C3-Chlorination of C2-Substituted Benzo[*b*]thiophene Derivatives in the Presence of Sodium Hypochlorite.

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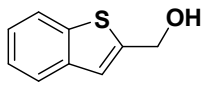
Supporting Information Index:

Scheme S1. Structure of compounds synthesized, and used in this work. The reference for the reported compounds is included below. Compounds that were previously reported, but that lacked a complete characterization, are labeled as Incomplete; and their full characterization is included herein. New compounds are also labeled accordingly, and their full characterization is included herein.



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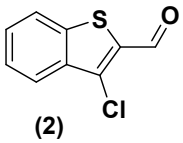

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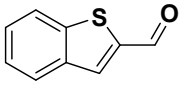

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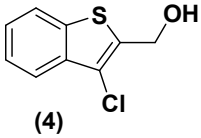

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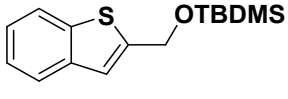

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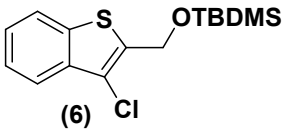

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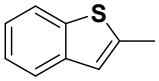

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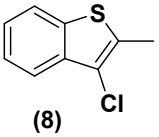

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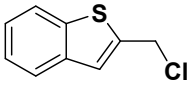

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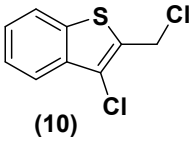

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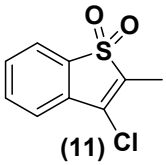

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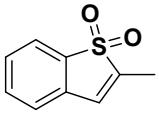

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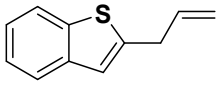

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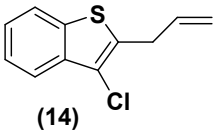

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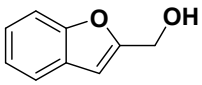

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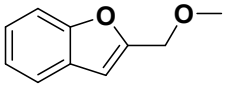

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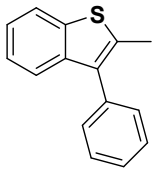

(17)

New compound

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Experimental Details

(A) General procedure for the chlorination in the presence of sodium hypochlorite pentahydrate. Prepare a solution of the desired benzothiophene in acetonitrile (0.5 M, 25 mL) and apply heat (70 °C), with stirring, followed by addition of an aqueous solution of sodium hypochlorite pentahydrate (2.67 M, 10 mL). Stir solution for 20 min, followed by addition of a second portion of a NaOCl•5H2O aqueous solution (2.5 M, 2.5 mL) with vigorous stirring. Cool the biphasic solution to room temperature and partition in water (50 mL) and methylene chloride (50 mL). Wash the aqueous layer with methylene chloride (2x 20mL). Combine the organic residues to wash with brine (30 mL), and dry over sodium sulfate. Concentrate under reduced pressure and purify.

(B) General procedure for the chlorination in the presence of sodium hypochlorite pentahydrate at room temperature.

Prepare a solution of the desired benzothiophene in acetonitrile (0.5 M, 25 mL), with stirring, followed by addition of an aqueous solution of sodium hypochlorite pentahydrate (2.67 M, 10 mL). Stir solution for 48 hr. Partition in water (50 mL) and methylene chloride (50 mL. was the aqueous layer with methylene chloride (2x 20 mL). Combine the organic residues to wash with brine (30 mL), and dry over sodium sulfate. Concentrate under reduced pressure and purify *via* column chromatography.

(C) General procedure for the chlorination in the presence of N-chlorosuccinimide.

Under anhydrous conditions, dissolve a mixture of the desired benzothiophene (0.2 M) and 1.1 equivalents of N-chlorosuccinimide in 10 mL dimethylformamide. Stir solution in at 65 ˚C in an oil bath for 90 minutes. Add 0.15 more equivalents of NCS and stir in the oil bath for an additional 30 minutes. Cool solution to ambient temperature, then partition in water (20 mL) and ethyl acetate (20 mL). Extract the aqueous layer with ethyl acetate (2x 10 mL); combine organic fractions, wash with brine (20 mL) and dry over sodium sulfate. Concentrate under reduced pressure and purify *via* flash column chromatography.

(D) General procedure for the chlorination in the presence of sodium hypochlorite pentahydrate in the absence of solvent (neat).

Charge a round bottom flask with the desired benzothiophene derivative and 5 molar equivalents of sodium hypochlorite pentahydrate. Submerge the reaction flask in an pre-heated oil bath (75 °C), with stirring for 1 h, followed by addition of 2 mol eq. of sodium hypochlorite pentahydrate, and stirring of the oil for additional 1 h. Cool the flask to rt and partition in water (20 mL) and ethyl acetate (20 mL). Extract the aqueous layer with ethyl acetate (2x 10 mL); combine organic fractions, wash with brine (20 mL) and dry over sodium sulfate. Concentrate under reduced pressure and purify *via* flash column chromatography.

Benzo[*b*]thiophene-2-carbaldehyde (3). Use procedure (A) with benzothiophene-2-methanol **1** (2.00 g, 12.2 mmol) and purify *via* flash column chromatography using a gradient from hexanes to 2% ethyl acetate in hexanes. Fast fraction yielded aldehyde **3** in the form of a red oil (0.720 g, 3.66 mmol, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.03 (s, 1H), 7.94 (d, J = 12 Hz, 1H), 7.90 (d, J = 12 Hz, 1H), 7.52 (t, J = 8 Hz, 1H), 7.44 (t, J = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.71, 143.40, 142.72, 138.58, 134.51, 128.21, 126.31, 125.30, 123.35; IR (neat): 3055, 2816, 2792, 2724, 1663, 1591, 1514 cm^{-1}; bp: >250 ˚C; GC-MS: 162, 133, 89.

3-Chlorobenzo[*b*]thiophene-2-methanol (4). A solution of chlorinated benzothiophene **5** (2.1 g, 6.7 mmol) in THF (20 mL), was treated with 3HF•TEA (2.2 mL, 13.4 mmol) and stirred for 1 h. The solution was then partitioned in a $NaHCO_3$ aq. solution (50 %) and ethyl acetate. The aqueous layer was then washed with ethyl acetate (x 2, 35 mL). The organic residues were combined, washed over brine (20 mL), and dried over sodium sulfate, followed by concentration under reduced pressure. Purification was achieved *via* flash column chromatography starting with hexanes, followed by a gradient to 20 % ethyl acetate, to yield alcohol **4** in the form of a white solid (1 g, 5 mmol, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 12 Hz, 2H), 7.48-7.37 (m, 2H), 4.99 (s, 2H), 2.03 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.13, 136.68, 125.5, 124.98, 122.76,

121.83, 117.85, 58.41; IR (neat): 3240, 3050, 2955, 2928, 2849,1562, 1535 cm^{-1}; mp: 91-92 ˚C; GC-MS: 198, 163, 135.

Alternative method for (4). A solution of aldehyde **2** (0.15 g, 0.76 mmol) in MeOH (6 mL) was cooled to 0 °C, followed by addition of sodium borohydride (0.075 g, 1.98 mmol). The suspension was stirred for 20 min and partitioned in ethyl acetate and water. The aqueous layer was then washed with ethyl acetate (x 2, 10 mL). The organic residues were combined, washed over brine (20 mL), and dried over sodium sulfate, followed by concentration under reduced pressure, to yield alcohol **4** in the form of a white solid (0.145 g, 0.73 mmol, 96 %). Spectroscopic data matched those obtained for the previous step.

Benzo[*b*]thiophen-2-ylmethoxy(*tert*-butyl)dimethylsilane (5). A solution of alcohol **1** (2g, 12.18 mmol) in dry pyridine (50 mL) was treated with *t*-butyldimethylsilyl chloride (2.2 g, 14.6 mmol) at once, and stirred for 2 h. The solution was then partitioned in water (75 mL) and ethyl acetate (125 mL). The organic residues were then washed with water (x 2, 40 mL) then brine (40 mL), and dried over sodium sulfate, followed by concentration under reduced pressure. Purification was achieved *via* flash column chromatography starting with hexanes, followed by a gradient to 10 % ethyl acetate, to yield silylated derivative **5** in the form of a clear oil that solidify over time (3.1 g, 11.1 mmol, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 12 Hz, 1H), 7.71 (d, J = 8 Hz, 1H), 7.36-7.26 (m, 2H), 7.15 (s, 1H), 0.98 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.29, 139.71, 124.10, 123.84, 123.28, 122.38, 119.77, 61.40, 25.90, 18.43, 5.21; IR (neat): 3063, 2926, 2897, 2854 cm^{-1}; mp: 39-40 ˚C; GC-MS: 221, 147.

2-Methylbenzo[*b*]thiophene (7). Charge a flame-dried flask with benzothiophene (5.5 g, 38.4 mmol), dissolve in tetrahydrofuran (125 mL) and cool to -78 °C. Add a solution of *n*-butyllithium in hexanes (25 mL, 1.6 M) dropwise (over 5 min) and stir with slow warming to room temperature for 1 hour. Cool the solution (-78 °C) and add iodomethane (4.8 mL, 77.1 mmol) dropwise and stir with slow warming to room temperature for 90 min. The solution was then partitioned over a NH_4Cl aq. solution (100 mL), followed by washing of the

organic residues with brine and drying over sodium sulfate. The clear solution was concentrated under reduced pressure to yield a yellow solid (5.2 g, 34.9 mmol, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8 Hz, 1H), 7.66 (d, *J* = 8 Hz, 1H), 7.33-7.24 (m, 2H), 6.99 (s, 1H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.88, 140.48, 139.71, 124.08, 123.36, 122.55, 122.01, 121.61, 16.18; IR (neat): 3060, 3049, 2942, 2914, 2849 cm^{-1}; mp: 51-53 ˚C; GC-MS: 147, 115.

3-Chloro-2-methylbenzo[*b*]thiophene (8). Use procedure (A) with 2-methylbenzo[*b*]thiophene **7** (1.00 g, 6.75 mmol) and purify *via* flash column chromatography using. The first collected fraction yielded chlorinated benzothiophene **8** in the form of a clear, greenish oil (0.735 g, 4.05 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8 Hz, 2H), 7.41 (t, J = 8 Hz, 2H), 7.34 (t, *J* = 8 Hz, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.01, 136.36, 133.25, 124.74, 124.69, 122.24, 121.29, 118.03, 13.76; IR (neat): 3059, 2916, 1681, 1569, 1543 cm^{-1}; bp: >250 ˚C; GC-MS: 182, 147.

2-Methylbenzo[*b*]thiophene-1,1-dioxide (12). Charged a round bottom flask with benzothiophene derivative **7** (1.00 g, 6.75 mmol) and dissolved with methanol (5 mL). A 0.44 M aqueous solution of Oxone® (9.57 g, 15.53 mmol, 2.3 equiv.) was added. Stirred at 90˚C for 40 minutes. Partitioned the mixture and ethyl acetate and water, washed organics with brine, dried with sodium sulfate and concentrated to dryness under reduced pressure to yield compound **12** in the form of a light pink solid (1.00 g, 5.60 mmol, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8 Hz, 1H), 7.51 (t, *J* = 8 Hz, 1H), 7.43 (t, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 1H), 6.77 (s, 1H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.99, 136.53, 133.62, 131.68, 129.34, 125.92, 124.30, 121.56, 9.11; IR (neat): 3065, 2921, 2852, 1597, 1581 cm^{-1}; GC-MS: 180, 137, 131, 115, 109.

2-Allylbenzo[*b*]thiophene (13). Charge a flame-dried flask with benzothiophene (16.2g, 120.7 mmol), dissolve in tetrahydrofuran (125 mL) and cool to -78 °C. Add a solution of *n*-butyllithium in hexanes (48 mL, 2.5 M) dropwise (over 5 min) and stir with slow warming to room temperature for 1 hour. Cool the solution (-

78 °C) and add allyl bromide (10.45 mL, 120.7 mmol) dropwise and stir with slow warming to room temperature for 90 min. The solution was then partitioned over a NH_4Cl aq. solution (100 mL), followed by washing of the organic residues with brine and drying over sodium sulfate. The clear solution was concentrated under reduced pressure to yield a yellow oil (21 g) as a mixture containing the desired product **13** along with benzothiophene (app. 15 % by NMR) and other minor impurities. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8 Hz, 1H), 7.68 (d, J = 8 Hz, 1H), 7.37-7.24 (m, 2H), 7.04 (s, 1H), 6.10-5.99 (m, 1H), 5.26-5.12 (m, 2H), 3.66 (d, J = 8 Hz, 2H); GC-MS: 174, 147, 129, 115.

Benzo[*b*]furan-2-methanol (15). Use same procedure as that previously reported for benzothiophene.[S1] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8 HZ, 1H), 7.51 (d, J = 8 Hz, 1H), 7.34-7.24 (m, 2H), 6.70 (s, 1H), 4.81 (s, 2H), 2.00 (s, 1H); IR (neat): 3313, 3065, 2932, 2868, 1604, 1586 cm^{-1}.

2-Methoxymethylbenzo[*b*]furan (16).[S12] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8 Hz, 1H), 7.48 (d, J = 8 Hz), 7.30-7.20 (m, 2H), 6.69 (s, 1H), 4.56 (s, 2H), 3.44 (s, 3H); IR (neat): 2987, 2924, 2853, 2822, 1602, 1586 cm^{-1}.

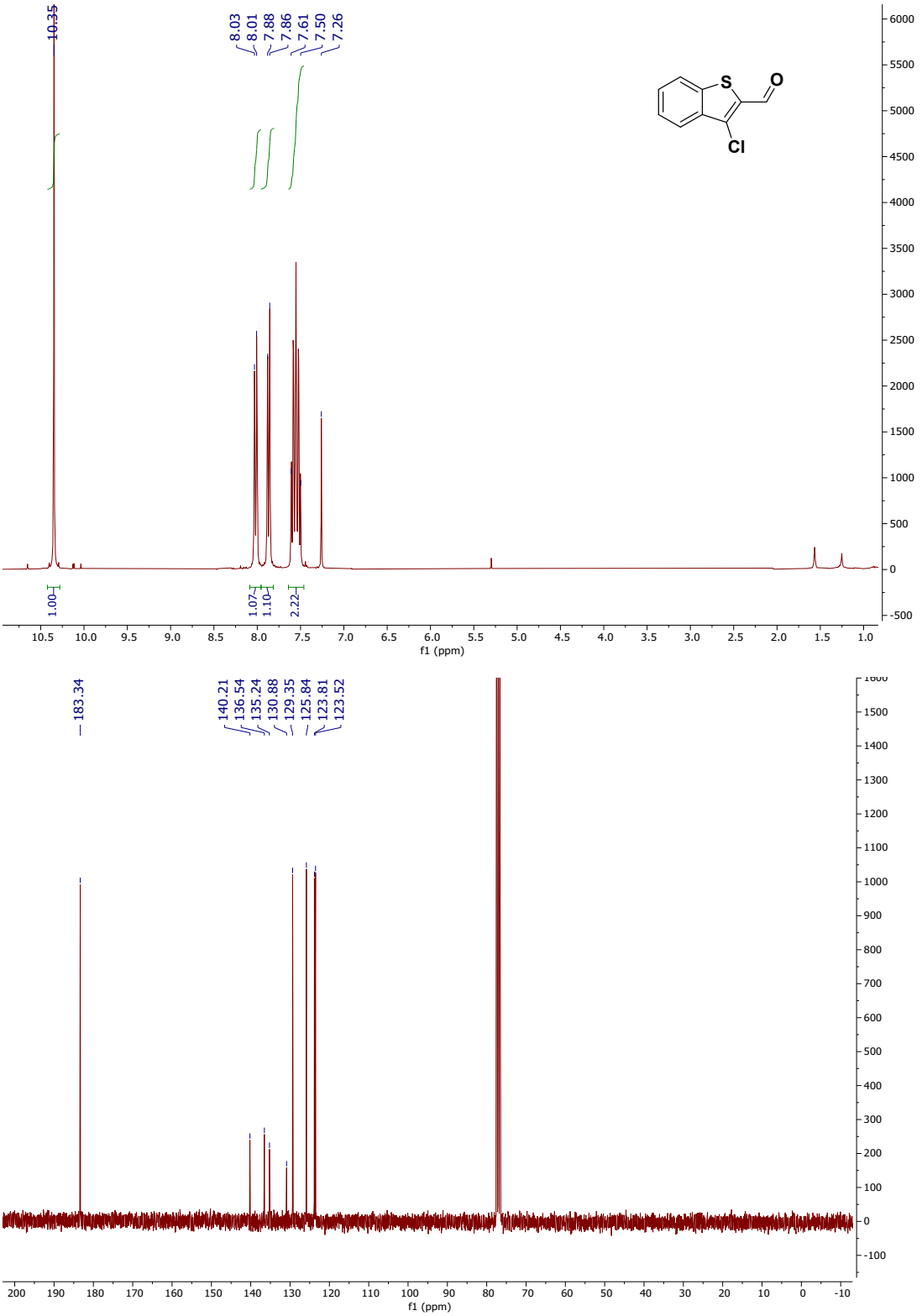


Figure S1. ^{1}H and ^{13}C-NMR of 3-chorobenzo[b]thiophene-2-carbaldehyde **2**.

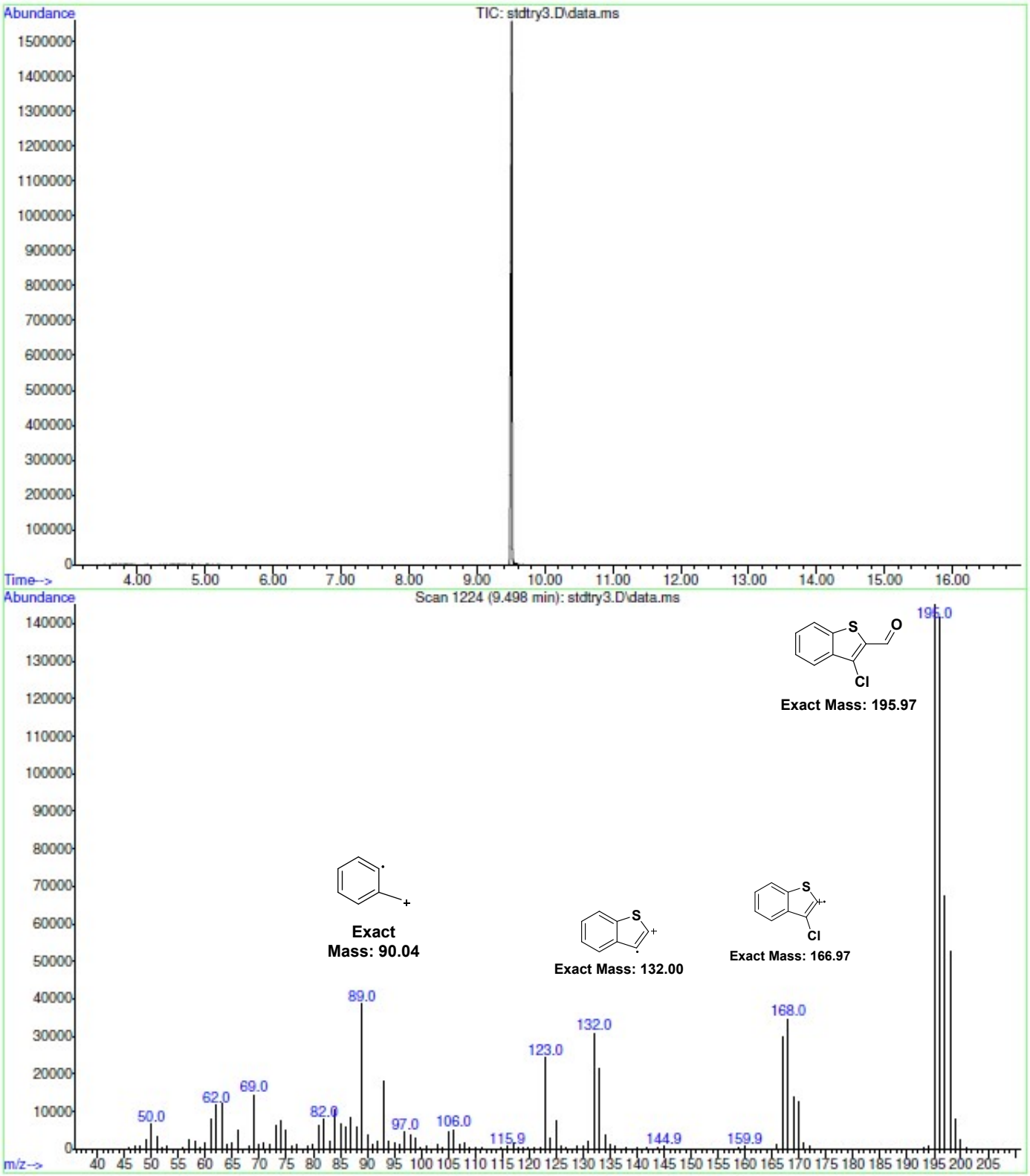
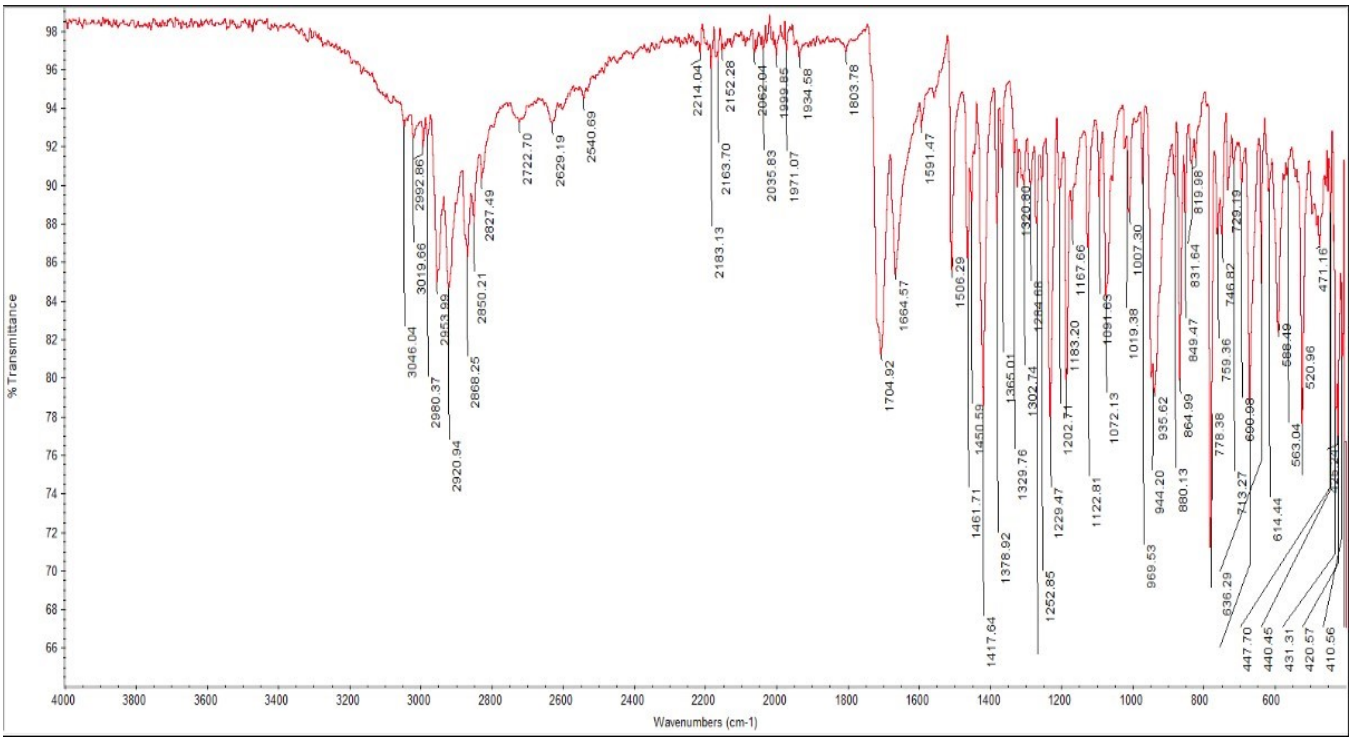


Figure S2. GC-MS of 3-chorobenzo[b]thiophene-2-carbaldehyde **2**



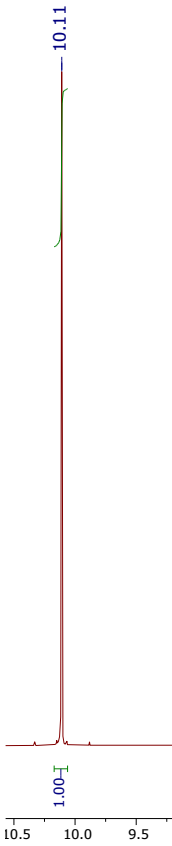


Figure S3. IR of 3-chorobenzo[b]thiophene-2-carbaldehyde **2** (top), and ^{1}H-NMR of benzo[b]thiophene-2-carbaldehyde **3**.

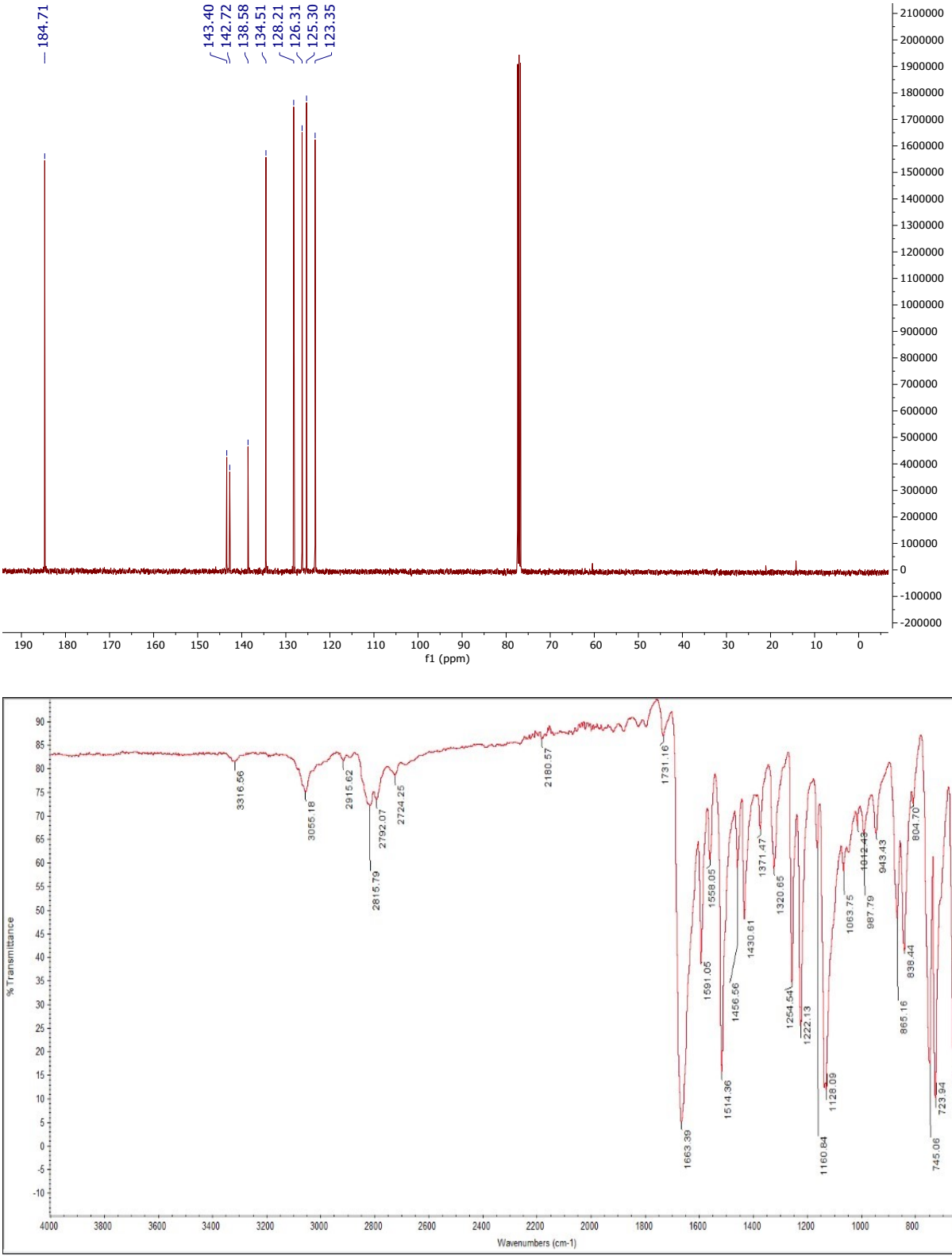


Figure S4. ^{13}C-NMR and IR of benzo[b]thiophene-2-carbaldehyde **3**.

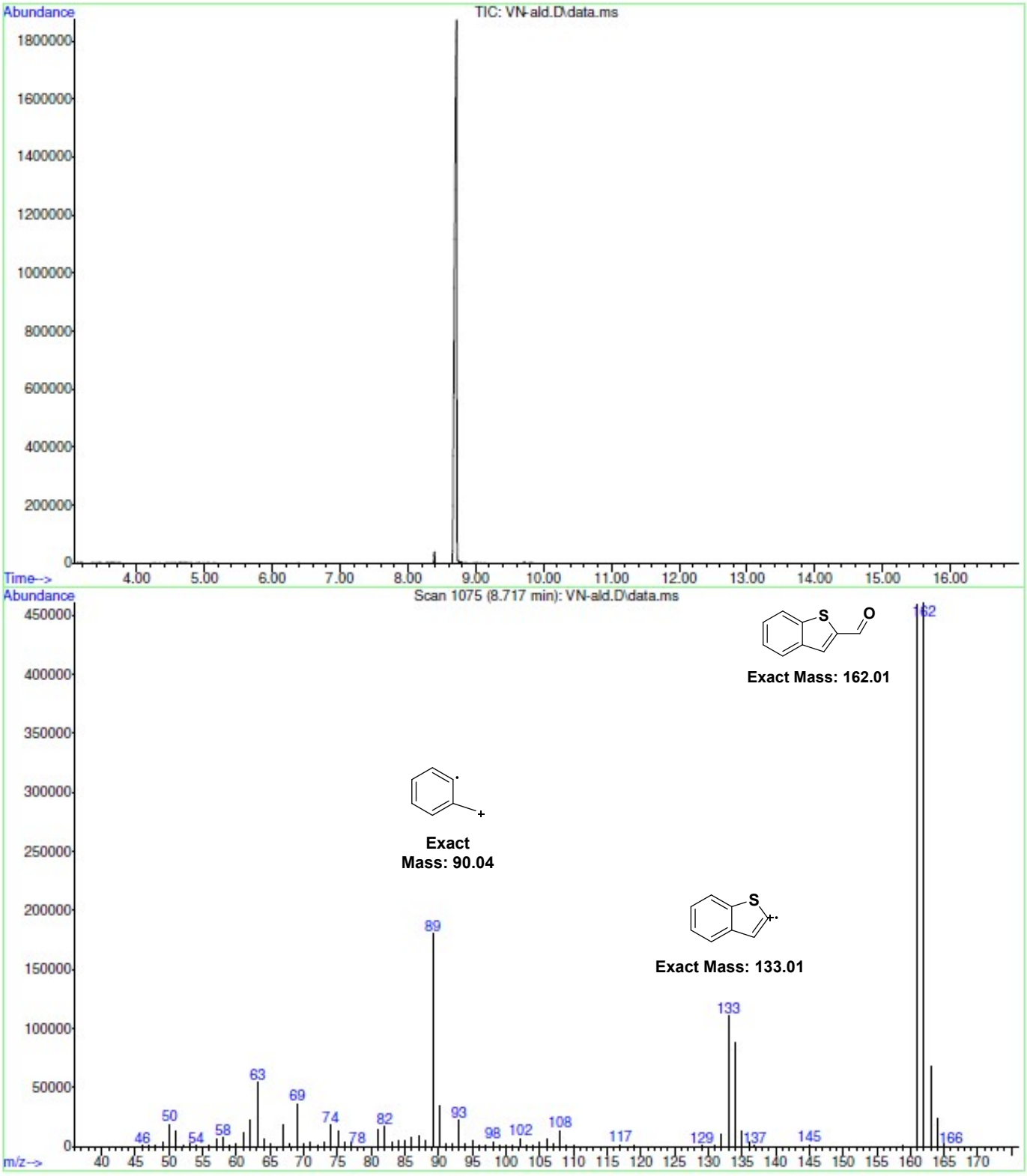


Figure S5. GC-MS of benzo[b]thiophene-2-carbaldehyde **3**.

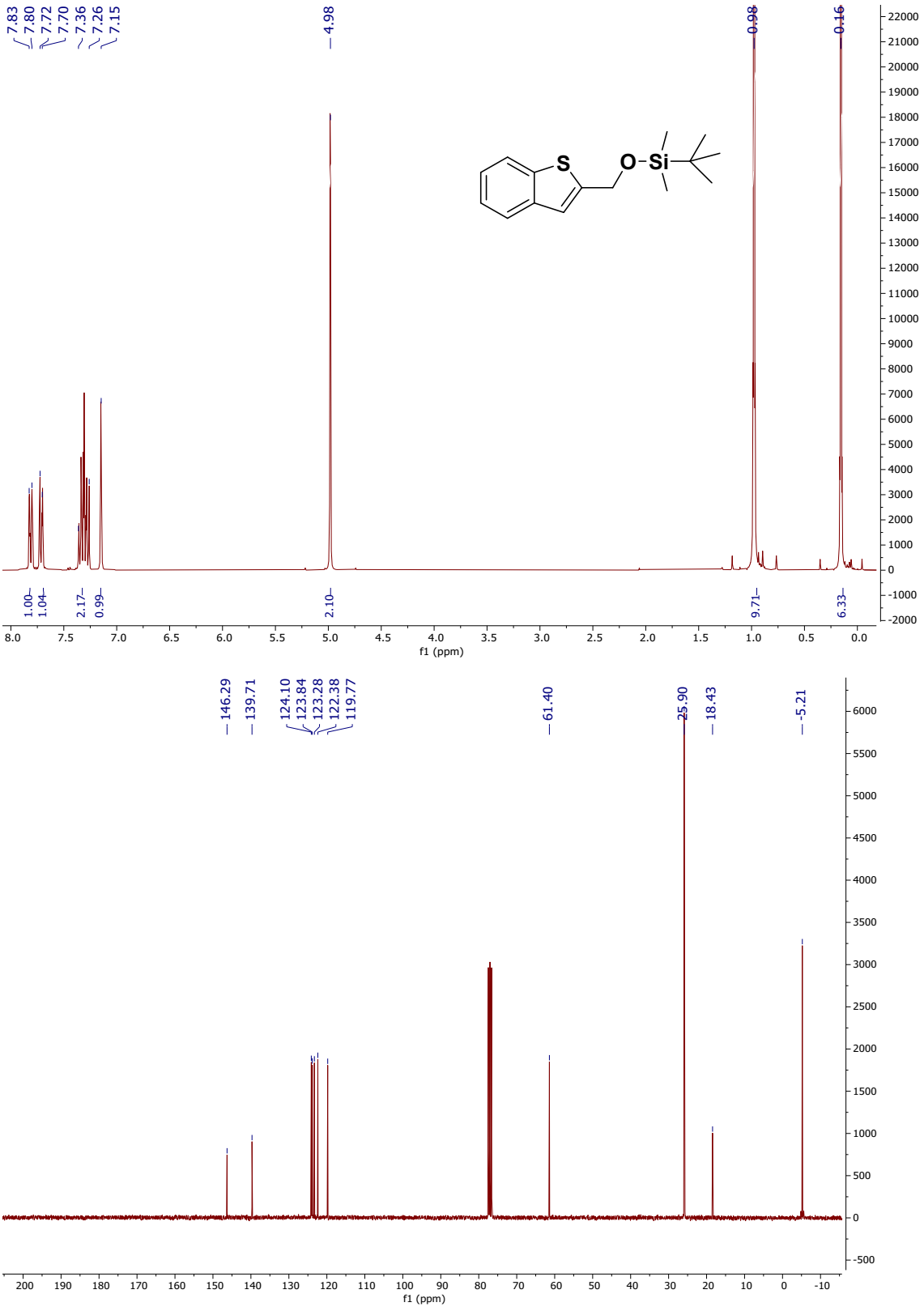


Figure S6. ^{1}H and ^{13}C-NMR of (Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **5**.

