Total Synthesis of (+)-Clavilactone A and (–)-Clavilactone B by Ring-Opening/Ring-Closing Metathesis

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Supporting Information

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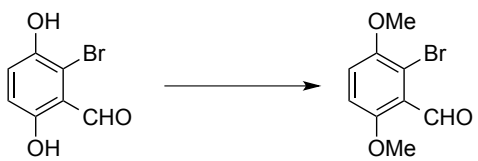
1. Experimental procedures for new compounds

General methods. Melting points are uncorrected. Specific rotations were measured in a 100 mm cell. ^{1}H NMR spectra were recorded at 500 MHz with tetramethylsilane as an internal standard on a JEOL JNM-ECA500 spectrometer. ^{13}C NMR spectra were recorded at 125 MHz. High-resolution mass spectra (HRMS) were measured by the EI mode (70 eV) on a JEOL JMS-GCmate spectrometer. Thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} plates. The crude reaction mixtures and extracted materials were purified by chromatography on Silica gel 60 (Merck) or Wakogel C-300 (Wako). Unless otherwise noted, reactions were carried out at room temperature. Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from the reaction mixture and the combined organic extracts by concentration under reduced pressure using an evaporator with bath at 35–45 °C.

2-Bromo-3,6-dimethoxybenzaldehyde (11).

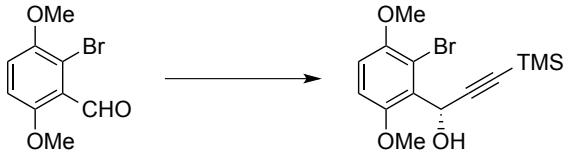


10 **11**

To a cooled (0 °C) stirred solution of **10** (2.46 g, 11.3 mmol) in DMF (110 mL) were added K_2CO_3 (4.71 g, 34.1 mmol) and Me_2SO_4 (3.2 mL, 34 mmol). After being stirred at room

temperature for 1.5 h, the mixture was diluted with EtOAc (170 mL) and washed with 1 M aqueous HCl (70 mL), H_2O (100 mL) and saturated brine (100 mL), respectively. The organic layer was dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 1.63 g (59%) of **11** and 230 mg (9%) of mono-methyl ether. Compound **11** was obtained as pale yellow crystals: mp 98.5–100 °C; TLC R_f 0.36 (EtOAc/hexane, 1:2); IR (KBr) 2959, 1691, 1567 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.89 (s, 3H), 6.93 (d, 1H, J = 9.2 Hz), 7.07 (d, 1H, J = 9.2 Hz), 10.41 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.6, 57.2, 111.5 (2C), 117.1 (2C), 150.4, 155.4, 190.9; HRMS calcd for $C_9H_9O_3Br$ (M^+) m/z 243.9735, found 243.9746.

(1*S*)-1-(2-Bromo-3,6-dimethoxyphenyl)-3-(trimethylsilyl)prop-2-yn-1-ol (12).



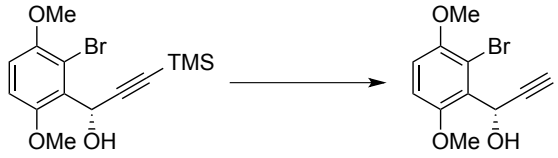
11 **12**

The following reaction was carried out under Ar. To a stirred solution of (*S*)-BINOL (2.37 g, 8.29 mmol) in CH_2Cl_2 (150 mL) were added *N*-methylimidazole (0.33 mL, 4.1 mmol), trimethylsilylacetylene (23 mL, 166 mmol) and Et_2Zn (1.00 M solution in hexane, 166 mL, 166 mmol), respectively. The mixture was stirred at room temperature for 24 h, and $Ti(OiPr)_4$ (6.2 mL, 21 mmol) was added. The mixture was stirred for 1 h, and then a solution of **11** (2.03 g, 8.28 mmol) in CH_2Cl_2 (15 mL) was added. After being stirred for 15 min, the mixture was quenched with saturated aqueous NH_4Cl (50 mL) at –78 °C and diluted with H_2O (50 mL). The precipitated solids were removed by filtration through a pad of Celite and washed well with CH_2Cl_2. The filtrate and washings were combined and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layers were washed with saturated brine (50 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:30) to provide 2.20 g (77%, 85% ee) of **12** as white crystals and (*S*)-BINOL was quantitatively recovered.

