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SUPPORTING INFORMATION

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Title: An Introverted Bis-Au Cavitand and Its Catalytic Dimerization of Terminal Alkynes
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Contents

1. General
2. ORTEP drawing of **2**•CH_2Cl_2 (Figure 1S).
3. Procedure for synthesis of dimethyl (Z)-2,14-diacetyl-7-methylpentadec-6-en-8-ynedioate by dimerization of methyl 2-acetyloct-7-ynoate (Scheme 2).
4. Reduction of **4**, **7**, **8**, **9**, and **10** for the structural elucidation.
5. Preparation of the diyne **11** (part (c) in Scheme 7).
6. The ^{1}H and ^{13}C NMR spectra for Scheme 2 of dimethyl (Z)-2,14-diacetyl-7-methylpentadec-6-en-8-ynedioate by dimerization of methyl 2-acetyloct-7-ynoate.
7. The ^{1}H and ^{13}C NMR spectra of all new compounds **2**, **3a**, **3b**, **3c**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**.

1. General Information.

All reactions sensitive to air or moisture were carried out under an argon or an nitrogen atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica 60F$_{254}$. Column chromatography was carried out with silica gel 60 $_{N}$ (Kanto Chemical Co.). LRMS were reported on the basis of DI (GC-2010 Plus; Shimadzu). HRMS were reported on the basis of TOF (time of flight)-MS (MADI-TOF or LCMS-IT-TOF; Shimadzu), and DART (Direct Analysis in Real Time)-MS. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with a 5 mm QNP probe at 400 MHz, 100 MHz, and 162 MHz, respectively. Chemical shifts are reported in ppm with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), CH_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

2. ORTEP drawing of **2**•CH_2Cl_2 (Figure 1S).

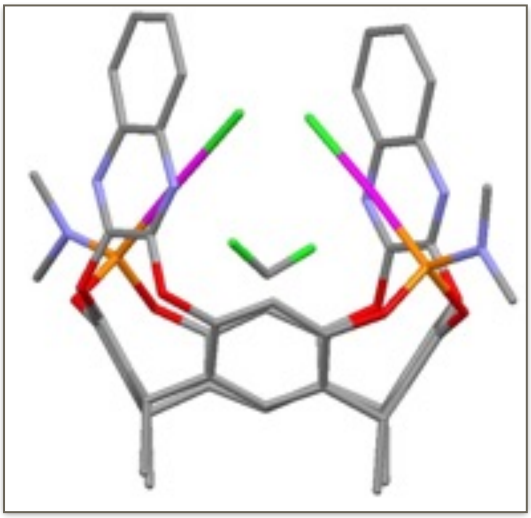

Figure 1S. ORTEP drawing of **2**•CH_2Cl_2 with thermal ellipsoids at the 50% probability level, which is illustrated with sticks from the side position for ease of viewing of an interior CH_2Cl_2. Hydrogen atoms are omitted for clarity. Each colorized atom is Cl for green, Au for magenta, P for orange, O for red, N for blue, and C for gray.

3. Procedure for synthesis of dimethyl (Z)-2,14-diacetyl-7-methylpentadec-6-en-8-ynedioate by dimerization of methyl 2-acetyloct-7-ynoate (Scheme 2).

To the reaction vessel charged with 0.55 mL of $CDCl_3$ was added **2** (5.5 mg, 0.0028 mmol) and AgOTf (1.5 mg, 0.0056 mmol), and the mixture was heated to 60 °C for 30 min. The starting methyl 2-acetyloct-7-ynoate (22 mg, 0.112 mmol) was added, and the reaction for 12 h indicated that a dimerized enyne product as a major adduct; no starting material remained. A a minor adduct, triketone that is derived from hydration of the terminal alkyne moiety was observed.[1] The major enyne of 10 mg (45% yield) as colorless oil form was obtained through purification by silica-gel column chromatography (eluent; hexane/EtOAc = 2/1). The stereochemistry of the dimer was determined by COSY and NOESY spectra that were listed in the section below. ^{1}H NMR (400 MHz, $CDCl_3$) 5.51 (t, J = 7.2 Hz, 1H), 3.73 (s, 6H), 3.46 (t, J = 6.4 Hz, 1H), 3.44 (t, J = 6.4 Hz, 1H), 2.34 (t, J = 6.8 Hz, 2H), 2.24-2.19 (m, 8H), 1.90-1.79 (m, 4H), 1.79 (s, 3H), 1.60-1.53 (m, 2H), 1.44-1.34 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) 203.4, 203.2, 170.5, 170.4, 135.4, 119.2, 93.5, 80.3, 59.7, 59.6, 52.51, 52.48, 30.1, 29.0 (two peaks are overlapped), 28.7, 27.9 (two peaks are overlapped), 27.0, 26.8, 23.6, 19.4 ppm. MS (MALDI-TOF) *m/z*: 393 ($[MH]^+$). HRMS (MALDI-TOF, *m/z*, $[MH]^+$) calcd for $C_{22}H_{33}O_6$: 393.2277, found 393.2101.

4. Reduction of **4**, **7**, **8**, **9**, and **10** for the structural elucidation.

To one-neck flask charged with the enyne (**4**, **7** - **10**) under H_2 atmosphere was added EtOAc and Pd/C (10 wt% of the starting enyne). After stirring for 8 h, the reaction mixture was filtered through a pad of celite, and the filtrate was concentrated in vacuo to give a mixture material of oils. Purification by silica-gel column chromatography (eluent; hexane only) afforded the corresponding alkanes. The physical property data are listed in the section below.

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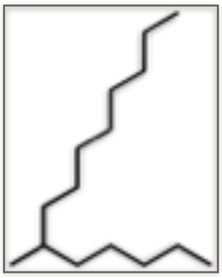
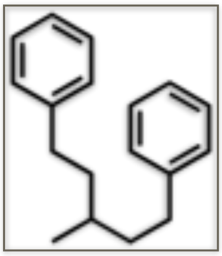
[1] This tri-ketone was already ensured in our previous report; see, M. P. Schramm, M. Kanaura, K. Ito, M. Ide, T. Iwasawa, *Eur. J. Org. Chem.* **2016**, 813-820.

7-methylpentadecane that is obtained through the reduction of **4**[2], known compound:



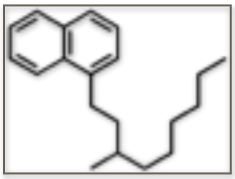
pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) 1.30-1.06 (m, 25H), 0.88 (t, J = 6.9 Hz, 6H), 0.81 (d, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 37.5 (two peaks are overlapped), 33.1, 32.34, 32.31, 30.4, 30.1 (two peaks are overlapped), 29.7, 27.5, 27.4, 23.07, 23.06, 20.1, 14.5 (two peaks are overlapped) ppm; MS (DI) m/z: 140 $[MH-C_6H_{13}]^+$, 226 $[M]^+$; IR (neat): 2956, 2922, 2852, 1465, 1377, 722 cm^{-1}.

(3-methylpentane-1,5-diyl)dibenzene that is obtained through the reduction of **7**: 93% yield (77 mg); colorless oil;



^{1}H NMR (400 MHz, $CDCl_3$) 7.28 (dd, J = 7.4 Hz, 7.4 Hz, 4H), 7.19-7.16 (m, 6H), 2.70-2.54 (m, 4H), 1.72-1.65 (m, 2H), 1.57-1.44 (m, 3H), 1.00 (d, J = 5.9 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 143.3, 128.7, 128.6, 125.9, 39.2, 32.7, 32.5, 19.9 ppm; IR (neat): 3025, 2922, 2856, 1603, 1495, 1453, 1377, 1058, 1030, 742 cm^{-1}; MS (LCMS-IT-TOF) m/z: 256 ($[M+NH_4]^+$); HRMS (DART, m/z, $[M+NH_4]^+$): calcd for $C_{18}H_{26}N$: 256.2060, Found 256.2035; Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.35; H, 9.19.

1-(3-methylnonyl)naphthalene that is obtained through the reduction of **8**: 84% yield (58 mg); colorless oil;



^{1}H NMR (400 MHz, $CDCl_3$) 8.04 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 7.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.50 (dd, J = 8.0 Hz, 6.8 Hz, 1H), 7.48 (dd, J = 8.4 Hz, 6.8 Hz, 1H), 7.39 (dd, J = 7.0 Hz, 7.0 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H), 3.15-2.98 (m, 2H), 1.78-1.72 (m, 1H), 1.59-1.51 (m, 2H), 1.44-1.18 (m, 10H), 1.02 (d, J = 6.3 Hz, 3H), 0.89 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 139.7, 134.3, 132.2, 129.1, 126.7, 126.1, 126.0, 125.9, 125.7, 124.2, 38.7, 37.3, 33.5, 32.3, 31.1, 30.0, 27.4, 23.1, 20.1, 14.5 ppm; IR (neat): 2953, 2922, 2853, 1461, 1376, 795, 722 cm^{-1}; MS (LCMS-IT-TOF) m/z: 268 $[M]^+$; HRMS (DART, m/z, $[M]^+$): calcd for $C_{20}H_{28}$: 268.2191, Found: 268.2192.

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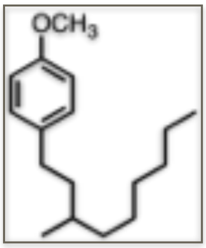
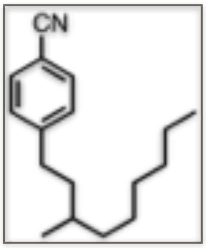
[2] W. H. Baarschers, M. A. Li. *Can. J. Chem.* **1983**, *61*, 1784.

1-methoxy-4-(3-methylnonyl)benzene that is obtained through the reduction of **9**: 98%



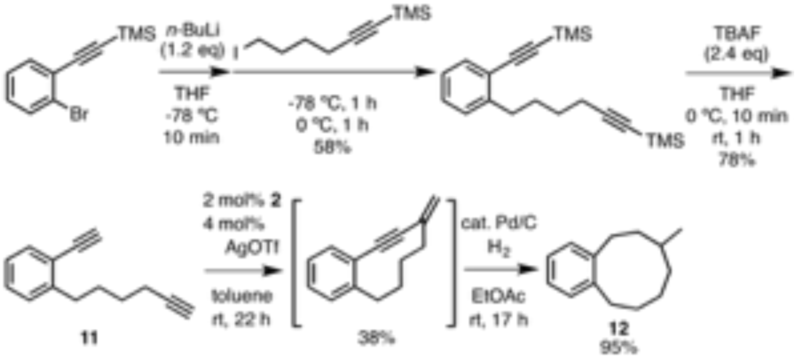
yield (41 mg); pale yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) 7.10 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H) 2.62-2.46 (m, 2H), 1.64-1.55 (m, 1H), 1.45-1.10 (m, 12H), 0.91 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) 157.9, 135.6, 129.5, 114.0, 55.6, 39.5, 37.3, 32.9, 32.7, 32.3, 30.0, 27.3, 23.0, 19.9, 14.5 ppm; MS (LCMS-IT-TOF) m/z: 248 [M]$^+$; IR (neat): 2923, 2853, 1612, 1510, 1464, 1441, 1300, 1243, 1175, 1038, 821 cm^{-1}; HRMS (DART, m/z, [M]$^+$): calcd for $C_{17}H_{28}O$: 248.2140, Found: 248.2150.

4-(3-methylnonyl)benzonitrile that is obtained through the reduction of **10**: 98% yield (42



mg); yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) 7.56 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 2.73-2.58 (m, 2H), 1.64-1.58 (m, 1H), 1.47-1.11 (m, 12H), 0.92 (d, J = 6.3 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$) 149.2 132.4, 129.5, 119.5, 109.7, 38.7, 37.1, 34.0, 32.7, 32.2, 29.9, 27.2, 23.0, 19.8, 14.4 ppm; MS (LCMS-IT-TOF) m/z: 244 [MH]$^+$; IR (neat): 2954, 2923, 2854, 2227, 1607, 1505, 1459, 1377, 821, 559 cm^{-1}; HRMS (DART, m/z, [MH]$^+$): calcd for $C_{17}H_{26}N$: 244.2060, Found: 244.2066.

5. Preparation of the diyne **11** (the part (c) in Scheme 7).



To the flask charged with ((2-bromophenyl)ethynyl)trimethylsilane (1.14 g, 4.5 mmol) in THF (45 mL) at -78 ºC was added slowly 3. 5 mL of n-BuLi (5.4 mmol, 1.54 M in hexane), and then 27 mL THF solution of (6-iodohex-1-yn-1-yl)trimethylsilane[3] (1.51 g, 5.4 mmol) was added dropwise over 3 min, and the mixture was stirred at -78 °C for 1 h. After additional stirring at 0 °C for 1 h, the reaction was quenched at 0 °C with satd. aq. NH_4Cl (50 mL). The mixture was diluted with EtOAc, and the aqueous layer was extracted with EtOAc three times. The combined organic phases were washed with brine, and dried over Na_2SO_4, and concentrated *in vacuo* to give a crude as an orange oil. Purification with silica-gel column chromatography (hexane/CH_2Cl_2 = 19/1) afforded the desired compound of trimethyl(6-(2-((trimethylsilyl)ethynyl)phenyl)hex-1-yn-1-yl)silane as a pale yellow oil of 1.14 g (58%). The following desilylation reaction of the bis-trimethylsilyl compound (628 mg, 1.9 mmol) was performed in THF (10 mL) at 0 °C by addition of TBAF (4.6 mmol, 1 M THF solution). After additional stirring at rt for 1 h, the reaction was quenched at 0 °C with satd. aq. NH_4Cl. The mixture was diluted with toluene, and the aqueous layer was extracted with toluene three times. The combined organic phases were washed with brine, and dried over Na_2SO_4, and concentrated *in vacuo* to give a crude as a brown oil. Purification with silica-gel column chromatography (hexane/$CHCl_3$ = 19/1) afforded the dine **11** as a colorless oil of 484 mg (78%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.47 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.27 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.2 Hz, 1H), 7.20 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.15 (ddd, *J* = 7.6 Hz, 7.6 Hz, 1.2 Hz, 1H), 3.24 (s, 1H), 2.81 (t, *J* = 7.7 Hz, 2H), 2.23 (dt, *J* = 7.2 Hz, 2.6 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.77 (tt, *J* = 7.7 Hz, 7.2 Hz, 2H), 1.60 (tt, *J* = 7.7 Hz, 7.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 145.2, 133.3, 129.2, 129.1, 126.1, 121.8, 84.8, 82.7, 81.0, 68.6, 34.1, 30.0, 28.5, 18.6 ppm; MS (LCMS-IT-TOF) *m/z*: 183 $[MH]^+$; IR (neat): 3294, 2939, 2861, 1483, 1446, 1259, 756, 623 cm^{-1}; HRMS (DART, *m/z*, $[MH]^+$): calcd for $C_{14}H_{15}$: 183.1168 $[MH]^+$, Found: 183.1162.

