Supplementary Information

Tactics for Probing Aryne Reactivity: Mechanistic Studies of Silicon-oxygen Bond Cleavage During the Trapping of (HDDA-generated) Benzynes by Silyl Ethers

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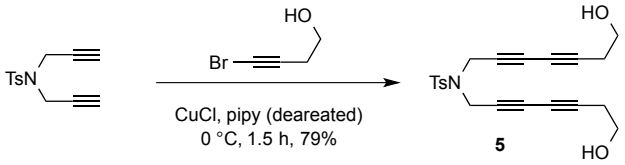
Contents of Supplementary Information **Page #**

General Experimental Protocols

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 (500 MHz) and Bruker Avance 500 (500 MHz) spectrometers. ^{1}H NMR chemical shifts in $CDCl_3$ are referenced to TMS (δ 0.00 ppm). Non-first order multiplets are identified as "nfom". ^{13}C NMR chemical shifts in $CDCl_3$ are referenced to chloroform (δ 77.16 ppm). TMS is present in some ^{13}C NMR samples (δ ca. 0.0 ppm). The following format is used to report resonances: chemical shift in ppm [multiplicity, coupling constant(s) in Hz, integral, and assignment]. ^{1}H NMR assignments are indicated by structure environment (e.g., CH_2CH_3). Infrared spectra were recorded on a Midac Corporation Prospect 4000 FT-IR spectrometer. The most intense and/or diagnostic peaks are reported, and all spectra were collected in attenuated total reflectance (ATR) mode as thin films on a 45° germanium window. High-resolution mass spectrometry (HRMS) measurements were made on via electrospray ionization (ESI) on a Bruker BioTOF II (ESI-TOF) instrument using PEG or PPG as an internal standard/calibrant. Samples were introduced as solutions in methanol or acetonitrile. MPLC refers to medium pressure liquid chromatography (25-200 psi) using hand-packed columns of Silasorb silica gel (18-32 μm, 60 Å pore size), a Waters HPLC pump, a Waters R401 differential refractive index detector, and a Gilson 116 UV detector. Flash chromatography was performed using E. Merck silica gel (230-400 mesh). Thin layer chromatography was performed on plastic-backed plates of silica gel and visualized by UV detection and/or a solution of phosphomolybdic acid. Piperidine for cross-coupling reactions was degassed by purging with N_2 gas immediately prior to use. Anhydrous methylene chloride was taken immediately prior to use after being passed through a column of activated alumina. Chloroform was stored over 4Å molecular sieves prior to use as a reaction solvent. Reported (external) reaction temperatures are the temperature of the heating bath. HDDA reactions, including those that were carried out at temperatures above the boiling point of the solvent, were typically performed in a screw-capped vial or culture tube fitted with an inert, teflon-lined cap. Those carried out in deuterated solvents were often performed directly in a capped 5 mm NMR sample tube.

_N,N_-bis(7-Hydroxyhepta-2,4-diyn-1-yl)-4-methylbenzenesulfonamide (5, prepared by the method reported in ref[1])



CuCl (20 mg, 0.2 mmol) was added to a solution of 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide[2] (247 mg, 1.0 mmol) and 4-bromo-3-butyn-1-ol[3] (326 mg, 2.2 mmol) in freshly deaerated piperidine (2 mL, 0.5 M) at 0 °C. After 1.5 h the reaction mixture was partitioned between EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted twice with EtOAc (2 x 15 mL) and the combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (1:2, hexanes-EtOAc) gave the tetrayne diol **5** (302 mg, 0.79 mmol, 79%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.0 Hz, Ar-H), 7.33 (2H, d, J = 8.0 Hz, Ar-H), 4.18 (4H, s, N-CH_2), 3.73 (4H, t, J = 6.5 Hz, CH_2OH), 2.52 (4H, t, J = 6.5 Hz, CH_2CH$_2$OH), 2.43 (3H, s, Ar-CH_3), and 2.04 (1H, br s, OH).

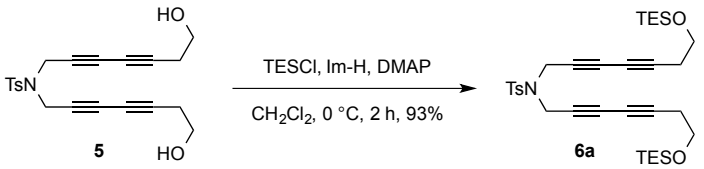
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 134.7, 129.8, 128.0, 77.3, 70.8, 68.8, 66.0, 60.7, 37.4, 23.7, and 21.7 ppm.

IR (neat): 3349 (OH), 2943, 2888, 1597, 1420, 1348, 1160, 1045, 815, and 750 cm^{-1}.

HR ESI-MS: $[C_{21}H_{21}NNaO_4S]^+$ requires 406.1083; found 406.1072.

TLC: R_f = 0.4 (1:2, Hex/EtOAc).

_N,N_-bis-{7-[(Triethylsilyl)oxy]hepta-2,4-diyn-1-yl}-4-methylbenzenesulfonamide (6a)



TESCl (69 mg, 0.46 mmol) was added to a solution of imidazole (31 mg, 0.46 mmol), DMAP (5 mg, 0.037 mmol), and diol **5** (70 mg, 0.183 mmol) in DCM (3 mL) at 0 °C with stirring. After 2 h the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the bis-TES-ether **6a** (103 mg, 0.17 mmol, 93%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.17 (4H, s, N-CH_2), 3.71 (4H, t, J = 7.0 Hz, CH_2OTES), 2.46 (4H, t, J = 7.0 Hz, CH_2CH$_2$OTES), 2.43 (3H, s, Ar-CH_3), 0.96 [18H, s, SiCH$_2$CH_3], and 0.60 [12H, s, SiCH_2CH$_3$].

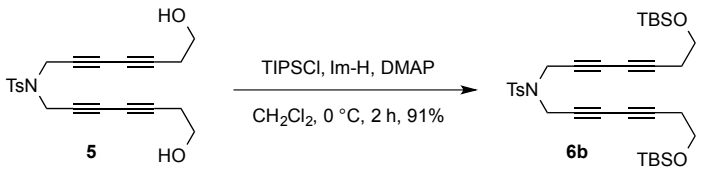
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 134.8, 129.8, 127.9, 77.8, 71.0, 68.3, 65.5, 61.1, 37.3, 23.7, 21.7, 6.8 and 4.5 ppm.

IR (neat): 2954, 2910, 2856, 2260, 1598, 1459, 1414, 1356, 1327, 1237, 1165, 1094, 1056, 1015, 1007, 903, and 813 cm^{-1}.

HR ESI-MS: $[C_{33}H_{49}NNaO_4SSi_2]^+$ requires 634.2813; found 634.2845.

TLC: R_f = 0.4 (9:1 Hex/EtOAc).

_N,N_-bis{7-[(*tert*-Butyldimethylsilyl)oxy]hepta-2,4-diyn-1-yl}-4-methylbenzenesulfonamide (6b)



TBSCl (60 mg, 0.40 mmol) was added to a solution of imidazole (28 mg, 0.40 mmol), DMAP (4 mg, 0.031 mmol), and diol **5** (60 mg, 0.157 mmol) in DCM (3 mL) at 0 °C with stirring. After 2 h the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the bis-TBS-ether **6b** (87 mg, 0.143 mmol, 91%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.17 (4H, s, N-CH_2), 3.71 (4H, t, J = 7.0 Hz, CH_2OTBS), 2.45 (4H, t, J = 7.0 Hz, CH_2CH$_2$OTBS), 2.43 (3H, s, Ar-CH_3), 0.89 [18H, s, SiC(CH_3)$_3$], and 0.07 [12H, s, Si^{t}Bu(CH_3)$_2$].

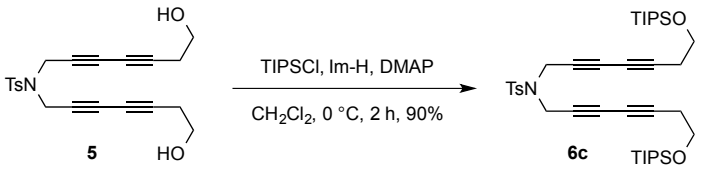
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 134.9, 129.8, 127.9, 78.0, 71.0, 68.3, 65.5, 61.4, 37.3, 26.0, 23.8, 21.7, 18.4, and -5.2 ppm.

IR (neat): 2954, 2930, 2857, 2261, 1598, 1469, 1357, 1275, 1259, 1165, 1105, 1007, 905, 839, 814, 766, 754, and 677 cm^{-1}.

HR ESI-MS: $[C_{33}H_{49}NNaO_4SSi_2]^+$ requires 634.2813; found 634.2829.

TLC: R_f = 0.4 (9:1 Hex/EtOAc).

_N,N_-bis{7-[(Triisopropylsilyl)oxy]hepta-2,4-diyn-1-yl}-4-methylbenzenesulfonamide (6c)



TIPSCl (90 mg, 0.471 mmol) was added to a solution of imidazole (32 mg, 0.471 mmol), DMAP (6 mg, 0.05 mmol), and diol **5** (60 mg, 0.157 mmol) in DCM (3 mL) at 0 °C with stirring. After 2 h the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the bis-TIPS-ether **6c** (97 mg, 0.14 mmol, 90%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.17 (4H, s, N-CH_2), 3.79 (4H, t, J = 7.0 Hz, CH_2OTIPS), 2.48 (4H, t, J = 7.0 Hz, CH_2CH$_2$OTIPS), 2.42 (3H, s, Ar-CH_3), 1.13-1.04 [6H, nfom, SiCH(CH$_3$)$_2$] and 1.05 [36H, d, J = 5.0 Hz, SiCH(CH_3)$_2$].

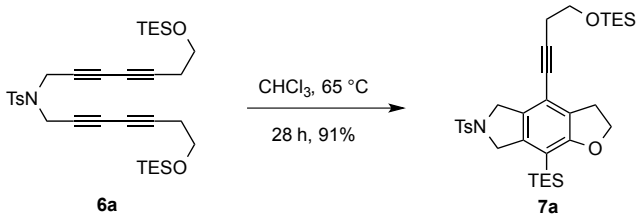
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 134.8, 129.8, 127.9, 77.9, 71.0, 68.2, 65.5, 61.7, 37.3, 23.8, 21.7, 18.0 and 12.0 ppm.

IR (neat): 2942, 2866, 2260, 1598, 1463, 1356, 1165, 1111, 1070, 1013, 996, 904, 882, 812, 745, and 685 cm^{-1}.

HR ESI-MS: $[C_{39}H_{61}NNaO_4SSi_2]^+$ requires 718.3752; found 718.3745.

TLC: R_f = 0.5 (9:1 Hex/EtOAc).

6-Tosyl-8-(triethylsilyl)-4-{4-[(triethylsilyl)oxy]but-1-yn-1-yl}-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindole (7a)



A solution of tetrayne **6a** (30 mg, 0.049 mmol) in chloroform (2 mL, 0.025 M) was placed in a screw-capped vial and heated in a 65 °C oil bath. After 28 h the reaction mixture was concentrated. Purification of the residue by MPLC (19:1, hexanes-EtOAc) yielded the tricyclic isoindole **7a** (27 mg, 0.0442 mmol, 91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (2H, d, J = 8.5 Hz, ArH), 7.31 (2H, d, J = 8.5 Hz, ArH), 4.55 (2H, s, N-CH_2), 4.52 (2H, s, N-CH_2), 4.47 (2H, br t, J = 8.5 Hz, CH_2OAr), 3.79 (2H, t, J = 7.0 Hz, CH_2OTES), 3.11 (2H, br t, J = 8.5 Hz, CH_2CH$_2$OAr), 2.67 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTES), 2.40 (3H, s, Ar-CH_3), 0.99 [9H, t, J = 8.0 Hz, OSi(CH$_2$CH_3)$_3$], 0.87 [9H, t, J = 7.0 Hz, ArSi(CH$_2$CH_3)$_3$], 0.78 [6H, q, J = 8.0 Hz, ArSi(CH_2CH$_3$)$_3$], and 0.64 [6H, q, J = 8.0 Hz, OSi(*C*H_2CH$_3$)$_3$].

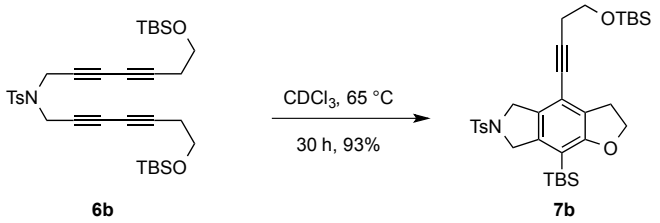
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 143.6, 141.2, 134.0, 129.9, 129.5, 128.0, 127.7, 116.3, 111.9, 95.0, 76.9, 70.9, 61.7, 55.7, 53.1, 29.2, 24.2, 21.6, 7.6, 6.9, 4.6, and 4.0 ppm.

IR (neat): 2954, 2876, 2260, 1597, 1459, 1388, 1346, 1237, 1163, 1097, 1056, 1004, 958, 816, 745, 671, 642, and 611cm^{-1}.

HR ESI-MS: $[C_{33}H_{49}NNaO_4SSi_2]^+$ requires 634.2813; found 634.2829.

TLC: R_f = 0.35 (9:1 Hex/EtOAc).

8-(*tert*-Butyldimethylsilyl)-4-{4-[(*tert*-butyldimethylsilyl)oxy]but-1-yn-1-yl}-6-tosyl-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindole (7b)



6b **7b**

A solution of tetrayne **6b** (30 mg, 0.049 mmol) in chloroform (2 mL, 0.025 M) was kept at 65 °C. After 30 h the reaction mixture was concentrated. Purification of the residue by MPLC (19:1, hexanes-EtOAc) yielded the tricyclic isoindole **7b** (28 mg, 0.046 mmol, 93%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (2H, d, J = 8.0 Hz, Ar-H), 7.32 (2H, d, J = 8.0 Hz, Ar-H), 4.58 (2H, s, N-CH_2), 4.55 (2H, s, N-CH_2), 4.47 (2H, br t, J = 8.5 Hz, -CH_2OAr), 3.82 (2H, t, J = 7.0 Hz, CH_2OTBS), 3.13 (2H, br t, J = 8.5 Hz, CH_2CH$_2$OAr), 2.68 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTBS), 2.42 (3H, s, Ar-CH_3), 0.94 [9H, s, OSiC(CH_3)$_3$], 0.85 [9H, s, Ar-SiC(CH_3)$_3$], 0.29 [6H, s, ArSi^{t}Bu(CH_3)$_2$], and 0.13 [6H, s, OSi^{t}Bu(CH_3)$_2$].

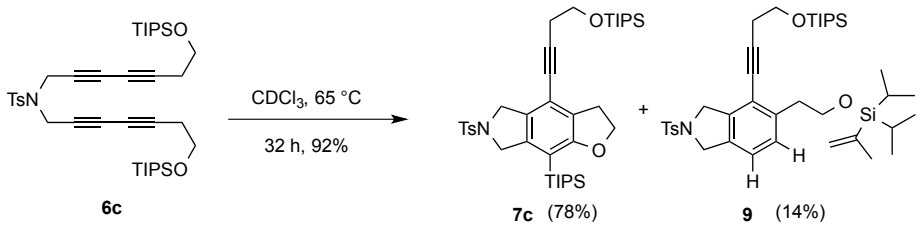
^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 143.6, 141.2, 133.9, 129.9, 129.4, 128.2, 127.7, 116.5, 112.2, 95.3, 76.8, 70.7, 60.0, 56.2, 53.2, 29.3, 26.7, 26.0, 24.2, 21.6, 18.6, 18.4, -3.3, and -5.1 ppm.

IR (neat): 2955, 2929, 2889, 2856, 2260, 1596, 1468, 1388, 1347, 1310, 1250, 1163, 1097, 1054, 960, 875, 837, 816, 783, 709, 670, 640, and 612 cm^{-1}.

HR ESI-MS: $[C_{33}H_{49}NNaO_4SSi_2]^+$ requires 634.2813; found 634.2837.

TLC: R_f = 0.35 (9:1 Hex/EtOAc).

6-Tosyl-8-(triisopropylsilyl)-4-{4-[(triisopropylsilyl)oxy]but-1-yn-1-yl}-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindole (7c) and 5-{2-[(Diisopropyl(prop-1-en-2-yl)silyl)oxy]ethyl}-2-tosyl-4-{4-[(triisopropylsilyl)oxy]but-1-yn-1-yl}isoindoline (9)



A solution of tetrayne **6c** (30 mg, 0.043 mmol) in chloroform (2 mL, 0.022 M) was kept at 65 °C. After 32 h the reaction mixture was concentrated. Purification of the residue by MPLC (19:1, hexanes-EtOAc) yielded the tricyclic isoindole **7c** (23 mg, 0.033 mmol, 78%). Further elution gave the bicyclic isoindole **9** (4 mg, 0.006 mmol, 14%).

Data for 7c:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (2H, d, *J* = 8.0 Hz, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H), 4.67 (2H, s, N-CH_2), 4.57 (2H, s, N-CH_2), 4.46 (2H, br t, *J* = 8.5 Hz, CH_2OAr), 3.91 (2H, t, *J* = 7.0 Hz, CH_2OTIPS), 3.14 (2H, br t, *J* = 8.5 Hz, CH_2CH$_2$OAr), 2.73 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$OTIPS), 2.43 (3H, s, Ar-CH_3), 1.48 [3H, septet, *J* = 7.5 Hz, ArSiC*H*(CH$_3$)$_2$], 1.22–1.10 [3H, m, OSiC*H*(CH$_3$)$_2$], 1.13 [18H, d, *J* = 5.5 Hz, OSiCH(CH_3)$_2$] and 1.05 [18H, d, *J* = 7.5 Hz, ArSiCH(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 143.6, 141.3, 133.8, 129.9, 129.8, 128.2, 127.7, 116.4, 111.1, 95.4, 76.8, 70.5, 62.3, 56.3, 53.1, 29.3, 24.3, 21.6, 18.9, 18.2, 12.5, and 12.1 ppm.

IR (neat): 2943, 2865, 2260, 1595, 1463, 1385, 1350, 1302, 1166, 1100, 1058, 997, 916, 882, 816, and 740 cm^{-1}.

HR ESI-MS: $[C_{39}H_{61}NNaO_4SSi_2]^+$ requires 718.3752; found 718.3782.

TLC: R_f = 0.4 (9:1 Hex/EtOAc).

Data for 9:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (2H, d, *J* = 8.0 Hz, O_2SArH), 7.35 (2H, d, *J* = 8.0 Hz, O_2SArH), 7.16 (1H, d, *J* = 8.0 Hz, ArH), 7.01 (1H, d, *J* = 8.0 Hz, Ar-H), 5.70 (1H, dq, *J* = 1.5, 3.0 Hz, $=CH_aH_b$), 5.33 (1H, dq, *J* = 1.0, 3.0 Hz, $=CH_aH_b$), 4.66 (2H, s, N-CH_2), 4.63 (2H, s, N-CH_2), 3.92 (2H, t, *J* = 7.0 Hz, CH_2OTIPS), 3.86 (2H, t, *J* = 7.0 Hz, CH_2OTIPS'), 3.02 (2H, t, *J* = 7.0 Hz, CH_2CH_2OTIPS), 2.73 (2H, t, *J* = 7.0 Hz, CH_2CH_2OTIPS'), 2.44 (3H, s, Ar-CH_3), 1.81 (3H, dd, *J* = 1.5, 1.5 Hz, olefinic-CH_3), 1.22–1.10 [3H, m, OSiC*H*$(CH_3)_2$], 1.12 [18H, d, *J* = 5.5 Hz, O'SiCH(C*H*$_3)_2$], 1.10–1.02 [2H, m, SiC*H*$(CH_3)_2$], 1.02 [6H, d, *J* = 7.0 Hz, OSiCH(C*H*$_3)_2$], and 1.01 [6H, d, *J* = 7.0 Hz, O'SiCH(C*H*$_3)_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 142.7, 140.4, 139.1, 134.1, 133.8, 130.0, 129.6, 128.0, 127.7, 121.4, 118.7, 95.6, 77.0, 63.8, 62.3, 54.4, 54.3, 37.8, 24.3, 23.6, 21.6, 18.2, 17.6, 17.5, 12.1, and 11.9 ppm.

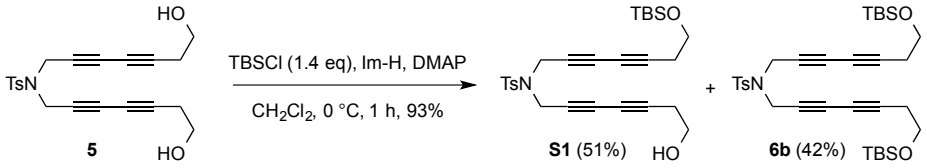
IR (neat): 2942, 2866, 2260, 1598, 1463, 1383, 1352, 1166, 1101, 1068, 995, 920, 882, 815, and 735 cm^{-1}.

HR ESI-MS: $[C_{39}H_{61}NNaO_4SSi_2]^+$ requires 718.3752; found 718.3751.

TLC: R_f = 0.35 (9:1 Hex/EtOAc).

Intramolecular Cross-over Experiment: Substrate Synthesis and Their Cyclization

N-{7-[(*tert*-Butyldimethylsilyl)oxy]hepta-2,4-diyn-1-yl}-*N*-(7-hydroxyhepta-2,4-diyn-1-yl)-4-methylbenzenesulfonamide (S1)



TBSCl (77 mg, 0.512 mmol) was added to a solution of imidazole (50 mg, 0.732 mmol), DMAP (5 mg, 0.037 mmol), and diol **5** (140 mg, 0.366 mmol) in DCM (3 mL) at 0 °C with stirring. After 1 h the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the bis-TBS-ether **6b** (94 mg, 0.154 mmol, 42%) as a pale yellow oil. Further elution with (1:1, hexanes:EtOAc) afforded the mono-hydroxy, mono-TBS-ether **S1** (93 mg, 0.187 mmol, 51%).

Data for S1

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.18 (2H, s, N-CH_2), 4.17 (2H, s, N-CH_2), 3.73 (2H, t, J = 6.0 Hz, CH_2OH), 3.71 (2H, t, J = 6.0 Hz, CH_2OTBS), 2.52 (2H, t, J = 6.0 Hz, CH_2CH$_2$OH), 2.45 (2H, t, J = 6.0 Hz, CH_2CH$_2$OTBS), 2.43 (3H, s, Ar-CH_3), 1.84 (1H, br s, OH), 0.89 [9H, s, SiC(CH_3)$_3$], and 0.06 [6H, s, Si(CH_3)$_2$].

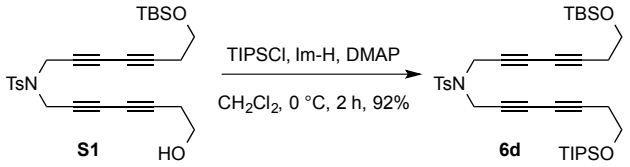
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 134.8, 129.8, 127.9, 78.0, 77.4, 71.1, 70.7, 68.8, 68.3, 66.1, 65.4, 61.4, 60.7, 37.4, 37.3, 26.0, 23.73, 23.70, 21.7, 18.4 and -5.2 ppm.

IR (neat): 2956, 2928, 2856, 2259, 1598, 1469, 1353, 1254, 1163, 1095, 1055, 902, 839, 815, 780, 747, and 677 cm^{-1}.

HR ESI-MS: $[C_{27}H_{35}NNaO_4SSi]^+$ requires 520.1948; found 520.1958.

TLC: R_f = 0.5 (1:1 Hex/EtOAc).

_N_-{7-[(_tert_-Butyldimethylsilyl)oxy]hepta-2,4-diyn-1-yl}-4-methyl-_N_-{7-[(triisopropylsilyl)-oxy]hepta-2,4-diyn-1-yl}benzenesulfonamide (6d)



TIPSCl (27 mg, 0.14 mmol) was added to a solution of imidazole (14 mg, 0.2 mmol), DMAP (1 mg, 0.01 mmol), and mono-alcohol **S1** (50 mg, 0.1 mmol) in DCM (3 mL) at 0 °C with stirring. After 2 h the reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (2 x 20 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the mono-TBS, mono-TIPS-ether **6d** (61 mg, 0.093 mmol, 92%) as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.17 (4H, s, two N-CH_2), 3.79 (2H, t, J = 7.0 Hz, CH_2OTIPS), 3.71 (2H, t, J = 7.0 Hz, CH_2OTBS), 2.49 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTIPS), 2.45 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTBS), 2.43 (3H, s, Ar-CH_3), 1.14-1.00 [3H, m, SiCH(CH$_3$)$_2$], 1.06 [18H, d, J = 5.0 Hz, Si(CH(CH_3)$_2$)], 0.90 [9H, s, SiC(CH_3)$_3$], and 0.07 [6H, s, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3, 134.9, 129.8, 128.0, 78.0, 77.4, 71.01, 70.98, 68.34, 68.3, 65.4 (2C), 61.6, 61.2, 37.3 (2C), 26.0, 23.83, 23.76, 21.7, 18.4, 18.1, 12.1, and -5.2 ppm.

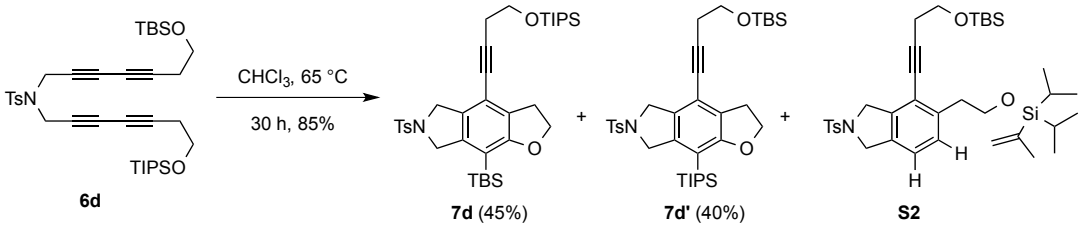
IR (neat): 2955, 2915, 2878, 2258, 1459, 1415, 1356, 1258, 1165, 1104, 1016, 905, 837, 763, 751, and 668 cm^{-1}.

HR ESI-MS: $[C_{36}H_{55}NNaO_4SSi_2]^+$ requires 676.3283; found 676.3315.

TLC: R_f = 0.4 (9:1 Hex/EtOAc).

8-(*tert*-Butyldimethylsilyl)-6-tosyl-4-{4-[(triisopropylsilyl)oxy]but-1-yn-1-yl}-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindole (7d) and

4-{4-[(*tert*-Butyldimethylsilyl)oxy]but-1-yn-1-yl}-6-tosyl-8-(triisopropylsilyl)-3,5,6,7-tetrahydro-2*H*-furo[2,3-f]isoindole (7d')



A solution of tetrayne **6d** (40 mg, 0.061 mmol) in chloroform (3 mL, 0.02 M) was kept at 65 °C. After 32 h the reaction mixture was concentrated. Purification of the residue by MPLC (25:1, hexanes:EtOAc) first gave the tricyclic isoindole **7d** (18 mg, 0.027 mmol, 45%) followed closely by the isomeric **7d'** (16 mg, 0.024 mmol, 40%). A trace of what was judged to be **S2**, the disproportionation dihydrogen-transfer product analogous to **9** (see above), was detected in the ^{1}H NMR spectrum of the crude product mixture, but it was not isolated.

Data for 7d

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (2H, d, J = 8.0 Hz, Ar-H), 7.30 (2H, d, J = 8.0 Hz, Ar-H), 4.56 (2H, s, N-CH_2), 4.53 (2H, s, N-CH_2), 4.45 (2H, br t, J = 9.0 Hz, CH_2OAr), 3.87 (2H, t, J = 7.0 Hz, CH_2OTIPS), 3.10 (2H, br t, J = 9.0 Hz, CH_2CH$_2$OAr), 2.69 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTIPS), 2.40 (3H, s, Ar-CH_3), 1.18-1.08 [3H, m, Si(CH(CH$_3$)$_2$)$_3$], 1.08 [18H, d, J = 6.0 Hz, Si(CH(CH_3)$_2$)$_3$], 0.82 [9H, s, SiC(CH_3)$_3$], and 0.27 [6H, s, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 143.6, 141.2, 133.9, 129.9, 129.4, 128.2, 127.7, 116.5, 112.2, 95.4, 76.8, 70.7, 62.3, 56.2, 53.2, 29.2, 26.7, 24.3, 21.6, 18.6, 18.2, 12.1, and -3.3 ppm.

IR (neat): 2954, 2865, 1596, 1463, 1388, 1349, 1308, 1249, 1166, 1098, 1056, 997, 881, 836, 813, and 782 cm^{-1}.

HR ESI-MS: $[C_{36}H_{55}NNaO_4SSi_2]^+$ requires 676.3283; found 676.3291.

TLC: R_f = 0.37 (9:1 Hex/EtOAc).

Data for 7d'

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (2H, d, *J* = 8.0 Hz, Ar-H), 7.29 (2H, d, *J* = 8.0 Hz, Ar-H), 4.65 (2H, s, N-CH_2), 4.53 (2H, s, N-CH_2), 4.43 (2H, br t, *J* = 9.0 Hz, CH_2OAr), 3.80 (2H, t, *J* = 7.0 Hz, CH_2OTBS), 3.11 (2H, br t, *J* = 9.0 Hz, CH_2CH$_2$OAr), 2.52 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$OTBS), 2.40 (3H, s, Ar-CH_3), 1.45 [3H, septet, *J* = 8.0 Hz, Si(C*H*(CH$_3$)$_2$)], 1.01 [18H, d, *J* = 8.0 Hz, Si(CH(CH_3)$_2$)], 0.92 [9H, s, SiC(CH_3)$_3$], and 0.11 [6H, s, Si(CH_3)$_2$].

