PREPARATION OF 2, 3-DIHYDROBENZO[*b*]THIOPHENE BEARING BENZYLIC QUATERNARY CARBON BY PALLADIUM-CATALYZED CASCADE REACTION

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Supporting Information

Table of Contents

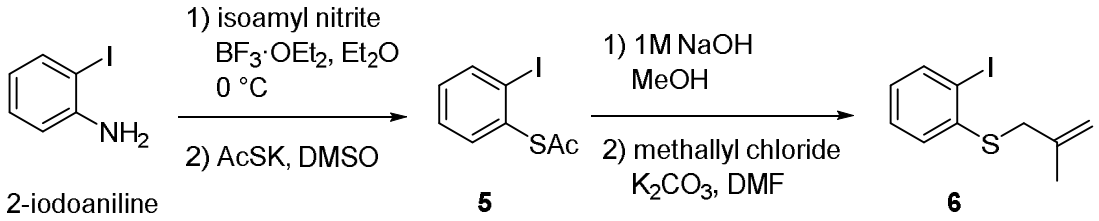
General Information.

^{1}H NMR, ^{13}C NMR spectra were recorded on a JEOL JNM-ECX500 spectrometer and a JEOL JNM-ECZR500 spectrometer. Chemical shifts are reported in ppm with the residual solvent resonance as internal standard ($CDCl_3$ ^{1}H, = 7.26 ppm, ^{13}C, = 77.16 ppm, CD_2Cl_2 ^{1}H, = 5.32 ppm, ^{13}C, = 53.84 ppm, CD_3OD ^{1}H, = 3.31 ppm, ^{13}C, = 49.00 ppm). The following abbreviations were used to explain the multiplecities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. All reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent, and phosphomolybdic acid and heat as developing agents. Kanto Chemical Silica Gel 60N (spherical, neutral, 62-210m partial size) was used for flash silica gel column chromatography. Preparative TLC (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254). TLC R*f*s of purified compounds were included.

Materials

THF, Et_2O were distilled from sodium/benzophenone ketyl, and methylene chloride, CH_3CN, and hexane from calcium hydride. DMF was distilled from CaH_2 under reduced pressure. Toluene was distilled from sodium. All reagents were purchased from Aldrich, TCI, Merck, or Kanto Chemical Co. Ltd.

Preparation of Compound 6



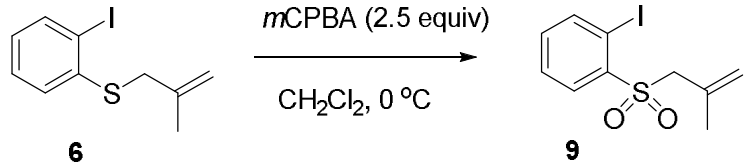
2-iodoaniline **5** **6**

A 50 mL round bottom flask was charged with $BF_3 \cdot Et_2O$ (2.3 mL, 18.2 mmol, 4.0 equiv) and cooled to ï 20 °C under argon atmosphere. To the reaction flask was added a solution of the 2-iodoaniline (1.00 g, 4.57 mmol, 1.0 equiv) in dry Et_2O (5 mL) dropwise with stirring over 5 min, followed by addition of a solution of isoamyl nitrite (1.87 g, 16.0 mmol, 3.5 equiv) in dry Et_2O (5 mL) over 0.5 h. The reaction mixture was stirred at the same temperature for 10 min after the end of addition and was wormed up to 5 °C. To the mixture was added 1.5 mL cold dry Et_2O and the resultant mixture was cooled at 0 °C for 15 min. The precipitated solid was collected by filtration, washed with chilled dry Et_2O and dried to give the diazonium salt. After briefly drying, the diazonium salt dissolved in 5 mL of DMSO was added dropwise to a stirred solution of potassium thioacetate (626 mg, 5.48 mmol, 1.2 equiv) in 10 mL DMSO. The mixture was stirred at room temperature for 40 min, and then, brine (10 mL) was added to the reaction mixture and the aqueous layer was extracted with Et_2O (10 mL×3), and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The solid residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 50/1) to afford **5** (406 mg, 33%, 2 steps) as a colorless oil:[1] R*f* = 0.52 (hexane/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.56 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.40 (ddd, *J* = 7.9, 7.7, 1.7 Hz, 1H), 7.09 (ddd, *J* = 7.7, 7.4, 1.7 Hz, 1H), 2.45 (s, 3H);^{13}C NMR (500 MHz, $CDCl_3$) ŭ 192.5, 140.4, 136.3, 134.1, 131.1, 129.1, 106.8, 30.5; HRMS (ESI) $[M+H]^+$ calculated for C_8H_8IOS: 278.9341, found: 278.9336.

A 50 mL round bottom flask was charged with **5** (931 mg, 3.35 mmol, 1.0 equiv), MeOH (35 mL), and 1M NaOH (8.4 mL, 8.40 mmol, 2.5 equiv) under argon atmosphere. The reaction mixture was stirred at room temperature under argon atmosphere for 30 min, and then, 2M HCl was added to the reaction mixture to maintain pH 5 and the mixture was concentrated under reduced pressure. The concentrate was extracted with Et_2O (10 mL×3) and the combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 50/1) to afford 2-iodobenzenethiol (395 mg, 50%) as a colorless oil: R*f* = 0.47 (hexane). A 30 mL round bottom flask was charged with 2-iodo benzenethiol (140 mg, 0.59 mmol, 1.0 equiv), K_2CO_3 (163 mg, 1.18 mmol, 2.0 equiv), DMF (5.9 mL), and methallyl chloride (107 mg, 1.18 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C under argon atmosphere for 2

days, and then, water (20 mL) was added to the reaction mixture and the aqueous layer was extracted with Et_2O (10 mL×3). The combined organic layer was washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 50/1) to afford **6** (161 mg, 94%) as a colorless oil: R*f* = 0.63 (hexane/ethyl acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.82 (d, *J* = 7.9 Hz, 1H), 7.25-7.30 (m, 2H), 6.86 (ddd, *J* = 7.4, 7.4, 1.7 Hz, 1H), 4.92 (s, 1H), 4.88 (s, 1H), 3.55 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 141.5, 140.0, 139.7, 128.8, 128.6, 127.2, 114.8, 100.7, 42.1, 21.7; HRMS (ESI) $[M+H]^+$ calculated for $C_{10}H_{12}IS$: 290.9704, found: 290.9699.

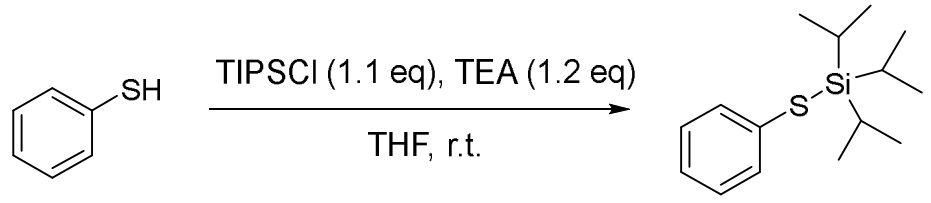
Preparation of Compound 9



6 **9**

A 30 mL round bottom flask charged with **6** (242 mg, 0.833 mmol, 1.0 equiv) and methylene chloride (8.3 mL) was cooled to 0 °C under argon atmosphere. Then, *m*CPBA(553 mg, 2.08 mmol, 2.5 equiv) was added to the stirred mixture. The reaction mixture was stirred at room temperature for 3 h, and then, saturated aq. $NaHCO_3$ (5 mL) was added to the reaction mixture. The aqueous layer was extracted with methylene chloride (5 mL×3) and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 4/1) to afford **9** (136 mg, 51%) as a white solid: R*f* = 0.41 (hexane/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 8.14 (dd, *J* = 7.9, 1.7 Hz, 1H), 8.11 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.53 (ddd, *J* = 7.9, 7.4, 1.1 Hz, 1H), 7.25 (ddd, *J* = 7.9, 7.4, 1.7 Hz, 1H), 5.03 (s, 1H), 4.84 (s, 1H), 4.11 (s, 2H), 1.88 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 142.8, 141.0, 134.5, 133.1, 132.4, 128.7, 121.3, 93.2, 60.9, 22.9; HRMS (ESI) $[M+Na]^+$ calculated for $C_{10}H_{12}IO_2S$: 344.9422, found: 344.9417.

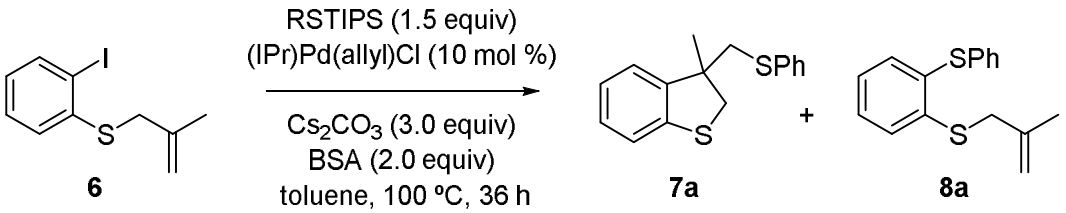
Preparation of Silyl thioether



benzenethiol PhSTIPS

A 100 mL round bottom flask was charged with benzenethiol (3.90 g, 35.6 mmol, 1.0 equiv), TIPSCl (8.3 mL, 39.2 mmol, 1.1 equiv), Et_3N (6.0 mL, 43.0 mmol, 1.2 equiv), and anhydrous THF (36 mL). The reaction mixture was stirred at room temperature under argon atmosphere. After 22 h, the slurry was filtered and the filtrate was washed with aqueous 10% KOH (20mL) solution. The aqueous layer was extracted with hexane (10 mL×3) and the combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by activated alumina column chromatography (hexane) to afford PhSTIPS (9.4 g, 99%) as a colorless oil.[2]

Typical Procedure of Palladium-Catalyzed Carbothiolation



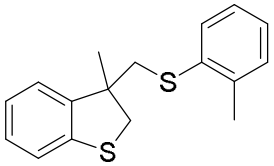
6 **7a** **8a**

A 10 mL test tube was charged with **6** (12.7 mg, 0.0438 mmol, 1.0 equiv), Cs_2CO_3 (43 mg, 0.131 mmol, 3.0 equiv), (IPr)Pd(allyl)Cl (2.5 mg, 0.0044 mmol, 0.1 equiv), PhSTIPS (18 mg, 0.0657 mmol, 1.5 equiv), BSA (17.9 mg, 0.0875 mmol, 2.0 equiv), and anhydrous toluene (880 µL, 0.05 mol/L). The reaction mixture was well degassed, and then, stirred at 100 °C under argon atmosphere. After 36 h, to the reaction mixture was added water (1 mL) at room temperature and the aqueous layer was extracted with EtOAc (1 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/methylene chloride = 40/1) to afford a mixture of **7a** and **8a** (10.5 mg, 96%, **7a**/**8a** = 97/3). The mixture was further purified by preparative thin-layer chromatography (PTLC) (hexane/methylene chloride as the eluent) to afford the **7a** (10.5 mg) as a colorless oil: R*f* = 0.50 (hexane/ methylene chloride = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.31-7.34 (m, 2H), 7.23-7.25 (m, 2H), 7.19-7.21 (m, 1H), 7.13-7.17 (m, 2H), 7.09-7.11 (m, 1H), 7.04-7.07 (m, 1H), 3.49 (d, *J* = 11.3 Hz, 1H), 3.33 (d, *J* = 13.0 Hz, 1H), 3.20 (d, *J* = 11.3 Hz, 1H), 3.16 (d, *J* = 13.0 Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 145.3, 141.1, 137.4, 129.4, 129.1, 128.3, 126.2, 124.6, 123.7, 122.8, 52.0, 44.0, 43.6, 24.5; HRMS (ESI) $[M+H]^+$ calculated for $C_{16}H_{17}S_2$: 273.0772, found: 273.0767.

8a: a colorless oil; R*f* = 0.51 (hexane/ methylene chloride = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.36-7.31 (m, 5H), 7.29-7.26 (m, 1H), 7.17 (ddd, *J* = 7.7, 6.5, 2.3 Hz, 1H), 7.10-7.06 (m, 2H), 4.86 (s, 1H), 4.84 (s, 1H), 3.56 (s, 2H), 1.86 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 140.6, 137.6, 137.4, 134.9, 131.8, 131.4, 130.4, 129.5, 127.5, 127.3, 126.9, 114.4, 41.4, 21.5; HRMS (ESI) $[M+H]^+$ calculated for $C_{16}H_{17}S_2$: 273.0772, found: 273.0767.