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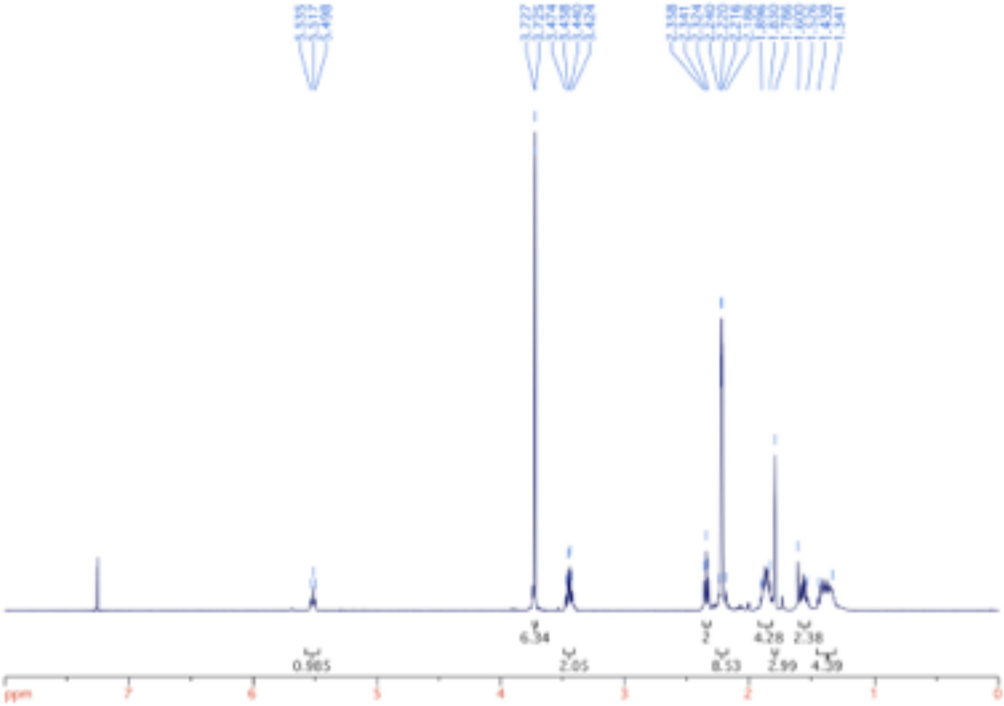
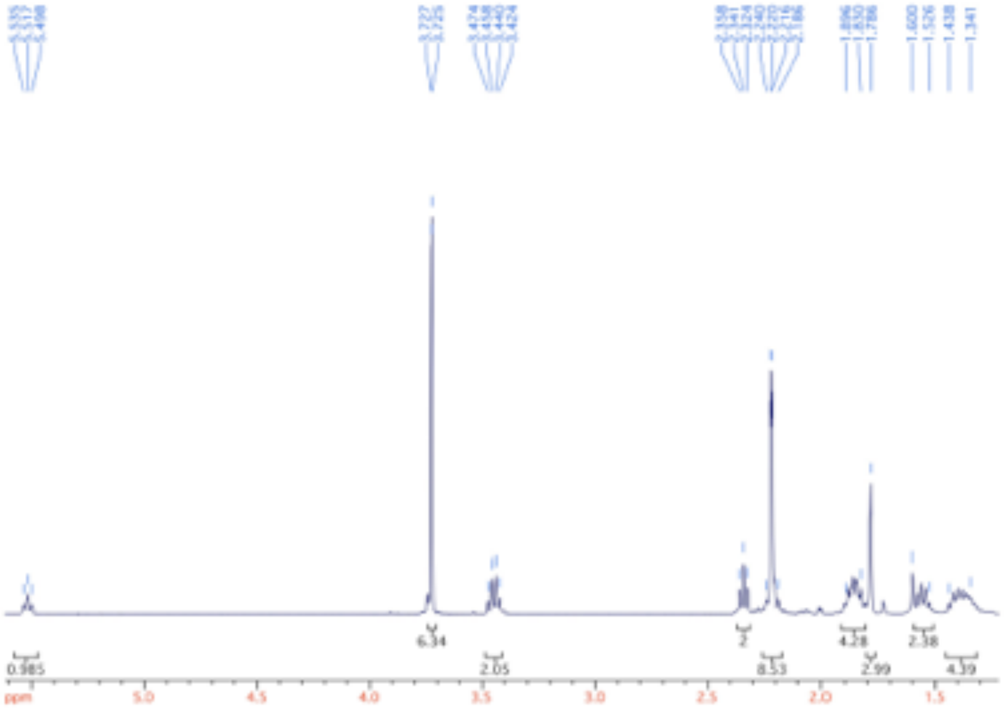
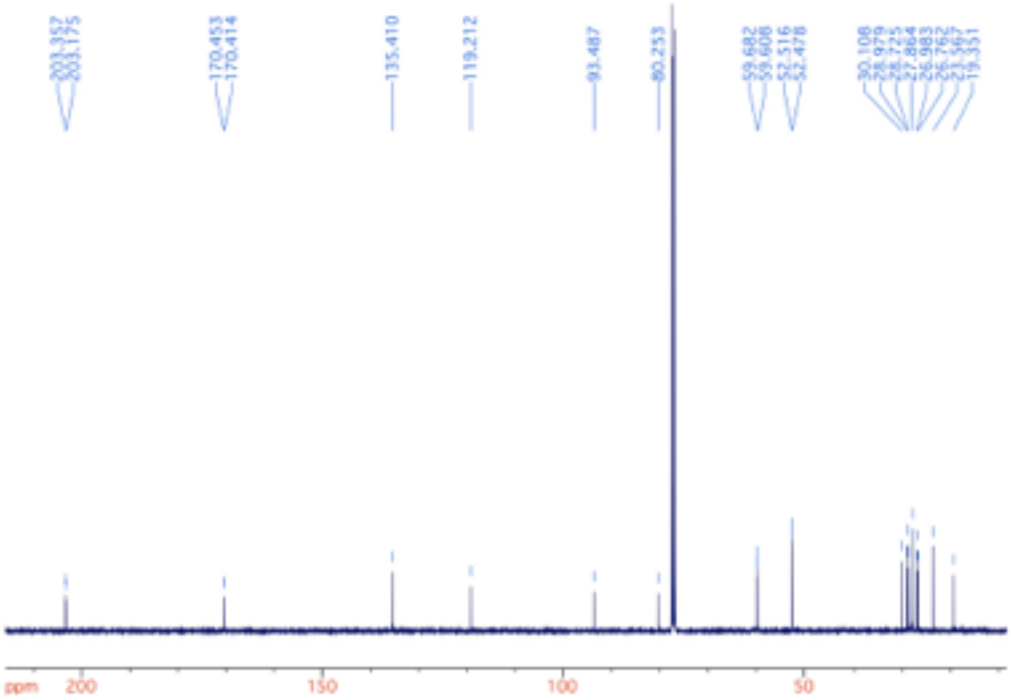
[3] C. Mukai, I. Nomura, S. Kitagaki, *J. Org. Chem.* **2003**, *68*, 1376-1385.

6. The ^{1}H and ^{13}C NMR spectra for Scheme 2 of dimethyl (Z)-2,14-diacetyl-7-methylpentadec-6-en-8-ynedioate by dimerization of methyl 2-acetyloct-7-ynoate.

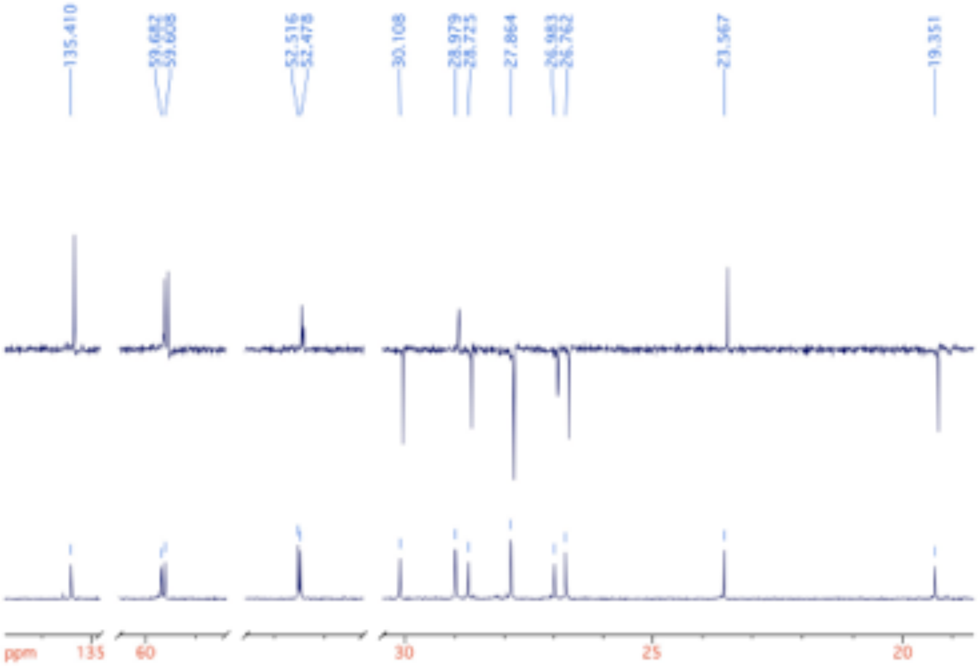


H NMR 400 MHz, CDCl3

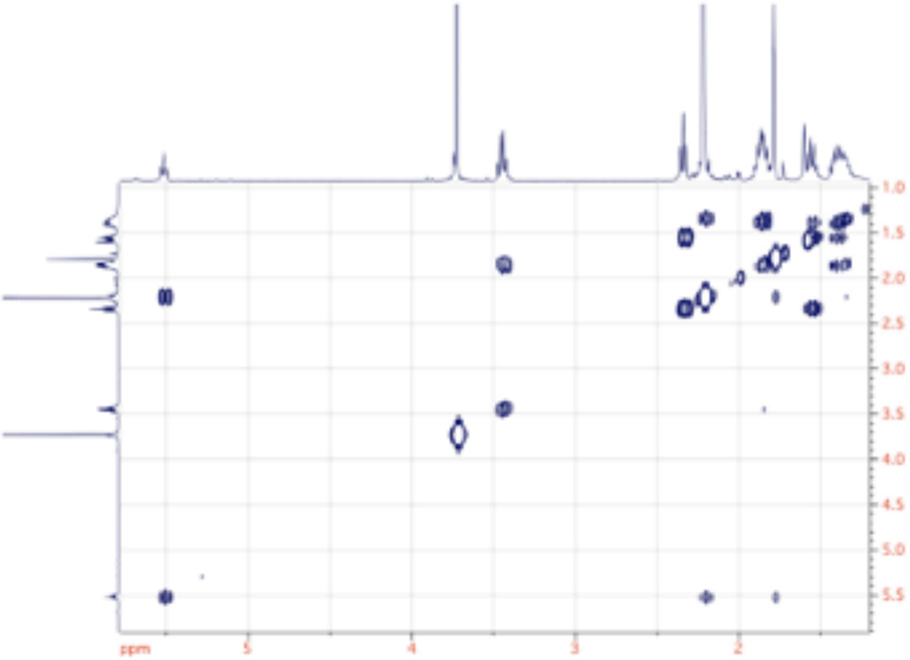




C NMR 100 MHz, CDCl3



C NMR and DEPT-135 stack plot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3
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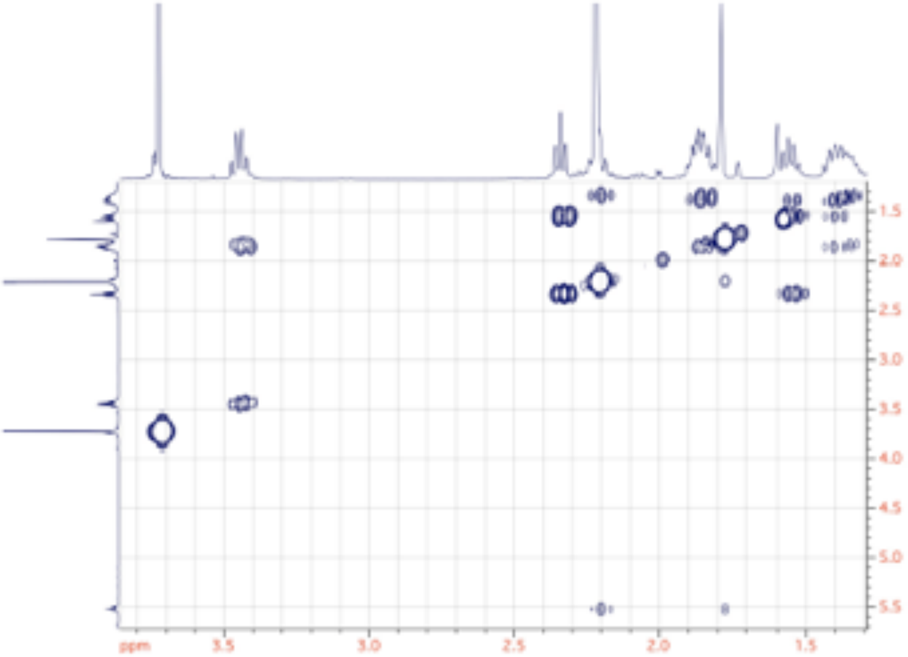
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

COSY


ppm
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3.0
2.5
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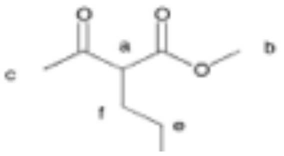
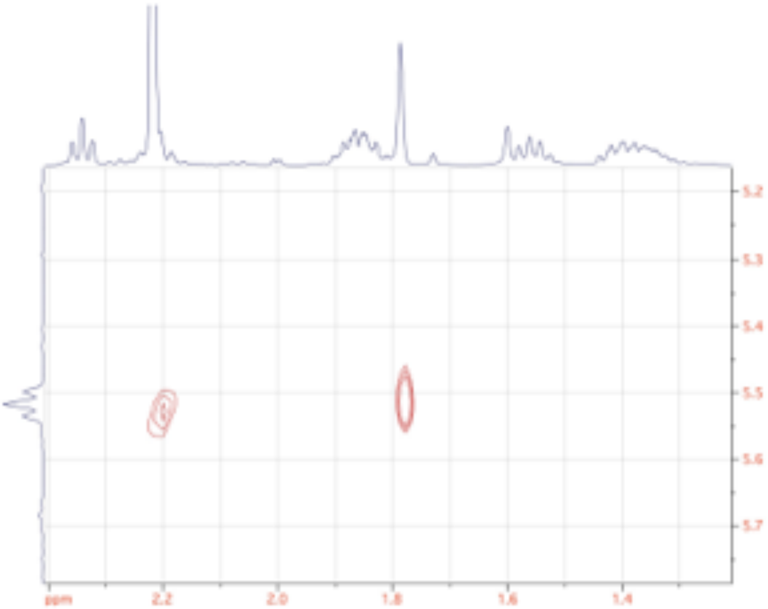
5.0
5.5

COSY





NOESY expansion showing relationship of alkene "z" proton to methyl protons (strong) and to g' (adjacent CH2) (moderate)

1.0
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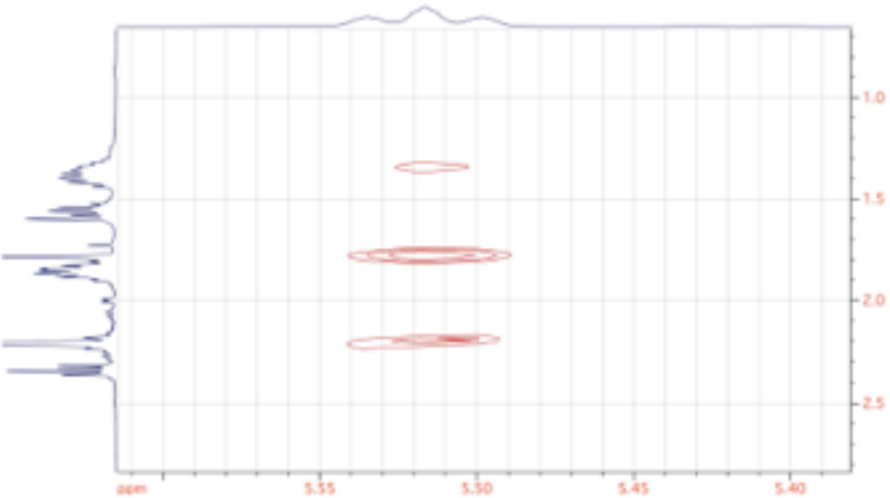
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5

S

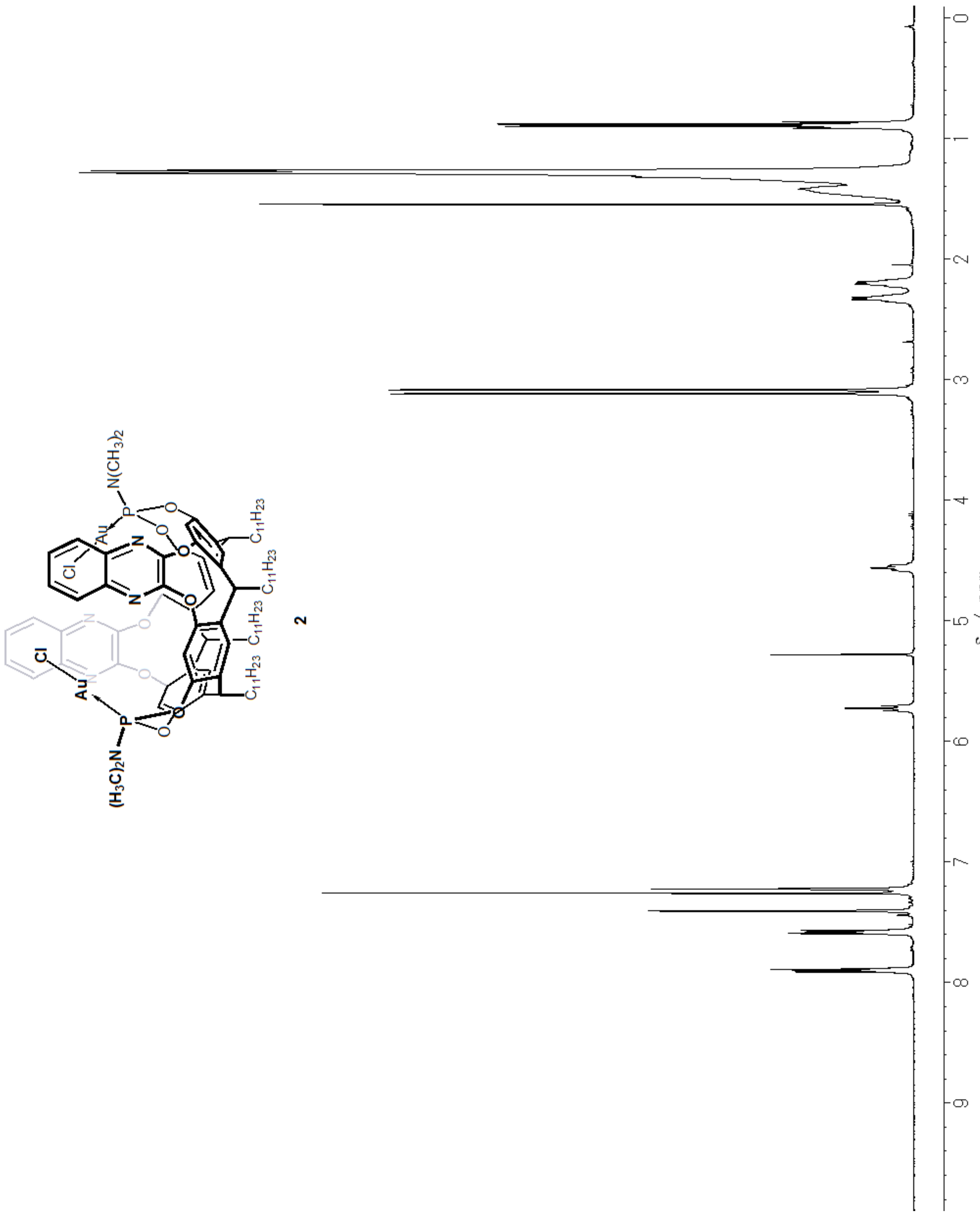


NOESY expansion (inverse axis compared to above) showing relationship of alkene "z" proton to methyl protons (strong), to adjacent g' (moderate) and to e' (weak).

