4-nitrobenzenesulfonamide (6o):**

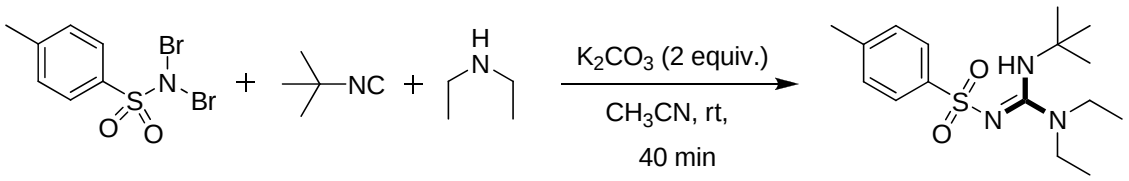


6o

Following the general procedure, compound **6o** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzenesulfonamide (180 mg) and 4-methyl piperidine (59 µL) in presence of K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 3:2). Yellow solid (76%, 145.1 mg); mp 141-143 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.27 (d, J = 8.7 Hz, 2H), 8.06 (d, J = 8.7

Hz, 2H), 4.76 (s, 1H), 3.96 (d, J = 12.9 Hz, 2H), 3.01 (t, J = 12.9 Hz, 2H), 1.79-1.60 (m, 3H), 1.38-1.23 (m, 2H), 1.11 (s, 9H), 0.96 (d, J = 6.6 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.2, 150.4, 148.7, 127.0, 123.7, 53.4, 49.3, 33.5, 30.8, 29.4, 21.4; **IR (KBr, cm^{-1})**: ν 3353, 2969, 2358, 1582, 1507, 1438, 1255, 1150, 1072, 873, 747, 702; **HRMS m/z (ESI)** calculated for $C_{17}H_{27}N_4O_4S$ $(M+H)^+$ 383.1747 found 383.1748.

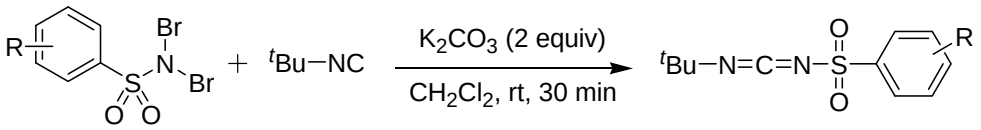
6. **Procedure for gram scale synthesis**:



1a, 1.0 g **2a** **3a** **4a** (77%, 760 mg)

To an ice cooled solution of *t*-butyl isocyanide (3.04 mmol, 1 equiv), K_2CO_3 (6.08 mmol, 2 equiv) and diethylamine (3.04 mmol, 1 equiv) in CH_3CN (20 mL), $TsNBr_2$ (3.04 mmol, 1g, 1 equiv) was added in portion. The resultant mixture was then allowed to stir at room temperature. After completion of the reaction as monitored by TLC, the reaction mixture was passed through a short pad of celite and washed with ethyl acetate. The solvent was concentrated under reduced pressure and the crude was purified by flash column chromatography using petroleum ether-ethyl acetate (7:3) as eluent to afford *N*-(*tert*-Butylamino-diethylamino-methylene)-4-methylbenzenesulfonamide (**4a**) with 77% yield (760 mg).

7. **General procedure for synthesis of sulfonyl carbodiimides and characterization**:

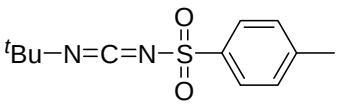


1 **2a** **7a-e**

To a stirred solution of *t*-Butyl isocyanide (0.5 mmol, 1.0 equiv) in CH_2Cl_2 (4 mL) at room temperature, dibromoarylsulfonamide (0.5 mmol, 1.0 equiv) and K_2CO_3 (1 mmol, 2.0 equiv) was added. After completion of the reaction, the reaction mixture was passed through a celite pad and

washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure. Purification by flash column chromatography using petroleum ether-ethyl acetate (9:1) afforded the product.

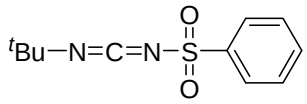
***N*-(*tert*-Butyliminomethylene)-4-methylbenzenesulfonamide (7a):**



7a

Following the general procedure, compound **7a** was prepared from *tert*-butyl isocyanide (57 μL) and *N,N*-dibromo-*p*-toluenesulfonamide (165 mg) in presence of K_2CO_3 (138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Semi solid (55%, 69.3 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.82 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H), 1.37 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 144.0, 138.0, 129.5, 126.5, 122.1, 59.6, 30.8, 21.4; **IR (KBr, cm^{-1})**: v 2978, 2929, 2162, 1597, 1381, 1340, 1165, 1089, 842, 752; **HRMS m/z (ESI)** calculated for $C_{12}H_{17}N_2O_2S$ $(M+H)^+$ 253.1005 found 253.1007.

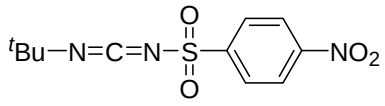
***N*-(*tert*-Butyliminomethylene)benzenesulfonamide (7b):**



7b

Following the general procedure, compound **7b** was prepared from *tert*-butyl isocyanide (57 μL) and *N,N*-dibromobenzenesulfonamide (158 mg) in presence of K_2CO_3 (138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Colorless oil (68%, 80.9 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.94 (d, J = 7.8 Hz, 2H), 7.62-7.51 (m, 3H), 1.37 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 140.9, 133.2, 129.0, 126.5, 121.4, 59.8, 30.8; **IR (KBr, cm^{-1})**: v 2983, 2167, 1592, 1394, 1157, 1081, 849, 741; **HRMS m/z (ESI)** calculated for $C_{11}H_{15}N_2O_2S$ $(M+H)^+$ 239.0848 found 239.0853.

***N*-(*tert*-Butyliminomethylene)-4-nitrobenzenesulfonamide (7c):**

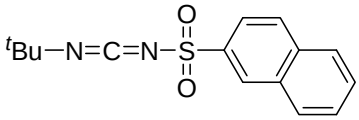


7c

Following the general procedure, compound **7c** was prepared from *tert*-butyl isocyanide (57 μL) and *N,N*-dibromo-4-nitrobenzenesulfonamide (180 mg) in presence of K_2CO_3 (138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). White solid (59%, 83.4 mg); mp 76-78 ^{o}C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.39 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.7 Hz, 2H), 1.47 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 150.0, 146.5, 127.8,

124.2, 117.7, 60.2, 30.8; **IR (KBr, cm^{-1})**: *v* 2995, 2916, 2158, 1588, 1376, 1323, 1184, 1096, 861, 755; **HRMS m/z (ESI)** calculated for $C_{11}H_{14}N_3O_4S$ $(M+H)^+$ 284.0699 found 284.0706.

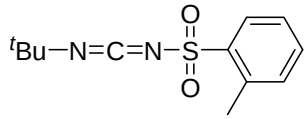
***N*-(*tert*-Butyliminomethylene)-2-naphthalenesulfonamide (7d):**



7d

Following the general procedure, compound **7d** was prepared from *tert*-butyl isocyanide (57 μL) and *N,N*-dibromo-2-naphthalenesulfonamide (183 mg) in presence of K_2CO_3 (138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Colorless oil (63%, 90.7 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.51 (s, 1H), 8.00-7.90 (m, 4H), 7.66-7.61 (m, 2H), 1.37 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 137.8, 134.9, 131.8, 129.4, 129.2, 128.9, 127.8, 127.7, 127.6, 121.8, 59.8, 30.8; **IR (KBr, cm^{-1})**: *v* 2932, 2162, 1593, 1329, 1181, 1077, 848, 752; **HRMS m/z (ESI)** calculated for $C_{15}H_{17}N_2O_2S$ $(M+H)^+$ 289.1005 found 289.1009.

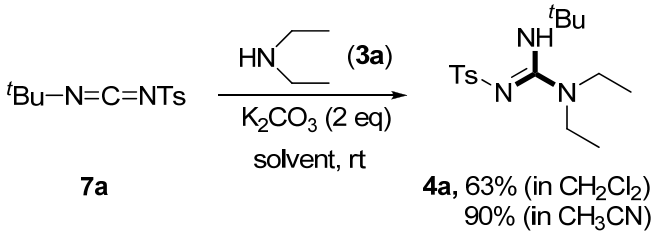
***N*-(*tert*-Butyliminomethylene)-2-methylbenzenesulfonamide (7e):**



7e

Following the general procedure, compound **7e** was prepared from *tert*-butyl isocyanide (57 μL) and *N,N*-dibromo-*o*-toluenesulfonamide (165 mg) in presence of K_2CO_3 (138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 9:1). Colorless oil (48%, 60.4 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.03 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.35-7.30 (m, 2H), 2.70 (s, 3H), 1.38 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 139.2, 137.6, 133.1, 132.4, 128.2, 126.0, 59.7, 30.9, 20.3; **IR (KBr, cm^{-1})**: *v* 2981, 2947, 2165, 1595, 1377, 1332, 1159, 1086, 844, 750; **HRMS m/z (ESI)** calculated for $C_{12}H_{17}N_2O_2S$ $(M+H)^+$ 253.1005 found 253.1012.

8. Synthesis of 4a from the carbodiimide (7a):

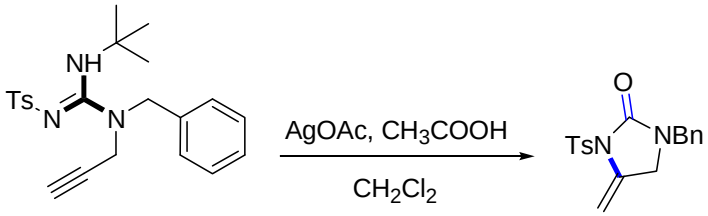


7a

4a, 63% (in CH_2Cl_2)
90% (in CH_3CN)

In the next step the carbodiimide *N*-(*tert*-Butyliminomethylene)-4-methylbenzenesulfonamide (**7a**) (0.5 mmol, 1.0 equiv) was added with diethylamine (0.5 mmol, 1equiv) in presence of K_2CO_3 in CH_3CN and allowed to stir for appropriate time at room temperature. The desired sulfonyl guanidine product **4a** was isolated in 90% yield.

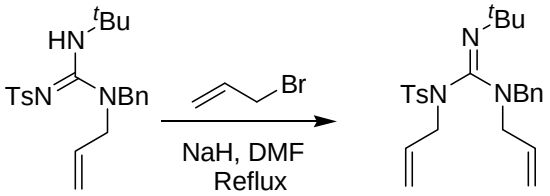
9. **Procedure for synthesis of 1-benzyl-4-methylidene-3-[(4-methylphenyl)sulfonyl]imidazolidin-2-one (8)**:



4j **8**, 63%

To a solution of *N*-[(Benzyl-prop-2-ynyl-amino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (**4j**, 0.20 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL), silver acetate (0.02 mmol, 0.1 equiv) and acetic acid (0.60 mmol, 3 equiv) was added and stirred at room temperature. After 2h (completion of the reaction as monitored by TLC), a saturated solution of $NaHCO_3$ was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, washed with water and dried over anhydrous Na_2SO_4. The residue was concentrated under reduced pressure and purified by flash chromatography using petroleum ether-ethyl acetate (4:1) as eluent to afford 1-benzyl-4-methylidene-3-[(4-methylphenyl)sulfonyl]imidazolidin-2-one (**8**). Colorless oil (63%, 43.0 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**:[7] δ 7.96 (d, J = 7.5 Hz, 2H), 7.36-7.29 (m, 5H), 7.14 (d, J = 3 Hz, 2H), 5.51 (s, br, 1H), 4.43 (s, br, 1H), 4.36 (s, 2H), 3.81 (s, 2H), 2.45 (s, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 152.8, 145.0, 135.3, 134.7, 134.2, 129.5, 128.7, 128.0, 127.9, 127.8, 91.8, 47.1, 47.0, 21.6; **IR (KBr, cm^{-1})**: ν 3412, 2924, 1741, 1658, 1436, 1377, 1273, 1176, 1087, 875, 754; **HRMS m/z (ESI)** calculated for $C_{18}H_{19}N_2O_3S$ $(M+H)^+$ 343.1110 found 343.1118.

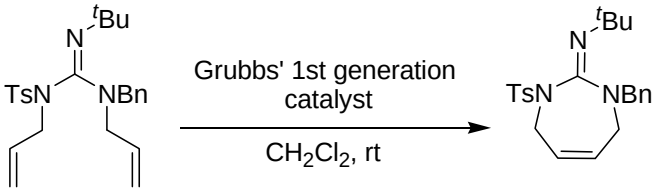
10. **Procedure for synthesis of *N*- Allyl-*N*-(*N*-allyl-*N*-benzyl-*N'*-*tert*-butylcarbamimidoyl)-4-methylbenzenesulfonamide (9)**:



4l **9**, 45%

To a solution of *N*-[(Allyl-benzyl-amino)-*tert*-butylamino-methylene]-4-methylbenzenesulfonamide (**4l**, 0.50 mmol, 1.0 equiv) in dry DMF (2 mL), NaH (1.0 mmol, 2.0 equiv) and allyl bromide (1.0 mmol, 2.0 equiv.) was added and refluxed under nitrogen atmosphere. After completion of the reaction (monitored by TLC), water was added and the aqueous layer was extracted using diethyl ether. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The crude mixture was purified by flash chromatography using petroleum ether-ethyl acetate (9:1) as eluent to afford *N*- Allyl-*N*-(*N*-allyl-*N*-benzyl-*N'*-*tert*-butylcarbamimidoyl)-4-methylbenzenesulfonamide (**9**). Colorless oil (45%, 98.7 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.86 (d, J = 8.1 Hz, 2H), 7.33-7.29 (m, 5H), 7.26-7.23 (m, 2H), 5.94-5.77 (m, 2H), 5.22-5.04 (m, 4H), 4.75 (d, J = 14.4 Hz, 1H), 4.43 (d, J = 14.1 Hz, 1H), 3.81 (s, br, 4H), 2.39 (s, 3H), 1.18 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 160.2, 141.9, 141.3, 136.2, 135.8, 133.0, 128.9, 128.5, 127.7, 126.2, 119.5, 116.9, 57.8, 53.6, 53.1, 51.5, 28.9, 21.4; **IR (KBr, cm^{-1})**: v 3336, 2917, 2369, 1660, 1501, 1371, 1283, 1089, 834, 749.

11. **Procedure for synthesis of {1-Benzyl-3-tosyl-1,3,4,7-tetrahydro-[1,3]diazepin-2-ylidene}-*tert*-butylamine (10)**:

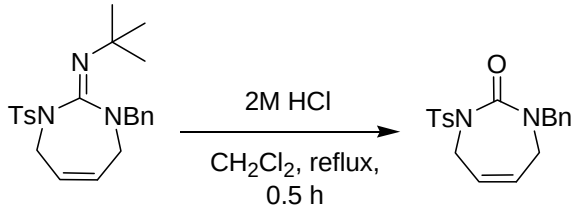


10, 53%

To a stirred solution of *N*-Allyl-*N*-(*N*-allyl-*N*-benzyl-*N'*-*tert*-butylcarbamimidoyl)-4-methylbenzenesulfonamide (**9**, 0.20 mmol, 1.0 equiv) in dry CH_2Cl_2 (2 mL), Grubbs' 1st generation catalyst (5 mol%) was added under nitrogen atmosphere. The resulting purple solution becomes brown after 10-15 min. The reaction was allowed to stir at room temperature

overnight under nitrogen atmosphere. After completion the reaction, the crude mixture was concentrated under reduced pressure and the residue was purified by flash chromatography using petroleum ether-ethyl acetate (4:1) as eluent to afford {1-Benzyl-3-tosyl-1,3,4,7-tetrahydro-[1,3]diazepin-2-ylidene}-*tert*-butylamine (**10**). White semi solid (53%, 43.5 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.84 (d, J = 7.8 Hz, 2H), 7.29 (s, br, 5H), 7.23 (d, J = 8.1 Hz, 2H), 5.56 (d, J = 10.2 Hz, 1H), 5.32 (d, J = 10.2 Hz, 1H), 4.81 (br, 1H), 4.53 (br, 1H), 3.89 (br, 2H), 3.56 (br, 2H), 2.39 (s, 3H), 1.18 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 161.9, 141.9, 141.3, 136.9, 128.9, 128.8, 128.4, 127.6, 126.4, 126.1, 125.4, 57.0, 56.8, 49.5, 45.5, 28.6, 21.4; **IR (KBr, cm^{-1})**: v 3412, 2924, 1741, 1658, 1436, 1377, 1273, 1176, 1087, 875, 754; **HRMS m/z (ESI)** calculated for $C_{23}H_{30}N_3O_2S$ $(M+H)^+$ 412.2053 found 412.2058.

12. **Procedure for synthesis of 1-Benzyl-3-tosyl-1,3,4,7-tetrahydro-[1,3]diazepin-2-one (11)**:



11, 81%

2M HCl solution (0.2 mL) was added to a stirred solution of {1-Benzyl-3-tosyl-1,3,4,7-tetrahydro-[1,3]diazepin-2-ylidene}-*tert*-butylamine (**10**, 0.1 mmol, 1.0 equiv.) in CH_2Cl_2 (0.5 mL) and the mixture was refluxed for 30 min. Then CH_2Cl_2 was evaporated and added $NaHCO_3$ solution. The mixture was was extracted with EtOAc, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the product 1-Benzyl-3-tosyl-1,3,4,7-tetrahydro-[1,3]diazepin-2-one (**11**) without any further chromatographic purification. Colorless semi solid (81%, 28.8 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**:[8] δ 7.73 (d, J = 8.1 Hz, 2H), 7.25-7.16 (m, 7H), 5.68-5.65 (m, 2H), 4.57 (s, 2H), 3.81-3.75 (m, 4H), 2.40 (s, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.3, 143.4, 136.7, 129.2, 128.5, 127.8, 126.7, 126.0, 125.3, 54.6, 48.4, 44.2, 21.4; **IR (KBr, cm^{-1})**: v 3081, 2933, 1681, 1459, 1256, 1080, 861, 742.

13. **References**:

1. a) M. Tajbakhsh, A. Khazaei, M. S. Mahalli and R. G. Vaghi, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2004, **179**, 1159; b) A. Khazaei, A. Rostami, Z. Tanbakouchian and Z. Zinati, *Catal. Commun.*, 2006, **7**, 214; c) A. J. Borah and P. Phukan, *Chem. Commun.*, 2012, **48**, 5491.

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3. T. Makino and K. Itoh, *J. Org. Chem.*, 2004, **69**, 395.

4. B. Kim, J. M. Beebe, Y. Jun, X. -Y. Zhu, C. D. Frisbie, *J. Am. Chem. Soc.*, 2006, 128, 4970.

5. Z. Zhang, B. Huang, G. Qiao, L. Zhu, F. Xiao, F. Chen, B. Fu and Z. Zhang, *Angew. Chem. Int. Ed.*, 2017, **56**, 4320.

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14. **Crystal structure data of *N*-(*tert*-Butylamino-dimethylamino-methylene)-4-nitrobenzenesulfonamide (6m)**

CCDC No. 1882434

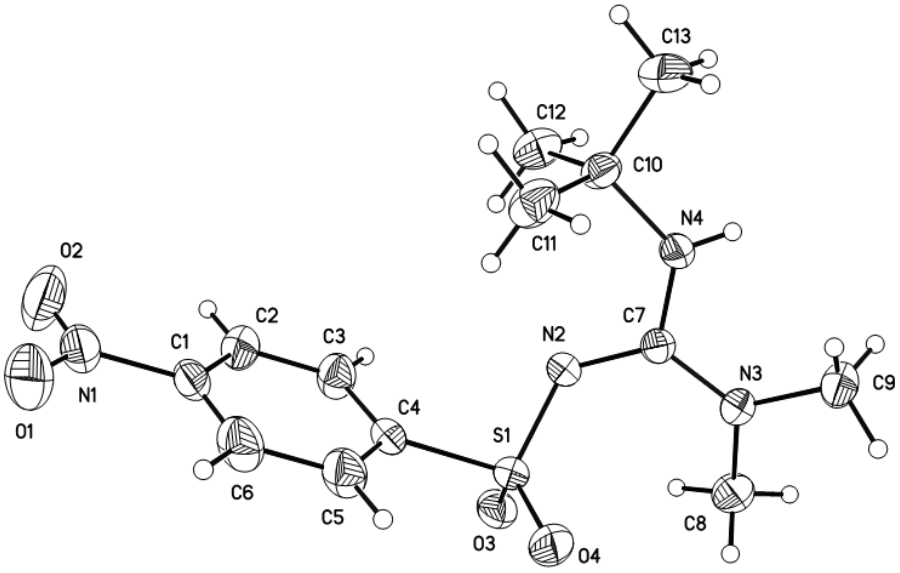


Figure: ORTEP of compound ***N*-(*tert*-Butylamino-dimethylamino-methylene)-4-nitrobenzenesulfonamide (6m)** with 35% probability ellipsoid

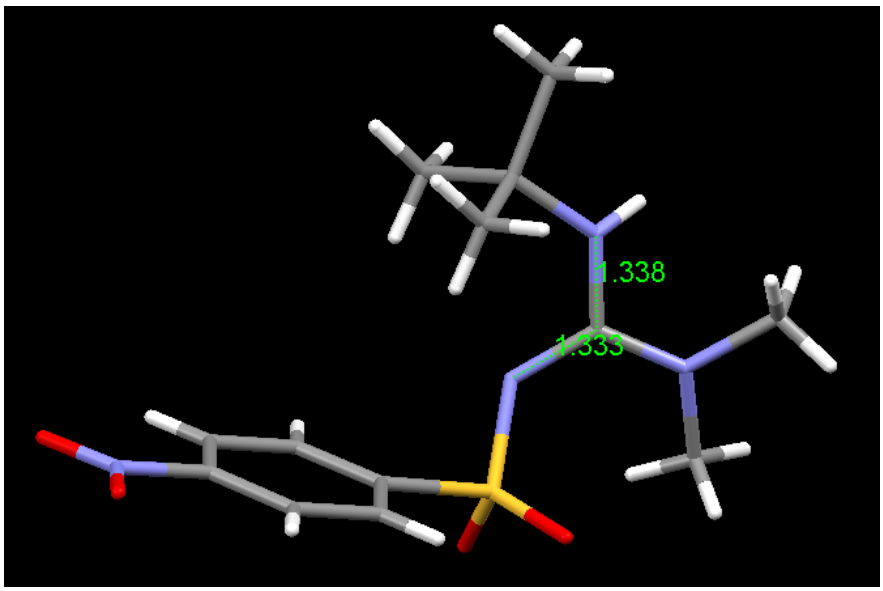
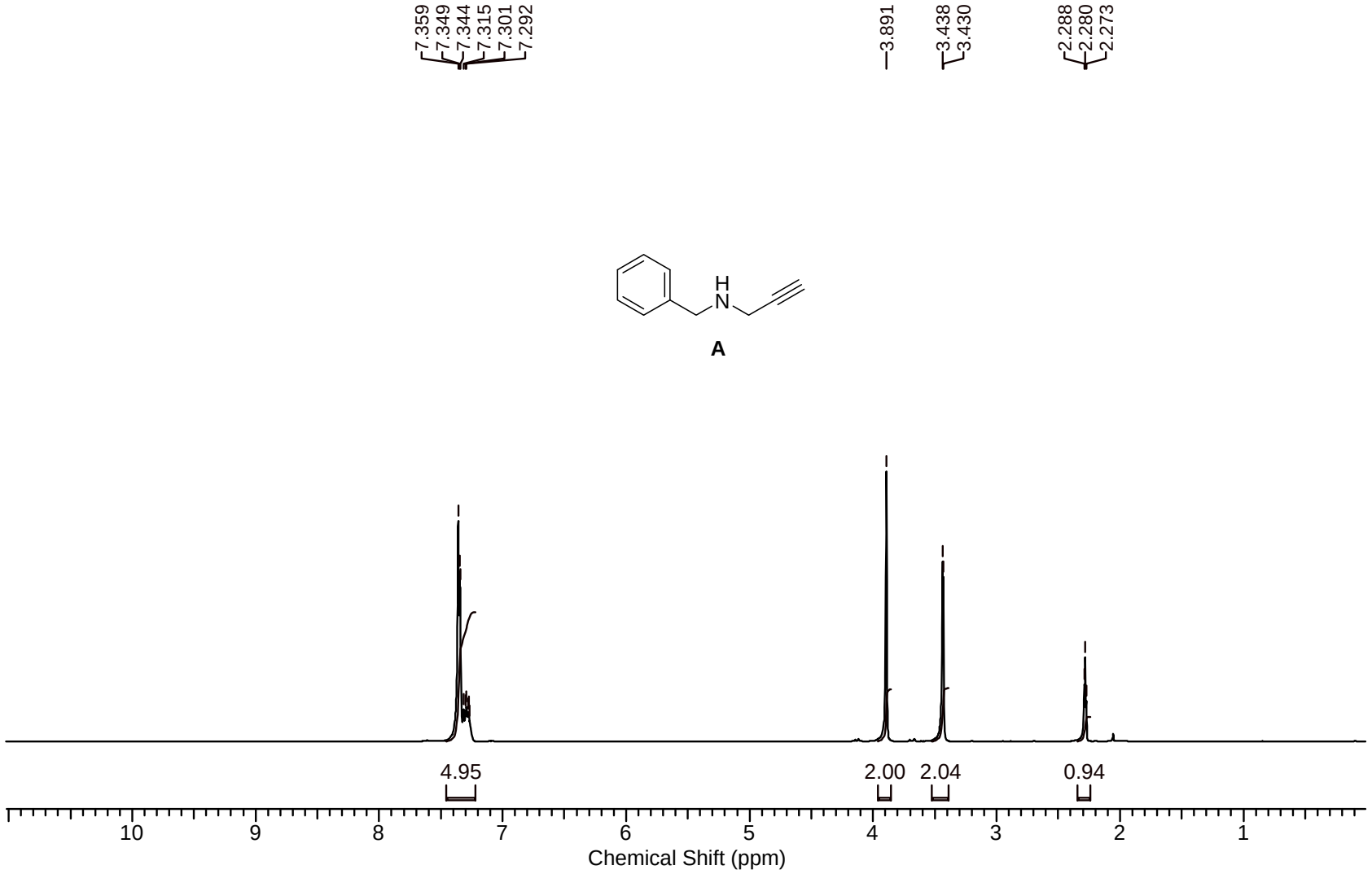


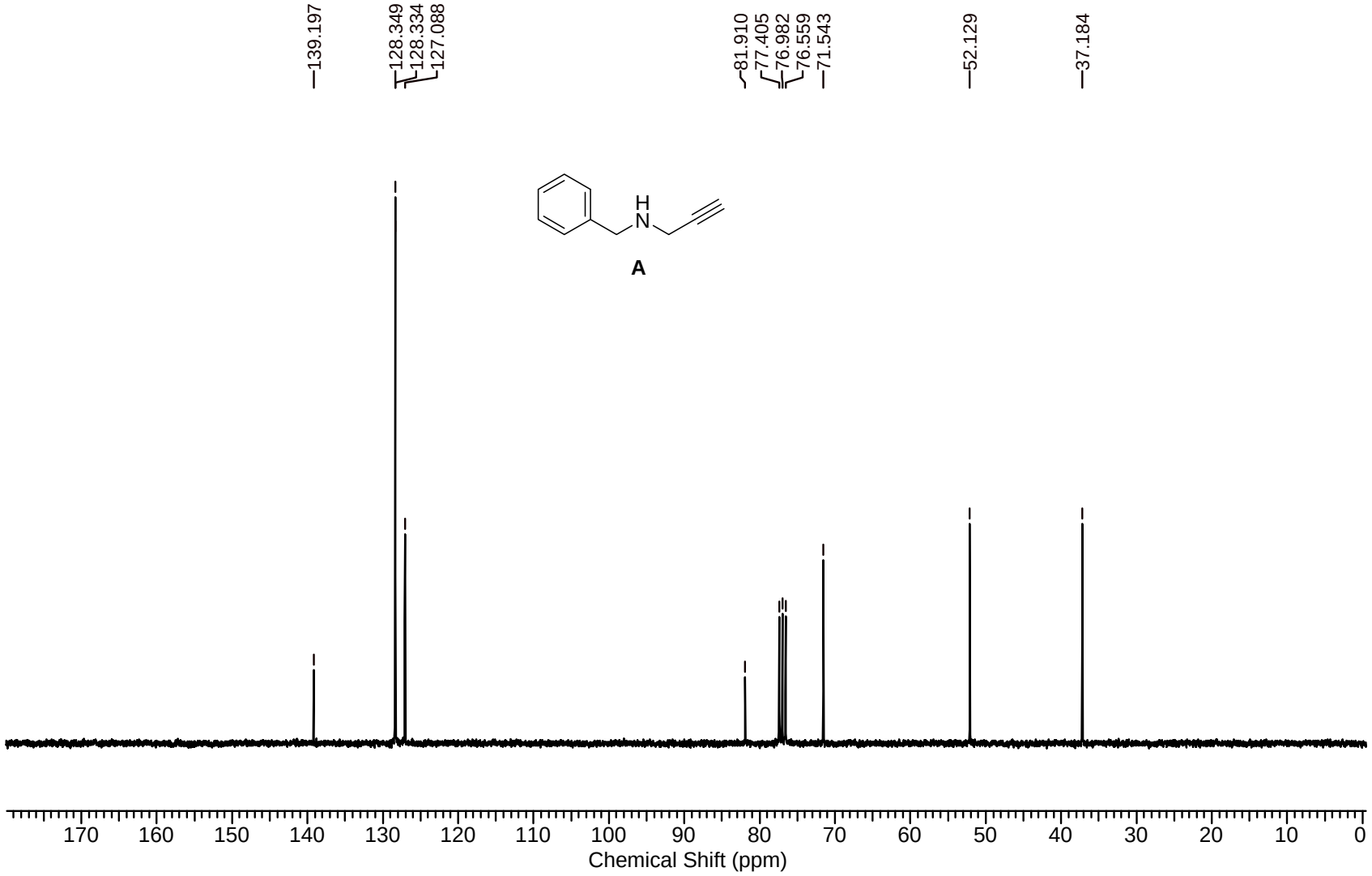
Figure: Bond length of C=NNs (1.333 Å) and C-NH(^{t}Bu) (1.338 Å) (Measured by using Mercury free version 1.4.1.

Table: Crystal structure data of *N*-(*tert*-Butylamino-dimethylamino-methylene)-4-nitrobenzenesulfonamide (6m)

Chemical formula	$C_{13}H_{20}N_4O_4S$
M_r	328.39
Crystal system	Monoclinic
Space group	$P2_1/c$
Temperature (K)	296
a, Å	5.8970 (4)
b, Å	12.6136 (9)
c, Å	21.8512 (16)
α, deg	90
β, deg	90.674 (4)
γ, deg	90
V (Å^3)	1625.2 (2)
Z	4
μ (mm^{-1})	0.22
No. of measured	14152
Observed [$I > 2\sigma(I)$] reflections	2733
R_1	0.045
$wR_{2(all)}$	0.145
GOF	1.12
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, -0.28
Diffractometer	Bruker *APEX-II* CCD diffractometer
CCDC No.	1882434

15. **^{1}H and ^{13}C NMR spectra of compounds**:

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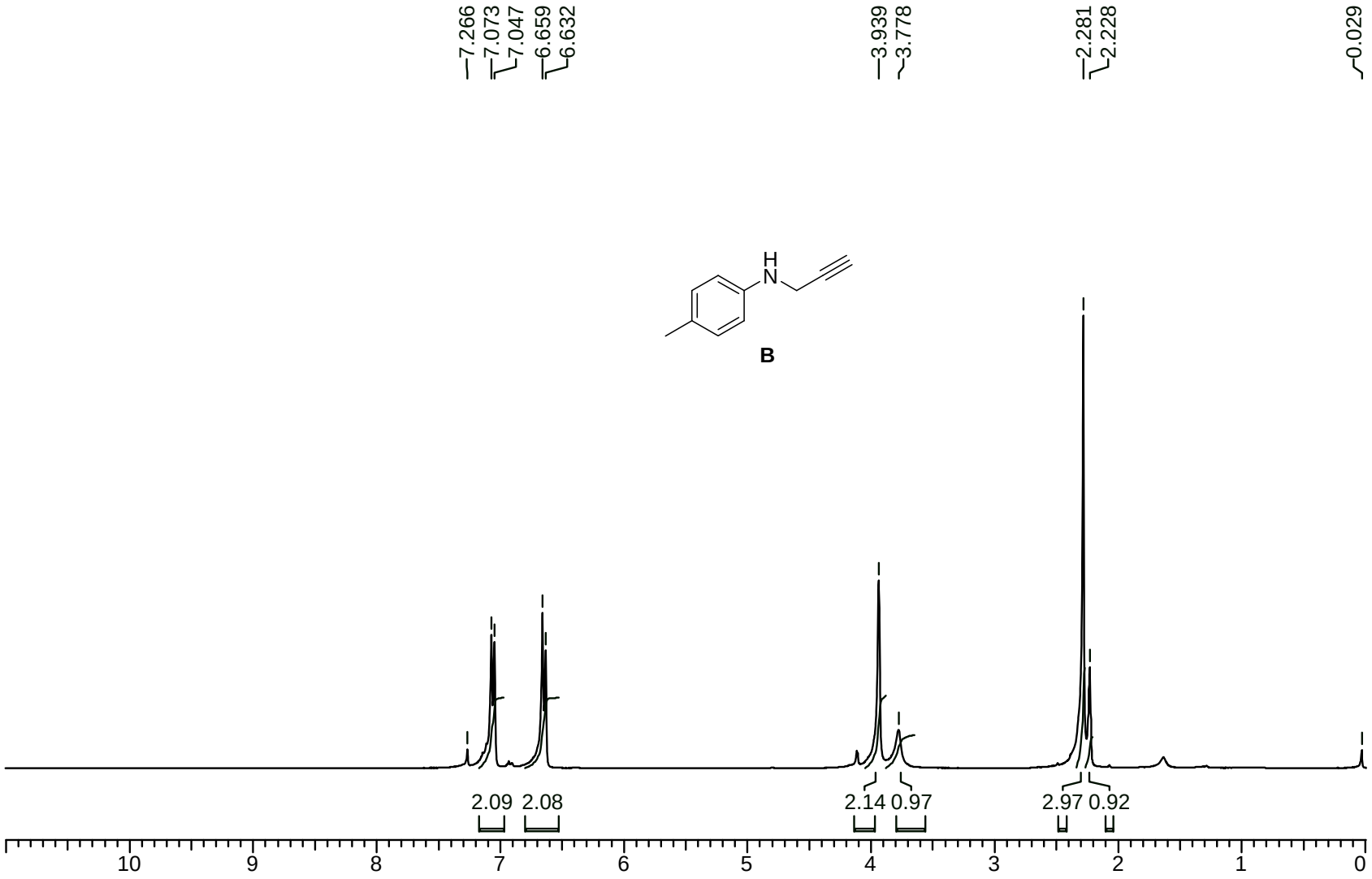
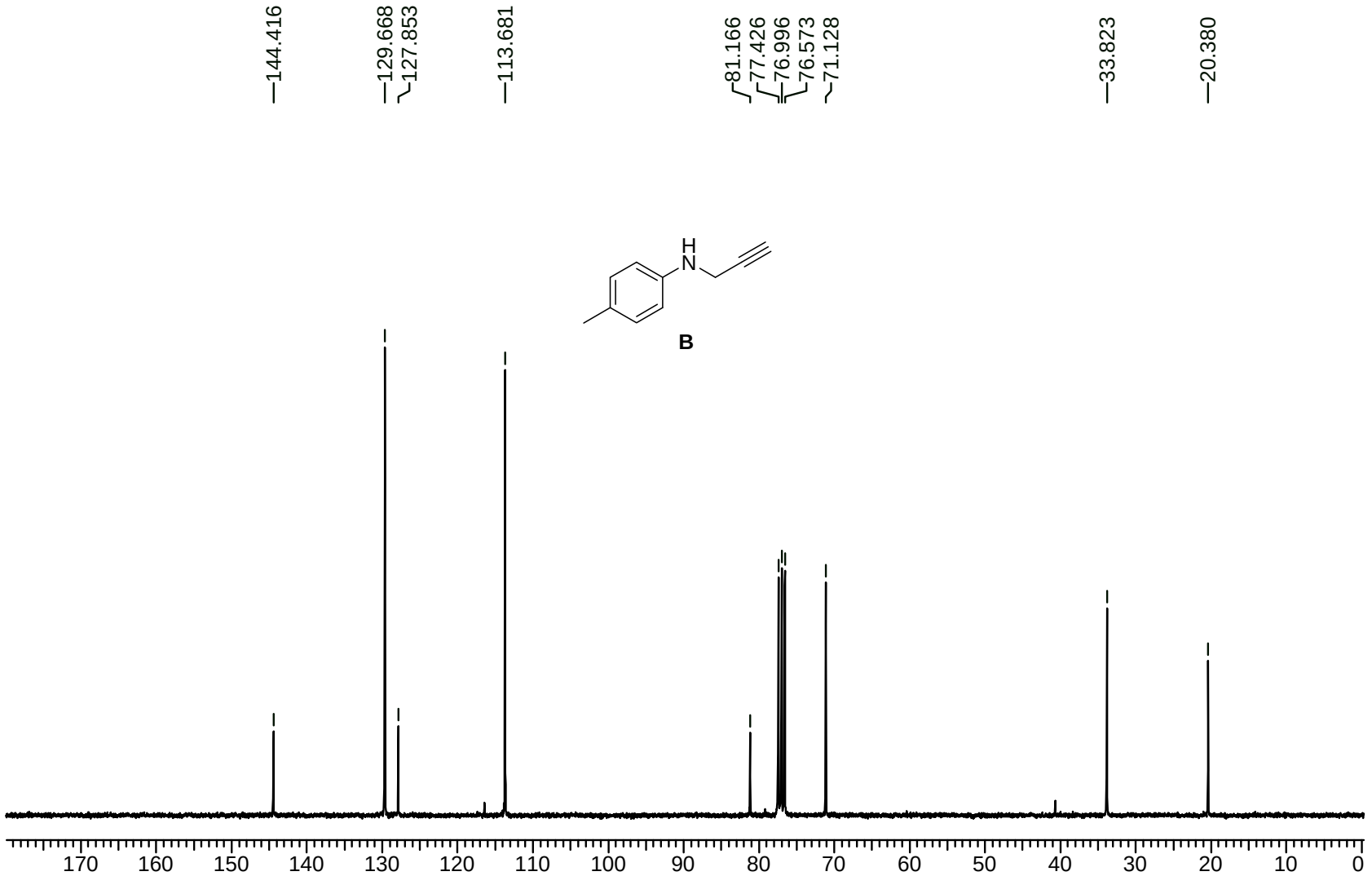
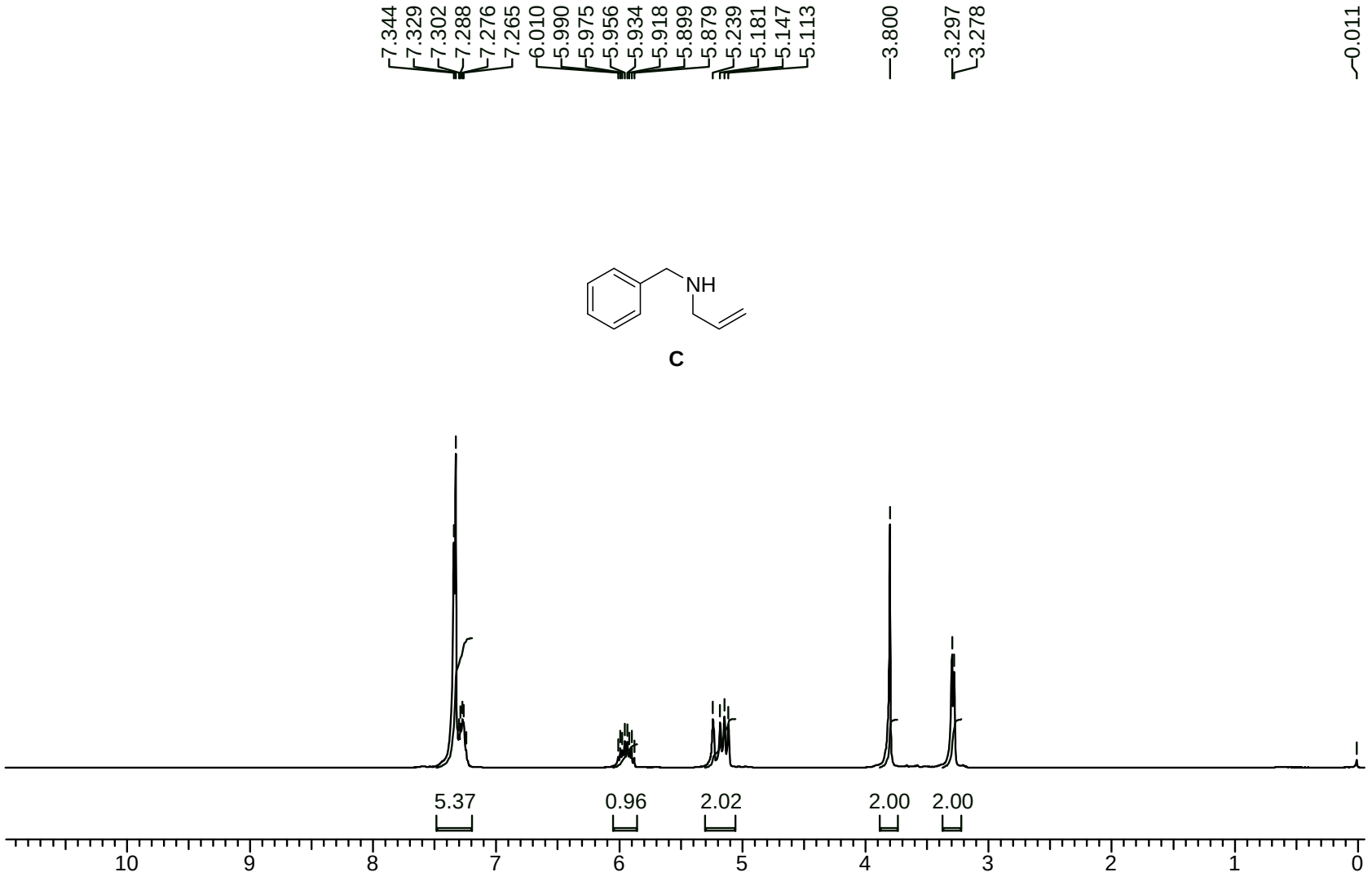
128.349
128.334
127.088
81.910
77.405
76.982
76.559
71.543
52.129
37.184
H
N
A
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.266
7.073
7.047
6.659
6.632
3.939
3.778
2.281
2.228
0.029
H
N
B
2.09
2.08
2.14
0.97
2.97
0.92
10
9
8
7
6
5
4
3
2
1
0


144.416
129.668
127.853
113.681
81.166
77.426
76.996
76.573
71.128
33.823
20.380
H
N
B
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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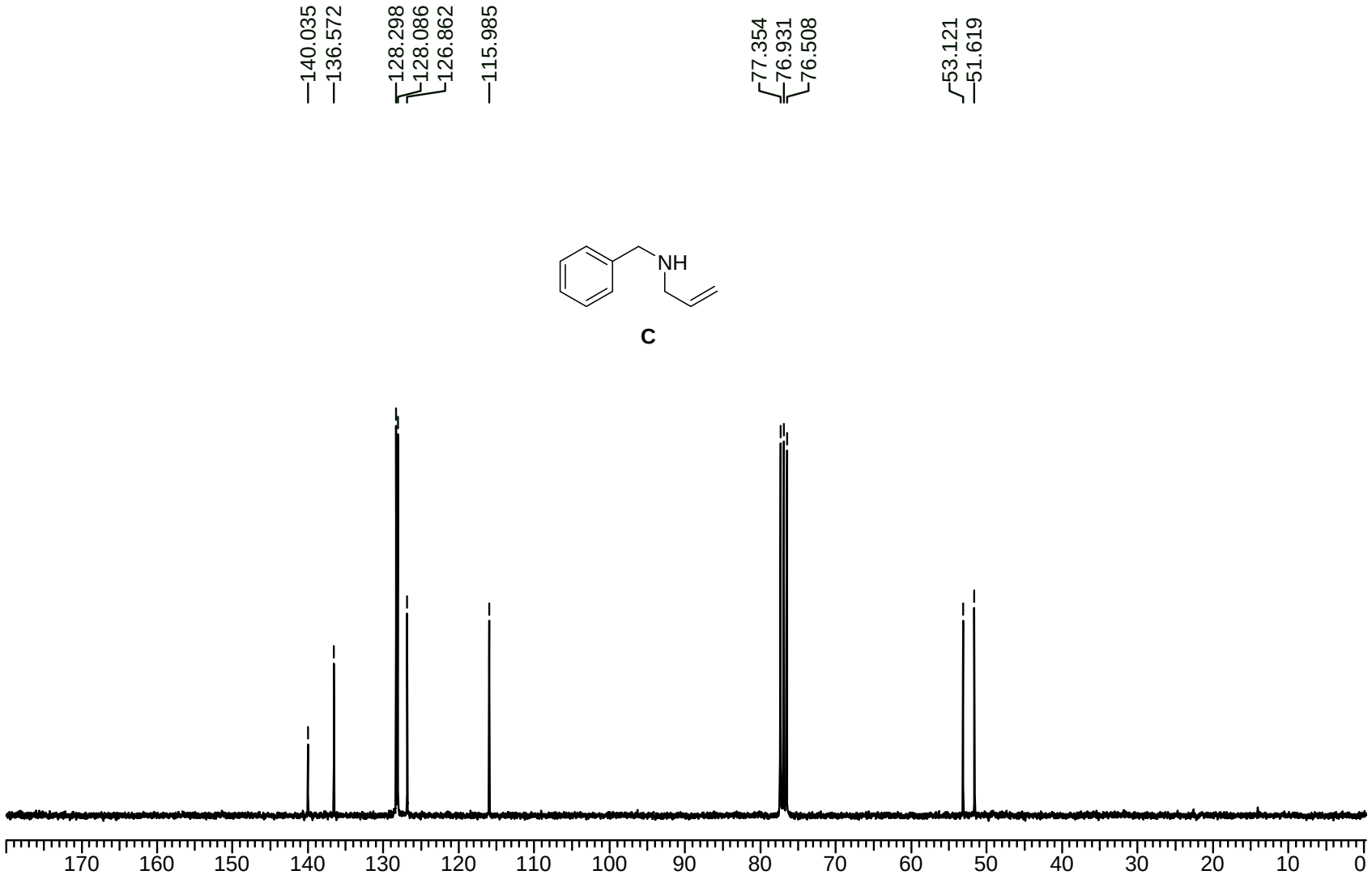
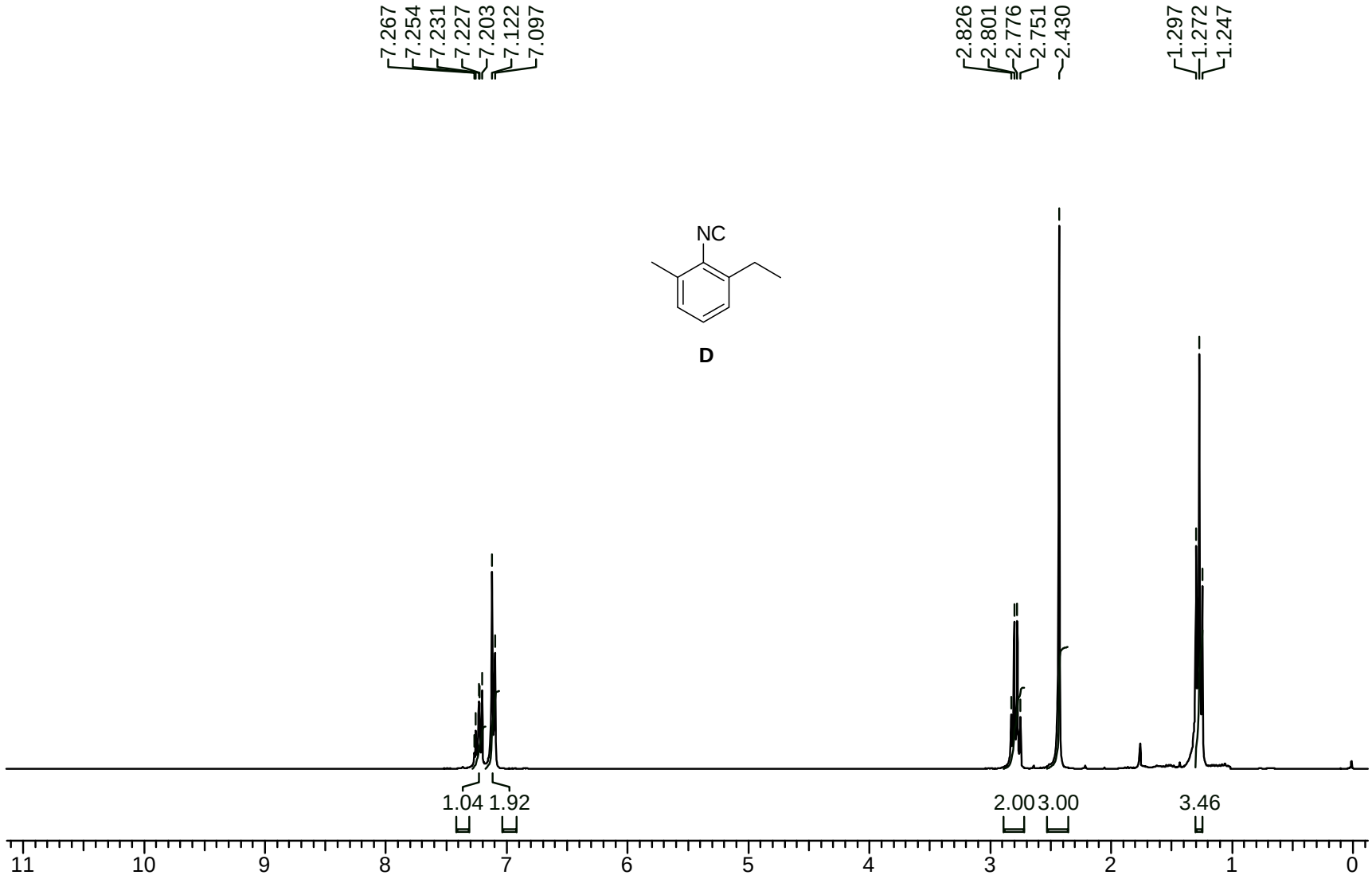
7.329
7.302
7.288
7.276
7.265
6.010
5.990
5.975
5.956
5.934
5.918
5.899
5.879
5.239
5.181
5.147
5.113
3.800
3.297
3.278
0.011
NH
C
5.37
0.96
2.02
2.00
2.00
10
9
8
7
6
5
4
3
2
1
0


140.035
136.572
128.298
128.086
126.862
115.985
77.354
76.931
76.508
53.121
51.619
NH
C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.254
7.231
7.227
7.203
7.122
7.097
2.826
2.801
2.776
2.751
2.430
1.297
1.272
1.247
NC
D
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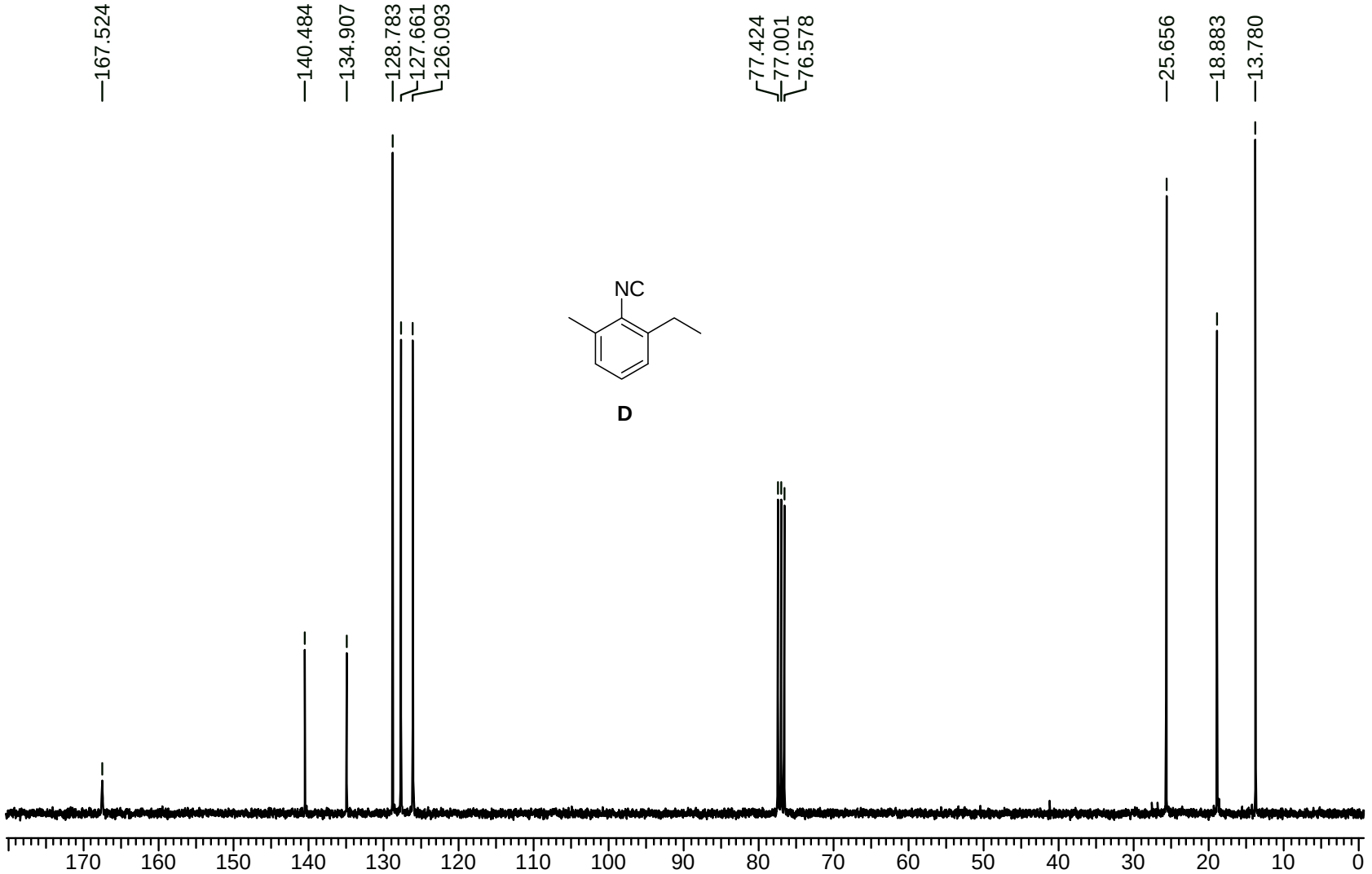
1.92
2.00
3.00
3.46
11
10
9
8
7
6
5
4
3
2
1
0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128.783
127.661
126.093
77.424
77.001
76.578
25.656
18.883
13.780
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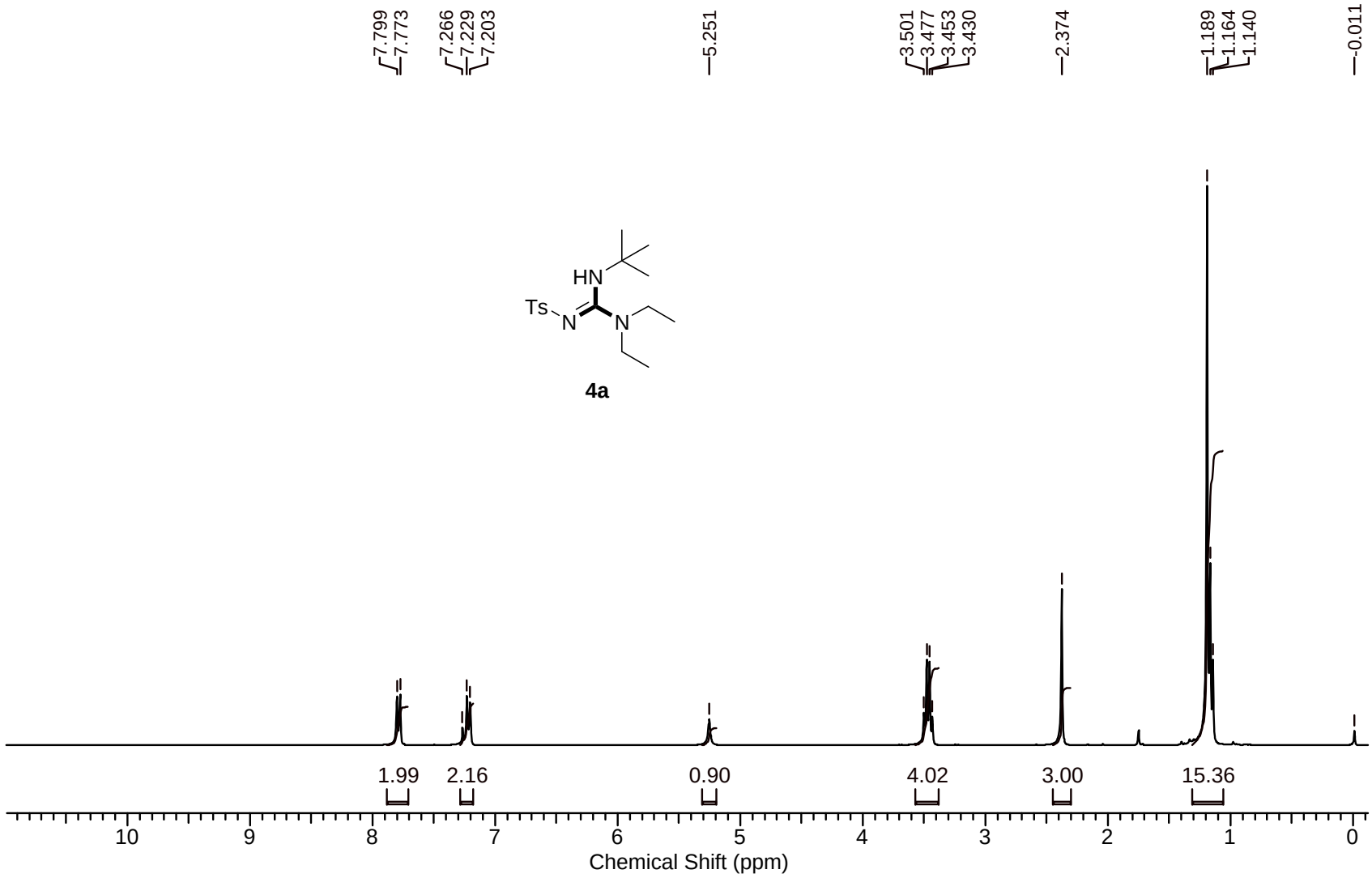
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

