Supplementary Information

Gold-Catalyzed Thioetherification of Allyl, Benzyl and Propargyl Phosphates

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1. Characterization of supported Au catalysts

1-1 Characterization of spent Au/ZrO_2 catalysts.

HAADF-STEM images and the size distribution histograms for Au/ZrO_2 catalysts before and after the reaction of **1a** and **2a** are shown in Fig. S1. Increase of the average particle diameter indicates that Au particles agglomerate during catalytic reaction. However, as shown in Fig. 1 in main manuscript, Au/ZrO_2 catalyst could be used for reactions repeatedly, suggesting that particle size of Au is not main factor for determining catalytic activity for the title reaction.

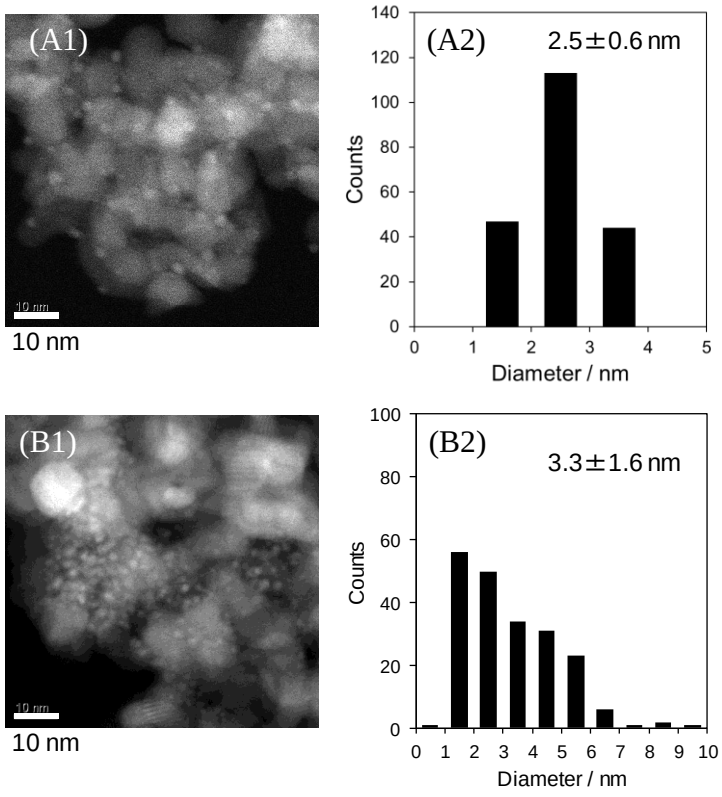


Fig. S1. HAADF-STEM images of Au/ZrO_2 catalyst (A1) before, and (B1) after the reaction of **1a** with **2a** and their particle size distribution histograms (A2 and B2).

1-2 Characterization of Au/ZrO_2 catalysts prepared at different calcination temperatures.

HAADF-STEM images and the size distribution histograms for Au/ZrO_2 catalysts prepared at different calcination temperatures are shown in Fig. S2. Calcination at a higher temperature increased the average Au NPs diameter.

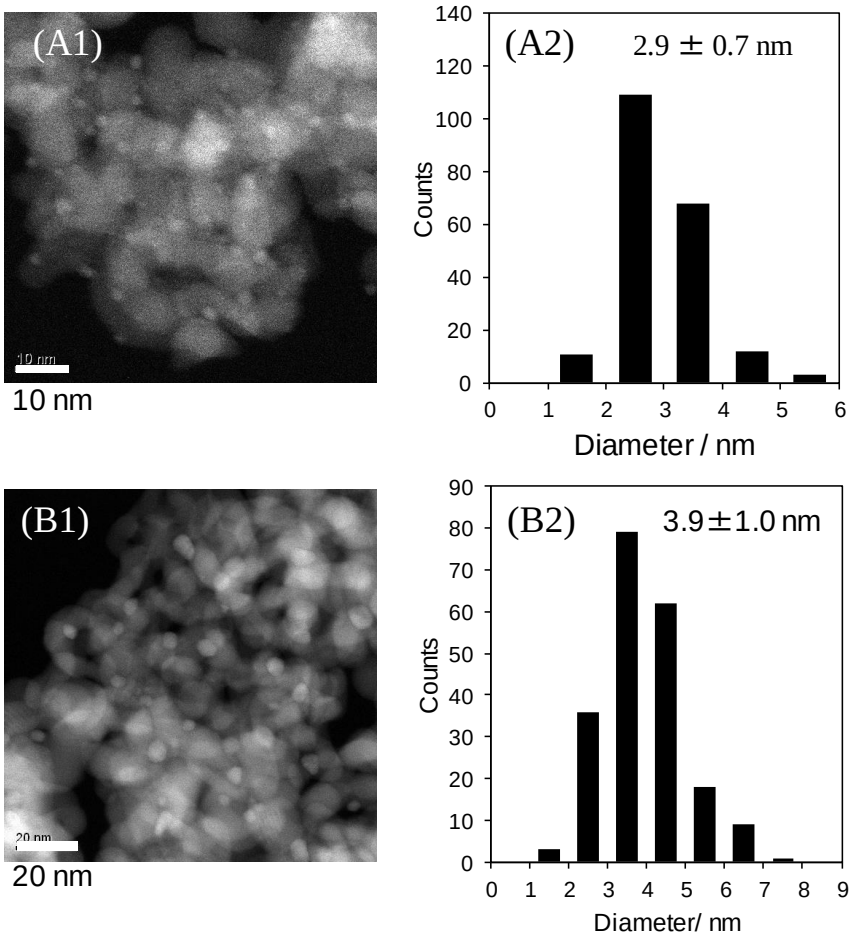


Fig. S2. HAADF-STEM images of Au/ZrO_2 catalyst calcined at 300 ^oC (A1) and 500 ^oC (B1) and their particle size distribution histograms (A2 and B2).

1-3 XRD patterns of supported Au catalysts.

XRD patterns of supported Au catalysts are shown in Fig. S3. Peaks due to (111) phase of crystalline Au particles were not identified at the patterns of Au/ZrO_2, Au/CeO_2, Au/TiO_2 and Au/Al_2O_3. In contrast, the peak appeared in the pattern of Au/SiO_2. These results are consistent with TEM data shown in Fig. 3 in the main manuscript.

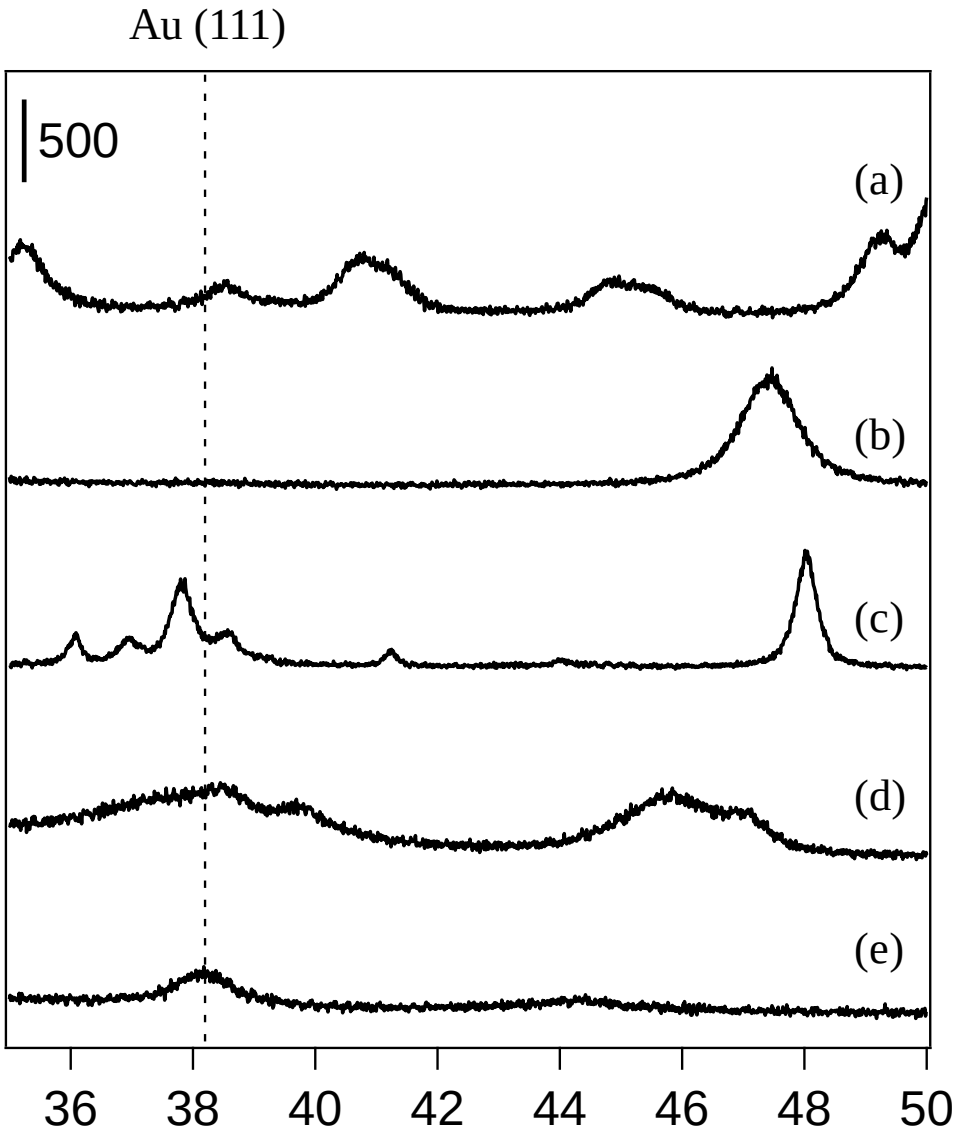


Fig. S3. XRD patterns of (a) Au/ZrO_2, (b1) Au/CeO_2, (c1) Au/TiO_2, (d1) Au/Al_2O_3, and (e) Au/SiO_2.

1-4 BET surface area of supported Au catalysts.

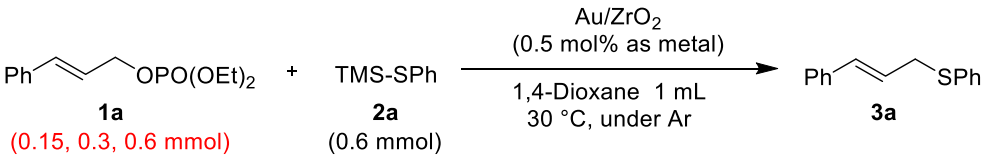
Table. S1. BET surface area of supported Au catalysts.

Catalyst[a]	BET surface area / $m^2 g^{-1}$
Au/ZrO_2	87
Au/CeO_2	117
Au/TiO_2	61
Au/Al_2O_3	171
Au/SiO_2	176

[a]Calcined at 300 ^{o}C.

2. Kinetic data for thioetherification of allyl phosphate

Reaction orders of substrates (**1a** and **2a**) for thioetherification of allyl phosphate were estimated by changing concentration of each substrate (Fig. S4 and S5). Increase of the concentration of **1a** decreased the reaction rate, and the reaction order for **1a** was estimated to be -0.5. On the other hand, reaction rate was increased by increasing of the concentration of **2a**, and the reaction order for **2a** was estimated to be 1.2. These results indicate that the C–S bond formation takes place in S_N2 manner.



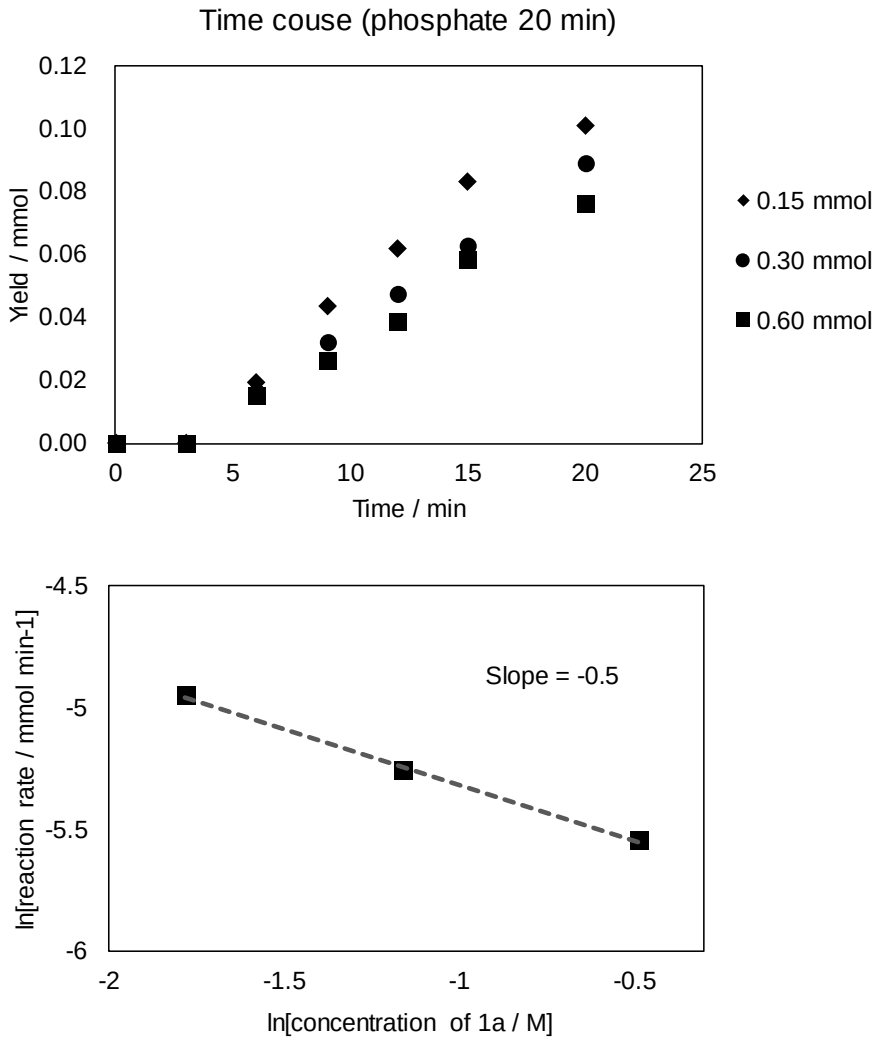
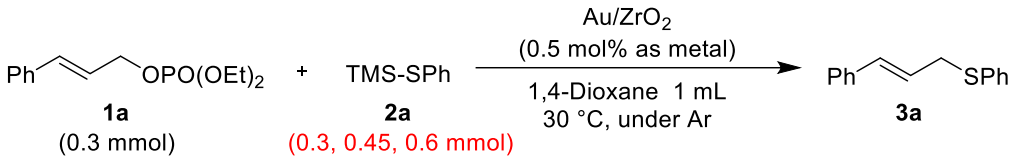
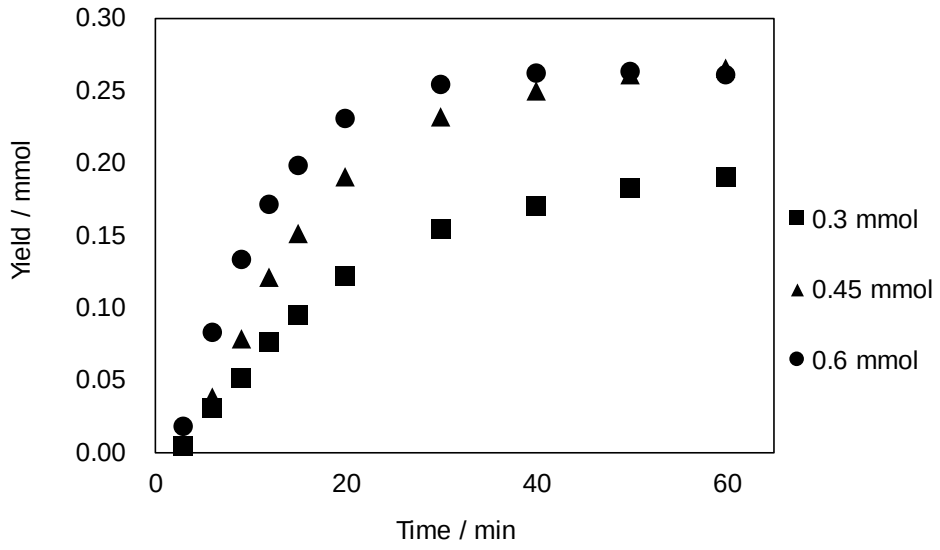


Fig. S4. Effect of concentration of **1a** on thioetherification over Au/ZrO_2.





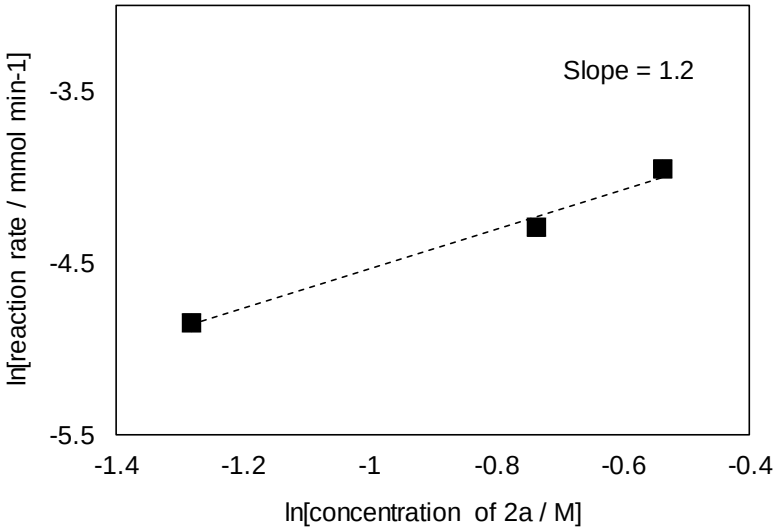
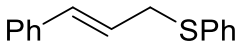


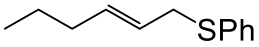
Fig. S5. Effect of concentration of **2a** on thioetherification over Au/ZrO_2.

3. Compound data



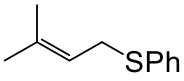
(*E*)-Cinnamyl phenyl sulfide (**3a**; CAS Registry Number 5848-60-2)

white solid; yield 92%, 62.5 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35-7.38 (m, 2H), 7.15-7.31 (m, 8H), 6.41(d, *J* = 15.8 Hz, 1H), 6.24(dt, *J* = 15.6 Hz, *J* = 7.2 Hz, 1H), 3.70(dd, *J* = 6.9 Hz, *J* = 1.1 Hz 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.7, 135.8, 132.7, 130.2, 128.8, 128.5, 127.5, 126.4, 126.3, 125.0, 37.1.



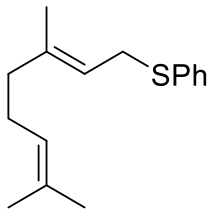
(E)-2-hexenyl phenyl sulfide, (**3b**; new compound)

yellow liquid; yield 99%, 57.1 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.14-7.33 (m, 5H), 5.44-5.56(m, 2H), 3.51(d, *J* = 5.8 Hz, 1H), 1.95(q, *J* = 6.8 Hz, 2H), 1.31(sextet, *J* = 7.4 Hz, 2H), 0.82(t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.2, 134.3, 129.8, 128.6, 126.0, 36.5, 34.3, 22.3, 13.5. HRMS (FAB) m/z $[M]^+$ calcd for 192.0973, found 192.0974.



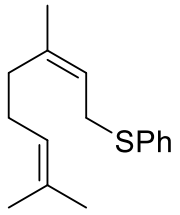
3-Methyl-2-butenyl phenyl sulfide (**3c**; CAS Registry Number 10276-04-7)

colorless liquid; yield 74%, 39.6 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.14-7.34 (m, 5H), 5.27-5.32(m, 1H), 3.54(d, *J* = 7.6 Hz, 2H), 1.71(s, 3H), 1.58(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.8, 136.4, 129.8, 128.7, 125.9, 119.2, 32.2, 25.7, 17.7.



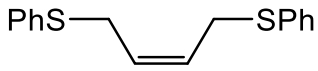
Geranyl phenyl sulfide (**3d**; CAS Registry Number 35162-74-4)

colorless liquid; yield 94% 69.5 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.14-7.34 (m, 5H), 5.28-5.32(m, 1H), 5.03-5.07(m, 1H), 3.54(d, *J* = 7.7 Hz, 2H), 1.98-2.05(m, 4H), 1.67(s, 3H), 1.59(s, 3H), 1.57(s,3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.9, 136.7, 131.6, 129.8, 128.6, 125.9, 123.9, 119.1, 39.5, 32.1, 26.4, 25.7, 17.7, 16.0.



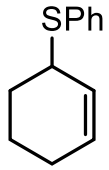
Neryl phenyl sulfide (**3e**; CAS Registry Number 35162-79-9)

yellow liquid; yield 94% 69.5 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.14-7.33 (m, 5H), 5.32(dt, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 5.09(m, 1H), 3.55(d, *J* = 7.8 Hz, 2H), 2.04(m, 4H), 1.72(d, *J* = 1.2 Hz, 3H), 1.68(s, 3H)1.60(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.0, 137.0, 132.0, 129.3, 128.7, 125.8, 123.8, 119.7, 31.9, 31.8 32.1, 26.5, 25.7, 23.4, 17.7.



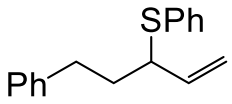
(*Z*)-1,4-bis(phenylsulfanyl)but-2-ene (**3f**; new compound)

colorless liquid, Yield 91% 74.4 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.17-7.33 (m, 10H), 5.61(ddd, *J* = 6.4 Hz, *J* = 4.8 Hz, *J* = 1.2 Hz, 2H), 3.40(dd, *J* = 4.7 Hz, *J* = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.6, 130.4, 128.8, 127.9, 126.5, 31.0. HRMS (FAB) m/z $[M]^+$ calcd for 272.0693, found 272.0699.



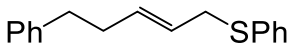
(2-Cyclohexenyl) phenyl sulfide (**3g**; CAS Registry Number 3467-73-0)

colorless liquid, Yield 86% 49.0 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.39-7.42 (m, 2H), δ7.18-7.30 (m, 3H), 5.74-5.85(m, 2H), 3.85(m, 1H), 1.58-2.06(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.8, 131.2, 130.4, 128.8, 126.8, 126.5, 43.8, 28.7, 24.9, 19.4.



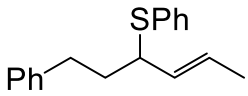
5-Phenyl-3-(phenylsulfanyl)pent-1-ene (**3h-α**; CAS Registry Number 81650-71-7)

colorless liquid, Yield 90% **(3h-α + 3h-γ),** 68.7 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.10-7.35 (m, 10H), 5.72 (ddd, *J* = 17.0 Hz, *J* = 9.1 Hz, *J* = 8.9 Hz, 1H), 4.98(dd, *J* = 10.0 Hz, *J* = 1.3 Hz, 1H), 4.89(d, *J* = 16.9 Hz, 1H), 3.56(dt, *J* = 8.4 Hz, *J* = 6.2 Hz, 1H), 2.69-2.83(m, 2H), 1.87-2.06(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.3, 138.5, 134.4, 132.7, 128.6, 128.5, 128.4, 127.0, 125.9, 116.1, 51.3, 35.6, 33.2.



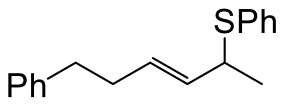
(*E)*-5-Phenyl-1-(phenylsulfanyl)pent-2-ene **(3h-γ**; CAS Registry Number 147330-95-8)

colorless liquid, Yield 90% (**3h-α + 3h-γ),** 68.7 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.10-7.35 (m, 10H), 5.54(m, 2H), 3.49(d, *J* = 5.8 Hz, 2H), 2.61(t, *J* = 7.6 Hz, *2*H), 2.29 (dt, *J* = 8.7 Hz, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.6, 136.1, 133.3, 129.8, 128.7, 128.4, 128.2, 126.1, 125.8, 125.6, 36.4, 35.6, 34.0.



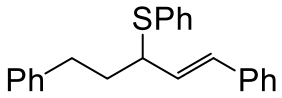
(*E*)-phenyl (1-phenylhex-4-en-3-yl) sulfide (**3i-α**; new compound)

Yellow liquid, Yield 93% (**3i-α** + **3i-γ**)**,** 74.9 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.08-7.38 (m, 10H), 5.29-5.46 (m, 2H), 3.54 (dt, *J* = 8.0Hz, *J* = 6.0 Hz, 1H), 2.54(m, *2*H), 1.84-2.04 (m, 2H), 1.62(d, *J* = 4.9 Hz, 3H); HRMS (FAB) m/z $[M]^+$ calcd for 268.1286, found 268.1288.



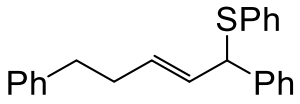
(*E)*-phenyl (6-phenylhex-3-en-2-yl) sulfide (**3i-γ**; new compound**)**

Yellow liquid, Yield 93% (**3i-α** + **3i-γ**)**,** 74.9 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.08-7.38 (m, 10H), 5.29-5.46 (m, 2H), 3.72(quin, *J* = 7.0 Hz, 1H), 2.65-2.81(m, *2*H), 2.21-2.27 (m, 2H), 1.34(d, *J* = 6.8 Hz, 3H); HRMS (FAB) m/z $[M]^+$ calcd for 268.1286, found 268.1288.



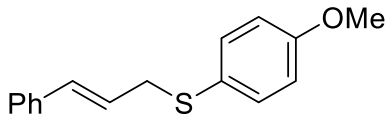
(*E*)-1,5-diphenylpent-1-en-3-yl phenyl sulfide (**3j-α**; new compound)

Yellow liquid, Yield 74% (**3j-α** + **3j-γ**)**,** 73.4 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.06-7.37 (m, 15H), 6.04-6.16 (m, 2H), 3.69(dt, *J* = 8.2 Hz, *J* = 6.2 Hz, 1H), 2.73-2.86(m, *2*H), 1.97 -2.16; HRMS (FAB) m/z $[M+H]^+$ calcd for 333.1520, found 333.1521.



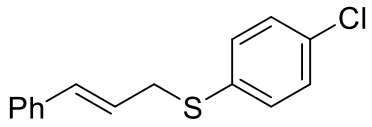
(*E*)-1,5-diphenylpent-2-en-1-yl phenyl sulfide **(3j-γ**; new compound)

Yellow liquid, Yield 74% (**3j-α + 3j-γ**)**,** 73.4 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.06-7.37 (m, 15H), 5.75(dd, *J* = 15.1 Hz, *J* = 8.0 Hz, 1H), 5.45(dt, *J* = 15.2 Hz, *J* = 6.8 Hz, 1H), 4.74(d, *J* = 8.4 Hz, 1H), 2.55(dt, *J* = 7.8 Hz, *J* = 6.8 Hz, 2H) 2.27(dt, *J* = 7.4 Hz, *J* = 7.3 Hz, 1H); HRMS (FAB) m/z $[M+H]^+$ calcd for 333.1520, found 333.1521.



