Supporting Information

N-tosyl-1,5,2,6-dithiadiazocane: a waste-free electrophilic sulfur reagent for an efficient synthesis of medium-ring S,N-heterocycles

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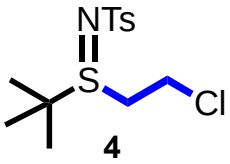
General

All chemicals were used as received from commercial suppliers. All moisture sensitive reactions were carried out under an atmosphere of dry argon using oven-dried glassware. Column chromatography was performed on Silicagel (Merck, 40-63μm). TLC was done on aluminum sheets pre-coated with silica gel 60 F254 (Merck). The TLC plates were visualized with short wavelength UV light, vanillin, Seebach stain or aq. $KMnO_4$ stain. Melting points were determined with Galenkamp Melting Point Aparatus and were uncorrected. Chemical shifts are given in parts per million relative to tetramethylsilane using the residual solvent peaks at δ = 7.28(^{1}H NMR) and 77.10 (^{13}C NMR) ppm in $CDCl_3$. High resolution mass spectra (HMS) were recorded on a time-of-flight (TOF) spectrometer with electrospray ionization (ESI). IR spectra were recorded in KBr pellets.

Abbreviations:

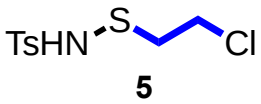
br s – broad singlet, d – doublet, dd – doublet of doublets, ddd – doublet of doublet of doublets, DEAD – diethyl azodicarboxylate, DCE – dichloroethane, DCM – dichloromethane, DMEDA – N,N′-Dimethylethylenediamine, EtOAc – ethyl acetate, m – multiplet, PIDA – phenyliodonium diacetate, q – quartet, s – singlet, t – triplet, td – triplet of doublets, THF – tetrahydrofuran

Compounds 2-6 (Figure 2)



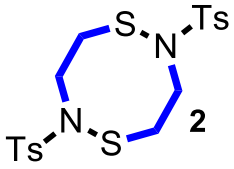
4

Chloramine-T trihydrate (0.523 mol, 147.5 g, 1.2 eq.) was added to MeOH (650 ml) in 2L flask. Afterwards, sulphide **3** (0.436 mol, 66.5 g, 1.0 eq.) was added dropwise. The mixture was stirred vigorously for 16 h, evaporated and diluted with water (1.4 L). The precipitate was filtered, washed with water and dried *in vacuo* to obtain 140 g of white crystalline sulfimide **4** (99%). It was used in the next step without further purification.[1]



5

2L flask was charged with 140 g of sulfimide **4** and dry toluene (400 ml). The mixture was stirred for 3.5 h at 80°C resulting in yellowish solution. The solution was cooled to room temperature and evaporated. To residue diethyl ether (200 ml) and petrol ether (400 ml) were added and the precipitate formed was filtered and washed with petrol ether. The solid was dried *in vacuo* to obtain 104 g of N-((2-chloroethyl)thio)-4-methylbenzenesulfonamide (90%). It was used in the next step without further purification.



2

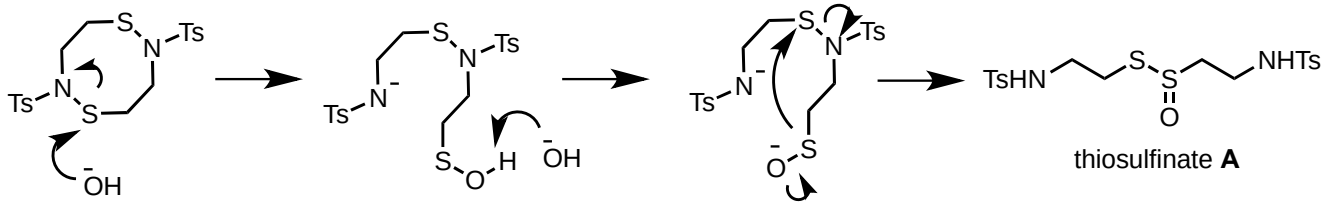
To an oven-dried flask NaH (60% suspension, 51 mmol, 2.04 g, 1.2 eq.) was added and washed twice with dry petrol ether. Dry THF (200 ml) was added and the suspension was cooled in an ice bath. Sulfonamide **5** (42.5 mmol, 11.3 g, 1.0 eq.) was added in portions and after 2.5 h, the reaction was quenched with 1M HCl, extracted with ethylacetate, washed with brine, dried with Na_2SO_4 and evaporated *in vacuo*. The residue was triturated with ethylacetate and filtered to provide 2.8 g of

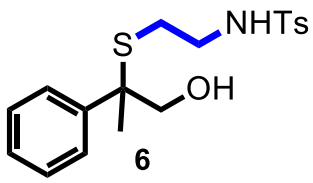
[1]Compounds **4** and **5** are reported in literature. However, in contrary to literature data, compound **4** failed to rearrange into compound **5** at room temperature. Our procedure was therefore modified and adopted to large scale preparation of **5**. See ref. [7] in the main text.

compound **2**. Filtrate was evaporated and further purified by column chromatography (DCM).The solid obtained was washed with diethyl ether to afford additional 0.7 g of compound **2** with total yield of 36%. R_f = 0.3 (DCM), **m.p**. 195°C (decomposes).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 3.81 (br s, 4H), 3.29 (br s, 4H), 2.45 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 134.9, 129.6, 127.5, 53.5, 39.4, 21.6; **FT-IR** ν_{max}/cm^{-1} 2923w, 1597w, 1335s, 1156s, 1091m, 872m, 813m, 679s; **HRMS-ESI$^+$**: m/z $[M+NH_4]^+$ calcd for $C_{18}H_{22}N_2O_4S_4$: 476.0801; found 476.0790.

Note: it is very important to keep the acidic medium during the quench. The sulfenamide **2** is sensitive to base and thiosulfinate **A** is obtained exclusively if only water is used for quenching.

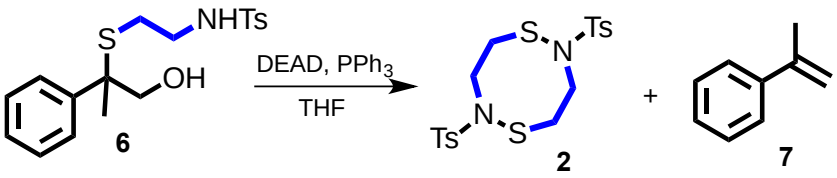




To a solution of diisopropylamine (0.6 mmol, 0.084 ml, 2.2 eq.) in dry THF (3 ml) under argon at -40°C 2.2M n-BuLi (0.6 mmol, 0.272 ml, 2.2 eq.) was added. The solution was cooled to -78°C and methyl 2-phenylpropanoate (0.6 mmol, 98.5 mg, 2.2 eq.) in dry THF (2 ml) was added. Stirring was continued for 40 min at -78°C and 10 min at room temperature. The solution of **2** (0.272 mmol, 125 mg, 1.0 eq.) in dry THF (5 ml) was added at -78°C. The cooling bath was removed after 0.5 h and the reaction mixture was stirred for an additional hour. Then, $LiAlH_4$ (0.545 mmol, 20.7 mg, 2.0 eq.) was added in one portion and stirring was continued for 3 h. The reaction mixture was quenched with solid $Na_2SO_4 \cdot 10H_2O$ and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) afforded **6** as colorless oil, 178 mg (89%).

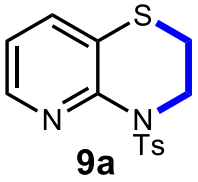
R_f = 0.35 (EtOAc/Hexanes 1:1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.44-7.48 (m, 2H), 7.23-7.37 (m, 5H), 4.84 (t, *J* = 6.4 Hz, 1H), 3.84-3.91 (m, 2H), 2.82-2.91 (m, 2H), 2.45 (s, 3H), 2.32-2.44 (m, 2H), 2.11 (br s, 1H), 1.66 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 142.4, 136.9, 129.7, 128.6, 127.4, 127.1, 126.9, 68.6, 54.1, 42.4, 29.1, 25.0, 21.5; **FT-IR** ν_{max}/cm^{-1} 3277m, 2925w, 1598w, 1446m, 1325s, 1158s, 1093s, 815m, 700m, 551s; **HRMS-ESI$^+$**: m/z $[M+Na]^+$ calcd for $C_{18}H_{23}NO_3S_2$: 388.1012; found 388.1008.



To a solution of **6** (0.125 mmol, 46 mg, 1.0 eq) in THF (8 ml) PPh_3 (0.164 mmol, 43 mg, 1.3 eq) was added followed by DEAD (0.16 mmol, 0.025 ml, 1.28 eq). After stirring for 1.3 h, the mixture was quenched with water and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) afforded **2**, 17 mg (59 %).

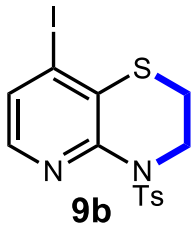
Compounds 9a-t (Table 1)



To diisopropylamine (0.577 mmol, 0.08 ml, 2.6 eq.) solution in dry THF (4 ml) under argon 2.2M n-BuLi (0.577 mmol, 0.262 ml, 2.6 eq.) was added at -40°C. The mixture was cooled to -78°C and 2-fluoropyridine (0.577 mmol, 0.05 ml, 2.6 eq.) in dry THF (3 ml) was added and solution was stirred for 1 h. The solution of **2** (0.222 mmol, 102 mg, 1.0 eq.) in dry THF (5 ml) was added dropwise and the mixture was stirred for additional 0.5 h and 3.5 h at 60°C. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) provided **9a** as colorless oil, 115 mg (84%).

R_f = 0.44 (EtOAc:Hexanes – 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-8.05 (m, 3H), 7.41 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.89 (dd, *J* = 8.0, 4.8 Hz, 1H), 4.19-4.23 (m, 2H), 3.27-3.32 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 143.6, 143.2, 138.4, 135.2, 129.2, 128.1, 121.1, 119.6, 45.4, 28.3, 21.6; **FT-IR** ν_{max}/cm^{-1} 2928w, 2361w, 1560w, 1421s, 1346m, 1161s, 1091m, 578m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{14}H_{14}N_2O_2S_2$: 307.0569; found 307.0575.

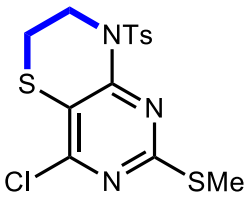


9b

To diisopropylamine (0.283 mmol, 0.04 ml, 2.6 eq.) solution in dry THF (3 ml) under argon 2.2M n-BuLi (0.283 mmol, 0.128 ml, 2.6 eq.) was added at -40°C. The mixture was cooled to -78°C and 2-fluoro-3-iodopyridine (0.283 mmol, 63 mg, 2.6 eq) in dry THF (2 ml) was added. The mixture was stirred for 1 h and then, solution of **2** (0.109 mmol, 50 mg, 1.0 eq.) in dry THF (3.5 ml) was added dropwise. The mixture was stirred for 0.5 h at -78°C and then for 3.5 h at 60°C. The mixture was diluted with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) provided **9b** as white solid, 76.4 mg (81%).

***R*f** = 0.56 (EtOAc:Hexanes – 1:3), **m.p**. 138-140°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 5.2 Hz, 1H), 7.41 (d, *J* = 5.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.17-4.24 (m, 2H), 3.32-3.38 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.9, 143.8, 142.3, 138.3, 130.1, 129.3, 128.1, 126.6, 107.5, 45.1, 31.0, 21.6; **FT-IR** ν_{max}/cm^{-1} 2919m, 2359m, 1534s, 1428s, 1350s, 1167s, 1090s, 864s, 749s, 660s, 578s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{14}H_{13}IN_2O_2S_2$: 432.9536; found 432.9546.



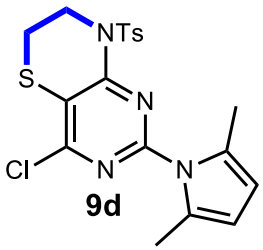
9c

To diisopropylamine (0.351 mmol, 0.05 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.351 mmol, 0.16 ml, 2.6 eq.) was added at -40°C. The mixture was cooled to -78°C and 4,6-dichloro-2-(methylthio)pyrimidine (0.351 mmol, 68.5 mg, 2.6 eq.) in dry THF (2 ml) was added. The solution was stirred for 3 h. Then, solution of **2** (0.135 mmol, 62 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise, the mixture was stirred for additional 0.5 h and allowed to reach room temperature. After 1 h, the mixture was diluted with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) provided **9c** as orange-yellow solid, 83 mg (79%).

***R*f**= 0.52 (EtOAc:Hexanes – 1:3), **m.p**. 164-165°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.35-4.40 (m, 2H), 3.23-3.29 (m, 2H), 2.45 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 155.7, 153.4, 144.6,

137.1, 129.4, 128.2, 110.9, 45.8, 27.2, 21.7, 14.1; **FT-IR** ν_{max}/cm^{-1} 2926m, 1534s, 1496s, 1361s, 1295s, 1174s, 1087s, 936s, 740s, 662s, 581s; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{14}H_{14}ClN_3O_2S_3$: 388.0009; found 388.0017.

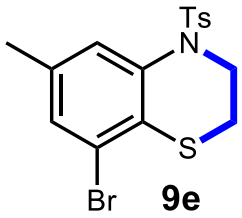


9d

To diisopropylamine (0.400 mmol, 0.056 ml, 2.6 eq.) solution in dry THF (4 ml) under argon 2.2M n-BuLi (0.398 mmol, 0.18 ml, 2.6 eq.) was added at -40°C. The solution was cooled to -78°C and 4,6-dichloro-2-(2,5-dimethyl-1H-pyrrol-1-yl)pyrimidine (0.398 mmol, 96.3 mg, 2.6 eq.) in dry THF (3 ml) was added. The mixture was stirred for 3 h. Then, solution of **2** (0.153 mmol, 70 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise. The mixture was stired for additional 0.5 h and allowed to reach room temperature. After 1 h, the mixture was diluted with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) provided **9d** as reddish solid, 117 mg (88%).

***R*f** = 0.53 (EtOAc:Hexanes – 1:3), **m.p**. 68-70°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.87 (s, 2H), 4.37-4.42 (m, 2H), 3.32-3.36 (m, 2H), 2.39 (s, 3H), 2.21 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 154.4, 151.3, 144.7, 136.4, 129.7, 129.3, 128.5, 113.6, 108.2, 45.6, 27.3, 21.5, 13.5; **FT-IR** ν_{max}/cm^{-1} 2925w, 1509s, 1440s, 1167s, 582s; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{19}H_{19}ClN_4O_2S_2$: 435.0711; found 435.0694.



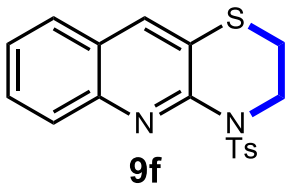
9e

To diisopropylamine (0.408 mmol, 0.057 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.408 mmol, 0.185 ml, 2.6 eq.) was added at -40°C. The solution was cooled to -78°C and 1,3-dibromo-5-methylbenzene (0.408 mmol, 102 mg, 2.6 eq.) in dry THF (3 ml) was added. The mixture was stirred for 0.5 h. Then, solution of **2** (0.157 mmol, 72 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise. The mixture was stirred for additional 0.5 h and allowed to reach room temperature, then CuI (0.031 mmol, 5.9 mg, 0.2 eq.), DMEDA (0.062 mmol, 0.007 ml, 0.4 eq.) and Cs_2CO_3 (0.628 mmol, 205

mg, 4.0 eq.) were added. The sealed vial was stirred at 70°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:7) provided **9e** as white solid, 92.5 mg (74%).

***R*f** = 0.6 (EtOAc:Hexanes – 1:5), **m.p**. 147-148°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.54 (m, 3H), 7.21-7.30 (m, 3H), 3.91-3.97 (m, 2H), 2.85-2.90 (m, 2H), 2.43 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.2, 137.2, 135.3, 135.0, 131.3, 129.9, 127.8, 127.1, 125.8, 120.3, 44.1, 26.7, 21.6, 20.7; **FT-IR** ν_{max}/cm^{-1} 2920w, 1430m, 1353s, 1164s, 828s, 732s, 581s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{16}BrNO_2S_2$: 399.9858; found 399.9852.

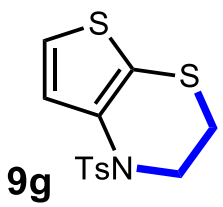


9f

To diisopropylamine (0.317 mmol, 0.044 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.317 mmol, 0.144 ml, 2.6 eq.) was added at -40°C. The solution was cooled to -78°C and 2-chloroquinoline (0.317 mmol, 51.8 mg, 2.6 eq.) in dry THF (2 ml) was added. The mixture was stirred for 2 h. Then, solution of **2** (0.122 mmol, 56 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise. The mixture was stirred for additional 0.5 h and allowed to reach room temperature. CuI (0.024 mmol, 4.6 mg, 0.2 eq.), DMEDA (0.048 mmol, 0.005 ml, 0.4 eq.) and Cs_2CO_3 (0.488 mmol, 159 mg, 4.0 eq.) were added and the sealed vial was stirred at 70°C for 72 h. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) provided **9f** as light yellow solid, 61 mg (70%).

***R*f** = 0.46 (EtOAc:Hexanes – 1:3), **m.p.** 128-129°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.0 Hz, 2H), 7.85 (s, 1H), 7.75-7.81 (m, 1H), 7.51-7.59 (m, 2H), 7.32-7.41 (m, 3H), 4.37-4.44 (m, 2H), 3.32-3.39 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 143.8, 143.6, 138.3, 133.2, 129.1, 128.74, 128.72, 127.6, 126.0, 125.82, 125.75, 120.0, 46.1, 28.1, 21.6; **FT-IR** ν_{max}/cm^{-1} 2928w, 1407m, 1354s, 1163s, 673s, 544m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{18}H_{16}N_2O_2S_2$: 357.0726; found 357.0729.

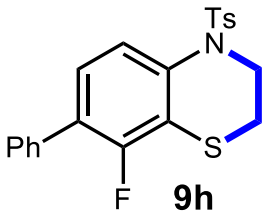


9g

To diisopropylamine (0.285 mmol, 0.04 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.285 mmol, 0.13 ml, 2.4 eq.) was added at 0°C. After 20 min, 3-bromothiophene (0.285 mmol, 46.5 mg, 2.4 eq.) in dry THF (2 ml) was added and the reaction mixture was stirred for 1 h. Then, solution of **2** (0.119 mmol, 54.5 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise and stirred for additional 0.5 h, then cooling bath was removed and CuI (0.095 mmol, 18 mg, 0.8 eq.), DMEDA (0.190 mmol, 0.020 ml, 1.6 eq.) and Cs_2CO_3 (0.475 mmol, 155 mg, 4.0 eq.) were added at room temperature. The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) provided **9g** as yellowish solid, 35.5 mg (48%).

***R*f**= 0.55 (EtOAc:Hexanes – 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 5.6 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 5.6 Hz, 1H), 4.00-4.04 (m, 2H), 2.58-2.62 (m, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 135.7, 130.3, 130.0, 127.2, 125.9, 119.8, 119.2, 45.2, 23.5, 21.6; **FT-IR** ν_{max}/cm^{-1} 2945m, 1597m, 1358s, 1166s, 756s, 674s, 569s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{13}H_{13}NO_2S_3$: 312.0181; found 312.0187.



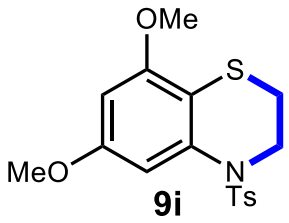
9h

To diisopropylamine (0.314 mmol, 0.044 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.314 mmol, 0.143 ml, 2.4 eq.) was added at -40°C. The solution was cooled to -78°C, 4-bromo-2-fluoro-1,1'-biphenyl (0.314 mmol, 78.8 mg, 2.4 eq.) in dry THF (2.5 ml) was added and the reaction mixture was stirred for 1 h. Then, solution of **2** (0.131 mmol, 60 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise and the mixture was stirred for additional 0.5 h and allowed to reach room temperature. CuI (0.131 mmol, 25 mg, 1.0 eq.), DMEDA (0.262 mmol, 0.028 ml, 2.0 eq.) and Cs_2CO_3 (0.524 mmol, 170 mg, 4.0 eq.) were added and the sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) provided **9h** as yellowish crystals, 92 mg (88%).

***R*f** = 0.73 (EtOAc/Hexanes 1:2), **m.p**. 104-105°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.53-7.60 (m, 4H), 7.43-7.50 (m, 2H), 7.37-7.43 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (t, *J* = 8.4 Hz, 1H), 4.02-4.07 (m, 2H), 2.83-2.88 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.8 (d, *J* = 243 Hz), 144.3, 137.2, 134.91, 134.90, 134.4 (d, *J* = 4.6 Hz), 130.0, 128.9 (d, *J* = 3.1 Hz), 128.5, 127.9, 127.1, 126.1, 125.9, 125.1 (d, *J* = 4.6

Hz), 123.1 (d, *J* = 3.6 Hz), 116.7 (d, *J* = 20.3 Hz), 44.1, 23.8, 21.6; **FT-IR** ν_{max}/cm^{-1} 2941w, 1470s, 1357s, 1165s, 681s, 549m; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{21}H_{18}FNO_2S_2$: 400.0836; found 400.0842.

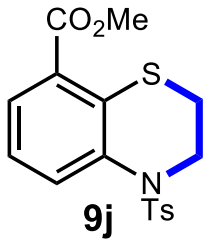


9i

To a solution of 1-bromo-2-iodo-3,5-dimethoxybenzene (0.408 mmol, 140 mg, 2.6 eq.) in dry THF (3 ml) cooled to -30°C under argon 1.3M *i*-PrMgCl-LiCl (0.408 mmol, 0.314 ml, 2.6 eq.) was added dropwise. After 1.5 h, solution of **2** (0.157 mmol, 72 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred at -30°C for 45 min. The mixture was diluted with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. The residue was dried in vacuum overnight. To the above crude dry THF (8 ml) was added followed CuI (0.126 mmol, 24 mg, 0.8 eq.), DMEDA (0.252 mmol, 0.027 ml, 1.6 eq.) and Cs_2CO_3 (0.629 mmol, 205 mg, 4.0 eq.) under argon. The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) afforded **9i** as yellowish oil, 90 mg (80%).

***R*f**= 0.4 (EtOAc/Hexanes 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.35 (d, *J* = 2.4 Hz, 1H), 3.97-4.02 (m, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 2.76-2.81 (m, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 155.7, 143.9, 137.4, 135.2, 129.8, 127.1, 108.1, 104.2, 97.2, 56.0, 55.6, 44.7, 24.2, 21.6; **FT-IR** ν_{max}/cm^{-1} 2936w, 1601m, 1458m, 1352m, 1164s, 669m, 542m; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{17}H_{19}NO_4S_2$: 366.0828; found 366.0836.



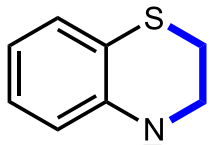
9j

To tetramethylpiperidine (0.595 mmol, 0.1 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.595 mmol, 0.27 ml, 2.6 eq.) was added at 0°C. The solution was cooled to -78°C, methyl 3-

bromobenzoate (0.595 mmol, 128 mg, 2.6 eq.) in dry THF (3 ml) was added and the reaction mixture was stirred for 2 h. To this solution, **2** (0.229 mmol, 105 mg, 1.0 eq.) in dry THF (6 ml) was added dropwise and the mixture was stirred for 2.5 h. After this time, CuI (0.183 mmol, 34.8 mg, 0.8 eq.), DMEDA (0.366 mmol, 0.039 ml, 1.6 eq.), Cs_2CO_3 (0.915 mmol, 298 mg, 4.0 eq.) were added and the cooling bath was removed. The sealed vial was stirred at 80°C overnight. After dilution with water and 1M HCl, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **9j** as brownish solid, 68 mg (41%).

***R*f** = 0.65 (EtOAc/Hexanes 1:2), **m.p**. 69-71°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 3.97-4.04 (m, 2H), 3.90 (s, 3H), 2.80-2.87 (m, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 144.1, 137.1, 135.3, 133.4, 132.6, 129.9, 129.8, 127.1, 127.0, 123.3, 52.2, 44.0, 26.1, 21.6; **FT-IR** ν_{max}/cm^{-1} 2948w, 1712s, 1357s, 1163s, 816s, 724s, 660s, 541s; **HRMS-ESI**$^+$: m/z $[M+H]^+$ calcd for $C_{17}H_{17}NO_4S_2$: 364.0672; found 364.0680.



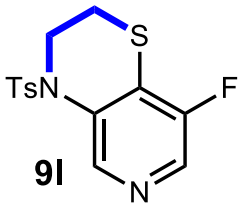
9k

To a solution of 2-bromoiodobenzene (0.251 mmol, 71 mg, 2.6 eq.) in dry THF (3 ml) cooled down to -40°C under argon 1.3M *i*-PrMgCl-LiCl (0.251 mmol, 0.193 ml, 2.6 eq.) was added dropwise. After 1 h, the temperature was lowered to -78°C and solution of **2** (0.096 mmol, 44 mg, 1.0 eq.) in dry THF (4 ml) was added. The reaction mixture was stirred at -78°C for 0.5 h and 1.5 h at room temperature. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. The residue dried in vacuum overnight. To the above crude dry THF (7 ml) was added under argon followed by CuI (0.077 mmol, 14.6 mg, 0.8 eq.), DMEDA (0.154 mmol, 0.0165 ml, 1.6 eq.) and Cs_2CO_3 (0.384 mmol, 125 mg, 4.0 eq.). The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4.5) afforded **9k** as yellowish crystals, 52 mg (89%).

***R*f** = 0.65 (EtOAc/Hexanes 1:3), **m.p**. 134-135°C (lit. 137-138°C).

^{1}H and ^{13}C NMR data are identical to those reported in literature.[2]

[2]X.-B. Xu, J. Liu, J.-J. Zhang, Y.-W. Wang, Y. Peng, *Org. Lett*., 2013, ***15***, 550.

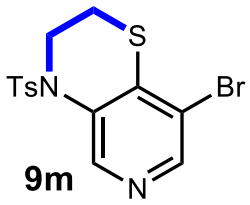


9l

To diisopropylamine (0.556 mmol, 0.078 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.554 mmol, 0.25 ml, 2.6 eq.) was added at -40°C. The solution was cooled to -78°C, 3-bromo-5-fluoropyridine (0.554 mmol, 97.5 mg, 2.6 eq.) in dry THF (3 ml) was added and the reaction mixture was stirred for 1 h. Then, solution of **2** (0.213 mmol, 98 mg, 1.0 eq.) in dry THF (5 ml) was added dropwise and stirred for 1 h. CuI (0.170 mmol, 32 mg, 0.8 eq.), DMEDA (0.340 mmol, 0.036 ml, 1.6 eq.) and Cs_2CO_3 (0.852 mmol, 277 mg, 4.0 eq.) were added and the cooling bath was removed. The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) provided **9l** as yellowish solid, 100 mg (72%).

R_f= 0.45 (EtOAc/Hexanes 1:2), **m.p**. 103-104°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.18 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.96-4.01 (m, 2H), 2.83-2.87 (m, 2H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1 (d, *J* = 252.4 Hz), 144.8, 143.3 (d, *J* = 4.1 Hz), 136.4, 132.5 (d, *J* = 22.1 Hz), 131.7, 130.2, 127.2, 126.2 (d, *J* = 16.3 Hz), 43.1, 23.6, 21.6; **FT-IR** ν_{max}/cm^{-1} 2932w, 1416m, 1353s, 1160s, 1090m, 720m, 584s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{14}H_{13}FN_2O_2S_2$: 325.0475; found 325.0480.

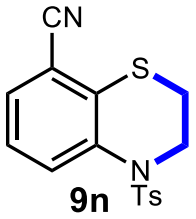


9m

To tetramethylpiperidine (0.545 mmol, 0.092 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.544 mmol, 0.247 ml, 2.6 eq.) was added at 0°C. The solution was cooled to -78°C, 3-bromo-5-fluoropyridine (0.544 mmol, 96 mg, 2.6 eq.) in dry THF (3 ml) was added and the reaction mixture was stirred for 1.5 h. Then, solution of **2** (0.209 mmol, 96 mg, 1.0 eq.) in dry THF (5 ml) was added dropwise and stirred for additional 1 h. The cooling bath was removed and the sealed vial was stirred at 80°C for 48 h. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) provided **9m** as white crystals, 80.5 mg (50%).

***R*$_f$**= 0.44 (EtOAc/Hexanes 1:2), **m.p**. 100-101°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.42 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 3.92-3.97 (m, 2H), 2.90-2.94 (m, 2H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 145.8, 144.8, 139.2, 138.5, 136.5, 135.6, 130.2, 127.3, 43.0, 26.4, 21.6; **FT-IR** ν_{max}/cm^{-1} 2940w, 1421s, 1352s, 1166s, 859m, 729m, 580s, 539m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{14}H_{13}BrN_2O_2S_2$: 386.9654; found 386.9658.

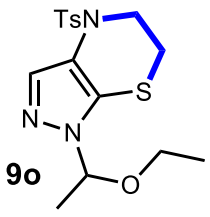


9n

To diisopropylamine (0.239 mmol, 0.033 ml, 2.6 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.239 mmol, 0.108 ml, 2.6 eq.) was added at -40°C. Mixture was cooled down to -78°C and 3-bromobenzonitrile (0.239 mmol, 43.5 mg, 2.6 eq.) in dry THF (2 ml) was added. The reaction mixture was stirred for 1 h. Then, solution of **2** (0.092 mmol, 42 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise and stirred for additional 0.5 h. CuI (0.092 mmol, 17.5 mg, 1.0 eq.), DMEDA (0.184 mmol, 0.020 ml, 2.0 eq.) and Cs_2CO_3 (0.368 mmol, 120 mg, 4.0 eq.) were added and the sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) provided **9n** as light yellow solid, 53 mg (88%).

***R*$_f$**= 0.45 (EtOAc:Hexanes – 1:3), **m.p**. 127-128°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.46-7.52 (m, 3H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 1H), 3.96-4.02 (m, 2H), 2.92-2.98 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 136.7, 135.3, 133.3, 132.0, 131.5, 130.1, 127.0, 124.4, 116.1, 110.3, 43.7, 25.8, 21.6; **FT-IR** ν_{max}/cm^{-1} 2929w, 2222w, 1346s, 1160s, 1083m, 799m, 727m, 662m, 543m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{14}N_2O_2S_2$: 331.0569; found 331.0578.



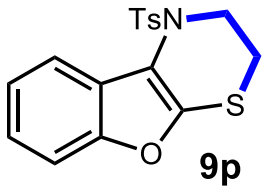
9o

To diisopropylamine (0.262 mmol, 0.037 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.262 mmol, 0.119 ml, 2.4 eq.) was added at -40°C. The mixture was cooled down to -78°C and

1-(1-ethoxyethyl)-4-iodo-1H-pyrazole (0.262 mmol, 70 mg, 2.4 eq.) in dry THF (2.5 ml) was added. The reaction mixture was stirred for 1 h. Then, solution of **2** (0.109 mmol, 50 mg, 1.0 eq.) in dry THF (3.5 ml) was added dropwise and the mixture was stirred for additional 0.5 h. CuI (0.044 mmol, 8.3 mg, 0.4 eq.), DMEDA (0.088 mmol, 0.009 ml, 0.8 eq.) and Cs_2CO_3 (0.436 mmol, 142 mg, 4.0 eq.) were added at room temperature. The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **9o** as white solid, 60 mg (75%).

***R*f** = 0.23 (EtOAc:Hexanes – 1:3), **m.p**. 70-72°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.43 (q, *J* = 6.0 Hz, 1H), 3.84-4.07 (m, 2H), 3.22-3.45 (m, 2H), 2.45-2.59 (m, 2H), 2.42 (s, 3H), 1.63 (d, *J* = 6.0 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 135.0, 134.0, 129.8, 127.3, 121.4, 117.6, 87.8, 64.0, 45.4, 22.7, 21.6, 20.4, 14.7; **FT-IR** ν_{max}/cm^{-1} 2982w, 1410m, 1356m, 1165s, 1058m, 668m, 593m, 549m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{21}N_3O_3S_2$: 368.1097; found 368.1102.

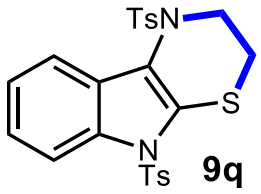


9p

To a solution of 2,3-dibromobenzofuran (0.370 mmol, 102 mg, 2.4 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.370 mmol, 0.168 ml, 2.4 eq.) was added dropwise. After 0.5 h, solution of **2** (0.152 mmol, 70 mg, 1.0 eq.) in dry THF (5 ml) was added and the mixture was stirred for 1.5 h. The cooling bath was removed and CuI (0.121 mmol, 23 mg, 0.8 eq.), DMEDA (0.242 mmol, 0.026 ml, 1.6 eq.) and Cs_2CO_3 (0.608 mmol, 198 mg, 4.0 eq.) were added at room temperature. The sealed vial was stirred at 80°C for 48 h. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) afforded **9p** as yellowish solid, 63 mg (60%).

***R*f** = 0.65 (EtOAc/Hexanes 1:3), **m.p**. 153-155°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.37-7.43 (m, 1H), 7.23-7.36 (m, 4H), 3.90-3.96 (m, 2H), 2.64-2.70 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 144.6, 142.1, 134.9, 130.1, 127.7, 125.3, 123.6, 123.3, 120.8, 115.1, 110.5, 45.3, 23.3, 21.7; **FT-IR** ν_{max}/cm^{-1} 3063m, 1595m, 1447s, 1357s, 1165s, 803s, 745s, 679s, 547s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{15}NO_3S_2$: 346.0566; found 346.0579.

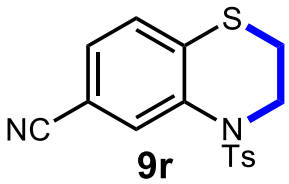


9q

To diisopropylamine (0.366 mmol, 0.05 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.366 mmol, 0.166 ml, 2.4 eq.) was added at -40°C. The solution was cooled to -78°C, 3-iodo-1-tosylindole (0.366 mmol, 145 mg, 2.4 eq.) in dry THF (2.5 ml) was added and reaction mixture was stirred for 1.5 h. Then, solution of **2** (0.152 mmol, 70 mg, 1.0 eq.) in dry THF (5 ml) was added dropwise and the mixture was stirred for additional 1 h. The cooling bath was removed and CuI (0.091 mmol, 17 mg, 0.6 eq.), DMEDA (0.182 mmol, 0.020 ml, 1.2 eq.) and Cs_2CO_3 (0.608 mmol, 198 mg, 4.0 eq.) were added at room temperature. The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **9q** as yellow oil, 132 mg (87%).

R_f = 0.3 (EtOAc/Hexanes 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.20 (m, 1H), 7.90-7.96 (m, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29-7.33 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.80-3.85 (m, 2H), 2.62-2.66 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 144.4, 135.5, 134.8, 134.7, 129.9, 129.8, 128.1, 127.6, 127.2, 124.8, 124.2, 124.0, 120.4, 117.8, 113.5, 44.5, 23.7, 21.72, 21.69; **FT-IR** ν_{max}/cm^{-1} 2927w, 1597m, 1446s, 1363s, 1167s, 1089s, 714s, 570s, 540s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{24}H_{22}N_2O_4S_3$: 499.0814; found 499.0816.



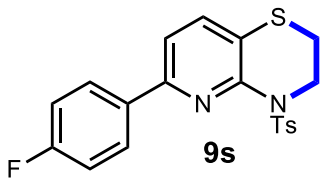
9r

To a solution of 3-bromo-4-iodobenzonitrile (0.493 mmol, 152 mg, 2.6 eq.) in dry THF (3 ml) cooled to -30°C under argon 1.3M *i*-PrMgCl-LiCl (0.493 mmol, 0.38 ml, 2.6 eq.) was added dropwise. After 1.5 h, solution of **2** (0.19 mmol, 87 mg, 1.0 eq.) in dry THF (5 ml) was added. The reaction mixture was stirred at -30°C for 45 min. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. The residue was dried *in vacuo* overnight. To the above crude dry THF (8 ml) was added under argon followed by CuI (0.152 mmol, 29 mg, 0.8 eq.), DMEDA (0.306

mmol, 0.033 ml, 1.6 eq.) and Cs_2CO_3 (0.76 mmol, 247 mg, 4.0 eq.). The sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) afforded **9r** as yellow to white crystals, 110 mg (88%).

***R*f**= 0.3 (EtOAc/Hexanes 1:3), **m.p**. 133-134°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.6 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.33 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 3.95-4.00 (m, 2H), 2.89-2.94 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 136.7, 134.8, 134.6, 131.0, 130.1, 128.8, 127.5, 127.1, 118.4, 107.8, 43.7, 25.6, 21.7; **FT-IR** ν_{max}/cm^{-1} 2931w, 2228s, 1347s, 1160s, 1068s, 777s, 690s, 584s, 536m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{14}N_2O_2S_2$: 331.0569; found 331.0579.

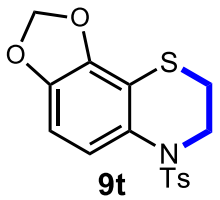


9s

To diisopropylamine (0.403 mmol, 0.056 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.403 mmol, 0.183 ml, 2.4 eq.) was added at -40°C. The solution was cooled to -78°C, 2-fluoro-6-(4-fluorophenyl)pyridine (0.403 mmol, 77 mg, 2.4 eq.) in dry THF (3 ml) was added and the reaction mixture was stirred for 1 h. Then, solution of **2** (0.168 mmol, 77 mg, 1.0 eq.) in dry THF (5 ml) was added dropwise and the mixture was stirred for additional 1 h. The cooling bath was removed and the sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) afforded **9s** as white solid, 70 mg (52%).

***R*f** = 0.43 (EtOAc/Hexanes 1:3), **m.p**. 199-201°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.66-7.72 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.25-7.28 (m, 3H), 7.04-7.11 (m, 2H), 4.31-4.36 (m, 2H), 3.31-3.36 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4 (d, *J* = 246.9 Hz), 150.5, 146.5, 143.5, 139.1, 136.0, 134.4 (d, *J* = 3.1 Hz), 129.3, 128.6 (d, *J* = 8.2 Hz), 127.5, 119.2, 116.0, 115.3 (d, *J* = 21.4 Hz), 45.7, 28.3, 21.6; **FT-IR** ν_{max}/cm^{-1} 2929w, 1509s, 1444s, 1329s, 1155s, 817s, 583m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{20}H_{17}FN_2O_2S_2$: 401.0788; found 401.0793.



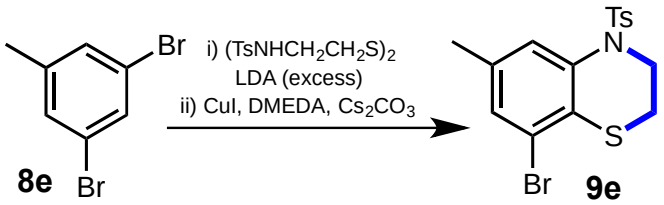
9t

To diisopropylamine (0.400 mmol, 0.056 ml, 2.4 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.398 mmol, 0.18 ml, 2.4 eq.) was added at -40°C. The solution was cooled to -78°C, 5-bromo-1,3-benzodioxole (0.398 mmol, 80 mg, 2.4 e.q) in dry THF (2.5 ml) was added and the reaction mixture was stirred for 1 h. Then, solution of **2** (0.166 mmol, 76 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise, the mixture was stirred for additional 0.5 h and allowed to reach room temperature. CuI (0.066 mmol, 13 mg, 0.4 eq.), DMEDA (0.132 mmol, 0.014 ml, 0.8 eq.) and Cs_2CO_3 (0.664 mmol, 216 mg, 4.0 eq.) were added and the sealed vial was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **9t** as yellowish solid, 100 mg (83%).

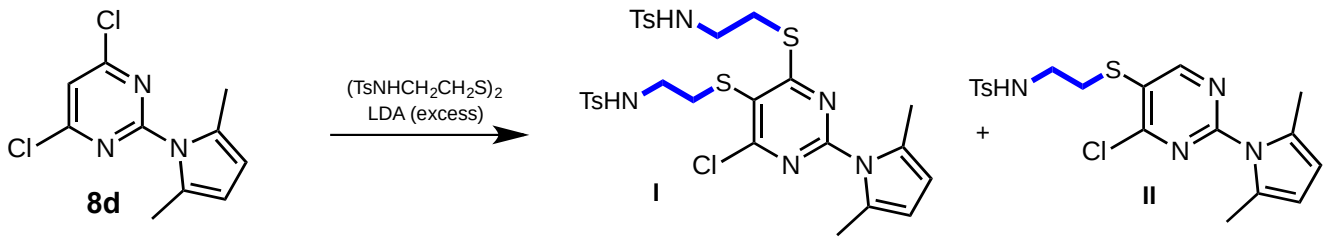
$\boldsymbol{R_f}$ = 0.7 (EtOAc/Hexanes 1:2), **m.p**. 128-129°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 3.98-4.03 (m, 2H), 2.83-2.88 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 143.9, 143.0, 137.3, 129.8, 128.2, 127.2, 121.5, 109.9, 104.4, 101.9, 44.8, 23.7, 21.6; **FT-IR** ν_{max}/cm^{-1} 2896w, 1457s, 1355s, 1163s, 945s, 810s, 691s, 568s, 536s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{15}NO_4S_2$: 350.0515; found 350.0523.

Control experiments with disulphide $(TsNHCH_2CH_2S)_2$



To diisopropylamine (0.998 mmol, 0.14 ml, 2.6 eq.) solution in dry THF (3 ml) under argon 2.2M n-BuLi (0.998 mmol, 0.454 ml, 2.6 eq.) was added at -40˚C. The solution was cooled to -78˚C and 1,3-dibromo-5-methylbenzene (0.384 mmol, 96 mg, 1.0 eq.) in dry THF (3 ml) was added. The reaction mixture was stirred for 1 h. Then, solution of **10** (0.307 mmol, 141 mg, 0.8 eq.) in dry THF (4 ml) was added dropwise, the mixture was stirred for additional 0.5 h and allowed to reach room temperature. CuI (0.154 mmol, 29.3 mg, 0.4 eq.), DMEDA (0.308 mmol, 0.033 ml, 0.8 eq.) and Cs_2CO_3 (0.614 mmol, 200 mg, 1.6 eq.) were added and the sealed vial was stirred at 80˚C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:7) provided **9e**, 5 mg (4 %).



To diisopropylamine (1.074 mmol, 0.15 ml, 2.6 eq.) solution in dry THF (4 ml) under argon 2.2M n-BuLi (1.074 mmol, 0.488 ml, 2.6 eq.) was added at -40˚C. The solution was cooled to -78˚C and 4,6-dichloro-2-(2,5-dimethyl-1H-pyrrol-1-yl)pyrimidine (0.413 mmol, 100 mg, 1.0 eq.) in dry THF (4 ml) was added. The reaction mixture was stirred for 3 h. A solution of **10** (0.330 mmol, 152 mg, 0.8 eq.) in dry THF (5 ml) was added dropwise, stirred for additional 0.5 h and allowed to reach room temperature. After 4 h water was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) provided **I** as dark red oil (39 mg) and **II** as brownish oil (115 mg).

R_f = 0.47 (**I**), 0.18 (**II**) (EtOAc:Hexanes – 1:2).

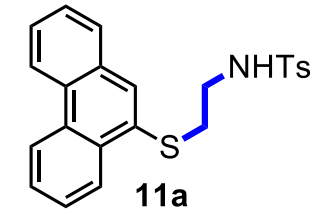
I

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.78 (m, 4H), 7.24-7.34 (m, 4H), 5.92 (s, 2H), 5.52 (t, *J* = 6.4 Hz, 1H), 5.43 (t, *J* = 6.4 Hz, 1H), 3.36-3.41 (m, 2H), 3.26-3.34 (m, 2H), 3.11-3.16 (m, 2H), 3.05-3.10 (m, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 2.38 (s, 6H); **FT-IR** ν_{max}/cm^{-1} 3277m, 1520s, 1429s, 1327m, 1158s, 813m, 661m, 550m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{28}H_{32}ClN_5O_4S_4$: 666.1098; found 666.1105.

II

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 5.92 (s, 2H), 5.09 (t, *J* = 6.0 Hz, 1H), 3.34-3.40 (m, 2H), 3.24-3.32 (m, 2H), 2.43 (s, 3H), 2.36 (s, 6H); **FT-IR** ν_{max}/cm^{-1} 3275m, 2924m, 1546s, 1427s, 1158s, 815s, 661m, 550m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{21}ClN_4O_2S_2$: 437.0867; found 437.0875.

Compounds 11-13 (Table 2)

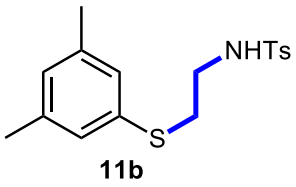


11a

To a solution of 9-bromophenanthrene (1.89 mmol, 488 mg, 2.6 eq.) in dry THF (7 ml) under argon at -78°C 2.2M n-BuLi (1.89 mmol, 0.863 ml, 2.6 eq.) was added. Mixture was stirred for 1 h and solution of **2** (0.73 mmol, 335 mg, 1.0 eq.) in dry THF (7 ml) was added dropwise. Coolant was removed after 0.5 h and mixture was stirred for 1 h, quenched with 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **11a** as off-white solid, 510 mg (86%).