D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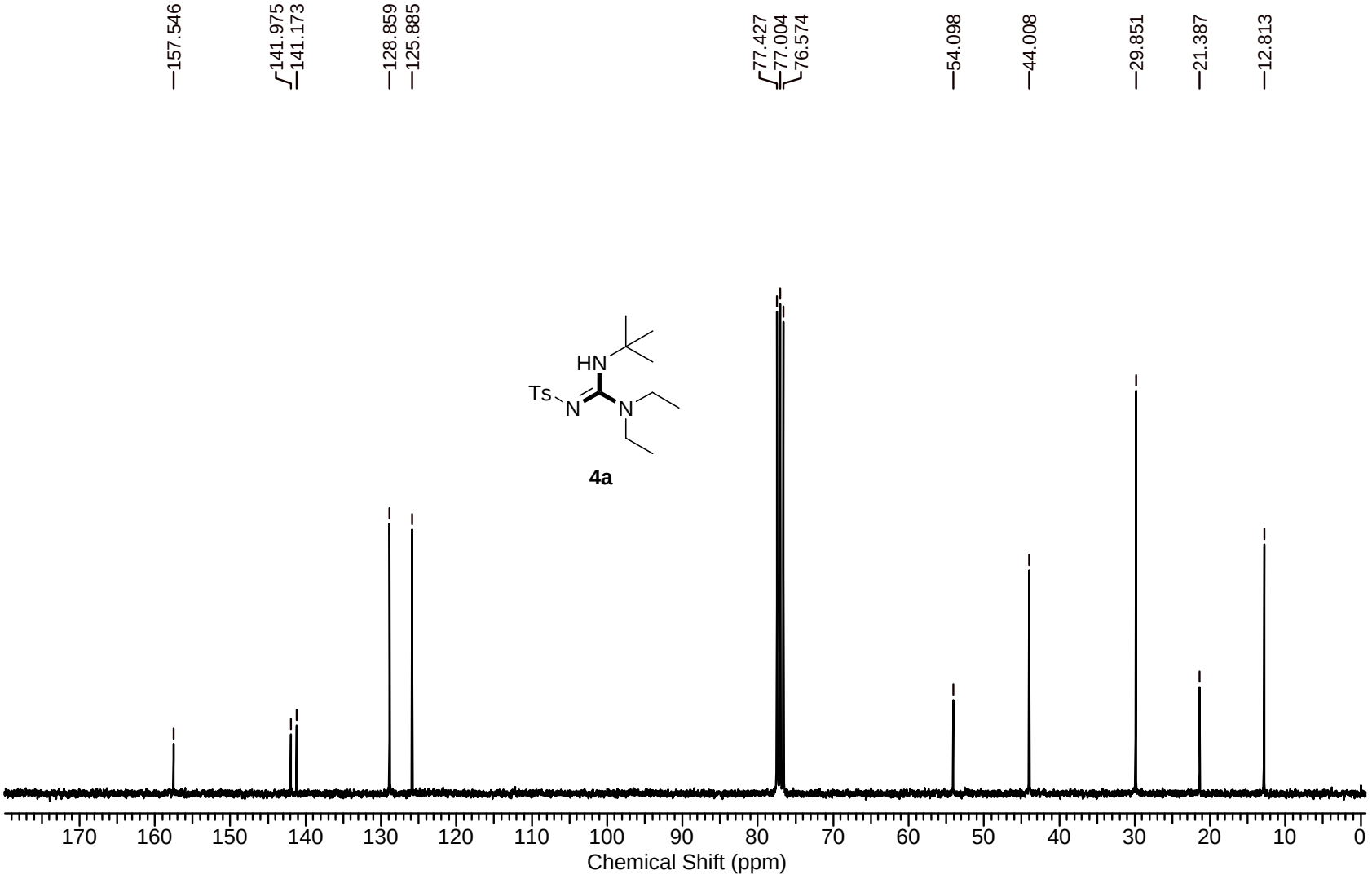
7.266
7.229
7.203
5.251
3.501
3.477
3.453
3.430
2.374
1.189
1.164
1.140
-0.011
HN
Ts
N
N
4a
1.99
2.16
0.90
4.02
3.00
15.36
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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141.173
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77.004
76.574
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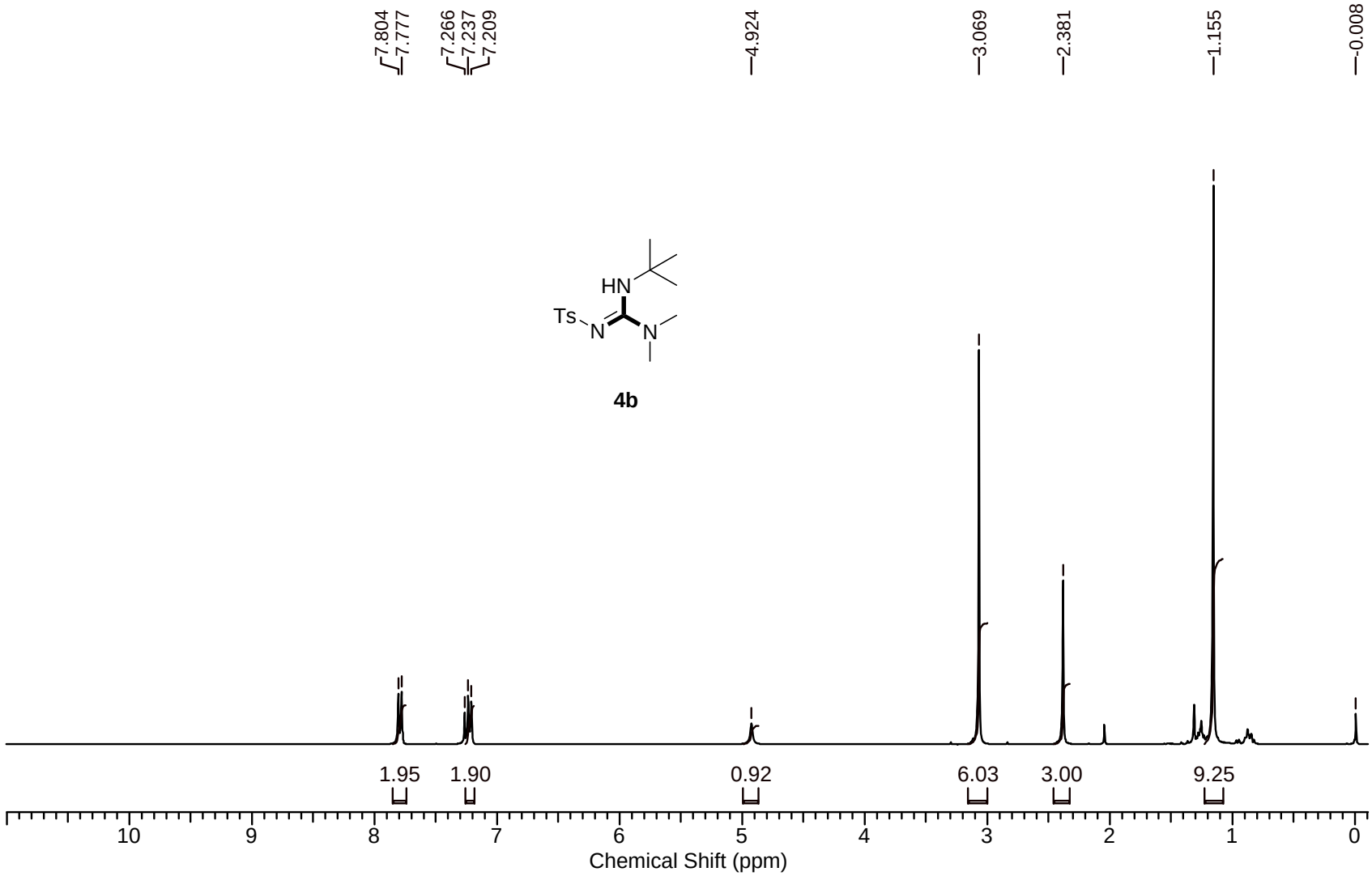
44.008
29.851
21.387
12.813
HN
Ts
N
N
4a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.266
7.237
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4.924
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2.381
1.155
-0.008
HN
Ts
N
N
4b
1.95
1.90
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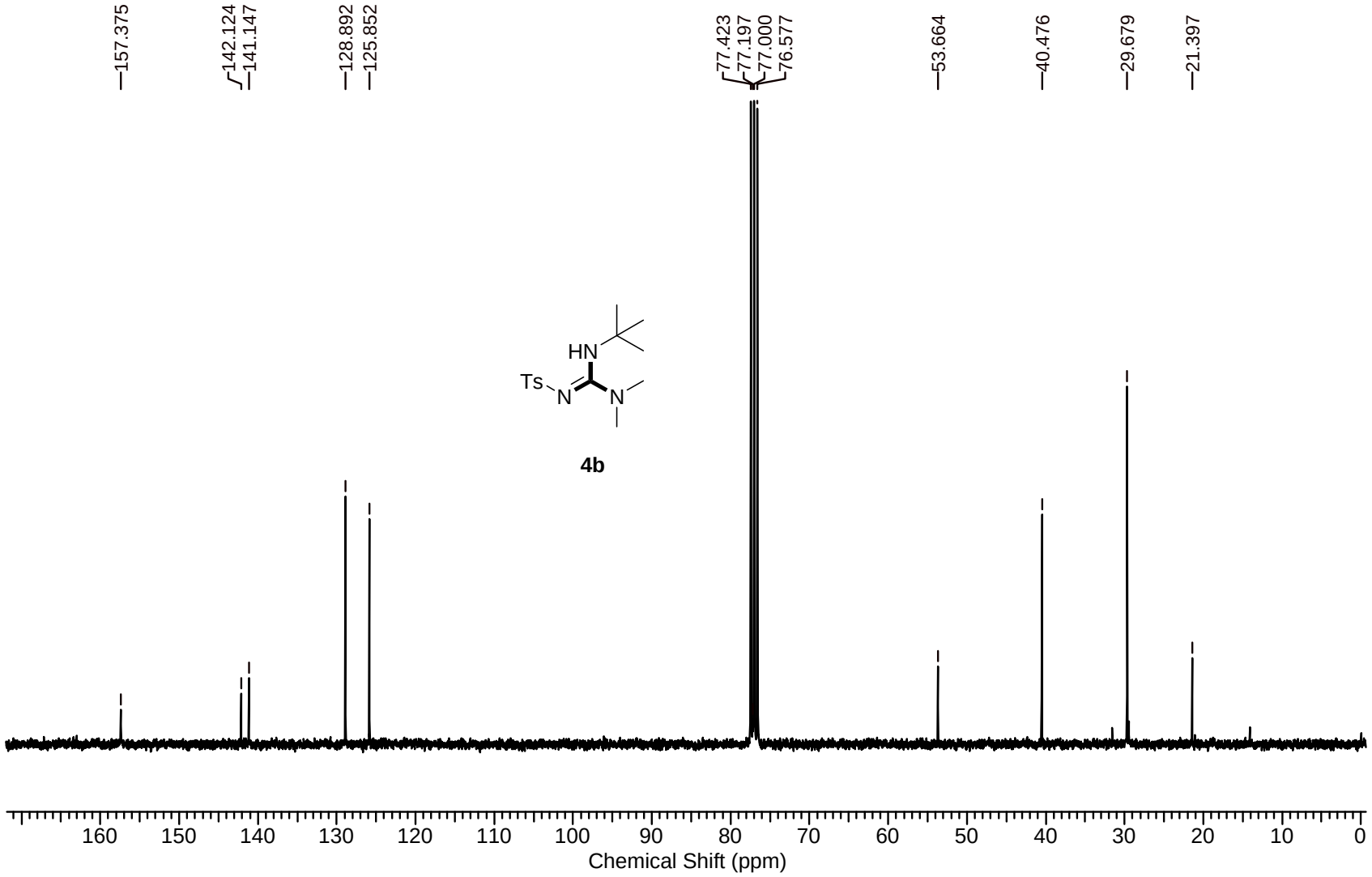
6.03
3.00
9.25
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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77.000
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21.397
HN
Ts
N
N
4b
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120
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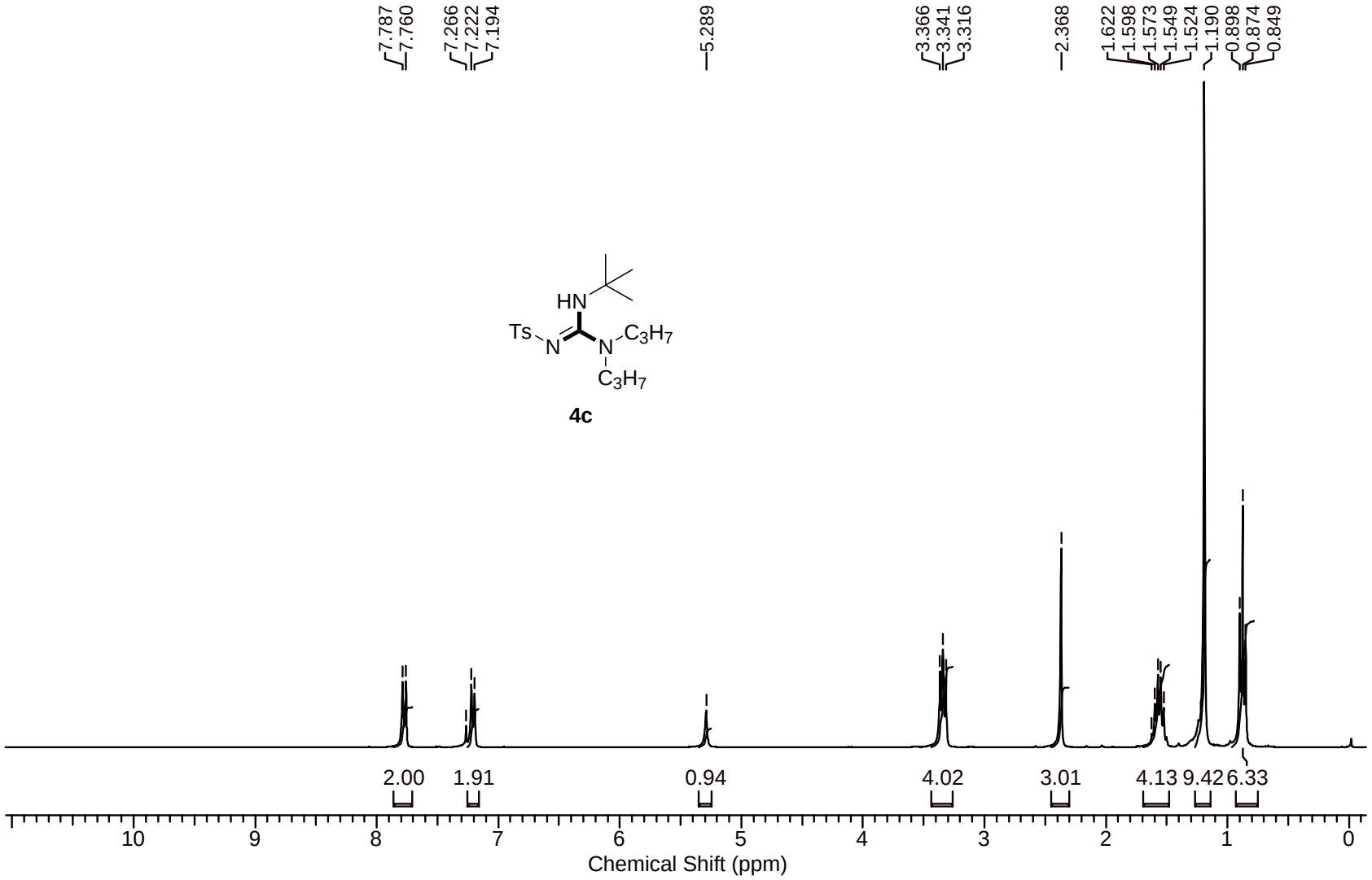
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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5.289
3.366
3.341
3.316
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1.622
1.598
1.573
1.549
1.524
1.190
0.898
0.874
0.849
HN
Ts
N
N
C3H7
C3H7
4c
2.00
1.91
0.94
4.02
3.01
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6.33
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5
4
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2
1
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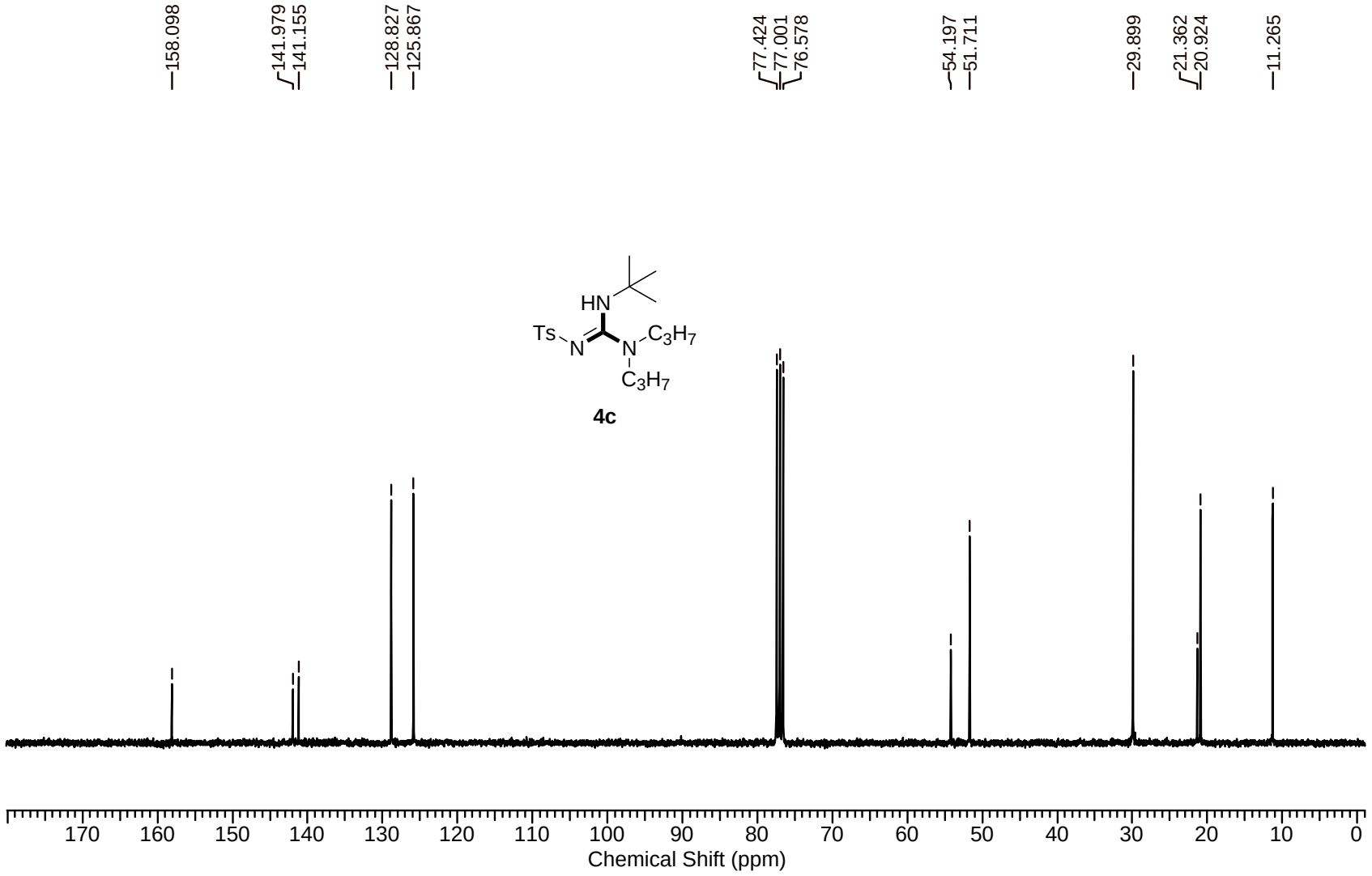
Chemical Shift (ppm)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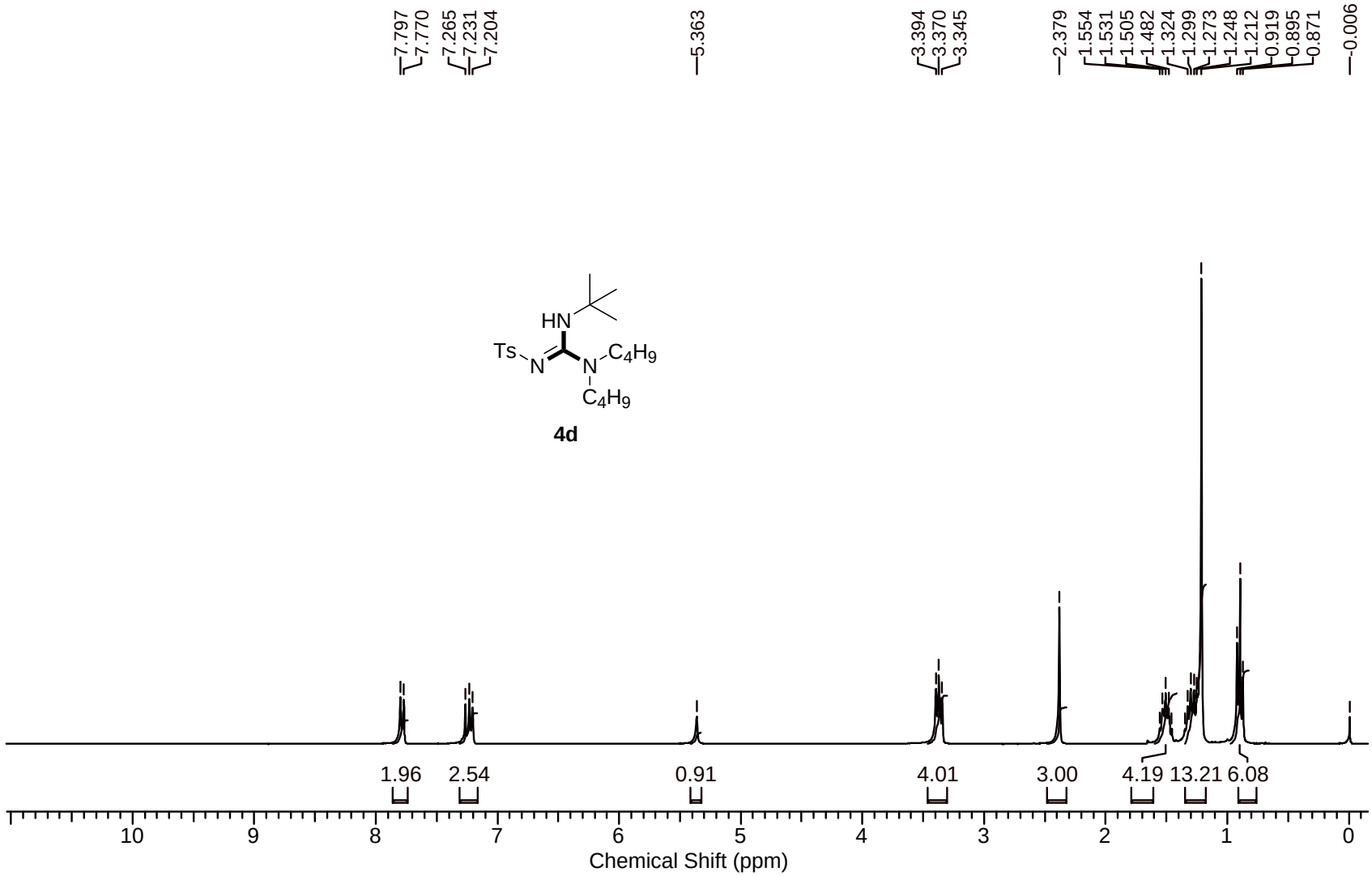
54.197
51.711
29.899
21.362
20.924
11.265
HN
Ts
N
N
C3H7
C3H7
4c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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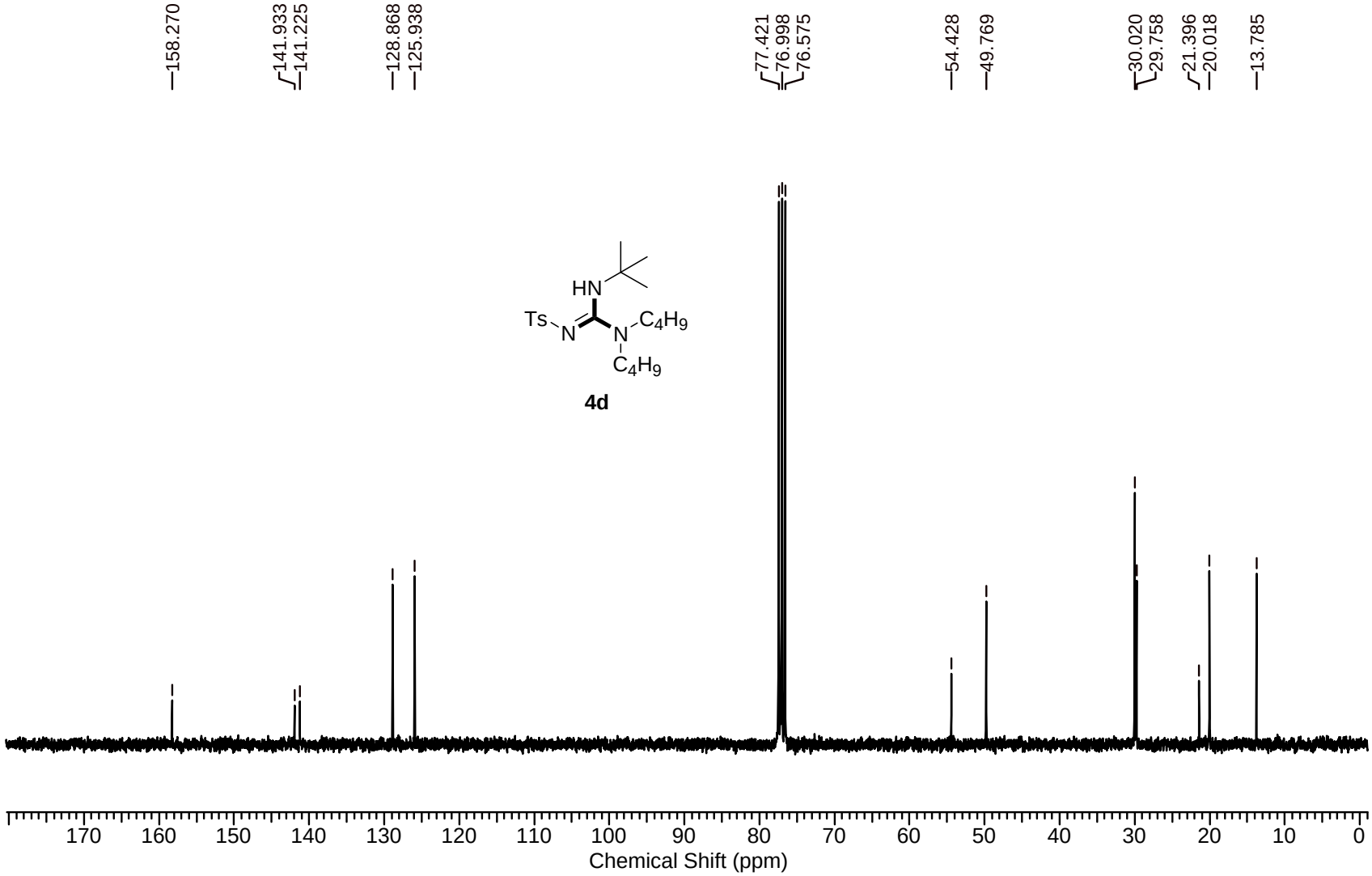
2.379
1.554
1.531
1.505
1.482
1.324
1.299
1.273
1.248
1.212
0.919
0.895
0.871
-0.006
HN
Ts
N
N
C4H9
C4H9
4d
1.96
2.54
0.91
4.01
3.00
4.19
13.21
6.08
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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125.938
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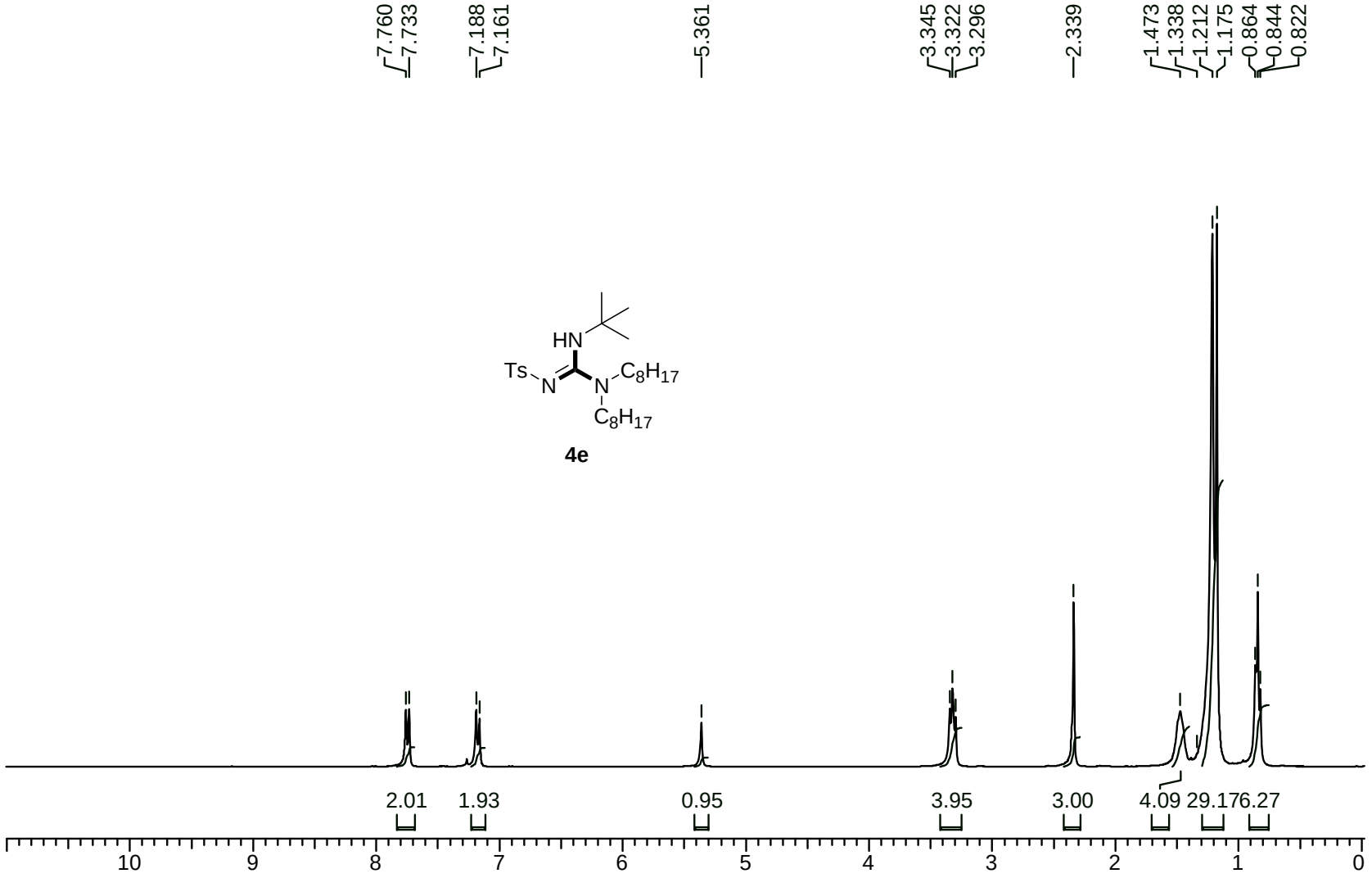
49.769
30.020
29.758
21.396
20.018
13.785
HN
Ts
N
N
C4H9
C4H9
4d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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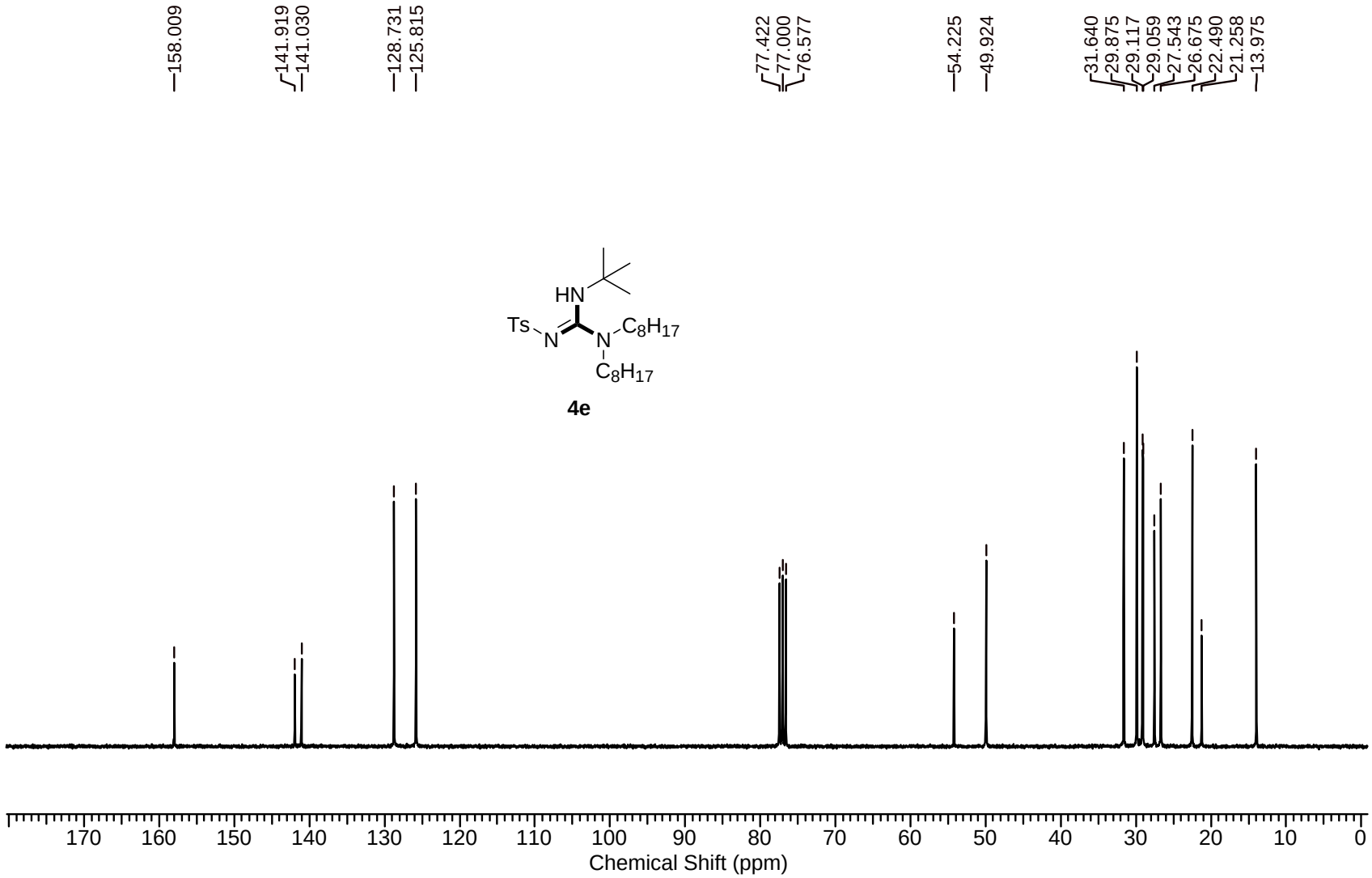
7.188
7.161
5.361
3.345
3.322
3.296
2.339
1.473
1.338
1.212
1.175
0.864
0.844
0.822
HN
Ts
N
N
C8H17
C8H17
4e
2.01
1.93
0.95
3.95
3.00
4.09
29.17
6.27
10
9
8
7
6
5
4
3
2
1
0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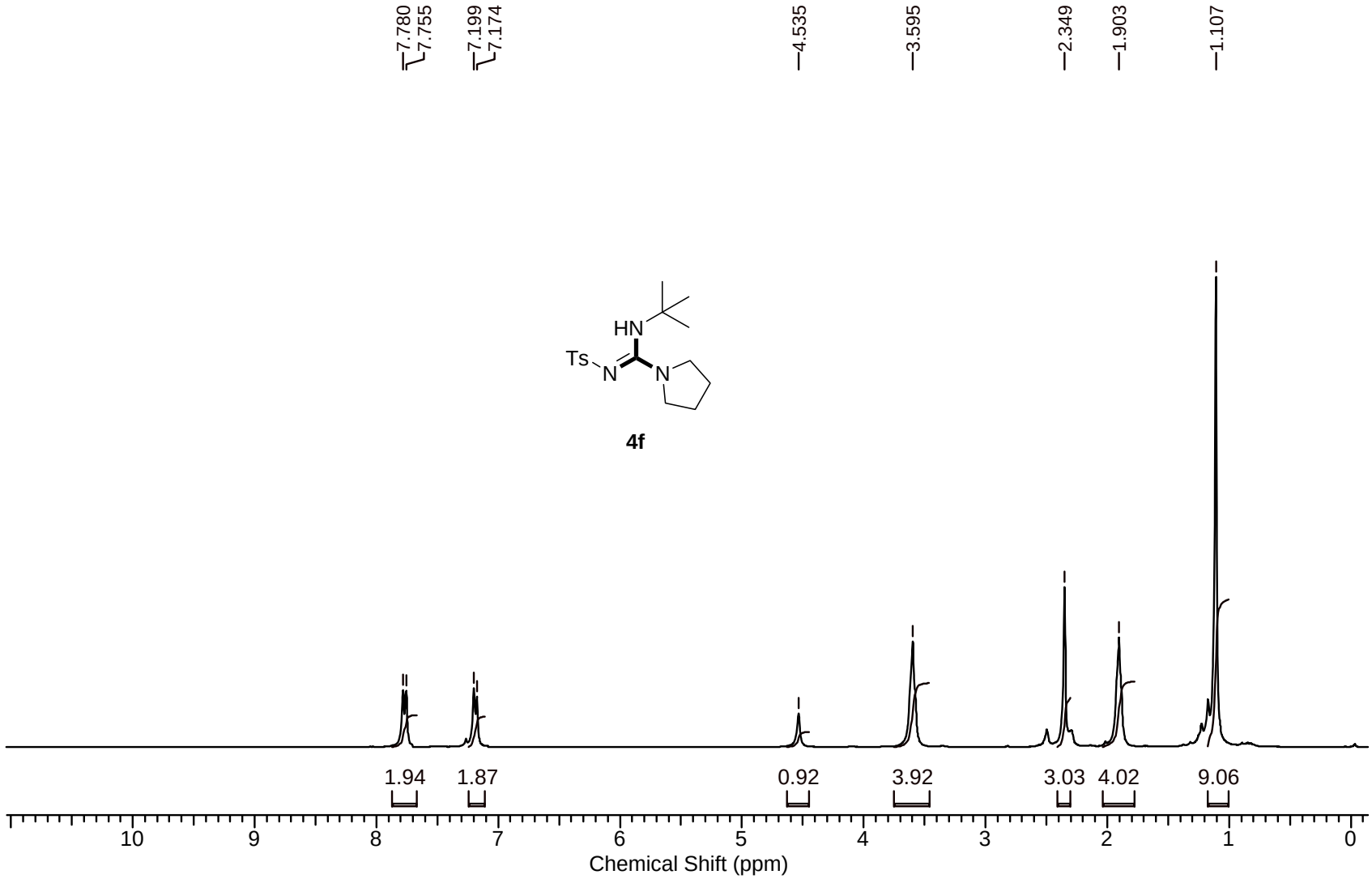
141.030
128.731
125.815
77.422
77.000
76.577
54.225
49.924
31.640
29.875
29.117
29.059
27.543
26.675
22.490
21.258
13.975
HN
Ts
N
N
C8H17
C8H17
4e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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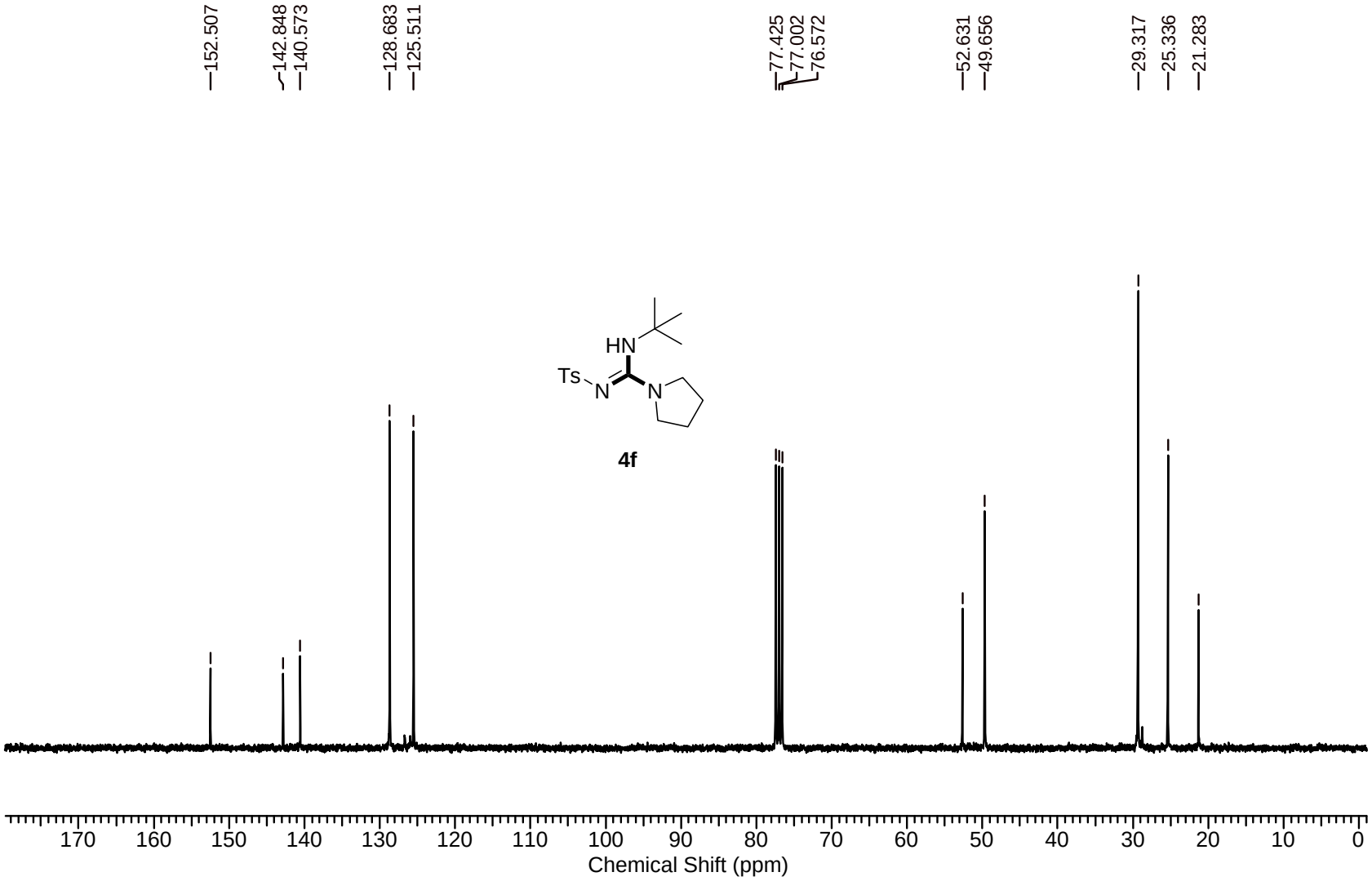
7.755
7.199
7.174
4.535
3.595
2.349
1.903
1.107
HN
Ts
N
N
4f
1.94
1.87
0.92
3.92
3.03
4.02
9.06
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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142.848
140.573
128.683
125.511
77.425
77.002
76.572
52.631
49.656
29.317
25.336
21.283
HN
Ts
N
N
4f
170
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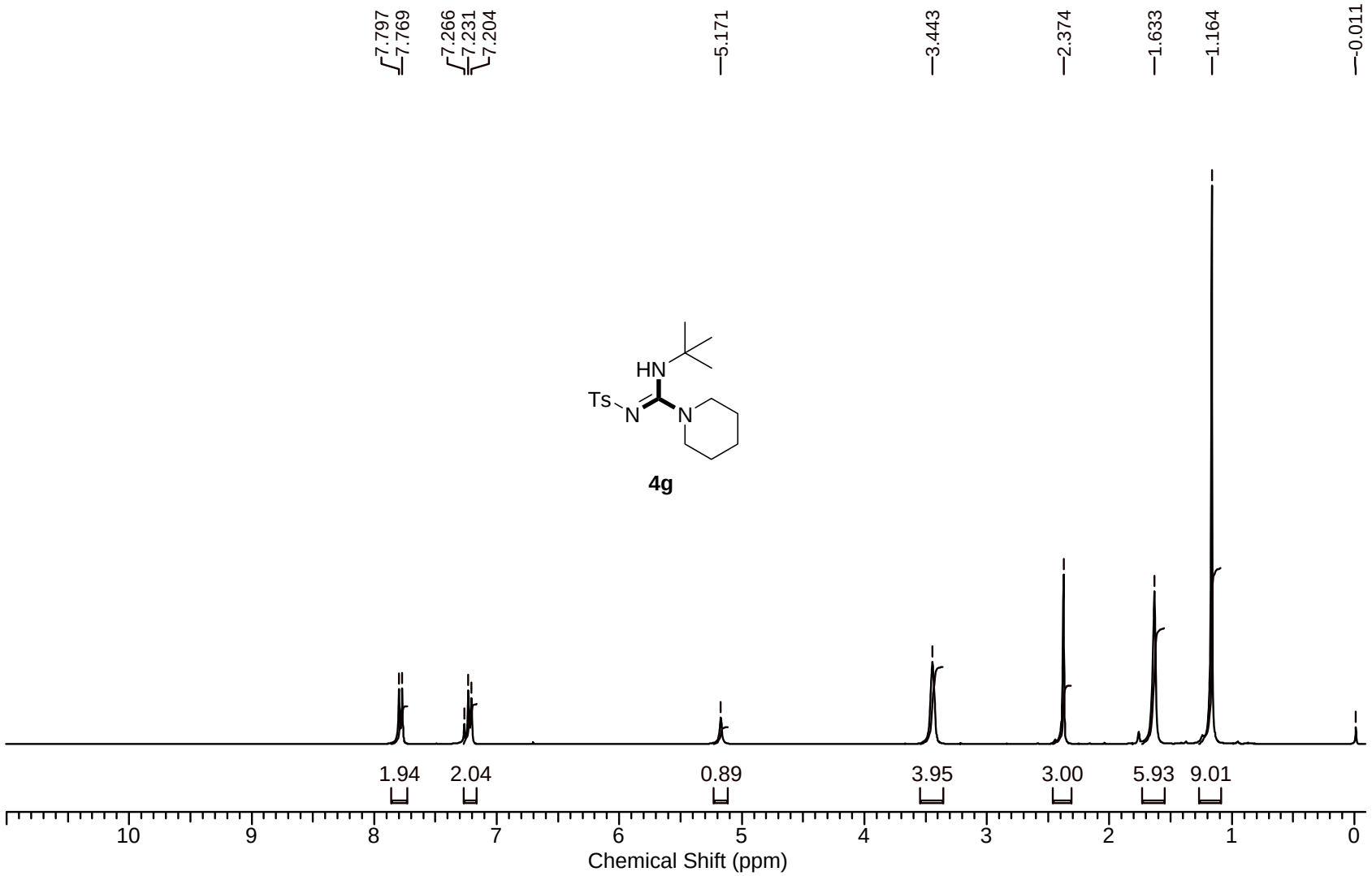
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.797
7.769
7.266
7.231
7.204
5.171
3.443
2.374
1.633
1.164
-0.011
HN
Ts
N
N
4g
1.94
2.04
0.89
3.95
3.00
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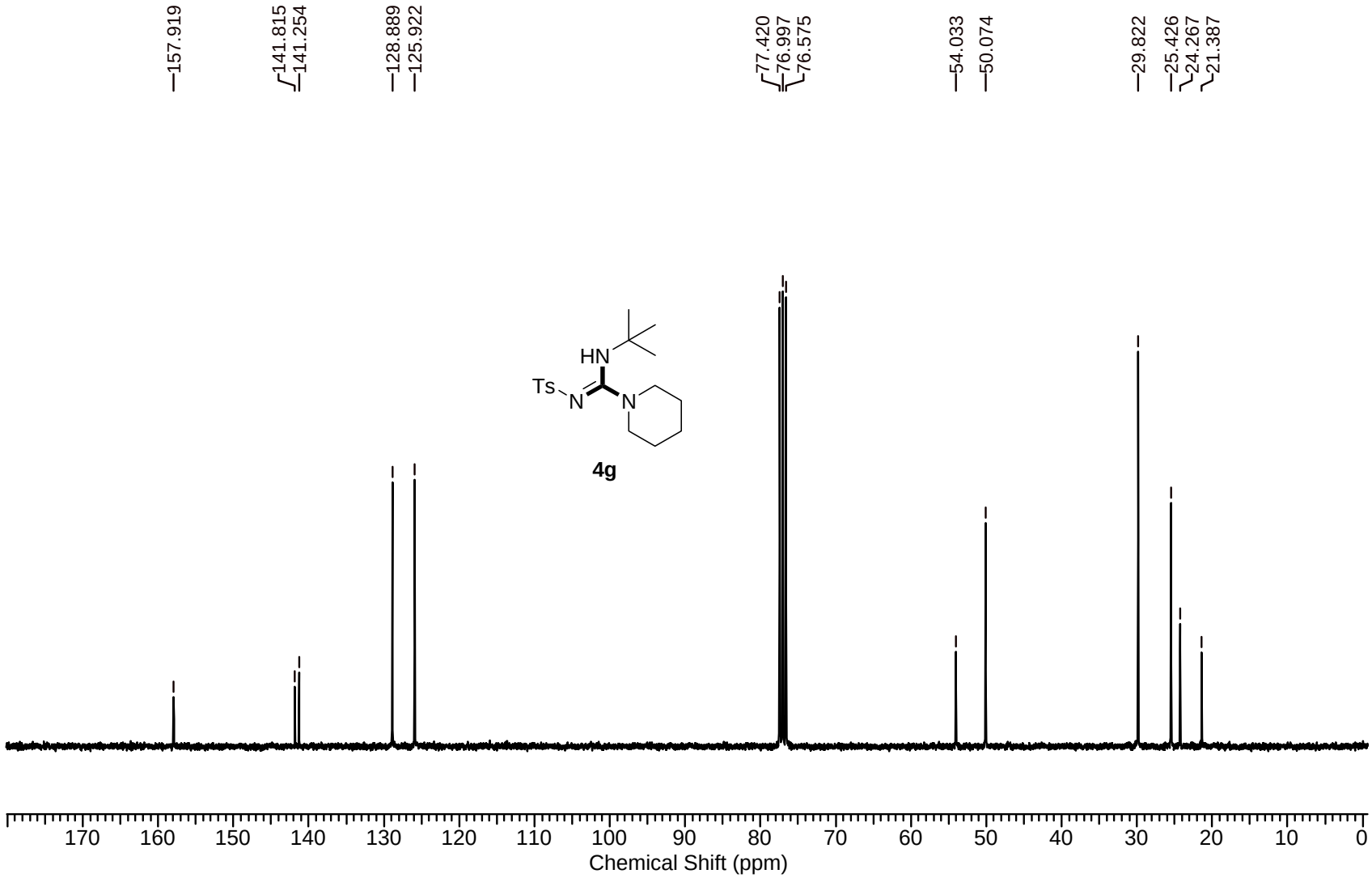
9.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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125.922
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76.997
76.575
54.033
50.074
29.822
25.426
24.267
21.387
HN
Ts
N
N
4g
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150
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130
120
110
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90
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40
30
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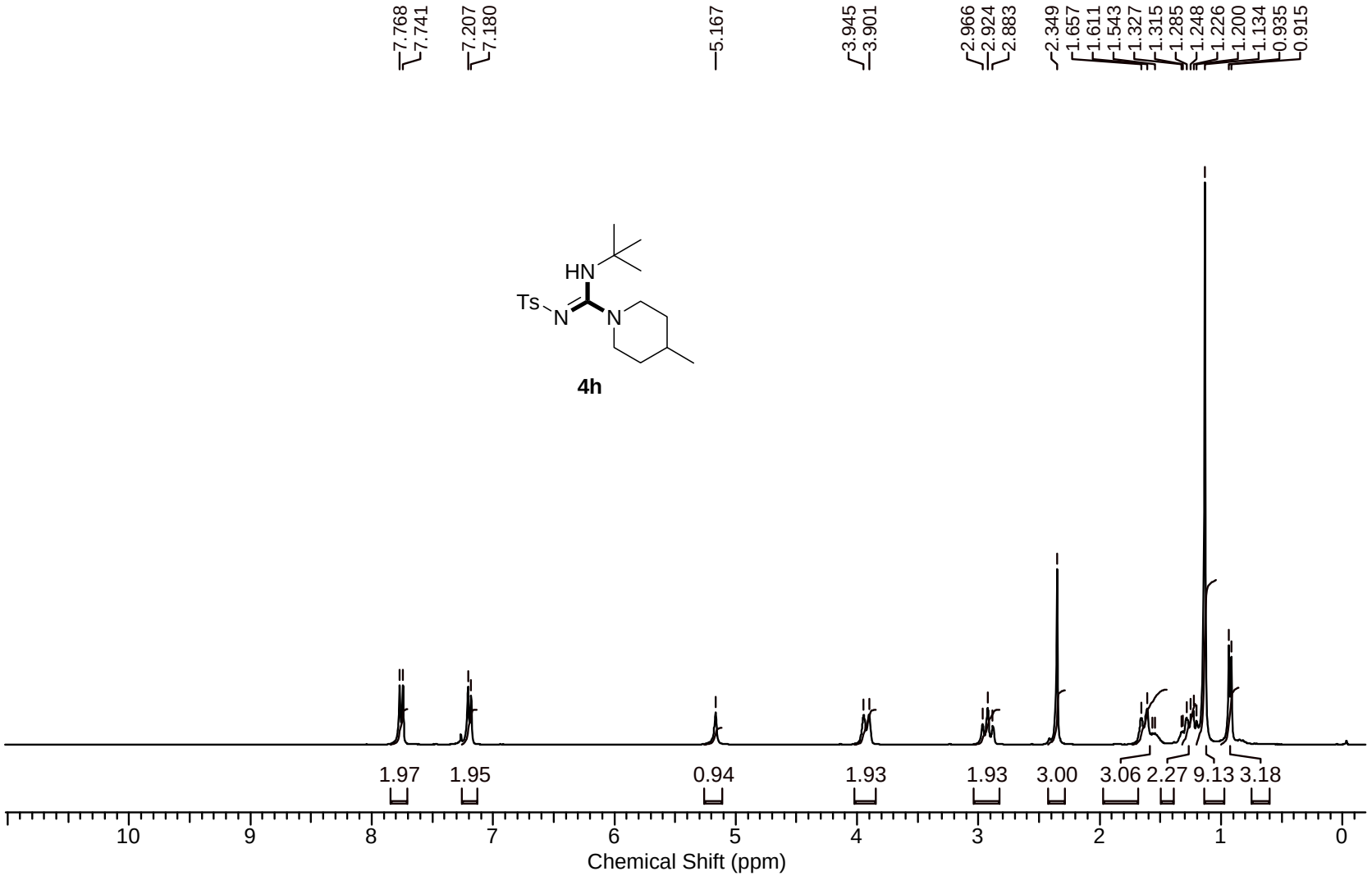
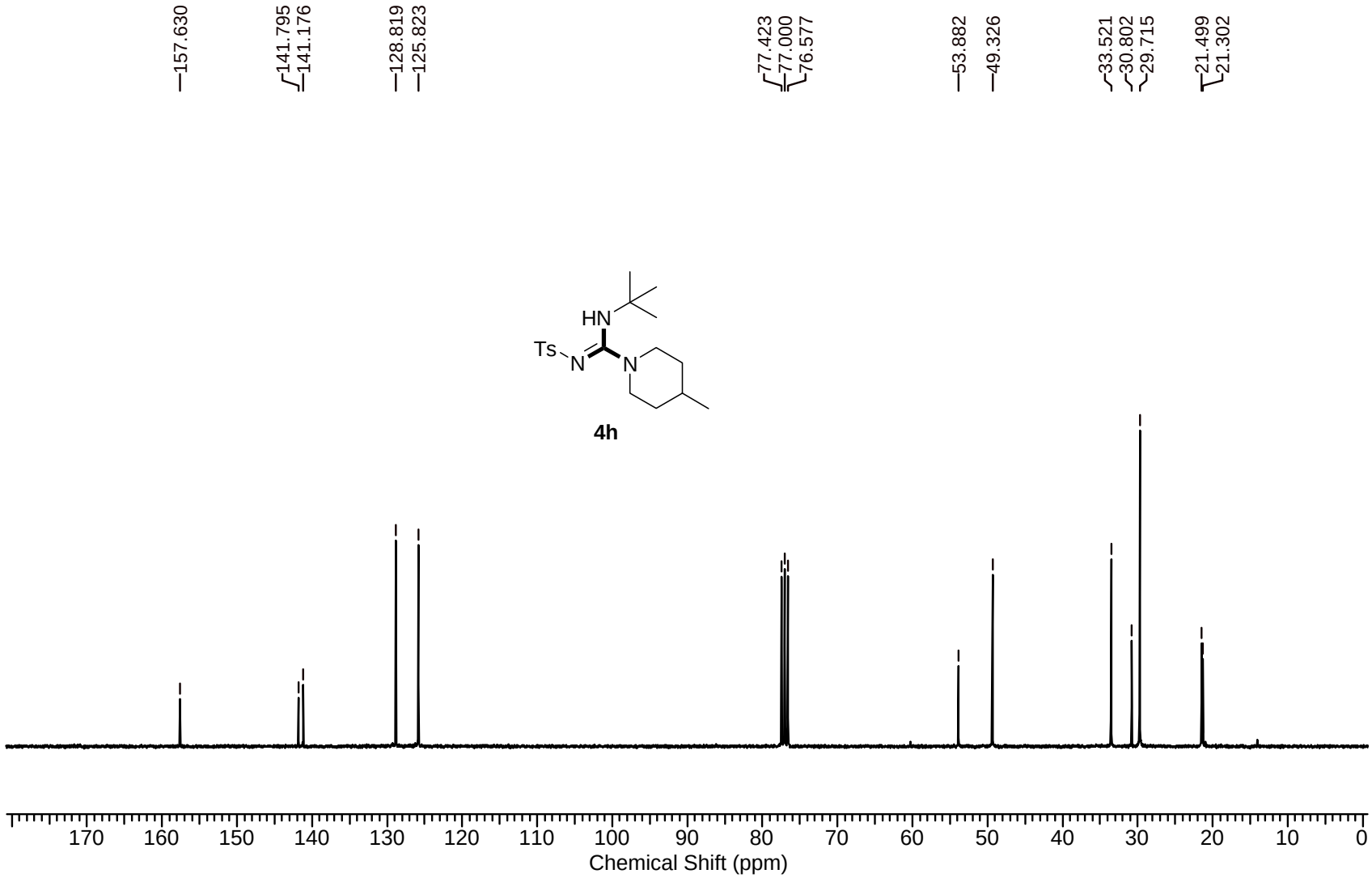
0
Chemical Shift (ppm)


7.768
7.741
7.207
7.180
5.167
3.945
3.901
2.966
2.924
2.883
2.349
1.657
1.611
1.543
1.327
1.315
1.285
1.248
1.226
1.200
1.134
0.935
0.915
HN
Ts
N
N
4h
1.97
1.95
0.94
1.93
1.93
3.00
3.06
2.27
9.13
3.18
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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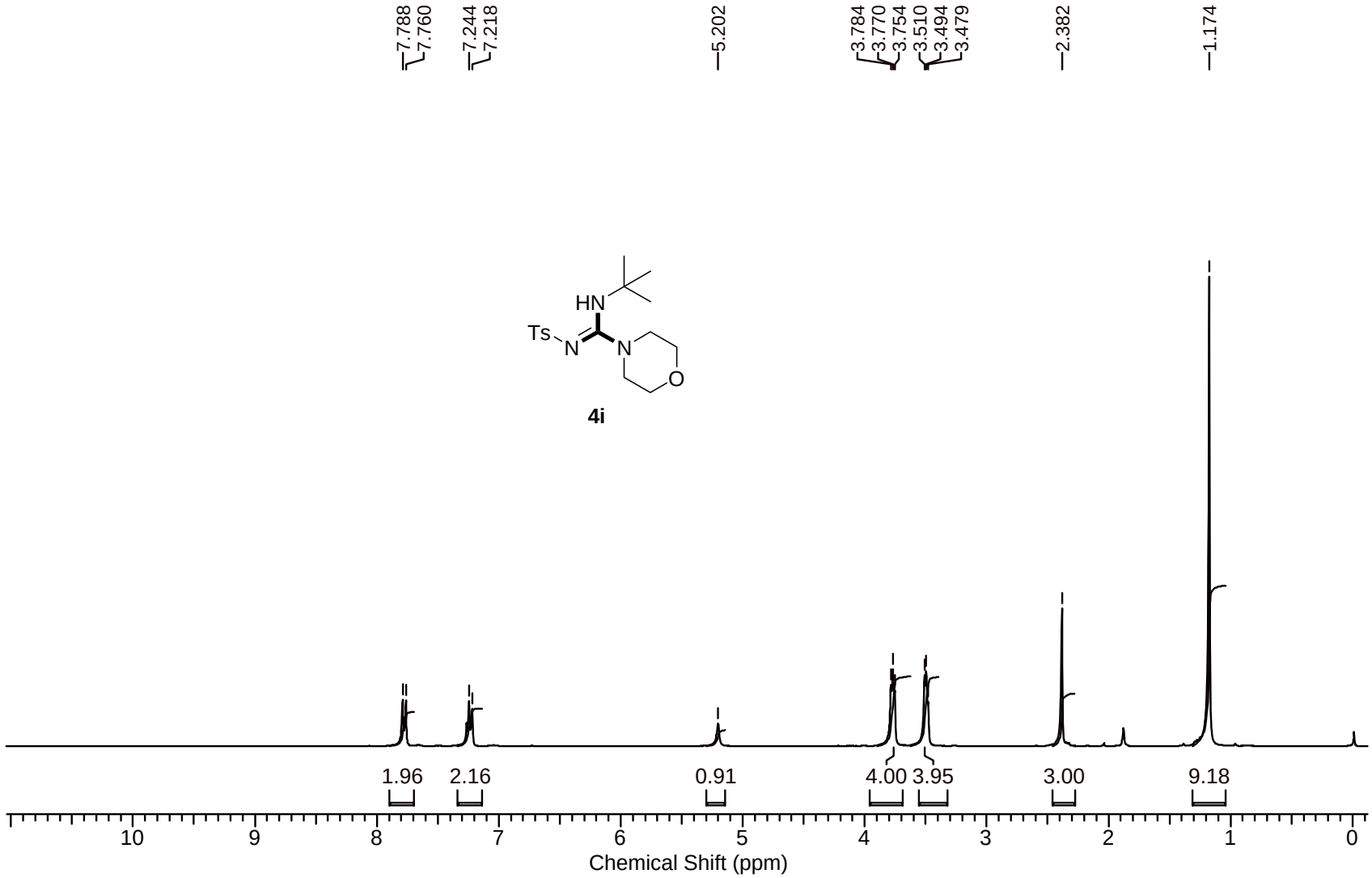
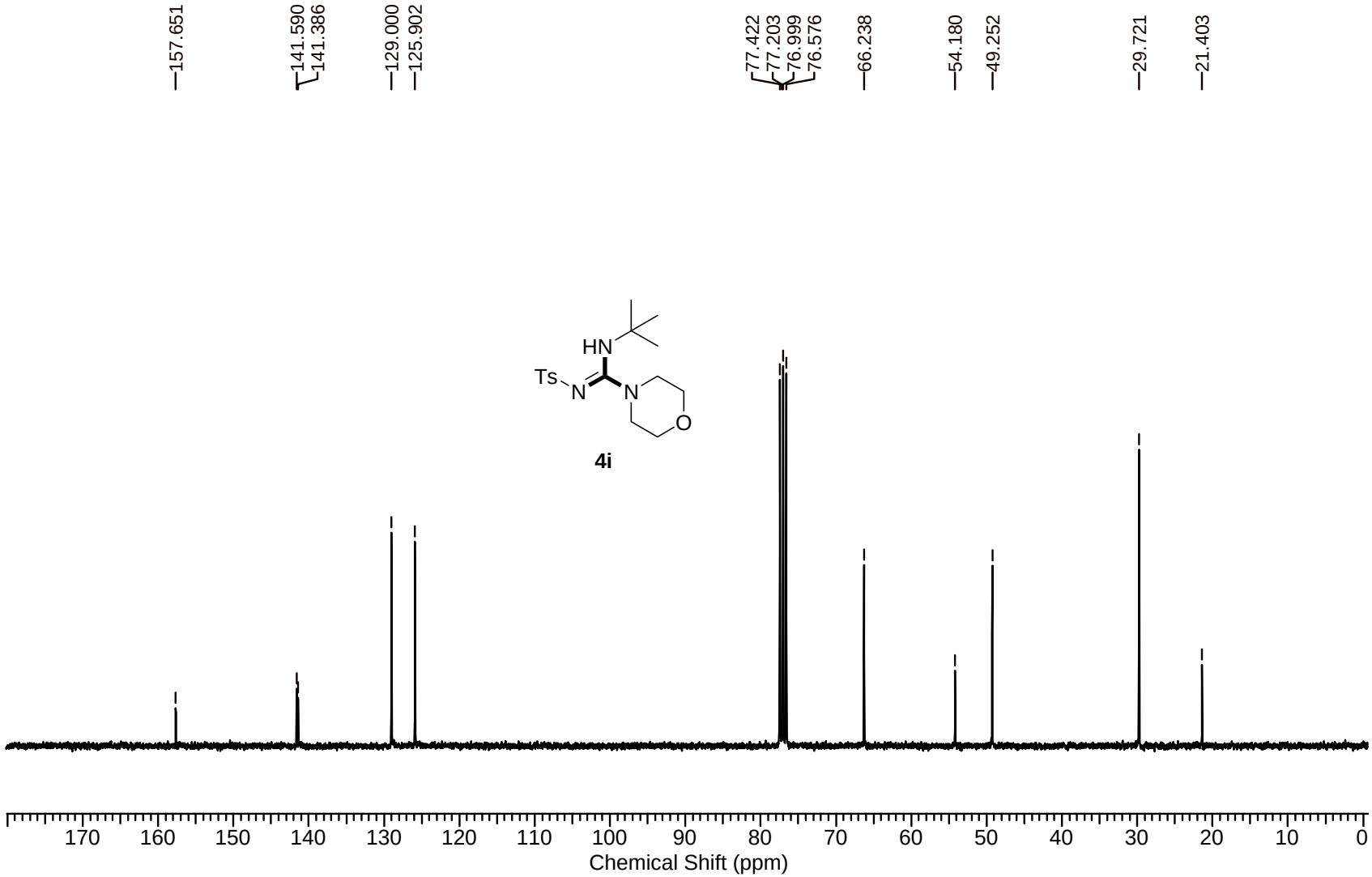
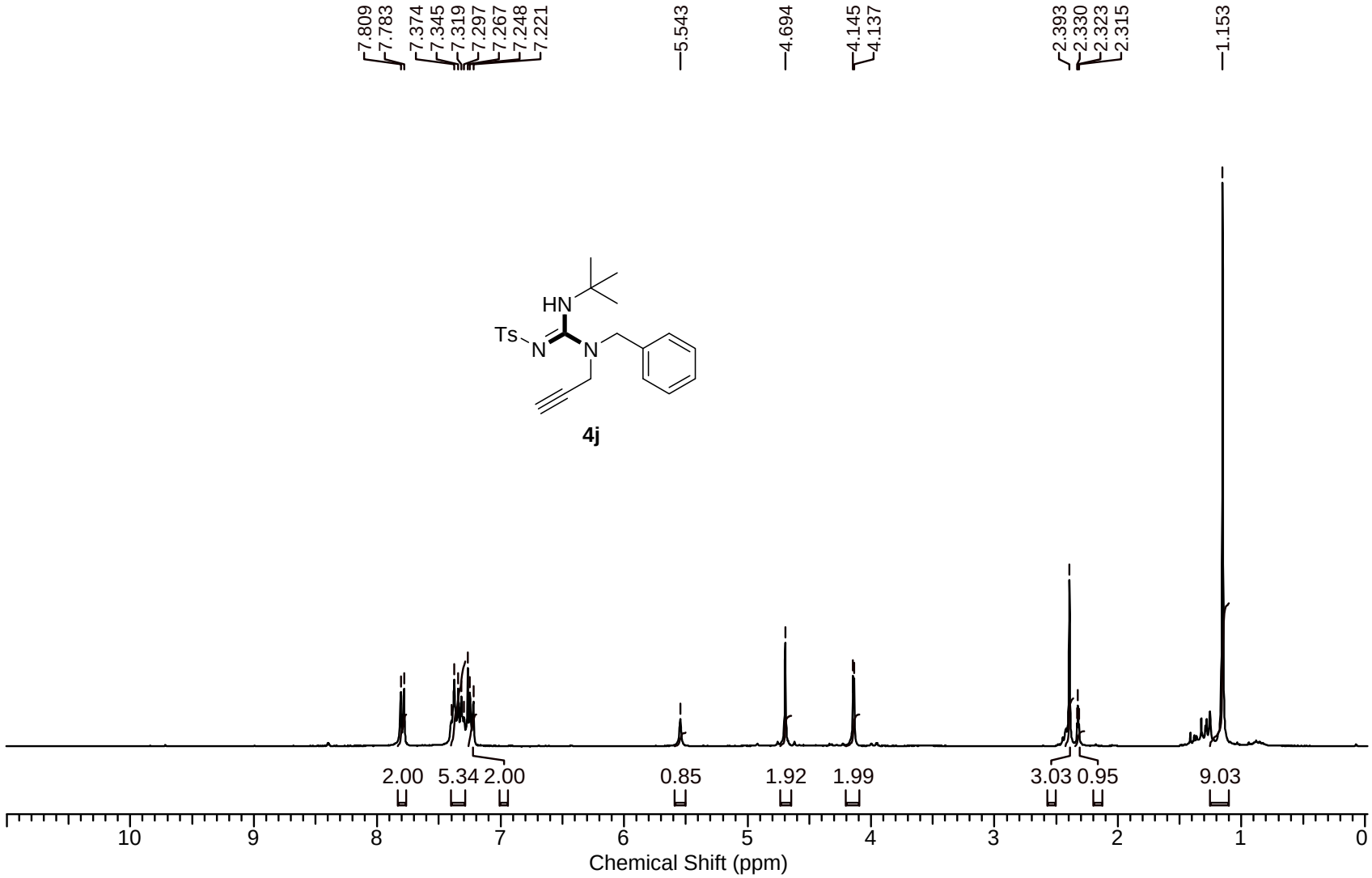
141.176
128.819
125.823
77.423
77.000
76.577
53.882
49.326
33.521
30.802
29.715
21.499
21.302
HN
Ts
N
N
4h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.788
7.760
7.244
7.218
5.202
3.784
3.770
3.754
3.510
3.494
3.479
2.382
1.174
HN
Ts
N
N
O
4i
1.96
2.16
0.91
4.00
3.95
3.00
9.18
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


