Supporting Information

Catalyst-dependent selectivity in sulfonium ylide cycloisomerisation reactions

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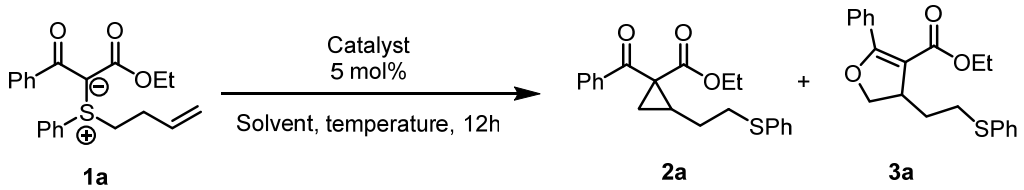
1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all reactions were performed under an argon atmosphere. All solvents were distilled from appropriate drying agents prior to use. All other reagents were used as received from commercial suppliers unless otherwise stated. Reaction progress was monitored by thin layer chromatography (TLC) performed on aluminium plates coated with silica gel F_{254} with 0.2 mm thickness. Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining using potassium permanganate. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck and co.). Infra-red (IR) spectra were recorded using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Wavenumbers (ν_{max}) are reported in cm^{-1}. Mass spectra were obtained using a Finnigan MAT 8200 or (70 eV) or an Agilent 5973 (70 eV) spectrometer, using electrospray ionization (ESI). All ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using a Bruker AV-400 or AV-600 spectrometer at 300K. Chemical shifts were given in parts per million (ppm, δ), referenced to the solvent peak of $CDCl_3$, defined at δ = 7.26 ppm (^{1}H NMR) and δ = 77.16 (^{13}C NMR). Coupling constants are quoted in Hz (*J*). ^{1}H NMR splitting patterns were designated as singlet (s), doublet (d), triplet (t), quartet (q), pentet (p), sextet (sex). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br).

2. Reaction optimization

Table S1. Survey of reaction conditions for selective formation of 2a and 3a.



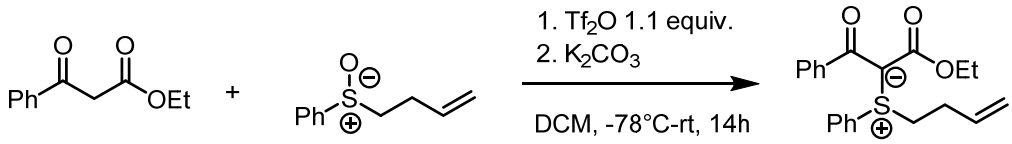
1a **2a** **3a**

Entry	Catalyst (5 mol%)	Solvent	Temperature	Yield **2a**[a]	Yield **3a**
1	$Au(PPh_3)$	Toluene	75°C	-	-
2	$Au(JohnPhos)(MeCN)SbF_6$	Toluene	75°C	95% (2:1 d.r.)	-
3	$Hg(OTf)_2$	Toluene	75°C	88% (1.1:1 d.r.)	-
4	$Pd_2(dba)_3$	Toluene	75°C	65% (1:1 d.r.)	-
5	$AuCl_3$	Toluene	75°C	40% (2:1 d.r.)	13%
6	$PdCl_2(MeCN)_2$	Dioxane	75°C	10% (1.2:1 d.r.)	82%
7	$PtCl_2$	Dioxane	75°C	-	65%
8	$PtCl_4$	Dioxane	75°C	-	40%
9	$CuBr{\cdot}SMe_2$	Dioxane	75°C	-	-
10	AgOTf	Dioxane	75°C	-	-
11	$[Rh(nbd)_2]BF_4$	Dioxane	75°C	-	-
12	$[Rh(cod)Cl]_2$	Dioxane	75°C	-	-
13	$[Ir(cod)_2Cl]_2$	Dioxane	75°C	-	-
14	$[Cp^*Ru(MeCN)_3](BF_4)_2$	Dioxane	75°C	-	-
15	$RuCl_3$	Dioxane	75°C	-	-
16	$Pd(OAc)_2$	Dioxane	75°C	-	-
17	$Au(JohnPhos)(MeCN)SbF_6$	DCE	75°C	83% (2:1 d.r.)	-
18	$Au(JohnPhos)(MeCN)SbF_6$	$CHCl_3$	75°C	75% (2:1 d.r.)	-
19	$Au(JohnPhos)(MeCN)SbF_6$	Dioxane	75°C	32% (2:1 d.r.)	-
20	$Au(JohnPhos)(MeCN)SbF_6$	THF	75°C	57% (2:1 d.r.)	-
21	$Au(JohnPhos)(MeCN)SbF_6$	MeCN	75°C	-	-
22	$Au(JohnPhos)(MeCN)SbF_6$	MeOH	75°C	-	-
23	$Au(JohnPhos)(MeCN)SbF_6$	Toluene	60°C	n.r.	-
24	$Au(JohnPhos)(MeCN)SbF_6$	Toluene	110°C	90% (1.3:1 d.r.)	-

3. Characterization

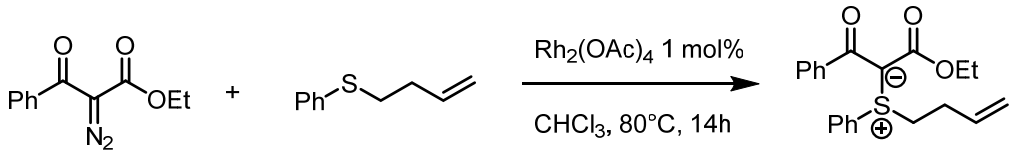
3.1 Synthesis of sulfonium ylides

General Procedure 1 (GP1):



The corresponding β-keto ester (1 mmol, 1 equiv.) and sulfoxide (1.1 mmol, 1.1 equiv.) were dissolved in anhydrous DCM (1 mL). The solution was cooled to -78°C and triflouromethansulfonic anhydride (0.19 mL, 1.1 equiv.) was added dropwise. The reaction mixture was stirred for 30 minutes at this temperature and allowed to warm up to room temperature. After 12 hours stirring at room temperature, the resulting solution was quenched with a saturated K_2CO_3 solution (5 mL). Water was added and the aqueous layer was extracted with DCM (3x 5 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo. The crude product was purified by column chromatography over silica (heptane/EtOAc = 7:3 to 2:8).

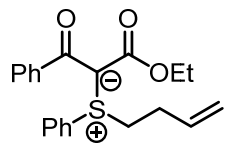
General Procedure 2 (GP2):



A oven dried Schlenk was charged with $Rh_2(OAc)_4$ (4.4 mg, 0.01 mmol, 1 mol%) and the corresponding sulfide (2 mmol, 2 equiv.) were dissolved in 1 mL anhydrous $CHCl_3$. The mixture was heated to 80°C and a solution of diazo compound (1 mmol) in 1 mL anhydrous $CHCl_3$ was added dropwise over 5 min. The reaction was stirred for 14 hours at 80°C before cooling down to room temperature. After evaporation of the solvent, the crude product was purified on column chromatography over silica (heptane/EtOAc = 7:3 to 2:8).

Characterization

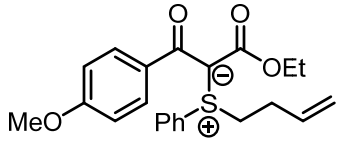
Ethyl 2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-3-oxo-3-phenylpropanoate (1a)



The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 7:3) to yield the title compound as a white solid (290 mg, 81%). **^{1}H-NMR** (400 Mhz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 2.55 (m, 2H), 3.55 (dt, *J* = 7.8, 11.7 Hz, 1H), 3.92 (q, *J* = 7.1 Hz, 2H), 4.41 (m, 1H), 5.19 (m, 2H), 5.86 (ddt, *J* = 6.7, 10.1, 16.9 Hz, 1H), 7.33 (m, 3H), 7.50 (m, 5H), 7.82 (m, 2H); **^{13}C-NMR** δ 14.1, 29.2, 41.4, 59.5, 72.3, 118.6, 127.5, 127.6, 128.7, 129.3, 129.9, 131.5, 131.7, 133.8, 143.5, 167.0, 190.9; **IR** (neat): 3059, 2977, 2933,

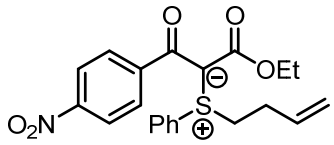
2902, 1649, 1585, 1553, 1443, 1365, 1328, 1275, 1148, 1060, 1025; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{21}H_{23}O_3S$, 377.1182; found 377.1184.

Ethyl 2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-3-(4-methoxyphenyl)-3-oxopropanoate (1b)



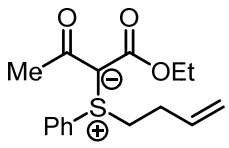
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 6:4) to yield the title compound as a white solid (349 mg, 90%). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.00 (t, *J* = 7.0 Hz, 3H), 2.55 (m, 2H), 3.55 (dt, *J* = 8.0, 12.0 Hz, 1H), 3.84 (s, 3H), 3.99 (q, *J* = 7.0 Hz, 2H), 4.40 (ddd, *J* = 5.5, 8.0, 12.0 Hz, 1H), 5.20 (m, 2H), 5.88 (ddt, *J* = 6.5, 10.0, 17.0 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 7.50 (m, 3H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.82 (m, 2H); **^{13}C-NMR** δ 14.2, 28.9, 41.2, 55.2, 59.2, 70.9, 112.4, 118.3, 128.2, 129.6, 129.8, 131.1, 131.7, 133.6, 135.3, 160.8, 166.8, 189.8; **IR** (neat): 3484, 3052, 2979, 2933, 2903, 2837, 1643, 1603, 1582, 1548, 1508, 1443, 1325, 1275, 1246, 1170, 1124, 1057, 1027; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{24}O_3SNa$, 407.1288; found 407.1295.

Ethyl 2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-3-(4-nitrophenyl)-3-oxopropanoate (1c)



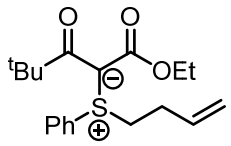
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 7:3) to yield the title compound as a white solid (372 mg, 93%). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.0 Hz, 3H), 2.55 (m, 2H), 3.63 (dt, *J* = 7.5, 12.0 Hz, 1H), 3.92 (q, *J* = 7.0 Hz, 2H), 4.39 (ddd, *J* = 6.0, 8.0, 12.0 Hz, 1H), 5.20 (m, 2H), 5.86 (ddt, *J* = 6.5, 10.5, 17.0 Hz, 1H), 7.52 (m, 5H), 7.83 (m, 2H), 8.17 (d, *J* = 8.8 Hz, 2H); **^{13}C-NMR** δ 14.1, 29.2, 41.0, 59.7, 73.7 118.9, 122.9, 128.0, 128.8, 130.0, 130.7, 131.9, 133.4, 147.7, 149.9, 166.3, 188.3; **IR** (neat): 3507, 3067, 2980, 2933, 2904, 2867, 1658, 1555, 1516, 1367, 1330, 1276, 1058; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{21}NO_5SNa$, 422.1033; found 422.1037.

Ethyl 2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-3-oxobutanoate (1d)



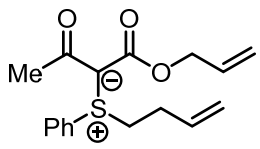
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 7:3) to yield the title compound as a white solid (129 mg, 44%). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.0 Hz, 3H), 2.4-2.5 (m, 2H), 2.49 (s, 3H), 2.47 (dt, *J* = 8.0, 11.5 Hz, 1H), 4.17 (m, 2H), 4.33 (ddd, *J* = 5.5, 8.0, 11.5 Hz, 1H), 5.18 (m, 2H), 5.84 (ddt, *J* = 6.5, 10.5, 17.0 Hz, 1H), 7.48 (m, 3H), 7.69 (m, 2H); **^{13}C-NMR** δ 14.5, 28.8, 29.9, 40.7, 59.2, 71.6, 118.2, 127.9, 129.5, 130.9, 131.2, 133.6, 167.0, 192.0; **IR** (neat): 3485, 3062, 2978, 2929, 2905, 1660, 1571, 1442, 1366, 1319, 1273, 1234, 1064, 1030; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1027.

Ethyl 2-(but-3-en-1-yl(phenyl)- λ⁴-sulfanylidene)-4,4-dimethyl-3-oxopentanoate (1e)



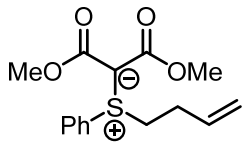
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 7:3) to yield the title compound as a white solid (268 mg, 80%). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.22 (t, *J* = 7.0 Hz, 3H), 1.33 (s, 9H), 2.46 (m, 2H), 3.41 (dt, *J* = 8.0, 11.5 Hz, 1H), 4.12 (m, 2H), 4.20 (ddd, *J* = 5.5, 8.0, 11.5 Hz, 1H), 5.17 (m, 2H), 5.85 (ddt, *J* = 6.5, 10.0, 17.0 Hz, 1H), 7.45 (m, 3H), 7.58 (m, 2H); **^{13}C-NMR** δ 14.6, 27.2, 28.9, 41.2, 43.4, 59.2, 71.1, 118.2, 127.1, 129.5, 130.4, 132.5, 134.9, 165.9, 200.4; **IR** (neat): 3507, 3063, 2976, 1950, 1905, 1866, 1667, 1567, 1442, 1261, 1307, 1263, 1243, 1215, 1156, 1052, 1023; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{19}H_{26}O_3SNa$, 357.1495; found 357.1499.

Allyl 2-(but-3-en-1-yl(phenyl)-λ⁴-sulfanylidene)-3-oxobutanoate (1f)



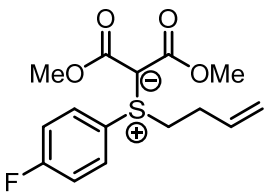
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 7:3) to yield the title compound as a white solid (164 mg, 54%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.42 (m, 2H), 2.47 (s, 3H), 3.46 (dt, *J* = 7.8, 11.7 Hz, 1H), 4.33 (ddd, *J* = 5.7, 7.8, 11.7 Hz, 1H), 4.61 (m, 2H), 5.22 (m, 4H), 5.82 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 5.93 (ddt, *J* = 5.5, 10.7, 17.2 Hz, 1H), 7.46 (m, 3H), 7.68 (m, 2H); **^{13}C-NMR** δ 29.1, 30.2, 41.0, 64.3, 71.8, 117.1, 118.5, 128.3, 129.8, 131.2, 133.6, 133.8, 166.8, 192.4; **IR** (neat): 2982, 2929, 1667, 1583, 1442, 1364, 1320, 1269, 1232, 1058, 1024; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{17}H_{21}O_3S$, 327.1031; found 327.1023.

Dimethyl 2-(but-3-en-1-yl(phenyl)-λ⁴-sulfanylidene)malonate (1g)



The compound was prepared following **GP2** and purified by column chromatography over silica (heptane/EtOAc = 9:1) to yield the title compound as white solid (112 mg, 38%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.48 (m, 2H), 3.41 (dt, *J* = 7.9, 11.7 Hz, 1H), 3.70 (s, 6H), 4.23 (ddd, *J* = 5.6, 7.9, 11.7 Hz, 1H), 5.18 (ddt, *J* = 6.7, 10.4, 23.2 Hz, 2H), 5.84 (ddt, J = 6.7, 10.4, 23.2 Hz, 1H), 7.48 (m, 3H), 7.66 (m, 2H); **^{13}C-NMR** δ 28.9, 41.8, 51.2, 56.2, 118.6, 127.9, 129.8, 131.2, 132.1, 133.8, 167.4; **IR** (neat): 3062, 2982, 2946, 2908, 2839, 1712, 1675, 1621, 132, 1304, 1235, 1180; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{18}O_4SNa$, 317.0818; found 317.0811.

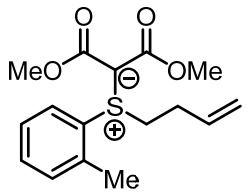
Dimethyl 2-(but-3-en-1-yl(4-fluorophenyl)-λ⁴-sulfanylidene)malonate (1h)



The compound was prepared following **GP2** and purified by column chromatography over silica (heptane/EtOAc = 9:1) to yield the title compound as white solid (41 mg, 13%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.47 (m, 2H), 3.40 (dt, *J* = 7.8, 11.7 Hz, 1H), 3.70 (s, 6H), 4.23 (ddd, *J* = 5.7, 7.9, 11.8 Hz, 1H), 5.17 (m, 2H),

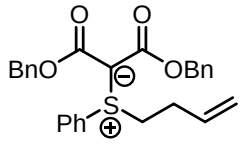
5.82 (ddt, *J* = 6.7, 9.9, 19.3 Hz, 1H), 7.17 (m, 2H), 7.73 (m, 2H); **^{13}C-NMR** δ 28.9, 41.9, 51.3, 117.2 (d, *J* = 22.7 Hz), 118.7, 127.5, 130.7 (d, *J* = 8.9 Hz), 133.6, 164.4 (d, *J* = 254 Hz), 167.3; **^{19}F-NMR** δ -107.4; **IR** (neat): 3070, 2983, 2948, 2924, 2852, 1713, 1678, 1624, 1590, 1493, 1318, 1182, 1160, 1073; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{17}FO_4SNa$, 335.0724; found 335.0725.

Dimethyl 2-(but-3-en-1-yl(o-tolyl)-λ^4-sulfanylidene)malonate (1i)



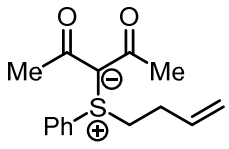
The compound was prepared following **GP2** and purified by column chromatography over silica (heptane/EtOAc = 9:1) to yield the title compound as white solid (37 mg, 12%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.47 (m, 2H), 2.57 (s, 3H), 3.37 (dt, *J* = 7.8, 12.0 Hz, 1H), 3.70 (s, 6H), 4.25 (ddd, *J* = 5.9, 8.0, 12.0 Hz, 1H), 5.15 (m, 2H), 5.83 (ddt, *J* = 6.7, 9.9, 16.7 Hz, 1H), 7.34 (m, 3H), 7.97 (d, *J* = 8.1 Hz, 1H); **^{13}C-NMR** δ 20.0, 28.9, 39.8, 51.1, 57.9, 118.4, 127.0, 129.5, 129.8, 131.7 (2C), 133.9, 139.4, 167.3; **IR** (neat): 3063, 2981, 2945, 2850, 1714, 1679, 1621, 1432, 1303, 1234, 1202, 1180, 1072; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_4SNa$, 331.0975; found 331.0976.

Dibenzyl 2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)malonate (1j)



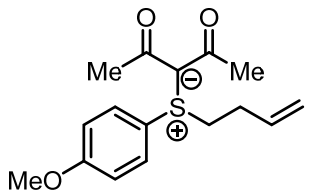
The compound was prepared following **GP2** and purified by column chromatography over silica (heptane/EtOAc = 6:4) to yield the title compound as white solid (49 mg, 11%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.46 (m, 2H), 3.37 (dt, *J* = 7.9, 11.6 Hz, 1H), 4.17 (ddd, *J* = 5.7, 7.9, 11.7 Hz, 1H), 5.11 (m, 2H), 5.18 (s, 4H), 5.77 (ddt, *J* = 6.7, 10.3, 17.0 Hz, 1H), 7.30 (m, 10H), 7.45 (m, 3H), 7.62 (m, 2H); **^{13}C-NMR** δ 28.7, 41.8, 56.3, 65.5, 118.6, 124.2, 127.6, 127.8, 128.5, 129.8, 131.2, 132.1, 133.7, 137.5, 166.6; **IR** (neat): 3063, 3031, 2929, 1718, 1682, 1443, 1378, 1282, 1220, 1053, 1028; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{27}H_{26}O_4SNa$, 469.1446; found 469.1446.

3-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)pentane-2,4-dione (1k)



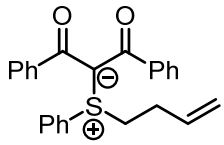
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 3:7) to yield the title compound as a white solid (220 mg, 84%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.42 (s, 6H), 2.50 (m, 2H), 3.48 (ddd, *J* = 7.2, 8.2, 11.8 Hz, 1H), 4.48 (ddd, *J* = 5.6, 7.2, 11.8 Hz, 1H), 5.20 (m, 2H), 5.82 (dddd, *J* = 5.9, 7.3, 9.9, 17.3 Hz, 1H), 7.48 (m, 3H), 7.66 (m, 2H); **^{13}C-NMR** δ 29.1, 30.2 (br. s), 41.3, 118.8, 128.0, 129.9, 131.1, 131.3, 133.8, 191.3 (ylidic carbon not visible in ^{13}C-NMR); **IR** (neat): 3001, 2923, 1608, 1575, 1443, 1364, 1322, 1237, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{18}O_2SNa$, 285.0920; found 285.0918.

3-(but-3-en-1-yl(4-methoxyphenyl)-λ^4-sulfanylidene)pentane-2,4-dione (1l)



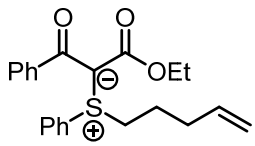
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 2:8) to yield the title compound as a white solid (73 mg, 25%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.40 (s, 6H), 2.43 (m, 2H), 3.47 (dt, *J* = 7.7, 11.8 Hz, 1H); 3.83 (s, 3H), 4.41 (ddd, *J* = 5.9, 7.2, 12.8 Hz, 1H), 5.16 (m, 2H), 5.81 (dddd, *J* = 6.1, 7.2, 9.5, 11.2 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 2H); **^{13}C-NMR** δ 29.2, 30.2 (br.s), 41.5, 55.7, 115.4, 118.6, 121.7, 130.9, 133.9, 162.3, 191.6, (ylidic carbon not visible in ^{13}C-NMR); **IR** (neat): 3077, 3003, 2978, 2923, 2840, 1578, 1496, 1462, 1441, 1364, 1324, 1302, 1256, 1178, 1084, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1021.

2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-1,3-diphenylpropane-1,3-dione (1m)



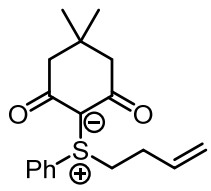
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 4:6) to yield the title compound as a white solid (220 mg, 57%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 2.59 (m, 2H), 3.66 (dt, *J* = 7.8, 11.8 Hz, 1H), 4.55 (ddd, *J* = 6.1, 7.8, 11.8 Hz, 1H), 5.18 (m, 2H), 5.86 (ddt, *J* = 6.7, 10.2, 16.9 Hz, 1H), 7.02 (m, 4H), 7.09 (m, 2H), 7.35 (m, 4H), 7.52 (m, 3H), 7.93 (m, 2H); **^{13}C-NMR** δ 29.5, 41.9, 86.9, 118.8, 127.6, 128.9, 129.1, 130.0, 130.1, 131.5, 131.8, 133.7, 142.2, 191.3; **IR** (neat): 3059, 2927, 2855, 2236, 1712, 1644, 1528, 1443, 1328, 1278; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{25}H_{23}O_2S$, 387.1419; found 387.1402.

Ethyl 3-oxo-2-(pent-4-en-1-yl(phenyl)-λ^4-sulfaneylidene)-3-phenylpropanoate (1n)



The compound was prepared following **GP2** and purified by column chromatography over silica (heptane/EtOAc = 6:4) to yield the title compound as a white solid (129 mg, 35%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.90 (tt, *J* = 6.9, 13.7 Hz, 2H), 2.30 (q, *J* = 7.1 Hz, 2H), 3.50 (ddd, *J* = 7.3, 8,5, 11.9 Hz, 1H), 3.93 (q, *J* = 7.1 Hz, 2H), 4.31 (ddd, *J* = 5.6, 8.5, 11.9 Hz, 1H), 5.10 (m, 2H), 5.78 (ddt, *J* = 6.7, 10.2, 16.9 Hz, 1H), 7.33 (m, 3H), 7.49 (m, 5H), 7.82 (m, 2H); **^{13}C-NMR** δ 14.1, 24.2, 32.2, 41.1, 59.5, 72.6, 116.9, 127.5, 127.6, 128.7, 129.3, 129.9, 131.5, 131.8, 136.4, 143.6, 167.1, 190.9; **IR** (neat): 3060, 2977, 2927, 2851, 1650, 1554, 1444, 1329, 1278, 1062, 746; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{22}H_{25}O_3S$, 369.1519; found 369.1526.

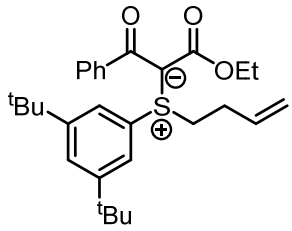
2-(but-3-en-1-yl(phenyl)-λ^4-sulfanylidene)-5,5-dimethylcyclohexane-1,3-dione (1o)



The compound was prepared following **GP1** and purified by column chromatography over silica (Heptane/EtOAc = 2:8) to yield the title compound as a white solid (142 mg, 47%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.05 (s, 6H), 2.35 (s, 4H), 2.40 (m, 2H), 3.65 (dt, *J* = 7.8, 12.1 Hz, 1H), 4.39 (ddd, J = 6.2, 8.1, 12.1 Hz, 1H), 5.13 (m, 2H), 5.79 (ddt, *J* = 6.7,

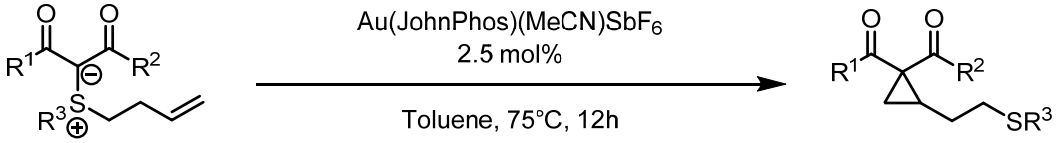
10.6, 14.9 Hz, 1H), 7.42-7.54 (m, 3H), 7.82 (m, 2H); **^{13}C-NMR** δ 28.6, 29.5, 31.5, 40.8, 51.9, 85.9, 118.8, 129.6, 130.1, 130.4, 132.0, 133.4, 192.7; **IR** (neat): 2955, 2933, 2887, 2867, 1557, 1475, 1443, 1411, 1329, 1312, 1281, 1223, 1141, 998, 919, 728, 685, 642, 614; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{18}H_{23}O_2S$, 303.1413; found 303.1423.

Ethyl 2-(but-3-en-1-yl(3,5-di-tert-butylphenyl)-λ^4-sulfanylidene)-3-oxo-3-phenylpropanoate (1p)



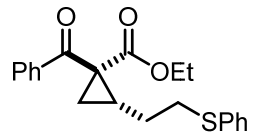
The compound was prepared following **GP1** and purified by column chromatography over silica (heptane/EtOAc = 6:4) to yield the title compound as a white solid (150 mg, 32%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.1 Hz, 3H), 1.33 (s, 18H), 2.55 (m, 2H), 3.50 (dt, *J* = 7.9, 11.8 Hz, 1H), 3.94 (m, 2H), 4.42 (ddd, *J* = 6.0, 7.9, 11.8 Hz, 1H), 5.19 (m, 2H), 5.88 (ddt, *J* = 6.8, 10.2, 16.9 Hz, 1H), 7.32 (m, 3H), 7.48 (m, 2H), 7.53 (t, *J* = 1.7 Hz, 1H), 7.65 (d, *J* = 1.7 Hz, 2H); **^{13}C-NMR** δ 14.2, 29.5, 31.4, 35.4, 42.2, 59.4, 72.4, 118.5, 122.9, 125.9, 127.4, 127.5, 129.1, 131.1, 134.0, 144.0, 153.0, 167.3, 190.9; **IR** (neat): 2962, 2904, 2868, 1647, 1585, 1552, 1364, 1326, 1273, 1248, 1061; **HRMS** (ESI): $[M+H]^+$ calculated for $C_{29}H_{39}O_3S$, 467.2620; found 467.2617.

3.2 Au(I)-catalyzed cyclopropanation



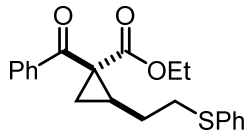
A round bottom flask was charged with a stirrer and Au(JohnPhos)(MeCN)SbF_6 (1.9 mg, 0.0025 mmol, 2.5 mol%). The corresponding sulfonium ylide (0.1 mmol) was dissolved in anhydrous toluene (1 mL) and added to the flask. The reaction was heated to 75°C and stirred for 14 hour at this temperature. The solvent was evaporated and the crude product was purified by column chromatography over silica (Heptane/EtOAc = 9:1).

Ethyl 1-benzoyl-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2a, major)



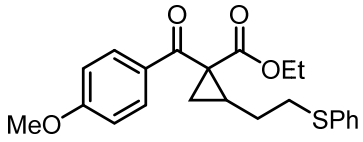
Title compound was obtained as colorless oil (22 mg, 63% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.41 (dd, *J* = 4.4, 9.0 Hz, 1H), 1.70 (dd, *J* = 4.4, 7.8 Hz, 1H), 1.91 (q, *J* = 7.4 Hz, 2H), 2.32 (dq, *J* = 7.4, 8.9 Hz, 1H), 3.02 (qt, *J* = 7.4, 13.0 Hz, 2H), 3.98 (m, 2H), 7.18 (m, 1H), 7.28 (m, 2H), 7.34 (m, 2H), 7.42 (m, 2H), 7.53 (m, 1H), 7.85 (m, 2H); **^{13}C-NMR** δ 13.8, 22.0, 26.0, 27.5, 33.2, 39.1, 61.5, 126.2, 128.2, 128.6, 129.1, 129.5, 132.9, 136.5, 137.6, 170.1, 195.2; **IR** (neat): 2923, 2852, 1723, 1677, 1443, 1309, 1271, 1210, 1179, 1147, 1094, 1073, 1023; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{22}O_3SNa$, 377.1187; found 377.1180.

Ethyl 1-benzoyl-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2a, minor)



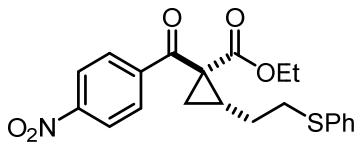
Title compound was obtained as colorless oil (11 mg, 32% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.1 Hz, 3H), 1.26 (m, 1H), 1.46 (dd, *J* = 4.4, 8.9 Hz, 1H), 1.62 (dd, *J* = 4.4, 7.4 Hz, 1H), 1.80 (m, 1H), 2.39 (tdd, *J* = 5.3, 7.5, 9.1 Hz, 1H), 2.96 (t, *J* = 7.2 Hz. 2H), 4.02 (m, 2H), 7.16 (m, 1H), 7.24 (m, 4H), 7.43 (m, 2H), 7.54 (m, 1H), 7.86 (m, 2H); **^{13}C-NMR** δ 13.8, 20.3, 28.4, 33.3, 38.1, 61.5, 126.2, 128.6 (2C), 129.1, 129.4, 133.1, 136.2, 137.7, 171.7, 194.1; **IR** (neat): 2923, 2853, 1723, 1677, 1444, 1308, 1271, 1209, 1179, 1148, 1094, 1072, 1024; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{22}O_3SNa$, 377.1187; found 377.1179.

Ethyl 1-(4-methoxybenzoyl)-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2b)



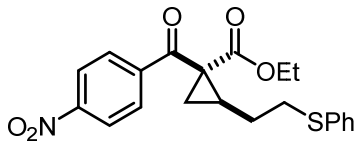
Title compound was obtained as colorless oil (35 mg, 92% yield, 1.8:1 mixture of diastereomers). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.1 Hz, 3H, major), 1.01 (t, *J* = 7.1 Hz, 3H, minor), 1.36 (dd, *J* = 4.4, 9.0 Hz, 1H, major), 1.44 (dd, *J* = 4.4, 8.7 Hz, 1H, minor), 1.56 (dd, *J* = 4.4, 7.3 Hz, 1H, minor), 1.66 (dd, *J* = 4.4, 7.6 Hz, 1H, major), 1.77 (m, 1H, minor), 1.90 (q, *J* = 7.5 Hz, 1H, major), 2.28 (m, 1H), 3.00 (m, 2H), 3.86 (s, 3H, major), 3.87 (s, 3H, minor), 4.04 (m, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.1-7.4 (m, 5H), 7.86 (m, 2H); **^{13}C-NMR** δ 14.0, 20.1, 21.3, 25.7, 27.5, 27.9, 28.6, 33.17, 33.21, 37.8, 38.7, 55.6, 61.5, 113.8, 126.09, 126.12, 129.0, 129.2, 129.4, 130.0, 130.6, 130.7, 131.0, 136.3, 136.5, 163.5, 163.6, 170.3, 171.9, 192.2, 193.2; **IR** (neat): 3058, 2961, 2933, 2839, 1721, 1669, 1599, 1575, 1308, 1257, 1214, 1171, 1147, 1093, 1072, 1024, 968, 909, 841, 800, 730, 690; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{24}O_4SNa$, 407.1288; found 407.1282.

Ethyl 1-(4-nitrobenzoyl)-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2b, major)



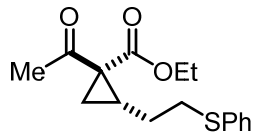
Title compound was obtained as colorless oil (14 mg, 34% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.1 Hz, 3H), 1.52 (dd, *J* = 4.4, 9.1 Hz, 1H), 1.77 (dd, *J* = 4.4, 7.9 Hz, 1H), 1.94 (q, *J* = 7.5 Hz, 2H), 2.37 (m, 1H), 3.02 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 7.20 (m, 1h), 7.31 (m, 4H), 7.97 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H); **^{13}C-NMR** δ 13.9, 22.9, 27.1, 27.3, 33.3, 39.2, 61.9, 123.9, 126.4, 129.0, 129.1, 129.7, 136.2, 142.7, 150.2, 169.3, 194.1; **IR** (neat): 3107, 3076, 2980, 2962, 2923, 2852, 1728, 1687, 1525, 1349, 1308, 1275, 1205, 1148, 1107, 1093, 1077, 1024, 861, 841, 745, 693; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{21}NO_5SNa$, 422.1033; found 422.1025.

Ethyl 1-(4-nitrobenzoyl)-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2c, minor)



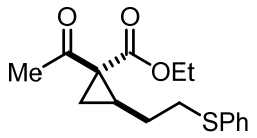
Title compound was obtained as colorless oil (9 mg, 22% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.1 Hz, 3H), 1.56 (dd, *J* = 4.4, 8.9 Hz, 1H), 1.69 (dd, *J* = 4.4, 7.5 Hz, 1H), 1.81 (m, 1H), 2.46 (m, 1H), 2.97 (t, *J* = 7.1 Hz, 2H), 4.04 (m, 2H), 7.18 (m, 1H), 7.25 (m, 4H), 7.97 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H); **^{13}C-NMR** δ 13.9, 20.8, 28.3, 29.5, 29.8, 33.3, 38.3, 61.9, 123.9, 126.5, 129.1, 129.4, 129.6, 135.9, 142.5, 150.3, 170.9, 192.9; **IR** (neat): 3108, 3076, 2981, 2961, 2924, 2852, 1726, 1685, 1525, 1350, 1316, 1265, 1208, 1152, 1093, 1068, 1023, 1011, 855, 749, 693; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{21}NO_5SNa$, 422.1033; found 422.1029.

Ethyl 1-acetyl-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2d, major)



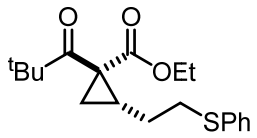
Title compound was obtained as colorless oil (15 mg, 52% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.38 (dd, *J* = 4.2, 9.0 Hz, 1H), 1.47 (m, 1H), 1.57 (dd, *J* = 4.2, 7.8 Hz, 1H), 1.76 (m, 1H), 2.37 (s, 3H), 2.94 (td, *J* = 2.2, 7.3 Hz, 2H), 4.20 (m, 2H), 7.19 (m, 1H), 7.31 (m, 4H); **^{13}C-NMR** δ 14.2, 20.9, 27.3, 30.6, 31.0, 33.4, 41.7, 61.6, 126.3, 129.1, 129.5, 136.2, 171.1, 201.8; **IR** (neat): 3057, 2980, 2961, 2851, 1721, 1699, 1439, 1357, 1270, 1186, 1126, 1095, 1068, 1024, 799, 738, 691; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1020.

Ethyl 1-acetyl-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2d, minor)



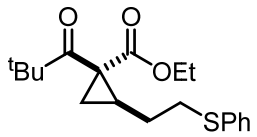
Title compound was obtained as colorless oil (7 mg, 24% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.26 (t, *J* = 7.1 Hz, 3H), 1.43 (m, 2H), 1.74 (ddt, *J* = 7.1, 14.3, 21.7 Hz, 2H), 2.06 (m, 1H), 2.36 (s, 3H), 2.96 (t, *J* = 7.5 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 7.18 (m, 1H), 7.30 (m, 4H); **^{13}C-NMR** δ 14.3, 23.5, 28.5, 29.5, 30.2, 33.0, 41.7, 61.7, 126.3, 129.1, 129.6, 136.2, 169.6, 202.7; **IR** (neat): 3058, 2980, 2961, 2925, 2853, 1721, 1696, 1439, 1358, 1311, 1262, 1189, 1123, 1070, 1024, 741, 692; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1024.

Ethyl 2-(2-(phenylthio)ethyl)-1-pivaloylcyclopropane-1-carboxylate (2e, major)



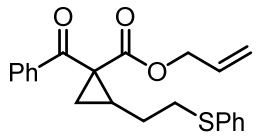
Title compound was obtained as colorless oil (15 mg, 46% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.16 (dd, *J* = 4.7, 8.9 Hz, 1H), 1.21 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.42 (dd, *J* = 4.7, 7.5 Hz, 1H), 1.79 (m, 2H), 1.95 (p, *J* = 7.6 Hz, 1H), 2.96 (m, 2H), 4.15 (m, 2H), 7.17 (m, 1H), 7.28 (m, 2H), 7.33 (m, 2H); **^{13}C-NMR** δ 14.2, 19.8, 24.9, 27.2, 28.3, 33.2, 39.5, 45.2, 61.6, 126.1, 129.0, 129.5, 136.5, 169.6, 210.1; **IR** (neat): 3058, 2959, 2928, 2870, 1730, 1693, 1479, 1440, 1393, 1366, 1304, 1223, 1193, 1173, 1156, 1086, 1024, 989, 738, 691; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{19}H_{26}O_3SNa$, 357.1495; found 357.1503.

Ethyl 2-(2-(phenylthio)ethyl)-1-pivaloylcyclopropane-1-carboxylate (2e, minor)



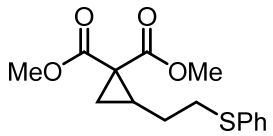
Title compound was obtained as colorless oil (10 mg, 29% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.18 (s, 9H), 1.21 (m, 1H), 1.27 (m, 4H), 1.37 (dd, *J* = 4.3, 9.3 Hz, 1H), 1.96 (m, 2H), 3.04 (m, 2H), 4.17 (m, 2H), 7.17 (m, 1H), 7.27 (m, 2H), 7.32 (m, 2H); **^{13}C-NMR** δ 14.2, 20.2, 27.5, 27.9, 29.9, 33.4, 38.9, 45.0, 61.7, 126.2, 129.1, 129.6, 136.2, 171.3, 210.4. **IR** (neat): 3059, 2966, 2932, 2871, 1728, 1692, 1479, 1440, 1392, 1365, 1263, 1224, 1195, 1172, 1158, 1093, 1067, 1024, 986, 739, 692. **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{19}H_{26}O_3SNa$, 357.1495; found 357.1502.

Allyl 1-benzoyl-2-(2-(phenylthio)ethyl)cyclopropane-1-carboxylate (2f)



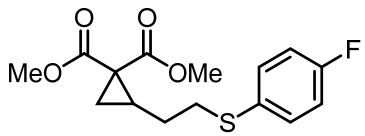
Title compound was obtained as colorless oil (34 mg, 93% yield, 2:1 mixture of diastereomers). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.41 (dd, *J* = 4.3, 9.0, 1H, minor) 1.4-1.5 (m, 2H), 1.4-1.5 (m, 1H, major), 1.60 (dd, *J* = 4.3, 7.8 Hz, 1H, minor), 1.65-1.8 (m, 2H), 1.65-1.8 (m, 1H, major), 2.07 (m, 1H, major), 2.17 (1H, minor), 2.36 (s, 3H, major), 2.38 (s, 3H, minor), 2.96 (t, *J* = 7.6 Hz, 2H), 4.61 (m, 2H), 5.30 (m, 2H), 5.89 (m, 1H), 7.18 (m, 1H), 7.29 (m, 4H); **^{3}C-NMR** δ 21.0, 23.5, 27.3, 28.5, 29.4, 30.4, 31.0, 33.0, 33.5, 41.6, 53.6, 66.3, 119.1, 119.7, 126.3, 129.08, 129.12, 129.5, 129.6, 131.6, 131.7, 136.2, 169.3, 202.5; **IR** (neat): 2921, 2852, 1723, 1695, 1650, 1439, 1358, 1311, 1265, 1183, 1121, 1068, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{22}O_3SNa$, 327.1025; found 327.1021.

Dimethyl 2-(2-(phenylthio)ethyl)cyclopropane-1,1-dicarboxylate (2g)



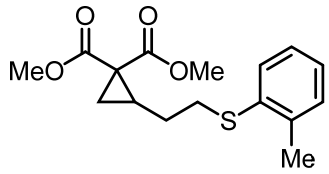
Title compound was obtained as colorless oil (26 mg, 89% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.40 (dd, *J* = 4.8, 7.6 Hz, 1H), 1.44 (m, 1H), 1.61 (m, 1H), 1.74 (td, J = 6.9, 14.5 Hz, 1H), 2.04 (m, 1H), 3.00 (m, 2H), 3.70 (s, 3H), 3.72 (s, 3H), 7.18 (m, 1H), 7.30 (m, 4H); **^{13}C-NMR** δ 21.1, 27.6, 29.0, 31.04, 32.9, 52.7, 52.8, 126.3, 129.1, 136.2, 168.5, 170.7; **IR** (neat): 3003, 2952, 2849, 1723, 1436, 1276, 1211, 1131, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{18}O_4SNa$, 317.0818; found 317.0811.

Dimethyl 2-(2-((4-fluorophenyl)thio)ethyl)cyclopropane-1,1-dicarboxylate (2h)



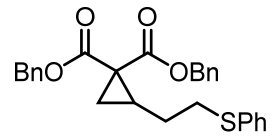
Title compound was obtained as colorless oil (28 mg, 89% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.41 (m, 2H), 1.64 (m, 2H), 2.01 (dq, *J* = 7.4, 8.9 Hz, 1H), 2.94 (m, 2H), 3.70 (s, 3H), 3.72 (s, 3H), 6.99 (m, 2H), 7.34 (m, 2H); **^{13}C-NMR** δ 21.1, 27.5, 29.0, 29.8, 34.2, 52.7, 52.8, 116.1 (d, *J* = 21.9 Hz), 130.9 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 8.0 Hz), 161.5 (d, *J* = 246 Hz), 168.5, 170.6; **^{19}F-NMR** δ -115.4; **IR** (neat): 3006, 3955, 3926, 2853, 2257, 1723, 1491, 1438, 1331, 1277, 1217, 1135; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{17}FO_4SNa$, 335.0724; found 335.0732.

Dimethyl 2-(2-(o-tolylthio)ethyl)cyclopropane-1,1-dicarboxylate (2i)



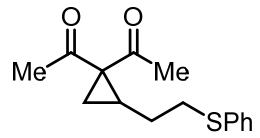
Title compound was obtained as colorless oil (27 mg, 89% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.43 (m, 2H), 1.63 (sex, *J* = 7.3 Hz, 1H), 1.75 (sex, *J* = 6.9 Hz, 1H), 2.05 (m, 1H), 2.37 (s, 3H), 2.97 (m, 2H), 3.71 (s, 3H), 3.73 (s, 3H), 7.13 (m, 3H), 7.26 (m, 1H); **^{13}C-NMR** δ 20.5, 21.1, 27.7, 28.8, 32.1, 34.1, 52.7, 52.8, 126.0, 126.5, 128.4, 130.3, 135.5, 137.9, 168.5, 170.6; **IR** (neat): 3007, 2954, 2925, 2851, 1723, 1438, 1331, 1277, 1214, 1135; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_4SNa$, 331.0975; found 331.0976.

Dibenzyl 2-(2-(phenylthio)ethyl)cyclopropane-1,1-dicarboxylate (2j)



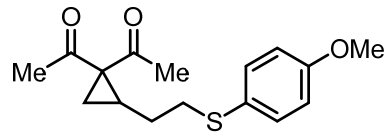
Title compound was obtained as colorless oil (31 mg, 70% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.45 (dt, *J* = 4.7, 8.7 Hz, 2H), 1.61 (sex, *J* = 7.4 Hz, H), 1.72 (sex, *J* = 7.2 Hz, 1H), 2.08 (m, 1H), 2.93 (t, *J* = 7.2 Hz, 2H), 5.13 (m, 4H), 7.17 (m, 2H), 7.2-7.35 (m, 13H); **^{13}C-NMR** δ 21.3, 27.8, 28.7, 29.8, 32.8, 34.3, 67.3, 67.6, 126.2, 128.1, 128.4, 128.5, 128.6, 128.7, 129.0, 129.4, 135.4, 135.6, 136.2, 167.9, 170.0; **IR** (neat): 3067, 3034, 2954, 2925, 2854, 1721, 1319, 1273, 1199, 1131; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{27}H_{26}O_4SNa$, 469.1444; found 469.1453.

1,1'-(2-(2-(phenylthio)ethyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (2k)



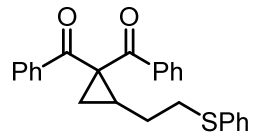
Reaction was performed at 75°C for 24 hour. Title compound was obtained as colorless oil (23 mg, 86% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.34 (dd, *J* = 4.8, 8.9 Hz, 1H), 1.45 (m, 1H), 1.53 (dd, *J* = 4.8, 7.5 Hz, 1H), 1.77 (sex, *J* = 7.0 Hz, 1H), 2.07 (m, 1H), 2.10 (s, 3H), 2.29 (s, 3H), 2.97 (t, *J* = 7.1 Hz, 2H), 7.19 (m, 1H), 7.30 (m, 4H); **^{13}C-NMR** δ 20.6, 27.0, 28.1, 29.3, 31.1, 33.4, 49.4, 126.4, 129.2, 129.6, 136.1, 203.2, 203.7; **IR** (neat): 3003, 2922, 2854, 1682, 1480, 1438, 1358, 1310, 1265, 1169, 1093, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{18}O_2SNa$, 285.0925; found 285.0907.

1,1'-(2-(2-((4-methoxyphenyl)thio)ethyl)cyclopropane-1,1-diyl)bis(ethan-1-one) (2l)



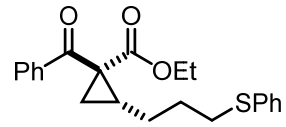
Reaction was performed at 75°C for 24 hour. Title compound was obtained as colorless oil (20 mg, 67% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.33 (dd, *J* = 4.8, 8.9 Hz, 1H), 1.41 (m, 1H), 1.52 (dd, *J* = 4.8, 7.6 Hz, 1H), 1.70 (sex, *J* = 7.0 Hz, 1H), 2.05 (m, 1H), 2.11 (s, 3H), 2.28 (s, 3H), 2.86 (t, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H); **^{13}C-NMR** δ 20.6, 27.0, 28.2, 29.3, 31.1, 35.5, 49.4, 55.5, 114.8, 126.1, 133.5, 159.3, 203.2, 203.8; **IR** (neat): 3003, 2925, 2837, 1684, 1592, 1493, 1461, 1441, 1359, 1282, 1243, 1172, 1097, 1029; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1021.

(2-(2-(phenylthio)ethyl)cyclopropane-1,1-diyl)bis(phenylmethanone) (2m)



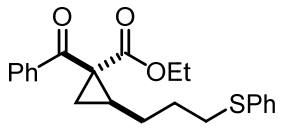
Reaction was performed at 75°C for 24 hour. Title compound was obtained as slightly yellow oil (20 mg, 51% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.41 (dd, *J* = 4.1, 8.7 Hz, 1H), 1.55 (m, 1H), 1.84 (m, 1H), 2.06 (dd, *J* = 4.1, 7.5 Hz, 1H), 2.82 (m, 1H), 3.00 (m, 2H), 7.2-7.4 (m, 10H), 7.71 (m, 4H), 7.96 (m, 2H); **^{13}C-NMR** δ 21.7, 27.3, 27.6, 33.3, 46.0, 126.1, 126.1, 128.57. 128.62, 128.7, 128.8, 128.9, 129.0, 129.3, 133.0, 133.2, 137.9, 138.3, 196.5, 197.5; **IR** (neat): 3060, 3028, 3003, 2960, 2922, 2853, 1658, 1596, 1479, 1447, 1317, 1298, 1267, 1212, 1175, 1074, 1024, 1001; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{25}H_{22}O_2SNa$, 409.1233; found 409.1231.

Ethyl 1-benzoyl-2-(3-(phenylthio)propyl)cyclopropane-1-carboxylate (2n, major)



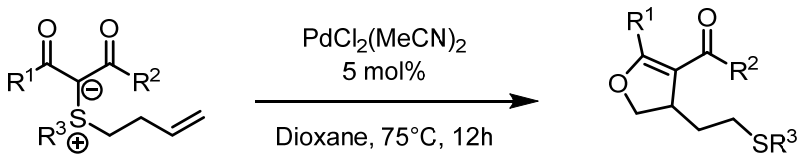
Title compound was obtained as colorless oil (7 mg, 18% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.1 Hz, 3H), 1.38 (dd, *J* = 4.3, 9.0 Hz, 1H), 1.74 (m, 5H), 2.20 (dq, *J* = 7.3, 8.8 Hz, 1H), 2.97 (m, 2H), 3.96 (m, 2H), 7.16 (m, 1H), 7.28 (m, 2H), 7.33 (m, 2H), 7.42 (m, 2H), 7.53 (m, 1H), 7.85 (m, 2H); **^{13}C-NMR** δ 13.8, 22.3, 26.4, 26.5, 28.8, 33.2, 39.1, 61.4, 126.0, 128.2, 128.6, 129.0, 129.3, 132.8, 136.7, 137.7, 170.2, 195.5; **IR** (neat): 3059, 2957, 2924, 2853, 1725, 1678, 1445, 1308, 1281, 1261, 1205, 1182, 1147, 1092, 1023, 968, 791, 737, 690, 663; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{24}O_3SNa$, 391.1338; found 391.1338.

Ethyl 1-benzoyl-2-(3-(phenylthio)propyl)cyclopropane-1-carboxylate (2n, minor)



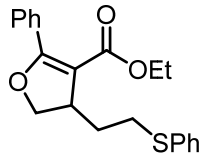
Title compound was obtained as colorless oil (3 mg, 7% yield). **^{1}H-NMR** ($CDCl_3$) δ 0.92 (t, *J* = 7.1 Hz, 3H), 1.42 (dd, *J* = 4.3, 8.9 Hz, 1H), 1.60 (dd, *J* = 4.3, 7.5 Hz, 1H), 1.65 (m, 1H), 1.75 (p, *J* = 7.2 Hz, 2H), 2.23 (m, 1H), 2.86 (m, 2H), 4.01 (m, 2H), 7.15 (m, 1H), 7.23 (m, 4H), 7.44 (m, 2H), 7.55 (m, 1H), 7.87 (m, 2H); **^{13}C-NMR** δ 13.8, 20.4, 27.5, 28.9, 29.0, 33.3, 38.1, 61.5, 126.1, 128.6 (2C), 129.0, 129.4, 133.0, 136.5, 137.9, 171.8, 194.4; **IR** (neat): 3058, 2959, 2923, 2853, 1722, 1677, 1446, 1323, 1258, 1212, 1151, 1092, 1070, 1023, 971, 797, 739, 690, 665; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{24}O_3SNa$, 391.1338; found 391.1338.

3.3 Pd(II)-catalyzed synthesis of dihydrofurans



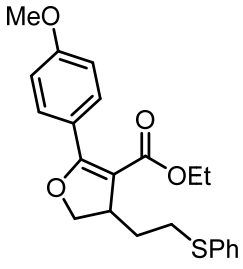
A round bottom flask was charged with a stirrer and $PdCl_2(MeCN)_2$ (1.3 mg, 0.005 mmol, 5 mol%). The corresponding sulfonium ylide (0.1 mmol) was dissolved in 1,4-dioxane (1 mL) and added to the flask. The reaction was heated to specified reaction temperature and stirred until full conversion (TLC). The solvent was evaporated and the crude product was purified by column chromatography (Heptane/EtOAc = 9:1).

Ethyl 2-phenyl-5-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3a)



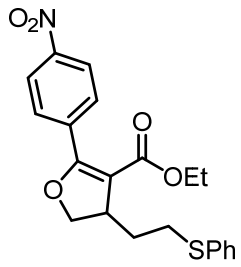
Reaction was performed at 75°C for 14 hour. Title compound was obtained as colorless oil (30 mg, 82% yield). **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.1 Hz, 3H), 1.93 (m, 1H), 2.15 (m, 1H), 2.99 (qdd, *J* = 6.1, 9.3, 13.0 Hz, 2H), 3.52 (tt, *J* = 4.0, 8.3 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 4.32 (dd, *J* = 4.4, 9.3 Hz, 1H), 4.56 (t, *J* = 9.3 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.36 (m, 4H), 7.42 (m, 1H), 7.72 (m, 2H); **^{13}C-NMR** δ 14.3, 31.0, 33.4, 43.3, 59.9, 75.2, 106.2, 126.1, 127.8, 129.1, 129.3, 129.6, 130.1, 130.6, 136.5, 165.2, 166.4; **IR** (neat): 3058, 2978, 2930, 2903, 1687, 1624, 1597, 1238, 1094, 1070; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{22}O_3SNa$, 377.1187; found 377.1179.

Ethyl 2-(4-methoxyphenyl)-5-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3b)



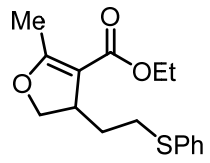
Reaction was performed at 55°C for 14 hour. Title compound was obtained as colorless oil (28 mg, 73% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.1 Hz, 3H), 1.92 (qd, *J* = 8.9, 14.3 Hz, 1H), 2.11 (m, 1H), 2.98 (m, 2H), 3.49 (tt, *J* = 3.9, 8.1 Hz, 1H), 3.83 (s, 3H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.29 (dd, *J* = 4.1, 9.3 Hz, 1H), 4.51 (t, *J* = 9.3 Hz, 1H), 6.89 (m, 2H), 7.17 (m, 1H), 7.28 (m, 2H), 7.34 (m, 2H), 7.77 (m, 2H); **^{13}C-NMR** δ 14.4, 31.0, 33.5, 43.3, 55.5, 59.8, 74.8, 104.8, 113.2, 122.3, 126.1, 129.1, 129.3, 131.5, 136.6, 161.5, 165.4, 166.3; **IR** (neat): 3074, 3057, 2976, 2955, 2933, 2901, 2838, 1682, 1604, 1508, 1478, 1462, 1440, 1371, 1302, 1253, 1174, 1145, 1114, 1090, 1068, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{22}H_{24}O_4SNa$, 407.1288; found 407.1281.

Ethyl 2-(4-nitrophenyl)-5-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3c)



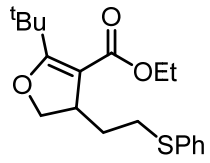
Reaction was performed at 75°C for 72 hour. Title compound was obtained as yellow oil (30 mg, 74% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.1 Hz, 3H), 1.93 (m, 1H), 2.17 (m, 1H), 2.99 (m, 2H), 3.58 (m, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.37 (dd, *J* = 4.7, 9.4 Hz, 1H), 4.61 (t, *J* = 9.6 Hz, 1H), 7.20 (m, 1H), 7.29 (m, 2H), 7.35 (m, 2H), 7.94 (m, 2H), 8.22 (m, 2H); **^{13}C-NMR** δ 14.3, 31.1, 33.3, 43.4, 60.3, 75.6, 109.1, 122.9, 126.3, 129.1, 129.4, 130.7, 136.2, 148.7, 163.4, 164.6; **IR** (neat): 3077, 2978, 2956, 2926, 2854, 1694, 1629, 1589, 1520, 1480, 1344, 1313, 1296, 1240, 1091, 1075; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{21}H_{21}NO_5SNa$, 422.1033; found 422.1036.

Ethyl 2-methyl-5-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3d)



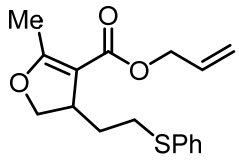
Reaction was performed at 55°C for 14 hour. Title compound was obtained as colorless oil (23 mg, 77% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.23 (t, *J* = 7.1 Hz, 3H), 1.77 (m, 1H), 2.06 (m, 1H), 2.19 (d, *J* = 1.1 Hz, 3H), 2.90 (m, 2H), 3.32 (m, 1H), 4.16 (m, 3H), 4.42 (t, *J* = 9.5 Hz, 1H), 7.17 (m, 1H), 7.31 (m, 4H); **^{13}C-NMR** δ 14.4, 14.5, 31.0, 33.3, 41.7, 59.6, 75.6, 105.8, 126.1, 129.0, 129.3, 136.5, 166.0, 169.5; **IR** (neat): 3057, 2960, 2919, 2850, 1691, 1636, 1439, 1384, 1336, 1304, 1258, 1224, 1170, 1124, 1078, 1017; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{16}H_{20}O_3SNa$, 315.1025; found 315.1021.

Ethyl 2-(tert-butyl)-5-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3e)



Reaction was performed at 55°C for 14 hour. Title compound was obtained as colorless oil (19 mg, 56% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.0 Hz, 3H), 1.29 (s, 9H), 1.79 (m, 1H), 1.97 (m, 1H), 2.88 (m, 2H), 3.31 (m, 1H), 4.12 (m, 3H), 4.29 (t, *J* = 9.5 Hz, 1H), 7.17 (m, 1H), 7.31 (m, 4H); **^{13}C-NMR** δ 14.4, 27.8, 30.5, 33.5, 34.7, 43.5, 59.6, 74.4, 103.8, 126.0, 129.0, 129.1, 136.7, 165.4, 178.3; **IR** (neat): 3075, 2957, 2934, 2906, 2870, 1696, 1594, 1480, 1300, 1259, 1228, 1198, 1165, 1110, 1071, 1057, 1024; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{19}H_{26}O_3SNa$, 357.1495; found 357.1487.

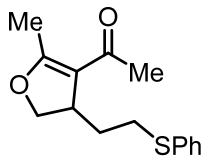
Allyl 2-methyl-4-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-carboxylate (3f)



Reaction was performed at 75°C for 14 hour. Title compound was obtained as colorless oil (23 mg, 75% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.71 (dtd, *J* = 6.2, 8.6, 14.5 Hz, 1H), 2.00 (m, 1H), 2.13 (d, *J* = 1.2 Hz, 3H), 2.82 (m, 2H), 3.27 (m, 1H), 4.10 (dd, *J* = 4.7, 9.4 Hz, 1H), 4.36 (t, *J* = 9.5 Hz, 1H), 5.17 (ddq, *J* = 1.6, 10.4, 32.9 Hz, 2H), 5.83 (ddt, *J* = 5.6, 10.5, 17.2 Hz, 1H), 7.10 (m, 1H), 7.23 (m, 4H); **^{13}C-NMR** δ 14.5, 31.1, 33.3, 41.7, 64.4, 75.8, 105.6, 117.8, 126.1, 129.1, 129.4, 132.9, 136.6, 165.6, 170.0; **IR** (neat): 3076, 3057, 2924, 2894, 1693, 1480,

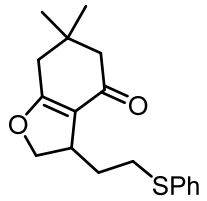
1439, 1387, 1334, 1306, 1281, 1253, 1225, 1129, 1073, 1025; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{17}H_{20}O_3SNa$, 327.1025; found 327.1027.

1-(2-methyl-4-(2-(phenylthio)ethyl)-4,5-dihydrofuran-3-yl)ethan-1-one (3k)



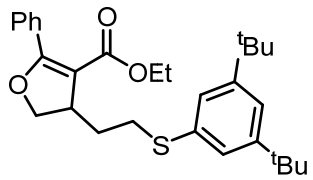
Reaction was perfomed at 75°C for 72 hour. Title compound was obtained as colorless oil (21 mg, 80% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.75 (dtd, *J* = 5.7, 8.8, 14.3 Hz, 1H), 2.00 (m, 1H), 2.20 (s, 3H), 2.21 (d, *J* = 0.9 Hz, 3H), 2.91 (m, 2H), 3.36 (m, 1H), 4.17 (dd, *J* = 4.1, 9.4 Hz, 1H), 4.38 (t, *J* = 9.4 Hz, 1H), 7.18 (m, 1H), 7.31 (m, 4H); **^{13}C-NMR** δ 15.5, 29.3, 31.3, 33.3, 42.2, 75.6, 117.0, 126.3, 129.1, 129.5, 136.4, 168.8, 194.0; **IR** (neat): 3056, 2954, 2920, 2851, 1664, 1613, 1586, 1479, 1438, 1386, 1369, 1224; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{15}H_{18}O_2SNa$, 285.0920; found 285.0929.

6,6-dimethyl-3-(2-(phenylthio)ethyl)-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3o)



Reaction was perfomed at 55°C for 72 hour. Title compound was obtained as colorless oil (12 mg, 41% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.09 (s, 6H), 1.76 (m, 1H), 2.16 (m, 1H), 2.21 (s, 2H), 2.27 (d, *J* = 1.3 Hz, 2H), 2.96 (qdd, *J* = 6.1, 9.2, 13.0 Hz, 2H), 3.37 (m, 1H), 4.26 (dd, *J* = 5.6, 9.5 Hz, 1H), 4.60 (t, *J* = 9.5 Hz, 1H), 7.17 (m, 1H), 7.31 (m, 4H); **^{13}C-NMR** δ 28.5, 29.0, 31.7, 33.4, 34.1, 38.0, 39.1, 51.5, 78.7, 114.9, 126.1, 129.1, 129.3, 136.6, 177.2, 194.7; **IR** (neat): 3059, 2957, 2926, 2891, 2870, 1630, 1469, 1439, 1402, 1221, 1055, 1025, 1012, 943, 930, 798, 742, 692; **HRMS** (ESI): $[M+Na]^+$ calculated for $C_{18}H_{22}O_2SNa$, 325.1233; found 325.1242.

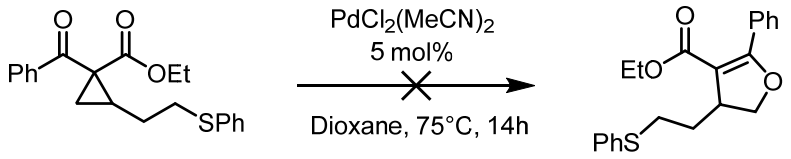
Ethyl 5-(2-((3,5-di-tert-butylphenyl)thio)ethyl)-2-phenyl-4,5-dihydrofuran-3-carboxylate (3p)



Reaction was perfomed at 75°C for 14 hour. Title compound was obtained as colorless oil (42 mg, 91% yield). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 18H), 1.95 (m, 1H), 2.16 (m, 1H), 3.00 (m, 2H), 3.52 (tt, *J* = 4.0, 8.2 Hz, 1H), 4.10 (m, 2H), 4.32 (dd, *J* = 4.3, 9.2 Hz, 1H), 4.56 (t, *J* = 9.4 Hz, 1H), 7.20 (d, *J* = 1.7 Hz, 2H), 7.24 (t, *J* = 1.7 Hz, 1H), 7.39 (m, 3H), 7.72 (m, 2H); **^{13}C-NMR** δ 14.3, 31.5, 31.5, 33.7, 35.1, 43.4, 59.8, 75.3, 106.4, 120.7, 123.7, 127.7, 129.6, 130.2, 130.6, 135.3, 151.6, 165.2, 166.3; **IR** (neat): 2961, 2867, 1687, 1623, 1594, 1574, 1446, 1365, 1242, 1094, 1069. **HRMS** (ESI): $[M+H]^+$ calculated for $C_{29}H_{39}O_3S$, 467.2614; found 467.2613.

4. Mechanistic studies

Isomerization of 2a under Pd-catalysis

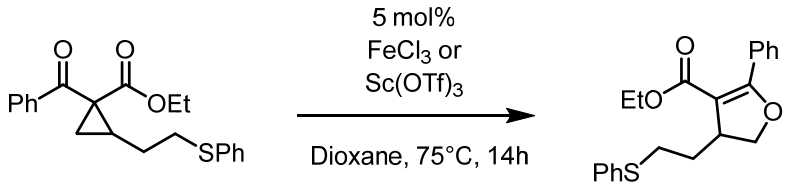


2a
mixture of 2:1 d.r.

3a

Exposure of **2a** under the reaction conditions for the dihydrofuran formation let to complete consumption of the cyclopropane but no dihydrofuran **3a** was observed.

Isomerization of 2a with different Lewis acids

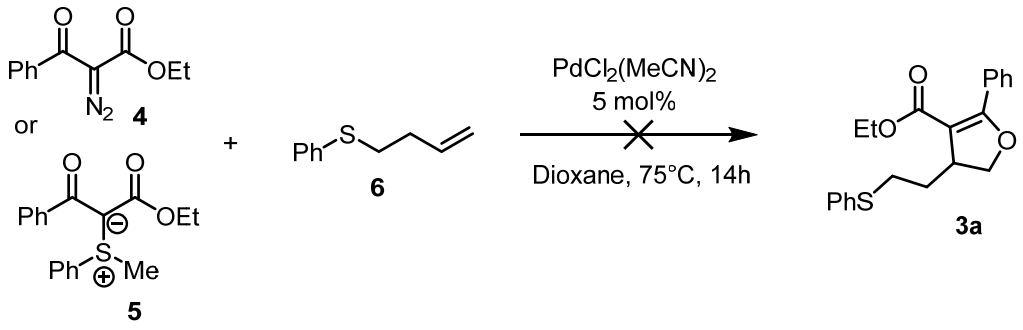


2a
mixture of 2:1 d.r.