7. The ^{1}H and ^{13}C NMR spectra of all new compounds **2**, **3a**, **3b**, **3c**, **4a**, **4b**, **5**, **6**, **7**, **8**, **9**, **10**, **11**, **12**.

Compound 2

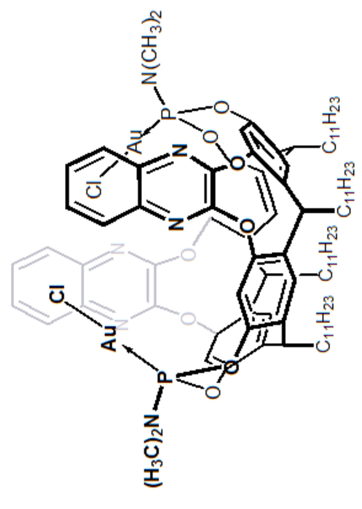
^{1}H NMR spectrum in $CDCl_3$



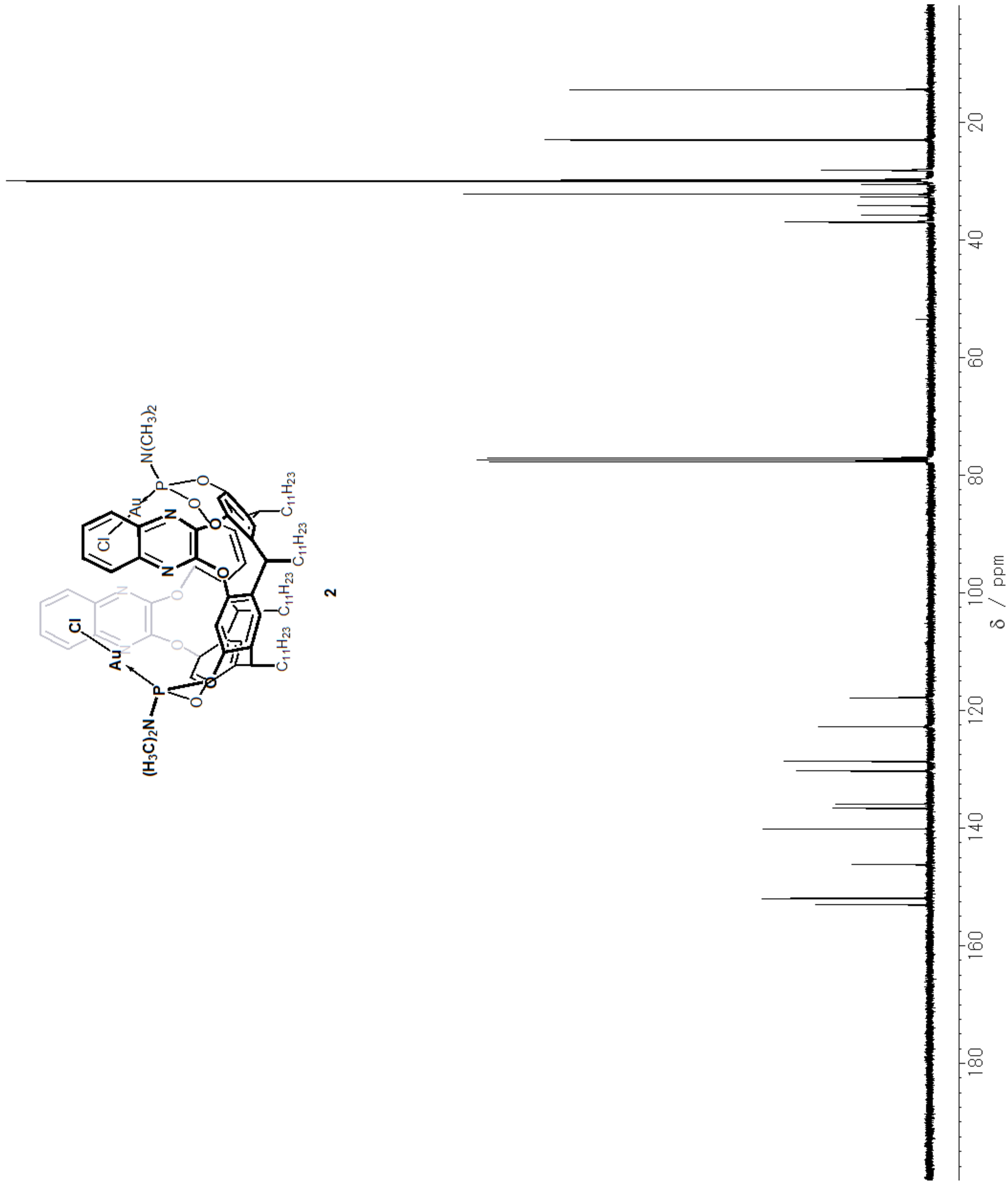
2

Compound 2

^{13}C NMR spectrum in $CDCl_3$

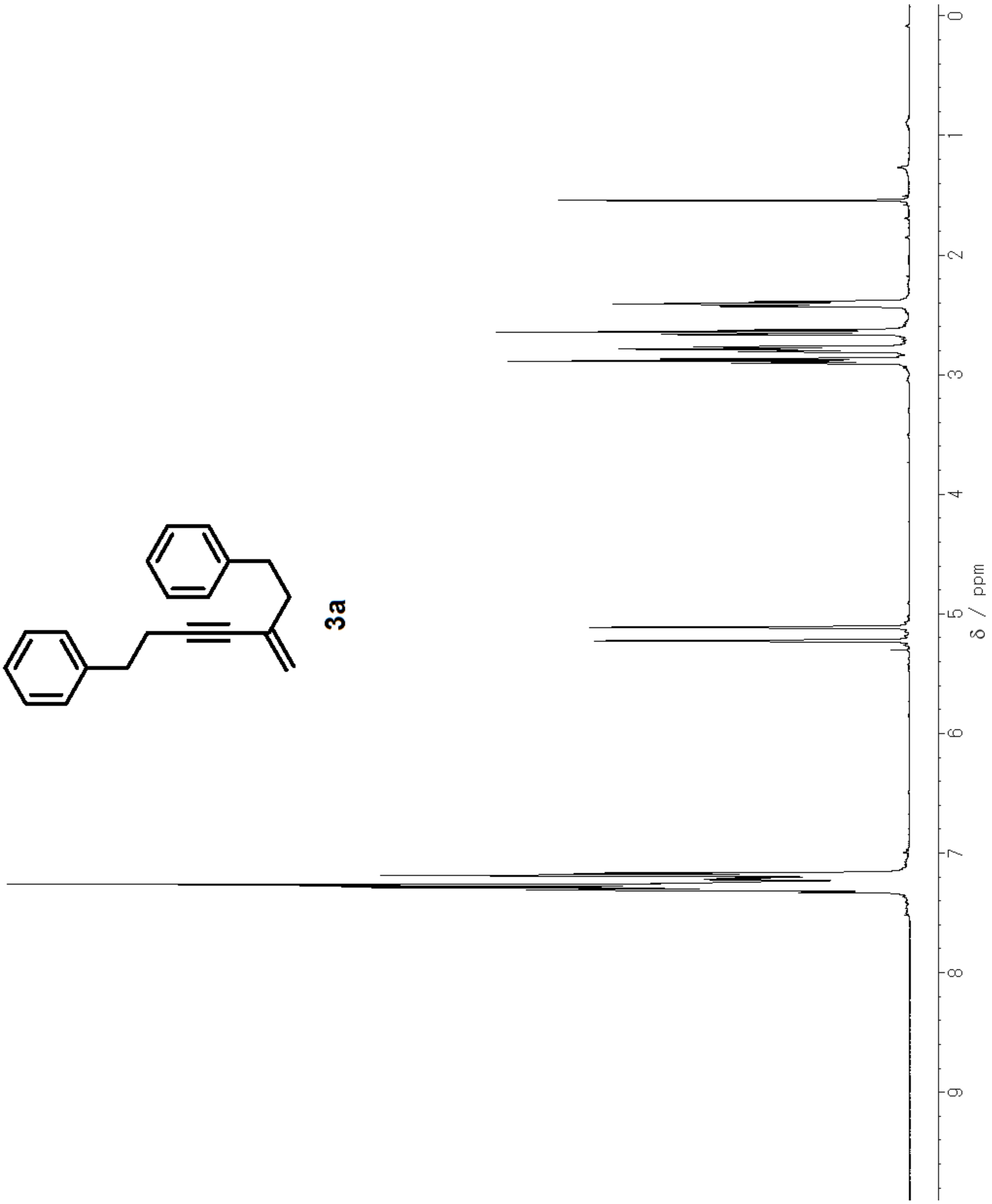


2



Compound 3a

^{1}H NMR spectrum in $CDCl_3$