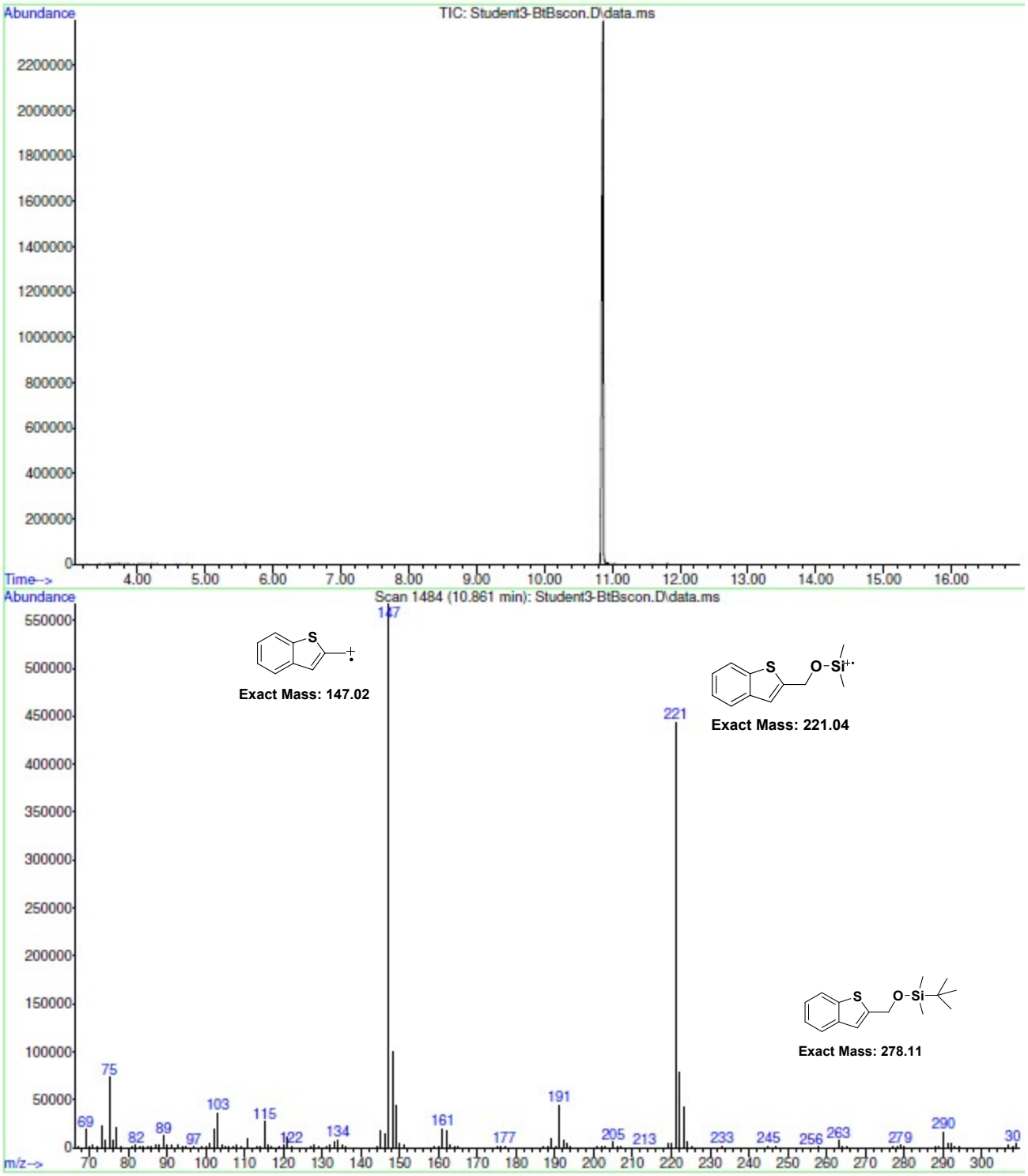


Figure S7. GC-MS of (Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **5**.

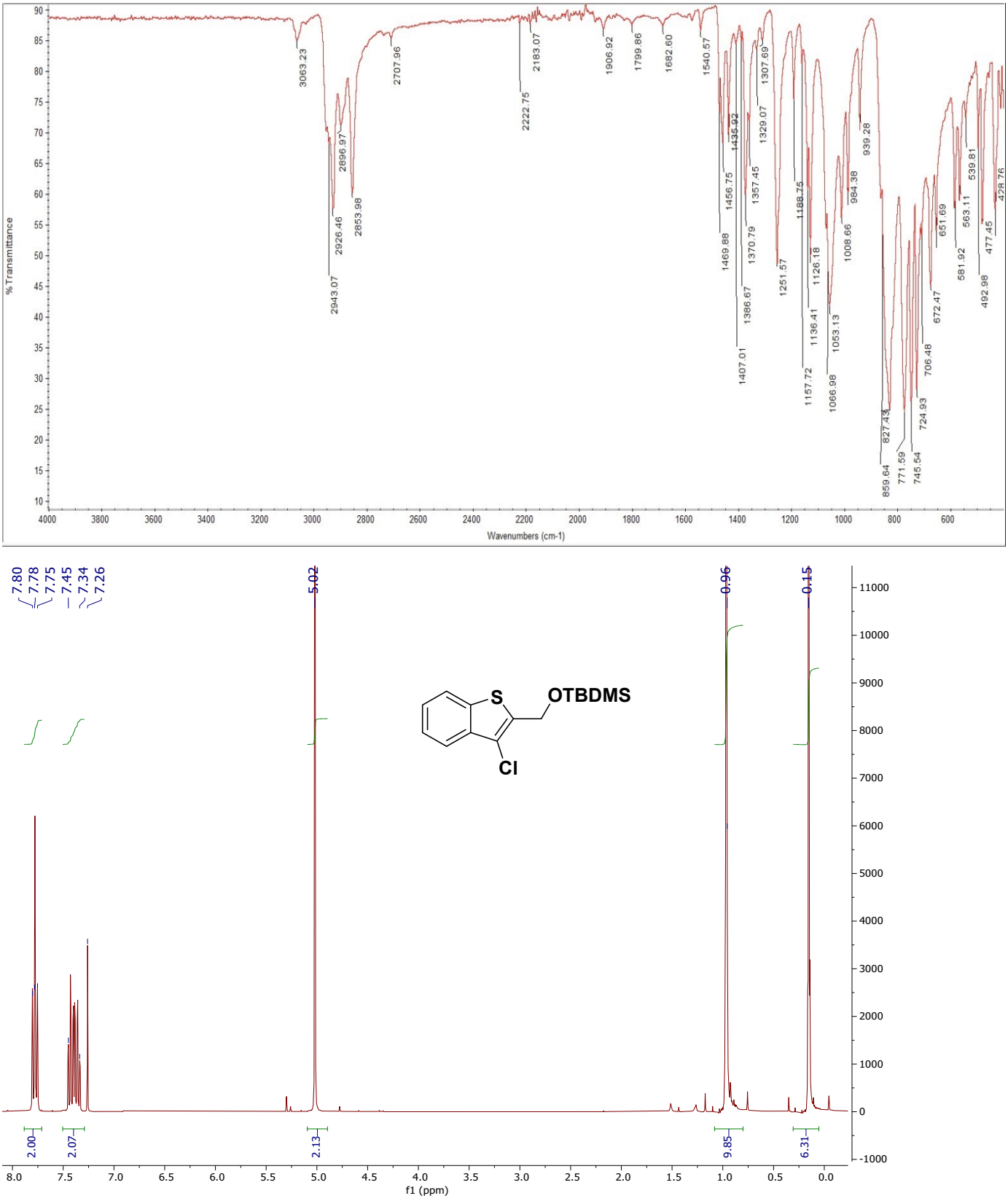


Figure S8. IR of (Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **5** (top) and ^{1}H-NMR of 3-chloro(Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **6** (bottom).

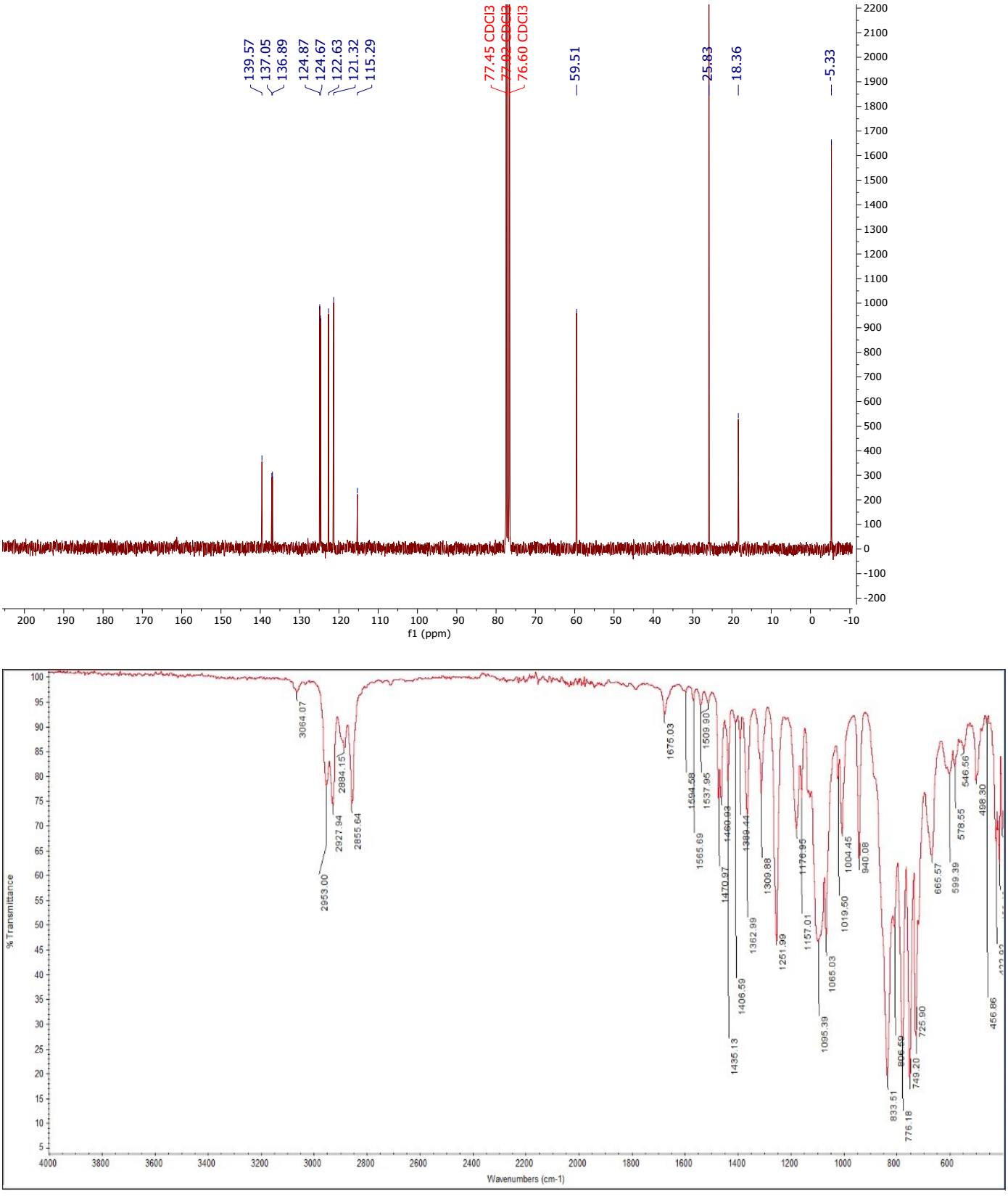


Figure S9. ^{13}C-NMR and IR of 3-chloro(Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **6**.

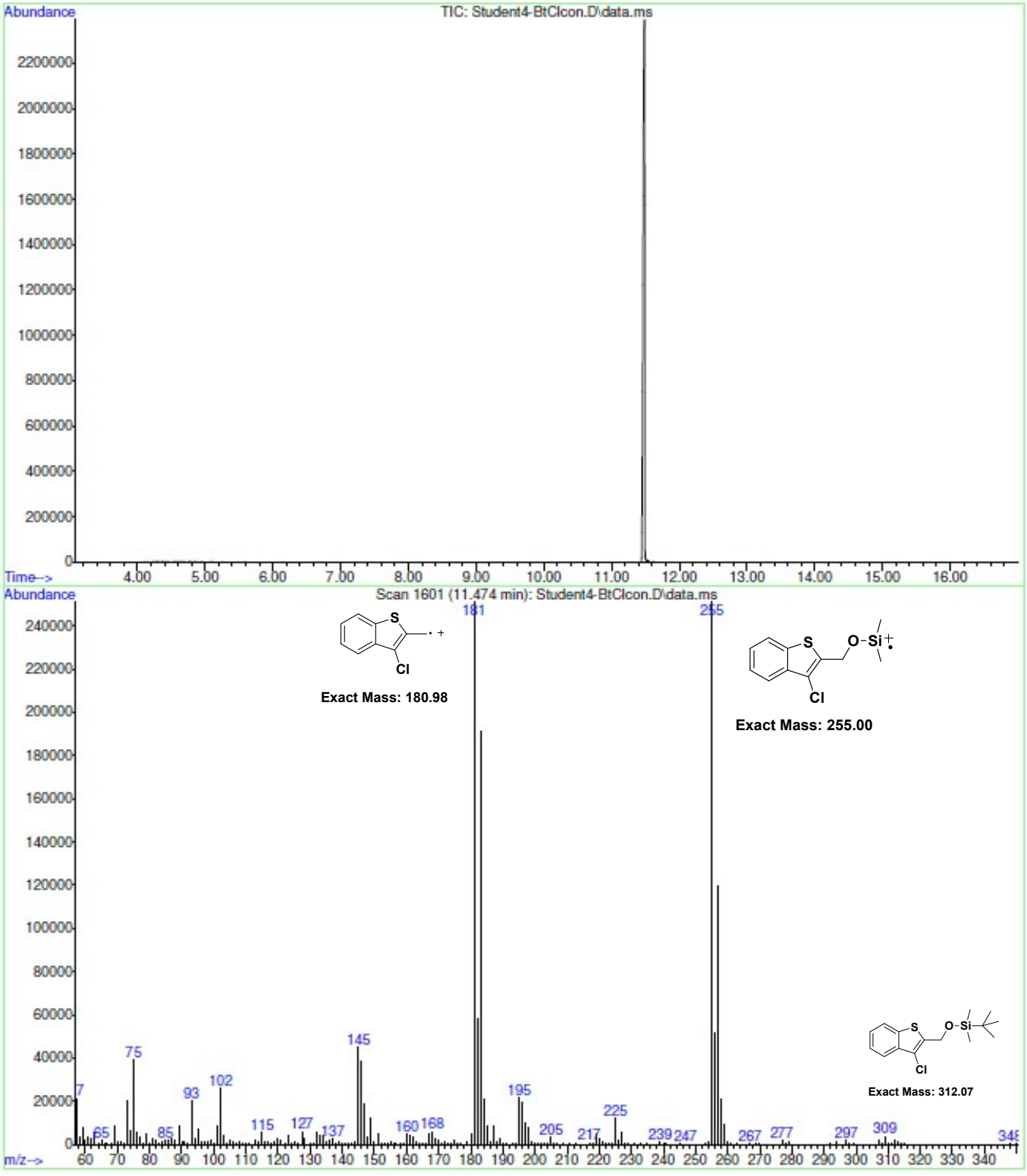


Figure S10. GC-MS of 3-chloro(Benzo[*b*]thiophen-2-ylmethoxy)(*tert*-butyl)dimethylsilane **6**.

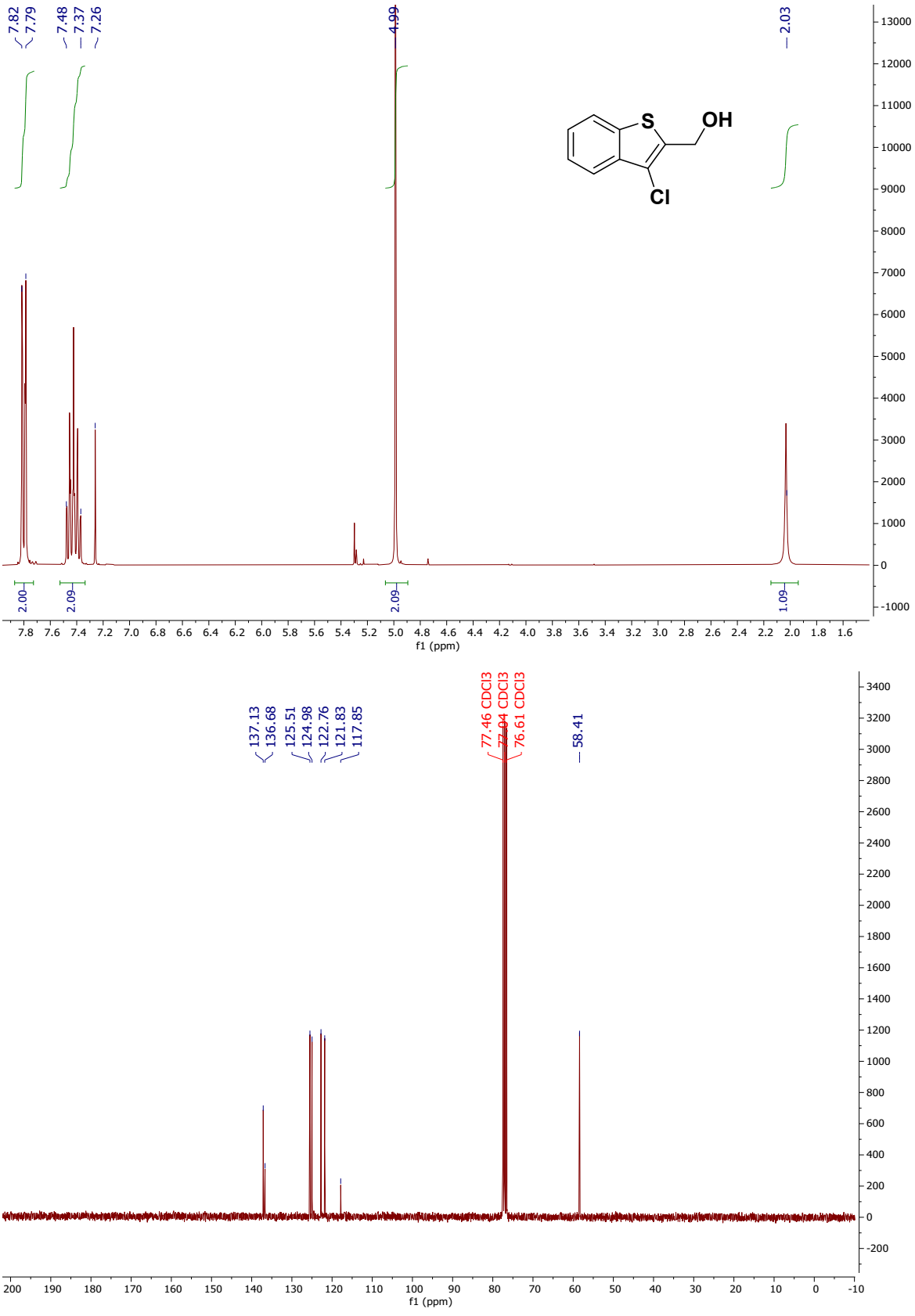


Figure S11. ^{1}H and ^{13}C-NMR of 3-chlorobenzo[*b*]thiophen-2-methanol **4**.

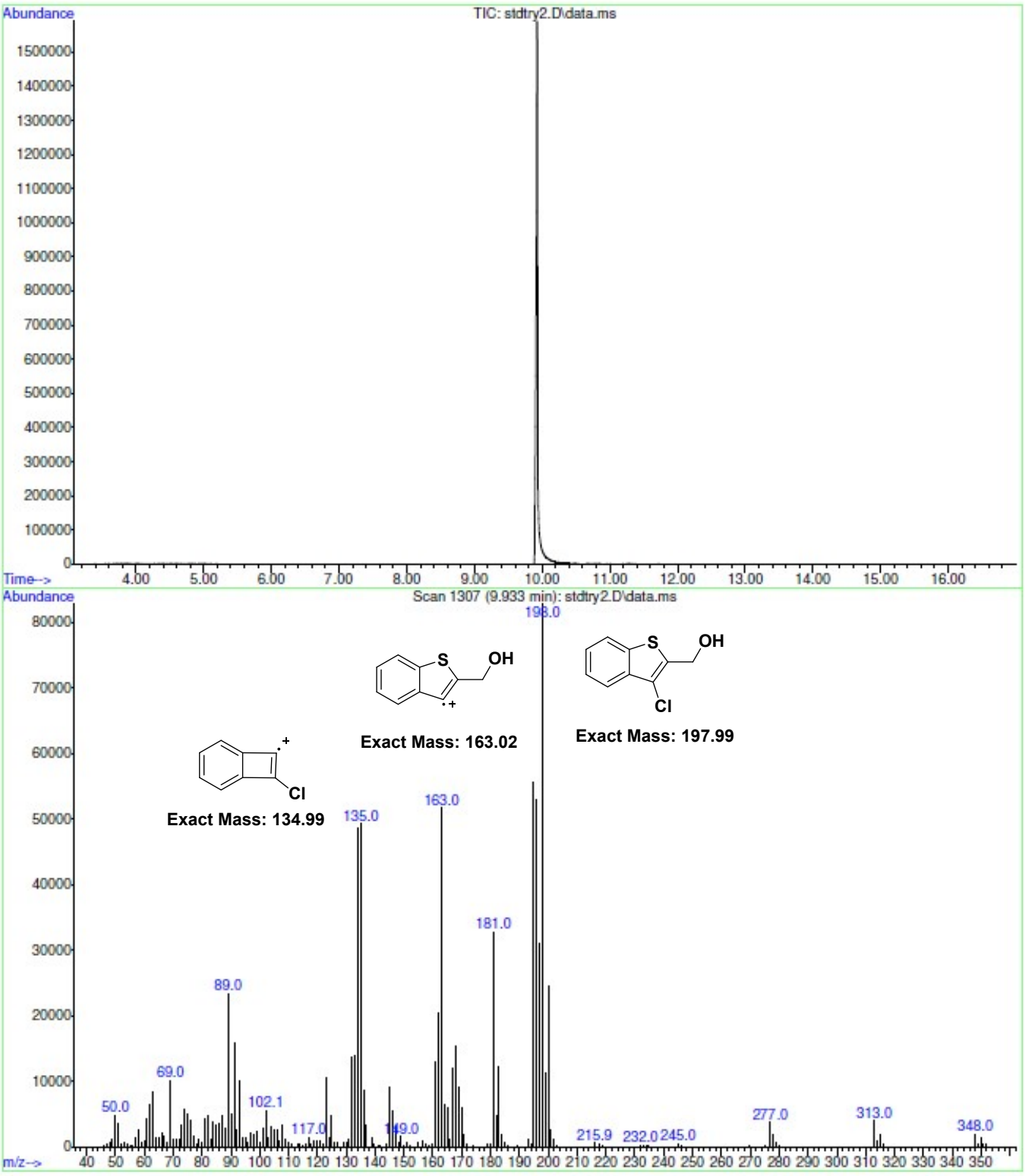


Figure S12. GC-MS of 3-chlorobenzo[*b*]thiophen-2-methanol **4**.

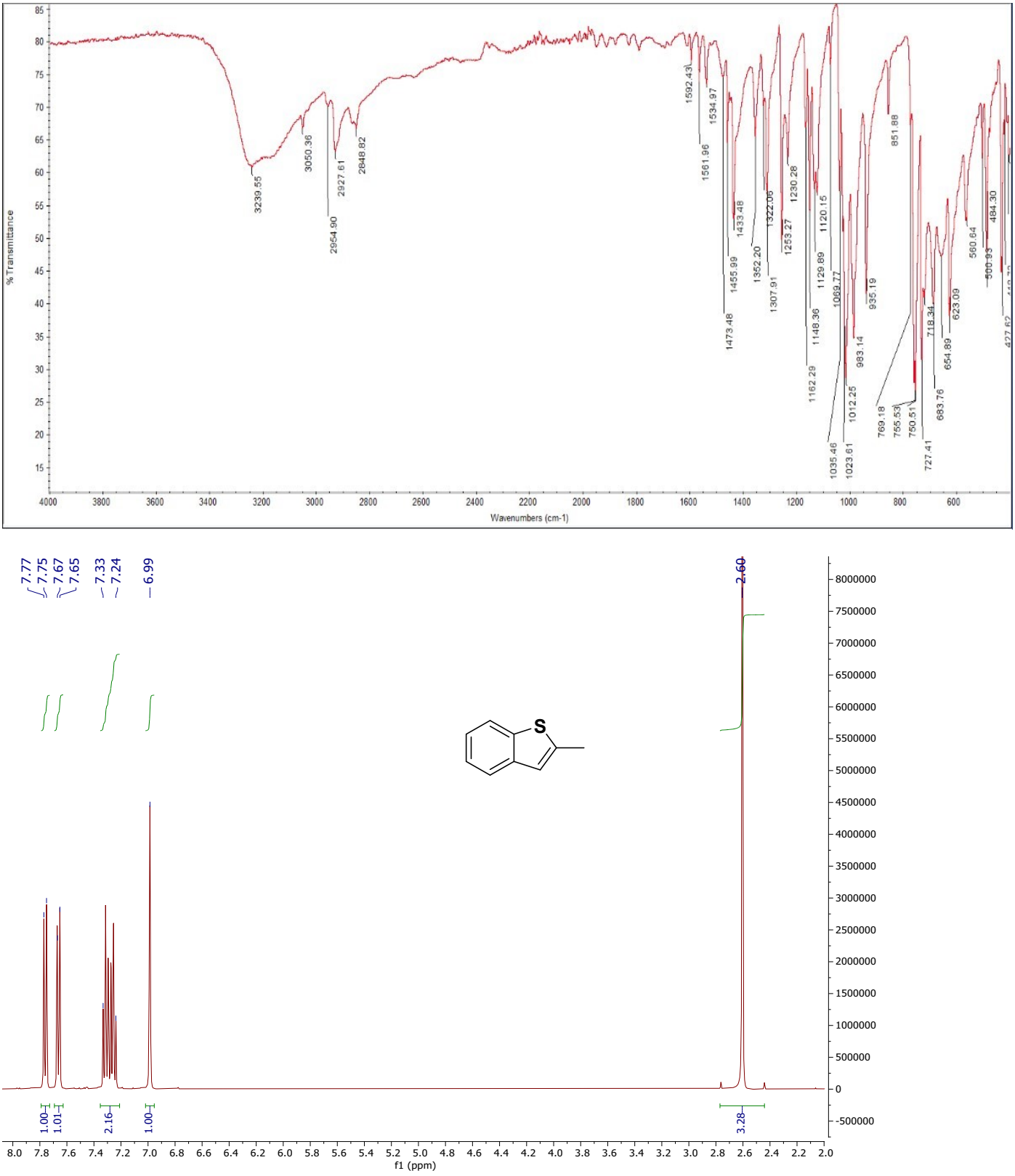


Figure S13. IR of 3-chlorobenzo[*b*]thiophen-2-methanol **4** (top) and ^{1}H-NMR of 2-methyl[*b*]benzothiophene **7**.

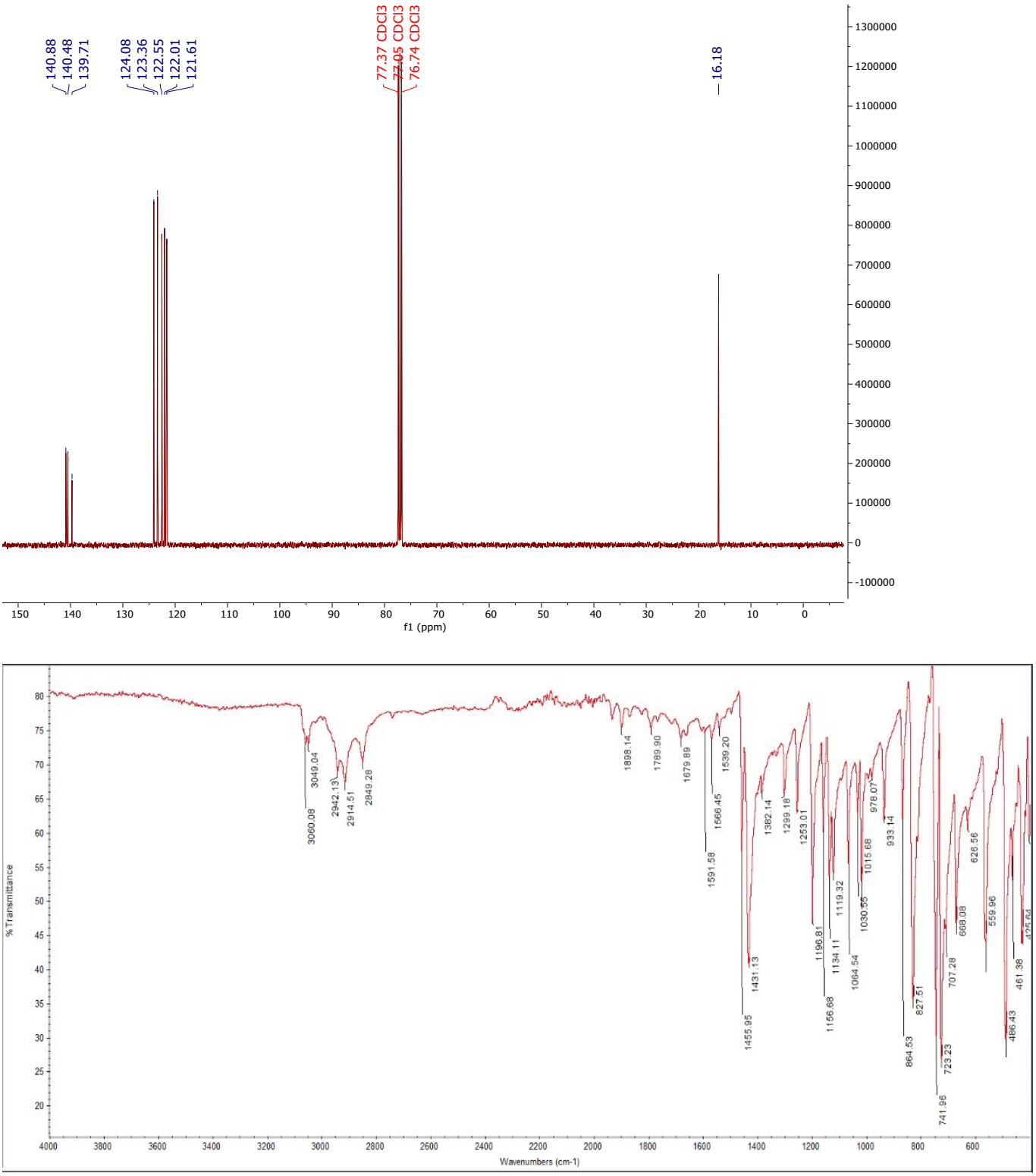


Figure S14. ^{13}C-NMR and IR of 2-methyl[*b*]benzothiophene **7**.

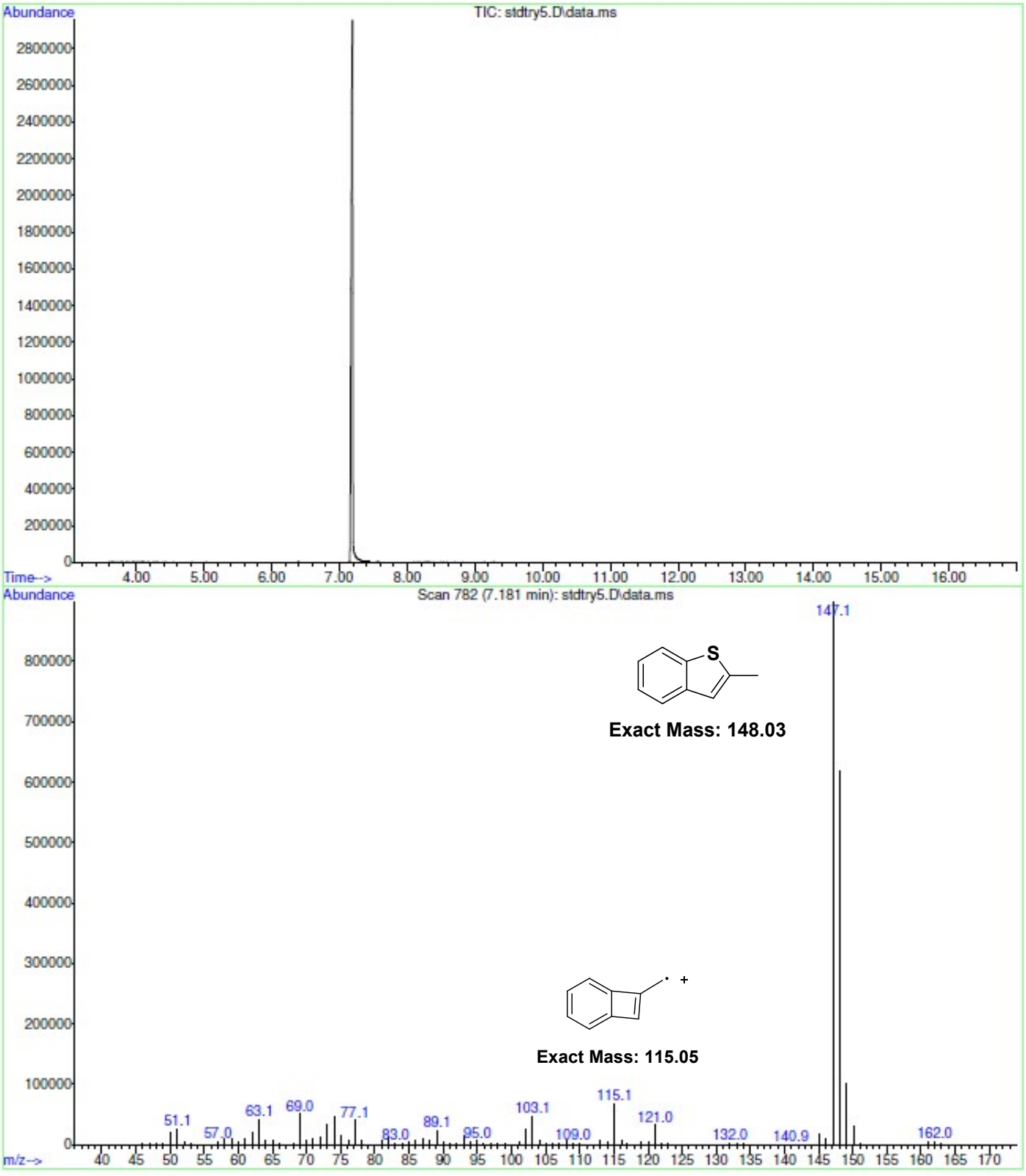


Figure S15. GC-MS and IR of 2-methyl[*b*]benzothiophene **7**.