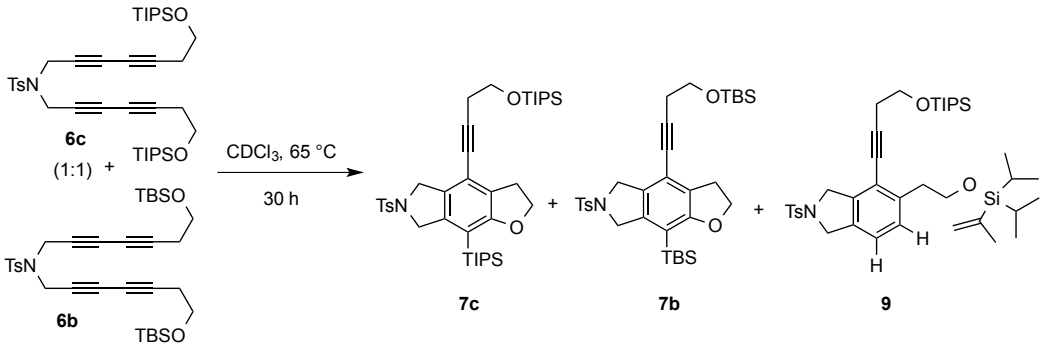
^{13}C NMR (125 MHz, $CDCl_3$): δ 166.2, 143.7, 141.4, 133.8, 129.9, 129.8, 128.2, 127.7, 116.3, 111.2, 95.3, 77.4, 70.5, 62.0, 56.3, 53.2, 29.3, 26.0, 24.2, 21.6, 18.9, 18.5, 12.5 and -5.1 ppm.

IR (neat): 2954, 2931, 2863, 1595, 1463, 1385, 1349, 1304, 1252, 1166, 1098, 1055, 997, 882, 836, and 778 cm^{-1}.

HR ESI-MS: $[C_{36}H_{55}NNaO_4SSi_2]^+$ requires 676.3283; found 676.3304.

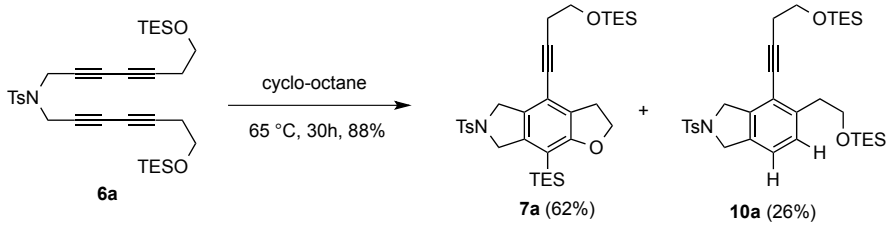
TLC: R_f = 0.35 (9:1 Hex/EtOAc).

Intermolecular Cross-over Experiment:



A nearly equimolar solution of tetraynes **6b** (12 mg, 0.02 mmol) and **6c** (14 mg, 0.02 mmol) in chloroform-*d* (1 mL) was kept at 65 °C. Reaction progress was followed by ^{1}H-NMR and LCMS. After 32 h only products **7b** and **7c** were observed; there was no evidence for the presence of cross-over products **7d** and **7d'**, whose presence would have been detected by both ^{1}H-NMR and LCMS analysis.

External Clock Reactions: Cyclization vs. Reduction by Cyclooctane
4-{4-[(Triethylsilyl)oxy]but-1-yn-1-yl}-5-{2-[(triethylsilyl)oxy]ethyl}-2-tosylisoindoline (10a)



A solution of tetrayne **6a** (50 mg, 0.082 mmol) in cyclooctane (4 mL, 0.02 M) was kept at 65 °C. After 30 h the cyclooctane solvent was removed by eluting the reaction mixture with hexanes through a small silica gel column. The column was then eluted with ethyl acetate to collect the products. Concentration of that polar eluent and purification of the resulting residue by MPLC (25:1, hexanes:EtOAc) gave the tricyclic isoindole **7a** (31 mg, 0.051 mmol, 62%) followed by the bicyclic isoindole **10a** (13 mg, 0.021 mmol, 26%).

Data for 10a

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (2H, d, *J* = 8.0 Hz, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H), 7.09 (1H, d, *J* = 7.8 Hz, Ar-H), 6.97 (1H, d, *J* = 7.8 Hz, Ar-H), 4.63 (2H, s, N-CH_2), 4.60 (2H, s, N-CH_2), 3.81 (2H, t, *J* = 7.0 Hz, ArCH$_2$CH_2OTES), 3.74 (2H, t, *J* = 7.0 Hz, CH$_2$CH_2OTES'), 2.95 (2H, t, *J* = 7.0 Hz, ArCH_2CH$_2$OTES), 2.69 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$OTES'), 2.40 (3H, s, Ar-CH_3), 0.99 [9H, t, *J* = 7.5 Hz, ArCH$_2$CH$_2$OSi(CH$_2$CH_3)$_3$], 0.91 [9H, t, *J* = 7.5 Hz, ≡CH$_2$CH$_2$O'Si(CH$_2$CH_3)$_3$], 0.65 [9H, q, *J* = 7.5 Hz, ArCH$_2$CH$_2$OSi(CH_2CH$_3$)$_3$], and 0.55 [9H, q, *J* = 7.5 Hz, CH$_2$CH$_2$OSi(CH_2CH$_3$)$_3$].

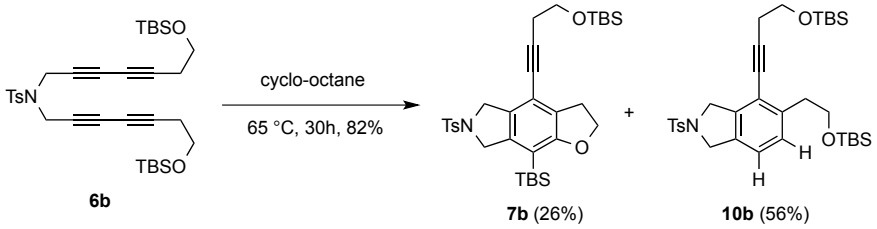
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 140.3, 139.1, 134.0, 133.9, 129.9, 129.5, 127.7, 121.5, 118.6, 95.4, 77.0, 63.1, 61.6, 54.31, 54.26, 37.8, 24.2, 21.6, 6.9, 6.8, 4.52, and 4.49 ppm.

IR (neat): 2954, 2913, 2876, 1598, 1457, 1414, 1352, 1239, 1166, 1098, 1006, 913, 812, and 778 cm^{-1}.

HR ESI-MS: $[C_{33}H_{51}NNaO_4SSi_2]^+$ requires 636.2970; found 636.2986.

TLC: R_f = 0.30 (9:1 Hex/EtOAc).

4-{4-[(*tert*-Butyldimethylsilyl)oxy]but-1-yn-1-yl}-5-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-tosylisoindoline (10b)



[BB-4-119] A solution of tetrayne **6b** (50 mg, 0.082 mmol) in cyclooctane (4 mL, 0.02 M) was kept at 65 °C. After 30 h solvent was removed by eluting the reaction mixture with hexanes through a small silica gel column. The column was then eluted with ethyl acetate to collect the products. Concentration of that polar eluent and purification of the resulting residue by MPLC using (25:1, hexanes:EtOAc) first gave the tricyclic isoindole **7b** (13 mg, 0.021 mmol, 26%) followed by the bicyclic, reduced isoindole **10b** (28 mg, 0.046 mmol, 56%).

Data for 10b

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (2H, d, J = 8.0 Hz, Ar-H), 7.31 (2H, d, J = 8.0 Hz, Ar-H), 7.09 (1H, d, J = 7.8 Hz, Ar-H), 6.97 (1H, d, J = 7.8 Hz, Ar-H), 4.62 (2H, s, N-CH_2), 4.60 (2H, s, N-CH_2), 3.81 (2H, t, J = 7.0 Hz, Ar-CH$_2$CH_2OTBS), 3.74 (2H, t, J = 7.0 Hz, CH_2OTBS), 2.93 (2H, t, J = 7.0 Hz, Ar-CH_2CH$_2$OTBS), 2.67 (2H, t, J = 7.0 Hz, CH_2CH$_2$OTBS), 2.40 (3H, s, Ar-CH_3), 0.92 [9H, s, Ar-CH$_2$CH$_2$OSiC(CH_3)$_3$], 0.85 [9H, s, CH$_2$CH$_2$OSiC(CH_3)$_3$], 0.10 [6H, s, Si(CH_3)$_2$], and -0.03 [6H, s, Si(CH_3)$_2$].

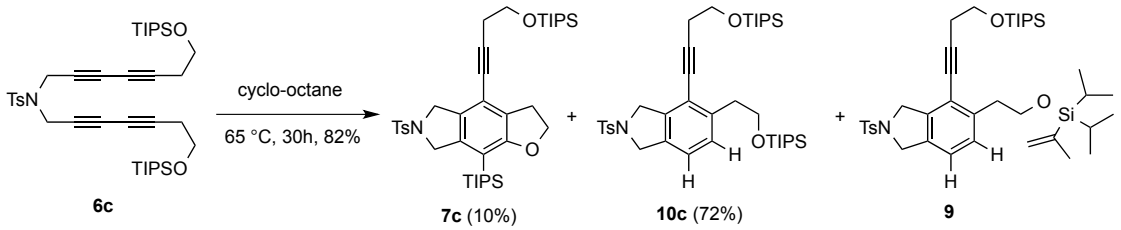
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 140.4, 139.1, 134.0, 133.9, 130.0, 129.6, 127.7, 121.4, 118.7, 95.6, 77.0, 63.4, 62.0, 54.3, 54.2, 37.8, 26.0 (2C), 24.2, 21.6, 18.46, 18.44, -5.1, and -5.3 ppm.

IR (neat): 2953, 2928, 2857, 1598, 1471, 1351, 1254, 1166, 1098, 1068, 915, 837, 814, and 778 cm^{-1}.

HR ESI-MS: $[C_{33}H_{51}NNaO_4SSi_2]^+$ requires 636.2970; found 636.2979.

TLC: R_f = 0.30 (9:1 Hex/EtOAc).

2-Tosyl-4-{4-[(triisopropylsilyl)oxy]but-1-yn-1-yl}-5-{-[(triisopropylsilyl)oxy]ethyl}-isoindoline (10c)



A solution of tetrayne **6c** (57 mg, 0.082 mmol) in cyclooctane (4 mL, 0.02 M) was kept at 65 °C. After 30 h the cyclooctane solvent was removed by eluting the reaction mixture with hexanes through a small silica gel column. The column was then eluted with ethyl acetate to collect the products. Concentration of that polar eluent and purification of the resulting residue by MPLC (25:1, hexanes:EtOAc) first gave the tricyclic isoindole **7c** (6 mg, 0.009 mmol, 10%) followed by the bicyclic isoindole **10c** (41 mg, 0.06 mmol, 72%).

Data for 10c

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (2H, d, *J* = 8.0 Hz, Ar-H), 7.31 (2H, d, *J* = 8.0 Hz, Ar-H), 7.12 (1H, d, *J* = 7.8 Hz, Ar-H), 6.97 (1H, d, *J* = 7.8 Hz, Ar-H), 4.62 (2H, s, N-CH_2), 4.60 (2H, s, N-CH_2), 3.88 (2H, t, *J* = 7.0 Hz, ArCH$_2$CH_2OTIPS), 3.81 (2H, t, *J* = 7.0 Hz, CH$_2$CH_2OTIPS), 2.96 (2H, t, *J* = 7.0 Hz, Ar-CH_2CH$_2$OTIPS), 2.69 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$OTIPS), 2.40 (3H, s, Ar-CH_3), 1.18-0.94 [6H, m, Si(C*H*(CH$_3$)$_2$)$_3$], 1.08 [18H, d, *J* = 6.0 Hz, Si(CH(CH_3)$_2$)$_3$], and 1.00 [18H, d, *J* = 6.0 Hz, Si(CH(CH_3)$_2$)$_3$].

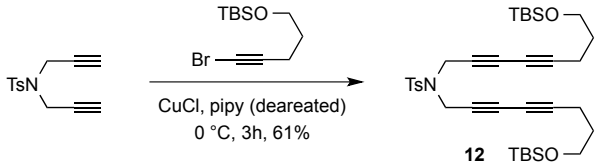
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 140.5, 139.0, 134.0, 133.8, 129.9, 129.6, 127.7, 121.4, 118.7, 95.6, 77.0, 63.7, 62.3, 54.35, 54.28, 37.9, 24.3, 21.6, 18.14, 18.10, 12.12, and 12.10 ppm.

IR (neat): 2942, 2913, 2866, 1598, 1464, 1383, 1352, 1247, 1166, 1100, 1069, 1015, 996, 919, and 814 cm^{-1}.

HR ESI-MS: $[C_{39}H_{63}NNaO_4SSi_2]^+$ requires 720.3909; found 720.3876.

TLC: R_f = 0.35 (9:1 Hex/EtOAc).

_N_-{7-[(*tert*-Butyldimethylsilyl)oxy]hepta-2,4-diyn-1-yl}-N-{8-[(*tert*-butyldimethylsilyl)oxy] octa-2,4-diyn-1-yl}-4-methylbenzenesulfonamide (12)



CuCl (10 mg, 0.1 mmol) was added to a solution of 4-methyl-*N,N*-di(prop-2-yn-1-yl)benzenesulfonamide[2] (125 mg, 0.51 mmol) and 1-(*tert*-butyldimethylsilyloxy)-5-bromo-4-pentyne[4] (307 mg, 1.1 mmol) in freshly deaerated piperidine (1 mL, 0.5 M) at 0 °C. After 3 h the reaction mixture was partitioned between EtOAc (20 mL) and saturated aqueous NH_4Cl (20 mL). The aqueous phase was extracted twice with EtOAc (2 x 15 mL), and the combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (9:1, hexanes:EtOAc) gave the tetrayne **12** (197 mg, 0.31 mmol, 61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (2H, d, J = 8.5 Hz, Ar-H), 7.32 (2H, d, J = 8.5 Hz, Ar-H), 4.18 (4H, s, N-CH_2), 3.66 (4H, t, J = 7.0 Hz, CH_2OTBS), 2.42 (3H, s, Ar-CH_3), 2.34 (4H, t, J = 7.0 Hz, Ar-CH_2), 1.70 (4H, tt, J = 7.0, 7.0 Hz, $CH_2CH_2CH_2$OTBS), 0.89 [18H, s, SiC(CH_3)$_3$], and 0.05 [12H, s, Si^{t}Bu(CH_3)$_2$].

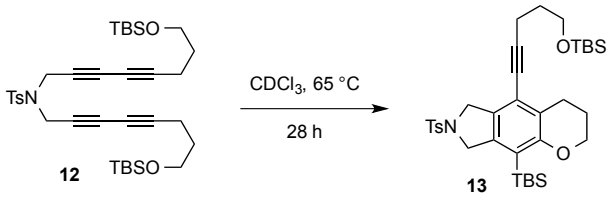
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.1, 134.8, 129.7, 127.8, 80.5, 71.0, 67.9, 64.4, 61.3, 37.2, 31.2, 25.9, 21.6, 18.3, 15.3 and -5.3 ppm.

IR (neat): 2954, 2930, 2857, 2257, 1598, 1471, 1358, 1252, 1165, 1103, 1007, 905, 893, 836, 814, and 778 cm^{-1}.

HR ESI-MS: $[C_{35}H_{53}NNaO_4SSi_2]^+$ requires 662.3126; found 662.3157.

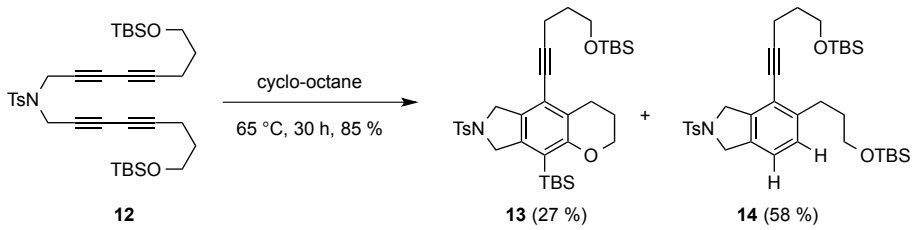
TLC: R_f = 0.4 (9:1 Hex/EtOAc).

9-(*tert*-Butyldimethylsilyl)-5-{5-[(*tert*-butyldimethylsilyl)oxy]pent-1-yn-1-yl}-7-tosyl-2,3,4,6,7,8-hexahydropyrano[2,3-f]isoindole (13)



A solution of tetrayne **12** (7 mg, 0.011 mmol) in chloroform-*d* (0.6 mL, 0.018 M) was kept at 65 °C for 28 h. Reaction was monitored by ^{1}H-NMR spectral analysis. Once the approximate reaction rate was known, the following experiment was performed on a scale suitable for isolation and characterization of product **13**.

9-(*tert*-Butyldimethylsilyl)-5-{5-[(*tert*-butyldimethylsilyl)oxy]pent-1-yn-1-yl}-7-tosyl-2,3,4,6,7,8-hexahydropyrano[2,3-f]isoindole (13) and 4-{4-[(*tert*-Butyldimethylsilyl)oxy}but-1-yn-1-yl}-5-{2-[(*tert*-butyldimethylsilyl)oxy]ethyl}-2-tosylisoindoline (14)



12 **13** (27 %) **14** (58 %)

A solution of tetrayne **12** (52 mg, 0.082 mmol) in cyclooctane (4 mL, 0.02 M) was kept at 65 °C. After 30 h the cyclooctane solvent was removed by eluting the reaction mixture with hexanes through a small silica gel column. The column was then eluted with ethyl acetate to collect the products. Concentration of that polar eluent and purification of the resulting residue by MPLC (25:1, hexanes:EtOAc) gave the tricyclic isoindole **13** (14 mg, 0.022 mmol, 27%) followed by the reduced bicyclic compound **14** (30 mg, 0.047 mmol, 58%).

Data for 13

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (2H, d, J = 8.2 Hz, Ar-H), 7.29 (2H, d, J = 8.0 Hz, Ar-H), 4.58 (2H, br s, N-CH_2), 4.53 (2H, br s, N-CH_2), 4.00 (2H, br t, J = 5.2 Hz, CH_2OAr), 3.74 (2H, 7, J = 6.8 Hz, CH_2OTBS), 2.77 (2H, br t, J = 6.6 Hz, ArCH_2CH$_2$CH$_2$OAr), 2.55 (2H, t, J = 7.0 Hz, ≡CH_2CH$_2$CH$_2$OTBS), 2.40 (3H, s, Ar-CH_3), 1.91 (2H, br tt, ΣJs = 23.7 Hz, ArCH$_2$CH_2CH$_2$OAr), 1.80 (2H, tt, J = 7.0, 7.0 Hz, CH_2CH$_2$OTBS), 0.92 [9H, s, OSiC(CH_3)$_3$], 0.83 [9H, s, Ar-SiC(CH_3)$_3$], 0.24 [6H, s, Ar-Si^{t}Bu(CH_3)$_2$], and 0.08 [6H, s, OSi^{t}Bu(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 143.6, 140.4, 133.9, 130.1, 129.9, 127.7, 122.4, 120.4, 119.6, 100.2, 76.1, 65.5, 61.7, 56.4, 53.4, 32.2, 27.1, 26.1, 24.2, 22.0, 21.6, 18.7, 18.5, 16.3, -2.1, and -5.1 ppm.

IR (neat): 2952, 2928, 2856, 2260, 1587, 1561, 1471, 1400, 1348, 1290, 1256, 1166, 1099, 1069, 975, 838, 814 and 778 cm^{-1}.

HR ESI-MS: $[C_{35}H_{53}NNaO_4SSi_2]^+$ requires 662.3126; found 662.3137.

TLC: R_f = 0.35 (9:1 Hex/EtOAc).

Data for 14

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (2H, d, *J* = 8.0 Hz, Ar-H), 7.32 (2H, d, *J* = 8.0 Hz, Ar-H), 7.06 (1H, d, *J* = 8.0 Hz, Ar-H), 6.97 (1H, d, *J* = 8.0 Hz, Ar-H), 4.63 (2H, s, N-CH_2), 4.60 (2H, s, N-CH_2), 3.74 (2H, t, *J* = 7.0 Hz, CH_2OTBS), 3.61 (2H, t, *J* = 7.0 Hz, CH_2OTBS), 2.76 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$CH$_2$OTBS), 2.54 (2H, t, *J* = 7.0 Hz, CH_2CH$_2$CH$_2$OTBS), 2.41 (3H, s, Ar-CH_3), 2.76 (2H, tt, *J* = 7.0, 7.0 Hz, CH$_2$CH_2CH$_2$OTBS), 2.54 (2H, tt, *J* = 7.0, 7.0 Hz, CH$_2$CH_2CH$_2$OTBS), 0.92 [9H, s, OSiC(CH_3)$_3$], 0.89 [9H, s, OSiC(CH_3)$_3$], 0.09 [6H, s, Si(CH_3)$_2$], and 0.04 [6H, s, Si(CH_3)$_2$].

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.71, 143.70, 139.0, 134.0, 133.4, 130.0, 128.5, 127.7, 121.4, 118.6, 98.7, 76.1, 62.7, 61.8, 54.34, 54.32, 33.7, 32.2, 30.6, 26.12, 26.10, 21.7, 18.5, 18.4, 16.3, and -5.1 (2C) ppm.

IR (neat): 2952, 2928, 2857, 1598, 1471, 1350, 1254, 1164, 1100, 1067, 965, 836, 814, and 777 cm^{-1}.

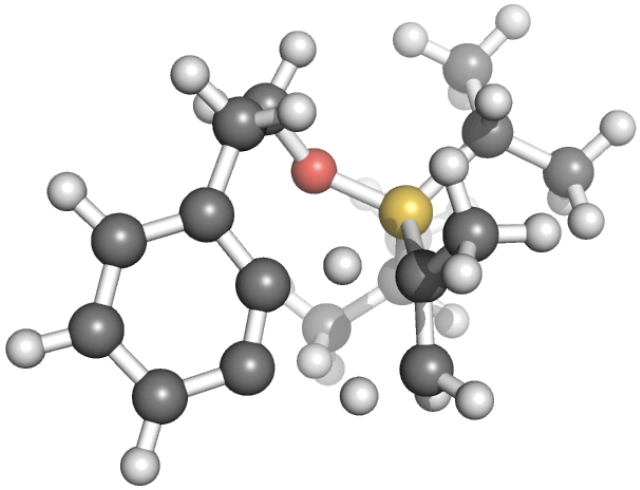
HR ESI-MS: $[C_{35}H_{55}NNaO_4SSi_2]^+$ requires 664.3283; found 664.3284.

TLC: R_f = 0.30 (9:1 Hex/EtOAc).

Computational Methodology

DFT calculations were performed with the Gaussian 09[5] software package. All geometries were optimized using the M06-2X functional.[6] The following basis sets were used: double-ζ split-valence 6-31G(d), triple-ζ split-valence 6-311G(d,p), and Dunning's correlation consistent, triple-ζ cc-pVTZ. Acetonitrile solvation was approximated by the continuum solvation model SMD [7] for both the geometry optimizations and the frequency calculations ["scrf=(SMD,solvent=acetonitrile)" keyword]. All calculations used the grid=ultrafine option to specify the integration grid used during the numerical integrations ["integral(grid=ultrafine)" keyword]. Harmonic vibrational frequency calculations were performed at 298 K to provide thermal corrections to the enthalpies. The optimized geometry for each reactant, intermediate, and product was found to have no imaginary frequencies; the optimized geometry for each transition structure (TS) was found to have one (and only one) imaginary frequency. Analysis of the imaginary frequency (by following the normal modes associated with each) for each TS identified it with each associated starting material and product.

Computed energy and geometry of 8-TS



M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -1028.473631 A.U.[a]

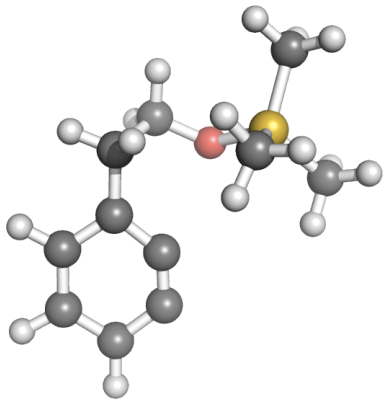
Imaginary frequency: -521.7727 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.471445	-0.005686	-0.575680
2	6	0	-3.694844	1.162290	-0.484598
3	6	0	-2.420866	1.135728	0.090853
4	6	0	-2.079500	-0.135832	0.526247
5	6	0	-2.732047	-1.251903	0.447673
6	6	0	-4.014156	-1.244358	-0.109947
7	1	0	-5.456352	0.058895	-1.032172
8	1	0	-4.091694	2.100571	-0.866089
9	1	0	-4.638942	-2.128773	-0.202899
10	6	0	-0.191508	-2.230342	1.392697
11	1	0	-1.333631	-2.237724	1.079421
12	1	0	-0.158501	-2.704948	2.377515
13	1	0	0.298451	-2.860457	0.648096
14	6	0	0.217274	-0.819599	1.407404
15	1	0	-0.886366	-0.246655	0.991954
16	14	0	1.237056	-0.065410	-0.022485
17	8	0	0.312247	0.995567	-0.910011
18	6	0	-1.467651	2.290329	0.229433
19	1	0	-1.985493	3.248232	0.103757
20	1	0	-1.052187	2.283392	1.246025

21	6	0	-0.309639	2.248825	-0.782574
22	1	0	-0.698779	2.498669	-1.775764
23	1	0	0.425210	3.018772	-0.507270
24	6	0	0.330941	-0.190321	2.789845
25	1	0	-0.491783	-0.521178	3.433671
26	1	0	1.270400	-0.489631	3.270930
27	1	0	0.313781	0.904275	2.756417
28	6	0	2.737031	0.800725	0.736243
29	1	0	2.358380	1.373991	1.596400
30	6	0	1.635435	-1.409267	-1.282248
31	1	0	2.017004	-2.280428	-0.729046
32	6	0	3.732550	-0.239413	1.270640
33	1	0	4.555302	0.241662	1.812449
34	1	0	3.258176	-0.955186	1.952595
35	1	0	4.175215	-0.814905	0.449109
36	6	0	3.424087	1.790615	-0.212903
37	1	0	2.722703	2.532817	-0.606846
38	1	0	4.230218	2.327465	0.301815
39	1	0	3.869781	1.277286	-1.070457
40	6	0	2.703622	-0.978485	-2.296019
41	1	0	3.682748	-0.827200	-1.830442
42	1	0	2.824262	-1.740798	-3.075494
43	1	0	2.416975	-0.043903	-2.792422
44	6	0	0.349676	-1.812836	-2.024165
45	1	0	0.539108	-2.667236	-2.684928
46	1	0	-0.472029	-2.080153	-1.350229
47	1	0	-0.002480	-0.978481	-2.638634

[a] Atomic Units = Hartrees

Computed energy and geometry of I



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -793.117704 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.111267	-0.998053	0.121095
2	6	0	4.126298	-0.034227	-0.012413
3	6	0	3.859705	1.339338	-0.123289
4	6	0	2.488893	1.582846	-0.093020
5	6	0	1.632208	0.694844	0.031945
6	6	0	1.736895	-0.678469	0.154165
7	1	0	3.389243	-2.044572	0.205405
8	1	0	5.158689	-0.367942	-0.032971
9	1	0	4.645359	2.076792	-0.223836
10	6	0	0.631015	-1.676567	0.300000
11	1	0	1.042176	-2.687371	0.249871
12	1	0	0.163054	-1.556582	1.281827
13	6	0	-0.433712	-1.517375	-0.786017
14	1	0	0.010349	-1.716095	-1.765070
15	1	0	-1.226258	-2.257741	-0.622125
16	8	0	-0.955633	-0.201267	-0.813938
17	14	0	-2.310463	0.298363	0.036710
18	6	0	-2.129952	-0.085990	1.859243
19	1	0	-2.988497	0.317713	2.406011
20	1	0	-2.097592	-1.163274	2.047424
21	1	0	-1.225447	0.364218	2.278718
22	6	0	-2.396702	2.137106	-0.250228
23	1	0	-3.258590	2.571586	0.264608
24	1	0	-1.496268	2.631766	0.125358
25	1	0	-2.489473	2.366249	-1.315343
26	6	0	-3.824473	-0.571806	-0.633678

27	1	0	-4.722186	-0.225717	-0.111652
28	1	0	-3.958588	-0.370323	-1.700254
29	1	0	-3.763069	-1.655535	-0.497228

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -792.947189 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.036817	-0.983305	0.139713
2	6	0	4.013023	0.022502	0.011526
3	6	0	3.689965	1.384087	-0.123542
4	6	0	2.309827	1.571105	-0.123308
5	6	0	1.485428	0.644877	0.000084
6	6	0	1.648405	-0.722387	0.142482
7	1	0	3.359970	-2.016950	0.244070
8	1	0	5.060351	-0.268841	0.014471
9	1	0	4.448091	2.153818	-0.220209
10	6	0	0.577963	-1.760683	0.288680
11	1	0	1.023407	-2.760087	0.254718
12	1	0	0.100781	-1.651026	1.269621
13	6	0	-0.486528	-1.654123	-0.808091
14	1	0	-0.041614	-1.918841	-1.773288
15	1	0	-1.290045	-2.375277	-0.603511
16	8	0	-0.996860	-0.341928	-0.931672
17	14	0	-2.193812	0.316945	0.040668
18	6	0	-1.715503	0.307692	1.855925
19	1	0	-2.419795	0.930286	2.421812
20	1	0	-1.748879	-0.698456	2.288115
21	1	0	-0.710709	0.716481	2.014244
22	6	0	-2.362289	2.072689	-0.575775
23	1	0	-3.144949	2.611393	-0.029848
24	1	0	-1.422765	2.621778	-0.445201
25	1	0	-2.618599	2.095284	-1.640577
26	6	0	-3.785443	-0.648767	-0.181297
27	1	0	-4.592800	-0.191027	0.402636
28	1	0	-4.100131	-0.666828	-1.230523
29	1	0	-3.684057	-1.685628	0.159120