157.651
141.590
141.386
129.000
125.902
77.422
77.203
76.999
76.576
66.238
54.180
49.252
29.721
21.403
HN
Ts
N
N
O
4i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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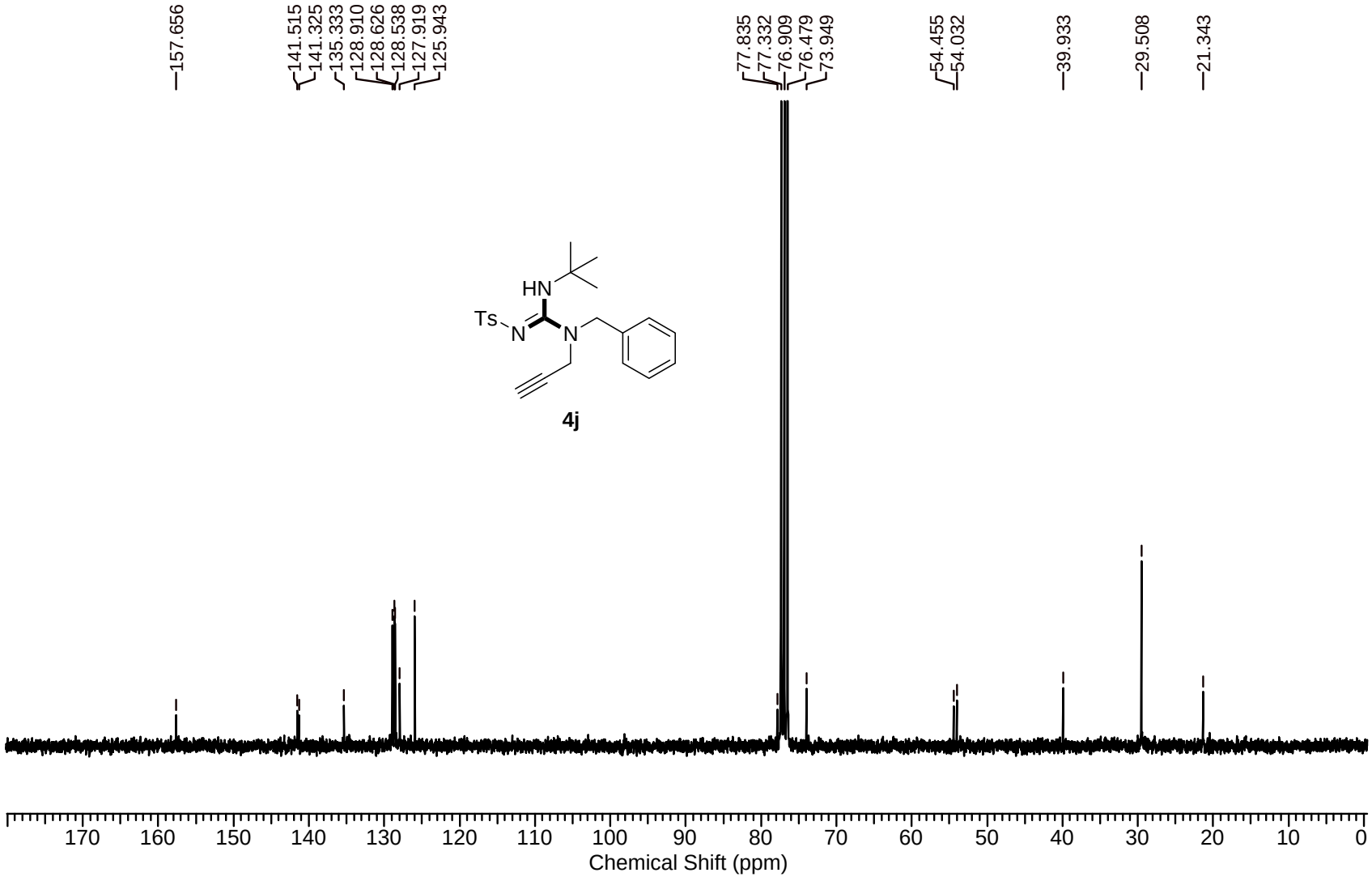
7.783
7.374
7.345
7.319
7.297
7.267
7.248
7.221
5.543
4.694
4.145
4.137
2.393
2.330
2.323
2.315
1.153
HN
Ts
N
N
2.00
5.34
2.00
0.85
1.92
1.99
3.03
0.95
9.03
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

4j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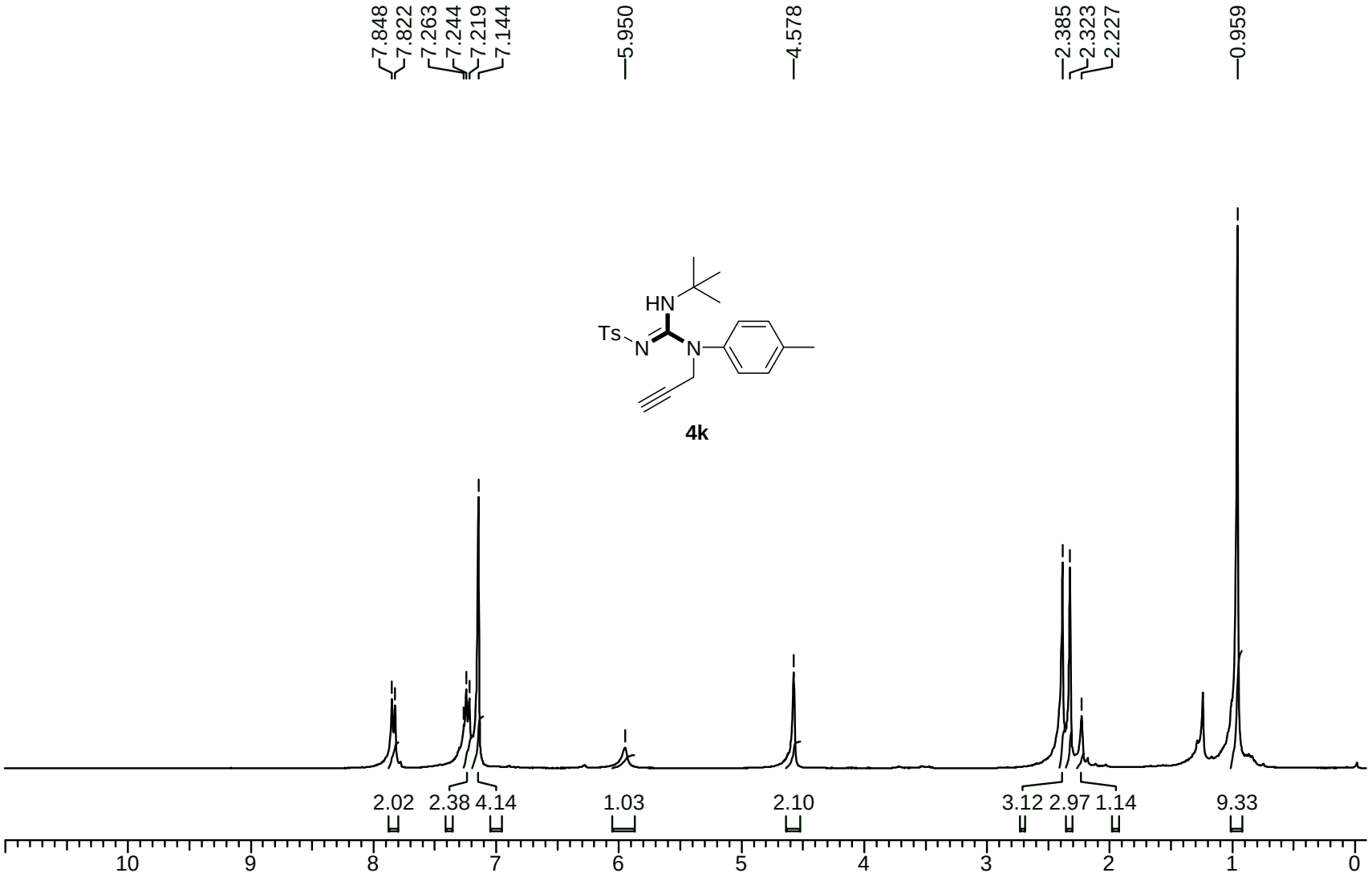
141.325
135.333
128.910
128.626
128.538
127.919
125.943
77.835
77.332
76.909
76.479
73.949
54.455
54.032
39.933
29.508
21.343
HN
Ts
N
N
4j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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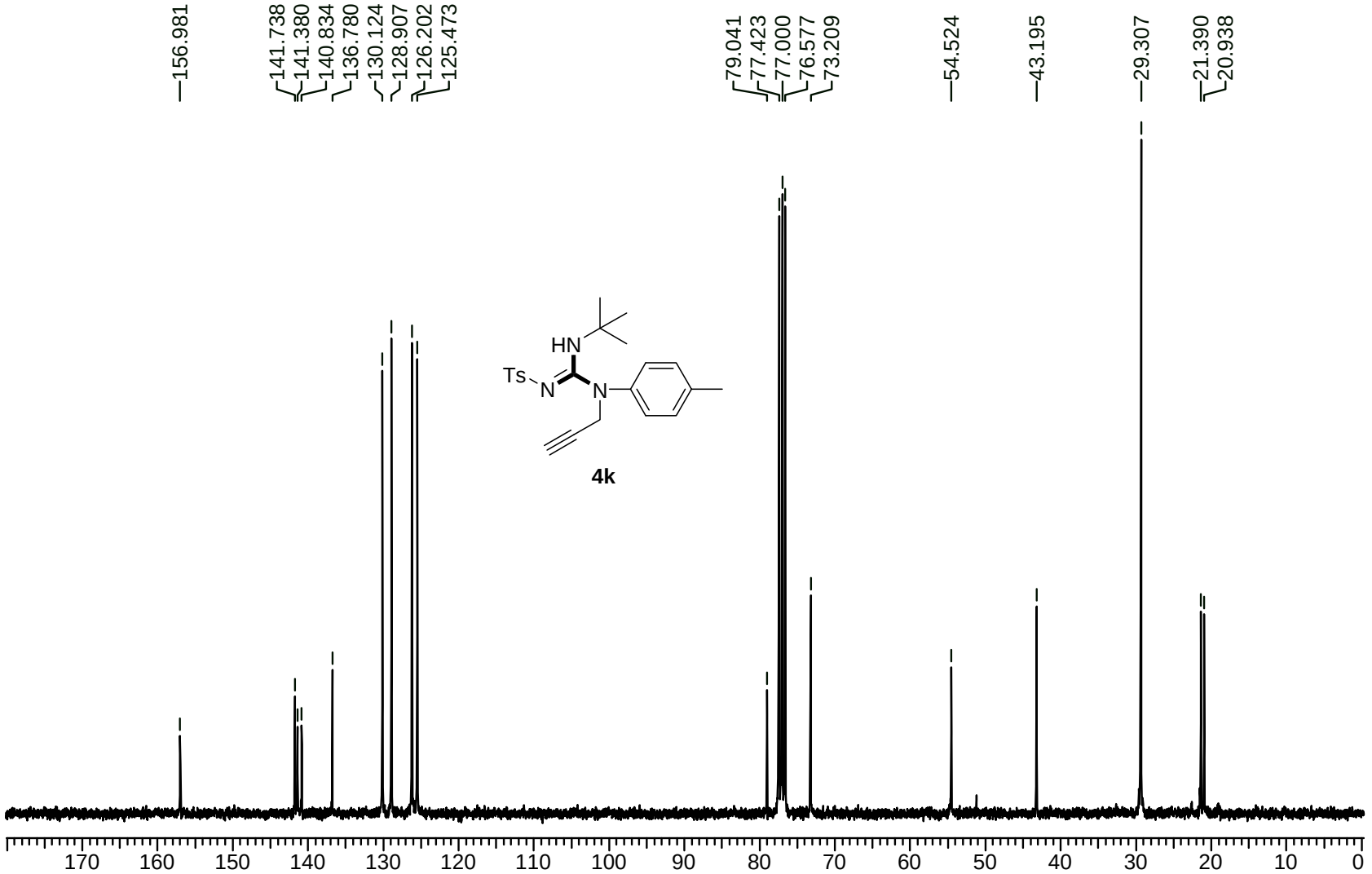
7.822
7.263
7.244
7.219
7.144
5.950
4.578
2.385
2.323
2.227
0.959
HN
Ts
N
N
2.02
2.38
4.14
1.03
2.10
3.12
2.97
1.14
9.33
10
9
8
7
6
5
4
3
2
1
0

4k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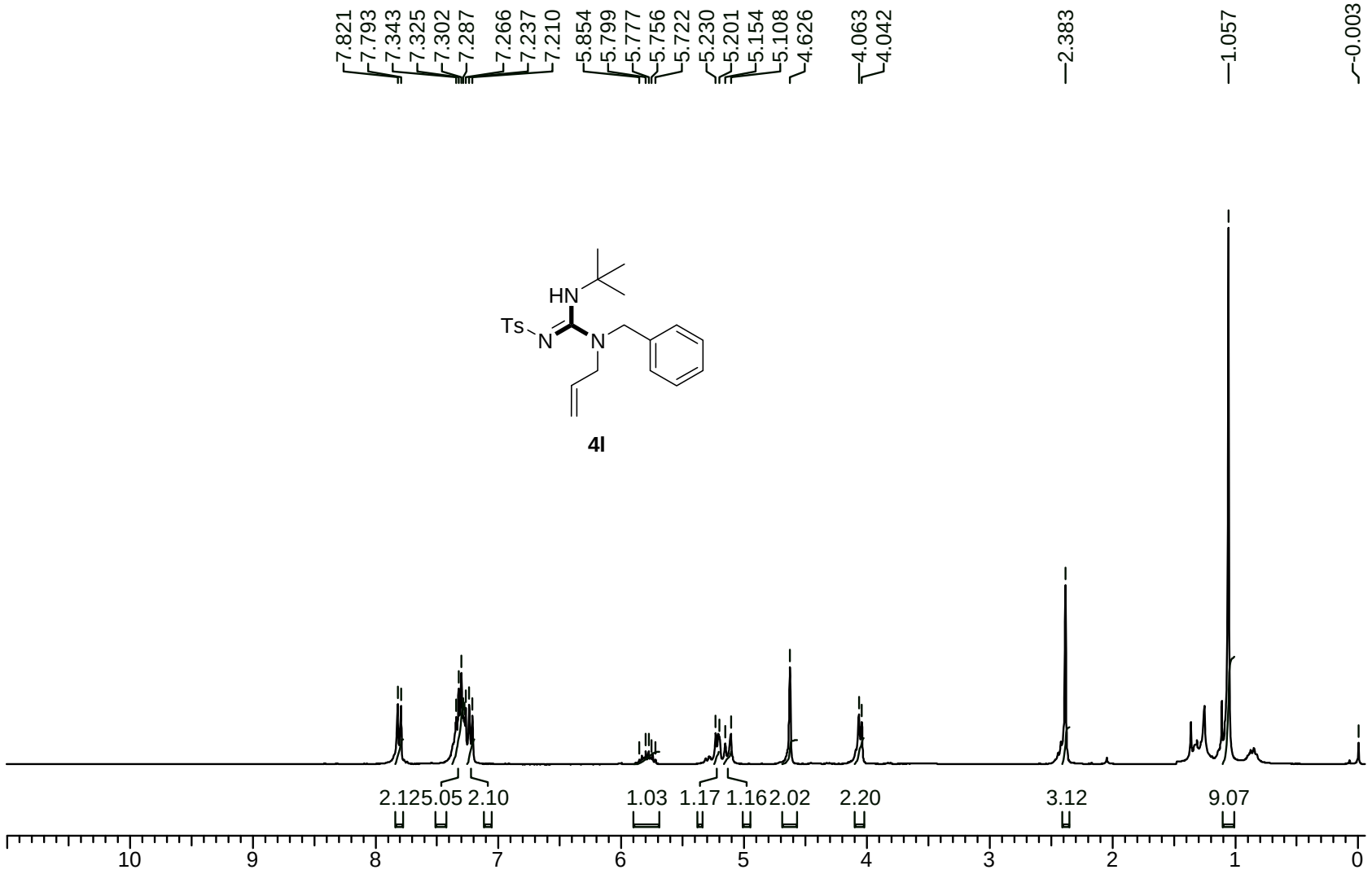
128.907
126.202
125.473
79.041
77.423
77.000
76.577
73.209
54.524
43.195
29.307
21.390
20.938
HN
Ts
N
N
4k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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7.343
7.325
7.302
7.287
7.266
7.237
7.210
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5.799
5.777
5.756
5.722
5.230
5.201
5.154
5.108
4.626
4.063
4.042
2.383
1.057
-0.003
HN
Ts
N
N
2.12
5.05
2.10
1.03
1.17
1.16
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2.20
3.12
9.07
10
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8
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6
5
4
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2
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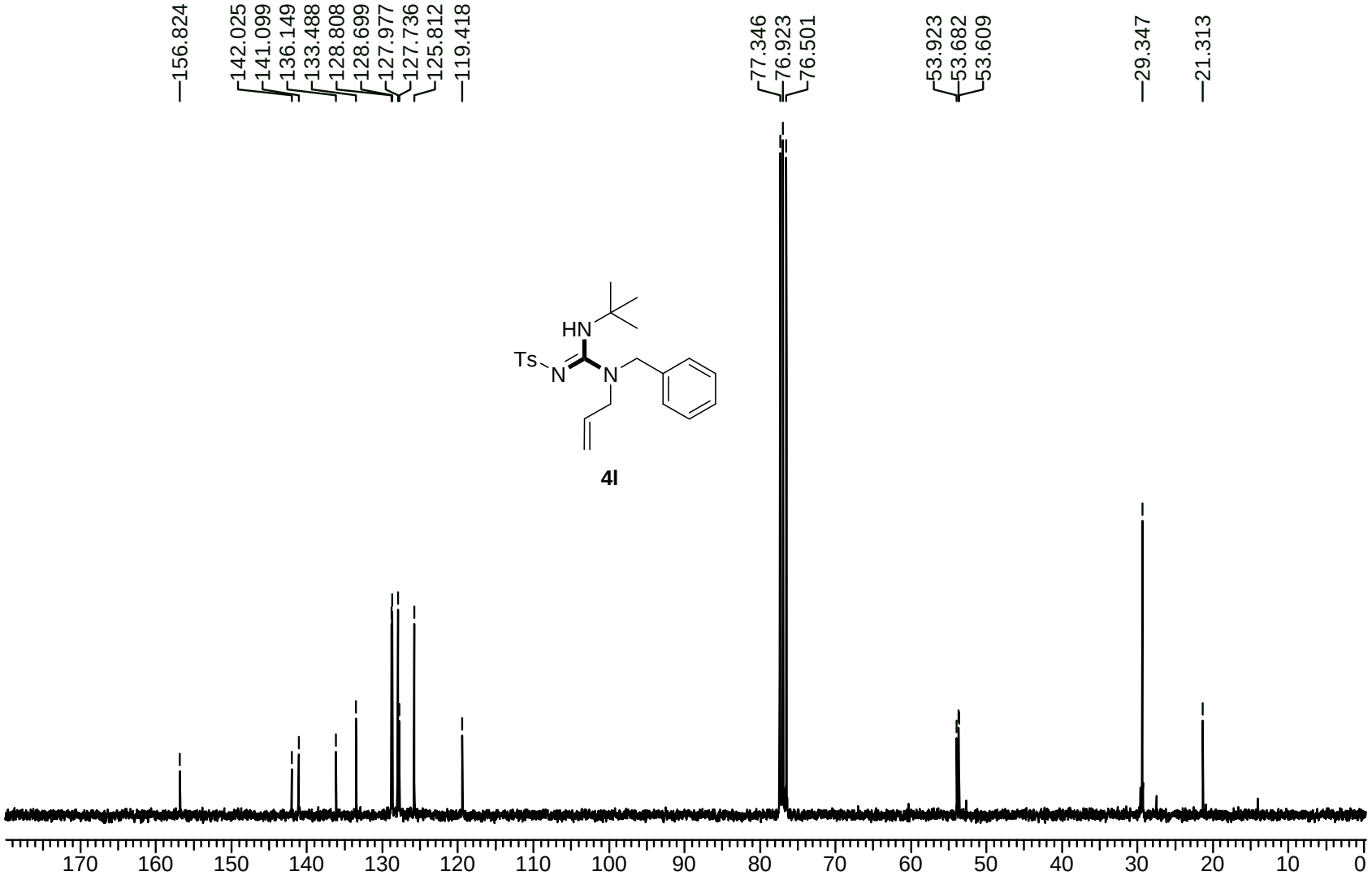
0

4l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141.099
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128.699
127.977
127.736
125.812
119.418
77.346
76.923
76.501
53.923
53.682
53.609
29.347
21.313
HN
Ts
N
N
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140
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20
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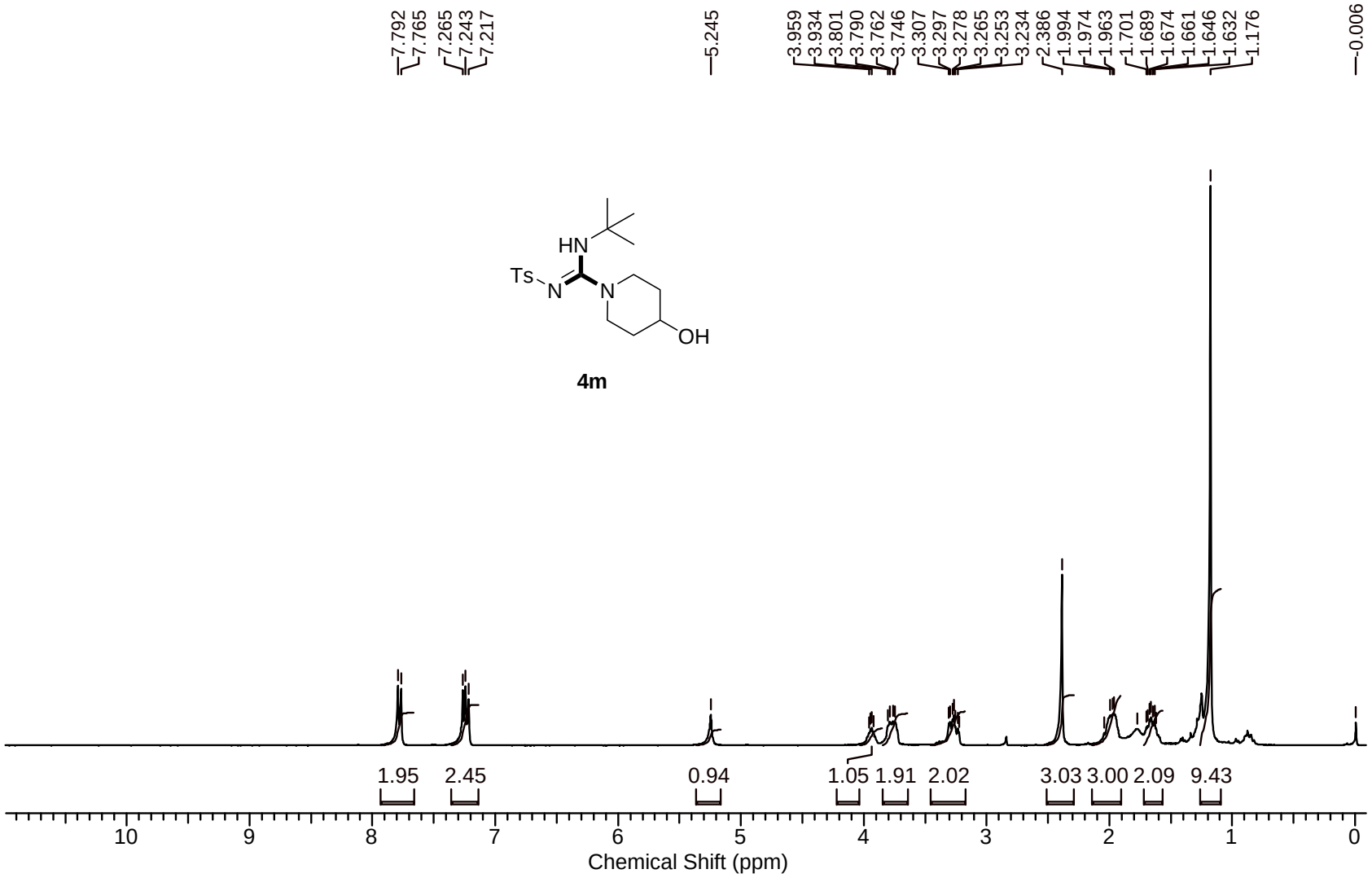
0

4l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3.934
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3.790
3.762
3.746
3.307
3.297
3.278
3.265
3.253
3.234
2.386
1.994
1.974
1.963
1.701
1.689
1.674
1.661
1.646
1.632
1.176
0.006
HN
Ts
N
N
OH
4m
1.95
2.45
0.94
1.05
1.91
2.02
3.03
3.00
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9.43
10
9
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7
6
5
4
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2
1
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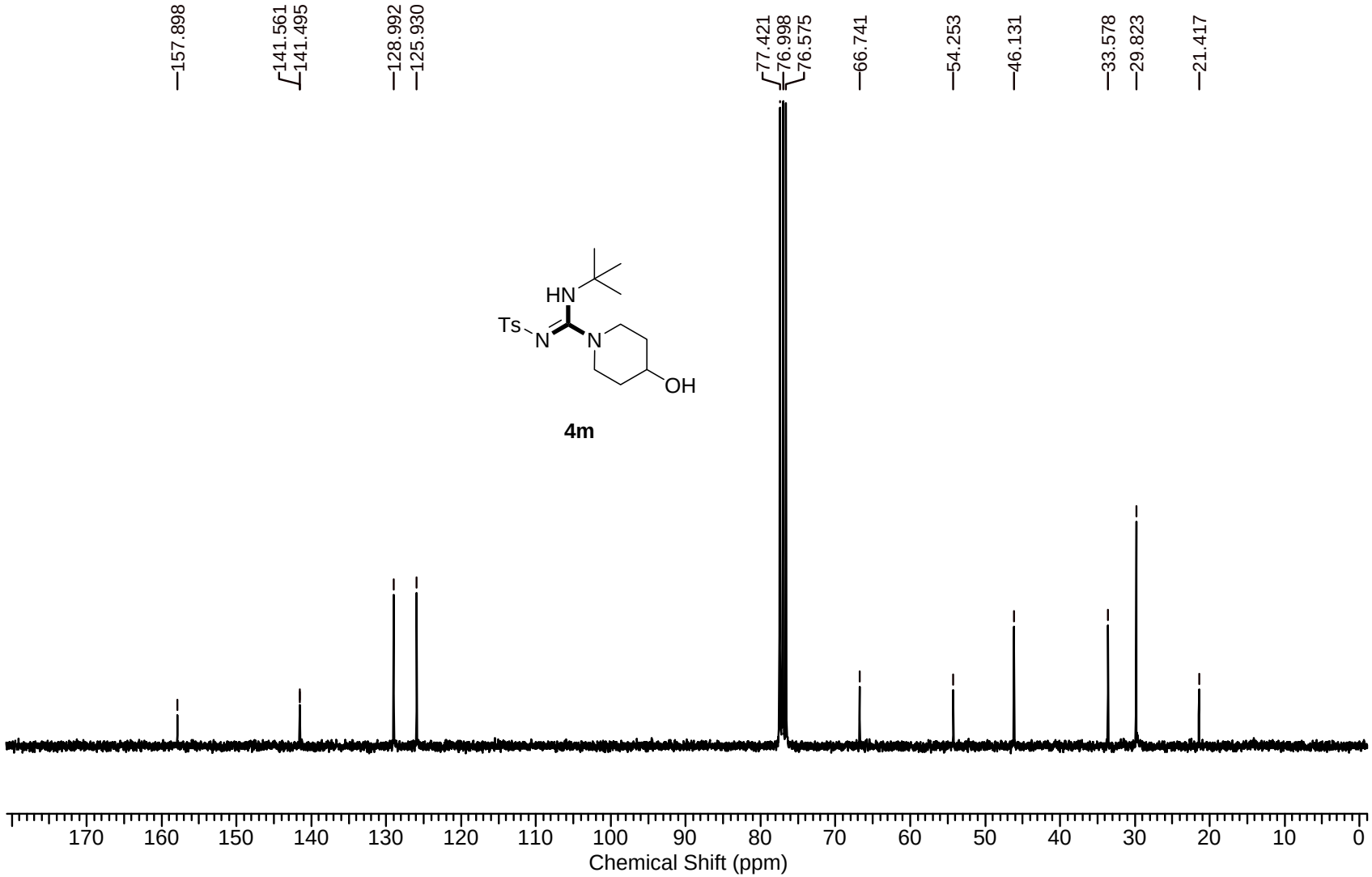
Chemical Shift (ppm)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141.495
128.992
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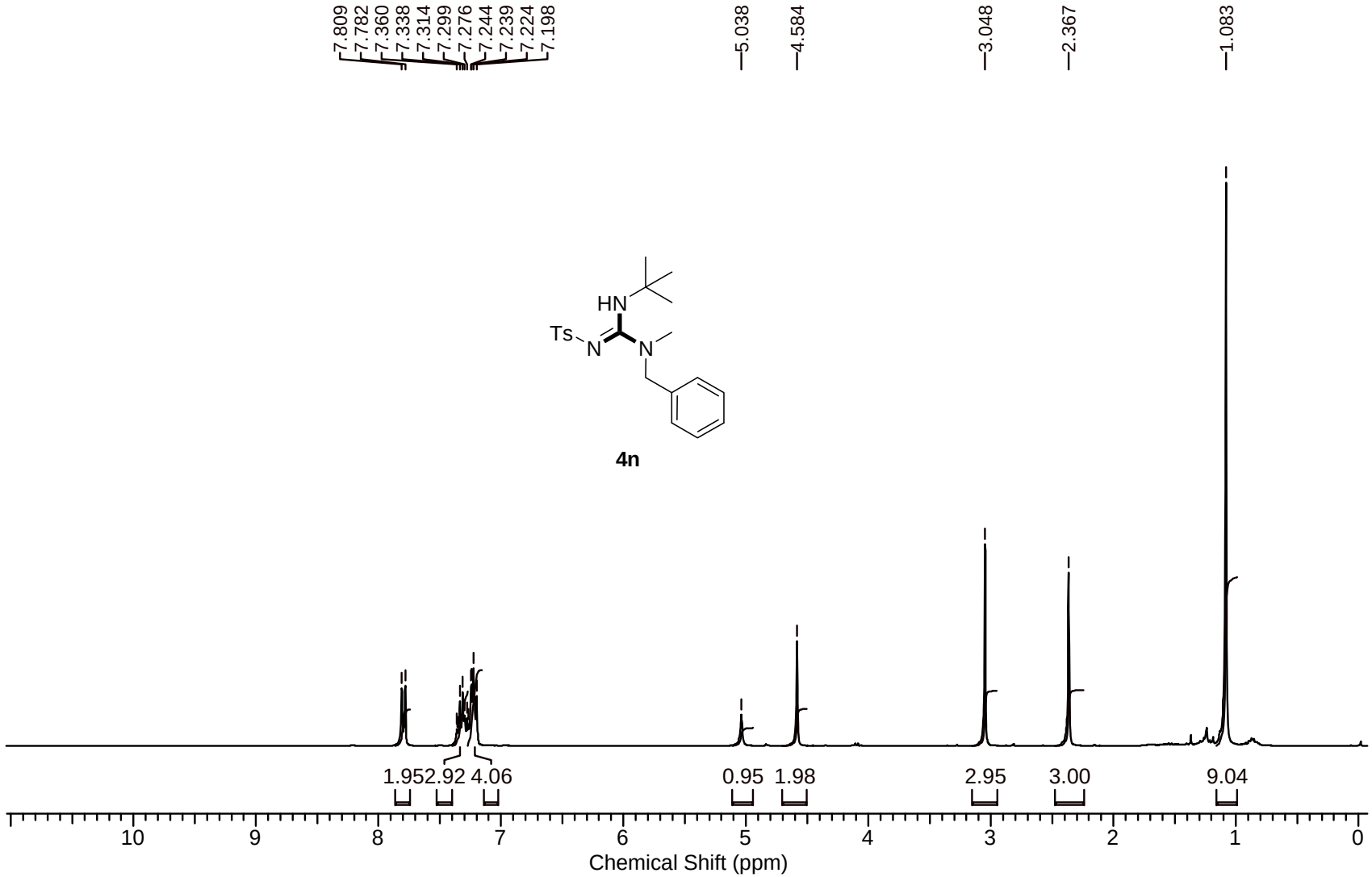
77.421
76.998
76.575
66.741
54.253
46.131
33.578
29.823
21.417
HN
Ts
N
N
OH
4m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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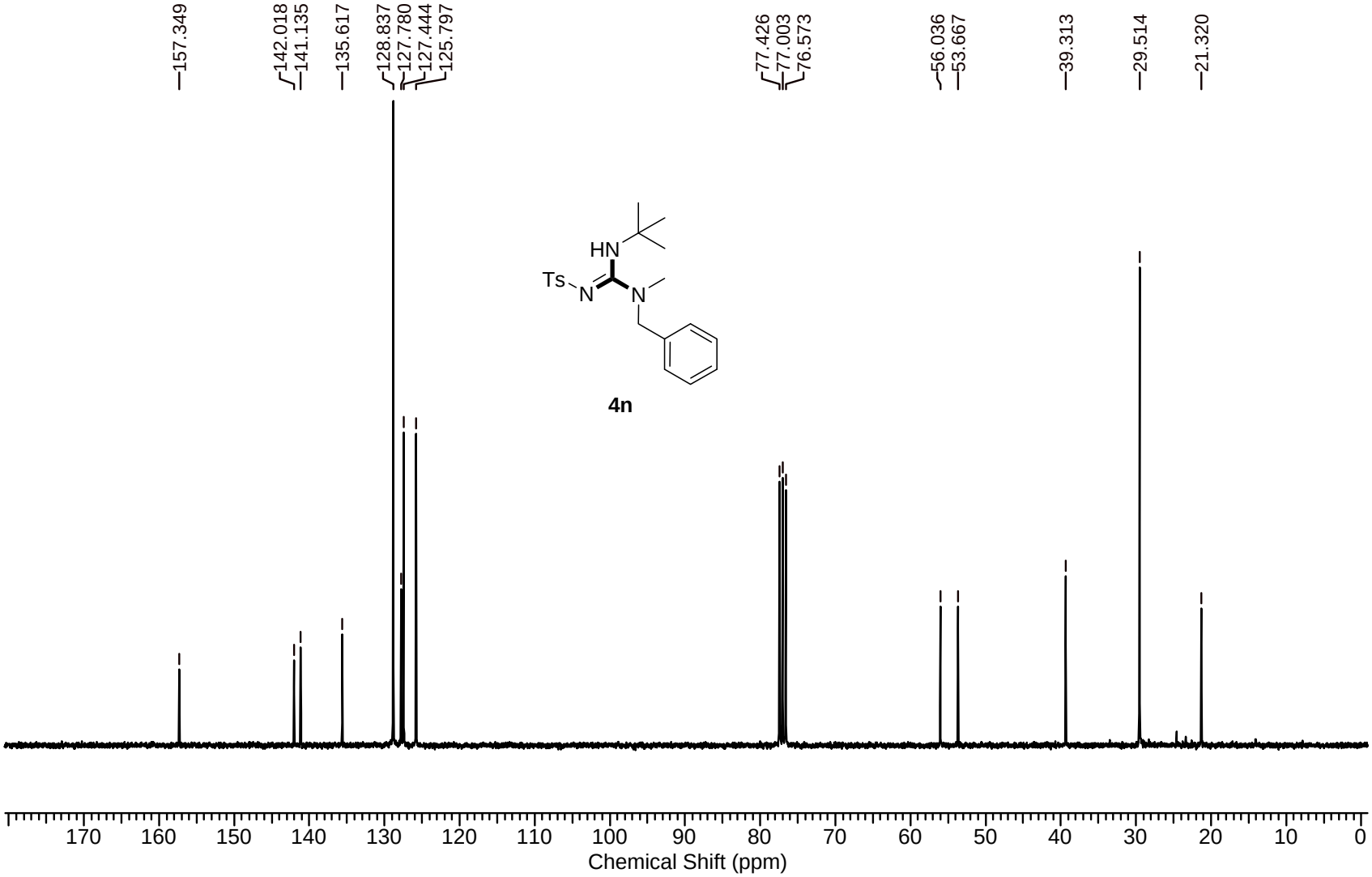
7.782
7.360
7.338
7.314
7.299
7.276
7.244
7.239
7.224
7.198
5.038
4.584
3.048
2.367
1.083
HN
Ts
N
N
1.95
2.92
4.06
0.95
1.98
2.95
3.00
9.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

4n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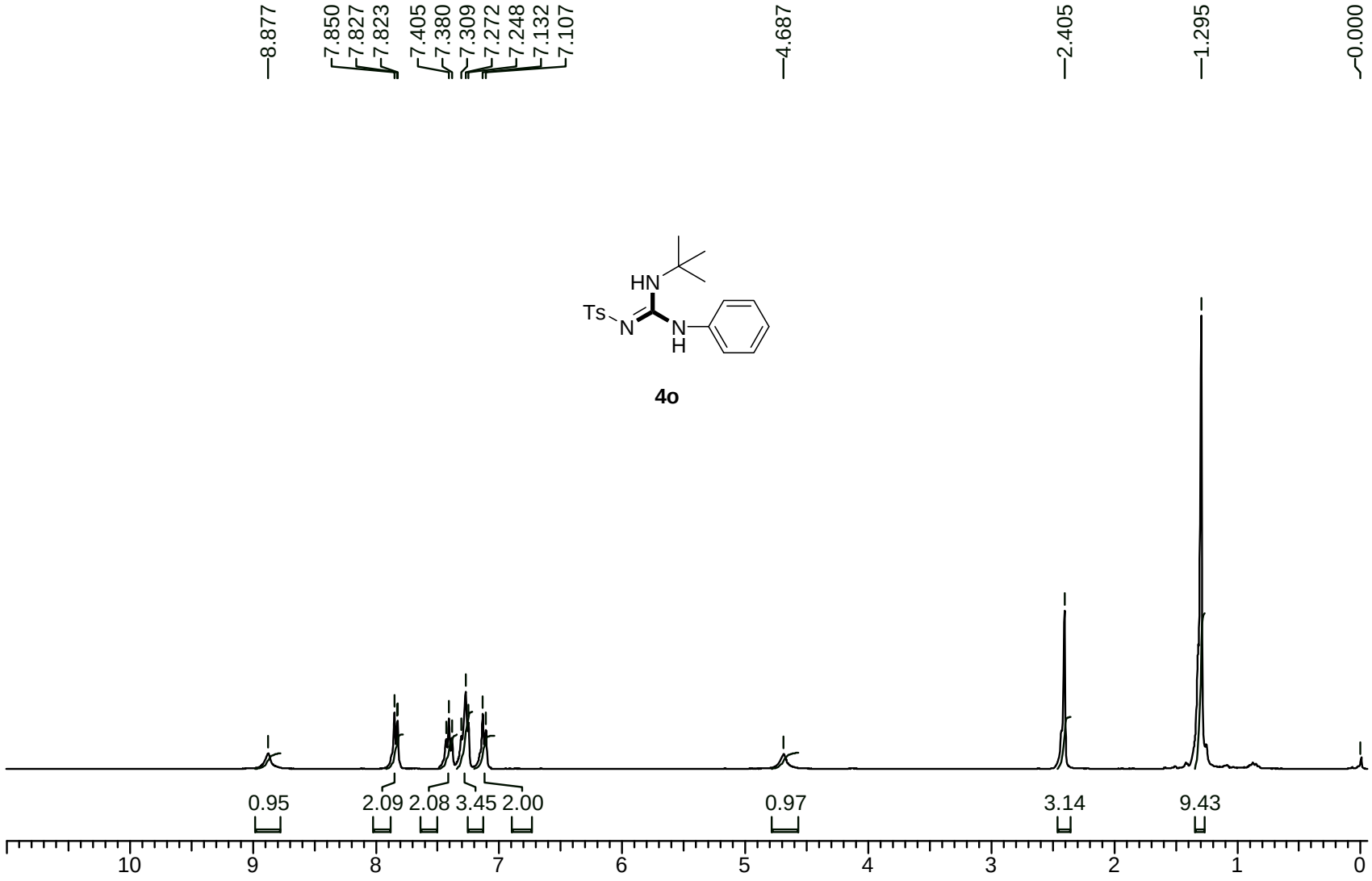
141.135
135.617
128.837
127.780
127.444
125.797
77.426
77.003
76.573
56.036
53.667
39.313
29.514
21.320
HN
Ts
N
N
4n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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7.309
7.272
7.248
7.132
7.107
4.687
2.405
1.295
0.000
HN
Ts
N
N
H
0.95
2.09
2.08
3.45
2.00
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3.14
9.43
10
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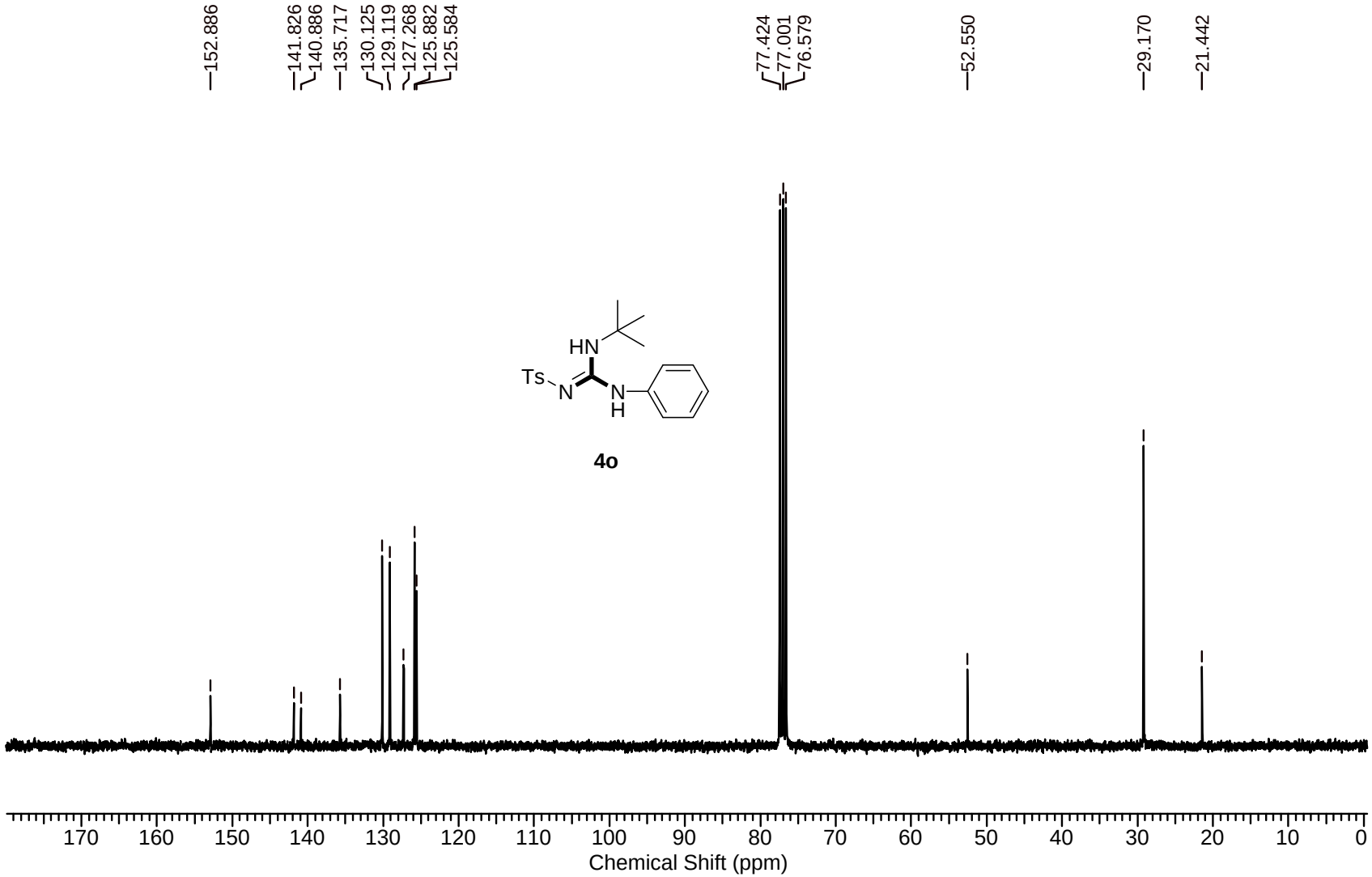
8
7
6
5
4
3
2
1
0

4o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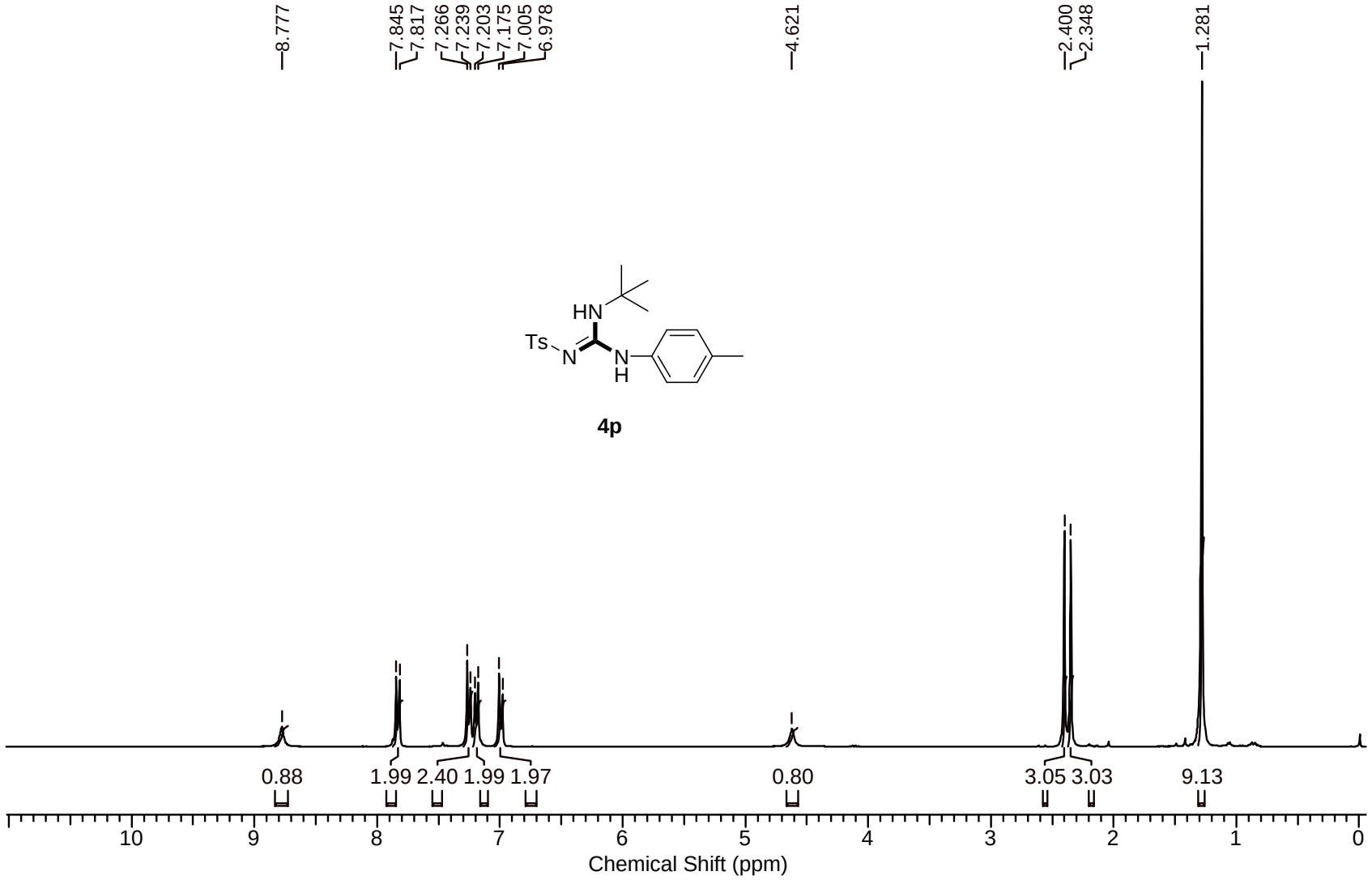
129.119
127.268
125.882
125.584
77.424
77.001
76.579
52.550
29.170
21.442
HN
Ts
N
N
H
4o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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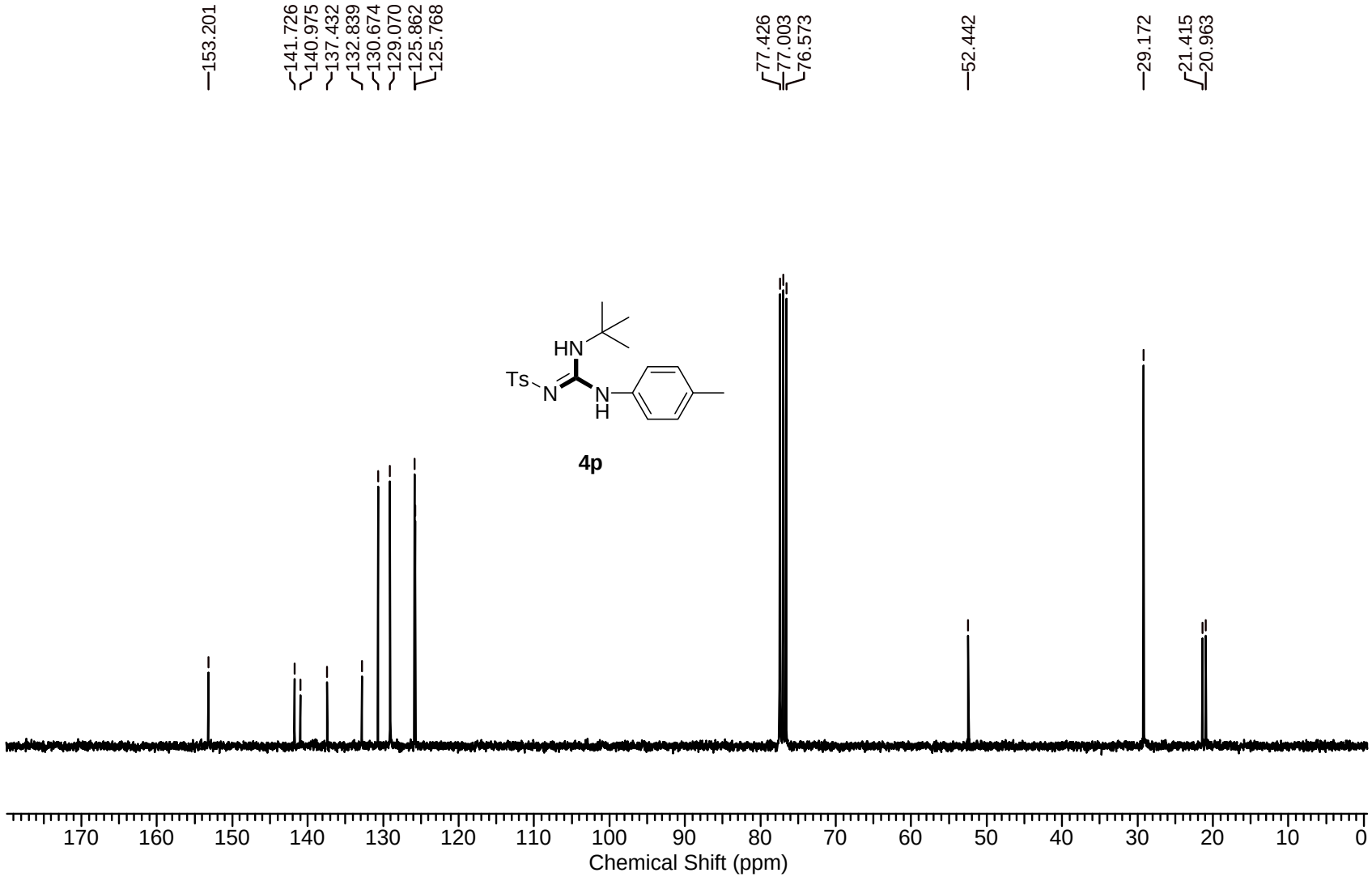
7.817
7.266
7.239
7.203
7.175
7.005
6.978
4.621
2.400
2.348
1.281
HN
Ts
N
N
H
0.88
1.99
2.40
1.99
1.97
0.80
3.05
3.03
9.13
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