***R*f** = 0.5 (EtOAc/Hexanes 1:2), **m.p**. 105-106°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.45 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.59-7.81 (m, 8H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.02 (t, *J* = 5.6 Hz, 1H), 3.07-3.19 (m, 4H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.7, 131.4, 131.3, 130.91, 130.87, 130.1, 129.6, 129.2, 128.2, 127.20, 127.17, 127.14, 127.08, 126.9, 125.7, 123.2, 122.6, 41.5, 33.9, 21.4; **FT-IR** ν_{max}/cm^{-1} 3254s, 1329s, 1159s, 1093m, 717m, 548m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{23}H_{21}NO_2S_2$: 408.1086; found 408.1096.

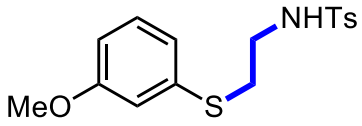


11b

A solution of 1-bromo-3,5-dimethylbenzene (0.691 mmol, 128 mg, 2.6 eq.) in dry THF (5 ml) was cooled to -78°C under argon and 2.2M n-BuLi (0.691 mmol, 0.314 ml, 2.6 eq.) was added dropwise. After 1 h, a solution of **2** (0.266 mmol, 122 mg, 1.0 eq.) in dry THF (5 ml) was added slowly. The reaction mixture was stirred at this temperature for additional 0.5 h and then allowed to reach room temperature. The mixture was quenched with 1M HCl solution, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **11b** as yellowish oil, 160.5 mg (90%).

***R*f**= 0.7 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 6.90 (s, 2H), 6.85 (s, 1H), 5.08 (t, *J* = 6.0 Hz, 1H), 3.13 (q, *J* = 6.4 Hz, 2H), 2.96 (t, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 138.8, 136.9, 133.2, 129.7, 128.9, 128.1, 127.1, 41.6, 34.0, 21.5, 21.2; **FT-IR** ν_{max}/cm^{-1} 3282s, 2921m, 1600m, 1448m, 1327s, 1159s, 1094s, 815m, 661m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{21}NO_2S_2$: 336.1086; found 336.1077.

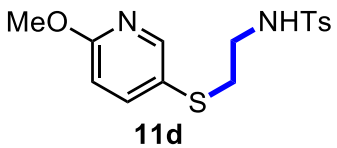


11c

To a solution of 1-bromo-3-methoxybenzene (0.652 mmol, 122 mg, 2.6 eq.) in dry THF (4 ml) under argon at -78°C 2.2M n-BuLi (0.652 mmol, 0.296 ml, 2.6 eq.) was added. The reaction mixture was stirred for 1 h and solution of **2** (0.251 mmol, 115 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for additional 1 h, then, cooling bath was removed and after 1 h, the mixture was quenched with 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **11c** as clear colourless oil, 118 mg (70%).

***R*f** = 0.5 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.82-6.86 (m, 2H), 6.77 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 4.95 (t, *J* = 6.0 Hz, 1H), 3.80 (s, 3H), 3.15 (q, *J* = 6.4 Hz, 2H), 3.00 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.0, 143.6, 136.9, 135.1, 130.0, 129.8, 127.1, 122.3, 115.6, 112.7, 55.3, 41.6, 33.9, 21.5; **FT-IR** ν_{max}/cm^{-1} 3281m, 2937m, 1590s, 1480m, 1326m, 1158s, 1094m, 662m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{16}H_{19}NO_3S_2$: 338.0879; found 338.0883.

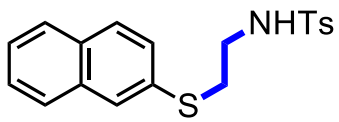


11d

A solution of 5-bromo-2-methoxypyridine (0.668 mmol, 126 mg, 2.6 eq.) in dry THF (4 ml) was cooled to -78°C under argon and 2.2M n-BuLi (0.668 mmol, 0.304 ml, 2.6 eq.) was added dropwise. The reaction mixture was stirred for 1 h, then, solution of **2** (0.257 mmol, 118 mg, 1.0 eq.) in dry THF (6 ml) was added. After 1 h, the cooling bath was removed, the reaction mixture was quenched with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) provided **11d** as white waxy solid, 156 mg (90%).

***R*f** = 0.43 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 2.4, 0.4 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.49 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.65 (dd, *J* = 8.4, 0.4 Hz, 1H), 4.97 (t, *J* = 6.0 Hz, 1H), 3.93 (s, 3H), 3.07 (q, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.4 Hz, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 151.1, 143.7, 143.4, 136.8, 129.8, 127.1, 121.4, 111.6, 53.7, 41.4, 36.1, 21.5; **FT-IR** ν_{max}/cm^{-1} 2949w, 1607s, 1495s, 1288s, 1158s, 690m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{15}H_{18}N_2O_3S_2$: 339.0832; found 339.0838.

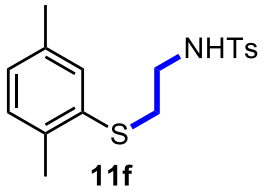


11e

To a solution of 2-bromonaphthalene (2.374 mmol, 492 mg, 2.6 eq.) in dry THF (7 ml) under argon at -78°C 2.2M n-BuLi (2.374 mmol, 1.08 ml, 2.6 eq.) was added dropwise. The mixture was stirred for 1 h and solution of **2** (0.913 mmol, 419 mg, 1.0 eq.) in dry THF (9 ml) was added dropwise. The cooling bath was removed after 0.5 h and the reaction mixture was stirred for an additional 1h. The reaction mixture was quenched with 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **11e** as whitish solid, 596 mg (91%).

***R*$_f$** = 0.53 (EtOAc/Hexanes 1:2), **m.p**. 73-74°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.83 (m, 1H), 7.71-7.76 (m, 3H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.46-7.54 (m, 2H), 7.34 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.02 (t, *J* = 6.0 Hz, 1H), 3.07-3.20 (m, 4H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.7, 133.6, 132.1, 131.1, 129.7, 128.9, 128.8, 127.9, 127.7, 127.2, 127.0, 126.8, 126.2, 41.5, 33.9, 21.5; **FT-IR** ν_{max}/cm^{-1} 3342s, 2932w, 1326s, 1150s, 1089m, 810s, 661m, 548m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{19}NO_2S_2$: 358.0930; found 358.0932.



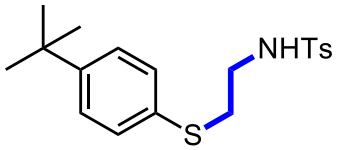
11f

A solution of 2-bromo-1,4-dimethylbenzene (0.659 mmol, 122 mg, 2.6 eq.) in dry THF (4 ml) was cooled to -78°C under argon and 2.2M n-BuLi (0.658 mmol, 0.3 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.253 mmol, 116 mg, 1.0 eq.) in dry THF (6 ml) was added. The reaction mixture was stirred for 0.5 h and then allowed to warm to room temperature. The mixture was quenched with 1M

HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) provided **11f** as clear colourless oil, 160 mg (94%).

R_f= 0.42 (EtOAc/Hexanes 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.09-6.93 (m, 3H), 4.93 (t, *J* = 6.0 Hz, 1H), 3.15 (q, *J* = 6.4 Hz, 2H), 2.95 (t, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.9, 136.2, 135.7, 132.7, 130.5, 130.3, 129.7, 127.8, 127.0, 41.7, 33.3, 21.5, 20.9, 19.9; **FT-IR** ν_{max}/cm^{-1} 3283s, 2923s, 1488m, 1326s, 1159s, 1094m, 814m, 662m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{21}NO_2S_2$: 336.1086; found 336.1084.



11g

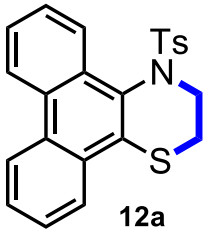
To a solution of 4-bromo-*tert*-butylbenzene (1.653 mmol, 352 mg, 2.6 eq.) in dry THF (7 ml) cooled to -78°C under argon 2.2M n-BuLi (1.653 mmol, 0.752 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.636 mmol, 292 mg, 1.0 eq.) in dry THF (7 ml) was added. The mixture was allowed to reach room temperature and then was quenched with 1M HCl solution, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:5) afforded **11g** as clear colourless oil, 415 mg (90%).

R_f = 0.3 (EtOAc/Hexanes 1:5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 4.97 (t, *J* = 6.0 Hz, 1H), 3.11 (q, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 143.5, 136.9, 131.1, 129.9, 129.8, 127.1, 126.2, 41.5, 34.6, 34.5, 31.2, 21.5; **FT-IR** ν_{max}/cm^{-1} 3284m, 2962m, 1327m, 1160s, 815m, 662m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{25}NO_2S_2$: 364.1399; found 364.1410.

Synthesis of benzomorpholines 12a-e

General procedure. To a round-bottomed flask containing compound **11** (1.0 eq.), PIDA (1.0-1.2 eq.), I_2 (1.0-1.2 eq.) and DCM (5.0-9.0 ml) was added. The mixture was stirred and illuminated with visible light using a 15W (≥798 lm) halogen lamp and aluminum foil reflective screen. After the time indicated, the mixture was diluted with DCM and sat. Na_2SO_3 solution, the water phase was extracted with DCM. The combined organic layers were dried with Na_2SO_4, filtered and evaporated *in vacuo*. Purification of the crude product was achieved by column chromatography.

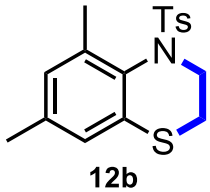


12a

11a 61.0 mg (0.15 mmol, 1.0 eq.), PIDA 48.3 mg (0.15 mmol, 1.0 eq.) and I_2 38 mg (0.15 mmol, 1.0 eq.) in 9 ml DCM. Reaction time – 4.5 h. Yield: 28 mg (46%).

R_f = 0.6 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.4 Hz, 1H), 8.61-8.67 (m, 1H), 8.49-8.54 (m, 1H), 8.07 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.59-7.76 (m, 4H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.79 (ddd, *J* = 14.4, 6.8, 2.4 Hz, 1H), 3.42 (ddd, *J* = 14.4, 12.0, 5.2 Hz, 1H), 3.25 (td, *J* = 12.0, 6.8 Hz, 1H), 3.05 (ddd, *J* = 12.0, 5.2, 2.4 Hz, 1H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 137.3, 131.0, 130.1, 129.63, 129.58, 129.5, 129.3, 129.2, 127.9, 127.6, 126.9, 126.6, 126.5, 125.4, 124.1, 123.1, 122.3, 45.9, 27.8, 21.6; **FT-IR** ν_{max}/cm^{-1} 2935w, 1488w, 1350s, 1161s, 724s, 757m, 662m, 553m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{23}H_{19}NO_2S_2$: 428.0749; found 428.0755.



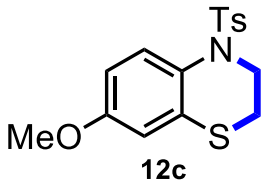
12b

11b 44.0 mg (0.131 mmol, 1.0 eq.), PIDA 42.0 mg (0.131 mmol, 1.0 eq.) and I_2 33 mg (0.131 mmol, 1.0 eq.) in 7 ml DCM. Reaction time – 5 h. Yield: 25 mg (57%).

R_f= 0.73 (EtOAc/Hexanes 1:3).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 0.8 Hz, 1H), 6.78 (d, *J* = 0.8 Hz, 1H), 4.51 (ddd, *J* = 14.4, 6.8, 2.8 Hz, 1H), 3.25 (dq, *J* = 11.2, 5.6 Hz, 1H), 2.98 (td, *J* = 11.2, 6.8 Hz, 1H), 2.82 (dq, *J* = 5.6, 2.8 Hz, 1H), 2.49 (s, 3H), 2.44 (s, 3H), 2.28 (s, 3H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 143.8, 139.1, 137.7, 137.2, 131.9, 131.7, 129.4, 129.1, 127.8, 125.5, 46.2, 27.0, 21.6, 20.9, 19.6; **FT-IR** ν_{max}/cm^{-1} 2924w, 1597m, 1345s, 1161s, 812m, 676s, 549s; **HRMS-ESI**$^+$: m/z $[M+H]^+$ calcd for $C_{17}H_{19}NO_2S_2$: 334.0930; found 334.0929.

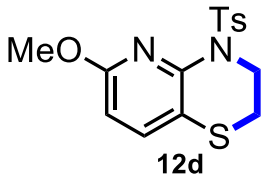


12c

11c 26.0 mg (0.077 mmol, 1.0 eq.), PIDA 24.8 mg (0.077 mmol, 1.0 eq.) and I_2 19.6 mg (0.077 mmol, 1.0 eq.) in 5 ml DCM. Reaction time – 4 h. Yield: 13 mg (50%).

***R*f** = 0.5 (EtOAc/Hexanes 1:2), **m.p**. 163-165°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.69 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 3.95-4.00 (m, 2H), 3.80 (s, 3H), 2.80-2.86 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 143.8, 137.3, 129.7 129.5, 129.2, 127.2, 127.1, 111.2, 110.8, 55.4, 44.8, 25.3, 21.6; **FT-IR** ν_{max}/cm^{-1} 2941w, 1596s, 1487s, 1342s, 1159s, 1059s, 819s, 676s, 545s; **HRMS-ESI**$^+$: m/z $[M+H]^+$ calcd for $C_{16}H_{17}NO_3S_2$: 336.0723; found 336.0730.

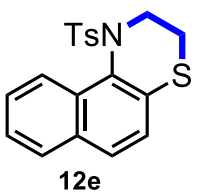


12d

11d 43.0 mg (0.127 mmol, 1.0 eq.), PIDA 49.0 mg (0.152 mmol, 1.2 eq.) and I_2 38.6 mg (0.152 mmol, 1.2 eq.) in 7 ml DCM. Reaction time –24 h. Yield: 17 mg (40%).

***R*f** = 0.68 (EtOAc/Hexanes 1:2), **m.p**. 137-139°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 1H), 4.26-4.31 (m, 2H), 3.58 (s, 3H), 3.25-3.30 (m, 2H), 2.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 144.0, 143.3, 139.5, 138.2, 129.3, 126.9, 110.6, 107.3, 53.9, 46.1, 28.1, 21.5; **FT-IR** ν_{max}/cm^{-1} 2937w, 1563s, 1468s, 1334s, 1158s, 924s, 807s, 687s, 583s; **HRMS-ESI**$^+$: m/z $[M+H]^+$ calcd for $C_{15}H_{16}N_2O_3S_2$: 337.0675; found 337.0679.

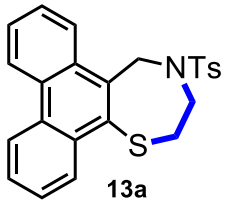


12e

11e 59.0 mg (0.165 mmol, 1.0 eq.), PIDA 49.0 mg (0.165 mmol, 1.0 eq.) and I_2 41.8 mg (0.165 mmol, 1.0 eq.) in 8 ml DCM. Reaction time –2.5 h. Yield: 40 mg (68%).

***R*f** = 0.65 (EtOAc/Hexanes 1:2), **m.p**. 122-124°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.54-7.60 (m, 1H), 7.43-7.50 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.8 Hz, 1H), 4.77 (ddd, *J* = 14.0, 6.0, 2.0 Hz, 1H), 3.24-3.33 (m, 1H), 3.18 (td, *J* = 12.0, 6.0 Hz, 1H), 2.94-3.00 (m, 1H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 137.1, 132.5, 132.1, 130.2, 129.7, 129.5, 127.9, 127.8, 127.4, 126.4, 125.6, 125.0, 124.5, 45.8, 26.8, 21.6; **FT-IR** ν_{max}/cm^{-1} 2930w, 1593m, 1349s, 1163s, 812s, 694s, 587s, 539m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{17}NO_2S_2$: 356.0773; found 356.0780.

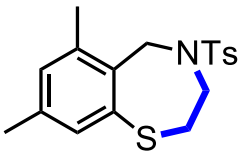


13a

To a solution of **11a** (0.103 mmol, 42 mg, 1.0 eq) in dry DCE (7 ml) under argon paraformaldehyde (0.216 mmol, 6.5 mg, 2.1 eq) was added followed by trifluoroacetic anhydride (0.309 mmol, 0.043 ml, 3.0 eq). The reaction mixture was cooled in an ice bath and methanesulfonic acid (1.03 mmol, 0.067 ml, 10.0 eq) was added. After 1 h, water was added and the mixture was allowed to reach room temperature, extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) afforded **13a** as off-white crystals, 40 mg (93%).

***R*f** = 0.66 (EtOAc/Hexanes 1:2), **m.p**. 191-192°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.0 Hz, 1H), 8.68-8.77 (m, 3H), 7.63-7.82 (m, 6H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 2H), 3.75 (br s, 2H), 2.98 (t, *J* = 5.2 Hz, 2H), 2.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 136.4, 135.7, 135.1, 131.7, 131.2, 130.3, 130.2, 129.9, 127.7, 127.5, 127.3, 127.0, 126.9, 126.7, 125.7, 122.9, 122.7, 51.7, 49.6, 34.3, 21.5; **FT-IR** ν_{max}/cm^{-1} 2923w, 1446w, 1335m, 1156s, 896m, 757s, 546s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{24}H_{21}NO_2S_2$: 420.1086; found 420.1098.

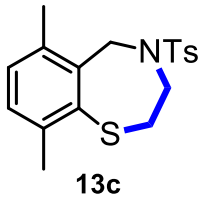


13b

To a solution of **11b** (0.125 mmol, 42 mg, 1.0 eq.) in dry DCE (4 ml) under argon paraformaldehyde (0.263 mmol, 7.9 mg, 2.1 eq.) was added followed by acetic anhydride (0.375 mmol, 0.035 ml, 3.0 eq.). The reaction mixture was cooled in an ice bath and methanesulfonic acid (1.25 mmol, 0.081 ml, 10.0 eq.) was added. After 30 min, water was added and the mixture was allowed to reach room temperature, extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:10) afforded **13b** as clear to white solid, 29.6 mg (68%).

***R*f**= 0.33 (EtOAc/Hexanes 1:10), **m.p**. 99-100°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7. 21 (s, 1H), 6.98 (s, 1H), 4.61 (s, 2H), 3.70 (br s, 2H), 2.77-2.82 (m, 2H), 2.59 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 138.0, 137.5, 137.0, 136.7, 136.2, 131.6, 131.5, 129.7, 127.1, 52.7, 49.6, 34.0, 21.5, 20.7, 20.3; **FT-IR** ν_{max}/cm^{-1} 2900m, 1444m, 1337s, 1161s, 876s, 696s, 589s, 545s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{18}H_{21}NO_2S_2$: 348.1086; found 348.1112.

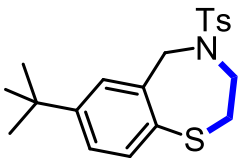


13c

To a solution of **11f** (0.095 mmol, 32 mg, 1.0 eq.) in dry DCE (5 ml) under argon paraformaldehyde (0.200 mmol, 6 mg, 2.1 eq.) was added, then trifluoroacetic anhydride (0.285 mmol, 0.04 ml, 3.0 eq.). Reaction mixture was cooled in an ice bath and methanesulfonic acid (0.95 mmol, 0.061 ml, 10.0 eq.) was added. After 40 min, water was added and the mixture was allowed to reach room temperature, extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:7) afforded **13c** as white solid, 26 mg (79%).

***R*f** = 0.7 (EtOAc/Hexanes 1:3), **m.p.** 127-129°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.03-7.09 (m, 2H), 4.65 (s, 2H), 3.67 (br s, 2H), 2.80 (t, *J* = 5.2 Hz, 2H), 2.60 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.4, 139.9, 137.8, 136.9, 135.9, 135.8, 130.2, 129.8, 129.4, 127.2, 52.3, 50.1, 33.7, 21.9, 21.5, 20.3; **FT-IR** ν_{max}/cm^{-1} 2919m, 1598m, 1448m, 1342s, 1165s, 880s, 710s, 546s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{18}H_{21}NO_2S_2$: 348.1086; found 348.1098.



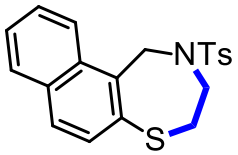
13d

To a solution of **11g** (0.160 mmol, 58 mg, 1.0 eq.) in dry DCE (8 ml) under argon paraformaldehyde (0.336 mmol, 10 mg, 2.1 eq.) was added, then trifluoroacetic anhydride (0.482 mmol, 0.067 ml, 3.0 eq.). Reaction mixture was cooled in an ice bath and methanesulfonic acid (1.6 mmol, 0.104 ml, 10.0 eq.) was added. After 1 h, the mixture was allowed to reach room temperature, stirred for 1 h and then,

quenched with water, extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:10) provided **13d** as white solid, 42 mg (70%).

***R*f** = 0.32 (EtOAc/Hexanes 1:10), **m.p**. 160-161°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.23 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 3.81 (br s, 2H), 2.66 (t, *J* = 4.8 Hz, 2H), 2.40 (s, 3H), 1.36 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.5, 143.2, 141.5, 137.3, 132.61, 132.60, 129.6, 127.7, 127.1, 125.0, 54.4, 52.3, 34.6, 33.7, 31.3, 21.5; **FT-IR** ν_{max}/cm^{-1} 2960m, 1442m, 1340s, 1165s, 819s, 720s, 662s, 546s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{20}H_{25}NO_2S_2$: 376.1399; found 376.1418.



13e

To a solution of **11e** (0.196 mmol, 70 mg, 1.0 eq.) in dry DCE (8 ml) under argon paraformaldehyde (0.412 mmol, 12.3 mg, 2.1 eq.) was added followed by trifluoroacetic anhydride (0.588 mmol, 0.083 ml, 3.0 eq.). The reaction mixture was cooled in ice bath and methanesulfonic acid (1.96 mmol, 0.127 ml, 10.0 eq.) was added. After 1 h, water was added and the mixture was allowed to reach room temperature, then, extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) afforded **13e** white crystals, 53.6 mg (74%).

***R*f** = 0.7 (EtOAc/Hexanes 1:2), **m.p.** 142-144°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.50-7.75 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 2H), 3.74-3.81 (m, 2H), 2.85-2.91 (m, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.9, 135.9, 135.8, 133.3, 132.7, 129.8, 129.7, 128.5, 128.3, 127.34, 127.25, 126.1, 124.6, 52.4, 48.5, 34.2, 21.5; **FT-IR** ν_{max}/cm^{-1} 2849m, 1446m, 1341s, 1163s, 821s, 667s, 549s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{20}H_{19}NO_2S_2$: 370.0930; found 370.0939.

Compounds 15-26 (Scheme 1)

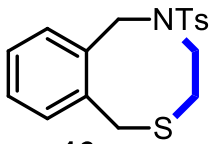
15

To a solution of 2-methylbenzyl alcohol (0.44 mmol, 54 mg, 2.6 eq.) in dry diethyl ether (6 ml) under argon at -78°C 2.2M n-BuLi (0.88 mmol, 0.4 ml, 5.2 eq.) was added dropwise. The reaction mixture was stirred for 24 h at room temperature. After cooling to -78°C, solution of **2** (0.17 mmol, 78 mg, 1.0 eq.)

in dry THF (4.5 ml) was added. The cooling bath was removed after 0.5 h and the reaction mixture was stirred for additional 1 h at room temperature. The mixture was quenched with 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **15** as white-brownish crystals, 77.5 mg (65%).

***R*f** = 0.3 (EtOAc/Hexanes 1:2), **m.p**. 74-76°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.17-7.41 (m, 6H), 5.18 (t, *J* = 6.4 Hz, 1H), 4.75 (s, 2H), 3.80 (s, 2H), 3.07 (q, *J* = 6.4 Hz, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 138.9, 137.0, 135.7, 130.4, 129.9, 129.8, 128.2, 128.0, 127.1, 63.2, 42.0, 33.2, 31.5, 21.5; **FT-IR** ν_{max}/cm^{-1} 3464s, 3131s, 2864m, 1318s, 1156s, 988s, 660m, 548s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{21}NO_3S_2$: 352.1036; found 352.1026.

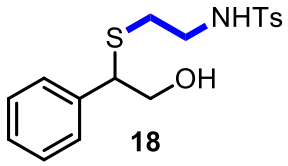


16

To a solution of **15** (0.09 mmol, 32 mg, 1.0 eq.) in THF (7 ml) PPh_3 (0.118 mmol, 31 mg, 1.3 eq.) was added followed by DEAD (0.118 mmol, 0.019 ml, 1.33 eq.). After 2 h, water was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3) afforded **16** as white needles, 26 mg (86%).

***R*f** = 0.7 (EtOAc/Hexanes 1:2), **m.p**. 135-136°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.19-7.34 (m, 4H), 4.44 (s, 2H), 4.01 (s, 2H), 3.57-3.62 (m, 2H), 2.48-2.53 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 137.0, 136.1, 134.3, 130.5, 129.91, 129.87, 129.1, 127.7, 127.2, 51.0, 50.4, 33.0, 29.4, 21.6; **FT-IR** ν_{max}/cm^{-1} 2923m, 1465m, 1332s, 1157s, 854m, 719s, 652m, 544s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{19}NO_2S_2$: 334.0930; found 334.0934.



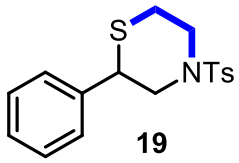
18

To diisopropylamine (0.503 mmol, 0.07 ml, 2.2 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.503 mmol, 0.228 ml, 2.2 eq.) was added at -40°C. The mixture was cooled to -78°C and methyl 2-phenylacetate (0.503 mmol, 75.5 mg, 2.2 eq.) in dry THF (2 ml) was added. The reaction mixture was stirred for 40 min at -78°C and 10 min at room temperature. Then, solution of **2** (0.229 mmol, 105 mg, 1.0 eq.) in dry THF (4.5 ml) was added dropwise at -78°C and the mixture was stirred for 0.5 h, then

allowed to reach room temperature. To the above solution, LAH (0.916 mmol, 34.7 mg, 4.0 eq.) was added in one portion. The suspension was stirred overnight, quenched with solid $Na_2SO_4 \cdot 10H_2O$ and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) provided **18** as colourless oil, 99 mg (62%).

***R*f**= 0.2 (EtOAc:Hexanes – 1:1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.24-7.37 (m, 7H), 4.43 (br s, 1H), 3.76-3.91 (m, 3H), 2.98-3.08 (m, 2H), 2.50-2.63 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 139.1, 136.9, 129.8, 128.9, 128.0, 127.9, 127.1, 65.9, 52.7, 42.2, 31.3, 21.5; **FT-IR** ν_{max}/cm^{-1} 3280s, 2924s, 1598m, 1324s, 1157s, 1093s, 701m, 661m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{21}NO_3S_2$: 352.1036; found 352.1049.

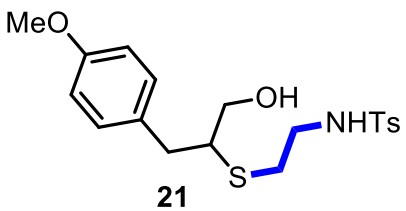


19

To a solution of **18** (0.087 mmol, 30.5 mg, 1.0 eq.) in THF (7 ml) PPh_3 (0.113 mmol, 29.6 mg, 1.3 eq.) was added followed by DEAD (0.113 mmol, 0.018 ml, 1.3 eq.). The mixture was stirred for 1 h and then, quenched with water, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:4) afforded **19** as white crystals, 25 mg (87%).

***R*f** = 0.72 (EtOAc/Hexanes 1:2), **m.p**. 95-97°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.29-7.40 (m, 7H), 4.12-4.22 (m, 2H), 4.09 (dd, *J* = 10.4, 2.8 Hz, 1H), 3.05-3.16 (m, 1H), 2.61-2.77 (m, 3H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.8, 138.6, 134.0, 129.9, 128.8, 128.2, 127.7, 127.4, 53.8, 47.1, 45.2, 28.7, 21.6; **FT-IR** ν_{max}/cm^{-1} 2905w, 1456w, 1343s, 1161s, 909s, 737m, 658m, 552m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{19}NO_2S_2$: 334.0930; found 334.0920.



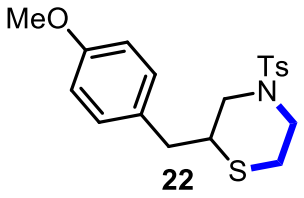
21

To diisopropylamine (0.374 mmol, 0.052 ml, 2.2 eq.) solution in dry THF (2 ml) under argon 2.2M n-BuLi (0.374 mmol, 0.17 ml, 2.2 eq.) was added at -40°C. The solution was cooled to -78°C, methyl 3-(4-methoxyphenyl)propionate (0.374 mmol, 72.6 mg, 2.2 eq.) in dry THF (2 ml) was added and the reaction mixture was stirred for 40 min at -78°C and 10 min at room temperature. After cooling the solution back

to -78°C, solution of **2** (0.170 mmol, 78 mg, 1.0 eq.) in dry THF (4 ml) was added dropwise and the mixture was stirred for 1 h. The cooling bath was removed and LAH (0.680mmol, 25.8 mg, 4.0 eq.) was added at once. The reaction mixture was stirred overnight, quenched with solid $Na_2SO_4 \cdot 10H_2O$ and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) provided **21** as colourless oil, 80 mg (59%).

***R*f**= 0.2 (EtOAc/Hexanes 1:1.5).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.12 (t, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.00 (t, *J* = 6.0 Hz, 1H), 3.82 (s, 3H), 3.48-3.73 (m, 2H), 2.92-3.12 (m, 2H), 2.81-2.90 (m, 2H), 2.47-2.70 (m, 3H), 2.44 (s, 3H), 2.21 (t, *J* = 5.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 143.5, 137.0, 130.5, 130.2, 129.8, 127.1, 113.9, 64.1, 55.3, 51.3, 42.5, 37.7, 31.5, 21.5; **FT-IR** ν_{max}/cm^{-1} 3281w, 2930w, 1513s, 1247m, 1158s, 815m, 661m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{25}NO_4S_2$: 396.1298; found 396.1307.

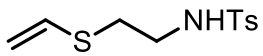


22

To a solution of **21** (0.141 mmol, 56 mg, 1.0 eq.) in THF (8 ml) PPh_3 (0.183 mmol, 48 mg, 1.3 eq.) was added followed by DEAD (0.183 mmol, 0.029 ml, 1.3 eq.). After stirring for 1.3 h, the mixture was quenched with water and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:3.5) afforded **22** as white crystals, 46 mg (86%).

***R*f** = 0.45 (EtOAc/Hexanes 1:3), **m.p.** 140-141°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 3.82 (s, 3H), 3.77 (dd, *J* = 12.0, 2.0 Hz, 2H), 3.02-3.13 (m, 1H), 2.62-2.94 (m, 6H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5, 143.7, 133.9, 130.1, 129.8, 129.6, 127.4, 114.0, 55.2, 52.5, 47.6, 41.8, 38.3, 27.0, 21.5; **FT-IR** ν_{max}/cm^{-1} 2920m, 1610m, 1511s, 1343s, 1243s, 1165s, 734s, 550s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{23}NO_3S_2$: 378.1192; found 378.1201.

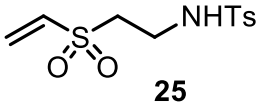


24

To a solution of **2** (0.392 mmol, 180 mg, 1.0 eq.) in dry THF (9 ml) under argon at -78°C 1.0M vinylmagnesium bromide (1.02 mmol, 1.02 ml, 2.6 eq.) was added. After stirring for 1 h, the mixture was quenched with water and 1M HCl, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **24** as off-white wax like solid, 170 mg (84%).

***R*f** = 0.53 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.20 (dd, *J* = 16.4, 10.0 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 5.18 (d, *J* = 16.4 Hz, 1H), 4.94 (t, *J* = 6.4 Hz, 1H), 3.20 (q, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 6.4 Hz, 2H), 2.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.7, 137.0, 130.5, 129.8, 127.1, 113.4, 42.0, 31.6, 21.5; **FT-IR** ν_{max}/cm^{-1} 3281s, 2919m, 1597m, 1332s, 1159s, 882s, 677s, 547s.

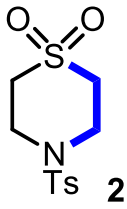


25

To a solution of **24** (0.377 mmol, 97 mg, 1.0 eq.) in THF/H_2O (4/4 ml) at 0°C Oxone (0.942 mmol, 580 mg, 2.5 eq.) was added. The mixture was stirred overnight at room temperature, then K_2CO_3 (0.942 mmol, 130 mg, 2.5 eq.) was added and stirring was continued overnight. After dilution with water, the mixture was extracted with DCM, dried with Na_2SO_4 and evaporated *in vacuo*. The residue was triturated with DCM and PE to give **25** as white solid, 108 mg (99%).

***R*f** = 0.46 (EtOAc/Hexanes 1:2), **m.p.**145-147°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.65 (dd, *J* = 16.8, 9.6 Hz, 1H), 6.44 (d, *J* = 16.8 Hz, 1H), 6.22 (d, *J* = 9.6 Hz, 1H), 5.28-5.37 (m, 1H), 3.40-3.49 (m, 2H), 3.16-3.25 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.0, 136.5, 136.0, 131.5, 130.0, 127.1, 53.7, 36.9, 21.6; **FT-IR** ν_{max}/cm^{-1} 3272s, 3055w, 1332s, 1291s, 1161s, 1127s, 777s, 547s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{11}H_{15}NO_4S_2$: 290.0515; found 290.0521.



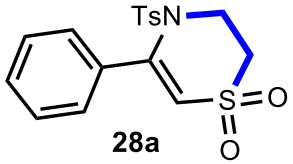
26

To a solution of **25** (0.131 mmol, 38 mg, 1.0 eq.) in THF (8 ml) K_2CO_3 (0.328 mmol, 45.3 mg, 2.5 eq.) was added. The reaction mixture was stirred at 80°C overnight. After dilution with water, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **26** as white solid, 37.6 mg (99%).

***R*f**= 0.3 (EtOAc/Hexanes 1:2), **m.p**. 188-190°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 3.66 (br s, 4H), 3.12-3.19 (m, 4H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.7, 133.8, 130.2, 127.3, 51.4, 44.8, 21.6; **FT-IR** ν_{max}/cm^{-1} 1344m, 1161m, 1128s, 903m, 722m, 600m, 549m.

Compounds 28a-k (Table 3)

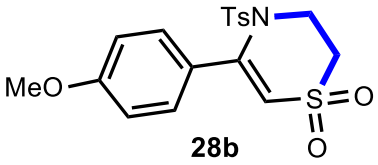


28a

To a solution of phenylacetylene (0.489 mmol, 50 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.489 mmol, 0.222 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.188 mmol, 86 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 0.5 h before removing the cooling bath and quenched with water (7 ml) at room temperature. Oxone (1.128 mmol, 693 mg, 6.0 eq.) was added and after 1.5 h K_2CO_3 (1.504 mmol, 208 mg, 8.0 eq.). After 8 h, 1M HCl was added and the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) afforded **28a** as white crystals, 130 mg (95%).

***R*f** = 0.46 (EtOAc/Hexanes 1:1), **m.p**. 107-108°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.48 (m, 3H), 7.26-7.40 (m, 6H), 5.89 (s, 1H), 4.48-4.53 (m, 2H), 3.20-3.25 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 145.4, 136.0, 135.1, 130.6, 130.1, 128.24, 128.19, 127.5, 114.7, 50.3, 46.4, 21.7; **FT-IR** ν_{max}/cm^{-1} 1594m, 1378s, 1290s, 1166s, 1118s, 879m, 616m, 550s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{17}NO_4S_2$: 364.0672; found 364.0678.

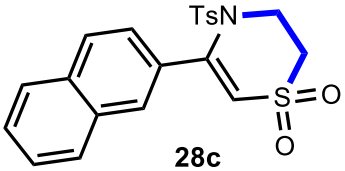


28b

To a solution of 1-ethynyl-4-methoxybenzene (0.360 mmol, 48 mg, 2.5 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.360 mmol, 0.164 ml, 2.5 eq.) was added dropwise. After 1 h, solution of **2** (0.144 mmol, 66 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1.5 h, quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.864 mmol, 531 mg, 6.0 eq.) and K_2CO_3 (1.152 mmol, 159 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 24 h, 1M HCl was added and the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **28b** as yellowish oil, 112 mg (99%).

R_f = 0.24 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.24-7.28 (m, 2H), 6.81-6.86 (m, 2H), 5.83 (s, 1H), 4.46-4.52 (m, 2H), 3.86 (s, 3H), 3.17-3.23 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 147.7, 145.4, 136.1, 130.1, 129.8, 127.5, 127.3, 113.7, 113.5, 55.4, 50.3, 46.3, 21.7; **FT-IR** ν_{max}/cm^{-1} 1607m, 1511m, 1295m, 1253m, 1166m, 1121m, 879m, 676m, 549m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{18}H_{19}NO_5S_2$: 394.0777; found 394.0782.



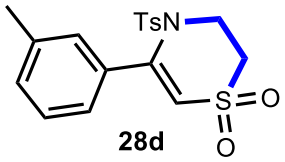
28c

To a solution of 2-ethynylnaphthalene (0.328 mmol, 50 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.328 mmol, 0.149 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.126 mmol, 58 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1.5 h, quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.756 mmol, 465 mg, 6.0 eq.) and K_2CO_3 (1.008 mmol, 139 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 24 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **28c** as yellowish solid, 96 mg (92%).

R_f = 0.3 (EtOAc/Hexanes 1:2), **m.p**. 150-151°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.70-7.74 (m, 2H), 7.51-7.61 (m, 2H), 7.39-7.45 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 4.56-4.60 (m, 2H), 3.28-

3.33 (m, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 145.4, 136.2, 134.1, 132.4, 132.3, 130.0, 128.5, 128.2, 128.0, 127.8, 127.6, 127.5, 126.8, 125.2, 115.0, 50.5, 46.4, 21.6; **FT-IR** ν_{max}/cm^{-1} 3059w, 1596m, 1370m, 1296s, 1169s, 1121s, 879m, 694m, 550m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{21}H_{19}NO_4S_2$: 414.0828; found 414.0833.

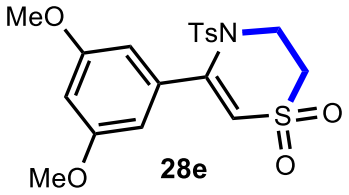


28d

To a solution of 1-ethynyl-3-methylbenzene (0.398 mmol, 46 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.398 mmol, 0.18 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.153 mmol, 70 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for additional 1 h, quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.918 mmol, 564 mg, 6.0 eq.) and K_2CO_3 (1.224 mmol, 169 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 20 h, 1M HCl was added and the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **28d** as dark reddish oil, 106 mg (92%).

***R*$_f$** = 0.4 (EtOAc/Hexanes 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20-7.25 (m, 2H), 7.12-7.17 (m, 1H), 7.01 (s, 1H), 5.88 (s, 1H), 4.47-4.54 (m, 2H), 3.24-3.31 (m, 2H), 2.47 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.0, 145.2, 137.9, 136.3, 134.9, 131.3, 130.0, 128.8, 128.2, 127.5, 125.5, 114.5, 50.6, 46.4, 21.6, 21.2; **FT-IR** ν_{max}/cm^{-1} 3051w, 1596m, 1357m, 1295m, 1165m, 1121m, 878m, 694m, 549m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{18}H_{19}NO_4S_2$: 378.0828; found 378.0836.



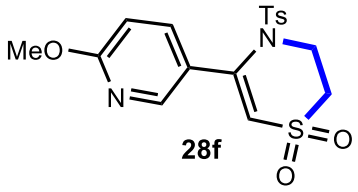
28e

To a solution of 1-ethynyl-3,5-dimethoxybenzene (0.510 mmol, 83 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.510 mmol, 0.232 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.196 mmol, 90 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1.5 h, quenched with water (7 ml) and allowed to reach room temperature. Oxone (1.176 mmol, 723 mg, 6.0 eq.) and K_2CO_3 (1.568 mmol, 217 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 24 h, another portion of Oxone (0.392 mmol, 241 mg, 2.0 eq.) and K_2CO_3 (0.392

mmol, 54 mg, 2.0 eq.) were added. The mixture was stirred overnight, 1M HCl was added, extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) afforded **28e** as slightly yellow solid, 164.5 mg (99%).

***R*f**= 0.36 (EtOAc/Hexanes 1:1.5), **m.p**. 111-113°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.49 (t, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 2H), 5.93 (s, 1H), 4.47-4.52 (m, 2H), 3.73 (s, 6H), 3.29-3.35 (m, 2H), 2.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.4, 147.7, 145.3, 136.6, 136.2, 129.9, 127.6, 114.5, 106.3, 102.9, 55.4, 50.7, 46.4, 21.6; **FT-IR** ν_{max}/cm^{-1} 3042m, 2945m, 1590s, 1425s, 1344s, 1297s, 1158s, 1119s, 886s, 720s, 542s; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{21}NO_6S_2$: 424.0883; found 424.0892.

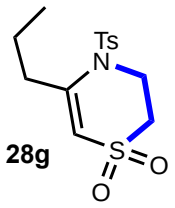


28f

To a solution of 5-ethynyl-2-methoxypyridine (0.369 mmol, 49 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.369 mmol, 0.167 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.142 mmol, 65 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1 h, then quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.852 mmol, 524 mg, 6.0 eq.) and K_2CO_3 (1.136 mmol, 157 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After 14 h, water was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **28f** as white crystals, 106 mg (95%).

***R*f** = 0.58 (EtOAc/Hexanes 1:2), **m.p**. 145-147°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 1.2 Hz, 1H), 7.56 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.86 (s, 1H), 4.49-4.54 (m, 2H), 3.99 (s, 3H), 3.15-3.21 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.5, 146.3, 145.8, 145.0, 138.6, 135.8, 130.3, 127.4, 124.5, 114.3, 110.5, 53.9, 50.0, 46.2, 21.7; **FT-IR** ν_{max}/cm^{-1} 1604m, 1372m, 1290m, 1170m, 1121m, 880m, 666m, 551m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{18}N_2O_5S_2$: 395.0730; found 395.0724.

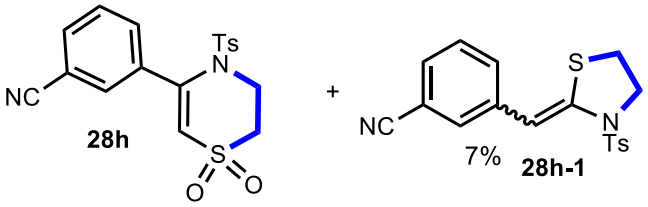


28g

To a solution of pent-1-yne (0.380 mmol, 26 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.380 mmol, 0.173 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.146 mmol, 67 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1 h, then quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.876mmol, 539 mg, 6.0 eq.) and K_2CO_3 (1.168 mmol, 161 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 13 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **28g** as yellowish solid, 80 mg (83%).

***R*f** = 0.47 (EtOAc/Hexanes 1:2), **m.p**. 120-122°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.69 (s, 1H), 4.32-4.39 (m, 2H), 3.00-3.07 (m, 2H), 2.56-2.65 (m, 2H), 2.48 (s, 3H), 1.48-1.60 (m, 2H), 0.87-0.97 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.2, 145.5, 136.5, 130.5, 126.8, 111.5, 49.5, 46.5, 37.6, 21.7, 21.5, 13.4; **FT-IR** ν_{max}/cm^{-1} 3063m, 2973m, 1595m, 1358s, 1167s, 910m, 817m, 681m, 600m, 541m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{14}H_{19}NO_4S_2$: 330.0828; found 330.0834.



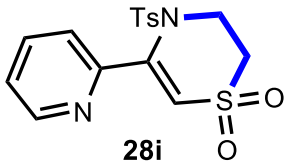
28h **28h-1**

To a solution of 3-ethynylbenzonitrile (0.351 mmol, 44.6 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.351 mmol, 0.16 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.135 mmol, 62 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1 h, then quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.810 mmol, 498 mg, 6.0 eq.) and K_2CO_3 (1.080 mmol, 149 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 19 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:1.5) afforded **28h** with inseparable isomer **28h-1** as yellowish solid, 82 mg (78%, including 7% of isomer).

***R*f**= 0.45 (EtOAc/Hexanes 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.74 (m, 2H), 7.48-7.56 (m, 1H), 7.31-7.45 (m, 5H), 5.93 (s, 1H), 4.49-4.54 (m, 2H), 3.24-3.29 (m, 2H), 2.49 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 145.3, 136.3,

135.8, 133.7, 132.4, 131.6, 130.4, 129.5, 127.3, 117.6, 116.2, 112.6, 50.3, 46.4, 21.7; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{18}H_{16}N_2O_4S_2$: 411.0444; found 411.0462.

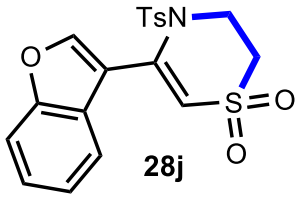


28i

To a solution of 2-ethynylpyridine (0.385 mmol, 40 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.385 mmol, 0.175 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.148 mmol, 68 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1 h, then quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.888 mmol, 546 mg, 6.0 eq.) and K_2CO_3 (1.184 mmol, 164 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 14 h, water was added and the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1.5:1) afforded **28i** as yellowish crystals, 83 mg (77%).

***R*$_f$** = 0.46 (EtOAc/Hexanes 2:1), **m.p**. 165-167°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.0 Hz, 1H), 7.74-7.84 (m, 3H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34-7.44 (m, 3H), 6.27 (s, 1H), 4.34-4.41 (m, 2H), 3.08-3.14 (m, 2H), 2.48 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.4, 149.2, 145.9, 145.7, 136.6, 135.1, 130.3, 127.9, 124.9, 123.7, 116.7, 49.6, 46.1, 21.8; **FT-IR** ν_{max}/cm^{-1} 3047m, 1582m, 1368s, 1299s, 1166s, 1123s, 767m, 694m, 549s; **HRMS-ESI**$^{+}$: m/z $[M+H]^{+}$ calcd for $C_{16}H_{16}N_2O_4S_2$: 365.0624; found 365.0626.

