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Gold superacid-catalyzed preparation of benzo[*c*]thiophenes

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Supporting Information

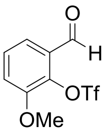
Contents

1. General experimental details

Commercially available products were used as received without any purification unless otherwise noted. Column chromatography was performed in a glass column with silica gel (particle size 70−200 µm, pore diameter 60 Å) using mixtures of ethyl acetate (EtOAc) and hexanes. NMR spectra were recorded at 300 and 400 MHz (^{1}H), 75 and 100 MHz (^{13}C) and 376 MHz (^{19}F) in $CDCl_3$ unless otherwise noted with tetramethylsilane (TMS) as internal standard. Low-resolution mass spectra were obtained with a single quadrupole mass spectrometer (ESI, 70 eV). High-resolution mass spectra were obtained with a time of flight (TOF) mass spectrometer (ESI or APCI). IR-spectra were obtained from a Perkin-Elmer Spectrum One BX FT-IR spectrophotometer.

2. Synthesis of 2-formyl-6-methoxyphenyl trifluoromethanesulfonate

2-Hydroxy-3-methoxybenzaldehyde was triflated according to a known literature procedure.[1] Spectral data are in accordance with reported values.[2]

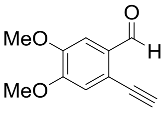


^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.70 (1H, s, C≡CH); 3.96 (3H, s, OCH_3); 7.31 (1H, dd, J = 8.1Hz, J = 1.6Hz, $CH_{arom.}$); 7.47 (1H, dd, J = 8.0Hz, J = 7.9Hz, $CH_{arom.}$); 7.53 (1H, dd, J = 8.0Hz, J = 1.6Hz, $CH_{arom.}$); 10.25 (1H, s, CHO). **Yield:** 90%.

3. Synthesis of *ortho*-ethynyl aromatic aldehydes

A number of 2-bromobenzaldehydes and 2-formyl-6-methoxyphenyl trifluoromethanesulfonate were subjected to a Sonogashira coupling and subsequent deprotection. 2-Ethynylbenzaldehyde is commercially available. Representative procedure: 5.32 g 2-bromo-4,5-dimethoxybenzaldehyde (21.2 mmol, 1 equiv), 0.30 g $PdCl_2(PPh_3)_2$ (0.43 mmol, 2 mol%) and 83 mg CuI (0.43 mmol, 2 mol%) were dissolved in 20 mL Et_3N in a 50 mL round-bottom flask under N_2-athmosphere. 3.70 mL TMS-acetylene was added in a dropwise fashion (26,0 mmol, 1.2 equiv) after which the reaction mixture was heated to reflux temperature. After completion of the reaction upon HPLC analysis, the solvent was removed *in vacuo* and the crude was then redissolved in ethyl acetate and filtered through a thick layer of Celite(r). The filtrate was concentrated *in vacuo*, then redissolved in methanol and TMS-deprotected by adding 0.99 g of K_2CO_3 (7.2 mmol, 0.33 equiv) and stirring for 15 minutes at room temperature. The solvent was removed *in vacuo* and the crude was dissolved in a $NaHCO_3$ solution with ethyl acetate and extracted 3 times (3x 20 mL). The combined organic fractions were dried using $MgSO_4$ and concentrated in vacuo. 3.83 g (20.1 mmol, 95%) of **1f** was obtained. The spectral data, if available, were in accordance with reported values. If necessary column chromatography or recrystallization was performed.

2-ethynyl-4,5-dimethxoybenzaldehyde **1f**:[3]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.39 (1H, s, C≡CH); 3.95 (3H, s, $C_{q\ arom.}OCH_3$); 3.97 (3H, s, $C_{q\ arom.}OCH_3$); 7.03 (1H, s, $CH_{arom.}$); 7.41 (1H, s, $CH_{arom.}$); 10.39 (1H, s, CHO). **Yield:**

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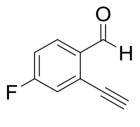
[1] L. J. Goossen, N. Rodríguez, C. Linder, *J. Am. Chem. Soc.*, 2008**, 130**, 15248.

[2] J. M. Saá, G. Martorell, A. García-Raso, *J. Org. Chem.*, 1992, **57**, 678.

[3] M. J. Kim, Y. R. Choi, H.-G. Jeon, P. Kang, M.-G. Choi, K.-S. Jeong, *Chem. Commun.*, 2013, **49**, 11412.

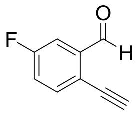
95%.

2-ethynyl-4-fluorobenzaldehyde **1b**:[4]



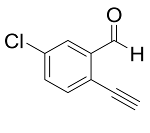
^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.51 (1H, s, $C\equiv CH$); 7.19 (1H, ddd, J = 8.6Hz, $^4J_{HF}$ = 8.4Hz, J = 2.5Hz, $CH_{arom.}$); 7.30 (1H, dd, $^4J_{HF}$ = 8.8Hz, J = 2.5Hz, $CH_{arom.}$); 7.97 (1H, dd, J = 8.6Hz, J_{HF} = 5.8Hz, $CH_{arom.}$); 10.46 (1H, s, CHO). **Yield:** 92%.

2-ethynyl-5-fluorobenzaldehyde **1c**:[4]



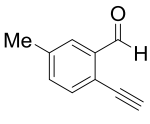
^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.44 (1H, s, $C\equiv CH$); 7.29 (1H, dd, $^3J_{HF}$ = 8.4Hz, J = 2.8Hz, $CH_{arom.}$); 7.58-7.64 (2H, m, 2x $CH_{arom.}$); 10.49 (1H, d, $^5J_{HF}$ = 3.2 Hz, CHO). **Yield:** 92%.

5-chloro-2-ethynylbenzaldehyde **1d**:[4]



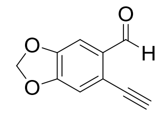
^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.50 (1H, s, $C\equiv CH$); 7.53 (1H, dd, J = 8.3Hz, J = 2.1Hz, $CH_{arom.}$); 7.56 (1H, dd, J= 8.3Hz, J = 0.6 Hz, $CH_{arom.}$); 7.90 (1H, dd, J = 2.1Hz, J = 0.6Hz, $CH_{arom.}$); 10.48 (1H, s, CHO). **Yield:** 94%.

2-ethynyl-5-methylbenzaldehyde **1e**:



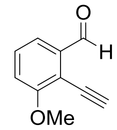
^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.38 (3H, s, CH_3); 3.41 (1H, s, $C\equiv CH$); 7.26 (1H, d, J = 8.3Hz, $CH_{arom.}$); 7.40 (1H, s, $CH_{arom.}$); 7.81 (1H, d, J = 8.3Hz, $CH_{arom.}$); 10.45 (1H, s, CHO). **Yield:** 72%.

6-ethynylbenzo[*d*][1,3]dioxole-5-carbaldehyde **1g**:[5]



^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.37 (1H, s, $C\equiv CH$); 6.08 (2H, s, CH_2); 6.99 (1H, s, $CH_{arom.}$); 7.35 (1H, s, $CH_{arom.}$); 10.38 (1H, s, CHO). **Yield:** 60%.

2-ethynyl-3-methoxybenzaldehyde **1h**:



^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.70 (1H, s, $C\equiv CH$); 3.96 (3H, s, OCH_3); 7.14 (1H, dd, J = 8.1Hz, J = 0.9Hz, $CH_{arom.}$); 7.44 (1H, dd, J = 8.1Hz, J = 7.9Hz, $CH_{arom.}$); 7.54 (1H, dd, J = 7.9Hz, J = 0.9Hz, $CH_{arom.}$); 10.55 (1H, s, CHO). **Yield:** 76%.

3-ethynylthiophene-2-carbaldehyde **1i**:[4]

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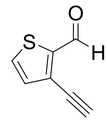
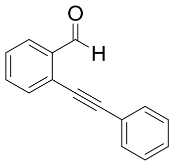
[4] M. Li, P. Xing, Z. Huang, B. Jiang, *Chin. J. Chem.*, 2013, **31**, 49.

[5] D. B. Grotjahn, K. P. C. Vollhardt, *Synthesis*, 1993, **1993**, 579.



^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.46 (1H, s, C≡CH); 7.22 (1H, d, J = 5.0Hz, CH$_{arom.}$); 7.68 (1H, dd, J = 5.0Hz, J = 1.3Hz, CH$_{arom.}$); 10.15 (1H, d, J = 1.3Hz, CHO). **Yield:** 87%.

2-(phenylethynyl)benzaldehyde **1j**:[6] instead of TMS-acetylene, phenylacetylene was used for the Sonogashira coupling.

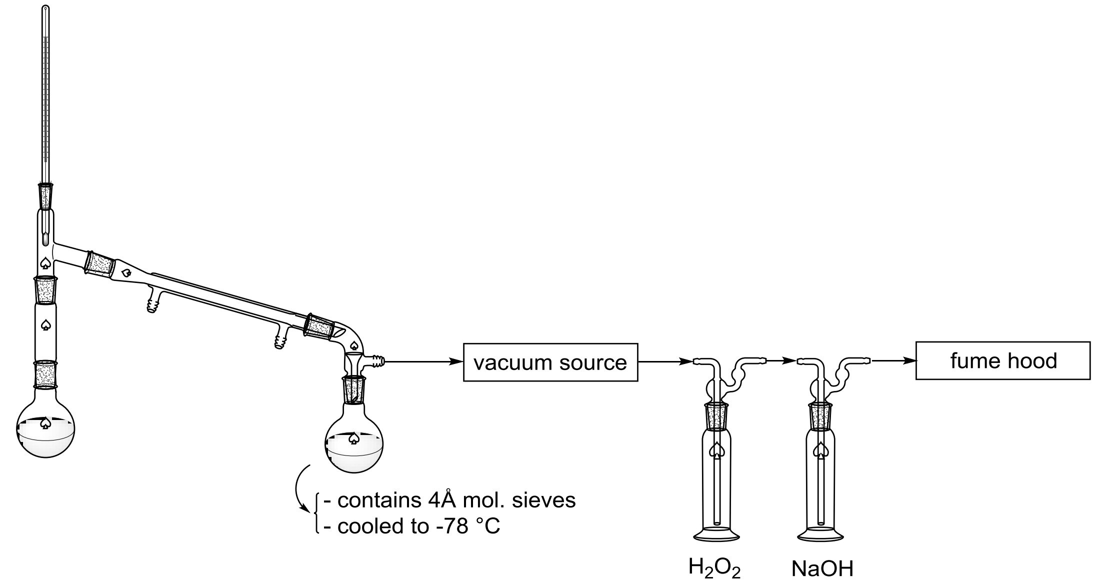


^{1}H-NMR (400 MHz, CDCl$_3$): δ 7.38-7.41 (3H, m, 3x CH$_{arom.}$); 7.44-7.48 (1H, m, CH$_{arom.}$); 7.55-7.67 (4H, m, 4x CH$_{arom.}$); 7.96 (1H, d, J = 8.2Hz, CH$_{arom.}$); 10.66 (1H, d, J = 0.8 Hz, CHO). **Yield:** 72%.

4. Synthesis of diallyl thioacetals

4.1 Distillation of allyl mercaptan

The following setup was used, as depicted in the figure below, due to the very pungent, unpleasant smell of the product: a round-bottom flask filled with allyl mercaptan was equipped with a vigreux column, a thermometer and standard distillation piece. To this distillation piece a water cooler was attached, which ended in a dry round-bottom flask filled with 4Å molecular sieves that was cooled to -78 °C. A pump was attached to the setup and all connections were sealed with vacuum grease. The outlet of the pump was connected to two washing flasks, the first one containing a H_2O_2 solution and the other one containing a 2M NaOH solution in order to oxidize or deprotonate any residual allyl mercaptan. Evidently, the distillation was performed in a working fume hood. After the distillation, all glassware was cleaned using a H_2O_2 solution. Allyl mercaptan was obtained as a colourless, clear liquid (33-35 °C, 380 mbar) and was stored at -20 °C under an inert atmosphere.



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[6] S. Zhu, H. Huang, Z. Zhang, T. Ma, H. Jiang, *J. Org. Chem.*, 2014, **79**, 6113.

4.2 Synthesis of crotyl mercaptan

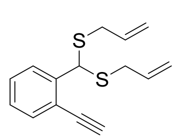
Crotyl mercaptan (but-2-ene-1-thiol) was prepared according to a literature procedure and used without further purification.[7] The same precautions as with the distillation of allyl mercaptan were taken due to the very pungent smell of the product.

4.3 Synthetic procedures

Method A: representative example: in a 25 mL round-bottom flask 0.4 g (3.1 mmol, 1 equiv) 2-ethynylbenzaldehyde and 0.5 g (6.8 mmol, 2.2 equiv) freshly distilled allyl mercaptan (380 mbar, 33-35 °C – CAUTION: very pungent smell, take precautions during distillation) were dissolved in 4 mL toluene and 2 mL acetic acid. The flask was cooled to 0 °C and 0.44 g (3.1 mmol, 1 equiv) $BF_3.OEt_2$ was added in a dropwise fashion. The reaction mixture was stirred at room temperature and the progress was monitored using HPLC. After completion, it was diluted with 8 mL dichloromethane and washed three times with water (8 mL). After drying with $MgSO_4$ and removal of the volatiles, the crude was purified by means of column chromatography. 0.67 g (2.57 mmol, 83%) of product was obtained.

Method B: representative example: in a 25 mL round-bottom flask 0.2 g (1.1 mmol, 1 equiv) 2-ethynyl-4,5-dimethoxybenzaldehyde and 34 mg (0.21 mmol, 0.2 equiv) anhydrous Cu(II)SO_4 were dissolved in 10 mL dry dichloromethane under N_2-athmosphere. 0.19 mL (2.31 mmol, 2.2 equiv) freshly distilled allyl mercaptan (380 mbar, 33-35 °C – CAUTION: very pungent smell, take precautions during distillation) was added to this flask in a dropwise fashion and the reaction mixture was heated to reflux temperature. The reaction progress was monitored using HPLC. After completion, the mixture was poured into water and extracted thrice using dichloromethane (3x 10 mL). After drying with $MgSO_4$ and removal of the volatiles, the crude was purified by means of column chromatography. 0.12 g (0.37 mmol, 34%) of product was obtained.

((2-ethynylphenyl)methylene)bis(allylsulfane) **2a**, prepared by method A:



^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.09 (2H, dd, J = 13.9Hz, J = 7.2Hz, 2 x $SC\underline{H}_aCH_b$); 3.29 (2H, dd, J = 13.9Hz, J = 7.2Hz, 2 x $SCH_aC\underline{H}_b$); 3.33 (1H, s, C≡CH); 5.08 (2H, dd, J = 9.9Hz, J = 1.1Hz, 2 x $CH{=}C\underline{H}_EH_Z$); 5.14 (2H, dd, J = 16.9Hz, J = 1.1Hz, 2 x $CH{=}CH_E\underline{H}_Z$); 5.47 (1H, s, CHS_2); 5.81 (2H, ddt, J = 16.9Hz, J = 9.9Hz, J = 7.2Hz, 2 x $C\underline{H}{=}CH_2$); 7.21 (1H, t, J = 7.7Hz, $CH_{arom.}$); 7.37 (1H, t, J = 7.7Hz, $CH_{arom.}$); 7.46 (1H, d, J = 7.7Hz, $CH_{arom.}$); 7.76 (1H, d, J = 7.7Hz, $CH_{arom.}$). **^{13}C-NMR (75 MHz, $CDCl_3$):** δ 35.6 (2 x SCH_2); 48.3 (CHS_2); 81.3 ($\underline{C}$≡CH); 82.9 (C≡$\underline{C}$H); 117.8 (2 x $CH{=}\underline{C}H_2$); 121.0 ($\underline{C}_{q\ arom.}$C≡CH); 127.6 ($CH_{arom.}$); 128.5 ($CH_{arom.}$); 129.5 ($CH_{arom.}$); 132.8 ($CH_{arom.}$); 133.7 (2 x $\underline{C}H{=}CH_2$); 142.8 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 187.1 (M - $[SCH_2CH{=}CH_2]^-$, 75). **HRMS (ESI):** m/z calcd for $C_{15}H_{16}S_2{+}H^+$ = 261.0771, found = 261.0765. **IR (cm^{-1}) ν $_{max}$:** 1634 ($CH{=}CH_2$); 3288 (C≡CH). **Chromatography:** hexanes/EtOAc 98/2. **R_f** = 0.21. **Yield:** 83%.

((2-ethynyl-4-fluorophenyl)methylene)bis(allylsulfane) **2b**, prepared by method A:

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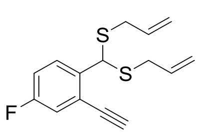
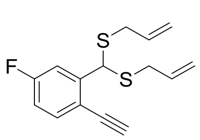
[7] C. G. Moore, B. R. Trego, *Tetrahedron*, 1962, **18**, 205.



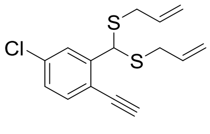
^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.08 (2H, dddd, J = 13.7Hz, J = 7.0Hz, J = 1.2Hz, J = 0.9Hz, 2x$SC\underline{H}_aCH_b$); 3.29 (2H, dddd, J = 13.7Hz, J = 7.3Hz, J = 1.2Hz, J = 0.9Hz, 2 x $SCH_aC\underline{H}_b$); 3.36 (1H, s, C≡CH); 5.08 (2H, dddd, J = 9.9Hz, J = 1.4Hz, J = 0.9Hz, J = 0.9Hz, 2 x $CH{=}C\underline{H}_EH_Z$); 5.13 (2H, ddt, J = 17.0Hz, J = 1.4Hz, J = 1.2Hz, J = 1.2Hz, 2x$CH{=}CH_E\underline{H}_Z$); 5.40 (1H, s, CHS_2); 5.79 (2H, dddd, J = 17.0Hz, J = 9.9Hz, J = 7.3Hz, J = 7.0Hz, 2x$C\underline{H}{=}CH_2$); 7.09 (1H, ddd, J = 8.6Hz, $^4J_{HF}$=8.4Hz, J = 2.7Hz, $CH_{arom.}$); 7.14 (1H, dd, $^4J_{HF}$ = 8.9Hz, J = 2.7Hz, $CH_{arom.}$); 7.75 (1H, dd, J = 8.6Hz, J_{HF} = 5.7Hz, $CH_{arom.}$). **^{13}C-NMR (100 MHz, CDCl$_3$):** δ 35.5 (2xSCH_2); 47.4 (CHS_2); 80.1 ($\underline{C}$≡CH); 83.7 (C≡$\underline{C}$H); 117.0 (d, $^2J_{CF}$ = 21.5Hz, $CH_{arom.}$); 117.8 (2 x $CH{=}\underline{C}H_2$); 119.0 (d, $^2J_{CF}$ = 23.4Hz, $CH_{arom.}$); 122.6 (d, $^3J_{CF}$ = 9.6Hz, $C_{q\ arom.}$); 130.4 (d, $^3J_{CF}$ = 8.9Hz, $CH_{arom.}$); 133.6 (2 x $\underline{C}H{=}CH_2$); 138.4 (d, $^4J_{CF}$ = 3.3Hz, $\underline{C}_{q\ arom.}CHS_2$); 161.3 (d, $^1J_{CF}$ = 247.7Hz, $C_{q\ arom.}F$). **^{19}F-NMR (376 MHz, CDCl$_3$): δ** -114.52 to -114.59 (m). **MS (ESI): m/z (%):** 205.0 (M - $[SCH_2CH{=}CH_2]^-$, 100). **HRMS (ESI):** m/z calcd for $C_{12}H_{10}FS^+$ (M - $[SCH_2CH{=}CH_2]^-$) = 205.0482, found = 205.0478. **IR (cm^{-1}) ν $_{max}$:** 1265; 1487; 1578; 1635 ($CH{=}CH_2$); 2912; 3081; 3296. **Chromatography:** hexanes/EtOAc 99/1. **R$_f$** = 0.21. **Yield:** 75%.

((2-ethynyl-5-fluorophenyl)methylene)bis(allylsulfane) **2c**, prepared by method A:



^{1}H-NMR (300 MHz, CDCl$_3$): δ 3.09 (2H, dd, J = 13.7Hz, J = 7.2Hz, 2 x $SC\underline{H}_aCH_b$); 3.30 (2H, dd, J = 13.7Hz, J = 7.2Hz, 2 x $SCH_aC\underline{H}_b$); 3.31 (1H, s, C≡CH); 5.08 (2H, dd, J = 9.9Hz, J = 1.6Hz, 2 x $CH{=}C\underline{H}_EH_Z$); 5.13 (2H, dd, J = 17.1Hz, J = 1.1Hz, 2 x $CH{=}CH_E\underline{H}_Z$); 5.40 (1H, d, $^5J_{HF}$ = 1.7Hz, CHS_2); 5.80 (2H, ddt, J = 17.1Hz, J = 9.9Hz, J = 7.2Hz, 2 x $C\underline{H}{=}CH_2$); 6.93 (1H, ddd, $^3J_{HF}$ = 8.3Hz, J = 8.3Hz, J = 2.7Hz, $CH_{arom.}$); 7.44 (1H, dd, J = 8.3Hz, $^4J_{HF}$ = 5.5Hz, $CH_{arom.}$); 7.50 (1H, dd, $^3J_{HF}$ = 9.6Hz, J = 2.7Hz, $C_{q\ arom.}CH_{arom.}CF$). **^{13}C-NMR (75 M, CDCl$_3$):** δ 35.6 (2 x SCH_2); 47.9 (CHS_2); 80.4 ($\underline{C}$≡CH); 82.6 (C≡$\underline{C}$H); 115.3 (d, $^2J_{CF}$ = 23.1Hz, $CH_{arom.}$); 115.7 (d, $^2J_{CF}$ = 24.2Hz, $CH_{arom.}$); 117.1 (d, $^4J_{CF}$ = 2.3Hz, $\underline{C}_{q\ arom.}$C≡CH); 118.0 (2 x $CH{=}\underline{C}H_2$); 133.5 (2 x $\underline{C}H{=}CH_2$); 134.6 (d, $^3J_{CF}$ = 9.2Hz, $CH_{arom.}$); 145.4 (d, $^3J_{CF}$ = 6.9Hz, $\underline{C}_{q\ arom.}CHS_2$); 163.1 (d, $^1J_{CF}$ = 250.4Hz, $C_{q\ arom.}F$). **^{19}F-NMR (282 Mhz, CDCl$_3$): δ** -108.48 to -108.55 (m). **MS (ESI): m/z (%):** 205.0 (M - $[SCH_2CH{=}CH_2]^-$, 100). **HRMS (ESI):** m/z calcd for $C_{15}H_{15}FS_2$ + H^+ = 279.0677, found = 279.0672. **IR (cm^{-1}) ν $_{max}$:** 1633 ($CH{=}CH_2$); 3301 (C≡CH). **Chromatography:** hexanes/EtOAc 98/2. **R$_f$** = 0.23. **Yield:** 86%.

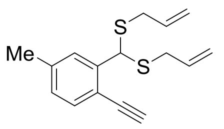
((5-chloro-2-ethynylphenyl)methylene)bis(allylsulfane) **2d**, prepared by method A:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.09 (2H, dddd, J = 13.7Hz, J = 7.1Hz, J = 1.2Hz, J = 0.8Hz, 2 x $SC\underline{H}_aCH_b$); 3.30 (2H, dddd, J = 13.7Hz, J = 7.4Hz, J = 1.2Hz, J = 0.8Hz, 2 x $SCH_aC\underline{H}_b$); 3.35 (1H, s, C≡CH); 5.08 (2H, dddd, J = 9.9Hz, J = 1.5Hz, J = 1.2Hz, J = 0.8Hz, 2x$CH{=}C\underline{H}_EH_Z$); 5.14 (2H, dddd, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, J = 0.8Hz, 2 x $CH{=}CH_E\underline{H}_Z$); 5.37 (1H, s, CHS_2); 5.80 (2H, dddd, J = 17.0Hz, J = 9.9Hz, J = 7.4Hz, J = 7.1Hz, 2 x $C\underline{H}{=}CH_2$); 7.20 (1H, dd, J = 8.3Hz, J = 2.2Hz, $CH_{arom.}$); 7.38 (1H, d, J = 8.3Hz, $CH_{arom.}$); 7.76 (1H, d, J = 2.2Hz, $CH_{arom.}$). **^{13}C-NMR (100**

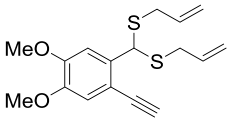
Mz, CDCl$_3$): δ 35.6 (2 x SCH_2); 47.7 (CHS_2); 80.2 ($\underline{C}\equiv CH$); 83.7 ($C\equiv\underline{C}H$); 118.0 (2 x $CH=\underline{C}H_2$); 119.4 ($C_{q\ arom.}$); 128.0 ($CH_{arom.}$); 128.7 ($\underline{C}H_{arom.}$); 133.4 (2 x $\underline{C}H=CH_2$); 133.8 ($CH_{arom.}$); 135.5 ($C_{q\ arom.}$); 144.3 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 221.0 (M – $[SCH_2CH=CH_2]^-$, 100). **HRMS (ESI):** m/z calcd for $C_{12}H_{10}ClS^+$ (M - $[SCH_2CH=CH_2]^-$) = 221.0186, found = 221.0185. **IR (cm^{-1}) ν$_{max}$:** 1475; 1588; 1634 ($CH=CH_2$); 2914; 3081; 3293. **Chromatography:** hexanes/EtOAc 99/1. **R$_f$** = 0,09. **Yield:** 70%.

((2-ethynyl-5-methylphenyl)methylene)bis(allylsulfane) **2e**, prepared by method A:



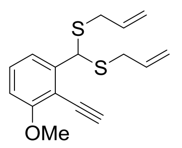
^{1}H-NMR (300 MHz, CDCl$_3$): δ 2.31 (3H, s, CH_3); 3.08 (2H, dd, J = 13.5Hz, J = 7.2Hz, 2x $SC\underline{H}_aH_b$); 3.28 (2H, dd, J = 13.5Hz, J = 7.2Hz, 2 x $SCH_a\underline{H}_b$); 3.29 (1H, s, $C\equiv CH$); 5.07 (2H, dd, J = 9.9Hz, J = 1.6Hz, 2 x $CH=C\underline{H}_EH_Z$); 5.13 (2H, dd, J = 16.9Hz, J = 1.6Hz, 2 x $CH=CH_E\underline{H}_Z$); 5.42 (1H, s, CHS_2); 5.80 (2H, ddt, J = 16.9Hz, J = 9.9Hz, J = 7.2Hz, 2 x $CH=CH_2$); 7.19 (1H, d, J = 8.3Hz, $CH_{arom.}$); 7.27 (1H, s, $CH_{arom.}$); 7.64 (1H, d, J = 8.3Hz, $CH_{arom.}$). **^{13}C-NMR (75 M, CDCl$_3$):** δ 21.0 (CH_3); 35.5 (2 x SCH_2); 48.0 (CHS_2); 81.4 ($\underline{C}\equiv CH$); 82.4 ($C\equiv\underline{C}H$); 117.8 (2 x $CH=\underline{C}H_2$); 120.8 ($\underline{C}_{q\ arom.}C\equiv CH$); 128.4 ($CH_{arom.}$); 130.5 ($CH_{arom.}$); 133.2 ($CH_{arom.}$); 133.8 (2 x $\underline{C}H=CH_2$); 137.5 ($\underline{C}_{q\ arom.}CH_3$); 139.4 ($\underline{C}_{q\ arom.}CHS_2$). **MS (ESI): m/z (%):** 201 (M – $[SCH_2CH=CH_2]^-$, 100). **HRMS (ESI):** m/z calcd for $C_{16}H_{18}S_2+H^+$ = 275.0928, found = 275.0921. **IR (cm^{-1}) ν $_{max}$:** 1634 ($CH=CH_2$); 3305 ($C\equiv CH$). **Chromatography:** hexanes/EtOAc 98/2. **R$_f$** = 0.19. **Yield:** 67%.

((2-ethynyl-4,5-dimethoxyphenyl)methylene)bis(allylsulfane) **2f**, prepared by method B:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.10 (2H, dddd, J = 13.6Hz, J = 7.0Hz, J = 1.2Hz, J = 1.0Hz, 2 x $SC\underline{H}_aCH_b$); 3.25 (1H, s, $C\equiv CH$); 3.27 (2H, dddd, J = 13.6Hz, J = 7.3Hz, J = 1.2Hz, J = 1.0Hz, 2 x $SCH_aC\underline{H}_b$); 3.87 (3H, s, $C_{q\ arom.}OCH_3$); 3.87 (3H, s, $C_{q\ arom.}OCH_3$); 5.08 (2H, dddd, J = 9.9Hz, J = 1.5Hz, J = 1.0Hz, J = 1.0Hz, 2 x $CH=C\underline{H}_EH_Z$); 5.15 (2H, dddd, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, J = 1.2Hz, 2 x $CH=CH_E\underline{H}_Z$); 5.42 (1H, s, CHS_2); 5.82 (2H, dddd, J = 17.0Hz, J = 9.9Hz, J = 7.3Hz, J = 7.0Hz, 2x$C\underline{H}=CH_2$); 6.90 (1H, s, $CH_{arom.}$); 7.26 (1H, s, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 35.6 (2 x SCH_2); 48.0 (CHS_2); 56.0 (2 x $C_qO\underline{C}H_3$); 81.3 ($C\equiv\underline{C}H$); 81.3 ($\underline{C}\equiv CH$); 110.8 ($CH_{arom.}$); 112.8 ($C_{q\ arom.}$); 114.2 ($CH_{arom.}$); 117.7 (2 x $CH=\underline{C}H_2$); 133.6 (2 x $\underline{C}H=CH_2$); 135.8 ($C_{q\ arom.}$); 148.1 ($C_{q\ arom.}$); 150.3 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 247.1 (M - $[SCH_2CH=CH_2]^-$, 75), 321.1 (M + H^+, 25). **HRMS (ESI):** m/z calcd for $C_{17}H_{20}O_2S_2+H^+$ = 321.0978, found = 321.0976. **IR (cm^{-1}) ν $_{max}$:** 1505; 1601; 1634 ($CH=CH_2$); 2912; 3280. **Chromatography:** hexanes/EtOAc 9/1. **R$_f$** = 0.20. **Yield:** 34%.

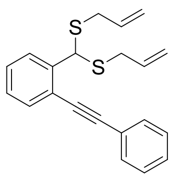
((2-ethynyl-3-methoxyphenyl)methylene)bis(allylsulfane) **2h**, prepared by method A:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.10 (2H, dddd, J = 13.5Hz, J = 7.0Hz, J = 1.2Hz, J = 0.9Hz, 2 x $SC\underline{H}_aCH_b$); 3.29 (2H, dddd, J = 13.5Hz, J = 7.3Hz, J = 1.2Hz, J = 0.9Hz, 2 x

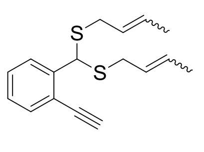
$SCH_aC\underline{H}_b$); 3.58 (1H, s, C≡CH); 3.90 (3H, s, OCH_3); 5.07 (2H, dddd, J = 10.0Hz, J = 1.5Hz, J = 0.9Hz, J = 0.9Hz, 2 x $CH{=}C\underline{H}_EH_Z$); 5.15 (2H, dddd, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, J = 1.2Hz, 2 x $CH{=}CH_E\underline{H}_Z$); 5.47 (1H, s, CHS_2); 5.81 (2H, dddd, J = 17.0Hz, J = 10.0Hz, J = 7.3Hz, J = 7.0Hz, 2 x $C\underline{H}{=}CH_2$); 6.81 (1H, dd, J = 7.9Hz, J = 1.3Hz, $CH_{arom.}$); 7.33 (1H, dd, J = 7.9Hz, J = 7.9Hz, $CH_{arom.}$); 7.37 (1H, dd, J = 7.9Hz, J = 1.3Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 35.5 (2 x SCH_2); 48.1 (CHS_2); 56.1 (OCH_3); 77.4 ($\underline{C}$≡CH); 87.2 (C≡$\underline{C}$H); 109.5 ($CH_{arom.}$); 110.1 ($C_{q\ arom.}$); 117.8 (2 x $CH{=}\underline{C}H_2$); 120.6 ($\underline{C}H_{arom.}$); 130.1 ($CH_{arom.}$); 133.7 (2 x $\underline{C}HCH_2$); 144.4 ($C_{q\ arom.}$); 160.6 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 217.1 (M – $[SCH_2CH{=}CH_2]^-$, 90), 291.1 (M + H^+, 10). **HRMS (ESI):** m/z calcd for $C_{13}H_{13}OS^+$ (M – $[SCH_2CH{=}CH_2]^-$) = 217.0682, found = 217.0683. **IR (cm^{-1}) ν$_{max}$:** 1270; 1468; 1573; 1633 ($CH{=}CH_2$); 2913; 3265. **Chromatography:** hexanes/EtOAc 96/4. **R$_f$** = 0.23. **Yield:** 45%.