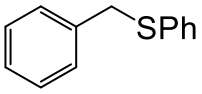
(*E*)- cinnamylsulfanyl-4-methoxybenzene (**3k**; new compound)

white solid; yield 90%, 69.2 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35 (d, *J* = 8.7 Hz 2H), 7.17-7.27 (m, 5H), 6.81(d, *J* = 8.7 Hz, 2H), 6.17-6.28(m, 2H), 3.76(s, 3H), 3.57(d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.2, 136.8, 134.4, 132.4, 128.4, 127.4, 126.2, 125.6, 125.5, 114.4, 55.3, 39.2. HRMS (FAB) m/z $[M]^+$ calcd for 256.0922, found 256.0914.



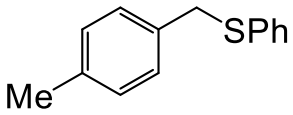
(*E*)- cinnamylsulfanyl-4-chlorobenzene (**3l**; CAS Registry Number 136811-66-0)

white solid; yield 82%, 64.2 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.18-7.31 (m, 10H), 6.40(d, *J* = 15.6 Hz, 2H), 6.21(dt, *J* = 15.6 Hz, *J* = 7.2 Hz, 2H), 3.67(d, *J* = 7.2 Hz, 2H), 3.57(d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.5, 134.2, 133.0, 132.5, 131.7, 128.9, 128.5, 127.7, 126.3, 124.6, 37.4.



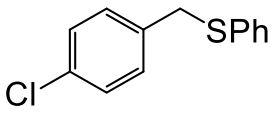
Benzyl phenyl sulfide (**5a**; CAS Registry Number 831-91-4)

white solid; yield 79%, 47.5 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.14-7.31 (m, 10H), 4.11(s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.4, 136.3, 129.7, 128.8, 128.5, 127.1, 126.3, 39.0.



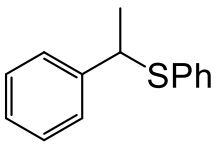
4-Methylbenzyl phenyl sulfide (**5b**; CAS Registry Number 5023-65-4)

white solid; yield 90%, 57.9 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.07-7.31 (m, 9H), 4.08 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.8, 136.6, 134.2, 129.5, 129.1, 128.8, 128.6, 126.1, 38.6, 21.1.



4-Chlorobenzyl phenyl sulfide (**5c**; CAS Registry Number 7693-30-3)

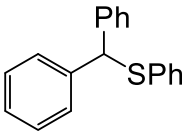
white solid; yield 92%, 64.8 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.16-7.29 (m, 9H), 4.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.1, 135.6, 132.9, 130.2, 130.1, 128.9, 128.5, 126.6, 38.5.



Phenyl 1-phenylethyl sulfide (**5d**; CAS Registry Number 21213-26-3)

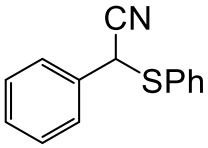
colorless liquid; yield 93%, 59.8 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.17-7.30 (m, 10H), 4.33 (q, J = 7.0 Hz, 1H), 1.62 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100

MHz, $CDCl_3$, ppm) δ 143.1, 135.0, 132.4, 128.6, 128.3, 127.2, 127.1, 127.1, 47.9, 22.3.



Diphenylmethyl phenyl sulfide (**5e**; CAS Registry Number 21122-20-3)

colorless liquid; yield 91%, 75.5 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39-7.42 (m, 4H), 7.09-7.30 (m, 11H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.9, 136.1, 130.4, 128.7, 128.5, 128.3, 127.2. 126.5, 57.4.

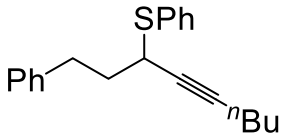


2-Phenyl-2-(phenylsulfanyl)acetonitrile (**5f**; new compound)

yellow liquid; yield 73%, 49.3 mg (0.30 mmol scale); hexane/EtOAc = 50/1; 1H NMR (400 MHz, CDCl3, ppm) δ 7.45-7.47 (m, 2H), 7.30-7.41 (m, 9H), 4.95 (s, 1H); 13C NMR (100 MHz, CDCl3, ppm) δ 135.3, 132.3, 130.1, 129.9, 129.2, 128.9, 128.9, 127.8, 117.8, 41.6. HRMS (FAB) m/z $[M]^+$ calcd for 225.0612, found 225.0622.

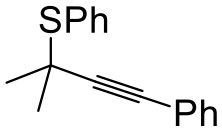
2-Hexynyl phenyl sulfide (**7a**; CAS Registry Number 72734-93-1)

yellow liquid; yield 60%, 33.1 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41-7.43 (m, 2H), 7.18-7.31 (m, 3H), 3.62 (t, *J* = 2.3 Hz, 2H), 2.13 (tt, *J* = 6.9, 2.3 Hz, 2H), 1.47 (sextet, *J* = 7.2 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.6, 129.7, 128.8, 126.5, 84.0, 75.6, 23.1, 22.1, 20.8, 13.4.



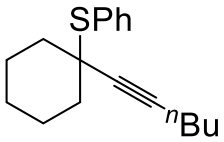
phenyl 1-phenylnon-4-yn-3-yl sulfide (**7b**; new compound)

brown liquid; yield 79%, 73.1 mg (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45-7.47 (m, 2H), 7.16-7.31 (m, 3H), 3.75-3.80 (m, 1H), 2.76-2.94 (m, 2H), 2.20(dt, *J* = 6.9 Hz, *J* = 2.2 Hz 2H), 1.98-2.05 (m, 2H), 1.33-1.49(m, 4H), 0.89(t, *J* = 7.2 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 141.1, 134.1, 132.6, 128.6, 128.5, 128.4, 127.4, 126.0, 85.5, 38.2, 37.0, 33.2, 30.8, 21.9, 18.5, 13.6. HRMS (FAB) m/z $[M]^+$ calcd for 308.1599, found 308.1591.



2-methyl-4-phenylbut-3-yn-2-yl phenyl sulfide (**7c**; new compound)

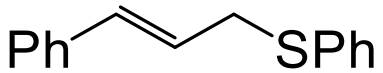
colorless oil; yield 41%, 30.2 mg, (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.68-7.70 (m, 2H), 7.26-7.39 (m, 8H), 1.63 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.9, 132.4, 131.4, 129.1, 128.4,128.1, 127.9, 123.2, 93.9, 83.2, 42.5, 30.4. HRMS (FAB) m/z $[M+H]^+$ calcd for 253.1051, found 253.1047.



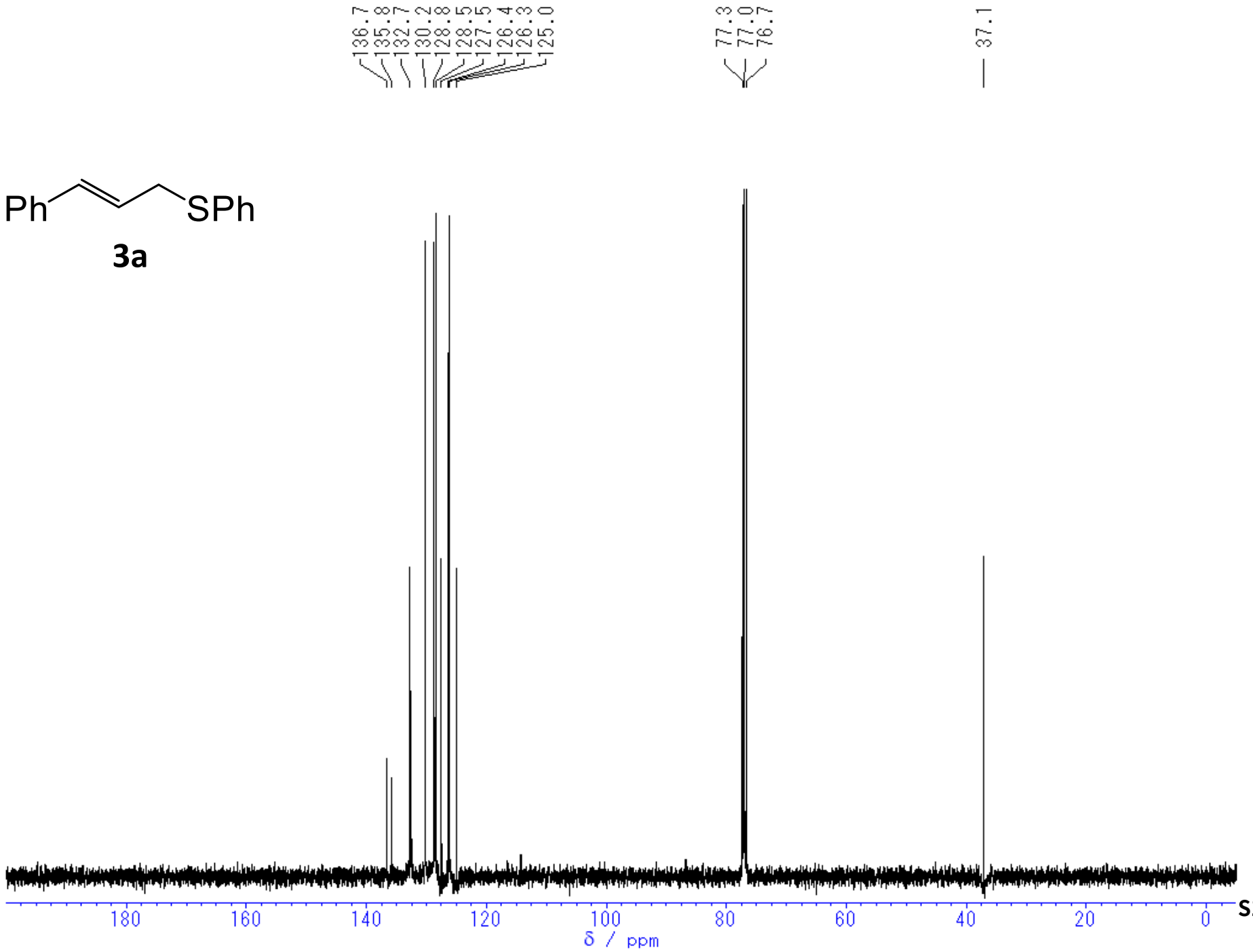
1-(hex-1-yn-1-yl)cyclohexyl phenyl sulfide (**7d**; new compound)

colorless oil; yield 29%, 23.7 mg, (0.30 mmol scale); hexane/EtOAc = 50/1; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.61-7.64 (m, 2H), 7.29-7.37 (m, 3H), 2.21 (t, *J* = 6.9 Hz 2H), 1.88-1.90 (m, 2H), 1.57-1.64(m, 8H), 1.32-1.50(m, 4H), 0.90(t, *J* = 7.2 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.8, 131.8, 128.6, 128.2, 85.8, 82.5, 48.0, 38.9, 31.0, 25.5, 23.5, 21.9, 18.5, 13.6. HRMS (FAB) m/z $[M+H]^+$ calcd for 273.1677, found 273.1677.

4. Copy of NMR charts for the products



3a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128.5
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Ph
SPh
3a
180
160
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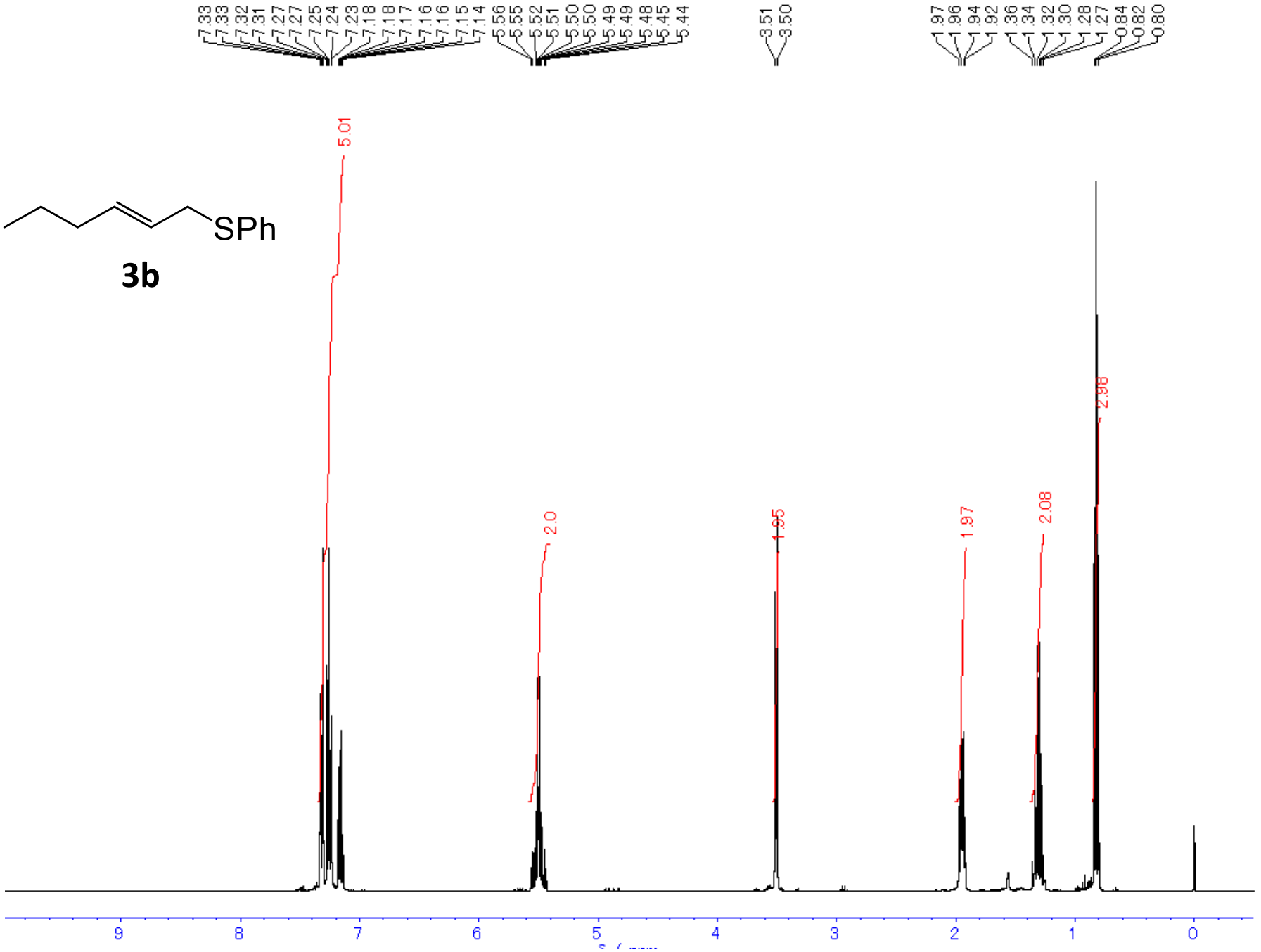
120
100
80
60
40
20
0
δ / ppm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3.50
1.97
1.96
1.94
1.92
1.36
1.34
1.32
1.30
1.28
1.27
0.84
0.82
0.80
SPh
3b
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1.97
2.08
2.98
9
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7
6
5
4
3
2
1
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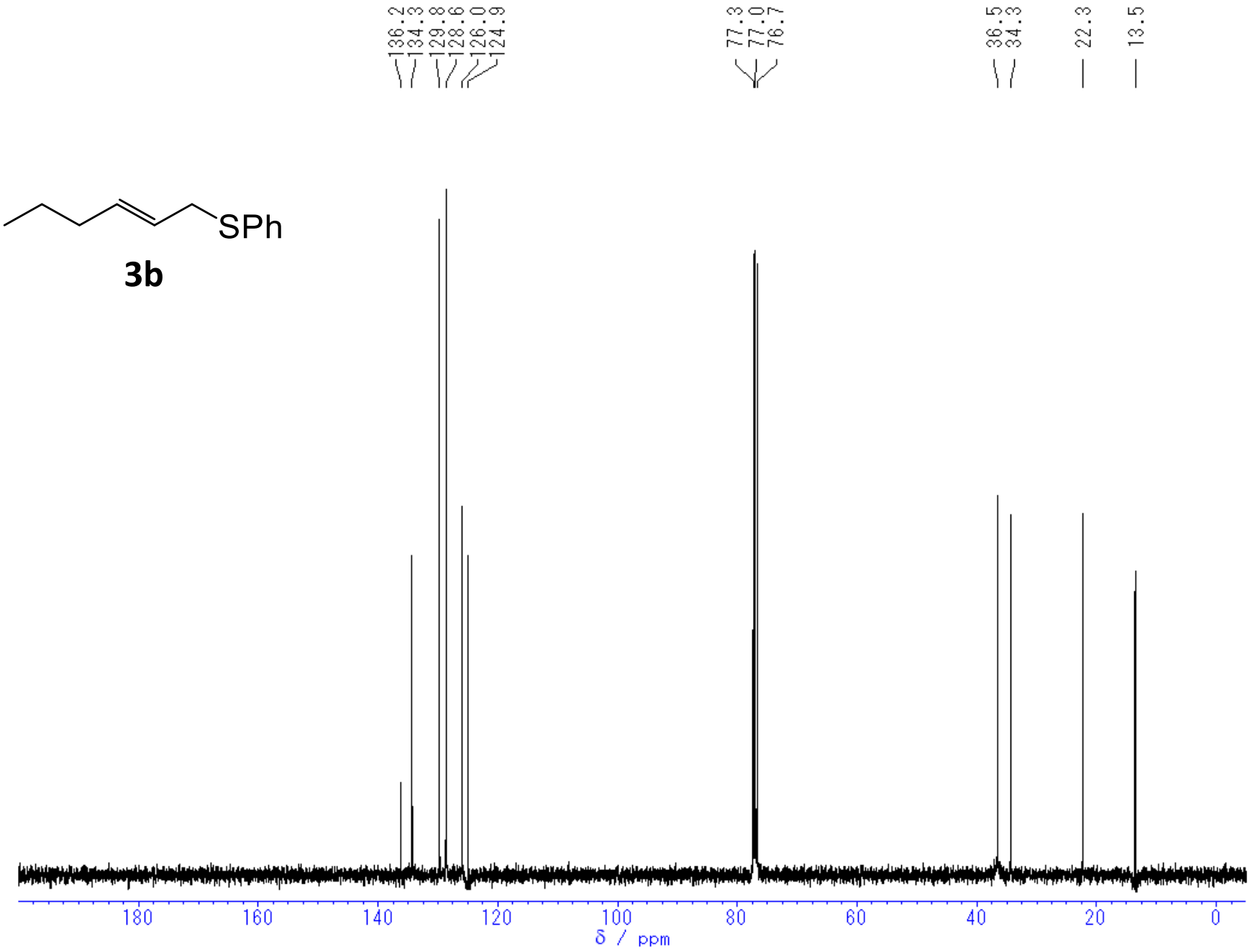
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34.3
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13.5
SPh
3b
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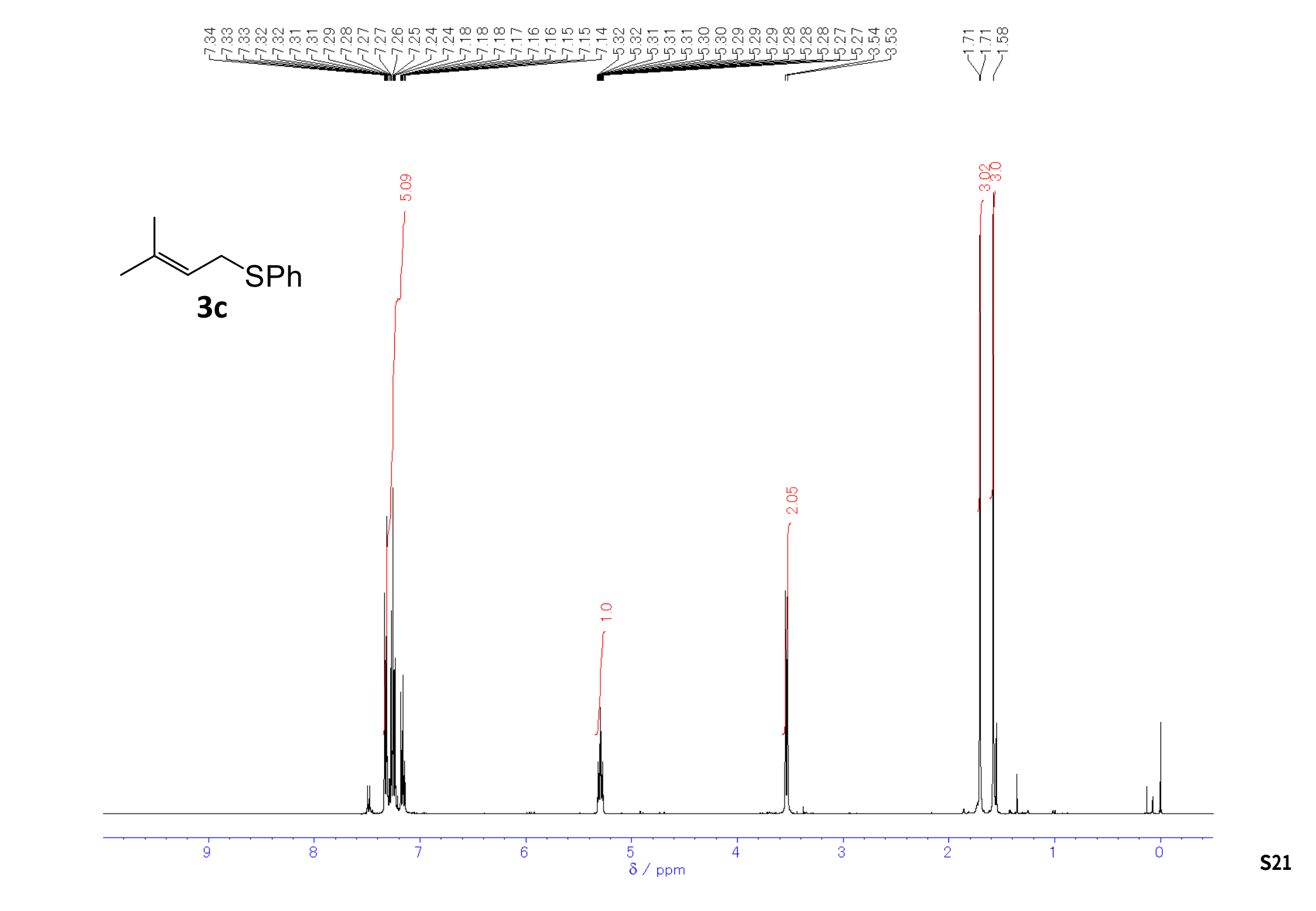
160
140
120
100
80
60
40
20
0
δ / ppm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7.14
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5.31
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5.27
5.27
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3.53
1.71
1.71
1.58
SPh
3c
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2.05
1.0
9
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6
5
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3
2
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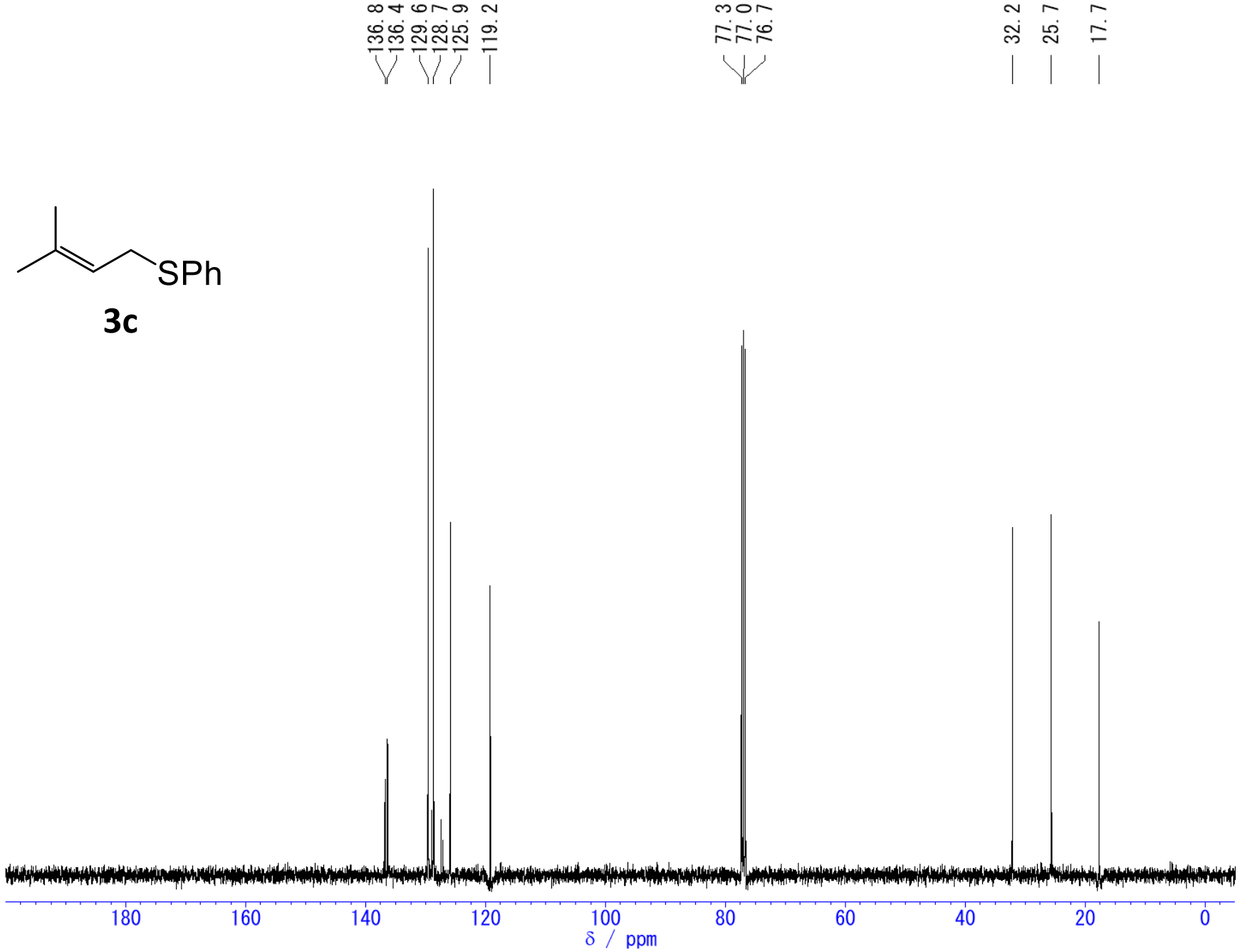
0
δ / ppm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136.4
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128.7
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119.2
77.3
77.0
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32.2
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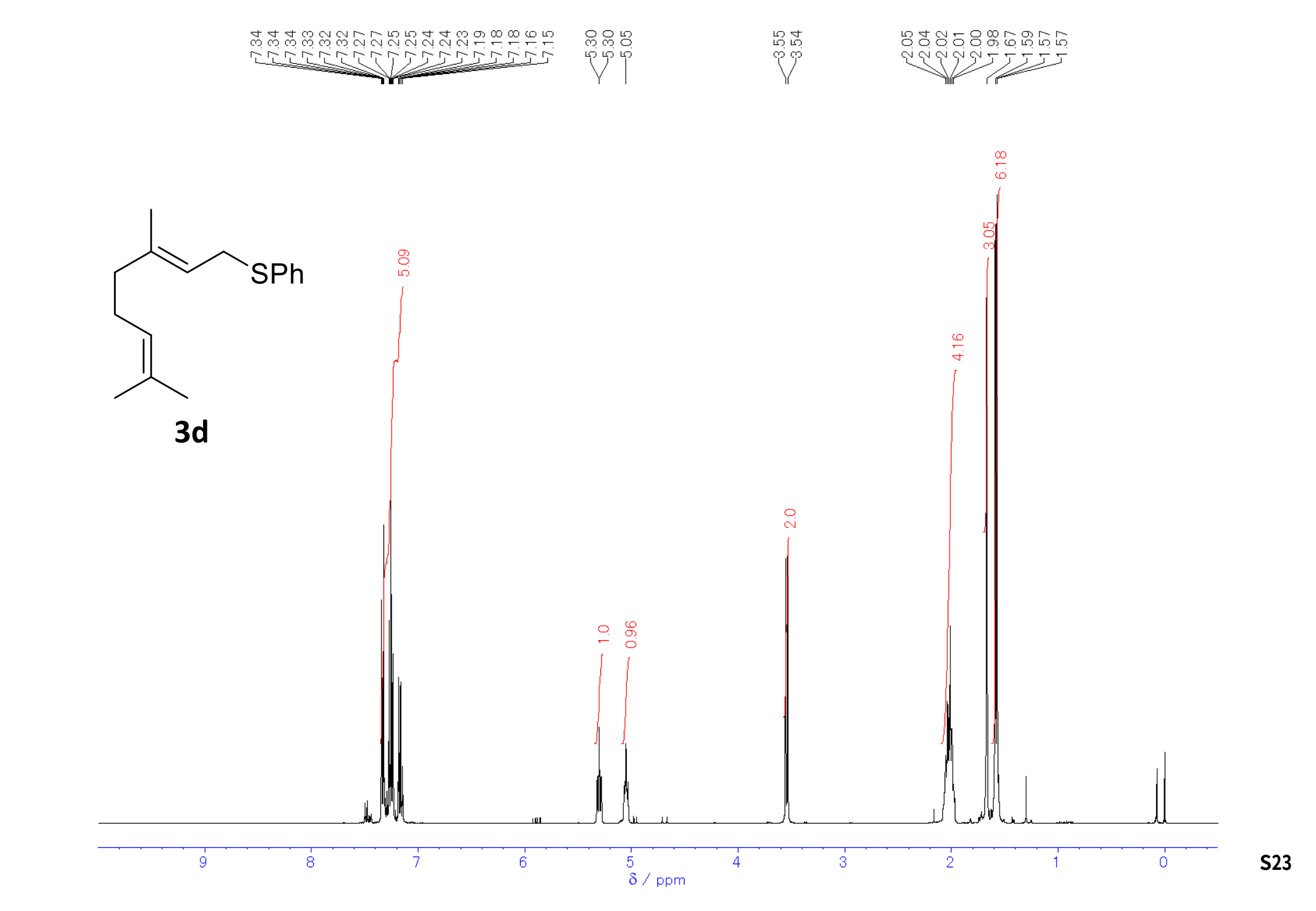
17.7
SPh
3c
180
160
140
120
100
80
60
40
20
0
δ / ppm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7.19
7.18
7.18
7.16
7.15
5.30
5.30
5.05
3.55
3.54
2.05
2.04
2.02
2.01
2.00
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1.67
1.59
1.57
1.57
SPh
3d
5.09
1.0
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3.05
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9
8
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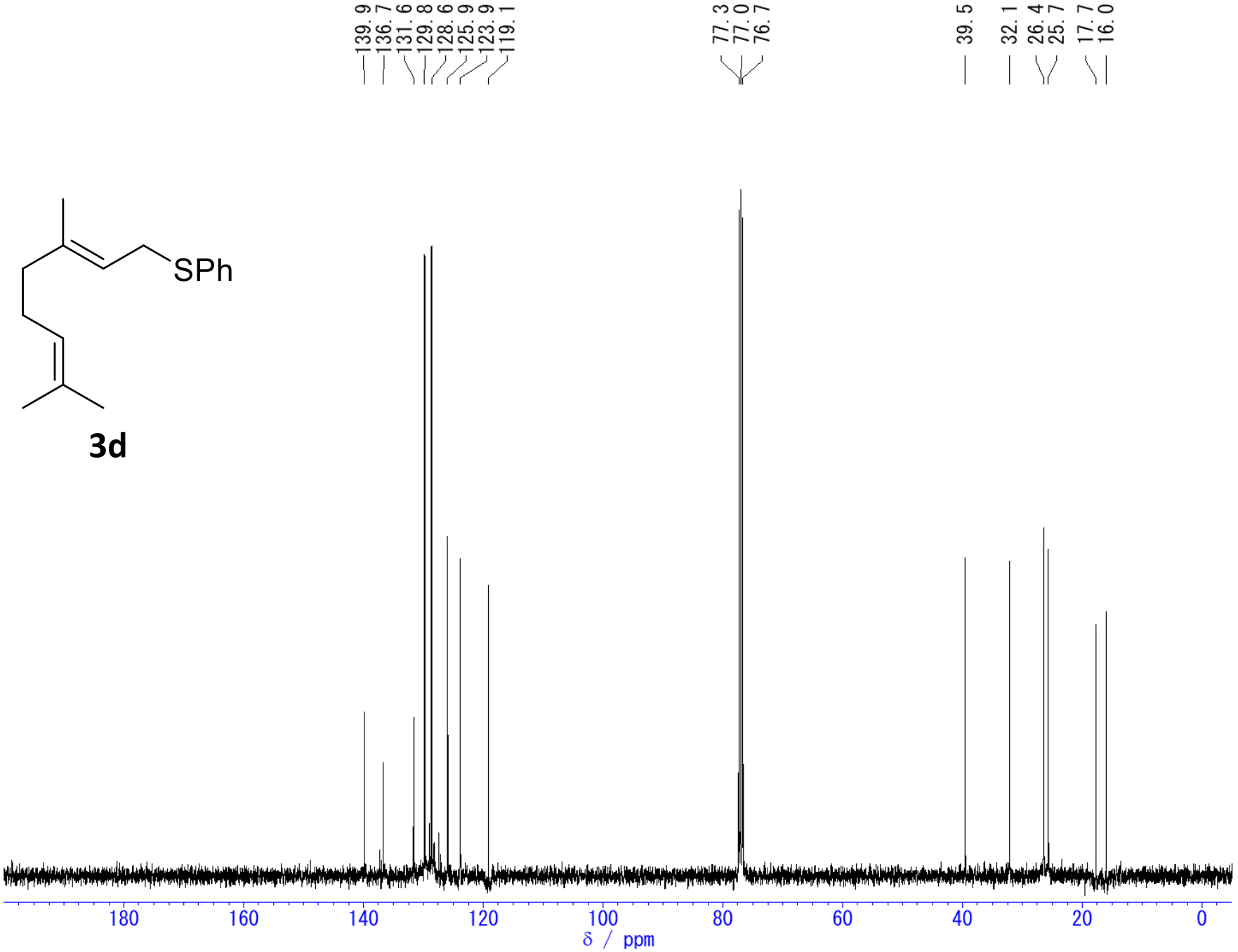
6
5
4
3
2
1
0
δ / ppm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131.6
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123.9
119.1
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32.1
26.4
25.7
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16.0
SPh
3d
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160
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120
100
80
60
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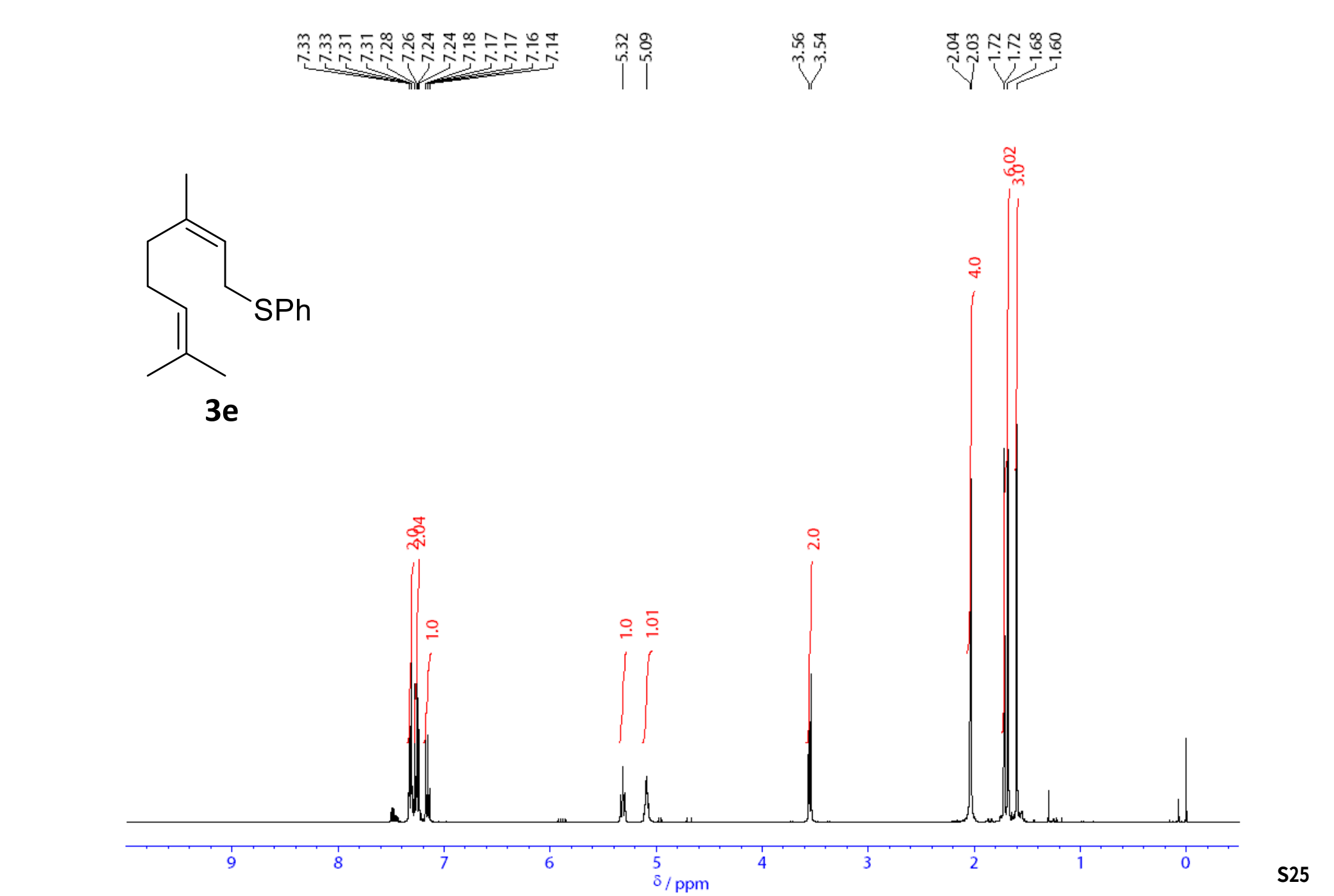
20
0
δ / ppm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5.32
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3.54
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2.03
1.72
1.72
1.68
1.60
SPh
3e
2.04
2.00
1.0
1.0
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3.02
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9
8
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6
5
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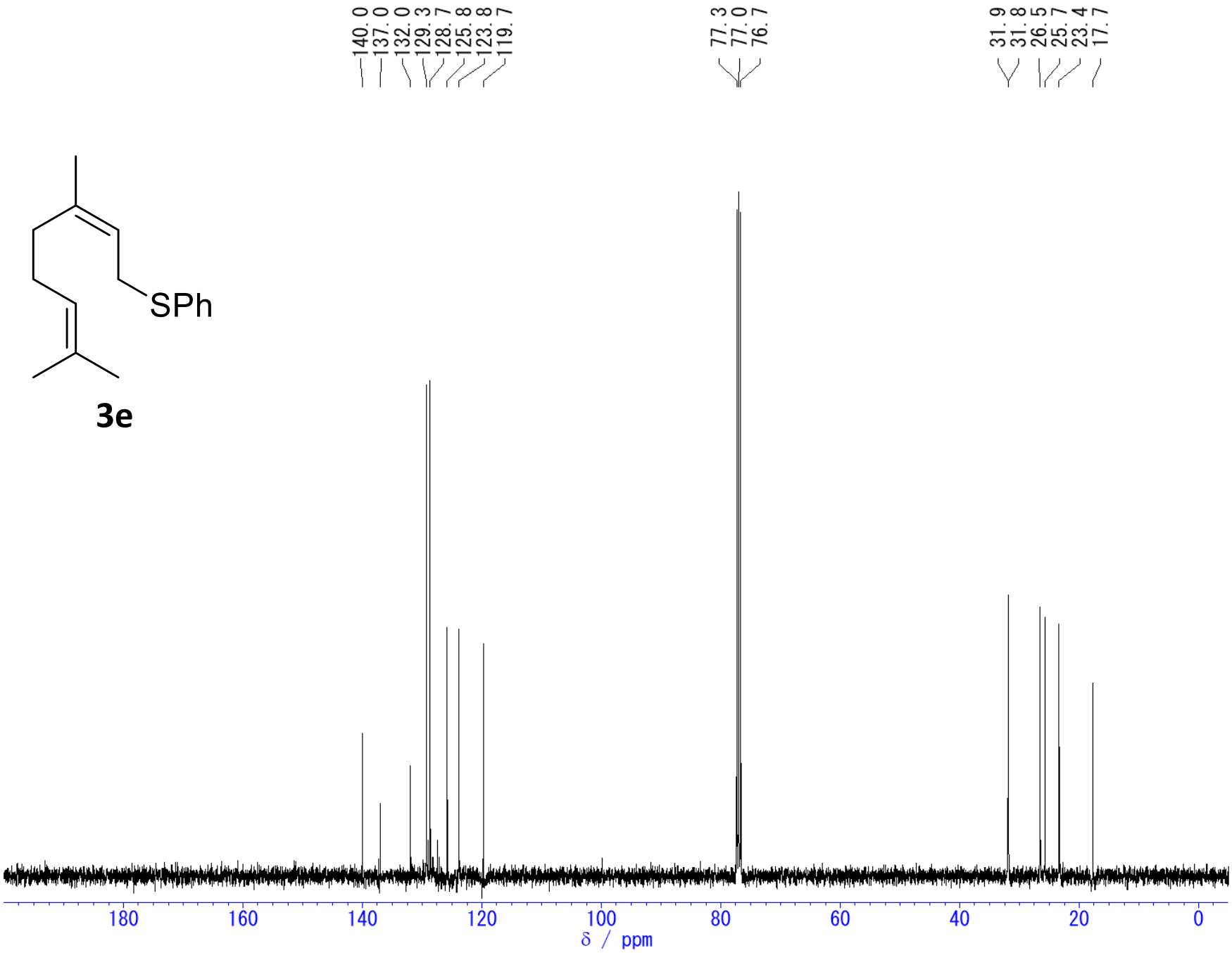
δ / ppm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17.7
SPh
3e
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100
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20
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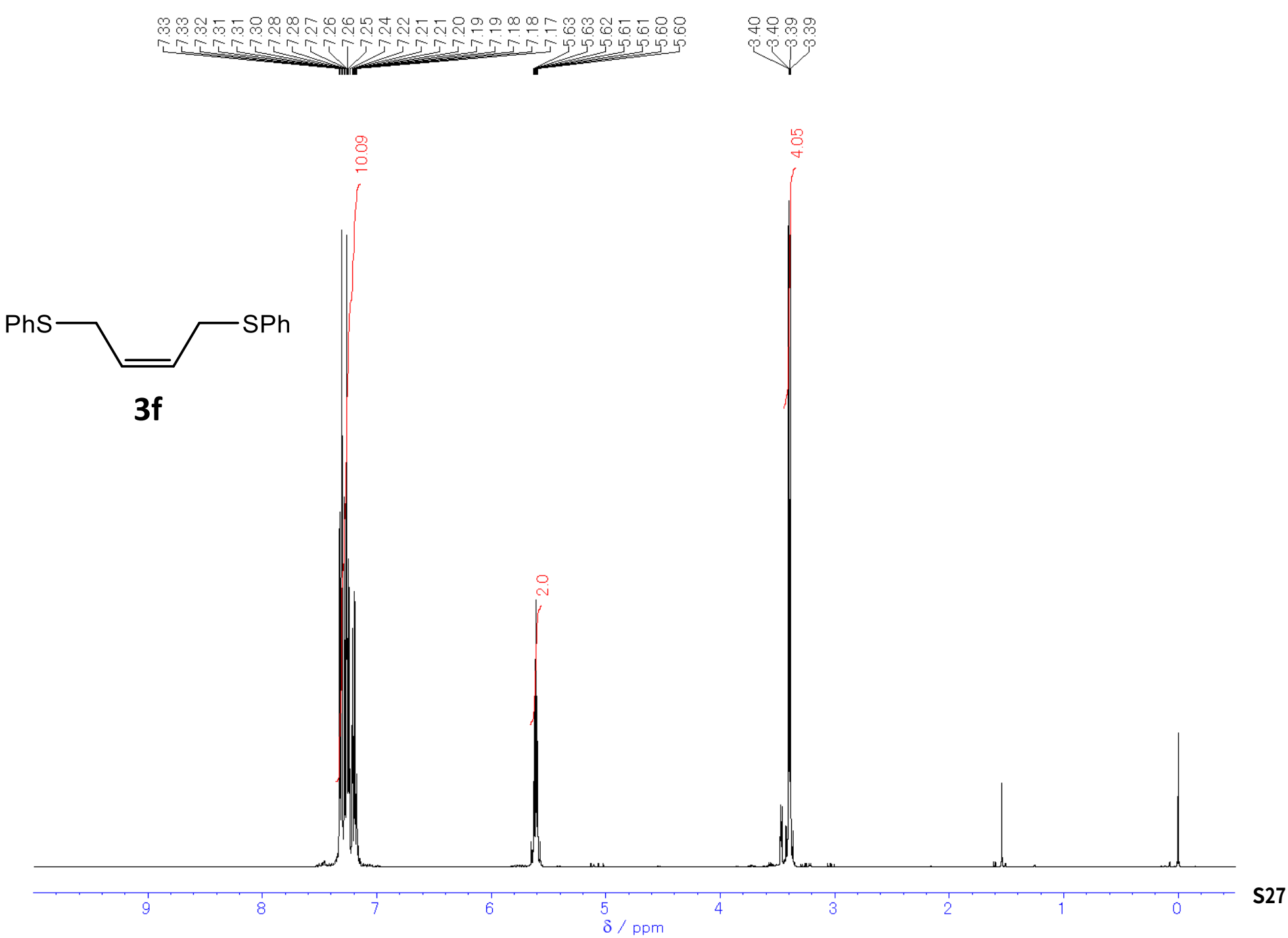
δ / ppm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7.17
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5.61
5.60
5.60
3.40
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3.39
10.09
4.05
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PhS
SPh
3f
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5
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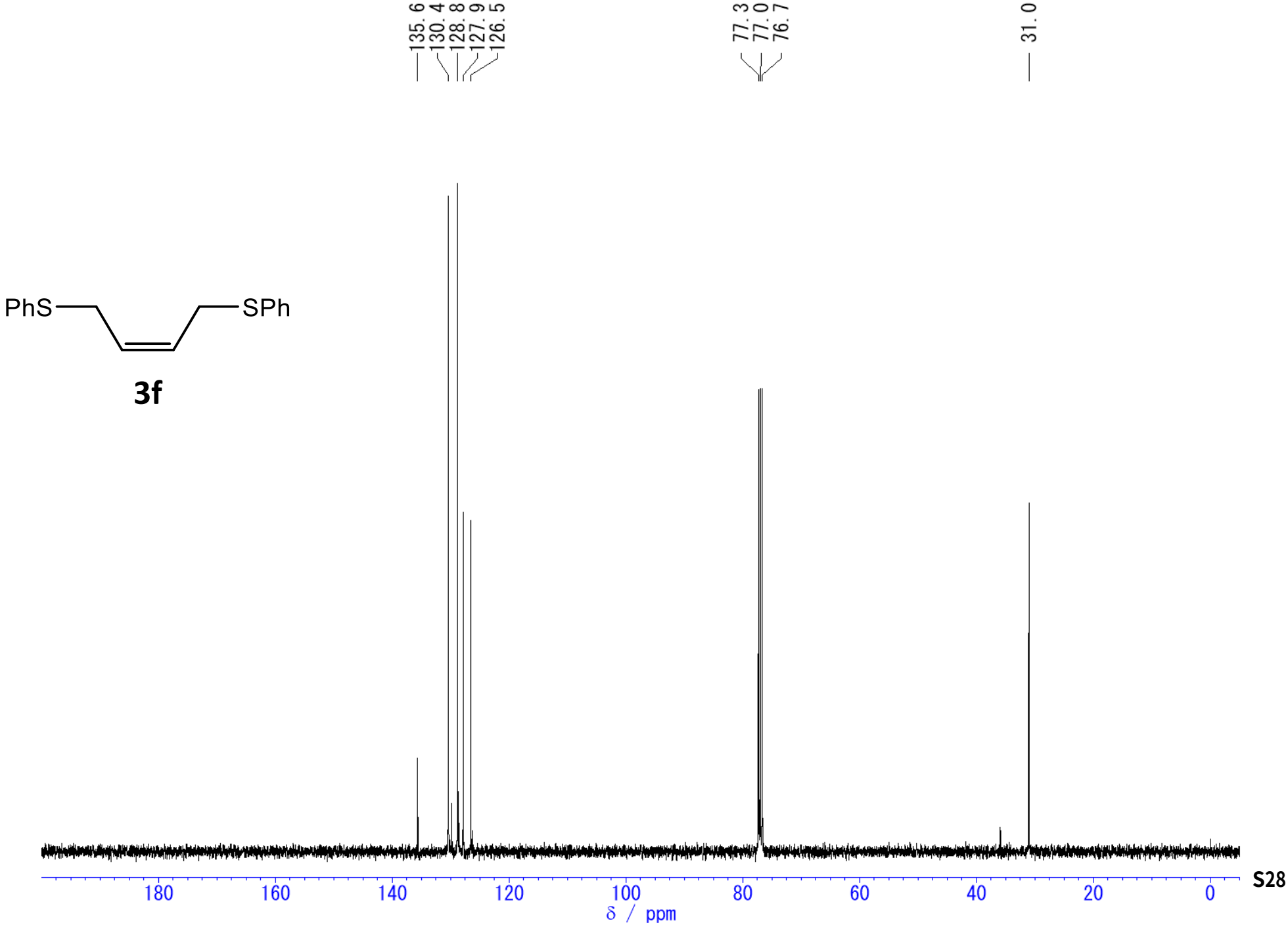
3
2
1
0
δ / ppm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31.0
PhS
SPh
3f
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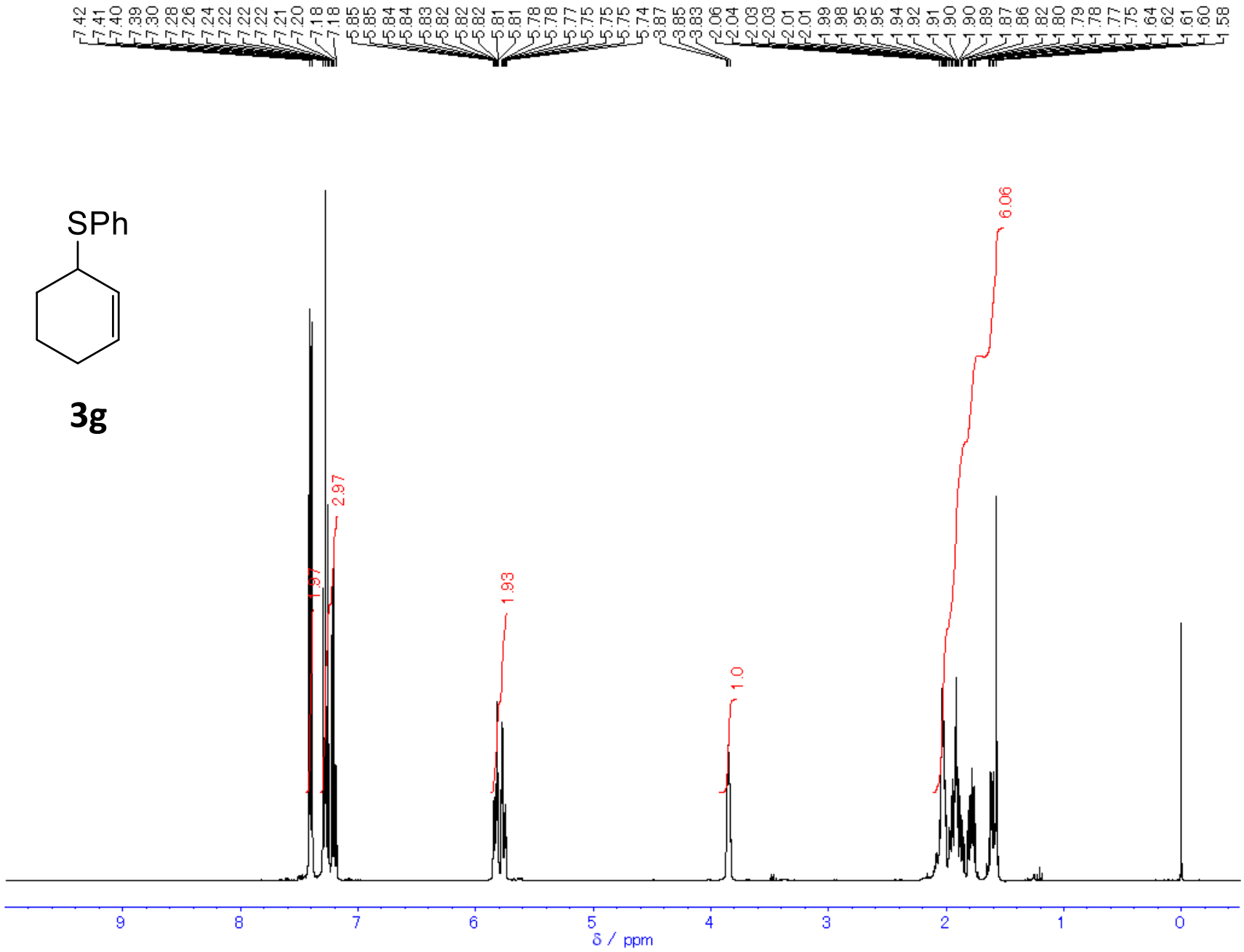
160
140
120
100
80
60
40
20
0
δ / ppm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3g
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5
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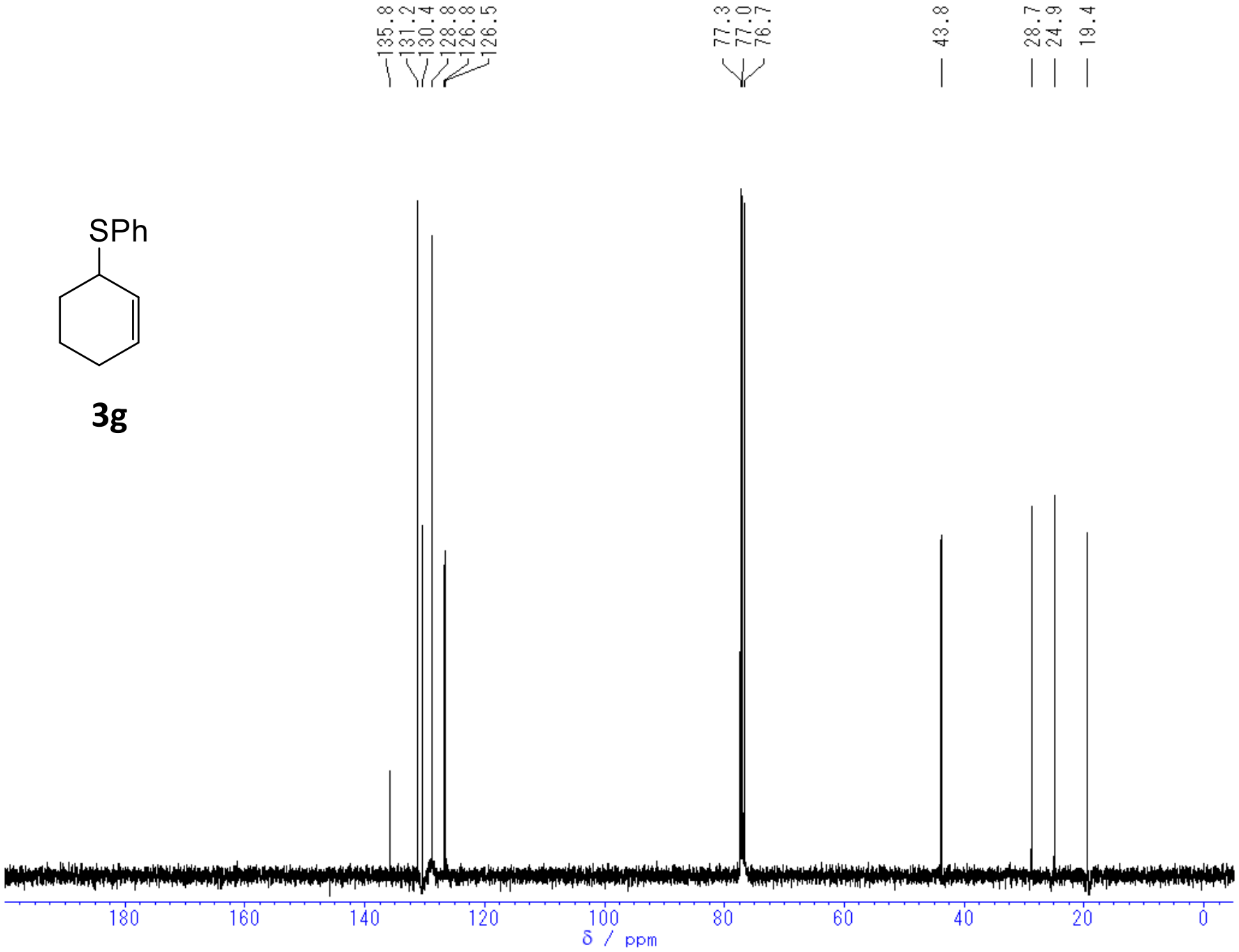
δ / ppm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19.4
SPh
3g
180
160
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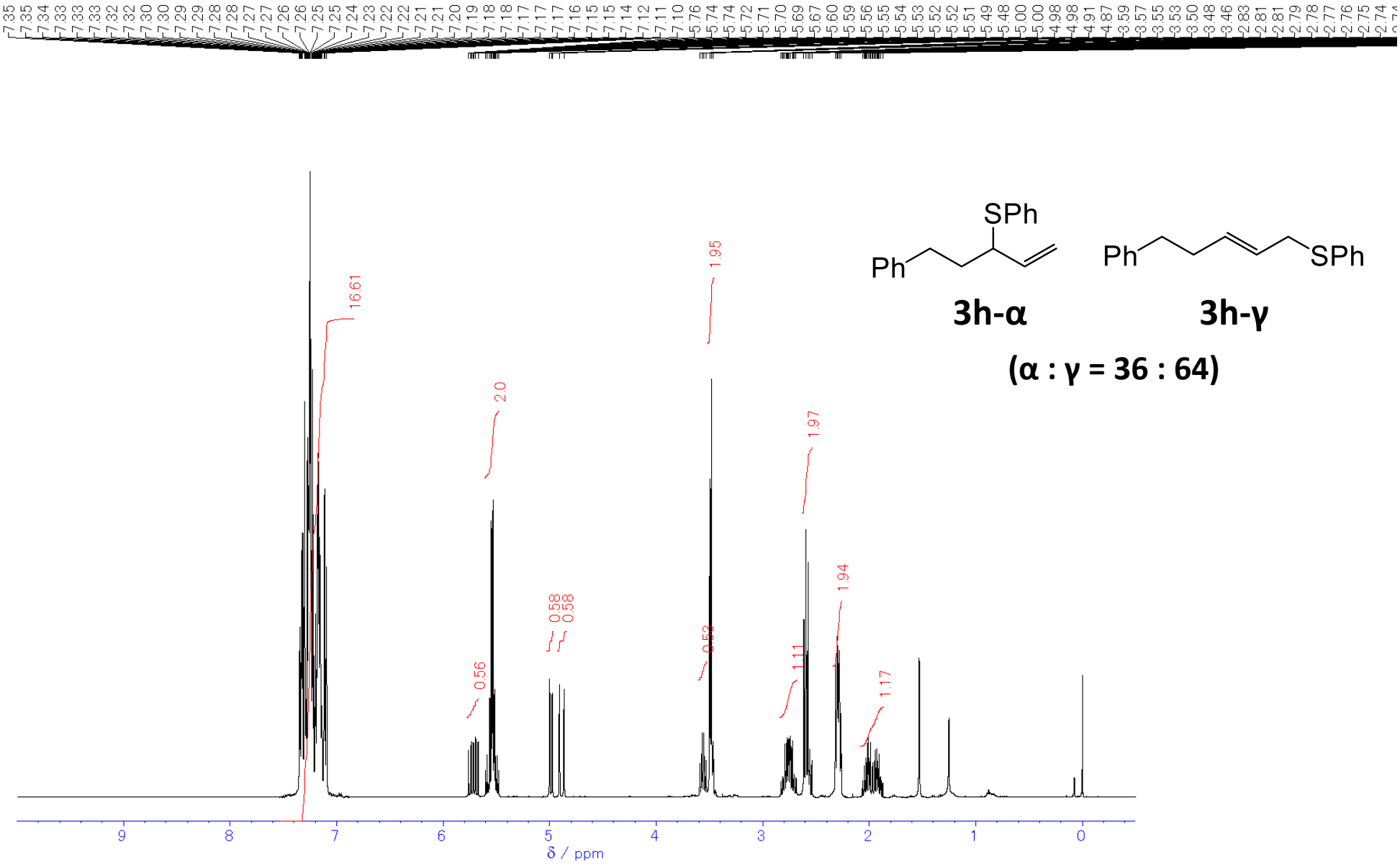
120
100
80
60
40
20
0
δ / ppm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Ph
3h-α
Ph
SPh
3h-γ
(α : γ = 36 : 64)
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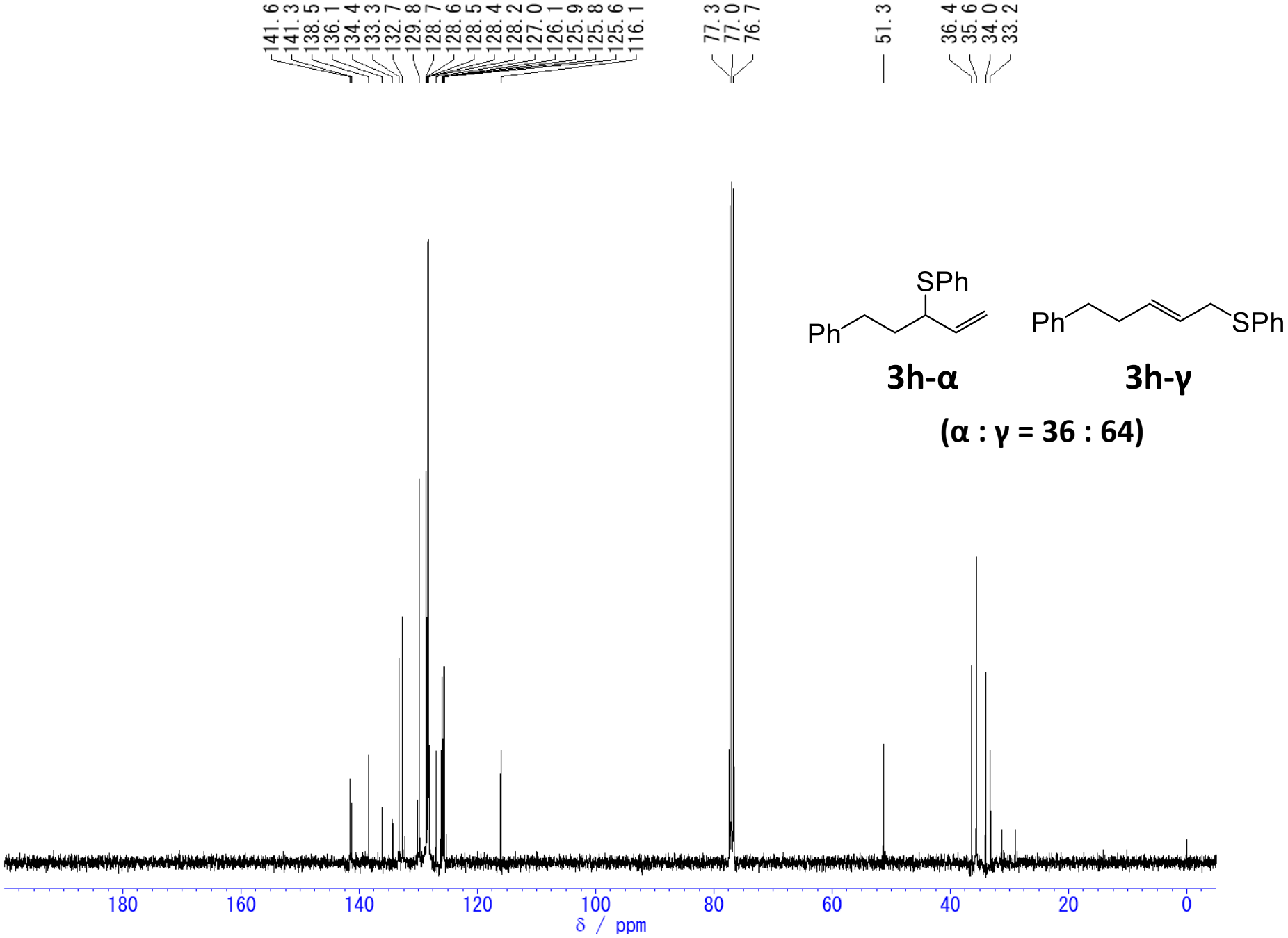
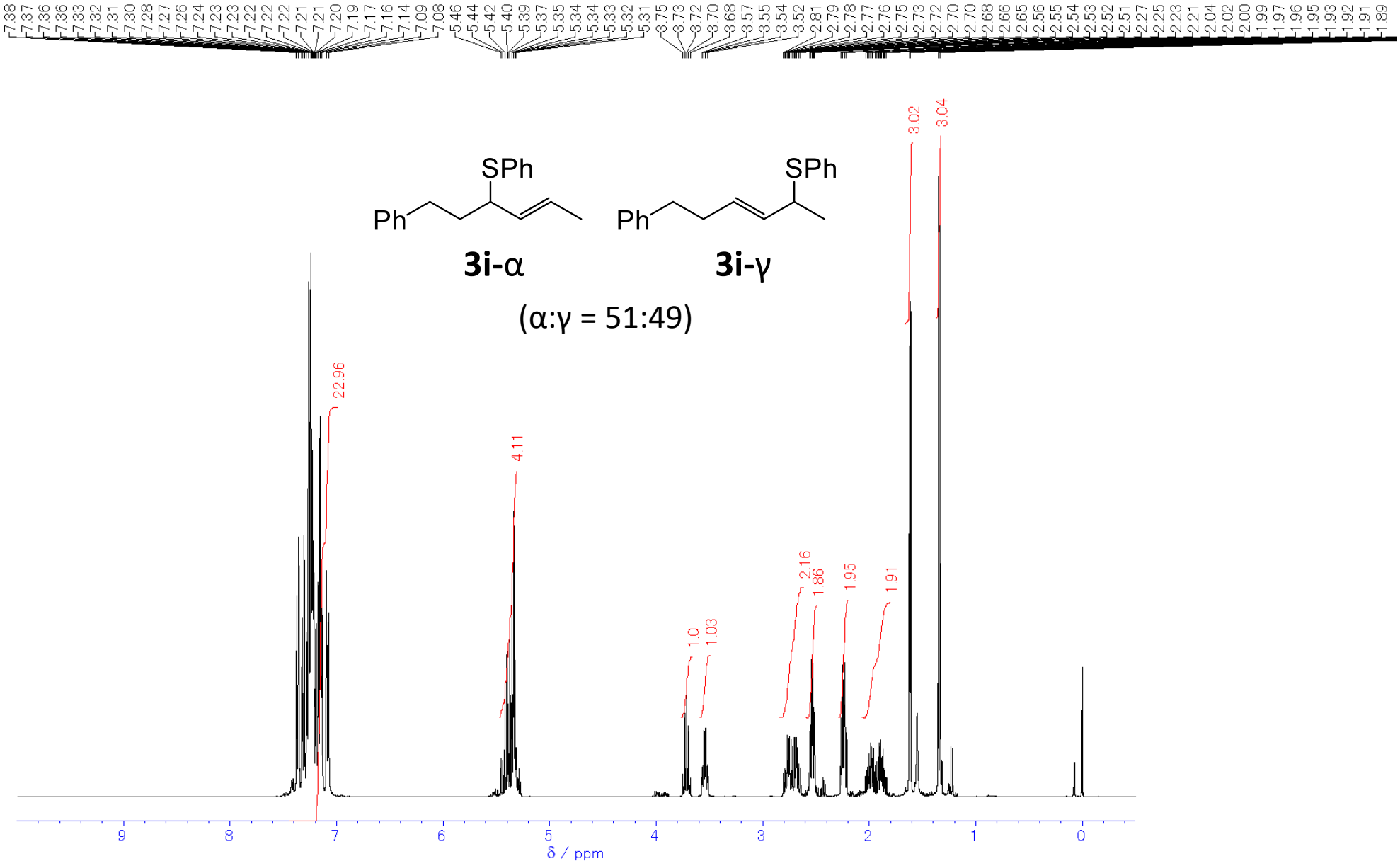
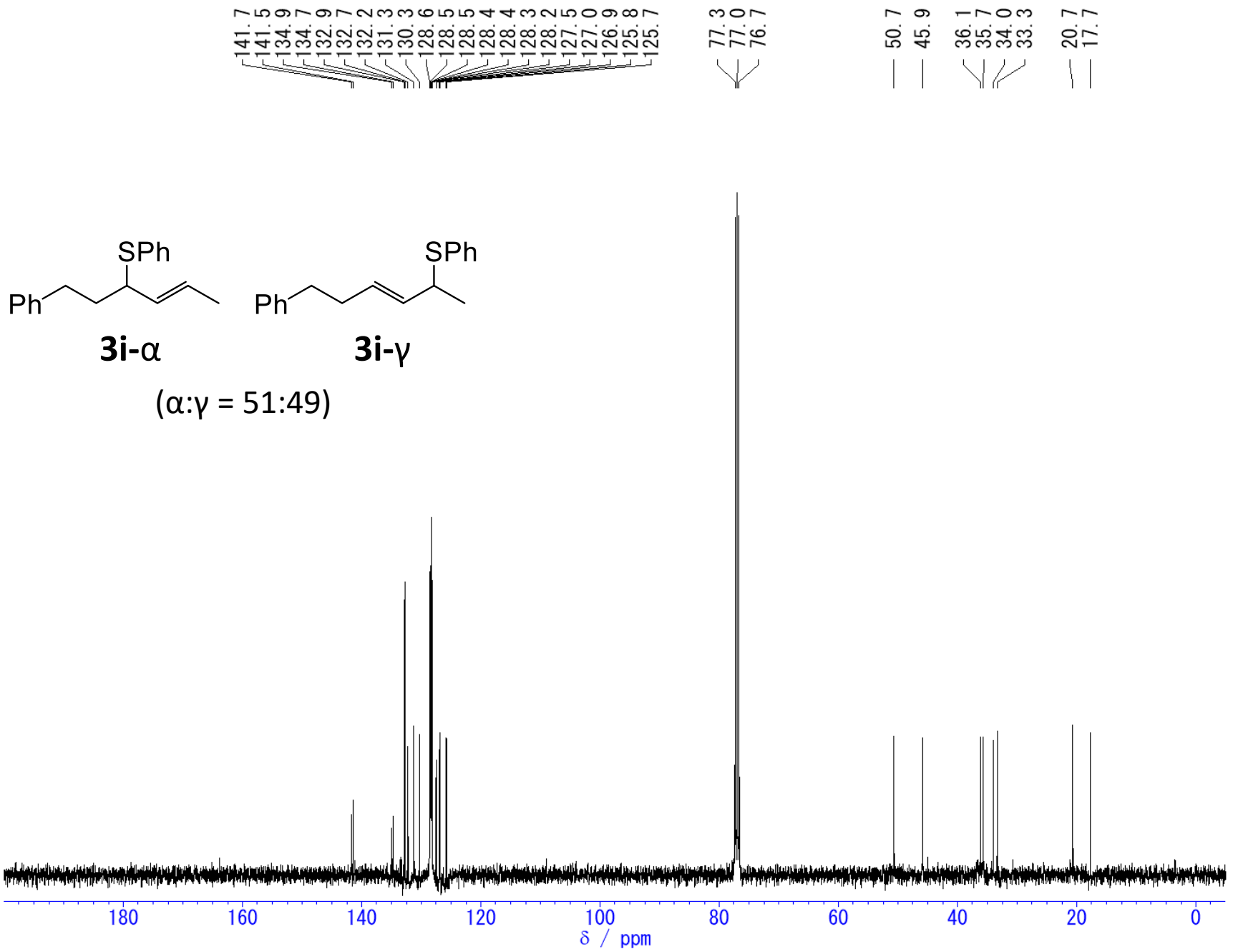
0.58
1.95
0.53
1.97
1.11
1.94
1.17
δ / ppm

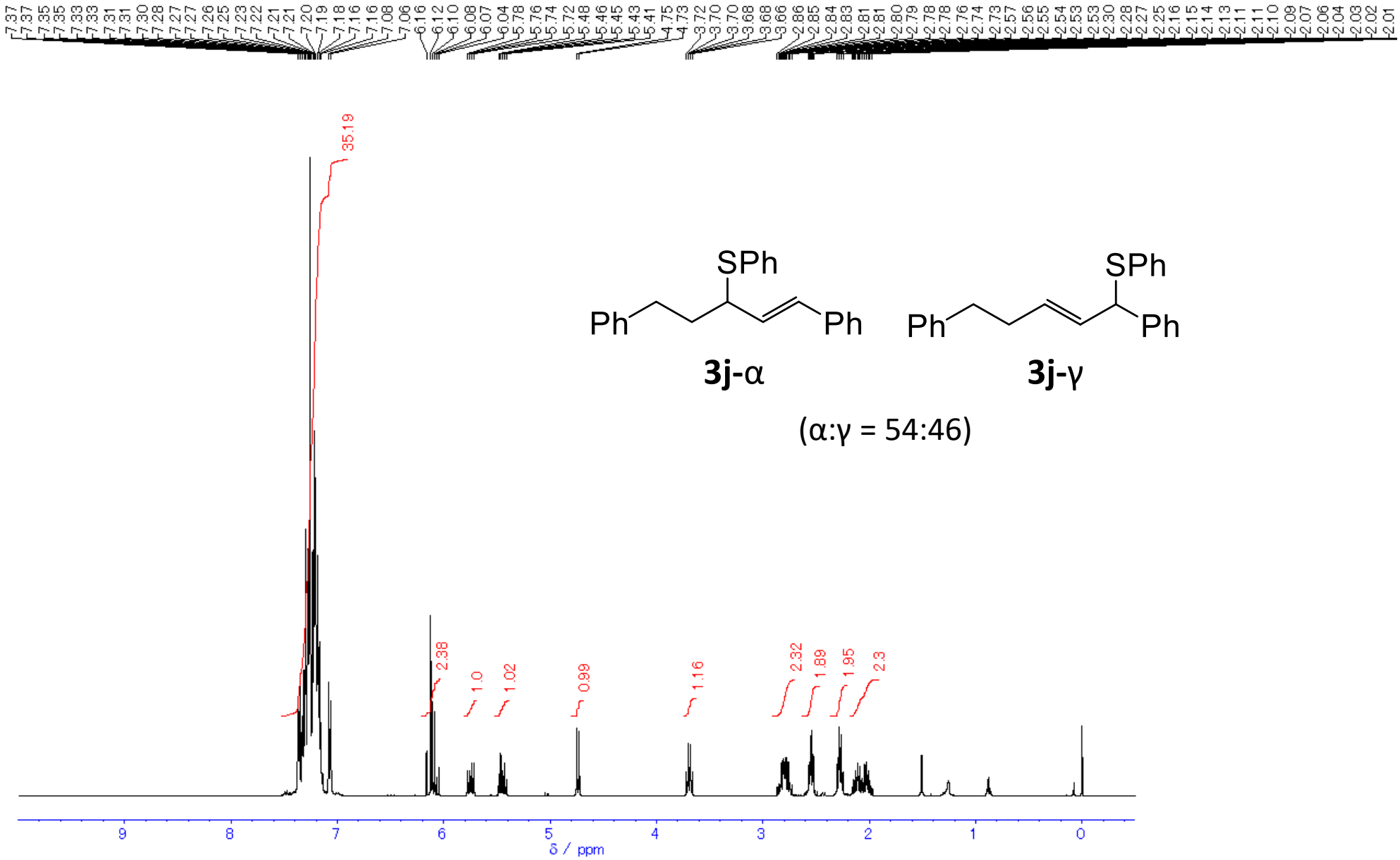


3h-α **3h-γ**

(α : γ = 36 : 64)


7.38 7.37 7.36 7.36 7.33 7.32 7.31 7.30 7.28 7.27 7.26 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.19 7.17 7.16 7.14 7.09 7.08
5.46 5.44 5.42 5.40 5.39 5.37 5.35 5.34 5.34 5.33 5.32 5.31
3.75 3.73 3.72 3.70 3.68 3.57 3.55 3.54 3.52
2.81 2.79 2.78 2.77 2.76 2.75 2.73 2.72 2.70 2.70 2.68 2.66 2.65 2.56 2.55 2.54 2.53 2.52 2.51 2.27 2.25 2.23 2.21 2.04 2.02 2.00 1.99 1.97 1.96 1.95 1.93 1.92 1.91 1.89
SPh
Ph
3i-α
SPh
Ph
3i-γ
(α:γ = 51:49)
22.96
4.11
1.0
1.03
2.16
1.86
1.95
1.91
3.02
3.04
9
8
7
6
5
4
3
2
1
0
δ / ppm

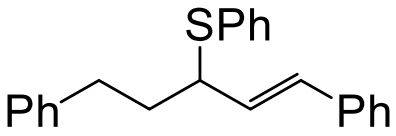

141.7
141.5
134.9
134.7
132.9
132.7
132.2
131.3
130.3
128.6
128.5
128.5
128.4
128.4
128.3
128.2
127.5
127.0
126.9
125.8
125.7
77.3
77.0
76.7
50.7
45.9
36.1
35.7
34.0
33.3
20.7
17.7
SPh
Ph
SPh
Ph
3i-α
3i-γ
(α:γ = 51:49)
180
160
140
120
100
80
60
40
20
0
δ / ppm



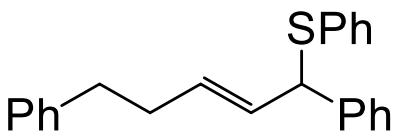
3j-α

3j-γ

(α:γ = 54:46)

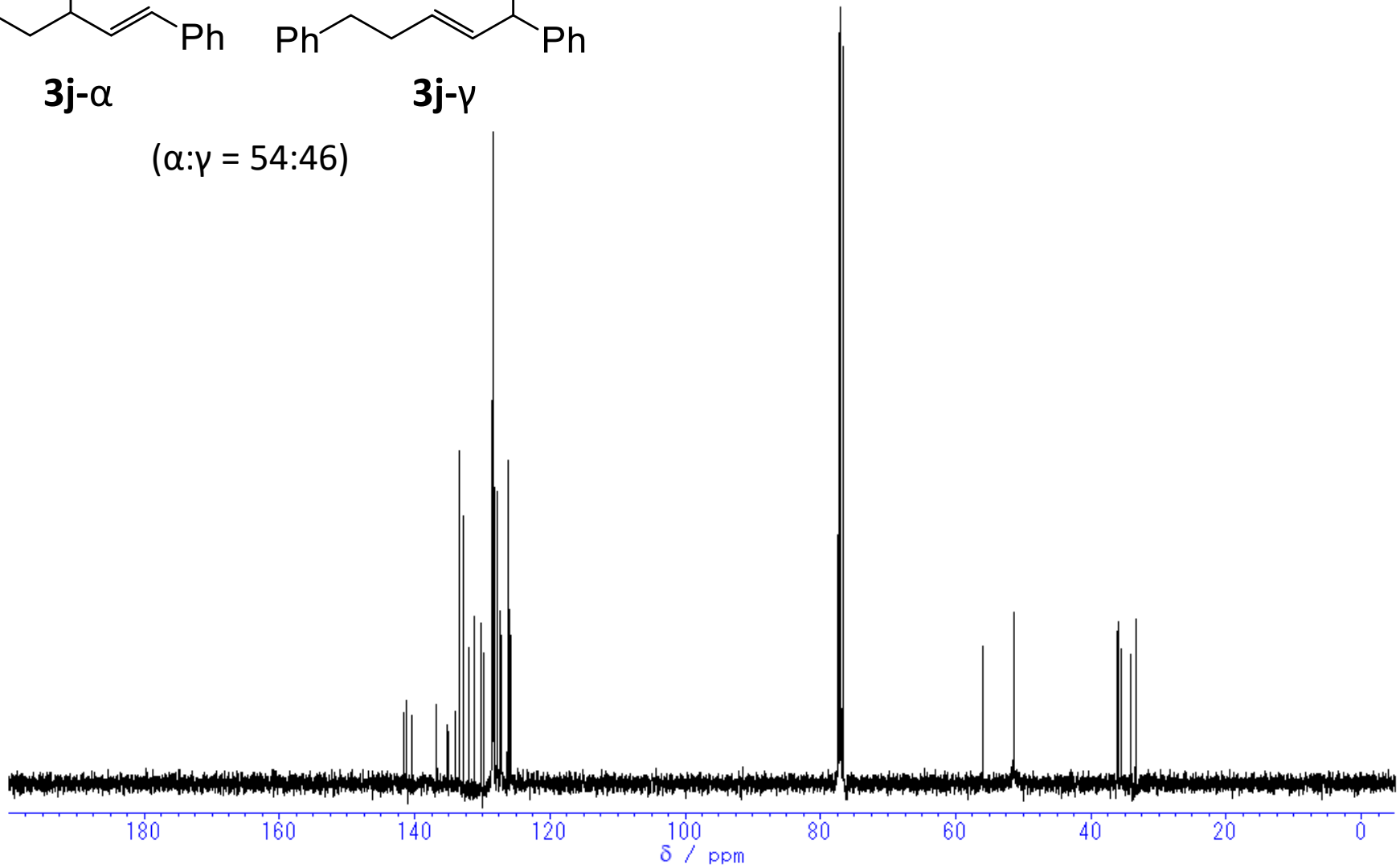


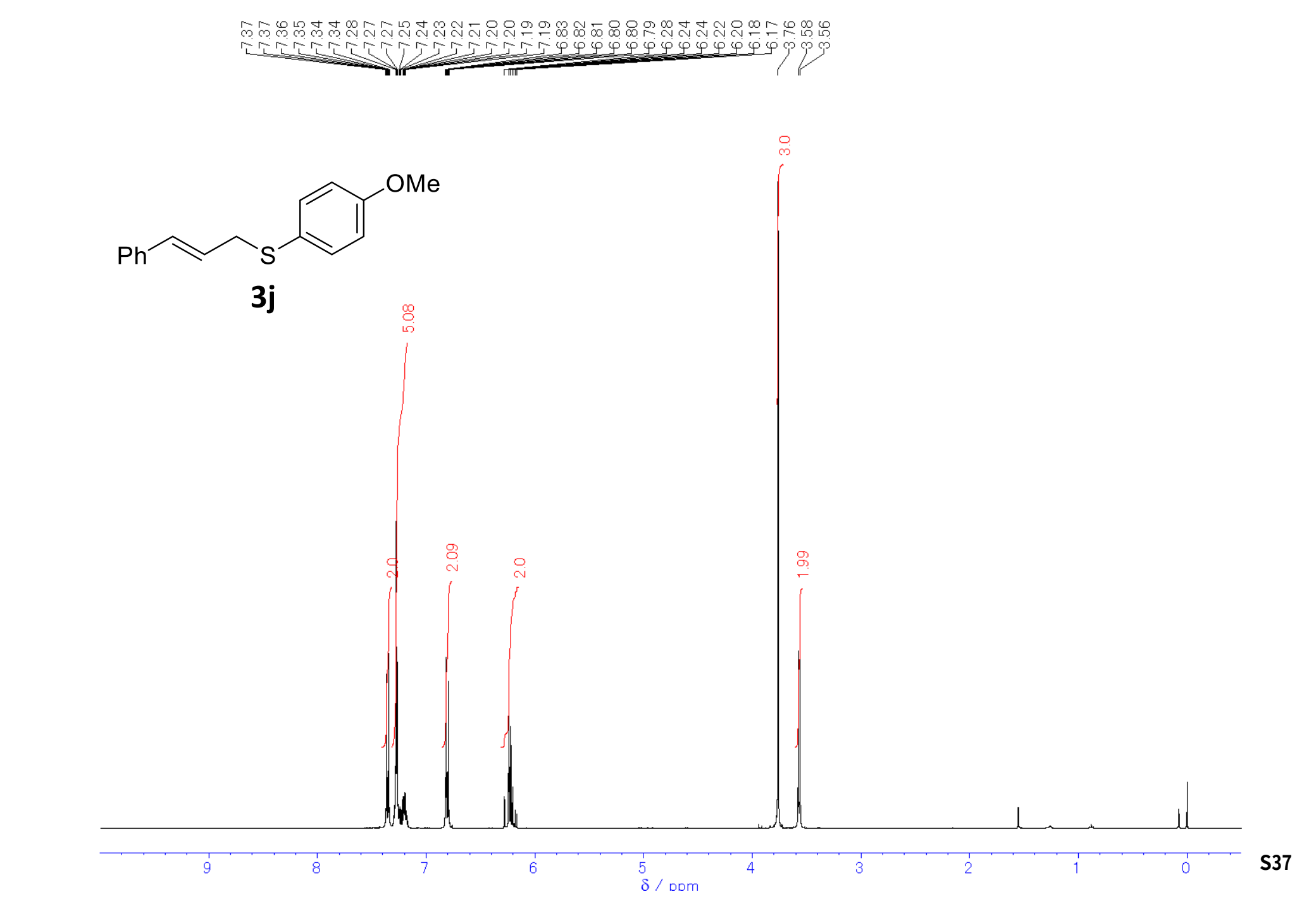
3j-α

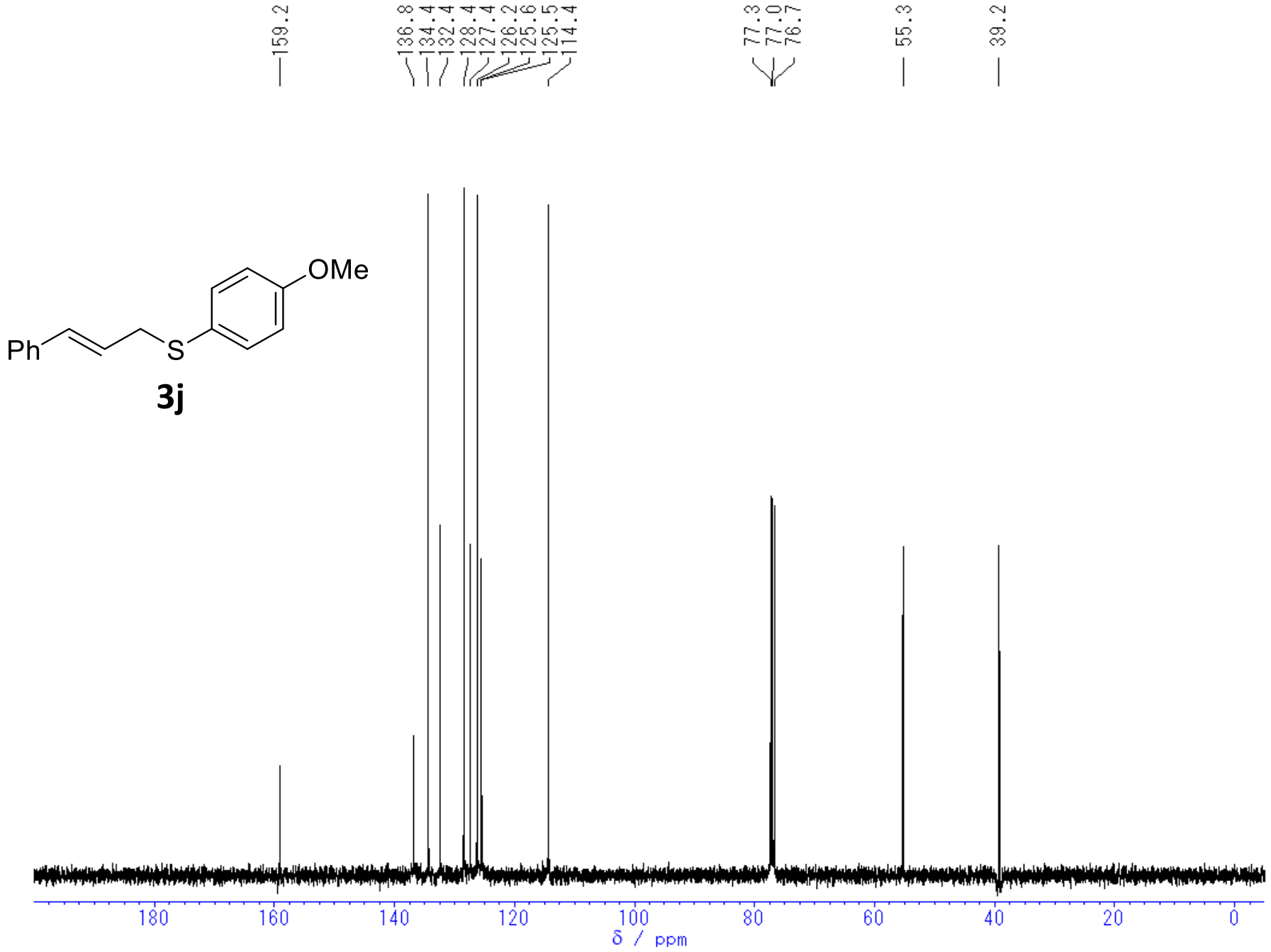


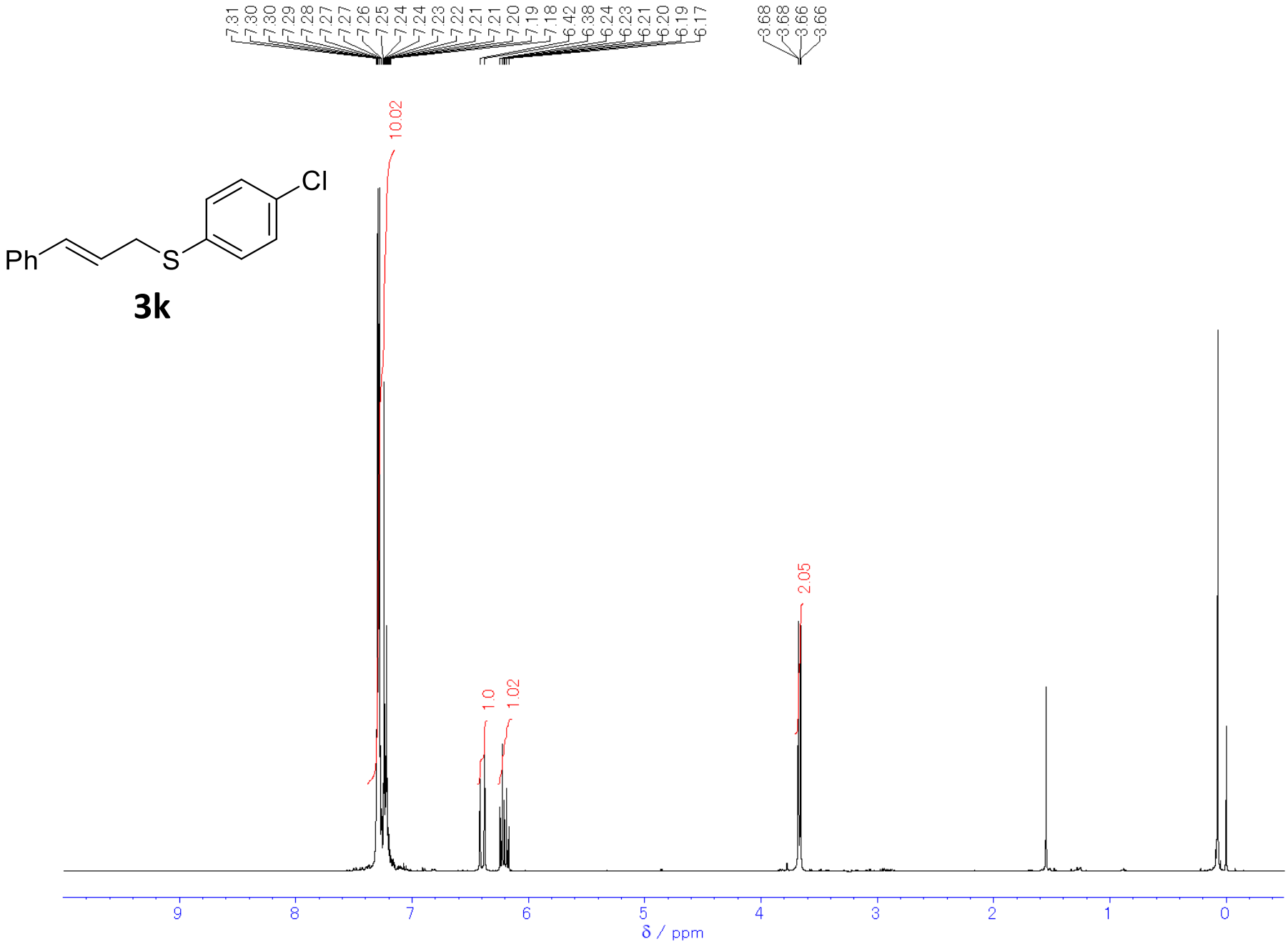
3j-γ

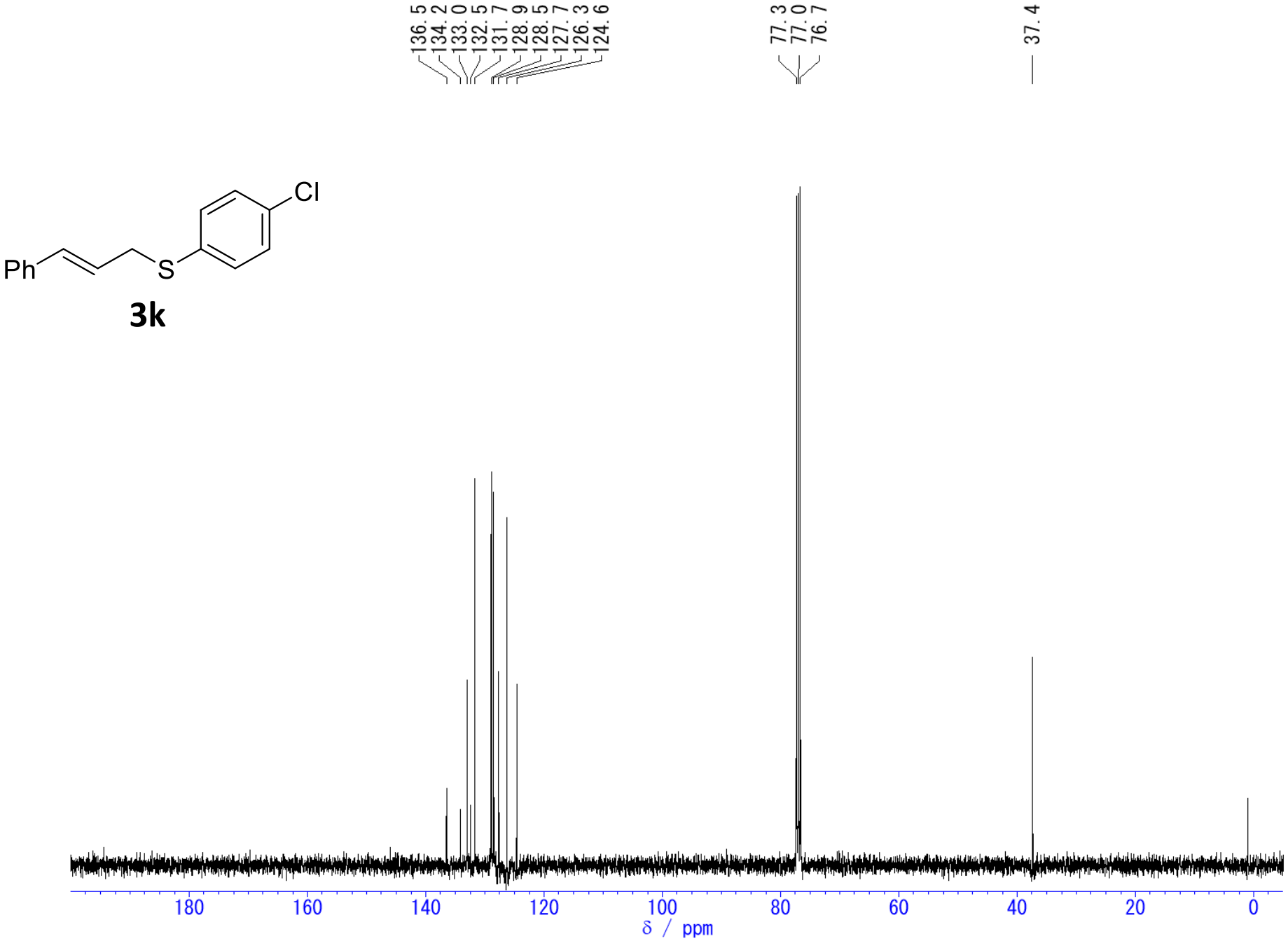
(α:γ = 54:46)

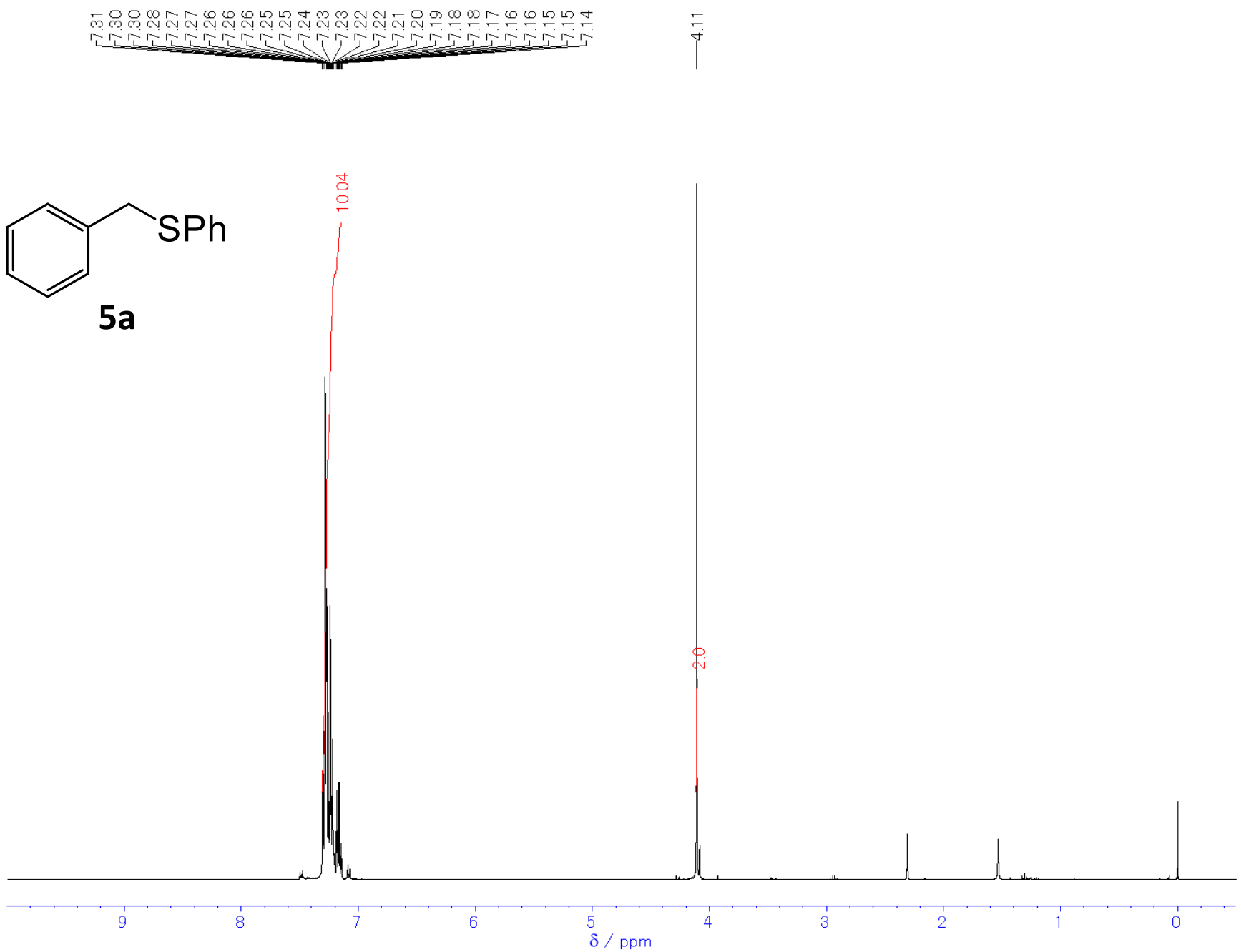


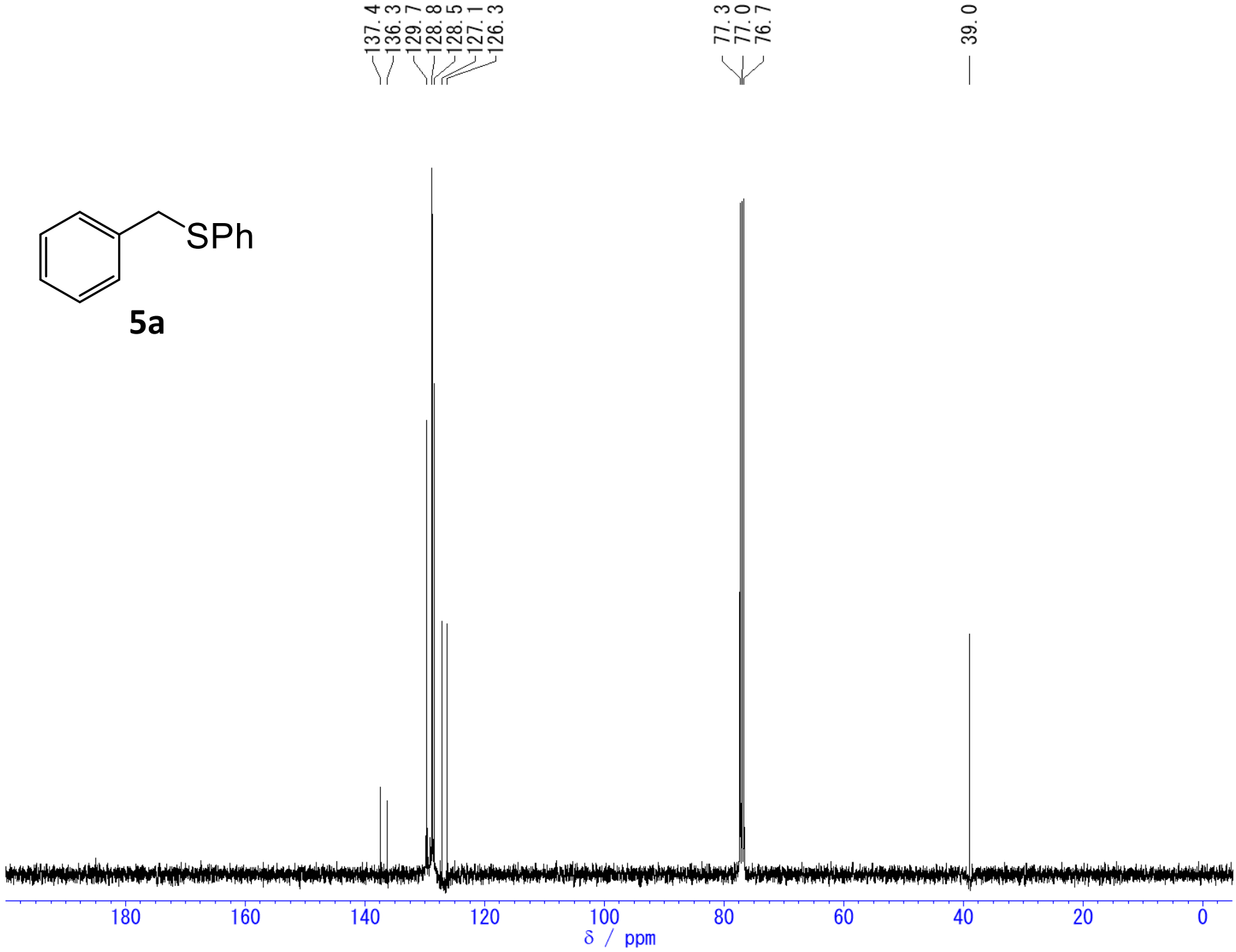

7.37
7.37
7.36
7.35
7.34
7.34
7.28
7.27
7.27
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.19
6.83
6.82
6.81
6.80
6.80
6.79
6.28
6.24
6.24
6.22
6.20
6.18
6.17
3.76
3.58
3.56
OMe
Ph
S
3j
3.0
5.08
2.0
2.09
2.0
1.99
9
8
7
6
5
4
3
2
1
0
δ / ppm

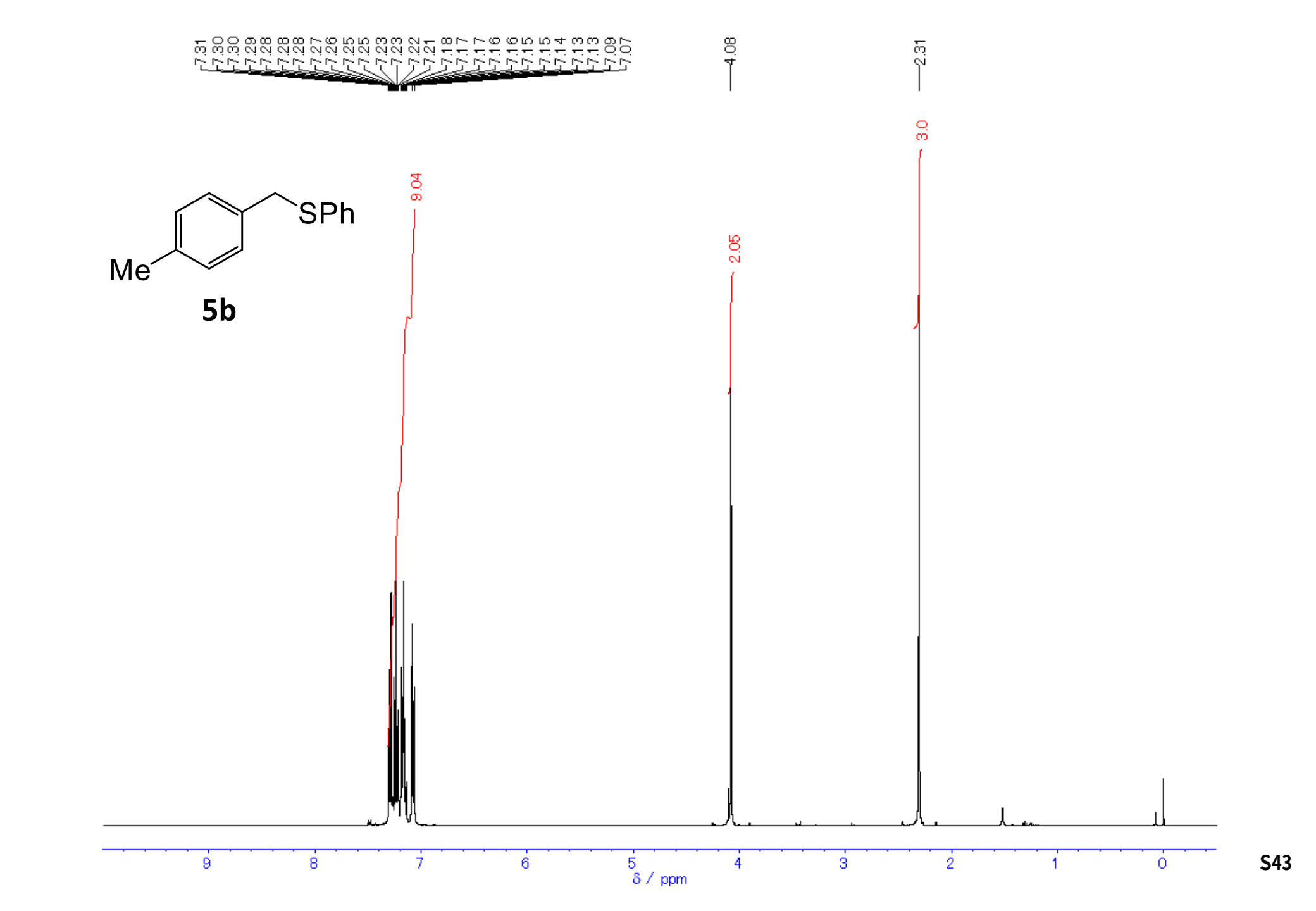

159.2
136.8
134.4
132.4
128.4
127.4
126.2
125.6
125.5
114.4
77.3
77.0
76.7
55.3
39.2
OMe
Ph
S
3j
180
160
140
120
100
80
60
40
20
0
δ / ppm

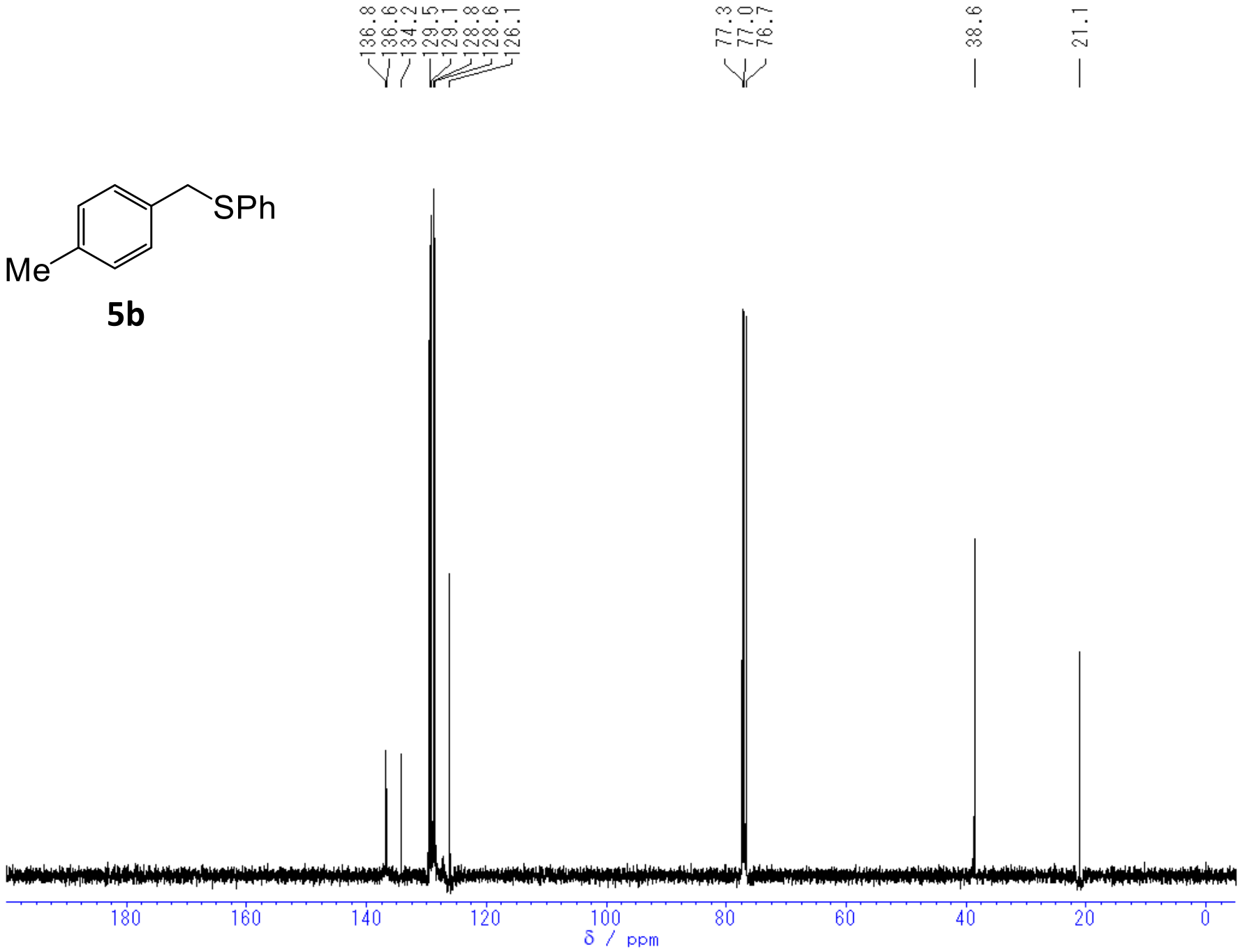

7.31
7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.21
7.21
7.20
7.19
7.18
6.42
6.38
6.24
6.23
6.21
6.20
6.19
6.17
3.68
3.68
3.66
3.66
10.02
Cl
Ph
S
3k
1.0
1.02
2.05
9
8
7
6
5
4
3
2
1
0
δ / ppm

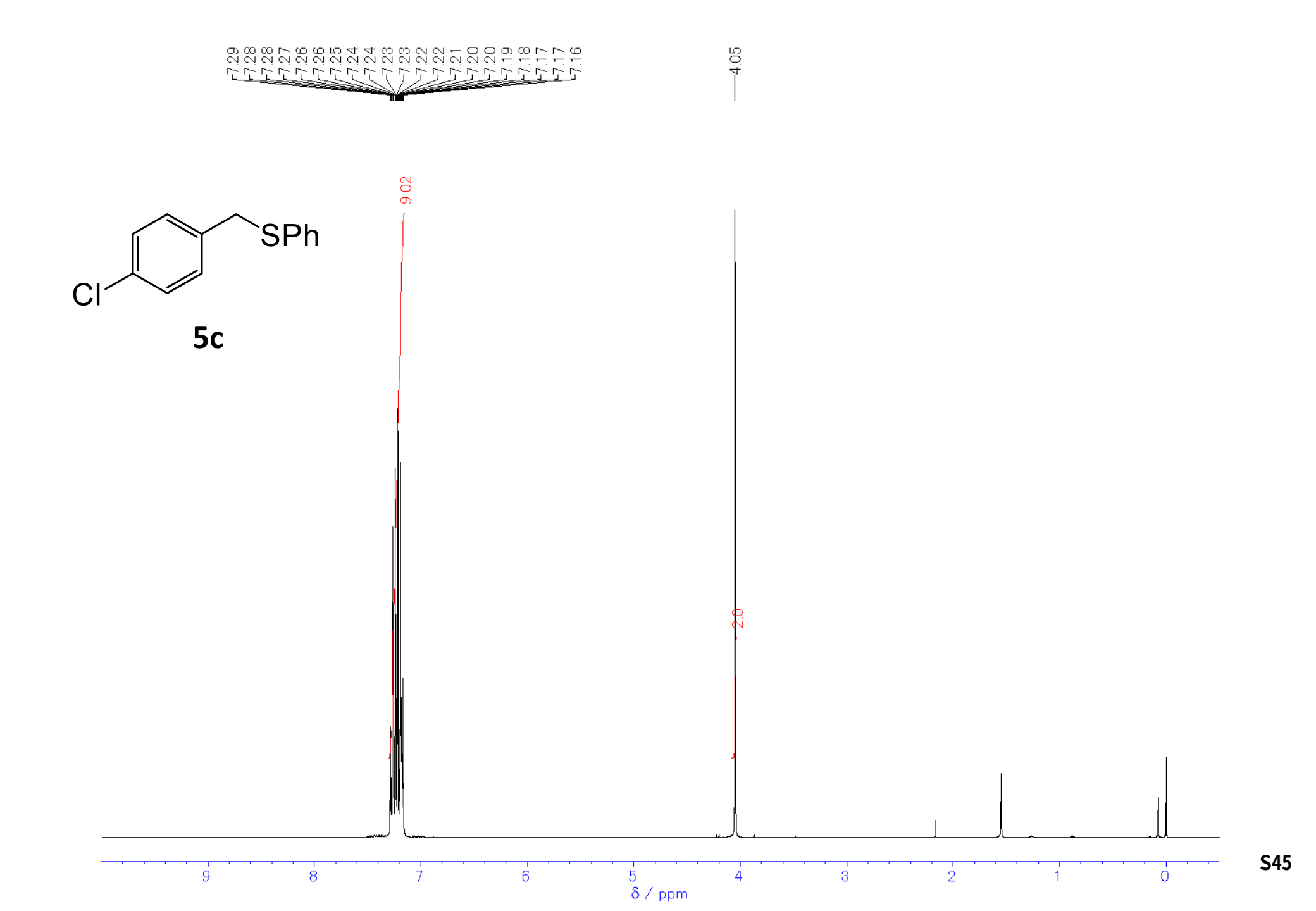

136.5
134.2
133.0
132.5
131.7
128.9
128.5
127.7
126.3
124.6
77.3
77.0
76.7
37.4
Cl
Ph
S
3k
180
160
140
120
100
80
60
40
20
0
δ / ppm

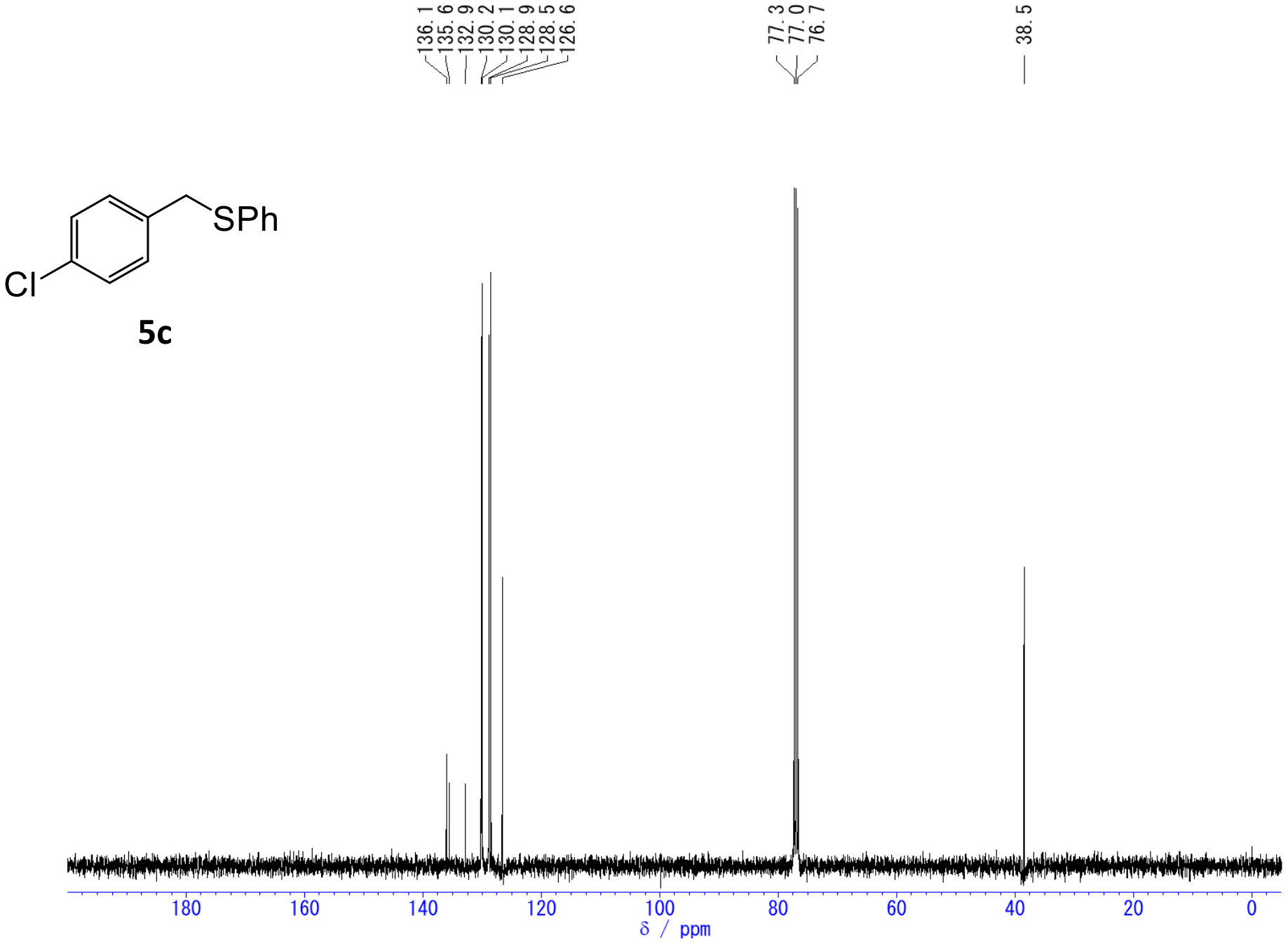

7.31
7.30
7.30
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.15
7.14
4.11
SPh
5a
10.04
2.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


137.4
136.3
129.7
128.8
128.5
127.1
126.3
77.3
77.0
76.7
39.0
SPh
5a
180
160
140
120
100
80
60
40
20
0
δ / ppm

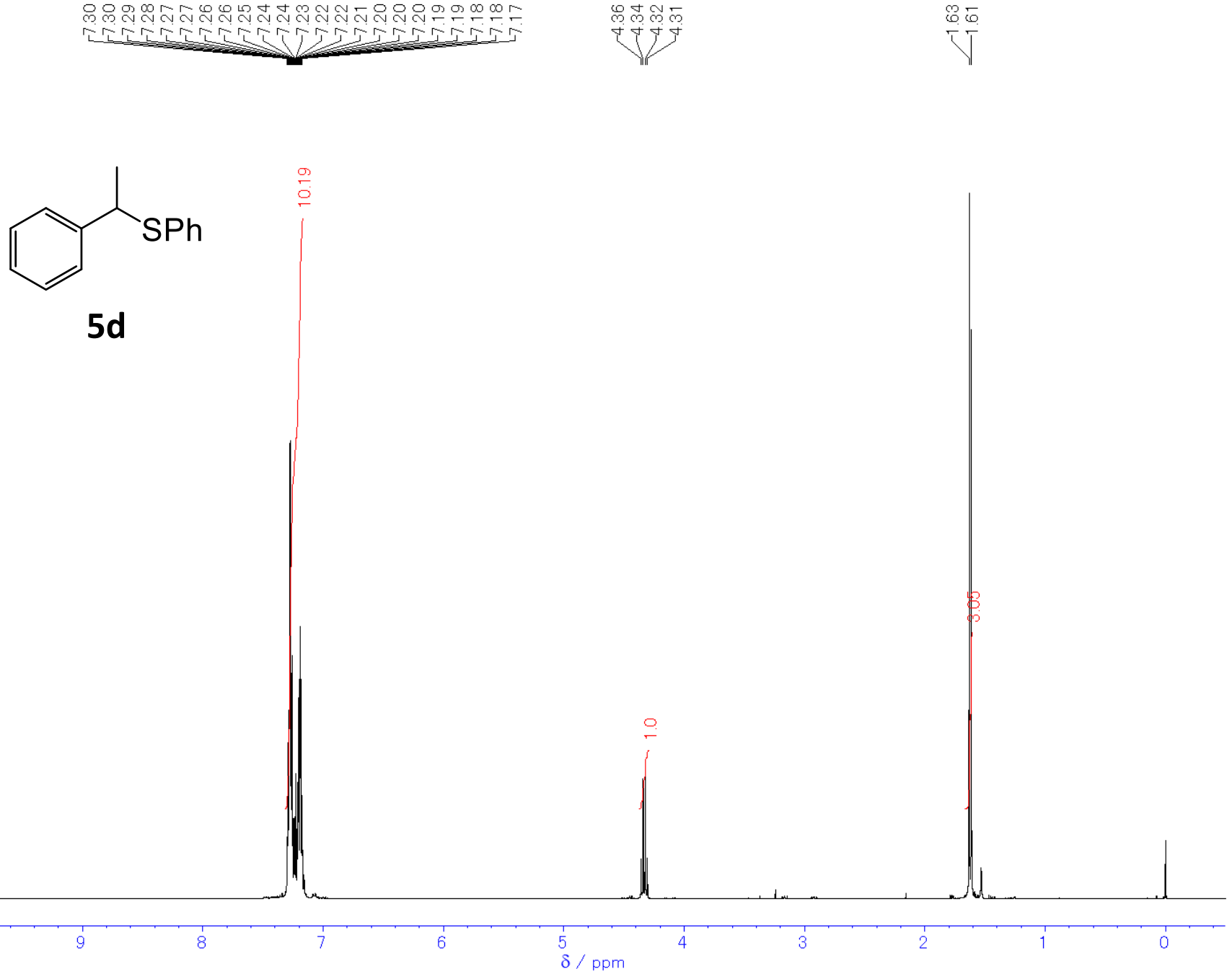

7.31
7.30
7.30
7.29
7.28
7.28
7.28
7.27
7.26
7.25
7.25
7.23
7.23
7.22
7.21
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.09
7.07
4.08
2.31
3.0
9.04
2.05
SPh
Me
5b
9
8
7
6
5
4
3
2
1
0
δ / ppm

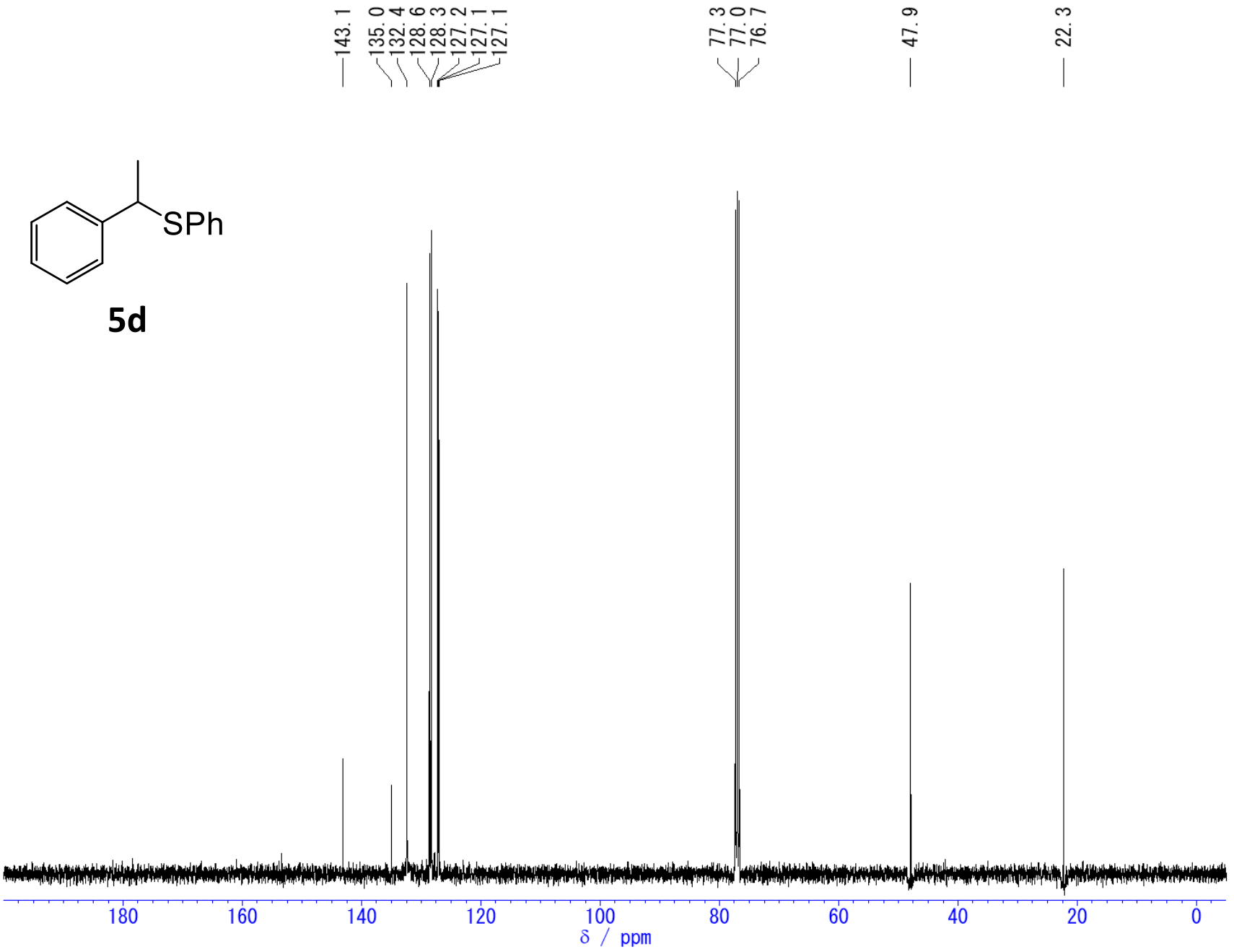

136.8
136.6
134.2
129.5
129.1
128.8
128.6
126.1
77.3
77.0
76.7
38.6
21.1
SPh
Me
5b
180
160
140
120
100
80
60
40
20
0
δ / ppm

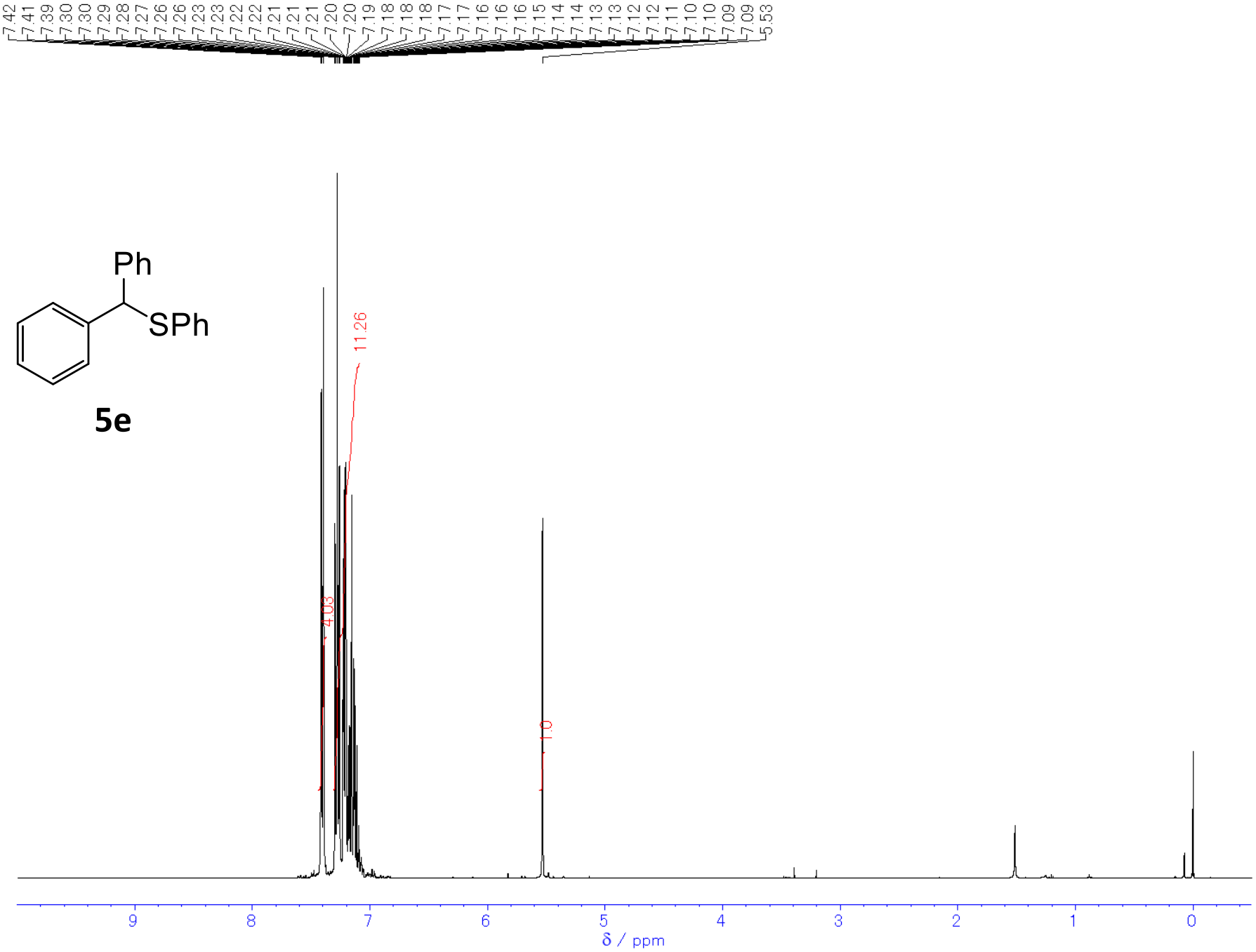

7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.20
7.20
7.19
7.18
7.17
7.17
7.16
4.05
9.02
2.0
SPh
Cl
5c
9
8
7
6
5
4
3
2
1
0
δ / ppm

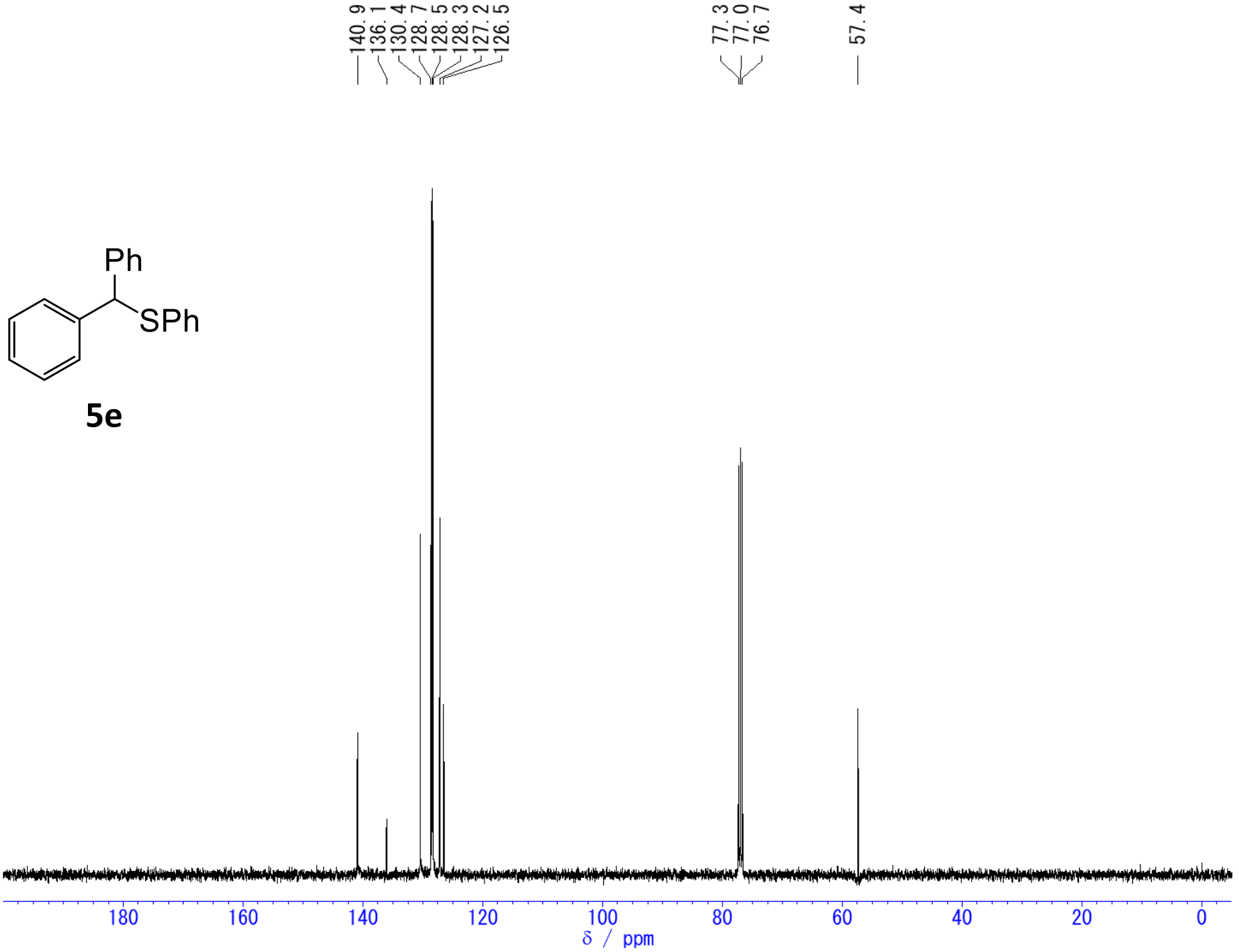

136.1
135.6
132.9
130.2
130.1
128.9
128.5
126.6
77.3
77.0
76.7
38.5
SPh
Cl
180
160
140
120
100
80
60
40
20
0
δ / ppm

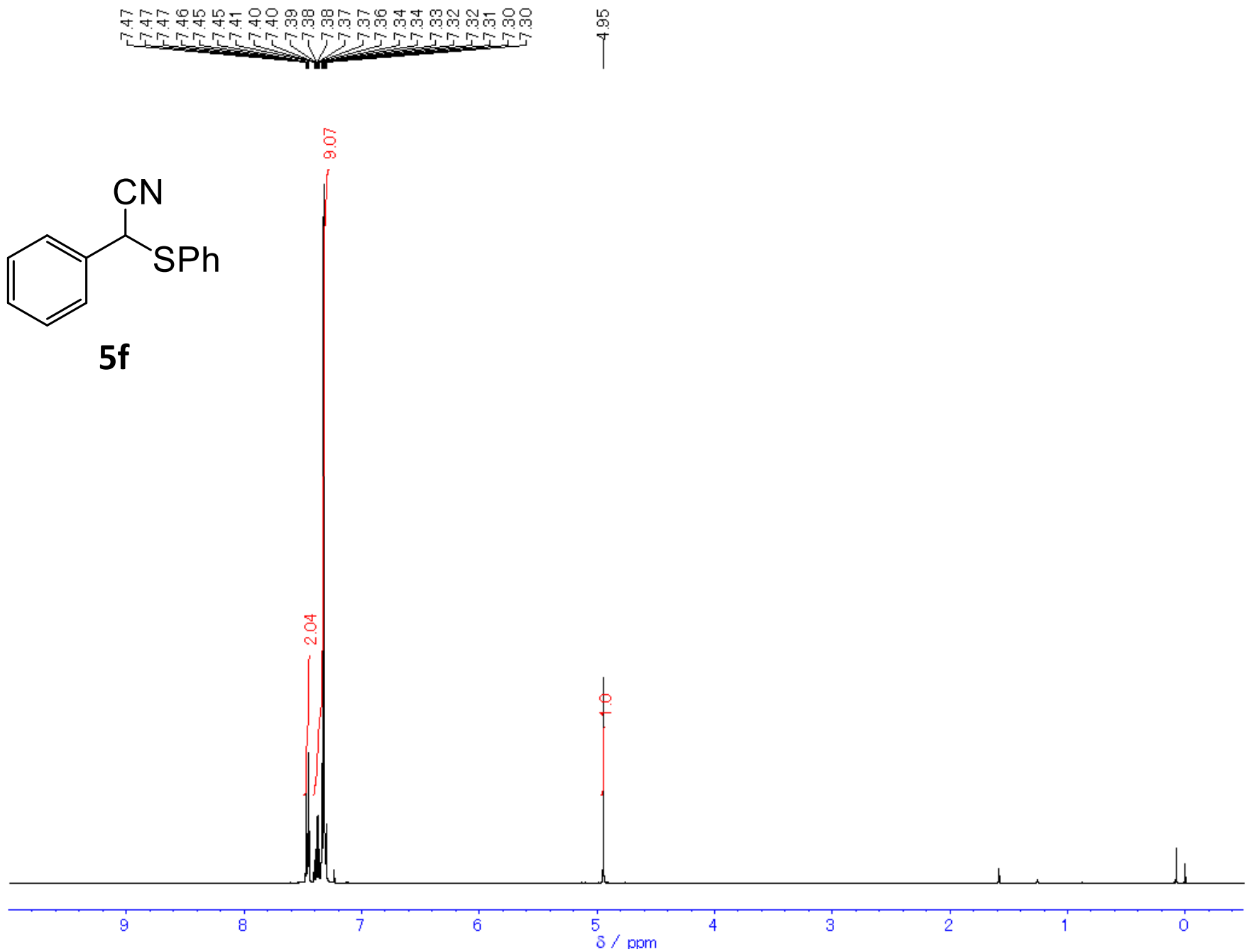
5c

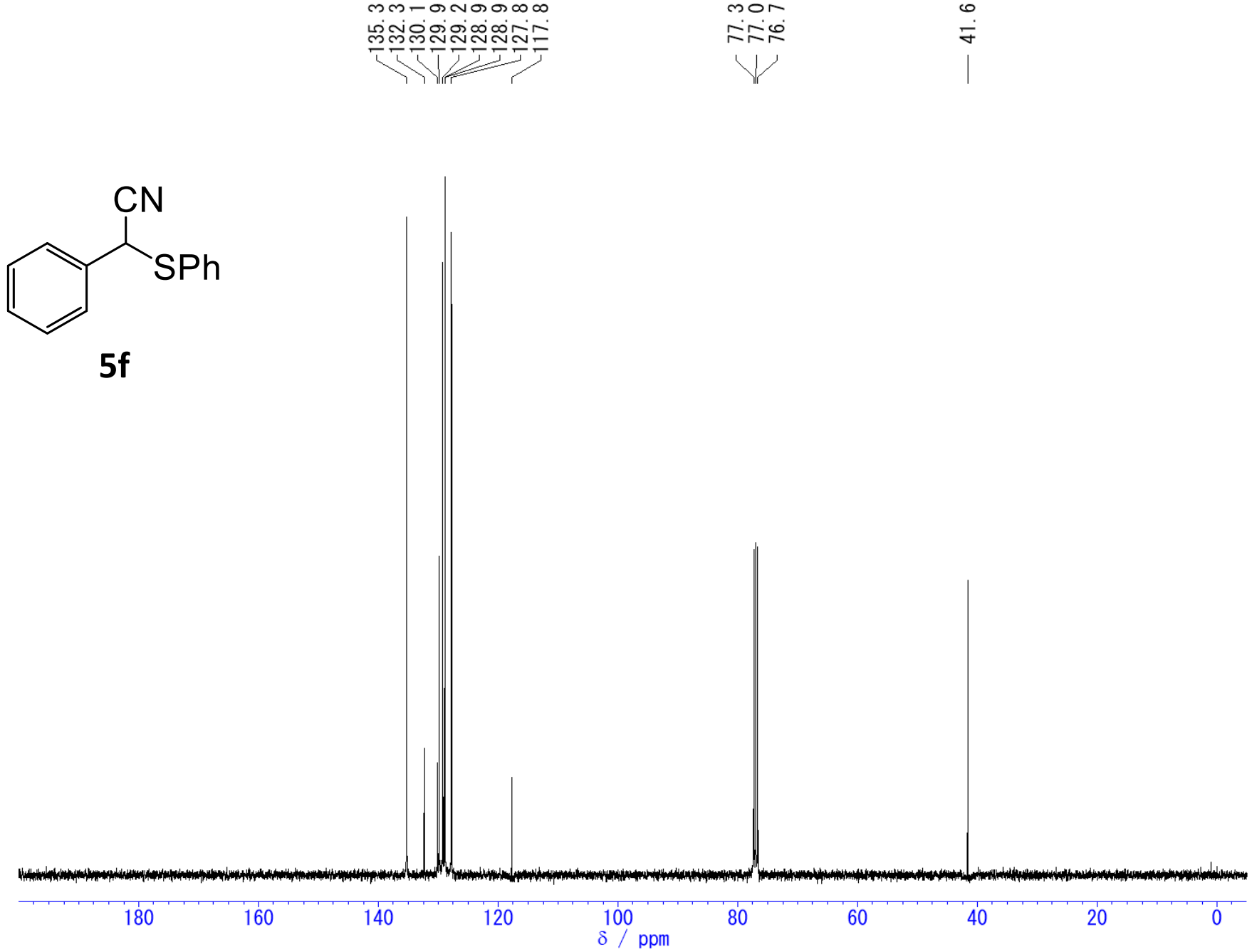

7.30
7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.20
7.19
7.19
7.18
7.18
7.17
4.36
4.34
4.32
4.31
1.63
1.61
SPh
5d
10.19
1.0
3.05
9
8
7
6
5
4
3
2
1
0
δ / ppm


143.1
135.0
132.4
128.6
128.3
127.2
127.1
127.1
77.3
77.0
76.7
47.9
22.3
SPh
5d
180
160
140
120
100
80
60
40
20
0
δ / ppm

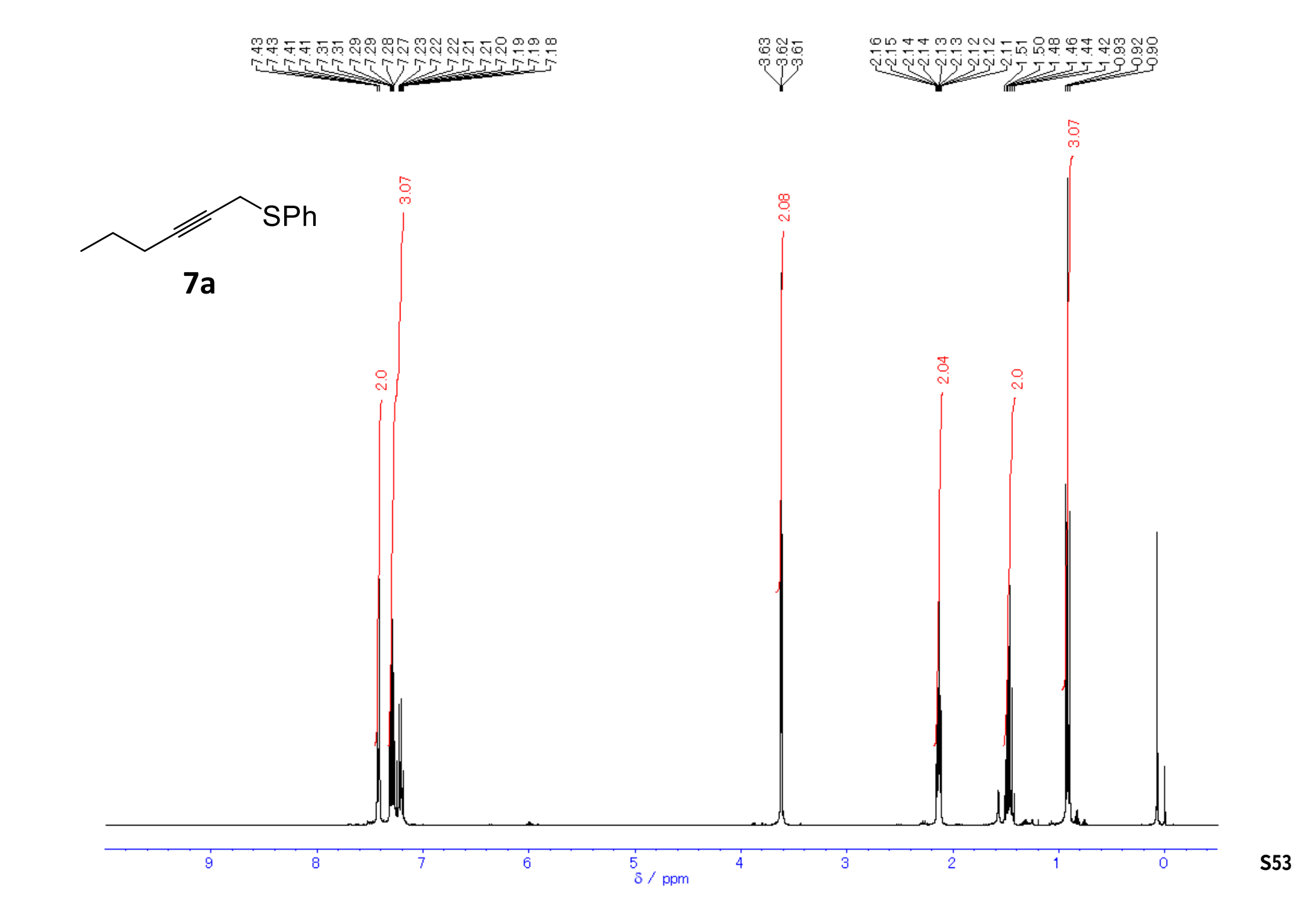

7.42
7.41
7.39
7.30
7.30
7.29
7.28
7.27
7.26
7.26
7.23
7.23
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.18
7.18
7.18
7.17
7.17
7.16
7.16
7.16
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.10
7.10
7.09
7.09
5.53
Ph
SPh
5e
11.26
4.03
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

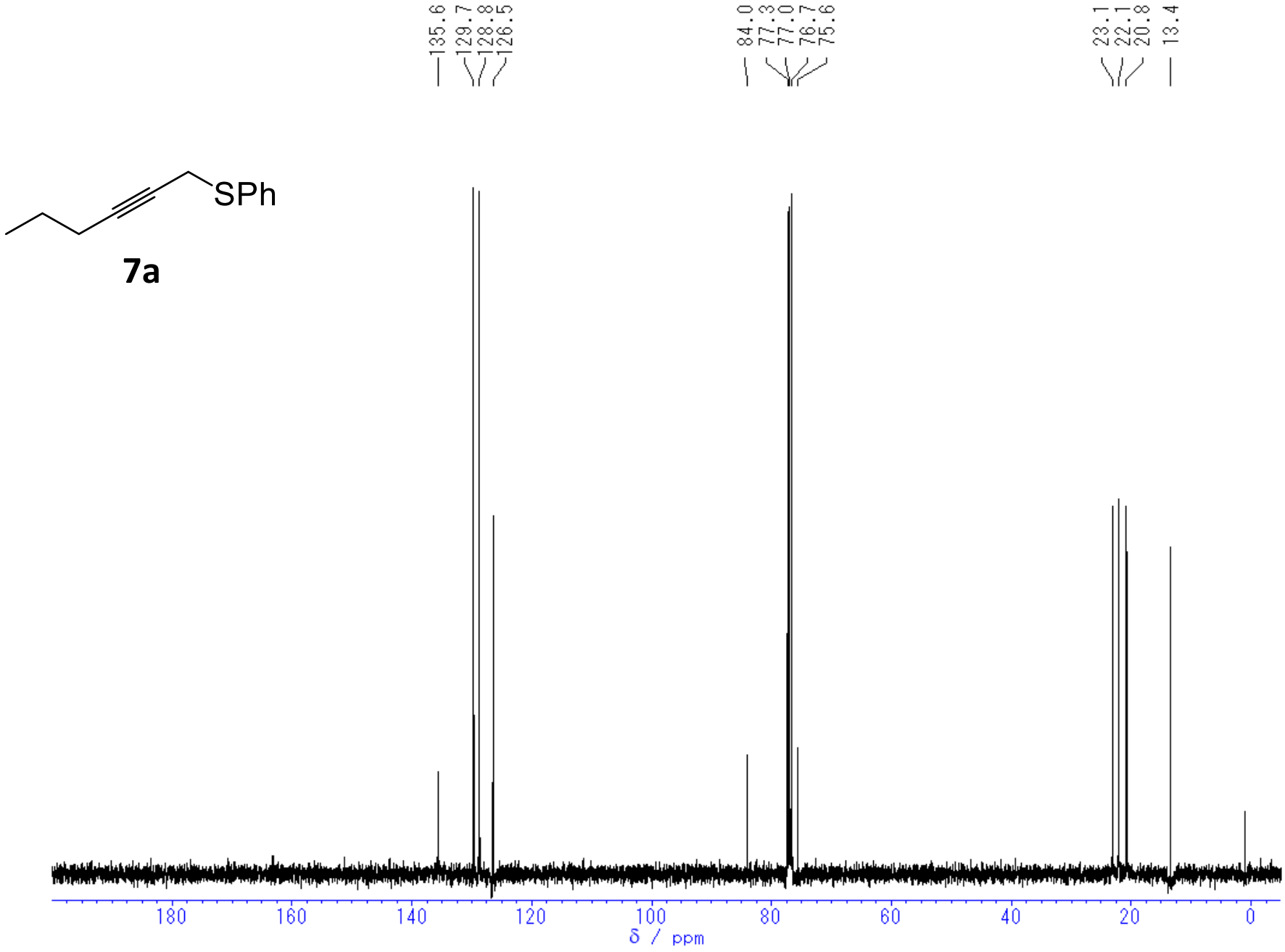

140.9
136.1
130.4
128.7
128.5
128.3
127.2
126.5
77.3
77.0
76.7
57.4
Ph
SPh
5e
180
160
140
120
100
80
60
40
20
0
δ / ppm

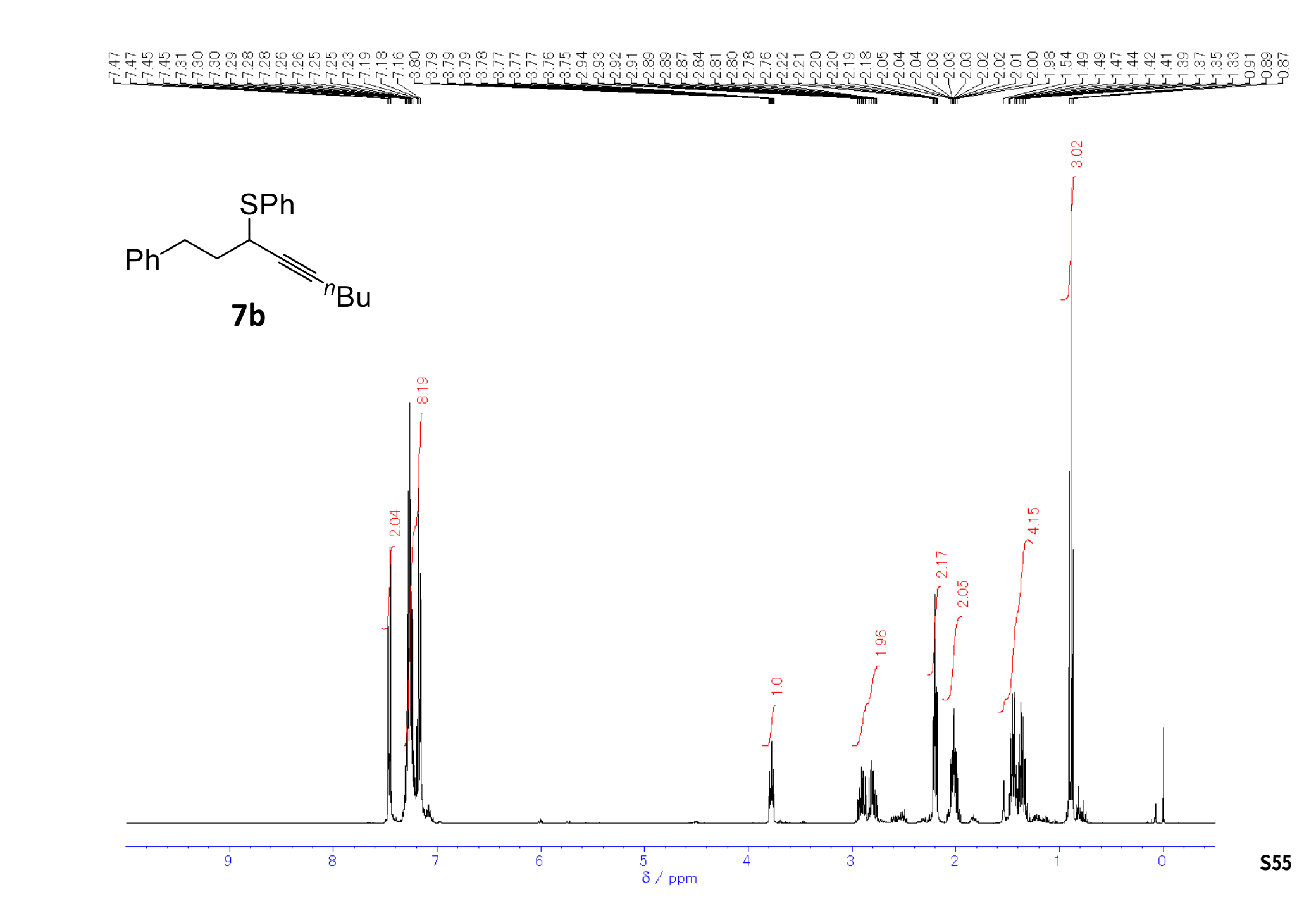

7.47
7.47
7.47
7.46
7.45
7.45
7.41
7.40
7.40
7.39
7.38
7.38
7.37
7.37
7.36
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
4.95
CN
SPh
5f
9.07
2.04
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

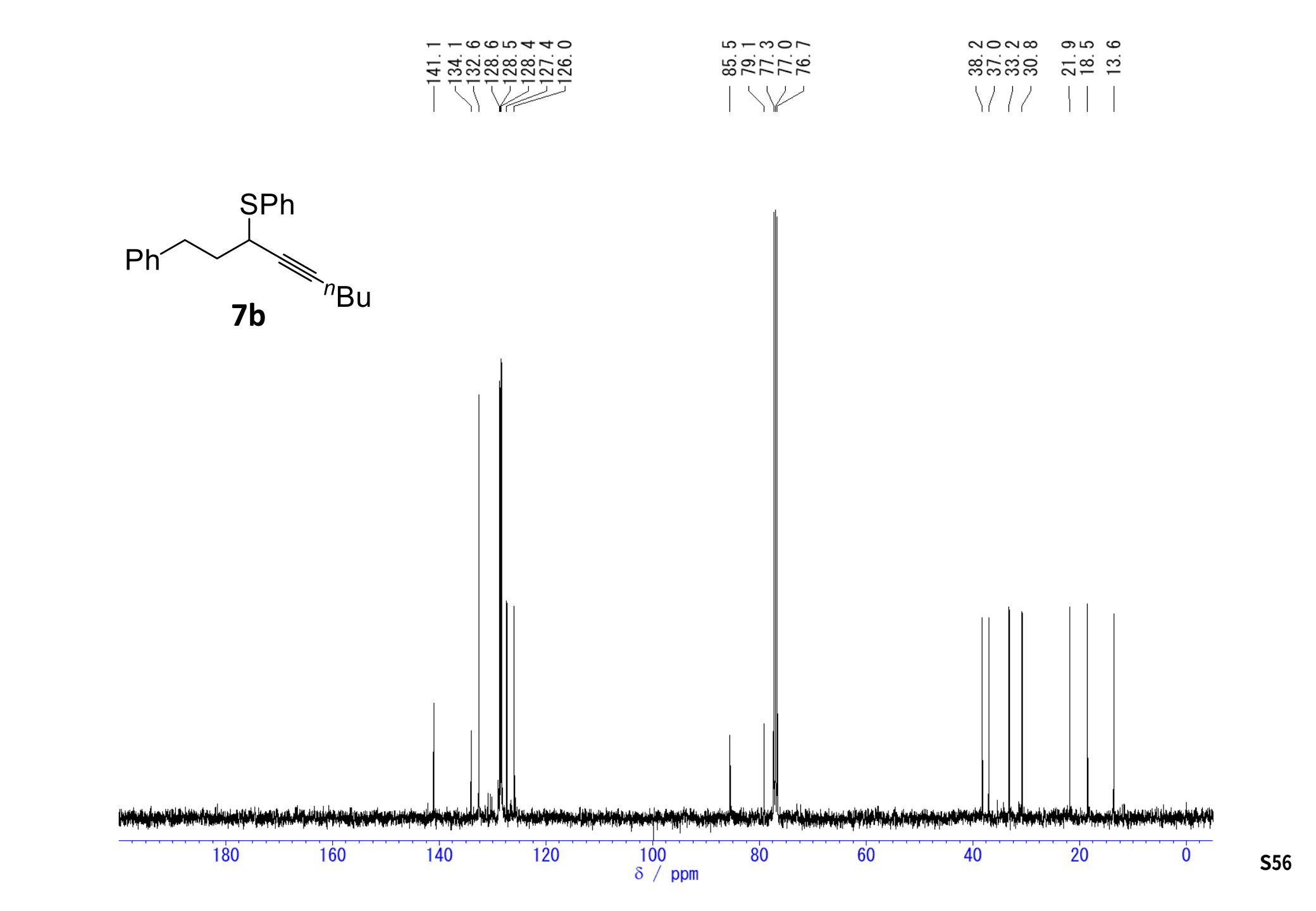

135.3
132.3
130.1
129.9
129.2
128.9
128.9
127.8
117.8
77.3
77.0
76.7
41.6
CN
SPh
180
160
140
120
100
80
60
40
20
0
δ / ppm

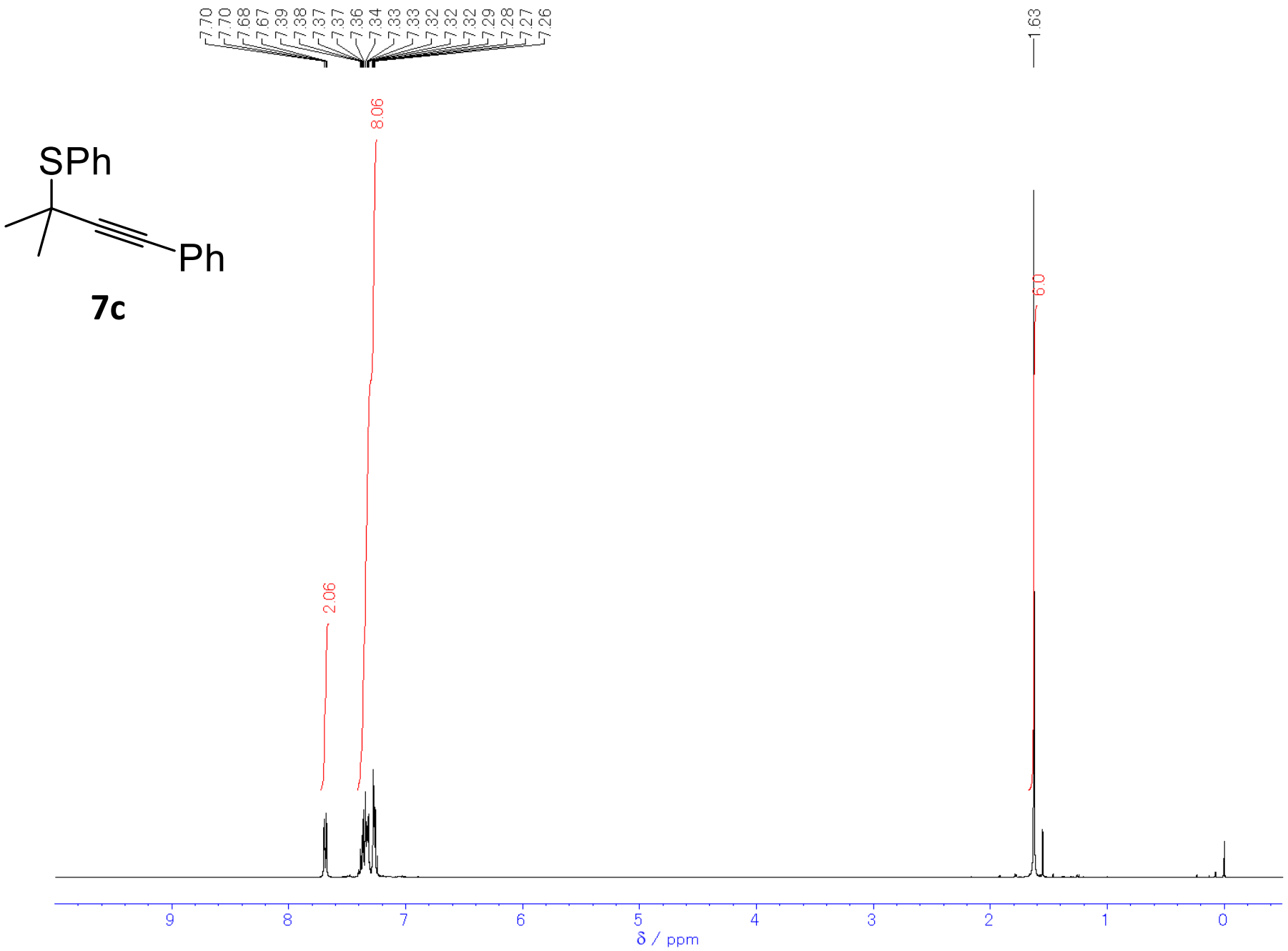
5f

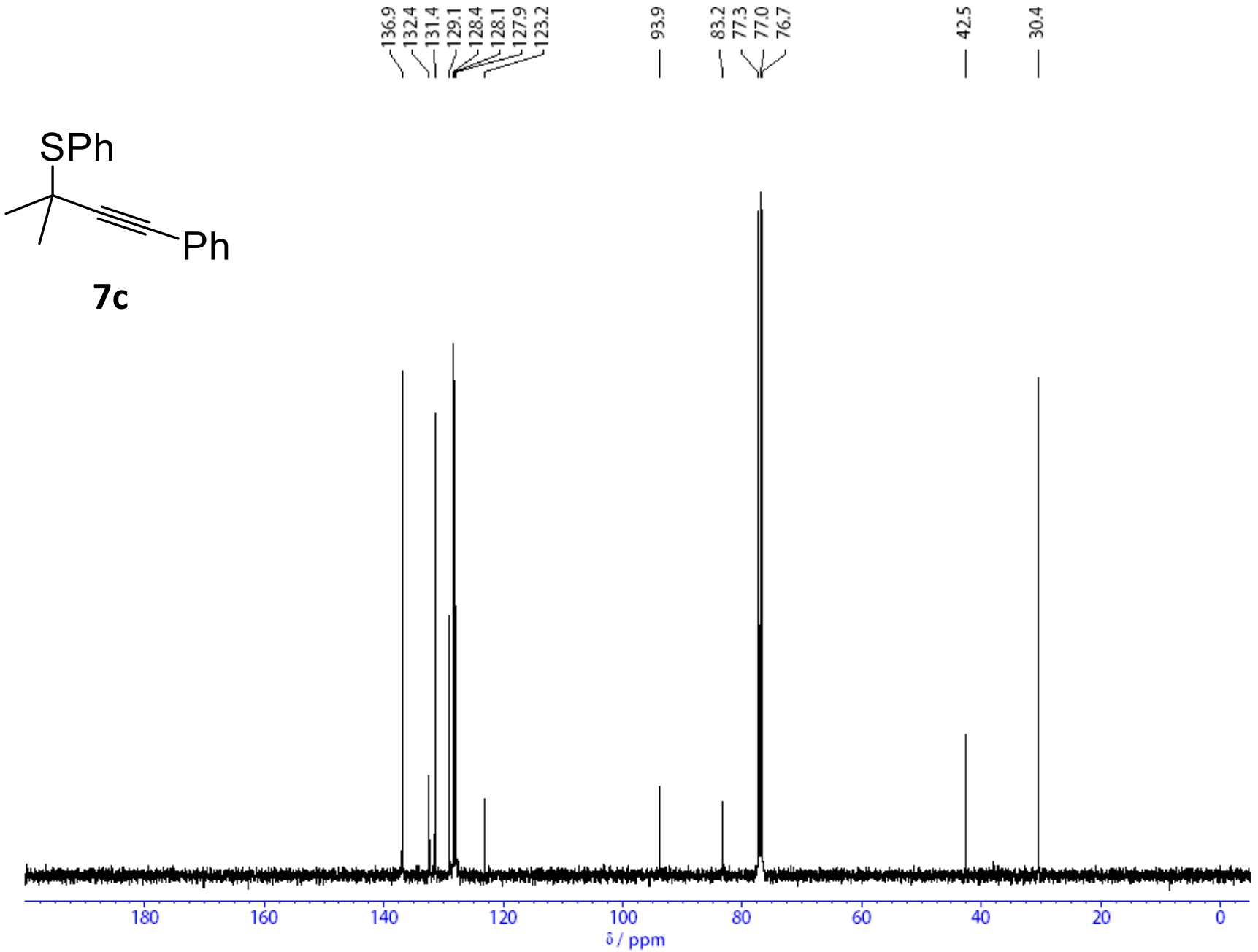

7.43
7.43
7.41
7.41
7.31
7.31
7.29
7.29
7.28
7.27
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.19
7.18
3.63
3.62
3.61
2.16
2.15
2.14
2.14
2.13
2.13
2.12
2.12
2.11
1.51
1.50
1.48
1.46
1.44
1.42
0.93
0.92
0.90
SPh
7a
2.0
3.07
2.08
2.04
2.0
3.07
9
8
7
6
5
4
3
2
1
0
δ / ppm

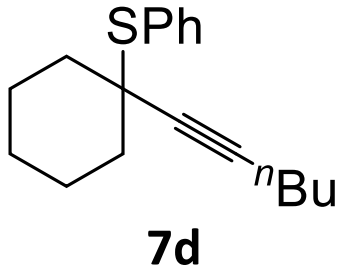

135.6
129.7
128.8
126.5
84.0
77.3
77.0
76.7
75.6
23.1
22.1
20.8
13.4
SPh
7a
180
160
140
120
100
80
60
40
20
0
δ / ppm


7.47 7.47 7.45 7.45 7.31 7.30 7.30 7.29 7.28 7.28 7.26 7.26 7.25 7.25 7.23 7.19 7.18 7.16 3.80 3.79 3.79 3.79 3.78 3.77 3.77 3.77 3.76 3.75 2.94 2.93 2.92 2.91 2.89 2.89 2.87 2.84 2.81 2.80 2.78 2.76 2.22 2.21 2.20 2.20 2.19 2.18 2.05 2.04 2.04 2.03 2.03 2.03 2.02 2.02 2.01 2.00 1.98 1.54 1.49 1.49 1.47 1.44 1.42 1.41 1.39 1.37 1.35 1.33 0.91 0.89 0.87
SPh
Ph
nBu
7b
3.02
8.19
2.04
4.15
2.17
2.05
1.96
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


141.1
134.1
132.6
128.6
128.5
128.4
127.4
126.0
85.5
79.1
77.3
77.0
76.7
38.2
37.0
33.2
30.8
21.9
18.5
13.6
SPh
Ph
nBu
7b
180
160
140
120
100
80
60
40
20
0
δ / ppm

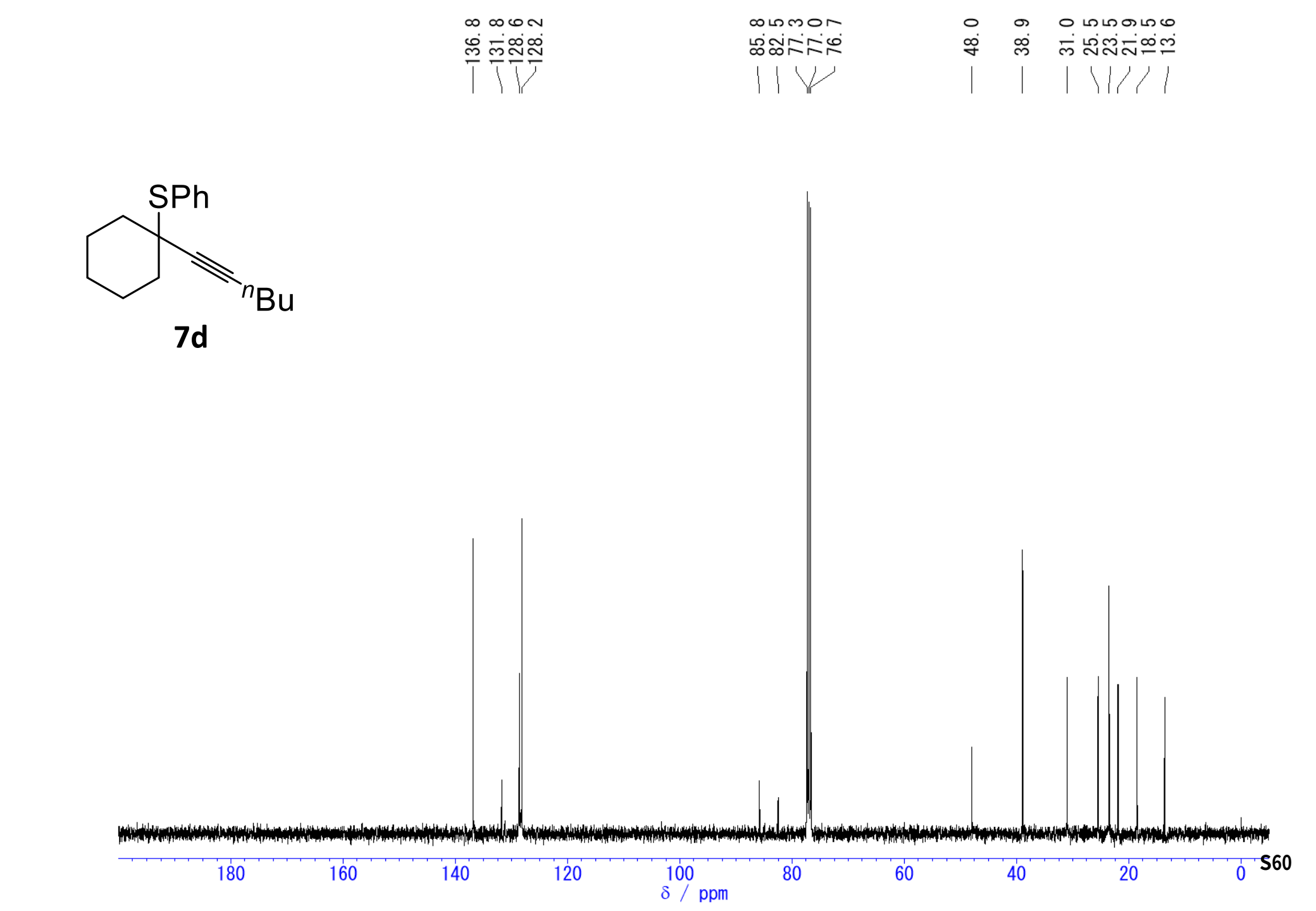

7.70
7.70
7.68
7.67
7.39
7.38
7.37
7.37
7.36
7.34
7.33
7.33
7.32
7.32
7.32
7.29
7.28
7.27
7.26
1.63
8.06
6.0
2.06
SPh
Ph
7c
9
8
7
6
5
4
3
2
1
0
δ / ppm


136.9
132.4
131.4
129.1
128.4
128.1
127.9
123.2
93.9
83.2
77.3
77.0
76.7
42.5
30.4
SPh
Ph
7c
180
160
140
120
100
80
60
40
20
0
δ / ppm

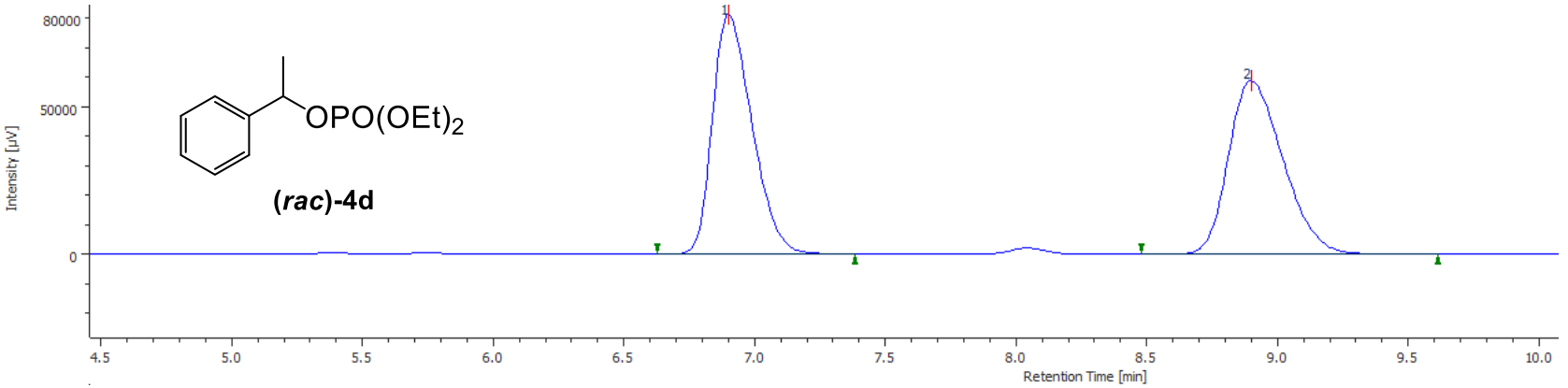

SPh
nBu

7d

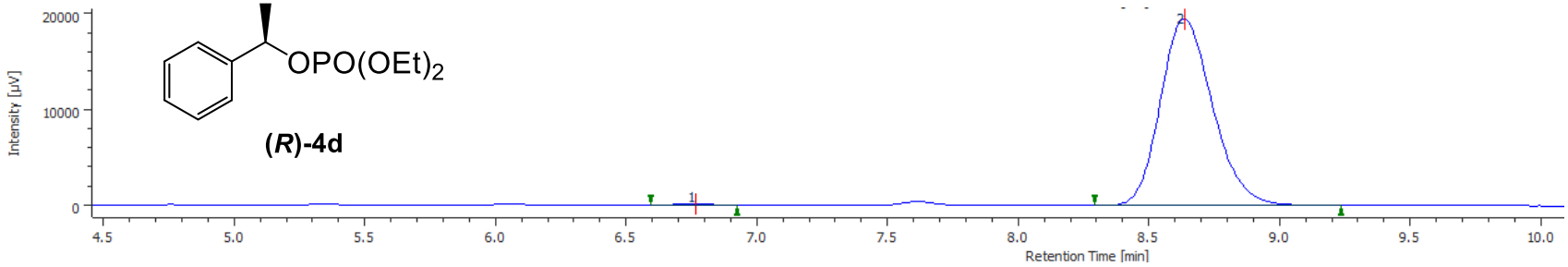
7.64 7.64 7.63 7.63 7.62 7.62 7.61 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.31 7.30 7.30 7.29
2.22 2.21 2.19 1.90 1.88 1.64 1.64 1.61 1.60 1.57 1.50 1.49 1.48 1.47 1.46 1.45 1.44 1.42 1.41 1.39 1.38 1.37 1.36 1.35 1.34 1.34 1.32 0.92 0.90 0.88
2.0
3.12
1.96
2.04
8.09
4.08
3.0
9
8
7
6
5
4
3
2
1
0
δ / ppm


136.8
131.8
128.6
128.2
85.8
82.5
77.3
77.0
76.7
48.0
38.9
31.0
25.5
23.5
21.9
18.5
13.6
SPh
nBu
7d
180
160
140
120
100
80
60
40
20
0
δ / ppm

5. HPLC traces of chiral compounds

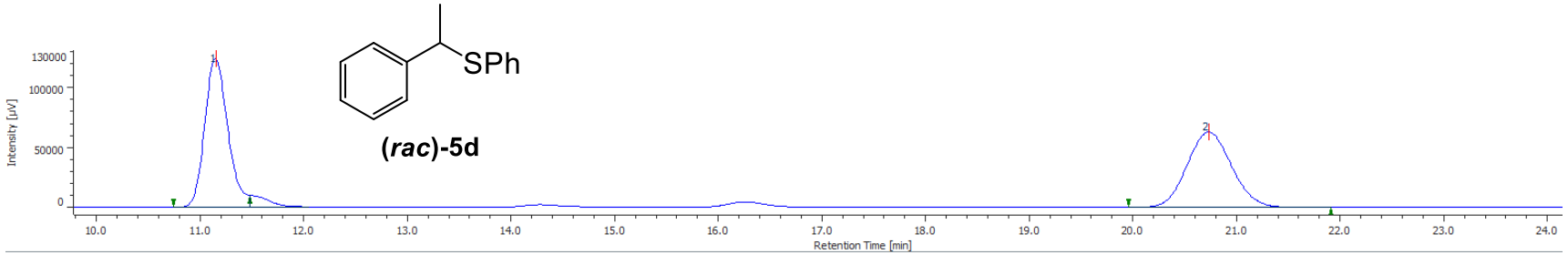


Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	6.900	846995	80833	1.343	49.961
2	8.900	848312	58571	1.273	50.039

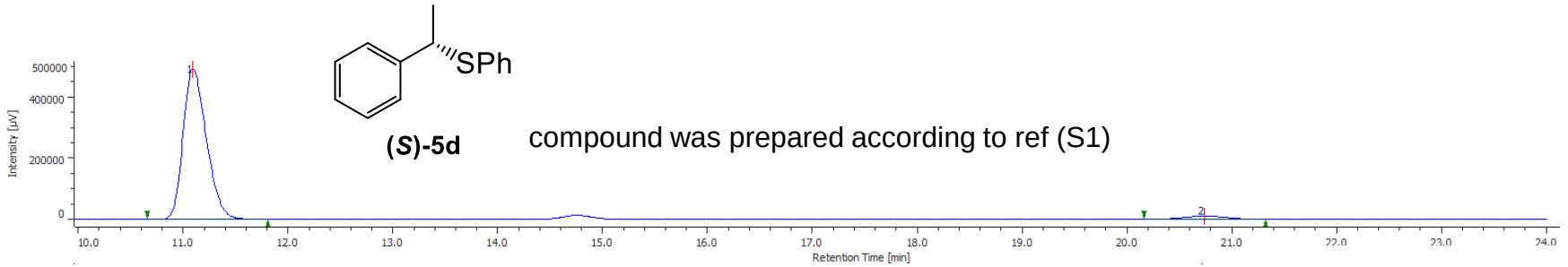


Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	6.767	1298	149	1.036	0.480
2	8.633	268877	19407	1.189	99.520

Daicel Chiralcel OJ- column; λ = 254 nm; hexane/isopropanol =90/10; flow rate = 1.0 mL/min; t_R(S) =6.8 min, t_R (R) = 8.6 min : ee = 99%



Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	11.150	1908094	123771	-	50.473
2	20.725	1872364	62692	1.076	49.527

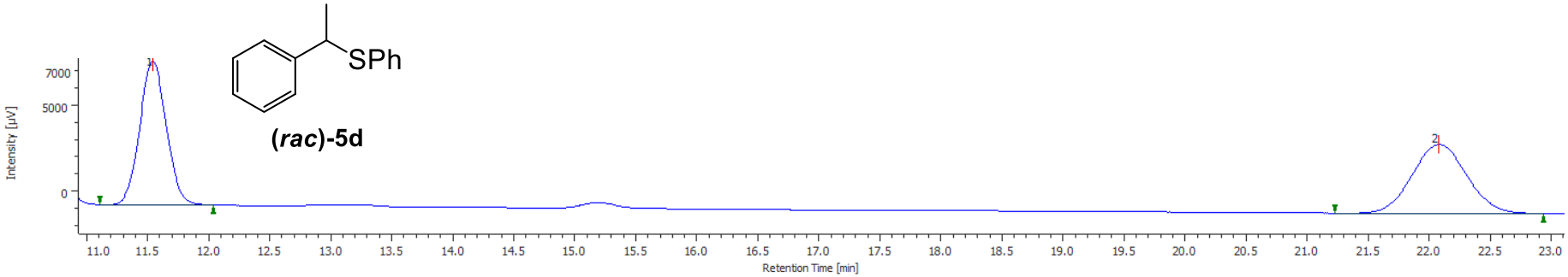


compound was prepared according to ref (S1)

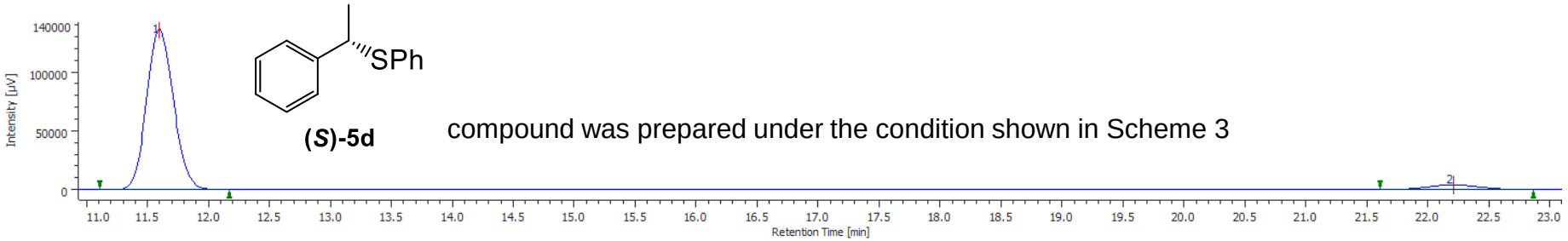
Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	11.092	7532455	487303	1.297	96.000
2	20.733	313881	10868	1.041	4.000

Ref (S1) Y. Kawano, N. Kaneko and T. Mukaiyama, *Chem. Lett.,* **2005,** *34,* 1612–1613.

Daicel Chiralcel OJ- column; λ = 254 nm; hexane/isopropanol =90/10; flow rate = 1.0 mL/min; t_R(S) =11.1 min, t_R (R) = 20.7 min : ee = 92%



Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	11.542	125622	8310	1.061	50.396
2	22.075	123648	4001	1.046	49.604



compound was prepared under the condition shown in Scheme 3

Number	Time / min	Area / µV s	Height / µV	Symmetry factor	Area (%)
1	11.600	2081826	136165	1.093	94.411
2	22.200	123235	4063	1.041	5.589

Daicel Chiralcel OJ- column; λ = 254 nm; hexane/isopropanol =90/10; flow rate = 1.0 mL/min; t_R(S) =11.6 min, t_R (R) = 22.2 min : ee = 89%