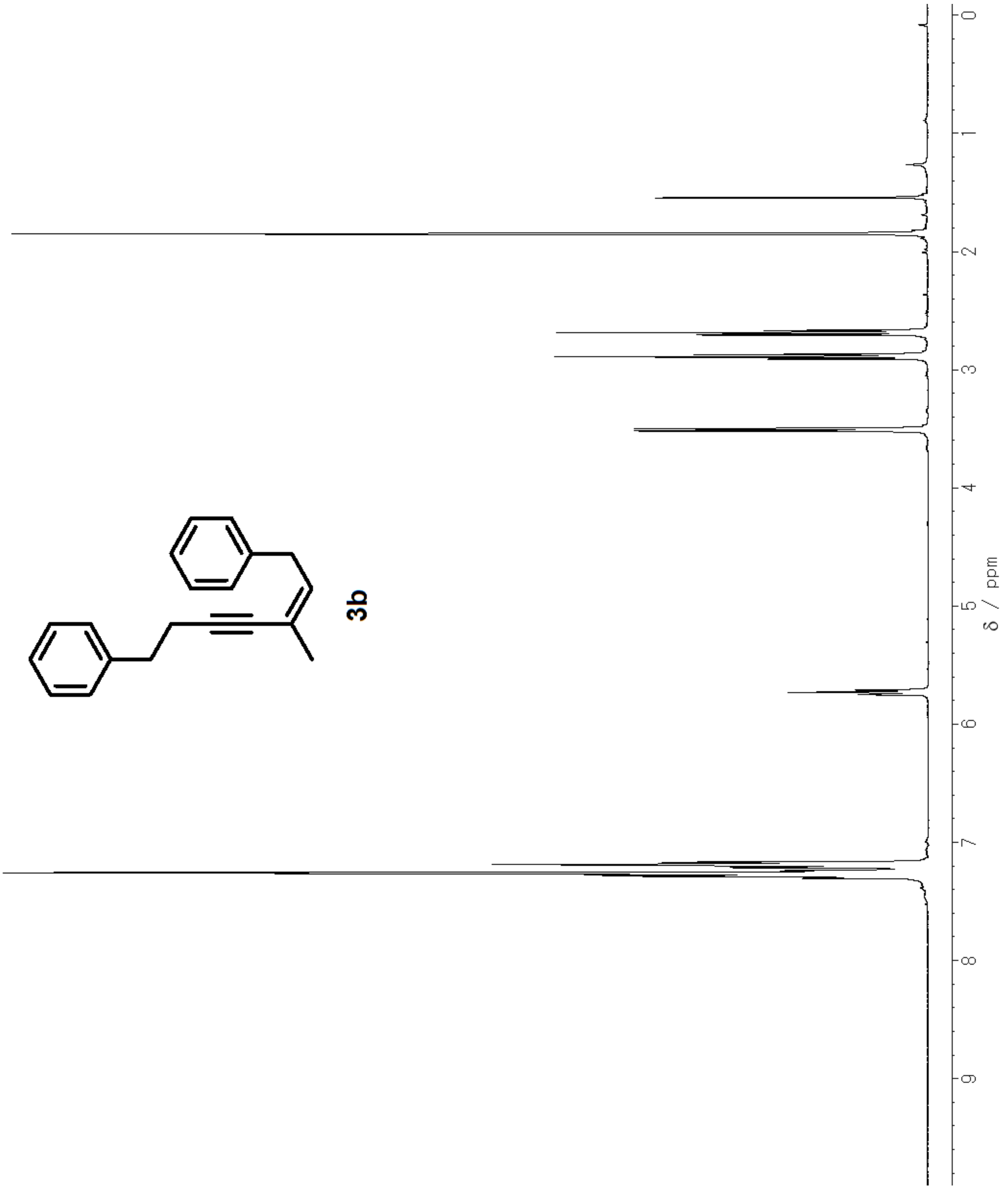
Compound 3a

^{13}C NMR spectrum in CDCl$_3$

3a

Compound 3b

^{1}H NMR spectrum in $CDCl_3$

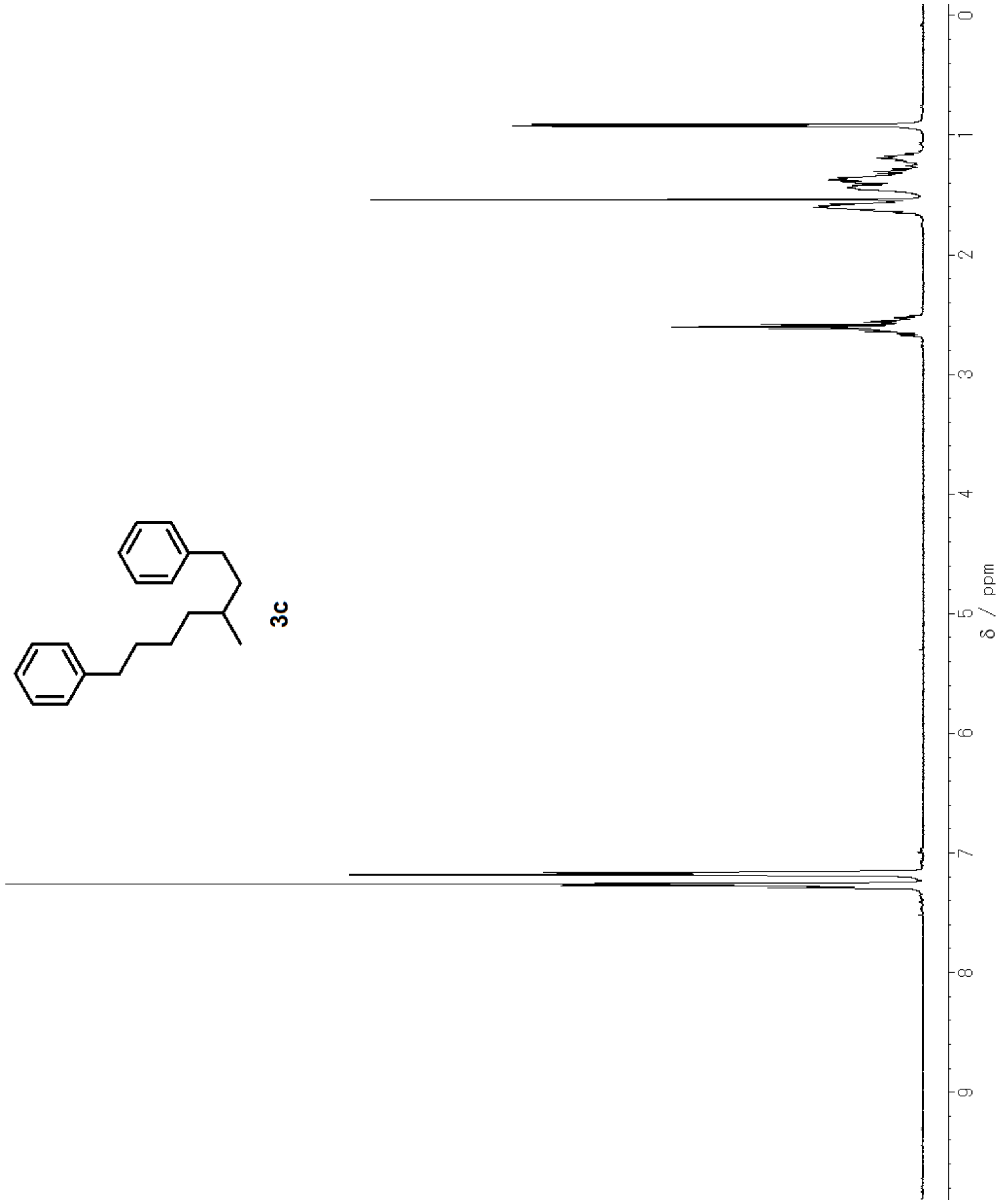


Compound 3b

^{13}C NMR spectrum in CDCl$_3$

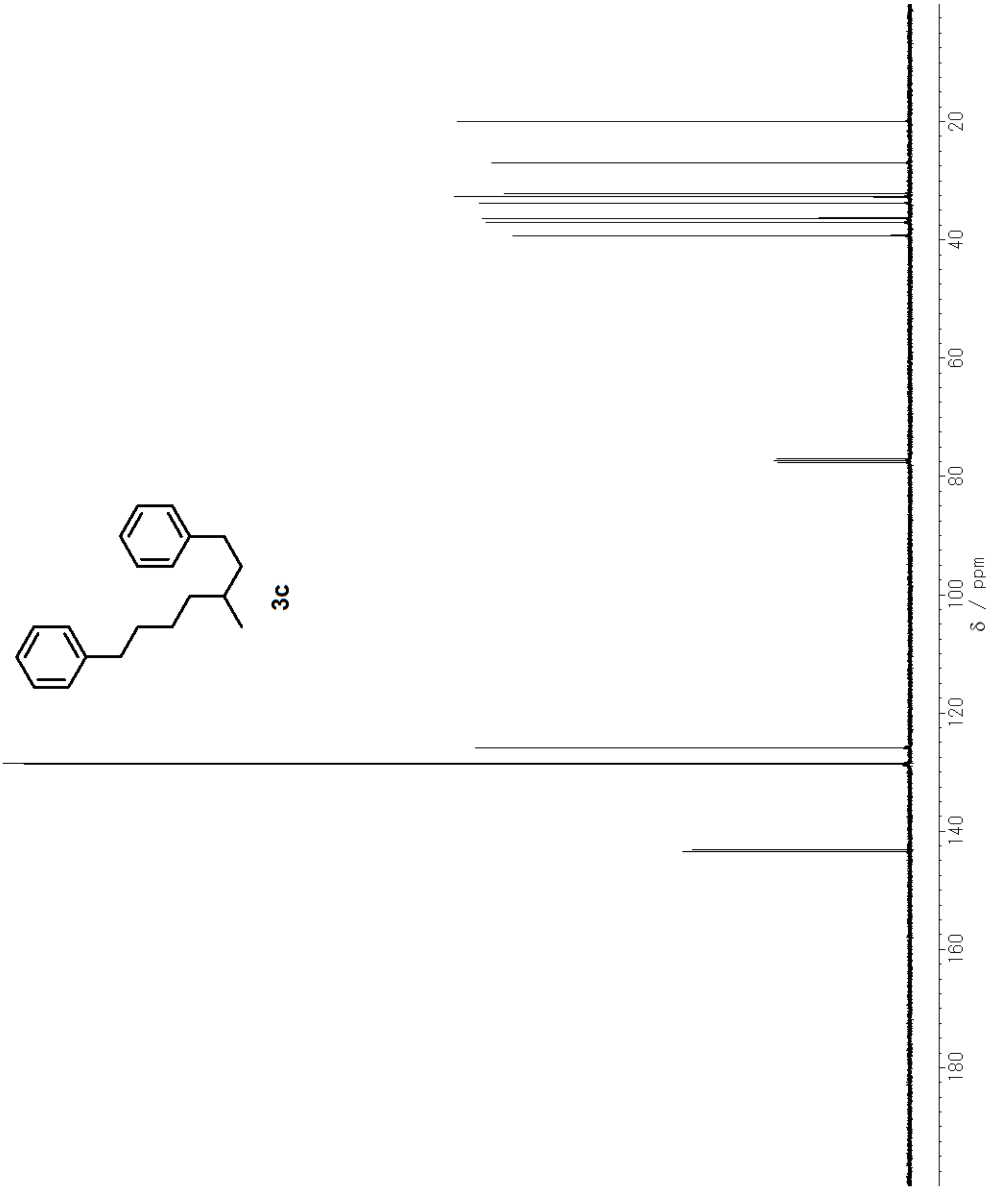
Compound 3c

^{1}H NMR spectrum in $CDCl_3$



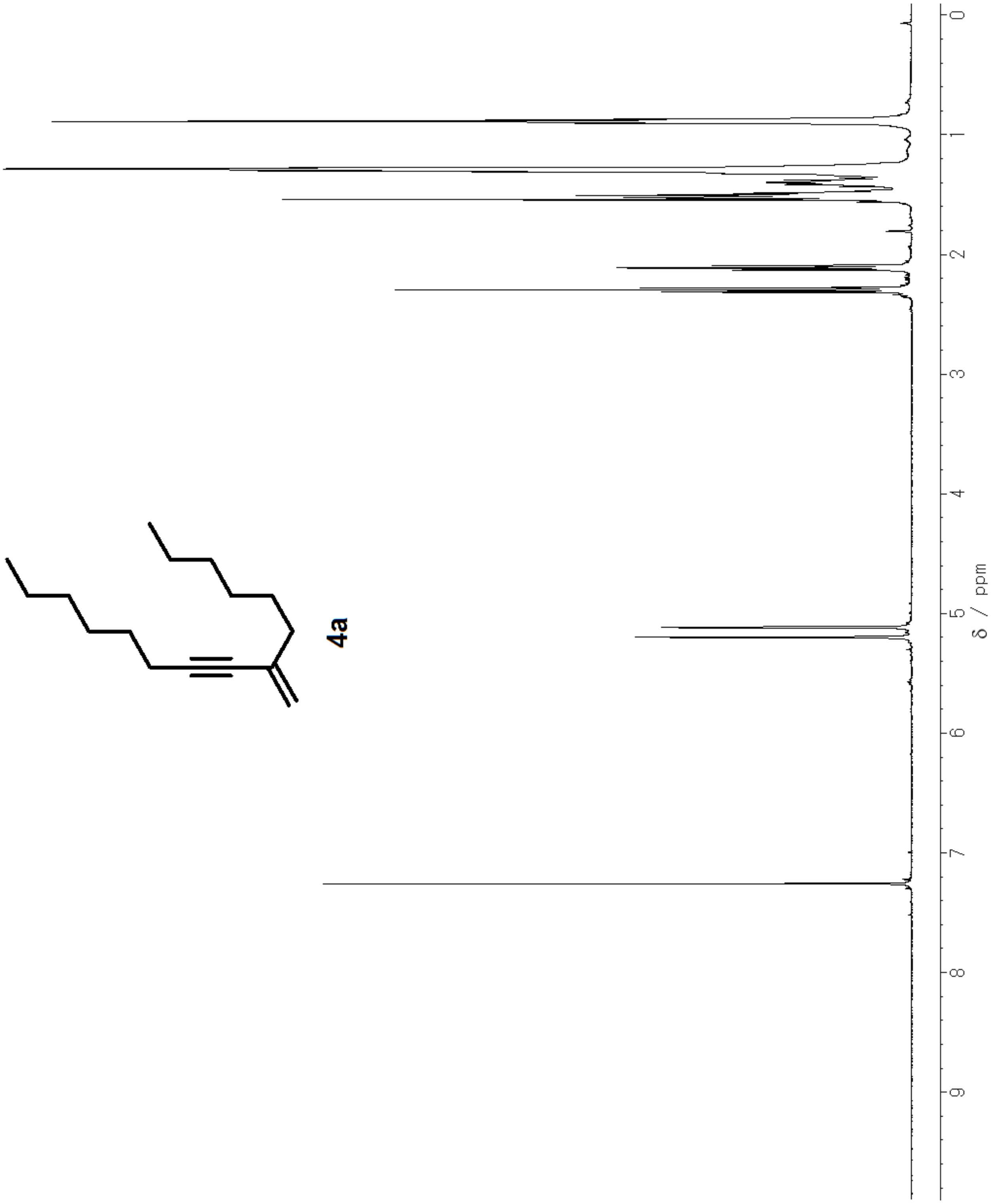
Compound 3c

^{13}C NMR spectrum in $CDCl_3$



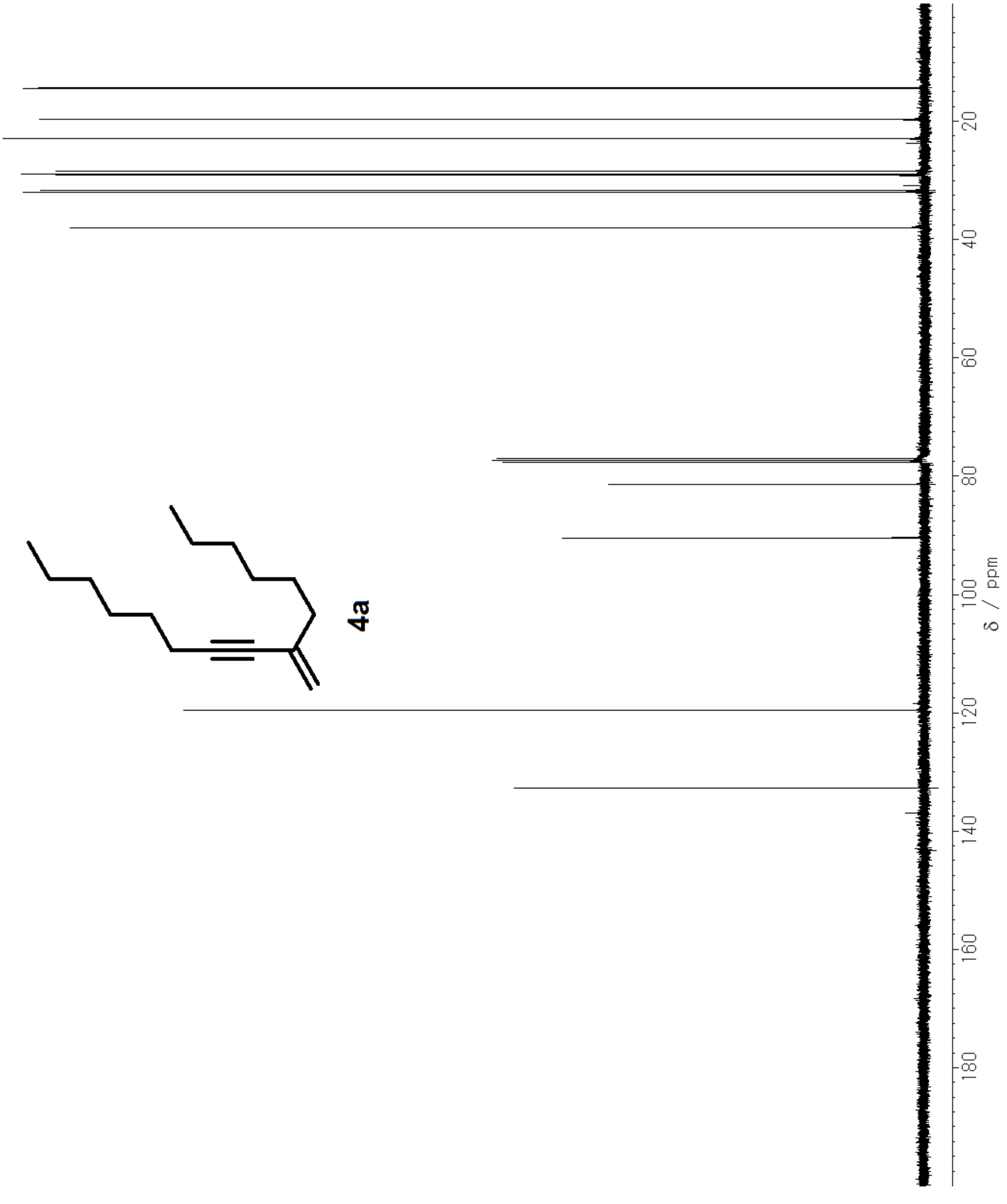
Compound 4a