[a] Atomic Units = Hartrees

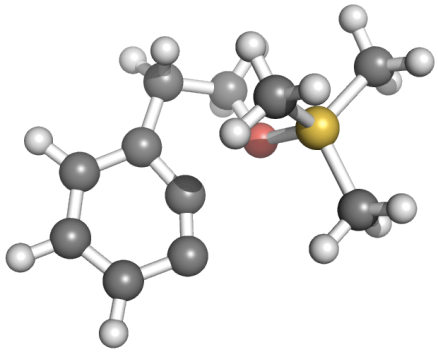
M06-2X/ccpVTZ

Sum of electronic and thermal Enthalpies = -793.181349 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.162187	-1.012205	0.113273
2	6	0	4.213509	-0.093670	-0.020563
3	6	0	4.005349	1.287924	-0.122962
4	6	0	2.649091	1.584984	-0.080343
5	6	0	1.758477	0.734978	0.042693
6	6	0	1.804182	-0.638777	0.157109
7	1	0	3.396300	-2.068153	0.188839
8	1	0	5.228868	-0.470253	-0.047702
9	1	0	4.818619	1.991530	-0.224112
10	6	0	0.665081	-1.595062	0.298158
11	1	0	1.037782	-2.616906	0.224718
12	1	0	0.211343	-1.476566	1.285352
13	6	0	-0.409485	-1.374696	-0.761190
14	1	0	0.019626	-1.511681	-1.756117
15	1	0	-1.193062	-2.129184	-0.634211
16	8	0	-0.937397	-0.064972	-0.687943
17	14	0	-2.399872	0.280632	0.038276
18	6	0	-2.424660	-0.392632	1.782901
19	1	0	-3.391383	-0.192728	2.251158
20	1	0	-2.271936	-1.474268	1.794192
21	1	0	-1.650928	0.070034	2.398714
22	6	0	-2.518094	2.138692	0.024710
23	1	0	-3.443856	2.470604	0.499121
24	1	0	-1.682481	2.584772	0.567619
25	1	0	-2.505169	2.524564	-0.996312
26	6	0	-3.781473	-0.496306	-0.952412
27	1	0	-4.752110	-0.246406	-0.518265
28	1	0	-3.771117	-0.138713	-1.983936
29	1	0	-3.698104	-1.585095	-0.969619

[a] Atomic Units = Hartrees

Computed energy and geometry of II



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -793.112966 A.U.[a]

Imaginary frequency: -163.4714 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.013861	-0.821534	0.366797
2	6	0	3.695884	0.400567	0.249491
3	6	0	3.052741	1.566140	-0.176619
4	6	0	1.670642	1.528038	-0.513676
5	6	0	1.220420	0.341792	-0.344513
6	6	0	1.651876	-0.897110	0.049004
7	1	0	3.532960	-1.713558	0.700953
8	1	0	4.752069	0.434741	0.496128
9	1	0	3.626418	2.486254	-0.250175
10	6	0	0.703993	-2.053174	0.096381
11	1	0	1.179743	-2.987190	-0.204735
12	1	0	0.323253	-2.177198	1.114754
13	6	0	-0.433388	-1.687163	-0.861787
14	1	0	-0.142414	-1.885799	-1.894464
15	1	0	-1.343369	-2.248513	-0.636644
16	8	0	-0.670642	-0.275777	-0.758478
17	14	0	-1.994338	0.343781	0.136873
18	6	0	-1.889794	-0.335964	1.870452
19	1	0	-2.705811	0.069302	2.477047
20	1	0	-1.974273	-1.426334	1.887255
21	1	0	-0.947130	-0.052125	2.347641
22	6	0	-1.811005	2.192495	0.092555
23	1	0	-2.721378	2.656979	0.484344
24	1	0	-0.968968	2.534235	0.698099
25	1	0	-1.665546	2.551158	-0.929914
26	6	0	-3.546438	-0.214084	-0.730383
27	1	0	-4.425933	0.181983	-0.213335

28	1	0	-3.569178	0.152778	-1.760234
29	1	0	-3.637329	-1.303453	-0.751322

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -792.942197 A.U.[a]

Imaginary frequency: -169.7033 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.968182	0.812981	0.382676
2	6	0	-3.630697	-0.421564	0.268993
3	6	0	-2.972238	-1.573616	-0.177832
4	6	0	-1.599599	-1.513885	-0.547312
5	6	0	-1.170673	-0.312950	-0.385374
6	6	0	-1.613387	0.914873	0.036276
7	1	0	-3.496313	1.692860	0.740506
8	1	0	-4.682179	-0.477038	0.539260
9	1	0	-3.533498	-2.505798	-0.238626
10	6	0	-0.675967	2.079853	0.089707
11	1	0	-1.160279	3.017273	-0.195960
12	1	0	-0.288158	2.199822	1.108310
13	6	0	0.457503	1.736666	-0.883809
14	1	0	0.159572	1.963354	-1.910858
15	1	0	1.371810	2.290766	-0.651888
16	8	0	0.698817	0.324436	-0.831937
17	14	0	1.936104	-0.355437	0.147748
18	6	0	1.465882	-0.150005	1.945027
19	1	0	2.214945	-0.631167	2.585238
20	1	0	1.420397	0.907449	2.228712
21	1	0	0.494985	-0.607851	2.163174
22	6	0	2.024729	-2.141104	-0.375249
23	1	0	2.814896	-2.660349	0.179145
24	1	0	1.080100	-2.662604	-0.194013
25	1	0	2.255469	-2.221147	-1.443174
26	6	0	3.524472	0.550338	-0.244843
27	1	0	4.368198	0.027548	0.221205
28	1	0	3.705562	0.579424	-1.325012
29	1	0	3.527439	1.578573	0.131440

[a] Atomic Units = Hartrees

M06-2X/ccpVTZ

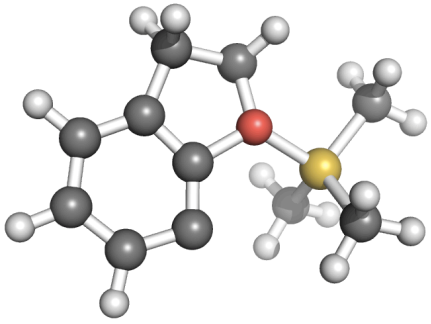
Sum of electronic and thermal Enthalpies = -793.175463 A.U.[a]

Imaginary frequency: -164.1869 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.014060	-0.823674	0.362346
2	6	0	3.698570	0.392997	0.246301
3	6	0	3.060459	1.559514	-0.173998
4	6	0	1.679248	1.528250	-0.504816
5	6	0	1.227631	0.344674	-0.337549
6	6	0	1.653509	-0.893816	0.049958
7	1	0	3.530284	-1.716922	0.691323
8	1	0	4.753838	0.422350	0.489017
9	1	0	3.635976	2.475852	-0.248032
10	6	0	0.705292	-2.044998	0.094628
11	1	0	1.175468	-2.977801	-0.210860
12	1	0	0.328226	-2.173250	1.111735
13	6	0	-0.433187	-1.671788	-0.854379
14	1	0	-0.149075	-1.871887	-1.887020
15	1	0	-1.341728	-2.230667	-0.626704
16	8	0	-0.666619	-0.263371	-0.747473
17	14	0	-1.995341	0.341982	0.133410
18	6	0	-1.918957	-0.357027	1.859272
19	1	0	-2.747365	0.034290	2.454332
20	1	0	-1.997094	-1.445964	1.857797
21	1	0	-0.988384	-0.075031	2.356090
22	6	0	-1.814204	2.190232	0.115379
23	1	0	-2.725615	2.646601	0.508643
24	1	0	-0.977440	2.521601	0.730554
25	1	0	-1.663273	2.562044	-0.899460
26	6	0	-3.535673	-0.208202	-0.756973
27	1	0	-4.419743	0.187141	-0.251768
28	1	0	-3.541942	0.159520	-1.784590
29	1	0	-3.624892	-1.295620	-0.780022

[a] Atomic Units = Hartrees

Computed energy and geometry of III



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -793.124734 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.198375	0.482288	0.036669
2	6	0	3.458829	-0.891791	0.078975
3	6	0	2.418036	-1.823990	0.011205
4	6	0	1.040094	-1.489997	-0.094204
5	6	0	0.927787	-0.130134	-0.120055
6	6	0	1.873671	0.880866	-0.067105
7	1	0	3.998951	1.212040	0.084402
8	1	0	4.485701	-1.233732	0.166397
9	1	0	2.705447	-2.874525	0.048108
10	6	0	1.245626	2.243601	-0.174148
11	1	0	1.656946	2.967400	0.529358
12	1	0	1.353949	2.641442	-1.186084
13	6	0	-0.219447	1.957346	0.144779
14	1	0	-0.430251	2.033321	1.212354
15	1	0	-0.929225	2.535983	-0.438258
16	8	0	-0.398446	0.536323	-0.226654
17	14	0	-1.946415	-0.346380	0.017966
18	6	0	-2.159798	-1.498537	-1.416851
19	1	0	-3.226611	-1.707607	-1.546585
20	1	0	-1.800460	-1.026523	-2.335728
21	1	0	-1.627103	-2.438536	-1.279574
22	6	0	-1.889452	-1.080516	1.719580
23	1	0	-2.907591	-1.329023	2.035744
24	1	0	-1.277700	-1.981187	1.763366
25	1	0	-1.490273	-0.352628	2.432981
26	6	0	-3.177582	1.044302	-0.065391
27	1	0	-4.178257	0.610437	0.032294
28	1	0	-3.053540	1.768296	0.743675
29	1	0	-3.139439	1.572951	-1.021469

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -792.953718 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.187445	-0.468167	-0.066262
2	6	0	3.429029	0.911302	-0.101432
3	6	0	2.378535	1.831911	0.008518
4	6	0	1.006703	1.484811	0.155068
5	6	0	0.919460	0.121855	0.168494
6	6	0	1.869226	-0.883939	0.074109
7	1	0	3.996665	-1.188275	-0.148971
8	1	0	4.450807	1.266260	-0.218525
9	1	0	2.658431	2.887820	-0.029012
10	6	0	1.250151	-2.252344	0.177621
11	1	0	1.641236	-2.966249	-0.550922
12	1	0	1.388909	-2.673096	1.179022
13	6	0	-0.227241	-1.965246	-0.093410
14	1	0	-0.467768	-2.026660	-1.157828
15	1	0	-0.921692	-2.557132	0.498793
16	8	0	-0.401053	-0.555104	0.310655
17	14	0	-1.922306	0.347107	-0.035427
18	6	0	-2.200564	1.559491	1.343950
19	1	0	-3.272851	1.777498	1.416407
20	1	0	-1.884271	1.126532	2.299435
21	1	0	-1.654277	2.491322	1.191705
22	6	0	-1.785298	1.010120	-1.766853
23	1	0	-2.786636	1.253243	-2.141537
24	1	0	-1.161411	1.904380	-1.817614
25	1	0	-1.358497	0.251893	-2.434006
26	6	0	-3.179763	-1.027847	0.052340
27	1	0	-4.175850	-0.585714	-0.072640
28	1	0	-3.051566	-1.774401	-0.738053
29	1	0	-3.166619	-1.537764	1.021625

[a] Atomic Units = Hartrees

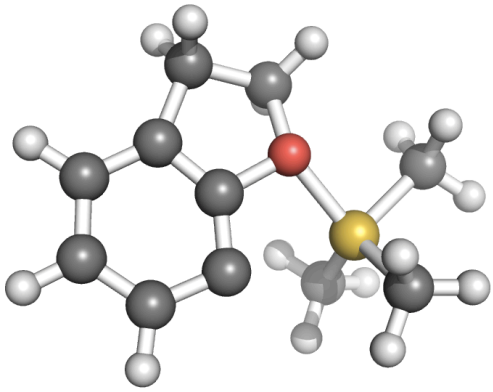
M06-2X/ccpVTZ

Sum of electronic and thermal Enthalpies = -793.186682 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.182143	0.487908	0.056617
2	6	0	3.447542	-0.881739	0.092841
3	6	0	2.415466	-1.816371	-0.002014
4	6	0	1.042231	-1.486293	-0.130587
5	6	0	0.920589	-0.129480	-0.145183
6	6	0	1.861015	0.881161	-0.068058
7	1	0	3.977402	1.218966	0.124255
8	1	0	4.472312	-1.219387	0.196257
9	1	0	2.706338	-2.863649	0.030652
10	6	0	1.232995	2.240299	-0.176238
11	1	0	1.623781	2.957233	0.542473
12	1	0	1.365413	2.649843	-1.178371
13	6	0	-0.235642	1.946743	0.103192
14	1	0	-0.472751	2.021784	1.163308
15	1	0	-0.931981	2.524517	-0.492898
16	8	0	-0.404388	0.528491	-0.275831
17	14	0	-1.934246	-0.345885	0.029905
18	6	0	-2.171786	-1.559219	-1.349149
19	1	0	-3.241887	-1.679469	-1.534158
20	1	0	-1.713942	-1.185261	-2.266673
21	1	0	-1.740170	-2.531081	-1.121050
22	6	0	-1.834674	-1.011395	1.755950
23	1	0	-2.845147	-1.216831	2.117072
24	1	0	-1.248811	-1.926258	1.813832
25	1	0	-1.390396	-0.268685	2.422757
26	6	0	-3.174109	1.032904	-0.086883
27	1	0	-4.169290	0.594231	0.021237
28	1	0	-3.053706	1.776739	0.701521
29	1	0	-3.137231	1.534663	-1.055166

[a] Atomic Units = Hartrees

Computed energy and geometry of IV



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -793.115579 A.U.[a]

Imaginary frequency: -163.8221 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.137571	-0.030714	0.056369
2	6	0	2.969904	-1.424588	0.082634
3	6	0	1.707561	-2.036191	-0.010065
4	6	0	0.518390	-1.284945	-0.156597
5	6	0	0.832104	0.036159	-0.220523
6	6	0	1.996704	0.751813	-0.092794
7	1	0	4.121752	0.410160	0.167022
8	1	0	3.849401	-2.048493	0.206652
9	1	0	1.675656	-3.121525	0.059851
10	6	0	1.653813	2.226756	-0.128655
11	1	0	2.166951	2.813813	0.632871
12	1	0	1.877290	2.657445	-1.107623
13	6	0	0.129742	2.218314	0.131032
14	1	0	-0.101467	2.278168	1.195450
15	1	0	-0.431634	2.956195	-0.434253
16	8	0	-0.292308	0.884074	-0.331632
17	14	0	-1.729449	-0.339012	0.021119
18	6	0	-2.304660	-1.351527	-1.440158
19	1	0	-3.380864	-1.232114	-1.599156
20	1	0	-1.792635	-1.005702	-2.343487
21	1	0	-2.065612	-2.408068	-1.308336
22	6	0	-1.786381	-0.995737	1.771109
23	1	0	-2.770036	-0.815719	2.216307
24	1	0	-1.554638	-2.061191	1.811334
25	1	0	-1.043558	-0.470870	2.381148
26	6	0	-2.925787	1.130698	0.054885

27	1	0	-3.942274	0.760568	0.226980
28	1	0	-2.696968	1.837509	0.859480
29	1	0	-2.934376	1.683181	-0.890271

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -792.948388 A.U.[a]

Imaginary frequency: -135.0053 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.143331	0.045112	0.063824
2	6	0	3.027622	-1.354911	0.091781
3	6	0	1.787726	-2.011082	-0.013052
4	6	0	0.566721	-1.312316	-0.175073
5	6	0	0.836505	0.020670	-0.238374
6	6	0	1.973524	0.782856	-0.099386
7	1	0	4.109818	0.525880	0.184401
8	1	0	3.930078	-1.946543	0.227226
9	1	0	1.798847	-3.099499	0.060036
10	6	0	1.582436	2.245453	-0.134343
11	1	0	2.073039	2.851017	0.631013
12	1	0	1.792924	2.691637	-1.111867
13	6	0	0.059666	2.184237	0.121966
14	1	0	-0.176216	2.220931	1.188310
15	1	0	-0.528521	2.911253	-0.433946
16	8	0	-0.316939	0.845044	-0.363894
17	14	0	-1.732839	-0.347162	0.025033
18	6	0	-2.304403	-1.384588	-1.424507
19	1	0	-3.383988	-1.272854	-1.579332
20	1	0	-1.799920	-1.050500	-2.338430
21	1	0	-2.062249	-2.440521	-1.279965
22	6	0	-1.732232	-1.001237	1.780517
23	1	0	-2.704009	-0.819268	2.254712
24	1	0	-1.502097	-2.068900	1.818268
25	1	0	-0.970765	-0.477264	2.371049
26	6	0	-2.956126	1.101069	0.075921
27	1	0	-3.965877	0.711498	0.258000
28	1	0	-2.735650	1.811136	0.882622
29	1	0	-2.988772	1.660330	-0.867048

[a] Atomic Units = Hartrees

M06-2X/ccpVTZ

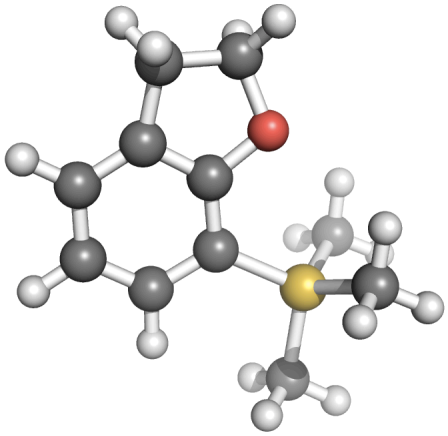
Sum of electronic and thermal Enthalpies = -793.176756 A.U.[a]

Imaginary frequency: -165.4977 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.123004	-0.035403	0.060352
2	6	0	2.951600	-1.425893	0.085402
3	6	0	1.691335	-2.033021	-0.013703
4	6	0	0.508672	-1.278758	-0.169100
5	6	0	0.824677	0.038515	-0.231366
6	6	0	1.988395	0.749096	-0.095388
7	1	0	4.106425	0.400710	0.177757
8	1	0	3.827114	-2.050955	0.214683
9	1	0	1.656181	-3.116144	0.057713
10	6	0	1.650005	2.222201	-0.126126
11	1	0	2.159209	2.804008	0.638967
12	1	0	1.879379	2.657945	-1.099243
13	6	0	0.127437	2.214828	0.124798
14	1	0	-0.108052	2.269419	1.186426
15	1	0	-0.428646	2.957850	-0.435323
16	8	0	-0.297070	0.887052	-0.348419
17	14	0	-1.708011	-0.337574	0.021596
18	6	0	-2.309403	-1.350851	-1.428318
19	1	0	-3.382636	-1.218153	-1.581444
20	1	0	-1.797929	-1.020742	-2.335417
21	1	0	-2.085142	-2.407691	-1.288576
22	6	0	-1.758078	-0.987675	1.773680
23	1	0	-2.734257	-0.797826	2.225747
24	1	0	-1.537038	-2.053402	1.814991
25	1	0	-1.006050	-0.468868	2.374014
26	6	0	-2.916165	1.124083	0.067964
27	1	0	-3.924827	0.744558	0.252092
28	1	0	-2.683547	1.830862	0.868821
29	1	0	-2.940326	1.675320	-0.875378

[a] Atomic Units = Hartrees

Computed energy and geometry of V



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -793.206783 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.418791	1.688131	-0.005979
2	6	0	1.302196	2.529640	-0.047917
3	6	0	0.015965	1.994439	-0.042624
4	6	0	-0.221993	0.608657	-0.005282
5	6	0	0.920772	-0.185719	0.026644
6	6	0	2.220168	0.318692	0.027953
7	1	0	3.421544	2.101649	0.000053
8	1	0	1.438501	3.604190	-0.081871
9	1	0	-0.830858	2.673645	-0.073104
10	6	0	3.170885	-0.847850	0.139803
11	1	0	4.012415	-0.793207	-0.550573
12	1	0	3.562581	-0.924774	1.157924
13	6	0	2.232758	-2.018036	-0.194508
14	1	0	2.289270	-2.275635	-1.255373
15	1	0	2.398527	-2.908258	0.408108
16	8	0	0.888145	-1.548446	0.072325
17	14	0	-1.945459	-0.159212	0.006667
18	6	0	-3.207499	1.226735	-0.038864
19	1	0	-4.219795	0.813192	0.003516
20	1	0	-3.091736	1.908294	0.808742
21	1	0	-3.126967	1.812077	-0.959476
22	6	0	-2.140626	-1.265475	-1.496406
23	1	0	-3.124346	-1.744451	-1.503984
24	1	0	-2.035671	-0.694563	-2.423441
25	1	0	-1.379447	-2.050127	-1.492492
26	6	0	-2.147718	-1.173865	1.571303
27	1	0	-3.135194	-1.643809	1.608220

28	1	0	-1.392866	-1.963548	1.614096
29	1	0	-2.036885	-0.550253	2.462974

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -793.041642 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.421984	-1.691189	0.005097
2	6	0	1.303557	-2.532635	0.045658
3	6	0	0.016530	-1.994894	0.041413
4	6	0	-0.221910	-0.607917	0.006617
5	6	0	0.924114	0.185127	-0.023706
6	6	0	2.224930	-0.319557	-0.027009
7	1	0	3.426193	-2.106535	-0.001293
8	1	0	1.439377	-3.609296	0.077790
9	1	0	-0.832508	-2.674801	0.070511
10	6	0	3.177053	0.847283	-0.130916
11	1	0	4.009138	0.797791	0.575192
12	1	0	3.592843	0.920280	-1.142059
13	6	0	2.234537	2.023283	0.180720
14	1	0	2.298227	2.313175	1.234969
15	1	0	2.396503	2.900708	-0.445927
16	8	0	0.890051	1.549356	-0.065697
17	14	0	-1.944722	0.158541	-0.006221
18	6	0	-3.211250	-1.229547	0.040727
19	1	0	-4.225704	-0.816357	-0.004920
20	1	0	-3.096346	-1.916136	-0.805504
21	1	0	-3.135059	-1.815008	0.963981
22	6	0	-2.148179	1.269087	1.498097
23	1	0	-3.129521	1.757441	1.495488
24	1	0	-2.059355	0.698652	2.429436
25	1	0	-1.380467	2.049997	1.504998
26	6	0	-2.155081	1.172458	-1.575643
27	1	0	-3.142664	1.647231	-1.607094
28	1	0	-1.397863	1.961903	-1.629188
29	1	0	-2.054792	0.547534	-2.470037

[a] Atomic Units = Hartrees

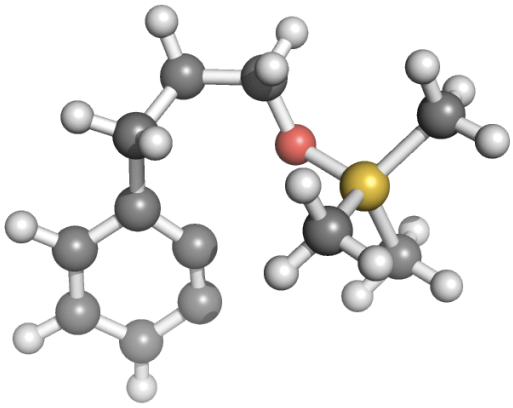
M06-2X/ccpVTZ

Sum of electronic and thermal Enthalpies = -793.266761 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.410186	1.689837	-0.006165
2	6	0	1.291849	2.524025	-0.046229
3	6	0	0.011740	1.982915	-0.041398
4	6	0	-0.220133	0.599152	-0.005710
5	6	0	0.924634	-0.186845	0.024455
6	6	0	2.219145	0.322644	0.028367
7	1	0	3.408888	2.108306	-0.000120
8	1	0	1.422169	3.597432	-0.079257
9	1	0	-0.836705	2.656946	-0.070388
10	6	0	3.176680	-0.835228	0.133398
11	1	0	4.010013	-0.775970	-0.563230
12	1	0	3.580744	-0.906545	1.144872
13	6	0	2.247138	-2.012796	-0.186386
14	1	0	2.308168	-2.286826	-1.240947
15	1	0	2.418970	-2.892050	0.427479
16	8	0	0.900705	-1.549459	0.070593
17	14	0	-1.945110	-0.162531	0.006263
18	6	0	-3.197718	1.229799	-0.037703
19	1	0	-4.210230	0.821955	0.000728
20	1	0	-3.078606	1.905574	0.811318
21	1	0	-3.109990	1.815975	-0.954586
22	6	0	-2.153069	-1.263798	-1.496887
23	1	0	-3.141074	-1.729226	-1.500517
24	1	0	-2.046264	-0.691638	-2.420488
25	1	0	-1.403077	-2.056205	-1.498734
26	6	0	-2.158441	-1.173886	1.569806
27	1	0	-3.150880	-1.628649	1.603920
28	1	0	-1.416194	-1.972317	1.615810
29	1	0	-2.042099	-0.550580	2.458435

[a] Atomic Units = Hartrees

Computed energy and geometry of VI



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -832.391922 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.118714	0.509202	0.617470
2	6	0	-3.841835	-0.663371	0.341866
3	6	0	-3.304097	-1.724101	-0.403053
4	6	0	-1.994770	-1.461835	-0.810152
5	6	0	-1.422667	-0.396427	-0.524005
6	6	0	-1.791535	0.727315	0.182781
7	1	0	-3.596211	1.300184	1.188890
8	1	0	-4.857238	-0.746767	0.715806
9	1	0	-3.869886	-2.622720	-0.614748
10	6	0	-1.012148	1.977118	0.475859
11	1	0	-1.728264	2.752826	0.754565
12	1	0	-0.383948	1.801370	1.358044
13	6	0	-0.126172	2.462755	-0.681037
14	1	0	-0.614874	2.262021	-1.639257
15	1	0	0.001355	3.546073	-0.603341
16	6	0	1.259085	1.841226	-0.674521
17	1	0	1.858429	2.249187	-1.495128
18	1	0	1.760598	2.107994	0.266040
19	8	0	1.177593	0.428361	-0.821180
20	14	0	2.072620	-0.609592	0.145373
21	6	0	1.440474	-0.522824	1.904529
22	1	0	1.993397	-1.220786	2.541489
23	1	0	1.562192	0.477978	2.329812
24	1	0	0.380539	-0.789945	1.955782
25	6	0	1.850381	-2.316008	-0.569671
26	1	0	2.466231	-3.036267	-0.022212
27	1	0	0.811288	-2.648664	-0.510018
28	1	0	2.157444	-2.342564	-1.618947

29	6	0	3.872319	-0.098662	0.088594
30	1	0	4.481695	-0.768782	0.703058
31	1	0	4.259757	-0.137779	-0.933824
32	1	0	4.018149	0.917705	0.466246

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -832.210755 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.256917	0.521997	0.408351
2	6	0	-3.921372	-0.692971	0.160962
3	6	0	-3.257023	-1.831890	-0.324015
4	6	0	-1.893584	-1.600950	-0.523566
5	6	0	-1.382743	-0.489087	-0.274158
6	6	0	-1.870560	0.710547	0.198656
7	1	0	-3.830423	1.369420	0.778868
8	1	0	-4.990765	-0.746445	0.349089
9	1	0	-3.779643	-2.764159	-0.513308
10	6	0	-1.153325	2.002570	0.473467
11	1	0	-1.913511	2.767250	0.660017
12	1	0	-0.578171	1.902155	1.404917
13	6	0	-0.207714	2.468401	-0.645183
14	1	0	-0.648196	2.256602	-1.626330
15	1	0	-0.084804	3.554959	-0.573642
16	6	0	1.177350	1.850030	-0.563828
17	1	0	1.829354	2.280107	-1.335433
18	1	0	1.617195	2.099800	0.414105
19	8	0	1.107593	0.442132	-0.745138
20	14	0	2.137001	-0.571415	0.112807
21	6	0	1.636752	-0.579534	1.920295
22	1	0	2.284400	-1.249527	2.498495
23	1	0	1.716721	0.418069	2.367754
24	1	0	0.603729	-0.924906	2.042654
25	6	0	1.961601	-2.266786	-0.652389
26	1	0	2.643317	-2.976981	-0.170079
27	1	0	0.943076	-2.654876	-0.550557
28	1	0	2.207432	-2.240800	-1.719803
29	6	0	3.898092	0.049078	-0.066936
30	1	0	4.596599	-0.611570	0.459975
31	1	0	4.198293	0.078644	-1.120720

32	1	0	4.023289	1.056601	0.345858

[a] Atomic Units = Hartrees

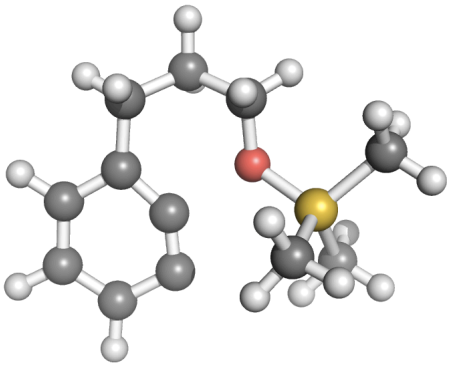
M06-2X/ccpVTZ

Sum of electronic and thermal Enthalpies = -832.458474 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.236930	0.548248	0.492097
2	6	0	-3.964928	-0.620679	0.229321
3	6	0	-3.385833	-1.755314	-0.351986
4	6	0	-2.032982	-1.560505	-0.619575
5	6	0	-1.457835	-0.495331	-0.353984
6	6	0	-1.863476	0.694044	0.204665
7	1	0	-3.746961	1.395297	0.937527
8	1	0	-5.018123	-0.642219	0.482476
9	1	0	-3.954460	-2.651497	-0.555346
10	6	0	-1.081333	1.939849	0.487996
11	1	0	-1.793951	2.718458	0.757581
12	1	0	-0.454554	1.769922	1.369704
13	6	0	-0.191561	2.415613	-0.668518
14	1	0	-0.666274	2.191149	-1.625979
15	1	0	-0.081674	3.499828	-0.609471
16	6	0	1.201099	1.819464	-0.636903
17	1	0	1.804022	2.229933	-1.451624
18	1	0	1.683981	2.107005	0.305219
19	8	0	1.149331	0.406504	-0.762928
20	14	0	2.166729	-0.576808	0.123340
21	6	0	1.670986	-0.515440	1.925420
22	1	0	2.322671	-1.154583	2.526053
23	1	0	1.744906	0.497976	2.326118
24	1	0	0.644466	-0.863459	2.060951
25	6	0	1.967901	-2.291757	-0.575495
26	1	0	2.650437	-2.985728	-0.080140
27	1	0	0.951241	-2.663217	-0.438259
28	1	0	2.193133	-2.303525	-1.643684
29	6	0	3.925572	0.026836	-0.073803
30	1	0	4.617320	-0.623607	0.466090
31	1	0	4.221778	0.033106	-1.124912
32	1	0	4.049114	1.038270	0.318946