3a

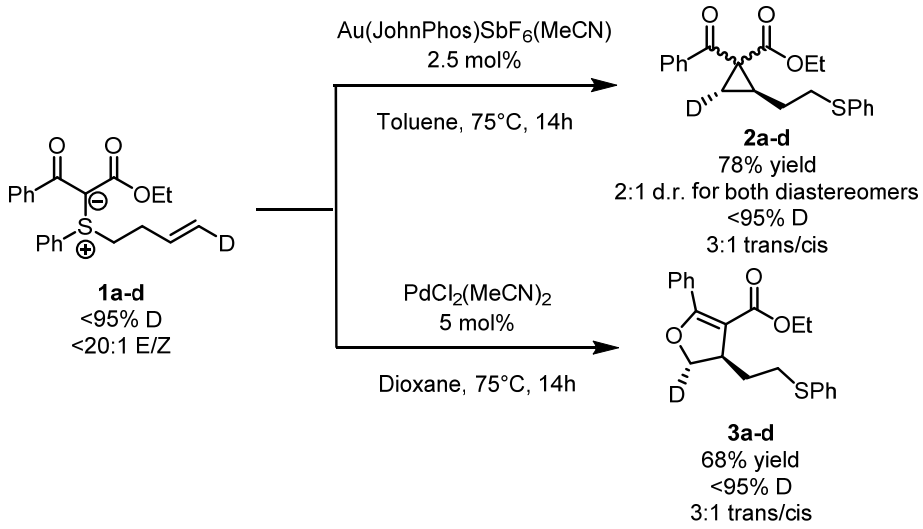
Reaction of **2a** with either 5 mol% $FeCl_3$ or $Sc(OTf)_3$ gave full conversion. In both reactions, the major compound observed was the dihydrofuran **3a** in yield 60-80%.

Probing a carbene intermediate

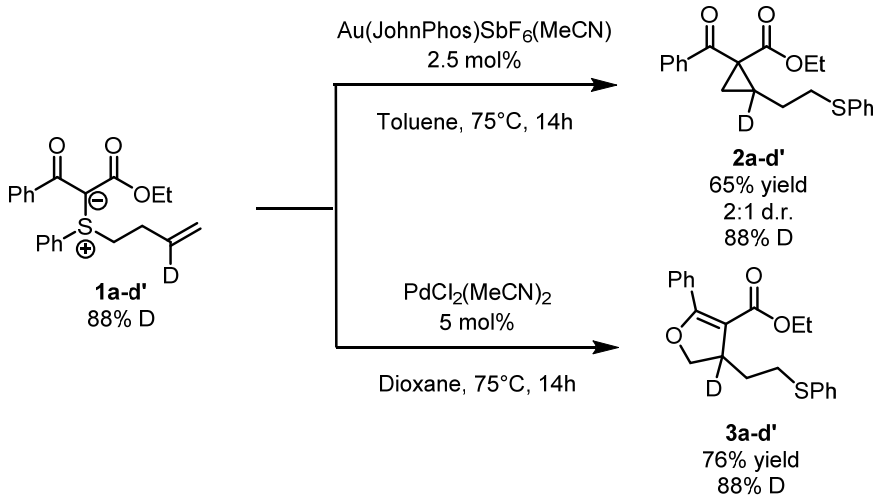


Performing the reaction with either diazo compound **4** in the presence of sulfide **6** and 5 mol% $PdCl_2(MeCN)_2$ or $Pd(OAc)_2$ let to full cons of the diazo compound, but no trace of dihydrofuran **3a** was found. Neither cyclopropane **2a** nor sulfonium ylide **1a** could be observed in the crude. The reaction with (phenylmethyl)sulfonium ylide **5** under the same reaction conditions gave no reaction and the sulfonium ylide could be recovered.

Deuterium labelling experiments

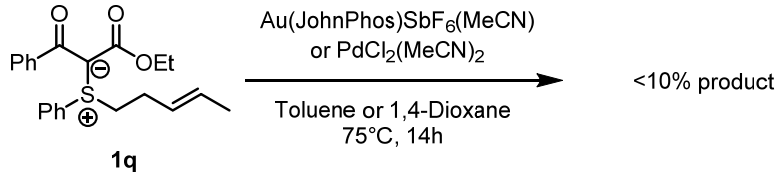


Performing the reaction with sulfonium ylide **1a**-d1, which was deuterated on the terminal position of the double bond (20:1 E/Z), gave full conversion to the cyclopropane **2a**-d1 and dihydrofuran **3a**-d1. For both products, the deuterium was incorporate on the expected position, however in similar 3:1 trans/cis ratio. This implies that the reaction is not fully stereospecific; but most importantly, it suggests that the first cyclization step is the same for both mechanisms.

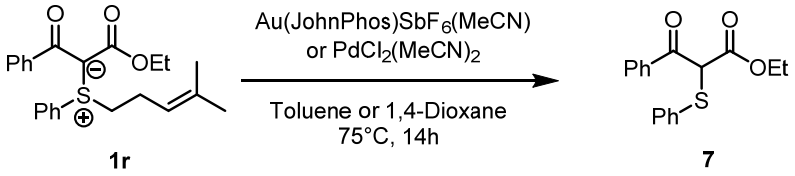


Performing the reaction with sulfonium ylide **1a**-d2, which was deuterated on the internal position of the double bond, gave the products with the deuterium label on the expected position.

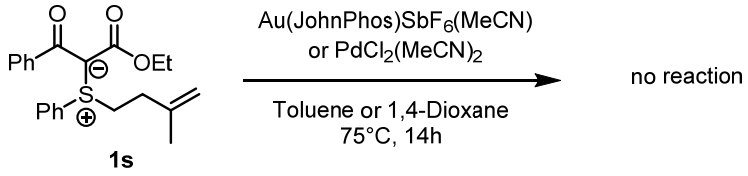
5. Di- and trisubstituted alkenes



The activation of sulfonium ylide **1q** led in both cases to low conversions, although trace amount of cyclopropane and dihydrofuran could be detected. Increasing the reaction temperature led to decomposition without improvement of yield of the products.



The activation of sulfonium ylide **1r** led in both cases to sulfide **7** in >70% yield, probably due to an intramolecular α,β-elimination.



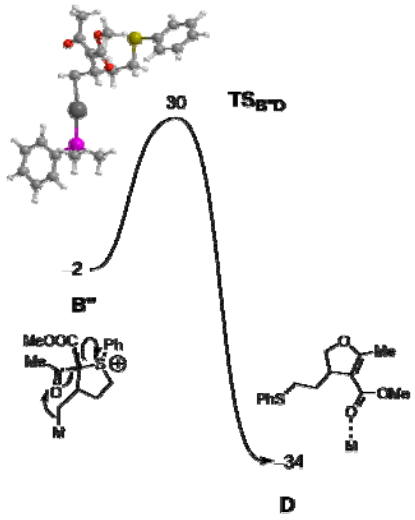
The reaction with sulfonium ylide **1s** gave no reaction in both cases. Increasing the reaction temperature to 100°C only led to small amounts of decomposition and no cyclopropane nor dihydrofuran were obtained.

6. Computational details

The computational results presented have been achieved in part using the Vienna Scientific Cluster (VSC). All calculations were performed using the GAUSSIAN 09 software package[1] and the PBE0 functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including 25 % mixture of Hartree-Fock[2] exchange with DFT[3] exchange-correlation, given by Perdew, Burke and Ernzerhof functional (PBE).[4] The basis set used for the geometry optimizations (basis b1) consisted of the Stuttgart/Dresden ECP (SDD) basis set[5] augmented with an *f*-polarization function[6] to describe the electrons of both Au and Pd, and a standard 6-31G(d,p) basis set[7] for all other atoms. Transition state optimizations were performed with the Synchronous Transit-Guided Quasi-Newton Method (STQN) developed by Schlegel *et al*,[8] following extensive searches of the Potential Energy Surface. Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition state and none for the minima. The transition states were further confirmed by following their vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. The electronic energies (E_{b1}) obtained at the PBE0/b1 level of theory were converted to free energy at 298.15 K and 1 atm (G_{b1}) by using zero point energy and thermal energy corrections based on structural and vibration frequency data calculated at the same level.

Single point energy calculations were performed on the geometries optimized at the PBE0/b1 level using the same functional and the same basis set for the metal atoms, and a standard 6-311++G(d,p) basis set[1] for the other elements (base b2). Solvent effects were considered in the single point energy calculations using the Polarizable Continuum Model (PCM) initially devised by Tomasi and coworkers[2] with radii and non-electrostatic terms of the SMD solvation model, developed by Truhlar *et al*.[3] The solvents were toluene for the Au-system and 1,4-dioxane for the Pd-catalysed reactions. The free energy values presented (G_{b2}^{soln}) were derived from the electronic energy values obtained at the PBE0/b2//PBE0/b1 level (E_{b2}^{soln}), according to the following expression: $G_{b2}^{soln} = E_{b2}^{soln} + G_{b1} - E_{b1} + E_{DFT\text{-}D3}$. The last term ($E_{DFT\text{-}D3}$) represents empirical correction for dispersion obtained means of Grimme DFT-D3 method[4] with Becke and Jonhson short distance damping.[5]

Figure S1. Free energy profile (kcal/mol) for the formation of the dihydrofuran with the Au catalyst. Free energy values relative to the initial reactant, A.



A pathway for formation of the dihydrofuran under Au catalysis was also calculated, and the corresponding free energy profile is represented in Figure 2. The mechanism starts with B", a Au alkyl complex similar to B and to B' but with a different conformation. The reaction occurs in a single step, with formation of a C–O bond between the ketone oxygen and the coordinated C-atom and simultaneous breaking of the S–C bond. In the final species, D, the dihydrofuran coordinates the metal by the $O_{C=O}$ atom of the ester group. In transition state $TS_{B''D}$ both C–O bond formation and C–S bond breaking are well advanced with bond distances of 2.11 and 3.16 Å, respectively. $TS_{B''D}$ is 30 kcal/mol less stable than the initial reagent, A, and, thus, the total reaction barrier is 37 kcal/mol, measured from B to $TS_{B''D}$. Overall, the process is rather favorable, from the thermodynamic point of view, with ΔG_R = –34 kcal/mol. Closing of the catalytic cycle, with liberation of the dihydrofuran, coordination of another substrate molecule and regeneration of A, has a modestly favorable energy balance: ΔG = –1 kcal/mol. However, comparison of the two mechanisms (cf. Figure 1 and Figure 2) shows a clear preference for the cyclopropanation reaction, due to a 21 kcal/mol lower overall barrier.

Figure S2. Free energy profile (kcal/mol) for the formation of carbene with the Au catalyst. Free energy values relative to the initial reactant, A.

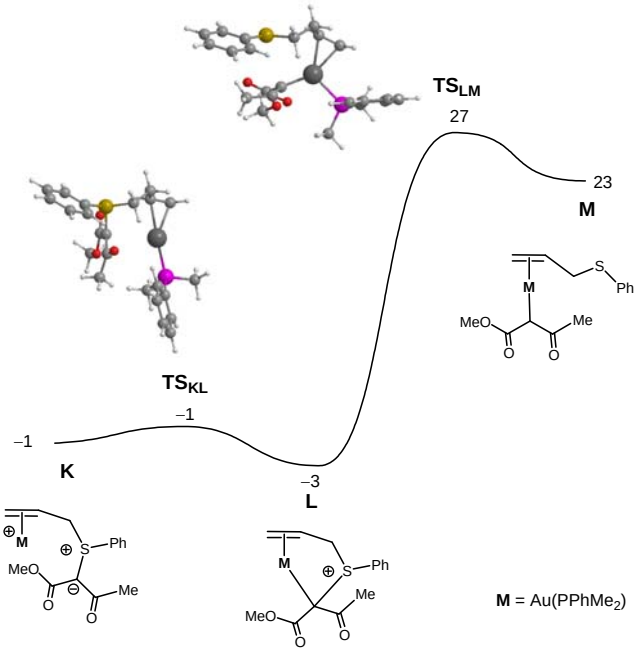
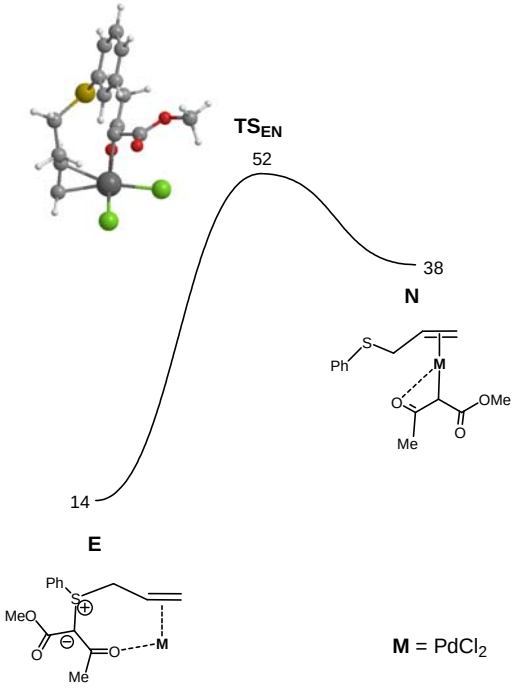


Figure S3. Free energy profile (kcal/mol) for the formation of carbene with the Pd catalyst. Free energy values relative to the separated reactants: [$PdCl_2(MeCN)_2$] and substrate.



The profiles in Figures S2 and S3 demonstrate that for both metallic systems carbene formation is not favourable neither from the kinetic nor from the thermodynamic point of view.

6.1 Atomic coordinates of the optimized species

Substrate

H	2.631935	-4.049479	-3.662106
H	4.341714	-4.572811	-3.500975
O	1.375608	-0.351427	-1.749370
S	3.027938	-2.003642	0.218347
H	0.980066	-1.176741	-5.281439
H	3.918532	-2.939421	-4.090273
H	1.354829	0.234634	-4.241945
O	4.568618	-3.750916	-1.212696
H	1.037767	-0.664841	0.412582
C	2.823768	-2.222435	-1.489847
C	1.961150	-1.330668	-2.212212
H	1.618540	-1.345636	1.967717
C	3.726908	-3.257753	-1.965953
C	0.422609	-2.719574	0.764954
C	-0.852936	-2.423257	1.495095
C	-2.036713	-2.257353	0.911431
C	3.984507	-0.529634	0.588047
C	3.615576	0.743737	0.151255
H	2.722866	0.867955	-0.454001
C	4.425738	1.823590	0.485852
H	4.151172	2.820431	0.153729
C	5.584617	1.633061	1.236912
C	5.947766	0.356363	1.654376
H	6.209976	2.483811	1.491441
H	6.855993	0.205827	2.229909
C	5.147463	-0.735153	1.328620
C	3.645428	-3.739676	-3.397154
O	1.812751	-1.662871	-3.516865
C	1.403301	-1.559975	0.915668
H	5.424418	-1.739869	1.633500
H	-0.044094	-0.786795	-3.863803
C	0.974206	-0.789872	-4.261849
H	-2.930589	-2.042209	1.488989
H	-2.153238	-2.333586	-0.166959
H	0.220053	-2.888793	-0.296763
H	0.875157	-3.638688	1.161402
H	-0.775799	-2.335036	2.579585

Cyclopropane product

H	0.709977	-0.306206	-3.878154
H	2.369133	0.067735	-3.342873
O	-1.782394	-1.411218	-0.565225
S	2.319691	0.511805	0.514367
H	0.958585	0.529609	-2.341092
O	2.460552	-2.269698	-2.492183
H	1.575448	-1.009079	2.208843
H	-2.757186	-0.345151	-3.943502
H	-2.812991	0.268873	-2.258718
C	0.384050	-2.022832	-1.403781
C	-1.001875	-1.473479	-1.492252
H	3.322977	-1.116019	1.976657
C	1.478176	-1.567391	-2.334299
C	2.183949	-2.299997	0.575851
C	0.791953	-2.452365	0.016884
C	0.441910	-3.486767	-0.978984
C	1.172837	1.483881	1.472123
C	-0.187046	1.158310	1.523206
H	-0.562418	0.295125	0.980061
C	-1.062736	1.950144	2.259483
H	-2.115977	1.687063	2.299314
C	-0.598185	3.082422	2.925072
C	0.750253	3.419609	2.857335
H	-1.287025	3.702067	3.491892
H	1.118953	4.301596	3.373317
C	1.636000	2.620350	2.139365
C	1.372738	-0.226968	-3.011899
O	-1.332413	-1.112421	-2.739863
C	2.364080	-1.065769	1.452592
H	2.692137	2.867879	2.095663
H	-3.392348	-1.371437	-2.616682
C	-2.659720	-0.608867	-2.890946
H	-0.505940	-4.006085	-0.880855
H	1.254057	-4.034502	-1.448629
H	2.928571	-2.327231	-0.225537
H	2.384067	-3.176813	1.206891
H	-0.005438	-2.221873	0.721657

Dihydrofurane product

H	5.253259	-2.126313	-1.235232
H	5.058404	-0.380989	-1.102228
O	0.241237	-2.029050	0.190519
S	0.676348	1.092857	4.611338
H	3.795148	-1.351502	-1.912736
O	4.668963	-1.415520	1.269005
H	0.822381	-1.303190	4.334906
H	0.793355	-2.015484	-3.437021
H	-0.279724	-1.241433	-2.226810
C	2.544986	-1.709436	0.558888
C	1.360039	-1.880254	-0.264846
H	2.410989	-0.575721	4.635418
C	3.836755	-1.499276	0.211182
C	1.718061	-0.423697	2.575469
C	2.433678	-1.683464	2.067609
C	3.918611	-1.757501	2.453093
C	0.483356	0.769074	6.353451
C	-0.516102	-0.096077	6.808830
H	-1.174574	-0.574869	6.089794
C	-0.670188	-0.330556	8.171204
H	-1.447467	-1.005973	8.517212
C	0.158498	0.310220	9.089679
C	1.145040	1.183610	8.641410
H	0.031331	0.132283	10.153580
H	1.791013	1.688491	9.354062
C	1.311840	1.409889	7.277619
C	4.513699	-1.330721	-1.097031
O	1.600311	-1.873474	-1.596284
C	1.474647	-0.461666	4.077656
H	2.083234	2.084922	6.919645
H	-0.044532	-2.999182	-2.194161
C	0.441276	-2.043227	-2.405671
H	4.222021	-2.767329	2.750800
H	4.209791	-1.054764	3.238162
H	0.760257	-0.340260	2.052702
H	2.315243	0.458780	2.311518
H	1.892017	-2.563797	2.433374

MeCN

N	-1.427715	1.193832	-0.459424
C	-0.580767	0.429062	-0.258035
C	0.482216	-0.529377	-0.003451
H	0.612743	-1.186861	-0.866843
H	1.423761	-0.007471	0.185739
H	0.238362	-1.140785	0.869113

[PdCl2(MeCN)2]

Pd	1.382326	1.381830	-0.009972
N	-0.625580	1.461949	-0.005502
N	1.462748	-0.626060	-0.006822
Cl	1.355175	3.649873	-0.013736
Cl	3.650375	1.355019	-0.015442
C	-1.753997	1.697374	-0.003476
C	1.698414	-1.754439	-0.005545
C	-3.163600	2.031285	-0.001302
H	-3.649297	1.619296	-0.889469
H	-3.644661	1.627090	0.892944
H	-3.272205	3.119245	-0.005764
C	2.032682	-3.163951	-0.003780
H	1.627330	-3.645702	0.889563
H	1.622080	-3.649163	-0.892835
H	3.120710	-3.272247	-0.006763

A

Au	-1.437261	-2.065868	-0.237366
P	-1.693207	-4.213522	0.603473
H	-1.909884	-2.274165	5.145499

C	-1.830218	-4.290129	2.408335
C	-1.812127	-3.118403	3.171624
H	-2.139291	-4.474416	6.265678
H	-2.744275	3.773341	0.003044
H	-2.173801	-6.556527	4.919214
C	-1.923731	-3.186451	4.557446
H	-3.897866	3.736659	-1.363664
O	1.501362	3.726331	-0.735233
C	-2.052749	-4.421768	5.184746
H	-1.980161	-6.453882	2.470467
S	0.273087	2.149091	-2.959526
C	-2.072117	-5.593277	4.429176
H	-0.322951	6.001259	1.482145
H	-2.610166	4.979500	-1.257049
H	1.105715	6.036165	0.401243
C	-1.961817	-5.531316	3.045497
H	-1.712524	-2.152408	2.682482
O	-2.510596	2.131814	-2.572766
H	1.784619	1.570784	-1.208903
H	-3.275381	-6.038516	0.314112
C	-0.539685	3.112016	-1.769638
H	-3.122942	-5.055681	-1.164483
C	0.282657	3.847090	-0.834861
H	-4.071524	-4.450160	0.213166
C	-3.184868	-5.019906	-0.073680
H	-0.477394	-6.321469	0.507113
H	0.621964	-4.923180	0.549354
H	-0.224989	-5.342609	-0.958472
H	2.230599	0.803122	-2.755864
C	-1.981139	2.999849	-1.864474
C	0.663246	-0.266277	-1.708448
C	-0.310450	-5.308327	0.130781
C	-0.553772	-0.021267	-0.855834
C	-1.846731	-0.126090	-1.315910
C	1.376246	3.146997	-3.956557
C	2.586358	3.674848	-3.503365
H	2.893218	3.534968	-2.474183
C	3.358810	4.420290	-4.388497
H	4.301638	4.838517	-4.049557
C	2.926933	4.640836	-5.695010
C	1.715400	4.112984	-6.132413
H	3.537907	5.227387	-6.374446
H	1.378215	4.282961	-7.150029
C	0.934372	3.355917	-5.264917
C	-2.865539	3.933766	-1.072152
O	-0.406919	4.672050	-0.028808
C	1.403945	1.022972	-2.074695
H	-0.008243	2.931516	-5.598105
H	0.924626	4.715970	1.574413
C	0.382973	5.396834	0.913245
H	-2.679211	0.277284	-0.746475
H	-2.055578	-0.398120	-2.347347
H	0.376726	-0.804128	-2.618737
H	1.379732	-0.895795	-1.165828
H	-0.381740	0.459538	0.108339

TS_{AB}

Au	-1.892498	-1.958602	-0.265030
P	-1.962378	-4.043891	0.741370
H	-1.031056	-1.858570	5.076826
C	-1.660162	-4.025139	2.531601
C	-1.431901	-2.815162	3.194049
H	-1.030759	-3.982771	6.356281
H	-3.024800	3.088331	-0.641741
H	-1.435897	-6.133843	5.190479
C	-1.206301	-2.801312	4.567821
H	-3.953243	3.433121	-2.134760
O	1.288015	2.982012	-0.703436
C	-1.206857	-3.993597	5.284979
H	-1.838490	-6.173739	2.765101
S	0.405039	2.071352	-3.448629
C	-1.434339	-5.203533	4.630947
H	-0.849500	4.875941	1.602571
H	-2.667528	4.537252	-1.553293
H	0.719915	5.079656	0.760822
C	-1.660810	-5.222057	3.260004
H	-1.433635	-1.884041	2.632601
O	-2.387311	2.171382	-3.533495
H	1.940121	1.116425	-1.879534
H	-3.592949	-5.842186	0.979571
C	-0.589286	2.585816	-2.100679
H	-3.790982	-4.961592	-0.557415
C	0.100953	3.156702	-0.947665
H	-4.366537	-4.239258	0.960675
C	-3.583891	-4.854147	0.510665
H	-0.861169	-6.210151	0.510012
H	0.254139	-4.859236	0.197933
H	-0.936210	-5.330803	-1.036574
H	1.988247	0.283896	-3.473706
C	-2.001032	2.727290	-2.511933
C	0.281899	-0.262832	-2.227226
C	-0.761107	-5.228779	0.037658
C	-0.703577	0.319759	-1.246784
C	-2.059029	-0.053495	-1.247229
C	1.598205	3.307572	-3.935554
C	2.741374	3.641529	-3.207396
H	2.937950	3.186700	-2.245106
C	3.601708	4.602531	-3.727889
H	4.495463	4.871864	-3.173751
C	3.320927	5.222210	-4.944242
C	2.175597	4.882037	-5.658859
H	4.000251	5.972376	-5.337399
H	1.958003	5.360703	-6.608237
C	1.309068	3.914791	-5.161084
C	-2.975503	3.493457	-1.656113
O	-0.699866	3.837068	-0.118714
C	1.345990	0.716277	-2.702722
H	0.420381	3.630661	-5.717329
H	0.385072	3.574503	1.643222
C	-0.061507	4.371809	1.044766
H	-2.713278	0.500032	-0.571535
H	-2.506280	-0.267782	-2.220251
H	-0.256161	-0.692992	-3.078702
H	0.804041	-1.087772	-1.724330
H	-0.275530	0.735226	-0.336314

B

Au	-1.863547	-1.971516	-0.275897
P	-2.084760	-4.100570	0.650939
H	-1.166323	-2.199543	5.119547
C	-1.816790	-4.206049	2.449534
C	-1.560338	-3.042299	3.180920
H	-1.267340	-4.386164	6.285539
H	-2.501034	2.772835	-0.184525
H	-1.722993	-6.457154	4.999182
C	-1.363488	-3.107784	4.558061
H	-3.729125	2.573196	-1.466570
O	1.328323	2.821200	-0.215449
C	-1.420746	-4.334621	5.211780
H	-2.075127	-6.353335	2.566387
S	0.584567	1.690069	-3.247194
C	-1.676712	-5.499366	4.489801
H	-0.001604	6.273343	-0.583510
H	-2.894866	4.117600	-1.281194
H	1.593690	5.481397	-0.792106
C	-1.874551	-5.436681	3.115545
H	-1.518739	-2.085495	2.665938
O	-1.925446	2.732496	-3.417890
H	2.342507	1.293212	-1.646363
H	-3.803081	-5.838584	0.808778
C	-0.405158	2.061599	-1.720543
H	-3.941426	-4.889320	-0.694408
C	0.377115	3.097077	-0.909320
H	-4.498890	-4.200076	0.843173
C	-3.740593	-4.834786	0.379000
H	-1.108296	-6.332227	0.358589
H	0.085920	-5.035830	0.109242
H	-1.111794	-5.391022	-1.152696
H	2.352104	0.096029	-2.992946
C	-1.746324	2.615884	-2.225009
C	0.742895	-0.186908	-1.506326
C	-0.947180	-5.340386	-0.072968
C	-0.451960	0.662903	-0.986945
C	-1.768958	-0.088236	-1.160638
C	1.413809	3.164297	-3.794906
C	2.608655	3.621661	-3.235729

H	3.082768	3.107256	-2.407367
C	3.193317	4.766960	-3.766544
H	4.128057	5.129963	-3.350929
C	2.589863	5.438673	-4.828486
C	1.396291	4.970339	-5.372556
H	3.057033	6.329412	-5.236973
H	0.929147	5.493535	-6.200549
C	0.799465	3.822691	-4.863061
C	-2.772003	3.033059	-1.209076
O	-0.102920	4.319500	-1.092887
C	1.732452	0.663440	-2.295545
H	-0.134064	3.449463	-5.272143
H	0.628614	5.152156	0.671476
C	0.581950	5.374248	-0.395948
H	-2.598667	0.485839	-0.733043
H	-1.985292	-0.213764	-2.232379
H	0.345585	-0.980240	-2.147215
H	1.259607	-0.676019	-0.676831
H	-0.281100	0.893642	0.068530

B'

Au	-0.559860	-1.872086	-0.918968
P	-0.838477	-3.559816	0.665979
H	-5.594887	-2.283702	1.067658
C	-2.514936	-3.698670	1.364659
C	-3.526257	-2.847448	0.908659
H	-6.103927	-3.972889	2.811379
H	-0.564022	0.353890	-5.098686
H	-4.318611	-5.488711	3.627492
C	-4.814487	-2.946865	1.428514
H	0.991143	0.338948	-5.996119
O	-2.177146	2.283209	-2.841794
C	-5.099515	-3.894908	2.406052
H	-2.040187	-5.325526	2.714922
S	1.319574	3.379648	-2.335639
C	-4.096834	-4.747561	2.865575
H	-0.584044	-5.993487	0.780807
H	-0.061686	1.772408	-6.029317
H	0.572875	-5.246888	-0.351741
C	-2.810587	-4.651629	2.347822
H	-3.300167	-2.108905	0.143301
O	2.238456	1.600169	-4.168365
H	-1.125687	-5.448007	-0.825181
H	0.127029	-4.249950	2.810988
H	1.631342	2.745677	-0.055577
H	0.057339	-2.479458	2.644600
H	1.307349	-3.402065	1.782635
H	-1.964351	4.906280	-5.473337
H	-2.665474	4.736697	-3.829288
C	0.220021	2.024530	-3.021753
C	-1.143962	2.616170	-3.361959
C	-0.458388	-5.226973	0.010980
H	3.092778	2.461158	-1.033971
C	1.029802	1.521143	-4.235889
C	1.542800	0.908409	-1.267550
C	0.267361	-3.414237	2.119826
C	0.156746	0.934751	-1.909026
C	-0.310973	-0.433159	-2.401042
C	0.240134	4.537866	-1.520841
C	-0.620632	4.200449	-0.473172
H	-0.683063	3.184851	-0.096887
C	-1.413272	5.194116	0.088690
H	-2.086815	4.943849	0.901952
C	-1.346403	6.502603	-0.388910
C	-0.486949	6.828050	-1.434513
H	-1.966512	7.272096	0.060331
H	-0.430987	7.847808	-1.801434
C	0.312830	5.845083	-2.009268
C	0.300932	0.945283	-5.408533
O	-1.020441	3.553192	-4.302803
C	2.009188	2.333893	-0.993891
H	0.990120	6.089714	-2.822039
H	-2.962893	3.475251	-5.051466
C	-2.241664	4.208285	-4.685675
H	-1.279562	-0.324963	-2.904572
H	0.403860	-0.830692	-3.135468
H	2.252749	0.406816	-1.930940
H	1.507810	0.339785	-0.333719
H	-0.578284	1.312317	-1.188089

$TS_{B'C}$

Au	-0.653304	-1.954298	-0.797789
P	-0.852326	-3.670315	0.737231
H	-5.650479	-2.556544	1.150350
C	-2.533050	-3.894463	1.387131
C	-3.565065	-3.045438	0.975764
H	-6.121616	-4.373326	2.771941
H	-0.399640	1.532690	-5.879850
H	-4.297369	-5.883948	3.507412
C	-4.853411	-3.218496	1.474434
H	1.364946	1.478693	-6.180041
O	-2.351170	1.956621	-2.337437
C	-5.116611	-4.238045	2.383927
H	-2.017394	-5.591018	2.636115
S	1.493118	3.417743	-2.354383
C	-4.092238	-5.088007	2.798179
H	-0.442003	-6.076068	0.771824
H	0.591067	2.911132	-5.436794
H	0.669648	-5.223232	-0.329278
C	-2.804751	-4.919165	2.303396
H	-3.358556	-2.250002	0.263871
O	1.815165	0.481713	-3.986116
H	-1.012816	-5.516955	-0.819545
H	0.125088	-4.322189	2.874314
H	1.220748	2.800144	-0.059275
H	-0.039345	-2.555923	2.728988
H	1.272200	-3.398361	1.872004
H	-2.549454	4.457449	-5.051993
H	-2.802029	4.414809	-3.275747
C	-0.108301	1.446906	-2.988376
C	-1.440240	2.155930	-3.110068
C	-0.362707	-5.280352	0.025679
H	2.875459	2.523291	-0.621833
C	0.848832	1.196274	-4.161321
C	1.500713	0.908794	-1.119469
C	0.230758	-3.470421	2.196406
C	0.103778	0.818675	-1.688964
C	-0.460261	-0.469493	-2.332237
C	0.516478	4.776222	-1.765917
C	-0.568866	4.623031	-0.896961
H	-0.847207	3.645688	-0.515018
C	-1.313300	5.738269	-0.526897
H	-2.151238	5.619366	0.153291
C	-0.993712	6.997987	-1.030898
C	0.078624	7.144449	-1.906592
H	-1.579319	7.863959	-0.738392
H	0.336070	8.124266	-2.296624
C	0.838495	6.038617	-2.274461
C	0.584878	1.820578	-5.499933
O	-1.472394	3.043213	-4.093238
C	1.820794	2.388819	-0.875193
H	1.687606	6.152850	-2.941586
H	-3.542148	3.160061	-4.304932
C	-2.679669	3.817369	-4.181432
H	-1.507749	-0.393986	-2.636709
H	0.181316	-0.938588	-3.076188
H	2.229542	0.457252	-1.792125
H	1.549721	0.384435	-0.158798
H	-0.630010	1.200638	-0.976447

C

Au	-0.419224	-1.717830	-1.198803
P	-0.692131	-3.072418	0.604288
H	-5.198188	-1.102105	1.121588
C	-2.302028	-2.858370	1.405118
C	-3.239182	-1.953559	0.896021
H	-5.739866	-2.439771	3.139148
H	0.188674	2.157717	-6.474112
H	-4.082497	-4.046077	4.046280
C	-4.473948	-1.805038	1.520987
H	1.880730	2.422702	-5.987666
O	-2.495043	1.044843	-3.142463
C	-4.776405	-2.556326	2.652477
H	-1.897031	-4.322425	2.955661
S	1.133569	3.489255	-2.087841
C	-3.845886	-3.459881	3.163853

H	-0.665002	-5.460855	1.043672
H	0.523316	3.075869	-5.006740
H	0.436449	-5.021757	-0.287170
C	-2.611529	-3.613277	2.544838
H	-3.006381	-1.365563	0.011445
O	1.771890	0.147358	-4.956583
H	-1.318996	-5.092757	-0.570597
H	0.428517	-3.479553	2.721153
H	0.909458	1.971224	-0.247834
H	0.524729	-1.768458	2.241041
H	1.573952	-2.973622	1.455112
H	-3.212950	2.712186	-6.370623
H	-3.443217	3.026323	-4.618957
C	-0.254305	0.659774	-3.864469
C	-1.659292	1.187523	-4.010877
C	-0.545210	-4.833843	0.155376
H	2.611178	2.158294	-0.695717
C	0.870546	0.954579	-4.856751
C	1.544366	0.730888	-1.908212
C	0.582304	-2.797576	1.879960
C	0.138335	0.474053	-2.426084
C	-0.225367	-0.768613	-3.324803
C	0.230277	4.446962	-0.885517
C	-1.134453	4.216872	-0.684032
H	-1.643404	3.451031	-1.263879
C	-1.836194	4.980512	0.244010
H	-2.896645	4.802832	0.397480
C	-1.184071	5.980420	0.962496
C	0.171391	6.219170	0.751938
H	-1.735259	6.579859	1.680860
H	0.679127	7.003735	1.304958
C	0.880804	5.455760	-0.171453
C	0.869359	2.242272	-5.621963
O	-1.884519	1.764863	-5.179161
C	1.601889	2.021735	-1.094036
H	1.936250	5.640100	-0.346221
H	-3.940291	1.460719	-5.309572
C	-3.214067	2.272984	-5.374892
H	-1.225664	-1.210899	-3.348395
H	0.601001	-1.334033	-3.751245
H	2.263251	0.745671	-2.731822
H	1.862743	-0.088981	-1.252088
H	-0.665567	0.828305	-1.777785

B”

Au	-1.151388	-1.464926	-0.313860
P	-2.300747	-3.101919	0.887423
H	2.080859	-4.891709	2.304376
C	-1.222464	-4.271729	1.775163
C	0.166112	-4.125669	1.697694
H	1.113152	-6.739527	3.647253
H	2.128573	3.941023	-3.445355
H	-1.348053	-7.008844	3.792603
C	1.003769	-5.012009	2.370161
H	3.204932	2.543248	-3.470916
O	-1.157767	2.351078	-4.156093
C	0.460322	-6.048048	3.122981
H	-2.838143	-5.449663	2.609407
S	-0.257766	4.071139	-1.579952
C	-0.922981	-6.200411	3.205418
H	-3.958156	-3.255124	2.687142
H	3.417961	3.767427	-2.211309
H	-4.172779	-1.790054	1.697754
C	-1.761448	-5.317377	2.535416
H	0.588178	-3.315404	1.108083
O	2.222121	1.925640	-0.885586
H	-2.863824	-1.867440	2.897065
H	-3.918206	-4.894545	0.464045
H	-2.230837	3.461829	-0.369369
H	-2.791128	-4.668184	-0.895707
H	-4.123924	-3.521808	-0.653773
H	1.585943	0.656591	-5.999410
H	0.411668	1.988397	-6.269239
C	0.266723	2.362219	-2.206142
C	-0.075065	2.127243	-3.673630
C	-3.435668	-2.446436	2.168309
H	-0.949466	4.082415	0.705522
C	1.792440	2.438567	-1.890104
C	-0.671611	1.982606	0.048430
C	-3.391525	-4.152552	-0.142743
C	-0.566806	1.363611	-1.343780
C	-0.059494	-0.073531	-1.408586
C	-1.438117	4.916779	-2.597012
C	-2.714508	4.425054	-2.880754
H	-3.027335	3.444621	-2.541281
C	-3.570376	5.206921	-3.643630
H	-4.564350	4.839025	-3.876364
C	-3.154216	6.450730	-4.120740
C	-1.877428	6.926054	-3.837706
H	-3.833297	7.051762	-4.717520
H	-1.557337	7.895184	-4.205981
C	-1.007010	6.159550	-3.069426
C	2.676113	3.238016	-2.812213
O	0.936052	1.543011	-4.302777
C	-1.166576	3.410181	-0.127161
H	-0.014099	6.527625	-2.828611
H	-0.160190	0.412929	-5.663531
C	0.667102	1.124902	-5.652332
H	-0.064842	-0.411028	-2.453660
H	0.977418	-0.117138	-1.062075
H	0.295240	1.951051	0.555464
H	-1.389825	1.419900	0.652312
H	-1.570129	1.399547	-1.792295

$TS_{B”D}$

Au	-0.601288	-1.455397	0.102494
P	-2.066726	-3.026987	0.941794
H	1.810475	-5.167806	3.140100
C	-1.255602	-4.274986	1.973561
C	0.125958	-4.235846	2.185774
H	0.451697	-6.963511	4.178844
H	2.359056	3.522076	-3.203052
H	-1.999140	-7.039534	3.807364
C	0.737688	-5.202670	2.978519
H	3.204835	2.192578	-3.996283
O	-1.201761	1.245958	-3.711787
C	-0.026014	-6.209627	3.560696
H	-3.095617	-5.340072	2.410571
S	-0.296923	4.262765	-1.852629
C	-1.403856	-6.253772	3.352894
H	-4.064968	-3.030593	2.329290
H	3.872668	2.859229	-2.483110
H	-3.935853	-1.543748	1.356464
C	-2.020182	-5.291408	2.562607
H	0.723259	-3.449410	1.730641
O	2.742815	1.013037	-1.293990
H	-2.926208	-1.748778	2.808011
H	-3.645572	-4.643730	0.044034
H	-2.024440	2.633435	-1.430527
H	-2.223384	-4.449069	-1.009517
H	-3.498452	-3.208374	-1.003590
H	0.613240	2.668550	-6.614444
H	-0.833163	3.141822	-5.670326
C	0.791535	1.355040	-2.464989
C	-0.022465	1.561129	-3.663850
C	-3.377082	-2.265365	1.957904
H	-1.706594	3.651818	-0.012849
C	2.179831	1.597696	-2.245280
C	-0.319715	2.022867	-0.235520
C	-2.946022	-3.919946	-0.384507
C	0.104701	0.923116	-1.223208
C	1.055614	-0.058778	-0.612553
C	-1.600272	5.149880	-2.677999
C	-2.541336	4.488678	-3.475482
H	-2.502651	3.408063	-3.587230
C	-3.519905	5.224446	-4.135757
H	-4.254571	4.710751	-4.749043
C	-3.551841	6.613691	-4.024644
C	-2.604920	7.269503	-3.243397
H	-4.313935	7.183302	-4.547722
H	-2.627007	8.351286	-3.152246
C	-1.632411	6.541498	-2.562856
C	2.954926	2.626461	-3.022648
O	0.658050	2.079343	-4.684977
C	-1.236095	3.086426	-0.822692
H	-0.901862	7.046843	-1.938599

H	-0.633598	1.447896	-6.190795
C	-0.108373	2.347786	-5.864780
H	1.468532	-0.854897	-1.235687
H	1.516371	0.108624	0.360455
H	0.581672	2.485469	0.185920
H	-0.839480	1.529041	0.597532
H	-0.813342	0.439999	-1.621505

D

Au	-1.324524	-0.553966	-1.370763
P	-2.641936	-1.635973	0.102800
H	0.781440	-5.192663	0.374555
C	-1.904593	-3.147382	0.781252
C	-0.699516	-3.638914	0.269100
H	-0.376966	-6.416481	2.193733
H	3.838186	1.146903	-4.055435
H	-2.515028	-5.552340	3.106197
C	-0.153001	-4.814118	0.777054
H	4.911010	2.156692	-3.048437
O	-0.265093	0.414499	-2.877758
C	-0.804425	-5.500578	1.797289
H	-3.497458	-3.483012	2.215700
S	-0.482729	3.737601	-1.983235
C	-2.006269	-5.016089	2.311221
H	-3.776885	-1.111679	2.195704
H	3.446865	2.840898	-3.813841
H	-3.584851	0.322854	1.159887
C	-2.557688	-3.844827	1.806091
H	-0.192656	-3.102346	-0.529275
O	3.778893	1.634658	-0.978542
H	-2.194733	-0.304770	2.075829
H	-4.860190	-2.629132	0.108172
H	-1.159791	1.993638	-0.446956
H	-4.057929	-2.808545	-1.471075
H	-4.758331	-1.240202	-1.007181
H	0.921995	1.390450	-6.180956
H	-0.541891	1.646679	-5.182426
C	1.778062	1.256824	-1.937586
C	0.852248	0.984156	-2.988904
C	-3.094690	-0.584073	1.523660
H	-0.992204	3.561470	0.353488
C	3.092520	1.608900	-2.117835
C	0.875641	2.512912	0.119842
C	-4.236631	-2.126611	-0.636867
C	1.506935	1.226515	-0.445312
C	2.943383	1.080377	0.063995
C	-2.234299	3.925813	-2.258804
C	-2.948379	2.933026	-2.937436
H	-2.425606	2.048170	-3.291044
C	-4.313077	3.090598	-3.165751
H	-4.863666	2.323701	-3.703581
C	-4.967362	4.238197	-2.722692
C	-4.255702	5.231219	-2.054089
H	-6.029916	4.363769	-2.908347
H	-4.761670	6.131368	-1.717925
C	-2.890860	5.079323	-1.823334
C	3.875203	1.961012	-3.326914
O	1.258151	1.327455	-4.196840
C	-0.521663	2.884345	-0.365565
H	-2.327604	5.856198	-1.314950
H	0.139365	0.003156	-5.357639
C	0.376355	1.067080	-5.296248
H	3.244458	0.034708	0.190832
H	3.151865	1.635280	0.980399
H	1.560045	3.352411	-0.061314
H	0.826914	2.392846	1.210077
H	0.905078	0.358796	-0.142624

E

Pd	-0.671405	2.112416	1.738901
C	0.493631	1.094645	-0.775938
C	-2.074833	1.338040	-1.021480
O	-3.180395	0.813262	-0.930309
O	0.721252	1.869504	0.181682
C	-0.826865	0.592836	-1.098499
S	-0.912927	-1.115225	-1.151491
C	-1.774597	-1.803589	-2.564084
C	-3.096633	-1.491569	-2.887317
C	-1.024006	-2.687333	-3.340938
C	-3.662438	-2.084240	-4.011357
C	-1.607771	-3.274284	-4.459765
C	-2.924846	-2.972184	-4.793084
C	-1.957027	-1.683226	0.274937
C	-1.949305	-0.746530	1.482433
C	-0.601266	-0.163026	1.839706
C	-0.223739	0.388773	3.042086
O	-1.888199	2.647706	-1.140794
C	-3.048334	3.465553	-0.957830
C	1.680893	0.692505	-1.603602
Cl	-0.659747	4.359356	1.313719
Cl	-2.433217	2.408211	3.155502
H	-3.648052	-0.783326	-2.277513
H	0.003385	-2.914885	-3.071382
H	-4.687876	-1.847271	-4.278335
H	-1.032514	-3.965582	-5.067803
H	-3.379597	-3.429425	-5.666849
H	-1.542291	-2.669174	0.507352
H	-2.972541	-1.796838	-0.104783
H	-2.335983	-1.329438	2.327812
H	-2.674485	0.052438	1.308813
H	0.220132	-0.411027	1.171813
H	0.831708	0.537189	3.257042
H	-0.912030	0.485388	3.875065
H	-3.426518	3.355338	0.060790
H	-2.704535	4.485908	-1.111998
H	-3.820691	3.190050	-1.679672
H	1.750883	1.396995	-2.440648
H	2.599412	0.755275	-1.017989
H	1.565069	-0.305017	-2.033889

TS_{EF}

Pd	-0.468266	2.800763	1.478608
C	0.498917	0.896015	-0.612473
C	-2.078675	0.977743	-0.624278
O	-3.174791	0.463470	-0.468775
O	0.770979	1.889582	0.067922
C	-0.802764	0.228476	-0.444235
S	-0.861611	-1.459260	-0.938778
C	-1.733409	-1.782110	-2.464304
C	-3.102395	-1.571227	-2.642092
C	-0.930502	-2.280571	-3.493666
C	-3.662278	-1.868828	-3.879921
C	-1.509023	-2.569289	-4.725136
C	-2.872617	-2.364404	-4.916111
C	-1.899803	-2.160315	0.410496
C	-1.913633	-1.179002	1.576984
C	-0.743512	-0.227162	1.621267
C	-0.793794	0.913381	2.457727
O	-1.869182	2.225197	-0.981894
C	-2.990347	3.125293	-0.938206
C	1.557425	0.358270	-1.534518
Cl	-0.144905	4.834631	0.390796
Cl	-1.816592	3.738684	3.050558
H	-3.703512	-1.153342	-1.842660
H	0.130096	-2.447281	-3.329749
H	-4.724302	-1.705967	-4.034655
H	-0.893923	-2.958744	-5.530076
H	-3.323619	-2.592193	-5.877133
H	-1.428847	-3.116783	0.650434
H	-2.896033	-2.339465	0.005768
H	-1.899247	-1.751395	2.513185
H	-2.836840	-0.596979	1.555059
H	0.235321	-0.703005	1.516400
H	0.077557	1.044991	3.103749
H	-1.750671	1.102281	2.941350
H	-3.471247	3.062911	0.039353
H	-2.550999	4.111796	-1.071336
H	-3.696123	2.872392	-1.732756
H	1.174841	0.248721	-2.554429
H	2.401462	1.048327	-1.529739
H	1.902566	-0.626902	-1.199933

F

Pd	-0.830868	2.625902	1.445583
C	0.510741	0.894891	-0.414395
C	-2.020041	0.890808	-0.341876

O	-3.112569	0.576191	0.083944
O	0.720976	1.954599	0.157855
C	-0.731984	0.131841	0.024572
S	-0.844755	-1.599309	-0.745033
C	-1.705109	-1.615380	-2.300767
C	-3.033539	-1.213282	-2.457732
C	-0.952073	-2.087395	-3.380198
C	-3.602808	-1.287141	-3.723746
C	-1.538453	-2.148786	-4.639696
C	-2.861378	-1.750314	-4.809662
C	-2.001027	-2.193377	0.553682
C	-1.762789	-1.302198	1.779725
C	-0.616960	-0.314830	1.514050
C	-0.584590	0.883398	2.459436
O	-1.783097	1.667489	-1.393249
C	-2.831179	2.572303	-1.788889
C	1.445036	0.388743	-1.462765
Cl	-0.920937	4.650769	0.179314
Cl	-2.546309	3.146095	2.837878
H	-3.602199	-0.821091	-1.620215
H	0.074477	-2.410450	-3.233652
H	-4.632936	-0.973833	-3.860836
H	-0.961701	-2.513655	-5.483485
H	-3.318854	-1.801375	-5.792914
H	-1.755425	-3.246941	0.702354
H	-3.012718	-2.102243	0.156875
H	-1.514140	-1.910083	2.653081
H	-2.670580	-0.734296	1.986839
H	0.329783	-0.878451	1.568737
H	0.388328	0.965874	2.956052
H	-1.370384	0.804163	3.212714
H	-2.714353	3.478964	-1.185325
H	-2.652044	2.785313	-2.841994
H	-3.805731	2.106933	-1.636278
H	0.902401	0.240918	-2.403625
H	2.238357	1.121604	-1.611161
H	1.881132	-0.573166	-1.169894

TS_{FG}

Pd	-0.748182	2.529404	1.529654
C	0.559029	1.009508	-0.309693
C	-1.999543	0.932008	-0.360424
O	-3.110809	0.607270	-0.002820
O	0.940640	1.969060	0.354492
C	-0.716092	0.354387	0.185353
S	-0.842681	-1.672059	-0.761917
C	-1.717940	-1.709596	-2.303484
C	-3.052635	-1.323347	-2.454999
C	-0.965281	-2.130410	-3.406276
C	-3.628101	-1.372748	-3.720071
C	-1.553263	-2.162705	-4.665556
C	-2.884947	-1.787669	-4.823138
C	-2.026380	-2.146534	0.552846
C	-1.797700	-1.246023	1.777756
C	-0.610675	-0.306059	1.568596
C	-0.493408	0.815651	2.589266
O	-1.709348	1.702032	-1.407714
C	-2.752086	2.563694	-1.892215
C	1.329137	0.533377	-1.491660
Cl	-0.841052	4.556817	0.281315
Cl	-2.634283	2.926780	2.720191
H	-3.626821	-0.957478	-1.610340
H	0.066141	-2.444050	-3.273543
H	-4.664807	-1.074536	-3.842553
H	-0.971280	-2.491791	-5.520771
H	-3.344912	-1.819193	-5.806028
H	-1.837708	-3.203332	0.754451
H	-3.032769	-2.035355	0.149108
H	-1.600808	-1.855102	2.664145
H	-2.691394	-0.645857	1.958174
H	0.307884	-0.914925	1.542275
H	0.506002	0.886119	3.028425
H	-1.262272	0.763011	3.359893
H	-2.740592	3.464264	-1.270549
H	-2.483515	2.804474	-2.919790
H	-3.715593	2.055225	-1.843815
H	0.665228	0.456184	-2.358361
H	2.134421	1.239165	-1.697118
H	1.748099	-0.460464	-1.297805

G

Pd	0.010406	2.378291	2.156801
C	0.414843	1.675437	-0.184749
C	-2.145780	1.944808	0.099561
O	-3.241766	1.478796	0.312615
O	1.376457	1.806752	0.605287
C	-0.849327	1.363944	0.526472
S	-0.766980	-2.050871	-1.209662
C	-1.495224	-2.653531	-2.717894
C	-2.172812	-1.797805	-3.591640
C	-1.343364	-4.001437	-3.050839
C	-2.709845	-2.293123	-4.775105
C	-1.863631	-4.486846	-4.247855
C	-2.552549	-3.637023	-5.108105
C	-2.252053	-1.442713	-0.326716
C	-1.915601	-1.004528	1.094478
C	-0.742538	-0.031597	1.215803
C	-0.457974	0.440341	2.612926
O	-1.949854	3.120591	-0.526080
C	-3.143889	3.844984	-0.835524
C	0.586666	1.768119	-1.653238
Cl	1.458776	3.385806	3.641022
Cl	-1.828157	3.105274	3.234481
H	-2.276027	-0.744633	-3.345920
H	-0.820544	-4.663684	-2.367622
H	-3.241598	-1.624263	-5.445793
H	-1.738205	-5.535470	-4.501613
H	-2.964884	-4.019042	-6.037276
H	-2.982319	-2.255672	-0.293230
H	-2.694695	-0.612577	-0.880723
H	-1.649402	-1.884248	1.693581
H	-2.815448	-0.560656	1.527748
H	0.150002	-0.522675	0.813243
H	0.461896	0.121851	3.104712
H	-1.319141	0.517245	3.274978
H	-3.676554	4.092606	0.085091
H	-2.814282	4.750468	-1.343014
H	-3.796831	3.253723	-1.481668
H	-0.142488	2.469758	-2.065401
H	1.604611	2.071153	-1.900369
H	0.370810	0.776642	-2.073462

G'

Pd	0.573676	1.270889	0.727675
C	-0.177476	2.600468	-1.073671
C	-2.124618	2.769179	0.620965
O	-3.154676	2.354299	1.101247
O	0.788669	1.825244	-1.341916
C	-1.200704	1.982917	-0.236072
S	-2.531493	-2.536323	-0.475362
C	-1.940317	-3.613388	-1.763974
C	-0.917111	-3.216883	-2.630650
C	-2.473399	-4.900274	-1.863244
C	-0.451595	-4.094075	-3.603923
C	-1.990679	-5.780043	-2.828845
C	-0.985448	-5.377583	-3.702960
C	-3.270237	-1.157197	-1.424319
C	-3.045530	0.170083	-0.712763
C	-1.557176	0.529265	-0.665870
C	-0.729023	-0.291852	0.280894
O	-1.651937	4.005827	0.846012
C	-2.413103	4.777308	1.778168
C	-0.131581	4.014987	-1.546097
Cl	2.608150	0.310592	1.180588
Cl	-0.088428	1.298320	2.884820
H	-0.478800	-2.226933	-2.536549
H	-3.265196	-5.204322	-1.185606
H	0.342553	-3.779923	-4.274871
H	-2.408460	-6.779975	-2.900665
H	-0.612922	-6.064012	-4.457470
H	-4.341171	-1.347061	-1.541397
H	-2.816192	-1.156591	-2.420318
H	-3.467393	0.154371	0.294597
H	-3.587404	0.952871	-1.256333
H	-1.144717	0.408396	-1.673889
H	-0.006665	-1.014614	-0.091740

H	-1.168457	-0.533590	1.245802
H	-2.417491	4.284937	2.752924
H	-1.911715	5.742437	1.838819
H	-3.441927	4.896773	1.430803
H	-1.128696	4.426210	-1.706250
H	0.363245	4.629769	-0.787806
H	0.465153	4.050194	-2.459955

$TS_{G'H}$

Pd	0.774054	1.962431	1.366969
C	-0.042454	2.935698	-0.810394
C	-2.029715	2.619893	0.840674
O	-2.948801	1.995299	1.309091
O	1.167010	2.795292	-0.599326
C	-0.926922	2.040351	0.008360
S	-1.550406	-2.469426	-0.824839
C	-1.687828	-3.785396	-2.019256
C	-0.715611	-3.942837	-3.010388
C	-2.756786	-4.682669	-1.947836
C	-0.820991	-4.981972	-3.930609
C	-2.858285	-5.719646	-2.870706
C	-1.892345	-5.869252	-3.862872
C	-2.514584	-1.170682	-1.679335
C	-2.530617	0.117940	-0.865156
C	-1.134504	0.696071	-0.688147
C	-0.281998	0.263992	0.444417
O	-1.835275	3.934375	1.016964
C	-2.730089	4.557448	1.947369
C	-0.574787	3.864776	-1.840805
Cl	2.646930	2.777833	2.360871
Cl	-0.087280	1.361883	3.365226
H	0.123091	-3.254031	-3.049534
H	-3.498853	-4.566157	-1.163574
H	-0.061540	-5.101559	-4.697954
H	-3.690272	-6.415315	-2.810354
H	-1.970814	-6.681680	-4.579465
H	-3.538367	-1.529550	-1.820067
H	-2.075210	-1.003978	-2.669435
H	-2.996310	-0.040880	0.109698
H	-3.160006	0.844016	-1.394709
H	-0.591783	0.676088	-1.639360
H	0.689759	-0.182159	0.232188
H	-0.809691	-0.117596	1.315209
H	-2.607313	4.103100	2.932669
H	-2.442713	5.607336	1.969559
H	-3.765039	4.442736	1.618079
H	-1.300253	3.350201	-2.478797
H	-1.105935	4.673523	-1.328333
H	0.242242	4.275197	-2.435296

H

Pd	1.557608	1.675703	1.313238
C	-0.107432	3.086104	-0.544741
C	-2.188158	2.534251	0.830810
O	-3.023674	1.826998	1.338145
O	1.055240	3.103125	-0.137638
C	-1.068082	2.045497	-0.042279
S	-1.646616	-2.359046	-0.892141
C	-1.753676	-3.775556	-1.967734
C	-0.628027	-4.191573	-2.682481
C	-2.946776	-4.496746	-2.072942
C	-0.698855	-5.315181	-3.502028
C	-3.016129	-5.611048	-2.903019
C	-1.892580	-6.022081	-3.617262
C	-2.527184	-1.126878	-1.915999
C	-2.634293	0.210313	-1.189209
C	-1.281833	0.837088	-0.938207
C	-0.532352	0.669996	0.349098
O	-2.110464	3.856939	1.010375
C	-3.080167	4.410816	1.909499
C	-0.547415	4.055329	-1.589050
Cl	3.229973	2.926611	2.103046
Cl	1.931308	0.062475	2.812076
H	0.299050	-3.634413	-2.587077
H	-3.812397	-4.186772	-1.494437
H	0.180923	-5.636874	-4.051867
H	-3.945825	-6.167241	-2.982188
H	-1.946474	-6.897512	-4.257911
H	-3.531355	-1.501991	-2.134250
H	-1.996353	-1.013193	-2.867825
H	-3.176188	0.096122	-0.247230
H	-3.227293	0.886528	-1.818638
H	-0.639749	0.857388	-1.820481
H	0.532216	0.383829	0.208890
H	-1.037914	0.183692	1.176314
H	-2.981772	3.952014	2.895144
H	-2.858917	5.475669	1.956663
H	-4.090080	4.239160	1.531084
H	-0.747679	3.511909	-2.519878
H	-1.478716	4.538301	-1.284696
H	0.231813	4.797943	-1.760876

$TS_{G'I}$

Pd	0.500319	1.008908	0.411055
C	-0.233222	2.459237	-1.194976
C	-2.097473	2.643237	0.599652
O	-3.115341	2.238936	1.120739
O	0.588072	1.608860	-1.665907
C	-1.290582	1.877636	-0.381370
S	-2.803509	-2.280104	-0.534577
C	-1.967574	-3.362200	-1.670482
C	-1.057363	-2.889228	-2.620464
C	-2.195907	-4.733603	-1.536850
C	-0.397636	-3.790975	-3.448066
C	-1.521532	-5.628260	-2.362500
C	-0.626993	-5.159371	-3.319982
C	-3.610309	-1.033017	-1.597888
C	-3.320364	0.336957	-1.006426
C	-1.803289	0.509641	-0.882949
C	-1.165552	-0.510591	0.025933
O	-1.548914	3.830708	0.891597
C	-2.185835	4.540362	1.955486
C	0.007482	3.914711	-1.444002
Cl	2.432383	-0.206815	0.672466
Cl	-0.008749	0.993745	2.624263
H	-0.851599	-1.826513	-2.712611
H	-2.900766	-5.092928	-0.793349
H	0.310596	-3.421677	-4.183435
H	-1.701237	-6.693877	-2.257597
H	-0.102328	-5.859339	-3.963007
H	-4.681791	-1.247692	-1.626250
H	-3.206025	-1.144594	-2.608134
H	-3.793801	0.452902	-0.029700
H	-3.735488	1.115846	-1.656181
H	-1.362893	0.381509	-1.878059
H	-0.386436	-1.191328	-0.304001
H	-1.475969	-0.566013	1.064998
H	-2.119269	3.961989	2.879453
H	-1.638803	5.477597	2.050808
H	-3.236321	4.727688	1.721281
H	-0.921611	4.482784	-1.495979
H	0.603614	4.329884	-0.626135
H	0.580225	4.005686	-2.369057

I

Pd	0.660384	0.814543	-0.407952
C	-0.539469	2.245264	-1.548922
C	-1.899568	2.329963	0.641886
O	-2.884534	1.953826	1.256572
O	0.044348	1.457041	-2.367976
C	-1.333774	1.599885	-0.512985
S	-3.063382	-2.086595	-0.398696
C	-1.885335	-3.018232	-1.377744
C	-0.536735	-2.676164	-1.454676
C	-2.395462	-4.145713	-2.025764
C	0.309939	-3.474869	-2.219434
C	-1.536012	-4.924608	-2.792122
C	-0.186326	-4.589093	-2.889077
C	-3.957277	-1.024583	-1.639304
C	-3.493512	0.411673	-1.391949
C	-2.046082	0.311594	-0.888374
C	-2.124650	-0.690218	0.267044
O	-1.221186	3.431888	0.968174
C	-1.662067	4.089648	2.155291
C	-0.322681	3.725931	-1.689906
Cl	2.530815	-0.464039	-0.863416

Cl	0.720024	0.410186	1.843300
H	-0.106030	-1.815026	-0.950192
H	-3.443204	-4.418284	-1.929564
H	1.357713	-3.195585	-2.276414
H	-1.921602	-5.801109	-3.303436
H	0.481415	-5.204571	-3.484093
H	-5.025473	-1.190717	-1.487156
H	-3.662112	-1.409442	-2.618151
H	-4.115978	0.905052	-0.640821
H	-3.552675	0.976028	-2.327239
H	-1.453620	-0.124664	-1.700555
H	-1.167818	-1.026726	0.676374
H	-2.726628	-0.288291	1.087024
H	-1.532514	3.431575	3.017246
H	-1.029874	4.971316	2.253155
H	-2.713875	4.374411	2.074079
H	-1.224977	4.296420	-1.463089
H	0.459366	4.058686	-1.003180
H	0.007140	3.914295	-2.713160

I’

Pd	-0.265153	1.188495	1.979534
C	0.452019	1.682614	-0.001494
C	-1.904886	2.625159	-0.275909
O	-2.974766	2.506166	-0.846480
O	1.151957	0.695248	0.416143
C	-0.990251	1.486755	0.004628
S	-1.832197	-2.534145	-0.364316
C	-1.820001	-3.099125	-2.053113
C	-2.060659	-2.255449	-3.139455
C	-1.529912	-4.451615	-2.234873
C	-2.009839	-2.784660	-4.423524
C	-1.483383	-4.966680	-3.527325
C	-1.722673	-4.135517	-4.617068
C	-3.373940	-1.547923	-0.162791
C	-2.901956	-0.193063	0.339371
C	-1.616577	0.157616	-0.423876
C	-0.714239	-1.071706	-0.270061
O	-1.442633	3.798240	0.161895
C	-2.338796	4.897376	0.016069
C	1.169578	2.941887	-0.406671
Cl	0.722949	0.298237	3.861501
Cl	-2.116778	1.932544	3.087751
H	-2.282298	-1.203251	-2.992651
H	-1.342064	-5.091271	-1.377746
H	-2.194213	-2.137930	-5.275498
H	-1.259308	-6.017793	-3.678063
H	-1.685291	-4.539643	-5.623977
H	-4.015989	-2.089312	0.534421
H	-3.852068	-1.507744	-1.145064
H	-2.699736	-0.209015	1.415842
H	-3.670887	0.560123	0.158308
H	-1.888999	0.269639	-1.485077
H	0.067760	-1.202501	-1.018507
H	-0.267120	-1.136202	0.725338
H	-3.239977	4.725283	0.608640
H	-1.799893	5.766373	0.391646
H	-2.617944	5.036924	-1.031380
H	2.180743	2.656625	-0.704183
H	0.664019	3.469222	-1.216823
H	1.240113	3.623715	0.444141

$TS_{I'J}$

Pd	-0.356638	1.333989	2.056677
C	0.389309	1.570676	0.103690
C	-1.948429	2.565434	-0.408392
O	-3.024294	2.347037	-0.930040
O	0.937445	0.439237	0.464576
C	-1.034521	1.476618	0.021508
S	-1.926822	-2.751223	-0.301186
C	-1.914202	-3.107495	-2.043542
C	-2.370795	-2.230417	-3.030239
C	-1.349267	-4.335300	-2.402320
C	-2.268015	-2.592738	-4.370028
C	-1.239343	-4.679523	-3.745155
C	-1.700319	-3.811598	-4.731169
C	-3.344547	-1.638604	-0.015365
C	-2.816829	-0.304047	0.499510
C	-1.546455	0.068335	-0.274327
C	-0.466847	-0.955429	0.015303
O	-1.480436	3.791621	-0.174706
C	-2.392211	4.853282	-0.459187
C	1.288902	2.719061	-0.218532
Cl	0.453006	0.584337	4.060477
Cl	-2.032704	2.539075	2.982377
H	-2.810453	-1.272625	-2.772093
H	-1.007998	-5.020047	-1.631363
H	-2.630395	-1.911400	-5.133834
H	-0.802069	-5.635091	-4.017846
H	-1.621162	-4.085370	-5.778657
H	-4.002163	-2.132440	0.703534
H	-3.887513	-1.538167	-0.957951
H	-2.586062	-0.357774	1.569453
H	-3.572594	0.472762	0.368181
H	-1.778803	0.039470	-1.348447
H	0.205048	-1.316772	-0.753420
H	-0.300253	-1.309626	1.025635
H	-3.277542	4.761662	0.173375
H	-1.853392	5.770776	-0.226921
H	-2.693215	4.834555	-1.509267
H	1.646854	2.595682	-1.248090
H	0.768729	3.670316	-0.134730
H	2.153707	2.692457	0.447310

J

Pd	-0.377649	1.250620	2.009270
C	0.275372	1.311700	-0.019567
C	-2.025688	2.434401	-0.416164
O	-3.213847	2.278333	-0.589178
O	0.752081	0.043268	0.037396
C	-1.128898	1.310116	-0.041405
S	-2.803515	-3.282867	-0.196028
C	-2.244300	-3.127998	-1.877524
C	-2.976479	-2.488846	-2.883590
C	-1.039193	-3.759731	-2.209409
C	-2.492059	-2.456617	-4.188041
C	-0.573815	-3.744084	-3.521078
C	-1.291758	-3.083300	-4.514107
C	-3.612174	-1.689551	0.174061
C	-2.715744	-0.573261	0.695974
C	-1.629033	-0.106982	-0.283780
C	-0.318045	-0.913078	-0.245956
O	-1.386700	3.592485	-0.582219
C	-2.234473	4.718130	-0.824436
C	1.300383	2.363682	-0.244168
Cl	0.240203	0.680926	4.103669
Cl	-1.421068	3.147704	2.611437
H	-3.933176	-2.026891	-2.660658
H	-0.468156	-4.261918	-1.433157
H	-3.068820	-1.950842	-4.957281
H	0.361131	-4.241855	-3.762214
H	-0.922930	-3.061808	-5.535000
H	-4.355067	-1.941719	0.936542
H	-4.173022	-1.356852	-0.703803
H	-2.256972	-0.875240	1.646419
H	-3.364106	0.282887	0.910788
H	-2.049778	-0.128652	-1.297852
H	-0.071456	-1.386207	-1.198446
H	-0.291132	-1.664238	0.544766
H	-2.895079	4.875216	0.030786
H	-1.564680	5.567552	-0.950348
H	-2.834217	4.560533	-1.723420
H	1.590683	2.349956	-1.301751
H	0.904360	3.345884	0.003836
H	2.187528	2.146840	0.355934

