Supporting Information

Unprecedented 1,3-*tert*-Butyl migration via C-N single bond scission of isonitrile: An expedient metal-free route to *N*-sulfonyl amidines

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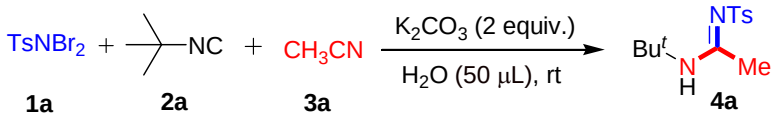
Table of contents:

1. **General Information:**

All the reactions were carried out in open atmosphere using oven-dried glassware. Distilled analytical grade solvents were used. Acetonitrile used for this purpose is of HPLC grade. 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); dd (doublet of doublets). 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.

2. Table S1: Optimization of reaction conditions[a]

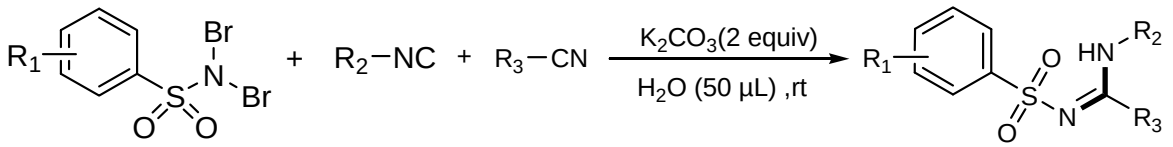


1a 2a 3a 4a

Entry	Acetonitrile / Solvent	Base (equiv)	Temp (ºC)	Yield[b] (%)
1	CH_3CN (2 mL)	K_2CO_3 (2)	RT	64
2	CH_3CN (1 equiv)	K_2CO_3 (2)	RT	63
3	CH_3CN (1 equiv) + DCM (2 mL)	K_2CO_3(2)	RT	51
4	CH_3CN (1 equiv) + $CHCl_3$ (2mL)	K_2CO_3(2)	RT	48
5	CH_3CN (1 equiv) + DCE (2 mL)	K_2CO_3(2)	RT	47
6	CH_3CN (1 equiv) + DCE (2 mL)	K_2CO_3(2)	80	Trace
7	CH_3CN (1 equiv) + H_2O (50 µL)	K_2CO_3(2)	RT	73
8	CH_3CN (1 equiv) + H_2O (50 µL)	K_2CO_3(2)	80	55
9	CH_3CN (1 equiv) + H_2O (50 µL)	K_2CO_3(1)	RT	48
10	CH_3CN (1 equiv) + H_2O (50 µL)	K_2CO_3(1.5)	RT	56
11	CH_3CN (1 equiv) + H_2O (50 µL)	KF (2)	RT	58
12	CH_3CN (1 equiv) + H_2O (50 µL)	$KHCO_3$(2)	RT	47
13	CH_3CN (1 equiv) + H_2O (50 µL)	Cs_2CO_3(2)	RT	37

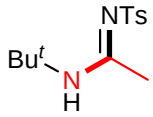
[a] Reaction condition: **1a** (0.5 mmol), **2a** (0.5 mmol), K_2CO_3 (1 mmol), 30 min; [b] Isolated yield.

3. General procedure for synthesis of sulfonyl amidines and characterization:



To a solution of isocyanide (0.5 mmol, 1.0 equiv) in nitrile (0.5 mmol, 1.0 equiv), *N,N*-dibromoarylsulfonamide (0.5 mmol, 1.0 equiv.) and K_2CO_3 (2 equiv.) was added and then followed by addition of 50 µL of H_2O. The reaction mixture was stirred 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 as eluent.

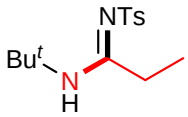
***N*-(*tert*-butyl)-*N'*-tosylacetimidamide (4a):**



4a

Following the general procedure, compound **4a** was prepared from *tert*- butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv, 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (73 %, 97 mg); mp 106-110 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.76 (d, J = 7.8 Hz, 2H), 7.24 (d, J = 7.8 Hz, 2H), 5.95 (br, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 1.32 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.3, 141.9, 140.7, 129.1, 125.9, 53.5, 28.1, 22.1, 21.4; **IR (KBr, cm^{-1})**: ν 3334, 1591, 1552, 1452, 1379; **HRMS m/z (ESI)** calculated for $C_{13}H_{21}N_2O_2S$ $(M+H)^+$ 269.1318, found 269.1323.

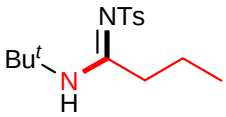
***N*-(*tert*-butyl)-*N'*-tosylpropionimidamide (4b):**



4b

Following the general procedure, compound **4b** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and propionitrile (35 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (71 %, 99 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.80 (d, J = 8.1 Hz, 2H), 7.25 (d, J= 8.1 Hz, 2H), 5.41 (br, 1H), 2.81 (q , J=7.5 Hz, 2H), 2.39 (s, 3H), 1.33 (s ,9H), 1.23 (t, J= 7.5 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**; δ 168.0, 141.7, 141.1, 129.0, 126.0, 53.2, 28.4, 28.2, 21.4, 11.6; **IR (KBr, cm^{-1})**: ν 3334, 1593, 1548, 1452, 1379; **HRMS m/z (ESI)** calculated for $C_{14}H_{23}N_2O_2S$ $(M+H)^+$ 283.1475, found 283.1491.

***N*-(*tert*-butyl)-*N'*-tosylbutyrimidamide (4c):**

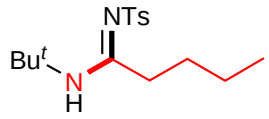


4c

Following the general procedure, compound **4c** was prepared from tert-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and butyronitrile (44 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Yellow semi solid (69 %, 101 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J =8.1 Hz, 2H), 7.24 (d, J=7.8 Hz, 2H), 5.54 (br, 1H), 2.70 (t, J=8.1 Hz, 2H), 2.38 (s, 3H), 1.68 (q, J=7.8 Hz, 2H), 1.31 (s, 9H), 0.96 (t, J=7.2 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**; δ 167.1, 141.7, 141.2, 129.0, 125.9, 53.2, 36.9, 28.2, 21.4, 21.0, 13.6; **IR(KBr, cm^{-1})**: ν

3321, 1591, 1550, 1452, 1381; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}N_2O_2S$ $(M+H)^+$ 297.1631, found 297.1656.

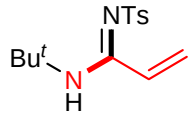
***N*-(*tert*-butyl)-*N'*-tosylpentanimidamide (4d):**



4d

Following the general procedure, compound **4d** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and valeronitrile (52 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (67 %, 103 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, *J*= 7.8 Hz, 2H), 7.24 (d, *J*= 8.1 Hz, 2H), 5.47 (br, 1H), 2.39 (s, 3H), 1.40-1.25 (m, 15H), 0.90 (t, *J*=7.2 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75MHz)**; δ 167.3, 141.7, 141.2, 129.0, 126.0, 53.2, 35.0, 29.6, 28.2, 22.4, 21.4, 13.7; **IR (KBr, cm^{-1})**: ν 3323, 1593, 1548, 1452, 1381; **HRMS m/z (ESI)** calculated for $C_{16}H_{27}N_2O_2S$ $(M+H)^+$ 311.1788, found 311.1784.

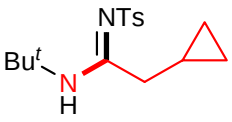
***N*-(*tert*-butyl)-*N'*-tosylacrylimidamide (4e):**



4e

Following the general procedure, compound **4e** was prepared from *tert*- butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and acrylonitrile (33 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (75 %, 103 mg); mp 120-124 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J*= 8.4 Hz, 2H), 7.11 (q, *J*=11.4 Hz, 1H), 5.62 (t, *J*=13.2 Hz, 2H), 5.48 (br, 1H), 2.40 (s, 3H) 1.38 (s, 9H); **^{13}C NMR ($CDCl_3$, 75MHz)**; δ 161.3, 142.0, 140.6, 132.2, 129.0, 126.2, 122.7, 53.6, 28.2, 21.4; **IR (KBr, cm^{-1})**: ν 3299, 1639, 1589, 1552, 1450, 1382; **HRMS m/z (ESI)** calculated for $C_{14}H_{21}N_2O_2S$ $(M+H)^+$ 281.1318, found 281.1322.

***N*-(*tert*-butyl)-2-cyclopropyl-*N'*-tosylacetimidamide (4f):**

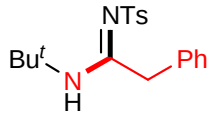


4f

Following the general procedure, compound **4f** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and cyclopropylacetonitrile (46 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (78 %, 120 mg); mp 110-114 °C ; **^{1}H NMR**

($CDCl_3$, 300 MHz): δ 7.79 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 6.22 (br, 1H), 2.86 (d, J = 6.9 Hz, 2H), 2.40 (s, 3H), 1.36 (s, 4H), 0.84 (s, 1H), 0.66 (d, J = 6.6 Hz, 2H), 0.27 (s, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 166.2, 141.7, 141.1, 129.0, 125.9, 53.1, 38.3, 31.5, 28.2, 6.4, 4.6; **IR (KBr, cm^{-1})**: ν 3323, 1573, 1554, 1448, 1382; **HRMS m/z (ESI)** calculated for $C_{16}H_{25}N_2O_2S$ $(M+H)^+$ 309.1631, found 309.1641.

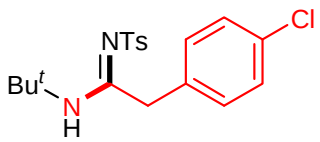
***N*-(*tert*-butyl)-2-phenyl-*N'*-tosylacetimidamide (4g):**



4g

Following the general procedure, compound **4g** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and benzylnitrile (57 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (67%, 114 mg); mp 130-134 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.86 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 7.2 Hz, 4H), 7.28 (d, J = 9.9 Hz, 1H), 7.20 (d, J = 6.6 Hz, 2H), 4.99 (br, 1H), 4.28 (s, 2H), 2.42 (s, 3H), 1.21 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.9, 141.9, 141.0, 133.5, 130.0, 129.4, 129.1, 128.1, 126.1, 53.3, 40.6, 28.0, 21.5; **IR (KBr, cm^{-1})**: ν 3332, 1591, 1552, 1446, 1379; **HRMS m/z (ESI)** calculated for $C_{18}H_{25}N_2O_2S$ $(M+H)^+$ 345.1631, found 345.1610.

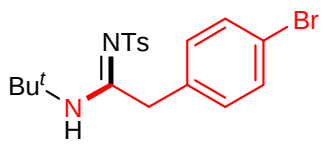
***N*-(*tert*-butyl)-2-(4-chlorophenyl)-*N'*-tosylacetimidamide (4h):**



4h

Following the general procedure, compound **4h** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-chlorobenzylnitrile (64 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Yellow semi solid (61 %, 115 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.84 (d, J = 8.4 Hz, 2H), 7.37-7.35 (m, 2H), 7.27 (d, J = 6 Hz, 2H), 7.23 (d, J = 15.3 Hz, 2H), 5.07 (br, 1H), 4.25 (s, 2H), 2.41 (s, 3H), 1.21 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.1, 142.1, 140.8, 132.5, 131.5, 129.7, 129.2, 126.4, 126.1, 53.6, 40.0, 28.1, 21.5; **IR (KBr, cm^{-1})**: ν 3334, 1597, 1556, 1452, 1382, 800; **HRMS m/z (ESI)** calculated for $C_{19}H_{24}ClN_2O_2S$ $(M+H)^+$ 379.1242, found 379.1241.

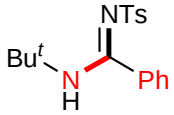
***N*-(*tert*-butyl)-2-(4-bromophenyl)-*N'*-tosylacetamidine (4i):**



4i

Following the general procedure, compound **4i** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-Bromobenzylnitrile (98 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Yellow solid (64%, 135 mg); mp 110-112 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.83 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 6.9 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 4.95 (br, 1H), 4.23 (s, 2H), 2.42 (s, 3H), 1.24 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.1, 142.0, 140.7, 132.4, 131.4, 129.6, 129.1, 126.4, 126.0, 53.5, 39.9, 28.0, 21.5; **IR (KBr, cm^{-1})**: ν 3334, 1593, 1554, 1448, 1382, 760; **HRMS m/z (ESI)** calculated for $C_{19}H_{24}BrN_2O_2S$ $(M+H)^+$ 423.0736, found 423.0728.

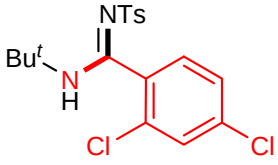
***N*-(*tert*-butyl)-*N'*-tosylbenzimidamide (4j)**



4j

Following the general procedure, compound **4j** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and benzonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (77 %, 127 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.62 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 6.6 Hz, 3H), 7.36 (t, J = 8.4 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.40 (br, 1H), 2.37 (s, 3H), 1.40 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.3, 141.6, 140.8, 135.2, 130.6, 128.8, 128.1, 127.5, 126.1, 54.0, 28.2, 21.4; **IR (KBr, cm^{-1})**: ν 3323, 1589, 1548, 1450, 1382; **HRMS m/z (ESI)** calculated for $C_{18}H_{23}N_2O_2S$ $(M+H)^+$ 331.1475, found 331.1553.

***N*-(tert-butyl)-2, 4-dichloro-*N'*-tosylbenzimidamide (4k):**

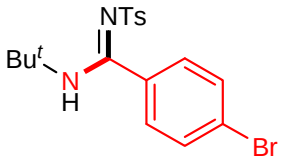


4k

Following the general procedure, compound **4k** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 2,4-dichlorobenzonitrile (1 equiv., 86 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (71 %, 141 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.77 (d, J = 7.8 Hz, 2H), 7.36-7.27 (m, 3H), 7.21

(d, J = 7.8 Hz, 2H), 5.21 (br, 1H), 2.40 (s, 3H), 1.45 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 159.7, 149.9, 144.6, 142.1, 136.6, 134.5, 132.0, 130.3, 129.8, 129.3, 128.9, 54.6, 28.7, 21.6; **IR (KBr, cm^{-1})**: ν 3348, 1591, 1550, 1452, 1381, 812; **HRMS m/z (ESI)** calculated for $C_{18}H_{21}Cl_2N_2O_2S$ $(M+H)^+$ 399.0695, found 399.0702.

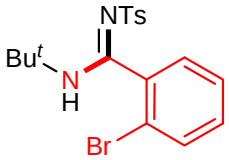
4-bromo-*N*-(*tert*-butyl)-*N'*-tosylbenzimidamide (4l):



4l

Following the general procedure, compound **4l** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-Bromobenzonitrile (1 equiv., 91 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow semi solid (74 %, 151 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.64 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 5.36 (br, 1H), 2.39 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 163.1, 141.9, 140.6, 134.1, 131.4, 129.2, 129.0, 126.1, 125.3, 54.3, 28.2, 21.4; **IR (KBr, cm^{-1})**: ν 3298, 1587, 1552, 1448, 1375; **HRMS m/z (ESI)** calculated for $C_{18}H_{22}BrN_2O_2S$ $(M+H)^+$ 409.0580, found 409.0589.

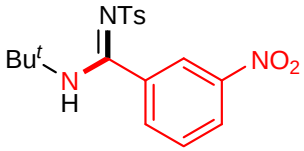
2-bromo-*N*-(*tert*-butyl)-*N'*-tosylbenzimidamide (4m):



4m

Following the general procedure, compound **4m** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 2-Bromobenzonitrile (1 equiv., 91 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (76 %, 154 mg); **^{1}H NMR (CDCl$_3$, 300 MHz)**: δ 7.67 (d, J = 8.1 Hz, 2H), 7.45-7.35 (m, 4H), 7.21 (d, J = 8.4 Hz, 2H), 5.27 (br, 1H), 2.39 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (CDCl$_3$, 75 MHz)**: δ 163.1, 141.9, 140.7, 137.0, 136.1, 133.7, 129.9, 129.0, 128.6, 126.9, 126.2, 54.3, 28.3, 21.5; **IR (KBr, cm^{-1})**: ν 3319, 1589, 1552, 1448, 1378, 737; **HRMS m/z (ESI)** calculated for $C_{18}H_{22}BrN_2O_2S$ $(M+H)^+$ 409.0580, found 409.0580.

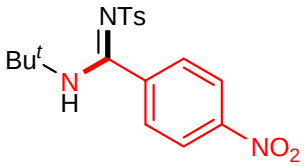
***N*-(*tert*-butyl)-3-nitro-*N'*-tosylbenzimidamide (4n):**



4n

Following the general procedure, compound **4n** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 3-Nitrobenzonitrile (74.05 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow semi solid (63%, 118 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)** δ 8.32 (d, J = 9.6 Hz, 1H), 8.09 (s, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.65 (d, J= 6.6 Hz, 2H), 7.61 (s, 1H), 7.21 (d, J=7.8 Hz, 2H), 5.34 (br, 1H), 2.39 (s, 3H), 1.46 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: 161.5, 147.6, 142.4, 140.2, 136.3, 134.2, 129.4, 129.1, 126.2, 125.3, 122.1, 54.8, 28.2, 21.4; **IR (KBr, cm^{-1})**: ν 3323, 1598, 1547, 1523, 1448, 1381; **HRMS m/z (ESI)** calculated for $C_{18}H_{22}N_3O_4S$ $(M+H)^+$ 376.1326, found 376.1325.

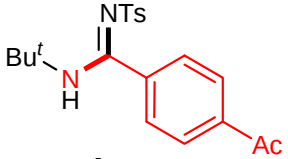
***N*-(*tert*-butyl)-4-nitro-*N'*-tosylbenzimidamide (4o)**:



4o

Following the general procedure, compound **4o** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-Nitrobenzonitrile (1 equiv., 74.05 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow semi solid (58 %, 109 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.21 (d, J = 8.7 Hz, 2H), 7.63 (q, J = 6.9 Hz, 4H), 7.22 (d, J = 8.1 Hz, 2H), 5.40 (br, 1H), 2.40 (s, 3H), 1.43 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 161.8, 148.7, 142.3, 141.1, 140.2, 129.1, 128.8, 126.2, 123.4, 54.8, 28.2, 21.5; **IR (KBr, cm^{-1})**: ν 3350, 1593, 1543, 1521, 1454, 1379; **HRMS m/z (ESI)** calculated for $C_{18}H_{22}N_3O_4S$ $(M+H)^+$ 376.1326, found 376.1330.

4-acetyl-*N*-(*tert*-butyl)-*N'*-tosylbenzimidamide (4p)

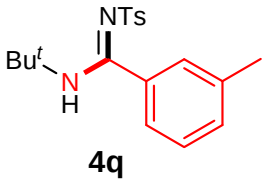


4p

Following the general procedure, compound **4p** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-Acetylbenzonitrile (1 equiv., 72.5 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow semi solid (71 %, 131 mg); **^{1}H NMR**

($CDCl_3$, 300 MHz): δ 7.96 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.21 (d, J= 8.4 Hz, 2H), 5.39 (br, 1H), 2.62 (s, 3H), 2.39 (s, 3H), 1.43 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)** :δ 197.4, 163.1, 142.0, 140.6, 139.5, 138.2, 129.0, 128.1, 127.9, 126.2, 54.4, 28.2, 26.7, 21.4; **IR (KBr, cm^{-1})**: v 3334, 1681, 1591, 1547, 1452, 1381; **HRMS m/z (ESI)** calculated for $C_{20}H_{25}N_2O_3S$ $(M+H)^+$ 373.1580, found 373.1582.

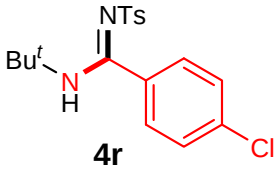
***N*-(*tert*-butyl)-3-methyl-*N'*-tosylbenzimidamide (4q):**



4q

Following the general procedure, compound **4q** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 3-Methylbenzonitrile (60 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (62 %, 105 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.64 (d, J = 7.8 Hz, 2H), 7.46 (s, 1H), 7.29 (d, J = 6.3 Hz, 2H), 7.21-7.16 (m, 3H), 5.31 (br, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.42 (s, 9H); **^{13}C NMR ($CDCl_3$, 75MHz)**: δ 164.6, 141.6, 140.9, 137.9, 132.4, 131.4, 128.8, 128.1, 127.9, 126.3, 124.8, 54.0, 28.3, 21.4, 21.3; **IR (KBr, cm^{-1})**: v 3299, 1589, 1567, 1450, 1379; **HRMS m/z (ESI)** calculated for $C_{19}H_{25}N_2O_2S$ $(M+H)^+$ 345.1631, found 345.1686.

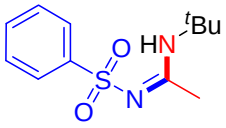
***N*-(*tert*-butyl)-4-chloro-*N'*-tosylbenzimidamide (4r):**



4r

Following the general procedure, compound **4r** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and 4-chlorobenzonitrile (1 equiv., 68.7 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (72 %, 131 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.67 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.26 (br, 1H), 2.39 (s, 3H), 1.41 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 163.1, 141.9, 140.7, 133.7, 129.9, 129.0, 128.6, 126.9, 126.2, 54.3, 28.3, 21.5; **IR(KBr, cm^{-1})**: v 3321, 1589, 1548, 1450, 1378, 780; **HRMS m/z (ESI)** calculated for $C_{18}H_{22}ClN_2O_2S$ $(M+H)^+$ 365.1085, found 365.1082.

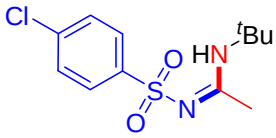
***N*-(*tert*-butyl)-*N'*(phenylsulfonyl)acetimidamide (5a)**:



5a

Following the general procedure, compound **5a** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-benzenesulfonamide (157 mg) and acetontrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (72 %, 91 mg); mp 104-106 °C; **^{1}H NMR ($CDCl_3$, 300 MHz):** δ 7.88 (d, J = 6 Hz, 2H), 7.44 (t ,J= 7.5 Hz, 3H), 6.01 (br, 1H), 2.32(s, 3H), 1.32(s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.5, 143.5, 131.4, 128.5, 125.9, 53.5, 28.0, 22.0; **IR (KBr, cm^{-1})**: ν 3319, 1598, 1541 1456, 1373; **HRMS m/z (ESI)** calculated for $C_{12}H_{15}N_2O_2S$ $(M+H)^+$ 255.1162, found 255.1160.

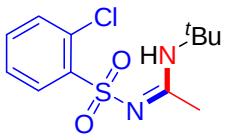
***N*-(*tert*-butyl)-*N'*-((4-chlorophenyl)sulfonyl)acetimidamide (5b)**:



5b

Following the general procedure, compound **5b** was prepared from *tert*-butylisocyanide (57 µL), *N,N*-dibromo-4-chlorobenzenesulfonamide (174 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (68 %, 98 mg); mp 116-118 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.85 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 5.64 (br, 1H), 2.38(s, 3H), 1.34(s, 9H); **^{13}C NMR ($CDCl_3$, 75MHz)**: 164.2, 142.1, 137.7, 128.8, 127.6, 53.7, 28.1, 22.5; **IR (KBr, cm^{-1})**: ν 3323, 1591, 1551, 1452, 1379, 744; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}ClN_2O_2S$ $(M+H)^+$ 289.0772, found 289.0834.

***N*-(*tert*-butyl)-*N'*-((2-chlorophenyl)sulfonyl)acetimidamide (5c)**:

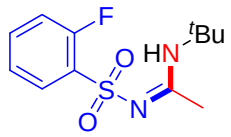


5c

Following the general procedure, compound **5c** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*2*-chlorobenzeneesulfonamide (174 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless Semi solid (67 %, 95 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.15 (t, J = 6 Hz, 1H), 7.47-7.37 (m, 3H), 5.48 (br, 1H), 2.41 (s, 3H), 1.34 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.4, 140.5, 132.6, 132.0,

131.4, 129.3, 126.6, 53.8, 28.3, 23.0; **IR (KBr, cm^{-1})**: *v* 3340, 1589, 1548, 1453, 1376; ; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}ClN_2O_2S$ $(M+H)^+$ 289.0772, found 289.0776.

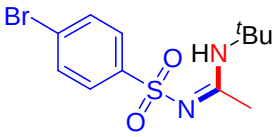
***N*-(*tert*-butyl)-*N'*-((2-fluorophenyl)sulfonyl)acetimidamide (5d)**:



5d

Following the general procedure, compound **5d** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*2*-fluorobenzeneesulfonamide (166 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless Semi solid (68 %, 92 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: *δ* 7.97 (q, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 5.7 Hz, 1H),7.25-7.16 (m, 2H), 5.60 (br, 1H), 2.40 (s, 3H), 1.33 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.3, 158.9 (J_{CF} = 253.7 Hz), 133.8 (J_{CF} = 8.2 Hz), 131.1, 128.6, 123.8 (J_{CF} = 3.8 Hz), 116.7 (J_{CF} = 21.82Hz), 53.8, 28.1, 22.7; **IR (KBr, cm^{-1})**: *v* 3319, 1593, 1552, 1450, 1382, 1024; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}FN_2O_2S$ $(M+H)^+$ 273.1068, found 273.1073.

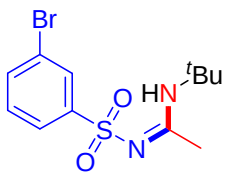
***N'*-((4-bromophenyl)sulfonyl)-*N*-(*tert*-butyl)acetimidamide (5e)**:



5e

Following the general procedure, compound 5e was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-bromobenzeneesulfonamide (197 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (71 %, 117 mg); mp 118-120 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: *δ* 7.79 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.7 Hz, 2H), 5.31 (br, 1H), 2.40 (s, 3H), 1.35 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: *δ* 164.3, 141.9, 140.7, 129.1, 126.0, 53.5, 28.1, 21.4; **IR (KBr, cm^{-1})**: *v* 3340, 1592, 1456, 1382, 750; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}BrN_2O_2S$ $(M+H)^+$ 333.0267, found 333.0271.

***N'*-((3-bromophenyl)sulfonyl)-*N*-(*tert*-butyl)acetimidamide (5f)**:

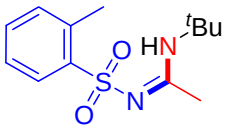


5f

Following the general procedure, compound **5f** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*3*-bromobenzeneesulfonamide (197 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica

gel (Petroleum ether: EtOAc = 7:3). Colorless Semi solid (70 %, 115 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.04 (s, 1H), 7.82 (d, J =8.1Hz, 1H), 7.62 (d, j=8.1 Hz, 1H), 7.34 (t, J=8.1 Hz, 1H), 5.82 (br, 1H), 2.36 (s, 3H), 1.34 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.4, 145.3, 134.5, 130.2, 129.1, 124.6, 122.4, 53.8, 28.1, 22.5; **IR (KBr, cm^{-1})**: ν 3321, 1591, 1554, 1453, 1384; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}BrN_2O_2S$ $(M+H)^+$ 333.0267, found 333.0271.

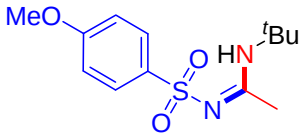
***N*-(*tert*-butyl)-*N'*-(o-tolylsulfonyl)acetimidamide (5g)**:



5g

Following the general procedure, compound **5g** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-methylbenzeneesulfonamide (164 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Semi solid (72 %, 96 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.03 (d, J = 8.4 Hz, 1H), 7.39 (t, J = 6.3 Hz, 1H), 7.27 (d, J = 6.3 Hz, 2H), 5.38 (br, 1H), 2.69 (s, 3H), 2.33 (s, 3H), 1.35 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.3, 141.3, 137.1, 132.0, 131.6, 127.5, 125.5, 53.6, 28.4, 22.6, 20.4; **IR (KBr, cm^{-1})**: ν 3321, 1592, 1550, 1448, 1380; **HRMS m/z (ESI)** calculated for $C_{13}H_{21}N_2O_2S$ $(M+H)^+$ 269.1318, found 269.1334.

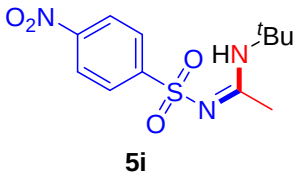
***N*-(*tert*-butyl)-*N'*-((4-methoxyphenyl)sulfonyl)acetimidamide (5h)**:



5h

Following the general procedure, compound **5h** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-methoxylbenzeneesulfonamide (172 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow solid (70 %, 99 mg); mp 124-126 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.80 (d, J = 9 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 5.97 (br, 1H), 383 (s, 3H), 2.30 (s, 3H), 1.32 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: 164.2, 161.8, 135.7, 127.9, 113.6, 55.4, 53.4, 28.1, 21.9; **IR (KBr, cm^{-1})**: ν 3334, 1590, 1548, 1438, 1384, 1265, 1141; **HRMS m/z (ESI)** calculated for $C_{13}H_{21}N_2O_3S$ $(M+H)^+$ 285.1267, found 285.1273.

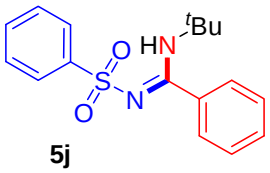
***N*-(*tert*-butyl)-*N'*-((4-nitrophenyl)sulfonyl)acetimidamide (5i)**:



5i

Following the general procedure, compound **5i** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzeneesulfonamide (179 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (79 %, 117 mg); mp 130-132 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.33 (d, J = 9 Hz, 2H), 8.11 (d, J = 8.7 Hz, 2H), 5.40 (br,1H), 2.46(s, 3H), 1.35 (s, 9H); **^{13}C NMR (CDCl3, 75 MHz)**: δ 164.3, 149.3, 149.1, 127.4, 123.9, 53.9, 28.1, 23.0; **IR (KBr, cm^{-1})**: ν 3348, 1591, 1562, 1527, 1452, 1382; **HRMS m/z (ESI)** calculated for $C_{12}H_{18}N_3O_4S$ $(M+H)^+$ 300.1013, found 300.1020.

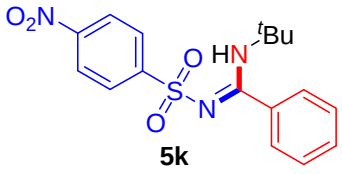
***N*-(*tert*-butyl)-*N'*-(phenylsulfonyl)benzimidamide (5j):**



5j

Following the general procedure, compound **5j** was prepared from *tert*-utyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (157 mg) and benzonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (78 %, 123 mg); mp 115-120 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.75 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 4H), 7.36 (d, J = 6.9 Hz, 4H), 5.42(br, 1H), 1.41 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.5, 143.6, 135.2, 131.2, 130.7, 128.3, 128.2, 127.5, 126.1, 54.1, 28.2; **IR (KBr, cm^{-1})**: ν 3319, 1592, 1548, 1446, 1381; **HRMS m/z (ESI)** calculated for $C_{17}H_{21}N_2O_2S$ $(M+H)^+$ 317.1318, found 317.1261.

***N*-(tert-butyl)-*N'*-((4-nitrophenyl)sulfonyl)benzimidamide (5k):**

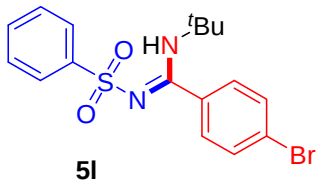


5k

Following the general procedure, compound **5k** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzenesulfonamide (179 mg) and benzonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (73 %, 131 mg); mp 190-192 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.25 (d, J = 8.7 Hz, 2H), 7.96 (d, J = 9 Hz, 2H), 7.51 (t, J = 7.5 Hz, 3H), 7.42 (t, J = 6.3 Hz, 2H), 5.54 (br, 1H), 1.40 (s, 9H); **^{13}C**

NMR ($CDCl_3$, 75 MHz): δ 165.0, 149.3, 149.1, 135.0, 131.3, 128.5, 127.5, 124.2, 123.7, 54.5, 28.2; **IR (KBr, cm^{-1})**: ν 3321, 1581, 1550, 1529, 1454, 1380; **HRMS m/z (ESI)** calculated for $C_{17}H_{20}N_3O_4S$ $(M+H)^+$ 362.1169, found 362.1179.

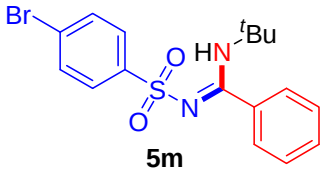
4-bromo-*N*-(*tert*-butyl)-*N'*-(phenylsulfonyl)benzimidamide (5l):



5l

Following the general procedure, compound **5l** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (157 mg) and 4-Bromobenzonitrile (1 equiv., 91 mg) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (76 %, 150 mg); mp 136-138°C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.76 (d, J = 7.2 Hz, 2H), 7.51 (d, J = 8.4 Hz, 3H), 7.43 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.38 (br, 1H), 1.40 (s, 9H); **^{13}C NMR ($CDCl_3$,75 MHz)**: δ 163.3, 143.4, 134.0, 133.4, 131.5, 129.2, 128.4, 126.1, 125.3, 54.3, 28.2; **IR (KBr, cm^{-1})**: ν 3323, 1589, 1550, 1452, 1382, 740; **HRMS m/z (ESI)** calculated for $C_{17}H_{20}BrN_2O_2S$ $(M+H)^+$ 395.0423, found 395.0422.

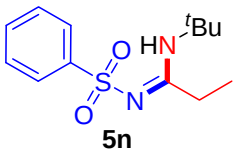
***N'*-((4-bromophenyl)sulfonyl)-*N*-(*tert*-butyl)benzimidamide (5m):**



5m

Following the general procedure, compound **5m** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-bromobenzenesulfonamide (197 mg) and benzonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (76 %, 150 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 6.3 Hz, 2H), 7.43 (t, J = 7.2 Hz, 3H), 7.35 (d, J = 8.7 Hz, 2H), 5.33 (br, 1H), 1.41 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 163.3, 143.4, 134.0, 131.7, 131.5, 129.2, 128.4, 126.2, 125.4 , 54.3, 28.2; **IR (KBr, cm^{-1})**: ν 3348, 1589, 1549, 1448, 1382, 738; **HRMS m/z (ESI)** calculated for $C_{17}H_{20}BrN_2O_2S$ $(M+H)^+$ 395.0423, found 395.0422.

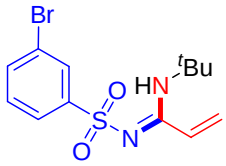
***N*-(*tert*-butyl)-*N'*-(phenylsulfonyl)propionimidamide (5n)**:



5n

Following the general procedure, compound **5n** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (157 mg) and propionitrile (35 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (69 %, 92 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.91 (t, J = 6.3 Hz, 2H), 7.46 (d, J = 6.6 Hz, 3H), 5.53 (br, 1H), 2.81 (q, J = 7.5 Hz, 2H), 1.32 (s, 9H), 1.23 (t, J = 7.5 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75MHz)**; δ 168.4, 143.9, 131.3, 128.4, 125.9, 53.2, 28.4, 28.1, 11.8; **IR (KBr, cm^{-1})**: ν 3298, 1587, 1549, 1450, 1378; **HRMS m/z (ESI)** calculated for $C_{13}H_{21}N_2O_2S$ $(M+H)^+$ 269.1318, found 269.1334.

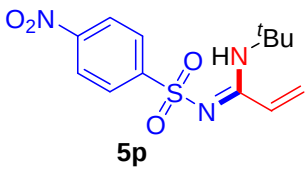
***N'*-((3-bromophenyl)sulfonyl)-*N*-(tert-butyl)acrylimidamide (5o):**



5o

Following the general procedure, compound **5o** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-3-bromobenzenesulfonamide (197 mg) and acrylonitrile (33 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow semi solid (70 %, 119 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.06 (s, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.34 (t, J = 8.1 Hz, 1H), 7.08 (q, J = 11.4 Hz, 1H), 5.67 (t, J = 10.8 Hz, 2H), 5.59 (br, 1H), 1.38 (s, 9H); **^{13}C NMR ($CDCl_3$, 75MHz)**; δ 161.6, 145.1, 134.6, 132.0, 130.1, 129.2, 124.8, 123.3, 122.3, 53.8, 28.1; **IR (KBr, cm^{-1})**: ν 3323, 1638, 1578, 1547, 1452, 1379, 737; **HRMS m/z (ESI)** calculated for $C_{13}H_{18}BrN_2O_2S$ $(M+H)^+$ 345.0267, found 345.0278.

***N*-(*tert*-butyl)-*N'*-((4-nitrophenyl)sulfonyl)acrylimidamide (5p):**

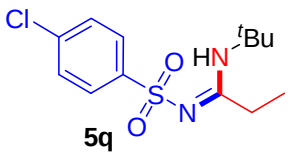


5p

Following the general procedure, compound **5p** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-Nitrobenzenesulfonamide (179 mg) and acrylonitrile (33 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Pale yellow solid (71 %, 110 mg); mp 118-120 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.32 (d, J = 9 Hz, 2H), 8.09 (d, J = 8.7 Hz, 2H), 7.08 (q, J = 11.1 Hz, 1H), 5.70 (t, J = 12 Hz, 3H), 1.37 (s, 9H); **^{13}C NMR ($CDCl_3$,**

75MHz); δ 161.8, 149.3, 148.9, 131.8, 127.5, 123.9, 123.8, 54.0, 28.1; **IR (KBr, cm^{-1})**: ν 3334, 1639, 1587, 1550, 1527, 1448, 1381; **HRMS m/z (ESI)** calculated for $C_{13}H_{18}N_3O_4S$ $(M+H)^+$ 312.1013, found 312.1022.

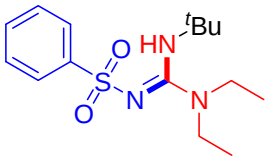
***N*-(*tert*-butyl)-*N'*-((4-chlorophenyl)sulfonyl)propionimidamide (5q):**



5q

Following the general procedure, compound **5q** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-chlorobenzenesulfonamide (174 mg) and propionitrile (35 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (71 %, 107 mg); mp 132-138 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.85 (d, J = 8.7 Hz, 2H), 7.42 (d, J = 8.7 Hz, 2H), 5.57 (br, 1H), 2.80 (q, J=7.8 Hz, 2H), 1.31 (s, 9H), 1.23 (t, J = 7.5 Hz, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**; δ 168.3, 142.4, 137.5, 128.7, 127.5, 53.3, 28.6, 28.1, 11.6; **IR (KBr, cm^{-1})**: ν 3319, 1591, 1552, 1450, 1378, 782. **HRMS m/z (ESI)** calculated for $C_{13}H_{20}ClN_2O_2S$ $(M+H)^+$ 303.0929, found 303.0927.

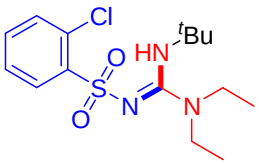
***N*-(*tert*-Butylamino-diethylamino-methylene)-benzenesulfonamide (7a) [2]:**



7a

Following the general procedure, compound **7a** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromobenzenesulfonamide (157 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (81 %, 125 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 (br, 1H), 3.39 (q, J = 7.2 Hz, 4H), 1.19-1.05 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.7, 144.7, 130.6, 128.1, 125.5, 53.5, 43.8, 29.4, 12.6**; IR (KBr, cm^{-1})**: ν 3325, 1586, 1547, 1448, 1376.

***N*-(*tert*-Butylamino-diethylamino-methylene)-2-chlorobenzenesulfonamide (7b) [2]:**

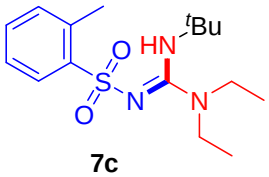


7b

Following the general procedure, compound **7b** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-chlorobenzenesulfonamide (174 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (74 %, 127 mg); mp 106-110 °C; **^{1}H NMR**

($CDCl_3$, 300 MHz): δ 8.06 (d, J = 7.5 Hz, 1H), 7.45 (d, J = 7.5 Hz, 1H), 7.35-7.30 (m, 2H), 5.10 (br, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.23-1.15 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.3, 141.8, 131.8, 131.7, 131.3, 128.7, 126.3, 53.9, 43.9, 29.7, 12.8; **IR (KBr, cm^{-1})**: ν 3329, 1593, 1547, 1454, 1378, 743.

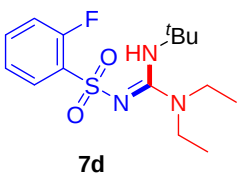
***N*-(*tert*-Butylamino-diethylamino-methylene)-2-methylbenzenesulfonamide (7c)[2]:**



7c

Following the general procedure, compound **7c** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*o*-toluenesulfonamide (164 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). colorless solid (75 %, 121 mg); mp 86-88 °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 (br, 1H), 3.45 (q, J = 7.2 Hz, 4H), 2.74 (s, 3H) 1.18-1.13 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.6, 142.7, 136.6, 131.8, 130.9, 126.7, 125.2, 53.9, 44.0, 29.8, 20.4, 12.8; **IR (KBr, cm^{-1})**: ν 3334, 1591, 1557, 1453, 1378.

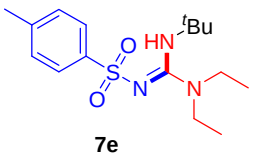
***N*-(*tert*-Butylamino-diethylamino-methylene)-2-fluorobenzenesulfonamide (7d)[2]:**



7d

Following the general procedure, compound **7d** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-2-fluorobenzenesulfonamide (166 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (69 %, 113 mg); mp 80-84 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.88 (t, J = 9Hz, 1H), 7.41 (t, J = 7.8 Hz 1H), 7.18-7.09 (m, 2H), 5.13 (br, 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} = 8.2 Hz), 132.5 (J_{CF} = 14.8 Hz), 128.3, 123.5, 116.5 (J_{CF} = 21.8 Hz), 53.9, 44.0, 29.6, 12.7; **IR (KBr, cm^{-1})**: ν 3331, 1592, 1558, 1447, 1381, 1056.

***N*-(*tert*-Butylamino-diethylamino-methylene)-4-methylbenzenesulfonamide (7e)[2]:**

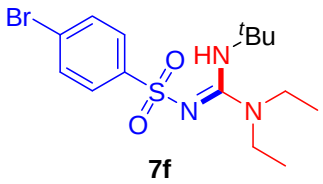


7e

Following the general procedure, compound **7e** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg)

and Diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (84%, 136 mg); mp 110-112 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 5.24 (br, 1H), 3.46 (q, J = 6.9 Hz, 4H), 2.38 (s, 3H), 1.93 (s, 9H) 1.14 (t, J = 7.2 Hz, 6H) ; **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 157.5, 141.9, 141.2, 128.9, 125.9, 54.1, 44.0, 29.8, 21.4, 12.8; **IR (KBr, cm^{-1})**: ν 3321, 1593, 1566, 1454, 1381.

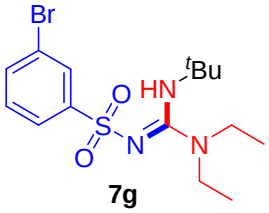
4-Bromo-*N*-(*tert*-butylamino-diethylamino-methylene)-benzenesulfonamide (7f) [2]:



7f

Following the general procedure, compound **7f** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-bromobenzenesulfonamide (197 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (78 %, 151 mg); mp 102-106 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.75 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 5.03 (br, 1H), 3.45 (q, J = 7.2 Hz, 4H), 1.18-1.15 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.5, 144.0, 131.4, 127.4, 125.1, 53.6, 43.9, 29.6, 12.7; **IR (KBr, cm^{-1})**: ν 3338, 1584, 1552, 1446, 1378, 742.

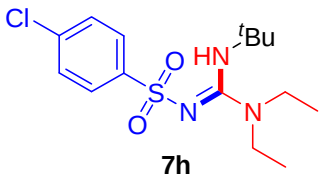
***N*-(*tert*-Butylamino-diethylamino-methylene)-3-bromobenzenesulfonamide (7g):**



7g

Following the general procedure, compound **7g** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-3-bromobenzenesulfonamide (174 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (74 %, 143 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 8.06 (s, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.33-7.28 (m, 1H), 5.02 (br, 1H), 3.48 (q, J = 7.2 Hz, 4H), 1.22-1.17 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.7, 146.7, 134.8, 132.2, 129.9,127.1, 124.4, 53.9, 44.1, 29.7, 12.8; **IR (KBr, cm^{-1})**: ν 3329, 1587, 1553, 1454, 1378, 743; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}BrN_3O_2S$ $(M+H)^+$ 390.0845, found 390.0843.

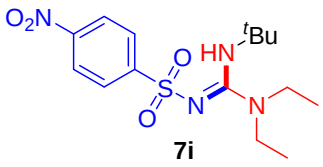
4-Chloro-*N*-(*tert*-Butylamino-diethylamino-methylene)-benzenesulfonamide (7h)



7h

Following the general procedure, compound **7h** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*4*-chlorobenzenesulfonamide (174 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (76 %, 131 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.85 (d, J = 8.7 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 5.02 (br, 1H), 3.49 (q, J = 7.2 Hz, 4H), 1.25-1.19 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 156.8, 143.5, 136.9, 128.5, 127.4, 53.9, 44.1, 29.7, 12.8; **IR (KBr, cm^{-1})**: ν 3334, 1591, 1556, 1454, 1373, 754; **HRMS m/z (ESI)** calculated for $C_{15}H_{25}ClN_3O_2S$ $(M+H)^+$ 346.1351, found 346.1365.

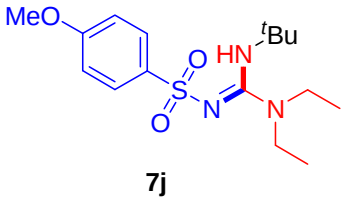
***N*-(*tert*-Butylamino-diethylamino-methylene)-4-nitrobenzenesulfonamide (7i)[2]:**



7i

Following the general procedure, compound **7i** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-nitrobenzenesulfonamide (179 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Yellow solid (78 %, 138 mg); **^{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 (br, 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 155.9, 150.7, 148.6, 126.9, 123.7, 53.4, 44.1, 29.5, 12.7; **IR (KBr, cm^{-1})**: ν 3329, 1593, 1554, 1529, 1453, 1373.

***N*-(*tert*-Butylamino-diethylamino-methylene)-4-methoxybenzenesulfonamide (7j)[2]:**

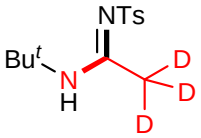


7j

Following the general procedure, compound **7j** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-4-methoxybenzenesulfonamide (172 mg) and diethyl cyanamide (58 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (79 %, 134 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 (br, 1H), 3.85 (s, 3H), 3.47 (q, J = 7.2 Hz, 4H), 1.21-1.15 (m, 15H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 161.3, 157.4, 137.0, 127.7, 113.3, 55.3, 54.0, 43.9, 29.7, 12.7; **IR (KBr, cm^{-1})**: ν 3326, 1589, 1548, 1450, 1384, 1268, 1147.

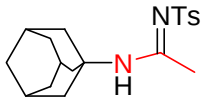
***N*-(*tert*-butyl)-*N'*-tosyl(acet-d$_3$)imidamide (4s):**



4s

Following the general procedure, compound **4s** was prepared from *tert*-butyl isocyanide (57 µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and $CDCl_3$ (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (64 %, 86 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.74 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 6.13 (br, 1H), 2.37 (s, 3H), 1.31 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 164.5, 141.8, 140.7, 129.1, 125.9, 53.4, 28.5, 28.0, 21.3; **IR (KBr, cm^{-1})**: ν 3323, 1593,1567, 1447, 1379; **HRMS m/z (ESI)** calculated for $C_{13}H_{18}D_3N_2O_2S$ $(M+H)^+$ 272.1507, found 272.1555.

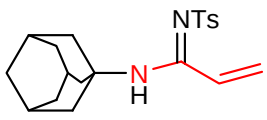
***N*-(adamantan-1-yl)-*N'*-tosylacetimidamide (8):**



8

Following the general procedure, compound **8** was prepared from 1-Adamantyl isocyanide (80.62 mg), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and acetonitrile(26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless semi solid (69 %, 118 mg); **^{1}H NMR ($CDCl_3$, 300 MHz):** δ 7.80 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 6.3 Hz, 2H), 5.29 (br, 1H), 2.40 (s, 3H), 2.35 (s, 3H), 2.02 (s, 8H), 1.68 (d, J =10.2 Hz, 2H), 1.62 (s, 6H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 163.7, 141.9, 140.8, 129.1, 126.0, 54.3, 40.7, 36.1, 29.2, 22.6, 21.4**;** **IR (KBr, cm-1)**: ν 3334, 1593, 1554, 1450, 1379; **HRMS m/z (ESI)** calculated for $C_{19}H_{27}N_2O_2S$ $(M+H)^+$ 347.1788, found 347.1794.

***N*-(adamantan-1-yl)-*N'*-tosylacrylimidamide (9):**

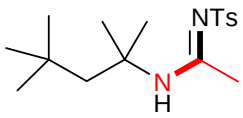


9

Following the general procedure, compound **9** was prepared from 1-Adamantyl isocyanide (80.62 mg), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and acrylonitrile (33 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether:

EtOAc = 7:3). Colorless semi solid (73 %, 130 mg); **^{1}H NMR ($CDCl_3$, 300 MHz):** δ 7.80 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.09 (q, J = 11.1 Hz, 1H), 5.61 (q, J = 11.4 Hz, 2H), 5.33 (br, 1H), 2.40 (s, 3H), 2.04 (s, 8H), 1.25 (s, 5H), 0.85 (t, J =8.1 Hz, 2H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 160.9, 141.9, 140.7, 132.3, 129.0, 126.1, 122.6, 54.3, 40.7, 36.1, 29.2, 21.5; **IR (KBr, cm-1)**: ν 3323, 1591, 1552, 1452, 1379; **HRMS m/z (ESI)** calculated for $C_{20}H_{27}N_2O_2S$ $(M+H)^+$ 359.1788, found 359.1801.

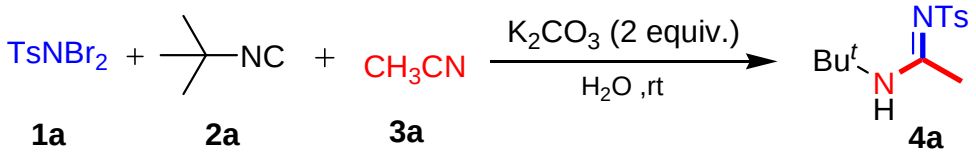
***N'*-tosyl-*N*-(2,4,4-trimethylpentan-2-yl)acetimidamide (10) :**



10

Following the general procedure, compound **10** was prepared from 1,1,3,3-Tetramethylbutylisocyanide (87µL), *N,N*-dibromo-*p*-toluenesulfonamide (164 mg) and acetonitrile (26 µL) in presence of water (50 µL) and K_2CO_3 (2 equiv., 138 mg). Purified by column chromatography on silica gel (Petroleum ether: EtOAc = 7:3). Colorless solid (70 %, 113 mg); mp 108-112 °C; **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.76 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H), 5.95 (br, 1H), 2.37 (s, 3H), 2.29 (s, 3H), 1.74 (s, 2H), 1.35 (s, 6H), 0.88 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 163.9, 141.8, 140.8, 129.0, 126.0, 57.3, 49.5, 31.5, 31.2, 28.9, 22.1, 21.4; **IR (KBr, cm^{-1})**: ν 3350, 1616, 1550, 1440, 1394; **HRMS m/z (ESI)** calculated for $C_{16}H_{28}N_3O_3S$ $(M+H)^+$ 325.1944, found 325.1958.

4. Procedure for gram scale synthesis:

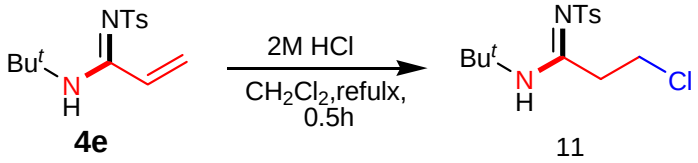


1a **2a** **3a** **4a**

To an ice cooled solution of *t*-butyl isocyanide (3.04 mmol, 1 equiv) in CH_3CN (3.04 mmol, 1 equiv) was added with $TsNBr_2$ (3.04 mmol, 1g, 1 equiv) and K_2CO_3 (6.08 mmol, 2 equiv) followed by addition of 304 µL of H_2O. The resultant mixture was 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-butyl-*N′*-tosylacetamidine (**4a**) with 72 % yield (585 mg).

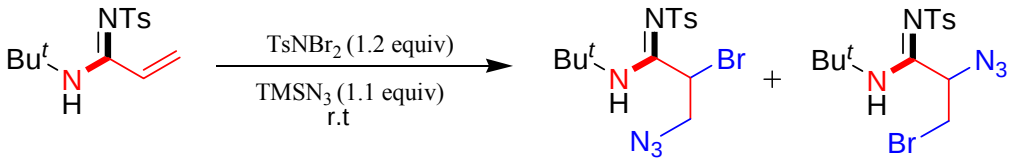
5. **Procedure for synthesis of *N-tert*-butyl-3-chloro-*N′*-tosylpropanamidine (11)**:



4e 11

2M HCl solution (0.2 mL) was added to a stirred solution of *N*-tert-butyl-*N′*-tosylacrylamidine (4e, 0.2 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL) and the mixture was refluxed for 30 min. Then $NaHCO_3$ solution was added to the reaction mixture and extracted with CH_2Cl_2 . The organic layer was dried over anhydrous Na_2SO_4. 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 the product *N*-tert-butyl-3-chloro-*N′*-tosylpropanamidine (11). Semi solid (84 %, 52 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.78 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 5.85 (br, 1H), 3.95 (t, J = 6.1 Hz, 2H), 3.17 (t, J = 6 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 162.8, 142.1, 140.6, 129.1, 125.9, 53.9, 41.7, 38.3, 28.1, 21.4; **IR (KBr, cm^{-1})**: ν 3334, 1593, 1557, 1447, 1381, 743; **HRMS m/z (ESI)** calculated for $C_{14}H_{21}Cl\,N_2O_2S$ $(M+H)^+$ 317.1085, found 317.1091.

6. **Procedure for synthesis of *N-tert*-butyl-2-azido-3-bromo-*N′*-tosylpropanamidine (12)**[3]:

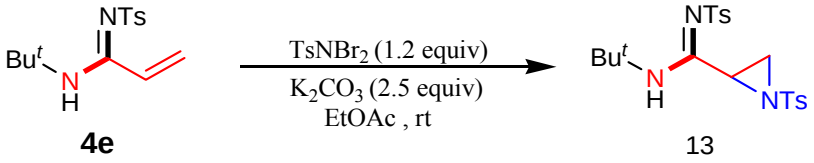


4e **12** **12'**

To a solution of *N*-tert-butyl-*N′*-tosylacrylamidine (4e, 0.2 mmol, 1.0 equiv.) and $TMSN_3$ (0.22 mmol, 1.1 equiv.) in acetonitrile (2 ml), $TsNBr_2$ (0.24 mmol, 1.2 equiv.) was added under nitrogen atmosphere and stirred. After completion of the reaction, sodium thiosulfate was added and the reaction mixture was stirred for 15 min. The reaction mixture was extracted with EtOAc.

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 (7:3) as eluent to afford the azidobromination product as a mixture of non separable regioisomers (**12**:**12′** = 85:15). Colorless semi solid (81 %, 77 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.79 (d, J = 8.4 Hz, 4H), 7.27 (d, J = 7.8 Hz, 4H), 8.34 (br, 1H), 8.22-8.19 (m, 2H), 6.00-5.97 (m, 1H), 4.30 0, (dd, J = 4.2Hz, 11.7 Hz, 1H), 4.16 (dd, J = 4.2 Hz, 13.8 Hz, 1H), 3.93 (dd, J = 3.9 Hz, 13.5 Hz, 1H), 2.40 (s, 6H), 1.33 (s, 18H). **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.7, 158.1, 142.6, 142.5, 139.9, 139.8, 129.2, 125.9, 55.8, 54.3, 54.1, 46.1, 46.0, 27.7, 21.5; **IR (KBr, cm^{-1})**: ν 3323, 2112, 1581, 1557, 1448, 1381,741; **HRMS m/z (ESI)** calculated for $C_{14}H_{21}Br\ N_5O_2S$ $(M+H)^+$ 402.0594, found 402.0688.

7. **Procedure for synthesis of *N*-*tert*-butyl-*N′*, 1-ditosylaziridine-2-carboxamidine (13)**[4]:



4e **13**

To a solution of *N*-tert-butyl-*N′*-tosylacrylamidine (4e, 0.2 mmol, 1.0 equiv.) and K_2CO_3 (0.5 mmol, 2.5 equiv.), in dry ethyl acetate (2 mL), a solution of $TsNBr_2$ (0.24 mmol, 1.2 equiv.) in dry ethyl acetate (2 mL) was added drop wise under nitrogen atmosphere at room temperature. After completion of the reaction, an aqueous solution of 10% sodium thiosulfate (5 mL) was added and the organic layer separated. The reaction mixture was extracted with EtOAc. Combined 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 (7:3) as eluent to afford the product *N*-tert-butyl-*N′*, 1-ditosylaziridine-2-carboxamidine (13). Colorless semi solid (84 %, 89 mg); **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 7.77 (t, J = 7.8 Hz, 4H), 7.38 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.5 Hz, 2H), 6.12 (br, 1H), 4.13 (dd J = 4.2 Hz, 8.1 Hz, 1H), 2.86 (d, J = 7.5 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.33 (d, J = 4.2 Hz, 1H) 1.22 (s, 9H); **^{13}C NMR ($CDCl_3$, 75 MHz)**: δ 158.3, 145.8, 142.4, 140.1, 132.3, 130.1, 129.2, 128.2, 126.0, 53.2, 37.6, 35.3, 27.7, 21.7, 21.4; **IR (KBr, cm^{-1})**: ν 3334, 1591 1551, 1448, 1378; **HRMS m/z (ESI)** calculated for $C_{21}H_{28}N_3O_4S_2$ $(M+H)^+$ 450.1516, found 450.1525.

8. **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) P. Phukan, P. Chakraborty and D. Kataki, *J. Org. Chem.* 2006, **71**, 7533-7537. (d) A. J. Borah and P. Phukan, *Chem. Commun.,* 2012, **48**, 5491.

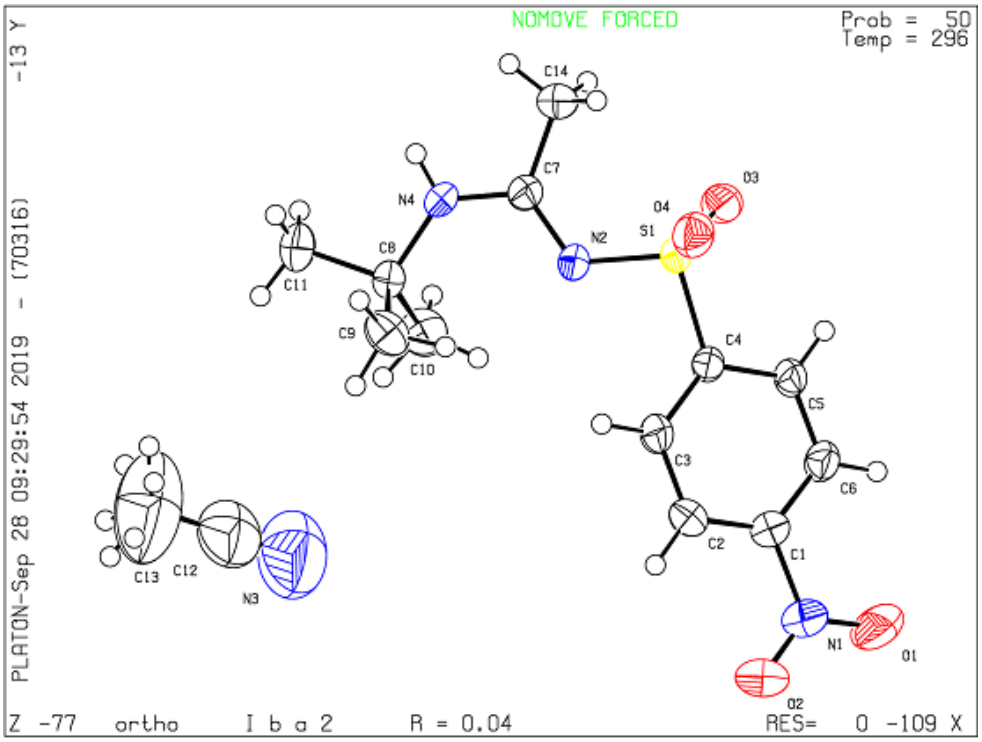
2. D. Hazarika, A. J. Borah, P. Phukan, *Chem. Commun.,* 2019, **55**, 1418-1421.