[a] Atomic Units = Hartrees

Computed energy and geometry of VII



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -832.388976 A.U.[a]

Imaginary frequency: -154.6740 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.287091	0.116342	0.224369
2	6	0	-3.514331	-1.257049	0.073288
3	6	0	-2.466463	-2.140184	-0.203536
4	6	0	-1.160276	-1.614142	-0.331691
5	6	0	-1.124694	-0.348295	-0.160513
6	6	0	-1.999404	0.672530	0.112034
7	1	0	-4.115008	0.787722	0.431496
8	1	0	-4.526842	-1.635525	0.169618
9	1	0	-2.676586	-3.200064	-0.317065
10	6	0	-1.706848	2.137756	0.280585
11	1	0	-2.599754	2.701699	0.002673
12	1	0	-1.519404	2.342131	1.340959
13	6	0	-0.503748	2.600060	-0.535560
14	1	0	-0.662509	2.392429	-1.597972
15	1	0	-0.383720	3.680367	-0.422928
16	6	0	0.786786	1.946406	-0.086199
17	1	0	1.633920	2.367059	-0.633564
18	1	0	0.943589	2.119078	0.985321
19	8	0	0.729713	0.531930	-0.340965
20	14	0	2.055428	-0.477675	0.066208
21	6	0	1.744723	-1.207424	1.754462
22	1	0	2.646295	-1.710529	2.117714
23	1	0	1.490290	-0.421102	2.471998
24	1	0	0.930753	-1.935004	1.740571
25	6	0	2.251909	-1.757986	-1.271937
26	1	0	3.206838	-2.277407	-1.140595
27	1	0	1.453247	-2.500658	-1.258906

28	1	0	2.265253	-1.282482	-2.256857
29	6	0	3.575764	0.609428	0.111582
30	1	0	4.443509	-0.015415	0.347029
31	1	0	3.764843	1.085385	-0.854721
32	1	0	3.513628	1.389672	0.874749

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -832.207909 A.U.[a]

Imaginary frequency: -160.9336 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.280752	0.103723	0.213072
2	6	0	-3.494158	-1.274635	0.079042
3	6	0	-2.434106	-2.150556	-0.186231
4	6	0	-1.132643	-1.617253	-0.323711
5	6	0	-1.110785	-0.343204	-0.166964
6	6	0	-1.997516	0.673006	0.093757
7	1	0	-4.117299	0.769697	0.413528
8	1	0	-4.504645	-1.662737	0.179918
9	1	0	-2.636664	-3.216323	-0.284779
10	6	0	-1.725143	2.144713	0.252555
11	1	0	-2.613633	2.699429	-0.065388
12	1	0	-1.580987	2.367969	1.318196
13	6	0	-0.496949	2.613692	-0.521756
14	1	0	-0.626409	2.428906	-1.594388
15	1	0	-0.373548	3.692863	-0.384604
16	6	0	0.777540	1.937618	-0.054073
17	1	0	1.646796	2.383636	-0.548159
18	1	0	0.895279	2.059231	1.031685
19	8	0	0.729760	0.540234	-0.382957
20	14	0	2.044437	-0.474512	0.062200
21	6	0	1.702424	-1.194474	1.753779
22	1	0	2.601767	-1.683552	2.146161
23	1	0	1.420593	-0.403722	2.459223
24	1	0	0.894687	-1.931148	1.728936
25	6	0	2.260232	-1.759022	-1.274520
26	1	0	3.154534	-2.360002	-1.070263
27	1	0	1.400446	-2.430316	-1.340211
28	1	0	2.396973	-1.279122	-2.250162
29	6	0	3.574297	0.606123	0.134997
30	1	0	4.440337	-0.027242	0.363127

31	1	0	3.772204	1.100539	-0.822520
32	1	0	3.514736	1.374798	0.912879

[a] Atomic Units = Hartrees

M06-2X/ccpVTZ

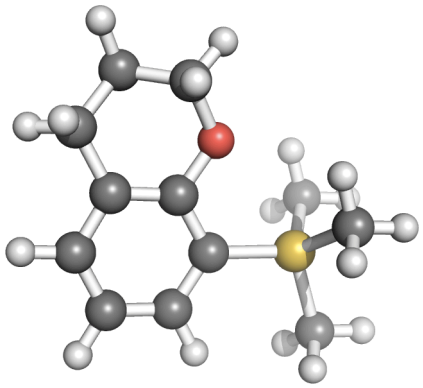
Sum of electronic and thermal Enthalpies = -832.453974 A.U.[a]

Imaginary frequency: -167.2388 cm^{-1}

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.272975	0.113668	0.231595
2	6	0	-3.499737	-1.255594	0.078605
3	6	0	-2.455309	-2.134272	-0.208515
4	6	0	-1.151849	-1.610463	-0.344274
5	6	0	-1.116161	-0.345752	-0.168991
6	6	0	-1.989467	0.669955	0.111563
7	1	0	-4.098113	0.783338	0.445034
8	1	0	-4.509484	-1.634615	0.180594
9	1	0	-2.665584	-3.191740	-0.324938
10	6	0	-1.702696	2.133195	0.276618
11	1	0	-2.595743	2.692781	-0.001078
12	1	0	-1.516293	2.340994	1.334425
13	6	0	-0.502816	2.594311	-0.537602
14	1	0	-0.665194	2.396818	-1.599327
15	1	0	-0.374636	3.670556	-0.417513
16	6	0	0.781189	1.929388	-0.096832
17	1	0	1.628980	2.350204	-0.638321
18	1	0	0.939726	2.091832	0.974095
19	8	0	0.722015	0.518666	-0.363226
20	14	0	2.044755	-0.473645	0.069216
21	6	0	1.737265	-1.153954	1.776839
22	1	0	2.638252	-1.643104	2.153918
23	1	0	1.480230	-0.348669	2.468911
24	1	0	0.926608	-1.882425	1.781584
25	6	0	2.246499	-1.793502	-1.227893
26	1	0	3.225073	-2.265920	-1.111283
27	1	0	1.482588	-2.565881	-1.158058
28	1	0	2.203640	-1.357694	-2.228061
29	6	0	3.562955	0.614901	0.079907
30	1	0	4.431271	-0.005672	0.314690
31	1	0	3.737995	1.074878	-0.894454
32	1	0	3.506611	1.404729	0.830442

[a] Atomic Units = Hartrees

Computed energy and geometry of VIII



M06-2X/6-311G(d,p)

Sum of electronic and thermal Enthalpies = -832.488052 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.923479	2.128566	0.039610
2	6	0	0.718544	2.817778	0.024949
3	6	0	-0.477693	2.101184	0.000102
4	6	0	-0.489160	0.704618	0.001631
5	6	0	0.749460	0.041054	0.029747
6	6	0	1.966877	0.732995	0.040302
7	1	0	2.862506	2.674303	0.042600
8	1	0	0.708997	3.901553	0.024561
9	1	0	-1.418040	2.643618	-0.019386
10	6	0	3.284671	-0.009791	0.027677
11	1	0	3.984664	0.505225	-0.634174
12	1	0	3.722997	0.007594	1.031255
13	6	0	3.077008	-1.457162	-0.409174
14	1	0	2.869836	-1.508072	-1.482186
15	1	0	3.963712	-2.060501	-0.206421
16	6	0	1.892211	-2.027091	0.345894
17	1	0	1.697315	-3.066351	0.085298
18	1	0	2.059085	-1.958742	1.427498
19	8	0	0.688693	-1.323834	0.021946
20	14	0	-2.098090	-0.287974	-0.020195
21	6	0	-2.237768	-1.323604	1.538912
22	1	0	-3.190546	-1.861854	1.559553
23	1	0	-1.430380	-2.058212	1.587801
24	1	0	-2.185314	-0.698782	2.435214
25	6	0	-3.528827	0.926907	-0.085368
26	1	0	-4.473505	0.374021	-0.105378
27	1	0	-3.549963	1.584214	0.788665
28	1	0	-3.493762	1.552345	-0.982026

29	6	0	-2.165015	-1.392792	-1.536617
30	1	0	-3.115850	-1.933437	-1.575833
31	1	0	-2.075964	-0.805351	-2.455213
32	1	0	-1.354801	-2.125226	-1.520662

[a] Atomic Units = Hartrees

M06-2X/6-31G(d)

Sum of electronic and thermal Enthalpies = -832.312045 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.927298	-2.129796	0.039409
2	6	0	-0.720668	-2.819736	0.024371
3	6	0	0.475940	-2.101057	-0.000436
4	6	0	0.488262	-0.702764	0.002422
5	6	0	-0.752558	-0.040350	0.031824
6	6	0	-1.971473	-0.732804	0.041314
7	1	0	-2.867943	-2.676812	0.041680
8	1	0	-0.710754	-3.905491	0.023065
9	1	0	1.418576	-2.643710	-0.021009
10	6	0	-3.289131	0.011085	0.028037
11	1	0	-3.993456	-0.503567	-0.633732
12	1	0	-3.731882	-0.003581	1.032285
13	6	0	-3.080059	1.458386	-0.410732
14	1	0	-2.872039	1.508664	-1.485660
15	1	0	-3.968748	2.063670	-0.210290
16	6	0	-1.894166	2.028421	0.345108
17	1	0	-1.697586	3.069613	0.082960
18	1	0	-2.064710	1.965213	1.428677
19	8	0	-0.691518	1.326104	0.025402
20	14	0	2.097539	0.286993	-0.020504
21	6	0	2.254058	1.313382	1.548357
22	1	0	3.198346	1.870709	1.552881
23	1	0	1.434071	2.034054	1.628216
24	1	0	2.236888	0.679419	2.442084
25	6	0	3.531482	-0.930588	-0.098582
26	1	0	4.479106	-0.378902	-0.119586
27	1	0	3.557950	-1.594687	0.772703
28	1	0	3.494725	-1.553843	-0.999118
29	6	0	2.167892	1.402517	-1.534660
30	1	0	3.118081	1.948760	-1.566743
31	1	0	2.088218	0.819681	-2.459412

32	1	0	1.354079	2.133894	-1.523739

[a] Atomic Units = Hartrees

M06-2X/ccpVTZ

Sum of electronic and thermal Enthalpies = -832.550958 A.U.[a]

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.916361	2.125432	0.039306
2	6	0	0.711822	2.808868	0.021628
3	6	0	-0.478484	2.088731	-0.003861
4	6	0	-0.486074	0.695371	-0.001117
5	6	0	0.752648	0.038317	0.028825
6	6	0	1.964953	0.733351	0.041640
7	1	0	2.851791	2.673597	0.043209
8	1	0	0.698043	3.890700	0.020012
9	1	0	-1.418936	2.626853	-0.025248
10	6	0	3.283066	-0.002000	0.033140
11	1	0	3.984076	0.519072	-0.619332
12	1	0	3.715212	0.012831	1.037240
13	6	0	3.086043	-1.445531	-0.409265
14	1	0	2.883552	-1.493588	-1.481291
15	1	0	3.973673	-2.043849	-0.207041
16	6	0	1.905389	-2.023779	0.339045
17	1	0	1.717302	-3.061396	0.073406
18	1	0	2.072462	-1.963013	1.419293
19	8	0	0.700322	-1.325550	0.021363
20	14	0	-2.098624	-0.289372	-0.019659
21	6	0	-2.253119	-1.306468	1.548500
22	1	0	-3.201835	-1.848071	1.558980
23	1	0	-1.444852	-2.034900	1.622333
24	1	0	-2.220506	-0.669380	2.434551
25	6	0	-3.520345	0.932511	-0.098983
26	1	0	-4.465854	0.385122	-0.116066
27	1	0	-3.537708	1.596315	0.767474
28	1	0	-3.477627	1.547467	-0.999955
29	6	0	-2.175553	-1.406738	-1.524745
30	1	0	-3.133063	-1.931617	-1.558118
31	1	0	-2.079137	-0.828546	-2.446003
32	1	0	-1.378669	-2.150373	-1.503802

[a] Atomic Units = Hartrees

IV. Reference for Supplementary Information

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[2] W. Oppolzer, A. Pimm, B. Stammen and W. E. Hume, Palladium-catalyzed intramolecular cyclizations of olefinic propargylic carbonates and application to the diastereoselective synthesis of enantiomerically pure (-)-α-thujone. *Helv. Chim. Acta.* 1997*,* **80,** 623–639.

[3] J. M. Montierth, D. R. DeMario, M. J. Kurth and N. E. Schore, The polymer-supported Cadiot-Chodkiewicz coupling of acetylenes to produce unsymmetrical diynes. *Tetrahedron* 1998, **54**, 11741–11748.

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[5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