K

Au	1.255610	-1.909612	-0.902309
P	-0.337060	-3.574851	-0.601158
C	-1.676902	-3.111897	0.524231
C	-2.066051	-1.769895	0.585990
C	-3.144535	-1.387155	1.375767
O	0.923813	0.216894	-4.117005
C	-3.825825	-2.342375	2.125303
S	0.261413	2.106359	-2.069909
C	-3.435102	-3.679670	2.077708
C	-2.367961	-4.070684	1.275778
O	-2.231741	1.212184	-0.813702
C	-0.808939	0.857885	-2.623459
C	-0.236618	0.116140	-3.728619
C	-1.103740	-4.076739	-2.181205
C	-2.056342	0.680379	-1.920922
C	2.167410	1.140447	-0.334829
C	0.432989	-5.096281	0.048611
C	2.461613	0.044008	-1.320309
C	3.299549	-1.010706	-1.051100
C	-0.580485	3.679655	-1.972038
C	-1.480601	4.031348	-0.965041
C	-2.045793	5.302140	-0.995103
C	-1.725071	6.197136	-2.014067
C	-0.828445	5.831569	-3.014265
C	-0.243607	4.569569	-2.994825
C	-3.167025	-0.154486	-2.512642
O	-1.093424	-0.760929	-4.291825
C	0.751929	1.715459	-0.351207
C	-0.570671	-1.476331	-5.412047
H	-1.540546	-1.012649	0.012064
H	-3.441417	-0.343261	1.389539
H	-4.663951	-2.047114	2.749294
H	-3.964950	-4.423059	2.665237
H	-2.082769	-5.118200	1.246306
H	-1.880756	-4.824327	-1.997774
H	-0.339432	-4.498081	-2.840332
H	-1.545076	-3.204875	-2.669650
H	2.874926	1.945636	-0.581583
H	2.406229	0.819485	0.685334
H	-0.290453	-5.915645	0.079961
H	0.822085	-4.917351	1.053474
H	1.259712	-5.387319	-0.604053
H	2.169477	0.215096	-2.364416
H	3.715047	-1.602821	-1.864428
H	3.759659	-1.130352	-0.070942
H	-1.755312	3.313083	-0.203076
H	-2.749261	5.589939	-0.219996
H	-2.175669	7.184885	-2.027021
H	-0.574148	6.529652	-3.805431
H	0.468273	4.279443	-3.761974
H	-4.066874	0.032299	-1.925039
H	-2.926787	-1.220626	-2.462220
H	-3.336246	0.081369	-3.564592
H	-0.008096	1.039202	0.043598
H	0.715123	2.647875	0.217144
H	-1.395175	-2.087718	-5.778558
H	0.272362	-2.106978	-5.117067
H	-0.234004	-0.786940	-6.188926

TS_{KL}

Au	1.009998	-1.570342	-1.004864
P	-0.446252	-3.359524	-0.662746
C	-1.865124	-3.054067	0.421807
C	-2.093009	-1.779060	0.946463
C	-3.190295	-1.550983	1.772522
O	0.911271	0.289161	-4.211892
C	-4.055798	-2.594583	2.083725
S	0.443086	2.120715	-2.069112
C	-3.832259	-3.869582	1.564450
C	-2.742880	-4.101776	0.734377
O	-1.891784	1.186832	-0.543048
C	-0.574937	0.744350	-2.415733
C	-0.150448	0.078933	-3.640181
C	-1.102761	-4.017238	-2.235588
C	-1.784223	0.598945	-1.626863
C	2.430193	1.229446	-0.407193
C	0.454631	-4.770540	0.072472
C	2.571766	0.070826	-1.360655
C	3.210074	-1.102636	-1.028458
C	-0.514973	3.628826	-2.035727
C	-1.329756	4.021568	-0.972683
C	-1.999573	5.237305	-1.064854
C	-1.865286	6.036838	-2.198324
C	-1.051525	5.631093	-3.252619
C	-0.363483	4.424839	-3.174040
C	-2.933415	-0.249144	-2.116247
O	-1.021959	-0.852165	-4.082391
C	1.059711	1.904500	-0.368418
C	-0.637336	-1.496925	-5.299530
H	-1.435439	-0.952378	0.694374
H	-3.367386	-0.553399	2.161422
H	-4.910683	-2.417072	2.729184
H	-4.509177	-4.683240	1.805786
H	-2.584504	-5.100266	0.334232
H	-1.793653	-4.843793	-2.047252
H	-0.272807	-4.377295	-2.849946
H	-1.620402	-3.223820	-2.778498
H	3.181815	1.968770	-0.715946
H	2.690889	0.920291	0.611048
H	-0.206512	-5.635669	0.176230
H	0.830672	-4.490259	1.058892
H	1.299164	-5.041208	-0.566432
H	2.396846	0.274548	-2.422478
H	3.563891	-1.780486	-1.801925
H	3.582083	-1.275207	-0.020017
H	-1.459984	3.376995	-0.112898
H	-2.637321	5.556522	-0.246426
H	-2.395822	6.982221	-2.258130
H	-0.940780	6.256351	-4.132776
H	0.287606	4.107196	-3.983344
H	-3.780825	-0.063613	-1.455311
H	-2.686629	-1.313197	-2.083321
H	-3.191567	-0.014685	-3.150795
H	0.297244	1.331356	0.162472
H	1.130279	2.900535	0.076066
H	-1.463951	-2.160563	-5.552712
H	0.285475	-2.066866	-5.164773
H	-0.481816	-0.763172	-6.092704

L

Au	0.467028	-1.160366	-1.165235
P	-0.791850	-3.159540	-0.934202
C	-1.689840	-3.188021	0.648418
C	-2.271727	-1.999970	1.110882
C	-3.001461	-1.995049	2.295592
O	0.569395	1.057669	-4.500363
C	-3.145618	-3.167967	3.032467
S	0.611594	1.993536	-1.928607
C	-2.563723	-4.349714	2.581197
C	-1.840482	-4.363751	1.392274
O	-2.048440	1.137019	-0.760824
C	-0.411967	0.571693	-2.371131
C	-0.113403	0.321390	-3.815989
C	-2.046142	-3.575261	-2.201044
C	-1.808771	0.618259	-1.847000
C	2.052428	1.136085	0.262104
C	0.298890	-4.628152	-0.943539
C	2.331910	-0.106044	-0.560271
C	2.357173	-1.395030	-0.025484
C	-0.295101	3.499571	-2.239197
C	-1.264602	4.005481	-1.370274
C	-1.891359	5.202342	-1.700140
C	-1.560580	5.871516	-2.877181
C	-0.599092	5.349012	-3.738446
C	0.045709	4.157325	-3.423758
C	-2.938929	0.070956	-2.678206
O	-0.636035	-0.821608	-4.279746
C	0.791852	1.918203	-0.115603
C	-0.409811	-1.062652	-5.676306
H	-2.161022	-1.074943	0.548380

H	-3.453332	-1.071500	2.644621
H	-3.710042	-3.161286	3.959988
H	-2.672943	-5.265036	3.154836
H	-1.395973	-5.295306	1.055306
H	-2.463008	-4.567708	-2.006530
H	-1.589489	-3.554624	-3.193879
H	-2.853635	-2.841687	-2.168666
H	2.926366	1.792896	0.181548
H	1.955467	0.867502	1.319610
H	-0.272979	-5.558472	-0.884319
H	0.999893	-4.578439	-0.107001
H	0.870170	-4.633728	-1.875813
H	2.868092	0.060033	-1.495156
H	2.915109	-2.184579	-0.521845
H	2.121199	-1.562644	1.023336
H	-1.539864	3.469247	-0.470029
H	-2.644911	5.610576	-1.033983
H	-2.055488	6.805966	-3.123419
H	-0.342267	5.871357	-4.654469
H	0.793291	3.733460	-4.086634
H	-3.789807	-0.123442	-2.023552
H	-2.667415	-0.809883	-3.256717
H	-3.232004	0.850927	-3.392499
H	-0.126359	1.476830	0.275168
H	0.856791	2.959244	0.212825
H	-0.947401	-1.981863	-5.904731
H	0.657519	-1.181491	-5.872717
H	-0.792647	-0.234128	-6.275381

TS_{LM}

Au	0.236475	-1.298829	-1.492154
P	-0.894592	-3.305433	-0.881722
C	-1.478562	-3.174547	0.825547
C	-2.276558	-2.069401	1.159854
C	-2.751825	-1.930089	2.458549
O	-0.001540	0.376073	-5.041180
C	-2.427740	-2.876910	3.429284
S	0.854769	2.405131	-1.832245
C	-1.627783	-3.967942	3.101566
C	-1.150580	-4.121017	1.802406
O	-2.549235	0.187874	-1.598806
C	-0.700162	-0.317116	-2.914829
C	-0.363533	-0.541336	-4.339508
C	-2.369911	-3.575811	-1.918184
C	-1.924251	0.487683	-2.608834
C	1.605662	0.869329	0.359401
C	0.096477	-4.824768	-1.036708
C	2.015914	-0.325815	-0.466788
C	1.911036	-1.635977	-0.014796
C	-0.193606	3.826137	-1.960058
C	-1.327656	4.034090	-1.168537
C	-2.113313	5.165516	-1.374235
C	-1.789424	6.081774	-2.370381
C	-0.665964	5.864894	-3.165734
C	0.133631	4.746737	-2.963677
C	-2.372968	1.565097	-3.547672
O	-0.458943	-1.816123	-4.717368
C	0.480847	1.755184	-0.178433
C	-0.117404	-2.065884	-6.093782
H	-2.524317	-1.322885	0.407118
H	-3.377394	-1.080125	2.713568
H	-2.800183	-2.763829	4.442808
H	-1.376592	-4.706802	3.856253
H	-0.534834	-4.982106	1.560939
H	-2.890349	-4.488263	-1.613307
H	-2.064839	-3.645674	-2.965686
H	-3.039148	-2.719586	-1.804405
H	2.506048	1.483229	0.495868
H	1.298107	0.526047	1.353987
H	-0.496441	-5.703538	-0.765537
H	0.982652	-4.772188	-0.400304
H	0.420500	-4.925633	-2.075759
H	2.659716	-0.125926	-1.323857
H	2.518909	-2.418028	-0.464035
H	1.506713	-1.841129	0.974166
H	-1.612141	3.323519	-0.399354
H	-2.987764	5.325498	-0.750300
H	-2.406668	6.961052	-2.524842
H	-0.401272	6.576210	-3.942177
H	1.018698	4.591188	-3.574216
H	-3.098164	2.201854	-3.041131
H	-2.853898	1.095707	-4.415228
H	-1.535740	2.153852	-3.925619
H	-0.463439	1.194452	-0.205347
H	0.356011	2.605151	0.498621
H	-0.322210	-3.122099	-6.257537
H	0.938253	-1.845475	-6.263608
H	-0.726617	-1.446781	-6.754885

M

Au	-0.040997	-1.100070	-1.314949
P	-0.839383	-3.322255	-0.979400
C	-1.498720	-3.465389	0.696201
C	-2.603392	-2.674183	1.047105
C	-3.128946	-2.759652	2.330869
O	-0.861332	0.665874	-4.756490
C	-2.555881	-3.617127	3.269100
S	1.578616	2.932030	-1.221706
C	-1.454299	-4.395558	2.924409
C	-0.920566	-4.322134	1.640976
O	-3.265207	-0.732073	-1.667757
C	-1.212730	-0.338552	-2.681391
C	-0.820088	-0.356135	-4.104526
C	-2.163342	-3.786587	-2.135583
C	-2.606701	0.043528	-2.350501
C	1.107166	1.038645	0.736262
C	0.461948	-4.574395	-1.204937
C	1.638836	-0.072640	-0.122190
C	1.577240	-1.414722	0.221613
C	0.496247	4.137783	-1.964417
C	0.327832	5.387264	-1.361988
C	-0.505107	6.334340	-1.950587
C	-1.160693	6.043182	-3.144672
C	-0.982514	4.802753	-3.752585
C	-0.154758	3.847214	-3.166865
C	-3.134758	1.352080	-2.851058
O	-0.395048	-1.537490	-4.543868
C	0.435231	2.190175	-0.005977
C	0.027501	-1.556192	-5.921725
H	-3.047761	-1.997809	0.320275
H	-3.988994	-2.154101	2.599536
H	-2.969534	-3.678553	4.271010
H	-1.010138	-5.066688	3.652935
H	-0.067668	-4.943221	1.385198
H	-2.523297	-4.792845	-1.902523
H	-1.772277	-3.752449	-3.156016
H	-2.976817	-3.063411	-2.043317
H	1.975319	1.433462	1.285817
H	0.417813	0.640060	1.489711
H	0.053923	-5.576108	-1.038287
H	1.297158	-4.404743	-0.522888
H	0.830946	-4.510179	-2.231904
H	2.316783	0.223761	-0.923643
H	2.272187	-2.118181	-0.230963
H	1.111506	-1.721545	1.156668
H	0.857918	5.615562	-0.442053
H	-0.632764	7.305142	-1.481039
H	-1.802533	6.787467	-3.606497
H	-1.480299	4.578381	-4.691608
H	-0.005484	2.883949	-3.646404
H	-4.138438	1.499228	-2.449478
H	-3.154365	1.352531	-3.945572
H	-2.480311	2.180293	-2.559442
H	-0.457266	1.832813	-0.531945
H	0.127543	2.954592	0.713049
H	0.287233	-2.591953	-6.131219
H	0.892807	-0.904721	-6.056321
H	-0.783987	-1.222235	-6.570774

TS_{EN}

Pd	-0.884621	1.824367	1.938677
C	0.662848	1.379978	-0.127457

C	-1.825765	1.406868	-0.930407
O	-2.976178	1.097120	-0.714546
O	0.987432	1.867090	1.008706
C	-0.668955	0.898256	-0.132829
S	-0.637841	-1.256282	-1.179820
C	-1.851380	-1.655908	-2.407693
C	-3.226365	-1.563937	-2.165524
C	-1.379167	-1.993525	-3.681398
C	-4.119420	-1.844874	-3.194880
C	-2.283377	-2.256699	-4.703603
C	-3.653956	-2.189544	-4.461557
C	-1.270081	-2.083355	0.340686
C	-1.671127	-1.219729	1.534688
C	-0.518792	-0.449254	2.134282
C	-0.487034	0.169478	3.365123
O	-1.443417	2.179765	-1.954658
C	-2.518347	2.716741	-2.730163
C	1.677687	1.292261	-1.213445
Cl	-1.242572	3.883265	1.033996
Cl	-2.965597	1.842178	2.883868
H	-3.593844	-1.243972	-1.196462
H	-0.310262	-2.064625	-3.860108
H	-5.186536	-1.777135	-3.005450
H	-1.914833	-2.528004	-5.688433
H	-4.358125	-2.402681	-5.260134
H	-0.465909	-2.769263	0.627018
H	-2.114287	-2.693360	0.011980
H	-2.058126	-1.916783	2.291399
H	-2.495049	-0.544102	1.286094
H	0.446040	-0.580479	1.648996
H	0.469967	0.465925	3.787419
H	-1.350022	0.182516	4.022324
H	-3.133977	3.369211	-2.106479
H	-2.047649	3.284988	-3.531693
H	-3.138048	1.913161	-3.135184
H	1.398136	1.989969	-2.009724
H	2.664372	1.549041	-0.823528
H	1.695882	0.289531	-1.649777

TS_{EN}

Pd	-0.946158	1.709570	2.218532
C	0.688482	2.386903	0.450740
C	-1.628192	2.003052	-0.778337
O	-2.737720	1.523403	-0.650451
O	0.961678	2.220445	1.732803
C	-0.604177	2.072614	0.227968
S	-0.601214	-2.173277	-1.387786
C	-1.976537	-2.267255	-2.518937
C	-3.043116	-1.362581	-2.471384
C	-1.953879	-3.261082	-3.501424
C	-4.087018	-1.477504	-3.386298
C	-2.989745	-3.352486	-4.427195
C	-4.061885	-2.466699	-4.366750
C	-1.407924	-2.502811	0.222020
C	-1.755685	-1.257922	1.048072
C	-0.517313	-0.544557	1.482261
C	-0.136800	-0.314716	2.780211
O	-1.158836	2.523369	-1.929700
C	-2.051602	2.419725	-3.041524
C	1.743378	2.839665	-0.489076
Cl	-1.482188	3.898593	2.400907
Cl	-3.021459	1.129411	2.912352
H	-3.057671	-0.561726	-1.737897
H	-1.125651	-3.962596	-3.529904
H	-4.917451	-0.778827	-3.336056
H	-2.963226	-4.126906	-5.188491
H	-4.874905	-2.545003	-5.082692
H	-0.725161	-3.156507	0.774963
H	-2.316530	-3.075974	0.021981
H	-2.347428	-1.550704	1.920611
H	-2.374500	-0.577039	0.453113
H	0.202962	-0.334367	0.692354
H	0.879265	-0.003874	3.009724
H	-0.776018	-0.622130	3.605086
H	-3.009636	2.888580	-2.806901
H	-1.557502	2.944450	-3.858685
H	-2.217884	1.372525	-3.307515
H	2.063974	3.845676	-0.199210
H	2.610600	2.175653	-0.419195
H	1.366378	2.858102	-1.511985

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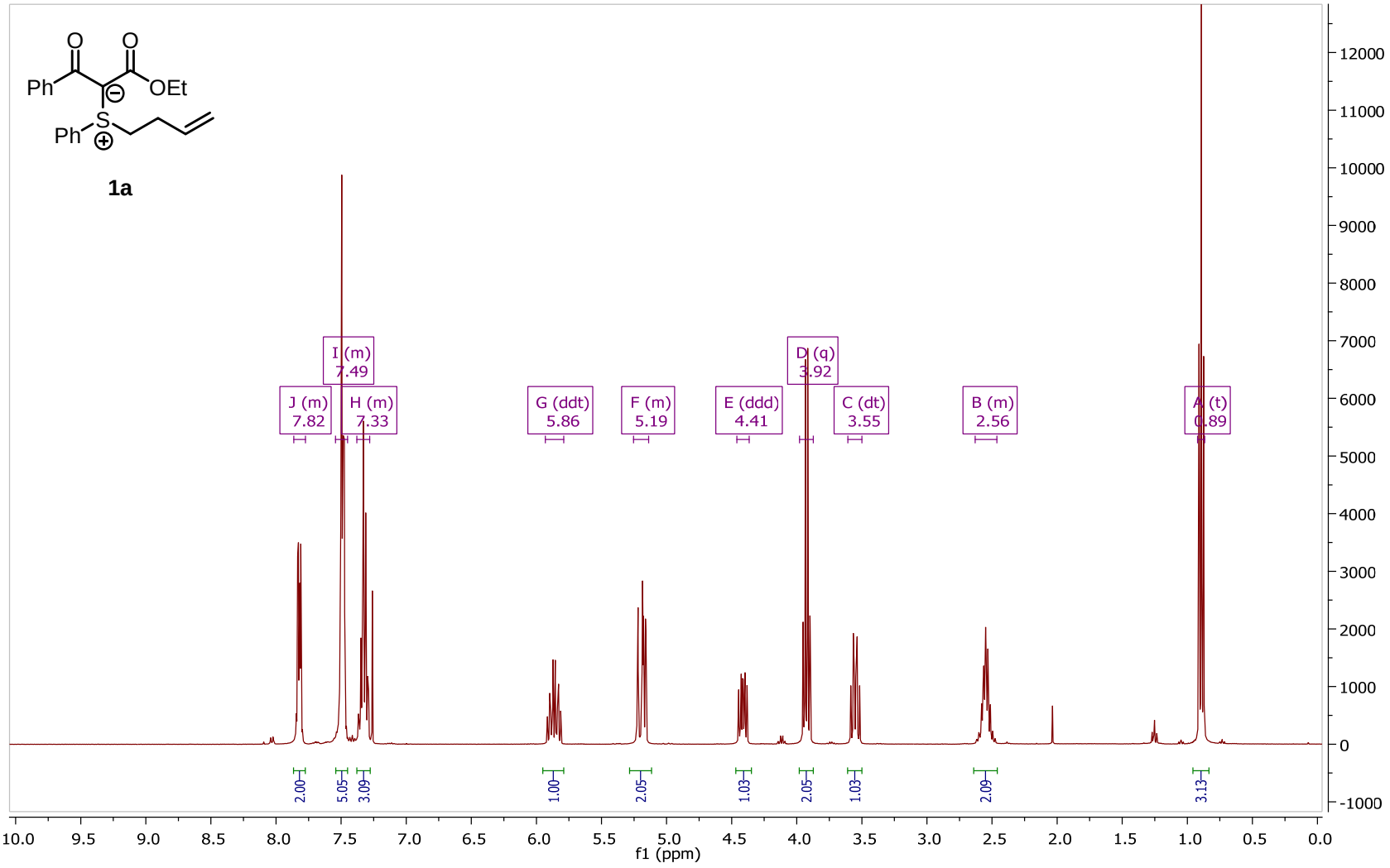
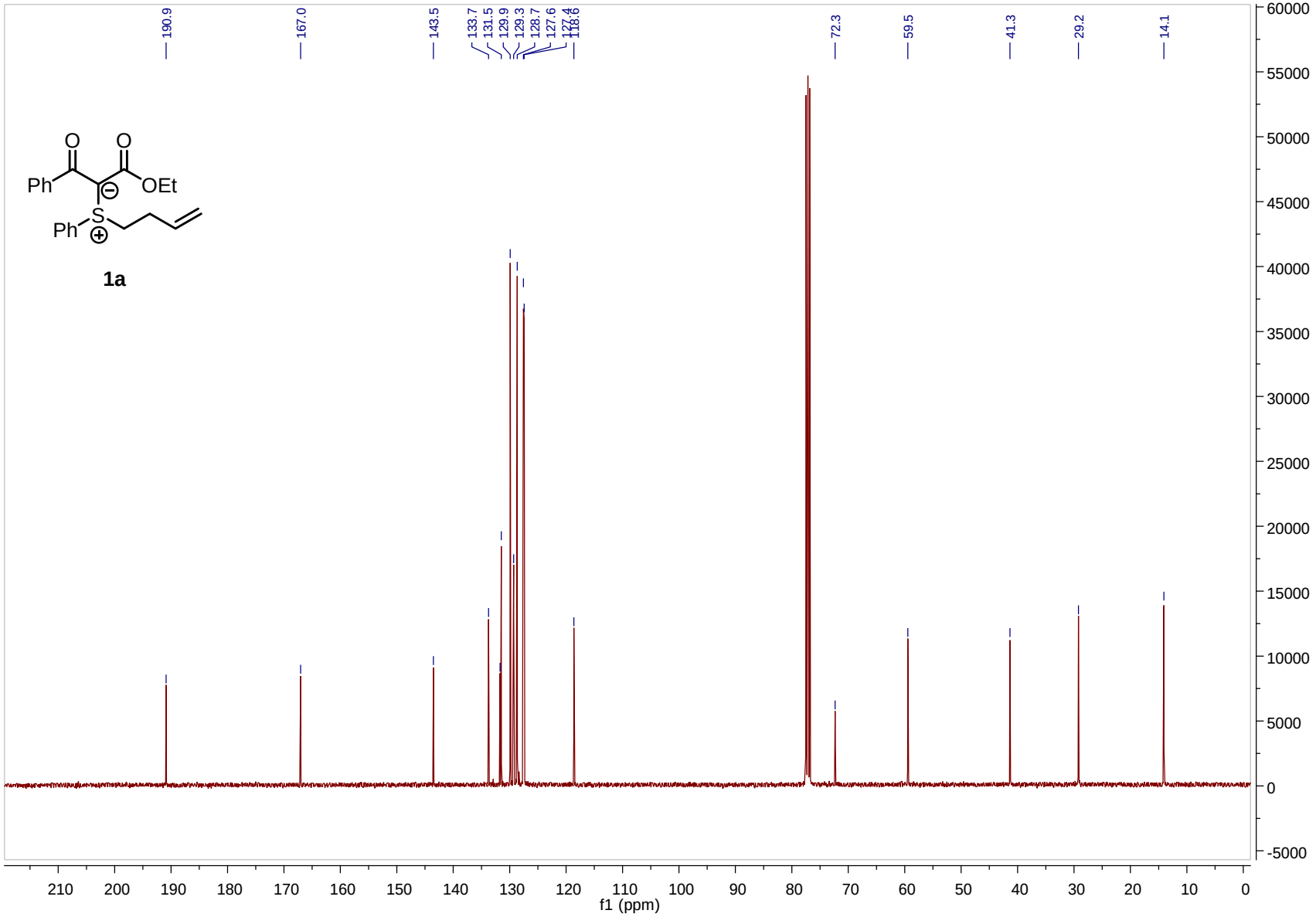
7. NMR Spectra

7.1 Sulfonium ylides

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143.5
133.7
131.5
129.9
129.3
128.7
127.6
127.4
118.6
72.3
59.5
41.3
29.2
14.1
O
O
Ph
OEt
S
Ph
1a
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
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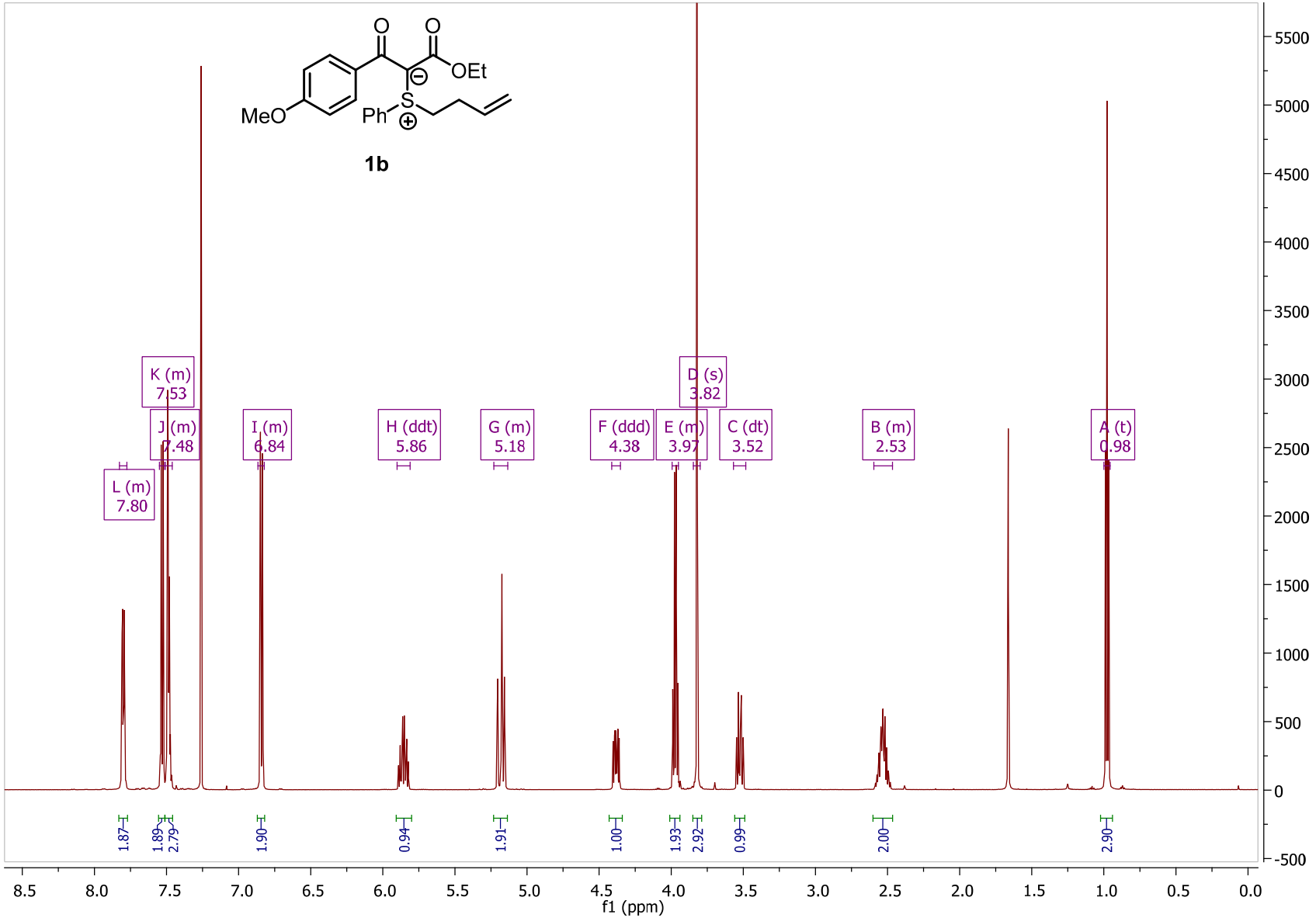
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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Ph
OEt
1b
K (m) 7.53
J (m) 7.48
L (m) 7.80
I (m) 6.84
H (ddt) 5.86
G (m) 5.18
F (ddd) 4.38
D (s) 3.82
E (m) 3.97
C (dt) 3.52
B (m) 2.53
A (t) 0.98
1.87
1.89
2.79
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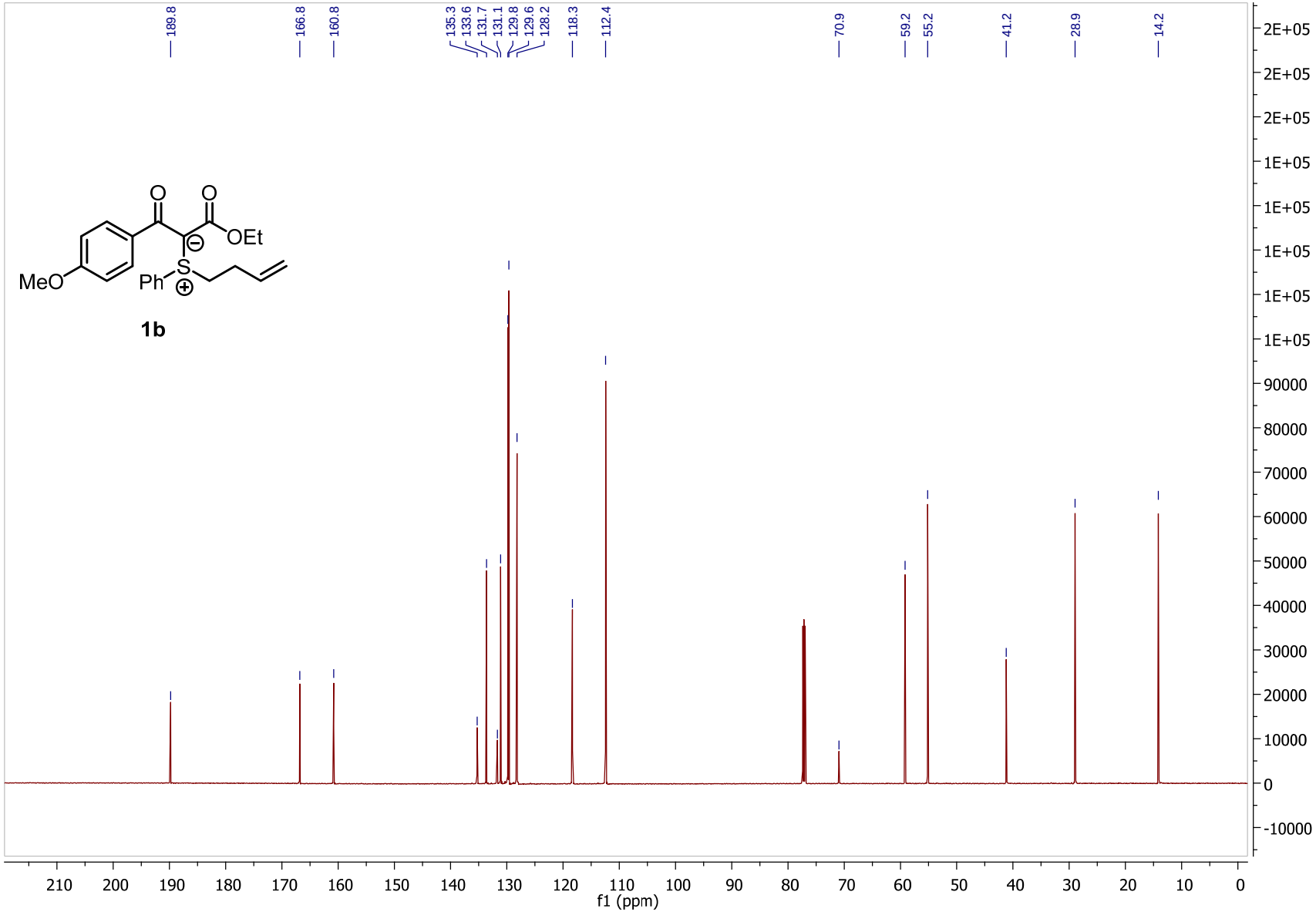
0.94
1.91
1.00
1.93
2.92
0.99
2.00
2.90
f1 (ppm)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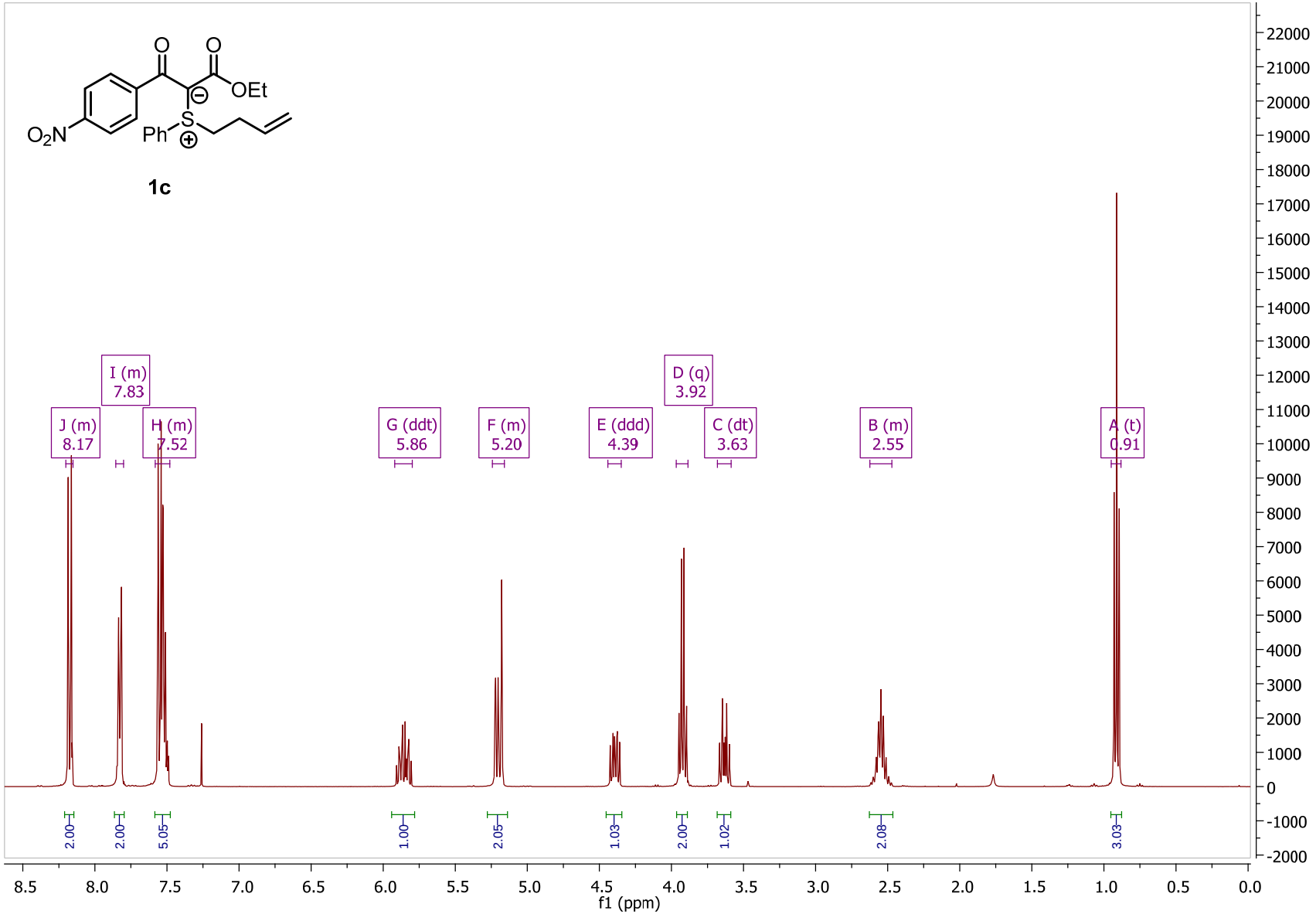
166.8
160.8
135.3
133.6
131.7
131.1
129.8
129.6
128.2
118.3
112.4
70.9
59.2
55.2
41.2
28.9
14.2
MeO
Ph
OEt
1b
f1 (ppm)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O
OEt
O_2N
Ph
S
1c
I (m)
7.83
J (m)
8.17
H (m)
7.52
G (ddt)
5.86
F (m)
5.20
E (ddd)
4.39
D (q)
3.92
C (dt)
3.63
B (m)
2.55
A (t)
0.91
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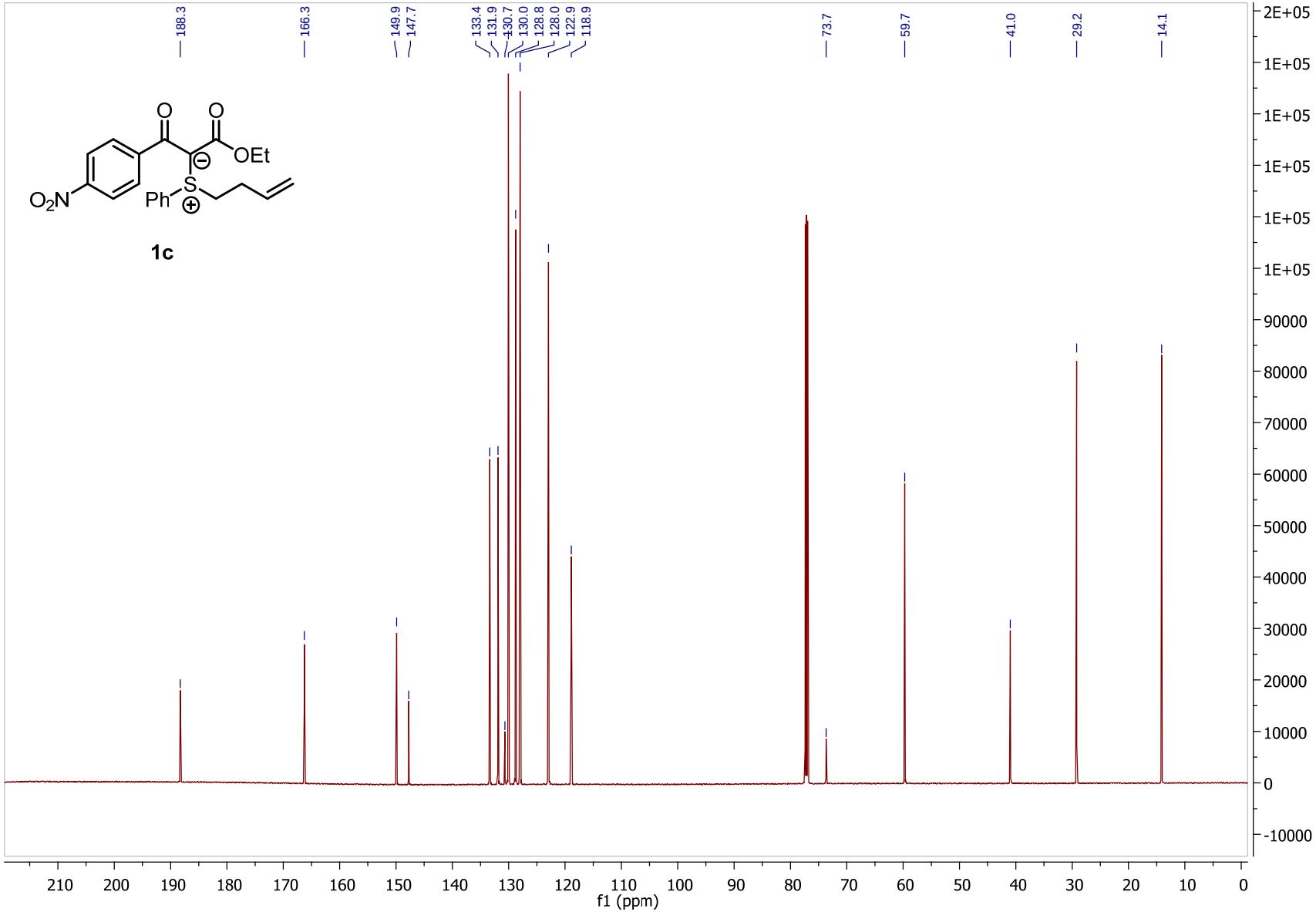
2.00
5.05
1.00
2.05
1.03
2.00
1.02
2.08
3.03
f1 (ppm)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133.4
131.9
130.7
130.0
128.8
128.0
122.9
118.9
73.7
59.7
41.0
29.2
14.1
O
O
OEt
O2N
Ph
S
1c
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
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130
120
110
100
90
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70
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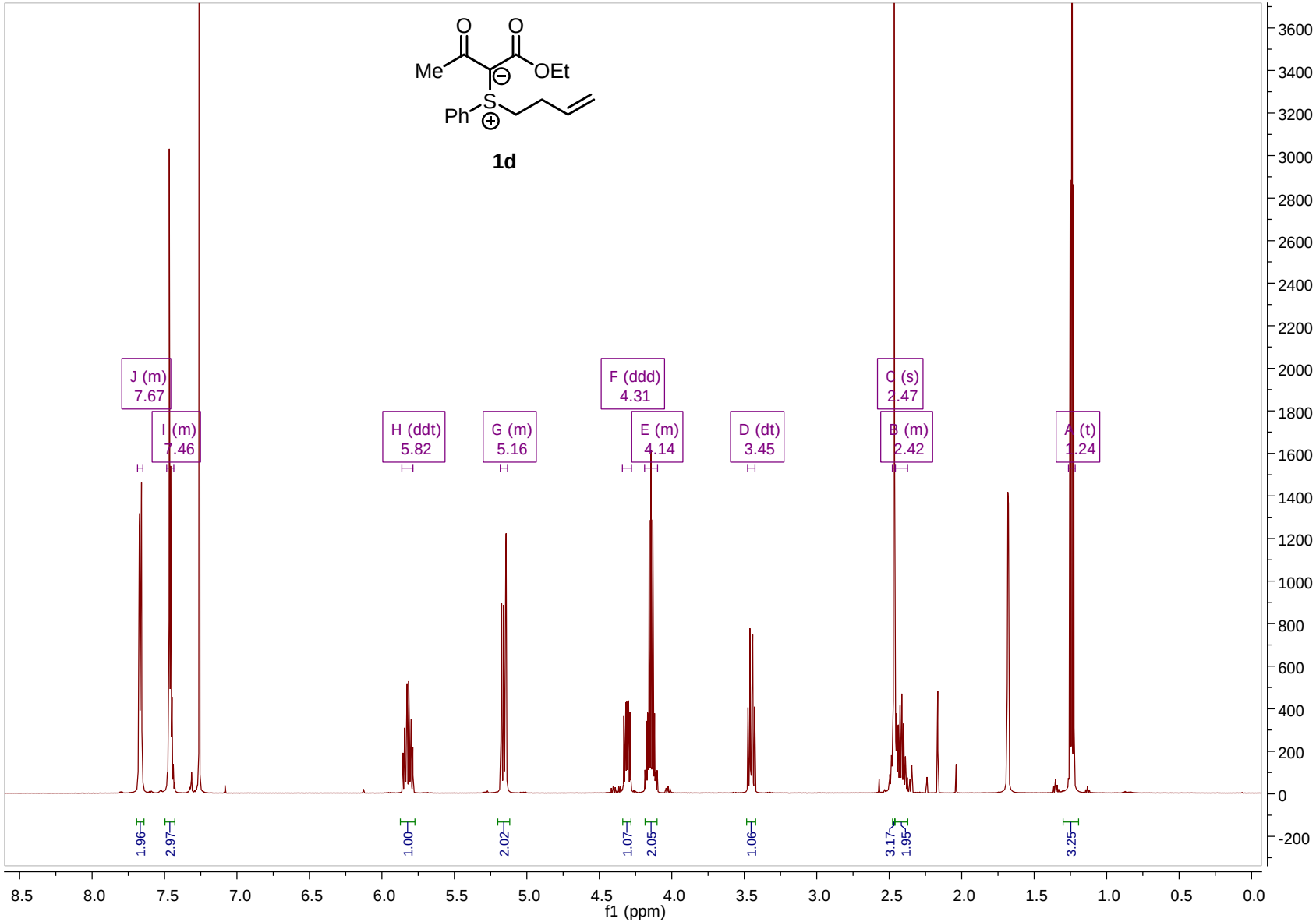
50
40
30
20
10
0
f1 (ppm)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O
O
OEt
Ph
S
1d
J (m)
7.67
I (m)
7.46
H (ddt)
5.82
G (m)
5.16
F (ddd)
4.31
E (m)
4.14
D (dt)
3.45
C (s)
2.47
B (m)
2.42
A (t)
1.24
1.96
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1.00
2.02
1.07
2.05
1.06
3.17
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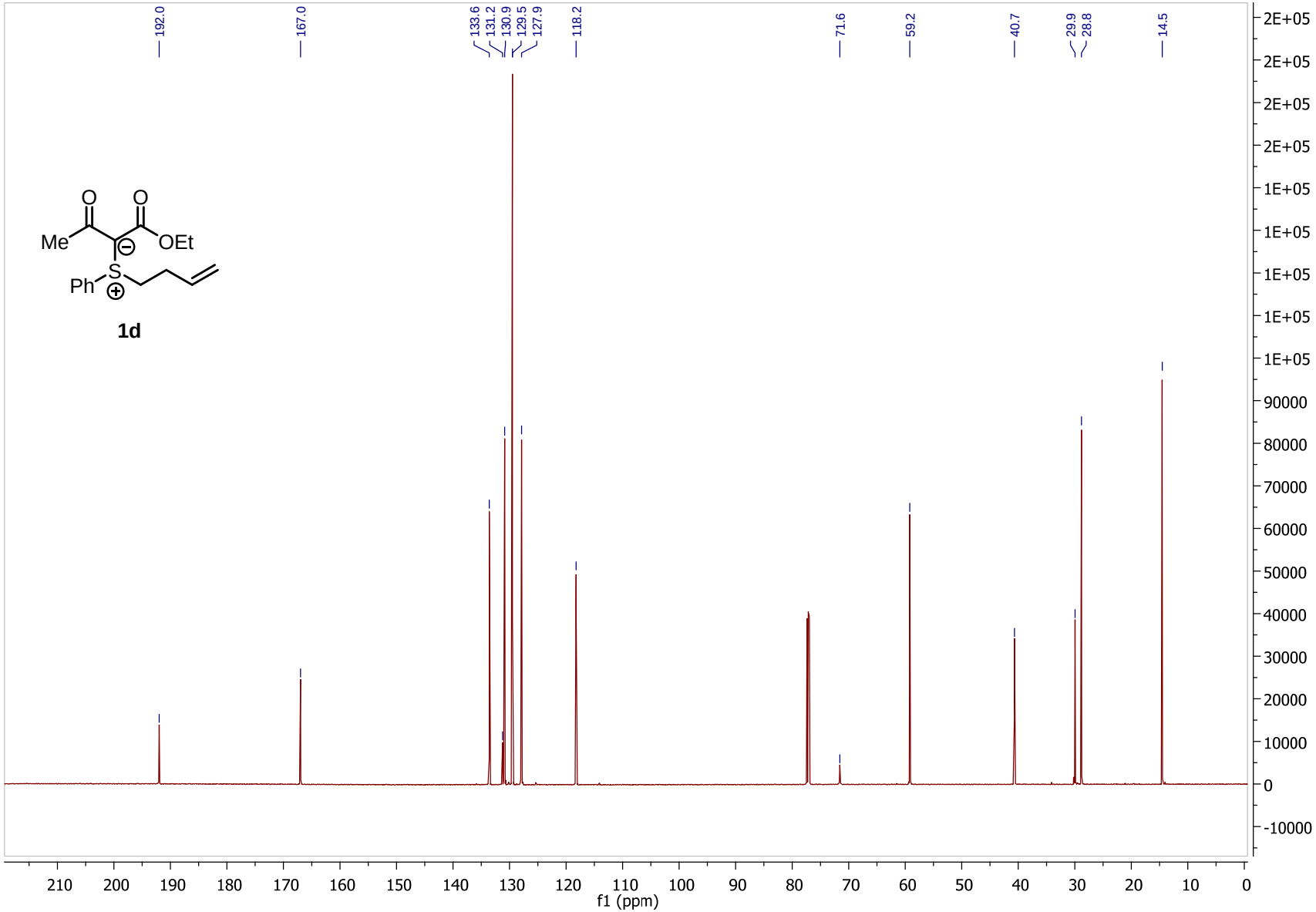
3.25
f1 (ppm)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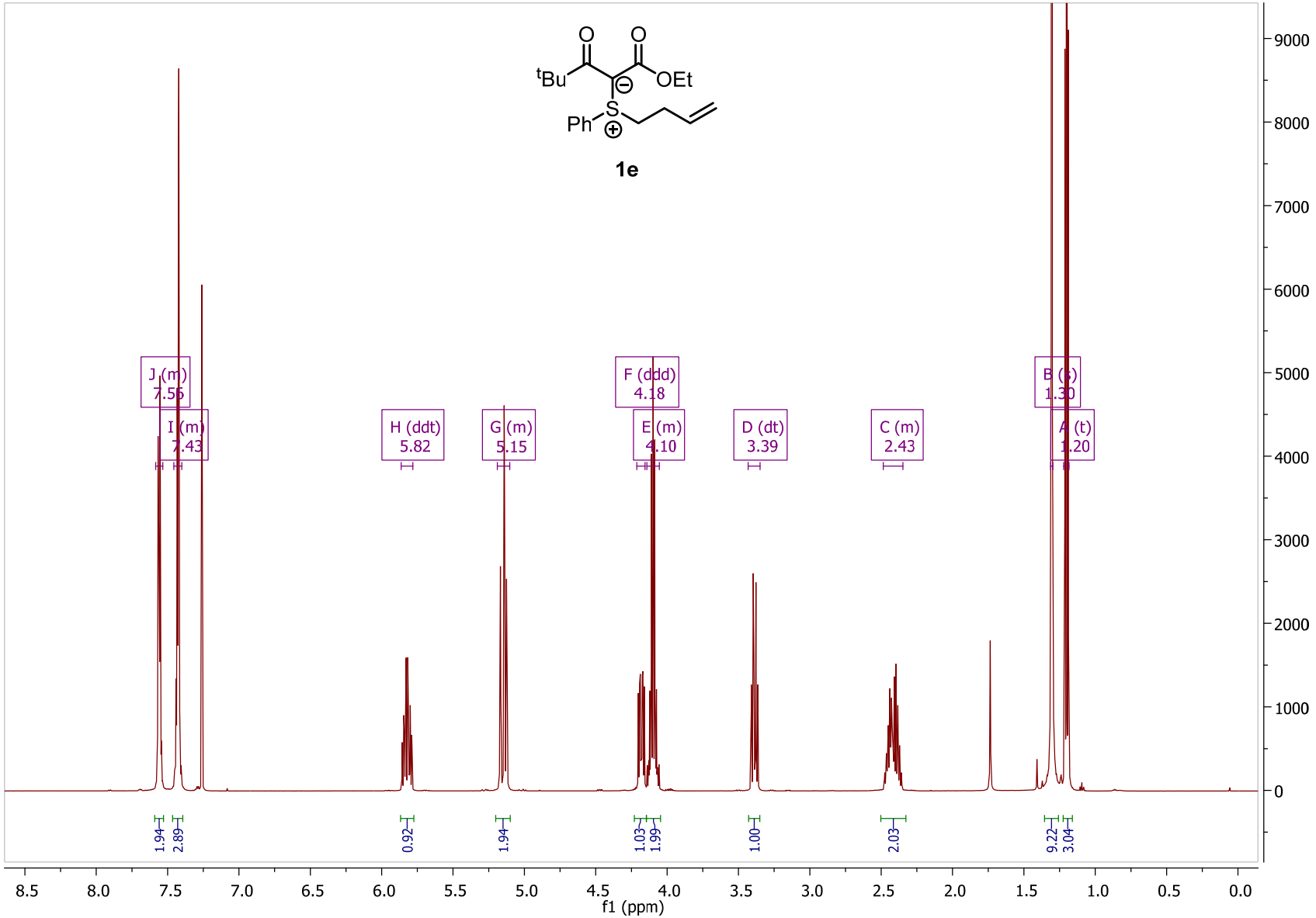
131.2
130.9
129.5
127.9
118.2
71.6
59.2
40.7
29.9
28.8
14.5
Me
O
O
OEt
Ph
S
1d
f1 (ppm)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J (m) 7.56
I (m) 7.43
H (ddt) 5.82
G (m) 5.15
F (ddd) 4.18
E (m) 4.10
D (dt) 3.39
C (m) 2.43
B (s) 1.30
A (t) 1.20
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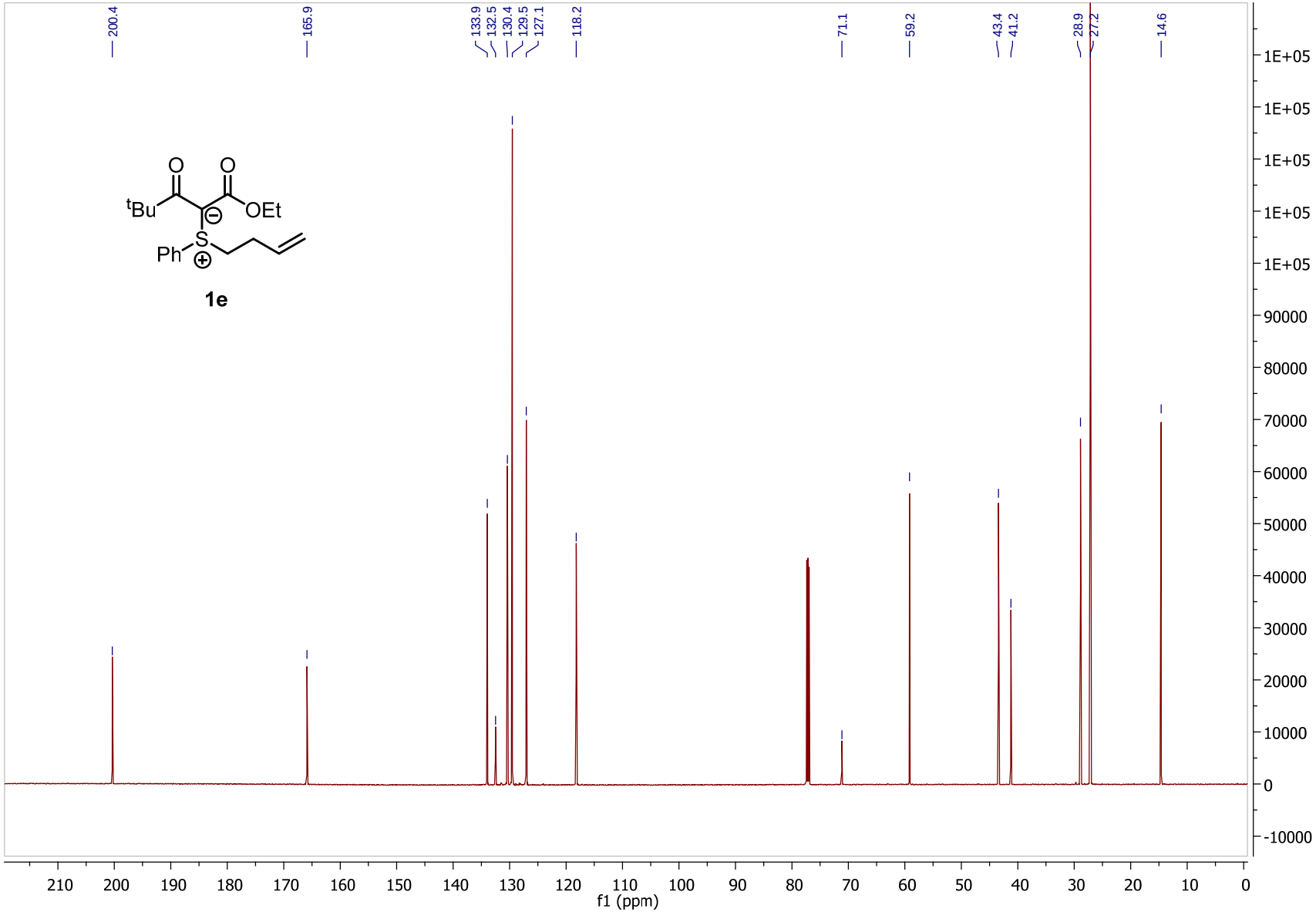
2.89
0.92
1.94
1.03
1.99
1.00
2.03
9.22
3.04
f1 (ppm)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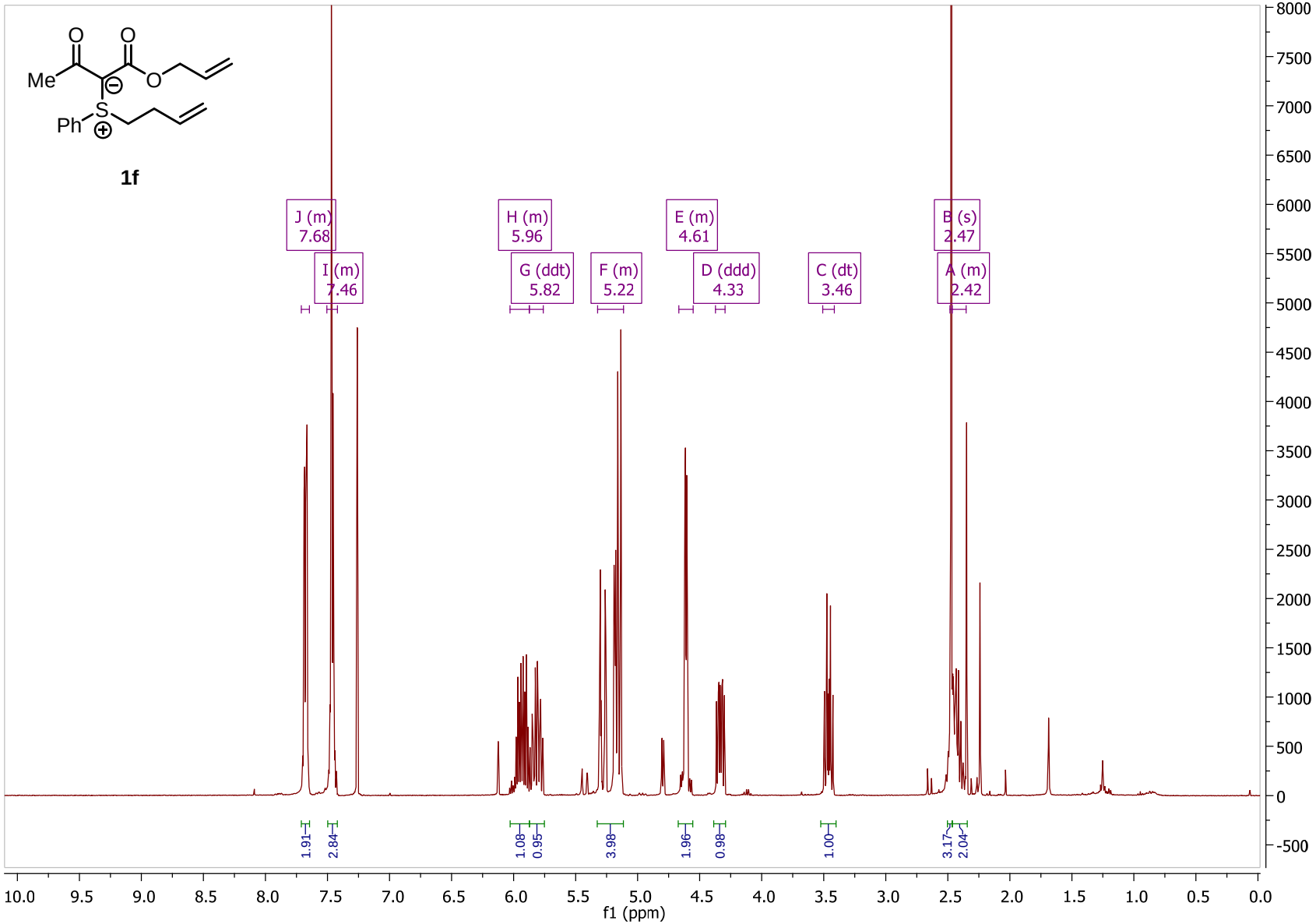
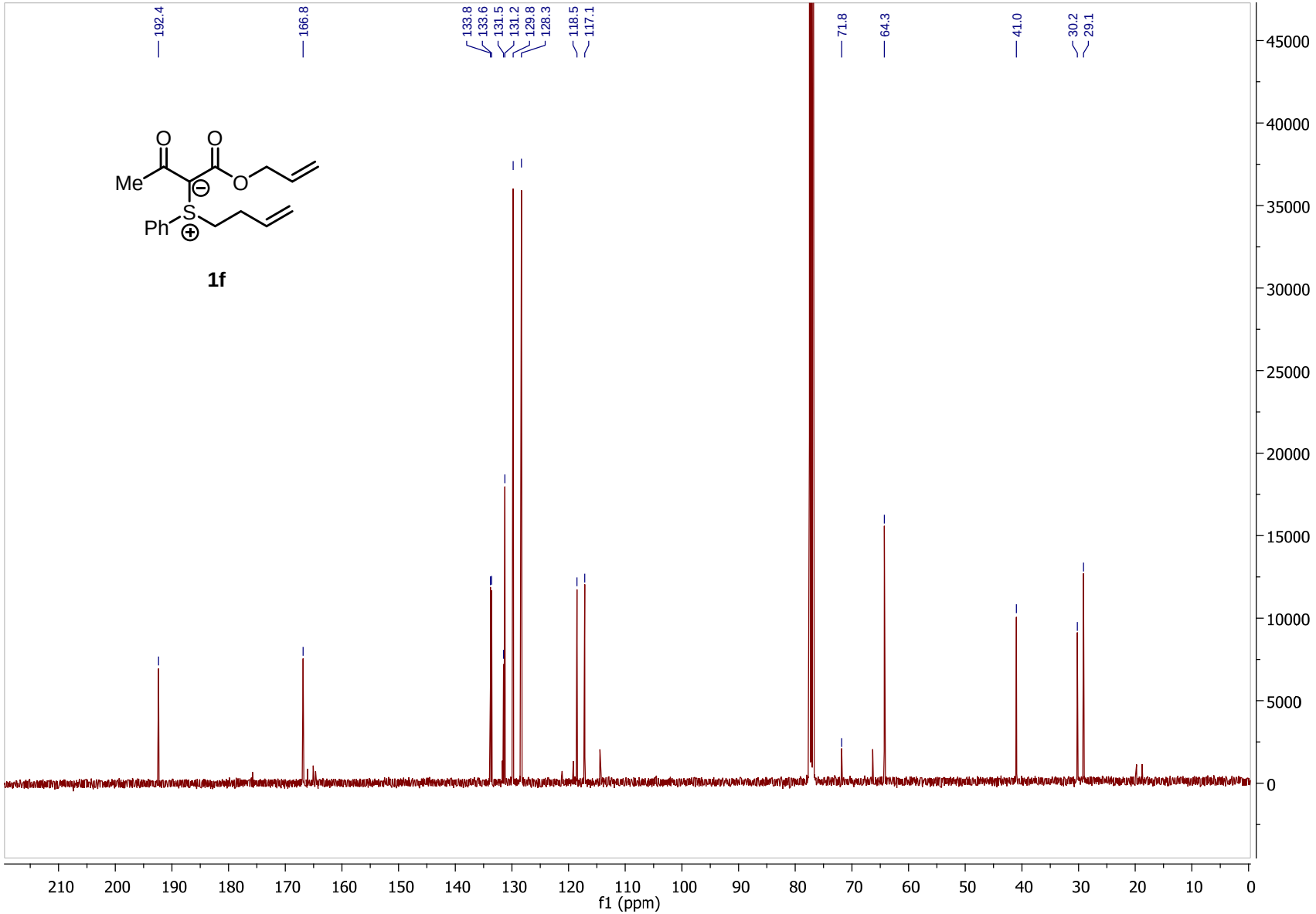
132.5
130.4
129.5
127.1
118.2
71.1
59.2
43.4
41.2
28.9
27.2
14.6
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
tBu
OEt
Ph
S

