Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

$Au(PPh_3)(OPOF_2)$-Catalyzed Intramolecular [4+2] Cycloaddition Reaction of Dienynes

Soo Min Kim, Ji Hoon Park and Young Keun Chung*

Intelligent Textile System Research Center, Department of Chemistry, College of Natural Sciences, Seoul National University, Seoul 151-747, Korea

E-mail : ykchung@snu.ac.kr

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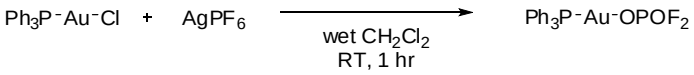
I . General Information

All solvents were dried and distilled according to standard methods before use. $Au(PPh_3)Cl$ was prepared according to the literature procedures.[S1] Commercially available reagents were used as received without further purification. Experiments were performed in a flame-dried glassware with a rubber septum under a positive pressure of nitrogen. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and acidic *p*-anisaldehyde, and heat as developing agent. Flash chromatography was carried out on Merck 60 silica gel (230 – 400 mesh). ^1H and ^{13}C NMR spectra were recorded with Bruker (300 MHz and 75 MHz) spectrometer. ^1H NMR spectra were taken in $CDCl_3$ and were referenced to residual TMS (0 ppm) and reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet). Chemical shifts of the ^{13}C NMR spectra were measured relative to $CDCl_3$ (77.00 ppm). Mass spectral data were obtained at the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Elemental analysis were performed on a Perkin Elmer EA 2400 analyzer. Melting points were determined by Barnstead-Electrothermal / Thermo Scientific Digital IA9100X1. Single crystal data for **1b**, **1c**, **11a** and $[Au(PPh_3)]OPOF_2$ were collected on an Enraf-Nonius CCD single crystal X-ray diffractometer at room temperature using graphite-monochromated MoK α radiation (λ= 0.71073Å). Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97. **1**,[S2] **2**,[S2] **5**,[S2] **6**,[S3] **14**,[S3] **15**,[S4] **17**,[S5] **1a**,[S6] **5a**,[S7] **6a**[S8] and $Au(PPh_3)NTf_2$[S9] were known compounds.

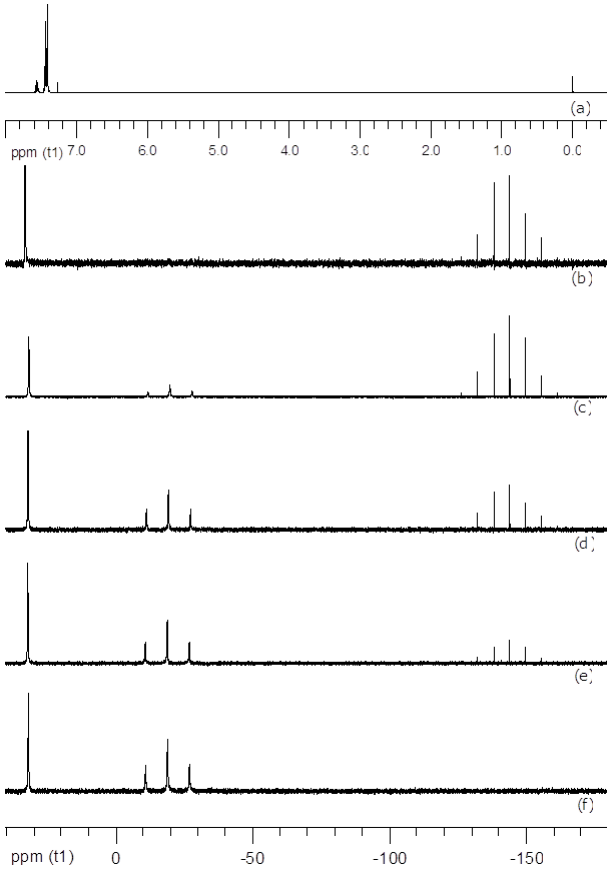
II . Synthesis of $Au(PPh_3)OPOF_2$.



To a flame-dried Schlenk tube capped with a rubber septum, $Au(PPh_3)Cl$ (99mg, 0.2 mmol) in wet CH_2Cl_2 (10 mL) and $AgPF_6$ (51mg, 0.2 mmol) were added. Immediately a white precipitate of AgCl was formed. The resulting solution was stirred for an hour at room temperature. The solution was filtered through a Celite pad and washed with CH_2Cl_2. The filterate was concentrated *in vacuo*. White solid (106mg, 95%). **^{31}P NMR (121.5 MHz, $CDCl_3$)** δ -20.1 (t, *J* (^{31}P-^{19}F) = 972 Hz), 31.6 (s) Hz. **Elemental analysis** calcd (%) for $C_{18}H_{15}AuF_2O_2P_2$: C 38.59, H 2.70; found : C 38.33, H : 2.69. **m.p.** dec.

NMR study of the transformation of $Au(PPh_3)PF_6$ into $Au(PPh_3)PF_2O_2$

According to the paper, *Inorg. Chem.* 1994, **33**, 2309, the amount of water seems to be meaningless because they said that "*It has not been possible to completely eliminate the water from $AgPF_6$ even after drying under P_2O_5 and a vacuum higher than 10^{-2}mmHg during 5 days*." In order to verify the above statement, we carried out some NMR experiments: (a) We first took ^{1}H NMR spectrum of $Au(PPh_3)PF_6$ prepared in a glove box. We only observed the peak due to the phenyl group, not due to water. (b-f) ^{31}P NMR spectra *vs* time: -144.1 ppm (PF_6), 20.1 ppm (PF_2O_2), and P, 31.6 ppm (PPh_3). Even though no water was detected, we could see the transformation of PF_6 into PF_2O_2 as time passed. As expected, when we use wet dichloromethane as a solvent, we could shorten the reaction time.



0.1 mmol of $Au(PPh_3)Cl$ and 0.1 mmol of $AgPF_6$ in 1 mL of $CDCl_3$.
(a) ^{1}H-NMR.
(b-f) ^{31}P-NMR, phosphine : 31.6 ppm, **PF_2O_2 : -20.1 ppm**, **PF_6 : -144.1**
(b) 5 min. (c) 35 min. (d) 70 min. (e) 100 min. (f) 130 min.

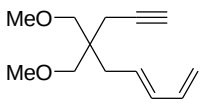
III. General Procedure for the Synthesis of Dienynes.

N-(*p*-Tolylsulfonamide) tethered dienynes were prepared as follows. To a flame-dried 100 mL schlenk flask capped with a rubber septum, 20 mL THF was injected via syringe under N_2 flow. 1.2 mL (1.2 eq.) of diisopropyl azodicarboxylate and 1.57g (1.2 eq.) of PPh_3 were added to the schlenk flask. After the solution was stirred for 10 min, 1.15 g (1.1 eq.) of 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide was added. Then, an alcohol (5 mmol) with (a) substituent(s) in a diene moiety was added, and the solution was stirred for 5 hours. After the resulting solution was concentrated, the mixture was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 10:1) to afford pure dienyne.

Compounds **3** and **4** were prepared as follows: To a flame-dried 100 mL schlenk flask equipped with a stirring bar, a suspension of $LiAlH_4$ (190 mg, 5 mmol) in 20 mL THF was stirred at 0°C. A solution of dimethyl 2-(penta-2,4-dienyl)-2-(prop-2-ynyl)malonate (**2**) (1.181g, 5 mmol) in 20 mL of THF was added slowly. The flask was removed from the bath, warmed to room temperature, and allowed to stir at room temperature for 12 hours. Then the solution was then cooled to 0°C and quenched with H_2O (10 mL) and 1N NaOH (10 mL). The The aqueous phase was extracted three times with Et_2O. The organic layers were combined, dried (Na_2SO_4), and concentrated. The mixture was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 1:1) to afford 766 mg (85% yield) of 2-(penta-2,4-dienyl)-2-(prop-2-ynyl)propane-1,3-diol (**S1**).

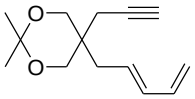
To a stirring suspension of NaH (425 mg, 60% disp. in mineral oil, 2.5 eq.) in 30 mL THF at 0°C, **S1** (766 mg, 4.25 mmol) was slowly added. After the solution was stirred for 1 hour at 0°C, iodomethane (0.8 mL, 3eq.) was slowly added, and it was slowly warmed to room temperature, and allowed to stir at room temperature for 12 hours. The reaction was quenched with 30 mL of saturated NH_4Cl solution. The organic layer was separated, and the aqueous phase was extracted twice with Et_2O. The combined organic phases were dried ($MgSO_4$) and concentrated. The mixture was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 15:1) to afford 673 mg (76% yield) of 6,6-bis(methoxymethyl)nona-1,3-dien-8-yne (**3**).

To a 100 mL schlenk flask, **S1** (766 mg, 4.25 mmol) and 20 mL acetone were added. The resulting solution was stirred at room temperature and then a few drops of H_2SO_4 were added. The solution was stirred for 12 hours. After the solution was concentrated, the mixture was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 15:1) to afford 328 mg (35% yield) of 2,2-dimethyl-5-(penta-2,4-dienyl)-5-(prop-2-ynyl)-1,3-dioxane (**4**).



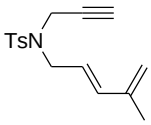
6,6-bis(methoxymethyl)nona-1,3-dien-8-yne (**3**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.98 (t, *J* = 2.6 Hz, 1 H), 2.20 (m, 4 H), 3.24 (m, 4 H), 3.32 (s, 3 H), 3.33 (s, 3 H), 4.99 (d, *J* = 10.1 Hz, 1 H), 5.12 (d, *J* = 16.8 Hz, 1 H), 5.67 (td, *J* = 7.8, 15.2 Hz, 1 H), 6.11 (dd, *J* = 10.5, 15.0 Hz, 1 H), 6.33 (td, *J* = 10.2, 16.9 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 22.0, 34.8, 42.2, 59.2, 70.2, 74.2, 81.1, 115.3, 129.8, 134.3, 137.0 ppm. **HRMS (EI)** calc. for $[C_{13}H_{20}O_2]^+$ 208.1463, found 208.1465.



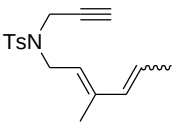
2,2-dimethyl-5-(penta-2,4-dienyl)-5-(prop-2-ynyl)-1,3-dioxane (**4**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 1.41 (s, 3 H), 2.04 (t, *J* = 2.7 Hz, 1 H), 2.21 (d, *J* = 7.8 Hz, 2 H), 2.35 (d, *J* = 2.7 Hz, 2 H), 3.65 (s, 4 H), 5.02 (dd, *J* = 1.3, 10.2 Hz, 1 H), 5.14 (dd, *J* = 1.4, 16.5 Hz, 1 H), 5.63 (td, *J* = 7.8, 15.3 Hz, 1 H), 6.14 (dd, *J* = 10.5, 14.9 Hz, 1 H), 6.31 (td, *J* = 10.2, 16.8 Hz, 1 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.9, 22.3, 25.4, 35.4, 35.8, 66.6, 71.0, 80.5, 98.0, 116.1, 128.0, 134.9, 136.6 ppm. **HRMS (EI)** calc. for $[C_{14}H_{20}O_2]^+$ 220.1463, found 220.1467.



4-methyl-*N*-(4-methylpenta-2,4-dienyl)-*N*-(prop-2-ynyl)benzenesulfonamide (**7**)

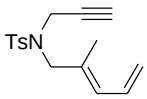
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.80 (s, 3 H), 2.04 (t, *J* = 2.3 Hz, 1 H), 2.42 (s, 3 H), 3.89 (d, *J* = 6.8 Hz, 2 H), 4.09 (d, *J* = 2.3 Hz, 2 H), 4.97 (s, 1 H), 5.00 (s, 1 H), 5.51 (td, *J* = 7.0, 15.6 Hz, 1 H), 6.30 (d, *J* = 15.6 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 18.4, 21.4, 35.7, 48.3, 73.7, 76.5, 117.4, 122.8, 127.6, 129.4, 136.0, 137.6, 140.9, 143.5 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1139.



4-methyl-*N*-(3-methylhexa-2,4-dienyl)-*N*-(prop-2-ynyl)benzenesulfonamide (*E* : *Z* = 3 : 7) (**8**)

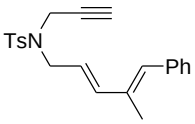
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.71-1.81 (m, 6 H), 2.00 (m, 0.7 H), 2.04 (s, 0.3 H), 2.43 (s, 3 H), 3.94 (d, *J* = 7.3 Hz, 2 H), 4.06 (d, *J* = 2.3 Hz, 0.6 H), 4.10 (d, *J* = 2.3 Hz, 1.4 H), 5.25 (t, *J* = 6.9 Hz, 1 H), 5.50 (qd, *J* = 7.1, 11.9 Hz, 0.7 H), 5.70 (m, 0.3 H), 5.78 (d, *J* = 11.6 Hz, 0.7 H), 6.05 (d, *J* = 15.7 Hz, 0.3 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.75 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 12.5, 14.7, 17.0, 18.2, 21.5, 35.6, 35.7, 43.86, 43.94, 73.5, 76.7, 77.2, 121.8, 122.3, 125.4, 125.6, 127.8, 129.4, 132.6,

134.9, 136.1, 138.6, 143.5 ppm. **HRMS (EI)** calc. for $[C_{17}H_{21}NO_2S]^+$ 303.1293, found 303.1291.



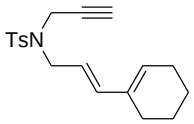
(*E*)-4-methyl-*N*-(2-methylpenta-2,4-dienyl)-*N*-(prop-2-ynyl)benzenesulfonamide (**9**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3 H), 1.97 (t, *J* = 2.2 Hz, 1 H), 2.42 (s, 3 H), 3.76 (s, 2 H), 4.01 (d, *J* = 1.8 Hz, 2 H), 5.13 (d, *J* = 10.4 Hz, 1 H), 5.19 (d, *J* = 17.2 Hz, 1 H), 6.01 (d, *J* = 10.8 Hz, 1 H), 6.56 (td, *J* = 10.5, 16.9 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 14.4, 21.5, 35.4, 53.9, 73.8, 76.2, 118.0, 127.7, 129.4, 130.0, 131.9, 132.3, 135.9, 143.5 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1138.



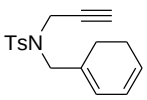
4-methyl-*N*-((2*E*,4*E*)-4-methyl-5-phenylpenta-2,4-dienyl)-*N*-(prop-2-ynyl)benzenesulfonamide (**10**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3 H), 2.04 (t, *J* = 2.2 Hz, 1 H), 2.43 (s, 3 H), 3.95 (d, *J* = 6.8 Hz, 2 H), 4.12 (d, *J* = 2.3 Hz, 2 H), 5.62 (td, *J* = 7.5, 15.5 Hz, 1 H), 6.40 (d, *J* = 15.5 Hz, 1 H), 6.49 (s, 1 H), 7.19-7.37 (m, 7 H), 7.76 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 13.8, 21.5, 35.8, 48.5, 73.7, 76.6, 122.0, 126.8, 127.7, 128.1, 129.1, 129.4, 132.3, 134.6, 136.1, 137.4, 140.1, 143.5 ppm. **HRMS (EI)** calc. for $[C_{22}H_{23}NO_2S]^+$ 365.1449, found 365.1448.



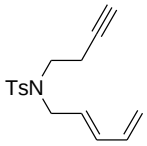
(*E*)-*N*-(3-cyclohexenylallyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (**11**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.56-1.70 (m, 4 H), 2.00 (t, *J* = 2.3 Hz, 1 H), 2.02-2.15 (m, 4 H), 2.42 (s, 3 H), 3.85 (d, *J* = 6.9 Hz, 2 H), 4.08 (d, *J* = 2.2 Hz, 2 H), 5.37 (td, *J* = 7.3, 15.6 Hz, 1 H), 5.74 (t, *J* = 3.7 Hz, 1 H), 6.18 (d, *J* = 15.6 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 22.3, 22.4, 24.4, 25.8, 35.6, 48.6, 73.5, 76.7, 118.4, 127.8, 129.4, 130.8, 134.9, 136.2, 138.7, 143.4 ppm. **HRMS (EI)** calc. for $[C_{19}H_{23}NO_2S]^+$ 329.1449, found 329.1454.



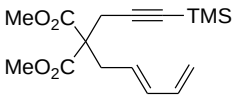
N-(cyclohexa-1,3-dienylmethyl)-4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (**12**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.96 (t, *J* = 2.2 Hz, 1 H), 2.17-2.10 (m, 4 H), 2.43 (s, 3 H), 3.79 (s, 2 H), 4.07 (d, *J* = 2.2 Hz, 2 H), 5.78-5.83 (m, 1 H), 5.84-5.89 (m, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 22.6, 23.4, 35.4, 51.8, 73.7, 76.3, 123.7, 124.0, 126.8, 127.7, 129.4, 131.7, 135.9, 143.4 ppm. **HRMS (EI)** calc. for $[C_{17}H_{19}NO_2S]^+$ 301.1136, found 301.1134.



(*E*)-*N*-(but-3-ynyl)-4-methyl-*N*-(penta-2,4-dienyl)benzenesulfonamide (**13**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.97 (t, *J* = 2.5 Hz, 1 H), 2.43 (s, 3 H), 2.45 (dt, *J* = 2.5, 7.8 Hz, 2 H), 3.29 (t, *J* = 7.5 Hz, 2 H), 3.89 (d, *J* = 6.7 Hz, 2 H), 5.18 (d, *J* = 16.2 Hz, 1 H), 5.10 (d, *J* = 9.5 Hz, 1 H), 5.50 (td, *J* = 7.1, 15.0 Hz, 1 H), 6.07-6.32 (m, 2 H), 7.30 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 19.4, 21.5, 46.0, 50.3, 70.1, 81.0, 118.3, 127.2, 127.8, 129.7, 134.8, 135.7, 136.9, 143.4 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1133.

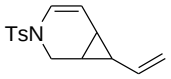


(*E*)-dimethyl 2-(penta-2,4-dienyl)-2-(3-(trimethylsilyl)prop-2-ynyl)malonate (**16**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 9 H), 2.81 (s, 2 H), 2.82 (d, *J* = 8.0 Hz, 2 H), 3.73 (s, 6 H), 5.03 (d, *J* = 9.5 Hz, 1 H), 5.14 (d, *J* = 16.2 Hz, 1 H), 5.49 (td, *J* = 7.7, 15.1 Hz, 1 H), 6.09-6.35 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 0.0, 24.2, 35.5, 52.7, 57.3, 88.4, 101.2, 116.7, 127.2, 135.5, 136.5, 170.0 ppm. **HRMS (EI)** calc. for $[C_{16}H_{24}O_4Si]^+$ 308.1444, found 308.1440.

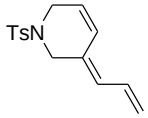
Ⅳ. General Procedure for $Au(PPh_3)(OPOF_2)$-Catalyzed Intramolecular [4+2] Cycloaddition Reaction of Dienynes

$[Au(PPh_3)OPOF_2]$ (25 μmol) and THF (2 mL) were added to a flame-dried Schlenk tube equipped with a stirring bar. To the solution was added a dienyne (0.5 mmol) along with 3 mL of THF. The mixture was stirred until the dienyne was completely disappeared (as checked by TLC) at room temperature. The mixture was purified by flash chromatography on silica gel (*n*-hexane/EtOAc = 10:1) to afford the desired [4+2] cycloaddition product.



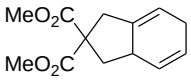
3-tosyl-7-vinyl-3-aza-bicyclo[4.1.0]hept-4-ene (**1b**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.17-1.27 (m, 2 H), 1.58 (m, 1 H), 2.44 (s, 3 H), 3.07 (dd, *J* = 3.0, 12.0 Hz, 1 H), 3.94 (d, *J* = 12.0 Hz, 1 H), 4.79 (dd, *J* = 1.6, 9.9 Hz, 1 H), 4.84 (dd, *J* = 1.6, 3.8 Hz, 1 H), 5.29 (m, 1 H), 5.42 (dd, *J* = 5.3, 8.0 Hz, 1 H), 6.35 (d, *J* = 8.0 Hz, 1 H), 7.33 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ □ 16.5, 21.5, 26.7, 30.9, 40.1, 110.7, 113.1, 121.4, 127.0, 129.8, 134.8,138.2, 143.7 ppm. **HRMS (EI)** calc. for $[C_{15}H_{17}NO_2S]^+$ 275.0980, found 275.0983. **m.p.** 98-100°C.



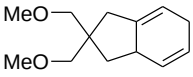
(*E*)-3-allylidene-1-tosyl-1,2,3,6-tetrahydropyridine (**1c**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.41 (s, 3 H), 3.78-3.82 (m, 2 H), 3.82 (s, 2 H), 5.17 (d, *J* = 10.2 Hz, 1 H), 5.25 (d, *J* = 16.8 Hz, 1 H), 5.74 (m, 1 H), 5.86 (d, *J* = 11.1 Hz, 1 H), 6.47-6.67 (m, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.8, 45.9, 49.6, 119.1, 122.9, 125.4, 127.4, 128.0, 129.1, 129.7, 131.0, 133.9, 143.8 ppm. **HRMS (EI)** calc. for $[C_{15}H_{17}NO_2S]^+$ 275.0980, found 275.0984. **m.p.** 134-136°C.



dimethyl 3,3a-dihydro-1*H*-indene-2,2(6*H*)-dicarboxylate (**2a**)

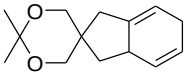
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.81 (t, *J* = 12.4 Hz, 1 H), 2.61-2.69 (m, 3 H), 2.81-2.94 (m, 1 H), 2.94-3.00 (m, 2 H), 3.71 (s, 3 H), 3.75(s, 3 H), 5.47-5.52 (m, 1 H), 5.73-5.78 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 26.9, 38.1, 38.3, 40.0, 52.6, 52.7, 57.1, 115.8, 125.1, 126.2, 138.4, 172.2, 172.8 ppm. **HRMS (EI)** calc. for $[C_{13}H_{16}O_4]^+$ 236.1049, found 236.1051.



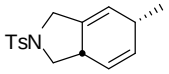
2,2-bis(methoxymethyl)-2,3,5,7a-tetrahydro-1*H*-indene (**3a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.00 (t, *J* = 12.1 Hz, 1 H), 1.90 (dd, *J* = 8.4, 12.5 Hz, 1 H), 2.07-2.10 (m, 2 H), 2.52-2.60 (m, 2 H), 2.73-2.86 (m, 1 H), 3.09 (s, 2 H), 3.23 (s, 2 H), 3.24 (s, 3 H), 3.28 (s, 3 H), 5.32-5.38 (m, 1 H), 5.59-5.72 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 27.0, 37.5, 37.6, 38.7, 44.5, 59.1, 59.2, 76.7, 77.2, 114.7, 124.3, 128.0, 141.1 ppm. **HRMS (EI)** calc. for $[C_{13}H_{20}O_2]^+$ 208.1463, found

208.1460.