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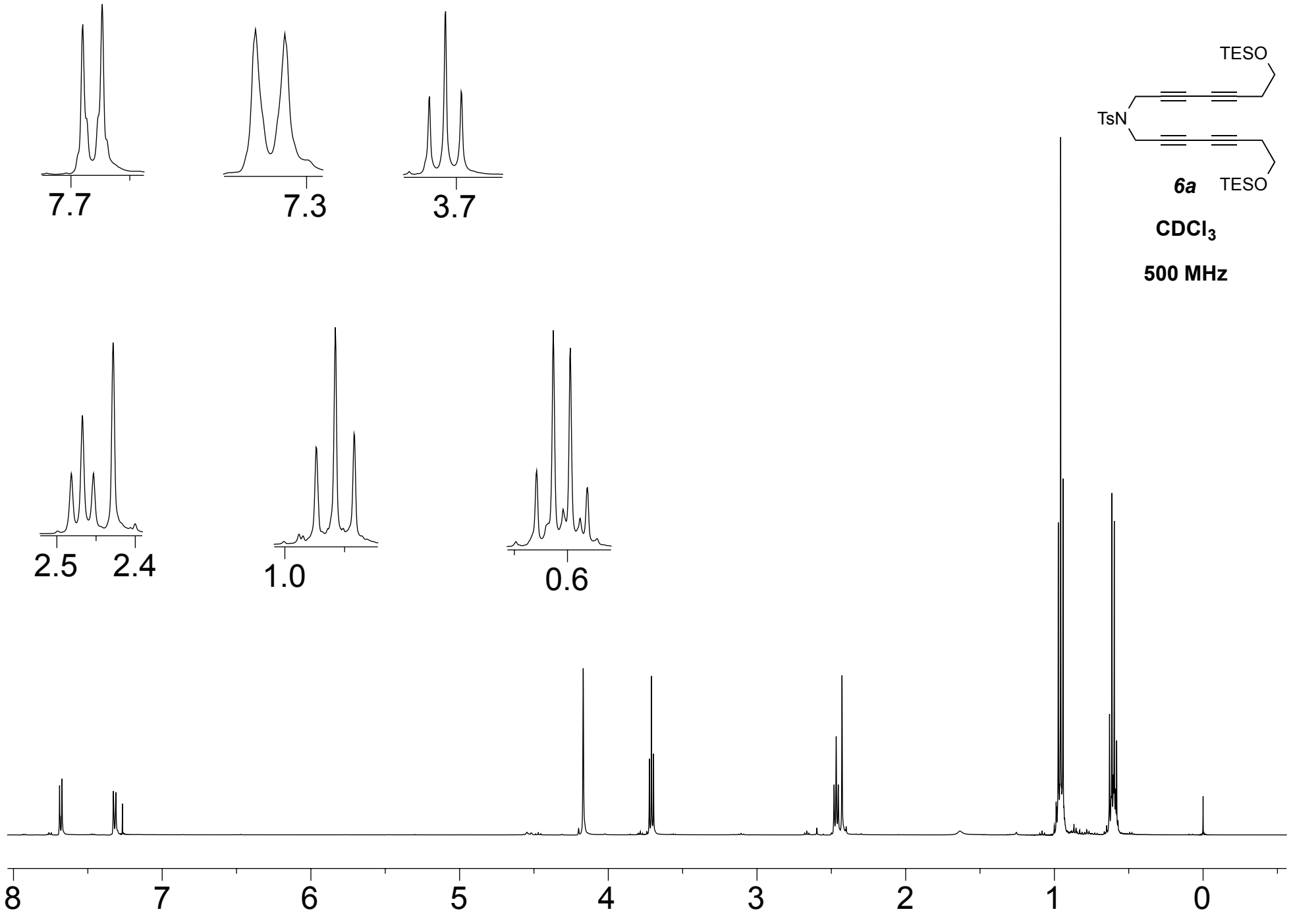
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7.3
3.7
2.5
2.4
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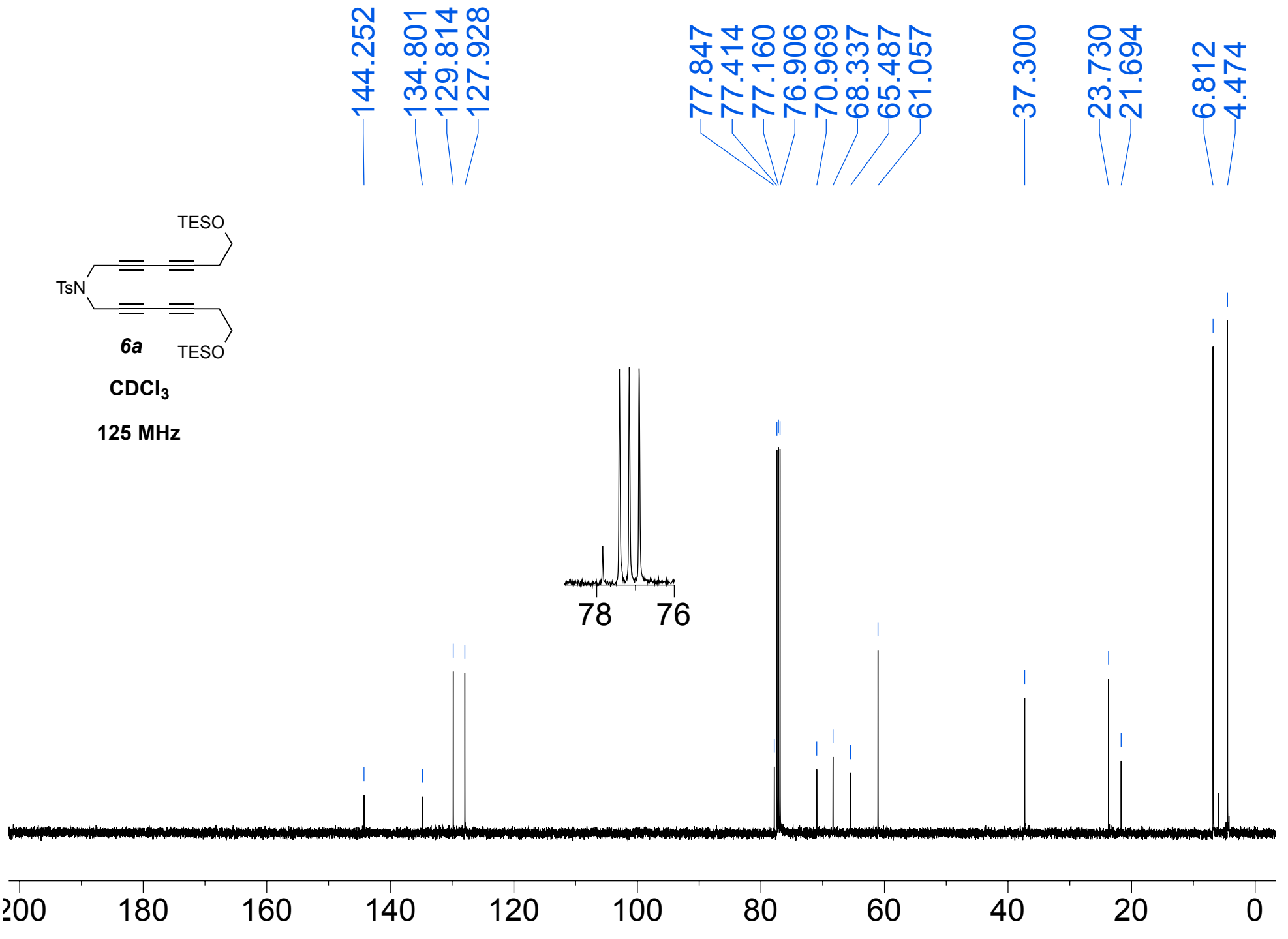
0.6
TESO
TsN
TESO
6a
CDCl3
500 MHz
8
7
6
5
4
3
2
1
0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77.414
77.160
76.906
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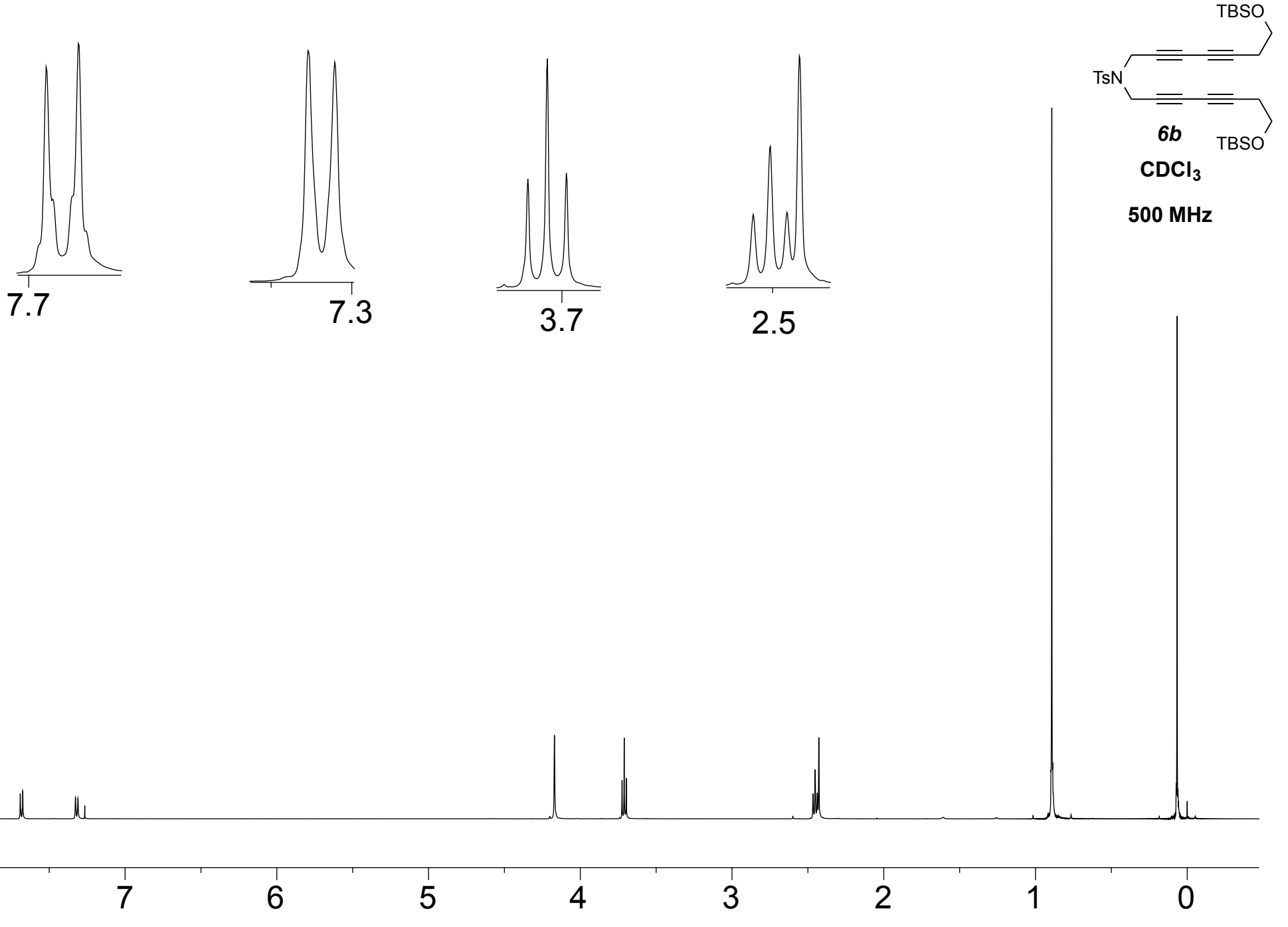
68.337
65.487
61.057
37.300
23.730
21.694
6.812
4.474
TESO
TsN
TESO
6a
CDCl3
125 MHz
78
76
200
180
160
140
120
100
80
60
40
20
0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TsN
TBSO
6b
CDCl3
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7.3
3.7
2.5
8
7
6
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3
2
1
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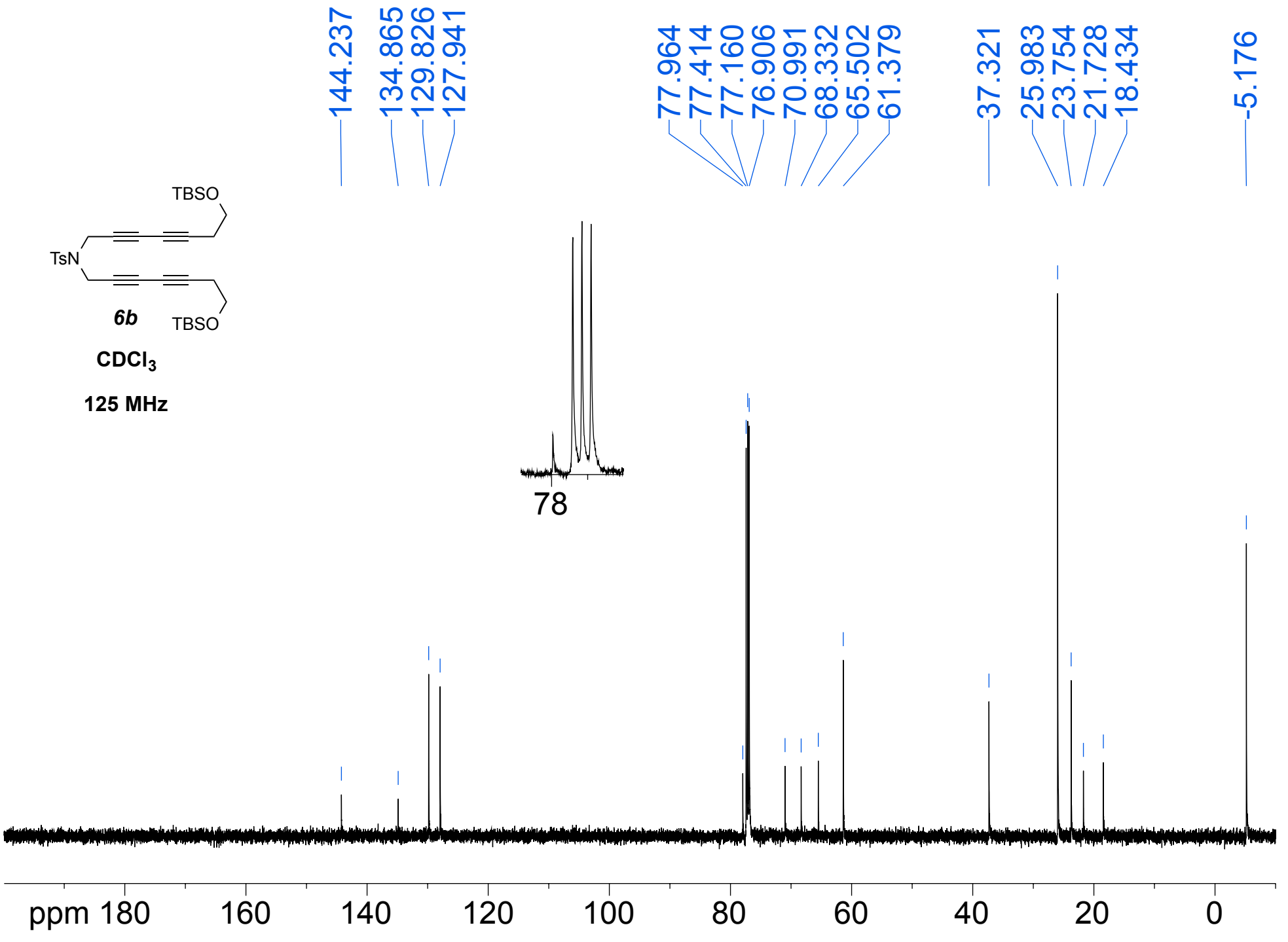
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77.160
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61.379
37.321
25.983
23.754
21.728
18.434
-5.176
TBSO
TsN
TBSO
6b
CDCl3
125 MHz
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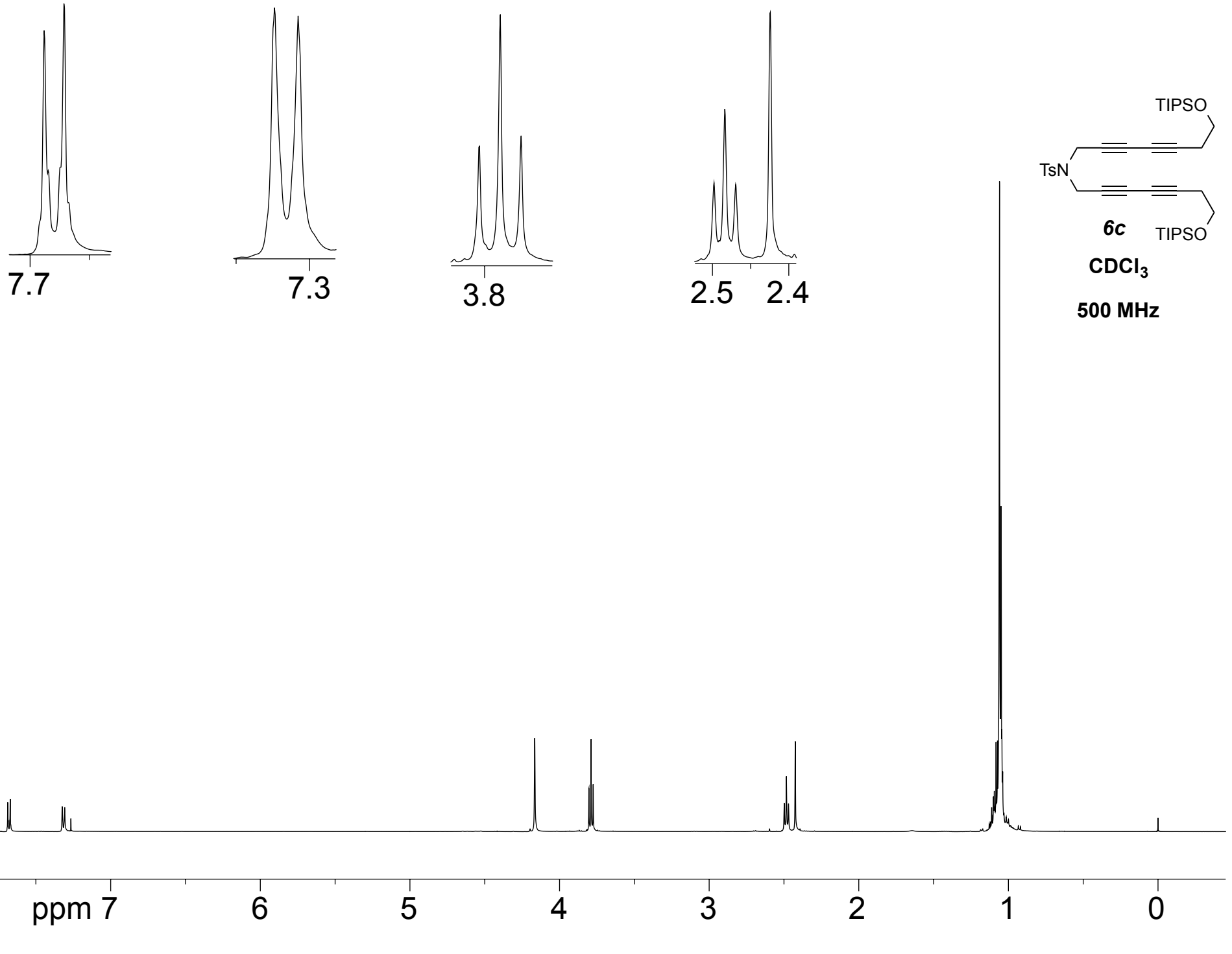
ppm 180
160
140
120
100
80
60
40
20
0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7.3
3.8
2.5
2.4
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TsN
TIPSO
6c
CDCl3
500 MHz
ppm 7
6
5
4
3
2
1
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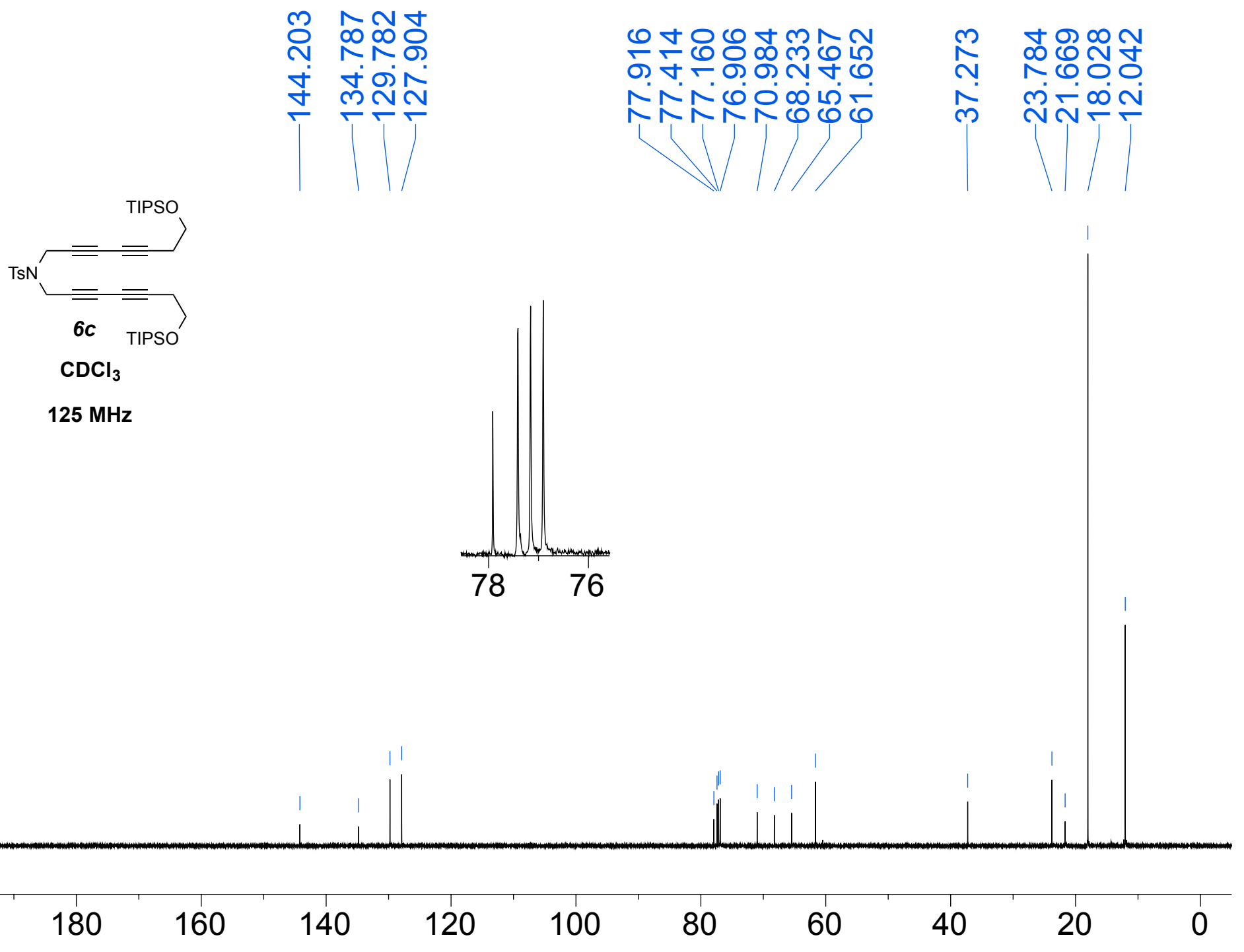
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37.273
23.784
21.669
18.028
12.042
TIPSO
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CDCl3
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76
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140
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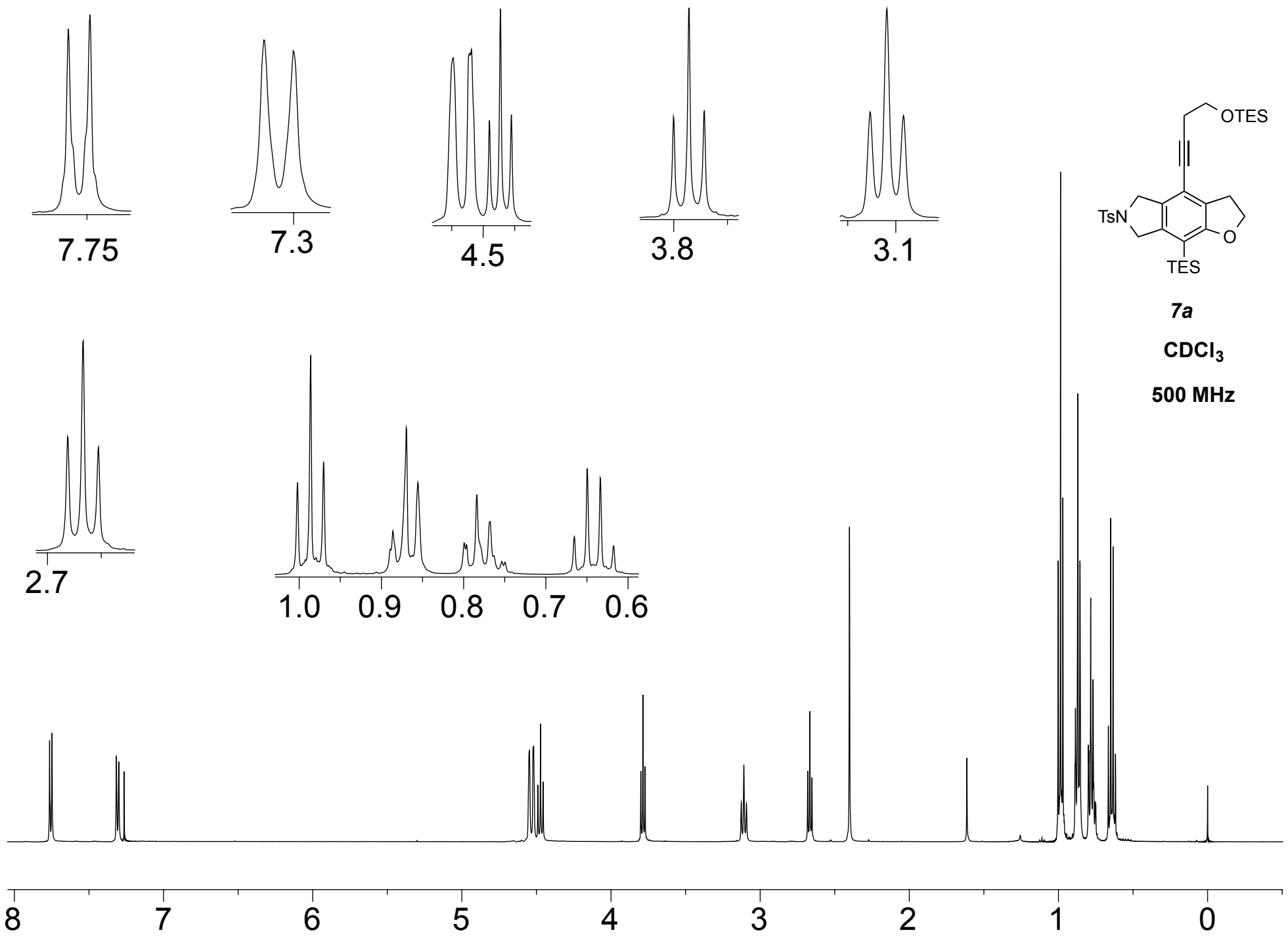
80
60
40
20
0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7.3
4.5
3.8
3.1
2.7
1.0
0.9
0.8
0.7
0.6
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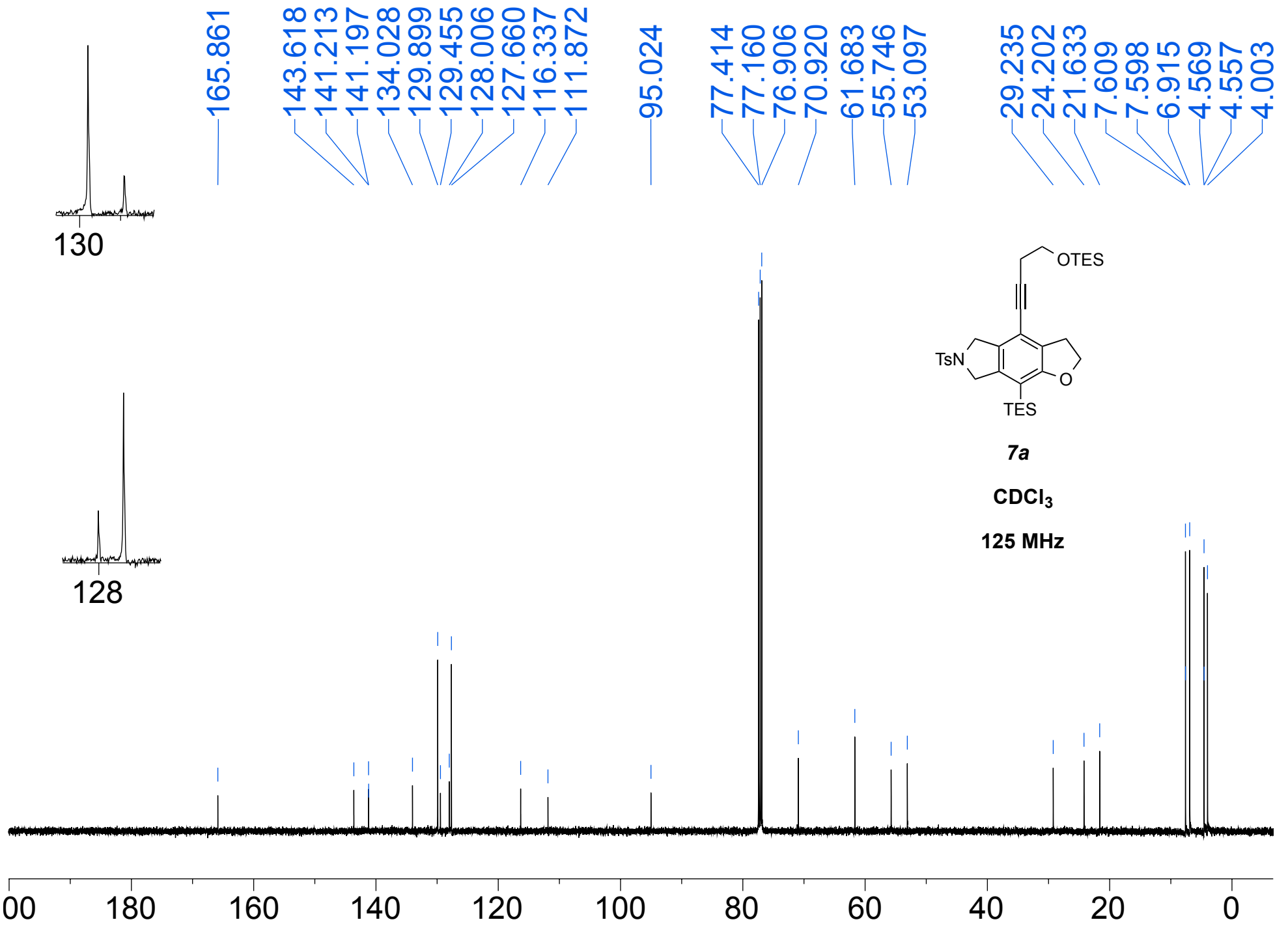
TsN
O
TES
7a
CDCl3
500 MHz
8
7
6
5
4
3
2
1
0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128.006
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77.414
77.160
76.906
70.920
61.683
55.746
53.097
29.235
24.202
21.633
7.609
7.598
6.915
4.569
4.557
4.003
130
128
OTES
TsN
O
TES
7a
CDCl3
125 MHz
00
180
160
140
120
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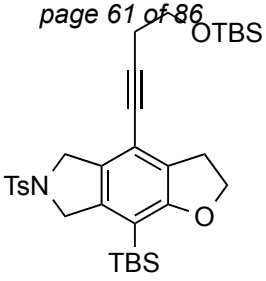
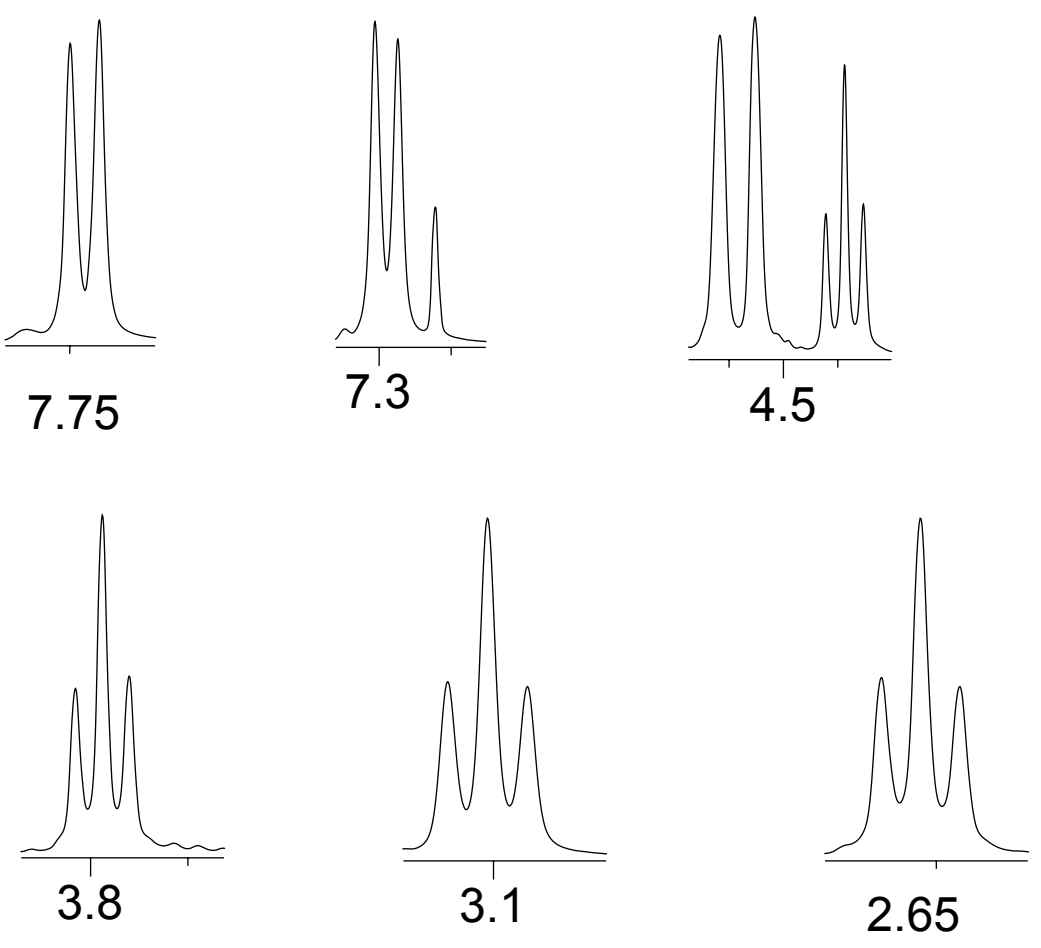
80
60
40
20
0