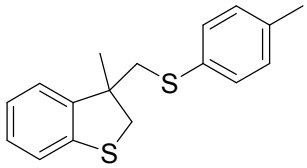
Characterization of the Title Products

3-methyl-3-(o-tolylthiomethyl)-2,3-dihydrobenzo[b]thiophene (7b)



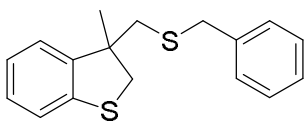
Purification by PTLC (hexane/methylene chloride as the eluent) afforded **7b** (11.3 mg) as a colorless oil: R*f* = 0.58 (hexane/methylene chloride = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.29 (d, *J* = 7.9 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H), 7.13-7.16 (m, 2H), 7.04-7.12 (m, 4H), 3.54 (d, *J* = 11.3 Hz, 1H), 3.30 (d, *J* = 12.5 Hz, 1H), 3.21 (d, *J* = 11.3 Hz, 1H), 3.10 (d, *J* = 12.5 Hz, 1H), 2.39 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 145.5, 141.1, 138.0, 136.4, 130.3, 128.9, 128.2, 126.6, 126.1, 124.6, 123.6, 122.8, 51.8, 44.0, 43.1, 24.6, 20.7; HRMS (ESI) $[M+H]^+$ calculated for $C_{17}H_{19}S_2$: 287.0928, found: 287.0923.

3-methyl-3-(p-tolylthiomethyl)-2,3-dihydrobenzo[b]thiophene (7c)



Purification by PTLC (hexane/methylene chloride as the eluent) afforded **7c** (14.3 mg) as a colorless oil: R*f* = 0.67 (hexane/methylene chloride = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.24 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 7.9, 1H), 7.14 (ddd, *J* = 7.4, 6.9, 1.7 Hz, 1H), 7.04-7.09 (m, 4H), 3.49 (d, *J* = 11.3 Hz, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 3.18 (d, *J* = 11.3 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.30 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 145.5, 141.1, 136.4, 133.7, 130.2, 129.9, 128.2, 124.6, 123.6, 122.8, 52.1, 44.4, 44.0, 24.5, 21.1; HRMS (ESI) $[M+H]^+$ calculated for $C_{17}H_{19}S_2$: 287.0928, found: 287.0922.

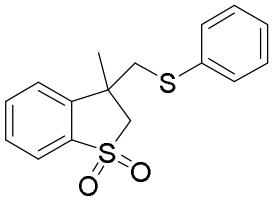
3-benzylthiomethyl-3-methyl-2,3-dihydrobenzo[b]thiophene (7d)



Purification by PTLC (hexane/methylene chloride as the eluent) afforded **7d** (12.8 mg) as a colorless oil: R*f* = 0.51 (hexane/methylene chloride = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.28-7.31 (m, 2H), 7.21-7.25 (m, 3H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.14 (ddd, *J* = 5.7, 5.7, 2.8 Hz, 1H),

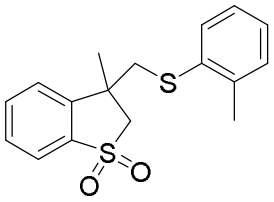
7.05-7.08 (m, 2H), 3.59 (d, *J* = 13.6 Hz, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.35 (d, *J* = 11.3 Hz, 1H), 3.19 (d, *J* = 11.3 Hz, 1H), 2.75 (d, *J* = 13.0 Hz, 1H), 2.72 (d, *J* = 13.0 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 145.4, 141.2, 138.4, 129.1, 128.6, 128.1, 127.2, 124.5, 123.8, 122.7, 51.6, 44.5, 40.8, 38.1, 24.5; HRMS (ESI) $[M+H]^+$ calculated for $C_{17}H_{19}S_2$: 287.0928, found: 287.0923.

3-methyl-3-phenylthiomethyl-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (10a)



Purification by PTLC (hexane/methylene chloride as the eluent) afforded **10a** (3.6 mg, 79 %) as a colorless oil: R*f* = 0.14 (hexane/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.71 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.56 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 7.48 (ddd, *J* = 7.4, 7.4, 1.1 Hz, 1H), 7.42 (d, *J* = 7.4, 1.1 Hz, 1H), 7.32 (m, 2H), 7.25 (m, 2H), 7.19 (m, 1H), 3.79 (d, *J* = 13.6 Hz, 1H), 3.44 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 13.6 Hz, 1H), 3.28 (d, *J* = 13.6 Hz, 1H), 1.62 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 143.9, 138.8, 135.8, 133.9, 130.4, 129.6, 129.3, 127.1, 124.7, 121.6, 60.8, 45.9, 44.2, 27.0; HRMS (ESI) $[M+H]^+$ calculated for $C_{16}H_{17}O_2S_2$: 305.0670, found: 305.0663.

3-methyl-3-(o-tolylthiomethyl)-2,3-dihydrobenzo[b]thiophene 1,1-dioxide (10b)

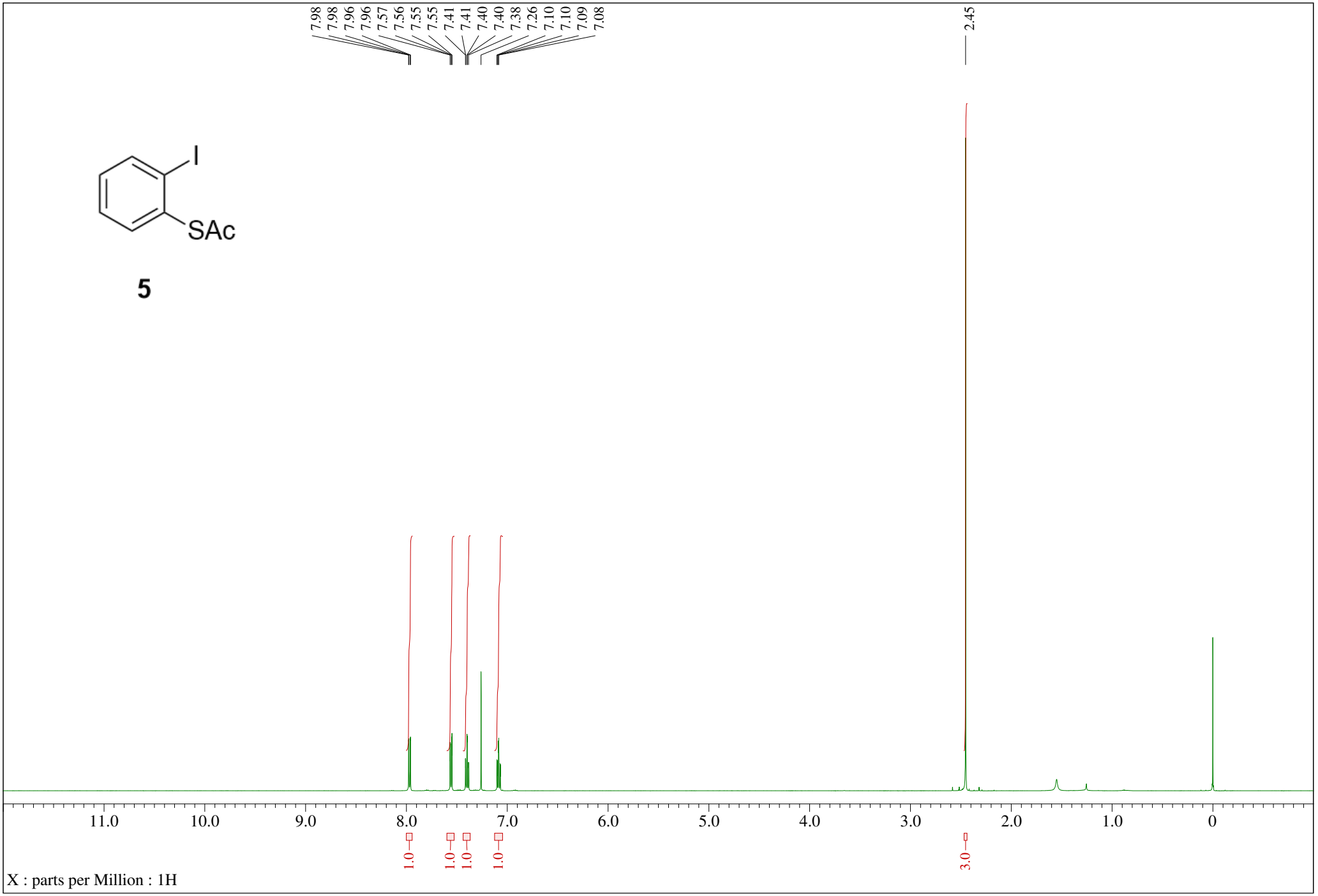


Purification by PTLC (hexane/methylene chloride as the eluent) afforded **10b** (10.4 mg, 64 %) as a colorless oil: R*f* = 0.24 (hexane/ethyl acetate = 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) ŭ 7.71 (dd, J = 7.9, 1.1 Hz, 1H), 7.56 (ddd, J = 7.9, 7.4, 1.1 Hz, 1H), 7.48 (ddd, J = 7.9, 7.4, 1.1 Hz, 1H), 7.41 (d, J = 7.9, 1.1 Hz, 1H), 7.28-7.30 (m, 1H), 7.10-7.16 (m, 2H), 3.82 (d, J = 13.6 Hz, 1H), 3.39 (d, J = 13.0 Hz, 1H), 3.30 (d, J = 13.0 Hz, 1H), 3.29 (d, J = 13.6 Hz, 1H), 2.36 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) ŭ 144.0, 138.9, 138.8, 134.8, 133.9, 130.6, 130.4, 129.5, 127.1, 126.8, 124.6, 121.6, 60.8, 45.3, 44.1, 27.2, 20.8; HRMS (ESI) $[M+H]^+$ calculated for $C_{17}H_{19}O_2S_2$: 319.0826, found: 319.0820.

References

[1] R. Liu, Y.-H. Li, J. Chang, Q. Xiao, and H.-J. Zhu, *Asian. J. Chem.*, 2010, **22**, 3059.