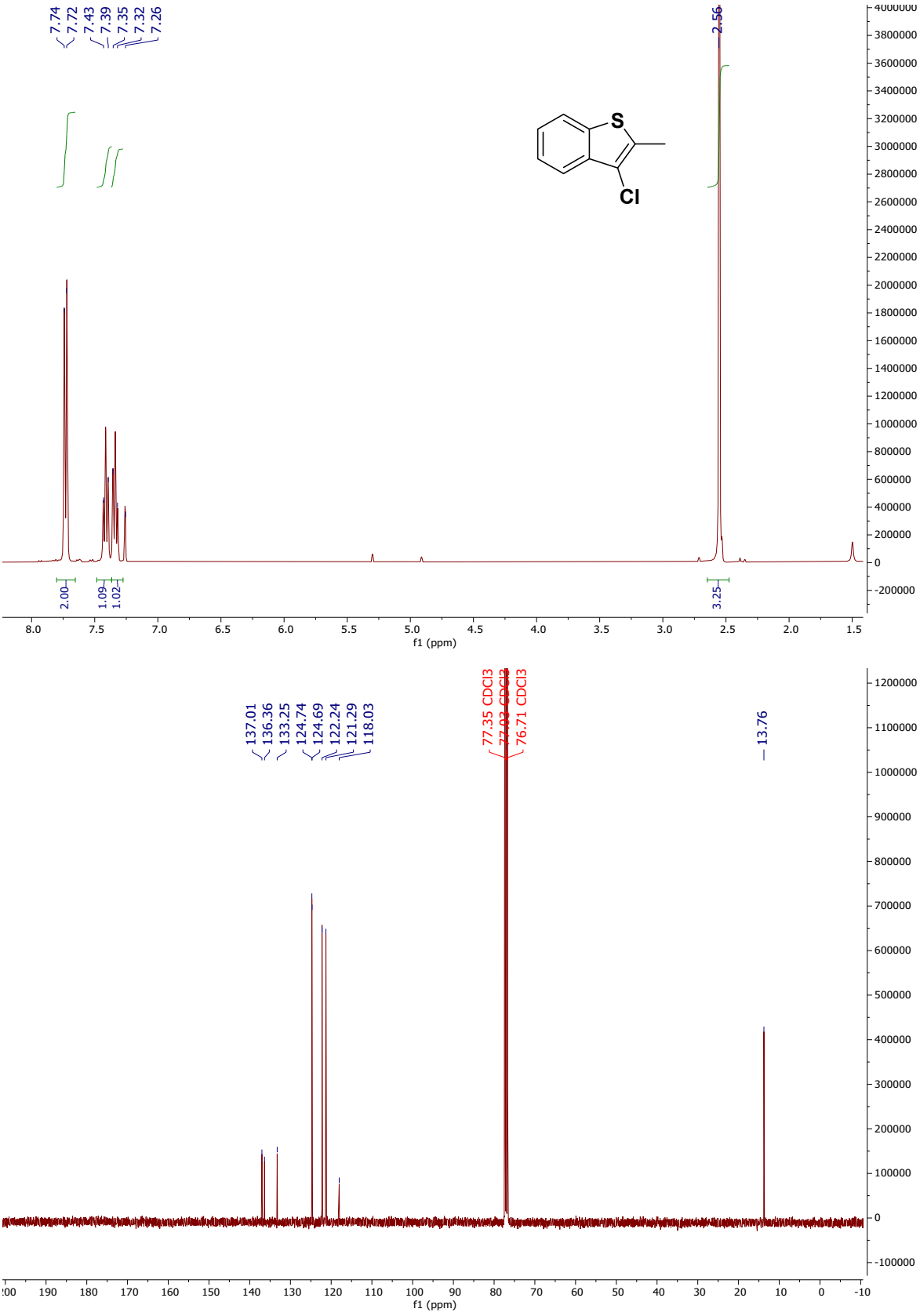


Figure S16. ^{1}H and ^{13}C-NMR of 3-chloro-2-methylbenzo[*b*]thiophene **8**.

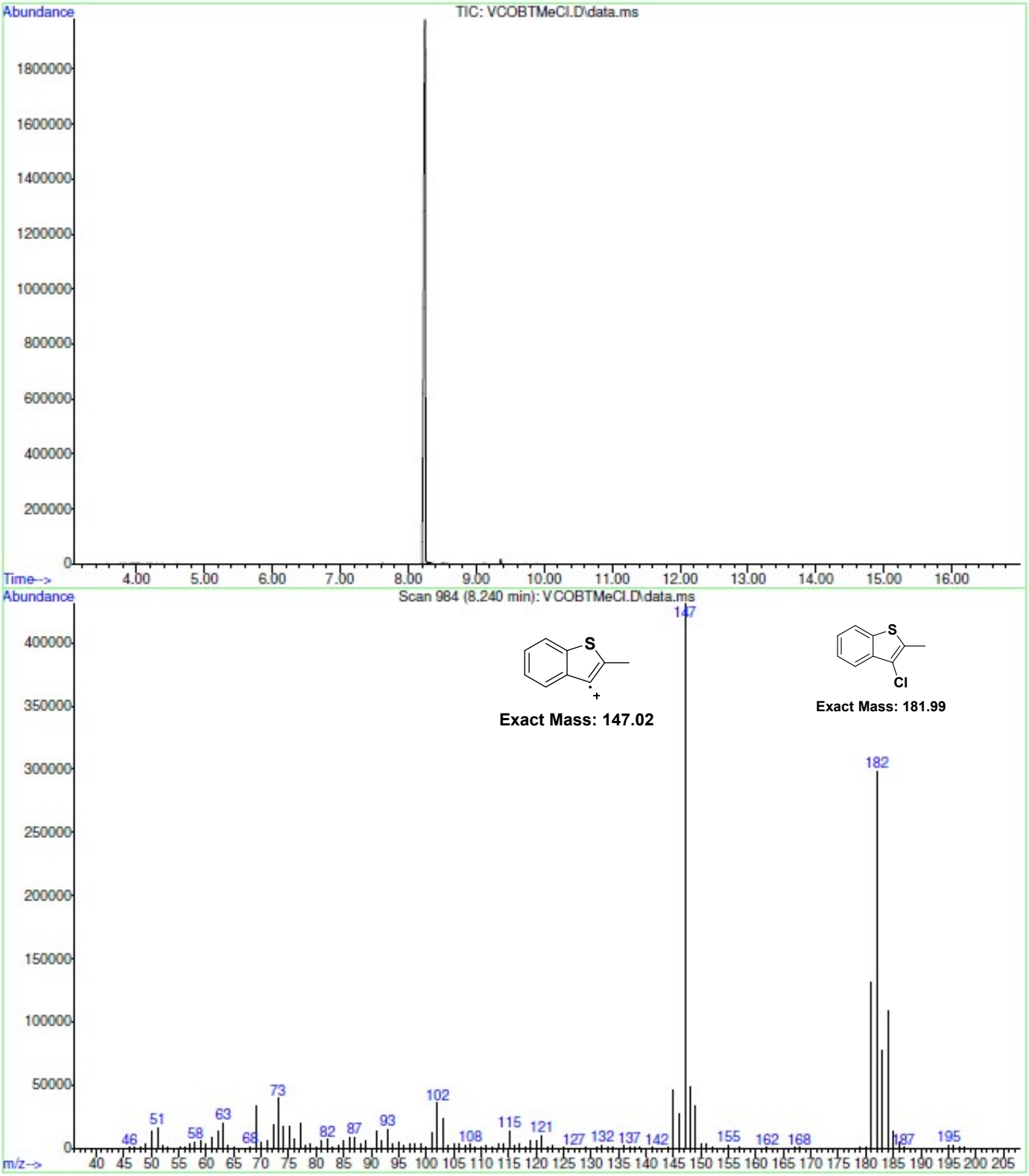
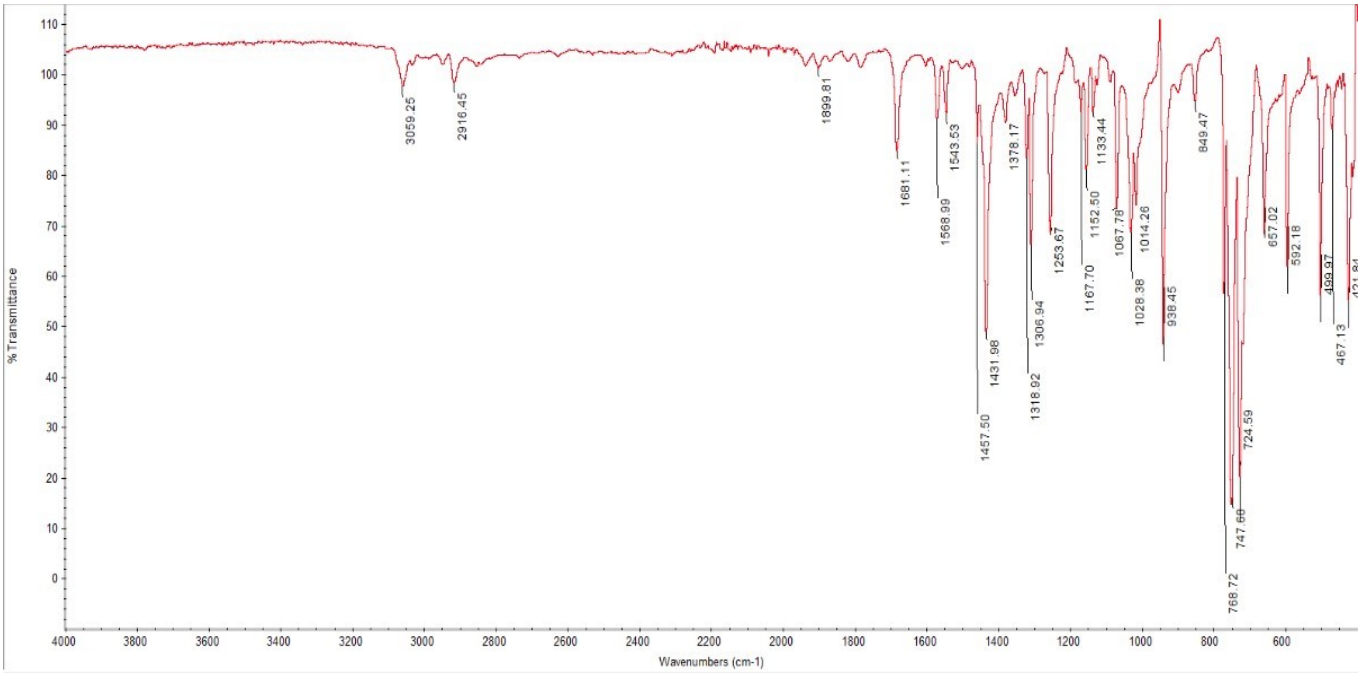


Figure S17. GC-MS of 3-chloro-2-methylbenzo[*b*]thiophene **8**.



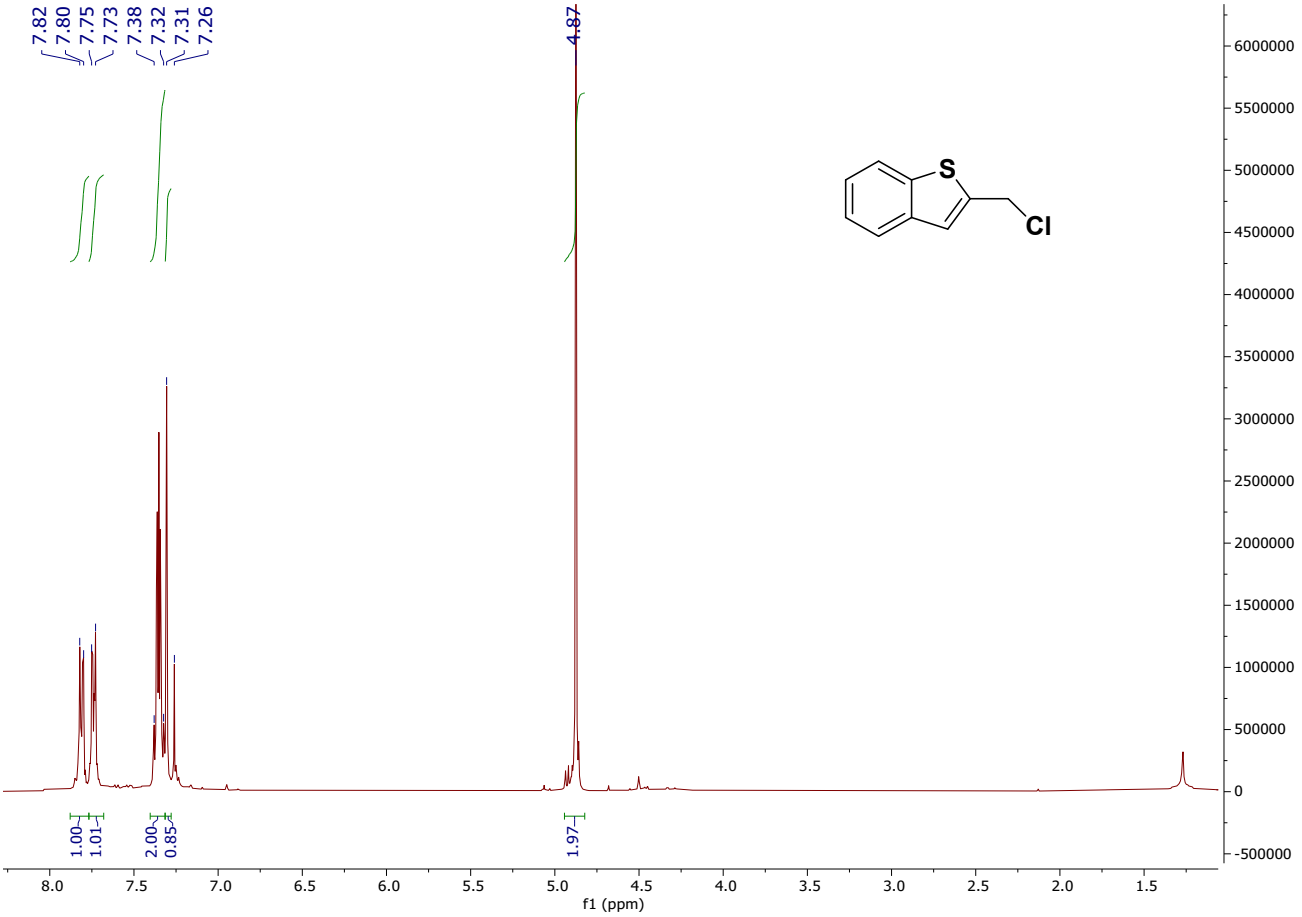
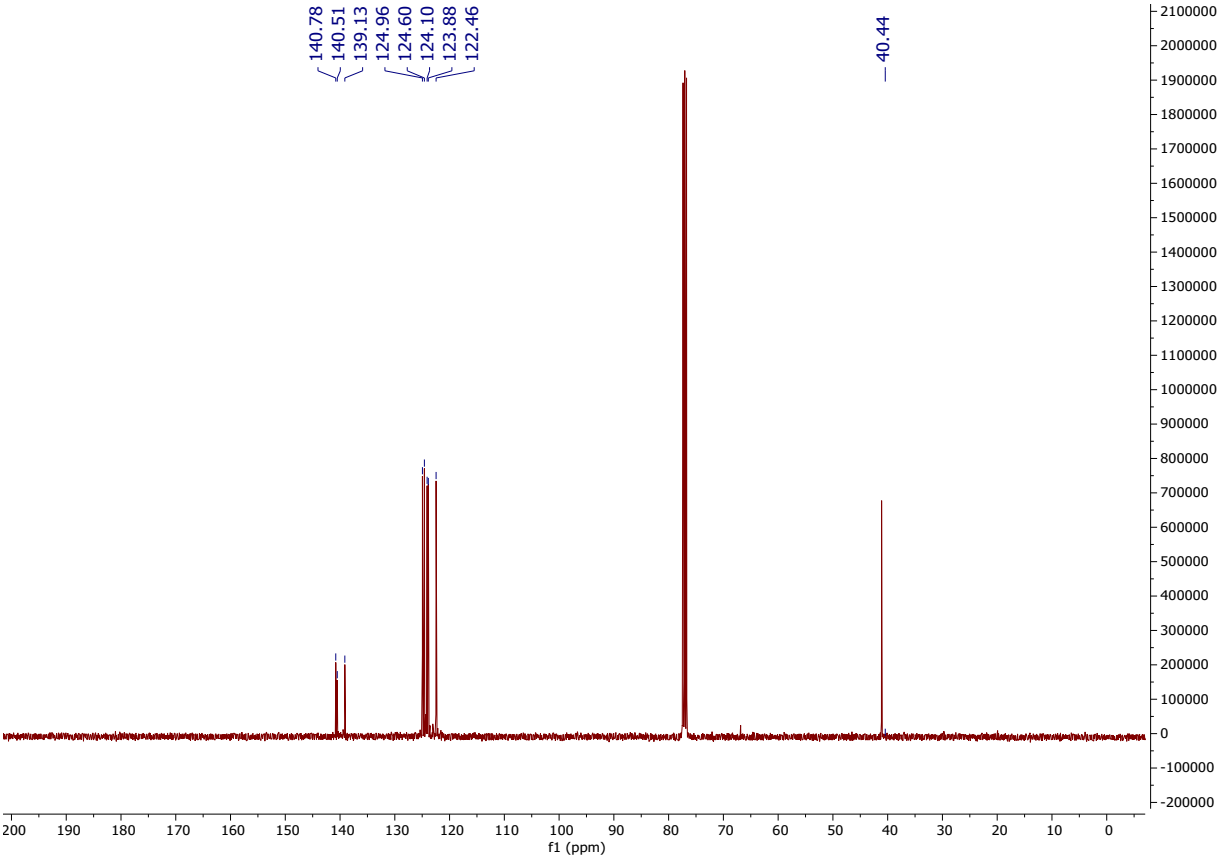


Figure S18. IR of 3-chloro-2-methylbenzo[*b*]thiophene **8** (top), and ^{1}H NMR of 2-chloromethylbenzo[*b*]thiophene **9** (bottom).



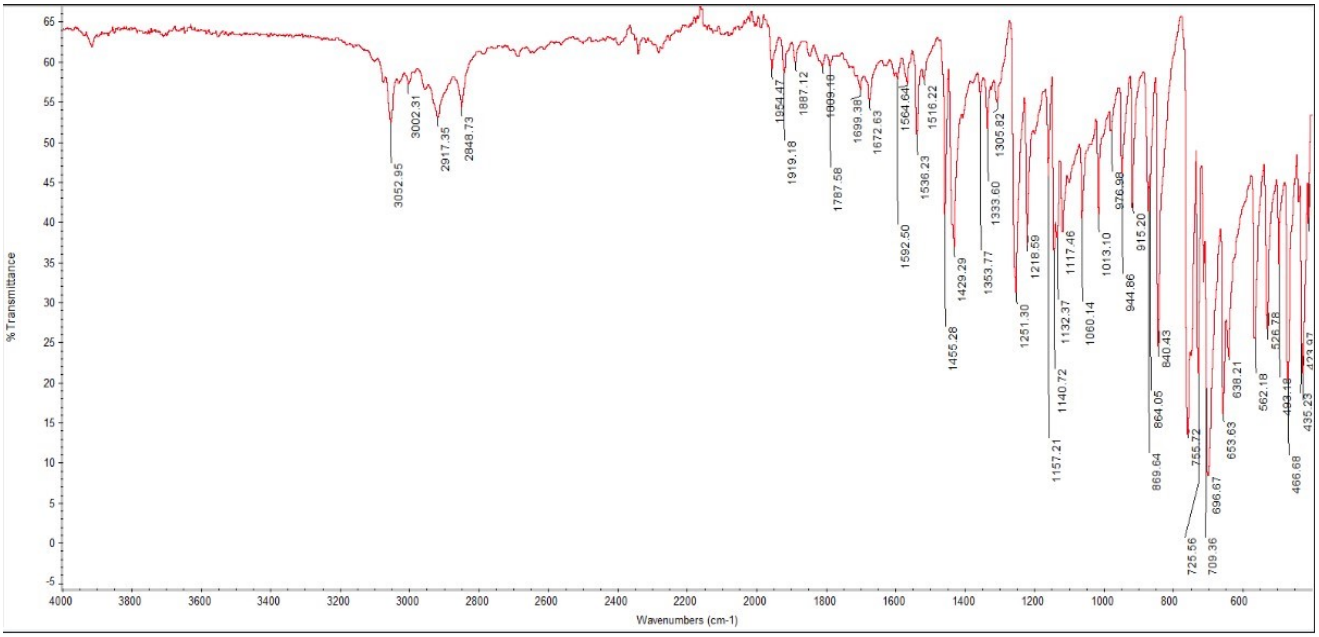


Figure S19. ^{13}C NMR and IR of 2-chloromethylbenzo[*b*]thiophene **9**.

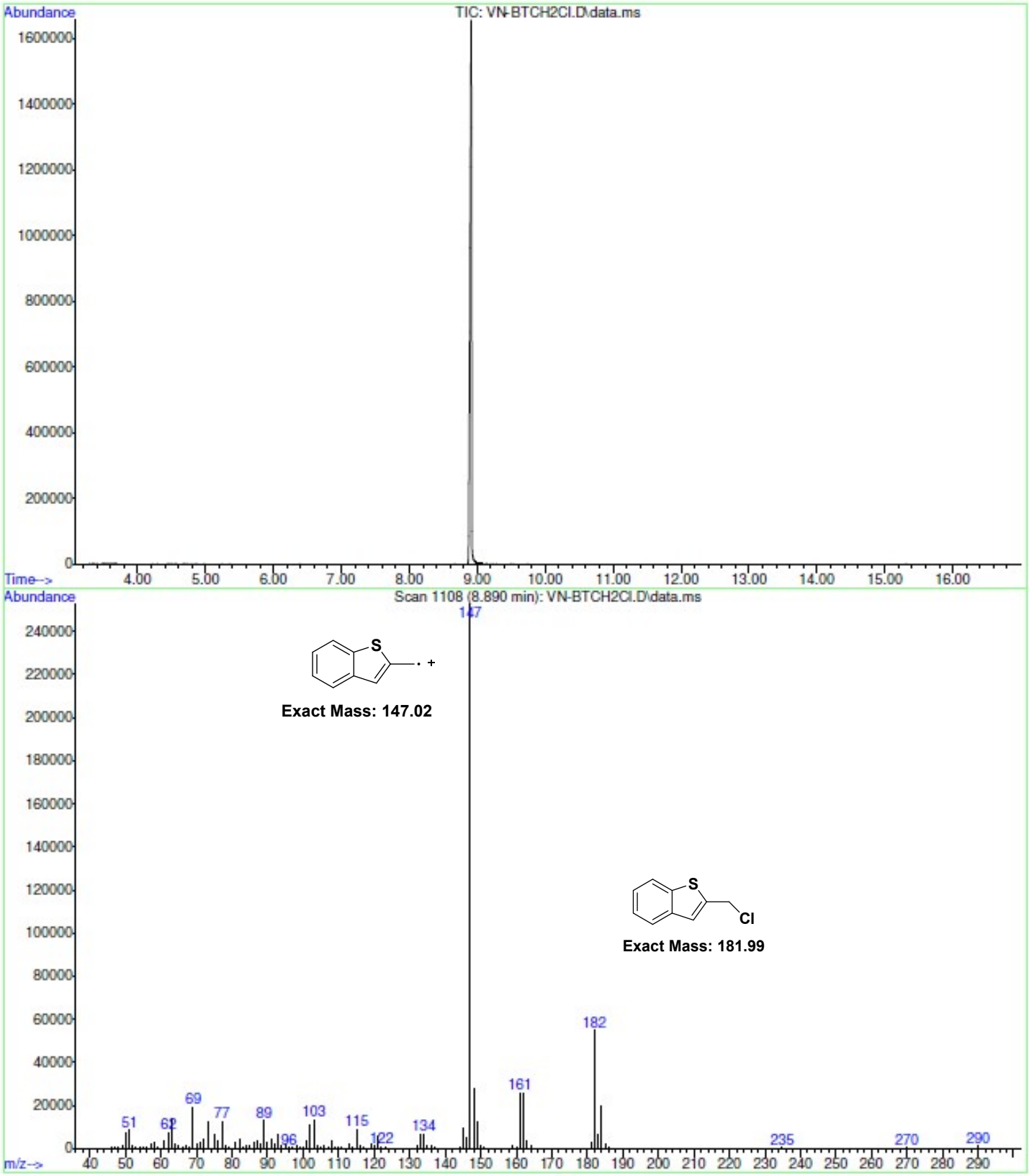


Figure S20. GC-MS of 2-chloromethylbenzo[*b*]thiophene **9**.

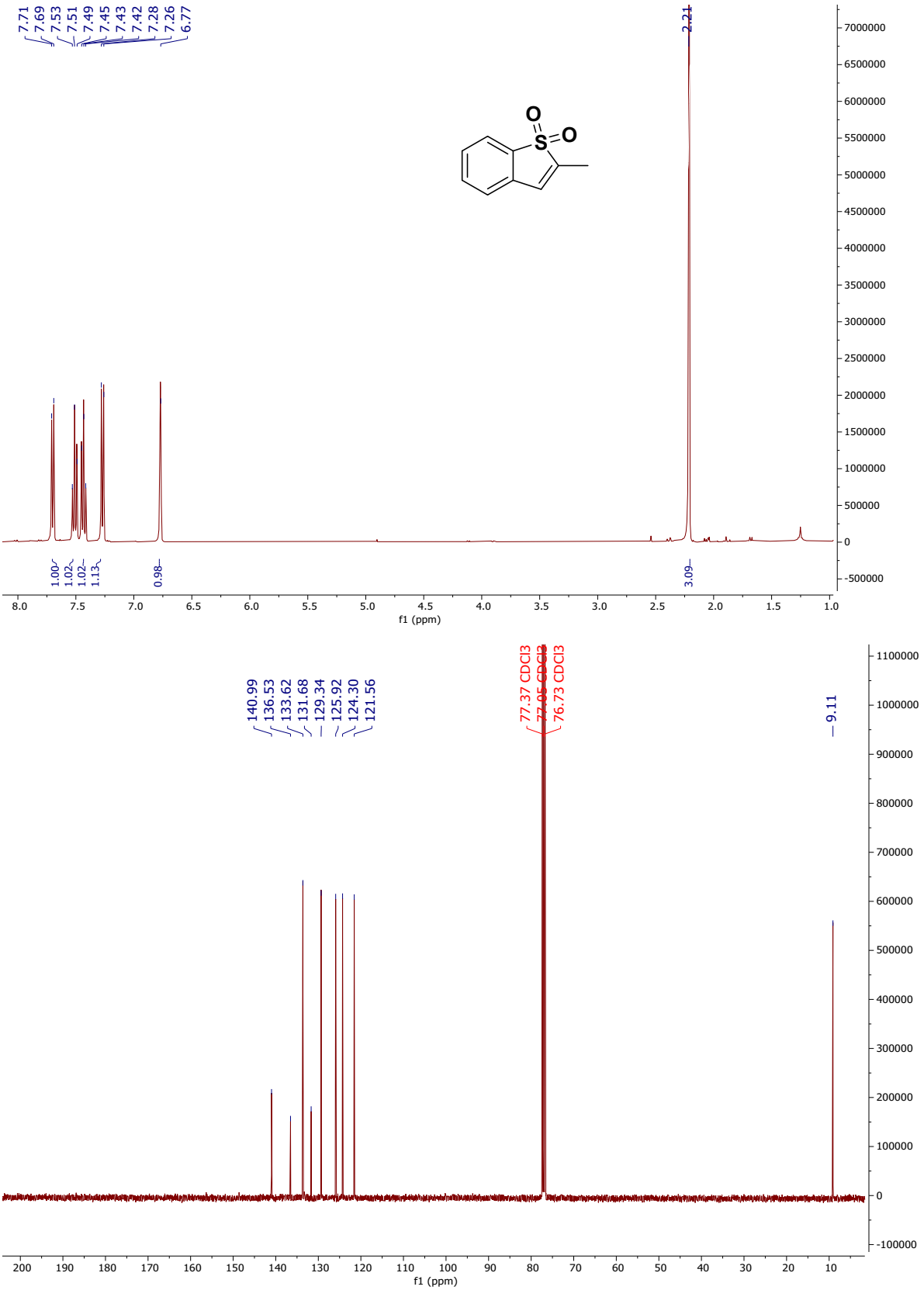


Figure S21. ^{1}H and ^{13}C-NMR, of 2-methylbenzo[*b*]thiophene 1,1-dioxide **12**.

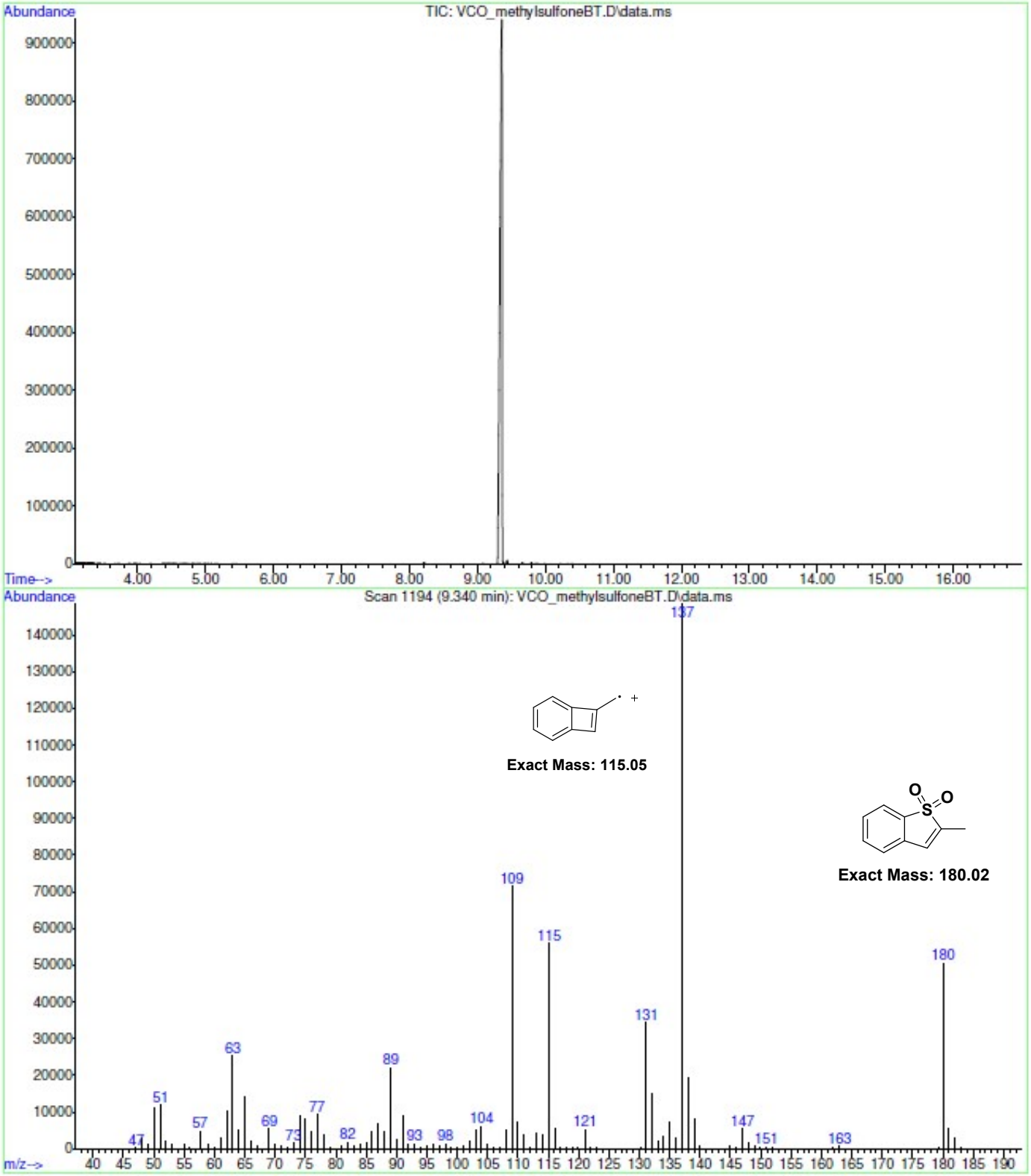


Figure S22. GC-MS of 2-methylbenzo[*b*]thiophene 1,1-dioxide **12**.

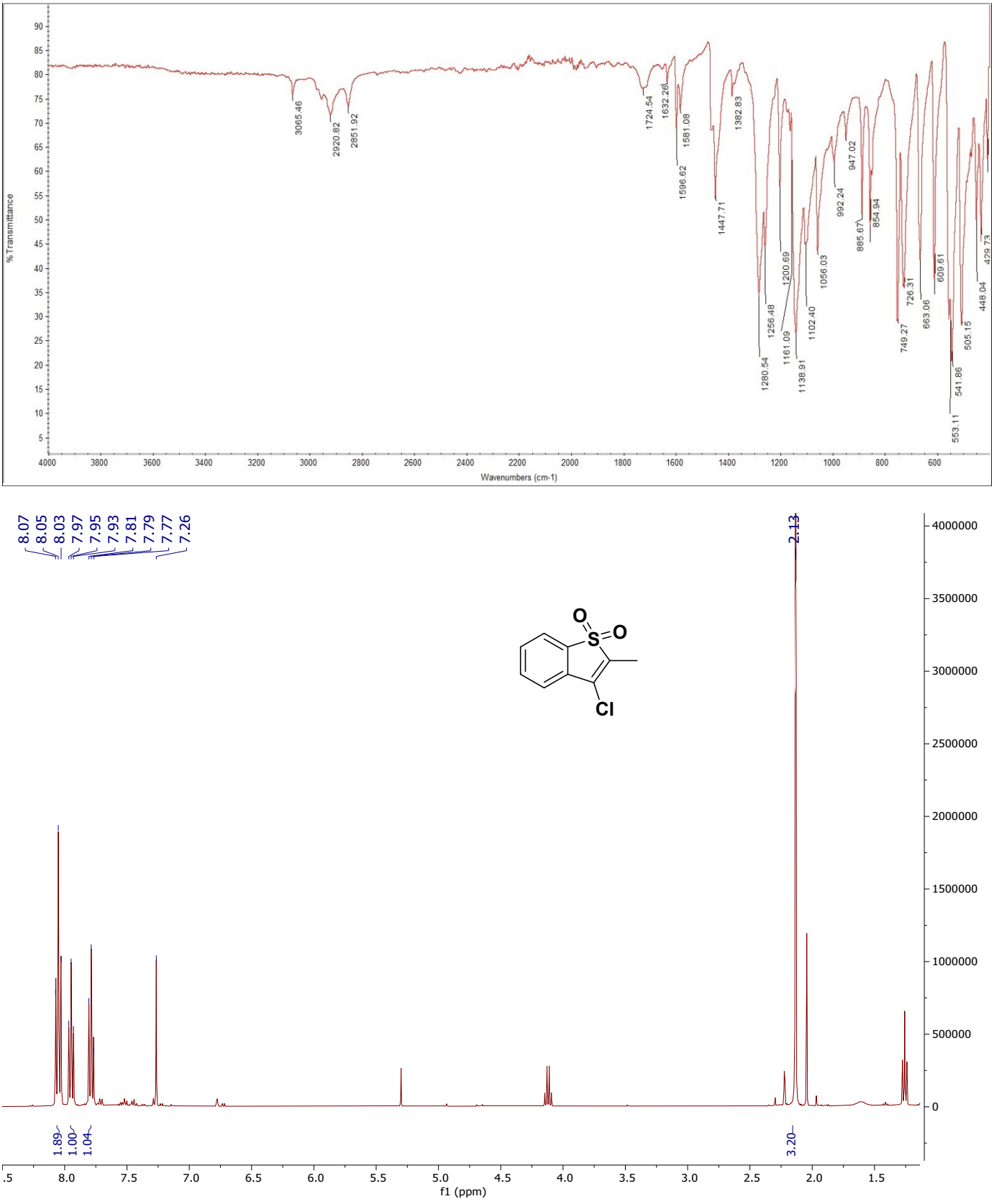


Figure S23. IR of 2-methylbenzo[*b*]thiophene 1,1-dioxide **10** (top) and ^{1}H-NMR of 3-chloro-2-methylbenzo[*b*]thiophene 1,1-dioxide **11**.

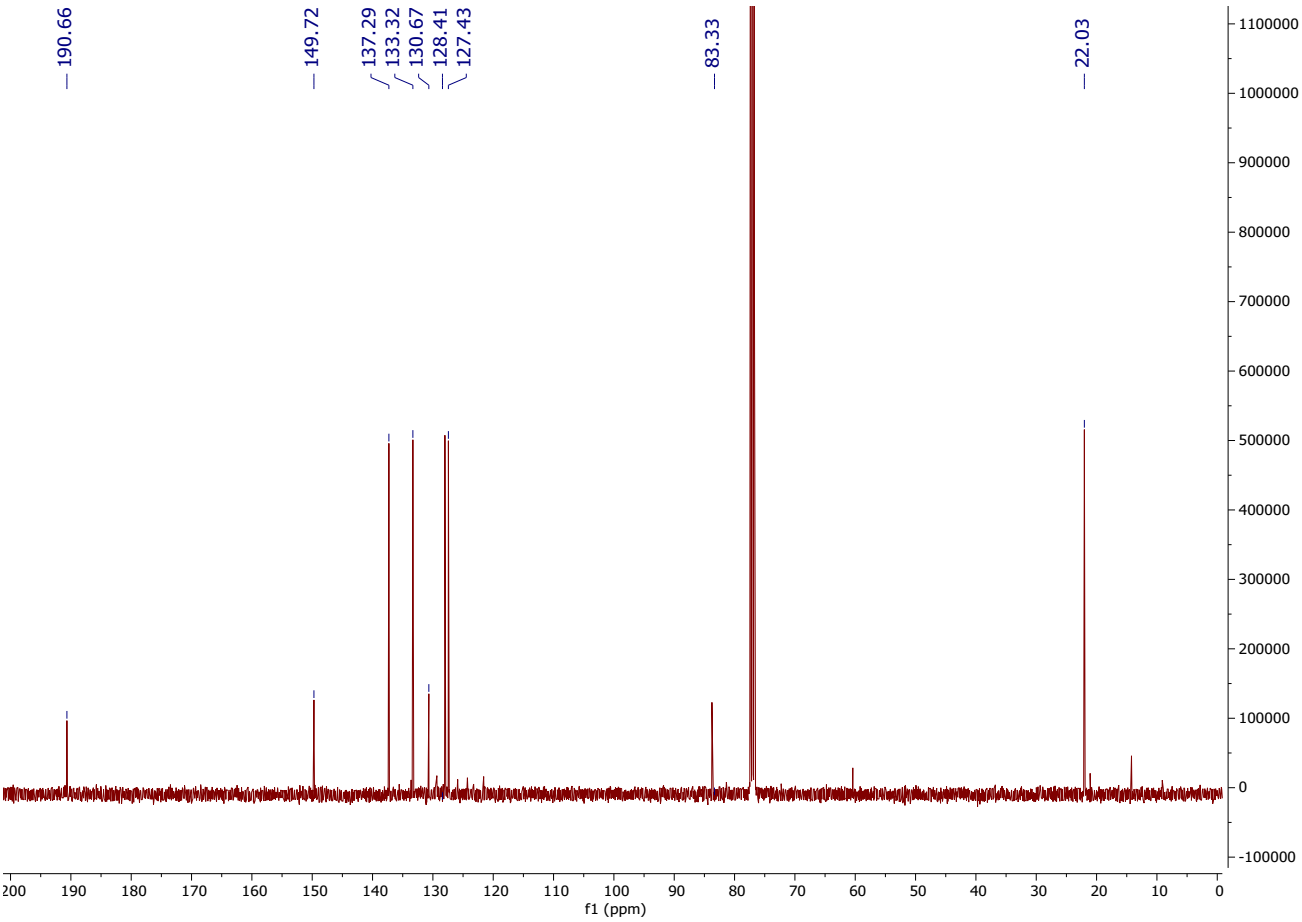


Figure S24. ^{13}C NMR and IR of 3-chloro-2-methylbenzo[*b*]thiophene 1,1-dioxide **11**.