^{1}H NMR spectrum in $CDCl_3$



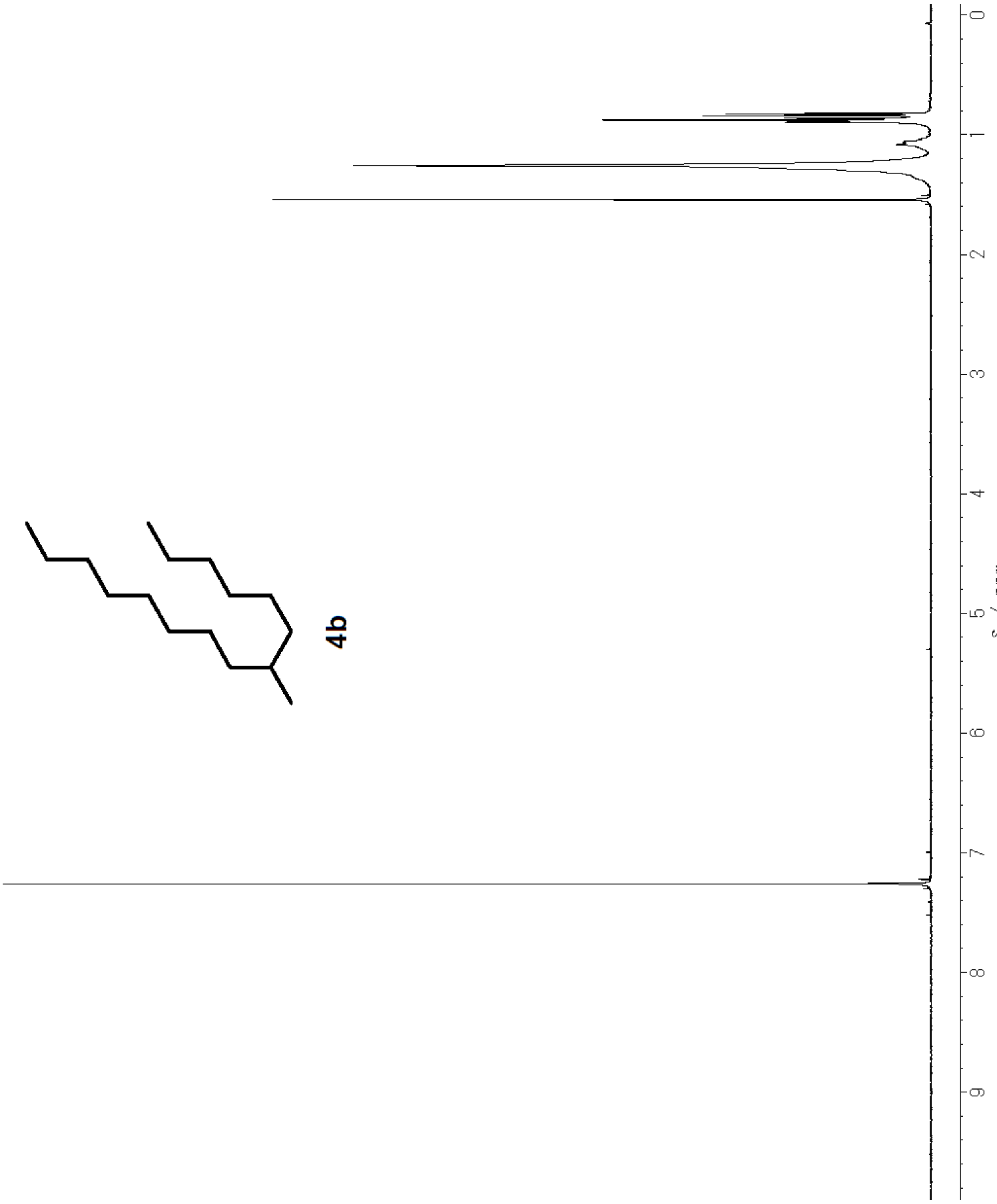
Compound 4a

^{13}C NMR spectrum in $CDCl_3$



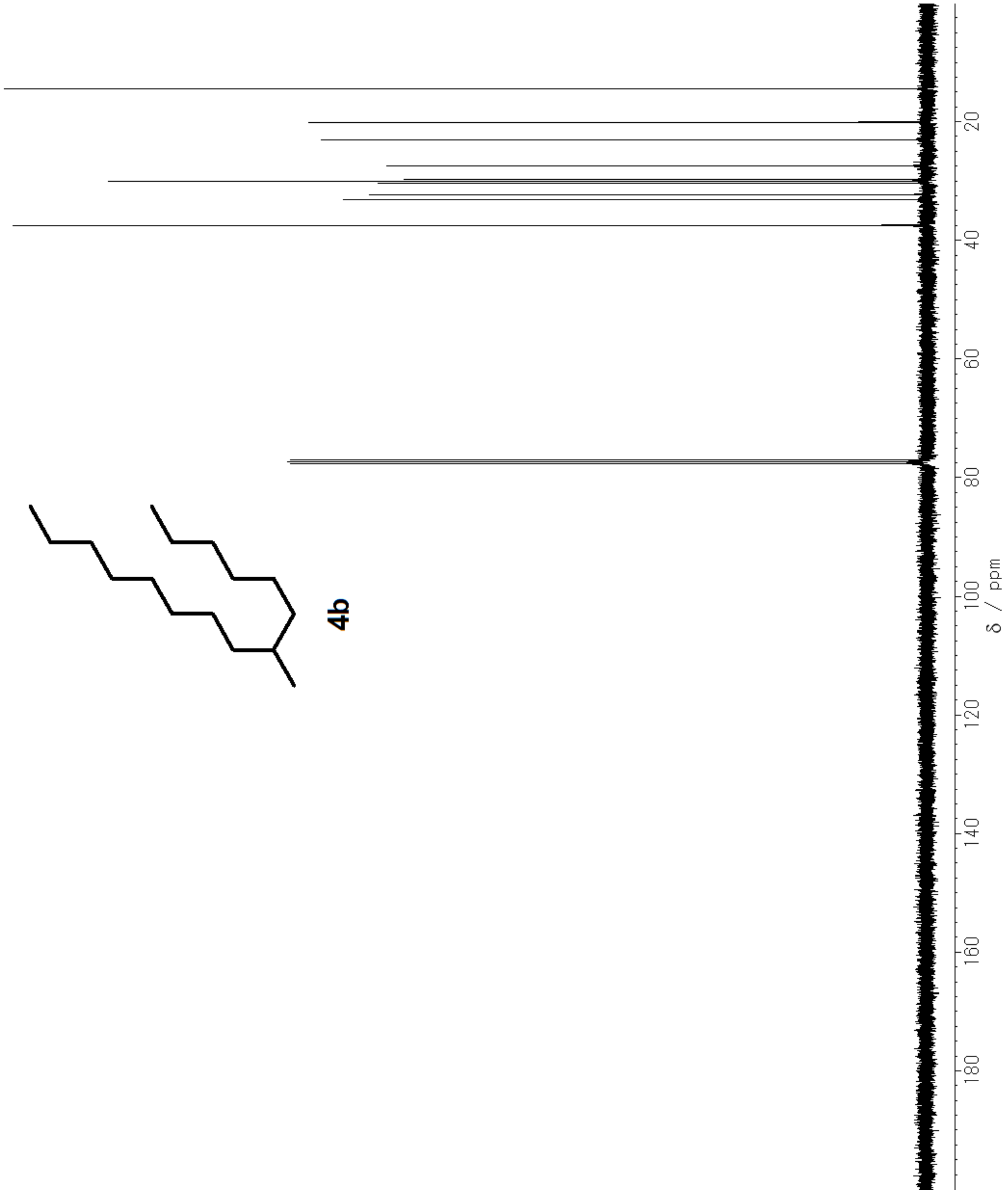
Compound 4b

^{1}H NMR spectrum in $CDCl_3$



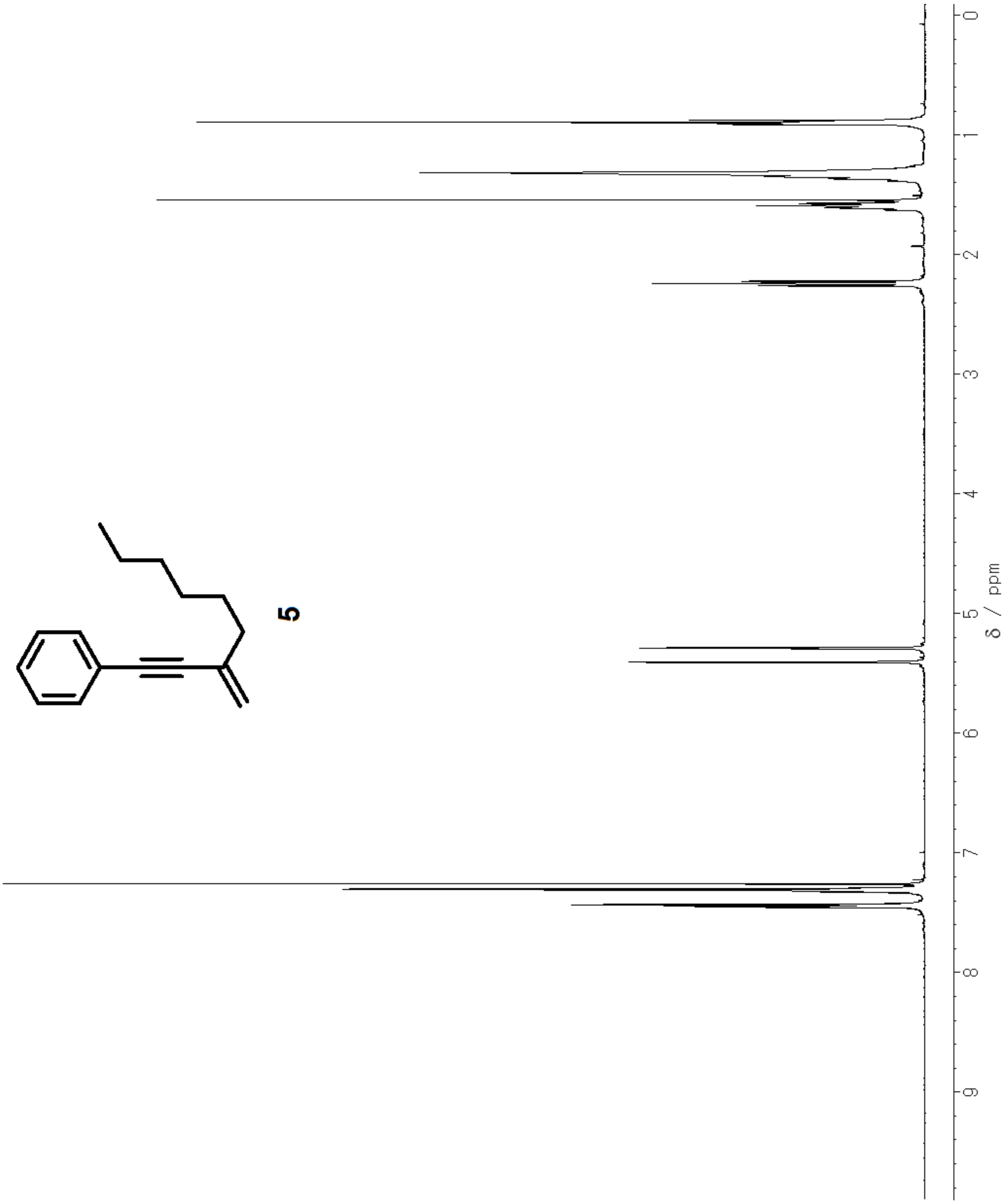
Compound 4b

^{13}C NMR spectrum in $CDCl_3$



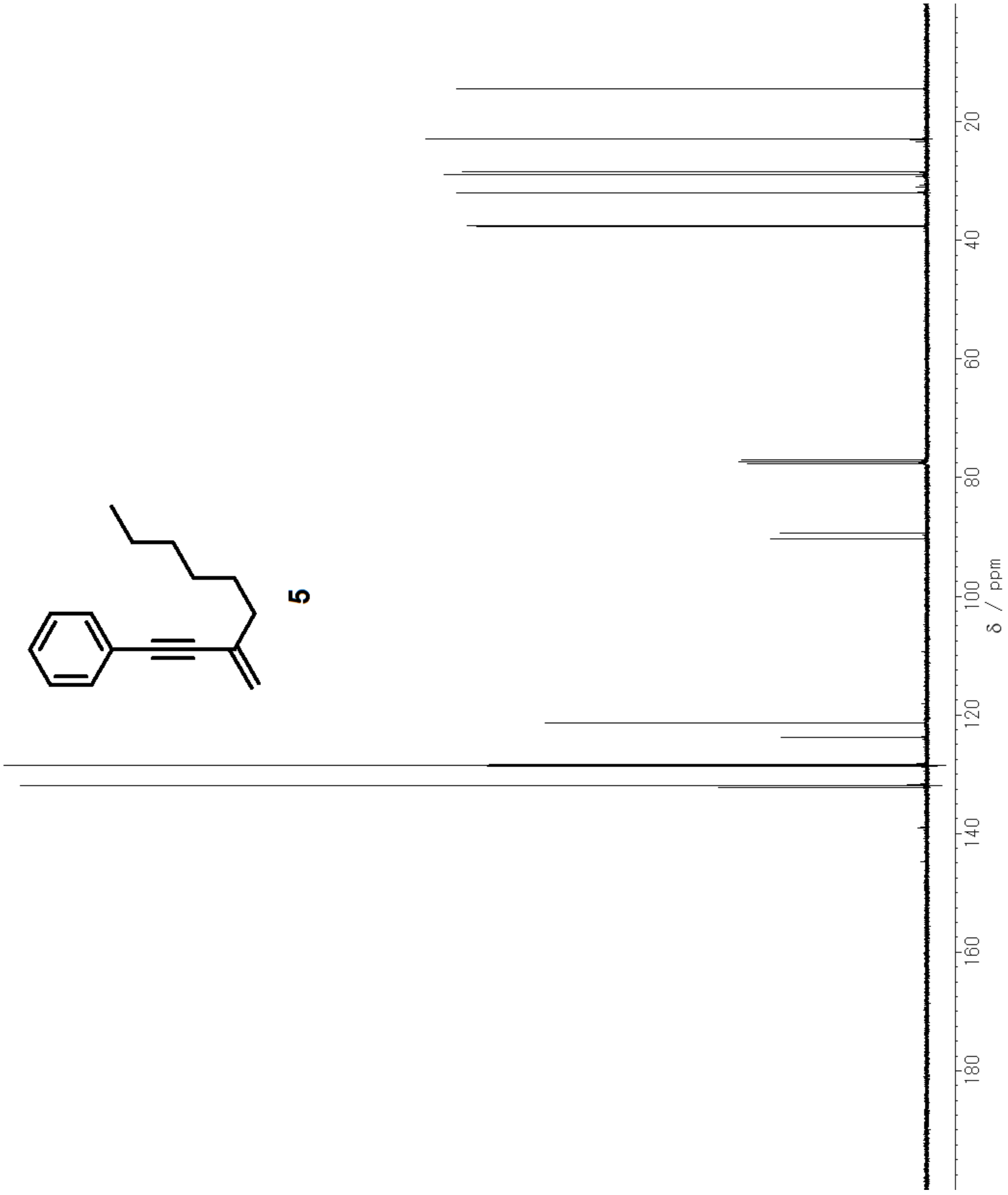
Compound 5

^{1}H NMR spectrum in $CDCl_3$



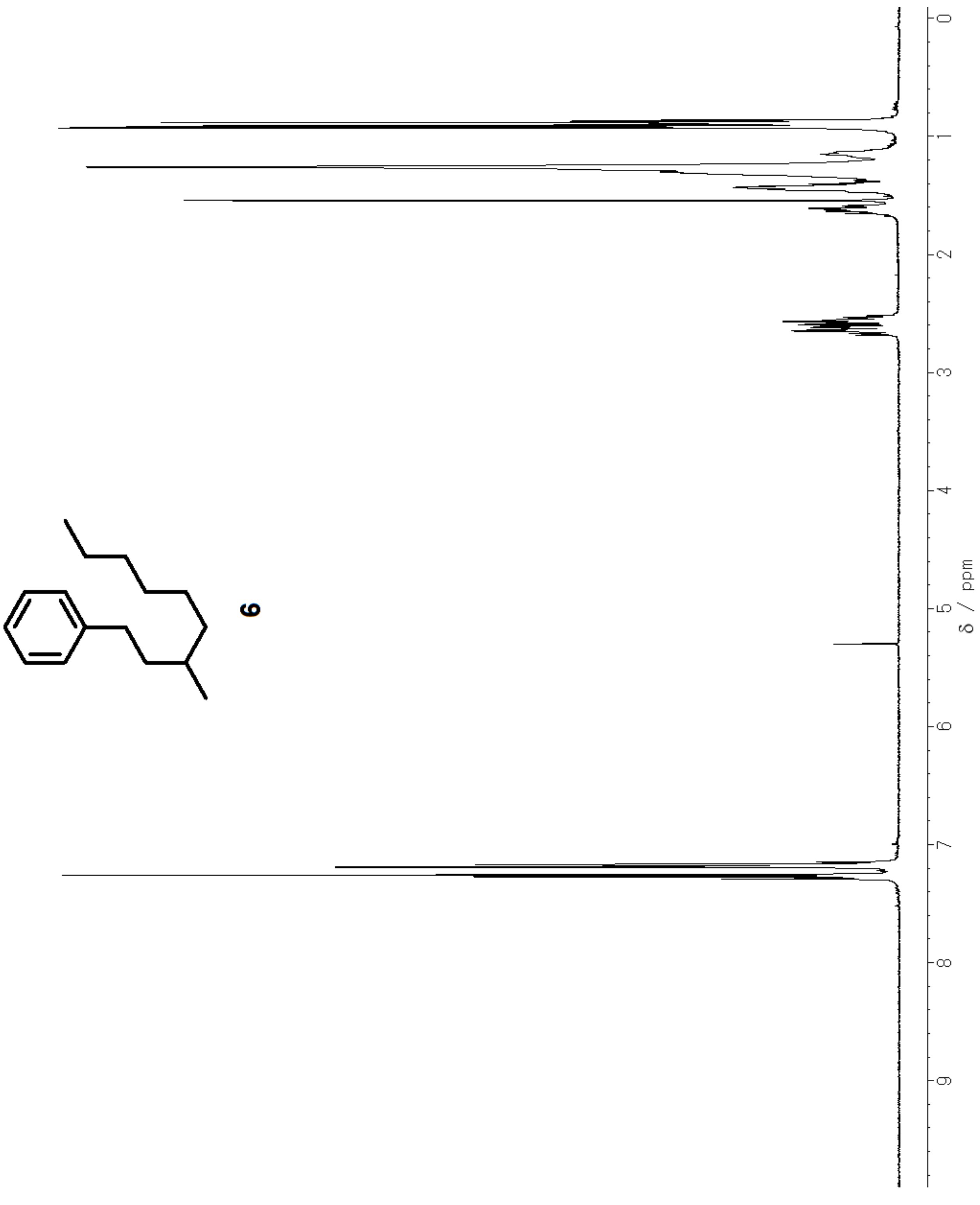
Compound 5