((2-(phenylethynyl)phenyl)methylene)bis(allylsulfane) **2j**, prepared by method A:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 3.10 (2H, dddd, J = 13.7Hz, J = 7.1Hz, J = 1.3Hz, J = 1.0Hz, 2 x $SC\underline{H}_aCH_b$); 3.32 (2H, dddd, J = 13.7Hz, J = 7.3Hz, J = 1.2Hz, J = 0.9Hz, 2 x $SCH_aC\underline{H}_b$); 5.02 (2H, dddd, J = 10.0Hz, J = 1.5Hz, J = 1.0Hz, J = 0.9Hz, 2 x $CH{=}C\underline{H}_EH_Z$); 5.15 (2H, dddd, J = 17.0Hz, J = 1.5Hz, J = 1.3Hz, J = 1.2Hz, 2 x $CH{=}CH_E\underline{H}_Z$); 5.54 (1H, s, CHS_2); 5.81 (2H, dddd, J = 17.0Hz, J = 10.0Hz, J = 7.3Hz, J = 7.1Hz, 2 x $C\underline{H}{=}CH_2$); 7.23-7.27 (1H, m, $CH_{arom.}$); 7.34-7.40 (4H, m, 4 x $CH_{arom.}$); 7.49-7.55 (3H, m, 3 x $CH_{arom.}$); 7.77 (1H, dd, J = 7.9 Hz, J = 1.1 Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 35.5 (2 x SCH_2); 48.2 (CHS_2); 87.1 ($\underline{C}$≡C); 94.8 (C≡$\underline{C}$); 117.8 (2 x $CH{=}\underline{C}H_2$); 122.1 ($C_{q\ arom.}$); 123.2 ($C_{q\ arom.}$); 127.7 ($CH_{arom.}$); 128.5 (3 x $CH_{arom.}$); 128.6 ($CH_{arom.}$); 129.0 ($CH_{arom.}$); 131.5 (2x $CH_{arom.}$); 132.2 ($CH_{arom.}$); 133.8 (2 x $\underline{C}H{=}CH_2$); 141.7 ($C_{q\ arom.}$); 160.6 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 263.1 (M - $[SCH_2CH{=}CH_2]^-$, 80). **HRMS (ESI):** m/z calcd for $C_{18}H_{15}S^+$ (M - $[SCH_2CH{=}CH_2]^-$) = 263.0889, found = 263.0886. **IR (cm^{-1}) ν$_{max}$:** 1422; 1442; 1491; 1636 ($CH{=}CH_2$); 2978. **Chromatography:** hexanes/EtOAc 98/2. **R$_f$** = 0.26. **Yield:** 69%.

((2-ethynylphenyl)methylene)bis(but-2-en-1-ylsulfane) **2k**, prepared by method A:



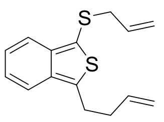
This compound was obtained as a mixture of *E*/*Z* stereoisomers in a 9/1 *E,E*/*Z,Z* ratio, according to ^{1}H-NMR integration. Spectral data are reported for the *E,E* isomer. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 1.68 (6H, dd, J = 6.1 Hz, J = 1.1 Hz, 2 x CH_3); 3.02 (2H, ddd, J = 13.5 Hz, J = 6.8 Hz, J = 1.0 Hz, 2 x $SC\underline{H}_aH_b$); 3.23 (2H, ddd, J = 13.5 Hz, J = 7.3 Hz, J = 0.9 Hz, 2 x $SCH_a\underline{H}_b$); 3.31 (1H, s, C≡CH); 5.39-5.56 (5H, m, 4 x CH= + CHS_2); 7.21 (1H, ddd, J = 7.7 Hz, J = 7.7 Hz, J = 1.3 Hz, $CH_{arom.}$); 7.37 (1H, ddd, J = 7.7 Hz, J =7.7 Hz, J = 1.3 Hz, $CH_{arom.}$); 7.45 (1H, dd, J = 7.7 Hz, J = 1.0 Hz, $CH_{arom.}$); 7.77 (1H, d, J = 7.7 Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 17.8 (2 x CH_3); 34.7 (2 x SCH_2); 47.6 (CHS_2); 81.4 ($\underline{C}$≡CH); 82.1 (C≡$\underline{C}$H); 120.9 ($\underline{C}_{q\ arom.}$C≡CH); 126.5 (2 x CH=); 127.4

(CH$_{arom.}$); 128.4 (CH$_{arom.}$); 128.8 (2 x CH=); 129.4 (CH$_{arom.}$); 132.7 (CH$_{arom.}$); 142.6 (C$_{q\ arom.}$). **MS (ESI): m/z (%):** 201.0 (M - [SCH$_2$CH=CHCH$_3$]$^-$, 95). **IR (cm^{-1}) ν$_{max}$:** 1220; 1444; 1475; 1665 (CH=CH); 2915. **Chromatography:** hexanes/EtOAc 99/1. **R$_f$** = 0.19. **Yield:** 87%.

5. Synthesis of benzo[*c*]thiophenes

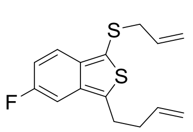
Representative example: 400 mg ((2-ethynylphenyl)methylene)bis(allylsulfane) (1.54 mmol, 1 equiv) was dissolved in 3 mL dichloromethane in a round-bottom flask and 5 mol% AuCl$_3$ was added. In case of a very slow reaction, another 5 mol% AuCl$_3$ was added to the reaction mixture, bringing the total to 10 mol% catalyst. The reaction progress was monitored using TLC and HPLC. When all starting material had been consumed, the crude reaction mixture was filtered over a small plug of silica gel. The resulting oil was purified by means of column chromatography. 0.27 g (1.05 mmol, 68%) of product was obtained.

1-(allylthio)-3-(but-3-en-1-yl)benzo[*c*]thiophene **3a**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.53 (2H, tddd, J = 7.6Hz, J = 6.6Hz, J = 1.4Hz, J = 1.2Hz, C$_q$CH$_2$C$\underline{H}_2$); 3.25 (2H, t, J = 7.6Hz, C$_q$C$\underline{H}_2$CH$_2$); 3.36 (2H, ddd, J = 7.4Hz, J = 1.2Hz, J = 0.8Hz, SC$\underline{H}_2$); 4.82 (1H, ddt, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, SCH$_2$CH=CH$_E\underline{H}_Z$); 4.93 (1H, ddt, J = 9.9Hz, J = 1.5Hz, J = 0.8Hz, SCH$_2$CH=C$\underline{H}_E$H$_Z$); 5.02 (1H, ddt, J = 10.3Hz, J = 1.7Hz, J = 1.2Hz, CH=C$\underline{H}_E$CH$_Z$); 5.08 (1H, ddt, J = 17.0Hz, J = 1.7Hz, J = 1.4Hz, CH=CH$_E$C$\underline{H}_Z$); 5.85 (1H, ddt, J = 17.0Hz, J = 9.9Hz, J = 7.4, SCH$_2$C$\underline{H}$); 5.86 (1H, ddt, J = 17.0Hz, J = 10.3Hz, J = 6.6Hz, C$_q$CH$_2$CH$_2$C$\underline{H}$); 7.03 (1H, ddd, J = 8.7Hz, J = 6.3Hz, J = 1.0Hz, CH$_{arom.}$); 7.11 (1H, ddd, J = 8.7Hz, J = 6.3Hz, J = 1.0Hz, CH$_{arom.}$); 7.52 (1H, dd, J = 8.7Hz, J = 1.0Hz, CH$_{arom.}$); 7.74 (1H, dd, J = 8.7Hz, J = 1.0Hz, CH$_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$): δ** 27.5 (C$_q\underline{C}$H$_2$CH$_2$); 35.7 (C$_q$CH$_2\underline{C}$H$_2$); 42.5 (SCH$_2$); 116.0 (C$_q$CH$_2$CH$_2$CH=$\underline{C}$H$_2$); 117.8 (SCH$_2$CH=$\underline{C}$H$_2$); 118.2 (C$_{q\ arom.}$); 120.2 (CH$_{arom.}$); 121.0 (CH$_{arom.}$); 122.6 (CH$_{arom.}$); 124.3 (CH$_{arom.}$); 133.8 ($\underline{C}$H=CH$_2$); 135.6 (C$_{q\ arom.}$); 137.1 ($\underline{C}$H=CH$_2$); 139.8 (C$_{q\ arom.}$); 142.4 (C$_{q\ arom.}$). **MS (ESI): m/z (%):** 277.1 (C$_{15}$H$_{16}$OS$_2$ + H$^+$ (S=O), 100). **HRMS (ESI):** m/z calcd for C$_{15}$H$_{16}$OS$_2$ + H$^+$ (S=O) = 277.0715, found = 277.0712. **IR (cm^{-1}) ν$_{max}$:** 1638 (CH=CH$_2$); 1691 (CH=CH$_2$). **Chromatography:** hexanes. **R$_f$** = 0.31. **Yield:** 68%.

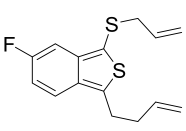
1-(allylthio)-3-(but-3-en-1-yl)-5-fluorobenzo[*c*]thiophene **3b**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.51 (2H, tddd, J = 7.6Hz, J = 6.7Hz, J = 1.4Hz, J = 1.3Hz, C$_q$CH$_2$C$\underline{H}_2$); 3.16 (2H, t, J = 7.6Hz, C$_q$CH$_2$); 3.35 (2H, ddd, J = 7.4Hz, J = 1.1Hz, J = 0.8Hz, SC$\underline{H}_2$); 4.81 (1H, ddt, J = 17.1Hz, J = 1.4Hz, J = 1.1Hz, SCH$_2$CH=CH$_E\underline{H}_Z$); 4.92 (1H, ddt, J = 9.8Hz, J = 1.4Hz, J = 0.8Hz, SCH$_2$CH=C$\underline{H}_E$H$_Z$); 5.03 (1H, ddt, J = 10.3Hz, J = 1.6Hz, J = 1.3Hz, CH=C$\underline{H}_E$CH$_Z$); 5.08 (1H, ddt, J = 17.0Hz, J = 1.6Hz, J = 1.4Hz, CH=CH$_E\underline{C}$H$_Z$); 5.84 (1H, ddt, J = 17.1Hz, J = 9.8Hz, J = 7.4, SCH$_2$C$\underline{H}$); 5.86 (1H, ddt, J = 17.0Hz, J = 10.3Hz, J = 6.7Hz, C$_q$CH$_2$CH$_2$C$\underline{H}$); 6.94 (1H, ddd, J = 9.4Hz, ^{3}J$_{HF}$ = 8.3Hz, J = 2.3Hz, CH$_{arom.}$); 7.07 (1H, ddd, ^{3}J$_{HF}$ = 10.3Hz, J = 2.3Hz, J = 0.6Hz, CH$_{arom.}$); 7.70

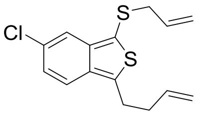
(1H, ddd, J = 9.4Hz, $^4J_{HF}$ = 5.5Hz, J = 0.6Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, $CDCl_3$):** δ 27.5 ($C_{q\,arom.}\underline{C}H_2$); 35.5 ($C_{q\,arom.}CH_2\underline{C}H_2$); 42.6 ($SCH_2$); 102.2 (d, $^2J_{CF}$ = 22.5Hz, $CH_{arom.}$); 116.1 ($CH{=}\underline{C}H_2$); 116.5 (d, $^2J_{CF}$ = 29.5Hz, $CH_{arom.}$); 118.0 ($SCH_2CH{=}\underline{C}H_2$); 119.9 ($C_{q\,arom.}$); 122.9 (d, $^3J_{CF}$ = 10.0Hz, $\underline{C}H_{arom.}$); 133.6 ($SCH_2\underline{C}H$); 134.7 (d, $^3J_{CF}$ = 9.0Hz, $C_{q\,arom.}$); 136.9 ($\underline{C}H_2{=}CH$); 137.8 (d, $^4J_{CF}$ = 9.4Hz, $C_{q\,arom.}$); 139.9 ($C_{q\,arom.}$); 159.7 (d, $^1J_{CF}$ = 244.9Hz, $C_{q\,arom.}F$). **^{19}F-NMR (282 M, $CDCl_3$):** δ -119.75 to -119.81 (m). **MS (ESI): m/z (%):** 279.1 (M + H^+, 100). **HRMS (ESI):** m/z calcd for $C_{15}H_{15}FOS_2 + H^+$ (S=O) = 295.0621, found = 295.0621. **IR (cm^{-1}) ν_{max}:** 1175; 1222; 1508; 1626 ($CH{=}CH_2$); 1693 ($CH{=}CH_2$); 2918. **Yield:** 74%.

1-(allylthio)-3-(but-3-en-1-yl)-4-fluorobenzo[*c*]thiophene **3c**:



^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.52 (2H, m, $C_qCH_2C\underline{H_2}$); 3.23 (2H, t, J = 7.6Hz, C_qCH_2); 3.33 (2H, d, J = 7.7Hz, $SC\underline{H_2}$); 4.80 (1H, d, J = 16.7Hz, $SCH_2CH{=}CH_E\underline{H_Z}$); 4.92 (1H, d, J = 9.9Hz, $SCH_2CH{=}C\underline{H_E}H_Z$); 5.03 (1H, d, J = 9.9Hz, $CH{=}C\underline{H_E}CH_Z$); 5.08 (1H, ddt, J = 17.1Hz, $CH{=}CH_E\underline{C}H_Z$); 5.77-5.93 (2H, m, $SCH_2C\underline{H}$ + $CH_2CH_2C\underline{H}$) 6.86 (1H, ddd, J = 9.5Hz, $^3J_{HF}$ = 8.3Hz, J = 2.2Hz, $FCC\underline{H}_{arom.}CH_{arom.}$); 7.31 (1H, dd, $^3J_{HF}$ = 9.9Hz, J = 2.2Hz, $FCCH_{arom.}C_{q\,arom.}$); 7.49 (1H, dd, J = 9.5Hz, $^4J_{HF}$ = 5.2Hz, $FCH_{arom.}C\underline{H}_{arom.}$). **^{13}C-NMR (75 M, $CDCl_3$):** δ 27.8 ($C_{q\,arom.}\underline{C}H_2CH_2$); 35.7 ($C_{q\,arom.}CH_2\underline{C}H_2$); 42.5 ($SCH_2$); 103.2 (d, $^2J_{CF}$ = 23.1Hz, $CH_{arom.}$); 115.1 (d, $^2J_{CF}$ = 28.8Hz, $CH_{arom.}$); 116.3 ($CH_2CH_2CH{=}\underline{C}H_2$); 116.9 (d, J_{CF} = 9.2Hz, $C_{q\,arom.}$); 118.0 ($SCH_2CH{=}\underline{C}H_2$); 122.1 (d, $^3J_{CF}$ = 9.2Hz, $\underline{C}H_{arom.}$); 133.2 ($C_{q\,arom.}$); 133.8 ($\underline{C}H{=}CH_2$); 136.9 ($\underline{C}H{=}CH_2$); 141.4 ($C_{q\,arom.}$); 142.5 (d, $^4J_{CF}$ = 9.2Hz, $C_{q\,arom.}$); 161.2 (d, $^1J_{CF}$ = 246.9Hz, $C_{q\,arom.}F$). **^{19}F-NMR (282 M, $CDCl_3$):** δ -117.3 (m). **MS (ESI): m/z (%):** 279.1 (M + H^+, 100). **HRMS (ESI):** m/z calcd for $C_{15}H_{16}FS_2 + H^+$ = 279.0672, found = 279.0666. **IR (cm^{-1}) ν_{max}:** 1625 ($CH{=}CH_2$); 1696 ($CH{=}CH_2$). **Chromatography:** hexanes. **R_f** = 0.25. **Yield:** 63%.

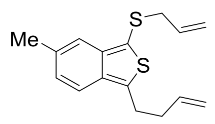
3-(allylthio)-1-(but-3-en-1-yl)-5-chlorobenzo[*c*]thiophene **3d**:



^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.50 (2H, tddd, J = 7.6Hz, J = 6.6Hz, J = 1.4Hz, J = 1.2Hz, $C_qCH_2C\underline{H_2}$); 3.22 (2H, t, J = 7.6Hz, $C_qC\underline{H_2}$); 3.34 (2H, ddd, J = 7.4Hz, J = 1.2Hz, J = 0.8Hz, $SC\underline{H_2}$); 4.81 (1H, ddt, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, $SCH_2CH{=}CH_E\underline{H_Z}$); 4.94 (1H, ddt, J = 10.0Hz, J = 1.5Hz, J = 0.8Hz, $SCH{=}C\underline{H_E}H_Z$); 5.02 (1H, ddt, J = 10.3Hz, J = 1.7Hz, J = 1.2Hz, $CH{=}C\underline{H_E}CH_Z$); 5.07 (1H, ddt, J = 17.0Hz, J = 1.7Hz, J = 1.4Hz, $SCH_2CH{=}CH_EC\underline{H_Z}$); 5.84 (1H, ddt, J = 17.0Hz, J = 10.0Hz, J = 7.4, $SCH_2C\underline{H}$); 5.84 (1H, ddt, J = 17.0Hz, J = 10.3Hz, J = 6.6Hz, $C_qCH_2CH_2C\underline{H}$); 6.96 (1H, dd, J = 9.2Hz, J = 1.9Hz, $CH_{arom.}$); 7.44 (1H, dd, J = 9.2Hz, J = 0.8Hz, $CH_{arom.}$); 7.72 (1H, dd, J = 1.9Hz, J = 0.8Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, $CDCl_3$):** δ 27.6 ($C_{q\,arom.}\underline{C}H_2$); 35.6 ($C_{q\,arom.}CH_2\underline{C}H_2$); 42.5 ($S\underline{C}H_2$); 116.2 ($CH{=}\underline{C}H_2$); 117.9 ($C_{q\,arom.}$); 118.0 ($SCH_2CH{=}\underline{C}H_2$); 119.5 ($CH_{arom.}$) ; 121.3 ($CH_{arom.}$) ; 124.1 ($CH_{arom.}$); 131.4 ($C_{q\,arom.}$); 133.6 ($SCH_2\underline{C}H{=}CH_2$); 133.7 ($C_{q\,arom.}$); 136.8 ($CH_2{=}\underline{C}H$); 141.1 ($C_{q\,arom.}$); 142.3 ($C_{q\,arom.}$). **MS (ESI): m/z (%):** 295.0 (M + H^+, 100). **HRMS (ESI):** m/z calcd for $C_{15}H_{15}ClS_2{+}H^+$ = 295.0377, found =

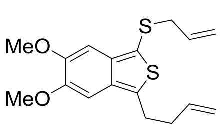
295.0370. **IR (cm^{-1}) ν $_{max}$:** 1219; 1273; 1425; 1604; 1638 ($C=CH_2$); 1698 ($C=CH_2$); 2918; 3078. **Yield:** 91%.

3-(allylthio)-1-(but-3-en-1-yl)-5-methylbenzo[*c*]thiophene **3e**:



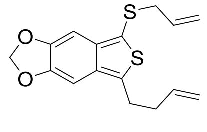
^{1}H-NMR (300 MHz, CDCl$_3$): δ 2.37 (3H, s, CH_3); 2.51 (2H, m, $CqCH_2C\underline{H}_2$); 3.20 (2H, t, J = 7.4Hz, C_qCH_2); 3.34 (2H, d, J = 7.2Hz, SCH_2); 4.81 (1H, d, J = 17.1Hz, $SCH_2CH=CH_E\underline{H}_Z$); 4.91 (1H, d, J = 9.1Hz, $SCH_2CH=C\underline{H}_EH_Z$); 5.02 (1H, d, J = 11.0Hz, $CH_2CH_2CH=C\underline{H}_EH_Z$); 5.08(1H, d, J = 17.1Hz, $CH_2CH_2CH=CH_E\underline{H}_Z$); 5.76-5.95 (2H, m, $SCH_2C\underline{H}+CH_2CH_2C\underline{H}$); 6.95 (1H,d, J = 8.9Hz, $CH_{arom.}$); 7.24 (1H, s, $CH_{arom.}$); 7.63 (1H, d, J = 8.9Hz, $CH_{arom.}$).**^{13}C-NMR (75 M, CDCl$_3$):** δ 21.8 (CH_3); 27.5 ($C_q\underline{C}H_2CH_2$); 35.7 ($CqCH_2\underline{C}H_2$); 42.6 (SCH_2); 115.9 ($CH_2CH_2CH=\underline{C}H_2$); 117.8 ($SCH_2CH=\underline{C}H_2$); 118.1 ($C_{q\ arom.}$); 118.3 ($C_q\underline{C}H_{arom.}$); 120.6 ($C_q\underline{C}H_{arom.}$); 127.6 ($CH_{arom.}$); 132.1 ($C_{q\ arom.}$); 133.9 ($\underline{C}H=CH_2$); 136.0 ($C_{q\ arom.}$); 137.3 ($\underline{C}H=CH_2$); 138.0 ($C_{q\ arom.}$); 141.4 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 291 ($C_{16}H_{18}OS_2$ + H$^+$ (S=O), 100). **IR (cm^{-1}) ν $_{max}$:** 1638 ($CH=CH_2$). **Yield:** 91%. **Chromatography:** hexanes. **R$_f$** = 0.30. **Yield:** 41%.

1-(allylthio)-3-(but-3-en-1-yl)-5,6-dimethoxybenzo[*c*]thiophene **3f**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.51 (2H, tddd, J = 7.7Hz, J = 6.6Hz, J = 1.8Hz, J = 1.5Hz, $C_qCH_2C\underline{H}_2$); 3.14 (2H, t, J = 7.7Hz, $C_qC\underline{H}_2$); 3.34 (2H, ddd, J = 7.4Hz, J = 1.5Hz, J = 1.2Hz, $SC\underline{H}_2$); 3.92 (3H, s, OCH_3); 3.97 (3H, s, OCH_3); 4.87 (1H, ddt, J = 17.0Hz, J = 1.5Hz, J = 1.2Hz, $SCH_2CH=CH_E\underline{H}_Z$); 4.94 (1H, ddt, J = 9.9Hz, J = 1.5Hz, J = 1.2Hz, $SCH_2CH=C\underline{H}_EH_Z$); 5.03 (1H, ddt, J = 10.3Hz, J = 1.8Hz, J = 1.5Hz, $CH=C\underline{H}_ECH_Z$); 5.10 (1H, ddt, J = 17.1Hz, J = 1.8Hz, J = 1.5Hz, $CH=CH_EC\underline{H}_Z$); 5.87 (1H, ddt, J = 17.0Hz, J = 9.9Hz, J = 7.4, $SCH_2C\underline{H}$); 5.89 (1H, ddt, J = 17.1Hz, J = 10.3Hz, J = 6.6Hz, $C_qCH_2CH_2C\underline{H}$); 6.65 (1H, s, $CH_{arom.}$); 6.96 (1H, s, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 27.6 ($C_{q\ arom.}\underline{C}H_2$); 35.3 ($C_{q\ arom.}CH_2\underline{C}H_2$); 42.4 ($S\underline{C}H_2$); 55.8 ($OCH_3$); 55.9 ($OCH_3$); 97.0 ($CH_{arom.}$); 98.0 ($CH_{arom.}$); 114.7 ($C_{q\ arom.}$); 115.8 ($CH=\underline{C}H_2$); 117.7 ($SCH_2CH=\underline{C}H_2$); 131.1 ($C_{q\ arom.}$); 134.0 ($SCH_2\underline{C}H=CH_2$); 136.2 ($C_{q\ arom.}$); 137.3 ($CH_2=\underline{C}H$); 139.0 ($C_{q\ arom.}$); 149.2 ($C_{q\ arom.}$); 150.6 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 337.1 ($C_{17}H_{20}O_3S_2$ + H$^+$ (S=O), 66), 321.1 (M + H$^+$, 33). **HRMS (ESI):** m/z calcd for $C_{17}H_{20}O_3S_2$ + H$^+$ (S=O) = 337.0927, found = 337.0928. **IR (cm^{-1}) ν $_{max}$:** 1230; 1352; 1490; 1638 ($CH=CH_2$); 1682 ($CH=CH_2$); 2932. **Yield:** 87%.

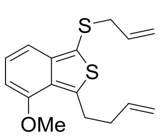
5-(allylthio)-7-(but-3-en-1-yl)thieno[3',4':4,5]benzo[1,2-*d*][1,3]dioxole **3g**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.47 (2H, tddd, J = 7.7Hz, J = 6.7Hz, J = 1.5Hz, J = 1.2Hz, $C_qCH_2C\underline{H}_2$); 3.08 (2H, t, J = 7.7Hz, $C_qC\underline{H}_2$); 3.32 (2H, ddd, J = 7.4Hz, J = 1.1Hz, J = 0.8Hz, $SC\underline{H}_2$); 4.85 (1H, ddt, J = 16.9Hz, J = 1.4Hz, J = 1.1Hz, $SCH_2CH=CH_E\underline{H}_Z$);

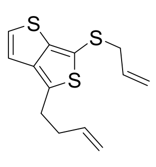
4.93 (1H, ddt, J = 9.9Hz, J = 1.4Hz, J = 0.8Hz, $SCH_2CH=C\underline{H}_EH_Z$); 5.01 (1H, ddt, J = 10.3Hz, J = 1.7Hz, J = 1.2Hz, $SCH_2CH=C\underline{H}_ECH_Z$); 5.07 (1H, ddt, J = 17.1Hz, J = 1.7Hz, J = 1.5Hz, $CH=CH_E\underline{C}H_Z$); 5.84 (1H, ddt, J = 16.9Hz, J = 9.9Hz, J = 7.4, $SCH_2C\underline{H}$); 5.85 (1H, ddt, J = 17.1Hz, J = 10.3Hz, J = 6.7Hz, $C_qCH_2CH_2C\underline{H}$); 5.95 (2H, s, OCH_2O); 6.72 (1H, s, $CH_{arom.}$); 6.99 (1H, s, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 27.7 ($C_{q\ arom.}\underline{C}H_2$); 35.4 ($C_{q\ arom.}CH_2\underline{C}H_2$); 42.3 ($S\underline{C}H_2$); 94.8 ($CH_{arom.}$); 96.0 ($CH_{arom.}$); 101.2 ($OCH_2O$); 115.5 ($C_{q\ arom.}$); 115.9 ($CH=\underline{C}H_2$); 117.7 ($SCH_2CH=\underline{C}H_2$); 132.3 ($C_{q\ arom.}$); 133.8 ($SCH_2\underline{C}H=CH_2$); 136.6 ($C_{q\ arom.}$); 137.1 ($CH_2=\underline{C}H$); 139.0 ($C_{q\ arom.}$); 140.4 ($C_{q\ arom.}$); 147.4 ($C_{q\ arom.}$); 148.8 ($C_{q\ arom.}$). **MS (ESI): m/z (%):** 305.0 (M + H$^+$, 100). **HRMS (ESI):** calcd for $C_{16}H_{16}O_2S_2 + H^+ = 305.0665$, found = 305.0665. **IR (cm^{-1}) ν$_{max}$:** 1213; 1336; 1594; 1638 ($C=CH_2$); 1684 ($C=CH_2$); 2360; 2901. **Chromatography:** hexanes/EtOAc 99/1. **R$_f$** = 0.16. **Yield:** 53% (2 steps).

1-(allylthio)-3-(but-3-en-1-yl)-4-methoxybenzo[*c*]thiophene **3h**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.51 (2H, tddd, J = 7.7Hz, J = 6.7Hz, J = 1.3Hz, J = 1.3Hz, $C_qCH_2C\underline{H}_2$); 3.34 (2H, ddd, J = 7.3Hz, J = 1.0Hz, J = 1.0Hz, $SC\underline{H}_2$); 3.42 (2H, t, J = 7.7Hz, $C_qC\underline{H}_2$); 3.90 (3H, s, OCH_3); 4.82 (1H, ddt, J = 17.1Hz, J = 1.4Hz, J = 1.0Hz, $SCH_2CH=CH_E\underline{H}_Z$); 4.93 (1H, ddt, J = 9.9Hz, J = 1.4Hz, J = 1.0Hz, $SCH_2CH=C\underline{H}_EH_Z$); 5.00 (1H, ddt, J = 10.3Hz, J = 1.9Hz, J = 1.3Hz, $CH=CH_ZC\underline{H}_E$); 5.06 (1H, ddt, J = 17.1Hz, J = 1.9Hz, J = 1.3Hz, $CH=C\underline{H}_ZCH_E$); 5.84 (1H, ddt, J = 17.1Hz, J = 9.9Hz, J = 7.3Hz, $SCH_2C\underline{H}$); 5.89 (1H, ddt, J = 17.1Hz, J = 10.3Hz, J = 6.7Hz, $C_qCH_2CH_2C\underline{H}$); 6.22 (1H, d, J = 7.2Hz, $CH_{arom.}$); 6.99 (1H, dd, J = 8.7Hz, J = 7.2Hz, $CH_{arom.}$); 7.31 (1H, d, J = 8.7Hz, $CH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 30.1 ($C_{q\ arom.}\underline{C}H_2$); 36.6 ($C_{q\ arom.}CH_2\underline{C}H_2$); 42.2 ($S\underline{C}H_2$); 55.0 ($O\underline{C}H_3$); 98.84 ($CH_{arom.}$); 113.5 ($CH_{arom.}$); 115.4 ($C_qCH_2CH_2CH=\underline{C}H_2$); 116.6 ($C_{q\ arom.}$); 117.8 ($SCH_2CH=\underline{C}H_2$); 124.9 ($\underline{C}H_{arom.}$); 128.3 ($C_{q\ arom.}$); 133.9 ($SCH_2\underline{C}H=CH_2$); 137.8 ($C_{q\ arom.}CH_2CH_2\underline{C}H=CH_2$); 141.8 ($C_{q\ arom.}$); 144.9 ($C_{q\ arom.}$); 155.1 ($C_{q\ arom.}OMe$). **MS (ESI): m/z (%):** 217.1 (M - $[SCH_2CH=CH_2]^{\cdot}$, 60). **HRMS (ESI):** calcd for $C_{16}H_{18}O_2S_2 + H^+$ (S=O) = 307.0821, found = 307.0827. **IR (cm^{-1}) ν$_{max}$:** 1428; 1528; 1614; 1638 ($CH=CH_2$); 1695 ($CH=CH_2$); 2911. **Yield:** 92%.

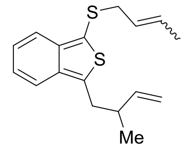
6-(allylthio)-4-(but-3-en-1-yl)thieno[3,4-*b*]thiophene **3i**:



^{1}H-NMR (400 MHz, CDCl$_3$): δ 2.46 (2H, tddd, J = 7.6Hz, J = 6.5Hz, J = 1.5Hz, J = 1.3Hz, $C_qCH_2C\underline{H}_2$); 3.04 (2H, t, J = 7.6Hz, $C_qC\underline{H}_2$); 3.41 (2H, ddd, J = 7.3Hz, J = 1.2Hz, J = 1.1Hz, $SC\underline{H}_2$); 4.95 (1H, ddt, J = 16.8Hz, J = 1.5Hz, J = 1.2Hz, $SCH_2CH=CH_E\underline{H}_Z$); 4.99 (1H, ddt, J = 10.2Hz, J = 1.5Hz, J = 1.1Hz, $SCH_2CH=C\underline{H}_EH_Z$); 5.02 (1H, ddt, J = 10.3Hz, J = 1.7Hz, J = 1.3Hz, $CH=C\underline{H}_ECH_Z$); 5.07 (1H, ddt, J = 17.1Hz, J = 1.7Hz, J = 1.5Hz, $CH=CH_EC\underline{H}_Z$); 5.84 (1H, ddt, J = 17.1Hz, J = 10.3Hz, J = 6.6Hz, $C_qCH_2CH_2C\underline{H}$); 5.88 (1H, ddt, J = 16.8Hz, J = 10.2Hz, J = 7.3, $SCH_2C\underline{H}$); 6.82 (1H, d, J = 5.6Hz, $CH_{arom.}$); 7.21 (1H, d, J = 5.6Hz, $SCH_{arom.}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 28.9 ($C_{q\ arom.}\underline{C}H_2$); 35.5 ($C_q$

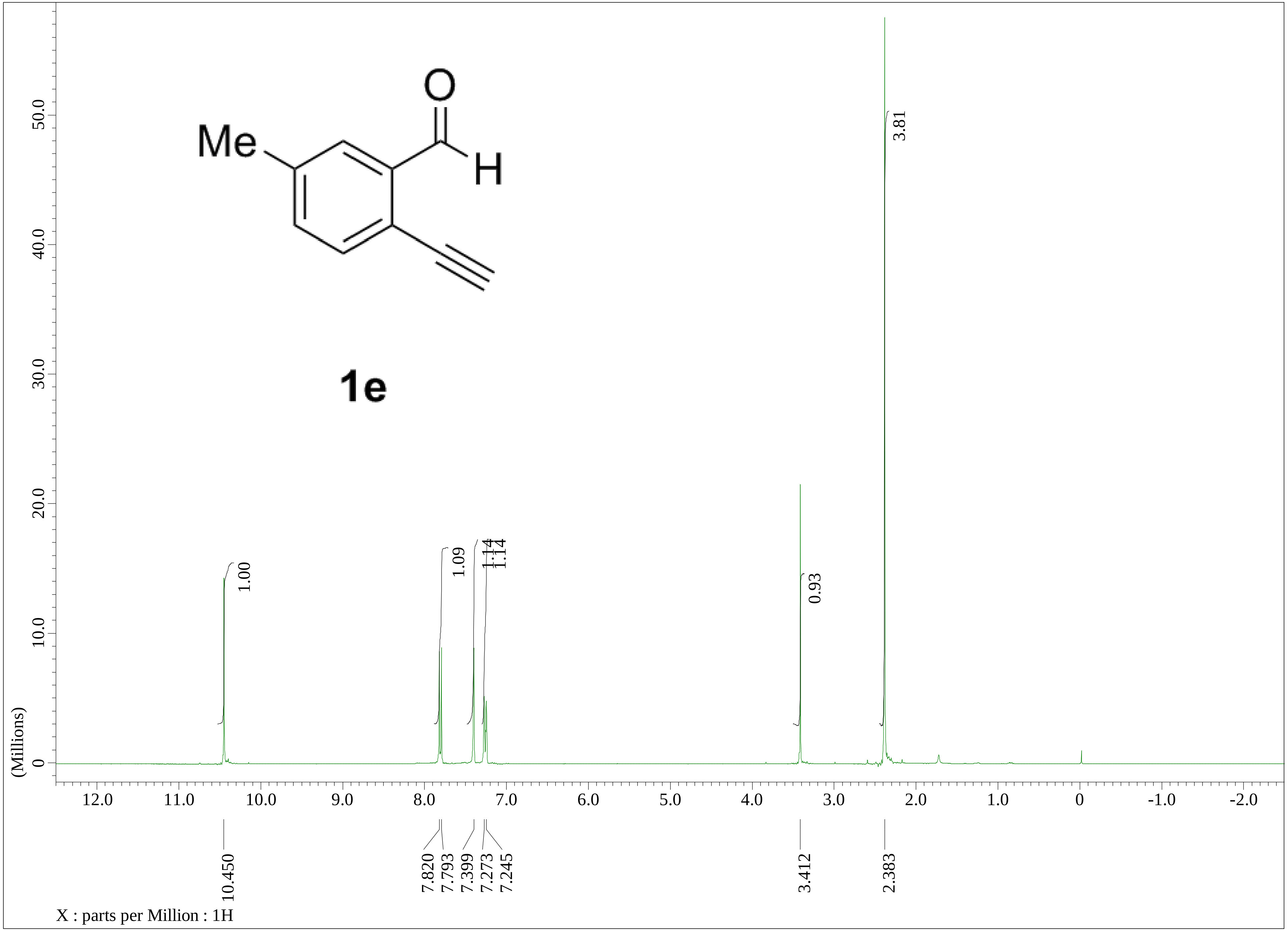
$_{\text{arom.}}$CH$_2\underline{\text{C}}$H$_2$); 41.0 (S$\underline{\text{C}}$H$_2$); 113.6 (C$_{\text{q arom.}}$); 116.0 (CH=$\underline{\text{C}}$H$_2$); 116.7 (CH$_{\text{arom.}}$); 118.0 (SCH$_2$CH=$\underline{\text{C}}$H$_2$); 130.9 (CH$_{\text{arom.}}$); 133.7 (SCH$_2\underline{\text{C}}$H); 136.1 (C$_{\text{q arom.}}$); 137.0 (CH$_2$=$\underline{\text{C}}$H); 144.4 (C$_{\text{q arom.}}$); 146.4 (C$_{\text{q arom.}}$). **MS (ESI): m/z (%):** 267.1 (M + H$^+$, 25), 283.1 ($C_{13}H_{14}OS_3$ + H$^+$ (S=O), 100). **HRMS (ESI):** calcd for $C_{13}H_{14}OS_3$ + H$^+$ (S=O) = 283.0280, found = 283.0276. **IR (cm^{-1}) ν $_{\text{max}}$:** 1220; 1425; 1639 (C=CH$_2$); 1841; 2913; 3077. **Chromatography:** hexanes/EtOAc 98/2. **R$_f$** = 0.24. **Yield:** 15% (2 steps).