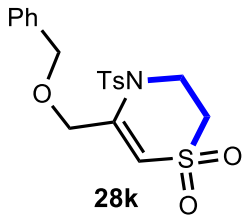


28j

To a solution of 3-ethynylbenzofuran (0.408 mmol, 58 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.408 mmol, 0.185 ml, 2.6 eq.) was added dropwise. After 1 h solution of **2** (0.157 mmol, 72 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 45 min, then quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.942 mmol, 579 mg, 6.0 eq.) and K_2CO_3 (1.256 mmol, 174 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 23 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **28j** as yellowish solid, 108 mg (85%).

***R*$_f$**= 0.2 (EtOAc/Hexanes 1:2), **m.p**. 171-173°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.38-7.44 (m, 3H), 7.31-7.37 (m, 1H), 7.18-7.24 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.07 (s, 1H), 4.57-4.63 (m, 2H), 3.29-3.35 (m, 2H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.79, 154.78, 146.0, 145.4, 138.7, 135.5, 130.0, 127.4, 125.3, 123.7, 120.0, 116.7, 114.3, 111.8, 50.5, 45.9, 21.6; **FT-IR** ν_{max}/cm^{-1} 1599m, 1370s, 1292s, 1167s, 1113s, 883m, 742m, 599s, 548s; **HRMS-ESI$^+$**: m/z $[M+NH_4]^+$ calcd for $C_{19}H_{17}NO_5S_2$: 421.0886; found 421.0895.

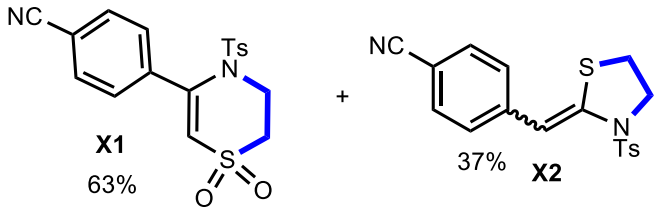


28k

To a solution of ((prop-2-ynyloxy)methyl)benzene (0.385 mmol, 56.3 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.385 mmol, 0.175 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.148 mmol, 68 mg, 1.0 eq.) in dry THF (5 ml) was added. The mixture was stirred for 1 h, quenched with water (7 ml) and allowed to reach room temperature. Oxone (0.888mmol, 546 mg, 6.0 eq.) and K_2CO_3 (1.184 mmol, 164 mg, 8.0 eq.) were added followed by water (3 ml) and THF (3 ml). After stirring for 20 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **28k** as off-white crystals, 100 mg (83%).

***R*$_f$** = 0.24 (EtOAc/Hexanes 1:2), **m.p**. 103-105°C.

1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.29-7.43 (m, 7H), 6.25 (s, 1H), 4.57 (s, 2H), 4.49 (s, 2H), 4.28-4.34 (m, 2H), 3.03-3.10 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.7, 145.2, 136.8, 135.7, 130.5, 128.6, 128.2, 127.9, 126.9, 110.5, 73.2, 68.5, 49.3, 46.3, 21.7; **FT-IR** ν_{max}/cm^{-1} 1599m, 1362s, 1301s, 1167s, 1116s, 752s, 680s, 590s, 546m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{19}H_{21}NO_5S_2$: 408.0934; found 408.0941.



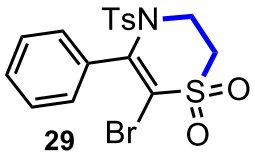
X1 63% 37% **X2**

To a solution of 4-ethynylbenzonitrile (0.369 mmol, 47 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78ºC under argon 2.2M n-BuLi (0.369 mmol, 0.168 ml, 2.6 eq.) was added dropwise. After 1 h solution of 2 (0.142 mmol, 65 mg, 1.0 eq.) in dry THF (5 ml) was added. Mixture was stirred for additional 1.5 h, quenched with water (7 ml), warmed to room temperature and Oxone (0.852 mmol, 524 mg, 6.0 eq.)

with K_2CO_3 (1.136 mmol, 157 mg, 8.0 eq.) were added. After 24 h, 1M HCl was added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded mixture of isomers **X1** and **X2** in 1.7 molar ratio (60 mg, 54 %).

R_f= 0.15 (EtOAc/Hexanes 1:2).

Compounds 29,31 (Scheme 2)

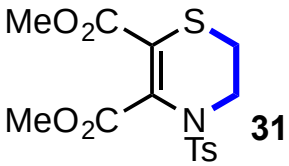


29

To a solution of phenylacetylene (0.783 mmol, 80 mg, 2.6 eq.) in dry THF (3 ml) cooled to -78°C under argon 2.2M n-BuLi (0.783 mmol, 0.356 ml, 2.6 eq.) was added dropwise. After 1 h, solution of **2** (0.301 mmol, 138 mg, 1.0 eq.) in dry THF (6 ml) was added. The mixture was stirred for 0.5 h, allowed to reach room temperature and quenched with water (9 ml). Oxone (1.806 mmol, 1.11 g, 6.0 eq.) and K_2CO_3 (2.408 mmol, 333 mg, 8.0 eq.) were added followed by water (4 ml) and THF (4 ml). After 20 h, another portion of Oxone (2.408 mmol, 1.48 g, 8.0 eq.) and K_2CO_3 (1.806 mmol, 250 mg, 6.0 eq.) was added followed by KBr (2.408 mmol, 287 mg, 8.0 eq.). The mixture was stirred for 3 h at room temperature, then, 1M HCl was added, the mixture was extracted with ethylacetate, washed with Na_2SO_3, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2.5) afforded **29** as brownish solid, 194 mg (73%).

R_f = 0.4 (EtOAc/Hexanes 1:2), **m.p**. 170-172°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.41 (m, 1H), 7.11-7.27 (m, 8H), 4.53-4.60 (m, 2H), 3.70-3.76 (m, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 144.9, 136.4, 132.7, 130.3, 130.2, 129.7, 127.9, 127.2, 110.2, 52.6, 46.0, 21.6; **FT-IR** ν_{max}/cm^{-1} 1380m, 1302m, 1166m, 1130m, 916m, 766m, 697m, 552m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{17}H_{16}BrNO_4S_2$: 443.9757; found 443.9762.



31

To a solution of **2** (0.081 mmol, 37 mg, 1.0 eq) and DMAP (0.089 mmol, 22 mg, 2.2 eq) in toluene (2 ml) at 0°C dimethyl but-2-ynedioate (0.324 mmol, 0.04 ml, 4.0 eq) in toluene (1 ml) was added dropwise

slowly. After 20 min, water and 1M HCl were added, the mixture was extracted with ethylacetate, dried with Na_2SO_4 and evaporated *in vacuo*. Purification by column chromatography (EtOAc:Hexanes – 1:2) afforded **31** as brownish oil, 30 mg (50 %).

R_f = 0.25 (EtOAc/Hexanes 1:2)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.56-3.61 (m, 2H), 2.76-2.81 (m, 2H), 2.47 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 164.3, 145.1, 134.9, 130.1, 129.9, 128.0, 122.4, 53.2, 53.1, 42.7, 25.9, 21.7; **FT-IR** ν_{max}/cm^{-1} 2952w, 1727s, 1571m, 1435m, 1293s, 1164s, 1091m, 820s, 735s, 559m; **HRMS-ESI$^+$**: m/z $[M+H]^+$ calcd for $C_{15}H_{17}NO_6S_2$: 371.0497; found 371.0488.

X-ray crystal structure of 2

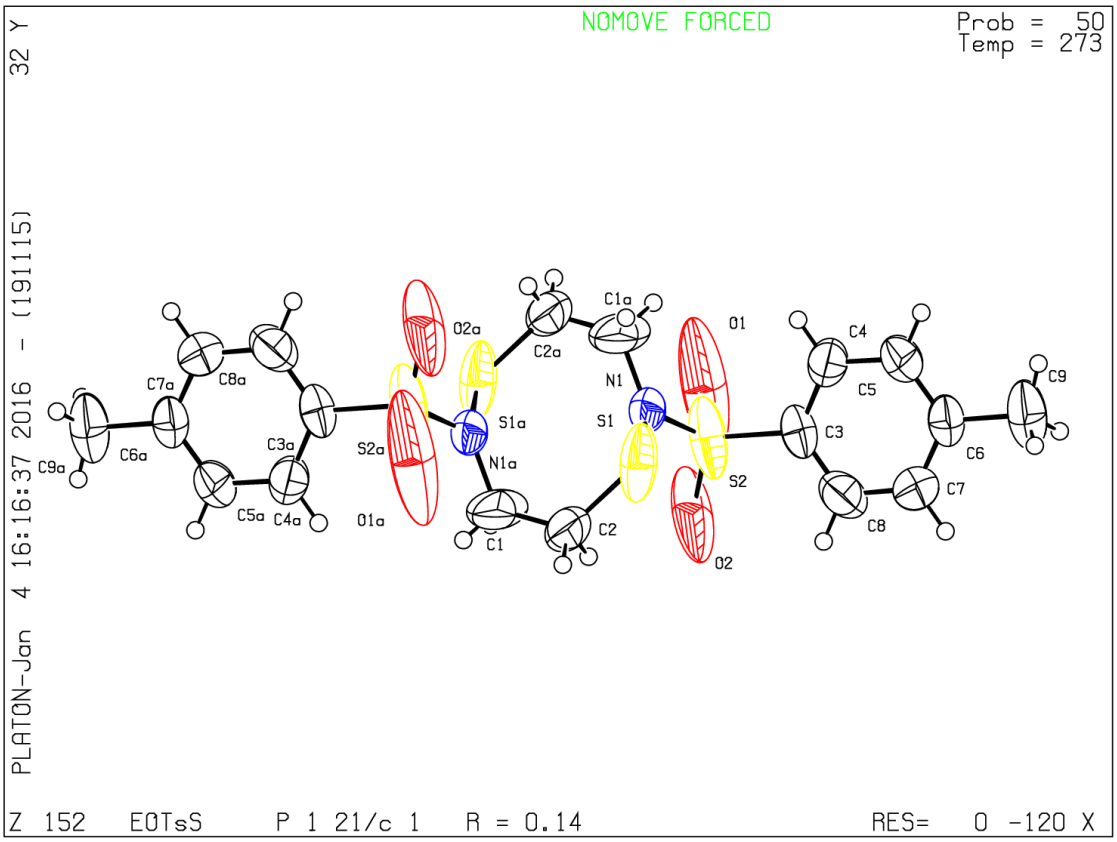


Figure S1. Thermal ellipsoid plot of **2** drawn at the 50% probability level.

Crystal Data

Empirical Formula	C12H12O2
Formula Weight	188.23
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.370 X 0.250 X 0.120 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 7.158(11) Å b = 10.19(2) Å c = 6.719(10) Å b = 96.46(2) o V = 486.8(13) Å3
Space Group	P21/c (#14)
Z value	2

Dcalc	1.284 g/cm^3
F000	200.00
m(MoKa)	0.863 cm^{-1}

Table S1. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
O1	C4	1.370(3)	O1	C7	1.427(3)
C2	C2^1	1.425(3)	C2	C3^1	1.428(3)
C2	C4	1.432(3)	C3	C5	1.368(3)
C4	C6	1.378(3)	C5	C6	1.410(3)

Table S2. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C4	O1	C7	117.91(11)	C2^1	C2	C3^1	119.78(13)
C2^1	C2	C4	118.32(11)	C3^1	C2	C4	121.91(11)
C2^1	C3	C5	119.60(12)	O1	C4	C2	114.24(11)
O1	C4	C6	124.91(14)	C2	C4	C6	120.85(12)
C3	C5	C6	121.74(13)	C4	C6	C5	119.72(15)

X-ray crystal structure of 12e

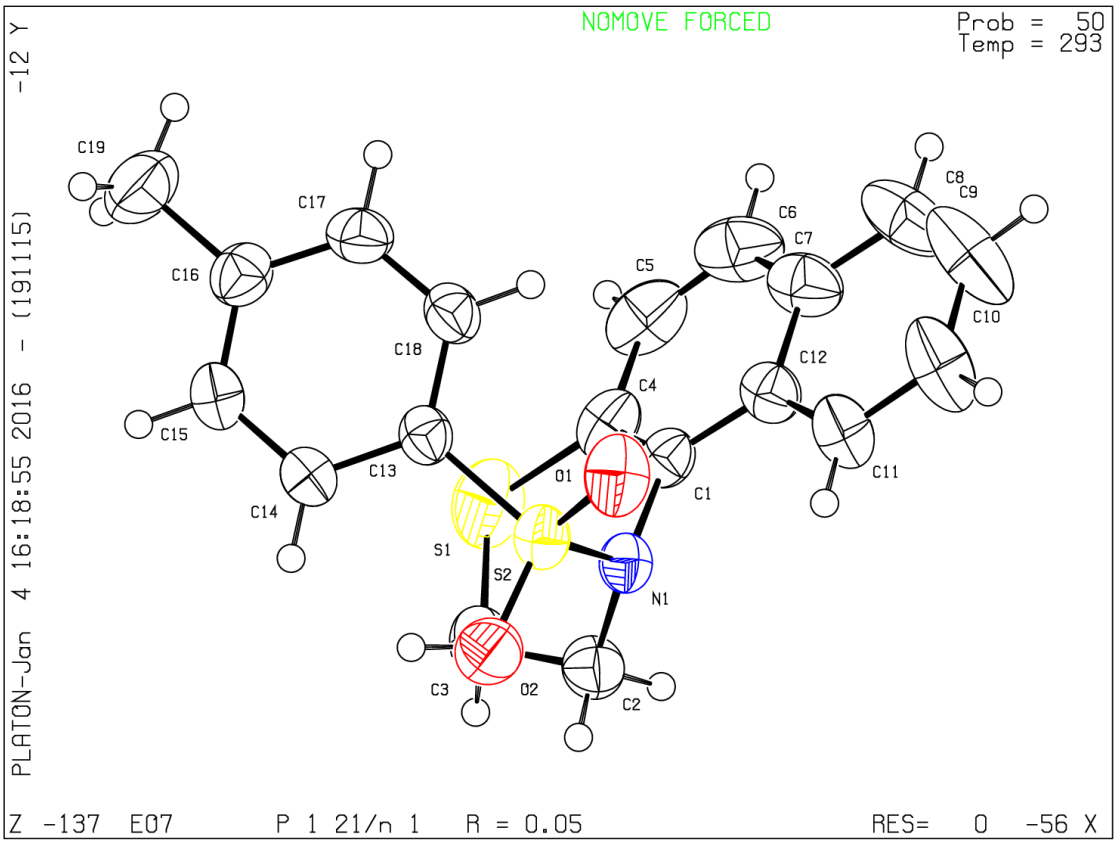


Figure S2. Thermal ellipsoid plot of **12e** drawn at the 50% probability level.

Crystal Data

Empirical Formula	C19H17NO2S2
Formula Weight	355.47
Crystal Color, Habit	colorless, block
Crystal Dimensions	0.360 X 0.350 X 0.300 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.920(8) Å b = 17.616(12) Å c = 10.628(8) Å b = 111.511(9) o V = 1728(3) Å3

Space Group P21/n (#14)

Z value	4
Dcalc	1.366 g/cm^3
F000	744.00
m(MoKa)	3.188 cm^{-1}

Table S3. Bond lengths (Å)

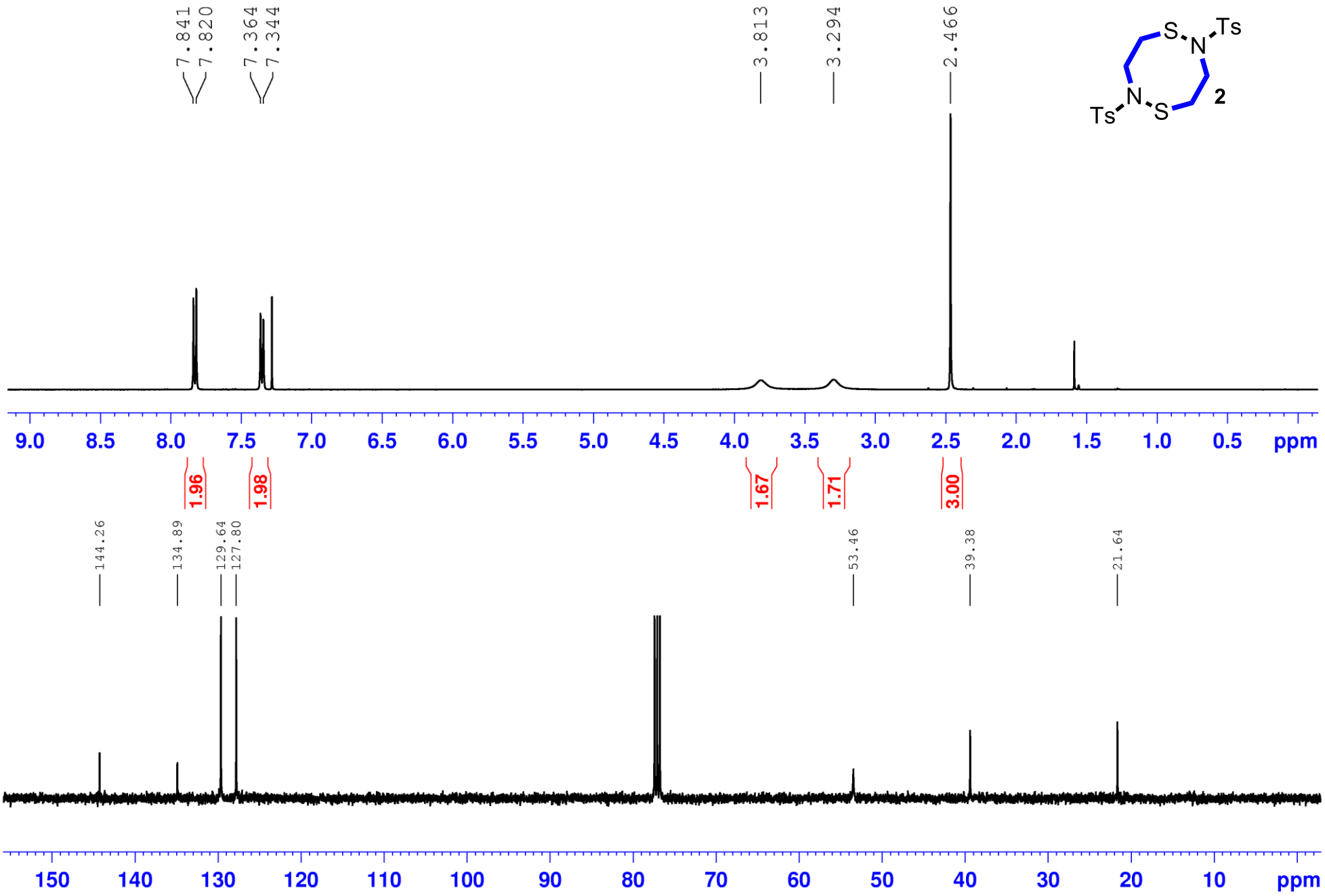
atom	atom	distance	atom	atom	distance
S1	C3	1.820(3)	S1	C4	1.759(3)
S2	O1	1.428(2)	S2	O2	1.4332(16)
S2	N1	1.6650(17)	S2	C13	1.767(3)
N1	C1	1.445(3)	N1	C2	1.482(3)
C1	C4	1.381(4)	C1	C12	1.429(3)
C2	C3	1.514(4)	C4	C5	1.425(3)
C5	C6	1.363(5)	C6	C7	1.413(5)
C7	C8	1.427(5)	C7	C12	1.426(3)
C8	C9	1.335(6)	C9	C10	1.396(5)
C10	C11	1.371(4)	C11	C12	1.411(4)
C13	C14	1.382(4)	C13	C18	1.394(3)
C14	C15	1.388(4)	C15	C16	1.383(3)
C16	C17	1.384(4)	C16	C19	1.509(4)
C17	C18	1.381(4)			

Table S4. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C3	S1	C4	104.34(12)	O1	S2	O2	119.94(11)
O1	S2	N1	107.26(9)	O1	S2	C13	106.61(10)
O2	S2	N1	105.76(9)	O2	S2	C13	108.82(11)
N1	S2	C13	107.96(9)	S2	N1	C1	116.68(12)
S2	N1	C2	117.96(13)	C1	N1	C2	114.23(15)
N1	C1	C4	119.64(18)	N1	C1	C12	119.79(18)
C4	C1	C12	120.53(17)	N1	C2	C3	113.94(18)
S1	C3	C2	113.12(17)	S1	C4	C1	124.88(15)
S1	C4	C5	115.6(2)	C1	C4	C5	119.5(3)

C4	C5	C6	120.6(3)	C5	C6	C7
	121.3(3)					
C6	C7	C8	122.6(3)	C6	C7	C12
	118.9(3)					
C8	C7	C12	118.5(3)	C7	C8	C9
	121.6(3)					
C8	C9	C10	120.2(3)	C9	C10	C11
	120.7(4)					
C10	C11	C12	121.0(3)	C1	C12	C7
	118.9(2)					
C1	C12	C11	123.28(17)	C7	C12	C11
	117.8(2)					
S2	C13	C14	119.98(14)	S2	C13	C18
	119.96(17)					
C14	C13	C18	120.1(2)	C13	C14	C15
	119.76(19)					
C14	C15	C16	121.1(3)	C15	C16	C17
	118.1(3)					
C15	C16	C19	120.8(3)	C17	C16	C19
	121.07(19)					
C16	C17	C18	122.05(18)	C13	C18	C17
	118.9(2)					