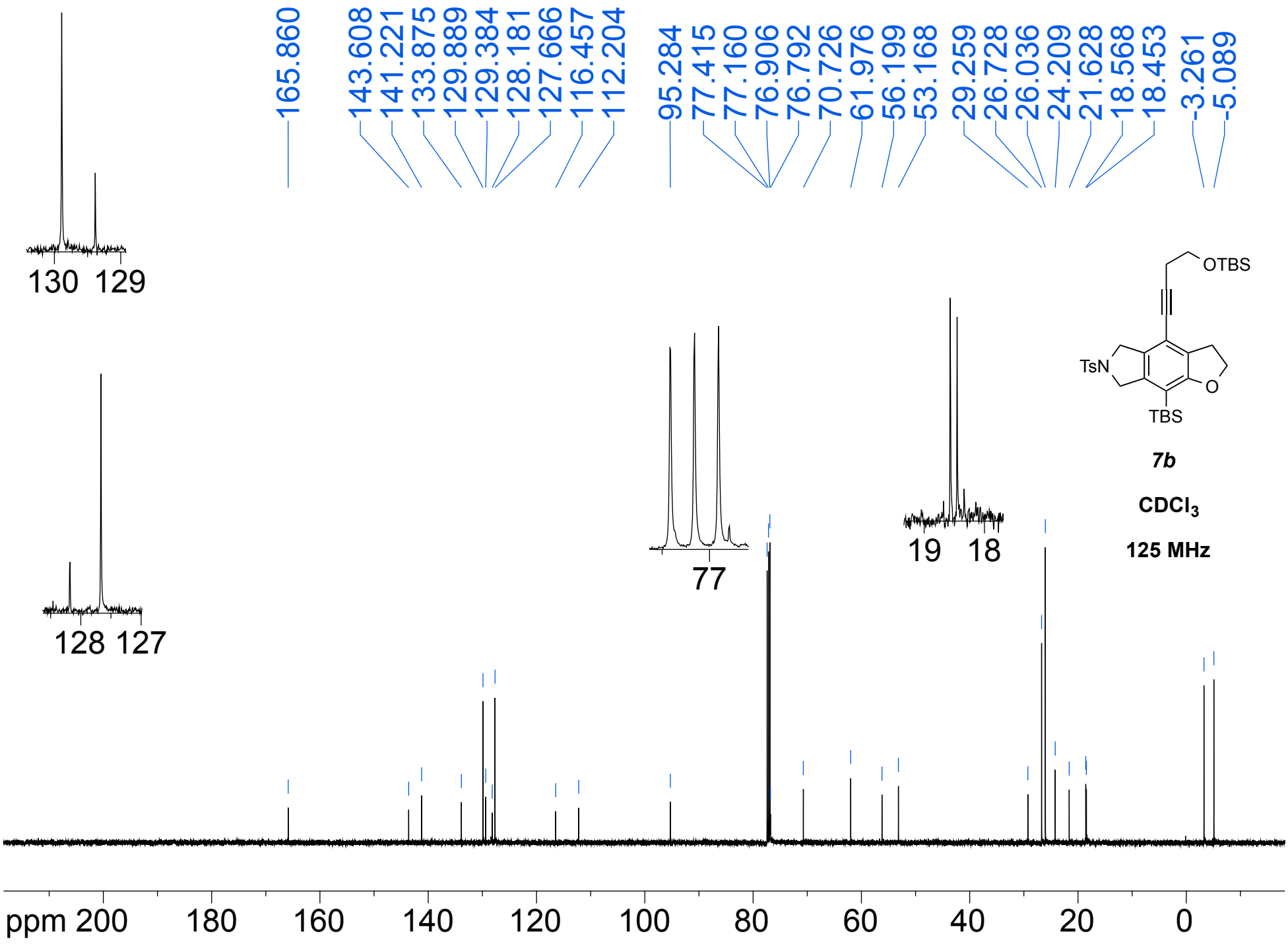


7b

$CDCl_3$

500 MHz

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77.160
76.906
76.792
70.726
61.976
56.199
53.168
29.259
26.728
26.036
24.209
21.628
18.568
18.453
-3.261
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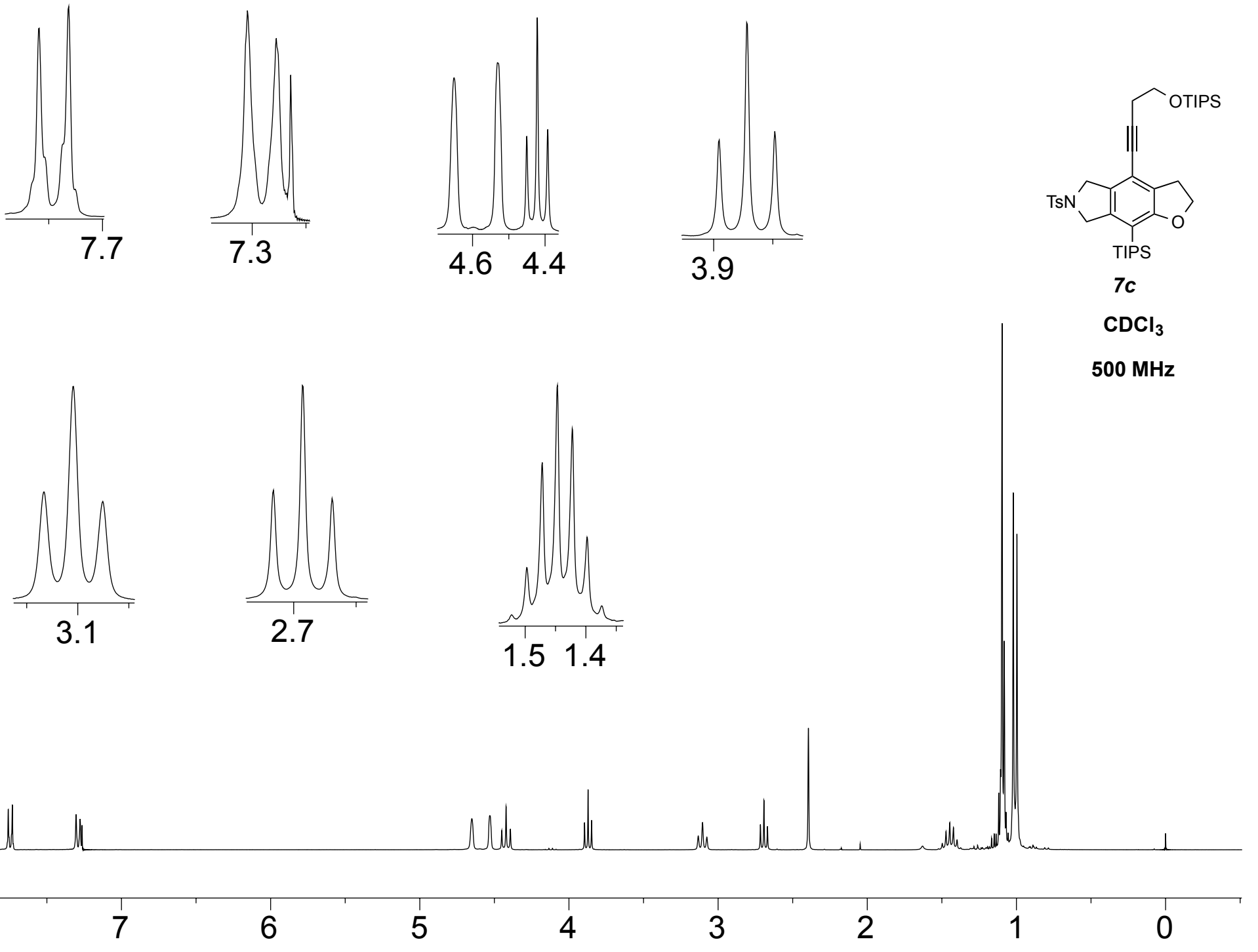
130 129
128 127
77
19 18
OTBS
TsN
O
TBS
7b
CDCl3
125 MHz
ppm 200 180 160 140 120 100 80 60 40 20 0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7.3
4.6
4.4
3.9
3.1
2.7
1.5
1.4
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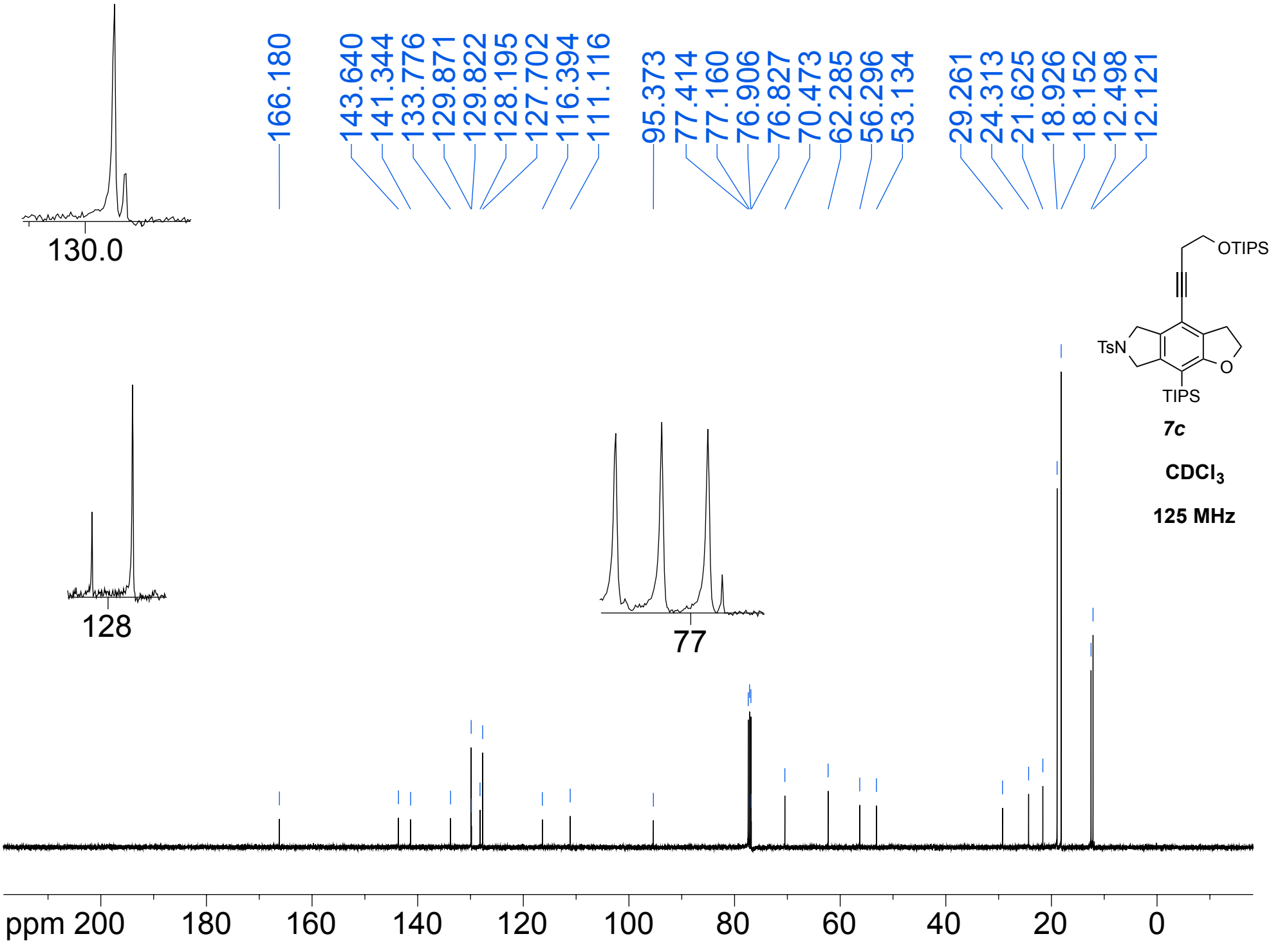
TsN
O
TIPS
7c
CDCl3
500 MHz
8
7
6
5
4
3
2
1
0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77.160
76.906
76.827
70.473
62.285
56.296
53.134
29.261
24.313
21.625
18.926
18.152
12.498
12.121
130.0
128
77
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TsN
O
TIPS
7c
CDCl3
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180
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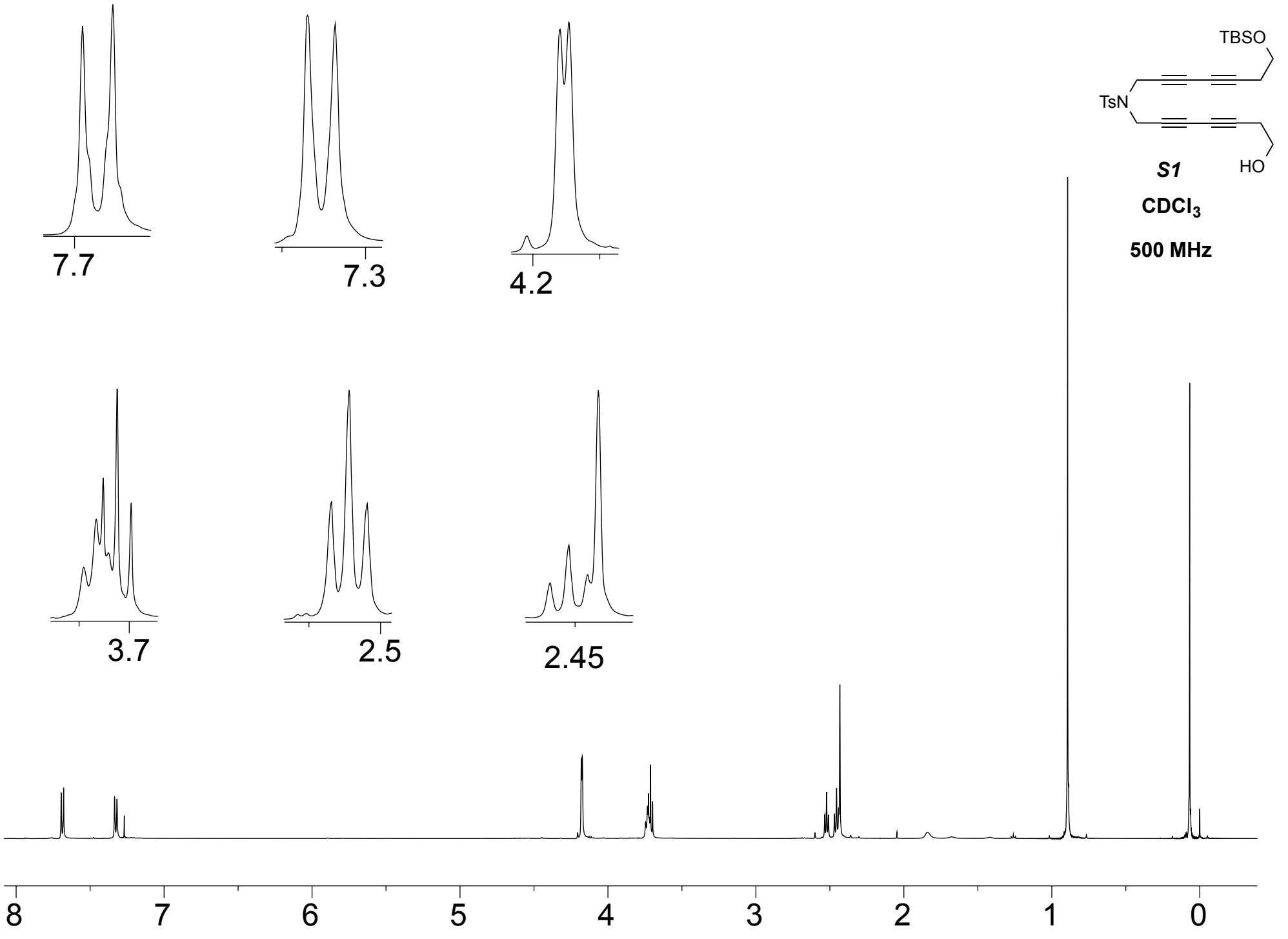
140
120
100
80
60
40
20
0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7.3
4.2
3.7
2.5
2.45
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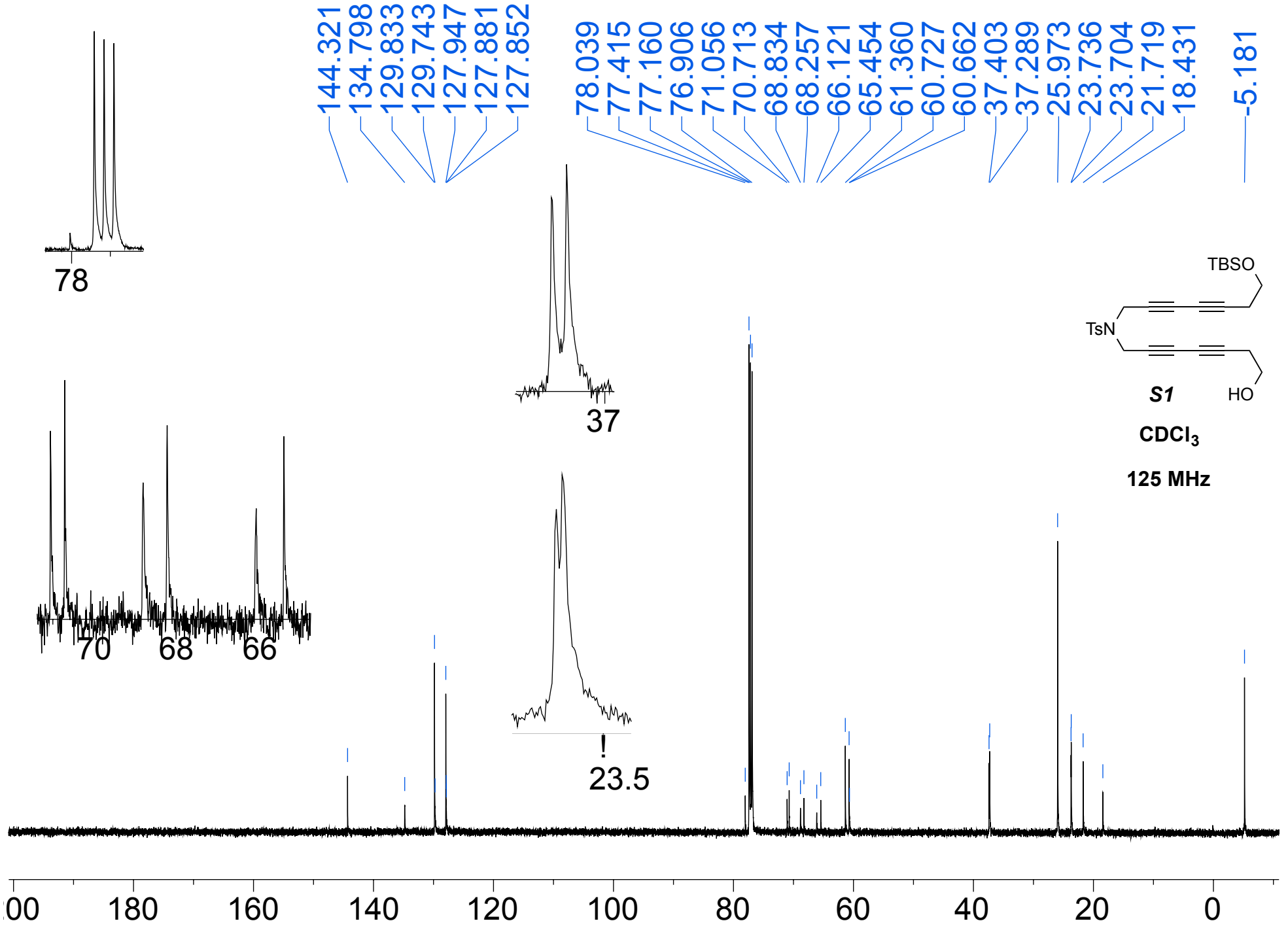
TsN
HO
S1
CDCl3
500 MHz
8
7
6
5
4
3
2
1
0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61.360
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25.973
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23.704
21.719
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78
37
70
68
66
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HO
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125 MHz
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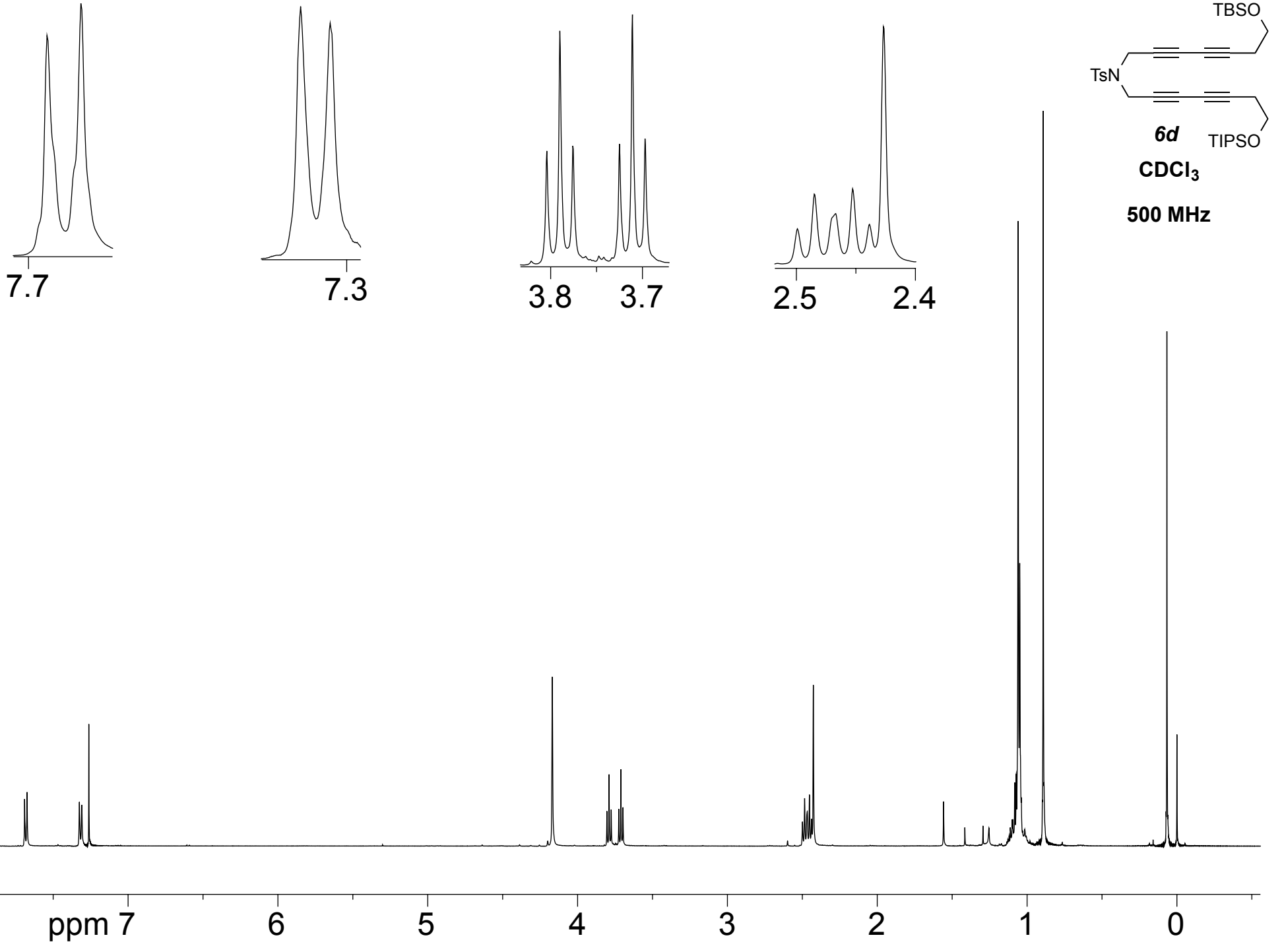
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TsN
TIPSO
6d
CDCl3
500 MHz
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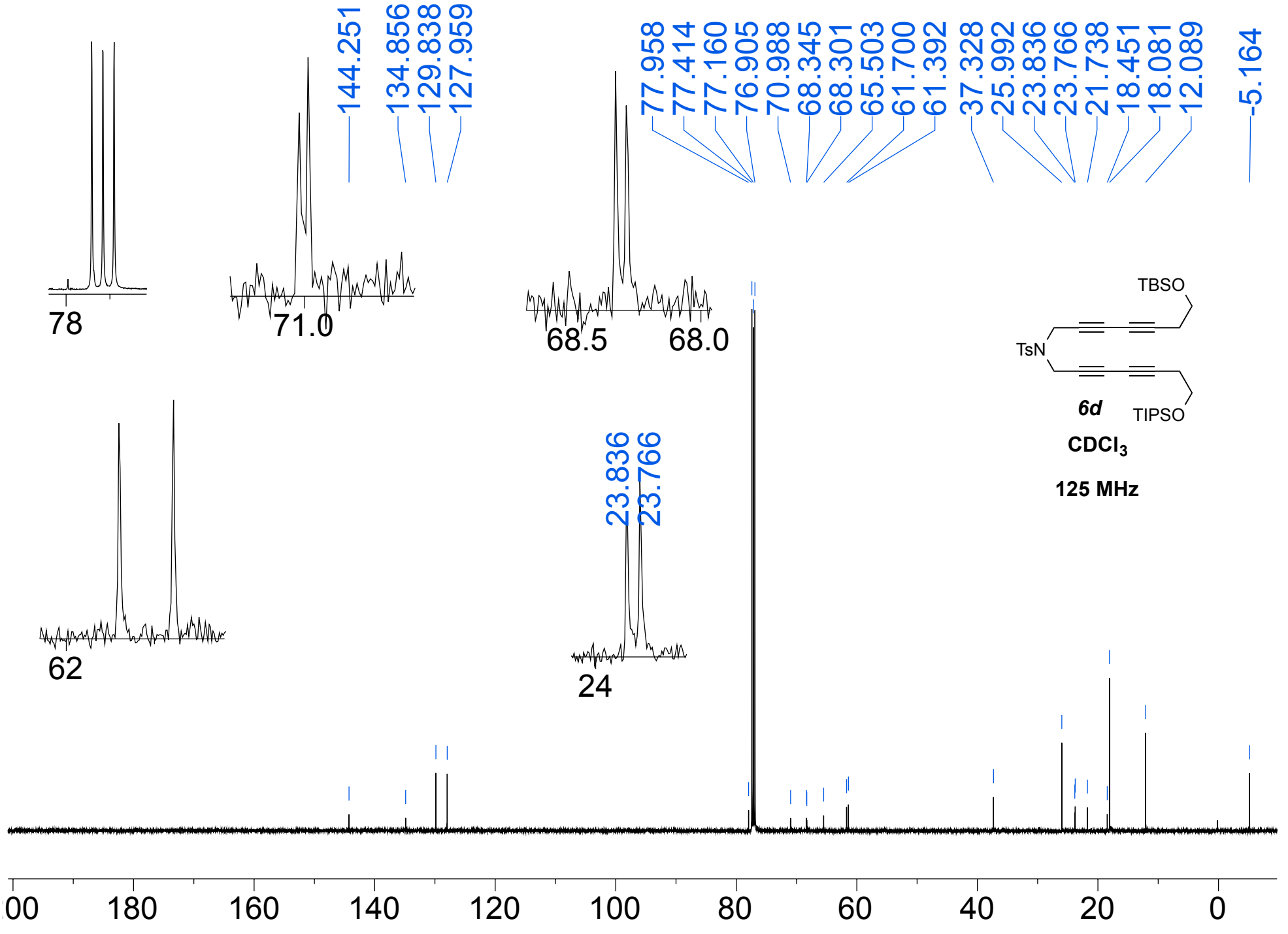
7.3
3.8
3.7
2.5
2.4
ppm 7
6
5
4
3
2
1
0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25.992
23.836
23.766
21.738
18.451
18.081
12.089
-5.164
78
71.0
68.5
68.0
62
24
23.836
23.766
TBSO
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140
120
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20
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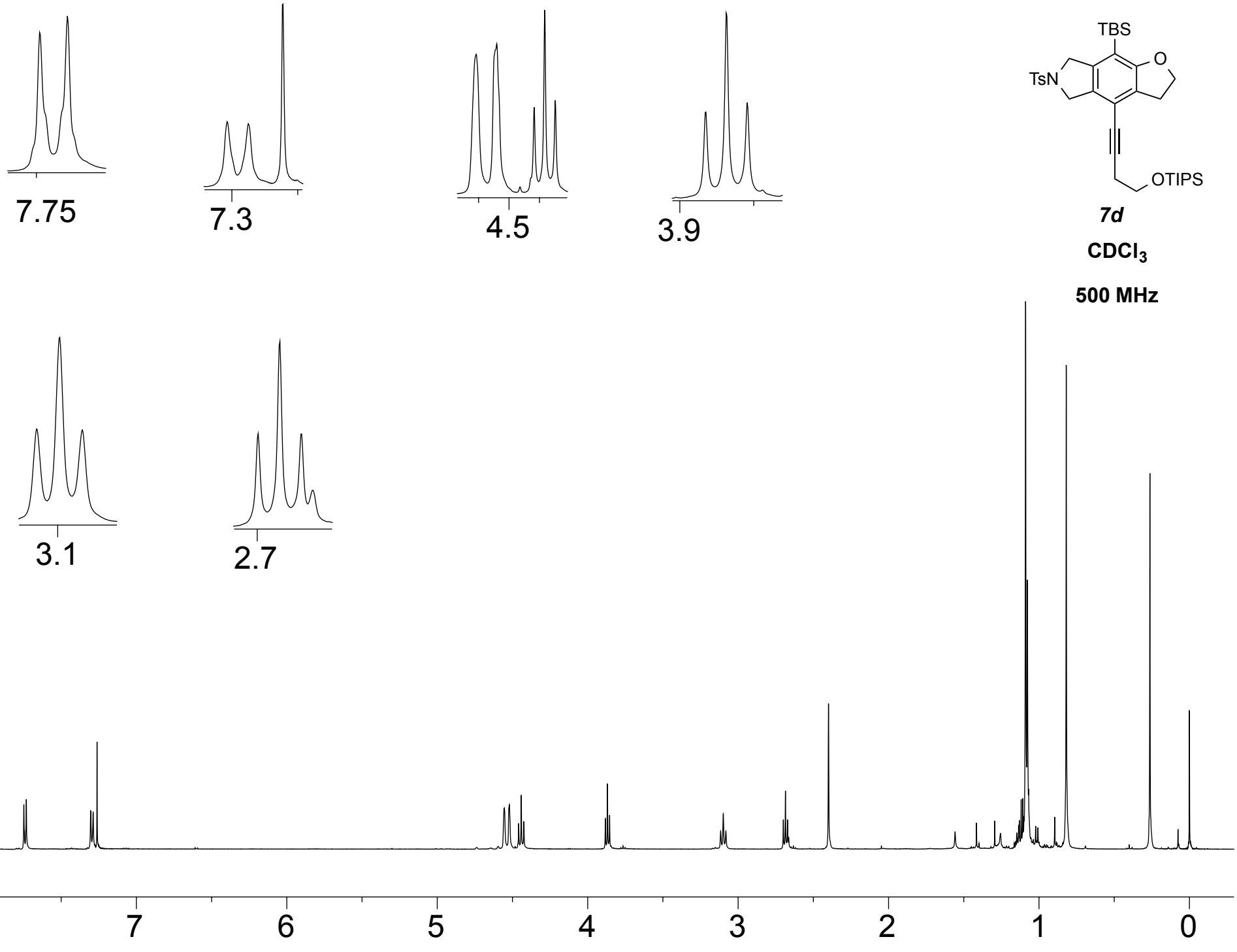
7.75
7.3
4.5
3.9
3.1
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TBS
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TsN
OTIPS
7d
CDCl3
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7
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4
3
2
1
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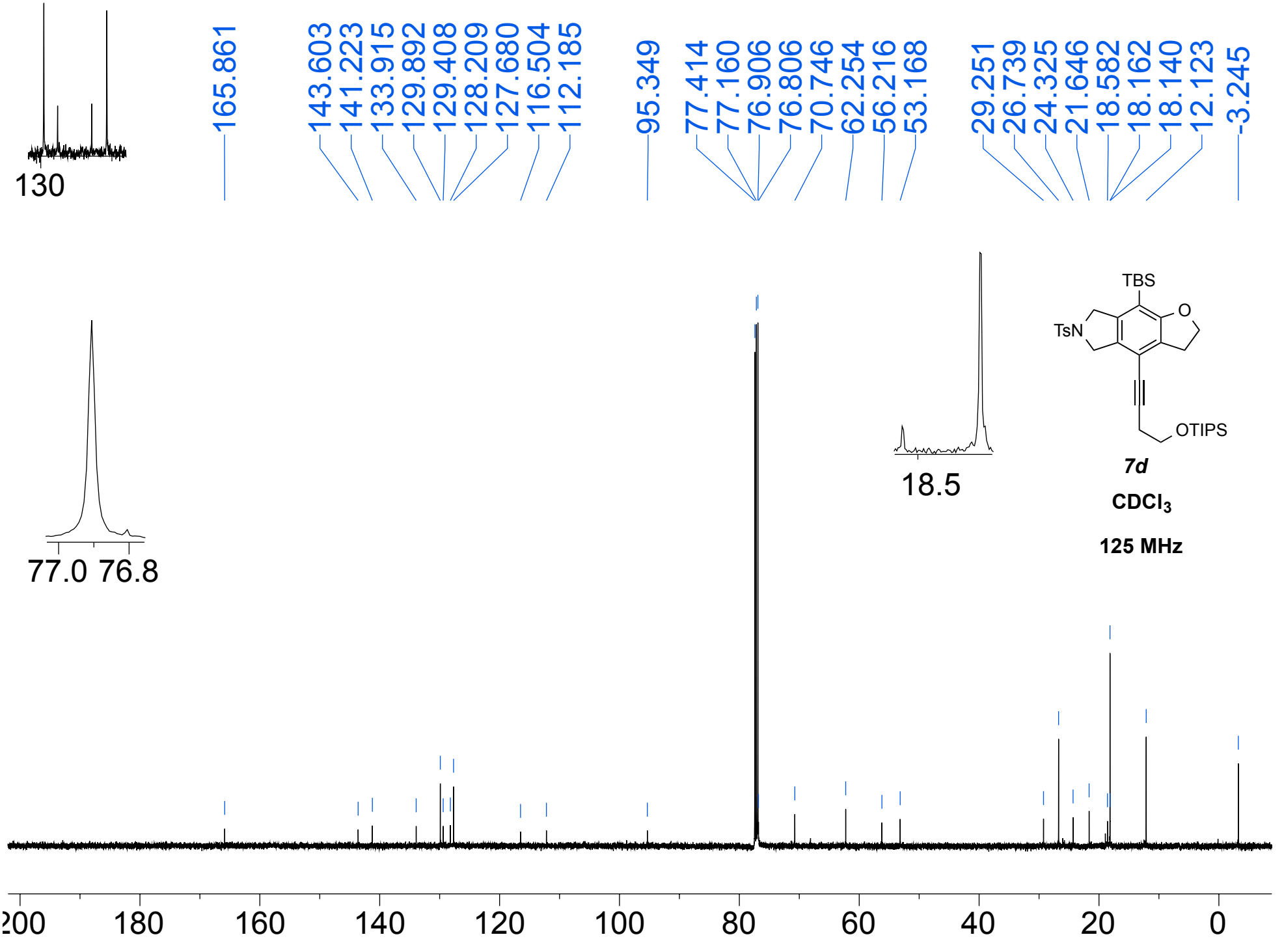
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112.185
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77.414
77.160
76.906
76.806
70.746
62.254
56.216
53.168
29.251
26.739
24.325
21.646
18.582
18.162
18.140
12.123
-3.245
77.0 76.8
18.5
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TsN
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125 MHz
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180
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140
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60
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20