1e


Me
O
O
O
Ph
S
1f
J (m) 7.68
I (m) 7.46
H (m) 5.96
G (ddt) 5.82
F (m) 5.22
E (m) 4.61
D (ddd) 4.33
C (dt) 3.46
B (s) 2.47
A (m) 2.42
1.91
2.84
1.08
0.95
3.98
1.96
0.98
1.00
3.17
2.04
f1 (ppm)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133.8
133.6
131.5
131.2
129.8
128.3
118.5
117.1
71.8
64.3
41.0
30.2
29.1
Me
O
O
O
Ph
S
1f
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
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120
110
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90
80
70
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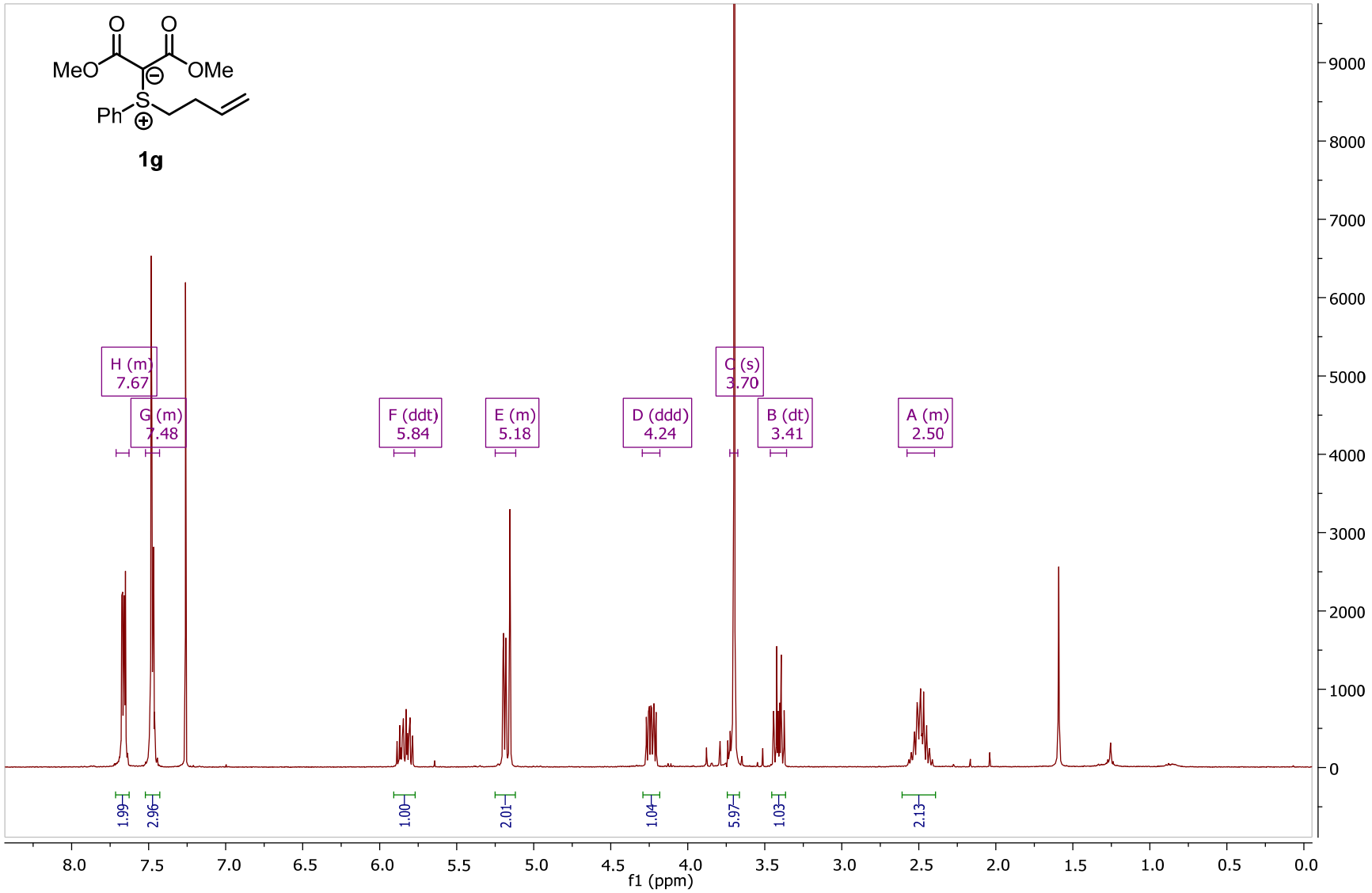
50
40
30
20
10
0
f1 (ppm)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OMe
Ph
1g
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G (m)
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F (ddt)
5.84
E (m)
5.18
D (ddd)
4.24
C (s)
3.70
B (dt)
3.41
A (m)
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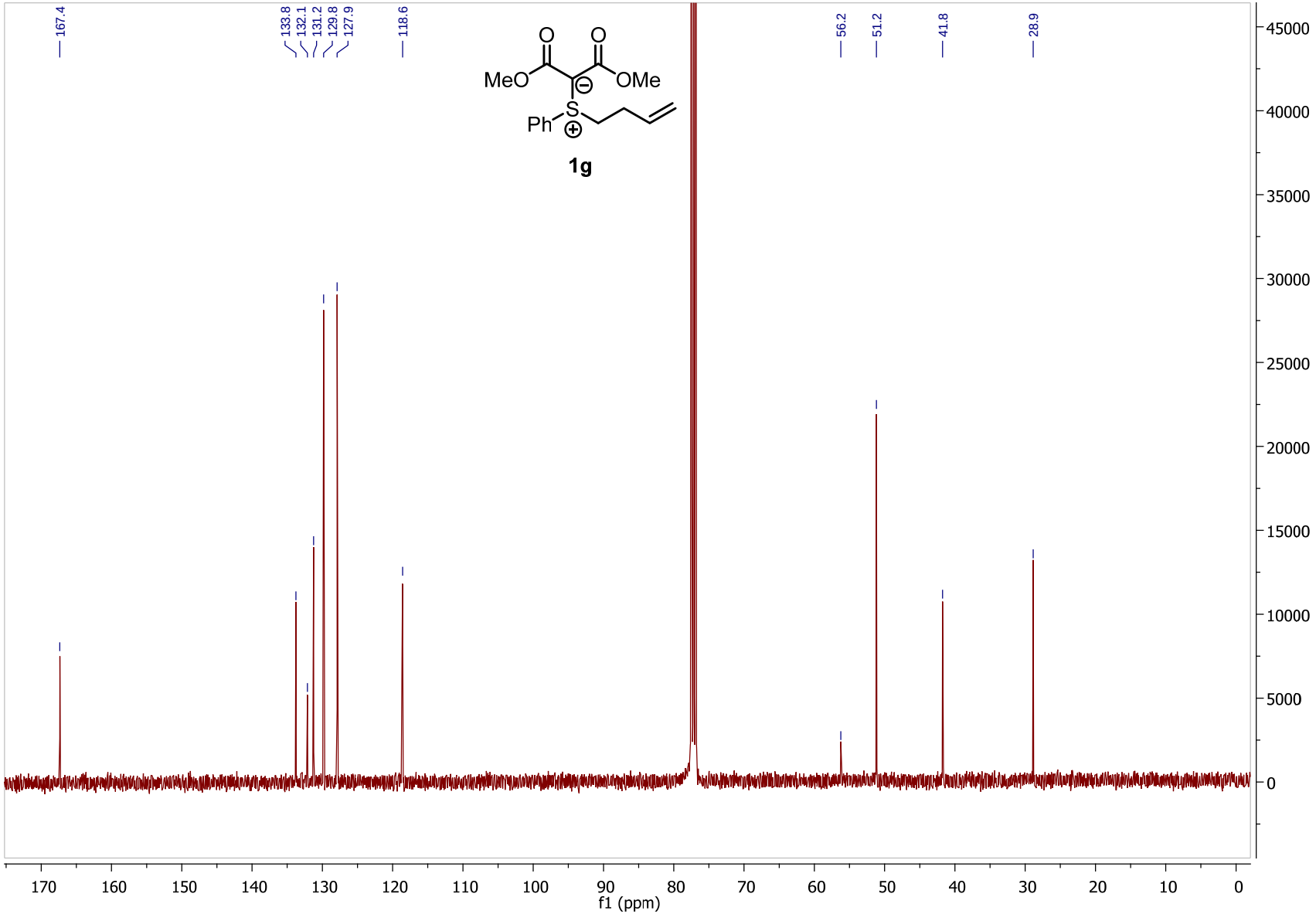
1.99
2.96
1.00
2.01
1.04
5.97
1.03
2.13
f1 (ppm)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133.8
132.1
131.2
129.8
127.9
118.6
56.2
51.2
41.8
28.9
MeO
OMe
Ph
S
1g
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
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150
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130
120
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90
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70
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50
40
30
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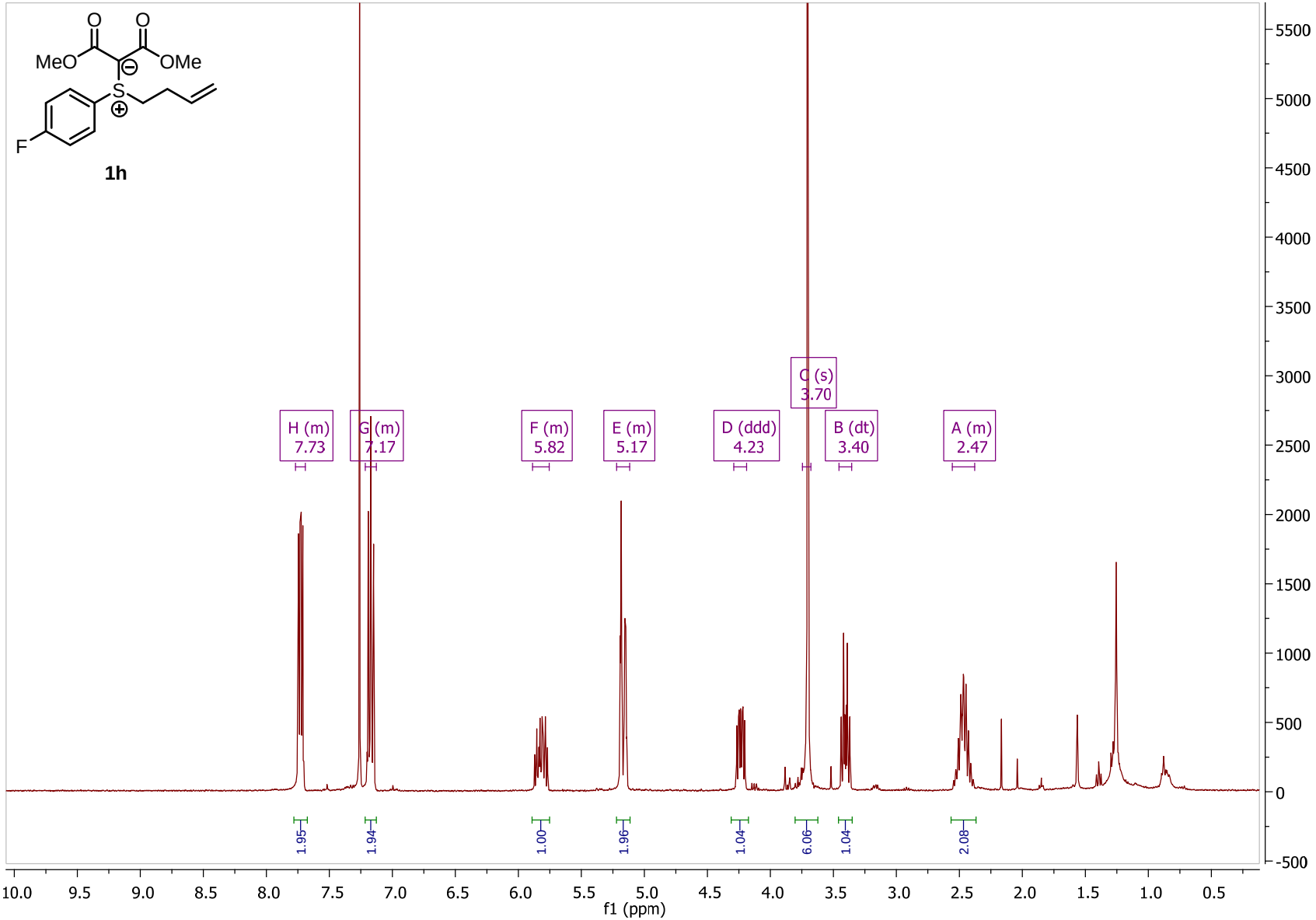
10
0
f1 (ppm)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OMe
F
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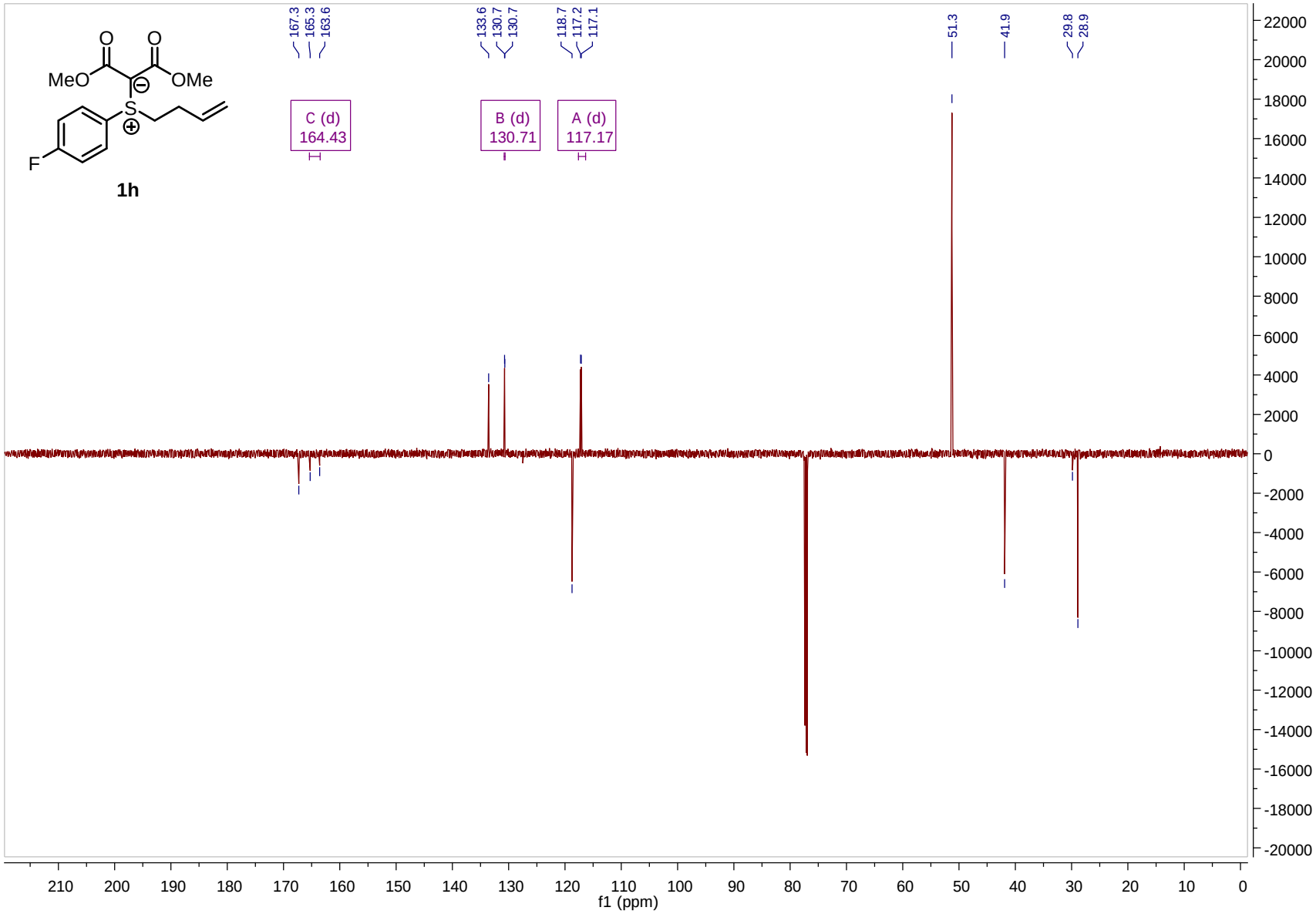
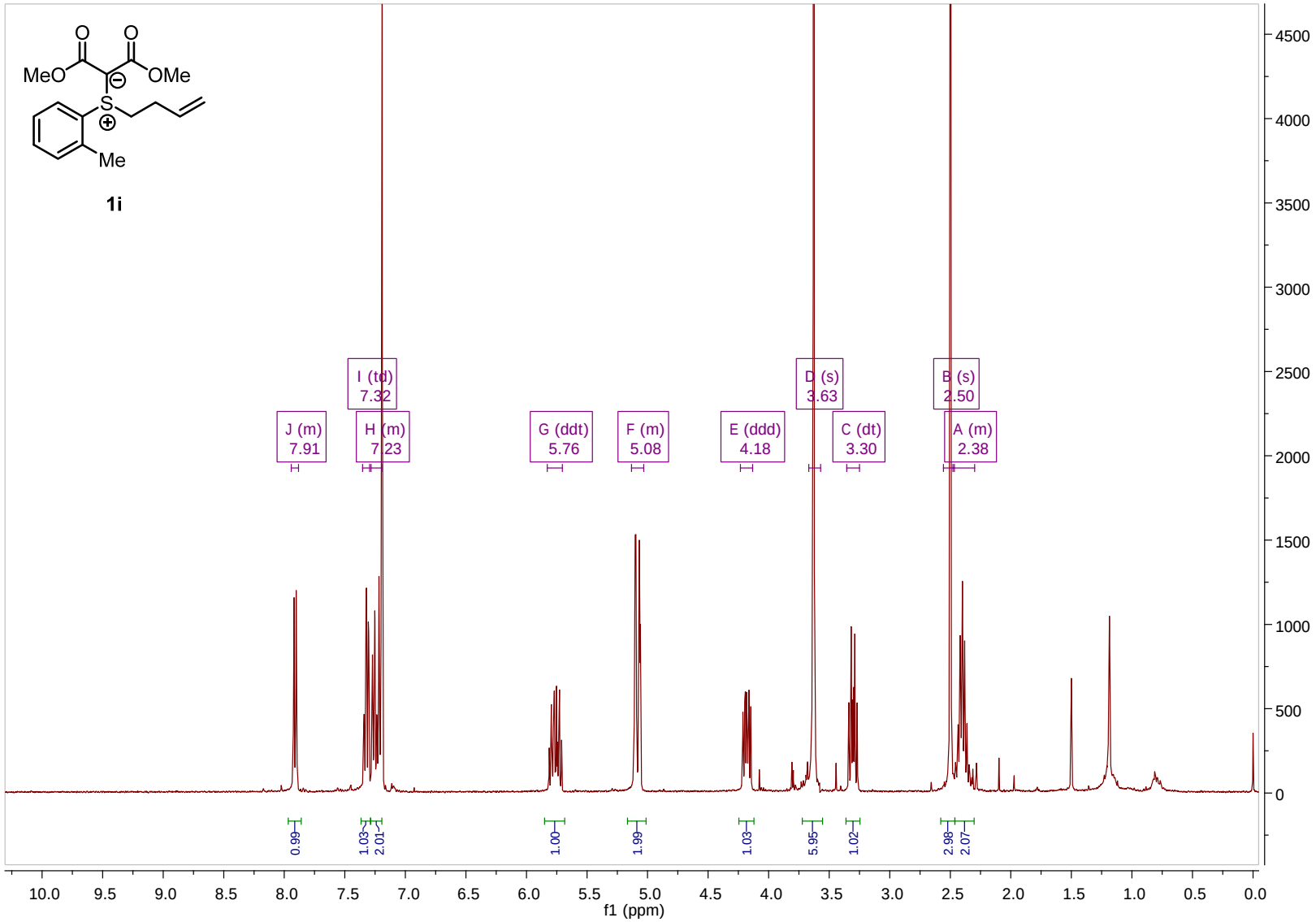
G (m) 7.17
F (m) 5.82
E (m) 5.17
D (ddd) 4.23
C (s) 3.70
B (dt) 3.40
A (m) 2.47
1.95
1.94
1.00
1.96
1.04
6.06
1.04
2.08
f1 (ppm)


MeO
OMe
F
1h
167.3
165.3
163.6
133.6
130.7
130.7
118.7
117.2
117.1
51.3
41.9
29.8
28.9
C (d)
164.43
B (d)
130.71
A (d)
117.17
f1 (ppm)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OMe
S
Me
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I (td) 7.32
H (m) 7.23
G (ddt) 5.76
F (m) 5.08
E (ddd) 4.18
D (s) 3.63
C (dt) 3.30
B (s) 2.50
A (m) 2.38
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2.01
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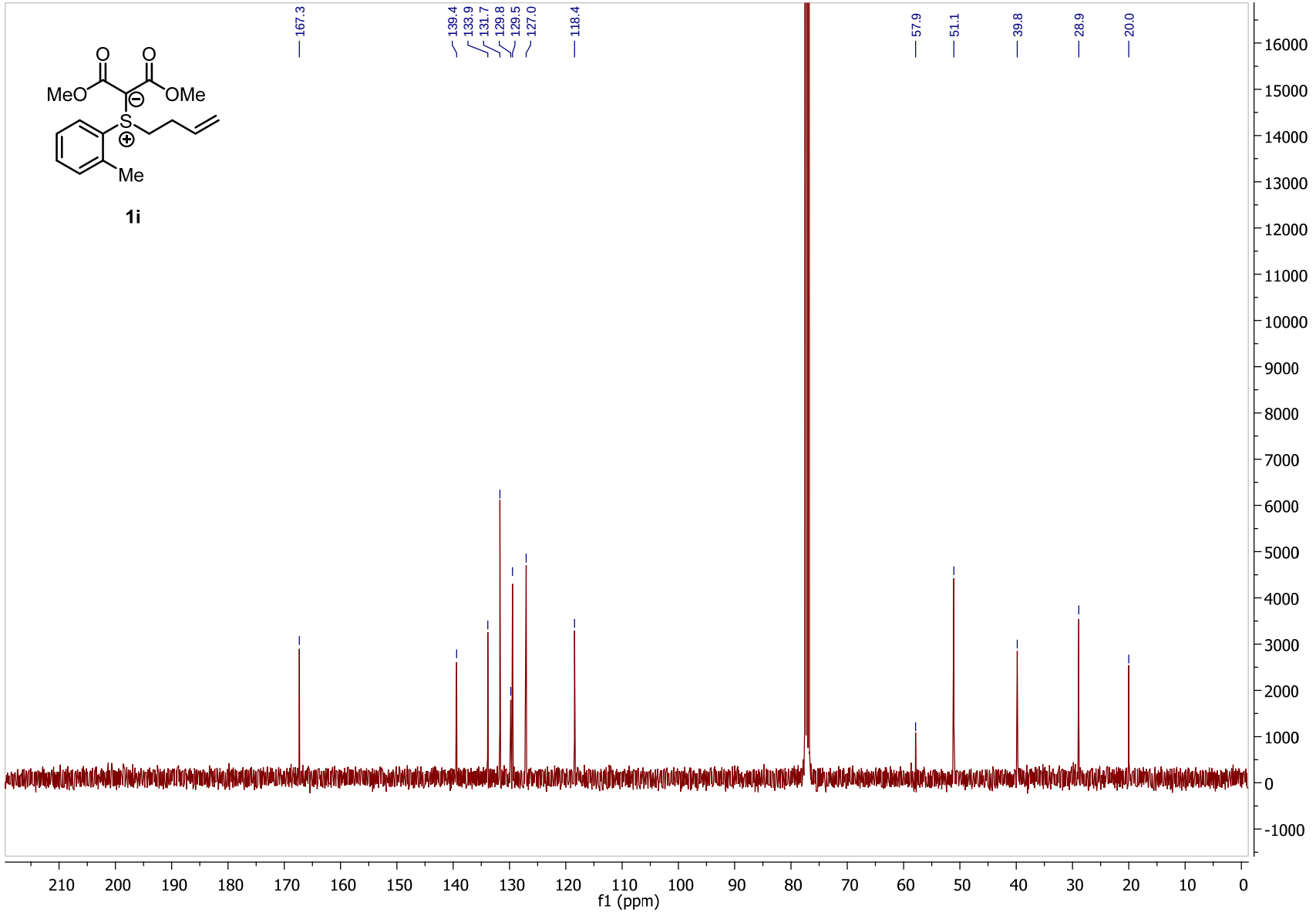
1.99
1.03
5.95
1.02
2.98
2.07
f1 (ppm)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118.4
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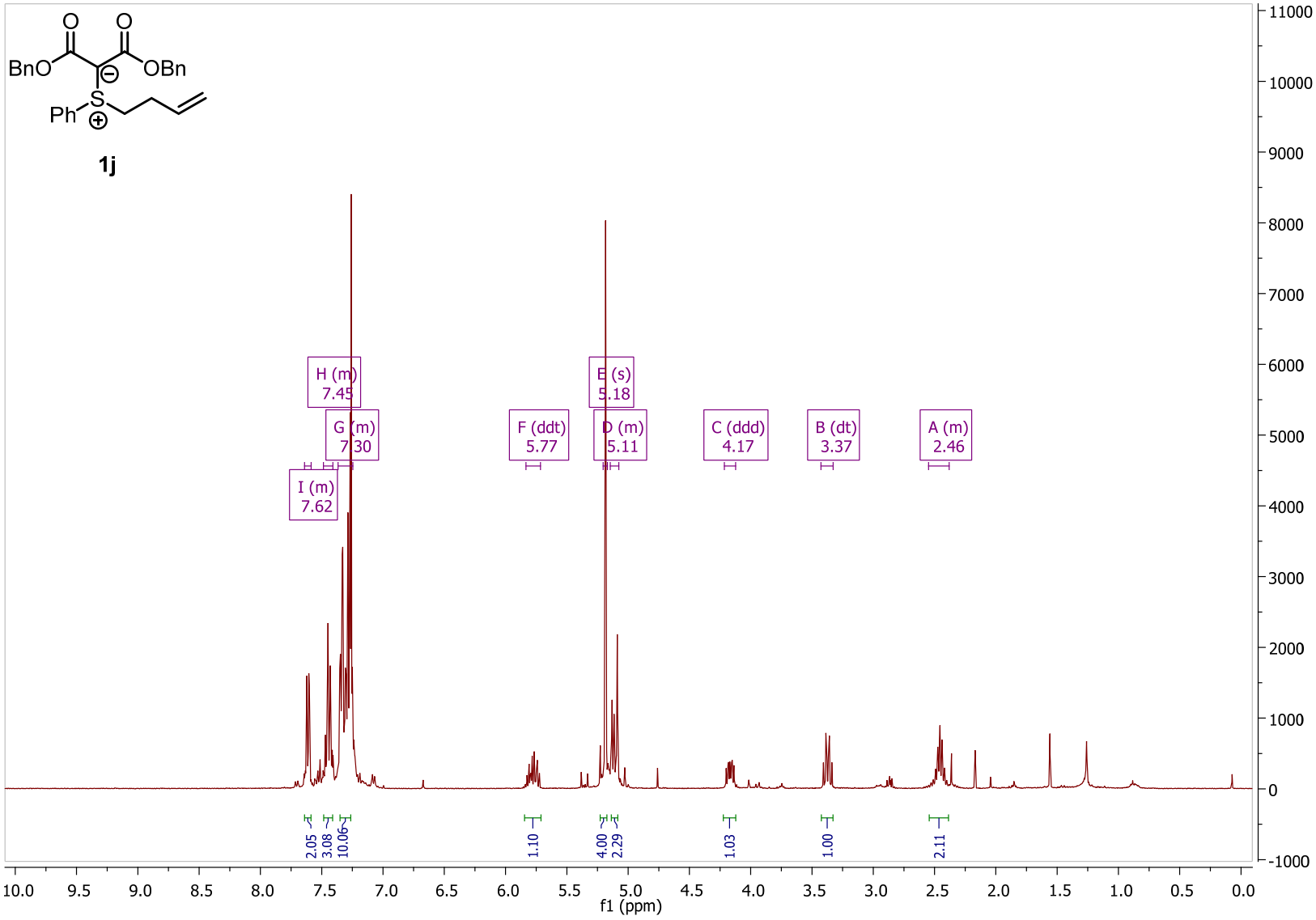
39.8
28.9
20.0
MeO
OMe
Me
1i
f1 (ppm)


BnO
OBn
Ph
S
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G (m)
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I (m)
7.62
F (ddt)
5.77
E (s)
5.18
D (m)
5.11
C (ddd)
4.17
B (dt)
3.37
A (m)
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3.08
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4.00
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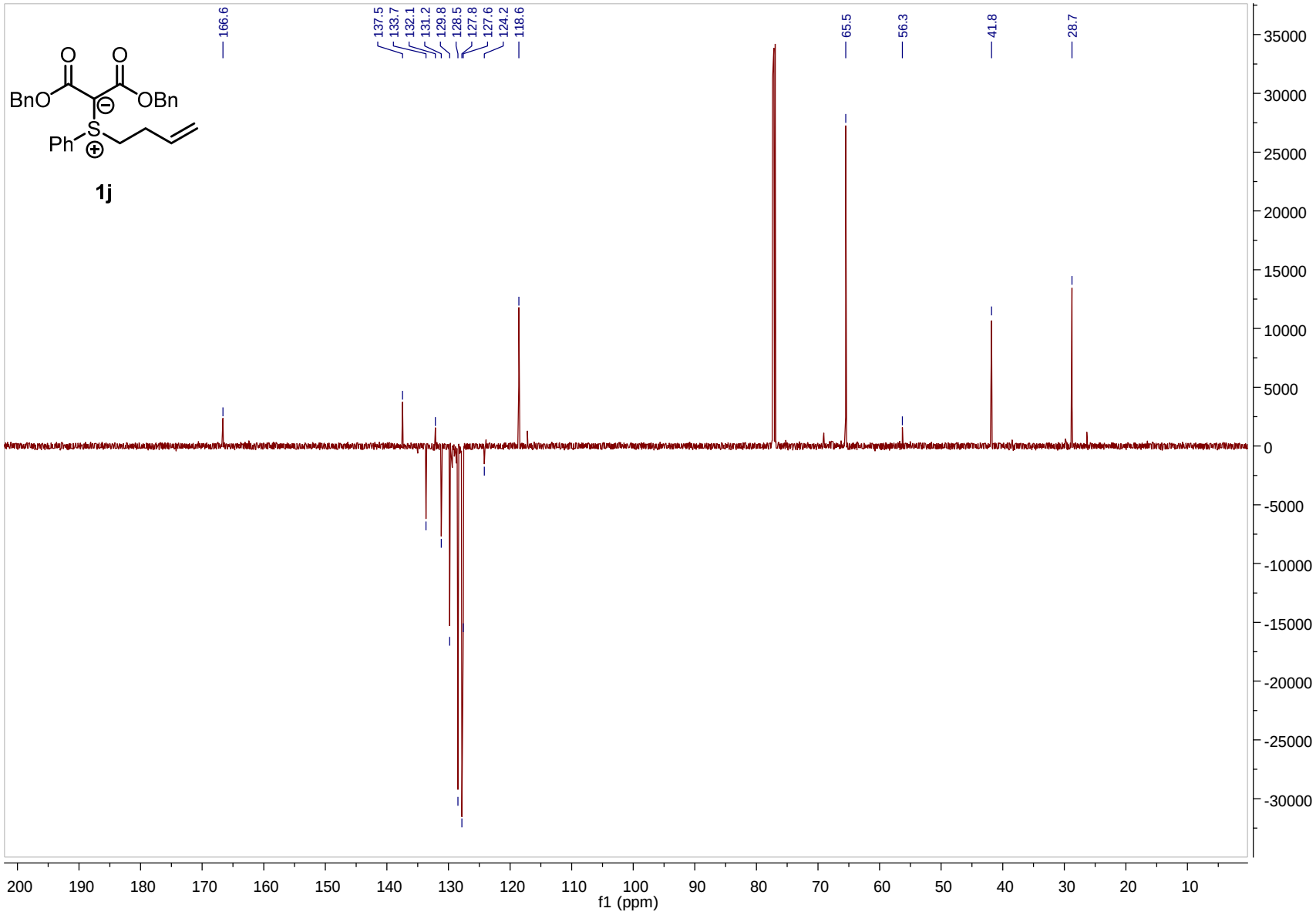
1.03
1.00
2.11
f1 (ppm)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127.8
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56.3
41.8
28.7
BnO
OBn
Ph
1j
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
-30000
200
190
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170
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130
120
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100
90
80
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60
50
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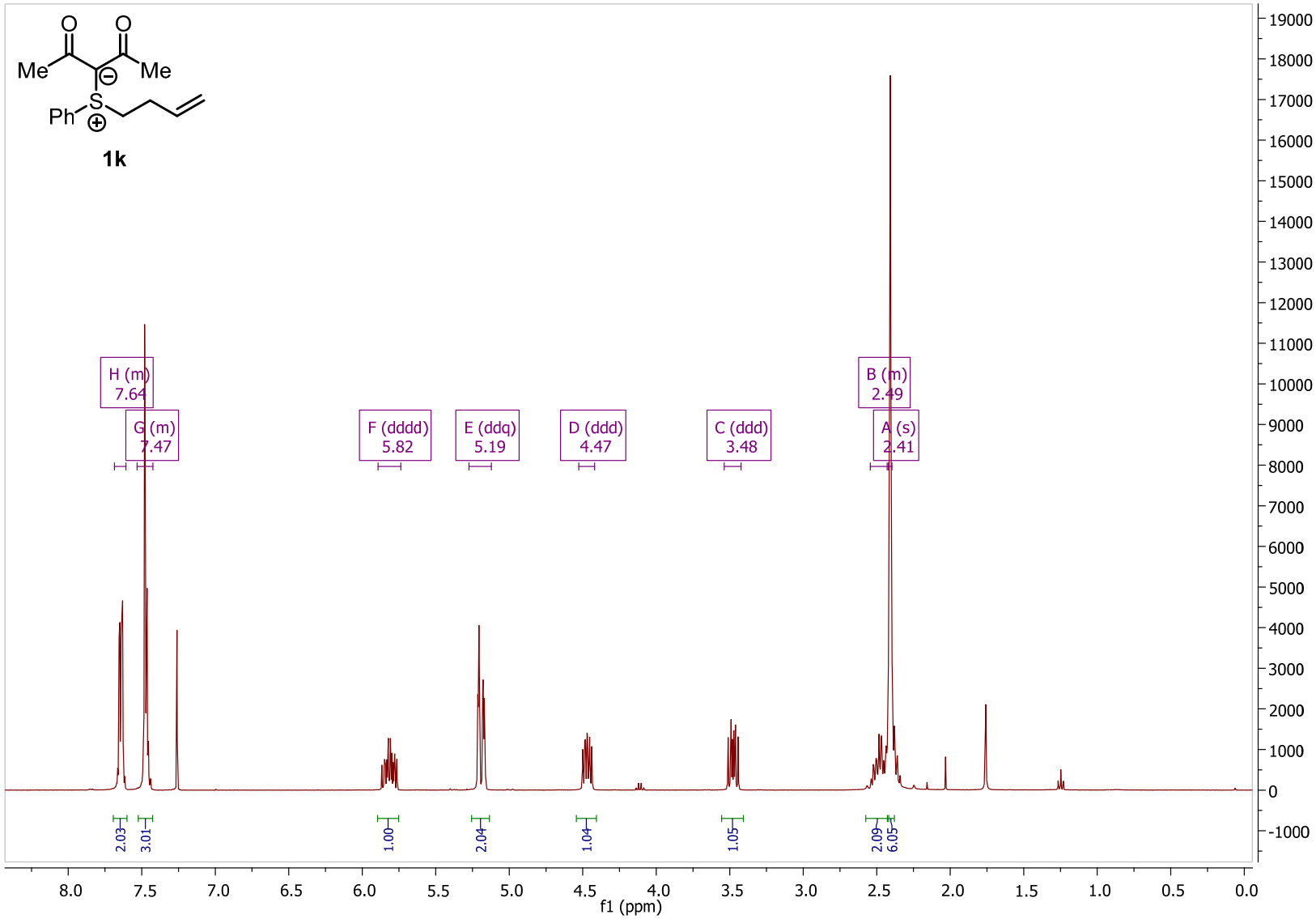
30
20
10
f1 (ppm)


1k
H (m)
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G (m)
7.47
F (dddd)
5.82
E (ddq)
5.19
D (ddd)
4.47
C (ddd)
3.48
B (m)
2.49
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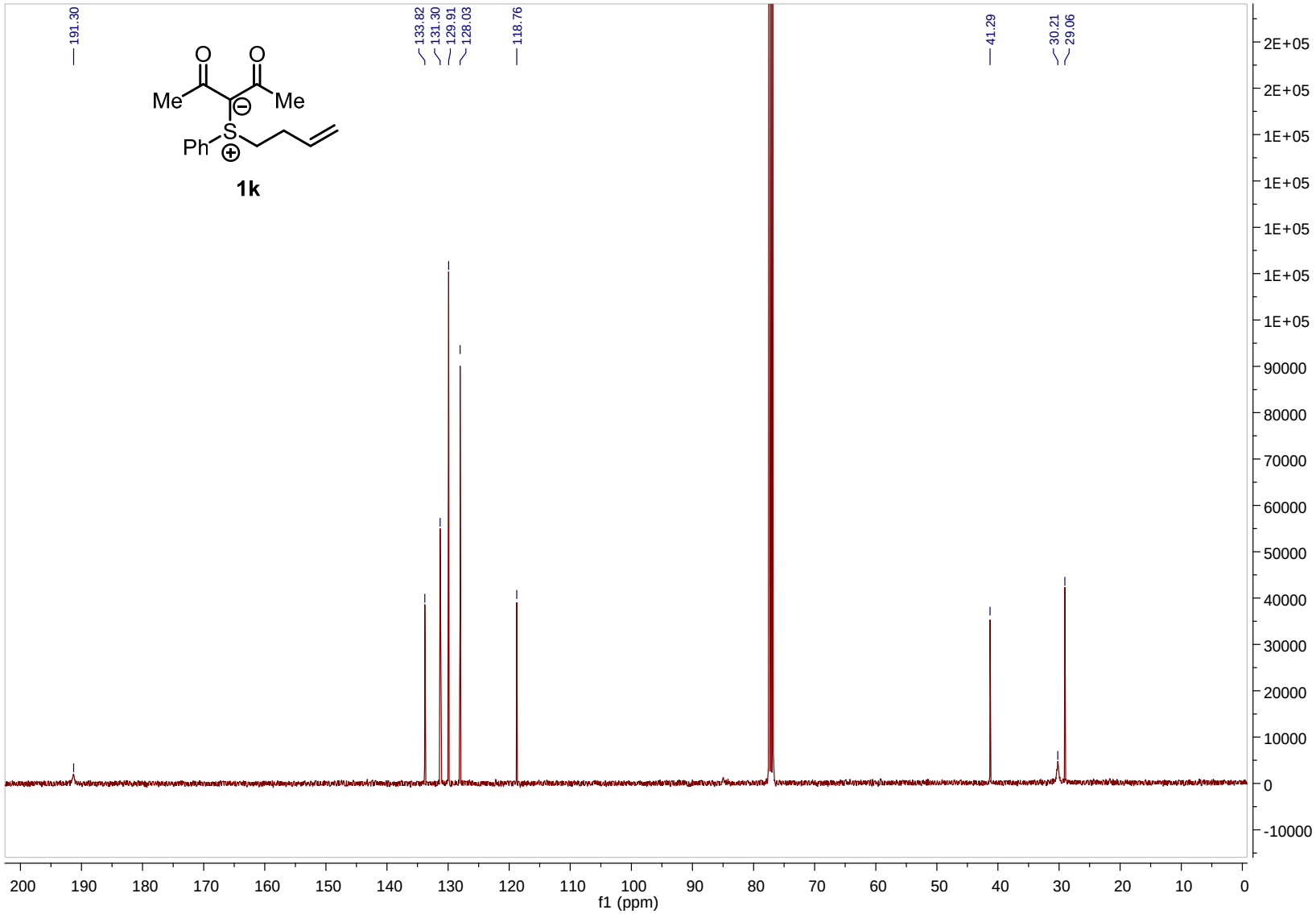
3.01
1.00
2.04
1.04
1.05
2.09
6.05
f1 (ppm)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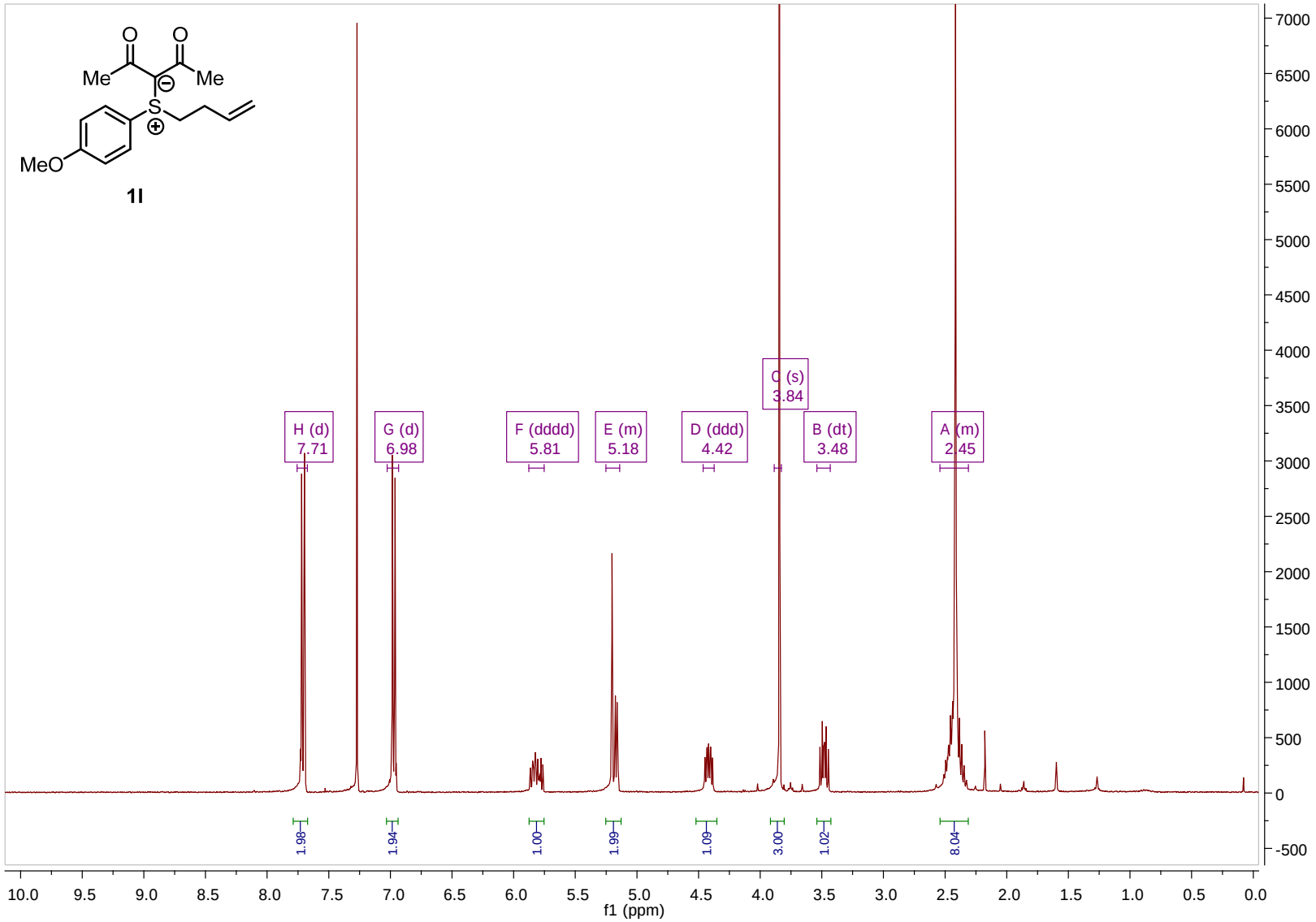
29.06
Me
Me
Ph
S
1k
f1 (ppm)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Me
S
MeO
1l
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G (d)
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F (dddd)
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E (m)
5.18
D (ddd)
4.42
C (s)
3.84
B (dt)
3.48
A (m)
2.45
1.98
1.94
1.00
1.99
1.09
3.00
1.02
8.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
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6000
5500
5000
4500
4000
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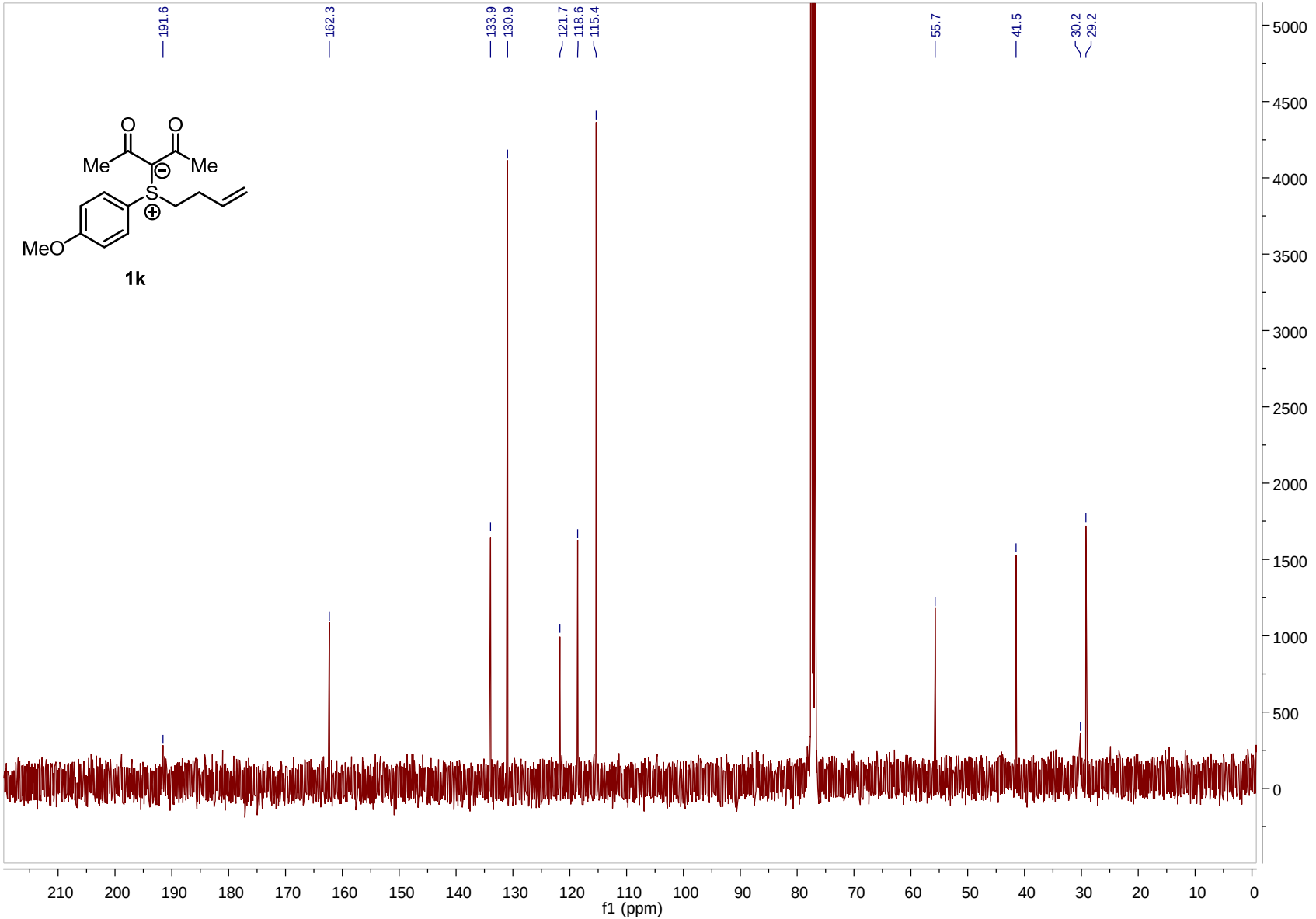
3000
2500
2000
1500
1000
500
0
-500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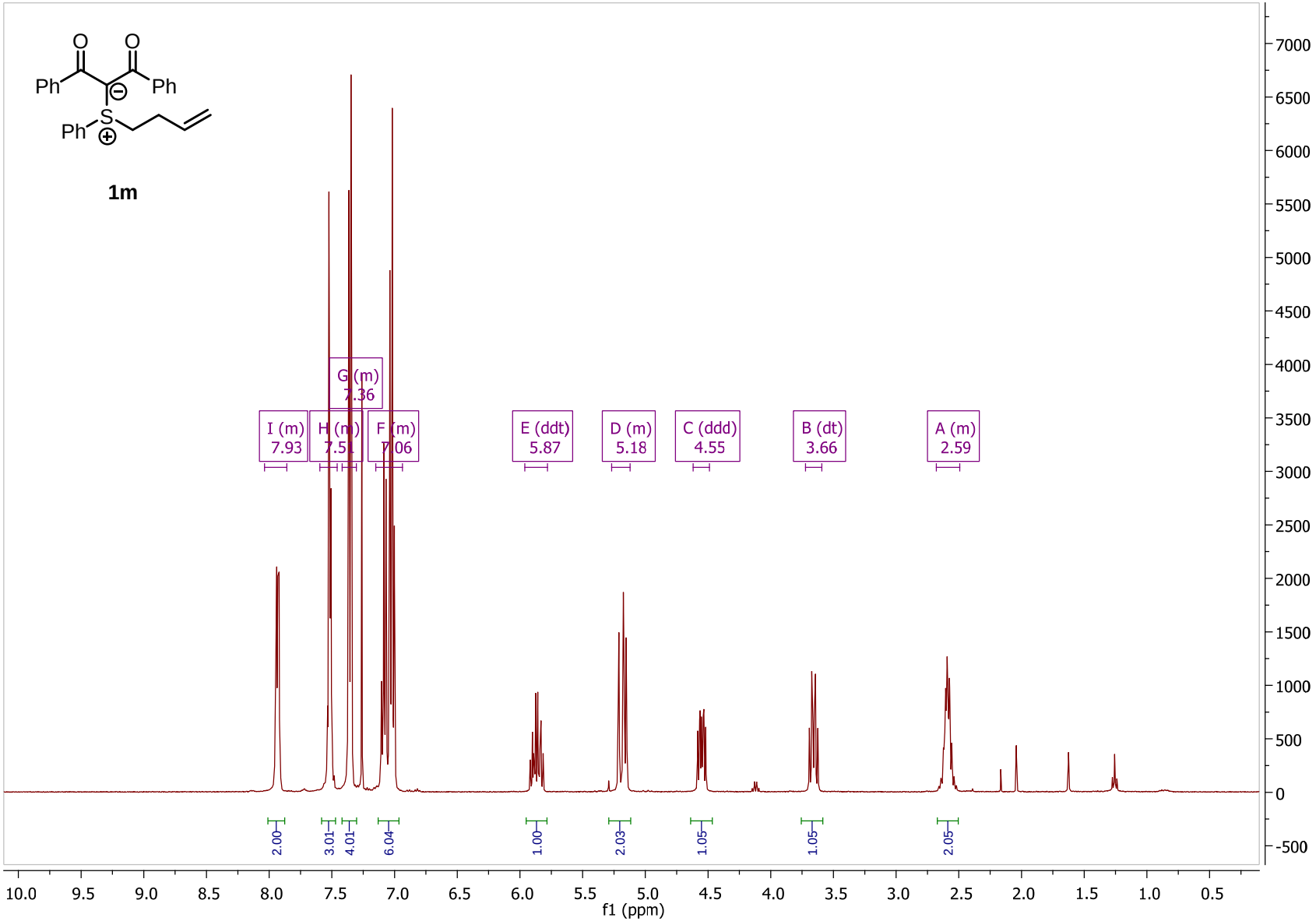
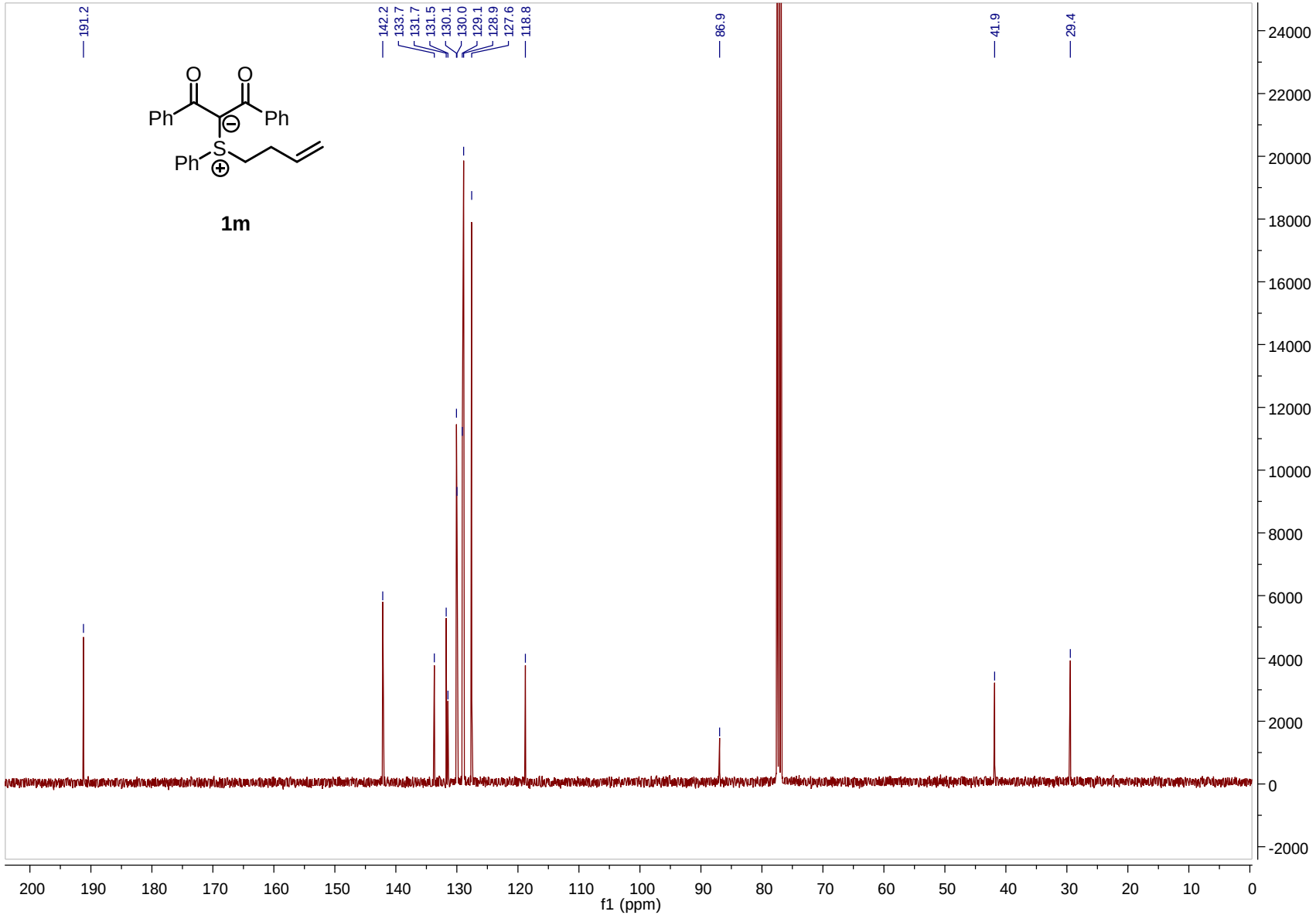
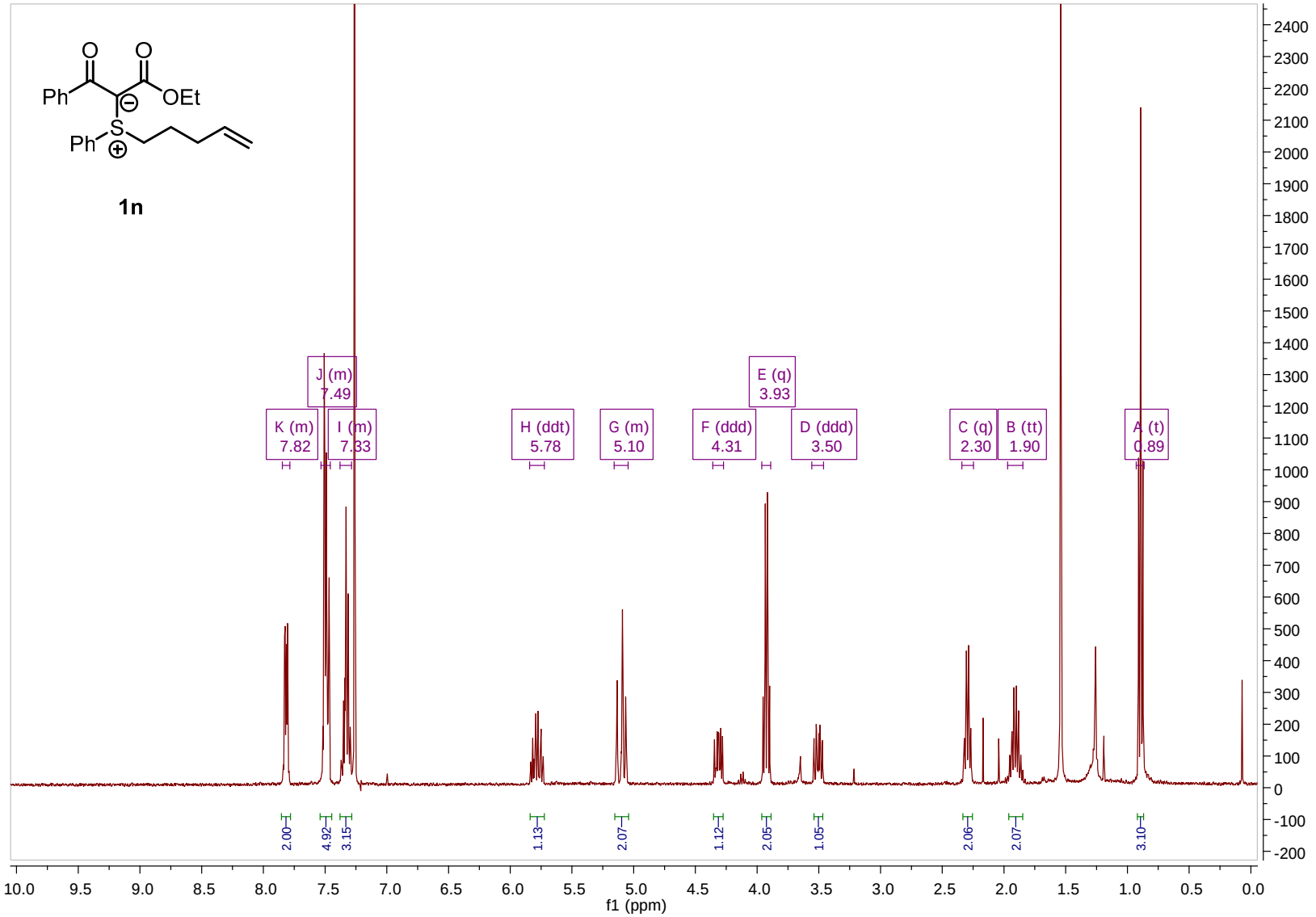
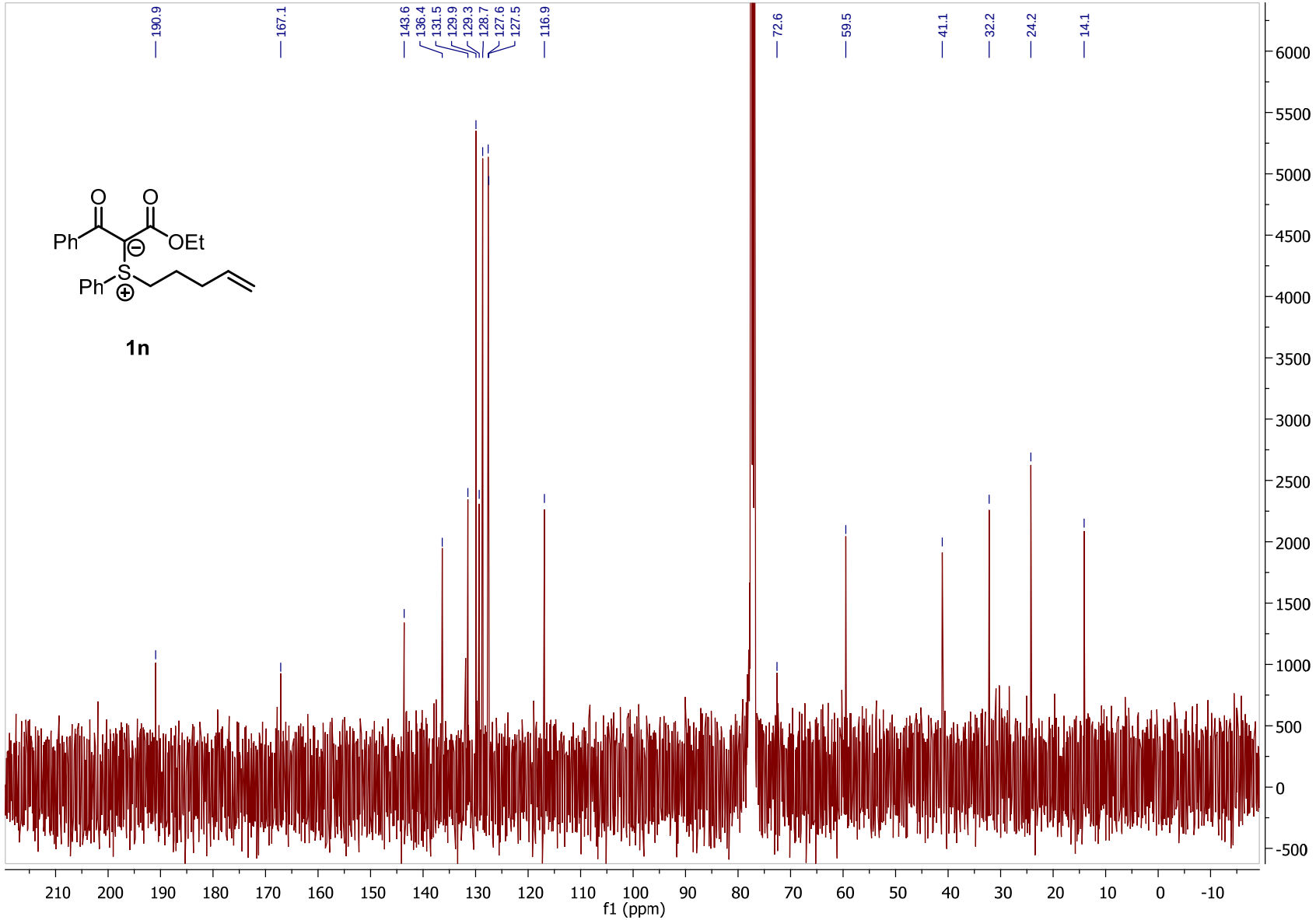
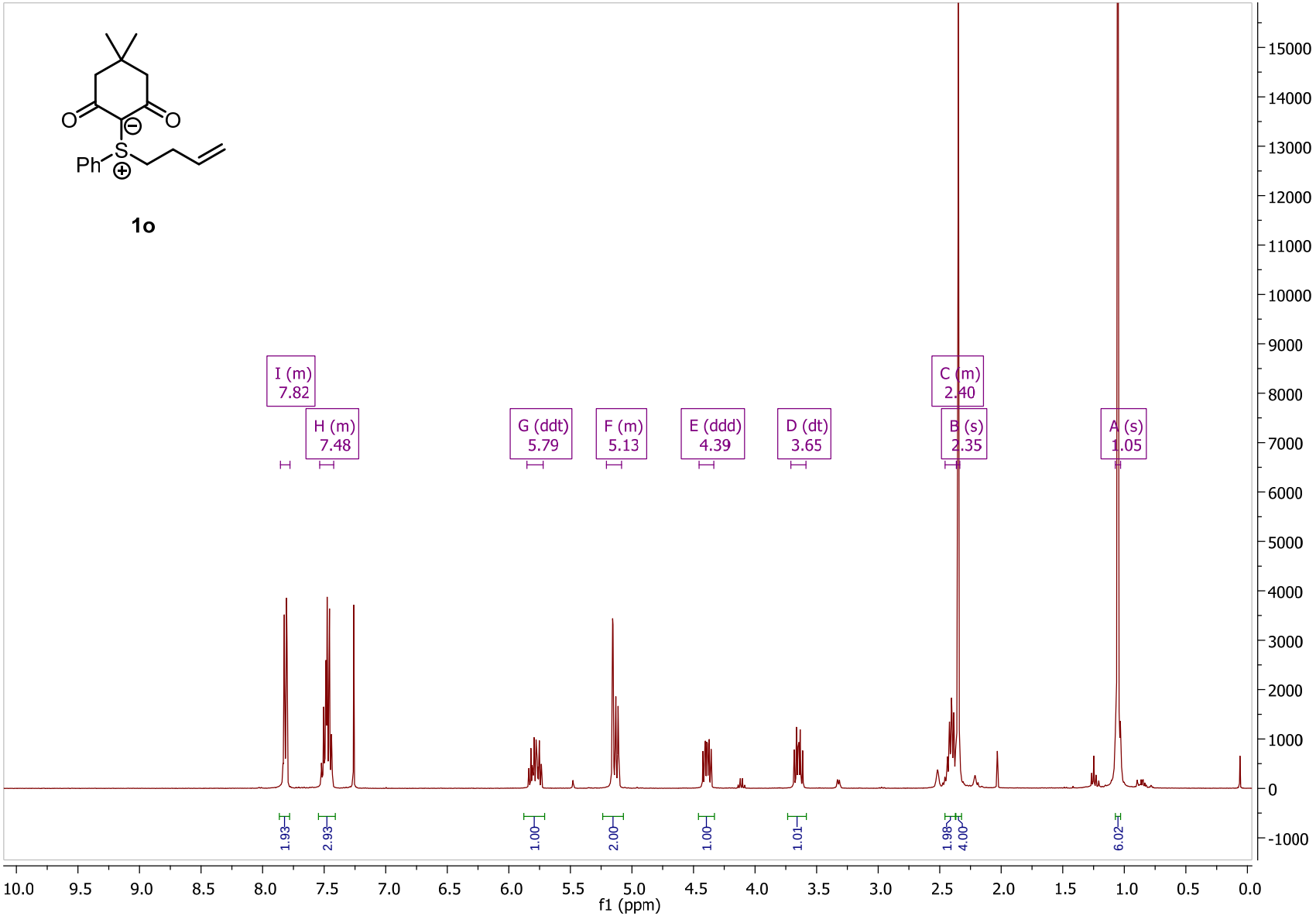
121.7
118.6
115.4
55.7
41.5
30.2
29.2
Me
Me
MeO
1k
f1 (ppm)