^{13}C NMR spectrum in CDCl$_3$



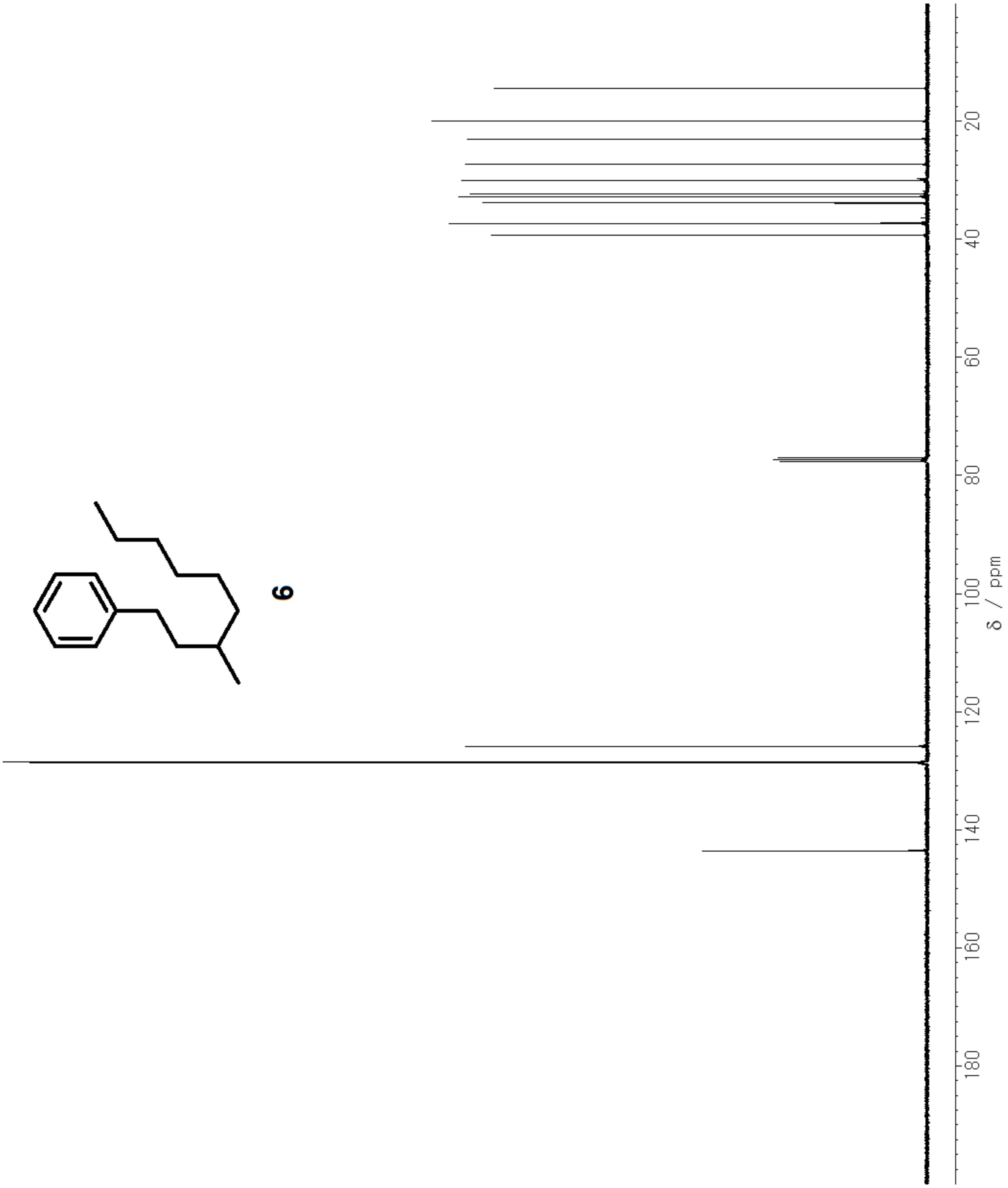
Compound 6

^{1}H NMR spectrum in $CDCl_3$



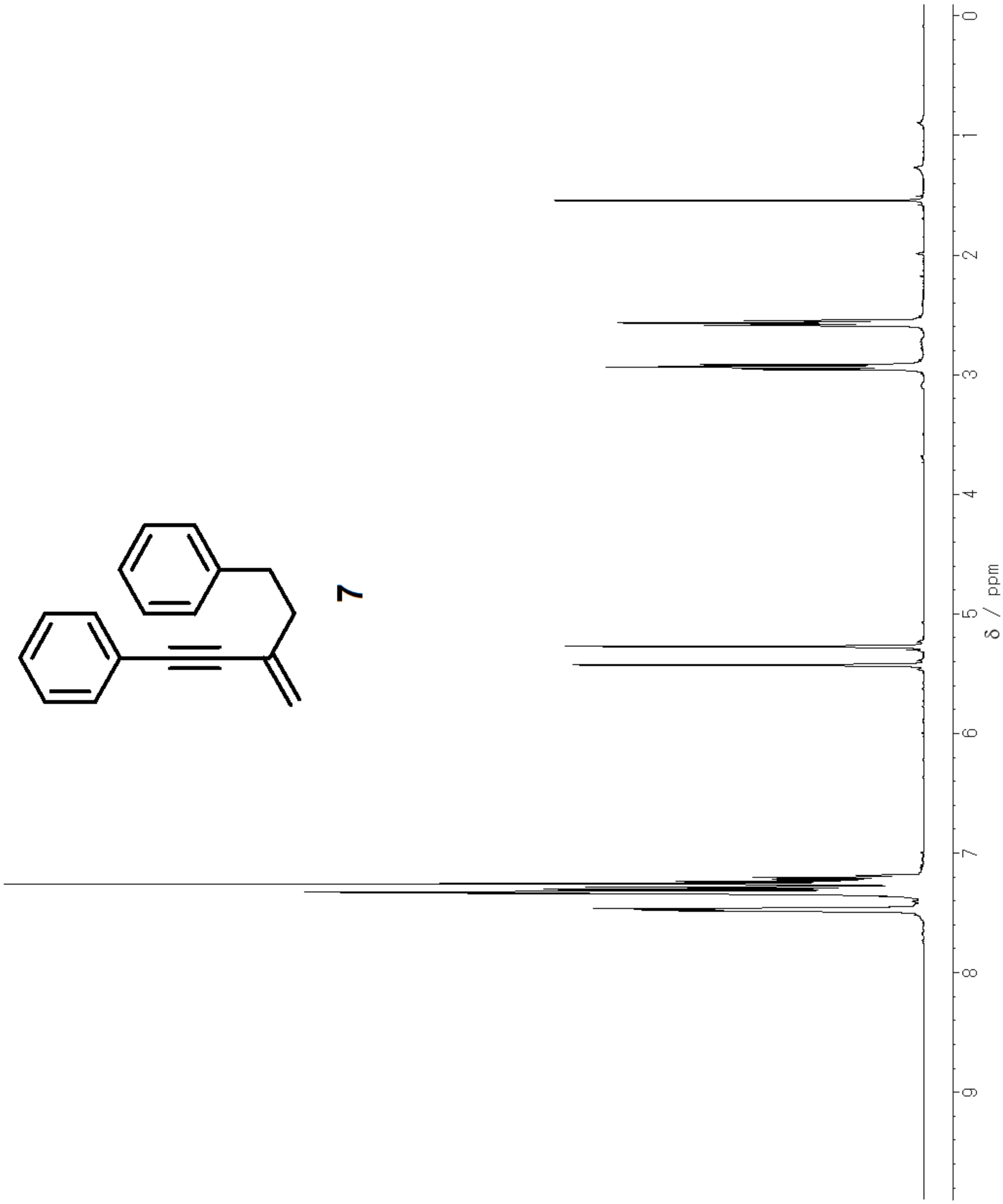
Compound 6

^{13}C NMR spectrum in $CDCl_3$



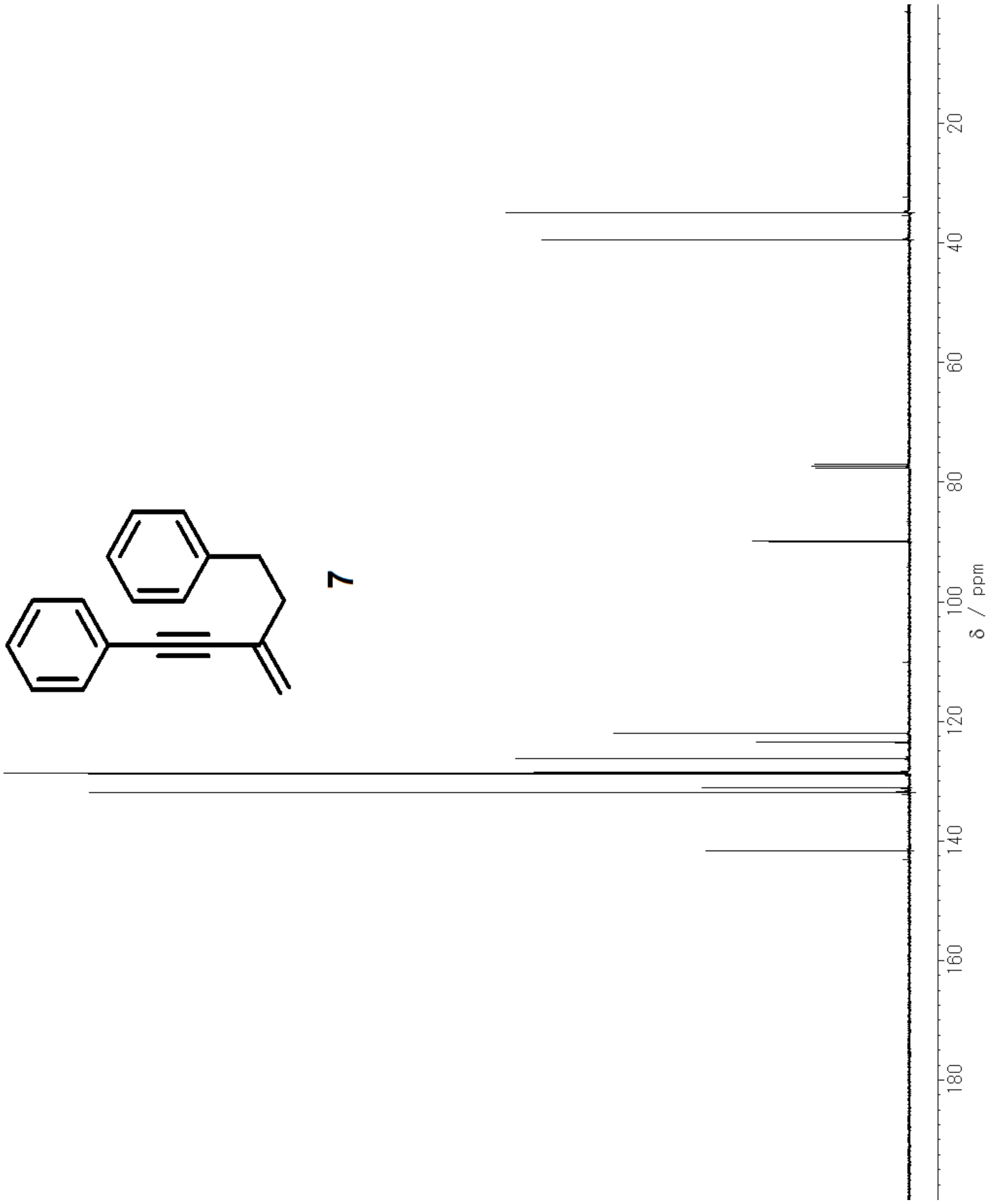
Compound 7

^{1}H NMR spectrum in $CDCl_3$


7

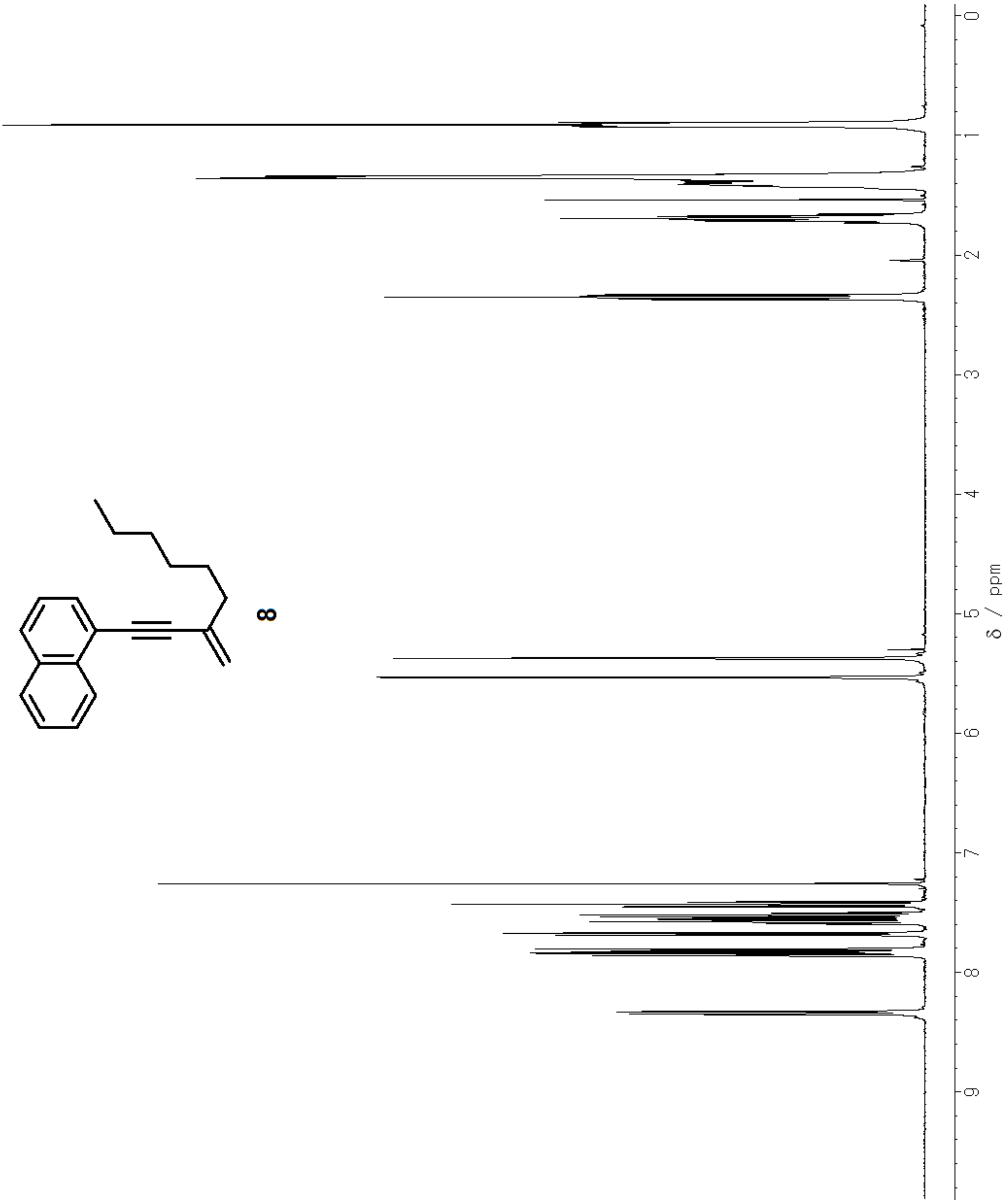
Compound 7

^{13}C NMR spectrum in CDCl$_3$



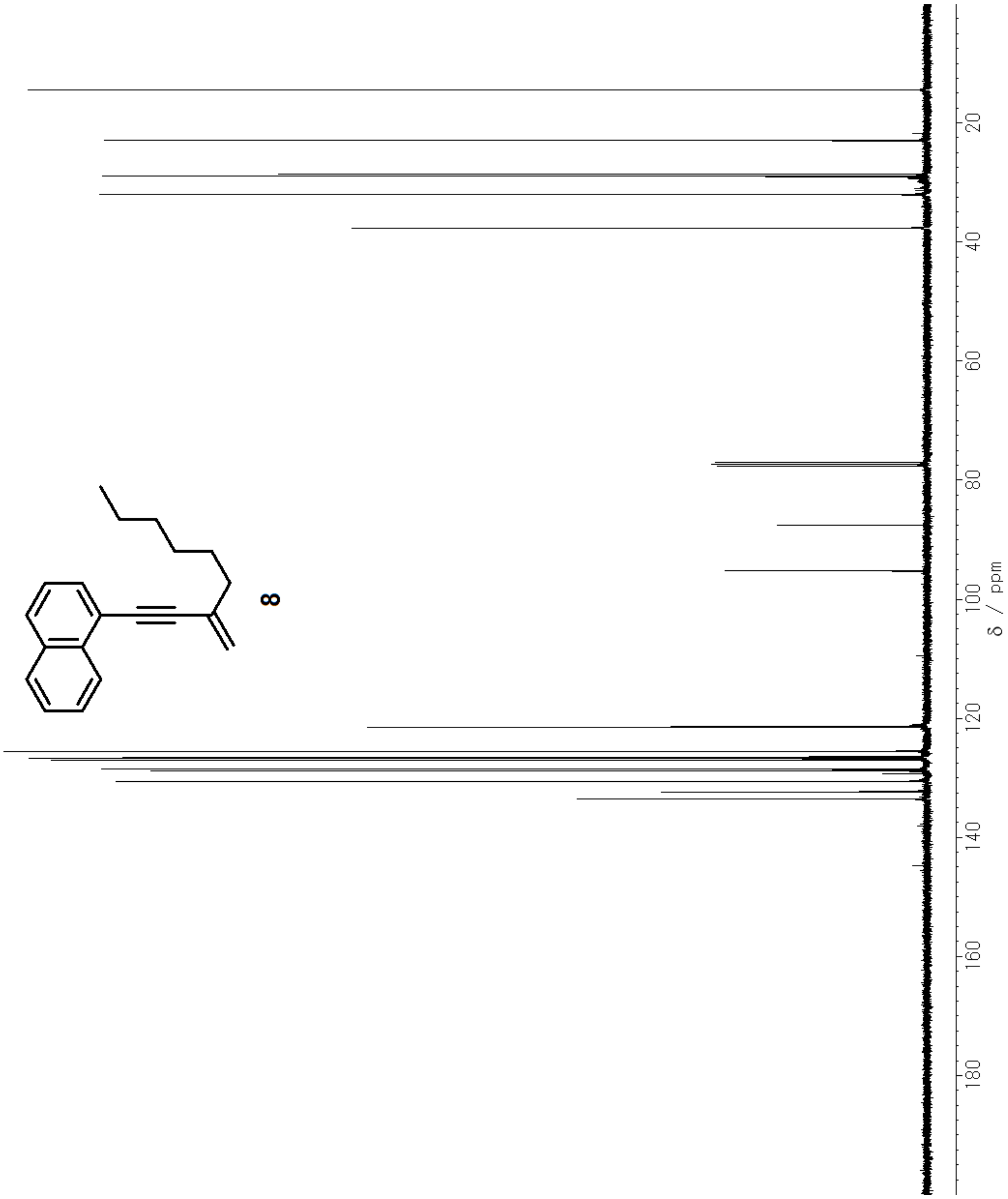
Compound 8