4p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130.674
129.070
125.862
125.768
77.426
77.003
76.573
52.442
29.172
21.415
20.963
HN
Ts
N
N
H
4p
170
160
150
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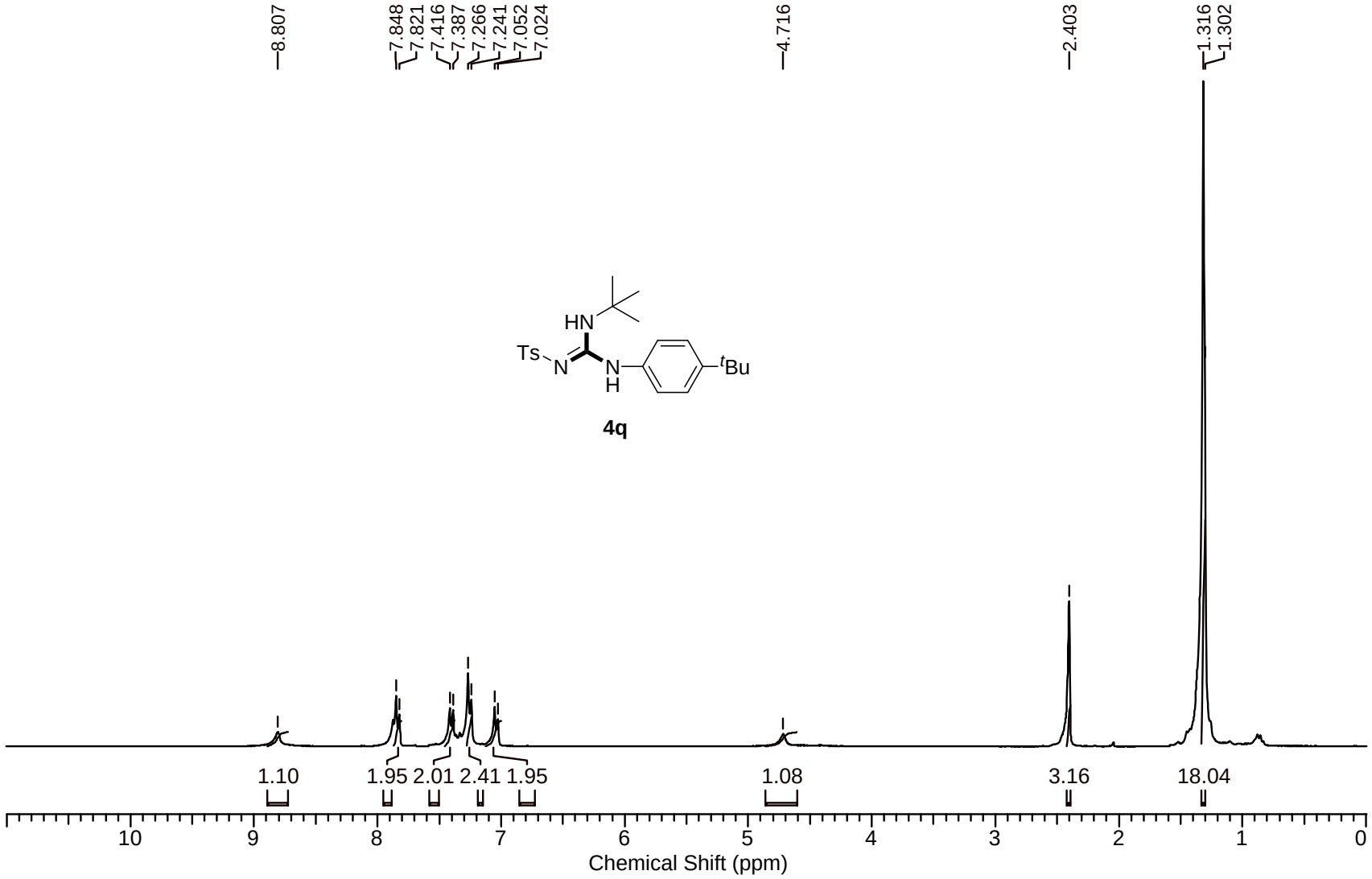
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.807
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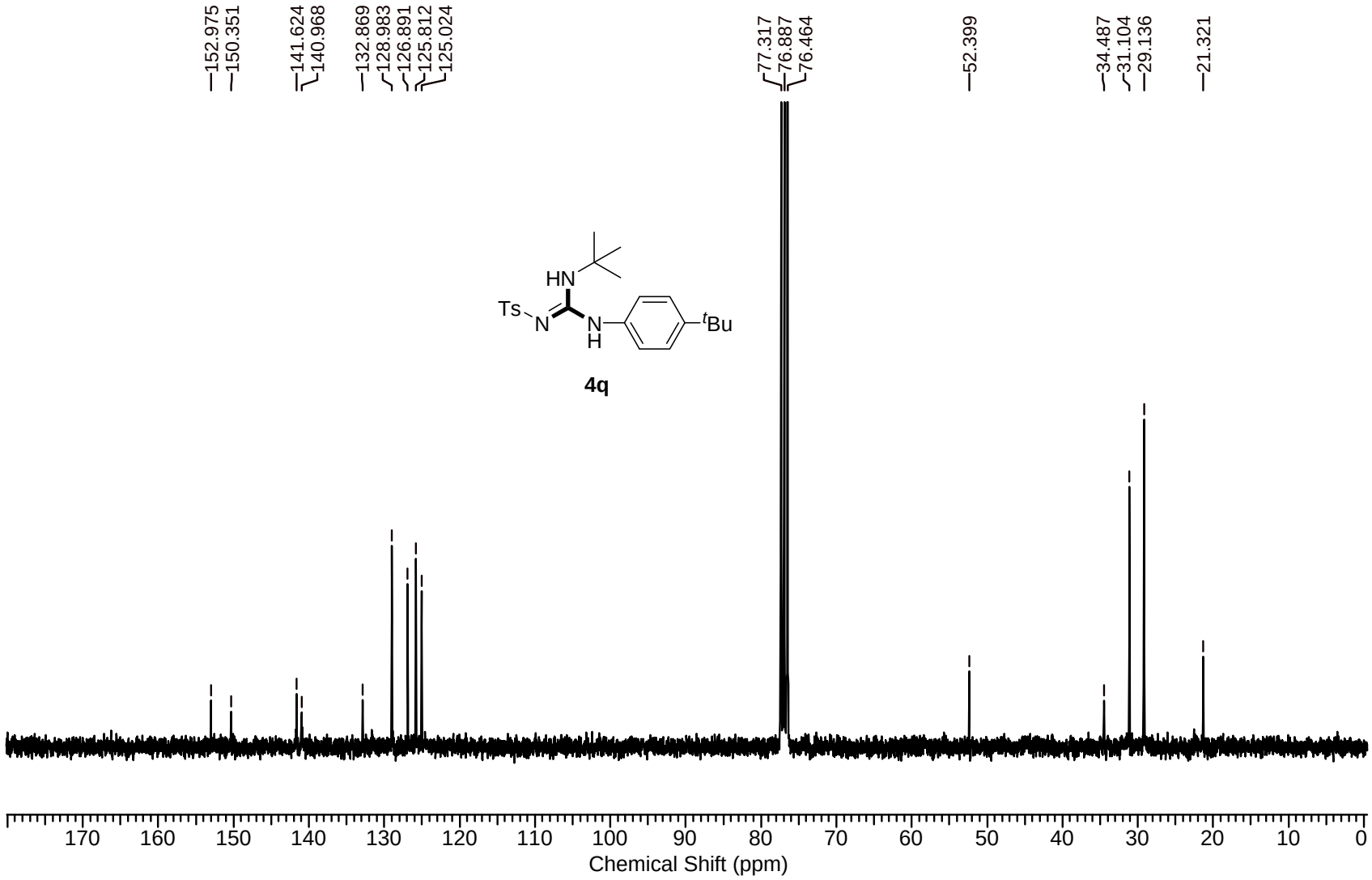
7.416
7.387
7.266
7.241
7.052
7.024
4.716
2.403
1.316
1.302
HN
Ts
N
N
H
tBu
4q
1.10
1.95
2.01
2.41
1.95
1.08
3.16
18.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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132.869
128.983
126.891
125.812
125.024
77.317
76.887
76.464
52.399
34.487
31.104
29.136
21.321
HN
Ts
N
N
H
tBu
4q
170
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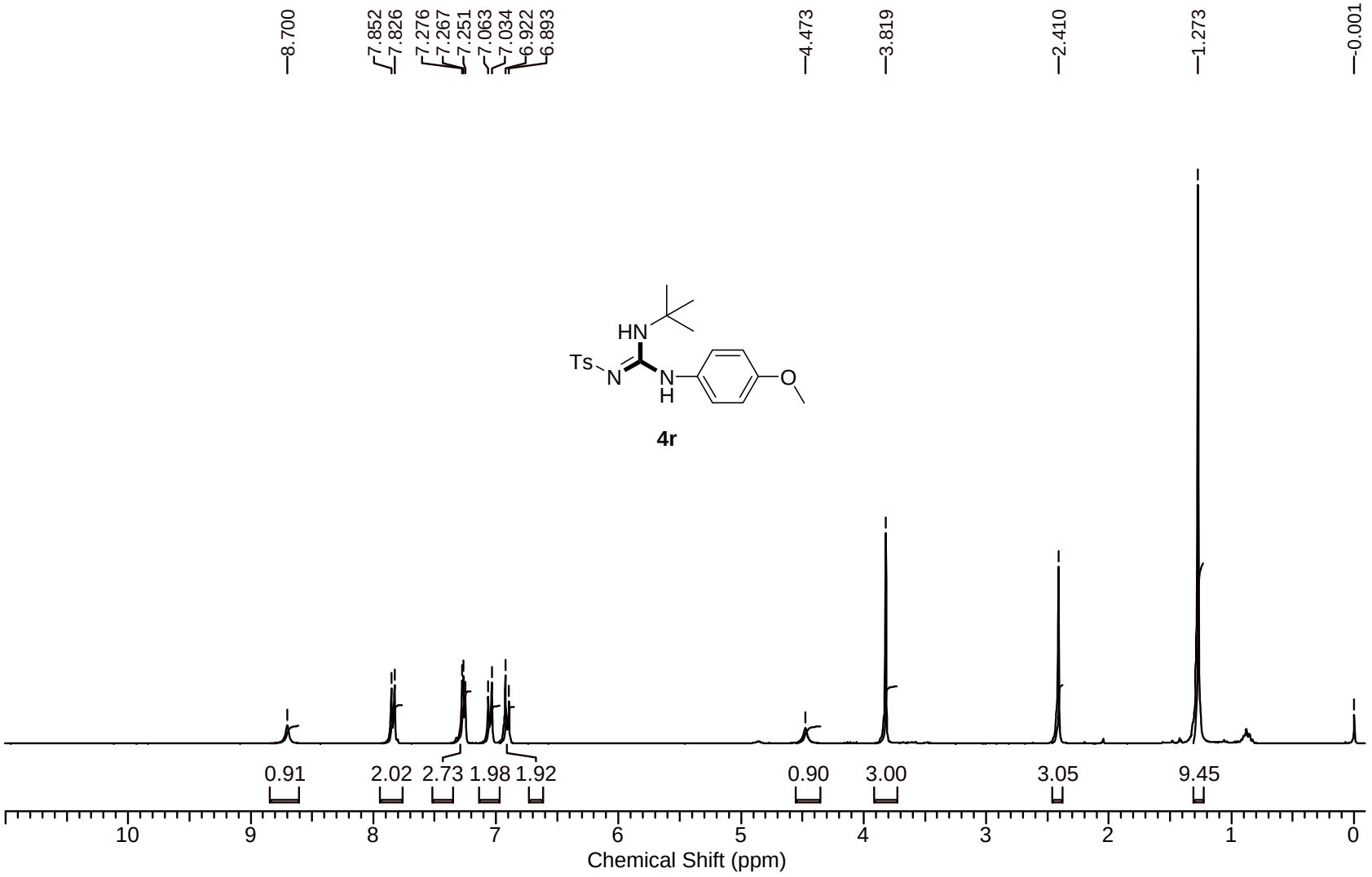
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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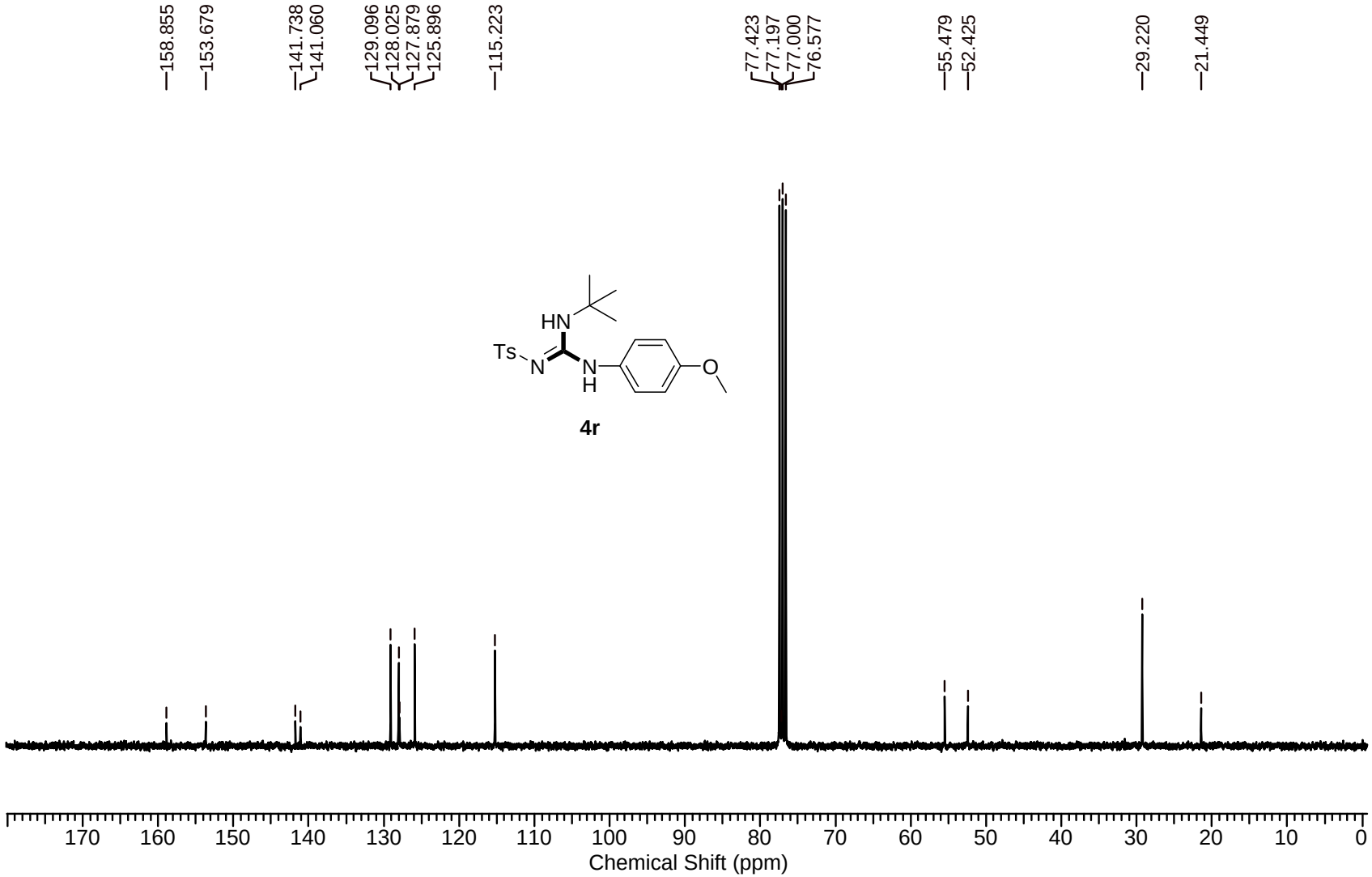
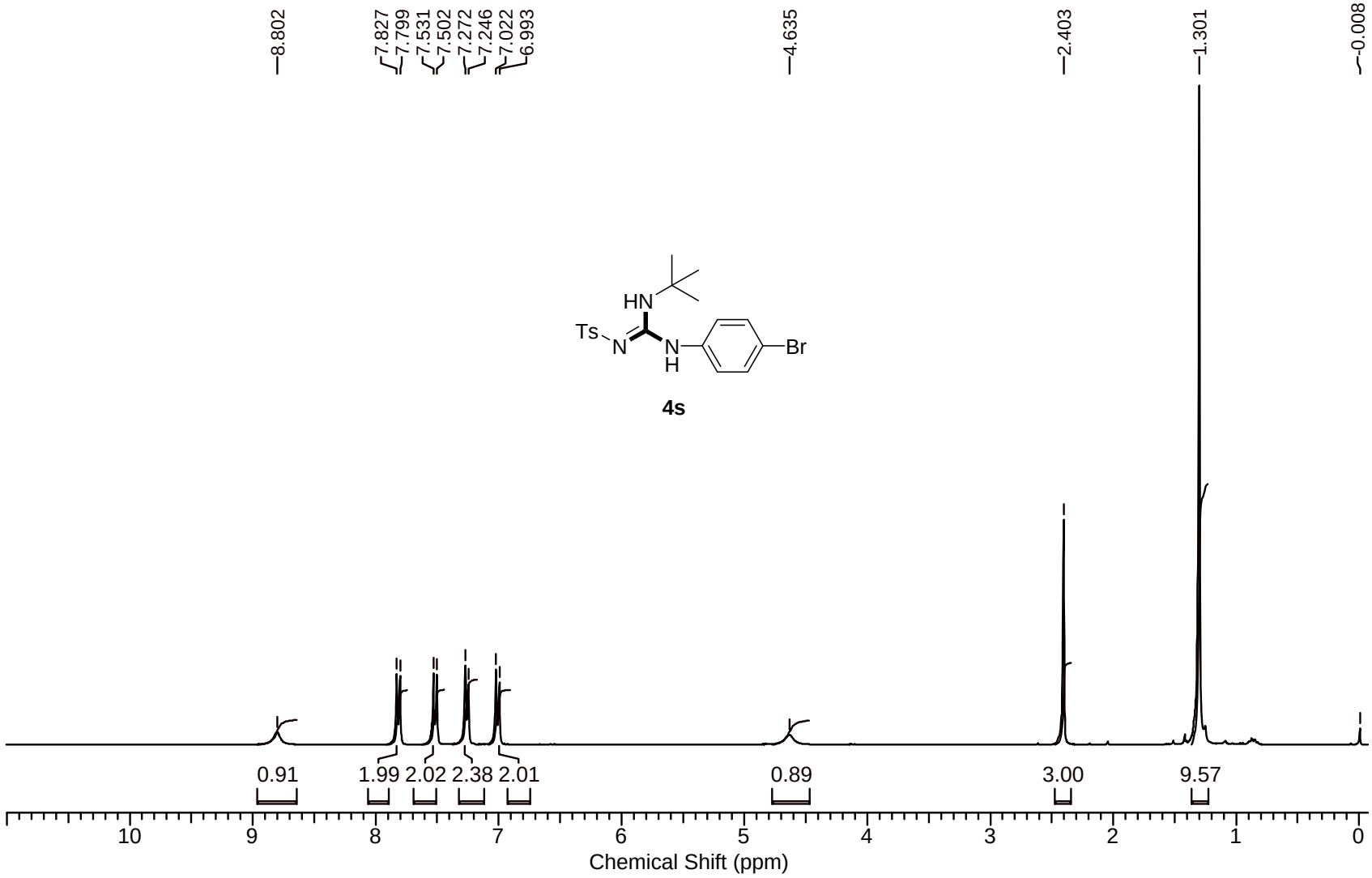
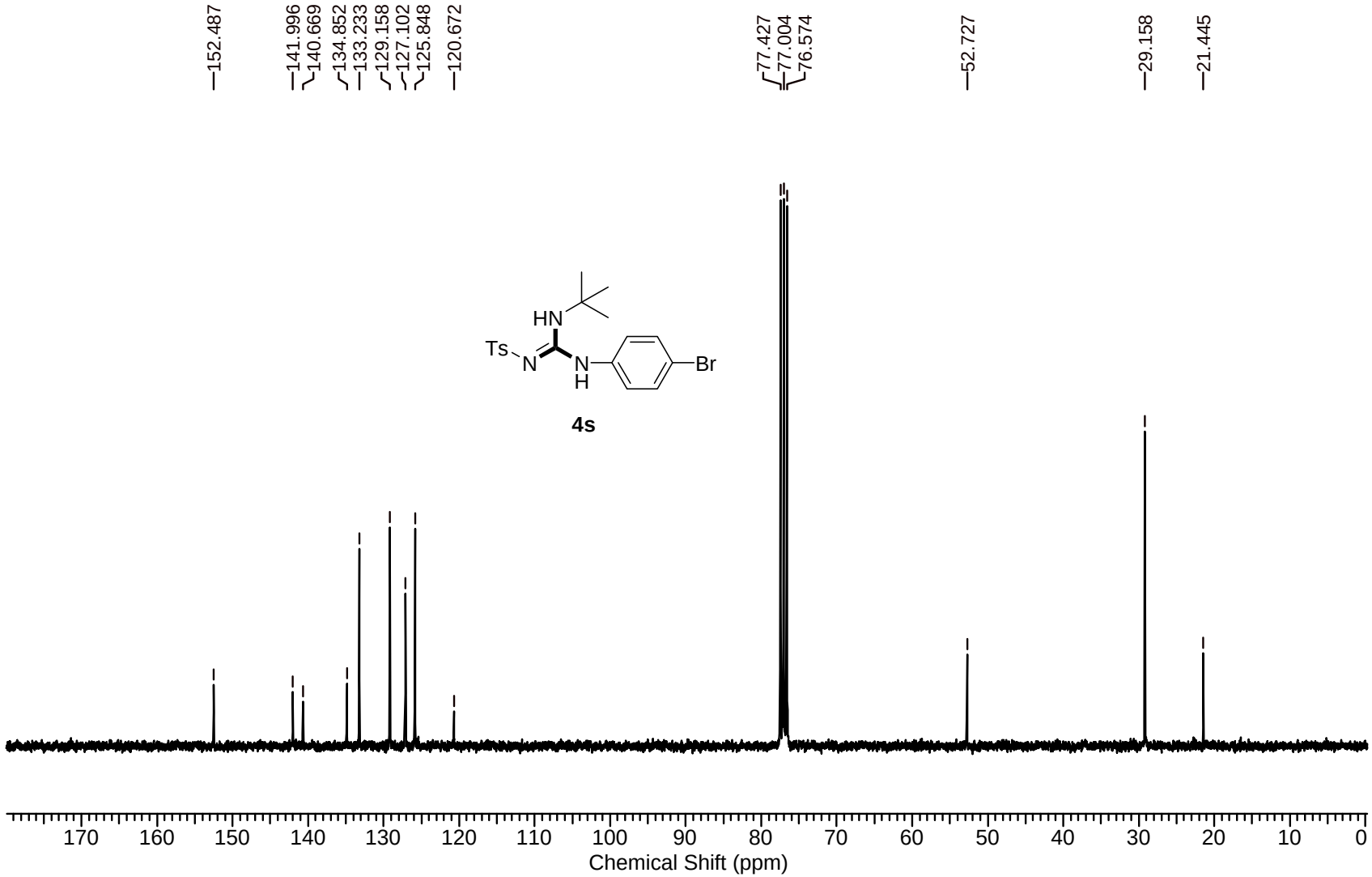
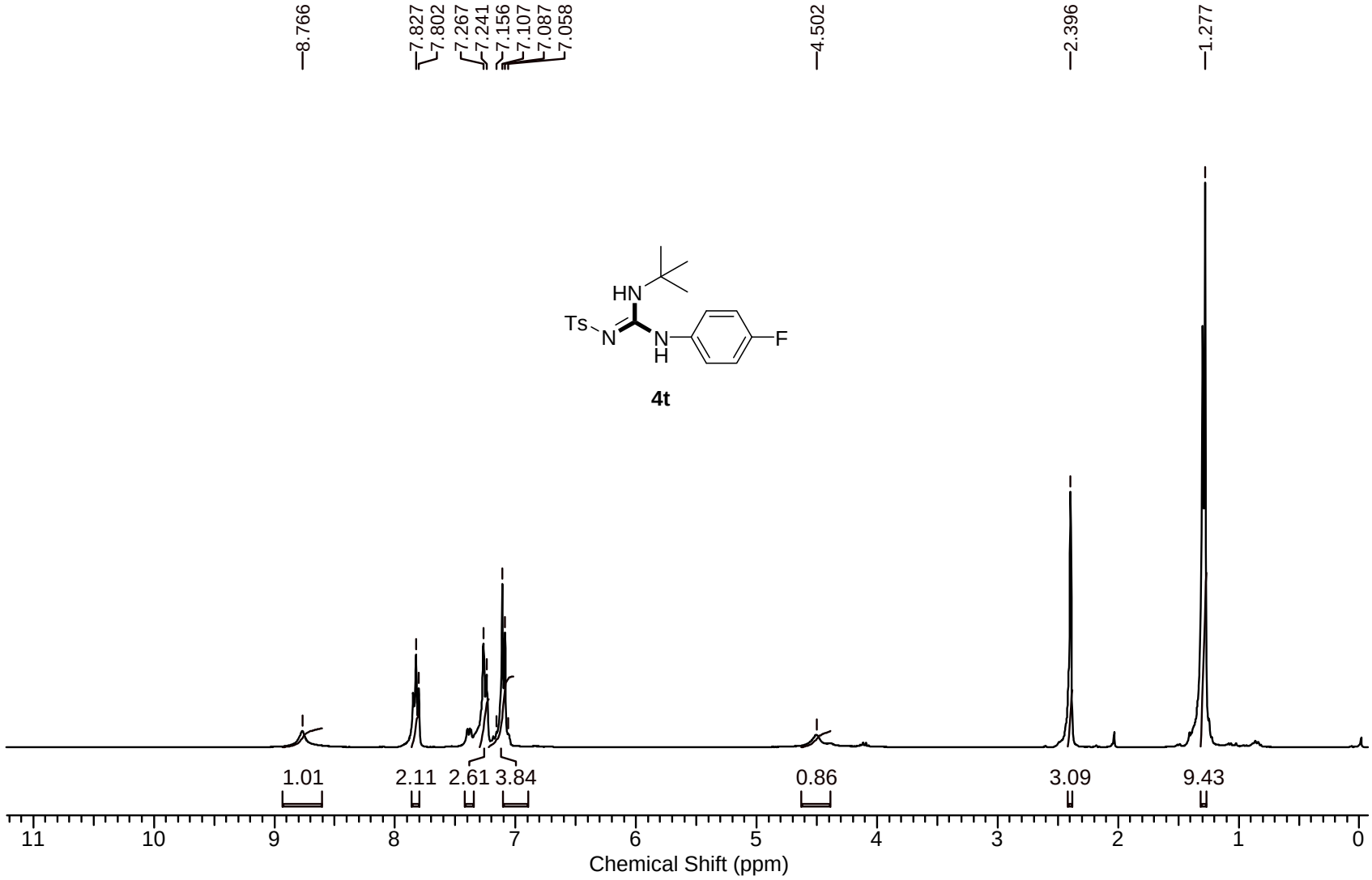
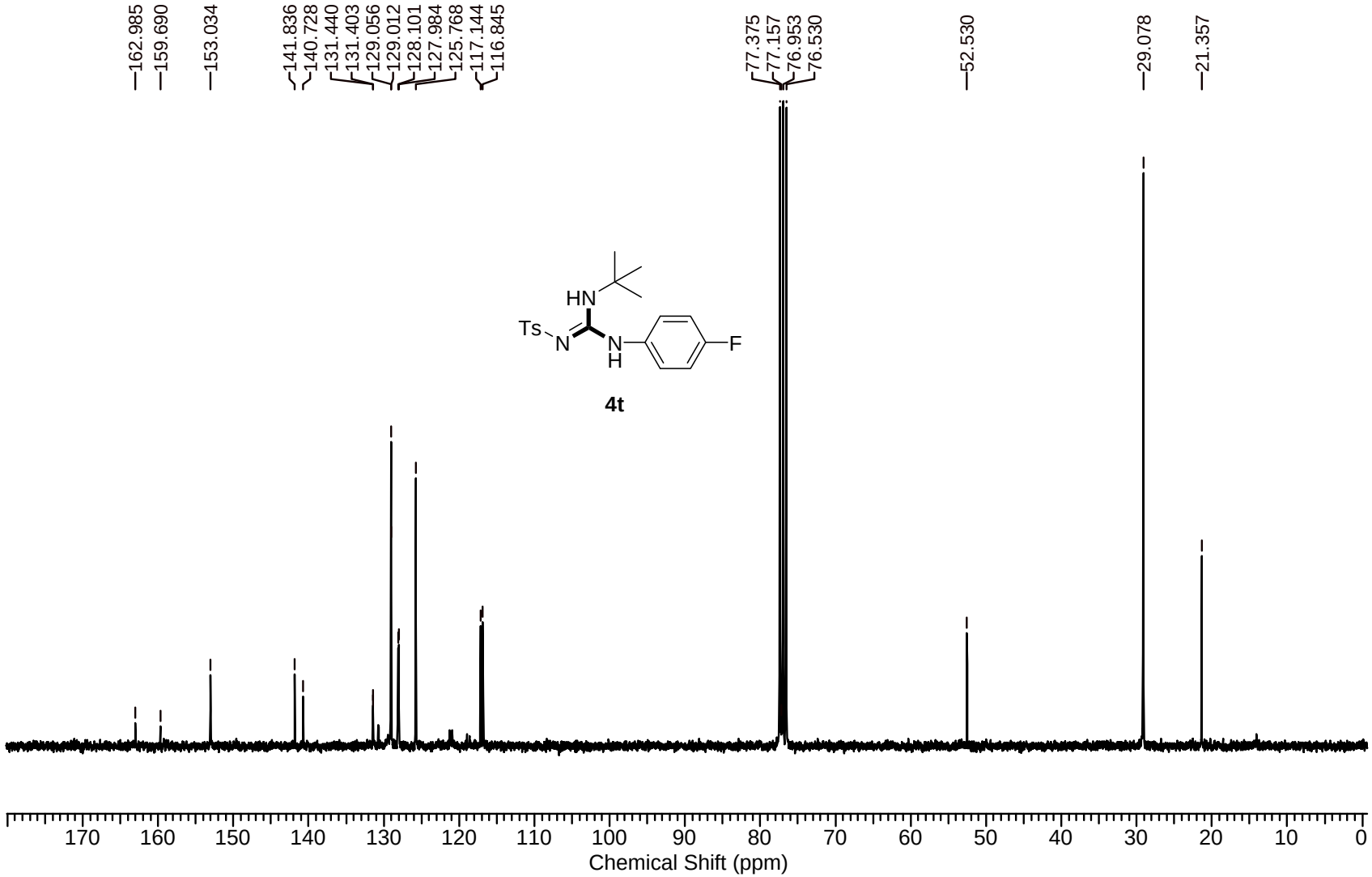
7.276
7.267
7.251
7.063
7.034
6.922
6.893
4.473
3.819
2.410
1.273
-0.001
HN
Ts
N
N
H
O
4r
0.91
2.02
2.73
1.98
1.92
0.90
3.00
3.05
9.45
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


158.855
153.679
141.738
141.060
129.096
128.025
127.879
125.896
115.223
77.423
77.197
77.000
76.577
55.479
52.425
29.220
21.449
HN
Ts
N
N
H
O
4r
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.802
7.827
7.799
7.531
7.502
7.272
7.246
7.022
6.993
4.635
2.403
1.301
-0.008
HN
Ts
N
N
H
Br
4s
0.91
1.99
2.02
2.38
2.01
0.89
3.00
9.57
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


152.487
141.996
140.669
134.852
133.233
129.158
127.102
125.848
120.672
77.427
77.004
76.574
52.727
29.158
21.445
HN
Ts
N
N
H
Br
4s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.766
7.827
7.802
7.267
7.241
7.156
7.107
7.087
7.058
4.502
2.396
1.277
HN
Ts
N
N
H
F
4t
1.01
2.11
2.61
3.84
0.86
3.09
9.43
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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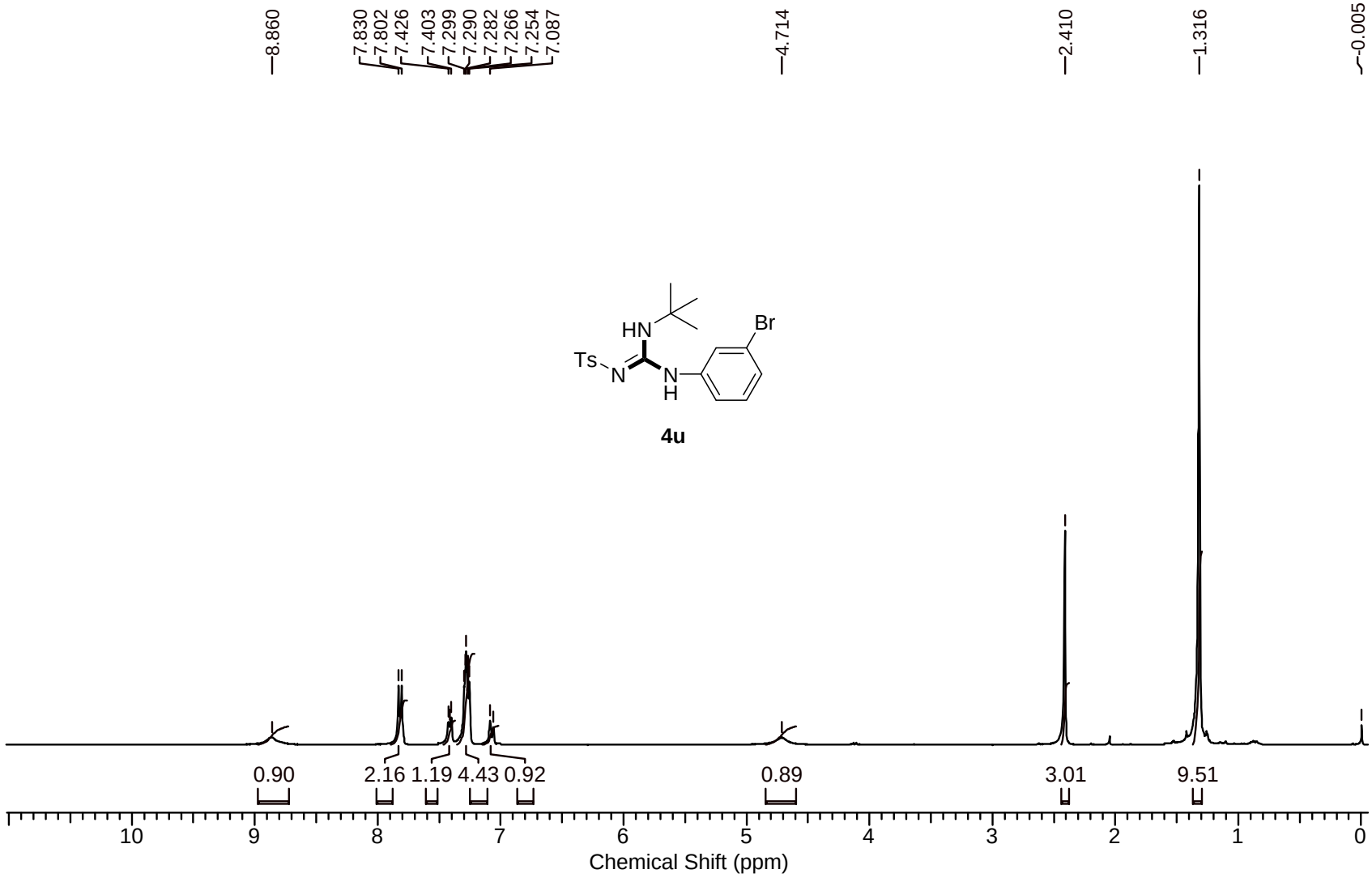
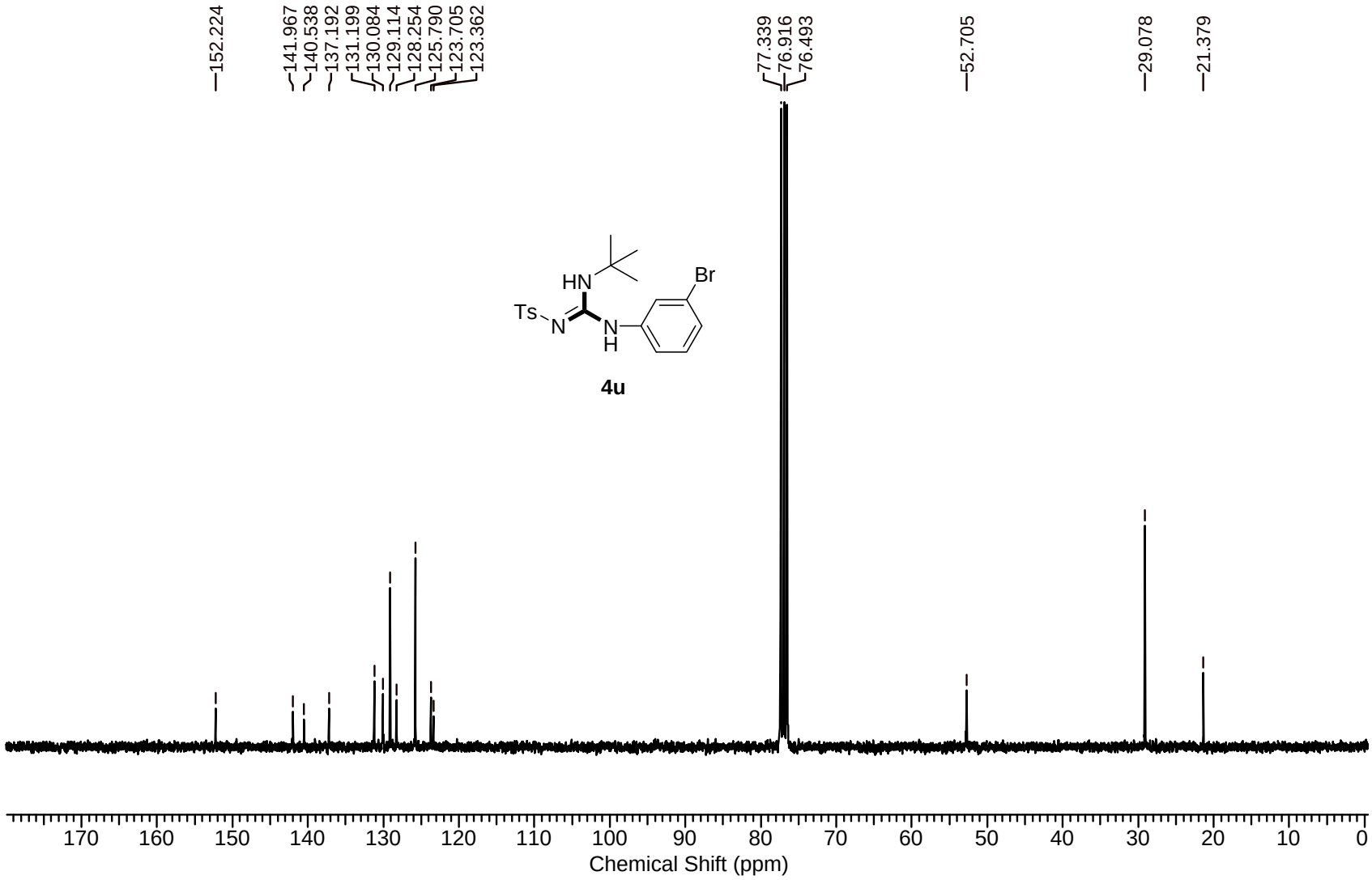
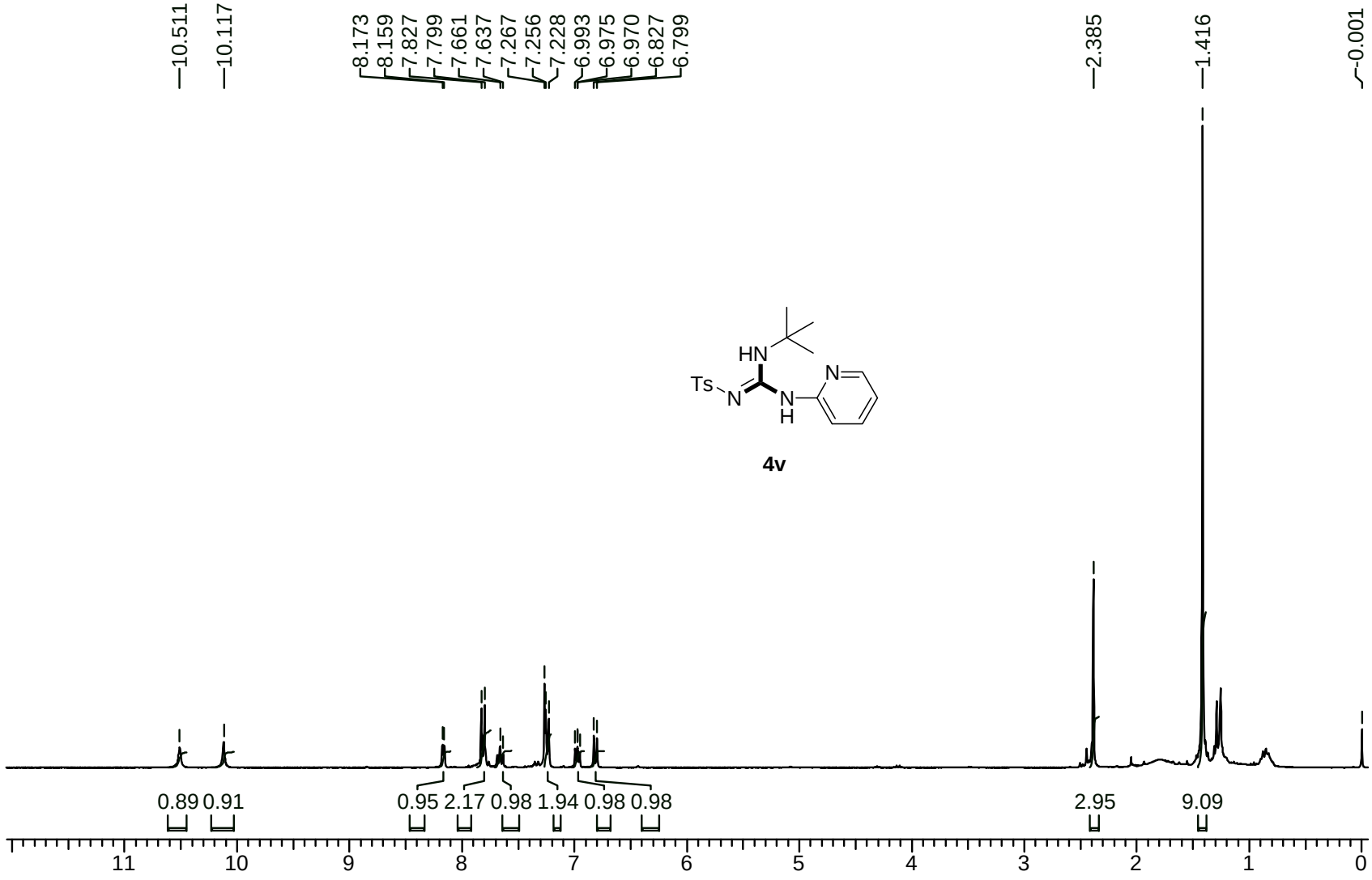
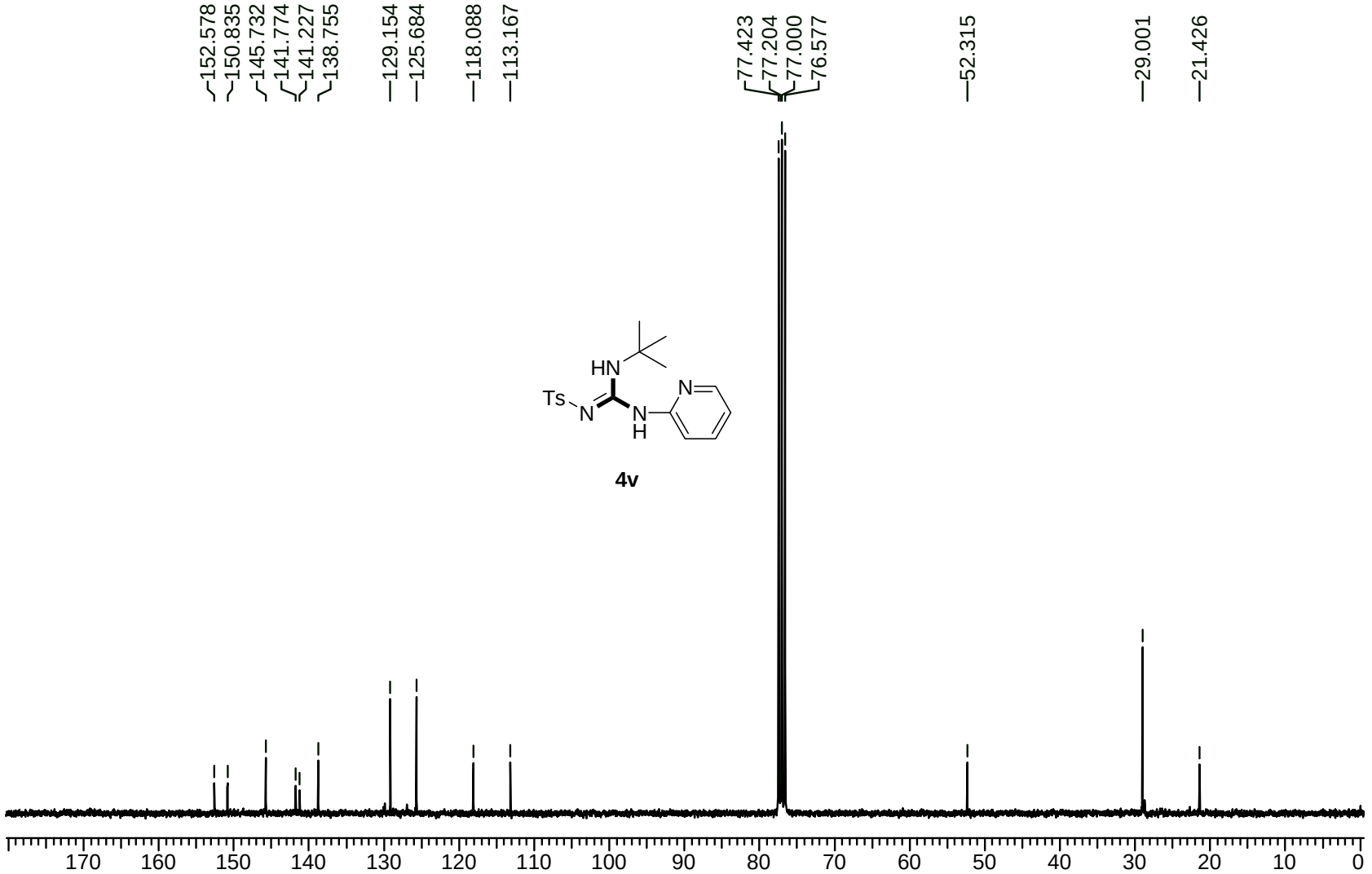
159.690
153.034
141.836
140.728
131.440
131.403
129.056
129.012
128.101
127.984
125.768
117.144
116.845
77.375
77.157
76.953
76.530
52.530
29.078
21.357
HN
Ts
N
N
H
F
4t
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.860
7.830
7.802
7.426
7.403
7.299
7.290
7.282
7.266
7.254
7.087
4.714
2.410
1.316
-0.005
HN
Br
Ts
N
N
H
4u
0.90
2.16
1.19
4.43
0.92
0.89
3.01
9.51
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

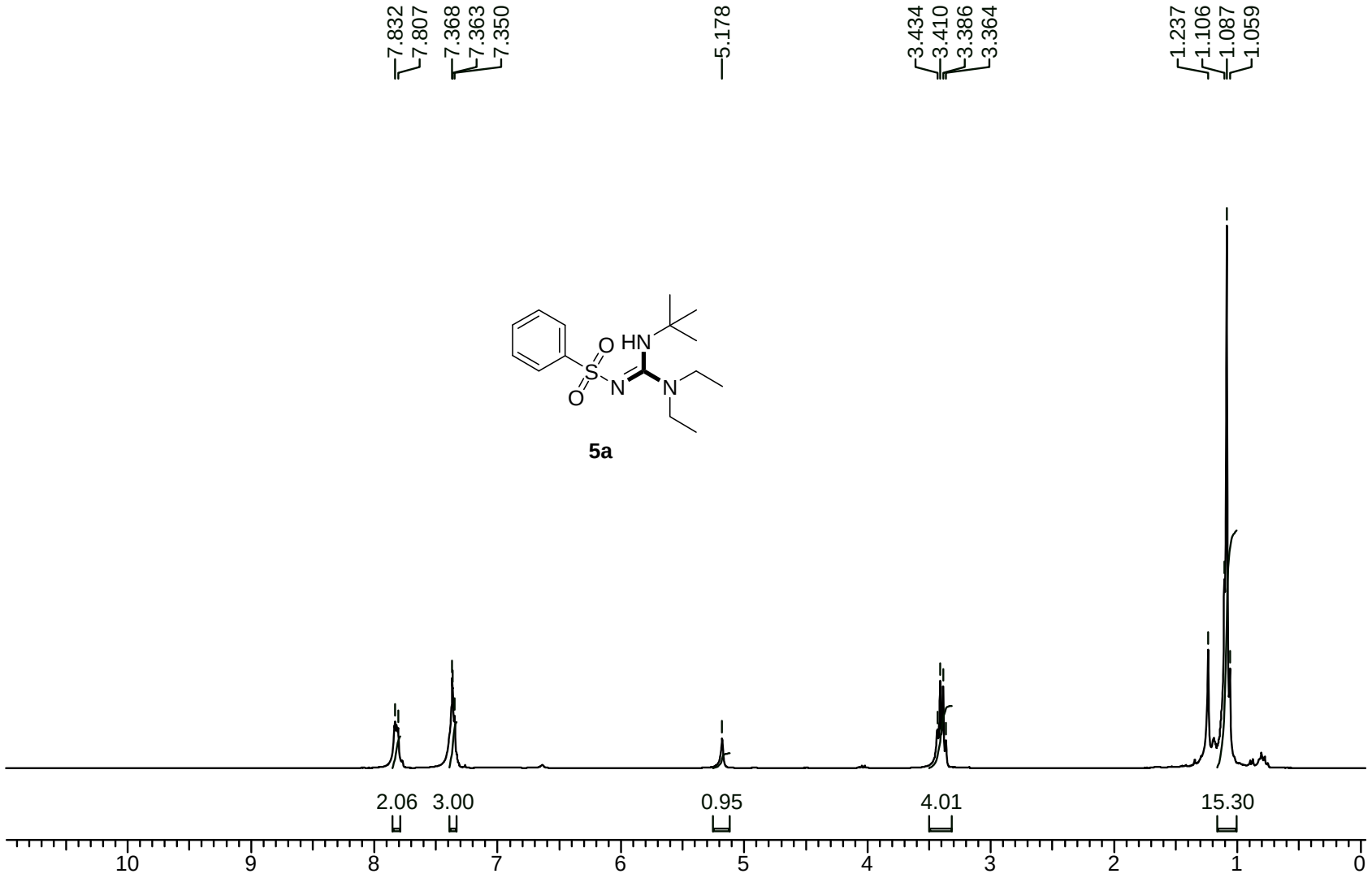

152.224
141.967
140.538
137.192
131.199
130.084
129.114
128.254
125.790
123.705
123.362
77.339
76.916
76.493
52.705
29.078
21.379
HN
Br
Ts
N
N
H
4u
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


10.511
10.117
8.173
8.159
7.827
7.799
7.661
7.637
7.267
7.256
7.228
6.993
6.975
6.970
6.827
6.799
2.385
1.416
-0.001
HN
Ts
N
N
H
N
0.89 0.91
0.95 2.17 0.98 1.94 0.98 0.98
2.95
9.09
11 10 9 8 7 6 5 4 3 2 1 0

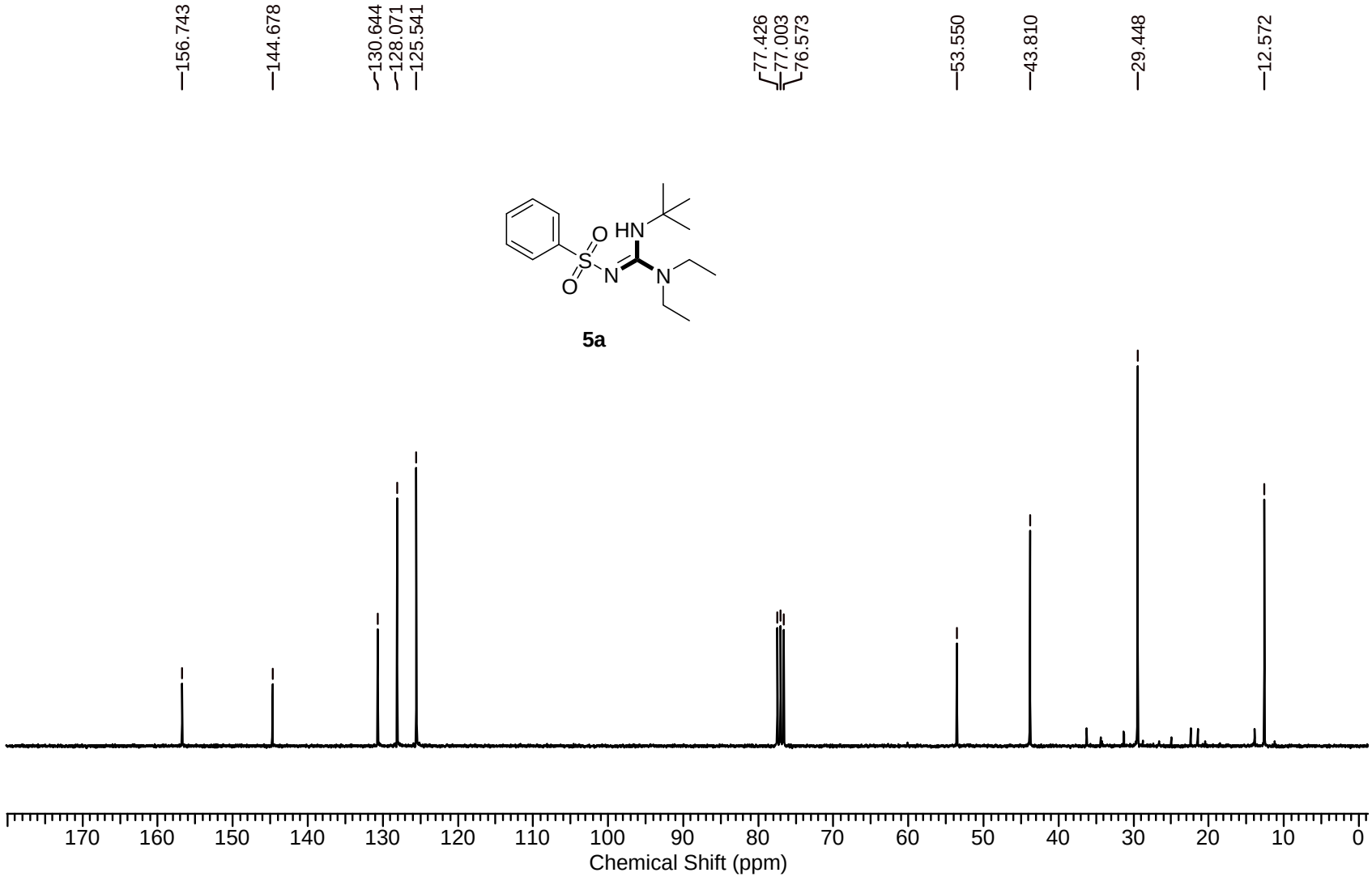
4v


152.578
150.835
145.732
141.774
141.227
138.755
129.154
125.684
118.088
113.167
77.423
77.204
77.000
76.577
52.315
29.001
21.426
HN
Ts
N
N
H
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

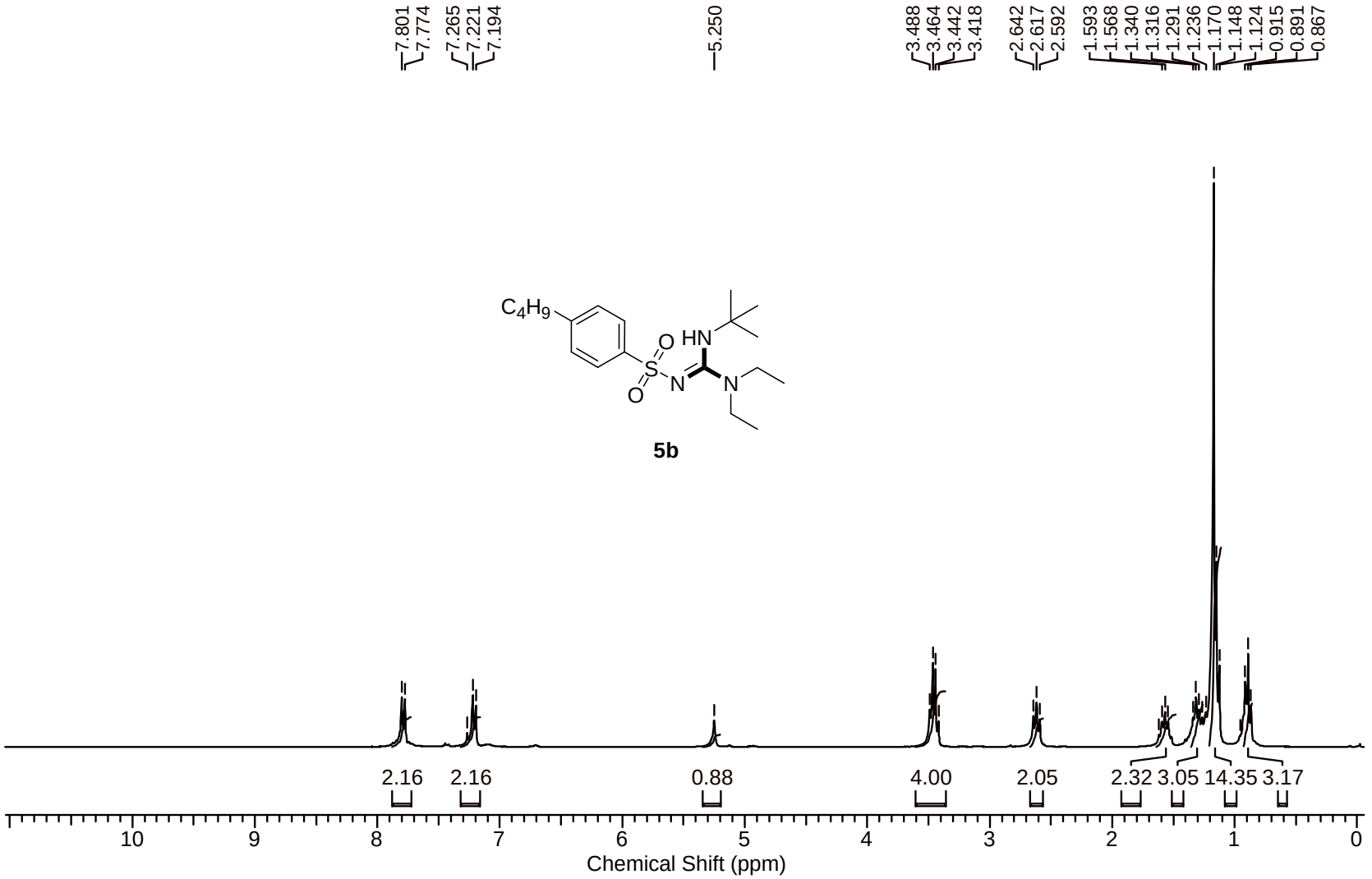
4v

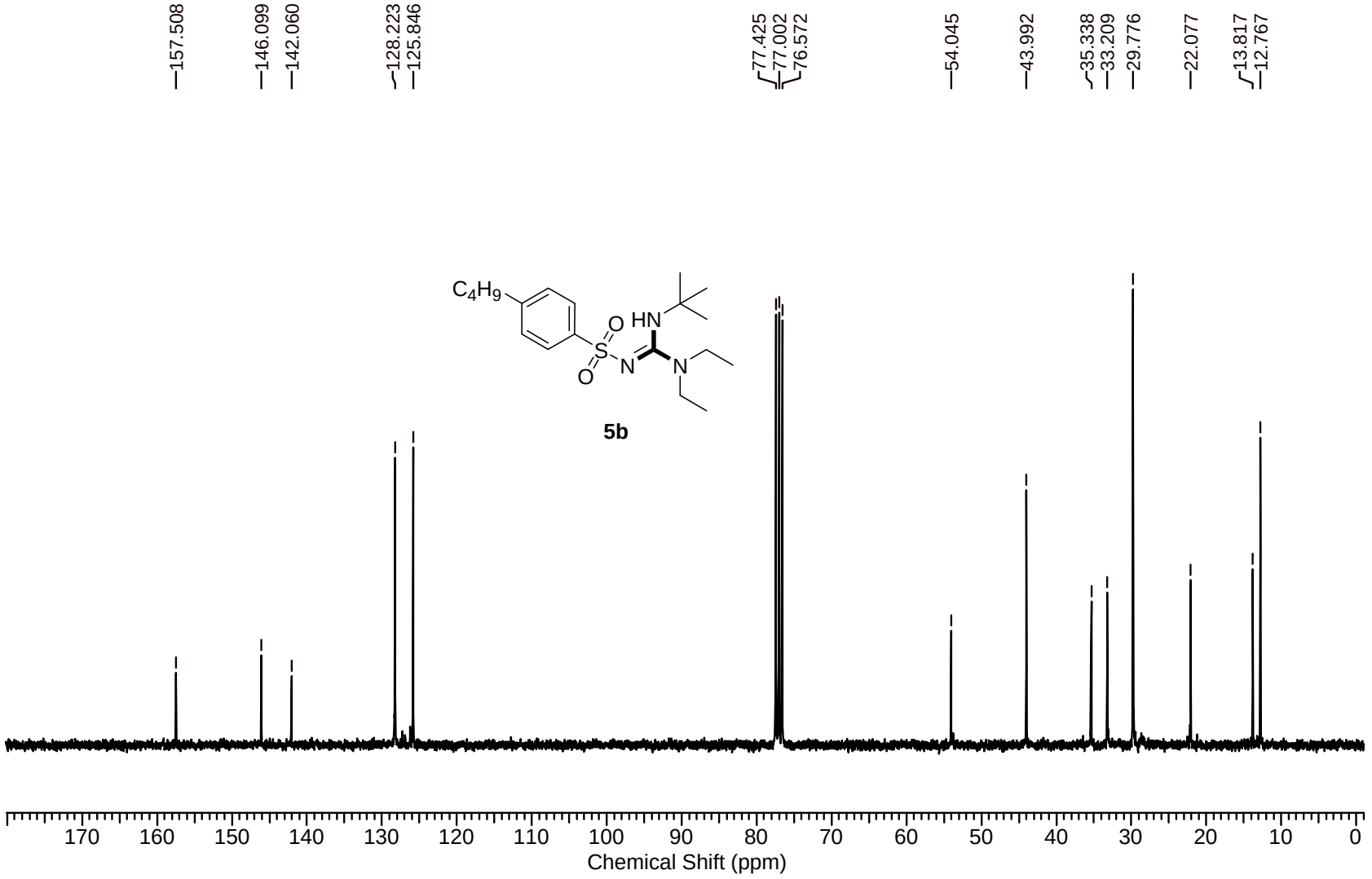

7.832
7.807
7.368
7.363
7.350
5.178
3.434
3.410
3.386
3.364
1.237
1.106
1.087
1.059
O
HN
S
O
N
N
2.06
3.00
0.95
4.01
15.30
10
9
8
7
6
5
4
3
2
1
0

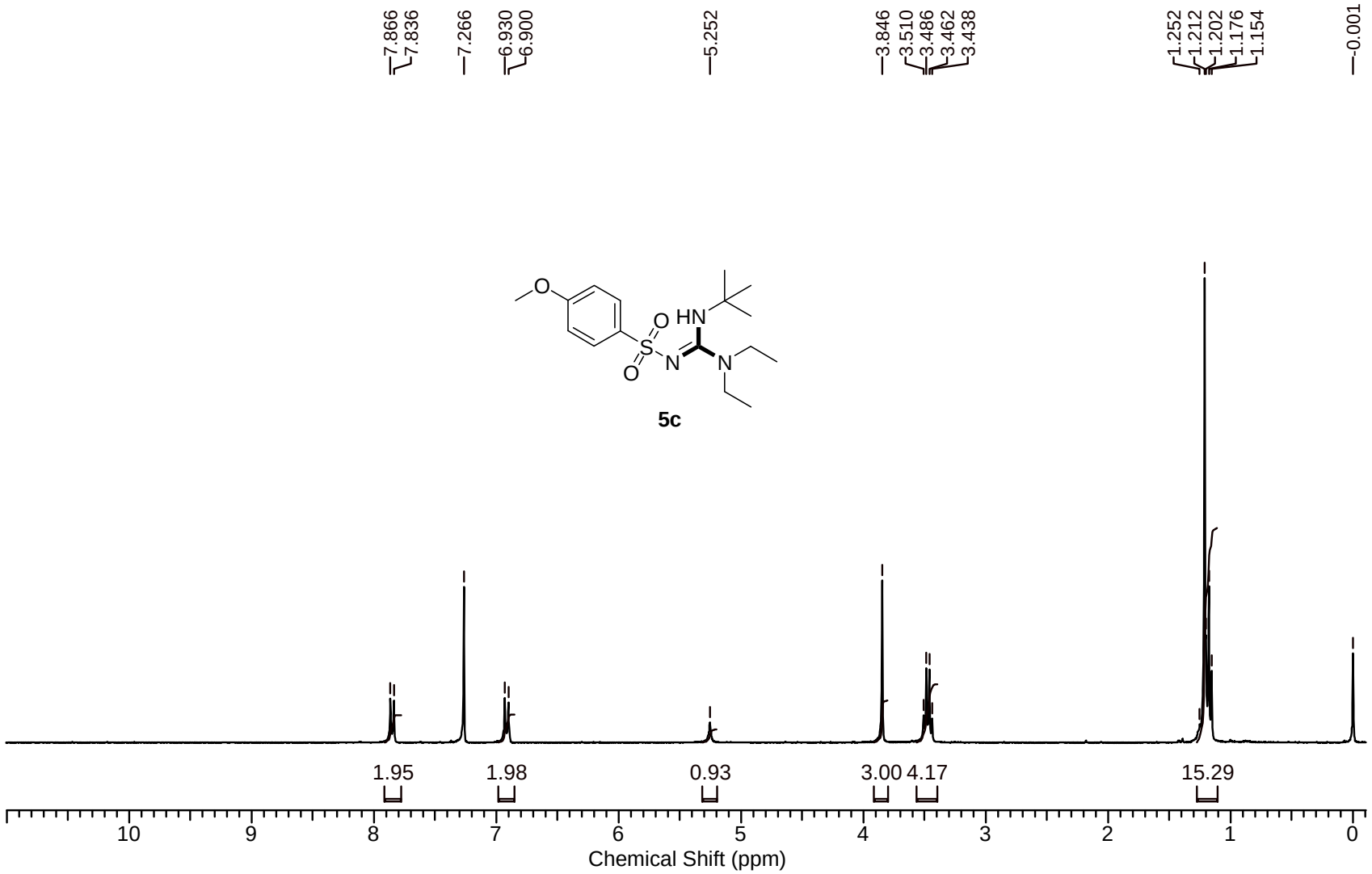
5a


156.743
144.678
130.644
128.071
125.541
77.426
77.003
76.573
53.550
43.810
29.448
12.572
O
HN
S
N
N
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