[2] Y. Hosoya, I. Kobayashi, K. Mizoguchi, and M. Nakada, *Org. Lett.*, 2019, **21**, 8280.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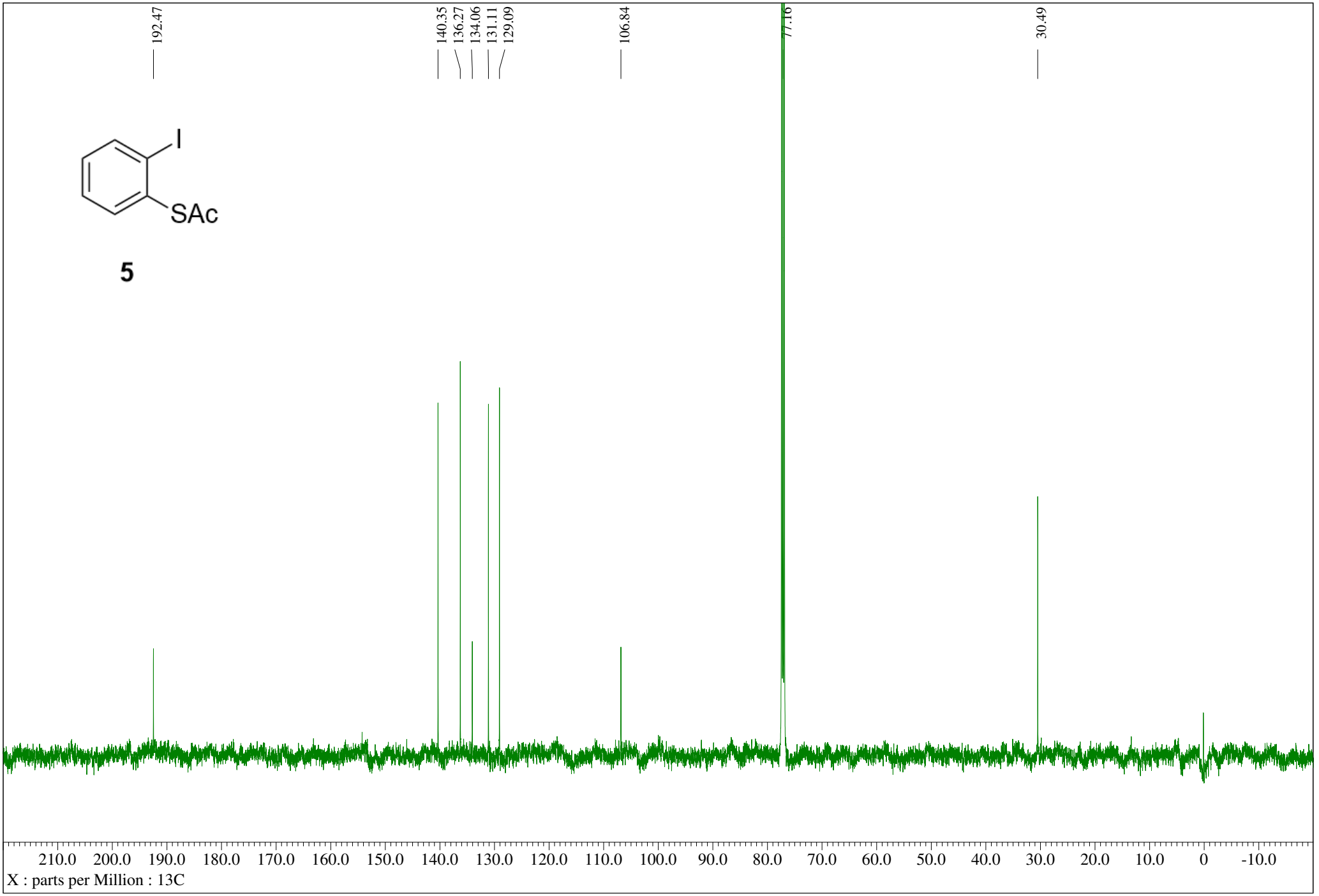
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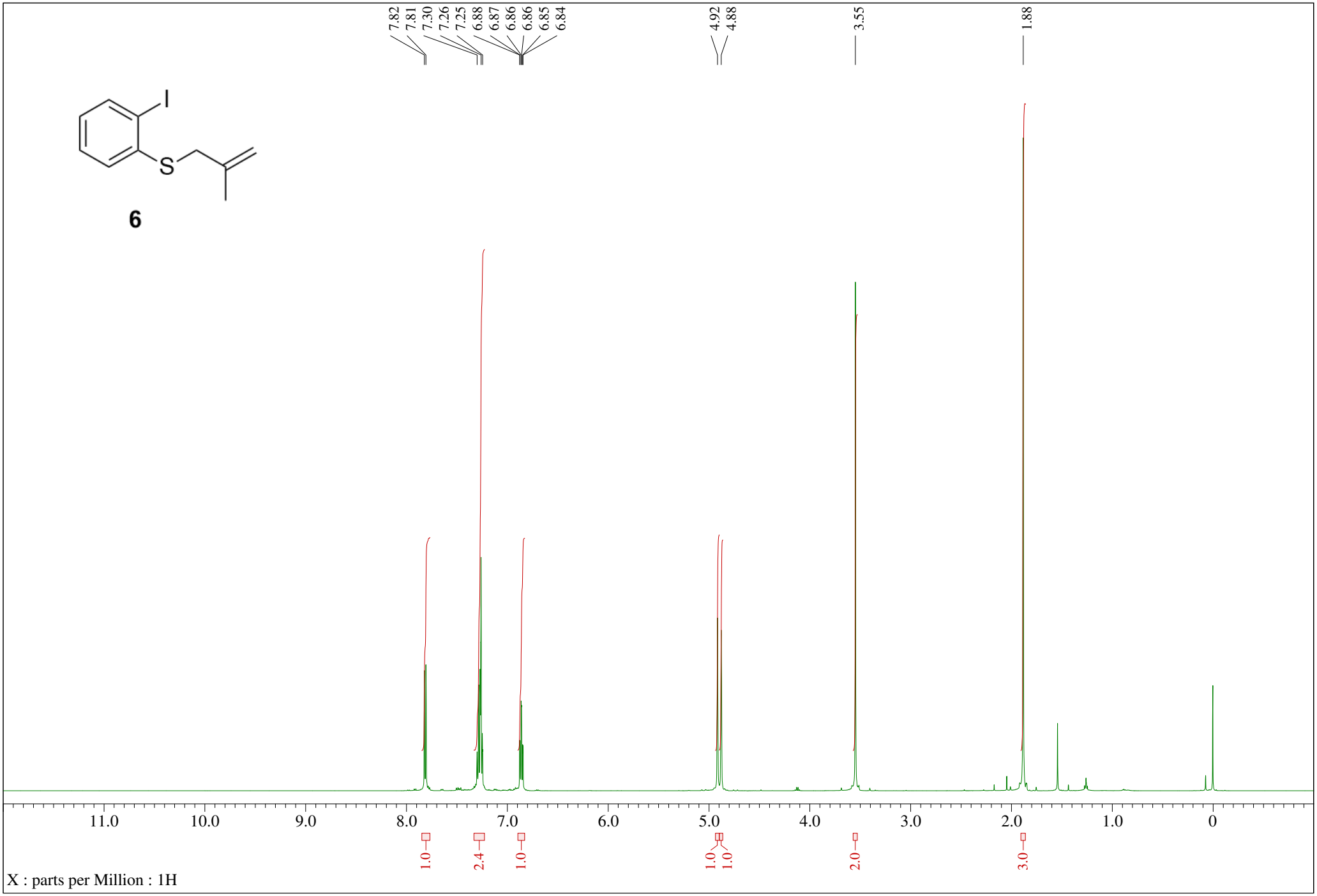
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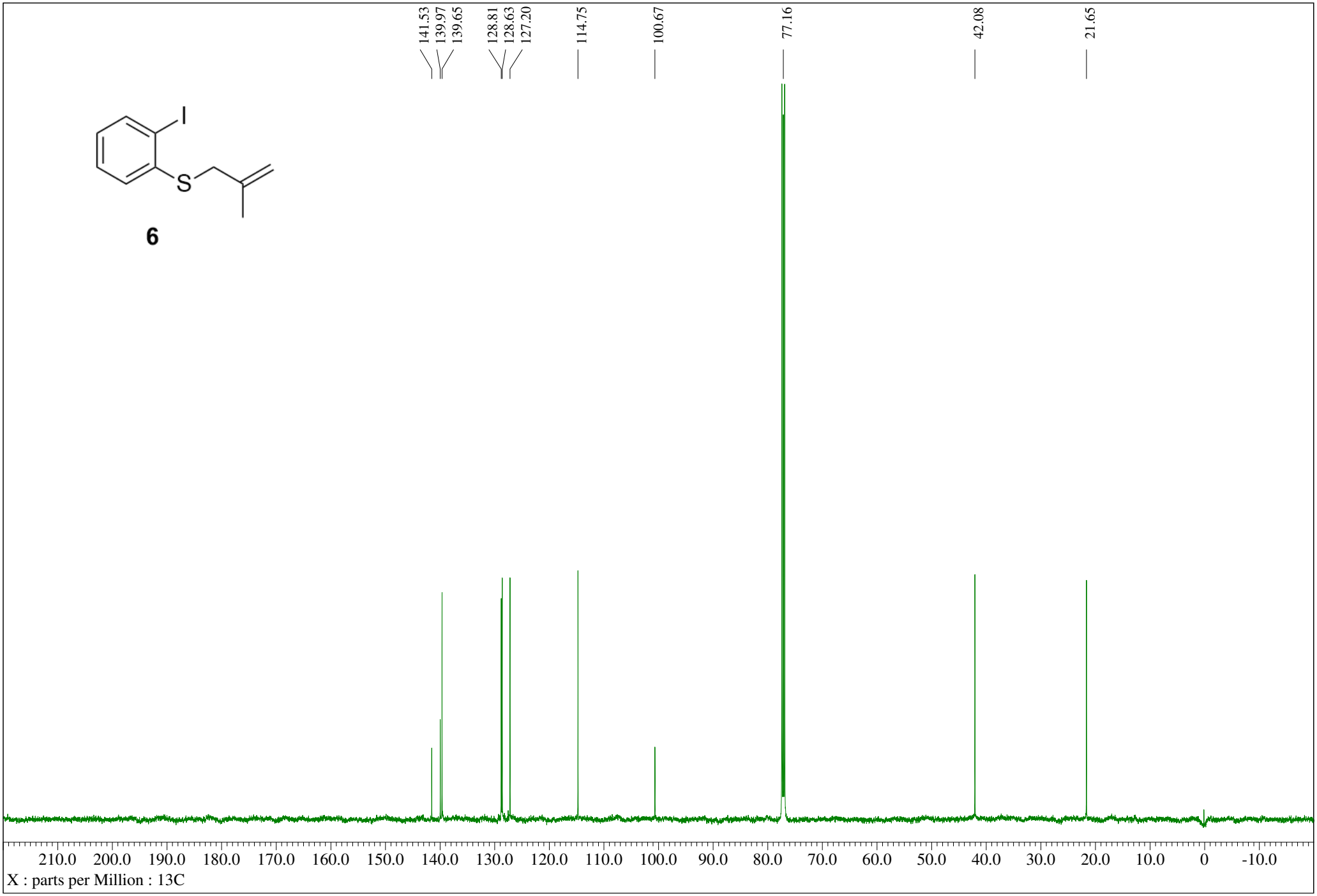
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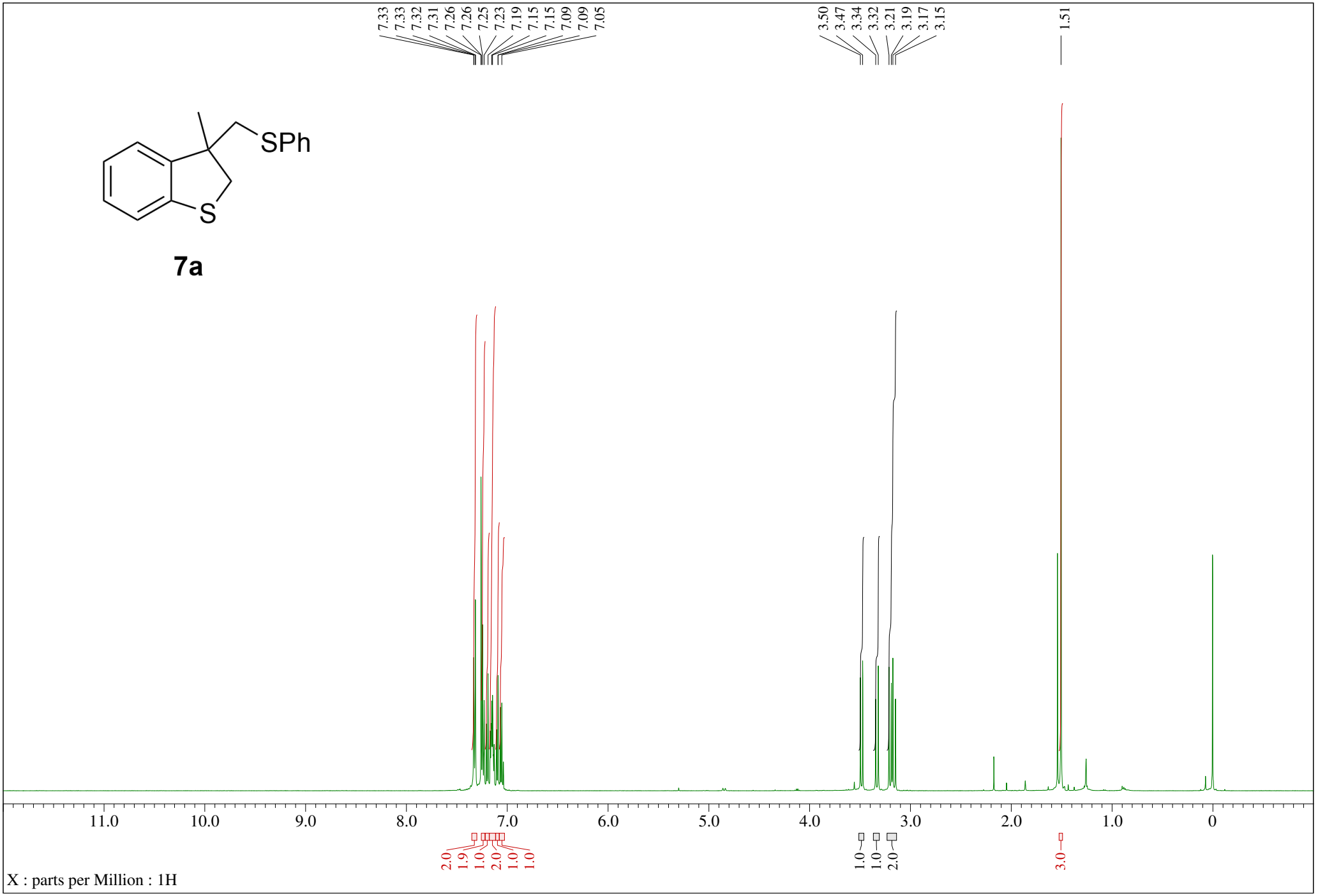
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1.51
SPh
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7a
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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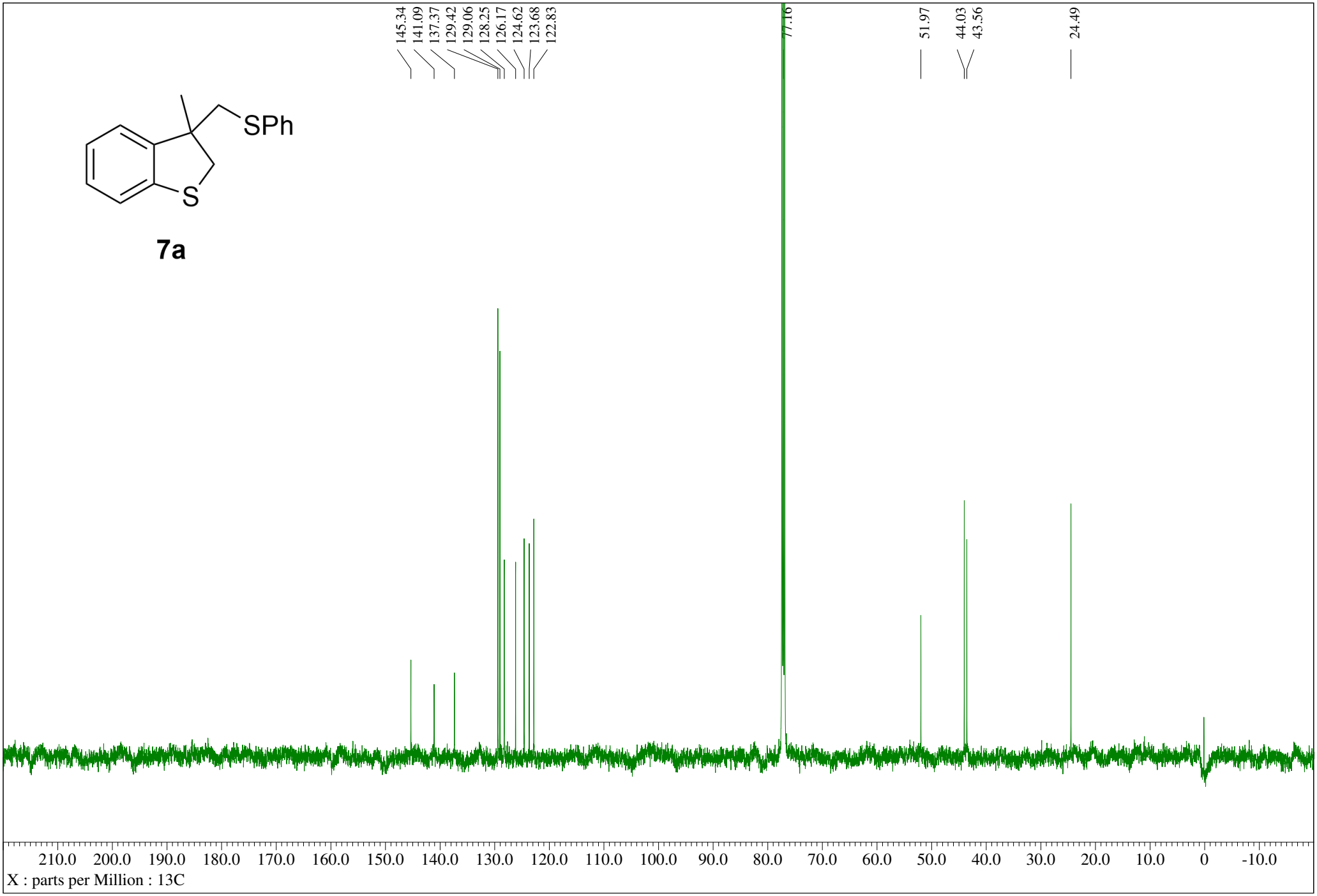
1.0
2.0
1.0
1.0
1.0
1.0
2.0
3.0
X : parts per Million : 1H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129.06
128.25