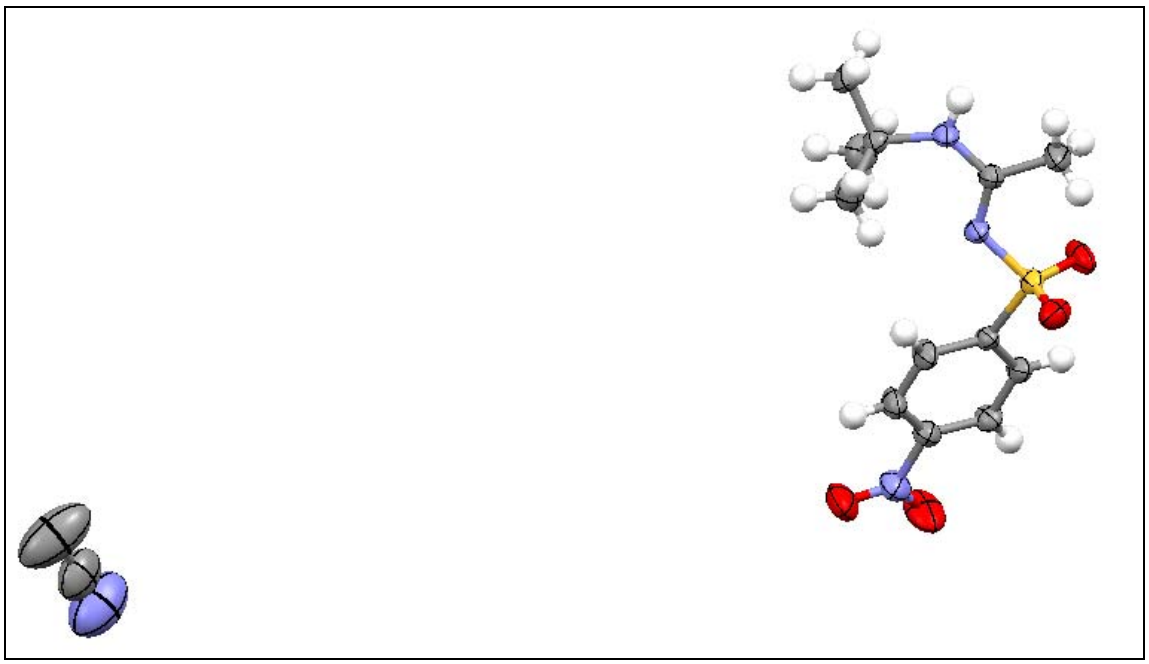
3. I. Saikia, P. Phukan, *Tetrahedron Letters*. 2009, **50**, 5083–5087.

4. I. Saikia, B. Kashyap and P. Phukan *Chem. Commun*., 2011, **47**, 2967–2969.

9. Crystal structure data of *N*-(*tert*-butyl)-*N'*-((4-nitrophenyl)sulfonyl)acetimidamide (5i):

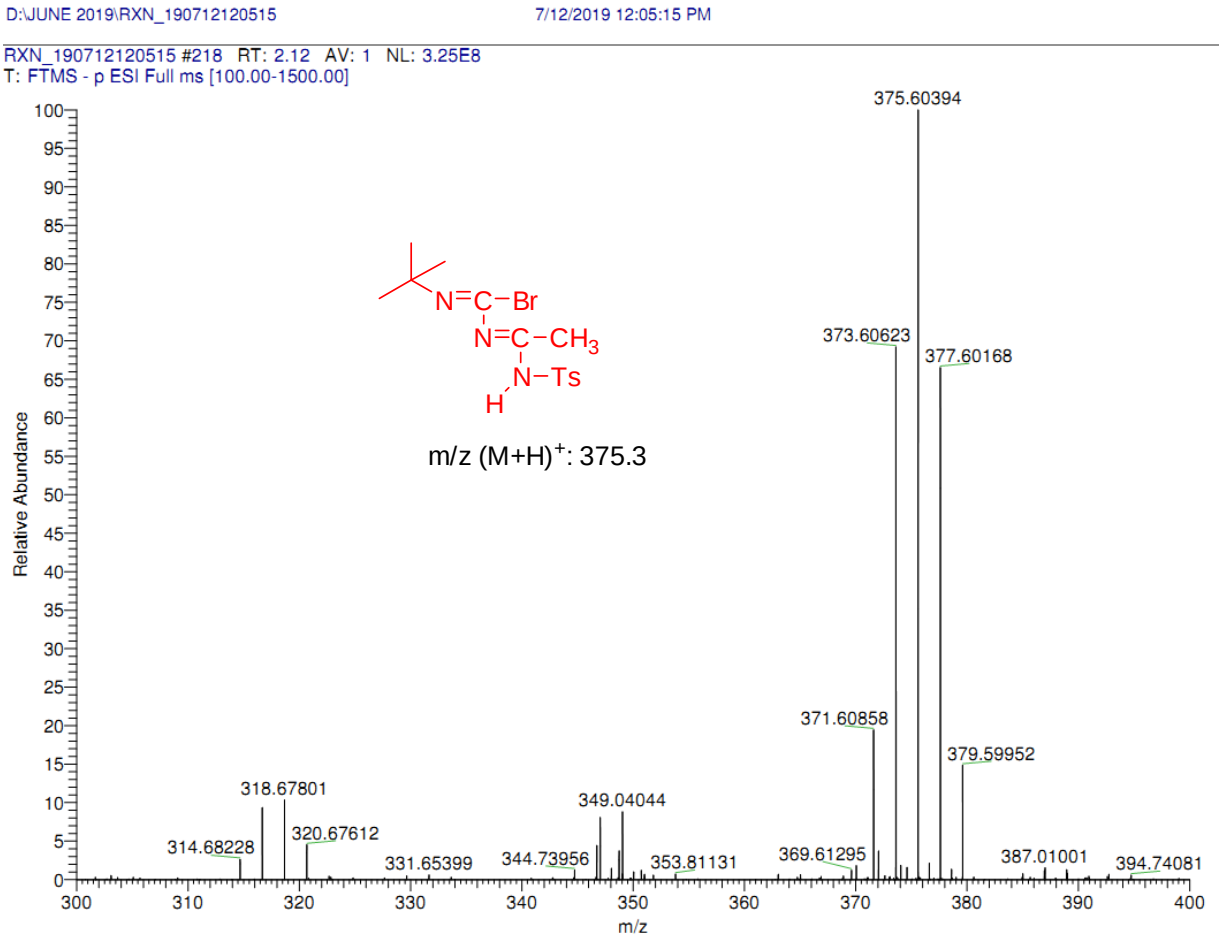
CCDC No. 1978583

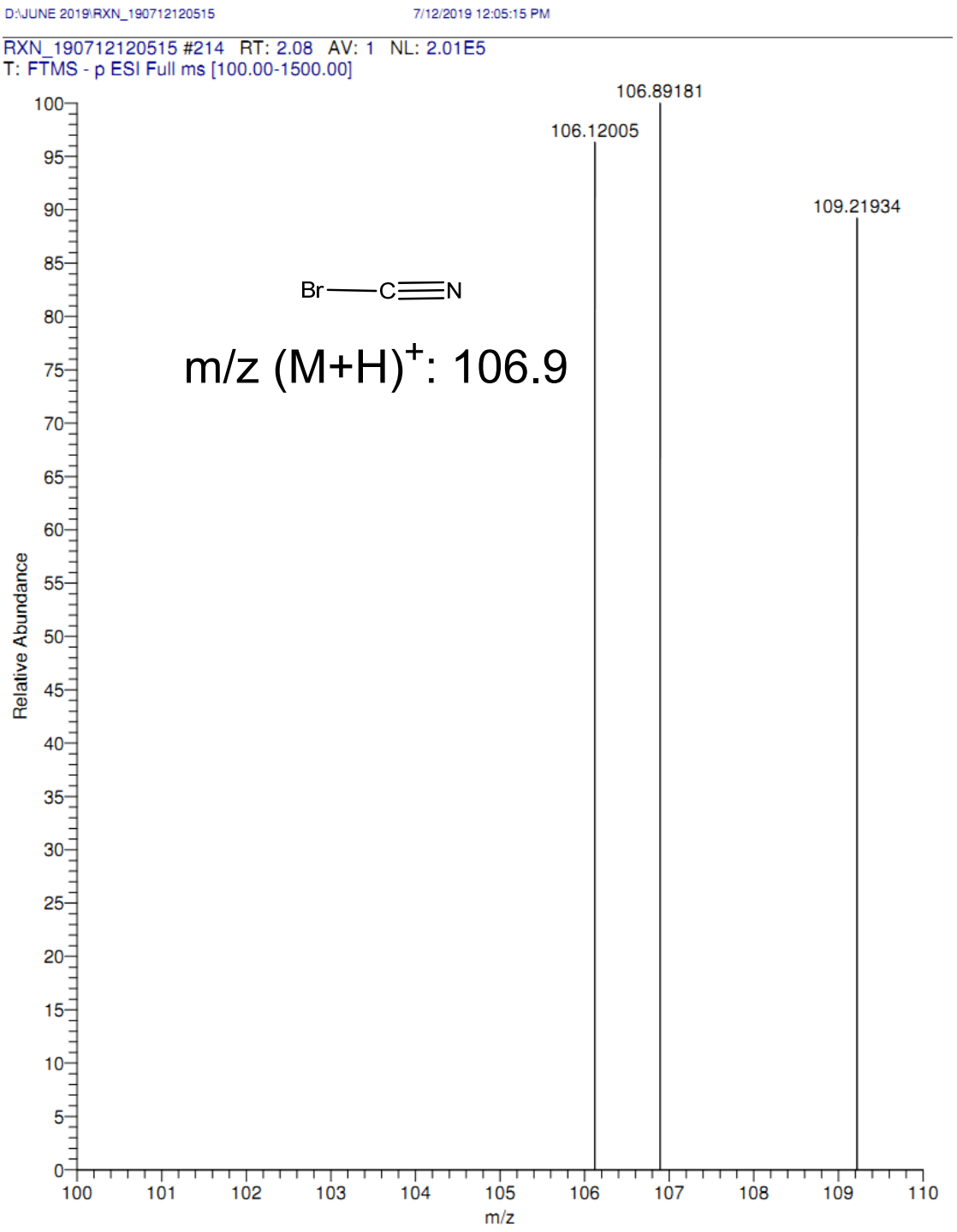




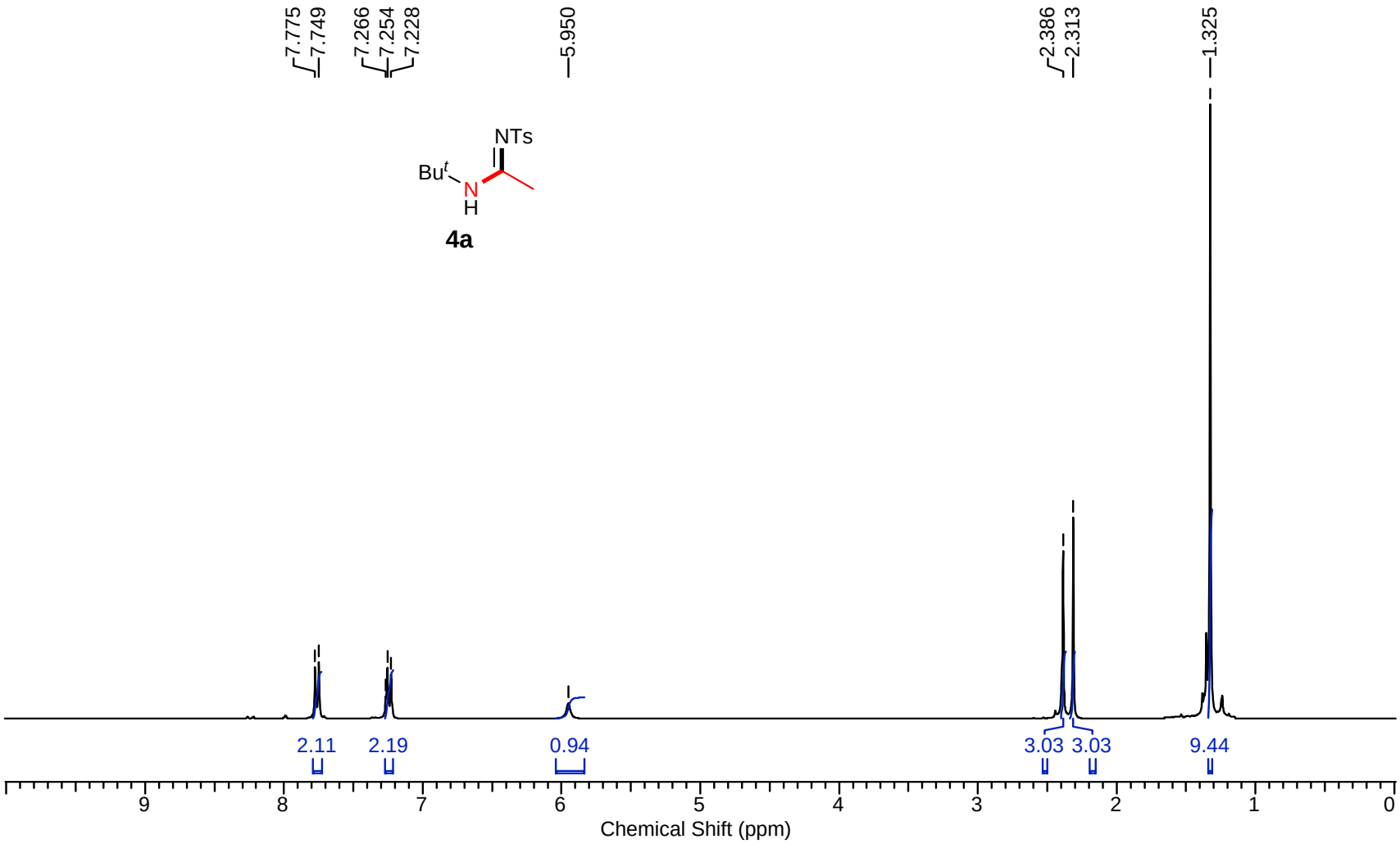
Moiety formula	$2(C_{12}H_{17}N_3O_4S)$, C_2H_3N
M_r	639.75
Crystal system	Orthorhombic
Space group	I b a 2
Temperature (K)	296
a, Å	29.306(4)
b, Å	9.4752(9)
c, Å	11.4635(11)
α, deg	90
β, deg	90
γ, deg	90
V (Å^3)	3183.2(6)
Z	4
μ (mm^{-1})	0.224
Nref	4270
Tmin	0.958
Tmax	0,973
R	0.0351
wR_2	0.0977
Diffractometer	Bruker *APEX-II* CCD diffractometer
CCDC No.	1978583

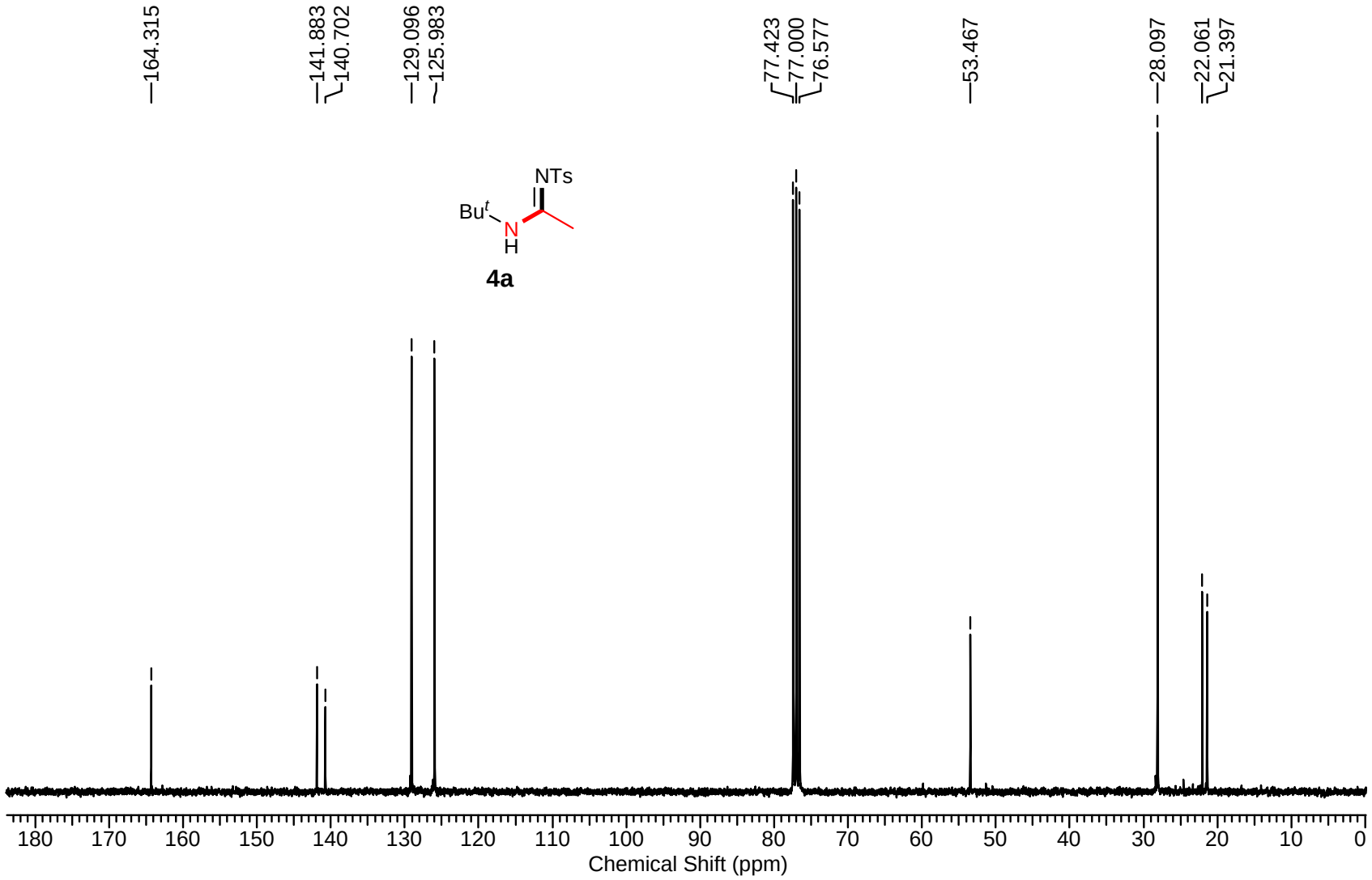
10. **LC-MS Spectrum of reaction mixture:**




D:\JUNE 2019\RXN_190712120515 7/12/2019 12:05:15 PM
RXN_190712120515 #214 RT: 2.08 AV: 1 NL: 2.01E5
T: FTMS - p ESI Full ms [100.00-1500.00]
106.89181
106.12005
109.21934
Br—C≡N
m/z (M+H)+: 106.9
Relative Abundance
m/z

11. ^{1}H and ^{13}C NMR spectra of compounds:

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77.000
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53.467
28.097
22.061
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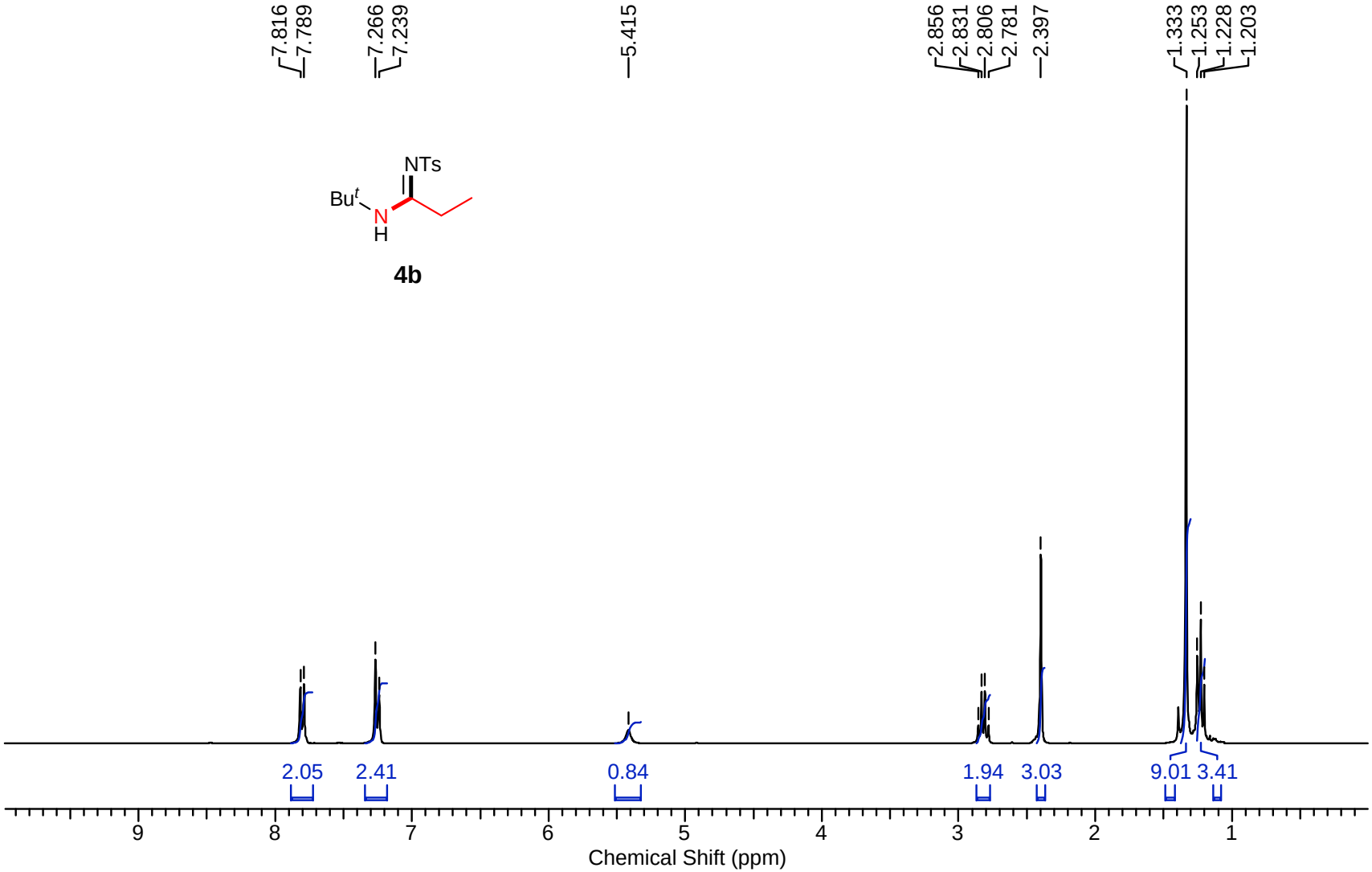
Bu^t
N
H
4a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)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1.203
NTs
Bu^t
N
H
4b
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2.41
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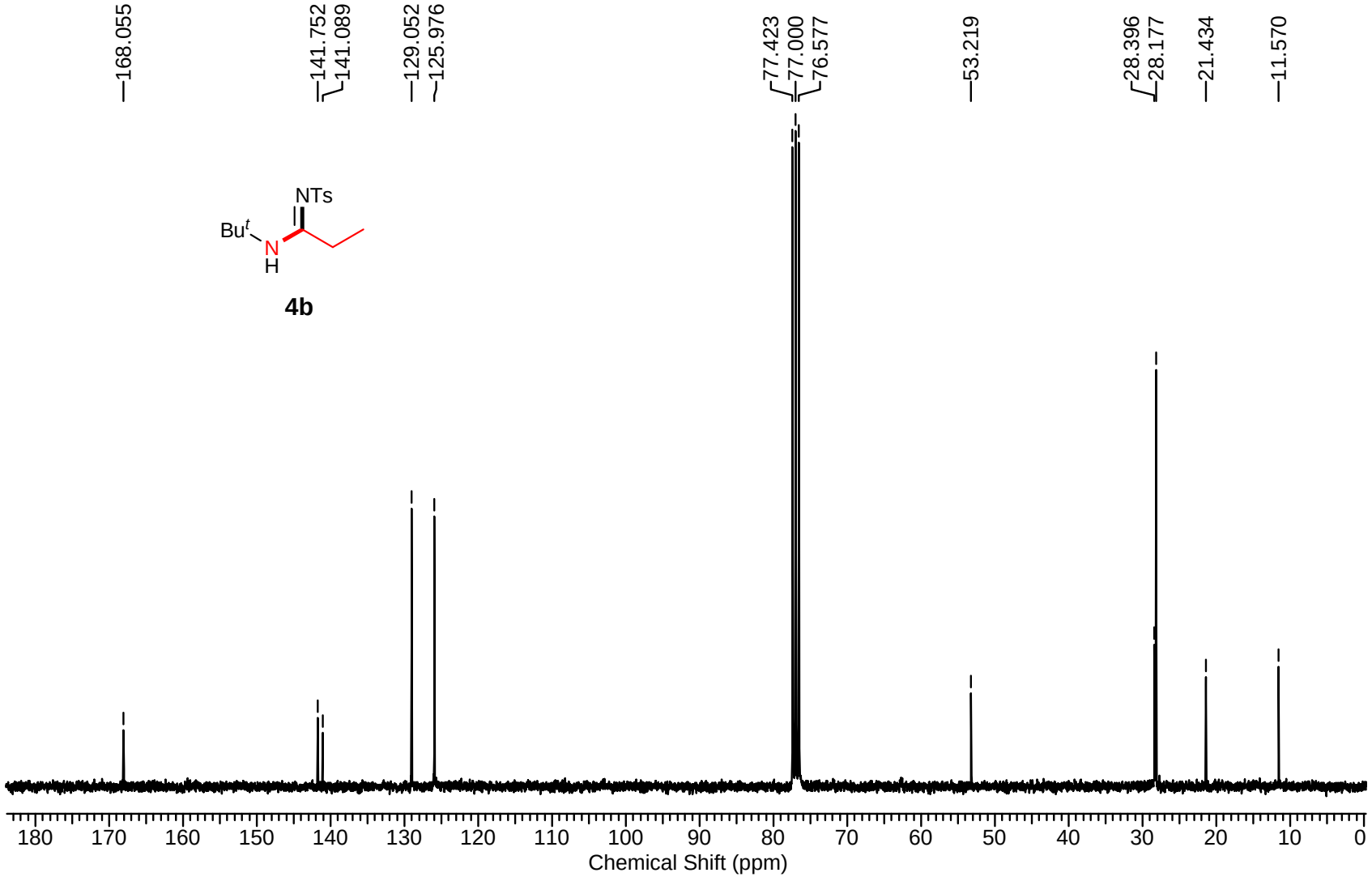
Chemical Shift (ppm)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4b
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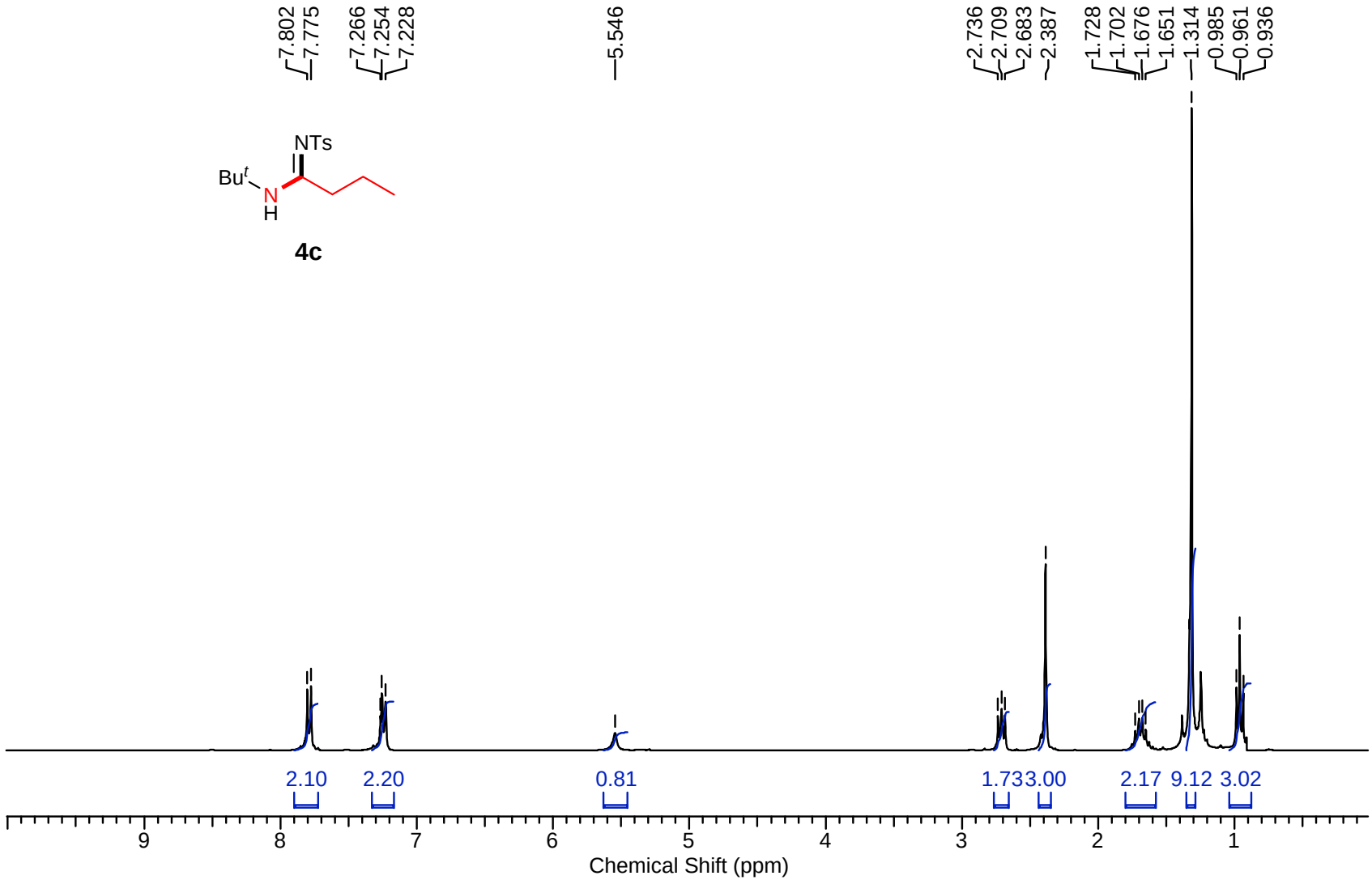
Chemical Shift (ppm)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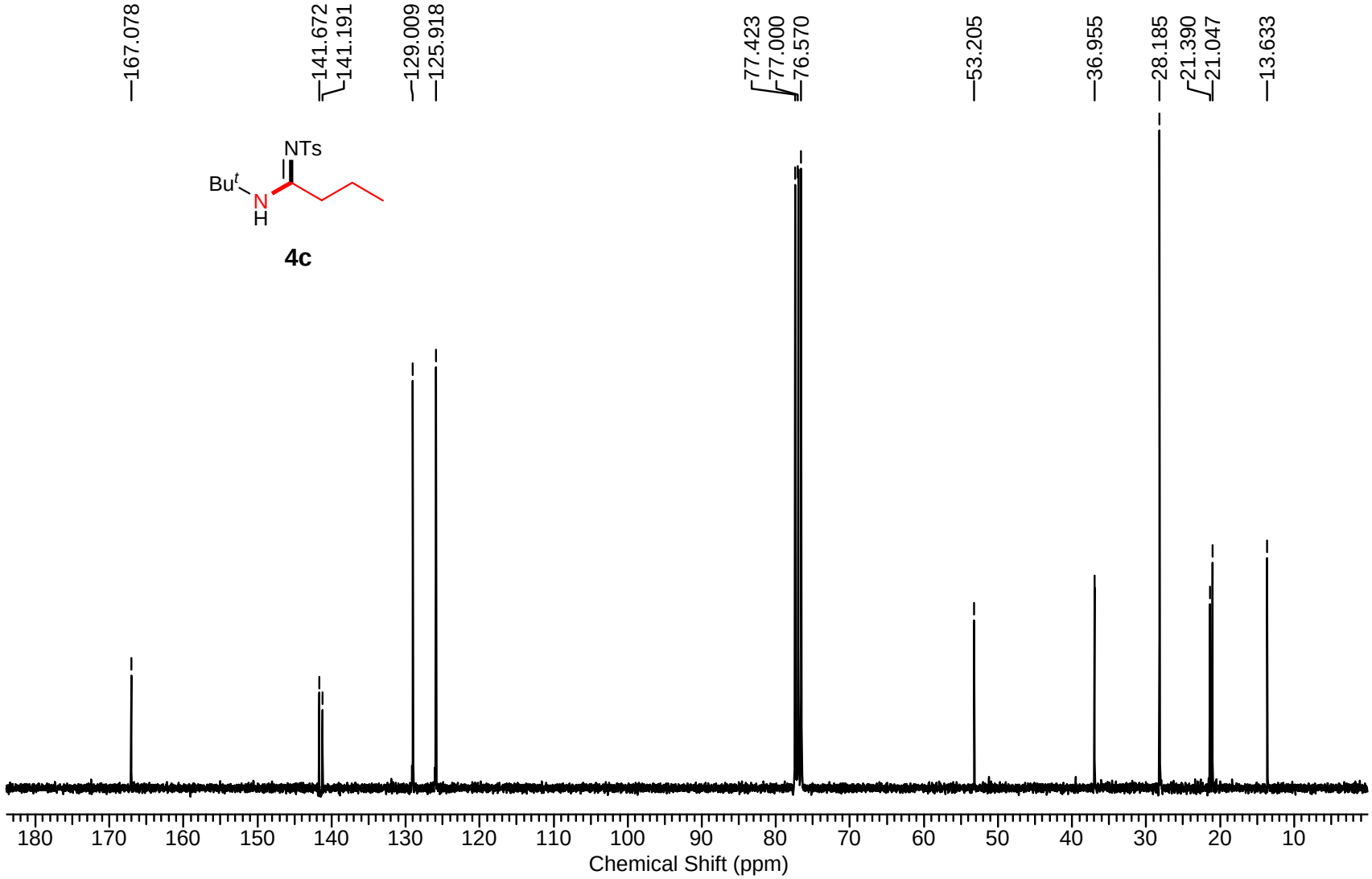
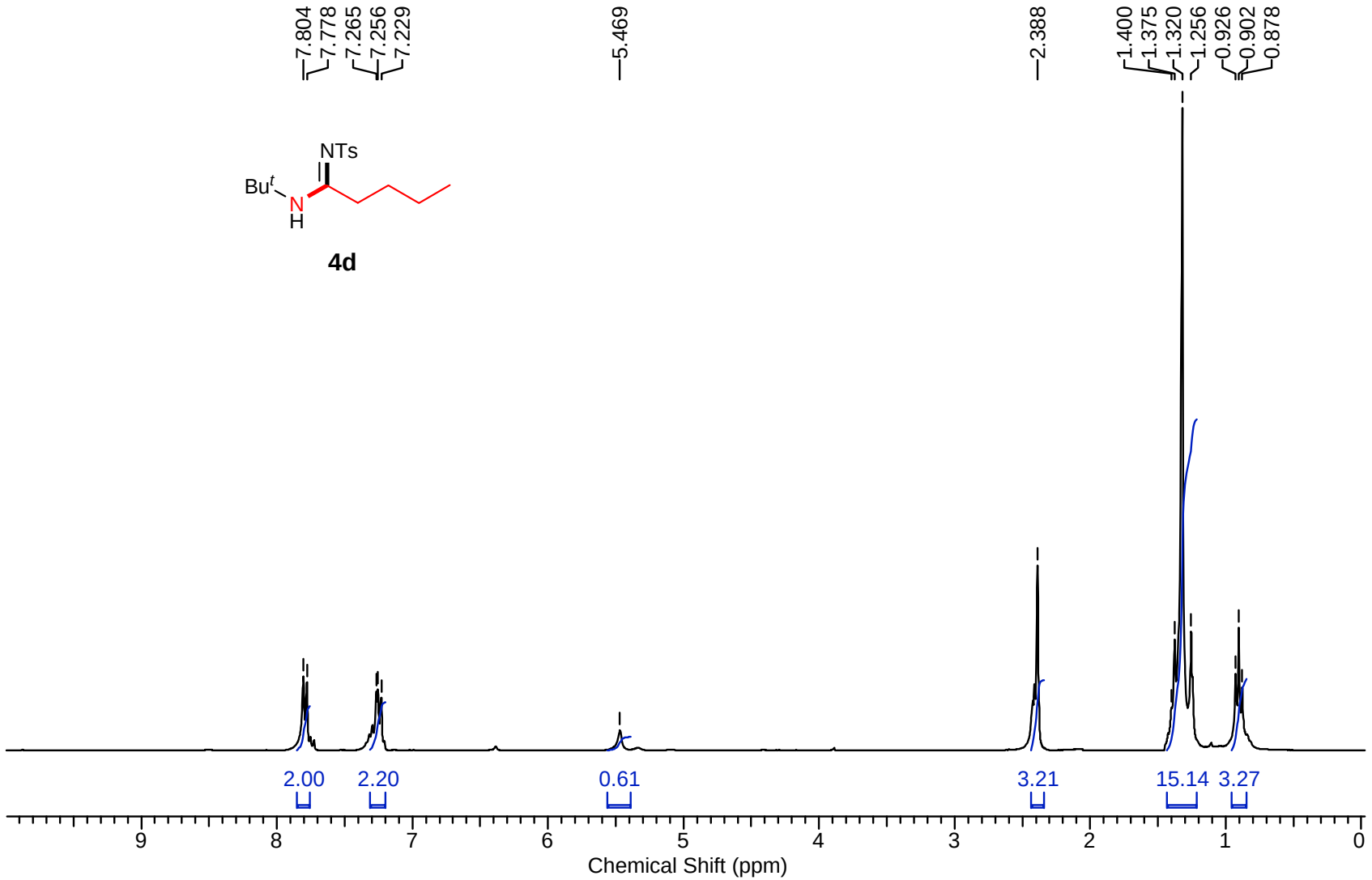
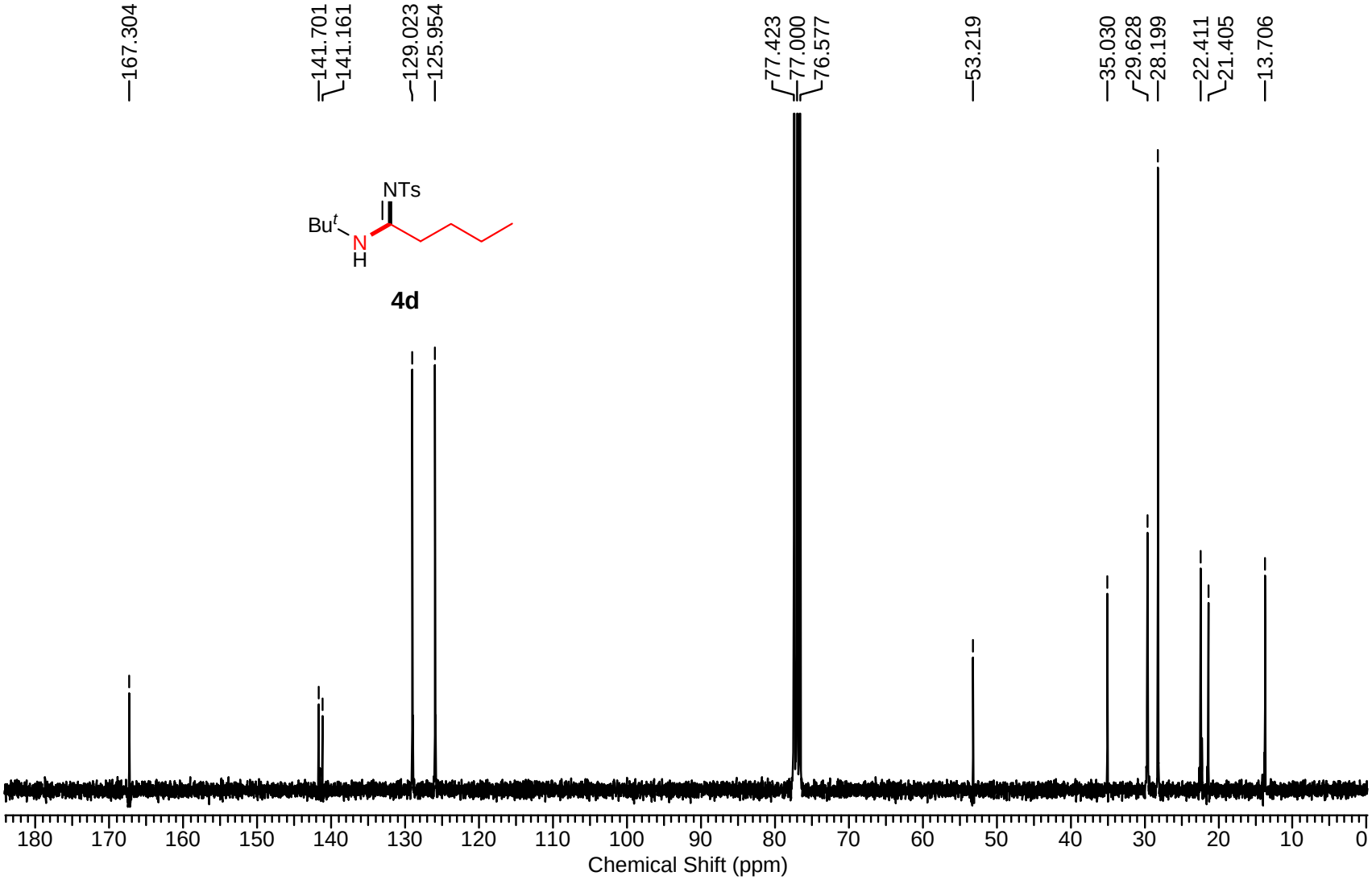
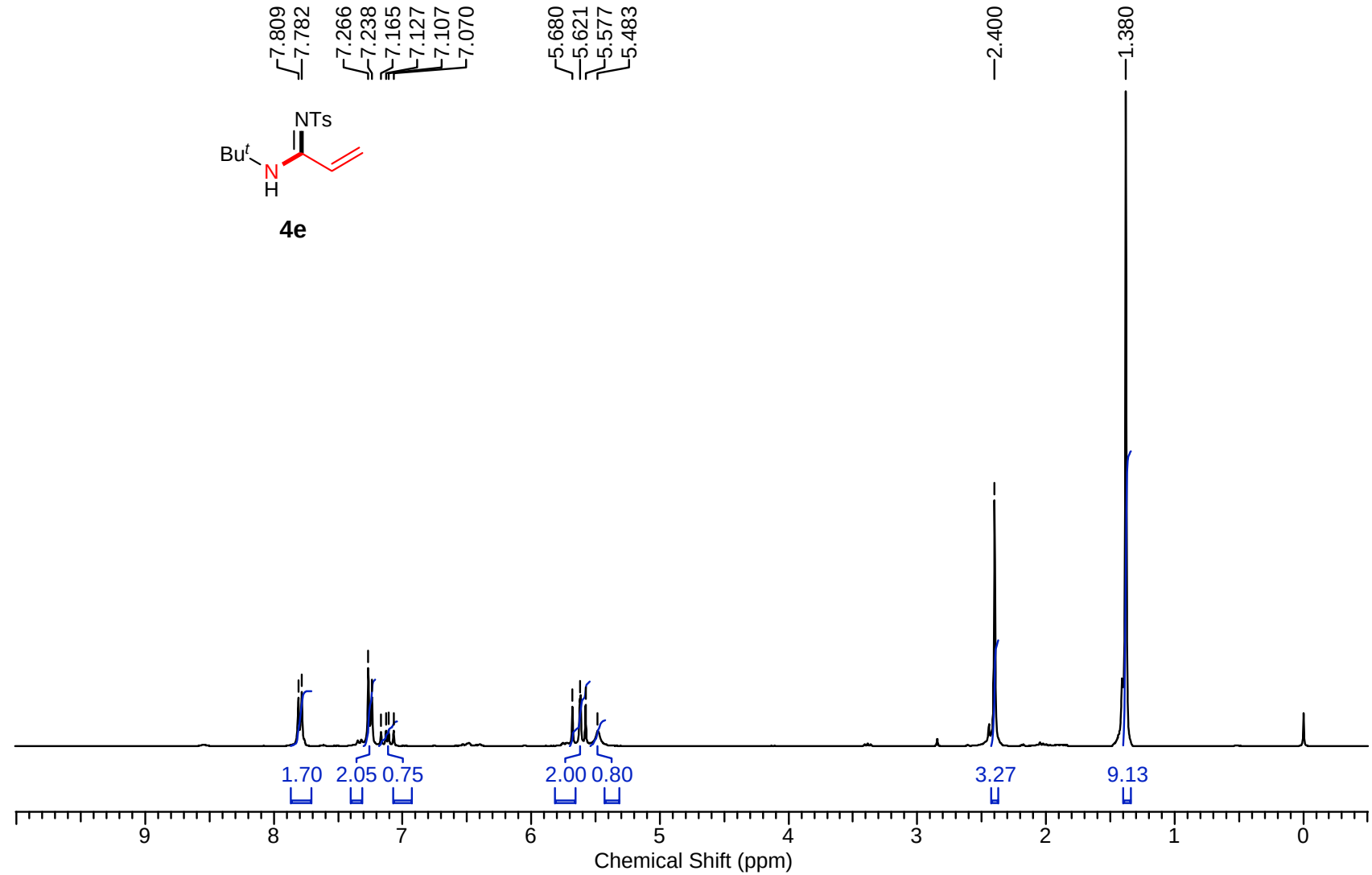
1.651
1.314
0.985
0.961
0.936
NTs
Bu^t
N
H
4c
2.10
2.20
0.81
1.73
3.00
2.17
9.12
3.02
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

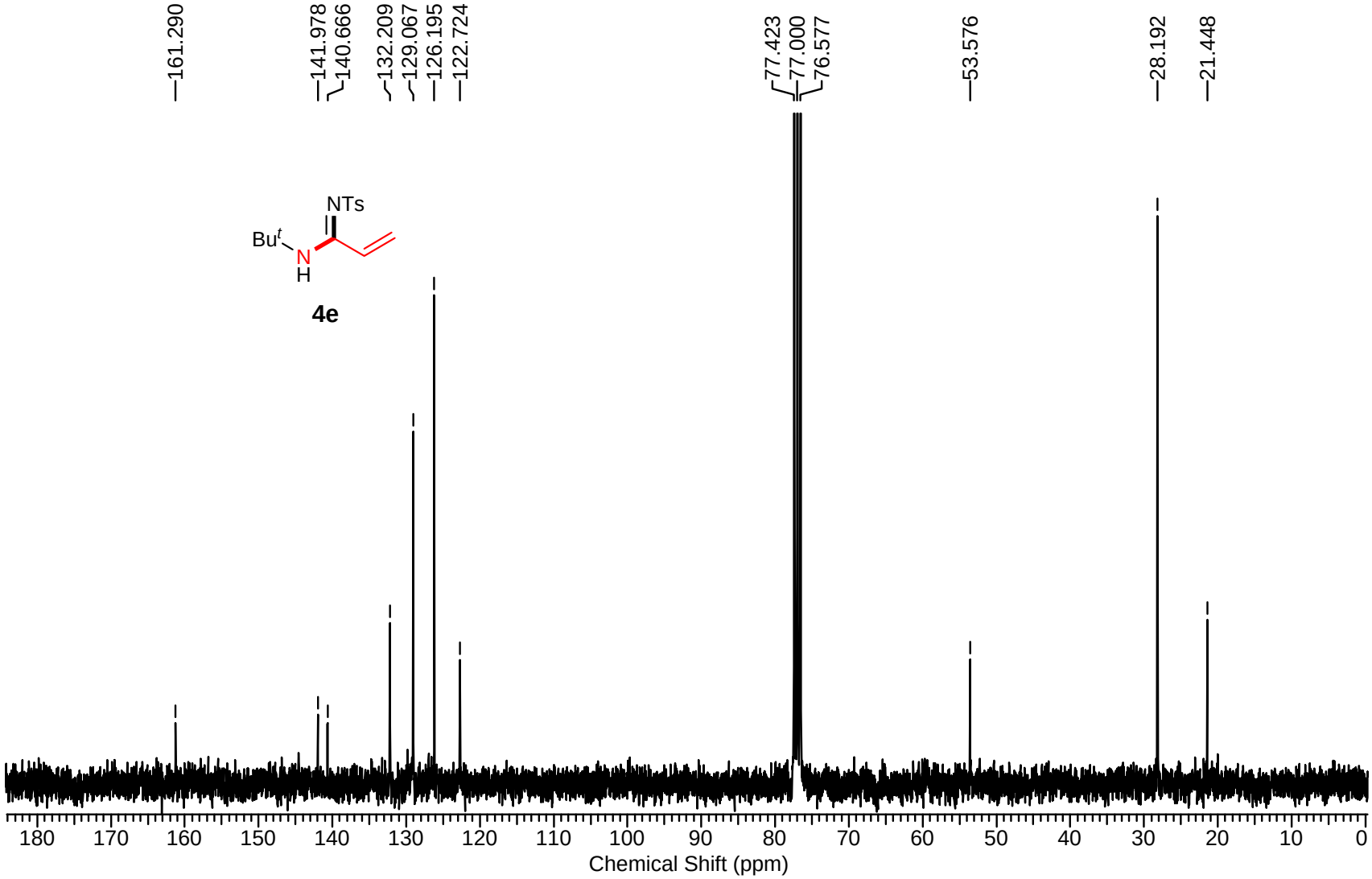

167.078
141.672
141.191
129.009
125.918
77.423
77.000
76.570
53.205
36.955
28.185
21.390
21.047
13.633
NTs
Bu^t
N
H
4c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

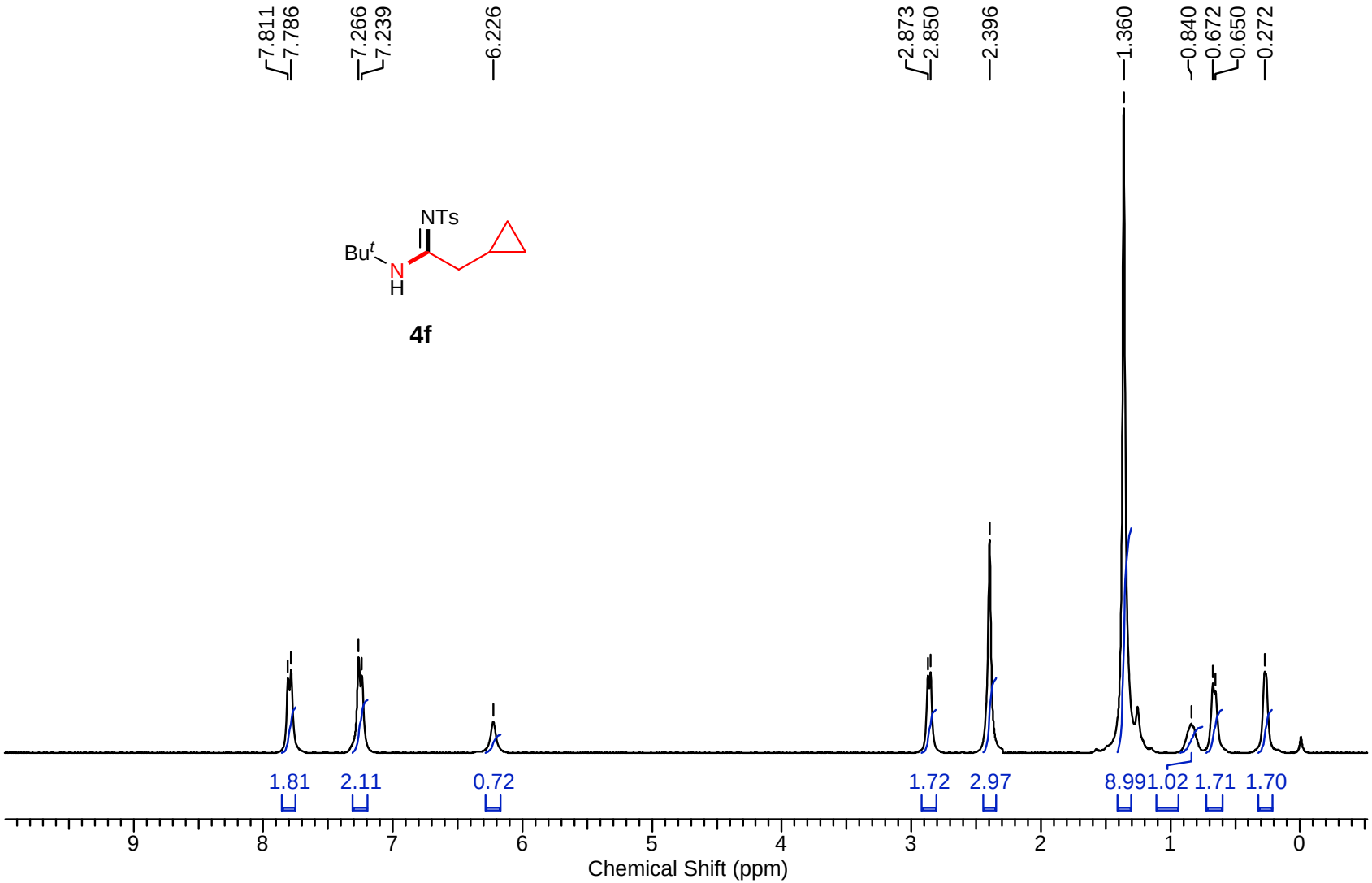

7.804
7.778
7.265
7.256
7.229
5.469
2.388
1.400
1.375
1.320
1.256
0.926
0.902
0.878
NTs
Bu^t
N
H
4d
2.00
2.20
0.61
3.21
15.14
3.27
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

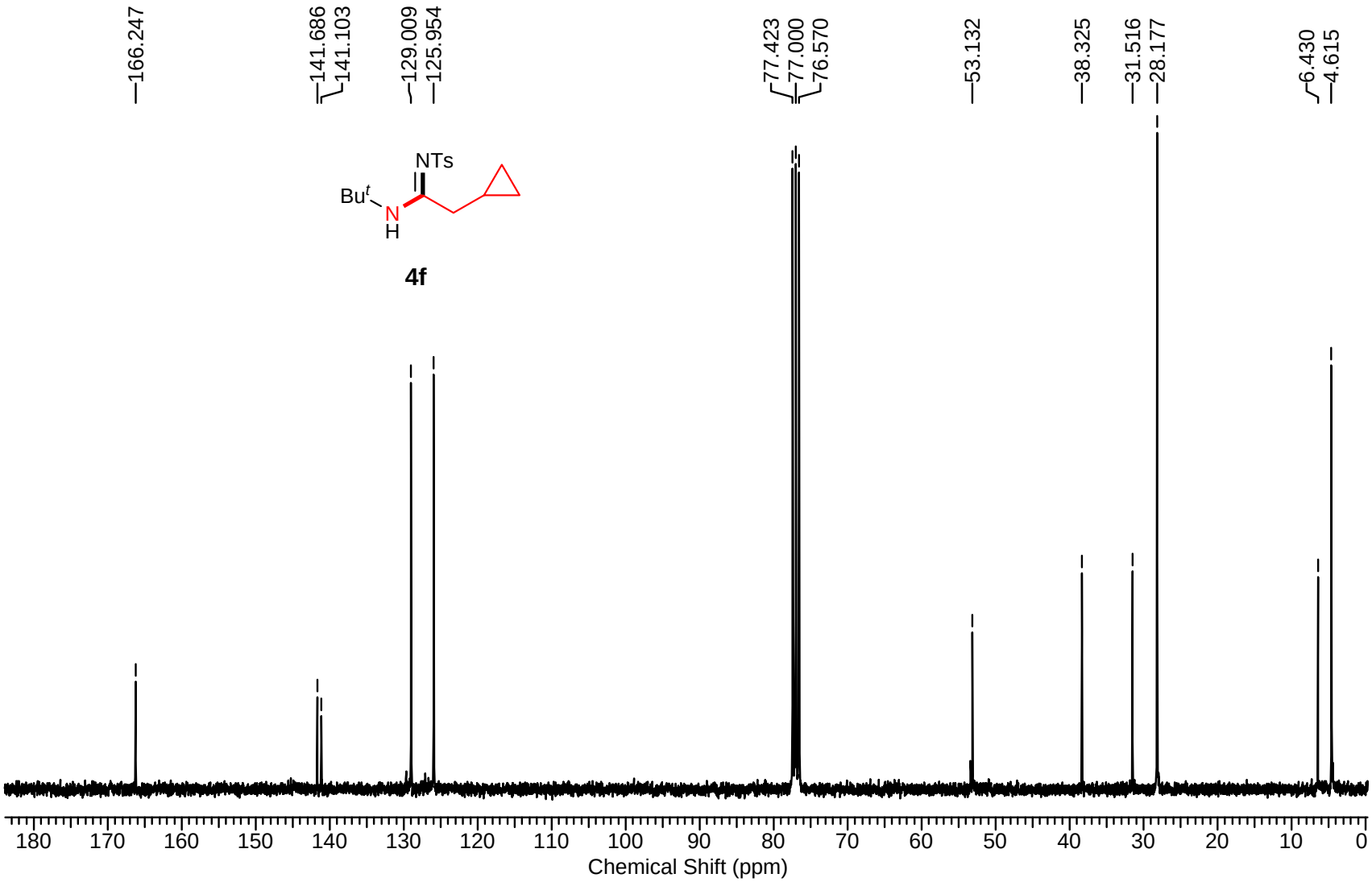

167.304
141.701
141.161
129.023
125.954
77.423
77.000
76.577
53.219
35.030
29.628
28.199
22.411
21.405
13.706
NTs
Bu^t
N
H
4d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

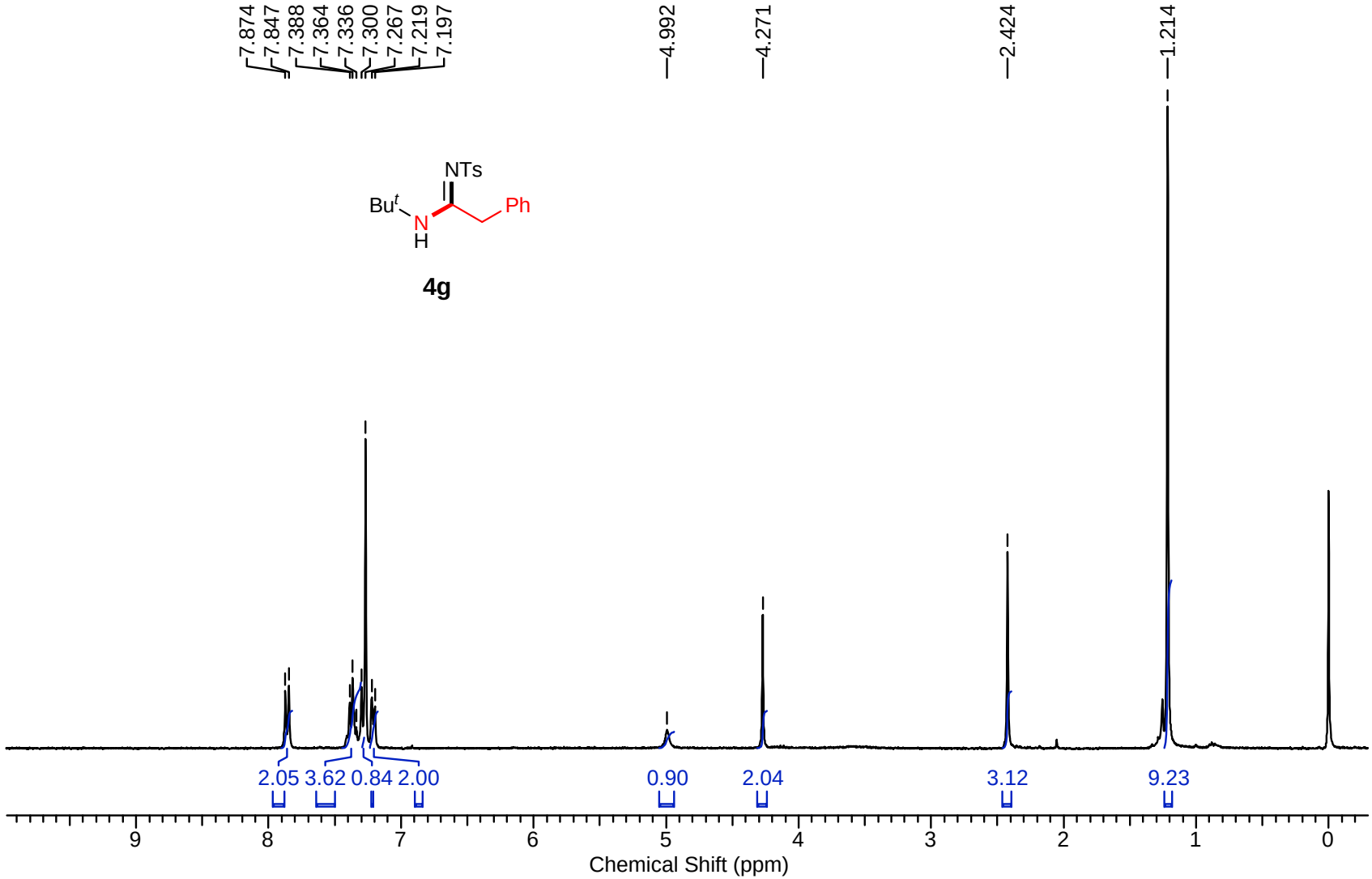

7.809
7.782
7.266
7.238
7.165
7.127
7.107
7.070
5.680
5.621
5.577
5.483
2.400
1.380
NTs
Bu^t
N
H
1.70
2.05
0.75
2.00
0.80
3.27
9.13
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