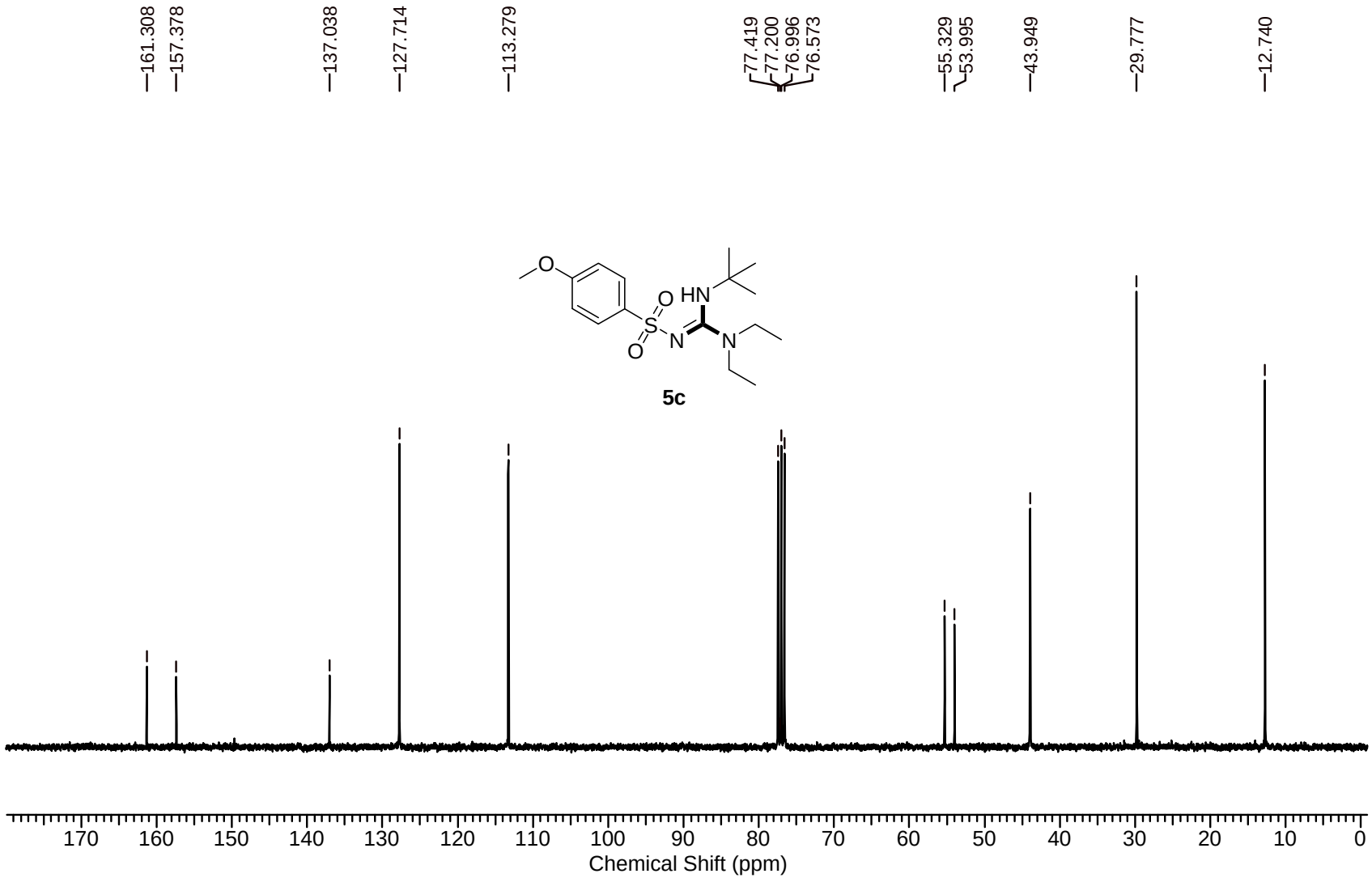
5a

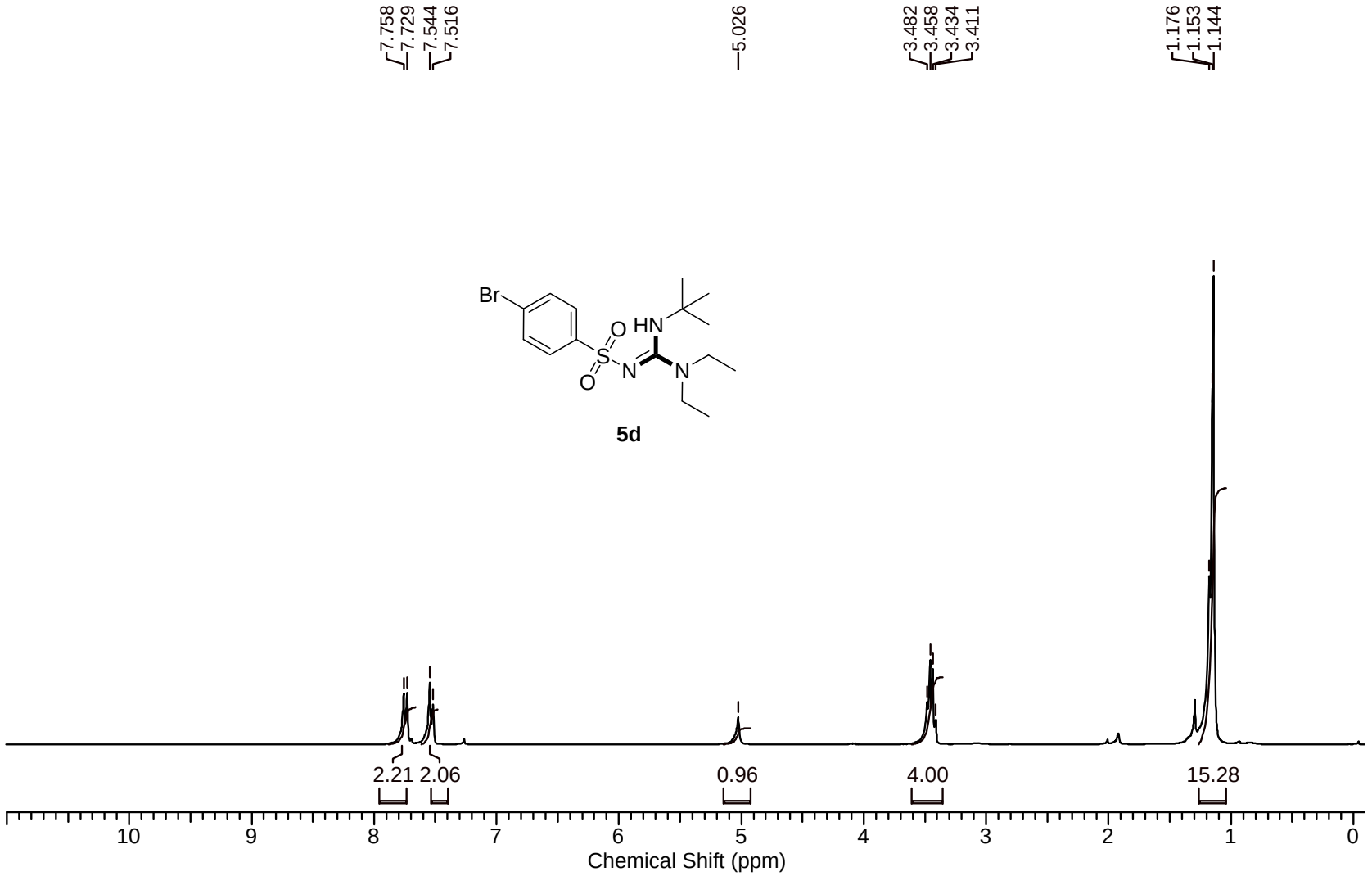

7.801
7.774
7.265
7.221
7.194
5.250
3.488
3.464
3.442
3.418
2.642
2.617
2.592
1.593
1.568
1.340
1.316
1.291
1.236
1.170
1.148
1.124
0.915
0.891
0.867
C4H9
O
HN
S
N
N
O
5b
2.16
2.16
0.88
4.00
2.05
2.32
3.05
14.35
3.17
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


157.508
146.099
142.060
128.223
125.846
77.425
77.002
76.572
54.045
43.992
35.338
33.209
29.776
22.077
13.817
12.767
C4H9
O
HN
S
O
N
N
5b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

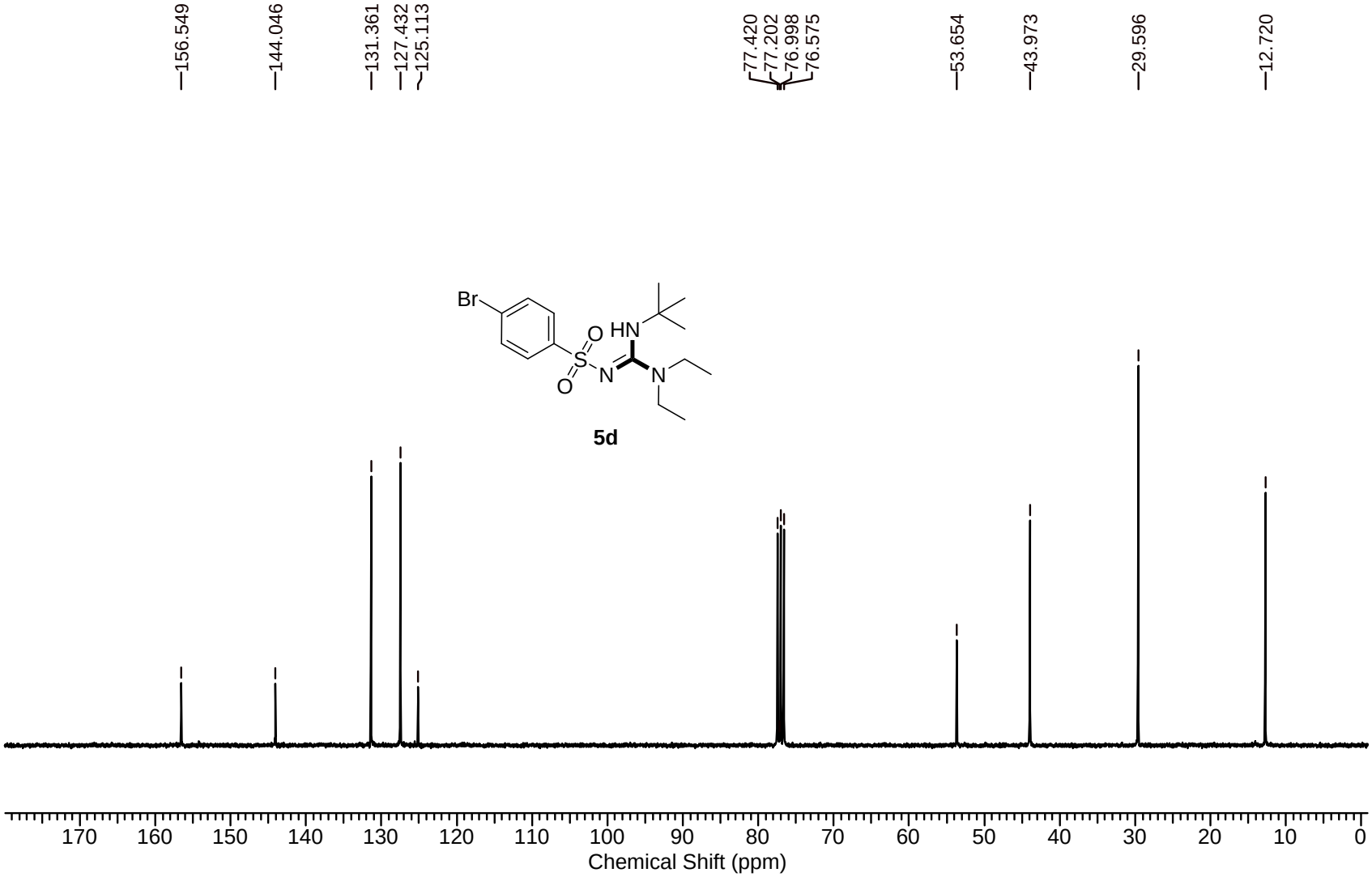

7.866
7.836
7.266
6.930
6.900
5.252
3.846
3.510
3.486
3.462
3.438
1.252
1.212
1.202
1.176
1.154
0.001
O
HN
O
S
O
N
N
1.95
1.98
0.93
3.00
4.17
15.29
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

5c

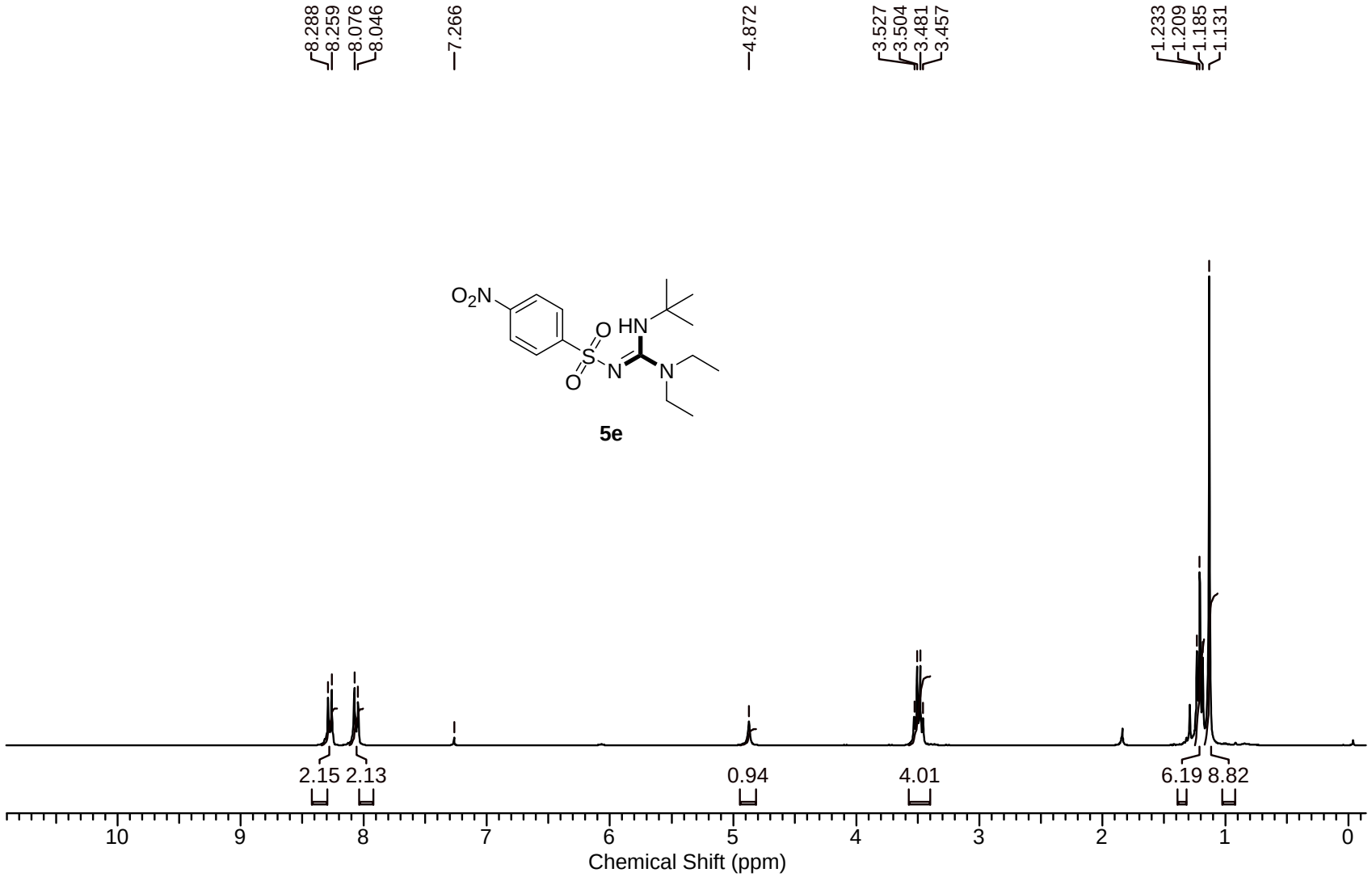

161.308
157.378
137.038
127.714
113.279
77.419
77.200
76.996
76.573
55.329
53.995
43.949
29.777
12.740
O
O
HN
S
N
N
O
5c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

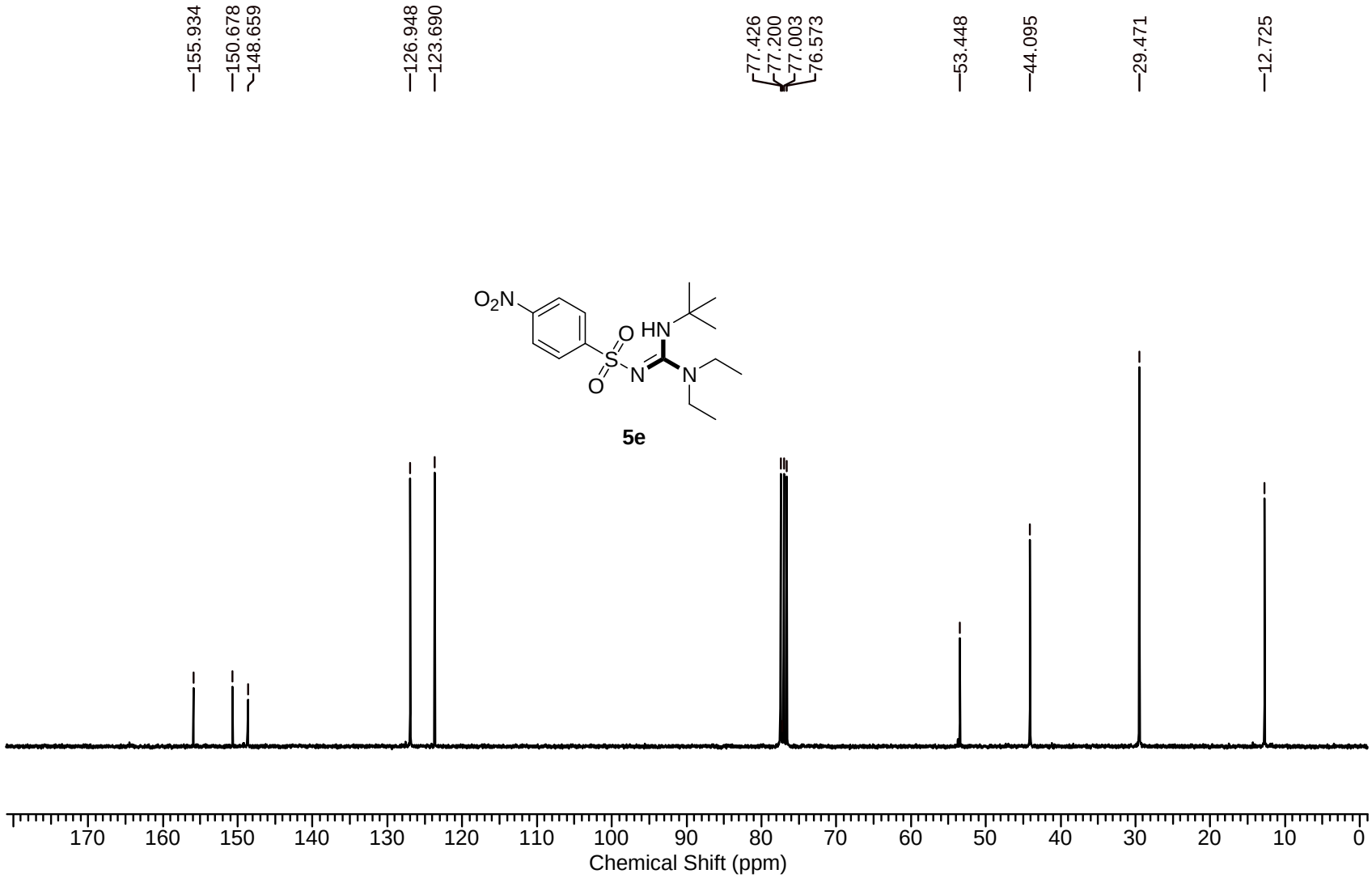

7.758
7.729
7.544
7.516
5.026
3.482
3.458
3.434
3.411
1.176
1.153
1.144
Br
O
HN
S
O
N
N
2.21
2.06
0.96
4.00
15.28
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

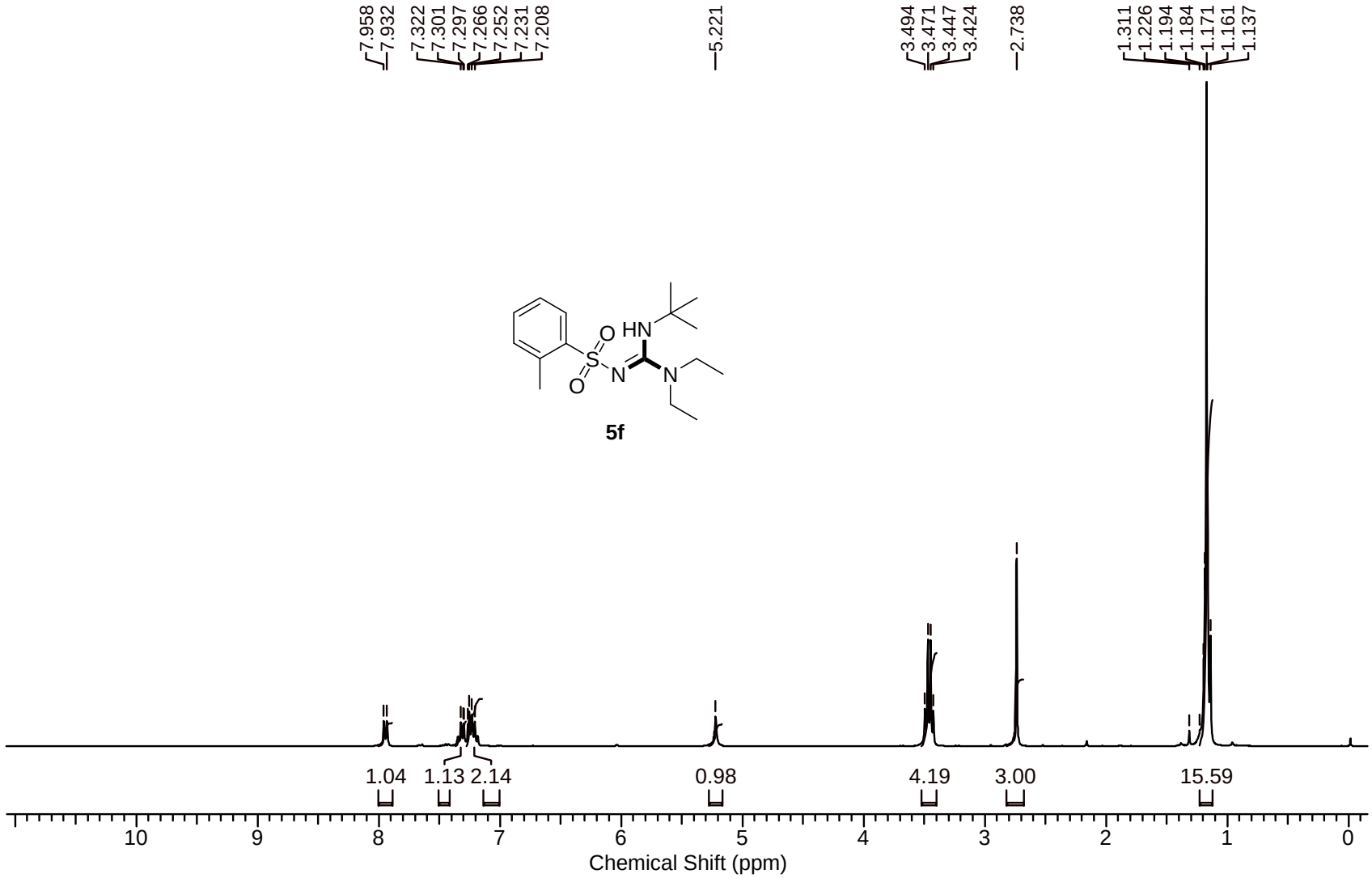
5d


156.549
144.046
131.361
127.432
125.113
77.420
77.202
76.998
76.575
53.654
43.973
29.596
12.720
Br
O
HN
S
O
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

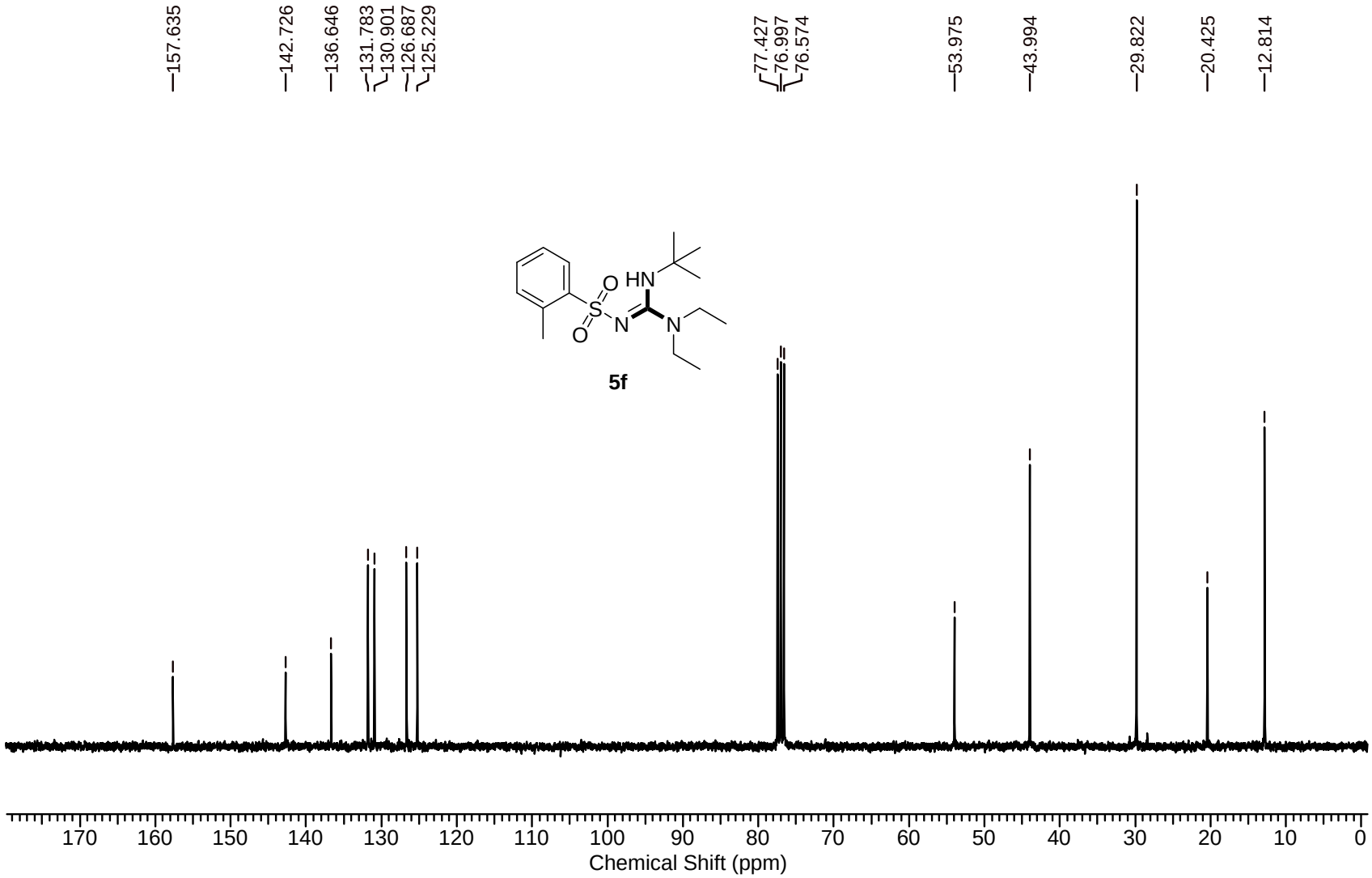
5d

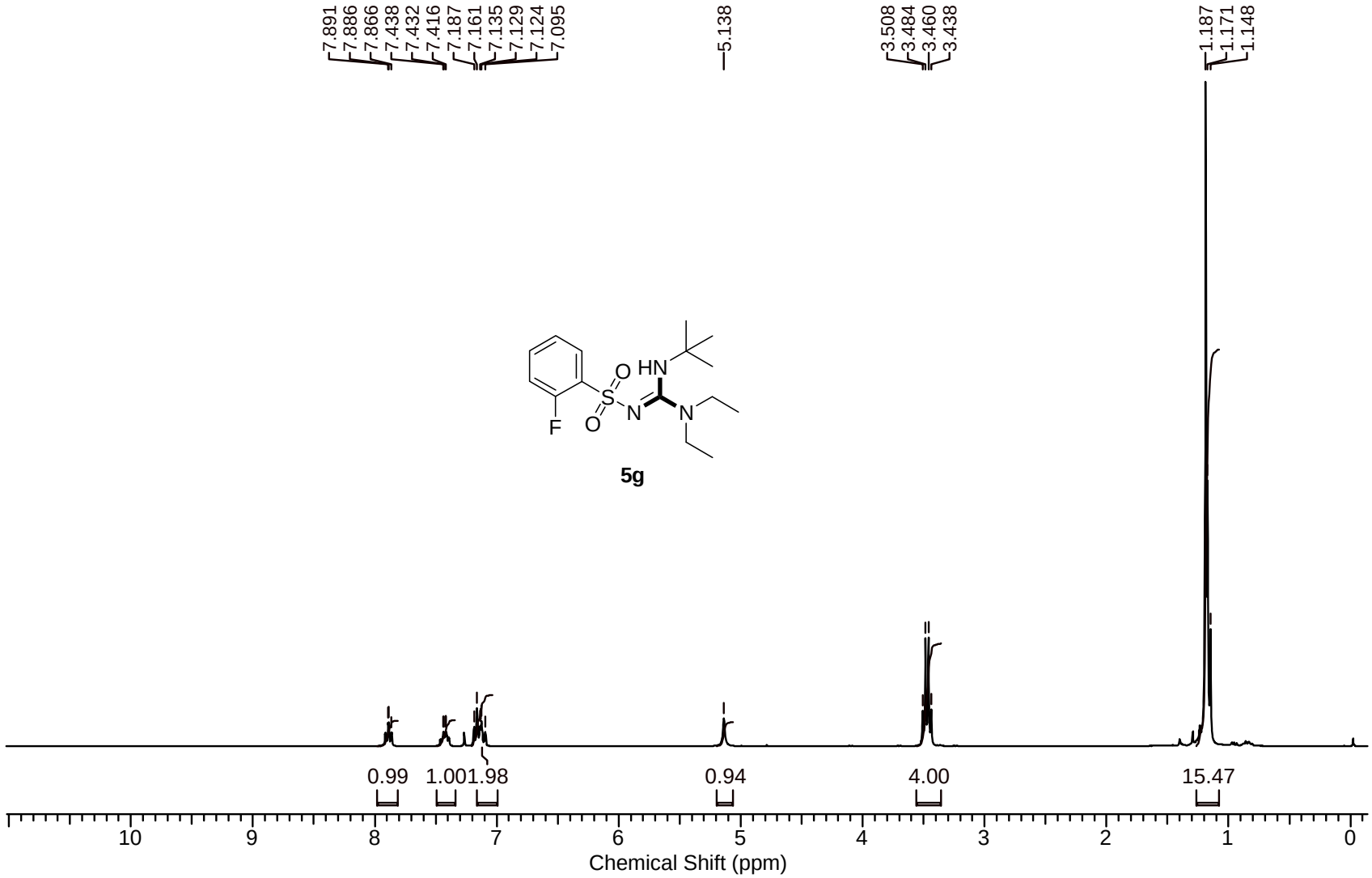

8.288
8.259
8.076
8.046
7.266
4.872
3.527
3.504
3.481
3.457
1.233
1.209
1.185
1.131
O2N
O
HN
S
O
N
N
5e
2.15
2.13
0.94
4.01
6.19
8.82
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


155.934
150.678
148.659
126.948
123.690
77.426
77.200
77.003
76.573
53.448
44.095
29.471
12.725
O2N
O
HN
S
N
O
N
5e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

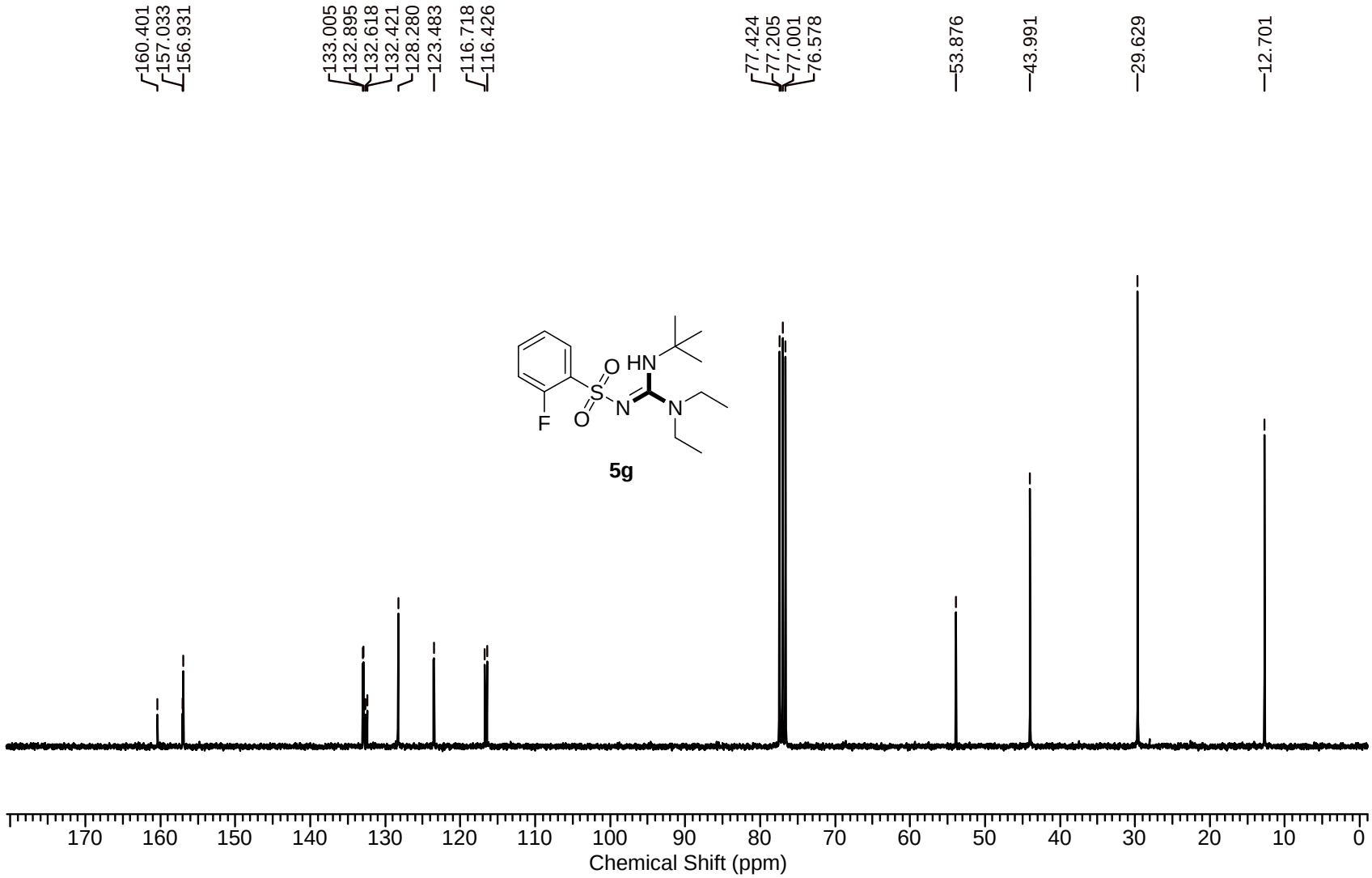

7.958
7.932
7.322
7.301
7.297
7.266
7.252
7.231
7.208
5.221
3.494
3.471
3.447
3.424
2.738
1.311
1.226
1.194
1.184
1.171
1.161
1.137
HN
O
S
O
N
N
1.04
1.13
2.14
0.98
4.19
3.00
15.59
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

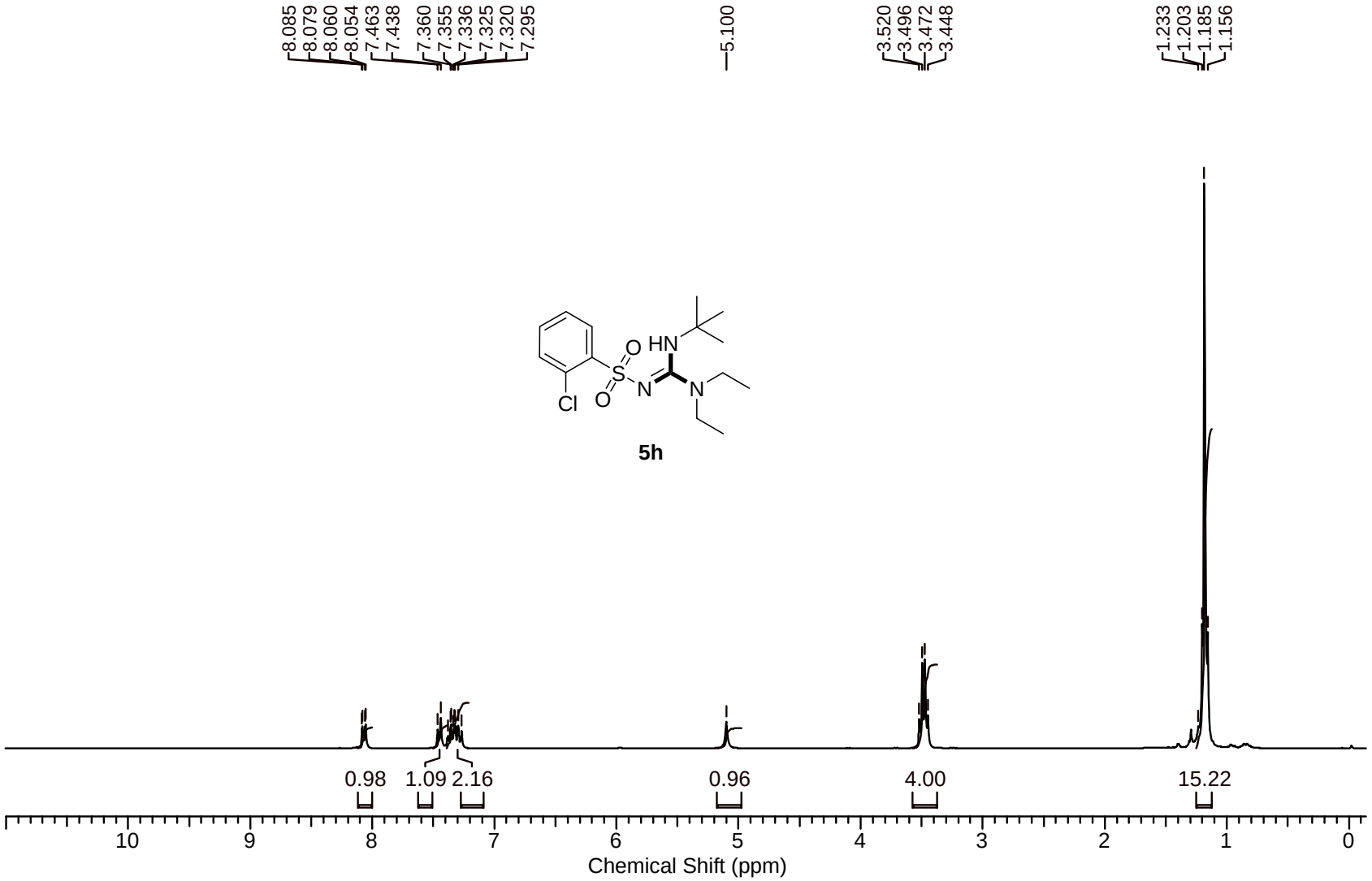
5f


157.635
142.726
136.646
131.783
130.901
126.687
125.229
77.427
76.997
76.574
53.975
43.994
29.822
20.425
12.814
O
HN
S
N
N
O
5f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

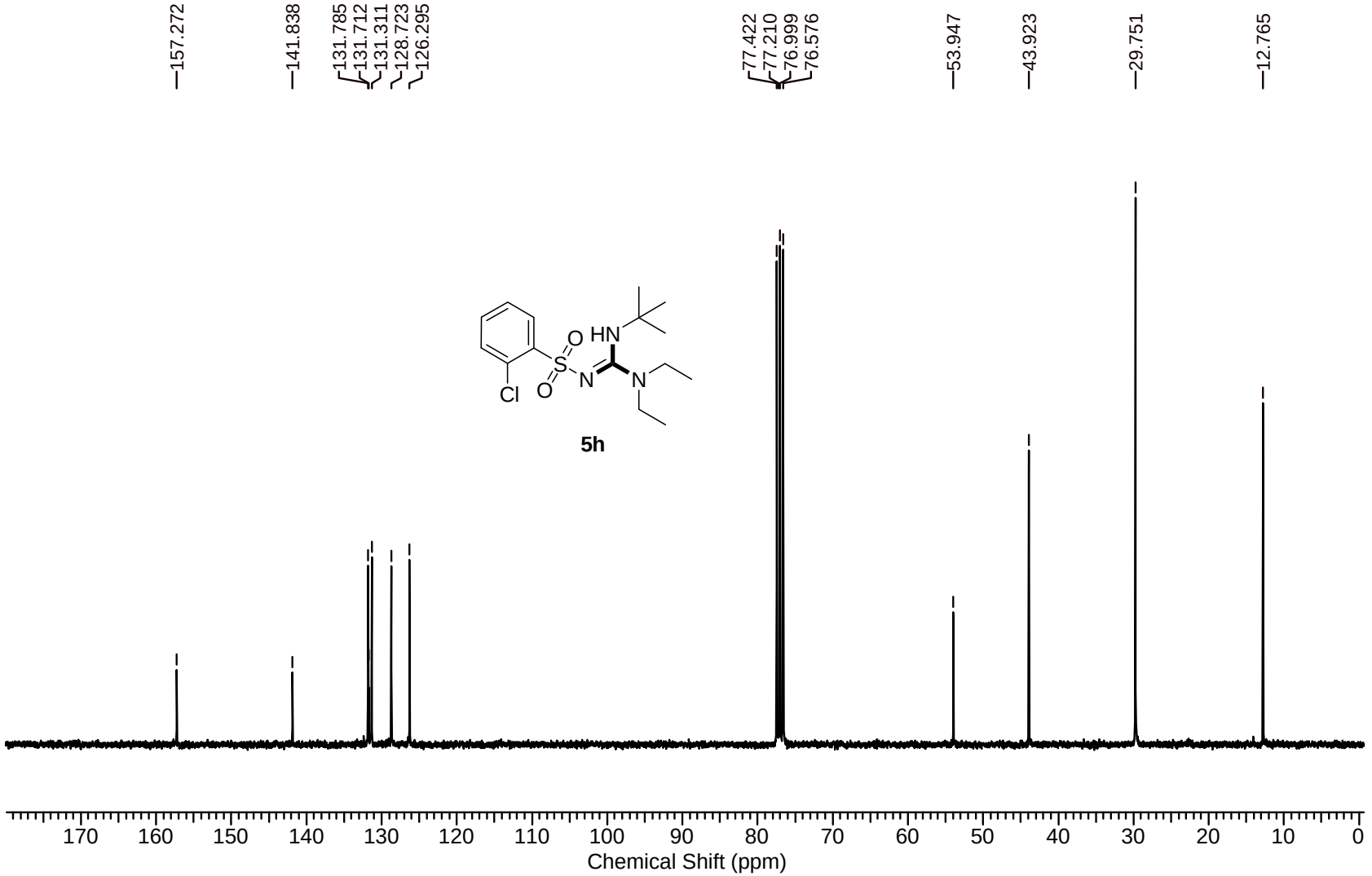

7.891
7.886
7.866
7.438
7.432
7.416
7.187
7.161
7.135
7.129
7.124
7.095
5.138
3.508
3.484
3.460
3.438
1.187
1.171
1.148
HN
O
S
N
N
O
F
0.99
1.00
1.98
0.94
4.00
15.47
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

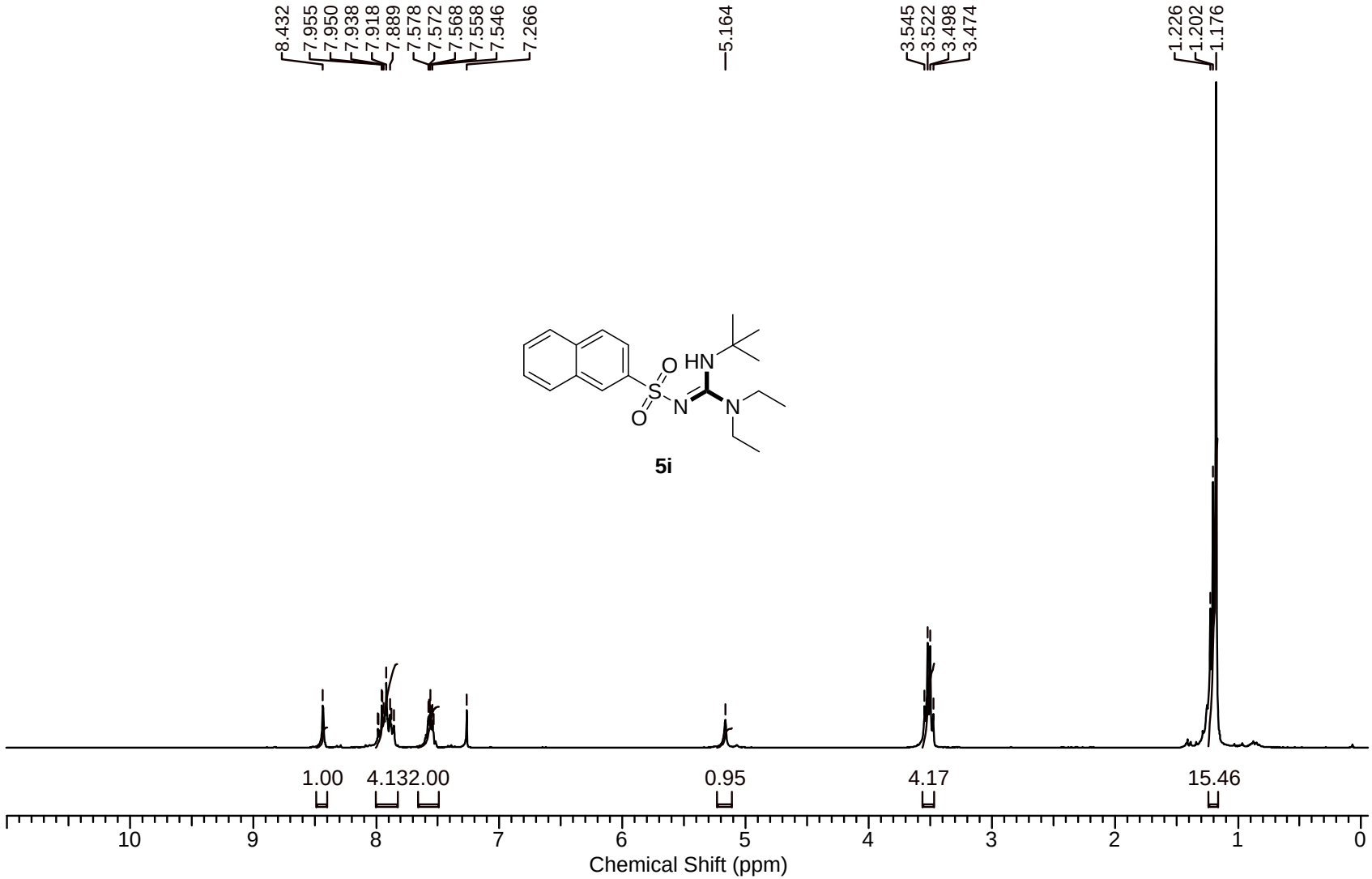
5g


160.401
157.033
156.931
133.005
132.895
132.618
132.421
128.280
123.483
116.718
116.426
77.424
77.205
77.001
76.578
53.876
43.991
29.629
12.701
O
HN
S
N
N
O
F
5g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

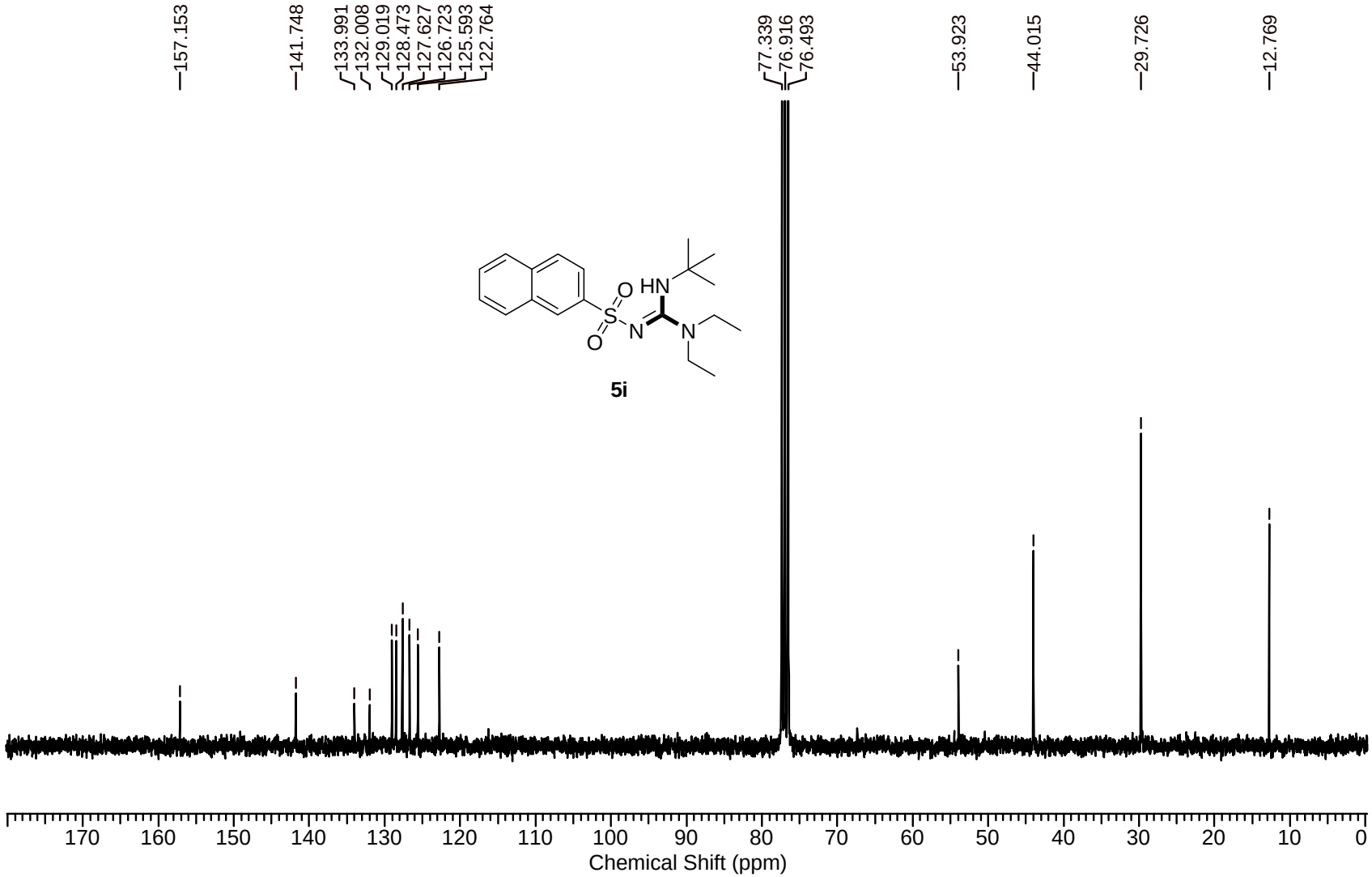

8.085
8.079
8.060
8.054
7.463
7.438
7.360
7.355
7.336
7.325
7.320
7.295
5.100
3.520
3.496
3.472
3.448
1.233
1.203
1.185
1.156
HN
O
S
O
N
N
Cl
0.98
1.09
2.16
0.96
4.00
15.22
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

5h

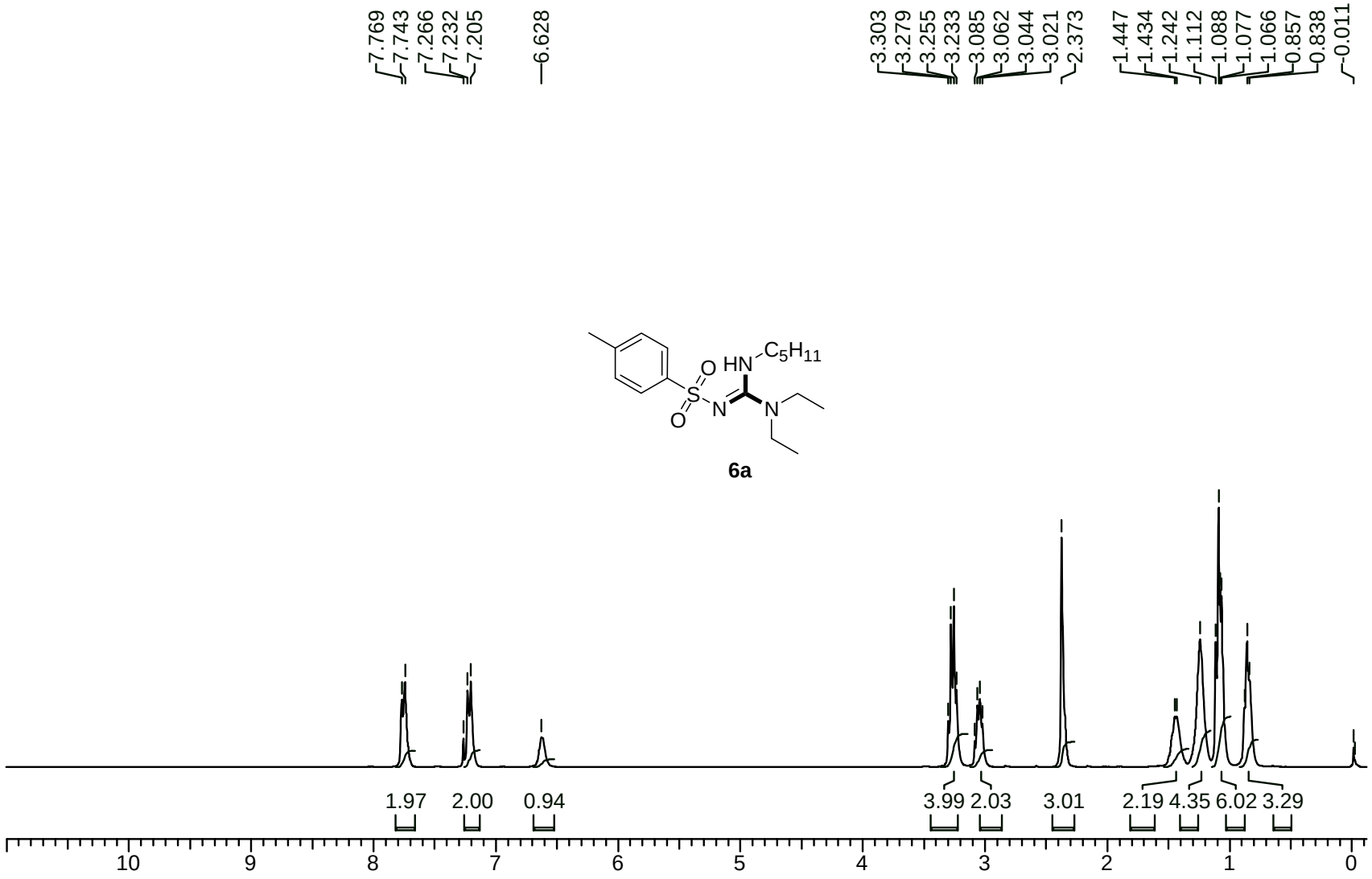

157.272
141.838
131.785
131.712
131.311
128.723
126.295
77.422
77.210
76.999
76.576
53.947
43.923
29.751
12.765
O
HN
S
N
N
O
Cl
5h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

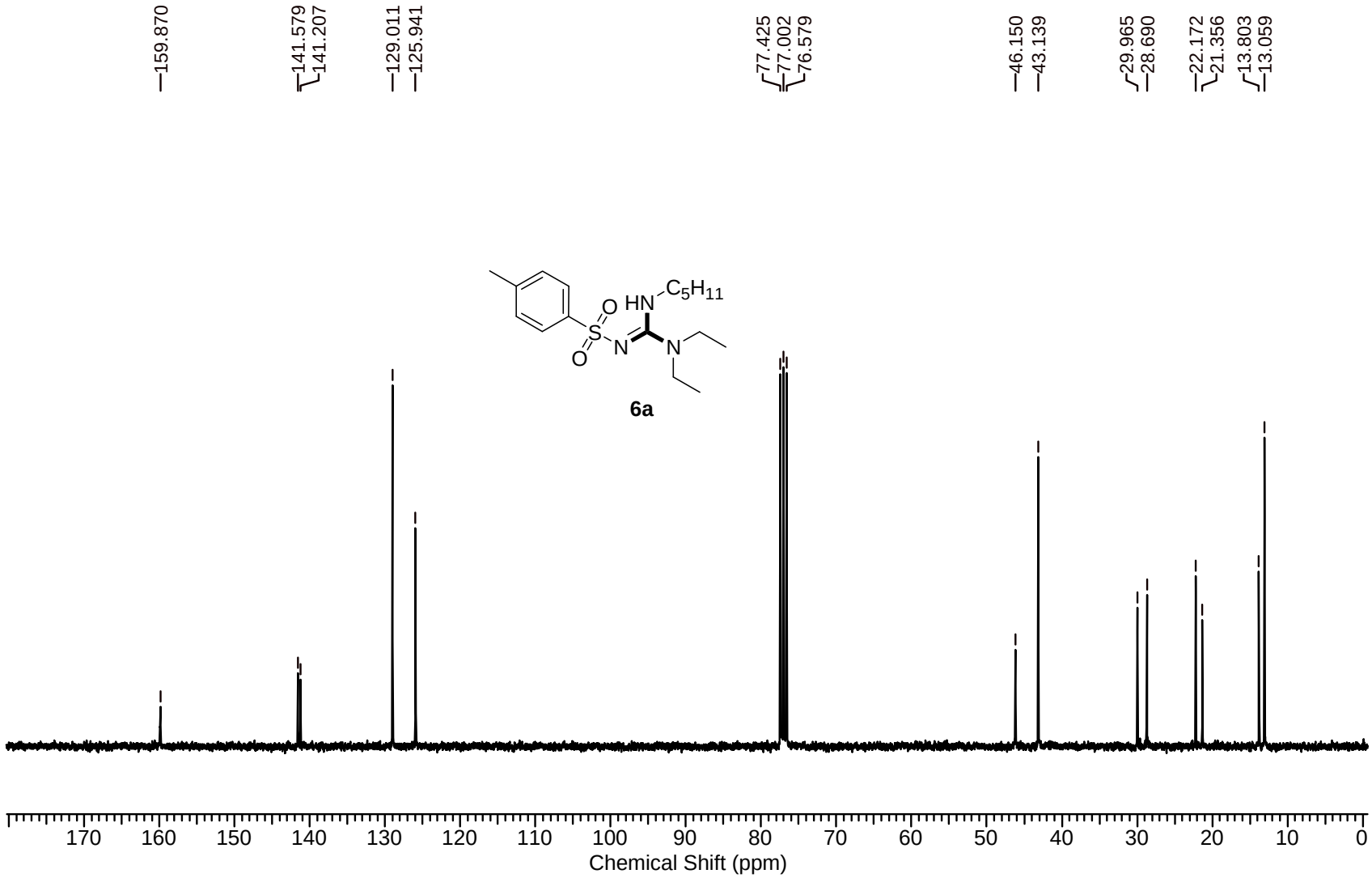

8.432
7.955
7.950
7.938
7.918
7.889
7.578
7.572
7.568
7.558
7.546
7.266
5.164
3.545
3.522
3.498
3.474
1.226
1.202
1.176
O
HN
S
O
N
N
1.00
4.13
2.00
0.95
4.17
15.46
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