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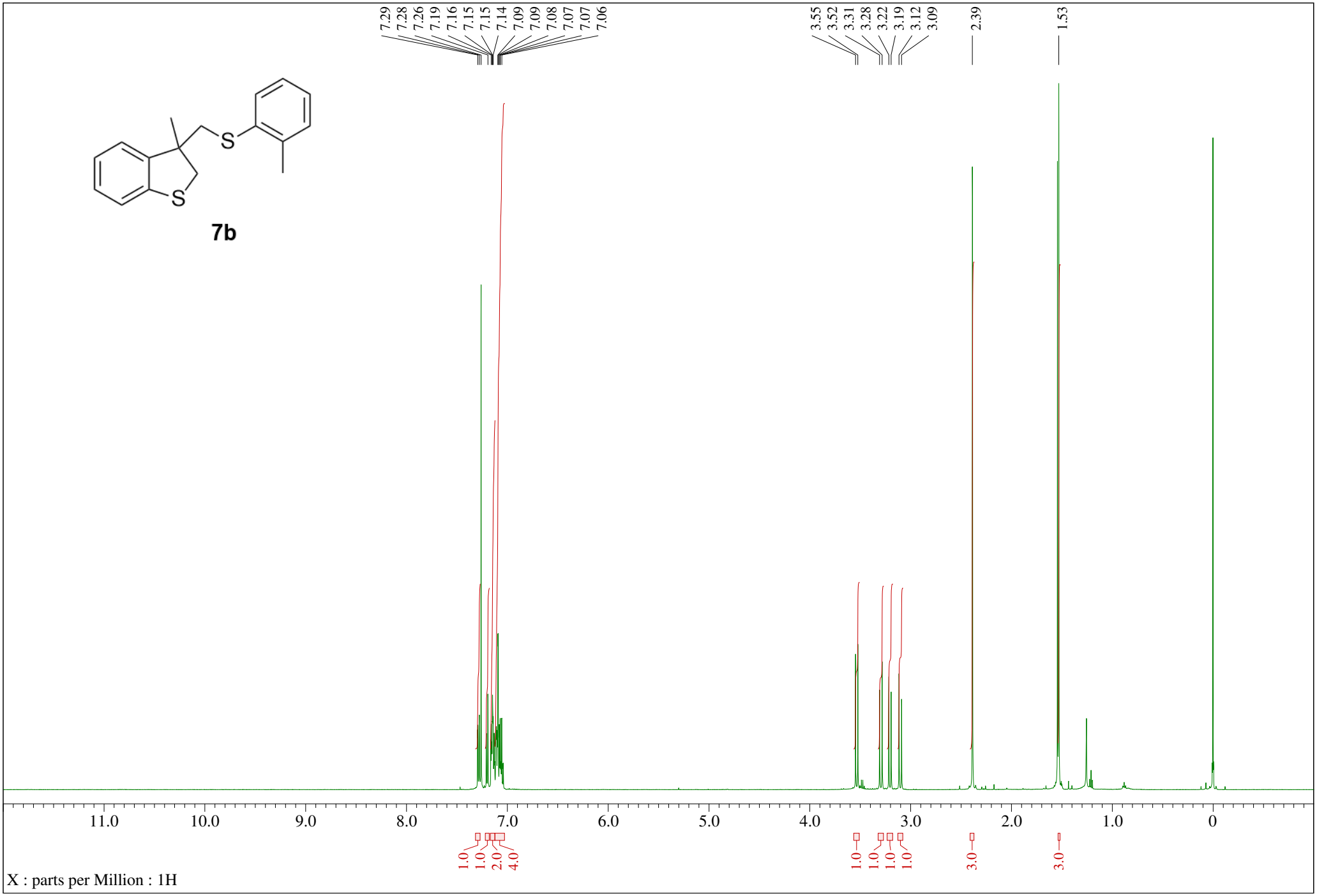
124.62
123.68
122.83
77.16
51.97
44.03
43.56
24.49
SPh
S
7a
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.14
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7.09
7.08
7.07
7.07
7.06
3.55
3.52
3.31
3.28
3.22
3.19
3.12
3.09
2.39
1.53
S
S
7b
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
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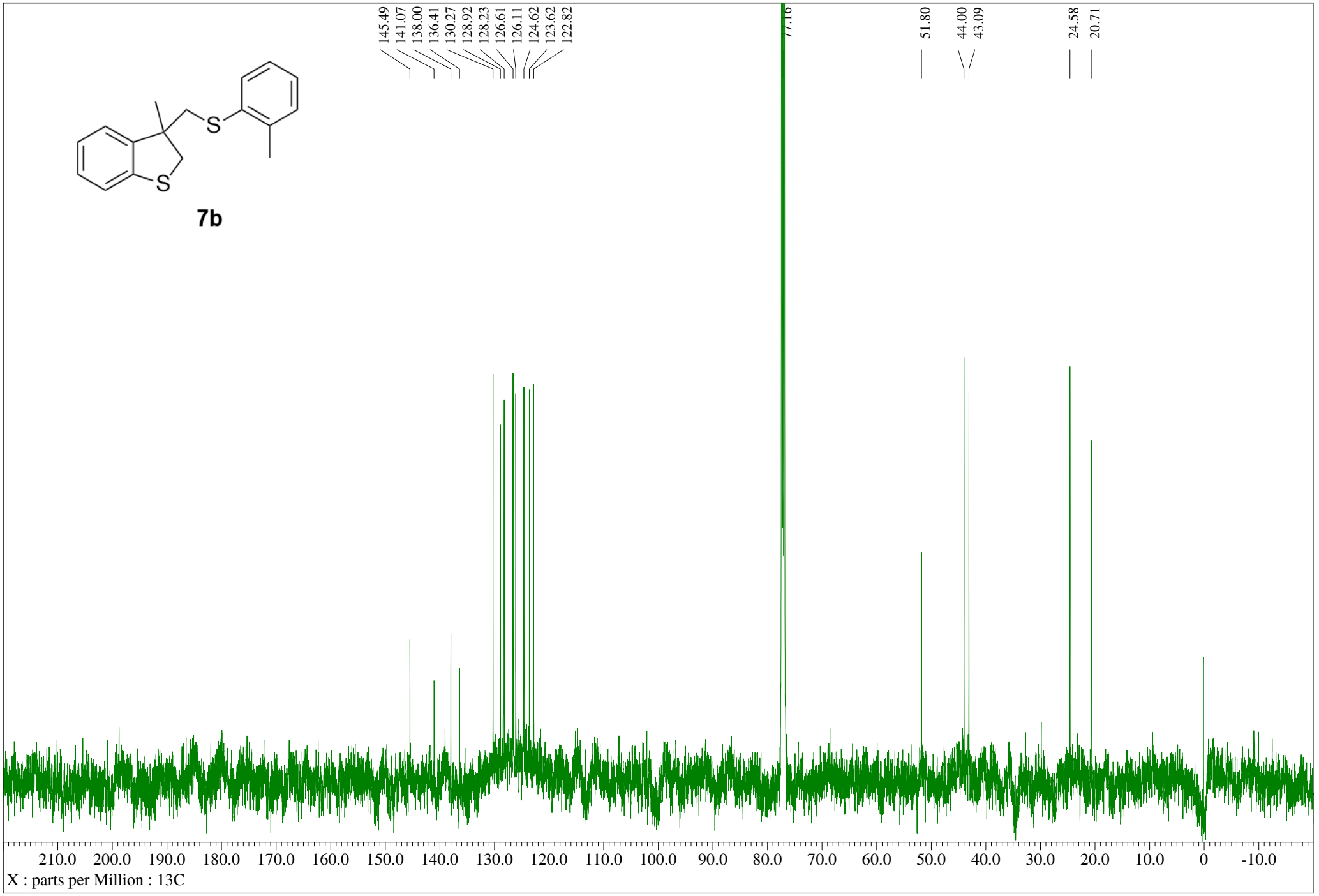
2.0
4.0
1.0
1.0
1.0
1.0
3.0
3.0
X : parts per Million : 1H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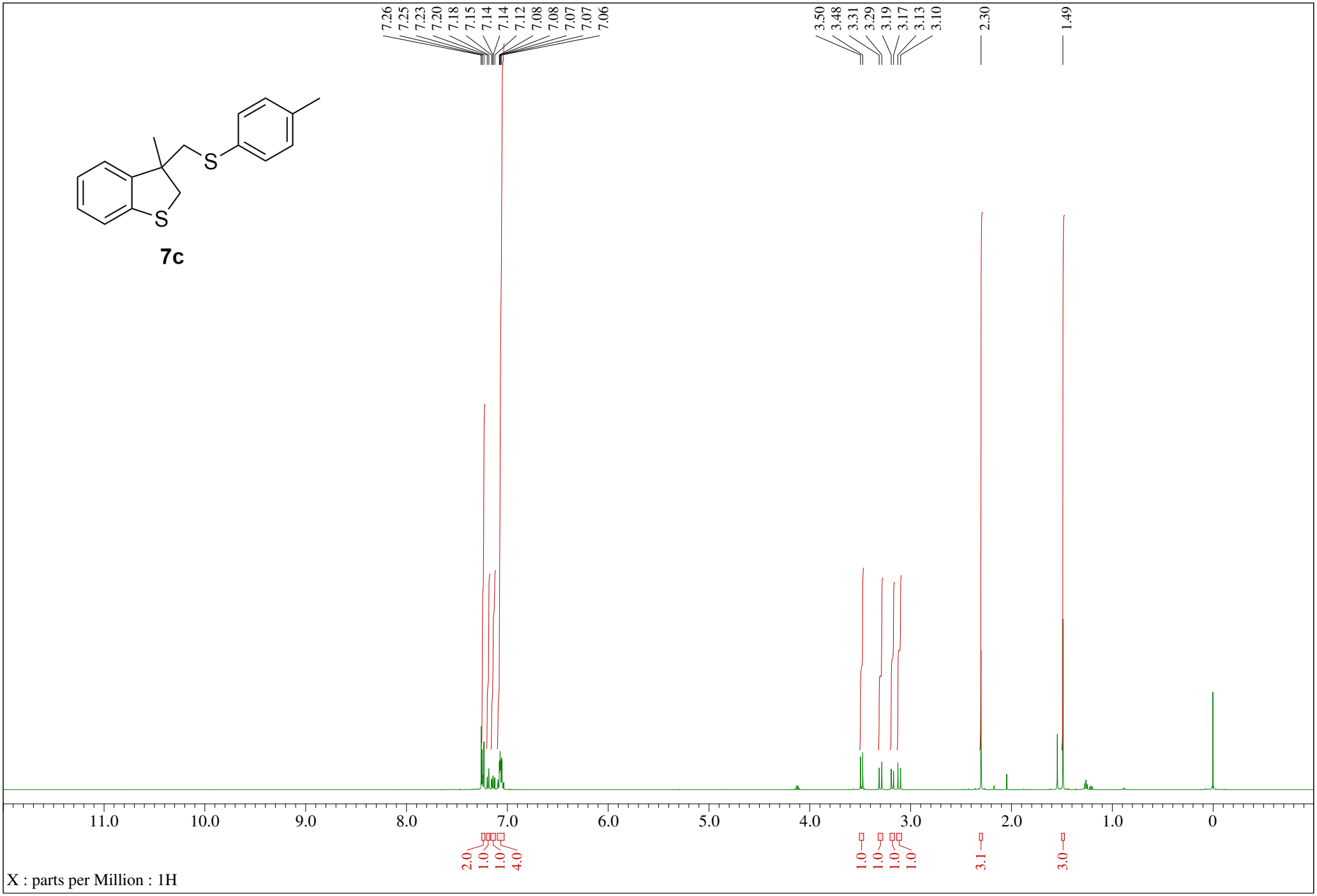
128.92
128.23
126.61
126.11
124.62
123.62
122.82
77.16
51.80
44.00
43.09
24.58
20.71
S
S
7b
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.15
7.14
7.14
7.12
7.08
7.08
7.07
7.07
7.06
3.50
3.48
3.31
3.29
3.19
3.17
3.13
3.10
2.30
1.49
S
S
7c
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.0