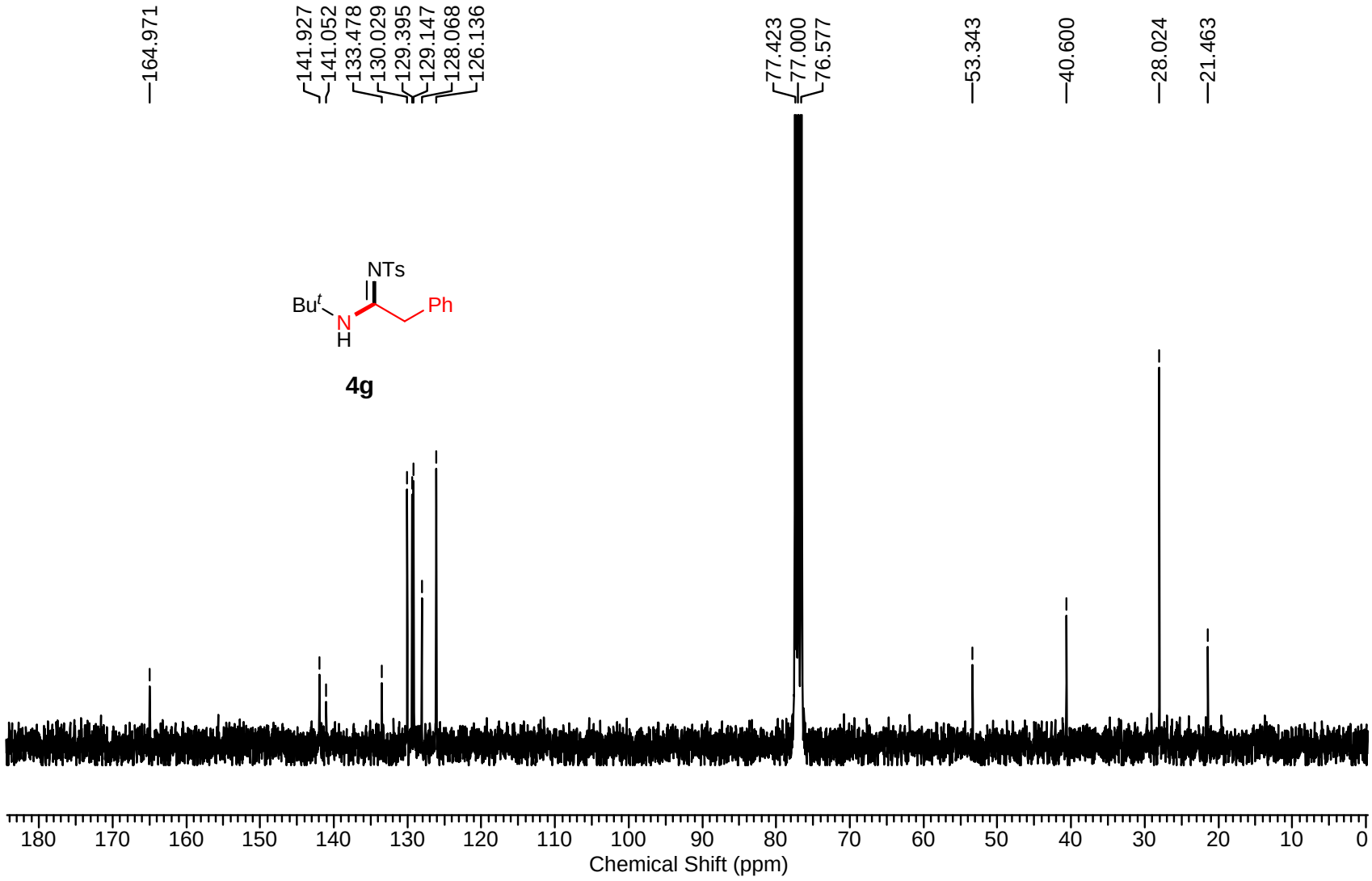
4e

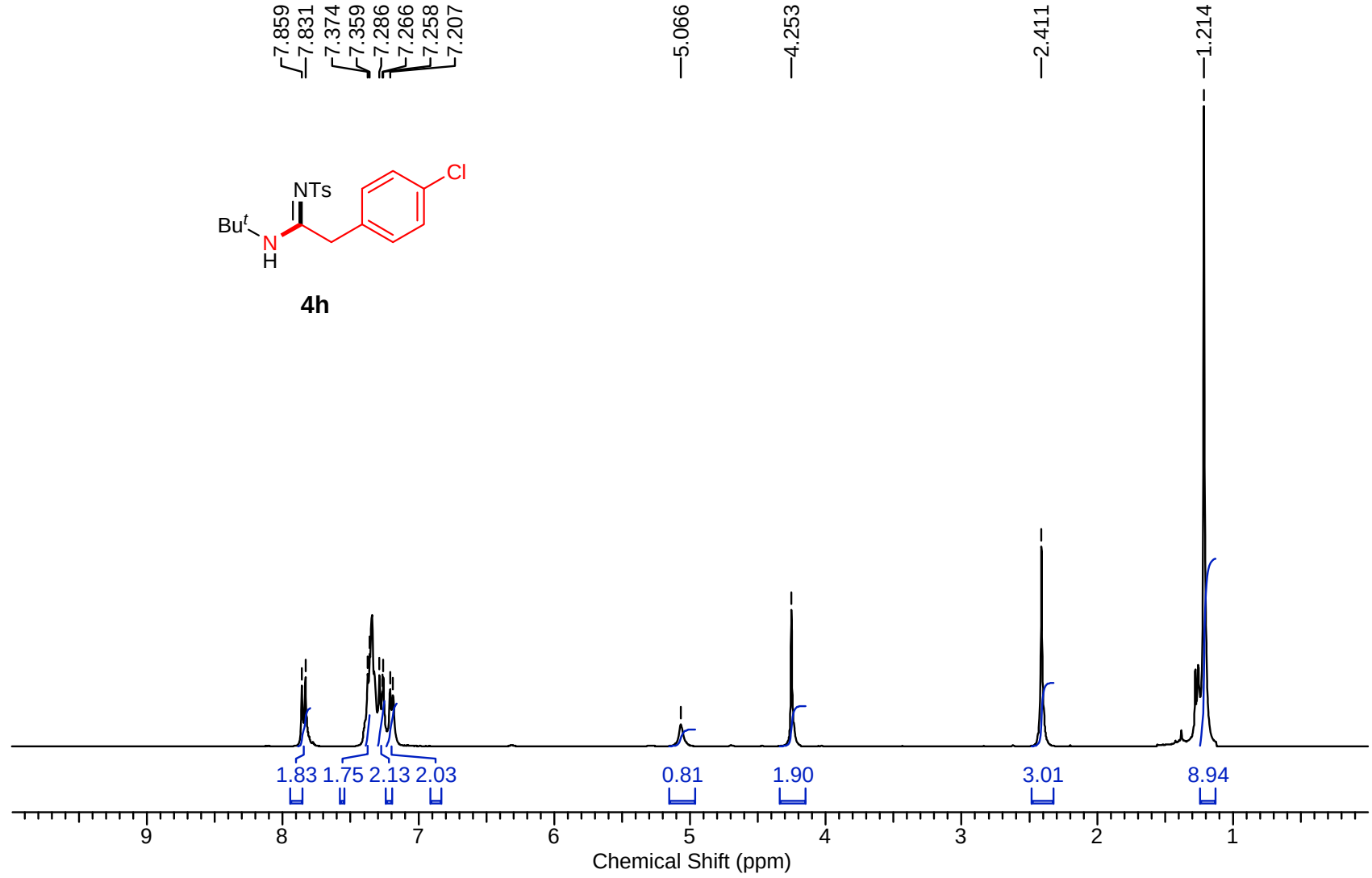

161.290
141.978
140.666
132.209
129.067
126.195
122.724
77.423
77.000
76.577
53.576
28.192
21.448
NTs
Bu^t
N
H
4e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.811
7.786
7.266
7.239
6.226
2.873
2.850
2.396
1.360
0.840
0.672
0.650
0.272
NTs
Bu^t
N
H
4f
1.81
2.11
0.72
1.72
2.97
8.99
1.02
1.71
1.70
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

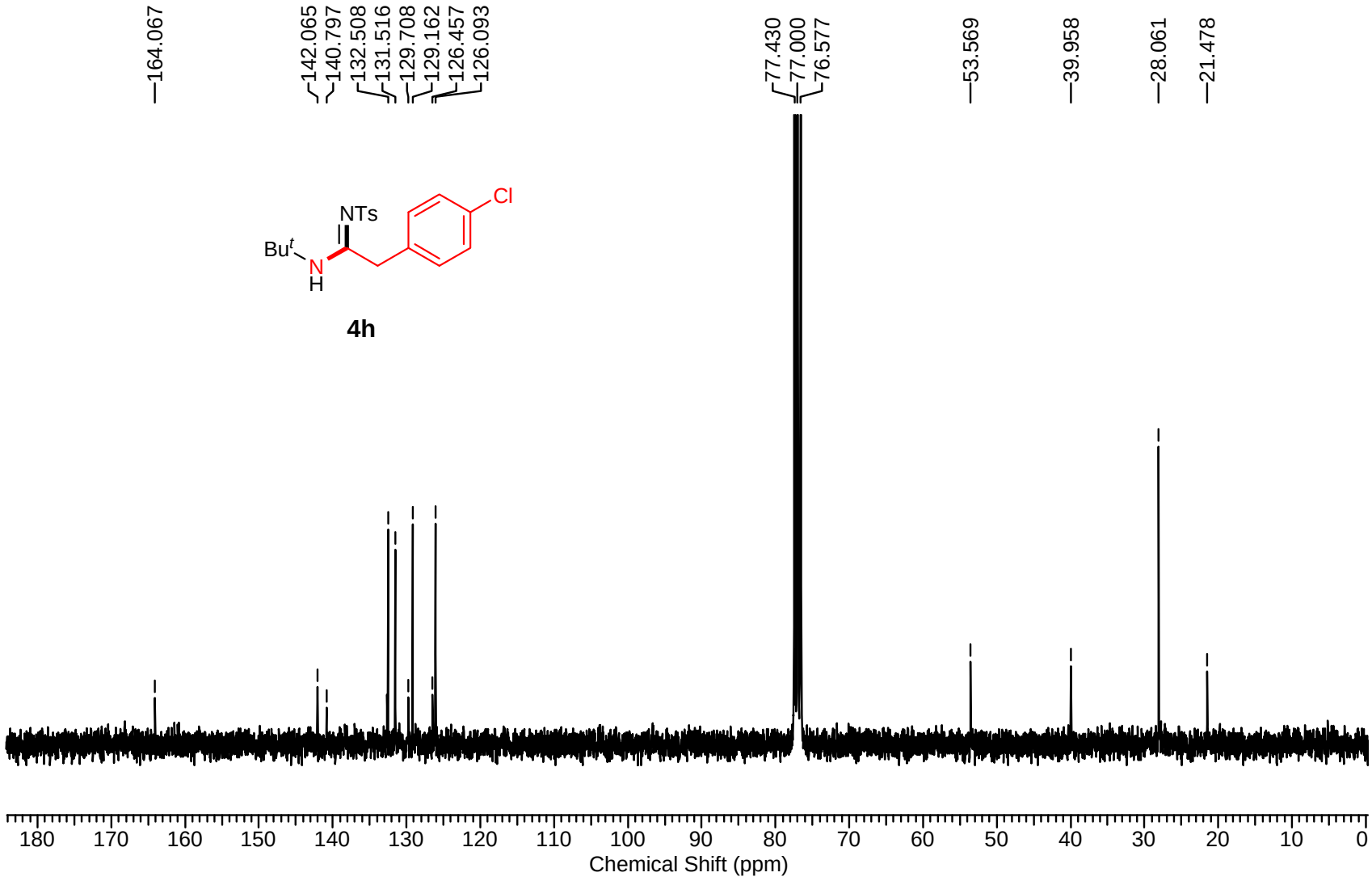

166.247
141.686
141.103
129.009
125.954
77.423
77.000
76.570
53.132
38.325
31.516
28.177
6.430
4.615
NTs
Bu^t
N
H
4f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

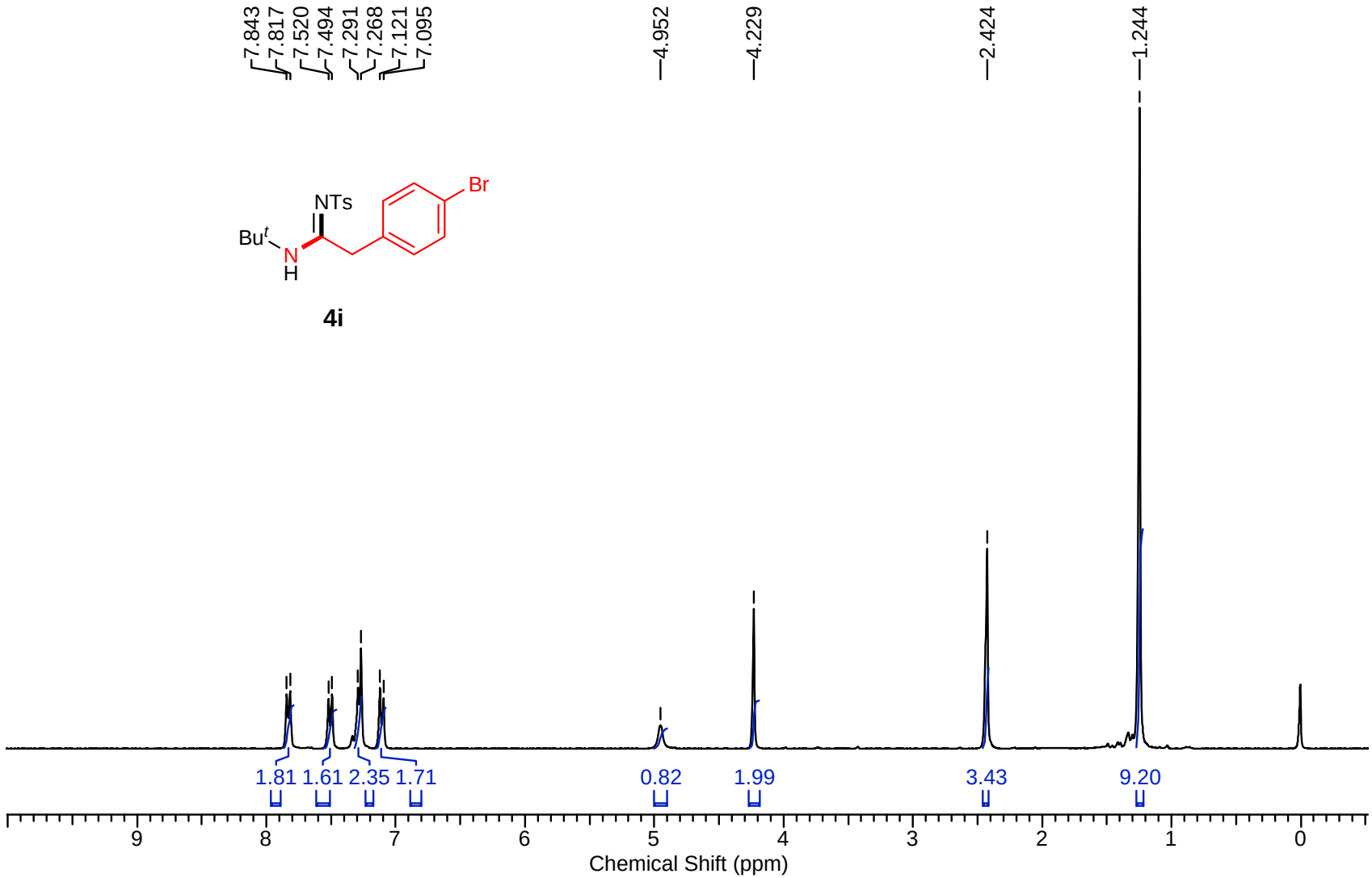

7.874
7.847
7.388
7.364
7.336
7.300
7.267
7.219
7.197
4.992
4.271
2.424
1.214
NTs
Bu^t
N
H
Ph
4g
2.05 3.62 0.84 2.00
0.90
2.04
3.12
9.23
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

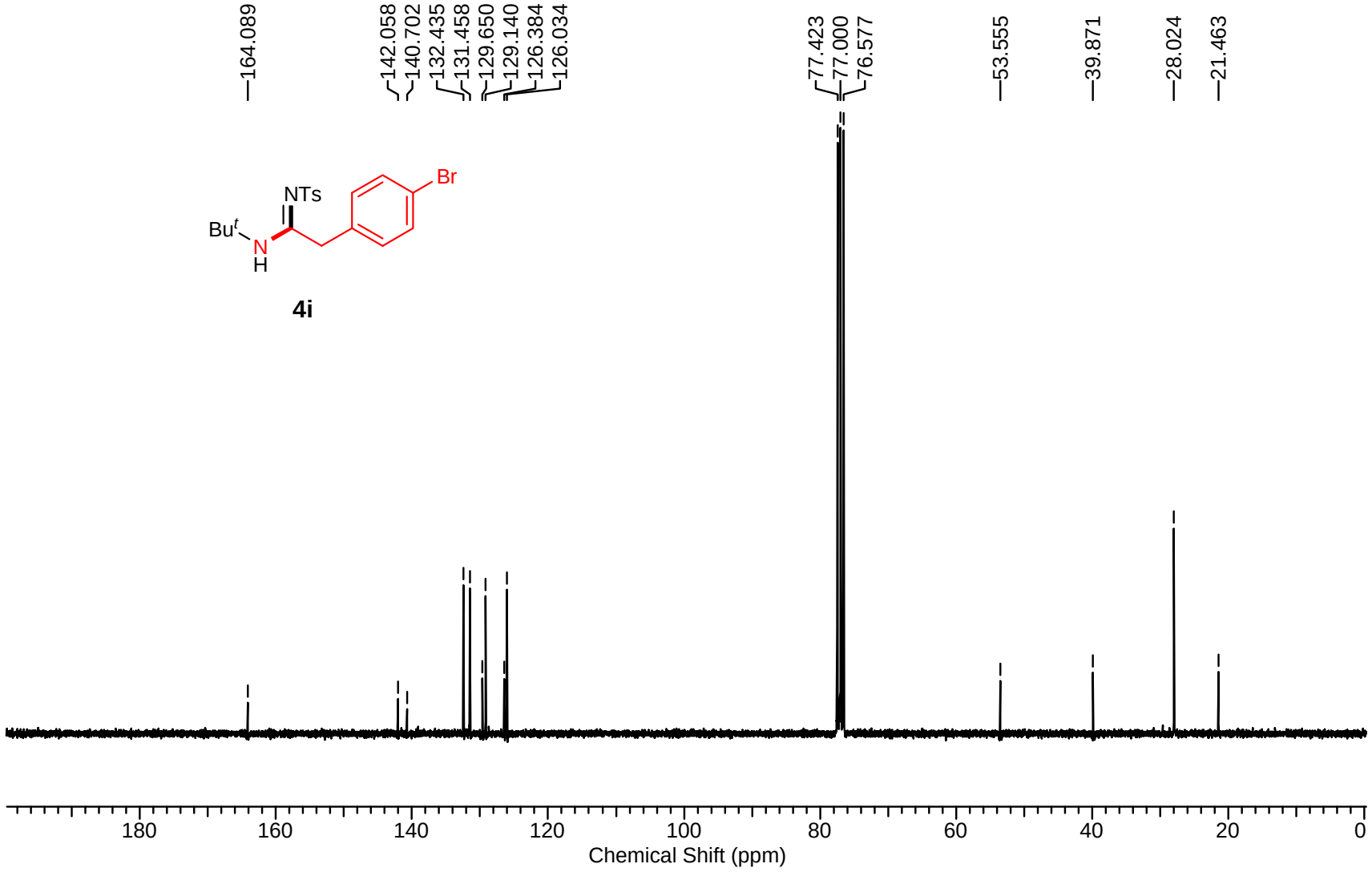

164.971
141.927
141.052
133.478
130.029
129.395
129.147
128.068
126.136
77.423
77.000
76.577
53.343
40.600
28.024
21.463
NTs
Bu^t
N
H
Ph
4g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

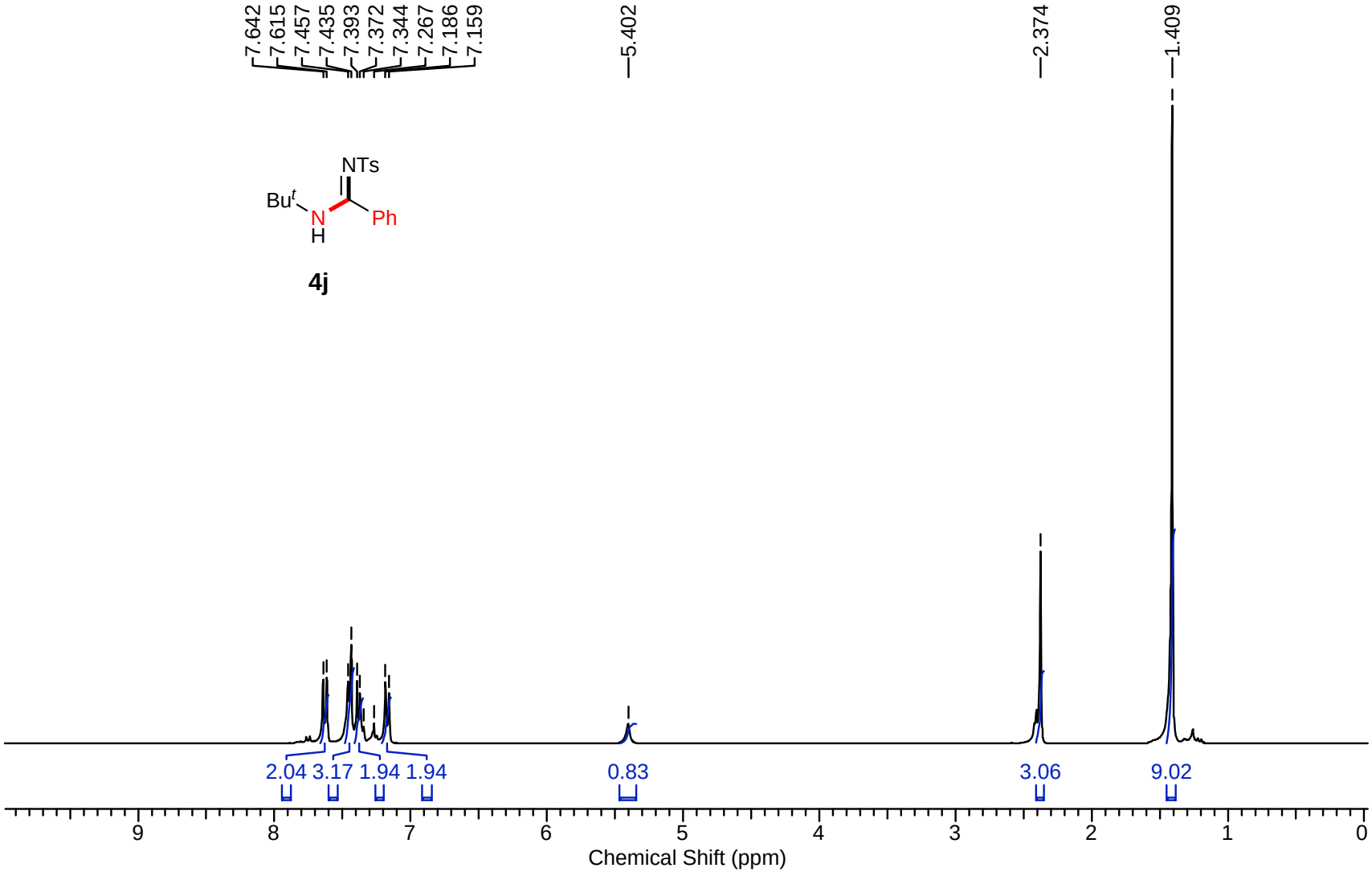

7.859
7.831
7.374
7.359
7.286
7.266
7.258
7.207
5.066
4.253
2.411
1.214
NTs
Cl
Bu^t
N
H
1.83
1.75
2.13
2.03
0.81
1.90
3.01
8.94
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

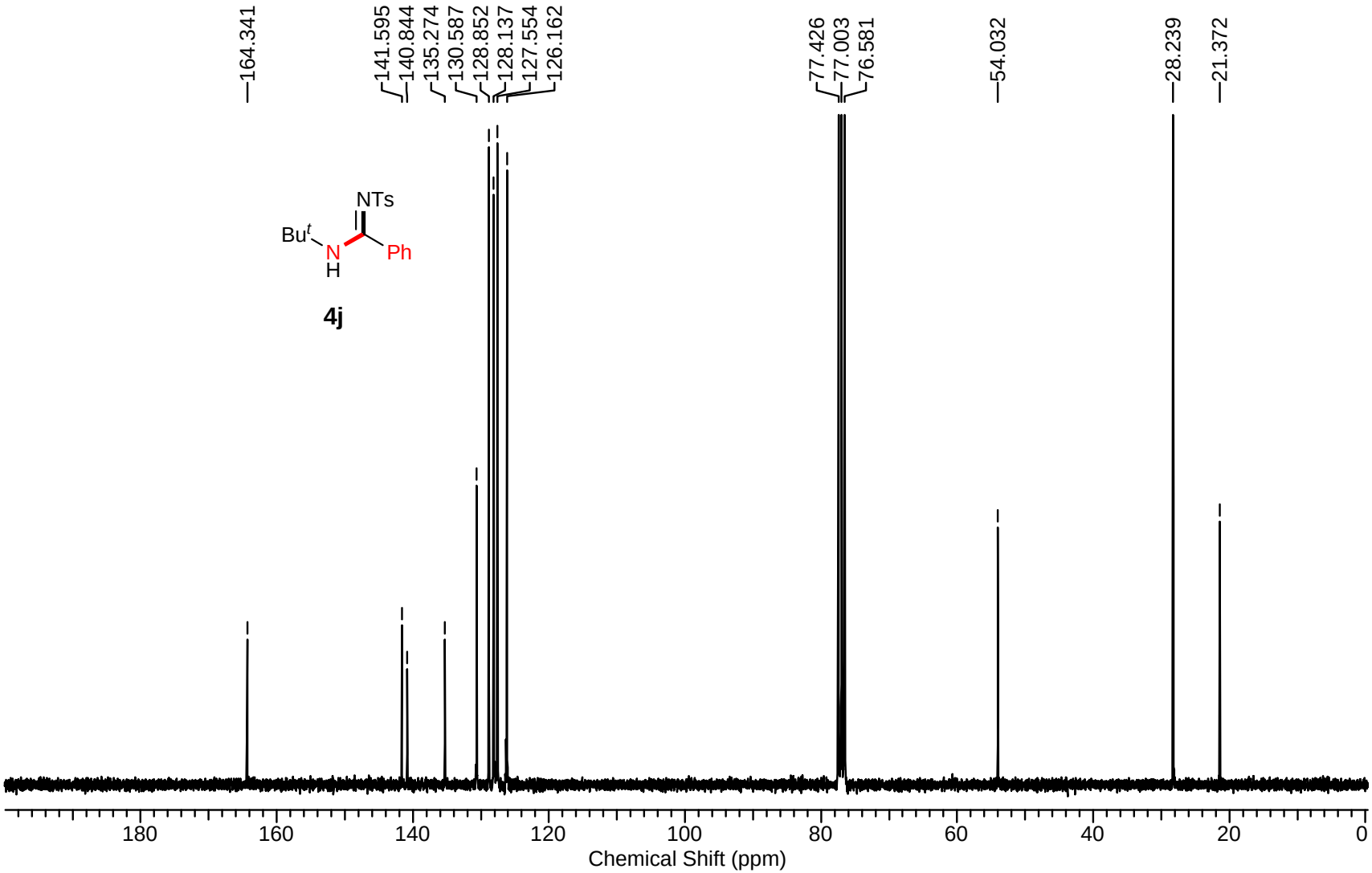
4h

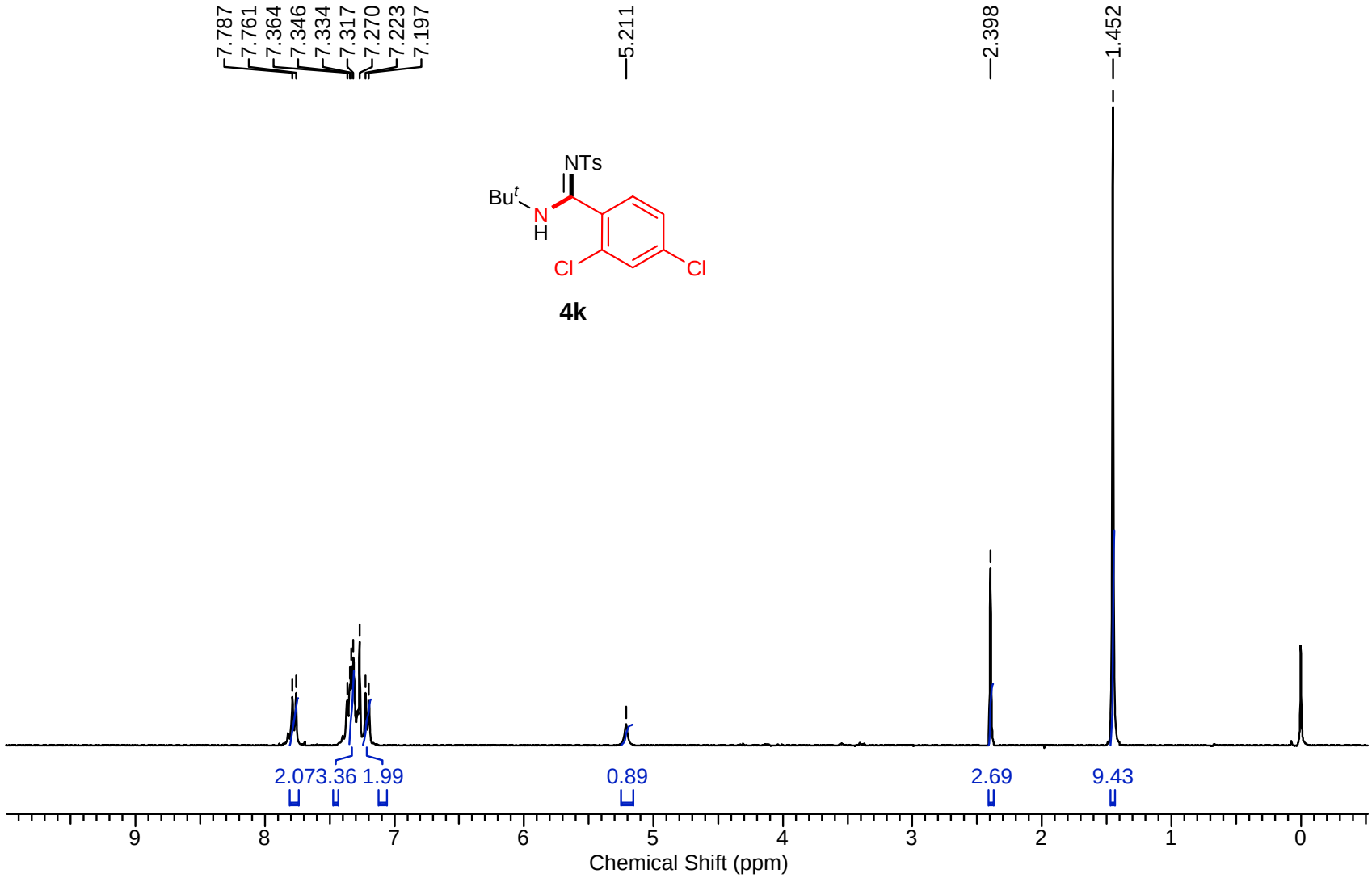

164.067
142.065
140.797
132.508
131.516
129.708
129.162
126.457
126.093
77.430
77.000
76.577
53.569
39.958
28.061
21.478
NTs
Cl
Bu^t
N
H
4h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.843
7.817
7.520
7.494
7.291
7.268
7.121
7.095
4.952
4.229
2.424
1.244
NTs
Br
Bu^t
N
H
4i
1.81
1.61
2.35
1.71
0.82
1.99
3.43
9.20
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

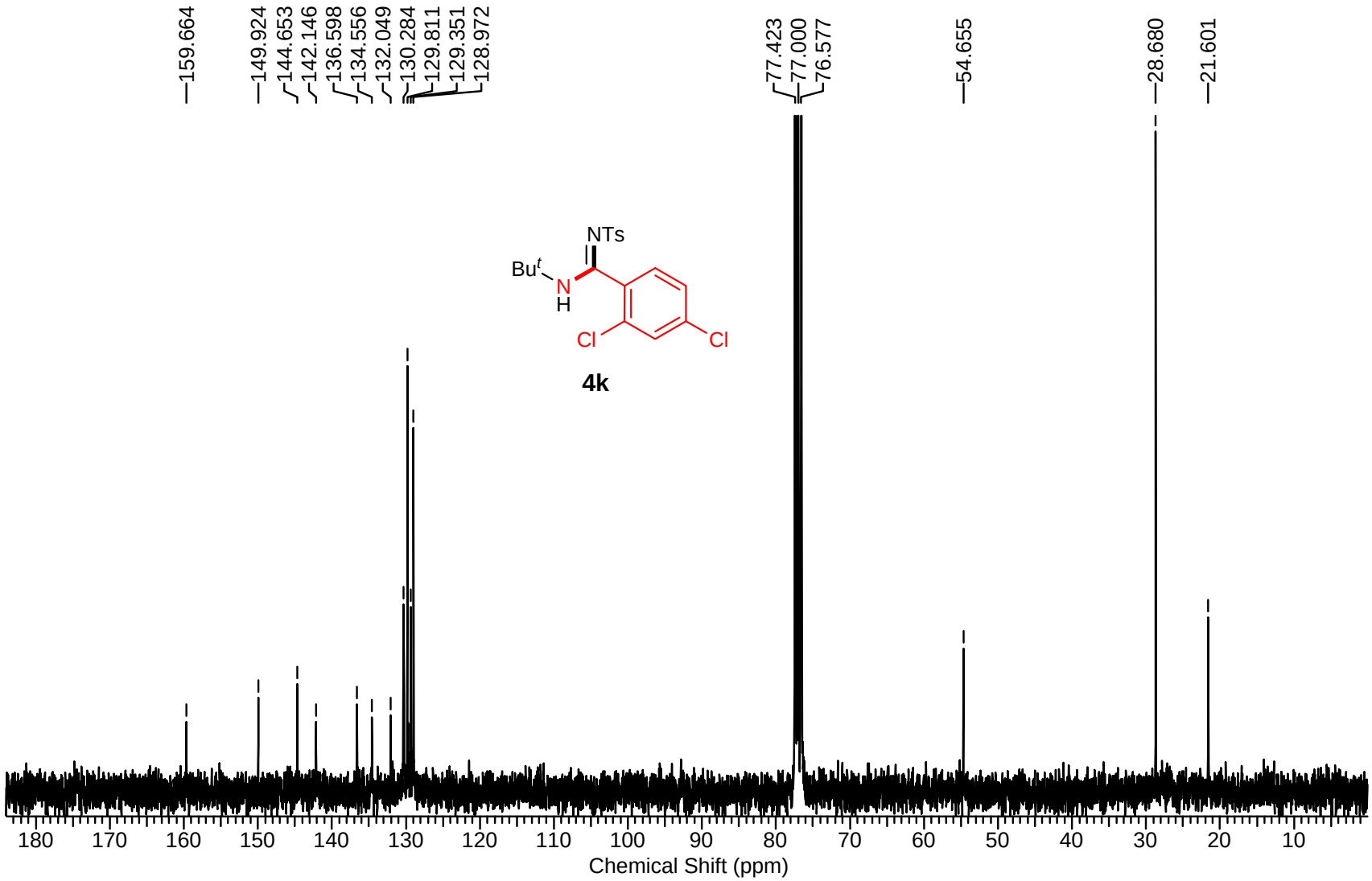

164.089
142.058
140.702
132.435
131.458
129.650
129.140
126.384
126.034
77.423
77.000
76.577
53.555
39.871
28.024
21.463
NTs
Br
Bu^t
N
H
4i
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

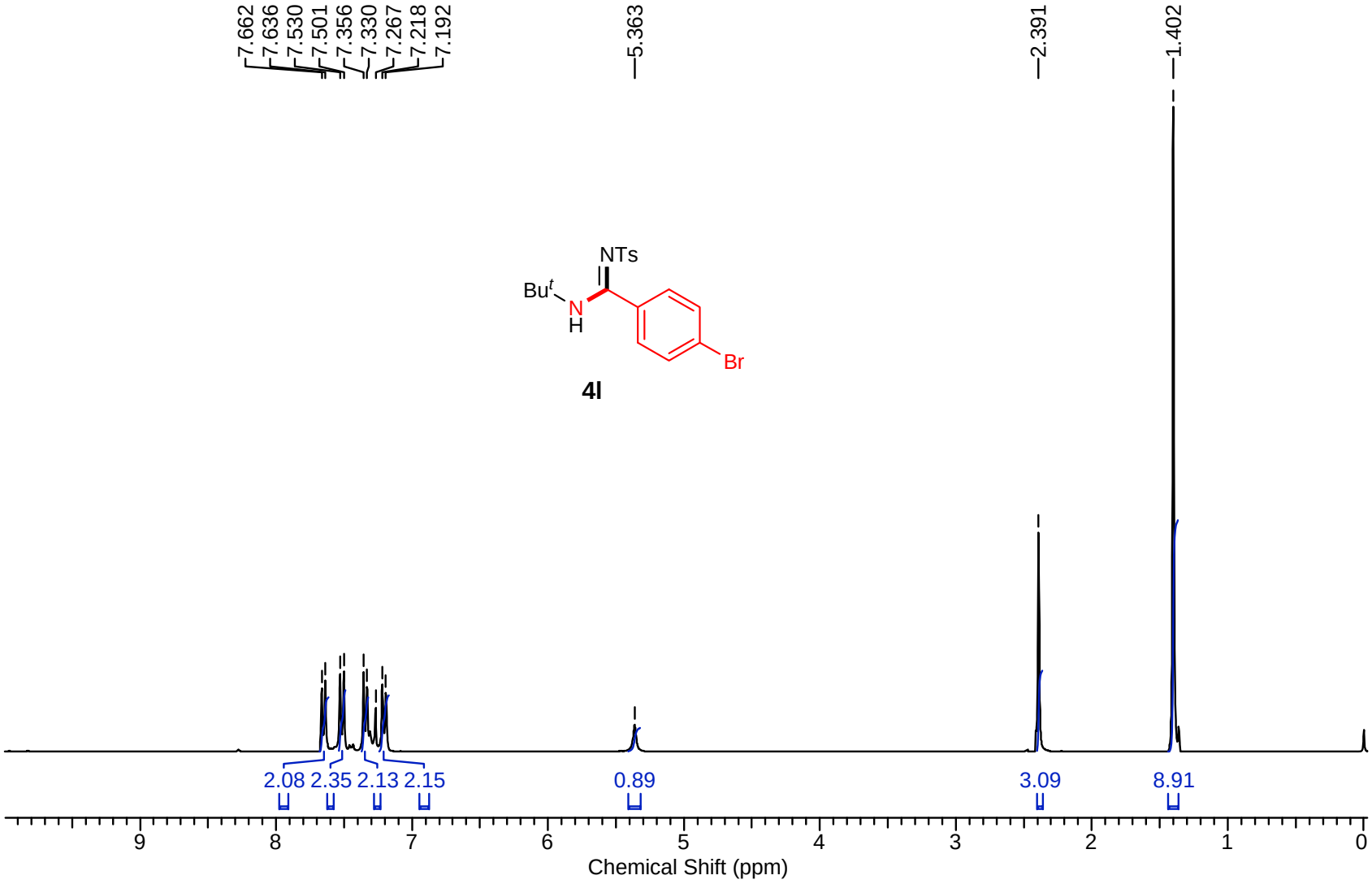

7.642
7.615
7.457
7.435
7.393
7.372
7.344
7.267
7.186
7.159
5.402
2.374
1.409
NTs
Bu^t
N
H
Ph
4j
2.04 3.17 1.94 1.94
0.83
3.06
9.02
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

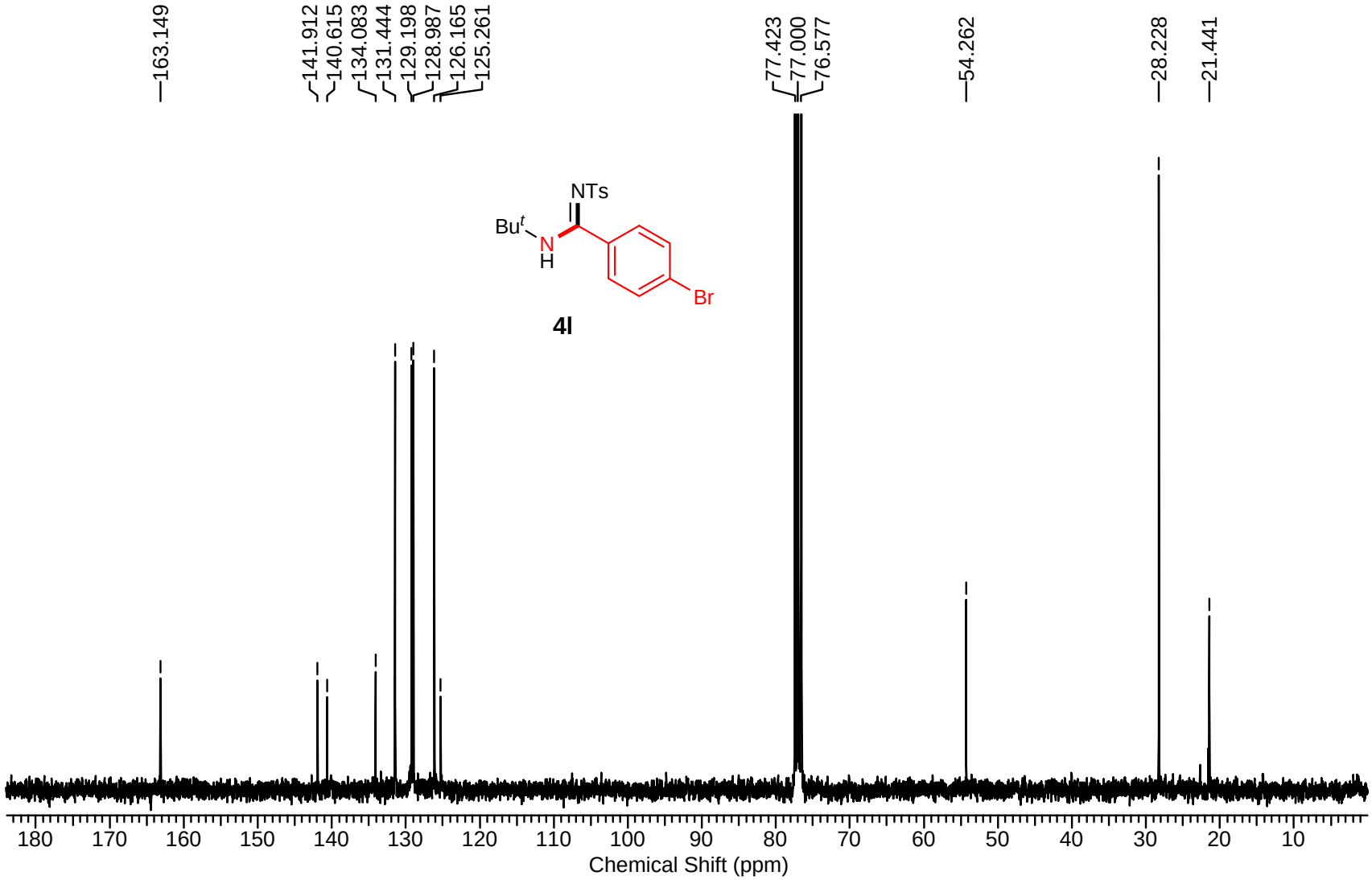

164.341
141.595
140.844
135.274
130.587
128.852
128.137
127.554
126.162
77.426
77.003
76.581
54.032
28.239
21.372
NTs
Bu^t
N
H
Ph
4j
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

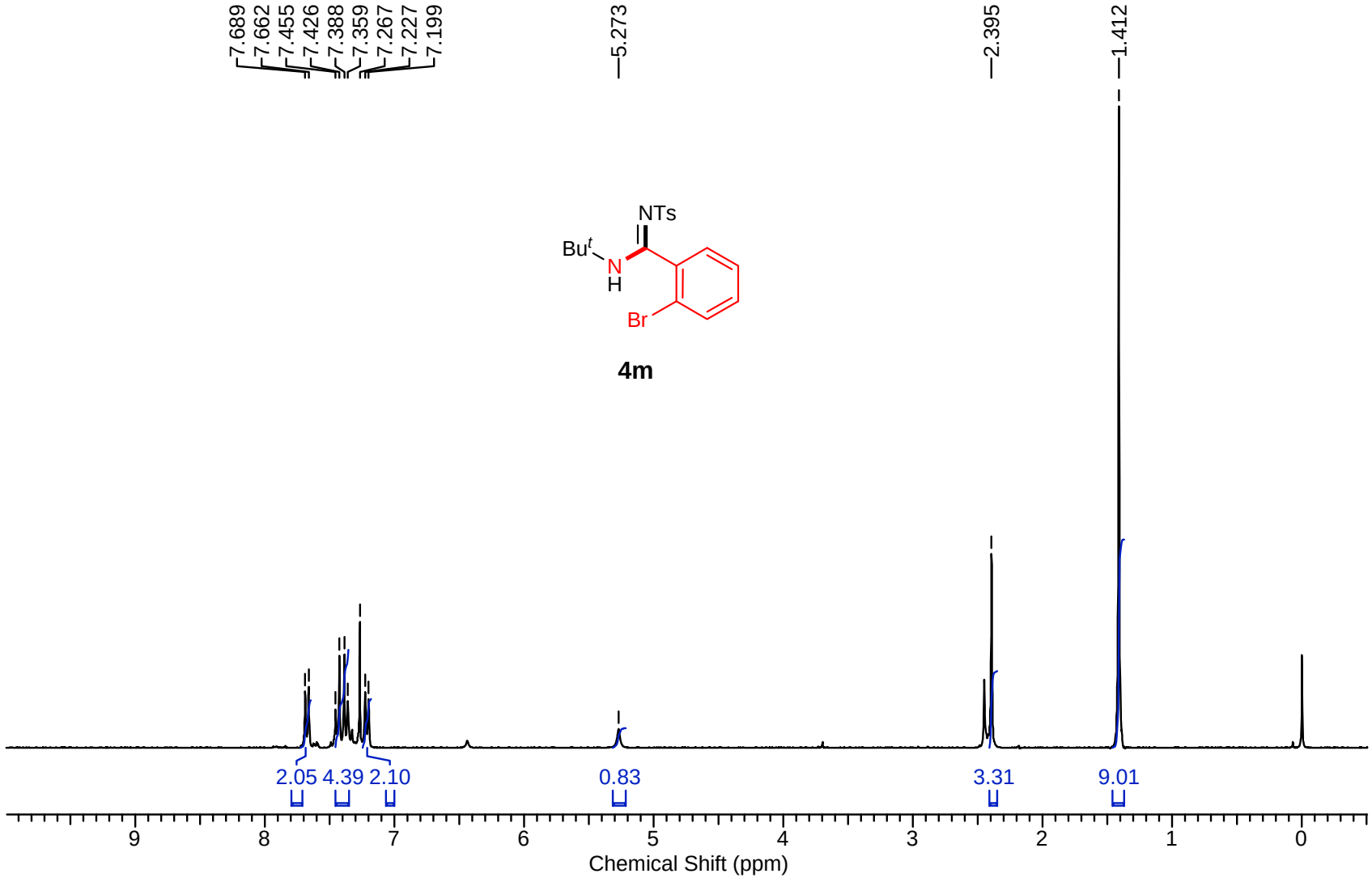

7.787
7.761
7.364
7.346
7.334
7.317
7.270
7.223
7.197
5.211
2.398
1.452
NTs
Bu^t
N
H
Cl
Cl
2.07
3.36
1.99
0.89
2.69
9.43
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

4k

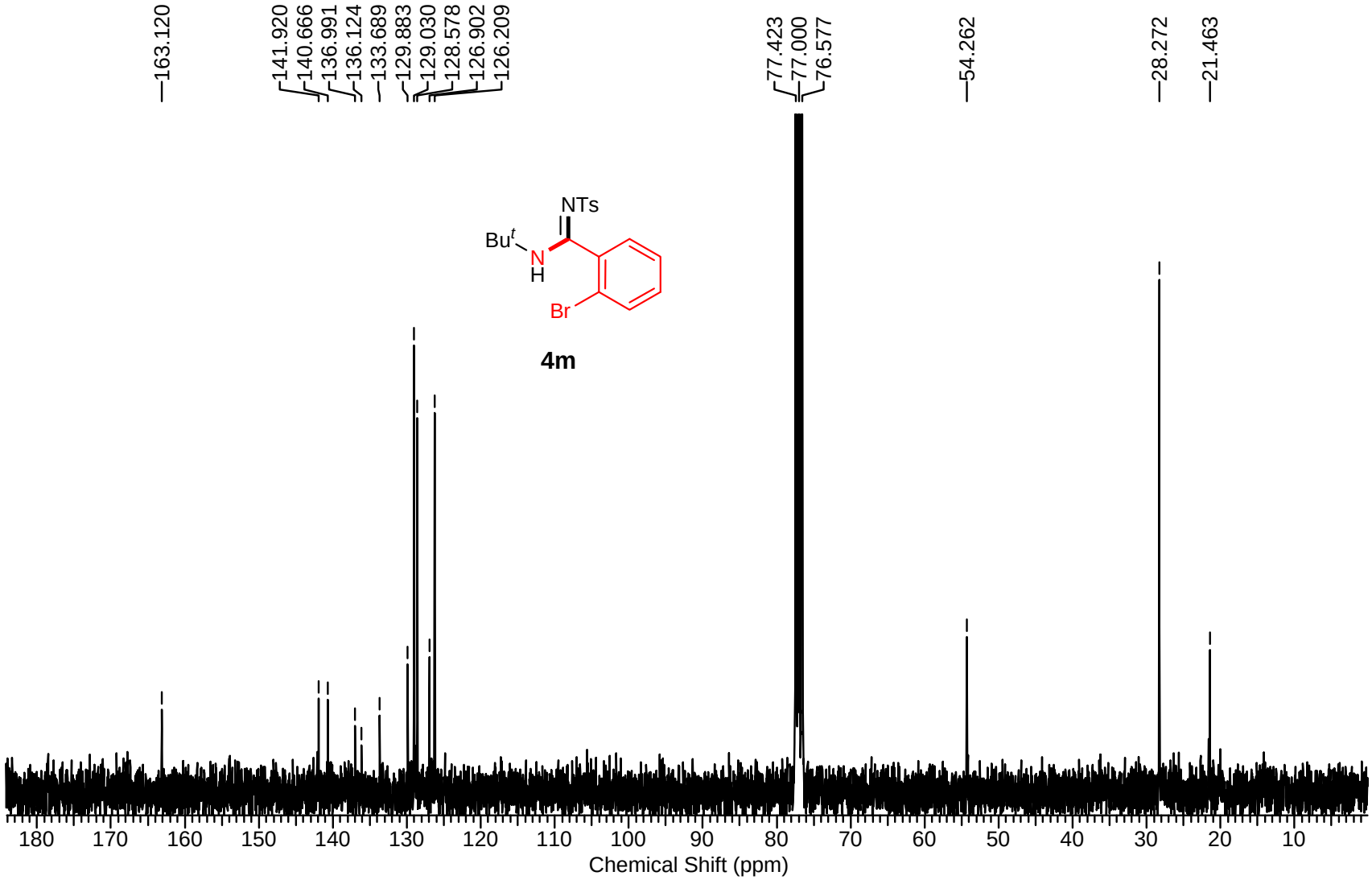

159.664
149.924
144.653
142.146
136.598
134.556
132.049
130.284
129.811
129.351
128.972
77.423
77.000
76.577
54.655
28.680
21.601
NTs
Bu^t
N
H
Cl
Cl
4k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

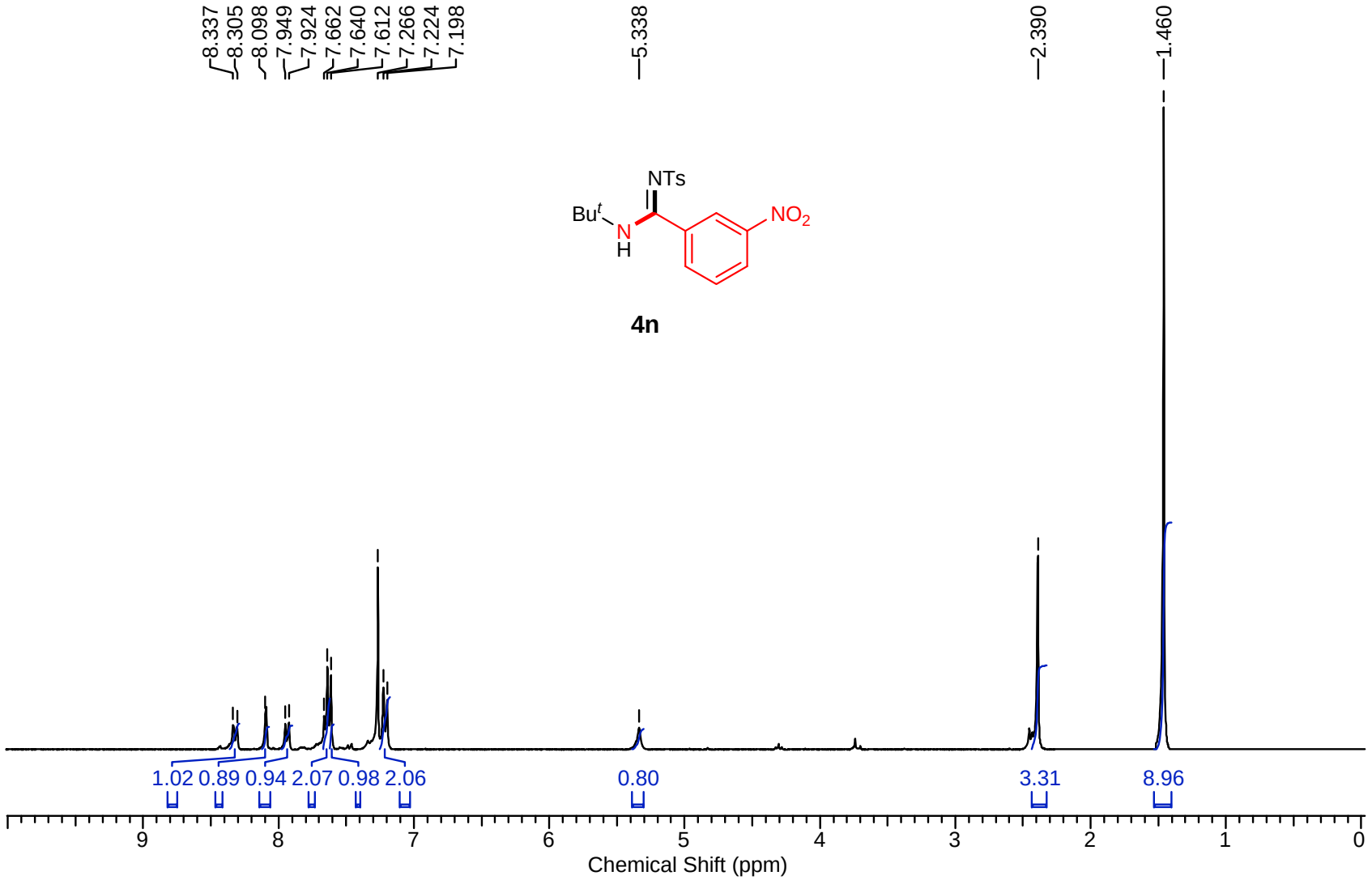

7.662
7.636
7.530
7.501
7.356
7.330
7.267
7.218
7.192
5.363
2.391
1.402
NTs
Bu^t
N
H
Br
4l
2.08 2.35 2.13 2.15
0.89
3.09
8.91
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

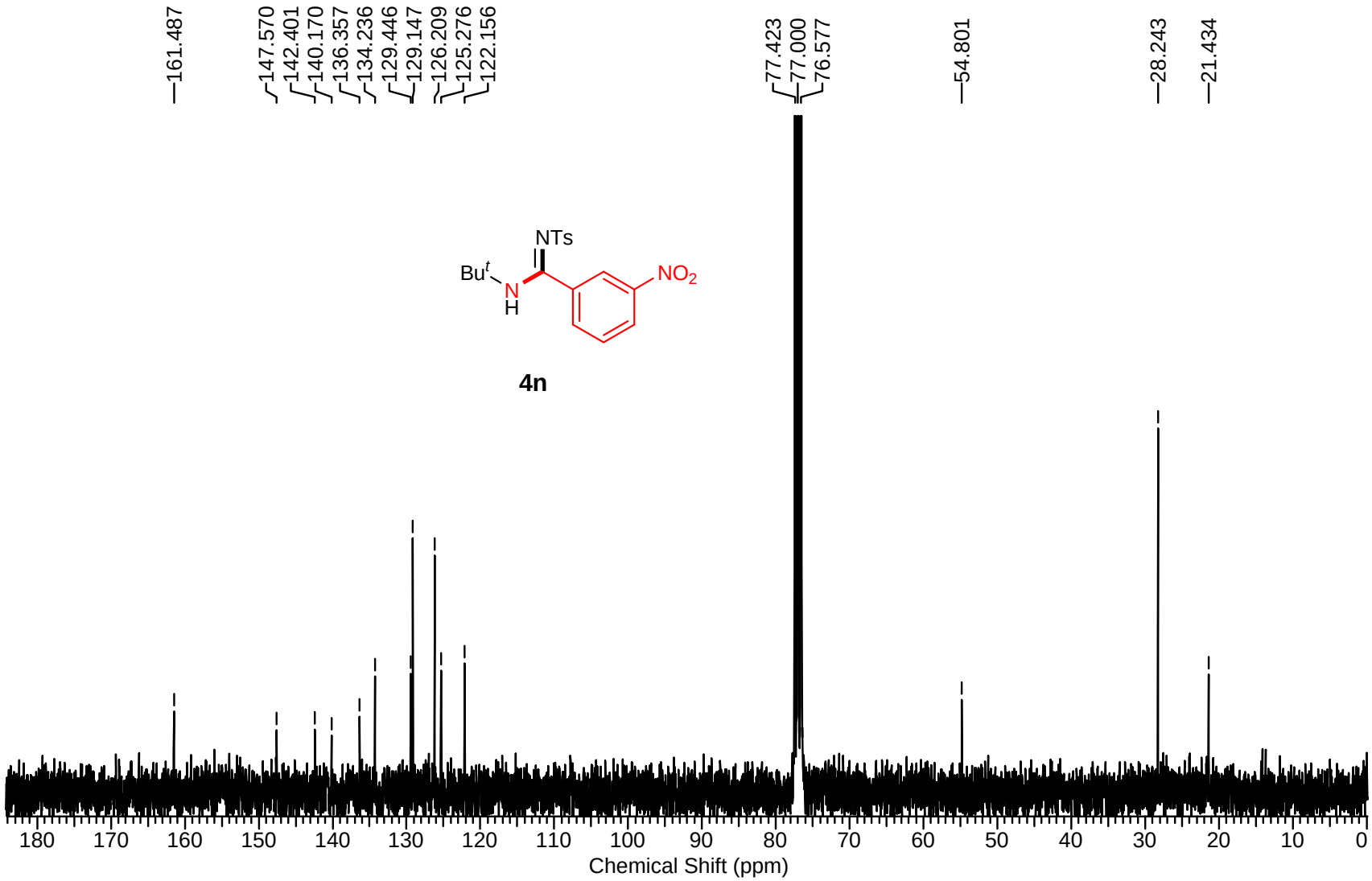

163.149
141.912
140.615
134.083
131.444
129.198
128.987
126.165
125.261
77.423
77.000
76.577
54.262
28.228
21.441
NTs
Bu^t
N
H
Br
4l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