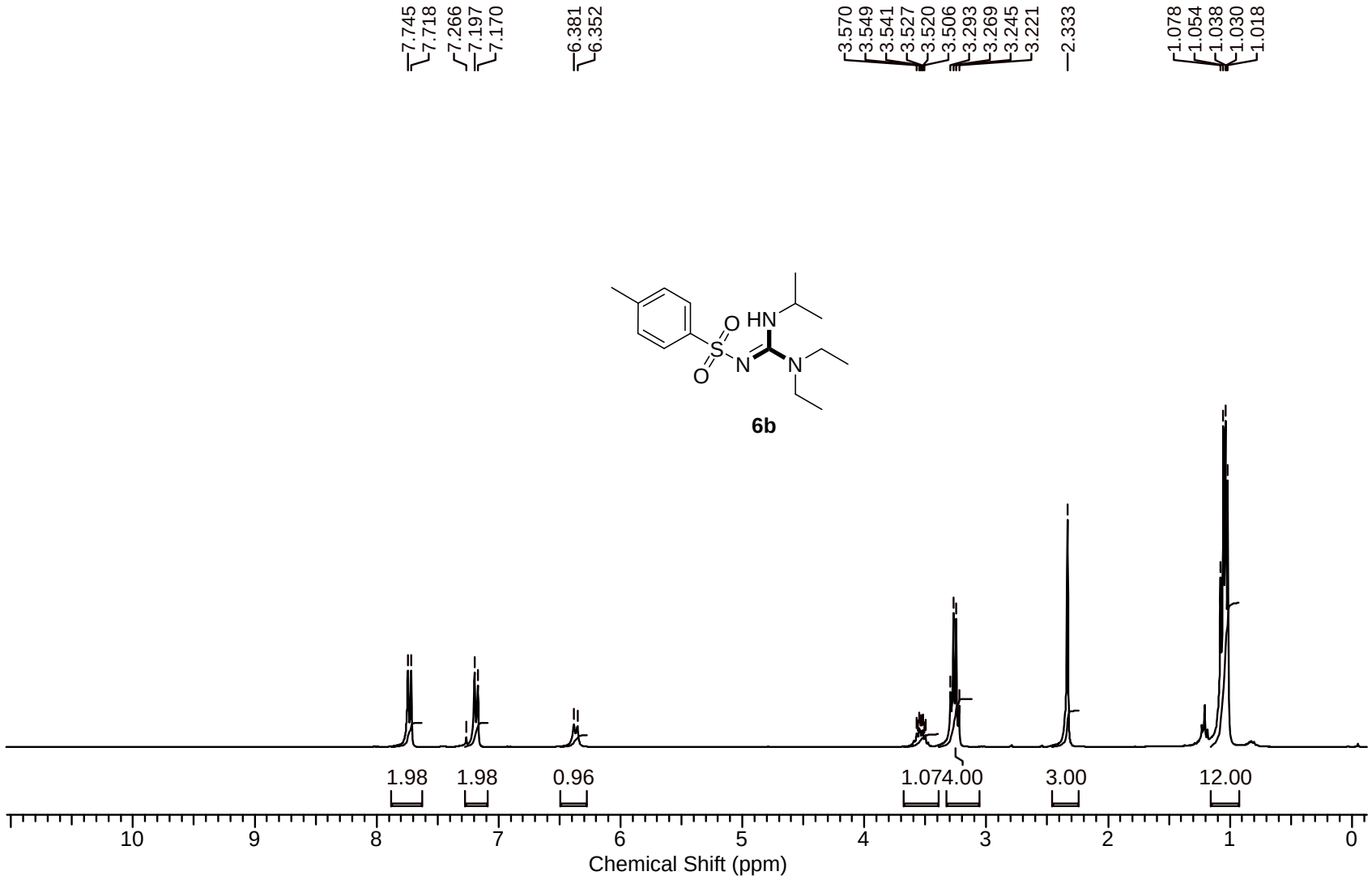
5i

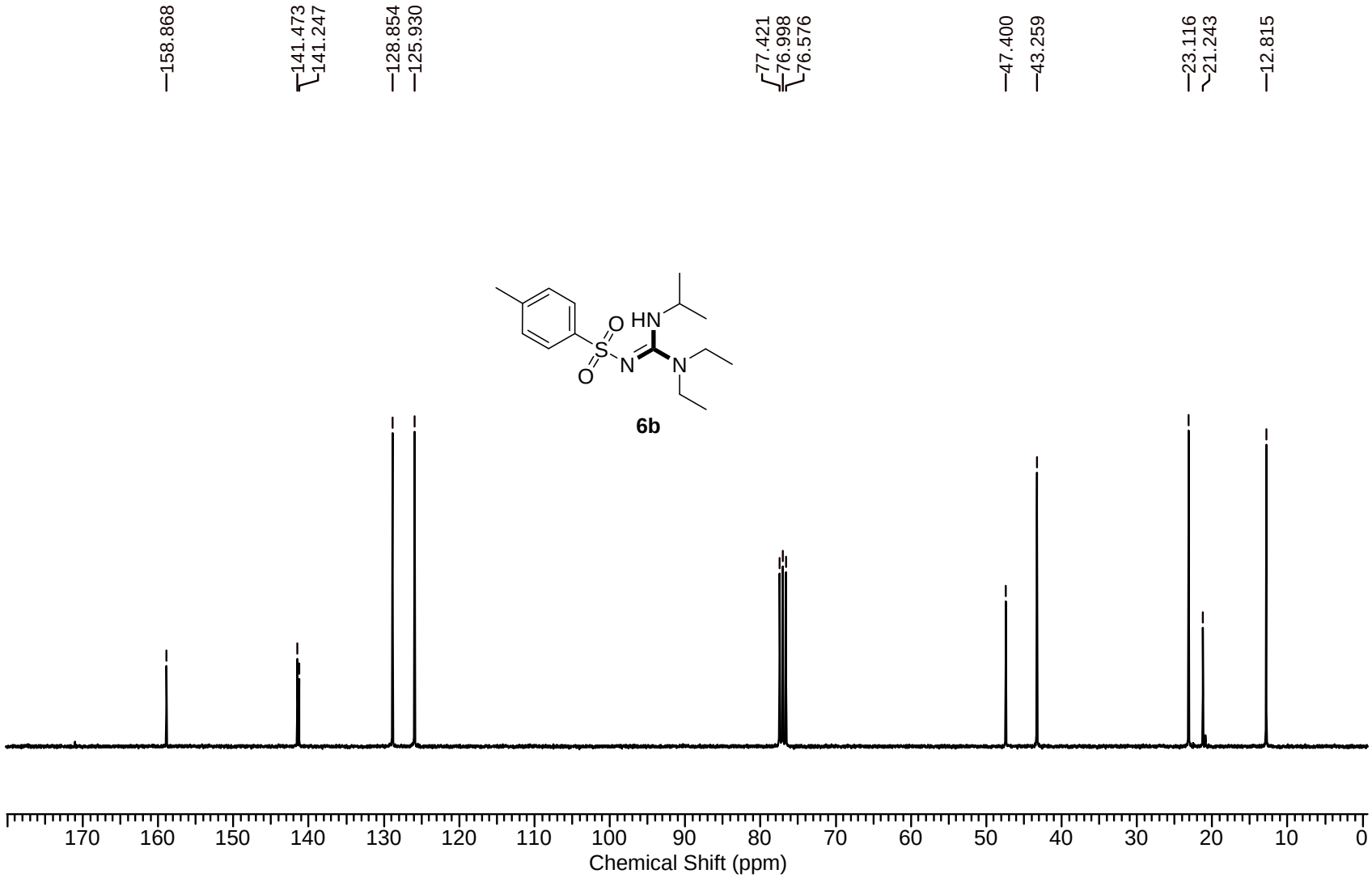

157.153
141.748
133.991
132.008
129.019
128.473
127.627
126.723
125.593
122.764
77.339
76.916
76.493
53.923
44.015
29.726
12.769
HN
O
S
O
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

5i

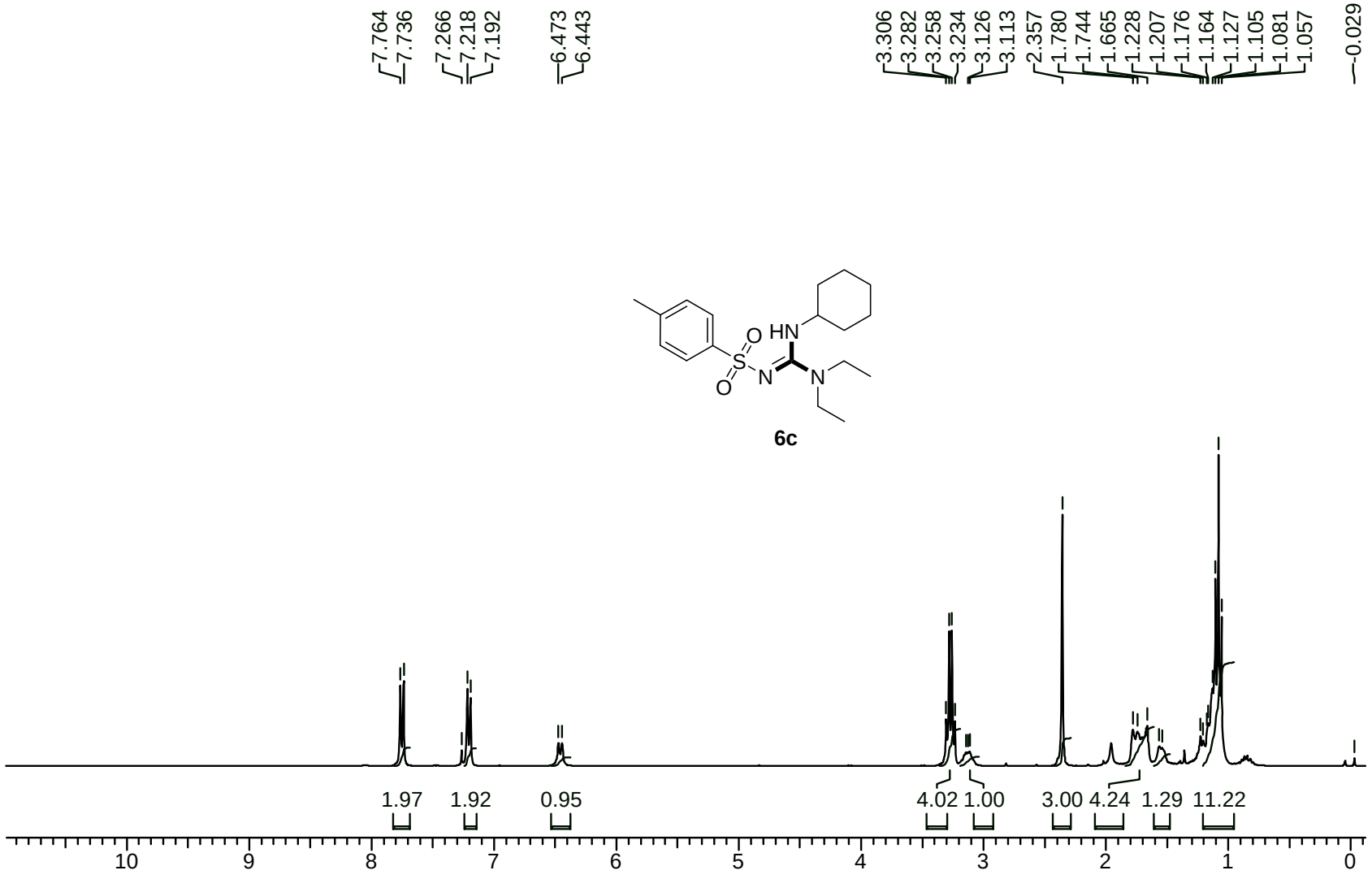

7.769
7.743
7.266
7.232
7.205
6.628
3.303
3.279
3.255
3.233
3.085
3.062
3.044
3.021
2.373
1.447
1.434
1.242
1.112
1.088
1.077
1.066
0.857
0.838
0.011
HN
C5H11
O
S
O
N
N
6a
1.97
2.00
0.94
3.99
2.03
3.01
2.19
4.35
6.02
3.29
10
9
8
7
6
5
4
3
2
1
0

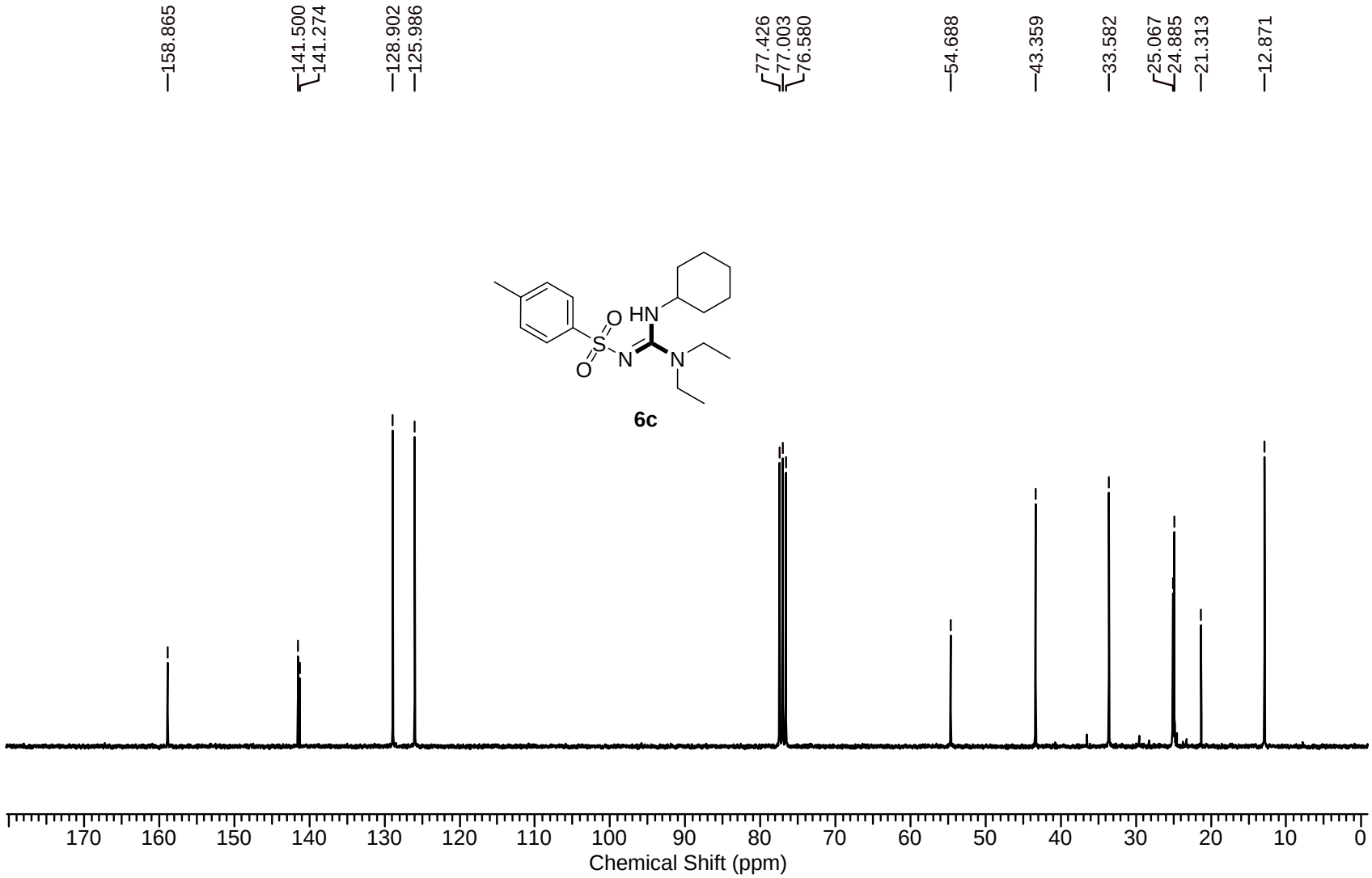

159.870
141.579
141.207
129.011
125.941
77.425
77.002
76.579
46.150
43.139
29.965
28.690
22.172
21.356
13.803
13.059
O
HN
C5H11
S
O
N
N
6a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

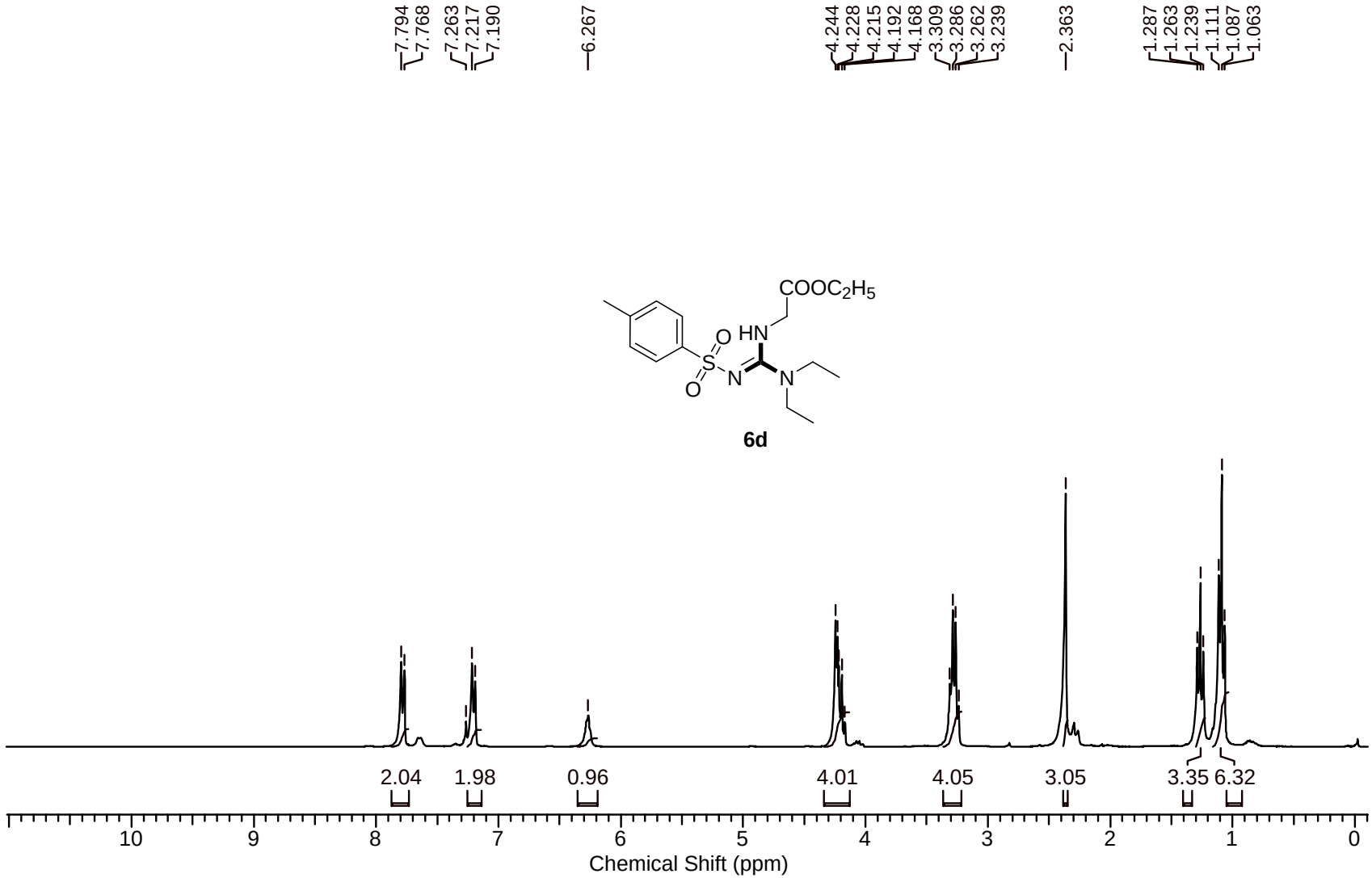

7.745
7.718
7.266
7.197
7.170
6.381
6.352
3.570
3.549
3.541
3.527
3.520
3.506
3.293
3.269
3.245
3.221
2.333
1.078
1.054
1.038
1.030
1.018
O
HN
S
N
N
O
6b
1.98
1.98
0.96
1.07
4.00
3.00
12.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

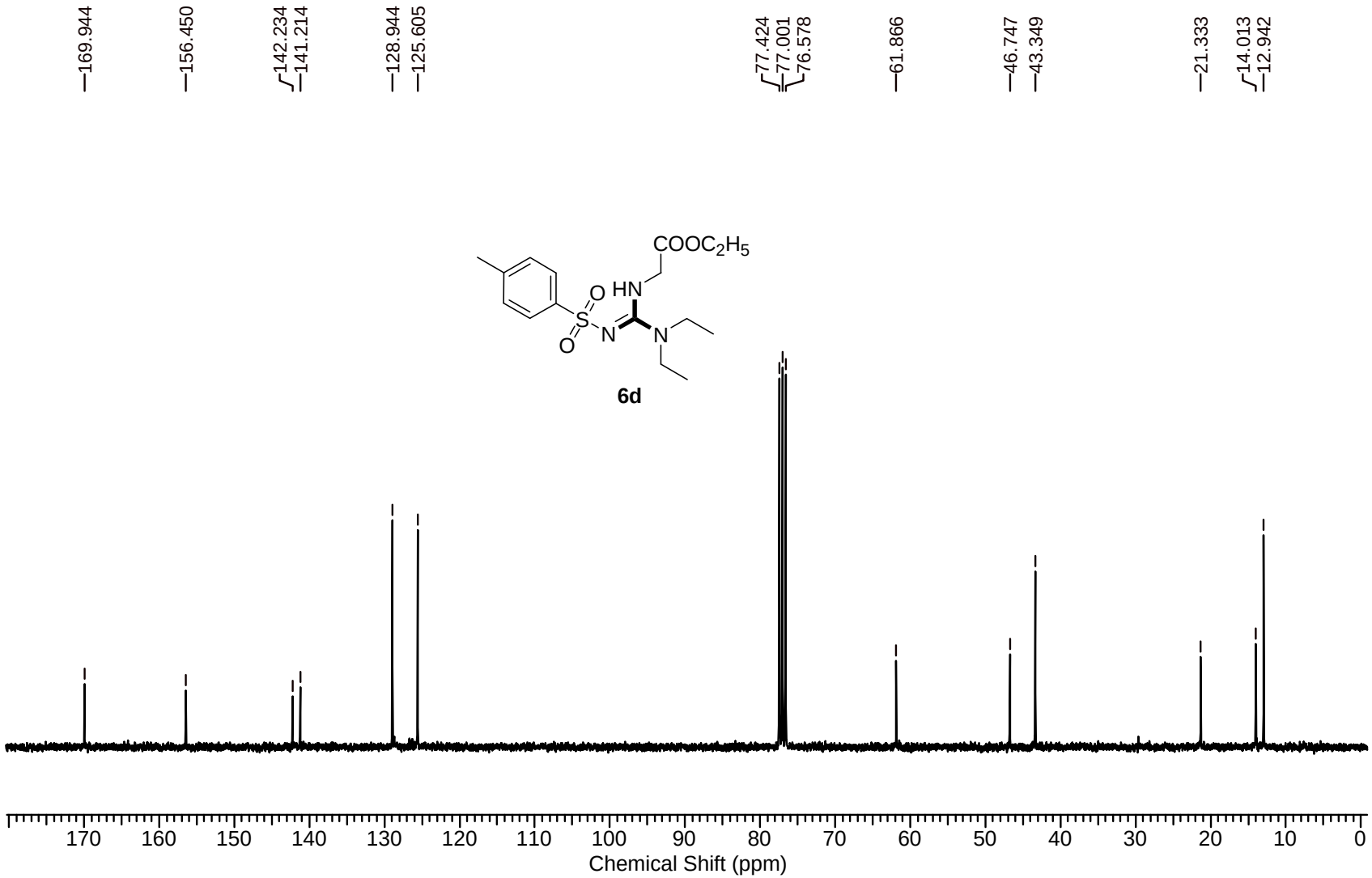

158.868
141.473
141.247
128.854
125.930
77.421
76.998
76.576
47.400
43.259
23.116
21.243
12.815
O
HN
S
O
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

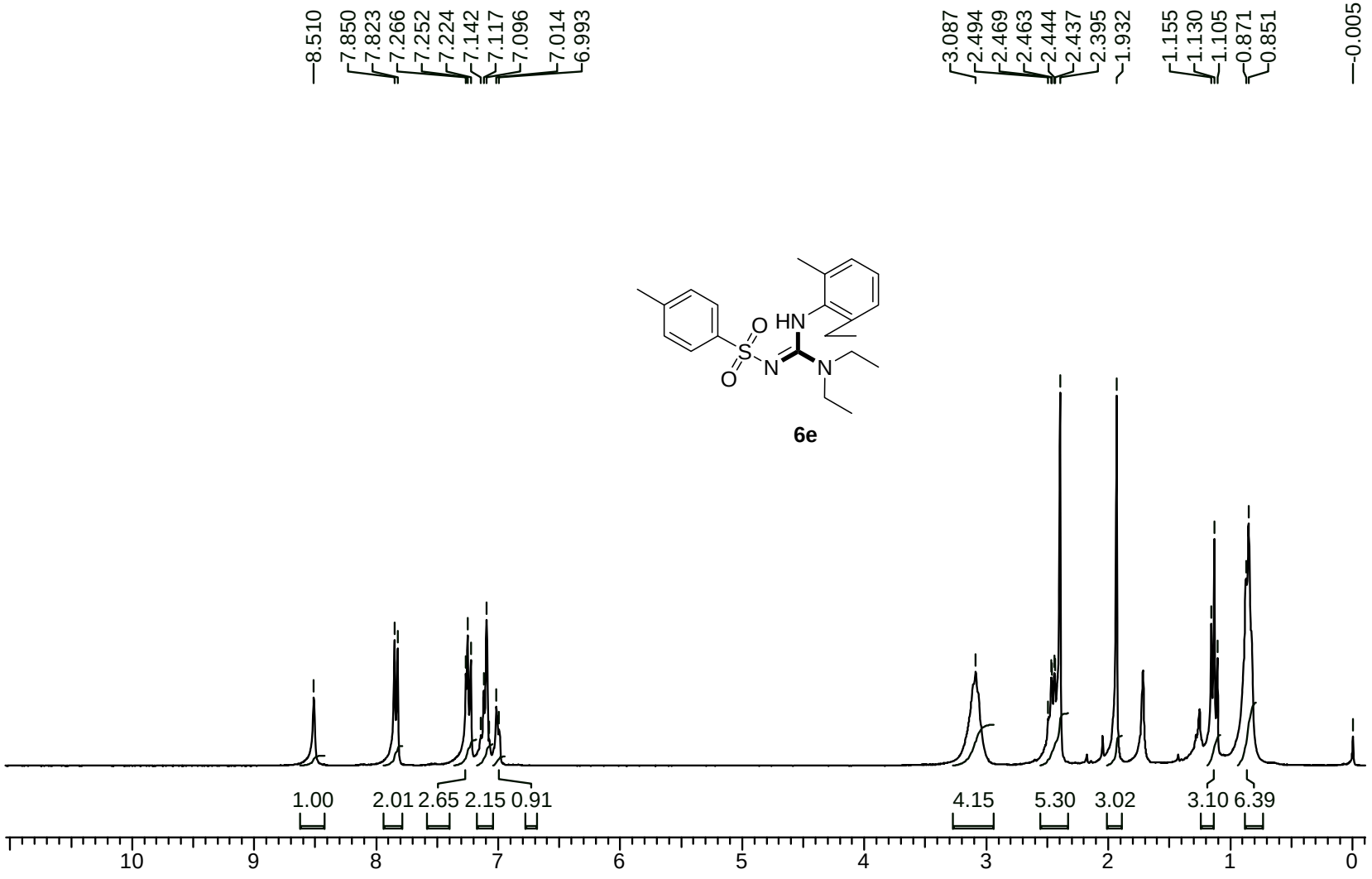
6b

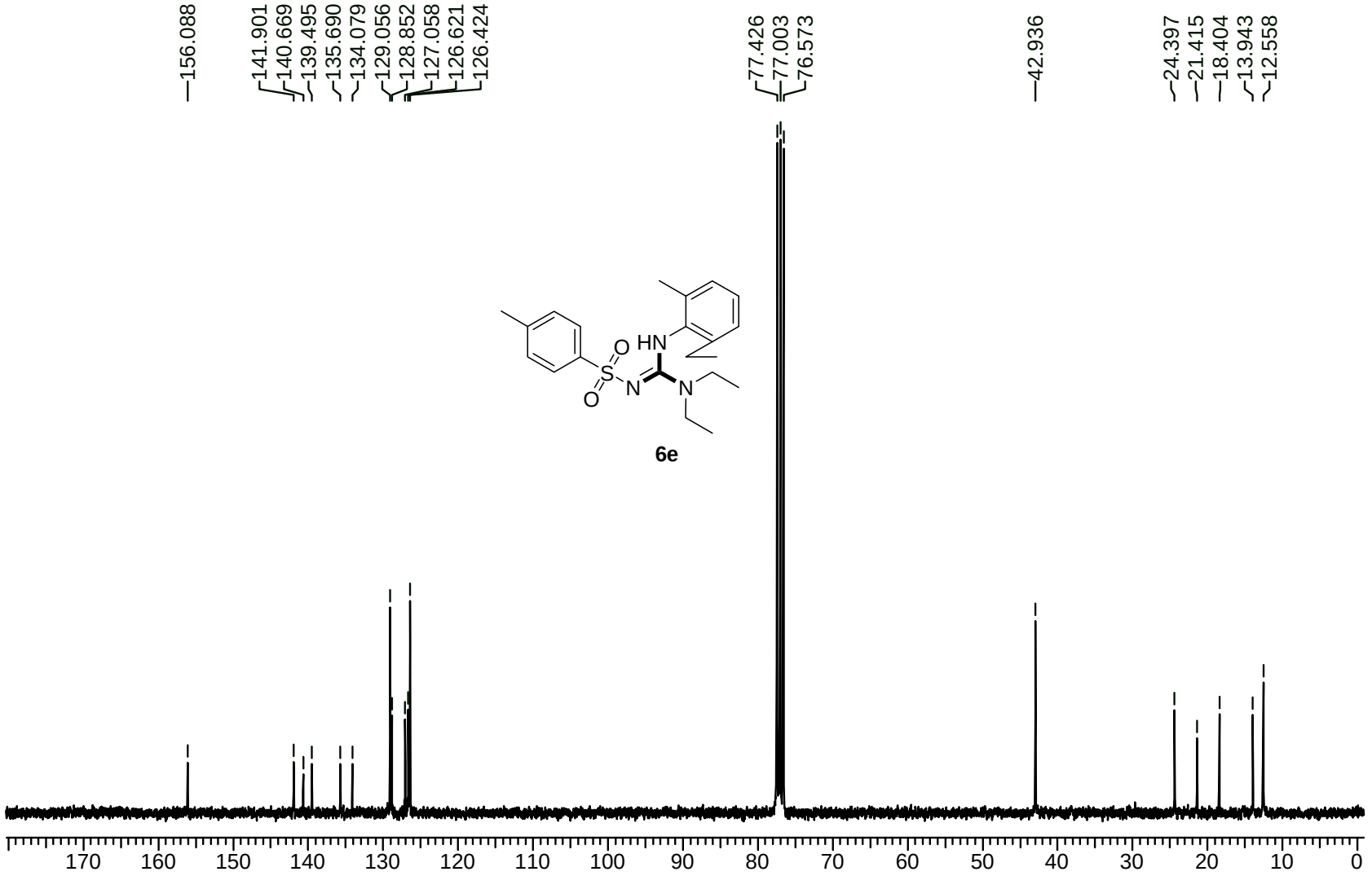

7.764
7.736
7.266
7.218
7.192
6.473
6.443
3.306
3.282
3.258
3.234
3.126
3.113
2.357
1.780
1.744
1.665
1.228
1.207
1.176
1.164
1.127
1.105
1.081
1.057
-0.029
O
HN
S
O
N
N
6c
1.97
1.92
0.95
4.02
1.00
3.00
4.24
1.29
11.22
10
9
8
7
6
5
4
3
2
1
0


158.865
141.500
141.274
128.902
125.986
77.426
77.003
76.580
54.688
43.359
33.582
25.067
24.885
21.313
12.871
O
HN
S
N
N
O
6c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

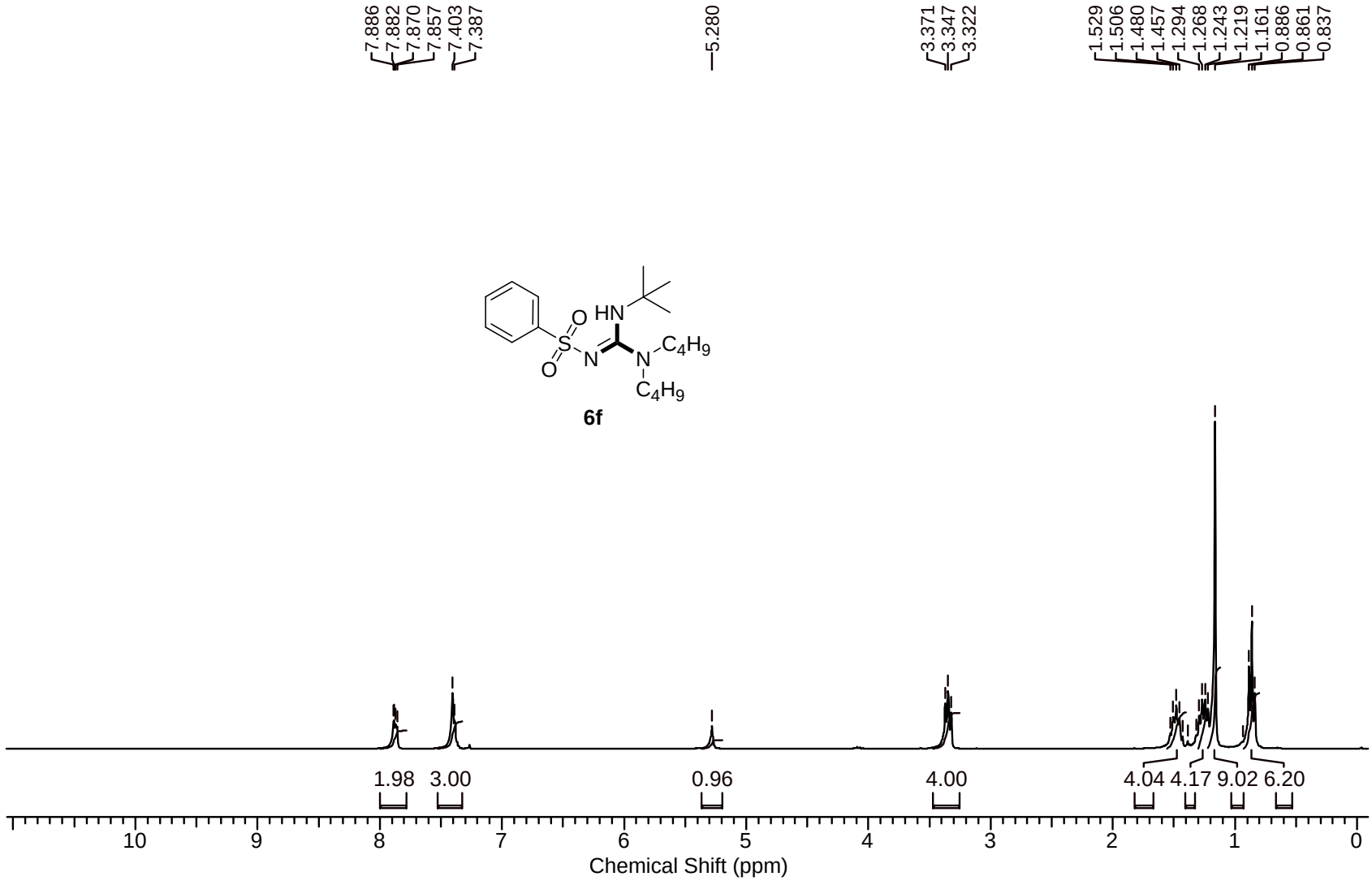

7.794
7.768
7.263
7.217
7.190
6.267
4.244
4.228
4.215
4.192
4.168
3.309
3.286
3.262
3.239
2.363
1.287
1.263
1.239
1.111
1.087
1.063
COOC2H5
HN
O
S
O
N
N
6d
2.04
1.98
0.96
4.01
4.05
3.05
3.35
6.32
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


169.944
156.450
142.234
141.214
128.944
125.605
77.424
77.001
76.578
61.866
46.747
43.349
21.333
14.013
12.942
COOC2H5
HN
O
S
O
N
N
6d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

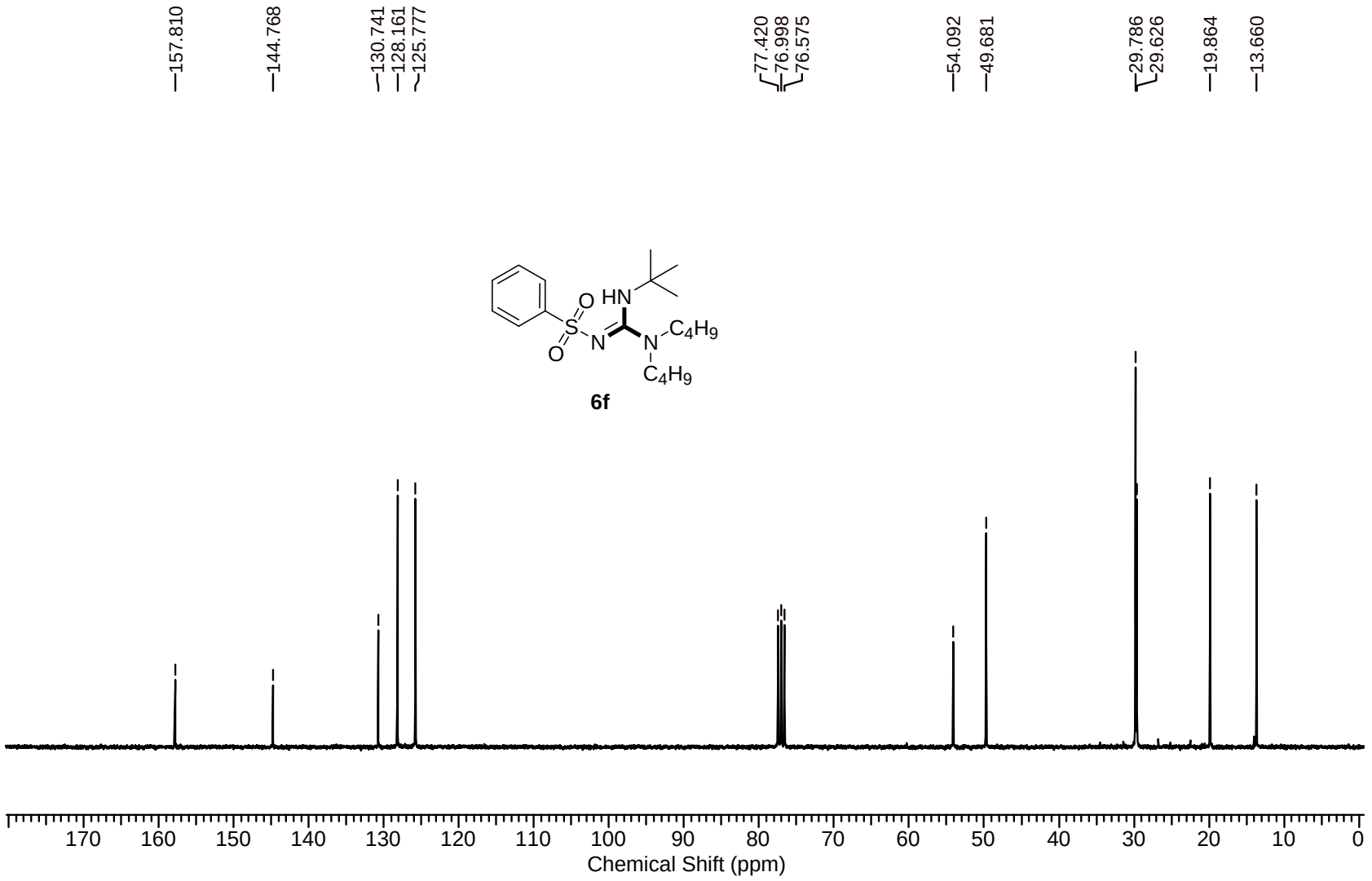

8.510
7.850
7.823
7.266
7.252
7.224
7.142
7.117
7.096
7.014
6.993
3.087
2.494
2.469
2.463
2.444
2.437
2.395
1.932
1.155
1.130
1.105
0.871
0.851
0.005
O
HN
S
N
N
O
6e
1.00
2.01
2.65
2.15
0.91
4.15
5.30
3.02
3.10
6.39
10
9
8
7
6
5
4
3
2
1
0

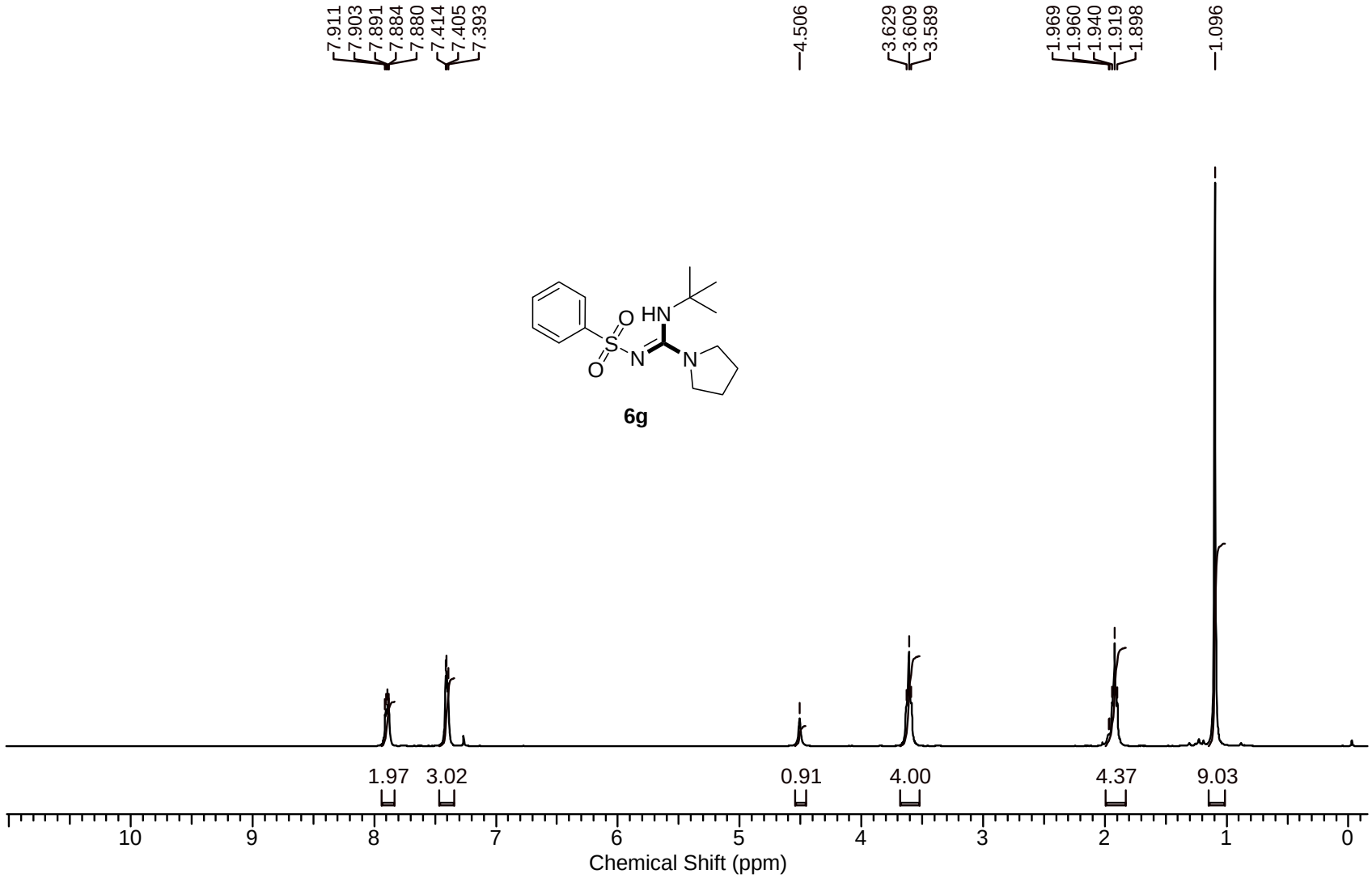

156.088
141.901
140.669
139.495
135.690
134.079
129.056
128.852
127.058
126.621
126.424
77.426
77.003
76.573
42.936
24.397
21.415
18.404
13.943
12.558
HN
O
S
O
N
N
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

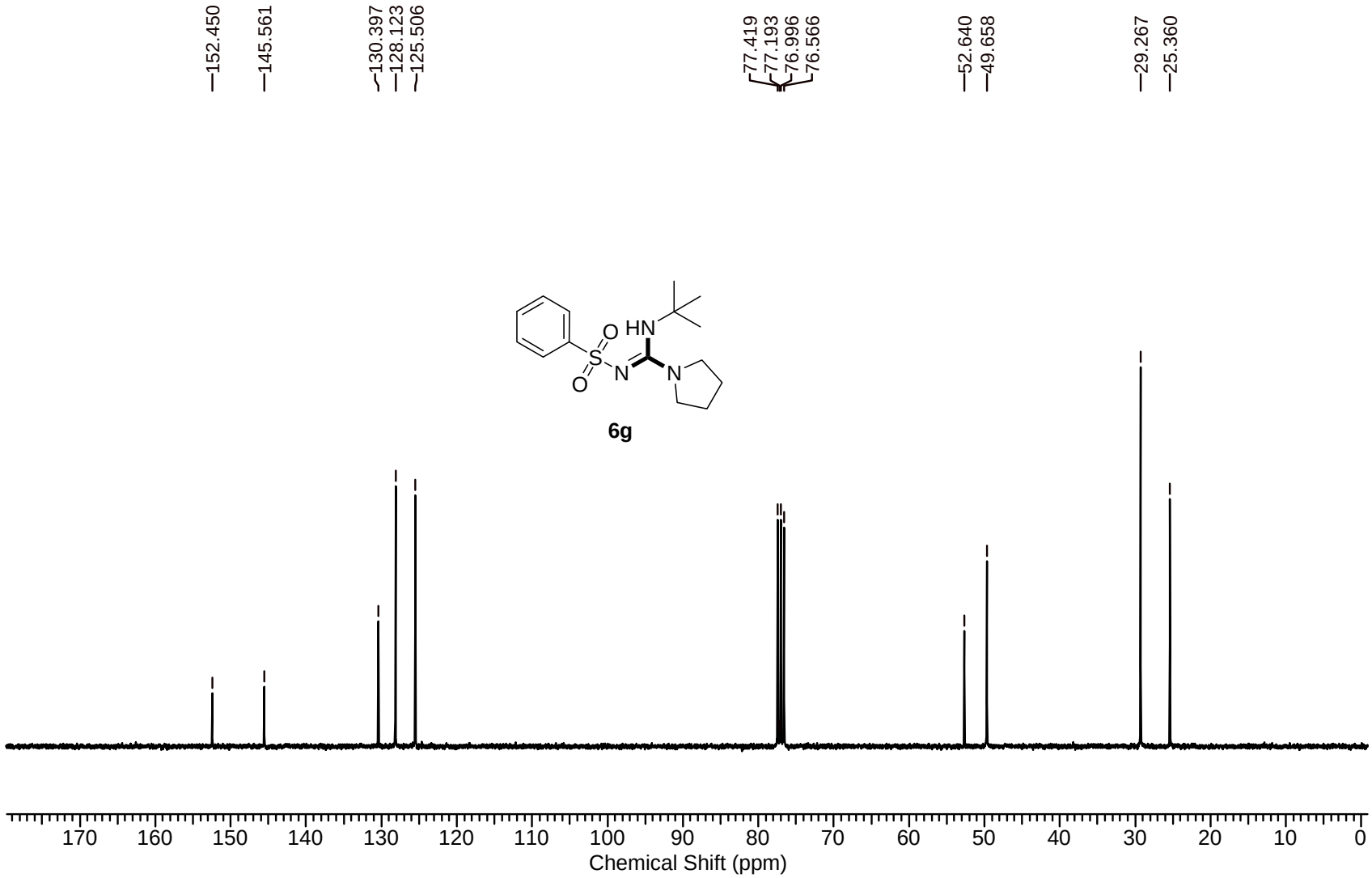
6e

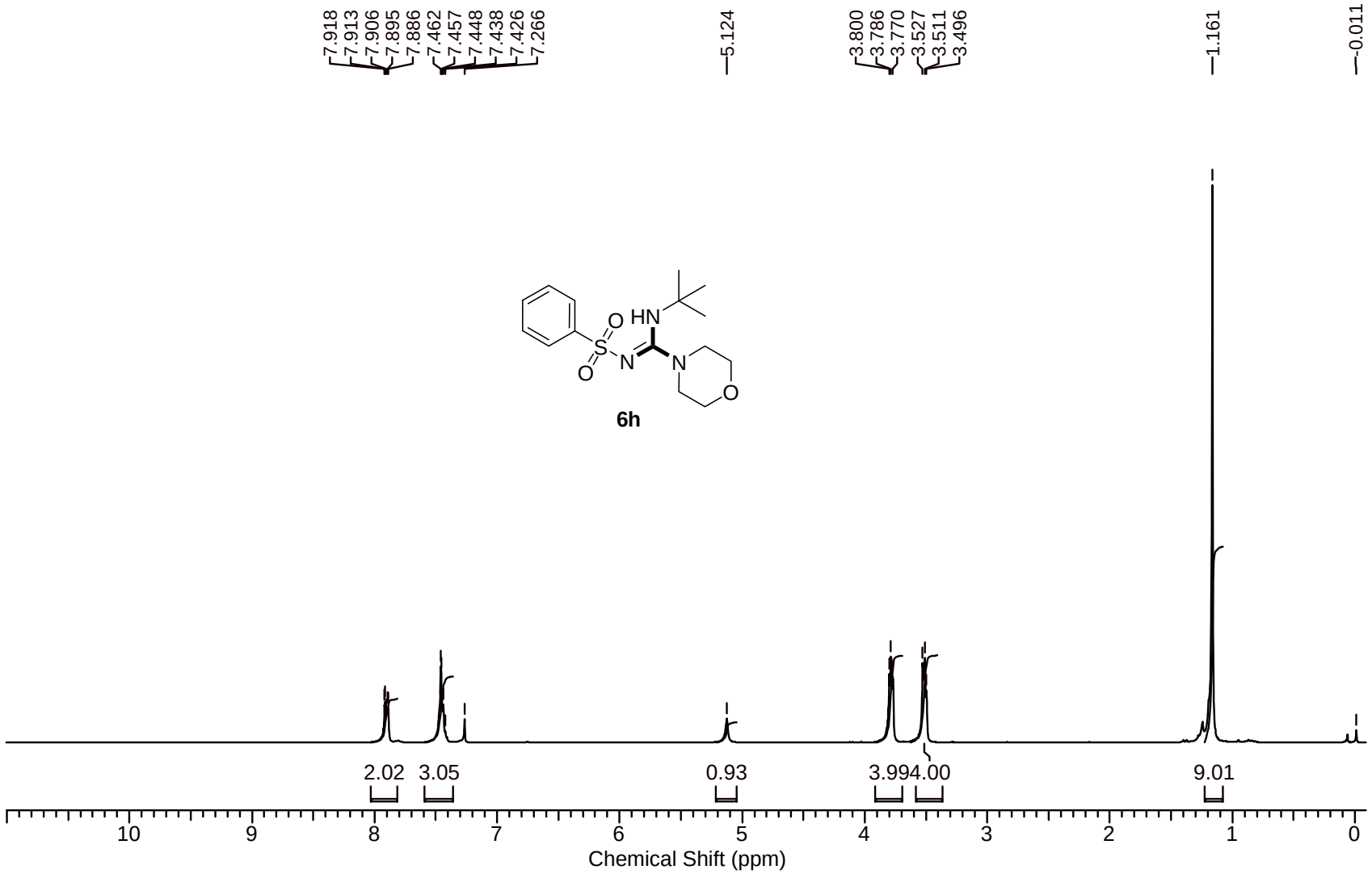

7.886
7.882
7.870
7.857
7.403
7.387
5.280
3.371
3.347
3.322
1.529
1.506
1.480
1.457
1.294
1.268
1.243
1.219
1.161
0.886
0.861
0.837
HN
O
S
O
N
N
C4H9
C4H9
1.98
3.00
0.96
4.00
4.04
4.17
9.02
6.20
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

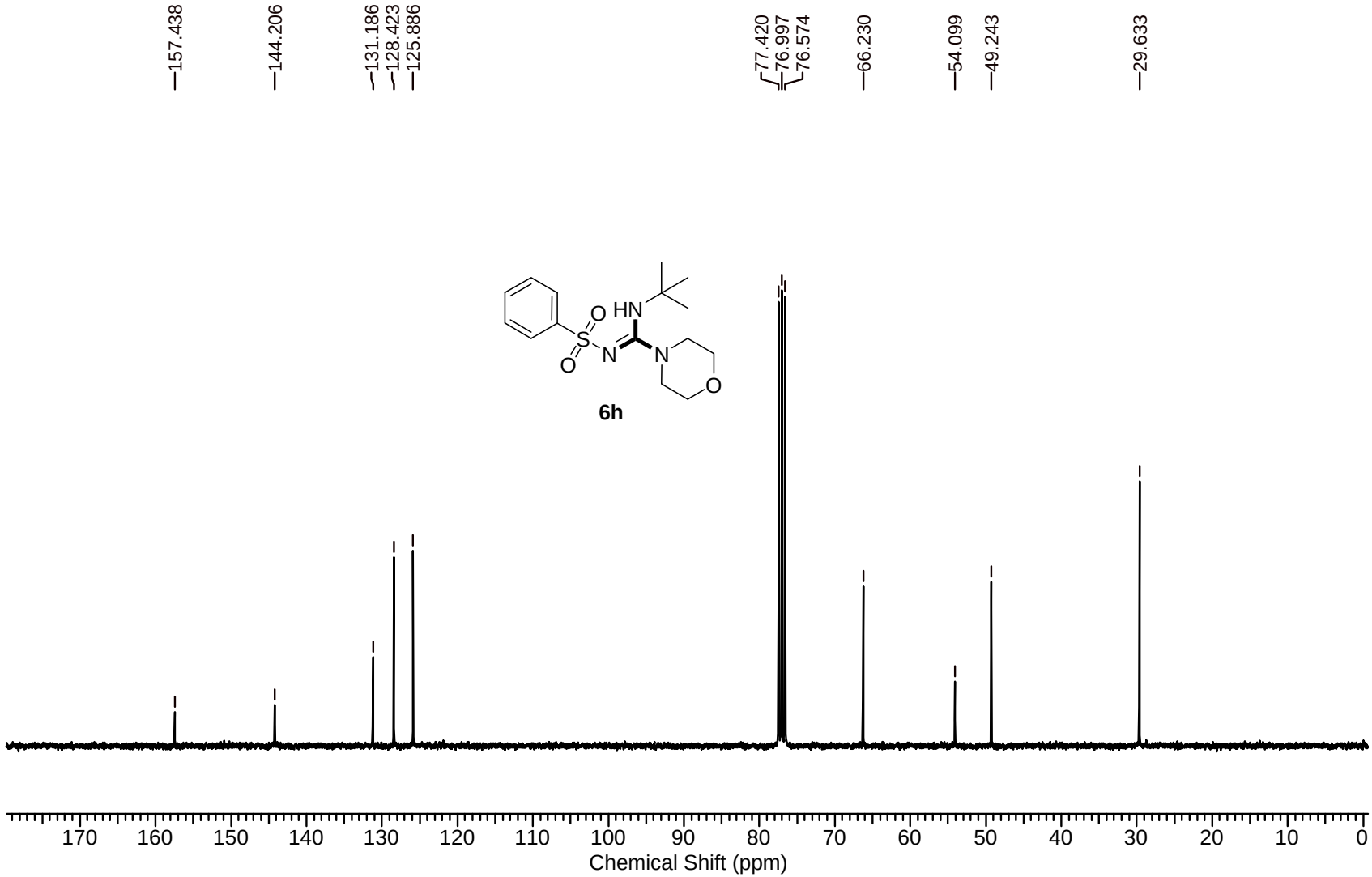
6f

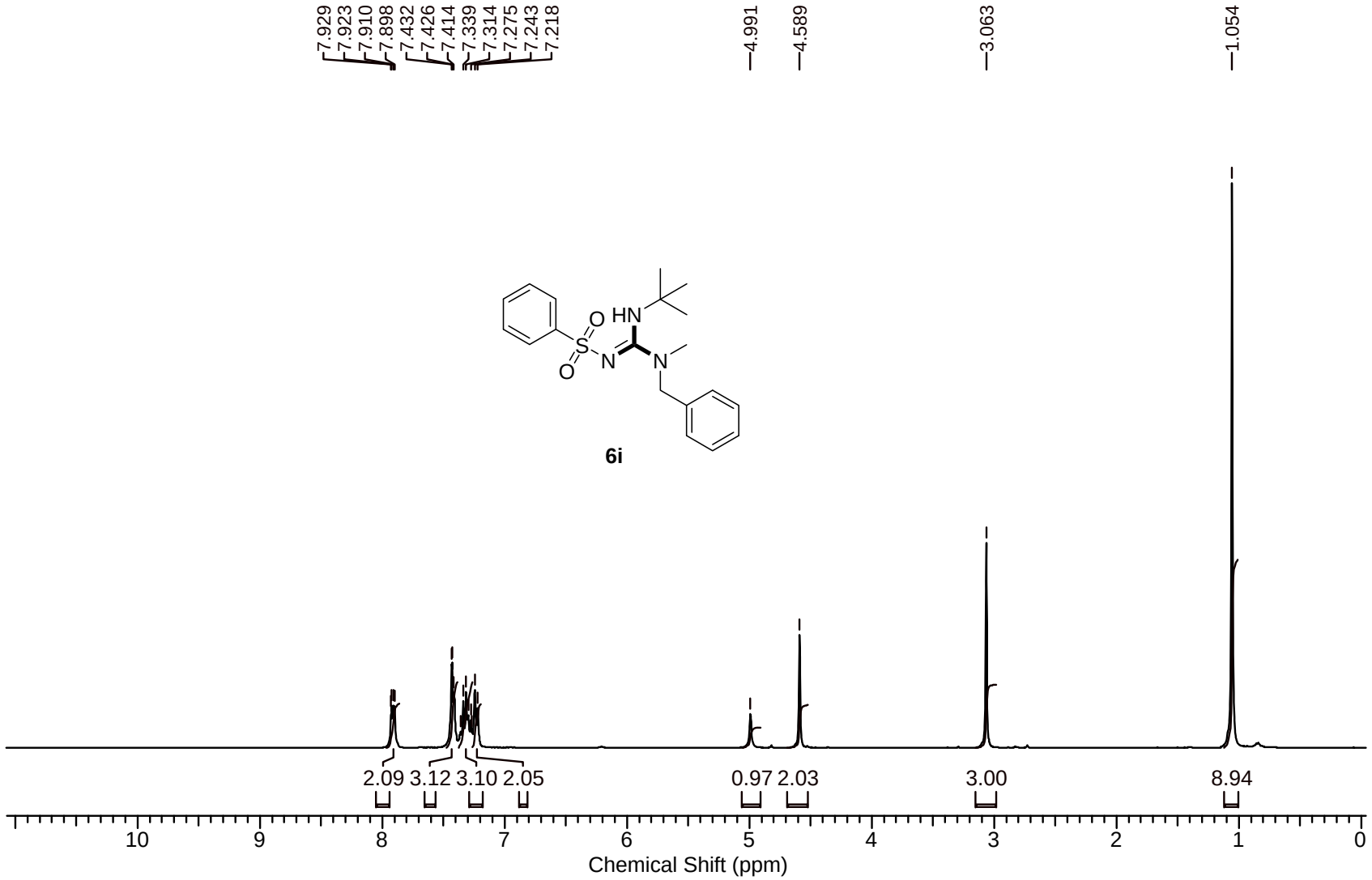

157.810
144.768
130.741
128.161
125.777
77.420
76.998
76.575
54.092
49.681
29.786
29.626
19.864
13.660
HN
O
S
O
N
N
C4H9
C4H9
6f
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