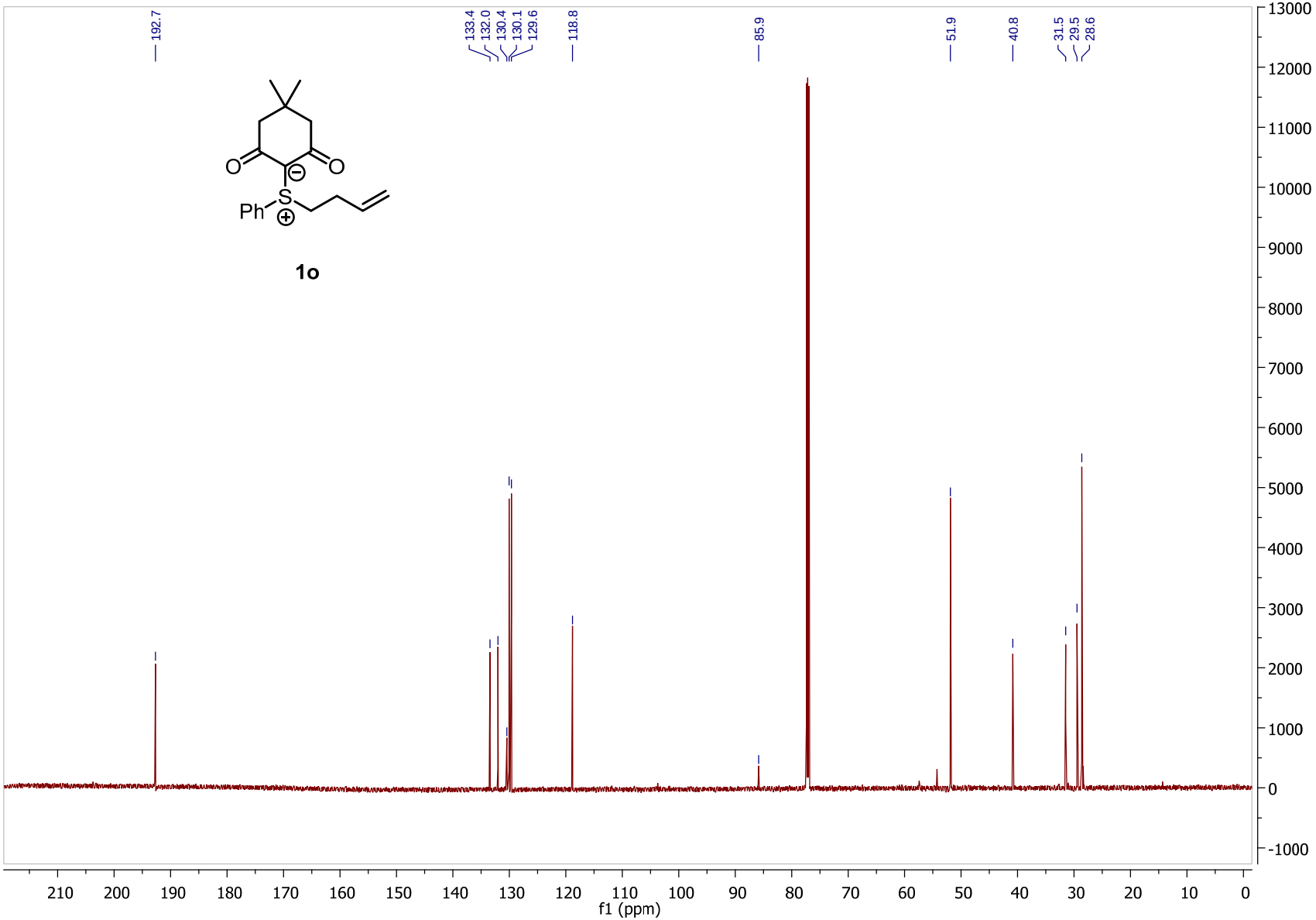

1m
I (m) 7.93
H (m) 7.51
G (m) 7.36
F (m) 7.06
E (ddt) 5.87
D (m) 5.18
C (ddd) 4.55
B (dt) 3.66
A (m) 2.59
2.00
3.01
4.01
6.04
1.00
2.03
1.05
1.05
2.05
f1 (ppm)

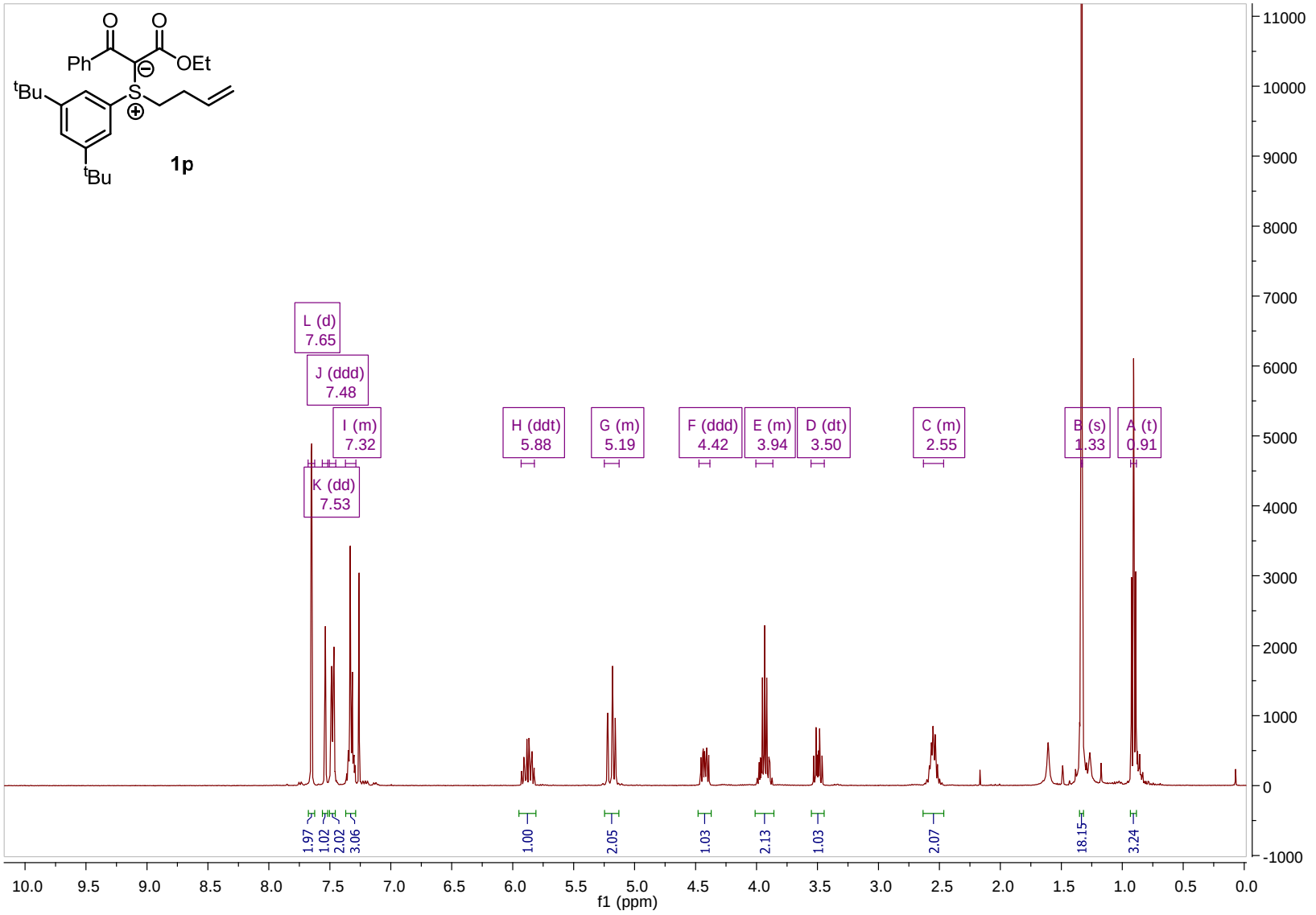

191.2
142.2
133.7
131.7
131.5
130.1
130.0
129.1
128.9
127.6
118.8
86.9
41.9
29.4
O
O
Ph
Ph
Ph
S
1m
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

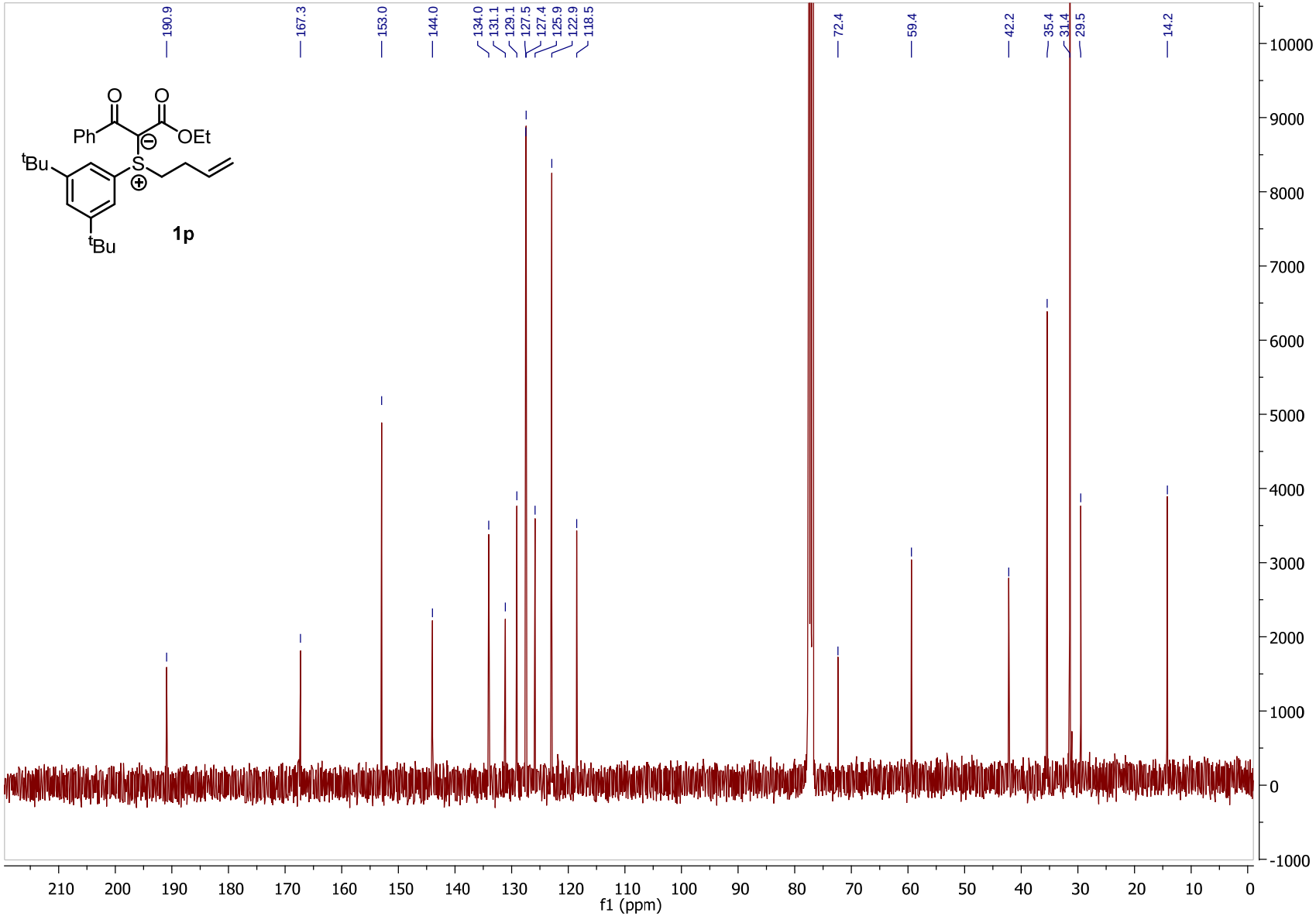

1n
J (m) 7.49
K (m) 7.82
I (m) 7.33
H (ddt) 5.78
G (m) 5.10
E (q) 3.93
F (ddd) 4.31
D (ddd) 3.50
C (q) 2.30
B (tt) 1.90
A (t) 0.89
2.00
4.92
3.15
1.13
2.07
1.12
2.05
1.05
2.06
2.07
3.10
f1 (ppm)


190.9
167.1
143.6
136.4
131.5
129.9
129.3
128.7
127.6
127.5
116.9
72.6
59.5
41.1
32.2
24.2
14.1
Ph
O
O
OEt
S
Ph
1n
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

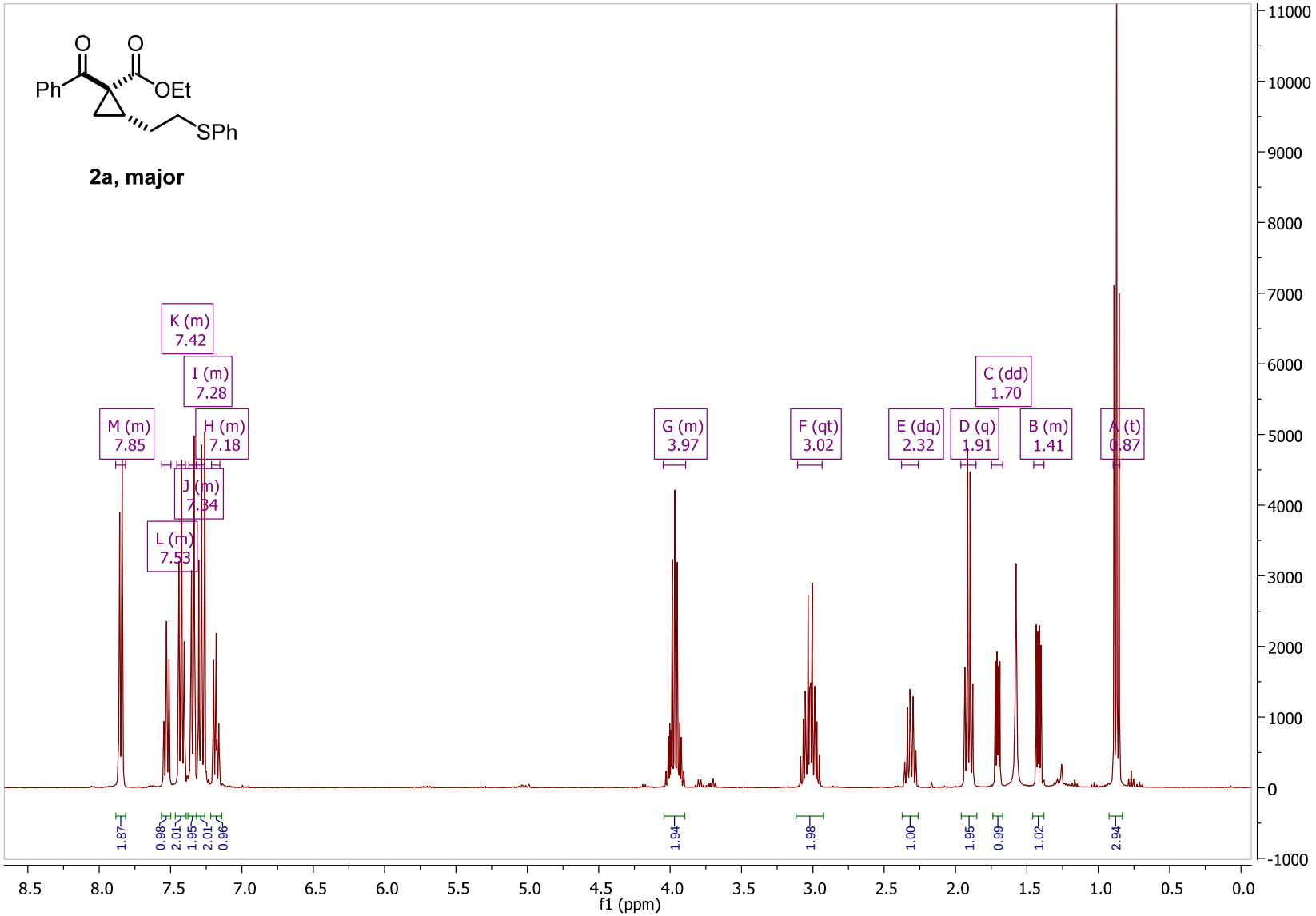

1o
I (m)
7.82
H (m)
7.48
G (ddt)
5.79
F (m)
5.13
E (ddd)
4.39
D (dt)
3.65
C (m)
2.40
B (s)
2.35
A (s)
1.05
1.93
2.93
1.00
2.00
1.00
1.01
1.98
4.00
6.02
f1 (ppm)

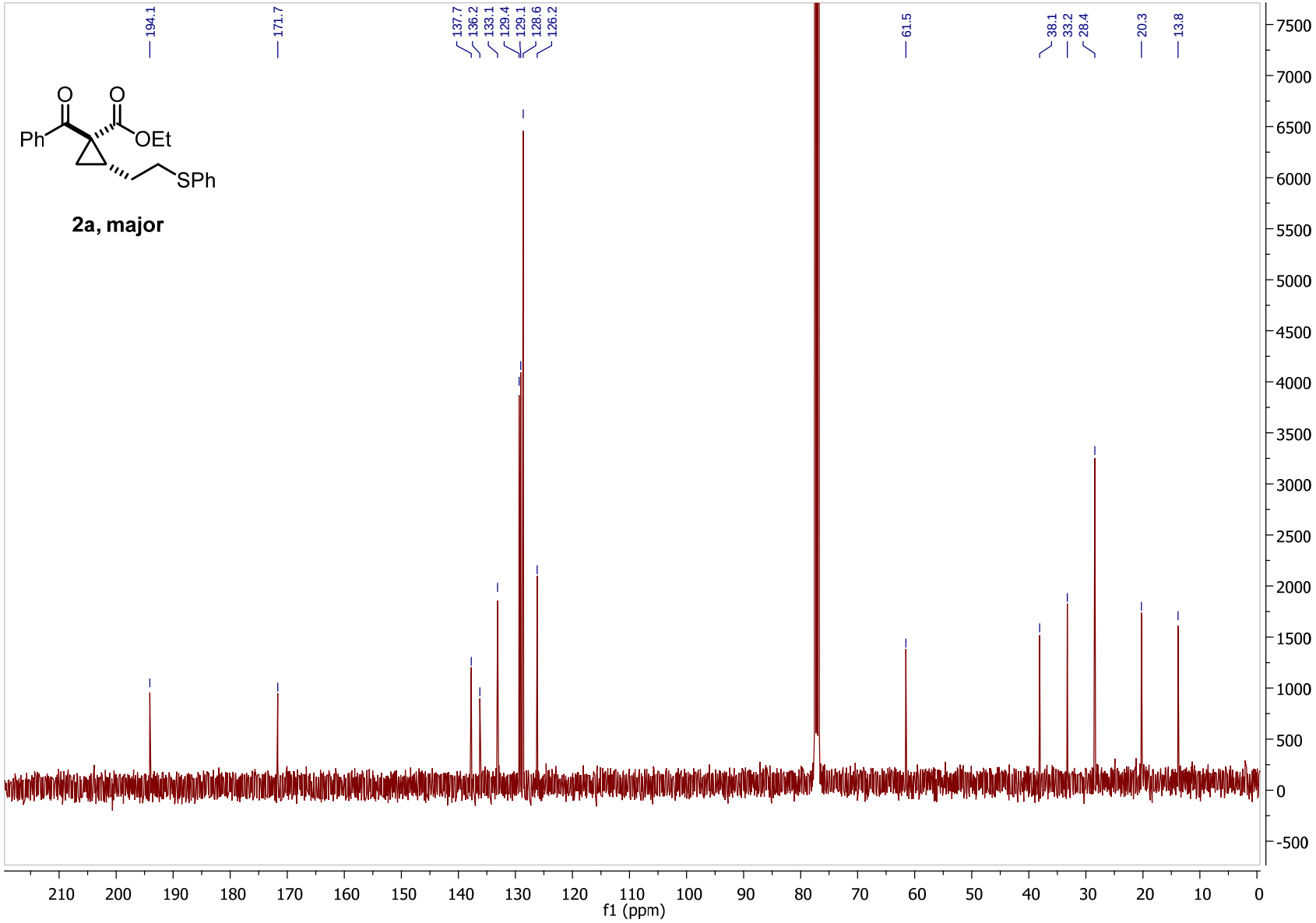

192.7
133.4
132.0
130.4
130.1
129.6
118.8
85.9
51.9
40.8
31.5
29.5
28.6
O
O
Ph
S
1o
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

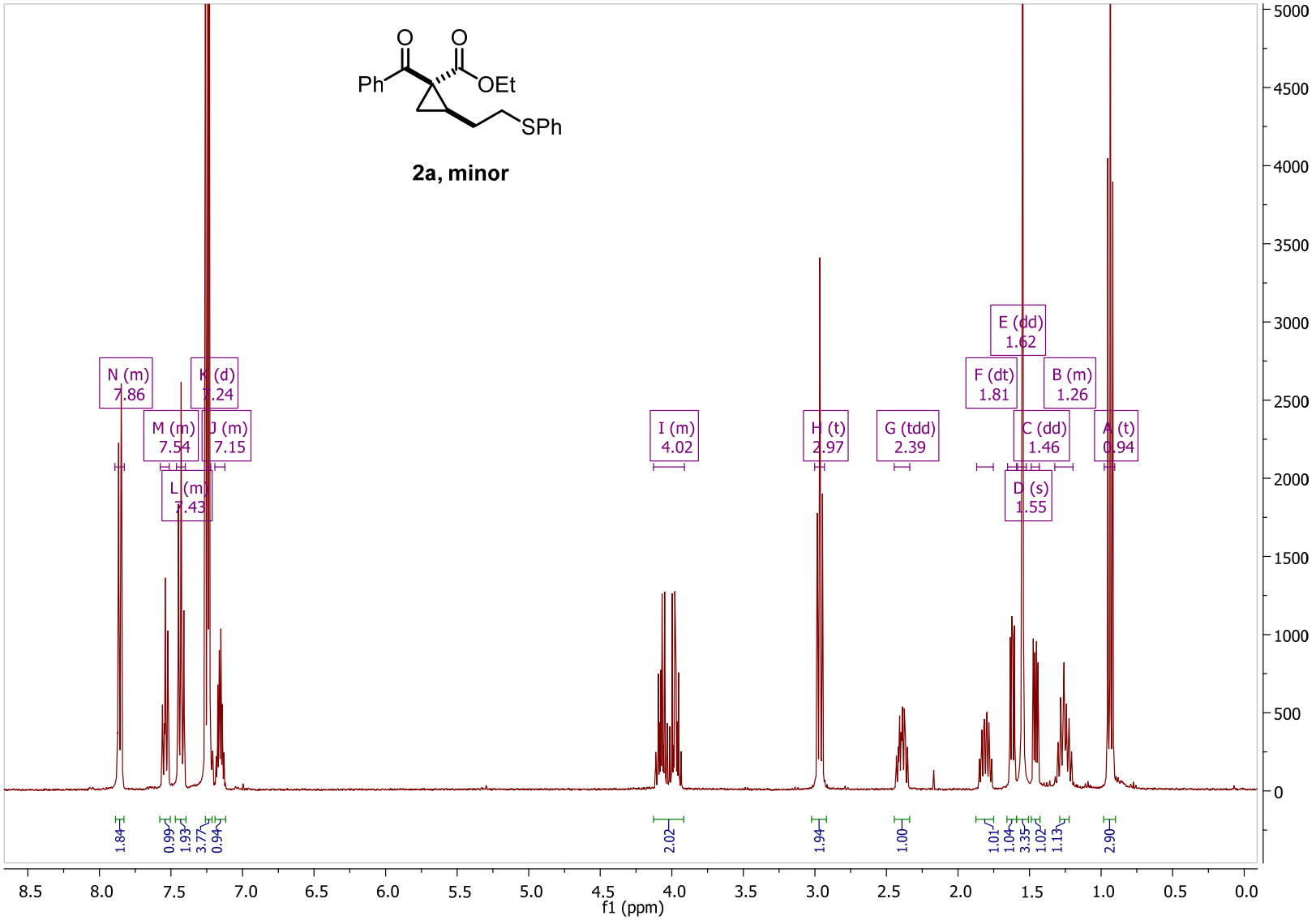

Ph
O
O
OEt
S
tBu
tBu
1p
L (d)
7.65
J (ddd)
7.48
I (m)
7.32
K (dd)
7.53
H (ddt)
5.88
G (m)
5.19
F (ddd)
4.42
E (m)
3.94
D (dt)
3.50
C (m)
2.55
B (s)
1.33
A (t)
0.91
1.97
1.02
2.02
3.06
1.00
2.05
1.03
2.13
1.03
2.07
18.15
3.24
f1 (ppm)

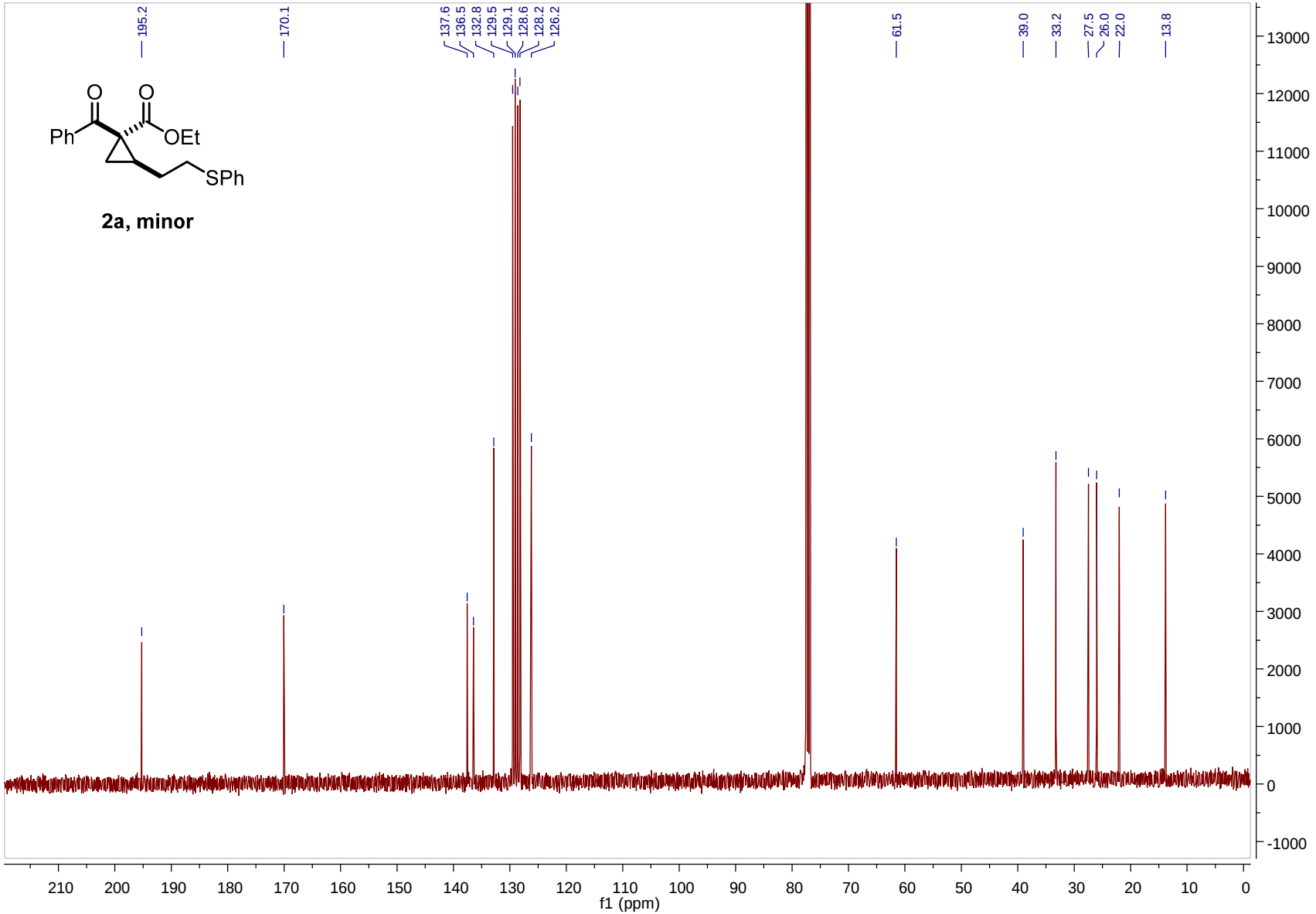

190.9
167.3
153.0
144.0
134.0
131.1
129.1
127.5
127.4
125.9
122.9
118.5
72.4
59.4
42.2
35.4
31.4
29.5
14.2
Ph
OEt
tBu
tBu
1p
f1 (ppm)

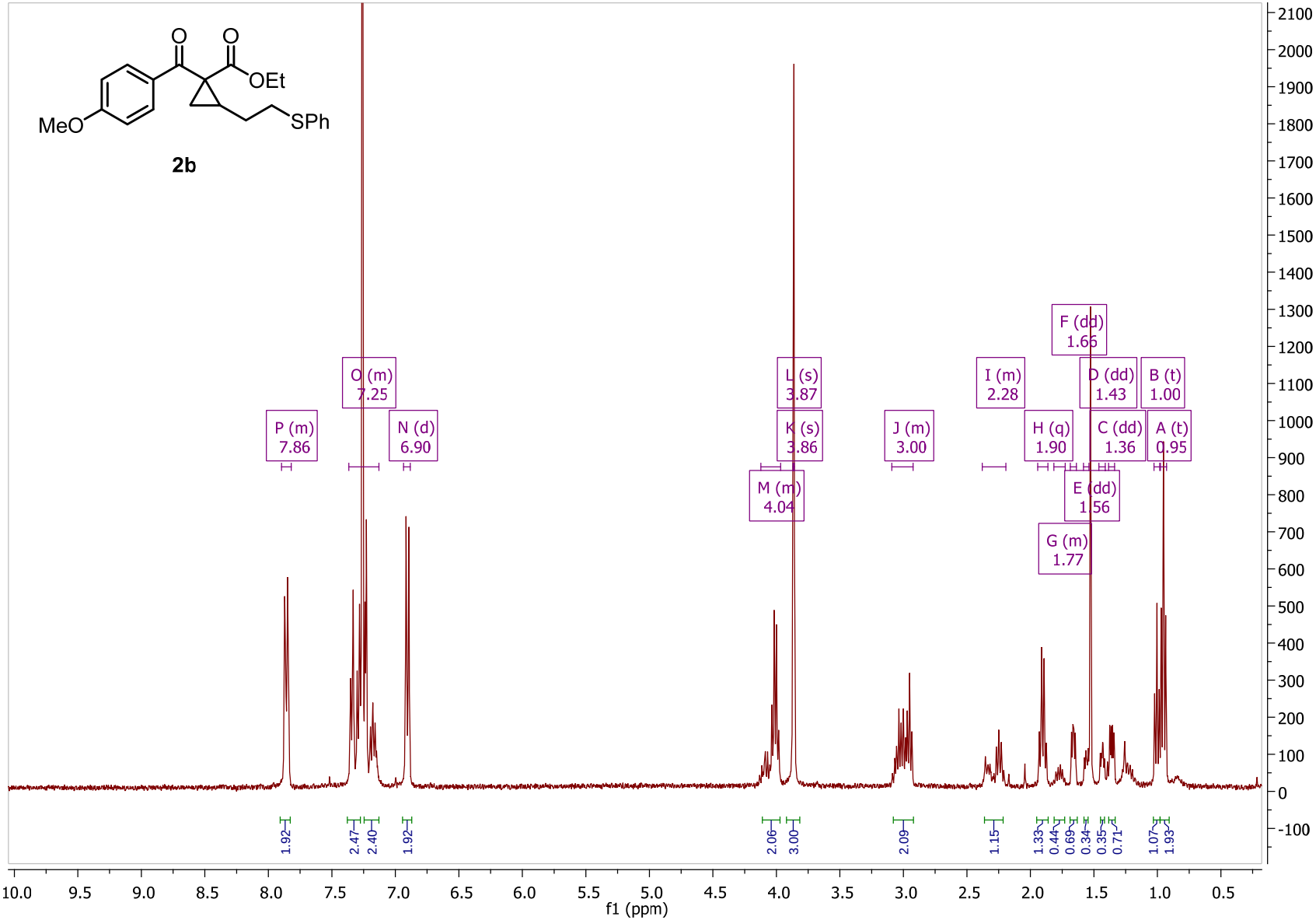
7.2 Cyclopropanes

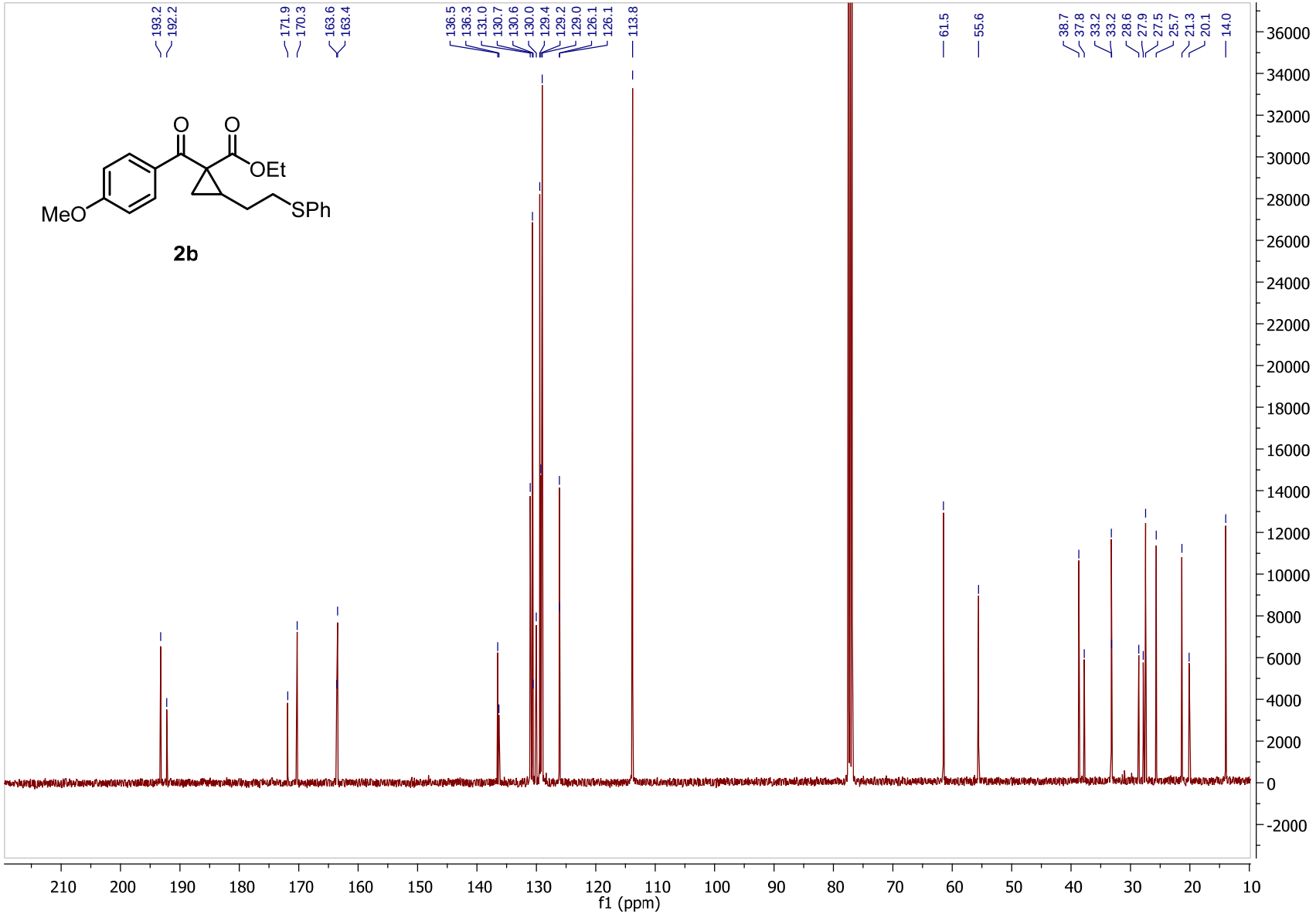


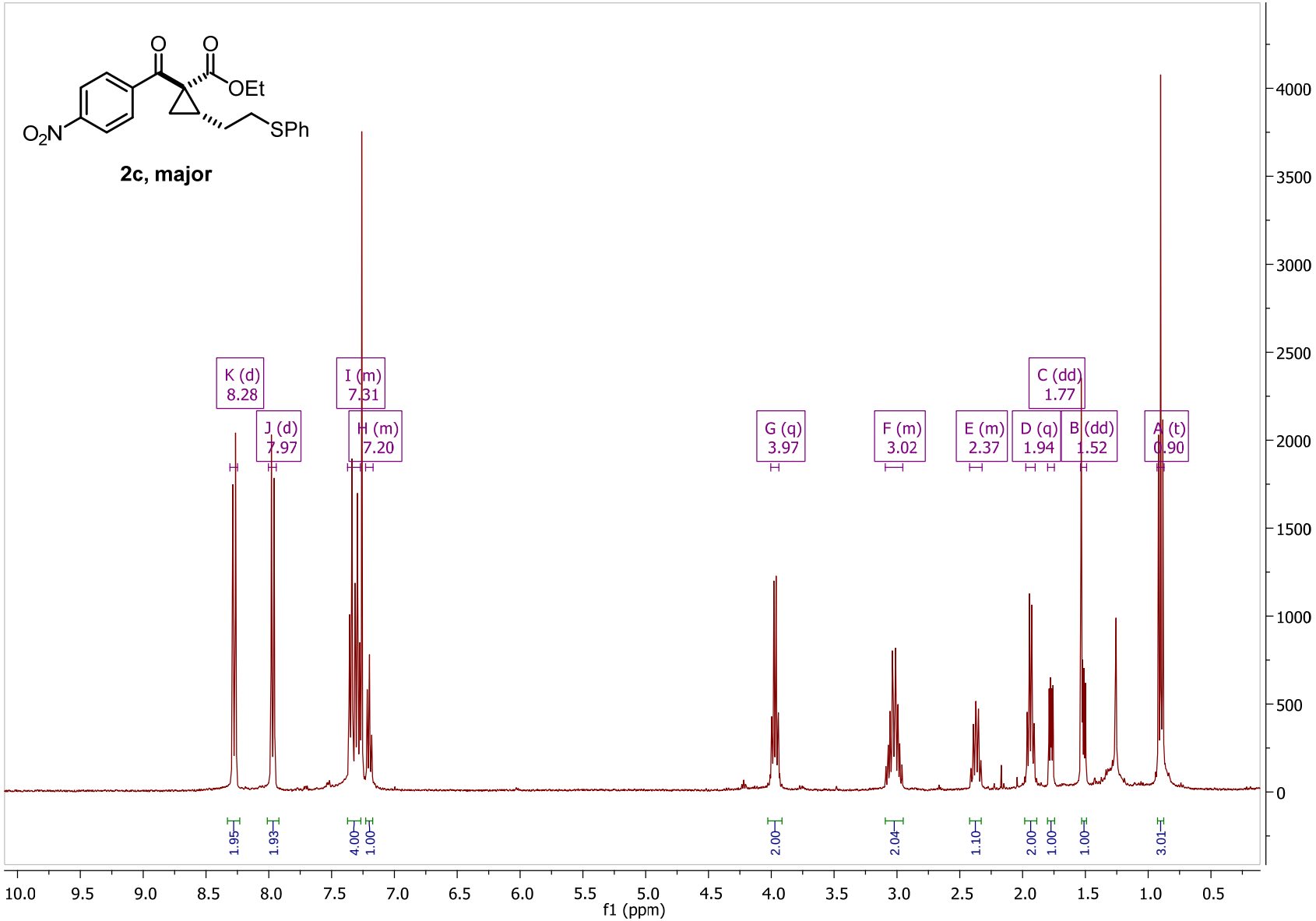

194.1
171.7
137.7
136.2
133.1
129.4
129.1
128.6
126.2
61.5
38.1
33.2
28.4
20.3
13.8
Ph
O
O
OEt
SPh
2a, major
f1 (ppm)

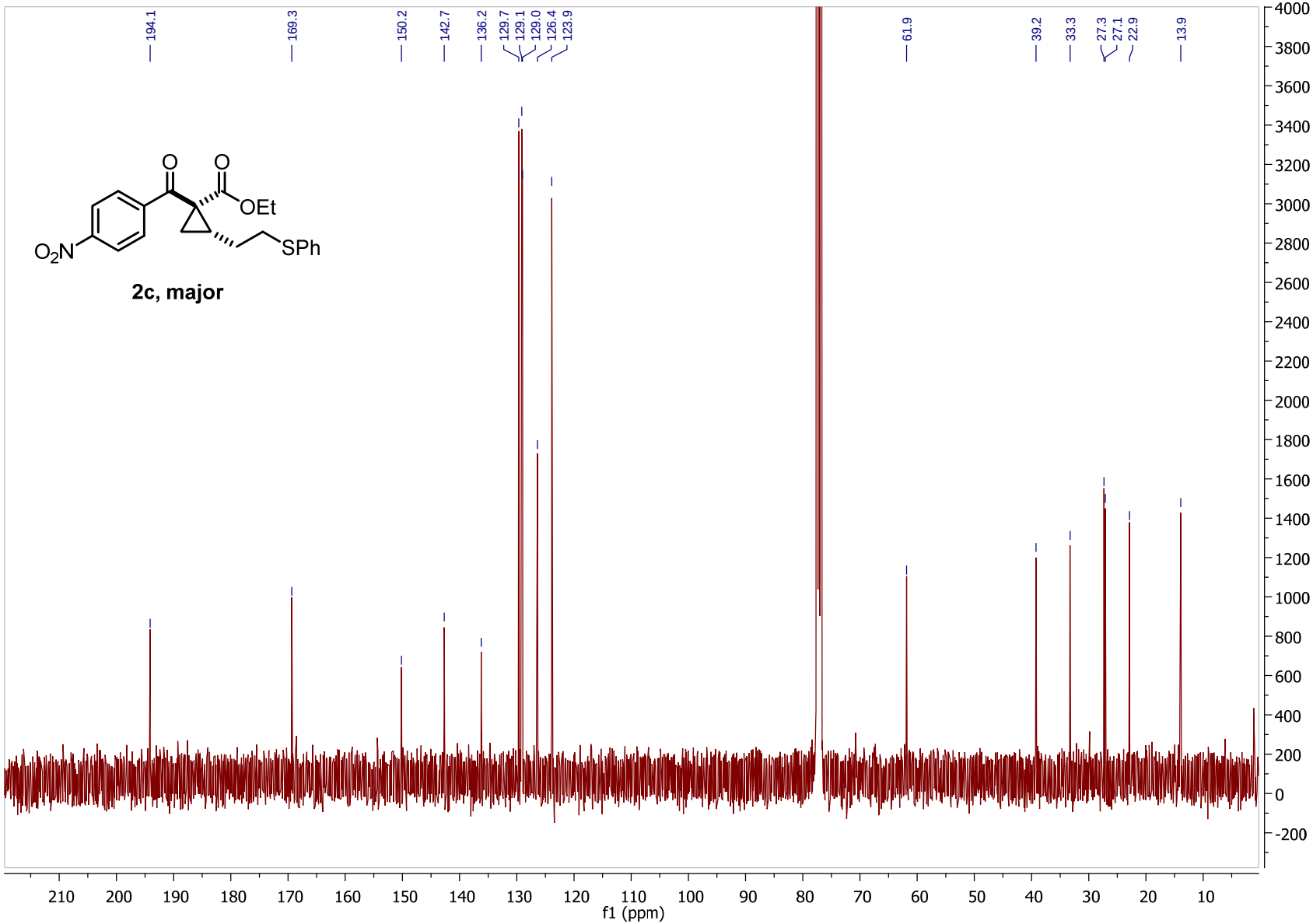

Ph
O
O
OEt
SPh
2a, minor
N (m) 7.86
K (d) 7.24
M (m) 7.54
J (m) 7.15
L (m) 7.43
I (m) 4.02
H (t) 2.97
G (tdd) 2.39
E (dd) 1.62
F (dt) 1.81
B (m) 1.26
C (dd) 1.46
A (t) 0.94
D (s) 1.55
1.84
0.99
1.93
3.77
0.94
2.02
1.94
1.00
1.01
1.04
3.35
1.02
1.13
2.90
f1 (ppm)

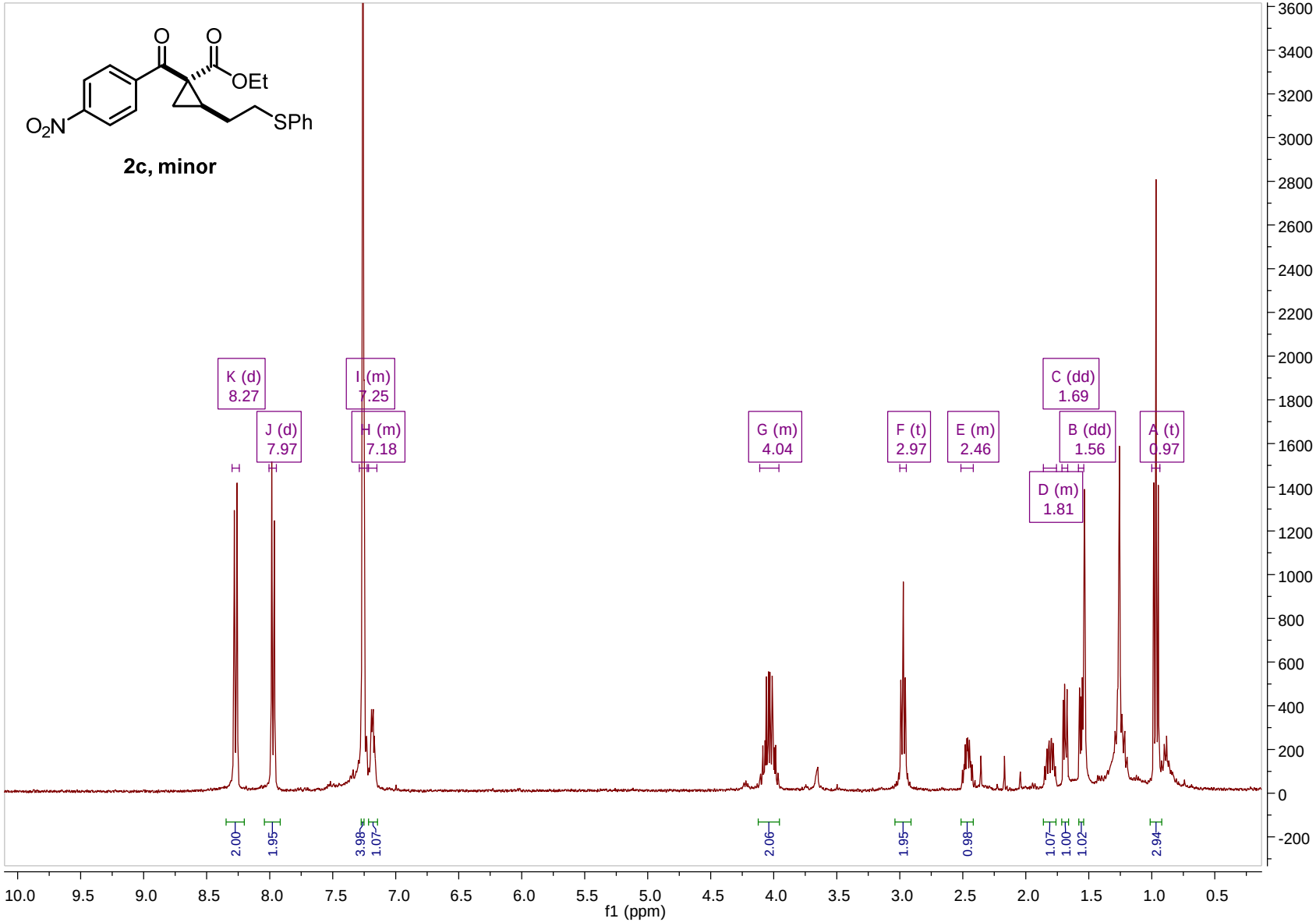

195.2
170.1
137.6
136.5
132.8
129.5
129.1
128.6
128.2
126.2
61.5
39.0
33.2
27.5
26.0
22.0
13.8
O
O
Ph
OEt
SPh
2a, minor
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

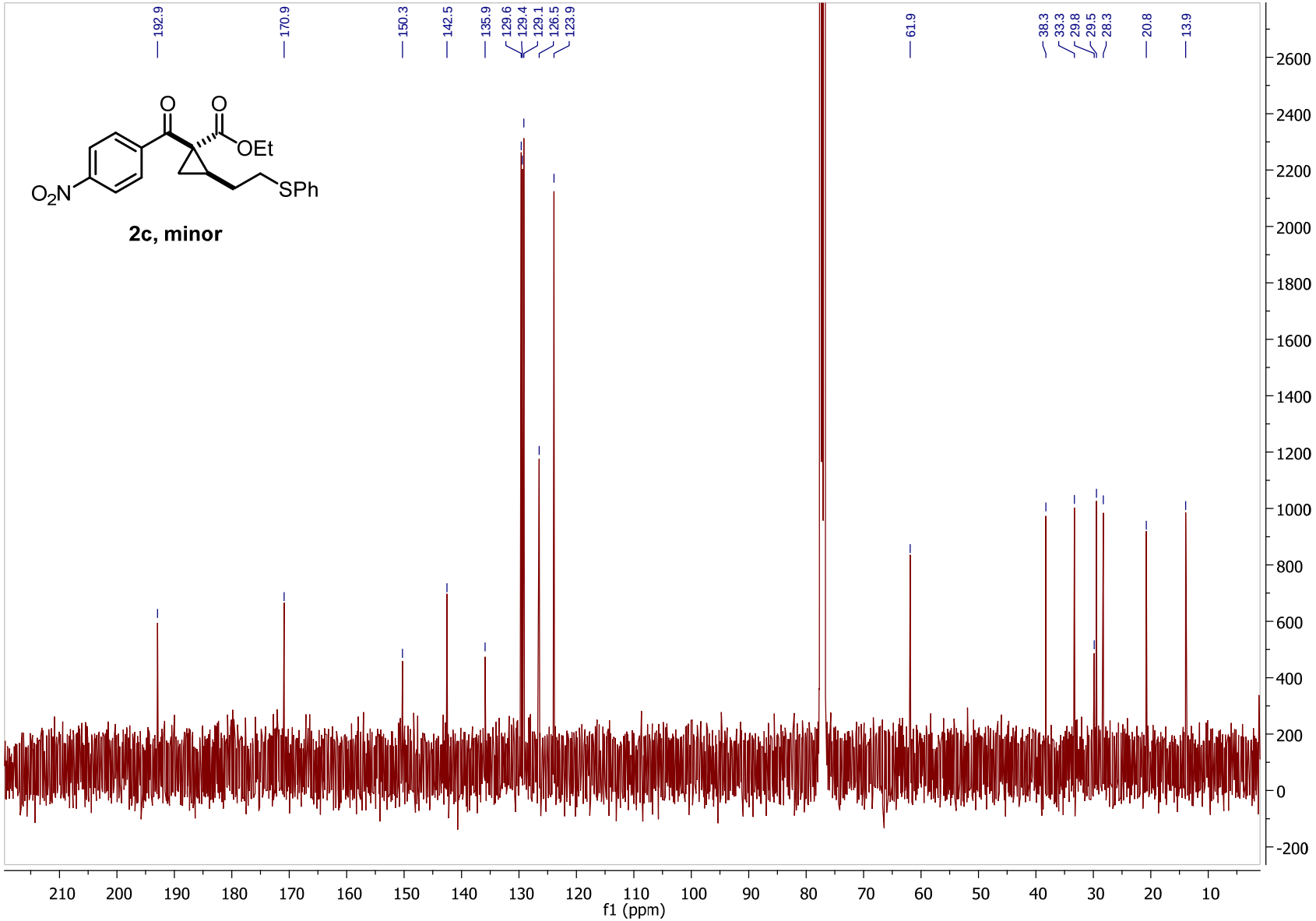

O
O
OEt
MeO
SPh
2b
P (m)
7.86
O (m)
7.25
N (d)
6.90
L (s)
3.87
K (s)
3.86
M (m)
4.04
J (m)
3.00
I (m)
2.28
F (dd)
1.66
H (q)
1.90
D (dd)
1.43
C (dd)
1.36
B (t)
1.00
A (t)
0.95
E (dd)
1.56
G (m)
1.77
1.92
2.47
2.40
1.92
2.06
3.00
2.09
1.15
1.33
0.44
0.69
0.34
0.35
0.71
1.07
1.93
f1 (ppm)

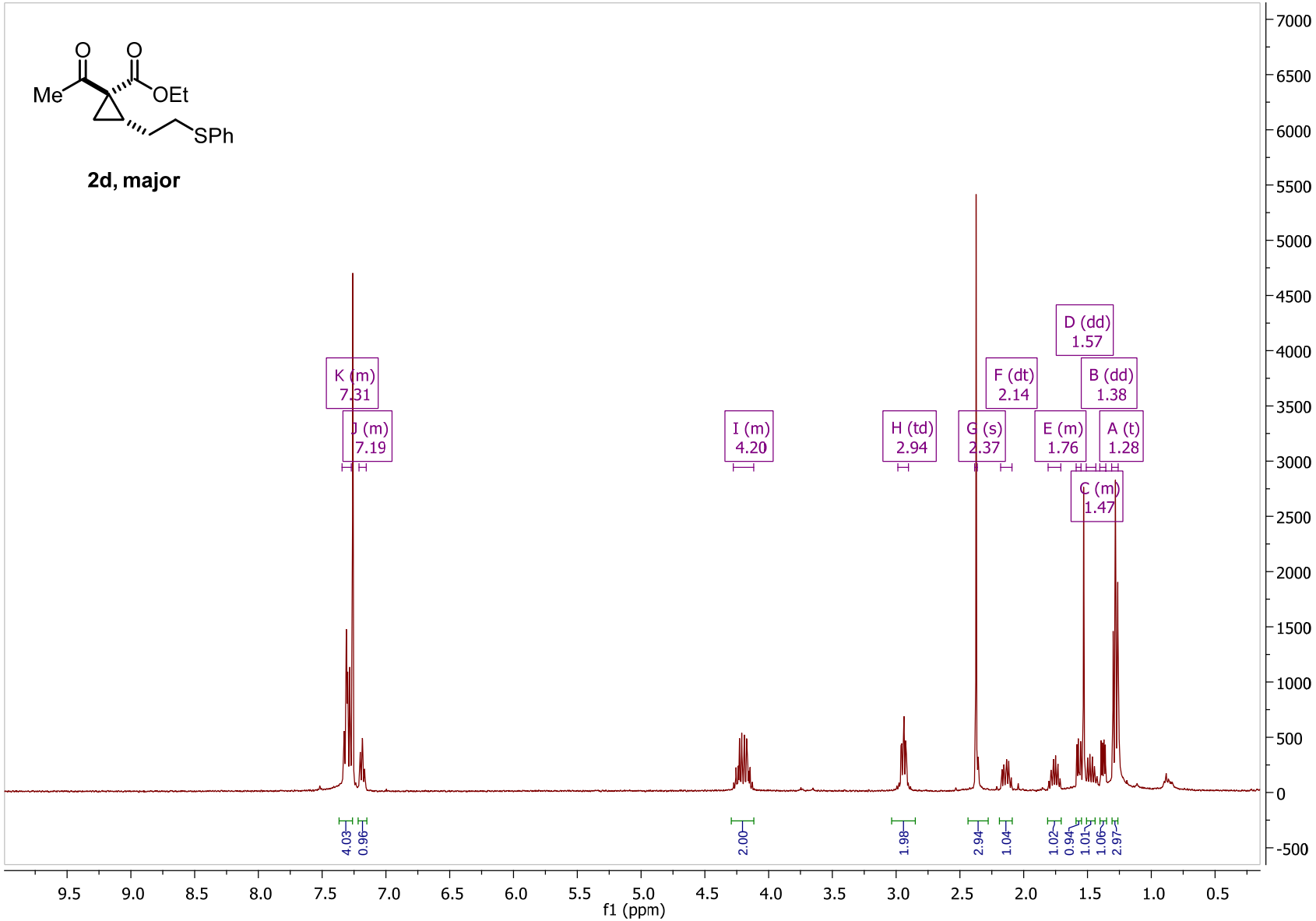

193.2
192.2
171.9
170.3
163.6
163.4
136.5
136.3
131.0
130.7
130.6
130.0
129.4
129.2
129.0
126.1
126.1
113.8
61.5
55.6
38.7
37.8
33.2
33.2
28.6
27.9
27.5
25.7
21.3
20.1
14.0
O
O
OEt
MeO
SPh
2b
f1 (ppm)

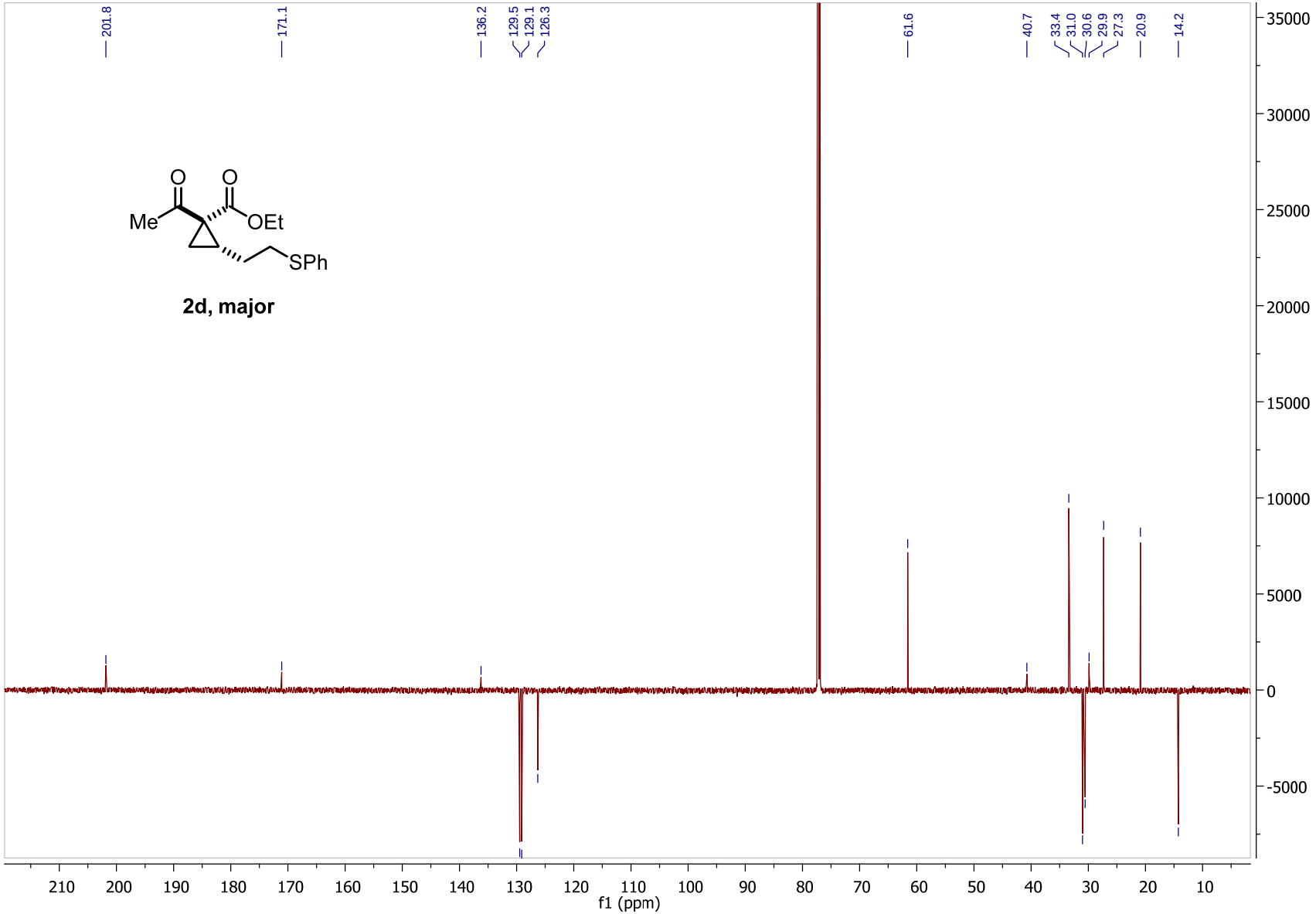

O
O
OEt
O_2N
SPh
2c, major
K (d) 8.28
J (d) 7.97
I (m) 7.31
H (m) 7.20
G (q) 3.97
F (m) 3.02
E (m) 2.37
D (q) 1.94
C (dd) 1.77
B (dd) 1.52
A (t) 0.90
1.95
1.93
4.00
1.00
2.00
2.04
1.10
2.00
1.00
1.00
3.01
f1 (ppm)

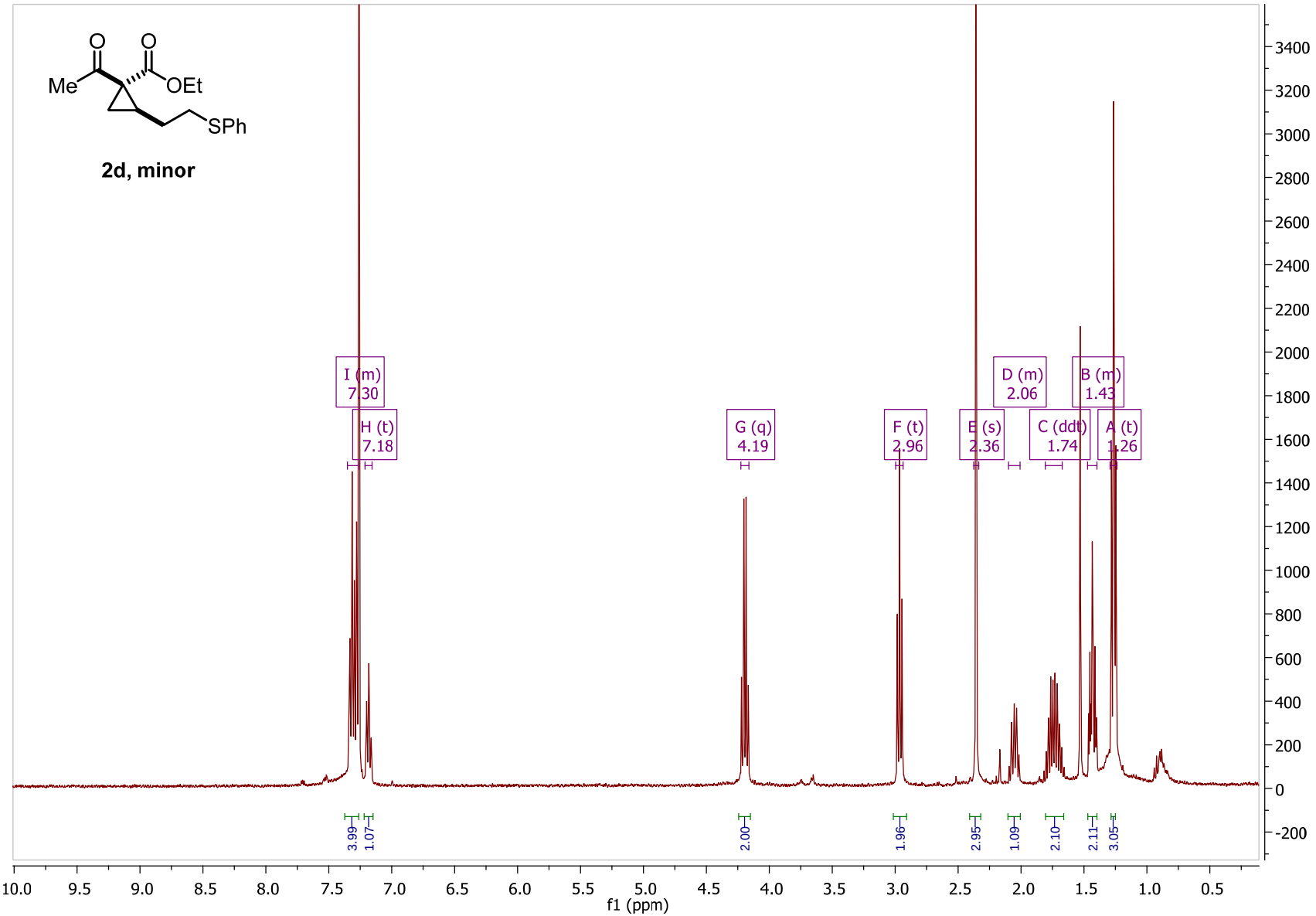

194.1
169.3
150.2
142.7
136.2
129.7
129.1
129.0
126.4
123.9
61.9
39.2
33.3
27.3
27.1
22.9
13.9
O
O
OEt
O2N
SPh
2c, major
f1 (ppm)