^{1}H NMR spectrum in $CDCl_3$



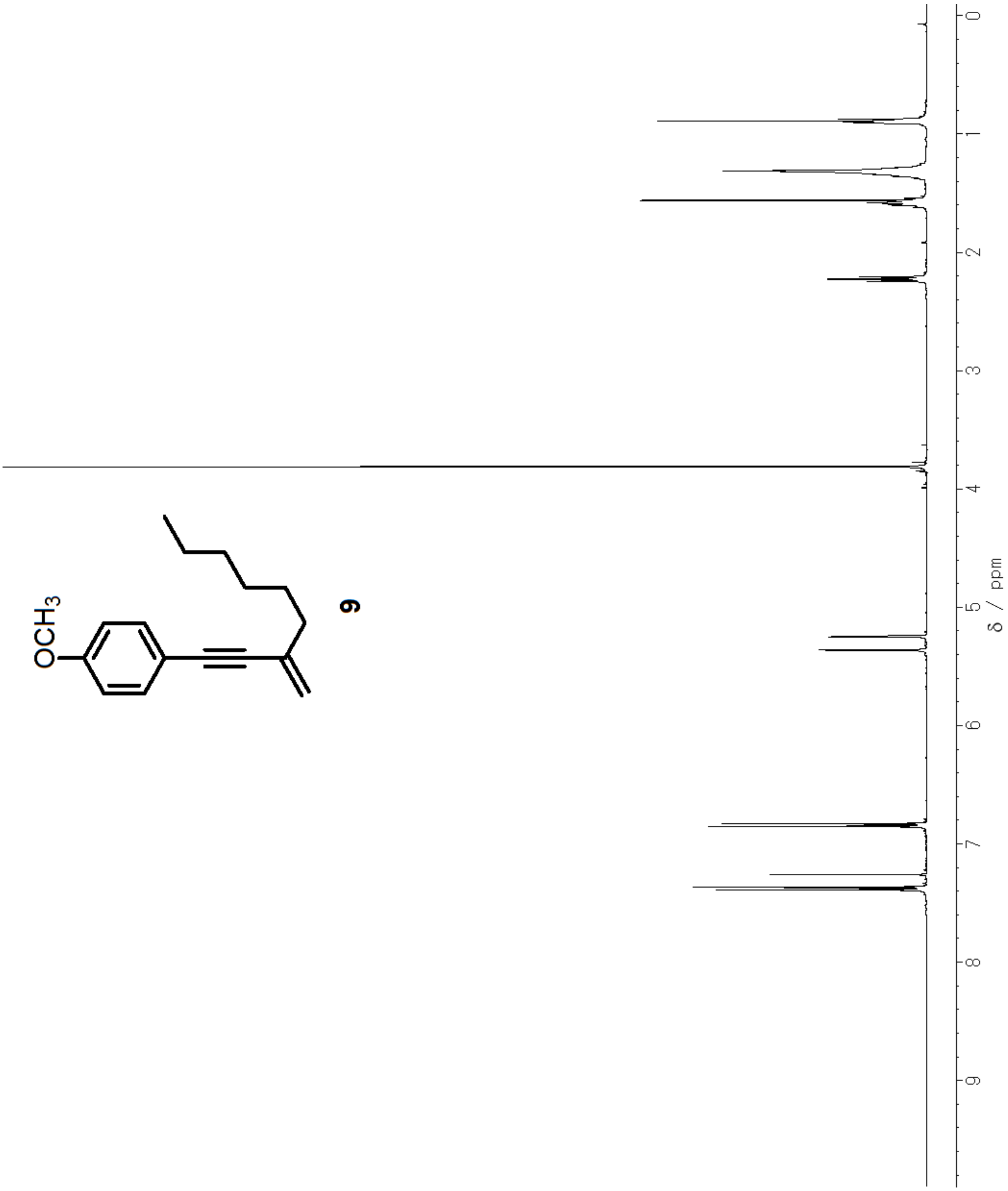
Compound 8

^{13}C NMR spectrum in CDCl$_3$



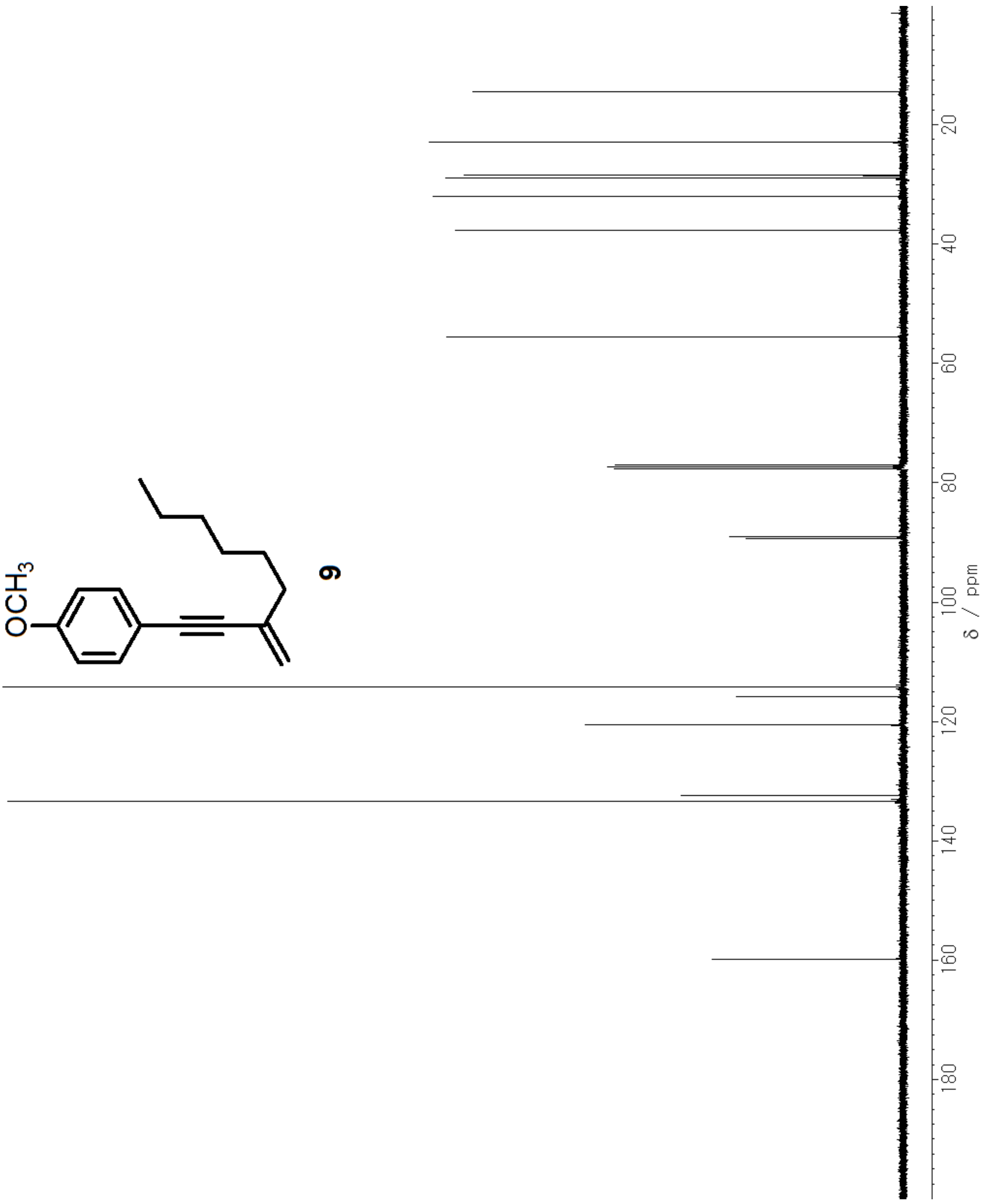
Compound 9

^{1}H NMR spectrum in $CDCl_3$



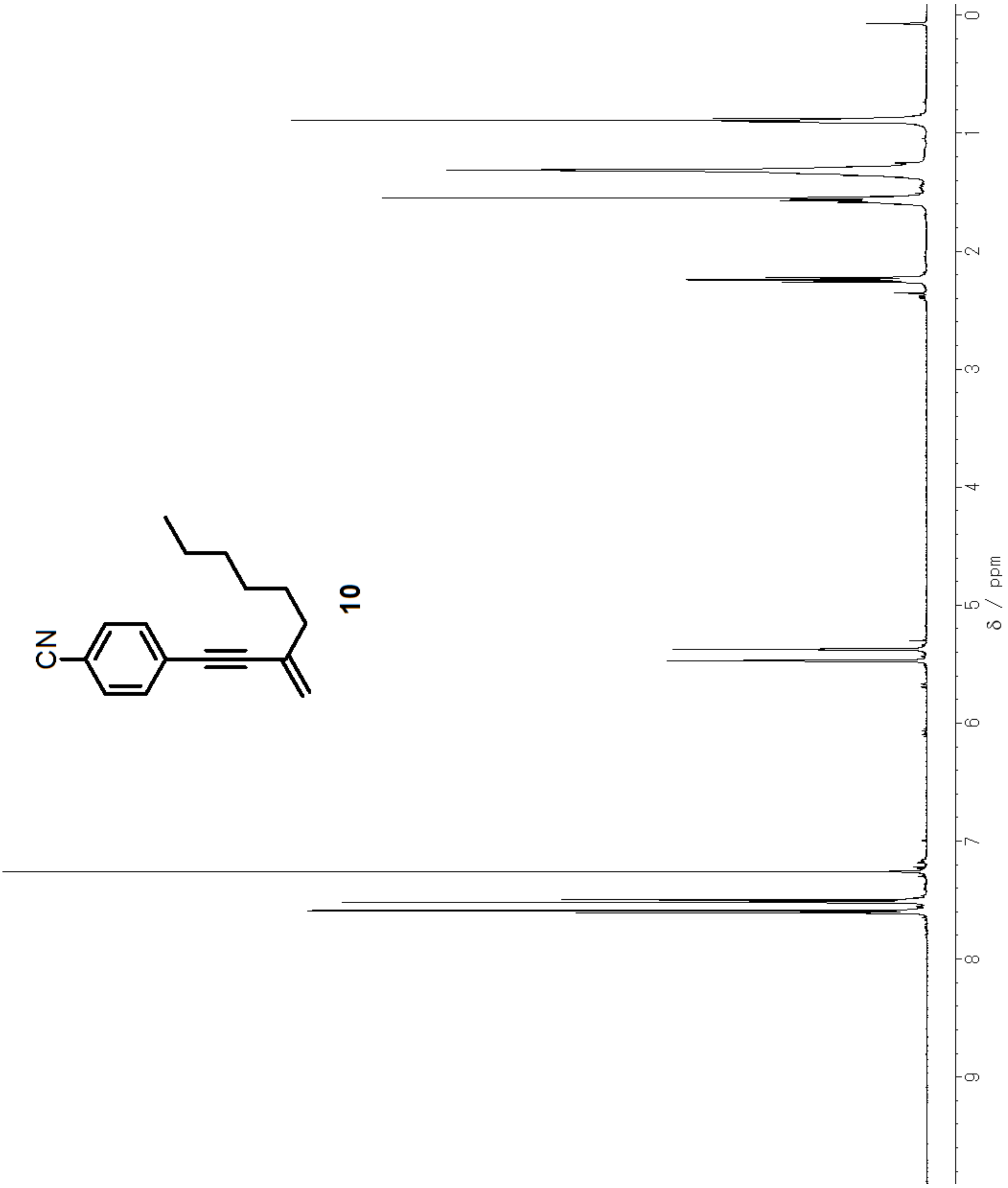
Compound 9

^{13}C NMR spectrum in CDCl$_3$



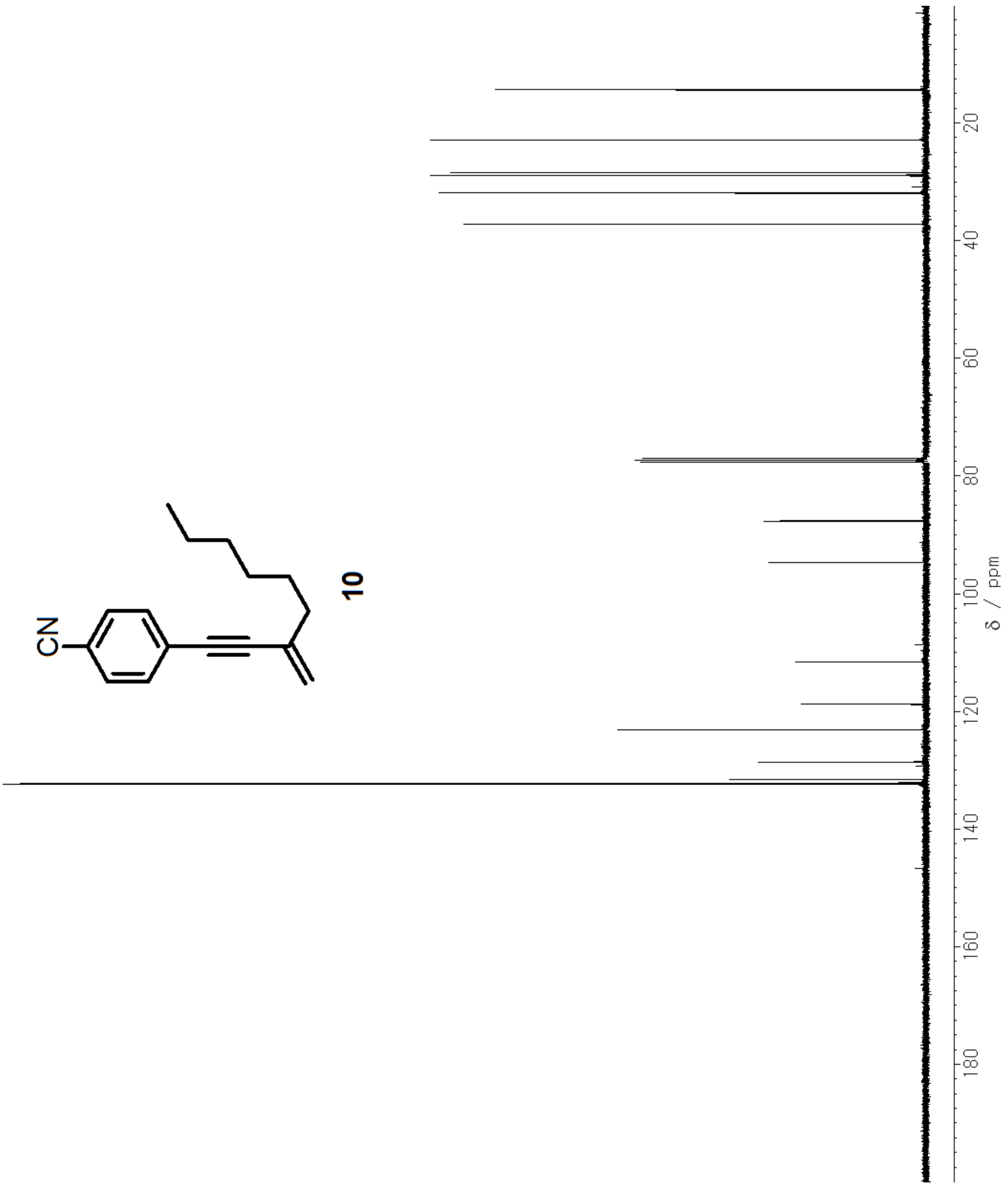
Compound 10

^{1}H NMR spectrum in $CDCl_3$



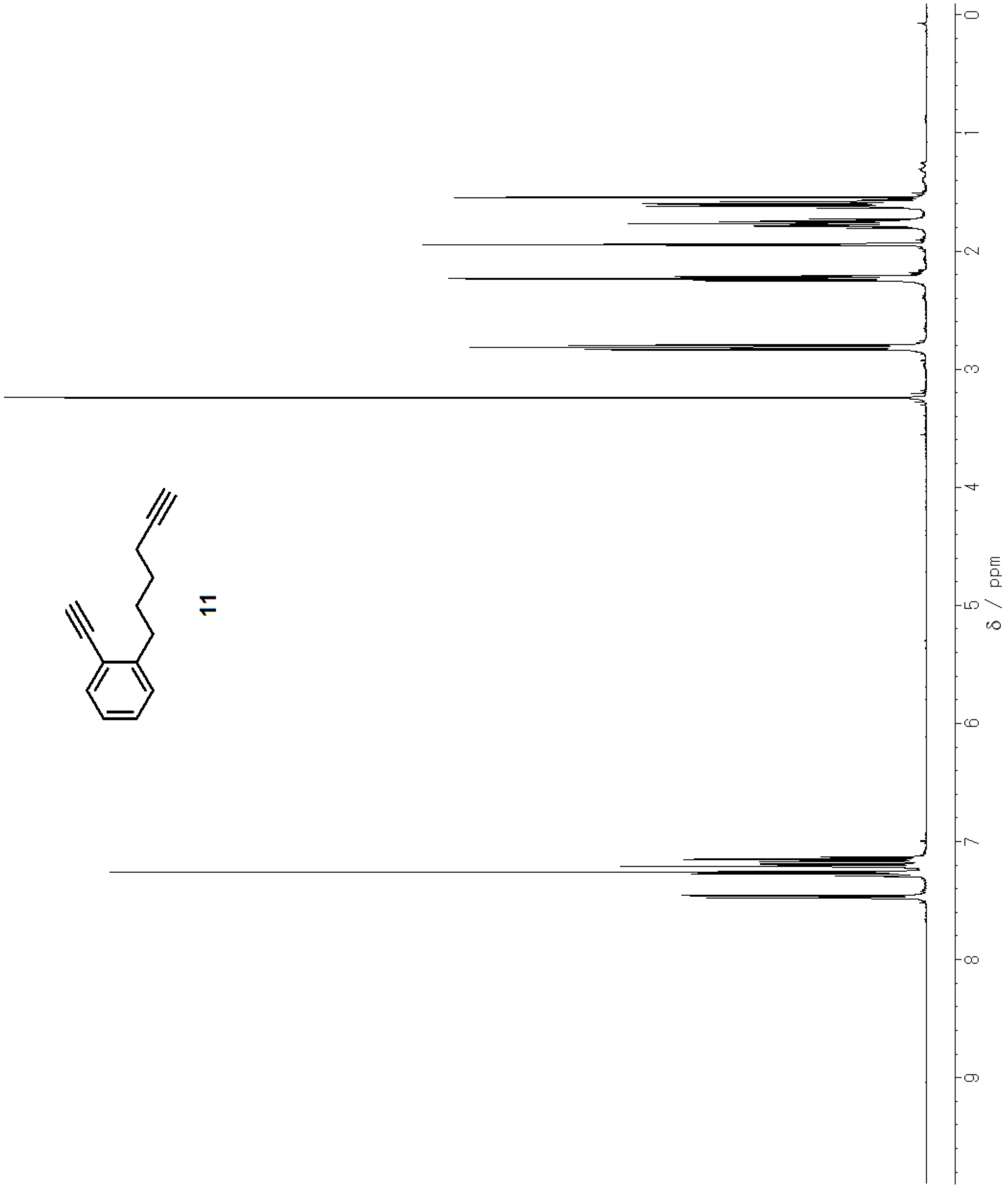
Compound 10