1-(but-2-en-1-ylthio)-3-(2-methylbut-3-en-1-yl)benzo[*c*]thiophene **3k**:



This compound was obtained as a mixture of *E*/*Z* stereoisomers in a 9/1 *E*/*Z* ratio, according to ^{1}H-NMR integration. Spectral data are reported for the *E* isomer. **^{1}H-NMR (400 MHz, CDCl$_3$):** δ 1.06 (3H, d, J = 7.0 Hz, C$\underline{\text{H}}_3$CH); 1.51 (3H, ddt, J = 6.5 Hz, J = 1.5 Hz, J = 0.8 Hz, CH=CHC$\underline{\text{H}}_3$); 2.61 (1H, sept, J = 7.0 Hz, CH$_3$C$\underline{\text{H}}$); 3.09 (1H, dd, J = 14.8 Hz, J = 7.0 Hz, C$\underline{\text{H}}_a$H$_b$); 3.20 (1H, dd, J = 14.8 Hz, J = 7.0 Hz, CH$_a\underline{\text{H}}_b$); 3.29 (2H, d, J = 7.5 Hz, SCH$_2$); 4.95 (1H, dm, J = 10.6 Hz, CH=C$\underline{\text{H}}_E$H$_Z$); 4.99 (1H, ddd, J = 17.1 Hz, J = 1.4 Hz, J = 1.4 Hz, CH=CH$_E\underline{\text{H}}_Z$); 5.10 (1H, dqt, J = 15.0 Hz, J = 6.5 Hz, 1.0 Hz, CH=C$\underline{\text{H}}$CH$_3$); 5.48 (1H, dtq, J = 15.0 Hz, J = 7.5 Hz, J = 1.5 Hz, C$\underline{\text{H}}$=CHCH$_3$); 5.82 (1H, ddd, J = 17.1 Hz, J = 10.6 Hz, J = 7.0 Hz, C$\underline{\text{H}}$=CH$_E$H$_Z$); 7.01 (1H, ddd, J = 8.7 Hz, J = 6.4 Hz, J = 1.0 Hz, CH$_{\text{arom.}}$); 7.10 Hz (1H, ddd, J = 8.7 Hz, J = 6.4 Hz, J = 1.0 Hz, CH$_{\text{arom.}}$); 7.50 (1H, d, J = 8.7 Hz, CH$_{\text{arom.}}$); 7.71 (1H, d, J = 8.7 Hz, CH$_{\text{arom.}}$). **^{13}C-NMR (100 M, CDCl$_3$):** δ 17.7 (CH$_3$); 19.6 (CH$_3$); 35.0 (CH$_2$); 40.1 (CH); 41.9 (SCH$_2$); 113.7 (CH=$\underline{\text{C}}$H$_2$); 118.9 (C$_{\text{q arom.}}$); 120.3 (CH$_{\text{arom.}}$); 121.0 (CH$_{\text{arom.}}$); 122.5 (CH$_{\text{arom.}}$); 124.0 (CH$_{\text{arom.}}$); 126.4 ($\underline{\text{C}}$H=CHCH$_3$); 129.2 (CH=$\underline{\text{C}}$HCH$_3$); 136.1 (C$_{\text{q arom.}}$); 138.3 (C$_{\text{q arom.}}$); 142.3 (C$_{\text{q arom.}}$); 143.0 ($\underline{\text{C}}$H=CH$_2$). **MS (ESI): m/z (%):** 289.0 (M + H$^+$, 100). **IR (cm^{-1}) ν $_{\text{max}}$:** 1220; 1444; 1665 (C=CH$_2$); 2915; 3288. **Chromatography:** hexanes. **R$_f$** = 0.23. **Yield:** 80%.

6. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra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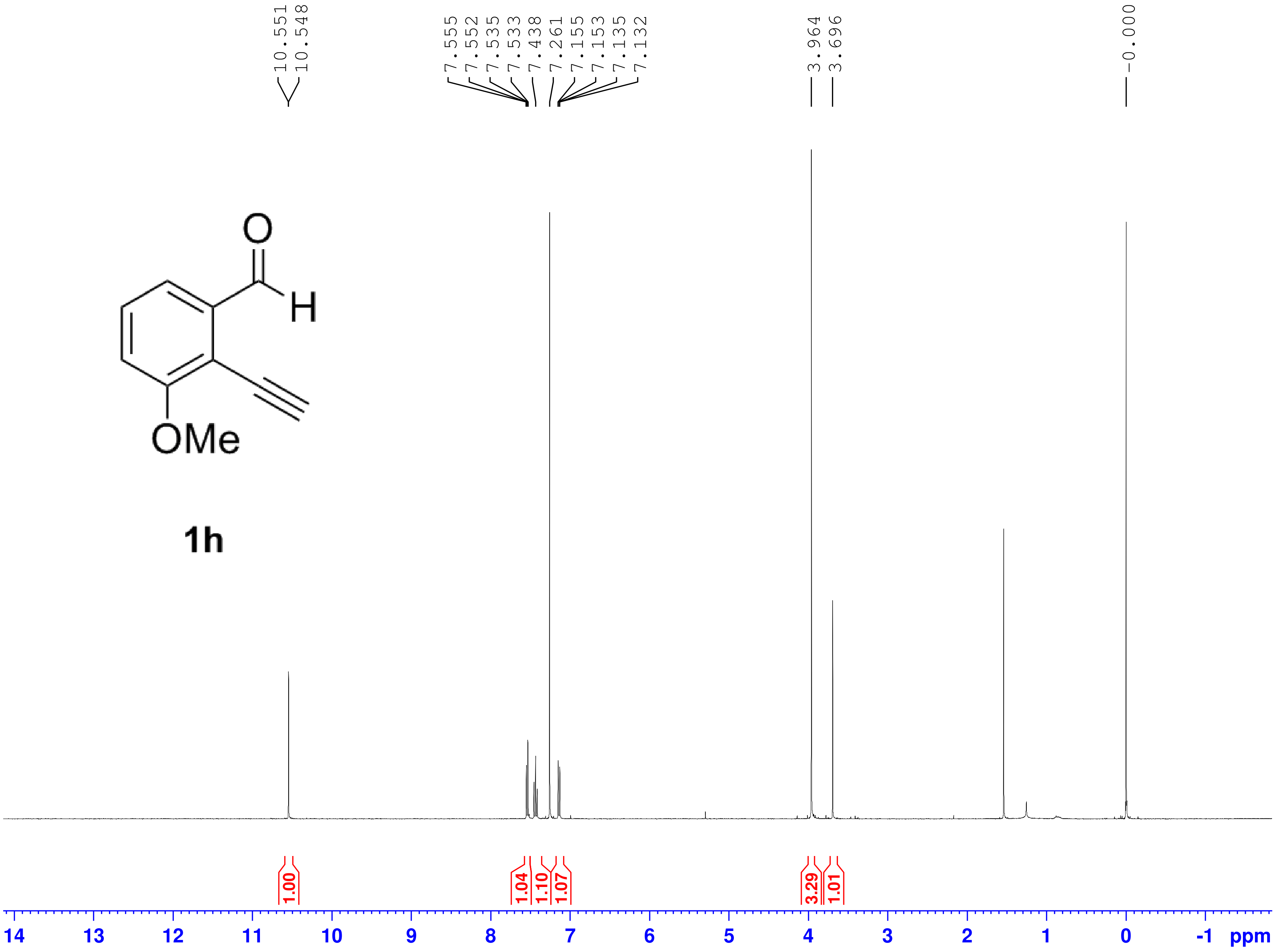
O
H
1e
(Millions)
0
10.0
20.0
30.0
40.0
50.0
1.00
1.09
1.14
1.14
0.93
3.81
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
10.450
7.820
7.793
7.399
7.273
7.245
3.412
2.383
X : parts per Million : 1H


10.551
10.548
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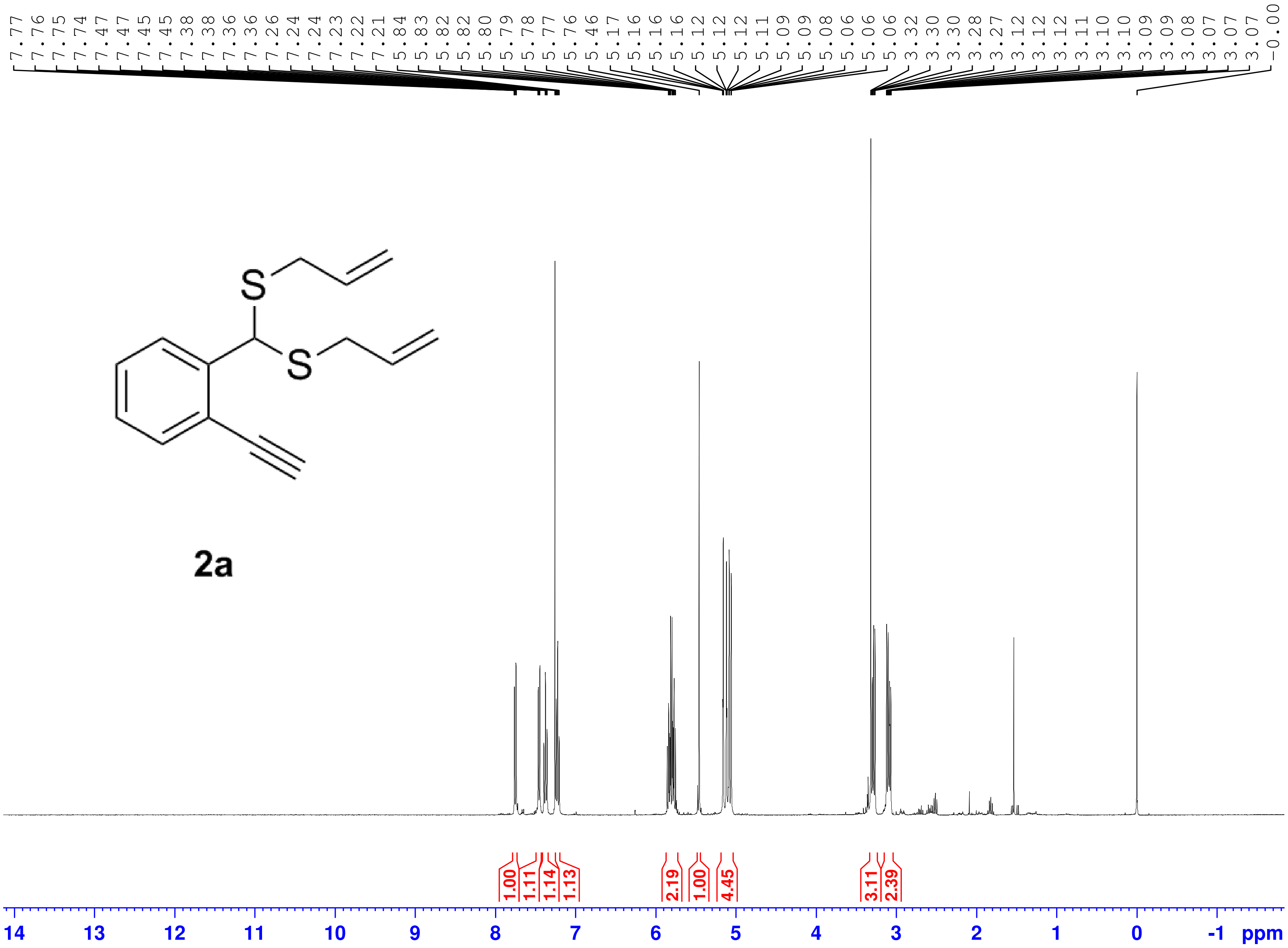
7.552
7.535
7.533
7.438
7.261
7.155
7.153
7.135
7.132
3.964
3.696
-0.000
O
H
OMe
1h
1.00
1.04
1.10
1.07
3.29
1.01
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm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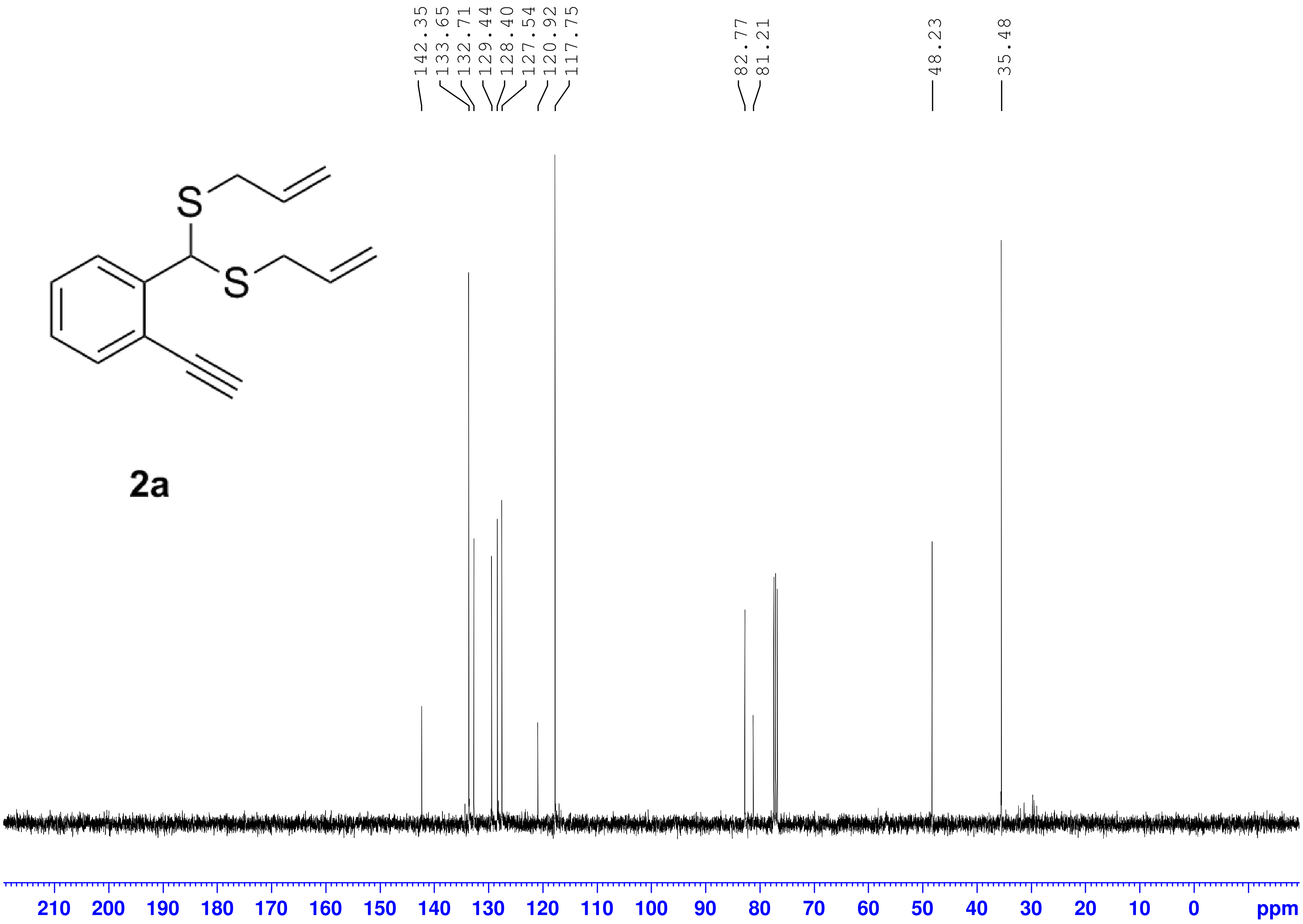
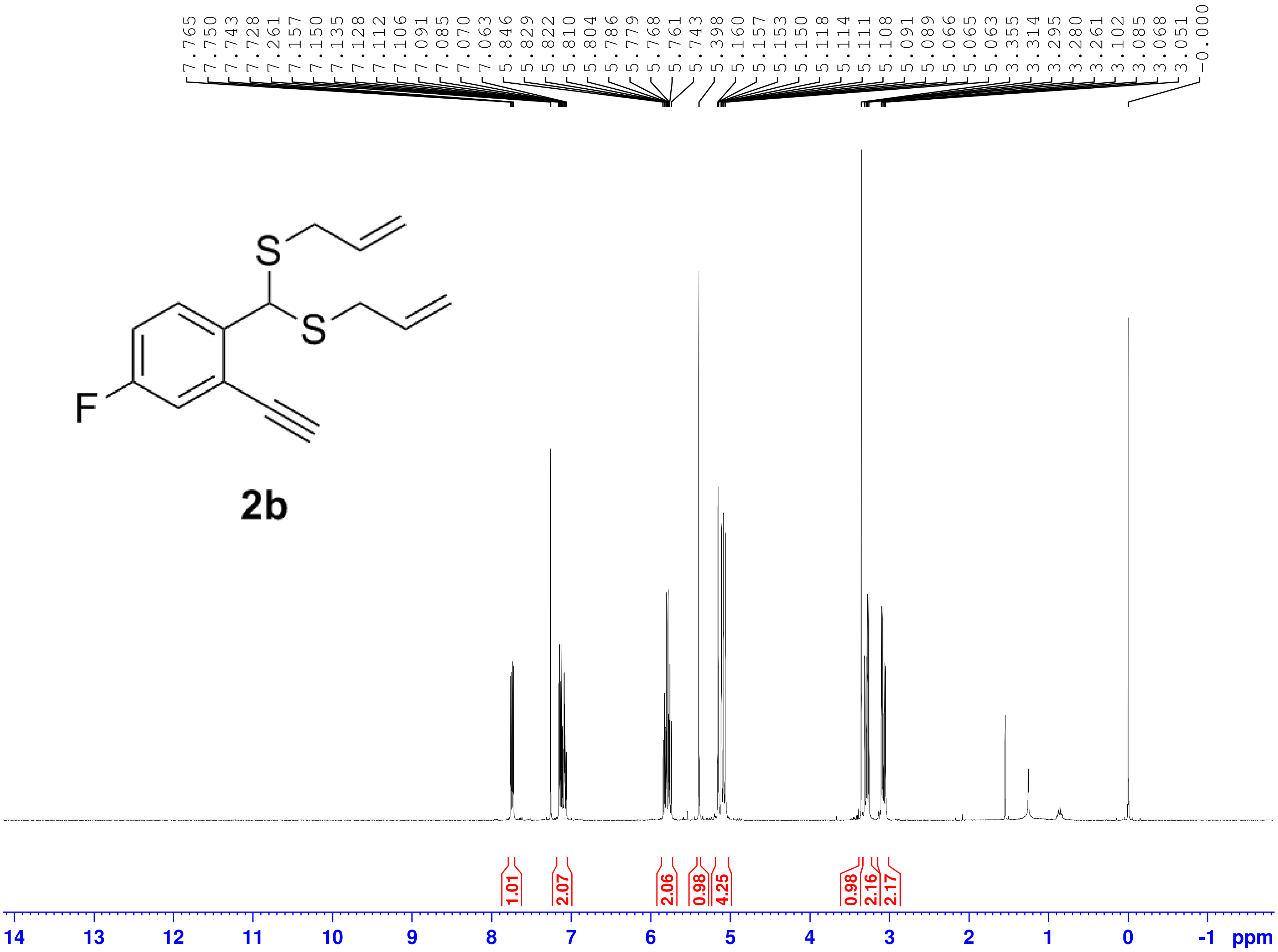
7.76
7.75
7.74
7.47
7.47
7.45
7.45
7.38
7.38
7.36
7.36
7.26
7.24
7.24
7.23
7.22
7.21
5.84
5.83
5.82
5.82
5.80
5.79
5.78
5.77
5.76
5.46
5.17
5.16
5.16
5.16
5.12
5.12
5.12
5.11
5.09
5.09
5.08
5.06
5.06
5.06
3.32
3.30
3.30
3.28
3.27
3.12
3.12
3.12
3.11
3.10
3.10
3.09
3.09
3.08
3.07
3.07
3.07
-0.00
S
S
2a
1.00
1.11
1.14
1.13
2.19
1.00
4.45
3.11
2.39
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm


142.35
133.65
132.71
129.44
128.40
127.54
120.92
117.75
82.77
81.21
48.23
35.48
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

2a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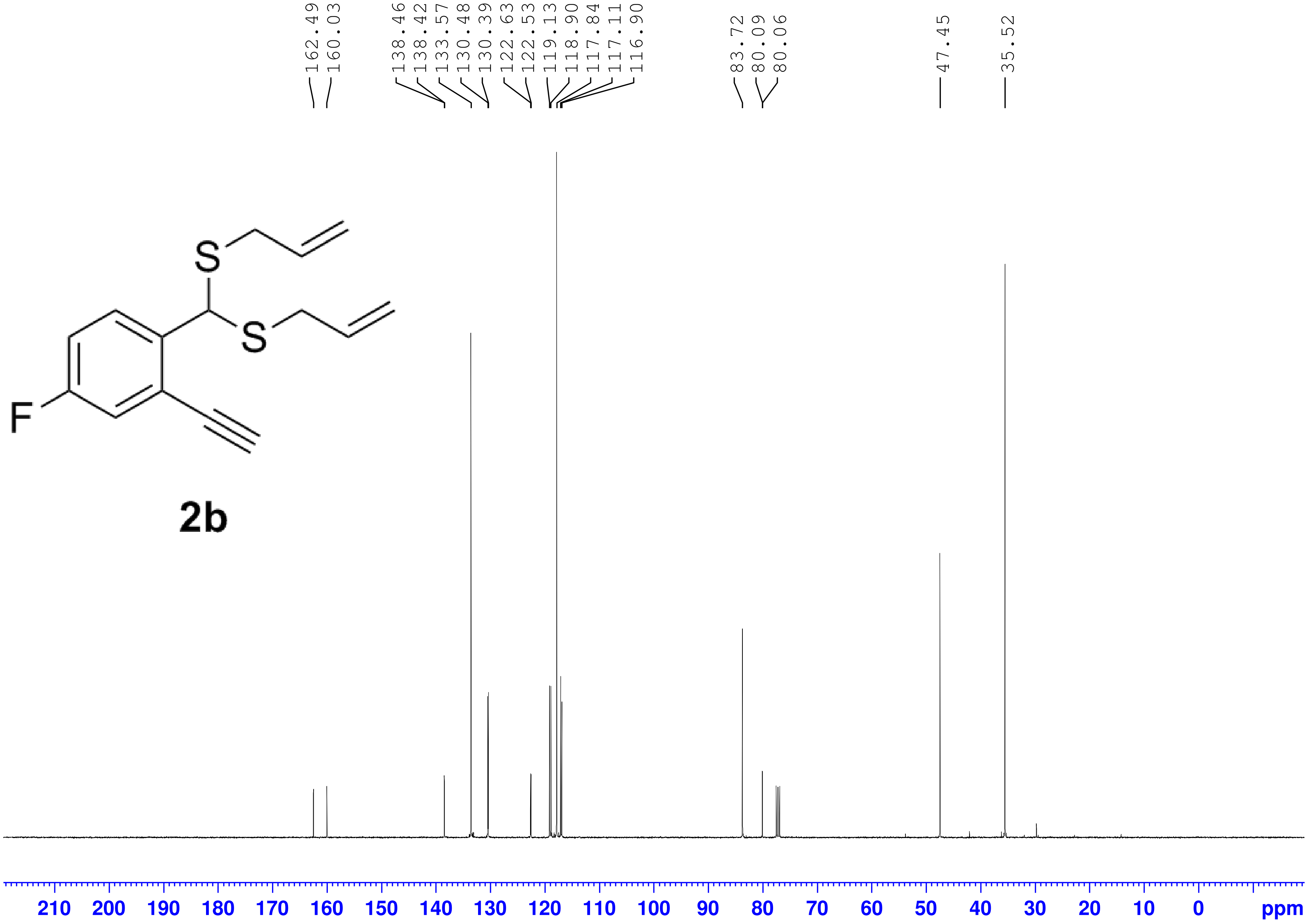
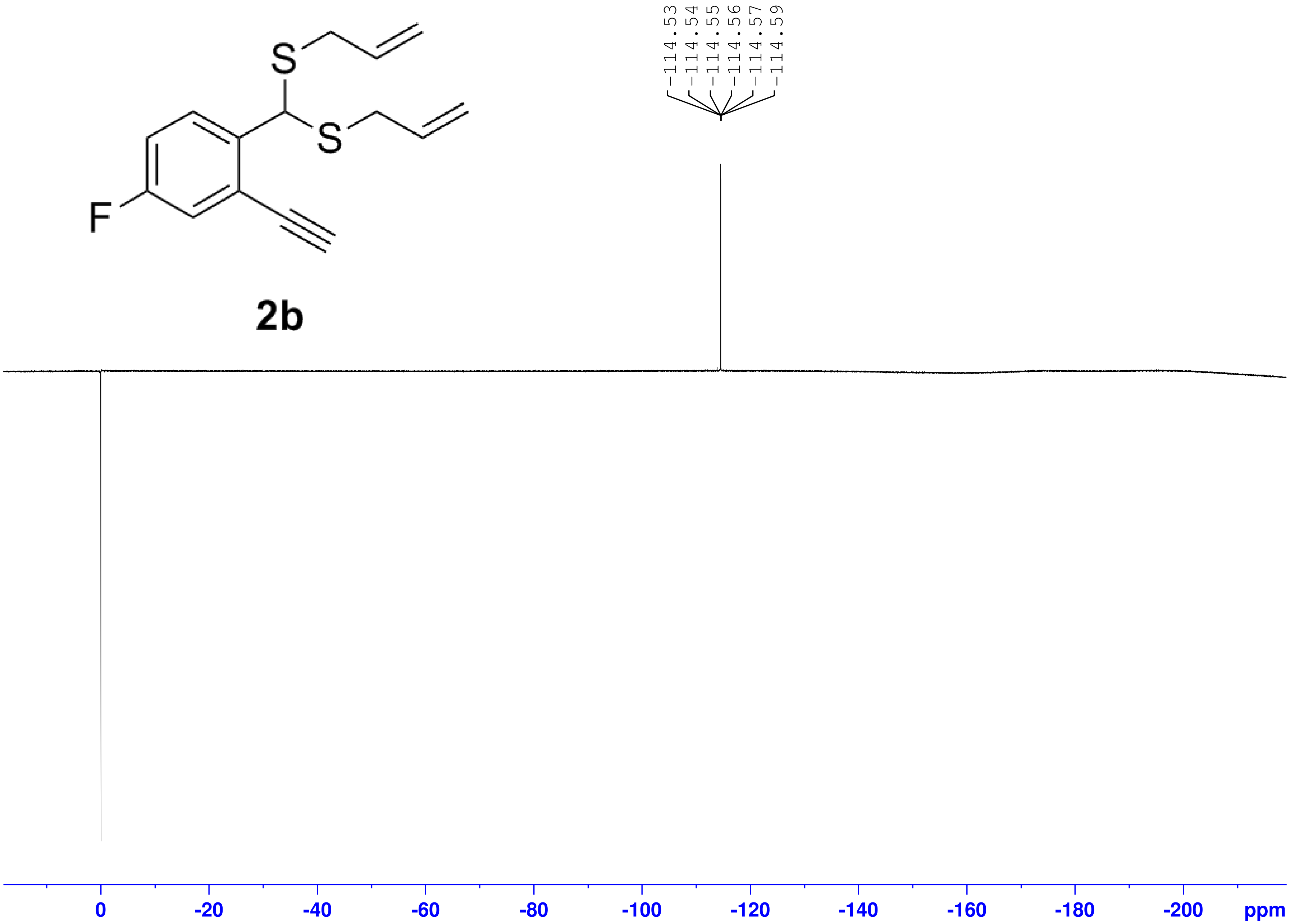
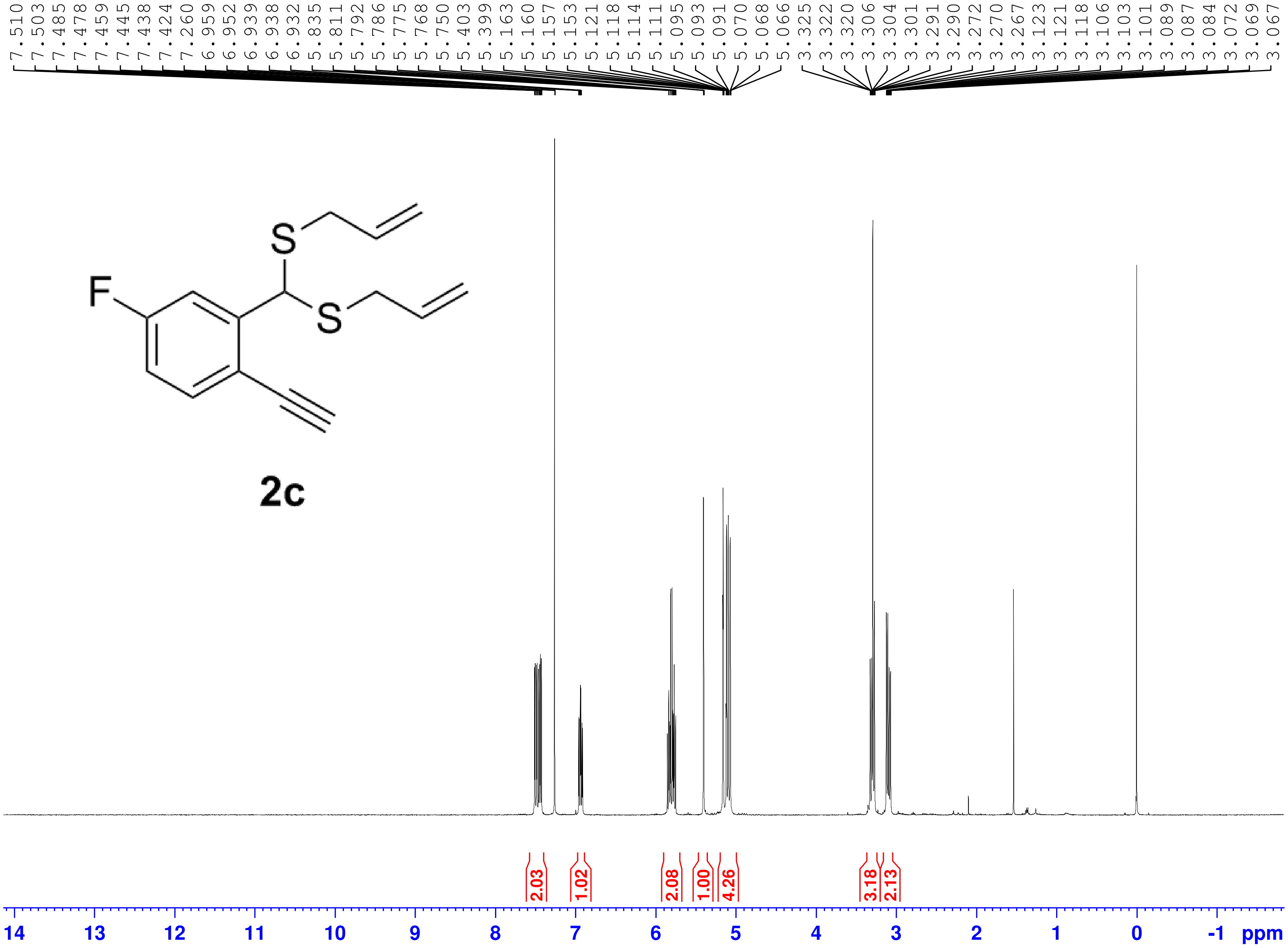
7.750
7.743
7.728
7.261
7.157
7.150
7.135
7.128
7.112
7.106
7.091
7.085
7.070
7.063
5.846
5.829
5.822
5.810
5.804
5.786
5.779
5.768
5.761
5.743
5.398
5.160
5.157
5.153
5.150
5.118
5.114
5.111
5.108
5.091
5.089
5.066
5.065
5.063
3.355
3.314
3.295
3.280
3.261
3.102
3.085
3.068
3.051
-0.000
S
S
F
1.01
2.07
2.06
0.98
4.25
0.98
2.16
2.17
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