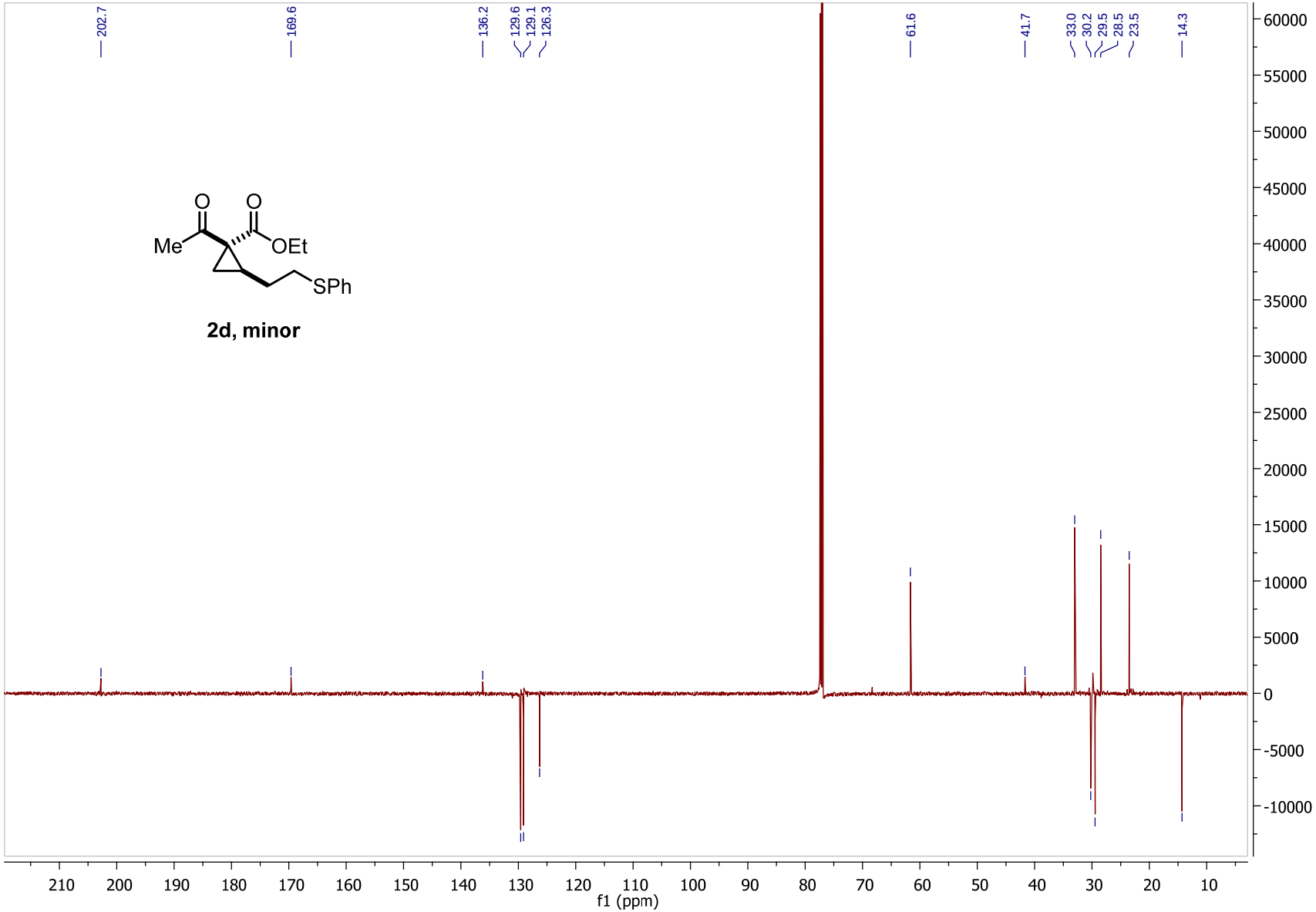

O
O
OEt
O2N
SPh
2c, minor
K (d)
8.27
J (d)
7.97
I (m)
7.25
H (m)
7.18
G (m)
4.04
F (t)
2.97
E (m)
2.46
C (dd)
1.69
B (dd)
1.56
A (t)
0.97
D (m)
1.81
2.00
1.95
3.98
1.07
2.06
1.95
0.98
1.07
1.00
1.02
2.94
f1 (ppm)

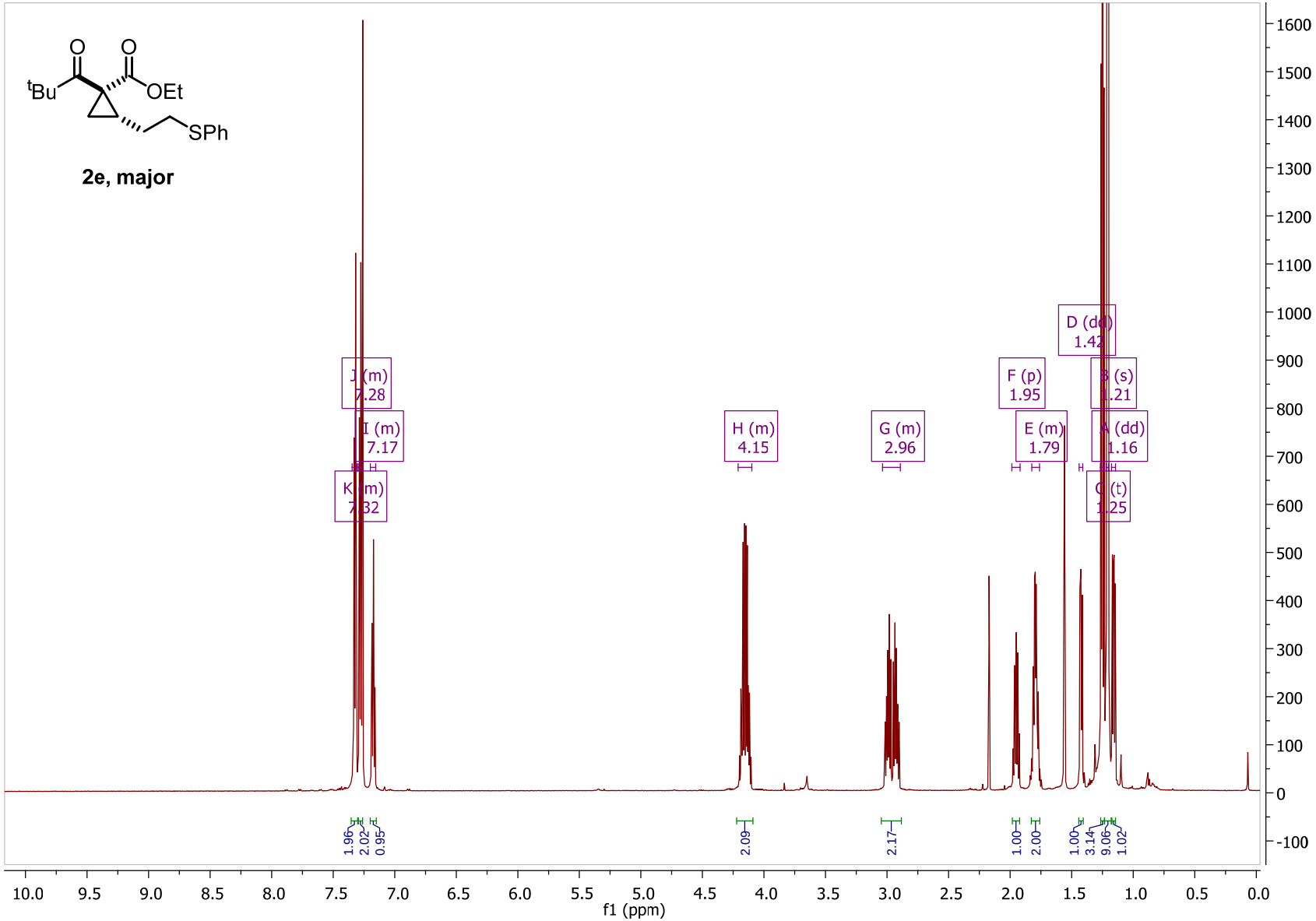

192.9
170.9
150.3
142.5
135.9
129.6
129.4
129.1
126.5
123.9
61.9
38.3
33.3
29.8
29.5
28.3
20.8
13.9
O
O
OEt
O2N
SPh
2c, minor
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

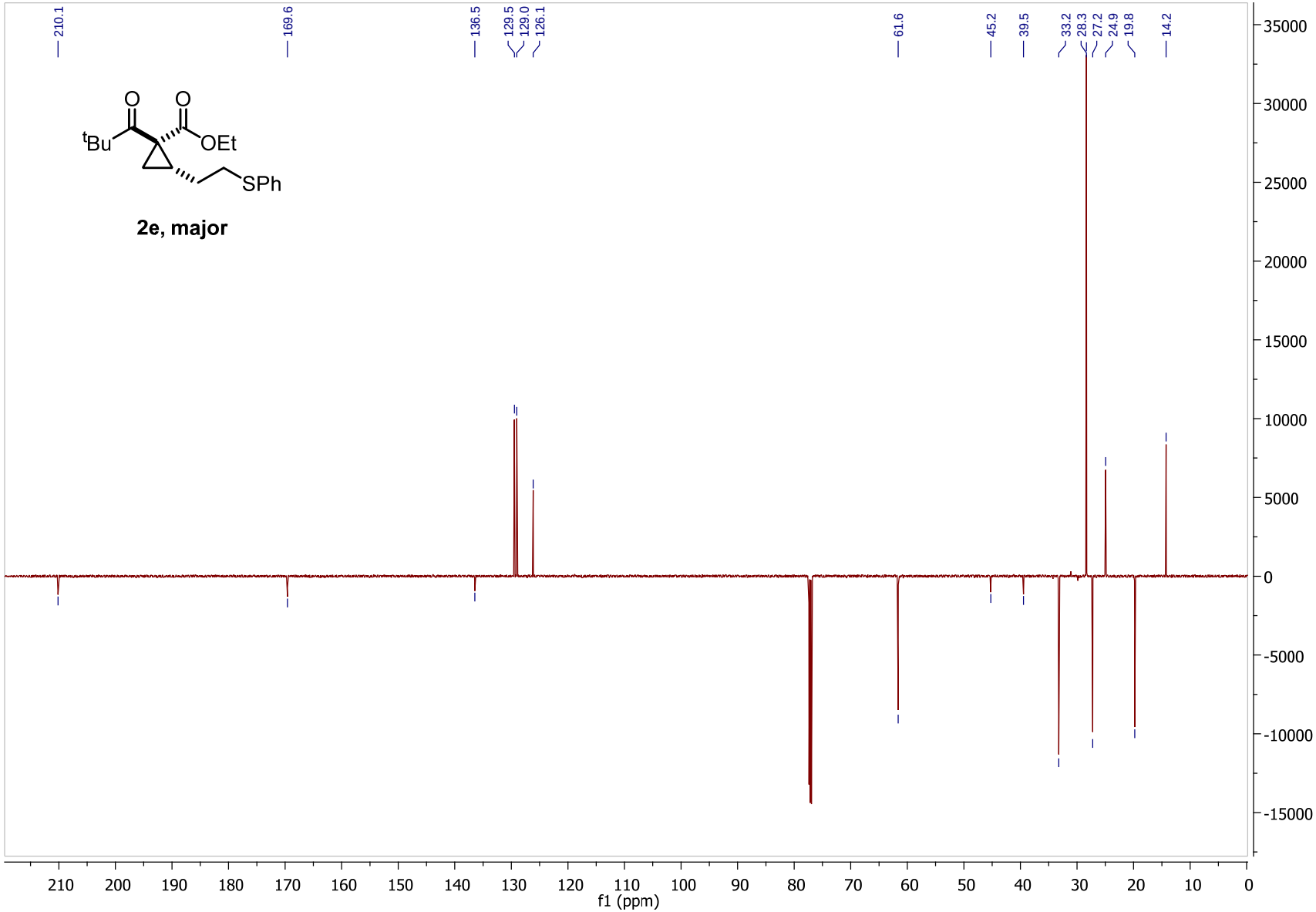

Me
O
O
OEt
SPh
2d, major
K (m)
7.31
J (m)
7.19
I (m)
4.20
H (td)
2.94
G (s)
2.37
F (dt)
2.14
E (m)
1.76
D (dd)
1.57
C (m)
1.47
B (dd)
1.38
A (t)
1.28
4.03
0.96
2.00
1.98
2.94
1.04
1.02
0.94
1.01
1.06
2.97
f1 (ppm)

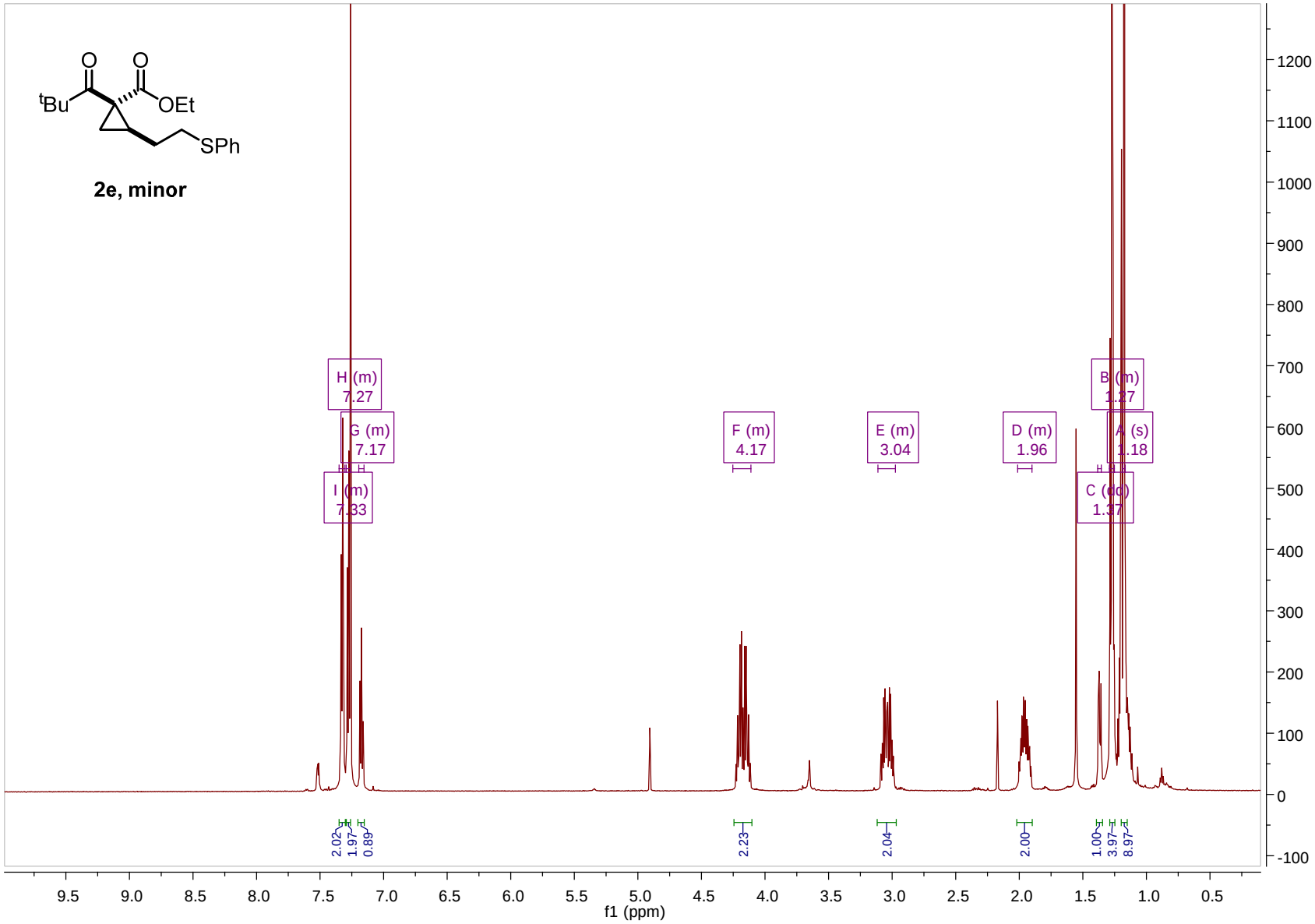

201.8
171.1
136.2
129.5
129.1
126.3
61.6
40.7
33.4
31.0
30.6
29.9
27.3
20.9
14.2
Me
OEt
SPh
2d, major
35000
30000
25000
20000
15000
10000
5000
0
-5000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

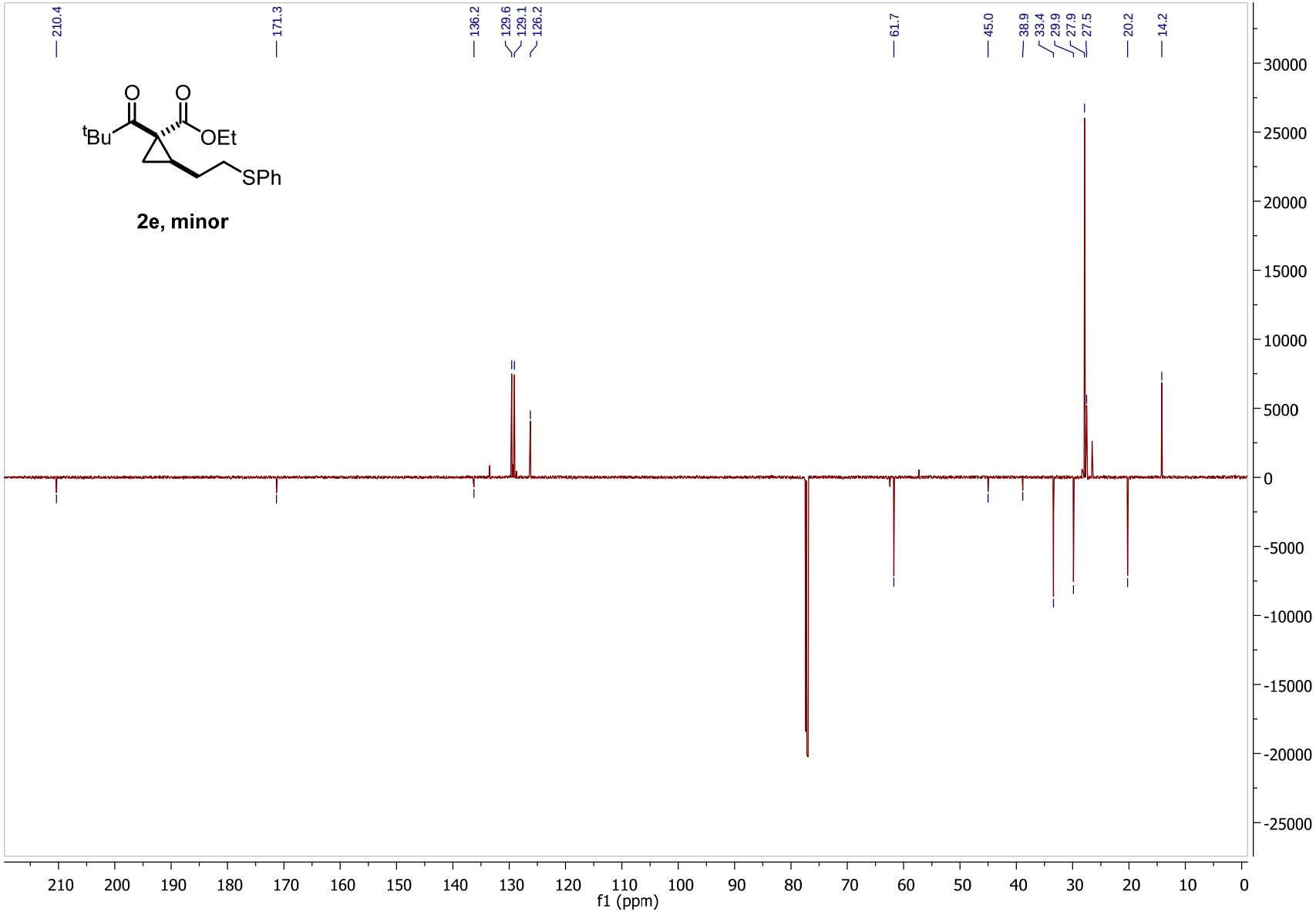

Me
O
O
OEt
SPh
2d, minor
I (m)
7.30
H (t)
7.18
G (q)
4.19
F (t)
2.96
E (s)
2.36
D (m)
2.06
C (ddt)
1.74
B (m)
1.43
A (t)
1.26
3.99
1.07
2.00
1.96
2.95
1.09
2.10
2.11
3.05
f1 (ppm)

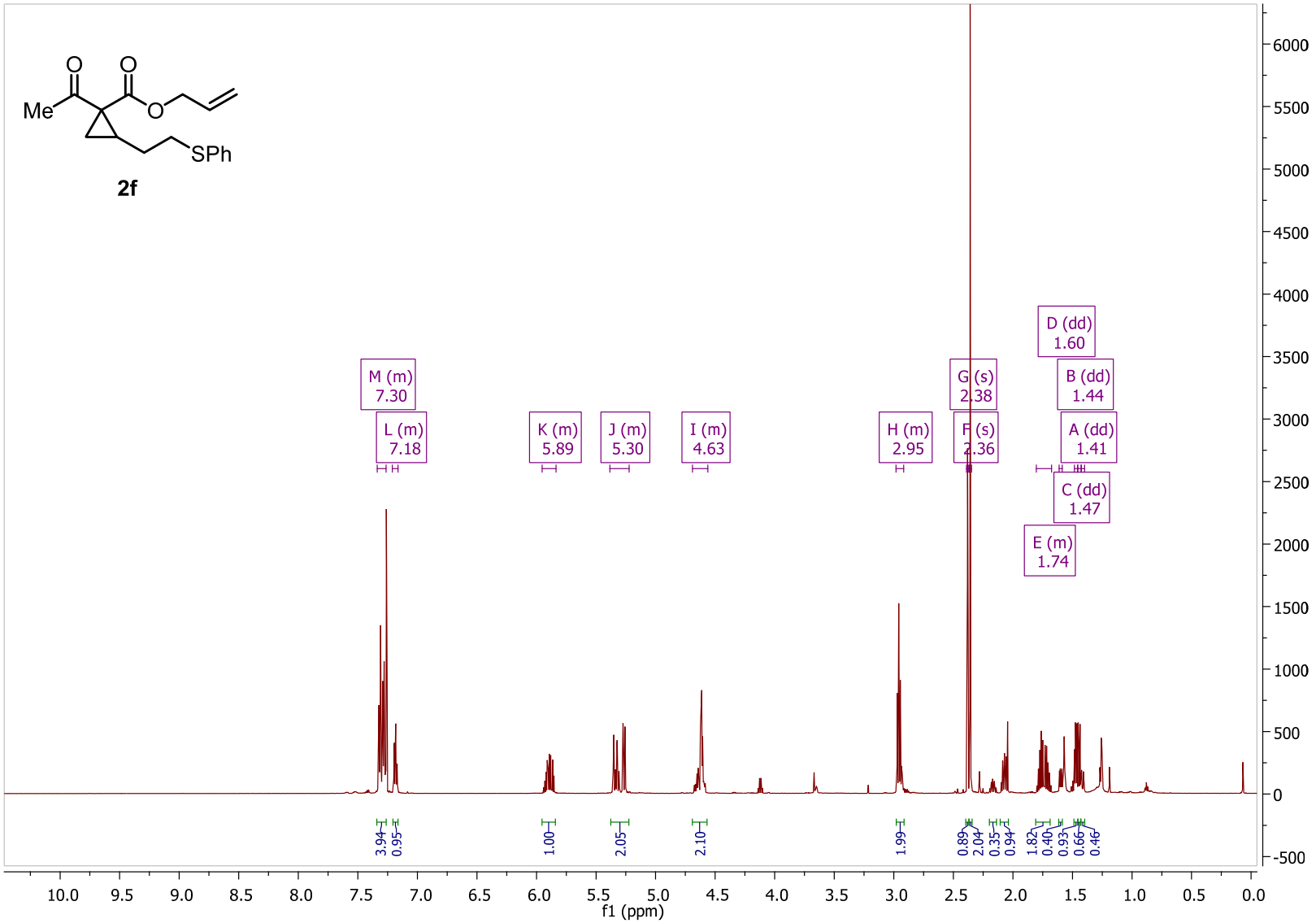

202.7
169.6
136.2
129.6
129.1
126.3
61.6
41.7
33.0
30.2
29.5
28.5
23.5
14.3
Me
OEt
SPh
2d, minor
f1 (ppm)

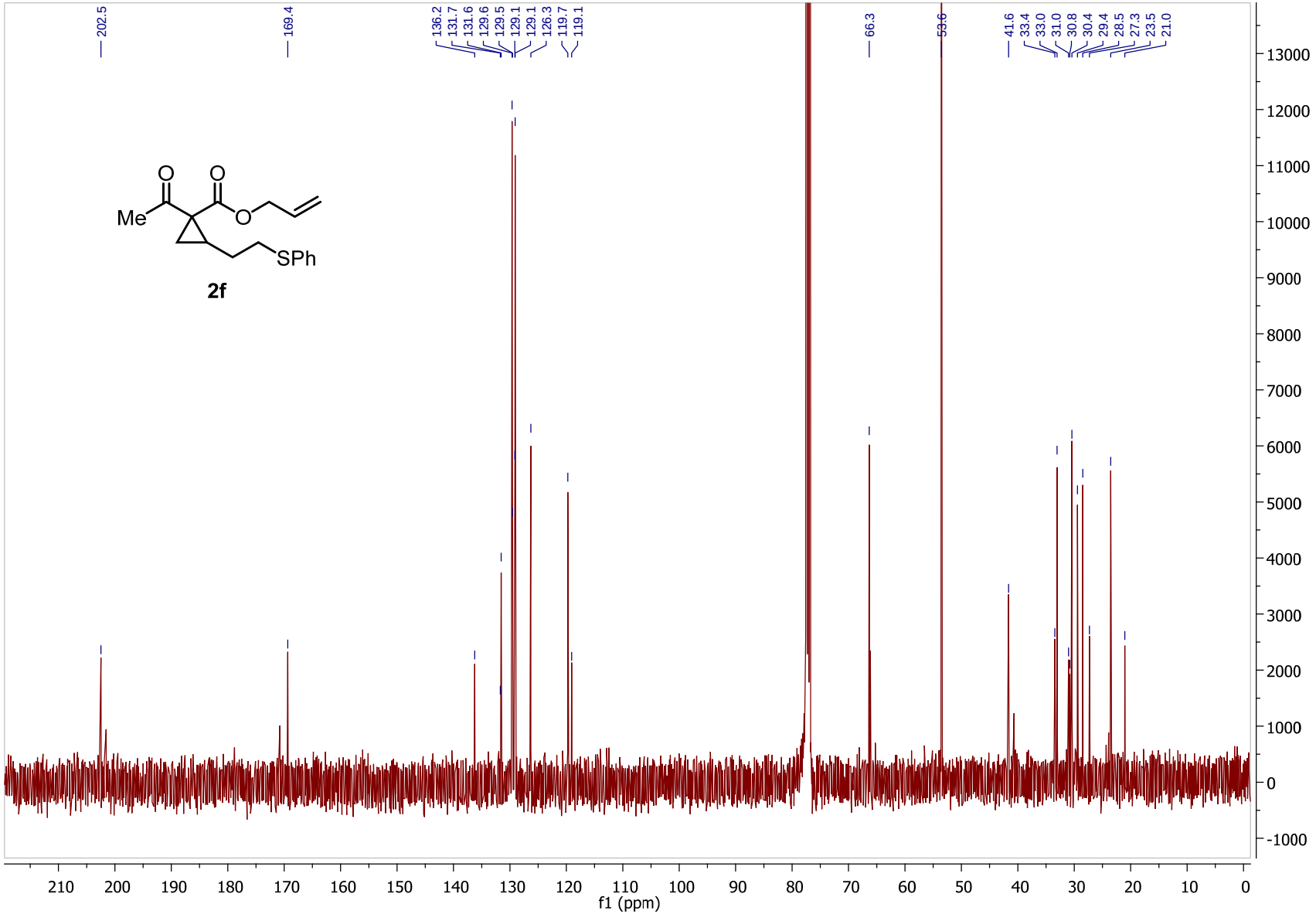

tBu
O
O
OEt
SPh
2e, major
H (m)
4.15
G (m)
2.96
F (p)
1.95
E (m)
1.79
D (dd)
1.42
A (dd)
1.16
C (t)
1.25
f1 (ppm)

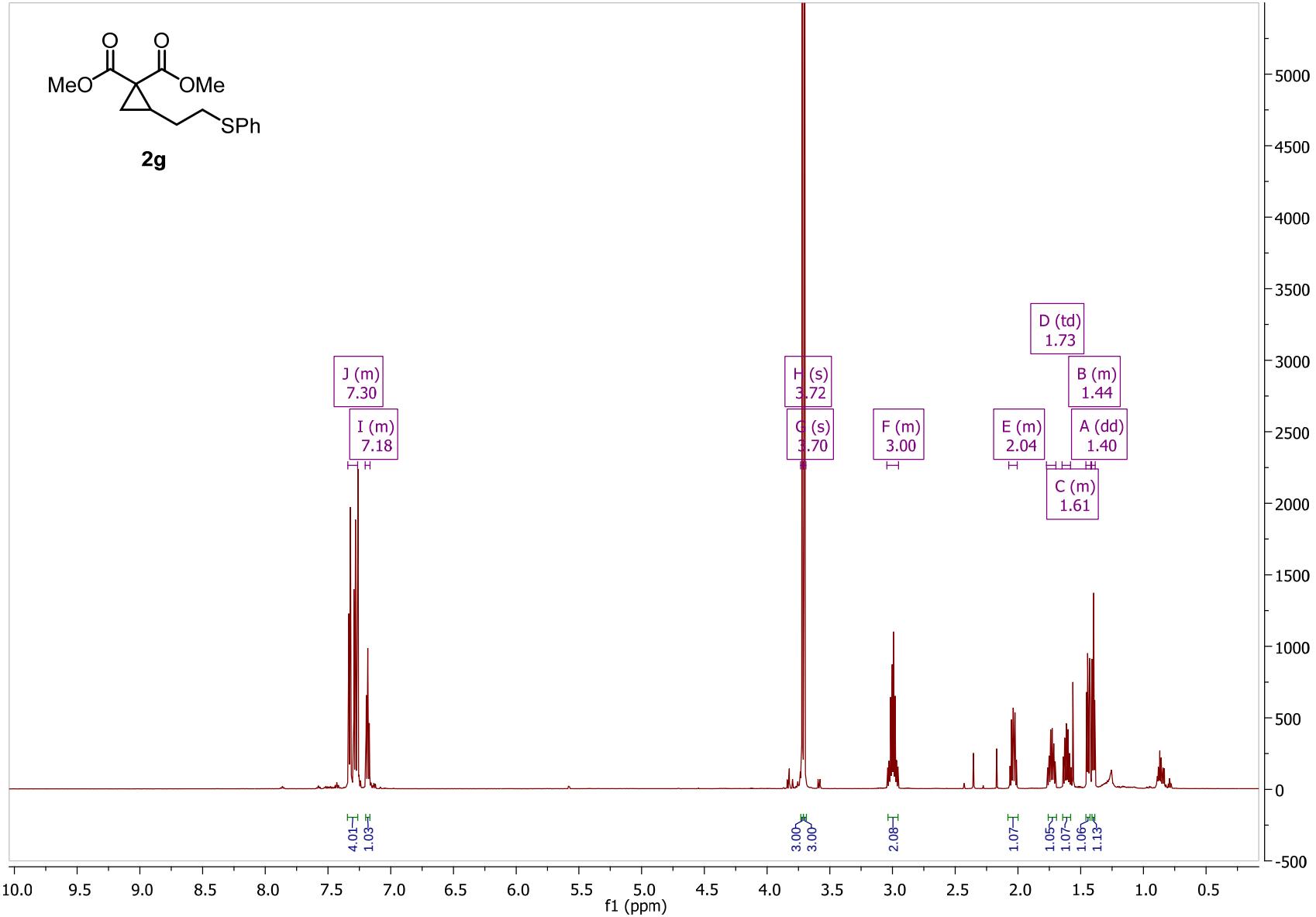

210.1
169.6
136.5
129.5
129.0
126.1
61.6
45.2
39.5
33.2
28.3
27.2
24.9
19.8
14.2
tBu
OEt
SPh
2e, major
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

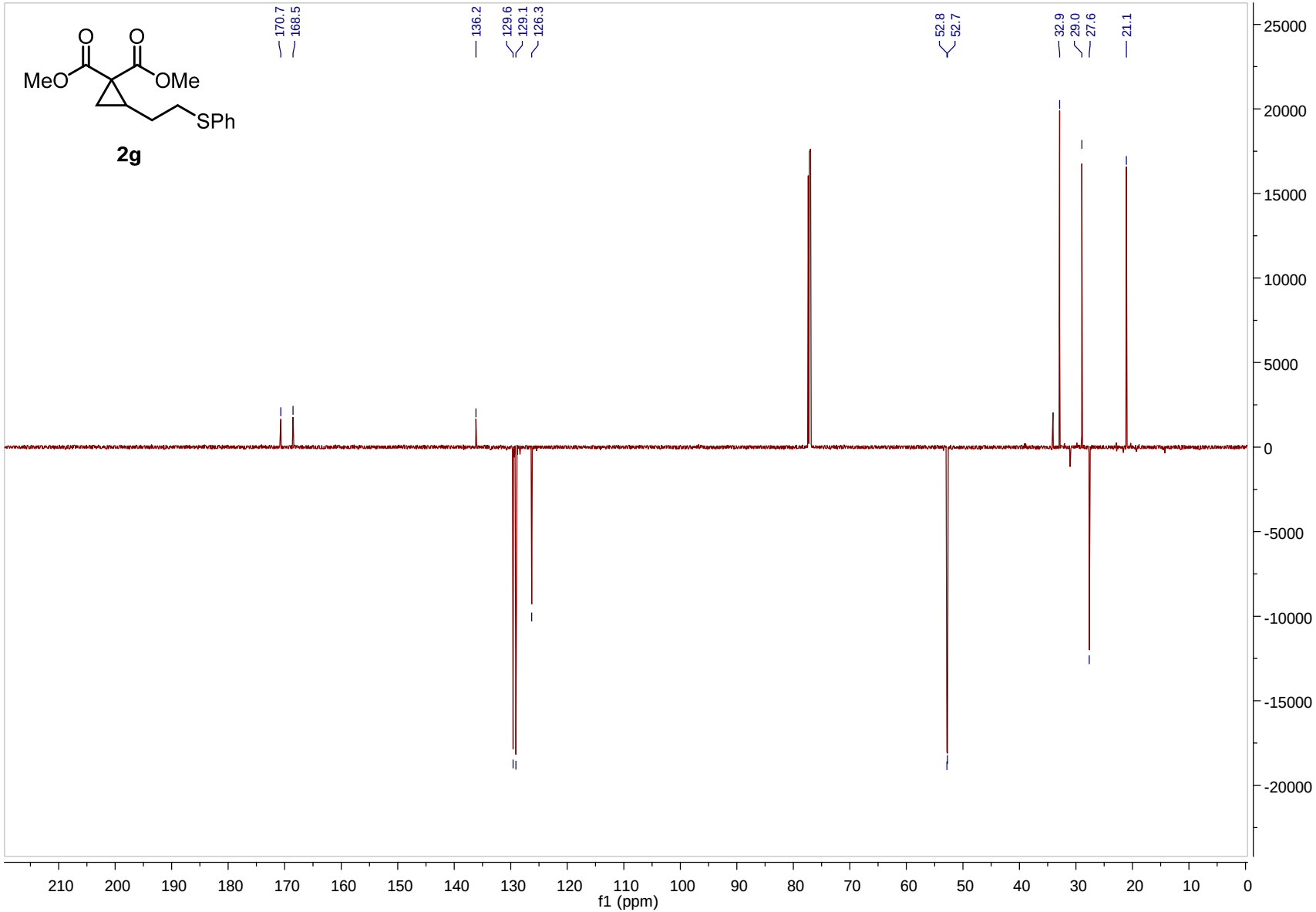

tBu
O
O
OEt
SPh
2e, minor
H (m)
7.27
G (m)
7.17
I (m)
7.33
F (m)
4.17
E (m)
3.04
D (m)
1.96
B (m)
1.27
A (s)
1.18
C (dd)
1.37
2.02
1.97
0.89
2.23
2.04
2.00
1.00
3.97
8.97
f1 (ppm)

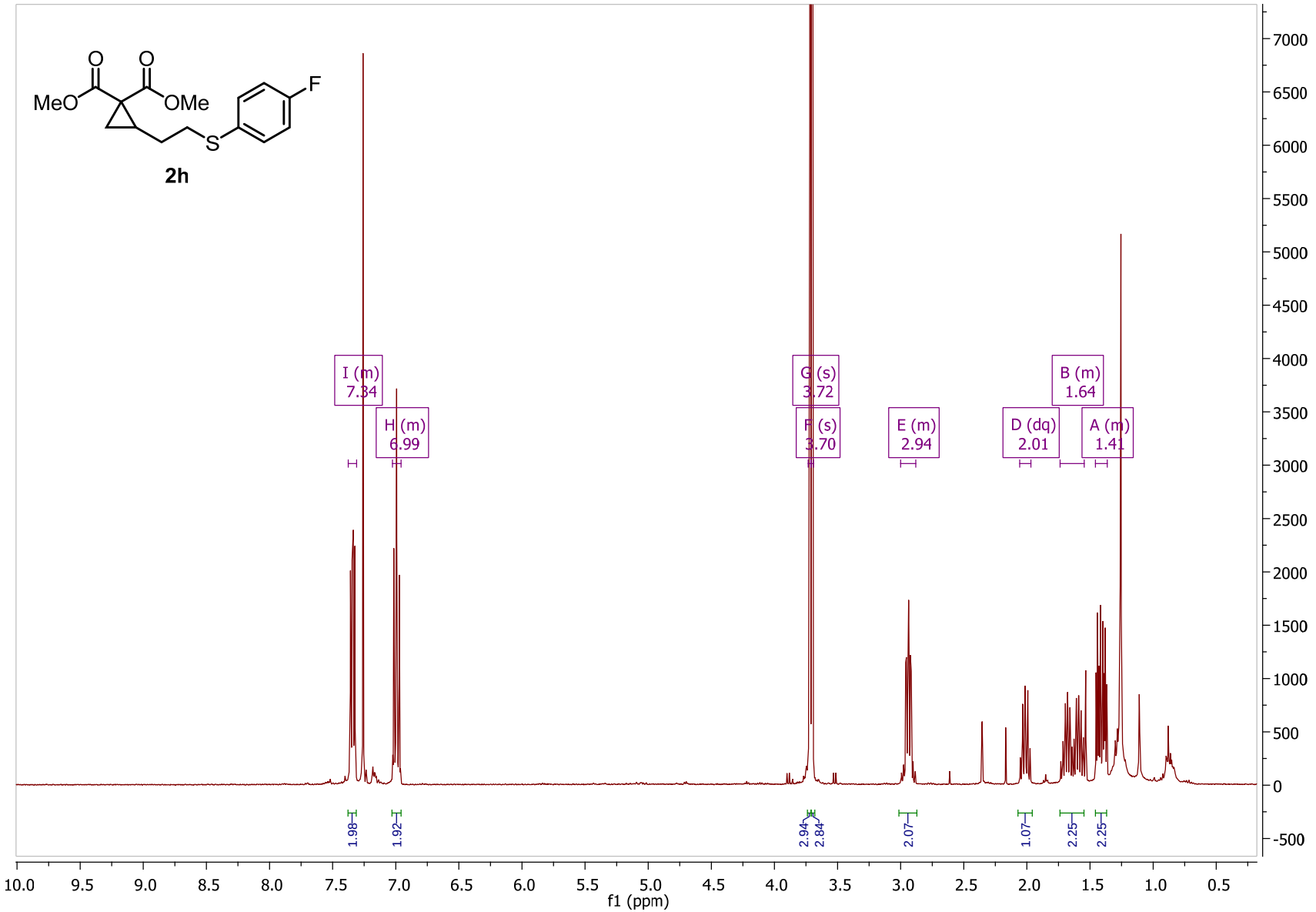

210.4
171.3
136.2
129.6
129.1
126.2
61.7
45.0
38.9
33.4
29.9
27.9
27.5
20.2
14.2
tBu
O
O
OEt
SPh
2e, minor
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

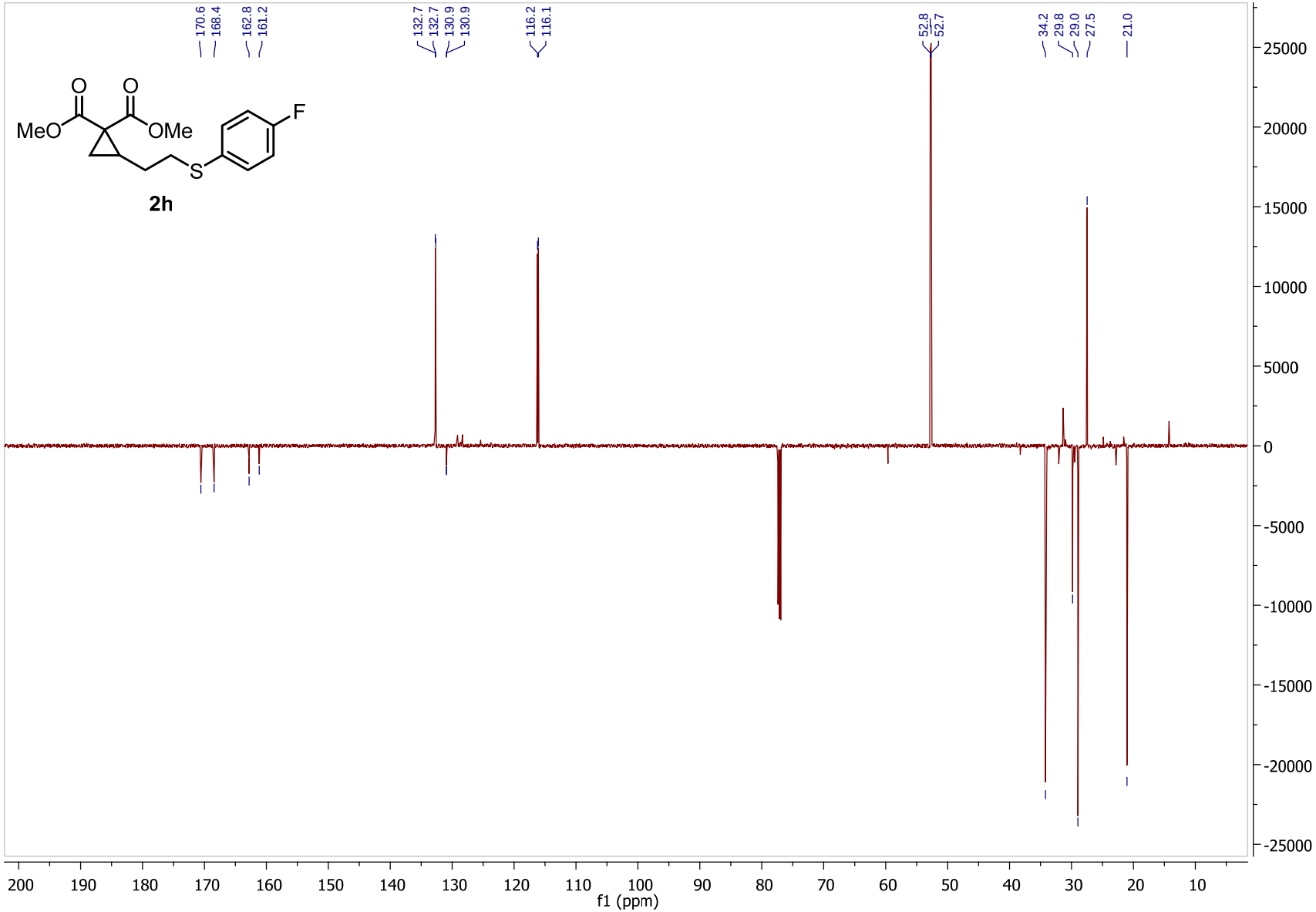

Me
SPh
2f
M (m)
7.30
L (m)
7.18
K (m)
5.89
J (m)
5.30
I (m)
4.63
H (m)
2.95
G (s)
2.38
F (s)
2.36
D (dd)
1.60
B (dd)
1.44
A (dd)
1.41
C (dd)
1.47
E (m)
1.74
3.94
0.95
1.00
2.05
2.10
1.99
0.89
2.04
0.35
0.94
1.82
0.40
0.93
0.66
0.46
f1 (ppm)

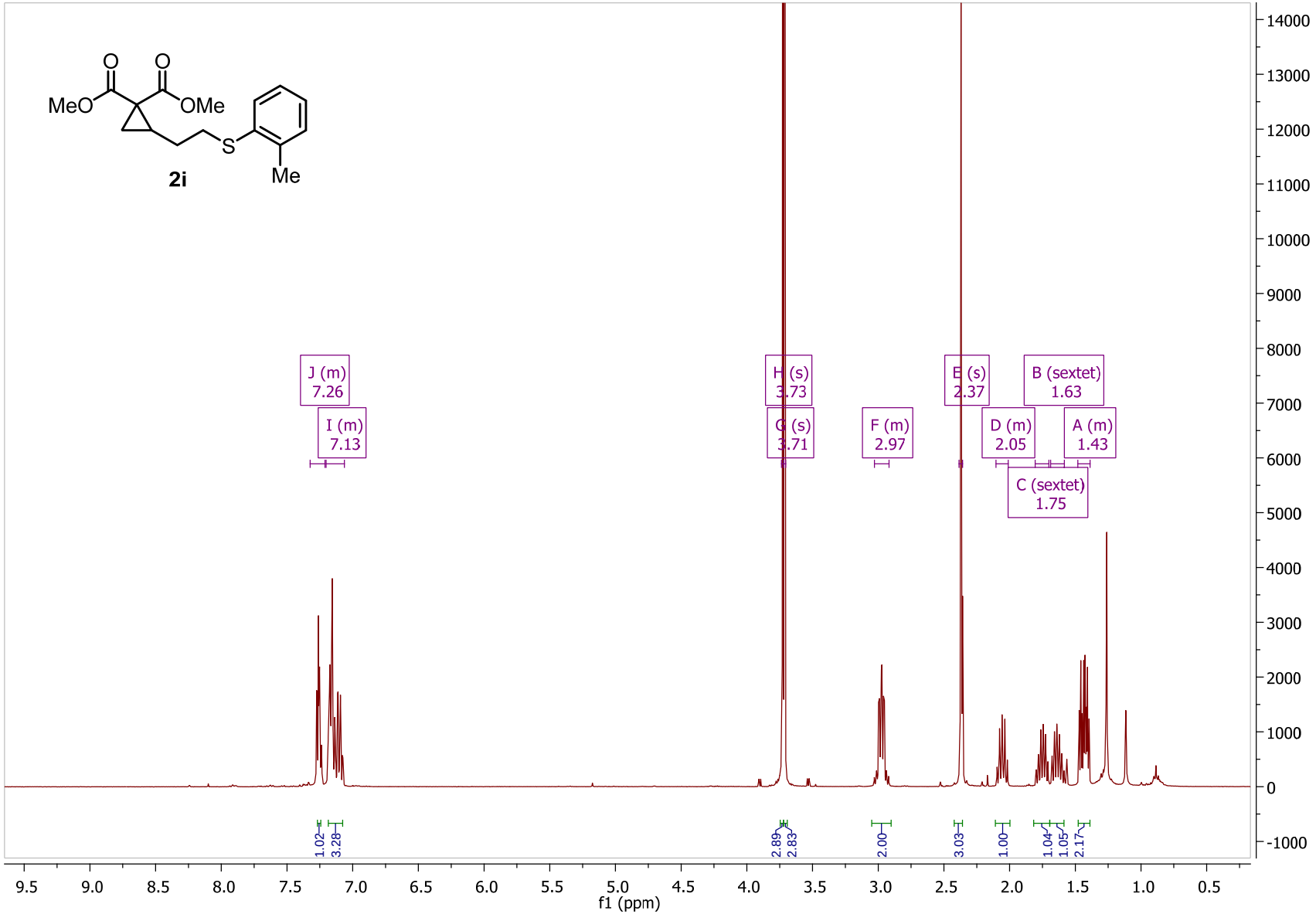

202.5
169.4
136.2
131.7
131.6
129.6
129.5
129.1
129.1
126.3
119.7
119.1
66.3
53.6
41.6
33.4
33.0
31.0
30.8
30.4
29.4
28.5
27.3
23.5
21.0
Me
O
O
O
SPh
2f
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

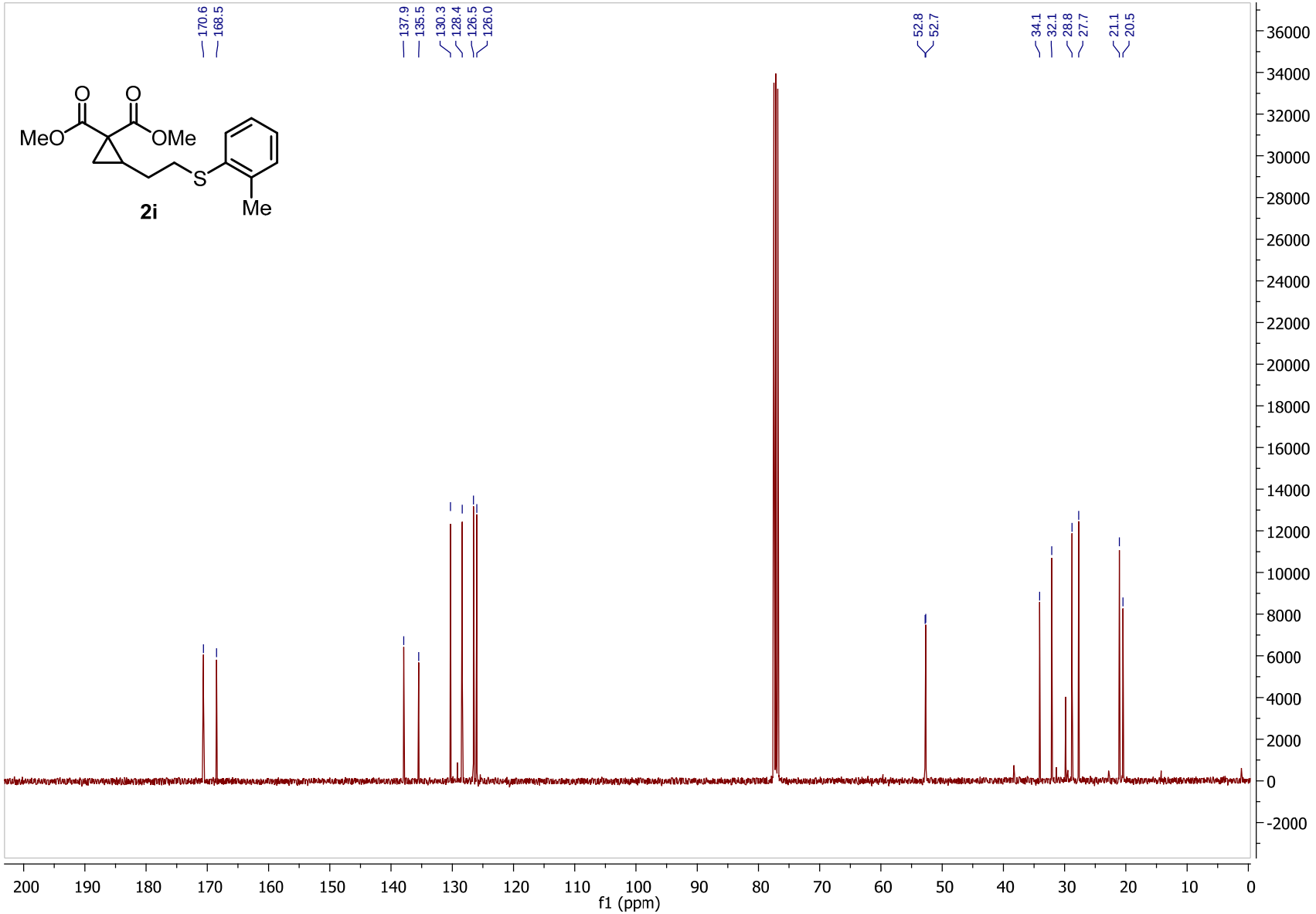

MeO
OMe
SPh
2g
J (m)
7.30
I (m)
7.18
H (s)
3.72
G (s)
3.70
F (m)
3.00
D (td)
1.73
B (m)
1.44
E (m)
2.04
A (dd)
1.40
C (m)
1.61
4.01
1.03
3.00
3.00
2.08
1.07
1.05
1.07
1.06
1.13
f1 (ppm)

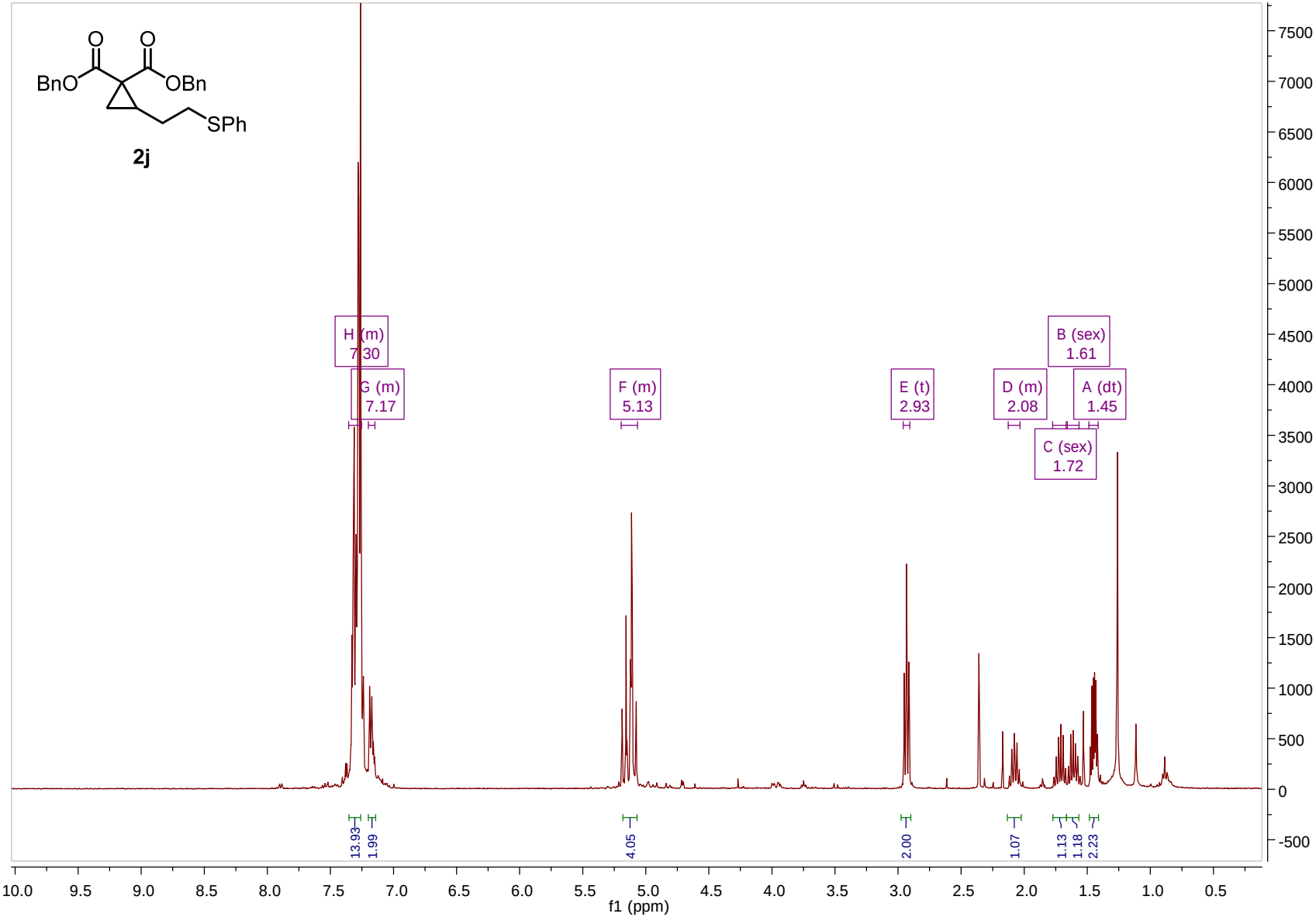

MeO
OMe
SPh
2g
170.7
168.5
136.2
129.6
129.1
126.3
52.8
52.7
32.9
29.0
27.6
21.1
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

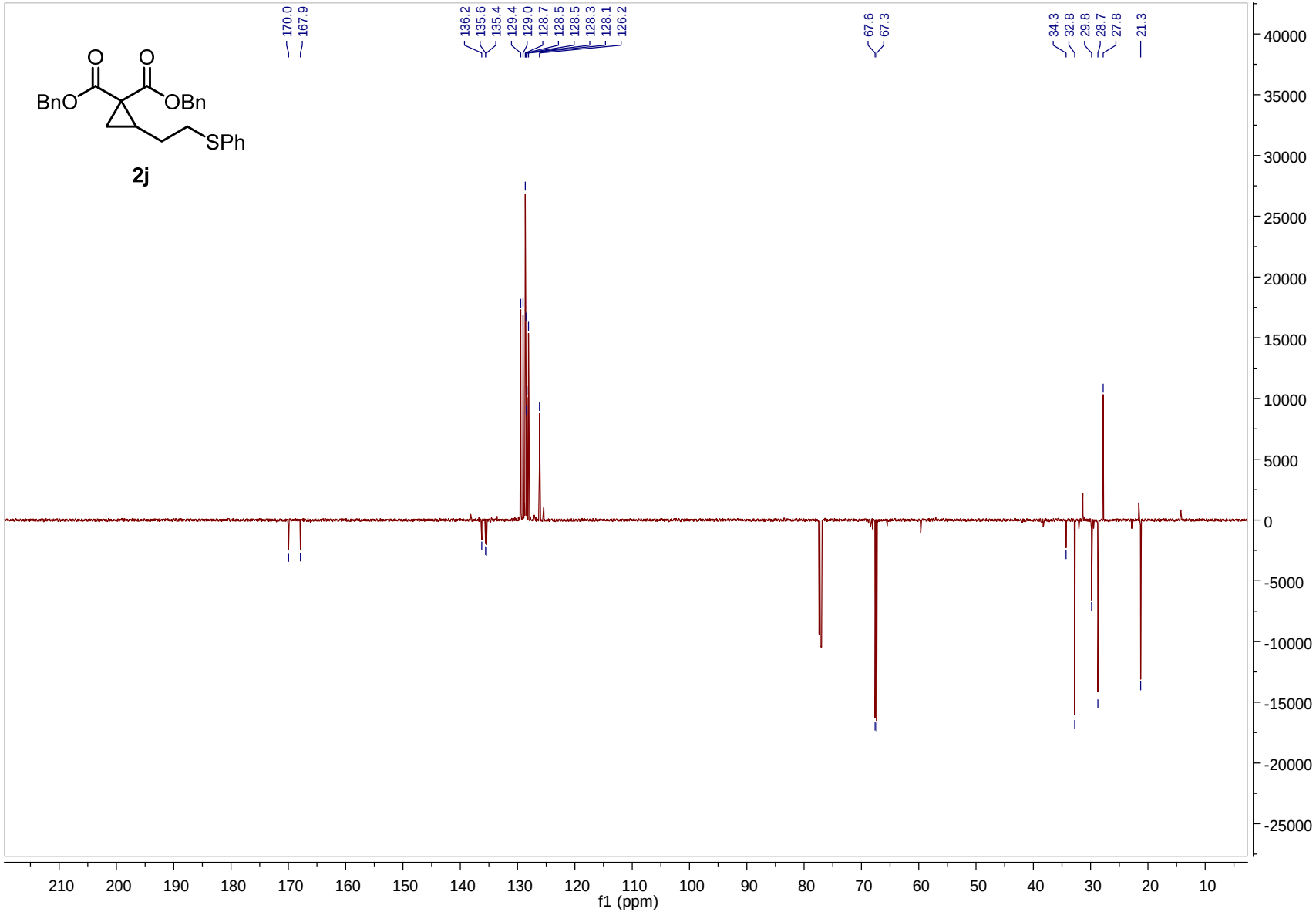

MeO
O
O
OMe
S
F
2h
I (m)
7.34
H (m)
6.99
G (s)
3.72
F (s)
3.70
E (m)
2.94
D (dq)
2.01
B (m)
1.64
A (m)
1.41
1.98
1.92
2.94
2.84
2.07
1.07
2.25
2.25
f1 (ppm)

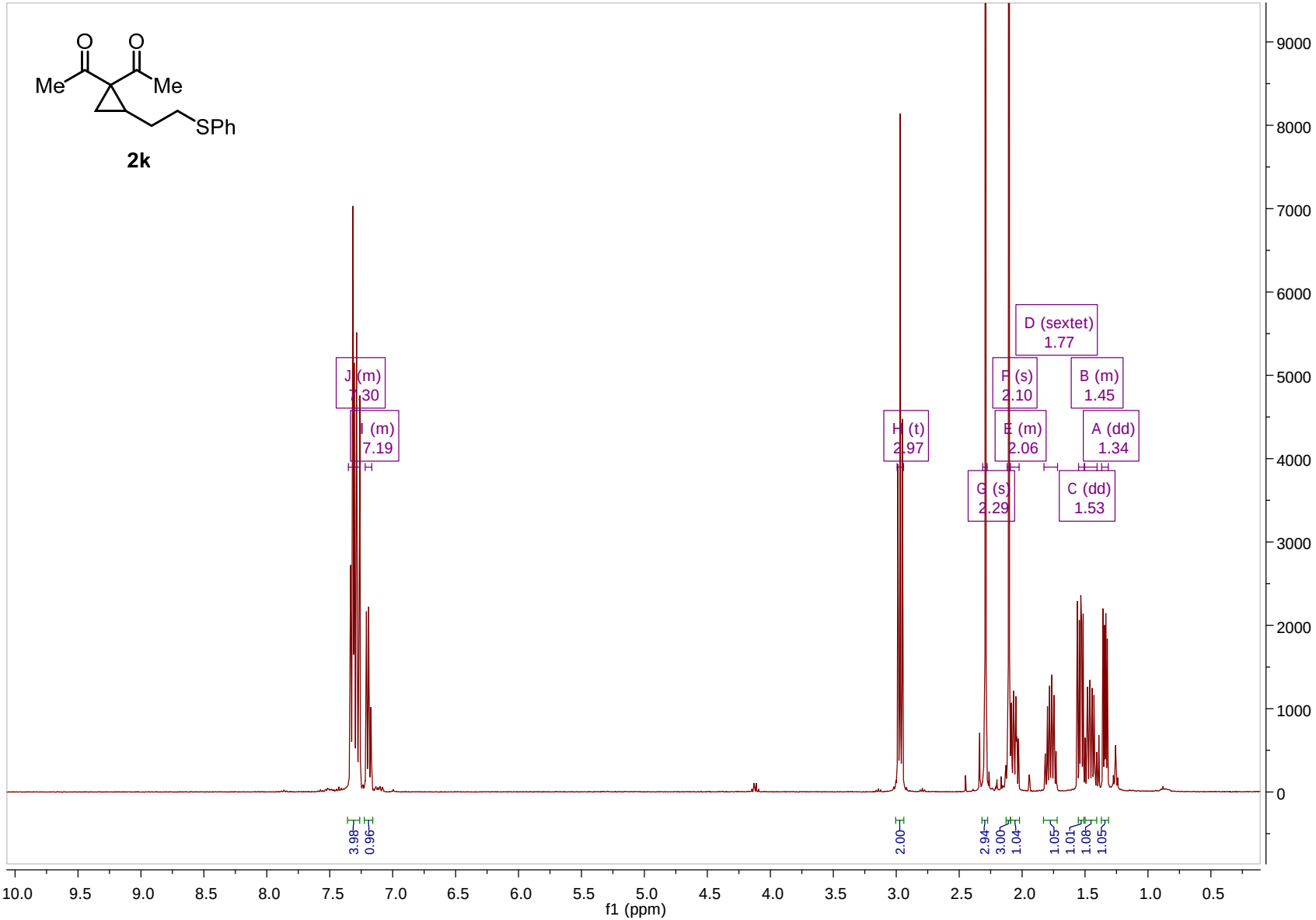

170.6
168.4
162.8
161.2
132.7
132.7
130.9
130.9
116.2
116.1
52.8
52.7
34.2
29.8
29.0
27.5
21.0
MeO
OMe
O
O
S
F
2h
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

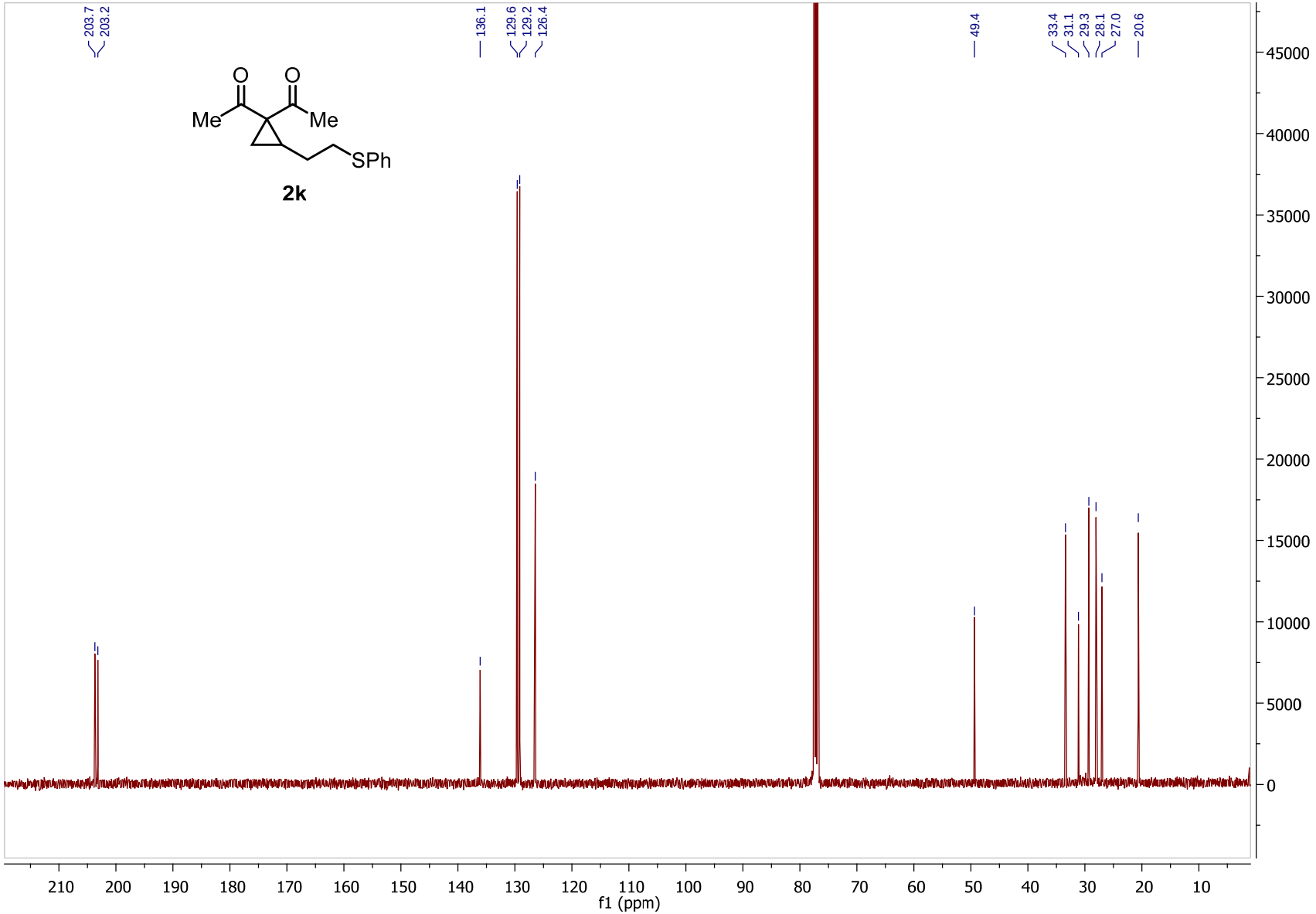

MeO
OMe
O
O
S
Me
2i
J (m)
7.26
I (m)
7.13
H (s)
3.73
G (s)
3.71
F (m)
2.97
E (s)
2.37
B (sextet)
1.63
D (m)
2.05
A (m)
1.43
C (sextet)
1.75
1.02
3.28
2.89
2.83
2.00
3.03
1.00
1.04
1.05
2.17
f1 (ppm)