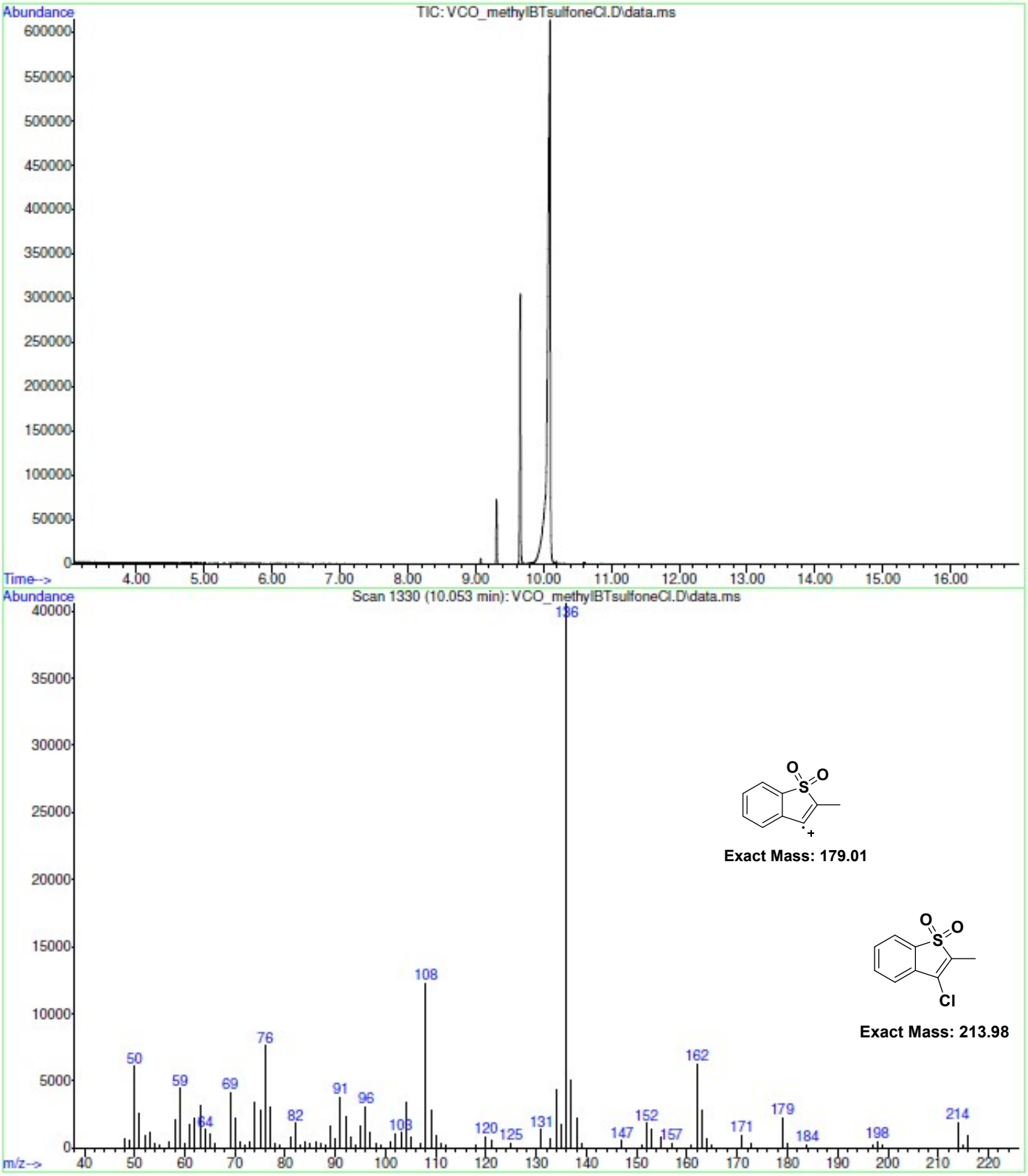


Figure S25. GC-MS of 3-chloro-2-methylbenzo[*b*]thiophene 1,1-dioxide **11**.

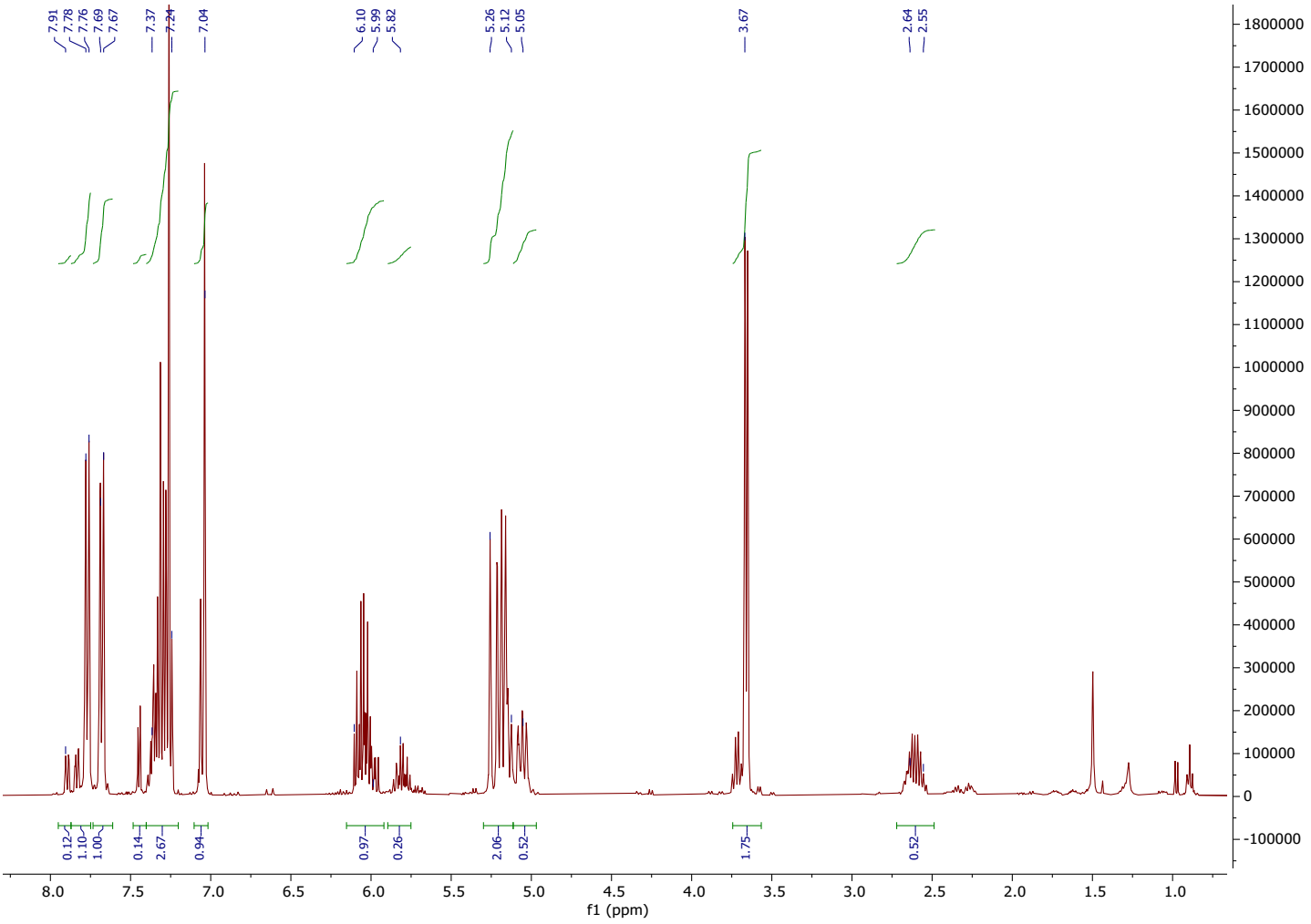


Figure S26. ^{1}H NMR of 2-allylbenzo[*b*]thiophene **13** w/ impurities.

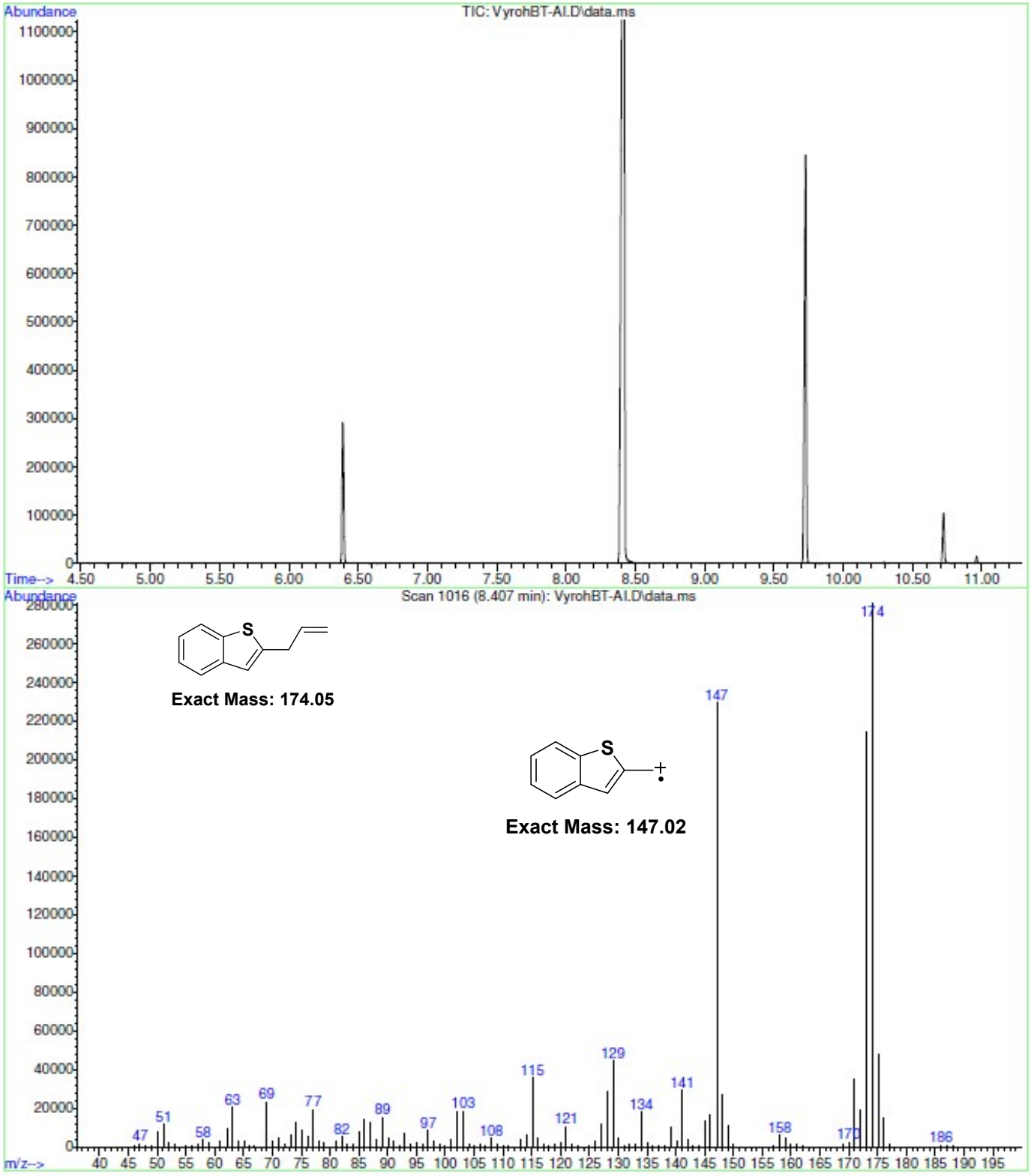


Figure S27. GC-MS of 2-allylbenzo[*b*]thiophene **13** w/ impurities.

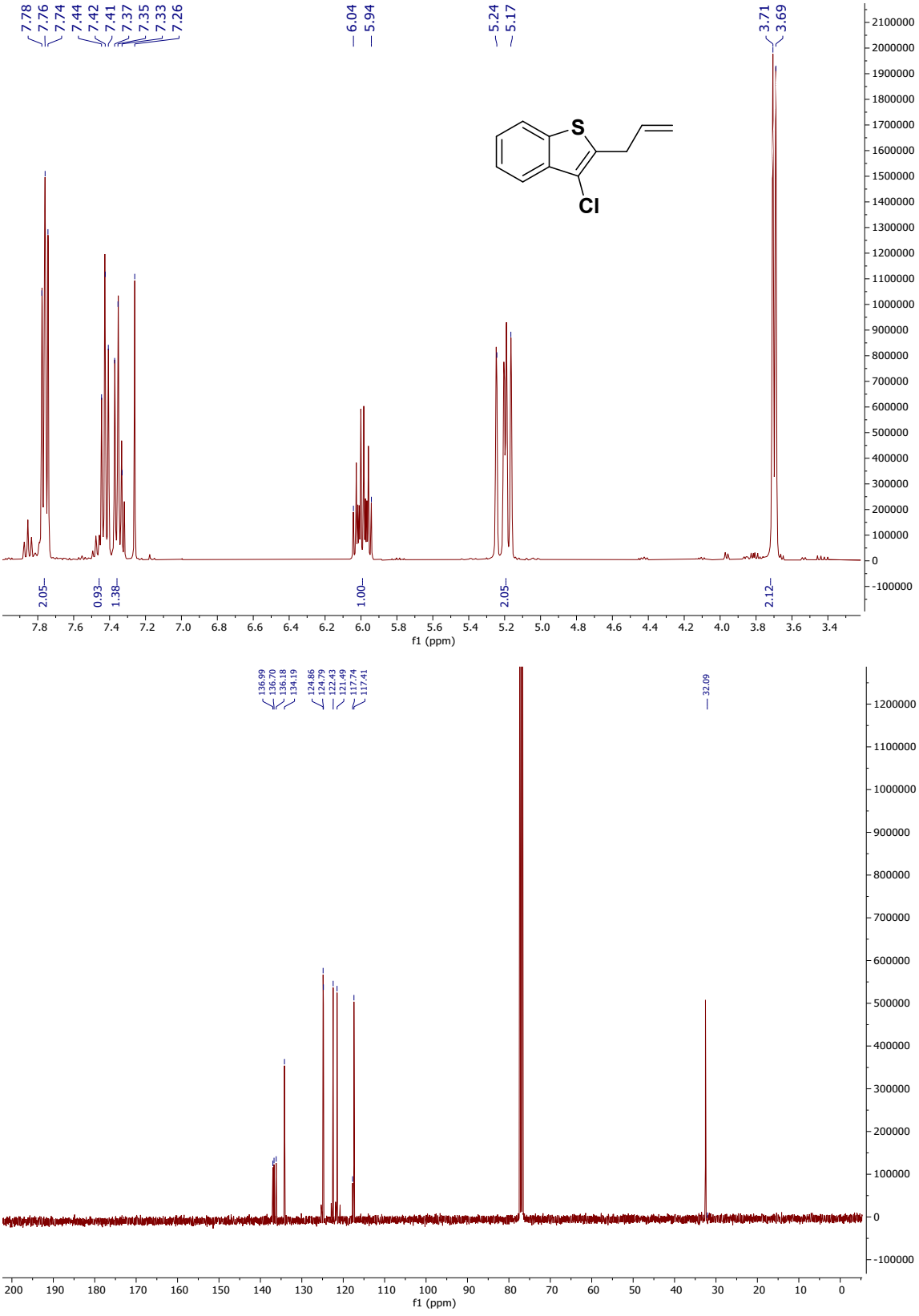


Figure S28. ^{1}H and ^{13}C NMR of 2-allyl-3-chlorobenzo[*b*]thiophene **14**.

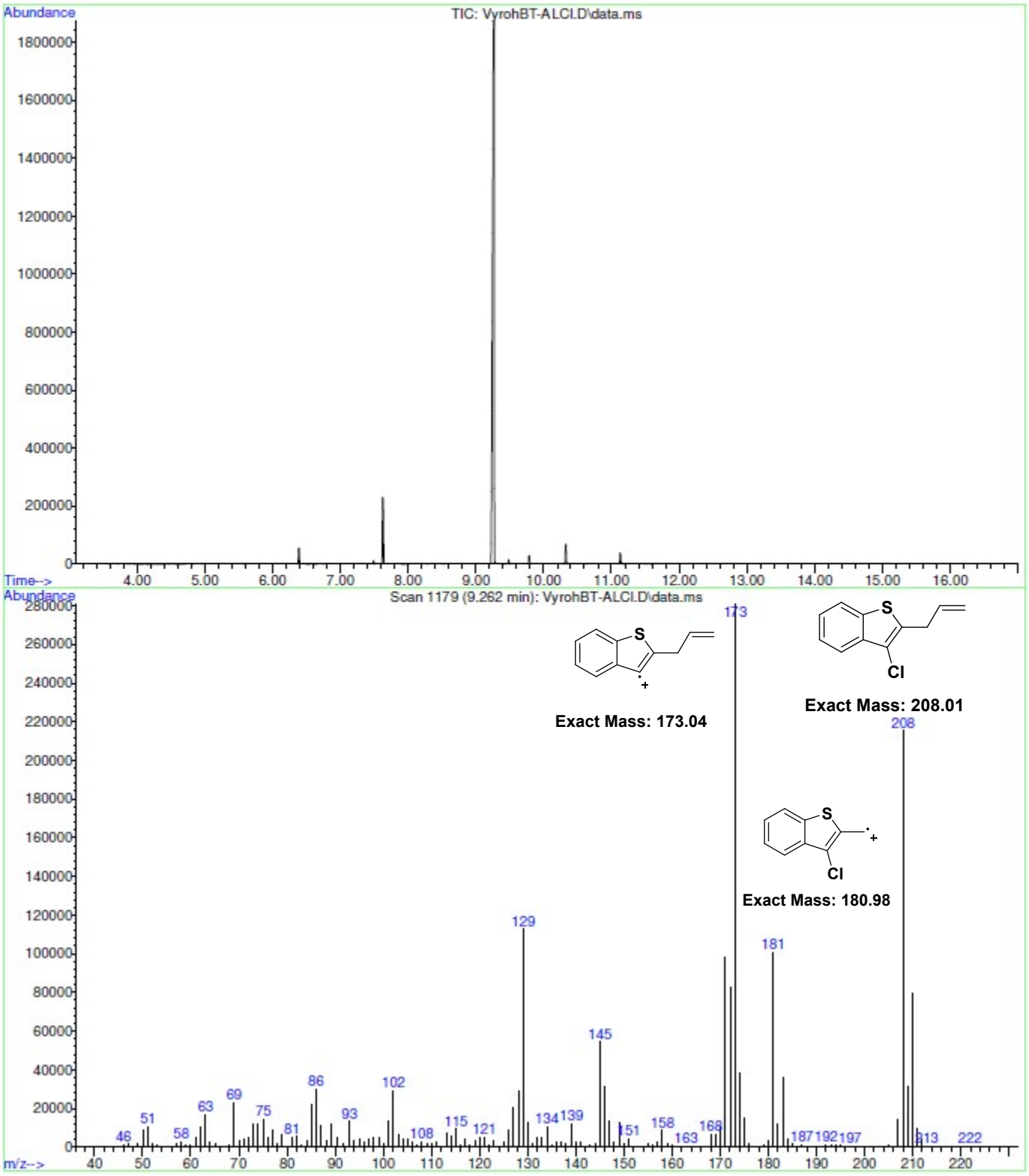


Figure S29. GC-MS of 2-allyl-3-chlorobenzo[*b*]thiophene **14**.

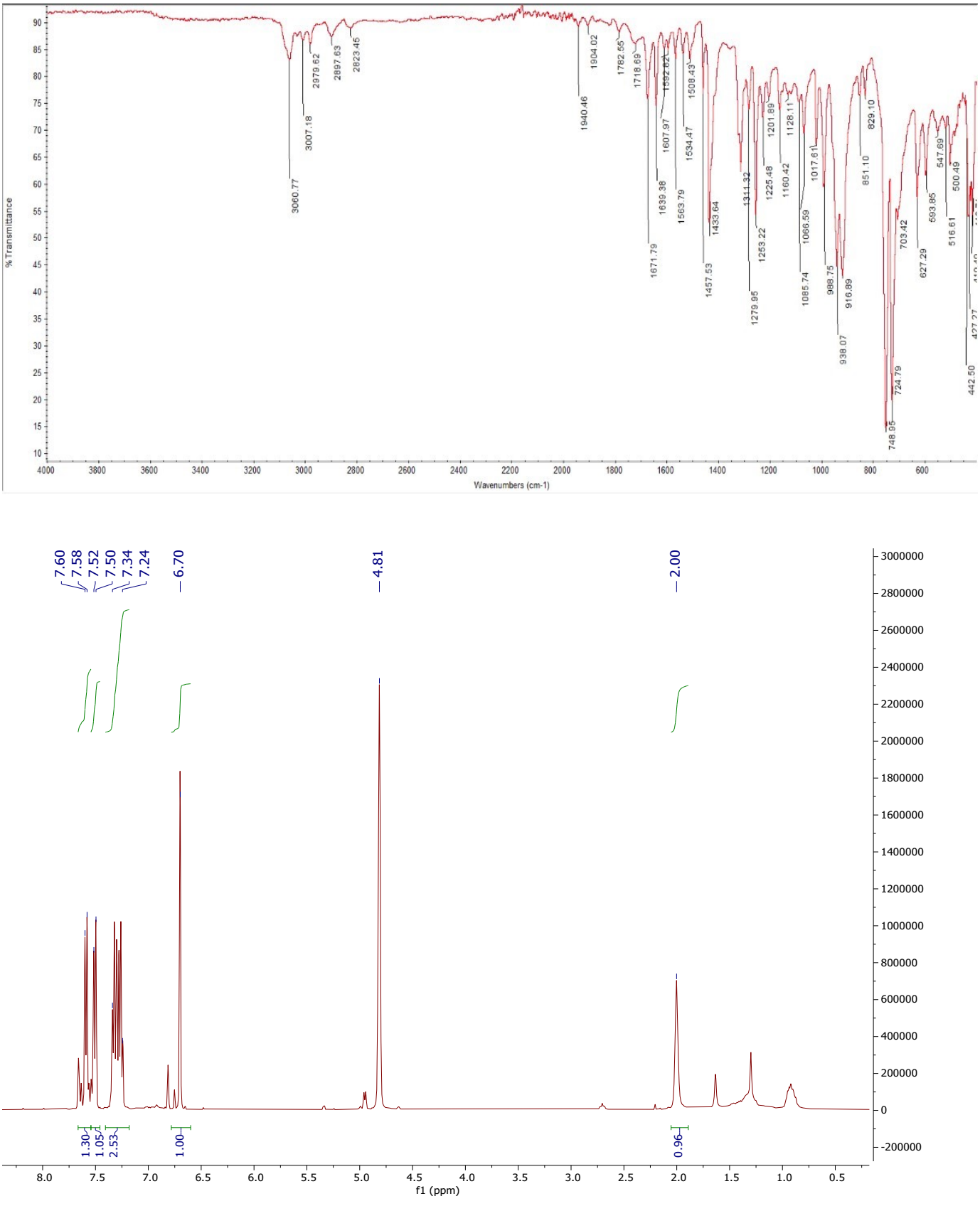


Figure S30. IR of 2-allyl-3-chlorobenzo[*b*]thiophene **14** (top); and ^{1}H-NMR of benzo[*b*]furan-2-methanol **15**.

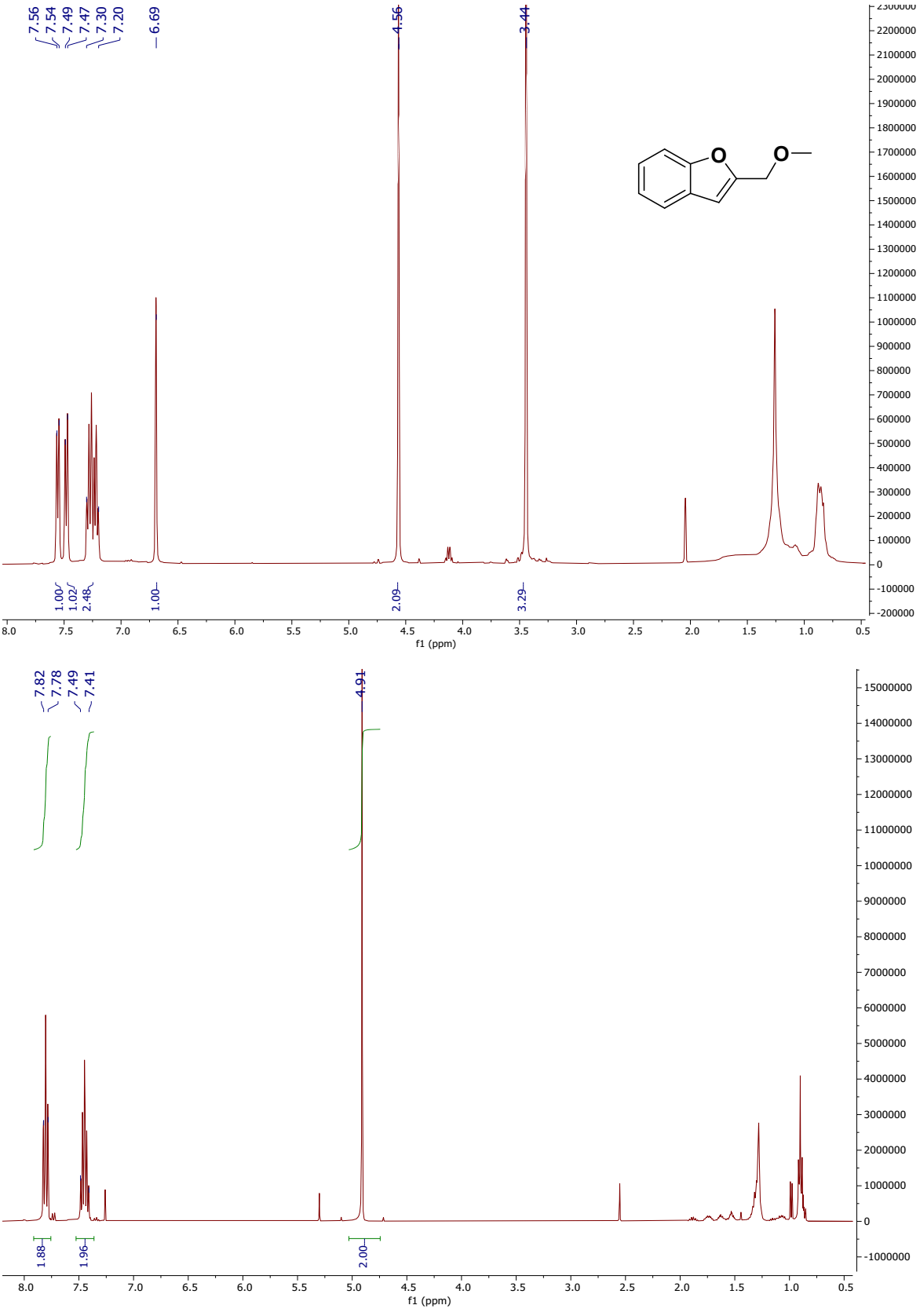


Figure S31. [1]H-NMR of 2-methoxymethylbenzofuran **16** (top); and 2-chloromethyl-3-chlorobenzo[*b*]thiophene **10** (bottom).

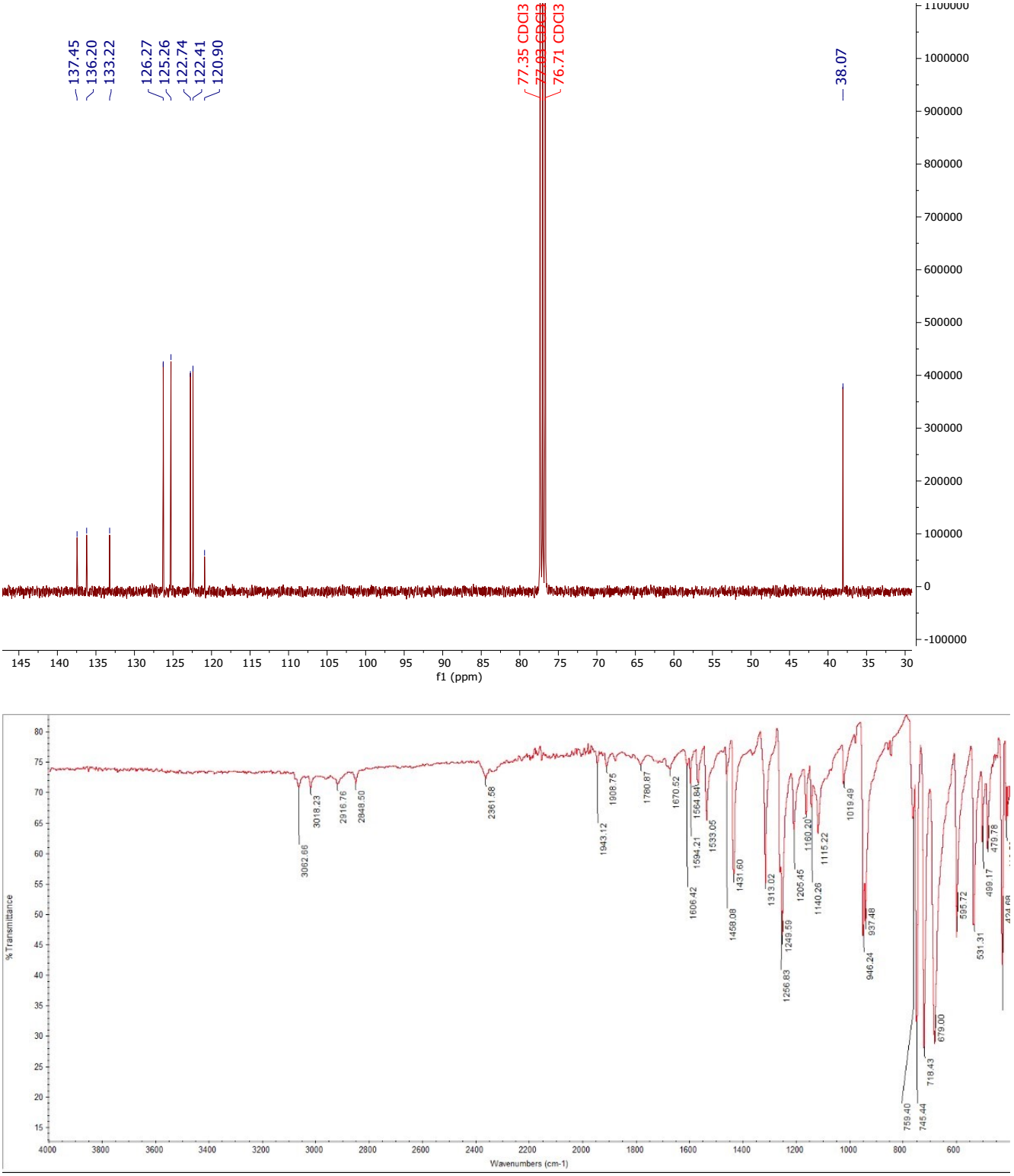


Figure S32. ^{13}C-NMR and IR of 2-chloromethyl-3-chlorobenzo[*b*]thiophene **10** (bottom).

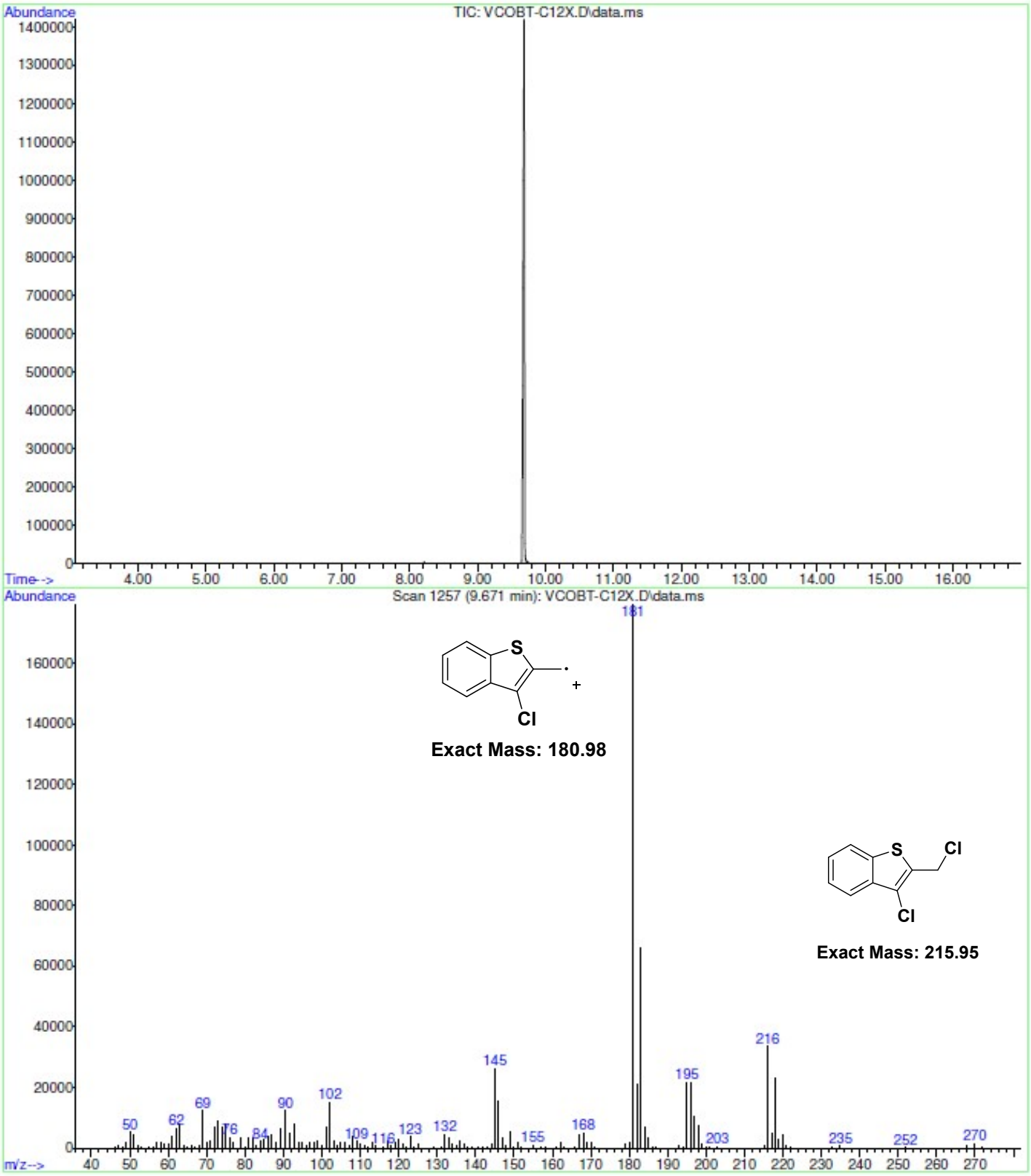


Figure S33. GC-MS 2-chloromethyl-3-chlorobenzo[*b*]thiophene **10** (bottom).