Copies of NMR spectra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S
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Ts
N
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2
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
1.96
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1.71
3.00
144.26
134.89
129.64
127.80
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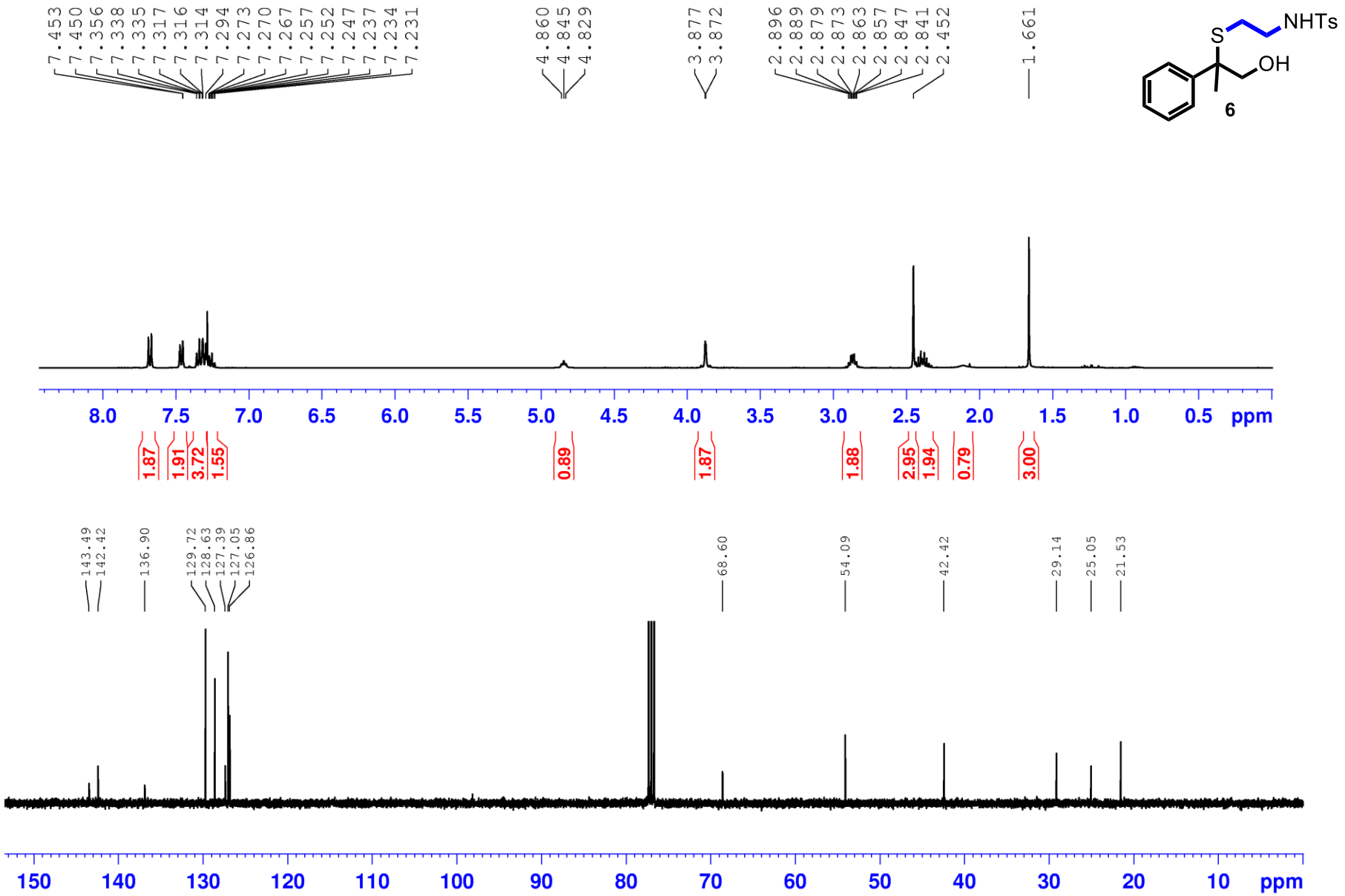
20
10
ppm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7.257
7.252
7.247
7.237
7.234
7.231
4.860
4.845
4.829
3.877
3.872
2.896
2.889
2.879
2.873
2.863
2.857
2.847
2.841
2.452
1.661
NHTs
S
OH
6
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.91
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1.55
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1.87
1.88
2.95
1.94
0.79
3.00
143.49
142.42
136.90
129.72
128.63
127.39
127.05
126.86
68.60
54.09
42.42
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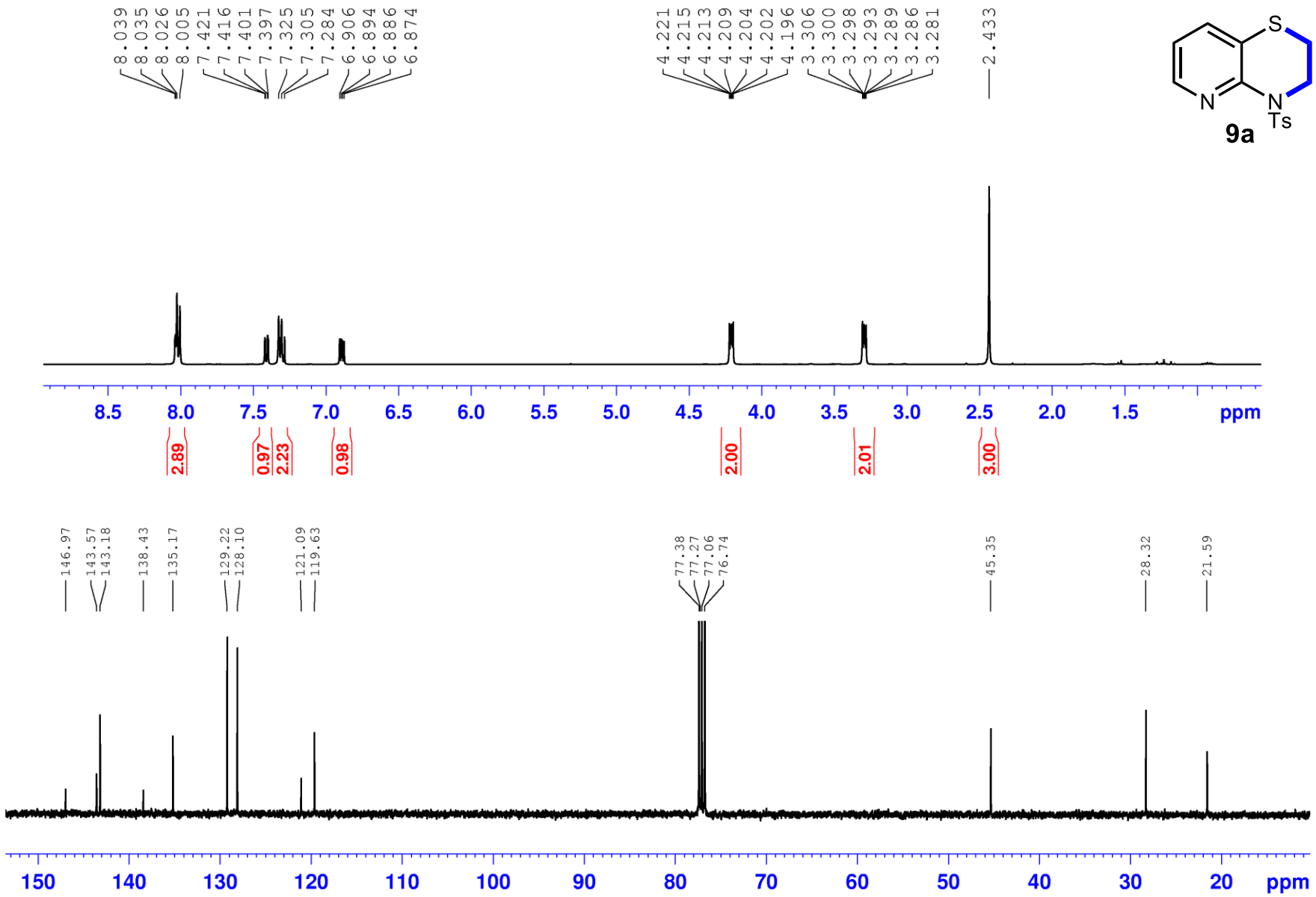
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7.397
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6.894
6.886
6.874
4.221
4.215
4.213
4.209
4.204
4.202
4.196
3.306
3.300
3.298
3.293
3.289
3.286
3.281
2.433
S
N
N
Ts
9a
8.5
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4.0
3.5
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3.00
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129.22
128.10
121.09
119.63
77.38
77.27
77.06
76.74
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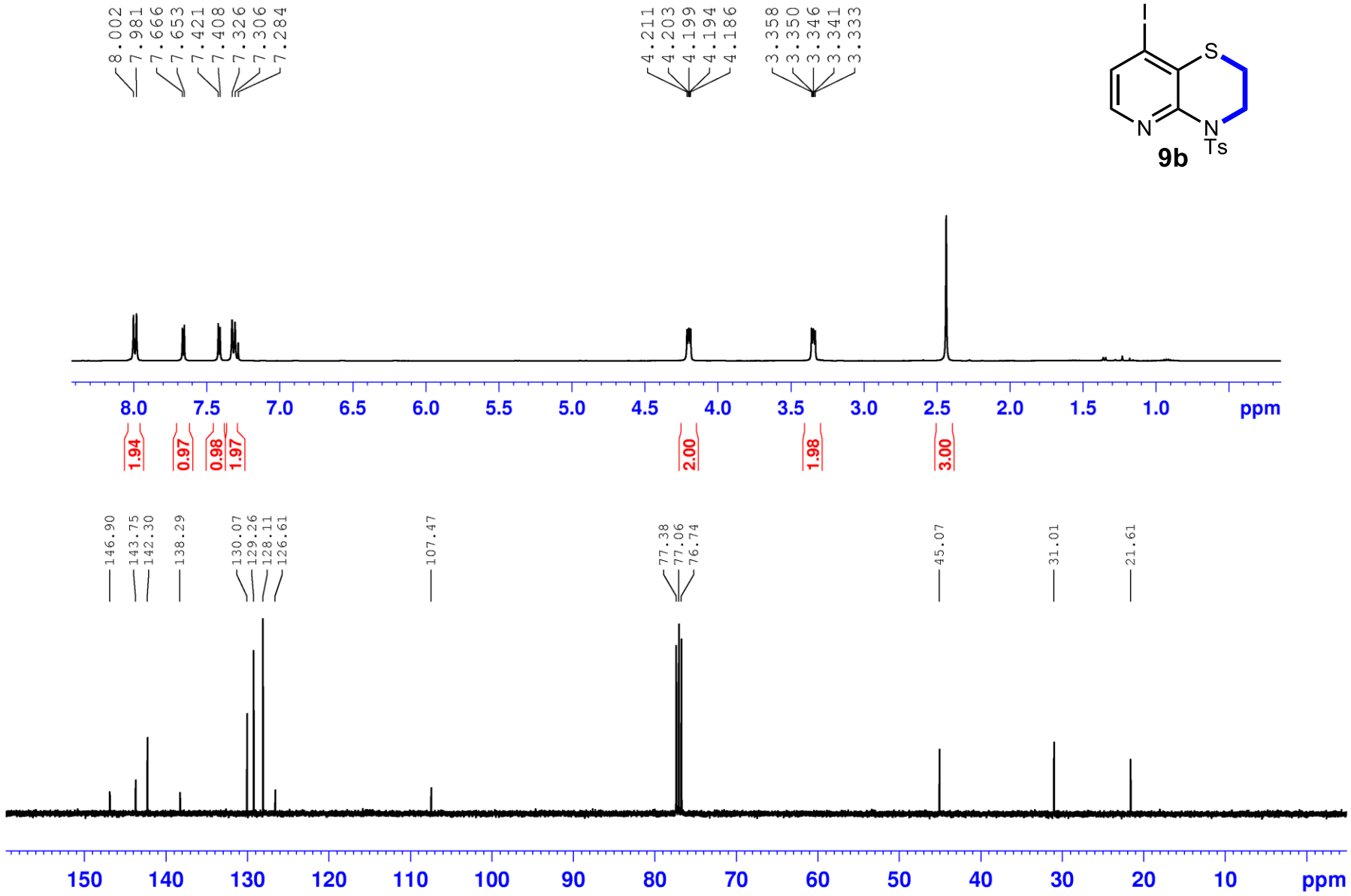
ppm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4.194
4.186
3.358
3.350
3.346
3.341
3.333
I
S
N
N
Ts
9b
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.00
1.98
3.00
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138.29
130.07
129.26
128.11
126.61
107.47
77.38
77.06
76.74
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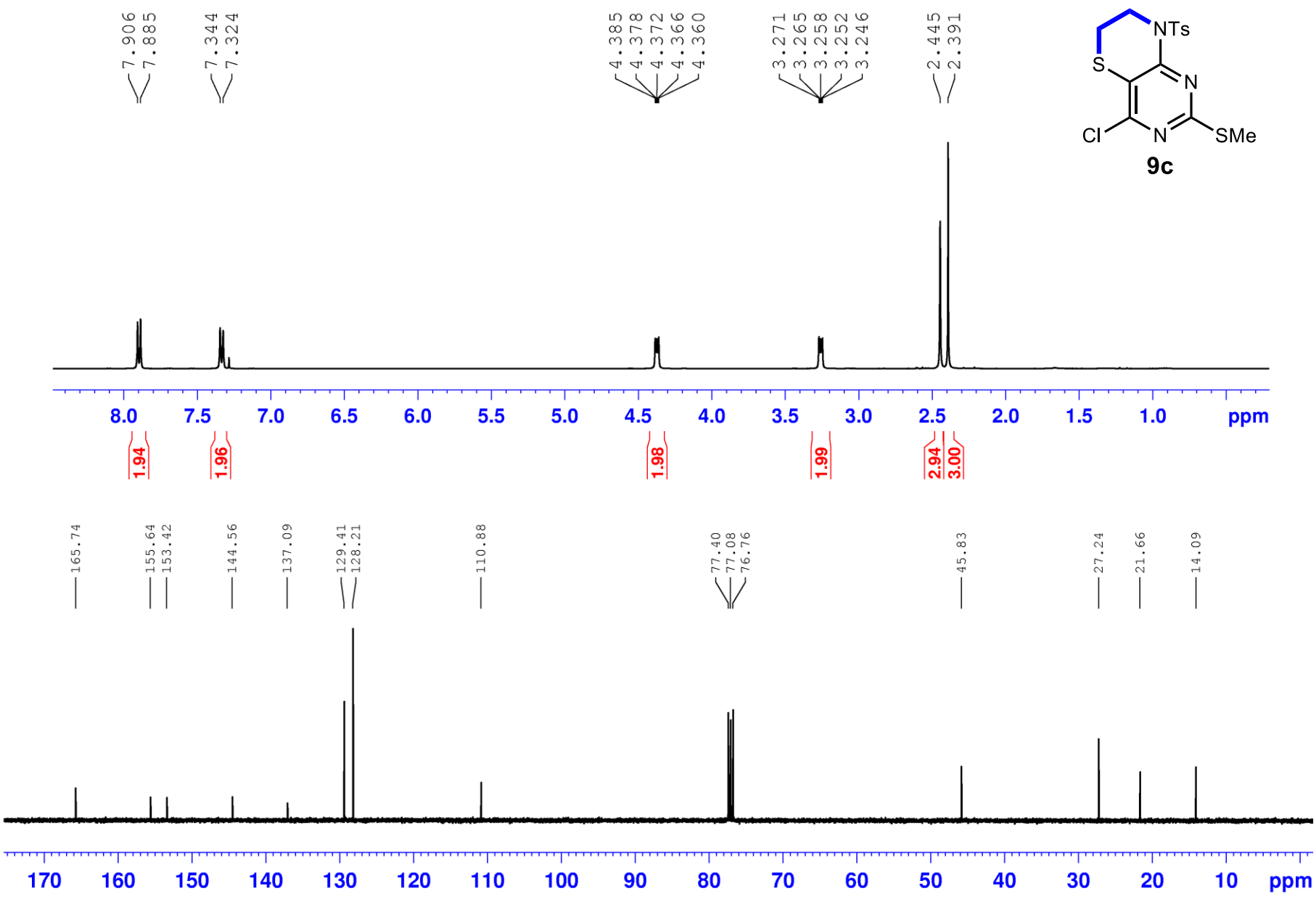
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3.246
2.445
2.391
NTs
S
N
Cl
N
SMe
9c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.94
1.96
1.98
1.99
2.94
3.00
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155.64
153.42
144.56
137.09
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128.21
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77.08
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21.66
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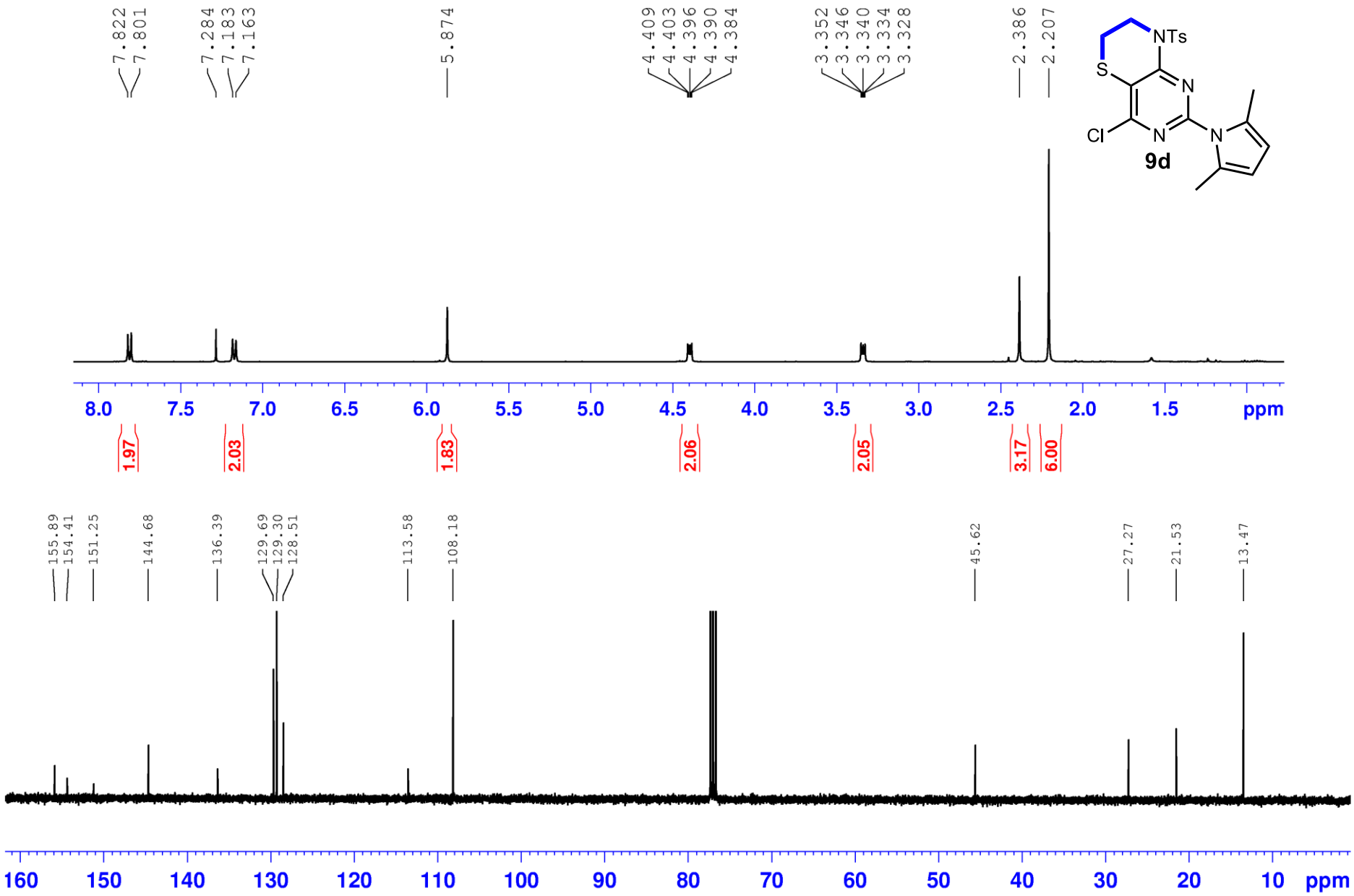
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3.340
3.334
3.328
2.386
2.207
NTs
S
N
Cl
N
N
9d
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4.0
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3.0
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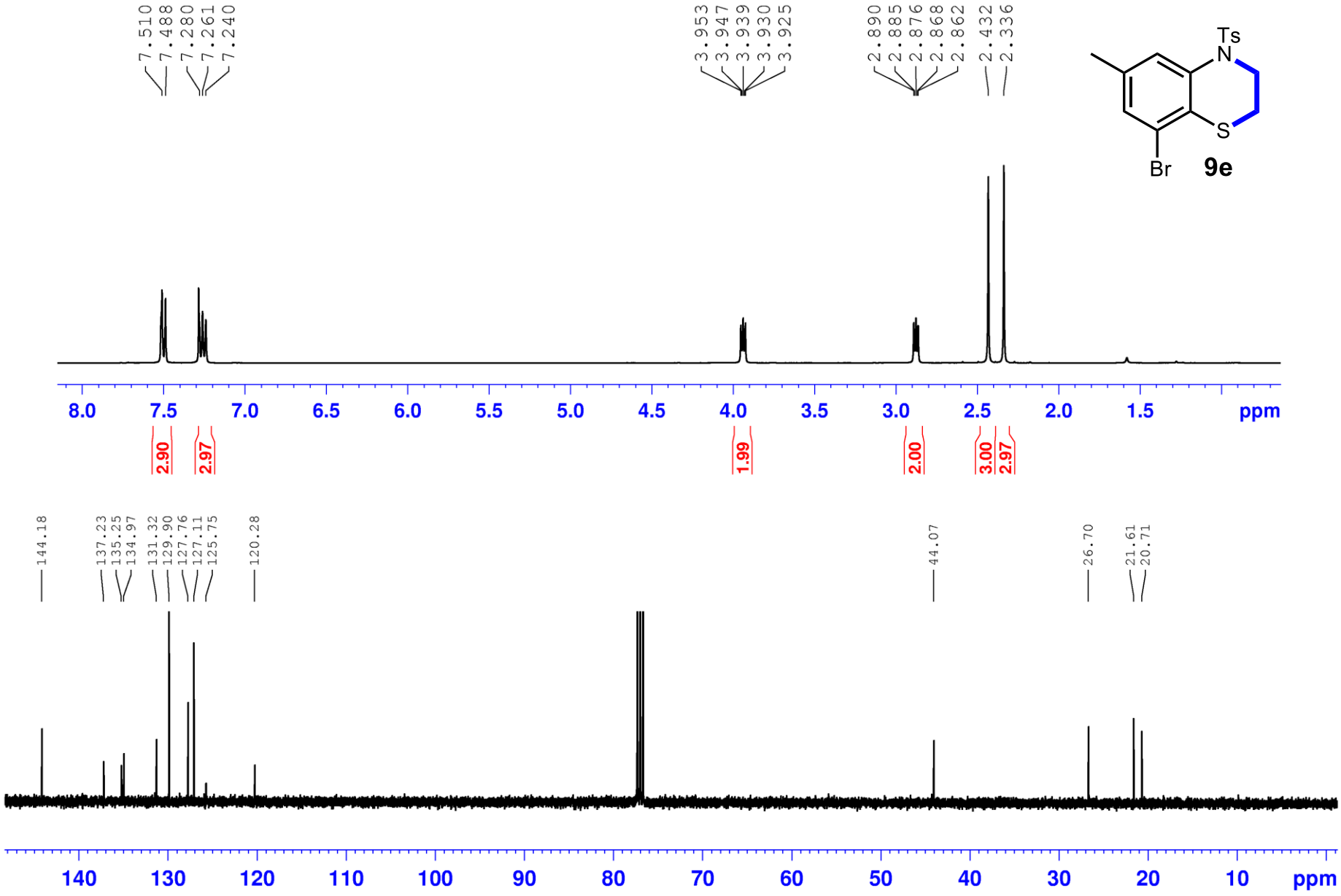
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2.336
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S
Br
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7.0
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6.0
5.5
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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2.97
1.99
2.00
3.00
2.97
144.18
137.23
135.25
134.97
131.32
129.90
127.76
127.11
125.75
120.28
44.07
26.70
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140
130
120
110
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70
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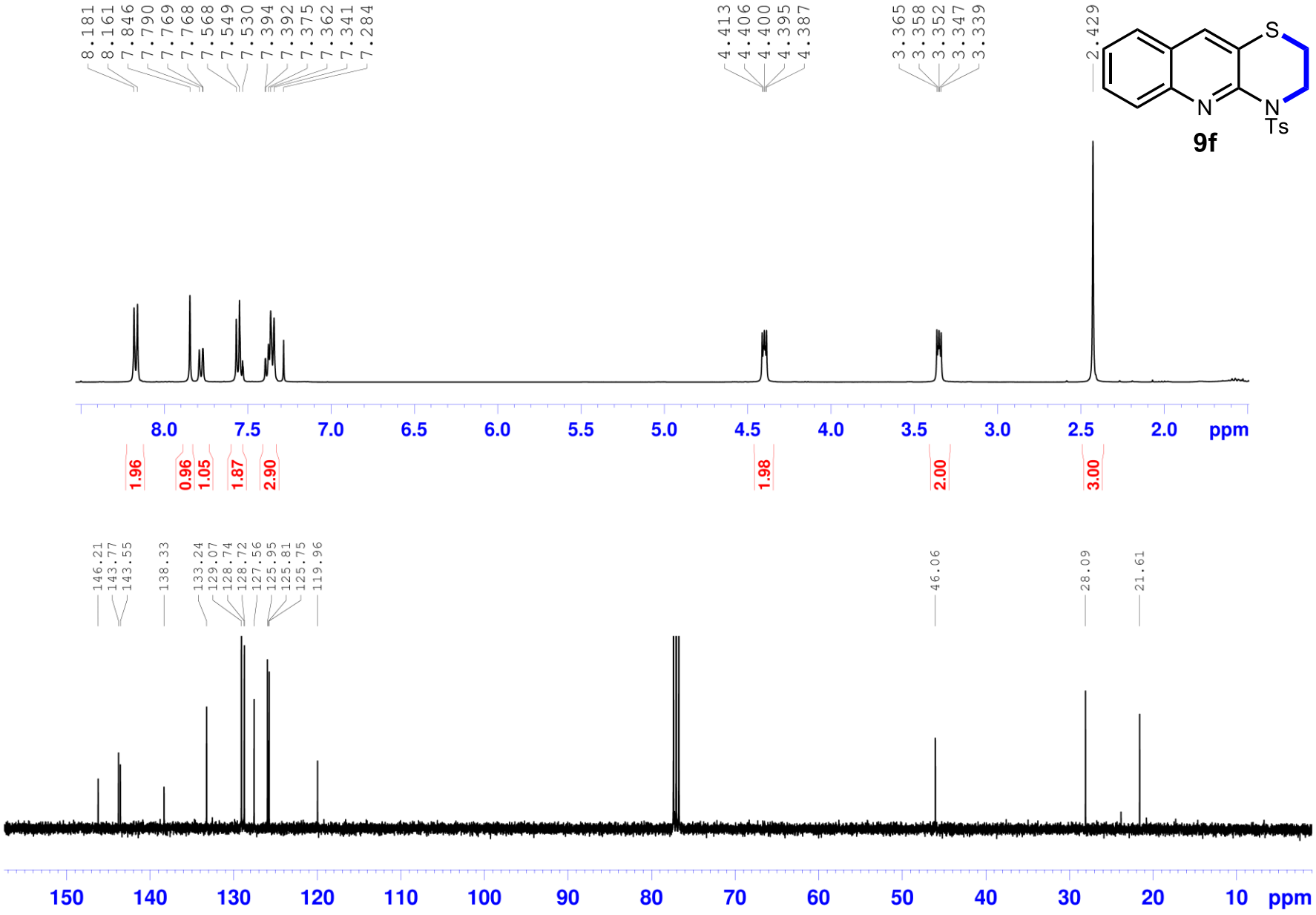
10
ppm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7.341
7.284
4.413
4.406
4.400
4.395
4.387
3.365
3.358
3.352
3.347
3.339
2.429
S
N
N
Ts
9f
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
ppm
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0.96
1.05
1.87
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1.98
2.00
3.00
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143.55
138.33
133.24
129.07
128.74
128.72
127.56
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20
10
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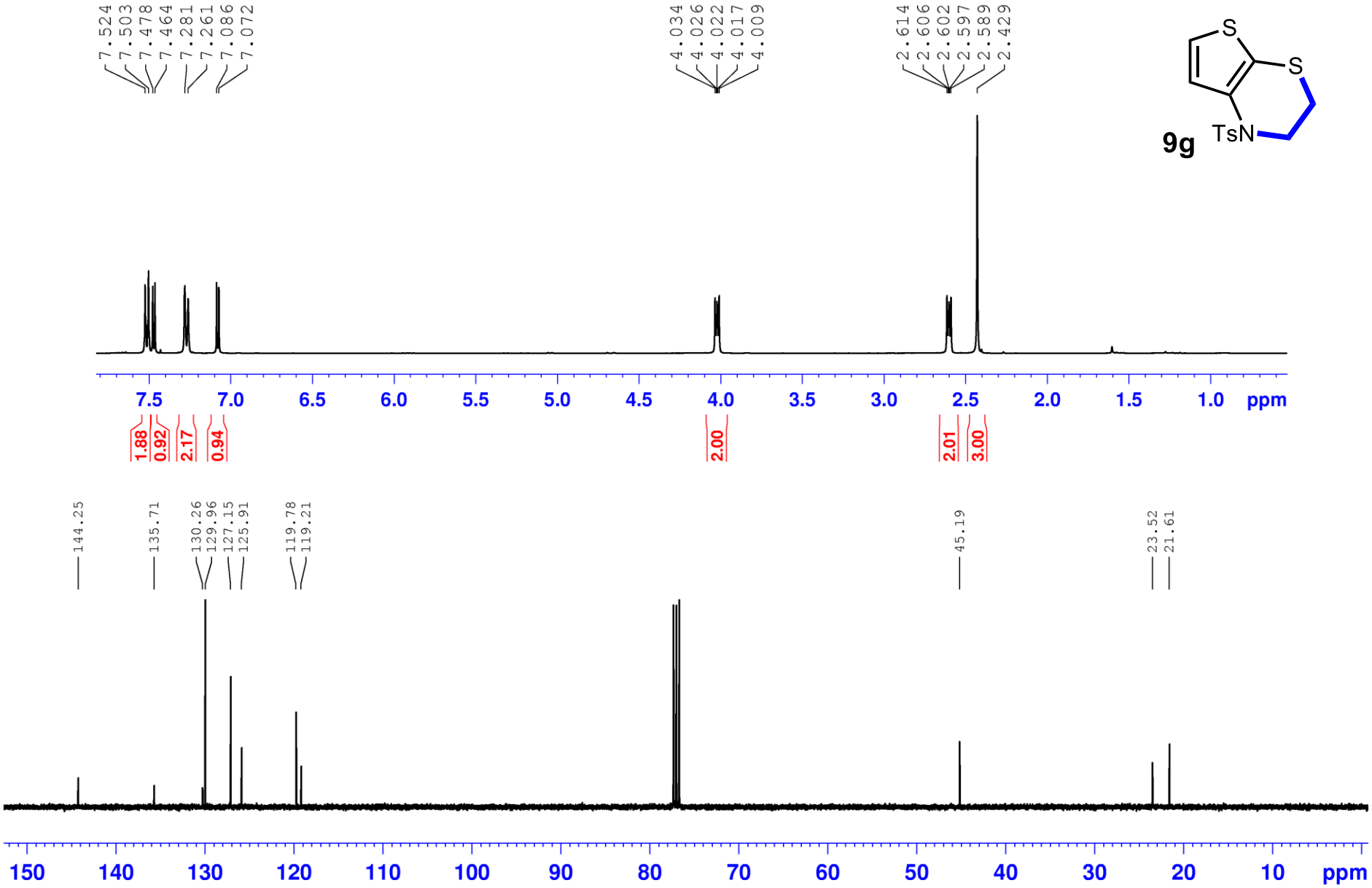
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2.606
2.602
2.597
2.589
2.429
S
S
TsN
9g
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.17
0.94
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2.01
3.00
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127.15
125.91
119.78
119.21
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50
40
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20
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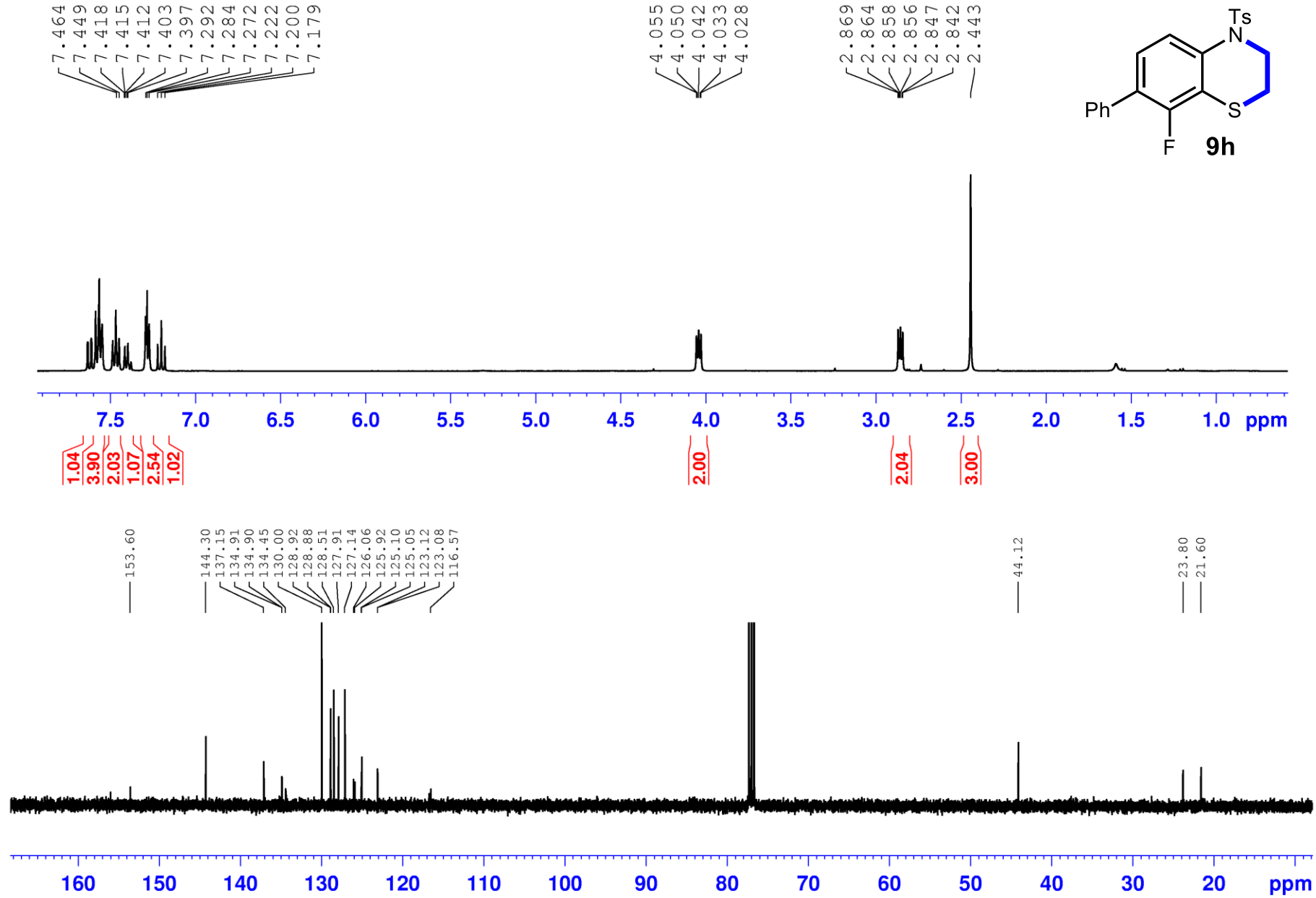
ppm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4.055
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4.033
4.028
2.869
2.864
2.858
2.856
2.847
2.842
2.443
Ts
N
Ph
S
F
9h
7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.04
3.90
2.03
1.07
2.54
1.02
2.00
2.04
3.00
153.60
144.30
137.15
134.91
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127.14
126.06
125.92
125.10
125.05
123.12
123.08
116.57
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80
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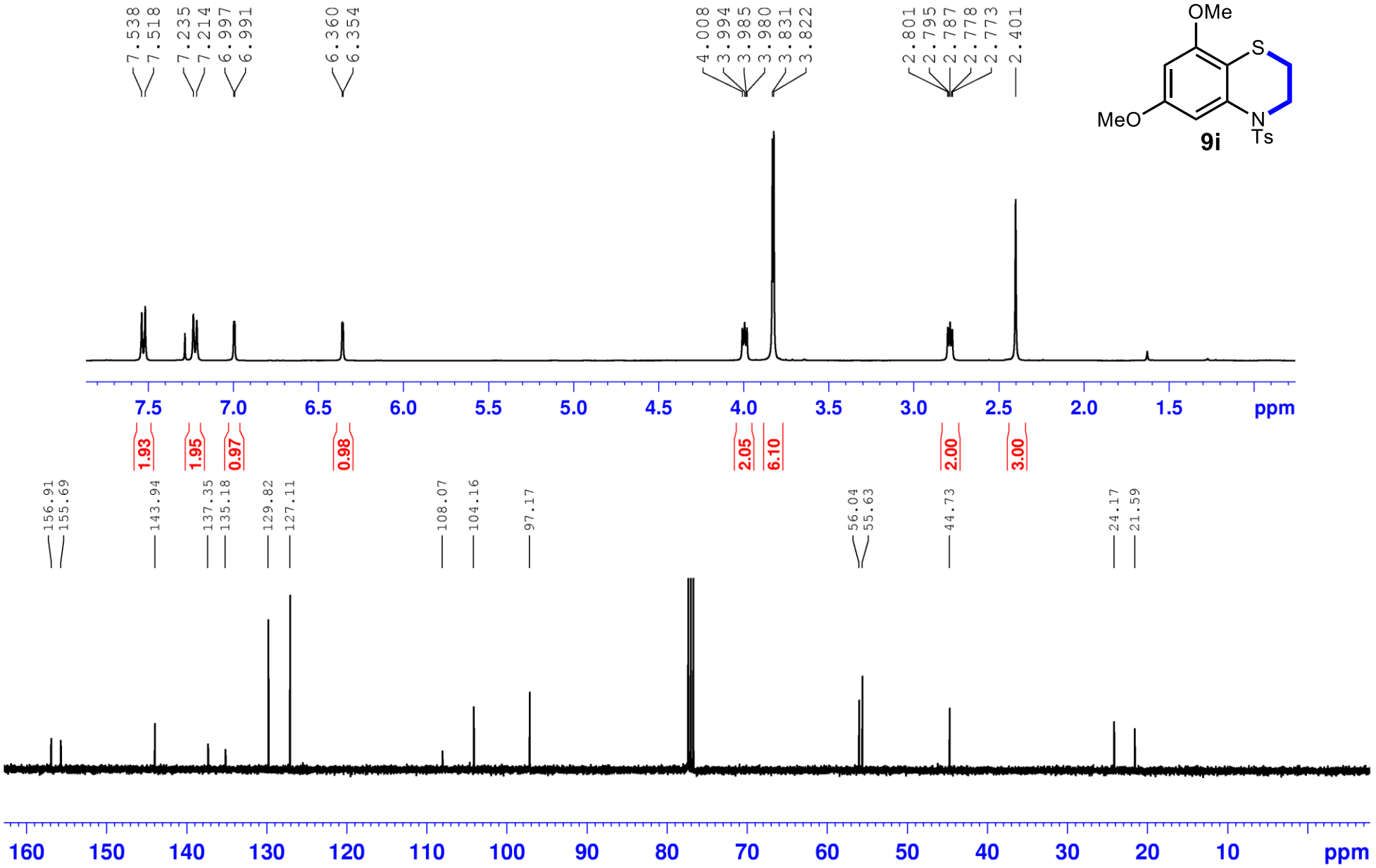
50
40
30
20
ppm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3.831
3.822
2.801
2.795
2.787
2.778
2.773
2.401
OMe
MeO
S
N
Ts
9i
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
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1.95
0.97
0.98
2.05
6.10
2.00
3.00
156.91
155.69
143.94
137.35
135.18
129.82
127.11
108.07
104.16
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56.04
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44.73
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150
140
130
120
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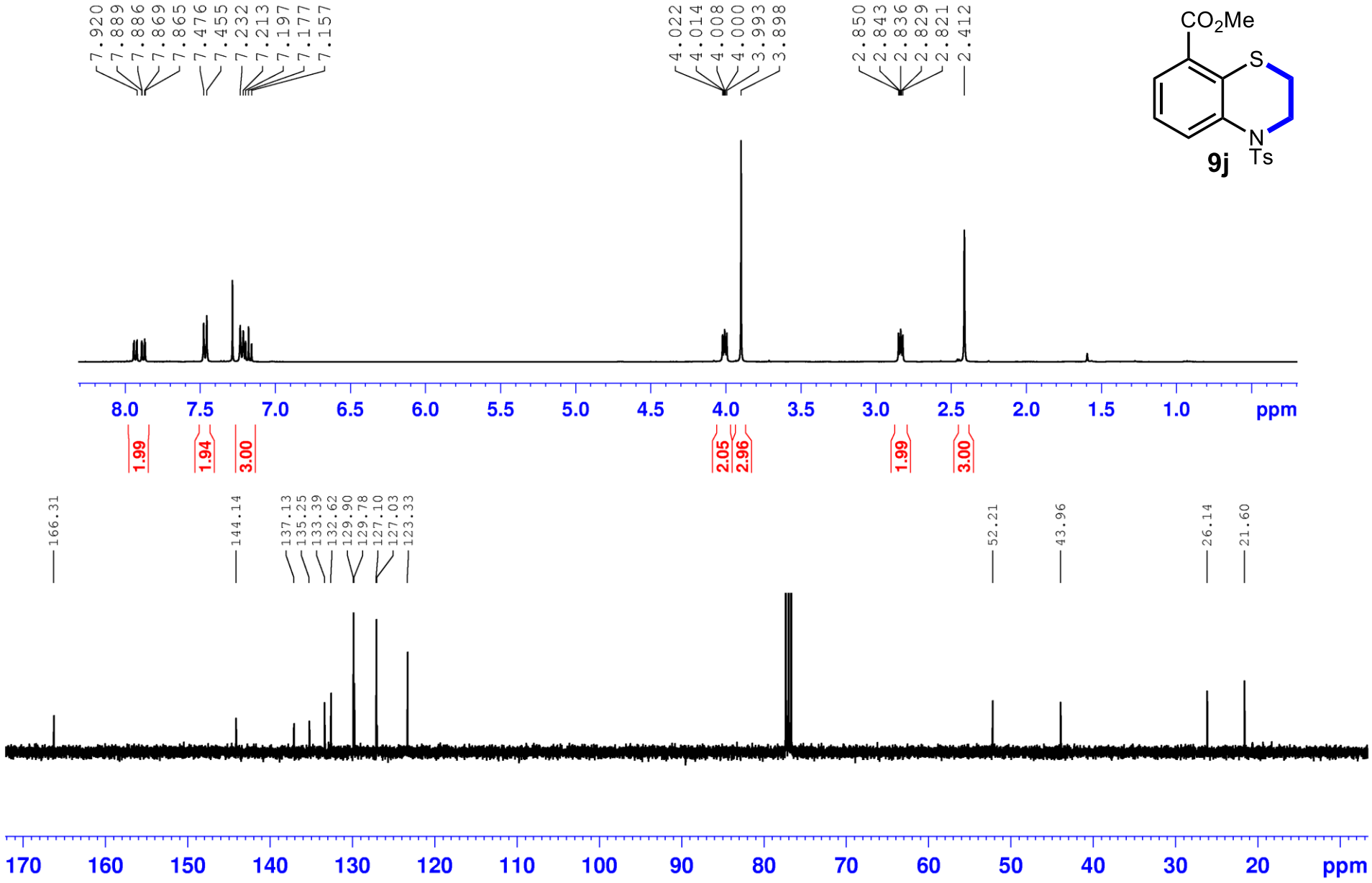
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4.022
4.014
4.008
4.000
3.993
3.898
2.850
2.843
2.836
2.829
2.821
2.412
CO2Me
S
N
Ts
9j
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.94
3.00
2.05
2.96
1.99
3.00
166.31
144.14
137.13
135.25
133.39
132.62
129.90
129.78
127.10
127.03
123.33
52.21
43.96
26.14
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80
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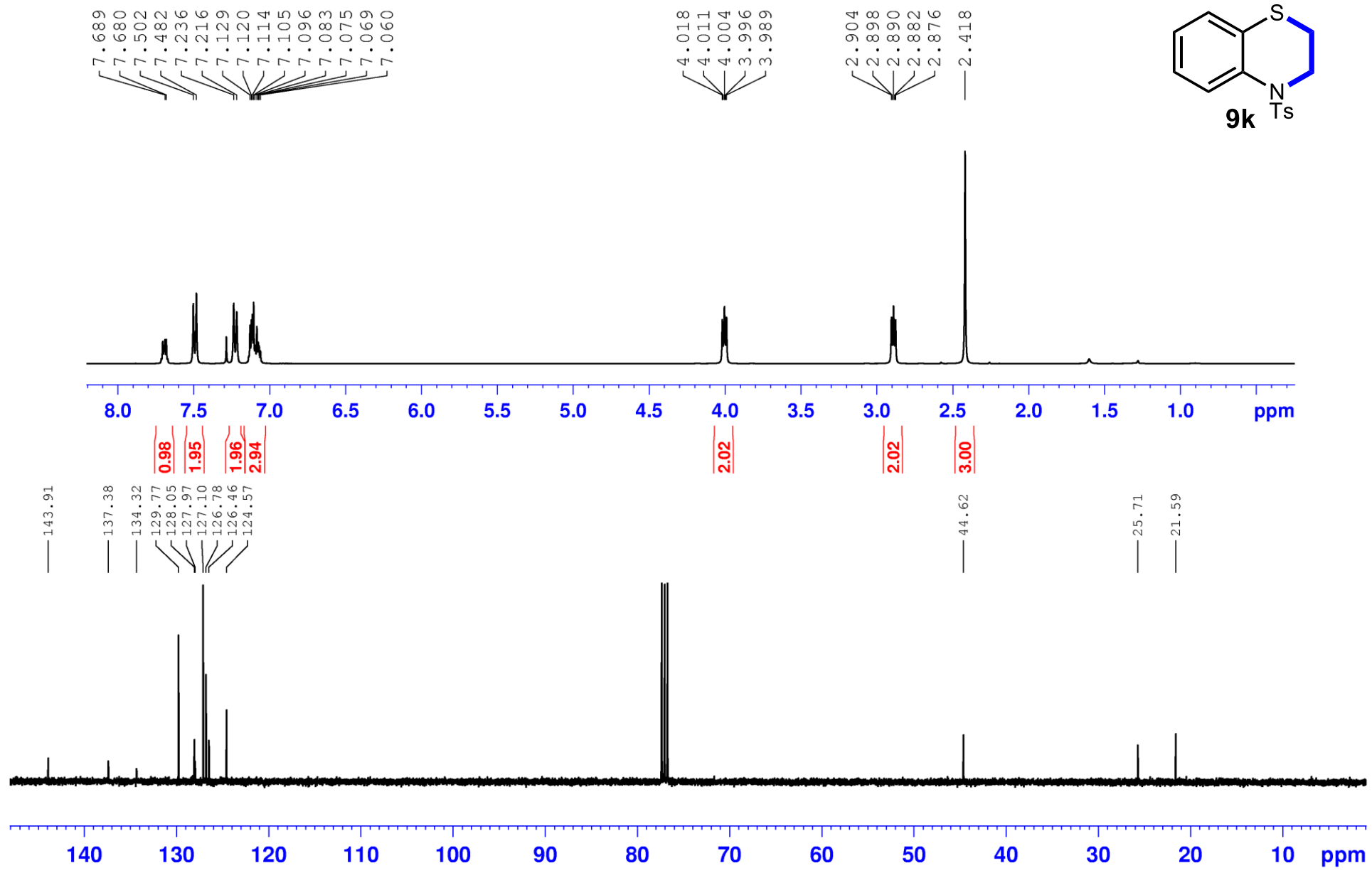
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4.011
4.004
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N
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6.0
5.5
5.0
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4.0
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3.0
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2.0
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ppm
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2.02
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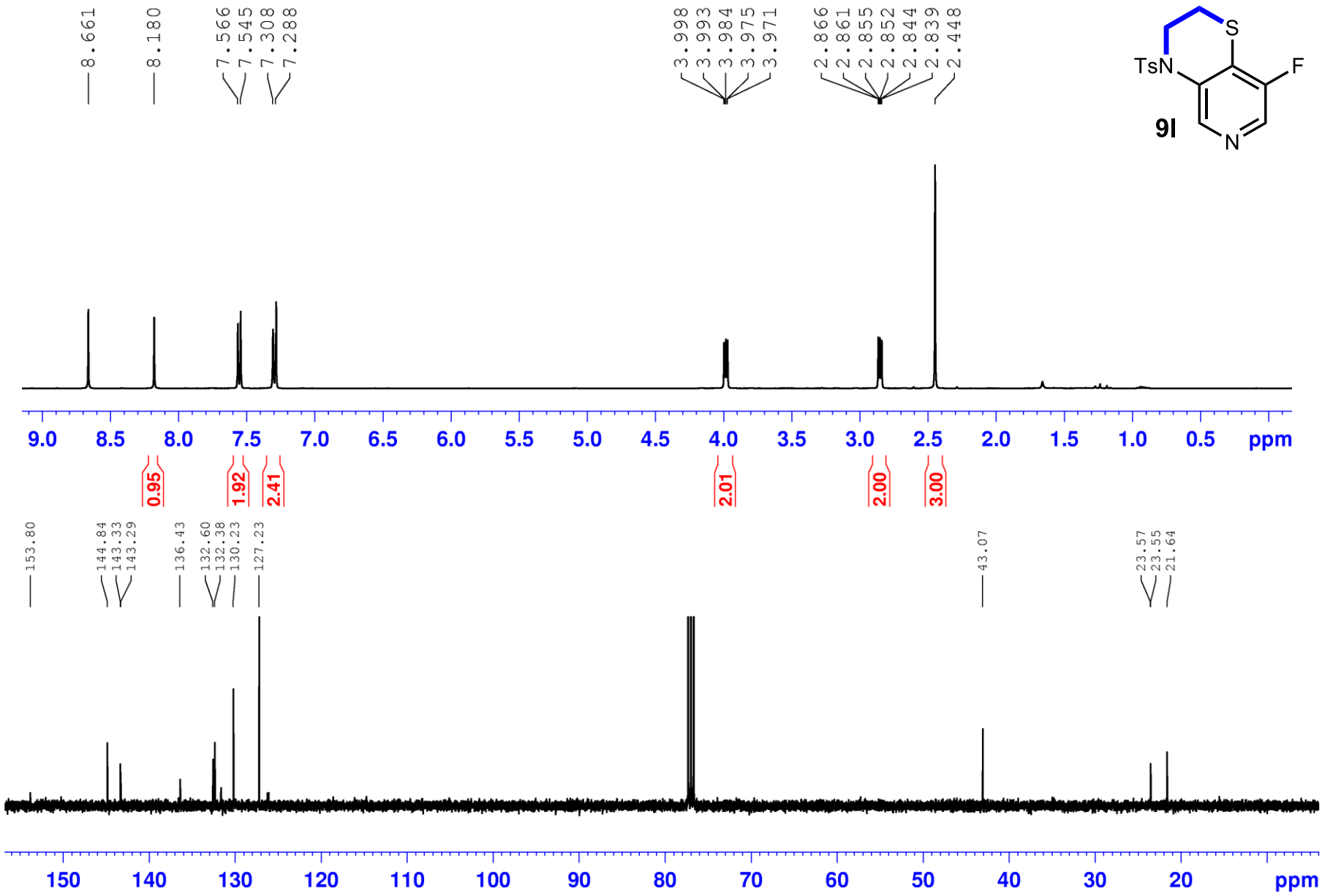
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3.975
3.971
2.866
2.861
2.855
2.852
2.844
2.839
2.448
TsN
S
F
N
9l
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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1.92
2.41
2.01
2.00
3.00
153.80
144.84
143.33
143.29
136.43
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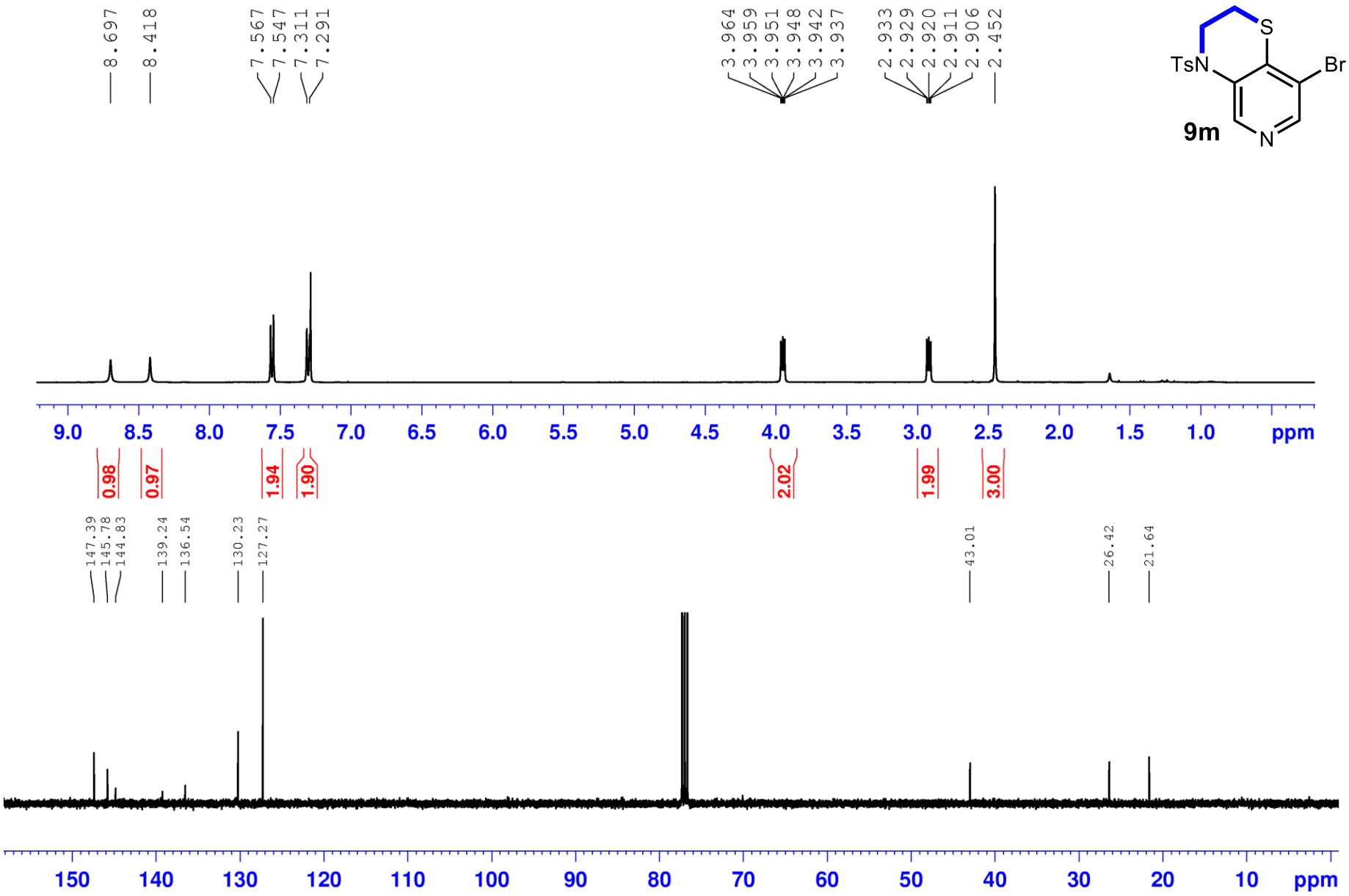
130.23
127.23
43.07
23.57
23.55
21.64
150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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3.937
2.933
2.929
2.920
2.911
2.906
2.452
TsN
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Br
N
9m
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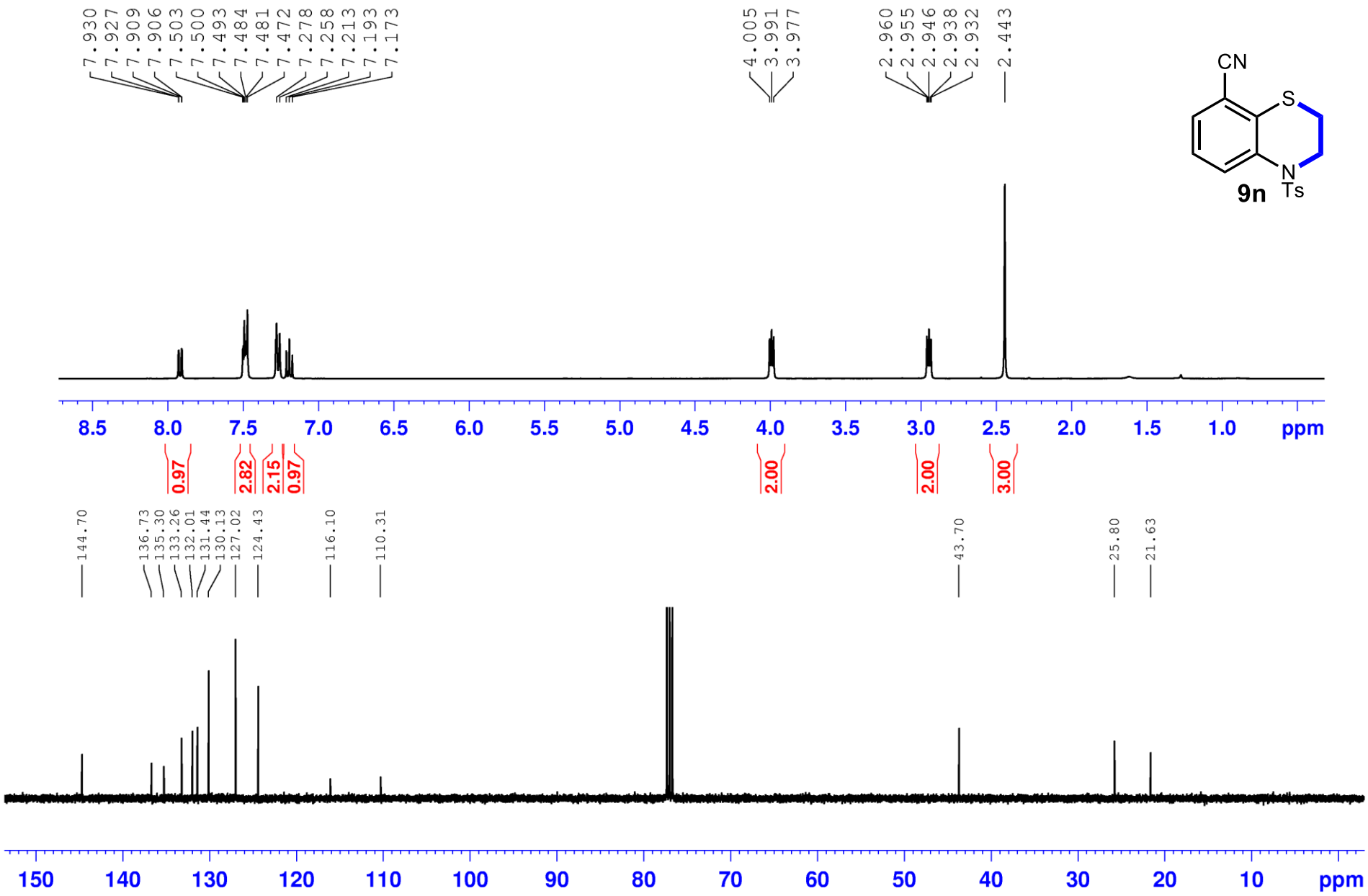
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.98
0.97
1.94
1.90
2.02
1.99
3.00
147.39
145.78
144.83
139.24
136.54
130.23
127.27
43.01
26.42
21.64
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.193
7.173
4.005
3.991
3.977
2.960
2.955
2.946
2.938
2.932
2.443
CN
S
N
Ts
9n
8.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.00
3.00
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133.26
132.01
131.44
130.13
127.02
124.43
116.10
110.31
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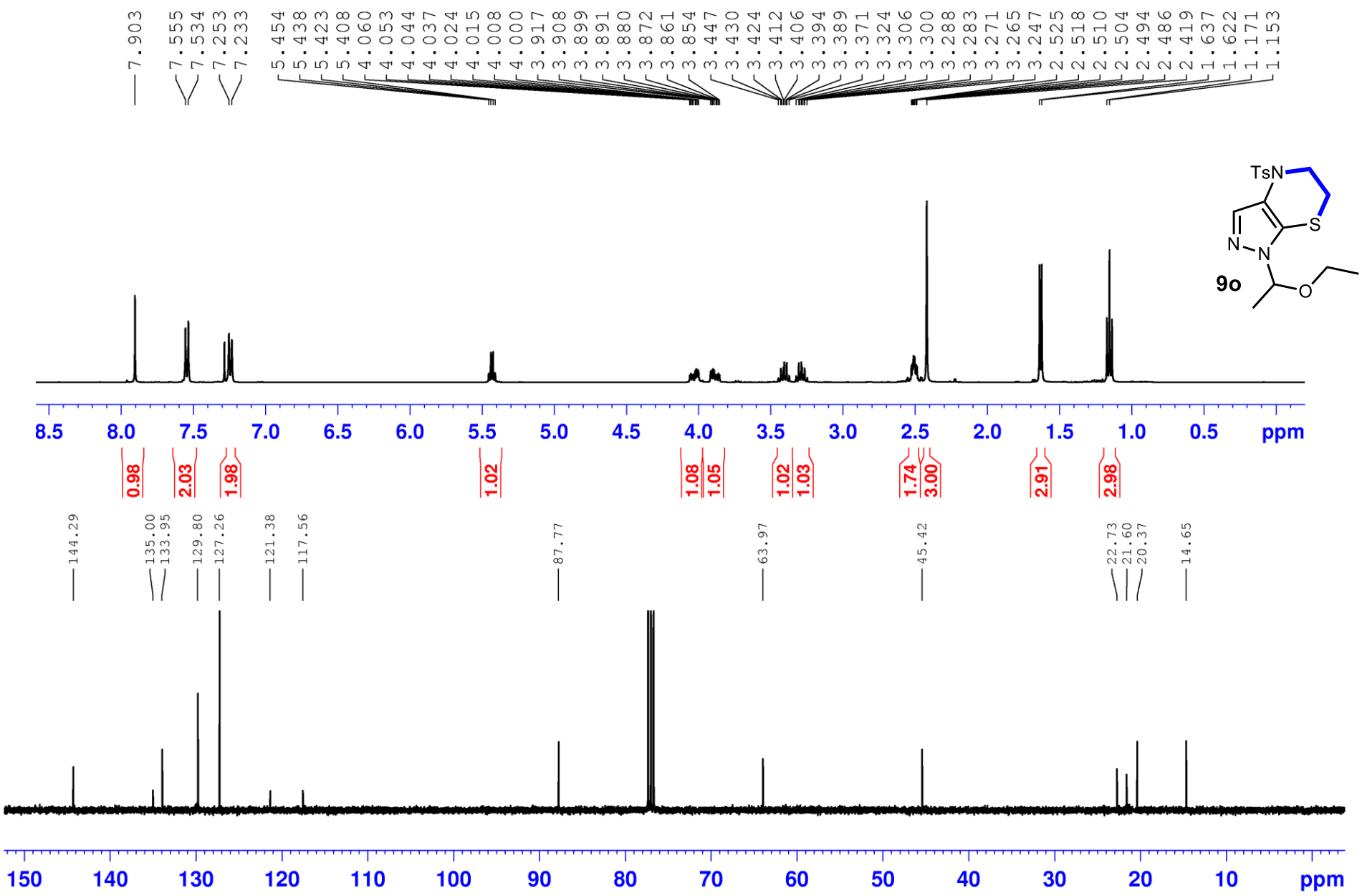