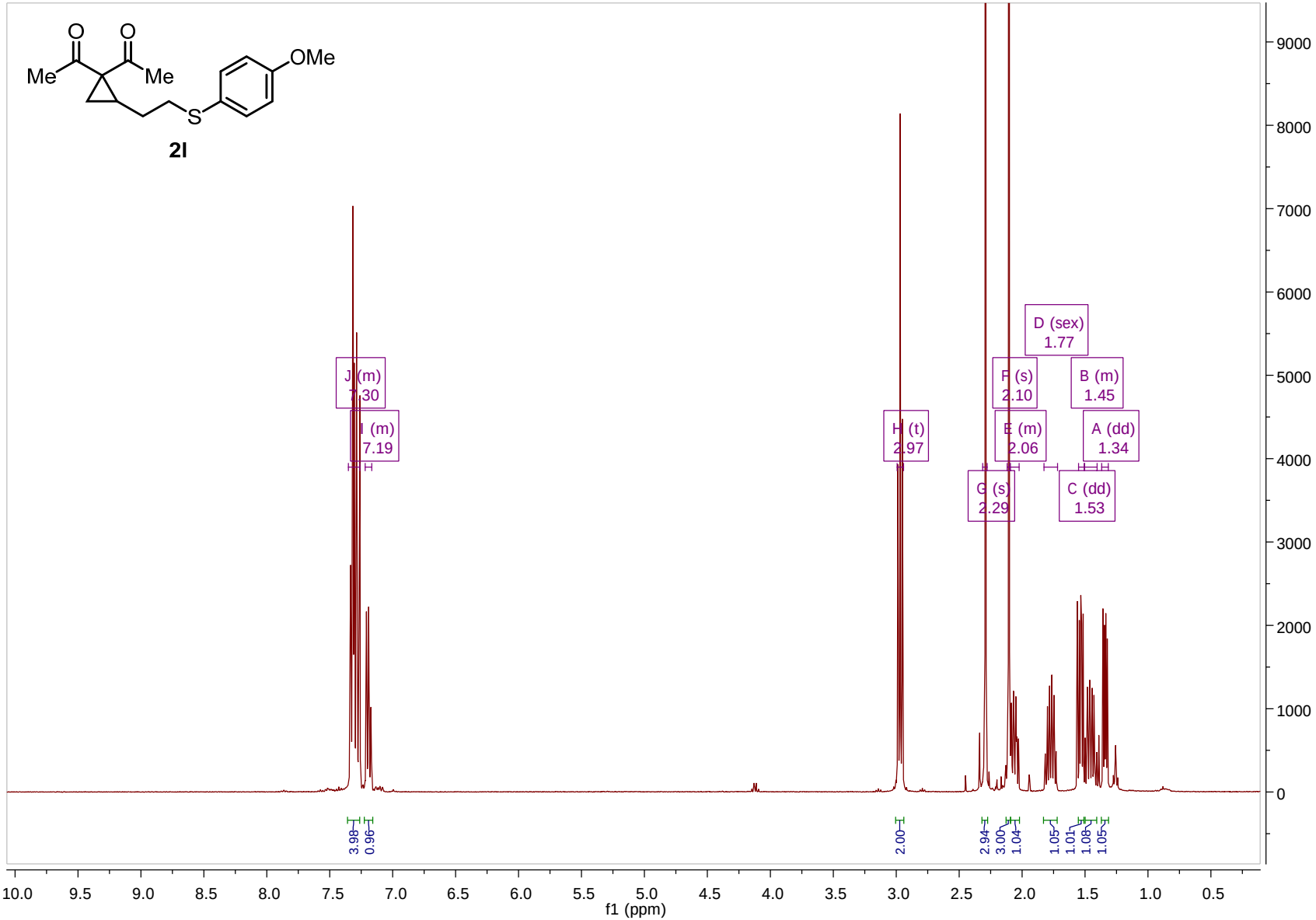

170.6
168.5
137.9
135.5
130.3
128.4
126.5
126.0
52.8
52.7
34.1
32.1
28.8
27.7
21.1
20.5
MeO
OMe
S
Me
2i
f1 (ppm)

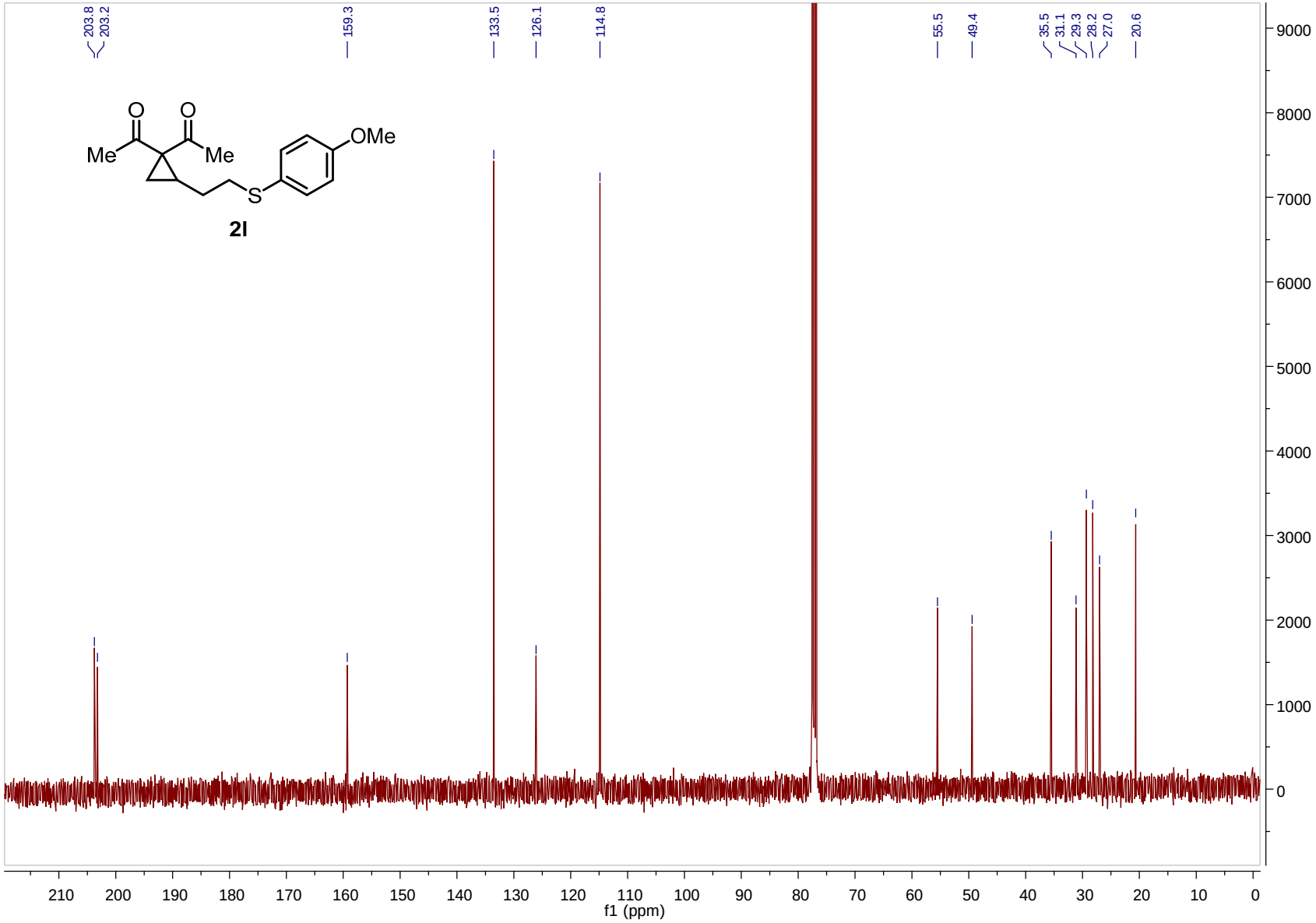

BnO
OBn
SPh
2j
H (m)
7.30
G (m)
7.17
F (m)
5.13
E (t)
2.93
D (m)
2.08
B (sex)
1.61
A (dt)
1.45
C (sex)
1.72
13.93
1.99
4.05
2.00
1.07
1.13
1.18
2.23
f1 (ppm)

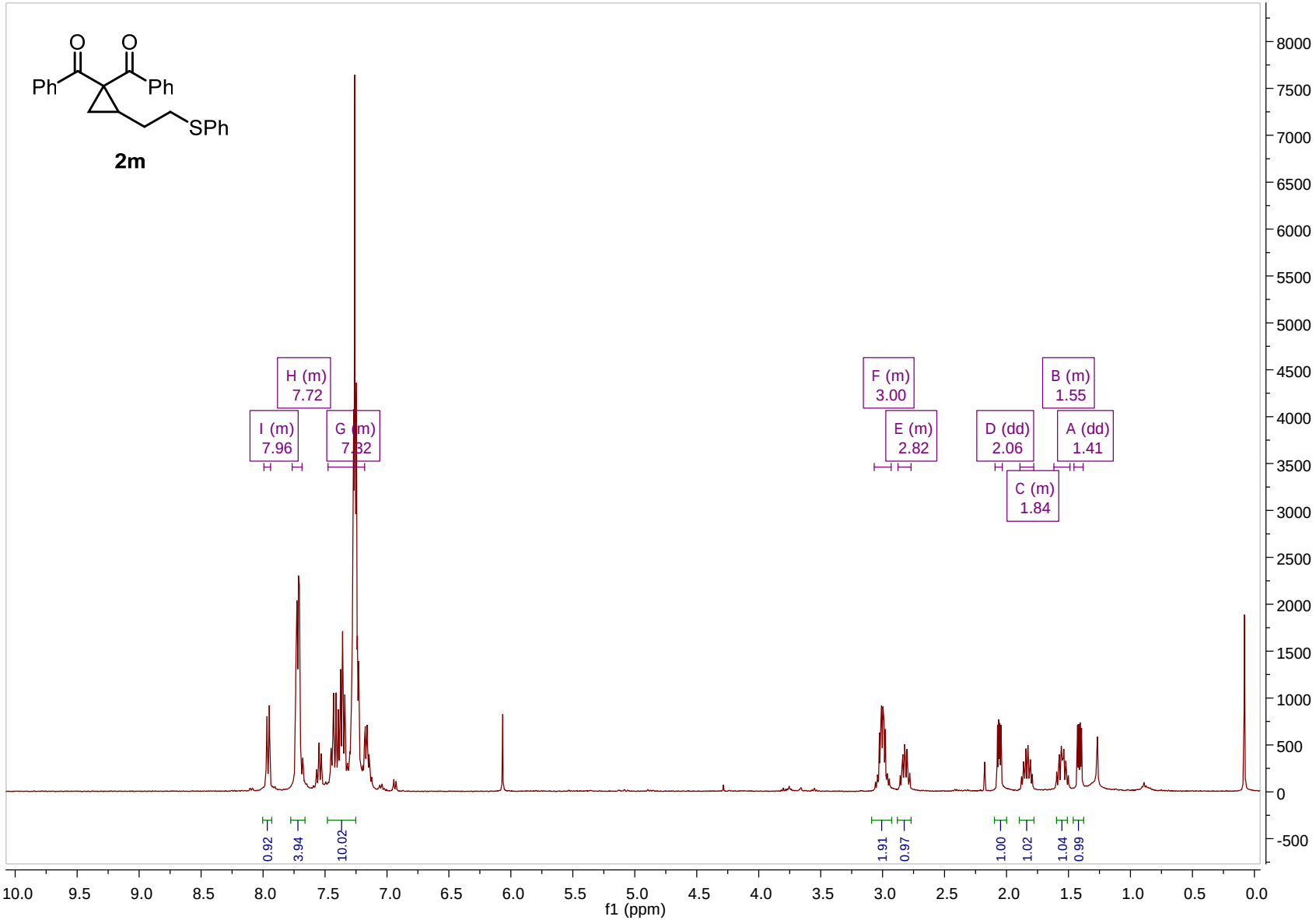

170.0
167.9
136.2
135.6
135.4
129.4
129.0
128.7
128.5
128.3
128.1
126.2
67.6
67.3
34.3
32.8
29.8
28.7
27.8
21.3
BnO
OBn
SPh
2j
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
-15000
-20000
-25000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

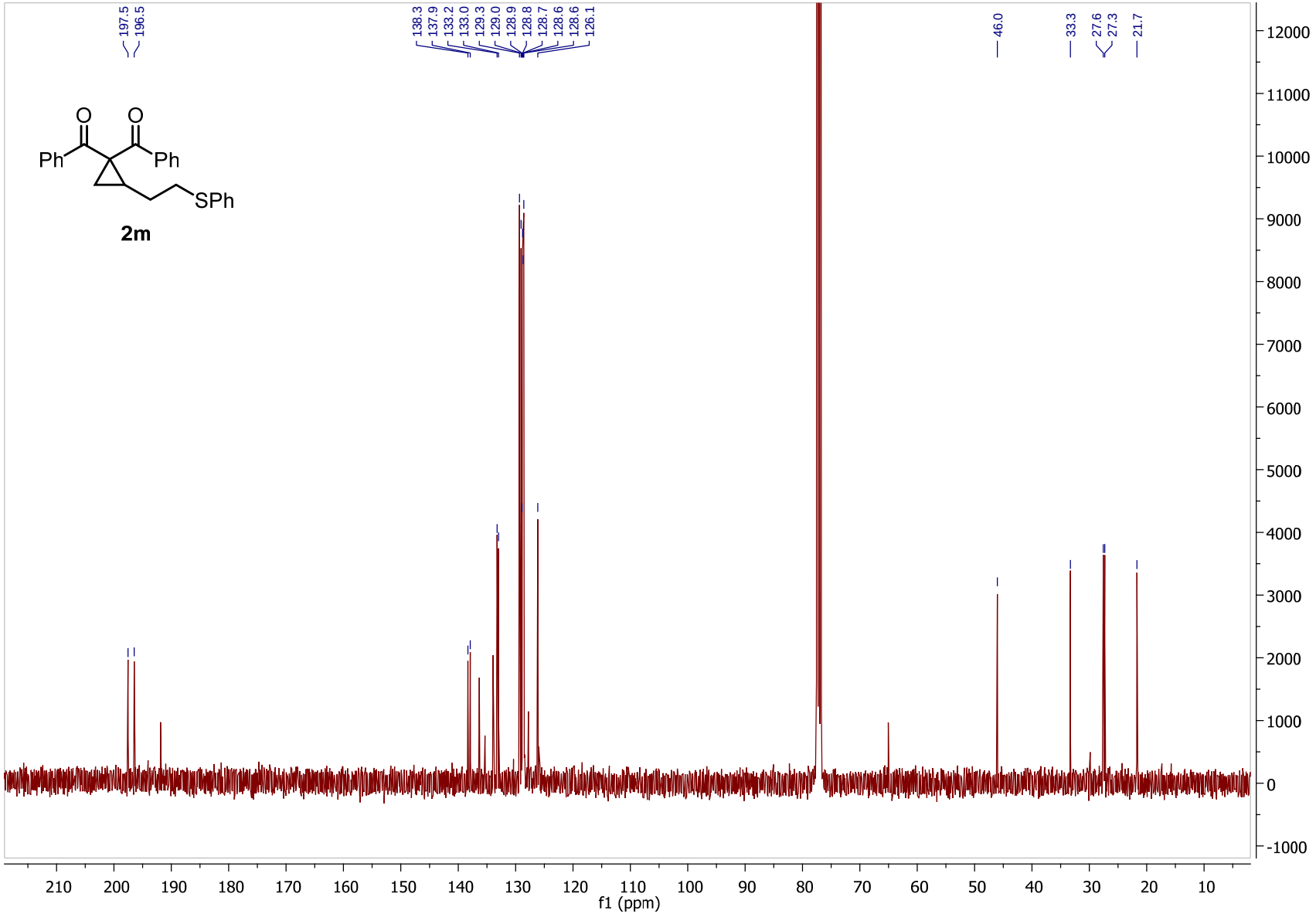

Me
Me
SPh
2k
J (m)
7.30
I (m)
7.19
H (t)
2.97
D (sextet)
1.77
F (s)
2.10
B (m)
1.45
E (m)
2.06
A (dd)
1.34
G (s)
2.29
C (dd)
1.53
3.98
0.96
2.00
2.94
3.00
1.04
1.05
1.01
1.08
1.05
f1 (ppm)

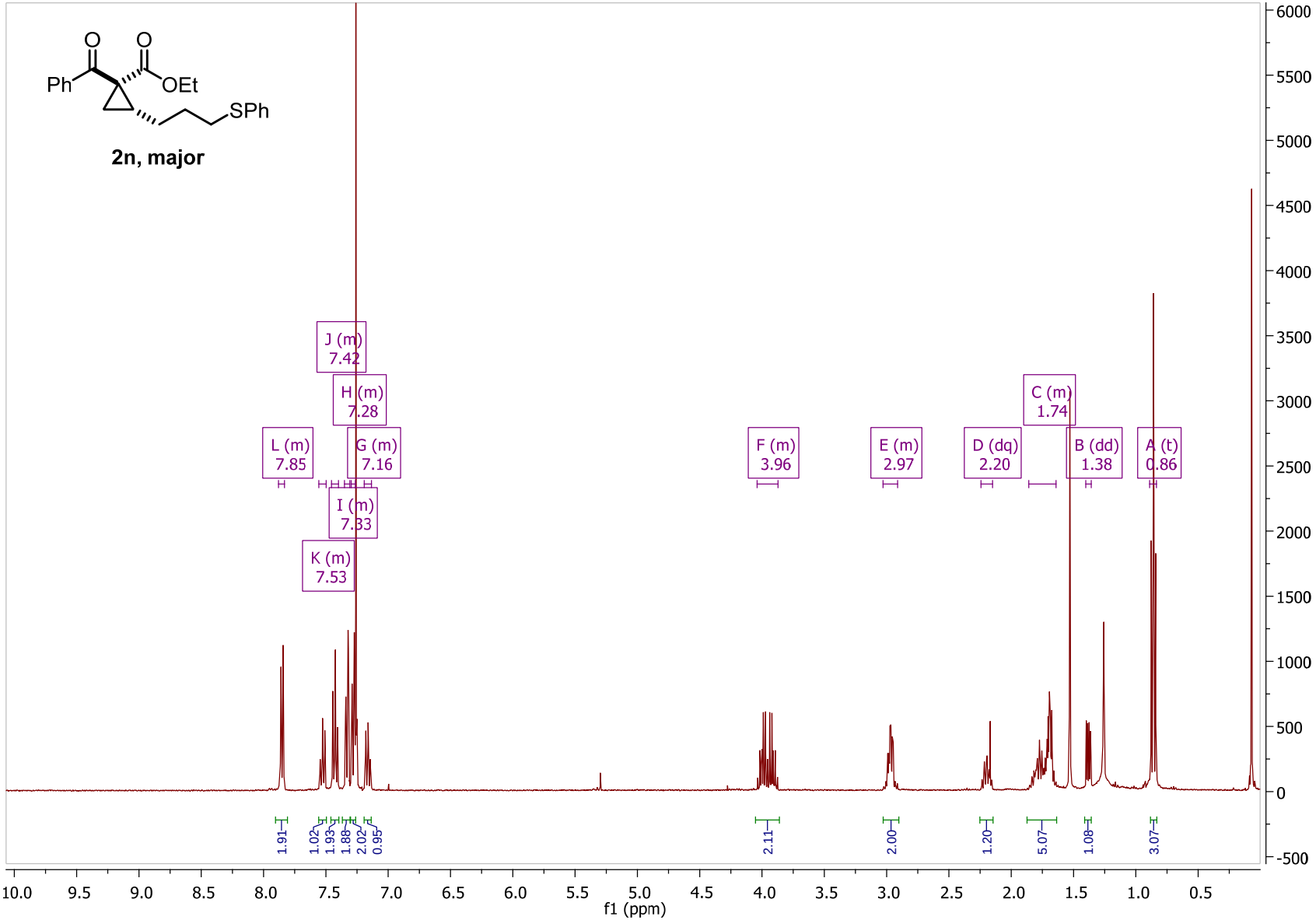

203.7
203.2
136.1
129.6
129.2
126.4
49.4
33.4
31.1
29.3
28.1
27.0
20.6
O
O
Me
Me
SPh
2k
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

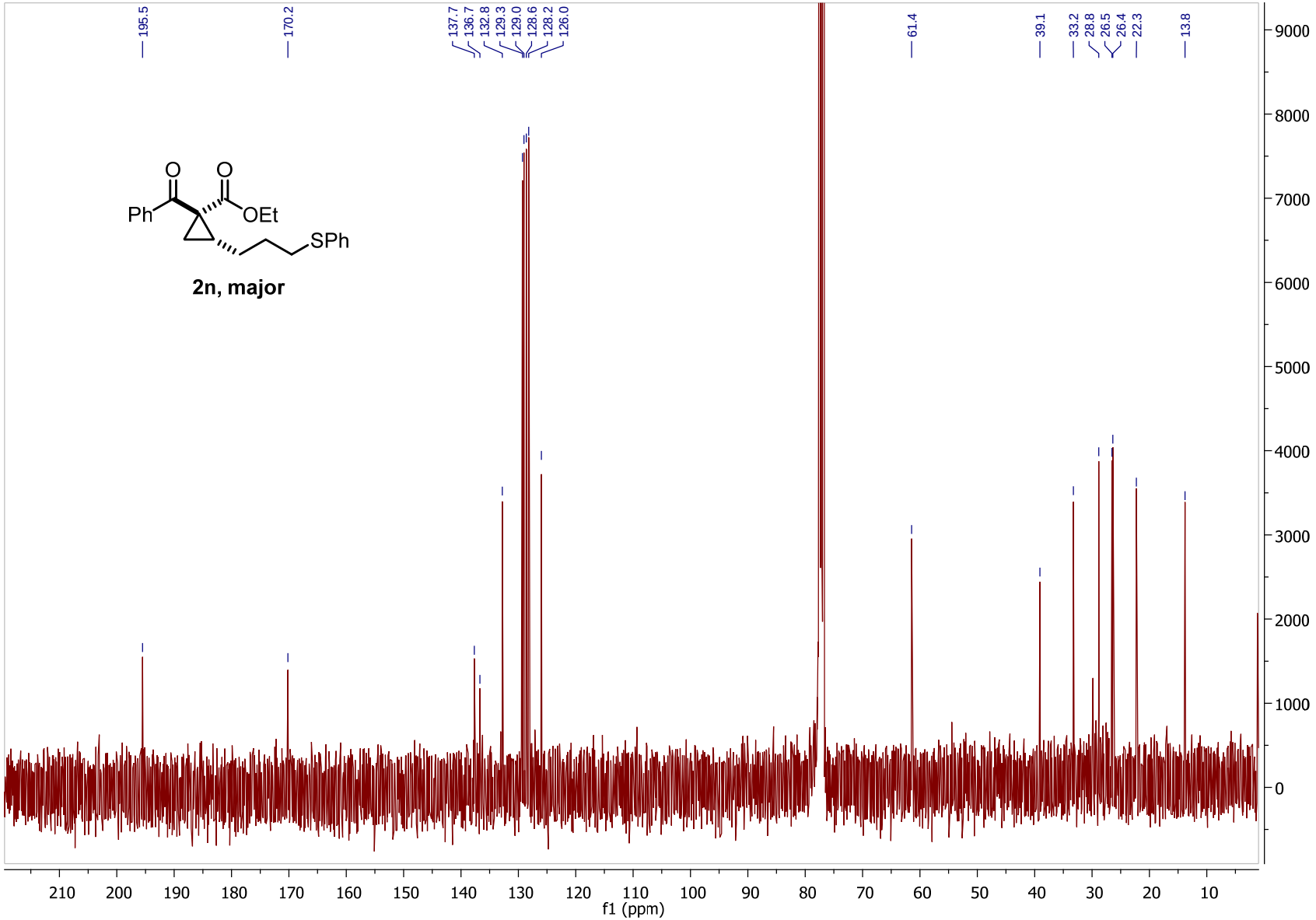

Me
O
O
Me
S
OMe
2l
J (m)
7.30
I (m)
7.19
H (t)
2.97
D (sex)
1.77
F (s)
2.10
B (m)
1.45
E (m)
2.06
A (dd)
1.34
G (s)
2.29
C (dd)
1.53
3.98
0.96
2.00
2.94
3.00
1.04
1.05
1.01
1.08
1.05
f1 (ppm)

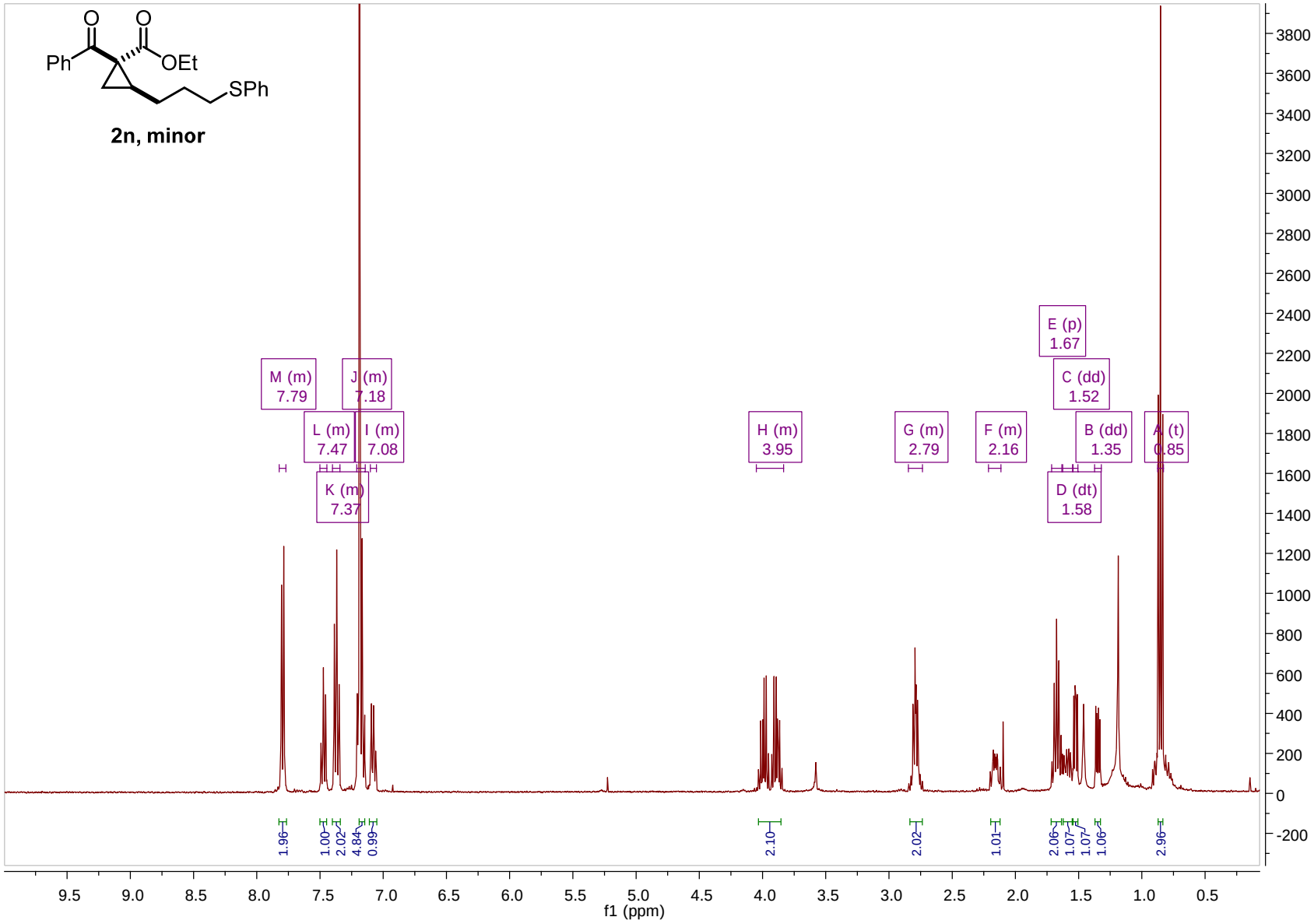

203.8
203.2
159.3
133.5
126.1
114.8
55.5
49.4
35.5
31.1
29.3
28.2
27.0
20.6
O
O
Me
Me
S
OMe
2l
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

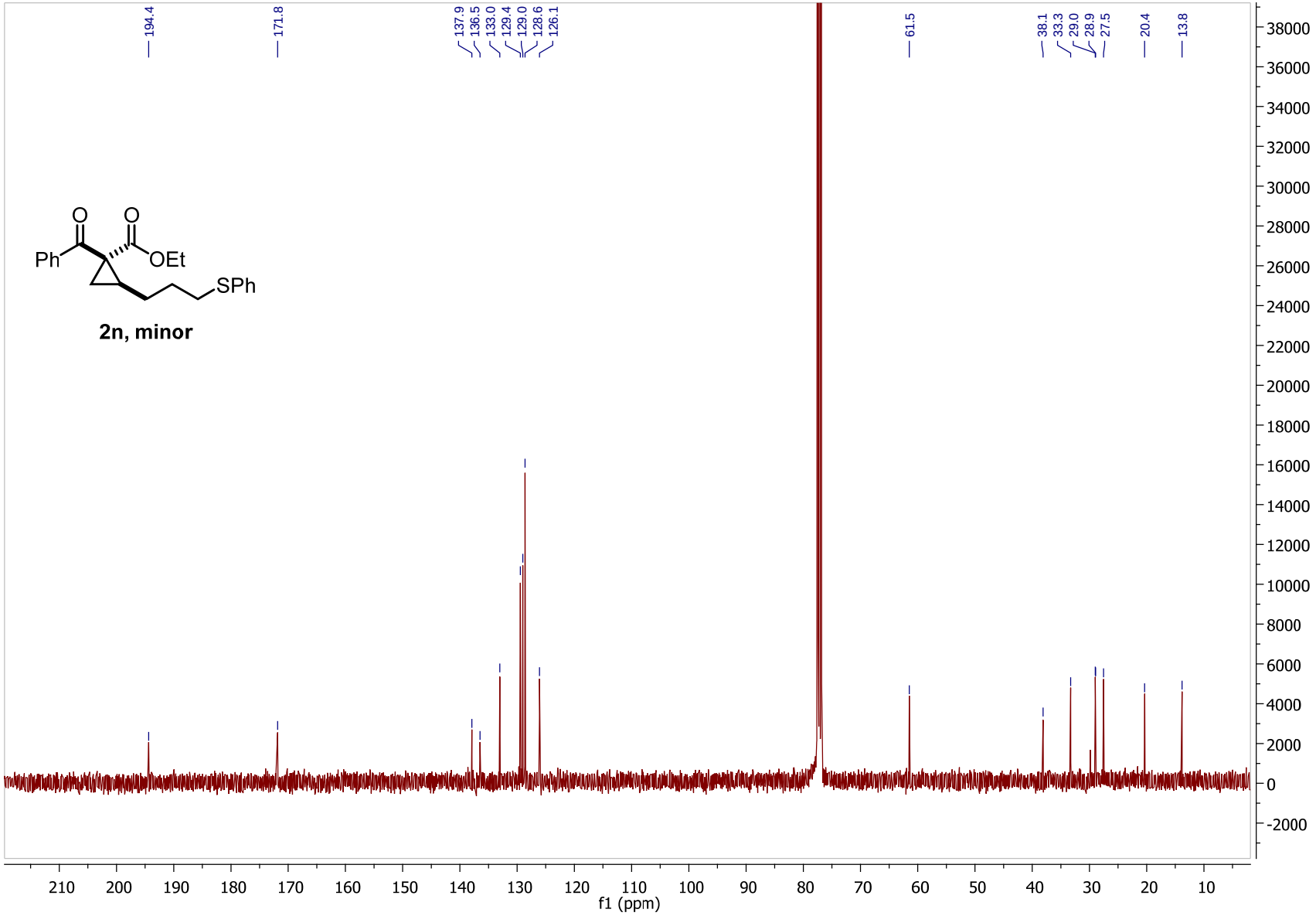

O
O
Ph
Ph
SPh
2m
H (m)
7.72
I (m)
7.96
G (m)
7.32
F (m)
3.00
E (m)
2.82
B (m)
1.55
D (dd)
2.06
A (dd)
1.41
C (m)
1.84
0.92
3.94
10.02
1.91
0.97
1.00
1.02
1.04
0.99
f1 (ppm)


197.5
196.5
138.3
137.9
133.2
133.0
129.3
129.0
128.9
128.8
128.7
128.6
128.6
126.1
46.0
33.3
27.6
27.3
21.7
O
O
Ph
Ph
SPh
2m
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

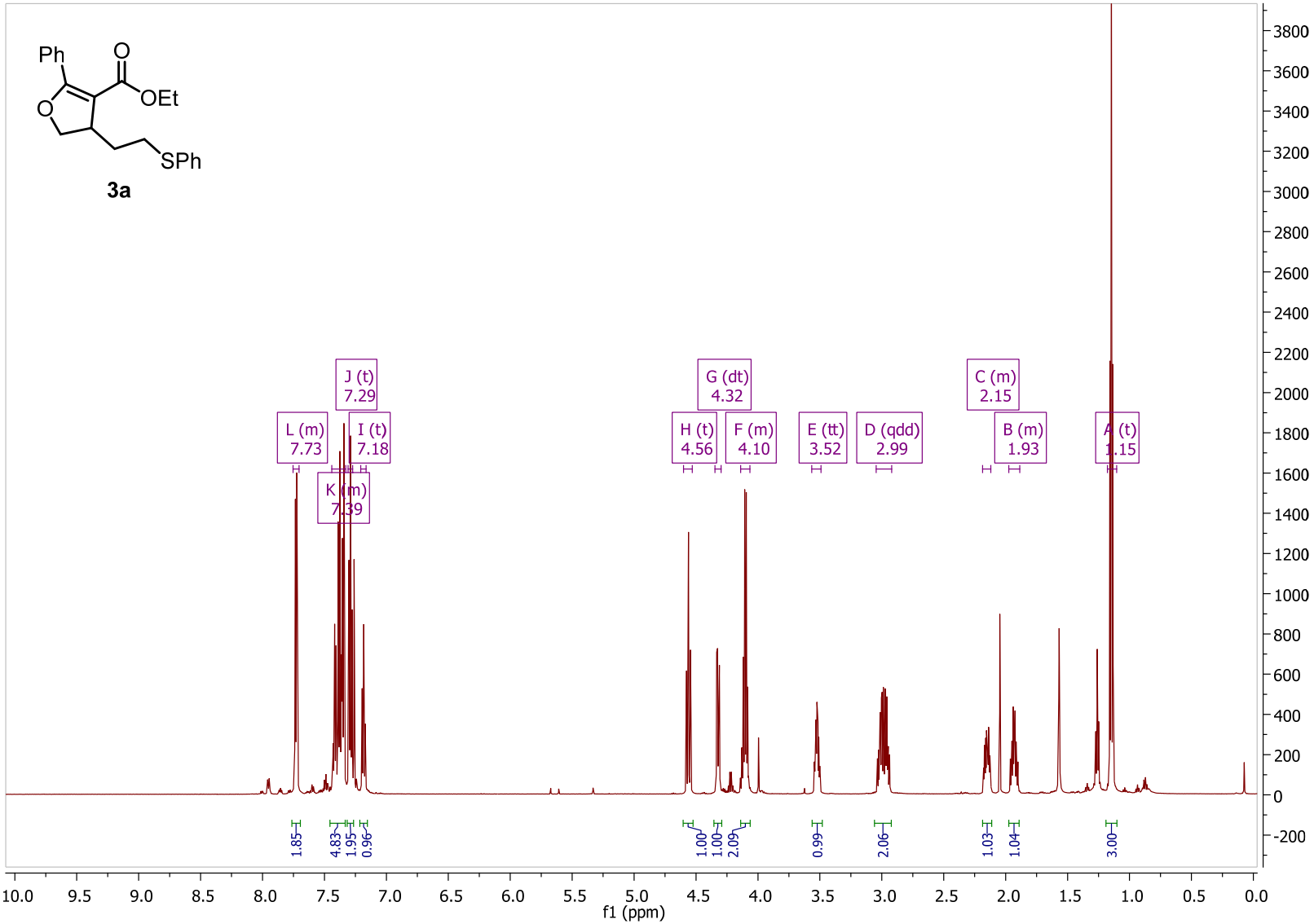

Ph
O
O
OEt
SPh
2n, major
J (m) 7.42
H (m) 7.28
L (m) 7.85
G (m) 7.16
I (m) 7.33
K (m) 7.53
F (m) 3.96
E (m) 2.97
D (dq) 2.20
C (m) 1.74
B (dd) 1.38
A (t) 0.86
1.91
1.02
1.93
1.88
2.02
0.95
2.11
2.00
1.20
5.07
1.08
3.07
f1 (ppm)

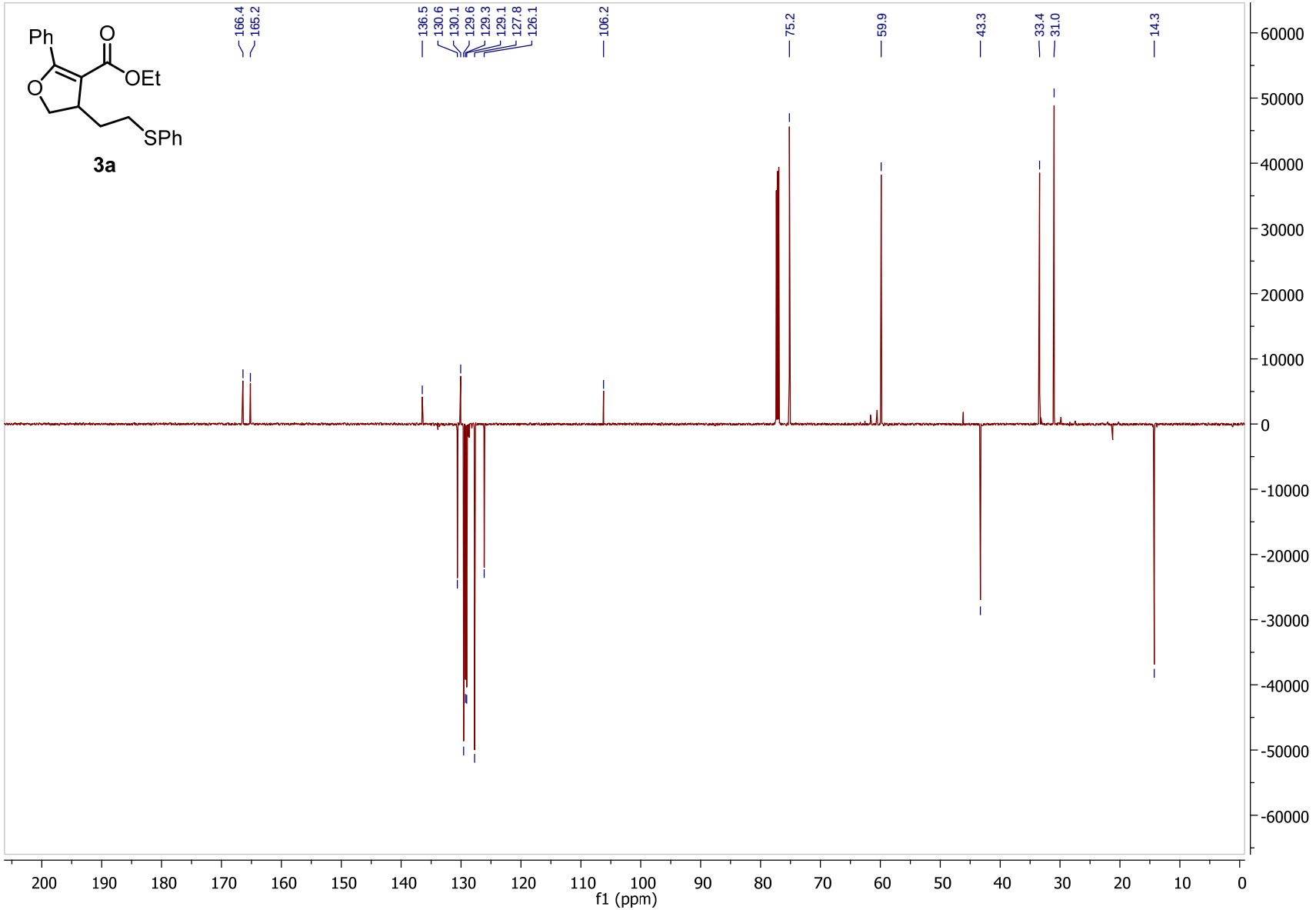

195.5
170.2
137.7
136.7
132.8
129.3
129.0
128.6
128.2
126.0
61.4
39.1
33.2
28.8
26.5
26.4
22.3
13.8
O
O
Ph
OEt
SPh
2n, major
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

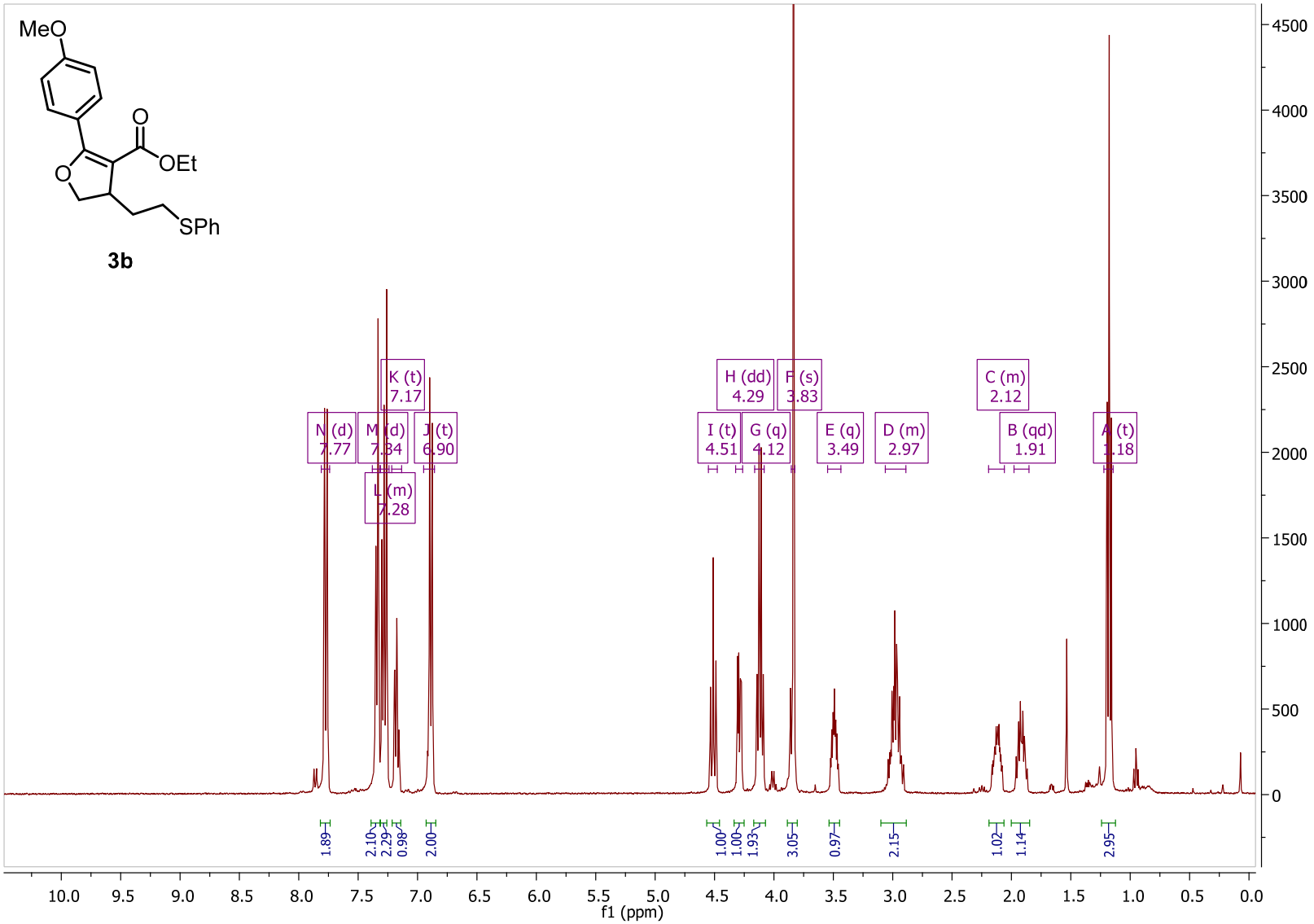

Ph
O
O
OEt
SPh
2n, minor
M (m) 7.79
J (m) 7.18
L (m) 7.47
I (m) 7.08
K (m) 7.37
H (m) 3.95
G (m) 2.79
F (m) 2.16
E (p) 1.67
C (dd) 1.52
B (dd) 1.35
D (dt) 1.58
A (t) 0.85
1.96
1.00
2.02
4.84
0.99
2.10
2.02
1.01
2.06
1.07
1.07
1.06
2.96
f1 (ppm)

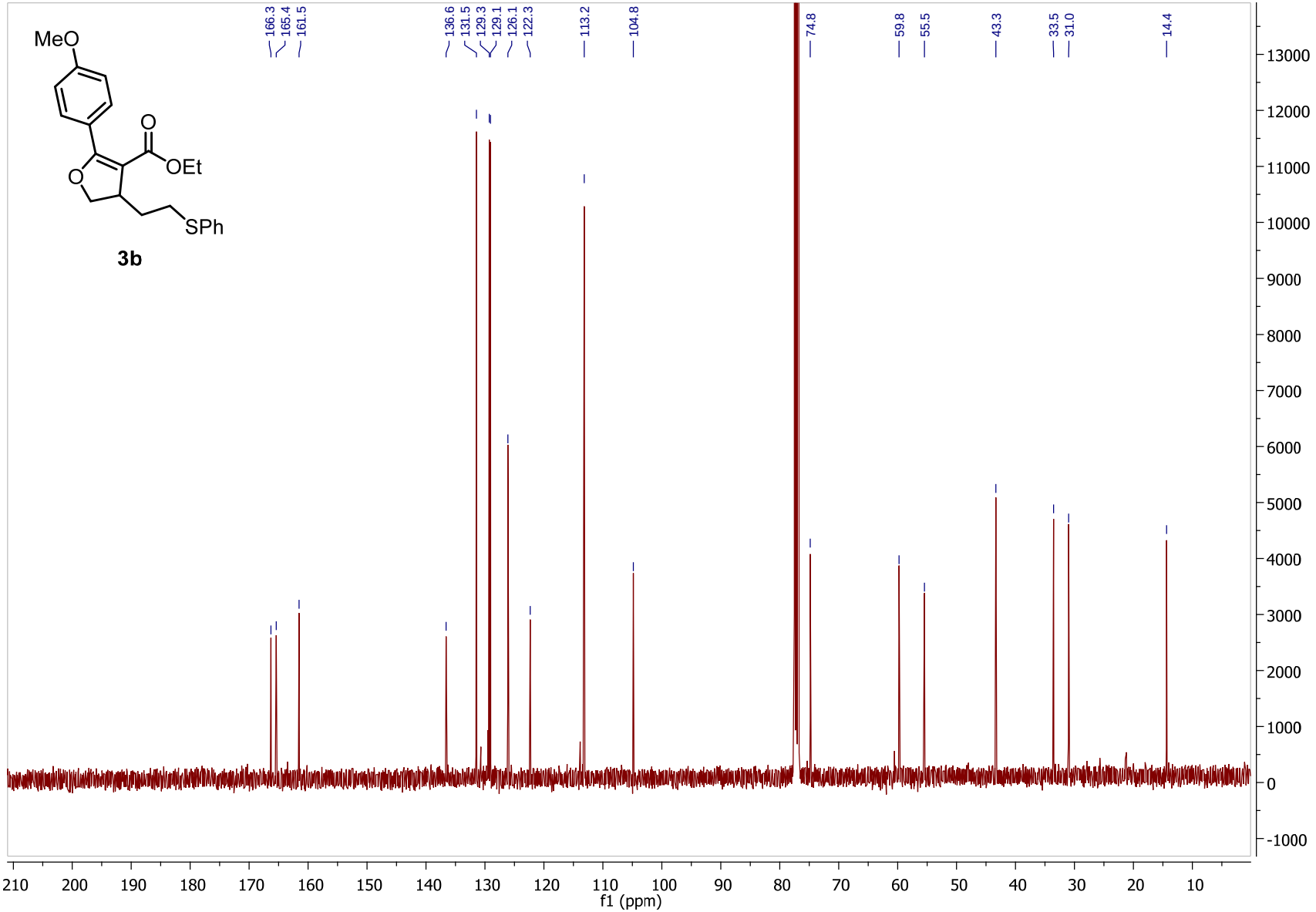

194.4
171.8
137.9
136.5
133.0
129.4
129.0
128.6
126.1
61.5
38.1
33.3
29.0
28.9
27.5
20.4
13.8
Ph
O
O
OEt
SPh
2n, minor
f1 (ppm)

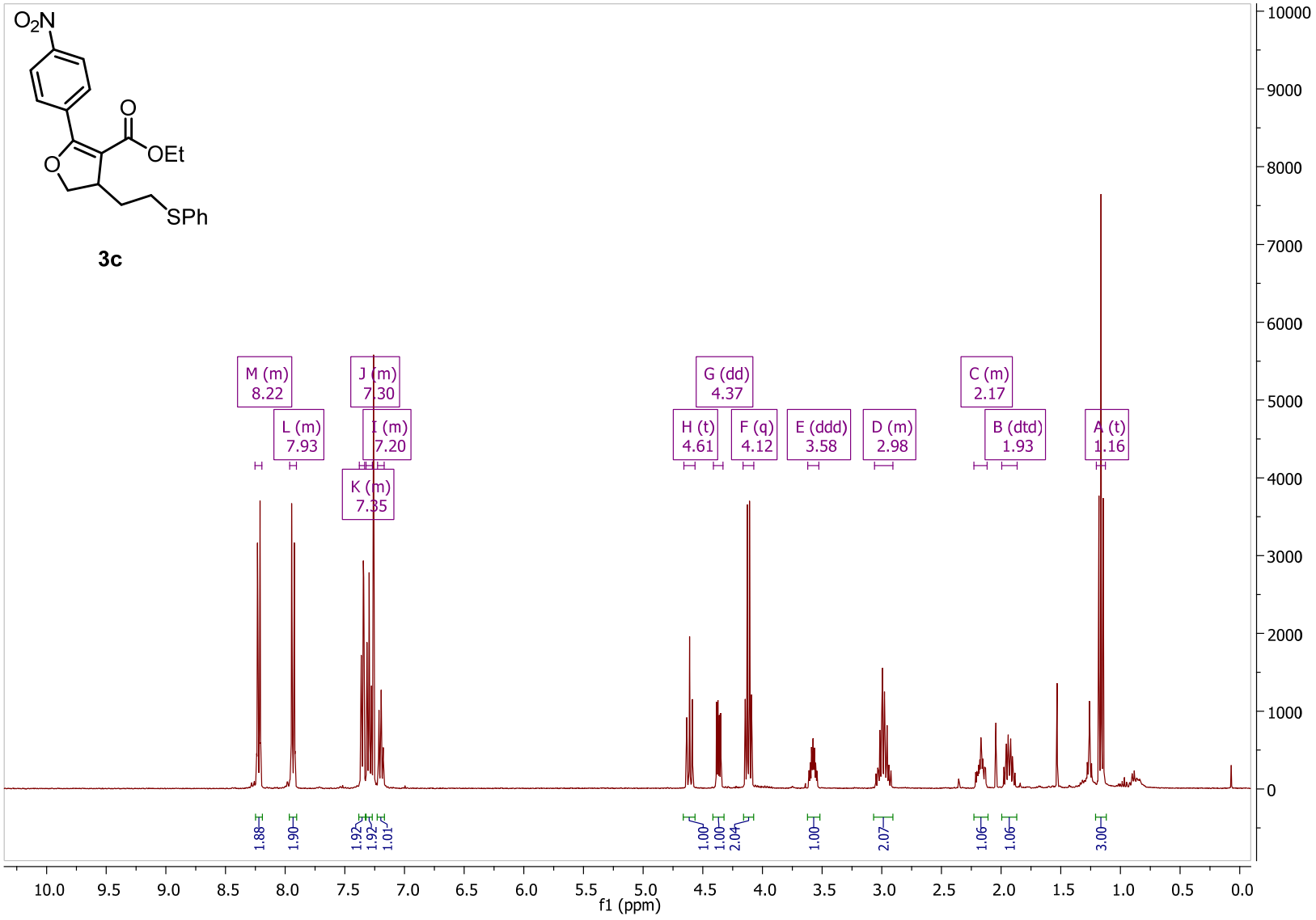
7.3 Dihydrofurans

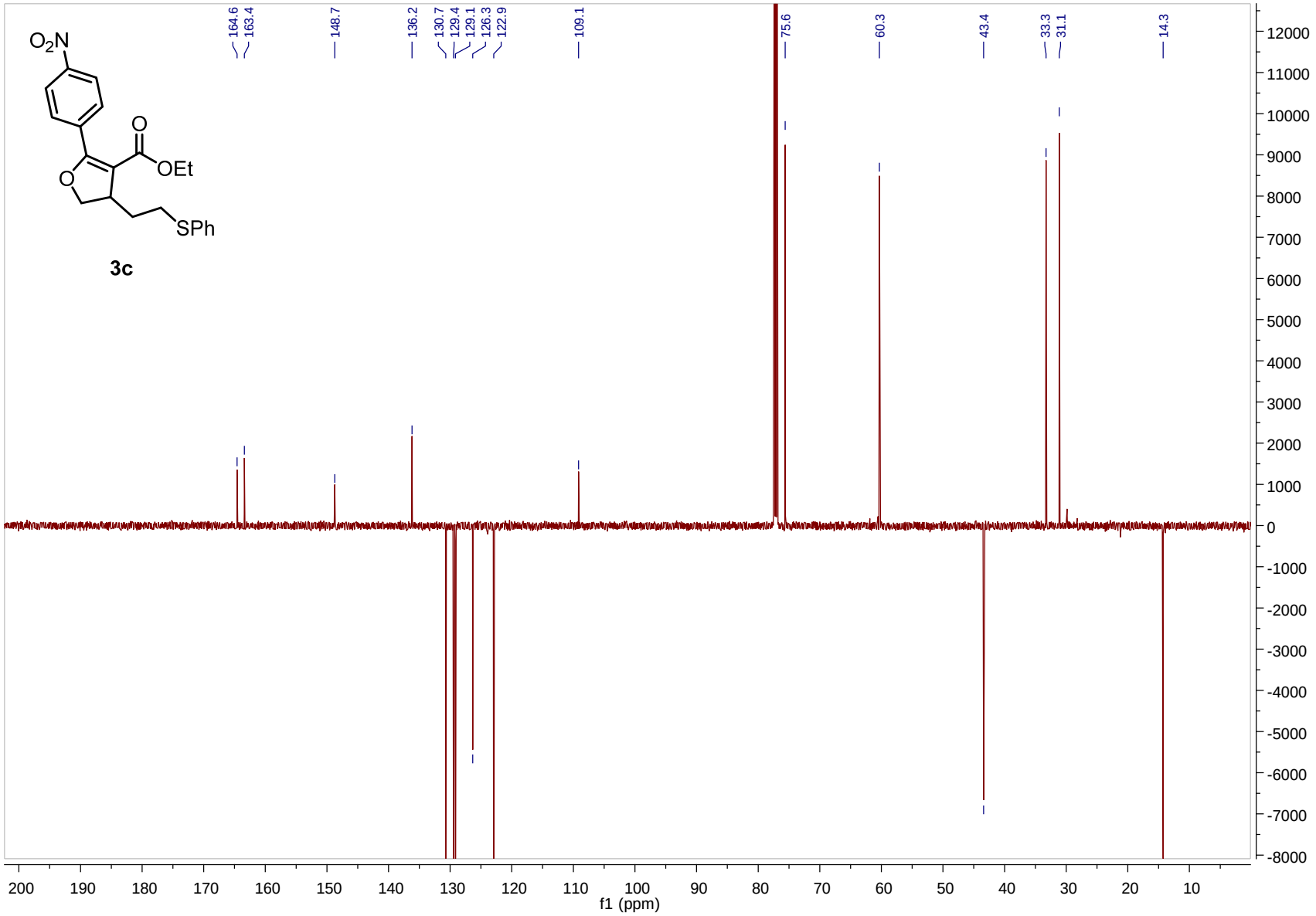


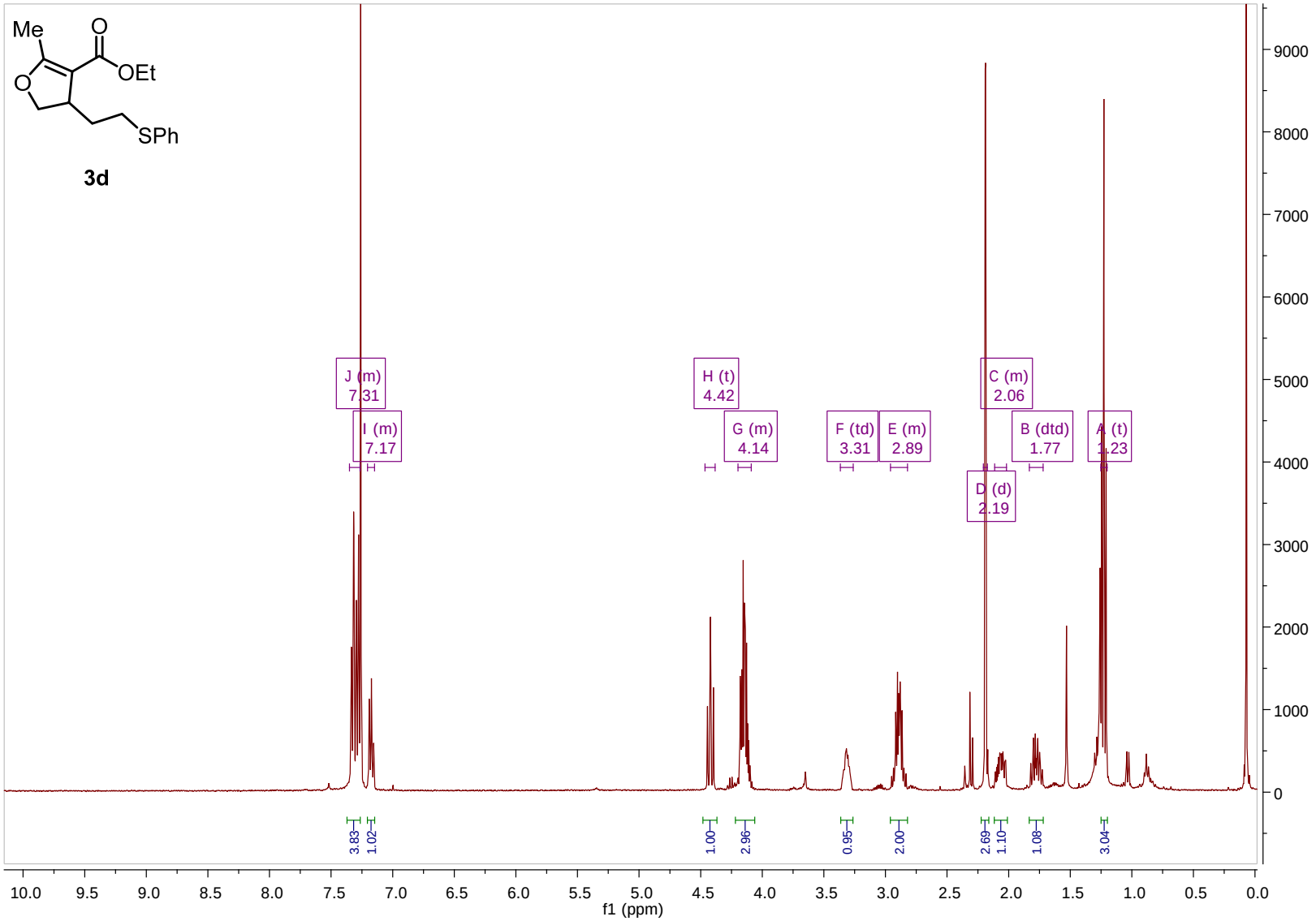

Ph
O
OEt
O
SPh
3a
166.4
165.2
136.5
130.6
130.1
129.6
129.3
129.1
127.8
126.1
106.2
75.2
59.9
43.3
33.4
31.0
14.3
60000
50000
40000
30000
20000
10000
0
-10000
-20000
-30000
-40000
-50000
-60000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

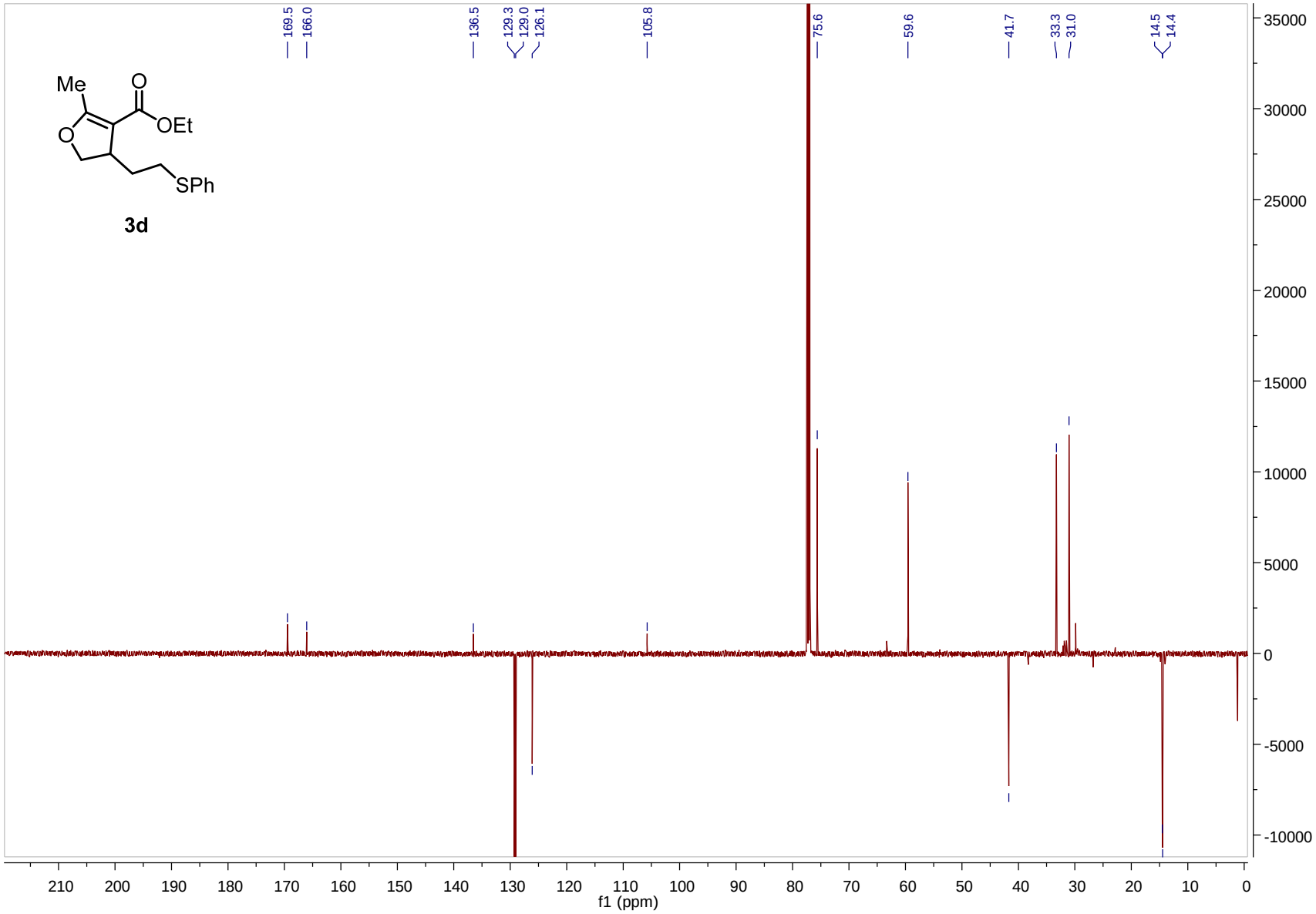

MeO
O
OEt
O
SPh
3b
K (t) 7.17
N (d) 7.77
M (d) 7.34
J (t) 6.90
L (m) 7.28
H (dd) 4.29
F (s) 3.83
I (t) 4.51
G (q) 4.12
E (q) 3.49
D (m) 2.97
C (m) 2.12
B (qd) 1.91
A (t) 1.18
1.89
2.10
2.29
0.98
2.00
1.00
1.00
1.93
3.05
0.97
2.15
1.02
1.14
2.95
4500
4000
3500
3000
2500
2000
1500
1000
500
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