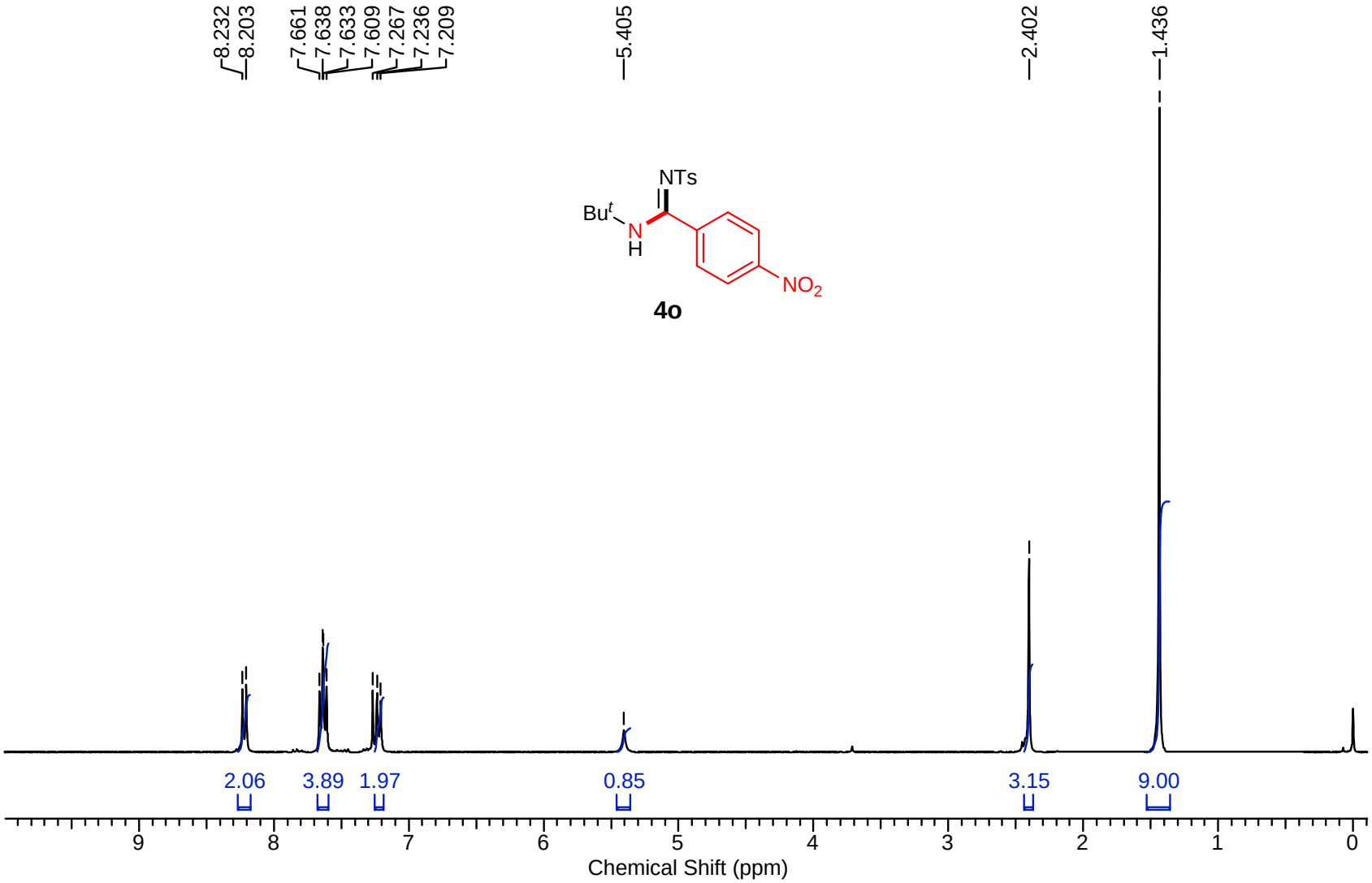

7.689
7.662
7.455
7.426
7.388
7.359
7.267
7.227
7.199
5.273
2.395
1.412
NTs
Bu^t
N
H
Br
2.05
4.39
2.10
0.83
3.31
9.01
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

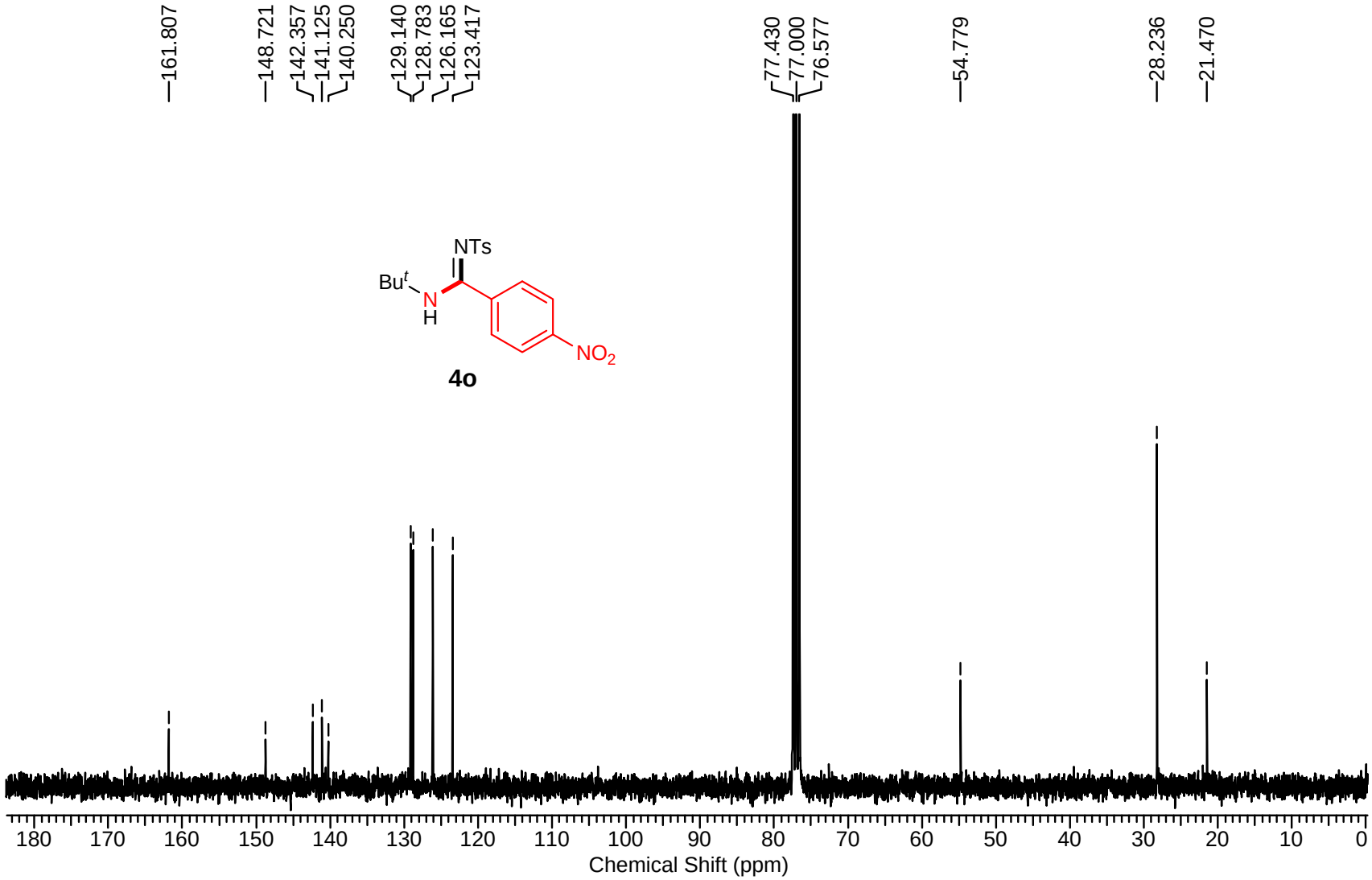
4m

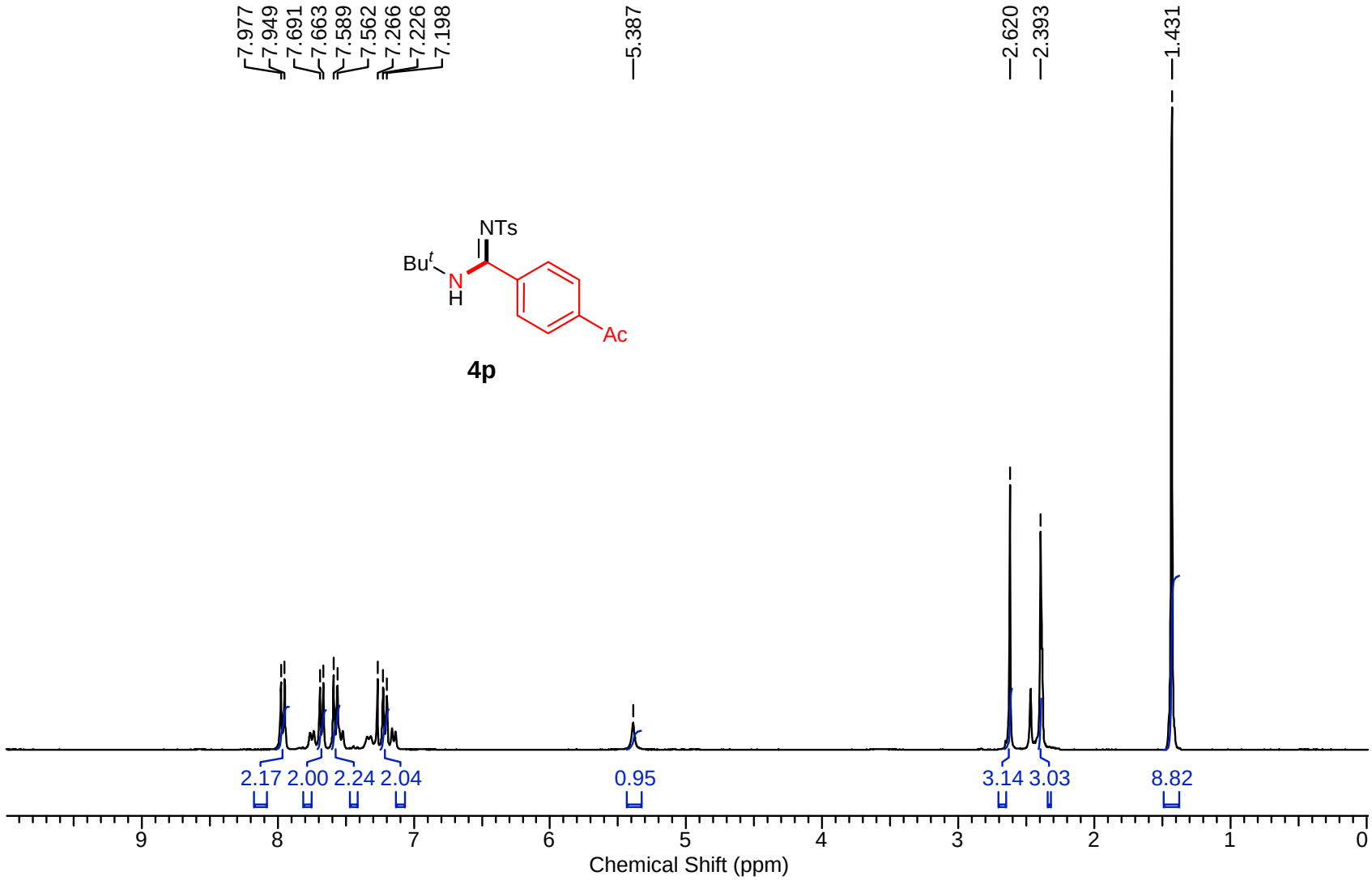

163.120
141.920
140.666
136.991
136.124
133.689
129.883
129.030
128.578
126.902
126.209
77.423
77.000
76.577
54.262
28.272
21.463
NTs
Bu^t
N
H
Br
4m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

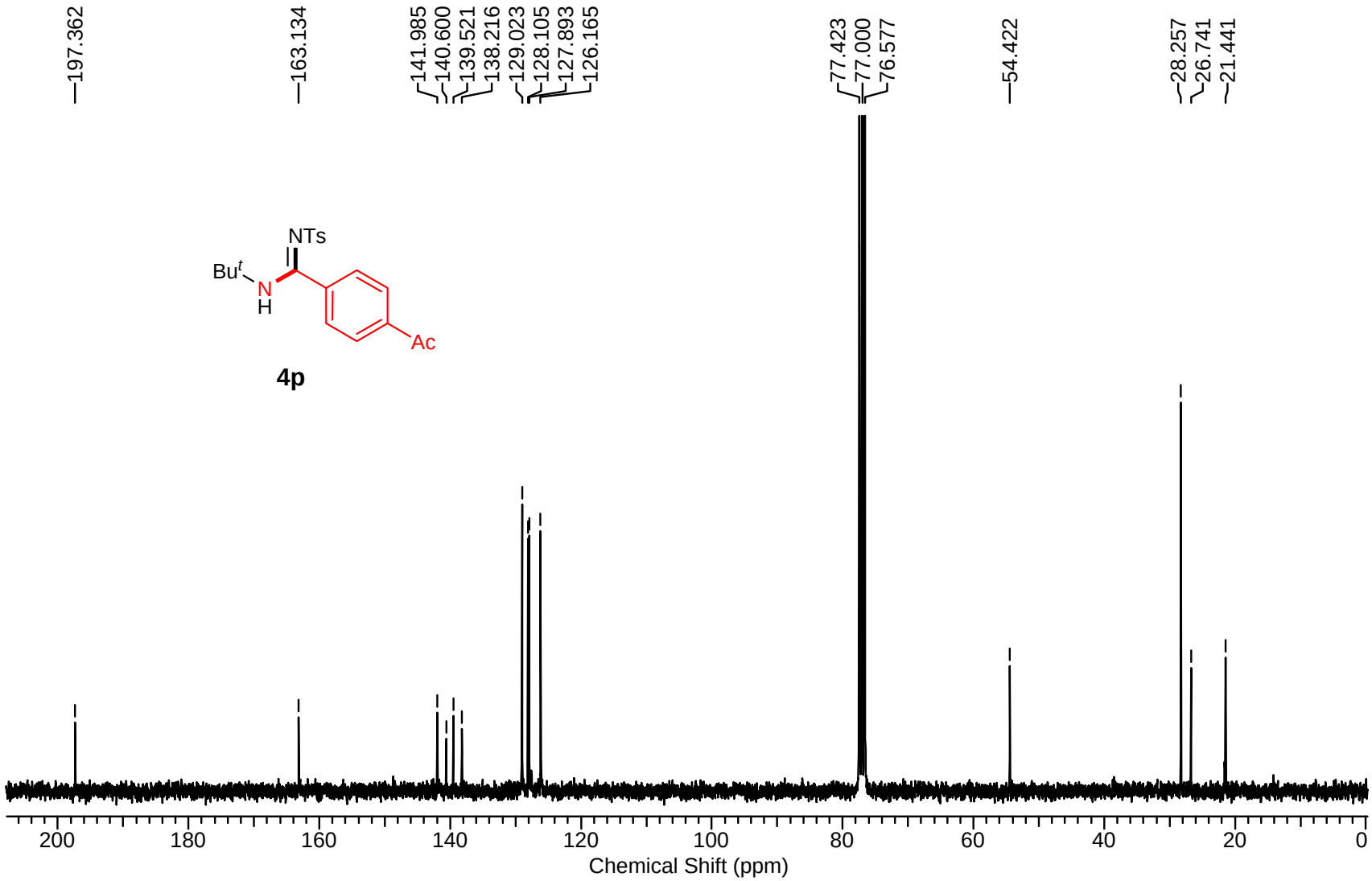

8.337
8.305
8.098
7.949
7.924
7.662
7.640
7.612
7.266
7.224
7.198
5.338
2.390
1.460
NTs
Bu^t
N
H
NO$_2$
4n
1.02 0.89 0.94 2.07 0.98 2.06
0.80
3.31
8.96
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

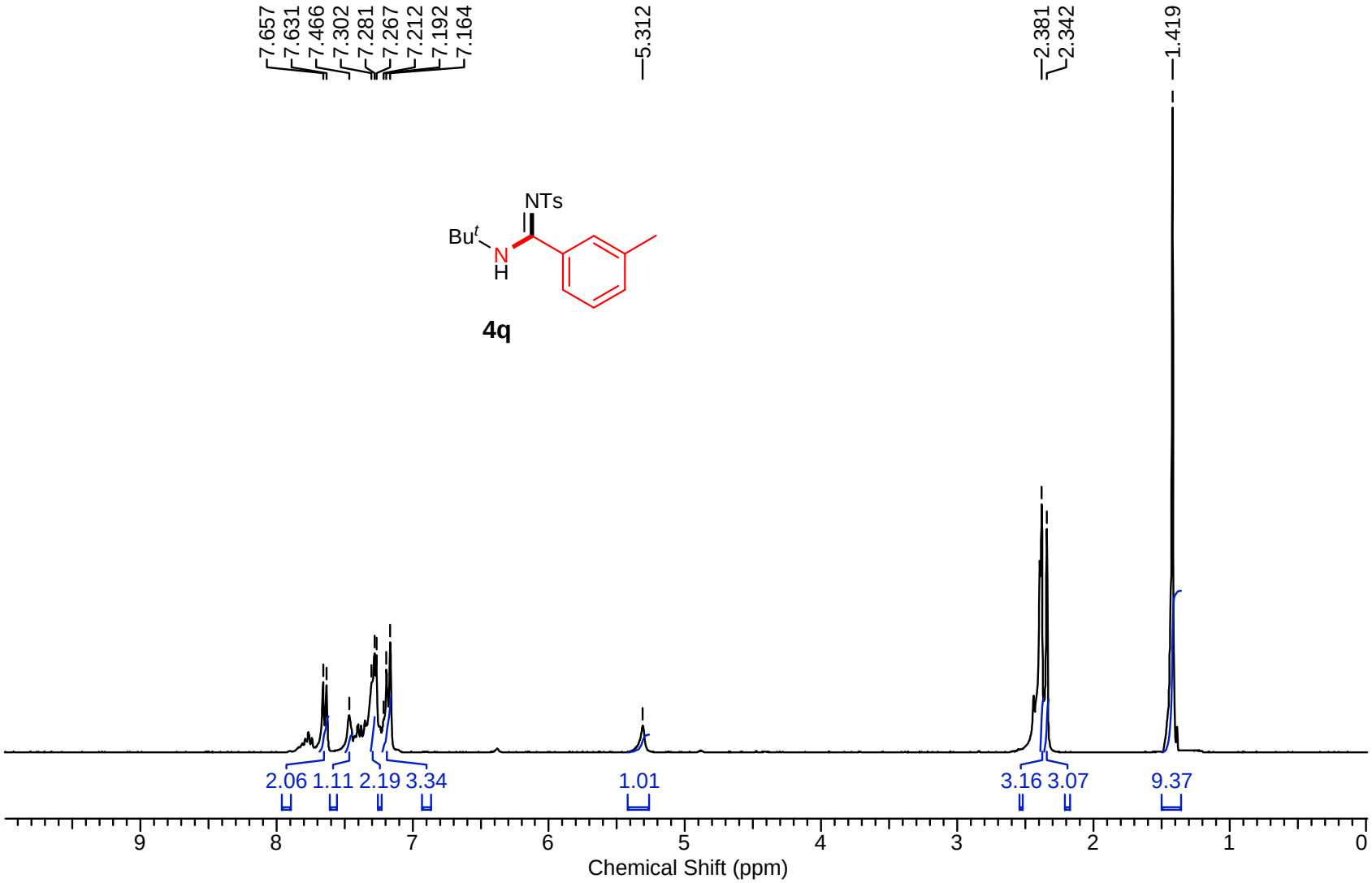

161.487
147.570
142.401
140.170
136.357
134.236
129.446
129.147
126.209
125.276
122.156
77.423
77.000
76.577
54.801
28.243
21.434
NTs
Bu^t
N
H
NO$_2$
4n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

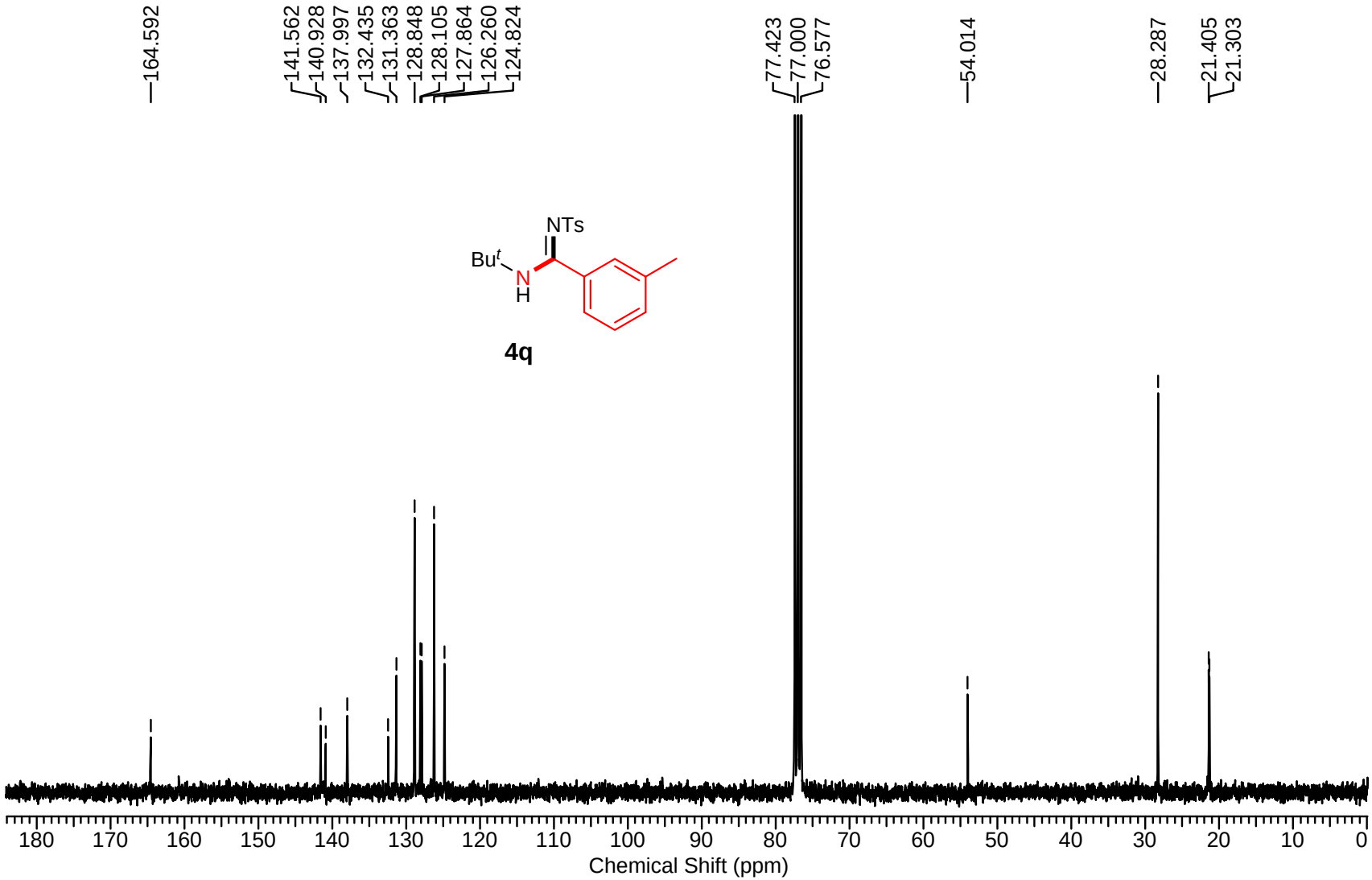

8.232
8.203
7.661
7.638
7.633
7.609
7.267
7.236
7.209
5.405
2.402
1.436
NTs
Bu^t
N
H
NO$_2$
4o
2.06
3.89
1.97
0.85
3.15
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

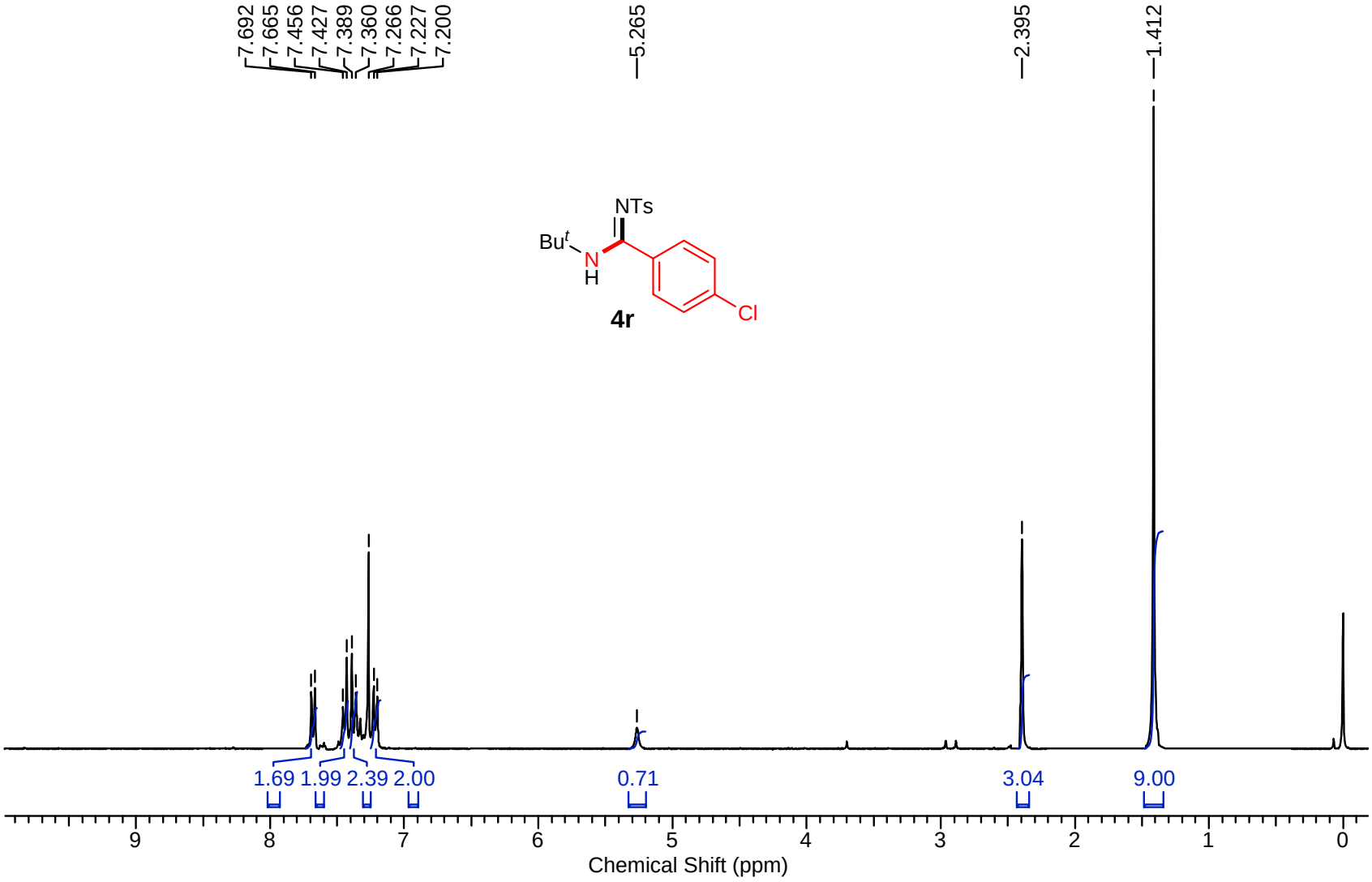

161.807
148.721
142.357
141.125
140.250
129.140
128.783
126.165
123.417
77.430
77.000
76.577
54.779
28.236
21.470
NTs
Bu^t
N
H
NO$_2$
4o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

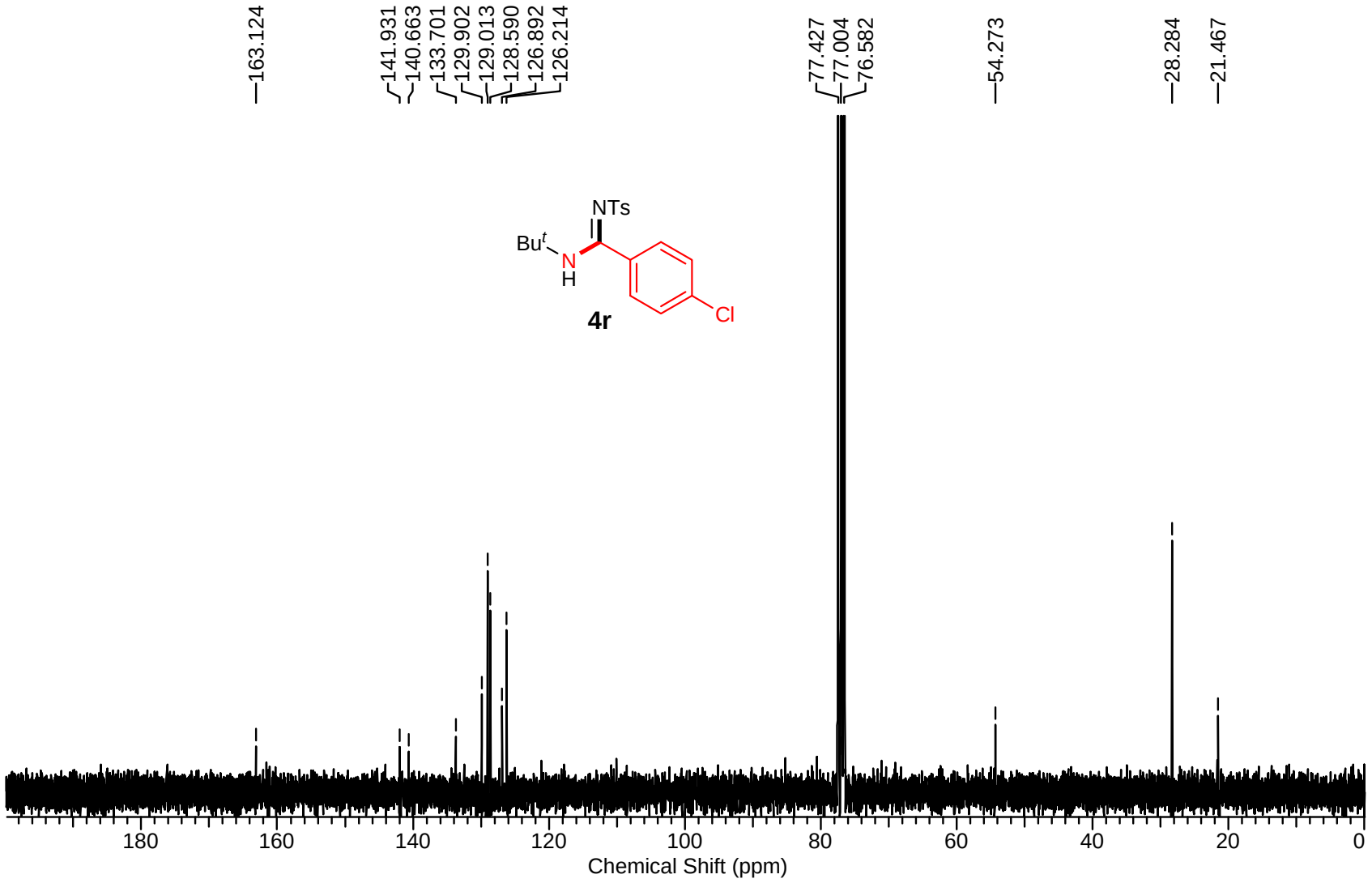

7.977
7.949
7.691
7.663
7.589
7.562
7.266
7.226
7.198
5.387
2.620
2.393
1.431
NTs
Bu^t
N
H
Ac
4p
2.17 2.00 2.24 2.04
0.95
3.14 3.03
8.82
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

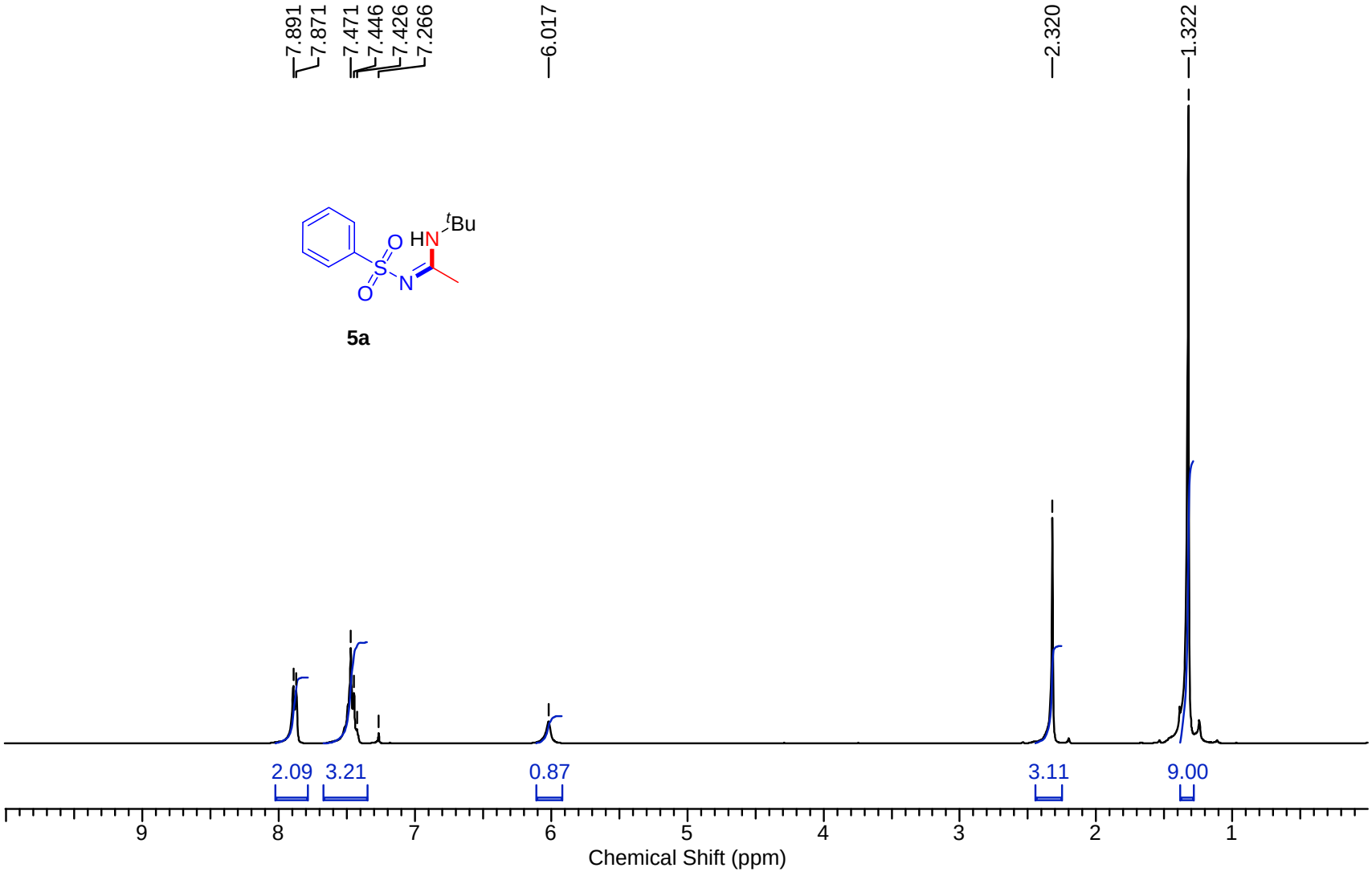

197.362
163.134
141.985
140.600
139.521
138.216
129.023
128.105
127.893
126.165
77.423
77.000
76.577
54.422
28.257
26.741
21.441
NTs
Bu^t
N
H
Ac
4p
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


7.657
7.631
7.466
7.302
7.281
7.267
7.212
7.192
7.164
5.312
2.381
2.342
1.419
NTs
Bu^t
N
H
4q
2.06 1.11 2.19 3.34
1.01
3.16 3.07
9.37
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

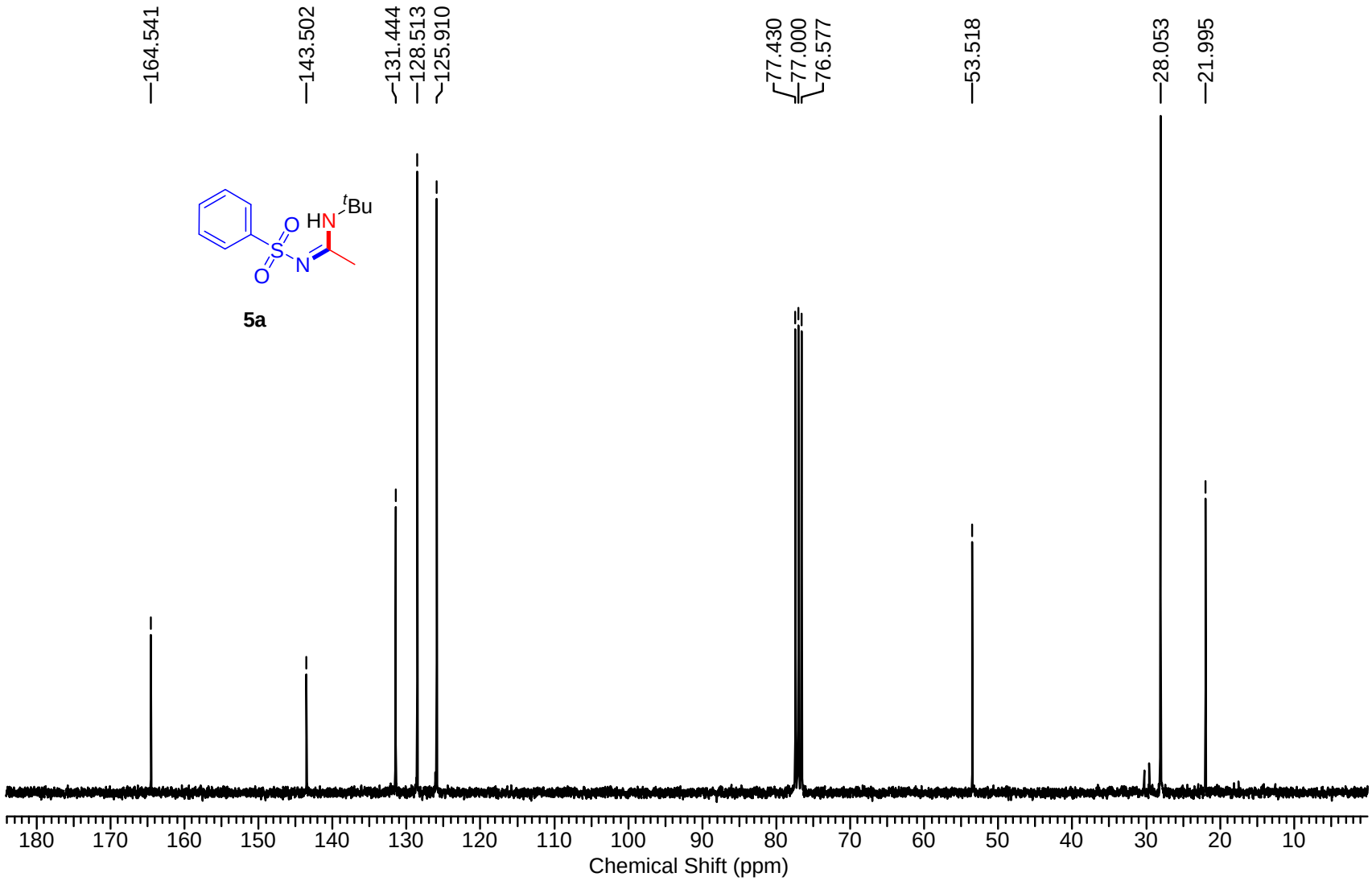

164.592
141.562
140.928
137.997
132.435
131.363
128.848
128.105
127.864
126.260
124.824
77.423
77.000
76.577
54.014
28.287
21.405
21.303
NTs
Bu^t
N
H
4q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

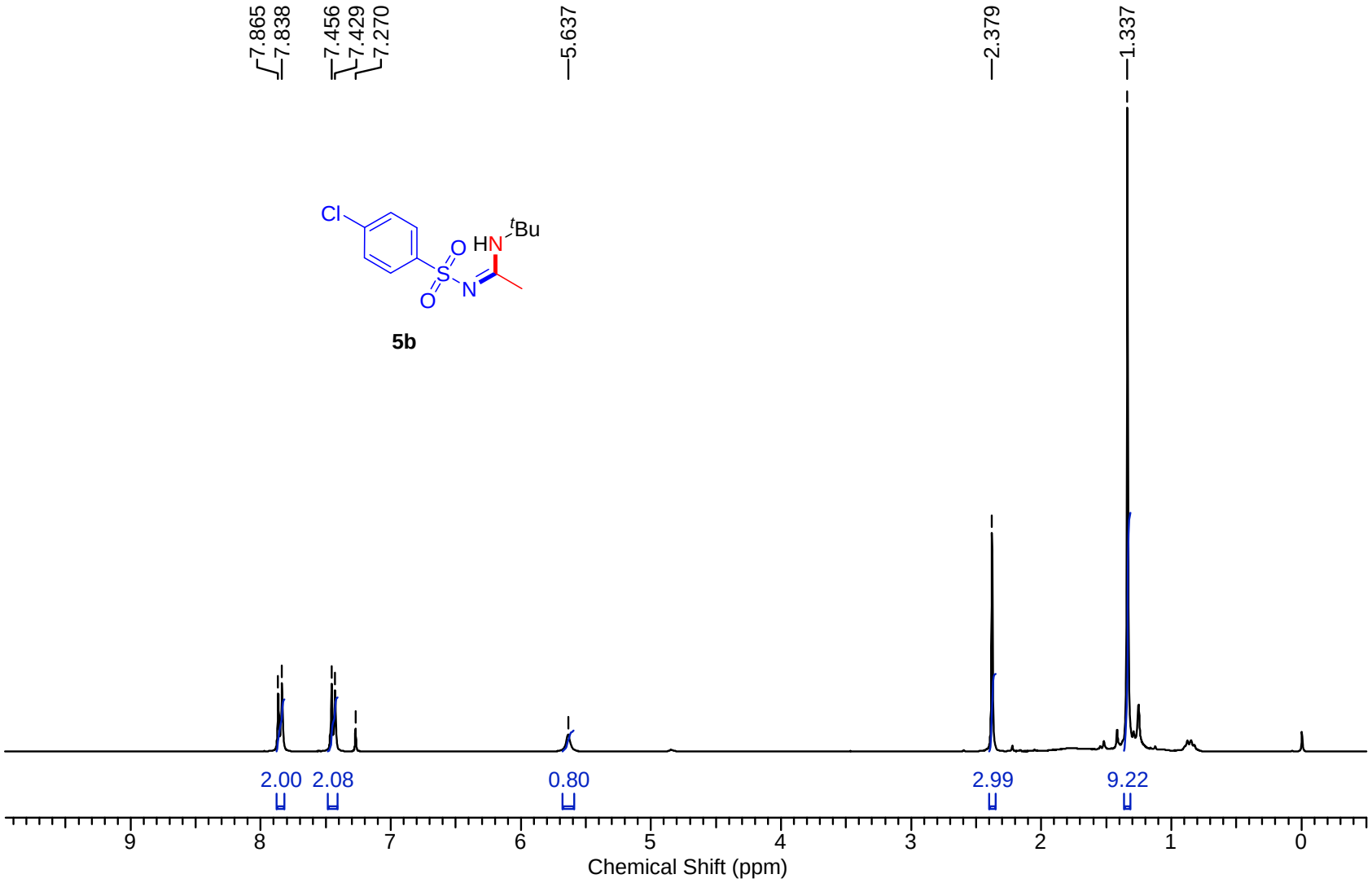

7.692
7.665
7.456
7.427
7.389
7.360
7.266
7.227
7.200
5.265
2.395
1.412
NTs
Bu^t
N
H
Cl
4r
1.69 1.99 2.39 2.00
0.71
3.04
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


163.124
141.931
140.663
133.701
129.902
129.013
128.590
126.892
126.214
77.427
77.004
76.582
54.273
28.284
21.467
NTs
Bu^t
N
H
Cl
4r
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

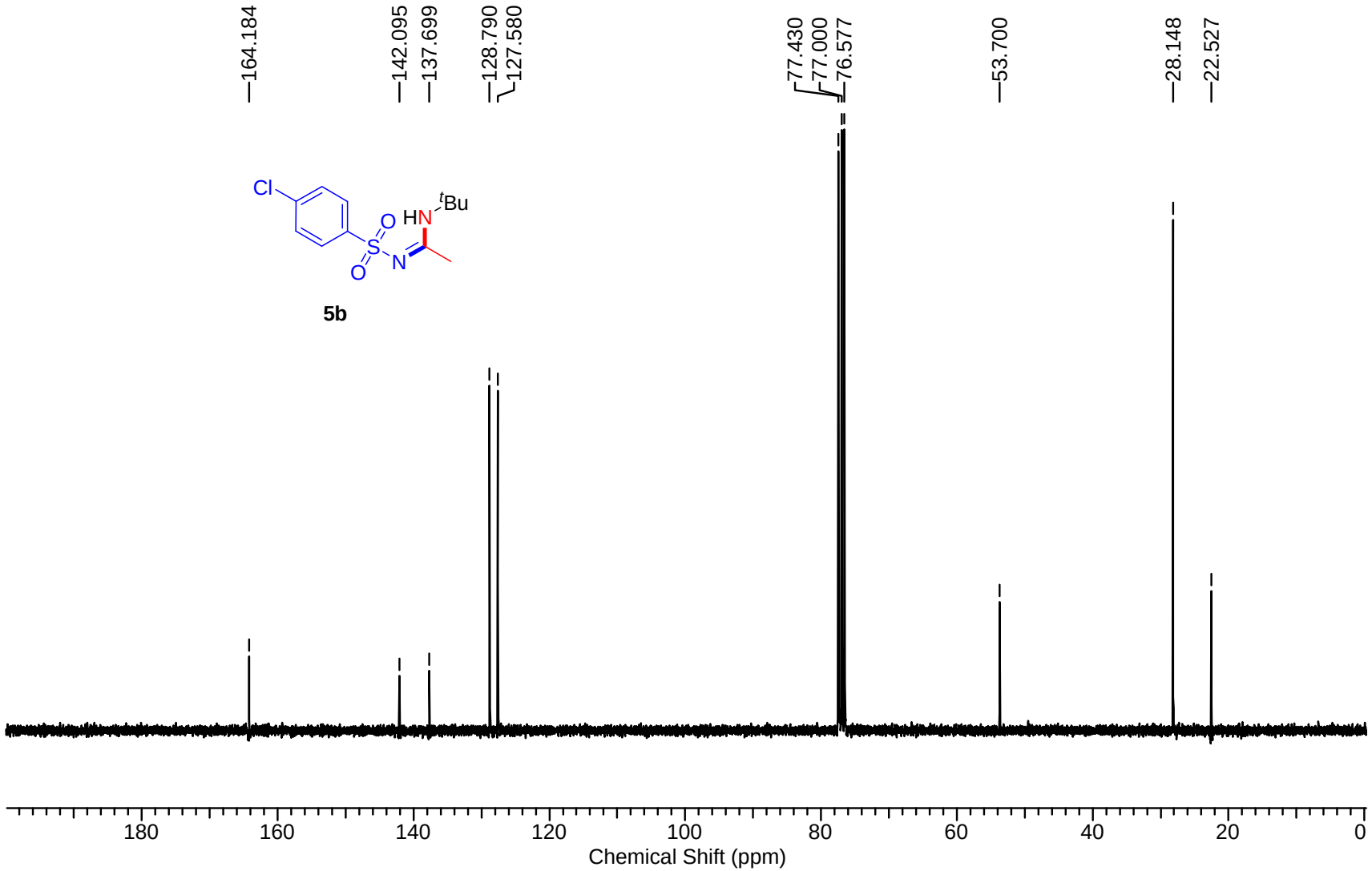

7.891
7.871
7.471
7.446
7.426
7.266
6.017
2.320
1.322
O
HN
tBu
S
O
N
2.09
3.21
0.87
3.11
9.00
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

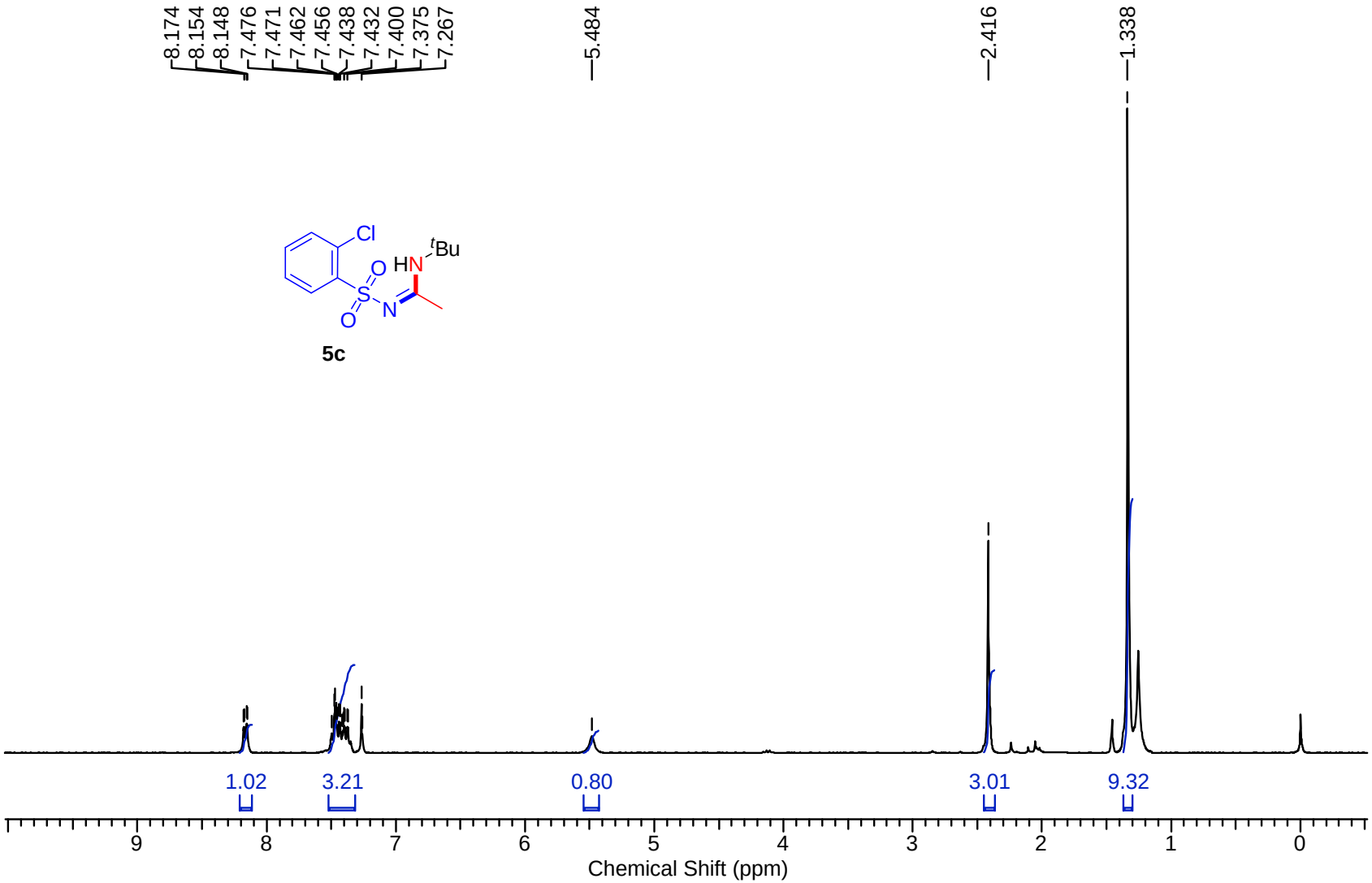
5a


164.541
143.502
131.444
128.513
125.910
77.430
77.000
76.577
53.518
28.053
21.995
O
HN
tBu
S
N
O
5a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

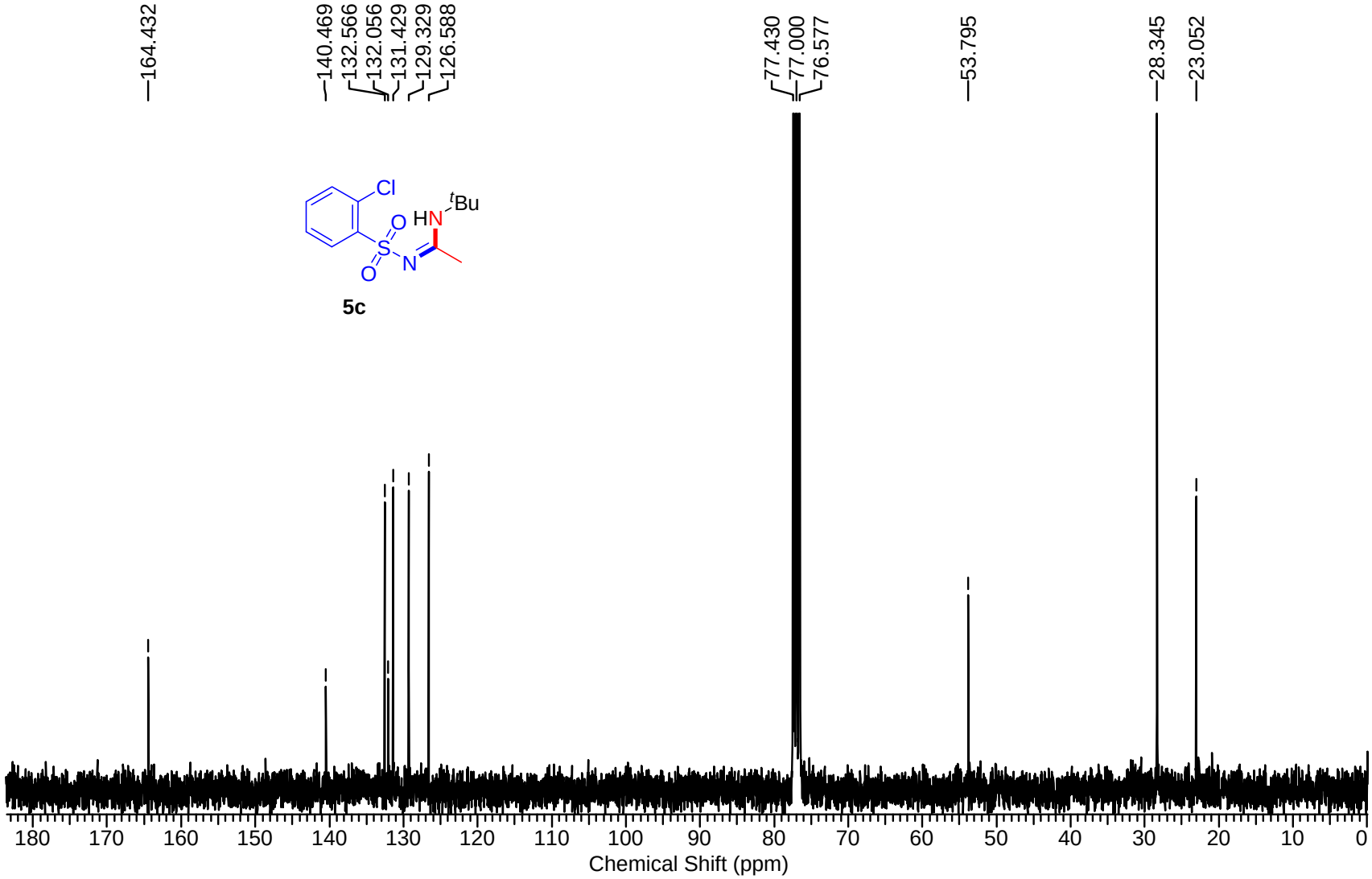

7.865
7.838
7.456
7.429
7.270
5.637
2.379
1.337
Cl
HN
tBu
O
S
O
N
2.00
2.08
0.80
2.99
9.22
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

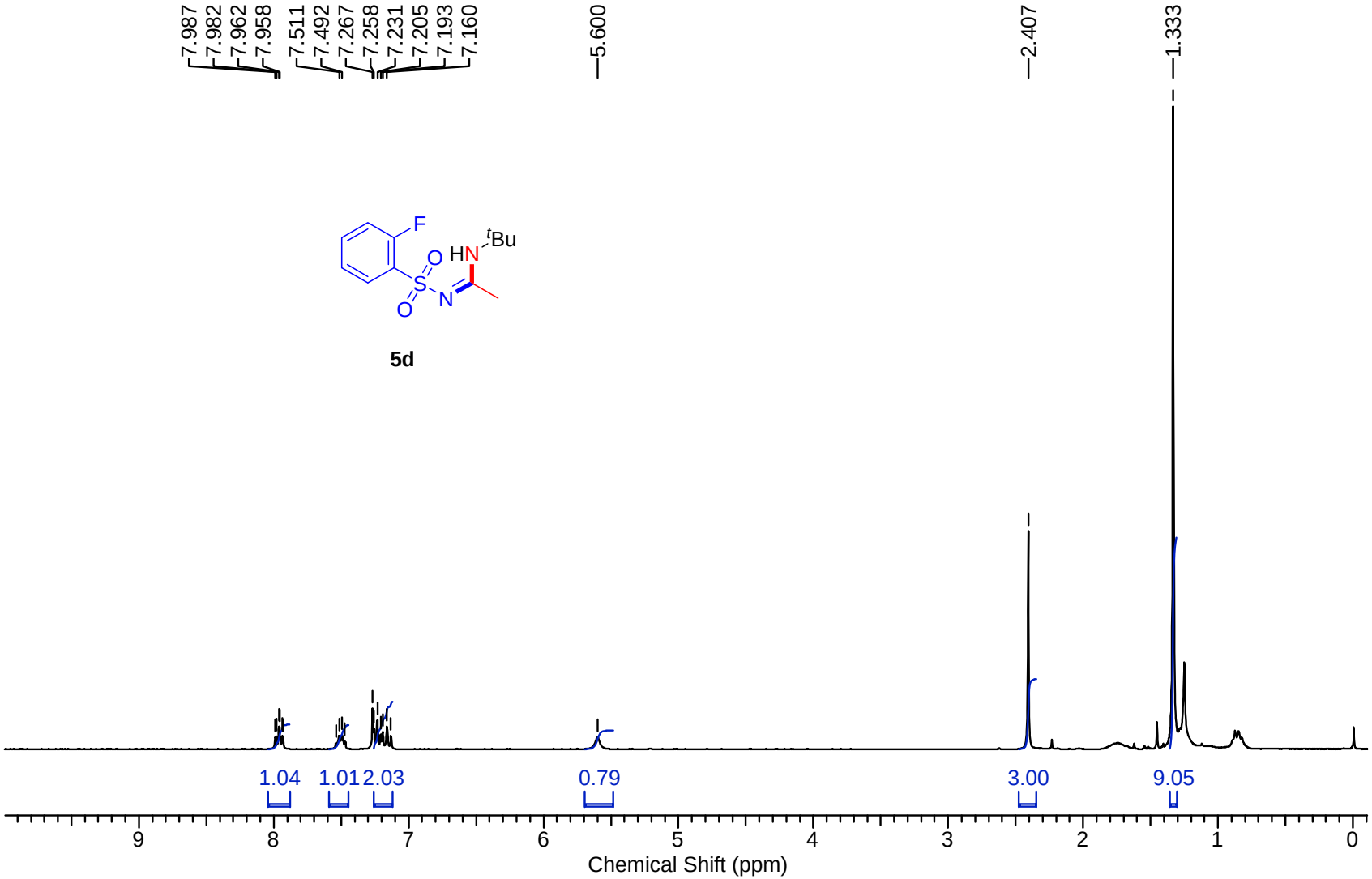
5b


164.184
142.095
137.699
128.790
127.580
77.430
77.000
76.577
53.700
28.148
22.527
Cl
O
HN
tBu
S
O
N
5b
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