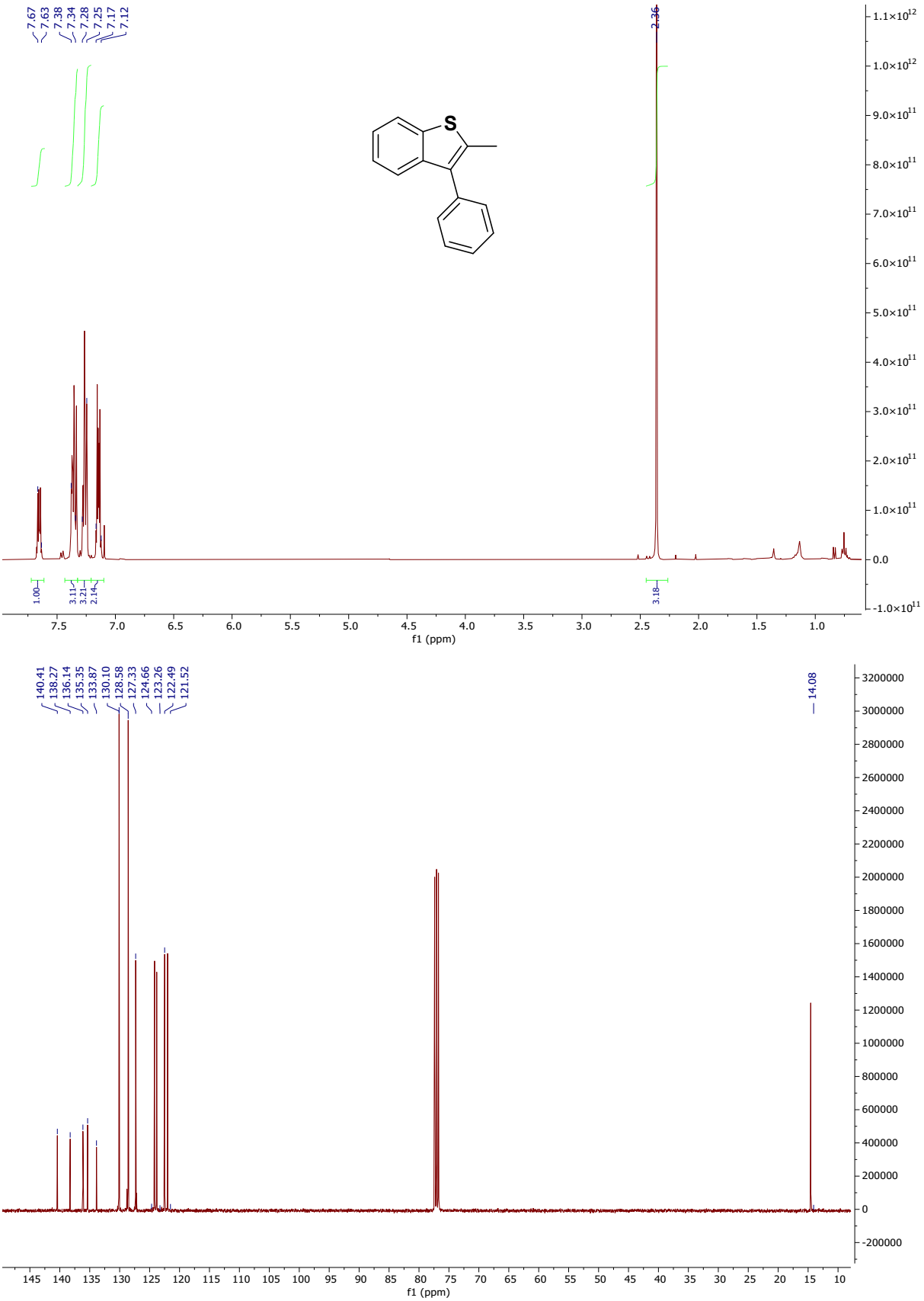
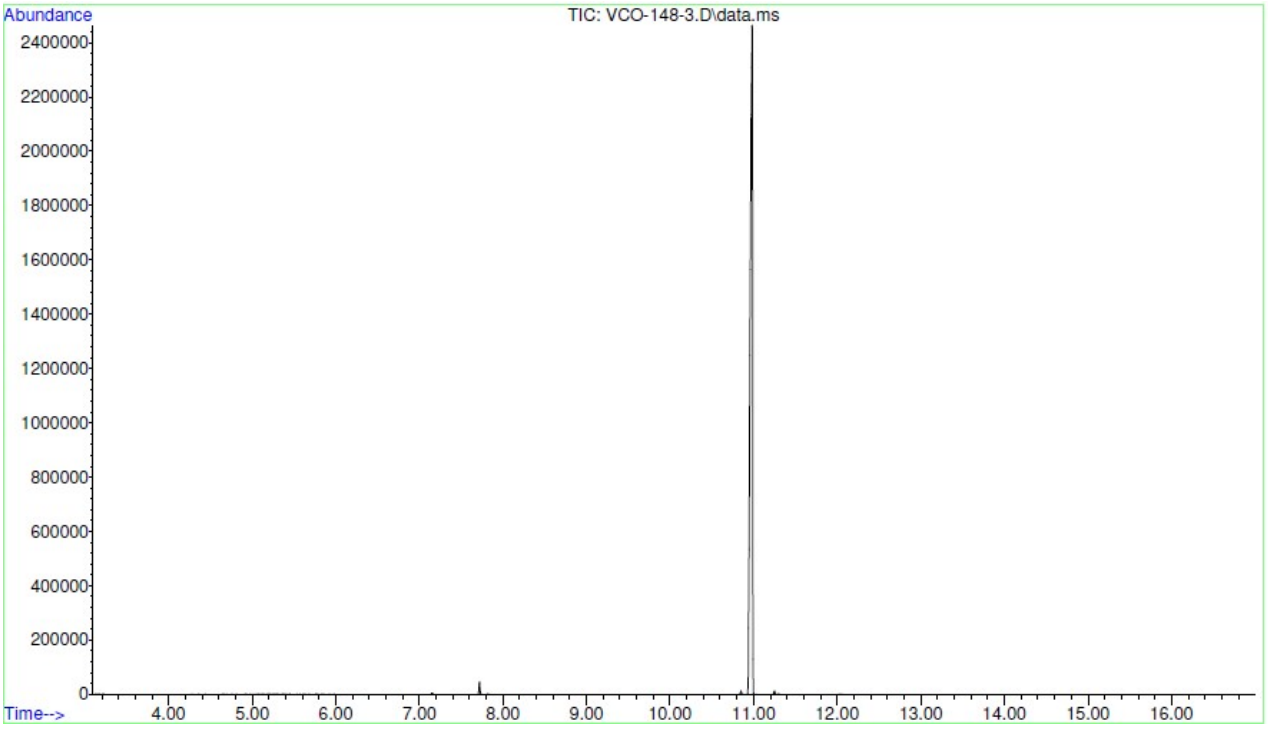
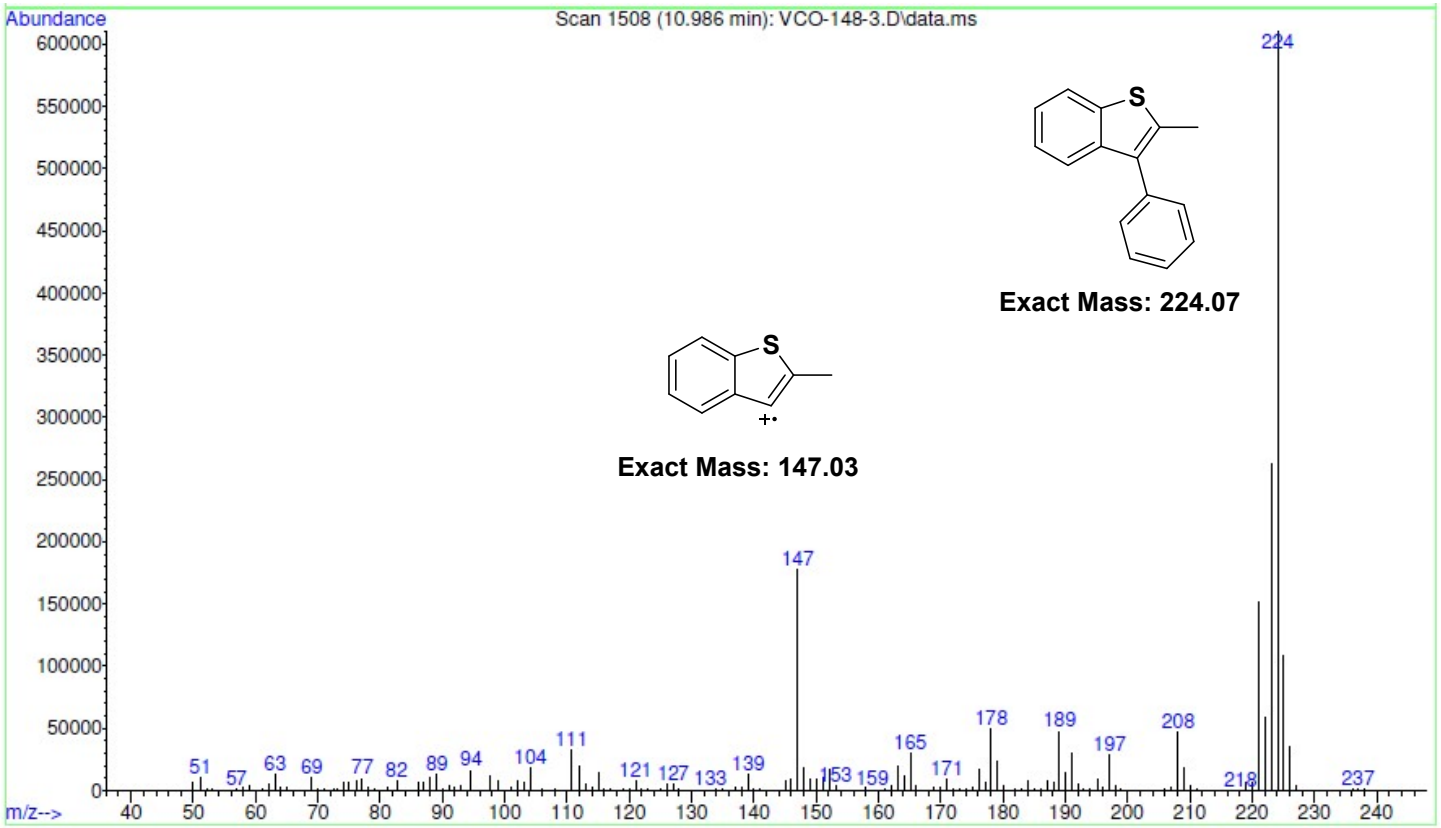


Figure S34. ^{1}H (top) and ^{13}C (bottom) NMR of2-Methyl-3-phenylbenzo[b]thiophene **17**.





Exact Mass: 224.07

Exact Mass: 147.03

Figure S35. GC-MS of2-Methyl-3-phenylbenzo[b]thiophene **17**.

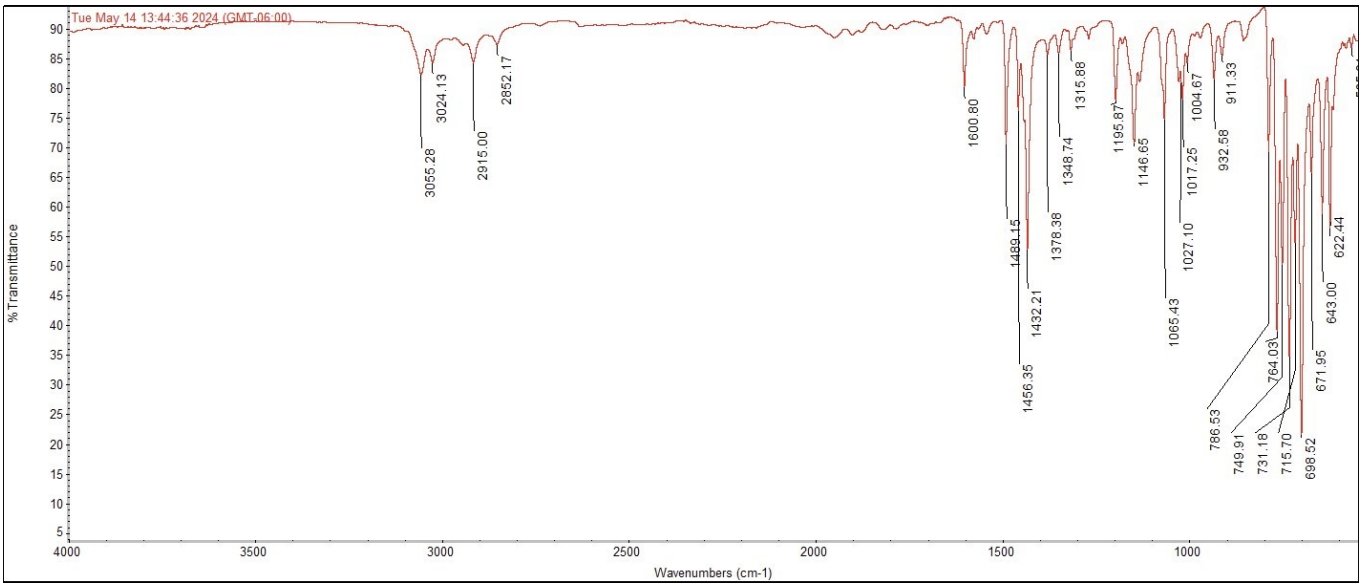


Figure S36. IR of2-Methyl-3-phenylbenzo[b]thiophene **17**.

We will first discuss statistical rate theory for treating a multi-step reaction and clarify the meaning of effective barrier height in the context of such a reaction.

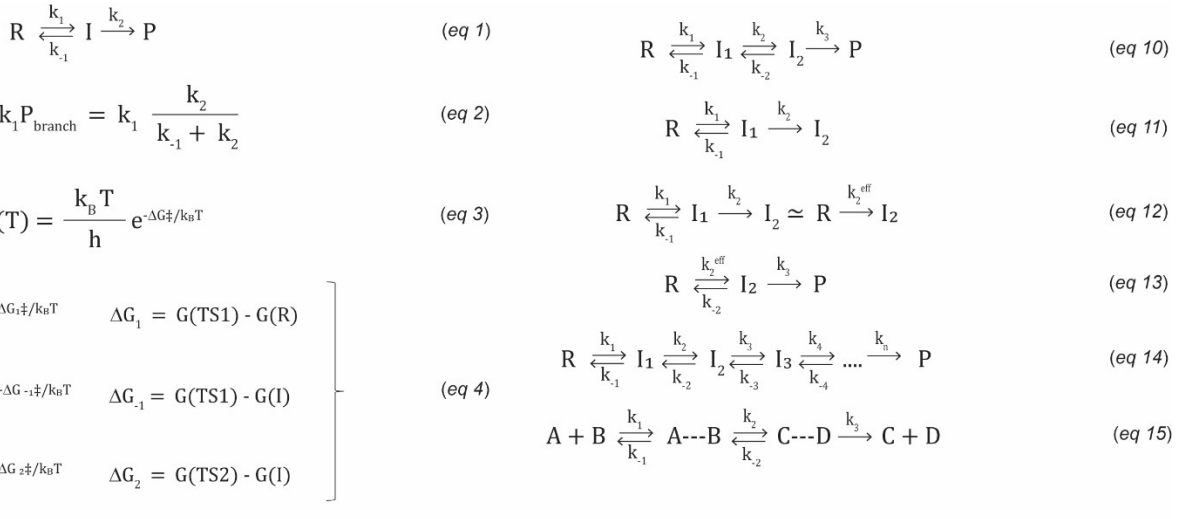
We start with a generic two-step reaction (eq 1), where R represents the reactant(s), I is the intermediate, and P represents the product(s). With a thermal distribution of energies for each species, the effective rate constant keff for the overall reaction can be given by invoking the detailed balance condition (eq 2), that is, the effective rate constant is the product of the rate constant for the first forward step to the intermediate, k1, and the branching ratio for the intermediate to reach the product as opposed to a path back to the reactant. The effective rate constant can be further explored by employing the canonical transition state theory for each elementary step (eq 3), where T is the temperature in Kelvin, k_B is the Boltzmann constant, h is the Planck constant, and $\Delta G‡$=G(TS)-Gr is the free energy difference between the transition state (TS) and the reactant of the corresponding elementary step [for example, R for the first forward step, I for the second forward step or the first backward step. Also note G(TS) is calculated without the reaction coordinate. For the two-step reaction considered above, there are two transition states, TS1 and TS2. Thus, the transition state rate constant for each step is given as the set of equations 4. Using these expressions, the branching ratio can be written more explicitly as equation 5. To analyze the effective rate constant, we consider three situations. First, if the transition state for the first step is much higher than that for the second step, G(TS1) $\gg$ G(TS2), then the branching ratio above is approximately one, Pbranch $\simeq$1, which renders the effective rate constant given as equation 6. That is, the effective barrier height is the barrier height for the first step, which equals to the free energy difference between the first transition state (the higher barrier) and the reactant. The second case occurs when the transition state for the second step is much higher than that for the first step, G(TS2) $\gg$ G(TS1), then the branching ratio is approximated by equation 7, which renders the effective rate constant as equation 8. That is, the effective barrier height equals the free energy difference between the second transition state (again the higher barrier) and the reactant.

The third case is when the transition state for the first step is approximately the same as that for the second step, G(TS1)$\simeq$G(TS2), then the branching ratio above is approximately half, Pbranch $\simeq$1/2, which renders the effective rate constant given as equation 9. In this situation one can still consider the dominant exponential contribution and treat the effective barrier height as the barrier height for the first step, with a multiplicative factor (1/2) for the rate constant.

Thus, in all three cases, the effective barrier height for the overall reaction equals to the free energy of the higher transition minus that of the reactant. The free energy difference between the transition state and the intermediate only enters the expression for the branching ratio, but not the expression for the overall rate constant. This is important as for a multi-step reaction one should always regard (approximately) the effective barrier height as the difference between a transition state and the reactant, and not a barrier height calculated from any intermediate. The above analysis can be generalized to reactions with more steps. Consider, for example, a three-step reaction (eq 10). Thereby one may separate the first effective step (eq 11), and use the above analysis for a two-step reaction to render it as an effective one-step reaction (eq 12). This effective step is then inserted into the three-step process and yield equation 13. This way, one is back to the analysis for a two-step reaction. Using this procedure, one may analyze a multi-step reaction (eq 14) and identify the effective barrier as the difference between the free energy of the highest transition state and that of the reactant. In another word, only the barrier of the rate-limiting step matters, in terms of transition state theory, for a complex, multi-step reaction. The relative free energy difference between any transition state and the adjacent intermediate only enters the expression for the branching ratio, and is essentially cancelled out in the final effective rate expression. The above discussions using transition state theory assume that there exists a transition state for each elementary step. Identifying such a transition state is straightforward in electronic

structure theory calculations whenever a saddle point can be obtained. For some steps considered in this paper, the process proceeds via a pre-reaction complex and sometimes a post-reaction complex, that is, the mechanism can be modeled as equation 15.

For the association reaction step (k1) there is no barrier along the potential energy profile from the reactants to the pre-reaction complex. However, in the language of variational transition state theory,47 a free energy barrier exists and serves as the transition state for the association reaction. This barrier is usually not high. In our case it is likely lower than the transition state for the isomerization reaction, which makes the scenario the second case in the above analysis for a two-step reaction. In that case, the effective barrier height equals the free energy difference between the second transition state (the saddle point identified in DFT calculations) and the reactants.



$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P \qquad (eq\ 1)$$

$$k_{eff} = k_1 P_{branch} = k_1 \frac{k_2}{k_{-1} + k_2} \qquad (eq\ 2)$$

$$k^{TST}(T) = \frac{k_B T}{h} e^{-\Delta G‡/k_B T} \qquad (eq\ 3)$$

$$\left.\begin{aligned} k_1 &= \frac{k_B T}{h} e^{-\Delta G_1‡/k_B T} \qquad \Delta G_1 = G(TS1) - G(R) \\ k_{-1} &= \frac{k_B T}{h} e^{-\Delta G_{-1}‡/k_B T} \qquad \Delta G_{-1} = G(TS1) - G(I) \\ k_2 &= \frac{k_B T}{h} e^{-\Delta G_2‡/k_B T} \qquad \Delta G_2 = G(TS2) - G(I) \end{aligned}\right\} \qquad (eq\ 4)$$

$$P_{branch} = \frac{k_2}{k_{-1} + k_2} = \frac{1}{k_{-1}/k_2 + 1} = \frac{1}{e^{-[G(TS1) - G(TS2)]/k_B T} + 1} \qquad (eq\ 5)$$

$$k_{eff} = k_1 P_{branch} \simeq k_1 = \frac{k_B T}{h} e^{-\Delta G‡/k_B T} = \frac{k_B T}{h} e^{-[G(TS1) - G(R)]/k_B T} \qquad (eq\ 6)$$

$$P_{branch} = \frac{1}{e^{-[G(TS1) - G(TS2)]/k_B T} + 1} \simeq \frac{1}{e^{-[G(TS1) - G(TS2)]/k_B T}} = e^{[G(TS1) - G(TS2)]/k_B T} \qquad (eq\ 7)$$

$$k_{eff} = k_1 P_{branch} \simeq \frac{k_B T}{h} e^{-\Delta G_1‡/k_B T} \bullet e^{[G(TS1) - G(TS2)]/k_B T} = \frac{k_B T}{h} e^{-[G(TS1) - G(R)]/k_B T} \bullet e^{[G(TS1) - G(TS2)]/k_B T} = \frac{k_B T}{h} e^{-[G(TS2) - G(R)]/k_B T} \qquad (eq\ 8)$$

$$k_{eff} = k_1 P_{branch} \simeq \frac{1}{2} k_1 = \frac{1}{2} \frac{k_B T}{h} e^{-\Delta G_1‡/k_B T} = \frac{1}{2} \frac{k_B T}{h} e^{-[\Gamma(TS1) - \Gamma(P)]/k_B T} \qquad (eq\ 9)$$

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I_2 \xrightarrow{k_3} P \qquad (eq\ 10)$$

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \xrightarrow{k_2} I_2 \qquad (eq\ 11)$$

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \xrightarrow{k_2} I_2 \simeq R \xrightarrow{k_2^{eff}} I_2 \qquad (eq\ 12)$$

$$R \underset{k_{-2}}{\overset{k_2^{eff}}{\rightleftharpoons}} I_2 \xrightarrow{k_3} P \qquad (eq\ 13)$$

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} I_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I_3 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} .... \xrightarrow{k_n} P \qquad (eq\ 14)$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A\text{---}B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C\text{---}D \xrightarrow{k_3} C + D \qquad (eq\ 15)$$

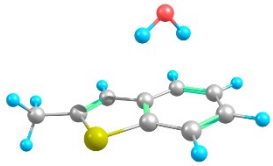
It is important to note that whenever H+ is mentioned, within the tables below, and discussion/calculations in general, it means adding H3O+ to one side and H2O to the other.

	Electronic Energy	Free Energy	Relative Electronic Energy	Relative Free Energy
Reactant	-1282.24069	-1282.128673		
M1 (BT-Me)	-745.9057306	-745.79633		
HOCl	-535.94765	-535.957229		
BT-Me + HOCl + H+	-1282.24069	-1282.128673	0	0
(M5) BT-Int1	-1281.82266	-1281.706824		
(M3-TS1) BT-Int1 + H+	-1282.20997	-1282.081938	19.27716526	29.32665648
Int1 Min1 (post)	-1281.887764	-1281.770314		
(M4) BT-Int1 Min1 (post) + H+	-1282.275073	-1282.145428	-21.57576142	-10.51392167
BT-Int1 Min2 (pre)	-1281.861708	-1281.744405		
(M2) BT-Int1 Min2 (pre) + H+	-1282.249017	-1282.119519	-5.225662545	5.744221963
(M6-TS2) BT-Int2	-1282.203188	-1282.074362	23.53272052	34.08066845
(M5) BT-Int2 Min1 (pre)	-1282.286913	-1282.160734	-29.00563787	-20.11858208
(M7) BT-Int2 Min2 (post)	-1282.231257	-1282.1051	5.91927559	14.79228144
BT-Int3	-1205.863271	-1205.753689		
(M9-TS3) BT-Int3 + H2O	-1282.292056	-1282.178618	-32.23256293	-31.34096198
BT-Int3 Min1 (post)	-1205.888297	-1205.779877		
(M10) BT-Int3 Min1 (post) + H2O	-1282.317081	-1282.204806	-47.93624545	-47.77418076
BT-Int3 Min2 (pre)	-1205.875229	-1205.765885		
(M8) BT-Int3 Min2 (pre) + H2O	-1282.304014	-1282.190814	-39.73643448	-38.99406784
BT-Me-Cl	-1205.504874	-1205.406382		
(M11) BT-Me-Cl + H3O+	-1282.320968	-1282.206425	-50.37500383	-48.79011864
H2O	-76.42878453	-76.424929		
H3O+	-76.81609385	-76.800043		
H+	-0.387309319	-0.375114		
HCl	-460.7999087	-460.811076		
Cl-	-460.3783687	-460.393391		
HOCl	-535.94765	-535.957229		
Sulfoxide	-821.0584693	-820.94762		
(M12) Sulfoxide + HCl + H+	-1282.245687	-1282.13381	-3.135926643	-3.223516302
Sulfone TS	-1356.97566	-1356.857663		
(M14 - TS2a) Sulfone TS + HCl + H+ - H	-1282.215228	-1282.086624	15.97774164	26.38614697
Sulfone TS Min1 (pre)	-1357.010676	-1356.893933		
(M13) Sulfone TS Min1 (pre) + HCl + H+	-1282.250244	-1282.122894	-5.995482414	3.6263774
Sulfone TS Min2 (post)	-1357.071654	-1356.954197		
(M15) Sulfone TS Min2 (post) + HCl + H	-1282.311222	-1282.183158	-44.25954335	-34.18985511
Sulfone	-896.2618135	-896.146587		
(M16) Sulfone + 2HCl + H+ - HOCl	-1282.30129	-1282.186624	-38.02728215	-36.36480303

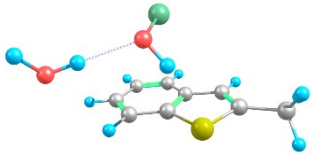
Table S1. Calculated values using acetonitrile as solvent. The assignment for each molecule M1-M16 correspond to those made on Figure 2.

	Electronic Energy	Free Energy	Relative Electronic Energy	Relative Free Energy
Reactant	-1358.675581	-1358.547039		
(M1) BT-Me	-822.3406216	-822.214696		
HOCl	-535.94765	-535.957229		
BT-Me + HOCl + H+	-1358.675581	-1358.547039	0	0
(M5) BT-Int1	-1358.26001	-1358.124323		
(M3-TS1) BT-Int1 + H+	-1358.647319	-1358.499437	17.73456493	29.87070722
BT-Int1 Min1 (pre)	-1358.297441	-1358.163017		
(M2) BT-Int1 Min1 (pre) + H+	-1358.68475	-1358.538131	-5.753812191	5.589854626
BT-Int1 Min2 (post)	-1358.325916	-1358.189248		
(M4) BT-Int1 Min2 (post) + H+	-1358.713225	-1358.564362	-23.62215775	-10.87034707
(M6-TS2) BT-Int2	-1358.634171	-1358.490367	25.98502137	35.56221838
(M5) BT-Int2 Min1 (pre)	-1358.717736	-1358.578598	-26.45300453	-19.80357231
(M7) BT-Int2 Min2 (post)	-1358.677955	-1358.528488	-1.490049106	11.64092873
BT-Int3	-1282.297792	-1282.170929		
(M9-TS3) BT-Int3 + H2O	-1358.726576	-1358.595858	-32.00011459	-30.63438628
BT-Int3 Min1 (post)	-1282.325538	-1282.197547		
(M10) BT-Int3 Min1 (post) + H2O	-1358.754323	-1358.622476	-49.4113383	-47.33743415
BT-Int3 Min2 (pre)	-1282.311212	-1282.182559		
(M8) BT-Int3 Min2 (pre) + H2O	-1358.739997	-1358.607488	-40.42152425	-37.93232177
BT-Me-Cl	-1281.940103	-1281.823949		
(M11) BT-Me-Cl + H3O+	-1358.756197	-1358.623992	-50.58732794	-48.28873855
H2O	-76.42878453	-76.424929		
H3O+	-76.81609385	-76.800043		
H+	-0.387309319	-0.375114		
HCl	-460.7999087	-460.811076		
Cl-	-460.3783687	-460.393391		
HOCl	-535.94765	-535.957229		
Sulfoxide	-821.0588543	-820.948015		
(M12) Sulfoxide + HCl + H+	-1282.246072	-1282.134205	47960.24277	47949.77926
Sulfone TS	-1356.976312	-1356.857928		
(M14 - TS2a) Sulfone TS + HCl + H+ - HOCl	-1282.21588	-1282.086889	47979.18858	47979.4705
Sulfone TS Min1 (pre)	-1357.01124	-1356.894558		
(M13) Sulfone TS Min1 (pre) + HCl + H+ - HOCl	-1282.250808	-1282.123519	47957.27109	47956.48482
Sulfone TS Min2 (post)	-1357.072044	-1356.95461		
(M15) Sulfone TS Min2 (post) + HCl + H+ - HOCl	-1282.311612	-1282.183571	47919.116	47918.80162
Sulfone	-896.2622188	-896.147		
(M16) Sulfone + 2HCl + H+ - HOCl	-1282.301695	-1282.187037	47925.33868	47916.62668

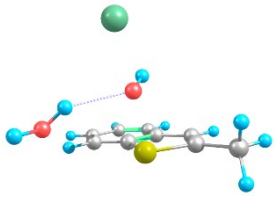
Table S2. Calculated values using an additional molecule of water, in the vicinity, at each step. The assignment for each molecule M1-M16 correspond to those made on Figure 2.



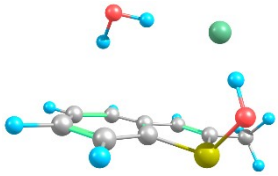
M1



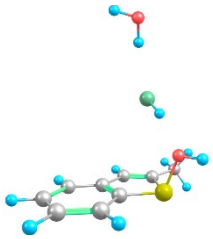
M2



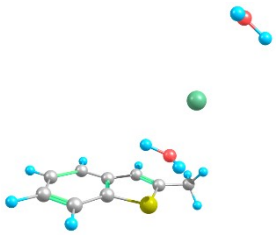
M3



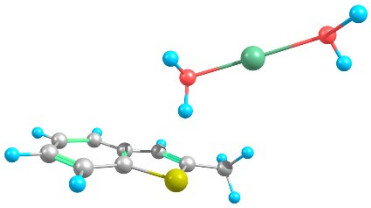
M4



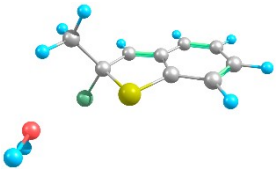
M5



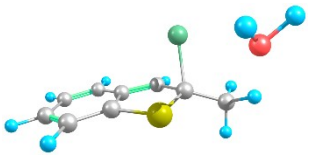
M6



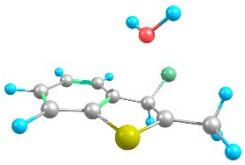
M7



M8



M9



M10

Table 2 structures.

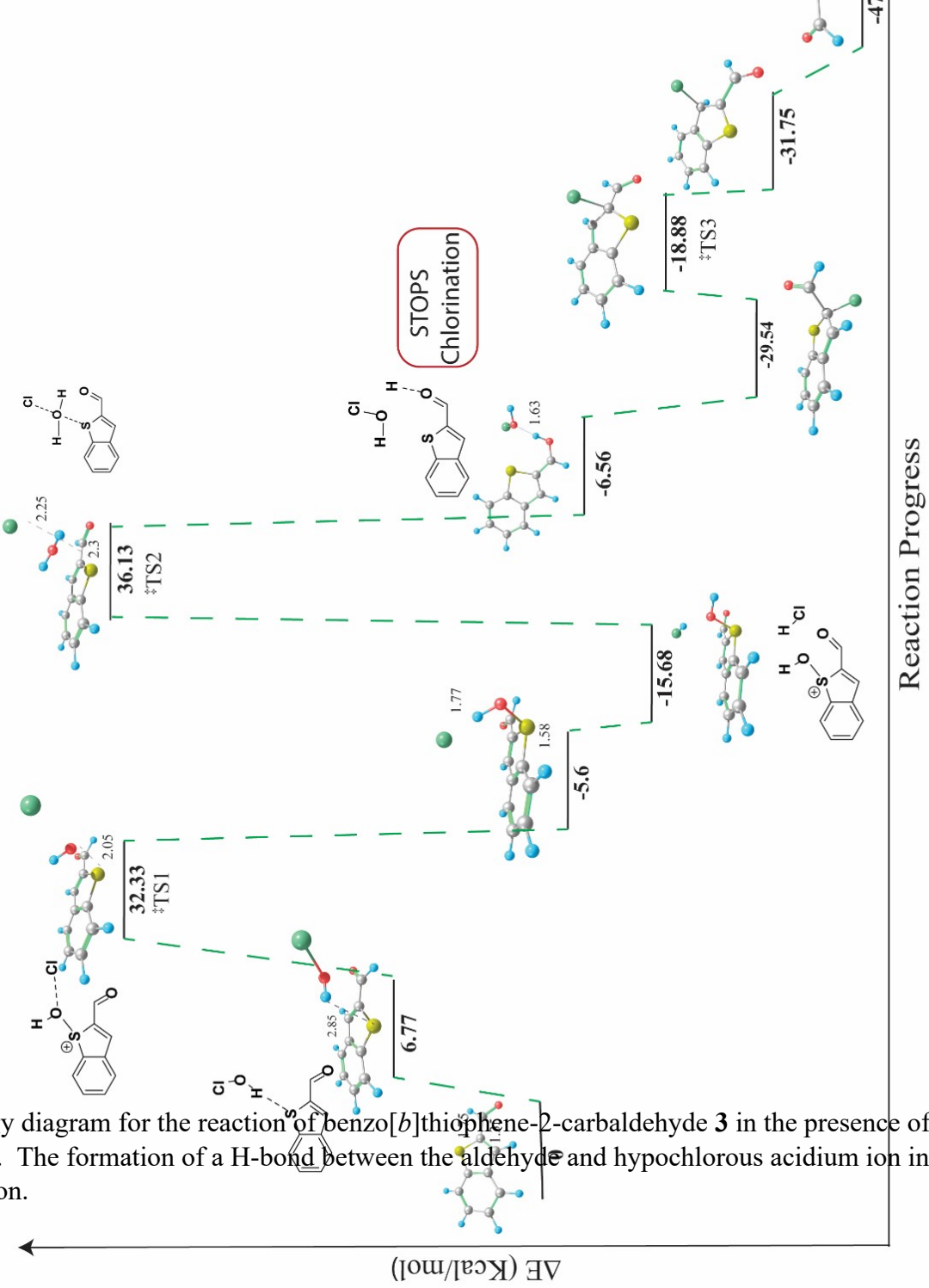


Figure S37. Energy diagram for the reaction of benzo[*b*]thiophene-2-carbaldehyde **3** in the presence of hypochlorous acid. The formation of a H-bond between the aldehyde and hypochlorous acidium ion inhibits the chlorination reaction.