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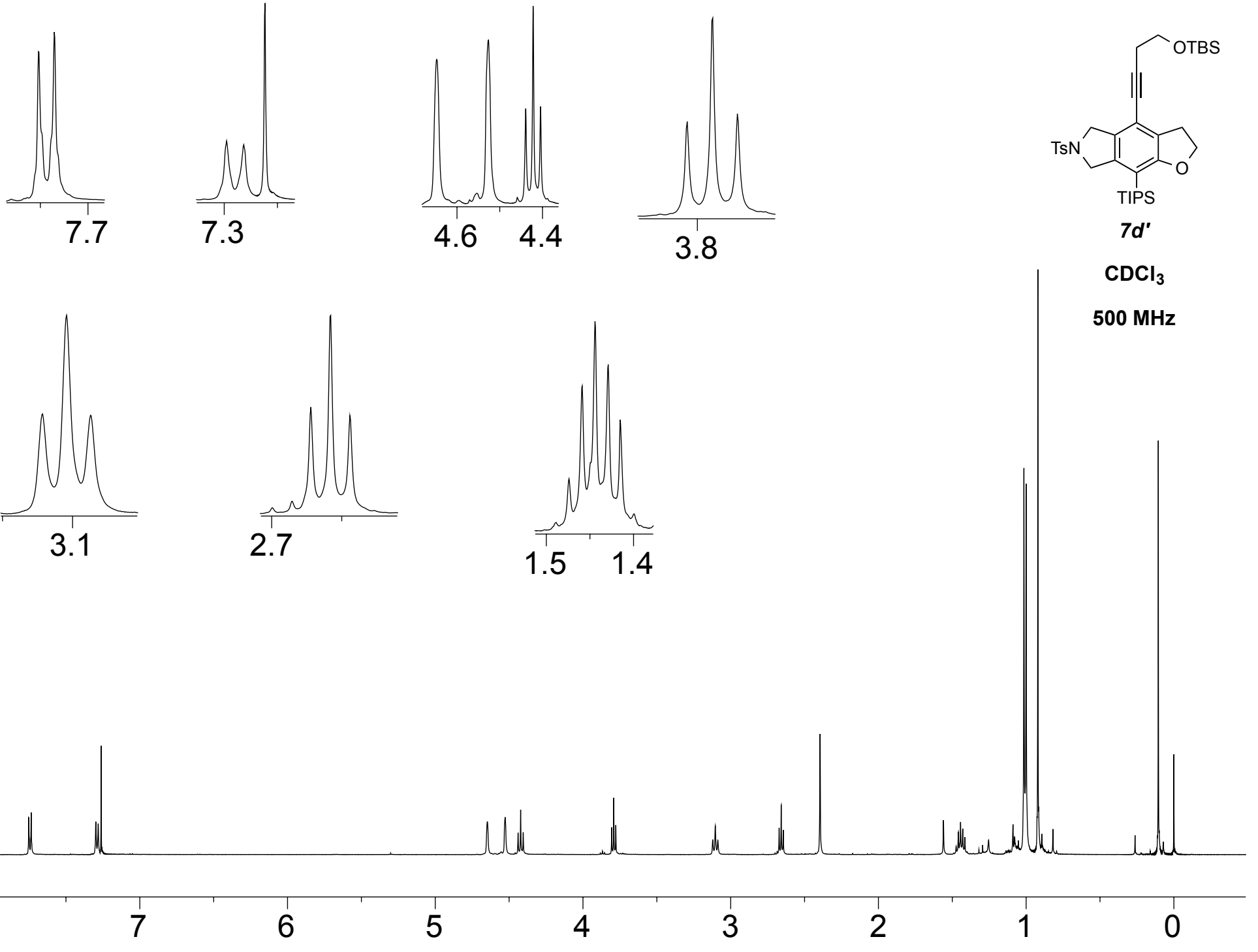
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7.3
4.6
4.4
3.8
3.1
2.7
1.5
1.4
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TsN
O
TIPS
7d'
CDCl3
500 MHz
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7
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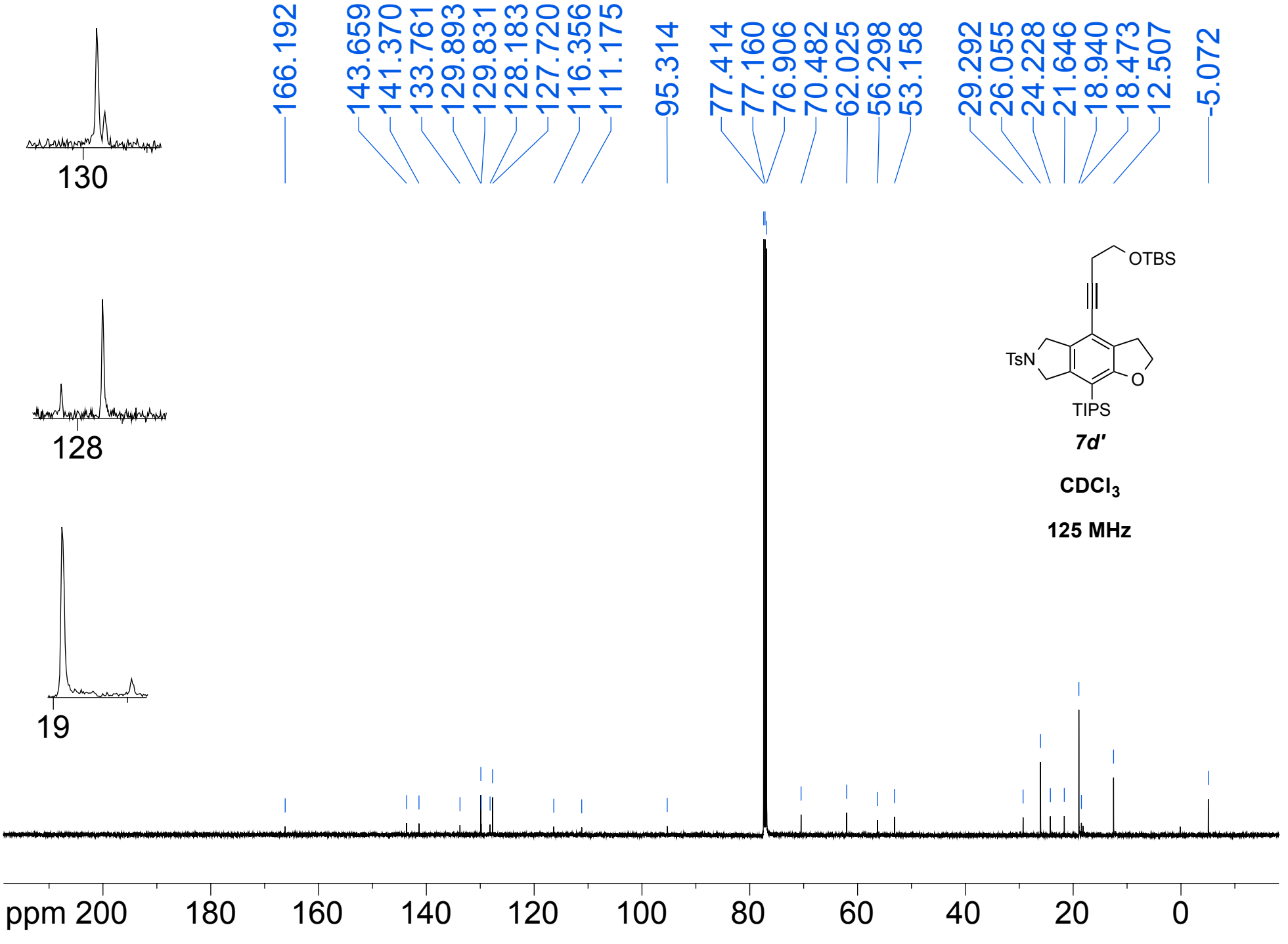
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77.414
77.160
76.906
70.482
62.025
56.298
53.158
29.292
26.055
24.228
21.646
18.940
18.473
12.507
-5.072
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19
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TsN
O
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7d'
CDCl3
125 MHz
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180
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140
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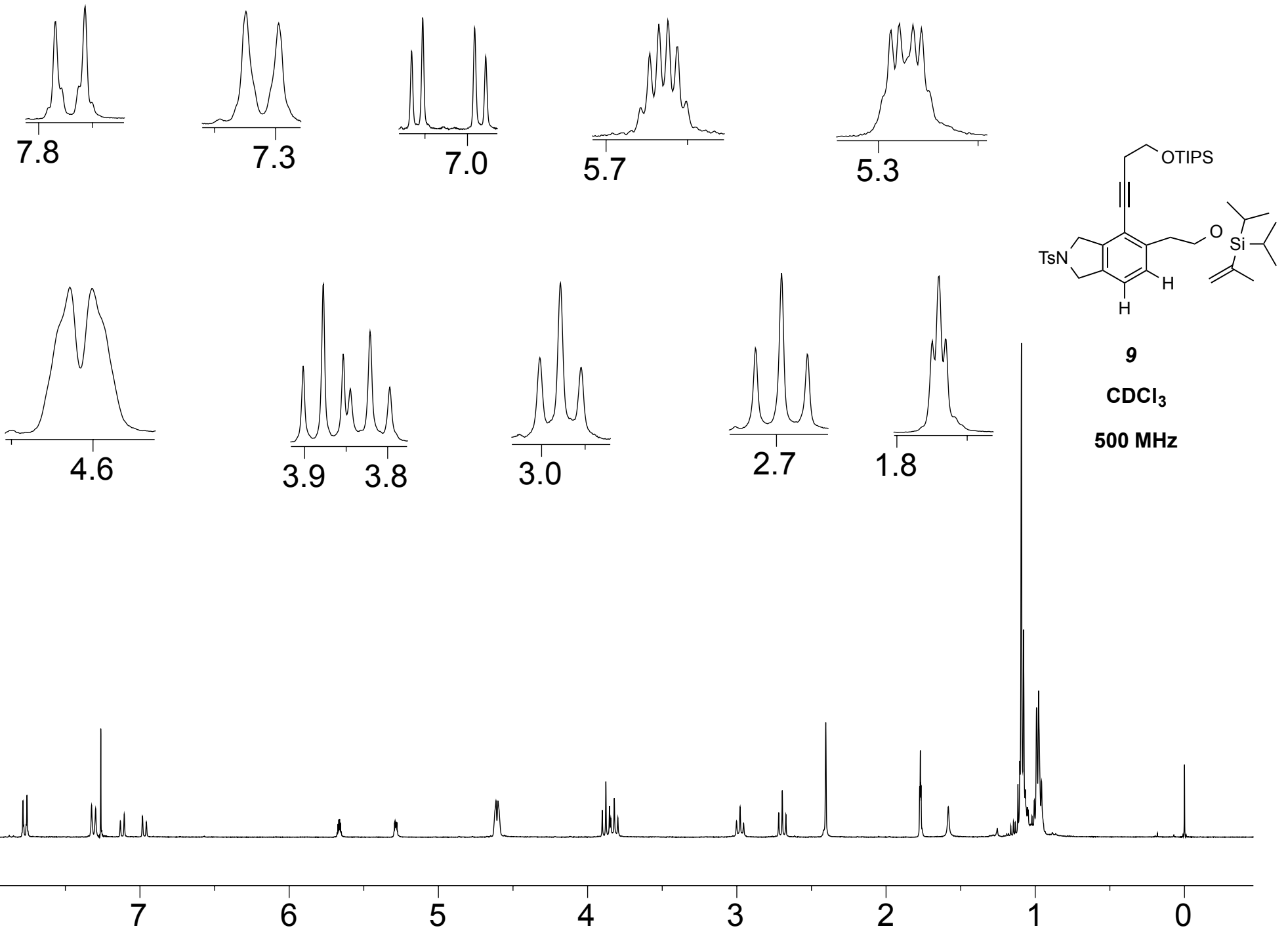
40
20
0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7.3
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5.7
5.3
4.6
3.9
3.8
3.0
2.7
1.8
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TsN
O
Si
H
H
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CDCl3
500 MHz
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7
6
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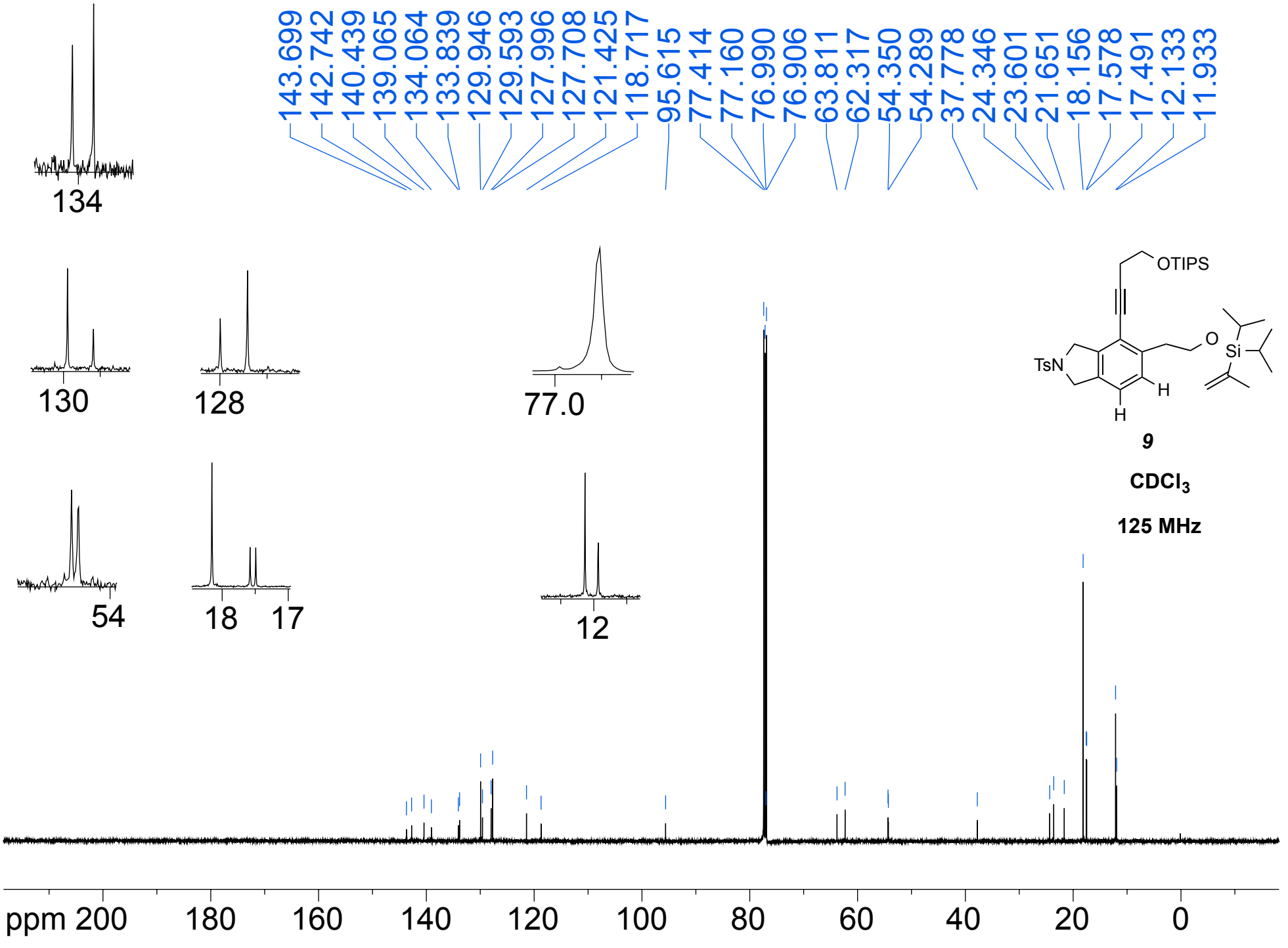
4
3
2
1
0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95.615
77.414
77.160
76.990
76.906
63.811
62.317
54.350
54.289
37.778
24.346
23.601
21.651
18.156
17.578
17.491
12.133
11.933
134
130
128
77.0
54
18
17
12
OTIPS
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Si
TsN
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H
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125 MHz
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180
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140
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20
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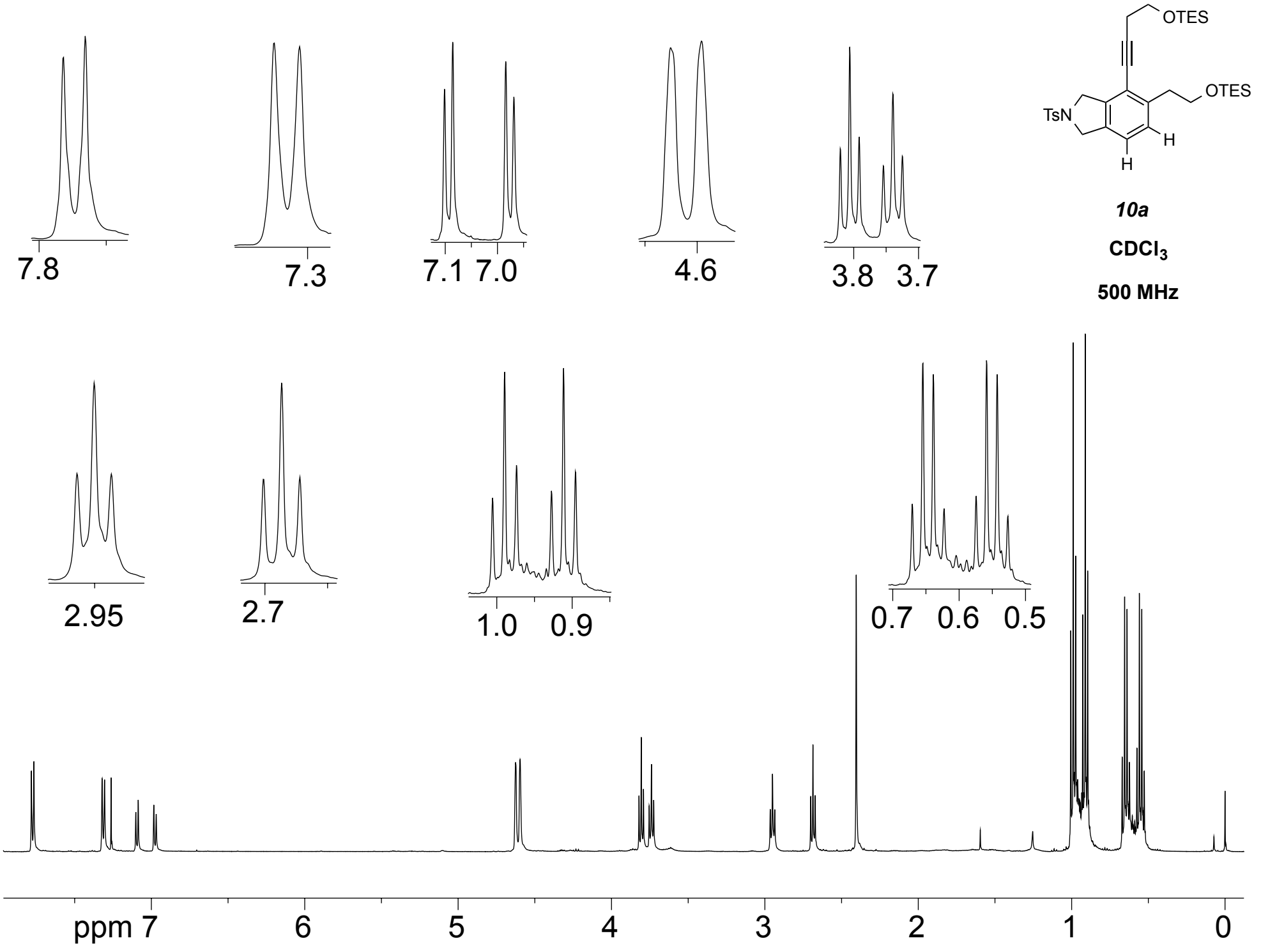
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OTES
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3
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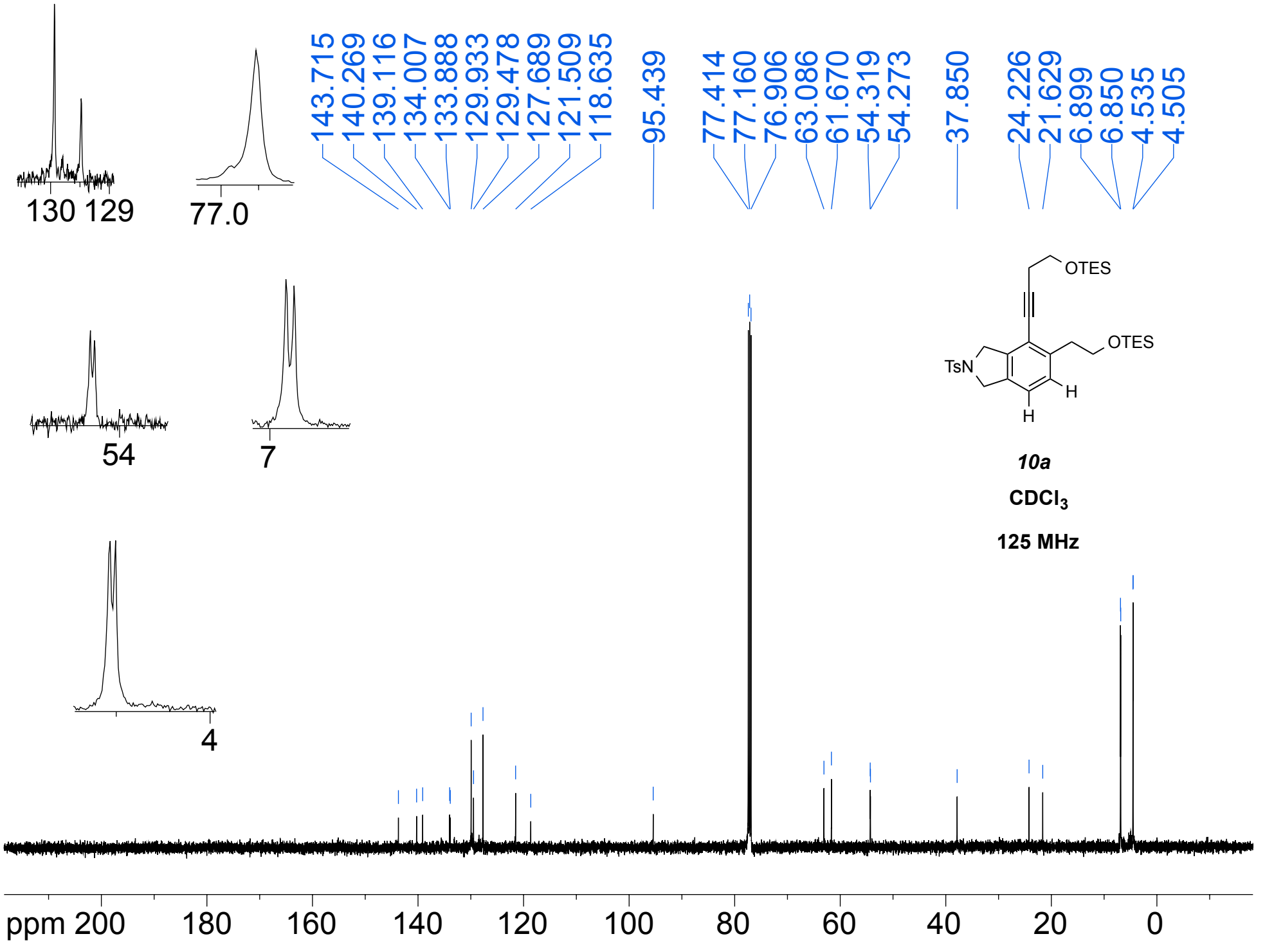
1
0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129.933
129.478
127.689
121.509
118.635
95.439
77.414
77.160
76.906
63.086
61.670
54.319
54.273
37.850
24.226
21.629
6.899
6.850
4.535
4.505
54
7
4
OTES
OTES
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140
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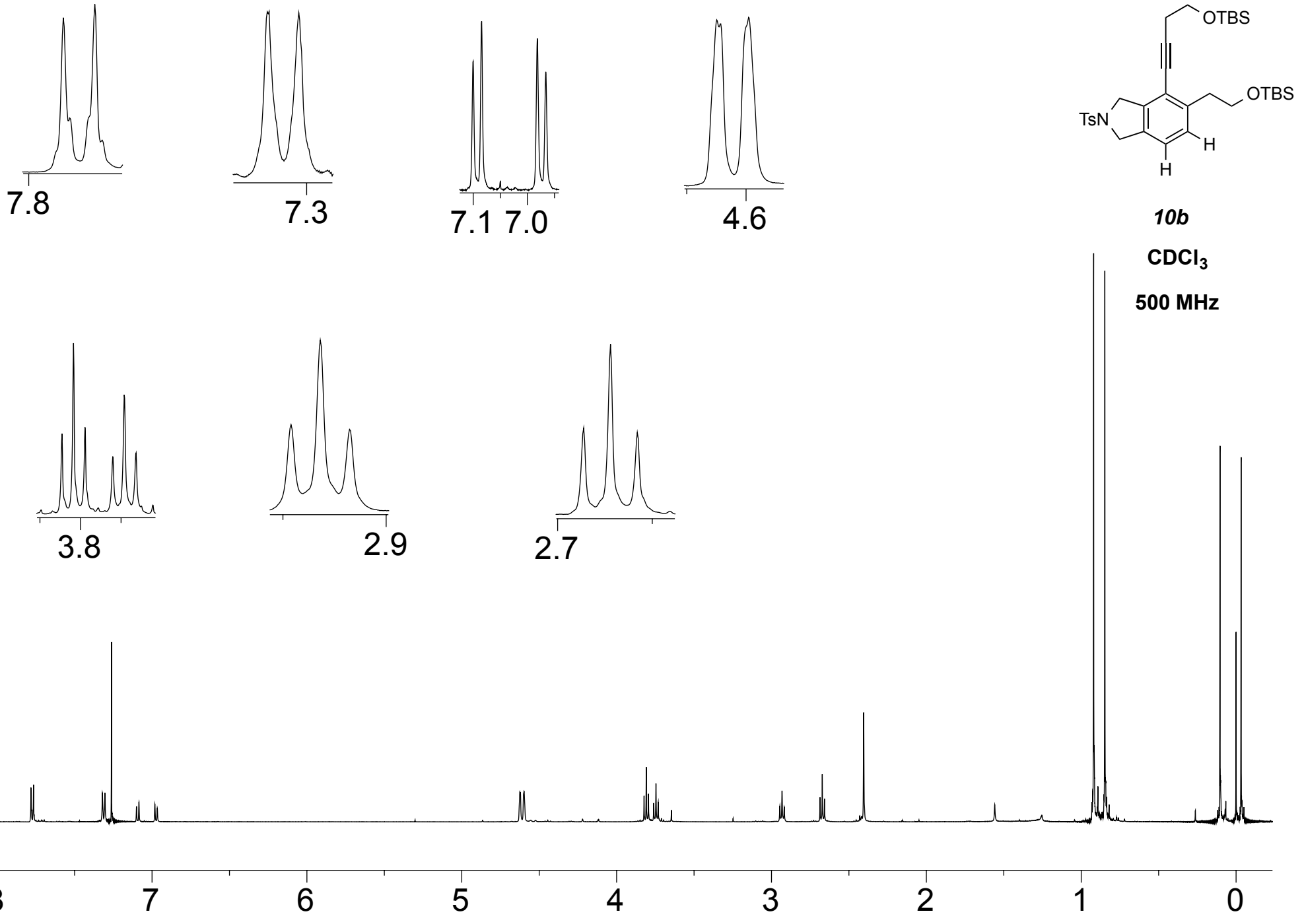
7.8
7.3
7.1 7.0
4.6
OTBS
OTBS
TsN
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2.9
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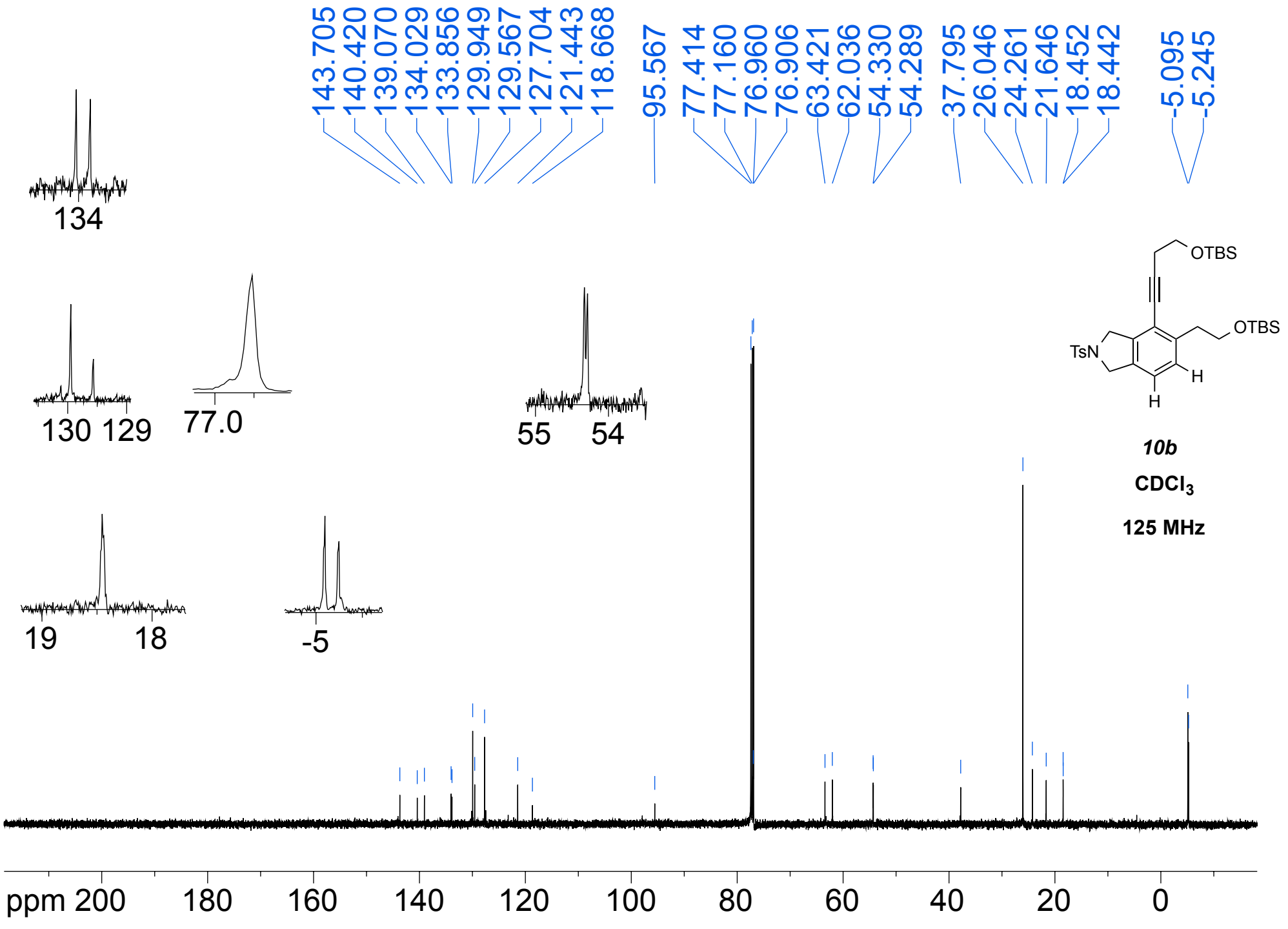
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76.960
76.906
63.421
62.036
54.330
54.289
37.795
26.046
24.261
21.646
18.452
18.442
-5.095
-5.245
134
130 129
77.0
55 54
19 18
-5
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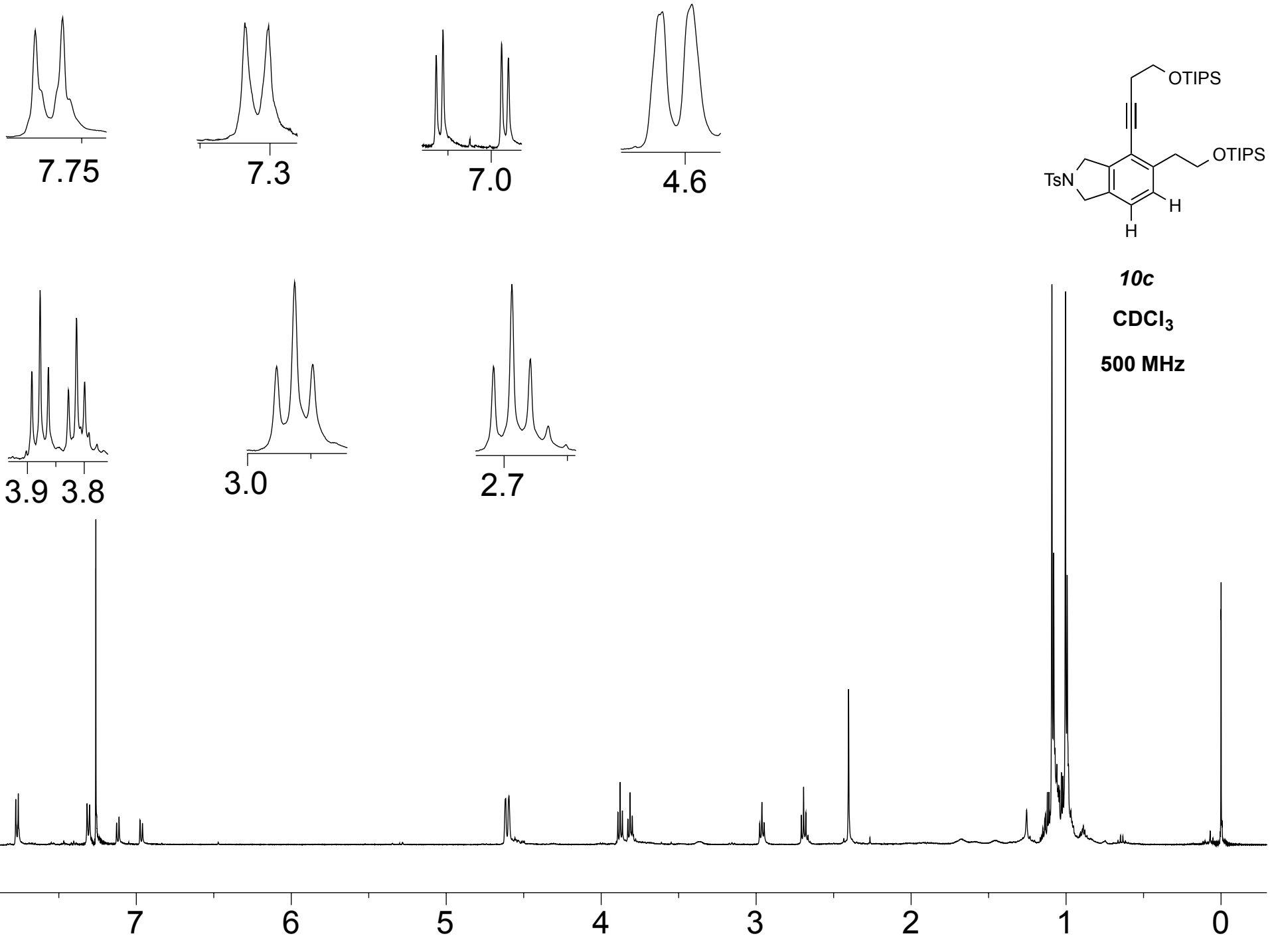
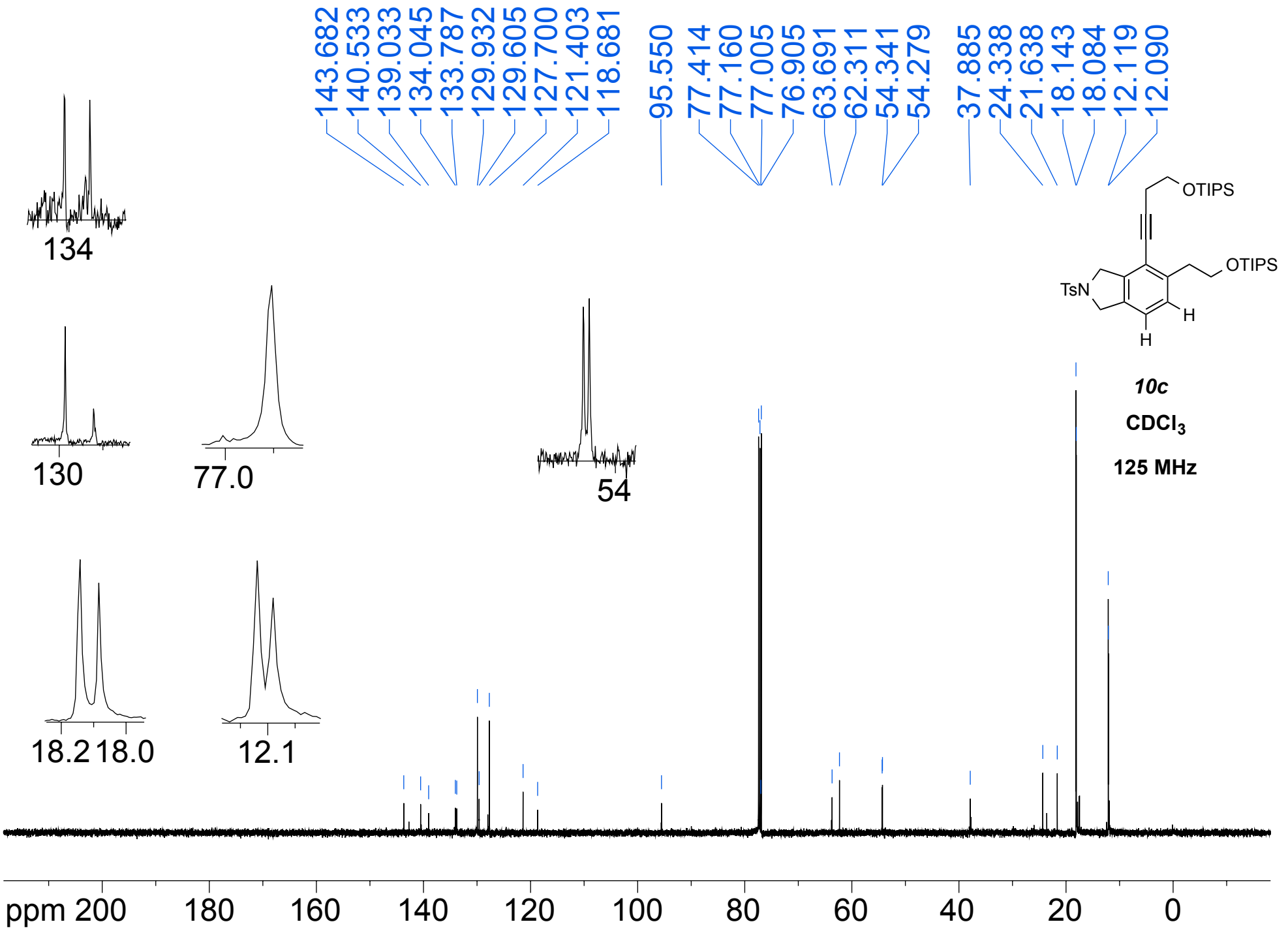
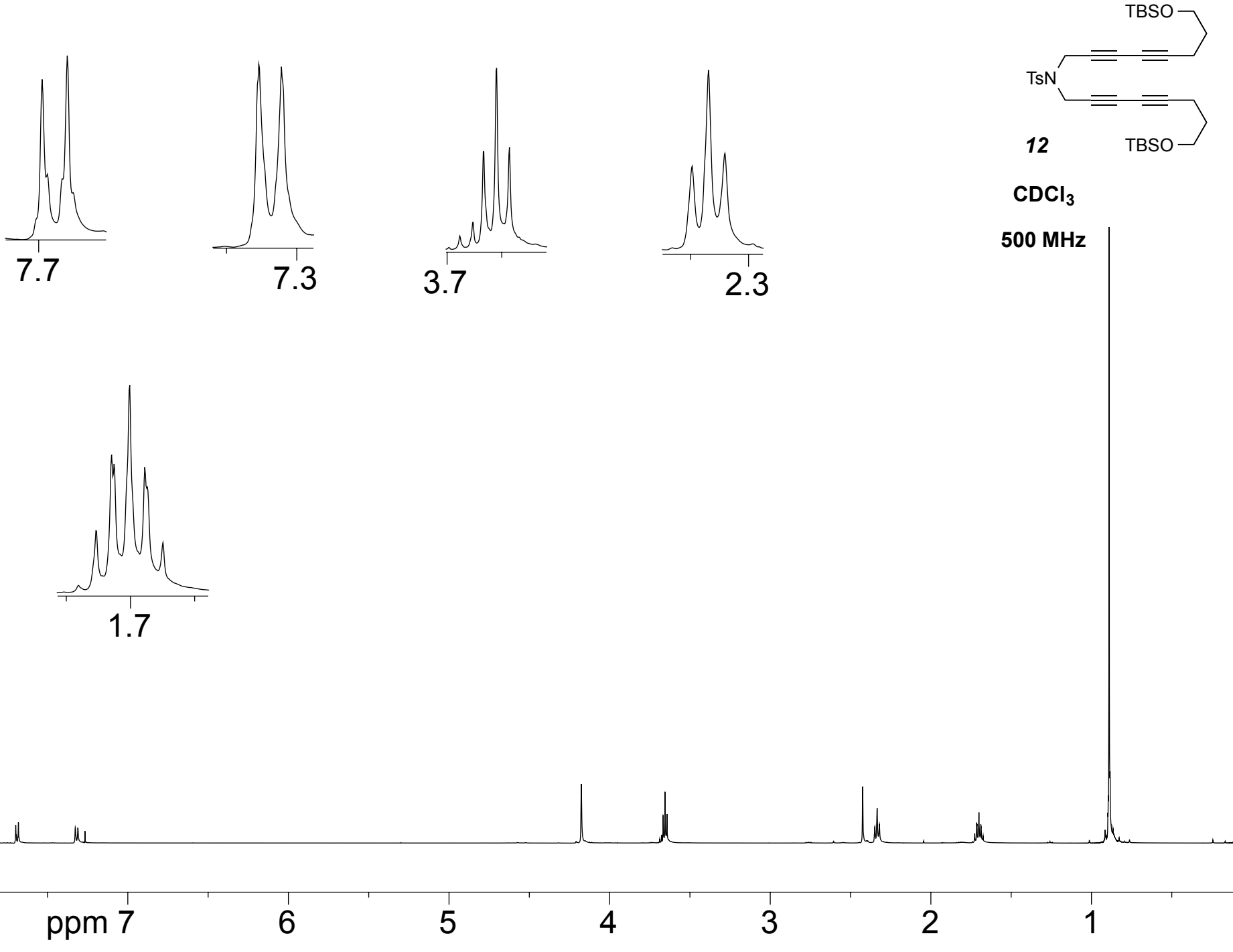
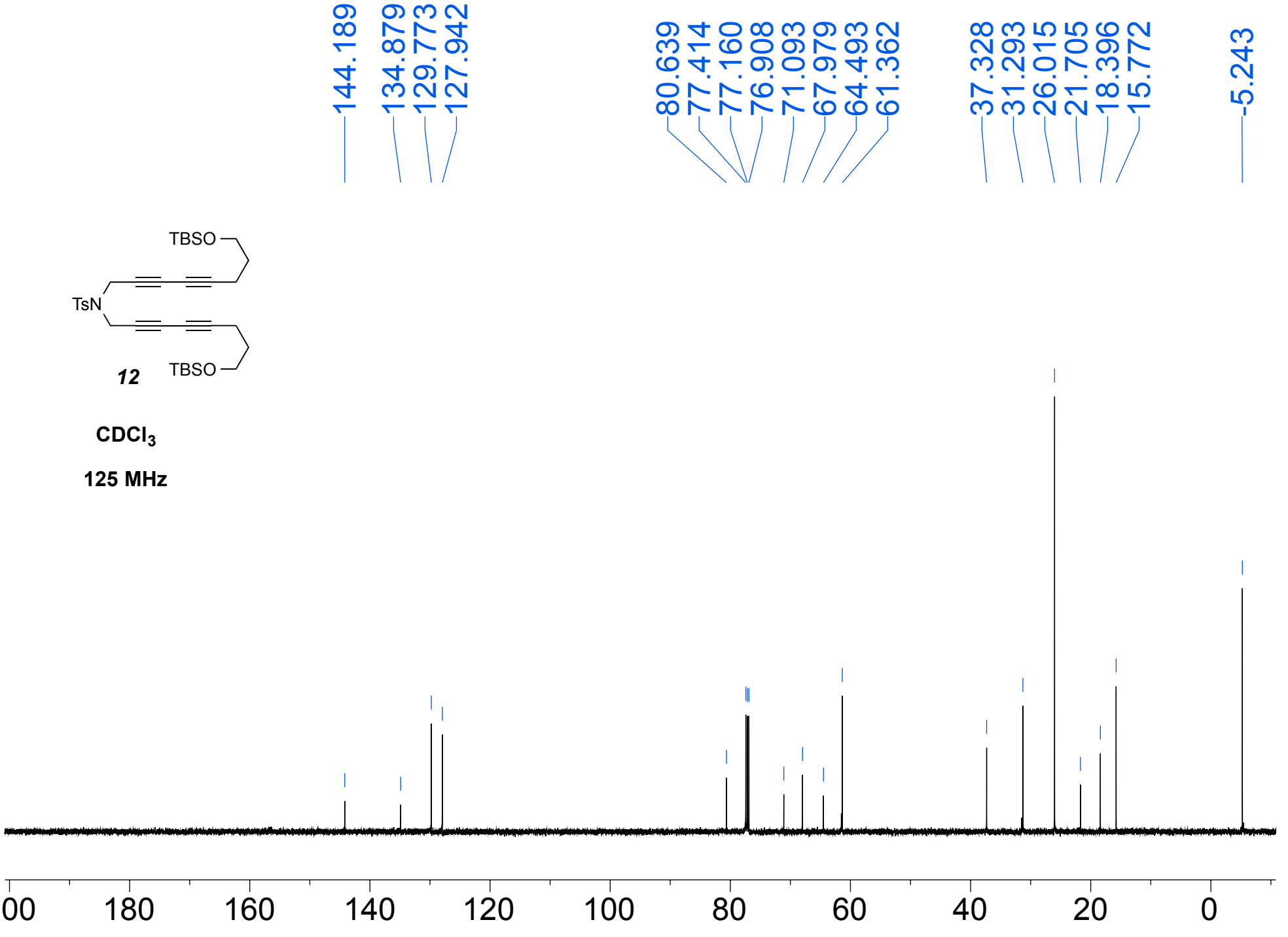
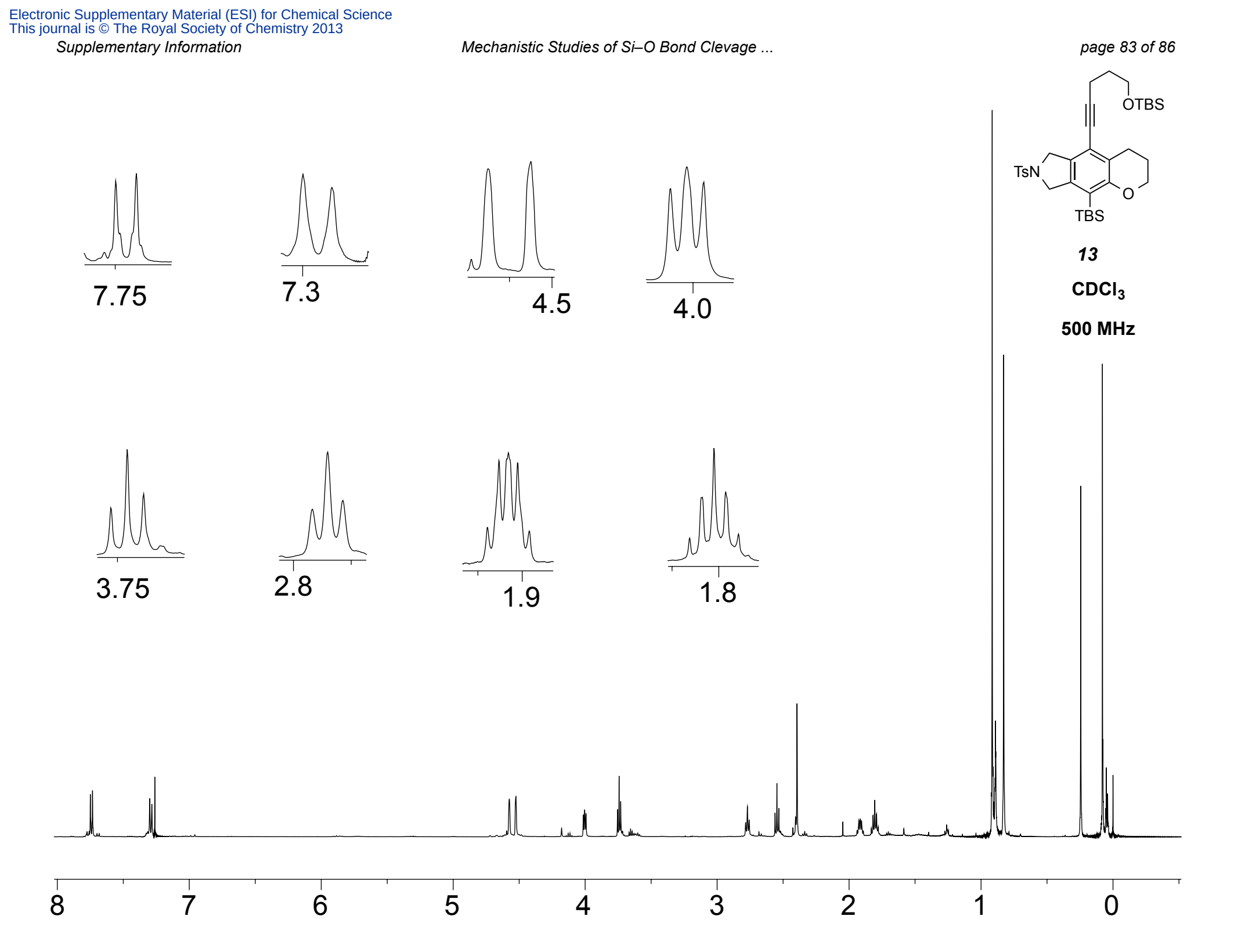
OTBS
TsN
H
H
10b
CDCl3
125 MHz
ppm 200 180 160 140 120 100 80 60 40 20 0