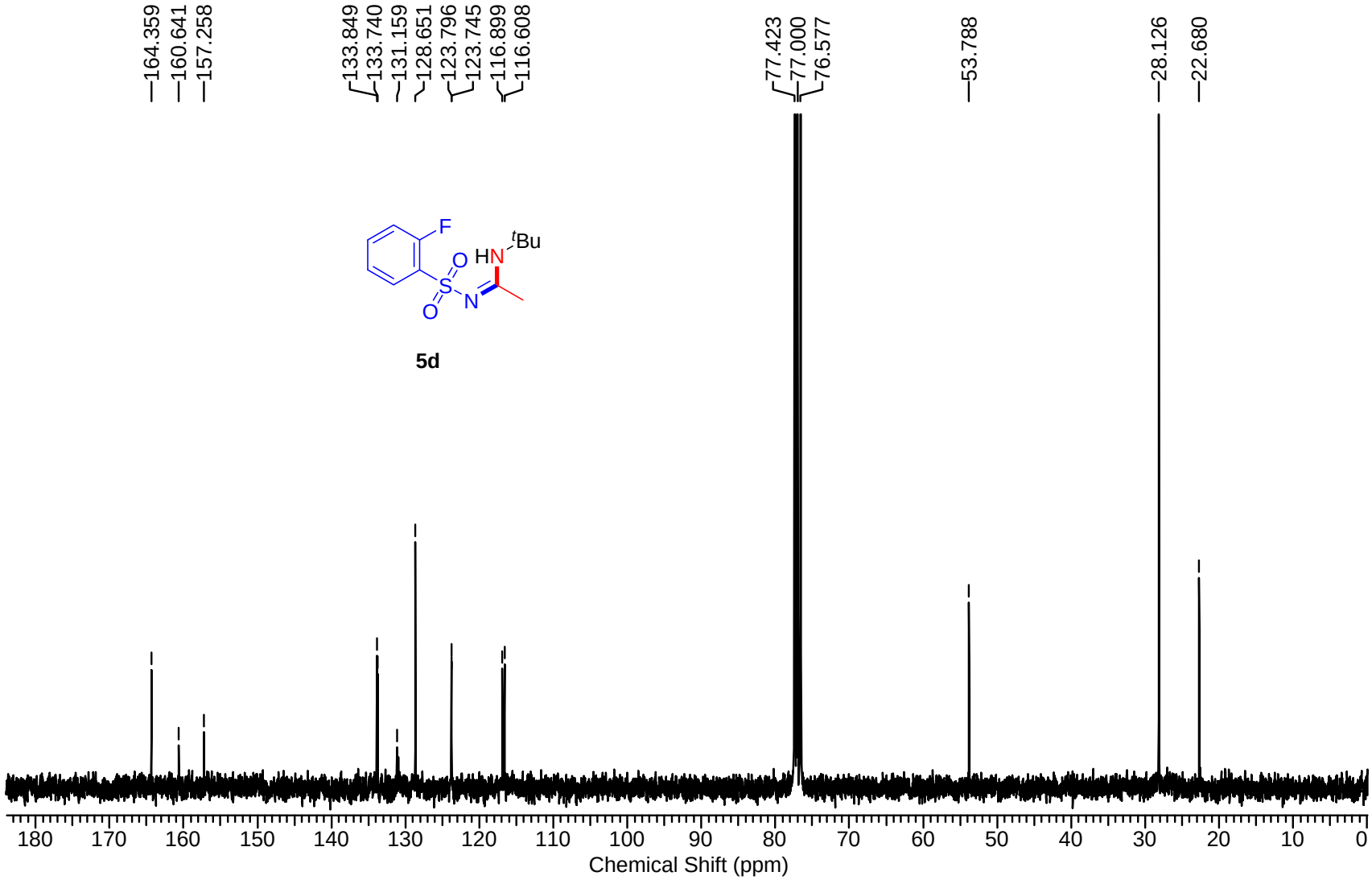

8.174
8.154
8.148
7.476
7.471
7.462
7.456
7.438
7.432
7.400
7.375
7.267
5.484
2.416
1.338
Cl
HN
tBu
O
S
O
N
1.02
3.21
0.80
3.01
9.32
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

5c

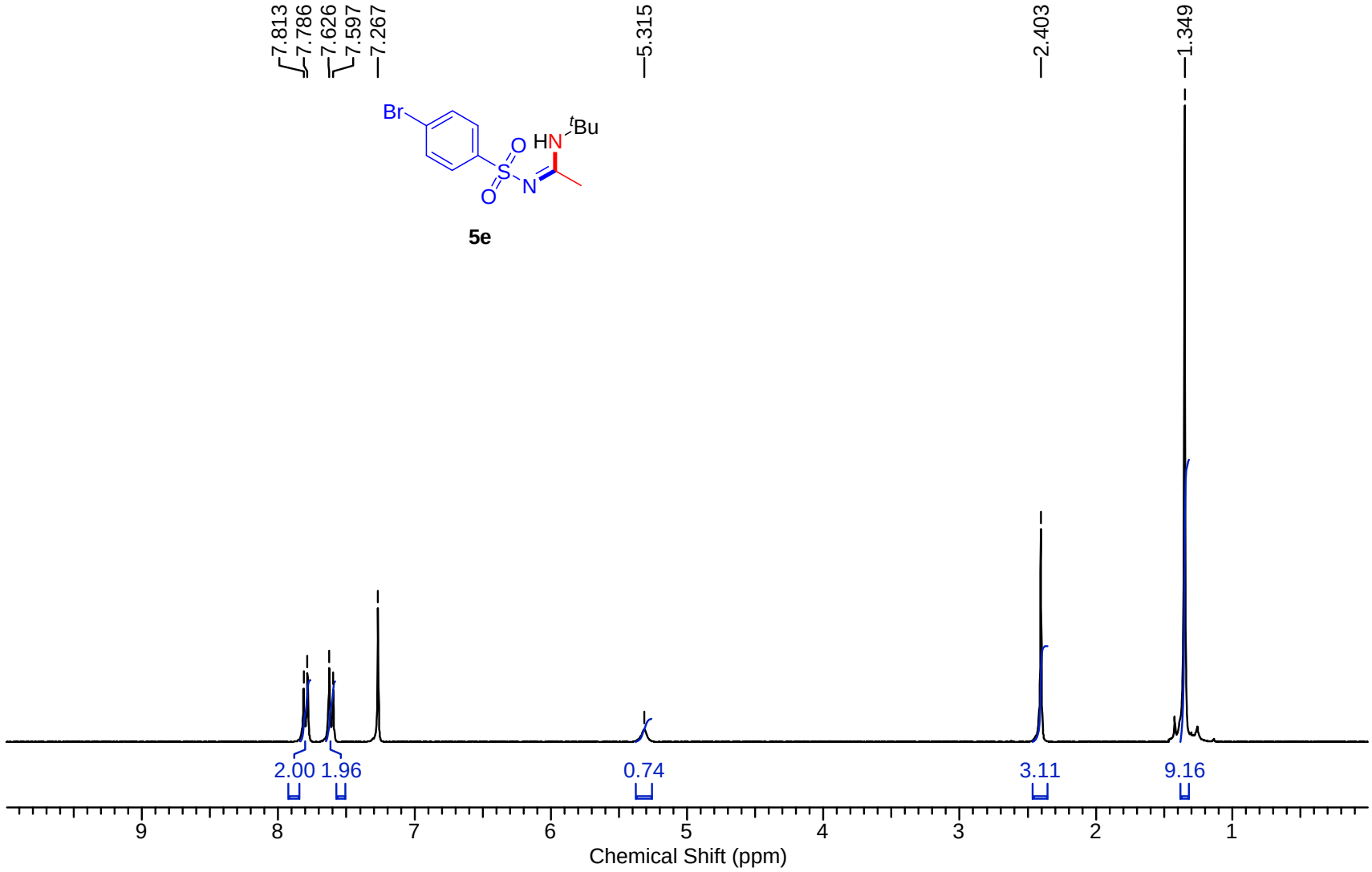

164.432
140.469
132.566
132.056
131.429
129.329
126.588
77.430
77.000
76.577
53.795
28.345
23.052
Cl
HN
tBu
O
S
O
N
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

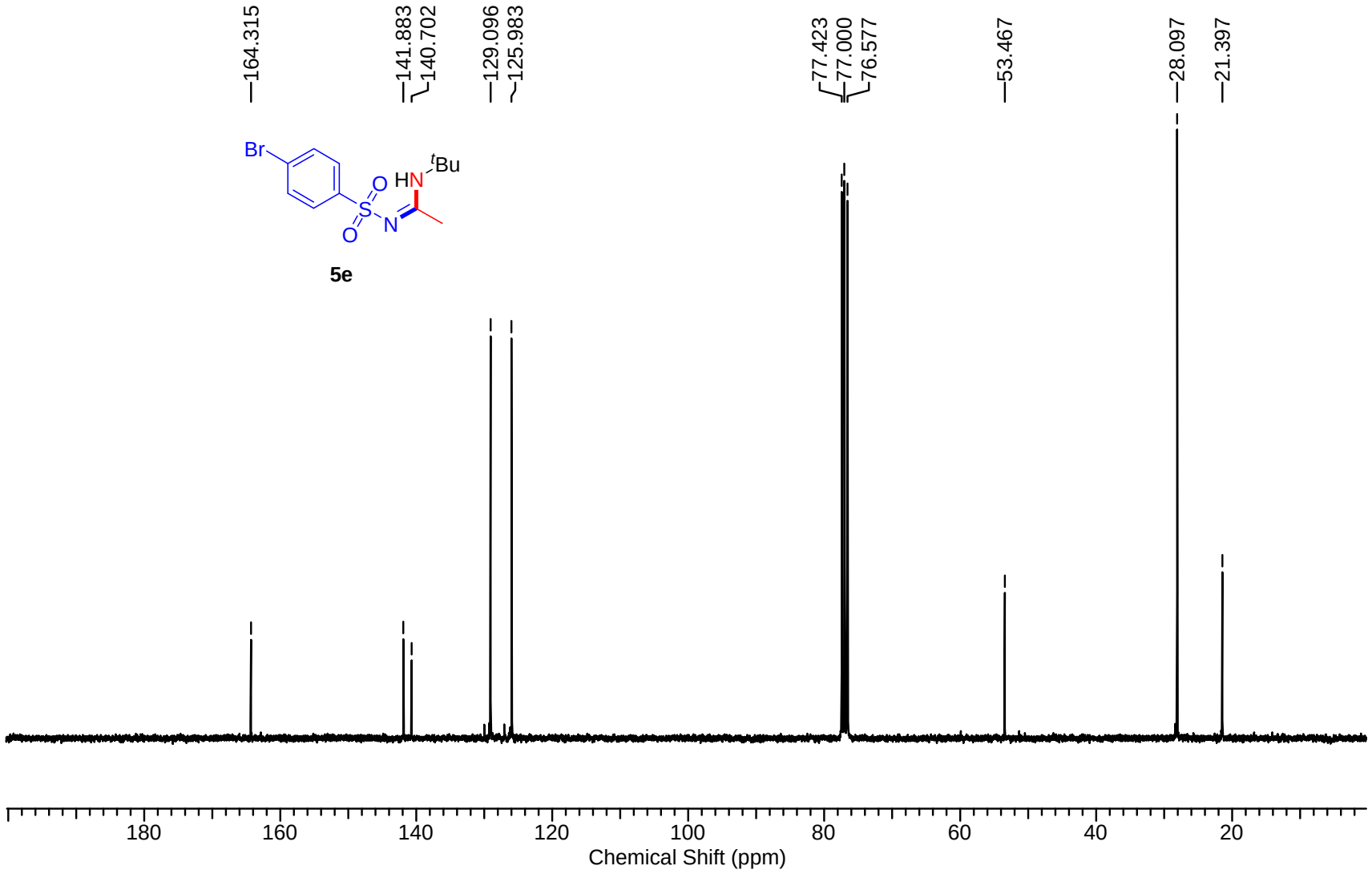

7.987
7.982
7.962
7.958
7.511
7.492
7.267
7.258
7.231
7.205
7.193
7.160
5.600
2.407
1.333
F
HN
tBu
O
S
O
N
O
1.04
1.01
2.03
0.79
3.00
9.05
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

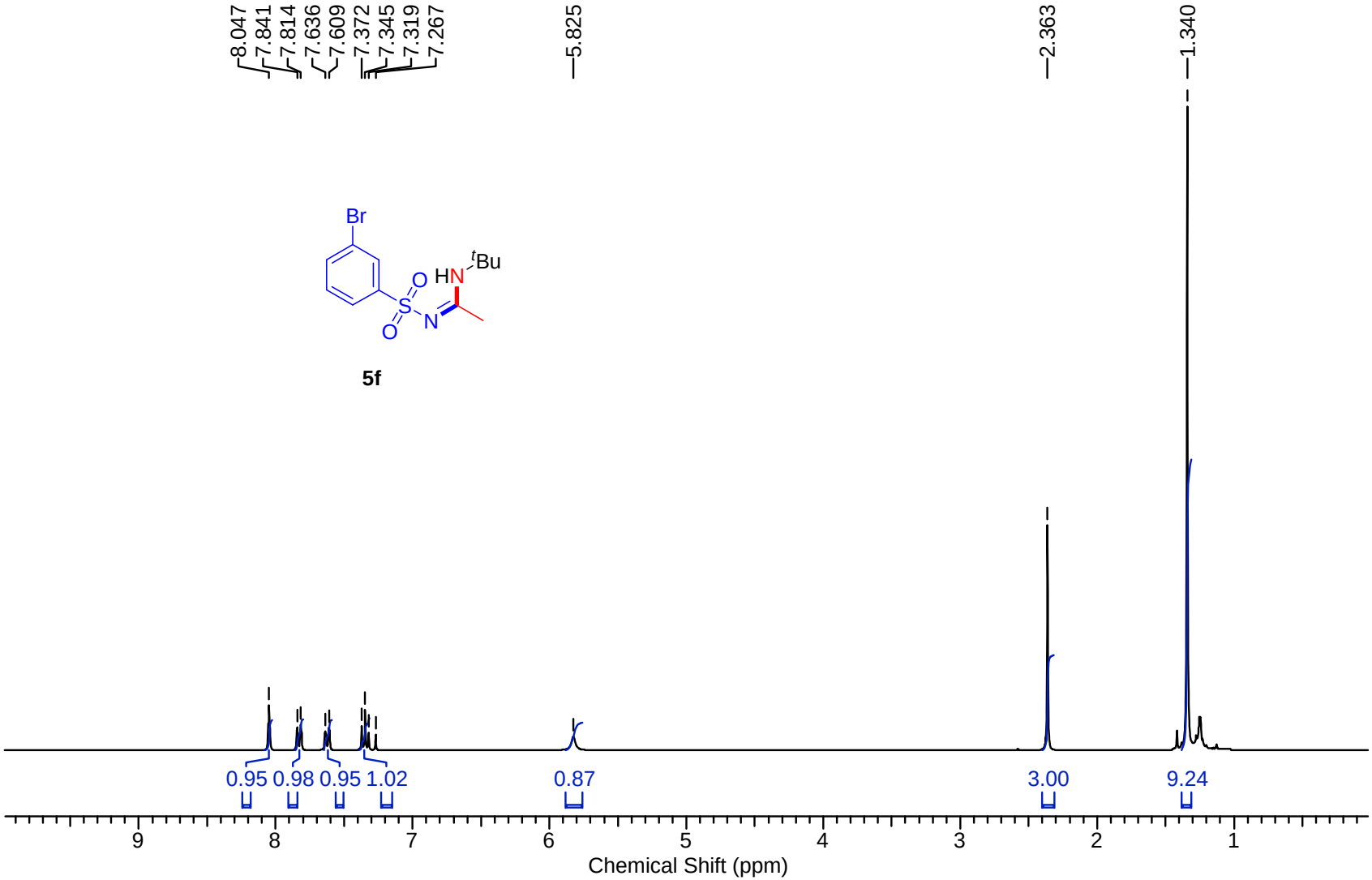
5d

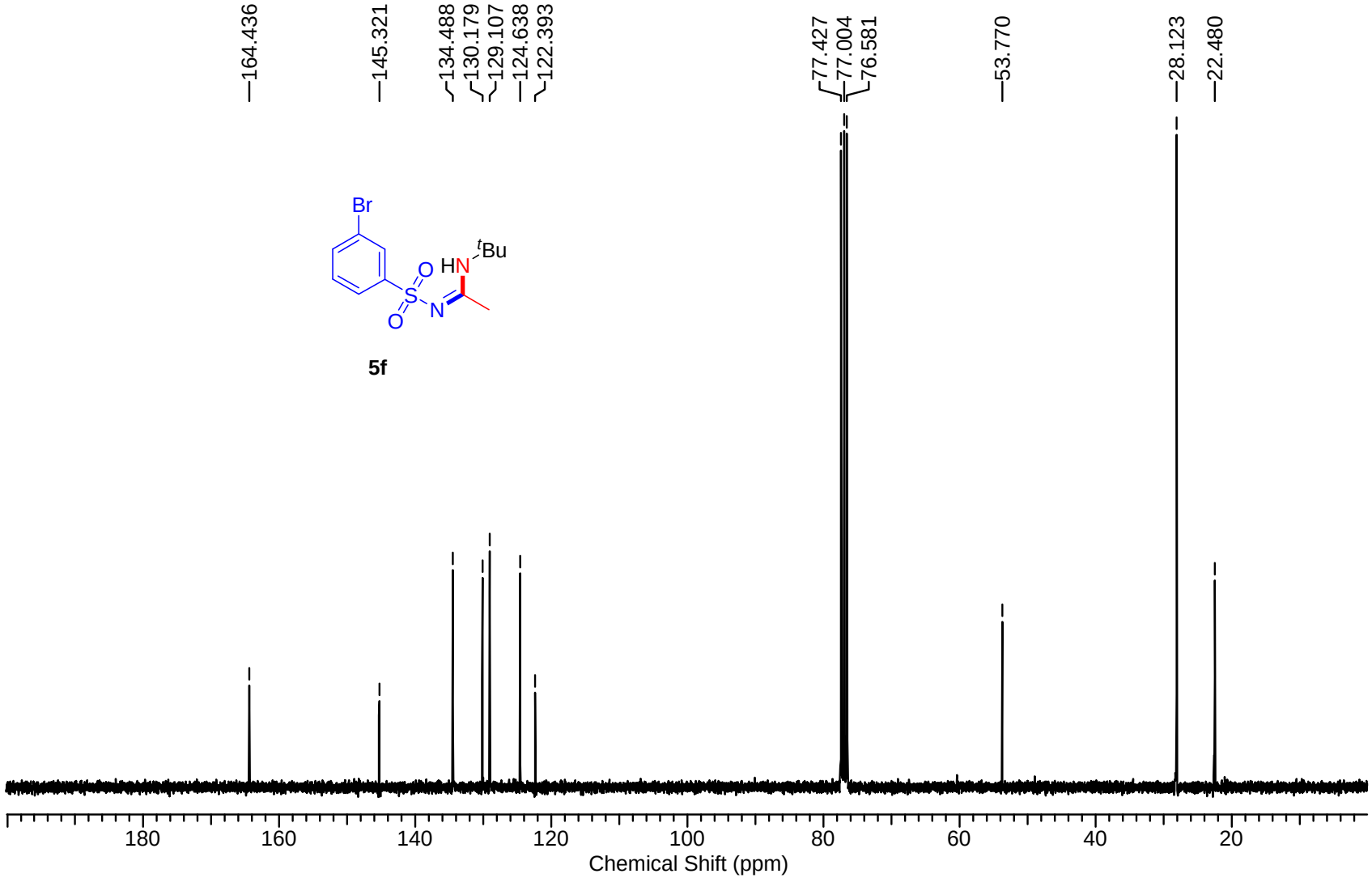

164.359
160.641
157.258
133.849
133.740
131.159
128.651
123.796
123.745
116.899
116.608
77.423
77.000
76.577
53.788
28.126
22.680
F
O
HN
tBu
S
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

5d

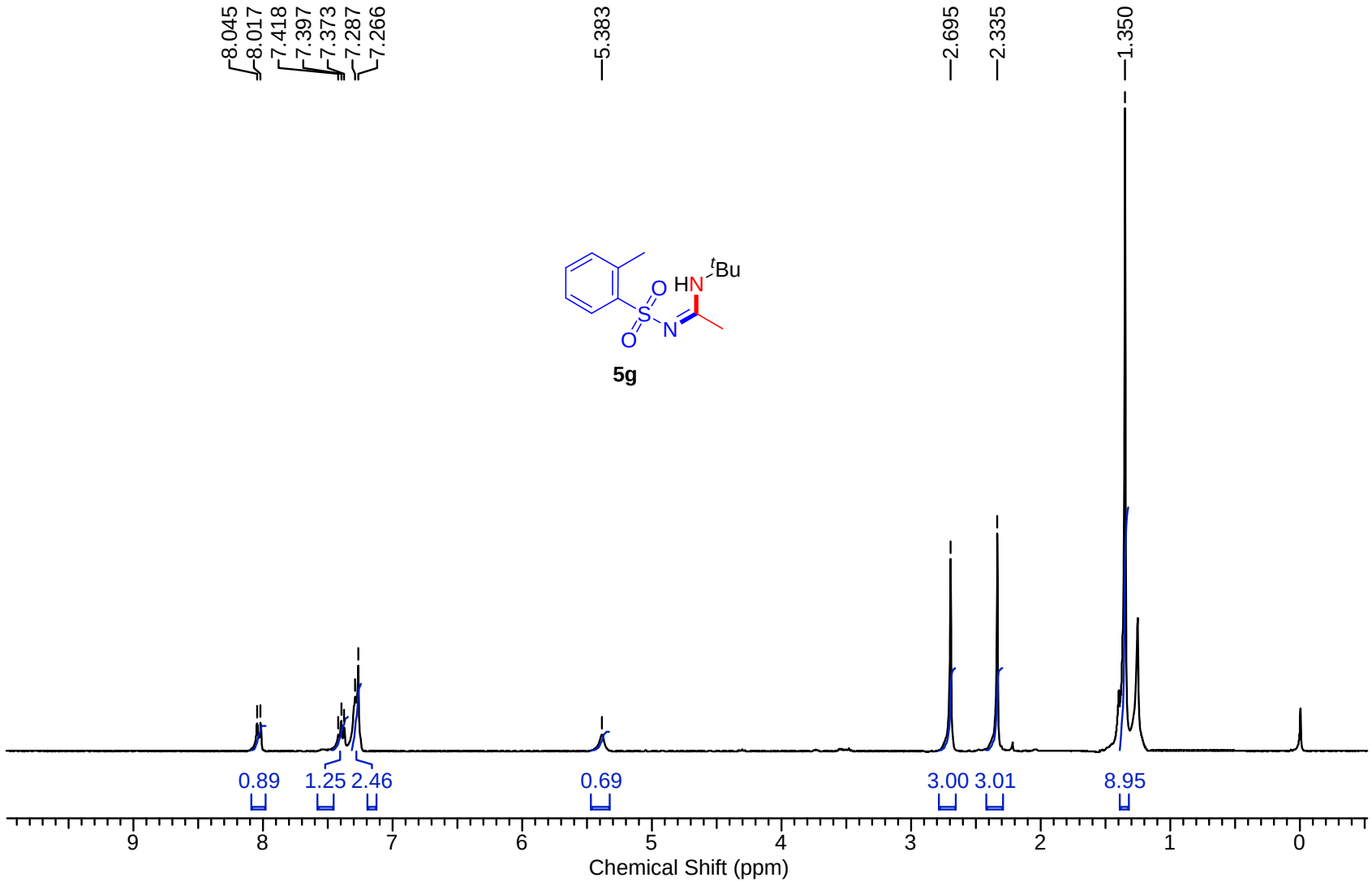

7.813
7.786
7.626
7.597
7.267
5.315
2.403
1.349
Br
O
HN
tBu
S
N
O
5e
2.00
1.96
0.74
3.11
9.16
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

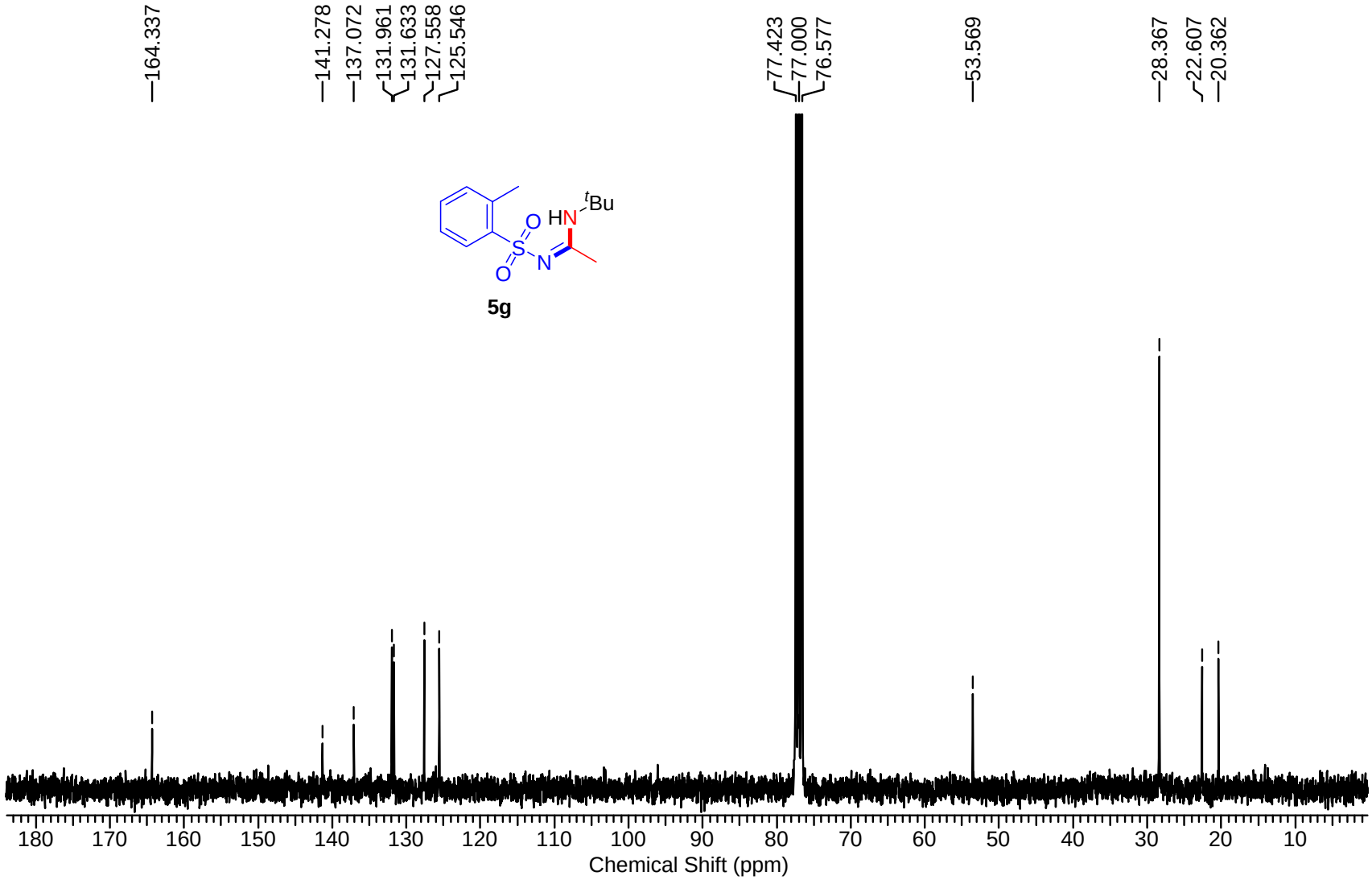

164.315
141.883
140.702
129.096
125.983
77.423
77.000
76.577
53.467
28.097
21.397
Br
HN
tBu
O
S
O
N
5e
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

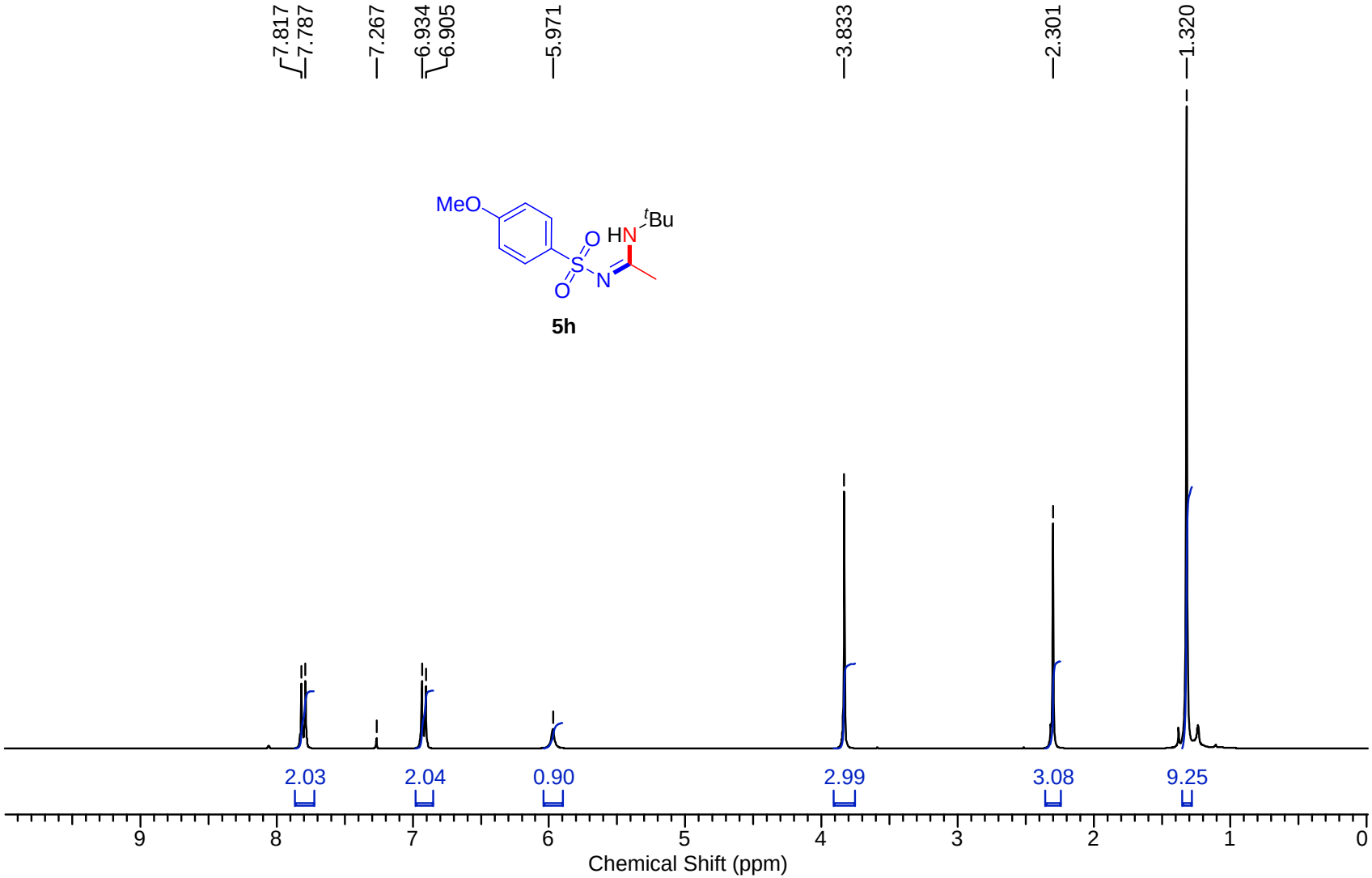

8.047
7.841
7.814
7.636
7.609
7.372
7.345
7.319
7.267
5.825
2.363
1.340
Br
O
HN
tBu
S
N
O
5f
0.95
0.98
0.95
1.02
0.87
3.00
9.24
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

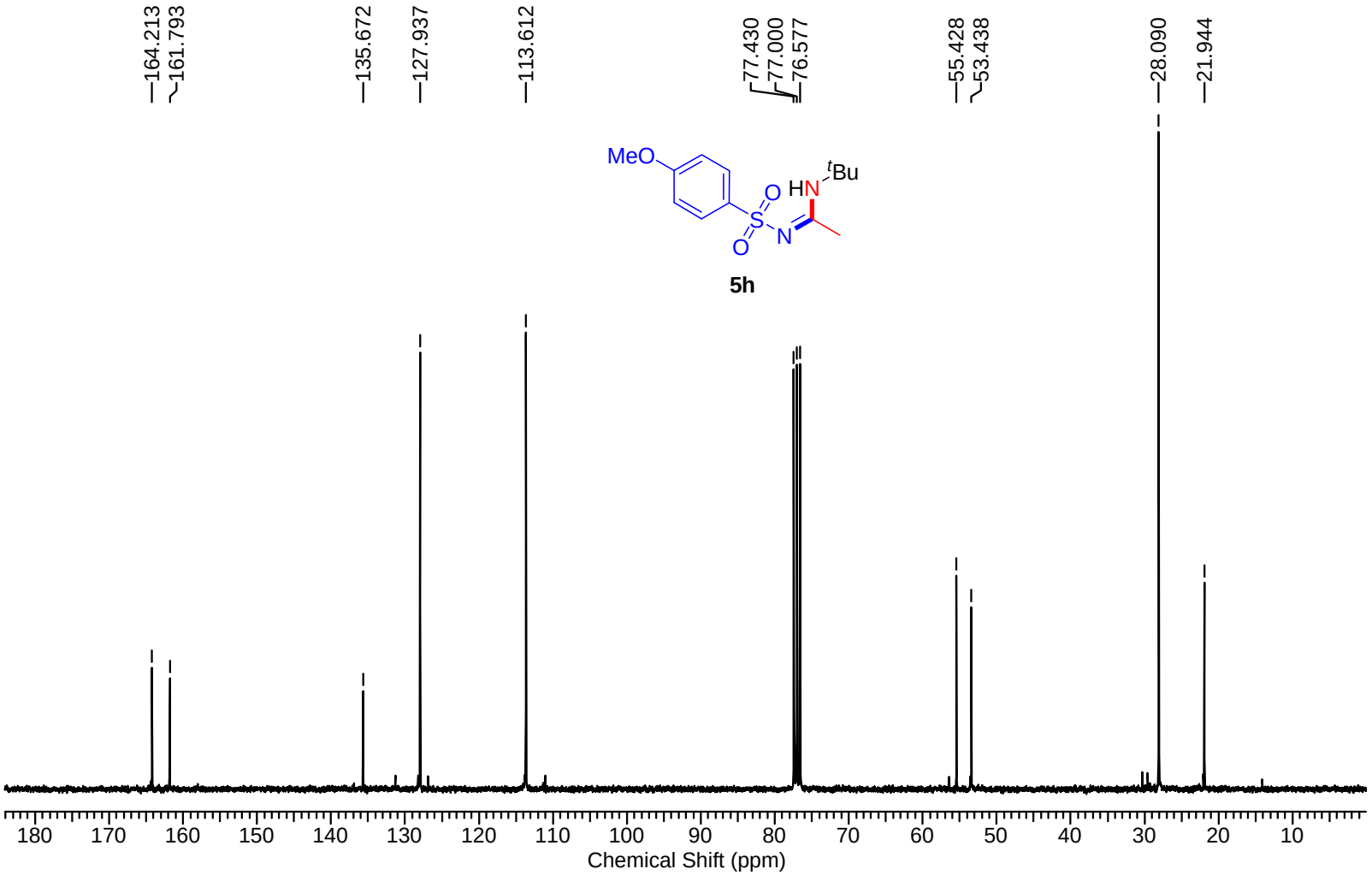

164.436
145.321
134.488
130.179
129.107
124.638
122.393
77.427
77.004
76.581
53.770
28.123
22.480
Br
HN
tBu
O
S
O
N
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

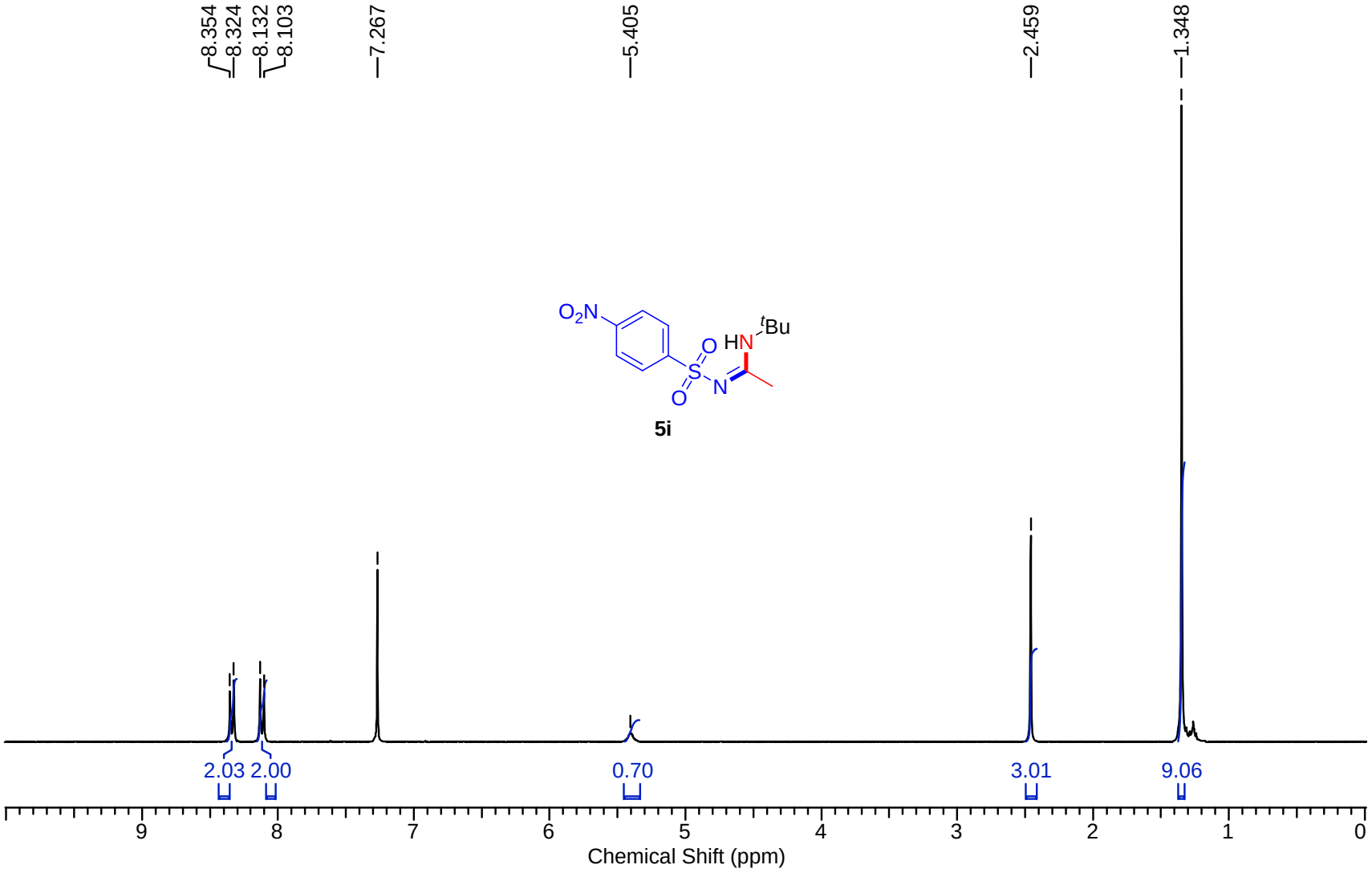
5f

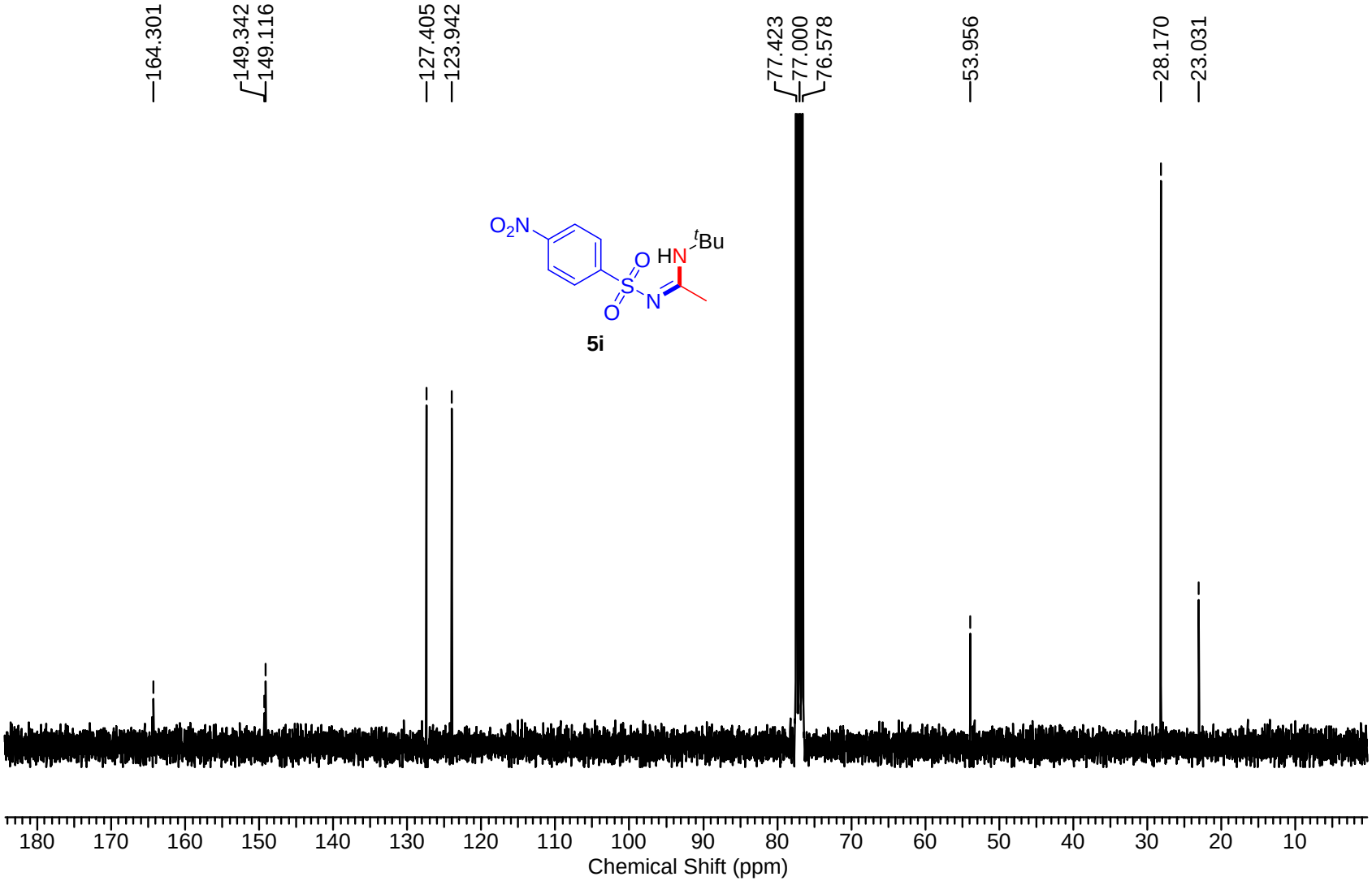

8.045
8.017
7.418
7.397
7.373
7.287
7.266
5.383
2.695
2.335
1.350
HN
tBu
O
S
O
N
5g
0.89
1.25
2.46
0.69
3.00
3.01
8.95
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

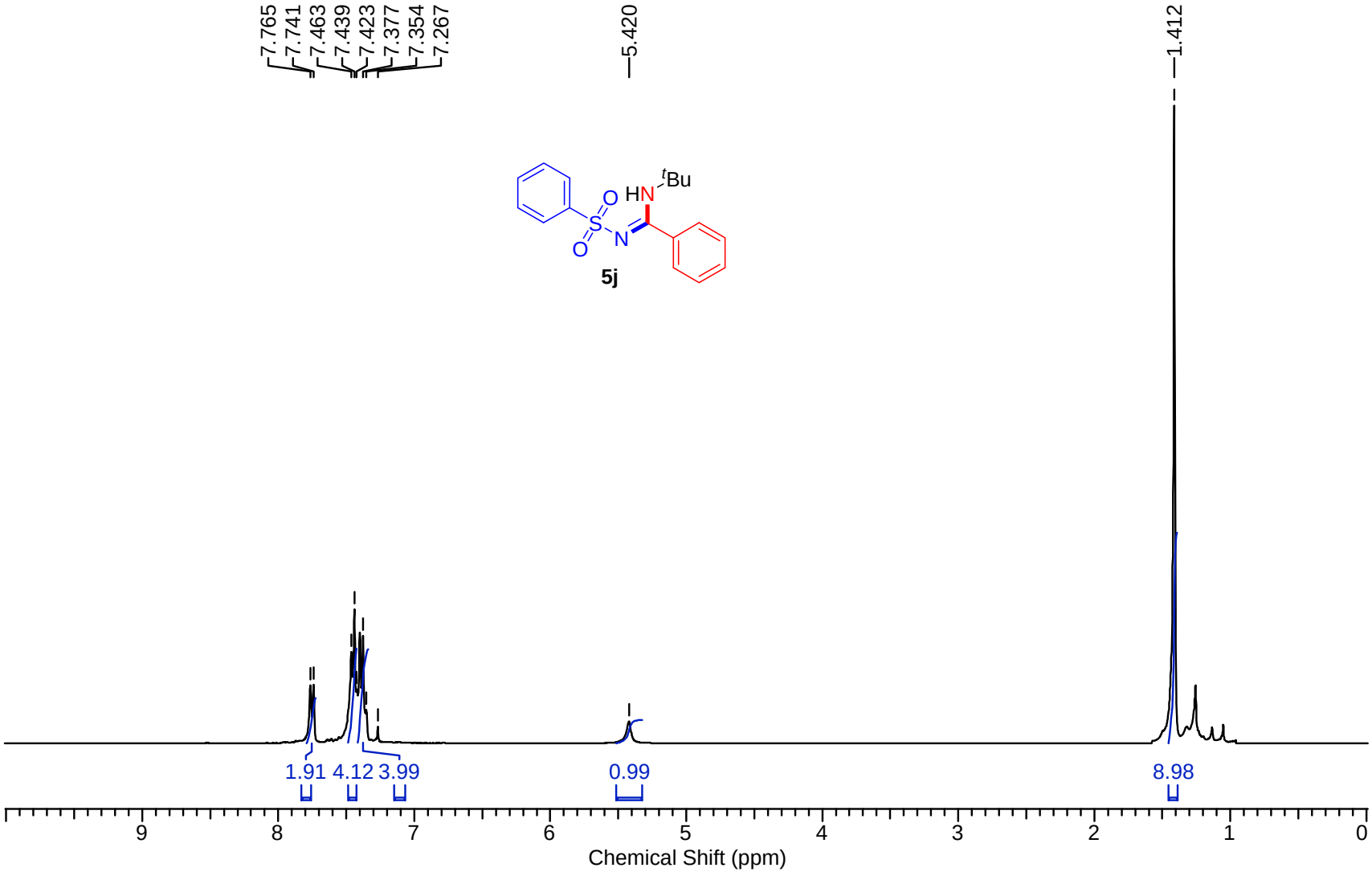

164.337
141.278
137.072
131.961
131.633
127.558
125.546
77.423
77.000
76.577
53.569
28.367
22.607
20.362
HN
tBu
O
S
O
N
5g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

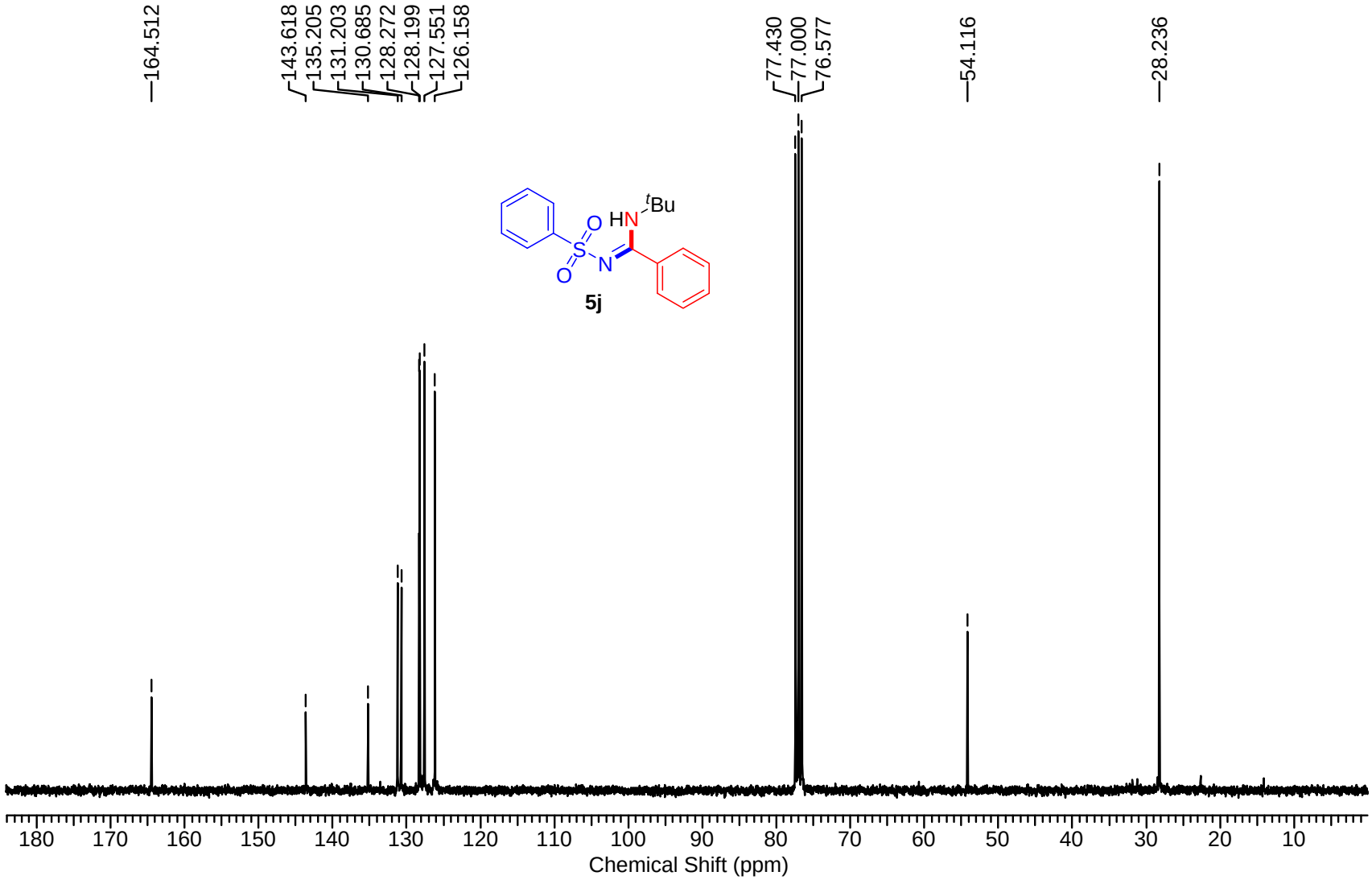

7.817
7.787
7.267
6.934
6.905
5.971
3.833
2.301
1.320
MeO
O
HN
tBu
S
O
N
5h
2.03
2.04
0.90
2.99
3.08
9.25
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

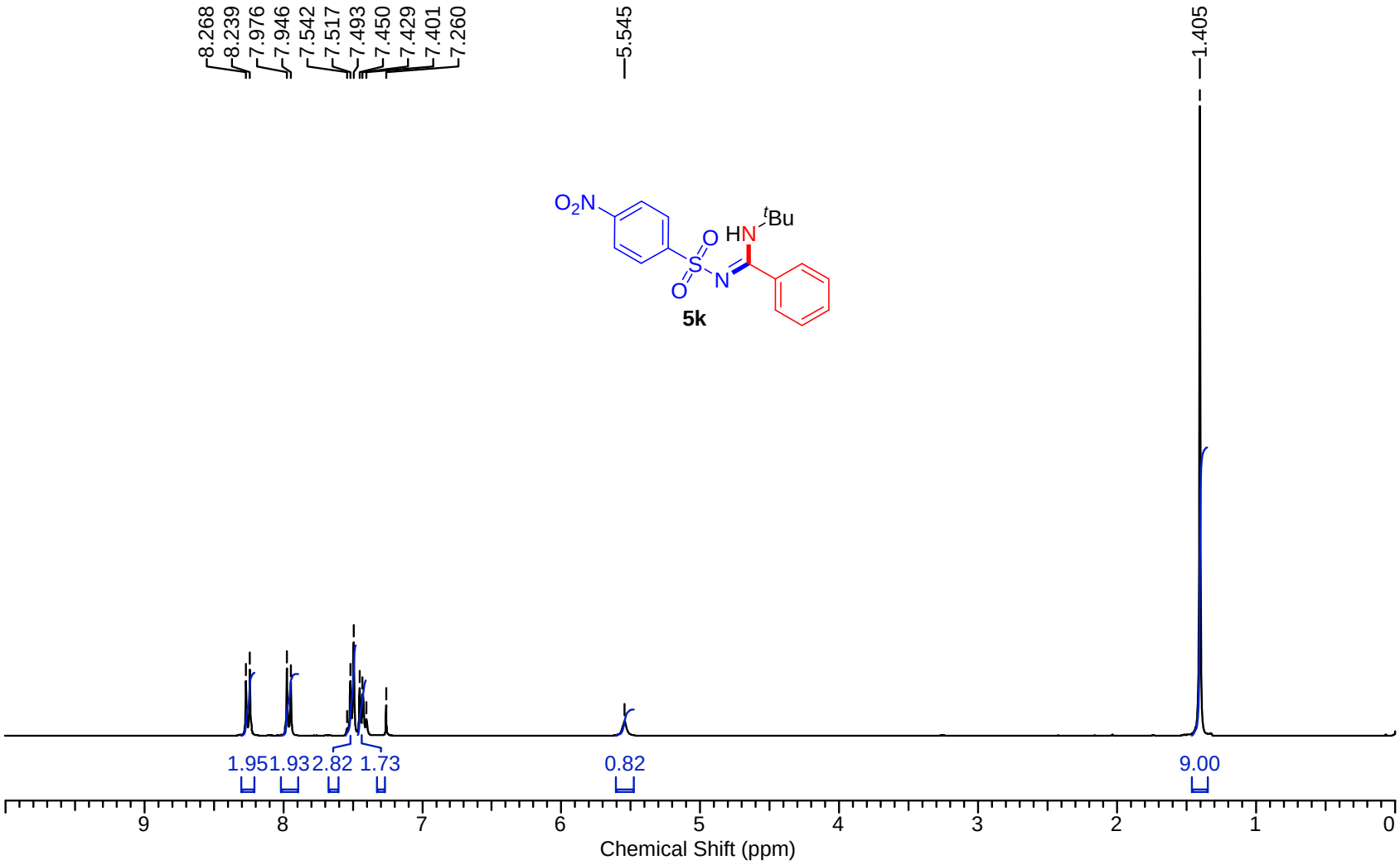

164.213
161.793
135.672
127.937
113.612
77.430
77.000
76.577
55.428
53.438
28.090
21.944
MeO
O
HN
tBu
S
O
N
5h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

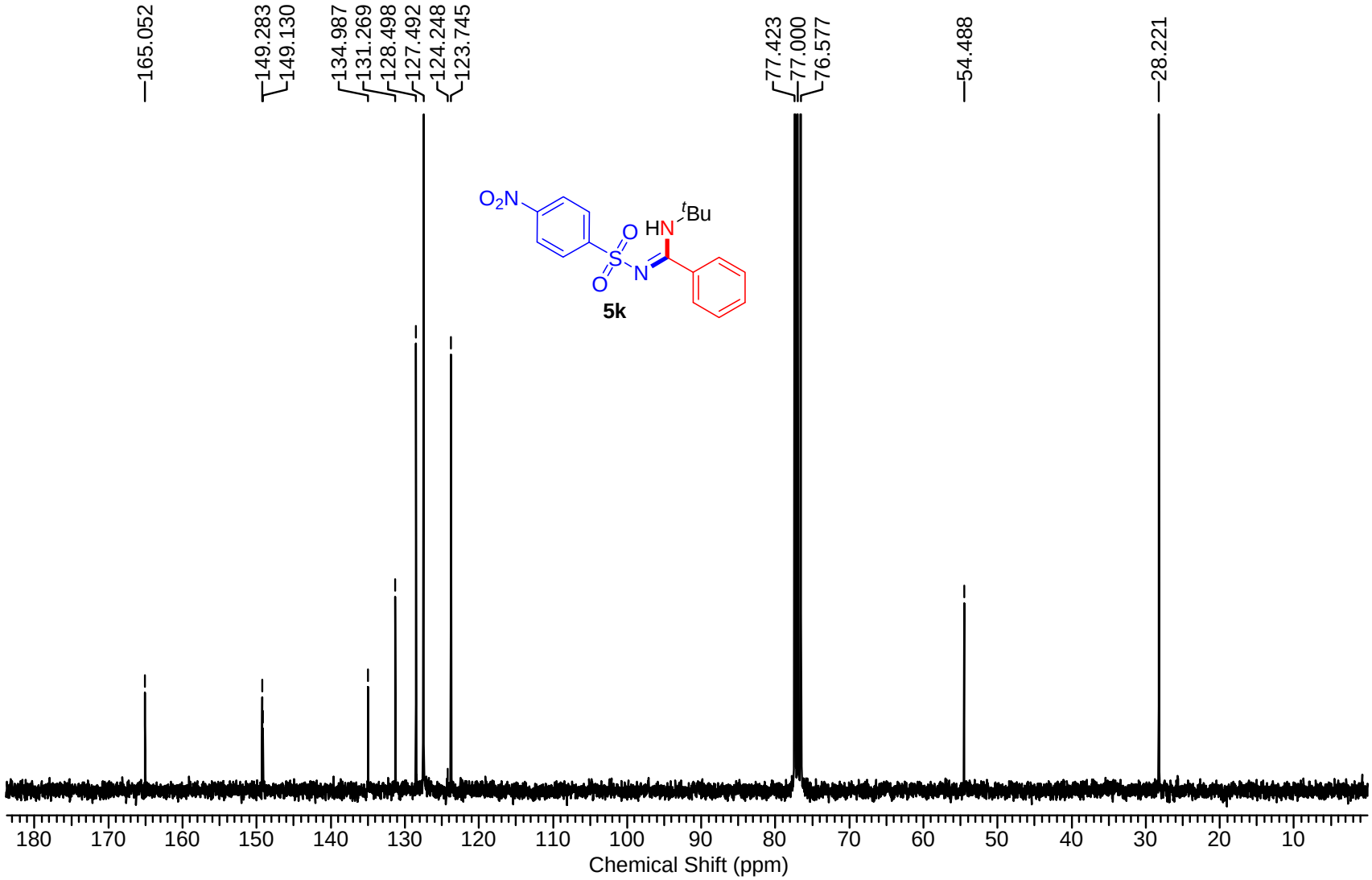

8.354
8.324
8.132
8.103
7.267
5.405
2.459
1.348
O2N
HN
tBu
O
S
O
N
5i
2.03
2.00
0.70
3.01
9.06
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

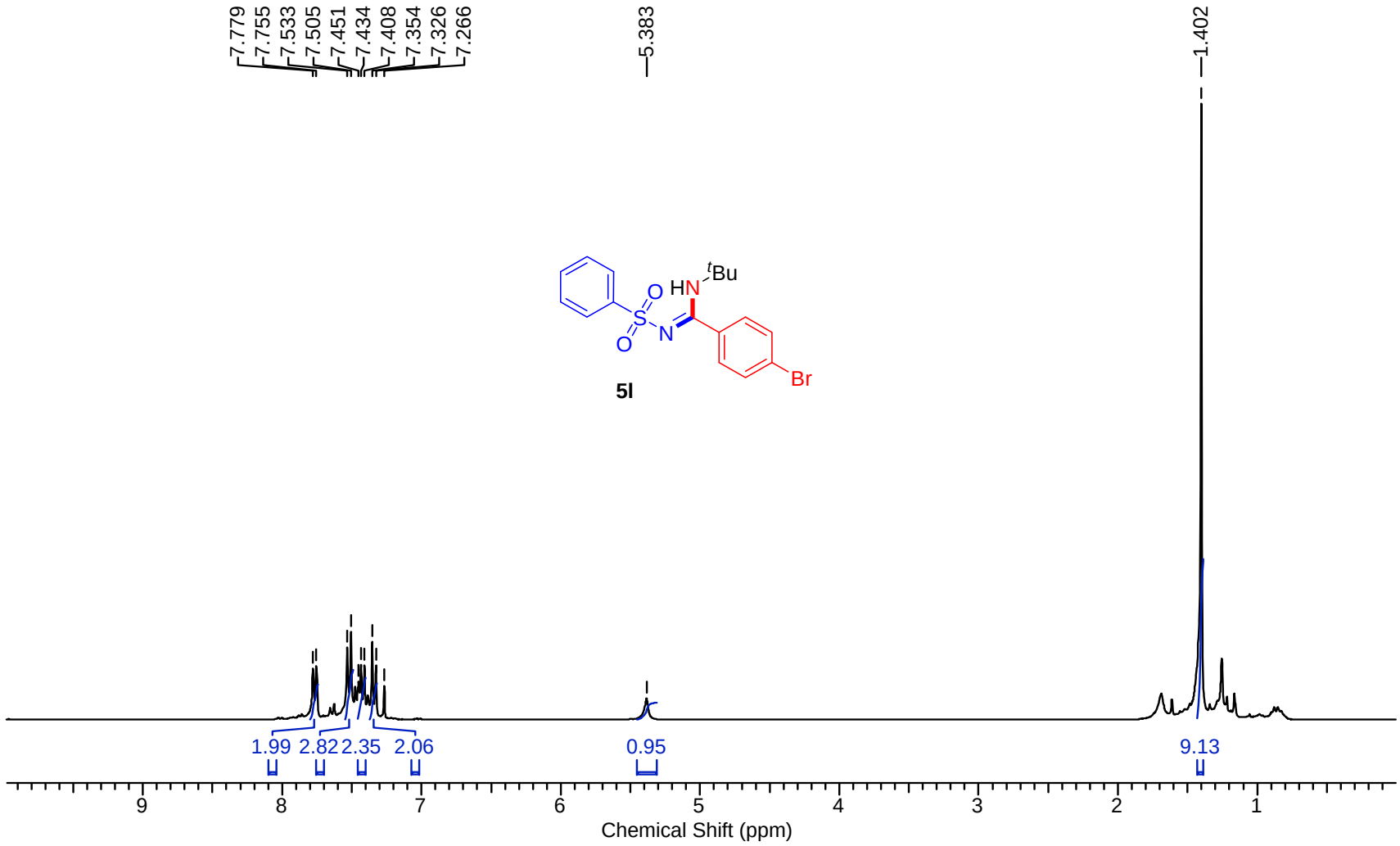

164.301
149.342
149.116
127.405
123.942
77.423
77.000
76.578
53.956
28.170
23.031
O2N
HN
tBu
S
O
O
N
5i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