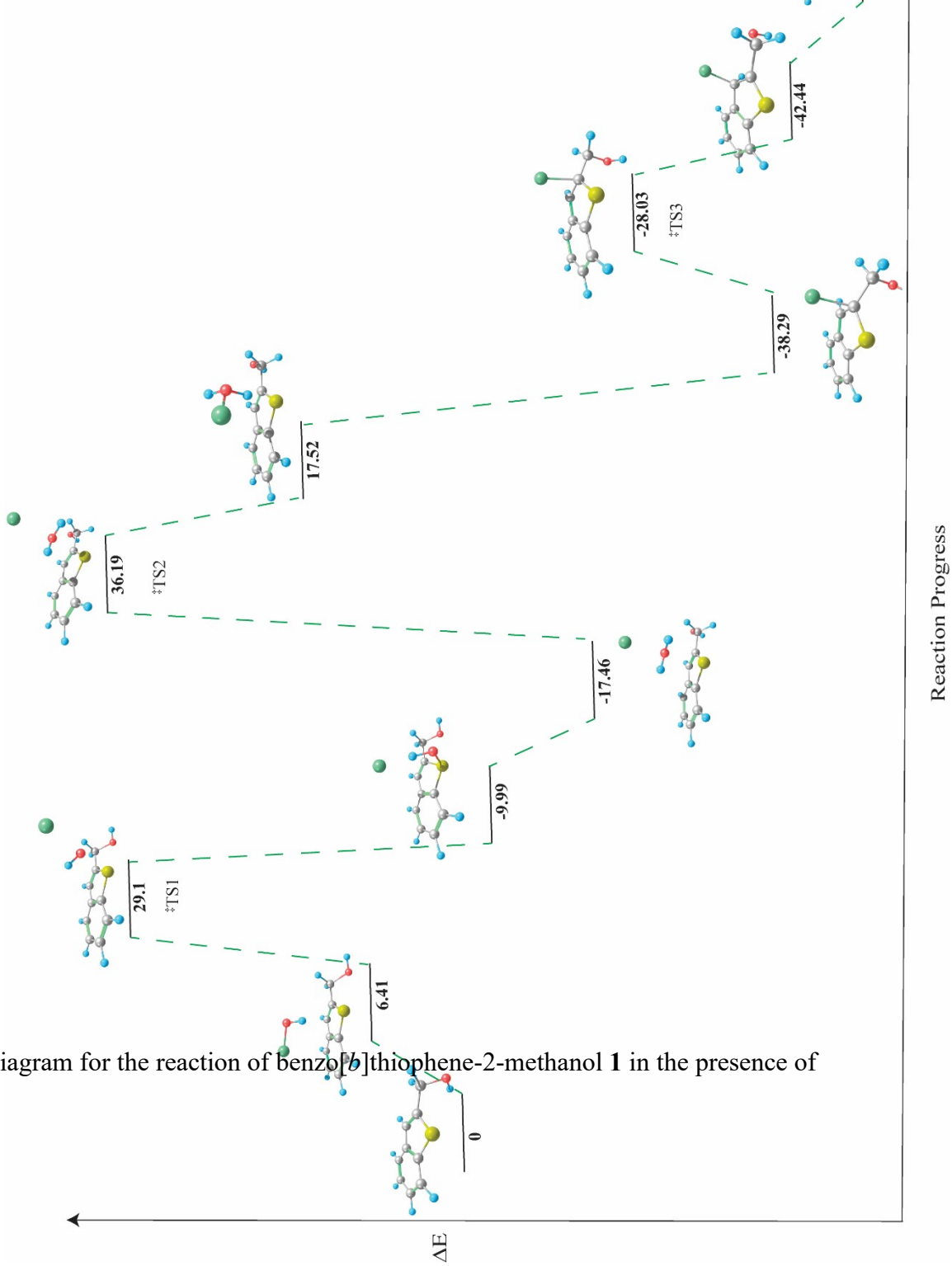


Figure S38. Energy diagram for the reaction of benzo[*b*]thiophene-2-methanol **1** in the presence of hypochlorous acid.

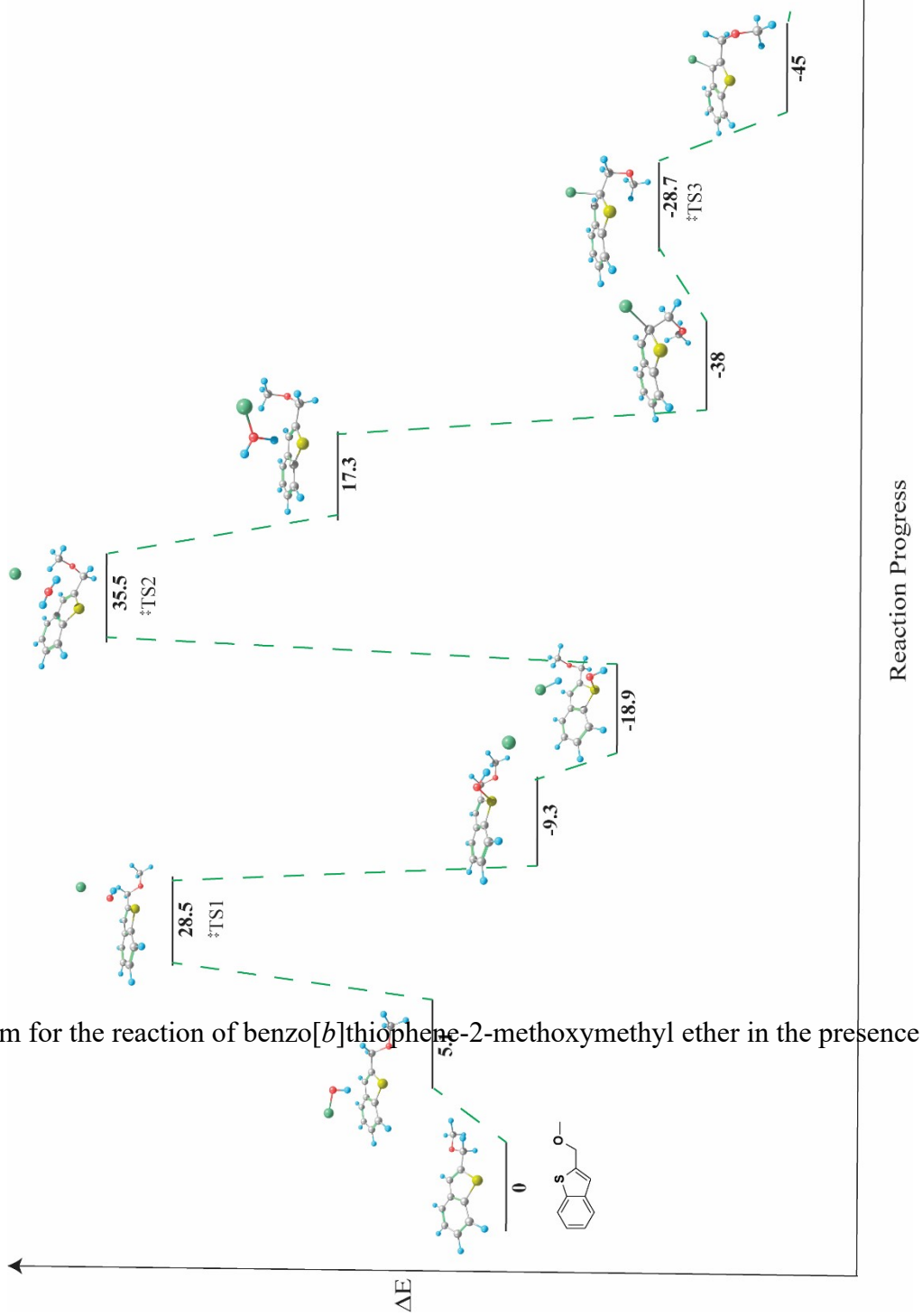


Figure S39. Energy diagram for the reaction of benzo[*b*]thiophene-2-methoxymethyl ether in the presence of hypochlorous acid.

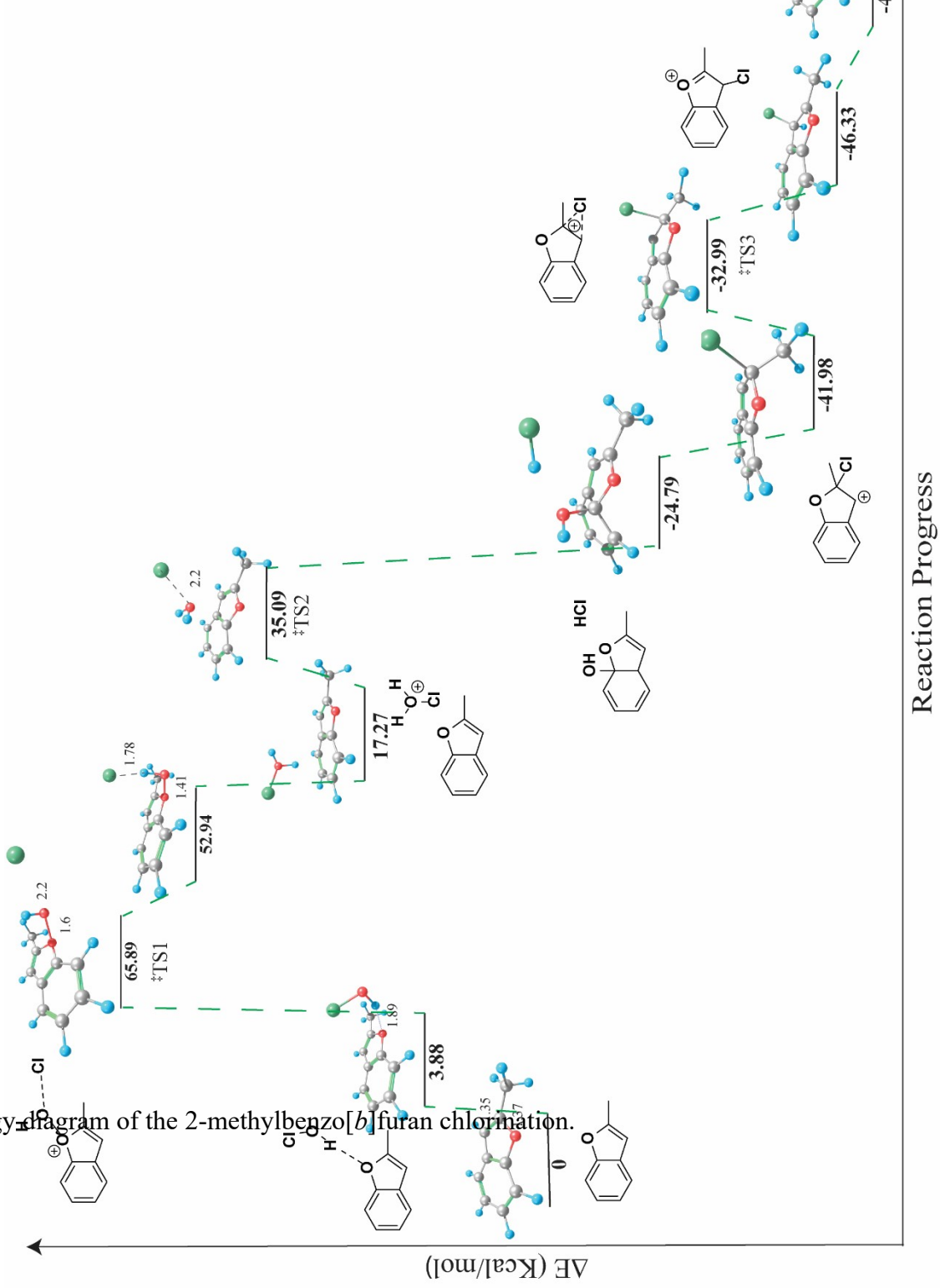
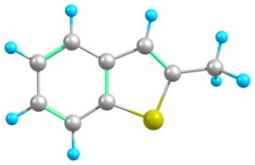


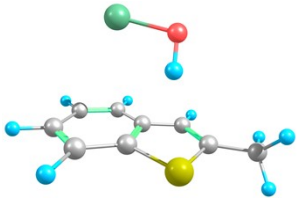
Figure S40. Energy diagram of the 2-methylbenzo[*b*]furan chlorination.

XYZ Coordinates for the chlorination of 2-methylbenzo[b]thiophene (7) and oxidation to sulfone



(Starting material)

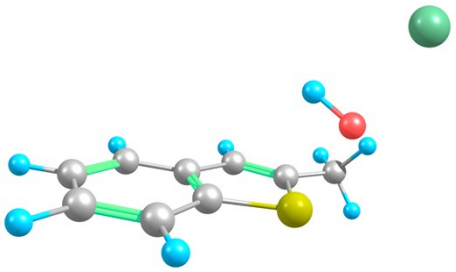
6	1.616374000	1.496307000	0.000094000
6	2.810364000	0.793683000	0.000198000
6	0.399971000	0.794518000	-0.000199000
1	3.752358000	1.332792000	0.000480000
6	2.817546000	-0.611212000	-0.000003000
6	0.427729000	-0.615433000	-0.000239000
1	3.762979000	-1.144151000	0.000059000
6	1.629339000	-1.327701000	-0.000199000
1	1.633078000	-2.413144000	-0.000140000
1	1.612382000	2.582435000	0.000366000
6	-0.949674000	1.305478000	-0.000282000
6	-1.896608000	0.337205000	0.000323000
16	-1.192876000	-1.273245000	0.000108000
1	-1.189522000	2.363704000	-0.000598000
6	-3.384481000	0.497576000	0.000023000
1	-3.834655000	0.034404000	0.883506000
1	-3.639656000	1.559605000	-0.000424000
1	-3.834319000	0.033753000	-0.883269000



pre-TS1

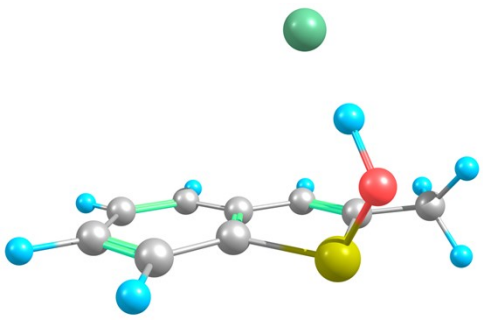
6	1.220668000	1.248914000	-1.453807000
6	2.376084000	1.504489000	-0.736607000
6	0.045033000	0.907178000	-0.768785000
1	3.287114000	1.766786000	-1.261075000
6	2.384425000	1.430953000	0.665503000
6	0.074766000	0.837791000	0.637013000
1	3.299062000	1.636785000	1.208351000
6	1.235885000	1.098972000	1.365972000
1	1.239693000	1.039945000	2.447615000
1	1.215985000	1.306446000	-2.536336000
6	-1.260953000	0.596303000	-1.298171000
6	-2.176871000	0.299587000	-0.348631000
16	-1.494367000	0.382704000	1.272271000
1	-1.491855000	0.593070000	-2.356237000
6	-3.612310000	-0.078156000	-0.525218000
1	-4.271510000	0.628177000	-0.016370000

1	-3.859819000	-0.081400000	-1.586727000
1	-3.810015000	-1.072611000	-0.119280000
8	-0.056601000	-2.463440000	0.042632000
1	-0.369307000	-1.702568000	0.561283000
17	1.611939000	-2.212150000	-0.133072000



TS1

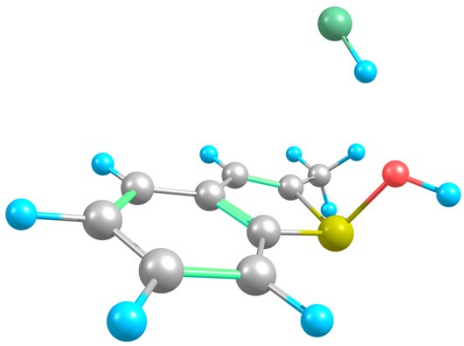
6	-2.862636000	0.261959000	1.058984000
6	-3.491331000	-0.920956000	0.681557000
6	-1.652287000	0.610905000	0.457414000
1	-4.431153000	-1.198104000	1.147421000
6	-2.932826000	-1.758142000	-0.290886000
6	-1.109770000	-0.245037000	-0.519093000
1	-3.440774000	-2.675085000	-0.569513000
6	-1.729957000	-1.427114000	-0.909121000
1	-1.292414000	-2.069639000	-1.665726000
1	-3.303691000	0.909830000	1.809747000
6	-0.814891000	1.777763000	0.687008000
6	0.299287000	1.816213000	-0.069838000
16	0.396651000	0.408140000	-1.142481000
1	-1.057875000	2.547761000	1.411388000
6	1.412048000	2.810993000	-0.094672000
1	1.498484000	3.287733000	-1.075451000
1	1.227536000	3.582985000	0.654833000
1	2.366147000	2.323810000	0.129833000
8	1.969792000	-0.573885000	-0.206694000
1	1.522544000	-0.645807000	0.661586000
17	3.652977000	-1.503656000	0.671825000



post-TS1

6	2.165291000	0.774790000	-1.257435000
6	3.226276000	0.141729000	-0.606767000
6	0.929180000	0.822118000	-0.629289000

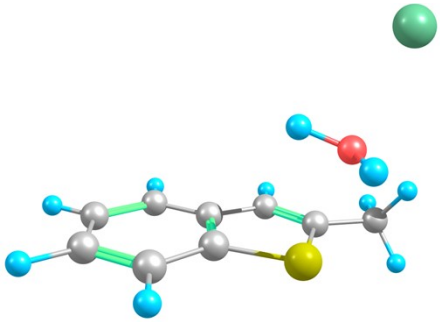
1	4.191723000	0.090005000	-1.094791000
6	3.069149000	-0.421653000	0.656787000
6	0.800728000	0.249247000	0.638945000
1	3.906834000	-0.907275000	1.140611000
6	1.838981000	-0.357507000	1.315465000
1	1.706913000	-0.778084000	2.304377000
1	2.299851000	1.216828000	-2.236912000
6	-0.332053000	1.380677000	-1.127516000
6	-1.377297000	1.248187000	-0.307314000
16	-0.840817000	0.533341000	1.260603000
1	-0.414755000	1.839781000	-2.105517000
6	-2.815180000	1.600645000	-0.453885000
1	-3.119607000	2.343963000	0.285417000
1	-2.983758000	2.003078000	-1.452182000
1	-3.440555000	0.713525000	-0.324886000
8	-1.570484000	-0.878949000	1.384707000
1	-1.446489000	-1.445608000	0.514819000
17	-1.159627000	-2.306322000	-1.038364000



pre-TS2

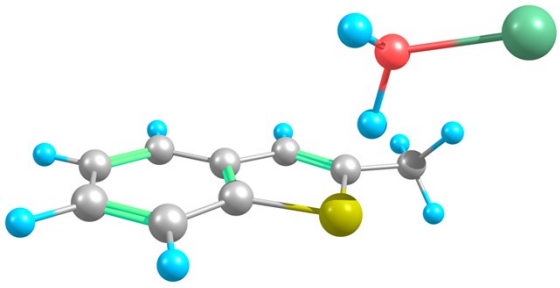
6	2.142549000	1.087125000	1.188275000
6	3.249375000	1.074850000	0.332933000
6	1.066581000	0.267022000	0.894082000
1	4.091637000	1.719556000	0.551009000
6	3.294788000	0.250083000	-0.786080000
6	1.141831000	-0.553348000	-0.236472000
1	4.164093000	0.258768000	-1.430476000
6	2.229026000	-0.604143000	-1.083608000
1	2.255662000	-1.264430000	-1.940912000
1	2.124370000	1.724198000	2.063498000
6	-0.202769000	0.117827000	1.617046000
6	-1.063377000	-0.759039000	1.094926000
16	-0.312147000	-1.555793000	-0.338718000
1	-0.436263000	0.696023000	2.503011000
6	-2.448633000	-1.155685000	1.462339000
1	-2.498846000	-2.208325000	1.745872000
1	-2.774892000	-0.543814000	2.302650000
1	-3.131832000	-0.989223000	0.625660000

8	-1.180460000	-0.861150000	-1.539546000
1	-1.989709000	0.980508000	-1.261736000
1	-1.423152000	-1.525195000	-2.206411000
17	-2.494074000	2.034452000	-0.712762000



TS2

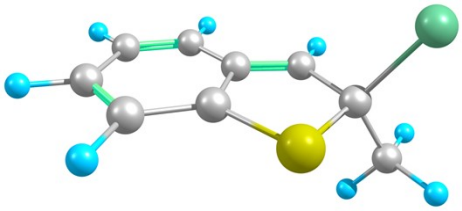
6	-2.728188000	0.125100000	1.285916000
6	-3.446333000	-0.979997000	0.805029000
6	-1.600037000	0.545073000	0.596804000
1	-4.326527000	-1.313481000	1.343708000
6	-3.054045000	-1.651506000	-0.349958000
6	-1.220540000	-0.148399000	-0.569901000
1	-3.625733000	-2.501826000	-0.703562000
6	-1.924611000	-1.239418000	-1.064761000
1	-1.610679000	-1.755303000	-1.965496000
1	-3.052308000	0.647405000	2.179724000
6	-0.698978000	1.652508000	0.885422000
6	0.310194000	1.798559000	-0.002097000
16	0.201302000	0.582981000	-1.271309000
1	-0.822469000	2.308632000	1.740240000
6	1.437396000	2.777447000	-0.023119000
1	1.441437000	3.361181000	-0.947325000
1	1.332905000	3.460253000	0.821878000
1	2.399627000	2.262772000	0.061321000
8	1.980331000	-0.637295000	-0.303942000
1	1.371647000	-1.243930000	0.176544000
1	2.209811000	-1.092408000	-1.146314000
17	3.715862000	-1.508167000	0.695986000



post-TS2

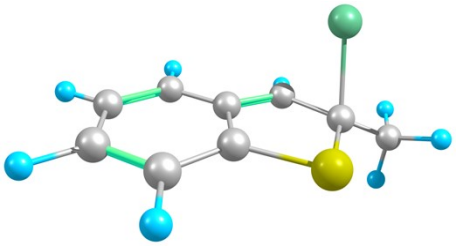
6	2.940860000	0.404505000	-0.958090000
6	3.601586000	-0.769691000	-0.626117000

6	1.694976000	0.672027000	-0.383070000
1	4.566310000	-0.983919000	-1.069449000
6	3.041244000	-1.682323000	0.274469000
6	1.155655000	-0.258433000	0.516407000
1	3.574989000	-2.591588000	0.521480000
6	1.806411000	-1.434795000	0.863101000
1	1.371219000	-2.134547000	1.565434000
1	3.378172000	1.110139000	-1.654372000
6	0.828019000	1.819236000	-0.582787000
6	-0.319491000	1.783939000	0.114614000
16	-0.406650000	0.312007000	1.124016000
1	1.079386000	2.640590000	-1.242408000
6	-1.441949000	2.765302000	0.165644000
1	-1.577350000	3.153498000	1.177066000
1	-1.220201000	3.597506000	-0.502042000
1	-2.382310000	2.307253000	-0.148788000
8	-2.019434000	-1.208585000	-0.706133000
1	-1.731098000	-2.141931000	-0.766727000
1	-1.415359000	-0.638232000	0.047787000
17	-3.695633000	-1.143577000	-0.386364000



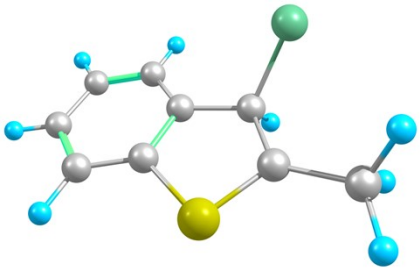
pre-TS3

6	-2.018554000	-1.558756000	0.090023000
6	-3.215542000	-0.937569000	-0.064991000
6	-0.828109000	-0.754648000	0.121465000
1	-4.135818000	-1.504805000	-0.092983000
6	-3.274907000	0.483437000	-0.193117000
6	-0.915784000	0.684549000	-0.015120000
1	-4.247818000	0.945126000	-0.317286000
6	-2.161099000	1.296719000	-0.168262000
1	-2.250545000	2.369477000	-0.269796000
1	-1.932948000	-2.633236000	0.192273000
6	0.448775000	-1.181778000	0.280589000
6	1.486482000	-0.113734000	0.308130000
16	0.596287000	1.475887000	0.035637000
1	0.750764000	-2.217878000	0.394204000
6	2.262957000	-0.086560000	1.622734000
1	1.573013000	0.085235000	2.450406000
1	2.768639000	-1.042048000	1.760383000
1	3.000782000	0.714368000	1.595081000
17	2.601649000	-0.430611000	-1.068893000



TS3

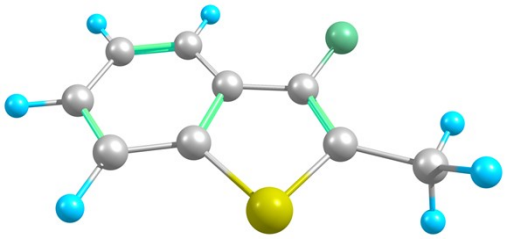
6	1.824778000	-1.432823000	-0.536135000
6	3.074297000	-0.918950000	-0.241296000
6	0.706091000	-0.597176000	-0.382874000
1	3.956923000	-1.537137000	-0.354204000
6	3.205418000	0.403591000	0.209725000
6	0.854003000	0.734870000	0.065473000
1	4.193877000	0.787921000	0.438840000
6	2.105880000	1.245716000	0.372243000
1	2.232100000	2.265063000	0.717833000
1	1.697616000	-2.454184000	-0.878378000
6	-0.651102000	-0.919848000	-0.655324000
6	-1.574102000	0.191333000	-0.367417000
16	-0.672260000	1.615313000	0.146186000
1	-0.977346000	-1.782746000	-1.228707000
6	-2.880435000	0.390478000	-1.075306000
1	-2.668906000	0.890539000	-2.024808000
1	-3.363931000	-0.567152000	-1.270802000
1	-3.543202000	1.022203000	-0.481921000
17	-1.809408000	-1.120745000	1.082861000



post-TS3

6	1.536611000	1.454078000	0.372522000
6	2.866827000	1.100708000	0.154733000
6	0.564509000	0.472348000	0.267982000
1	3.636216000	1.858779000	0.228715000
6	3.223274000	-0.211527000	-0.154169000
6	0.941348000	-0.829616000	-0.045579000
1	4.263354000	-0.462953000	-0.317857000
6	2.256811000	-1.208043000	-0.259321000
1	2.523106000	-2.229141000	-0.498801000
1	1.263986000	2.475127000	0.610855000
6	-0.908024000	0.610470000	0.503034000
6	-1.551626000	-0.719813000	0.208024000
16	-0.469130000	-1.902103000	-0.141178000

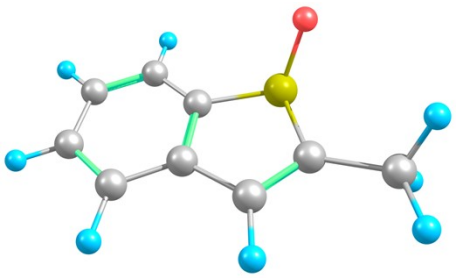
1	-1.123064000	0.842139000	1.552889000
6	-3.008446000	-0.936951000	0.247749000
1	-3.404150000	-0.539622000	1.186731000
1	-3.461841000	-0.353463000	-0.561390000
1	-3.275130000	-1.984503000	0.135644000
17	-1.673182000	1.908081000	-0.461635000



Product (8)

6	-1.411178000	1.538853000	-0.000013000
6	-2.768847000	1.265134000	0.000012000
6	-0.502548000	0.471417000	-0.000012000
1	-3.481483000	2.083354000	0.000027000
6	-3.236592000	-0.059757000	0.000015000
6	-0.982715000	-0.850712000	0.000006000
1	-4.304528000	-0.251945000	0.000022000
6	-2.351646000	-1.127836000	0.000005000
1	-2.711109000	-2.151708000	0.000003000
1	-1.046131000	2.561392000	-0.000005000
6	0.940525000	0.489159000	-0.000012000
6	1.532022000	-0.729651000	0.000005000
16	0.330184000	-2.006079000	-0.000019000
6	2.986527000	-1.071367000	0.000028000
1	3.249487000	-1.659891000	-0.883833000
1	3.584985000	-0.158612000	-0.000769000
1	3.249789000	-1.658533000	0.884707000
17	1.820163000	1.987163000	-0.000004000

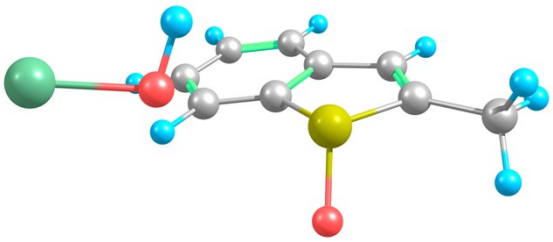
***S*-oxidation can occur after post-TS2 to provide methylated sulfoxide, and subsequent *S*-oxidation to the sulfone**



Sulfoxide

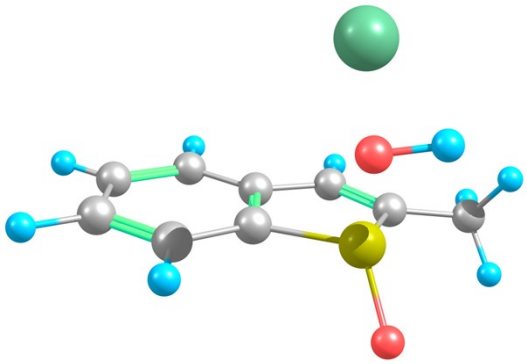
6	-1.940271000	-1.478452000	0.128007000
6	-3.050161000	-0.632915000	0.119662000
6	-0.671360000	-0.921740000	0.013738000

1	-4.042205000	-1.056485000	0.219381000
6	-2.904517000	0.746694000	-0.013404000
6	-0.548380000	0.462782000	-0.132060000
1	-3.779473000	1.384688000	-0.011063000
6	-1.636207000	1.313905000	-0.156936000
1	-1.512513000	2.383620000	-0.278507000
1	-2.062098000	-2.550378000	0.229657000
6	0.632535000	-1.594885000	0.051256000
6	1.683089000	-0.777097000	-0.062688000
16	1.164732000	0.929360000	-0.376869000
1	0.725639000	-2.666823000	0.184875000
6	3.145369000	-1.050542000	-0.012347000
1	3.619899000	-0.426465000	0.749490000
1	3.320849000	-2.097886000	0.232113000
1	3.620696000	-0.826095000	-0.970138000
8	1.651615000	1.822445000	0.757842000



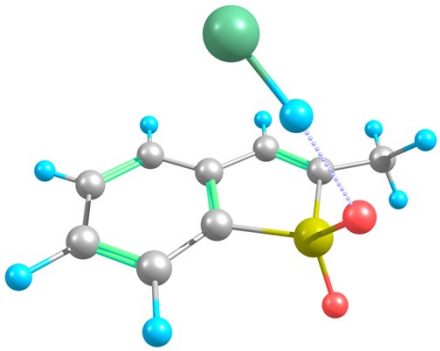
pre-TS2a

6	2.763324000	0.828854000	-1.070510000
6	3.321284000	-0.348505000	-0.571861000
6	1.462514000	1.161818000	-0.708374000
1	4.338122000	-0.610052000	-0.838887000
6	2.594814000	-1.190306000	0.268511000
6	0.744320000	0.292992000	0.118251000
1	3.051586000	-2.093380000	0.654108000
6	1.277818000	-0.880609000	0.615435000
1	0.697147000	-1.532592000	1.255871000
1	3.335764000	1.480271000	-1.720315000
6	0.698430000	2.368803000	-1.045778000
6	-0.526149000	2.416095000	-0.512658000
16	-0.934914000	0.874433000	0.342810000
1	1.111408000	3.161969000	-1.659022000
6	-1.573312000	3.472767000	-0.566488000
1	-1.876996000	3.755697000	0.444808000
1	-1.187510000	4.354718000	-1.077288000
1	-2.462344000	3.119357000	-1.094206000
8	-1.221924000	1.161045000	1.811290000
8	-1.686766000	-1.998102000	0.446577000
1	-1.801487000	-1.985175000	-0.515294000
17	-1.307627000	-3.612595000	0.814267000



TS2a

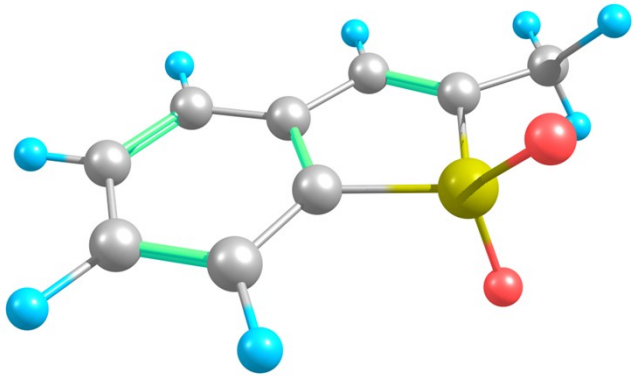
6	2.741737000	0.679630000	-0.847041000
6	3.467164000	-0.357687000	-0.257671000
6	1.444613000	0.917957000	-0.413420000
1	4.482972000	-0.545025000	-0.583296000
6	2.910860000	-1.157553000	0.738085000
6	0.913390000	0.100208000	0.586022000
1	3.494779000	-1.955085000	1.179429000
6	1.599627000	-0.944183000	1.169811000
1	1.145033000	-1.567044000	1.930365000
1	3.181079000	1.291636000	-1.625387000
6	0.507613000	1.958787000	-0.861807000
6	-0.685902000	1.957364000	-0.259955000
16	-0.778068000	0.546258000	0.860679000
1	0.780713000	2.690397000	-1.613791000
6	-1.878143000	2.837395000	-0.380196000
1	-2.159775000	3.234550000	0.597749000
1	-1.646512000	3.668587000	-1.045395000
1	-2.732009000	2.289153000	-0.783687000
8	-1.126689000	0.920246000	2.257852000
8	-1.588216000	-1.267572000	0.286344000
1	-2.488110000	-0.942141000	0.105397000
17	-2.188308000	-3.224803000	-0.090685000



post-TS2a

6	2.625409000	0.518896000	-1.072579000
6	3.341627000	-0.507879000	-0.452176000
6	1.370554000	0.848537000	-0.581891000
1	4.321521000	-0.773420000	-0.829597000
6	2.820422000	-1.197665000	0.639152000

6	0.876651000	0.144232000	0.514873000
1	3.394417000	-1.990027000	1.102389000
6	1.557405000	-0.875884000	1.143695000
1	1.134008000	-1.407005000	1.987343000
1	3.037926000	1.046777000	-1.923996000
6	0.437126000	1.875597000	-1.090469000
6	-0.727595000	1.964689000	-0.448577000
16	-0.764243000	0.736379000	0.861905000
1	0.695718000	2.506302000	-1.932868000
6	-1.920259000	2.833335000	-0.632009000
1	-2.111811000	3.417973000	0.270881000
1	-1.753164000	3.513362000	-1.466304000
1	-2.806733000	2.228668000	-0.838282000
8	-0.889182000	1.355089000	2.177156000
8	-1.752091000	-0.308366000	0.532325000
1	-1.269395000	-1.438192000	-0.832485000
17	-0.739240000	-2.105556000	-1.821632000

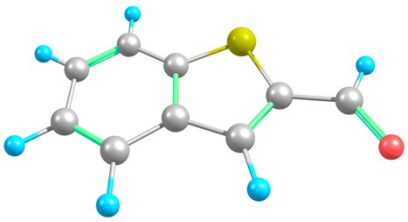


Sulfone

6	-2.140407000	1.476787000	0.000027000
6	-3.212376000	0.581138000	-0.000013000
6	-0.847394000	0.972675000	-0.000034000
1	-4.224827000	0.965911000	0.000044000
6	-3.004138000	-0.795580000	-0.000097000
6	-0.668342000	-0.409628000	-0.000199000
1	-3.850761000	-1.470333000	-0.000110000
6	-1.706808000	-1.316104000	-0.000156000
1	-1.527293000	-2.384302000	-0.000252000
1	-2.311914000	2.546654000	0.000143000
6	0.422037000	1.729848000	0.000120000
6	1.531409000	0.991548000	0.000209000
16	1.081153000	-0.749454000	0.000044000
1	0.432900000	2.813479000	0.000172000
6	2.976365000	1.342947000	-0.000089000
1	3.469990000	0.933727000	-0.884924000
1	3.092471000	2.426050000	0.001460000
1	3.471124000	0.931049000	0.882854000

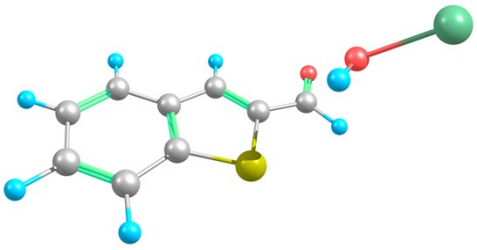
8	1.503302000	-1.388172000	-1.246768000
8	1.502670000	-1.388423000	1.246932000

XYZ Coordinates for the chlorination of benzo[b]thiophene-2-carbaldehyde (3)



Starting Material (3)