10
ppm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4.024
4.015
4.008
4.000
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3.908
3.899
3.891
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3.872
3.861
3.854
3.447
3.430
3.424
3.412
3.406
3.394
3.389
3.371
3.324
3.306
3.300
3.288
3.283
3.271
3.265
3.247
2.525
2.518
2.510
2.504
2.494
2.486
2.419
1.637
1.622
1.171
1.153
TsN
S
N
N
O
9o
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5.0
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1.08
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1.02
1.03
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135.00
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121.38
117.56
87.77
63.97
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22.73
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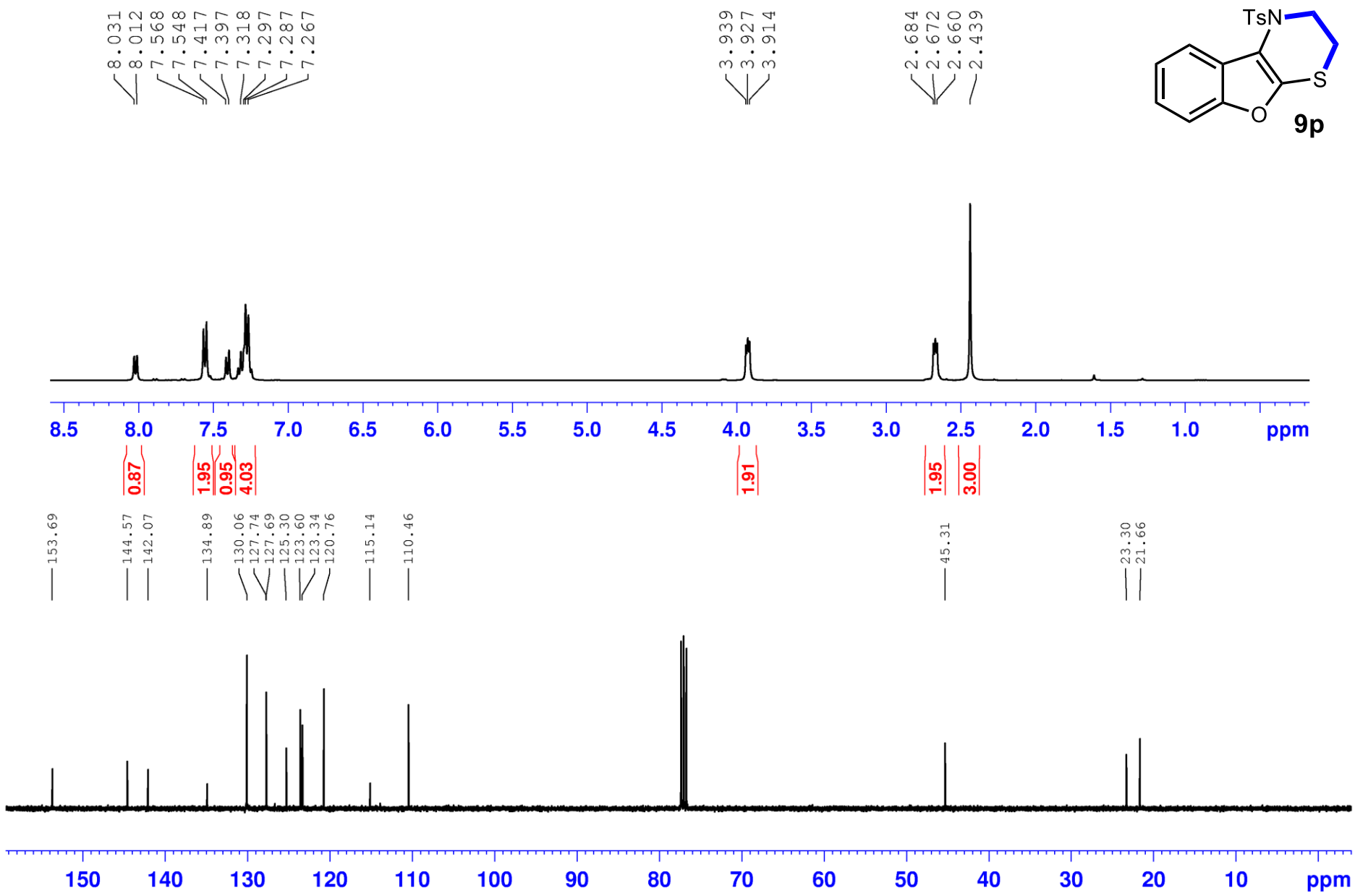
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3.927
3.914
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2.672
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2.439
TsN
S
O
9p
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3.0
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ppm
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1.95
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127.69
125.30
123.60
123.34
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110.46
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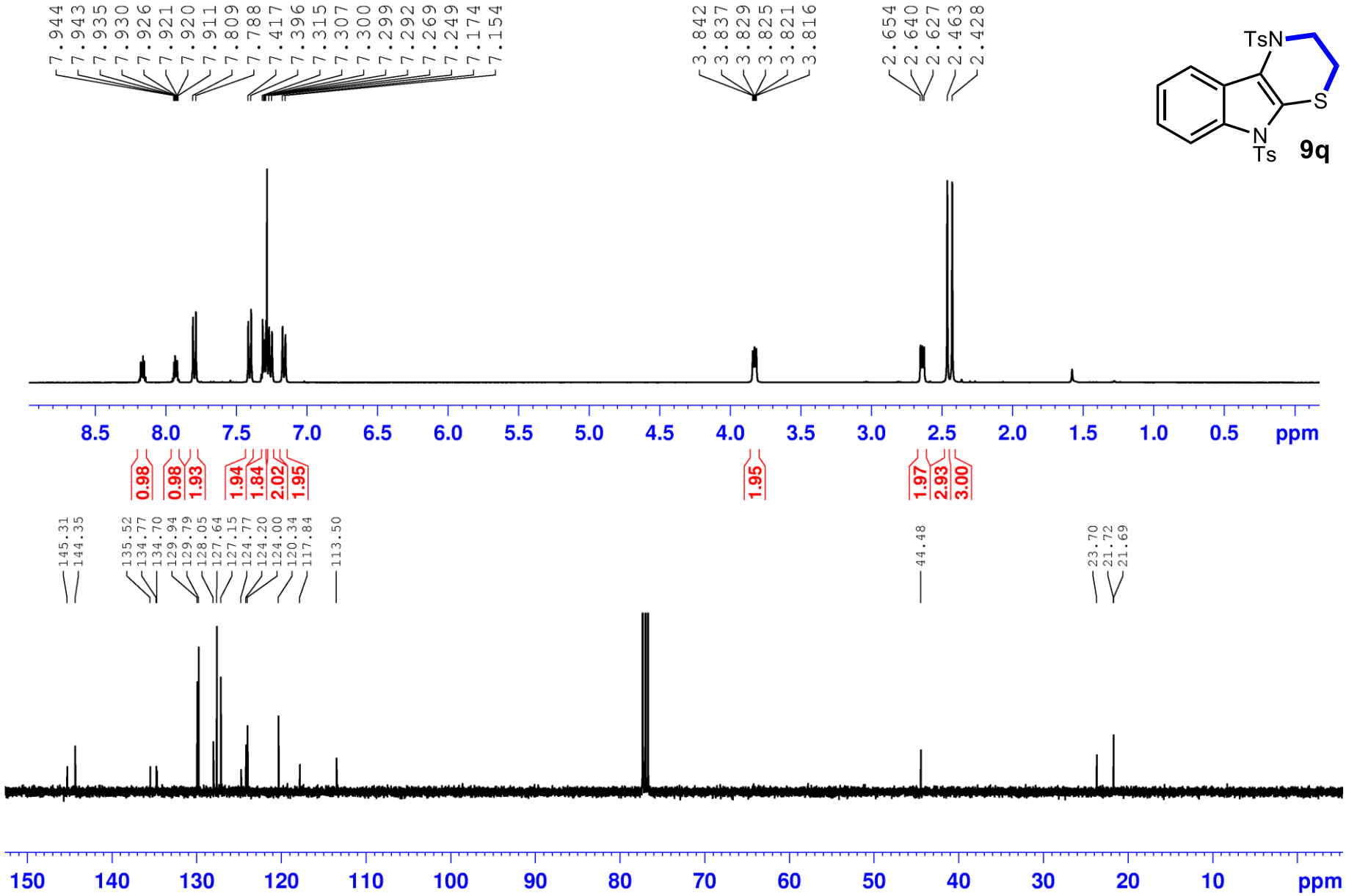
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7.396
7.315
7.307
7.300
7.299
7.292
7.269
7.249
7.174
7.154
3.842
3.837
3.829
3.825
3.821
3.816
2.654
2.640
2.627
2.463
2.428
TsN
S
N
Ts
9q
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98
0.98
1.93
1.94
1.84
2.02
1.95
1.95
1.97
2.93
3.00
145.31
144.35
135.52
134.77
134.70
129.94
129.79
128.05
127.64
127.15
124.77
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117.84
113.50
44.48
23.70
21.72
21.69
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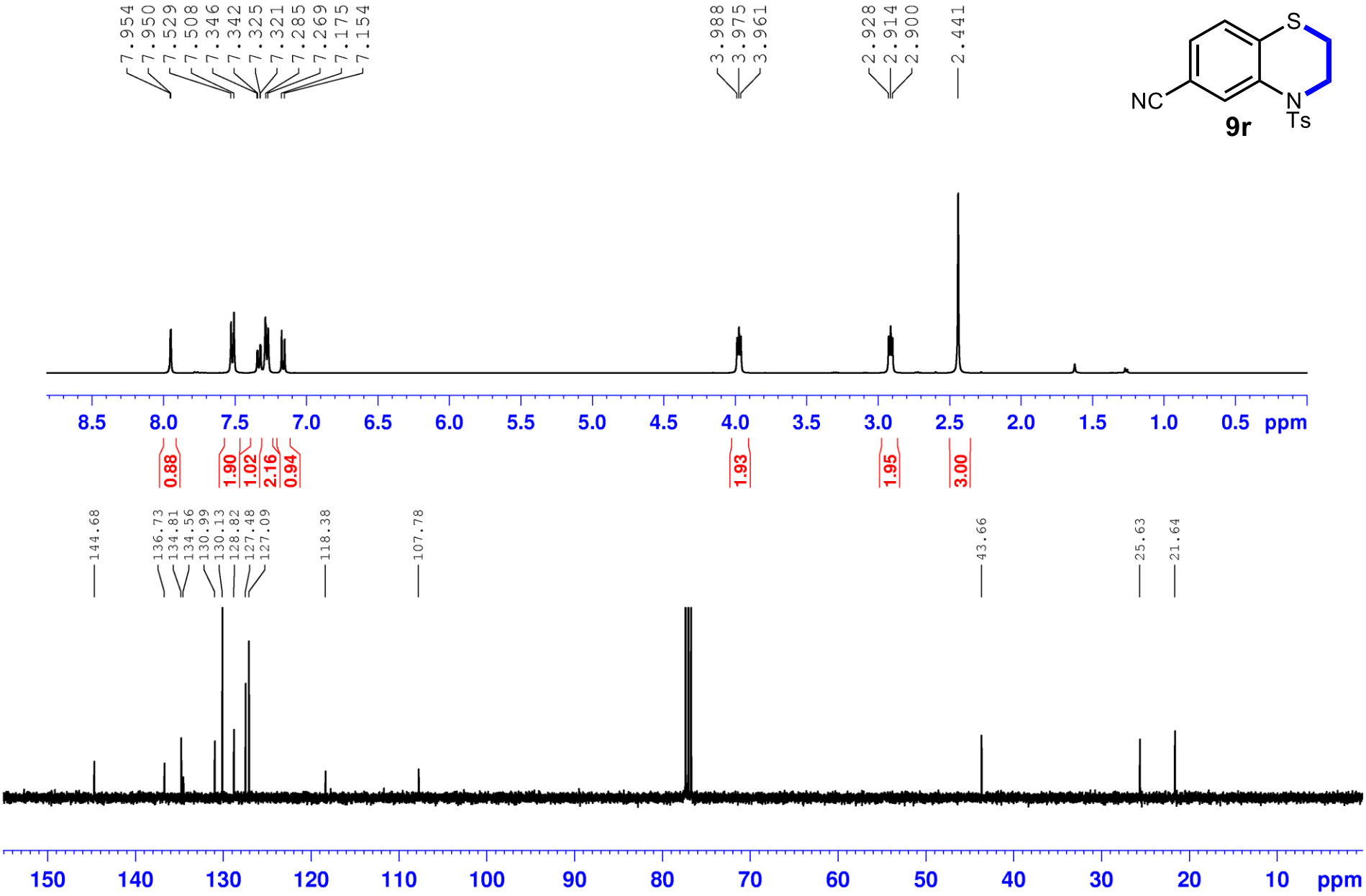
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7.321
7.285
7.269
7.175
7.154
3.988
3.975
3.961
2.928
2.914
2.900
2.441
NC
S
N
Ts
9r
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.02
2.16
0.94
1.93
1.95
3.00
144.68
136.73
134.81
134.56
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130.13
128.82
127.48
127.09
118.38
107.78
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140
130
120
110
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50
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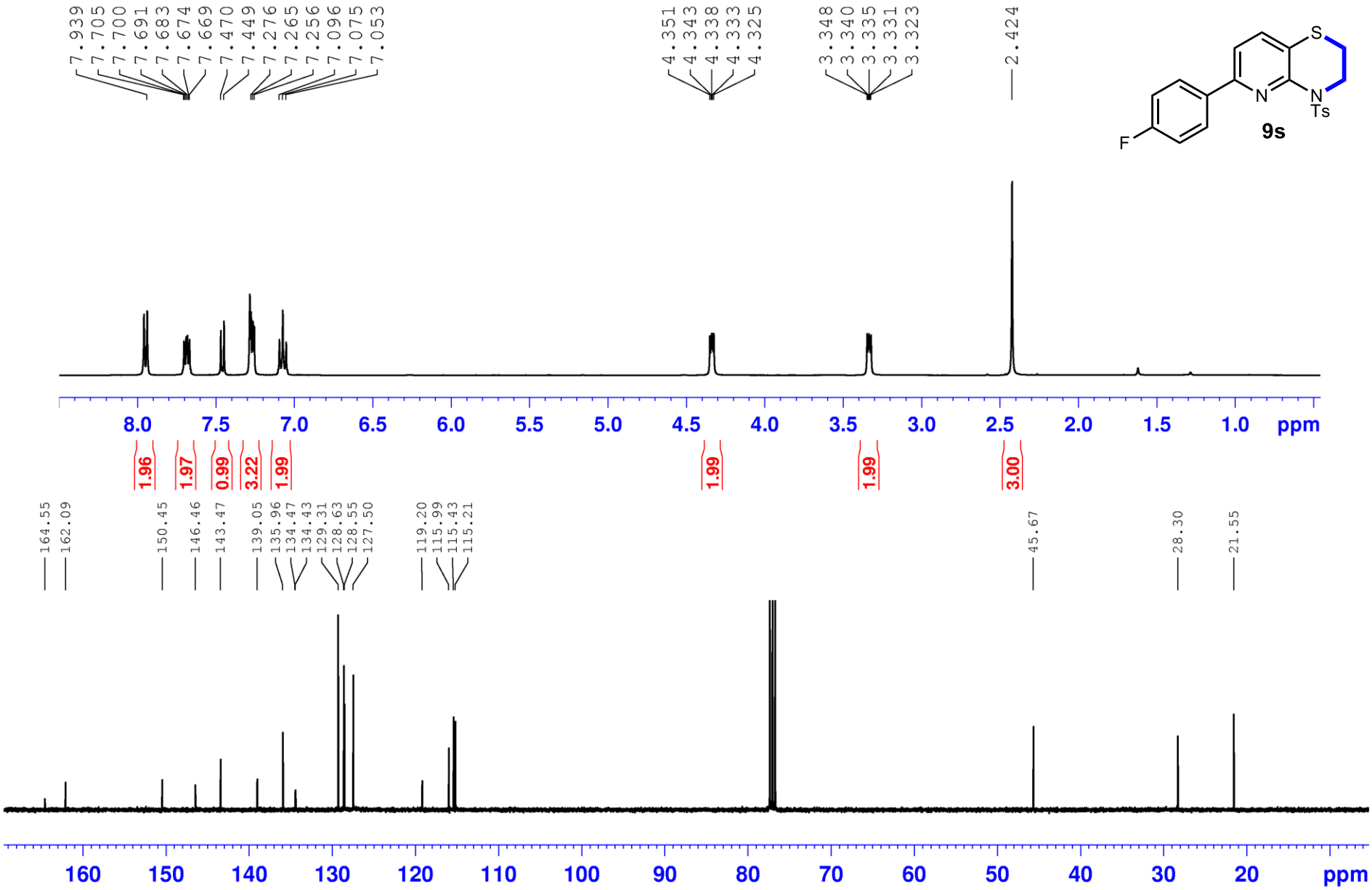
30
20
10
ppm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7.096
7.075
7.053
4.351
4.343
4.338
4.333
4.325
3.348
3.340
3.335
3.331
3.323
2.424
S
N
N
Ts
F
9s
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.97
0.99
3.22
1.99
1.99
1.99
3.00
164.55
162.09
150.45
146.46
143.47
139.05
135.96
134.47
134.43
129.31
128.63
128.55
127.50
119.20
115.99
115.43
115.21
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28.30
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130
120
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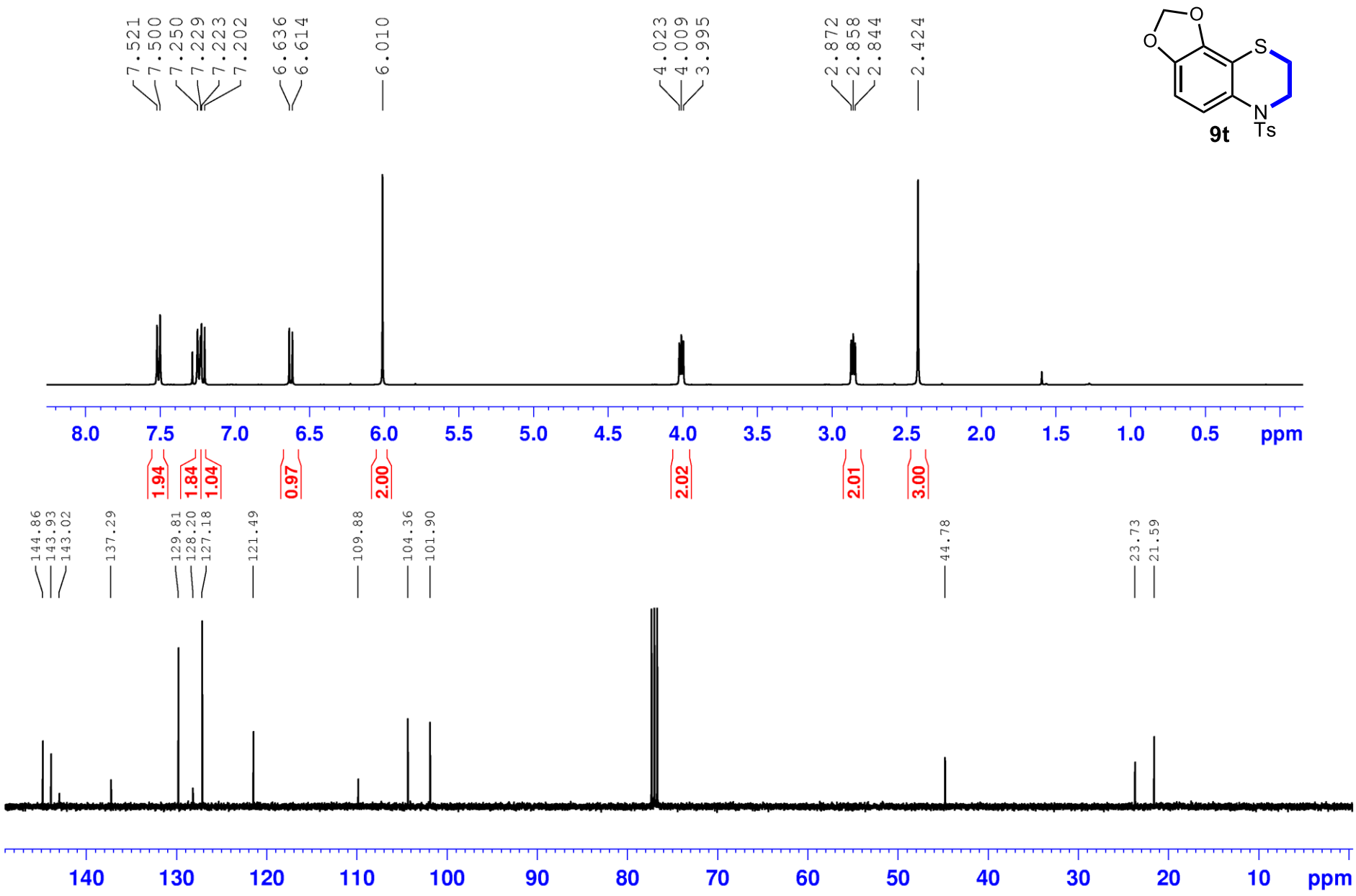
80
70
60
50
40
30
20
ppm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4.009
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2.872
2.858
2.844
2.424
O
O
S
N
Ts
9t
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
1.84
1.04
0.97
2.00
2.02
2.01
3.00
144.86
143.93
143.02
137.29
129.81
128.20
127.18
121.49
109.88
104.36
101.90
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130
120
110
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70
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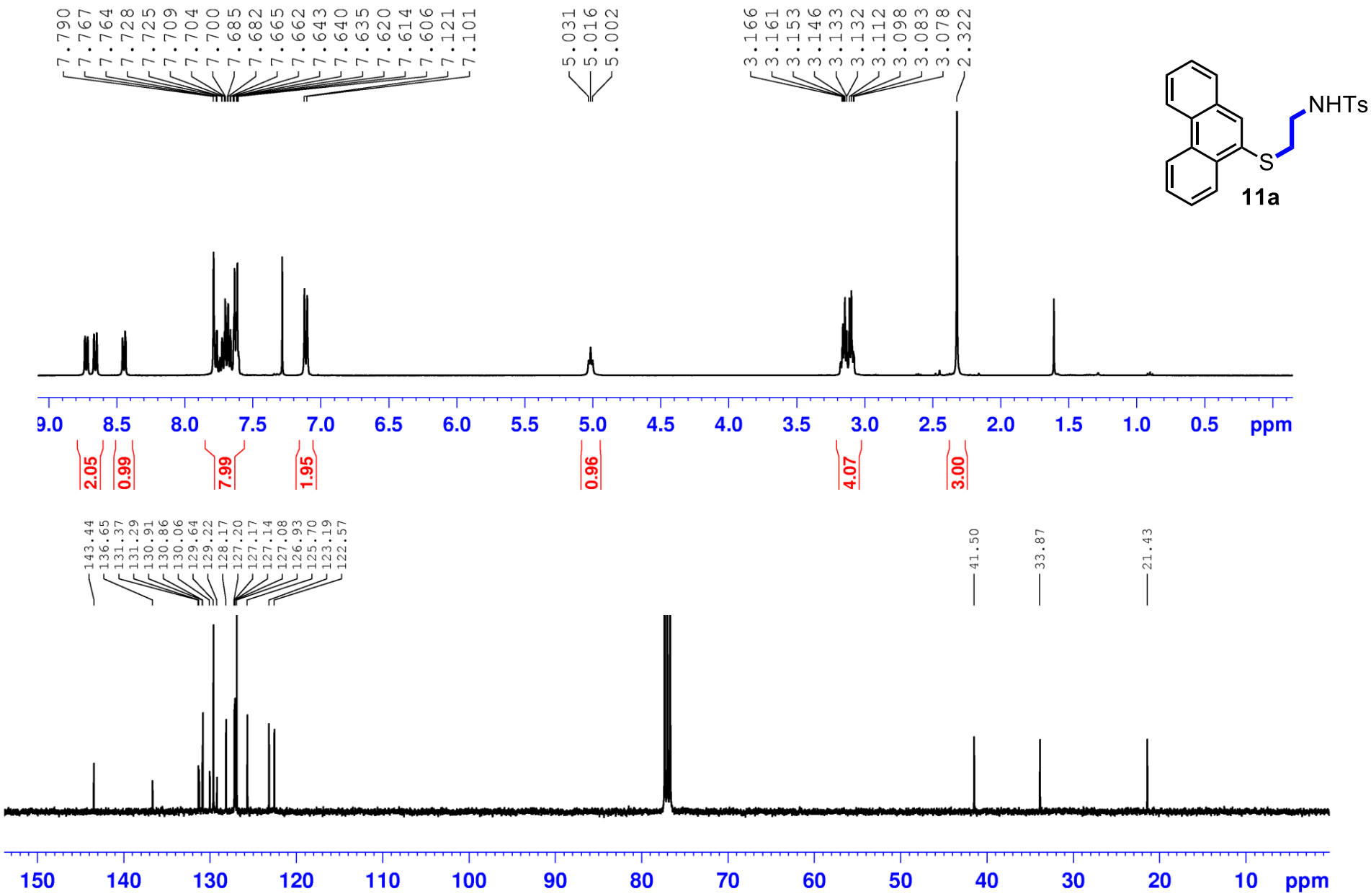
50
40
30
20
10
ppm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7.700
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7.682
7.665
7.662
7.643
7.640
7.635
7.620
7.614
7.606
7.121
7.101
5.031
5.016
5.002
3.166
3.161
3.153
3.146
3.133
3.132
3.112
3.098
3.083
3.078
2.322
NHTs
S
11a
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
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0.96
4.07
3.00
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131.29
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130.86
130.06
129.64
129.22
128.17
127.20
127.17
127.14
127.08
126.93
125.70
123.19
122.57
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150
140
130
120
110
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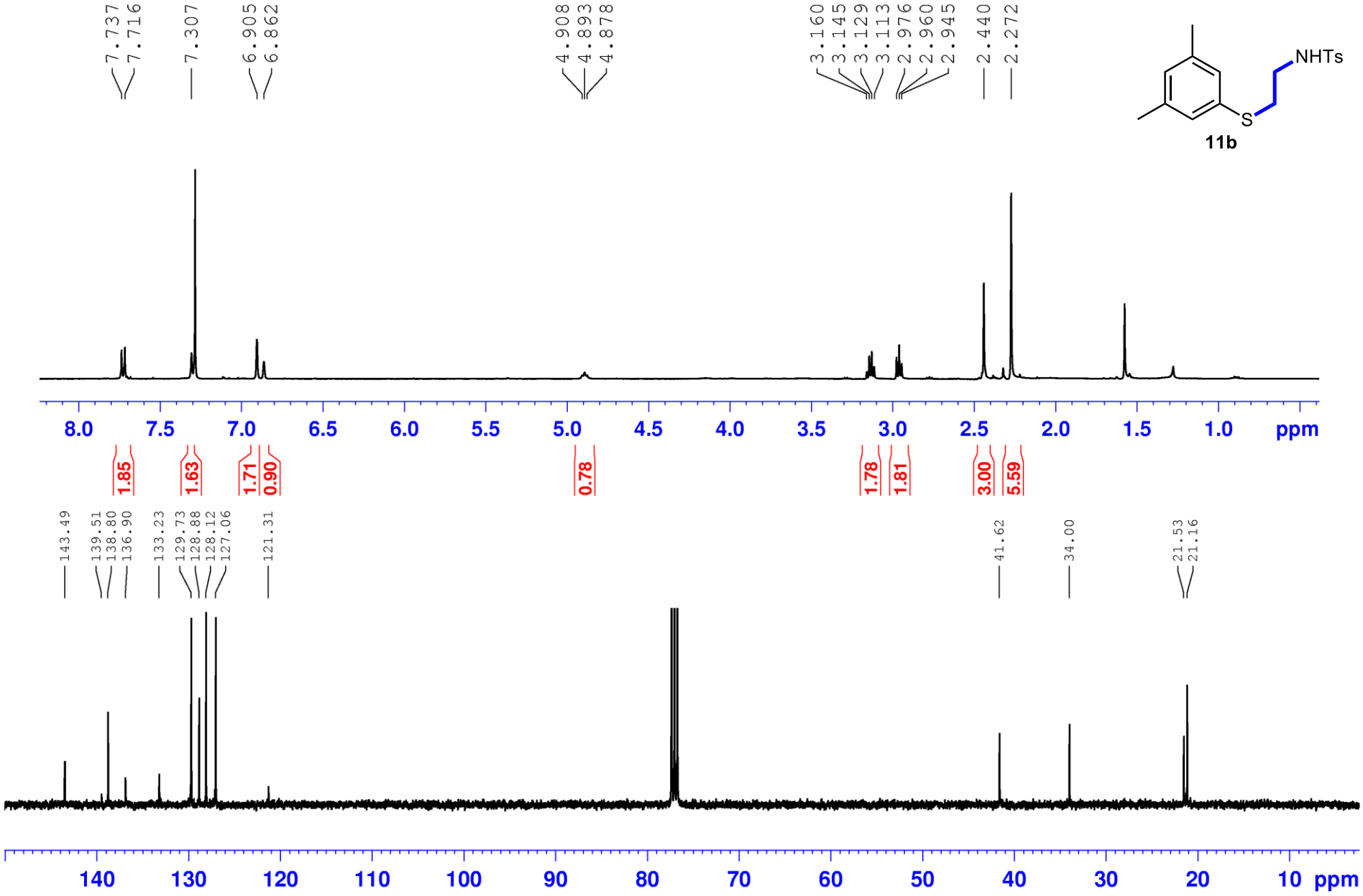
70
60
50
40
30
20
10
ppm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4.878
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3.145
3.129
3.113
2.976
2.960
2.945
2.440
2.272
NHTs
S
11b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.85
1.63
1.71
0.90
0.78
1.78
1.81
3.00
5.59
143.49
139.51
138.80
136.90
133.23
129.73
128.88
128.12
127.06
121.31
41.62
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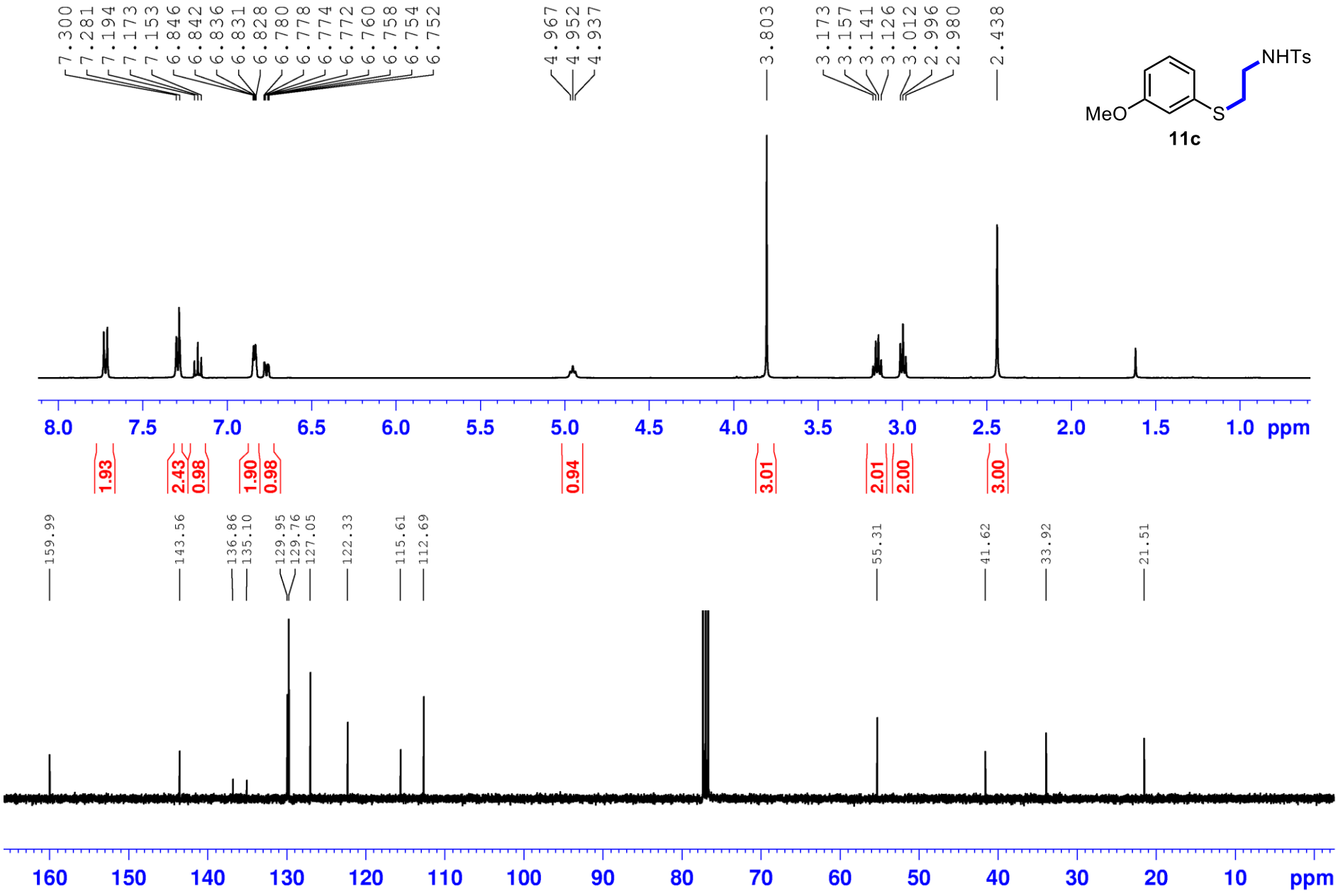
40
30
20
10
ppm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6.828
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6.774
6.772
6.760
6.758
6.754
6.752
4.967
4.952
4.937
3.803
3.173
3.157
3.141
3.126
3.012
2.996
2.980
2.438
NHTs
MeO
S
11c
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7.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.43
0.98
1.90
0.98
0.94
3.01
2.01
2.00
3.00
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135.10
129.95
129.76
127.05
122.33
115.61
112.69
55.31
41.62
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130
120
110
100
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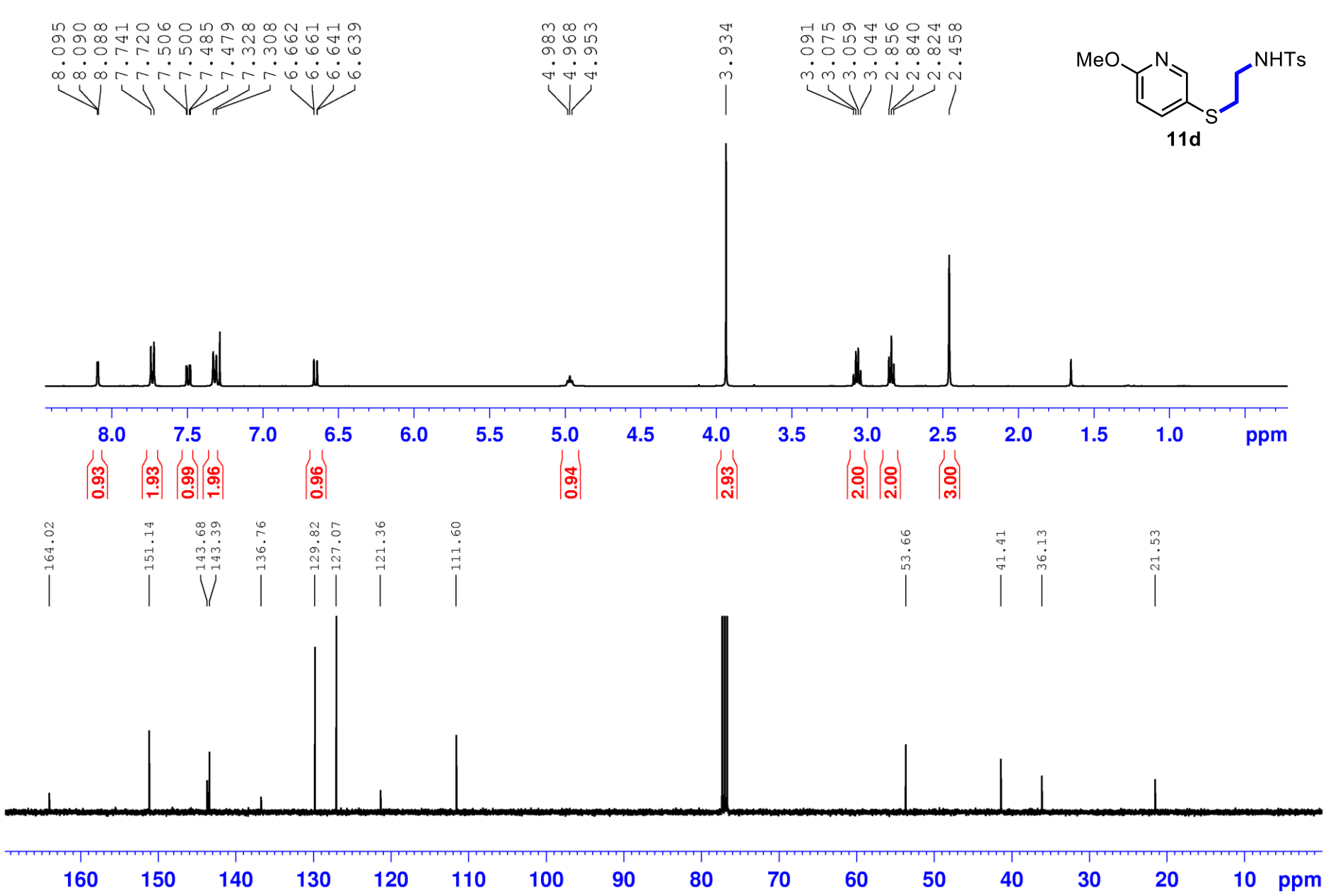
80
70
60
50
40
30
20
10
ppm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7.485
7.479
7.328
7.308
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6.661
6.641
6.639
4.983
4.968
4.953
3.934
3.091
3.075
3.059
3.044
2.856
2.840
2.824
2.458
MeO
N
NHTs
S
11d
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.93
0.99
1.96
0.96
0.94
2.93
2.00
2.00
3.00
164.02
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143.39
136.76
129.82
127.07
121.36
111.60
53.66
41.41
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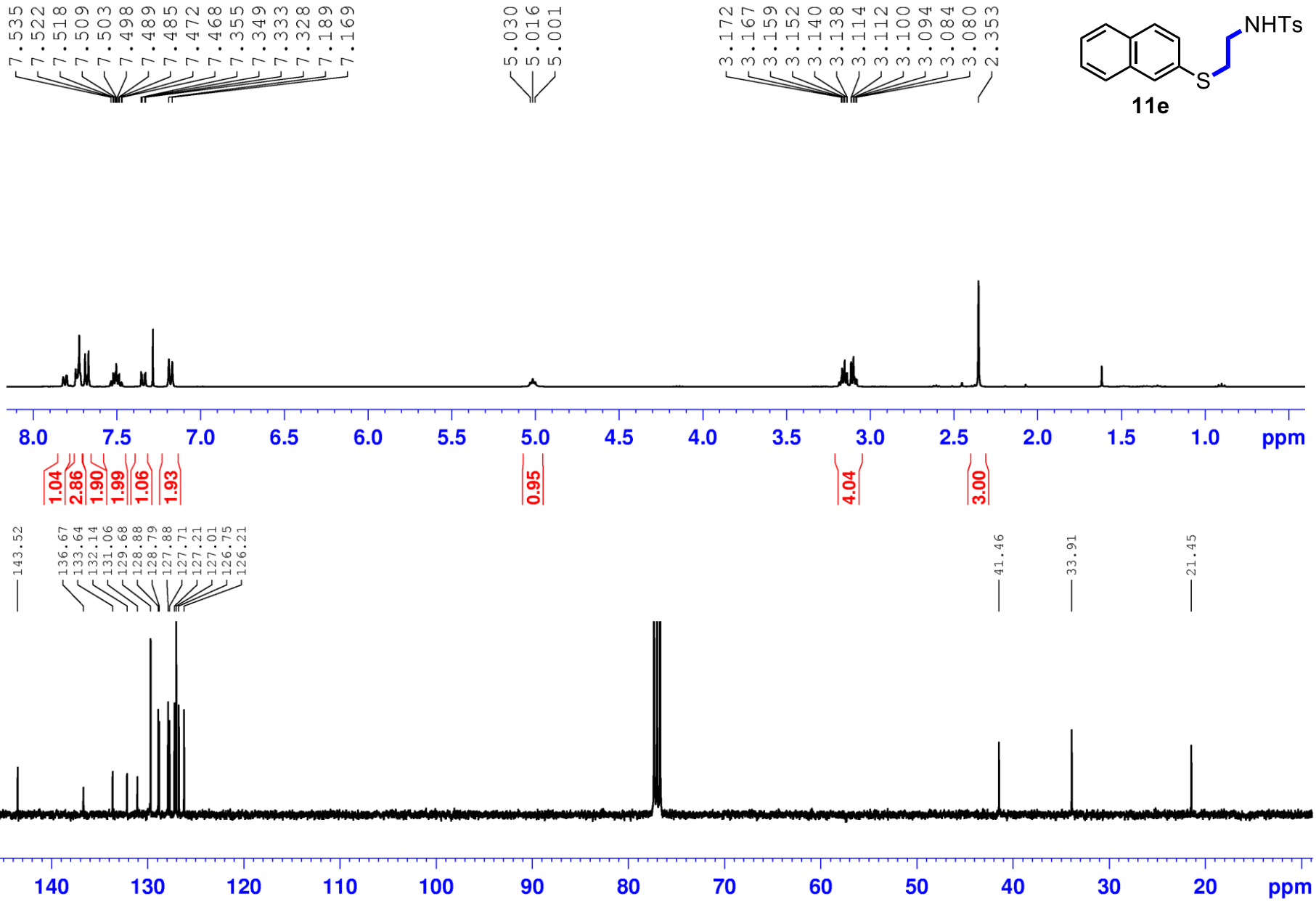
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.468
7.355
7.349
7.333
7.328
7.189
7.169
5.030
5.016
5.001
3.172
3.167
3.159
3.152
3.140
3.138
3.114
3.112
3.100
3.094
3.084
3.080
2.353
NHTs
S
11e
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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ppm
1.04
2.86
1.90
1.99
1.06
1.93
0.95
4.04
3.00
143.52
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133.64
132.14
131.06
129.68
128.88
128.79
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127.01
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21.45
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120
110
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80
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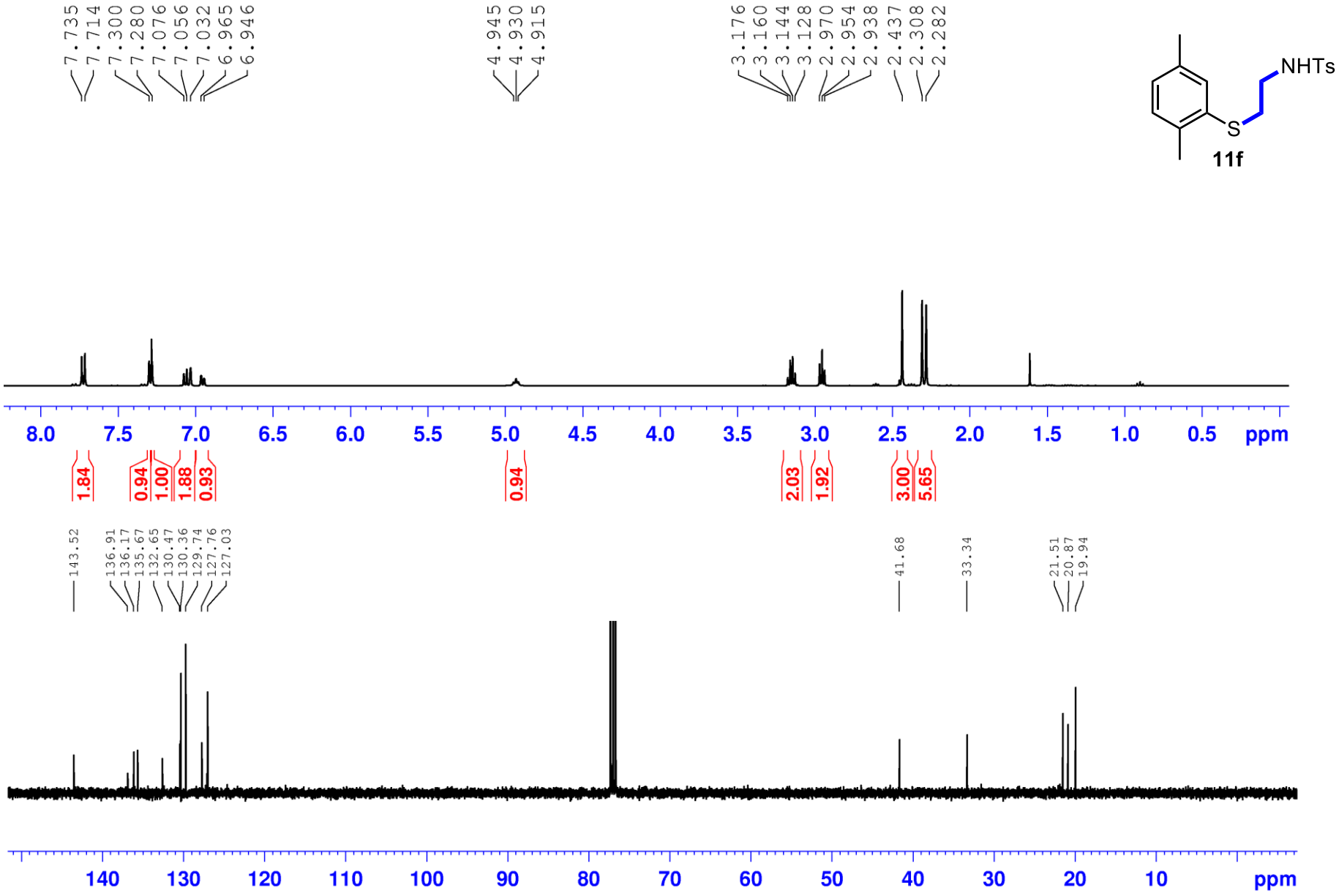
50
40
30
20
ppm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4.915
3.176
3.160
3.144
3.128
2.970
2.954
2.938
2.437
2.308
2.282
NHTs
S
11f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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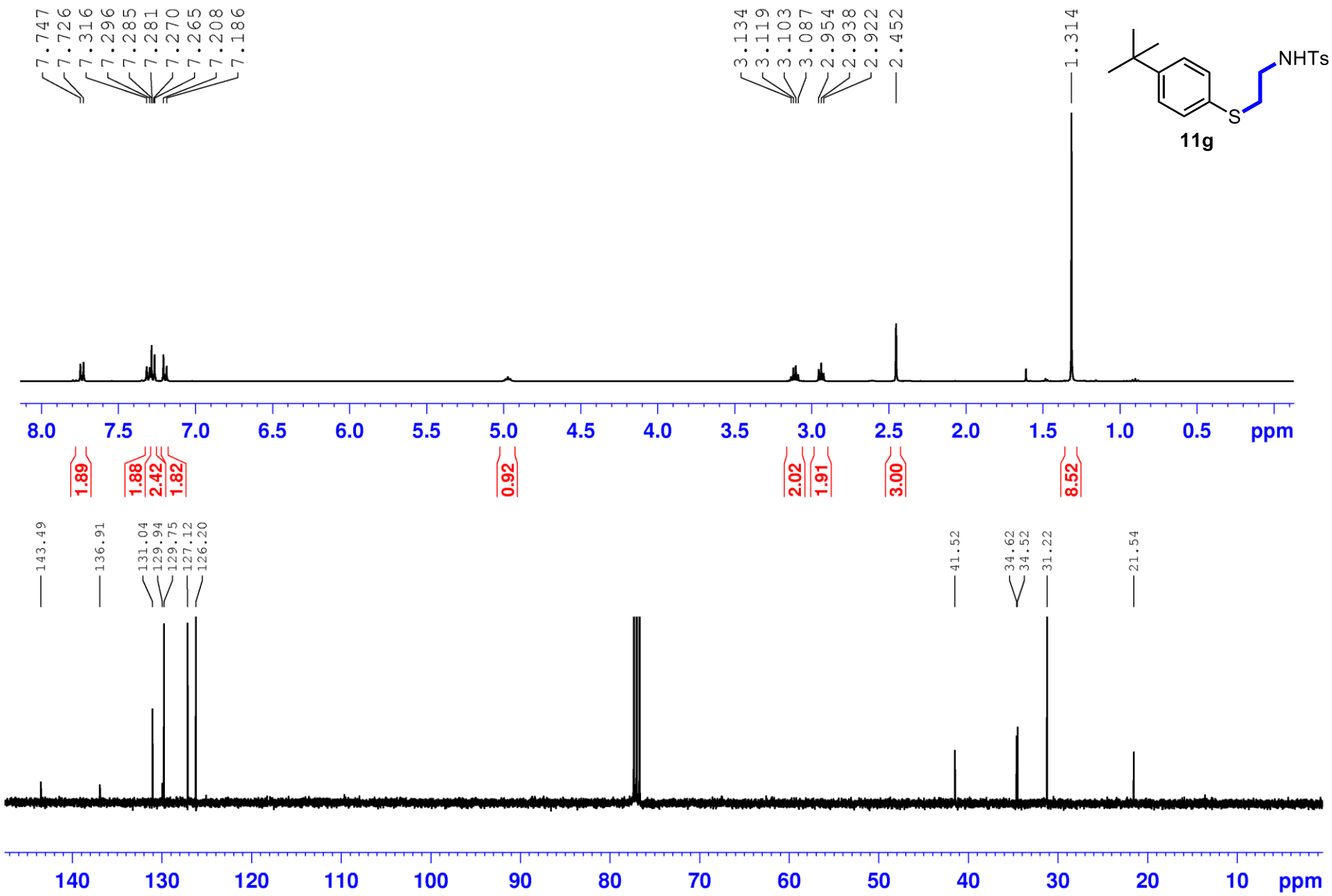
0.94
1.00
1.88
0.93
0.94
2.03
1.92
3.00
5.65
143.52
136.91
136.17
135.67
132.65
130.47
130.36
129.74
127.76
127.03
41.68
33.34
21.51
20.87
19.94
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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3.119
3.103
3.087
2.954
2.938
2.922
2.452
1.314
NHTs
S
11g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.88
2.42
1.82
0.92
2.02
1.91
3.00
8.52
143.49
136.91
131.04
129.94
129.75
127.12
126.20
41.52
34.62
34.52
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130
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70
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50
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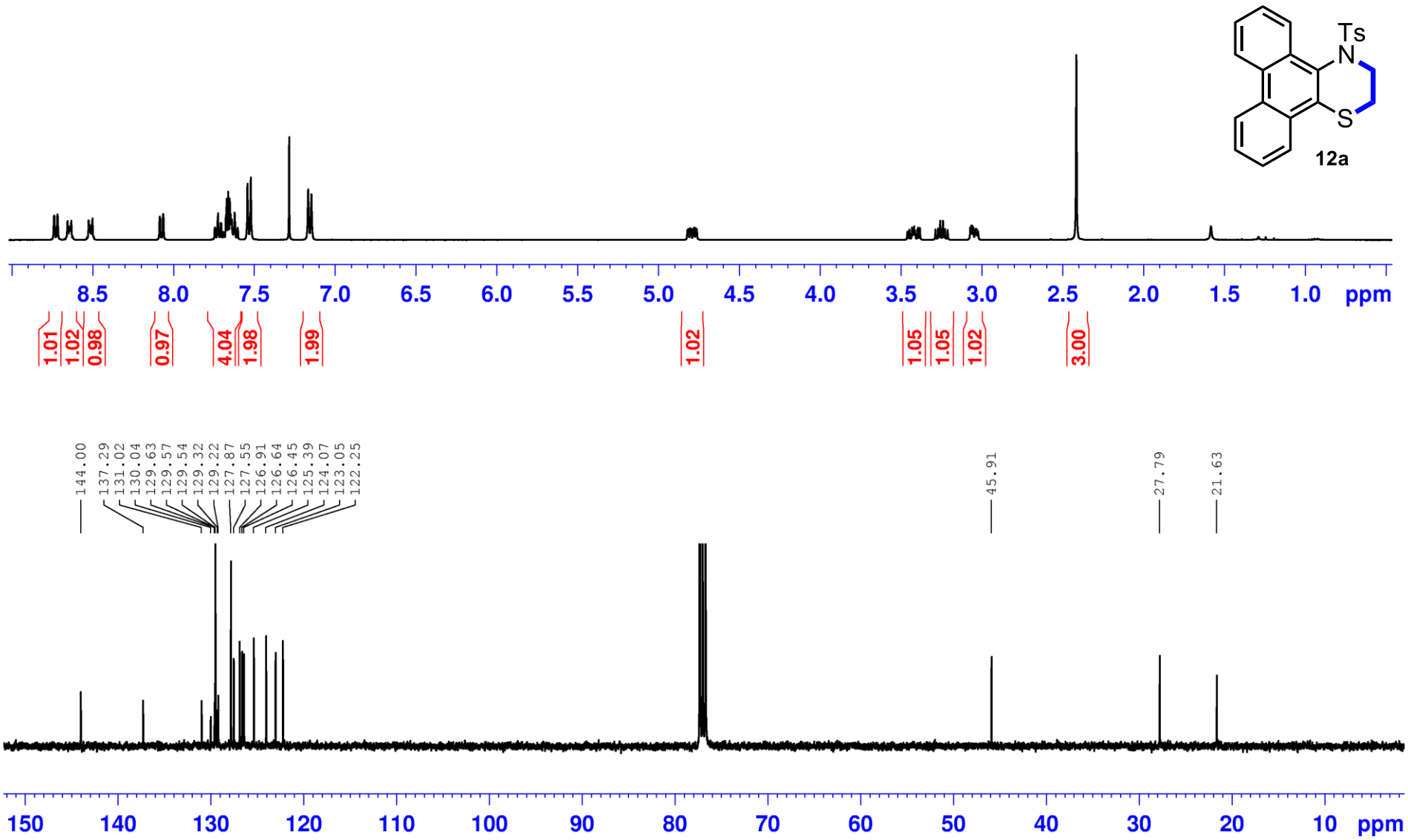
30
20
10
ppm