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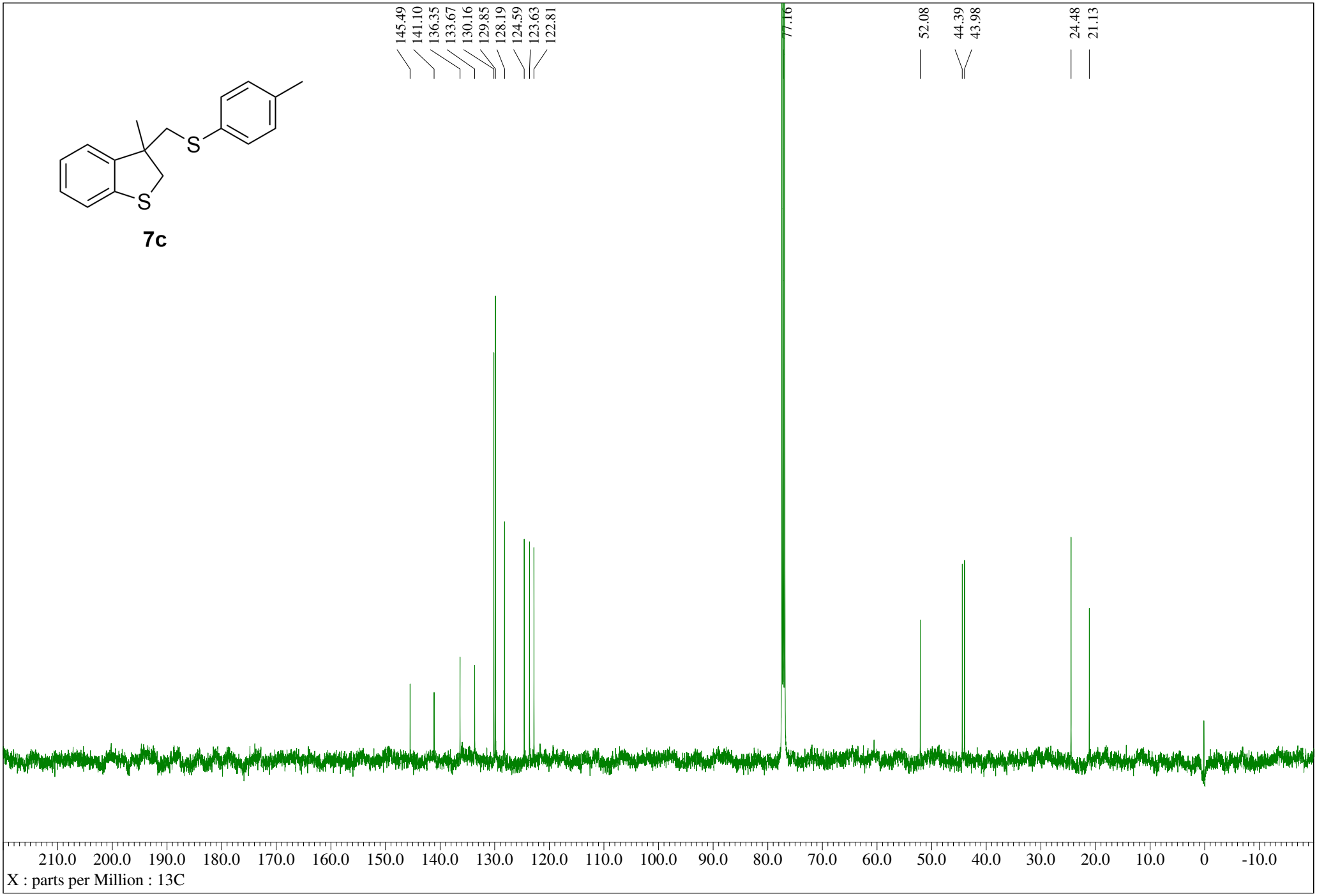
4.0
1.0
1.0
1.0
1.0
3.1
3.0
X : parts per Million : 1H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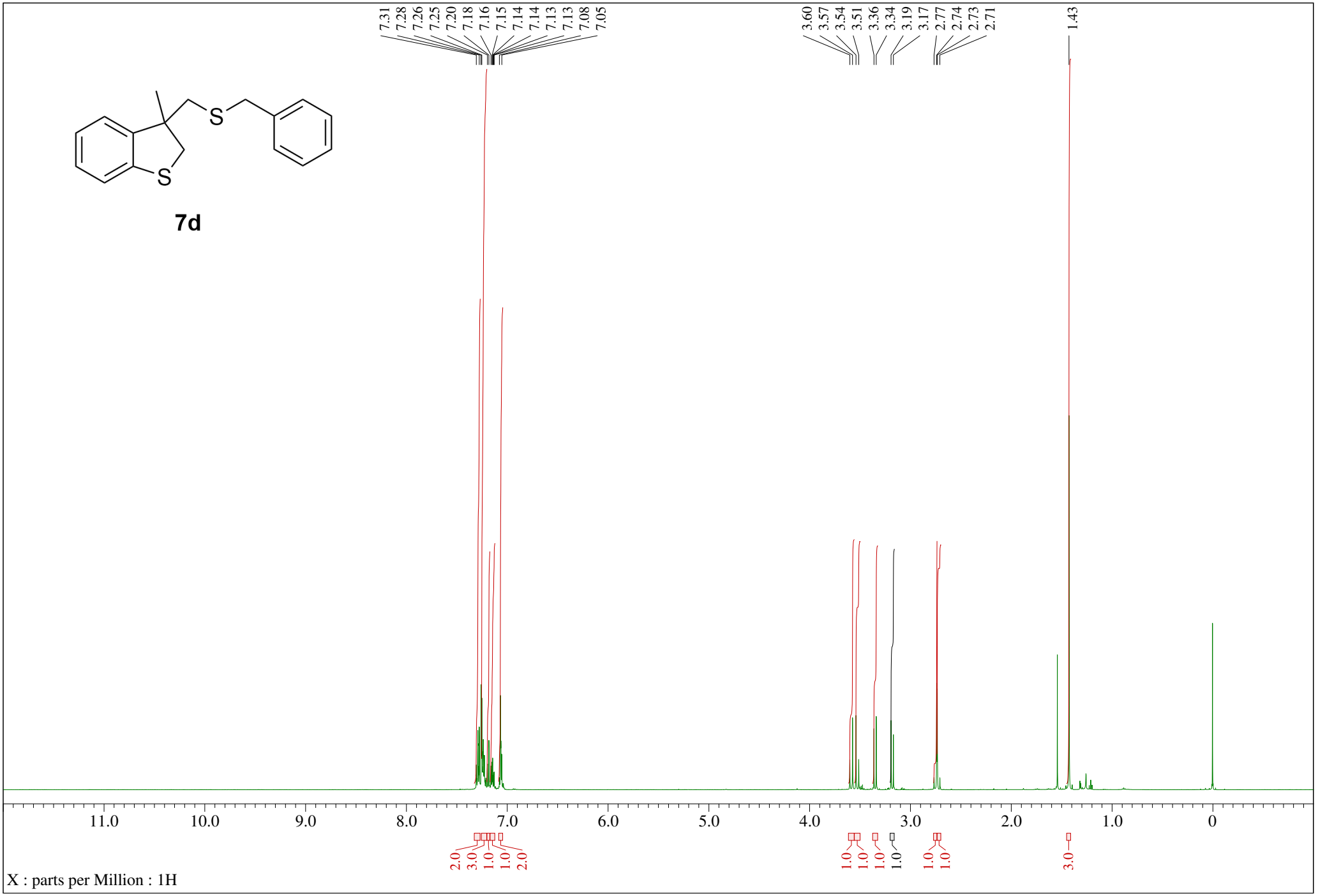
130.16
129.85
128.19
124.59
123.63
122.81
77.16
52.08
44.39
43.98
24.48
21.13
S
S
7c
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.15
7.14
7.14
7.13
7.13
7.08
7.05
3.60
3.57
3.54
3.51
3.36
3.34
3.19
3.17
2.77
2.74
2.73
2.71
1.43
S
S
7d
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.0
3.0
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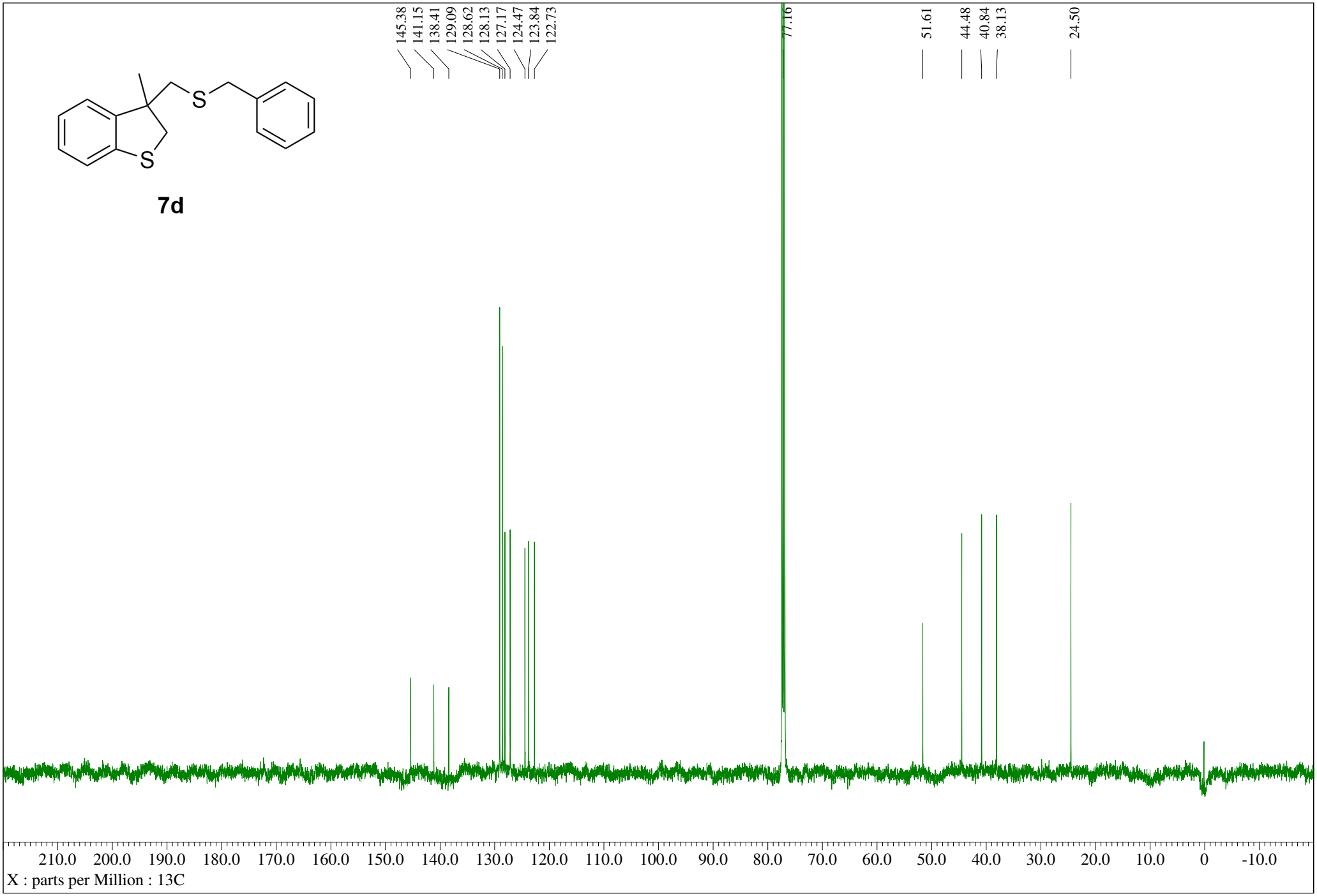
3.0
X : parts per Million : 1H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129.09
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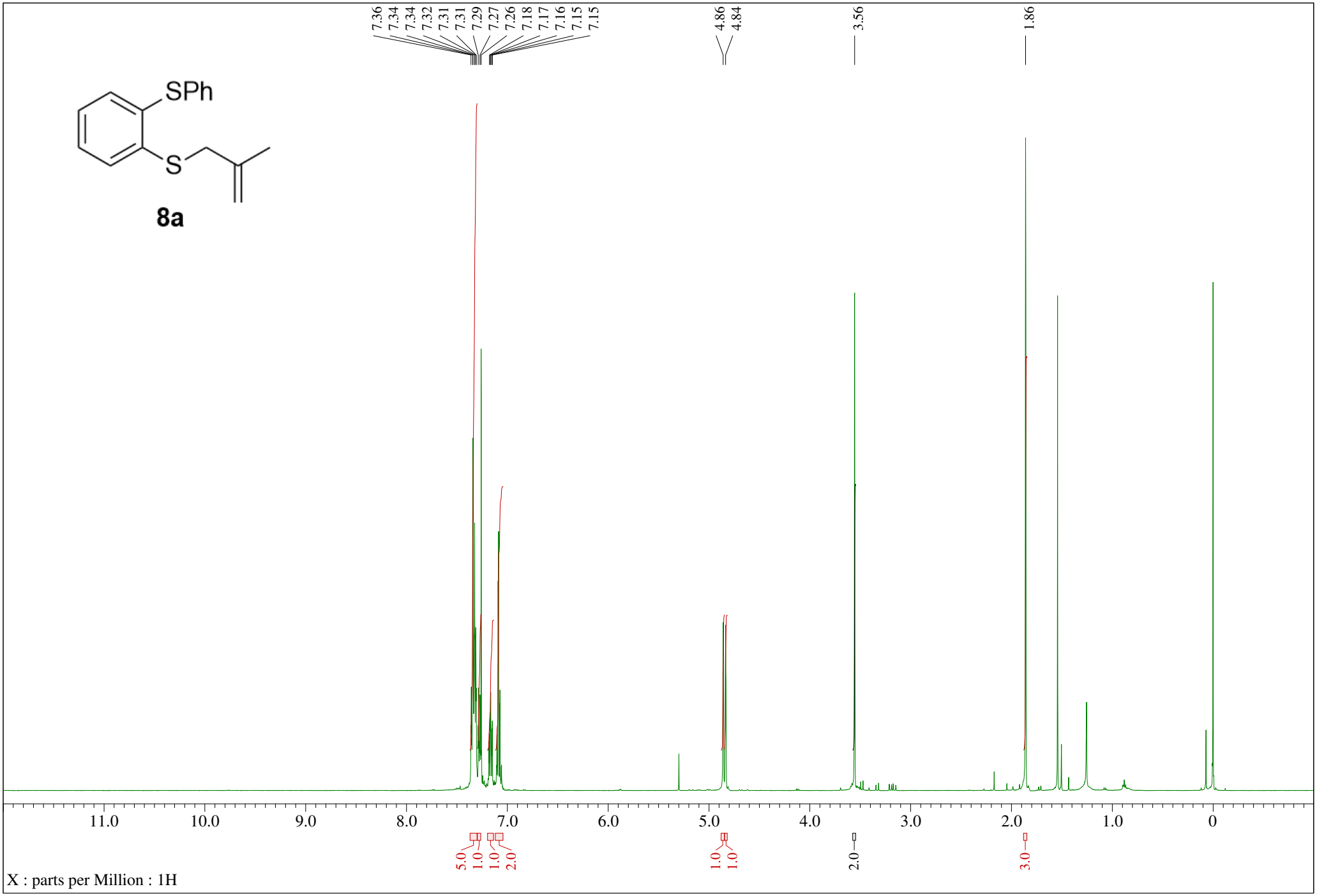
128.13
127.17
124.47
123.84
122.73
77.16
51.61
44.48
40.84