2b

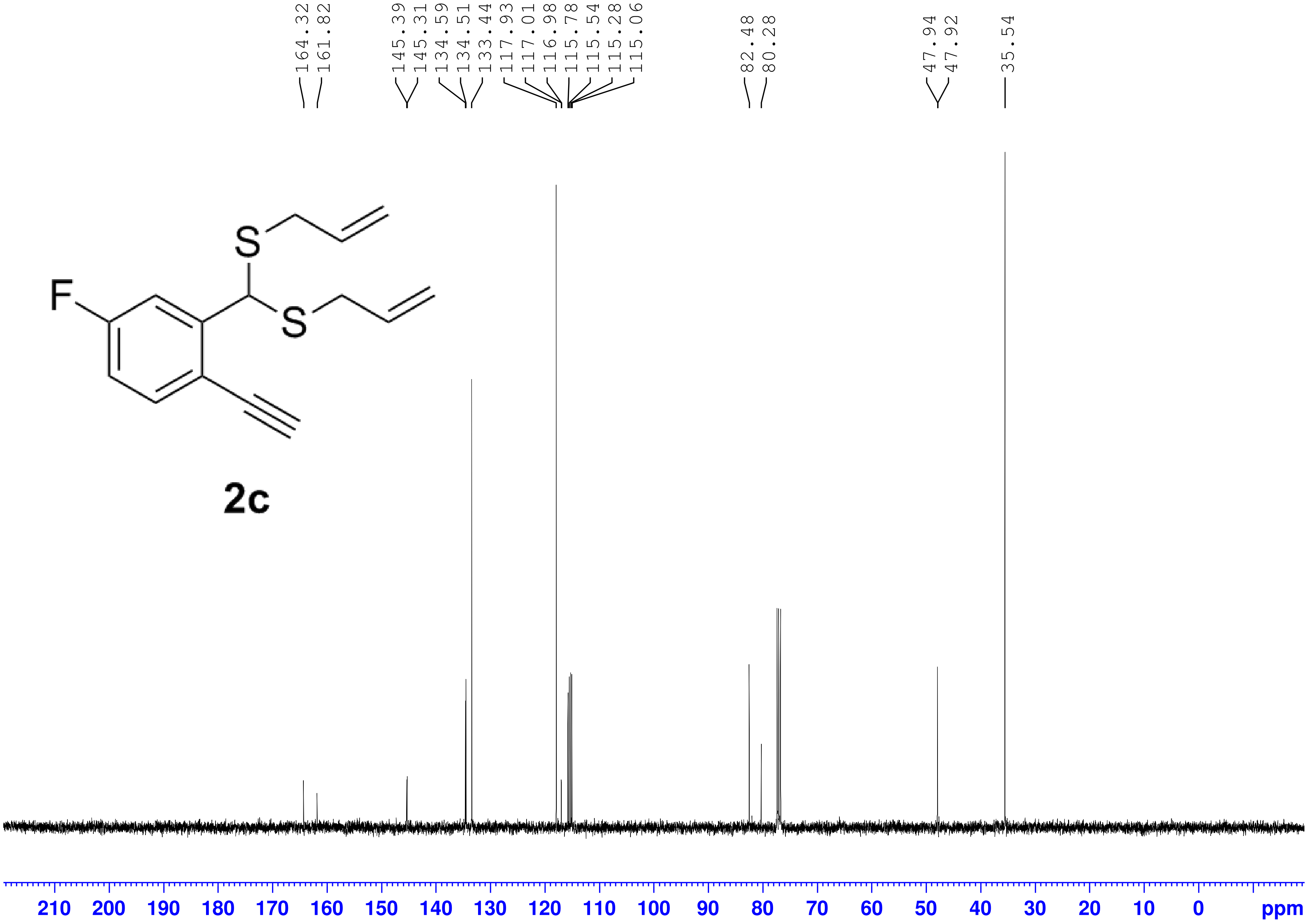

162.49
160.03
138.46
138.42
133.57
130.48
130.39
122.63
122.53
119.13
118.90
117.84
117.11
116.90
83.72
80.09
80.06
47.45
35.52
S
S
F
2b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-114.53
-114.54
-114.55
-114.56
-114.57
-114.59
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
S
S
F

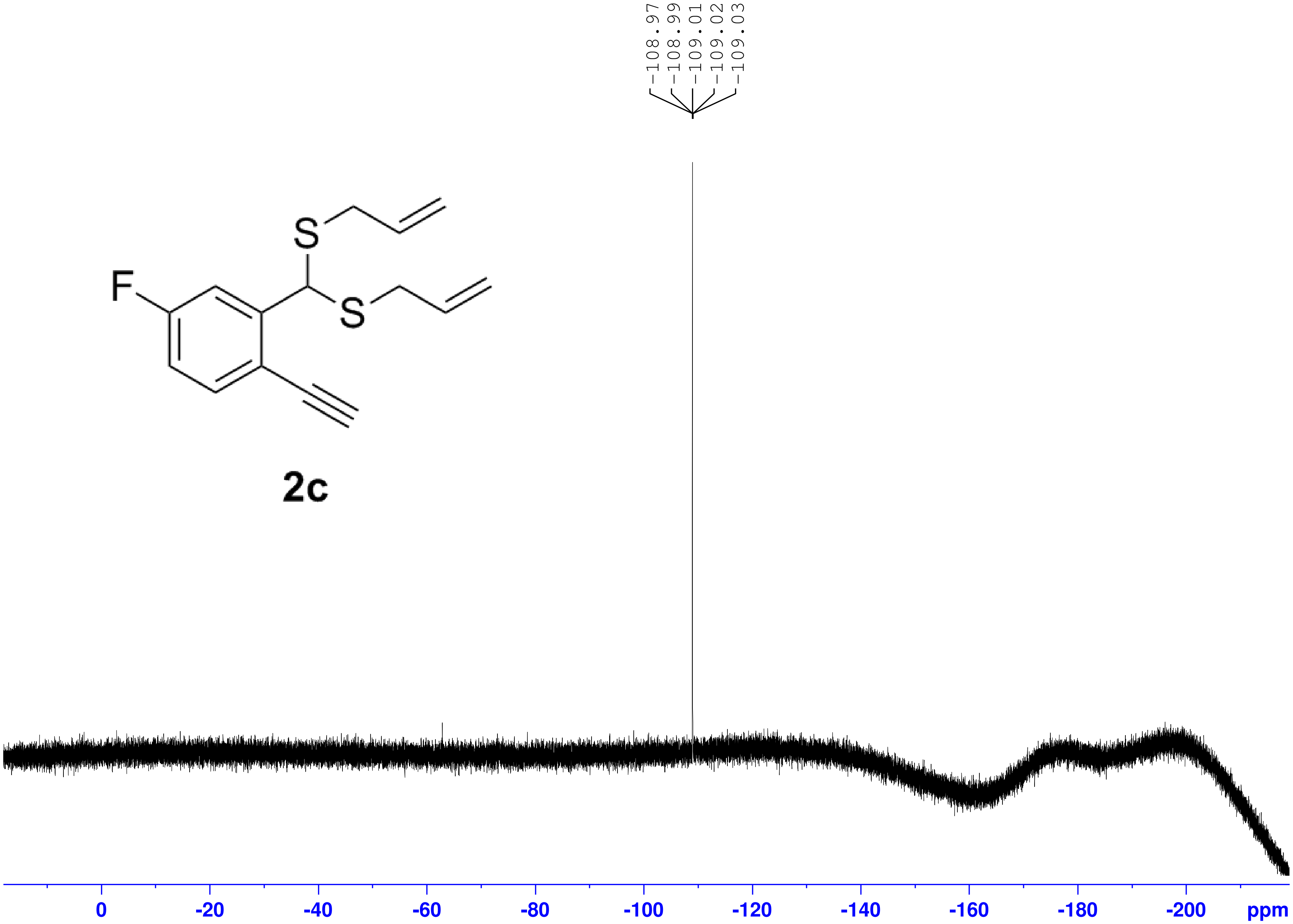
2b


7.510
7.503
7.485
7.478
7.459
7.445
7.438
7.424
7.260
6.959
6.952
6.939
6.938
6.932
5.835
5.811
5.792
5.786
5.775
5.768
5.750
5.403
5.399
5.163
5.160
5.157
5.153
5.121
5.118
5.114
5.111
5.095
5.093
5.091
5.070
5.068
5.066
3.325
3.322
3.320
3.306
3.304
3.301
3.291
3.290
3.272
3.270
3.267
3.123
3.121
3.118
3.106
3.103
3.101
3.089
3.087
3.084
3.072
3.069
3.067
F
S
S
2.03
1.02
2.08
1.00
4.26
3.18
2.13
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

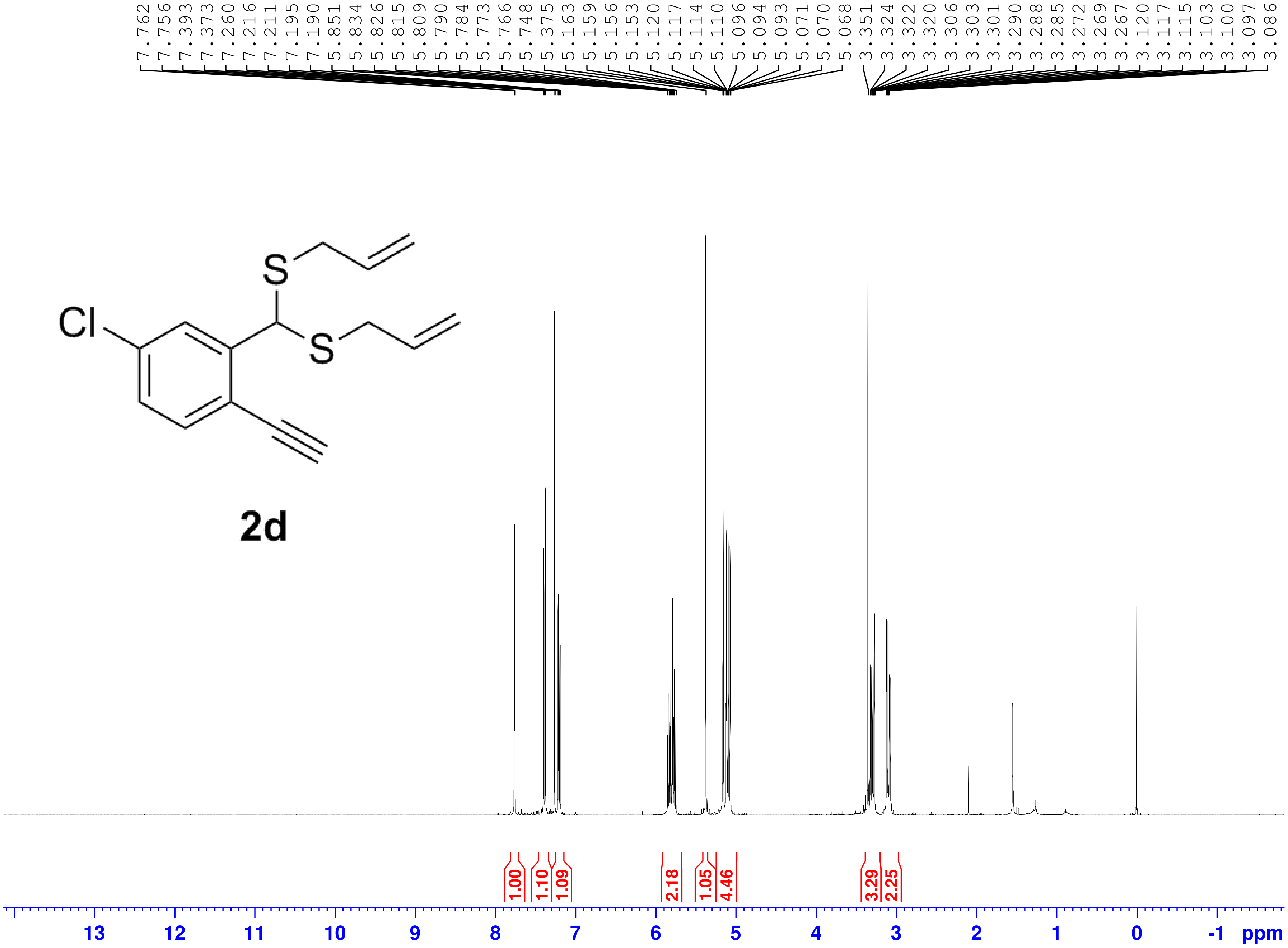
2c


164.32
161.82
145.39
145.31
134.59
134.51
133.44
117.93
117.01
116.98
115.78
115.54
115.28
115.06
82.48
80.28
47.94
47.92
35.54
F
S
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2c


F
S
S
-108.97
-108.99
-109.01
-109.02
-109.03
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

2c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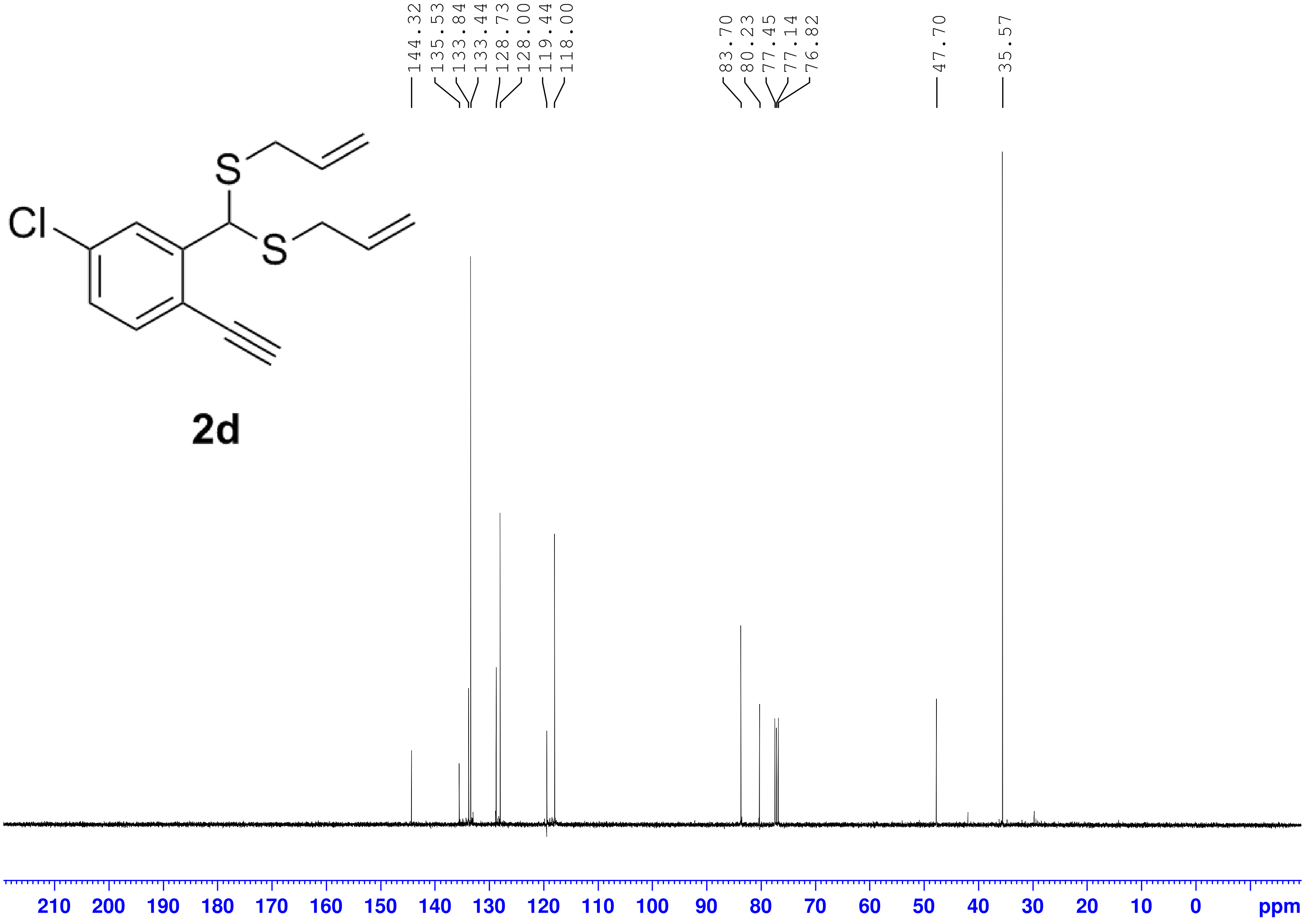
7.756
7.393
7.373
7.260
7.216
7.211
7.195
7.190
5.851
5.834
5.826
5.815
5.809
5.790
5.784
5.773
5.766
5.748
5.375
5.163
5.159
5.156
5.153
5.120
5.117
5.114
5.110
5.096
5.094
5.093
5.071
5.070
5.068
3.351
3.324
3.322
3.320
3.306
3.303
3.301
3.290
3.288
3.285
3.272
3.269
3.267
3.120
3.117
3.115
3.103
3.100
3.097
3.086
Cl
S
S
2d
1.00
1.10
1.09
2.18
1.05
4.46
3.29
2.25
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

Cl
S
S

2d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133.44
128.73
128.00
119.44
118.00
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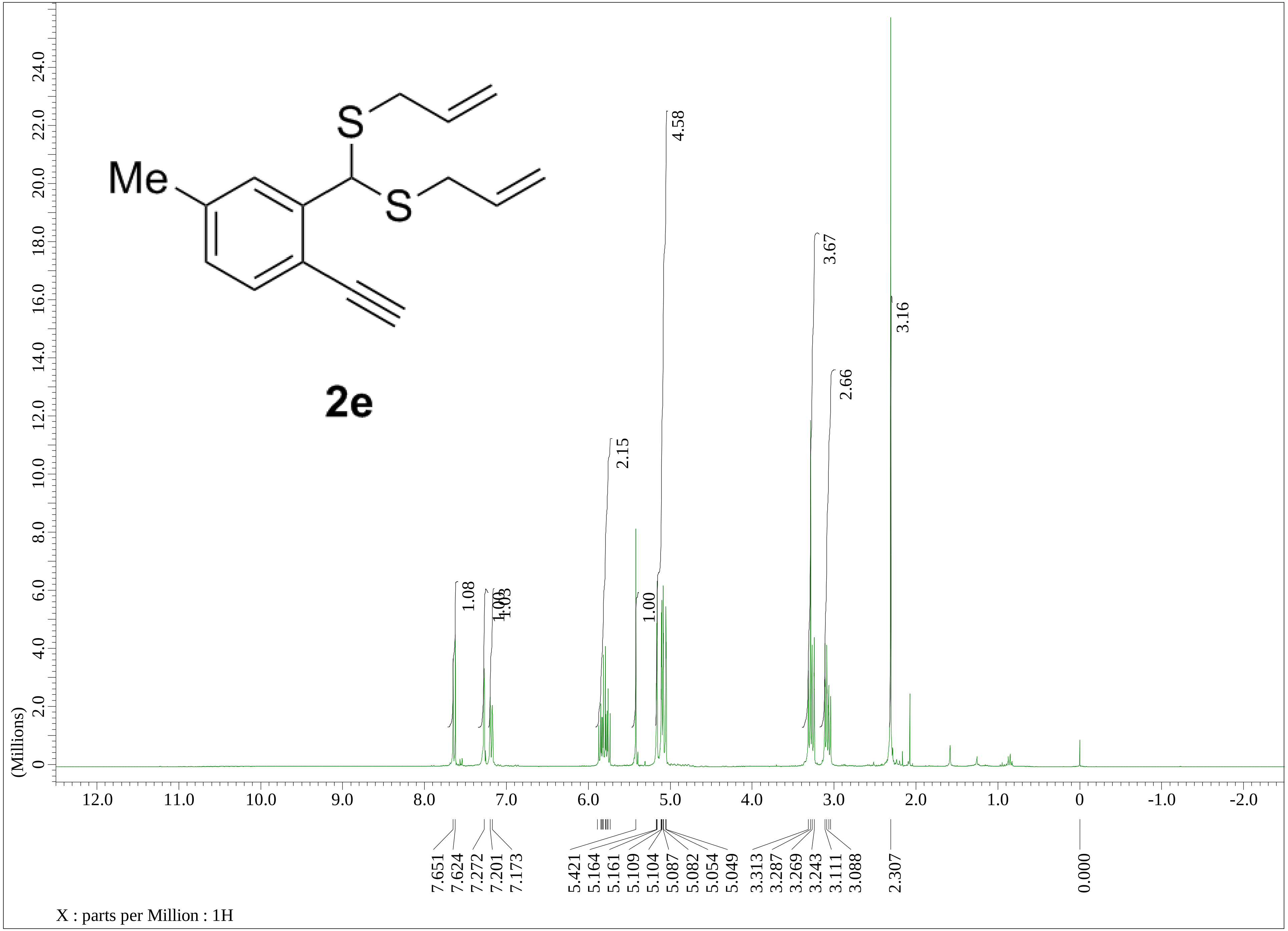
80.23
77.45
77.14
76.82
47.70
35.57
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me
S
S
2e
(Millions)
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22.0
20.0
18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
1.08
1.00
1.03
2.15
1.00
4.58
3.67
2.66
3.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.651
7.624
7.272
7.201
7.173
5.421
5.164
5.161
5.109
5.104
5.087
5.082
5.054
5.049
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3.269
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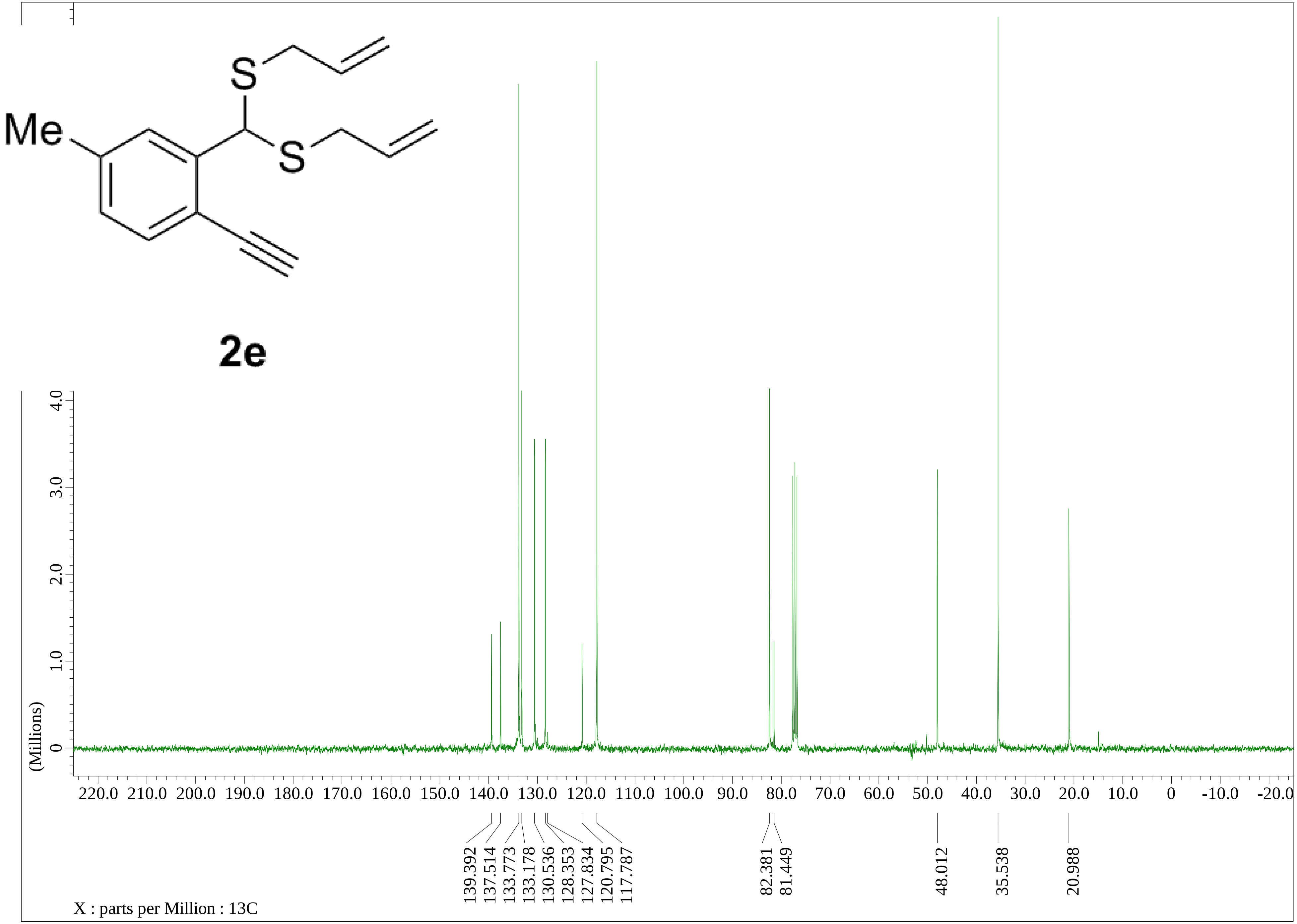
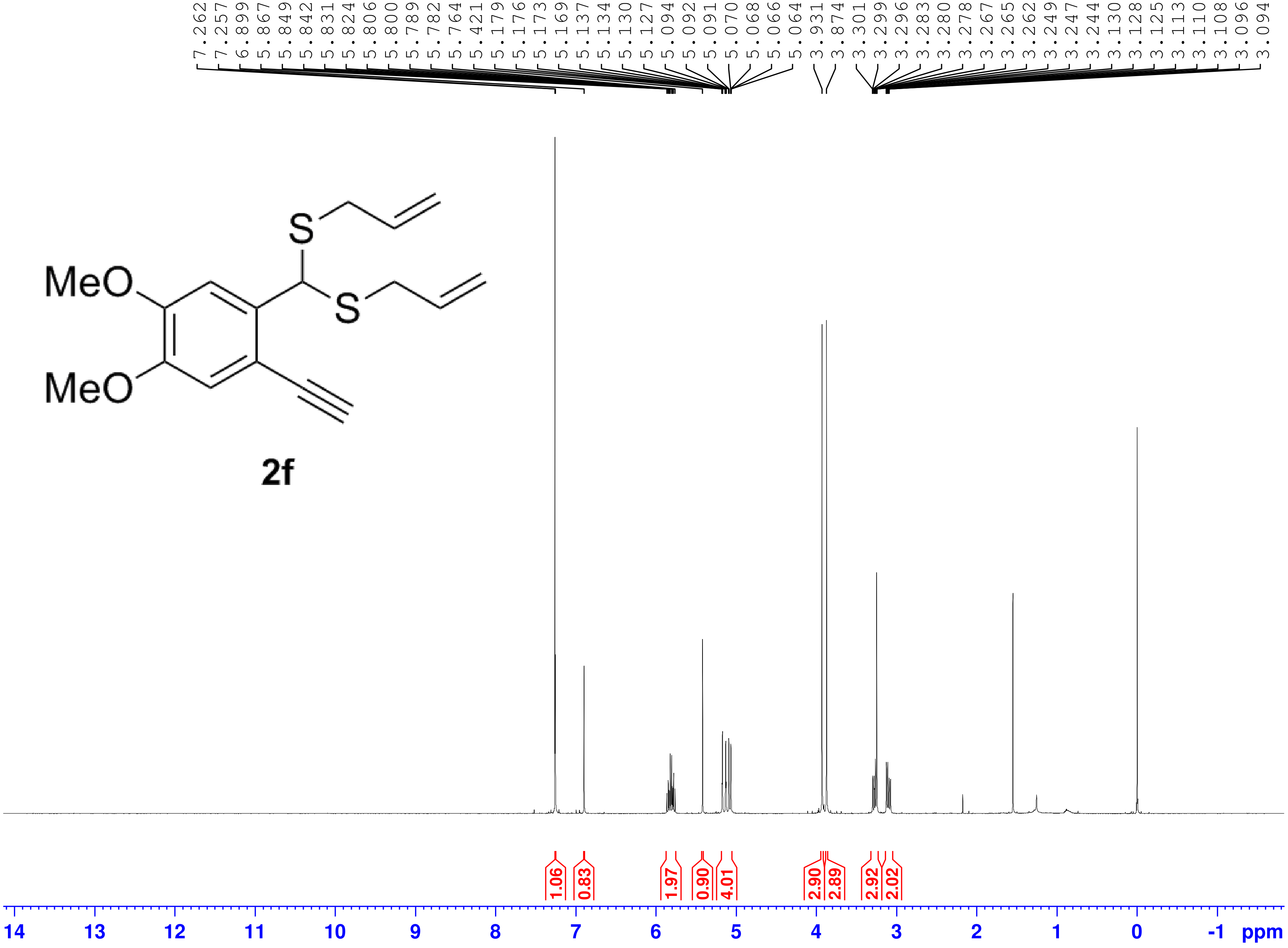
3.111
3.088
2.307
0.000
X : parts per Million : 1H


Me
S
S
2e
(Millions)
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
139.392
137.514
133.773
133.178
130.536
128.353
127.834
120.795
117.787
82.381
81.449
48.012
35.538
20.988
X : parts per Million : 13C


7.262
7.257
6.899
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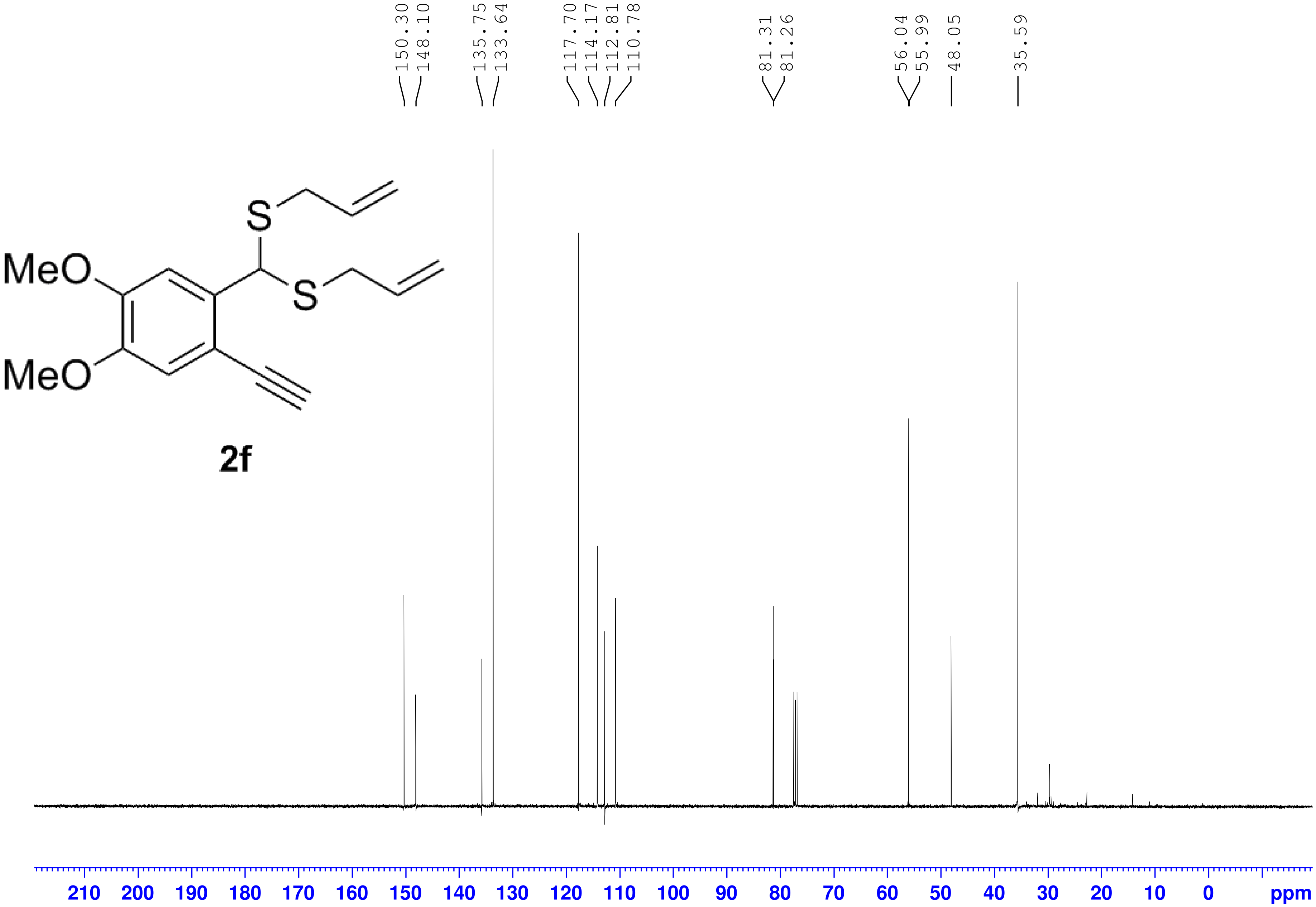
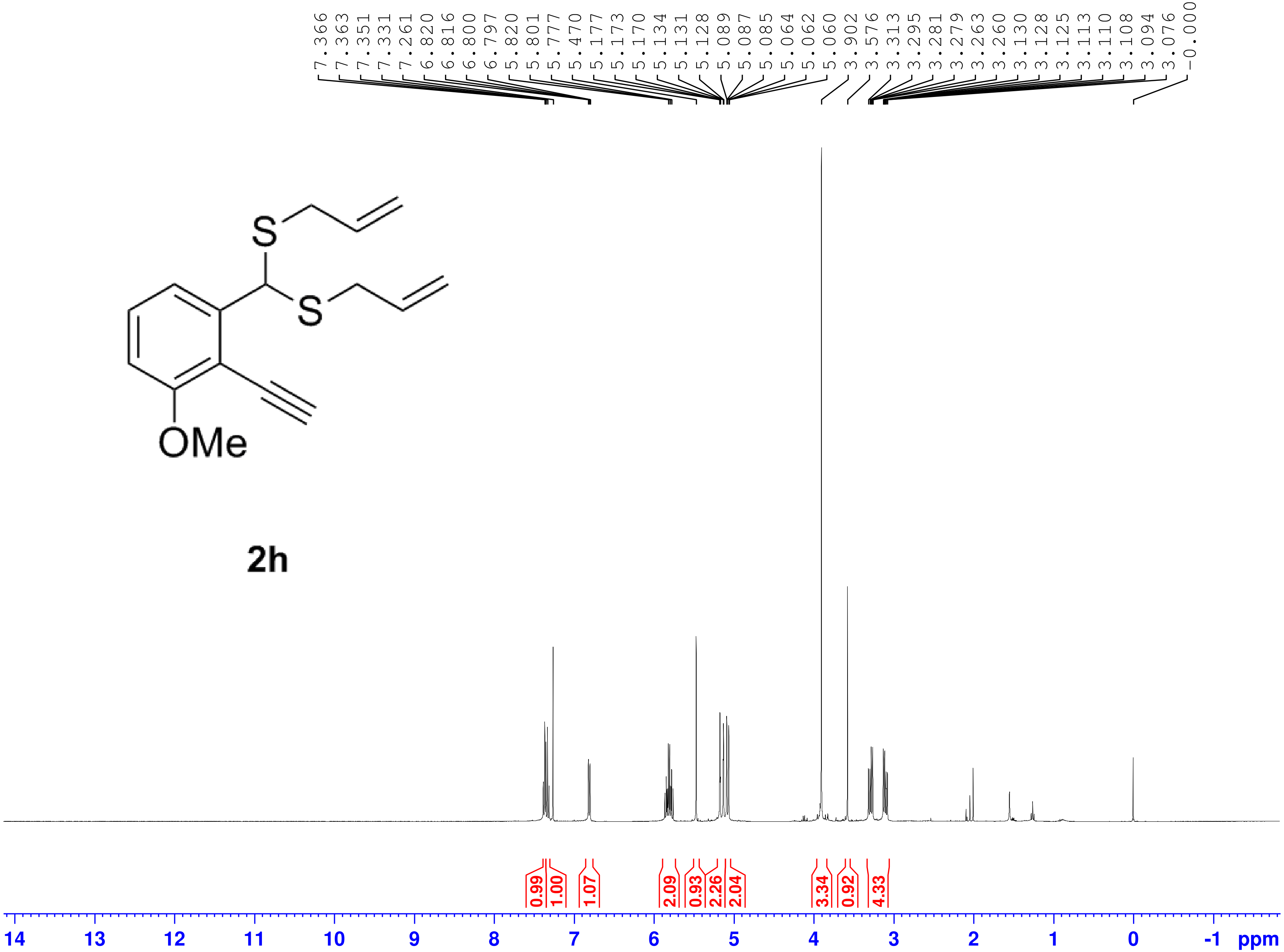
5.849
5.842
5.831
5.824
5.806
5.800
5.789
5.782
5.764
5.421
5.179
5.176
5.173
5.169
5.137
5.134
5.130
5.127
5.094
5.092
5.091
5.070
5.068
5.066
5.064
3.931
3.874
3.301
3.299
3.296
3.283
3.280
3.278
3.267
3.265
3.262
3.249
3.247
3.244
3.130
3.128
3.125
3.113
3.110
3.108
3.096
3.094
MeO
MeO
S
S
1.06
0.83
1.97
0.90
4.01
2.90
2.89
2.92
2.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