Ts
N
S
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.02
0.98
0.97
4.04
1.98
1.99
1.02
1.05
1.05
1.02
3.00
144.00
137.29
131.02
130.04
129.63
129.57
129.54
129.32
129.22
127.87
127.55
126.91
126.64
126.45
125.39
124.07
123.05
122.25
45.91
27.79
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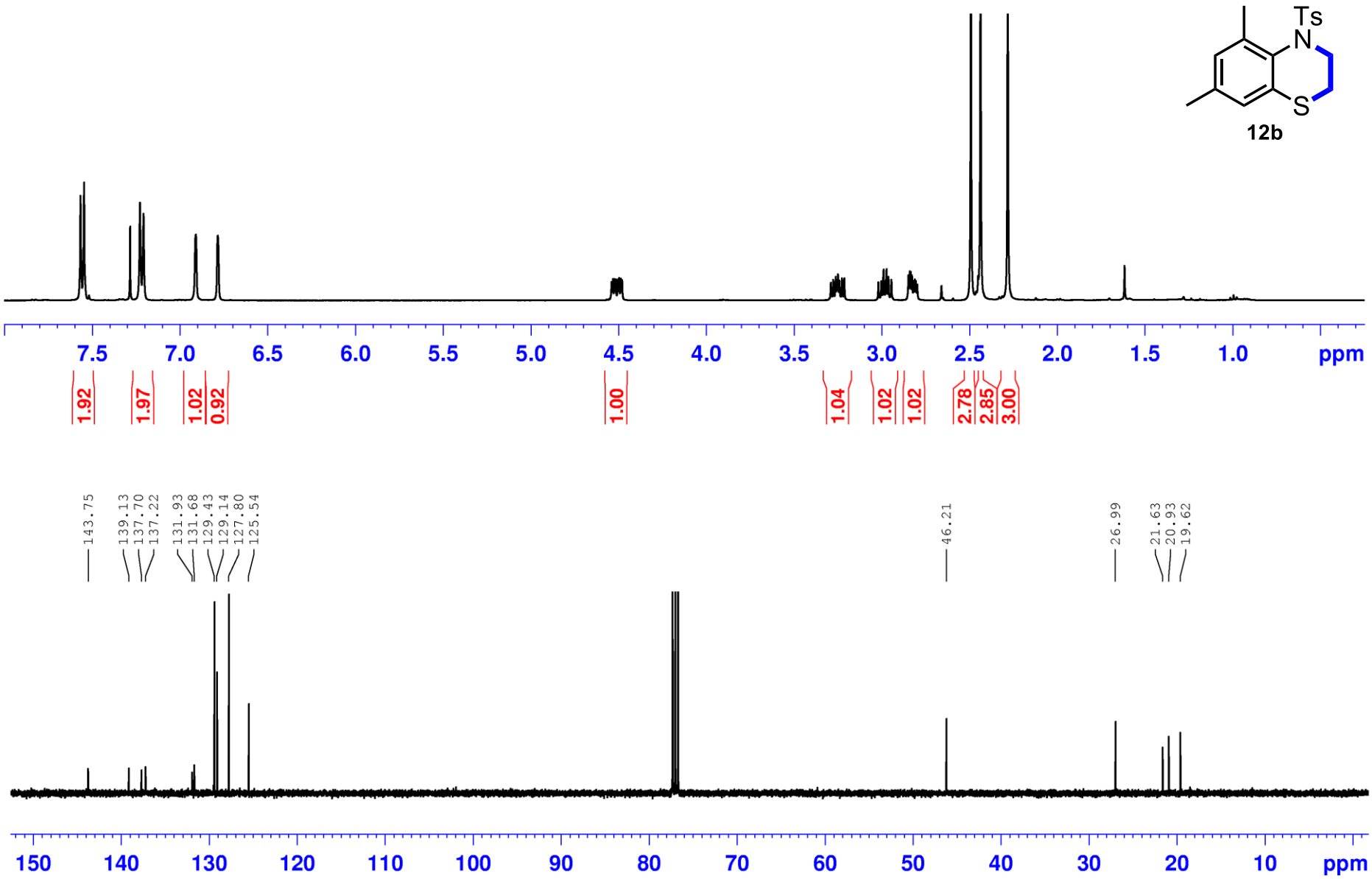
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
S
12b
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.92
1.97
1.02
0.92
1.00
1.04
1.02
1.02
2.78
2.85
3.00
143.75
139.13
137.70
137.22
131.93
131.68
129.43
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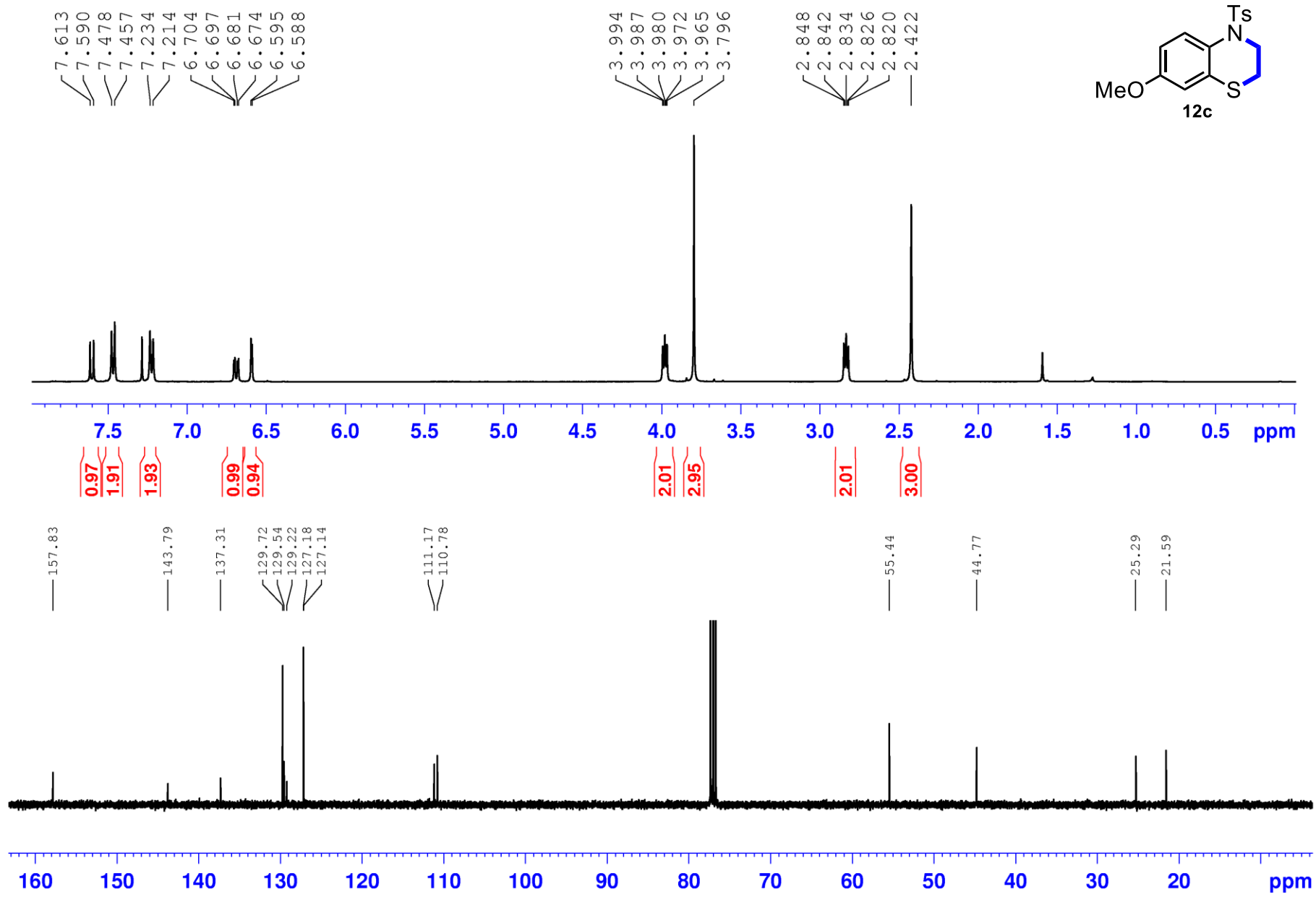
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Ts
N
MeO
S
12c
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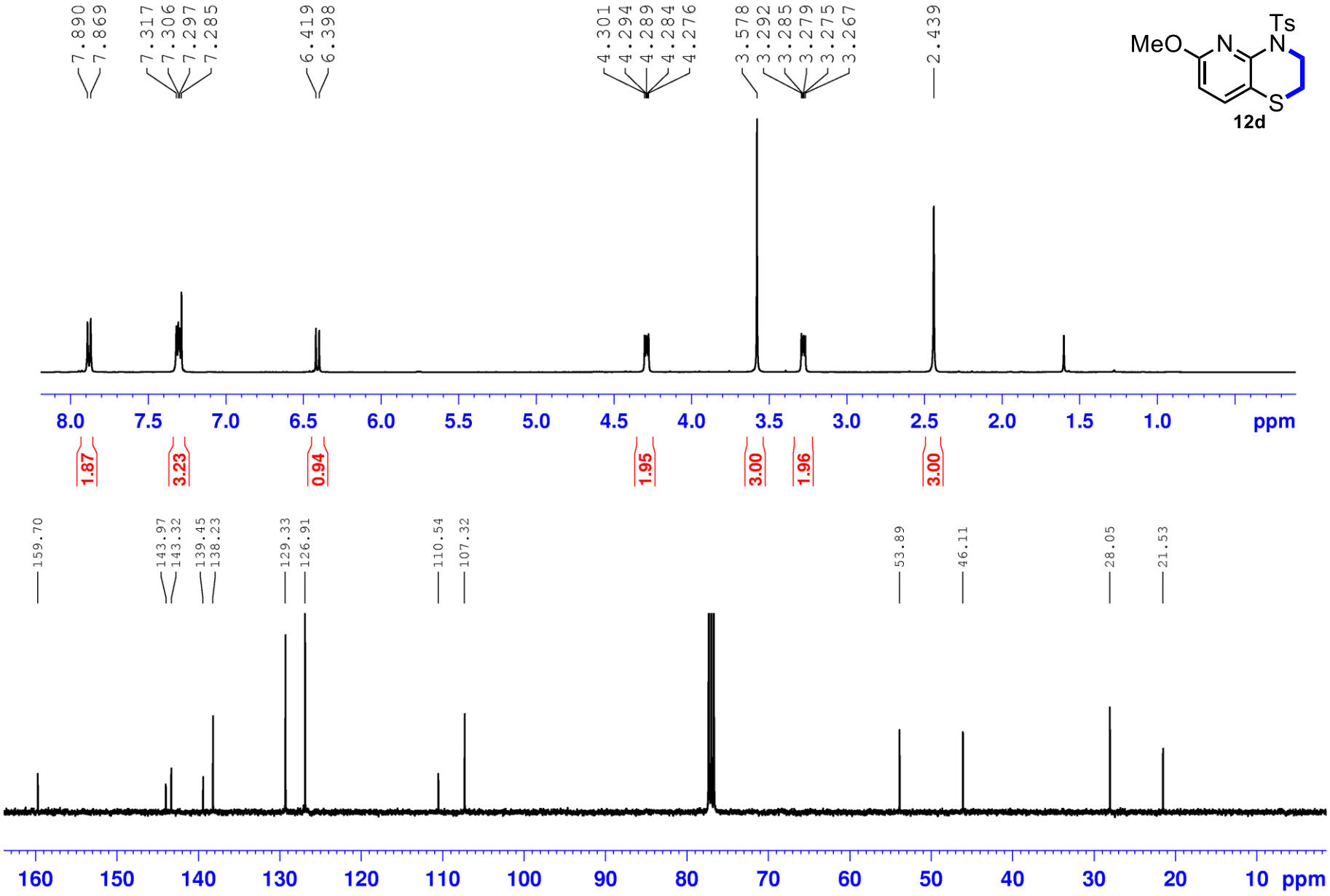
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MeO
N
N
Ts
S
12d
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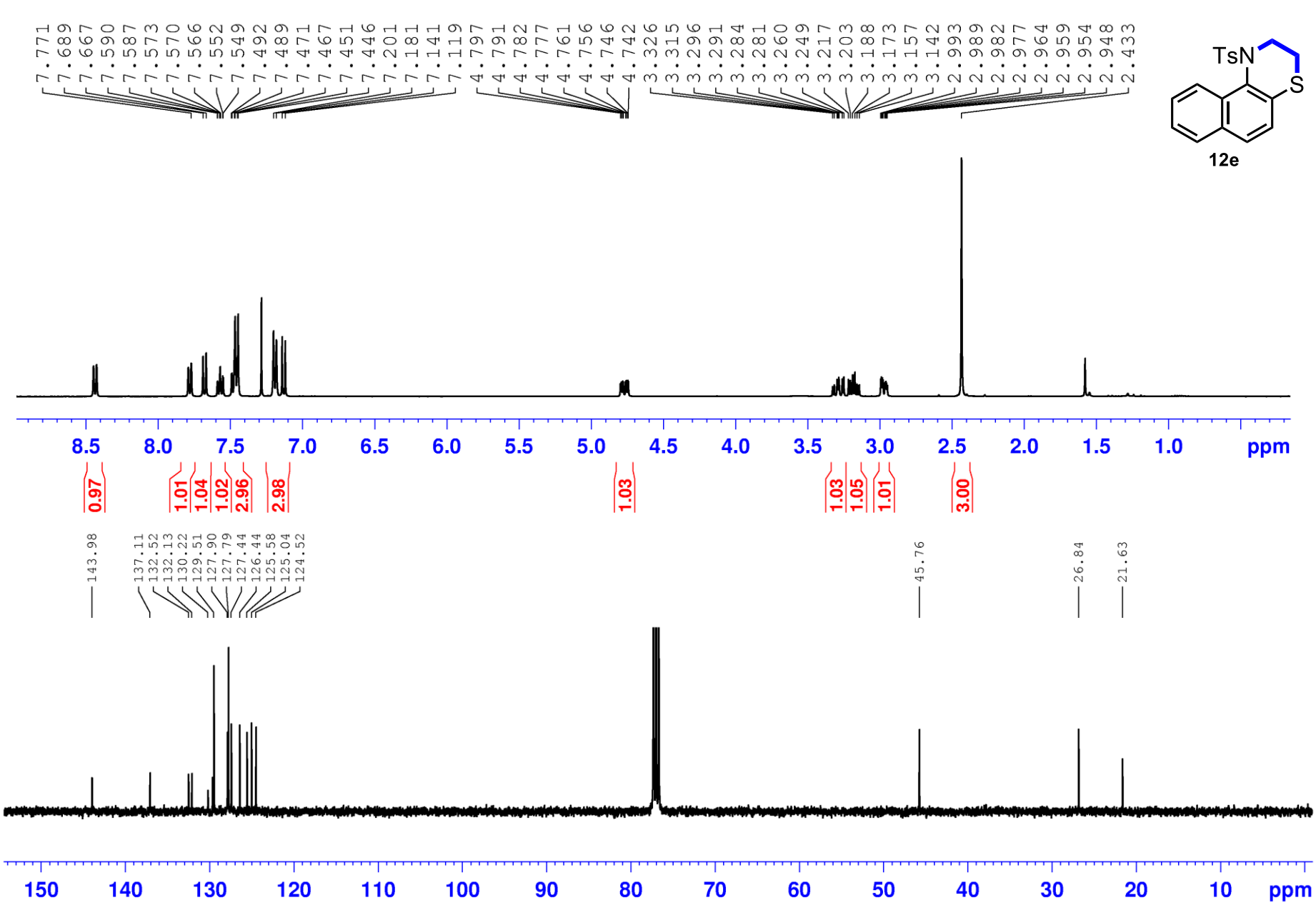
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7.451
7.446
7.201
7.181
7.141
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4.791
4.782
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4.761
4.756
4.746
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3.315
3.296
3.291
3.284
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2.954
2.948
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TsN
S
12e
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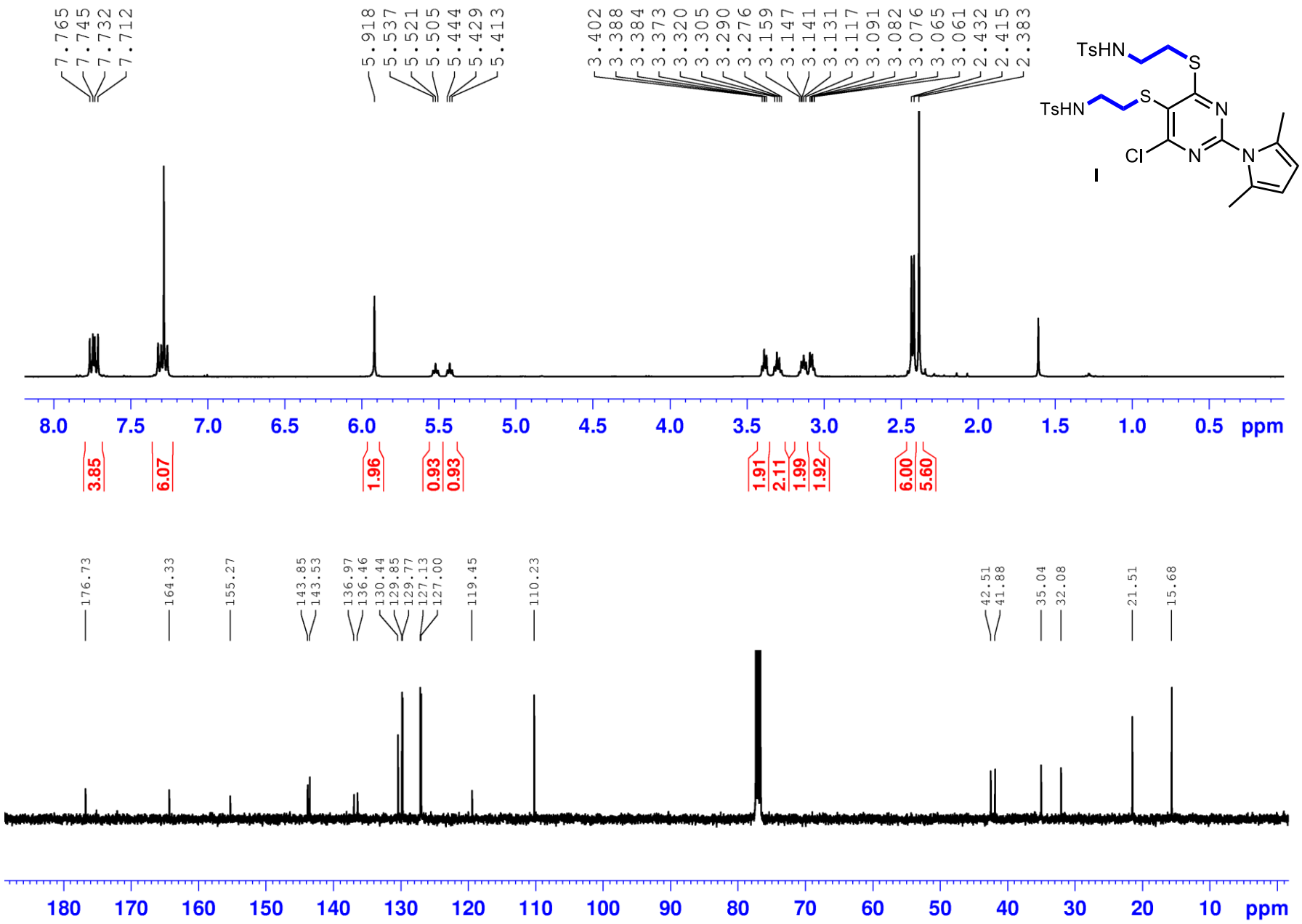
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3.076
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3.061
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2.383
TsHN
S
TsHN
S
N
Cl
N
N
I
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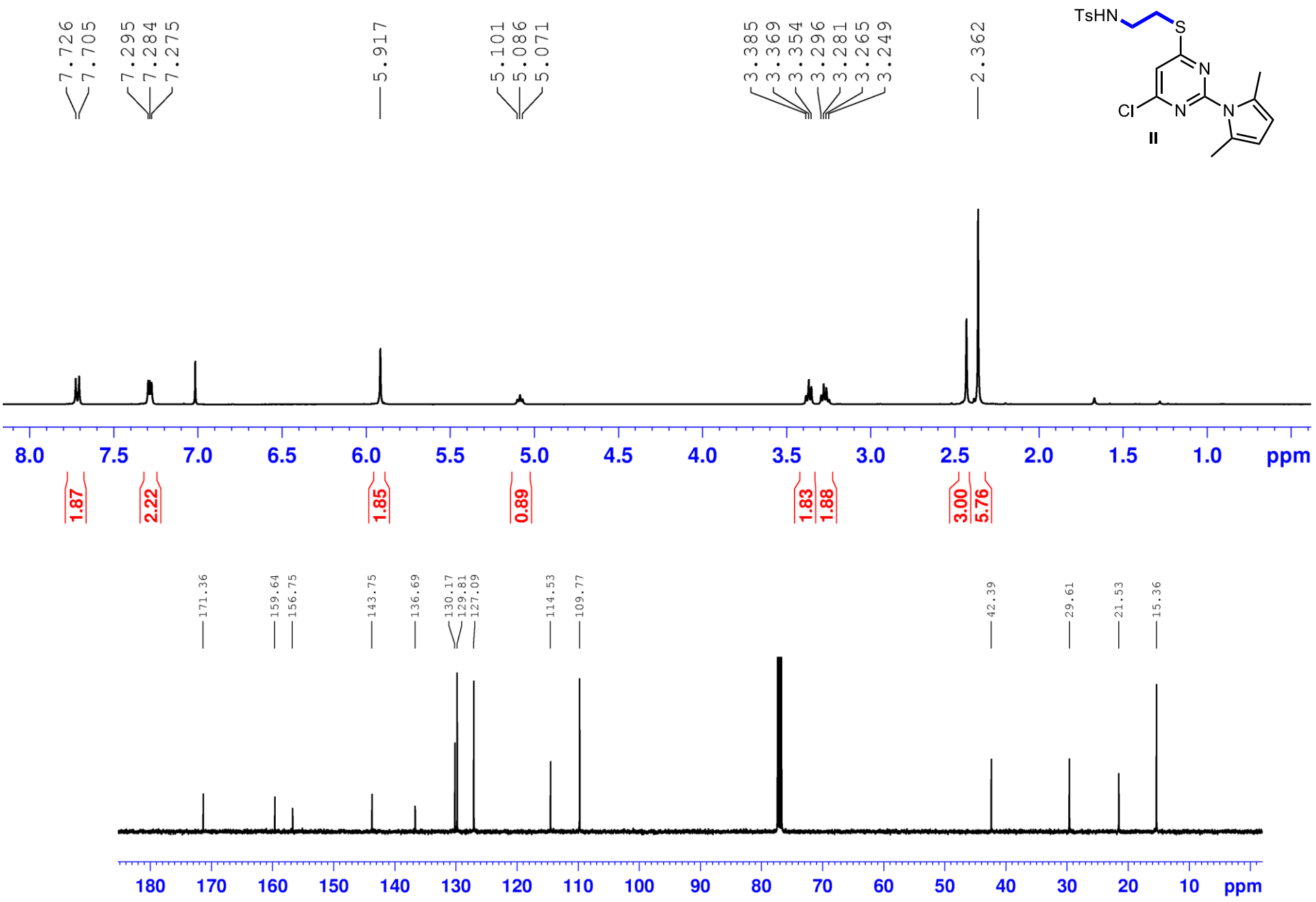
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3.265
3.249
2.362
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S
N
Cl
N
N
II
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5.5
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4.5
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3.0
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2.0
1.5
1.0
ppm
1.87
2.22
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0.89
1.83
1.88
3.00
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143.75
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130.17
129.81
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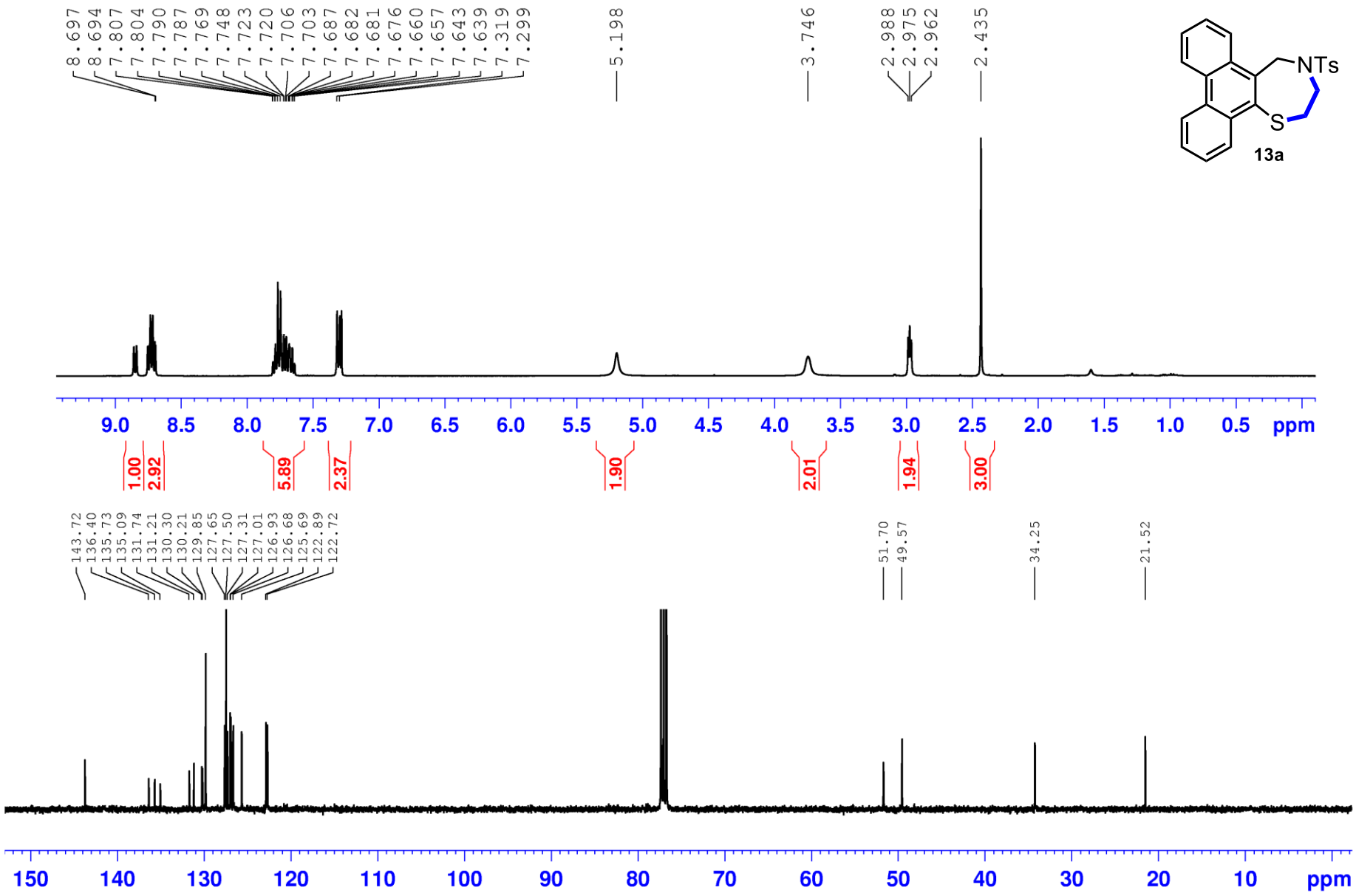
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7.687
7.682
7.681
7.676
7.660
7.657
7.643
7.639
7.319
7.299
5.198
3.746
2.988
2.975
2.962
2.435
NTs
S
13a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
2.92
5.89
2.37
1.90
2.01
1.94
3.00
143.72
136.40
135.73
135.09
131.74
131.21
130.30
130.21
129.85
127.65
127.50
127.31
127.01
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21.52
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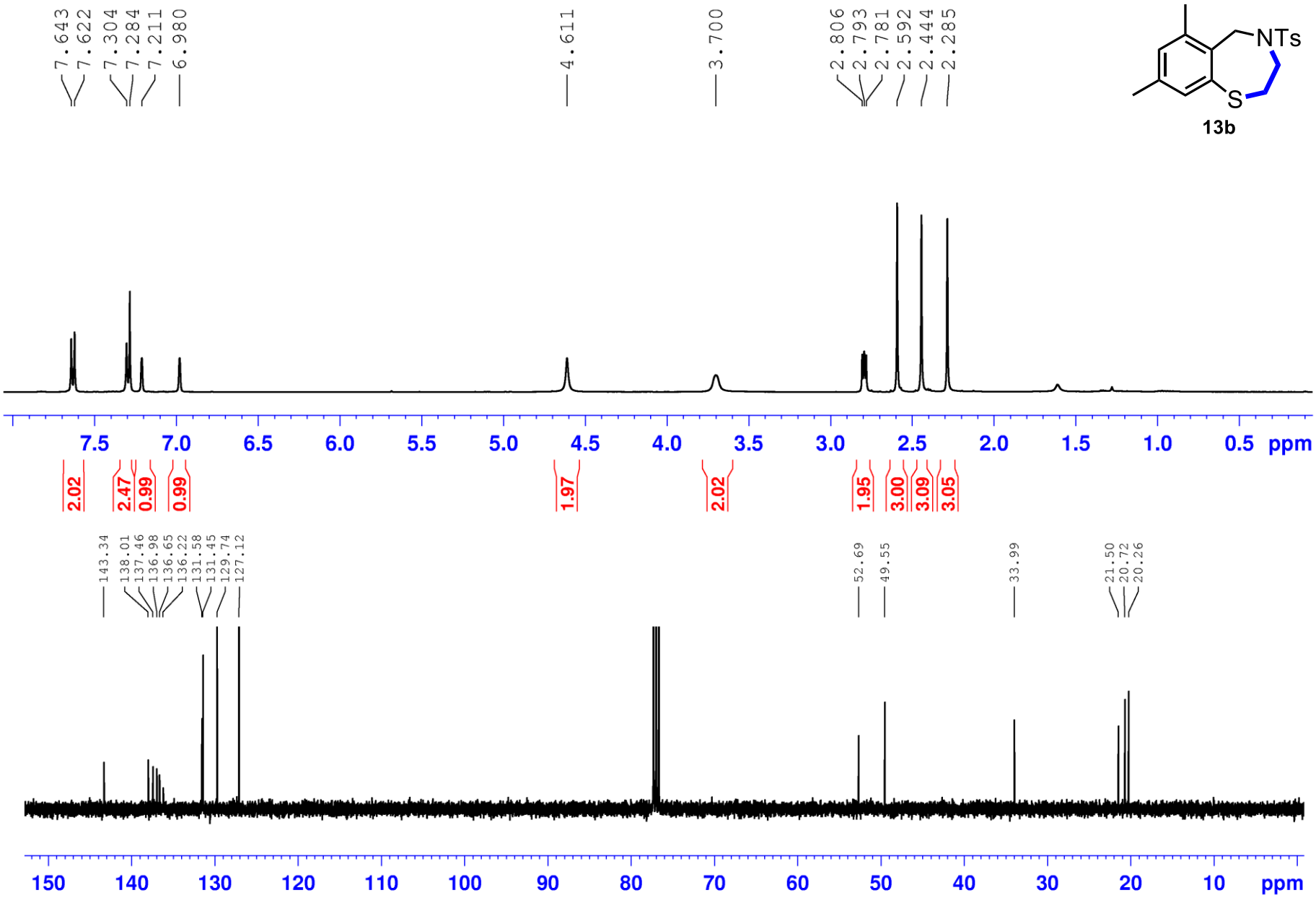
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S
13b
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ppm
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0.99
1.97
2.02
1.95
3.00
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3.05
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136.98
136.65
136.22
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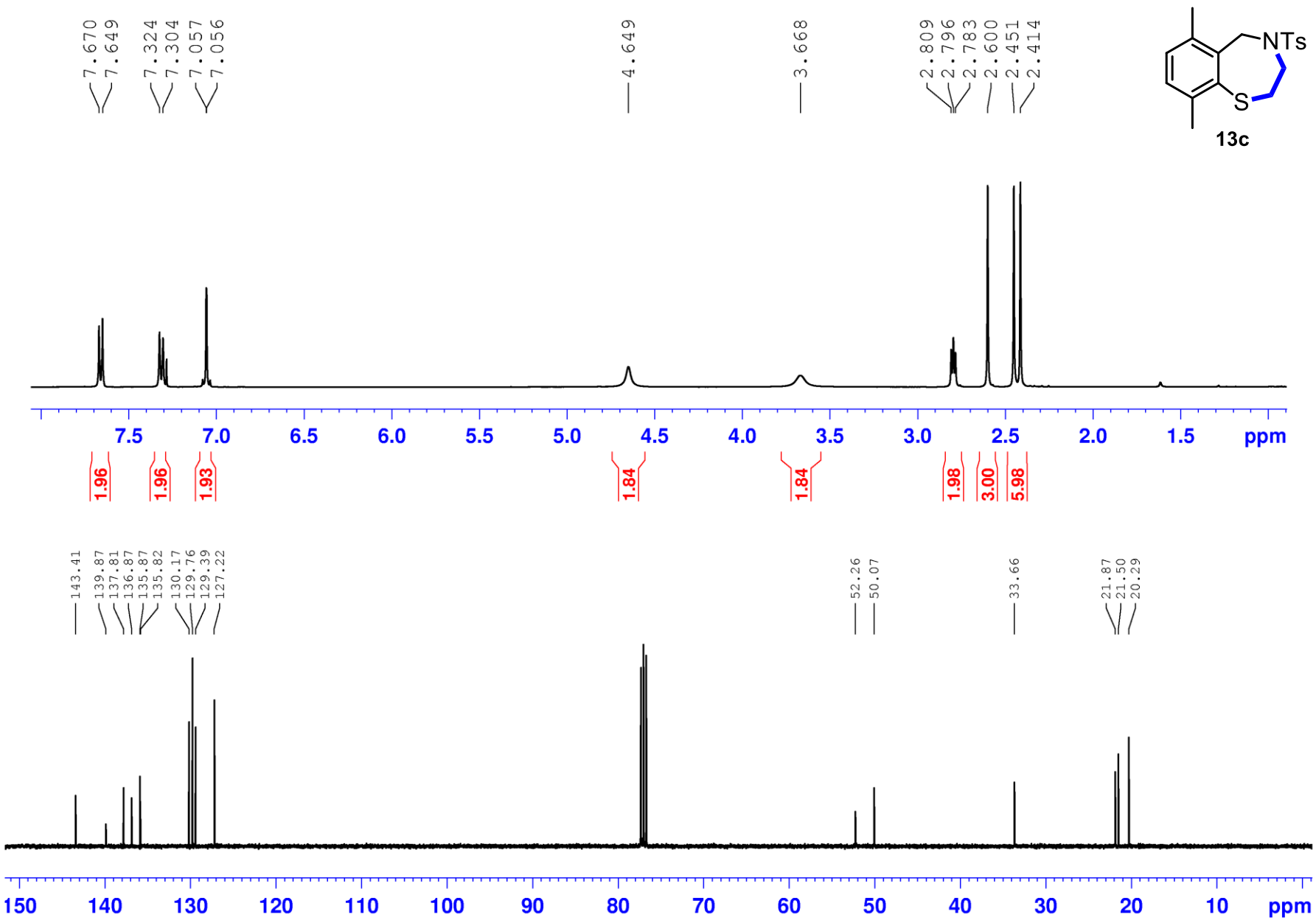
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NTs
S
13c
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4.0
3.5
3.0
2.5
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129.39
127.22
52.26
50.07
33.66
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20
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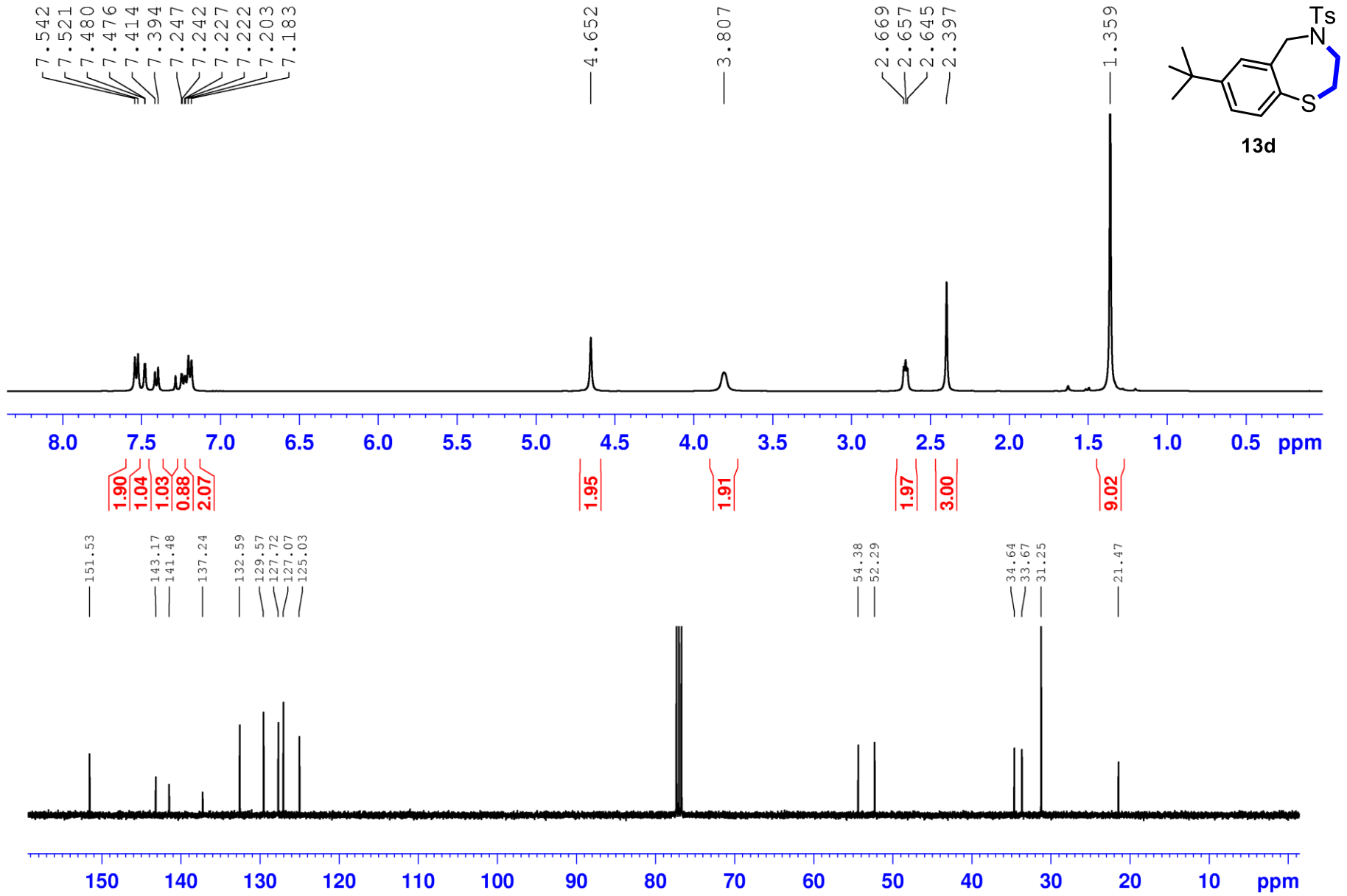
ppm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2.657
2.645
2.397
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Ts
N
S
13d
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5.0
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3.0
2.5
2.0
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127.07
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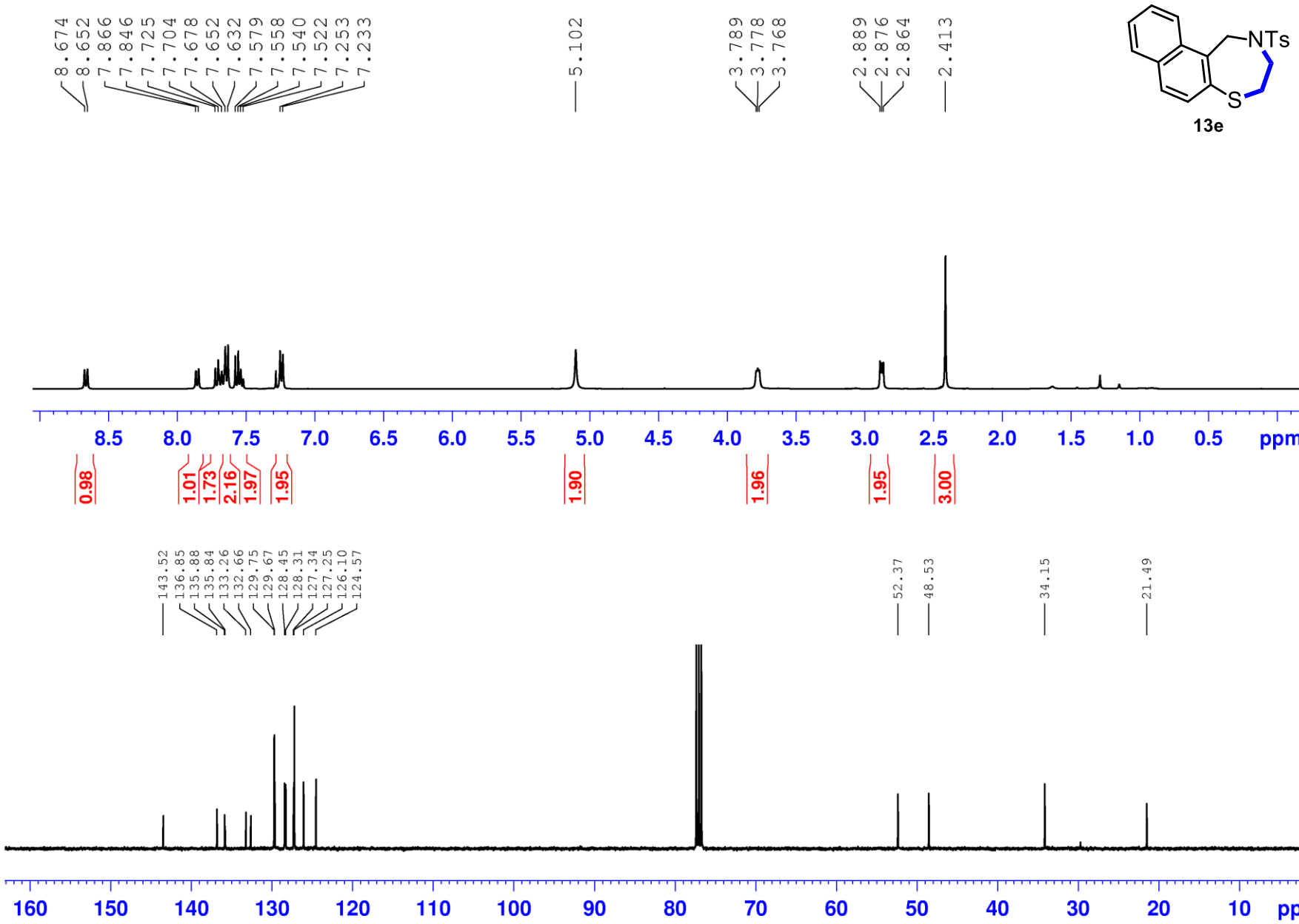
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NTs
S
13e
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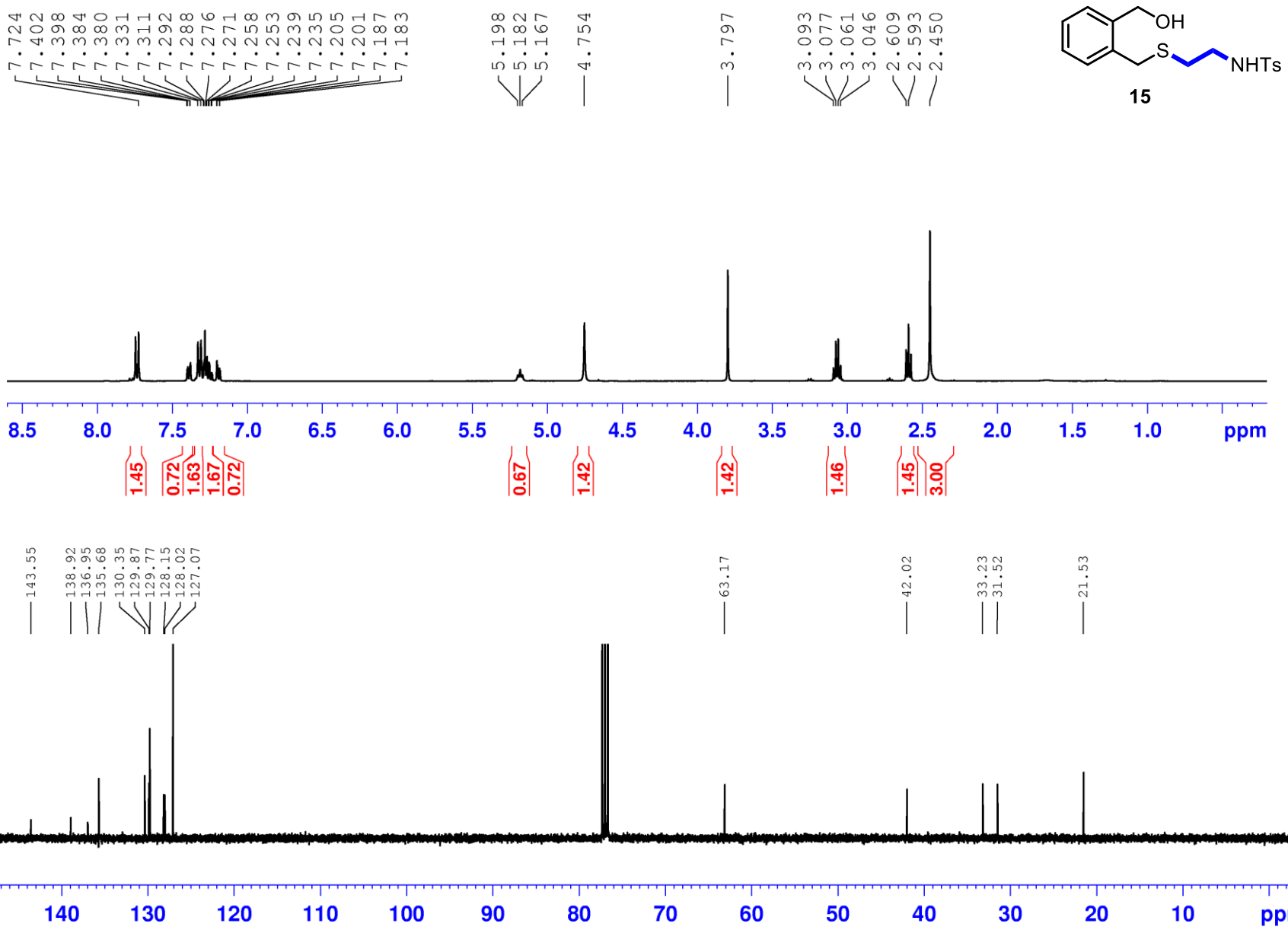
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7.205
7.201
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OH
S
NHTs
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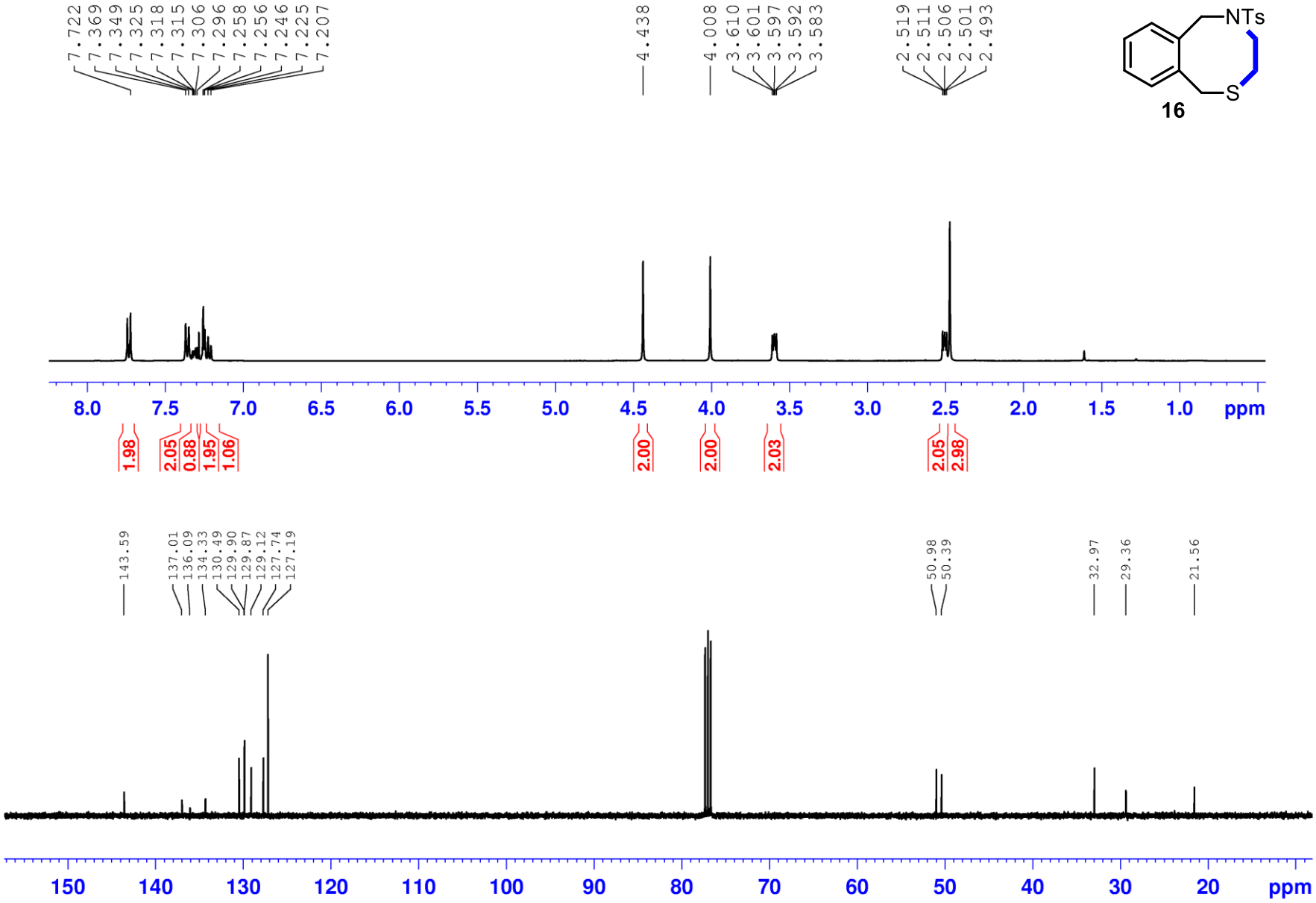
20
10
ppm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3.592
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2.511
2.506
2.501
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NTs
S
16
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5.0
4.5
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ppm
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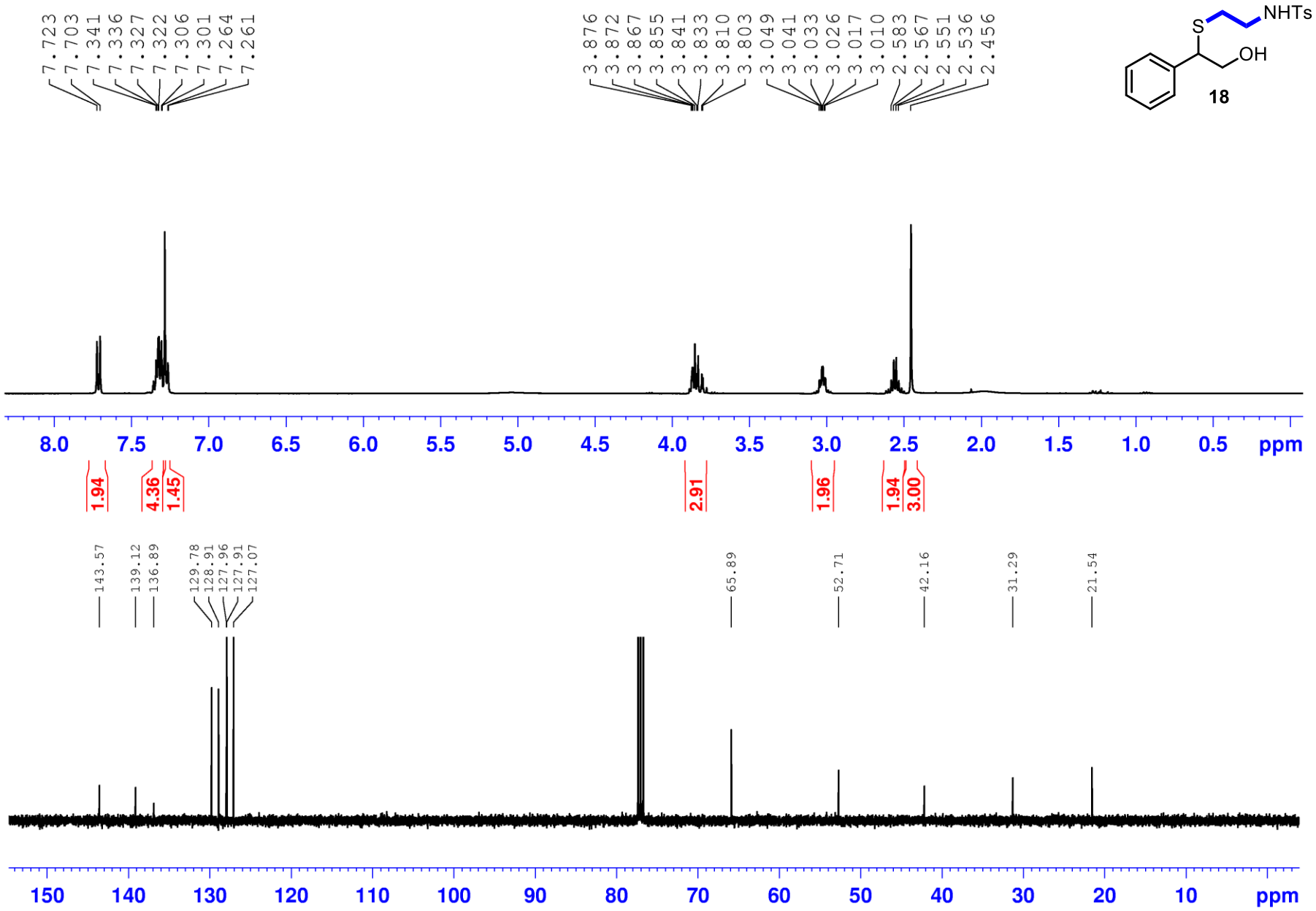
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S
OH
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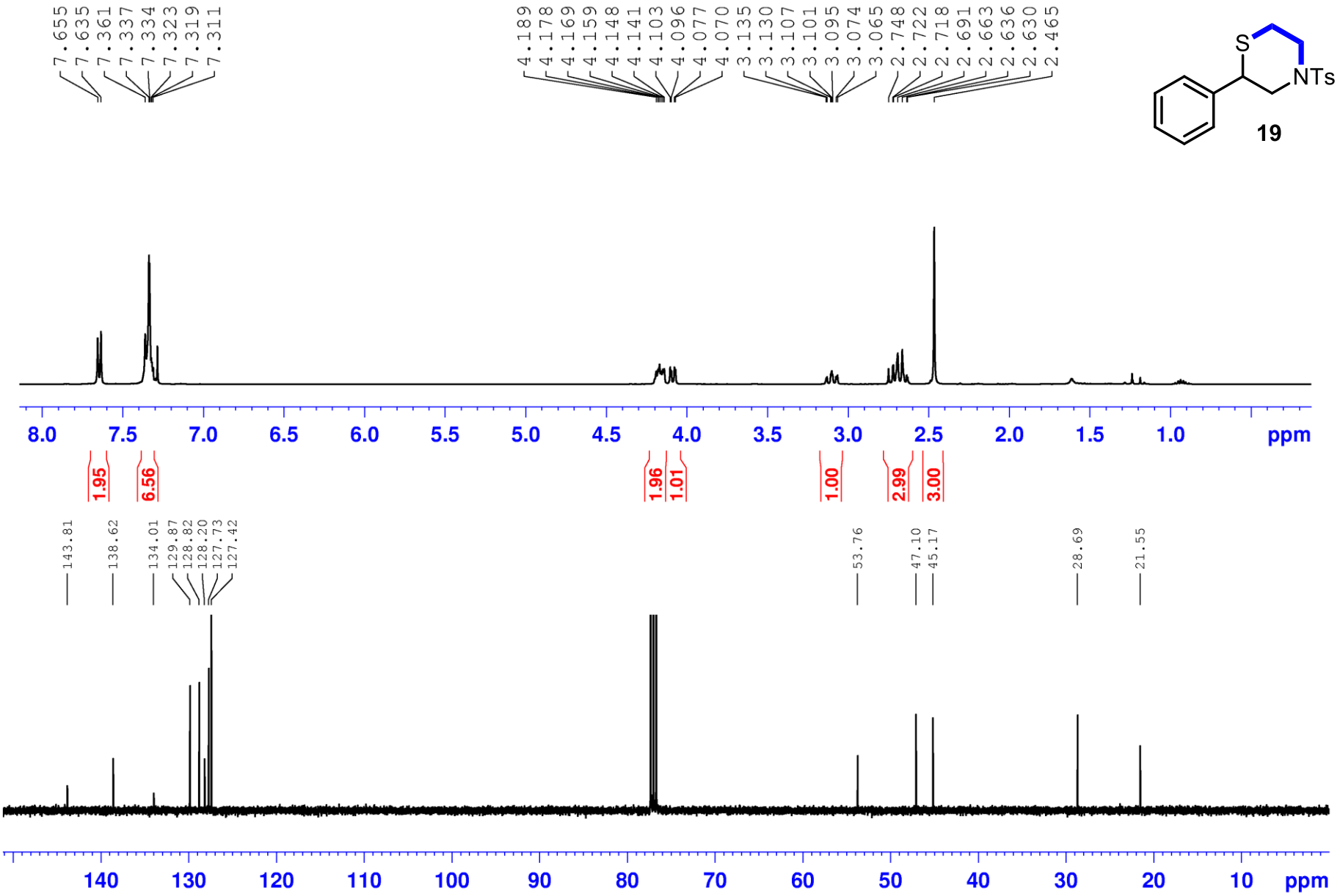
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S
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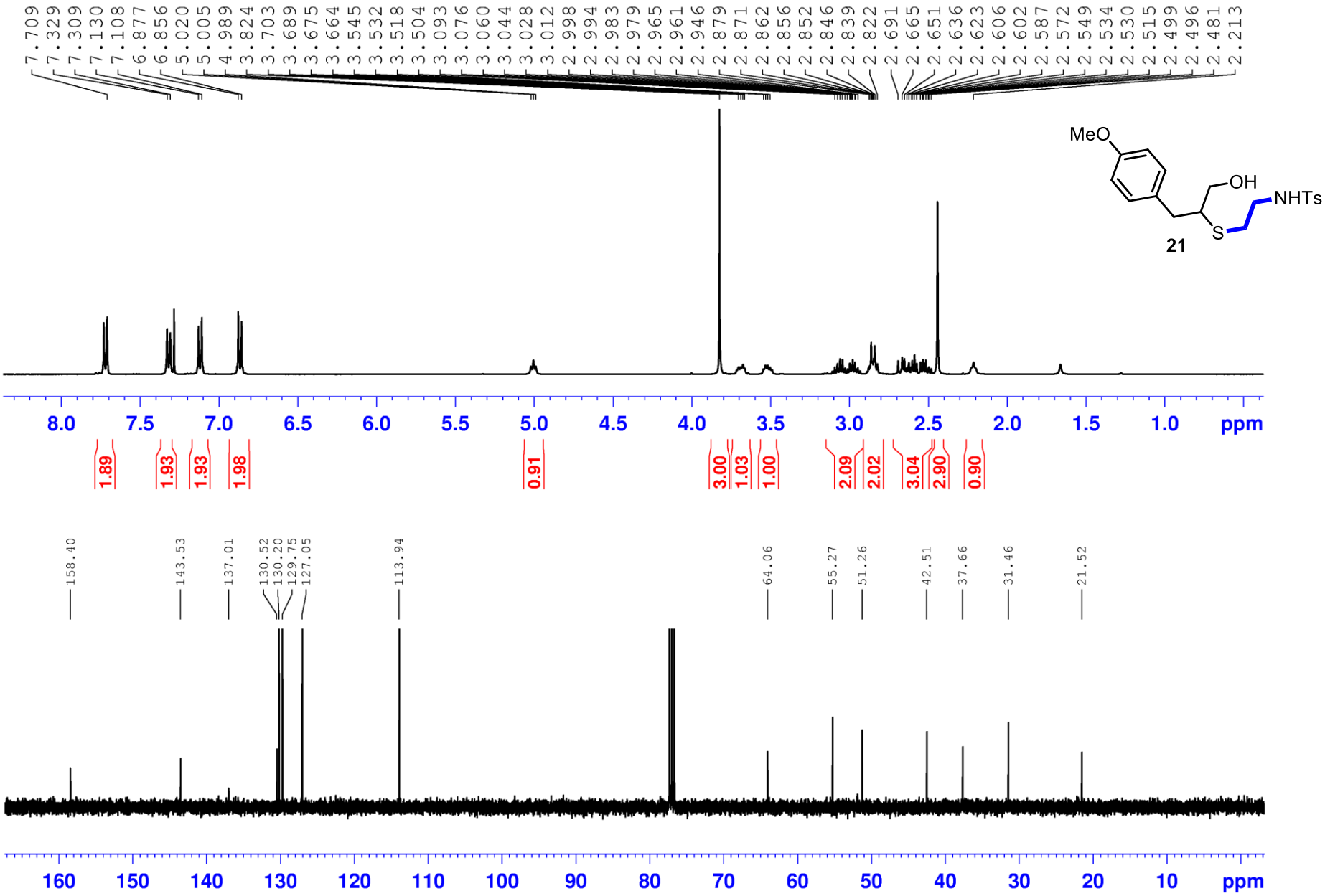