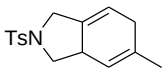

(**4a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.00 (t, *J* = 12.0 Hz, 1 H), 1.35 (s, 6 H), 1.99 (dd, *J* = 8.3, 12.6 Hz, 1 H), 2.07-2.28 (m, 2 H), 2.53-2.62 (m, 2 H), 2.68-2.83 (m, 1 H), 3.42-3.53 (m, 2 H), 3.52-3.69 (m, 2 H), 5.34-5.44 (m, 1 H), 5.59-5.74 (m, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 23.4, 24.3, 27.0, 37.3, 38.6, 38.9, 39.3, 69.4, 69.5, 97.7, 115.4, 124.7, 127.7, 140.2 ppm. **HRMS (EI)** calc. for $[C_{14}H_{20}O_2]^+$ 220.1463, found 220.1465.



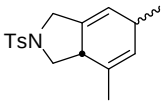
6-methyl-2-tosyl-2,3,3a,6-tetrahydro-1*H*-isoindole (**6a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.04 (d, *J* = 7.4 Hz, 3 H), 2.42 (s, 3 H), 2.66 (dd, *J* = 8.9, 11.1 Hz, 1 H), 2.75 (m, 1 H), 2.93 (m, 1 H), 3.73 (d, *J* = 13.2 Hz, 1 H), 3.83 (t, *J* = 8.3 Hz, 1 H), 4.01 (m, 1 H), 5.37 (m, 1 H), 5.57-5.65 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 21.5, 30.9, 38.0, 50.6, 52.8, 121.9, 123.5, 127.5, 129.7, 133.3, 133.9, 134.1, 143.4 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1139.



5-methyl-2-tosyl-2,3,3a,6-tetrahydro-1*H*-isoindole (**7a**)

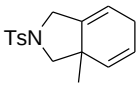
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.66 (s, 3 H), 2.41 (s, 3 H), 2.49 (t, *J* = 5.5 Hz, 1 H), 2.61 (dd, *J* = 8.8, 11.3 Hz, 2 H), 2.88-3.03 (m, 1 H), 3.68-3.75 (m, 1 H), 3.80 (t, *J* = 8.3 Hz, 1 H), 3.96-4.05 (m, 1 H), 5.31-5.36 (m, 1 H), 5.51-5.56 (m, 1 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 8.3 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 22.7, 31.6, 33.0, 50.5, 53.1, 117.0, 117.5, 127.4, 129.6, 133.7, 134.4, 134.8, 143.3 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1139.



4,6-dimethyl-2-tosyl-2,3,3a,6-tetrahydro-1*H*-isoindole (*syn* : *anti* = 3 : 7) (**8a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.90 (m, 3 H), 1.57 (s, 3 H), 2.33 (s, 3 H), 2.53-2.69 (m, 2 H), 2.82 (m, 1 H), 3.65 (d, *J* = 12.9 Hz, 1 H), 3.78 (t, *J* = 8.1 Hz, 1 H), 3.94 (dd, *J* = 1.3, 13.0 Hz, 1 H), 5.19 (m, 0.3 H), 5.30 (m, 1 H), 5.47 (m, 0.7 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 20.7, 21.1, 21.4, 21.6, 31.8, 32.7, 41.5, 41.6, 50.6, 50.7, 52.2, 123.6, 127.2, 127.3, 127.5,

129.2, 129.4, 129.6, 133.5, 133.6, 133.7, 133.8, 143.3 ppm. **HRMS (EI)** calc. for $[C_{17}H_{21}NO_2S]^+$ 303.1293, found 303.1289.



3a-methyl-2-tosyl-2,3,3a,6-tetrahydro-1*H*-isoindole (**9a**)

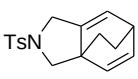
^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.91 (s, 3 H), 2.33 (s, 3 H), 2.46-2.54 (m, 2 H), 2.78 (d, *J* = 8.7 Hz, 1 H), 3.32 (d, *J* = 8.7 Hz, 1 H), 3.63-3.71 (m, 1 H), 3.97-4.05 (m, 1 H), 5.42 (s, 1 H), 5.57-5.66 (m, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 25.4, 26.3, 41.0, 49.9, 58.5, 116.8, 124.6, 127.3, 129.5, 129.6, 133.8, 138.8, 143.2 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1139.

5-methyl-6-phenyl-2-tosyl-2,3,3a,6-tetrahydro-1*H*-isoindole (**10a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.40 (s, 3 H), 2.44 (s, 3 H), 2.77 (dd, *J* = 8.9, 11.3 Hz, 1 H), 3.02 (m, 1 H), 3.73 (d, *J* = 8.7 Hz, 1 H), 3.79 (d, *J* = 13.4 Hz, 1 H), 3.89 (t, *J* = 8.3 Hz, 1 H), 4.01 (m, 1 H), 5.40 (m, 1 H), 5.50 (m, 1 H), 6.90-6.97 (m, 2 H), 7.18-7.27 (m, 3 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 21.9, 39.0, 47.3, 50.7, 53.5, 118.1, 122.0, 126.6, 127.4, 128.4, 129.7, 133.1, 134.1, 136.6, 143.4, 143.5 ppm. **HRMS (EI)** calc. for $[C_{22}H_{23}NO_2S]^+$ 365.1449, found 365.1453.

2-tosyl-2,3,4a,5,6,7,8,9a-octahydro-1*H*-benzo[*f*]isoindole (**11a**)

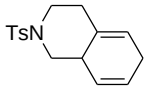
^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.93 (dq, *J* = 3.0, 12.8 Hz, 1 H), 1.16 (m, 1 H), 1.40 (m, 1 H), 1.70-1.79 (m, 2 H), 1.84 (m, 1 H), 1.97 (t, *J* = 13.3 Hz, 1 H), 2.23 (m, 1 H), 2.42 (s, 3 H), 2.51 (t, *J* = 12.0 Hz, 1 H), 2.67 (dd, *J* = 8.9, 11.2 Hz, 1 H), 2.93 (m, 1 H), 3.70-3.84 (m, 2 H), 3.97 (m, 1 H), 5.26-5.33 (m, 2 H), 7.31 (d, *J* = 7.9 Hz, 2 H), 7.71 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 26.1, 27.2, 35.0, 35.1, 38.1, 38.9, 50.6, 53.3, 114.6, 122.7, 127.5, 129.7, 133.4, 134.3, 141.3, 143.3 ppm. **HRMS (EI)** calc. for $[C_{19}H_{23}NO_2S]^+$ 329.1449, found 329.1454.



(**12a**)

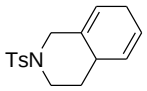
^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.24-1.34 (m, 4 H), 2.44 (s, 3 H), 3.46 (d, *J* = 9.6 Hz, 1 H), 3.59 (dd, *J* = 1.9, 13.7 Hz, 1 H), 3.64 (m, 1 H), 3.76 (d, *J* = 9.6 Hz, 1 H), 4.08 (dd, *J* = 1.3, 13.6 Hz, 1 H), 5.93 (m, 1 H),

6.07 (d, *J* = 7.3 Hz, 1 H), 6.25 (m, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.73 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 26.4, 30.0, 38.5, 49.1, 50.8, 55.2, 122.6, 128.0, 129.6, 132.1, 134.9, 135.2, 143.7, 145.8 ppm. **HRMS (EI)** calc. for $[C_{17}H_{19}NO_2S]^+$ 301.1136, found 301.1134.



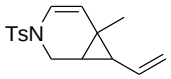
2-tosyl-1,2,3,4,6,8a-hexahydroisoquinoline (**13a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.94 (t, *J* = 11.3Hz, 1 H), 2.13-2.24 (m, 2 H), 2.33 (d, *J* = 11.6 Hz, 1 H), 2.41 (s, 3 H), 2.57-2.67 (m, 2 H), 2.92 (m, 1 H), 3.82-3.92 (m, 2 H), 5.39-5.49 (m, 2 H),5.75 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 8.1 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.4, 26.5, 33.8, 36.5, 47.8, 52.4, 118.4, 124.3, 126.3, 127.5, 129.6, 133.3, 133.4, 143.4 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1140.



2-tosyl-1,2,3,4,4a,7-hexahydroisoquinoline (**14a**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.46 (m, 1 H), 1.79 (m, 1 H), 2.34-2.51 (m, 5 H), 2.61-2.71 (m, 2 H), 2.83 (d, *J* = 11.9 Hz, 1 H), 3.86 (m, 1 H), 4.11 (d, *J* = 12.0 Hz, 1 H), 5.49 (d, *J* = 9.9 Hz, 1 H), 5.59-5.69 (m, 2 H), 7.32 (d, *J* = 7.8 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 21.5, 26.5, 32.7, 35.4, 46.8, 52.7, 120.9, 123.9, 127.1, 127.8, 129.5, 130.8, 133.1, 143.4 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1137.



6-methyl-3-tosyl-7-vinyl-3-aza-bicyclo[4.1.0]hept-4-ene (**17b**)

^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.08 (s, 3 H), 1.19 (m, 1 H), 1.32 (m, 1 H), 2.43 (s, 3 H), 3.05 (dd, *J* = 2.5, 11.8 Hz, 1 H), 3.92 (d, *J* = 11.8 Hz, 1 H), 4.82 (dd, *J* = 1.3, 16.9 Hz, 1 H), 4.94 (dd, *J* = 1.5, 10.3 Hz, 1 H), 5.21 (d, *J* = 8.1 Hz, 1 H), 5.39 (ddd, *J* = 9.1, 10.1, 17.0 Hz, 1 H), 6.32 (d, *J* = 8.1 Hz, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 2 H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 18.1, 19.5, 21.5, 32.3, 35.0, 40.0, 115.5, 117.1, 120.3, 127.1, 129.8, 134.7, 135.5, 143.7 ppm. **HRMS (EI)** calc. for $[C_{16}H_{19}NO_2S]^+$ 289.1136, found 289.1135.

V. X-ray analysis

Diffraction data were measured by a Bruker-Nonius CCD single-crystal X-ray diffractometer at room temperature by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO. The structure was solved by direct methods using SHELXS-97, and refined by full-matrix least-squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically and hydrogen atoms except some were treated as idealized contributions.

Table S1. Crystal data and structure refinement for **1b**.

Empirical formula	C_{15} H_{17} N O_2 S	
Formula weight	275.36	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 1 21/n 1	
Unit cell dimensions	*a* = 11.4368(9) Å	α = 90 deg.
	b = 9.3232(4) Å	β = 103.023(3) deg.
	c = 13.8085(11) Å	γ = 90 deg.
Volume	1434.50(17) $Å^3$	
Z, Calculated density	4, 1.275 Mg/m^3	
Absorption coefficient	0.223 mm^{-1}	
F(000)	584	
Crystal size	0.1 x 0.1 x 0.1 mm	
Theta range for data collection	2.09 to 27.50 deg.	
Limiting indices	-14<h<14, -12<k<10, -17<l<17	
Reflections collected / unique	5731 / 3274 [R(int) = 0.0404]	
Completeness to theta = 27.50	99.5 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3274 / 0 / 173	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1406	
R indices (all data)	R1 = 0.1103, wR2 = 0.1754	
Largest diff. peak and hole	0.339 and -0.483 $e.A^{-3}$	

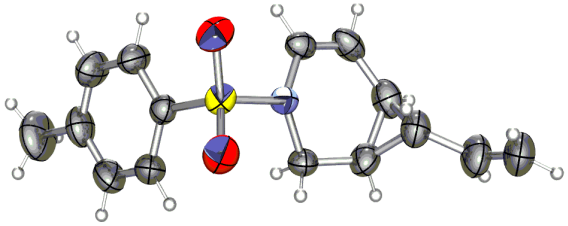


Figure S1. An ORTEP drawing of **1b** with 30% probability of thermal ellipsoids.

Table S2. Crystal data and structure refinement for **1c**.

Empirical formula	C_{15} H_{17} N O_2 S	
Formula weight	275.36	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Orthorhombic, P 21 21 21	
Unit cell dimensions	*a* = 8.0592(2) Å	α = 90 deg.
	b = 10.6389(4) Å	β = 90 deg.
	c = 16.7180(7) Å	γ = 90 deg.
Volume	1433.42(9) $Å^3$	
Z, Calculated density	4, 1.276 Mg/m^3	
Absorption coefficient	0.223 mm^{-1}	
F(000)	584	
Crystal size	0.10 x 0.10 x 0.10 mm	
Theta range for data collection	2.81 to 27.47 deg.	
Limiting indices	-10<h<10, -13<k<13, -21<l<21	
Reflections collected / unique	3269 / 3269 [R(int) = 0.0000]	
Completeness to theta = 27.47	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9780 and 0.9780	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3269 / 0 / 172	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0989	
R indices (all data)	R1 = 0.0443, wR2 = 0.1034	
Absolute structure parameter	-0.13(7)	
Largest diff. peak and hole	0.237 and -0.311 $e.A^{-3}$	

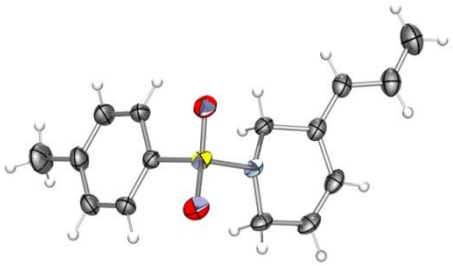


Figure S2. An ORTEP drawing of **1c** with 30% probability of thermal ellipsoids.

Table S3. Crystal data and structure refinement for $Au(PPh_3)PF_2O_2$.

Empirical formula	$C_{18}\ H_{15}\ Au\ F_2\ O_2\ P_2$	
Formula weight	560.21	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 21/c	
Unit cell dimensions	*a* = 10.9034(6) Å	α = 90 deg.
	b = 9.1653(5) Å	β = 100.487(3) deg.
	c = 18.9173(10) Å	γ = 90 deg.
Volume	1858.88(17) $Å^3$	
Z, Calculated density	4, 2.002 Mg/m^3	
Absorption coefficient	8.113 mm^{-1}	
F(000)	1064	
Crystal size	0.2 x 0.1 x 0.1 mm	
Theta range for data collection	3.24 to 27.51 deg.	
Limiting indices	-14<h<14, -11<k<10, -24<l<24	
Reflections collected / unique	7191 / 4232 [R(int) = 0.0501]	
Completeness to theta = 27.47	99.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.4975 and 0.4975	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4232 / 0 / 227	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0478, wR2 = 0.1156	
R indices (all data)	R1 = 0.0670, wR2 = 0.1261	
Extinction coefficient	0.0008(3)	
Largest diff. peak and hole	0.960 and -1.686 $e.A^{-3}$	

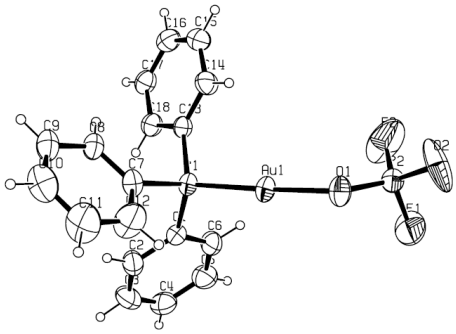


Figure S3. An ORTEP drawing of $Au(PPh_3)OPOF_2$ with 30% probability of thermal ellipsoids.

Table S4. Crystal data and structure refinement for **11a**.

Empirical formula	C19 H23 N O2 S	
Formula weight	329.44	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system, Space group	Monoclinic, P -1	
Unit cell dimensions	*a* = 10.7154(6) Å	α = 90.017(3)°.
	b = 12.3673(8) Å	β= 98.585(4)°.
	c = 13.3603(9) Å	γ = 90.014(4)°.
Volume	1750.68(19) $Å^3$	
Z, Calculated density	4, 1.250 Mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	704	
Crystal size	0.4 x 0.2 x 0.1 mm^3	
Theta range for data collection	1.65 to 27.40°.	
Index ranges	-13<h<12, -15<k<15, -14<l<17	
Reflections collected / Independent reflections	11188 / 7851 [R(int) = 0.0306]	
Completeness to theta = 27.40°	98.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9809 and 0.9264	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7851 / 0 / 415	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.0949, wR2 = 0.2341	
R indices (all data)	R1 = 0.1678, wR2 = 0.2662	
Largest diff. peak and hole	0.348 and -0.377 $e.Å^{-3}$	

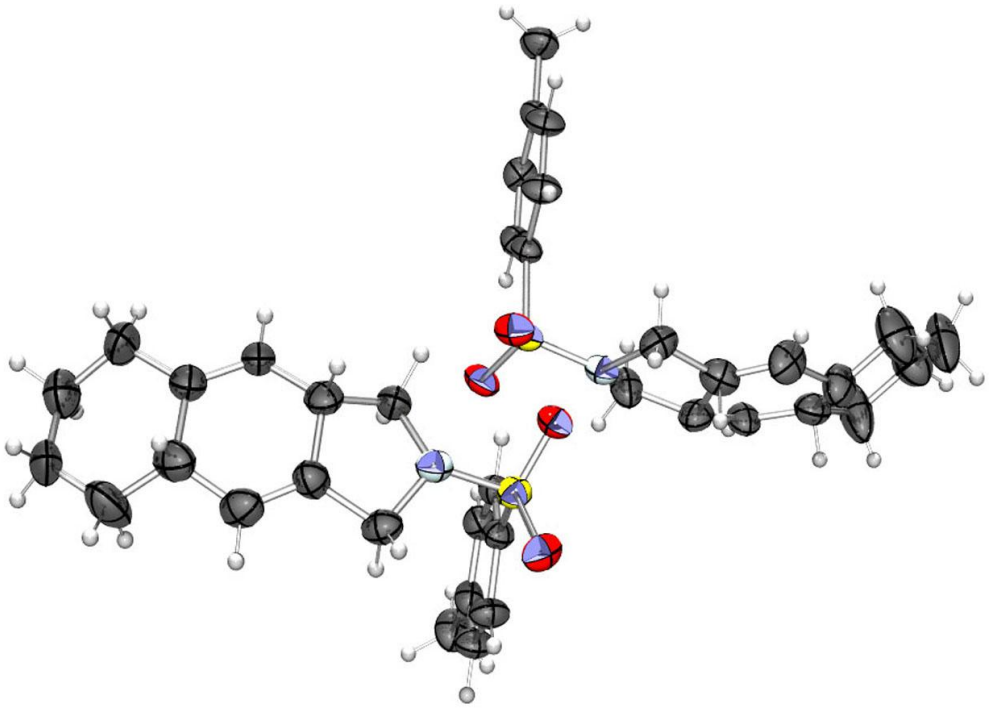


Figure S3. An ORTEP drawing of **11a** with 30% probability of thermal ellipsoids.

VI. References

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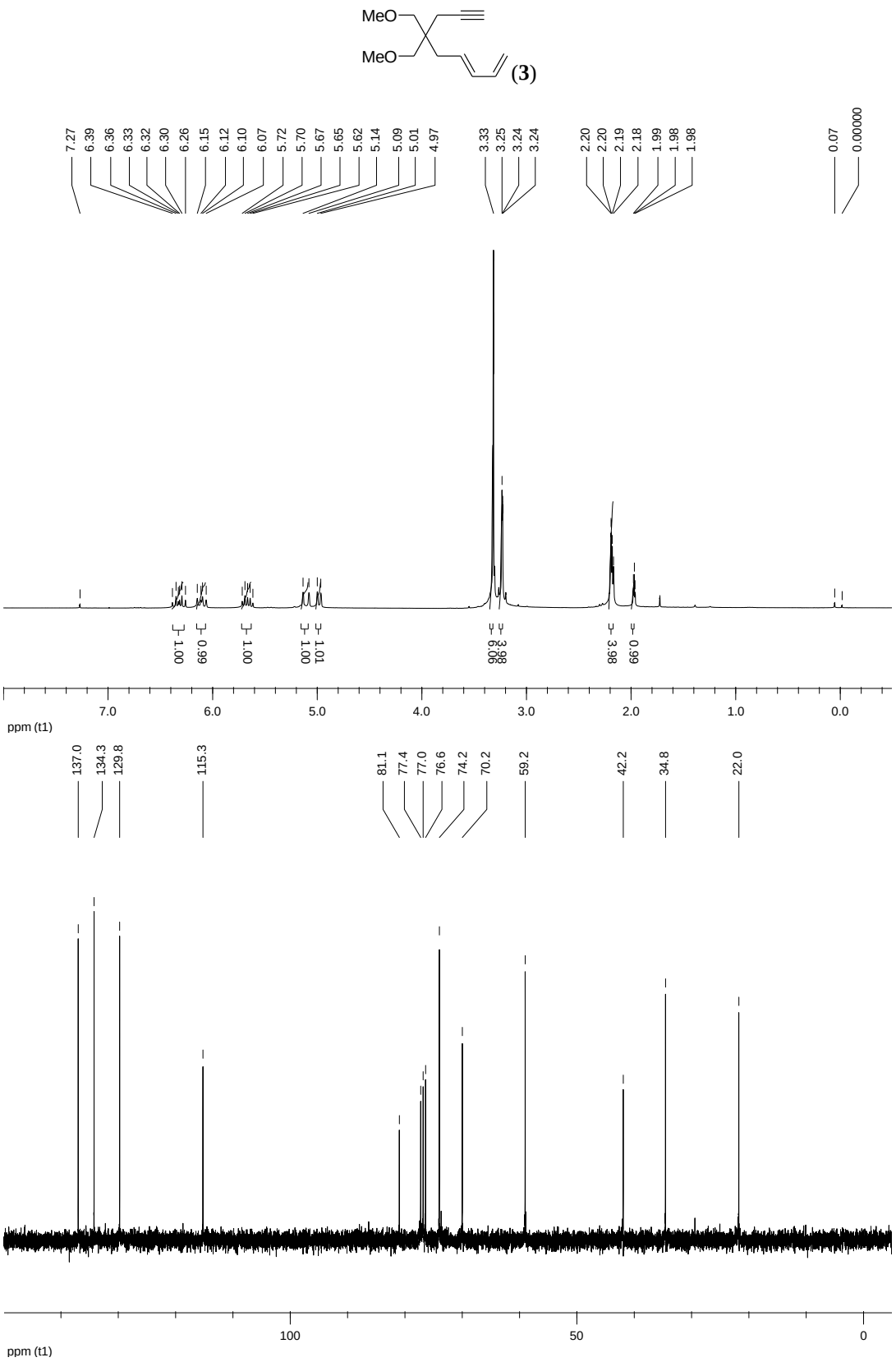
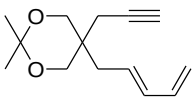
VII. ^{1}H NMR and ^{13}C NMR spectra