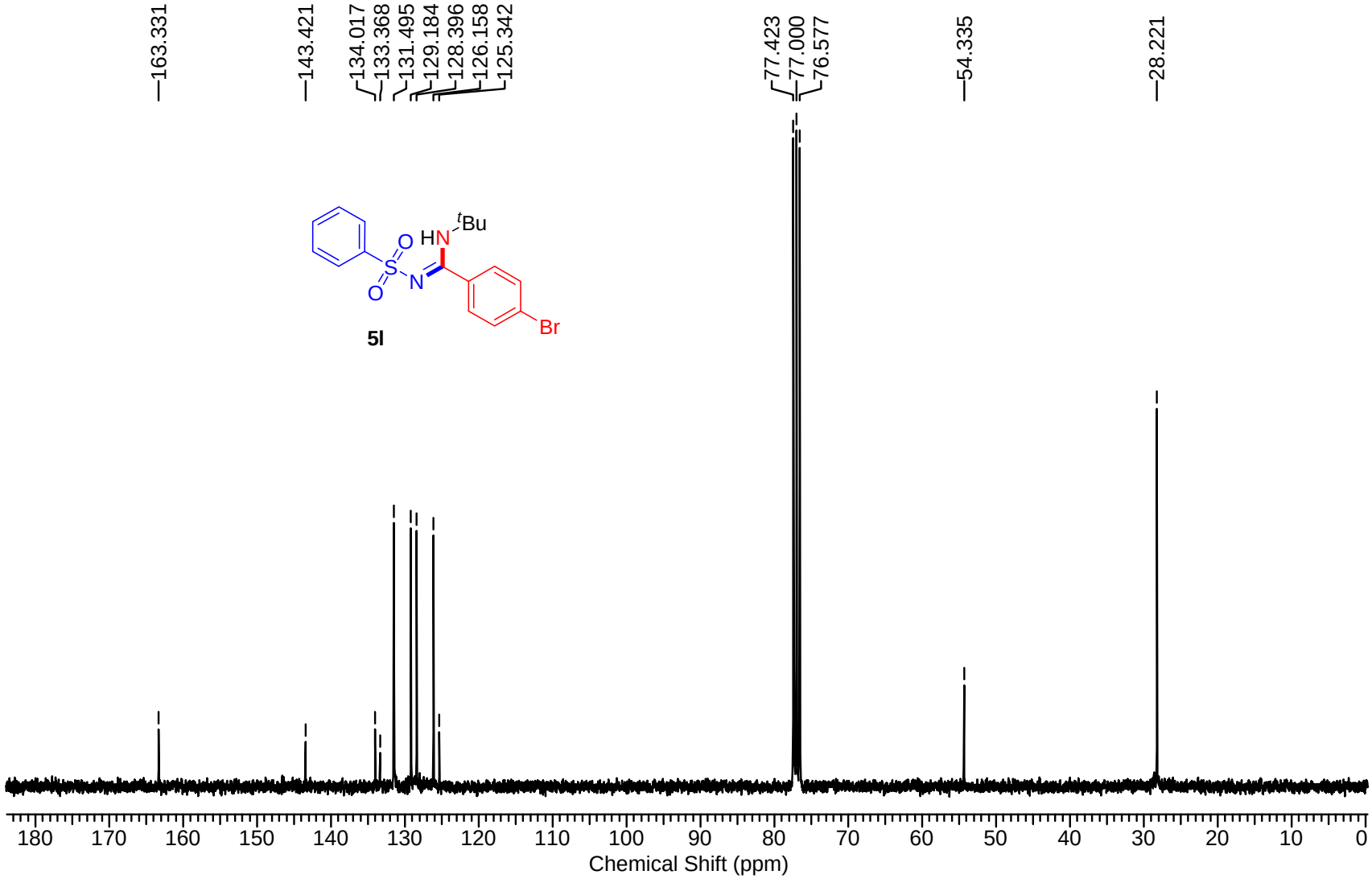

7.765
7.741
7.463
7.439
7.423
7.377
7.354
7.267
5.420
1.412
HN
tBu
O
S
O
N
5j
1.91
4.12
3.99
0.99
8.98
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

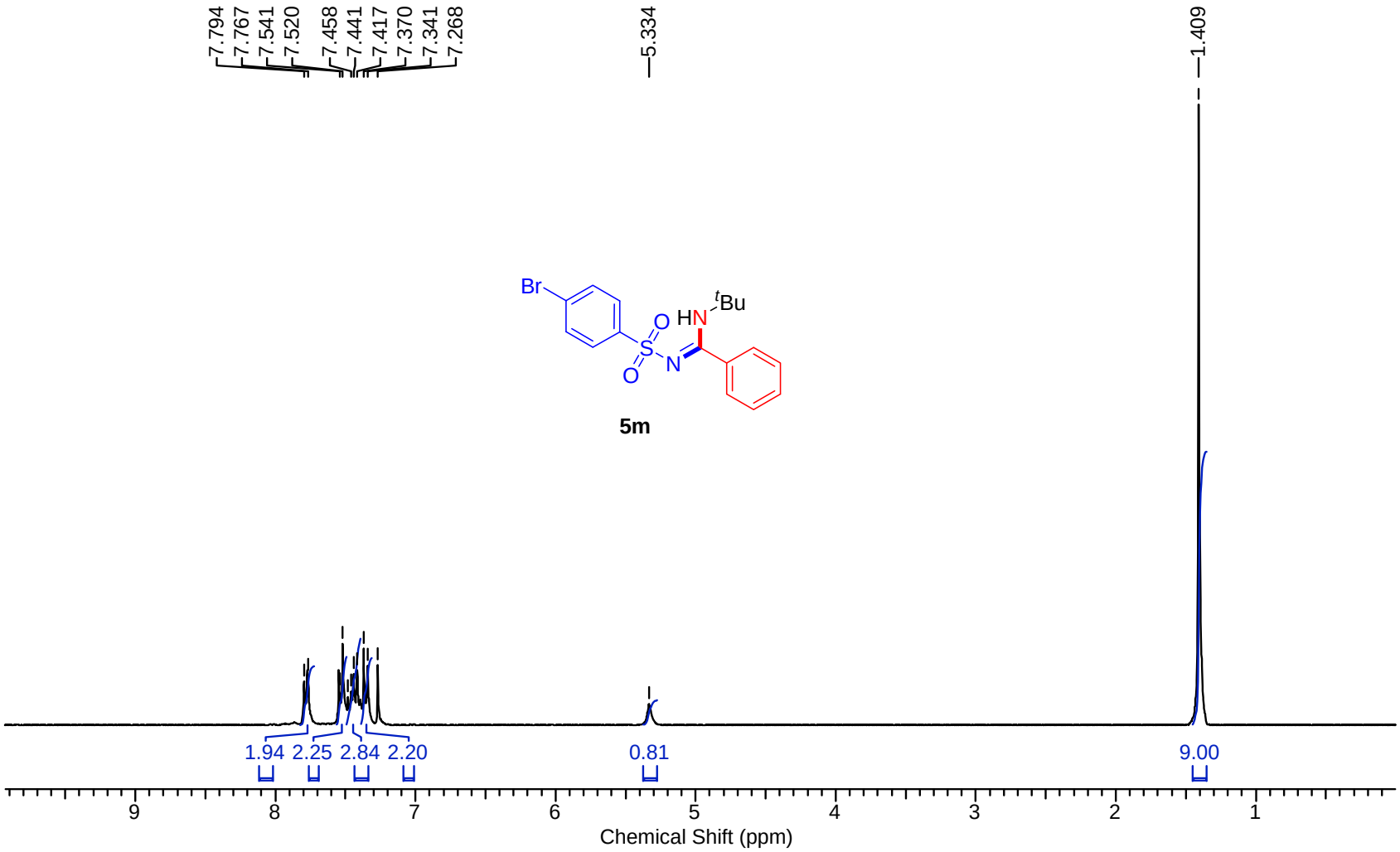

164.512
143.618
135.205
131.203
130.685
128.272
128.199
127.551
126.158
77.430
77.000
76.577
54.116
28.236
O
HN
tBu
S
O
N
5j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


8.268
8.239
7.976
7.946
7.542
7.517
7.493
7.450
7.429
7.401
7.260
5.545
1.405
O2N
HN
tBu
O
S
O
N
5k
1.95
1.93
2.82
1.73
0.82
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

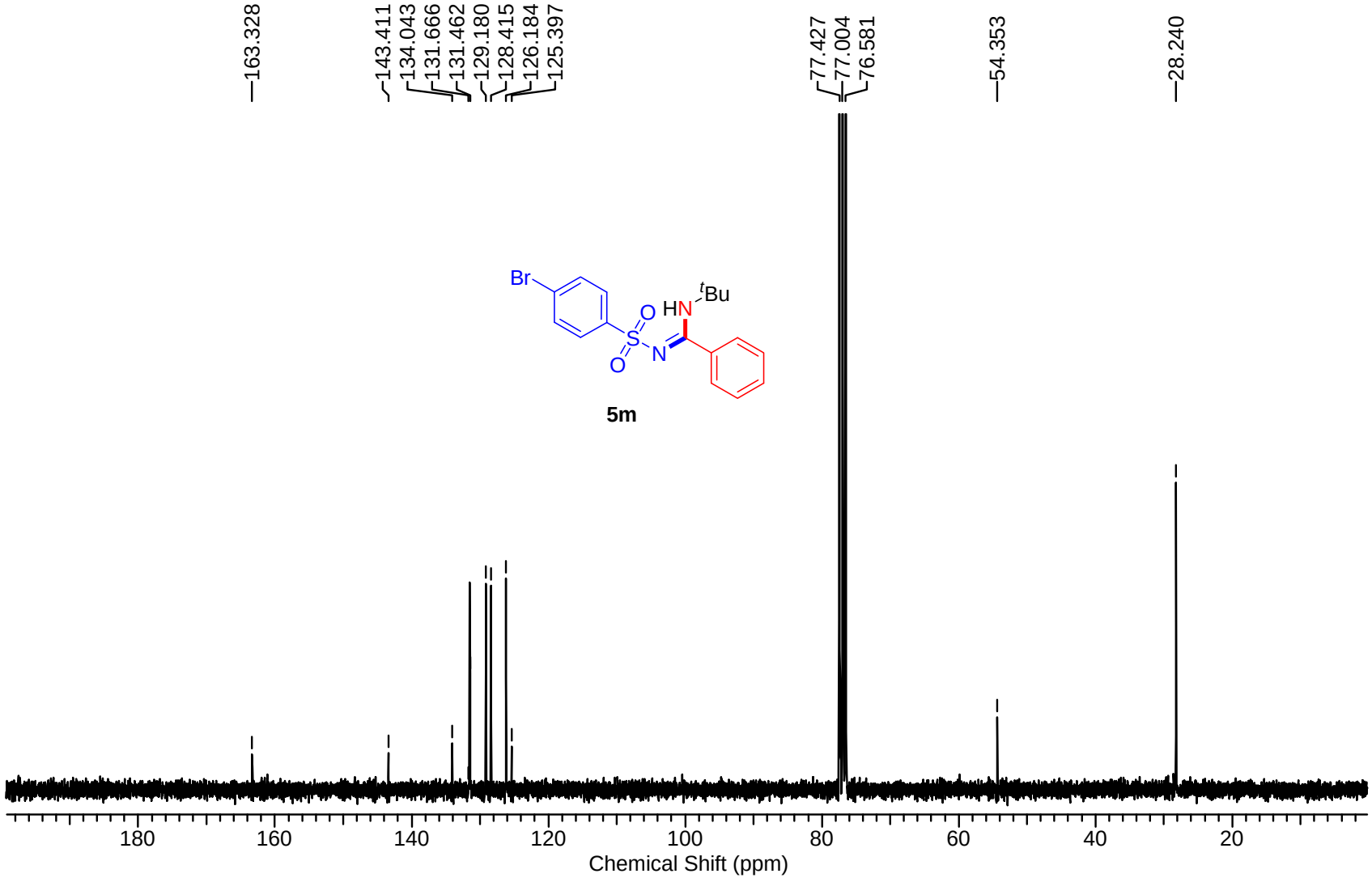

165.052
149.283
149.130
134.987
131.269
128.498
127.492
124.248
123.745
77.423
77.000
76.577
54.488
28.221
O2N
HN
tBu
O
S
O
N
5k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

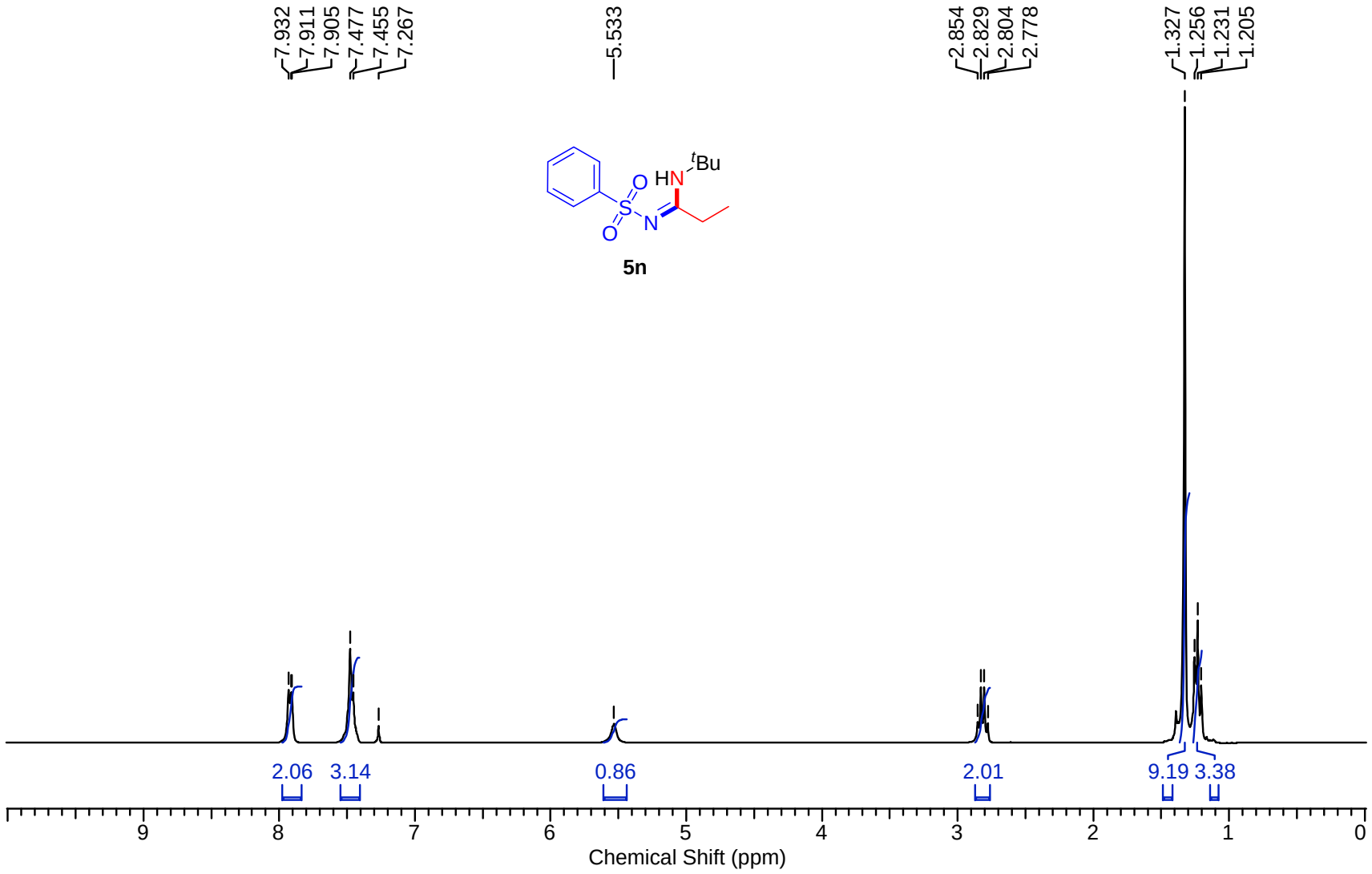

7.779
7.755
7.533
7.505
7.451
7.434
7.408
7.354
7.326
7.266
5.383
1.402
HN
tBu
O
S
O
N
Br
5l
1.99
2.82
2.35
2.06
0.95
9.13
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


163.331
143.421
134.017
133.368
131.495
129.184
128.396
126.158
125.342
77.423
77.000
76.577
54.335
28.221
HN
tBu
O
S
O
N
Br
5l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.794
7.767
7.541
7.520
7.458
7.441
7.417
7.370
7.341
7.268
5.334
1.409
Br
O
HN
tBu
S
O
N
1.94
2.25
2.84
2.20
0.81
9.00
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

5m


163.328
143.411
134.043
131.666
131.462
129.180
128.415
126.184
125.397
77.427
77.004
76.581
54.353
28.240
Br
O
HN
tBu
S
O
N
5m
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)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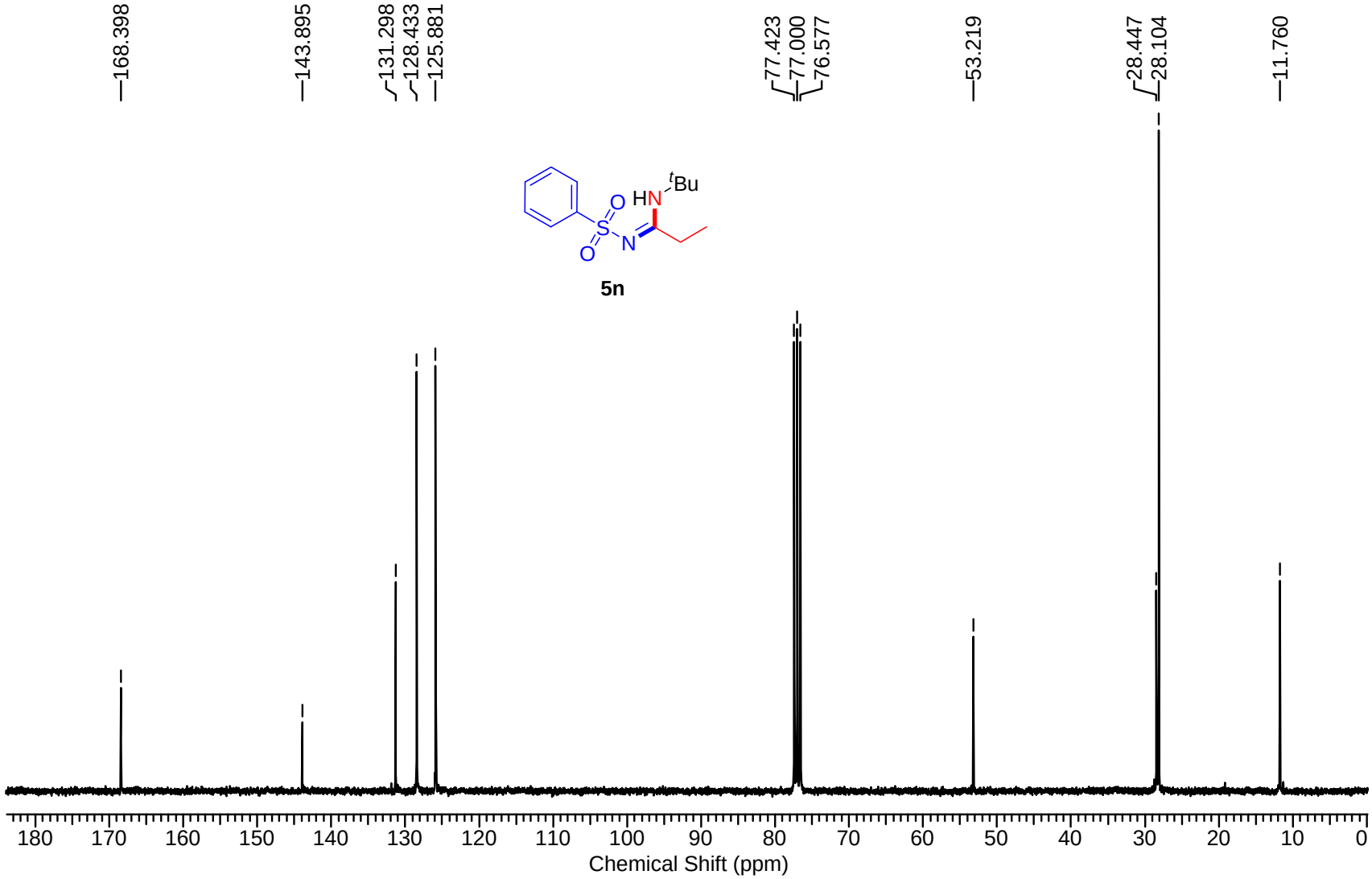
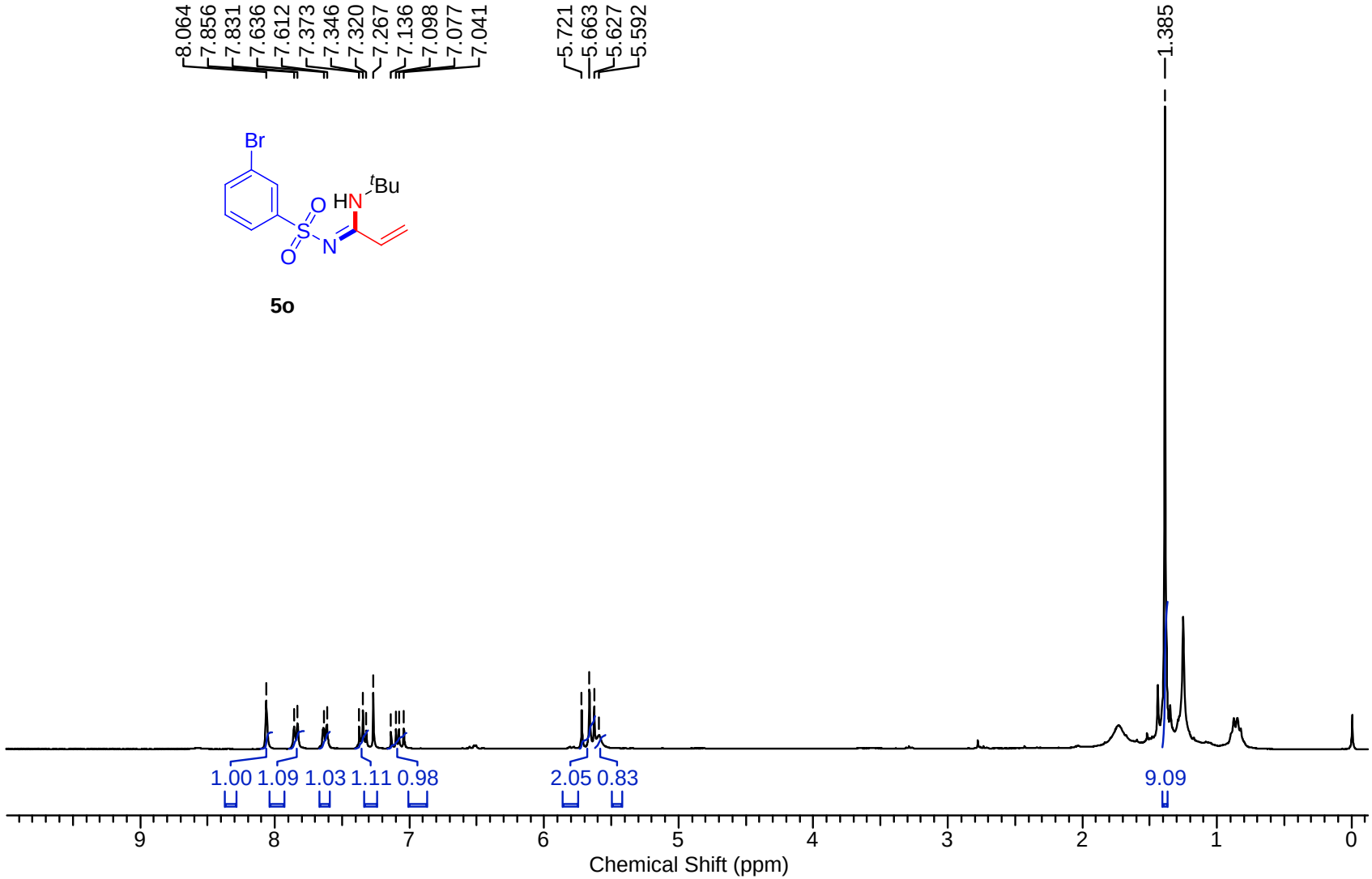
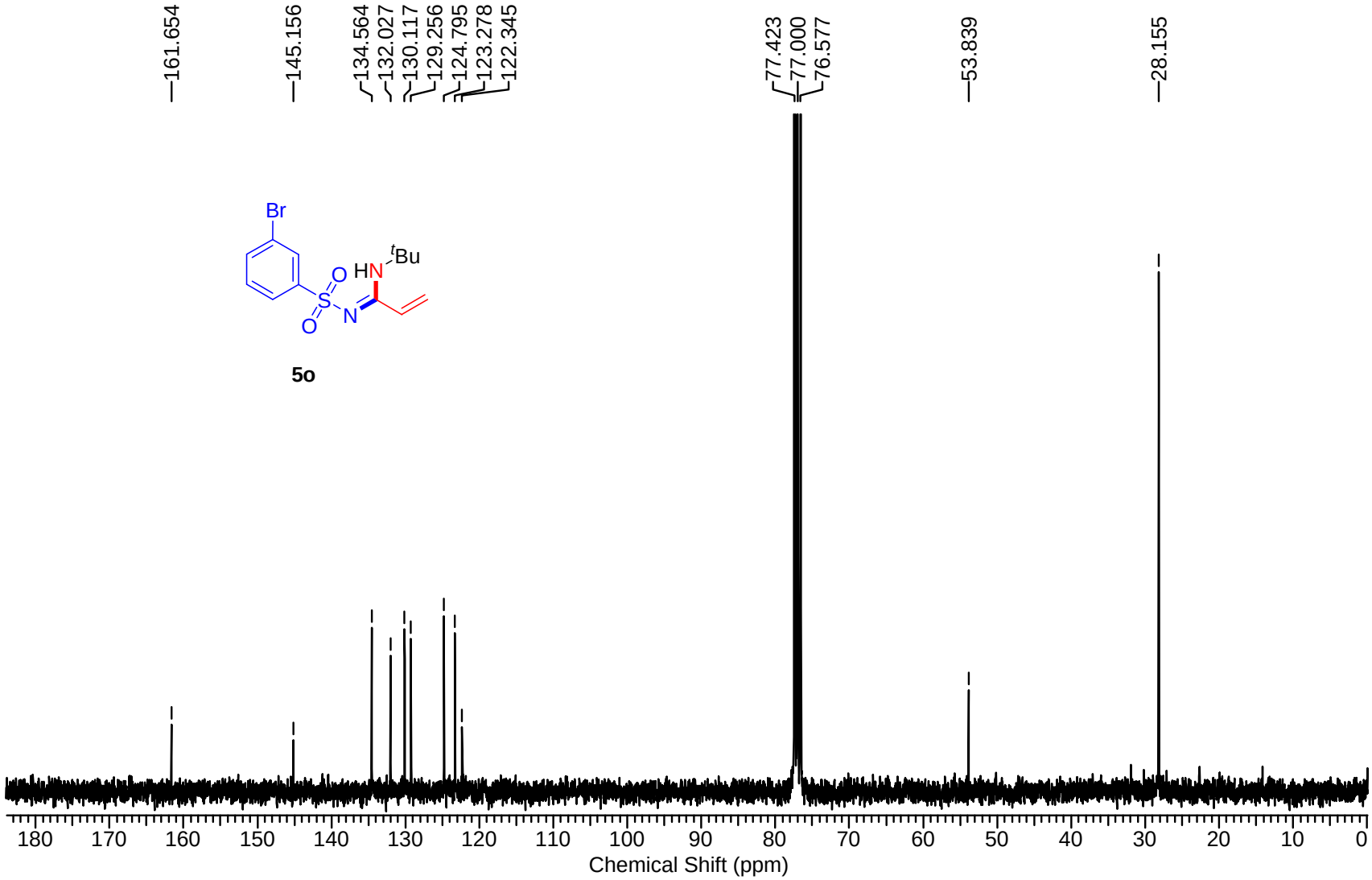
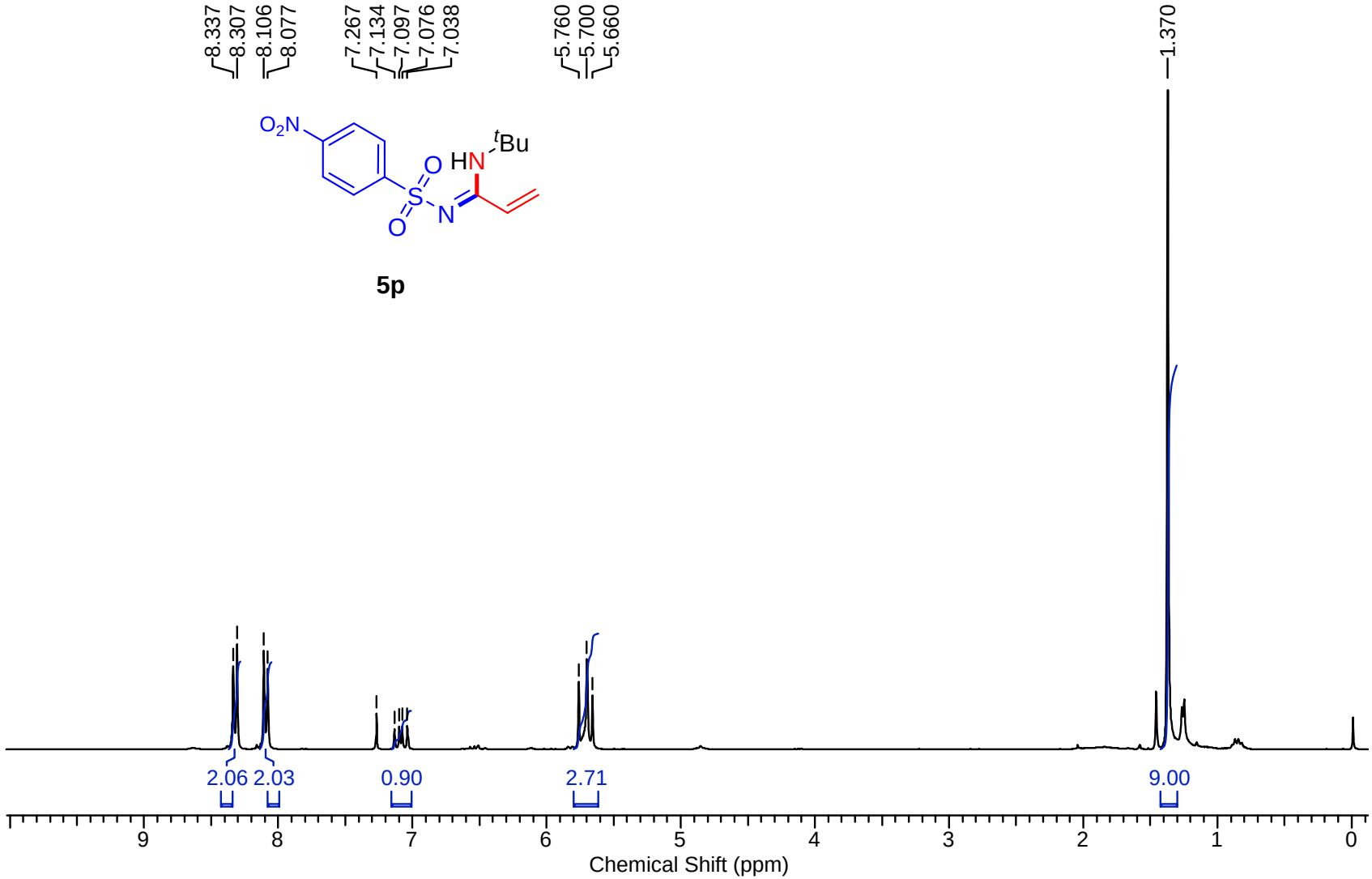
7.911
7.905
7.477
7.455
7.267
5.533
2.854
2.829
2.804
2.778
1.327
1.256
1.231
1.205
HN
tBu
O
S
O
N
5n
2.06
3.14
0.86
2.01
9.19
3.38
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

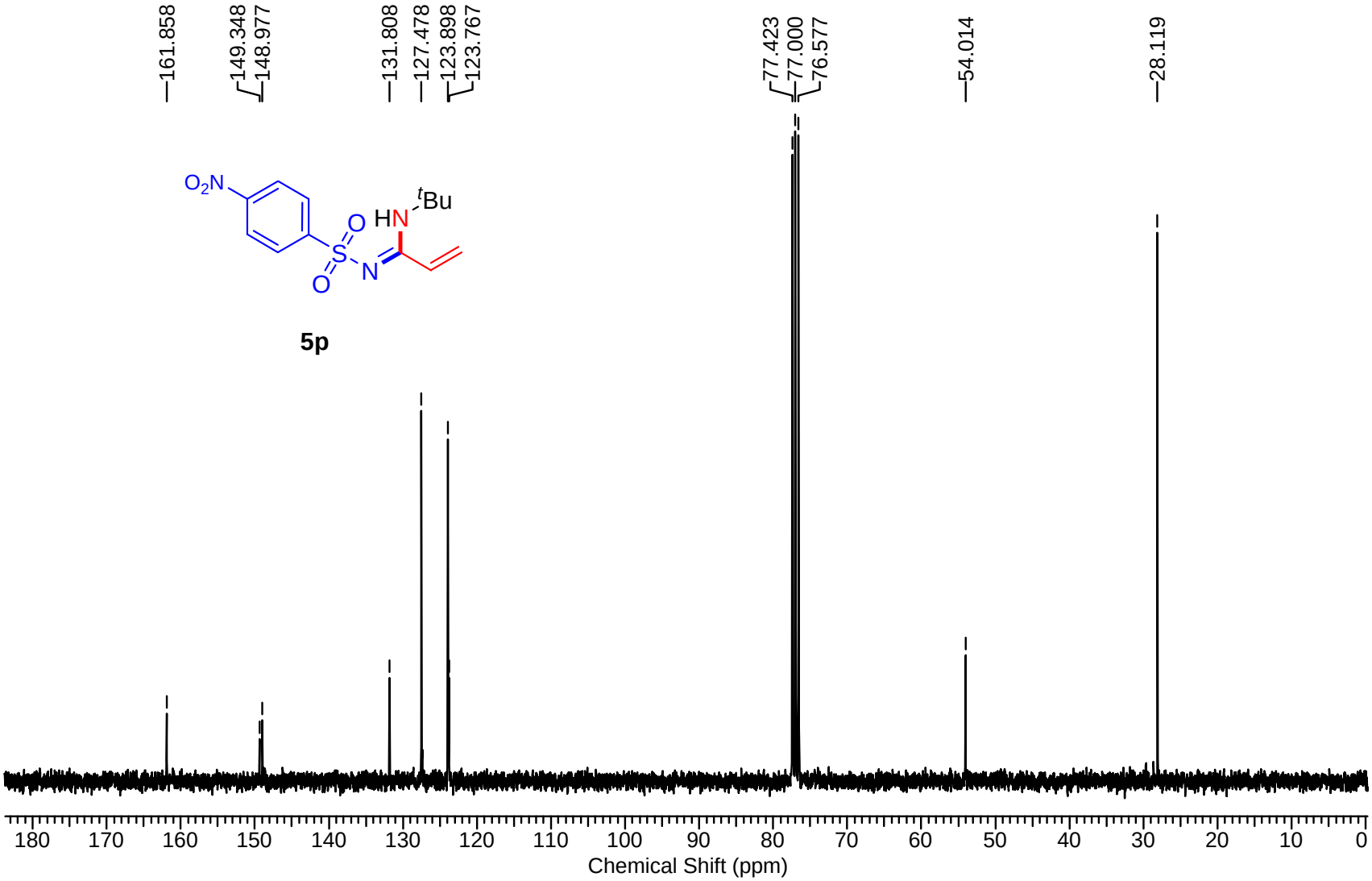

168.398
143.895
131.298
128.433
125.881
77.423
77.000
76.577
53.219
28.447
28.104
11.760
O
HN
tBu
S
O
N
5n
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.064
7.856
7.831
7.636
7.612
7.373
7.346
7.320
7.267
7.136
7.098
7.077
7.041
5.721
5.663
5.627
5.592
1.385
Br
O
HN
tBu
S
N
O
1.00 1.09 1.03 1.11 0.98
2.05 0.83
9.09
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

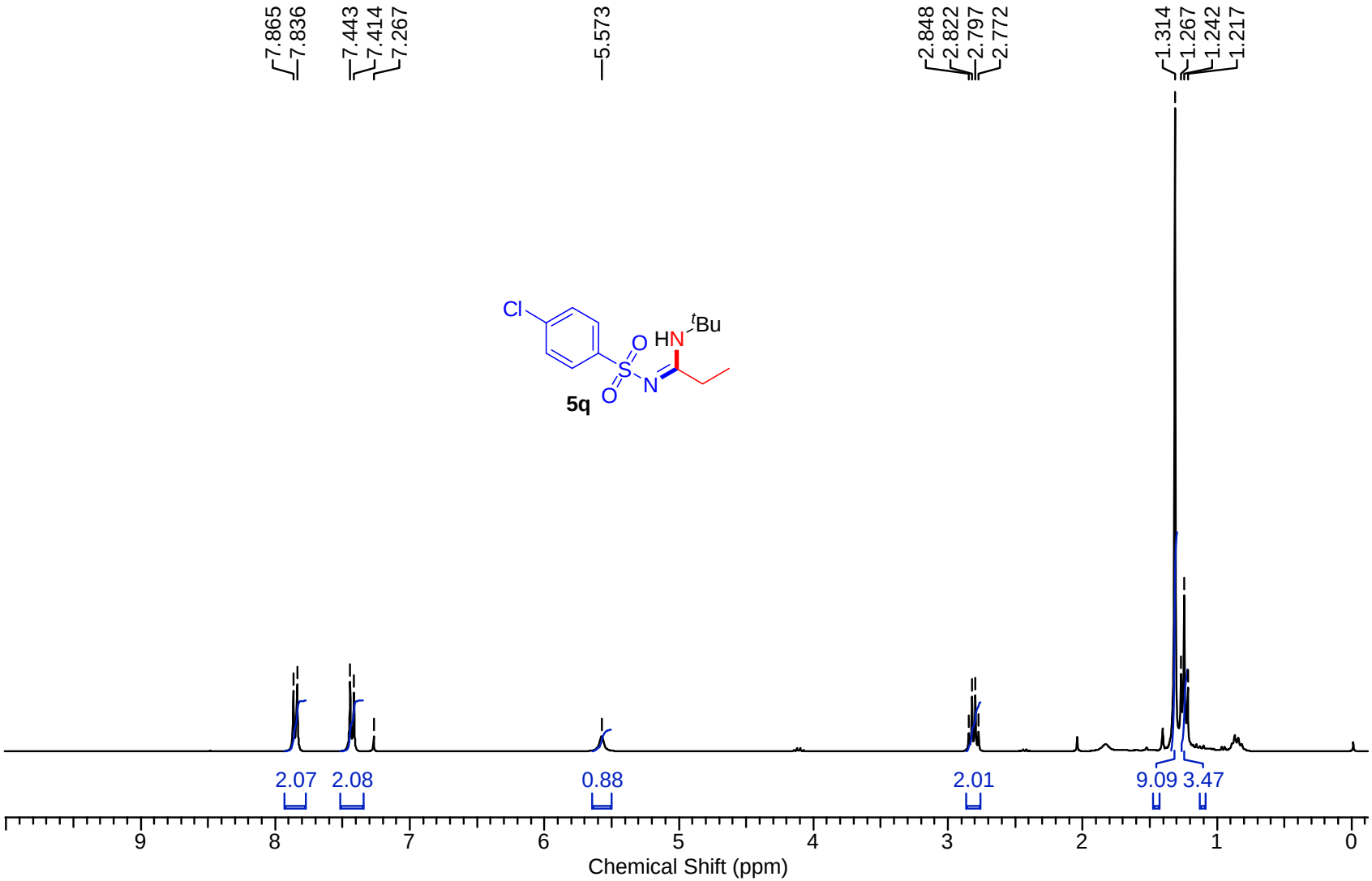
5o

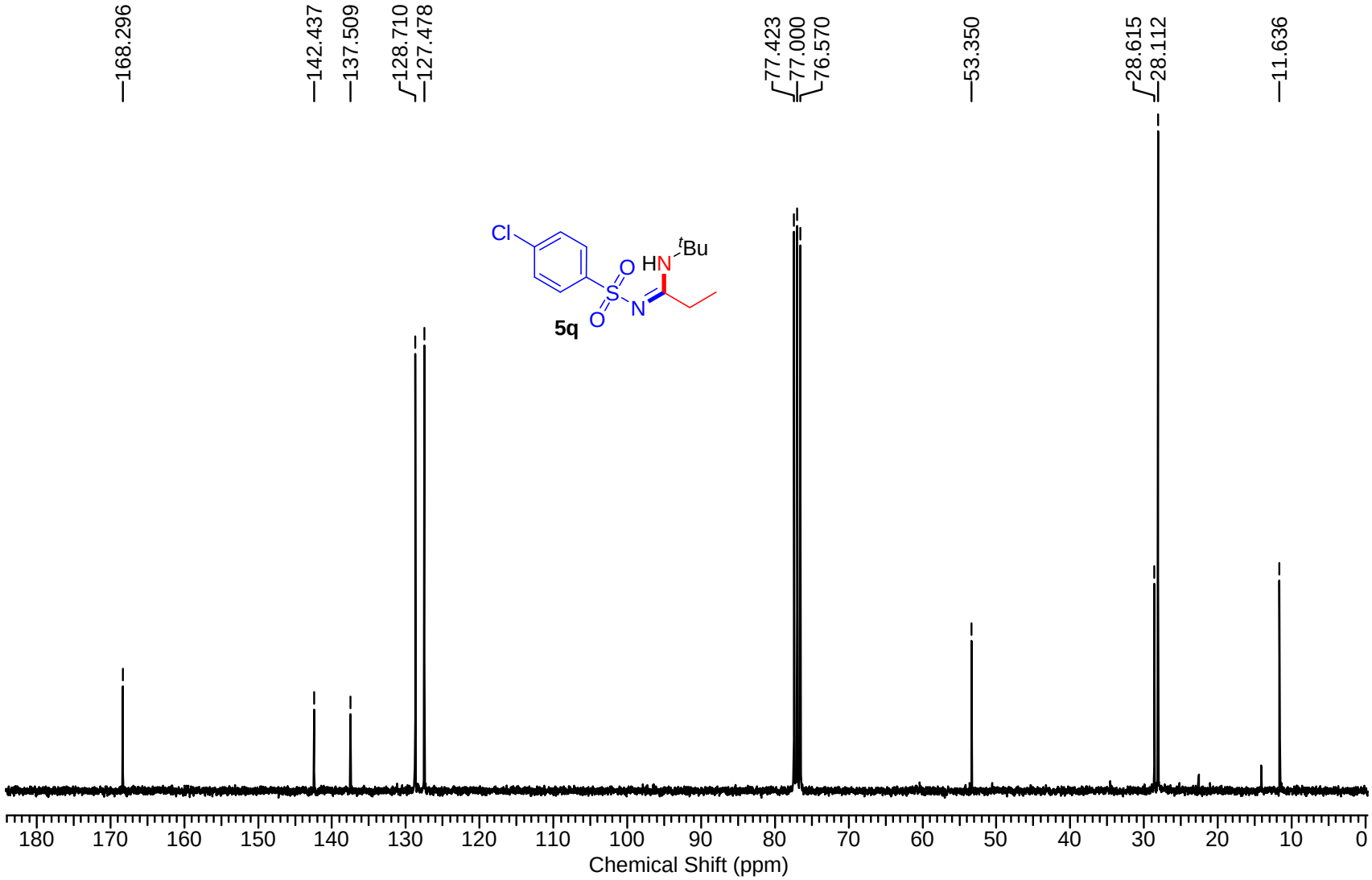

161.654
145.156
134.564
132.027
130.117
129.256
124.795
123.278
122.345
77.423
77.000
76.577
53.839
28.155
Br
O
HN
tBu
S
N
O
5o
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

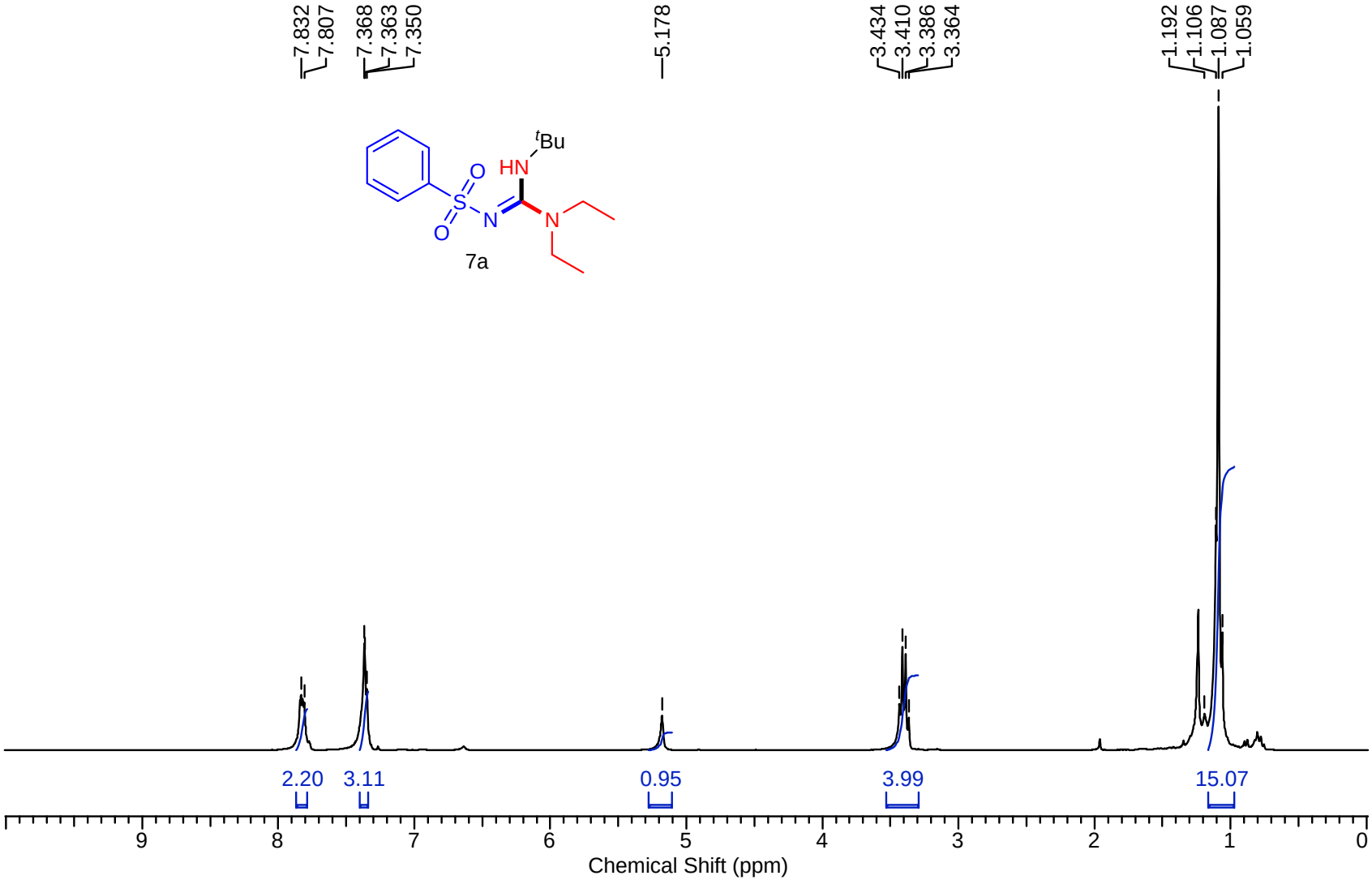

8.337
8.307
8.106
8.077
7.267
7.134
7.097
7.076
7.038
5.760
5.700
5.660
1.370
O2N
O
HN
tBu
S
N
O
5p
2.06
2.03
0.90
2.71
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

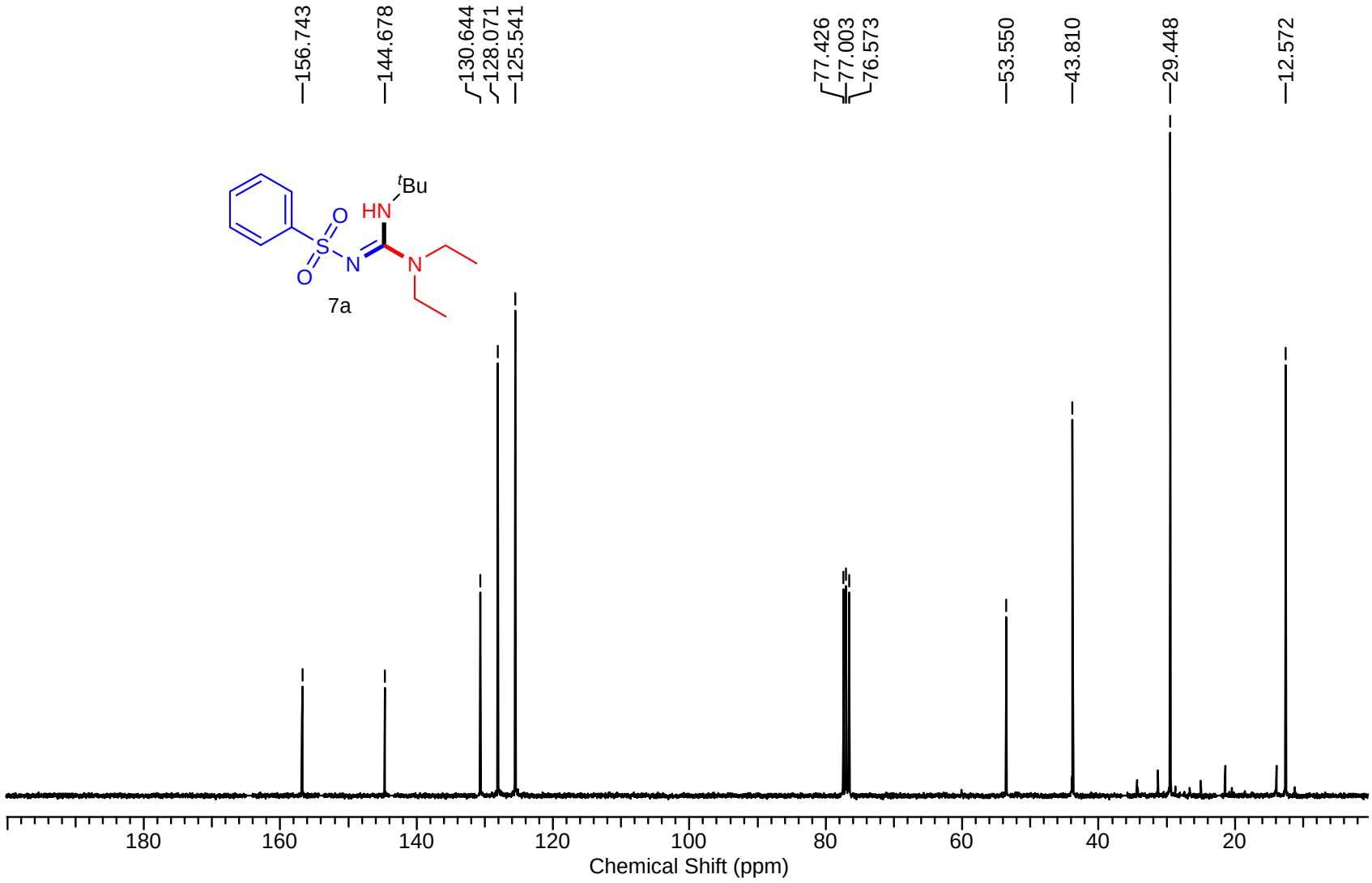

161.858
149.348
148.977
131.808
127.478
123.898
123.767
77.423
77.000
76.577
54.014
28.119
O2N
HN
tBu
O
S
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

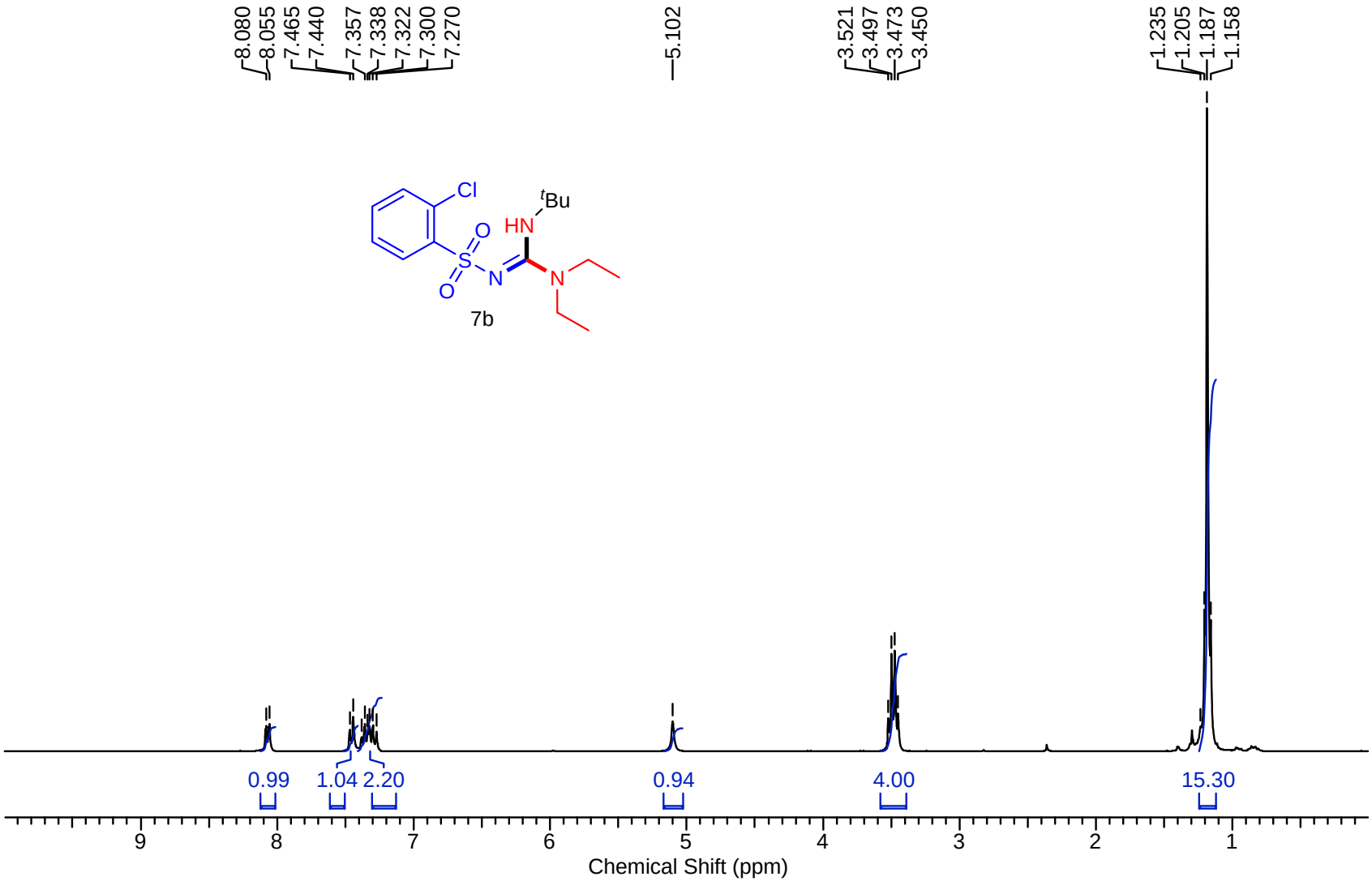
5p

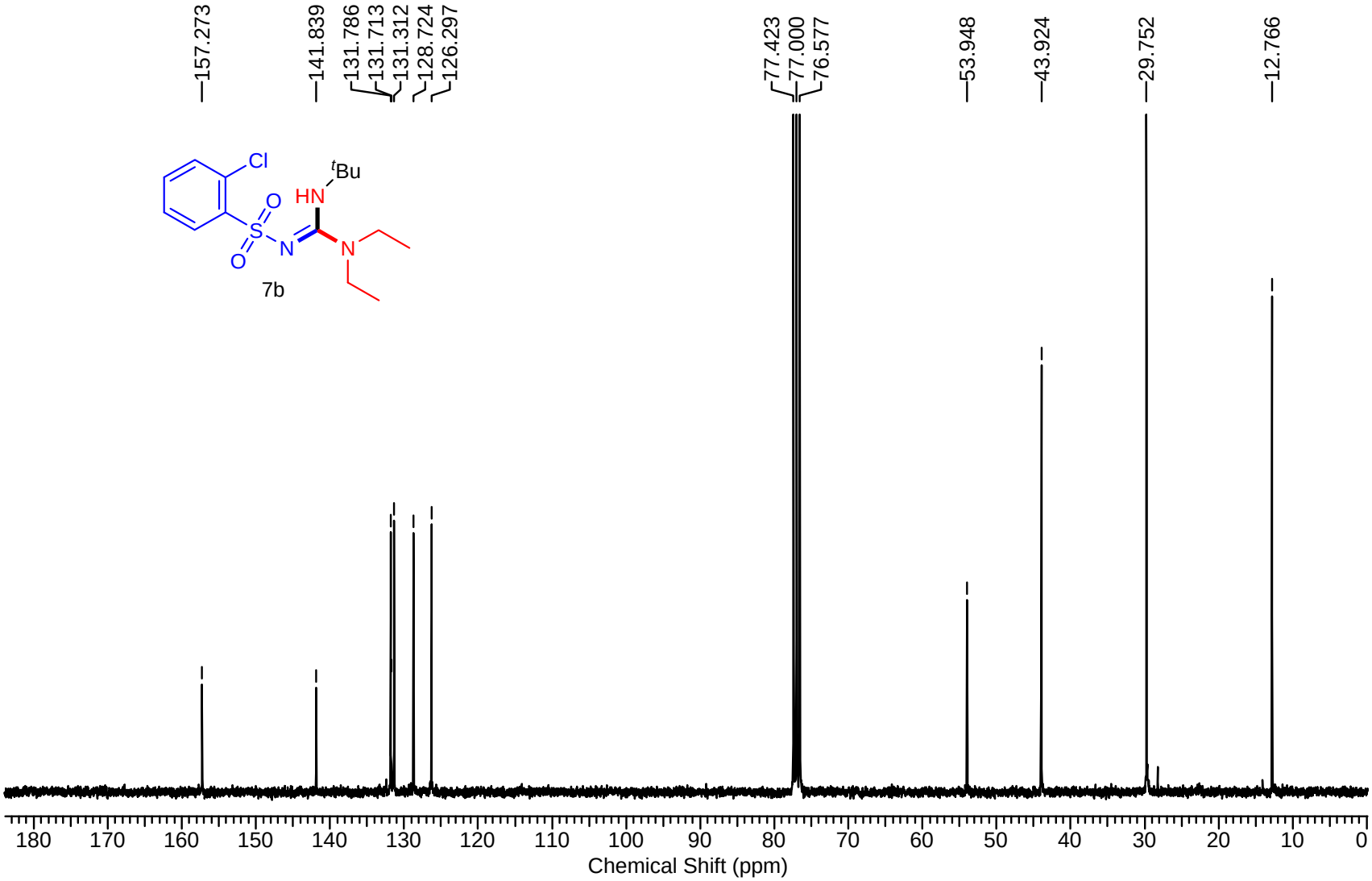

7.865
7.836
7.443
7.414
7.267
5.573
2.848
2.822
2.797
2.772
1.314
1.267
1.242
1.217
Cl
O
HN
tBu
S
N
O
5q
2.07
2.08
0.88
2.01
9.09
3.47
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