2f



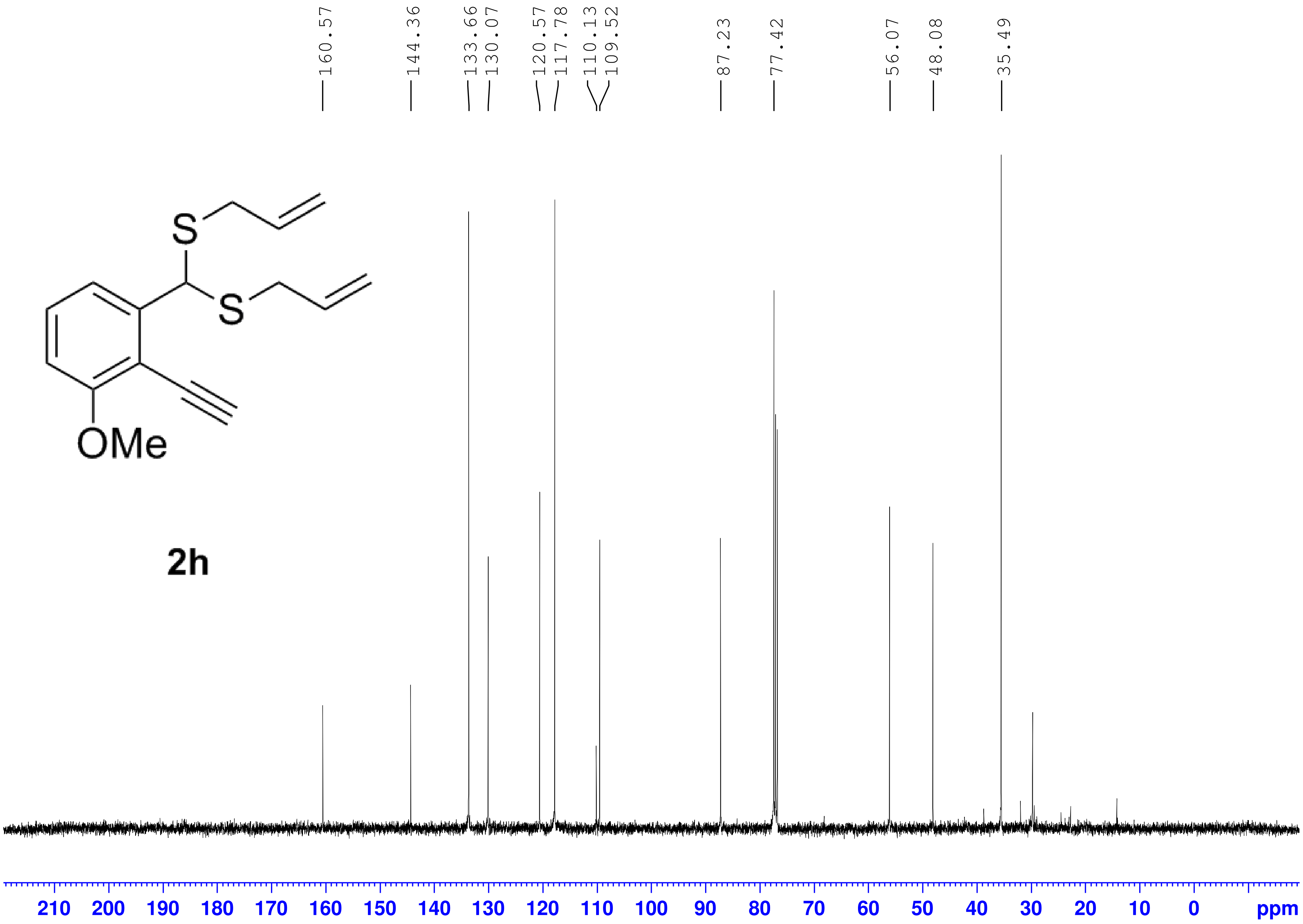
150.30
148.10
135.75
133.64
117.70
114.17
112.81
110.78
81.31
81.26
56.04
55.99
48.05
35.59
MeO
MeO
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

2f


S
S
OMe

2h

7.366
7.363
7.351
7.331
7.261
6.820
6.816
6.800
6.797
5.820
5.801
5.777
5.470
5.177
5.173
5.170
5.134
5.131
5.128
5.089
5.087
5.085
5.064
5.062
5.060
3.902
3.576
3.313
3.295
3.281
3.279
3.263
3.260
3.130
3.128
3.125
3.113
3.110
3.108
3.094
3.076
-0.000
0.99
1.00
1.07
2.09
0.93
2.26
2.04
3.34
0.92
4.33
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm



2h

160.57
144.36
133.66
130.07
120.57
117.78
110.13
109.52
87.23
77.42
56.07
48.08
35.49
S
S
OMe
210
200
190
180
170
160
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130
120
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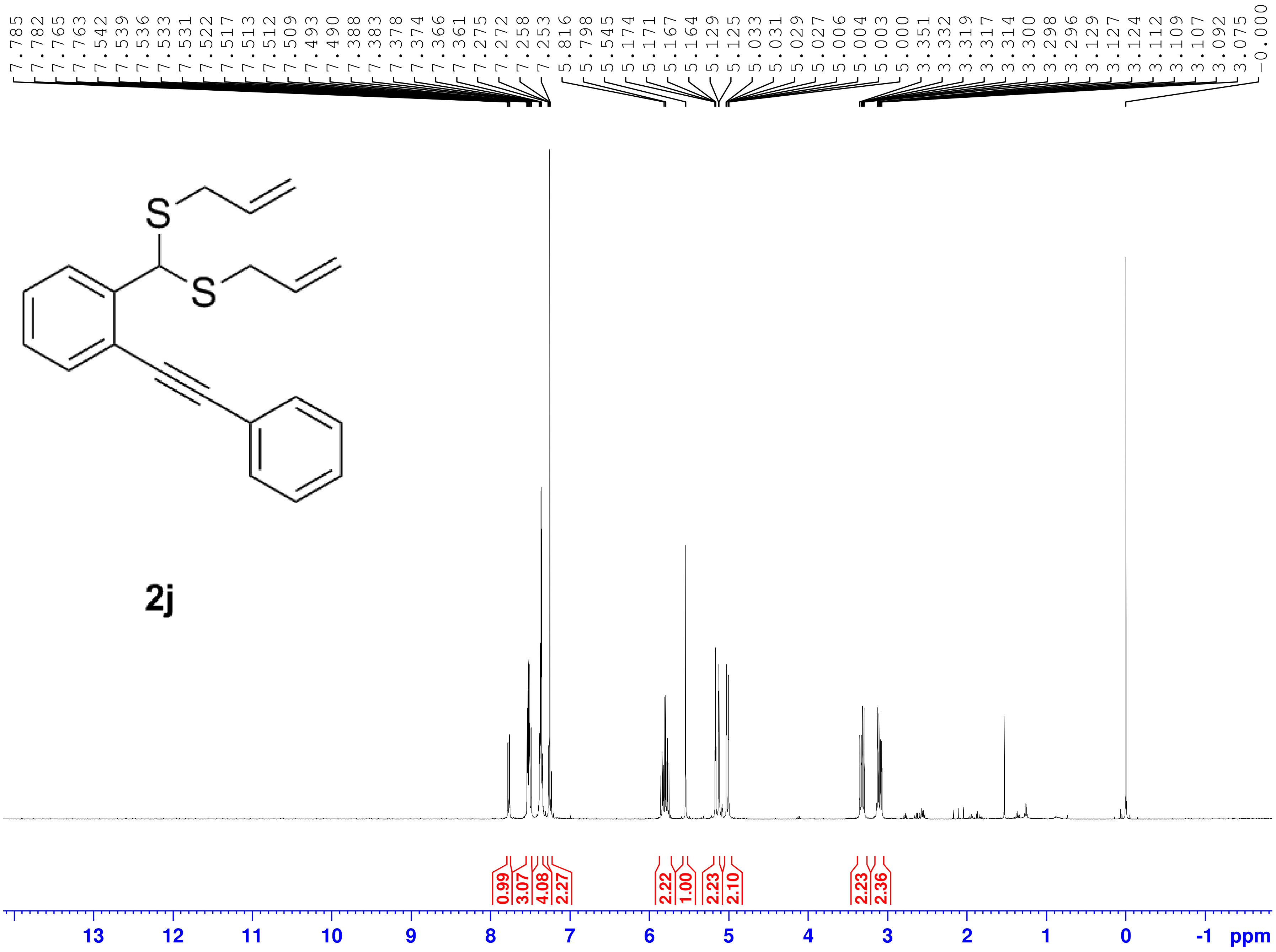
100
90
80
70
60
50
40
30
20
10
0
ppm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7.513
7.512
7.509
7.493
7.490
7.388
7.383
7.378
7.374
7.366
7.361
7.275
7.272
7.258
7.253
5.816
5.798
5.545
5.174
5.171
5.167
5.164
5.129
5.125
5.033
5.031
5.029
5.027
5.006
5.004
5.003
5.000
3.351
3.332
3.319
3.317
3.314
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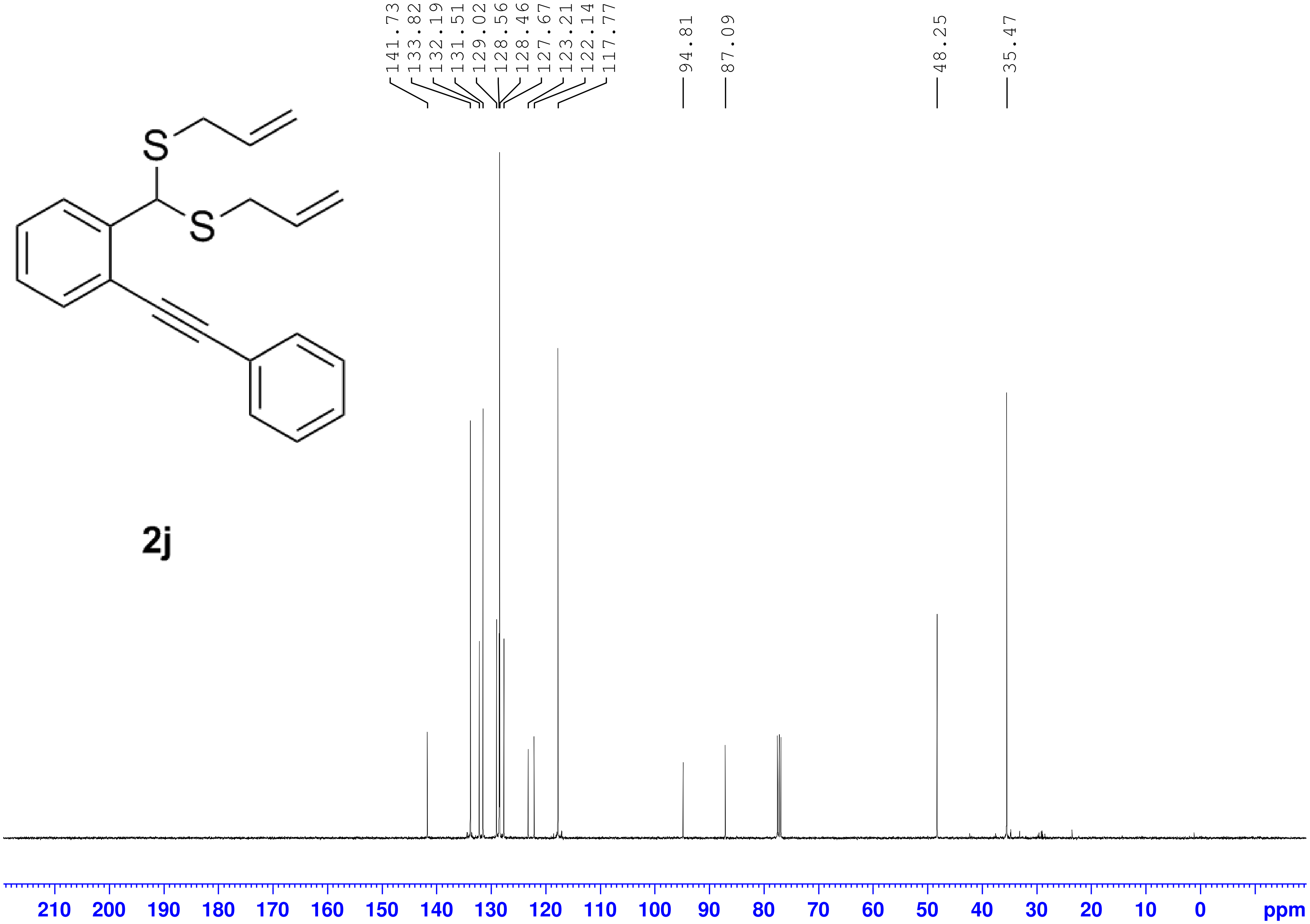
3.296
3.129
3.127
3.124
3.112
3.109
3.107
3.092
3.075
-0.000
S
S
2j
0.99
3.07
4.08
2.27
2.22
1.00
2.23
2.10
2.23
2.36
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm



2j

141.73
133.82
132.19
131.51
129.02
128.56
128.46
127.67
123.21
122.14
117.77
94.81
87.09
48.25
35.47
S
S
210
200
190
180
170
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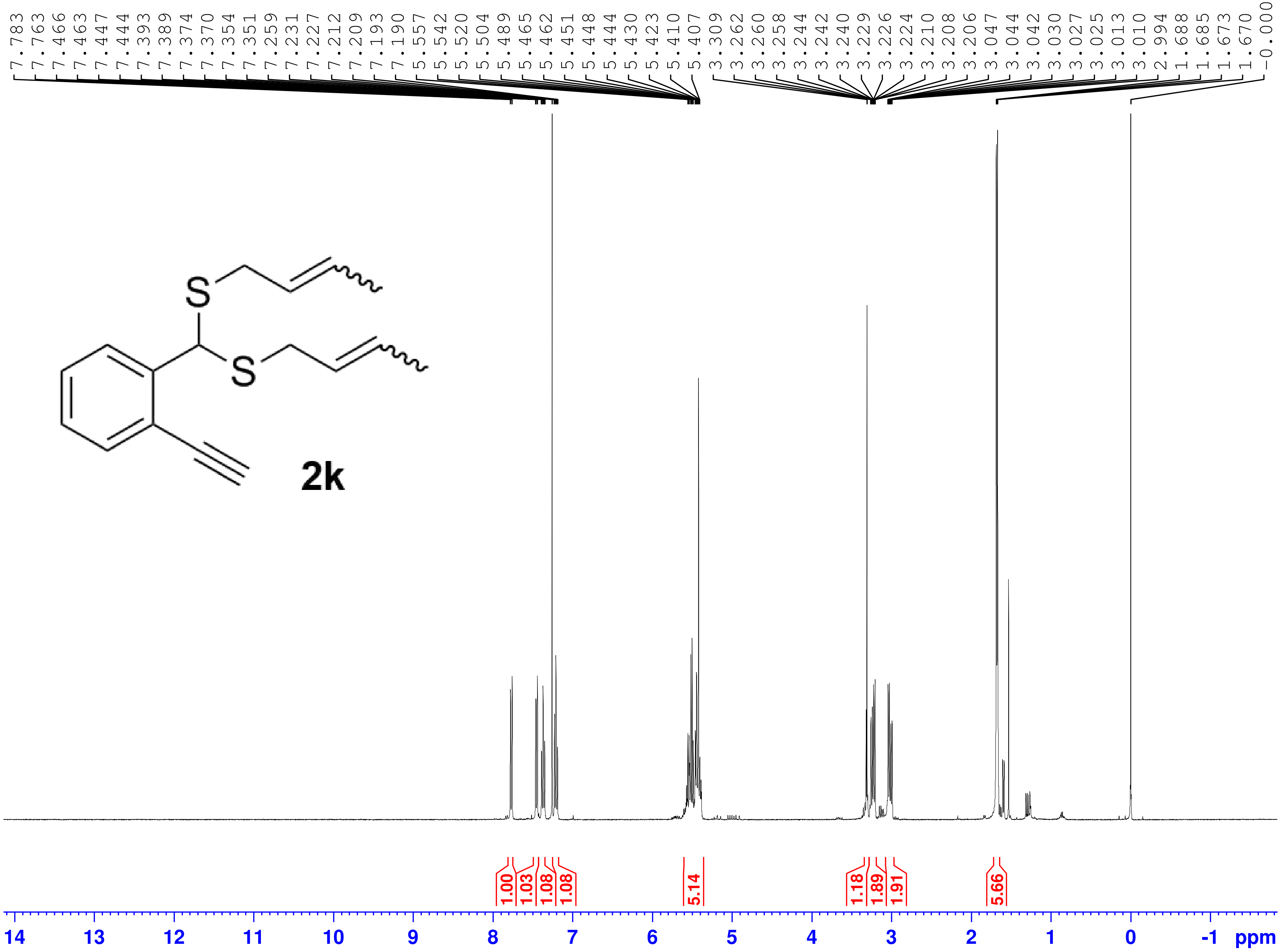
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.393
7.389
7.374
7.370
7.354
7.351
7.259
7.231
7.227
7.212
7.209
7.193
7.190
5.557
5.542
5.520
5.504
5.489
5.465
5.462
5.451
5.448
5.444
5.430
5.423
5.410
5.407
3.309
3.262
3.260
3.258
3.244
3.242
3.240
3.229
3.226
3.224
3.210
3.208
3.206
3.047
3.044
3.042
3.030
3.027
3.025
3.013
3.010
2.994
1.688
1.685
1.673
1.670
-0.000
S
S
2k
1.00
1.03
1.08
1.08
5.14
1.18
1.89
1.91
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14
13
12
11
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9
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5
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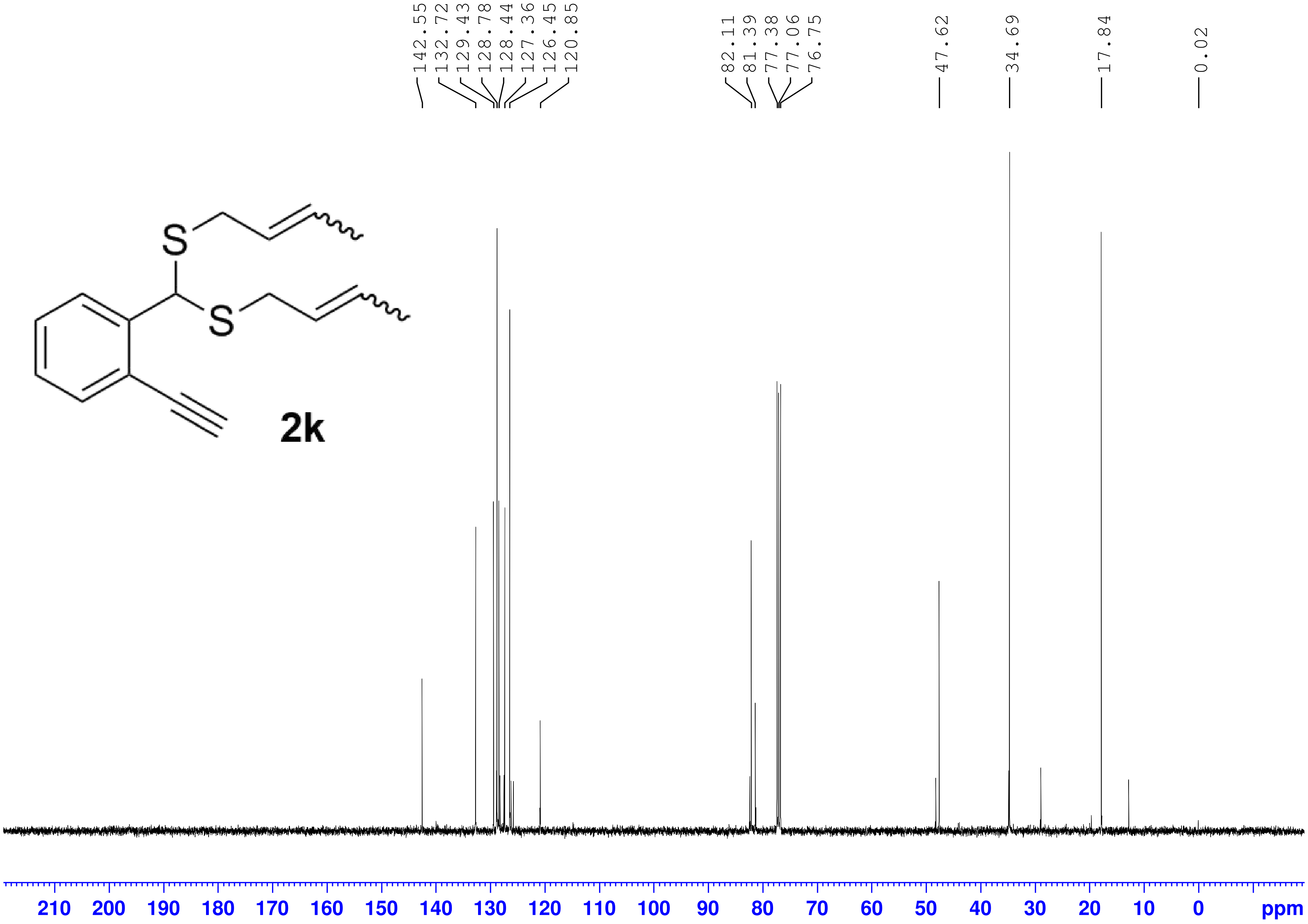
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132.72
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128.78
128.44
127.36
126.45
120.85
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81.39
77.38
77.06
76.75
47.62
34.69
17.84
0.02
S
S
2k
210
200
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180
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140
130
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80
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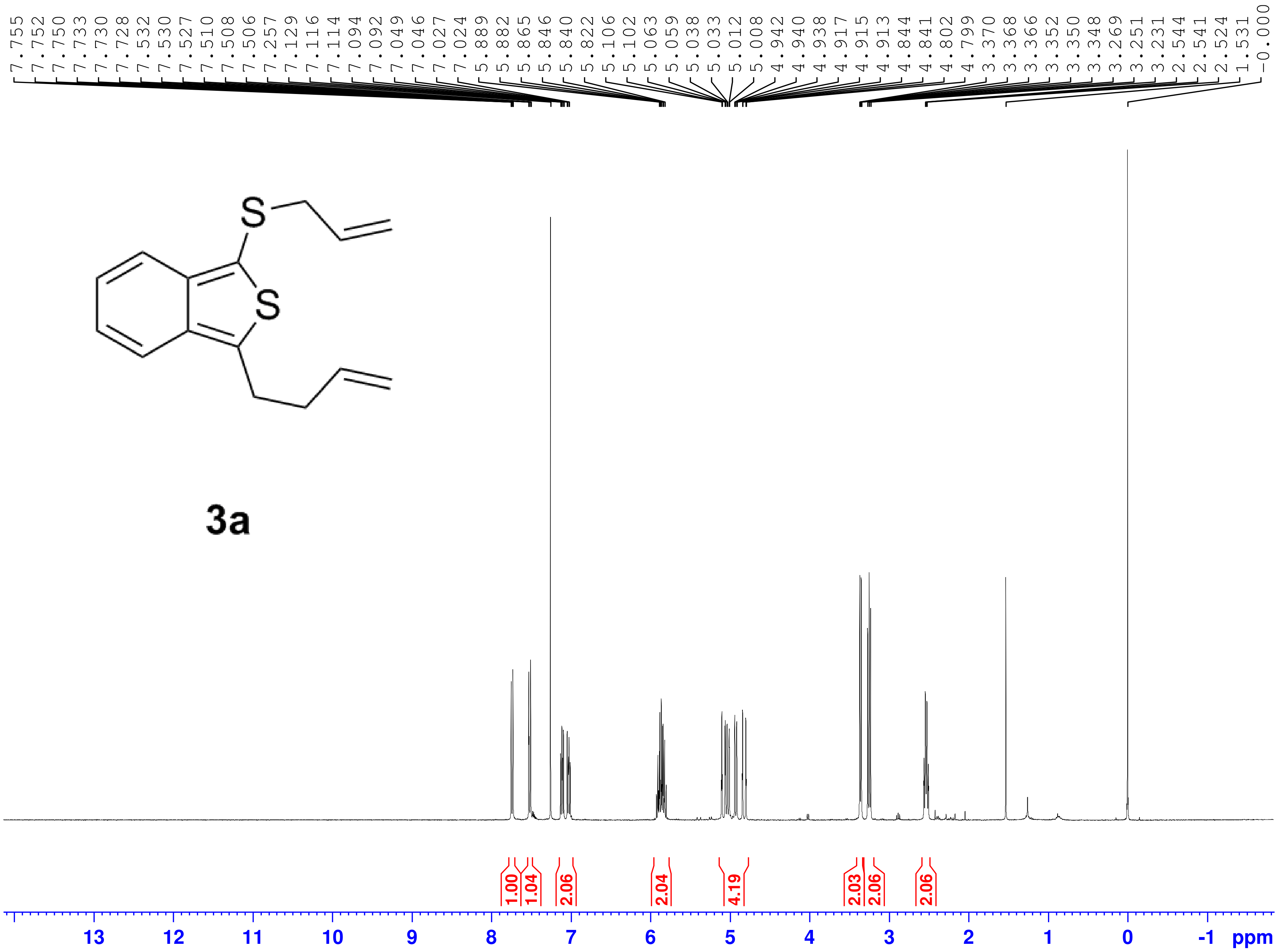
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7.752
7.750
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7.530
7.527
7.510
7.508
7.506
7.257
7.129
7.116
7.114
7.094
7.092
7.049
7.046
7.027
7.024
5.889
5.882
5.865
5.846
5.840
5.822
5.106
5.102
5.063
5.059
5.038
5.033
5.012
5.008
4.942
4.940
4.938
4.917
4.915
4.913
4.844
4.841
4.802
4.799
3.370
3.368
3.366
3.352
3.350
3.348
3.269
3.251
3.231
2.544
2.541
2.524
1.531
-0.000
S
S
3a
1.00
1.04
2.06
2.04
4.19
2.03
2.06
2.06
13
12
11
10
9
8
7
6
5
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3
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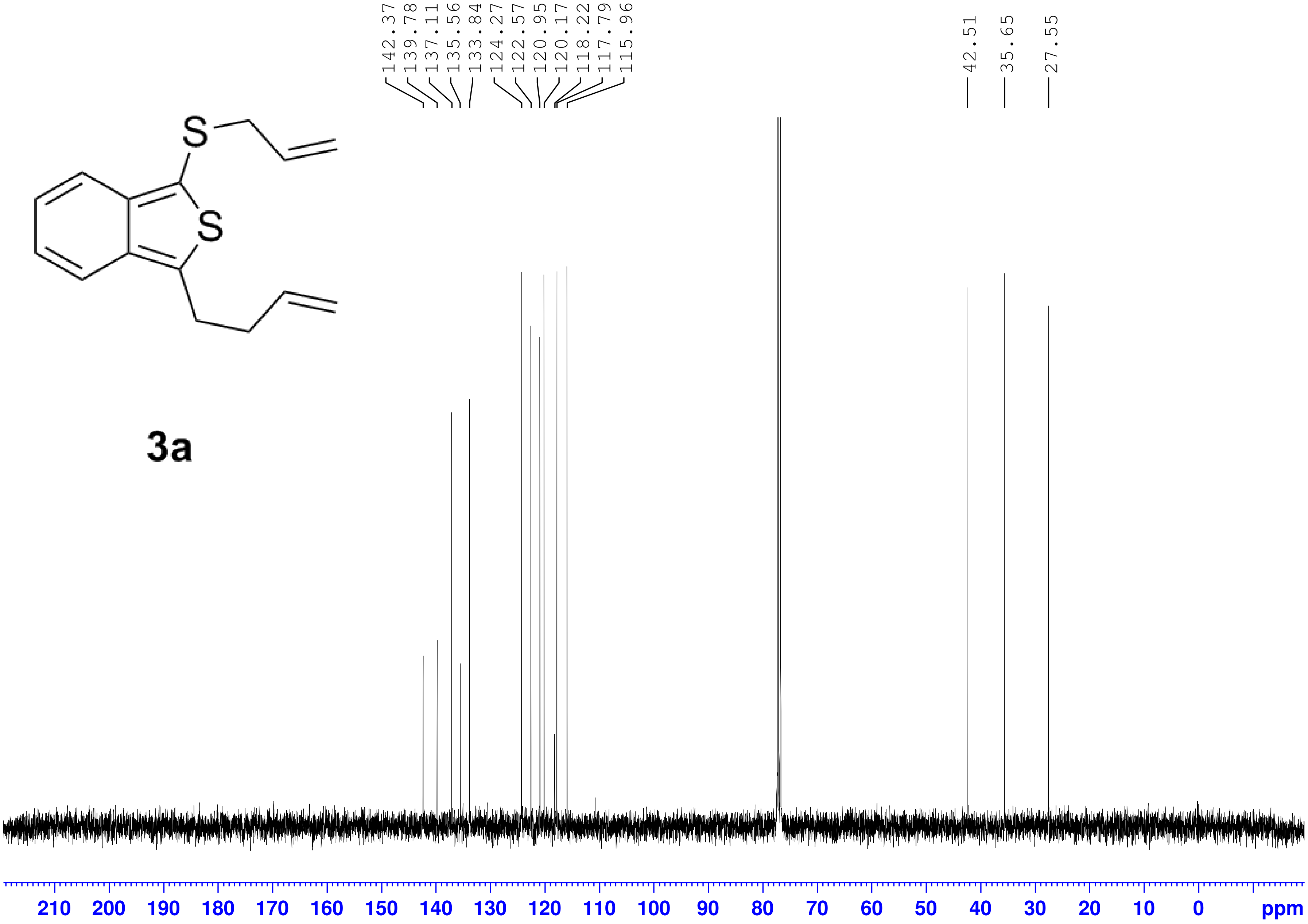
ppm