38.13
24.50
S
S
7d
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.34
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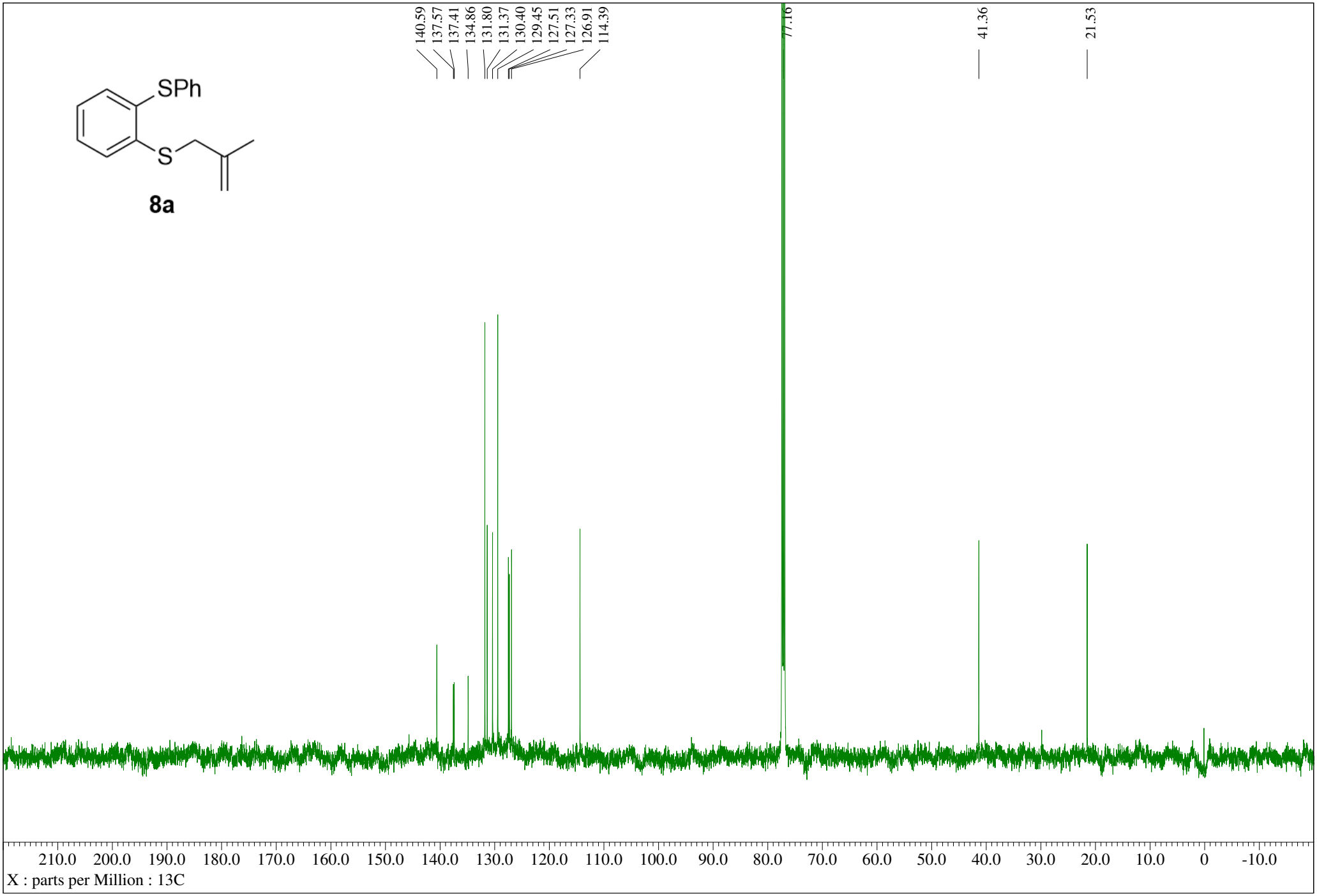
7.31
7.29
7.27
7.26
7.18
7.17
7.16
7.15
7.15
4.86
4.84
3.56
1.86
SPh
S
8a
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
5.0
1.0
1.0
2.0
1.0
1.0
2.0
3.0
X : parts per Million : 1H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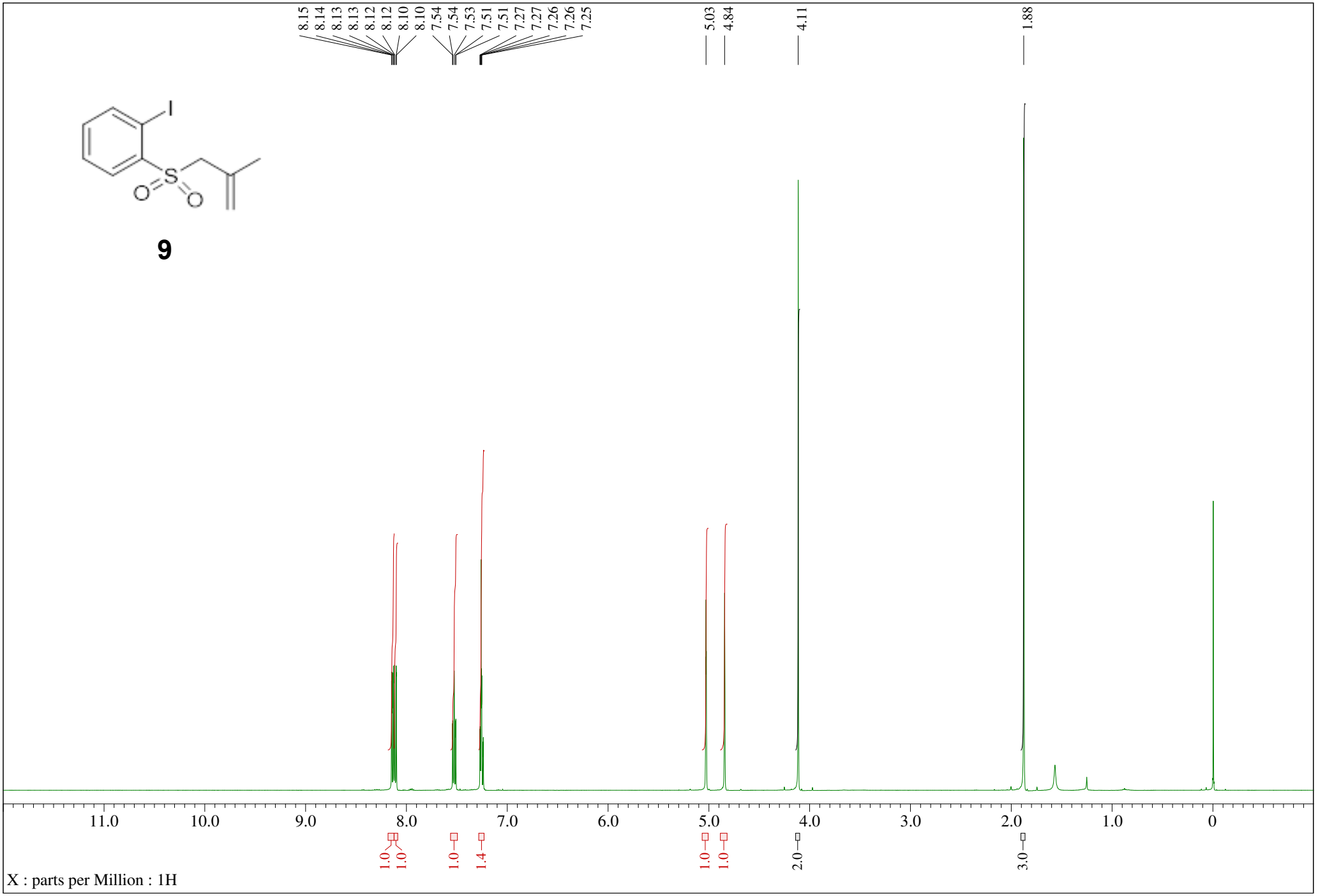
137.41
134.86
131.80
131.37
130.40
129.45
127.51
127.33
126.91
114.39
77.16
41.36
21.53
SPh
S
8a
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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8.13
8.12
8.12
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8.10
7.54
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7.53
7.51
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7.27
7.27
7.26
7.26
7.25
5.03
4.84
4.11
1.88
I
S
O