^{13}C NMR spectrum in CDCl$_3$



Compound 11

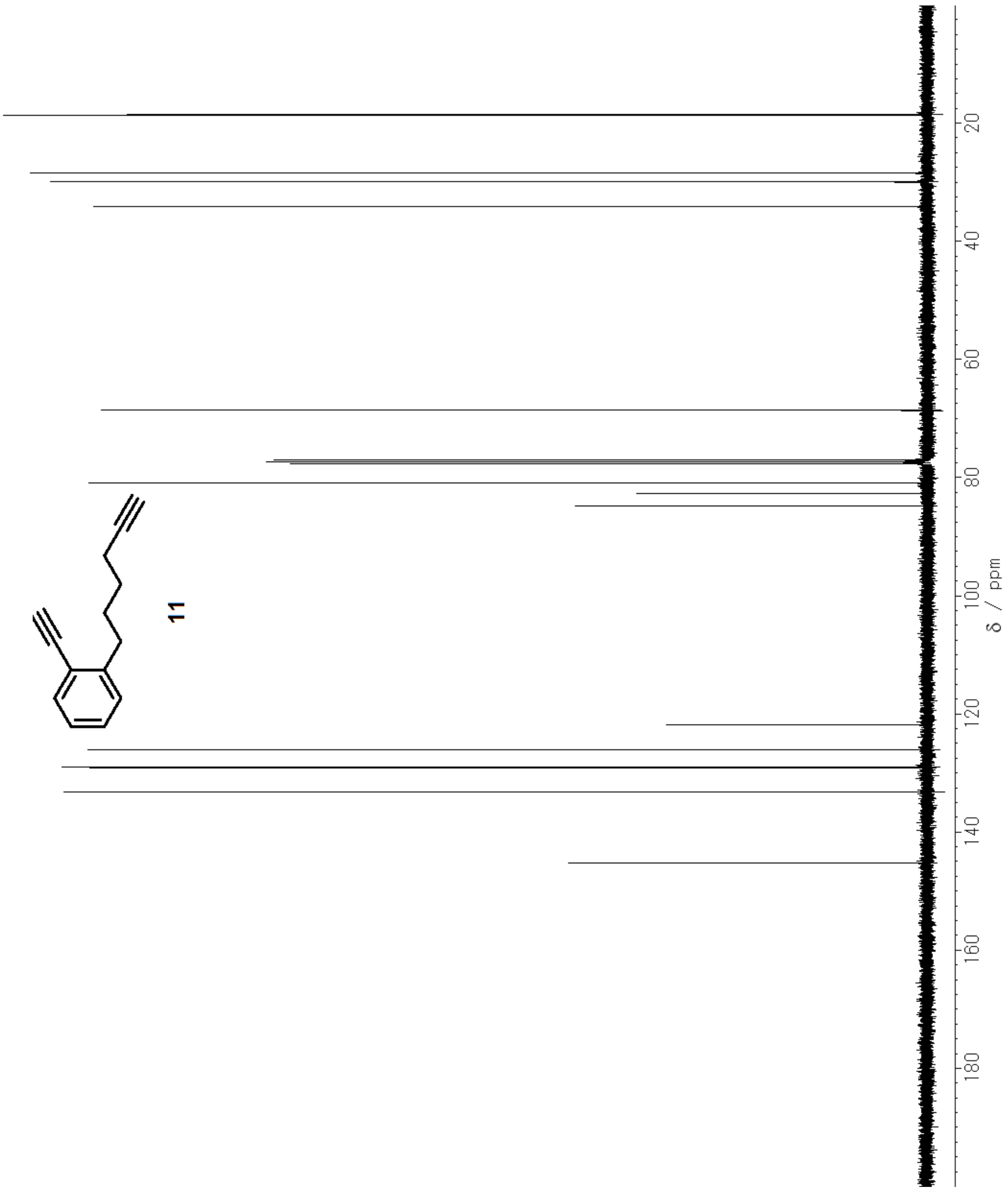
^{1}H NMR spectrum in CDCl$_3$



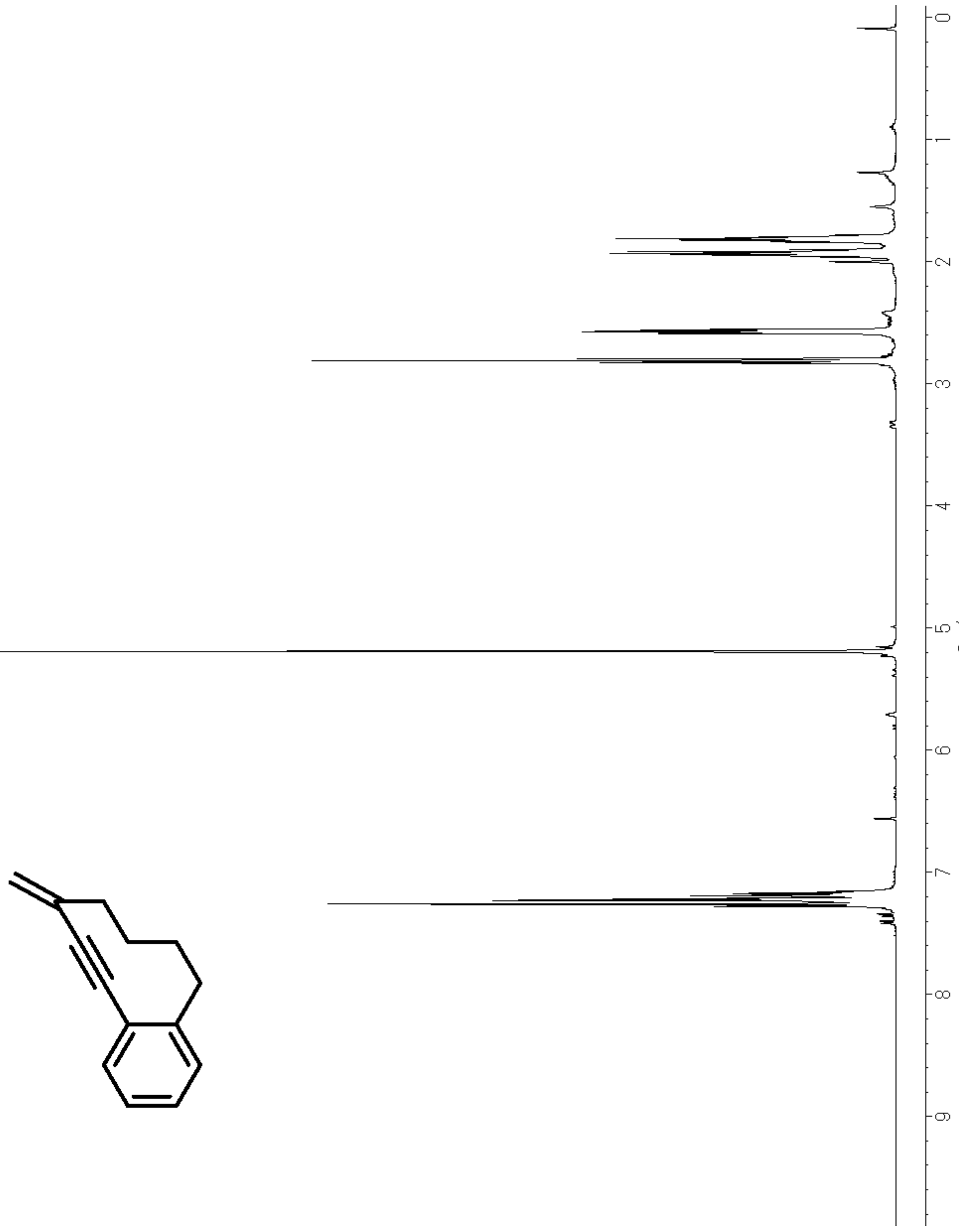
11

Compound 11

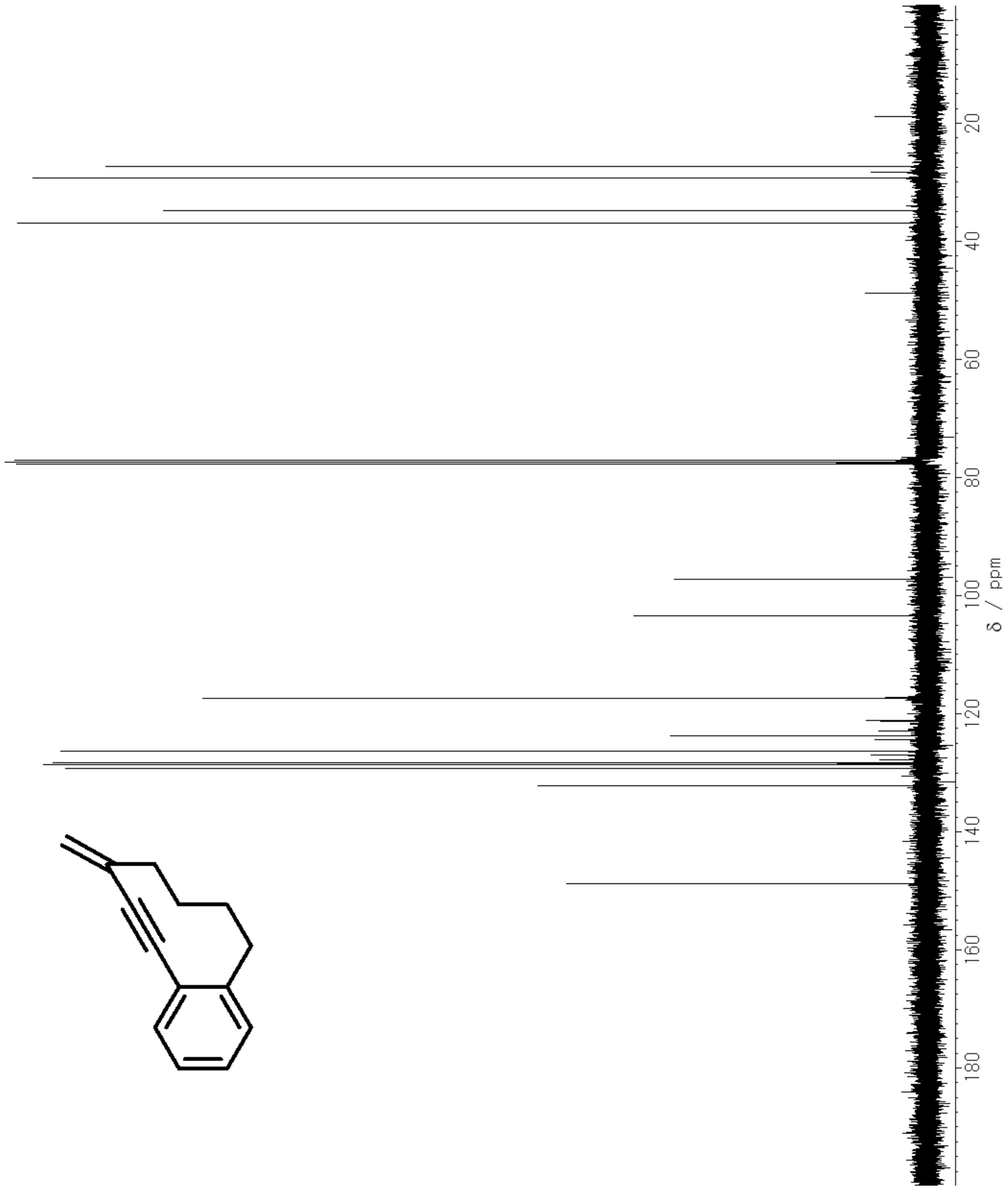
^{13}C NMR spectrum in CDCl$_3$



^{1}H NMR spectrum in $CDCl_3$

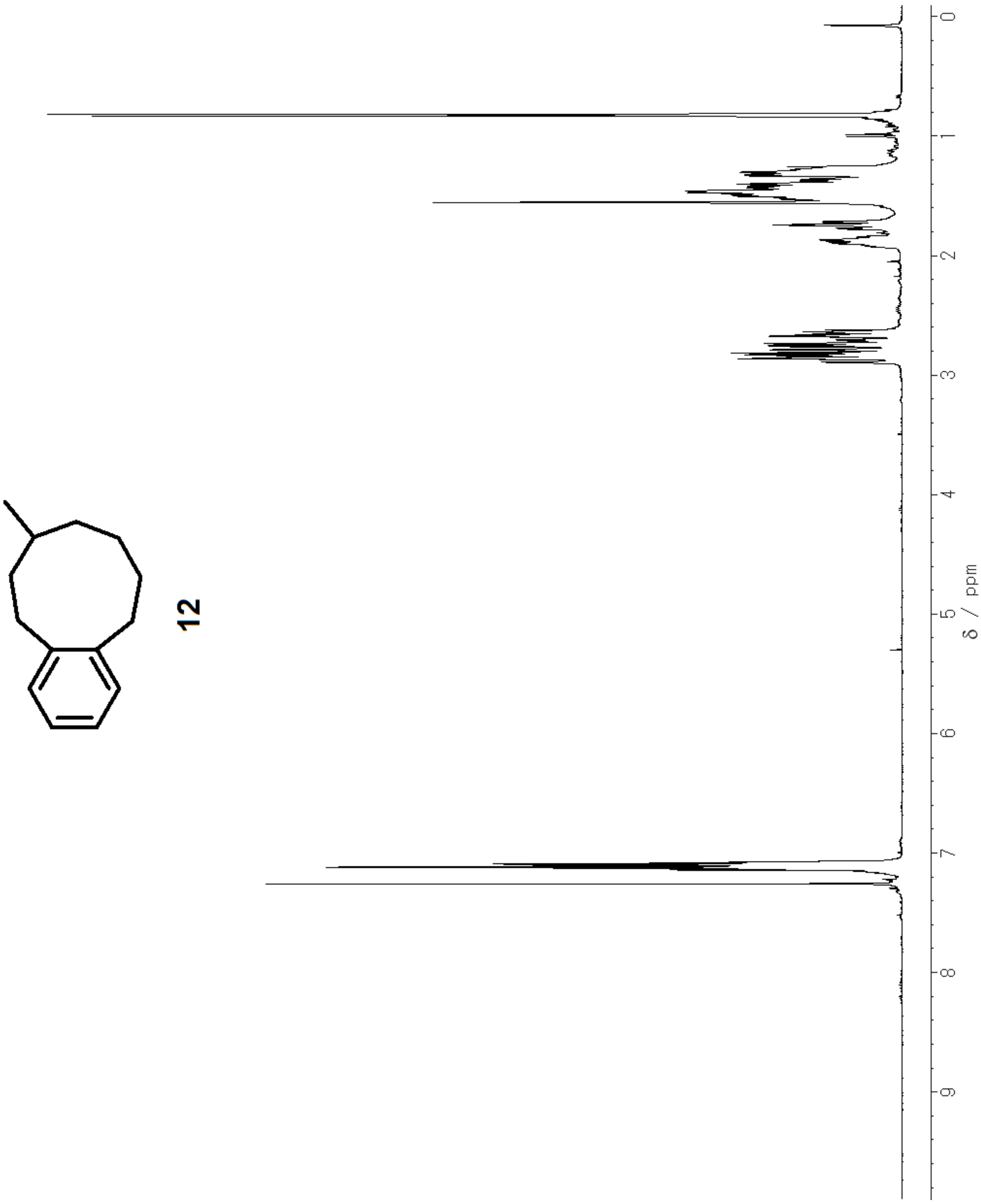


^{13}C NMR spectrum in $CDCl_3$



Compound 12

^{1}H NMR spectrum in $CDCl_3$



12

Compound 12

^{13}C NMR spectrum in $CDCl_3$