3a

142.37
139.78
137.11
135.56
133.84
124.27
122.57
120.95
120.17
118.22
117.79
115.96
42.51
35.65
27.55
210
200
190
180
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140
130
120
110
100
90
80
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20
10
0
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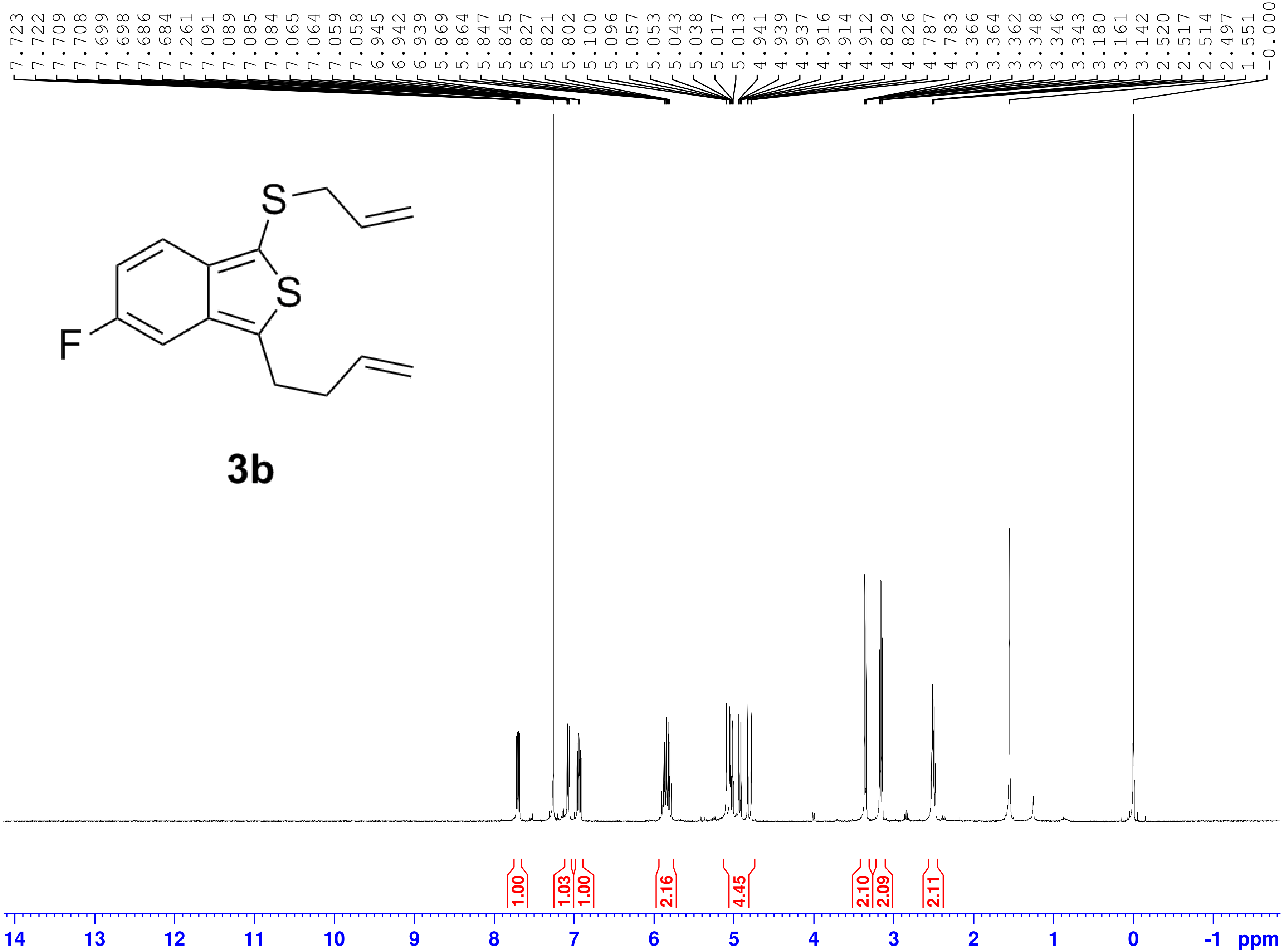
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7.709
7.708
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7.684
7.261
7.091
7.089
7.085
7.084
7.065
7.064
7.059
7.058
6.945
6.942
6.939
5.869
5.864
5.847
5.845
5.827
5.821
5.802
5.100
5.096
5.057
5.053
5.043
5.038
5.017
5.013
4.941
4.939
4.937
4.916
4.914
4.912
4.829
4.826
4.787
4.783
3.366
3.364
3.362
3.348
3.346
3.343
3.180
3.161
3.142
2.520
2.517
2.514
2.497
1.551
-0.000
S
S
F
3b
1.00
1.03
1.00
2.16
4.45
2.10
2.09
2.11
14
13
12
11
10
9
8
7
6
5
4
3
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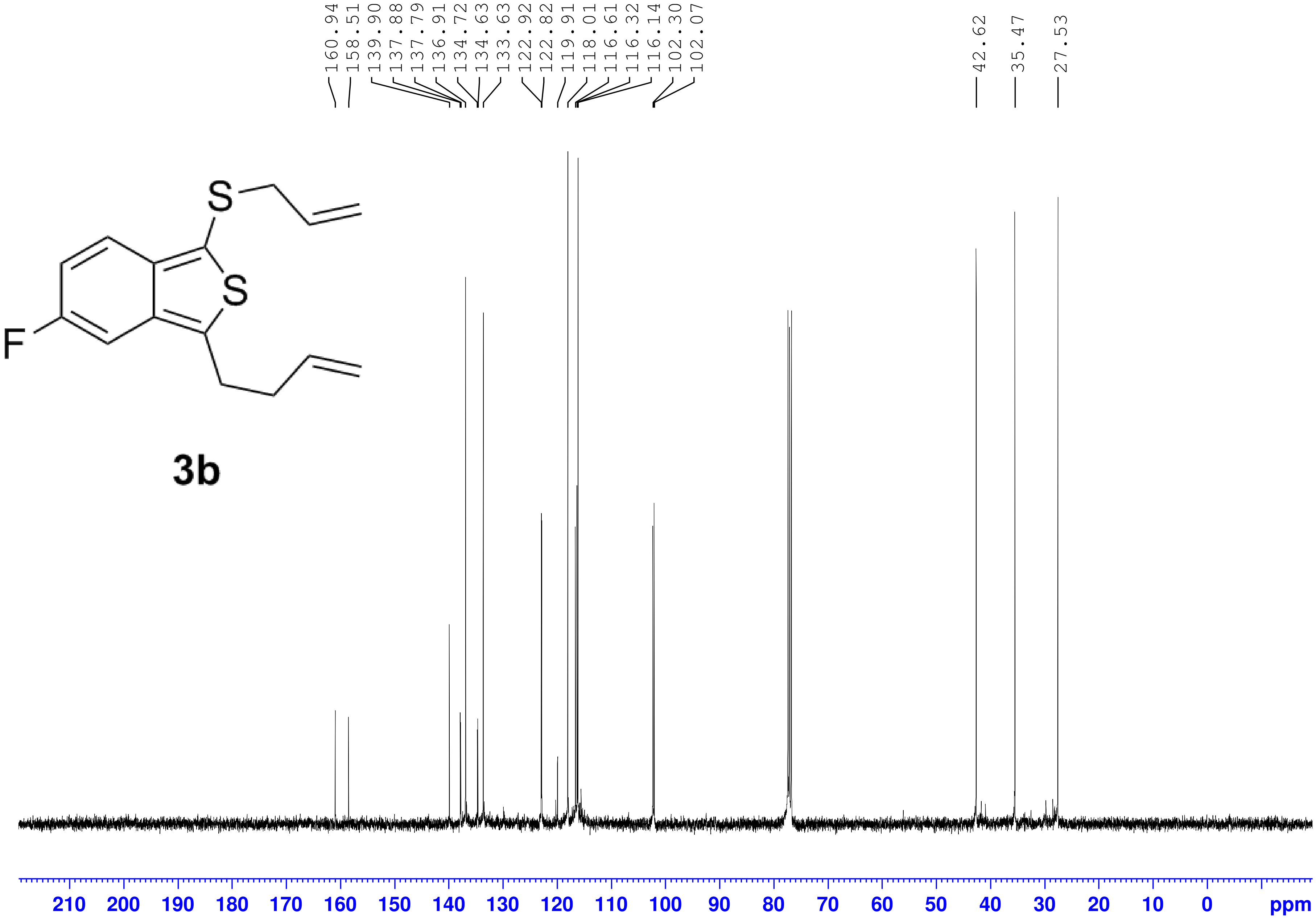
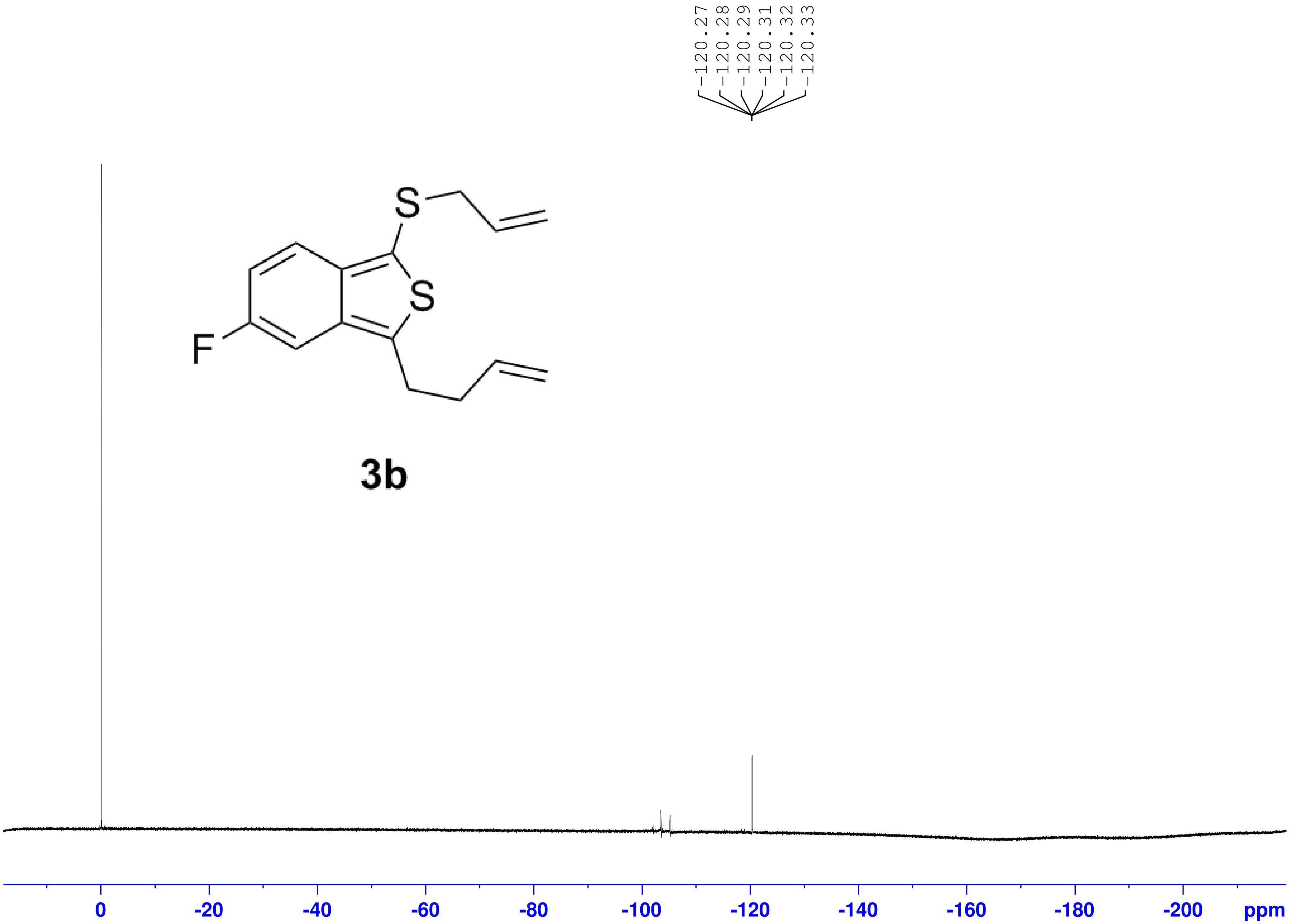
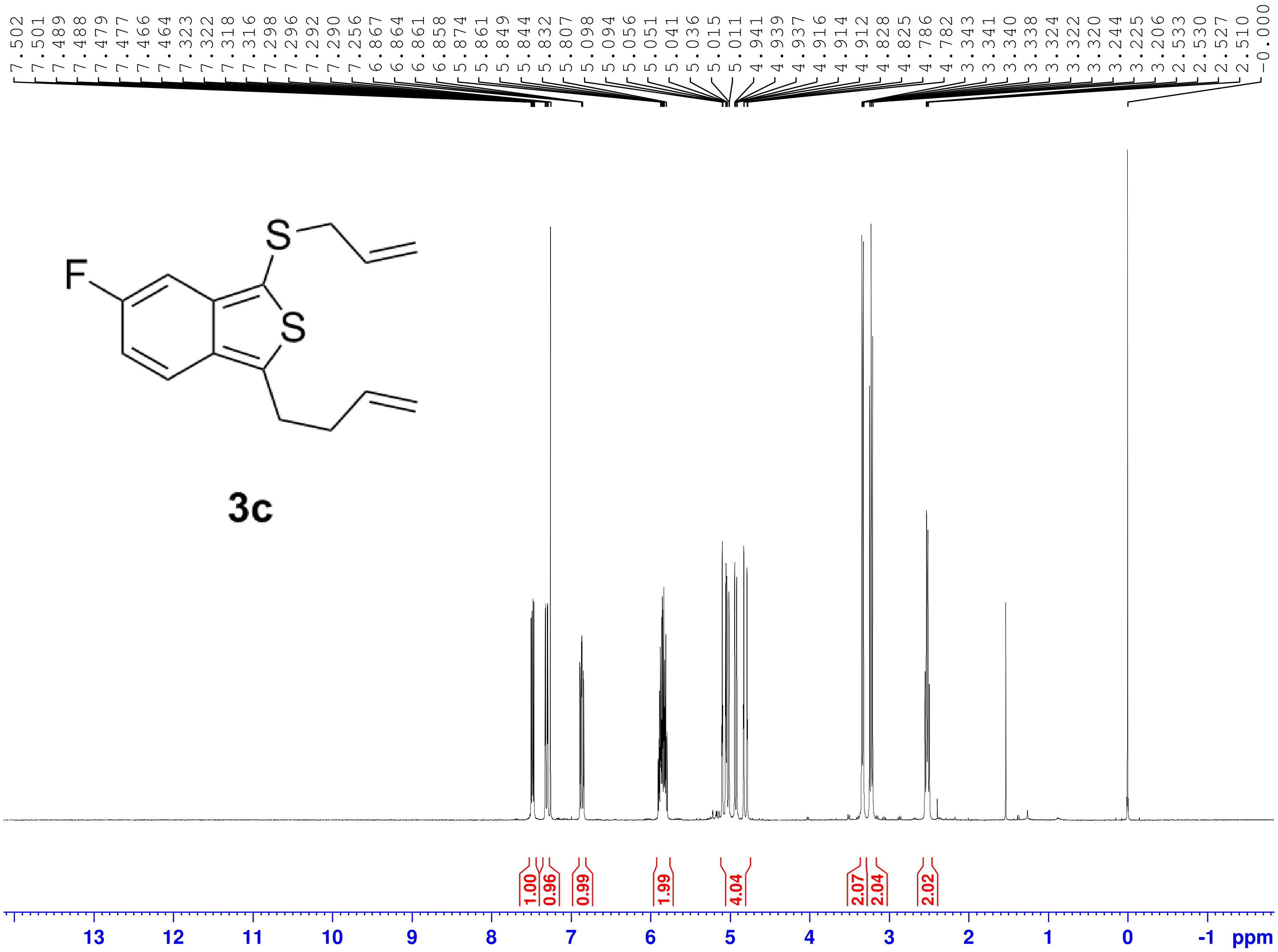
-1
ppm



3b

160.94
158.51
139.90
137.88
137.79
136.91
134.72
134.63
133.63
122.92
122.82
119.91
118.01
116.61
116.32
116.14
102.30
102.07
42.62
35.47
27.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-120.27
-120.28
-120.29
-120.31
-120.32
-120.33
F
S
S
3b
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm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7.501
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7.488
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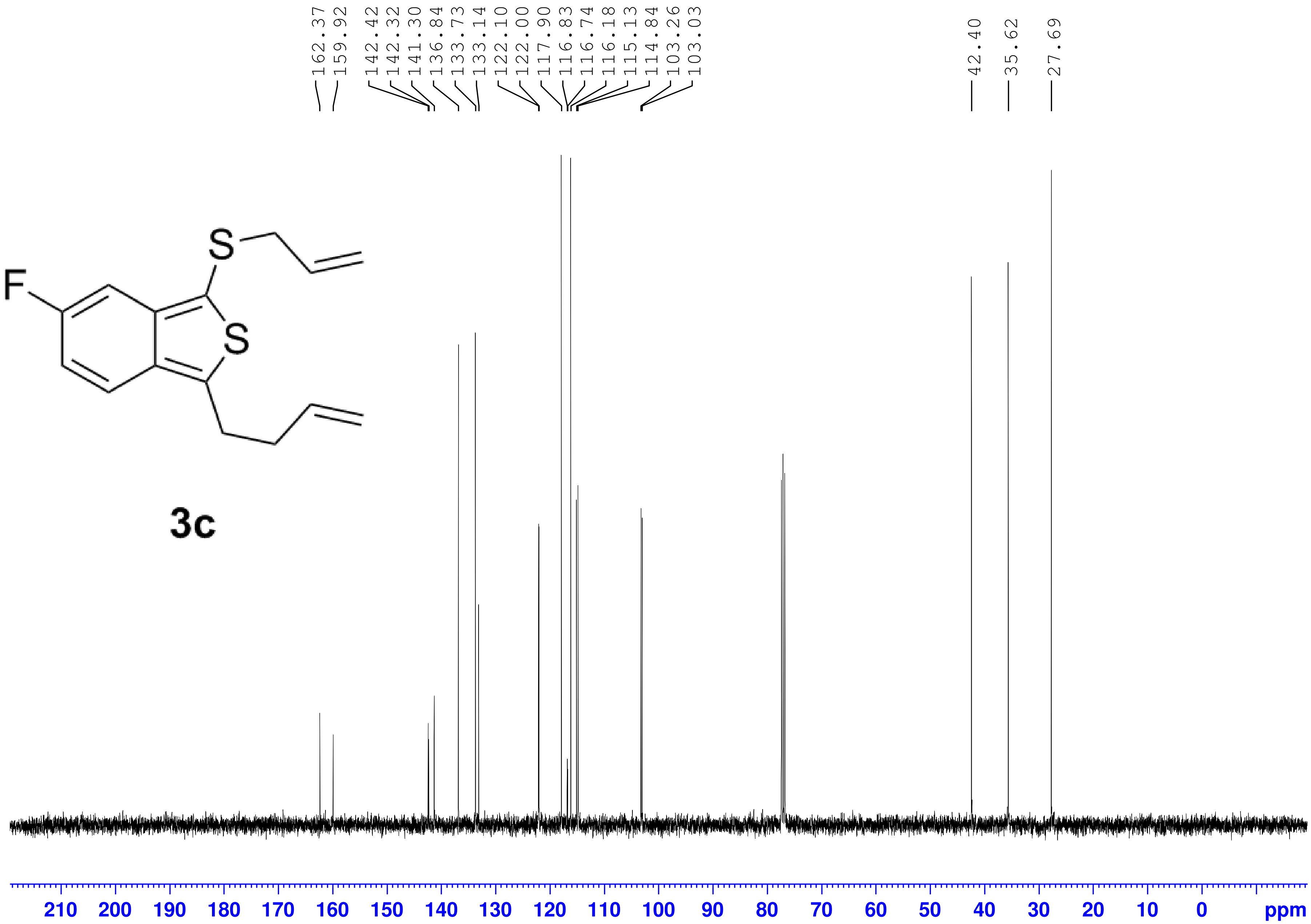
7.477
7.466
7.464
7.323
7.322
7.318
7.316
7.298
7.296
7.292
7.290
7.256
6.867
6.864
6.861
6.858
5.874
5.861
5.849
5.844
5.832
5.807
5.098
5.094
5.056
5.051
5.041
5.036
5.015
5.011
4.941
4.939
4.937
4.916
4.914
4.912
4.828
4.825
4.786
4.782
3.343
3.341
3.340
3.338
3.324
3.322
3.320
3.244
3.225
3.206
2.533
2.530
2.527
2.510
-0.000
F
S
S
1.00
0.96
0.99
1.99
4.04
2.07
2.04
2.02
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

3c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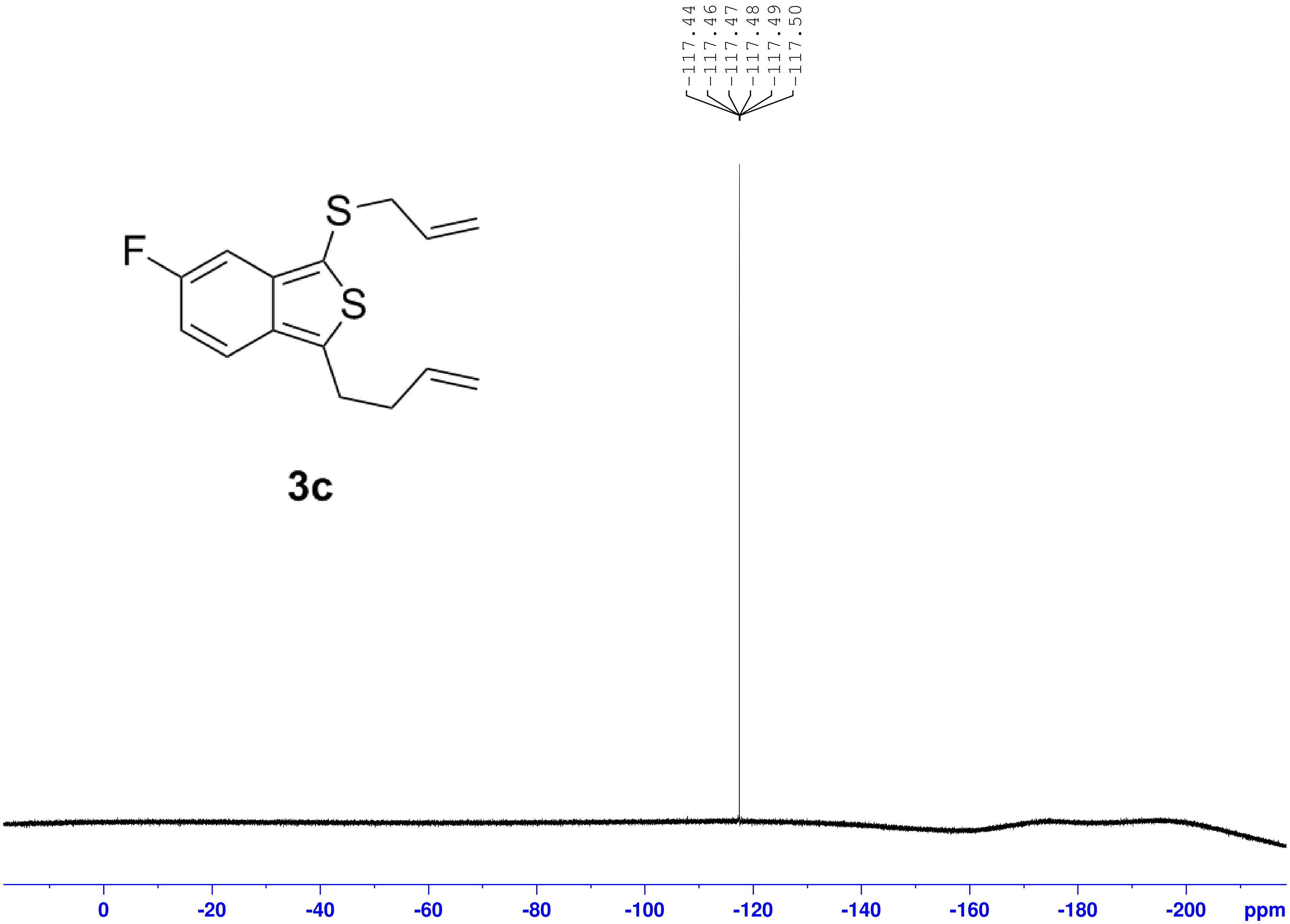
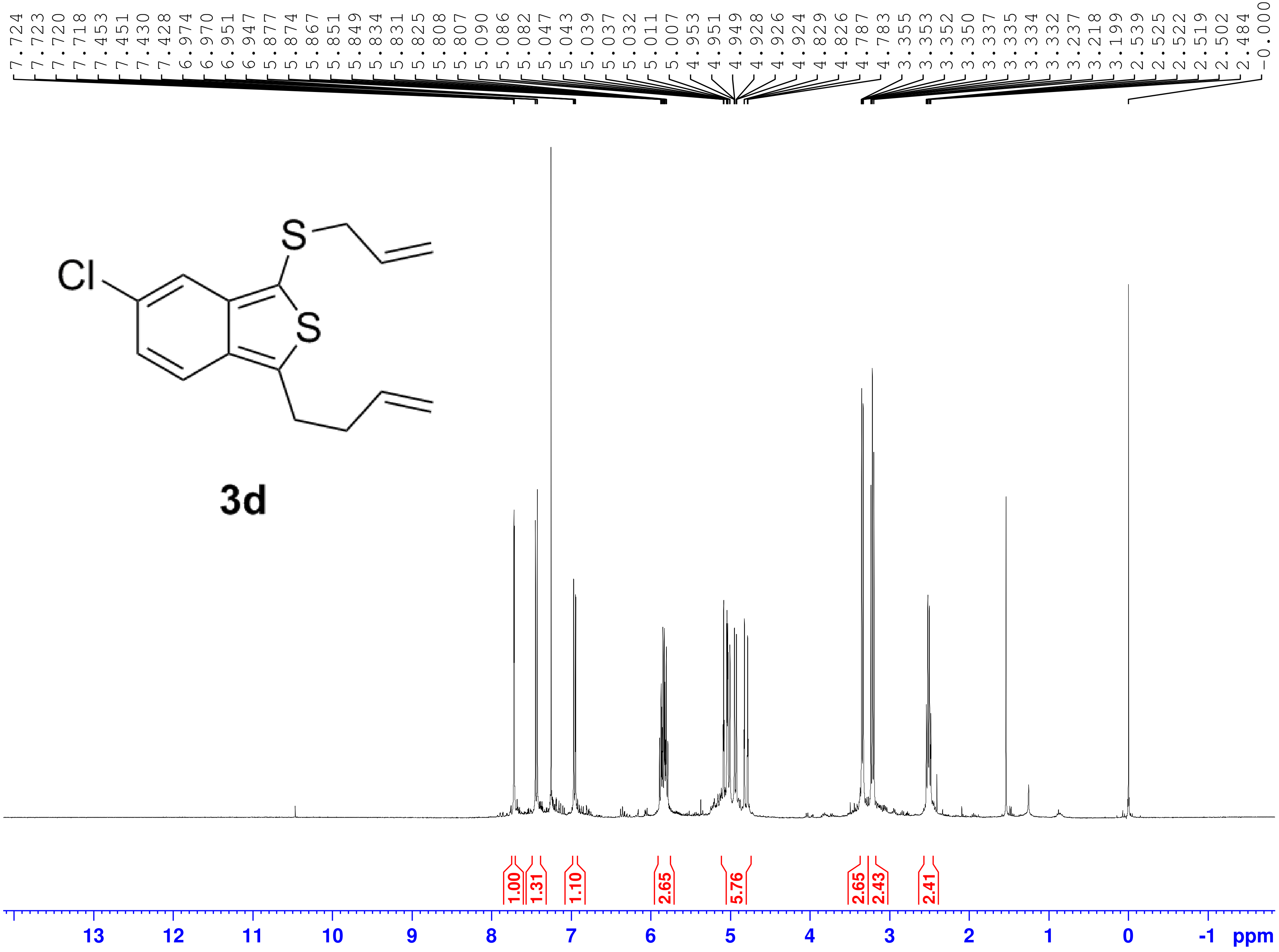
159.92
142.42
142.32
141.30
136.84
133.73
133.14
122.10
122.00
117.90
116.83
116.74
116.18
115.13
114.84
103.26
103.03
42.40
35.62
27.69
F
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

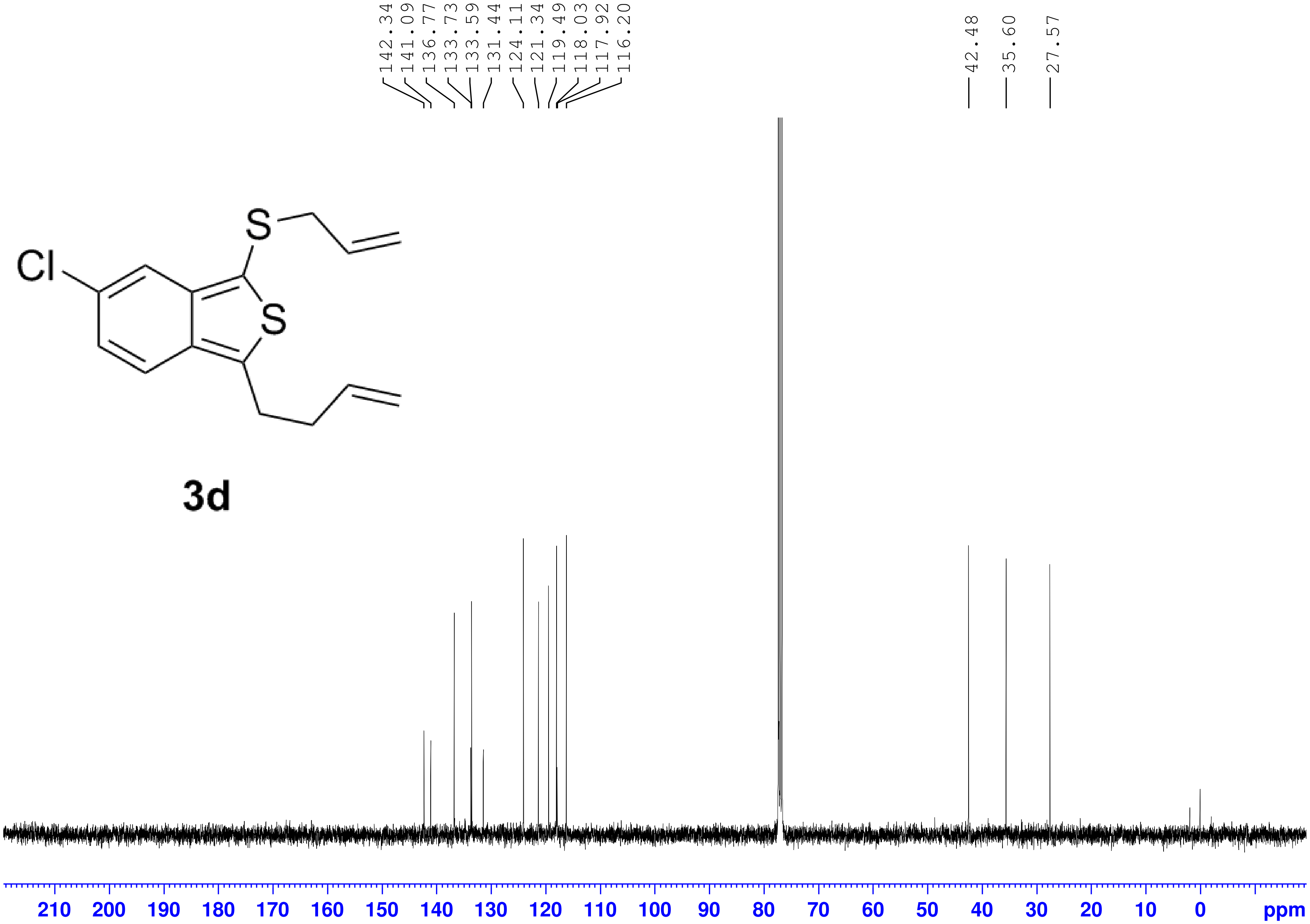
3c



3c

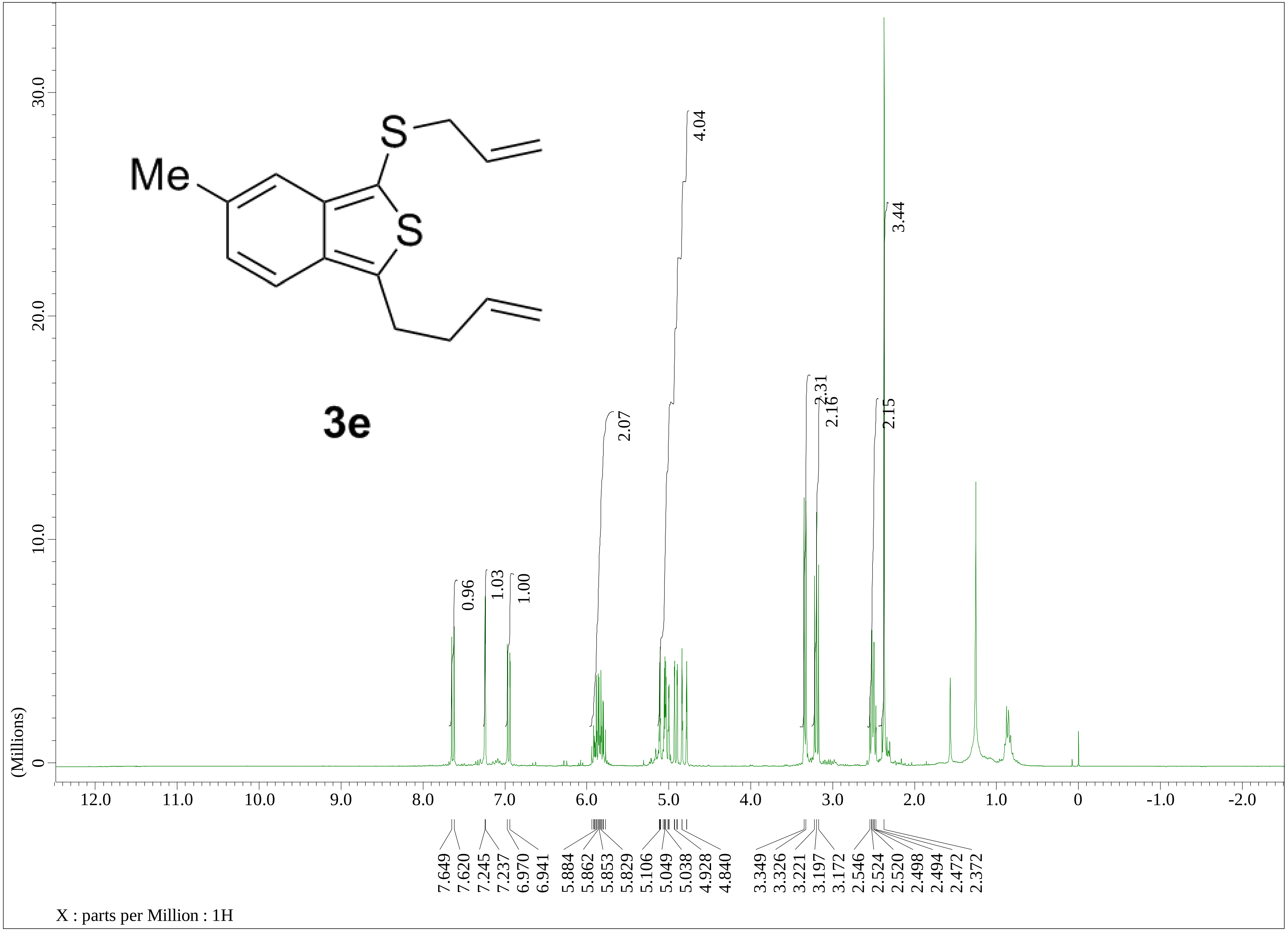
-117.44
-117.46
-117.47
-117.48
-117.49
-117.50
F
S
S
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