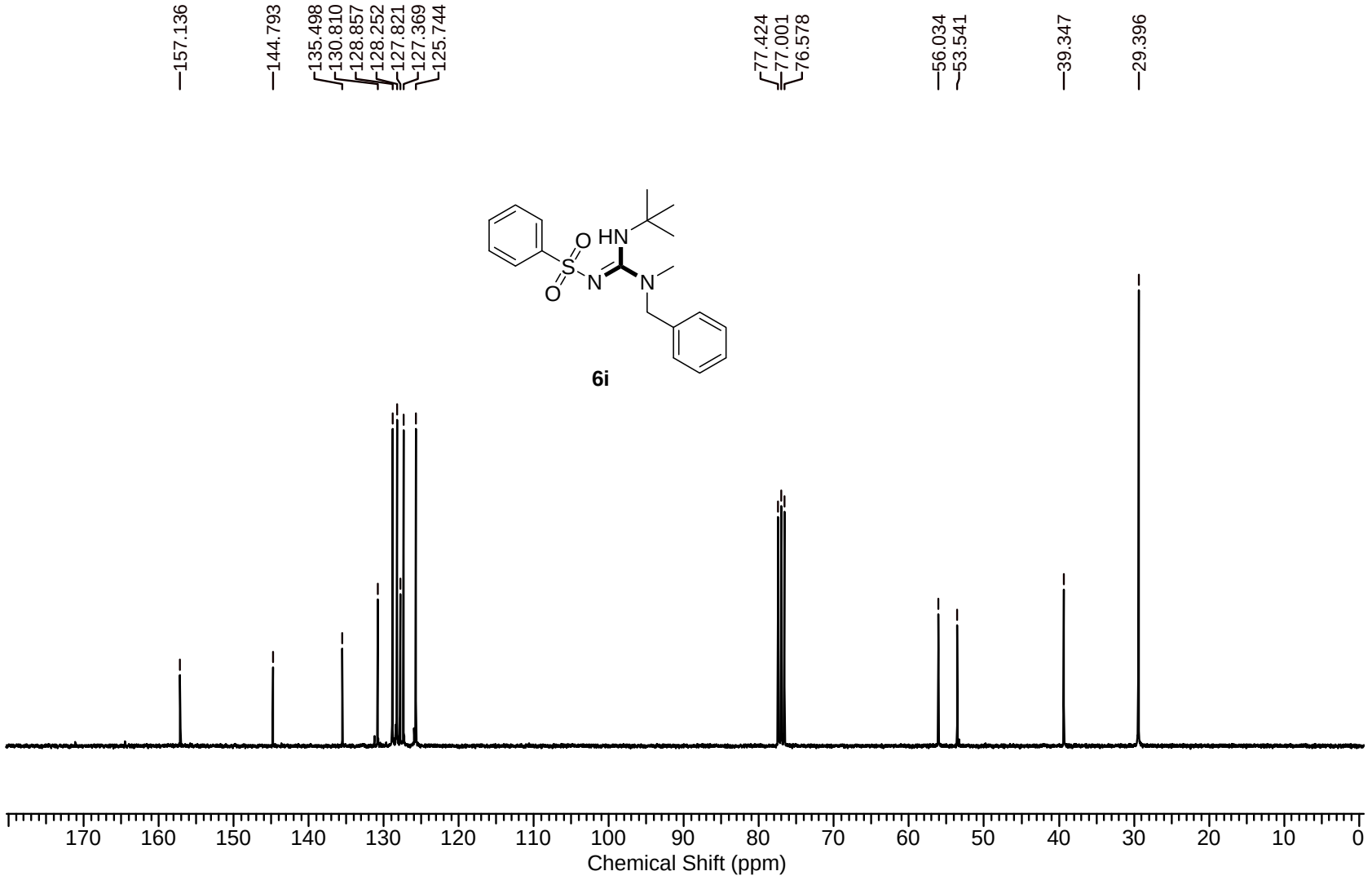

7.911
7.903
7.891
7.884
7.880
7.414
7.405
7.393
4.506
3.629
3.609
3.589
1.969
1.960
1.940
1.919
1.898
1.096
O
HN
S
N
N
O
6g
1.97
3.02
0.91
4.00
4.37
9.03
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

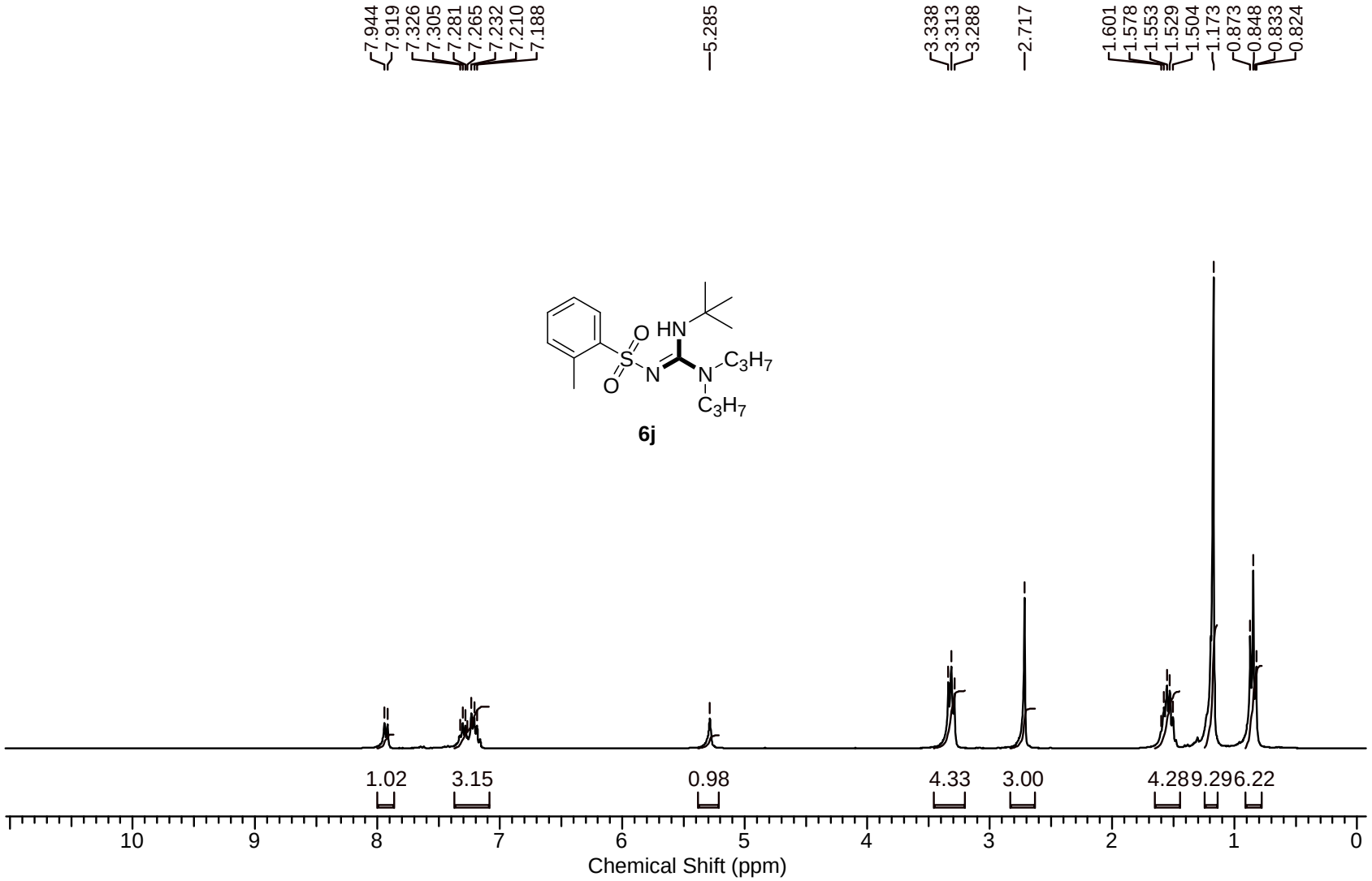

152.450
145.561
130.397
128.123
125.506
77.419
77.193
76.996
76.566
52.640
49.658
29.267
25.360
O
HN
S
O
N
N
6g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.918
7.913
7.906
7.895
7.886
7.462
7.457
7.448
7.438
7.426
7.266
5.124
3.800
3.786
3.770
3.527
3.511
3.496
1.161
-0.011
HN
O
S
O
N
N
O
6h
2.02
3.05
0.93
3.99
4.00
9.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

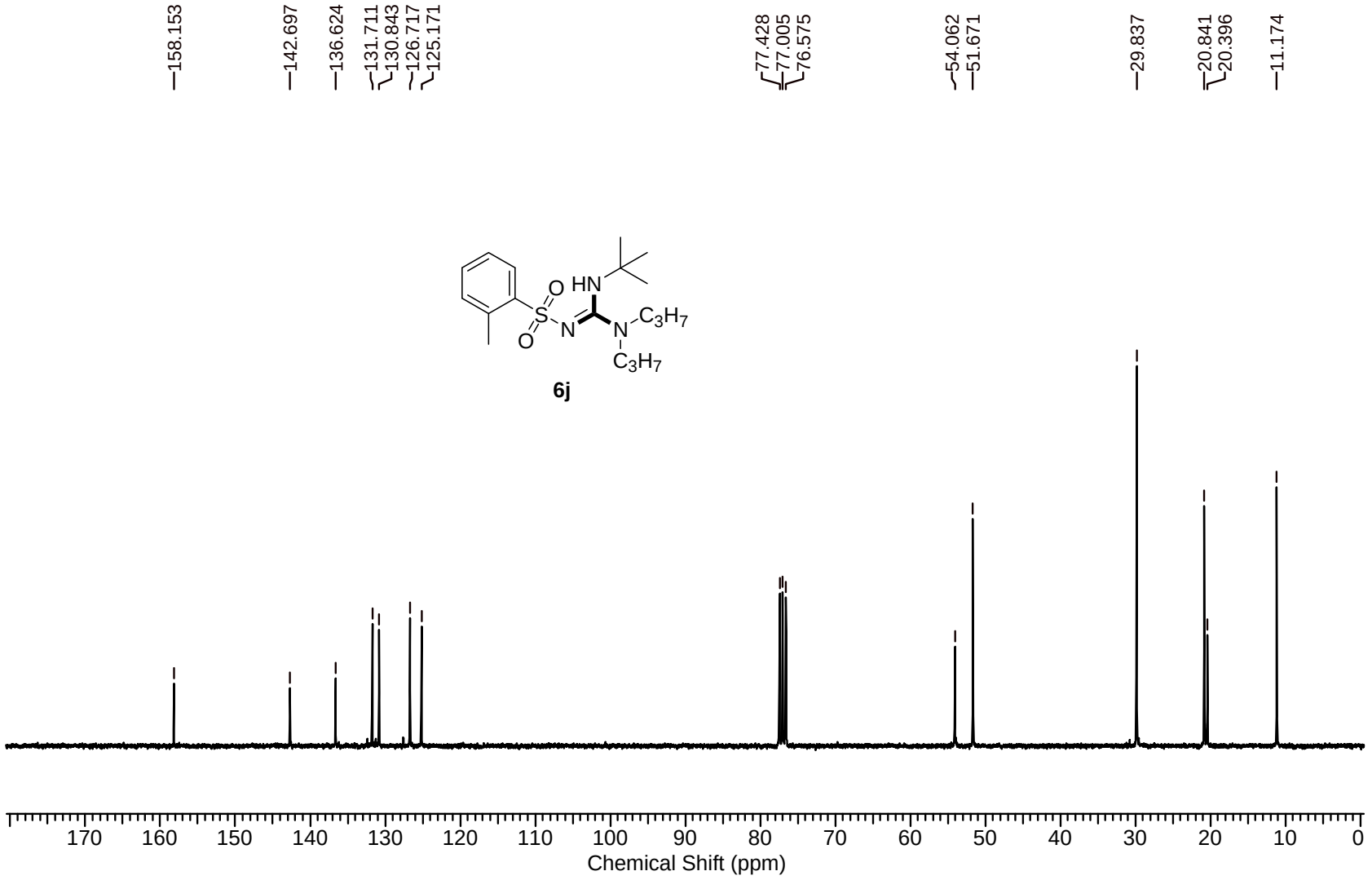

157.438
144.206
131.186
128.423
125.886
77.420
76.997
76.574
66.230
54.099
49.243
29.633
O
HN
S
O
N
N
O
6h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

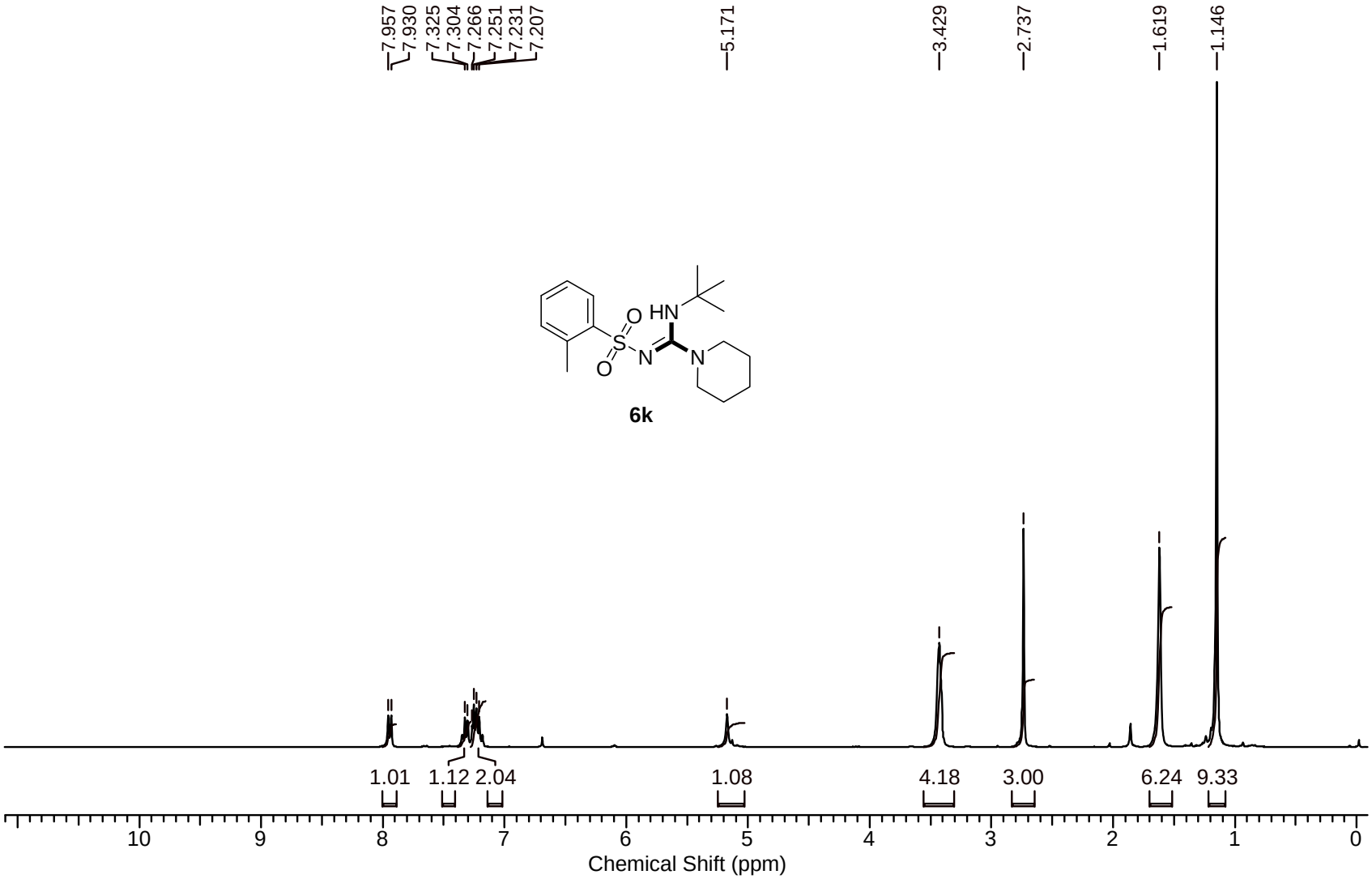

7.929
7.923
7.910
7.898
7.432
7.426
7.414
7.339
7.314
7.275
7.243
7.218
4.991
4.589
3.063
1.054
HN
O
S
O
N
N
6i
2.09 3.12 3.10 2.05
0.97 2.03
3.00
8.94
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

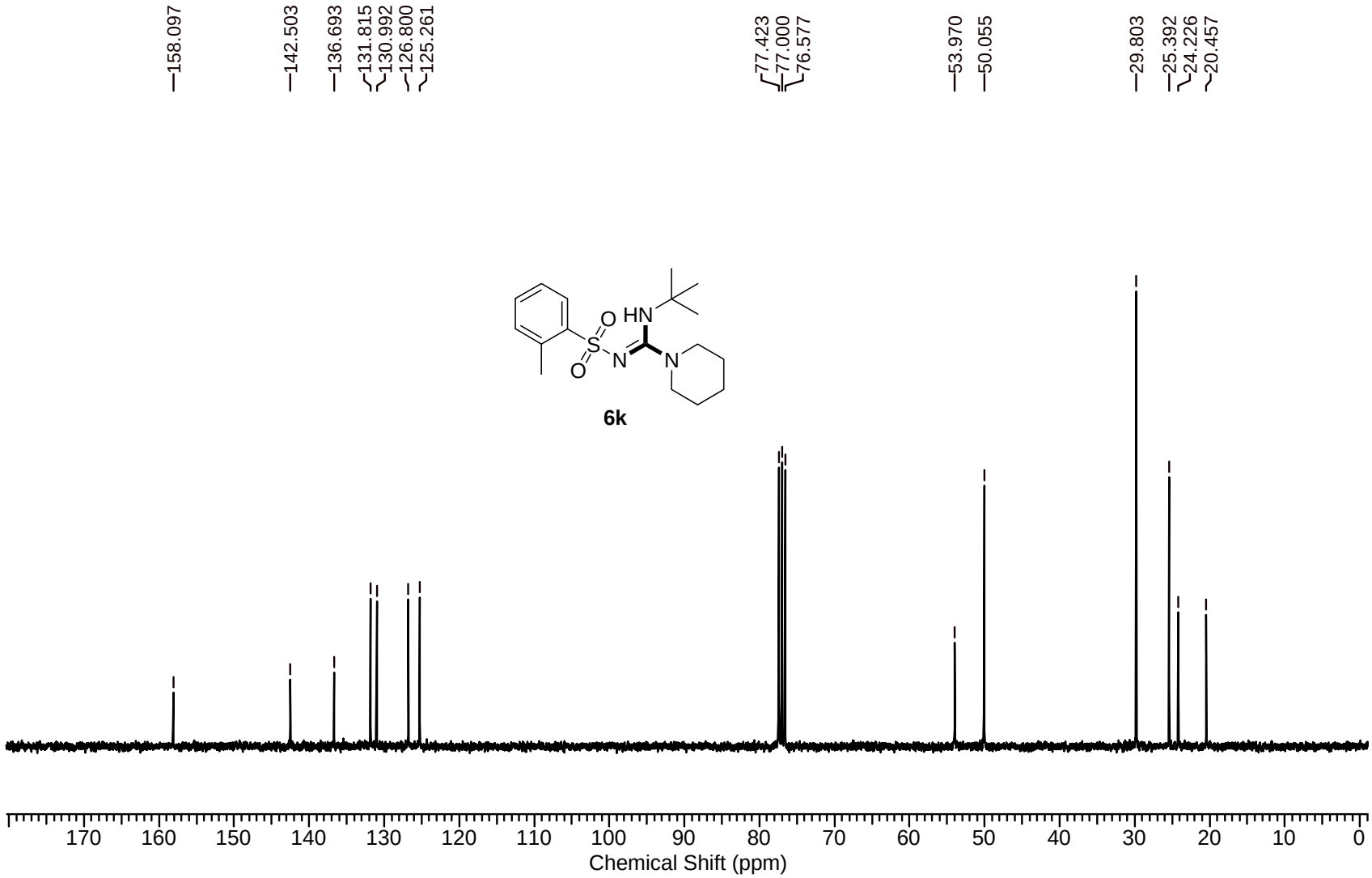

157.136
144.793
135.498
130.810
128.857
128.252
127.821
127.369
125.744
77.424
77.001
76.578
56.034
53.541
39.347
29.396
O
HN
S
O
N
N
6i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

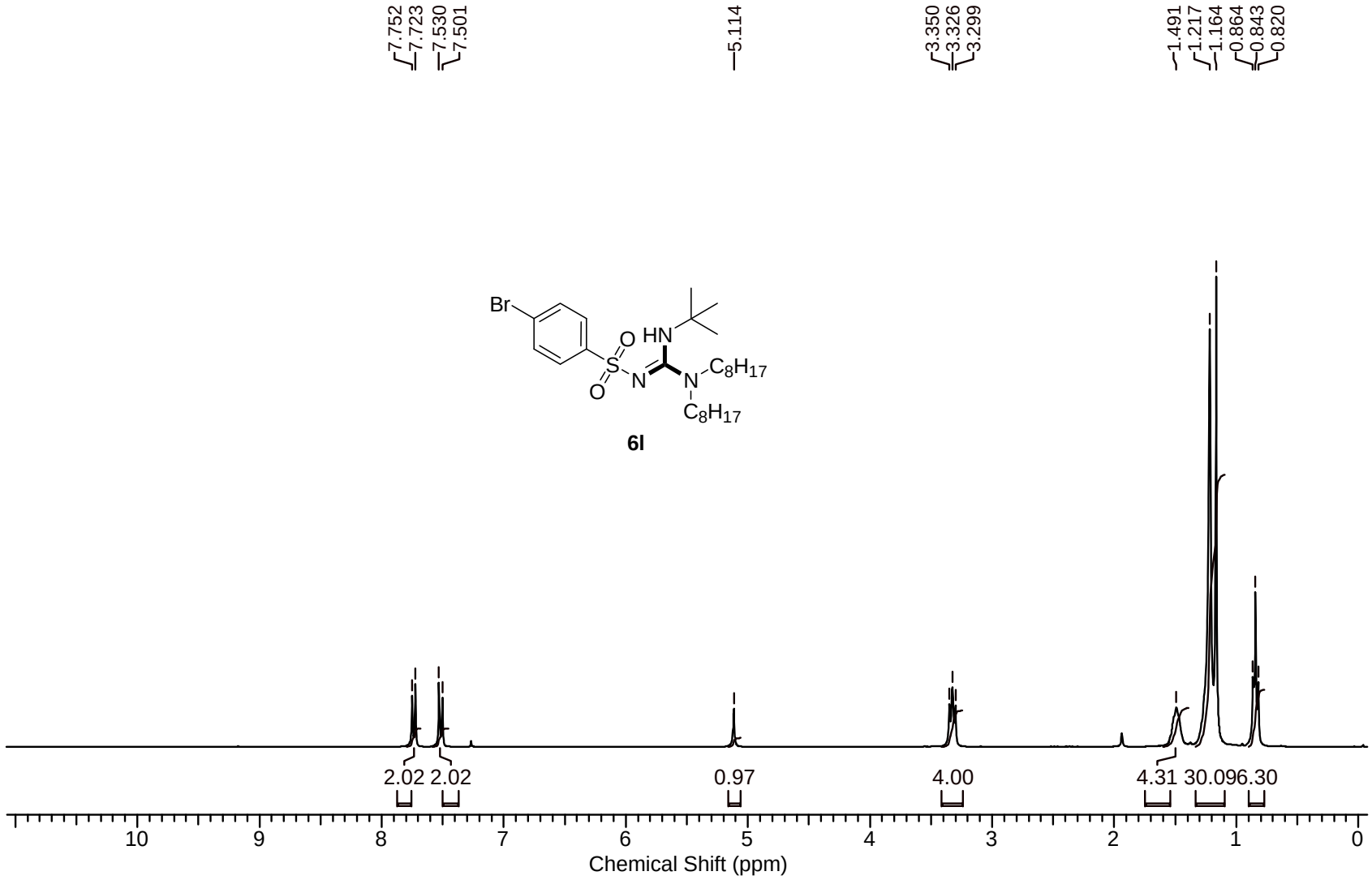

7.944
7.919
7.326
7.305
7.281
7.265
7.232
7.210
7.188
5.285
3.338
3.313
3.288
2.717
1.601
1.578
1.553
1.529
1.504
1.173
0.873
0.848
0.833
0.824
HN
O
S
O
N
N
C3H7
C3H7
1.02
3.15
0.98
4.33
3.00
4.28
9.29
6.22
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

6j

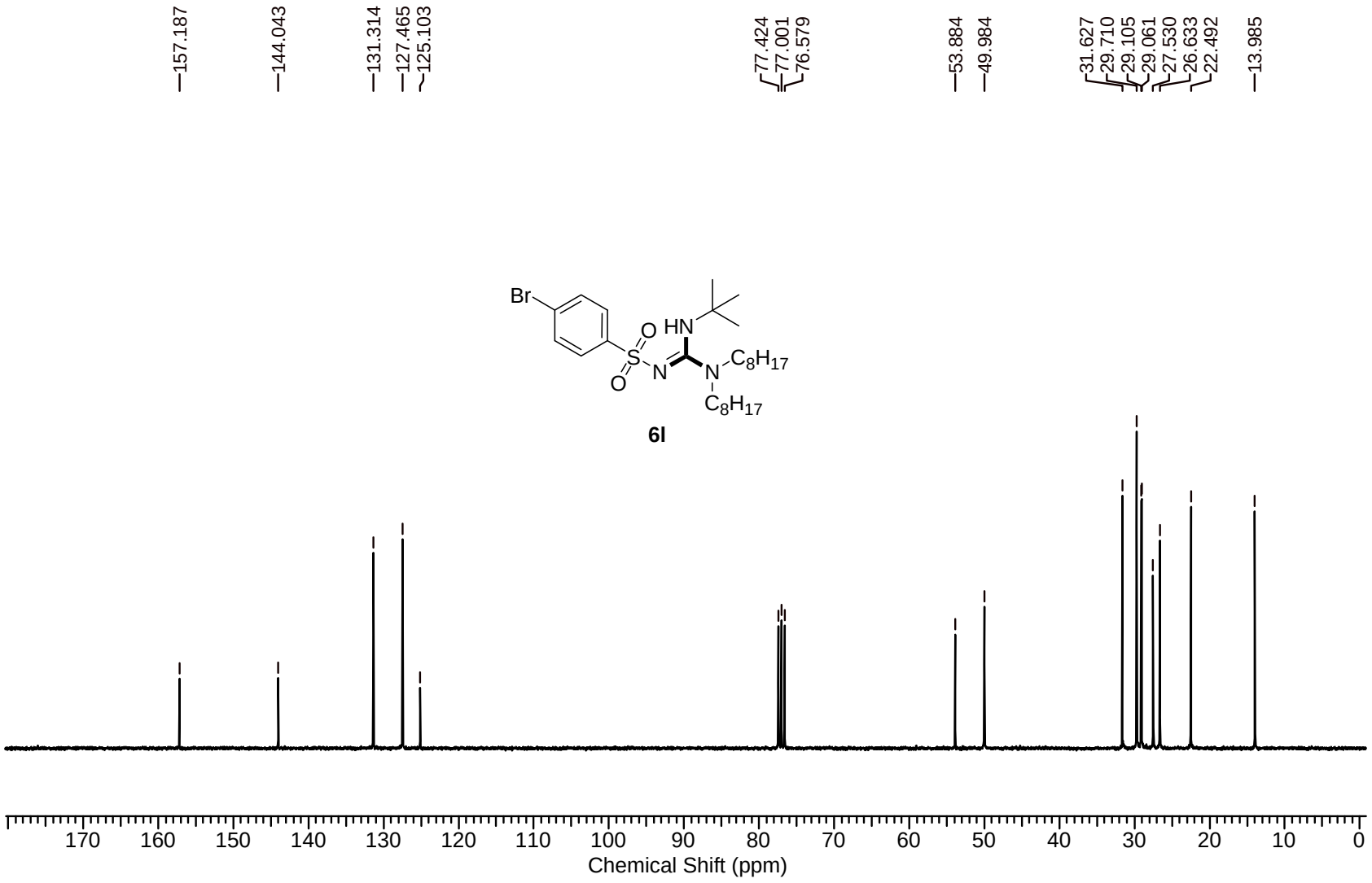

158.153
142.697
136.624
131.711
130.843
126.717
125.171
77.428
77.005
76.575
54.062
51.671
29.837
20.841
20.396
11.174
HN
O
S
O
N
N
C3H7
C3H7
6j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.957
7.930
7.325
7.304
7.266
7.251
7.231
7.207
5.171
3.429
2.737
1.619
1.146
HN
O
S
O
N
N
6k
1.01
1.12
2.04
1.08
4.18
3.00
6.24
9.33
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

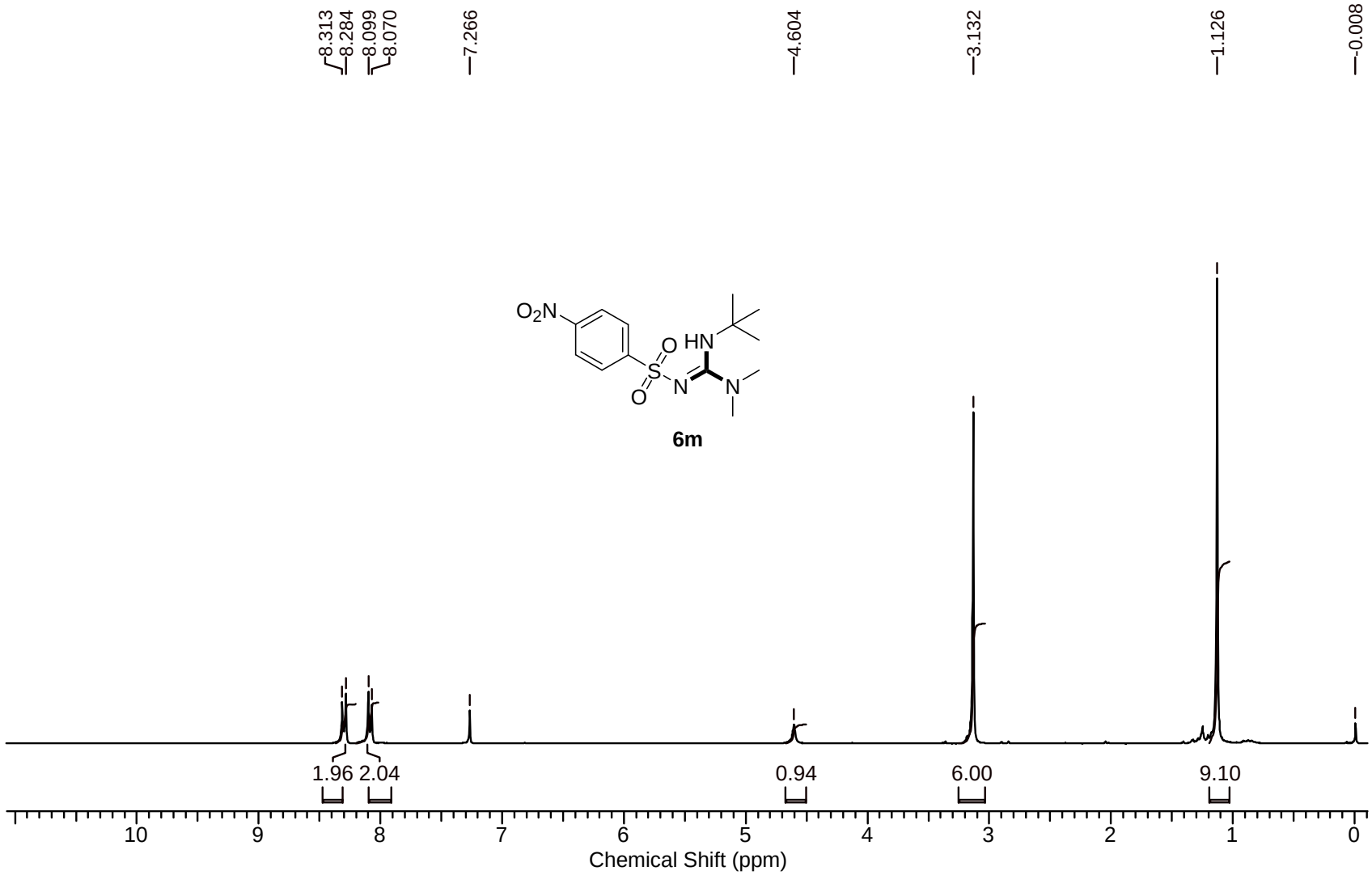

158.097
142.503
136.693
131.815
130.992
126.800
125.261
77.423
77.000
76.577
53.970
50.055
29.803
25.392
24.226
20.457
O
HN
S
O
N
N
6k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

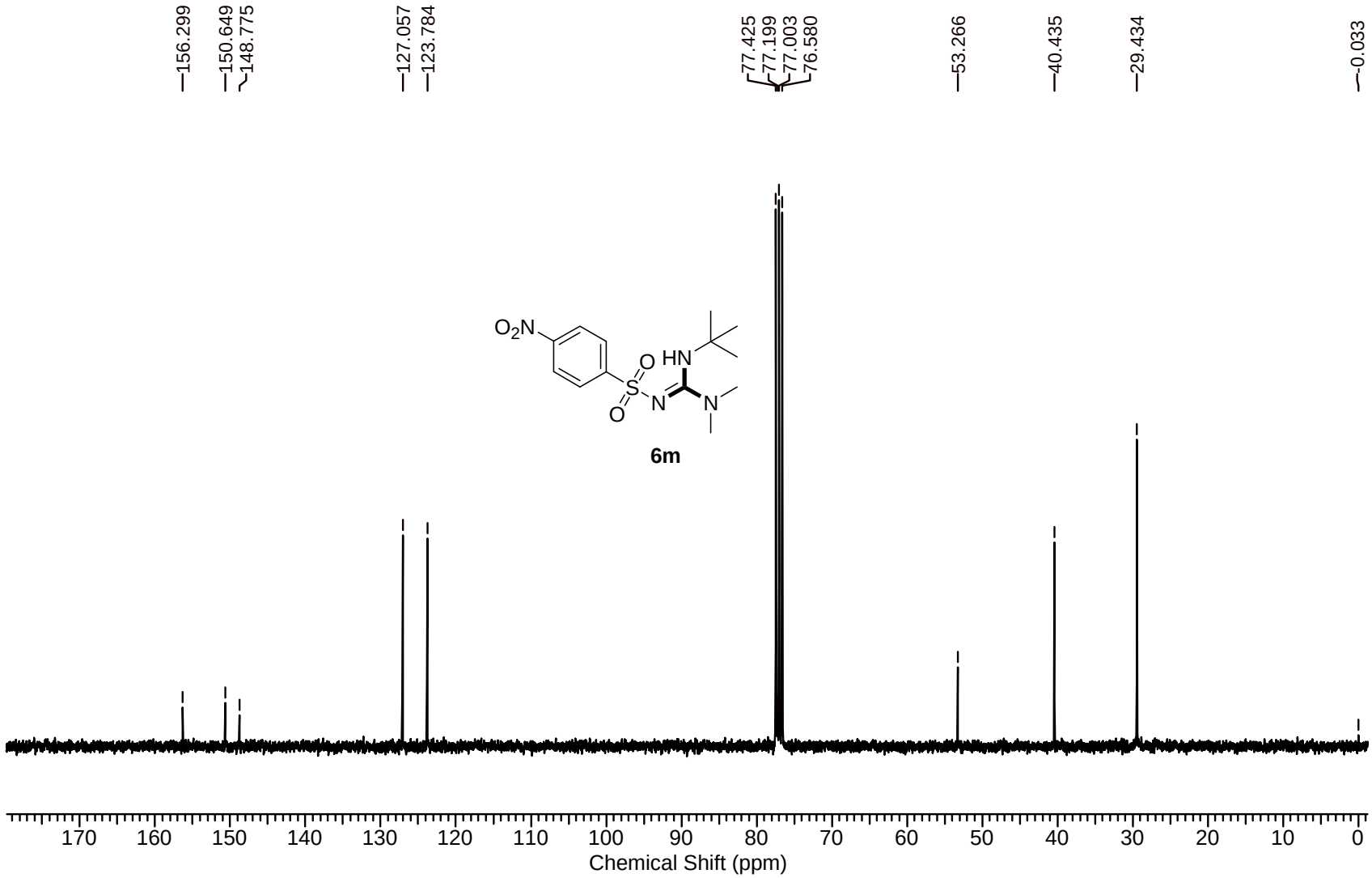

7.752
7.723
7.530
7.501
5.114
3.350
3.326
3.299
1.491
1.217
1.164
0.864
0.843
0.820
Br
O
HN
S
O
N
N
C_8H_{17}
C_8H_{17}
2.02
2.02
0.97
4.00
4.31
30.09
6.30
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

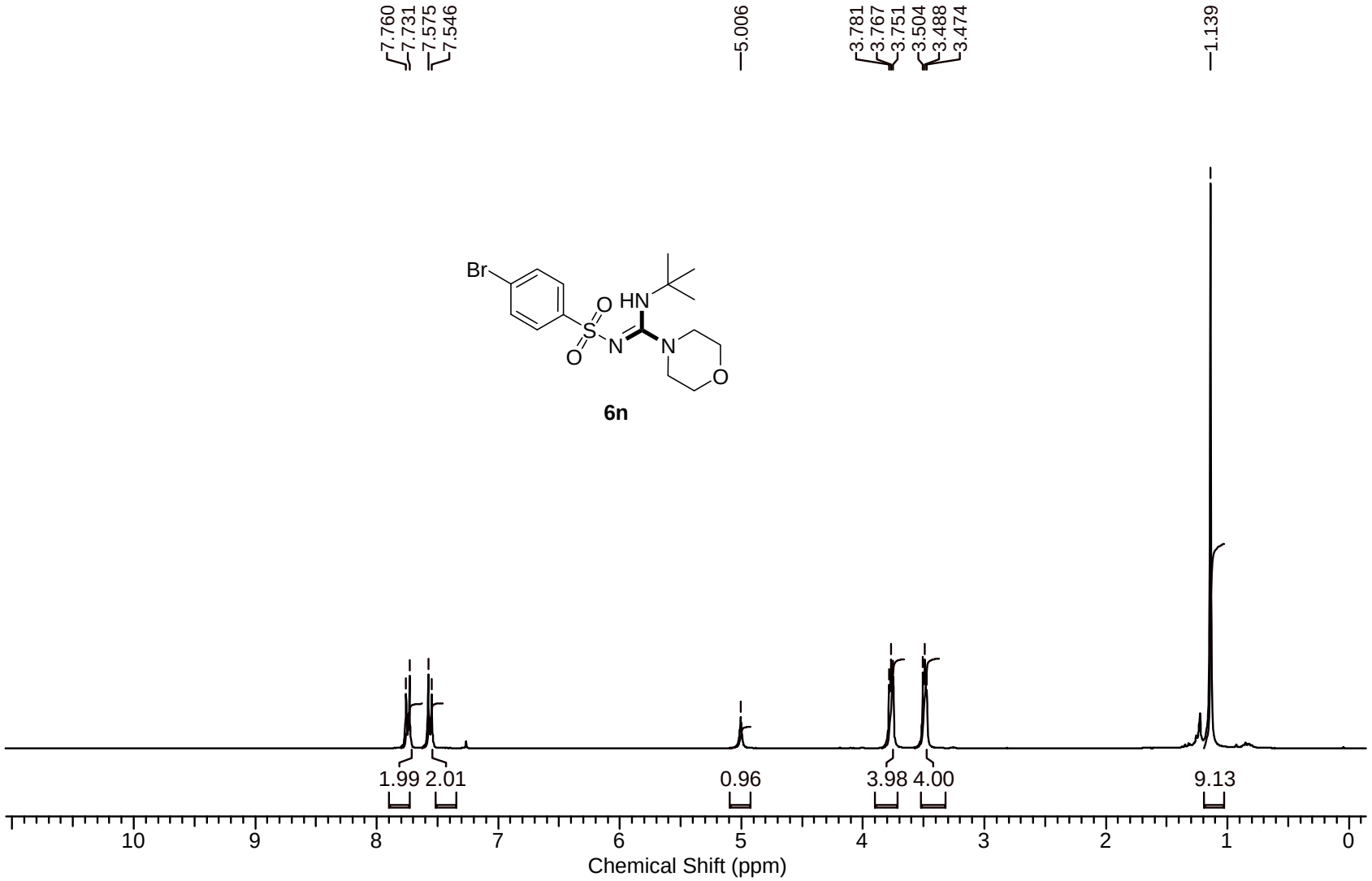
6l


157.187
144.043
131.314
127.465
125.103
77.424
77.001
76.579
53.884
49.984
31.627
29.710
29.105
29.061
27.530
26.633
22.492
13.985
Br
O
HN
S
N
N
C_8H_{17}
O
C_8H_{17}
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

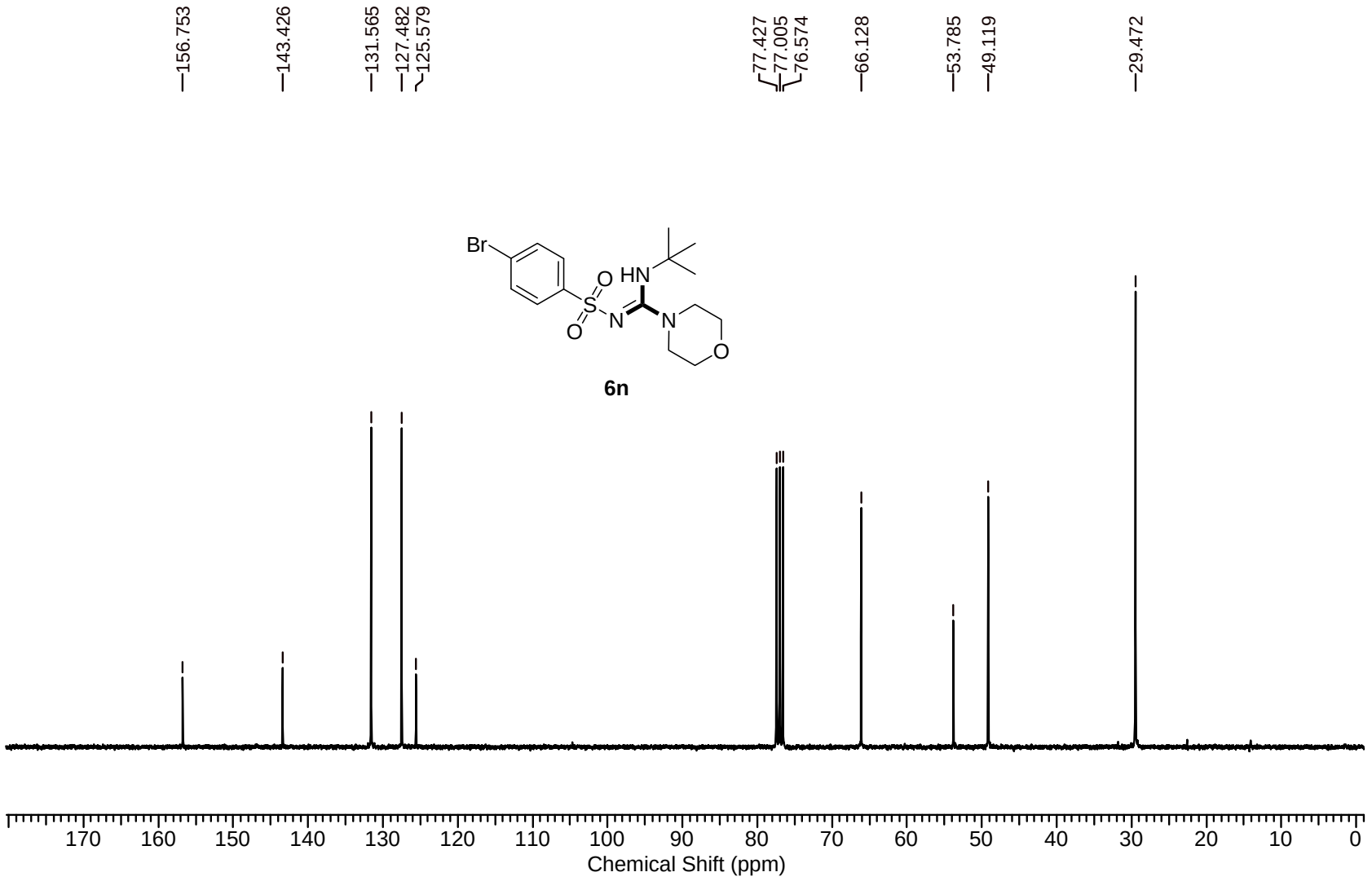
6l

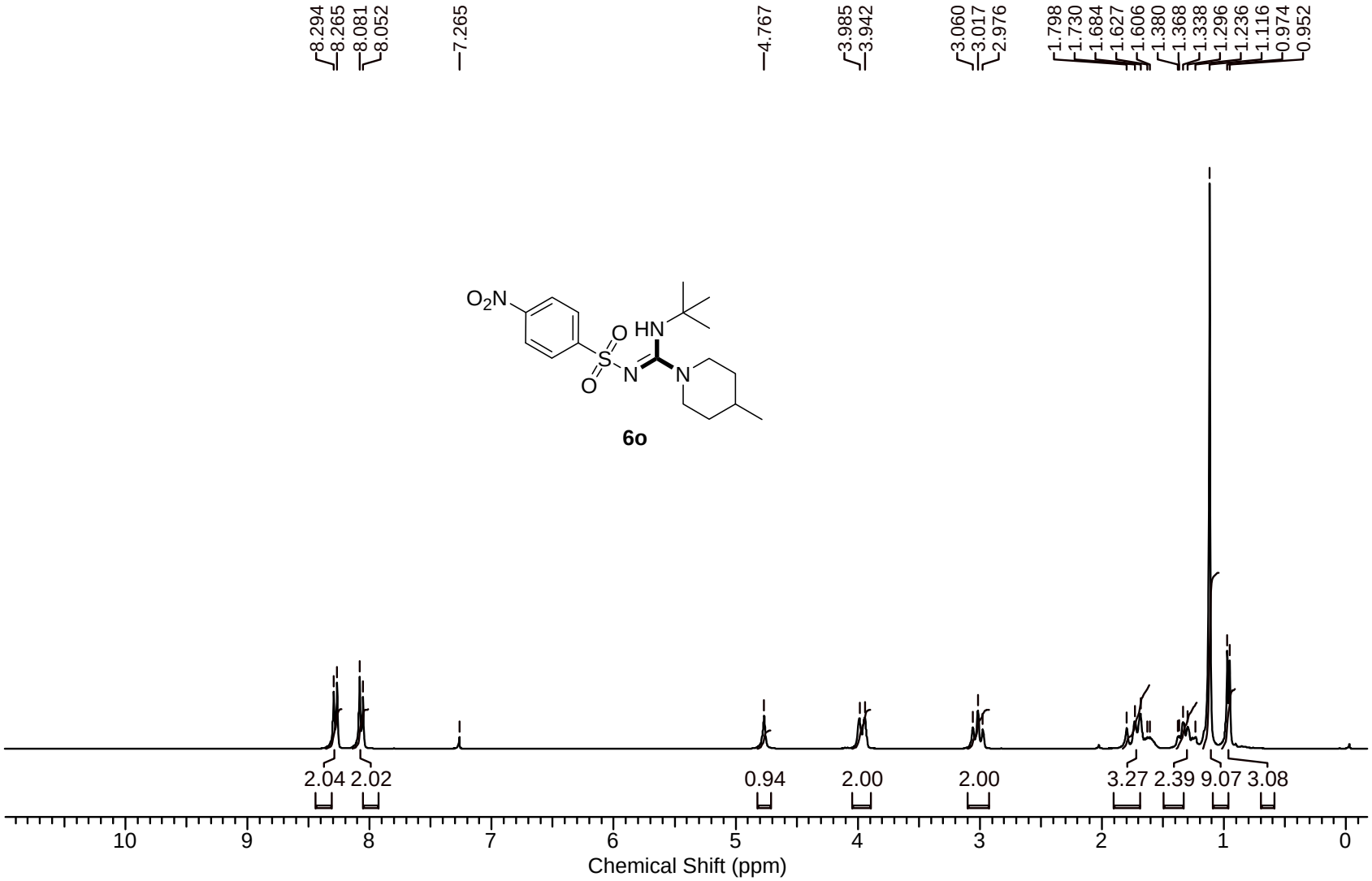

8.313
8.284
8.099
8.070
7.266
4.604
3.132
1.126
0.008
O2N
O
HN
S
O
N
N
6m
1.96
2.04
0.94
6.00
9.10
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

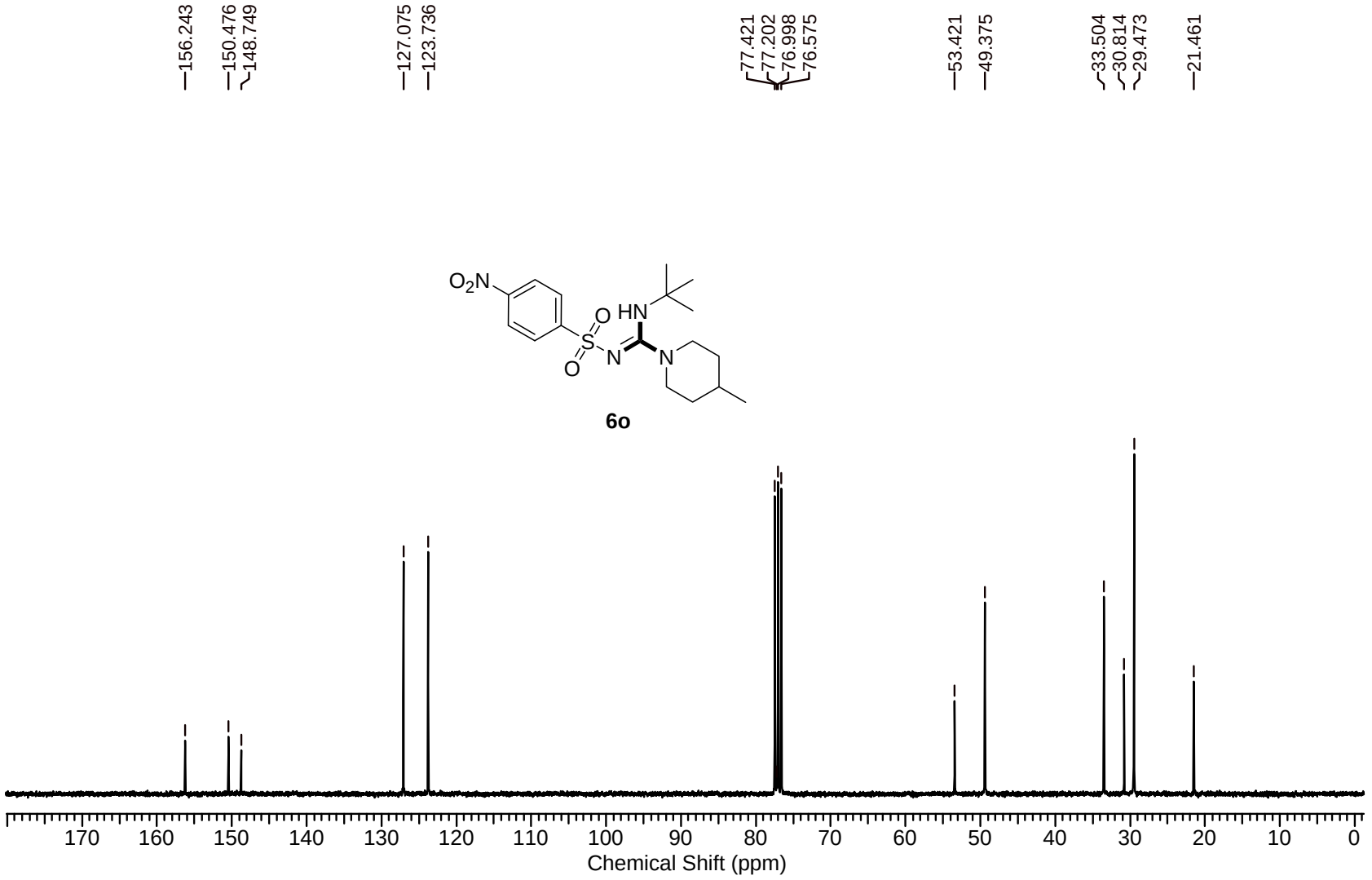

156.299
150.649
148.775
127.057
123.784
77.425
77.199
77.003
76.580
53.266
40.435
29.434
-0.033
O2N
O
HN
S
O
N
N
6m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

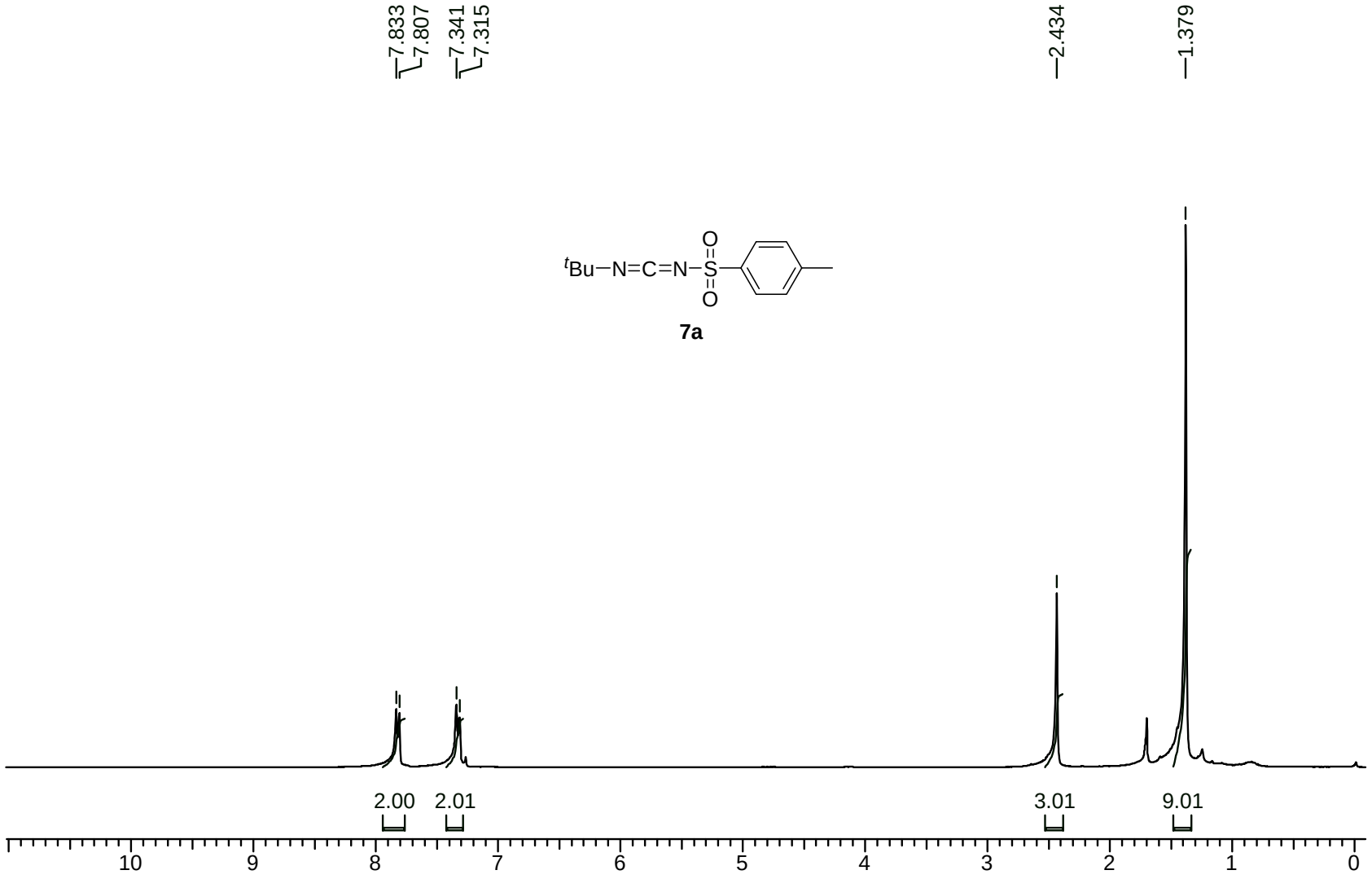

7.760
7.731
7.575
7.546
5.006
3.781
3.767
3.751
3.504
3.488
3.474
1.139
Br
O
HN
S
O
N
N
O
1.99
2.01
0.96
3.98
4.00
9.13
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

6n

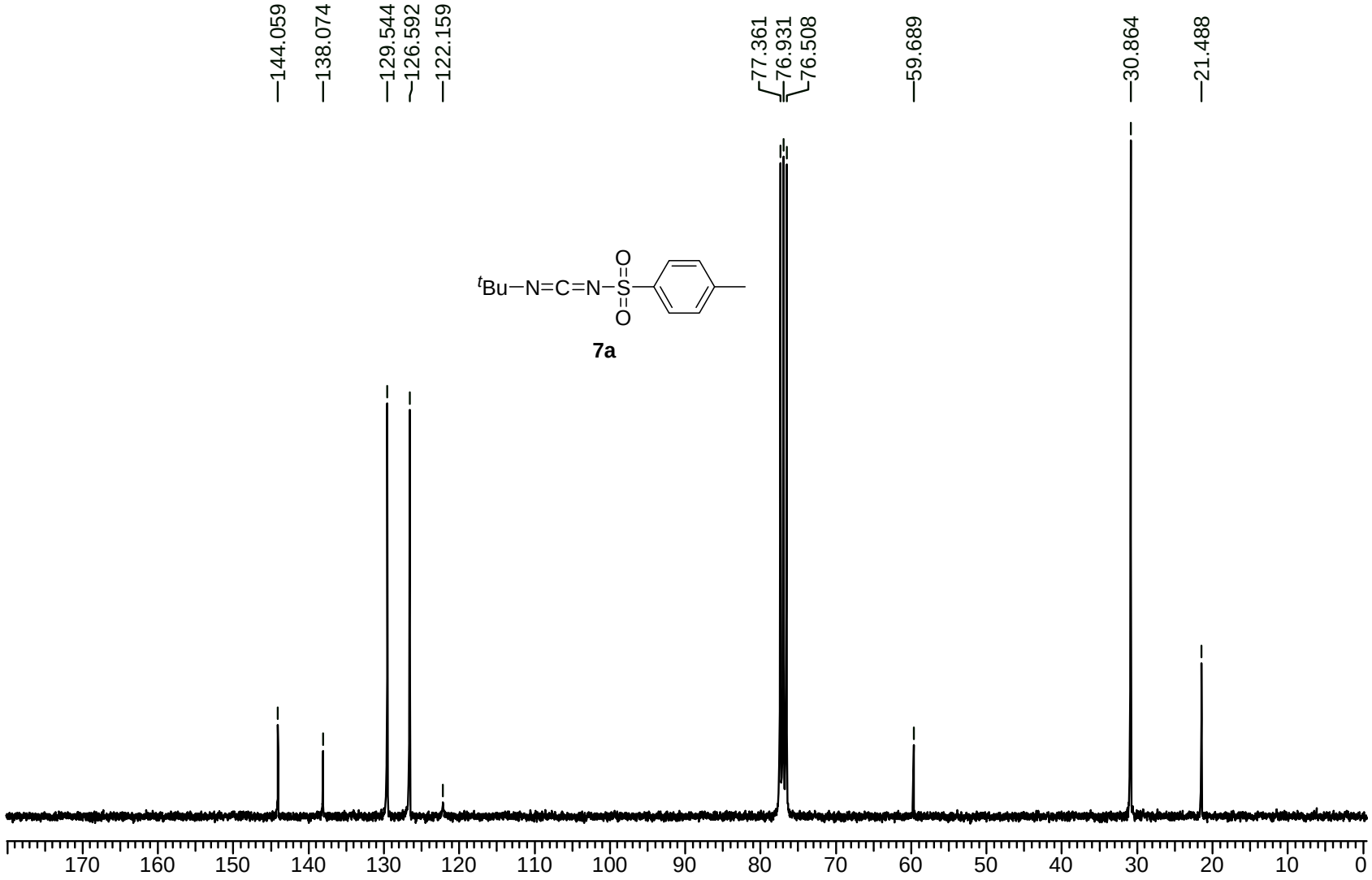

156.753
143.426
131.565
127.482
125.579
77.427
77.005
76.574
66.128
53.785
49.119
29.472
Br
O
HN
S
O
N
N
O
6n
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

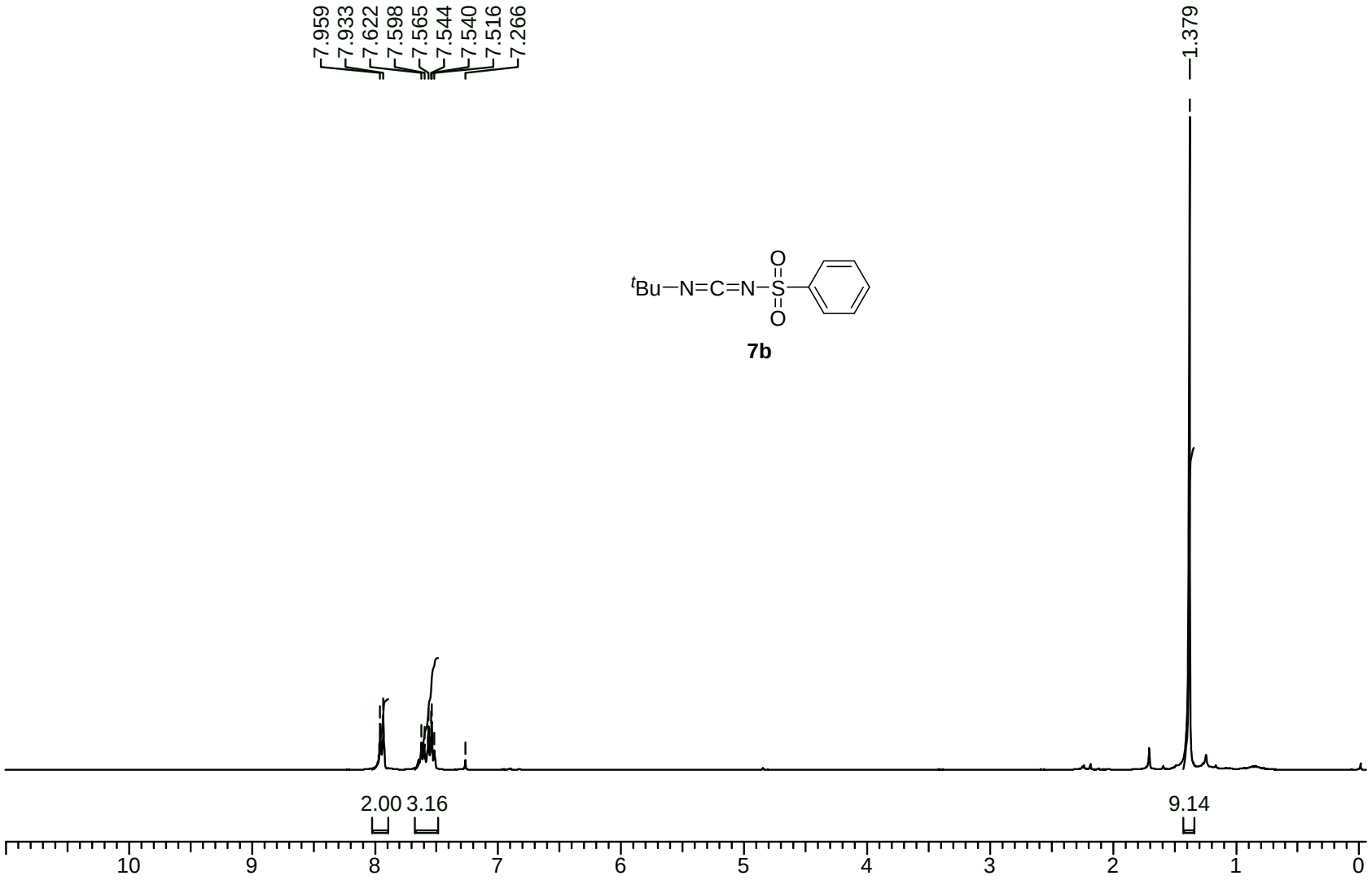

8.294
8.265
8.081
8.052
7.265
4.767
3.985
3.942
3.060
3.017
2.976
1.798
1.730
1.684
1.627
1.606
1.380
1.368
1.338
1.296
1.236
1.116
0.974
0.952
O2N
O
HN
S
N
O
N
6o
2.04 2.02
0.94
2.00
2.00
3.27 2.39 9.07 3.08
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