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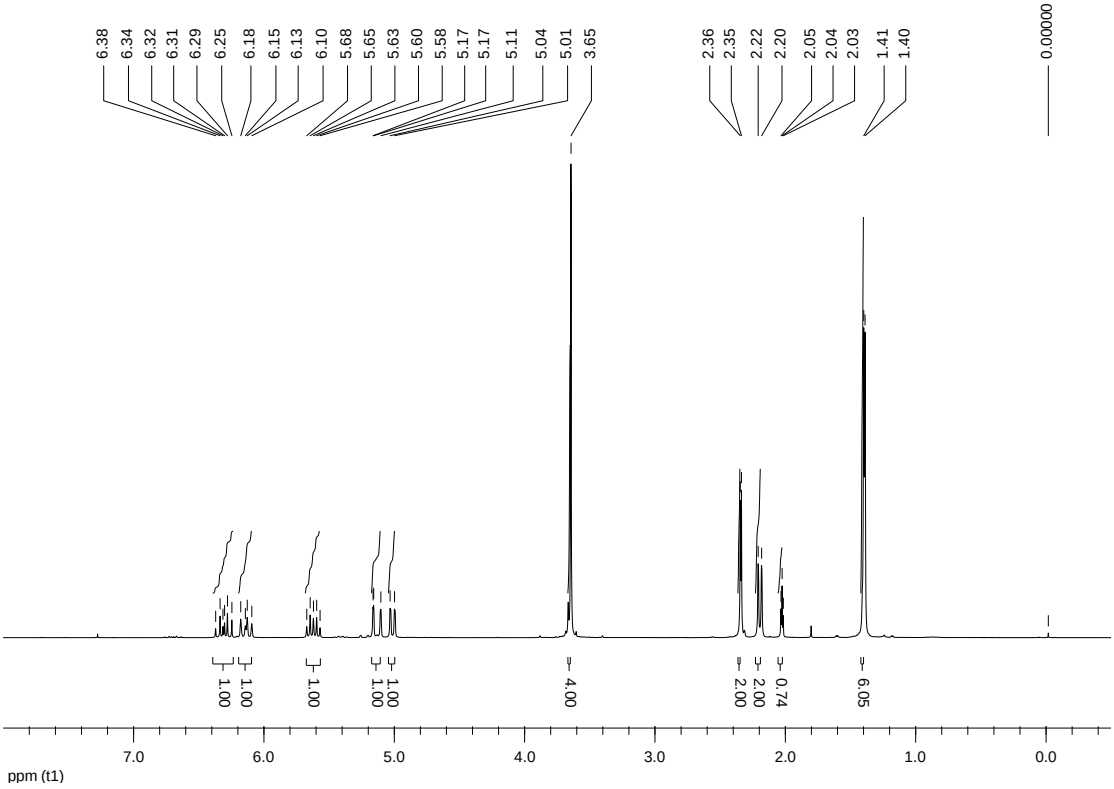
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6.25
6.18
6.15
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6.10
5.68
5.65
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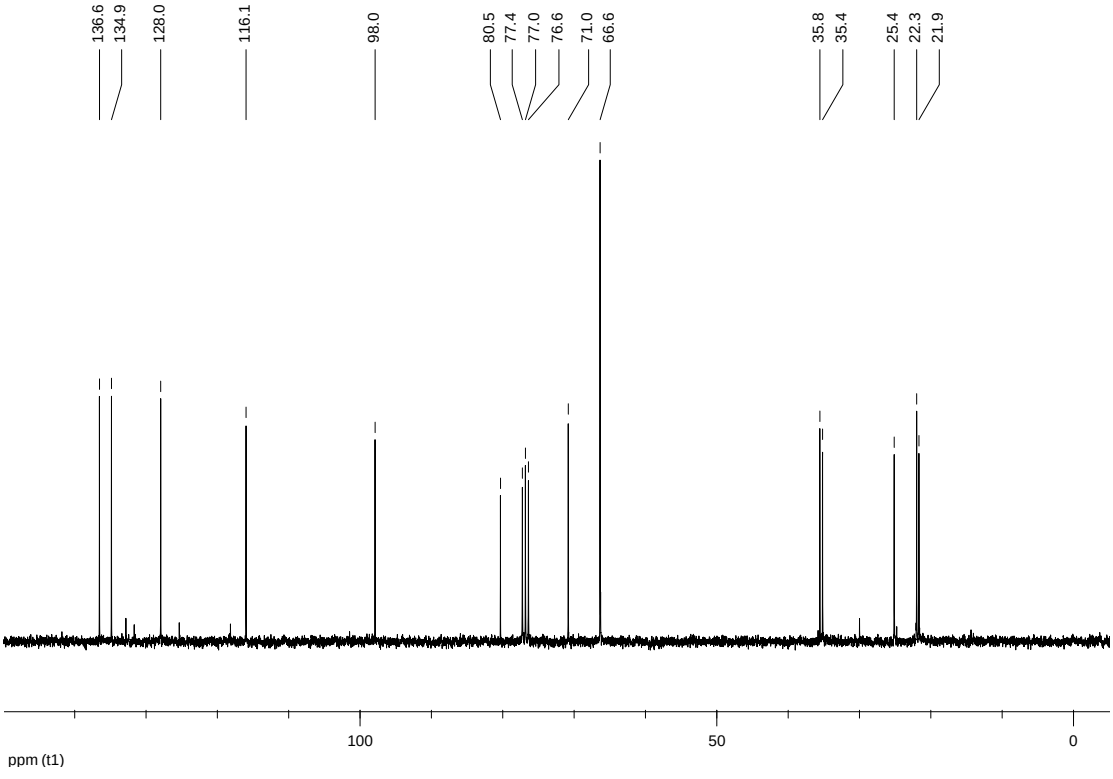
5.60
5.58
5.17
5.17
5.11
5.04
5.01
3.65
2.36
2.35
2.22
2.20
2.05
2.04
2.03
1.41
1.40
0.00000
1.00
1.00
1.00
1.00
1.00
4.00
2.00
2.00
0.74
6.05
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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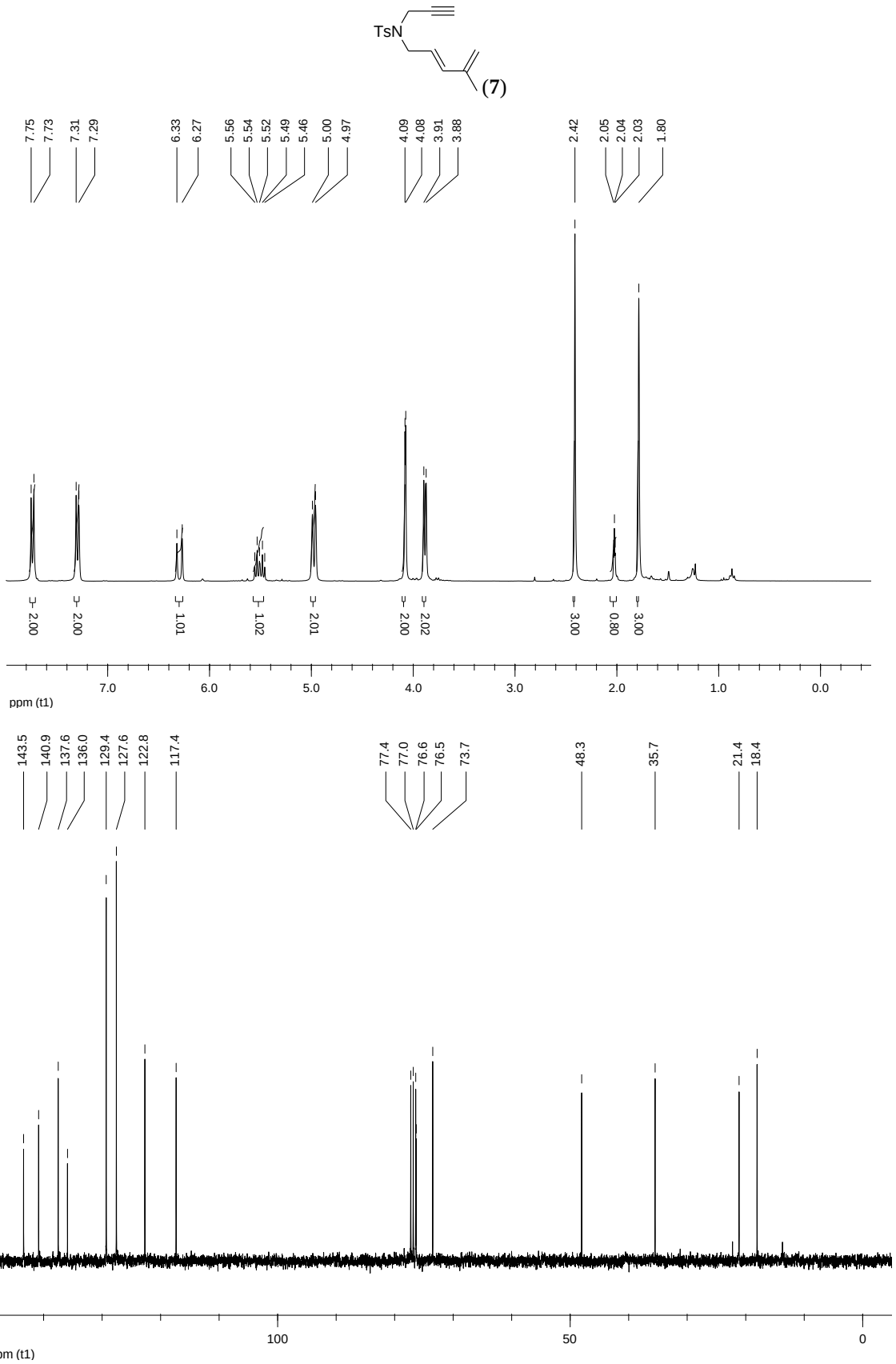
134.9
128.0
116.1
98.0
80.5
77.4
77.0
76.6
71.0
66.6
35.8
35.4
25.4
22.3
21.9
100
50
0
ppm (t1)


TsN
(7)
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7.73
7.31
7.29
6.33
6.27
5.56
5.54
5.52
5.49
5.46
5.00
4.97
4.09
4.08
3.91
3.88
2.42
2.05
2.04
2.03
1.80
2.00
2.00
1.01
1.02
2.01
2.00
2.02
3.00
0.80
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.5
140.9
137.6
136.0
129.4
127.6
122.8
117.4
77.4
77.0
76.6
76.5
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35.7
21.4
18.4
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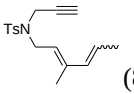
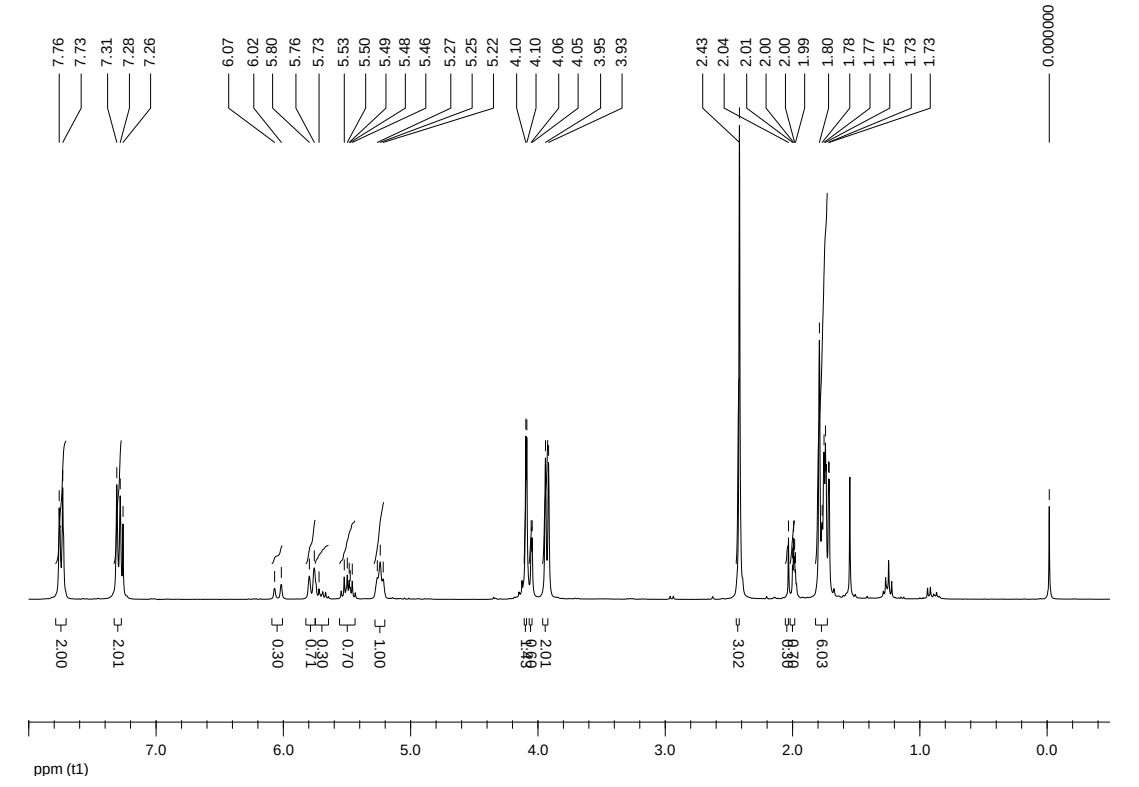
50
0
ppm (t1)


TsN

(8)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6.02
5.80
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5.73
5.53
5.50
5.49
5.48
5.46
5.27
5.25
5.22
4.10
4.06
4.05
3.95
3.93
2.43
2.04
2.01
2.00
2.00
1.99
1.80
1.78
1.77
1.75
1.73
1.73
0.000000
2.00
2.01
0.30
0.71
0.70
1.00
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3.02
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7.0
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2.0
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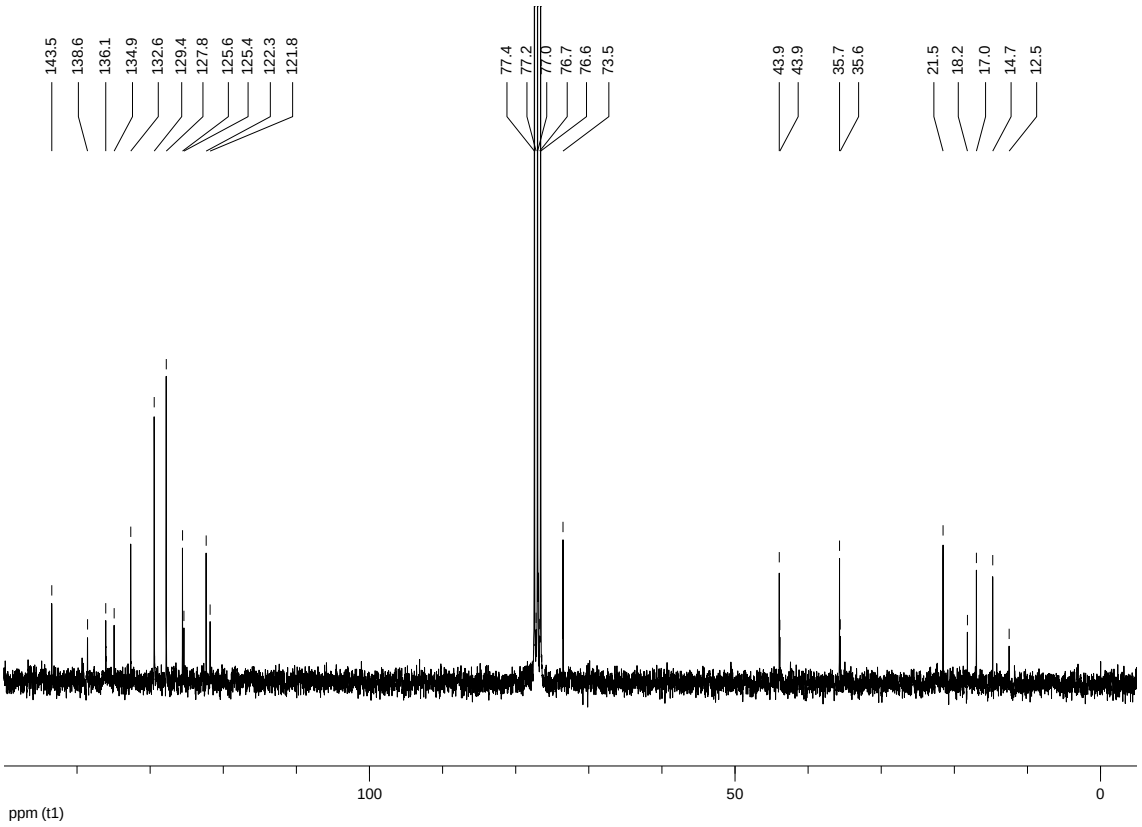
0.0
ppm (t1)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138.6
136.1
134.9
132.6
129.4
127.8
125.6
125.4
122.3
121.8
77.4
77.2
77.0
76.7
76.6
73.5
43.9
43.9
35.7
35.6
21.5
18.2
17.0
14.7
12.5
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50
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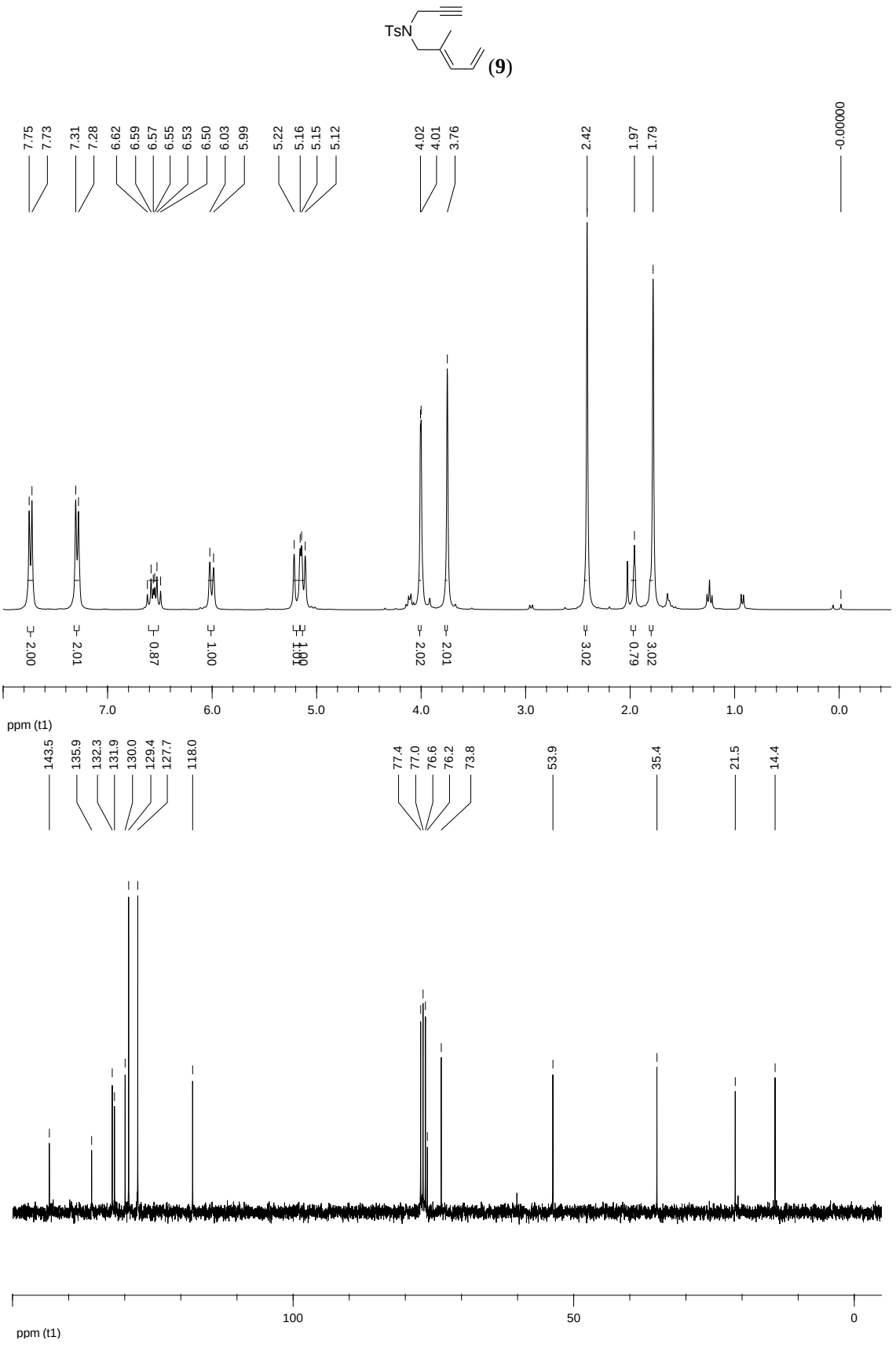
ppm (t1)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6.55
6.53
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6.03
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5.22
5.16
5.15
5.12
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4.01
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1.79
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2.01
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1.00
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2.02
2.01
3.02
0.79
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.5
135.9
132.3
131.9
130.0
129.4
127.7
118.0
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77.0
76.6
76.2
73.8
53.9
35.4
21.5
14.4
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50
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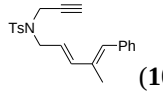
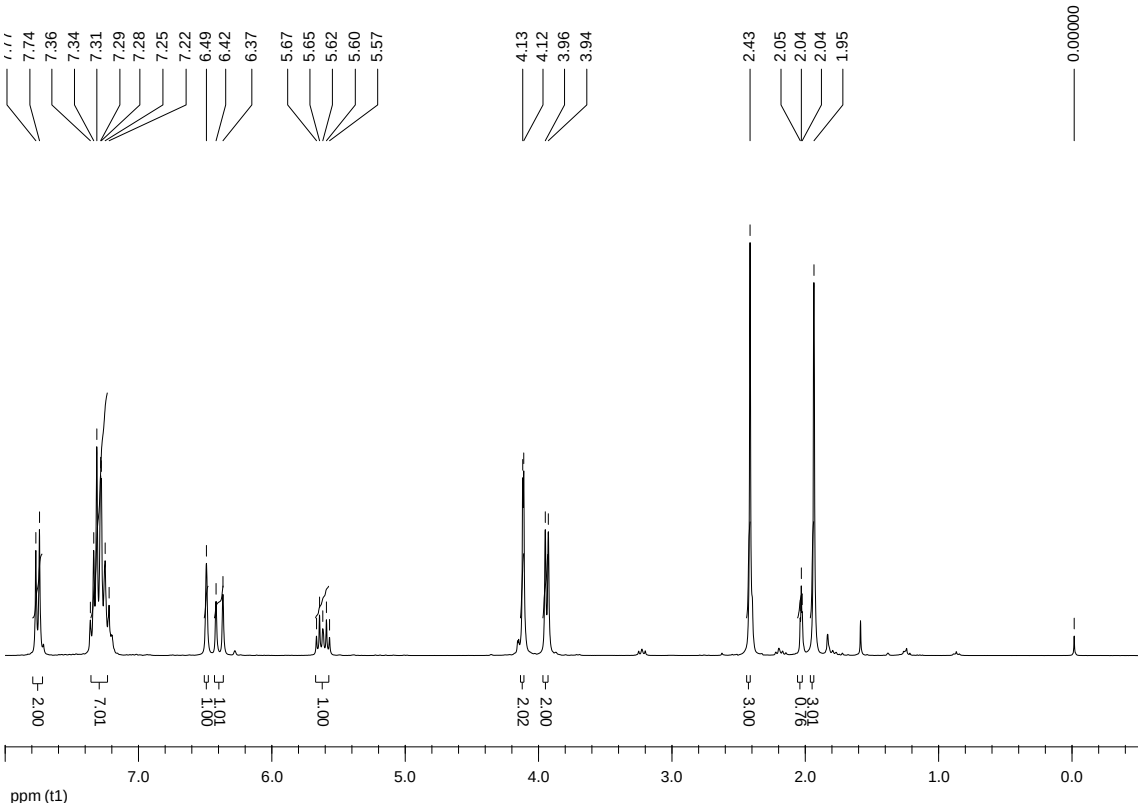
ppm (t1)