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MeO
OH
NHTs
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60
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40
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20
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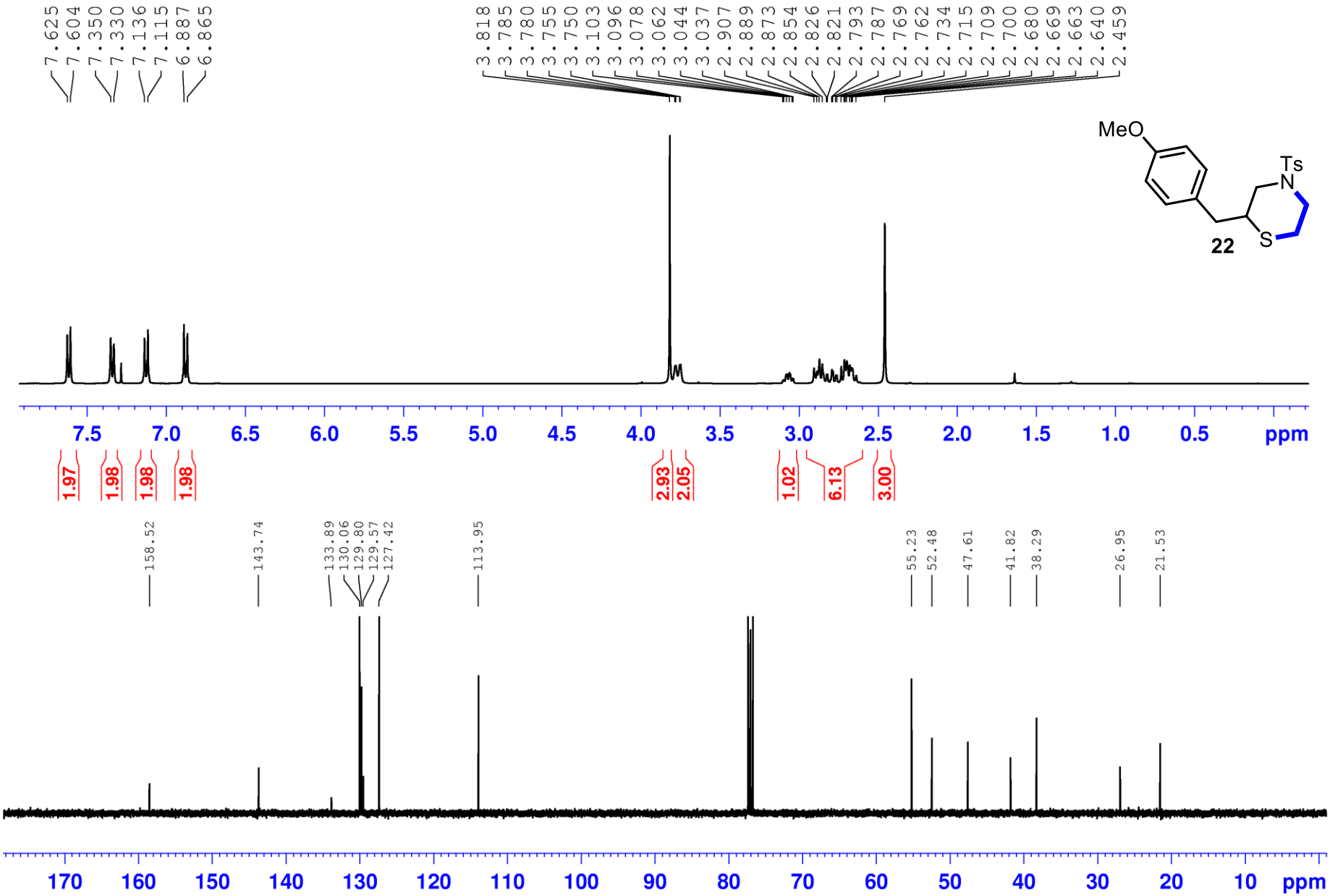
ppm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3.750
3.103
3.096
3.078
3.062
3.044
3.037
2.907
2.889
2.873
2.854
2.826
2.821
2.793
2.787
2.769
2.762
2.734
2.715
2.709
2.700
2.680
2.669
2.663
2.640
2.459
MeO
Ts
N
S
22
7.5
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6.5
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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ppm
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1.98
1.98
2.93
2.05
1.02
6.13
3.00
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143.74
133.89
130.06
129.80
129.57
127.42
113.95
55.23
52.48
47.61
41.82
38.29
26.95
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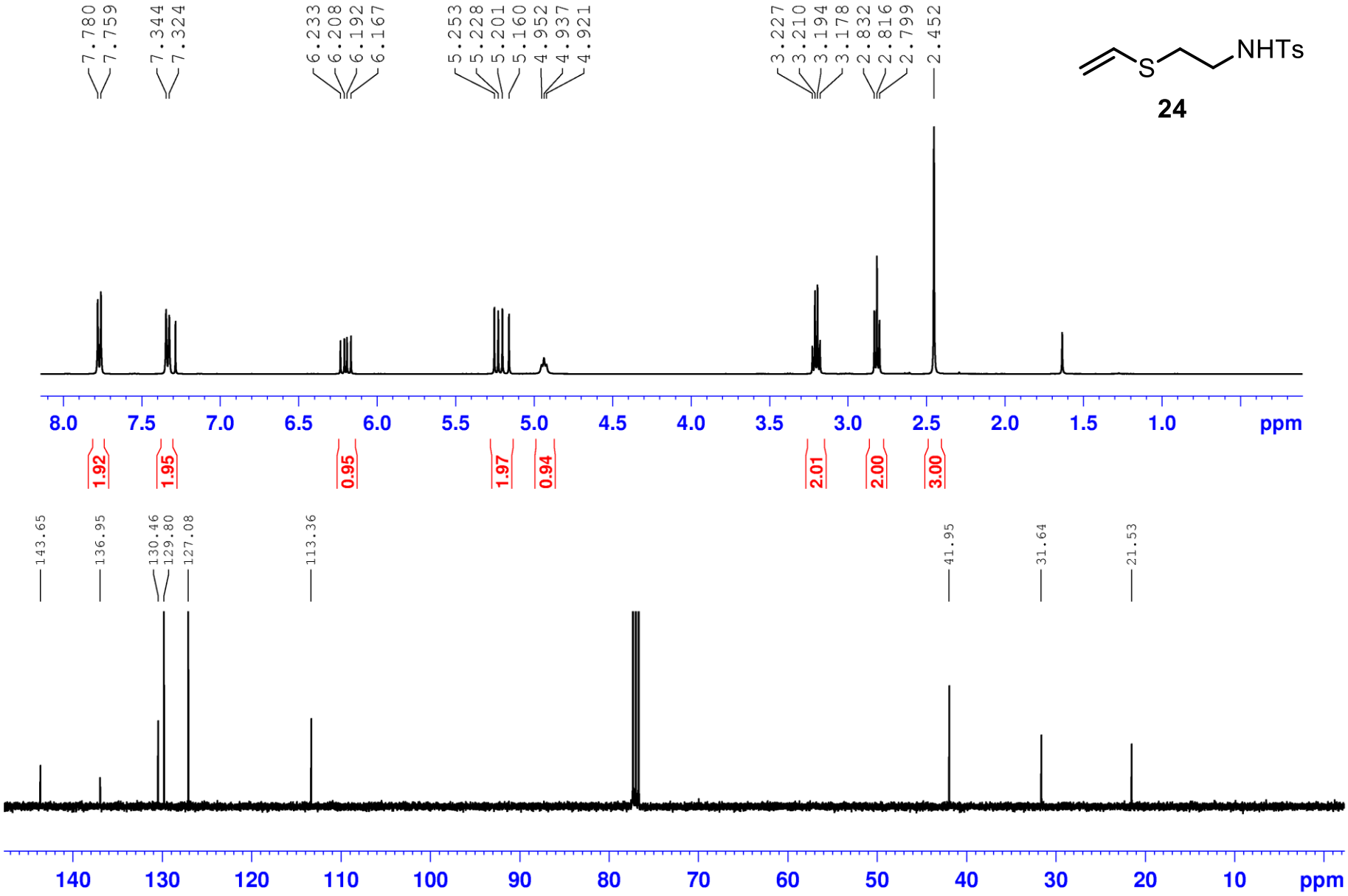
ppm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5.201
5.160
4.952
4.937
4.921
3.227
3.210
3.194
3.178
2.832
2.816
2.799
2.452
NHTs
S
24
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
ppm
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1.97
0.94
2.01
2.00
3.00
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130.46
129.80
127.08
113.36
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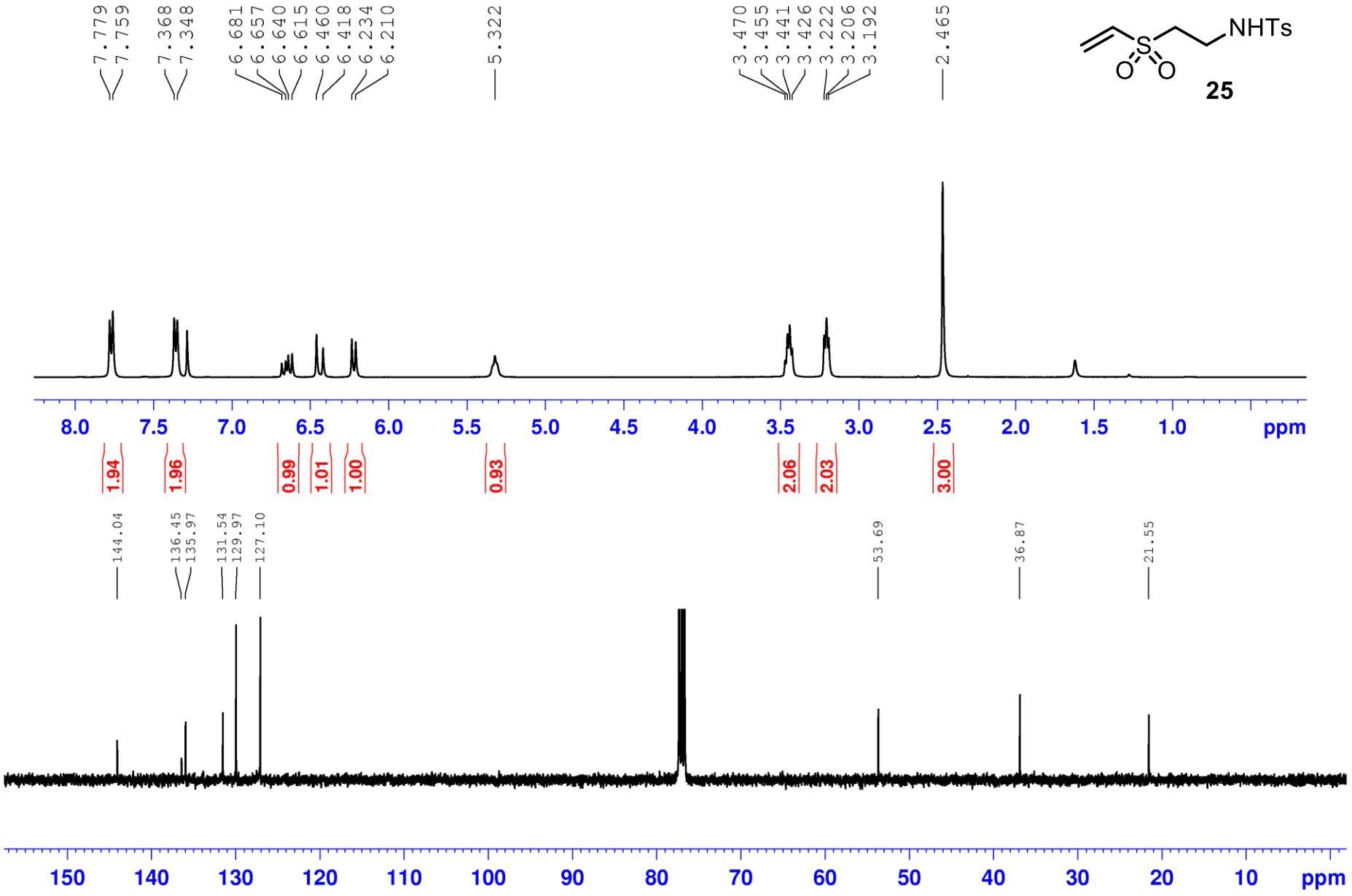
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3.455
3.441
3.426
3.222
3.206
3.192
2.465
NHTs
25
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7.0
6.5
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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0.99
1.01
1.00
0.93
2.06
2.03
3.00
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135.97
131.54
129.97
127.10
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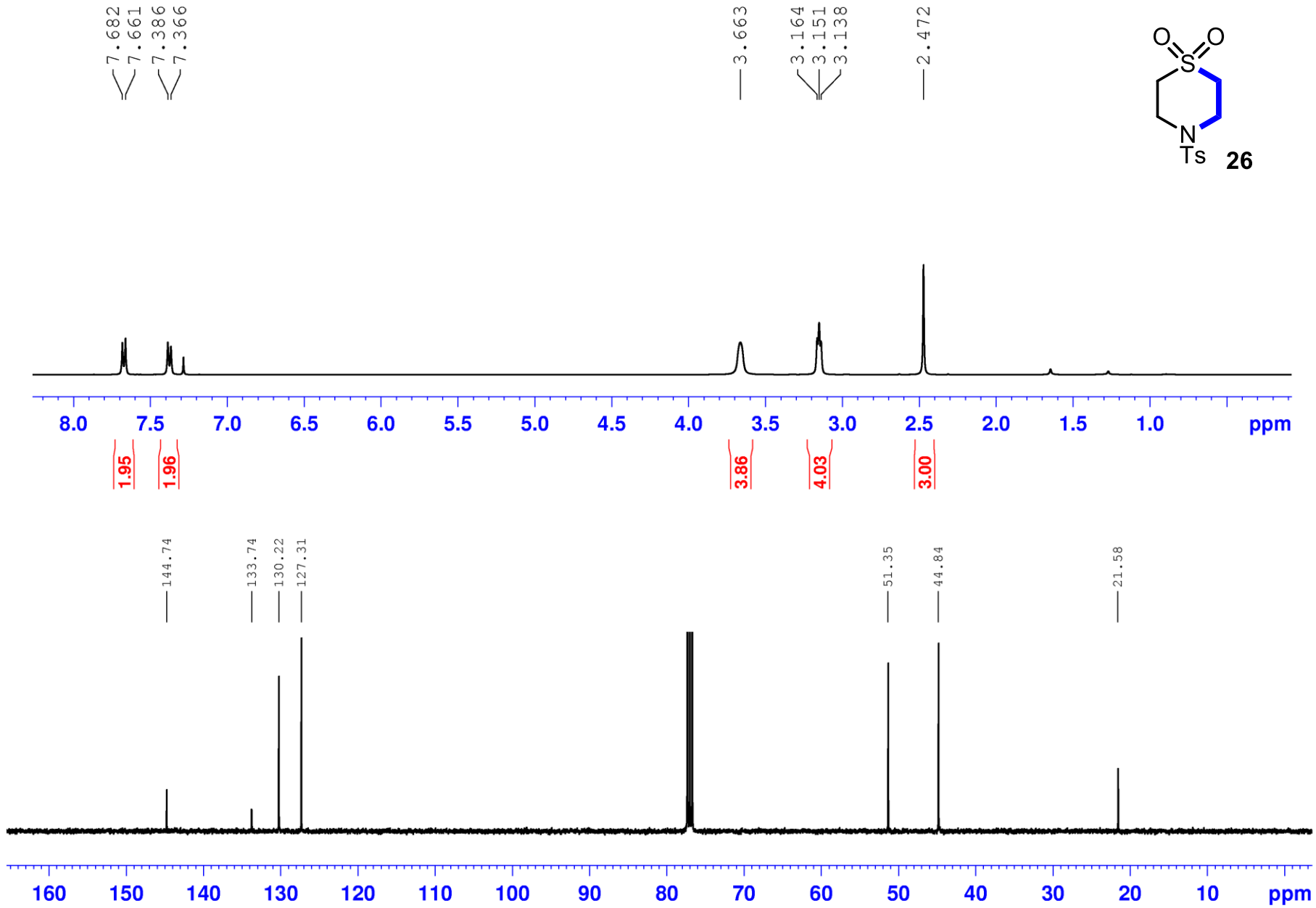
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3.138
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O
S
N
Ts
26
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.96
3.86
4.03
3.00
144.74
133.74
130.22
127.31
51.35
44.84
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150
140
130
120
110
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70
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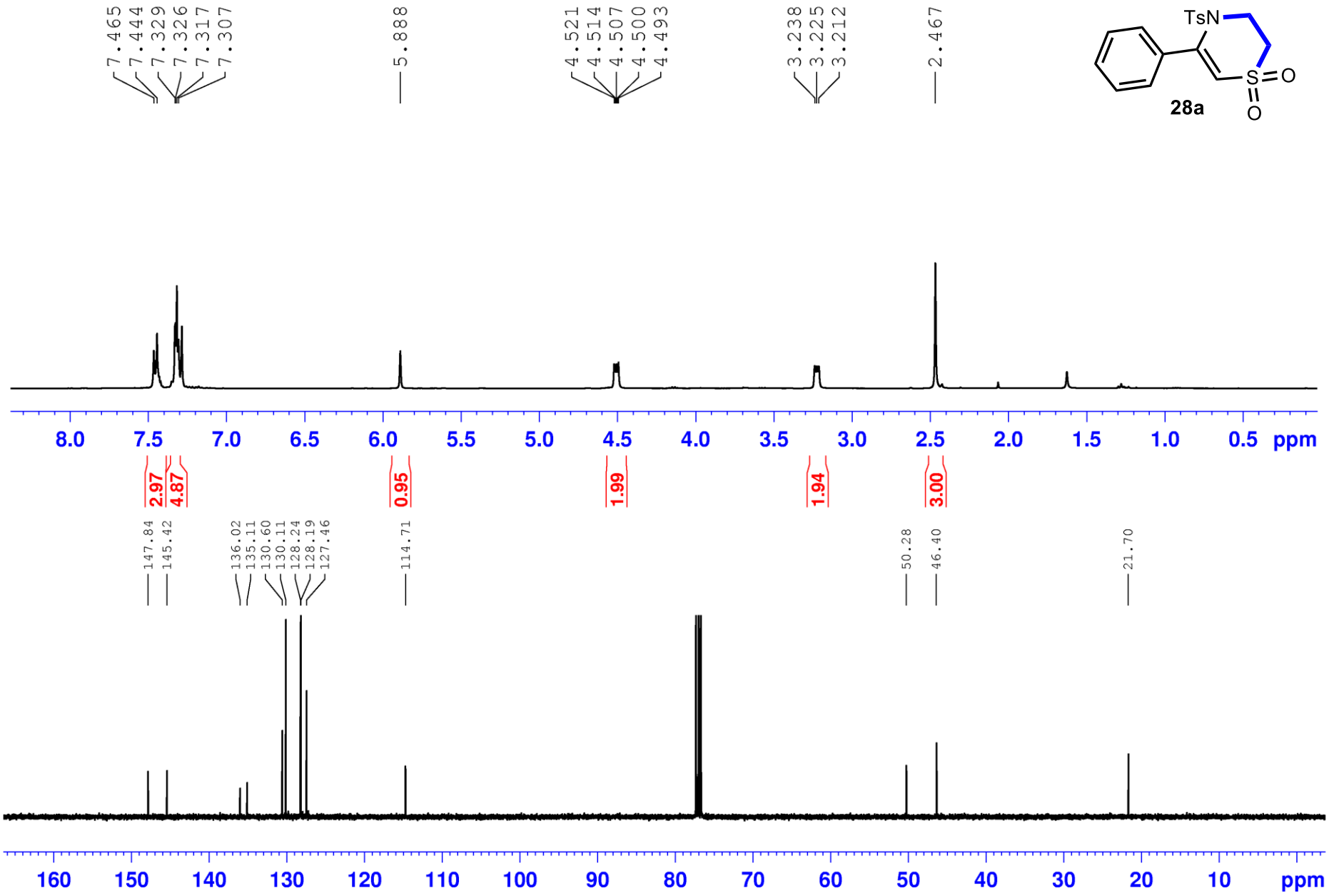
50
40
30
20
10
ppm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4.507
4.500
4.493
3.238
3.225
3.212
2.467
TsN
S
O
O
28a
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.97
4.87
0.95
1.99
1.94
3.00
147.84
145.42
136.02
135.11
130.60
130.11
128.24
128.19
127.46
114.71
50.28
46.40
21.70
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150
140
130
120
110
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70
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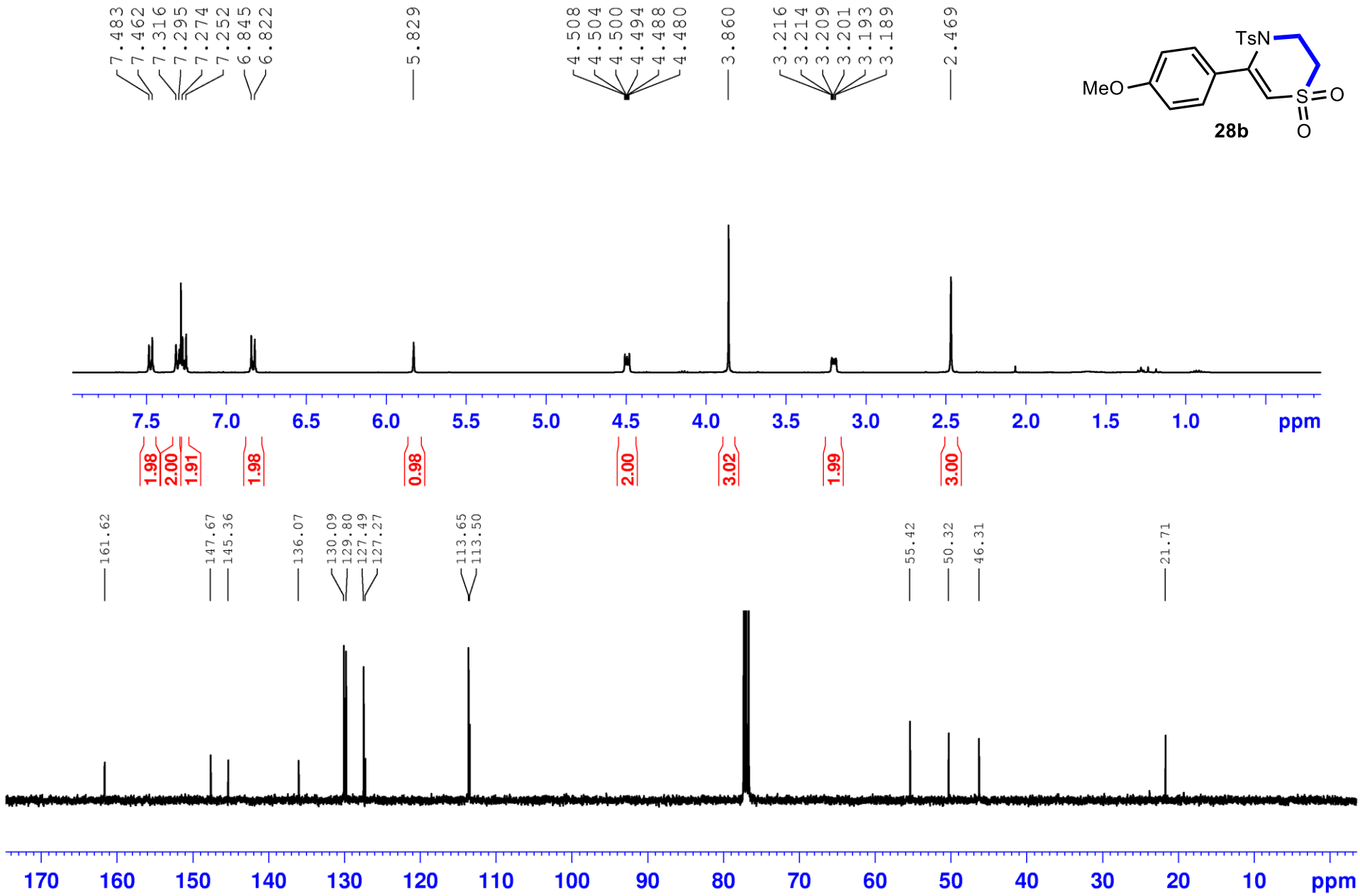
30
20
10
ppm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7.252
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6.822
5.829
4.508
4.504
4.500
4.494
4.488
4.480
3.860
3.216
3.214
3.209
3.201
3.193
3.189
2.469
TsN
MeO
S
O
O
28b
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.00
1.91
1.98
0.98
2.00
3.02
1.99
3.00
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147.67
145.36
136.07
130.09
129.80
127.49
127.27
113.65
113.50
55.42
50.32
46.31
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150
140
130
120
110
100
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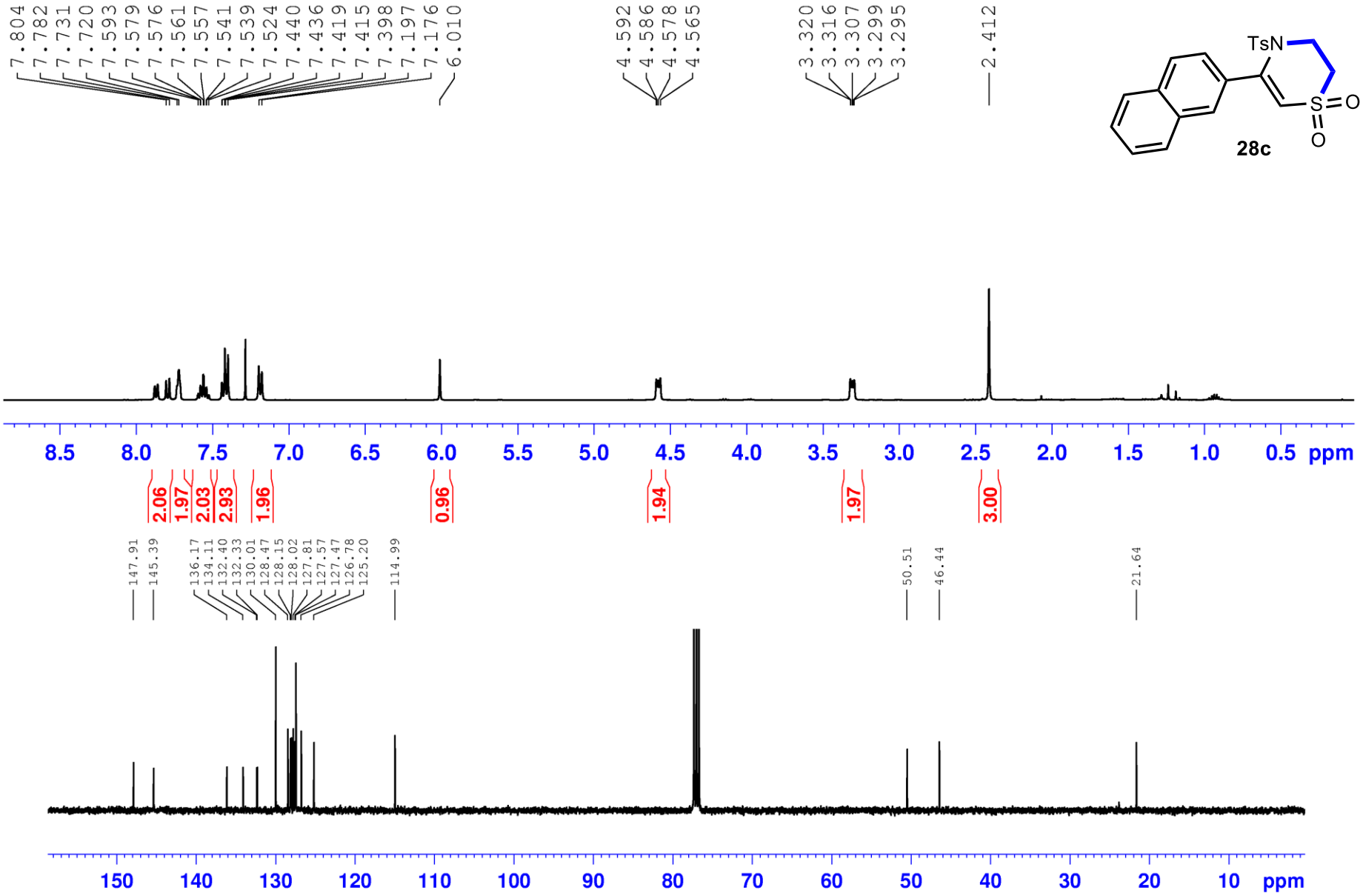
80
70
60
50
40
30
20
10
ppm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7.557
7.541
7.539
7.524
7.440
7.436
7.419
7.415
7.398
7.197
7.176
6.010
4.592
4.586
4.578
4.565
3.320
3.316
3.307
3.299
3.295
2.412
TsN
S
O
O
28c
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.06
1.97
2.03
2.93
1.96
0.96
1.94
1.97
3.00
147.91
145.39
136.17
134.11
132.40
132.33
130.01
128.47
128.15
128.02
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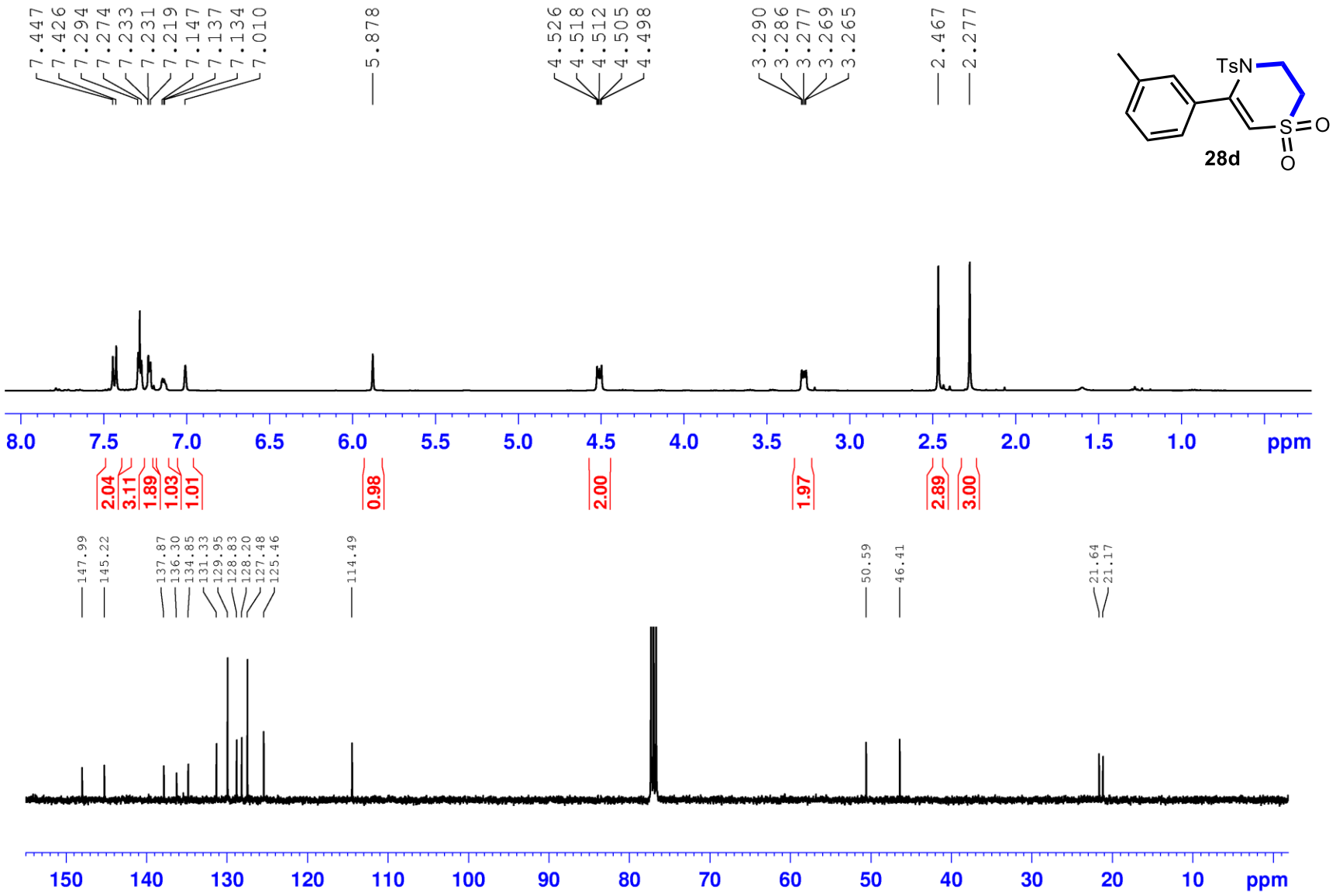
127.57
127.47
126.78
125.20
114.99
50.51
46.44
21.64
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.231
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7.147
7.137
7.134
7.010
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4.518
4.512
4.505
4.498
3.290
3.286
3.277
3.269
3.265
2.467
2.277
TsN
S
O
O
28d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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1.03
1.01
0.98
2.00
1.97
2.89
3.00
147.99
145.22
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136.30
134.85
131.33
129.95
128.83
128.20
127.48
125.46
114.49
50.59
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140
130
120
110
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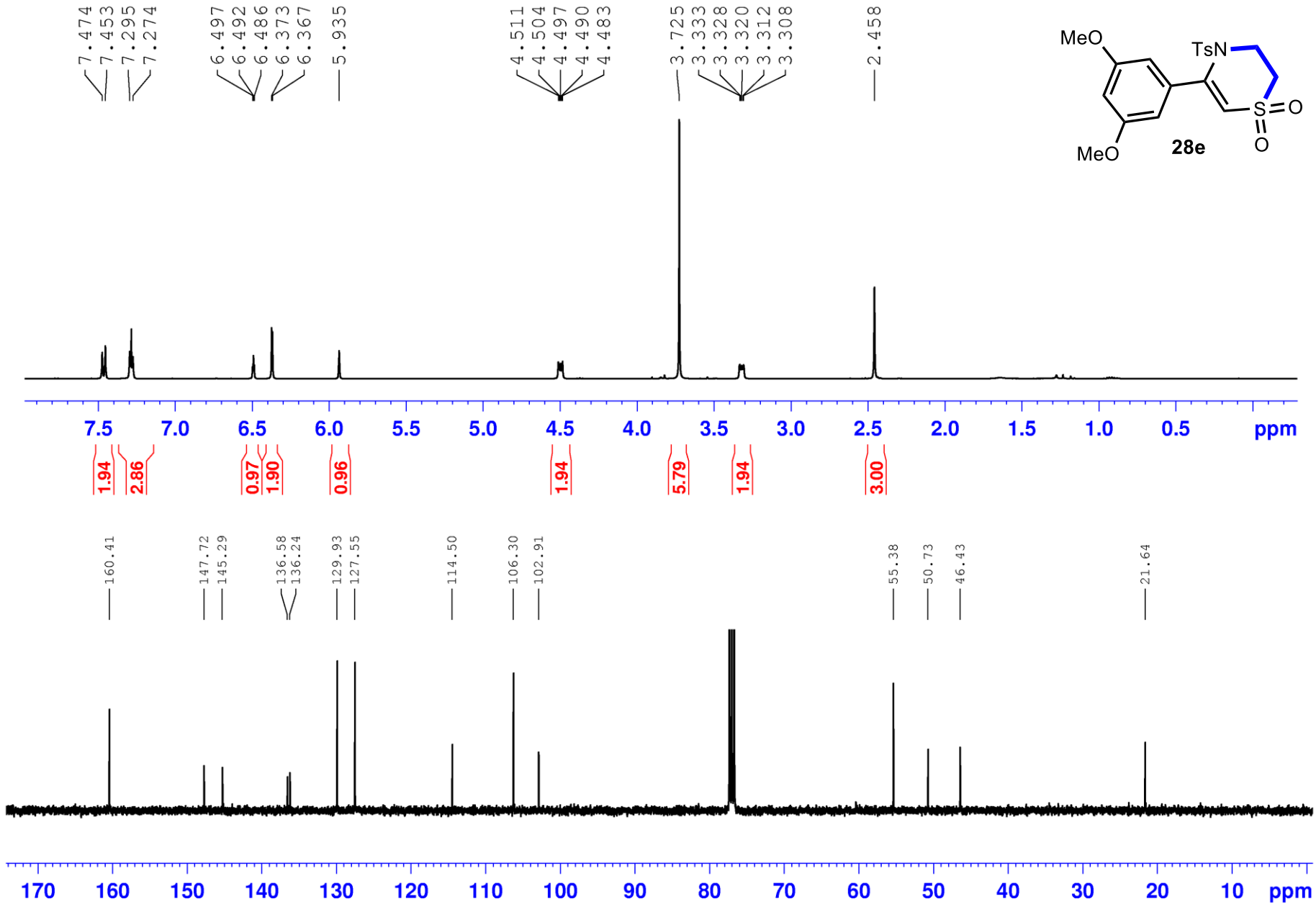
80
70
60
50
40
30
20
10
ppm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4.504
4.497
4.490
4.483
3.725
3.333
3.328
3.320
3.312
3.308
2.458
MeO
TsN
S
O
O
MeO
28e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
2.86
0.97
1.90
0.96
1.94
5.79
1.94
3.00
160.41
147.72
145.29
136.58
136.24
129.93
127.55
114.50
106.30
102.91
55.38
50.73
46.43
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150
140
130
120
110