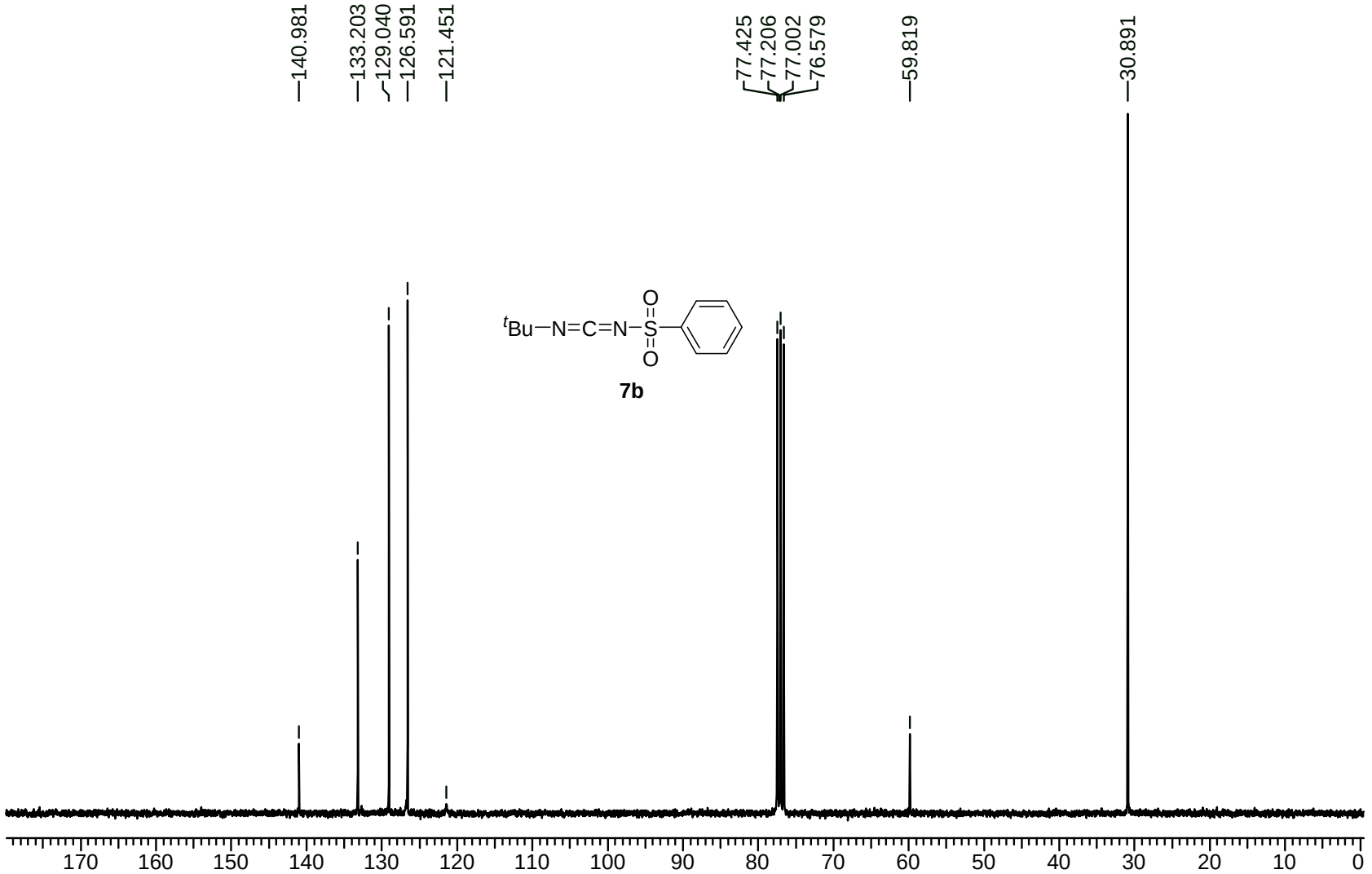

156.243
150.476
148.749
127.075
123.736
77.421
77.202
76.998
76.575
53.421
49.375
33.504
30.814
29.473
21.461
O2N
O
HN
S
O
N
N
6o
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

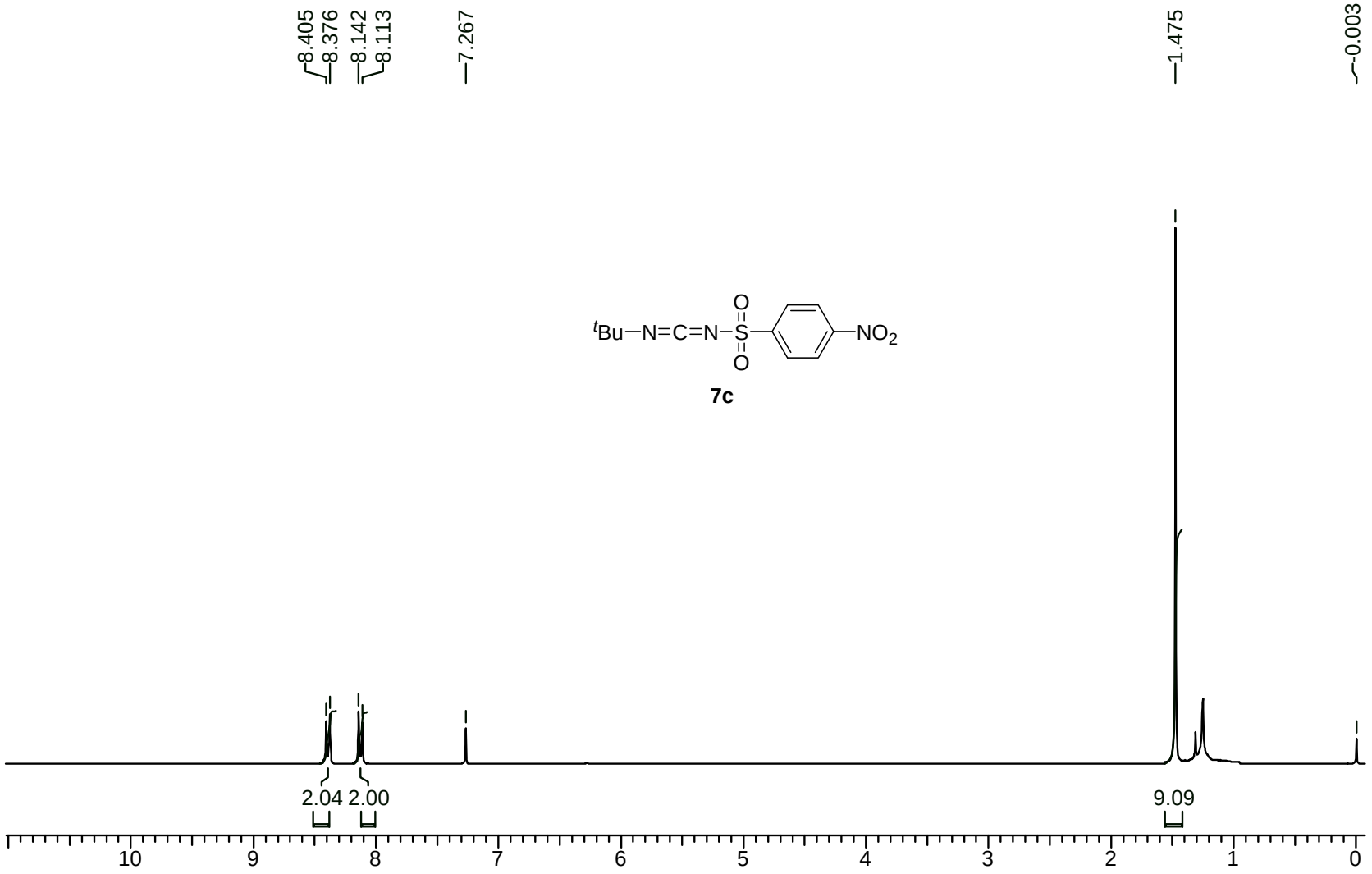

7.833
7.807
7.341
7.315
2.434
1.379
tBu–N=C=N–S
O
O
2.00
2.01
3.01
9.01
10
9
8
7
6
5
4
3
2
1
0

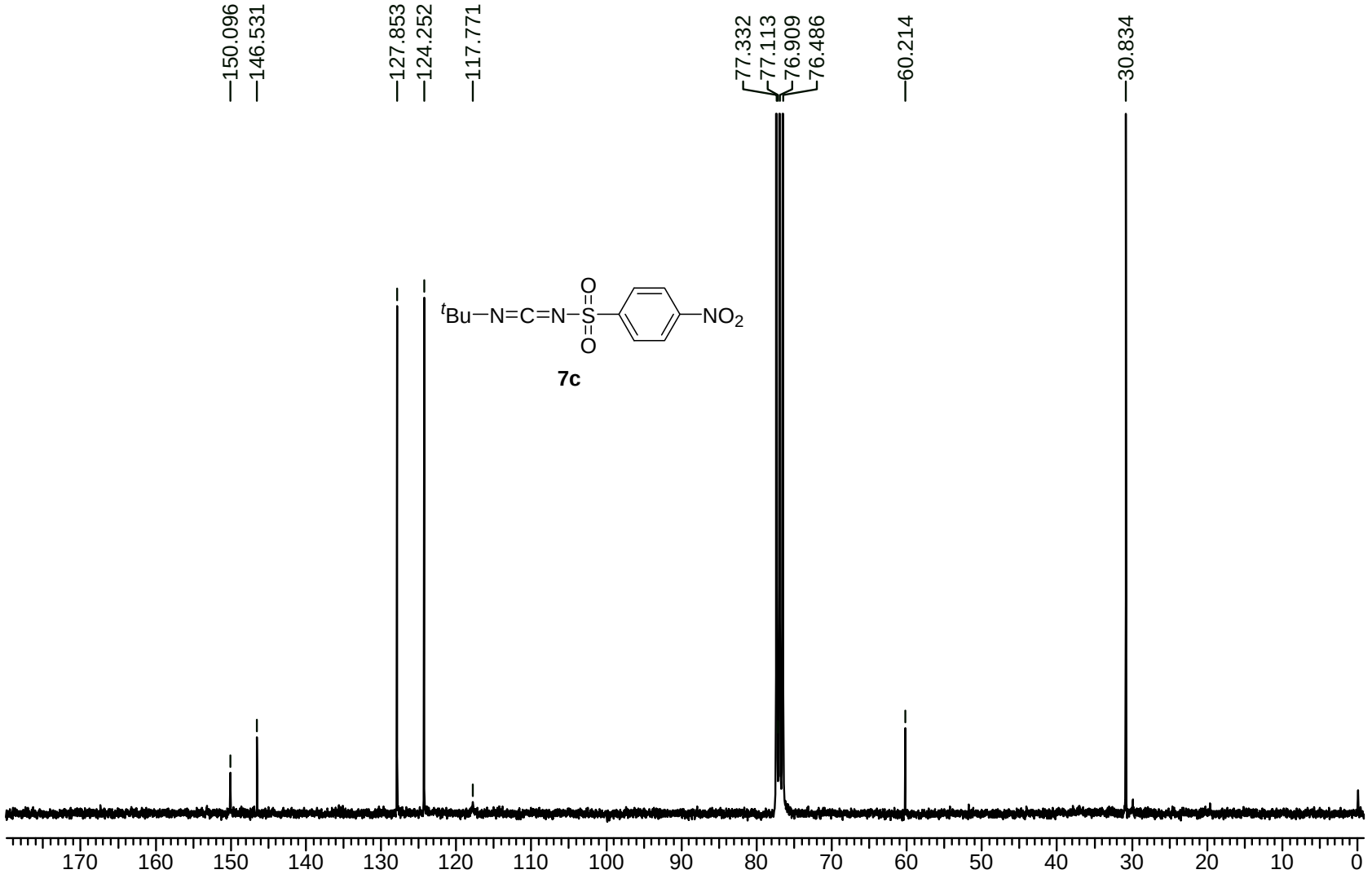
7a

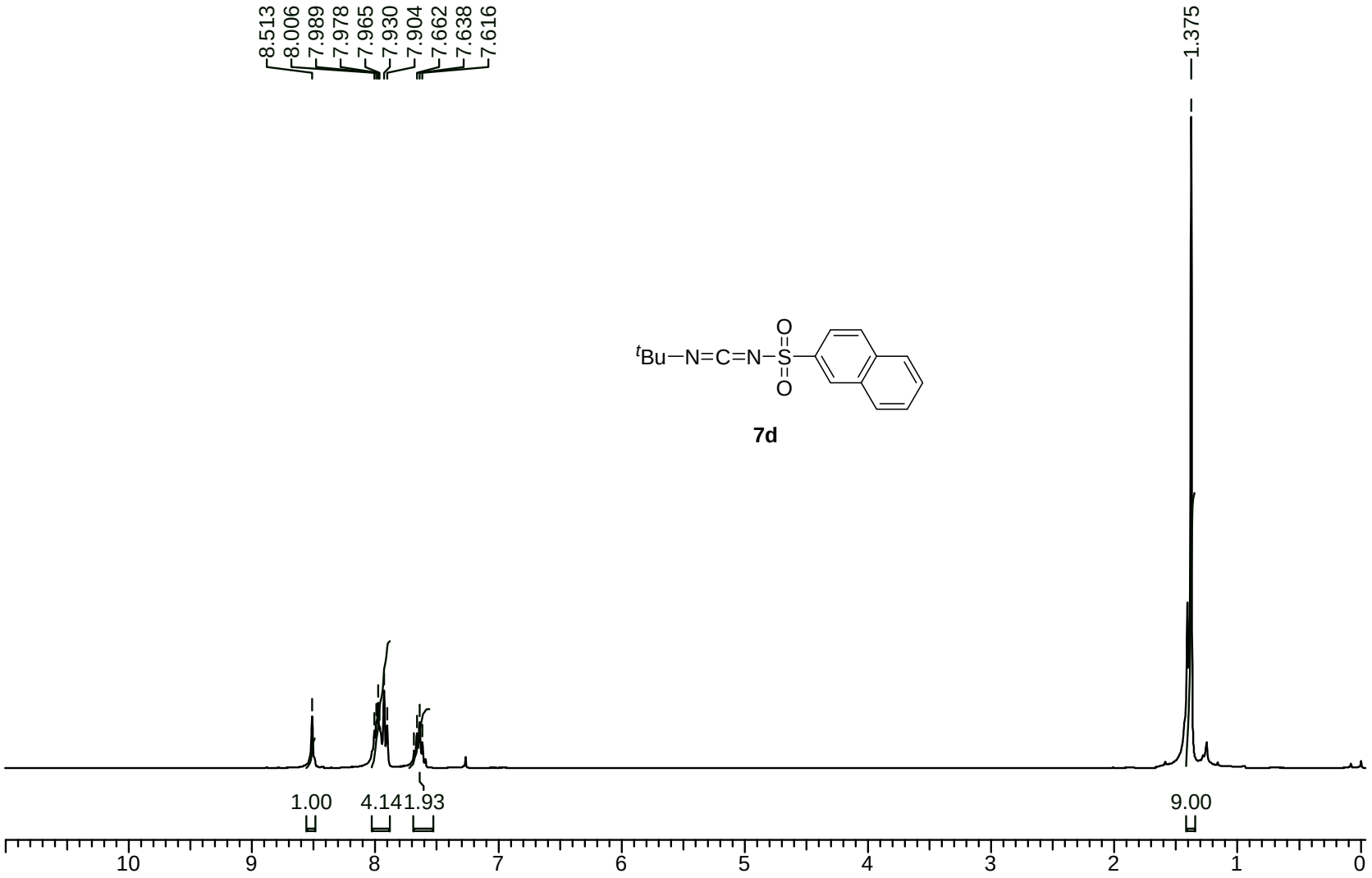

144.059
138.074
129.544
126.592
122.159
77.361
76.931
76.508
59.689
30.864
21.488
tBu–N=C=N–S(=O)(=O)–
7a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

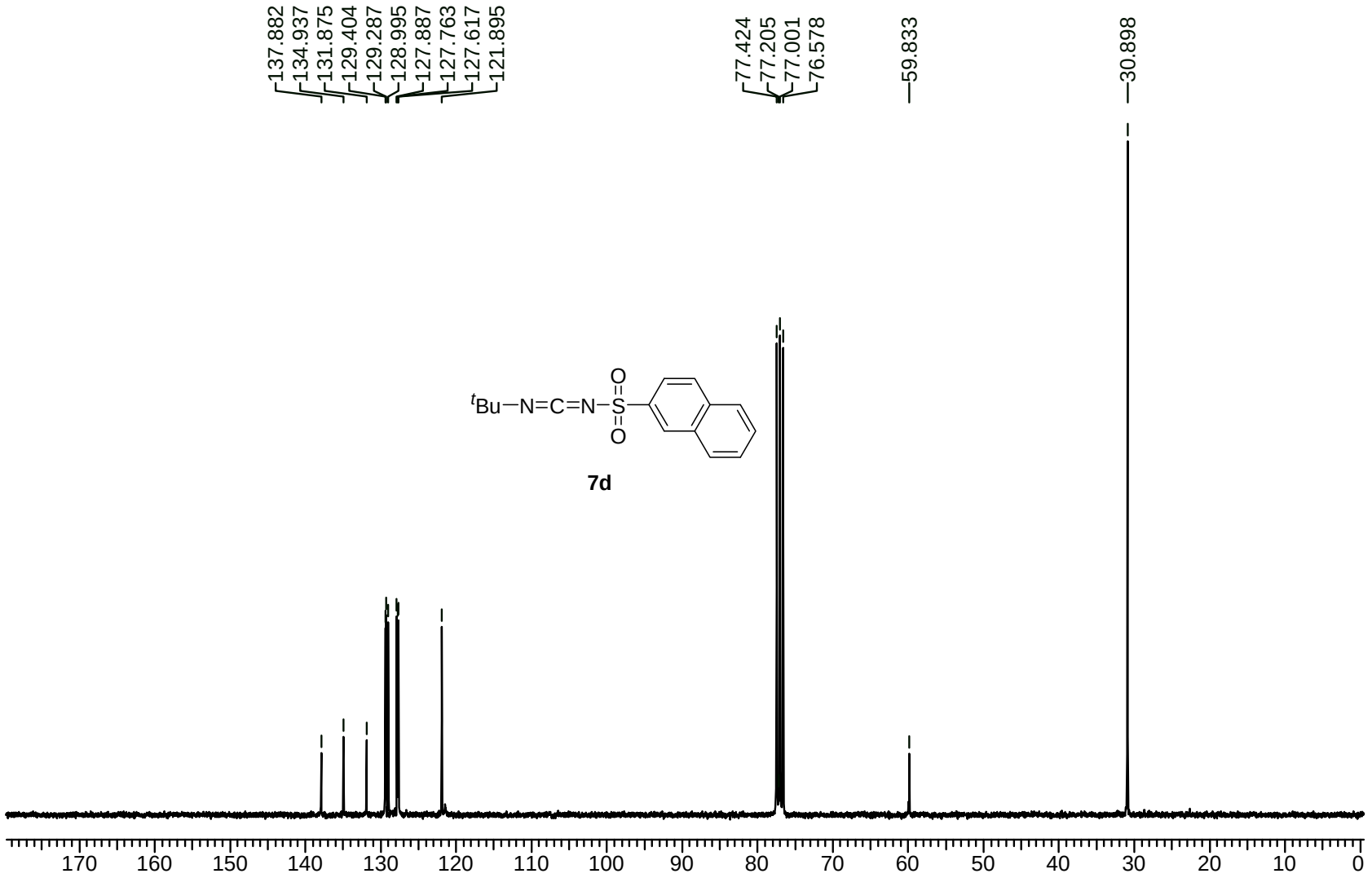

7.959
7.933
7.622
7.598
7.565
7.544
7.540
7.516
7.266
1.379
tBu—N=C=N—S(=O)(=O)—
7b
2.00
3.16
9.14
10
9
8
7
6
5
4
3
2
1
0

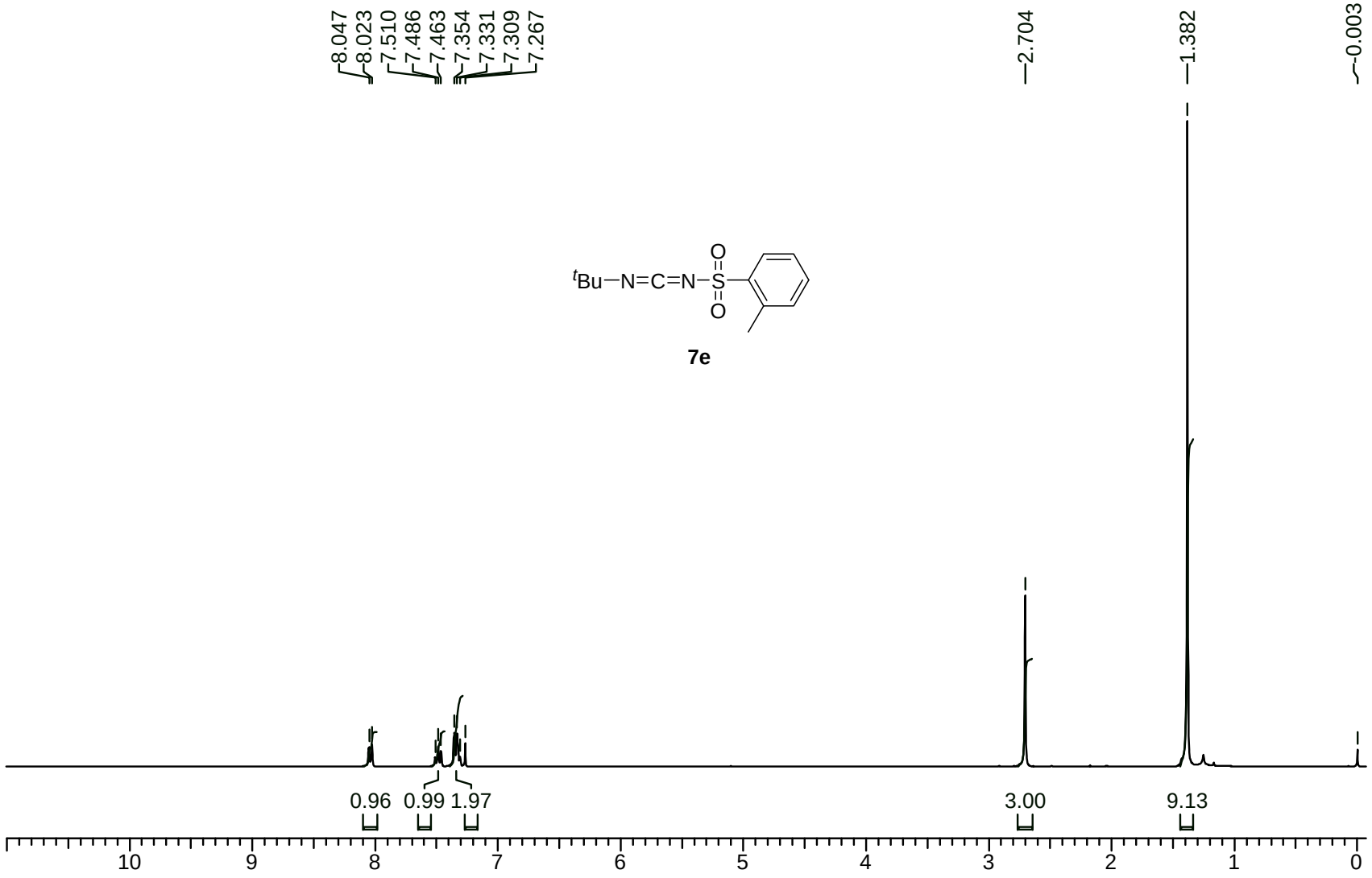

140.981
133.203
129.040
126.591
121.451
77.425
77.206
77.002
76.579
59.819
30.891
tBu—N=C=N—S(=O)(=O)—C6H5
7b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

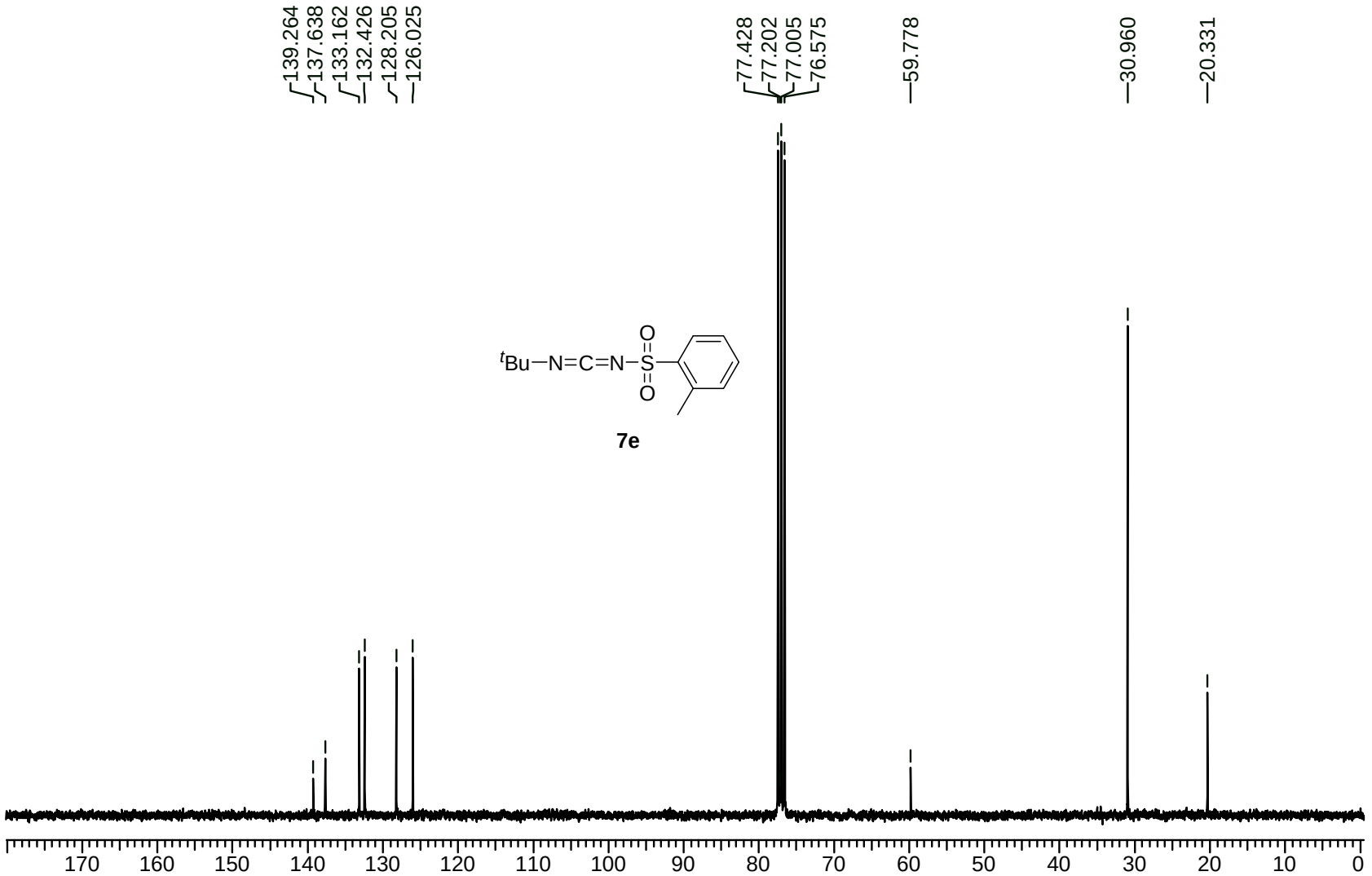

8.405
8.376
8.142
8.113
7.267
1.475
0.003
O
tBu—N=C=N—S
O
NO2
7c
2.04
2.00
9.09
10
9
8
7
6
5
4
3
2
1
0

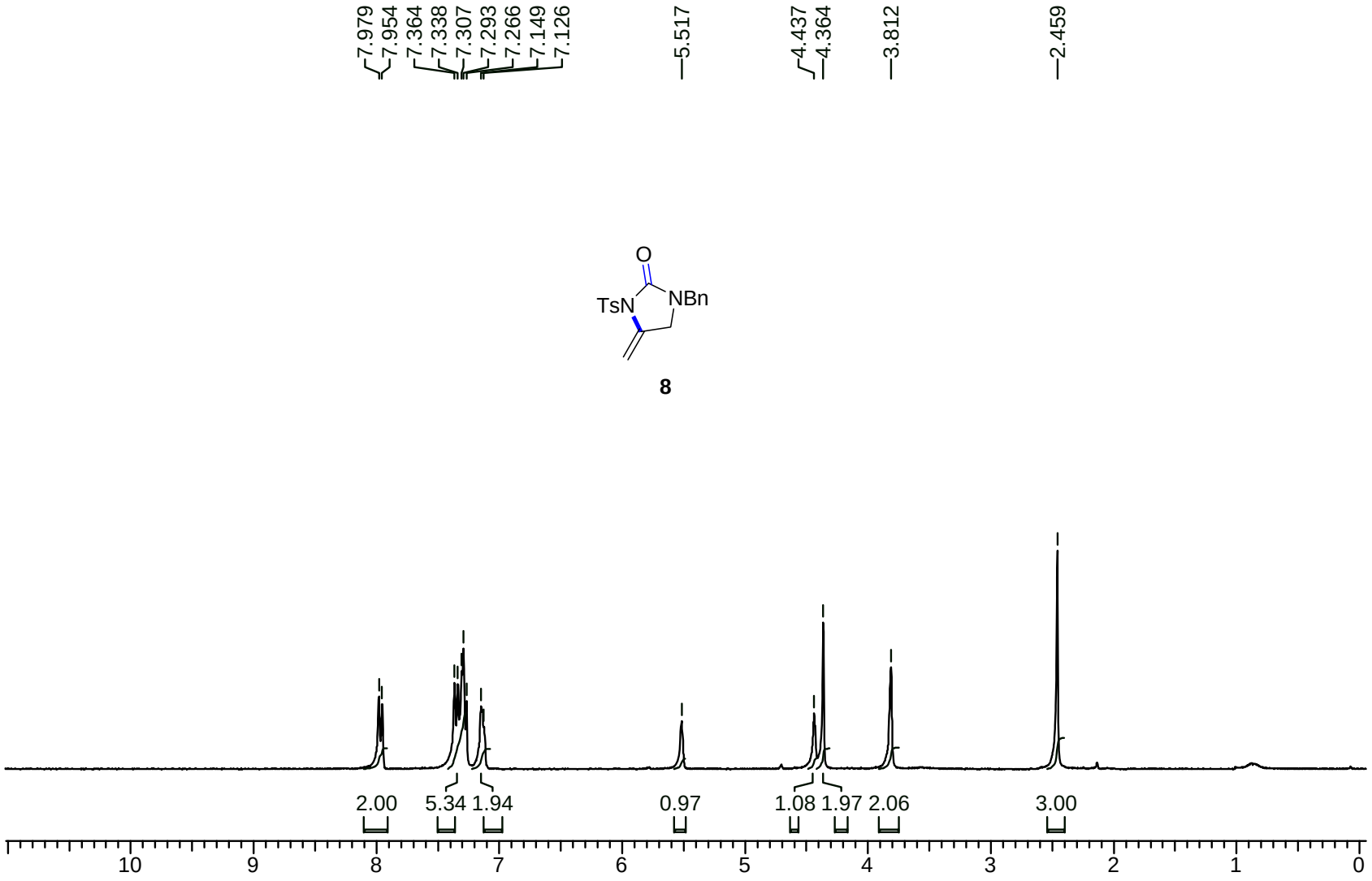

150.096
146.531
127.853
124.252
117.771
77.332
77.113
76.909
76.486
60.214
30.834
tBu—N=C=N—S(=O)(=O)—C6H4—NO2
7c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.513
8.006
7.989
7.978
7.965
7.930
7.904
7.662
7.638
7.616
1.375
tBu—N=C=N—S(=O)(=O)
7d
1.00
4.14
1.93
9.00
10
9
8
7
6
5
4
3
2
1
0

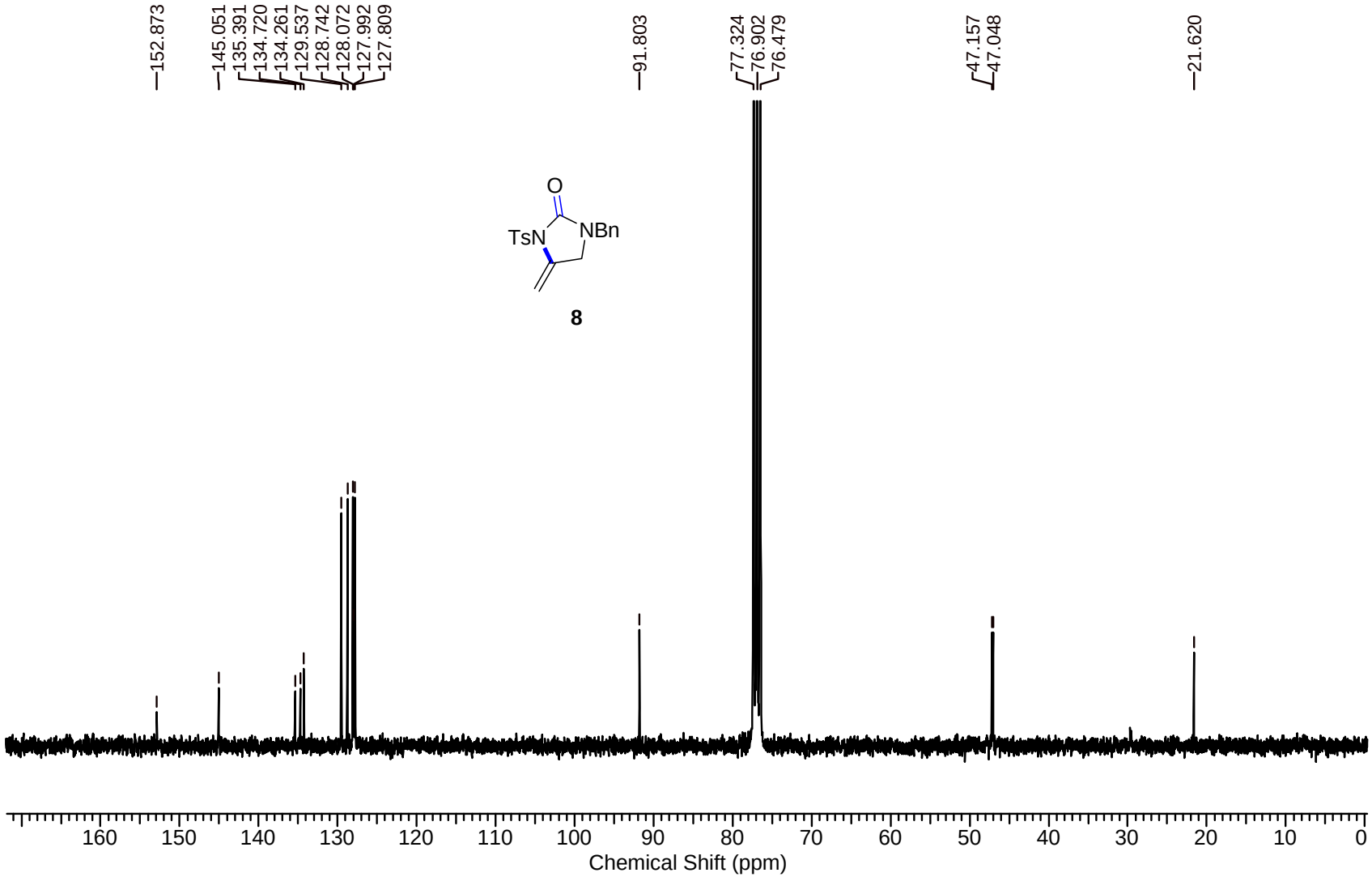

137.882
134.937
131.875
129.404
129.287
128.995
127.887
127.763
127.617
121.895
77.424
77.205
77.001
76.578
59.833
30.898
tBu—N=C=N—S(=O)(=O)
7d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

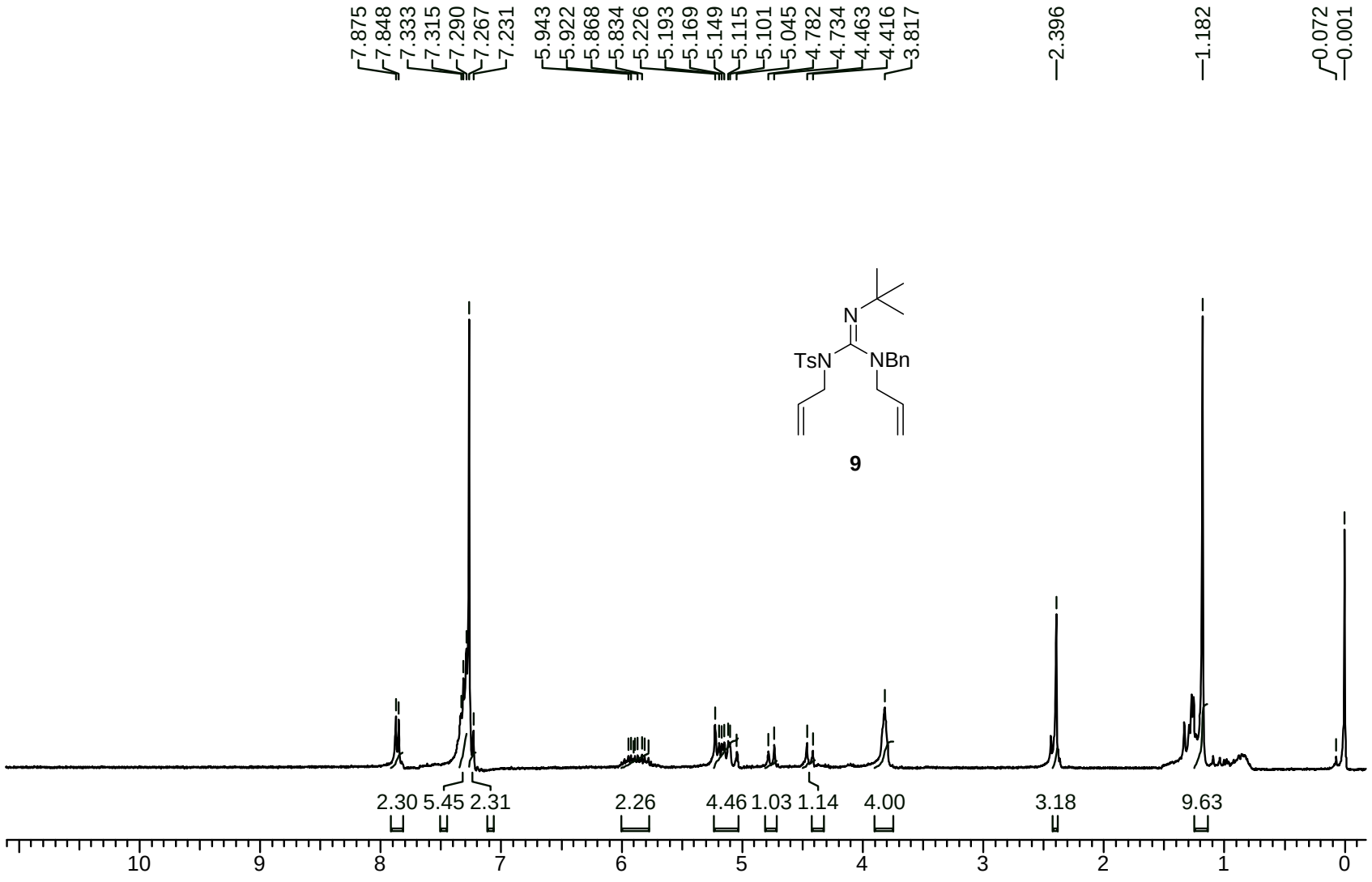

8.047
8.023
7.510
7.486
7.463
7.354
7.331
7.309
7.267
2.704
1.382
0.003
tBu–N=C=N–S(=O)(=O)–C6H4–CH3
7e
0.96
0.99
1.97
3.00
9.13
10
9
8
7
6
5
4
3
2
1
0

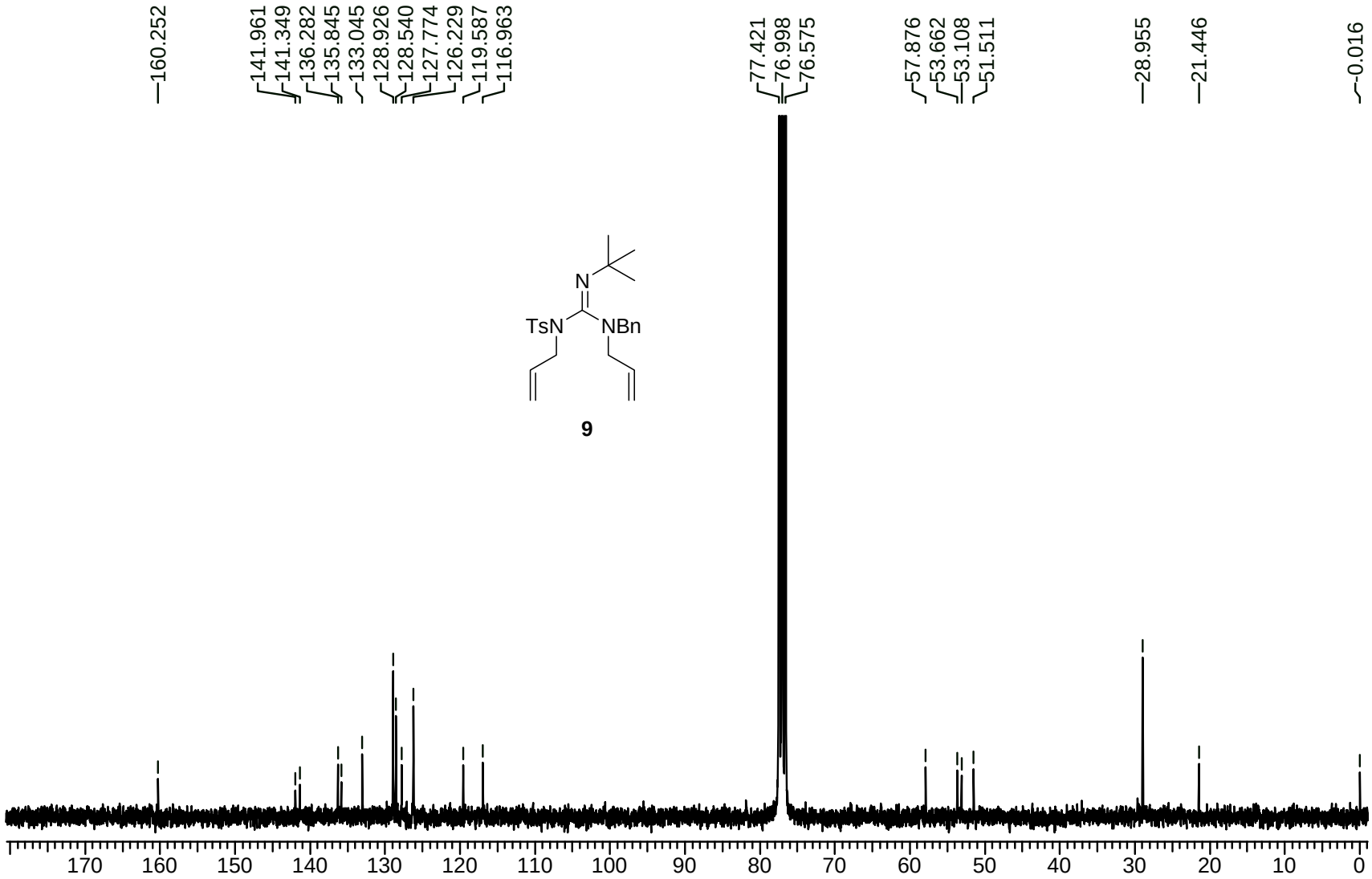

139.264
137.638
133.162
132.426
128.205
126.025
77.428
77.202
77.005
76.575
59.778
30.960
20.331
tBu—N=C=N—S(=O)(=O)—
7e
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.979
7.954
7.364
7.338
7.307
7.293
7.266
7.149
7.126
5.517
4.437
4.364
3.812
2.459
O
TsN
NBn
2.00
5.34
1.94
0.97
1.08
1.97
2.06
3.00
10
9
8
7
6
5
4
3
2
1
0

8


152.873
145.051
135.391
134.720
134.261
129.537
128.742
128.072
127.992
127.809
91.803
77.324
76.902
76.479
47.157
47.048
21.620
O
TsN
NBn
8
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.875
7.848
7.333
7.315
7.290
7.267
7.231
5.943
5.922
5.868
5.834
5.226
5.193
5.169
5.149
5.115
5.101
5.045
4.782
4.734
4.463
4.416
3.817
2.396
1.182
0.072
0.001
N
TsN
NBn
9
2.30 5.45 2.31 2.26 4.46 1.03 1.14 4.00 3.18 9.63
10 9 8 7 6 5 4 3 2 1 0


160.252
141.961
141.349
136.282
135.845
133.045
128.926
128.540
127.774
126.229
119.587
116.963
77.421
76.998
76.575
57.876
53.662
53.108
51.511
28.955
21.446
-0.016
N
TsN
NBn
9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
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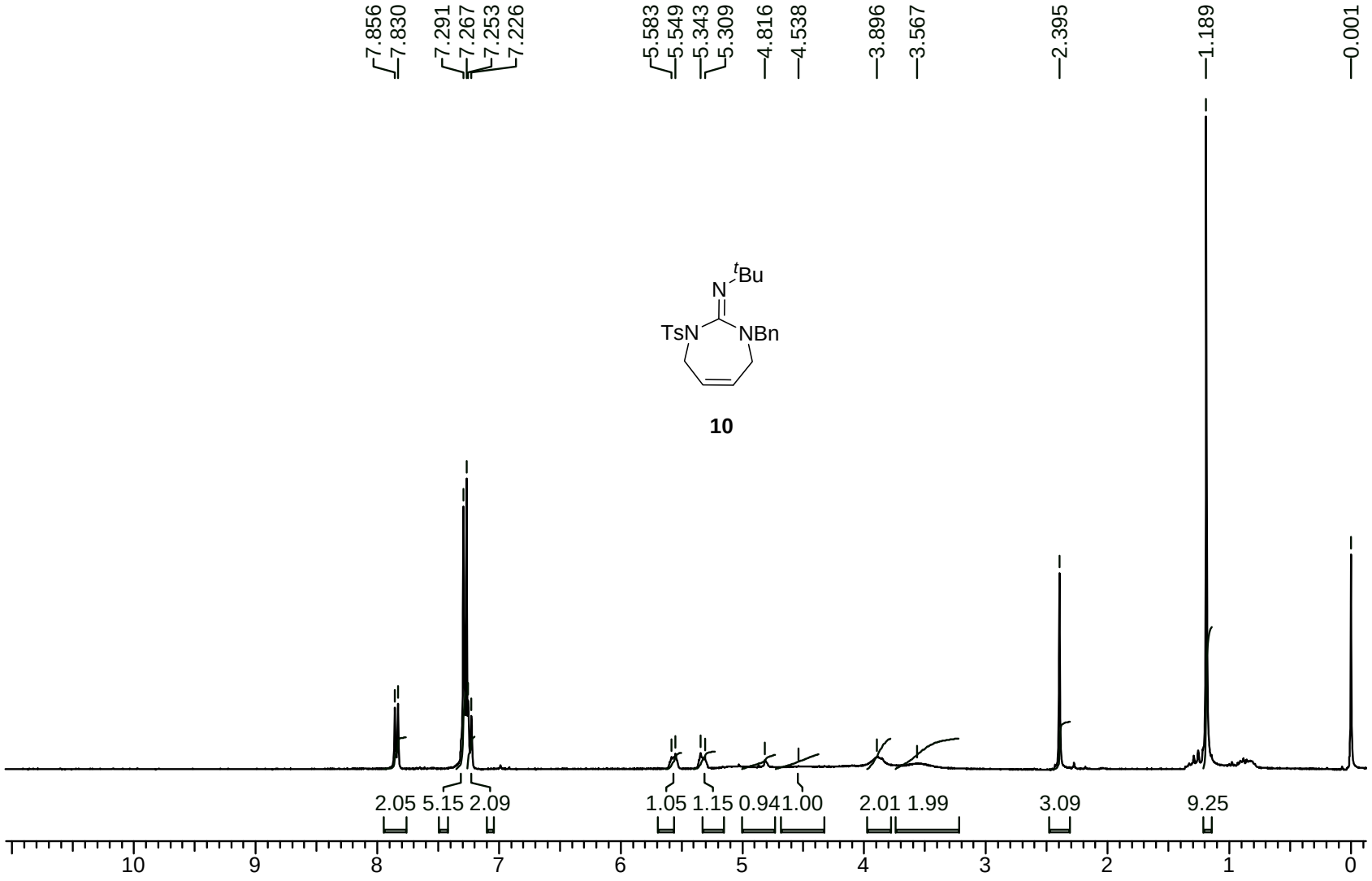
10
0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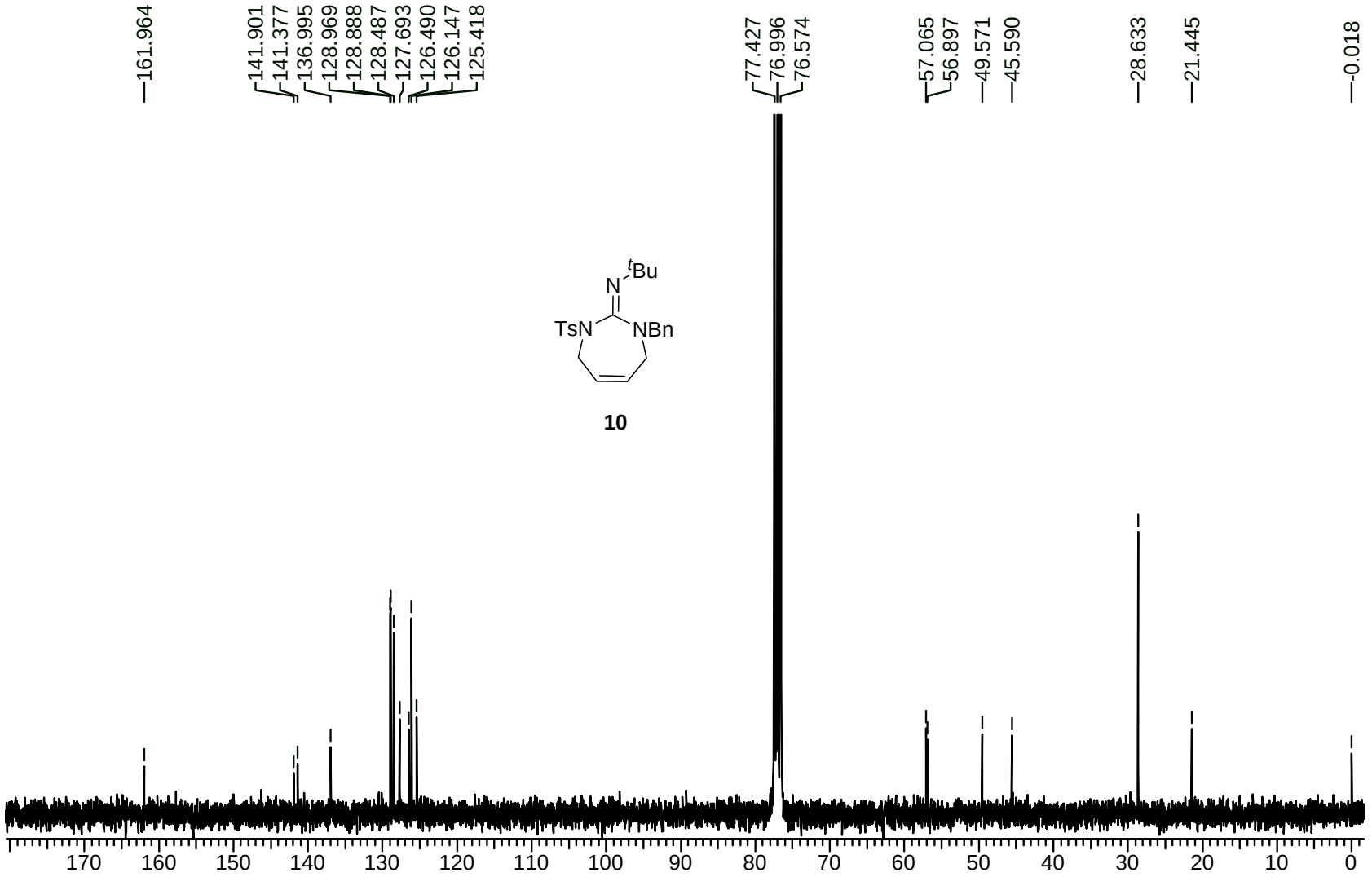
7.830
7.291
7.267
7.253
7.226
5.583
5.549
5.343
5.309
4.816
4.538
3.896
3.567
2.395
1.189
0.001
tBu
N
TsN
NBn
2.05 5.15 2.09
1.05 1.15 0.94 1.00
2.01 1.99
3.09
9.25
10
9
8
7
6
5
4
3
2
1
0

10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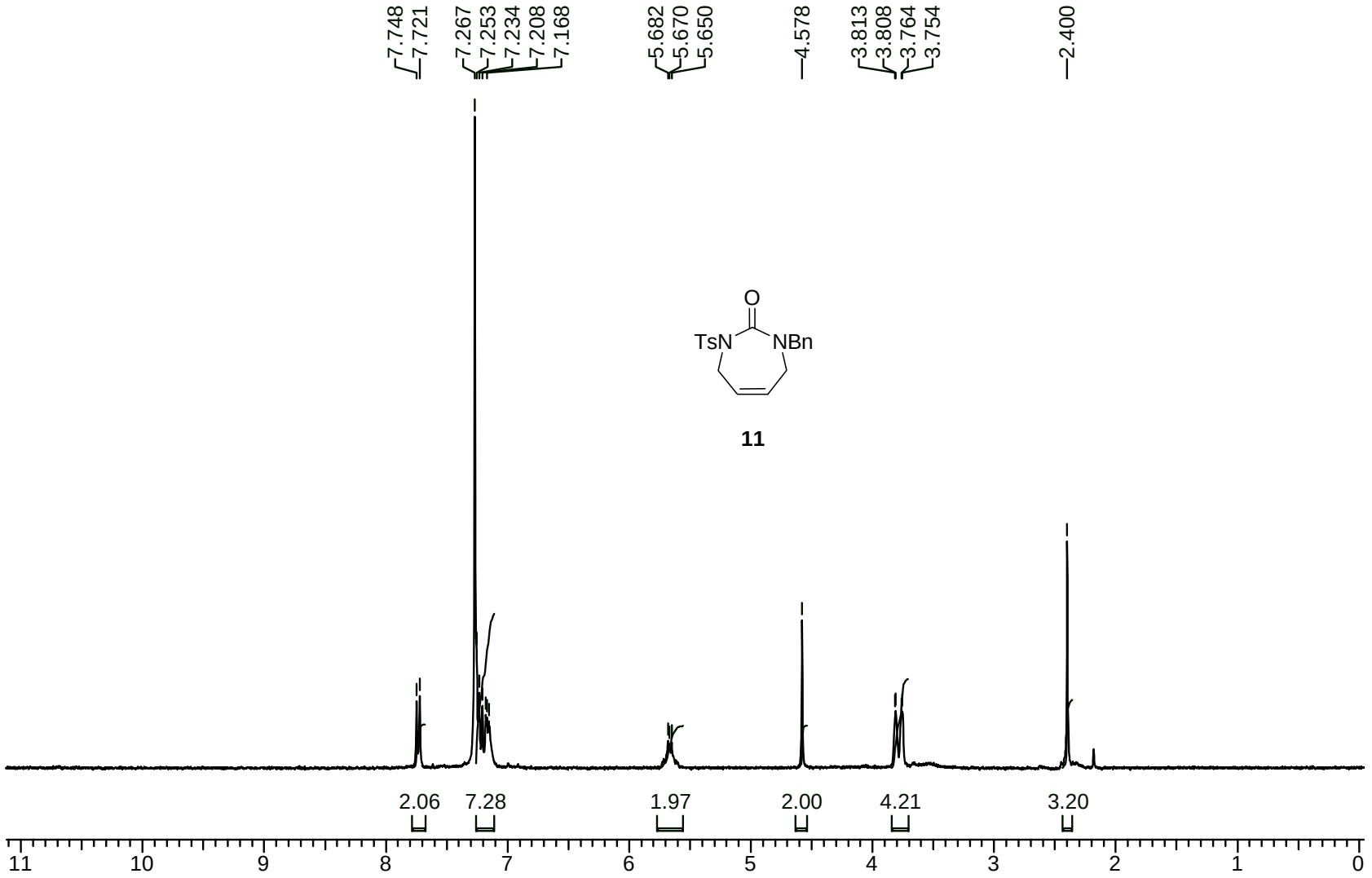
141.901
141.377
136.995
128.969
128.888
128.487
127.693
126.490
126.147
125.418
77.427
76.996
76.574
57.065
56.897
49.571
45.590
28.633
21.445
-0.018
tBu
N
TsN
NBn
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

10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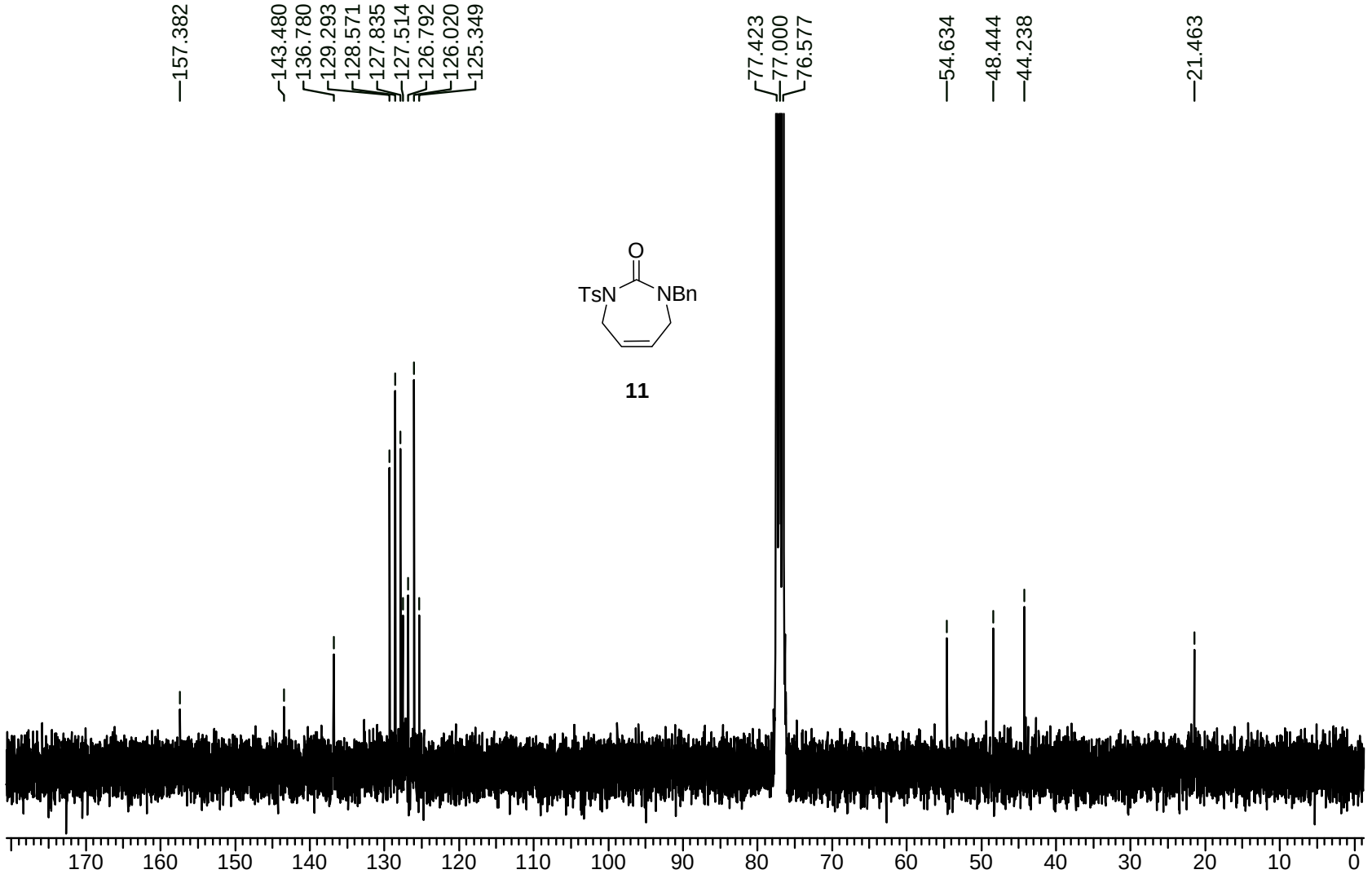
7.721
7.267
7.253
7.234
7.208
7.168
5.682
5.670
5.650
4.578
3.813
3.808
3.764
3.754
2.400
O
TsN
NBn
11
2.06
7.28
1.97
2.00
4.21
3.20
11
10
9
8
7
6
5
4
3
2
1
0


157.382
143.480
136.780
129.293
128.571
127.835
127.514
126.792
126.020
125.349
77.423
77.000
76.577
54.634
48.444
44.238
21.463
O
TsN
NBn
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0