TsN
Ph

(10)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5.62
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5.57
4.13
4.12
3.96
3.94
2.43
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2.04
2.04
1.95
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1.00
2.02
2.00
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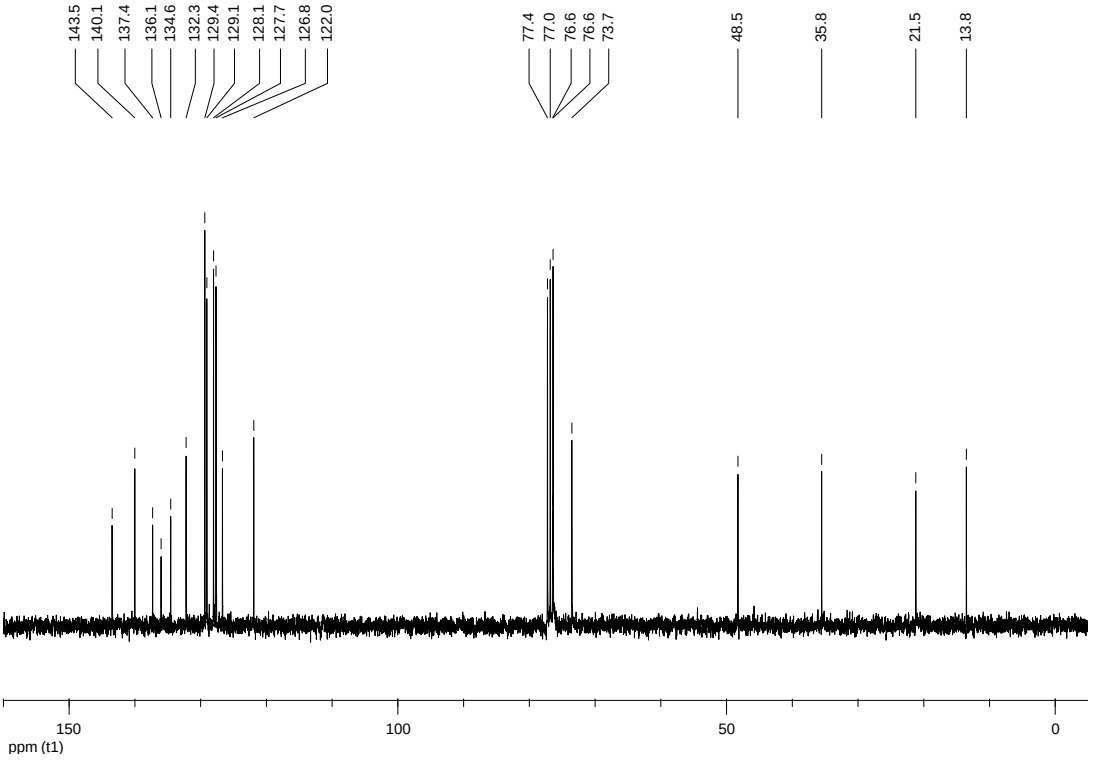
ppm (t1)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129.1
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127.7
126.8
122.0
77.4
77.0
76.6
76.6
73.7
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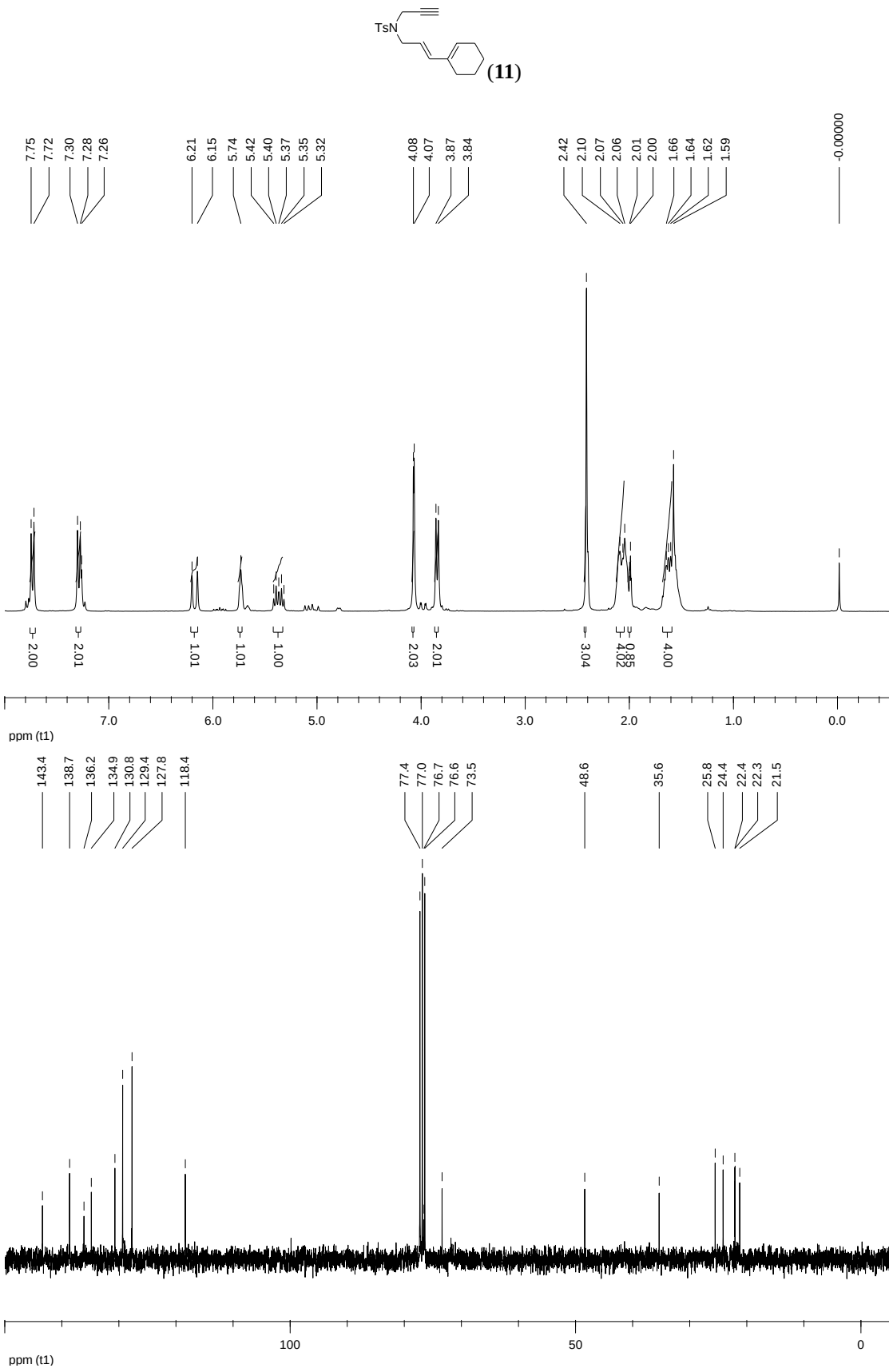
35.8
21.5
13.8
150
100
50
0
ppm (t1)


TsN
(11)
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7.28
7.26
6.21
6.15
5.74
5.42
5.40
5.37
5.35
5.32
4.08
4.07
3.87
3.84
2.42
2.10
2.07
2.06
2.01
2.00
1.66
1.64
1.62
1.59
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2.01
1.01
1.01
1.00
2.03
2.01
3.04
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0.42
4.00
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6.0
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4.0
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0.0
ppm (t1)
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134.9
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129.4
127.8
118.4
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76.7
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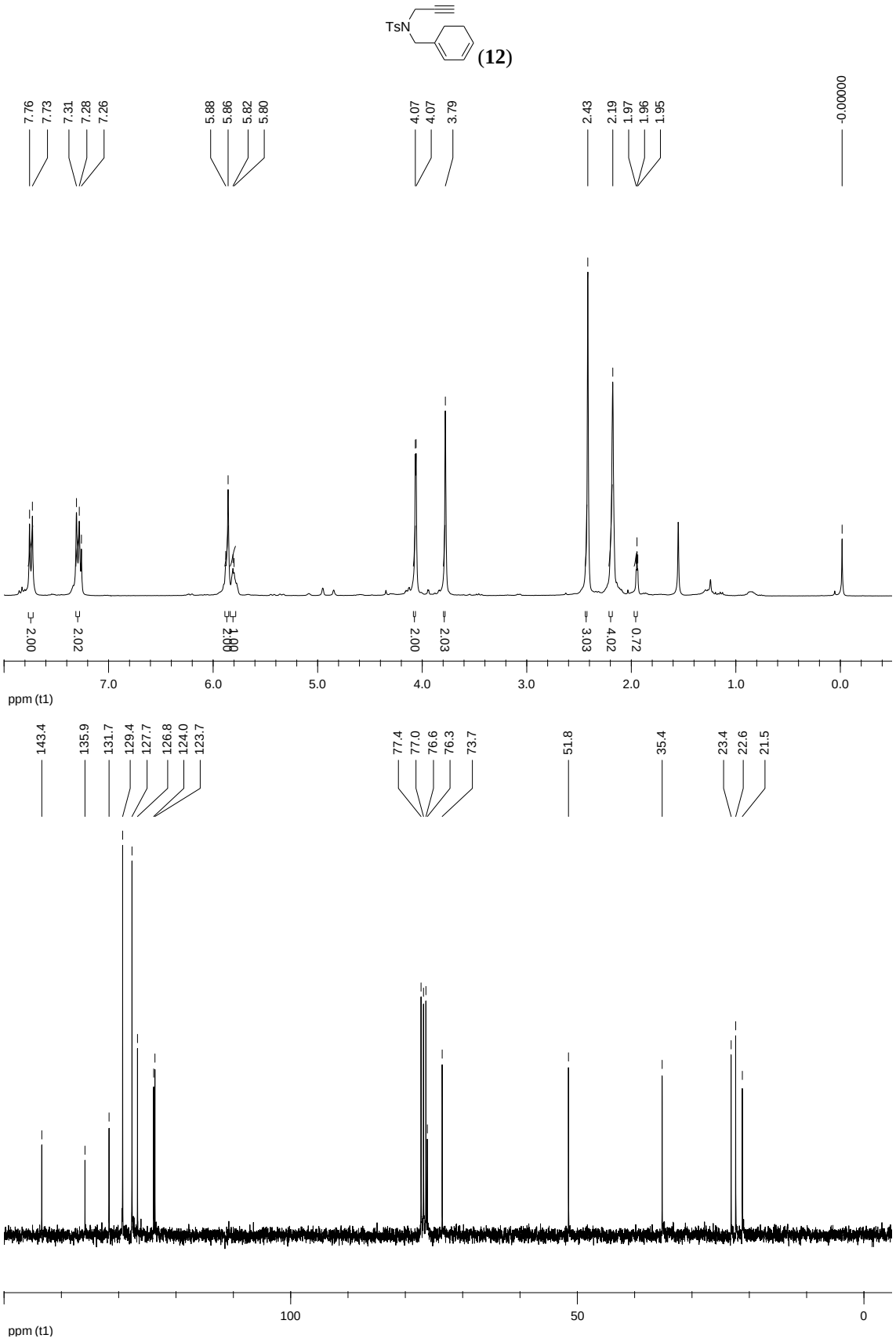
ppm (t1)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4.07
3.79
2.43
2.19
1.97
1.96
1.95
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2.00
2.02
1.00
2.00
2.03
3.03
4.02
0.72
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
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131.7
129.4
127.7
126.8
124.0
123.7
77.4
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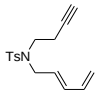
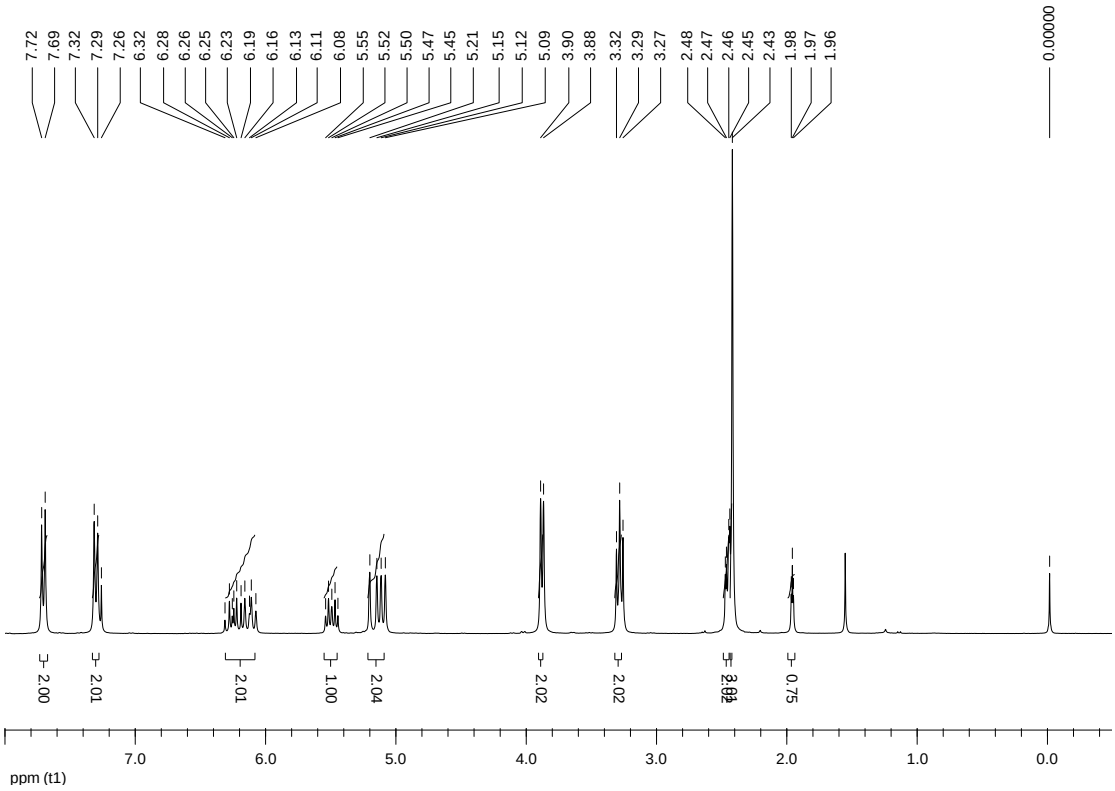
ppm (t1)


TsN

(13)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3.29
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2.02
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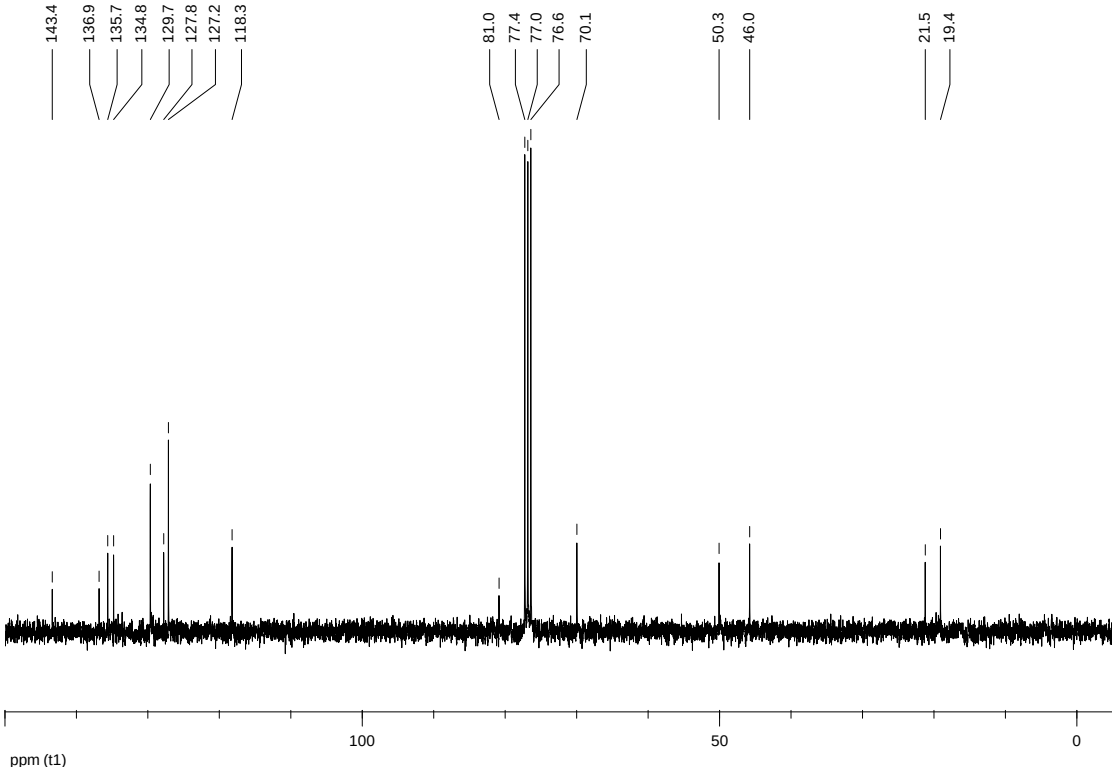
ppm (t1)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127.2
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19.4
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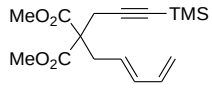
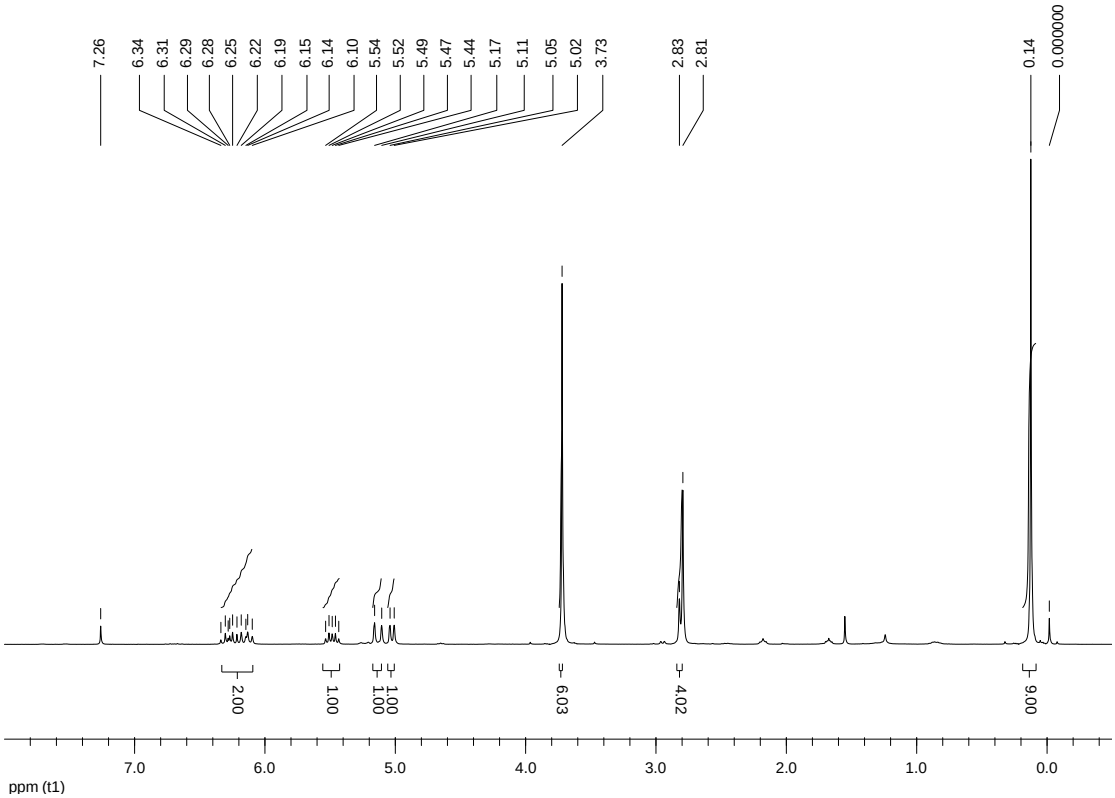
50
0
ppm (t1)