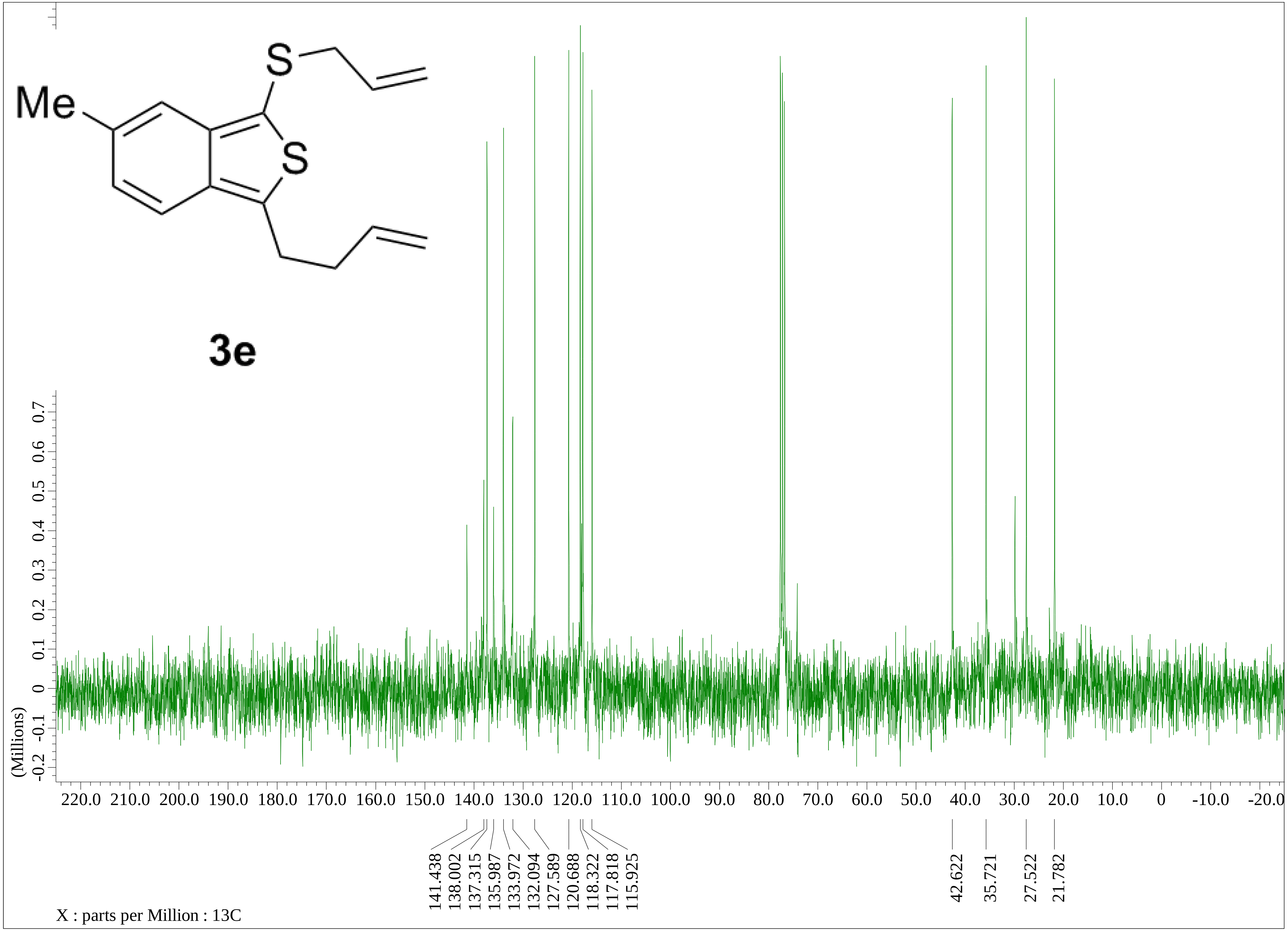

7.724
7.723
7.720
7.718
7.453
7.451
7.430
7.428
6.974
6.970
6.951
6.947
5.877
5.874
5.867
5.851
5.849
5.834
5.831
5.825
5.808
5.807
5.090
5.086
5.082
5.047
5.043
5.039
5.037
5.032
5.011
5.007
4.953
4.951
4.949
4.928
4.926
4.924
4.829
4.826
4.787
4.783
3.355
3.353
3.352
3.350
3.337
3.335
3.334
3.332
3.237
3.218
3.199
2.539
2.525
2.522
2.519
2.502
2.484
-0.000
Cl
S
S
3d
1.00
1.31
1.10
2.65
5.76
2.65
2.43
2.41
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

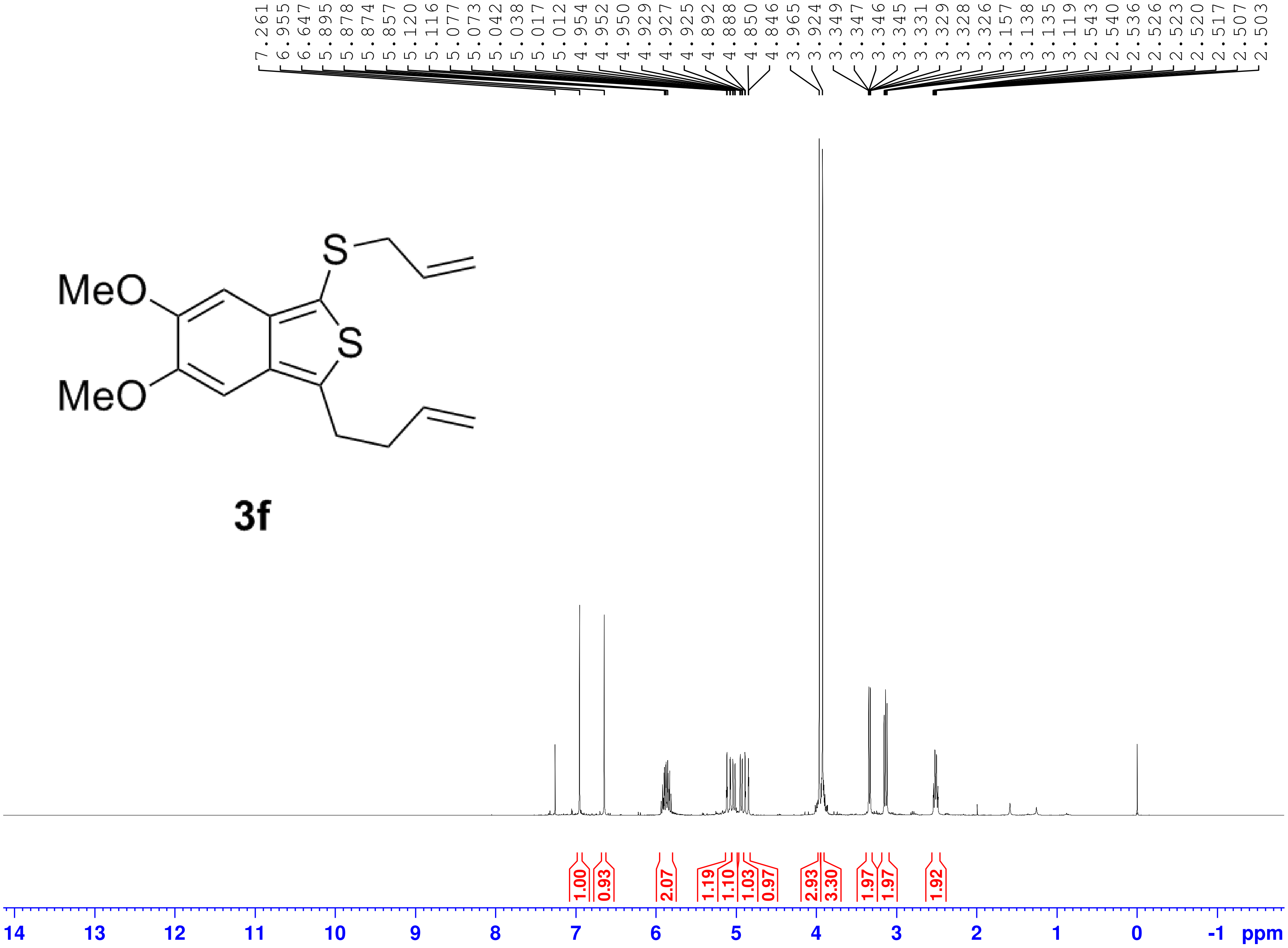

Cl
S
S

3d

142.34
141.09
136.77
133.73
133.59
131.44
124.11
121.34
119.49
118.03
117.92
116.20
42.48
35.60
27.57
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Me
S
S
3e
30.0
20.0
10.0
0
(Millions)
0.96
1.03
1.00
2.07
4.04
2.31
2.16
2.15
3.44
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.649
7.620
7.245
7.237
6.970
6.941
5.884
5.862
5.853
5.829
5.106
5.049
5.038
4.928
4.840
3.349
3.326
3.221
3.197
3.172
2.546
2.524
2.520
2.498
2.494
2.472
2.372
X : parts per Million : 1H


Me
S
S
3e
(Millions)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
141.438
138.002
137.315
135.987
133.972
132.094
127.589
120.688
118.322
117.818
115.925
42.622
35.721
27.522
21.782
X : parts per Million : 13C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6.955
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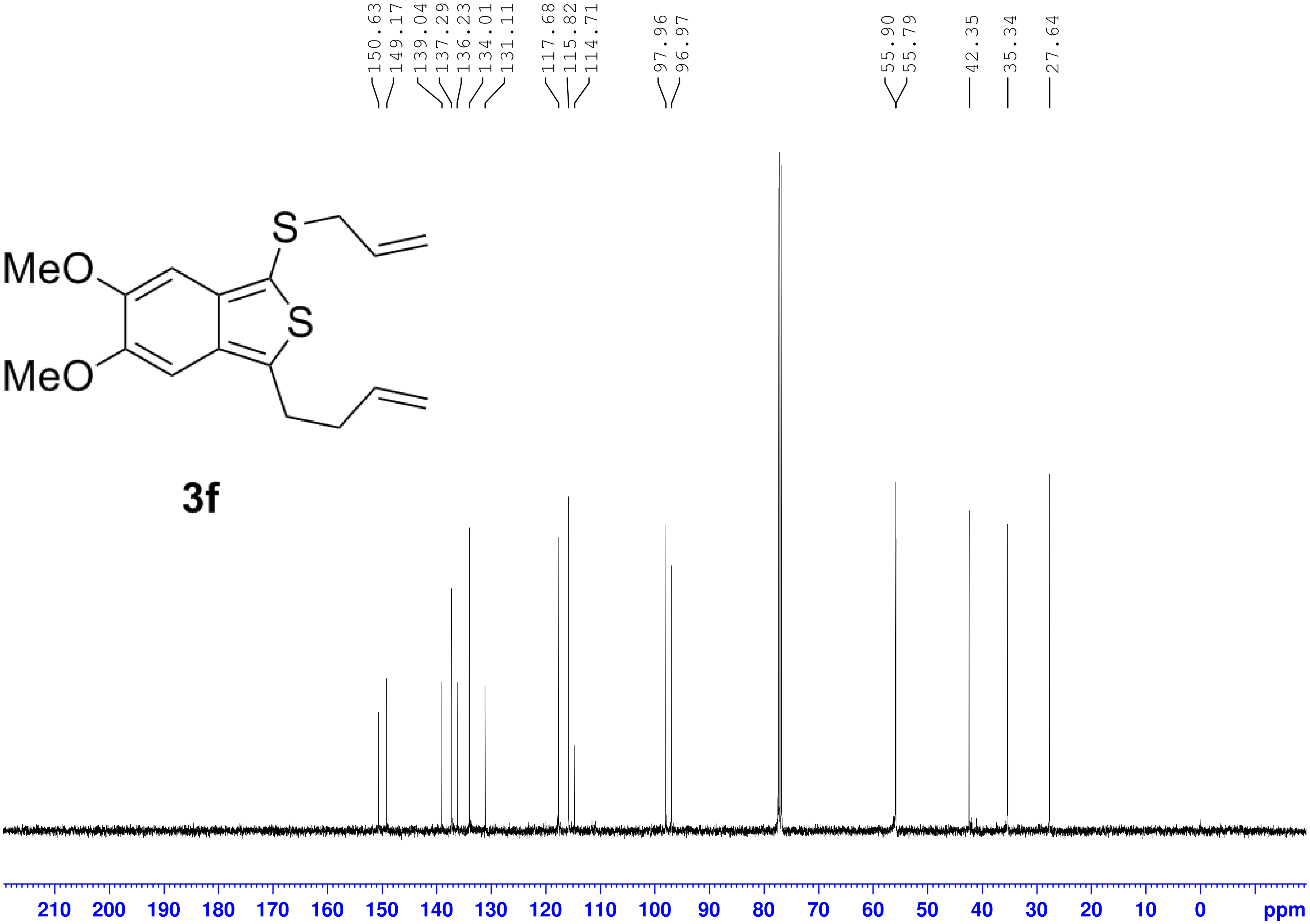
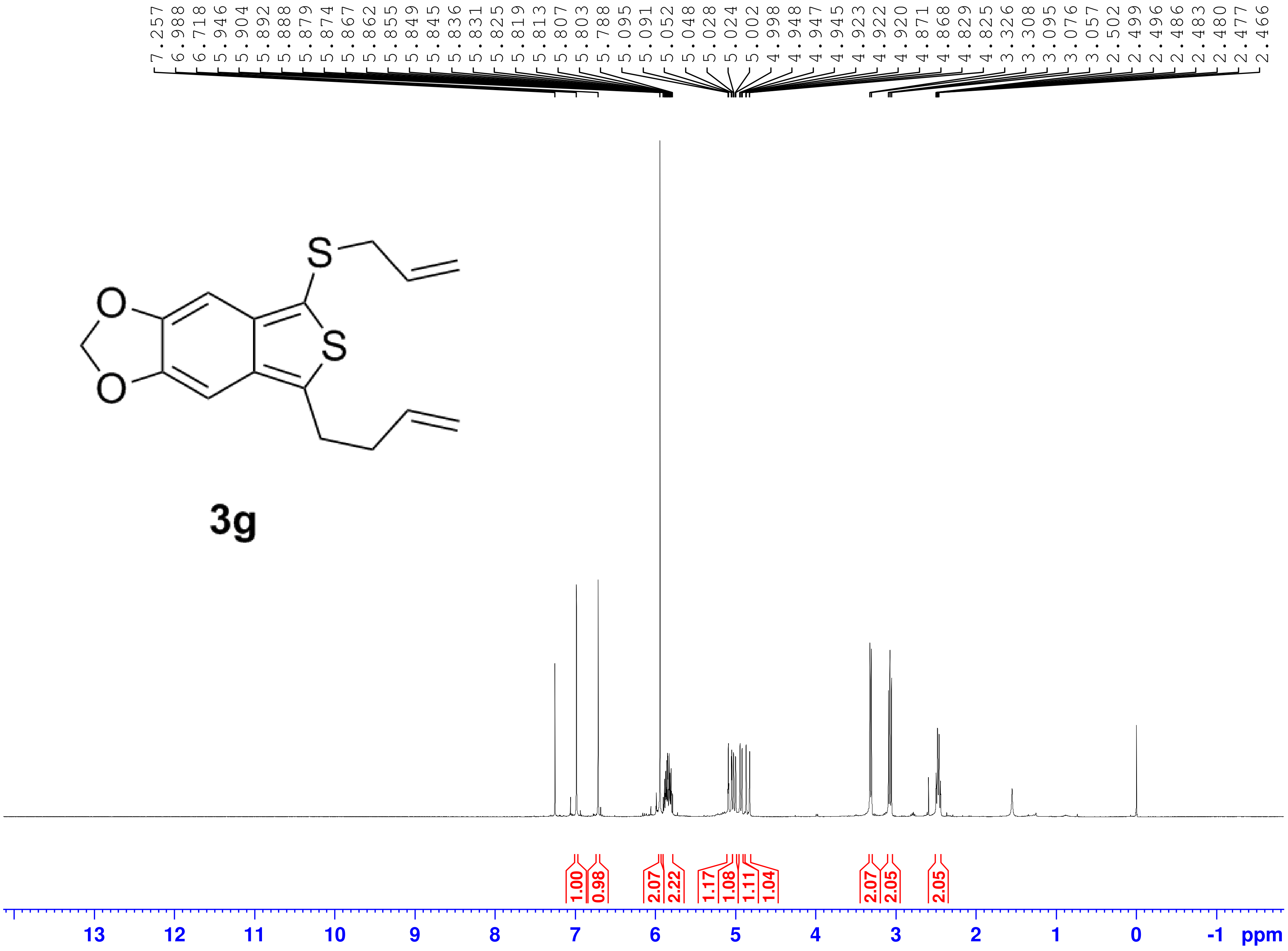
5.120
5.116
5.077
5.073
5.042
5.038
5.017
5.012
4.954
4.952
4.950
4.929
4.927
4.925
4.892
4.888
4.850
4.846
3.965
3.924
3.349
3.347
3.346
3.345
3.331
3.329
3.328
3.326
3.157
3.138
3.135
3.119
2.543
2.540
2.536
2.526
2.523
2.520
2.517
2.507
2.503
MeO
MeO
S
S
3f
1.00
0.93
2.07
1.19
1.10
1.03
0.97
2.93
3.30
1.97
1.97
1.92
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

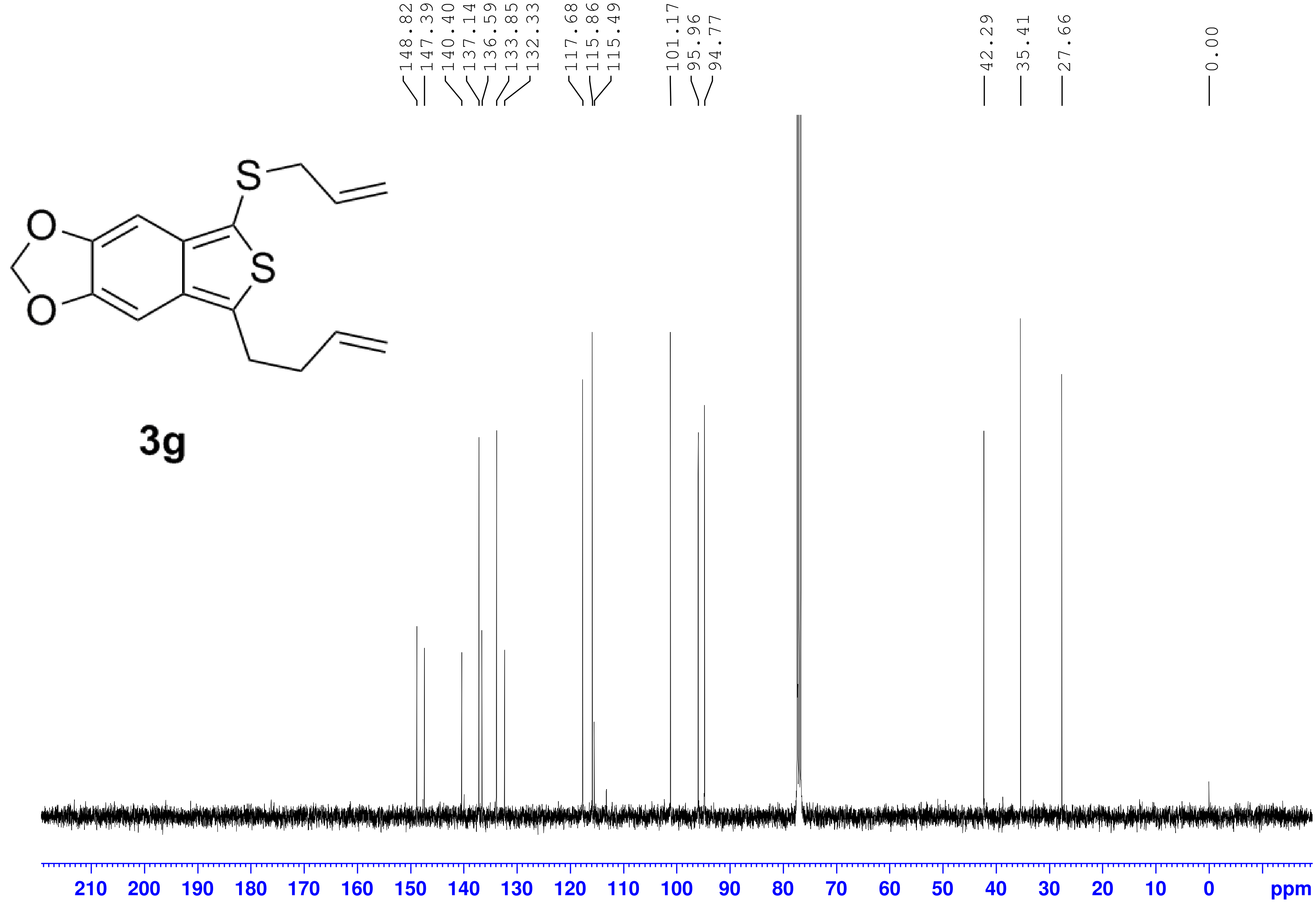

150.63
149.17
139.04
137.29
136.23
134.01
131.11
117.68
115.82
114.71
97.96
96.97
55.90
55.79
42.35
35.34
27.64
MeO
MeO
S
S
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3f



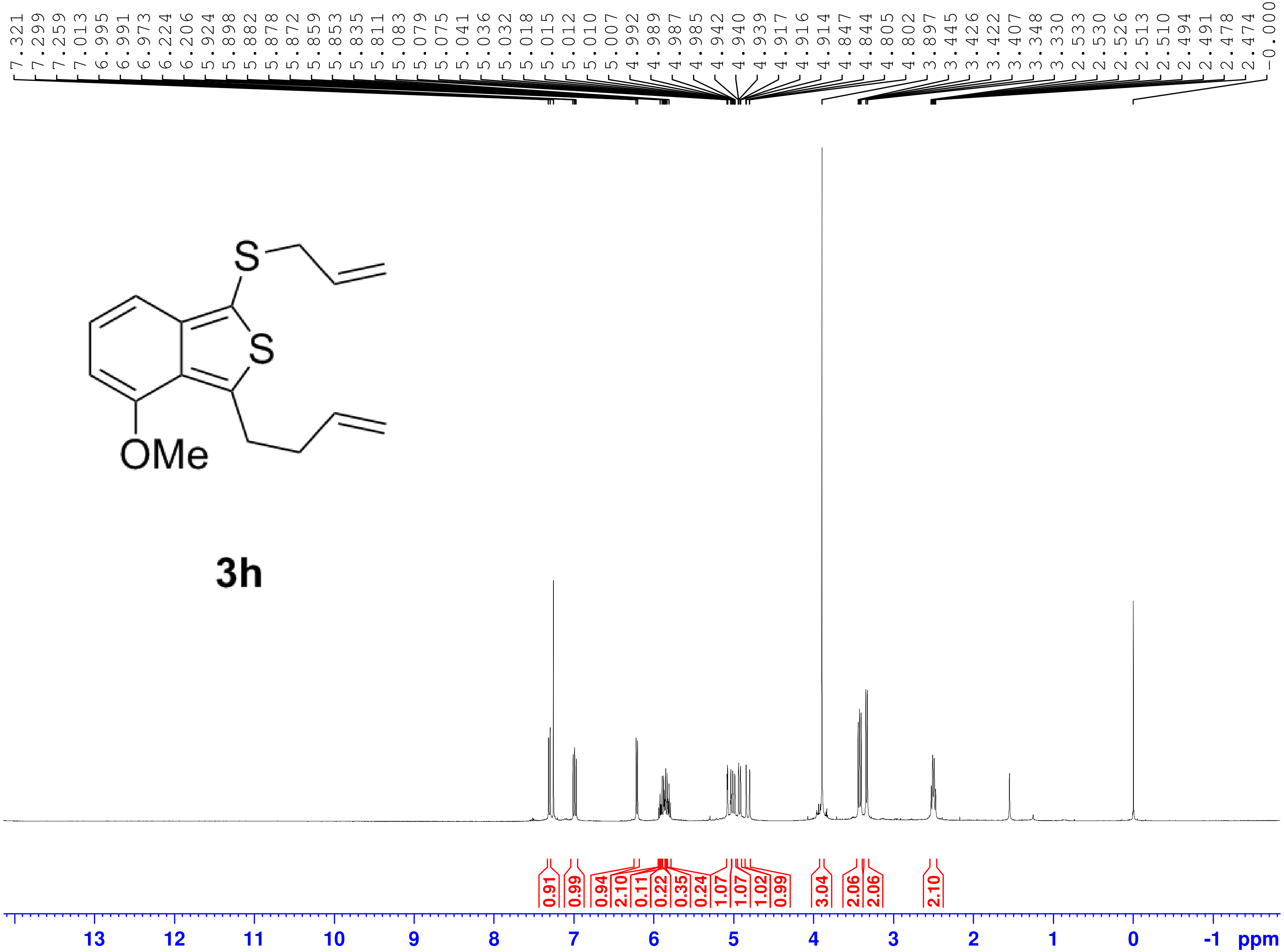
3g

7.257
6.988
6.718
5.946
5.904
5.892
5.888
5.879
5.874
5.867
5.862
5.855
5.849
5.845
5.836
5.831
5.825
5.819
5.813
5.807
5.803
5.788
5.095
5.091
5.052
5.048
5.028
5.024
5.002
4.998
4.948
4.947
4.945
4.923
4.922
4.920
4.871
4.868
4.829
4.825
3.326
3.308
3.095
3.076
3.057
2.502
2.499
2.496
2.486
2.483
2.480
2.477
2.466
1.00
0.98
2.07
2.22
1.17
1.08
1.11
1.04
2.07
2.05
2.05
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm



3g

148.82
147.39
140.40
137.14
136.59
133.85
132.33
117.68
115.86
115.49
101.17
95.96
94.77
42.29
35.41
27.66
0.00
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.321
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7.259
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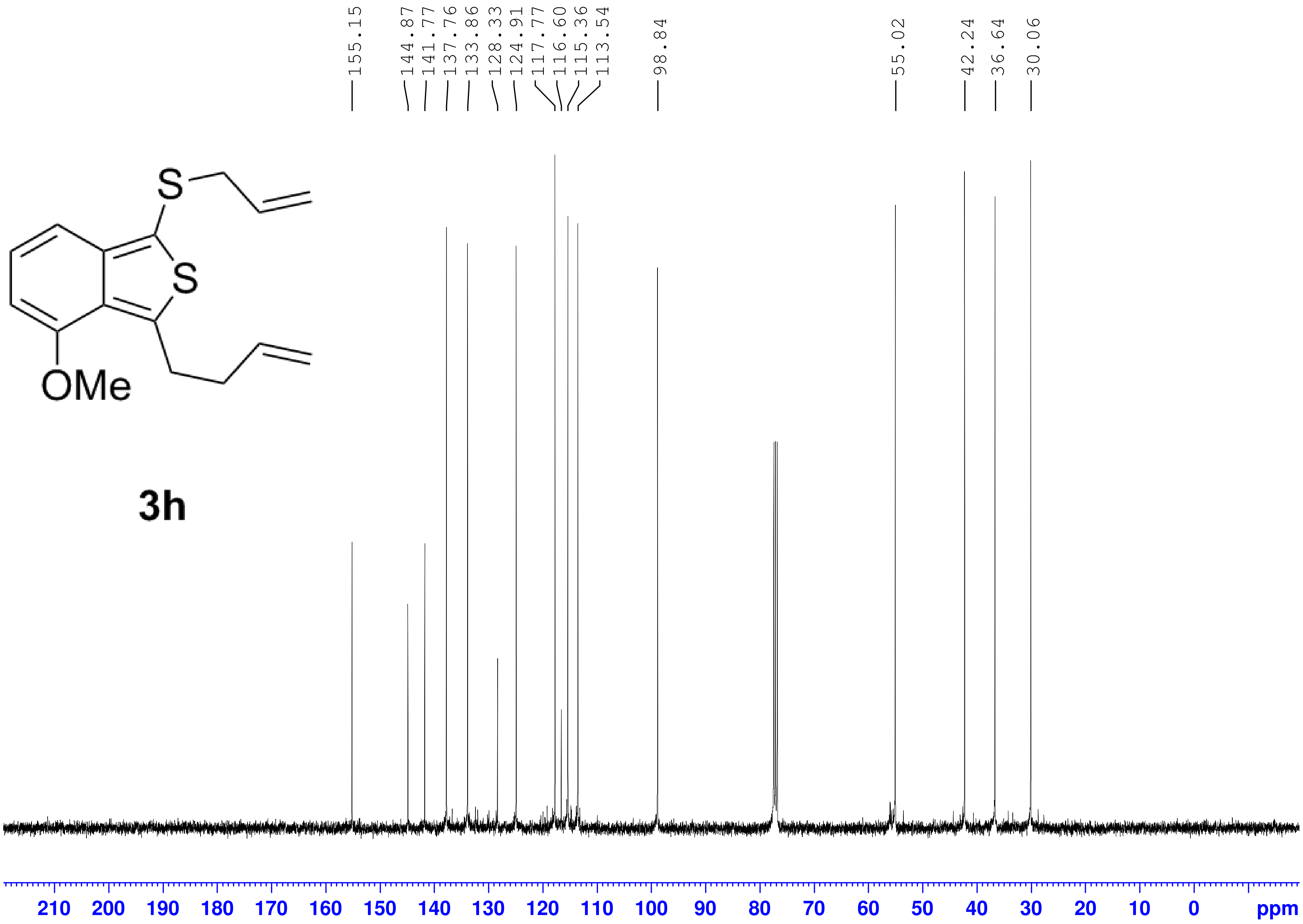
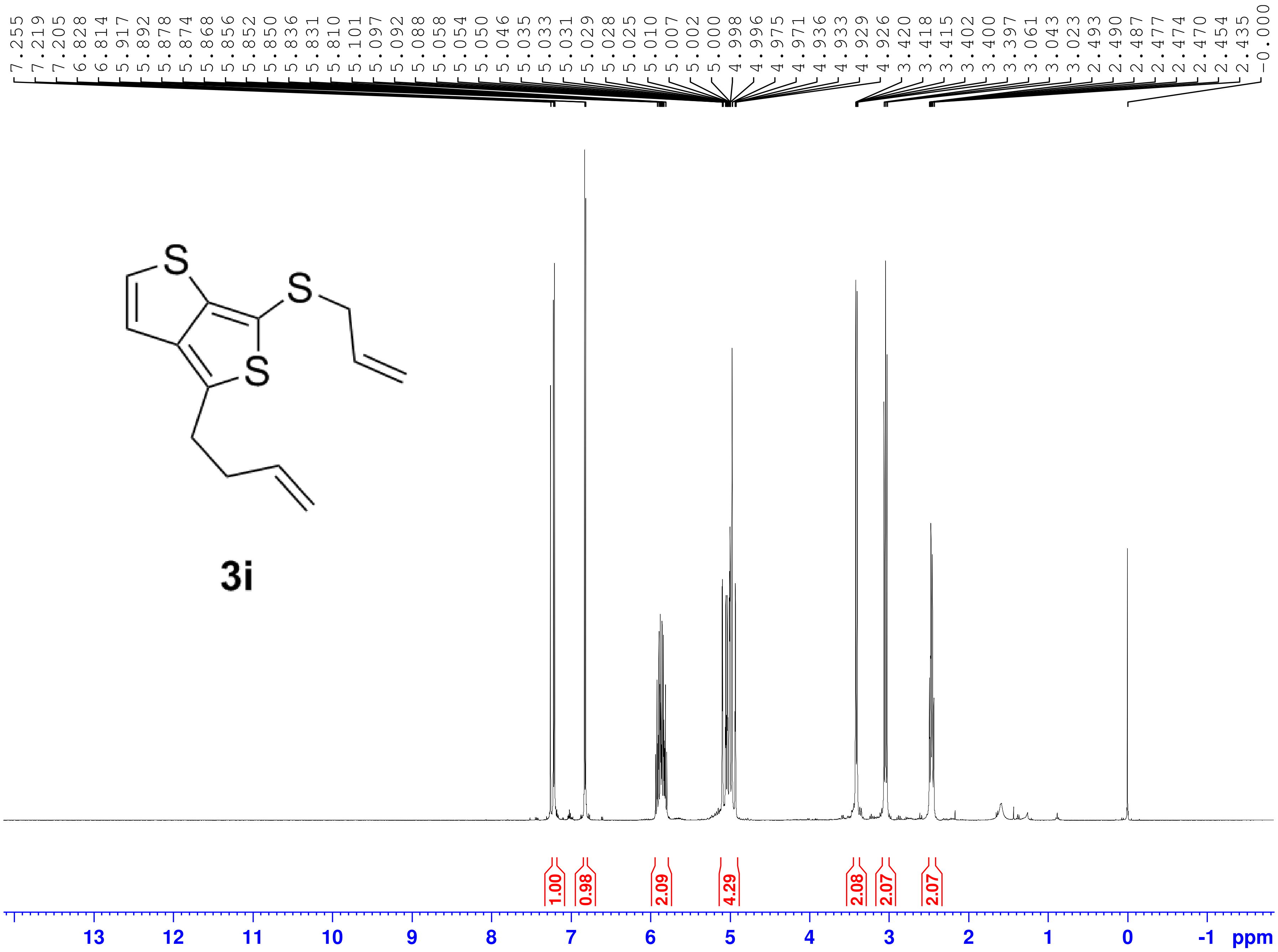
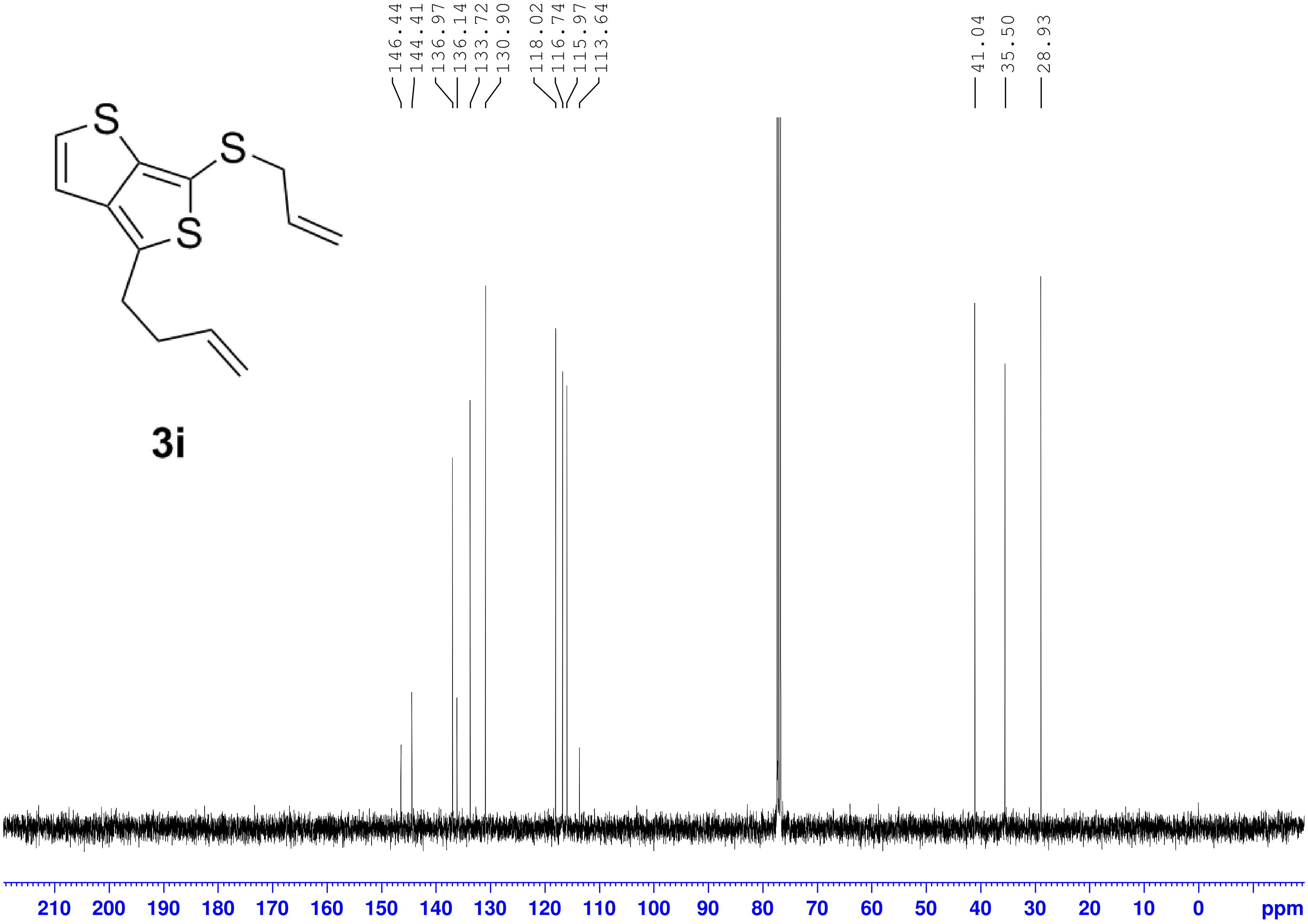
6.995
6.991
6.973
6.224
6.206
5.924
5.898
5.882
5.878
5.872
5.859
5.853
5.835
5.811
5.083
5.079
5.075
5.041
5.036
5.032
5.018
5.015
5.012
5.010
5.007
4.992
4.989
4.987
4.985
4.942
4.940
4.939
4.917
4.916
4.914
4.847
4.844
4.805
4.802
3.897
3.445
3.426
3.422
3.407
3.348
3.330
2.533
2.530
2.526
2.513
2.510
2.494
2.491
2.478
2.474
-0.000
S
S
OMe
0.91
0.99
0.94
2.10
0.11
0.22
0.35
0.24
1.07
1.07
1.02
0.99
3.04
2.06
2.06
2.10
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