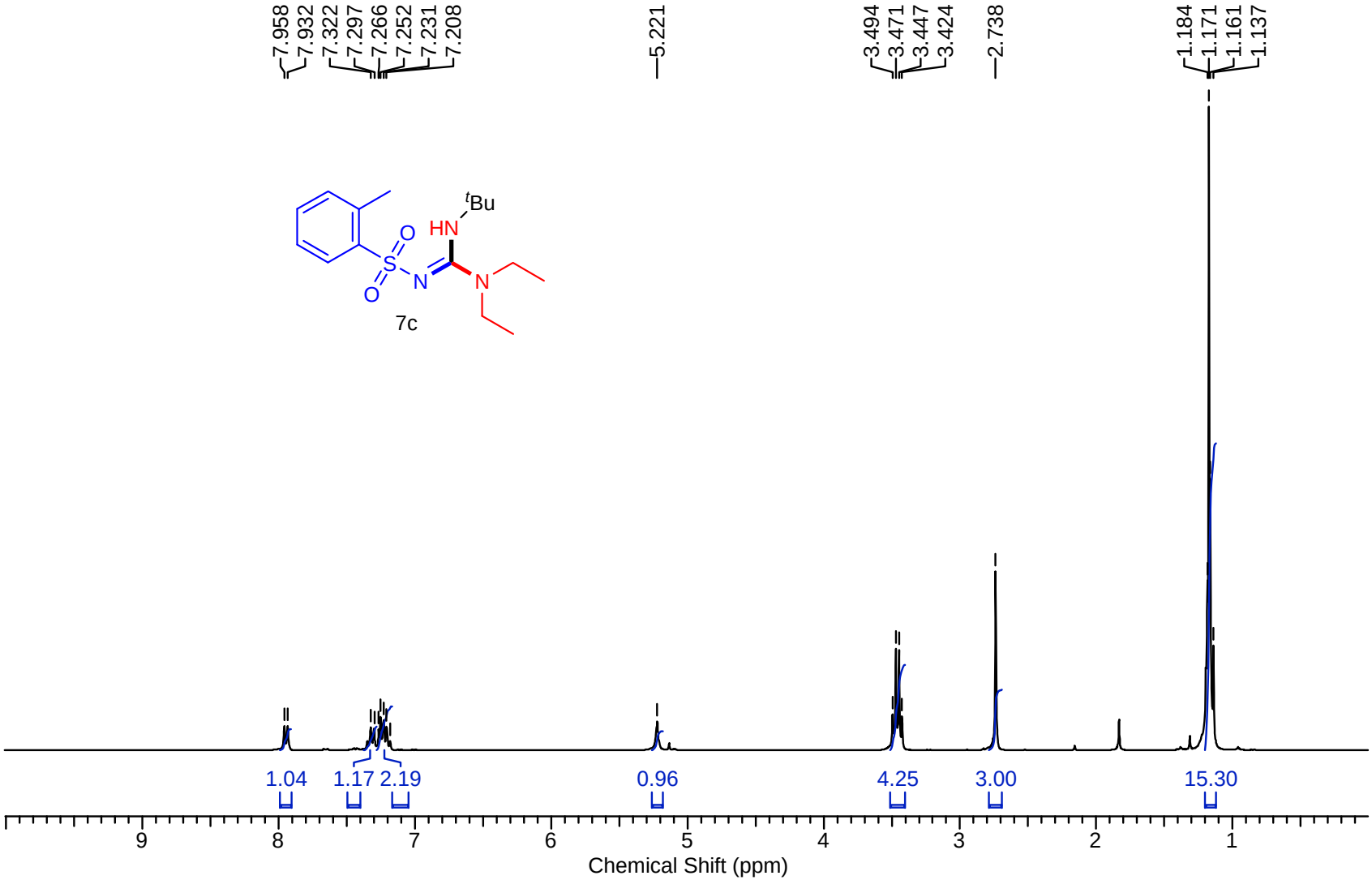

168.296
142.437
137.509
128.710
127.478
77.423
77.000
76.570
53.350
28.615
28.112
11.636
Cl
O
HN
tBu
S
O
N
5q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

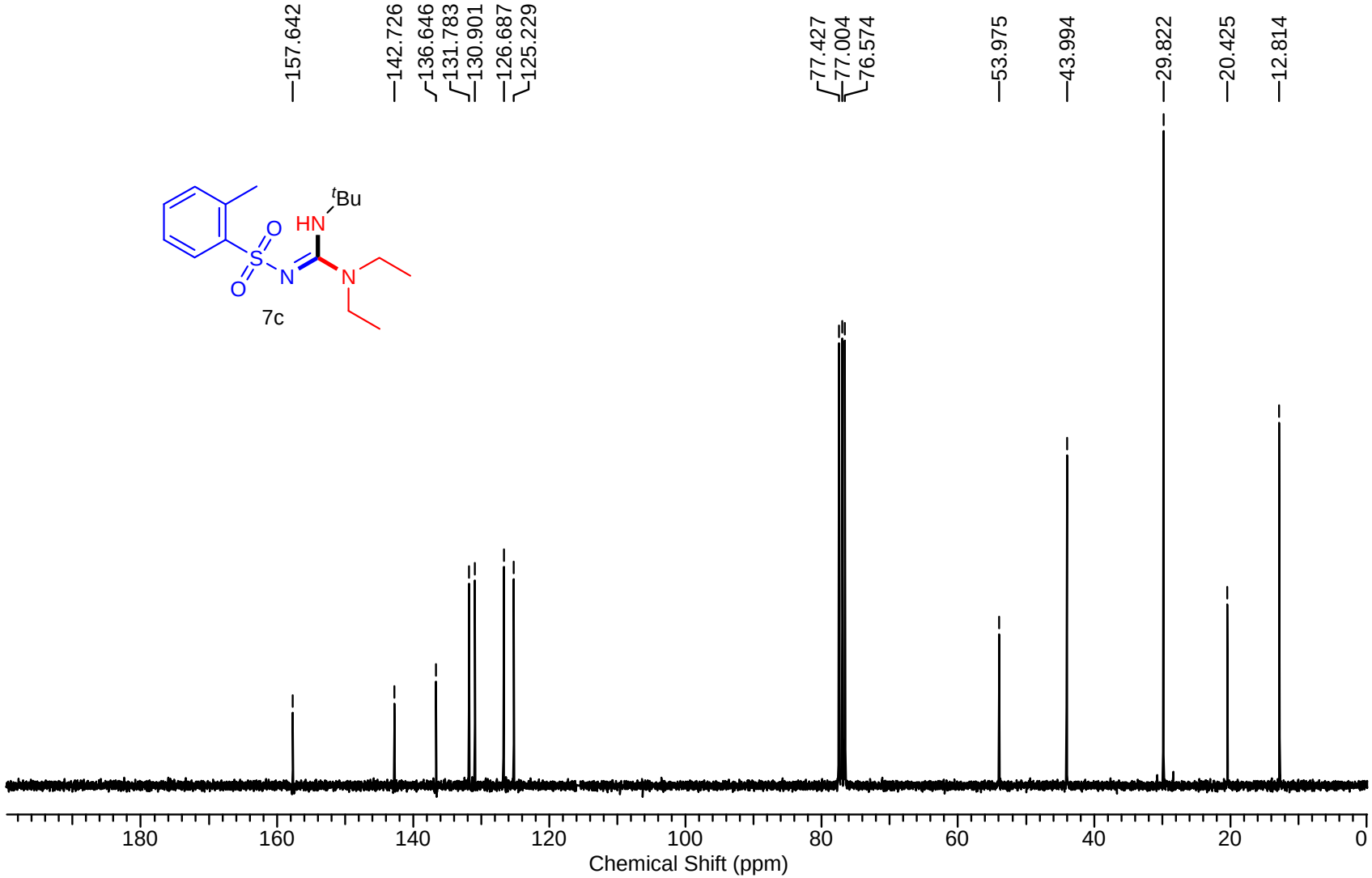

7.832
7.807
7.368
7.363
7.350
5.178
3.434
3.410
3.386
3.364
1.192
1.106
1.087
1.059
tBu
HN
O
S
O
N
N
7a
2.20
3.11
0.95
3.99
15.07
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

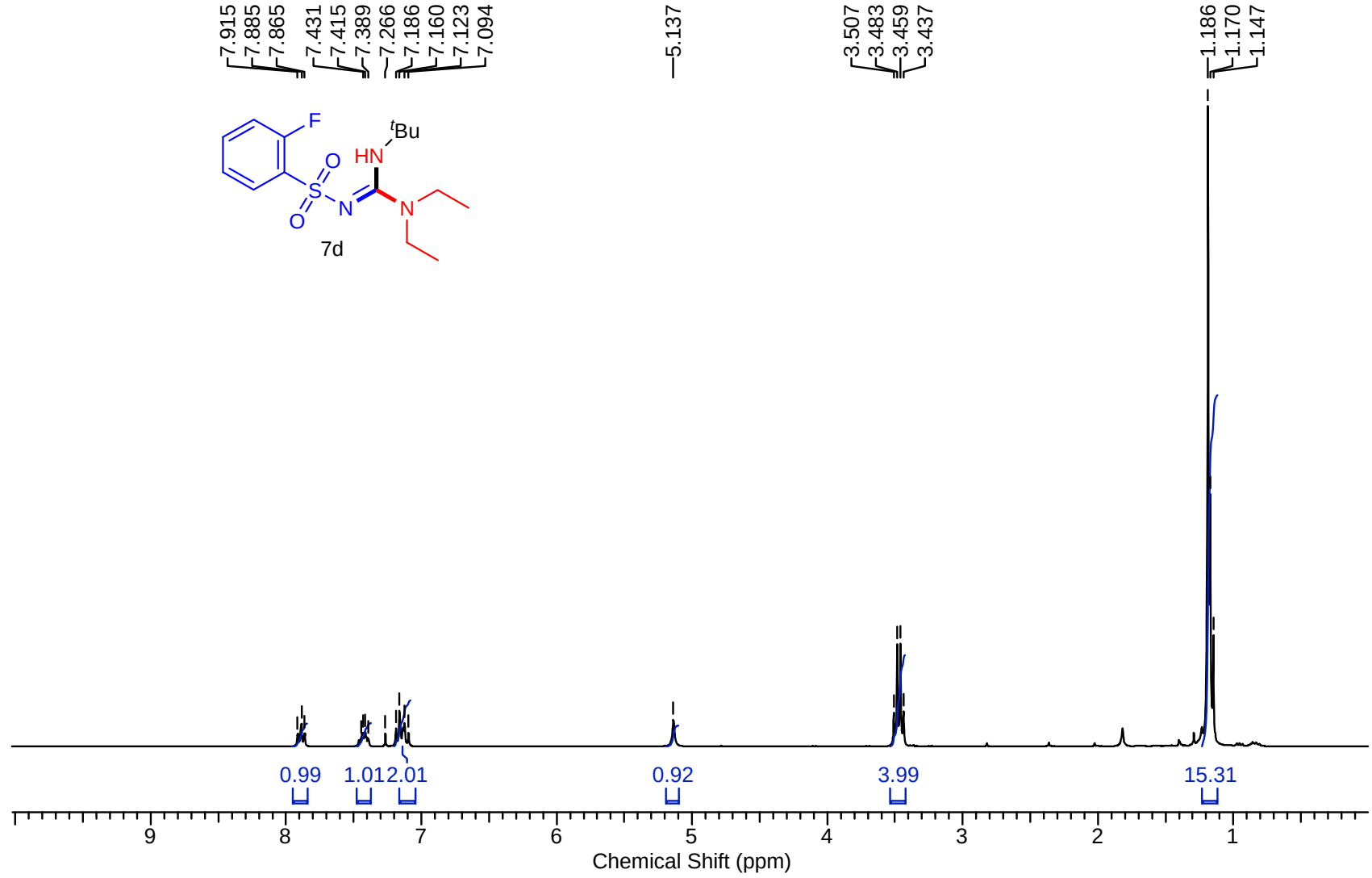

156.743
144.678
130.644
128.071
125.541
77.426
77.003
76.573
53.550
43.810
29.448
12.572
tBu
HN
O
S
O
N
N
7a
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

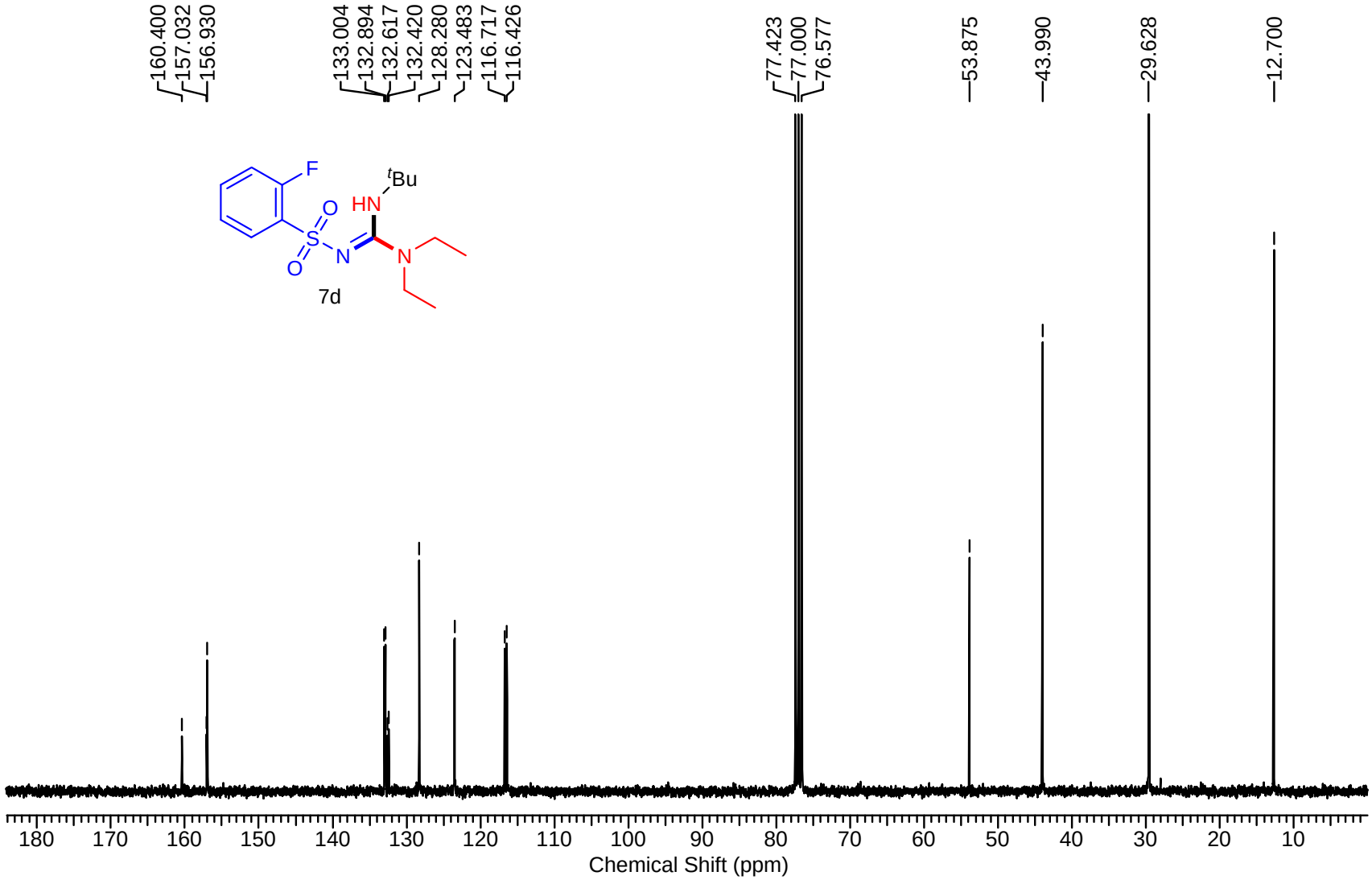

8.080
8.055
7.465
7.440
7.357
7.338
7.322
7.300
7.270
5.102
3.521
3.497
3.473
3.450
1.235
1.205
1.187
1.158
Cl
tBu
HN
O
S
O
N
N
7b
0.99
1.04
2.20
0.94
4.00
15.30
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

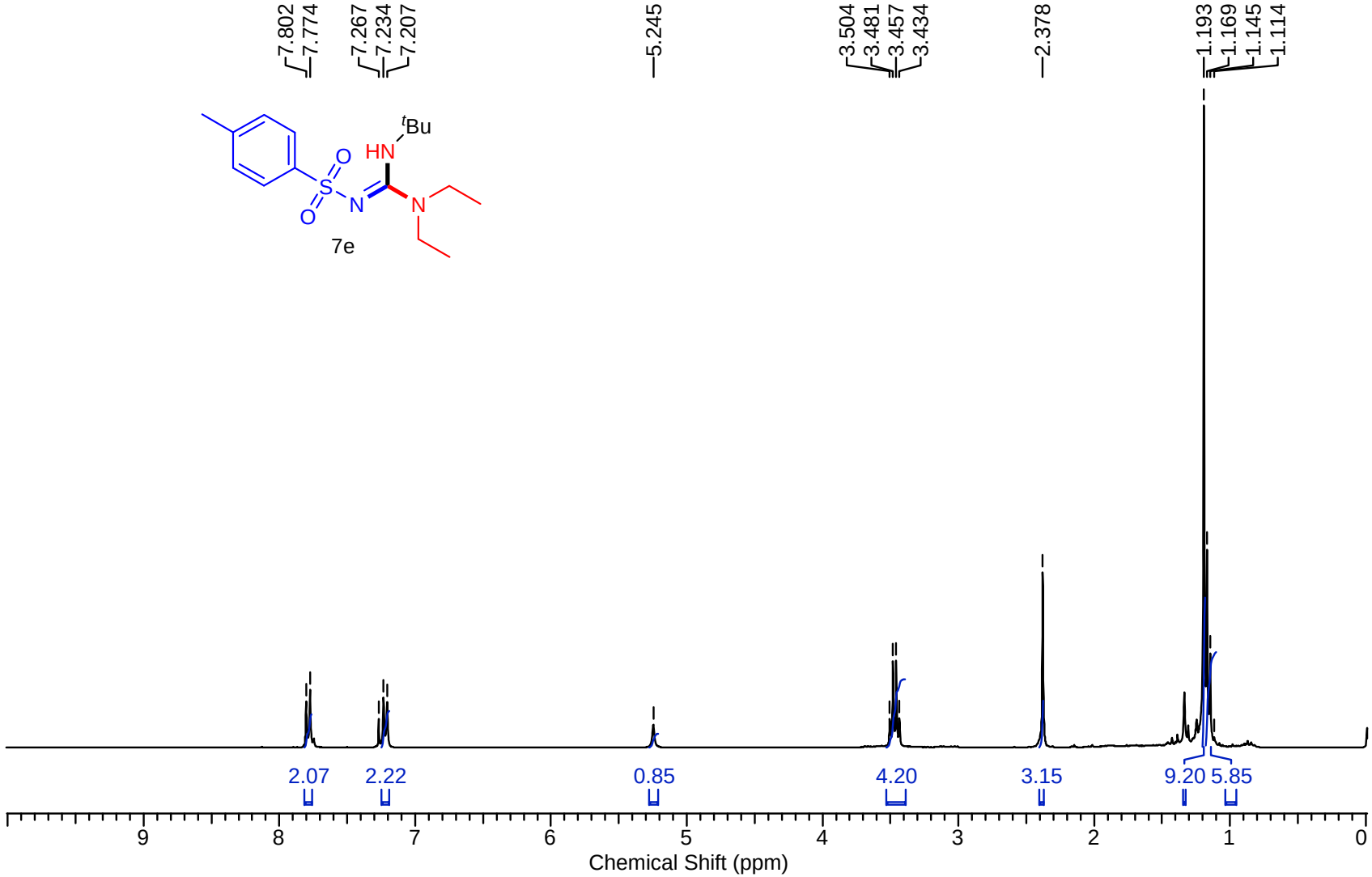

157.273
141.839
131.786
131.713
131.312
128.724
126.297
77.423
77.000
76.577
53.948
43.924
29.752
12.766
Cl
tBu
HN
O
S
O
N
N
7b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

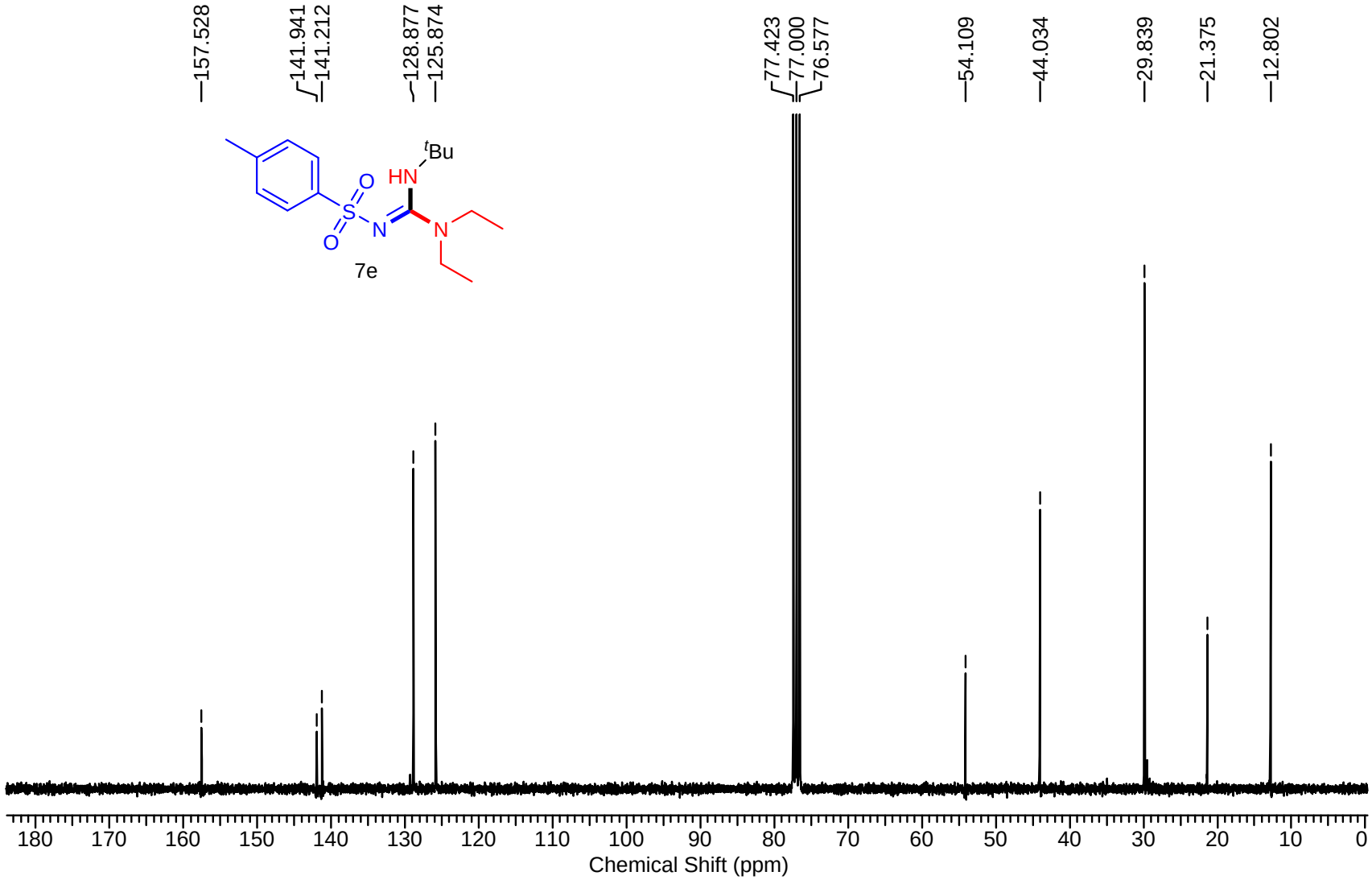

7.958
7.932
7.322
7.297
7.266
7.252
7.231
7.208
5.221
3.494
3.471
3.447
3.424
2.738
1.184
1.171
1.161
1.137
tBu
HN
O
S
O
N
N
7c
1.04
1.17
2.19
0.96
4.25
3.00
15.30
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

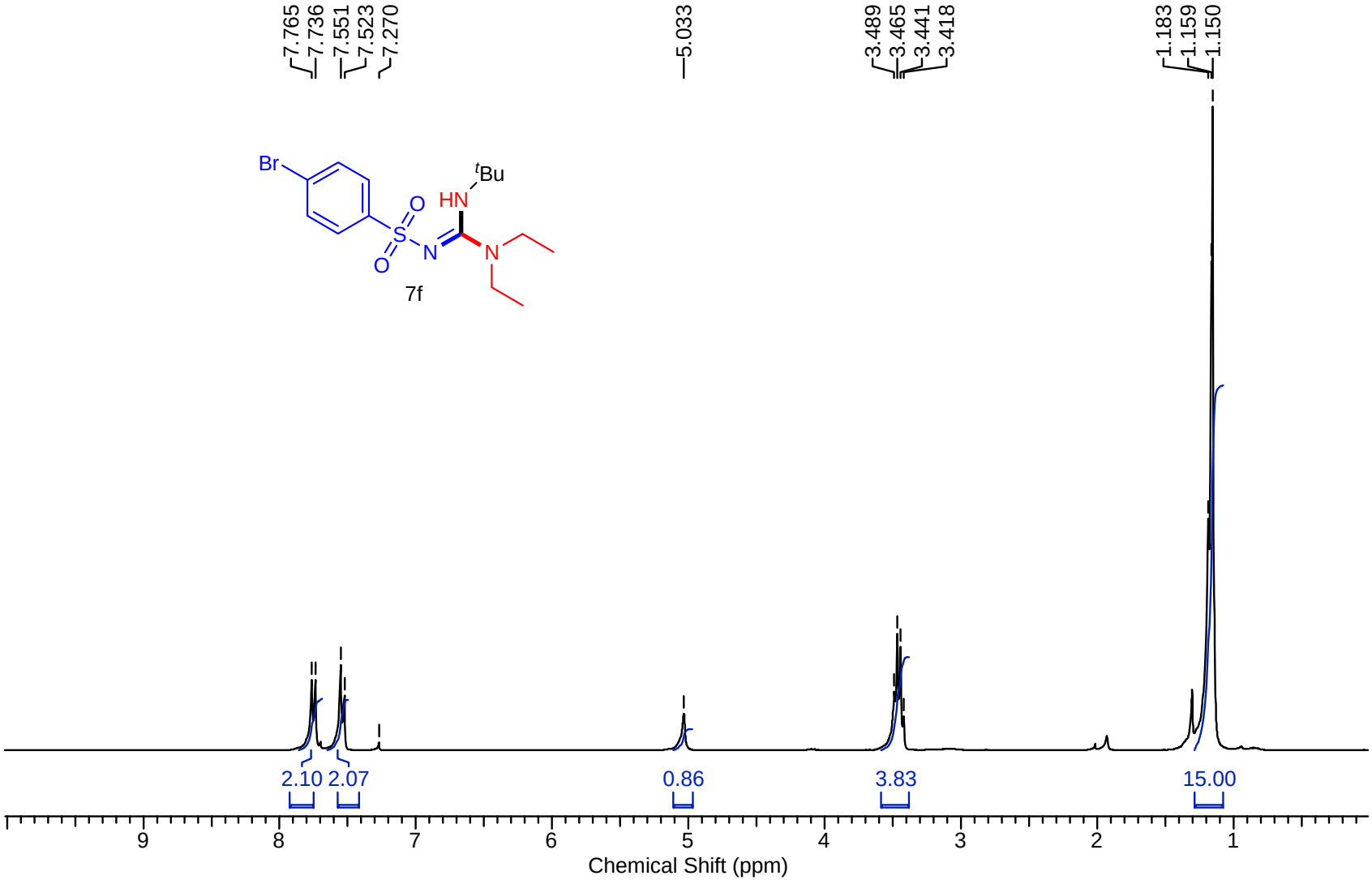

157.642
142.726
136.646
131.783
130.901
126.687
125.229
77.427
77.004
76.574
53.975
43.994
29.822
20.425
12.814
tBu
HN
O
S
O
N
N
7c
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

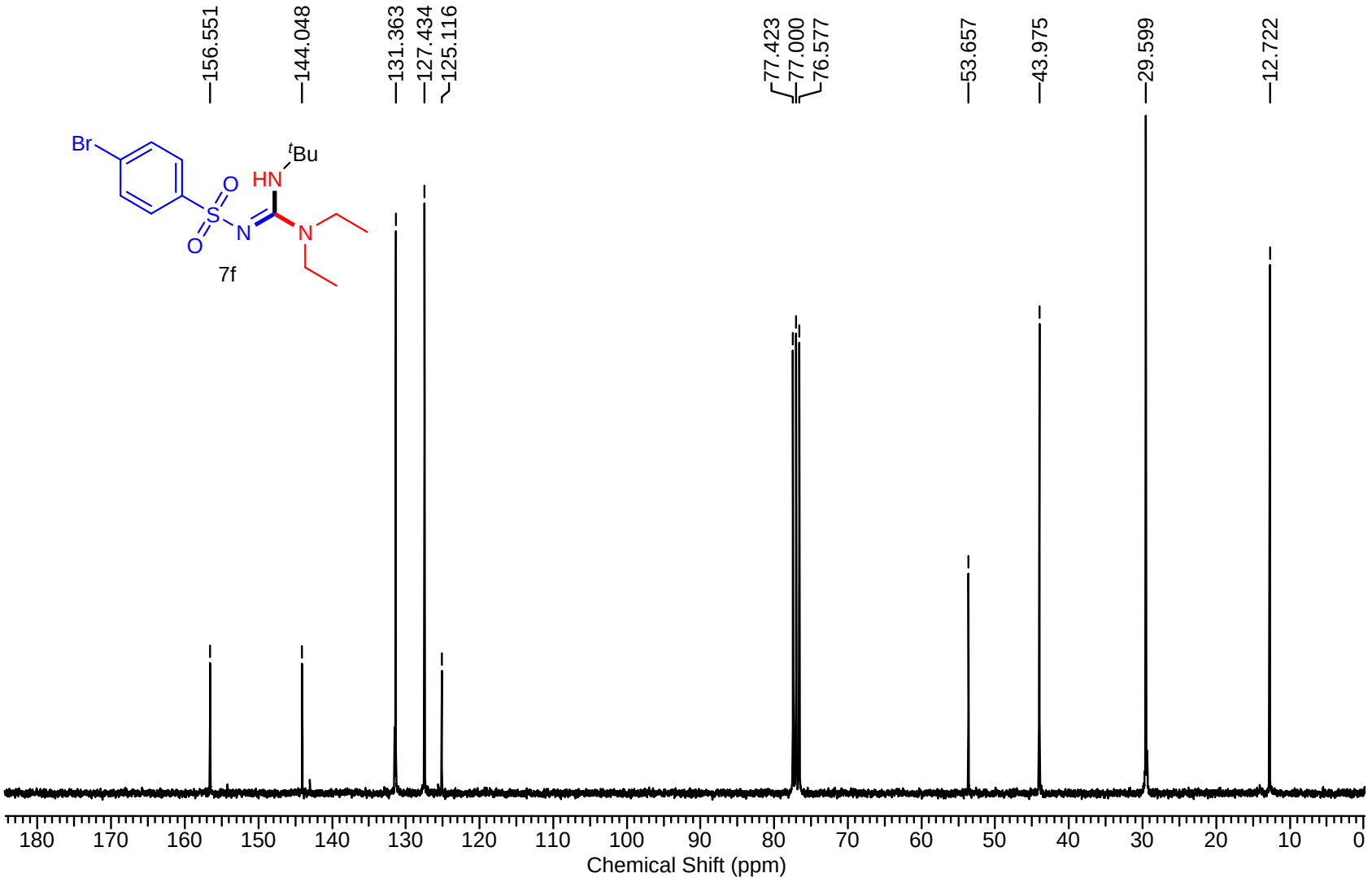

7.915
7.885
7.865
7.431
7.415
7.389
7.266
7.186
7.160
7.123
7.094
5.137
3.507
3.483
3.459
3.437
1.186
1.170
1.147
F
O
S
O
N
HN
tBu
N
7d
0.99
1.01
2.01
0.92
3.99
15.31
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


160.400
157.032
156.930
133.004
132.894
132.617
132.420
128.280
123.483
116.717
116.426
77.423
77.000
76.577
53.875
43.990
29.628
12.700
F
O
S
O
N
HN
tBu
N
7d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


7.802
7.774
7.267
7.234
7.207
5.245
3.504
3.481
3.457
3.434
2.378
1.193
1.169
1.145
1.114
tBu
HN
O
S
O
N
N
7e
2.07
2.22
0.85
4.20
3.15
9.20
5.85
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


157.528
141.941
141.212
128.877
125.874
77.423
77.000
76.577
54.109
44.034
29.839
21.375
12.802
tBu
HN
O
S
O
N
N
7e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.765
7.736
7.551
7.523
7.270
5.033
3.489
3.465
3.441
3.418
1.183
1.159
1.150
Br
HN
tBu
O
S
O
N
N
7f
2.10
2.07
0.86
3.83
15.00
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)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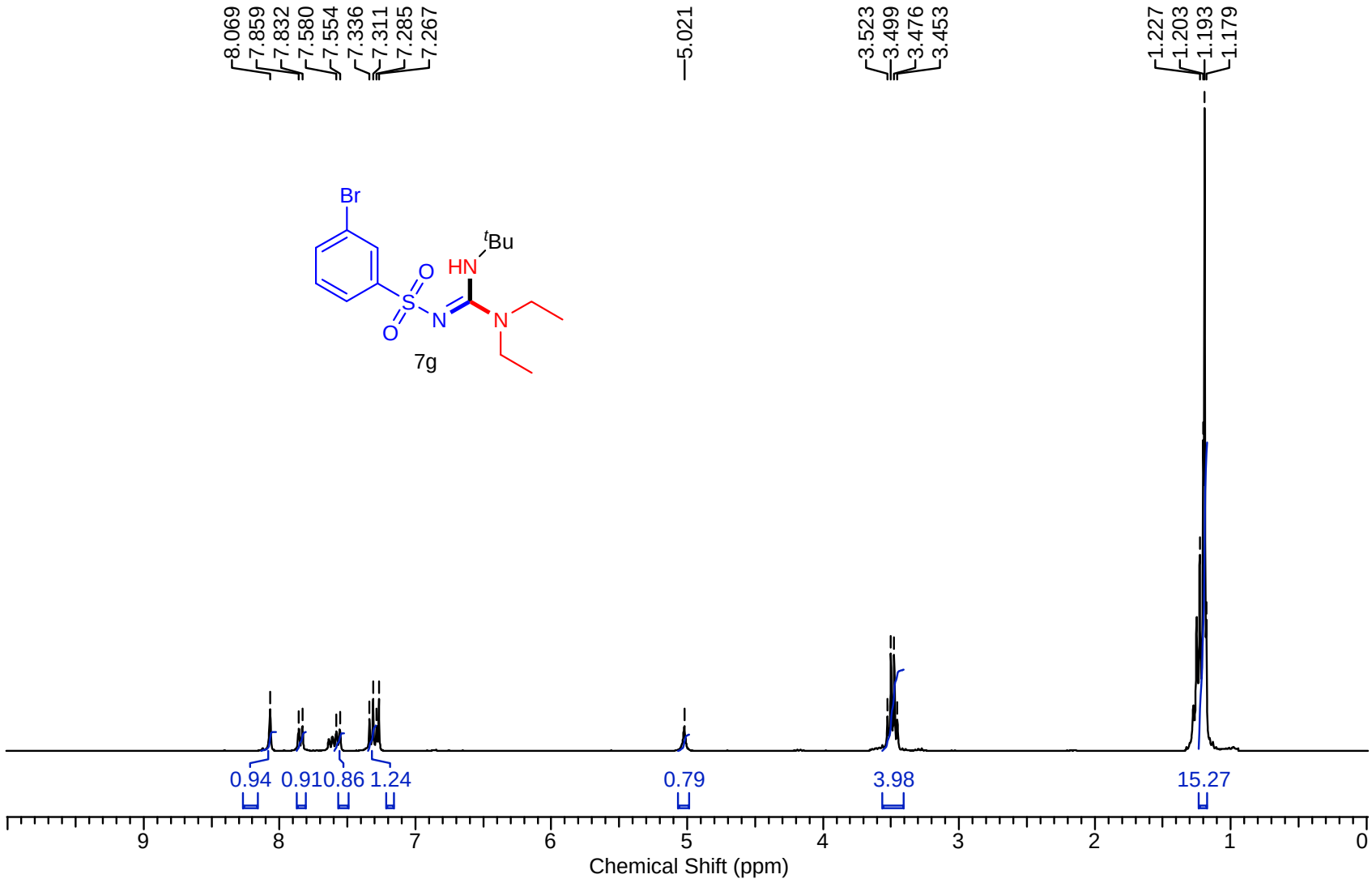
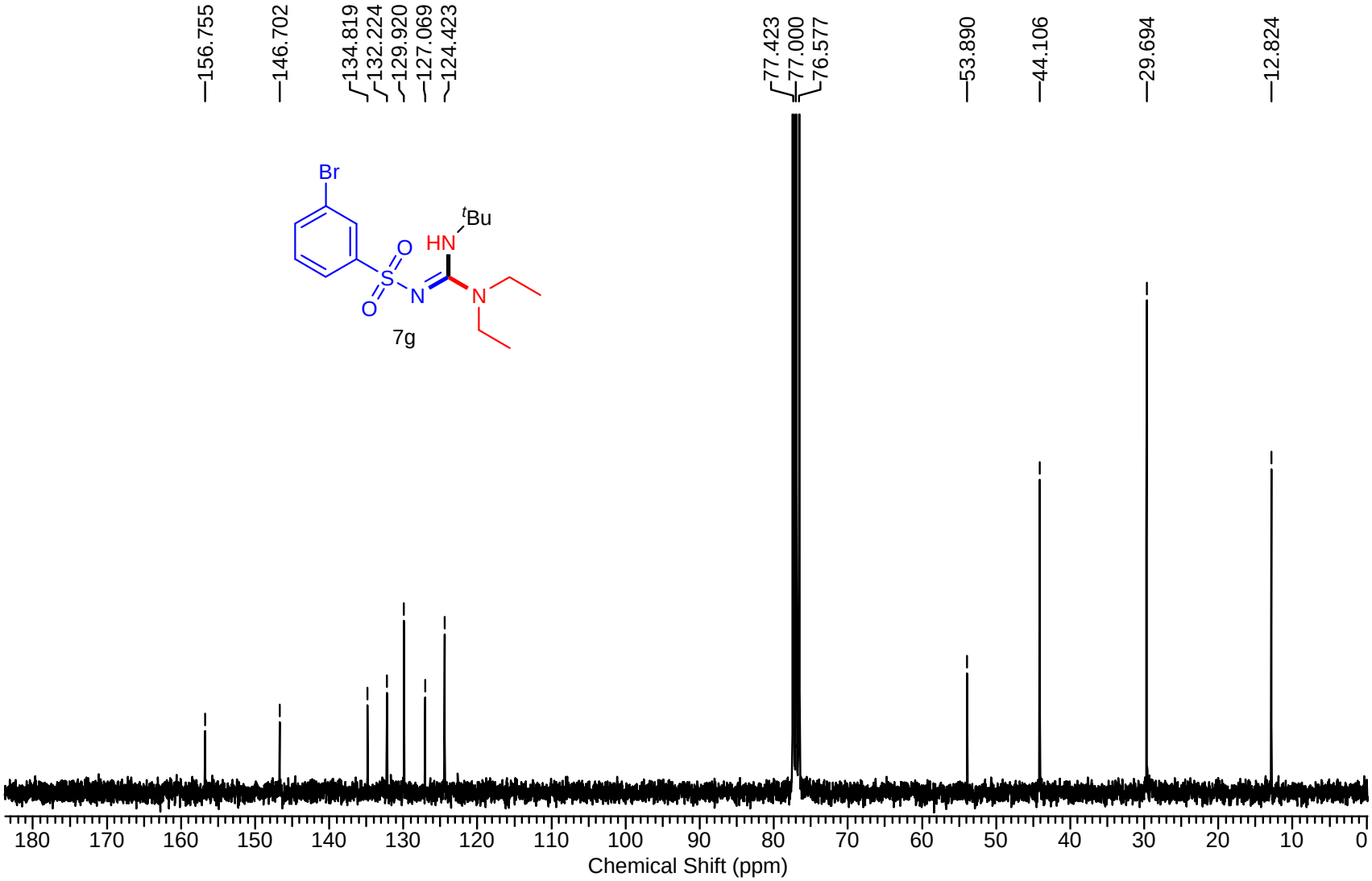
144.048
131.363
127.434
125.116
77.423
77.000
76.577
53.657
43.975
29.599
12.722
Br
tBu
HN
O
S
O
N
N
7f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


8.069
7.859
7.832
7.580
7.554
7.336
7.311
7.285
7.267
5.021
3.523
3.499
3.476
3.453
1.227
1.203
1.193
1.179
Br
tBu
HN
O
S
O
N
N
7g
0.94
0.91
0.86
1.24
0.79
3.98
15.27
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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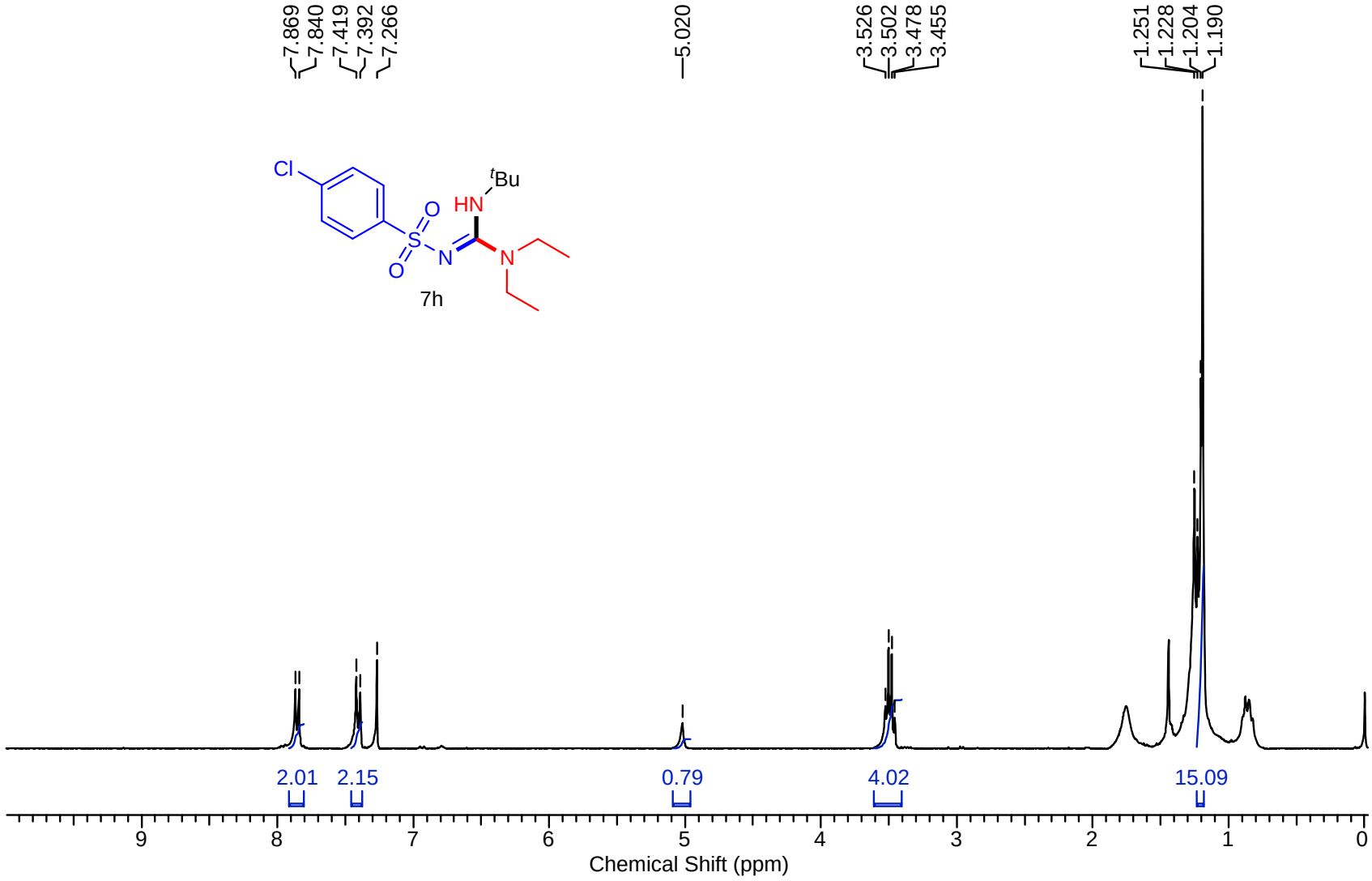
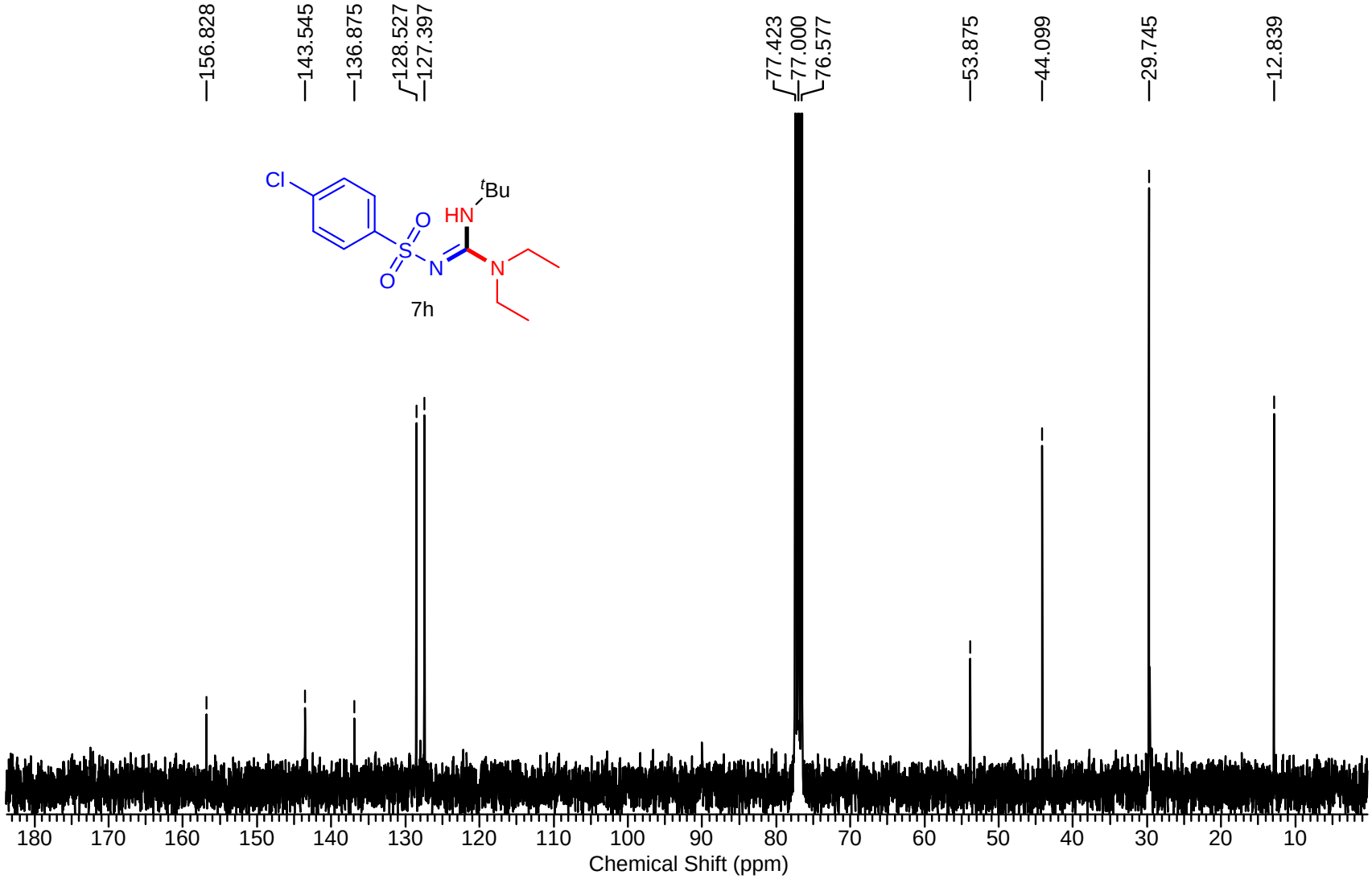
132.224
129.920
127.069
124.423
77.423
77.000
76.577
53.890
44.106
29.694
12.824
Br
tBu
HN
O
S
O
N
N
7g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


7.869
7.840
7.419
7.392
7.266
5.020
3.526
3.502
3.478
3.455
1.251
1.228
1.204
1.190
Cl
tBu
HN
O
S
N
O
N
7h
2.01
2.15
0.79
4.02
15.09
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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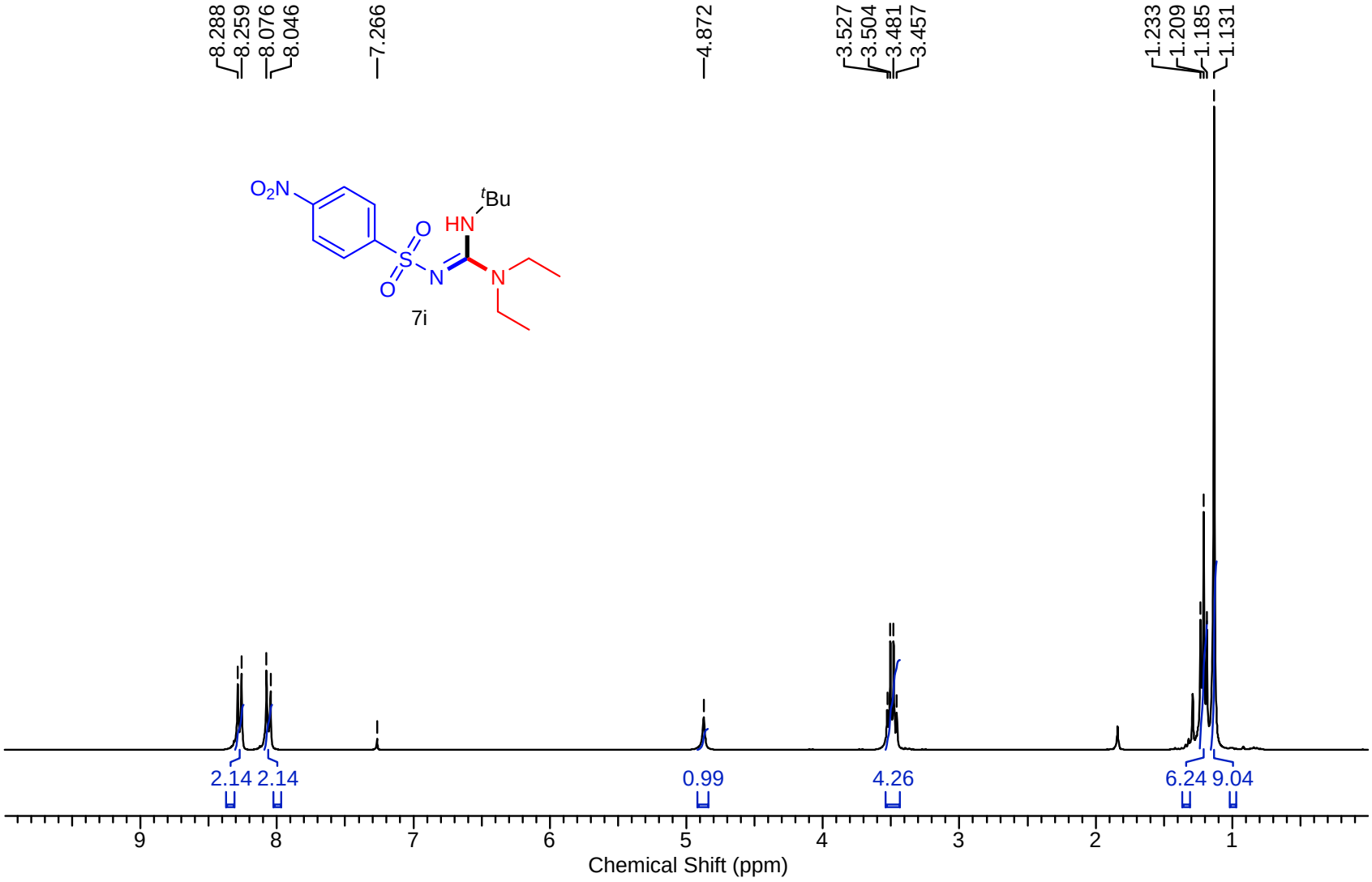
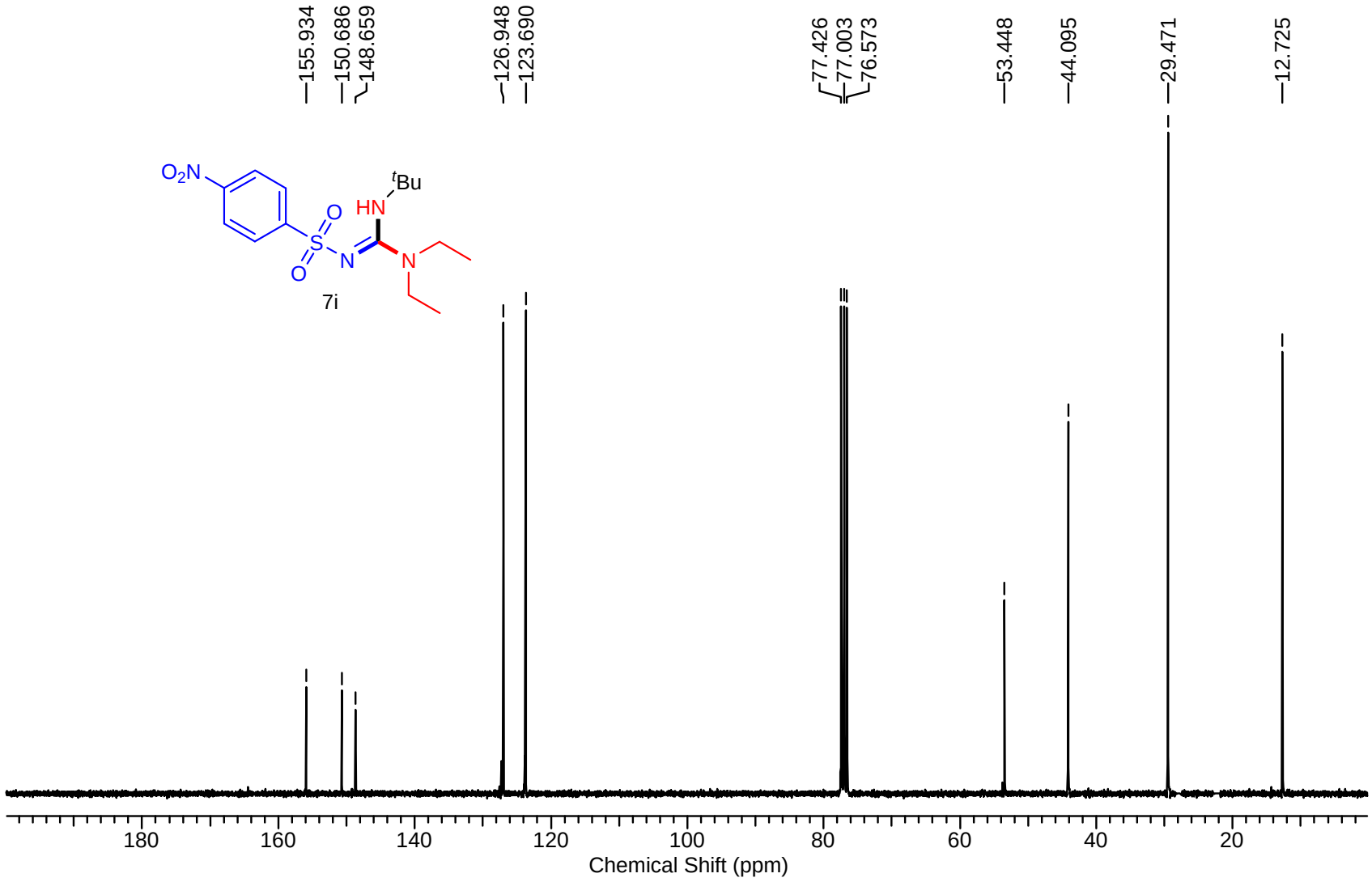
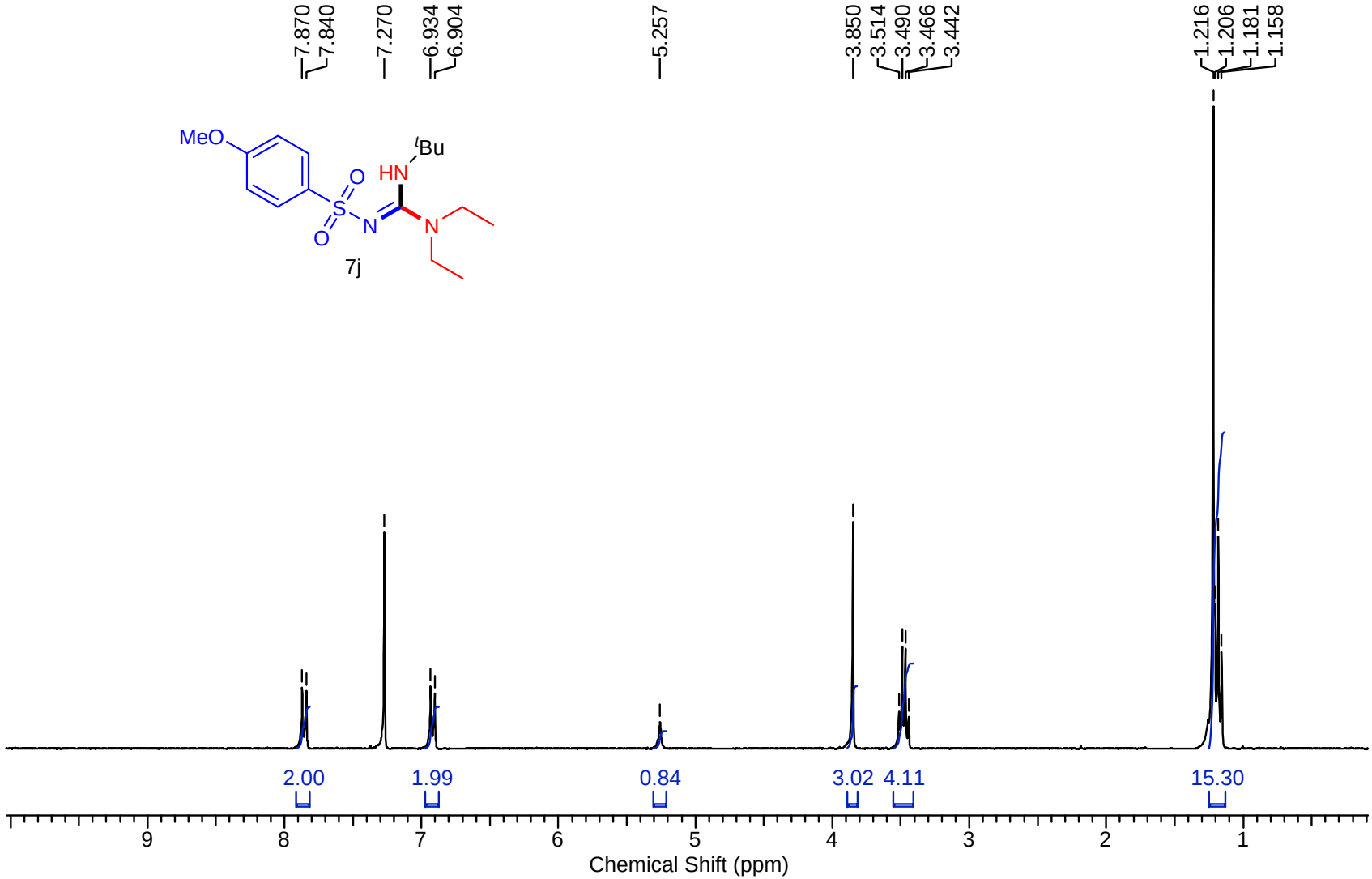
136.875
128.527
127.397
77.423
77.000
76.577
53.875
44.099
29.745
12.839
Cl
HN
tBu
O
S
O
N
N
7h
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