O
9
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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1.0
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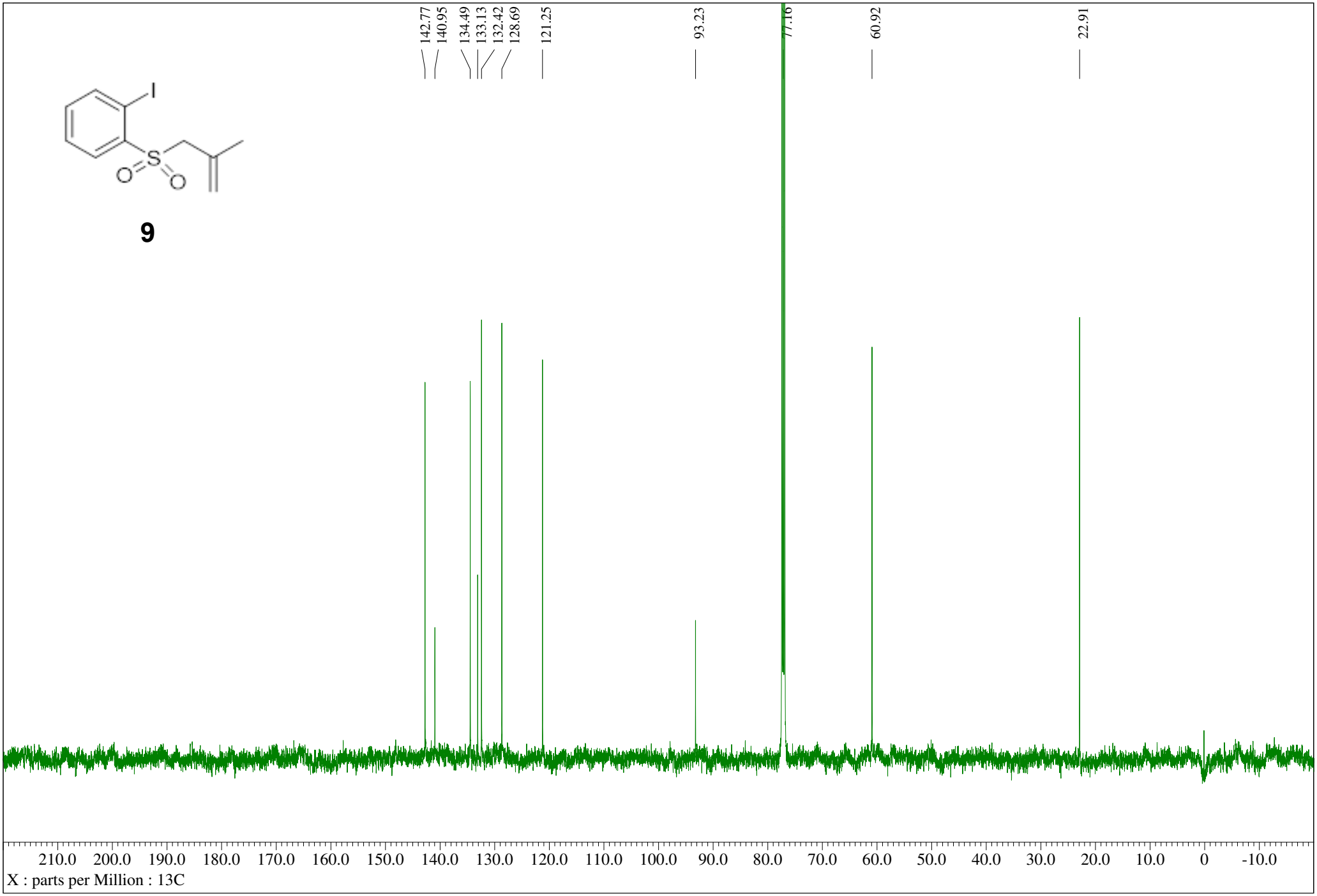
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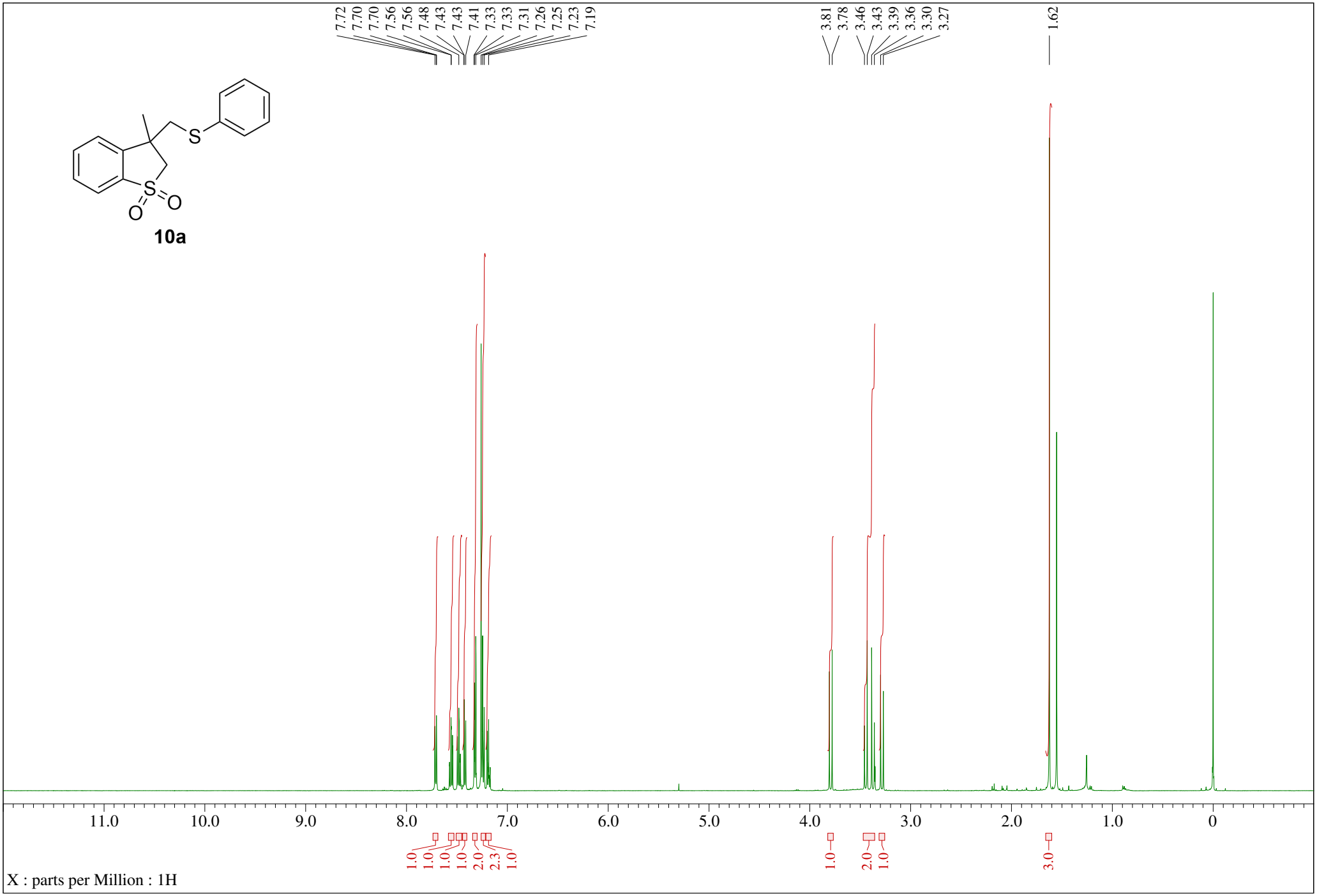
134.49
133.13
132.42
128.69
121.25
93.23
77.16
60.92
22.91
I
S
O
O
9
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.70
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7.43
7.41
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7.33
7.31
7.26
7.25
7.23
7.19
3.81
3.78
3.46
3.43
3.39
3.36
3.30
3.27
1.62
S
S
O
O
10a
11.0
10.0
9.0
8.0
7.0
6.0
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4.0
3.0
2.0
1.0
0
1.0
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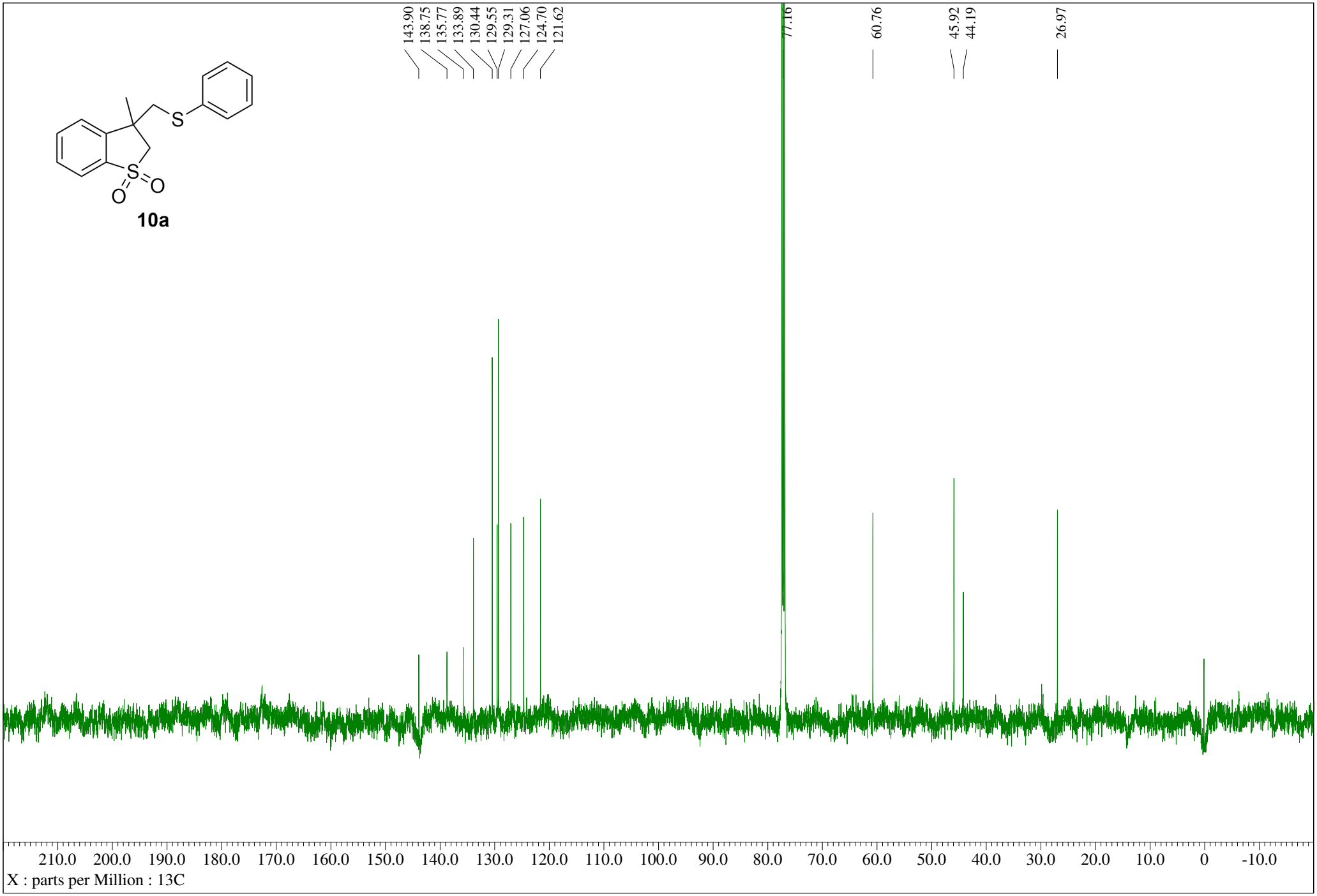
3.0
X : parts per Million : 1H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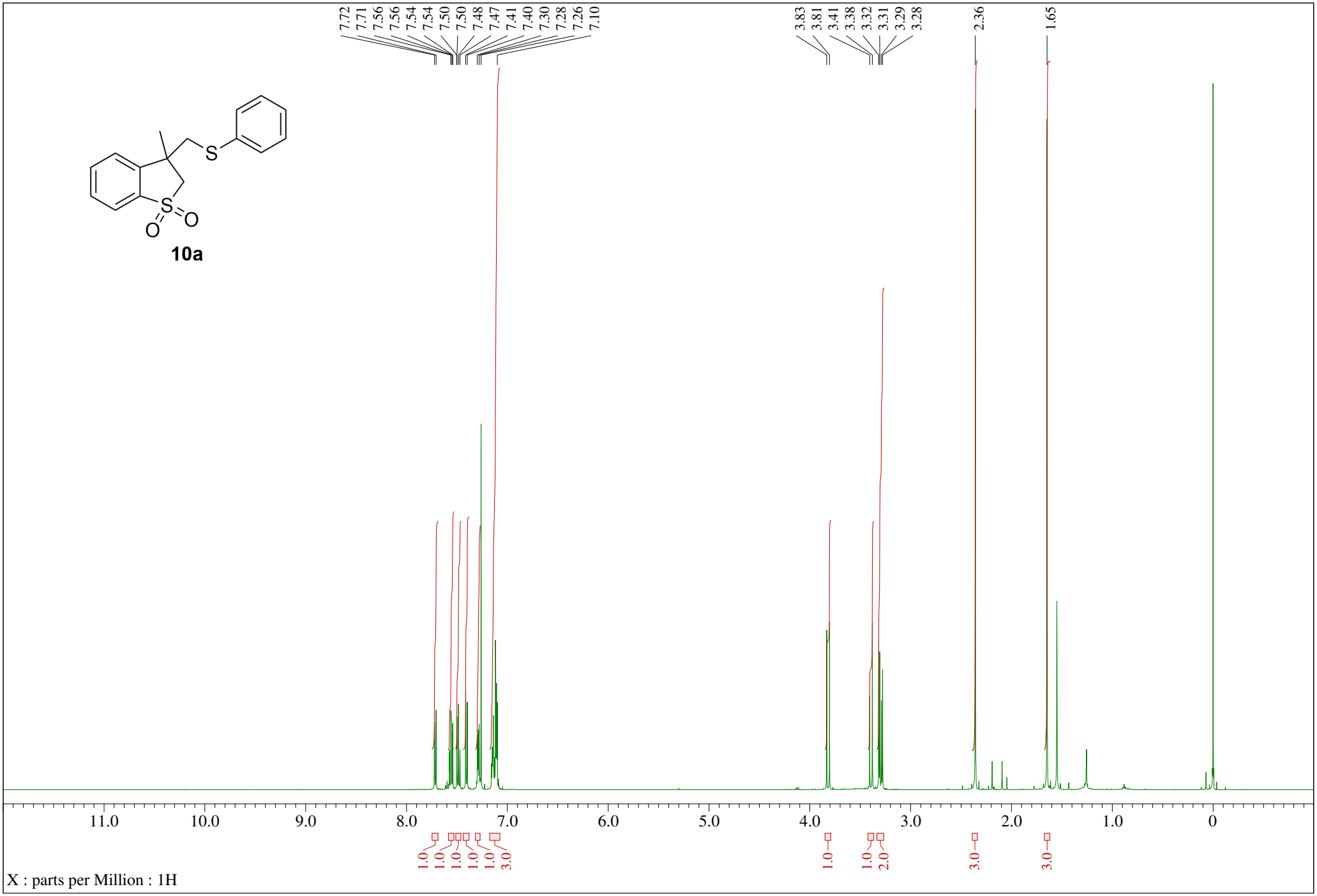