MeO2C
TMS
MeO2C

(**16**)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5.49
5.47
5.44
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5.11
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5.02
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2.81
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0.000000
2.00
1.00
1.00
1.00
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7.0
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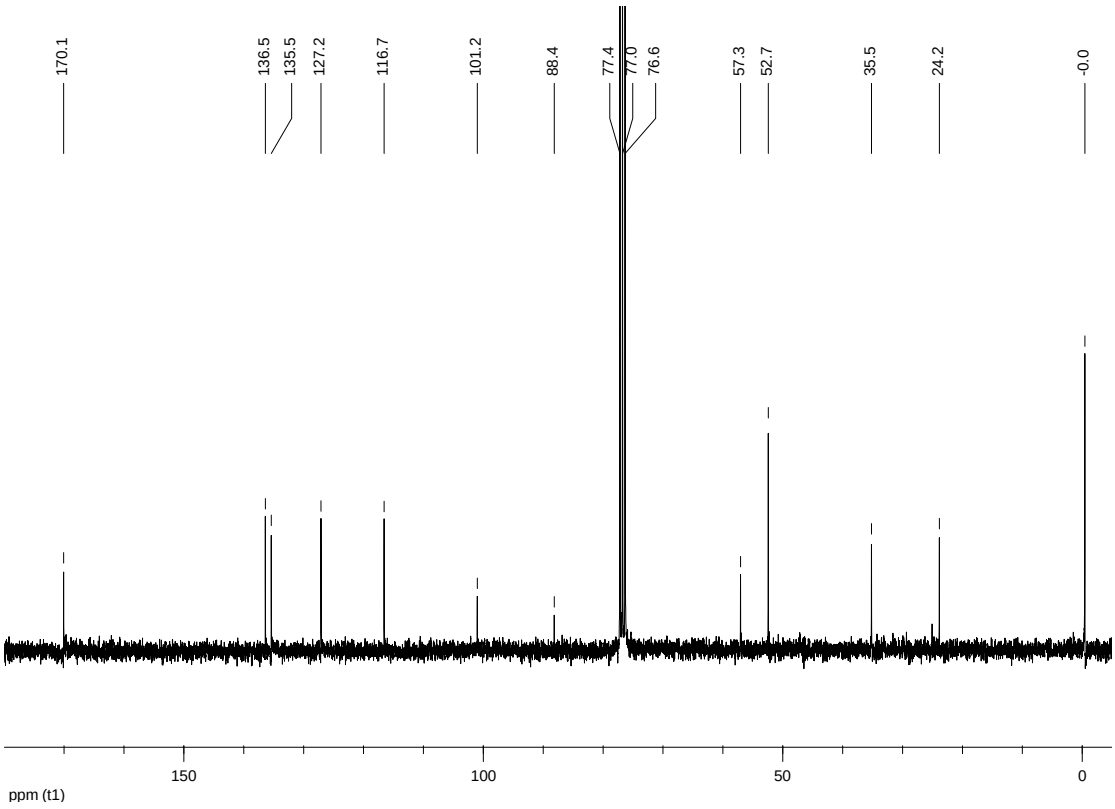
1.0
0.0
ppm (t1)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101.2
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76.6
57.3
52.7
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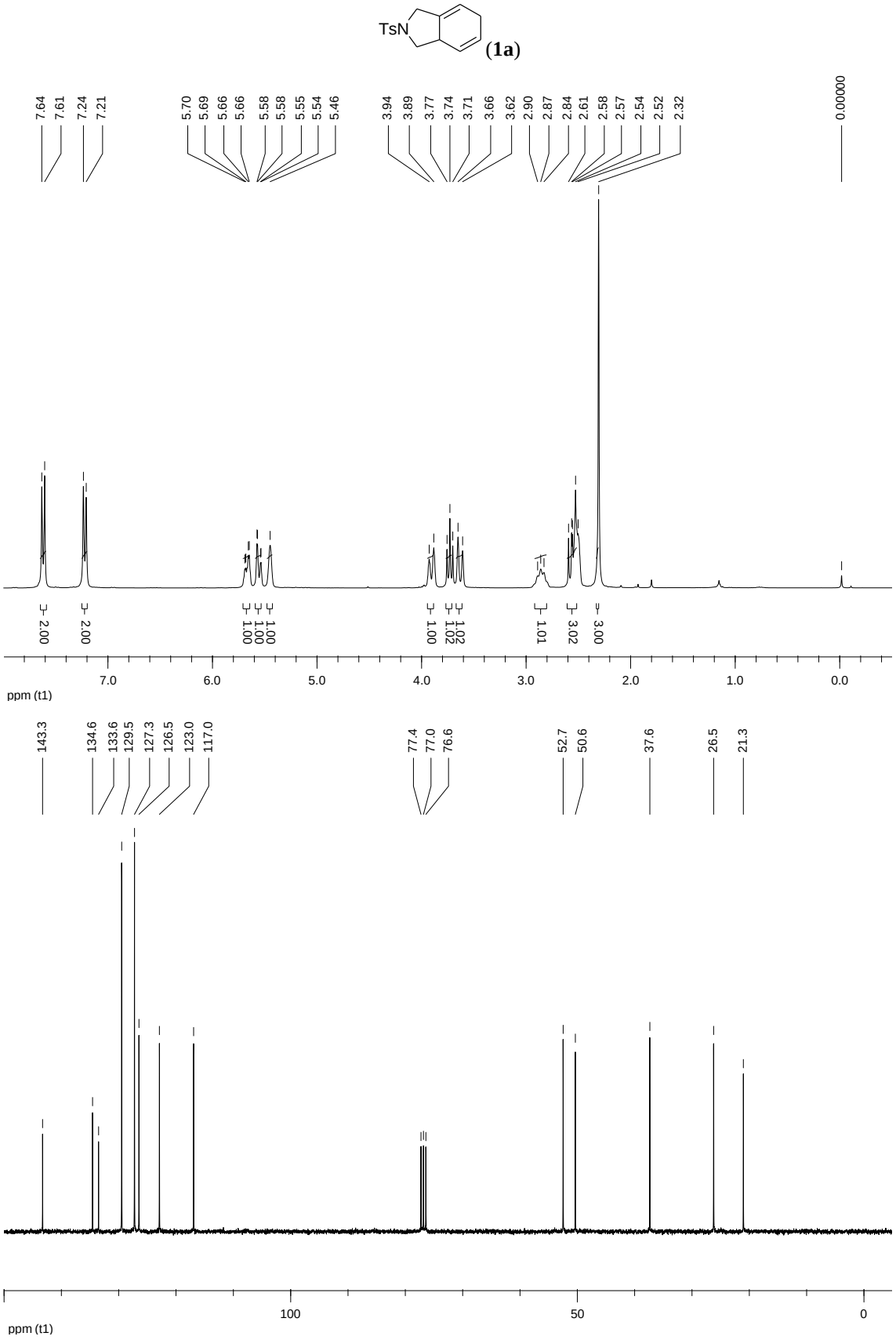
24.2
-0.0
150
100
50
0
ppm (t1)


TsN
(1a)
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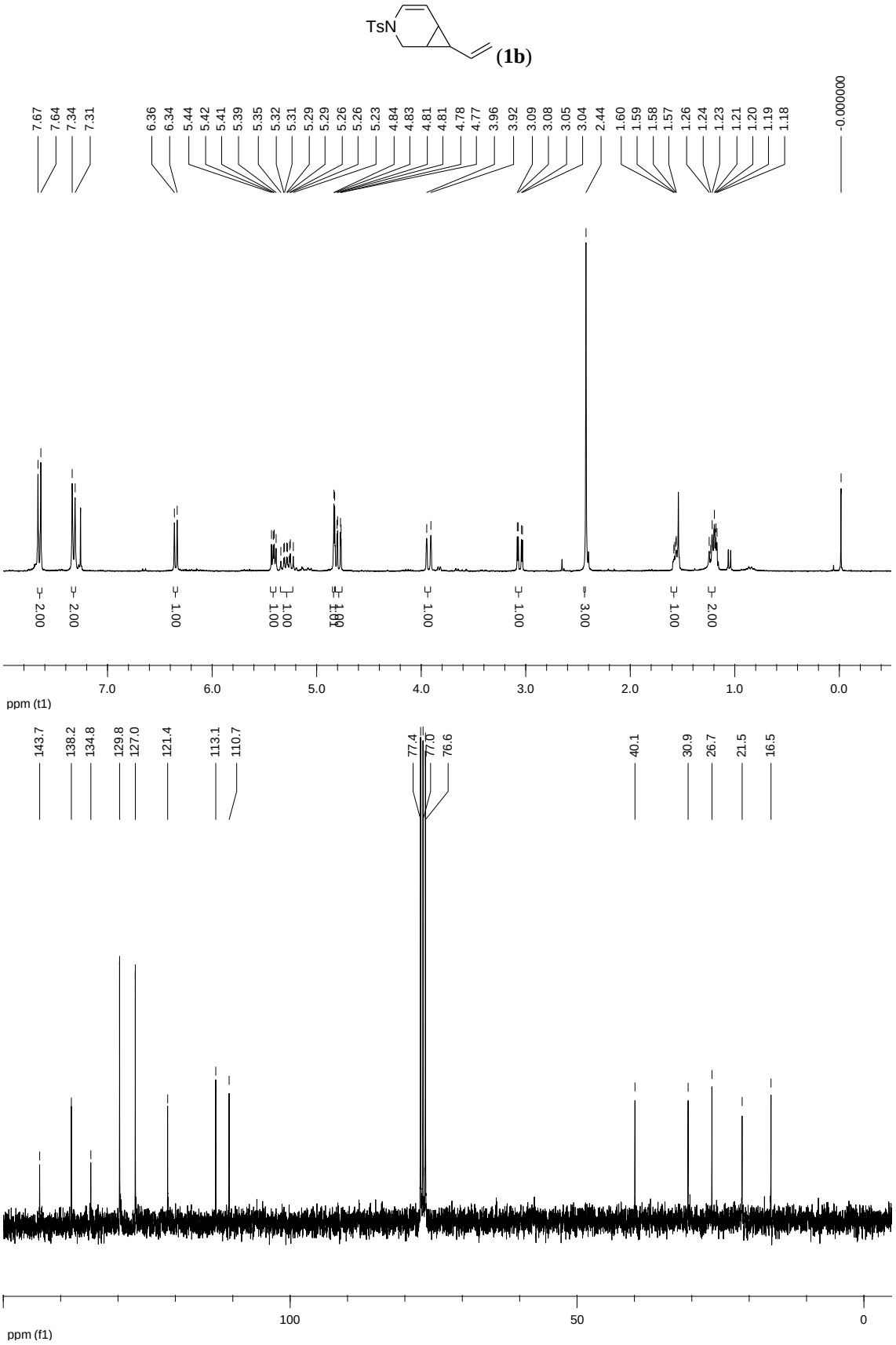
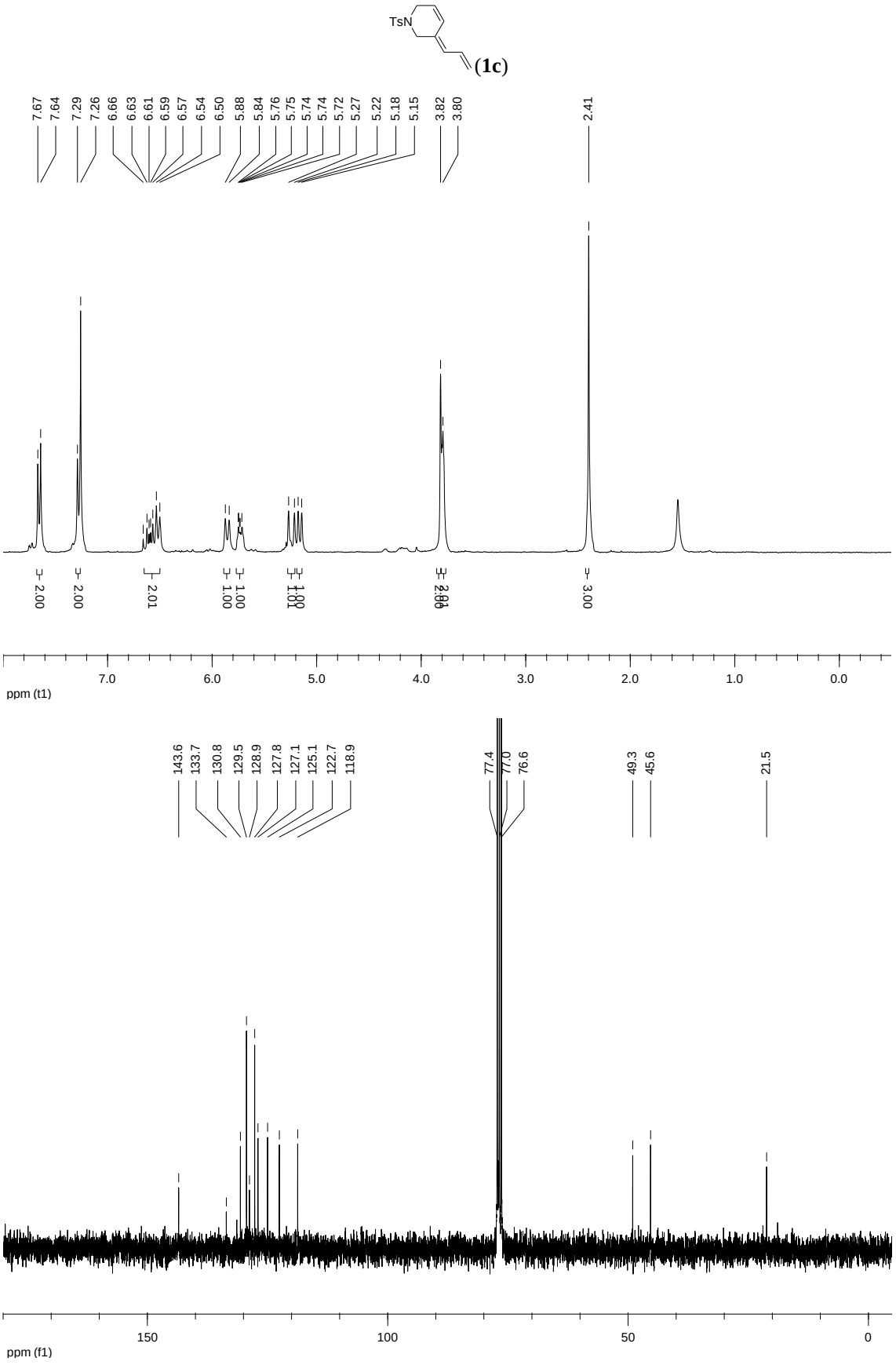
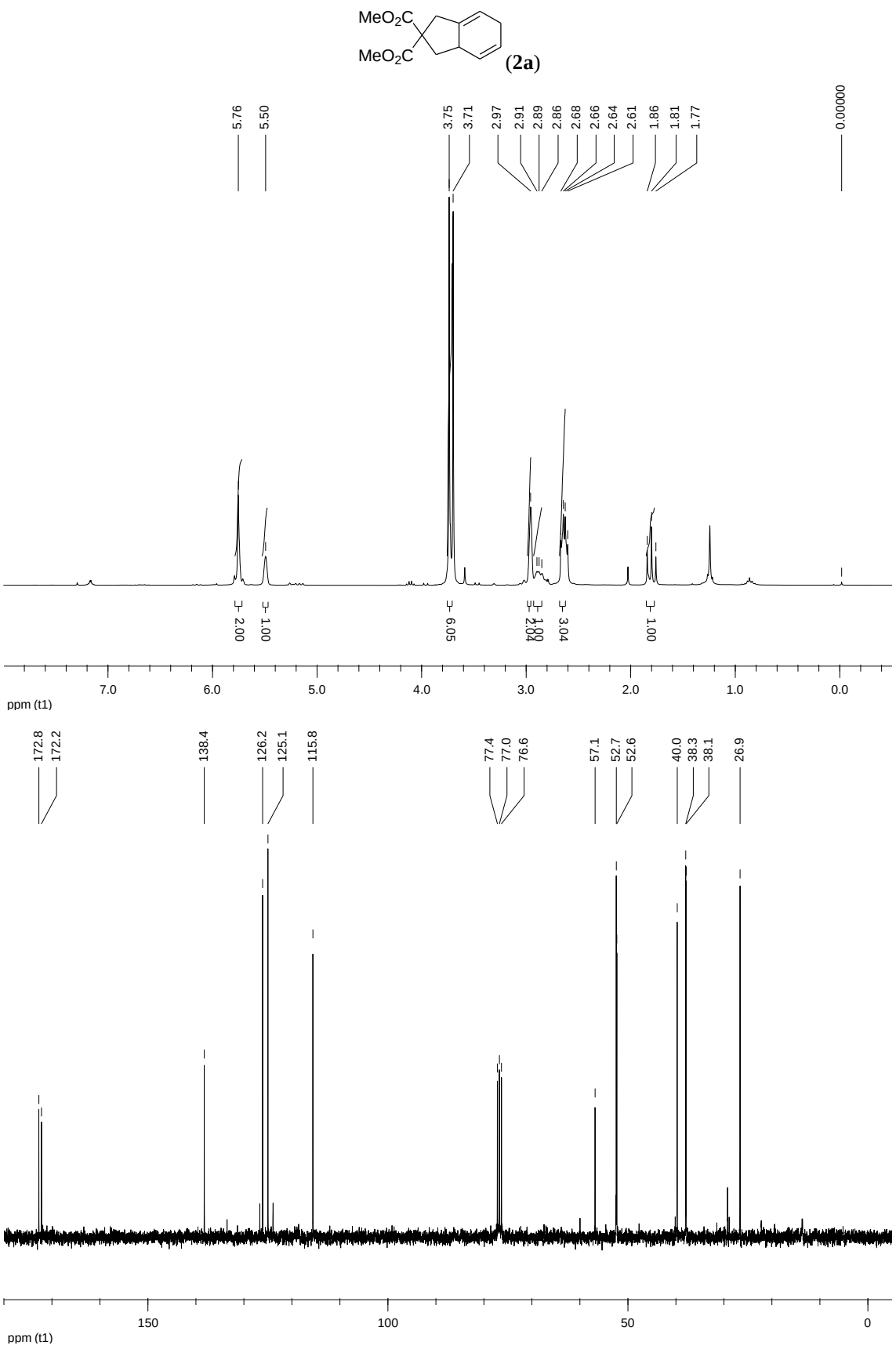
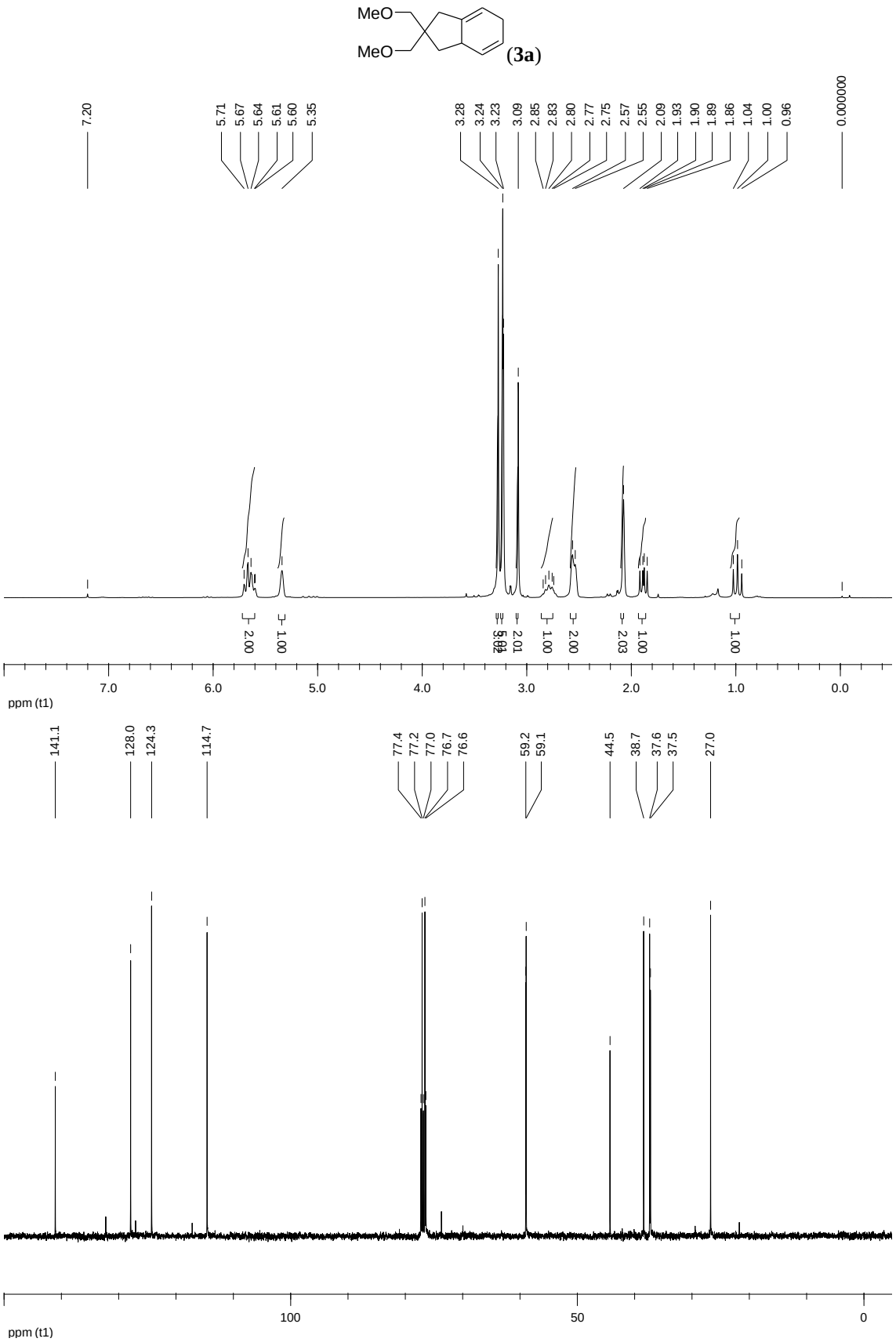
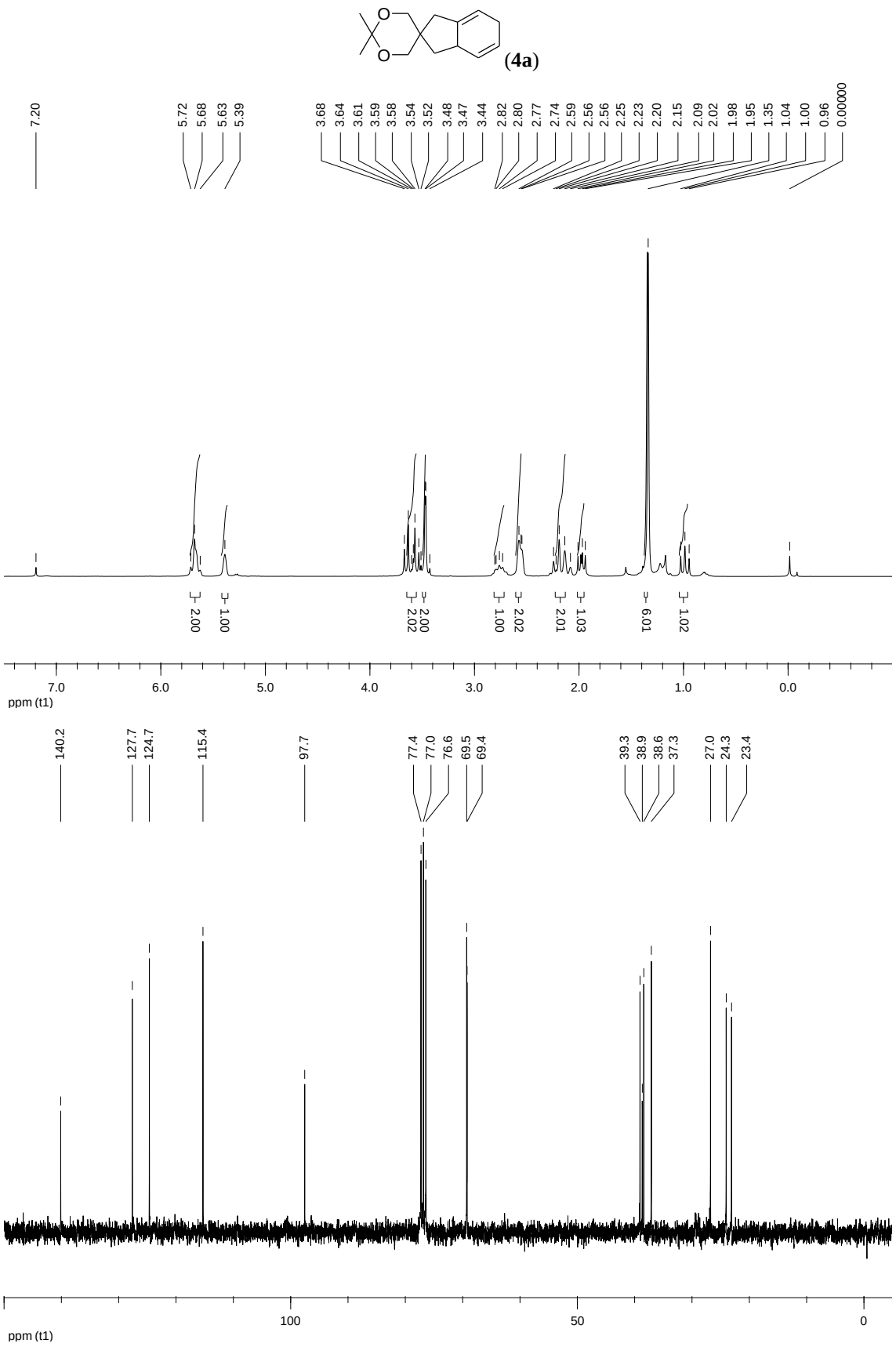
7.24
7.21
5.70
5.69
5.66
5.66
5.58
5.58
5.55
5.54
5.46
3.94
3.89
3.77
3.74
3.71
3.66
3.62
2.90
2.87
2.84
2.61
2.58
2.57
2.54
2.52
2.32
0.00000
2.00
2.00
1.00
1.00
1.00
1.00
1.02
1.02
1.01
3.02
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.3
134.6
133.6
129.5
127.3
126.5
123.0
117.0
77.4
77.0
76.6
52.7
50.6
37.6
26.5
21.3
100
50
0
ppm (t1)