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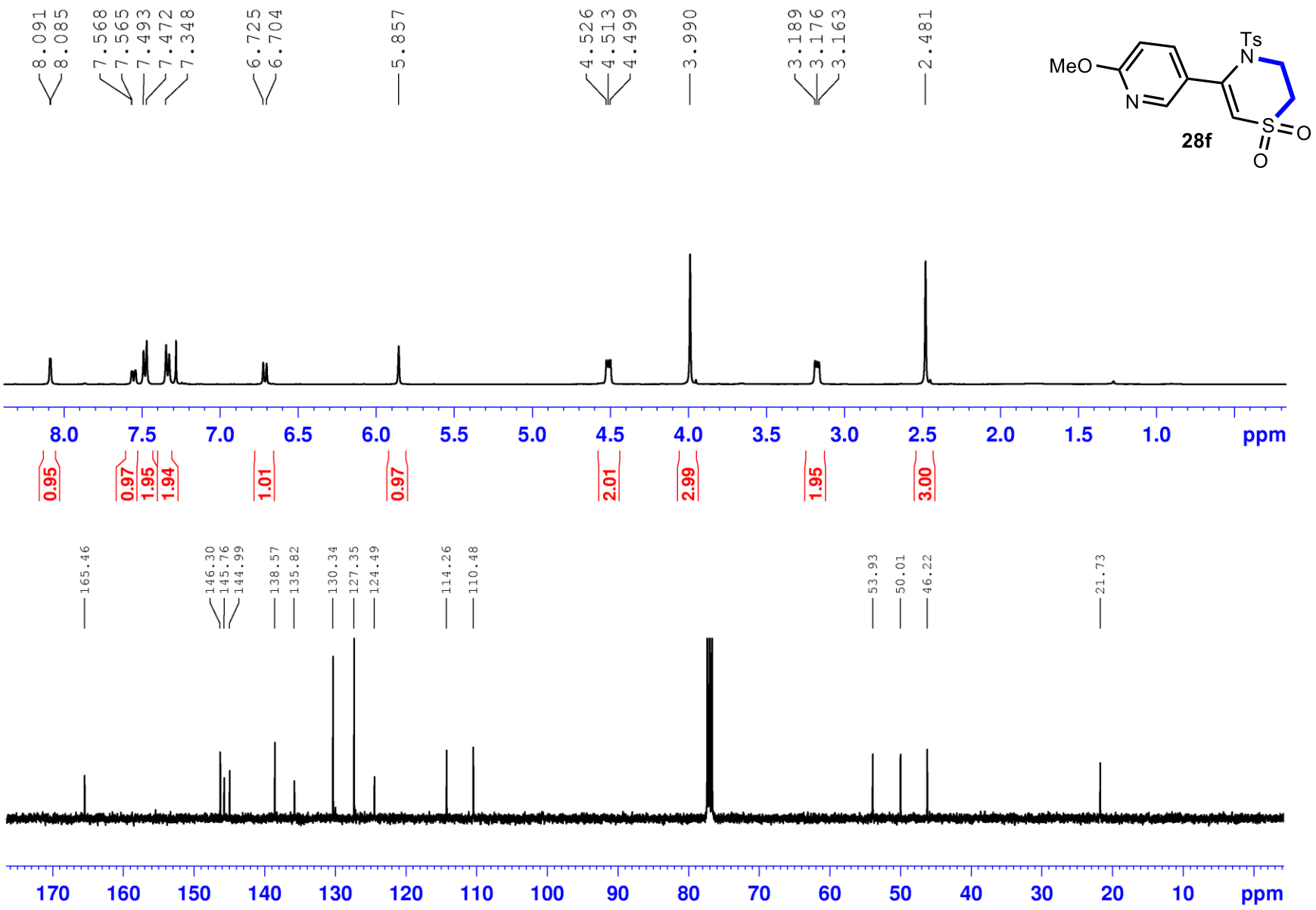
90
80
70
60
50
40
30
20
10
ppm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5.857
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4.513
4.499
3.990
3.189
3.176
3.163
2.481
MeO
N
Ts
N
S
O
O
28f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.95
0.97
1.95
1.94
1.01
0.97
2.01
2.99
1.95
3.00
165.46
146.30
145.76
144.99
138.57
135.82
130.34
127.35
124.49
114.26
110.48
53.93
50.01
46.22
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40
30
20
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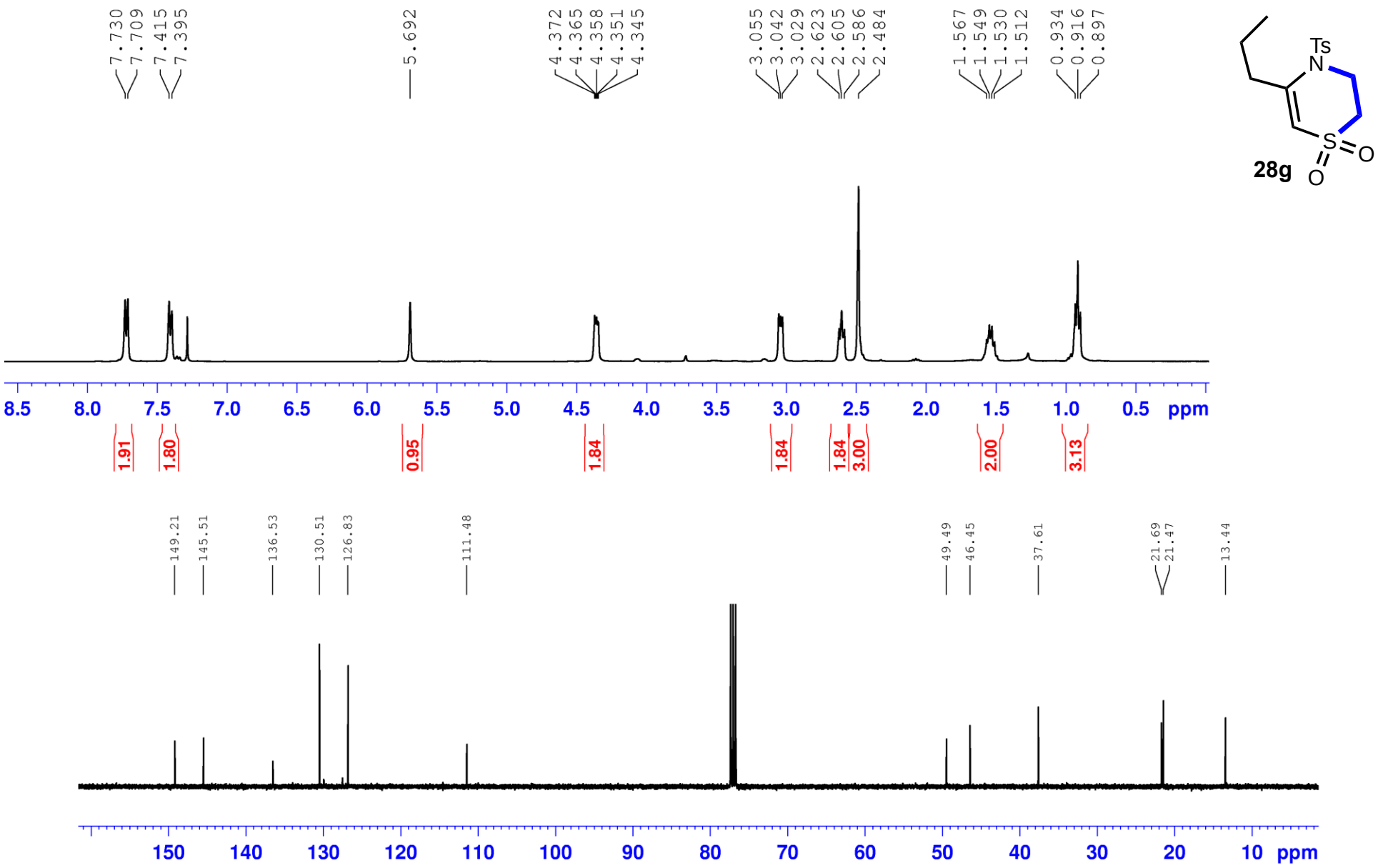
ppm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4.351
4.345
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3.042
3.029
2.623
2.605
2.586
2.484
1.567
1.549
1.530
1.512
0.934
0.916
0.897
Ts
N
S
O
O
28g
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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1.80
0.95
1.84
1.84
1.84
3.00
2.00
3.13
149.21
145.51
136.53
130.51
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49.49
46.45
37.61
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21.47
13.44
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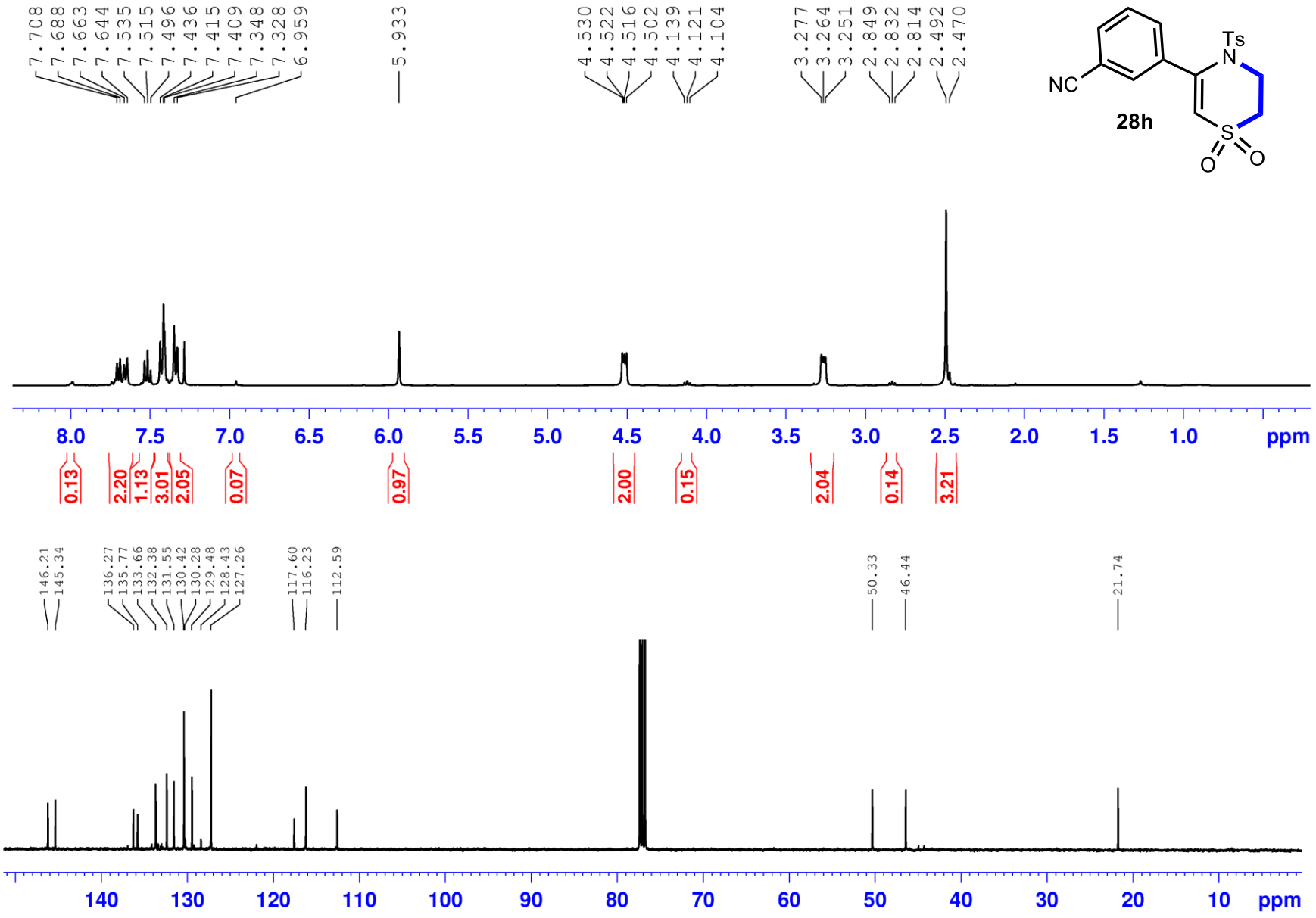
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7.348
7.328
6.959
5.933
4.530
4.522
4.516
4.502
4.139
4.121
4.104
3.277
3.264
3.251
2.849
2.832
2.814
2.492
2.470
NC
Ts
N
S
O
O
28h
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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2.20
1.13
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2.05
0.07
0.97
2.00
0.15
2.04
0.14
3.21
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145.34
136.27
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130.42
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129.48
128.43
127.26
117.60
116.23
112.59
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70
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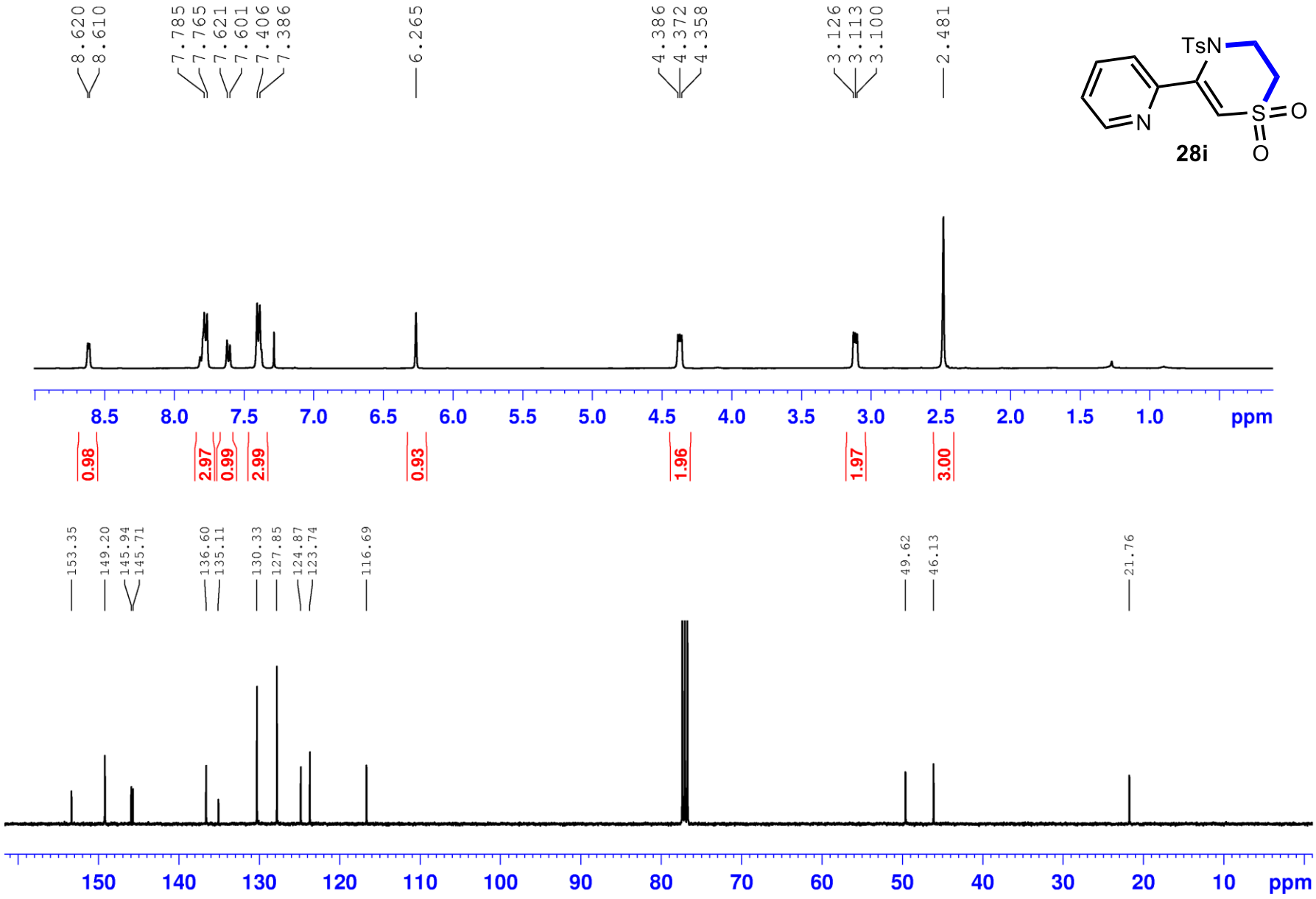
30
20
10
ppm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7.601
7.406
7.386
6.265
4.386
4.372
4.358
3.126
3.113
3.100
2.481
TsN
N
S
O
O
28i
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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0.99
2.99
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1.96
1.97
3.00
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145.94
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135.11
130.33
127.85
124.87
123.74
116.69
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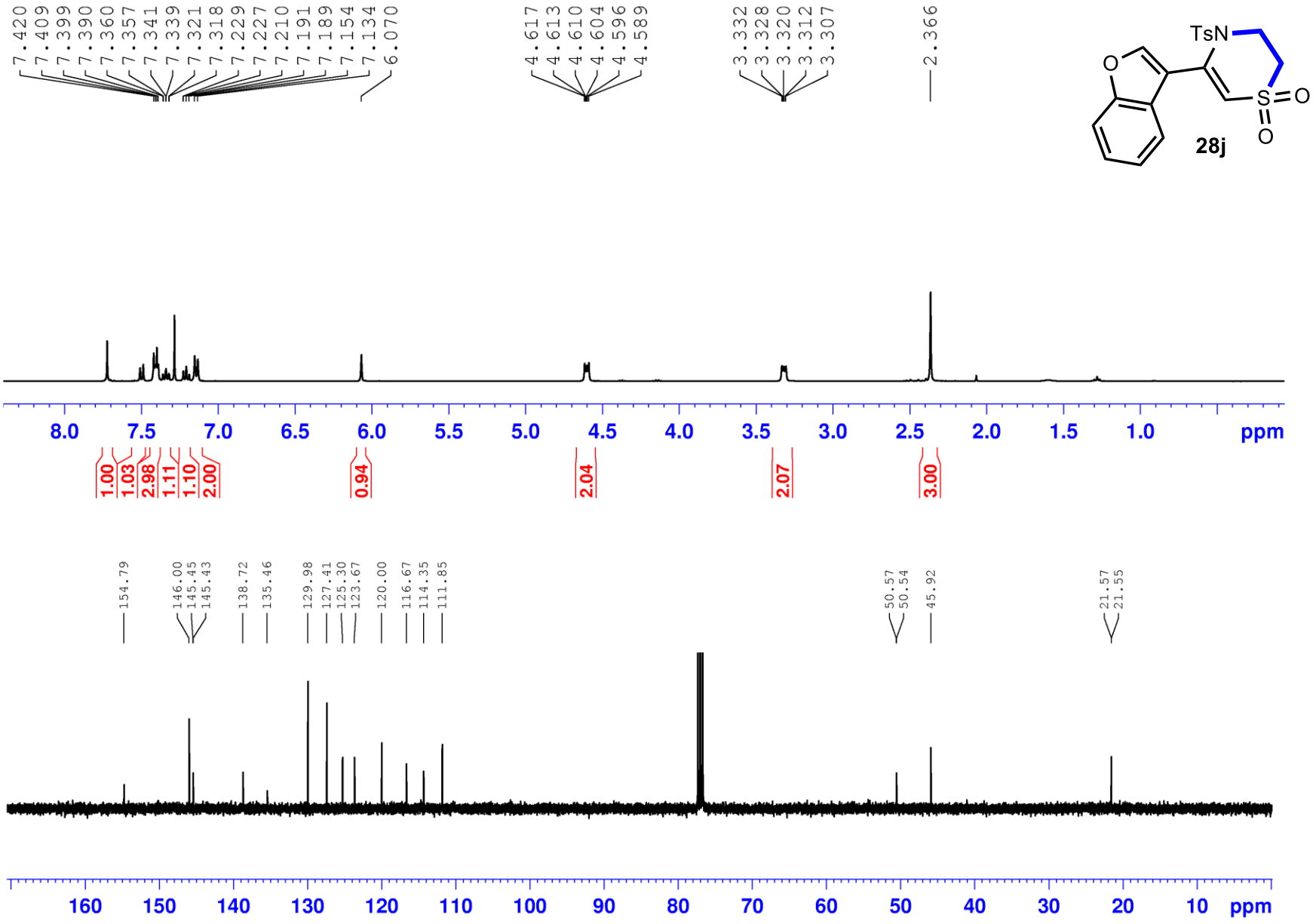
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7.318
7.229
7.227
7.210
7.191
7.189
7.154
7.134
6.070
4.617
4.613
4.610
4.604
4.596
4.589
3.332
3.328
3.320
3.312
3.307
2.366
TsN
O
S
O
O
28j
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.03
2.98
1.11
1.10
2.00
0.94
2.04
2.07
3.00
154.79
146.00
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138.72
135.46
129.98
127.41
125.30
123.67
120.00
116.67
114.35
111.85
50.57
50.54
45.92
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120
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70
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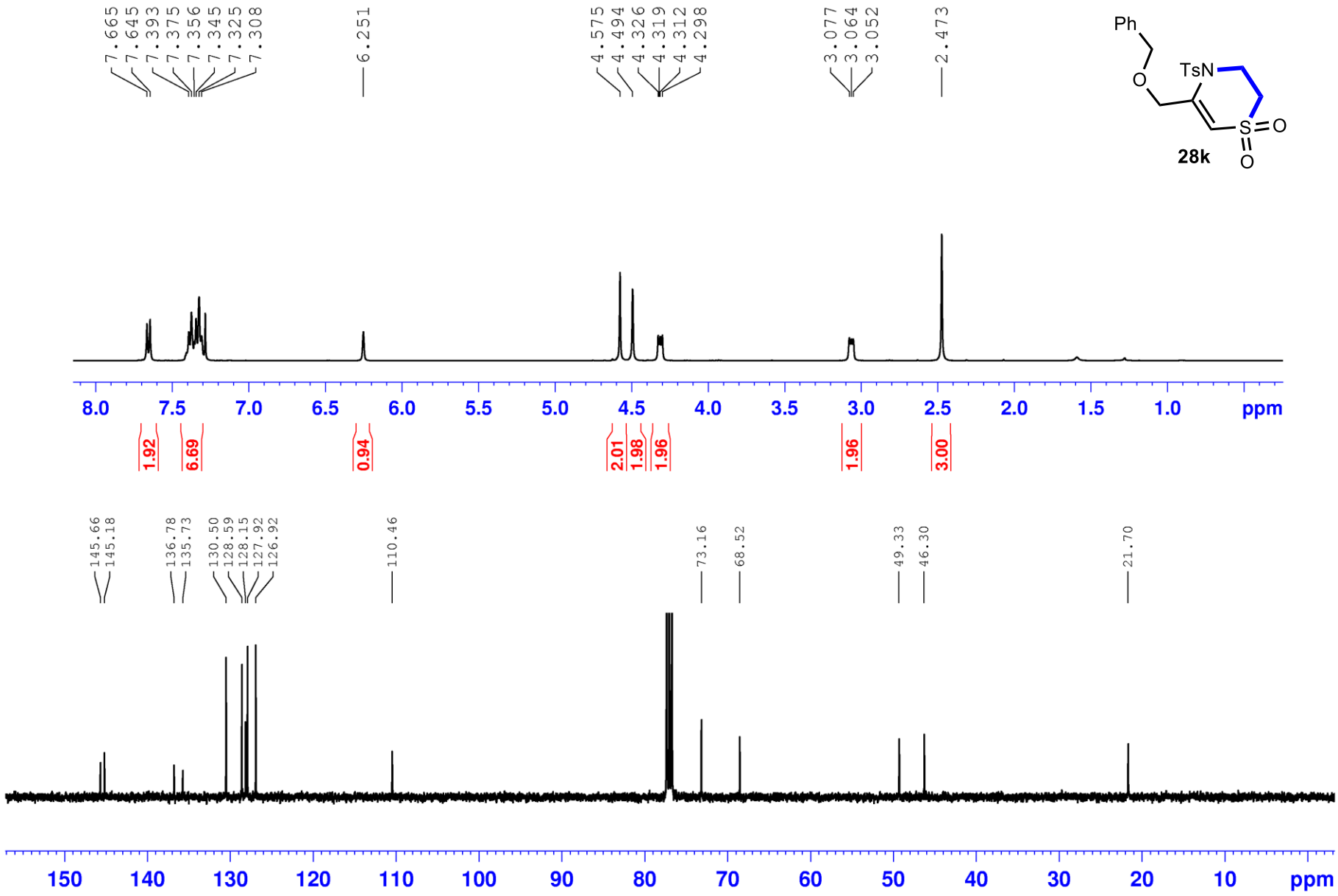
30
20
10
ppm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7.345
7.325
7.308
6.251
4.575
4.494
4.326
4.319
4.312
4.298
3.077
3.064
3.052
2.473
Ph
O
TsN
S
O
O
28k
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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6.69
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1.98
1.96
1.96
3.00
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136.78
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130.50
128.59
128.15
127.92
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68.52
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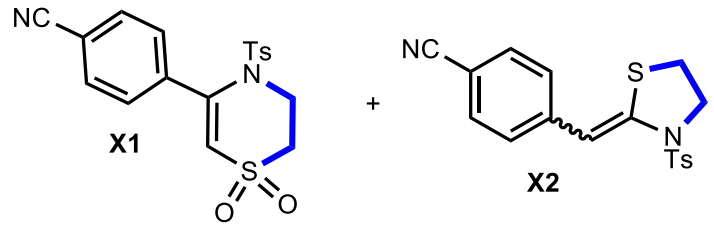
ppm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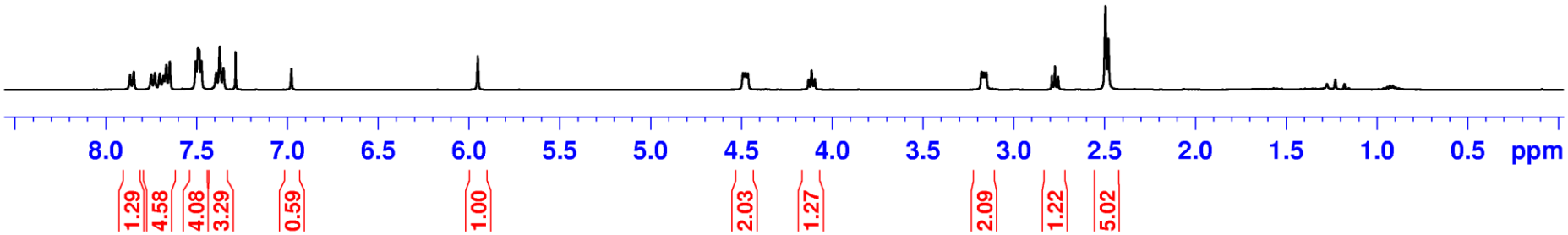
Ts
N
S
O
O
X1
+
NC
S
N
Ts
X2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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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4.08
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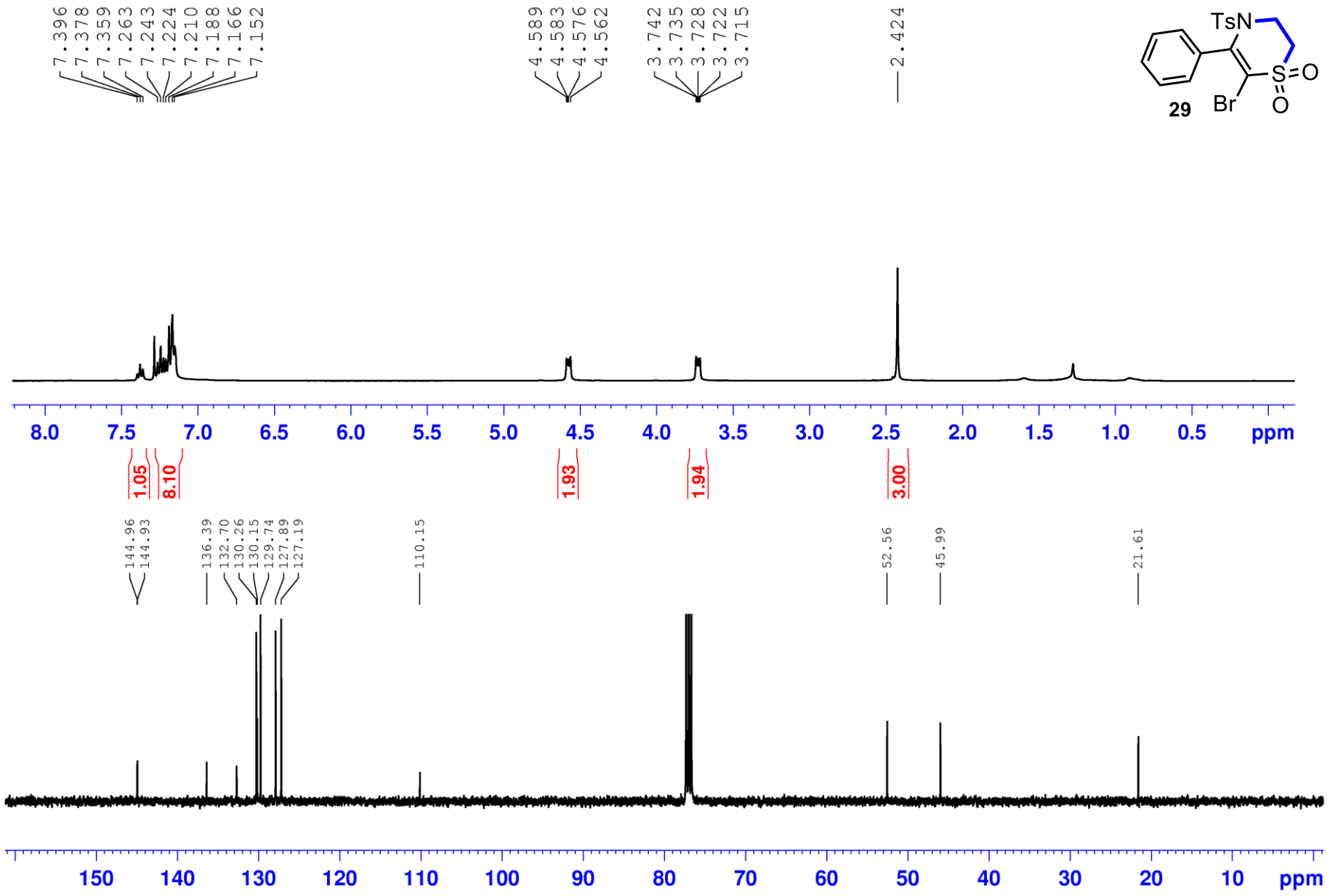
0.59
1.00
2.03
1.27
2.09
1.22
5.02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7.152
4.589
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3.742
3.735
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3.722
3.715
2.424
TsN
S=O
O
Br
29
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.05
8.10
1.93
1.94
3.00
144.96
144.93
136.39
132.70
130.26
130.15
129.74
127.89
127.19
110.15
52.56
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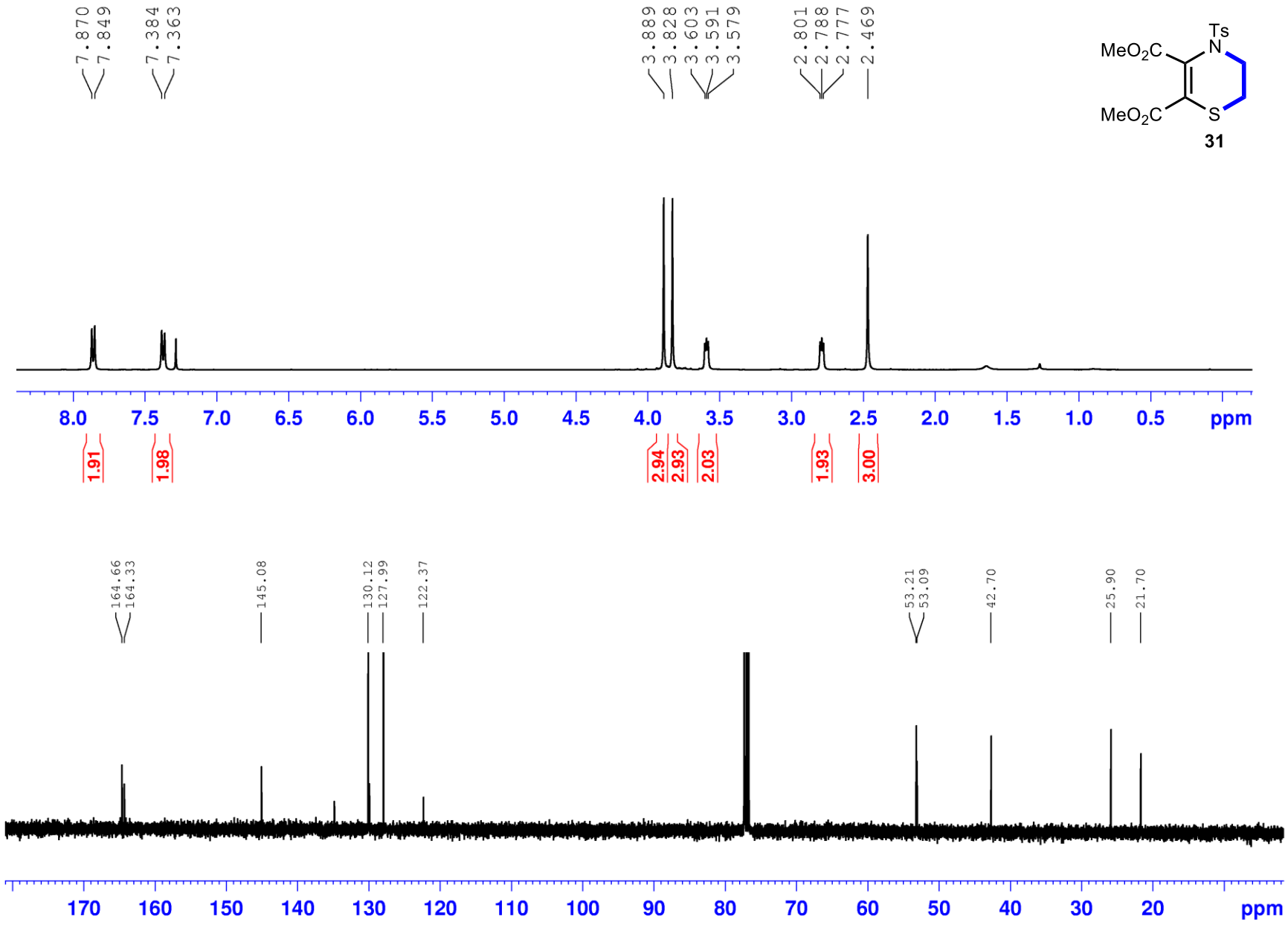
21.61
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.849
7.384
7.363
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3.828
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2.801
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2.777
2.469
Ts
N
MeO2C
MeO2C
S
31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.98
2.94
2.93
2.03
1.93
3.00
164.66
164.33
145.08
130.12
127.99
122.37
53.21
53.09
42.70
25.90
21.70
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm