Catalytic asymmetric Michael reaction of methyl alkynyl ketone catalyzed by diphenylprolinol silyl ether

Nariyoshi Umekubo, Yujiro Hayashi*

Department of Chemistry, Graduate School of Science, Tohoku University 6-3 Aramaki-Aza Aoba-ku, Sendai, Miyagi 980-8579, Japan

SUPPORTING INFORMATION

Experimental procedures and Characterization data

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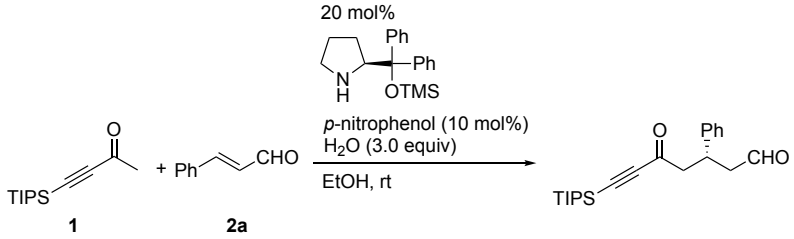
1. Materials and Methods

General Methods.

General Remarks: All reactions were carried out under argon atmosphere and monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plates (0.25 mm thickness). Specific optical rotations were measured using a JASCO P-1020 polarimeter and a JASCO DIP-370 polarimeter. FT-IR spectra were recorded on a JASCO FT/IR-410 spectrometer and a Perkin Elmer spectrum BX FT-IP spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent-400 MR (400 MHz for ^{1}H NMR, 100 M Hz for ^{13}C NMR) instrument. Data for ^{1}H NMR are reported as chemical shift (δ ppm), integration multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quintet = quin, septet = sep, dd = doublet of doublets, ddd = doublet of doublet of doublets, dt = double of triplets, td = triplet of doublets, m = multiplet, brs = broad singlet), coupling constant (Hz), Data for ^{13}C NMR are reported as chemical shift. High resolution ESI-TOF mass spectra were measured by Themo Orbi-trap instrument. HPLC analysis was performed on a HITACHI Elite LaChrom Series HPLC, UV detection monitored at appropriate wavelength respectively, using CHIRALPACK® IG (0.46 cm × 25 cm).

2. Experimental Procedures

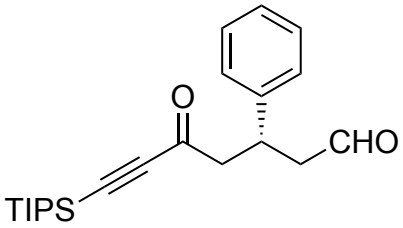
2.1. Typical procedure of asymmetric Michael reaction using alkynyl ketone



To a solution of cinnamaldehyde **1** (23.5 mg, 0.18 mmol) and 4-(triisopropylsilyl)but-3-yn-2-one **2a** (33.7 mg, 0.15 mmol) in EtOH (600 μL), H_2O (8.1 μL, 0.45 mmol), diphenylprolinol silyl ether (9.7 mg, 0.030 mmol), *p*-nitrophenol (2.1 mg, 0.015 mmol) were added at room temperature. After stirred the reaction mixture at this temperature for 3 hours, its solvent was removed under reduced pressure. The residue was directly purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 12:1) to give the target compound (37.1 mg, 0.104 mmol) in 69% yield.

2.2. Compounds information

(*R*)-5-Oxo-3-phenyl-7-(triisopropylsilyl)hept-6-ynal (3a)



Yield: 69% (36.8 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$) δ 1.05-1.15 (m, 21H), 2.79-2.82 (m, 2H), 2.95 (d, *J* = 7.2 Hz, 2H), 3.90 (quin, *J* = 7.2, 1H), 7.20-7.24 (m, 3H), 7.29-7.33 (m, 2H), 9.66 (t, *J* = 2.0 Hz, 1H)

^{13}C NMR ($CDCl_3$) δ 200.4, 185.1, 142.1, 128.9, 128.9, 127.3, 127.1, 127.1, 104.0, 96.7, 51.6, 49.3, 35.9, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 10.9, 10.9, 10.9

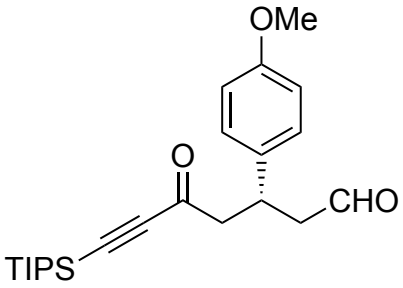
HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{32}O_2SiNa$: 379.2064, found: 379.2064

IR(neat)ν 2145, 1726, 1677, 1463, 1386, 1222, 1116, 1073, 997, 883, 7000, 679, 586, 457, 410 cm^{-1}

$[\alpha]_D^{26}$ -20.1 (*c* 2.0, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.40

(*R*)-3-(4-Methoxyphenyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3b)



Yield: 68% (39.3 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$) δ 1.06-1.15 (m, 21H), 2.75-2.78 (m, 2H), 2.92 (d, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.85 (quin, *J* = 7.2 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 9.65 (t, *J* = 2.0 Hz, 1H)

^{13}C NMR ($CDCl_3$) δ 200.7, 185.3, 158.6, 134.1, 128.3, 128.3, 114.2, 114.2, 104.1, 96.6, 55.2, 51.9, 49.5, 34.9, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 11.0, 11.0, 11.0

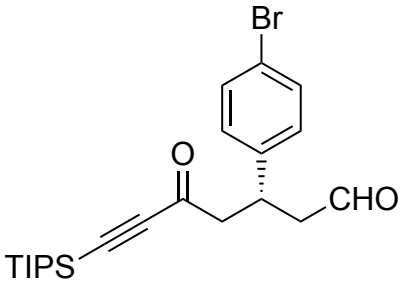
HRMS (ESI): $[M+Na]^+$ calcd for $C_{23}H_{34}O_3SiNa$: 409.2169, found: 409.2169

IR(neat)ν 2145, 1726, 1677, 1463, 1386, 1222, 1116, 1073, 997, 883, 7000, 679, 586, 457, 410 cm^{-1}

$[\alpha]_D^{26}$ -15.5 (*c* 1.5, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.20

(*R*)-3-(4-Bromophenyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3c)



Yield: 61% (37.9 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.06-1.11 (m, 21H), 2.80 (dt, *J* = 1.6, 6.8 Hz, 2H), 2.92 (dd, *J* = 2.4, 7.2 Hz, 2H), 3.86 (quin, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 9.66 (t, *J* = 1.2 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.8, 188.9, 141.2, 132.0, 132.0, 129.1, 129.1, 121.0, 104.0, 91.6, 51.3, 49.2, 34.9, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 11.0, 11.0, 11.0

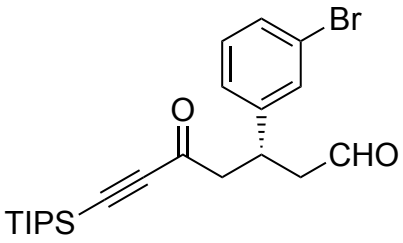
HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{31}BrO_2SiNa$: 457.1169, found: 457.1172

IR(neat)ν 2145, 1726, 1677, 1489, 1463, 1118, 1074, 1011, 883, 821, 681, 404 cm^{-1}

$[\alpha]_D^{26}$ -19.5 (*c* 1.7, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

(*R*)-3-(3-Bromophenyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3d)



Yield: 64% (41.6 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.06-1.17 (m, 21H), 2.81 (ddd, *J* = 1.6, 5.6, 7.2 Hz, 2H), 2.93 (dd, *J* = 1.2, 6.8 Hz, 2H), 3.86 (quin, *J* = 7.2 Hz, 1H), 7.16-7.18 (m, 2H), 7.34-7.38 (m, 2H), 9.70 (t, *J* =1.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.7, 184.6, 144.6, 130.5, 130.4, 130.3, 126.2, 122.9, 103.9, 97.1, 51.2, 49.1, 35.0, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 11.0, 11.0, 11.0

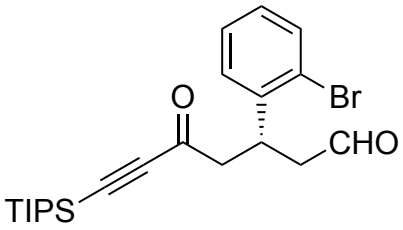
HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{31}BrO_2SiNa$: 457.1169, found: 457.1173

IR(neat)ν 2145, 1726, 1677, 1568, 1463, 1428, 1221, 1117, 1074, 997, 882, 784, 679, 587, 440, 408 cm^{-1}

$[\alpha]_D^{26}$ -38.5 (*c* 0.50, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

(*R*)-3-(2-Bromophenyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3e)



Yield: 70% (45.6 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.07-1.15 (m, 21H), 2.85 (dd, *J* = 1.6, 7.2 Hz, 2H), 2.94 (dd, *J* = 8.0, 17.6 Hz, 1H), 3.03 (dd, *J* = 6.0, 16.8 Hz, 1H), 4.37 (quin, *J* = 7.2 Hz, 1H), 7.09 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.21 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.28 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.56 (dd, *J* = 1.2, 8.0 Hz, 1H), 9.68 (t, *J* = 1.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1, 184.8, 140.8, 133.5, 128.6, 128.1, 127.9, 124.3, 103.8, 96.9, 49.8, 47.9, 34.5, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 11.0, 11.0, 11.0

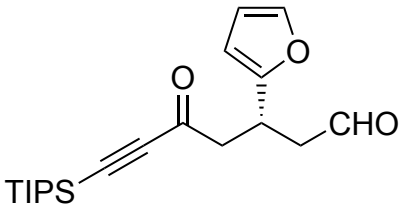
HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{31}BrO_2SiNa$: 457.1169, found: 457.1170

IR(neat)ν 2146, 1726, 1676, 1470, 1223, 1110, 1022, 883, 755, 681, 585, 450 cm^{-1}

$[\alpha]_D^{26}$ +3.40 (*c* 1.9, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

(*R*)-3-(Furan-2-yl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3f)



Yield: 78% (40.8 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04-1.17 (m, 21H), 2.79 (dt, *J* = 1.6, 5.6 Hz, 2H), 2.90 (dd, *J* = 7.6, 17.2 Hz, 1H), 3.02 (dd, *J* = 6.8, 16.8 Hz, 1H), 3.99 (quin, *J* = 7.6 Hz, 1H), 6.06 (d, *J* = 3.2 Hz, 1H), 6.26 (dd, *J* = 1.6, 3.2 Hz, 1H), 7.30 (t, *J* = 0.80 Hz, 1H), 9.72 (t, *J* = 2.0 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.1, 184.7, 154.9, 141.7, 110.2, 105.9, 103.8, 96.9, 48.7, 46.6, 29.0, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 10.9, 10.9, 10.9

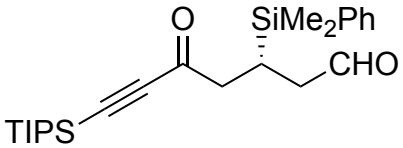
HRMS (ESI): $[M+Na]^+$ calcd for $C_{20}H_{30}O_3SiNa$: 369.1856, found: 369.1858

IR(neat)ν 2146, 1727, 1679, 1464, 1218, 1115, 1072, 1015, 883, 734, 681, 597 cm^{-1}

$[\alpha]_D^{26}$ -4.41 (*c* 1.5, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.20

(*R*)-3-(Dimethyl(phenyl)silyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3g)



Yield: 71% (44.1 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.33 (s, 6H), 1.08-1.12 (m, 21H), 2.01-2.16 (m, 1H), 2.34 (ddd, *J* = 2.0, 8.0, 17.6 Hz, 1H), 2.49 (dd, *J* = 9.6, 16.8 Hz, 1H), 2.50 (ddd, *J* = 1.6, 5.6, 17.6 Hz, 1H), 2.69 (dd, *J* = 4.8, 16.8 Hz, 1H), 7.34-7.39 (m, 3H), 7.47-7.50 (m, 2H), 9.62 (t, *J* = 1.2 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.5, 187.1, 136.2, 133.9, 133.9, 129.5, 128.0, 128.0, 104.0, 96.4, 46.0, 44.1, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 15.4, 11.0, 11.0, 11.0, -4.37, -4.46

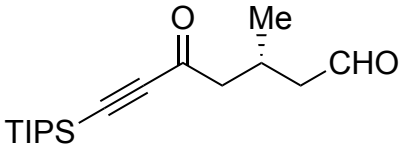
HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{38}O_2Si_2Na$: 437.2303, found: 437.2303

IR(neat)ν 2145, 1725, 1677, 1462, 1427, 1253, 1212, 1112, 1069, 997, 883, 836, 778, 736, 701, 681, 471 cm^{-1}

$[\alpha]_D^{26}$ -5.02 (*c* 1.5, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.50

(*R*)-3-Methyl-5-oxo-7-(triisopropylsilyl)hept-6-ynal (3h)



Yield: 55% (24.3 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04 (d, *J* = 6.8 Hz, 3H), 1.08-1.16 (m, 21H), 2.35 (ddd, *J* = 2.4, 8.0, 17.2 Hz, 1H), 2.48-2.60 (m, 2H), 2.60-2.66 (dd, *J* = 6.4, 16.4 Hz, 1H), 2.72 (quin, *J* = 6.8 Hz, 1H), 9.75 (t, *J* = 1.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 201.3, 186.2, 104.2, 96.2, 51.9, 50.0, 24.6, 20.0, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 10.8, 10.8, 10.8

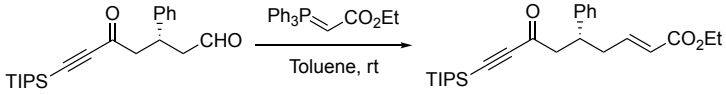
HRMS (ESI): $[M+Na]^+$ calcd for $C_{17}H_{30}O_2SiNa$: 317.1907, found: 317.1907

IR(neat)ν 2145, 1726, 1673, 1463, 1163, 1072, 996, 918, 883, 701, 680, 505 cm^{-1}

$[\alpha]_D^{26}$ +20.6 (*c* 0.20, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.60

2.3. Typical procedure of Wittig reaction to determine the value of *ee*

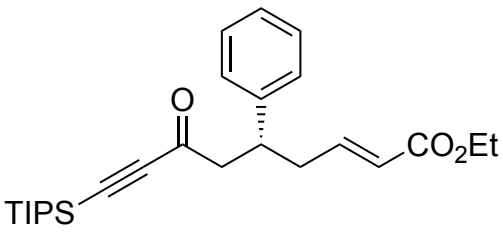


To a solution of aldehyde (37.1 mg, 0.10 mmol) in toluene (300 μL), $Ph_3P{=}CHCO_2Et$ (69.6 mg, 0.20 mmol) was added at room temperature. After stirring the reaction mixture at this temperature for 1 hour, the reaction mixture was directly purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 3:1) to give the target compound.

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 12.7 min, minor isomer t_R = 24.9 min) (95% *ee*).

2.4. Compounds information

Ethyl (*R*,*E*)-7-oxo-5-phenyl-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 73% (31.2 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.94-1.17 (m, 21H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.51-2.60 (m, 2H), 2.90 (d, *J* = 3.6 Hz, 2H), 3.48 (quin, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.78 (d, *J* = 15.6 Hz, 1H), 6.78 (dd, *J* = 7.6, 15.6 Hz, 1H), 7.17-7.23 (m, 2H), 7.26-7.32 (m, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.6, 166.2, 145.6, 142.3, 128.7, 128.7, 127.4, 127.4, 127.0, 123.5, 104.1, 96.5, 60.2, 51.5, 40.7, 38.6, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0,11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{38}O_3SiNa$: 449.2482, found: 449.2480

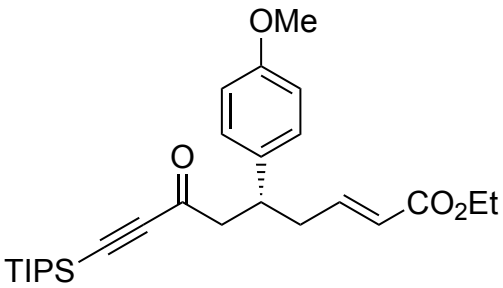
IR(neat)ν 2145, 1721, 1677, 1463, 1367, 1264, 1207, 1160, 1109, 1075 1041, 997, 883, 838, 762, 700, 679 cm^{-1}

$[\alpha]_D^{26}$ -7.14 (*c* 1.8, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.40

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 12.7 min, minor isomer t_R = 24.9 min) (95% *ee*).

Ethyl (*R*,*E*)-5-(4-methoxyphenyl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 80% (36.5 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04-1.17 (m, 21H), 1.25 (t, *J* = 7.2 Hz, 3H), 2.45-2.58 (m, 2H), 2.85 (d, *J* = 7.6 Hz, 2H), 3.43 (quin, *J* = 7.2 Hz, 1H), 3.78 (s, 3H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 15.6 Hz, 1H), 6.79 (td, *J* = 7.2, 15.6 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.8, 166.2, 158.4, 145.8, 134.3, 128.3, 128.3, 123.4, 114.1, 114.1, 104.2, 96.5, 60.2, 55.2, 51.8, 40.0, 38.8, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0, 11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{27}H_{40}O_4SiNa$: 479.2588, found: 479.2593

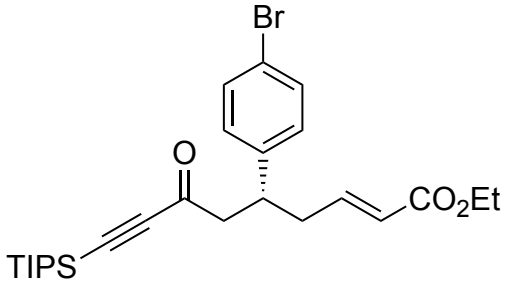
IR(neat)ν 2146, 1718, 1675, 1513, 1458, 1251, 1038, 827, 419 cm^{-1}

$[\alpha]_D^{26}$ -2.84 (*c* 0.20, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.20

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 20.6 min, minor isomer t_R = 39.3 min) (95% *ee*).

Ethyl (*R*,*E*)-5-(4-bromophenyl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 81% (40.8 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.06-1.14 (m, 21H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.50-2.59 (m, 2H), 2.87 (dd, *J* = 0.80, 8.0 Hz, 2H), 3.43 (quin, *J* = 7.2 Hz, 1H), 4.15 (t, *J* = 7.2 Hz, 2H), 5.76 (d, *J* = 15.6 Hz, 1H), 6.74 (td, *J* =7.2, 15.6 Hz, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.1, 166.1, 145.0, 141.2, 131.9, 131.9, 129.1, 129.1, 123.8, 120.8, 104.1, 96.8, 60.3, 51.3, 40.2, 38.4, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0, 11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{37}BrO_3SiNa$: 527.1588, found: 527.1589

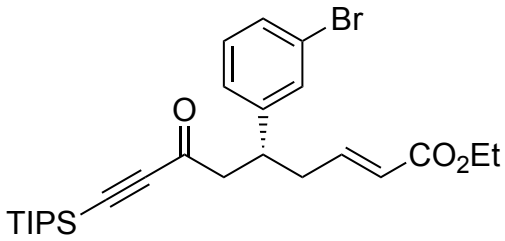
IR(neat)ν 2145, 1720, 1677, 1464, 1206, 1101, 882, 679 cm^{-1}

$[\alpha]_D^{26}$ +2.65 (*c* 1.0, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 12.7 min, minor isomer t_R = 20.3 min) (94% *ee*).

Ethyl (*R*,*E*)-5-(3-bromophenyl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 78% (39.3 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.07-1.15 (m, 21H), 1.26 (t, *J* = 7.2 Hz, 3H), 2.46-2.59 (m, 2H), 2.87 (d, *J* = 7.2 Hz, 2H), 3.43 (quin, *J* = 7.2 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 5.78 (d, *J* = 15.6 Hz, 1H), 6.75 (td, *J* = 7.6, 15.6 Hz, 1H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.33-7.36 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.0, 166.1, 145.0, 144.7, 130.4, 130.3, 130.2, 126.2, 123.9, 122.8, 104.0, 96.9, 60.3, 51.2, 40.3, 38.4, 18.7, 18.7, 18.5, 18.5, 18.4, 18.4, 14.2, 11.0, 11.0, 11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{37}BrO_3SiNa$: 527.1588, found: 527.1586

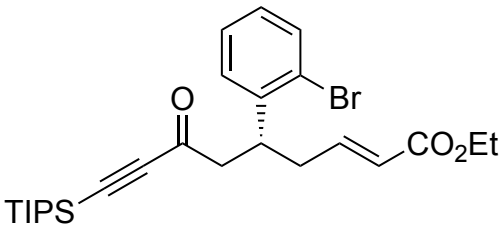
IR(neat)ν 2146, 1719, 1677, 1464, 1367, 1270, 1206, 1113, 882, 680 cm^{-1}

$[\alpha]_D^{26}$ -10.9 (*c* 0.65, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 11.4 min, minor isomer t_R = 20.4 min) (95% *ee*).

Ethyl (*R*,*E*)-5-(2-bromophenyl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 70% (435.3 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05-1.17 (m, 21H), 1.26 (t, *J* =7.2 Hz, 3H), 2.52-2.64 (m, 2H), 2.86 (dd, *J* = 8.0, 16.4 Hz, 1H), 2.92 (dd, *J* = 6.8, 16.0 Hz, 1H), 4.06 (quin, *J* = 7.2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.78 (d, *J* = 15.6 Hz, 1H), 6.80 (td, *J* = 7.2, 15.6 Hz, 1H), 7.08 (dt, *J* =1.6, 7.6 Hz, 1H), 7.17 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 1H), 7.55 (dd, *J* = 0.80, 8.0 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.1, 166.1, 145.0, 140.9, 133.4, 128.4, 127.8, 127.8, 124.8, 123.8, 103.9, 96.7, 60.2, 49.8, 39.0, 37.0, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0, 11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{26}H_{37}BrO_3SiNa$: 527.1588, found: 527.1588

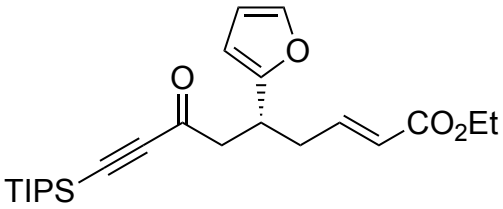
IR(neat)ν 2146, 1721, 1676, 1470, 1367, 1267, 1205, 1162, 1107, 1024, 996 920, 883, 756, 680, 585, 452, 420 cm^{-1}

$[\alpha]_D^{26}$ -14.1 (*c* 1.7, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.45

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 9.05 min, minor isomer t_R = 9.91 min) (95% *ee*).

Ethyl (*R*,*E*)-5-(furan-2-yl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 65% (27.0 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.04-1.17 (m, 21H), 1.27 (t, *J* = 7.2 Hz, 3H), 2.50-2.64 (m, 2H), 2.82 (dd, *J* = 6.8, 16.4 Hz, 1H), 2.94 (dd, *J* = 7.2, 16.4 Hz, 1H), 3.61 (quin, *J* = 6.8 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 5.81 (d, *J* = 15.6 Hz, 1H), 6.04 (d, *J* = 3.2 Hz, 1H), 6.26 (dd, *J* = 2.0, 3.2 Hz, 1H), 6.82 (td, *J* = 7.6, 15.6 Hz, 1H), 7.31 (d, *J* = 1.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 185.0, 166.1, 155.2, 145.1, 141.6, 123.7, 110.1, 105.9, 103.9, 96.7, 60.3, 48.7, 36.0, 33.9, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0, 11.0

HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{36}O_4SiNa$: 439.2275, found: 439.2272

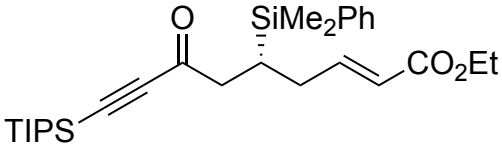
IR(neat)ν 2146, 1720, 1681, 1464, 1367, 1267, 1161, 1110, 883, 733, 664 cm^{-1}

$[\alpha]_D^{26}$ +1.04 (*c* 0.75, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.20

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 11.9 min, minor isomer t_R = 16.5 min) (94% *ee*).

Ethyl (*R*,*E*)-5-(dimethyl(phenyl)silyl)-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 85% (41.1 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.32 (s, 3H), 0.33 (s, 3H), 1.05-1.15 (m, 21H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.79-1.86 (m, 1H), 2.14 (dquin, *J* = 1.2, 8.0 Hz, 1H), 2.30-2.37 (m, 1H), 2.47 (dd, *J* = 8.4, 16.4 Hz, 1H), 2.57 (dd, *J* = 5.6, 16.8 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 5.72 (d, *J* = 15.6 Hz, 1H), 6.79 (td, *J* = 7.2, 15.6 Hz, 1H), 7.33-7.40 (m, 3H), 7.46-7.50 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.5, 166.1, 147.8, 136.7, 136.7, 133.9, 129.4, 128.0, 122.7, 122.7, 104.1, 96.1, 60.1, 45.7, 32.6, 21.1, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 11.0, 11.0, 11.0, -4.11, -4.11

HRMS (ESI): $[M+Na]^+$ calcd for $C_{28}H_{44}O_3Si_2Na$: 507.2721, found: 507.2723

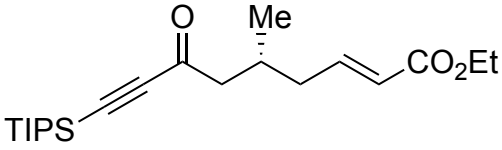
IR(neat)ν 2145, 1720, 1676, 1464, 1428, 1367, 1261, 1186, 1112, 1044, 997, 883, 835, 775, 736, 701, 680, 472 cm^{-1}

$[\alpha]_D^{26}$ -6.45 (*c* 2.1, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.50

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 7.84 min, minor isomer t_R = 9.32 min) (98% *ee*).

Ethyl (*R*,*E*)-5-methyl-7-oxo-9-(triisopropylsilyl)non-2-en-8-ynoate



Yield: 60% (21.8 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.99 (d, *J* = 6.8 Hz, 3H), 1.08-1.16 (m, 21H), 1.29 (t, *J* = 7.2 Hz, 3H), 2.10-1.17 (m, 1H), 2.22-2.30 (m, 1H), 2.30-2.39 (m, 1H), 2.41 (dd, *J* = 7.6, 15.6 Hz, 1H), 2.57 (dd, *J* = 6.0, 15.6

Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 5.84 (dd, J = 1.2, 15.6 Hz, 1H), 6.90 (td, J = 7.2, 15.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.8, 166.3, 146.4, 123.4, 104.2, 96.0, 52.1, 38.9, 29.3, 19.6, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 14.2, 10.9, 10.9, 10.9, 10.9

HRMS (ESI): $[M+Na]^+$ calcd for $C_{21}H_{36}O_3SiNa$: 387.2326, found: 387.2325

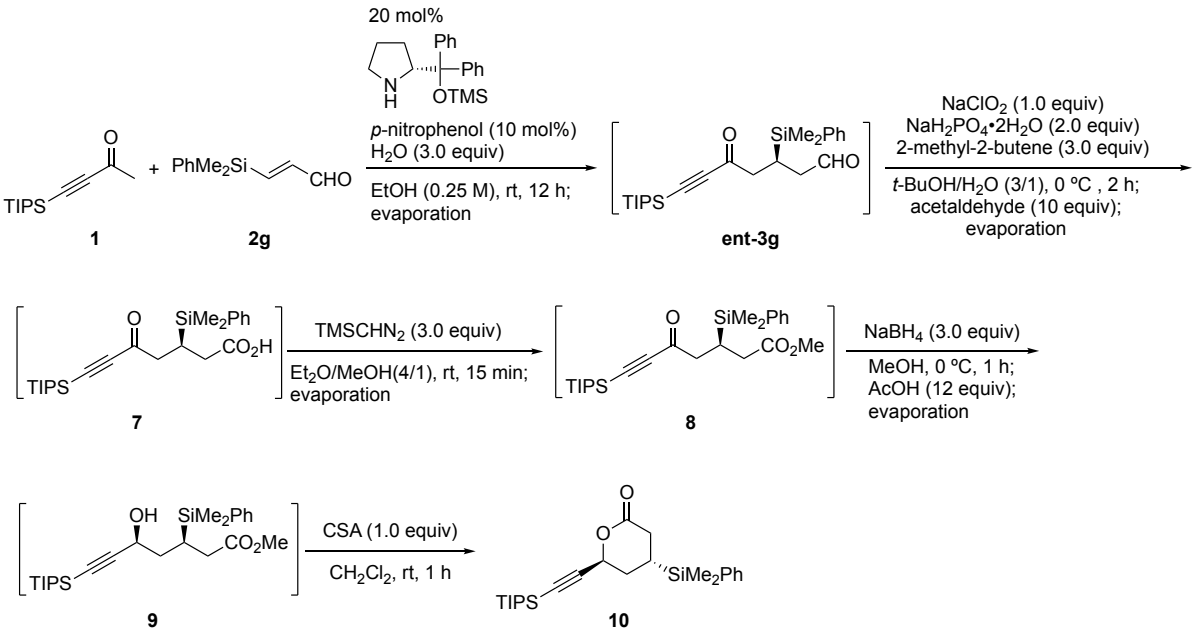
IR(neat)ν 2146, 1727, 1677, 1462, 1070, 882, 682, 522, 483, 459, 431, 421, 413 cm^{-1}

$[\alpha]_D^{26}$ +10.8 (*c* 0.15, $CHCl_3$)

R_f (*n*-Hexane: EtOAc =3:1, color reagent: Hanessian's stain reagent): 0.60

The enantiomeric ratio was determined by HPLC using CHIRALPACK® IG (*n*-Hexane: *i*-PrOH = 66:1; flow rate 1.0 ml/min, major isomer t_R = 5.91 min, minor isomer t_R = 6.39 min) (76% *ee*).

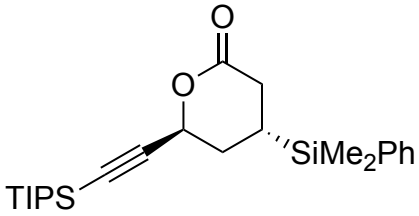
2.5. One-pot procedure of providing compound 10 from compound 1 and compound 2g



To a solution of aldehyde **2g** (114 mg, 0.60 mmol) and 4-(triisopropylsilyl)but-3-yn-2-one **1** (112 mg, 0.50 mmol) in EtOH (2.0 mL), H_2O (27 μL, 1.5 mmol), diphenylprolinol silyl ether (32.5 mg, 0.10 mmol) and *p*-nitrophenol (7.0 mg, 0.050 mmol) were added at room temperature. After stirred at this temperature for 12 hours, its solvent was removed by evaporation under reduced pressure. To a solution of the residue in *t*-BuOH/H_2O = (3/1) (0.8 mL), $NaH_2PO_4 \cdot H_2O$ (312 mg, 1.0 mmol), 2-methyl-2-butene (160 μL, 1.5 mmol) and $NaClO_2$ (45 mg, 0.5 mmol) were added at 0 ºC. After stirred at this temperature for 2 hours, the oxidant in the reaction mixture was quenched by acetaldehyde (0.14 mL, 2.5 mmol). Its solvent and excess amount of acetaldehyde were removed by evaporation under reduced pressured. To a solution of the residue in Et_2O: MeOH = (4:1) (1.0 mL), $TMSCHN_2$ (2.0 M in Et_2O, 75 μL, 1.5 mmol) was added at room temperature. After stirred at this temperature for 15 minutes, its solvent was removed by evaporation under reduced pressure. To a solution of the residue in MeOH (1.0 mL), sodium borohydride (56.0 mg, 1.5 mmol) was added at 0 ºC. After stirred at this temperature for 1 hour, the reductant was quenched by acetic acid (0.24 mL, 6.0 mmol). Its solvent and acetic acid were removed by evaporation under reduced pressure. To a solution of the residue

in CH_2Cl_2 (1.5 mL), CSA (117 mg, 0.5 mmol) was added at room temperature. After stirred at this temperature for 1 hour, the reaction mixture was quenched by sat. aq. $NaHCO_3$ (5 mL) and diluted by EtOAc (5 mL). After separated, the aqueous layer was extracted with EtOAc (5 mL) for three times. The combined organic layers were washed by brine (10 mL), dried over on sodium sulfate, and evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 10:1) to give desired compound **10** (85.0 mg, 0.21 mmol) in 42% isolated yield.

(*4R,6S*)-4-(Dimethyl(phenyl)silyl)-6-((triisopropylsilyl)ethynyl)tetrahydro-2H-pyran-2-one (10)



Yield: 42% (85.0 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.33 (s, 3H), 0.33 (s, 3H), 1.02-1.11 (m, 21H), 1.78-2.00 (m, 3H), 2.27 (dd, *J* =12.0, 18.0 Hz, 1H), 2.62 (ddd, *J* = 1.6, 6.0, 18.0 Hz, 1H), 5.19 (dd, *J* = 3.2, 4.4 Hz, 1H), 7.35-7.42 (m, 3H), 7.45-7.48 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.1, 135.3, 133.8, 133.8, 129.7, 128.1, 128.1, 103.7, 89.1, 70.4, 30.7, 29.8, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 15.6, 11.0, 11.0, 11.0, -5.65, -5.76

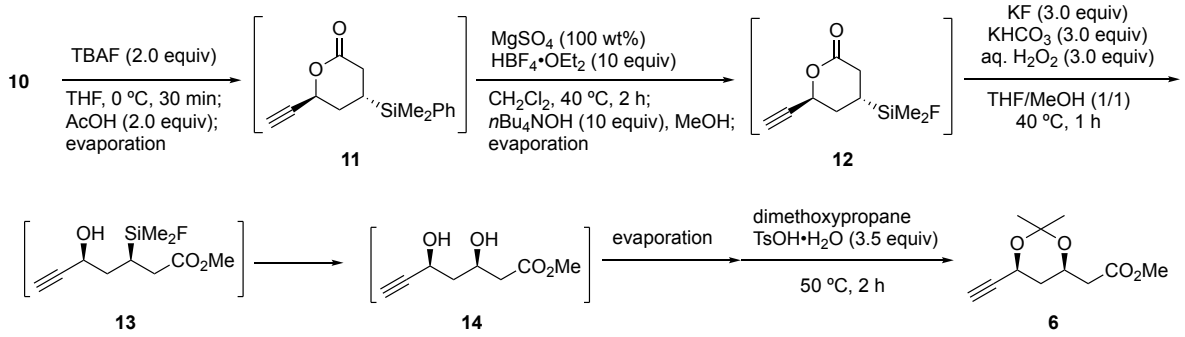
HRMS (ESI): $[M+Na]^+$ calcd for $C_{24}H_{38}O_2Si_2Na$: 437.2303, found: 437.2300

IR(neat)ν 2943, 2865, 2317, 1746, 1464, 1261, 1065, 977, 883, 814, 702, 668 cm^{-1}

$[\alpha]_D^{26}$ +43.9 (*c* 1.5, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.45

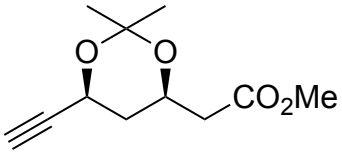
2.6. One-pot procedure of providing compound 6 from compound 10



To a solution of compound **10** (82.8 mg, 0.20 mmol) in THF, TBAF (1.0 M in THF, 300 μL, 0.30 mmol) was added at 0 ºC. After stirred at this temperature for 30 minutes, acetic acid (34.3 μL, 0.60 mmol) was added. Then solvent was removed by evaporation under reduced pressure. To a solution of the residue in

CH_2Cl_2 (0.30 mL), $MgSO_4$ (82.8 mg) and $HBF_4{\cdot}OEt_2$ (272 μL, 2.0 mmol) were added at 40 ºC. After stirred at this temperature for 2 hours, TBAOH (10% in MeOH, 5.2 mL, 2.0 mmol) was added. Then solvent was removed by evaporation under reduced pressure. To a solution of the residue in THF: MeOH = (1:1) (0.30 mL), KF (34.9 mg, 0.60 mmol), $KHCO_3$ (60.0 mg, 0.60 mmol) and aq. H_2O_2 (35% in H_2O, 40.2 μL, 0.60 mmol) were added at 40 ºC. After stirred at this temperature for 2 hours, solvent was removed by evaporation under reduced pressure. To a solution of the residue in 2,2-dimethoxy propane (0.60 mL), $TsOH{\cdot}H_2O$ (133 mg, 0.70 mmol) was added at 50 ºC. After stirred at this temperature for 2 hours, the reaction mixture was quenched by sat. aq. $NaHCO_3$ (5 mL) and diluted by EtOAc (5 mL). The aqueous layer was extracted with EtOAc (5 mL) for three times. The combined organic layers were washed with brine (20 mL), dried over on sodium sulfate. Its solvent was removed by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 4:1) to give corresponding compound **6** (17.0 mg, 0.080 mmol) in 40% isolated yield.

Methyl 2-((4*R*,6*S*)-6-ethynyl-2,2-dimethyl-1,3-dioxan-4-yl)acetate (6)



Yield: 40% (17.0 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 3H), 1.47 (s, 3H), 1.67 (t, *J* =13.2 Hz, 1H), 1.85 (td, *J* = 2.4, 16.8 Hz, 1H), 2.40 (dd, *J* = 6.0, 16.0 Hz, 1H), 2.45 (d, *J* = 2.0 Hz, 1H), 2.56 (dd, *J* = 7.2, 16.0 Hz, 1H), 3.69 (s, 3H), 4.31 (dsext, *J* = 2.4, 6.4 Hz, 1H), 4.69 (td, *J* = 2.4, 11.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0, 99.6, 82.2, 72.9, 65.4, 60.0, 51.7, 40.8, 36.7, 30.0, 19.3

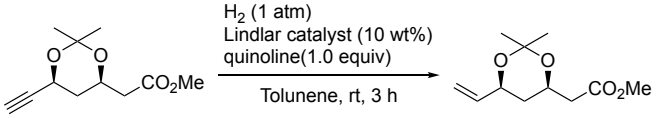
HRMS (ESI): $[M+Na]^+$ calcd for $C_{11}H_{16}O_4Na$: 235.0941, found: 235.0940

IR(neat)ν 3276, 2926, 2126, 1728, 1462, 1381, 1262, 1200, 1166, 1123, 1011, 924, 845, 743, 665, 557 cm^{-1}

$[\alpha]_D^{26}$ -1.97 (*c* 1.1, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.40

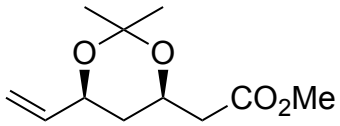
2.7. Lindlar reduction of compound 6 to determine its absolute configuration



To a solution of compound **7** (12.7 mg, 0.060 mmol) in toluene (1.0 mL), Lindlar's catalyst (2.0 mg) and quinolone (7.11 μL, 0.060 mmol) were added at room temperature under H_2 atmosphere (1 atm). After stirred at this condition for 3 hours, the residue was filtrated by Celite®. The solvent was removed by evaporation under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-Hexane: EtOAc

= 4:1) to give corresponding compound **15** (11.7 mg, 0.055 mmol) in 91% isolated yield. All Spectrum data of target compound were matched to reported data[1]. The reported value of optical rotation is $[\alpha]_D^{20}$ -2.8 (*c* 1.4, $CHCl_3$) and observed one was $[\alpha]_D^{27}$ -2.9 (*c* 1.0 $CHCl_3$). Thus, absolute configuration of compound **15** is same to reported one.

Methyl 2-((4*R*,6*S*)-2,2-dimethyl-6-vinyl-1,3-dioxan-4-yl)acetate (15)



Yield: 91% (11.7 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.30 (q, *J* = 12.8, 1H), 1.41 (s, 3H), 1.49 (s, 3H), 1.66 (td, *J* = 2.4, 12.8 Hz, 1H), 2.40 (dd, *J* = 6.4, 15.6 Hz, 1H), 2.57 (dd, *J* = 6.8, 15.6 Hz, 1H), 3.69 (s, 3H), 4.32-4.41 (m, 2H), 5.13 (td, *J* = 1.6, 10.4 Hz, 1H), 5.26 (td, *J* = 1.2, 17.2 Hz, 1H), 5.81 (ddd, *J* = 6.0, 10.4, 17.2 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.3, 138.4, 115.6, 98.9, 70.0, 65.6, 51.7, 41.1, 36.2, 30.0, 19.7

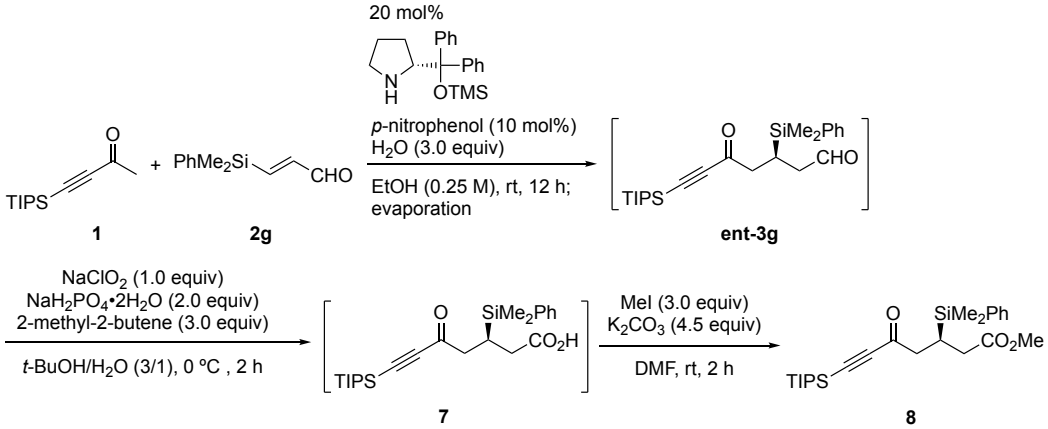
HRMS (ESI): $[M+Na]^+$ calcd for $C_{11}H_{18}O_4$ Na: 237.1097, found: 237.1097

IR(neat)ν 2994, 2951, 1740, 1438, 1381, 1314, 1259, 1200, 1169, 1097, 999, 925, 848 cm^{-1}

$[\alpha]_D^{27}$ -2.9 (*c* 1.0, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.35

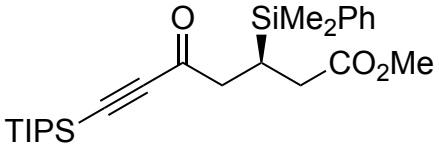
2.8. Preparation of compound 8



To a solution of aldehyde **2g** (1.33 g, 7.0 mmol) and 4-(triisopropylsilyl)but-3-yn-2-one **1** (1.57 g, 7.0 mmol) in EtOH (21 mL), H_2O (378 μL, 21 mmol), diphenylprolinol silyl ether (456 mg, 1.4 mmol) and *p*-nitrophenol (97.4 mg, 0.70 mmol) were added at room temperature. After stirred the reaction mixture at this temperature for 3 hours, its solvent was removed under reduced pressure. To a solution of the residue in *t*-BuOH: H_2O = (3:1) (21 mL), $NaH_2PO_4 \cdot H_2O$ (2.18 g, 14 mmol), 2-methyl-2-butene (2.23 mL, 21 mmol) and $NaClO_2$ (633 mg, 7.0 mmol) were added at 0 ºC. After stirred at this temperature for 2 hours, the reaction mixture was quenched by sat. aq. sodium hyposulfite (50 mL). The residue was diluted by EtOAc (20 mL). After separated,

the aqueous layer was extracted with EtOAc (30 mL) for three times. The combined organic layers were evaporated under reduced pressure. The residue was directly used without further purification. To a solution of crude material in DMF (30 mL), MeI (2.18 mL, 35 mmol) and K_2CO_3 (7.26 g, 75 mmol) were added at room temperature. After stirred at this temperature for 2 hours, the reaction mixture was quenched by sat. aq. ammonium chloride (60 mL). The residue was diluted by EtOAc (30 mL). After separated, the aqueous layer was extracted with EtOAc (50 mL) for three times. The combined organic layers were washed by brine, dried over on sodium sulfate, and evaporated under reduced pressure. The crude material was purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 15:1) to give the target compound **8** (1.71 g, 3.85 mmol) in 55% yield.

Methyl (*R*)-3-(dimethyl(phenyl)silyl)-5-oxo-7-(triisopropylsilyl)hept-6-ynoate (8)



Yield: 55% (1.71 g)

Physical State: Brown oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.33 (s, 6H), 1.07-1.15 (m, 21H), 2.05-2.12 (m, 1H), 2.26 (dd, *J* = 8.0, 15.6 Hz, 1H), 2.41 (dd, *J* = 6.0, 15.6 Hz, 1H), 2.55 (dd, *J* = 8.8, 16.8 Hz, 1H), 2.66 (dd, *J* = 8.8, 16.8 Hz, 1H) 3.56 (s, 3H), 7.33-7.39 (m, 3H), 7.48-7.50 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 187.2, 173.3, 136.4, 133.9, 133.9, 129.4, 127.9, 127.9, 104.0, 95.7, 51.4, 46.0, 34.4, 32.8, 18.5, 18.5, 18.5, 18.5, 18.5, 18.5, 11.0, 11.0, 11.0, -4.48, -4.52

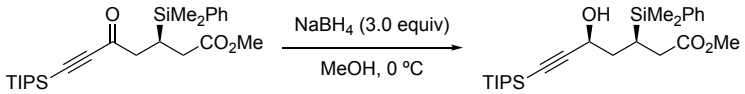
HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{40}O_3Si_2Na$: 467.2408, found: 467.2411

IR(neat)ν 2946, 2867, 2146, 1721, 1676, 1464, 1428, 1367, 1261, 1185, 1112, 1044, 997, 883, 835, 815, 775, 736, 701, 680, 581 cm^{-1}

$[\alpha]_D^{26}$ +14.3 (*c* 0.90, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 3:1, color reagent: Hanessian's stain reagent): 0.55

2.9. Stereo-selective reduction of compound 8

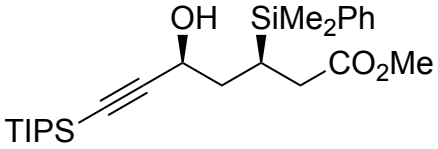


8 **9**

To a solution of compound **8** (44.5 mg, 0.10 mmol) in MeOH (300 μL), sodium borohydride (11.3 mg, 0.30 mmol) was added at 0 °C. After stirred at this temperature for 1 hour, the reaction mixture was quenched by sat. aq. ammonium chloride (5 mL). The residue was diluted by EtOAc (5 mL). After separated, the aqueous layer was extracted with EtOAc (5 mL) for three times. The combined organic layers were washed by brine (20 mL) and dried over on sodium sulfate. The solvent was removed by evaporation under reduced pressure.

The residue was purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 8:1) to give the target compound **9** (39.2 mg, 0.088 mmol) in 88% yield.

Methyl (3*R*,5*S*)-3-(dimethyl(phenyl)silyl)-5-hydroxy-7-(triisopropylsilyl)hept-6-ynoate (9)



Yield: 88% (39.2 mg)

Physical State: Brown oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.321 (s, 6H), 1.03-1.14 (m, 21H), 1.60-1.66 (m, 1H), 1.70-1.81 (m, 1H), 1.87-1.95 (m, 1H), 2.39 (dd, *J* = 8.0, 16.4 Hz, 1H), 2.46 (dd, *J* = 8.0, 16.4 Hz, 1H), 3.60 (d, *J* = 0.80 Hz, 3H), 4.31 (dd, *J* = 4.0, 8.8 Hz, 1H), 7.34-7.36 (m, 3H), 7.48-7.50 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.5, 137.0, 133.9, 133.9, 129.3, 127.9, 127.9, 108.6, 85.4, 61.2, 51.9, 39.1, 34.2, 18.6, 18.6, 18.6, 18.6, 18.6, 18.6, 11.1, 11.1, 11.1, -4.32, -4.87

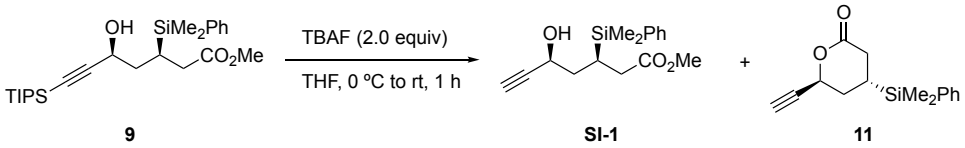
HRMS (ESI): $[M+Na]^+$ calcd for $C_{25}H_{42}O_3Si_2Na$: 469.2565, found: 469.2564

IR(neat)ν 2944, 2866, 2169, 1739, 1463, 1252, 1113, 1017, 883, 834, 816, 774, 735, 701, 678 cm^{-1}

$[\alpha]_D^{26}$ -3.04 (*c* 2.5, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.45

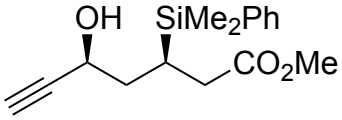
2.10. Deprotection of compound 9



9 **SI-1** **11**

To a solution of compound **9** (133 mg, 0.30 mmol) in THF (0.90 mL), TBAF (1.0 M in THF, 0.60 mL, 0.60 mmol) was added at 0 °C with stirring. Then, the reaction temperature was elevated to room temperature. After stirred at this temperature for 1 hour, the reaction mixture was quenched by sat. aq. ammonium chloride (20 mL). The residue was diluted by EtOAc (10 mL). After separated, aqueous layer was extracted with EtOAc (10 mL) for three times. The combined organic layers were dried over on sodium sulfate and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (*n*-Hecane/EtOAc = 1/6~1/2) to give desired alcohol **SI-1** (23.5 mg, 27%) and undesired lactone **11** (47.2 mg, 61%).

Methyl (3*R*,5*S*)-3-(dimethyl(phenyl)silyl)-5-hydroxyhept-6-ynoate (SI-1)



Yield: 27% (23.5 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.322 (s, 6H), 1.57-1.64 (m, 1H), 1.67-1.73 (m, 1H), 1.94 (ddd, *J* = 2.8, 9.6, 12.8 Hz, 1H), 2.22 (dd, *J* = 8.4, 16.8 Hz, 1H), 2.42-2.43 (m, 1H), 2.47 (dd, *J* = 3.6, 17.2 Hz, 1H), 3.63 (s, 3H), 4.27 (d, *J* = 9.6 Hz, 1H), 7.35-7.37 (m, 3H), 7.49-7.51 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 175.9, 136.7, 133.9, 133.9, 129.3, 127.9, 127.9, 84.8, 72.7, 60.3, 52.0, 38.9, 34.0, 16.8, -4.47, -4.92

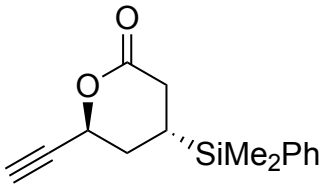
HRMS (ESI): $[M+Na]^+$ calcd for $C_{16}H_{22}O_3SiNa$: 313.1230, found: 313.1235

IR(neat)ν 3448, 3291, 3070, 2952, 2116, 1733, 1428, 1253, 1113, 1043, 816, 775, 736, 702 cm^{-1}

$[\alpha]_D^{26}$ -18.2 (*c* 0.50, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.25

(4*R*,6*S*)-4-(Dimethyl(phenyl)silyl)-6-ethynyltetrahydro-2H-pyran-2-one (11)



Yield: 61% (47.2 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) 0.343 (s, 3H), 0.347 (s, 3H), 1.83-1.96 (m, 3H), 2.24-2.36 (s, 1H), 2.58 (dd, *J* = 2.0, 10.0 Hz, 1H), 2.64 (dd, *J* = 4.2, 16.4 Hz, 1H), 5.14 (quin, *J* = 2.0 Hz, 1H), 7.36-7.42 (m, 2H), 7.46-7.50 (m, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.0, 135.2, 133.8, 133.8, 129.8, 128.1, 128.1, 80.2, 75.6, 69.4, 30.6, 29.2, 15.3, -5.60, -5.69

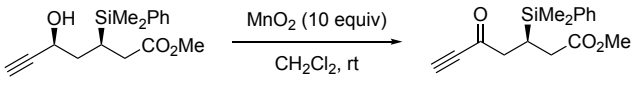
HRMS (ESI): $[M+Na]^+$ calcd for $C_{15}H_{18}O_2SiNa$: 281.0968, found: 281.0964

IR(neat)ν 3265, 2954, 2092, 1735, 1683, 1428, 1253, 1113, 816, 776, 737, 702 cm^{-1}

$[\alpha]_D^{26}$ +53.9 (*c* 1.0, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.30

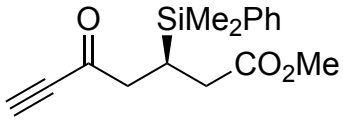
2.11. Oxidation of compound SI-1



SI-1 **16**

To a solution of alcohol **SI-1** (20 mg, 0.076 mmol) in CH_2Cl_2 (1.0 mL), Mn_2O (65.4 mg, 0.76 mmol) was added at room temperature. After stirred at this temperature for 1 hour, its solvent was removed under reduced pressure. The residue was diluted by EtOAc and filtrated by silica gel. After removed its solvent under reduced pressure, the reaction mixture was purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 3:1) to give desired ketone **16** (16.9 mg, 0.058 mmol) in 76%.

Methyl (*R*)-3-(dimethyl(phenyl)silyl)-5-oxohept-6-ynoate (16)



Yield: 76% (16.9 mg)

Physical State: Colorless oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.326 (s, 6H), 2.02-2.09 (m, 1H), 2.22 (dd, *J* = 8.8, 15.6 Hz, 1H), 2.41 (dd, *J* = 5.6, 15.6 Hz, 1H), 2.58-2.70 (m, 2H), 3.20 (s, 1H), 3.57 (s, 3H), 7.35-7.40 (m, 3H), 7.48-7.51 (m, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 186.8, 173.5, 136.2, 133.9, 133.9, 129.5, 128.0, 128.0, 81.3, 78.6, 51.6, 45.8, 34.2, 17.6, -4.56, -4.61

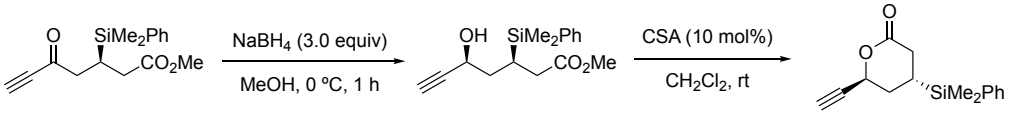
HRMS (ESI): $[M+Na]^+$ calcd for $C_{16}H_{20}O_3SiNa$: 311.1074, found: 311.1079

IR(neat)ν 3281, 2925, 2359, 1719, 1439, 1263, 1015, 763 cm^{-1}

$[\alpha]_D^{26}$ -8.80 (*c* 0.050, $CHCl_3$)

R_f (*n*-Hexane: EtOAc = 2:1, color reagent: Hanessian's stain reagent): 0.60

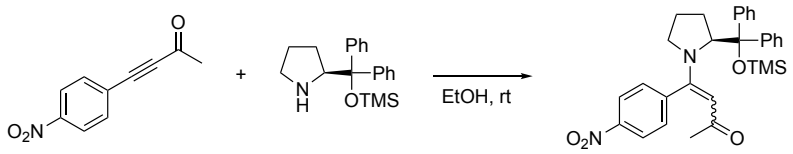
2.12. Reduction & intramolecular lactonization of compound 16



16 **11**

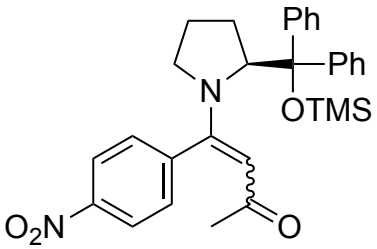
To a solution of compound **16** (14.4 mg, 0.050 mmol) in MeOH (150 μL), sodium borohydride (5.68 mg, 0.15 mmol) was added at 0 ºC. After stirred at this temperature for 1 hour, the reaction mixture was quenched by sat. aq. ammonium chloride (0.5 mL). The residue was diluted by EtOAc (0.5 mL). After separated, the aqueous layer was extracted with EtOAc (1 mL) for three times. The combined organic layers were washed by brine (3 mL) and dried over sodium sulfate. The solvent was removed by evaporation under reduced pressure. It was difficult to determine the value of diastereo ratio because the both of peaks were overlap in ^{1}H-NMR spectrum. To distinguished its peaks, alcohol was converted to lactone. To a solution of the residue in CH_2Cl_2 (0.5 mL), CSA (2.32 mg, 0.0020 mmol) was added at room temperature. After stirred at this temperature for 1 hour, the residue was directly purified by column chromatography (*n*-Hexane: EtOAc = 5:1) to give diastereomixtures of compound **11** (9.8 mg, 0.038 mmol) with *syn*: *anti* = 3:1. *Syn*: *anti* ratio means that the diastereo ratio of the compound **11**.

2.13. A side-reaction in asymmetric Michael reaction



To a solution of 4-(4-nitrophenyl)but-3-yn-2-one (18.9 mg, 0.10 mmol) in EtOH (100 μL), (*S*)-2-(diphenyl((trimethylsilyl)oxy)methyl)pyrrolidine (32.5 mg, 0.10 mmol) was added at room temperature. After stirred at this temperature for 1 hour, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by column chromatography on silica gel (*n*-Hexane: EtOAc = 3:1 with 1% Et_3N) to give adduct (38.5 mg, 0.075 mmol) in 75%.

(*S*)-4-(2-(Diphenyl((trimethylsilyl)oxy)methyl)pyrrolidin-1-yl)-4-(4-nitrophenyl)but-3-en-2-one



E/Z mixtures

Yield: 75% (38.5 mg)

Physical State: Yellow oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.15 (s, 9H), 0.83-0.93 (m, 1H), 1.21-1.28 (m, 1H), 1.85 (s, 3H), 1.93-2.04 (m, 2H) 2.15-2.22 (m, 1H), 3.47 (ddd, *J* = 5.6, 9.6, 11.2 Hz, 1H), 4.80 (dd, *J* = 7.2, 9.2 Hz, 1H), 5.40 (brs, 1H), 7.29-7.43 (m, 10 H), 8.00-8.19 (m, 4H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 193.9, 163.0, 158.8, 158.8, 147.3, 147.3, 142.3, 142.1, 141.4, 129.3, 129.3, 129.3, 129.3, 128.1, 128.1, 127.8, 127.8, 127.7, 127.7, 127.5, 127.5, 83.2, 66.1 44.0, 30.8, 27.3, 22.1, 2.09, 2.09, 2.09

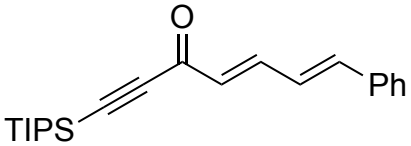
HRMS (ESI): $[M+Na]^+$ calcd for $C_{30}H_{34}N_2O_4SiNa$: 537.2180, found: 537.2180

IR(neat)ν 2956, 1661, 1601, 1523, 1493, 1345, 1252, 1182, 1069, 969, 840, 755, 704 cm^{-1}

R_f (*n*-Hexane: EtOAc = 1:2, color reagent: Hanessian's stain reagent): 0.10

2.14. Compounds information about side-product

(4*E*,6*Z*)-7-Phenyl-1-(triisopropylsilyl)hepta-4,6-dien-1-yn-3-one (4)



E/Z mixtures. (The presented structure is major isomer determined by coupling constant.)

Physical State: Brawn oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96-1.04 (m, 21H), 6.35 (d, *J* = 15.2 Hz, 1H), 6.96-6.97 (m, 2H) 7.32-7.44

(m, 3H), 7.49-7.52 (m, 2H), 7.67 (ddd, *J* = 3.6, 6.8, 15.6 Hz, 1H)

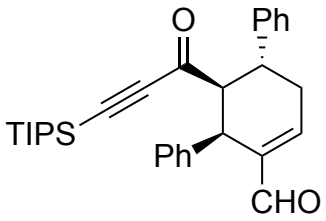
^{13}C NMR ($CDCl_3$, 100 MHz) δ 177.8, 148.4, 142.7, 135.7, 131.9, 129.6, 128.9, 128.9, 127.5, 127.5, 126.4, 102.9, 95.7, 18.6, 18.6, 18.6, 18.6, 18.6, 18.6, 11.1, 11.1, 11.1

HRMS (ESI): $[M+Na]^+$ calcd for $C_{22}H_{30}OSiNa$: 361.1958, found: 361.1959

IR(neat)ν 2946, 2866, 2151, 1615, 1462, 1231, 1105, 997, 881, 754, 679 cm^{-1}

R_f (*n*-Hexane: EtOAc = 3:1, color reagent: Hanessian's stain reagent): 0.85

(1'*R*,2'*S*,3'*R*)-2'-(3-(Triisopropylsilyl)propioloyl)-1',2',3',6'-tetrahydro-[1,1':3',1''-terphenyl]-4'-carbaldehyde (5)



Diastereomeric mixtures. (The presented structure is major isomer determined by coupling constant.)

Physical State: Brawn oil

^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.96-1.04 (m, 21H), 2.46 (tdd, *J* = 2.4, 10.4, 21.2 Hz, 1H), 3.01 (td, *J* = 5.6, 21.2 Hz, 1H), 3.46 (dd, *J* = 4.8, 12.4 Hz, 1H), 3.52 (ddd, *J* = 5.4, 10.8, 12.4 Hz, 1H), 4.58 (d, *J* = 4.8 Hz, 1H), 7.08 (t, *J* = 1.2 Hz, 1H), 7.14-7.33 (m, 10 H), 9.47 (s, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.8, 191.6, 149.2, 143.4, 141.8, 137.4, 129.3, 129.3, 128.7, 128.7 128.4, 128.4, 127.3, 127.3, 126.7, 126.7, 104.2, 97.5, 56.8, 41.3, 36.7, 36.0, 18.5, 18.5, 18.5, 18.4, 18.4, 18.4, 10.9, 10.9, 10.9

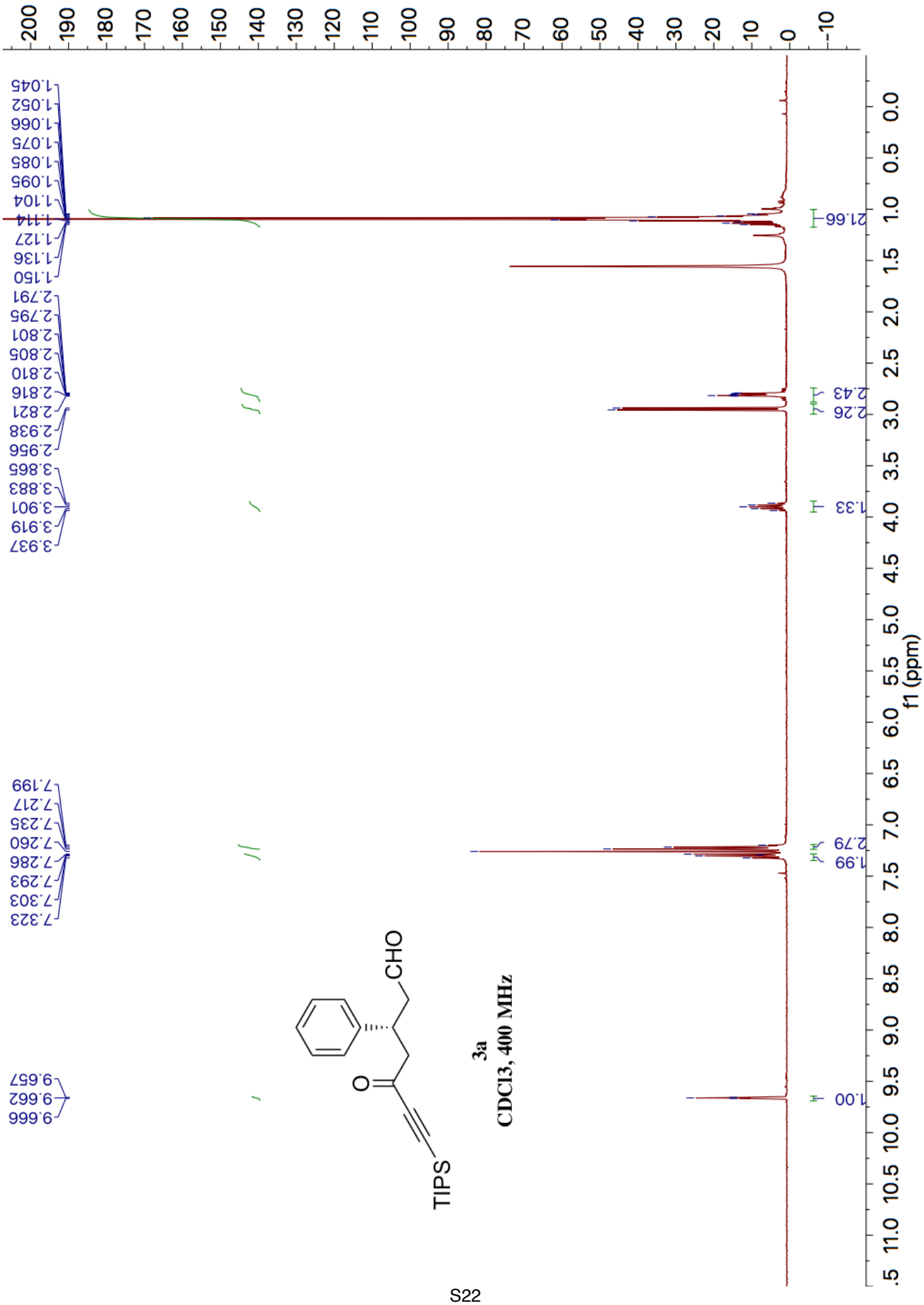
HRMS (ESI): $[M+Na]^+$ calcd for $C_{31}H_{38}O_2SiNa$: 493.2533, found: 493.2538

IR(neat)ν 3428, 3030, 2945, 2866, 2146, 1726, 1685, 1494, 1460, 1374, 1204, 1148, 1074, 997, 957, 882, 758, 701, 583 cm^{-1}

R_f (*n*-Hexane: EtOAc = 3:1, color reagent: Hanessian's stain reagent): 0.20

3. References

[1] Y. Gu, B. B. Snider, *Org. Lett.* **2003**, *5*, 4385.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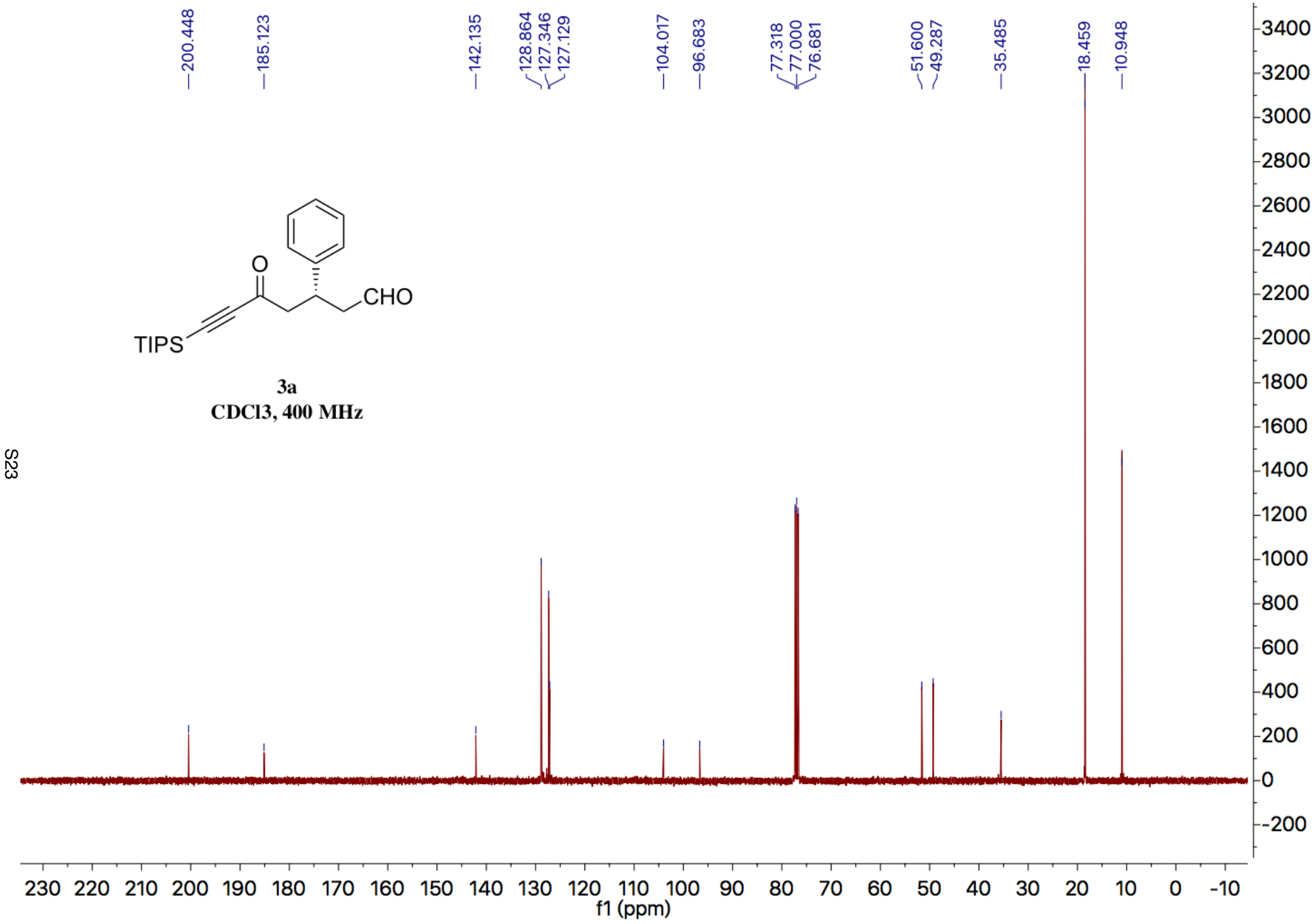
O
TIPS
3a
CDCl3, 400 MHz
f1 (ppm)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127.346
127.129
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96.683
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77.000
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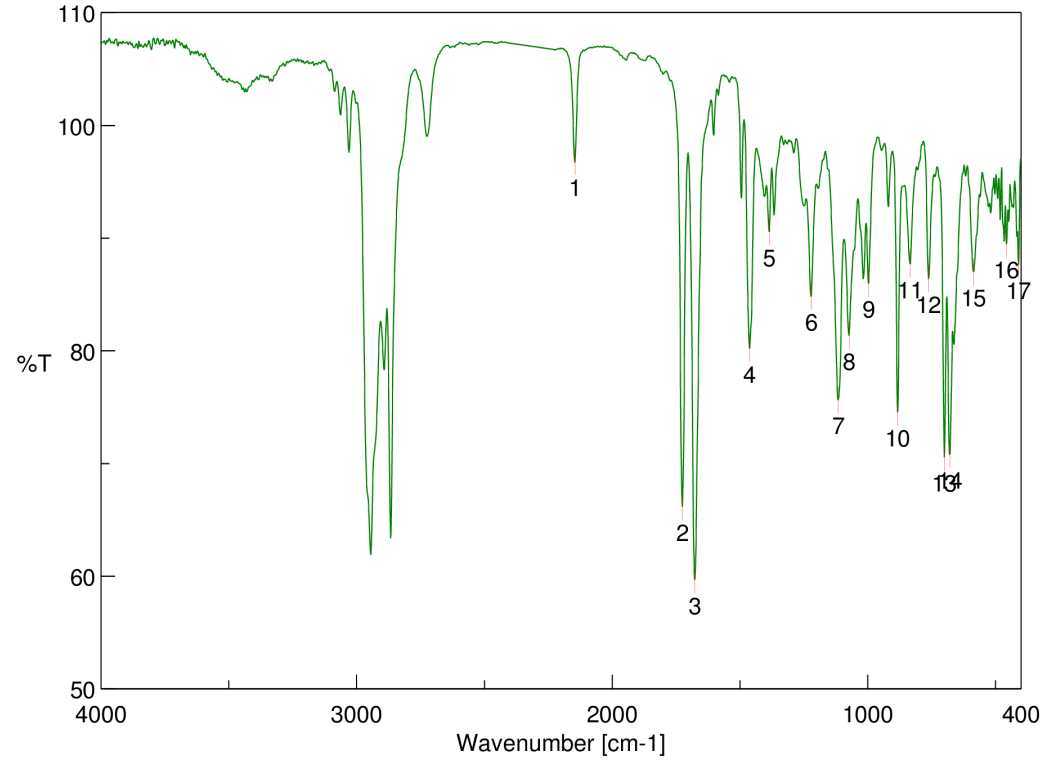
49.287
35.485
18.459
10.948
O
CHO
TIPS
3a
CDCl3, 400 MHz
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
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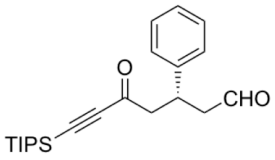
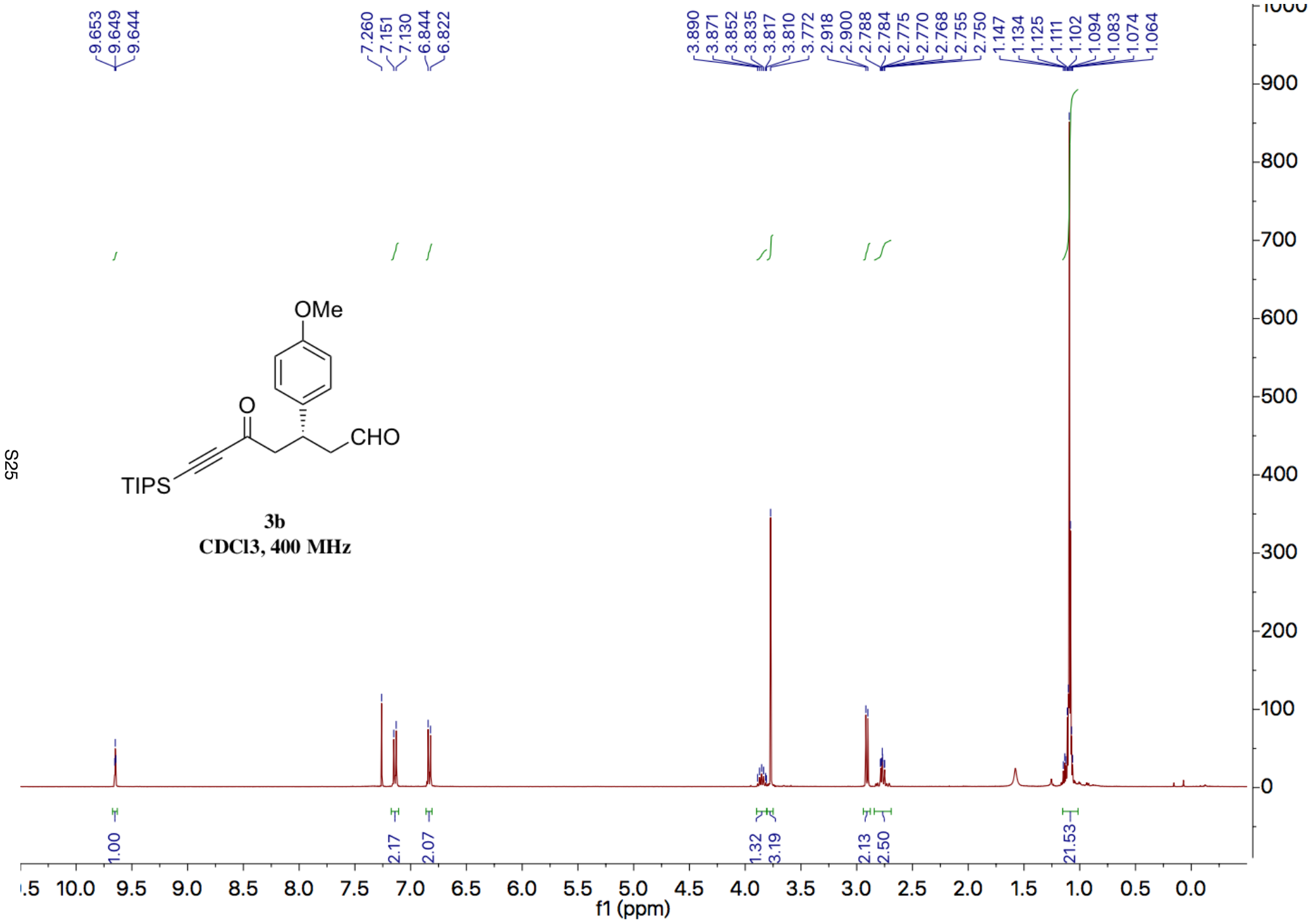
3	1676.8	59.6778	4	1462.74	80.2008
5	1385.6	90.5405	6	1221.68	84.8352
7	1115.62	75.6454	8	1073.19	81.371
9	997.017	85.9852	10	883.238	74.5744
11	834.062	87.7047	12	761.744	86.3906
13	700.034	70.576	14	678.82	70.8001
15	586.254	87.0057	16	457.047	89.4714
17	409.799	87.6601			




9.653
9.649
9.644
7.260
7.151
7.130
6.844
6.822
3.890
3.871
3.852
3.835
3.817
3.810
3.772
2.918
2.900
2.788
2.784
2.775
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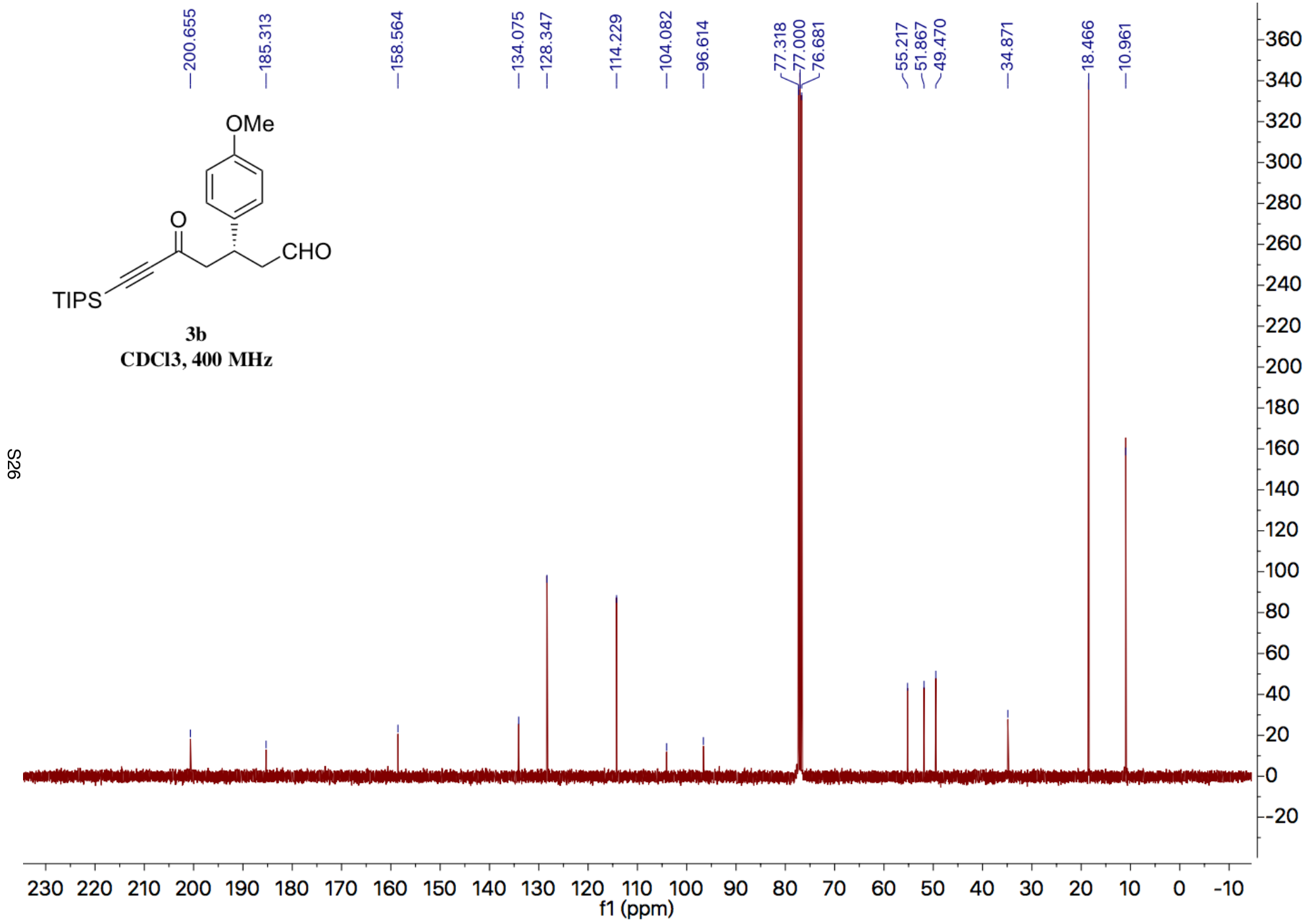
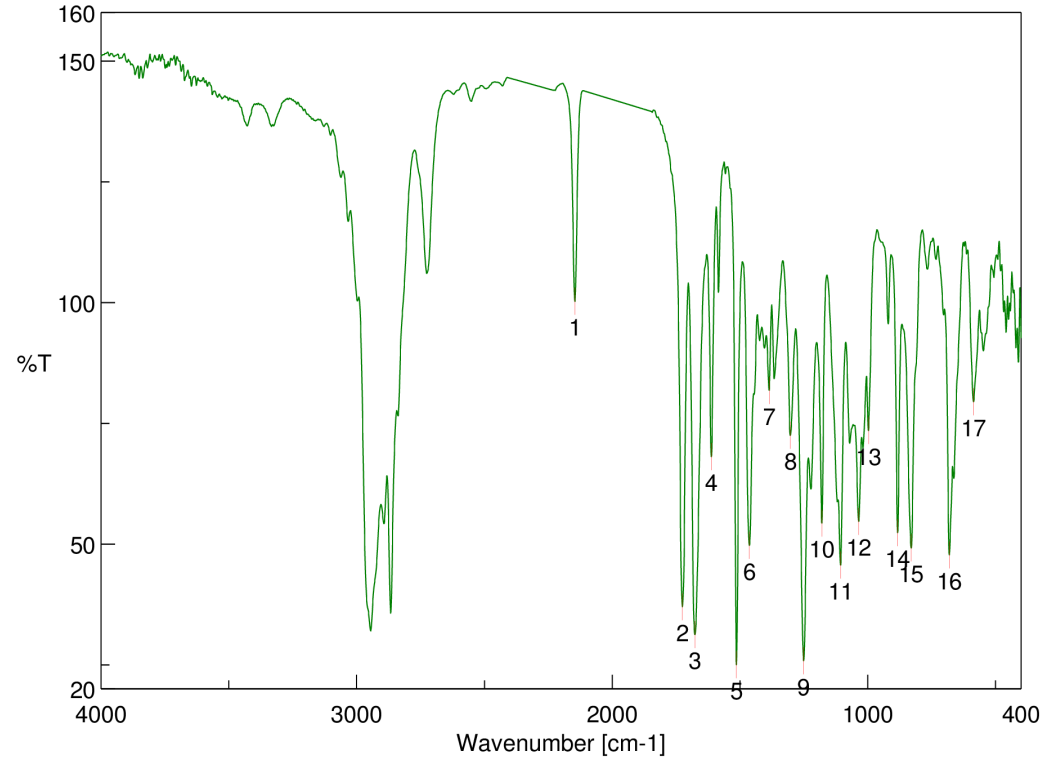
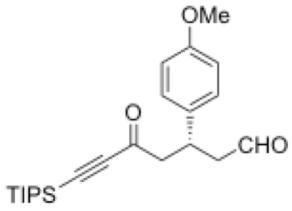
2.755
2.750
1.147
1.134
1.125
1.111
1.102
1.094
1.083
1.074
1.064
OMe
O
CHO
TIPS
3b
CDCl3, 400 MHz
1.00
2.17
2.07
1.32
3.19
2.13
2.50
21.53
f1 (ppm)

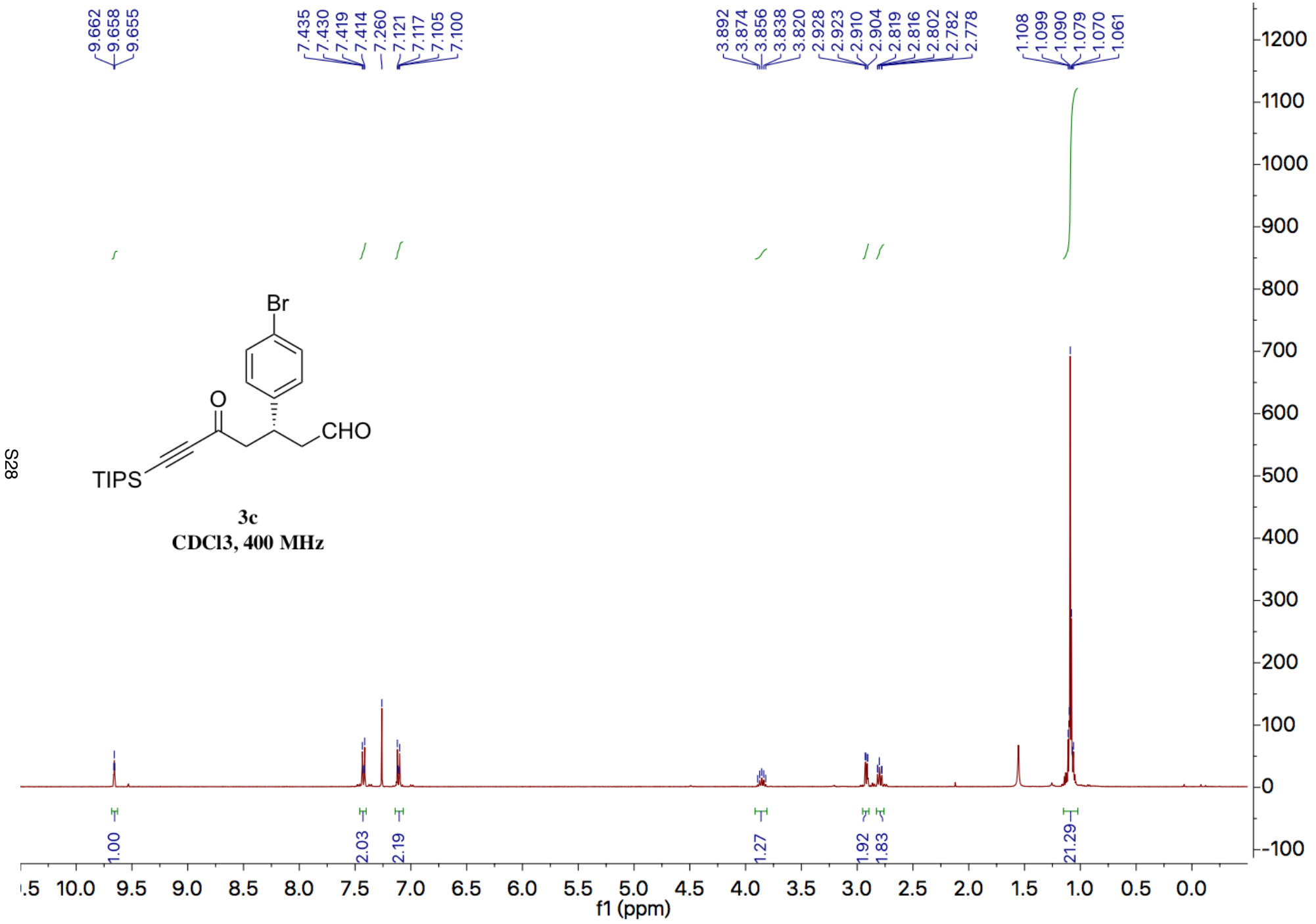

200.655
185.313
158.564
134.075
128.347
114.229
104.082
96.614
77.318
77.000
76.681
55.217
51.867
49.470
34.871
18.466
10.961
OMe
O
CHO
TIPS
3b
CDCl3, 400 MHz
f1 (ppm)

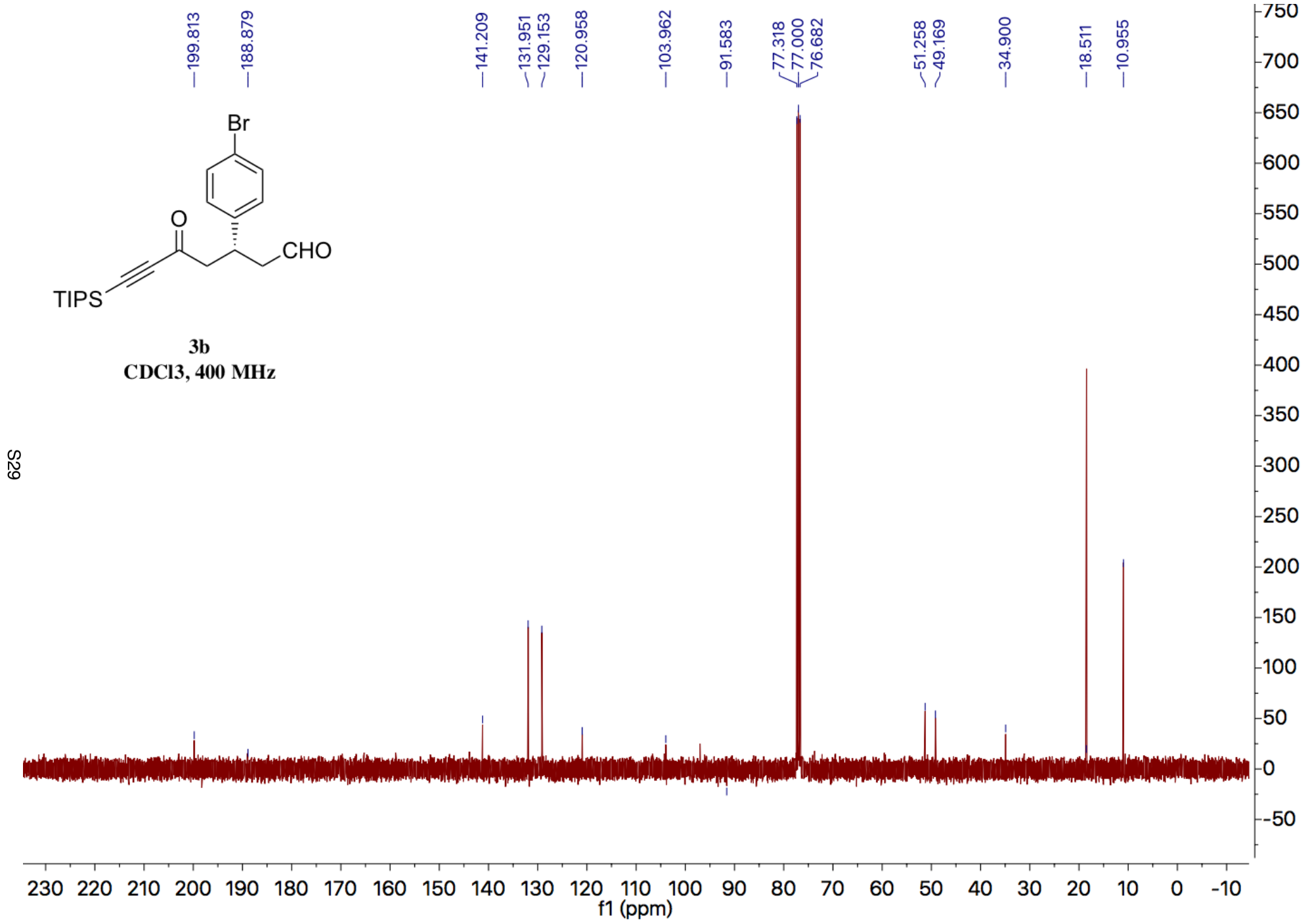


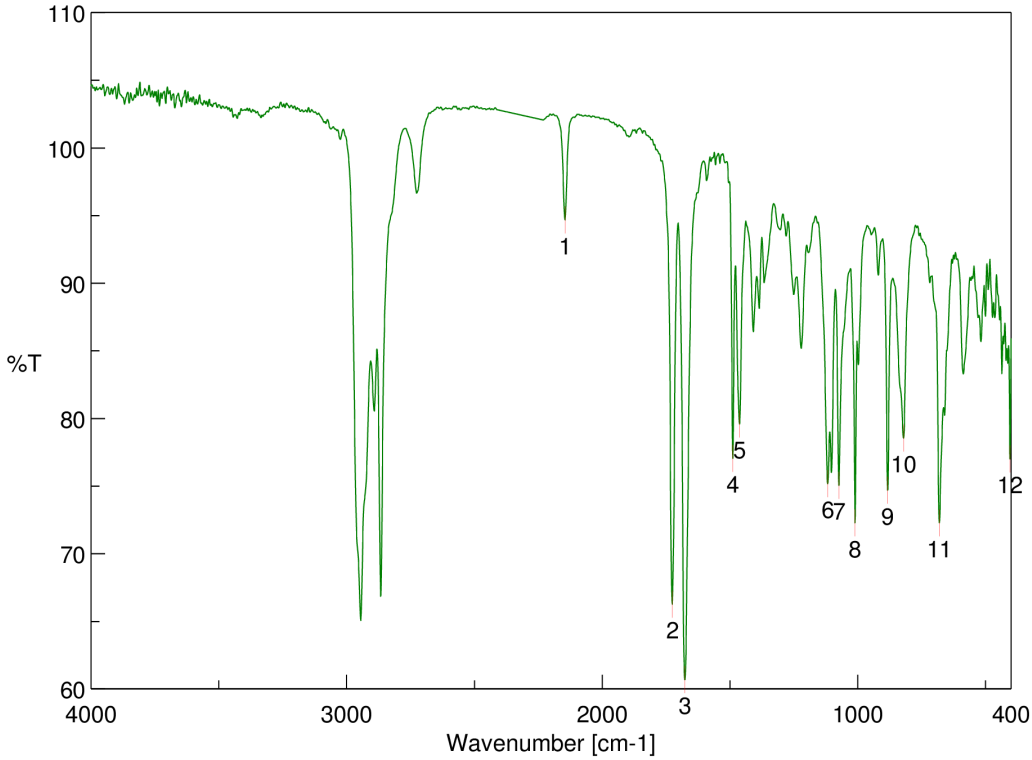
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	100.199	2	1725.01	36.9878
3	1675.84	31.2231	4	1612.2	68.0906
5	1513.85	25.0181	6	1463.71	49.7064
7	1385.6	81.7601	8	1302.68	72.4826
9	1250.61	25.8514	10	1179.26	54.3048
11	1105.98	45.6517	12	1035.59	54.6377
13	997.017	73.504	14	883.238	52.306
15	830.205	49.1953	16	680.749	47.7322
17	586.254	79.4357			



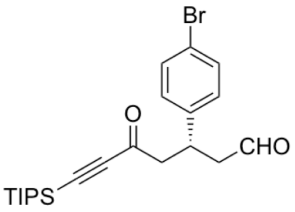

9.662
9.658
9.655
7.435
7.430
7.419
7.414
7.260
7.121
7.117
7.105
7.100
3.892
3.874
3.856
3.838
3.820
2.928
2.923
2.910
2.904
2.819
2.816
2.802
2.782
2.778
1.108
1.099
1.090
1.079
1.070
1.061
Br
O
CHO
TIPS
3c
CDCl3, 400 MHz
1.00
2.03
2.19
1.27
1.92
1.83
21.29
f1 (ppm)

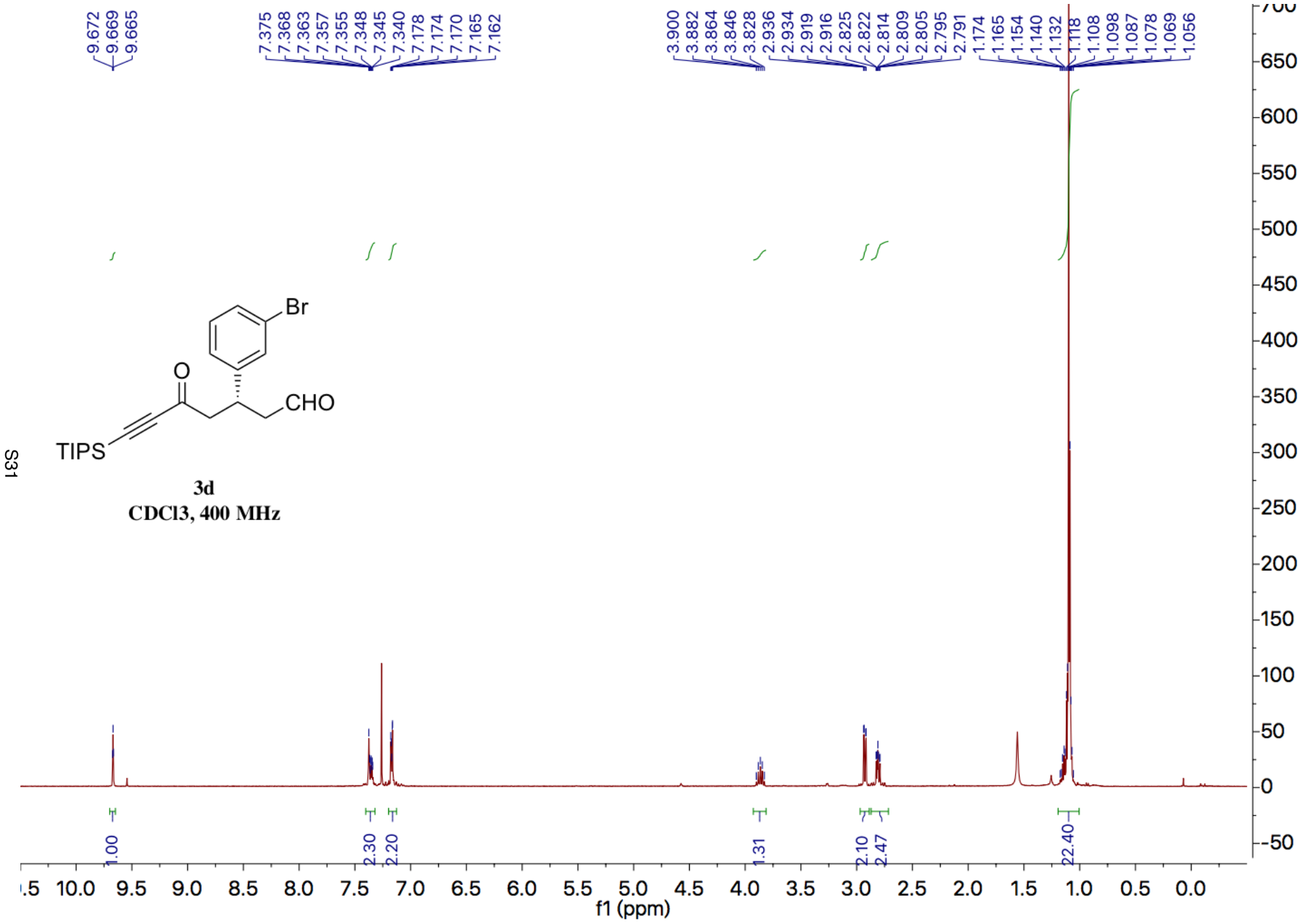

199.813
188.879
141.209
131.951
129.153
120.958
103.962
91.583
77.318
77.000
76.682
51.258
49.169
34.900
18.511
10.955
Br
O
CHO
TIPS
3b
CDCl3, 400 MHz
f1 (ppm)

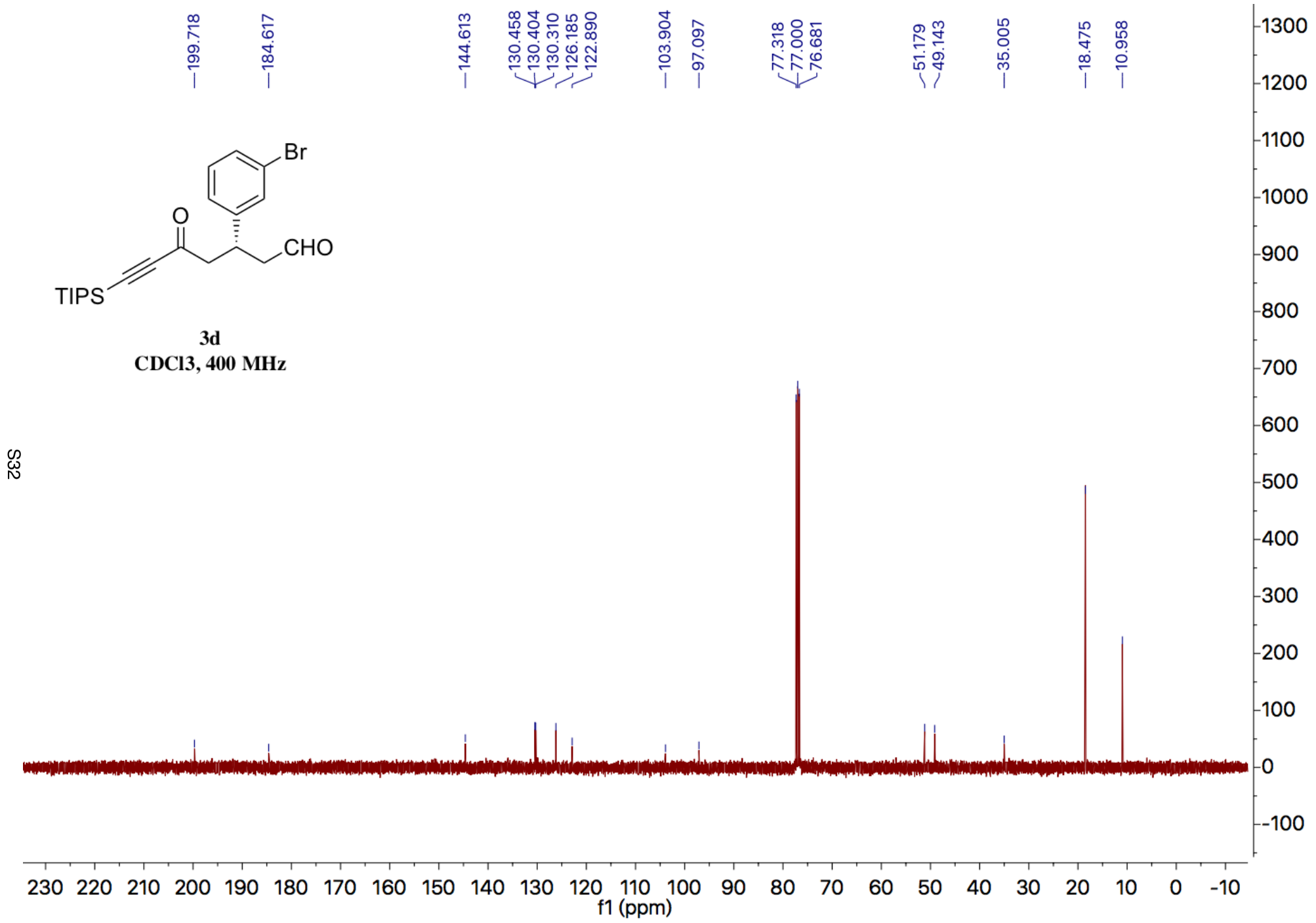


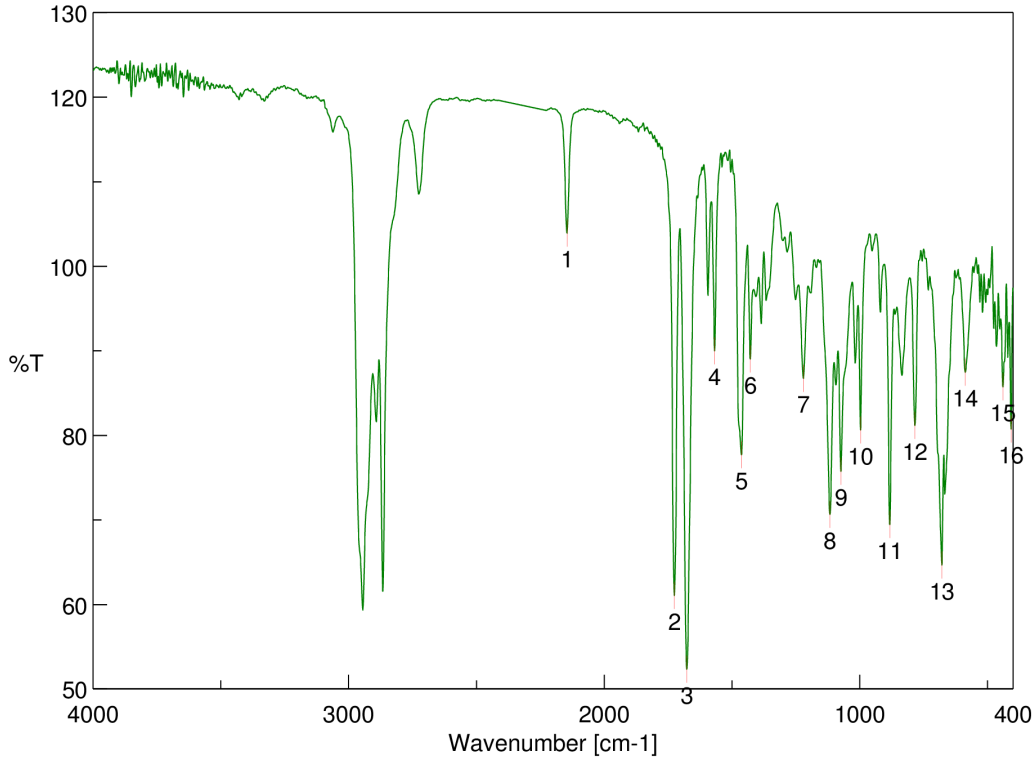
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2145.42	94.6656	2	1725.98	66.2595
3	1676.8	60.68	4	1488.78	77.0398
5	1462.74	79.5739	6	1117.55	75.1742
7	1074.16	75.0461	8	1010.52	72.2698
9	883.238	74.6965	10	820.563	78.5467
11	680.749	72.2851	12	404.014	77.0076



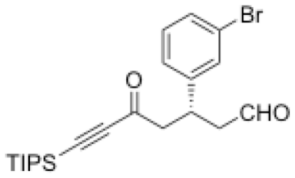

9.672
9.669
9.665
7.375
7.368
7.363
7.357
7.355
7.348
7.345
7.340
7.178
7.174
7.170
7.165
7.162
3.900
3.882
3.864
3.846
3.828
2.936
2.934
2.919
2.916
2.825
2.822
2.814
2.809
2.805
2.795
2.791
1.174
1.165
1.154
1.140
1.132
1.118
1.108
1.098
1.087
1.078
1.069
1.056
Br
O
CHO
TIPS
3d
CDCl3, 400 MHz
1.00
2.30
2.20
1.31
2.10
2.47
22.40
f1 (ppm)

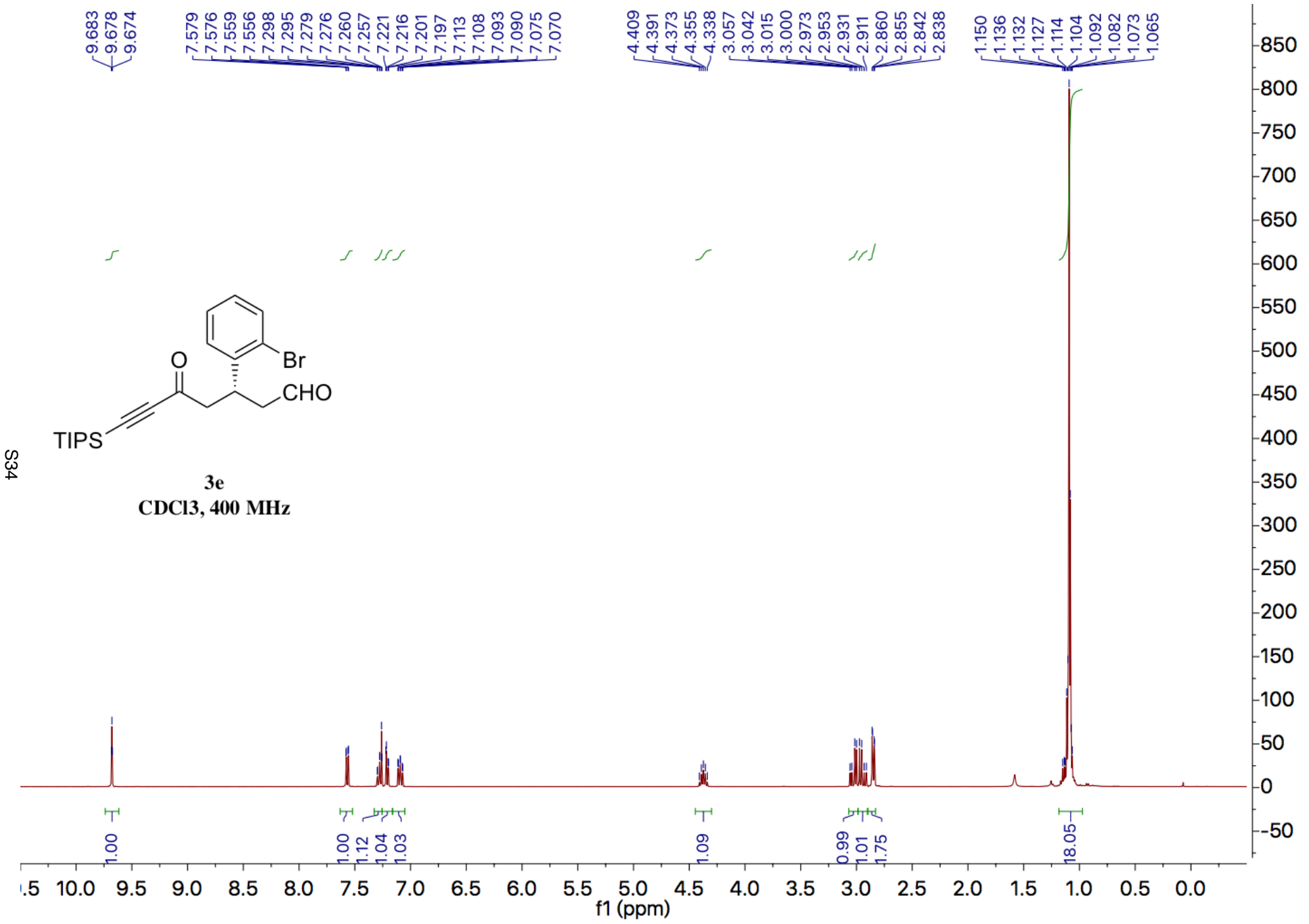

199.718
184.617
144.613
130.458
130.404
130.310
126.185
122.890
103.904
97.097
77.318
77.000
76.681
51.179
49.143
35.005
18.475
10.958
Br
O
CHO
TIPS
3d
CDCl3, 400 MHz
f1 (ppm)



[ピーク検出結果]

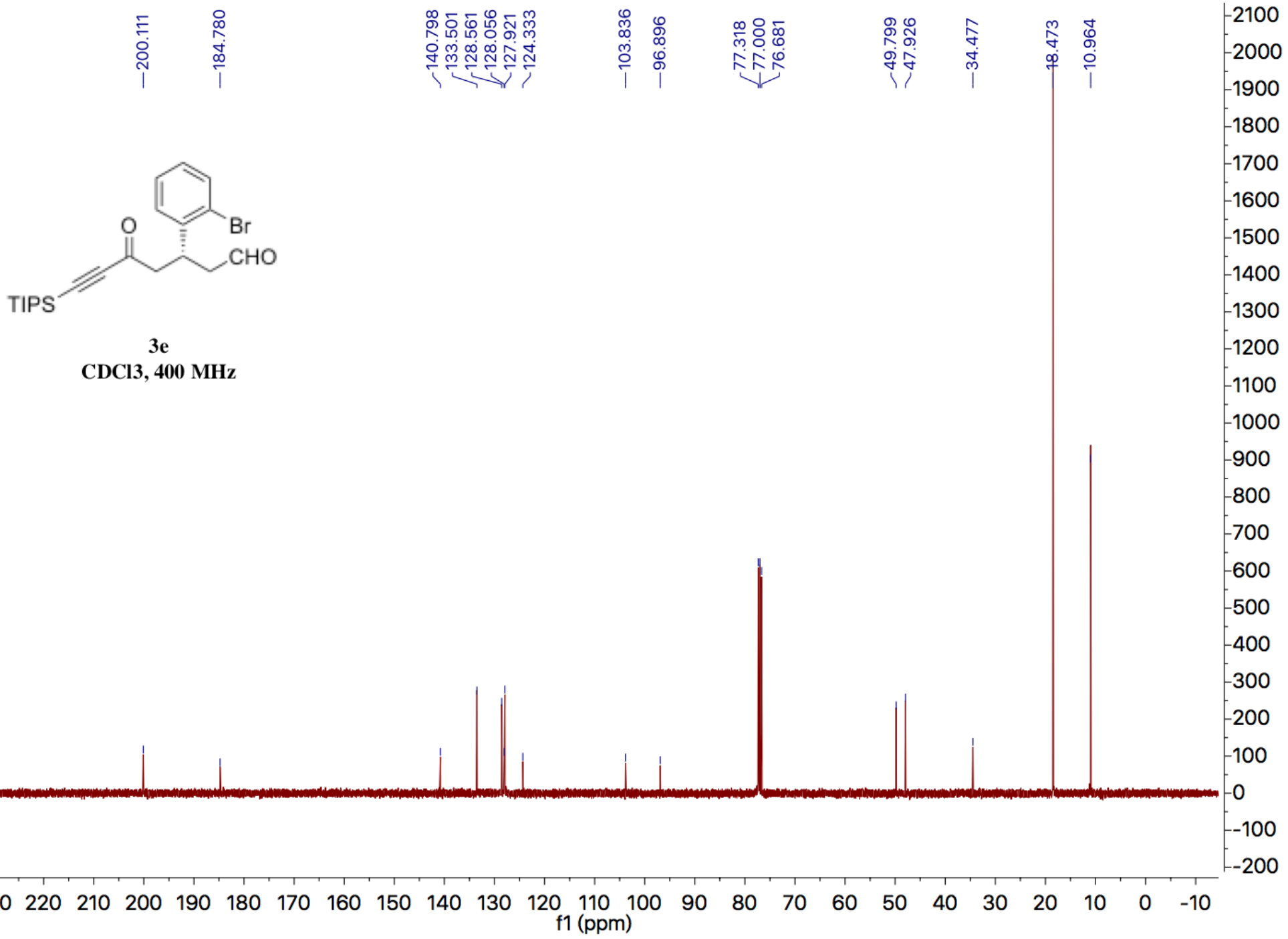
No.	位置	強度	No.	位置	強度
1	2145.42	103.905	2	1725.98	61.0608
3	1676.8	52.3179	4	1567.84	89.9908
5	1462.74	77.6846	6	1428.03	89.0289
7	1220.72	86.7059	8	1116.58	70.6369
9	1074.16	75.7458	10	997.017	80.6148
11	882.274	69.4399	12	783.922	81.1542
13	678.82	64.6436	14	587.218	87.4619
15	439.69	85.7071	16	407.871	80.7341

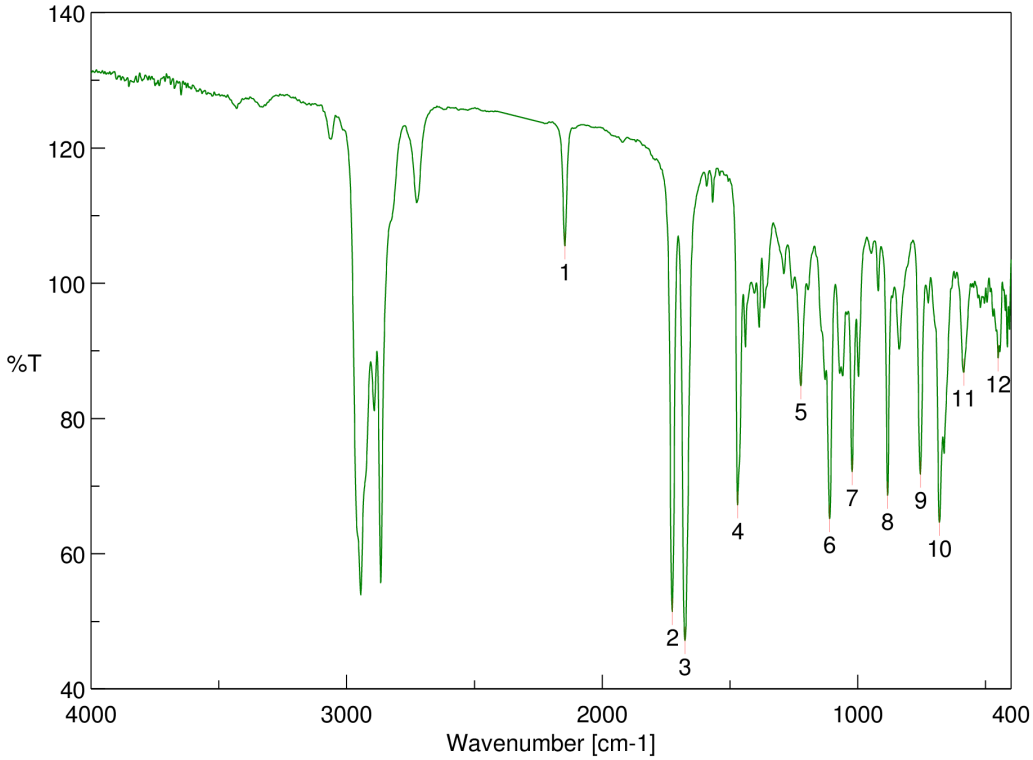




3e

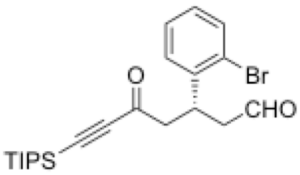
CDCl3, 400 MHz

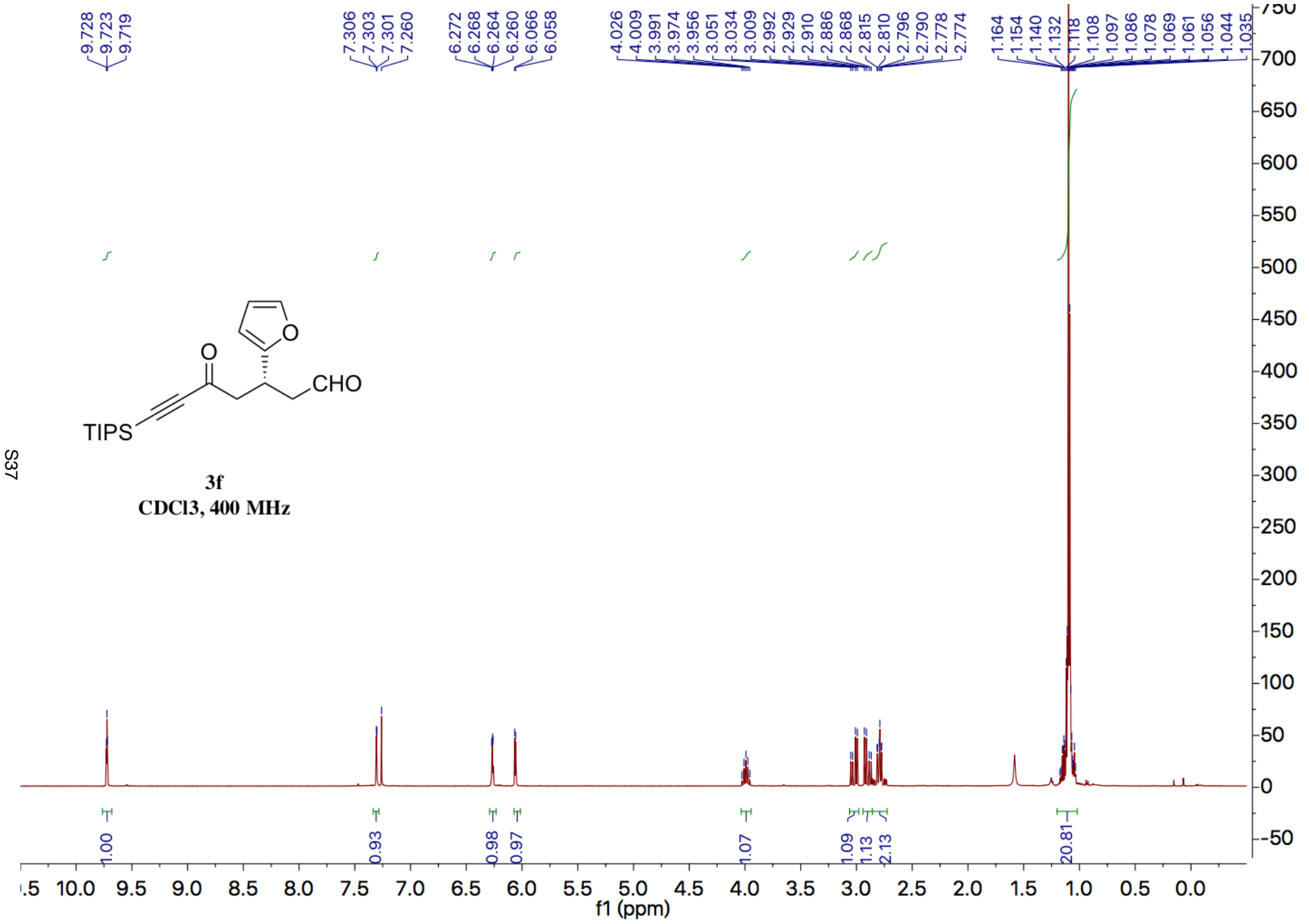

200.111
184.780
140.798
133.501
128.561
128.056
127.921
124.333
103.836
96.896
77.318
77.000
76.681
49.799
47.926
34.477
18.473
10.964
O
Br
CHO
TIPS
3e
CDCl3, 400 MHz
f1 (ppm)



[ピーク検出結果]

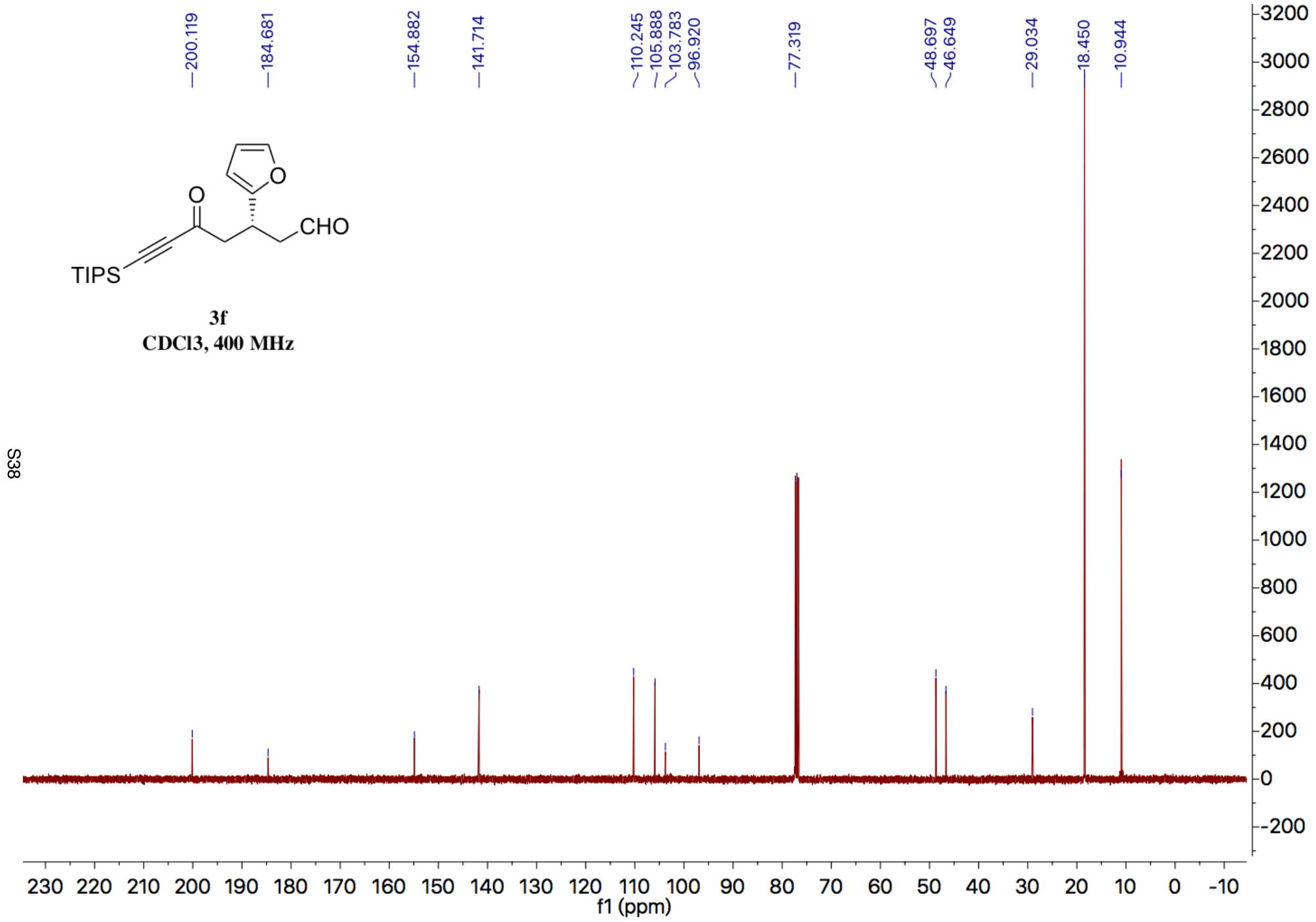
No.	位置	強度	No.	位置	強度
1	2146.38	105.491	2	1725.98	51.4454
3	1675.84	47.1698	4	1470.46	67.212
5	1222.65	84.8335	6	1109.83	65.1583
7	1022.09	72.1303	8	883.238	68.6319
9	754.995	71.7331	10	680.749	64.6486
11	585.29	86.8128	12	450.297	88.9388

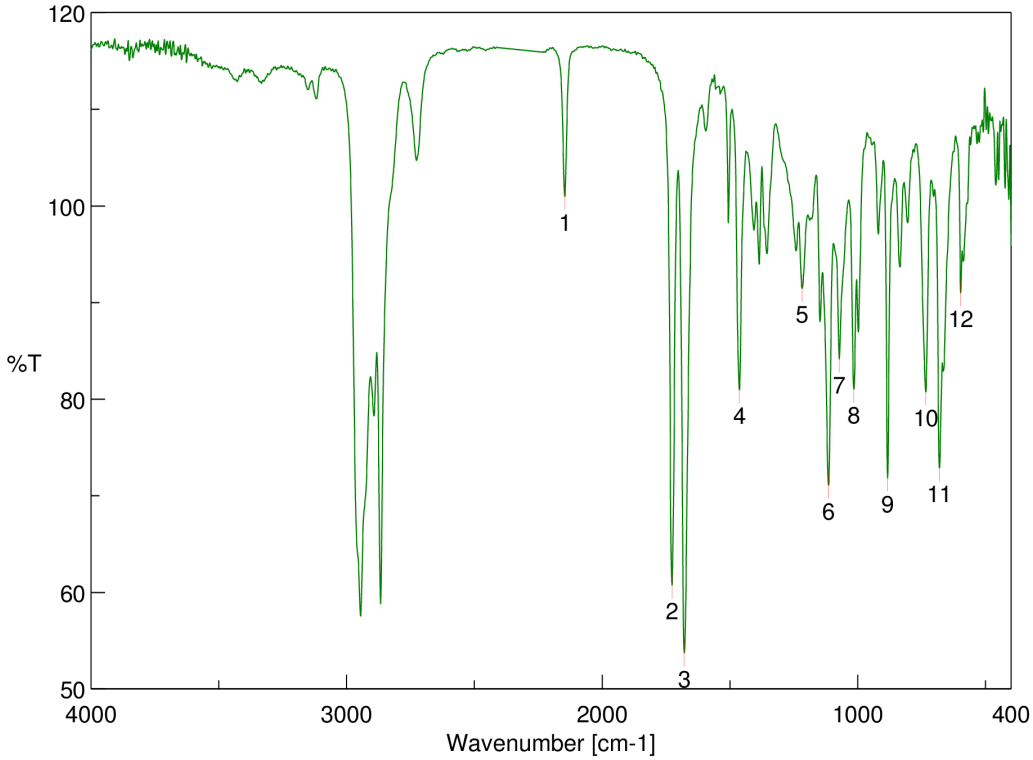




3f

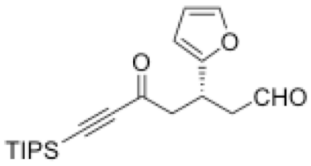
CDCl3, 400 MHz

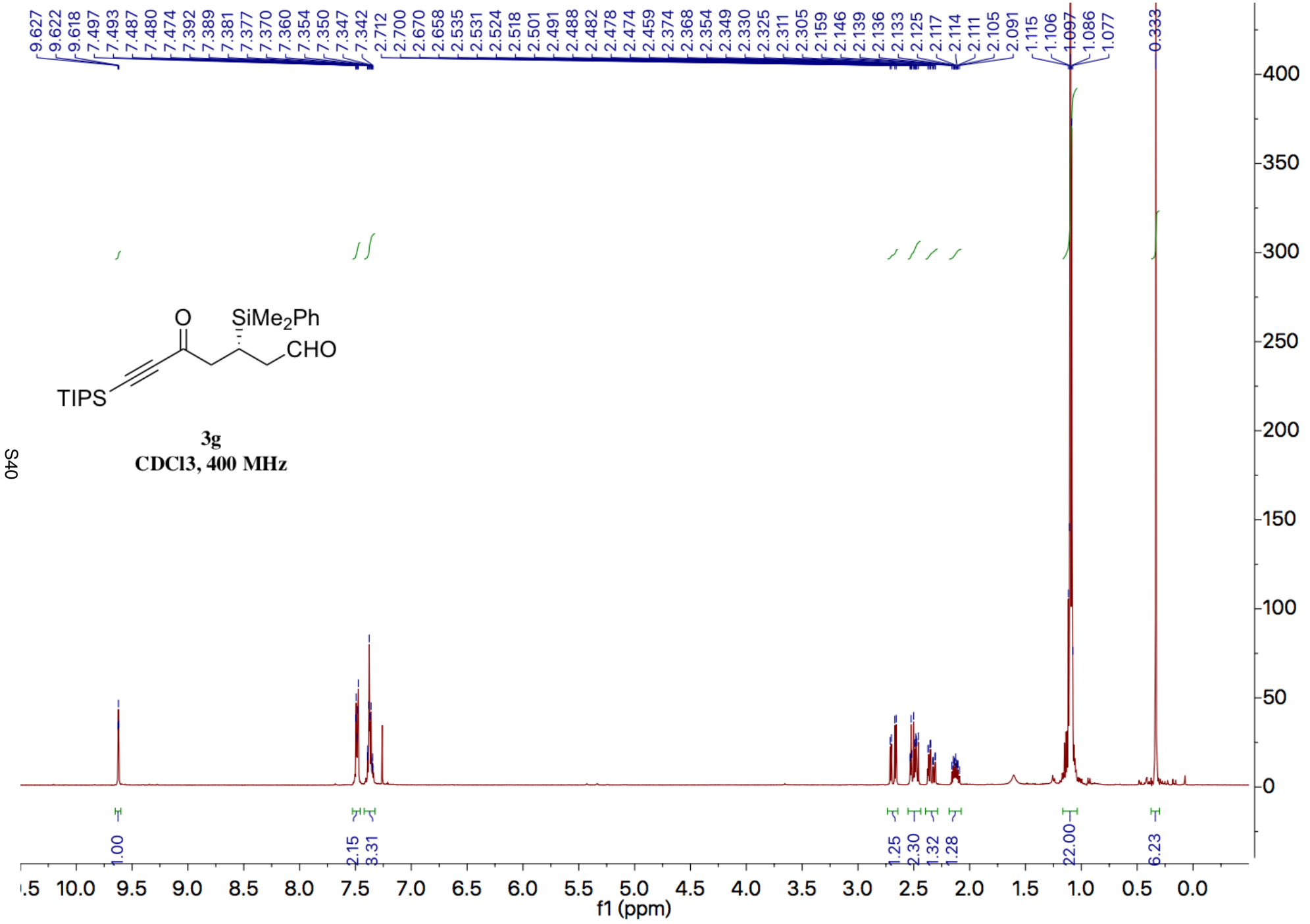

200.119
184.681
154.882
141.714
110.245
105.888
103.783
96.920
77.319
48.697
46.649
29.034
18.450
10.944
O
O
CHO
TIPS
3f
CDCl3, 400 MHz
f1 (ppm)

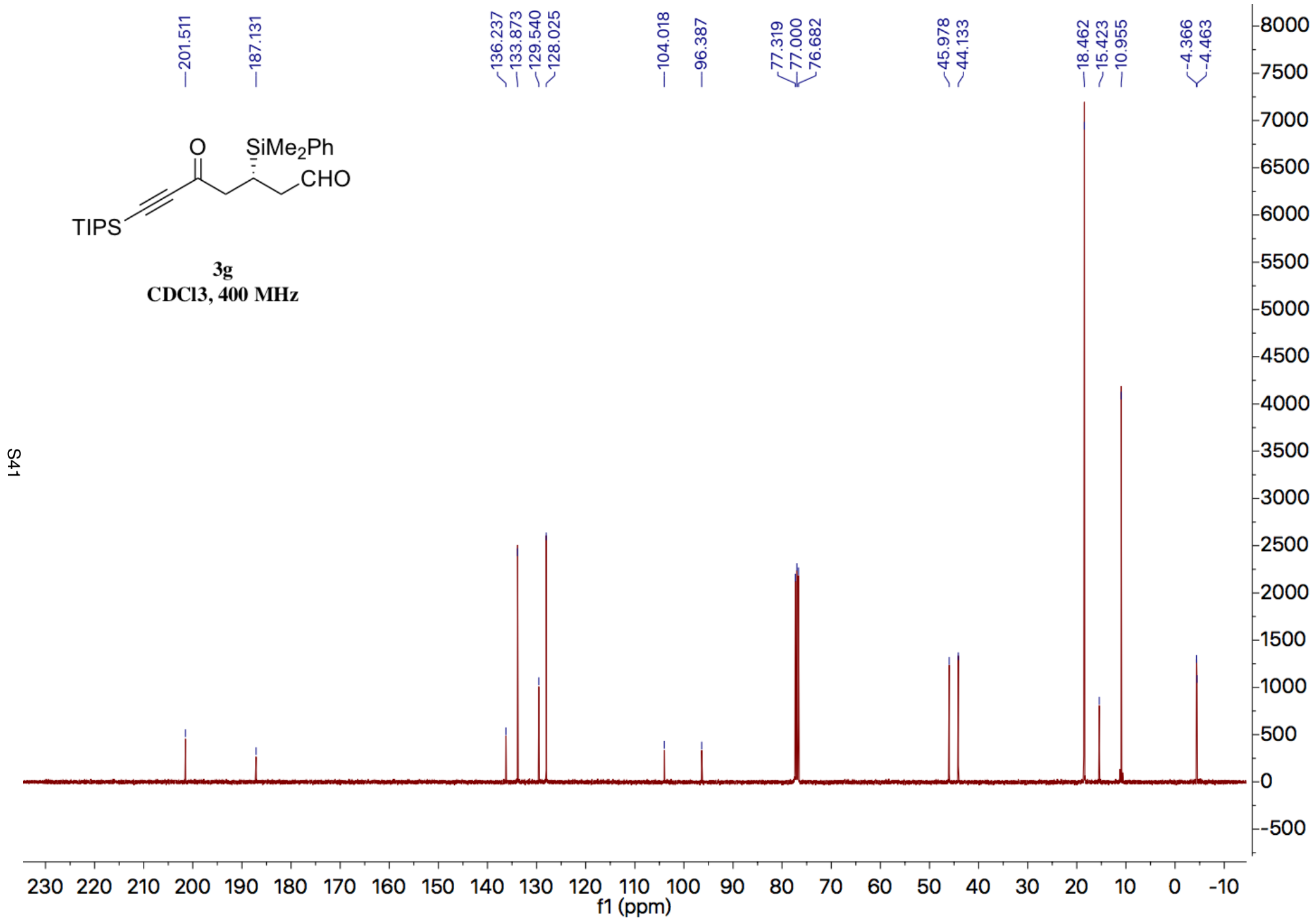


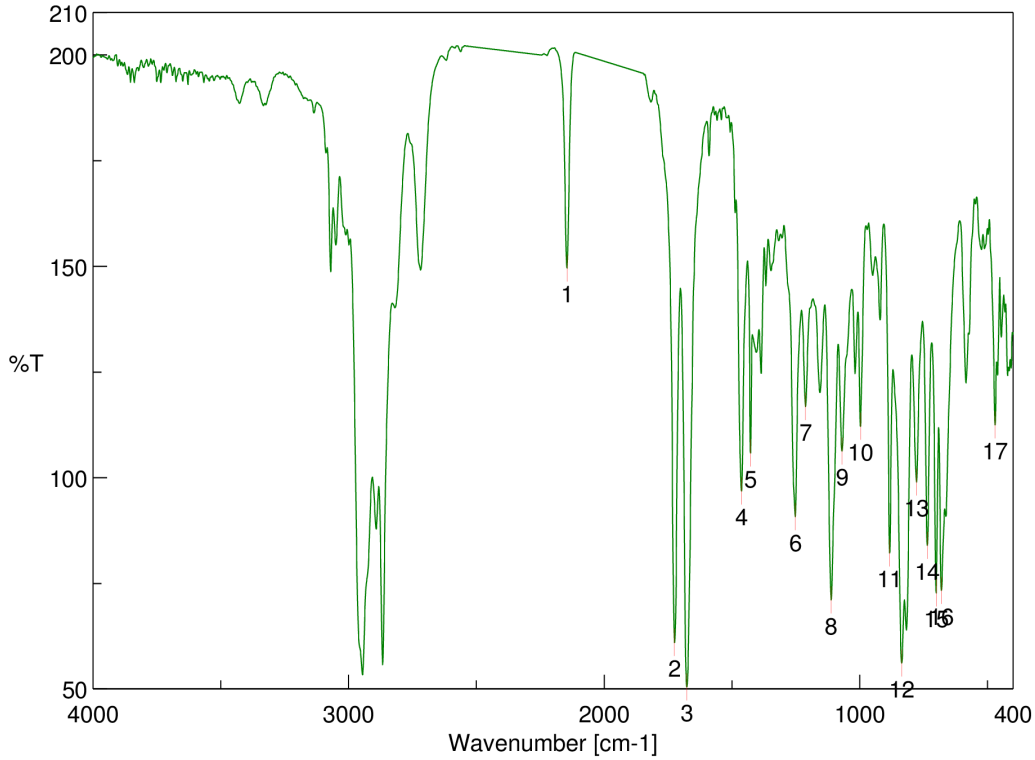
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	100.971	2	1726.94	60.748
3	1678.73	53.7382	4	1463.71	80.9579
5	1217.83	91.4577	6	1114.65	71.0891
7	1072.23	84.1533	8	1015.34	81.0283
9	883.238	71.8622	10	733.782	80.7281
11	680.749	72.8752	12	596.861	90.9865



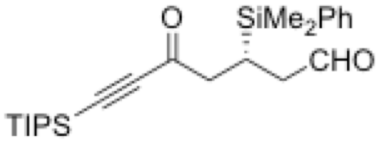

9.627
9.622
9.618
7.497
7.493
7.487
7.480
7.474
7.392
7.389
7.381
7.377
7.370
7.360
7.354
7.350
7.347
7.342
2.712
2.700
2.670
2.658
2.535
2.531
2.524
2.518
2.501
2.491
2.488
2.482
2.478
2.474
2.459
2.374
2.368
2.354
2.349
2.330
2.325
2.311
2.305
2.159
2.146
2.139
2.136
2.133
2.125
2.117
2.114
2.111
2.105
2.091
1.115
1.106
1.097
1.086
1.077
0.333
O
SiMe2Ph
CHO
TIPS
3g
CDCl3, 400 MHz
S40
400
350
300
250
200
150
100
50
0
1.00
2.15
3.31
1.25
2.30
1.32
1.28
22.00
6.23
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)

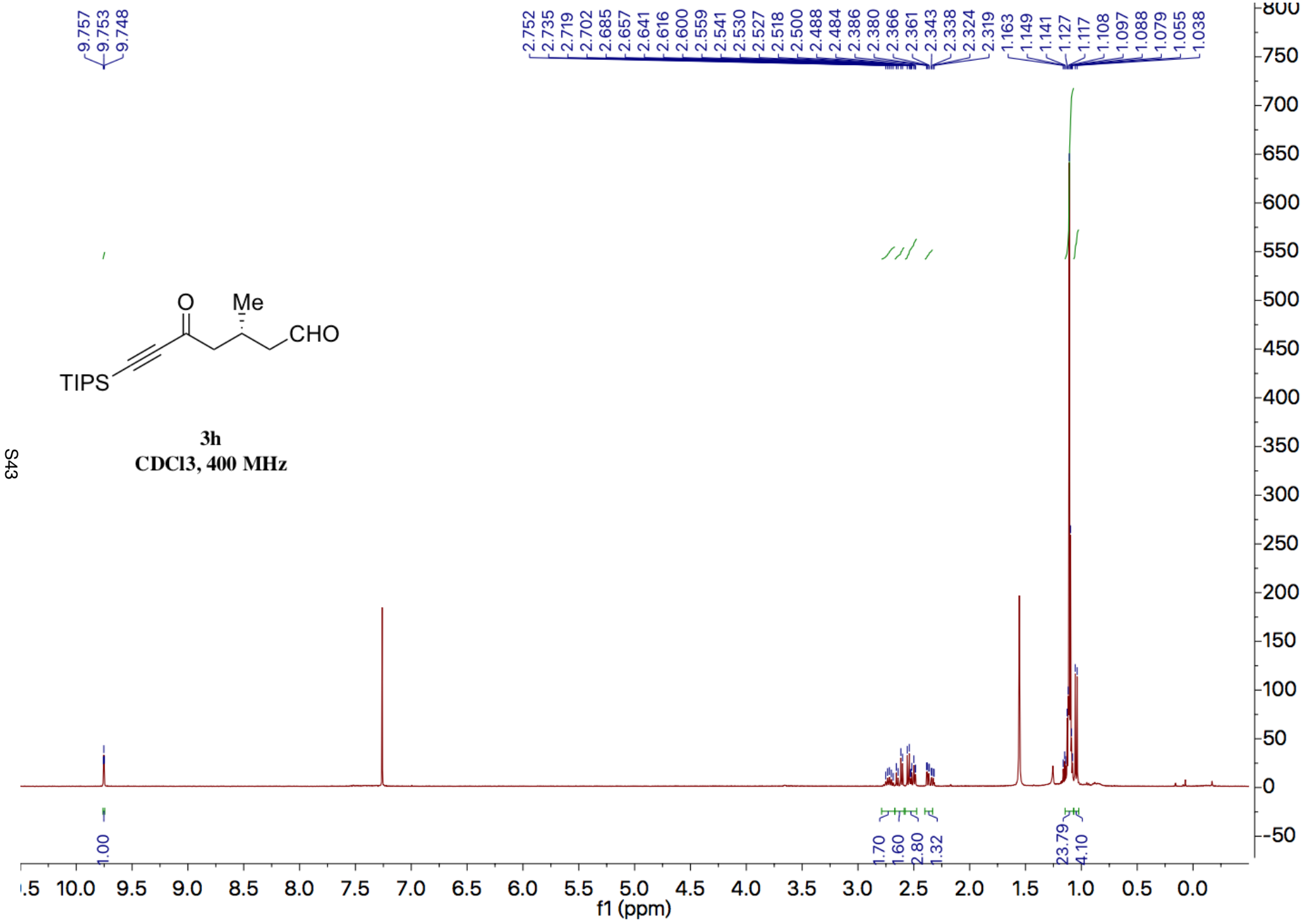

201.511
187.131
136.237
133.873
129.540
128.025
104.018
96.387
77.319
77.000
76.682
45.978
44.133
18.462
15.423
10.955
-4.366
-4.463
O
SiMe2Ph
CHO
TIPS
3g
CDCl3, 400 MHz
f1 (ppm)

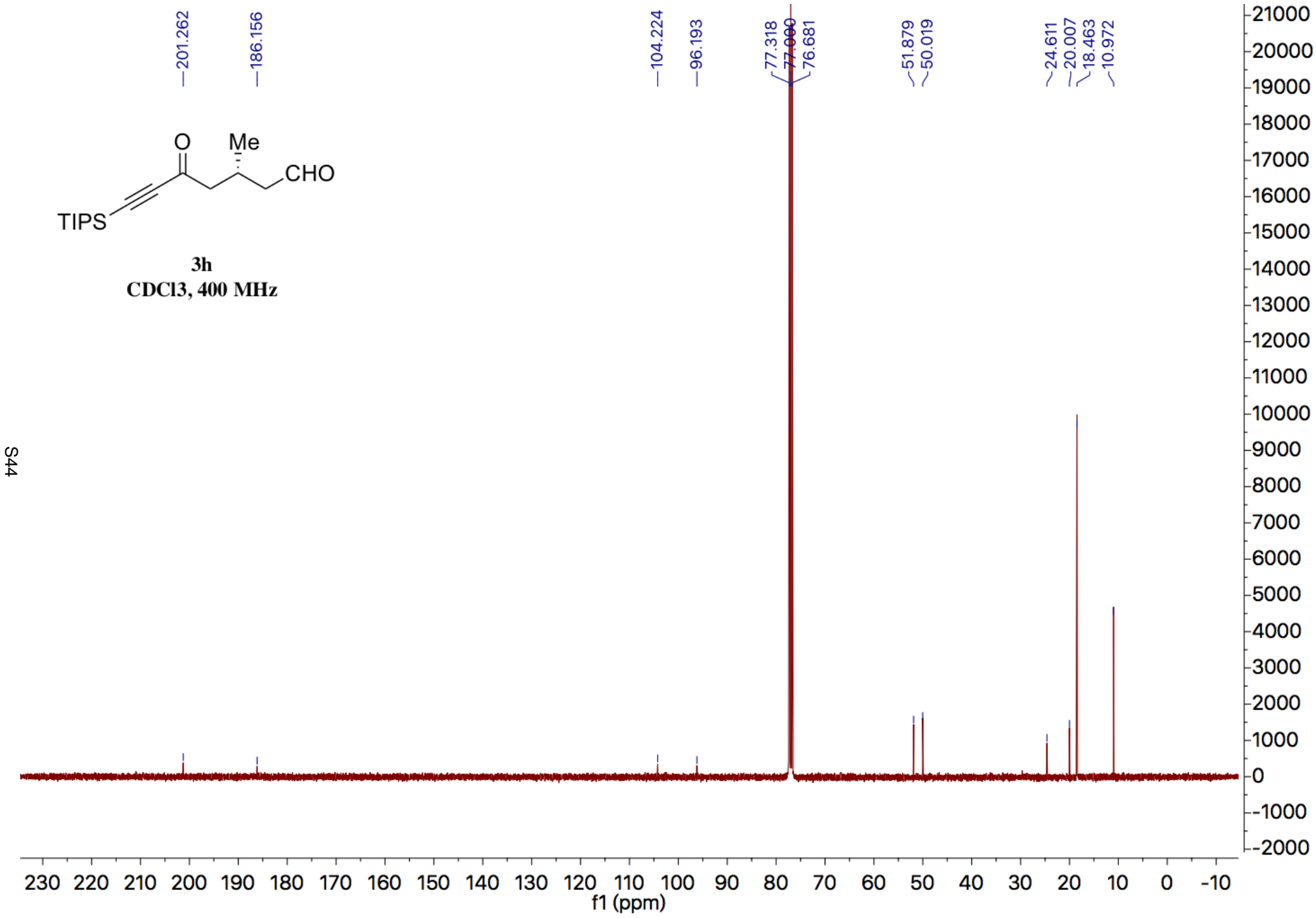


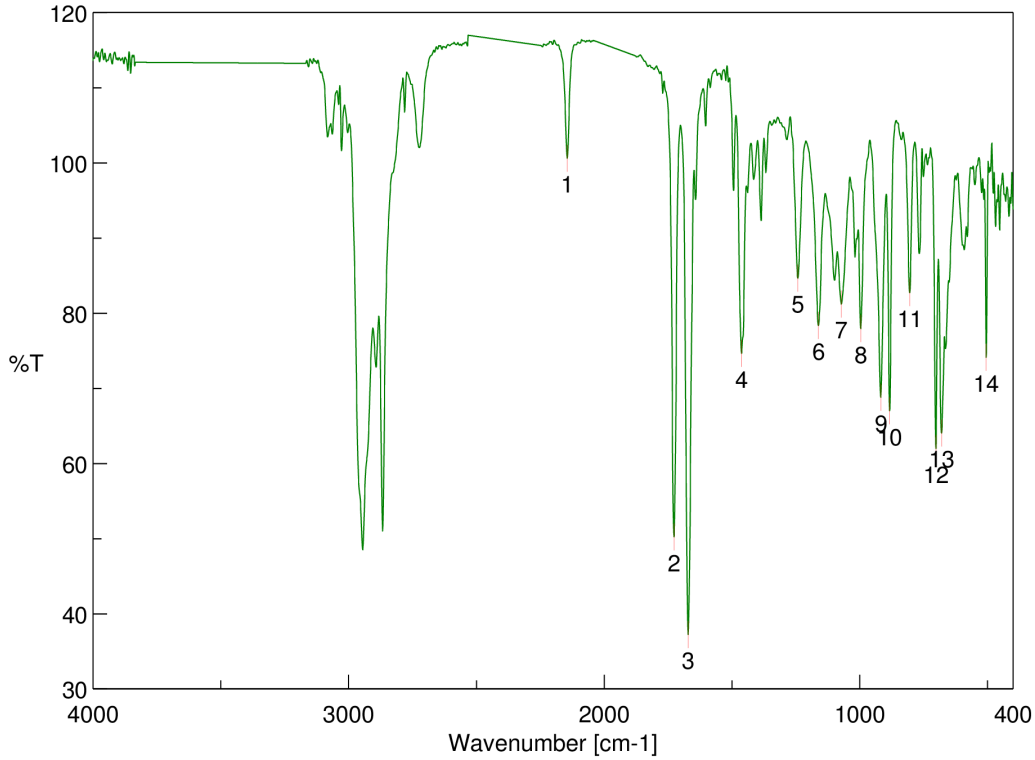
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2145.42	149.562	2	1725.01	60.9598
3	1676.8	50.4834	4	1462.74	96.8409
5	1427.07	105.773	6	1252.54	90.7543
7	1212.04	116.774	8	1111.76	71.0225
9	1069.33	106.275	10	997.017	112.131
11	883.238	82.1869	12	835.99	56.1477
13	778.136	98.9593	14	735.71	83.9728
15	700.998	72.7094	16	680.749	73.2955
17	470.546	112.448			



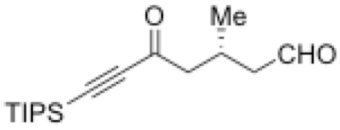

9.757
9.753
9.748
2.752
2.735
2.719
2.702
2.685
2.657
2.641
2.616
2.600
2.559
2.541
2.530
2.527
2.518
2.500
2.488
2.484
2.386
2.380
2.366
2.361
2.343
2.338
2.324
2.319
1.163
1.149
1.141
1.127
1.117
1.108
1.097
1.088
1.079
1.055
1.038
O
Me
CHO
TIPS
3h
CDCl3, 400 MHz
1.00
1.70
1.60
2.80
1.32
23.79
4.10
f1 (ppm)

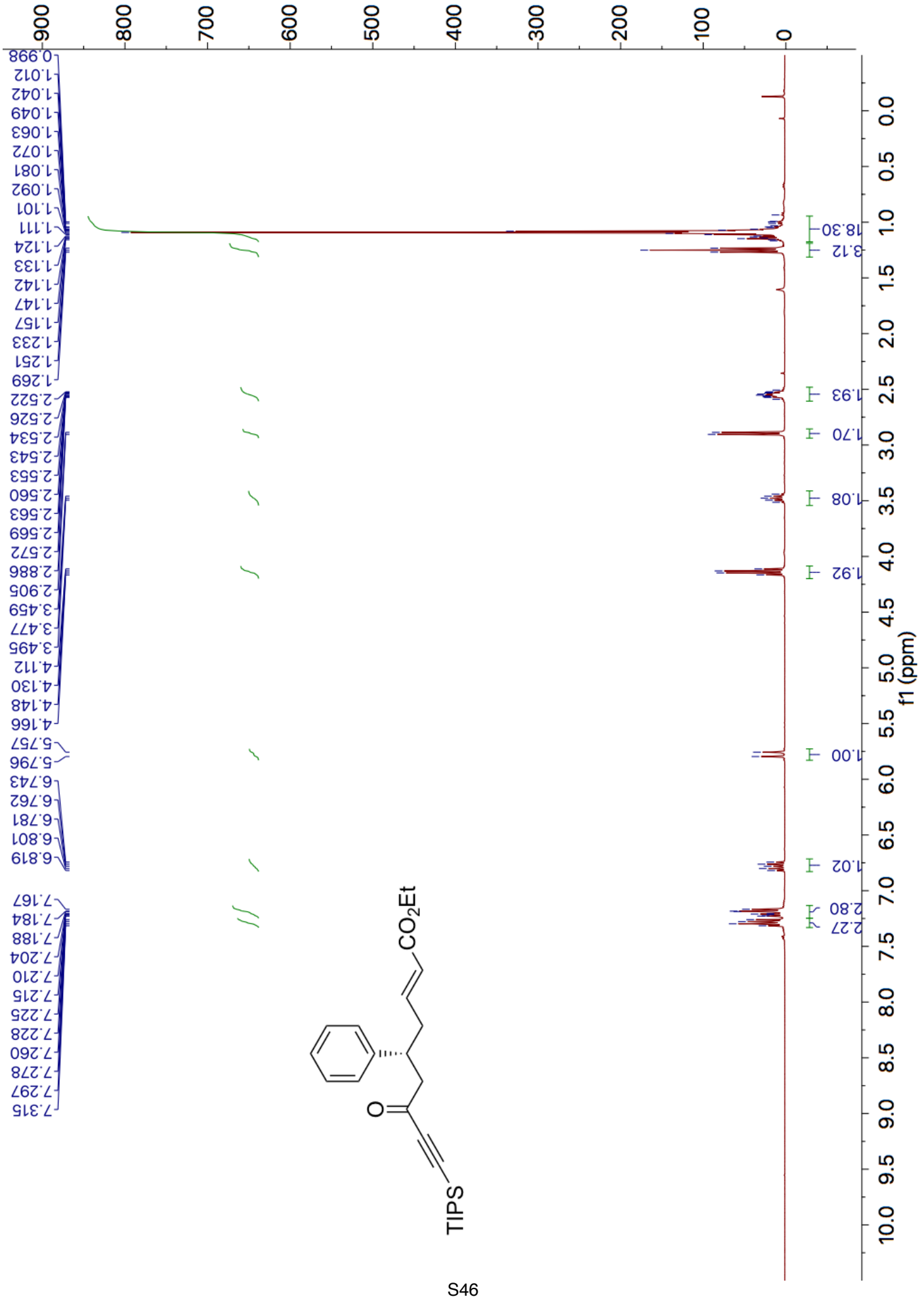

201.262
186.156
104.224
96.193
77.318
77.000
76.681
51.879
50.019
24.611
20.007
18.463
10.972
O
Me
CHO
TIPS
3h
CDCl3, 400 MHz
f1 (ppm)

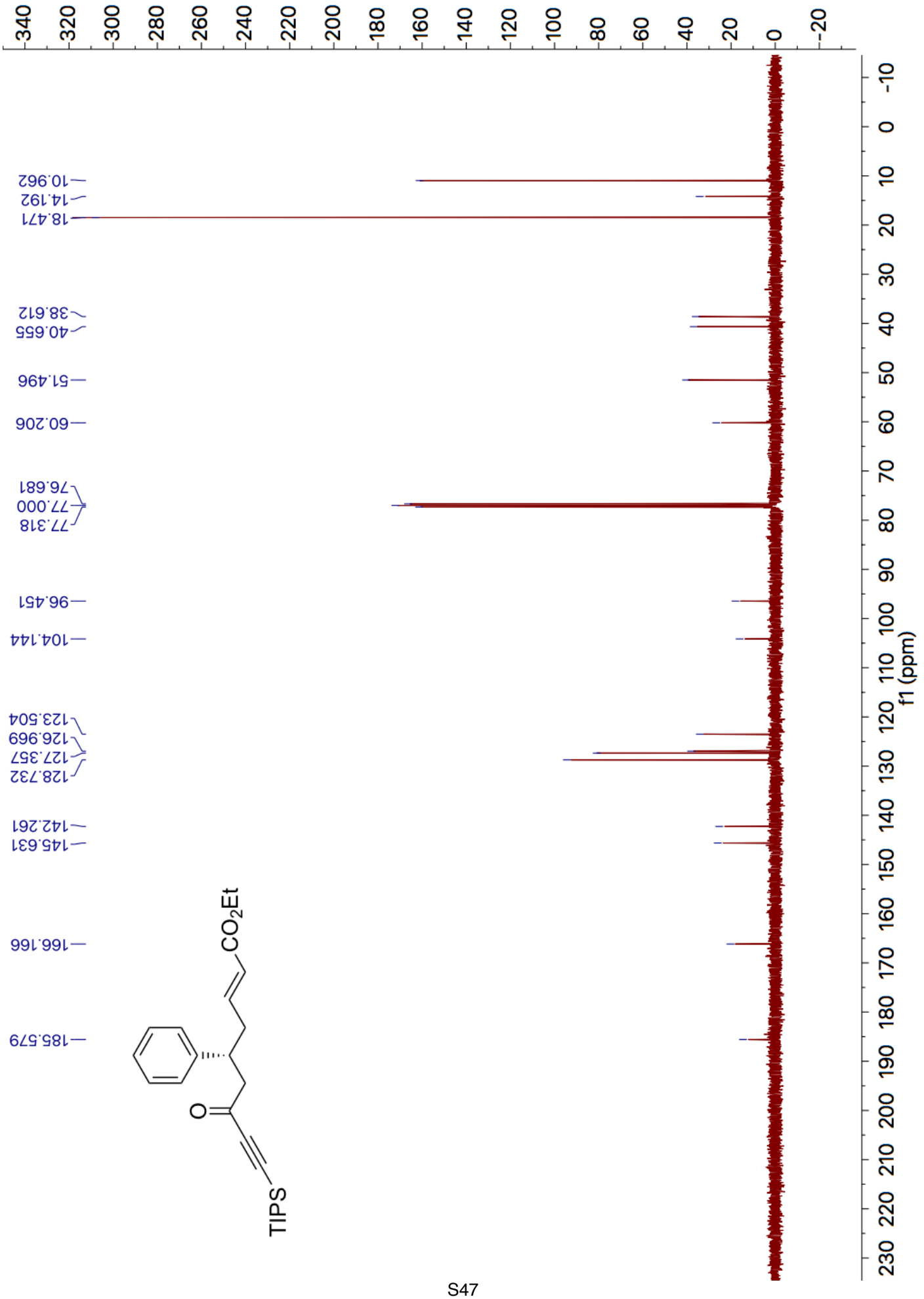


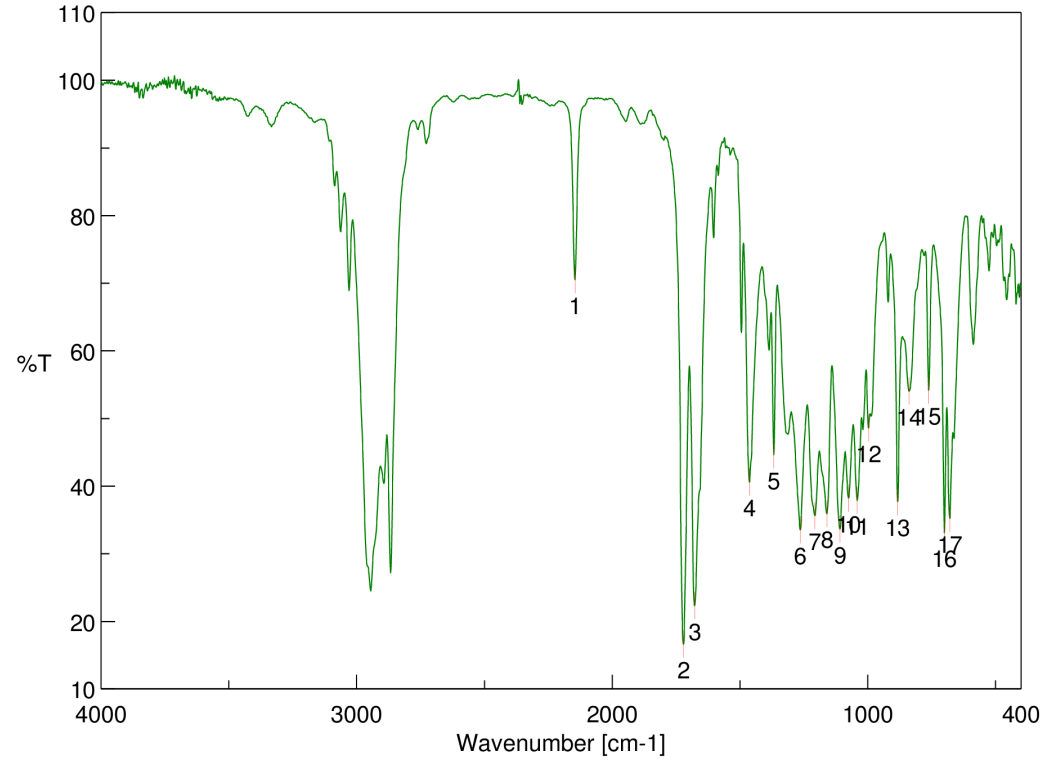
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2144.46	100.583	2	1726.94	50.2365
3	1671.02	37.2193	4	1462.74	74.643
5	1241.93	84.6359	6	1161.9	78.3419
7	1072.23	81.215	8	996.053	77.9284
9	917.95	68.8086	10	883.238	67.0089
11	804.171	82.7392	12	701.962	61.976
13	679.785	64.0461	14	505.258	74.1117



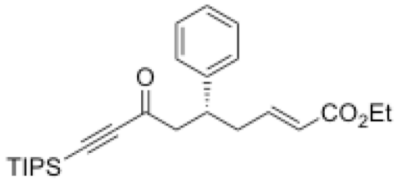

CO2Et
O
TIPS
f1 (ppm)

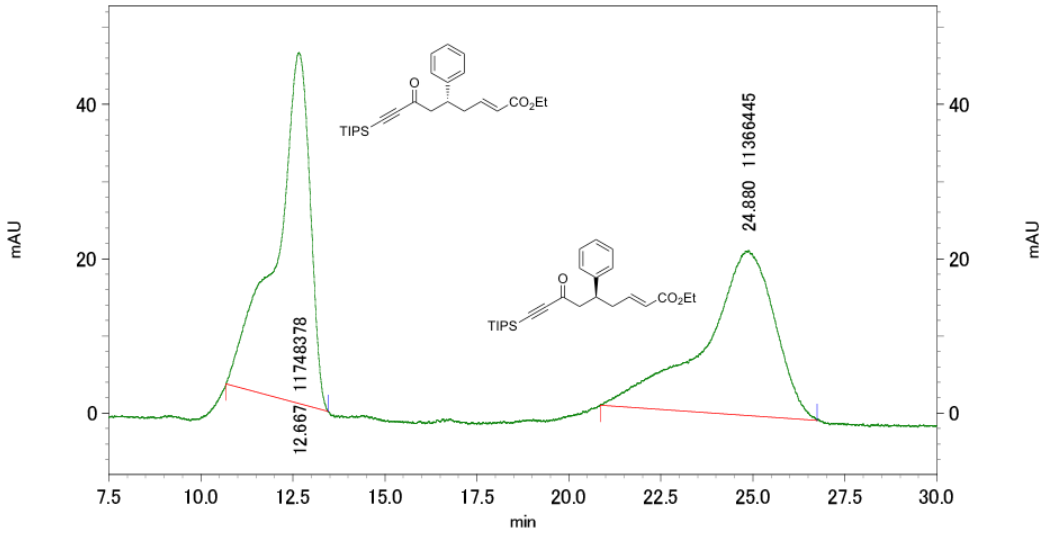

10.962
14.192
18.471
38.612
40.655
51.496
60.206
76.681
77.000
77.318
96.451
104.144
123.504
126.969
127.357
128.732
142.261
145.631
166.166
185.579
CO2Et
TIPS
O
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2145.42	70.4999	2	1721.16	16.6109
3	1676.8	22.3269	4	1462.74	40.5704
5	1367.28	44.627	6	1264.11	33.5003
7	1207.22	35.6323	8	1159.97	35.9157
9	1108.87	33.6187	10	1075.12	38.2352
11	1041.37	37.8997	12	997.017	48.5932
13	883.238	37.7165	14	837.919	54.0177
15	761.744	54.1649	16	700.034	33.1012
17	678.82	35.2257			



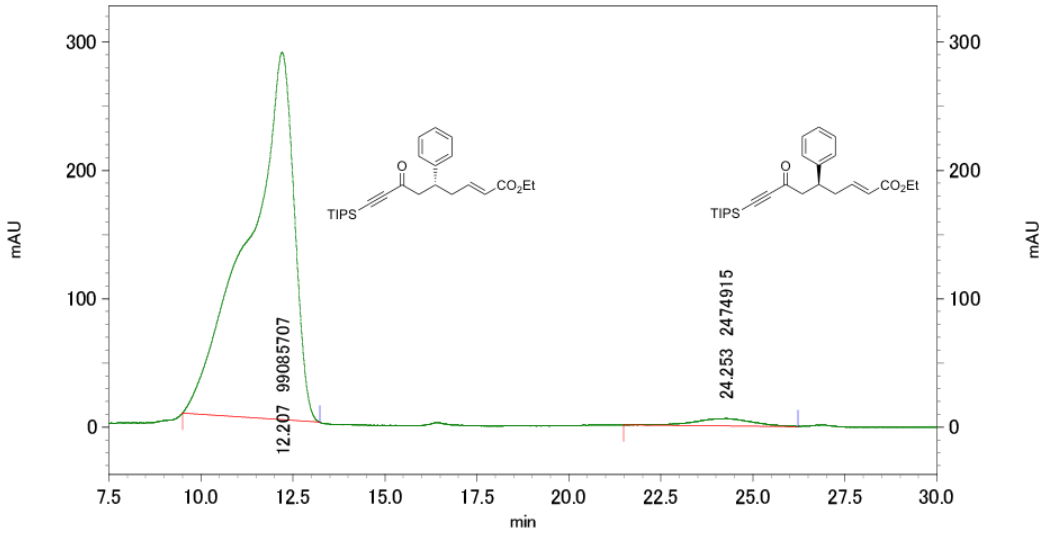


Result

1: 238 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	12.667	50.826
2	24.880	49.174

トータル		100.000
Total		

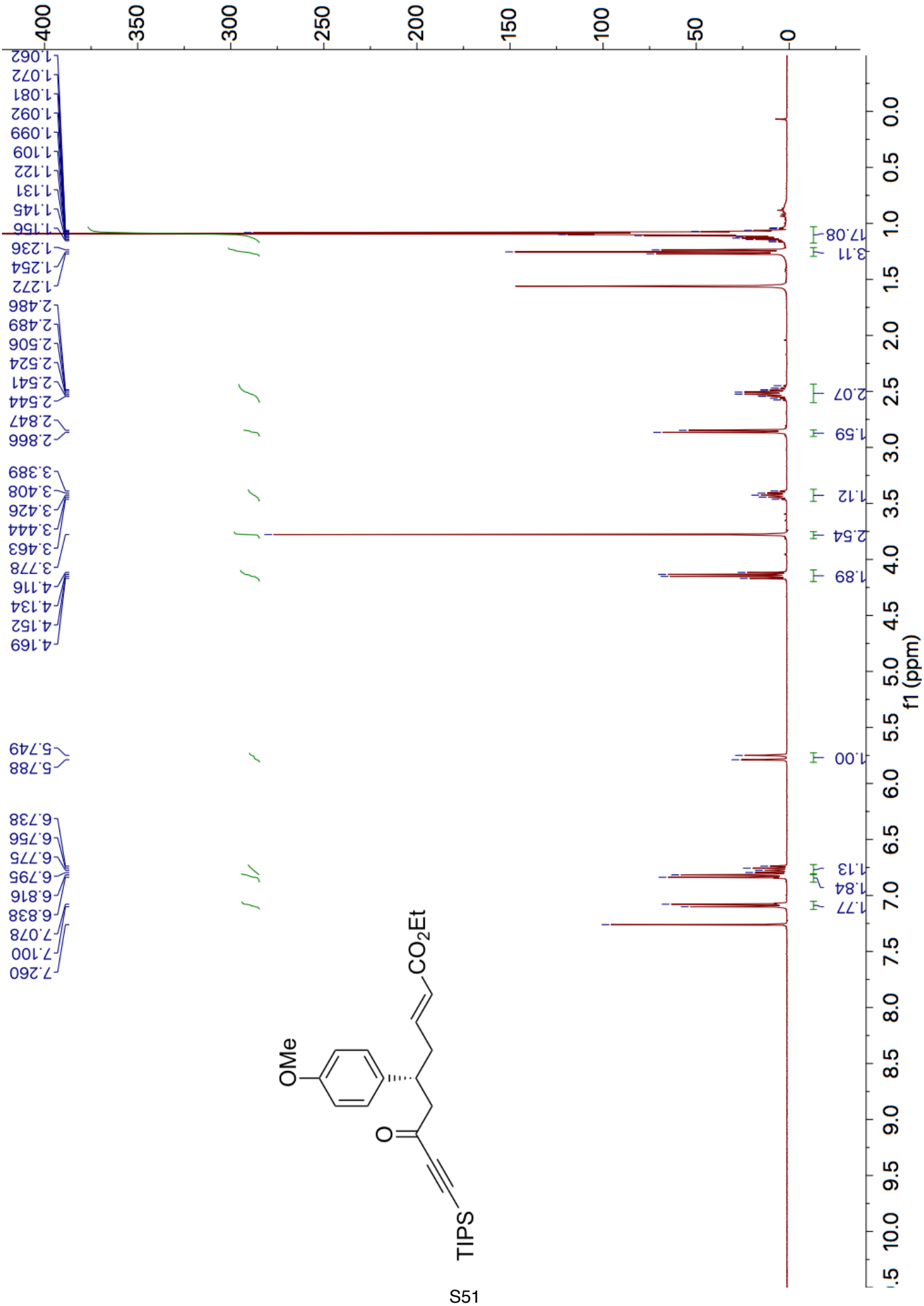


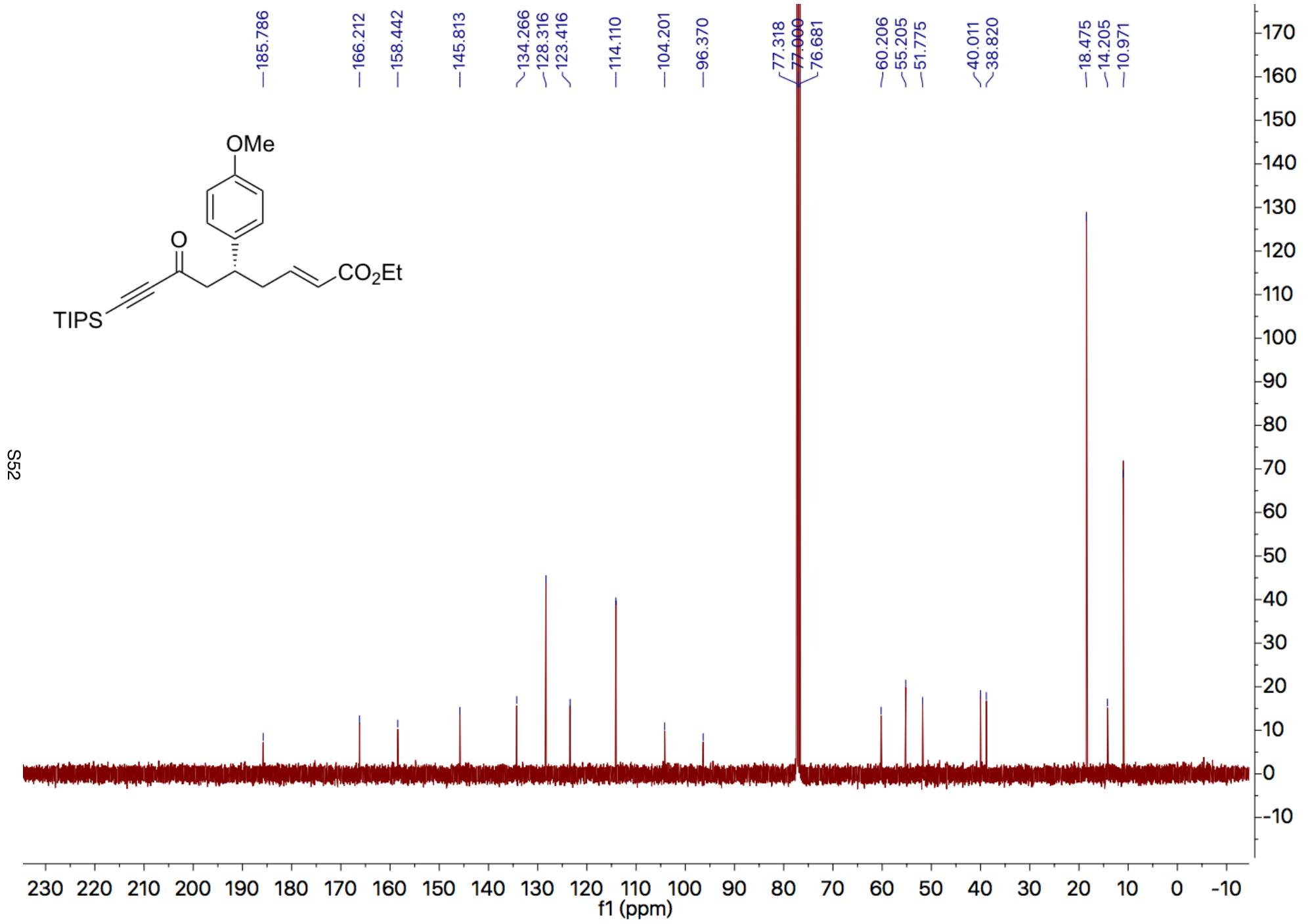
Result

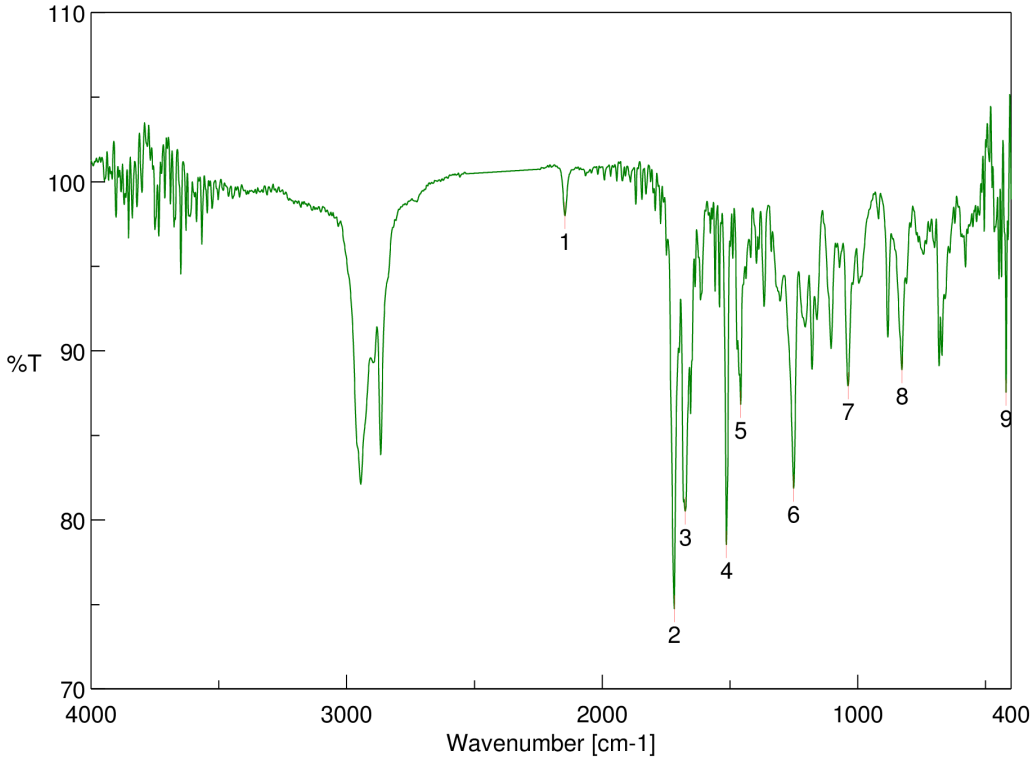
1: 238 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	12.207	97.563
2	24.253	2.437

トータル		100.000
Total		

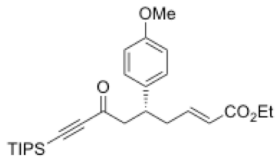

1.062
1.072
1.081
1.092
1.099
1.109
1.122
1.131
1.145
1.156
1.236
1.254
1.272
2.486
2.489
2.506
2.524
2.541
2.544
2.847
2.866
3.389
3.408
3.426
3.444
3.463
3.778
4.116
4.134
4.152
4.169
5.749
5.788
6.738
6.756
6.775
6.795
6.816
6.838
7.078
7.100
7.260
17.08
3.11
2.07
1.59
1.12
2.54
1.89
1.00
1.13
1.84
1.77
f1 (ppm)
OMe
CO2Et
O
TIPS

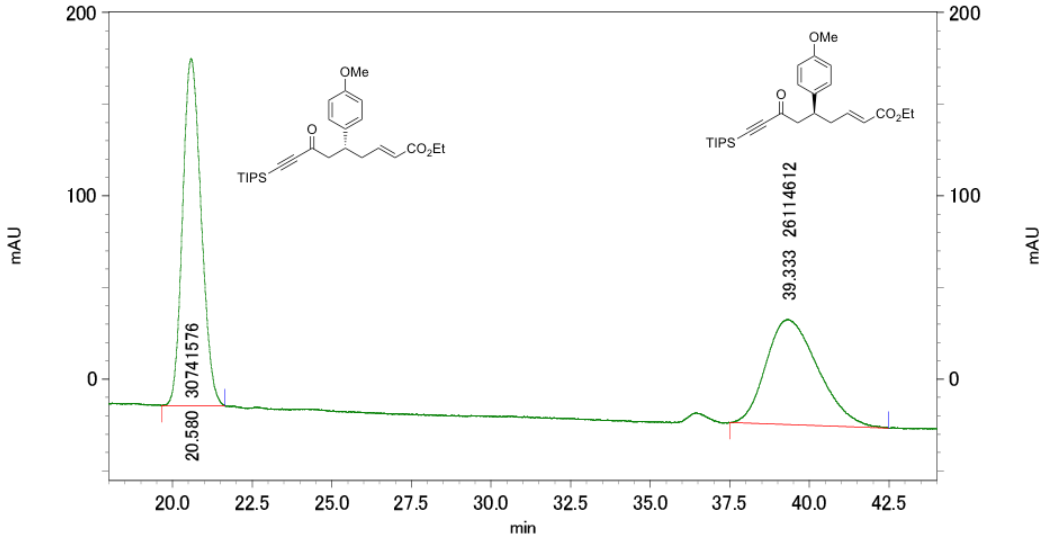

185.786
166.212
158.442
145.813
134.266
128.316
123.416
114.110
104.201
96.370
77.318
77.000
76.681
60.206
55.205
51.775
40.011
38.820
18.475
14.205
10.971
OMe
O
CO2Et
TIPS
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	97.9915	2	1718.26	74.7363
3	1674.87	80.5174	4	1513.85	78.543
5	1457.92	86.8269	6	1250.61	81.8696
7	1037.52	87.923	8	827.312	88.8837
9	419.442	87.5454			

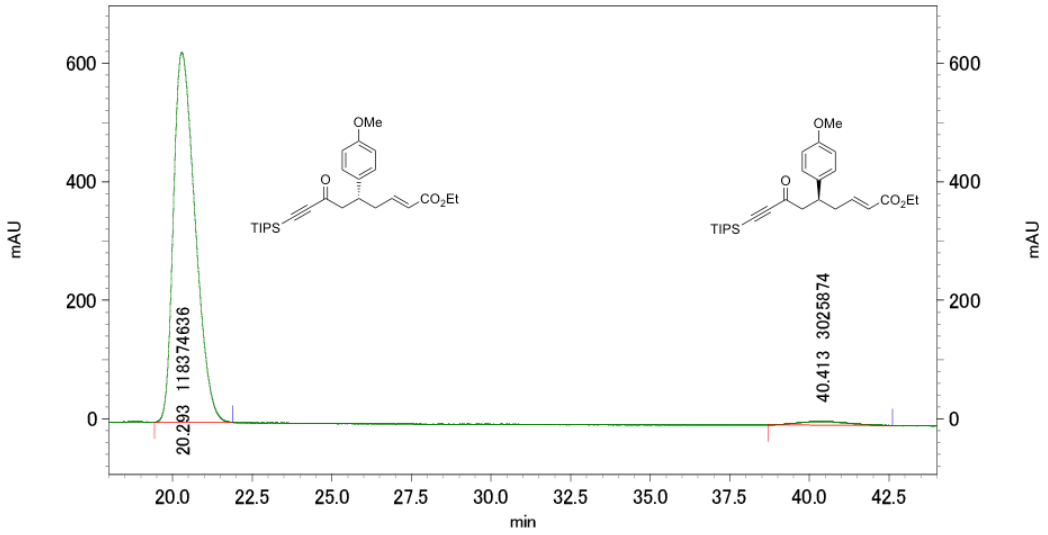




Result

1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	20.580	54.069
2	39.333	45.931
トータル Total		100.000

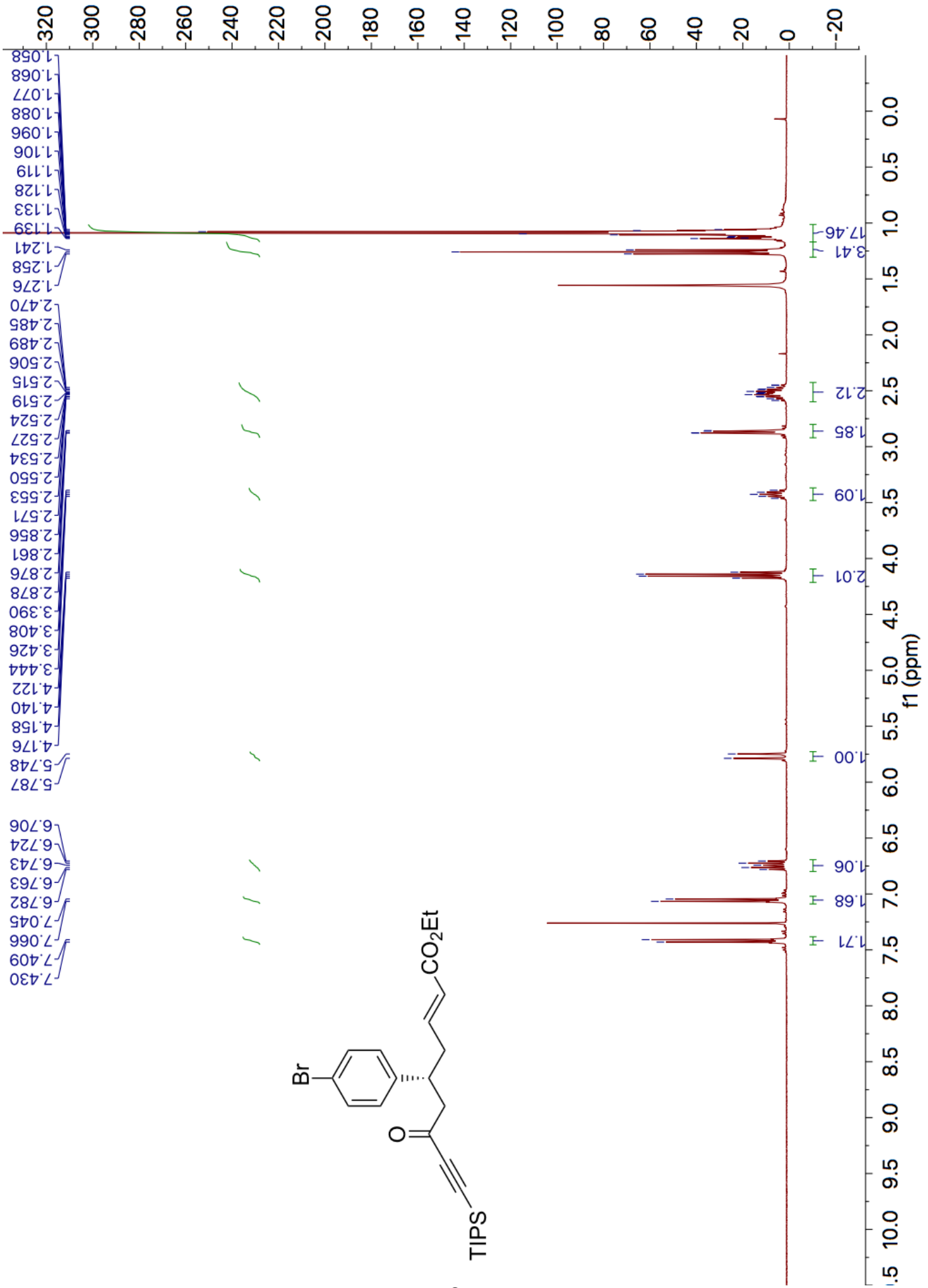


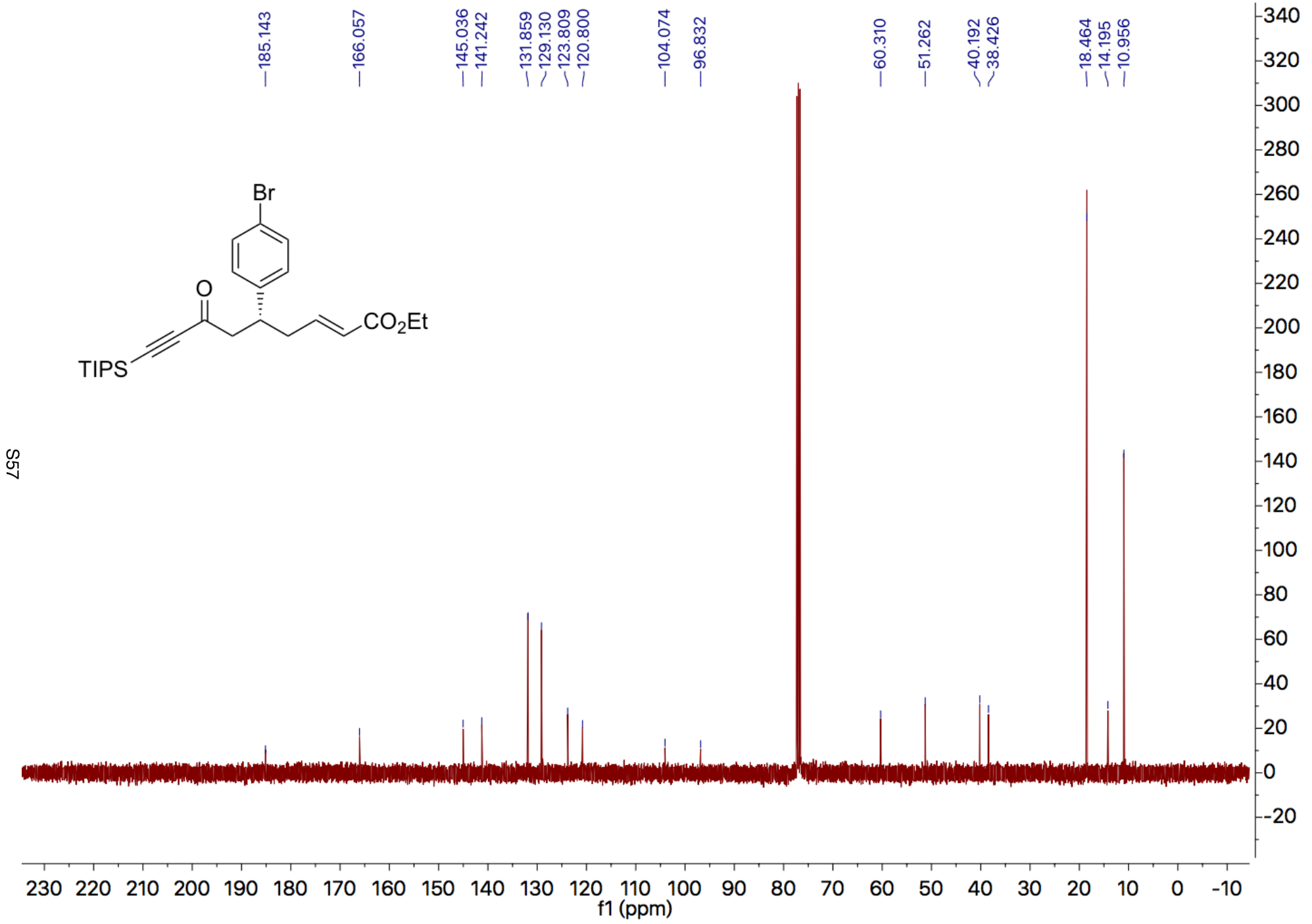
Result

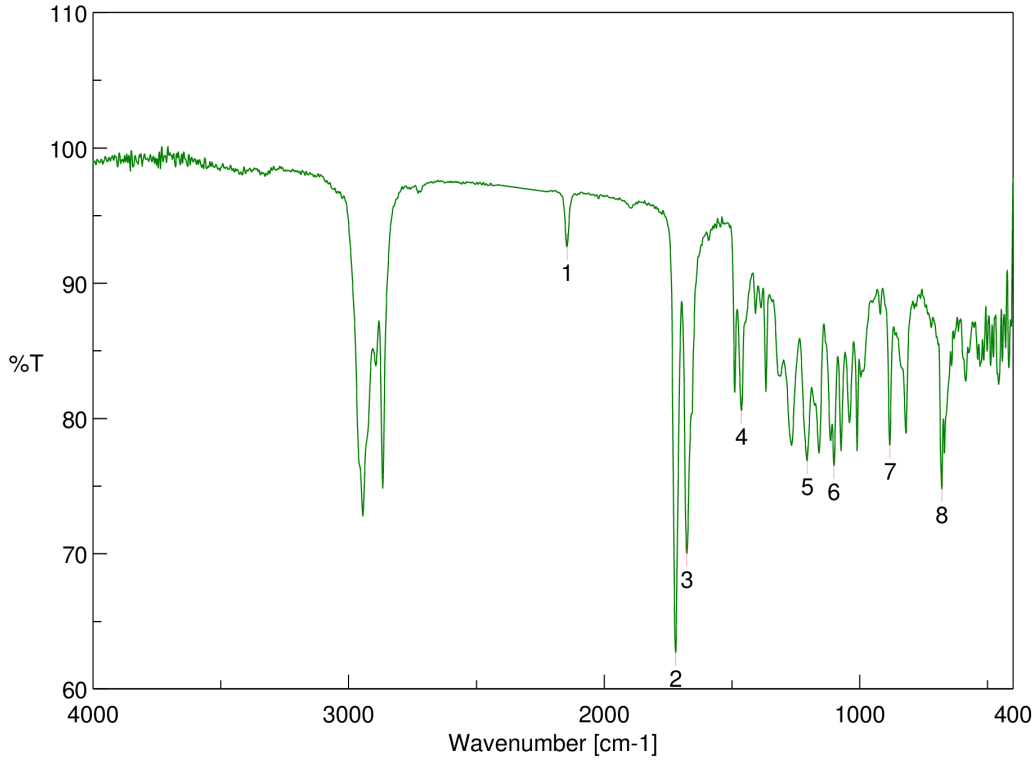
1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	20.293	97.508
2	40.413	2.492
トータル		100.000

Total

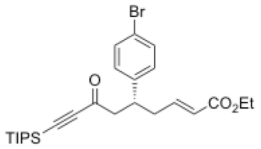

Br
O
CO2Et
TIPS
f1 (ppm)

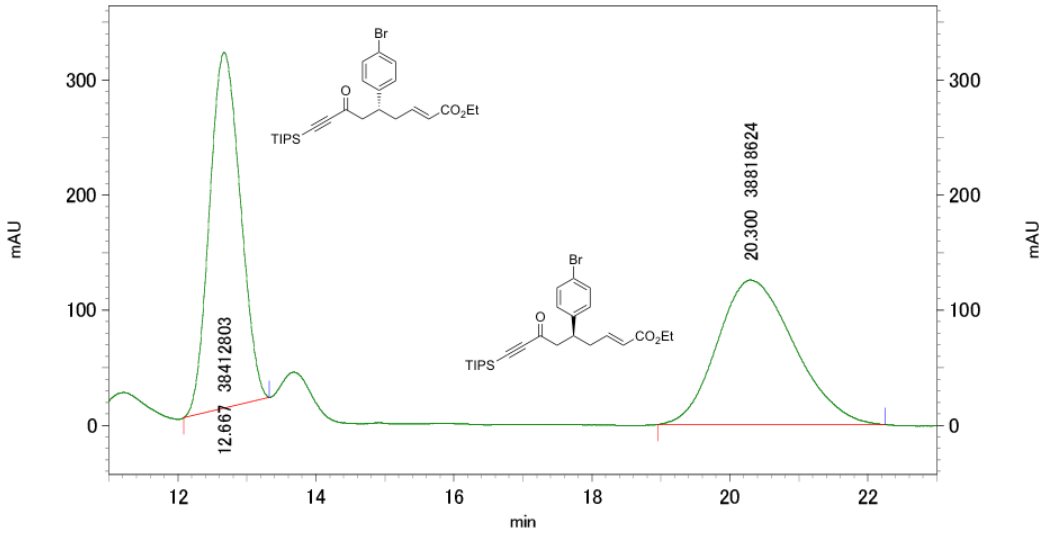

185.143
166.057
145.036
141.242
131.859
129.130
123.809
120.800
104.074
96.832
60.310
51.262
40.192
38.426
18.464
14.195
10.956
Br
O
CO2Et
TIPS
S57
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2145.42	92.6808	2	1720.19	62.7037
3	1676.8	70.0386	4	1463.71	80.5901
5	1206.26	76.8825	6	1101.15	76.5214
7	882.274	78.0259	8	678.82	74.7902



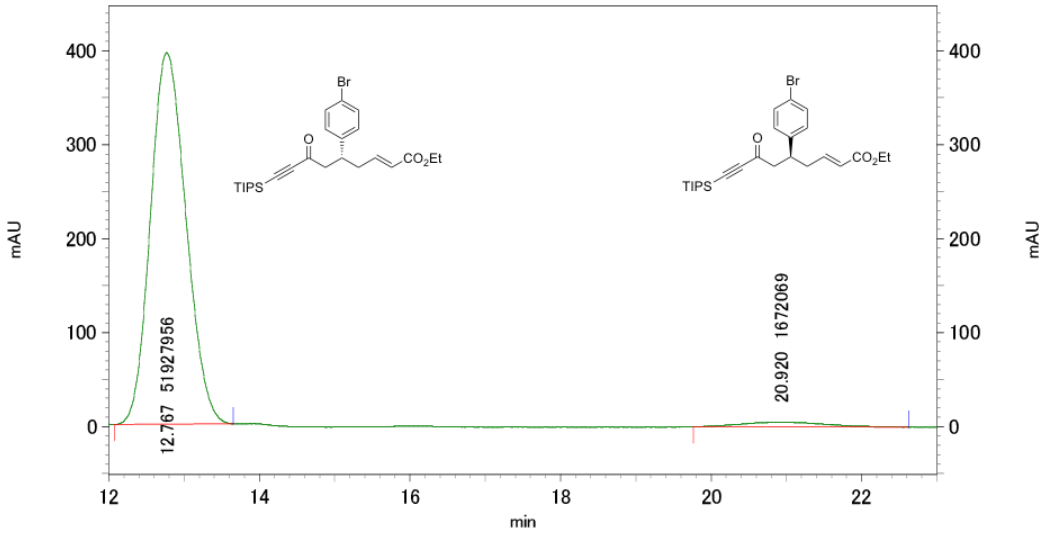


Result

1: 234 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	12.667	49.737
2	20.300	50.263

トータル		100.000
Total		



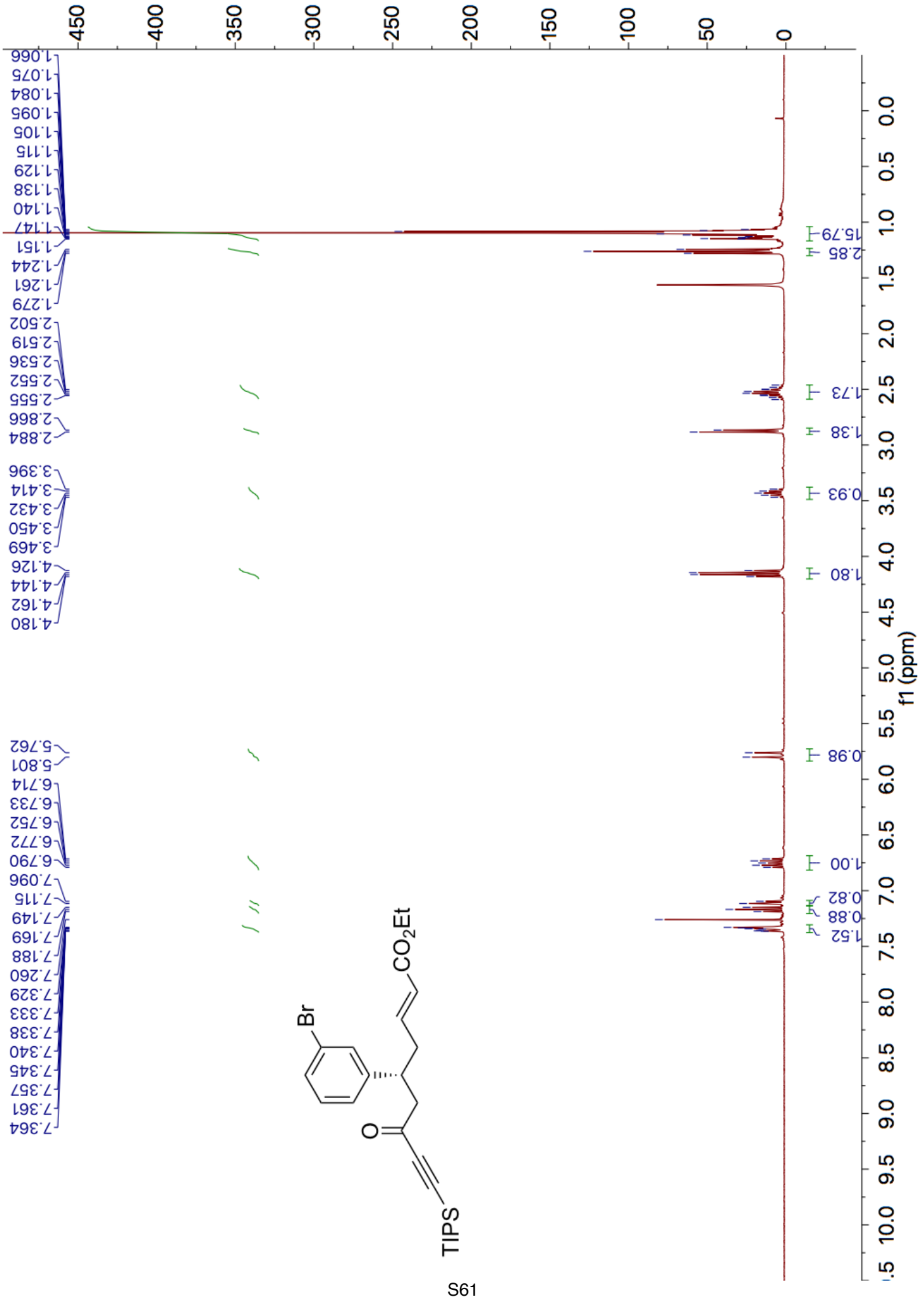
Result

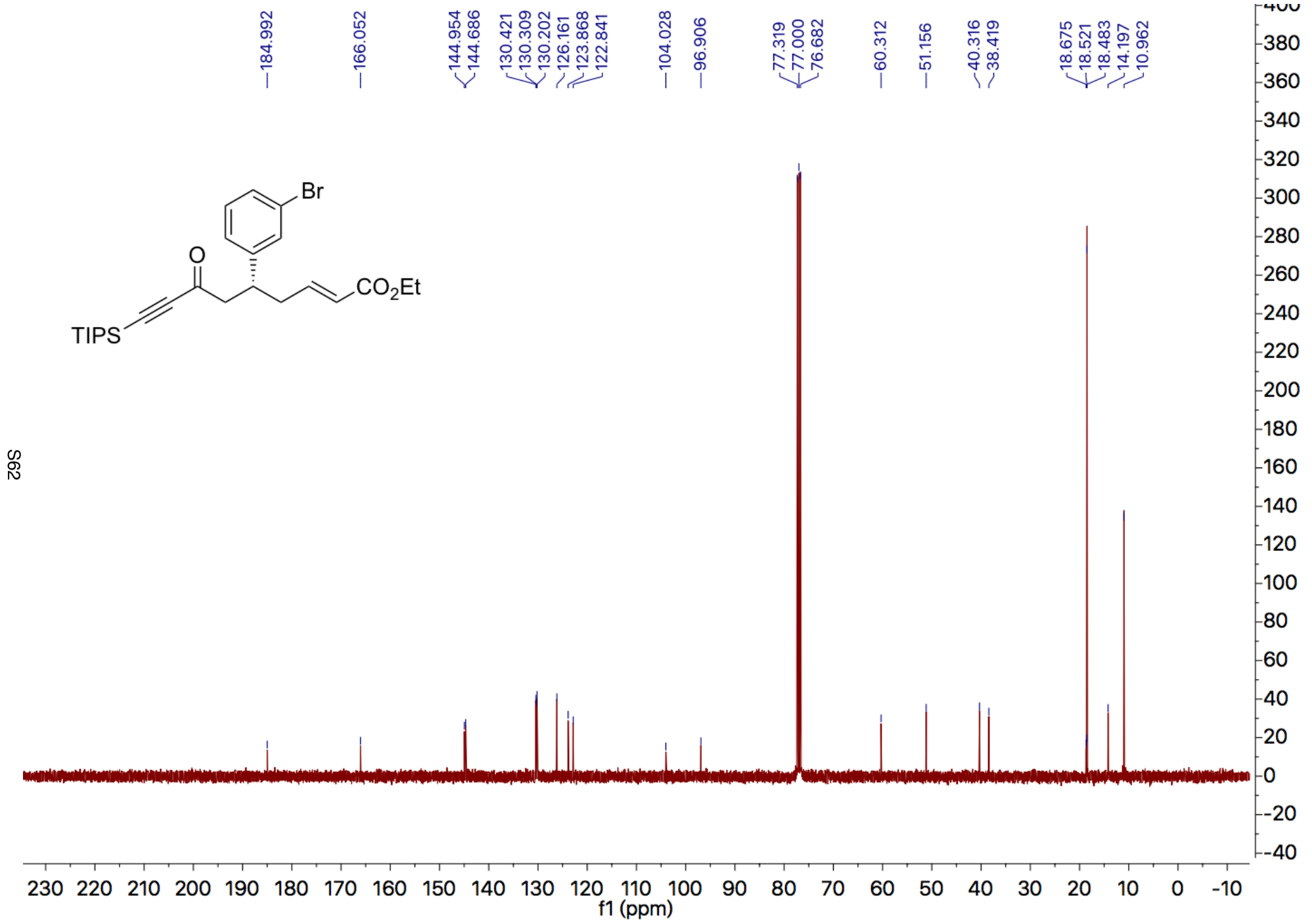
1: 233 nm, 4 nm結果

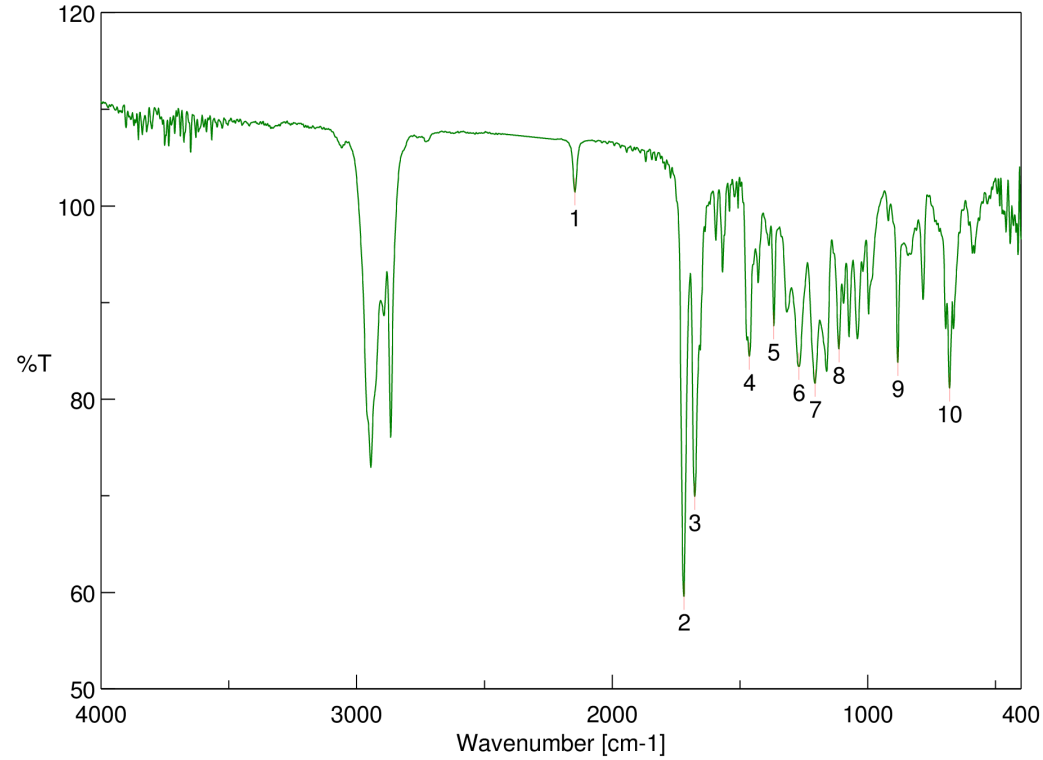
Pk #	Retention time / min	Integration/ %
1	12.767	96.880
2	20.920	3.120

ﾄｰﾀﾙ		100.000

Total

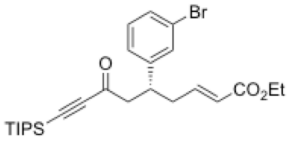

Br
CO2Et
O
TIPS
f1 (ppm)

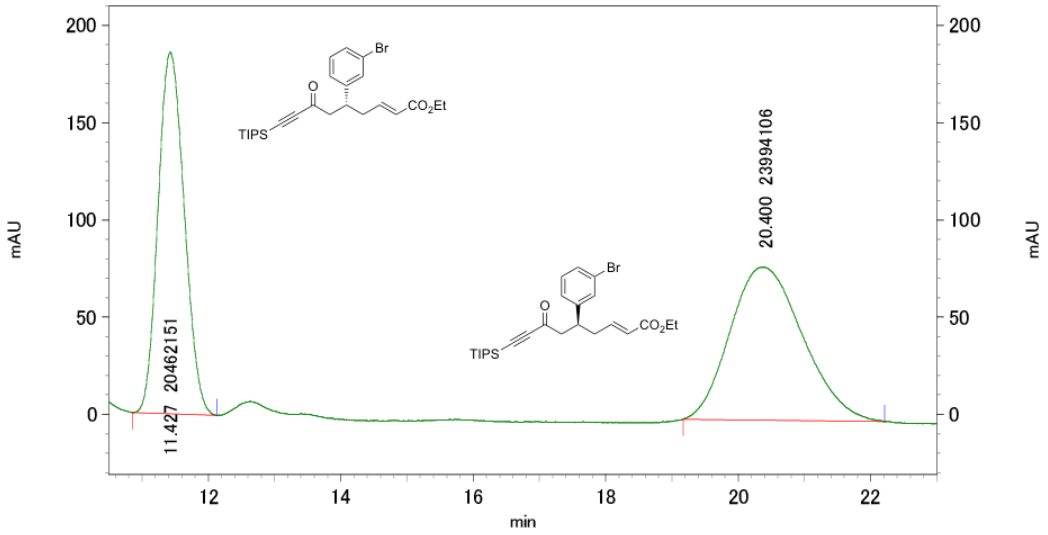

184.992
166.052
144.954
144.686
130.421
130.309
130.202
126.161
123.868
122.841
104.028
96.906
77.319
77.000
76.682
60.312
51.156
40.316
38.419
18.675
18.521
18.483
14.197
10.962
Br
O
CO2Et
TIPS
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	101.433	2	1719.23	59.5812
3	1676.8	69.9177	4	1463.71	84.4217
5	1367.28	87.5675	6	1269.9	83.3779
7	1206.26	81.6407	8	1112.73	85.1871
9	882.274	83.7914	10	679.785	81.126



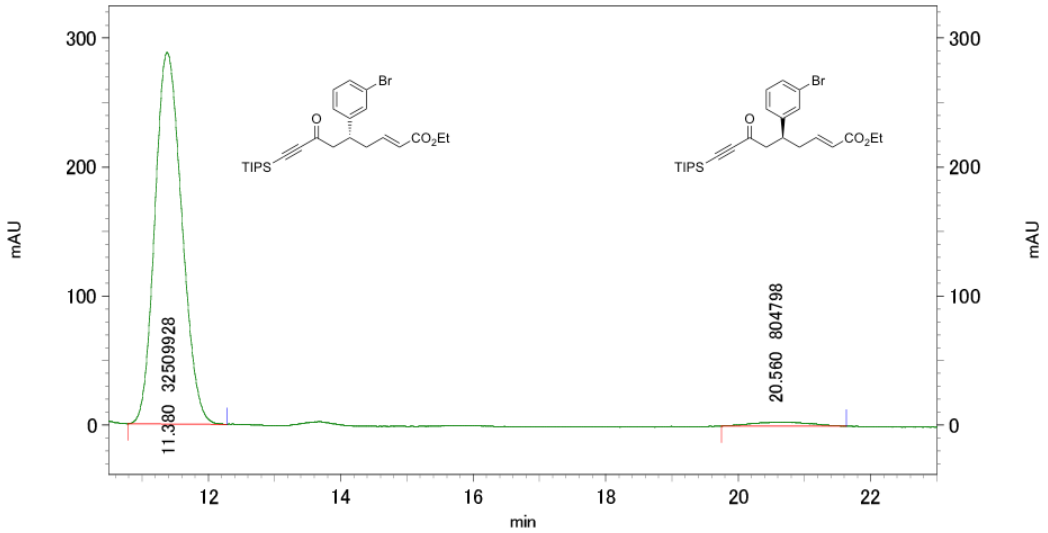


Result

1: 234 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	11.427	46.028
2	20.400	53.972

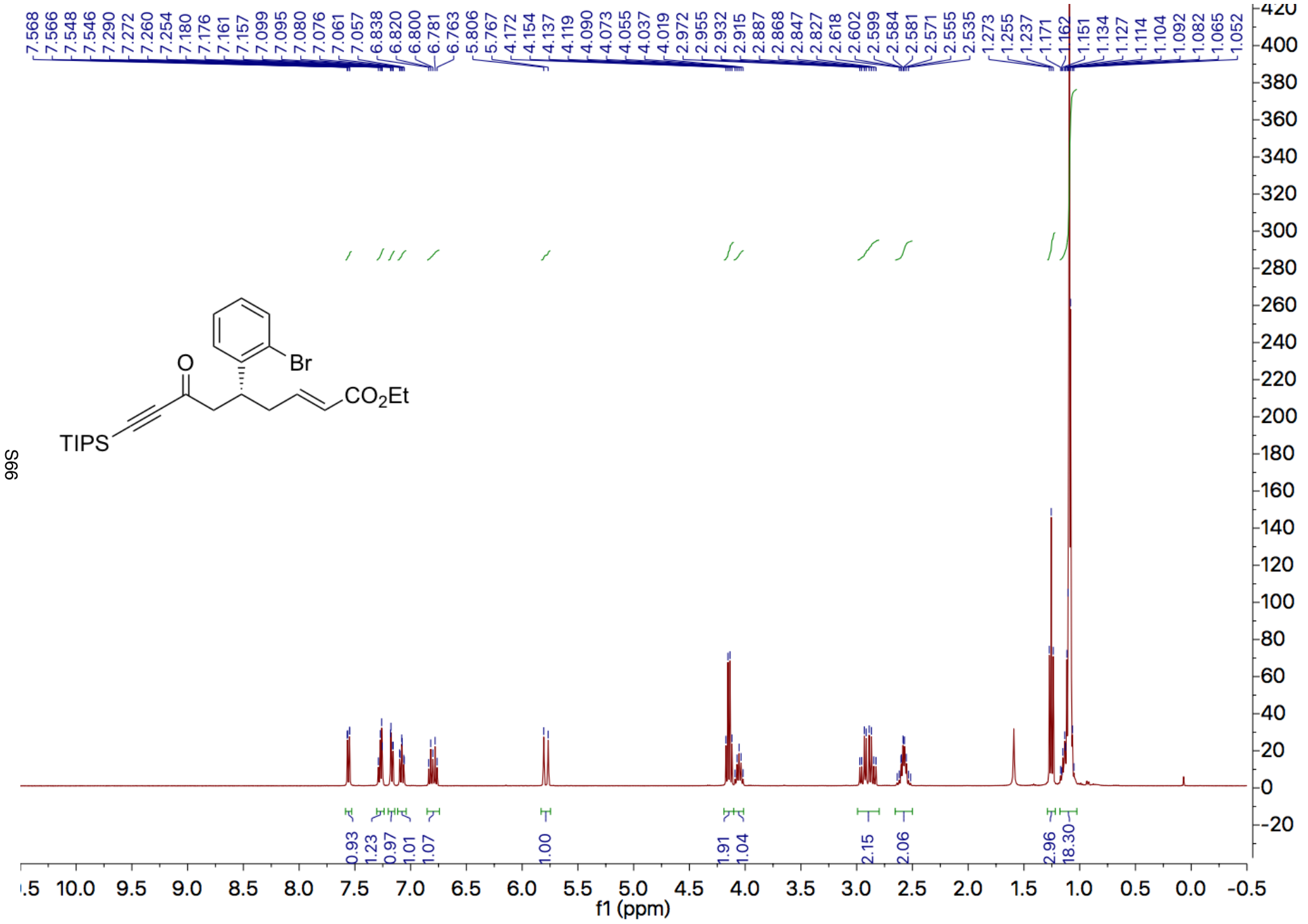
トータル		100.000
Total		

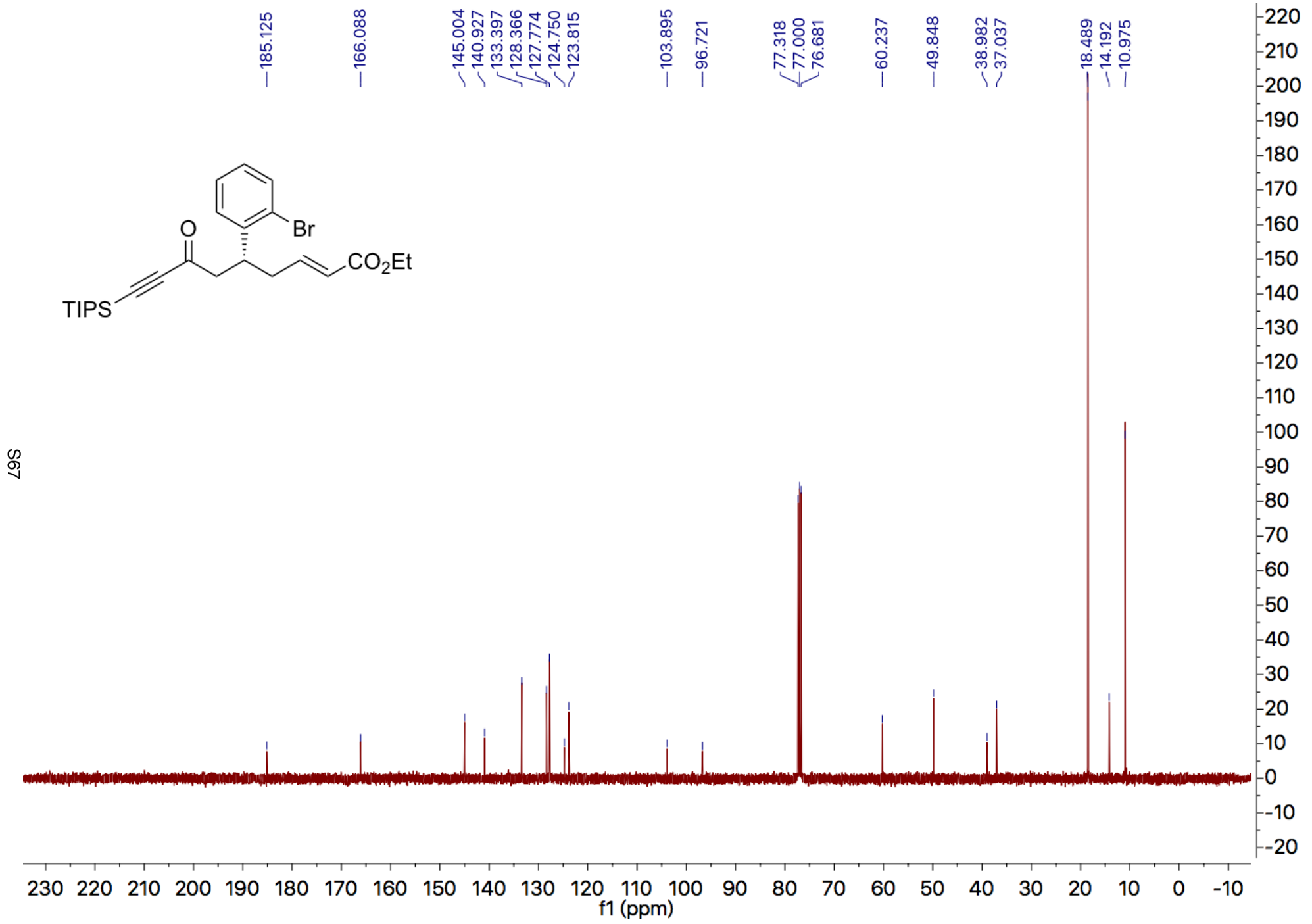


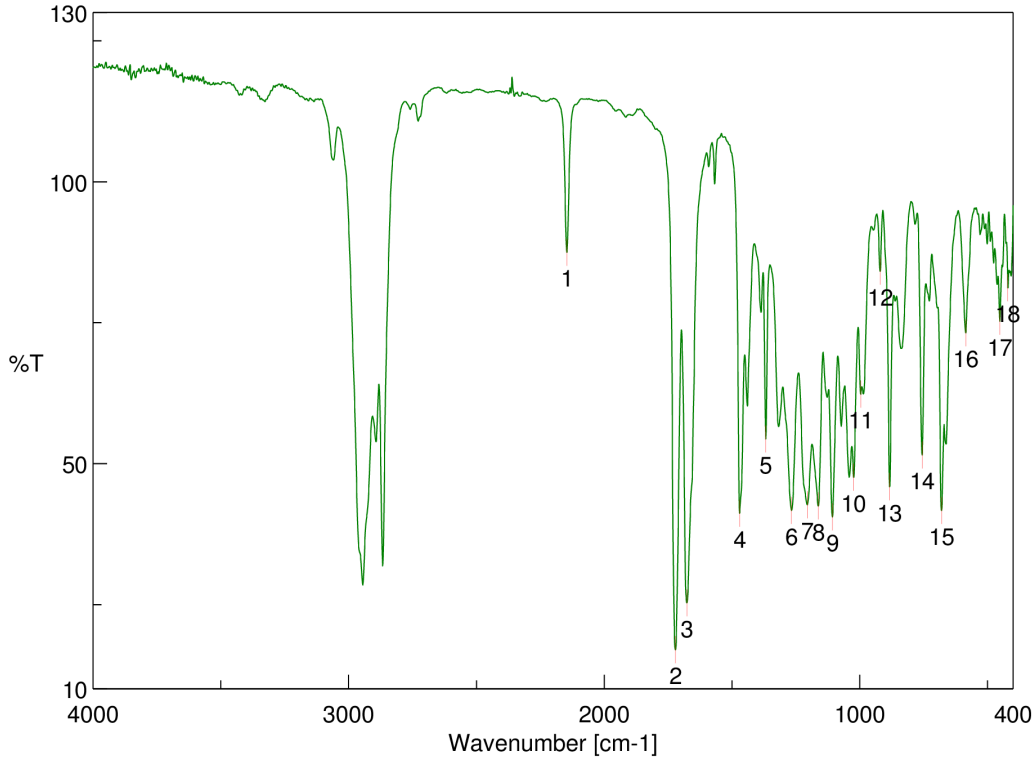
Result

1: 234 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	11.380	97.584
2	20.560	2.416
トータル		100.000
Total		

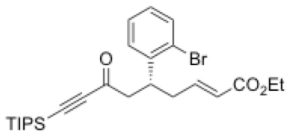

7.568 7.566 7.548 7.546 7.290 7.272 7.260 7.254 7.180 7.176 7.161 7.157 7.099 7.095 7.080 7.076 7.061 7.057 6.838 6.820 6.800 6.781 6.763 5.806 5.767 4.172 4.154 4.137 4.119 4.090 4.073 4.055 4.037 4.019 2.972 2.955 2.932 2.915 2.887 2.868 2.847 2.827 2.618 2.602 2.599 2.584 2.581 2.571 2.555 2.535 1.273 1.255 1.237 1.171 1.162 1.151 1.134 1.127 1.114 1.104 1.092 1.082 1.065 1.052
O
Br
CO2Et
TIPS
S66
0.93 1.23 0.97 1.01 1.07 1.00 1.91 1.04 2.15 2.06 2.96 18.30
f1 (ppm)

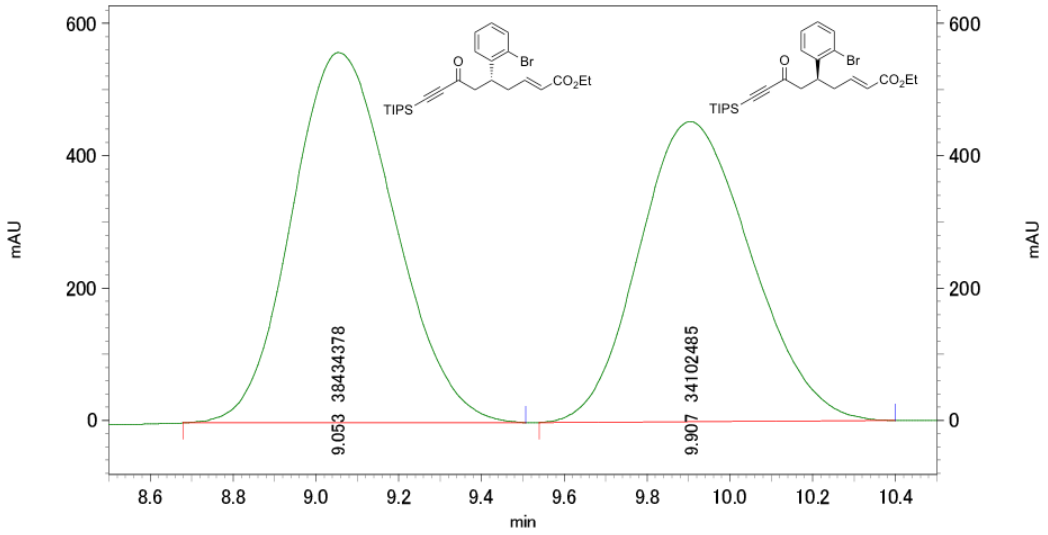

185.125
166.088
145.004
140.927
133.397
128.366
127.774
124.750
123.815
103.895
96.721
77.318
77.000
76.681
60.237
49.848
38.982
37.037
18.489
14.192
10.975
O
Br
CO2Et
TIPS
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	87.4447	2	1721.16	16.9312
3	1675.84	25.2578	4	1470.46	41.1771
5	1367.28	54.3629	6	1267	41.6697
7	1205.29	42.6426	8	1161.9	42.4444
9	1106.94	40.5302	10	1024.02	47.5424
11	996.053	62.2804	12	919.879	84.0874
13	883.238	45.8727	14	755.959	51.4923
15	679.785	41.676	16	585.29	73.1495
17	452.225	75.2175	18	420.406	81.1371



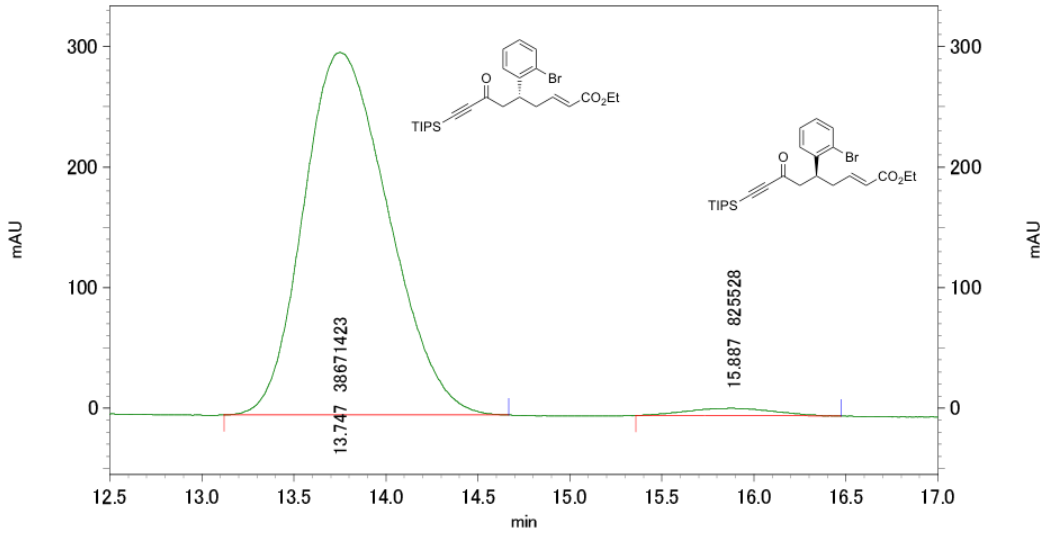


Result

1: 234 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	9.053	52.986
2	9.907	47.014

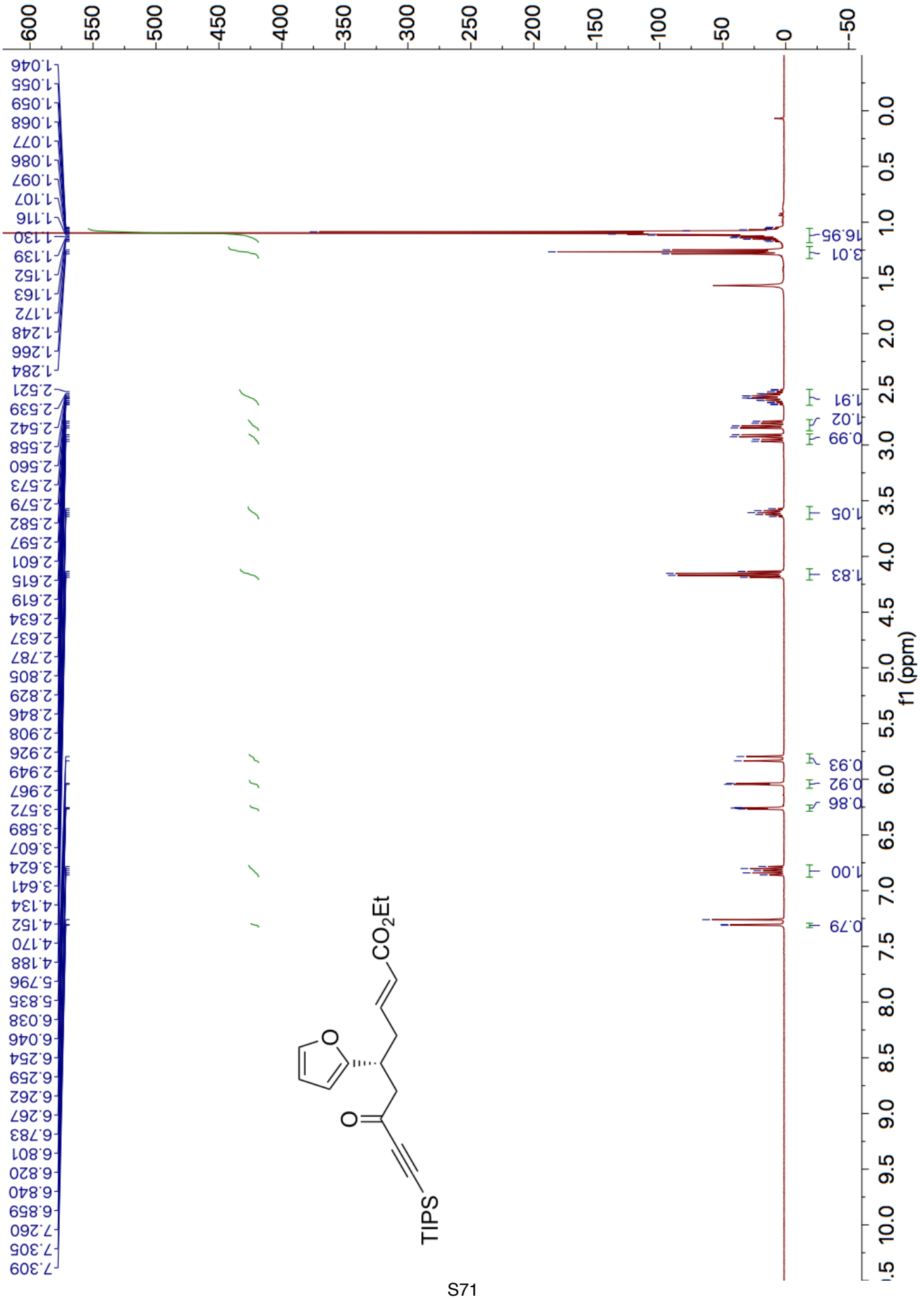
ﾄｰﾀﾙ		100.000
Total		

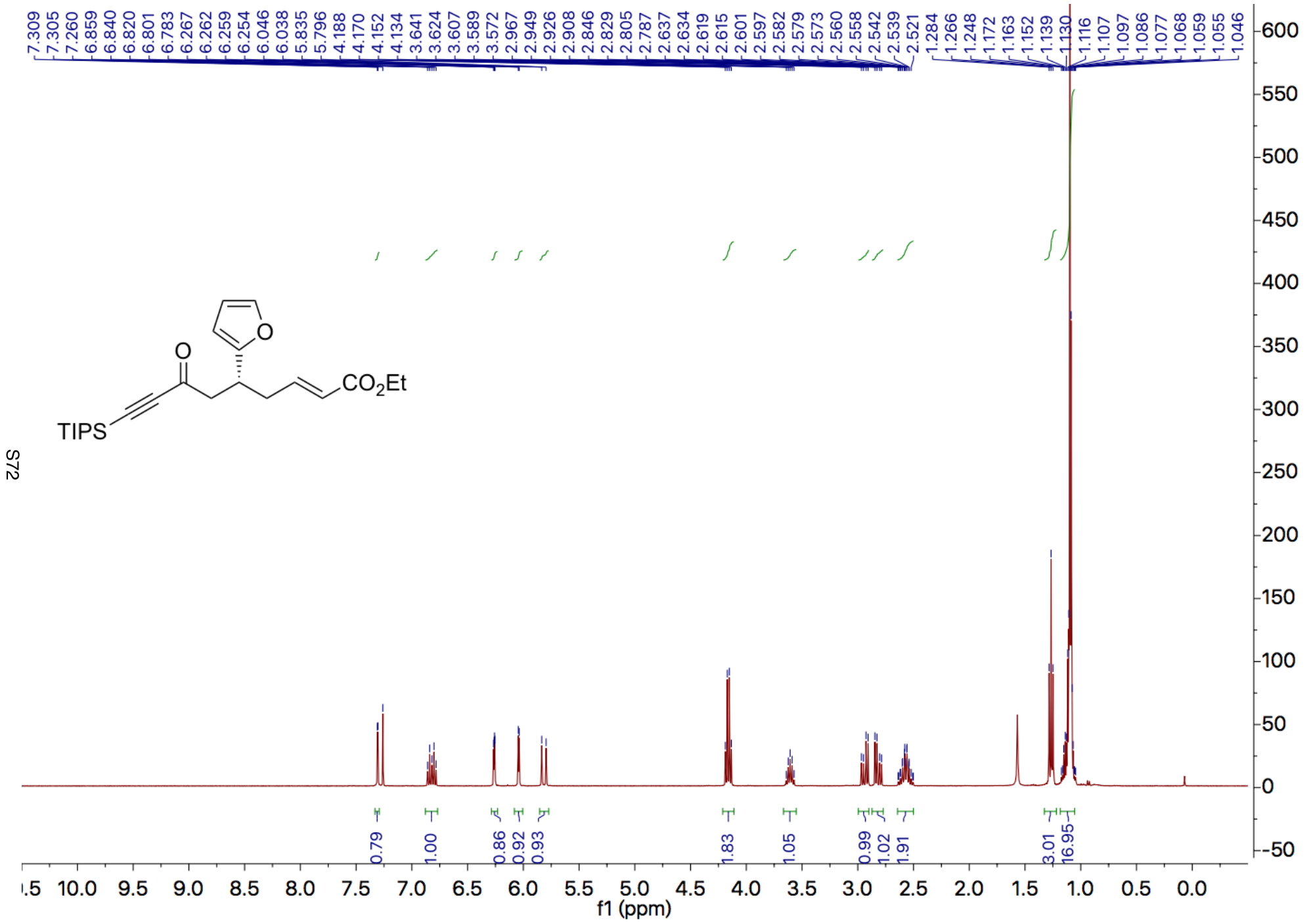


Result

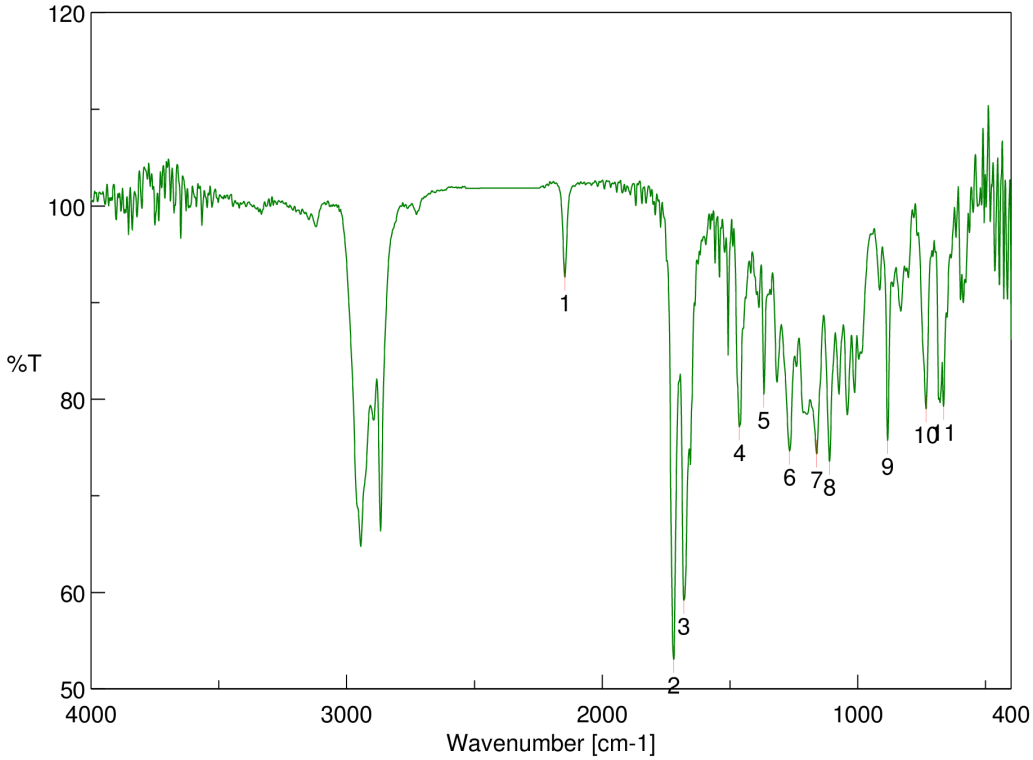
1: 234 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	13.747	97.910
2	15.887	2.090
トータル Total		100.000


CO2Et
TIPS
O
O
f1 (ppm)

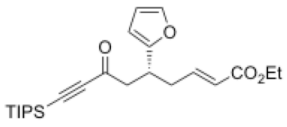

7.309 7.305 7.260 6.859 6.840 6.820 6.801 6.783 6.267 6.262 6.259 6.254 6.046 6.038 5.835 5.796 4.188 4.170 4.152 4.134 3.641 3.624 3.607 3.589 3.572 2.967 2.949 2.926 2.908 2.846 2.829 2.805 2.787 2.637 2.634 2.619 2.615 2.601 2.597 2.582 2.579 2.573 2.560 2.558 2.542 2.539 2.521 1.284 1.266 1.248 1.172 1.163 1.152 1.139 1.130 1.116 1.107 1.097 1.086 1.077 1.068 1.059 1.055 1.046
O
O
CO2Et
TIPS
0.79 1.00 0.86 0.92 0.93 1.83 1.05 0.99 1.02 1.91 3.01 16.95
f1 (ppm)

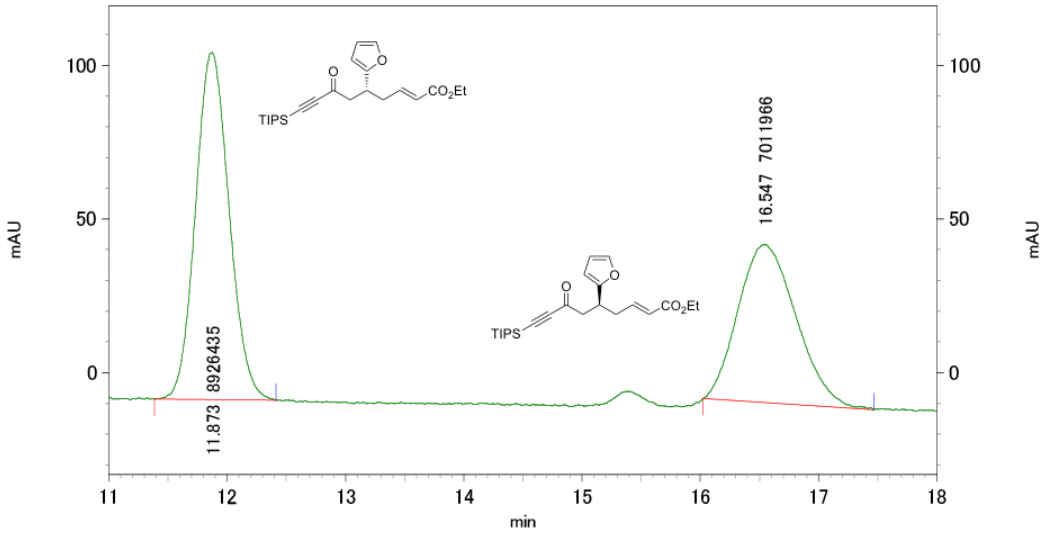
S72



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	92.6141	2	1720.19	53.0539
3	1680.66	59.1653	4	1463.71	77.1184
5	1367.28	80.4945	6	1267	74.6197
7	1160.94	74.3223	8	1109.83	73.5718
9	883.238	75.7183	10	732.817	78.9756
11	664.357	79.2511			



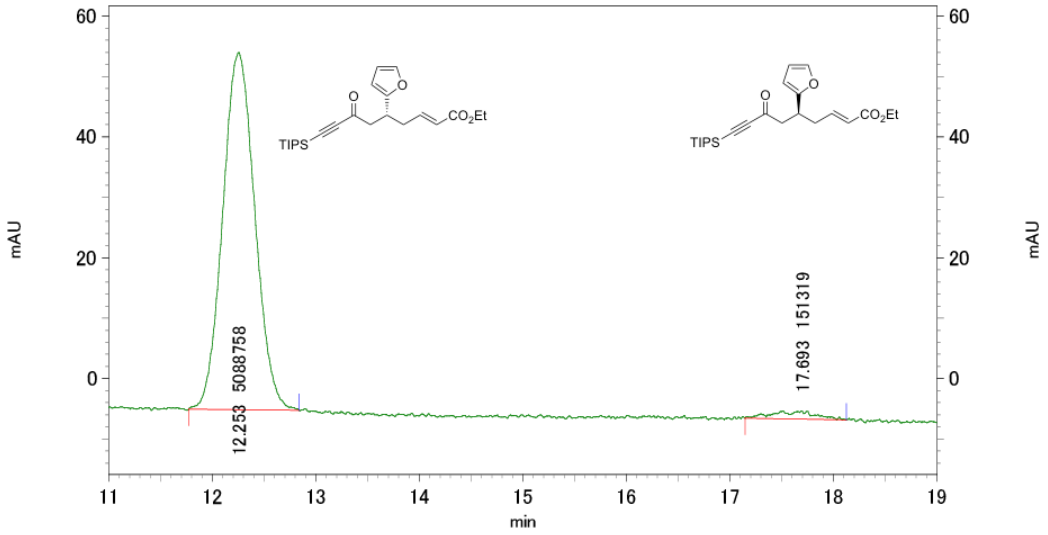


Result

1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	11.873	56.006
2	16.547	43.994

トータル		100.000
Total		

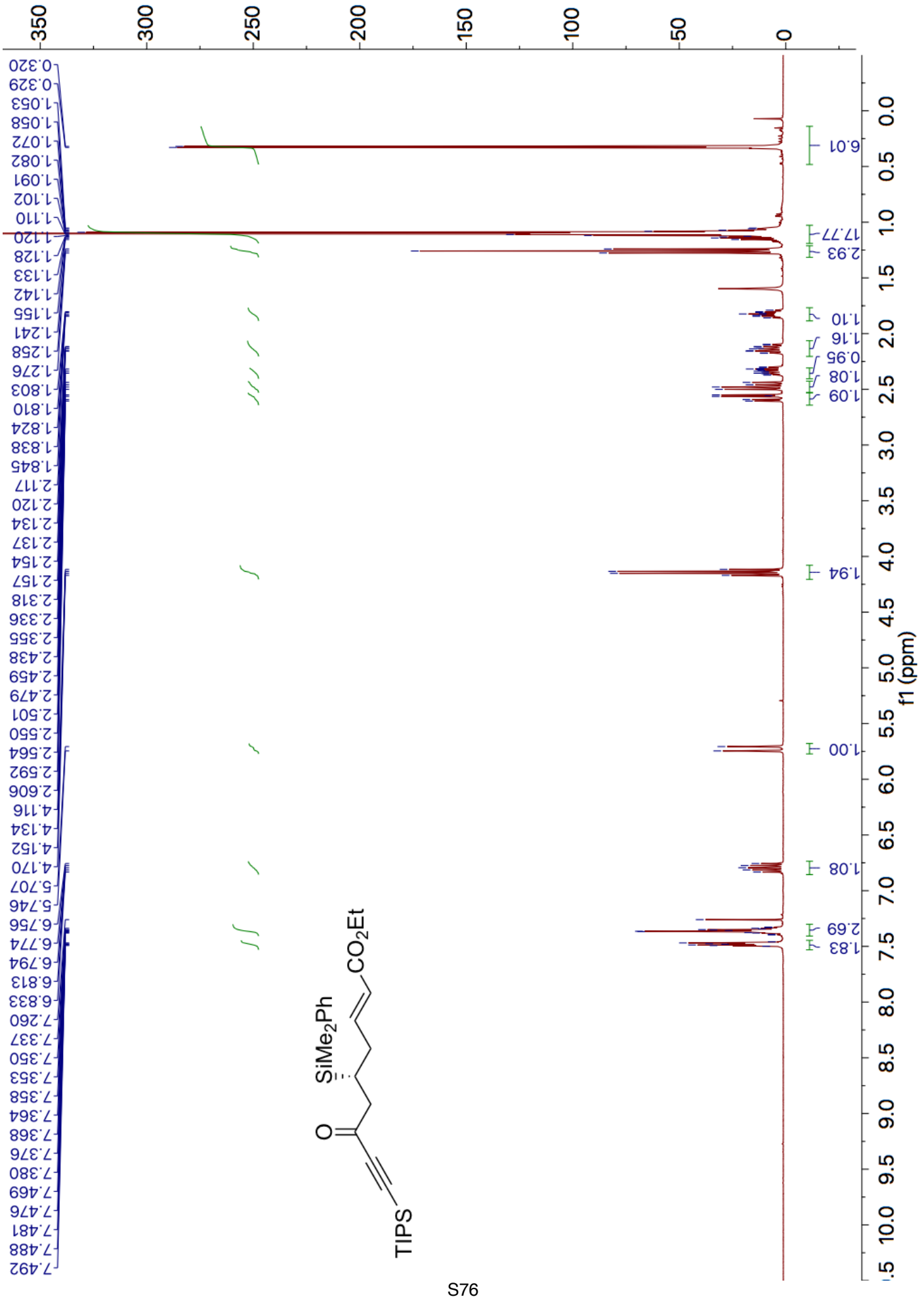


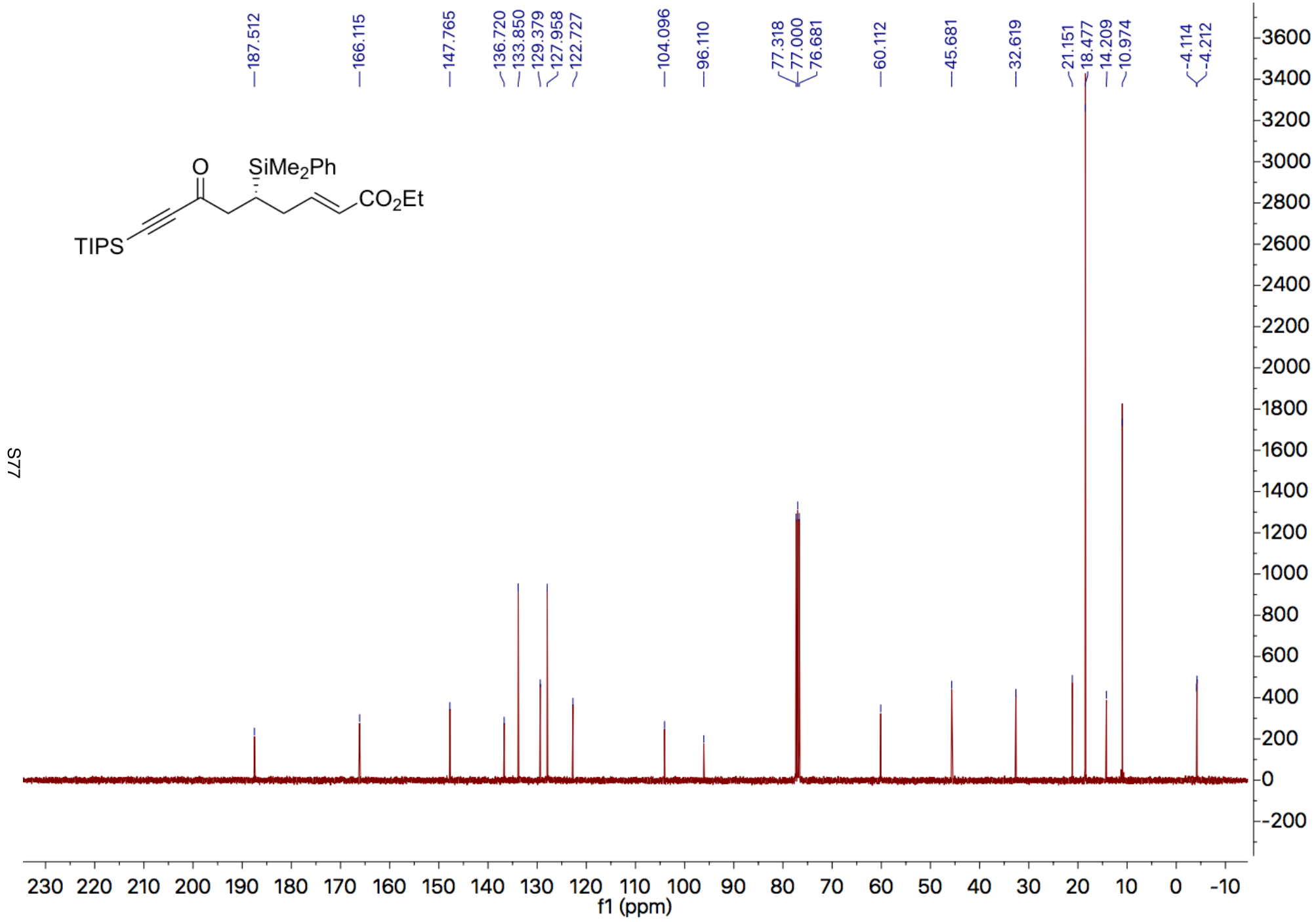
Result

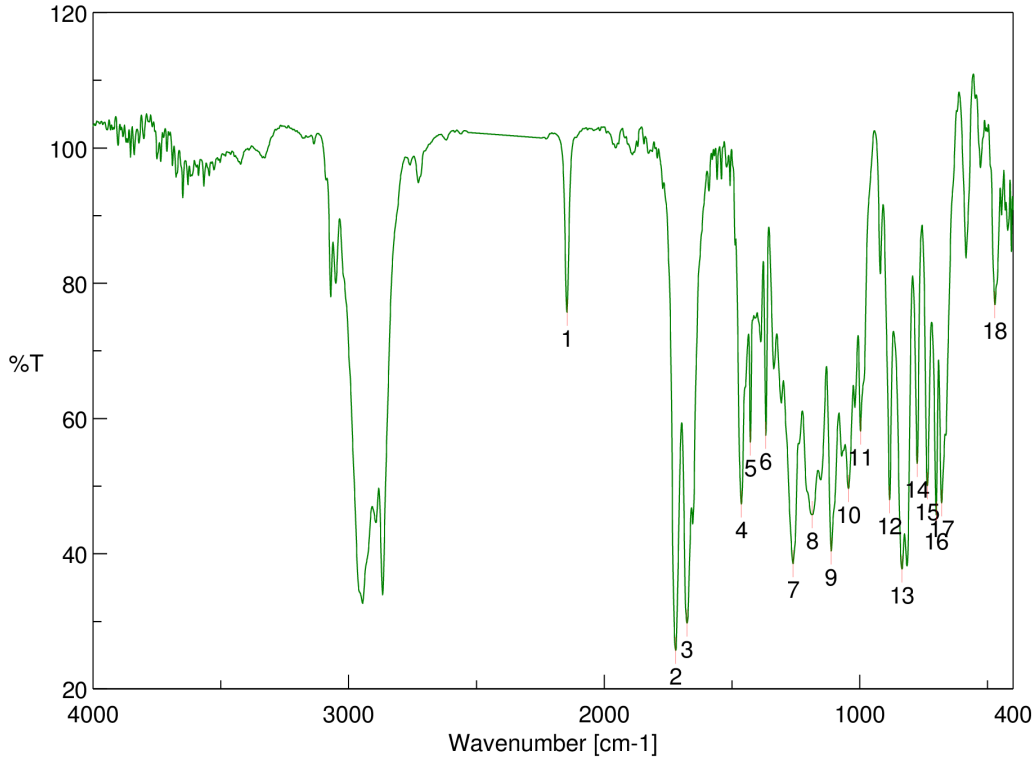
1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	12.253	97.112
2	17.693	2.888

ﾄｰﾀﾙ		100.000
Total		

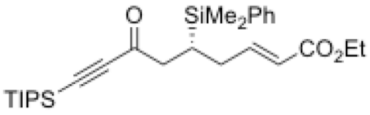

SiMe2Ph
CO2Et
O
TIPS
f1 (ppm)

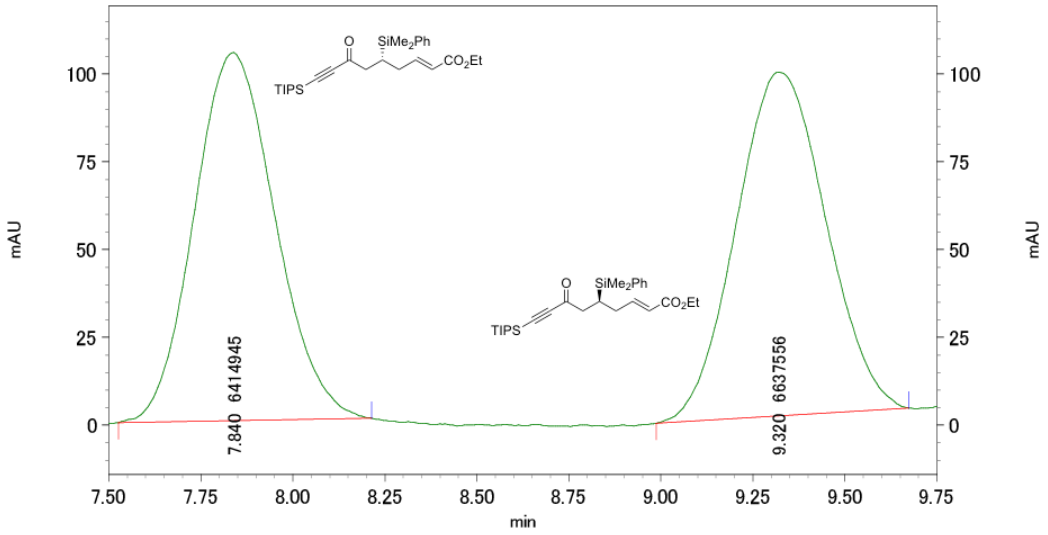

187.512
166.115
147.765
136.720
133.850
129.379
127.958
122.727
104.096
96.110
77.318
77.000
76.681
60.112
45.681
32.619
21.151
18.477
14.209
10.974
-4.114
-4.212
O
SiMe2Ph
CO2Et
TIPS
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2145.42	75.6876	2	1720.19	25.7176
3	1675.84	29.7196	4	1463.71	47.3614
5	1428.03	56.479	6	1367.28	57.4964
7	1261.22	38.5372	8	1186.01	45.7387
9	1111.76	40.3718	10	1044.26	49.6385
11	997.017	58.1297	12	883.238	47.9641
13	835.026	37.7479	14	775.244	53.3237
15	735.71	50.0408	16	700.998	45.7245
17	679.785	47.497	18	471.51	76.8163



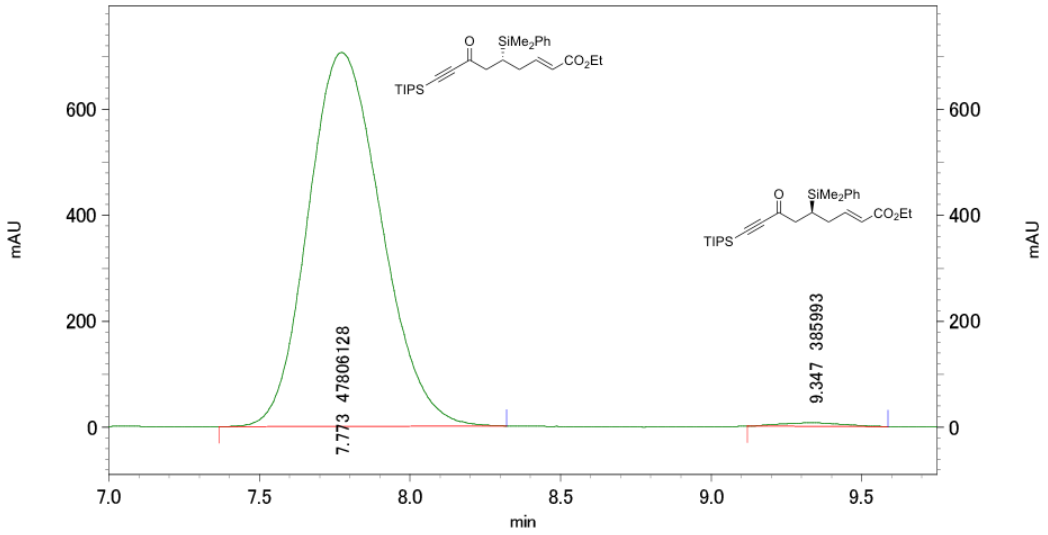


Result

1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	7.840	49.147
2	9.320	50.853

ﾄｰﾀﾙ		100.000
Total		



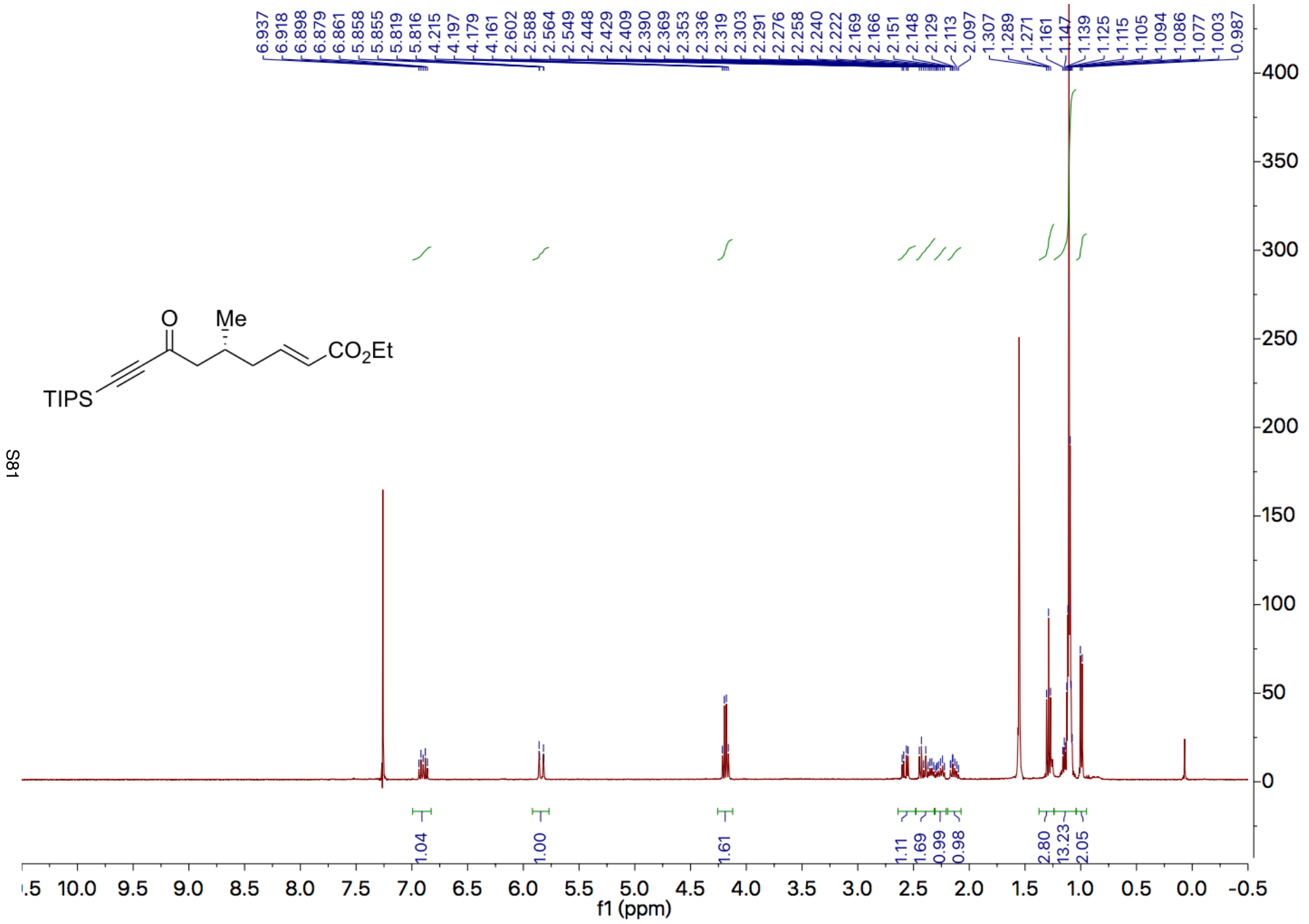
Result

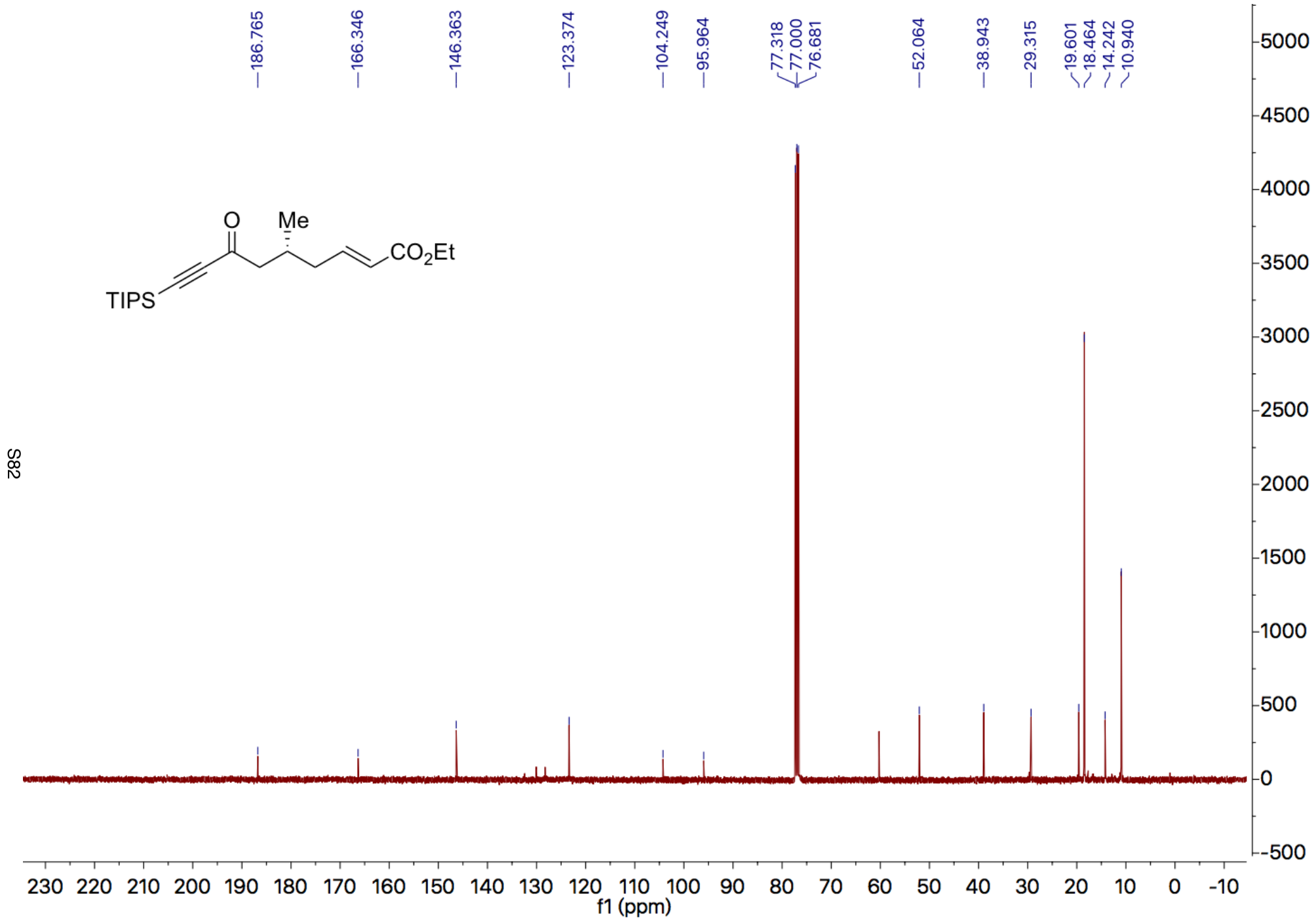
1: 213 nm, 4 nm結果

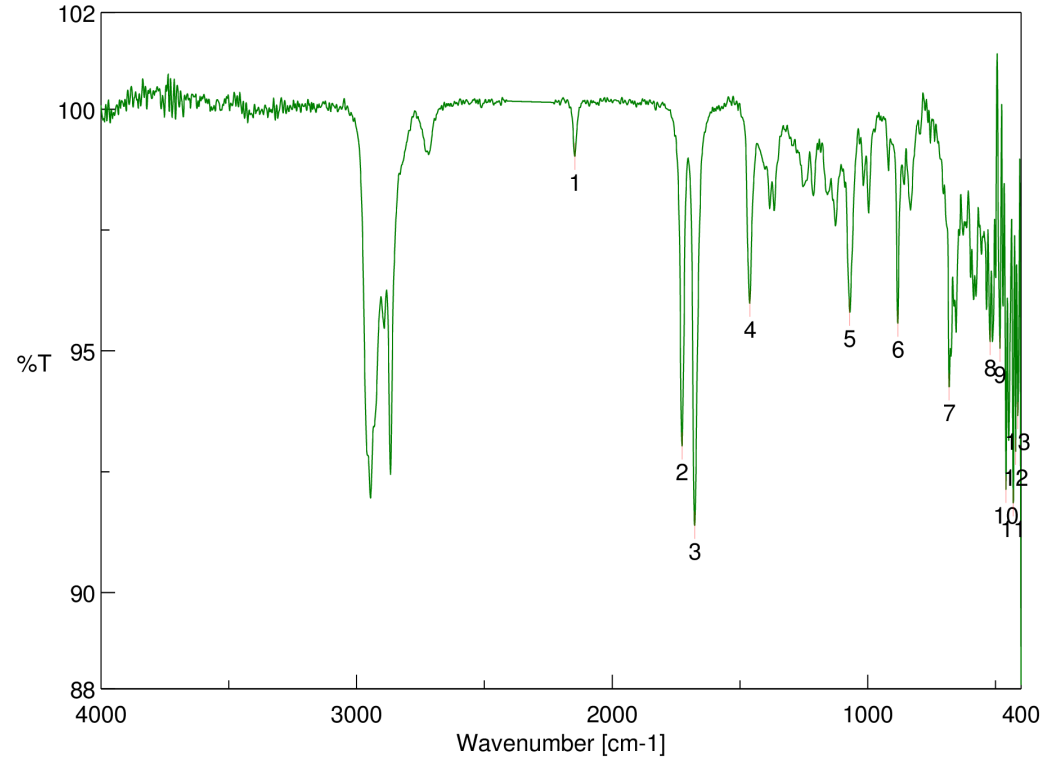
Pk #	Retention time / min	Integration/ %
1	7.773	99.199
2	9.347	0.801

ﾄｰﾀﾙ		100.000

Total

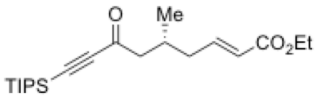

6.937
6.918
6.898
6.879
6.861
5.858
5.855
5.819
5.816
4.215
4.197
4.179
4.161
2.602
2.588
2.564
2.549
2.448
2.429
2.409
2.390
2.369
2.353
2.336
2.319
2.303
2.291
2.276
2.258
2.240
2.222
2.169
2.166
2.151
2.148
2.129
2.113
2.097
1.307
1.289
1.271
1.161
1.147
1.139
1.125
1.115
1.105
1.094
1.086
1.077
1.003
0.987
O
Me
CO2Et
TIPS
S81
1.04
1.00
1.61
1.11
1.69
0.99
0.98
2.80
13.23
2.05
f1 (ppm)

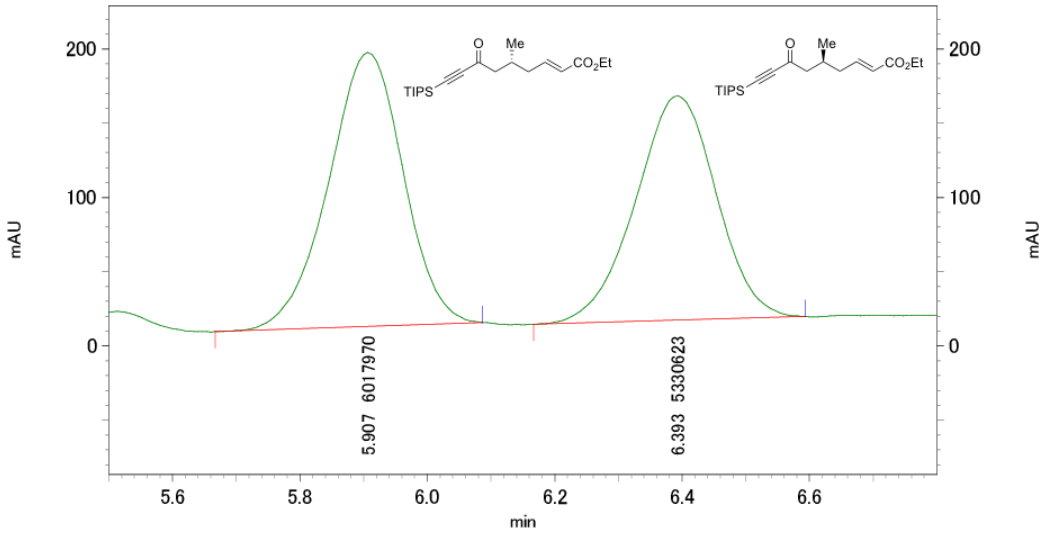

186.765
166.346
146.363
123.374
104.249
95.964
77.318
77.000
76.681
52.064
38.943
29.315
19.601
18.464
14.242
10.940
O
Me
CO2Et
TIPS
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2146.38	99.0249	2	1726.94	93.0258
3	1676.8	91.3858	4	1461.78	95.983
5	1070.3	95.798	6	882.274	95.5699
7	681.713	94.2521	8	521.65	95.1872
9	483.081	95.0478	10	458.975	92.1311
11	431.012	91.8513	12	421.37	92.919
13	412.692	93.659			

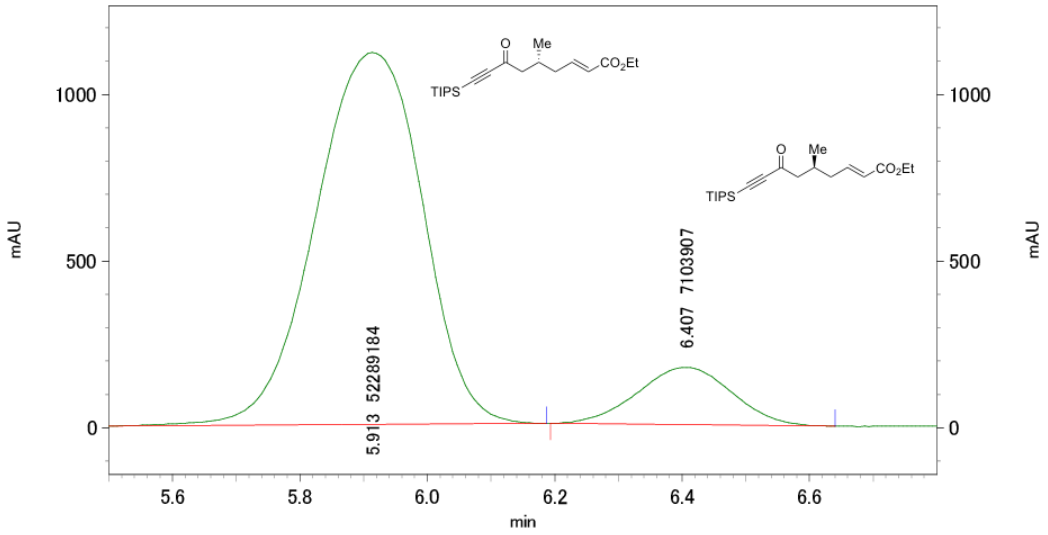




Result

1: 213 nm, 4 nm結果

Pk #	Retention time / min	Integration/ %
1	5.907	53.028
2	6.393	46.972
トータル Total		100.000

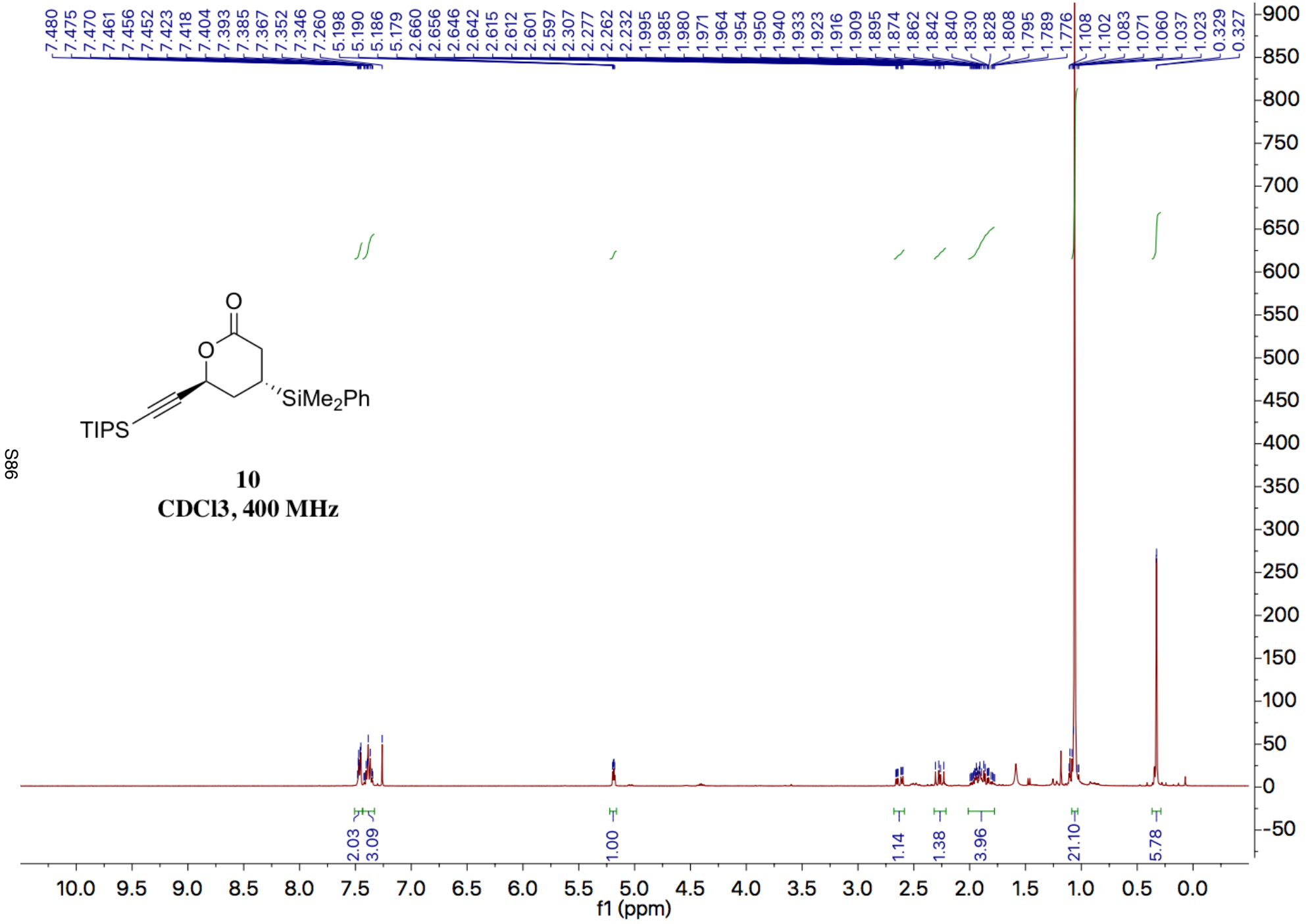


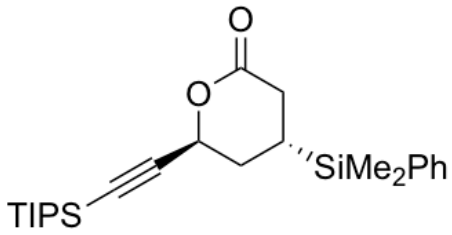
Result

1: 213 nm, 4 nm結果

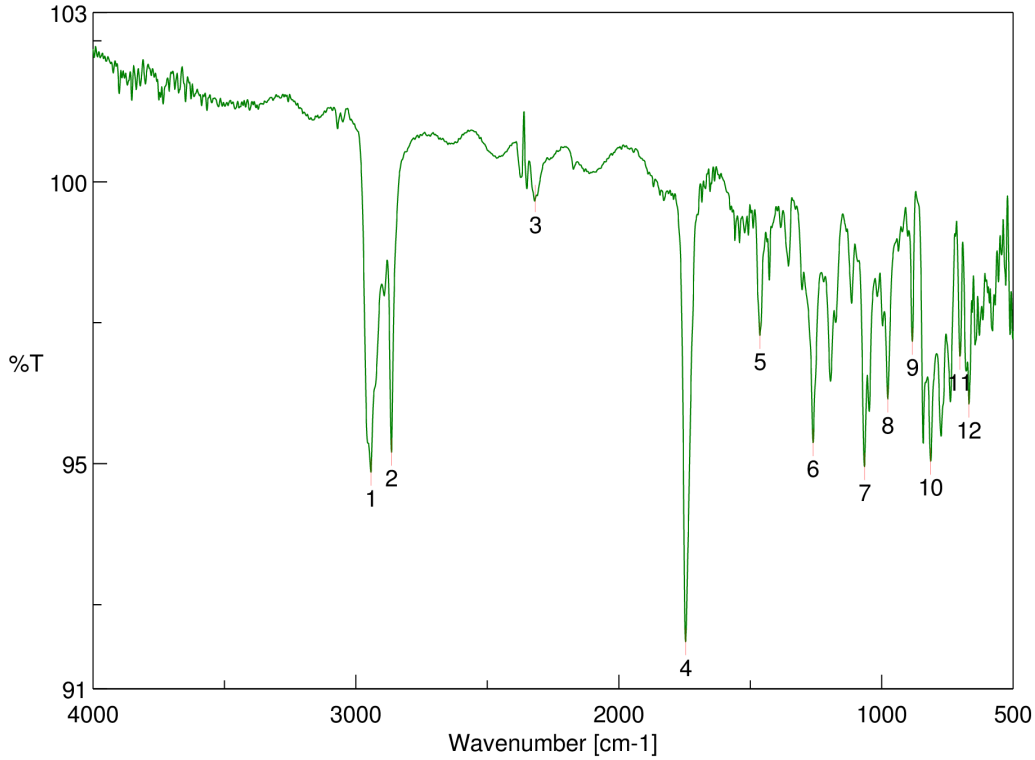
Pk #	Retention time / min	Integration/ %
1	5.913	88.039
2	6.407	11.961

トータル		100.000
Total		


7.480 7.475 7.470 7.461 7.456 7.452 7.423 7.418 7.404 7.393 7.385 7.367 7.352 7.346 7.260 5.198 5.190 5.186 5.179 2.660 2.656 2.646 2.642 2.615 2.612 2.601 2.597 2.307 2.277 2.262 2.232 1.995 1.985 1.980 1.971 1.964 1.954 1.950 1.940 1.933 1.923 1.916 1.909 1.895 1.874 1.862 1.842 1.840 1.830 1.828 1.808 1.795 1.789 1.776 1.108 1.102 1.083 1.071 1.060 1.037 1.023 0.329 0.327
O
O
SiMe2Ph
TIPS
10
CDCl3, 400 MHz
2.03
3.09
1.00
1.14
1.38
3.96
21.10
5.78
f1 (ppm)

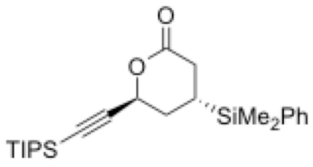


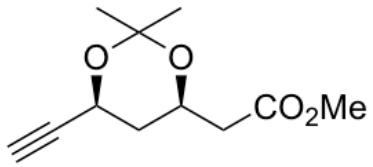
10
CDCl3, 100 MHz



[ピーク検出結果]

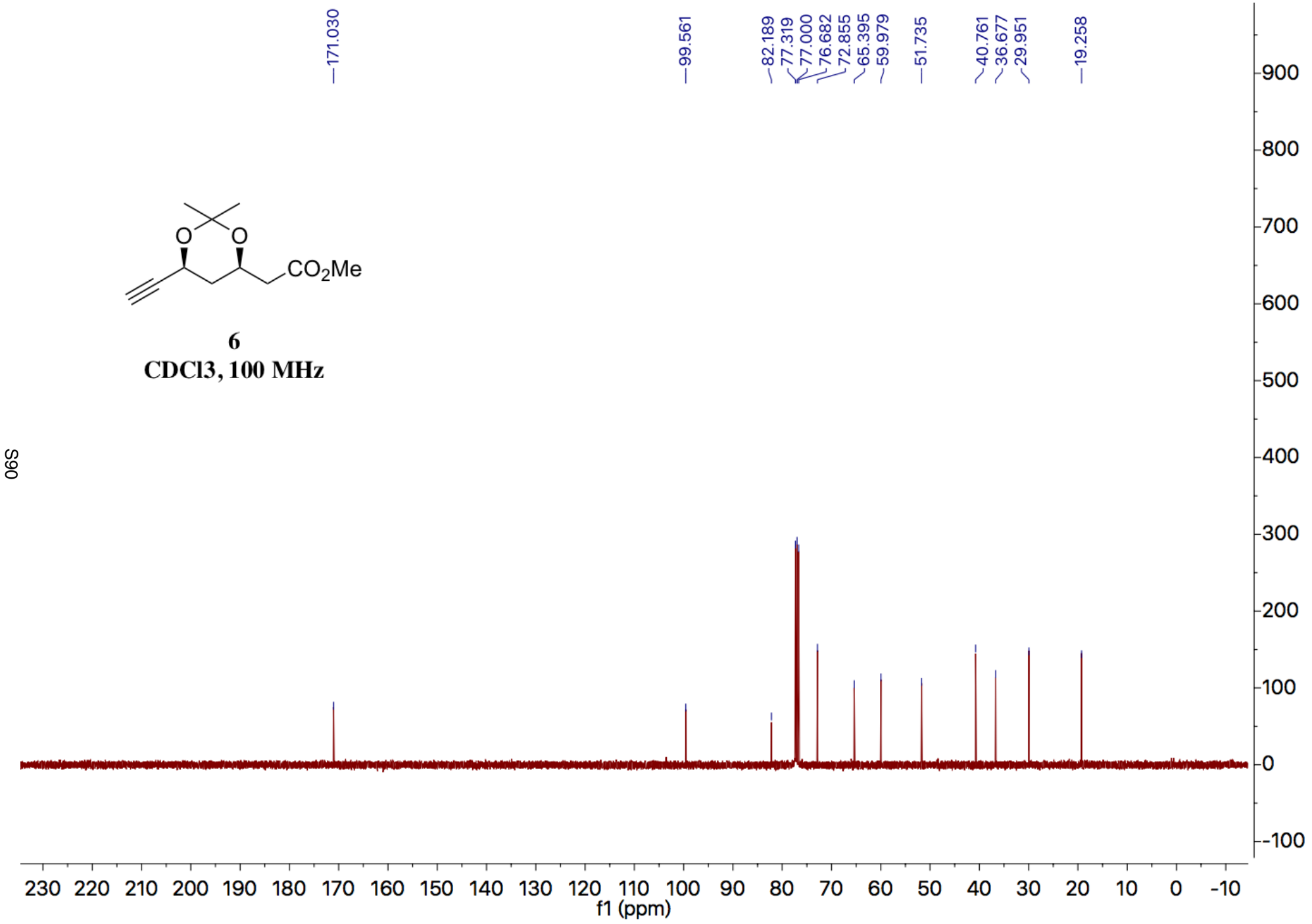
No.	位置	強度	No.	位置	強度
1	2942.84	94.8446	2	2864.74	95.2006
3	2317.05	99.6995	4	1746.23	91.8394
5	1463.71	97.2725	6	1261.22	95.3701
7	1065.48	94.9429	8	976.769	96.146
9	883.238	97.1658	10	813.813	95.0414
11	701.962	96.9027	12	668.214	96.0529

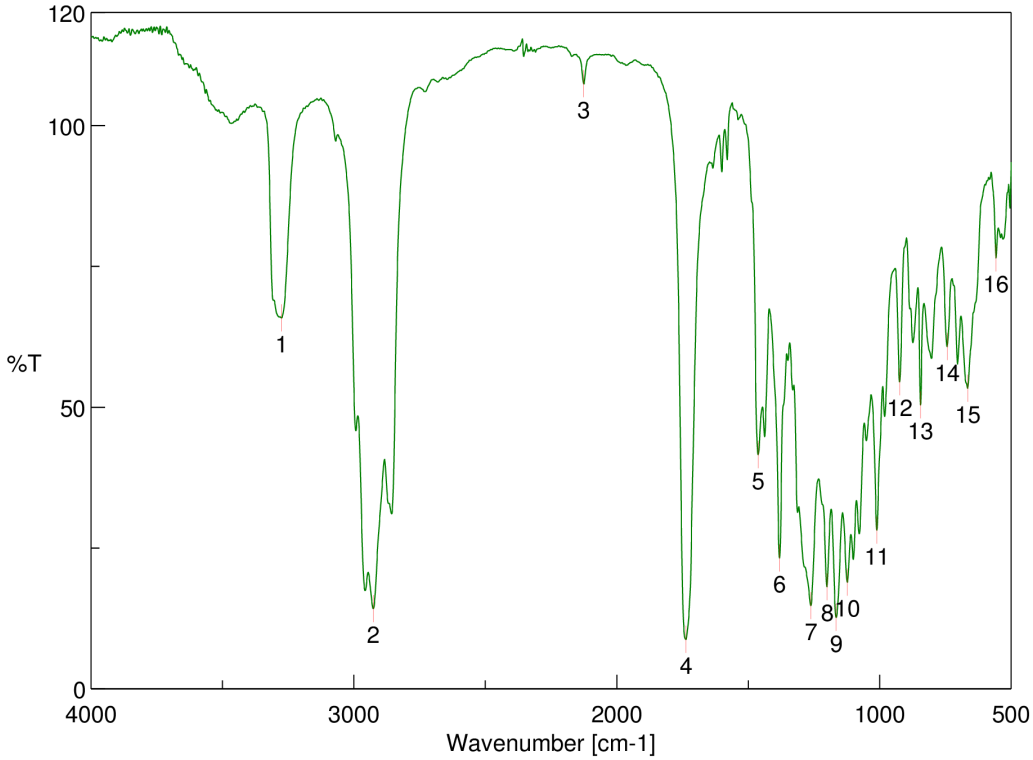




6

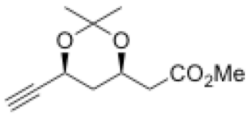
CDCl3, 400 MHz

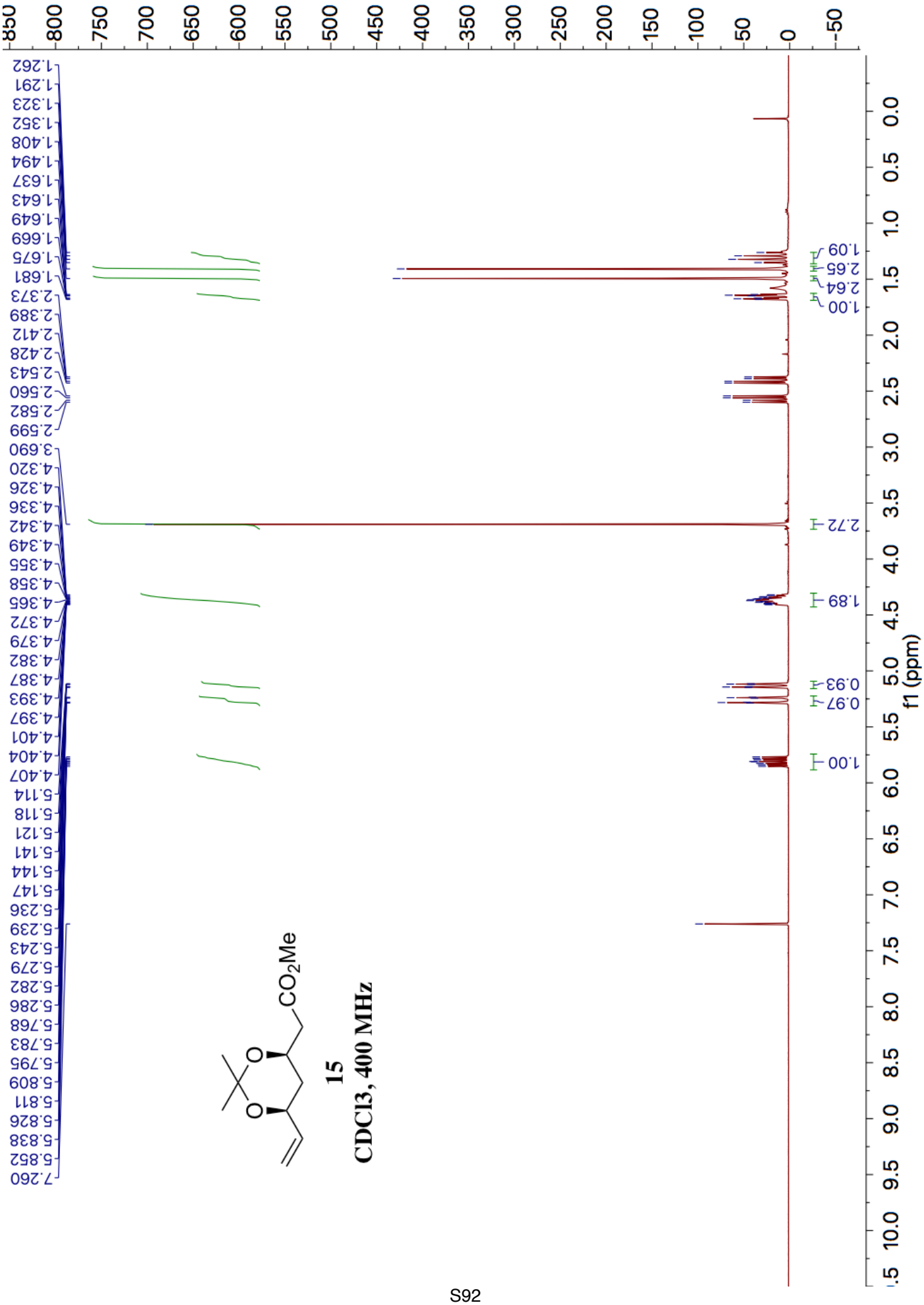

171.030
99.561
82.189
77.319
77.000
76.682
72.855
65.395
59.979
51.735
40.761
36.677
29.951
19.258
CO2Me
6
CDCl3, 100 MHz
S90
f1 (ppm)

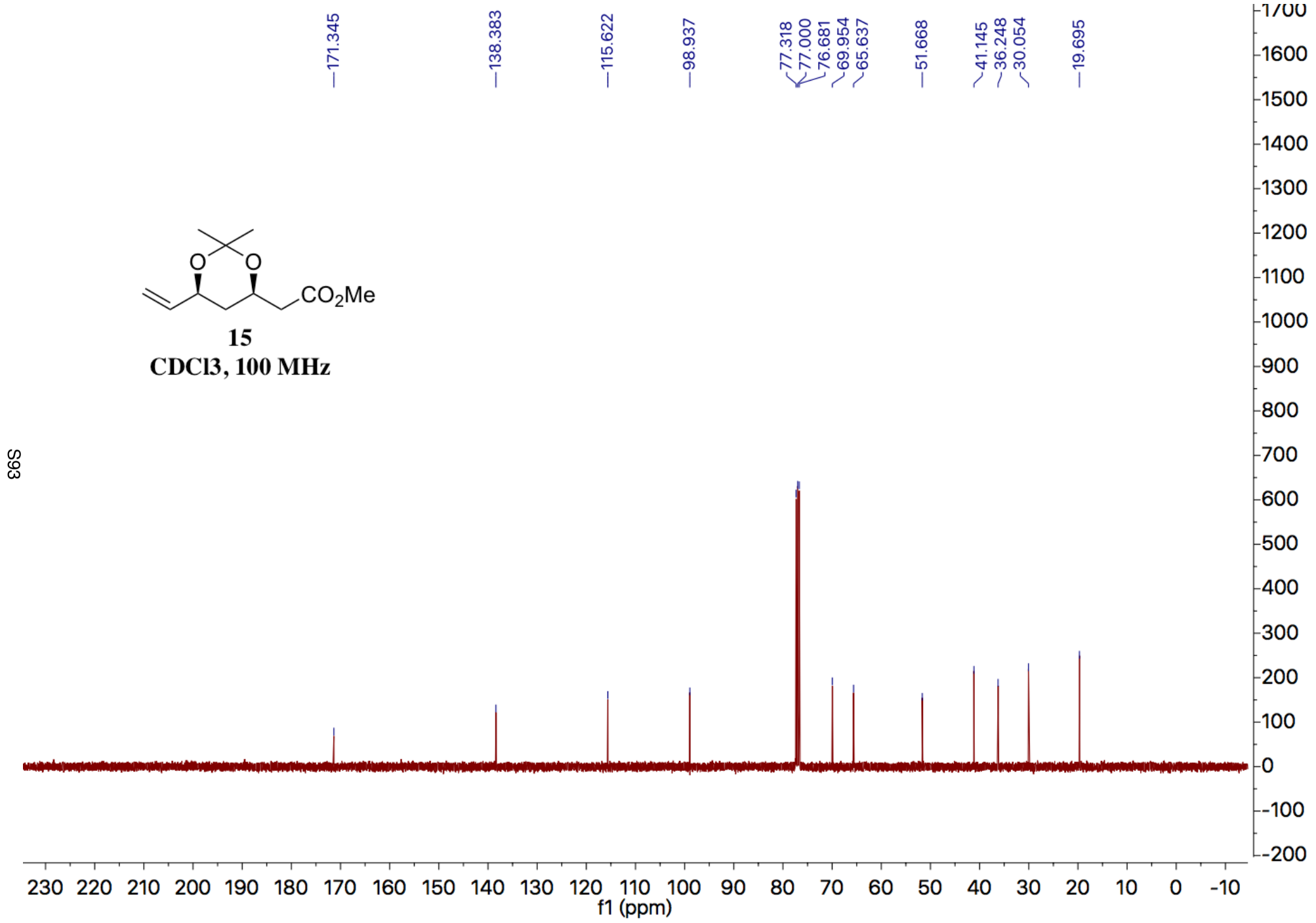


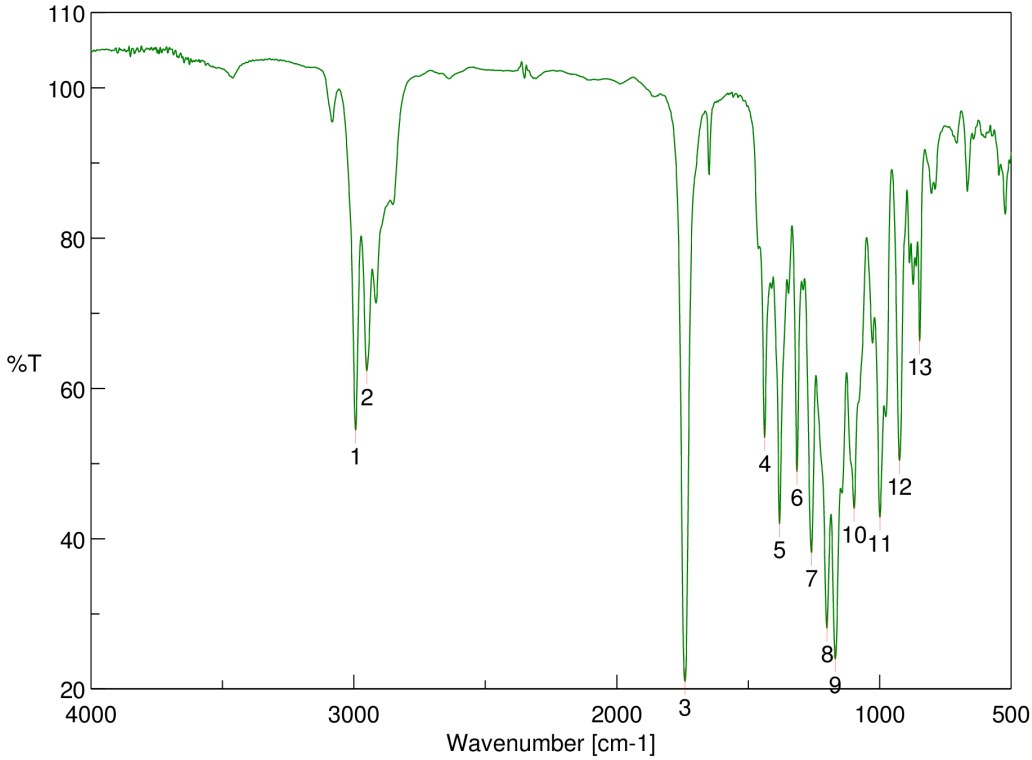
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3275.5	65.7972	2	2926.45	14.2363
3	2126.13	107.341	4	1737.55	8.77249
5	1462.74	41.5256	6	1380.78	23.2454
7	1262.18	14.8	8	1200.47	18.1388
9	1165.76	12.663	10	1123.33	18.9334
11	1010.52	28.1406	12	923.736	54.4708
13	844.669	50.3803	14	743.424	60.7057
15	665.321	53.3182	16	557.327	76.4504



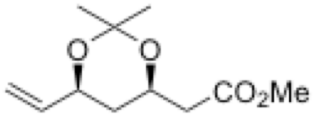

CO2Me
15
CDCl3, 400 MHz
f1 (ppm)

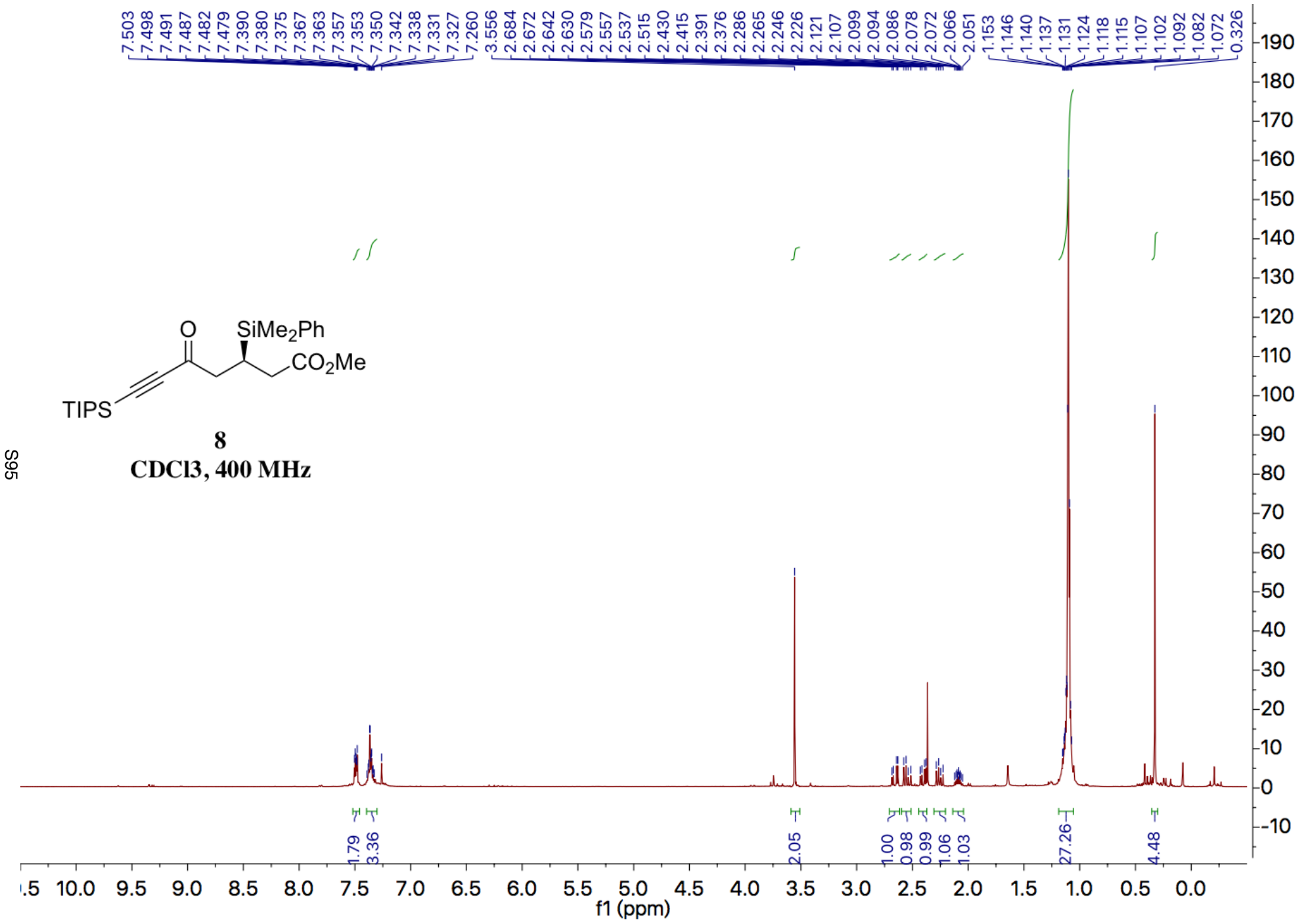

171.345
138.383
115.622
98.937
77.318
77.000
76.681
69.954
65.637
51.668
41.145
36.248
30.054
19.695
O
O
CO2Me
15
CDCl3, 100 MHz
S93
f1 (ppm)

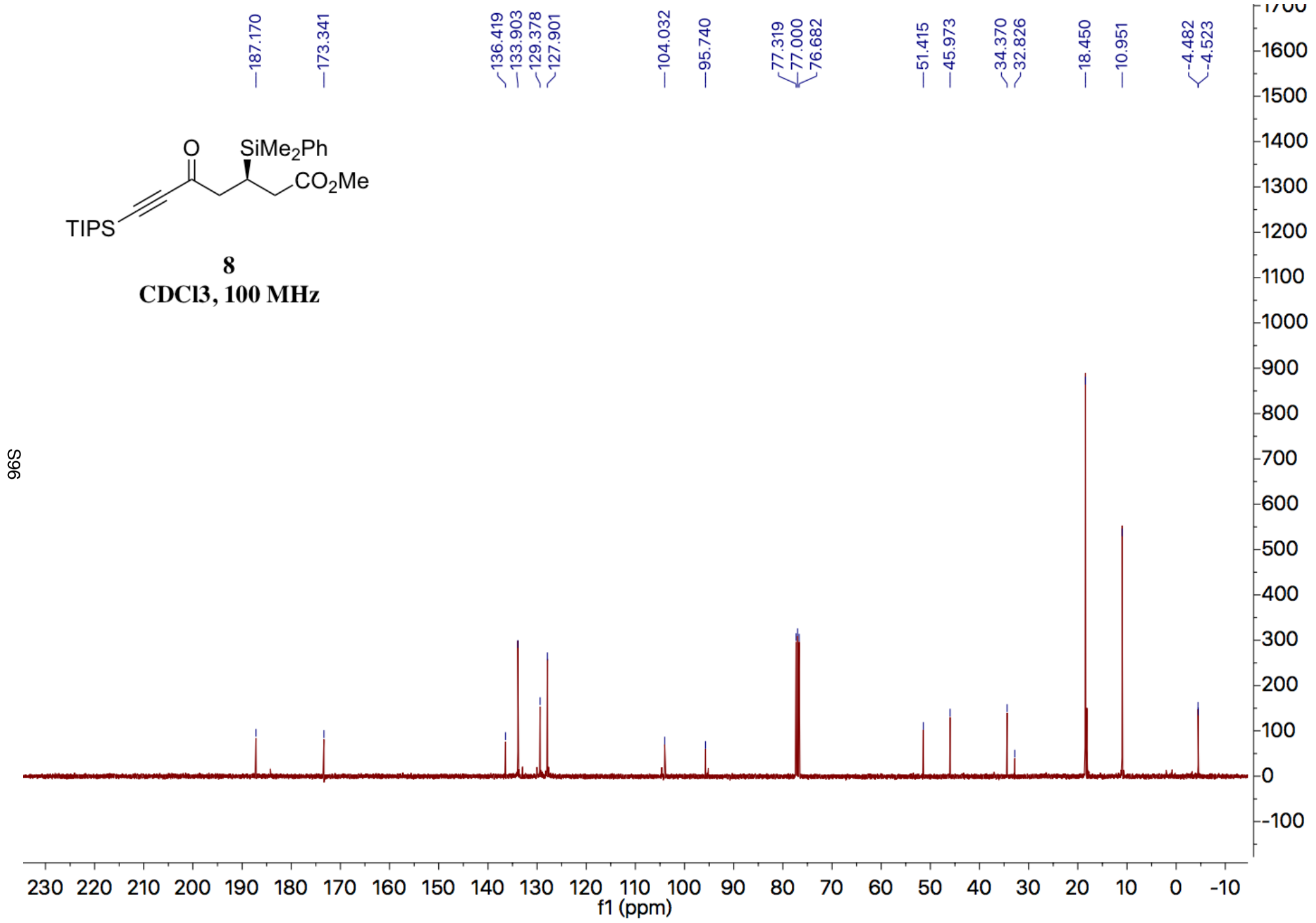


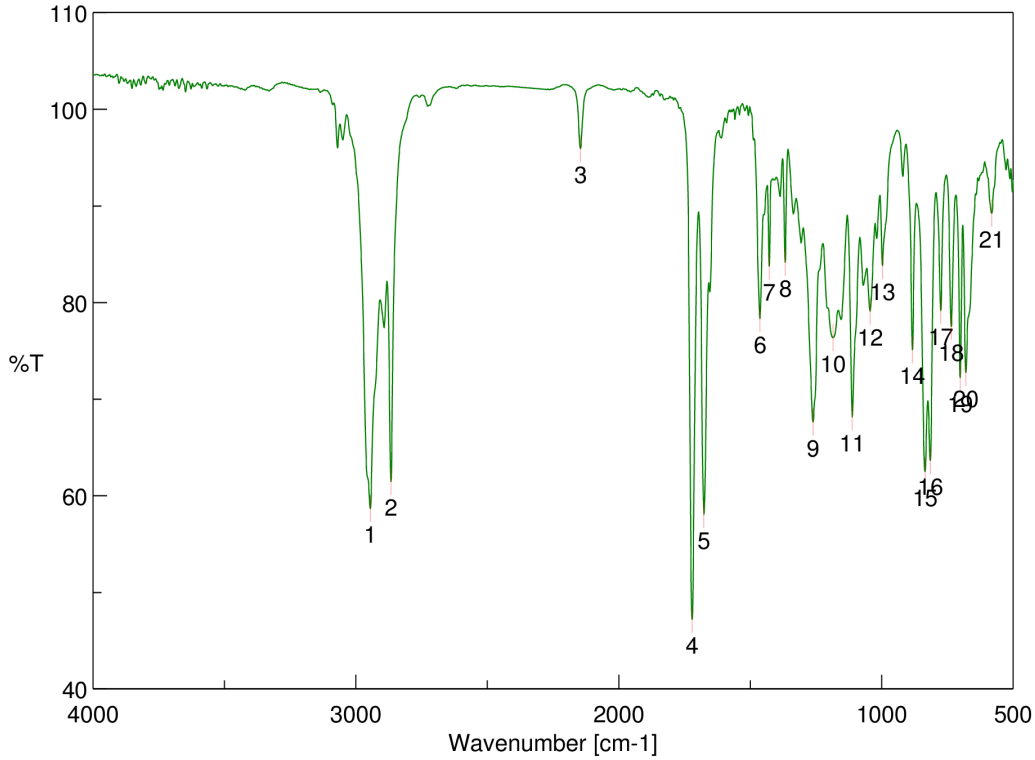
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2993.94	54.4669	2	2950.55	62.3311
3	1740.44	21.0265	4	1437.67	53.4662
5	1380.78	41.9869	6	1314.25	48.9695
7	1259.29	38.1736	8	1200.47	28.1254
9	1168.65	24.002	10	1097.3	44.0488
11	998.946	42.8603	12	924.7	50.4298
13	847.561	66.3477			



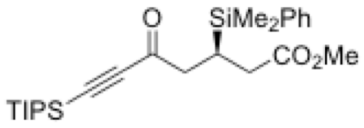

7.503 7.498 7.491 7.487 7.482 7.479 7.390 7.380 7.375 7.367 7.363 7.357 7.353 7.350 7.342 7.338 7.331 7.327 7.260
3.556 2.684 2.672 2.642 2.630 2.579 2.557 2.537 2.515 2.430 2.415 2.391 2.376 2.286 2.265 2.246 2.226 2.121 2.107 2.099 2.094 2.086 2.078 2.072 2.066 2.051
1.153 1.146 1.140 1.137 1.131 1.124 1.118 1.115 1.107 1.102 1.092 1.082 1.072 0.326
O
SiMe2Ph
CO2Me
TIPS
8
CDCl3, 400 MHz
S95
1.79
3.36
2.05
1.00
0.98
0.99
1.06
1.03
27.26
4.48
f1 (ppm)

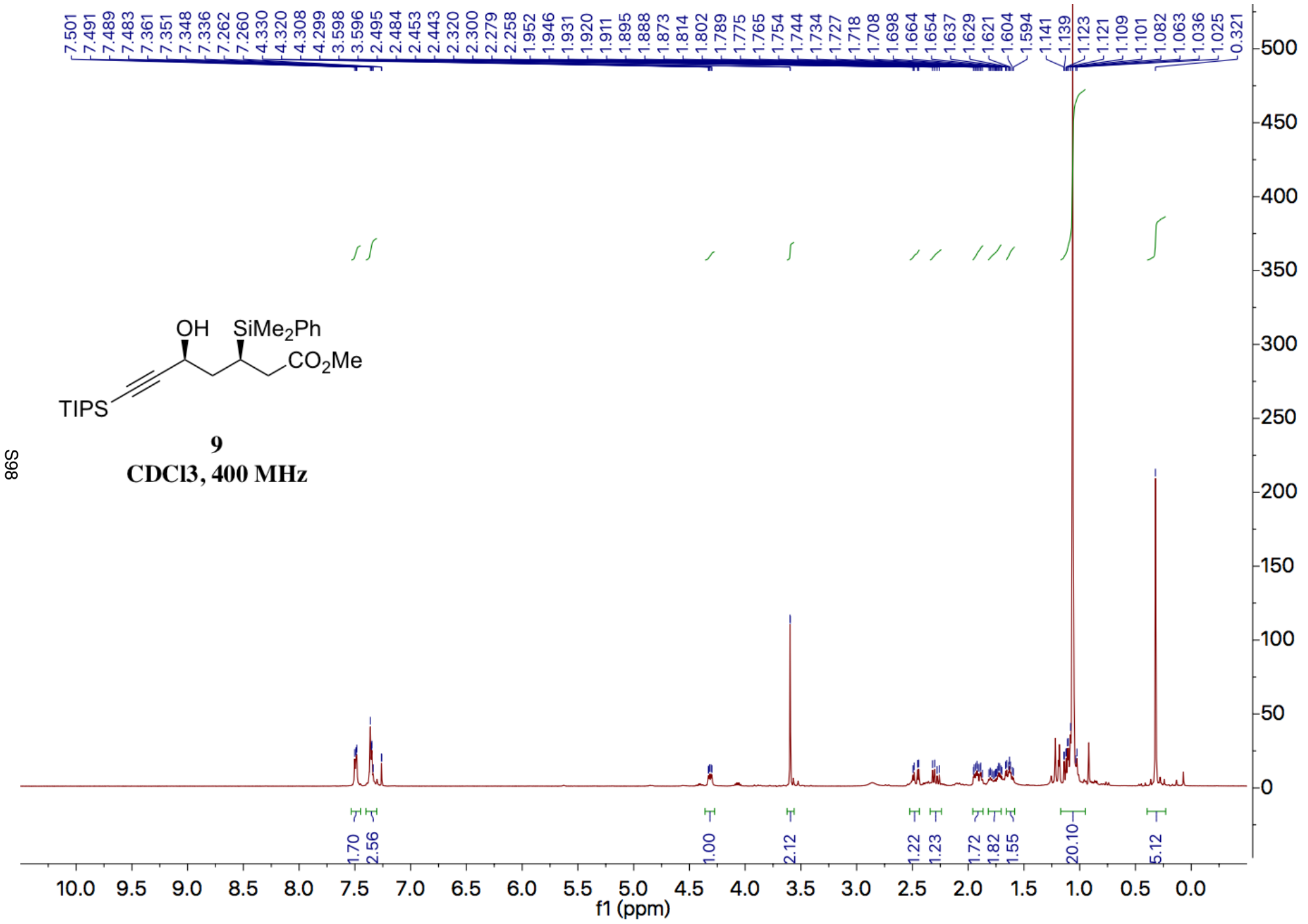

187.170
173.341
136.419
133.903
129.378
127.901
104.032
95.740
77.319
77.000
76.682
51.415
45.973
34.370
32.826
18.450
10.951
-4.482
-4.523
O
SiMe2Ph
CO2Me
TIPS
8
CDCl3, 100 MHz
S96
f1 (ppm)

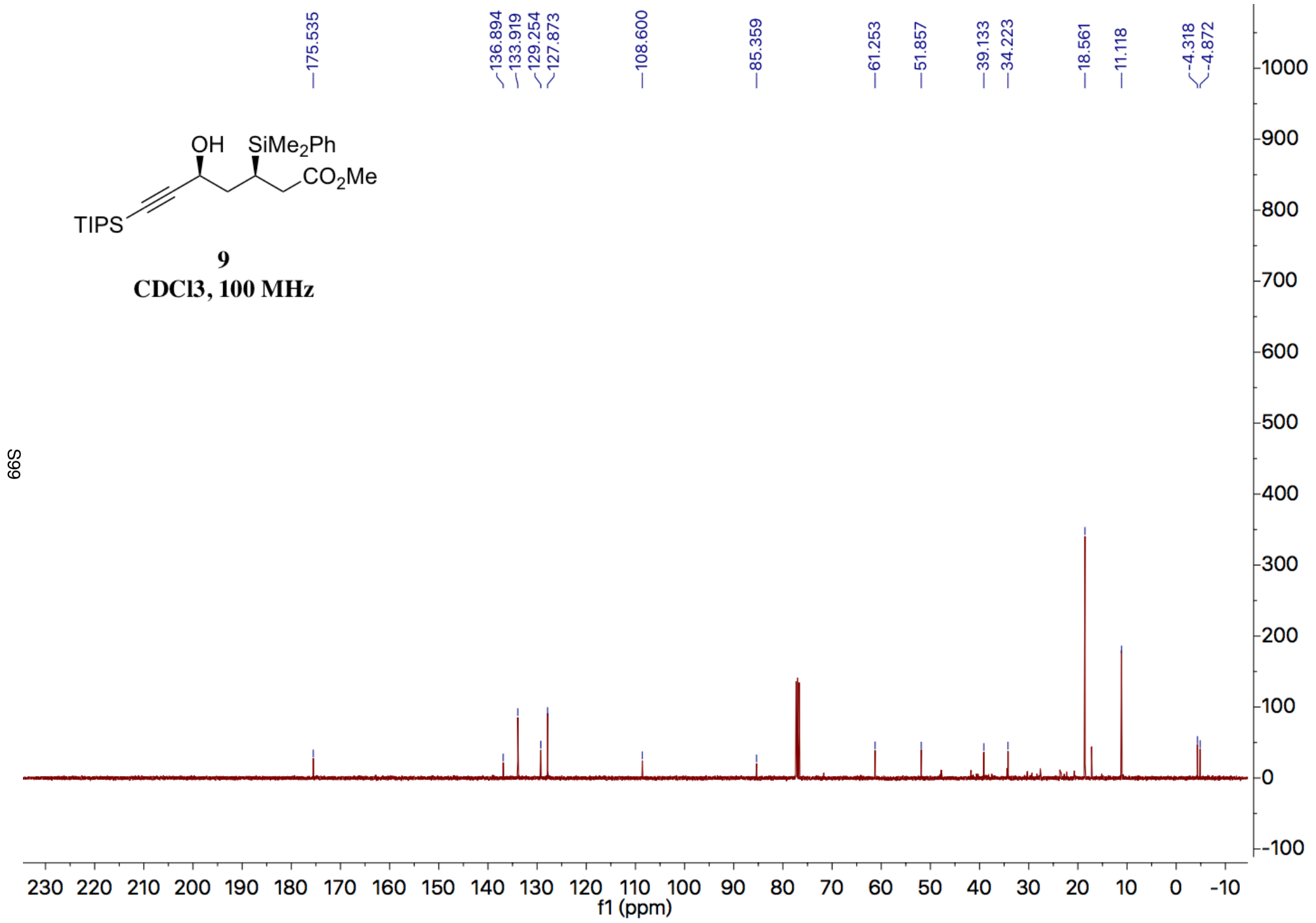


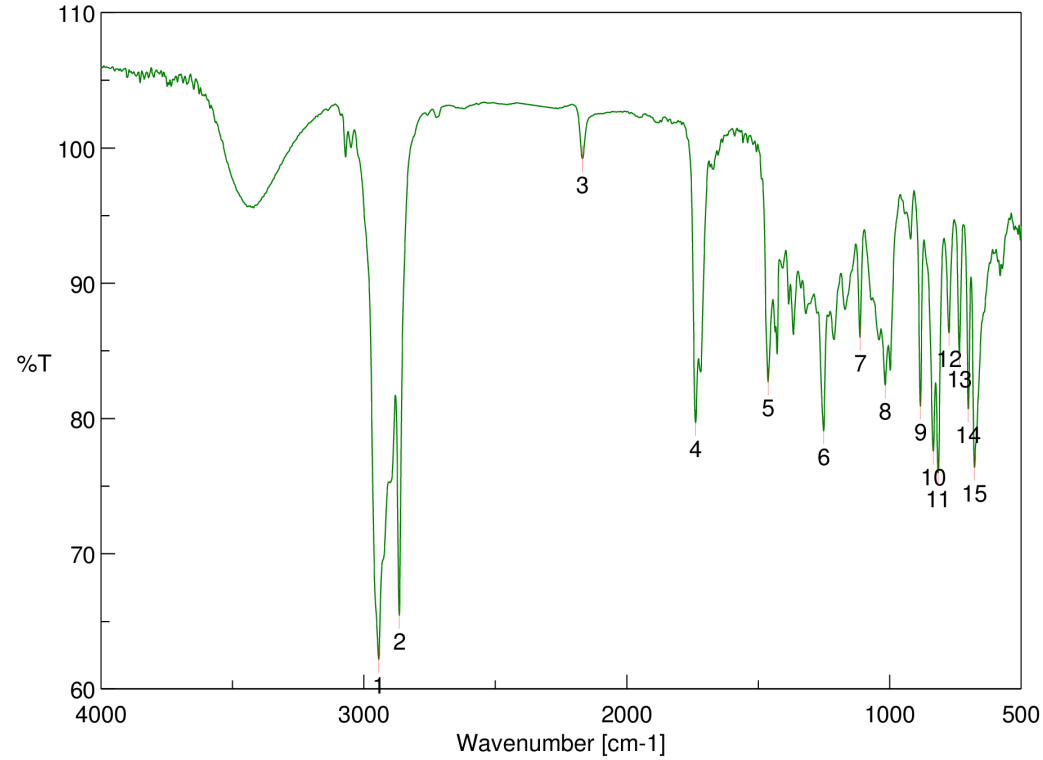
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2945.73	58.6823	2	2866.67	61.4764
3	2146.38	95.9173	4	1721.16	47.1943
5	1675.84	58.0542	6	1463.71	78.3429
7	1428.03	83.7596	8	1367.28	84.1687
9	1261.22	67.6144	10	1185.04	76.3495
11	1111.76	68.1392	12	1044.26	79.1067
13	997.017	83.8152	14	883.238	75.1082
15	835.026	62.4803	16	814.777	63.6394
17	775.244	79.1549	18	735.71	77.5064
19	700.998	72.2065	20	679.785	72.7306
21	581.433	89.2305			



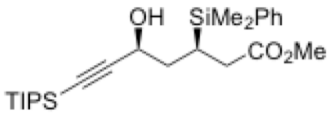

OH
SiMe2Ph
CO2Me
TIPS
9
CDCl3, 400 MHz
S98
f1 (ppm)

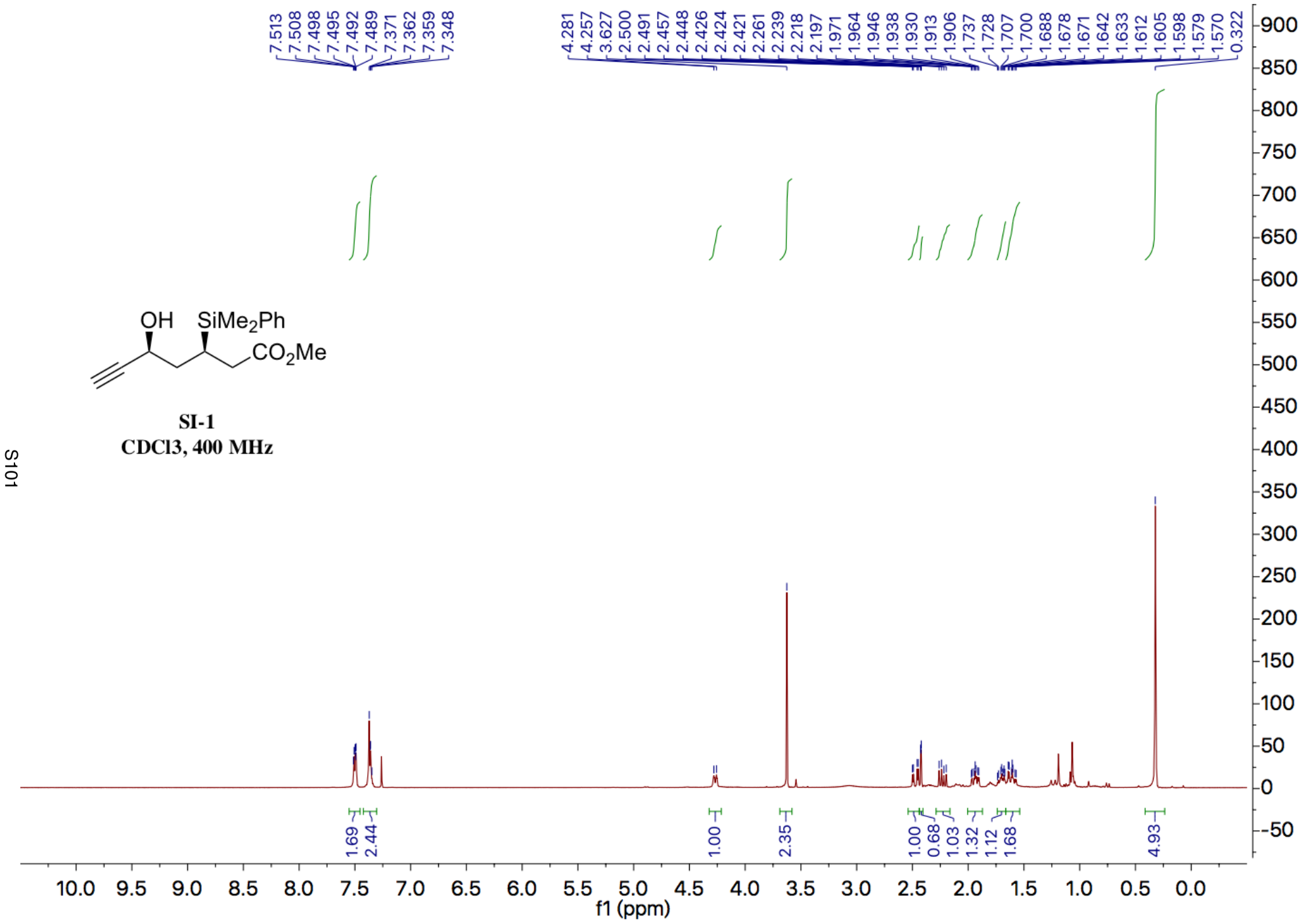

175.535
136.894
133.919
129.254
127.873
108.600
85.359
61.253
51.857
39.133
34.223
18.561
11.118
-4.318
-4.872
OH
SiMe2Ph
CO2Me
TIPS
9
CDCl3, 100 MHz
66S
f1 (ppm)

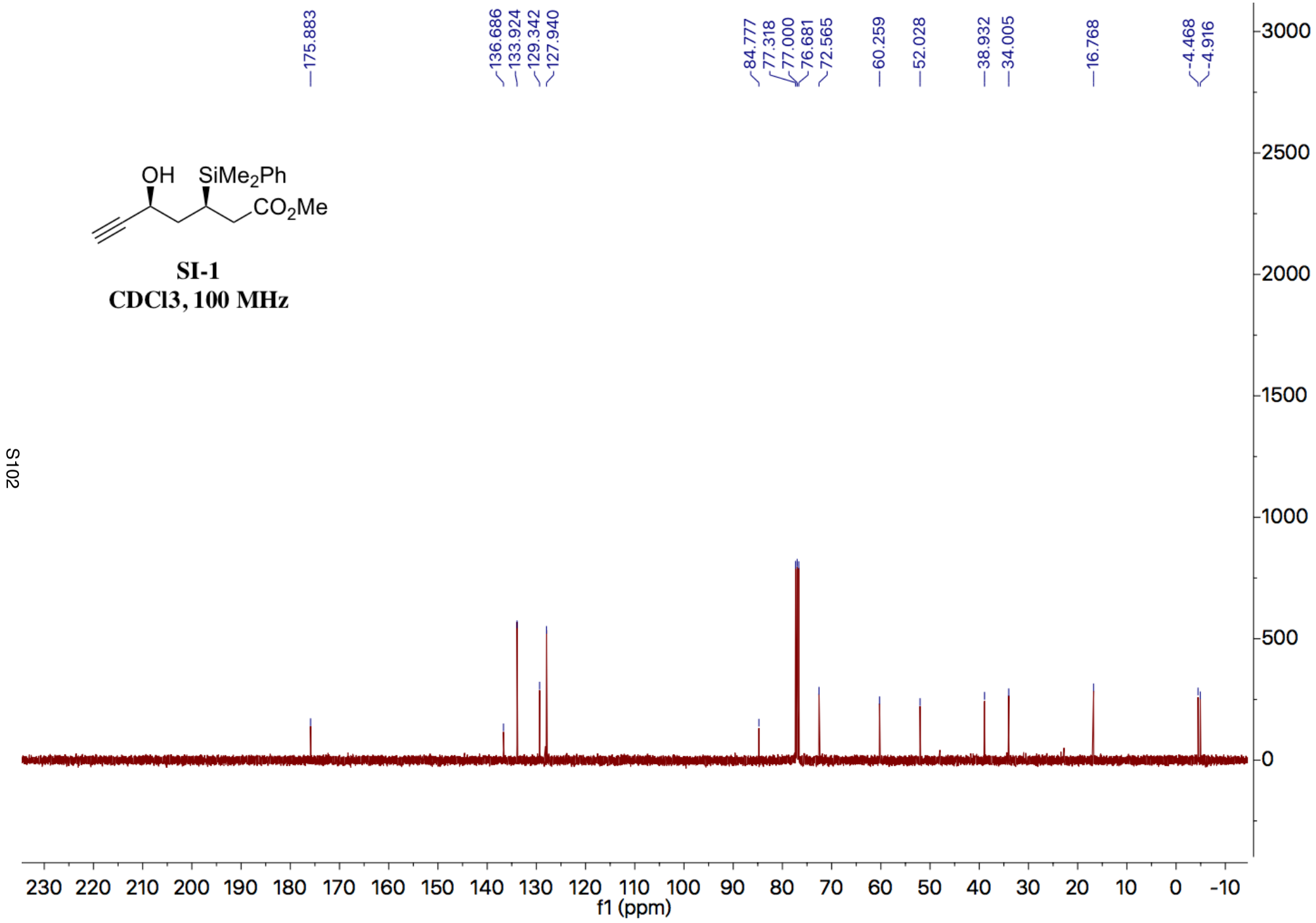


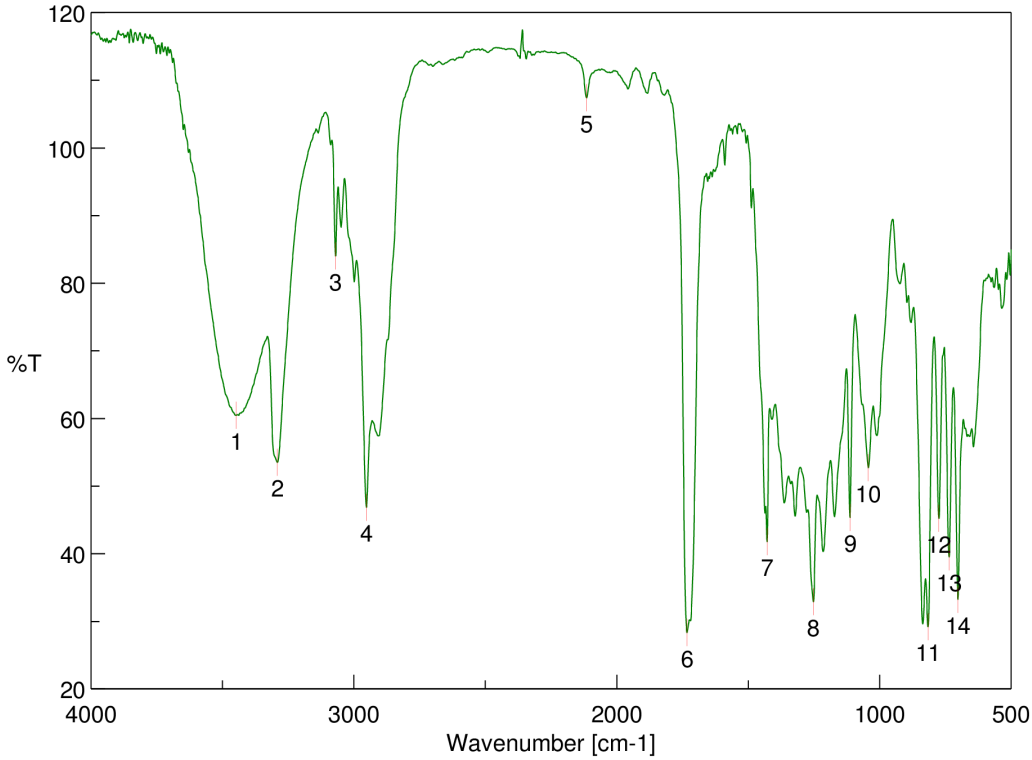
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2943.8	62.1929	2	2865.7	65.4572
3	2168.56	99.2111	4	1738.51	79.6888
5	1462.74	82.6987	6	1251.58	79.0866
7	1112.73	86.0092	8	1017.27	82.4702
9	883.238	80.9175	10	834.062	77.581
11	815.742	75.9845	12	774.279	86.3283
13	734.746	84.8487	14	700.998	80.6979
15	677.856	76.3981			



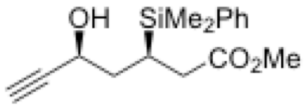

7.513
7.508
7.498
7.495
7.492
7.489
7.371
7.362
7.359
7.348
4.281
4.257
3.627
2.500
2.491
2.457
2.448
2.426
2.424
2.421
2.261
2.239
2.218
2.197
1.971
1.964
1.946
1.938
1.930
1.913
1.906
1.737
1.728
1.707
1.700
1.688
1.678
1.671
1.642
1.633
1.612
1.605
1.598
1.579
1.570
0.322
OH
SiMe2Ph
CO2Me
SI-1
CDCl3, 400 MHz
1.69
2.44
1.00
2.35
1.00
0.68
1.03
1.32
1.12
1.68
4.93
f1 (ppm)

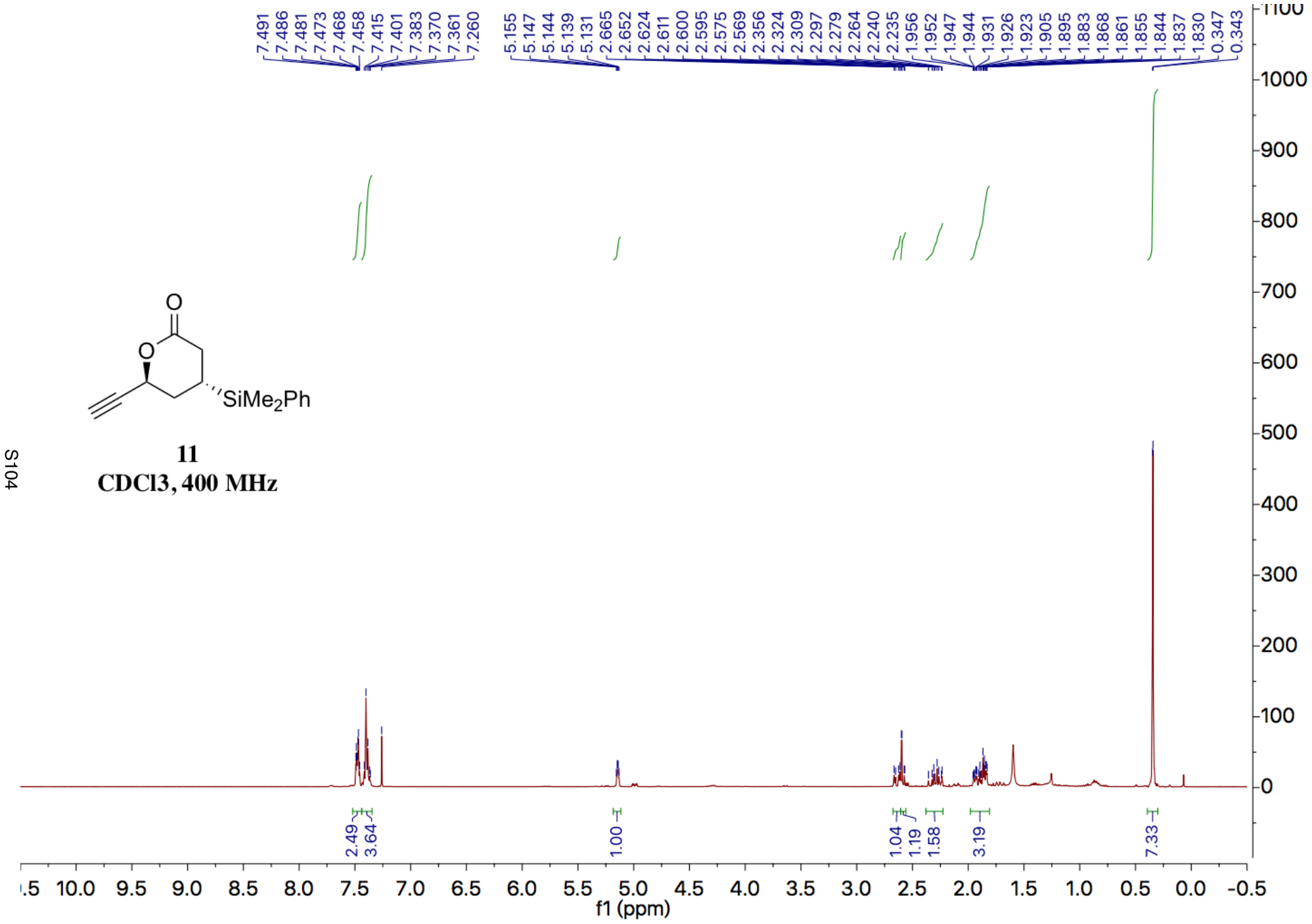

175.883
136.686
133.924
129.342
127.940
84.777
77.318
77.000
76.681
72.565
60.259
52.028
38.932
34.005
16.768
-4.468
-4.916
OH
SiMe2Ph
CO2Me
SI-1
CDCl3, 100 MHz
3000
2500
2000
1500
1000
500
0
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

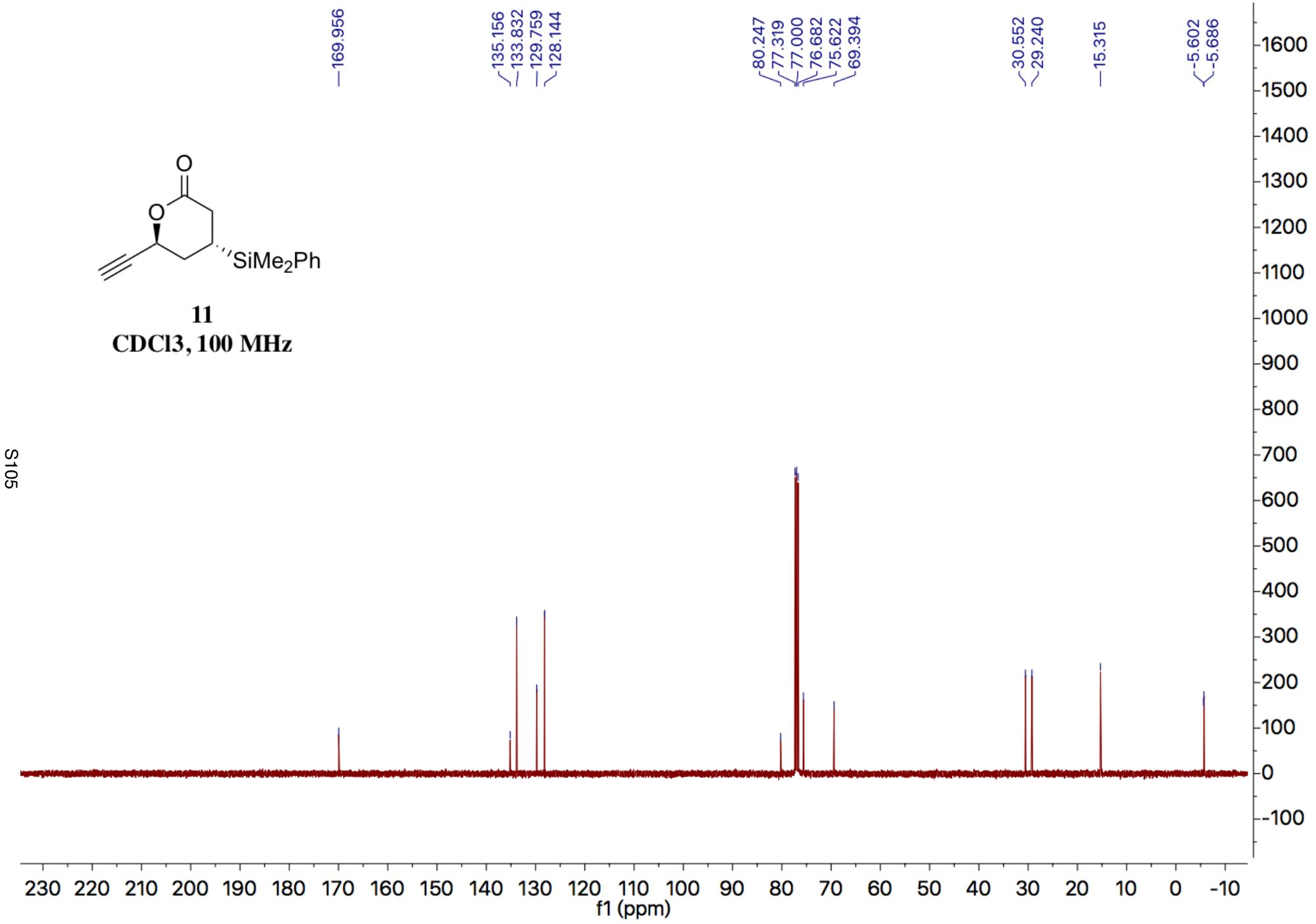


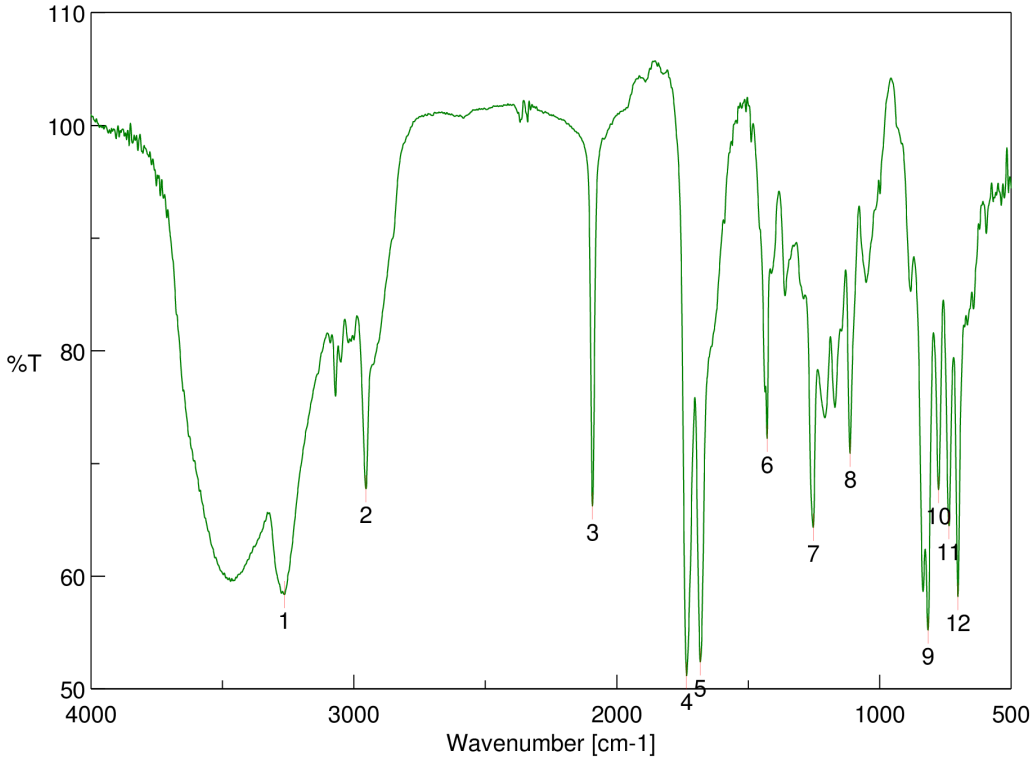
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3448.1	60.4343	2	3290.93	53.482
3	3070.12	83.9826	4	2952.48	46.8548
5	2115.53	107.401	6	1732.73	28.3173
7	1428.03	41.7521	8	1252.54	32.9056
9	1112.73	45.3577	10	1043.3	52.6983
11	815.742	29.1785	12	775.244	45.2074
13	735.71	39.5002	14	701.962	33.2348



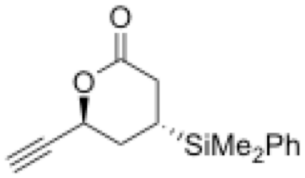

7.491
7.486
7.481
7.473
7.468
7.458
7.415
7.401
7.383
7.370
7.361
7.260
5.155
5.147
5.144
5.139
5.131
2.665
2.652
2.624
2.611
2.600
2.595
2.575
2.569
2.356
2.324
2.309
2.297
2.279
2.264
2.240
2.235
1.956
1.952
1.947
1.944
1.931
1.926
1.923
1.905
1.895
1.883
1.868
1.861
1.855
1.844
1.837
1.830
0.347
0.343
O
O
SiMe2Ph
11
CDCl3, 400 MHz
2.49
3.64
1.00
1.04
1.19
1.58
3.19
7.33
f1 (ppm)

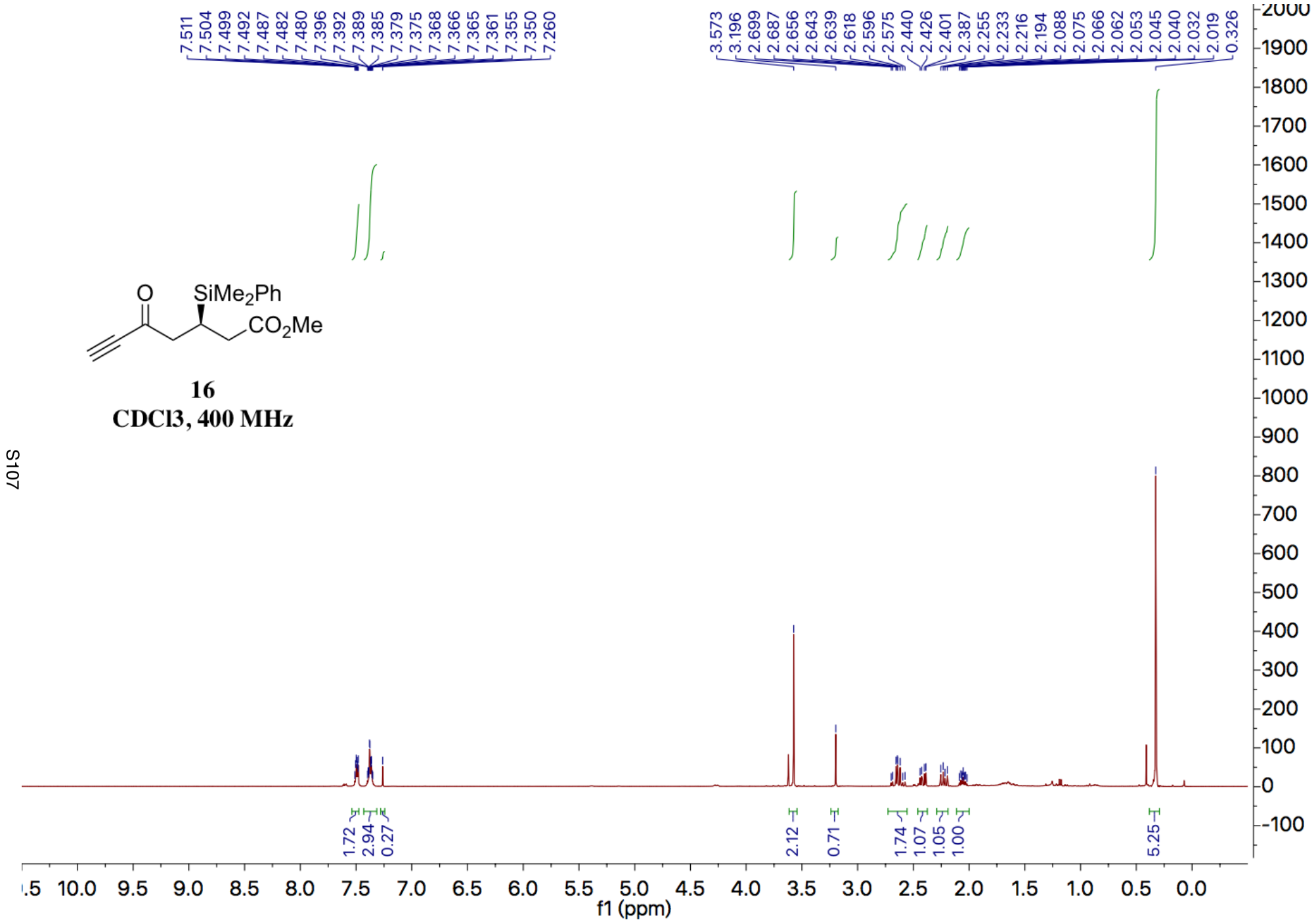

169.956
135.156
133.832
129.759
128.144
80.247
77.319
77.000
76.682
75.622
69.394
30.552
29.240
15.315
-5.602
-5.686
O
O
SiMe2Ph
11
CDCl3, 100 MHz
f1 (ppm)

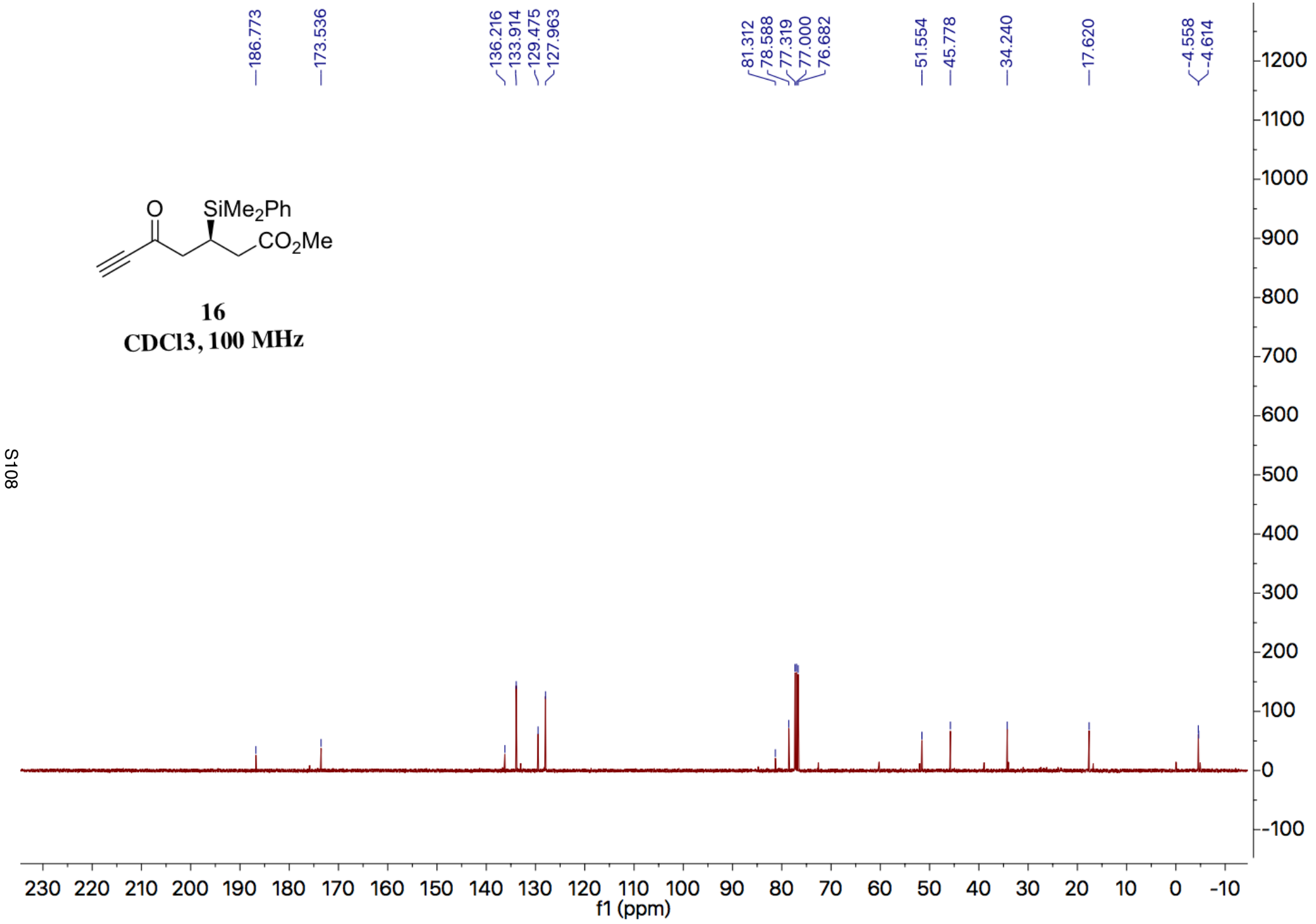


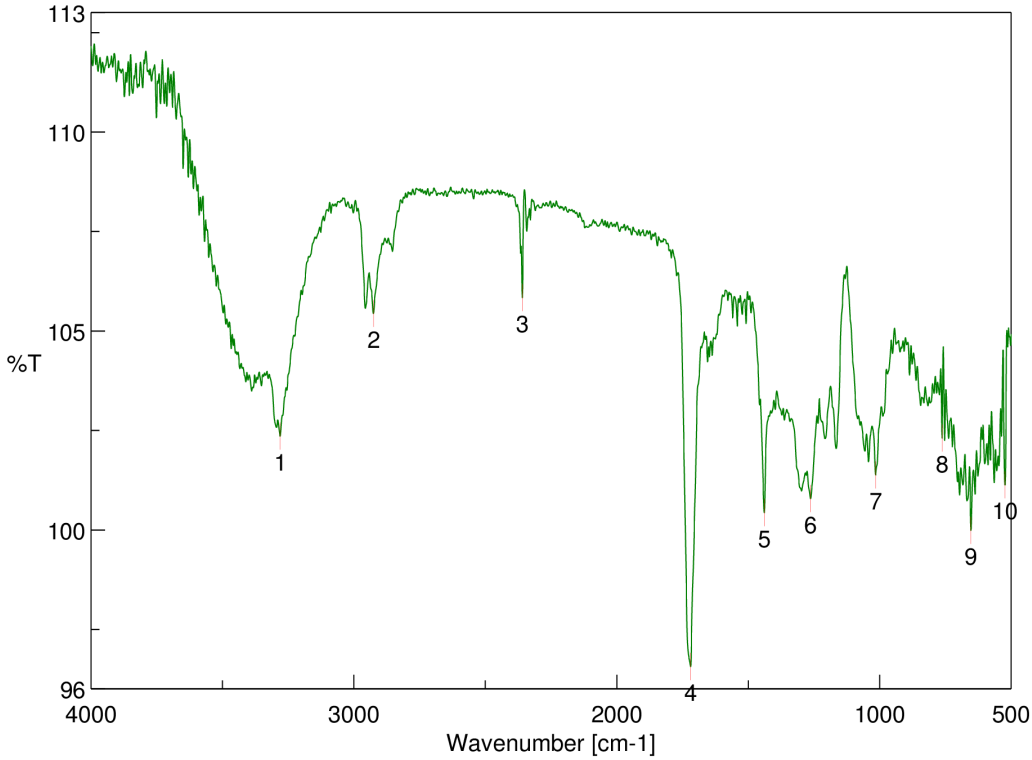
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3264.89	58.3741	2	2954.41	67.7418
3	2092.39	66.2368	4	1734.66	51.1806
5	1682.59	52.3871	6	1428.03	72.2198
7	1252.54	64.3294	8	1112.73	70.8925
9	815.742	55.2062	10	776.208	67.6755
11	736.674	64.471	12	701.962	58.1863



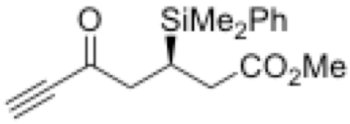

7.511
7.504
7.499
7.492
7.487
7.482
7.480
7.396
7.392
7.389
7.385
7.379
7.375
7.368
7.366
7.365
7.361
7.355
7.350
7.260
3.573
3.196
2.699
2.687
2.656
2.643
2.639
2.618
2.596
2.575
2.440
2.426
2.401
2.387
2.255
2.233
2.216
2.194
2.088
2.075
2.066
2.062
2.053
2.045
2.040
2.032
2.019
0.326
O
SiMe2Ph
CO2Me
16
CDCl3, 400 MHz
S107
1.72
2.94
0.27
2.12
0.71
1.74
1.07
1.05
1.00
5.25
f1 (ppm)

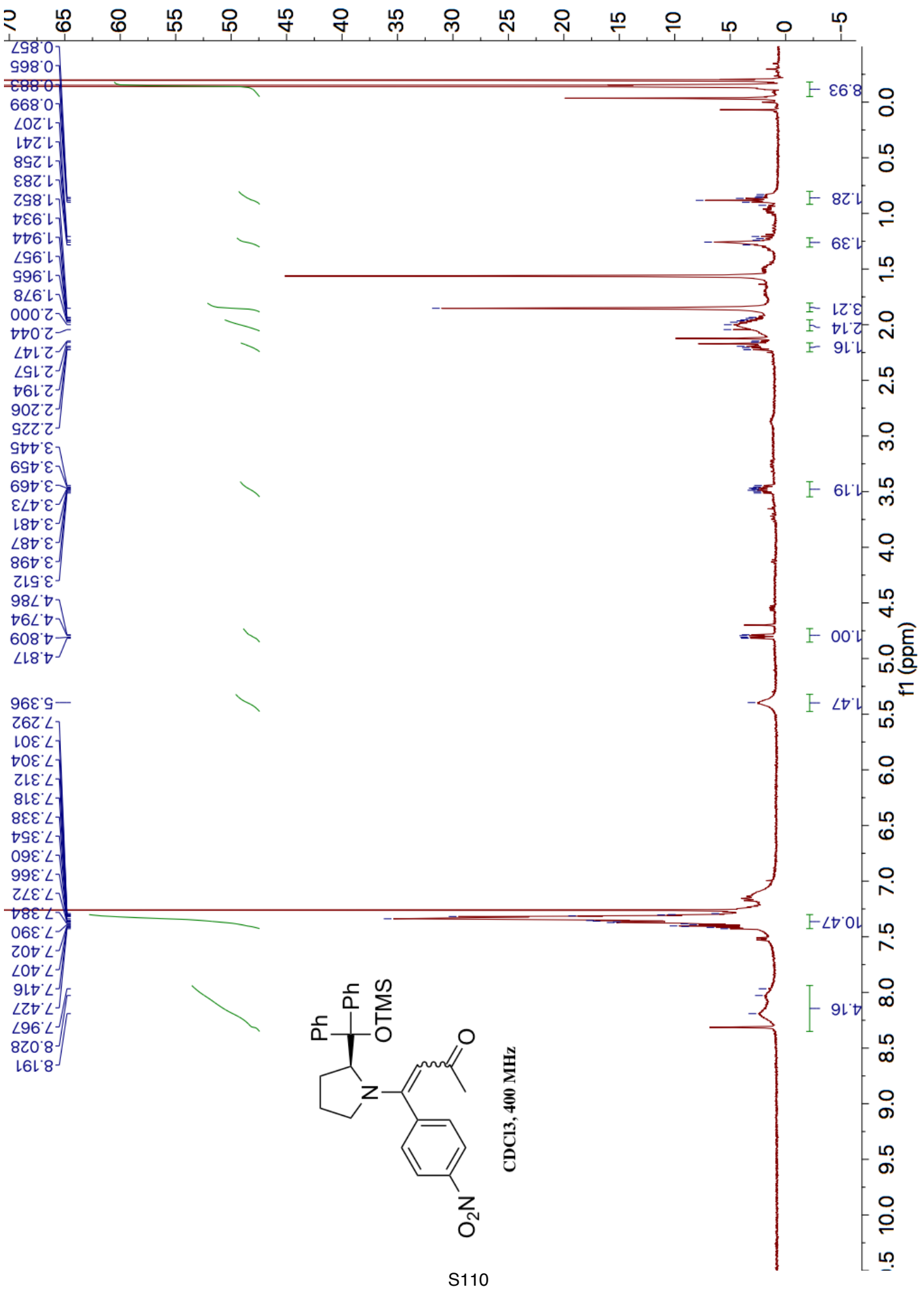

186.773
173.536
136.216
133.914
129.475
127.963
81.312
78.588
77.319
77.000
76.682
51.554
45.778
34.240
17.620
-4.558
-4.614
O
SiMe2Ph
CO2Me
16
CDCl3, 100 MHz
f1 (ppm)

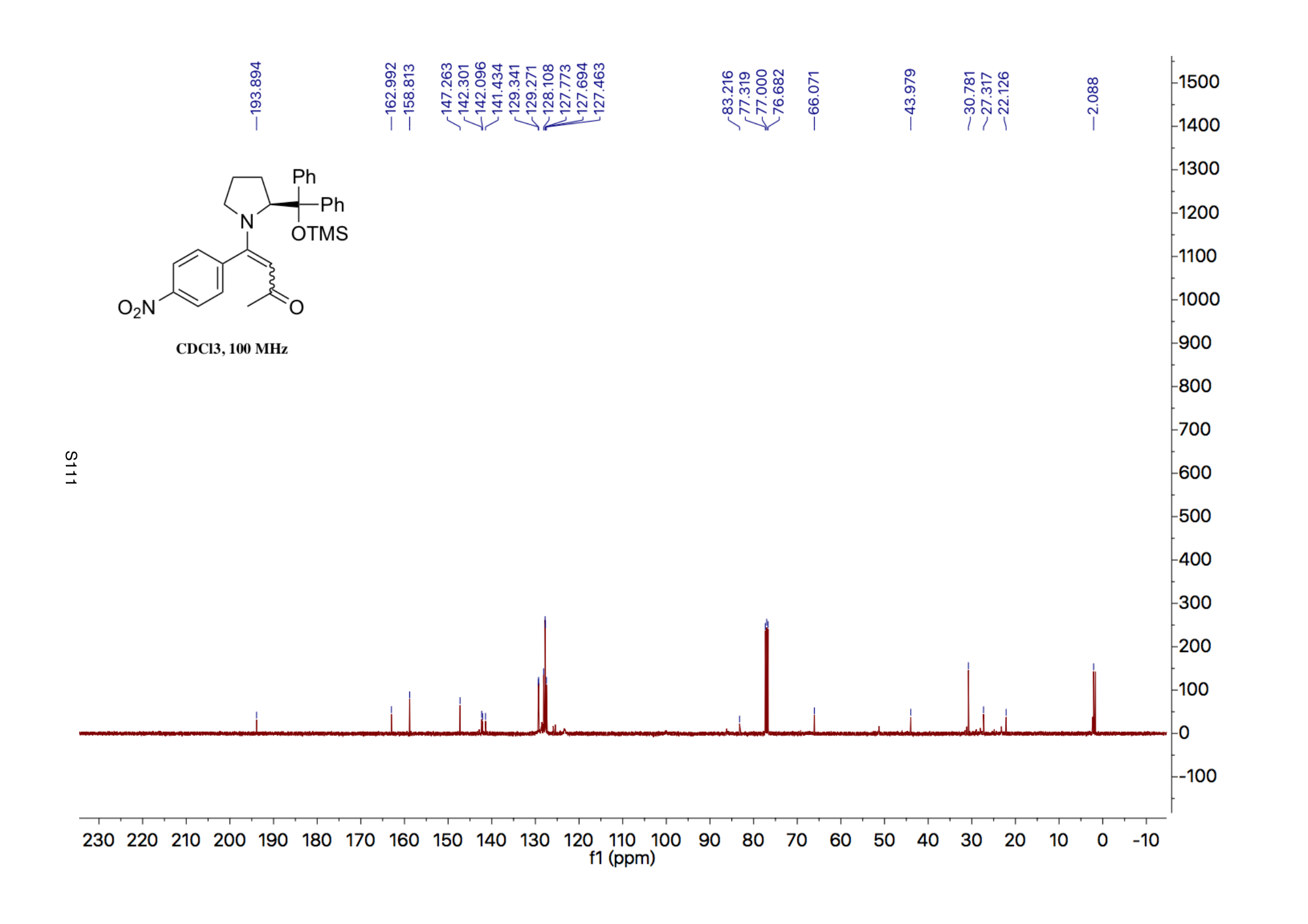


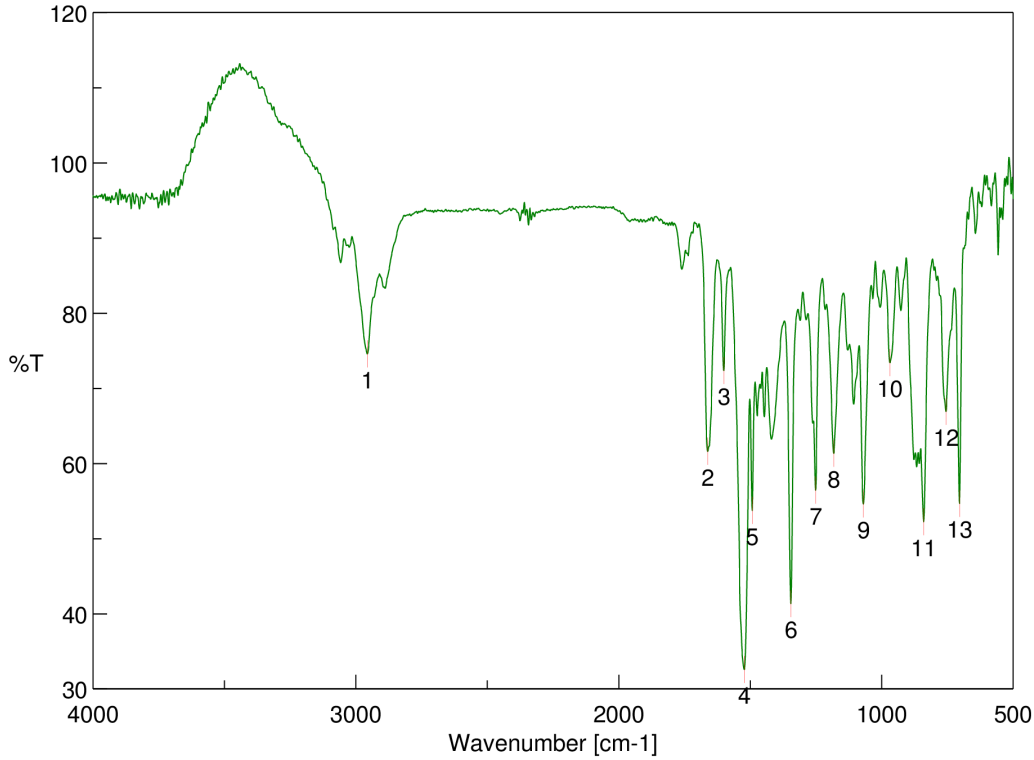
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3280.32	102.35	2	2925.48	105.435
3	2359.48	105.835	4	1719.23	96.5608
5	1438.64	100.429	6	1263.15	100.784
7	1015.34	101.38	8	762.709	102.304
9	652.786	99.9851	10	523.579	101.126



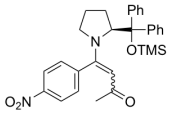

Ph
Ph
OTMS
N
O
O2N
CDCl3, 400 MHz
f1 (ppm)

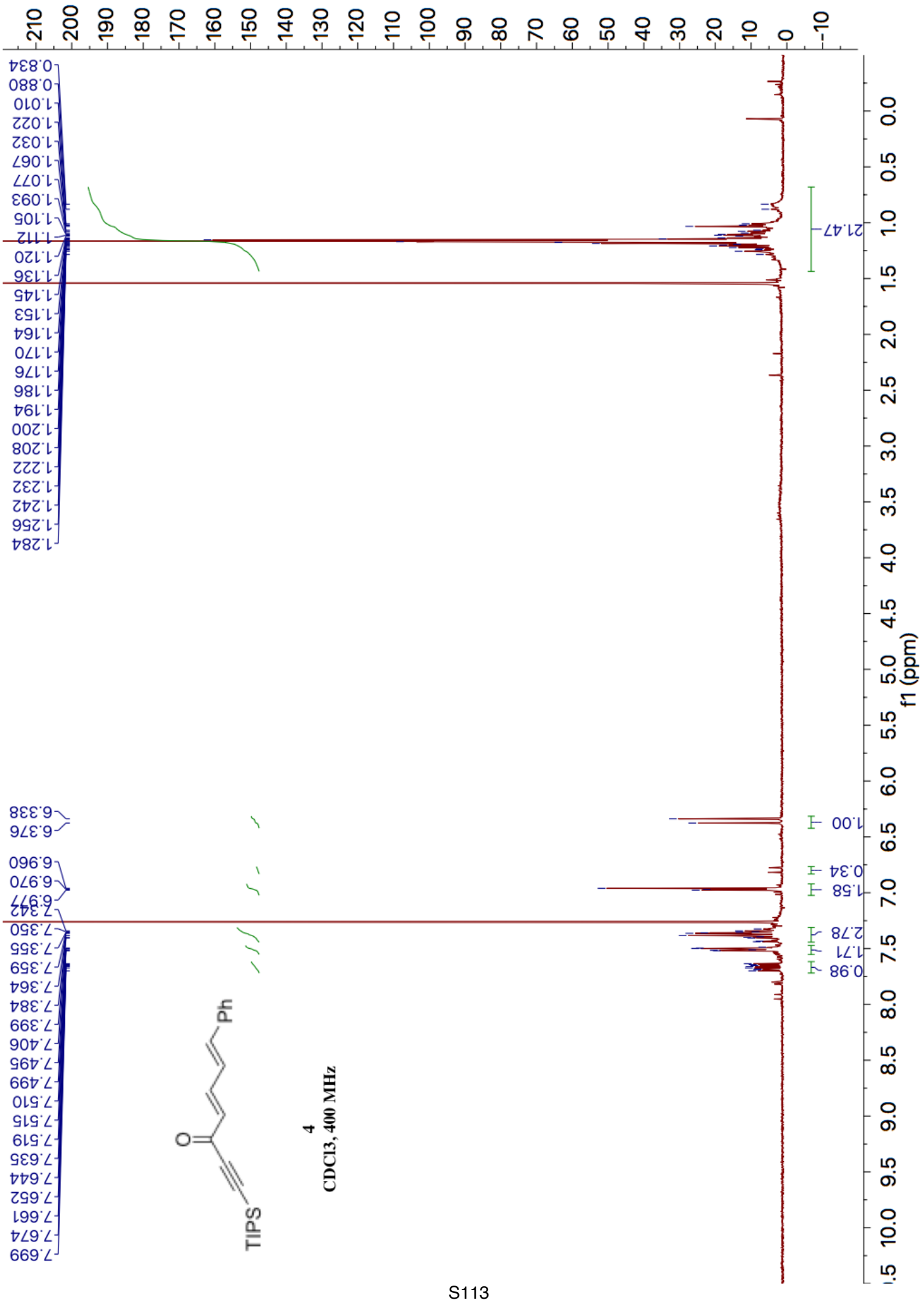

193.894
162.992
158.813
147.263
142.301
142.096
141.434
129.341
129.271
128.108
127.773
127.694
127.463
83.216
77.319
77.000
76.682
66.071
43.979
30.781
27.317
22.126
2.088
Ph
Ph
N
OTMS
O2N
O
CDCl3, 100 MHz
f1 (ppm)

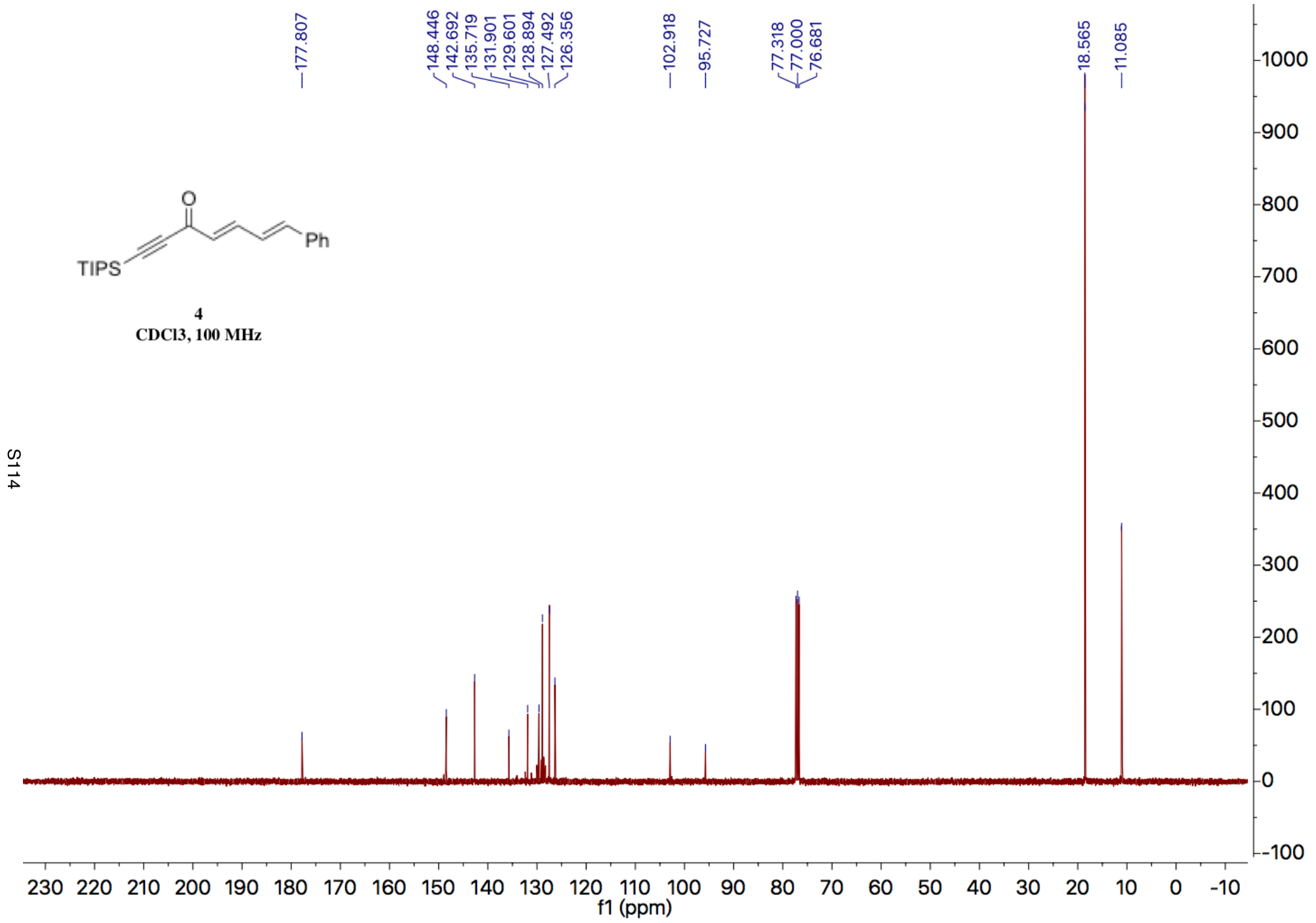


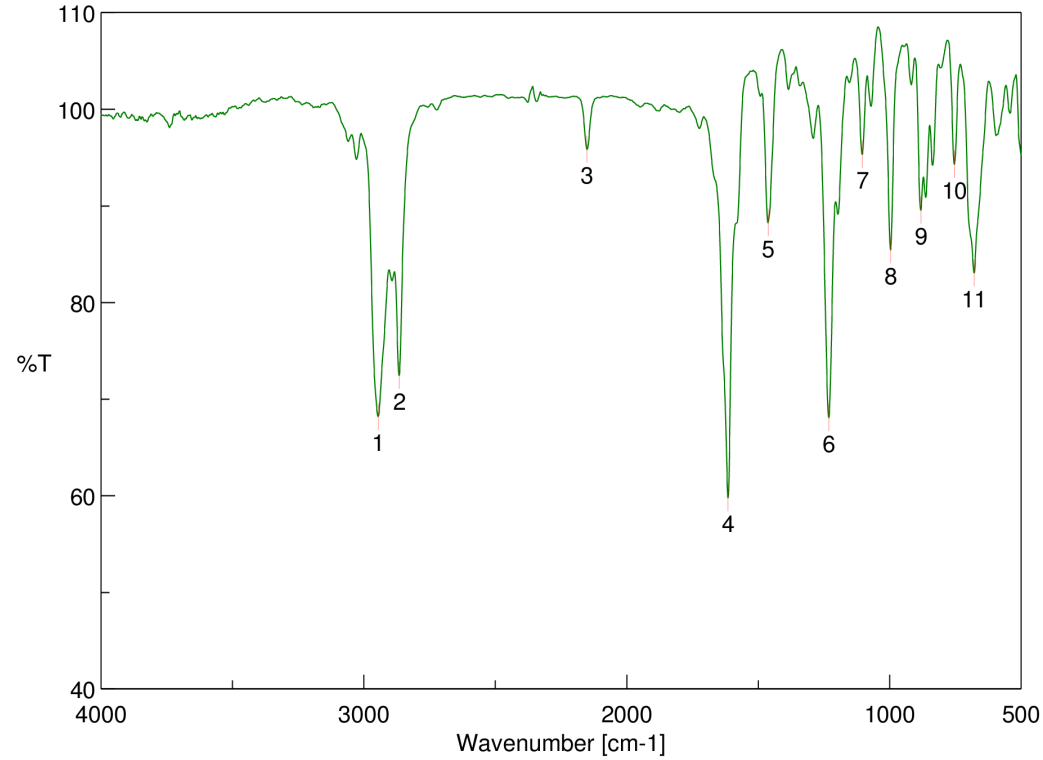
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2956.34	74.5878	2	1661.37	61.612
3	1600.63	72.3715	4	1522.52	32.5978
5	1492.63	53.7373	6	1345.11	41.365
7	1251.58	56.4595	8	1182.15	61.3301
9	1069.33	54.6235	10	969.055	73.3985
11	839.847	52.2597	12	754.995	66.9187
13	703.89	54.6881			



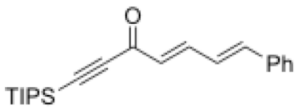

4
CDCl3, 400 MHz
TIPS
O
Ph
f1 (ppm)
21.47
1.00
0.34
1.58
2.78
1.71
0.98

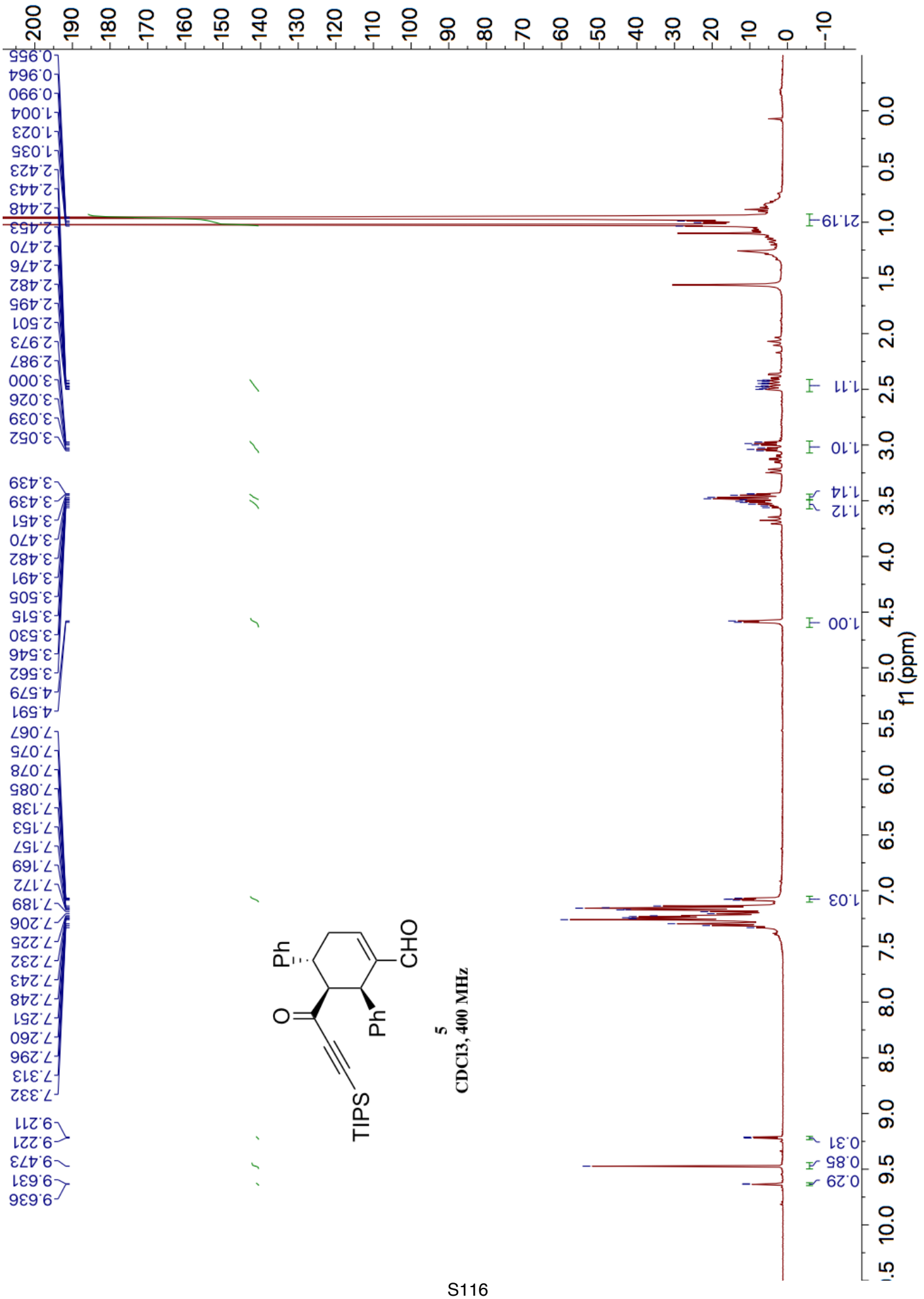

177.807
148.446
142.692
135.719
131.901
129.601
128.894
127.492
126.356
102.918
95.727
77.318
77.000
76.681
18.565
11.085
O
TIPS
Ph
4
CDCl3, 100 MHz
f1 (ppm)

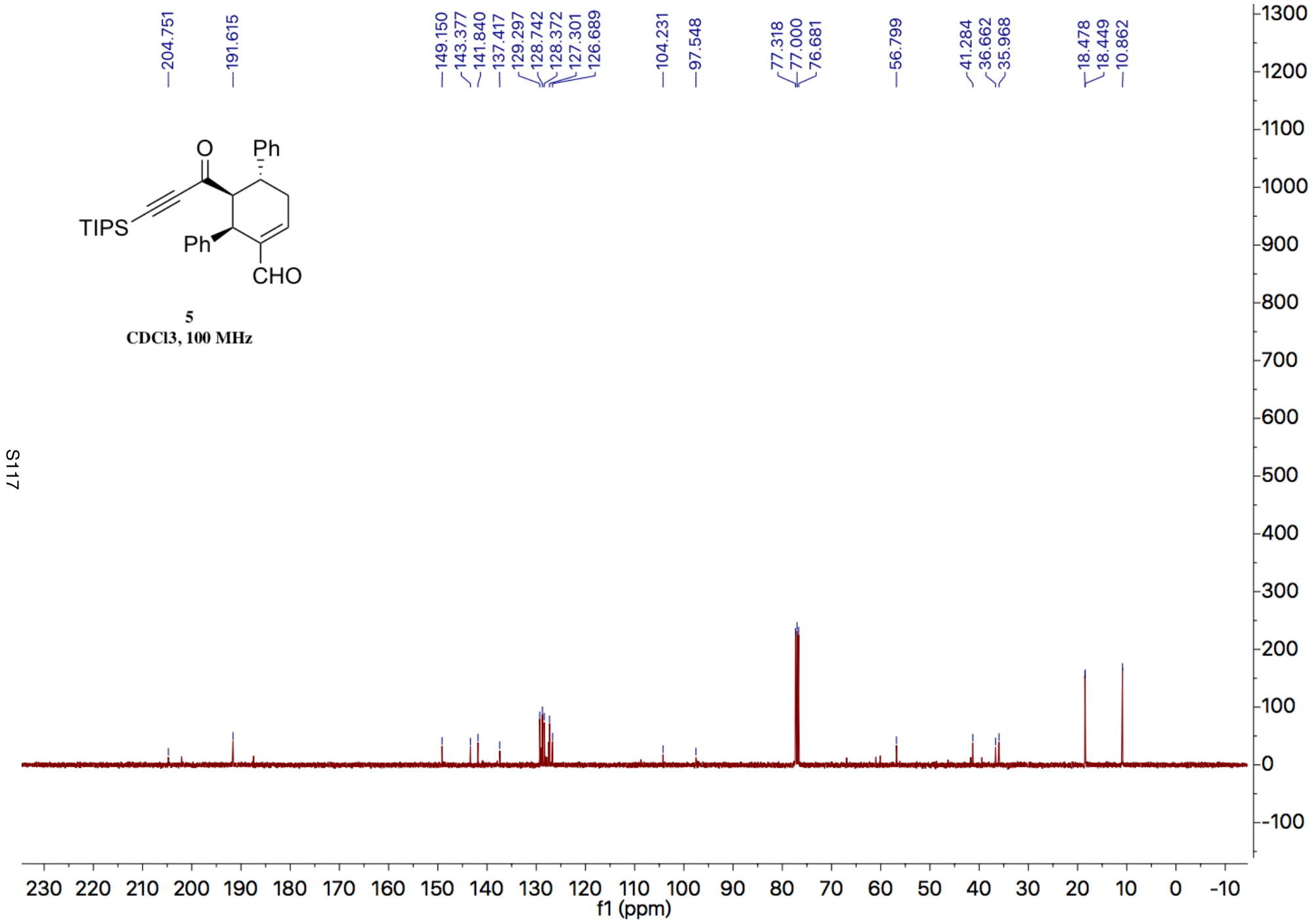


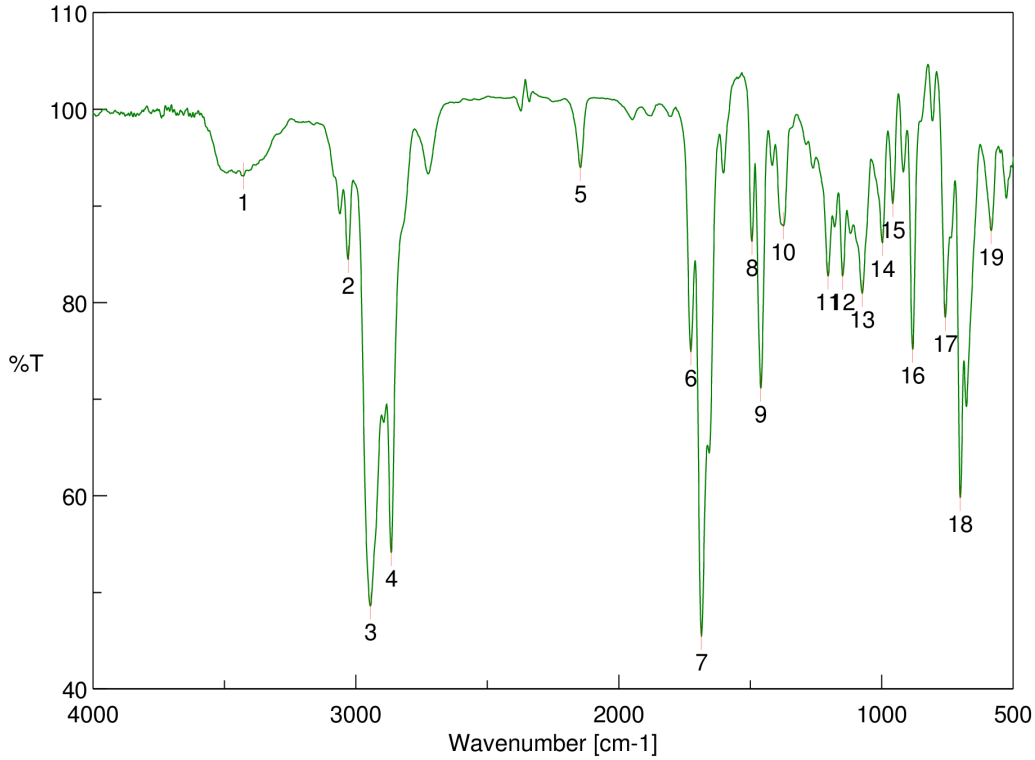
[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	2945.73	68.2095	2	2865.7	72.4437
3	2151.2	95.8311	4	1615.09	59.7909
5	1462.74	88.2471	6	1231.33	68.0951
7	1104.05	95.3236	8	997.017	85.4369
9	881.309	89.5574	10	754.031	94.2852
11	678.82	83.051			




Ph
O
CHO
Ph
TIPS
5
CDCl3, 400 MHz
f1 (ppm)


204.751
191.615
149.150
143.377
141.840
137.417
129.297
128.742
128.372
127.301
126.689
104.231
97.548
77.318
77.000
76.681
56.799
41.284
36.662
35.968
18.478
18.449
10.862
O
Ph
TIPS
Ph
CHO
5
CDCl3, 100 MHz
f1 (ppm)



[ピーク検出結果]

No.	位置	強度	No.	位置	強度
1	3427.85	93.0799	2	3029.62	84.4673
3	2944.77	48.5802	4	2865.7	54.1167
5	2146.38	93.9593	6	1725.98	74.888
7	1685.48	45.4608	8	1493.6	86.3172
9	1459.85	71.1445	10	1374.03	87.9066
11	1204.33	82.7268	12	1148.4	82.734
13	1074.16	80.9327	14	997.017	86.1704
15	957.484	90.2174	16	882.274	75.1639
17	757.888	78.4606	18	700.998	59.8131
19	583.361	87.4175