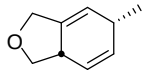

TsN
(1b)
7.67
7.64
7.34
7.31
6.36
6.34
5.44
5.42
5.41
5.39
5.35
5.32
5.31
5.29
5.29
5.26
5.26
5.23
4.84
4.83
4.81
4.81
4.78
4.77
3.96
3.92
3.09
3.08
3.05
3.04
2.44
1.60
1.59
1.58
1.57
1.26
1.24
1.23
1.21
1.20
1.19
1.18
-0.000000
2.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
1.00
2.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.7
138.2
134.8
129.8
127.0
121.4
113.1
110.7
77.4
77.0
76.6
40.1
30.9
26.7
21.5
16.5
100
50
0
ppm (f1)


TsN
(1c)
7.67
7.64
7.29
7.26
6.66
6.63
6.61
6.59
6.57
6.54
6.50
5.88
5.84
5.76
5.75
5.74
5.74
5.72
5.27
5.22
5.18
5.15
3.82
3.80
2.41
2.00
2.00
2.01
1.00
1.00
1.01
2.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.6
133.7
130.8
129.5
128.9
127.8
127.1
125.1
122.7
118.9
77.4
77.0
76.6
49.3
45.6
21.5
150
100
50
0
ppm (f1)

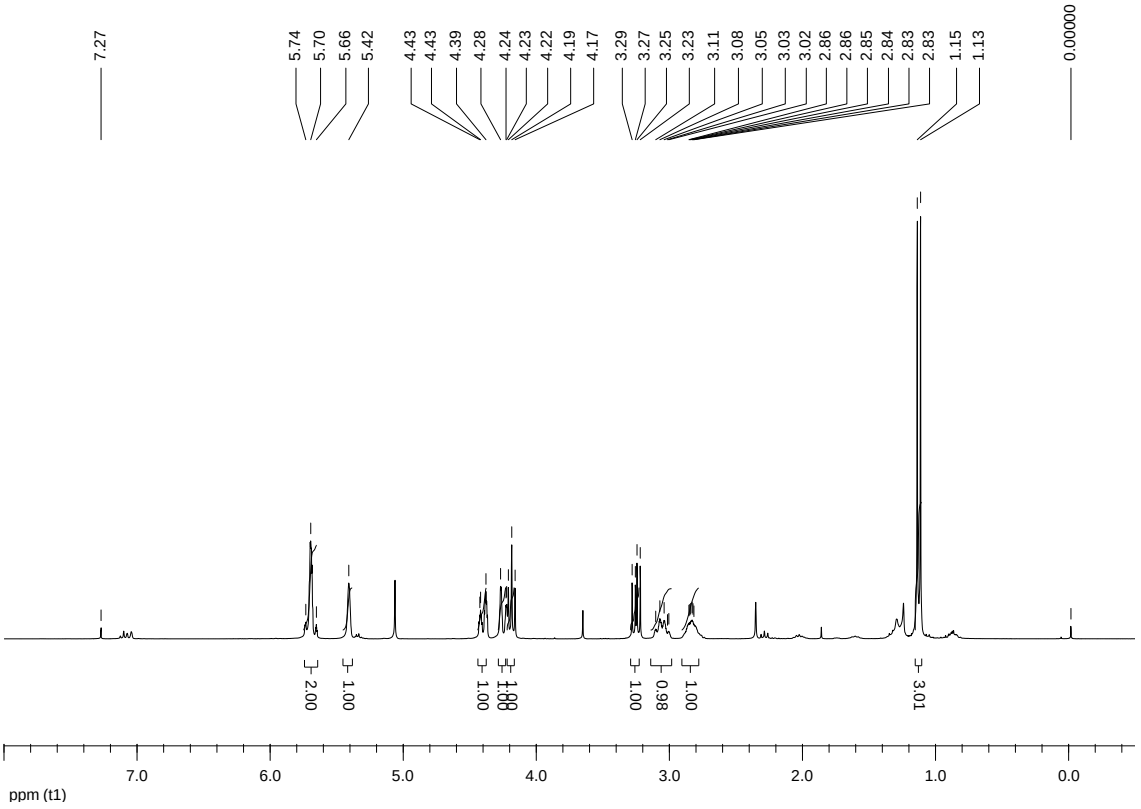

MeO2C
MeO2C
(2a)
5.76
5.50
3.75
3.71
2.97
2.91
2.89
2.86
2.68
2.66
2.64
2.61
1.86
1.81
1.77
0.00000
2.00
1.00
6.05
2.08
1.00
3.04
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
172.8
172.2
138.4
126.2
125.1
115.8
77.4
77.0
76.6
57.1
52.7
52.6
40.0
38.3
38.1
26.9
150
100
50
0
ppm (t1)

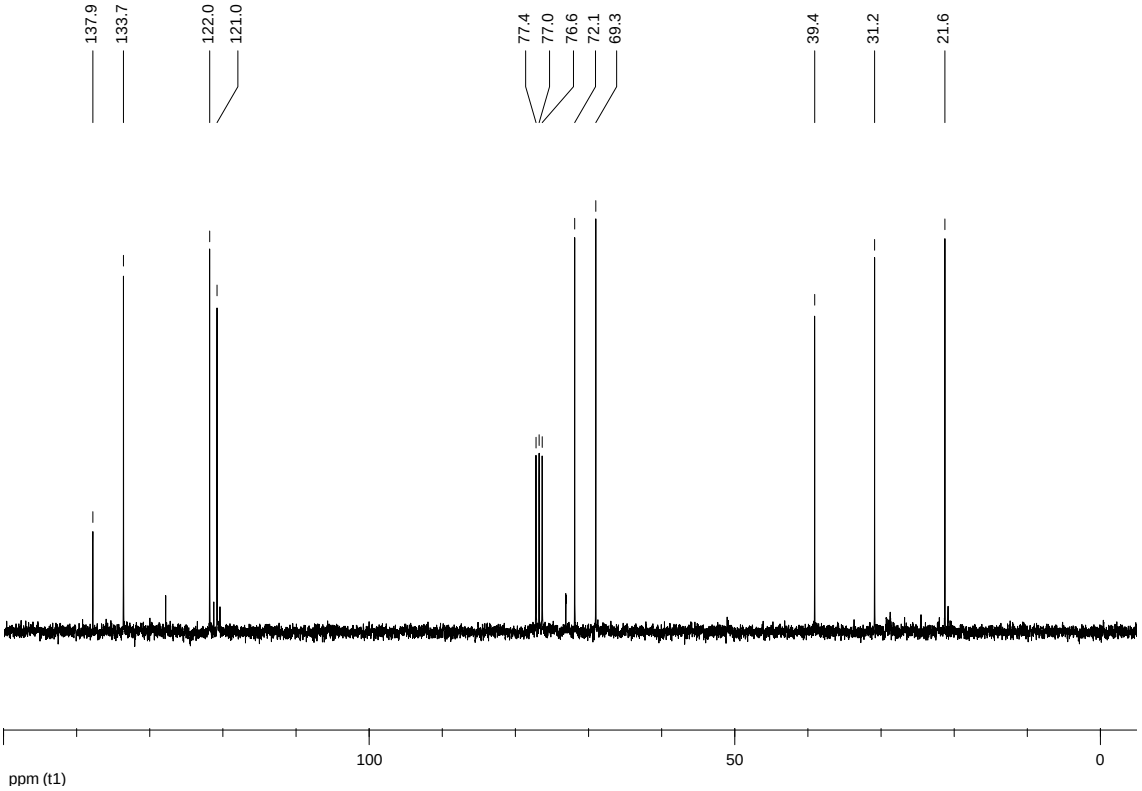

MeO
MeO
(3a)
7.20
5.71
5.67
5.64
5.61
5.60
5.35
3.28
3.24
3.23
3.09
2.85
2.83
2.80
2.77
2.75
2.57
2.55
2.09
1.93
1.90
1.89
1.86
1.04
1.00
0.96
0.000000
2.00
1.00
2.01
1.00
2.00
2.03
1.00
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
141.1
128.0
124.3
114.7
77.4
77.2
77.0
76.7
76.6
59.2
59.1
44.5
38.7
37.6
37.5
27.0
100
50
0
ppm (t1)

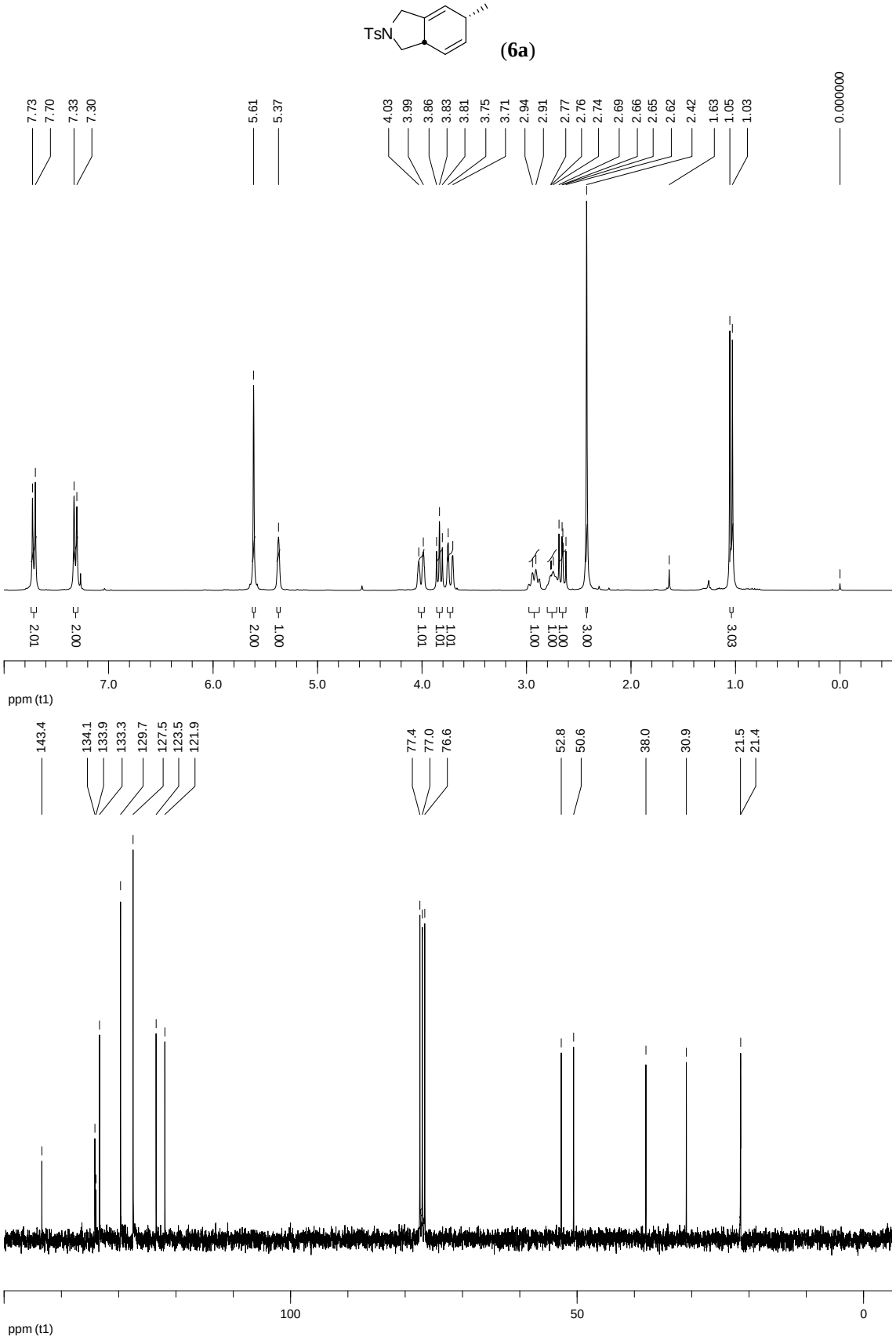

(4a)
7.20
5.72
5.68
5.63
5.39
3.68
3.64
3.61
3.59
3.58
3.54
3.52
3.48
3.47
3.44
2.82
2.80
2.77
2.74
2.59
2.56
2.56
2.25
2.23
2.20
2.15
2.09
2.02
1.98
1.95
1.35
1.04
1.00
0.96
0.00000
2.00
1.00
2.02
2.00
1.00
2.02
2.01
1.03
6.01
1.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
140.2
127.7
124.7
115.4
97.7
77.4
77.0
76.6
69.5
69.4
39.3
38.9
38.6
37.3
27.0
24.3
23.4
100
50
0
ppm (t1)

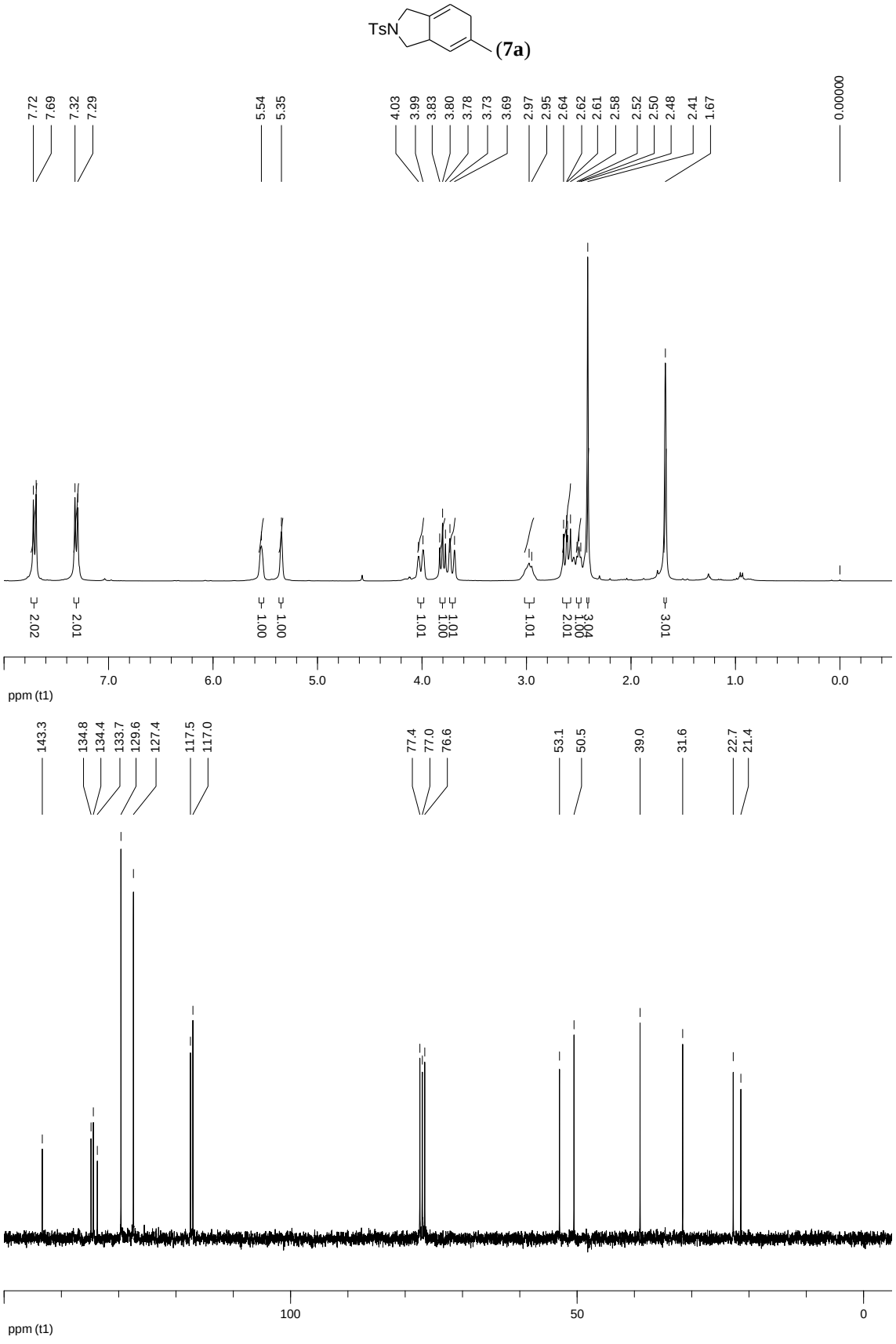


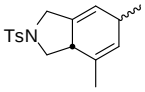
(5a)


7.27
5.74
5.70
5.66
5.42
4.43
4.43
4.39
4.28
4.24
4.23
4.22
4.19
4.17
3.29
3.27
3.25
3.23
3.11
3.08
3.05
3.03
3.02
2.86
2.86
2.85
2.84
2.83
2.83
1.15
1.13
0.00000
2.00
1.00
1.00
1.00
0.98
1.00
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

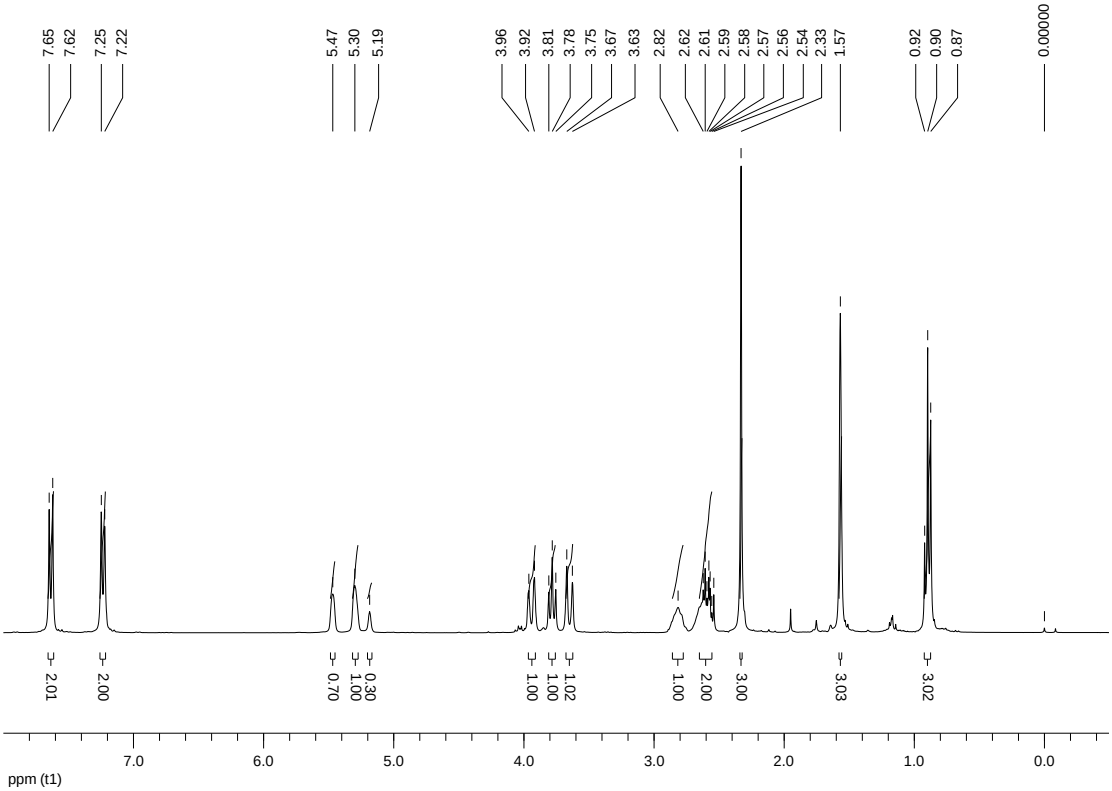

137.9
133.7
122.0
121.0
77.4
77.0
76.6
72.1
69.3
39.4
31.2
21.6
100
50
0
ppm (t1)