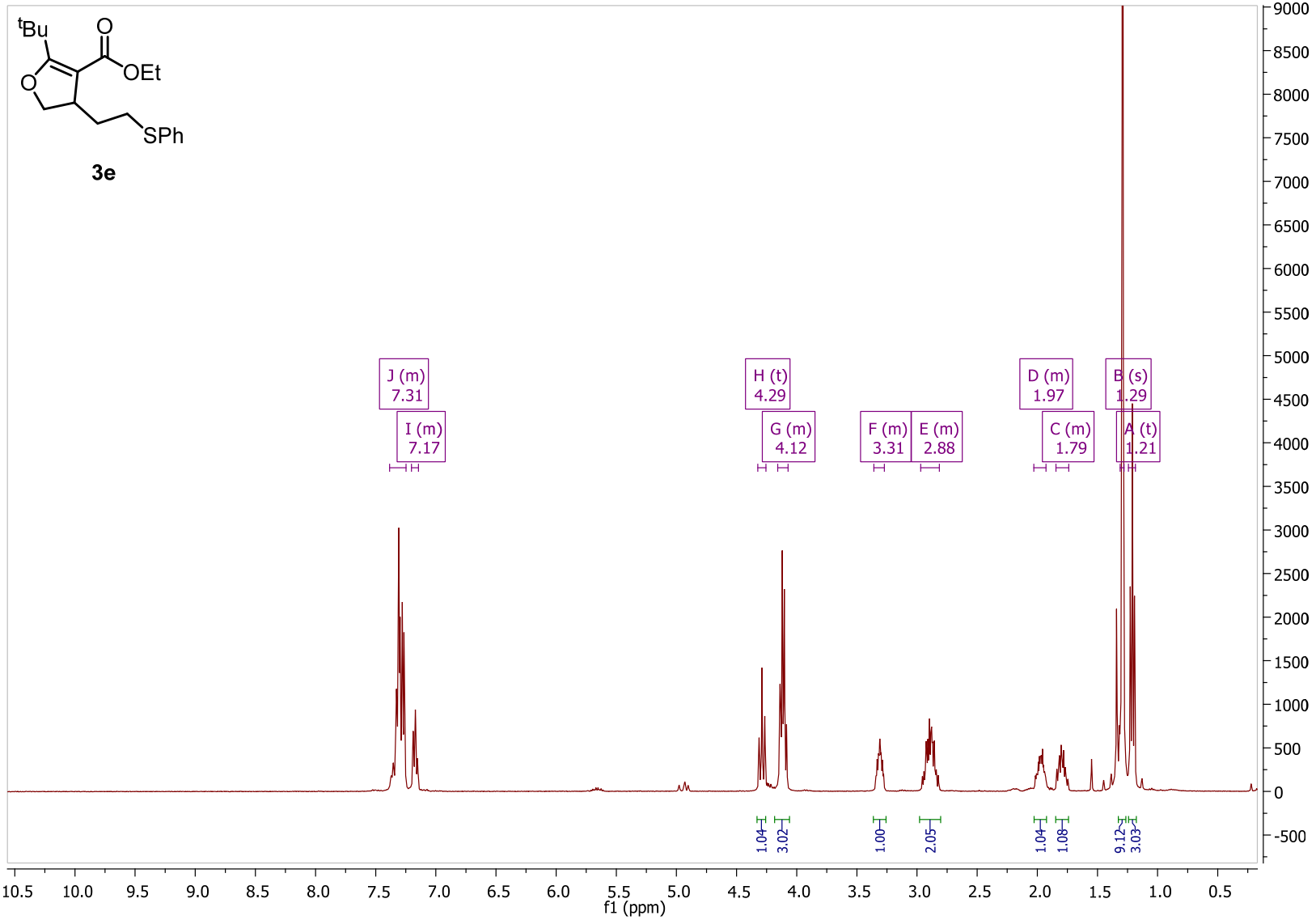

MeO
O
OEt
O
SPh
3b
166.3
165.4
161.5
136.6
131.5
129.3
129.1
126.1
122.3
113.2
104.8
74.8
59.8
55.5
43.3
33.5
31.0
14.4
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

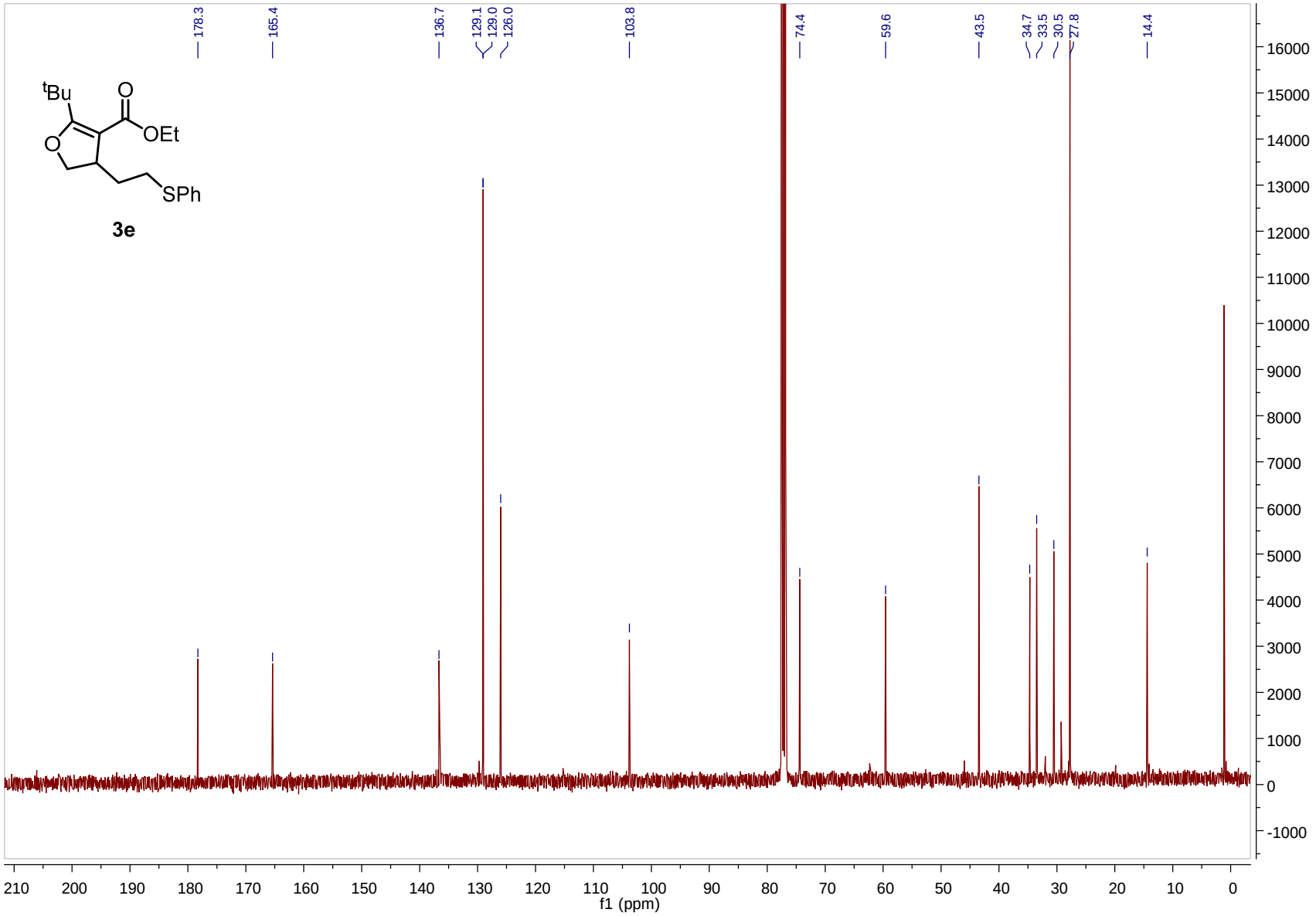

O2N
O
OEt
O
SPh
3c
M (m) 8.22
L (m) 7.93
J (m) 7.30
I (m) 7.20
K (m) 7.35
G (dd) 4.37
H (t) 4.61
F (q) 4.12
E (ddd) 3.58
D (m) 2.98
C (m) 2.17
B (dtd) 1.93
A (t) 1.16
1.88
1.90
1.92
1.92
1.01
1.00
1.00
2.04
1.00
2.07
1.06
1.06
3.00
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

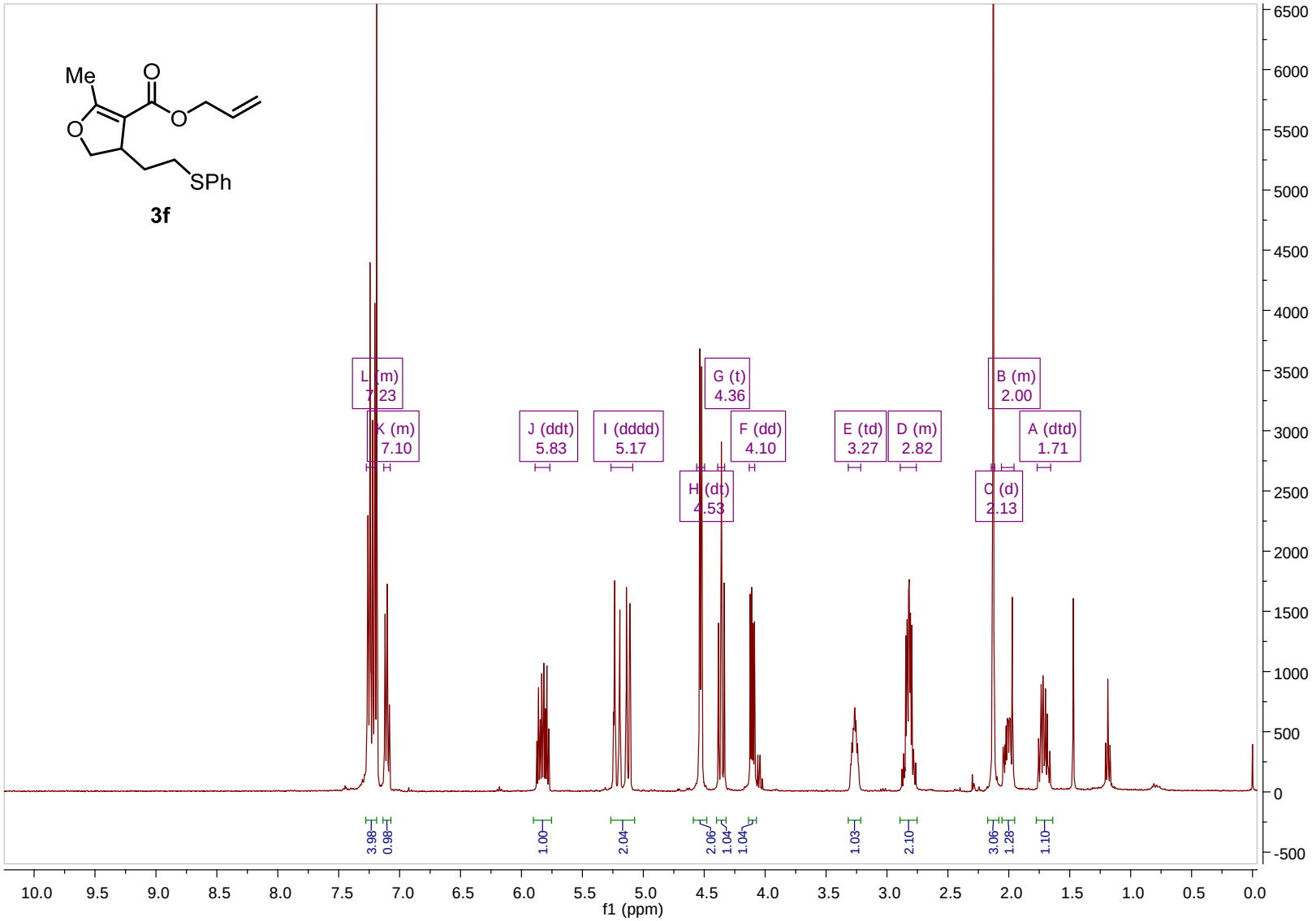

O2N
O
OEt
O
SPh
3c
164.6
163.4
148.7
136.2
130.7
129.4
129.1
126.3
122.9
109.1
75.6
60.3
43.4
33.3
31.1
14.3
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
-5000
-6000
-7000
-8000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

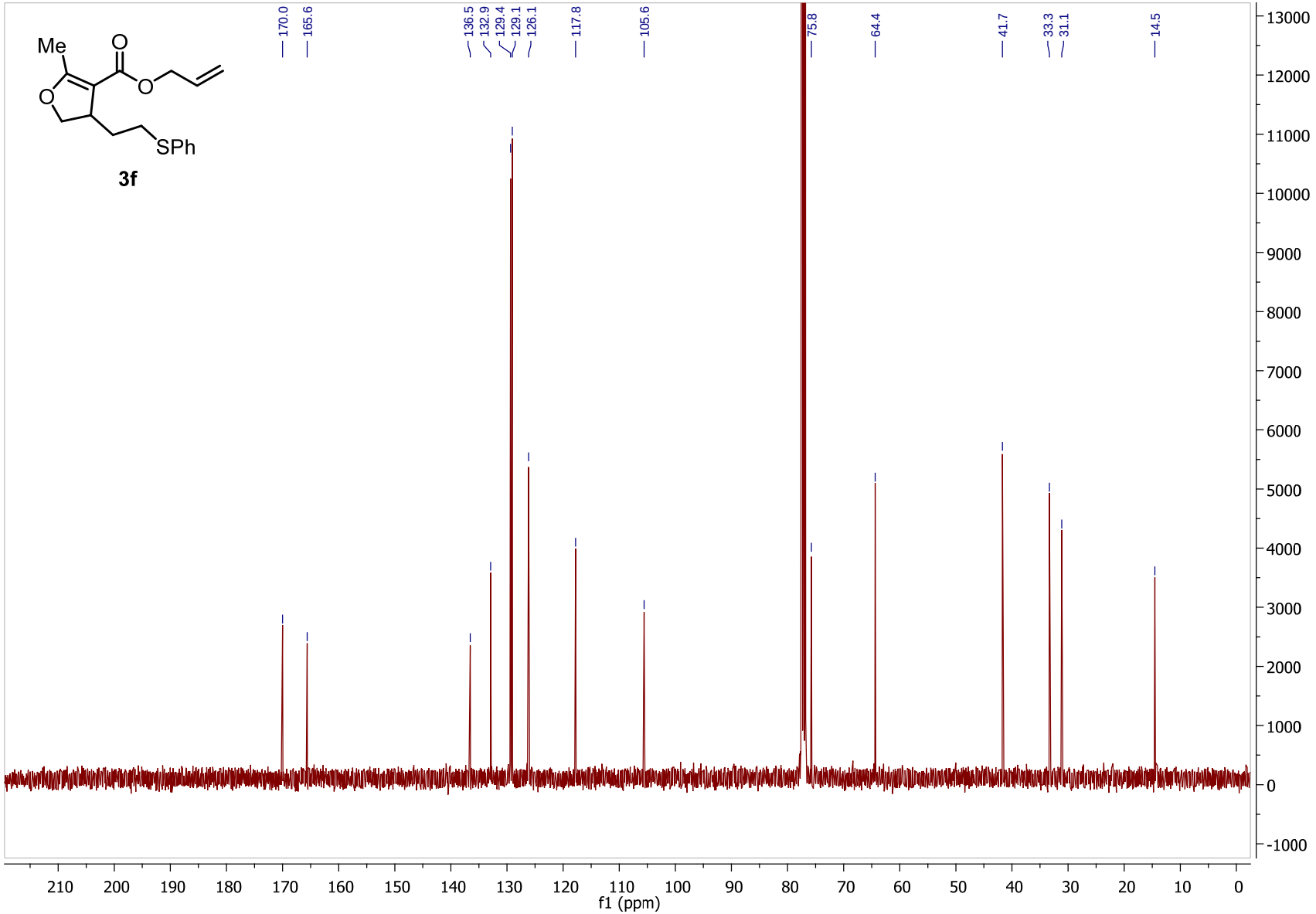

Me
O
OEt
O
SPh
3d
J (m)
7.31
I (m)
7.17
H (t)
4.42
G (m)
4.14
F (td)
3.31
E (m)
2.89
C (m)
2.06
D (d)
2.19
B (dtd)
1.77
A (t)
1.23
3.83
1.02
1.00
2.96
0.95
2.00
2.69
1.10
1.08
3.04
f1 (ppm)

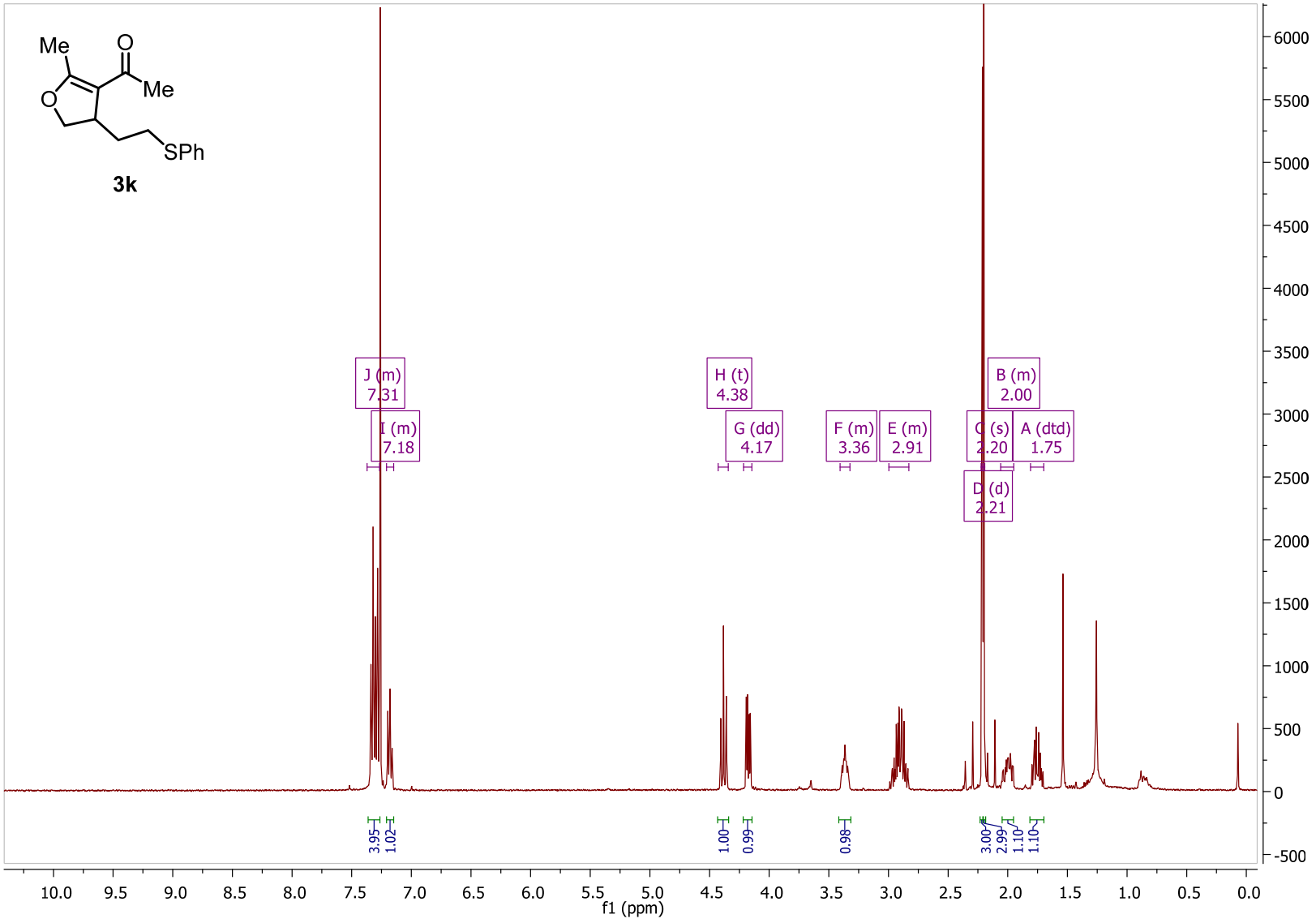

Me
O
OEt
O
SPh
3d
169.5
166.0
136.5
129.3
129.0
126.1
105.8
75.6
59.6
41.7
33.3
31.0
14.5
14.4
35000
30000
25000
20000
15000
10000
5000
0
-5000
-10000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

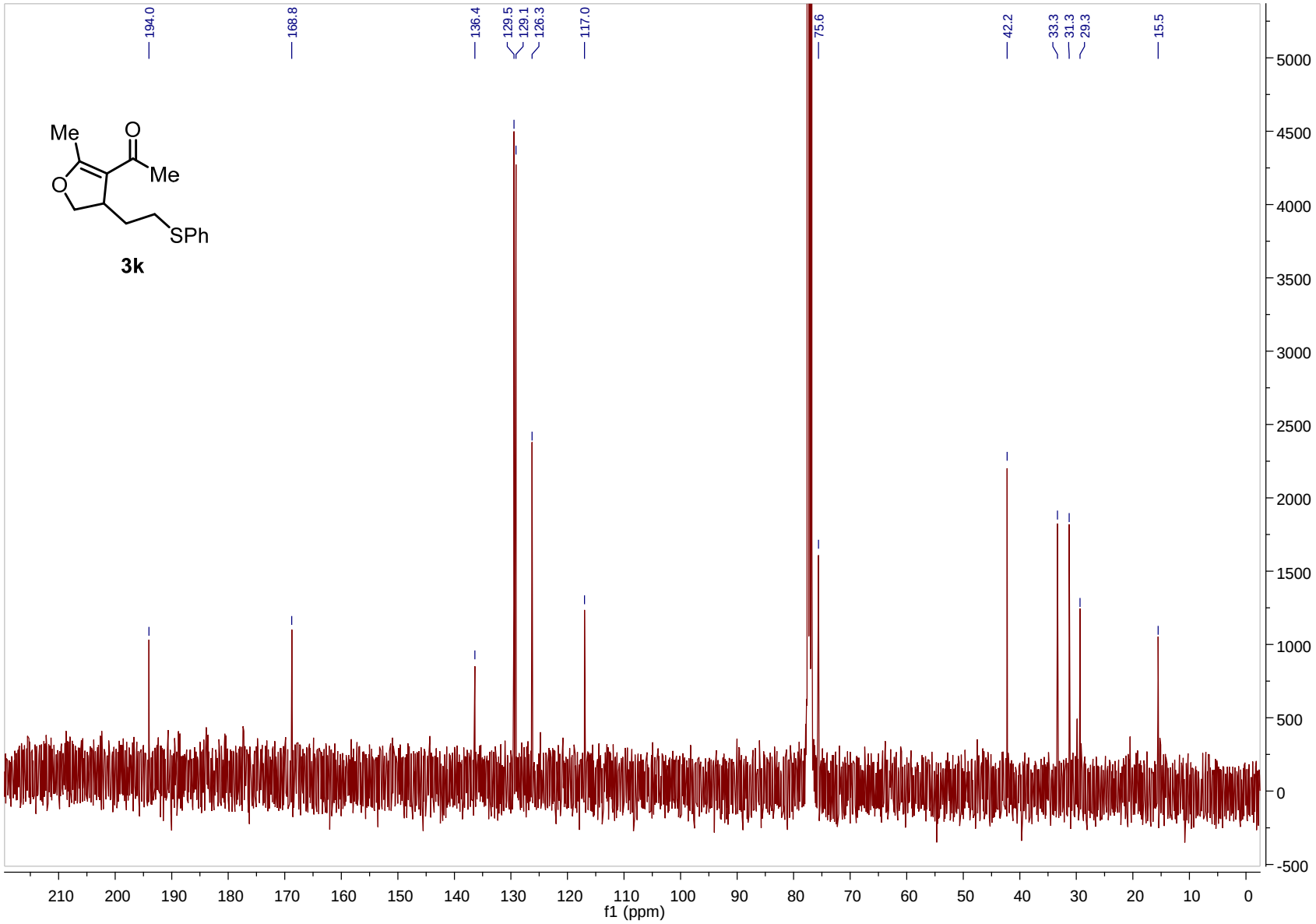

tBu
O
OEt
O
SPh
3e
J (m) 7.31
I (m) 7.17
H (t) 4.29
G (m) 4.12
F (m) 3.31
E (m) 2.88
D (m) 1.97
C (m) 1.79
B (s) 1.29
A (t) 1.21
1.04
3.02
1.00
2.05
1.04
1.08
9.12
3.03
f1 (ppm)

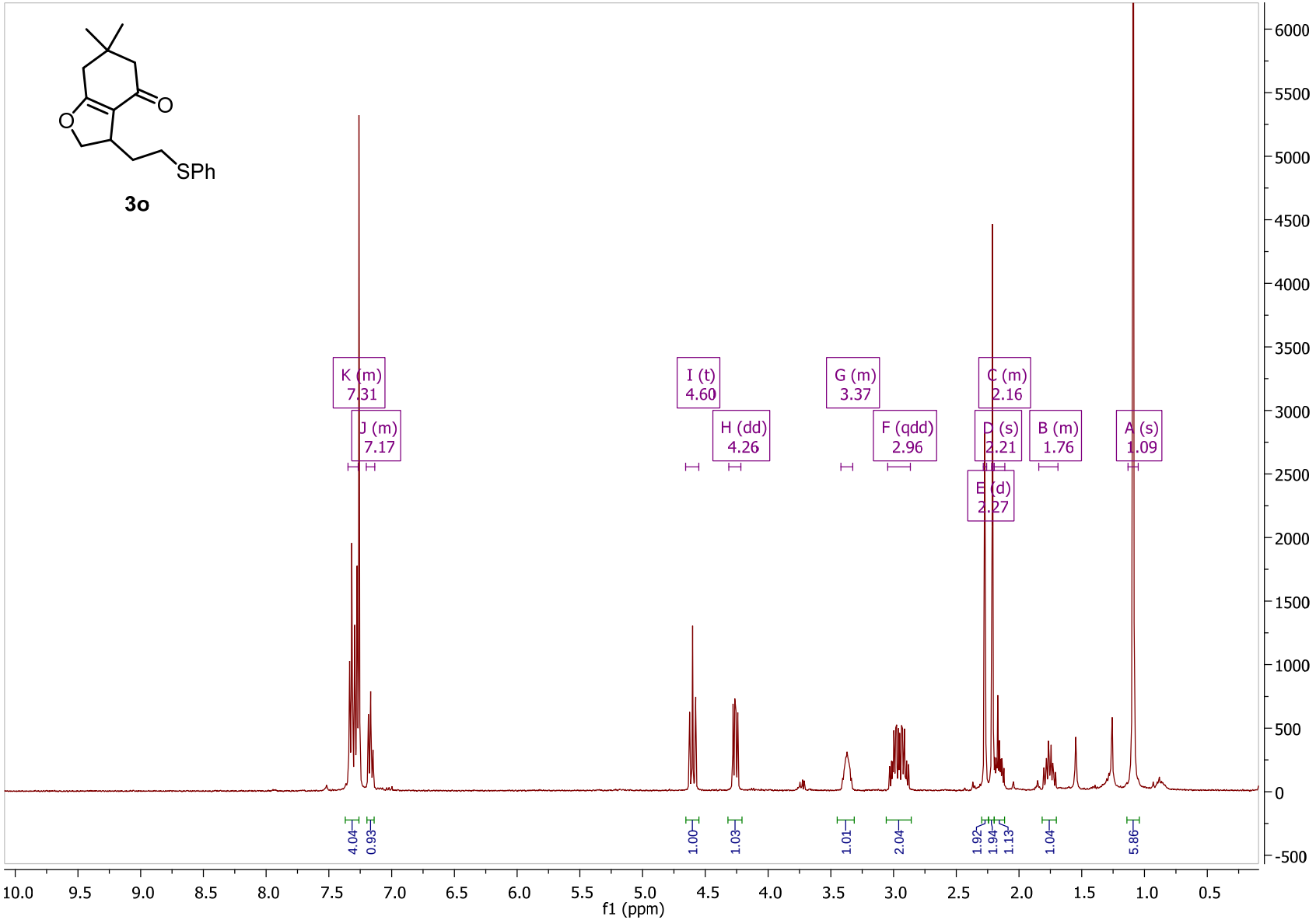

178.3
165.4
136.7
129.1
129.0
126.0
103.8
74.4
59.6
43.5
34.7
33.5
30.5
27.8
14.4
tBu
O
OEt
O
SPh
3e
f1 (ppm)

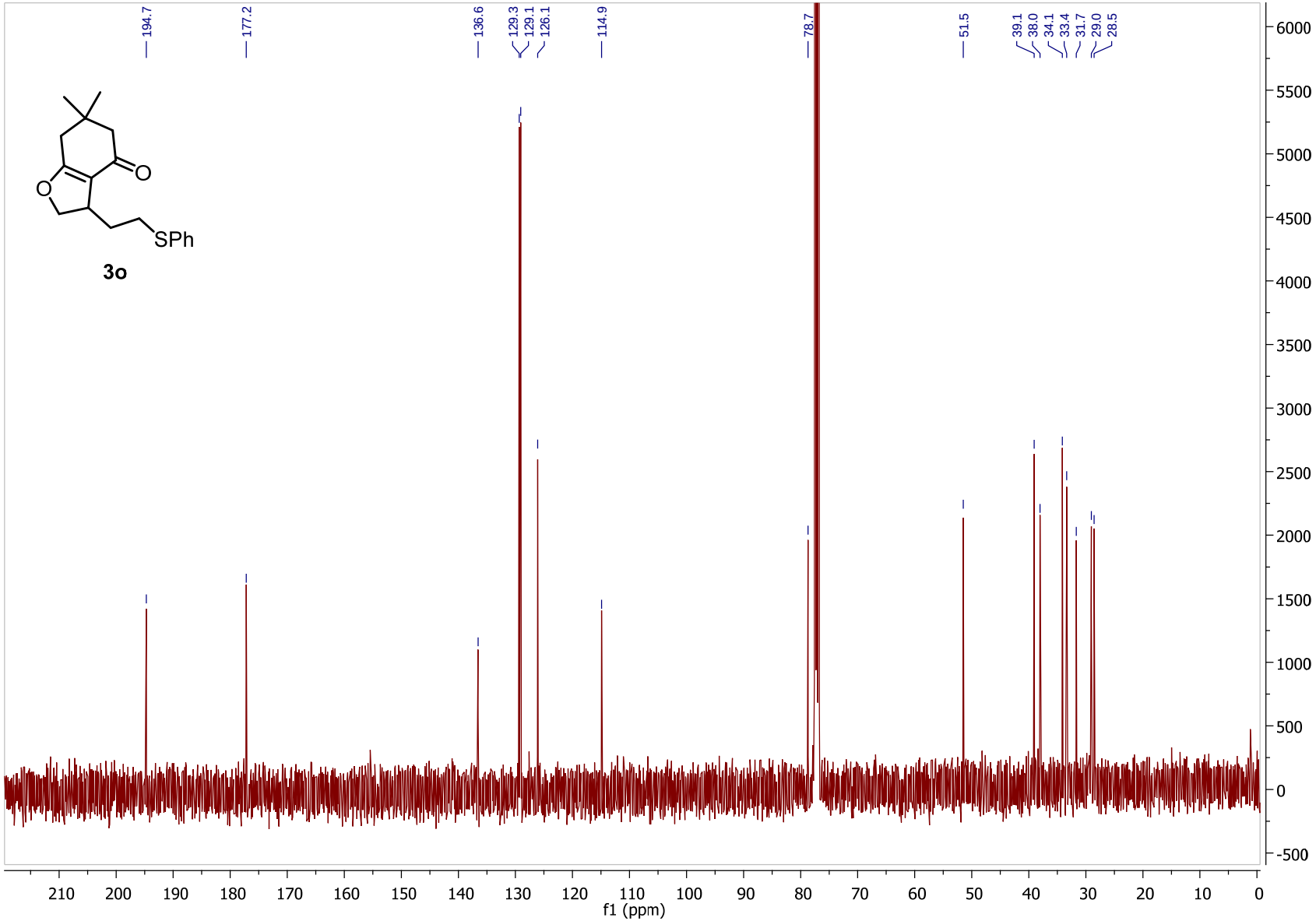

Me
O
O
O
SPh
3f
L (m)
7.23
K (m)
7.10
J (ddt)
5.83
I (dddd)
5.17
G (t)
4.36
H (dt)
4.53
F (dd)
4.10
E (td)
3.27
D (m)
2.82
B (m)
2.00
C (d)
2.13
A (dtd)
1.71
3.98
0.98
1.00
2.04
2.06
1.04
1.04
1.03
2.10
3.06
1.28
1.10
f1 (ppm)

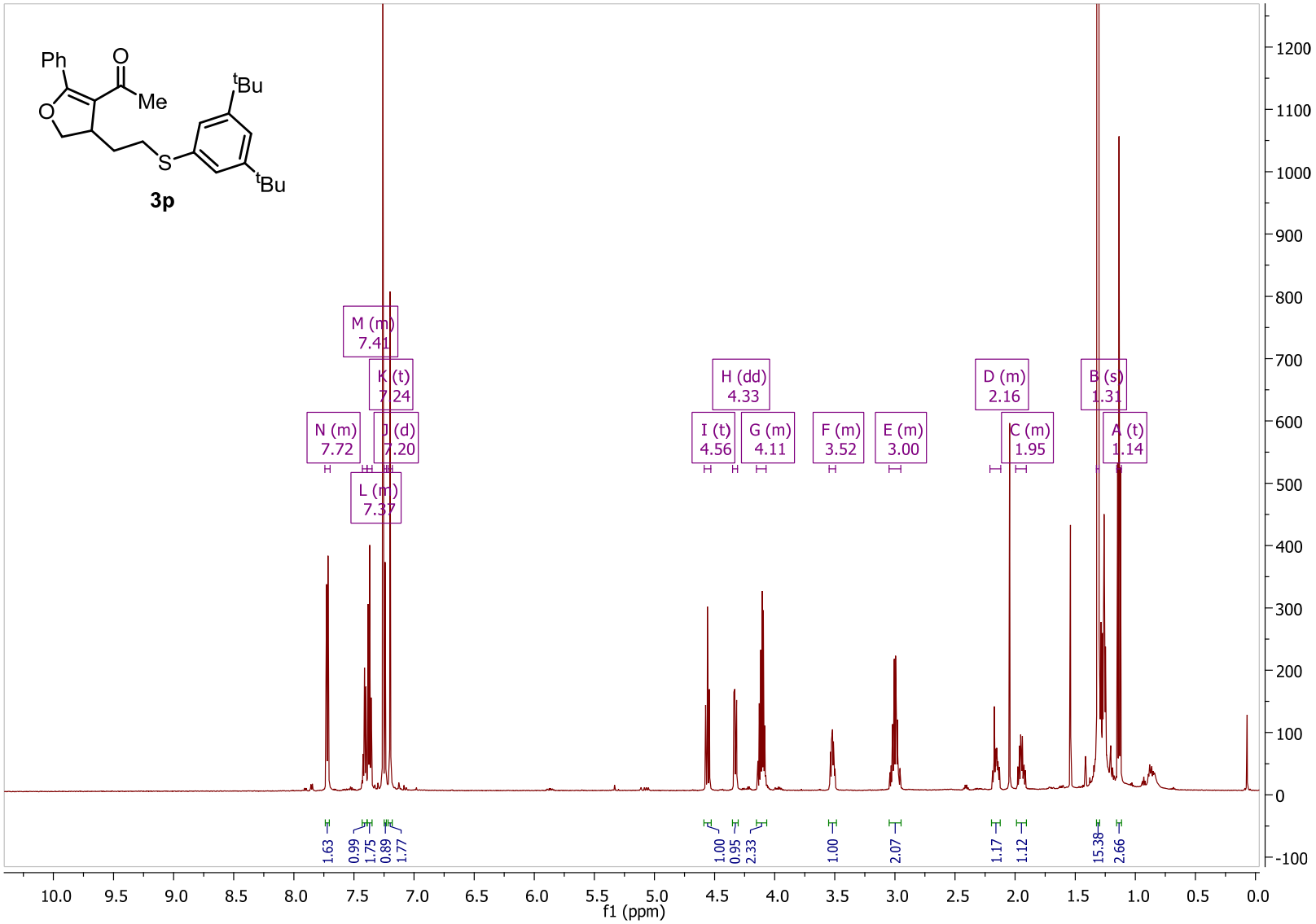

Me
O
O
O
SPh
3f
170.0
165.6
136.5
132.9
129.4
129.1
126.1
117.8
105.6
75.8
64.4
41.7
33.3
31.1
14.5
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

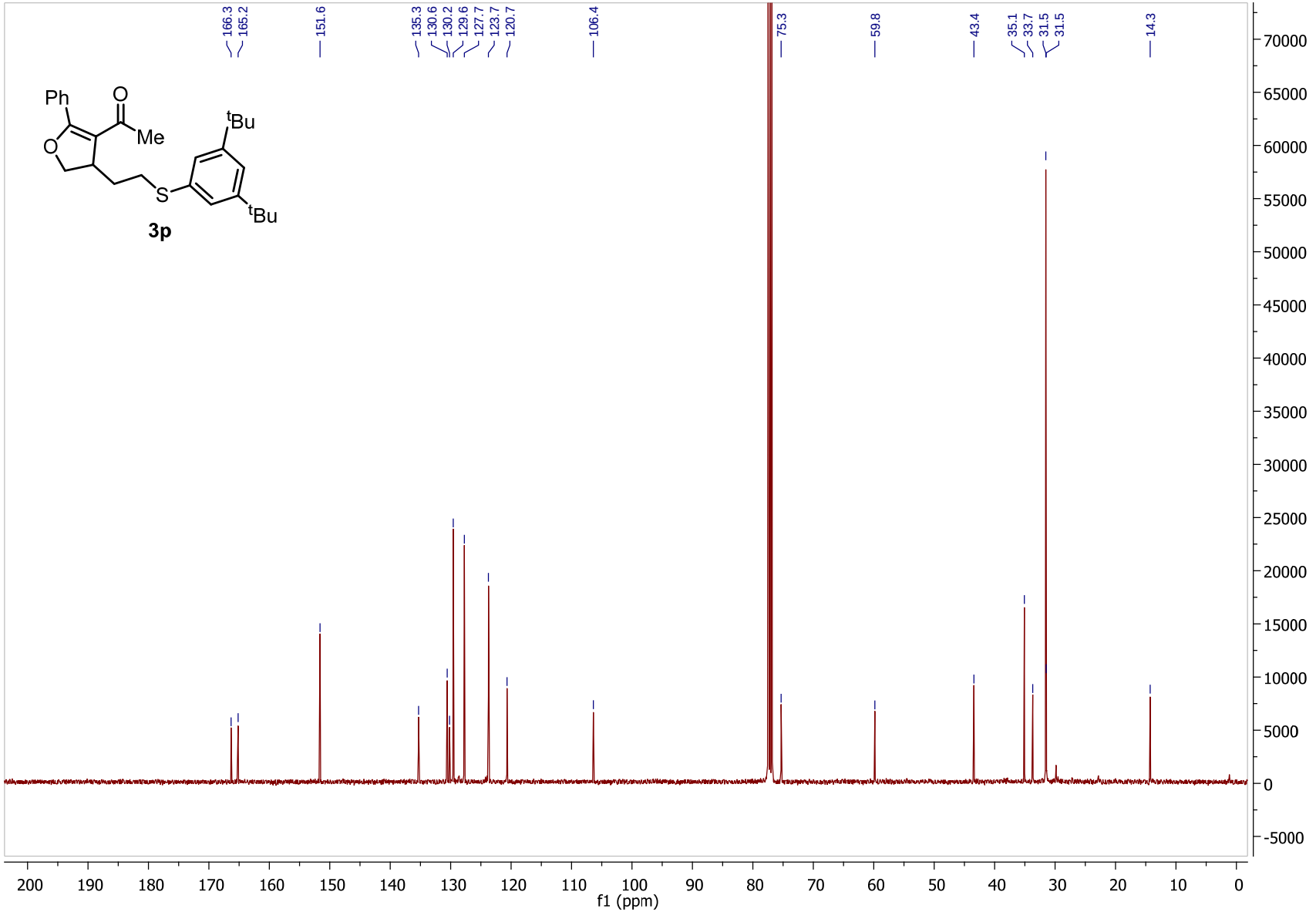

Me
O
Me
O
SPh
3k
J (m)
7.31
I (m)
7.18
H (t)
4.38
G (dd)
4.17
F (m)
3.36
E (m)
2.91
B (m)
2.00
C (s)
2.20
A (dtd)
1.75
D (d)
2.21
3.95
1.02
1.00
0.99
0.98
3.00
2.99
1.10
1.10
f1 (ppm)


194.0
168.8
136.4
129.5
129.1
126.3
117.0
75.6
42.2
33.3
31.3
29.3
15.5
Me
O
Me
O
SPh
3k
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

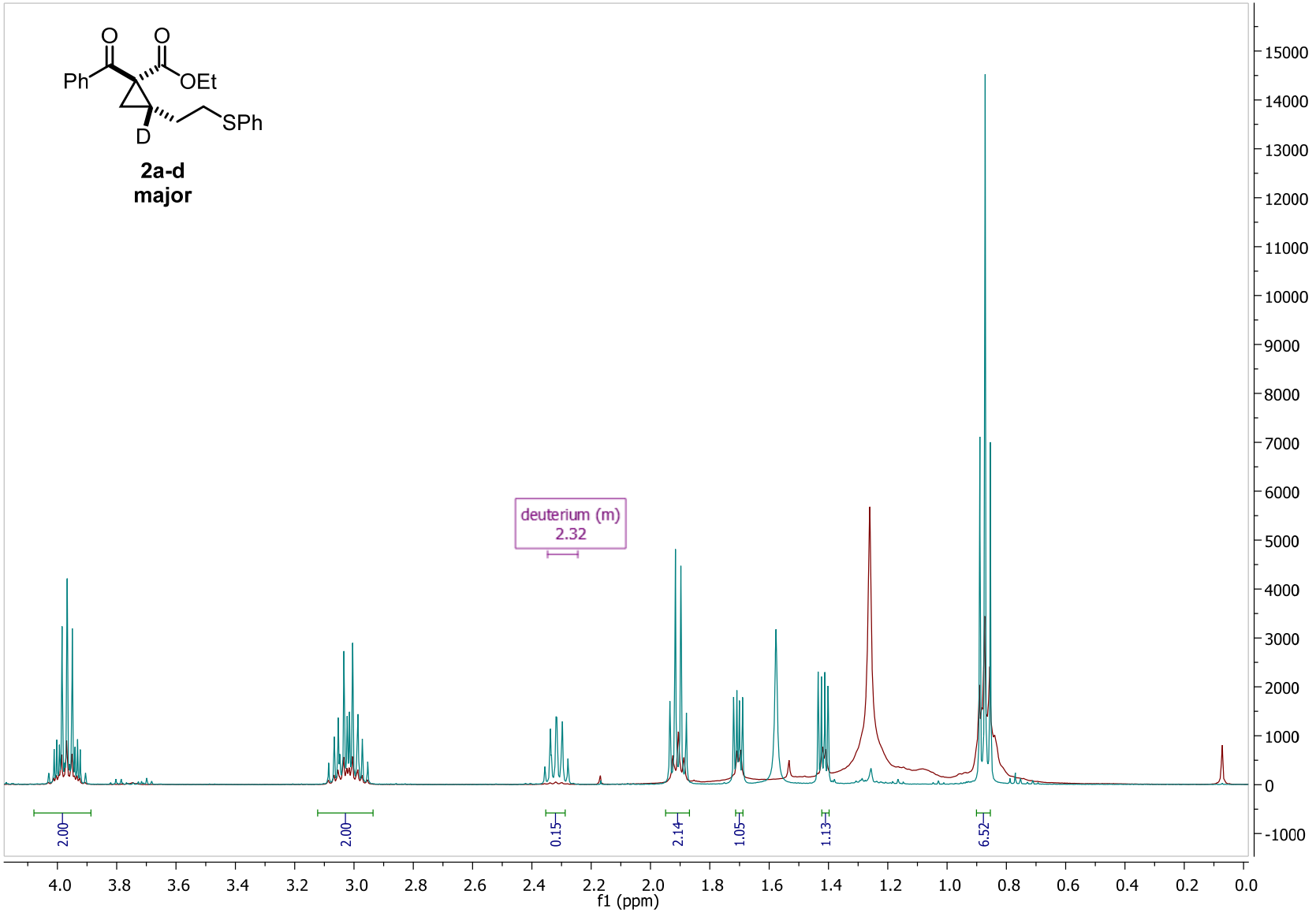

SPh
3o
K (m)
7.31
J (m)
7.17
I (t)
4.60
H (dd)
4.26
G (m)
3.37
F (qdd)
2.96
C (m)
2.16
D (s)
2.21
E (d)
2.27
B (m)
1.76
A (s)
1.09
4.04
0.93
1.00
1.03
1.01
2.04
1.92
1.94
1.13
1.04
5.86
f1 (ppm)

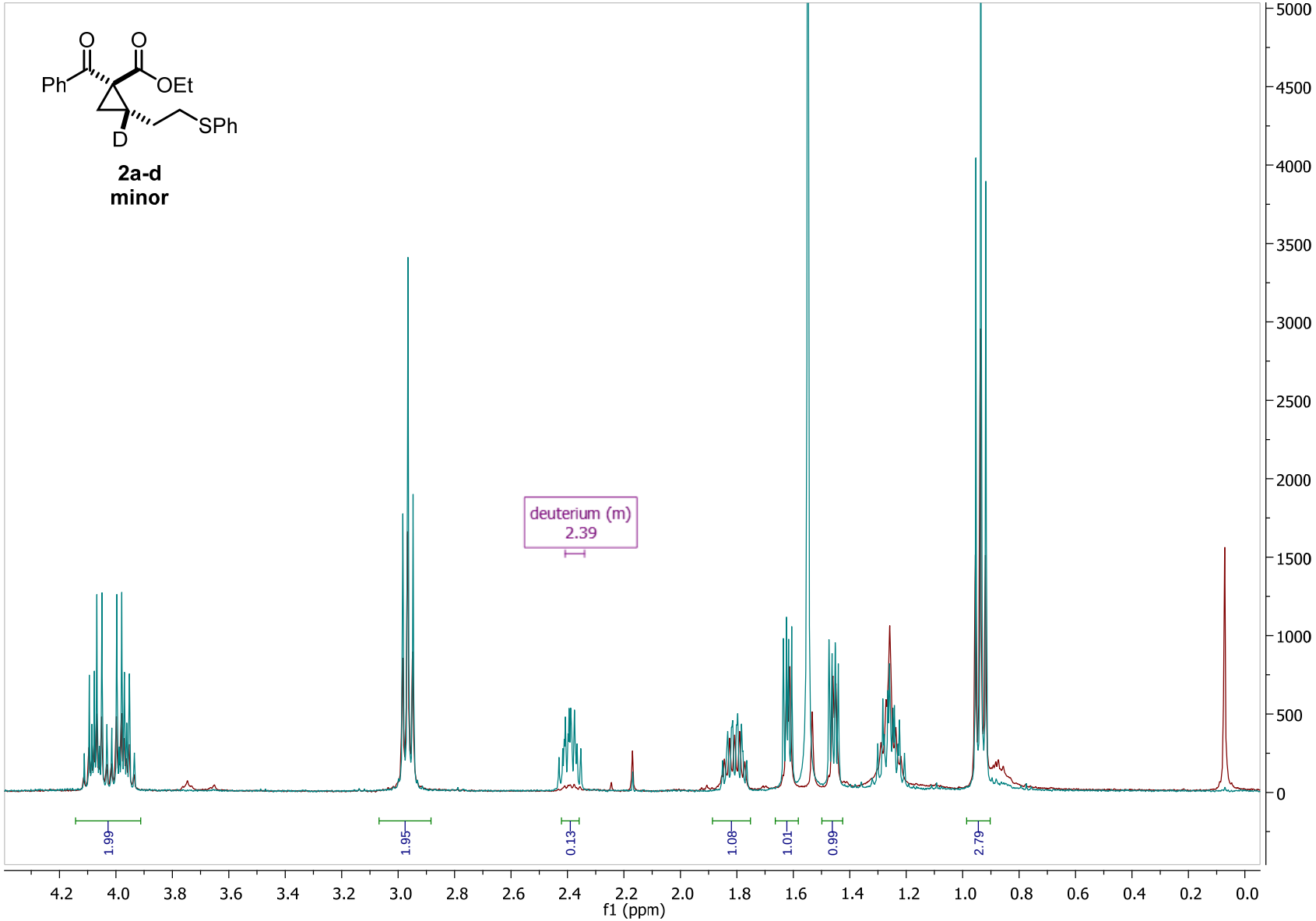

194.7
177.2
136.6
129.3
129.1
126.1
114.9
78.7
51.5
39.1
38.0
34.1
33.4
31.7
29.0
28.5
O
O
SPh
3o
f1 (ppm)

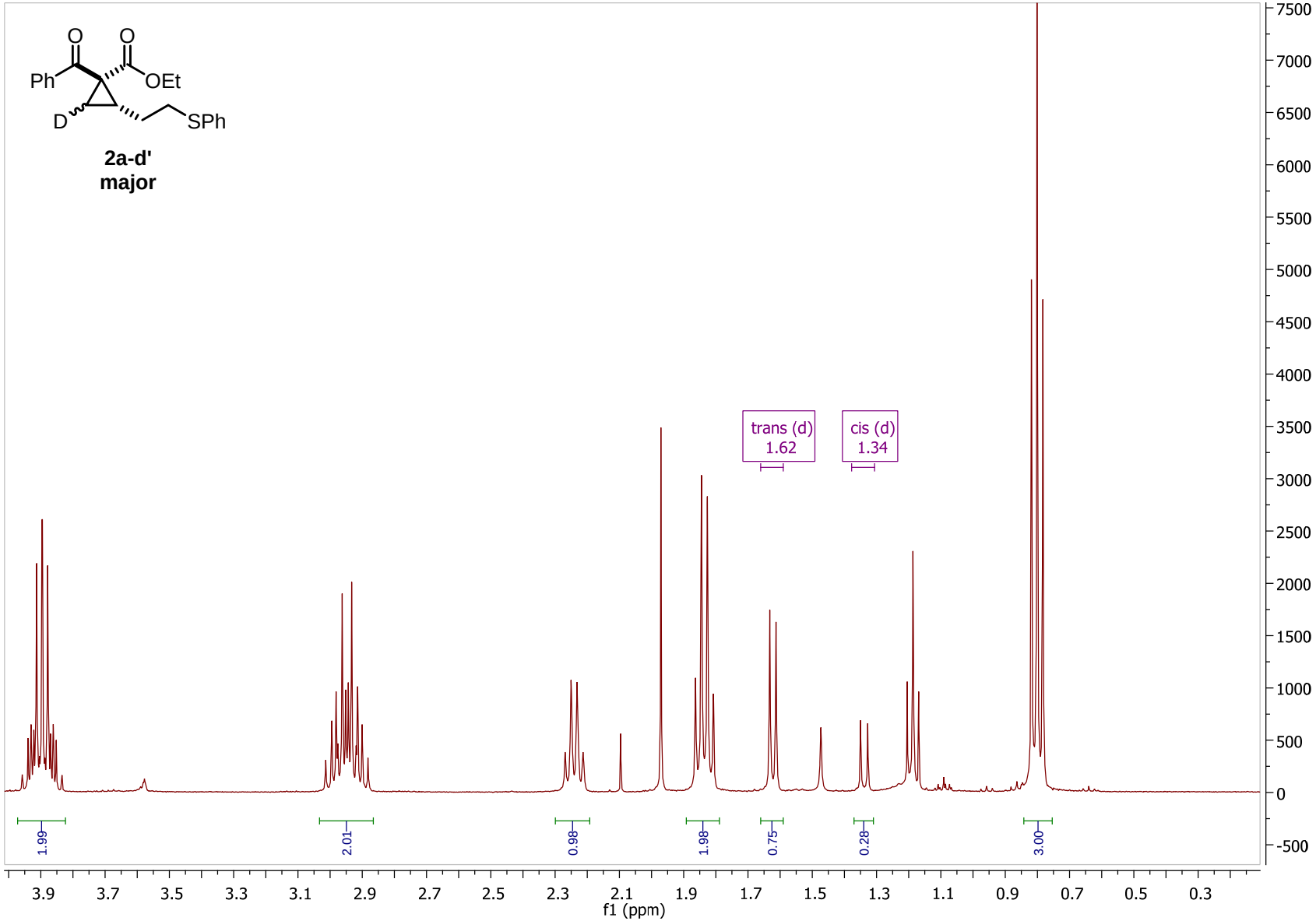

Ph
O
Me
O
S
tBu
tBu
3p
M (m)
7.41
K (t)
7.24
N (m)
7.72
J (d)
7.20
L (m)
7.37
H (dd)
4.33
I (t)
4.56
G (m)
4.11
F (m)
3.52
E (m)
3.00
D (m)
2.16
C (m)
1.95
B (s)
1.31
A (t)
1.14
1.63
0.99
1.75
0.89
1.77
1.00
0.95
2.33
1.00
2.07
1.17
1.12
15.38
2.66
f1 (ppm)

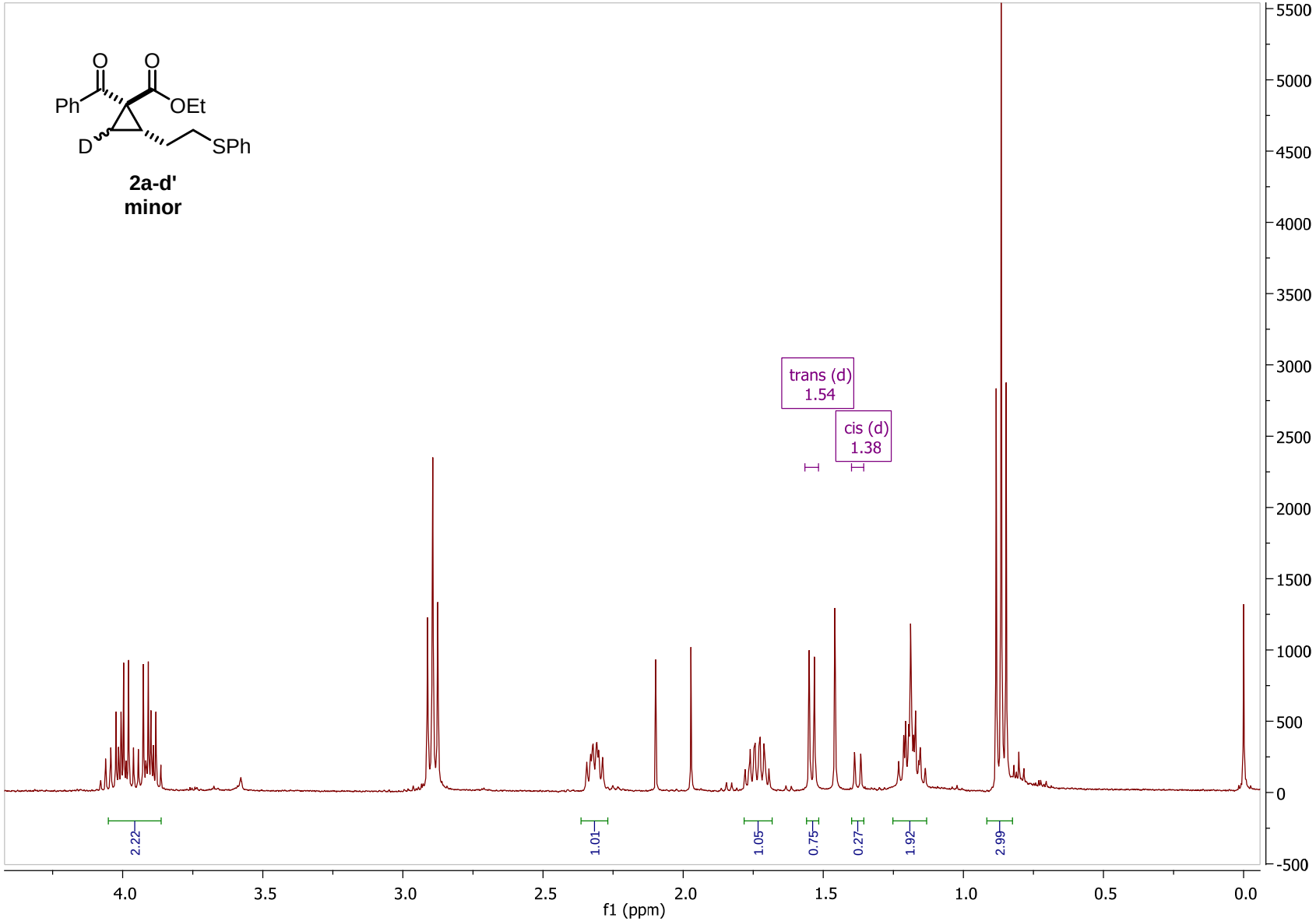

166.3
165.2
151.6
135.3
130.6
130.2
129.6
127.7
123.7
120.7
106.4
75.3
59.8
43.4
35.1
33.7
31.5
31.5
14.3
Ph
O
Me
O
S
tBu
tBu
3p
f1 (ppm)

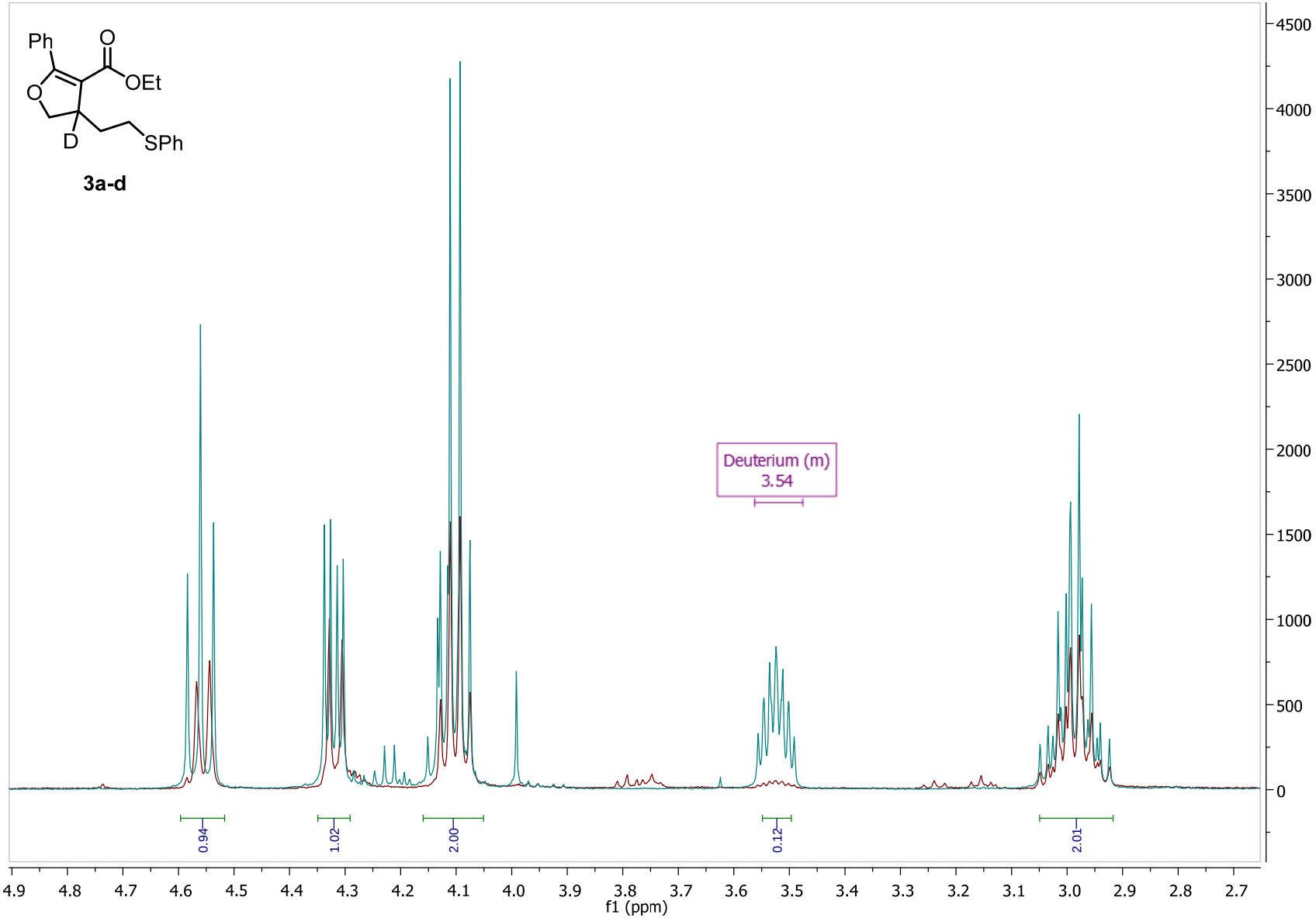
7.4 Deuterium experiments

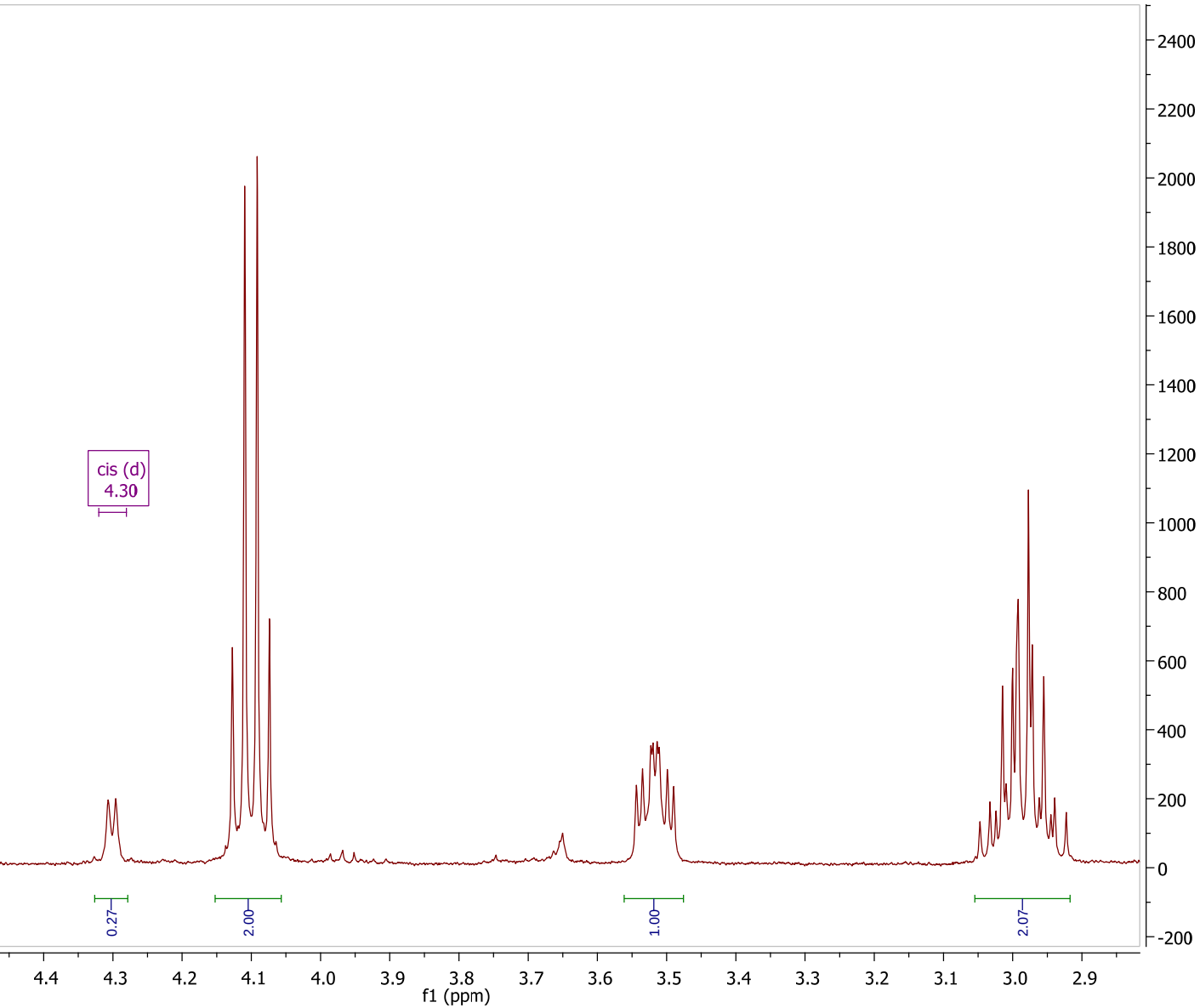



O
O
Ph
OEt
SPh
D
2a-d
minor
deuterium (m)
2.39
1.99
1.95
0.13
1.08
1.01
0.99
2.79
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
f1 (ppm)


O
O
Ph
OEt
D
SPh
2a-d'
major
trans (d)
1.62
cis (d)
1.34
1.99
2.01
0.98
1.98
0.75
0.28
3.00
f1 (ppm)


O
O
Ph
OEt
D
SPh
2a-d'
minor
trans (d)
1.54
cis (d)
1.38
2.22
1.01
1.05
0.75
0.27
1.92
2.99
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Ph
O
OEt
O
D
SPh
3a-d
Deuterium (m)
3.54
0.94
1.02
2.00
0.12
2.01
f1 (ppm)


cis (d)
4.30
0.27
2.00
1.00
2.07
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
f1 (ppm)