133.89
130.44
129.55
129.31
127.06
124.70
121.62
77.16
60.76
45.92
44.19
26.97
S
S
O
O
10a
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C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7.56
7.54
7.54
7.50
7.50
7.48
7.47
7.41
7.40
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7.28
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7.10
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3.41
3.38
3.32
3.31
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1.0
0
1.0
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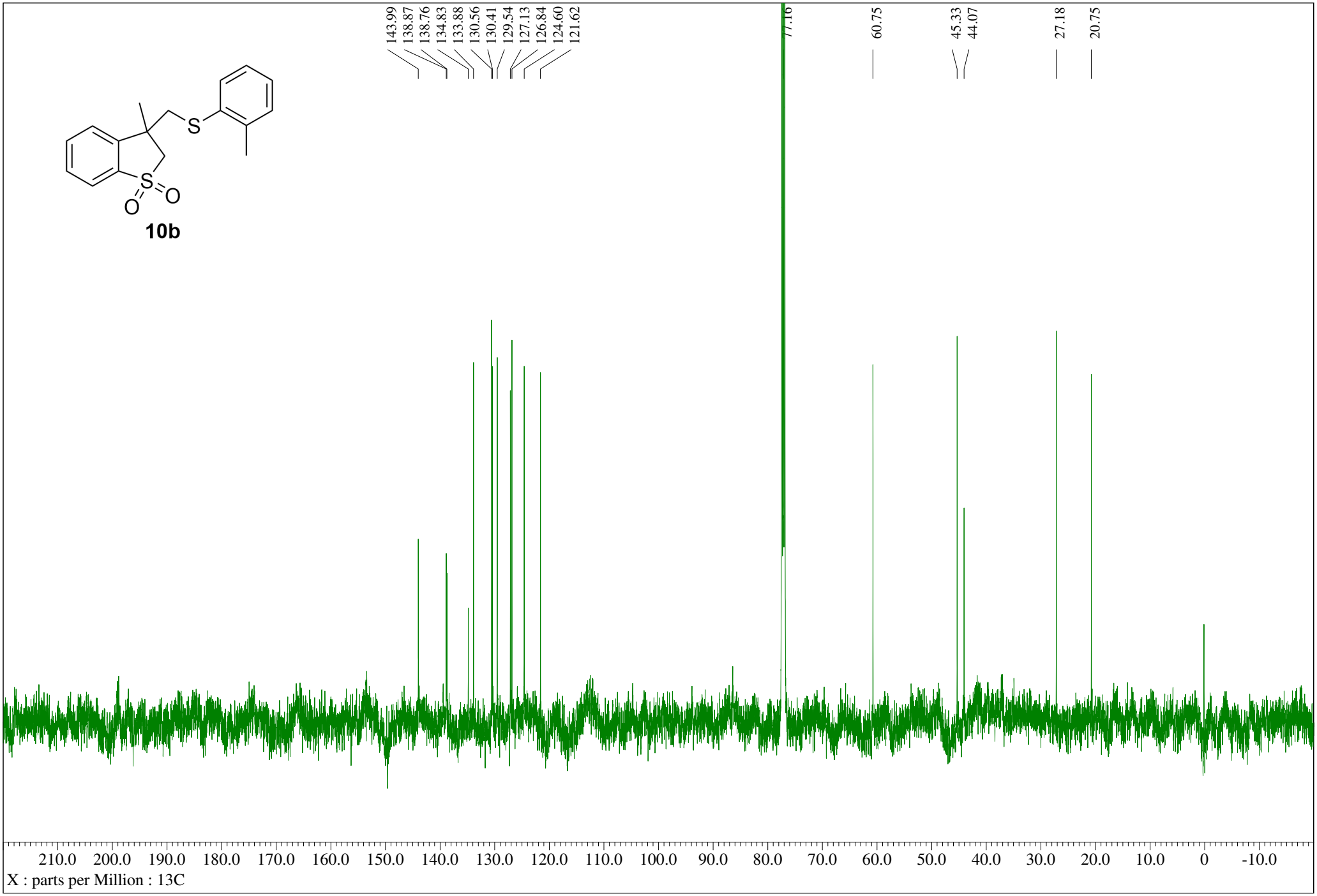
3.0
X : parts per Million : 1H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130.41
129.54
127.13
126.84
124.60
121.62
77.16
60.75
45.33
44.07
27.18
20.75
S
S
O
O
10b
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0
X : parts per Million : 13C