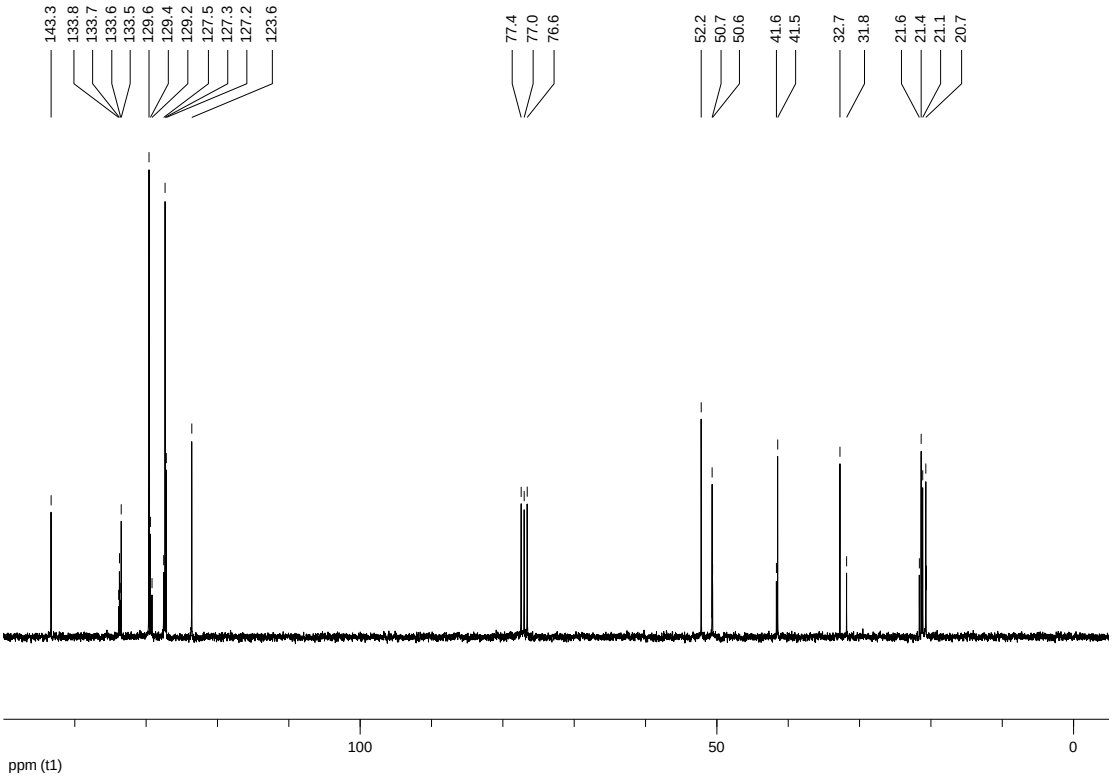

TsN
(6a)
7.73
7.70
7.33
7.30
5.61
5.37
4.03
3.99
3.86
3.83
3.81
3.75
3.71
2.94
2.91
2.77
2.76
2.74
2.69
2.66
2.65
2.62
2.42
1.63
1.05
1.03
0.000000
2.01
2.00
2.00
1.00
1.01
1.01
1.01
1.00
1.00
1.00
3.00
3.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.4
134.1
133.9
133.3
129.7
127.5
123.5
121.9
77.4
77.0
76.6
52.8
50.6
38.0
30.9
21.5
21.4
100
50
0
ppm (t1)

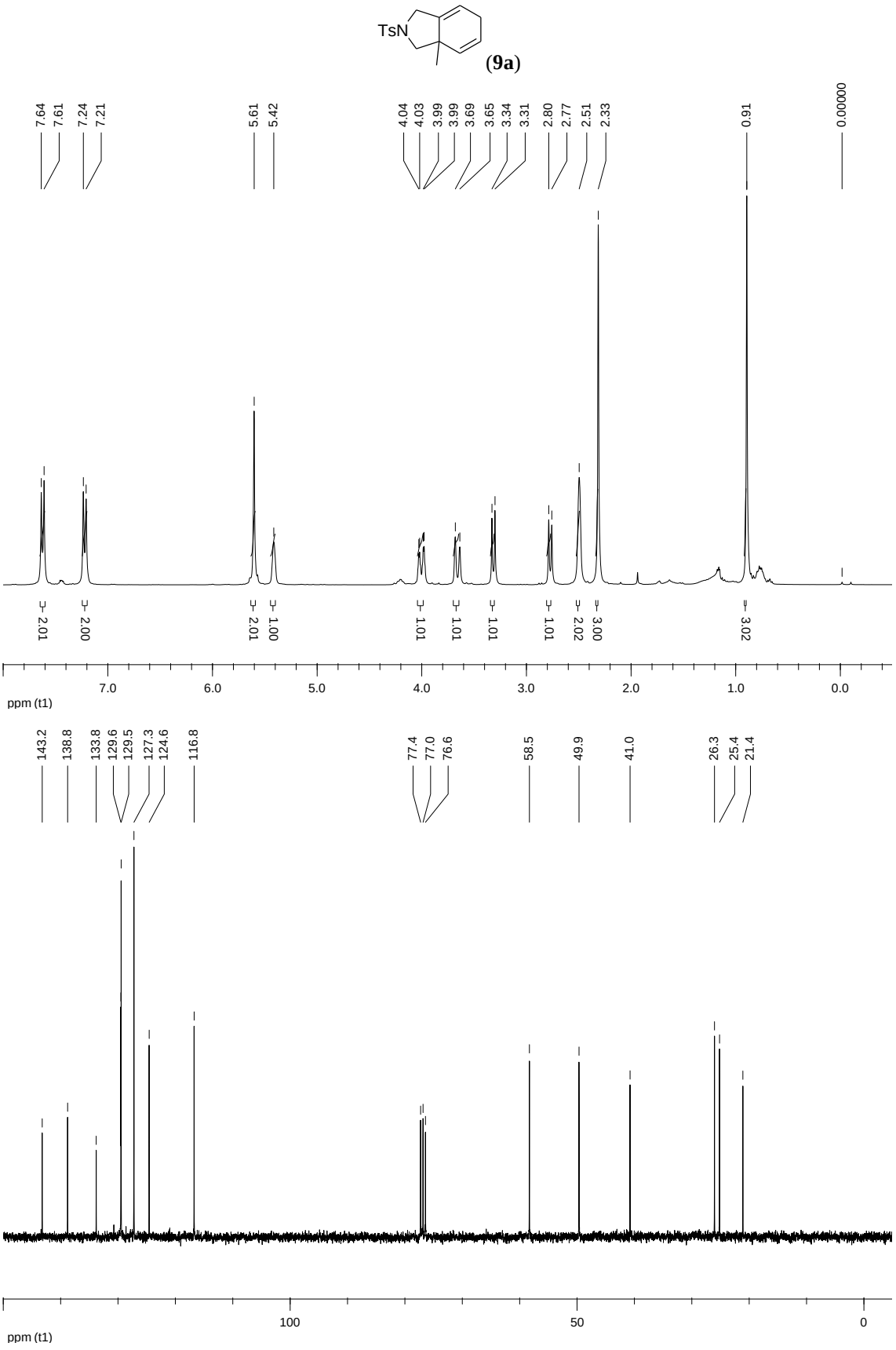

TsN
(7a)
7.72
7.69
7.32
7.29
5.54
5.35
4.03
3.99
3.83
3.80
3.78
3.73
3.69
2.97
2.95
2.64
2.62
2.61
2.58
2.52
2.50
2.48
2.41
1.67
0.00000
2.02
2.01
1.00
1.00
1.01
1.00
1.01
2.01
1.00
3.04
3.01
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.3
134.8
134.4
133.7
129.6
127.4
117.5
117.0
77.4
77.0
76.6
53.1
50.5
39.0
31.6
22.7
21.4
100
50
0
ppm (t1)


TsN

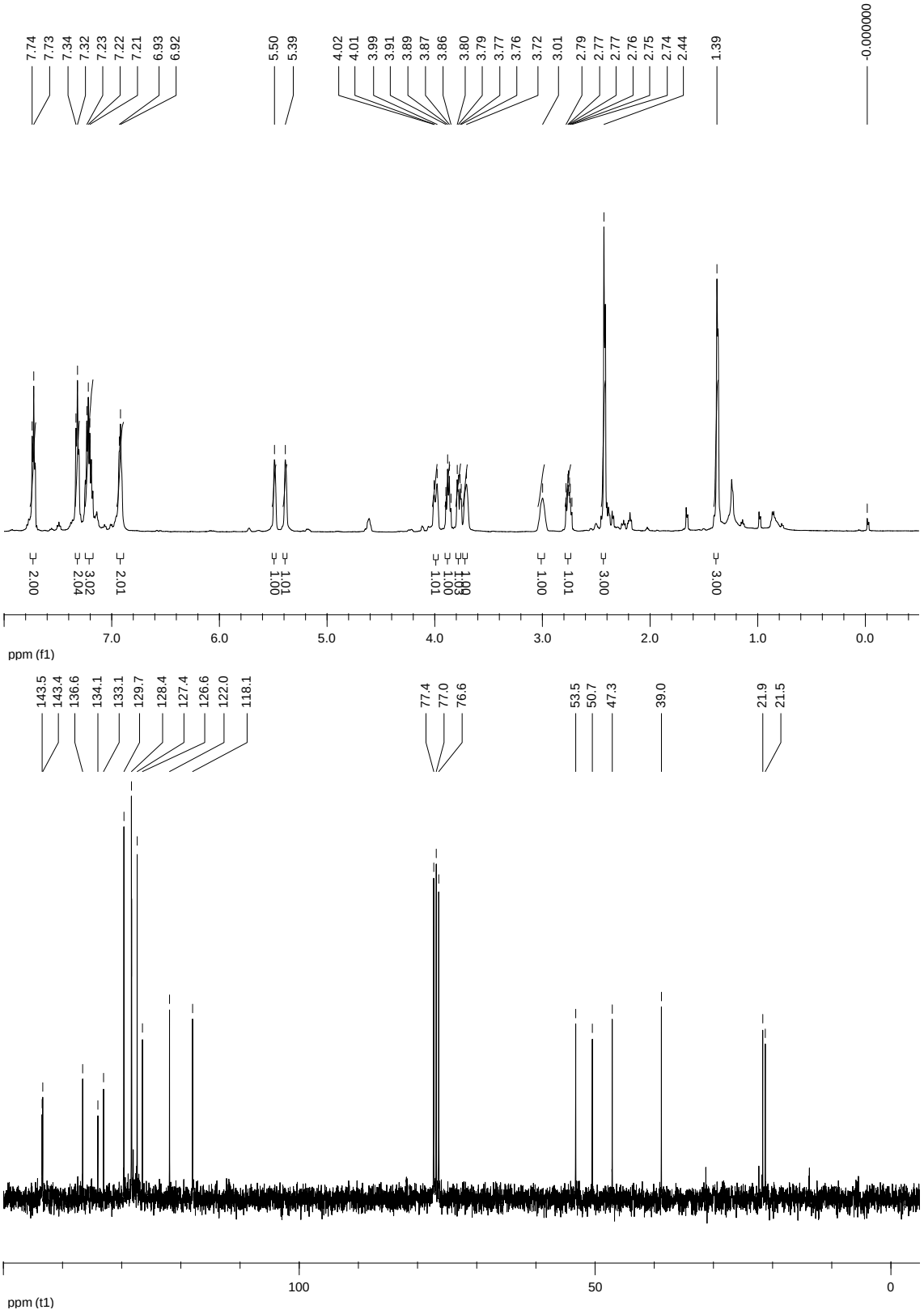
(8a)

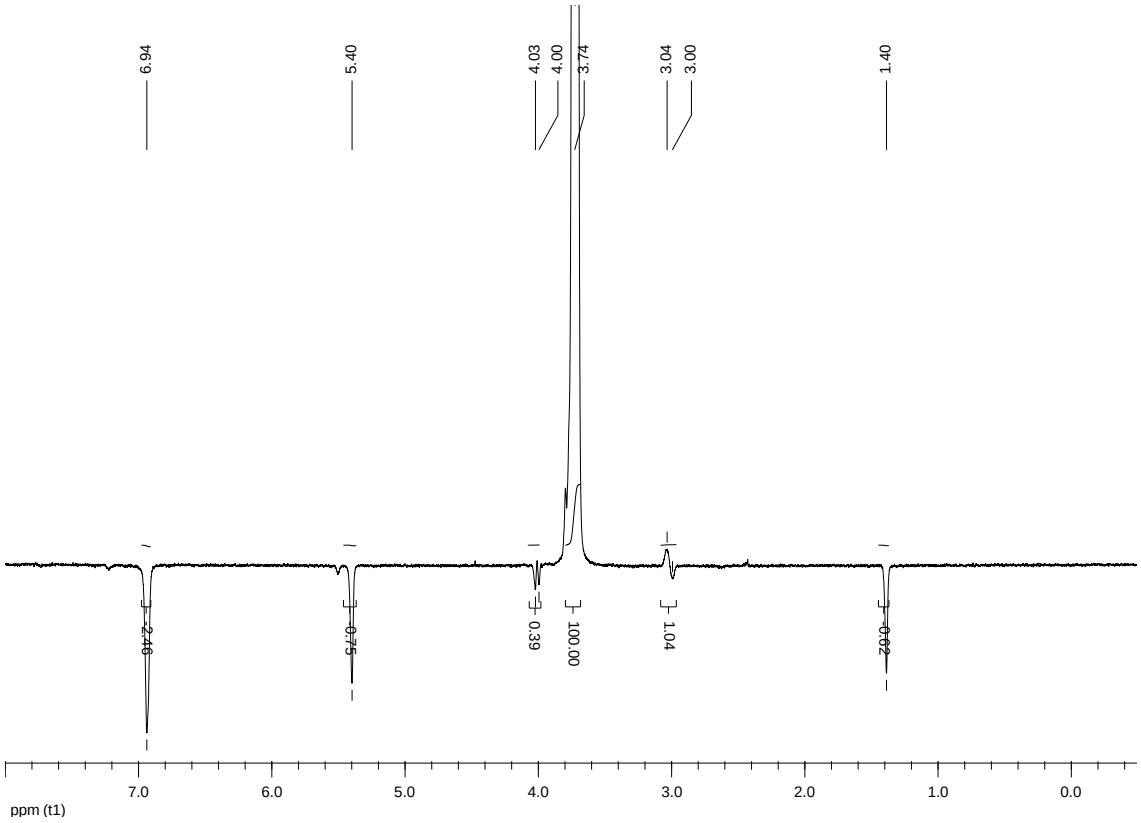

7.65
7.62
7.25
7.22
5.47
5.30
5.19
3.96
3.92
3.81
3.78
3.75
3.67
3.63
2.82
2.62
2.61
2.59
2.58
2.57
2.56
2.54
2.33
1.57
0.92
0.90
0.87
0.00000
2.01
2.00
0.70
1.00
0.30
1.00
1.02
1.00
1.00
2.00
3.00
3.03
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


143.3
133.8
133.7
133.6
133.5
129.6
129.4
129.2
127.5
127.3
127.2
123.6
77.4
77.0
76.6
52.2
50.7
50.6
41.6
41.5
32.7
31.8
21.6
21.4
21.1
20.7
100
50
0
ppm (t1)

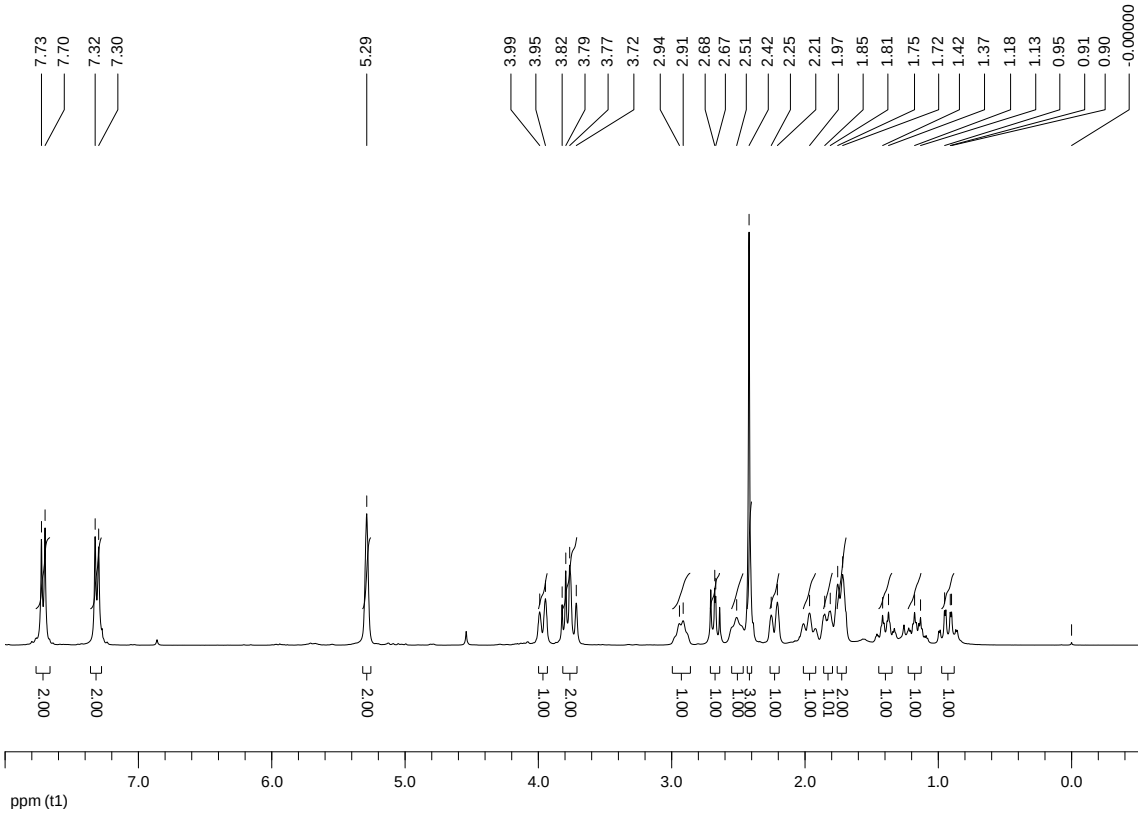

TsN
(9a)
7.64
7.61
7.24
7.21
5.61
5.42
4.04
4.03
3.99
3.99
3.69
3.65
3.34
3.31
2.80
2.77
2.51
2.33
0.91
0.00000
2.01
2.00
2.01
1.00
1.01
1.01
1.01
1.01
2.02
3.00
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.2
138.8
133.8
129.6
129.5
127.3
124.6
116.8
77.4
77.0
76.6
58.5
49.9
41.0
26.3
25.4
21.4
100
50
0
ppm (t1)

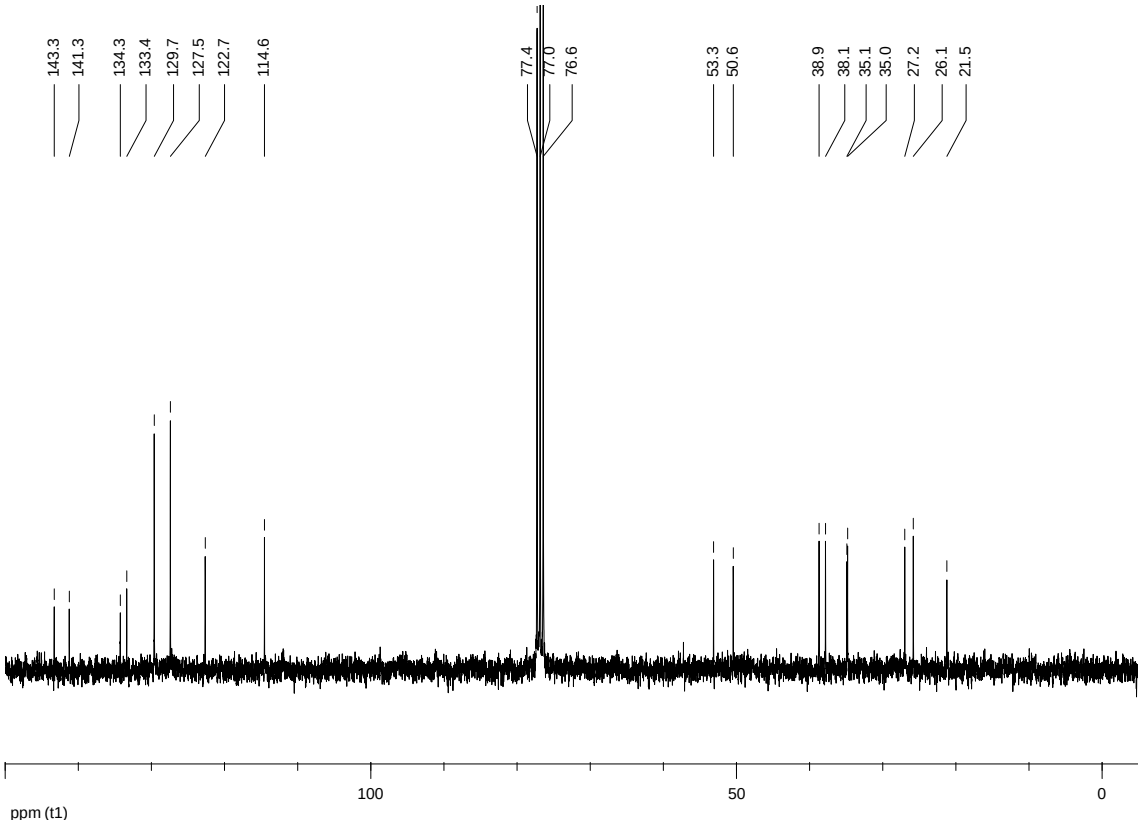
(10a)