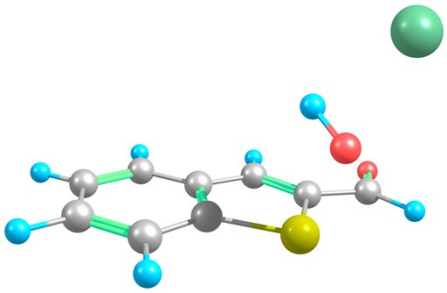
6	-1.700201000	1.606541000	0.000004000
6	-2.966708000	1.061401000	-0.000076000
6	-0.582325000	0.750508000	0.000061000
1	-3.833915000	1.710162000	-0.000153000
6	-3.149667000	-0.335711000	-0.000067000
6	-0.785029000	-0.646563000	0.000042000
1	-4.154329000	-0.740976000	-0.000092000
6	-2.071034000	-1.199529000	0.000018000
1	-2.215089000	-2.272830000	0.000042000
1	-1.554557000	2.680455000	-0.000025000
6	0.808553000	1.087223000	0.000080000
6	1.613285000	-0.010326000	0.000082000
16	0.720896000	-1.514685000	0.000059000
1	1.195303000	2.098176000	-0.000062000
6	3.082652000	-0.015147000	-0.000220000
1	3.565101000	-1.006798000	-0.000950000
8	3.745747000	0.997047000	0.000094000



pre-TS1

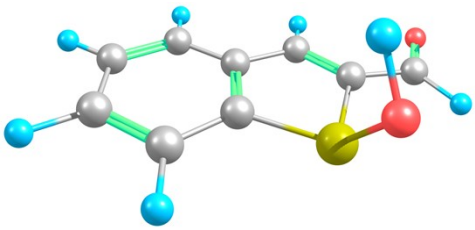
6	2.977243000	0.734581000	-1.160326000
6	3.970131000	-0.209518000	-0.997384000
6	1.792766000	0.623627000	-0.409173000
1	4.885764000	-0.133979000	-1.570880000
6	3.809016000	-1.274886000	-0.090943000
6	1.649651000	-0.450628000	0.494205000
1	4.602161000	-2.004392000	0.020005000
6	2.655866000	-1.407845000	0.660379000
1	2.534707000	-2.227955000	1.357165000
1	3.097334000	1.556185000	-1.856803000
6	0.639385000	1.473983000	-0.415479000
6	-0.325985000	1.055873000	0.444662000
16	0.116863000	-0.396407000	1.317848000
1	0.532482000	2.356701000	-1.032780000

6	-1.627523000	1.701000000	0.684583000
1	-2.266998000	1.230659000	1.447958000
8	-2.571033000	-0.674128000	-0.456331000
1	-1.994010000	-1.434243000	-0.285682000
17	-4.120546000	-1.331401000	-0.678003000
8	-1.985875000	2.693657000	0.093625000



TS1

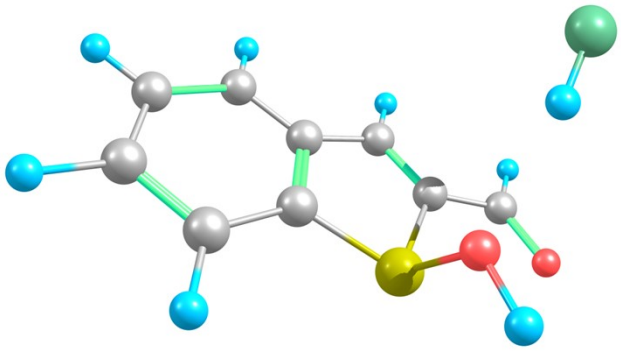
6	2.881491000	0.249632000	-0.998326000
6	3.520137000	-0.941260000	-0.682082000
6	1.659707000	0.542060000	-0.387976000
1	4.466869000	-1.180909000	-1.149550000
6	2.960461000	-1.838285000	0.234910000
6	1.118099000	-0.372712000	0.533079000
1	3.478646000	-2.760597000	0.465721000
6	1.748467000	-1.565446000	0.860135000
1	1.316073000	-2.257316000	1.571552000
1	3.316272000	0.946467000	-1.704374000
6	0.814752000	1.699656000	-0.560767000
6	-0.311309000	1.662126000	0.189119000
16	-0.410265000	0.203711000	1.177014000
1	1.045440000	2.526807000	-1.220659000
6	-1.375678000	2.680968000	0.248142000
1	-2.213715000	2.474157000	0.932239000
8	-1.804610000	-0.939418000	0.197836000
1	-1.438071000	-0.827807000	-0.697622000
17	-3.315867000	-2.168655000	-0.700197000
8	-1.337175000	3.687735000	-0.415786000



post-TS1

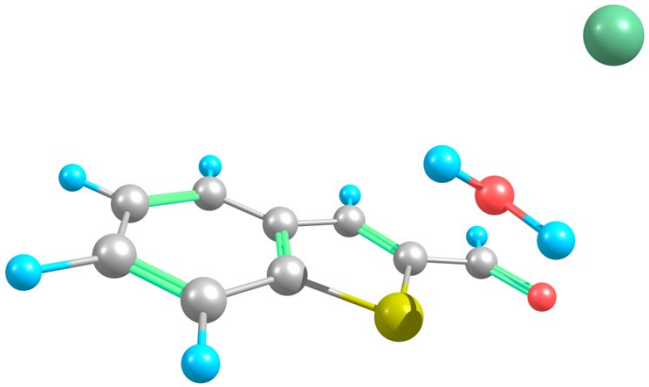
6	1.953815000	1.477570000	-1.035398000
6	3.192237000	0.969872000	-0.640714000
6	0.818852000	1.056711000	-0.355998000
1	4.085823000	1.279254000	-1.167877000
6	3.300105000	0.073996000	0.419584000

6	0.957465000	0.162464000	0.710755000
1	4.272316000	-0.306093000	0.706255000
6	2.169196000	-0.338162000	1.132216000
1	2.247657000	-1.024877000	1.965192000
1	1.873615000	2.179098000	-1.856359000
6	-0.572655000	1.399155000	-0.613148000
6	-1.458186000	0.785592000	0.190811000
16	-0.628953000	-0.184675000	1.449054000
1	-0.882337000	2.091184000	-1.388104000
6	-2.927873000	0.935110000	0.190876000
1	-3.475877000	0.443799000	1.009109000
8	-0.949972000	-1.713390000	1.158668000
1	-0.755694000	-1.961100000	0.151043000
17	-0.372582000	-2.215886000	-1.560500000
8	-3.495789000	1.562108000	-0.667359000



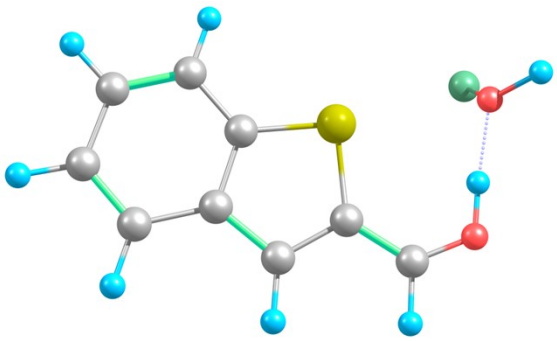
pre-TS2

6	-2.425019000	-1.096725000	1.148279000
6	-3.557892000	-0.925735000	0.346879000
6	-1.293397000	-0.352350000	0.858438000
1	-4.447165000	-1.506296000	0.556624000
6	-3.566041000	-0.021662000	-0.708925000
6	-1.329910000	0.553343000	-0.210587000
1	-4.456771000	0.094960000	-1.312518000
6	-2.438277000	0.755633000	-1.001391000
1	-2.444207000	1.471921000	-1.812615000
1	-2.427234000	-1.792734000	1.977469000
6	-0.000027000	-0.364389000	1.534171000
6	0.903708000	0.479580000	1.011740000
16	0.215574000	1.419838000	-0.346319000
1	0.218050000	-1.004531000	2.381919000
6	2.310442000	0.720935000	1.352070000
1	2.706382000	0.112781000	2.178219000
8	0.917465000	0.686919000	-1.625205000
1	1.861134000	-1.159489000	-1.406376000
1	1.285908000	1.356795000	-2.226534000
17	2.439718000	-2.144665000	-0.808308000
8	2.977283000	1.522669000	0.745470000



TS2

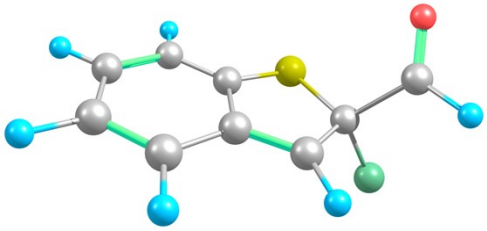
6	-2.806710000	0.132110000	1.336137000
6	-3.662796000	-0.776484000	0.698892000
6	-1.635058000	0.502948000	0.696559000
1	-4.578667000	-1.075402000	1.192367000
6	-3.361971000	-1.292192000	-0.556684000
6	-1.343466000	-0.036360000	-0.573582000
1	-4.042027000	-1.987654000	-1.030955000
6	-2.189029000	-0.924426000	-1.222795000
1	-1.951355000	-1.322453000	-2.200916000
1	-3.057456000	0.543570000	2.305834000
6	-0.611144000	1.430370000	1.134132000
6	0.396061000	1.573651000	0.240817000
16	0.155403000	0.597098000	-1.195620000
1	-0.642235000	1.957614000	2.080188000
6	1.632666000	2.358335000	0.348372000
1	1.720287000	2.980485000	1.251102000
8	1.678738000	-0.927646000	-0.388996000
1	1.078818000	-1.699114000	-0.339355000
1	2.194715000	-1.040981000	-1.212819000
17	3.229394000	-2.161677000	0.679262000
8	2.493819000	2.306542000	-0.495262000



post-TS2 – Chlorination stops here

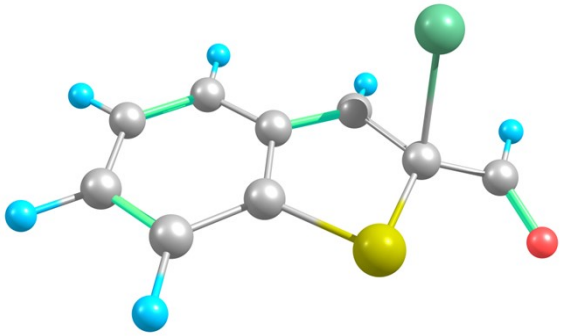
6	-3.518016000	0.768668000	0.336719000
6	-4.253566000	-0.384738000	0.225554000
6	-2.118562000	0.704244000	0.144131000
1	-5.326077000	-0.361893000	0.368836000

6	-3.622994000	-1.613248000	-0.076163000
6	-1.503804000	-0.537167000	-0.157673000
1	-4.228170000	-2.508190000	-0.157067000
6	-2.258976000	-1.708173000	-0.270411000
1	-1.790901000	-2.656237000	-0.500417000
1	-3.985295000	1.718126000	0.567479000
6	-1.175695000	1.746951000	0.211882000
6	0.121711000	1.314677000	-0.032079000
16	0.214033000	-0.407595000	-0.360520000
1	-1.416493000	2.780128000	0.431864000
6	1.184206000	2.219125000	0.016345000
1	0.957229000	3.260446000	0.232458000
8	3.230718000	-0.453079000	-0.682116000
1	3.885183000	-0.586947000	-1.385524000
1	2.682409000	1.045097000	-0.358357000
17	3.730986000	-1.383192000	0.641861000
8	2.424908000	1.988481000	-0.159435000



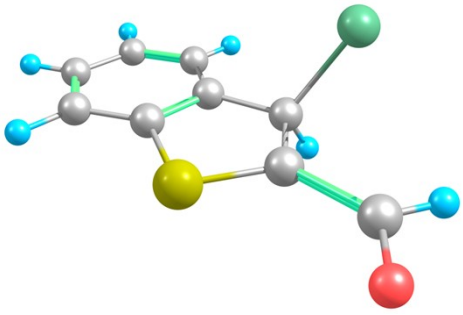
pre-TS3

6	-2.212689000	-1.443478000	0.560482000
6	-3.397164000	-0.821607000	0.332285000
6	-0.998583000	-0.732251000	0.265584000
1	-4.334289000	-1.318810000	0.541708000
6	-3.420668000	0.507076000	-0.190399000
6	-1.052337000	0.613991000	-0.270123000
1	-4.384935000	0.971454000	-0.362941000
6	-2.282304000	1.230195000	-0.488607000
1	-2.346907000	2.234545000	-0.883807000
1	-2.152182000	-2.448640000	0.957294000
6	0.271466000	-1.174598000	0.428291000
6	1.325206000	-0.189283000	0.057598000
16	0.485168000	1.299848000	-0.576894000
1	0.552499000	-2.153638000	0.802320000
6	2.229390000	0.121624000	1.295284000
1	2.810134000	-0.753890000	1.624676000
17	2.411991000	-0.915169000	-1.164089000
8	2.289406000	1.194910000	1.799775000



TS3

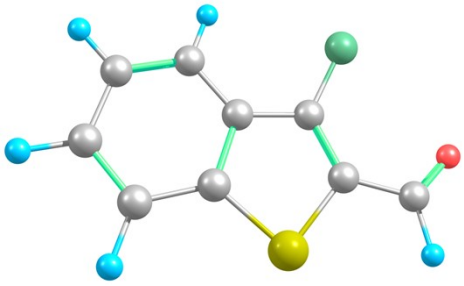
6	-2.138981000	1.251720000	-0.714016000
6	-3.344798000	0.638980000	-0.429724000
6	-0.956959000	0.556607000	-0.425540000
1	-4.275001000	1.148940000	-0.641617000
6	-3.370046000	-0.640797000	0.139390000
6	-0.997482000	-0.734162000	0.140029000
1	-4.325281000	-1.102985000	0.357124000
6	-2.204193000	-1.344630000	0.433853000
1	-2.247280000	-2.334412000	0.868399000
1	-2.094639000	2.244297000	-1.144422000
6	0.376727000	0.997172000	-0.657939000
6	1.360322000	0.005772000	-0.198203000
16	0.601999000	-1.449912000	0.374967000
1	0.655482000	1.807728000	-1.321051000
6	2.774067000	-0.080940000	-0.765404000
1	3.189096000	0.867439000	-1.135613000
17	1.392013000	1.508906000	1.068348000
8	3.351185000	-1.122769000	-0.784861000



post-TS3

6	2.030529000	1.223801000	0.421861000
6	3.260223000	0.611598000	0.182023000
6	0.881677000	0.461936000	0.302943000
1	4.167313000	1.196210000	0.268420000
6	3.346427000	-0.737655000	-0.164886000
6	0.988862000	-0.884299000	-0.051491000
1	4.315064000	-1.186348000	-0.342713000
6	2.201899000	-1.516837000	-0.287728000
1	2.254326000	-2.564293000	-0.553663000
1	1.972327000	2.271811000	0.689112000

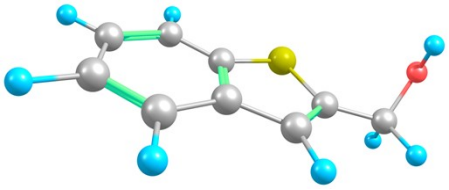
6	-0.533968000	0.889490000	0.532387000
6	-1.400482000	-0.296673000	0.249846000
16	-0.593060000	-1.650833000	-0.162299000
1	-0.705052000	1.221096000	1.562723000
6	-2.905166000	-0.285092000	0.340923000
1	-3.348758000	0.645025000	0.720383000
17	-1.061692000	2.235164000	-0.532375000
8	-3.542189000	-1.245696000	0.018454000



Product (not observed)

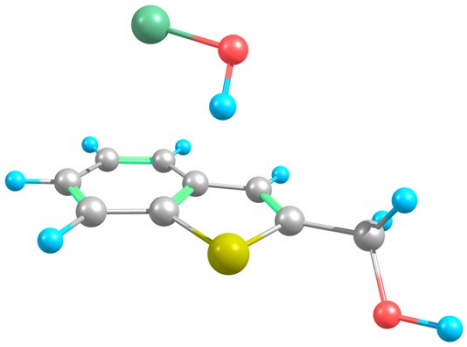
6	1.672378000	1.519695000	-0.000113000
6	3.016776000	1.214327000	-0.000182000
6	0.738811000	0.469180000	0.000041000
1	3.749606000	2.011493000	-0.000292000
6	3.452727000	-0.125263000	-0.000113000
6	1.186301000	-0.865185000	0.000063000
1	4.514607000	-0.339001000	-0.000157000
6	2.551696000	-1.172325000	0.000028000
1	2.888809000	-2.201224000	0.000092000
1	1.329822000	2.547484000	-0.000106000
6	-0.694091000	0.530944000	0.000173000
6	-1.300410000	-0.691566000	0.000191000
16	-0.132046000	-1.995060000	0.000112000
6	-2.729632000	-1.033352000	-0.000236000
1	-2.945176000	-2.115285000	-0.000495000
17	-1.516790000	2.042432000	0.000130000
8	-3.625852000	-0.222824000	-0.000271000

XYZ Coordinates for the chlorination of benzo[b]thiophene-2-methanol (1)



Starting material (1)

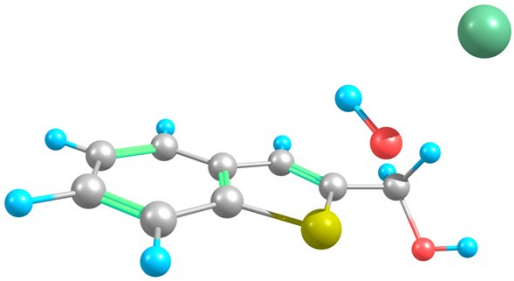
6	2.012664000	1.481381000	0.059720000
6	3.188996000	0.758883000	0.145771000
6	0.789883000	0.799186000	-0.042430000
1	4.136004000	1.279076000	0.224196000
6	3.171578000	-0.646079000	0.133730000
6	0.791948000	-0.609450000	-0.054837000
1	4.103747000	-1.193885000	0.202179000
6	1.978033000	-1.342190000	0.035798000
1	1.964678000	-2.425368000	0.027106000
1	2.025583000	2.565329000	0.070873000
6	-0.545907000	1.333149000	-0.134085000
6	-1.498168000	0.375285000	-0.220328000
16	-0.829195000	-1.244324000	-0.183715000
1	-0.772049000	2.392374000	-0.135581000
6	-2.979625000	0.568774000	-0.346628000
1	-3.189753000	1.642227000	-0.317686000
1	-3.334884000	0.177928000	-1.301746000
8	-3.710537000	-0.130247000	0.649690000
1	-3.438307000	0.199847000	1.512302000



pre-TS1

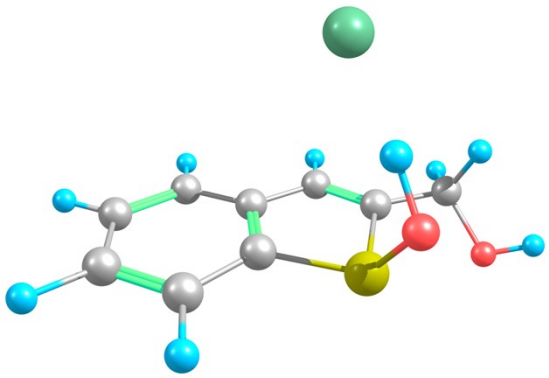
6	1.516054000	-1.277837000	1.450784000
6	2.626766000	-1.615519000	0.699118000
6	0.341595000	-0.872167000	0.799071000
1	3.538098000	-1.926104000	1.195771000
6	2.589026000	-1.564620000	-0.704115000
6	0.324486000	-0.823357000	-0.607806000
1	3.469682000	-1.835383000	-1.273998000
6	1.440007000	-1.173685000	-1.371329000
1	1.409391000	-1.133294000	-2.453377000
1	1.544444000	-1.320030000	2.533579000

6	-0.926460000	-0.484040000	1.366718000
6	-1.846385000	-0.145362000	0.436649000
16	-1.234909000	-0.290320000	-1.203974000
1	-1.124656000	-0.456812000	2.430954000
6	-3.230591000	0.371875000	0.657089000
1	-3.488372000	0.233736000	1.711472000
1	-3.262305000	1.443312000	0.430742000
8	0.414744000	2.469647000	-0.055299000
1	0.049445000	1.739876000	-0.583800000
17	2.072657000	2.131301000	0.064175000
8	-4.120410000	-0.336003000	-0.194470000
1	-4.974019000	0.106820000	-0.177646000



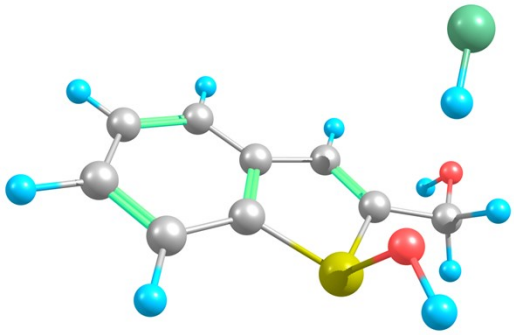
TS1

6	2.987935000	0.325324000	-1.082462000
6	3.762589000	-0.675954000	-0.507719000
6	1.715069000	0.574739000	-0.570732000
1	4.751205000	-0.877731000	-0.901267000
6	3.287966000	-1.424563000	0.573538000
6	1.256516000	-0.192042000	0.513529000
1	3.909601000	-2.198436000	1.006119000
6	2.024265000	-1.187362000	1.104403000
1	1.651776000	-1.761814000	1.943191000
1	3.363182000	0.908188000	-1.915098000
6	0.734004000	1.560173000	-0.995326000
6	-0.403843000	1.534532000	-0.280408000
16	-0.354030000	0.313735000	1.000687000
1	0.897260000	2.245813000	-1.817345000
6	-1.663236000	2.316024000	-0.454550000
1	-1.473863000	3.125321000	-1.165836000
1	-2.439081000	1.661912000	-0.867452000
8	-1.679093000	-1.065333000	0.167803000
1	-1.170652000	-1.197742000	-0.651757000
17	-3.128815000	-2.410753000	-0.592353000
8	-2.055771000	2.809223000	0.815924000
1	-2.963753000	3.121203000	0.756994000



post-TS1

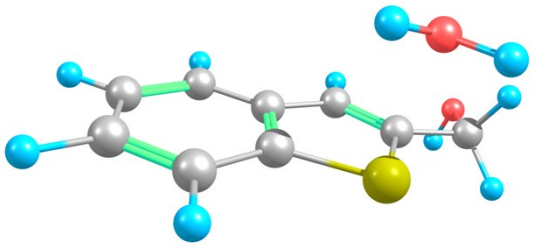
6	-2.325168000	-0.898733000	-1.312977000
6	-3.447103000	-0.593971000	-0.539319000
6	-1.068241000	-0.780829000	-0.739035000
1	-4.432698000	-0.670605000	-0.981431000
6	-3.323618000	-0.197421000	0.789382000
6	-0.972274000	-0.378747000	0.596542000
1	-4.208222000	0.033557000	1.368877000
6	-2.066007000	-0.103366000	1.391120000
1	-1.959267000	0.188160000	2.428332000
1	-2.430001000	-1.216603000	-2.342929000
6	0.244172000	-1.004870000	-1.355116000
6	1.282288000	-0.773779000	-0.550505000
16	0.729611000	-0.411907000	1.122872000
1	0.357895000	-1.305767000	-2.389773000
6	2.753568000	-0.763042000	-0.787133000
1	2.953855000	-1.217337000	-1.761723000
1	3.101819000	0.276126000	-0.808753000
8	1.181892000	1.085895000	1.427174000
1	0.913948000	1.730555000	0.646700000
17	0.405568000	2.713566000	-0.763350000
8	3.363592000	-1.475146000	0.274424000
1	4.304667000	-1.275634000	0.281151000



pre-TS2

6	2.136194000	0.124404000	-1.741017000
6	3.385224000	-0.239192000	-1.226053000
6	1.109146000	0.401345000	-0.855539000
1	4.192959000	-0.464764000	-1.911003000
6	3.613810000	-0.310894000	0.143561000

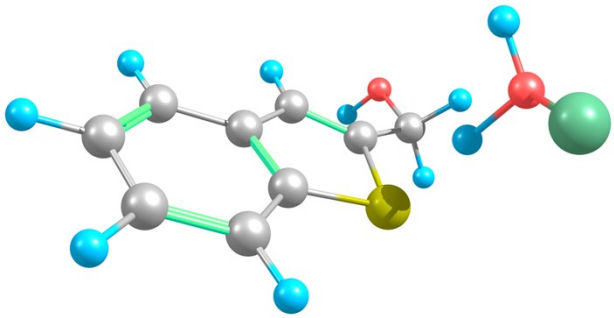
6	1.369553000	0.322876000	0.516214000
1	4.590341000	-0.591988000	0.515684000
6	2.594845000	-0.011005000	1.053267000
1	2.763556000	-0.047532000	2.121783000
1	1.973592000	0.189180000	-2.809488000
6	-0.278481000	0.784662000	-1.144983000
6	-1.043920000	0.989798000	-0.071700000
16	-0.079421000	0.787406000	1.427164000
1	-0.664275000	0.873951000	-2.152920000
6	-2.505291000	1.328809000	0.045608000
1	-2.631505000	2.240822000	0.637197000
1	-3.018789000	0.517991000	0.569610000
8	-0.669096000	-0.642191000	1.962121000
1	-1.455128000	-1.993188000	0.634140000
1	-0.807988000	-0.607278000	2.923605000
17	-1.943143000	-2.453552000	-0.467992000
8	-3.087409000	1.436276000	-1.227318000
1	-2.873036000	2.297186000	-1.601940000



TS2

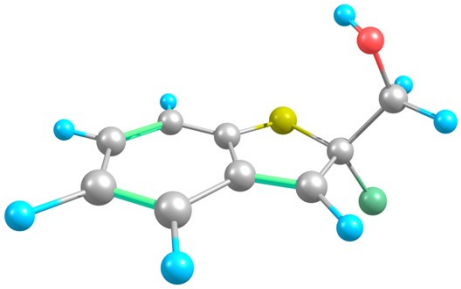
6	2.520885000	0.442886000	-1.384225000
6	3.509658000	-0.459069000	-0.965523000
6	1.407763000	0.637844000	-0.581537000
1	4.380170000	-0.616491000	-1.589755000
6	3.396115000	-1.146375000	0.236312000
6	1.313033000	-0.071831000	0.627914000
1	4.173817000	-1.833490000	0.543357000
6	2.283184000	-0.958727000	1.064153000
1	2.187954000	-1.487970000	2.003908000
1	2.626452000	0.983308000	-2.316858000
6	0.267019000	1.515164000	-0.784041000
6	-0.645299000	1.468906000	0.213322000
16	-0.163507000	0.355410000	1.466512000
1	0.149101000	2.156259000	-1.648123000
6	-1.951053000	2.214272000	0.324501000
1	-2.032002000	2.679310000	1.311533000
1	-2.777746000	1.507271000	0.221334000

8	-1.471384000	-1.376424000	0.470167000
1	-0.772682000	-2.057003000	0.539532000
1	-2.056052000	-1.519165000	1.241369000
17	-2.699014000	-2.676682000	-0.813236000
8	-2.084844000	3.154516000	-0.712151000
1	-1.537663000	3.921832000	-0.514867000



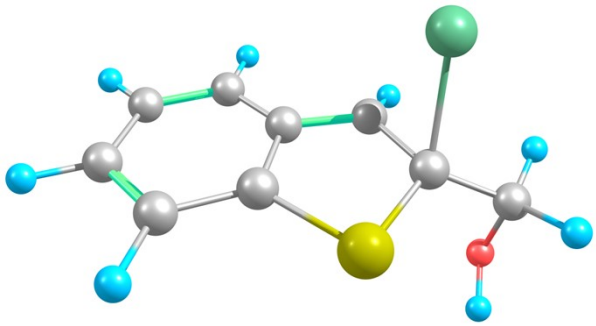
post-TS2

6	-0.366267000	2.828727000	-0.833095000
6	0.837782000	3.449148000	-0.532228000
6	-0.635642000	1.566955000	-0.294884000
1	1.053938000	4.426186000	-0.946619000
6	1.778329000	2.832767000	0.300685000
6	0.321772000	0.973140000	0.538633000
1	2.711287000	3.335393000	0.523263000
6	1.529658000	1.581525000	0.852628000
1	2.251620000	1.101859000	1.501705000
1	-1.093221000	3.308709000	-1.477291000
6	-1.810644000	0.732896000	-0.474993000
6	-1.759173000	-0.437525000	0.180139000
16	-0.257167000	-0.594881000	1.123642000
1	-2.655399000	1.019864000	-1.087632000
6	-2.777337000	-1.544264000	0.226941000
1	-2.993992000	-1.802410000	1.268746000
1	-2.370489000	-2.436134000	-0.255258000
8	1.205357000	-2.333713000	-0.657069000
1	1.014203000	-2.126722000	-1.594951000
1	0.645296000	-1.657564000	0.025952000
17	2.894317000	-2.279416000	-0.392617000
8	-3.946630000	-1.198884000	-0.477263000
1	-4.432657000	-0.540449000	0.030003000



pre-TS3

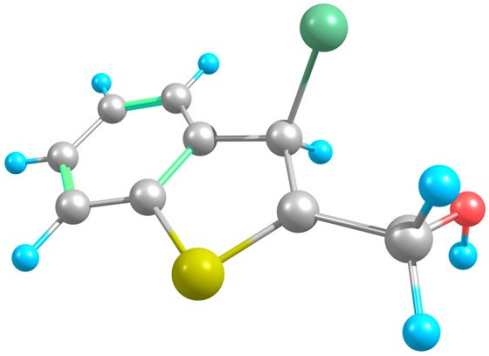
6	2.135811000	1.510407000	0.411124000
6	3.339897000	0.913482000	0.215259000
6	0.944562000	0.754317000	0.141272000
1	4.261220000	1.444871000	0.410578000
6	3.403419000	-0.432830000	-0.252429000
6	1.038156000	-0.608316000	-0.339490000
1	4.381184000	-0.877002000	-0.400475000
6	2.286783000	-1.197599000	-0.528883000
1	2.381396000	-2.214311000	-0.884646000
1	2.045365000	2.528799000	0.766992000
6	-0.339182000	1.161457000	0.293862000
6	-1.373837000	0.135992000	-0.004028000
16	-0.481875000	-1.340952000	-0.633523000
1	-0.645922000	2.144428000	0.636481000
6	-2.192027000	-0.216151000	1.273299000
1	-2.694245000	0.698145000	1.591359000
1	-2.944279000	-0.958483000	0.999405000
17	-2.501417000	0.778442000	-1.232245000
8	-1.353472000	-0.636034000	2.308943000
1	-1.184342000	-1.581017000	2.233376000



TS3

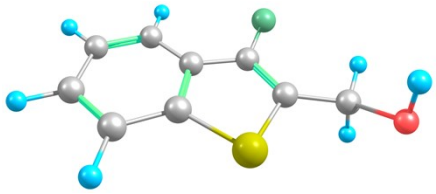
6	2.038758000	1.162040000	0.955625000
6	3.283815000	0.619569000	0.693335000
6	0.908200000	0.504594000	0.456923000
1	4.175510000	1.102908000	1.069718000
6	3.397647000	-0.553092000	-0.063217000
6	1.037028000	-0.678267000	-0.296220000
1	4.381299000	-0.961935000	-0.260156000
6	2.282877000	-1.216396000	-0.571024000
1	2.392275000	-2.123706000	-1.150272000

1	1.927902000	2.072618000	1.531111000
6	-0.458632000	0.880759000	0.634861000
6	-1.382860000	-0.037967000	-0.040759000
16	-0.517298000	-1.355702000	-0.795702000
1	-0.812595000	1.567060000	1.395695000
6	-2.801655000	-0.268155000	0.463072000
1	-3.236941000	0.695542000	0.724822000
1	-3.401386000	-0.730503000	-0.322389000
17	-1.322405000	1.640098000	-1.065567000
8	-2.727943000	-1.039537000	1.631911000
1	-2.675940000	-1.974614000	1.406485000



post-TS3

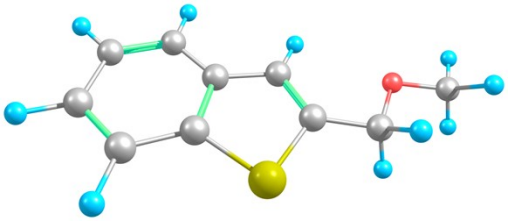
6	1.814295000	1.422459000	0.497822000
6	3.150722000	1.048592000	0.368623000
6	0.834877000	0.469376000	0.270407000
1	3.926180000	1.784542000	0.539163000
6	3.506103000	-0.255437000	0.025463000
6	1.212616000	-0.824564000	-0.075743000
1	4.551019000	-0.522520000	-0.066693000
6	2.532925000	-1.224661000	-0.201816000
1	2.797830000	-2.240141000	-0.465438000
1	1.543062000	2.437298000	0.763082000
6	-0.648787000	0.640027000	0.369449000
6	-1.279958000	-0.679857000	0.026656000
16	-0.206171000	-1.869594000	-0.296499000
1	-0.980417000	0.933769000	1.369843000
6	-2.770123000	-0.852008000	-0.031887000
1	-3.074645000	-0.536132000	-1.036590000
1	-3.039323000	-1.904173000	0.081357000
17	-1.287307000	1.885122000	-0.755012000
8	-3.404133000	-0.013132000	0.893281000
1	-3.423703000	-0.444723000	1.754384000



Product 4 (not obtained in the chlorination since oxidation was observed)

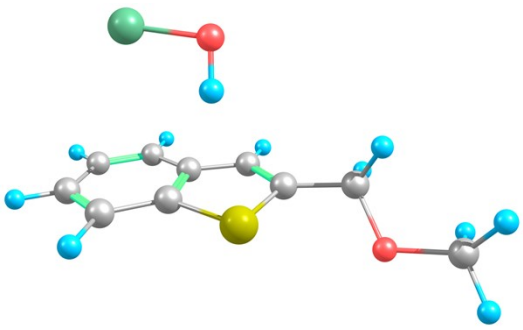
6	-2.027723000	1.265148000	0.087523000
6	-3.276964000	0.673311000	0.130843000
6	-0.893325000	0.447926000	-0.005974000
1	-4.162429000	1.292937000	0.201892000
6	-3.413500000	-0.724073000	0.083081000
6	-1.041699000	-0.948880000	-0.055769000
1	-4.401716000	-1.166305000	0.117347000
6	-2.302990000	-1.546568000	-0.008096000
1	-2.408193000	-2.623942000	-0.044839000
1	-1.917154000	2.342511000	0.124755000
6	0.499985000	0.811525000	-0.057968000
6	1.355312000	-0.232607000	-0.145496000
16	0.501304000	-1.759106000	-0.163807000
6	2.851531000	-0.220093000	-0.262125000
1	3.139881000	-0.378293000	-1.303308000
1	3.223656000	0.760046000	0.047643000
17	1.002562000	2.471768000	-0.018529000
8	3.456985000	-1.267638000	0.473161000
1	3.301894000	-1.114340000	1.411031000

XYZ Coordinates for the chlorination of benzo[b]thiophene-2-methoxymethyl ether (not synthesized)



Starting Material

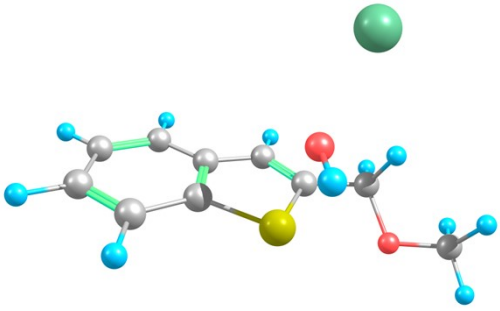
6	2.030718000	1.703443000	0.000007000
6	3.359126000	1.314770000	0.000098000
6	1.024609000	0.725241000	-0.000066000
1	4.139558000	2.066204000	0.000148000
6	3.709835000	-0.044959000	0.000123000
6	1.396656000	-0.632615000	-0.000044000
1	4.755125000	-0.329571000	0.000177000
6	2.734866000	-1.030077000	0.000056000
1	3.004353000	-2.079316000	0.000043000
1	1.760901000	2.753449000	-0.000001000
6	-0.408533000	0.893384000	-0.000127000
6	-1.077338000	-0.281014000	-0.000059000
16	-0.009866000	-1.670407000	-0.000254000
1	-0.907764000	1.852606000	-0.000108000
6	-2.560028000	-0.493988000	0.000045000
1	-2.855739000	-1.074236000	0.885512000
1	-2.855858000	-1.074185000	-0.885415000
8	-3.197489000	0.758779000	0.000126000
6	-4.606546000	0.631151000	0.000265000
1	-4.950511000	0.096149000	-0.891741000
1	-4.950334000	0.096142000	0.892335000
1	-5.022146000	1.637007000	0.000310000



pre TS1

6	1.921515000	-1.265677000	1.444872000
6	3.036145000	-1.580235000	0.688965000
6	0.737893000	-0.879666000	0.797744000
1	3.954451000	-1.875610000	1.182035000
6	2.993384000	-1.525566000	-0.714004000
6	0.715967000	-0.826360000	-0.608816000
1	3.877257000	-1.778146000	-1.287245000