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
tBu
HN
O
S
O
N
N
7i
2.14
2.14
0.99
4.26
6.24
9.04
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


155.934
150.686
148.659
126.948
123.690
77.426
77.003
76.573
53.448
44.095
29.471
12.725
O2N
tBu
HN
O
S
O
N
N
7i
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)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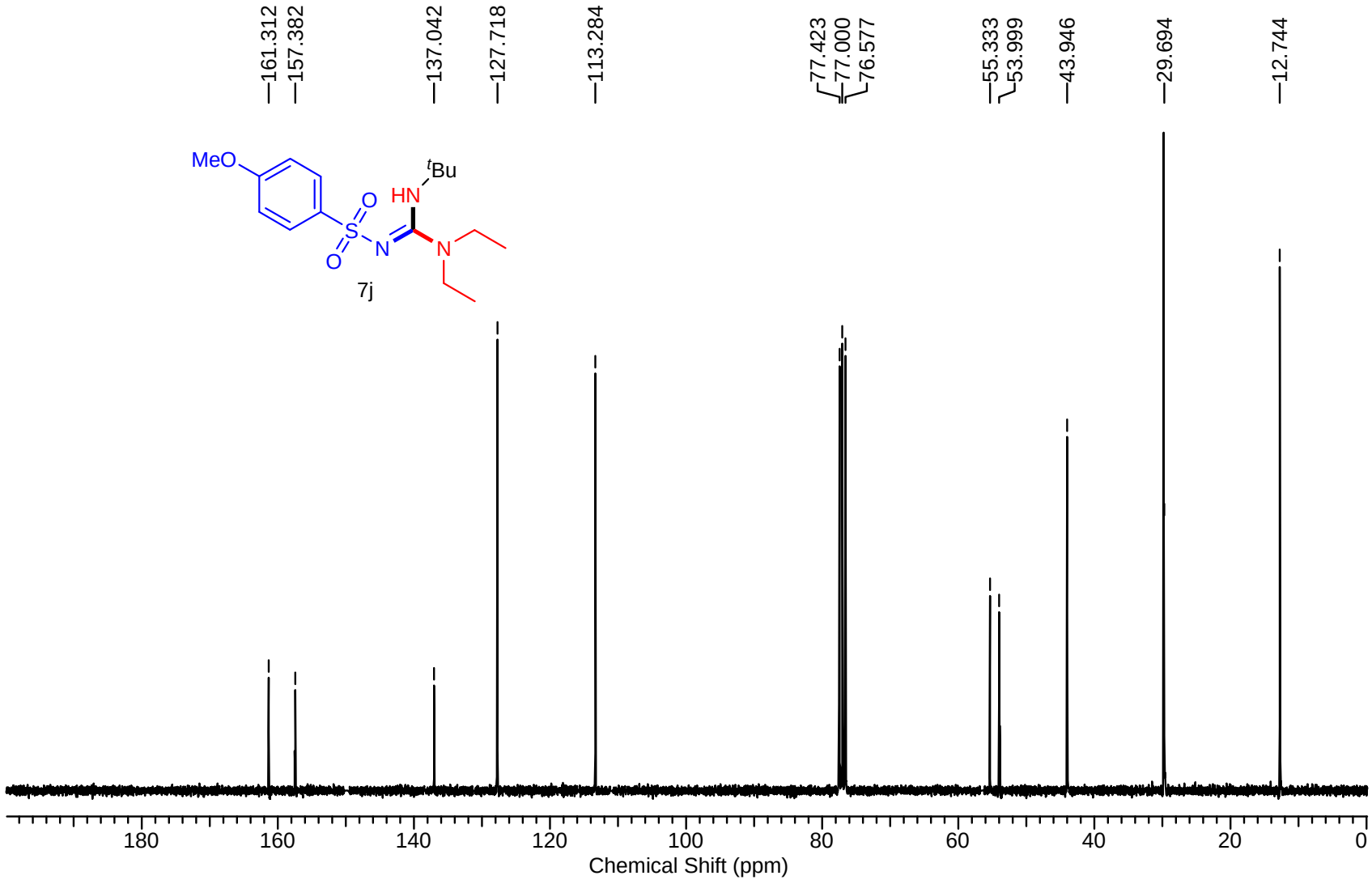
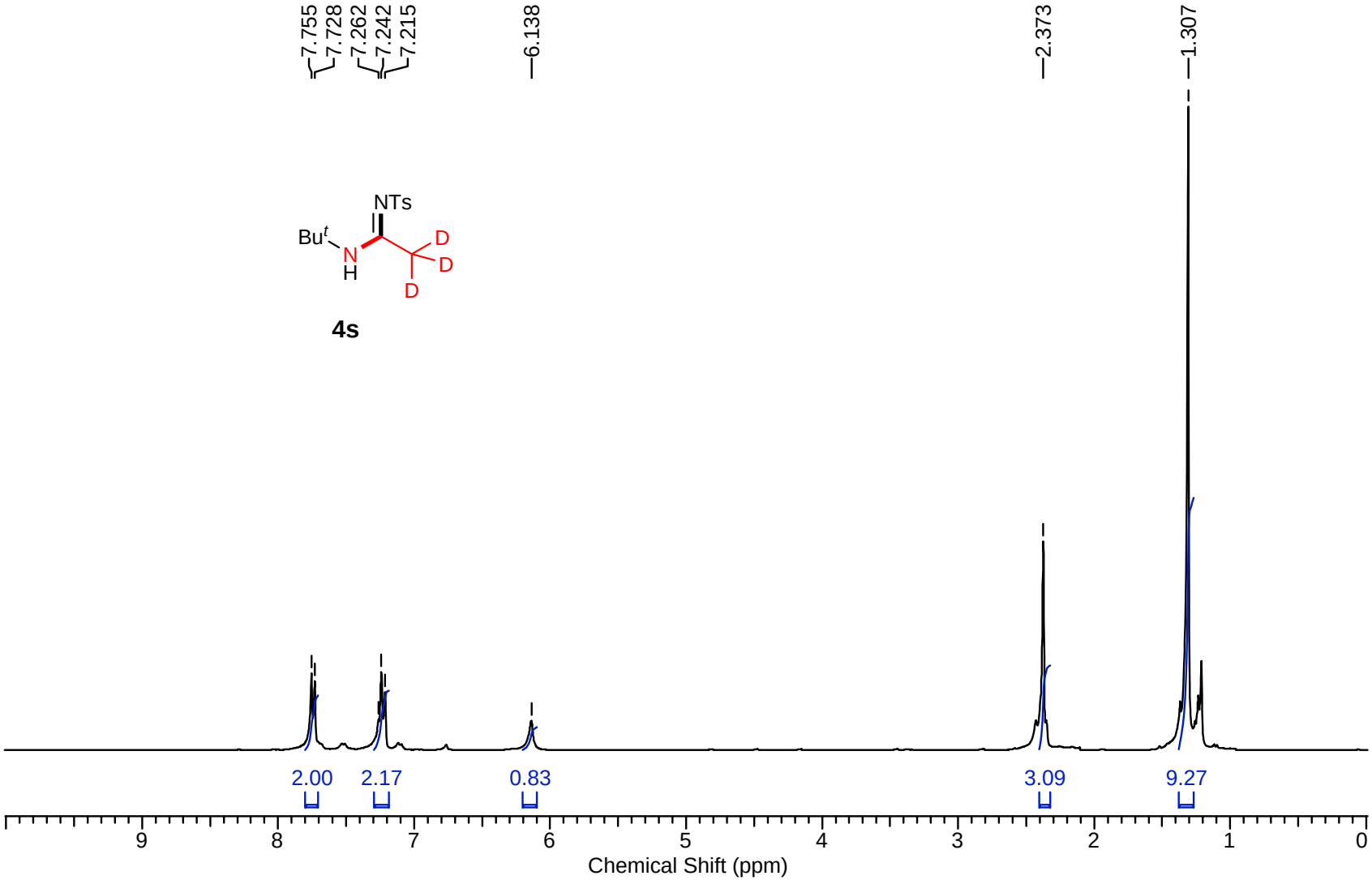
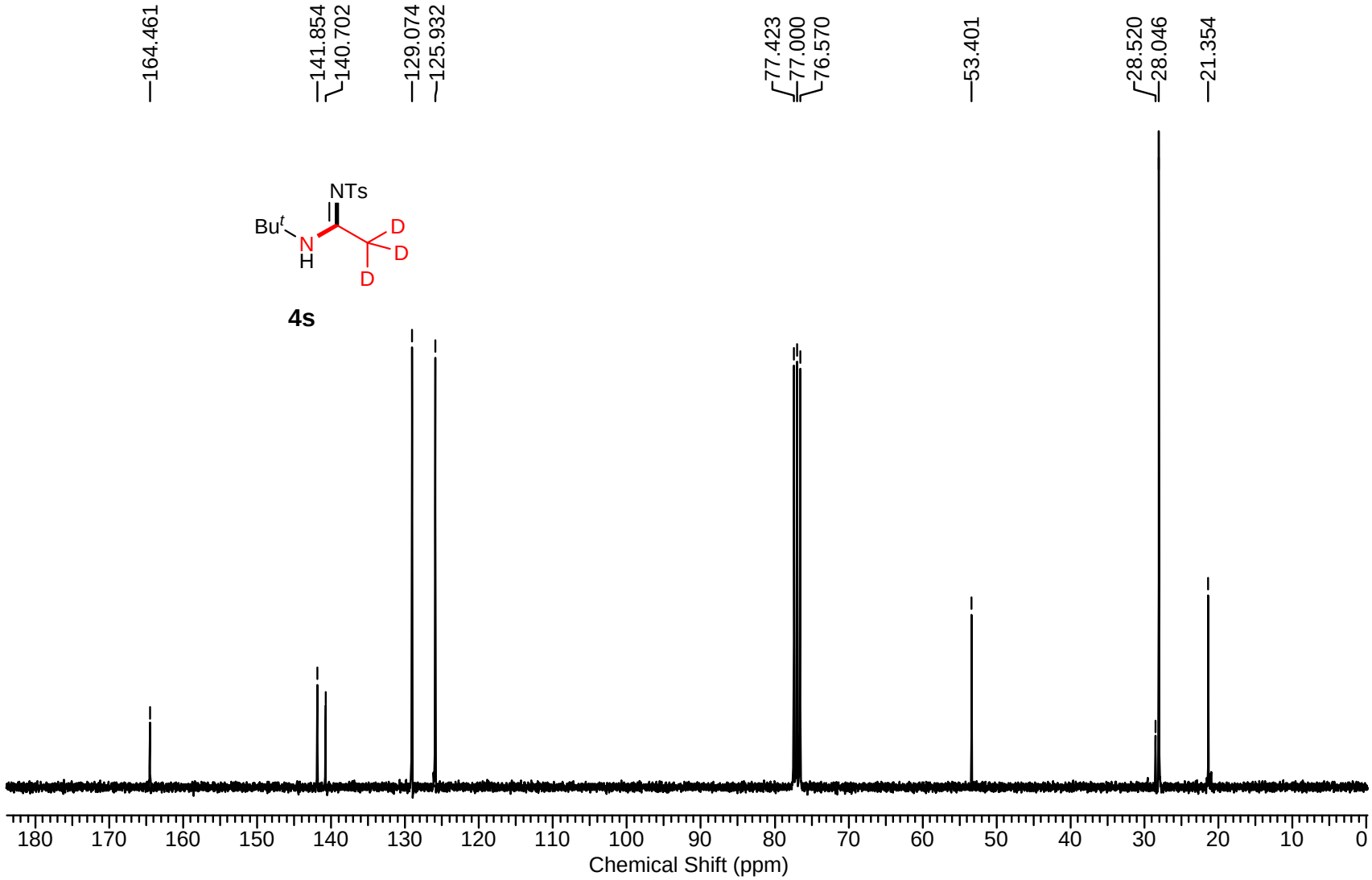
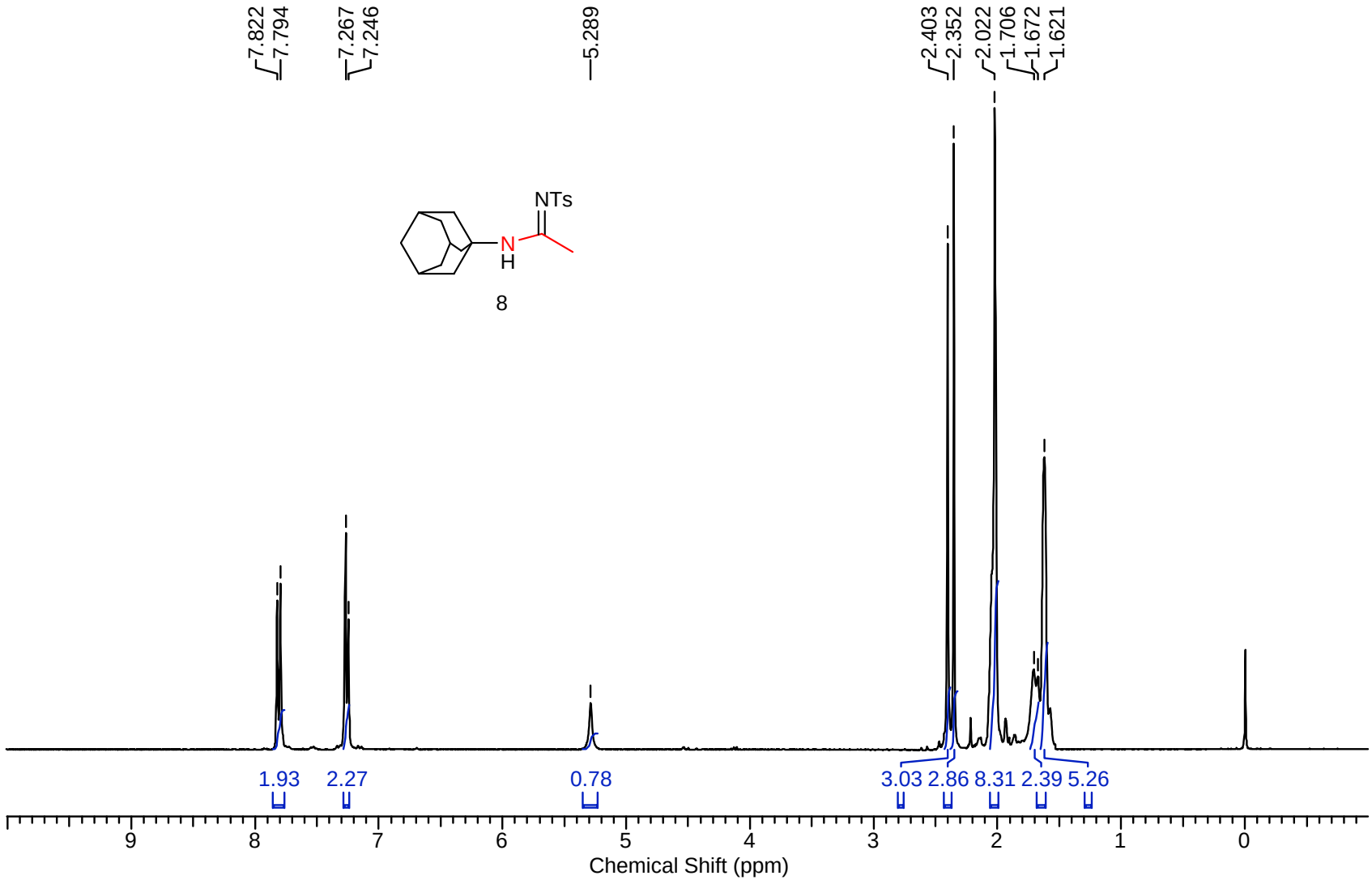
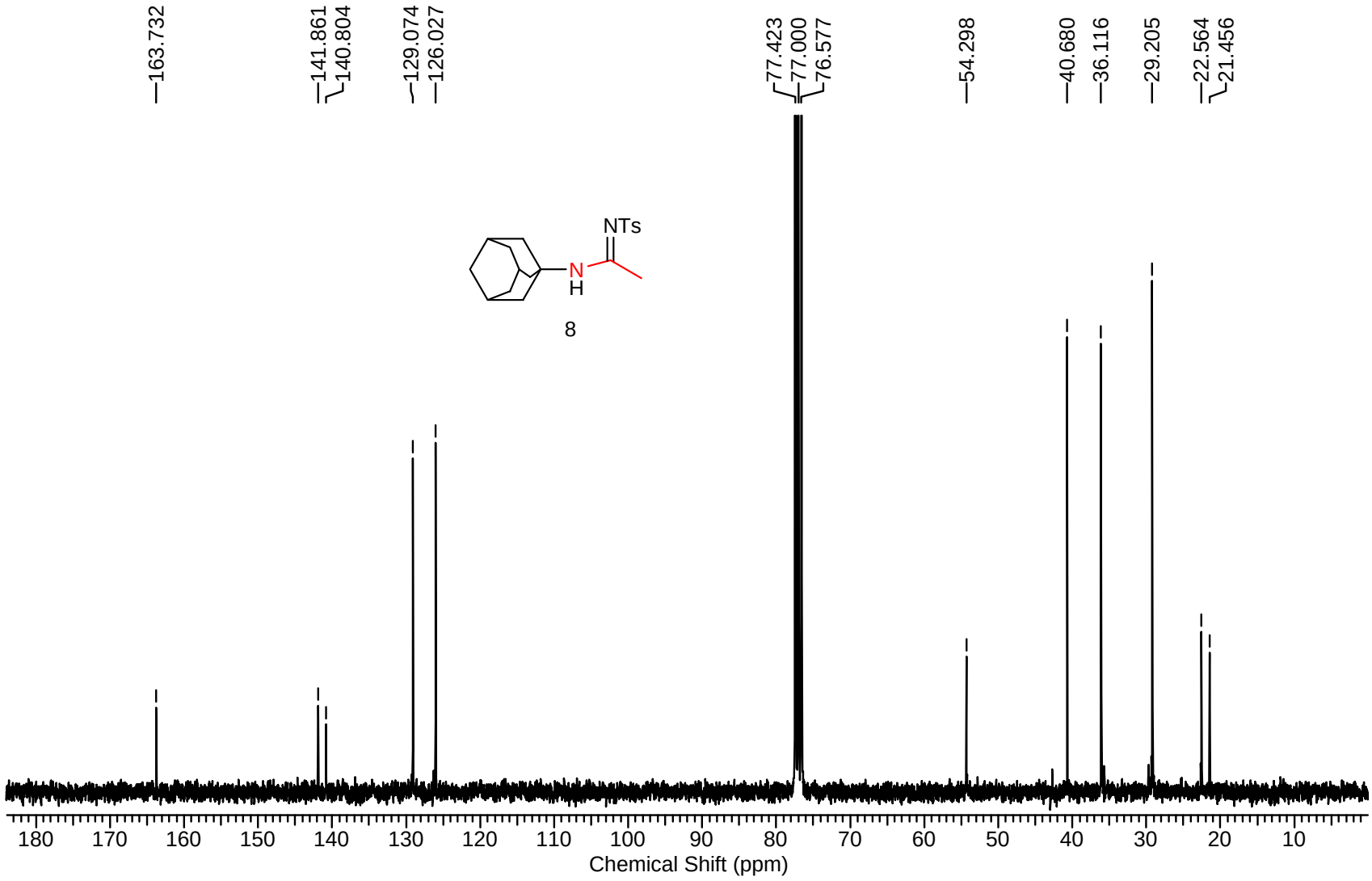
7.840
7.270
6.934
6.904
5.257
3.850
3.514
3.490
3.466
3.442
1.216
1.206
1.181
1.158
MeO
tBu
HN
O
S
O
N
N
7j
2.00
1.99
0.84
3.02
4.11
15.30
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

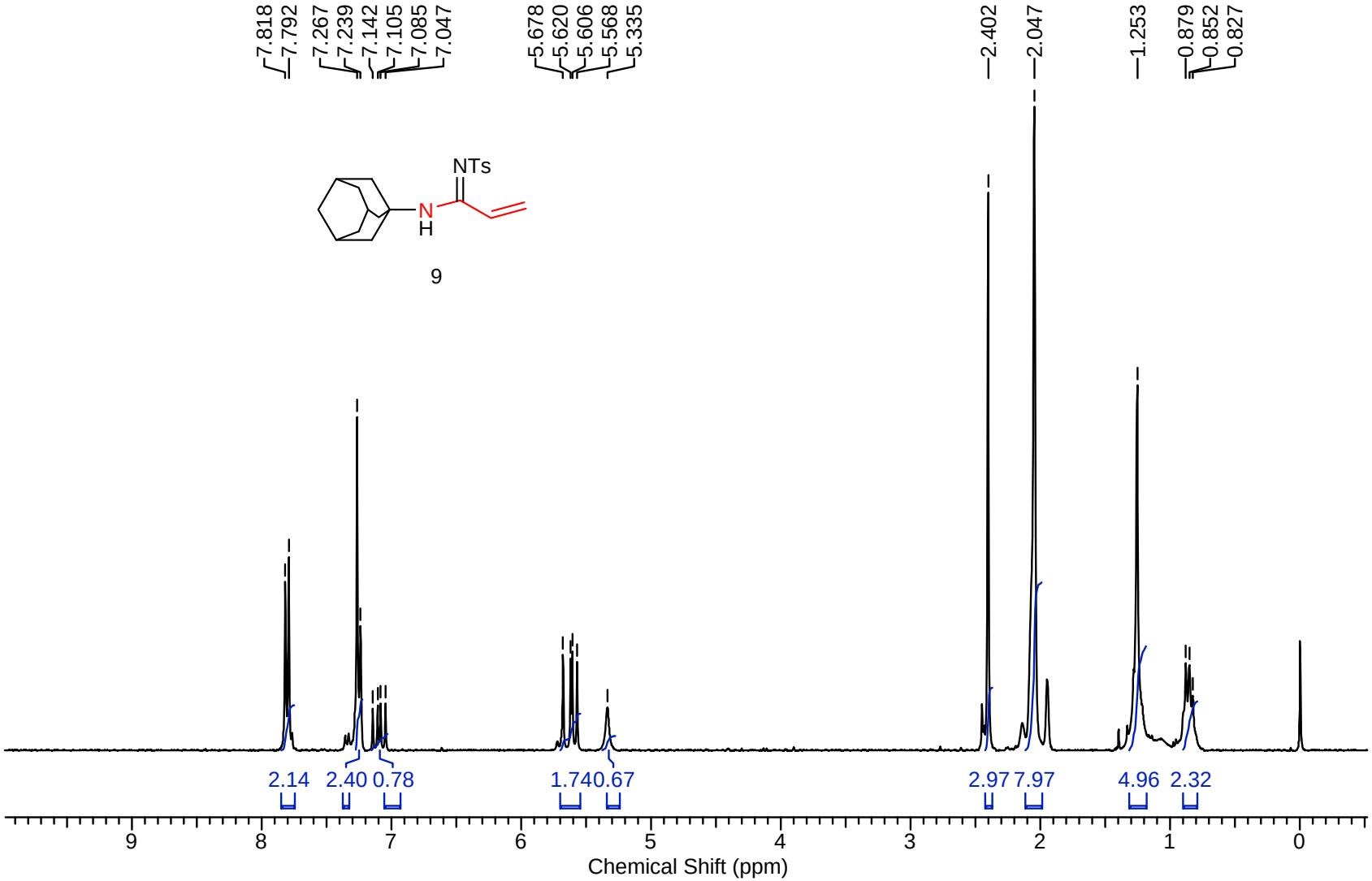

161.312
157.382
137.042
127.718
113.284
77.423
77.000
76.577
55.333
53.999
43.946
29.694
12.744
MeO
tBu
HN
O
S
O
N
N
7j
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

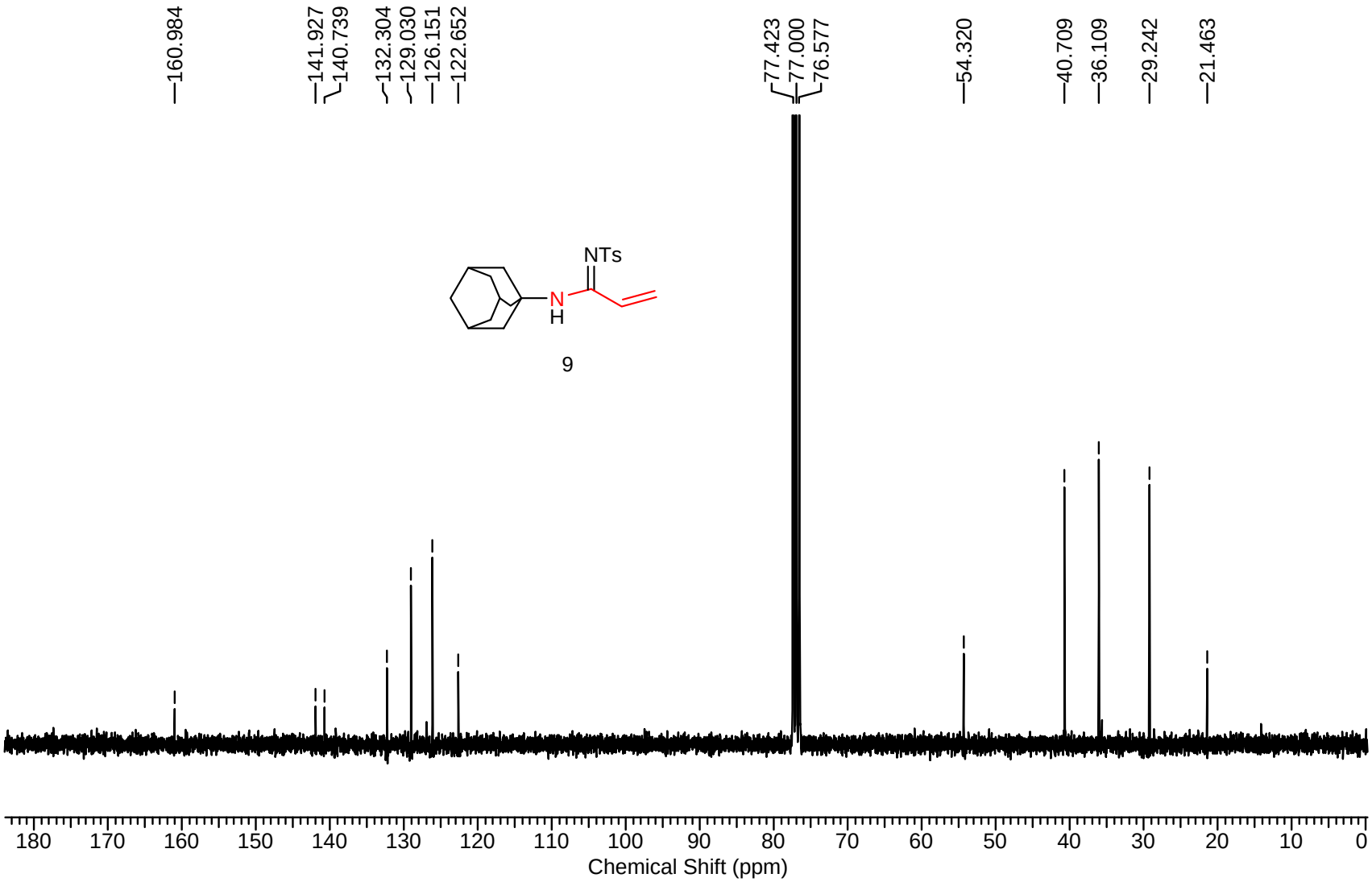

7.755
7.728
7.262
7.242
7.215
6.138
2.373
1.307
NTs
Bu^t
N
H
D
D
D
4s
2.00
2.17
0.83
3.09
9.27
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

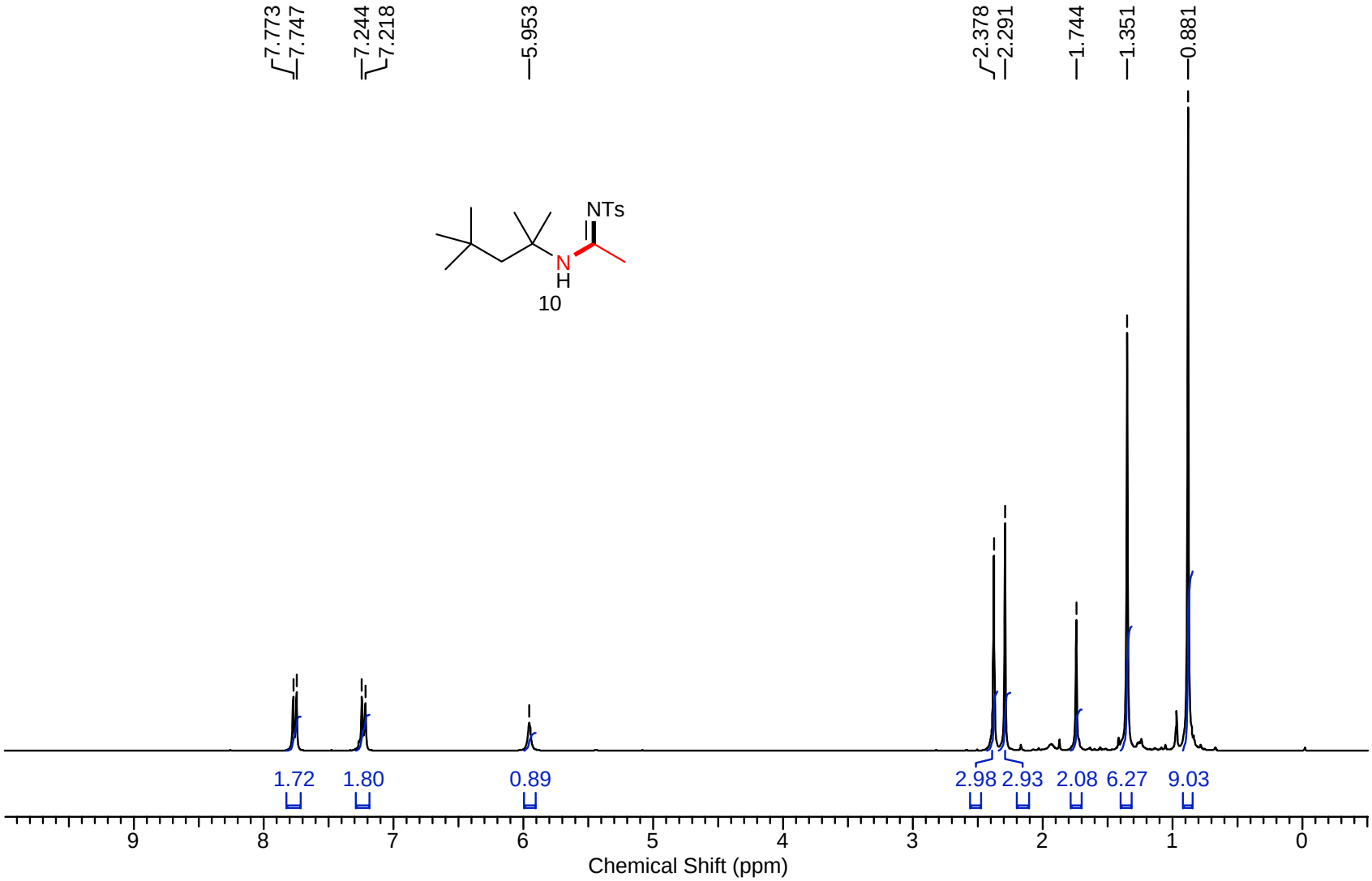

164.461
141.854
140.702
129.074
125.932
77.423
77.000
76.570
53.401
28.520
28.046
21.354
NTs
Bu^t
N
H
D
D
D
4s
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

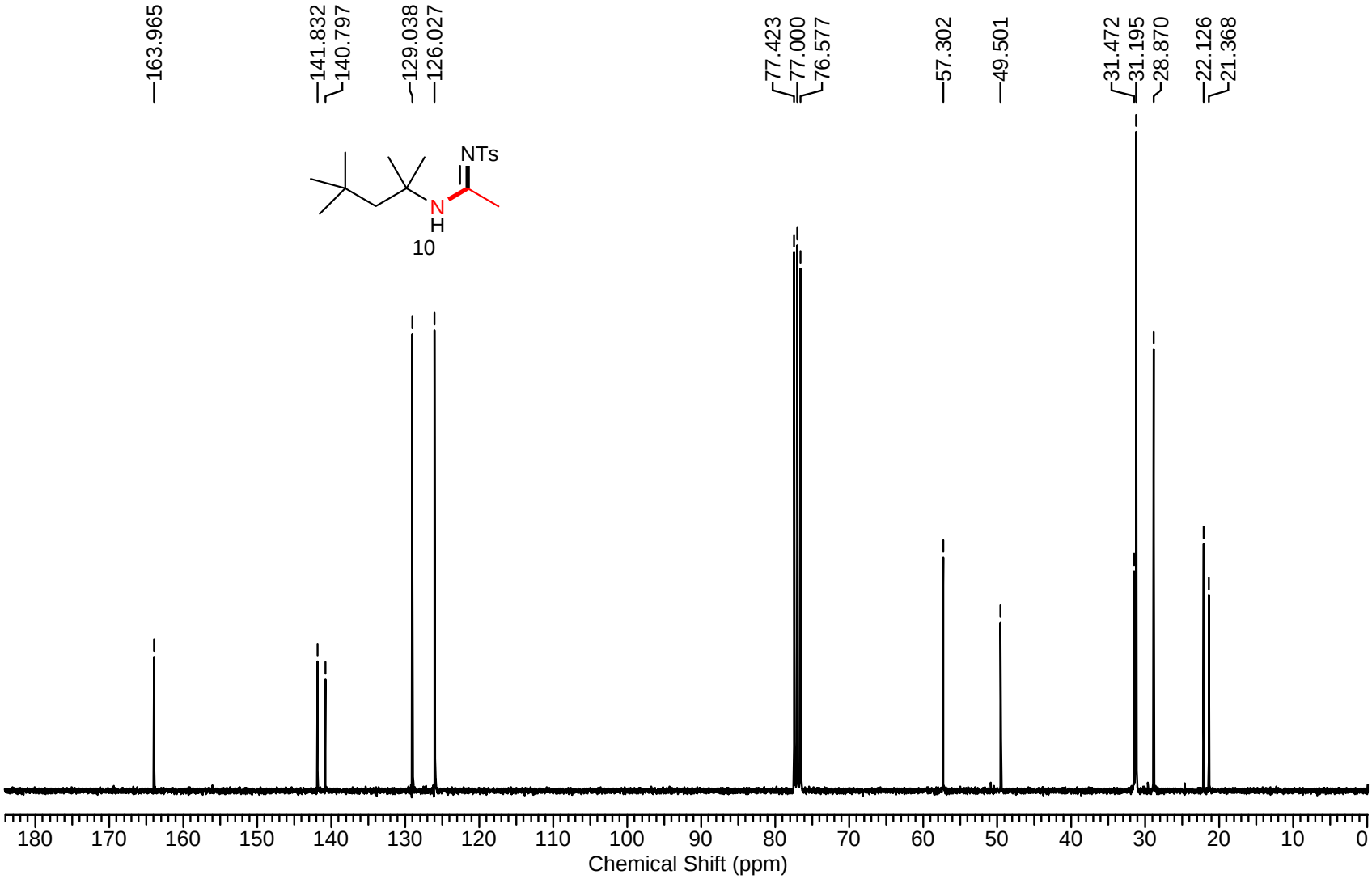

7.822
7.794
7.267
7.246
5.289
2.403
2.352
2.022
1.706
1.672
1.621
NTs
N
H
8
1.93
2.27
0.78
3.03
2.86
8.31
2.39
5.26
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

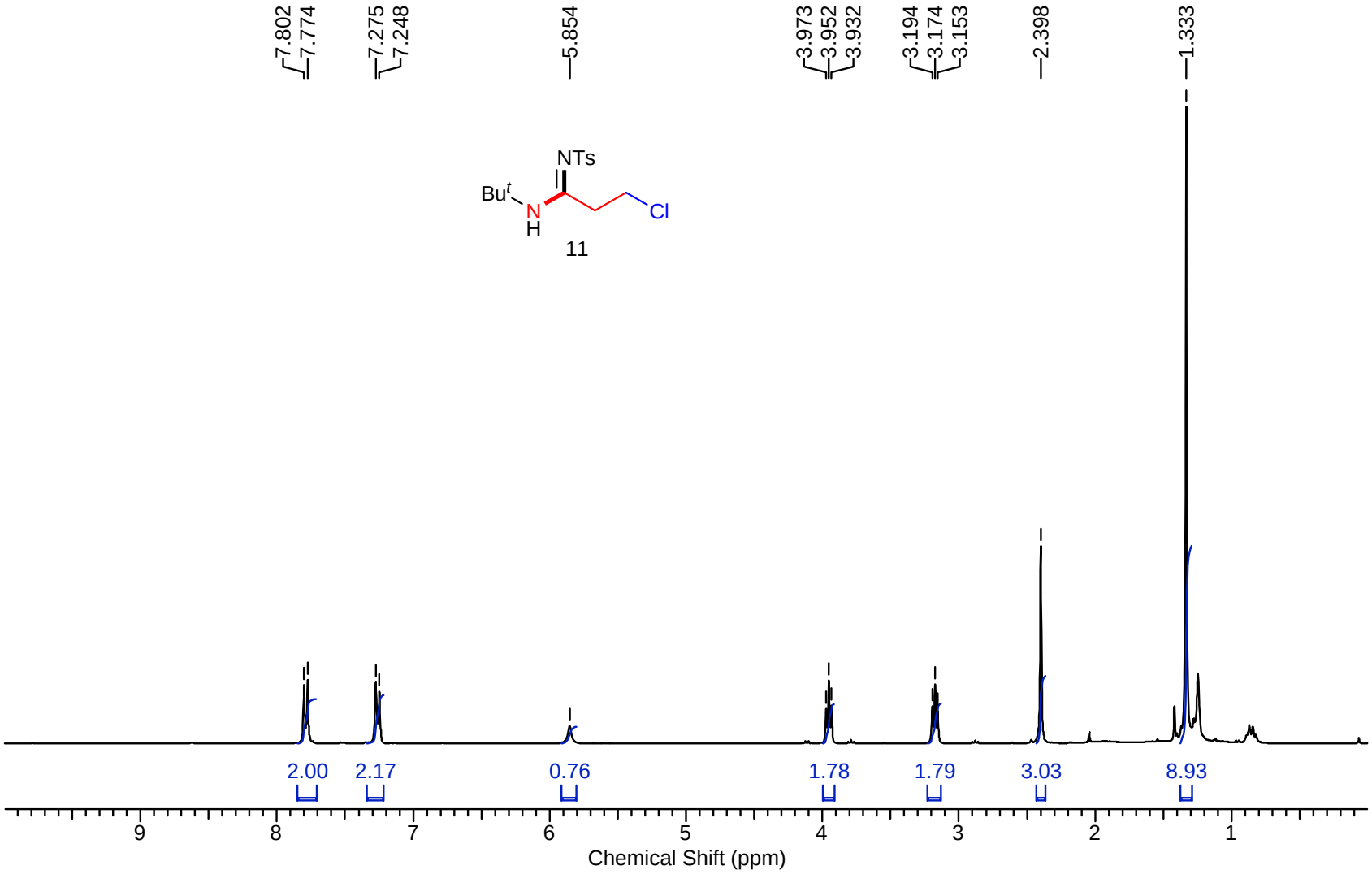

163.732
141.861
140.804
129.074
126.027
77.423
77.000
76.577
54.298
40.680
36.116
29.205
22.564
21.456
NTs
N
H
8
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

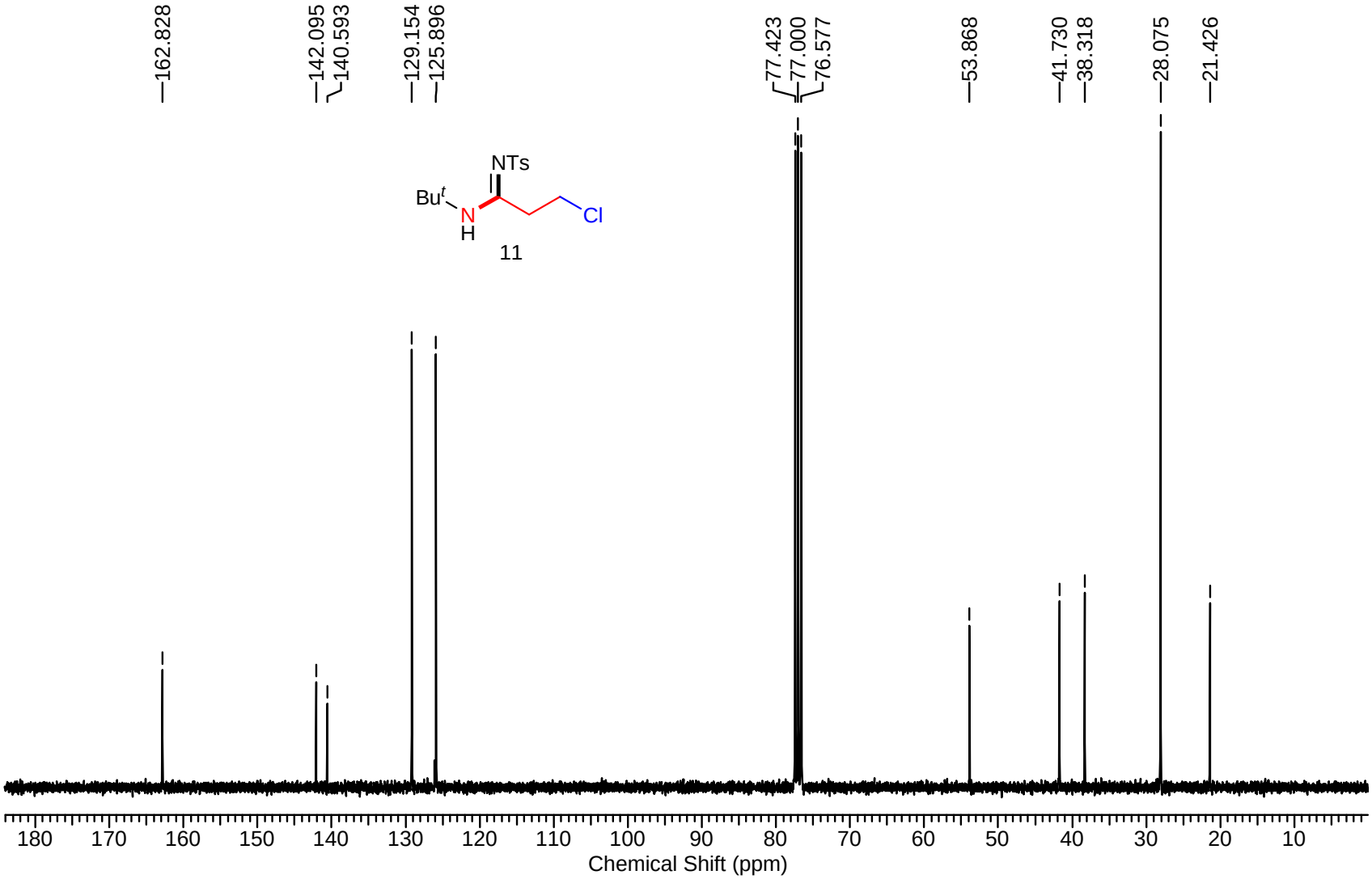

7.818
7.792
7.267
7.239
7.142
7.105
7.085
7.047
5.678
5.620
5.606
5.568
5.335
2.402
2.047
1.253
0.879
0.852
0.827
NTs
N
H
9
2.14
2.40
0.78
1.74
0.67
2.97
7.97
4.96
2.32
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

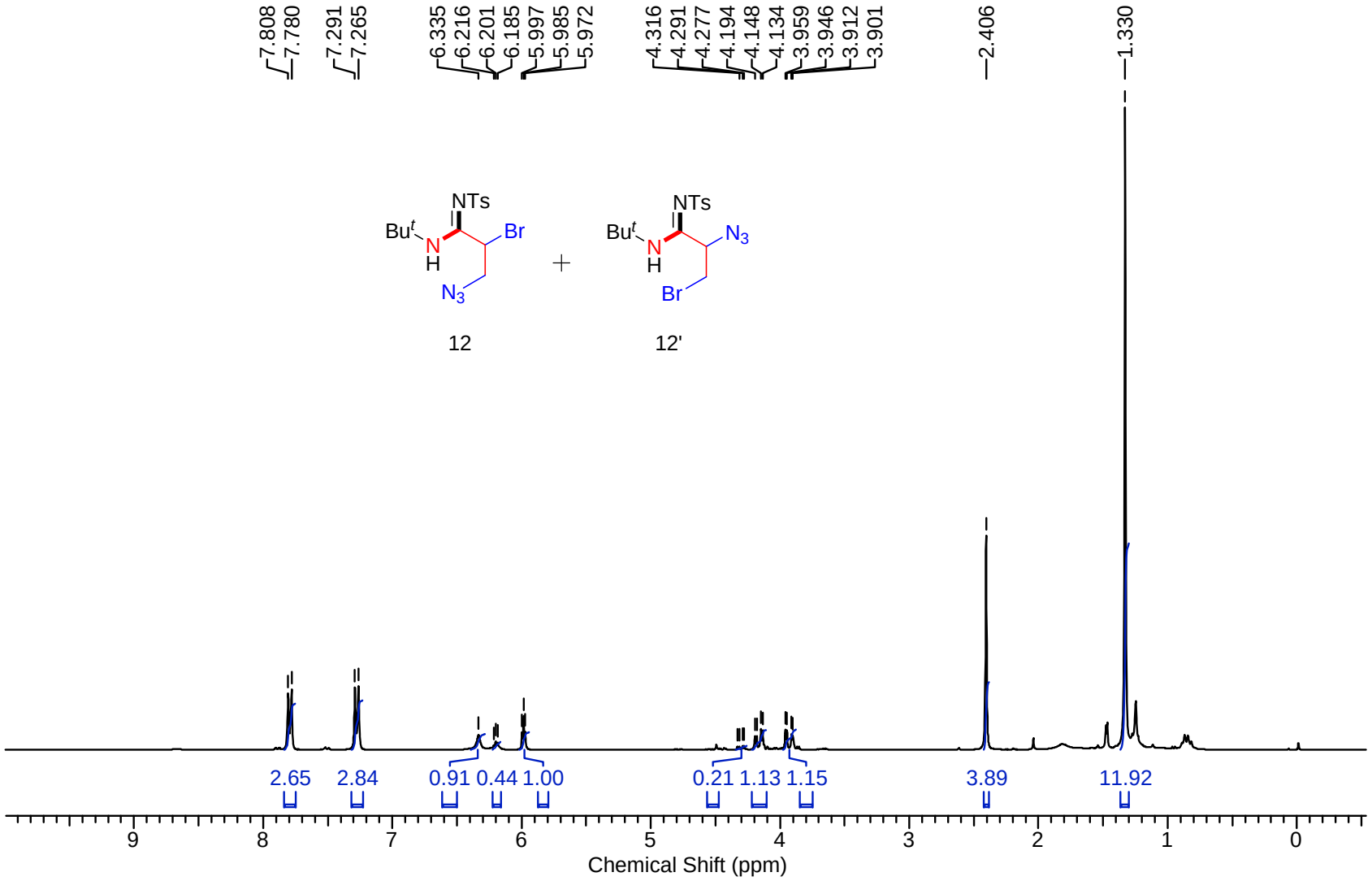

160.984
141.927
140.739
132.304
129.030
126.151
122.652
77.423
77.000
76.577
54.320
40.709
36.109
29.242
21.463
NTs
N
H
9
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

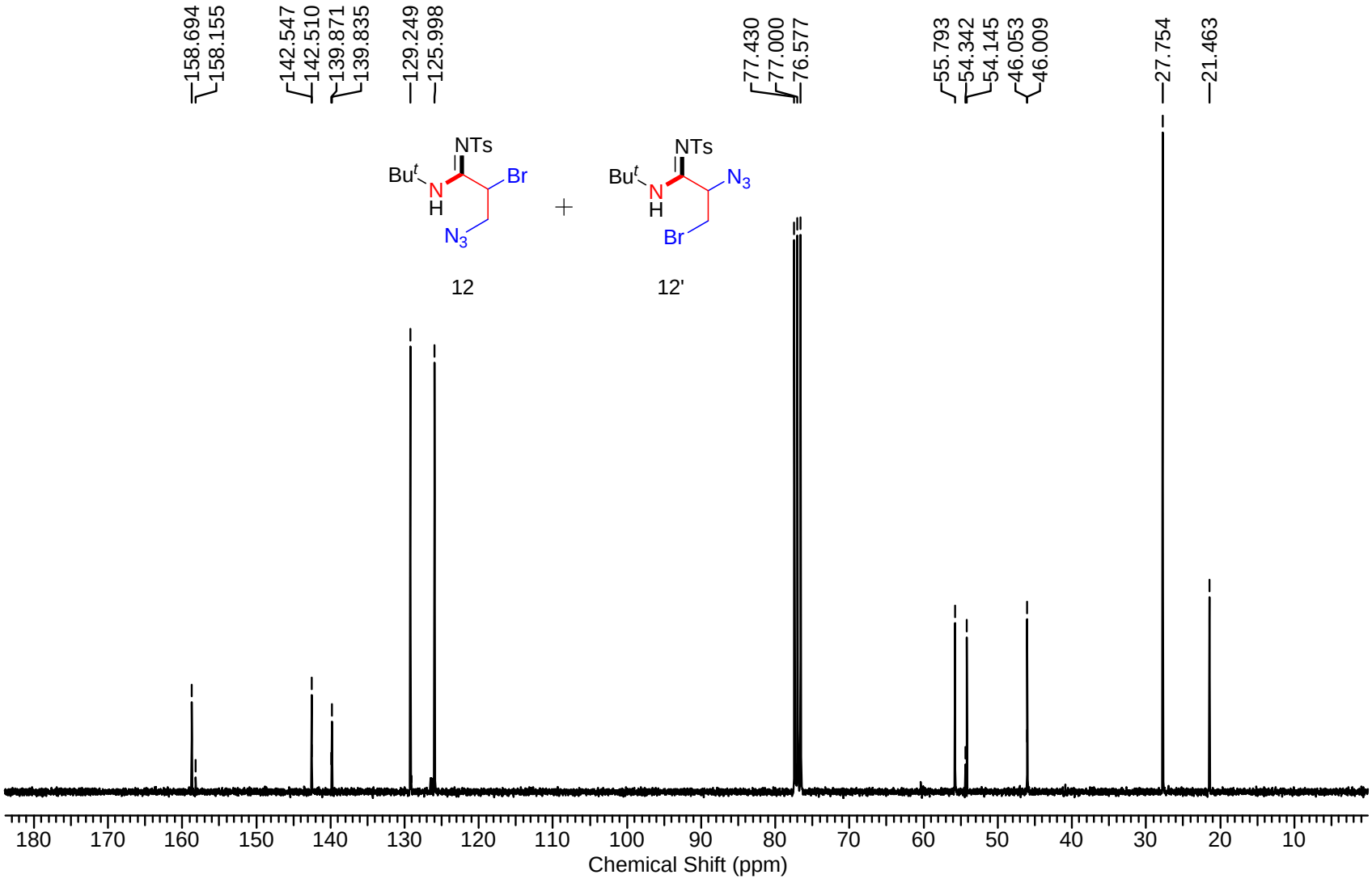

7.773
7.747
7.244
7.218
5.953
2.378
2.291
1.744
1.351
0.881
NTs
N
H
10
1.72
1.80
0.89
2.98
2.93
2.08
6.27
9.03
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

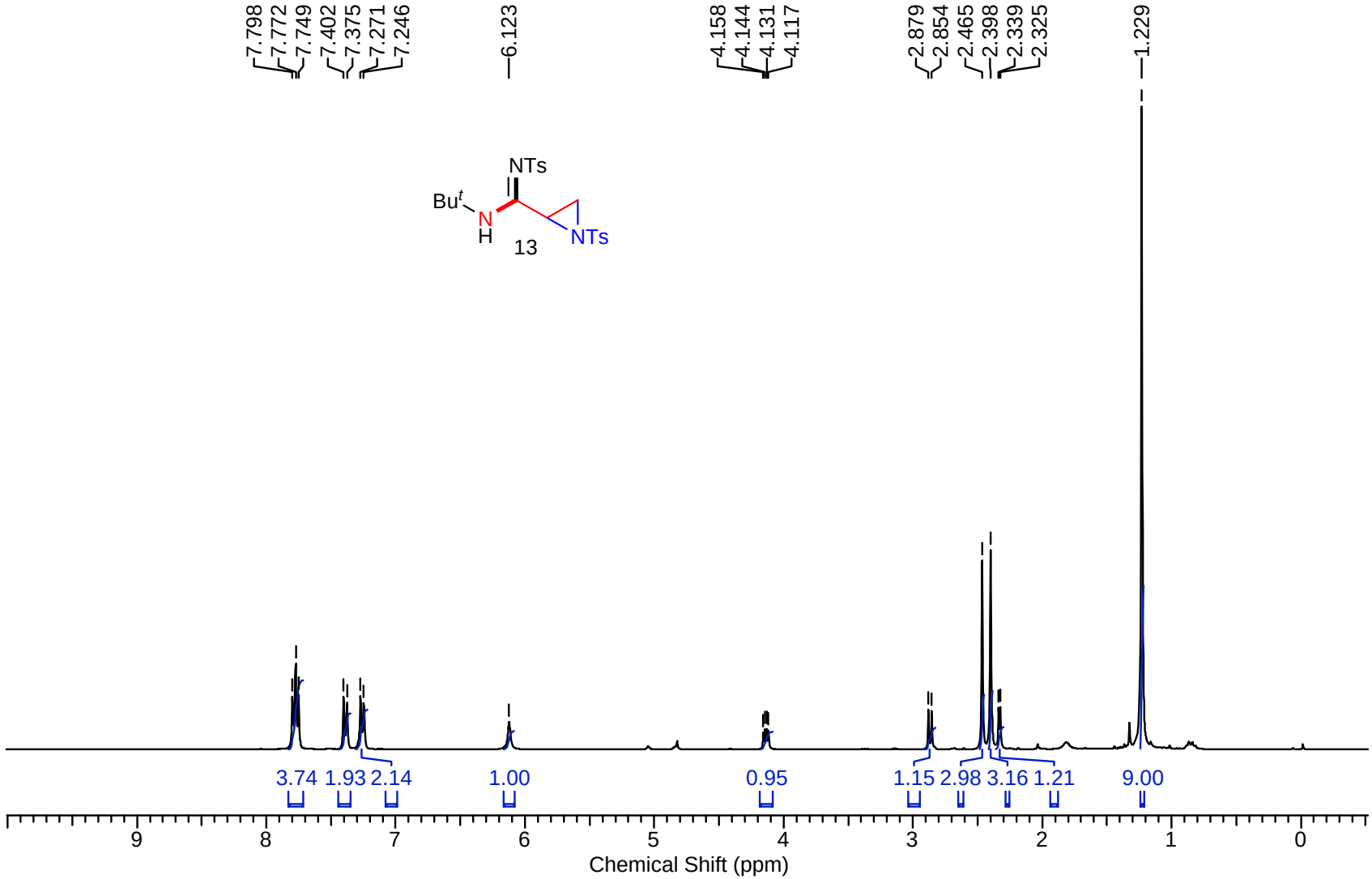

163.965
141.832
140.797
129.038
126.027
77.423
77.000
76.577
57.302
49.501
31.472
31.195
28.870
22.126
21.368
NTs
N
H
10
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

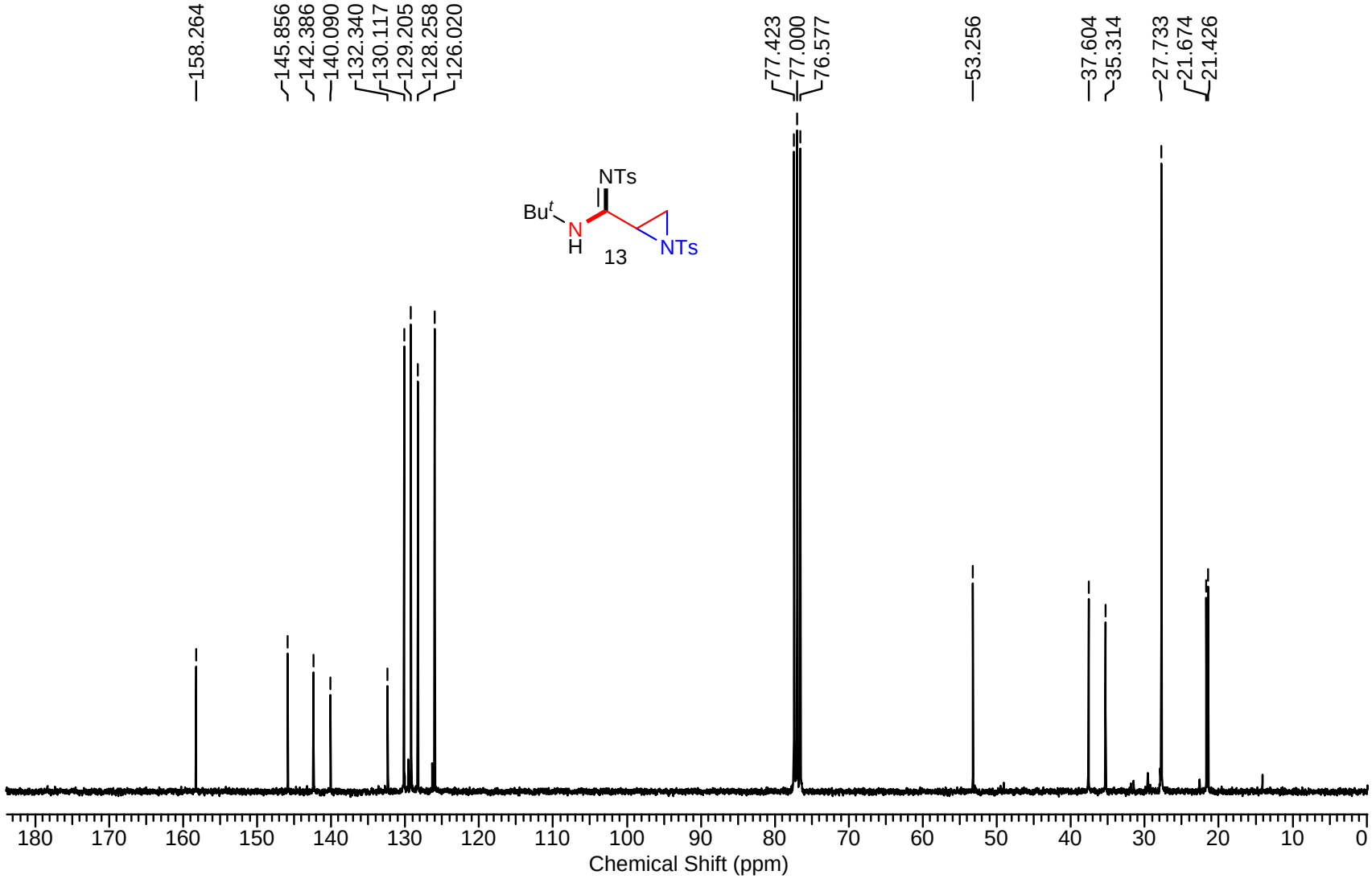

7.802
7.774
7.275
7.248
5.854
3.973
3.952
3.932
3.194
3.174
3.153
2.398
1.333
NTs
Bu^t
N
H
Cl
11
2.00
2.17
0.76
1.78
1.79
3.03
8.93
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)


162.828
142.095
140.593
129.154
125.896
77.423
77.000
76.577
53.868
41.730
38.318
28.075
21.426
NTs
Bu^t
N
H
Cl
11
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)


7.808
7.780
7.291
7.265
6.335
6.216
6.201
6.185
5.997
5.985
5.972
4.316
4.291
4.277
4.194
4.148
4.134
3.959
3.946
3.912
3.901
2.406
1.330
NTs
Bu^t
N
H
Br
N$_3$
12
+
NTs
Bu^t
N
H
N$_3$
Br
12'
2.65
2.84
0.91
0.44
1.00
0.21
1.13
1.15
3.89
11.92
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


158.694
158.155
142.547
142.510
139.871
139.835
129.249
125.998
77.430
77.000
76.577
55.793
54.342
54.145
46.053
46.009
27.754
21.463
NTs
Bu^t
N
H
Br
N$_3$
12
+
NTs
Bu^t
N
H
N$_3$
Br
12'
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)


7.798
7.772
7.749
7.402
7.375
7.271
7.246
6.123
4.158
4.144
4.131
4.117
2.879
2.854
2.465
2.398
2.339
2.325
1.229
NTs
Bu^t
N
H
NTs
13
3.74
1.93
2.14
1.00
0.95
1.15
2.98
3.16
1.21
9.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


158.264
145.856
142.386
140.090
132.340
130.117
129.205
128.258
126.020
77.423
77.000
76.577
53.256
37.604
35.314
27.733
21.674
21.426
NTs
Bu^t
N
H
NTs
13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)