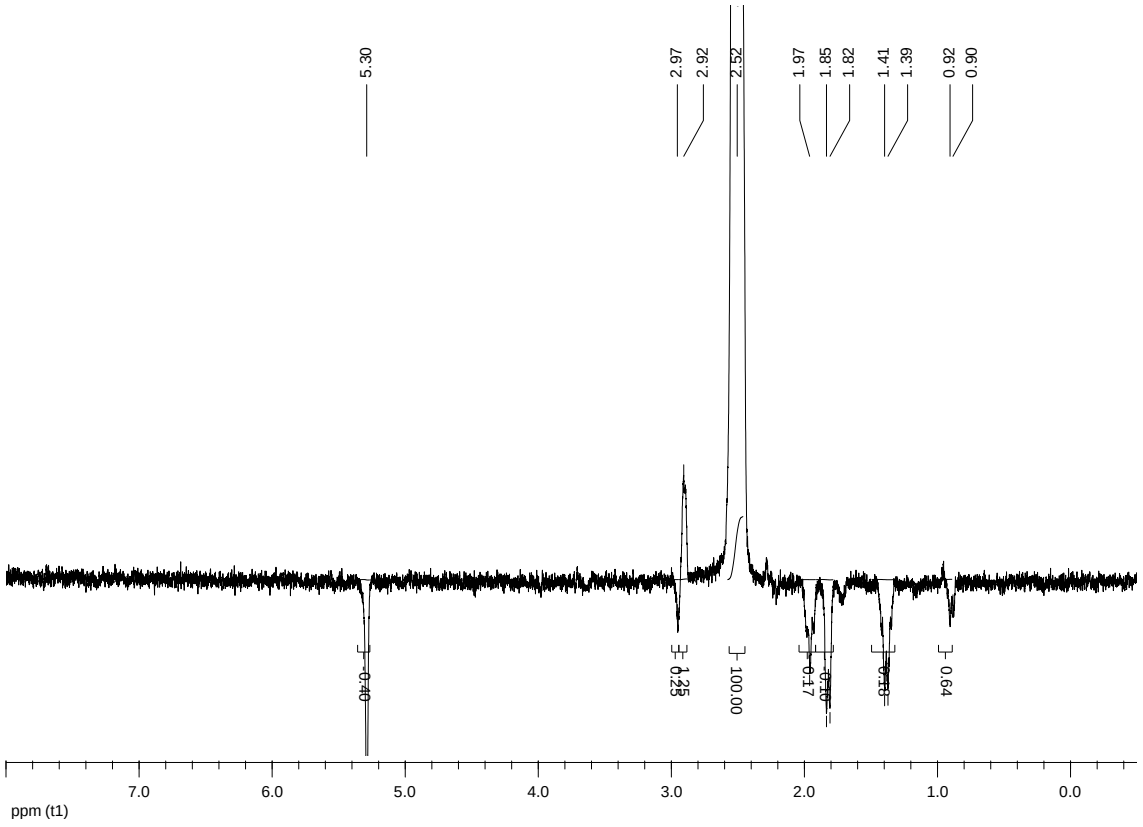

7.74
7.73
7.34
7.32
7.23
7.22
7.21
6.93
6.92
5.50
5.39
4.02
4.01
3.99
3.91
3.89
3.87
3.86
3.80
3.79
3.77
3.76
3.72
3.01
2.79
2.77
2.77
2.76
2.75
2.74
2.44
1.39
-0.000000
2.00
2.04
3.02
2.01
1.00
1.01
1.00
1.00
1.00
1.01
3.00
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
143.5
143.4
136.6
134.1
133.1
129.7
128.4
127.4
126.6
122.0
118.1
77.4
77.0
76.6
53.5
50.7
47.3
39.0
21.9
21.5
100
50
0
ppm (t1)

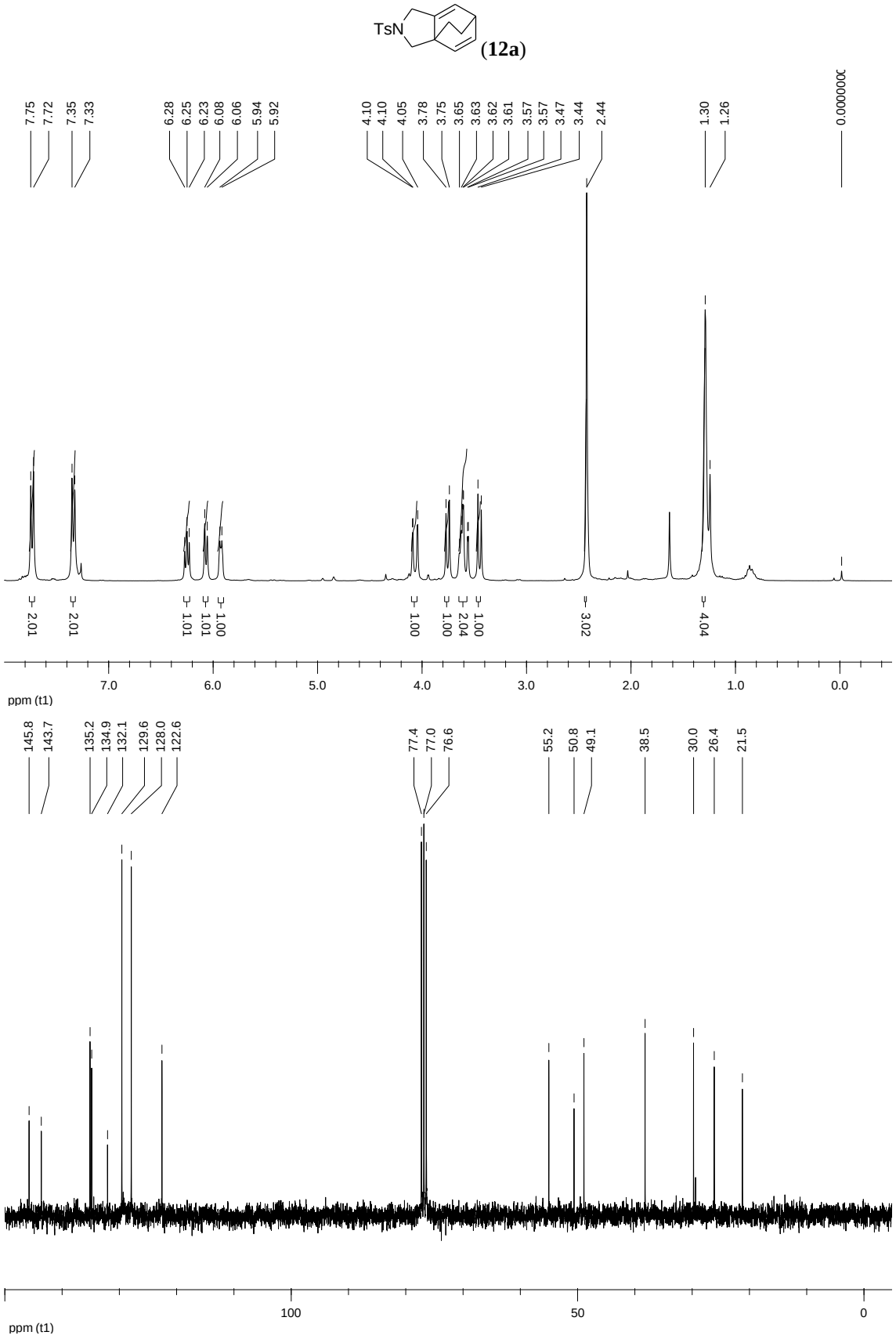

6.94
5.40
4.03
4.00
3.74
3.04
3.00
1.40
2.46
0.75
0.39
100.00
1.04
0.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

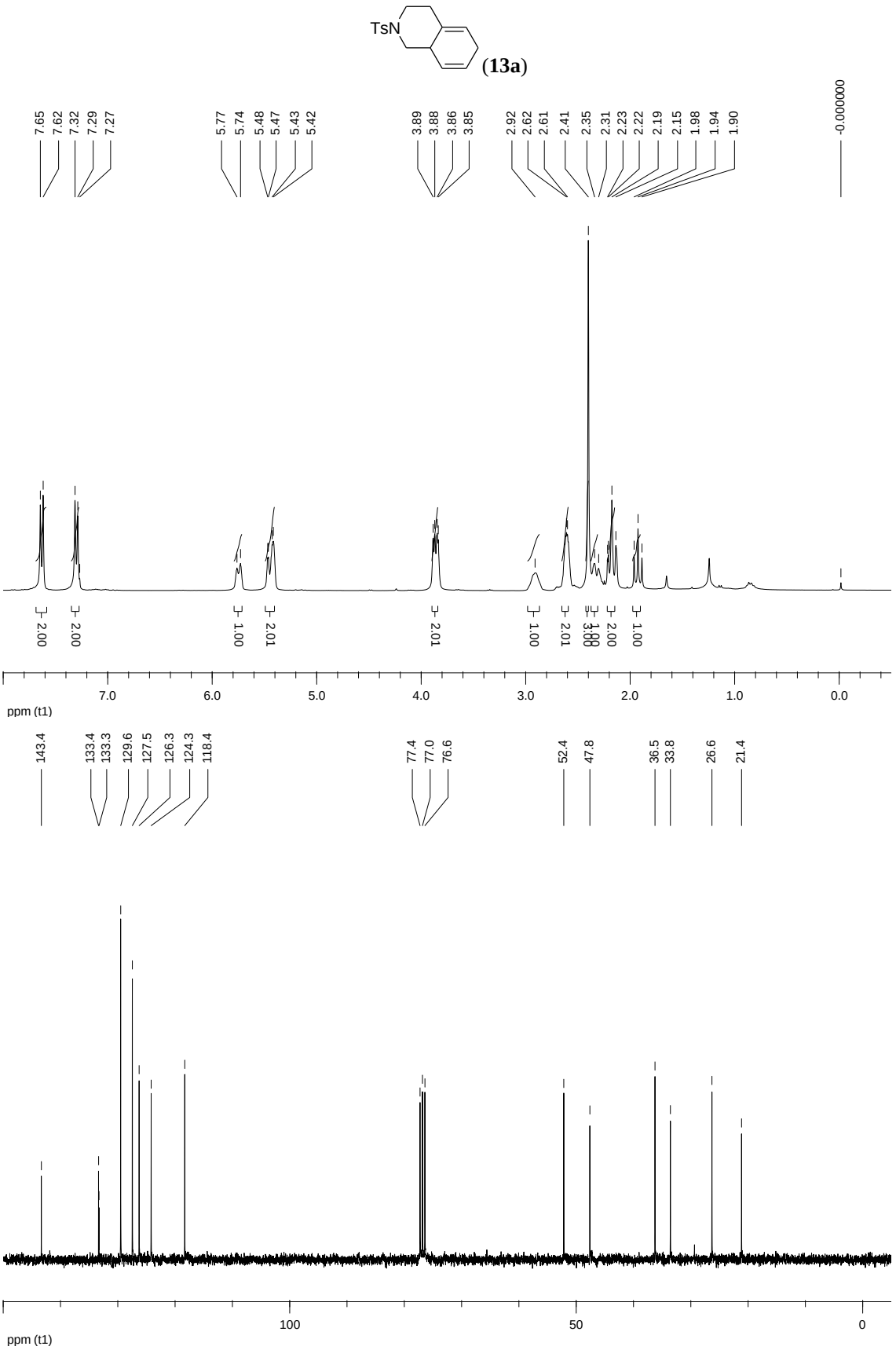
(11a)

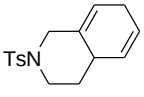

7.73
7.70
7.32
7.30
5.29
3.99
3.95
3.82
3.79
3.77
3.72
2.94
2.91
2.68
2.67
2.51
2.42
2.25
2.21
1.97
1.85
1.81
1.75
1.72
1.42
1.37
1.18
1.13
0.95
0.91
0.90
-0.00000
2.00
2.00
2.00
1.00
2.00
1.00
1.00
3.00
1.00
1.00
1.01
2.00
1.00
1.00
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


143.3
141.3
134.3
133.4
129.7
127.5
122.7
114.6
77.4
77.0
76.6
53.3
50.6
38.9
38.1
35.1
35.0
27.2
26.1
21.5
100
50
0
ppm (t1)

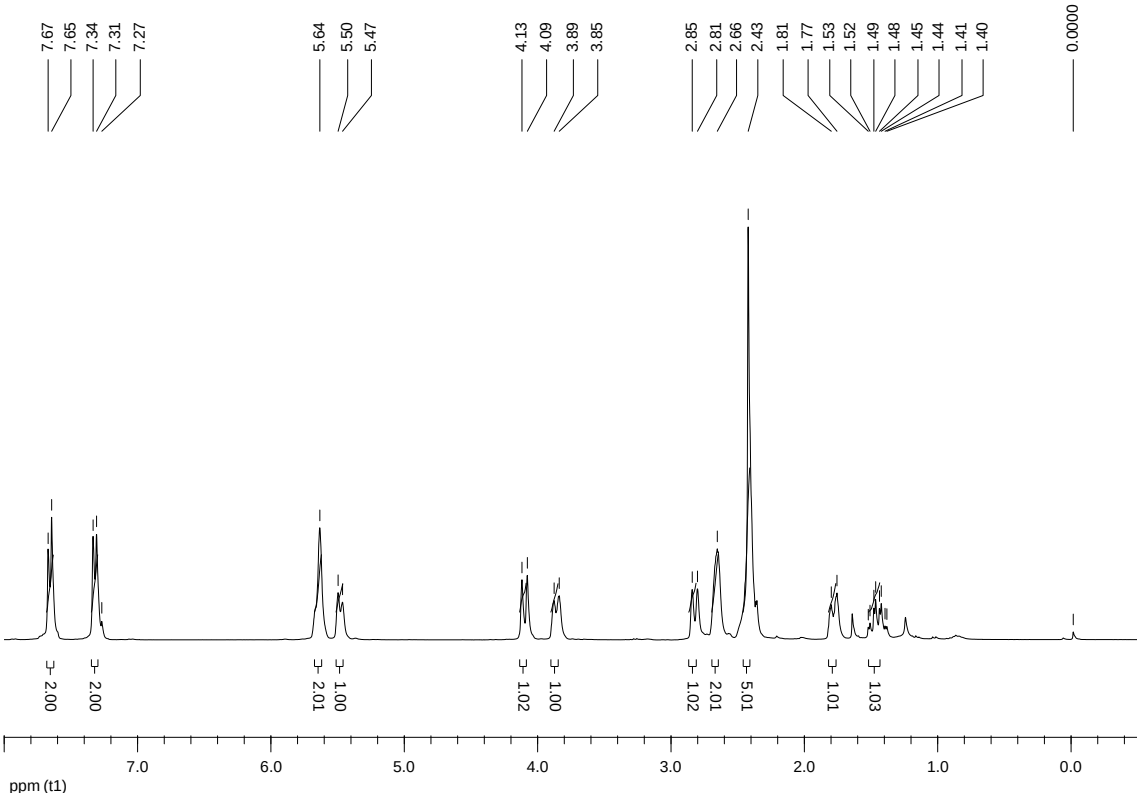

5.30
2.97
2.92
2.52
1.97
1.85
1.82
1.41
1.39
0.92
0.90
0.40
1.25
100.00
0.17
0.10
0.15
0.94
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

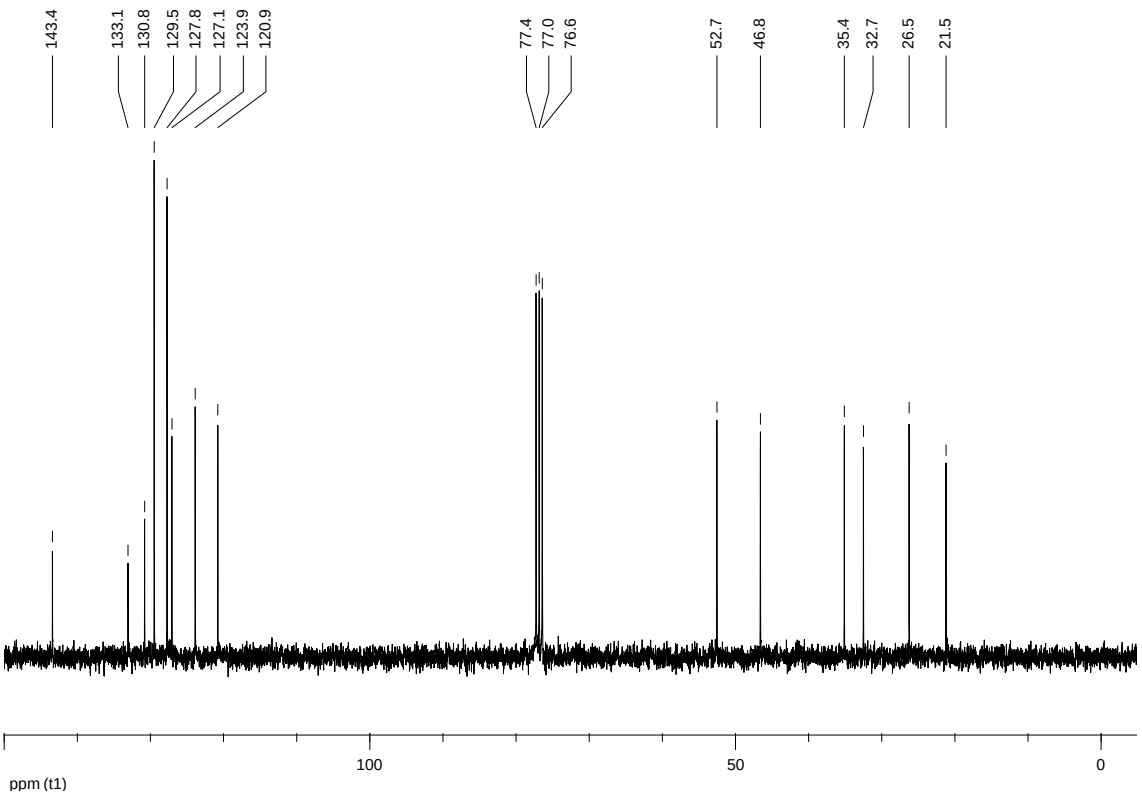

TsN
(12a)
7.75
7.72
7.35
7.33
6.28
6.25
6.23
6.08
6.06
5.94
5.92
4.10
4.10
4.05
3.78
3.75
3.65
3.63
3.62
3.61
3.57
3.57
3.47
3.44
2.44
1.30
1.26
0.000000
2.01
2.01
1.01
1.01
1.00
1.00
1.00
2.04
1.00
3.02
4.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
145.8
143.7
135.2
134.9
132.1
129.6
128.0
122.6
77.4
77.0
76.6
55.2
50.8
49.1
38.5
30.0
26.4
21.5
100
50
0
ppm (t1)

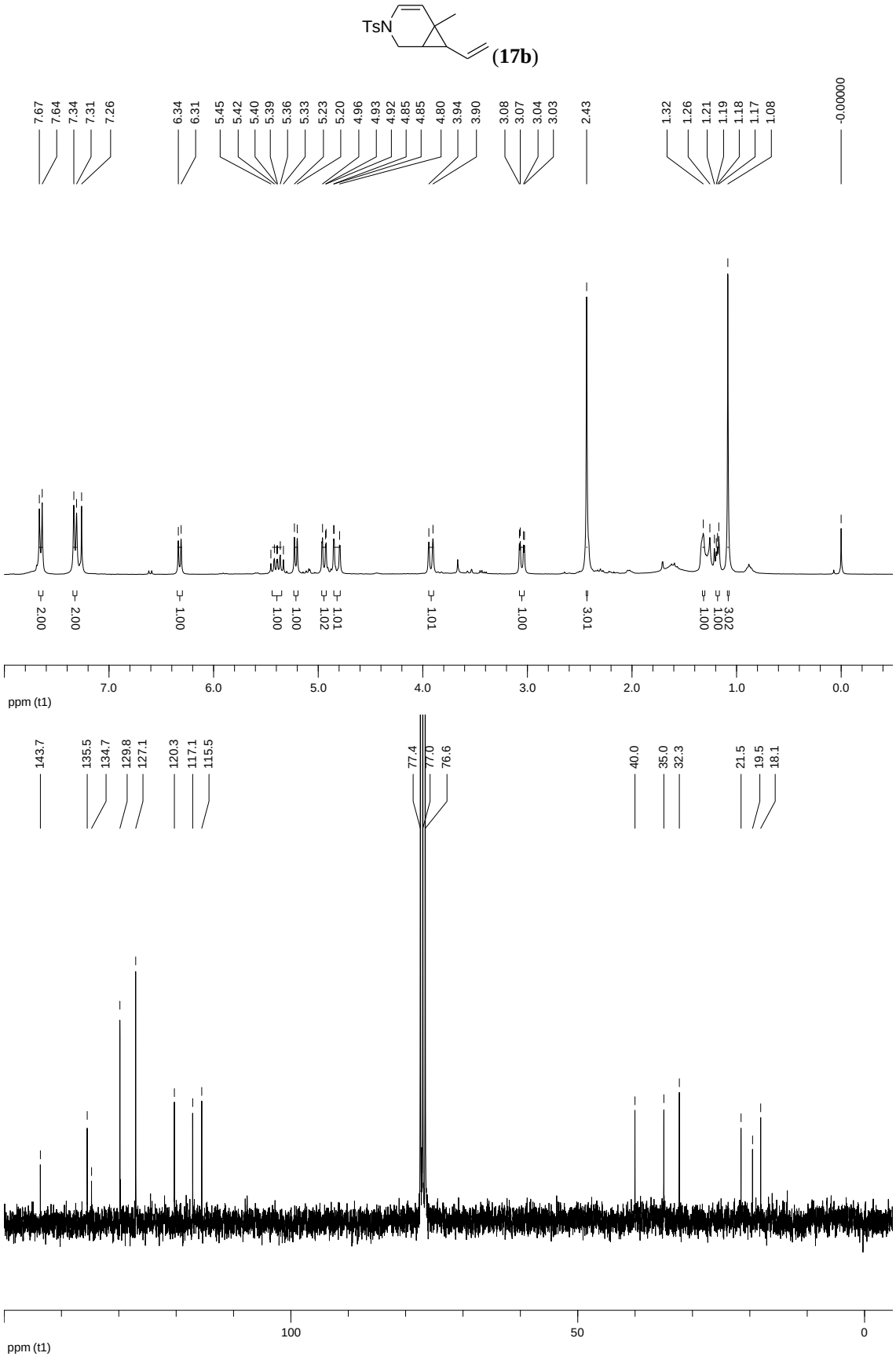

TsN
(13a)
7.65
7.62
7.32
7.29
7.27
5.77
5.74
5.48
5.47
5.43
5.42
3.89
3.88
3.86
3.85
2.92
2.62
2.61
2.41
2.35
2.31
2.23
2.22
2.19
2.15
1.98
1.94
1.90
-0.000000
2.00
2.00
1.00
2.01
2.01
1.00
2.01
3.00
2.00
1.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.4
133.4
133.3
129.6
127.5
126.3
124.3
118.4
77.4
77.0
76.6
52.4
47.8
36.5
33.8
26.6
21.4
100
50
0
ppm (t1)


TsN

(14a)


7.67
7.65
7.34
7.31
7.27
5.64
5.50
5.47
4.13
4.09
3.89
3.85
2.85
2.81
2.66
2.43
1.81
1.77
1.53
1.52
1.49
1.48
1.45
1.44
1.41
1.40
0.0000
2.00
2.00
2.01
1.00
1.02
1.00
1.02
2.01
5.01
1.01
1.03
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


143.4
133.1
130.8
129.5
127.8
127.1
123.9
120.9
77.4
77.0
76.6
52.7
46.8
35.4
32.7
26.5
21.5
100
50
0
ppm (t1)


TsN
(17b)
7.67
7.64
7.34
7.31
7.26
6.34
6.31
5.45
5.42
5.40
5.39
5.36
5.33
5.23
5.20
4.96
4.93
4.92
4.85
4.85
4.80
3.94
3.90
3.08
3.07
3.04
3.03
2.43
1.32
1.26
1.21
1.19
1.18
1.17
1.08
-0.00000
2.00
2.00
1.00
1.00
1.00
1.02
1.01
1.01
1.00
3.01
1.00
1.00
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
143.7
135.5
134.7
129.8
127.1
120.3
117.1
115.5
77.4
77.0
76.6
40.0
35.0
32.3
21.5
19.5
18.1
100
50
0
ppm (t1)