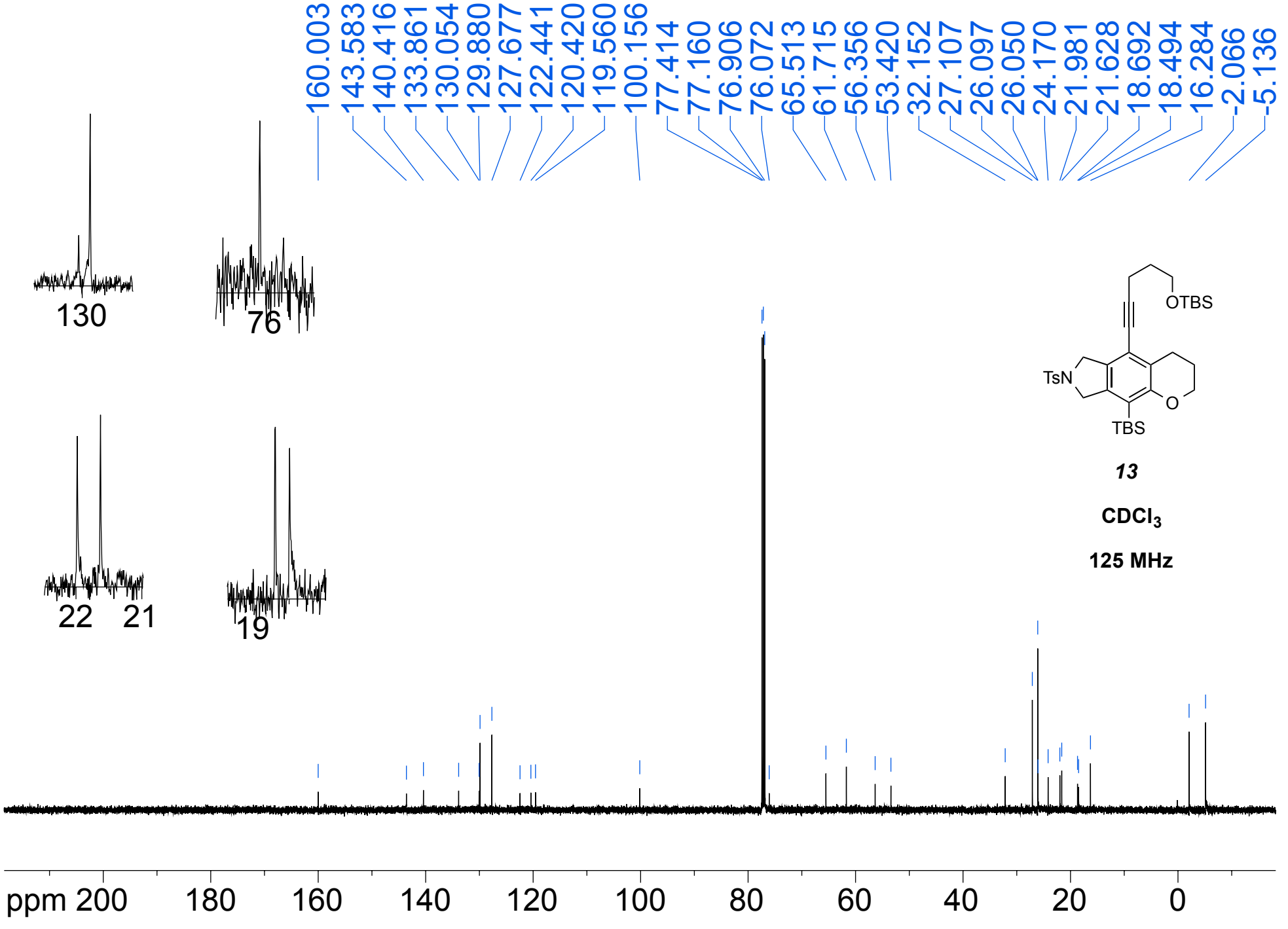

7.75
7.3
7.0
4.6
3.9 3.8
3.0
2.7
OTIPS
OTIPS
TsN
H
H
10c
CDCl3
500 MHz
8
7
6
5
4
3
2
1
0

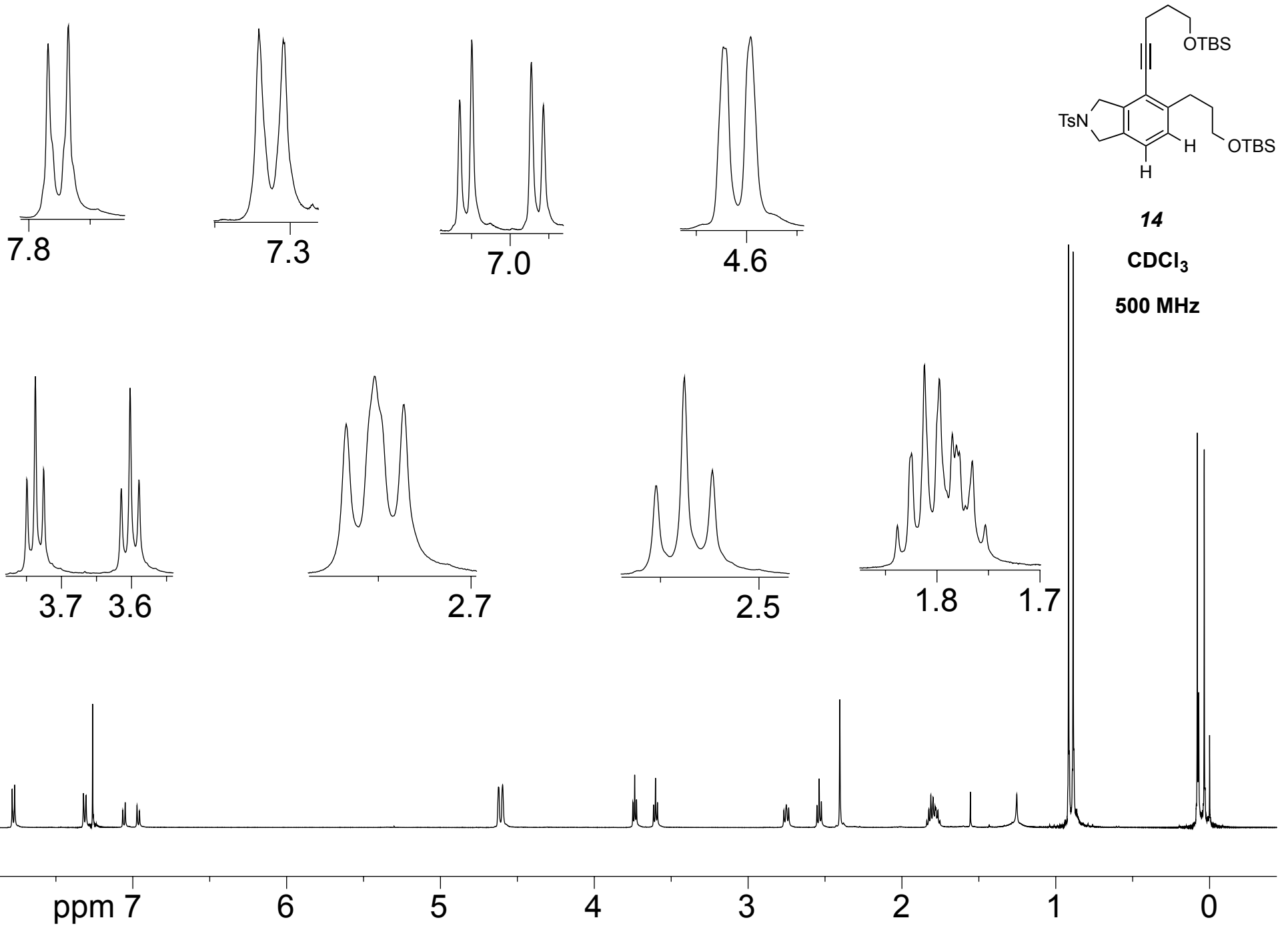

143.682
140.533
139.033
134.045
133.787
129.932
129.605
127.700
121.403
118.681
95.550
77.414
77.160
77.005
76.905
63.691
62.311
54.341
54.279
37.885
24.338
21.638
18.143
18.084
12.119
12.090
134
130
77.0
54
18.2 18.0
12.1
OTIPS
OTIPS
TsN
H
H
10c
CDCl3
125 MHz
ppm 200
180
160
140
120
100
80
60
40
20
0

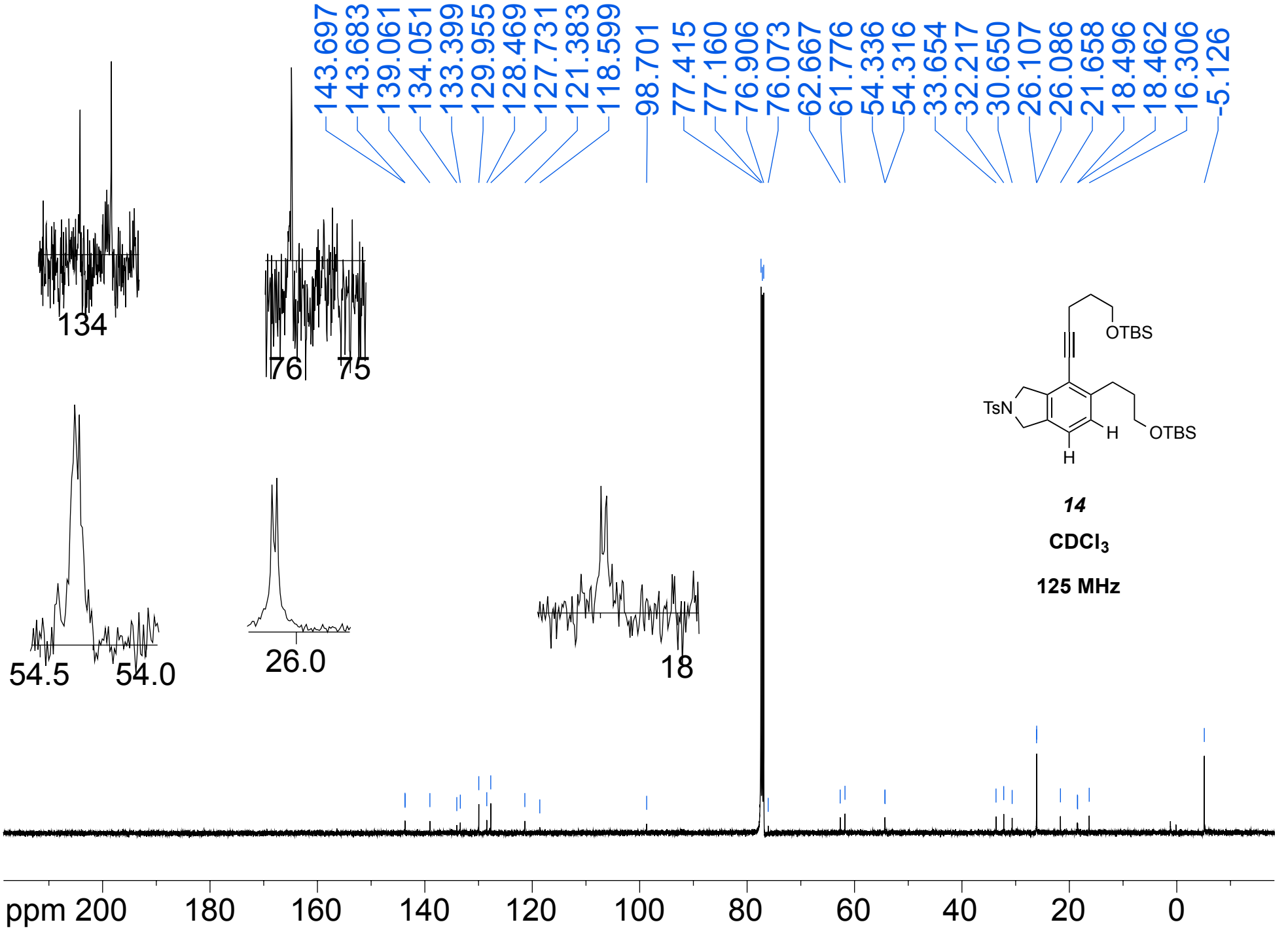

TBSO
TsN
TBSO
12
CDCl3
500 MHz
7.7
7.3
3.7
2.3
1.7
ppm 7
6
5
4
3
2
1
0


144.189
134.879
129.773
127.942
80.639
77.414
77.160
76.908
71.093
67.979
64.493
61.362
37.328
31.293
26.015
21.705
18.396
15.772
-5.243
TBSO
TsN
TBSO
12
CDCl3
125 MHz
00
180
160
140
120
100
80
60
40
20
0


OTBS
TsN
O
TBS
13
CDCl3
500 MHz
7.75
7.3
4.5
4.0
3.75
2.8
1.9
1.8
8
7
6
5
4
3
2
1
0


160.003
143.583
140.416
133.861
130.054
129.880
127.677
122.441
120.420
119.560
100.156
77.414
77.160
76.906
76.072
65.513
61.715
56.356
53.420
32.152
27.107
26.097
26.050
24.170
21.981
21.628
18.692
18.494
16.284
-2.066
-5.136
130
76
22
21
19
OTBS
TsN
O
TBS
13
CDCl3
125 MHz
ppm 200
180
160
140
120
100
80
60
40
20
0


OTBS
TsN
H
OTBS
H
14
CDCl3
500 MHz
7.8
7.3
7.0
4.6
3.7
3.6
2.7
2.5
1.8
1.7
ppm 7
6
5
4
3
2
1
0


143.697
143.683
139.061
134.051
133.399
129.955
128.469
127.731
121.383
118.599
98.701
77.415
77.160
76.906
76.073
62.667
61.776
54.336
54.316
33.654
32.217
30.650
26.107
26.086
21.658
18.496
18.462
16.306
-5.126
134
76
75
54.5
54.0
26.0
18
OTBS
TsN
H
OTBS
H
14
CDCl3
125 MHz
ppm 200
180
160
140
120
100
80
60
40
20
0