3h


155.15
144.87
141.77
137.76
133.86
128.33
124.91
117.77
116.60
115.36
113.54
98.84
55.02
42.24
36.64
30.06
S
S
OMe
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

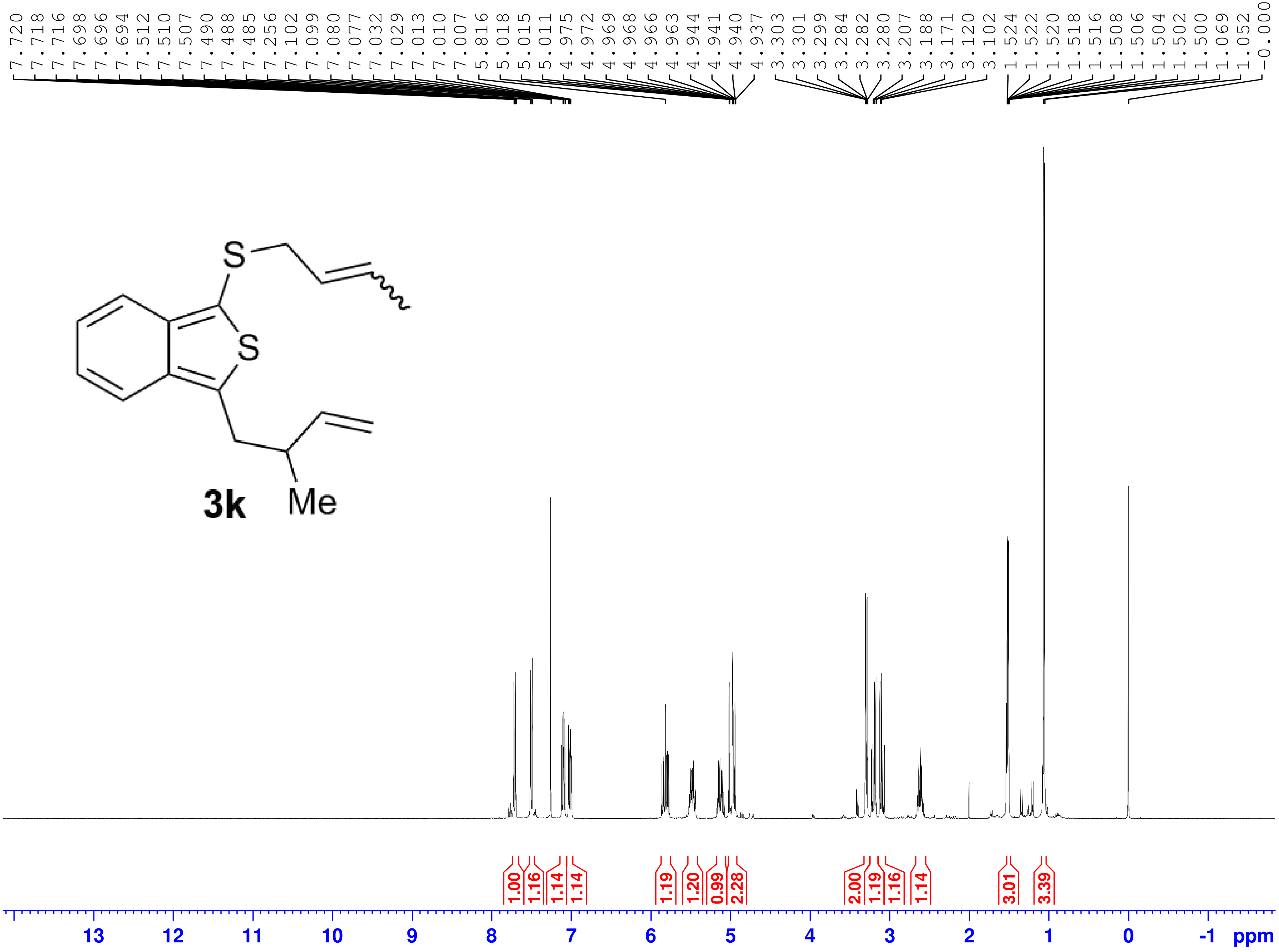

7.255
7.219
7.205
6.828
6.814
5.917
5.892
5.878
5.874
5.868
5.856
5.852
5.850
5.836
5.831
5.810
5.101
5.097
5.092
5.088
5.058
5.054
5.050
5.046
5.035
5.033
5.031
5.029
5.028
5.025
5.010
5.007
5.002
5.000
4.998
4.996
4.975
4.971
4.936
4.933
4.929
4.926
3.420
3.418
3.415
3.402
3.400
3.397
3.061
3.043
3.023
2.493
2.490
2.487
2.477
2.474
2.470
2.454
2.435
-0.000
S
S
S
1.00
0.98
2.09
4.29
2.08
2.07
2.07
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
ppm

3i



3i

146.44
144.41
136.97
136.14
133.72
130.90
118.02
116.74
115.97
113.64
41.04
35.50
28.93
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.102
7.099
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7.077
7.032
7.029
7.013
7.010
7.007
5.816
5.018
5.015
5.011
4.975
4.972
4.969
4.968
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4.963
4.944
4.941
4.940
4.937
3.303
3.301
3.299
3.284
3.282
3.280
3.207
3.188
3.171
3.120
3.102
1.524
1.522
1.520
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1.516
1.508
1.506
1.504
1.502
1.500
1.069
1.052
-0.000
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S
Me
3k
1.00
1.16
1.14
1.14
1.19
1.20
0.99
2.28
2.00
1.19
1.16
1.14
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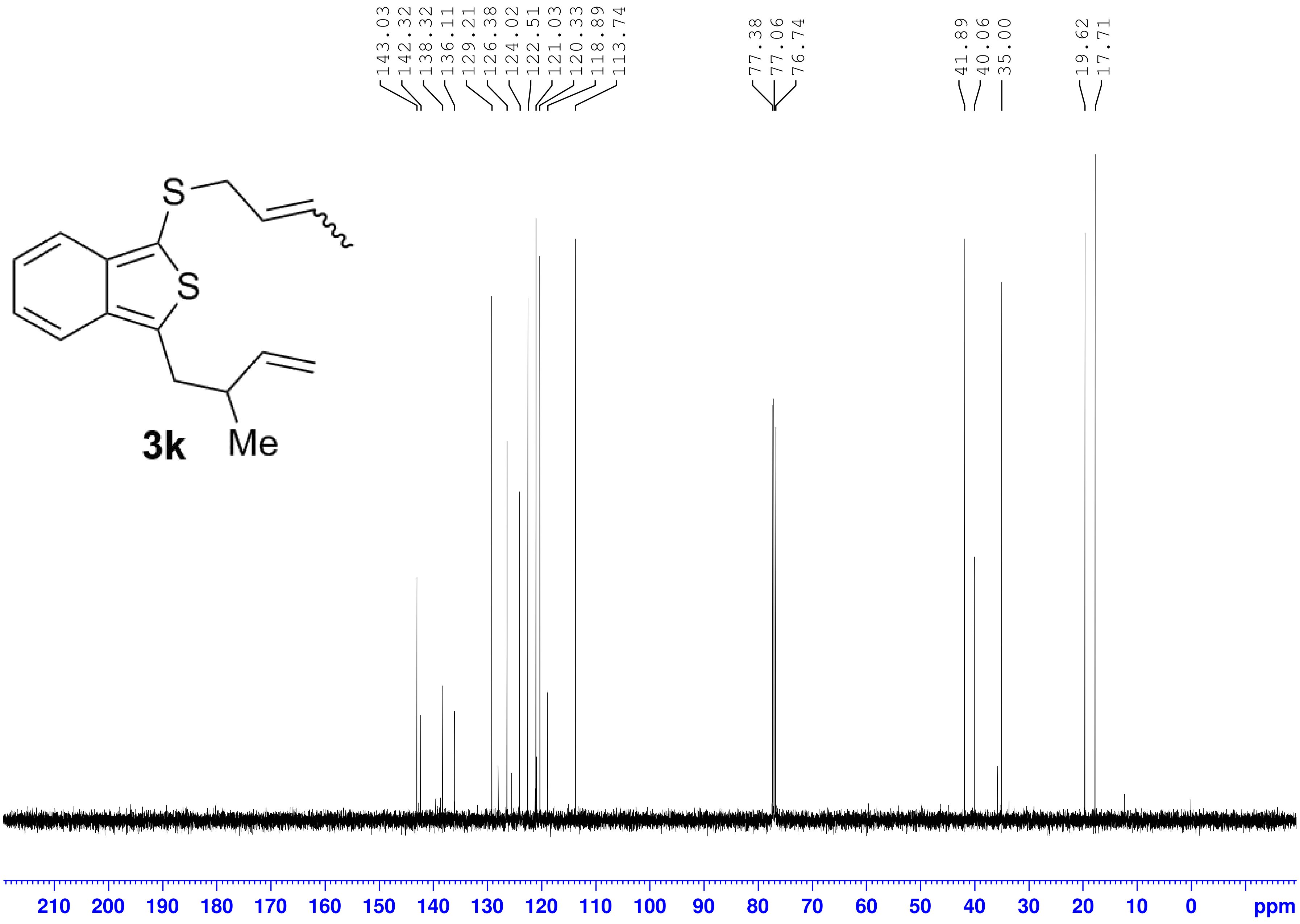
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77.06
76.74
41.89
40.06
35.00
19.62
17.71
S
S
Me
3k
210
200
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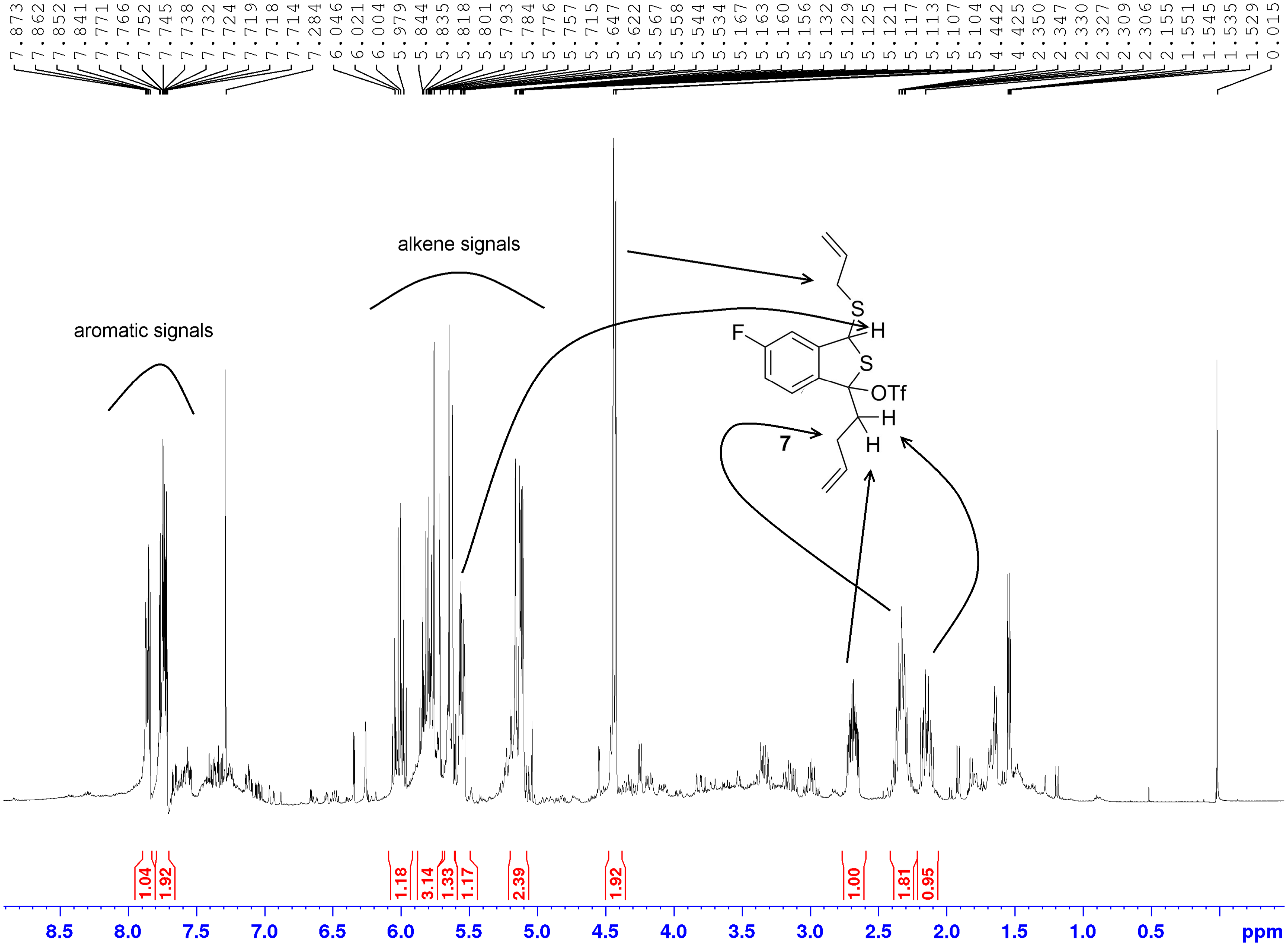
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7.714
7.284
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6.021
6.004
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5.835
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5.793
5.784
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5.544
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2.327
2.309
2.306
2.155
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1.545
1.535
1.529
0.015
alkene signals
aromatic signals
S
F
H
S
OTf
H
7
H
1.04
1.92
1.18
3.14
1.33
1.17
2.39
1.92
1.00
1.81
0.95
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8.0
7.5
7.0
6.5
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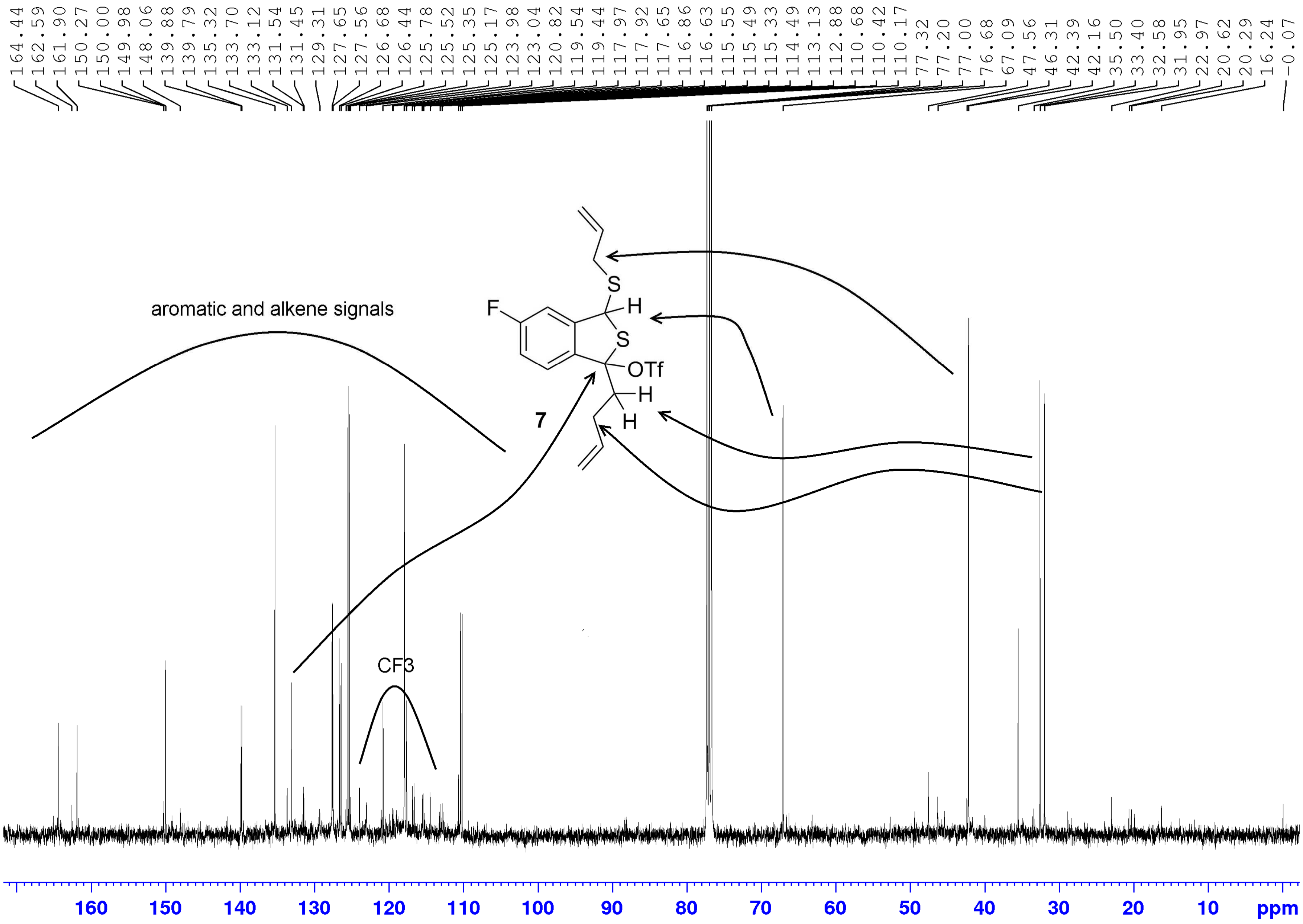
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126.68
126.44
125.78
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125.35
125.17
123.98
123.04
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117.65
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114.49
113.13
112.88
110.68
110.42
110.17
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77.20
77.00
76.68
67.09
47.56
46.31
42.39
42.16
35.50
33.40
32.58
31.95
22.97
20.62
20.29
16.24
-0.07
aromatic and alkene signals
F
S
H
S
OTf
H
H
7
CF3
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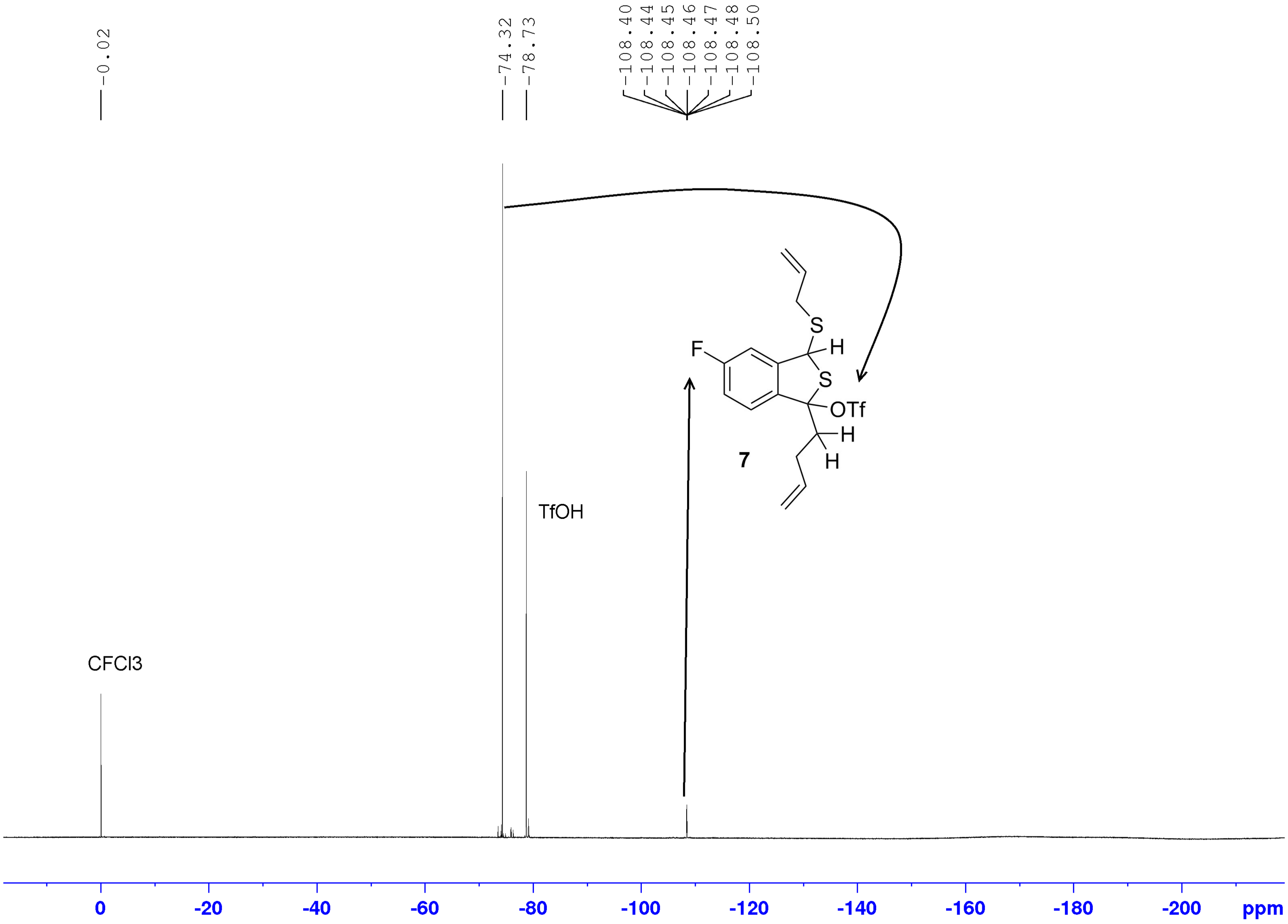
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

-0.02
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-78.73
-108.40
-108.44
-108.45
-108.46
-108.47
-108.48
-108.50
CFCl3
TfOH
F
S
H
S
OTf
H
H
7
0
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-40
-60
-80
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-120
-140
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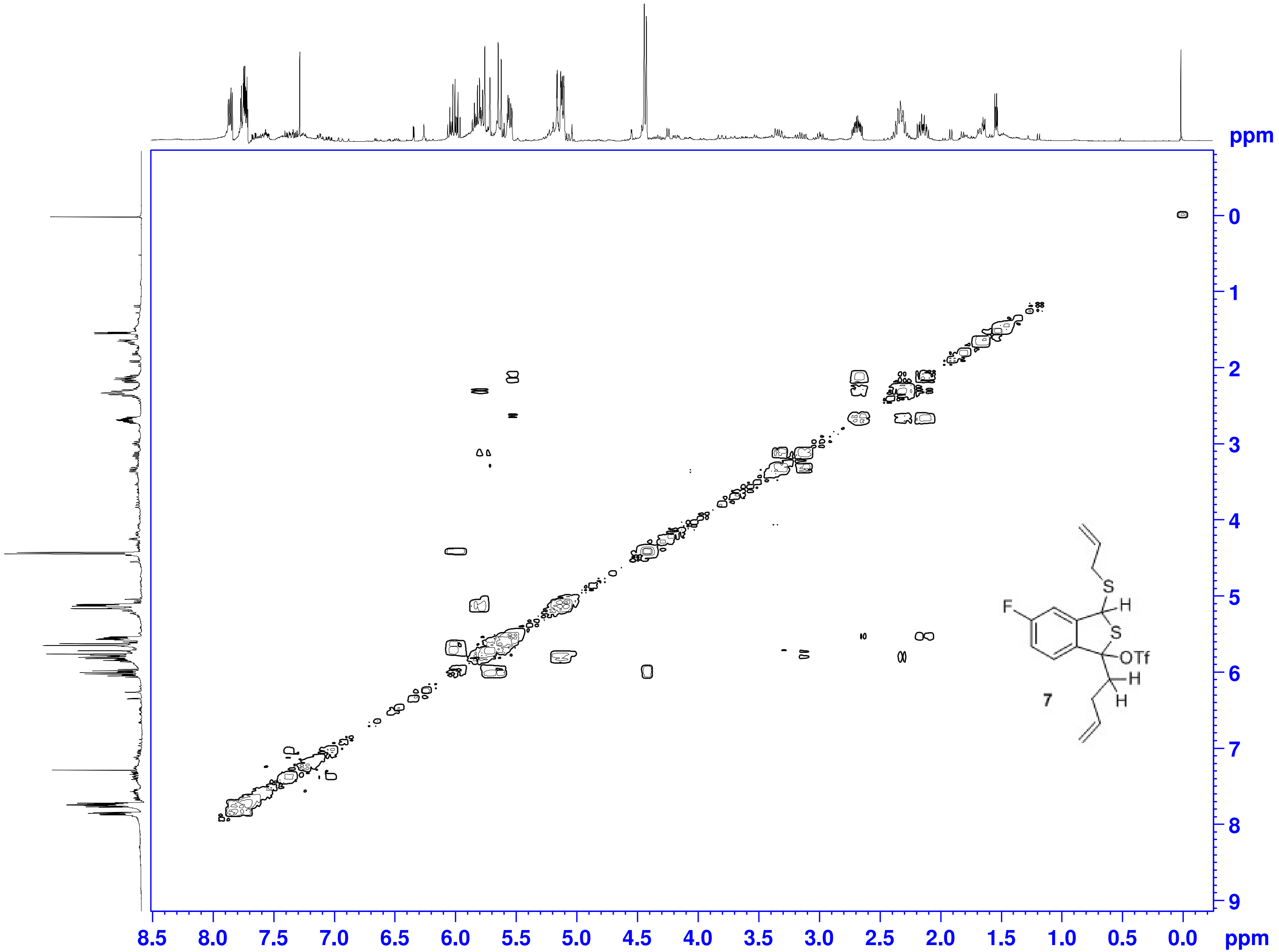
-180
-200
ppm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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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ppm
0
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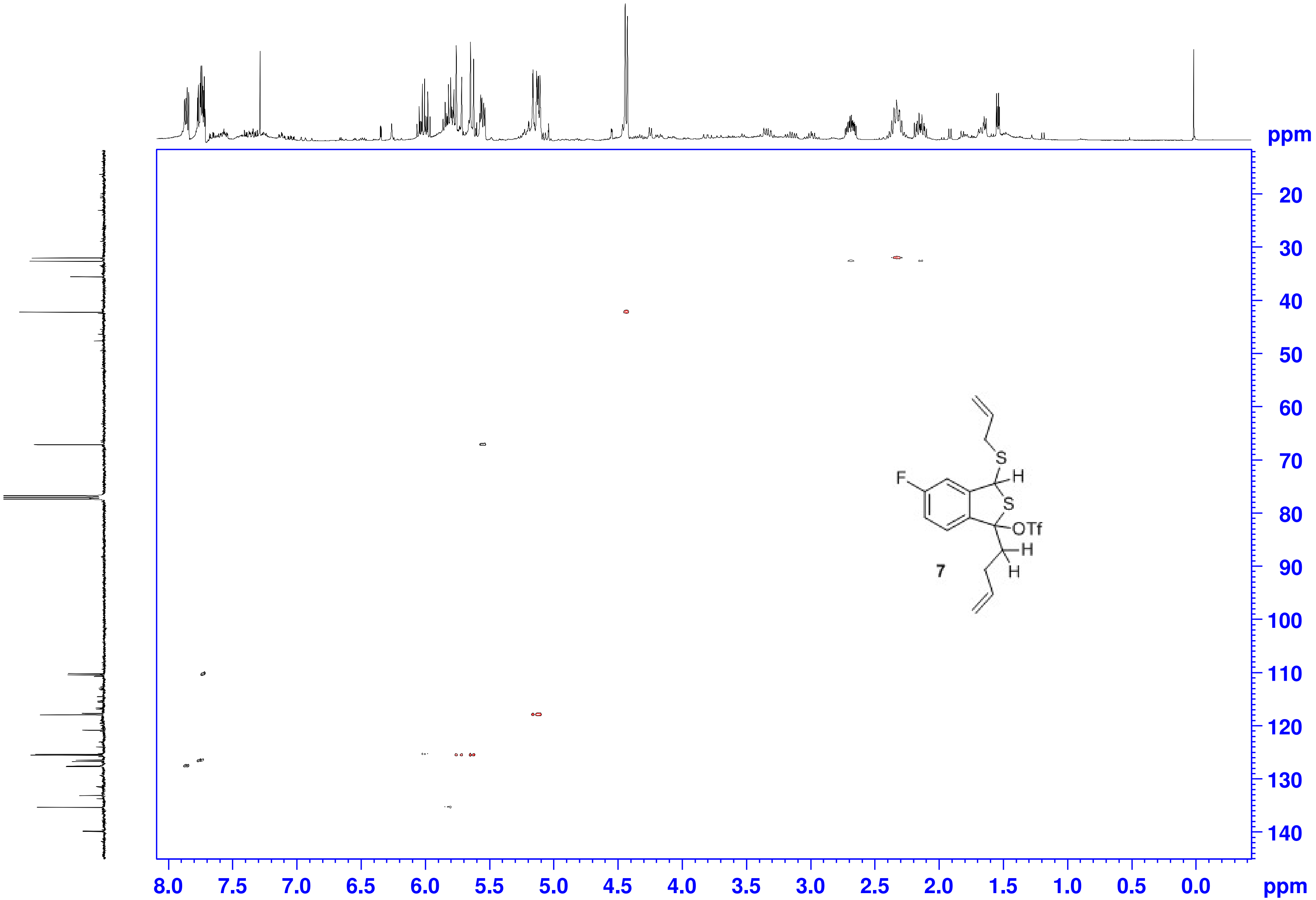
2
3
4
5
6
7
8
9
F
S
H
S
OTf
H
H
7


ppm
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50
60
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100
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120
130
140
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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
0.5
0.0
ppm
F
S
H
S
OTf
H
H

7