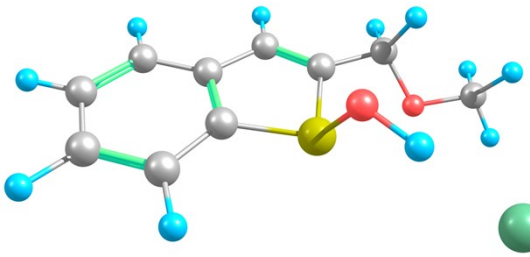
6	1.835532000	-1.153397000	-1.376694000
1	1.801178000	-1.109997000	-2.458506000
1	1.953728000	-1.310956000	2.527432000
6	-0.535194000	-0.515885000	1.370516000
6	-1.463262000	-0.190256000	0.444045000
16	-0.854067000	-0.317604000	-1.198433000
1	-0.730272000	-0.494867000	2.435451000
6	-2.855294000	0.300999000	0.669205000
1	-3.117195000	0.160388000	1.725258000
1	-2.917147000	1.374928000	0.443174000
8	0.735704000	2.471267000	-0.039835000
1	0.379716000	1.739415000	-0.571773000
17	2.401198000	2.164012000	0.059965000
8	-3.738847000	-0.410927000	-0.170385000
6	-5.067325000	0.063814000	-0.057655000
1	-5.438106000	-0.053728000	0.966436000
1	-5.128503000	1.120518000	-0.340273000
1	-5.681422000	-0.527844000	-0.733771000



TS1

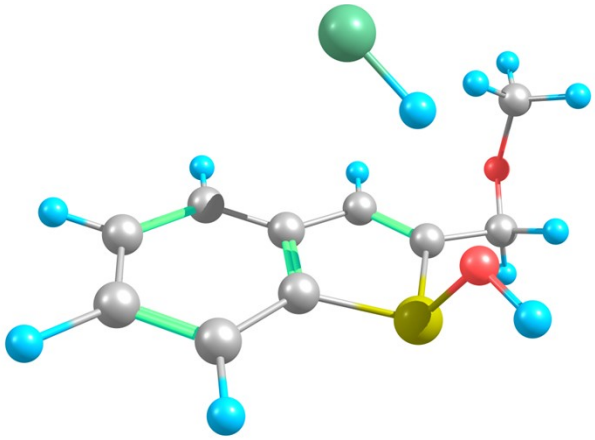
6	2.916931000	-1.010542000	1.211226000
6	4.002685000	-0.512599000	0.498611000
6	1.636966000	-0.876454000	0.676113000
1	5.000214000	-0.608834000	0.909334000
6	3.827786000	0.107395000	-0.741621000
6	1.483963000	-0.248204000	-0.570289000
1	4.687470000	0.487093000	-1.279467000
6	2.559471000	0.242352000	-1.298036000
1	2.418393000	0.718262000	-2.260320000
1	3.058074000	-1.497094000	2.168901000
6	0.363251000	-1.315299000	1.226761000
6	-0.691216000	-1.030152000	0.446466000
16	-0.203935000	-0.218661000	-1.046503000
1	0.271346000	-1.816231000	2.182410000
6	-2.149637000	-1.211248000	0.695257000
1	-2.288776000	-1.874876000	1.557191000
1	-2.601940000	-0.237365000	0.930971000
8	-0.786095000	1.644483000	-0.309478000
1	-0.971063000	2.037662000	-1.179580000

17	-1.373837000	3.463223000	0.597238000
8	-2.741091000	-1.745098000	-0.467938000
6	-4.149405000	-1.840462000	-0.349531000
1	-4.426299000	-2.502751000	0.477464000
1	-4.592397000	-0.852903000	-0.182311000
1	-4.524132000	-2.252980000	-1.284013000



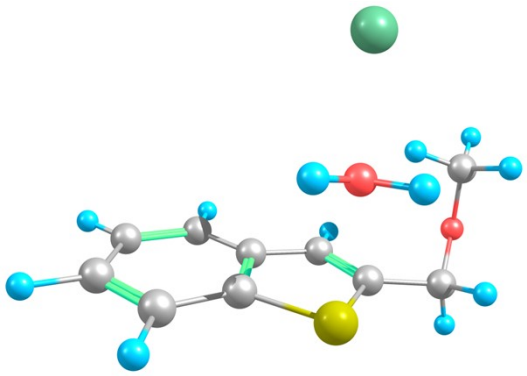
post-TS1

6	-3.479568000	-1.053294000	-0.167167000
6	-4.308141000	0.055045000	0.024428000
6	-2.105773000	-0.876796000	-0.102395000
1	-5.382168000	-0.070423000	-0.033682000
6	-3.781577000	1.315524000	0.291042000
6	-1.603630000	0.399207000	0.171907000
1	-4.444285000	2.159271000	0.434008000
6	-2.400242000	1.504602000	0.386278000
1	-1.978662000	2.476515000	0.609537000
1	-3.898482000	-2.031986000	-0.366034000
6	-1.041307000	-1.871008000	-0.297862000
6	0.194949000	-1.384730000	-0.185269000
16	0.166719000	0.342692000	0.301885000
1	-1.248582000	-2.907133000	-0.536986000
6	1.546840000	-1.970599000	-0.407883000
1	1.473696000	-3.063672000	-0.438874000
1	1.937005000	-1.621975000	-1.374816000
8	0.700972000	1.107545000	-0.999004000
1	1.555163000	1.634942000	-0.718848000
17	3.046946000	2.427297000	-0.076276000
8	2.378706000	-1.523102000	0.636329000
6	3.743818000	-1.831857000	0.406732000
1	3.890004000	-2.914282000	0.336692000
1	4.095443000	-1.357363000	-0.515138000
1	4.305651000	-1.443115000	1.253201000



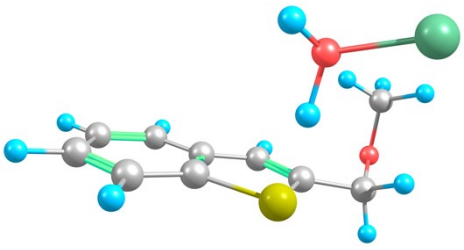
pre-TS2

6	-1.958605000	0.316263000	-1.837134000
6	-3.269107000	0.288435000	-1.348183000
6	-0.951711000	-0.235399000	-1.064727000
1	-4.062653000	0.727318000	-1.940007000
6	-3.575950000	-0.293062000	-0.122795000
6	-1.291263000	-0.818180000	0.160302000
1	-4.598185000	-0.300953000	0.232206000
6	-2.575526000	-0.880858000	0.657755000
1	-2.802180000	-1.350004000	1.606570000
1	-1.732810000	0.764958000	-2.796348000
6	0.490445000	-0.290125000	-1.332217000
6	1.220033000	-0.879511000	-0.382923000
16	0.159632000	-1.489850000	0.927775000
1	0.941851000	0.134782000	-2.220992000
6	2.708923000	-1.091661000	-0.279740000
1	2.953866000	-2.110527000	-0.587463000
1	3.031637000	-0.964189000	0.761986000
8	0.513107000	-0.402392000	2.097879000
1	0.149873000	1.579047000	1.669557000
1	0.575604000	-0.846074000	2.960462000
17	-0.272286000	2.559289000	0.943682000
8	3.382337000	-0.211841000	-1.133932000
6	3.505543000	1.099419000	-0.596452000
1	2.524790000	1.536595000	-0.383547000
1	4.099613000	1.078849000	0.322161000
1	4.013097000	1.701837000	-1.346471000



TS2

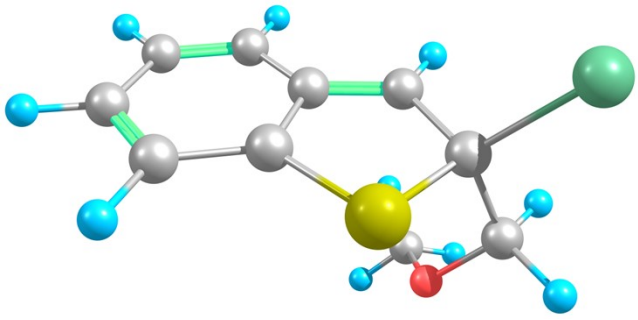
6	-2.372512000	-0.640545000	-1.616624000
6	-3.552431000	0.020589000	-1.249176000
6	-1.366175000	-0.791575000	-0.672641000
1	-4.341321000	0.142343000	-1.980500000
6	-3.728451000	0.512930000	0.037349000
6	-1.562356000	-0.274652000	0.619763000
1	-4.650150000	1.013538000	0.304211000
6	-2.724637000	0.368793000	1.004911000
1	-2.857851000	0.749322000	2.009638000
1	-2.247419000	-1.034354000	-2.617761000
6	-0.082856000	-1.449113000	-0.798516000
6	0.663096000	-1.424747000	0.335664000
16	-0.146337000	-0.572575000	1.610770000
1	0.265127000	-1.920435000	-1.709734000
6	2.051429000	-1.993552000	0.525992000
1	1.978301000	-3.056636000	0.760431000
1	2.553988000	-1.494688000	1.363707000
8	0.820122000	1.491323000	0.806104000
1	0.139687000	2.084039000	1.183050000
1	1.569065000	1.527320000	1.434375000
17	1.648690000	3.070905000	-0.477637000
8	2.803592000	-1.883088000	-0.653040000
6	3.182689000	-0.545971000	-0.943326000
1	2.307304000	0.086158000	-1.129118000
1	3.762834000	-0.123643000	-0.115521000
1	3.797601000	-0.575974000	-1.840164000



post-TS2

6	-2.890781000	-1.100988000	-0.954865000
6	-3.926258000	-0.179215000	-0.916909000
6	-1.722069000	-0.843424000	-0.231131000

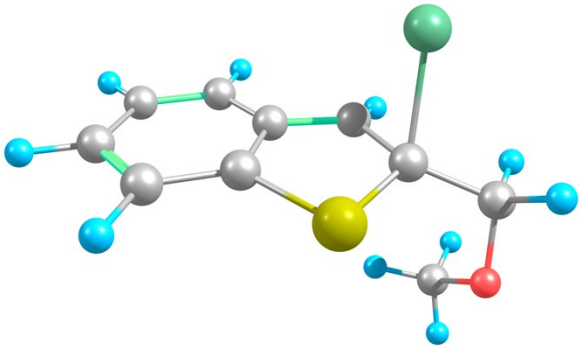
1	-4.834518000	-0.371777000	-1.474630000
6	-3.817339000	0.997410000	-0.166193000
6	-1.638467000	0.341714000	0.513808000
1	-4.638822000	1.702780000	-0.149426000
6	-2.668607000	1.272060000	0.565558000
1	-2.581973000	2.177251000	1.152916000
1	-2.978927000	-2.012830000	-1.533292000
6	-0.525370000	-1.655331000	-0.118532000
6	0.425317000	-1.126597000	0.668824000
16	-0.082949000	0.434405000	1.354276000
1	-0.395897000	-2.603732000	-0.624971000
6	1.773127000	-1.702524000	1.026724000
1	1.689987000	-2.259097000	1.962882000
1	2.505044000	-0.899267000	1.180783000
8	1.225250000	1.940988000	-0.733013000
1	0.736585000	2.750633000	-0.986883000
1	0.740719000	1.422819000	0.115581000
17	2.861938000	2.325483000	-0.424287000
8	2.218162000	-2.603377000	0.046868000
6	2.714314000	-1.953104000	-1.113389000
1	1.942532000	-1.335795000	-1.584340000
1	3.574355000	-1.324076000	-0.860907000
1	3.024631000	-2.731494000	-1.807457000



pre-TS3

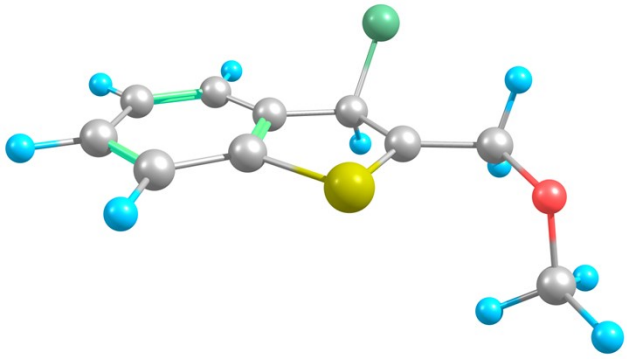
6	-2.169162000	0.429637000	1.486671000
6	-3.385428000	0.297625000	0.898771000
6	-1.005702000	0.010541000	0.755517000
1	-4.286182000	0.604216000	1.412699000
6	-3.491781000	-0.249009000	-0.416811000
6	-1.141940000	-0.551989000	-0.572770000
1	-4.479453000	-0.340038000	-0.854186000
6	-2.405610000	-0.667997000	-1.155710000
1	-2.530231000	-1.079643000	-2.147765000
1	-2.047013000	0.845148000	2.478899000
6	0.288209000	0.071894000	1.160225000
6	1.284084000	-0.350211000	0.145549000
16	0.338530000	-1.043647000	-1.266339000
1	0.624138000	0.425669000	2.129949000

6	2.154174000	0.855153000	-0.354407000
1	2.711883000	1.235506000	0.506720000
1	2.855983000	0.449752000	-1.084694000
17	2.389592000	-1.564165000	0.844539000
8	1.368644000	1.829892000	-0.956391000
6	1.072911000	2.950346000	-0.129878000
1	0.520023000	2.651608000	0.766838000
1	1.991949000	3.462623000	0.164813000
1	0.451678000	3.619222000	-0.720832000



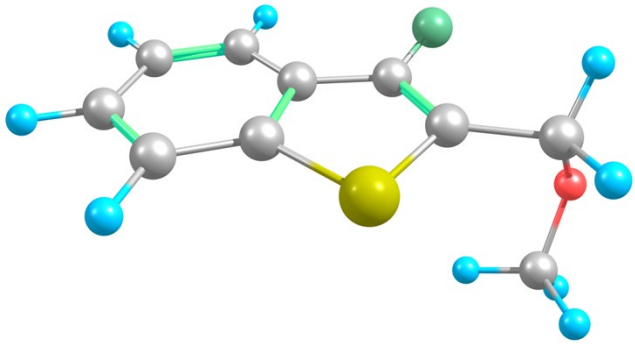
TS3

6	2.223796000	0.493035000	1.408325000
6	3.438161000	-0.027718000	0.999557000
6	1.100024000	0.269911000	0.603837000
1	4.323479000	0.125016000	1.602282000
6	3.530251000	-0.749684000	-0.196843000
6	1.205489000	-0.465331000	-0.592559000
1	4.490792000	-1.146458000	-0.502538000
6	2.422252000	-0.977906000	-1.009534000
1	2.512817000	-1.541984000	-1.928252000
1	2.132201000	1.061492000	2.325451000
6	-0.239628000	0.701838000	0.849520000
6	-1.161215000	0.297596000	-0.222787000
16	-0.340429000	-0.666252000	-1.424105000
1	-0.610245000	1.037148000	1.811917000
6	-2.668136000	0.107130000	-0.037784000
1	-2.992920000	0.743855000	0.793041000
1	-3.170688000	0.422273000	-0.951945000
17	-0.840486000	2.233910000	-0.374414000
8	-2.973313000	-1.233948000	0.176306000
6	-2.511770000	-1.734130000	1.425136000
1	-1.417852000	-1.806673000	1.443862000
1	-2.853050000	-1.096215000	2.246292000
1	-2.928254000	-2.731770000	1.538949000



post-TS3

6	2.581737000	0.808378000	0.562906000
6	3.659004000	-0.054882000	0.371226000
6	1.304567000	0.339867000	0.302107000
1	4.663322000	0.298517000	0.567608000
6	3.465248000	-1.364715000	-0.065997000
6	1.133302000	-0.968657000	-0.138872000
1	4.317558000	-2.017235000	-0.205687000
6	2.186428000	-1.848315000	-0.329519000
1	2.024877000	-2.863219000	-0.668596000
1	2.735847000	1.825372000	0.903097000
6	0.007422000	1.068618000	0.478502000
6	-1.089890000	0.150011000	0.020038000
16	-0.579180000	-1.340485000	-0.426724000
1	-0.178707000	1.309330000	1.531097000
6	-2.527828000	0.535271000	-0.052309000
1	-2.809686000	1.026110000	0.889897000
1	-2.610617000	1.294146000	-0.841257000
17	-0.072394000	2.620257000	-0.413378000
8	-3.343069000	-0.547023000	-0.371804000
6	-3.866298000	-1.226958000	0.769565000
1	-3.063610000	-1.601290000	1.411810000
1	-4.512536000	-0.558961000	1.343969000
1	-4.446458000	-2.064887000	0.391634000

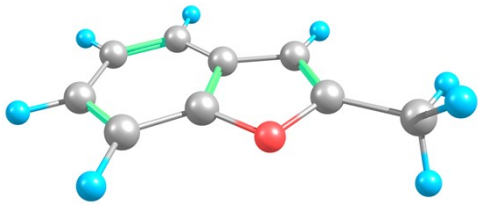


Product

6	2.173261000	1.336019000	0.271911000
6	3.439472000	0.811553000	0.450565000
6	1.114340000	0.466171000	-0.024975000
1	4.266480000	1.471814000	0.681122000

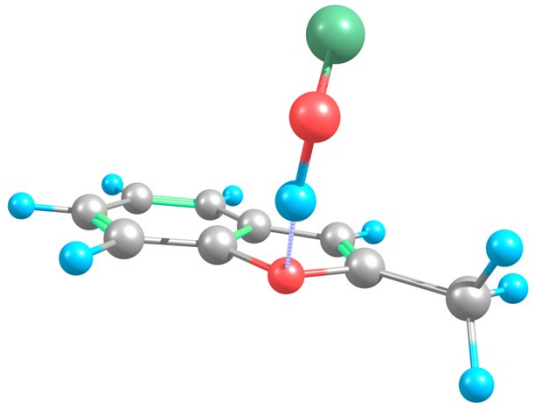
6	3.669969000	-0.570603000	0.336986000
6	1.356720000	-0.914988000	-0.135649000
1	4.670757000	-0.959003000	0.481465000
6	2.637620000	-1.444364000	0.043014000
1	2.815316000	-2.509217000	-0.045228000
1	1.990427000	2.400734000	0.357950000
6	-0.275498000	0.756233000	-0.258663000
6	-1.045566000	-0.323448000	-0.527749000
16	-0.103212000	-1.793091000	-0.509240000
6	-2.530284000	-0.347490000	-0.776020000
1	-2.780670000	0.407623000	-1.522714000
1	-2.825441000	-1.330343000	-1.162196000
17	-0.897152000	2.372462000	-0.204652000
8	-3.282542000	-0.026287000	0.374928000
6	-3.143371000	-0.978017000	1.414407000
1	-3.382004000	-1.985383000	1.053804000
1	-2.126979000	-0.975510000	1.821579000
1	-3.844549000	-0.699213000	2.198753000

XYZ Coordinates for the chlorination of 2-methylbenzo[b]furan



Starting Material

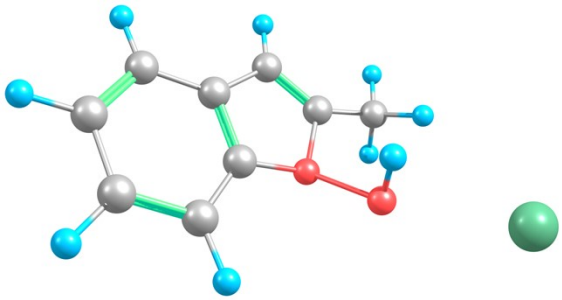
6	-1.491770000	-1.406524000	-0.000056000
6	-2.626797000	-0.606760000	0.000027000
6	-0.238920000	-0.783208000	-0.000025000
1	-3.606294000	-1.069782000	0.000025000
6	-2.533219000	0.794299000	0.000128000
6	-0.180305000	0.616043000	0.000092000
1	-3.438862000	1.388583000	0.000170000
6	-1.299037000	1.434501000	0.000171000
1	-1.209605000	2.513490000	0.000206000
1	-1.573682000	-2.486932000	-0.000089000
6	1.138219000	-1.221651000	0.000067000
6	1.896679000	-0.101627000	-0.000095000
8	1.117676000	1.029679000	-0.000071000
1	1.511042000	-2.233596000	0.000130000
6	3.362780000	0.124823000	-0.000187000
1	3.663824000	0.691688000	0.883527000
1	3.882644000	-0.831826000	-0.000146000
1	3.663737000	0.691570000	-0.884005000



pre-TS1

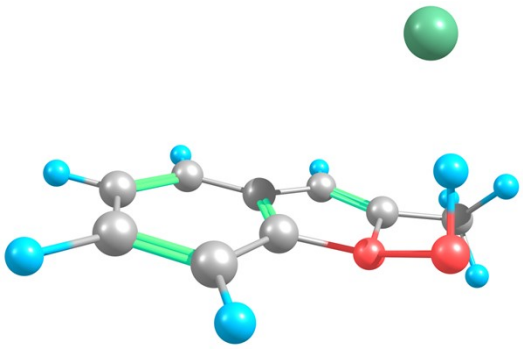
6	2.500549000	0.668352000	-0.930951000
6	3.232473000	-0.406824000	-0.444403000
6	1.232652000	0.906794000	-0.390799000
1	4.216154000	-0.609525000	-0.850429000
6	2.725246000	-1.240539000	0.564164000
6	0.760608000	0.058025000	0.614534000
1	3.323000000	-2.070656000	0.920033000
6	1.468822000	-1.019806000	1.118325000
1	1.062934000	-1.651580000	1.898492000

1	2.899988000	1.305942000	-1.710337000
6	0.177584000	1.871965000	-0.610473000
6	-0.823577000	1.554102000	0.236722000
8	-0.490791000	0.453444000	1.006045000
1	0.166820000	2.689307000	-1.313893000
6	-2.173400000	2.115802000	0.481732000
1	-2.281264000	2.423930000	1.523787000
1	-2.334210000	2.978312000	-0.162683000
1	-2.941965000	1.367985000	0.266449000
8	-2.388037000	-1.551398000	0.578614000
1	-1.789266000	-0.916173000	1.012318000
17	-1.993959000	-1.398890000	-1.064360000



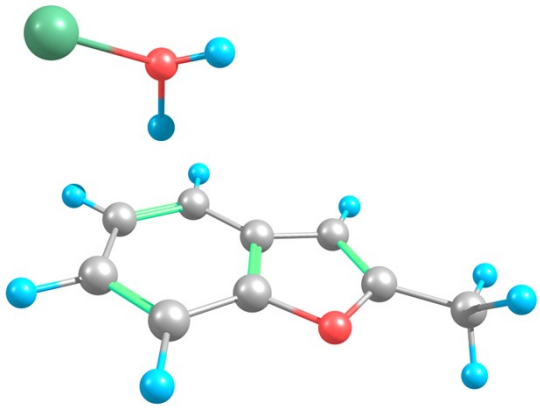
TS1 – High Energy transition state

6	2.911599000	0.180940000	-0.765604000
6	3.263846000	-1.114236000	-0.389691000
6	1.673236000	0.663563000	-0.356339000
1	4.220362000	-1.513794000	-0.702604000
6	2.414575000	-1.913097000	0.380987000
6	0.874197000	-0.163300000	0.419118000
1	2.721199000	-2.915294000	0.651297000
6	1.174024000	-1.443309000	0.815902000
1	0.496159000	-2.038992000	1.412228000
1	3.578947000	0.794088000	-1.357438000
6	0.949247000	1.918497000	-0.533013000
6	-0.222384000	1.842099000	0.101595000
8	-0.297030000	0.552169000	0.753597000
1	1.295187000	2.790281000	-1.066804000
6	-1.388986000	2.716556000	0.326591000
1	-1.547389000	2.874872000	1.394834000
1	-1.197844000	3.674205000	-0.154562000
1	-2.293001000	2.276117000	-0.098397000
8	-1.648726000	-0.236520000	0.447521000
1	-1.577540000	-0.404511000	-0.517956000
17	-3.530950000	-1.422849000	-0.539224000



post-TS1

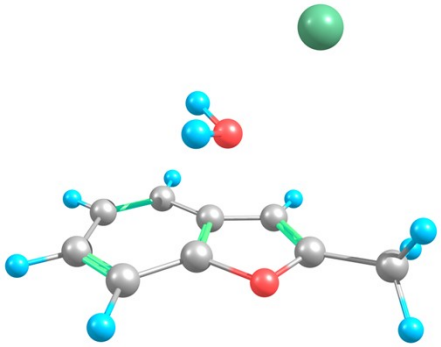
6	2.229069000	0.931594000	-1.003119000
6	3.152623000	0.045100000	-0.454382000
6	0.945256000	0.953464000	-0.465229000
1	4.154001000	0.004353000	-0.864030000
6	2.820827000	-0.798150000	0.610126000
6	0.682016000	0.105550000	0.594774000
1	3.563702000	-1.477873000	1.007035000
6	1.546471000	-0.781409000	1.180310000
1	1.257848000	-1.419585000	2.004038000
1	2.494955000	1.580628000	-1.827392000
6	-0.276962000	1.688106000	-0.773454000
6	-1.257293000	1.309177000	0.041743000
8	-0.658696000	0.368093000	1.008711000
1	-0.396328000	2.430091000	-1.548098000
6	-2.685671000	1.582627000	0.262430000
1	-2.864400000	1.925886000	1.282669000
1	-2.988063000	2.359288000	-0.438541000
1	-3.279666000	0.684935000	0.078535000
8	-1.435520000	-0.736660000	1.422916000
1	-1.536351000	-1.259352000	0.516405000
17	-1.564117000	-1.888011000	-1.154284000



pre-TS2

6	0.272013000	-0.531901000	1.621357000
6	1.260944000	-1.327274000	1.027995000
6	-0.868752000	-0.214871000	0.865610000
1	2.136265000	-1.602872000	1.604978000
6	1.128345000	-1.796963000	-0.294398000

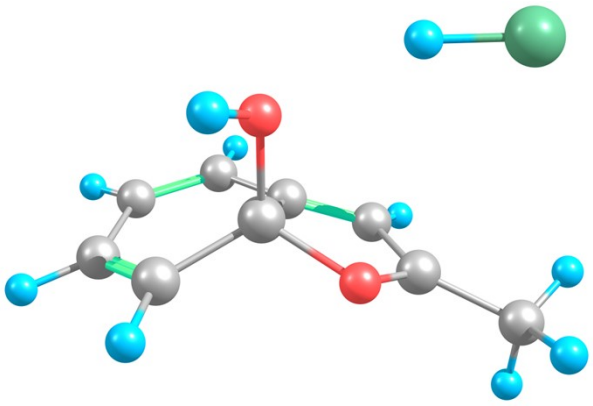
6	-0.961431000	-0.702926000	-0.445407000
1	1.914448000	-2.407441000	-0.719531000
6	0.008626000	-1.489027000	-1.052617000
1	-0.109313000	-1.840434000	-2.069513000
1	0.375925000	-0.196060000	2.646434000
6	-2.073988000	0.540446000	1.082197000
6	-2.783329000	0.456862000	-0.068397000
8	-2.121064000	-0.293425000	-1.008989000
1	-2.372761000	1.068702000	1.972926000
6	-4.095492000	1.004083000	-0.485439000
1	-4.777371000	0.194847000	-0.754475000
1	-4.529679000	1.578583000	0.330749000
1	-3.978325000	1.653130000	-1.355726000
8	2.076785000	1.318039000	0.393248000
1	1.555646000	0.463731000	0.741019000
1	1.478798000	1.959044000	-0.045575000
17	3.372881000	0.900076000	-0.642986000



TS2

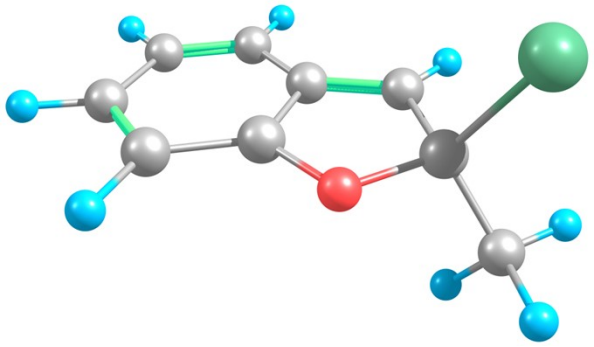
6	2.049699000	-0.242683000	-1.447300000
6	2.953716000	-0.895873000	-0.656016000
6	1.010394000	0.480734000	-0.802094000
1	3.770014000	-1.443546000	-1.108943000
6	2.867586000	-0.866922000	0.772443000
6	0.915696000	0.418315000	0.628330000
1	3.626026000	-1.385903000	1.345098000
6	1.859769000	-0.204649000	1.439080000
1	1.786956000	-0.177447000	2.517588000
1	2.131046000	-0.238709000	-2.526050000
6	-0.016784000	1.335803000	-1.213096000
6	-0.676798000	1.736216000	-0.058875000
8	-0.103013000	1.214361000	1.048918000
1	-0.287526000	1.628751000	-2.214671000
6	-1.881171000	2.547299000	0.145968000
1	-1.718574000	3.272404000	0.946095000
1	-2.165816000	3.049678000	-0.775014000
1	-2.695897000	1.884297000	0.463589000
8	-0.847393000	-1.159124000	0.208973000

1	-0.469924000	-1.766437000	-0.454242000
1	-0.764699000	-1.617519000	1.065895000
17	-2.947118000	-1.735112000	-0.127830000



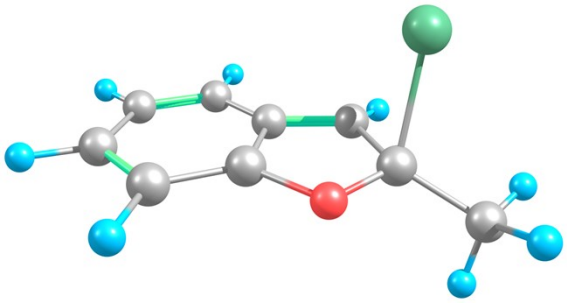
post-TS2 – Unexpected intermediate – leading to unexpected reactivity

6	-1.967091000	-0.068643000	1.569413000
6	-3.075910000	-0.242889000	0.820575000
6	-0.769082000	0.277090000	0.855798000
1	-4.029590000	-0.414332000	1.304621000
6	-3.069438000	-0.111603000	-0.647320000
6	-0.657656000	-0.173508000	-0.581981000
1	-4.024560000	-0.108267000	-1.156904000
6	-1.936861000	0.002541000	-1.345000000
1	-1.894778000	0.070258000	-2.425219000
1	-1.991610000	-0.045170000	2.650316000
6	0.292777000	1.064970000	1.141470000
6	0.986353000	1.274021000	-0.094128000
8	0.452724000	0.650341000	-1.090836000
1	0.558623000	1.538571000	2.073618000
6	2.151874000	2.130235000	-0.332769000
1	2.605755000	1.914045000	-1.296517000
1	1.800127000	3.168990000	-0.316348000
1	2.863262000	2.014414000	0.485517000
8	-0.213467000	-1.486862000	-0.602994000
1	-0.434628000	-1.901396000	-1.448858000
1	1.716800000	-1.720430000	-0.060344000
17	2.893338000	-1.337517000	0.319083000



pre-TS3

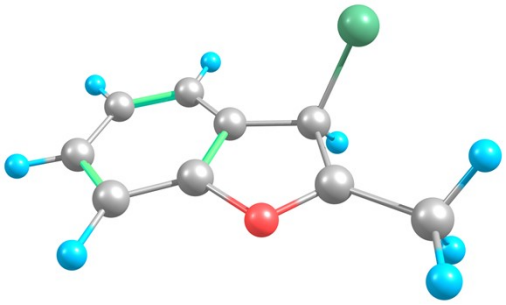
6	2.016065000	1.439300000	0.022693000
6	3.117391000	0.660888000	-0.125727000
6	0.749384000	0.772010000	0.120124000
1	4.100978000	1.103473000	-0.202783000
6	3.006137000	-0.768845000	-0.183010000
6	0.679331000	-0.667931000	0.053432000
1	3.919796000	-1.339705000	-0.304028000
6	1.814919000	-1.456197000	-0.095285000
1	1.756395000	-2.534147000	-0.141650000
1	2.064587000	2.518980000	0.070753000
6	-0.524245000	1.200682000	0.282012000
6	-1.432226000	0.012625000	0.327124000
8	-0.553013000	-1.114023000	0.159839000
1	-0.892922000	2.214481000	0.373271000
6	-2.226434000	-0.154070000	1.604268000
1	-1.540878000	-0.202473000	2.451473000
1	-2.900765000	0.691840000	1.724944000
1	-2.799238000	-1.078334000	1.541280000
17	-2.499164000	0.076900000	-1.107398000



TS3

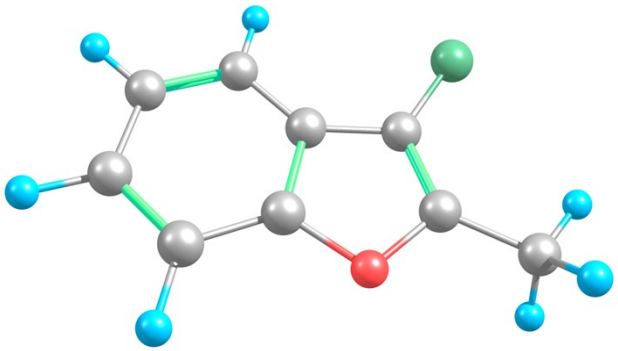
6	-1.798229000	-1.292440000	0.619033000
6	-2.978217000	-0.700928000	0.213671000
6	-0.621050000	-0.546490000	0.463122000
1	-3.913884000	-1.233038000	0.320775000
6	-2.984172000	0.589459000	-0.346211000
6	-0.662179000	0.741095000	-0.094750000
1	-3.929673000	1.017998000	-0.655825000
6	-1.824897000	1.342821000	-0.518604000
1	-1.834715000	2.334907000	-0.947761000

1	-1.771702000	-2.287636000	1.042801000
6	0.740418000	-0.792922000	0.766792000
6	1.477117000	0.409144000	0.342168000
8	0.592124000	1.303593000	-0.146571000
1	1.166843000	-1.571255000	1.385095000
6	2.728304000	0.971020000	0.909876000
1	2.445648000	1.564949000	1.781968000
1	3.404558000	0.175386000	1.211658000
1	3.203744000	1.617817000	0.173750000
17	1.884095000	-0.963084000	-1.015911000



post-TS3

6	-1.508466000	-1.355779000	0.444074000
6	-2.807088000	-0.933329000	0.153555000
6	-0.493118000	-0.423433000	0.323572000
1	-3.622931000	-1.639917000	0.235656000
6	-3.079498000	0.377448000	-0.240132000
6	-0.807780000	0.859688000	-0.072250000
1	-4.099210000	0.669023000	-0.456161000
6	-2.063047000	1.327382000	-0.365092000
1	-2.245192000	2.349265000	-0.667827000
1	-1.302670000	-2.374894000	0.745509000
6	0.984568000	-0.468926000	0.552829000
6	1.386247000	0.945792000	0.189816000
8	0.381536000	1.641638000	-0.140837000
1	1.271054000	-0.674832000	1.587946000
6	2.722604000	1.527551000	0.213916000
1	3.025665000	1.594300000	1.266805000
1	3.424080000	0.846007000	-0.272063000
1	2.730660000	2.513300000	-0.242379000
17	1.868219000	-1.620807000	-0.486619000



Product (not observed)

6	1.372037000	-1.468093000	-0.000022000
6	2.717567000	-1.128199000	0.000047000
6	0.437472000	-0.430396000	-0.000034000
1	3.465655000	-1.911494000	0.000060000
6	3.132057000	0.213653000	0.000103000
6	0.874978000	0.897483000	0.000019000
1	4.190763000	0.442077000	0.000150000
6	2.213260000	1.256624000	0.000089000
1	2.518858000	2.295098000	0.000116000
1	1.052043000	-2.503201000	-0.000055000
6	-0.999047000	-0.329825000	-0.000066000
6	-1.325868000	0.983450000	-0.000005000
8	-0.189800000	1.749331000	-0.000063000
6	-2.619719000	1.701893000	0.000093000
1	-2.702579000	2.336740000	-0.884522000
1	-3.439329000	0.985183000	-0.000340000
1	-2.702884000	2.335989000	0.885222000
17	-2.098856000	-1.656152000	-0.000086000