Recrystallization of the obtained **12** (85% ee, 2.20 g) from acetone/hexane (1:20) provided 1.75 g (80%) of optically pure **12** (>99% ee): mp 82–84 °C; TLC R_f 0.54 (EtOAc/hexane, 1:2); $[\alpha]^{26}_D$ –11.2 (*c* 1.78, $CHCl_3$); IR (KBr) 3546, 2960, 2175 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.14 (s, 9H), 3.84 (s, 3H), 3.90 (s, 3H), 4.09 (d, 1H, J = 11.4 Hz, OH), 5.96 (d, 1H, J = 11.4 Hz), 6.82 (d, 1H, J = 9.0 Hz), 6.89 (d, 1H, J = 9.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ –0.2 (3C), 56.8, 56.9, 63.5, 89.0, 104.8, 111.3, 112.0, 113.1, 130.7, 150.7, 152.3; HRMS calcd for $C_{14}H_{19}O_3BrSi$ (M^+) m/z 342.0287,

found 342.0287; HPLC analysis (column, Daicel Chiralcel OJ-H 0.46 cmΦ × 25 cm, 2-propanol/hexane = 1:15, flow rate = 0.5 mL/min); t_R (min) = 31.4 for **12**, 46.1 for *ent*-**12**.

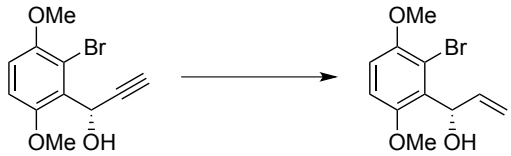
(1*S*)-1-(2-Bromo-3,6-dimethoxyphenyl)prop-2-yn-1-ol (13).



12 **13**

To a cooled (0 °C) stirred solution of **12** (1.03 g, 3.00 mmol) in MeOH (30 mL) was added K_2CO_3 (234 mg, 1.69 mmol). The mixture was stirred at room temperature for 2.5 h, diluted with H_2O (60 mL) and extracted with CH_2Cl_2 (30 mL × 6). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 814 mg (100%) of **13** as white crystals: mp 44–47 °C; TLC R_f 0.41 (EtOAc/hexane, 1:2); $[\alpha]^{26}_D$ +5.9 (*c* 1.74, $CHCl_3$); IR (KBr) 3537, 3289, 2949 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.51 (d, 1H, *J* = 2.3 Hz), 3.85 (s, 3H), 3.92 (s, 3H), 4.29 (d, 1H, *J* = 11.5 Hz, OH), 6.01 (dd, 1H, *J* = 11.5, 2.3 Hz), 6.83 (d, 1H, *J* = 8.9 Hz), 6.90 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.7, 56.9, 63.2, 72.4, 83.2, 111.4, 111.5, 113.0, 129.8, 150.7, 152.1; HRMS calcd for $C_{11}H_{11}O_3Br$ (M^+) *m/z* 269.9892, found 269.9904.

(1*S*)-1-(2-Bromo-3,6-dimethoxyphenyl)prop-2-en-1-ol (8).

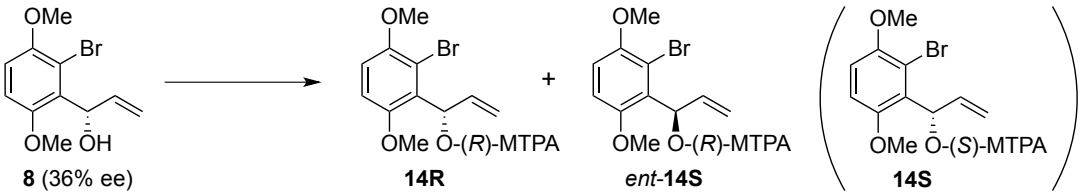


13 **8**

A solution of **13** (814 mg, 3.00 mmol) in EtOAc (30 mL) was stirred under atmospheric hydrogen for 1.5 h in the presence of Lindlar catalyst (86.9 mg) and pyridine (0.12 mL, 1.49 mmol). Additional Lindlar catalyst (total 221 mg) was added in several portions during the course of the reaction. The mixture was stirred under atmospheric hydrogen for total 7 h. The catalyst was removed by filtration through a Celite pad and washed well with EtOAc. The combined filtrate and washings were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 820 mg (100%) of **8** as white crystals: mp 53–54 °C; TLC R_f 0.41 (EtOAc/hexane, 1:2); $[\alpha]^{27}_D$ –7.5 (*c* 1.12, $CHCl_3$); IR (KBr) 3536, 2939, 1575 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.85 (s, 3H), 4.17 (d, 1H, *J* = 10.8 Hz, OH), 5.12 (dt, 1H, *J* = 10.5, 1.4 Hz), 5.26 (dt, 1H, *J* = 17.3, 1.4 Hz), 5.77 (br dd, 1H, *J* = 10.8, 5.2 Hz), 6.14 (ddd, 1H, *J* = 17.3, 10.5, 5.2 Hz), 6.79 (d, 1H, *J* = 9.1 Hz), 6.85 (d, 1H, *J* = 9.1

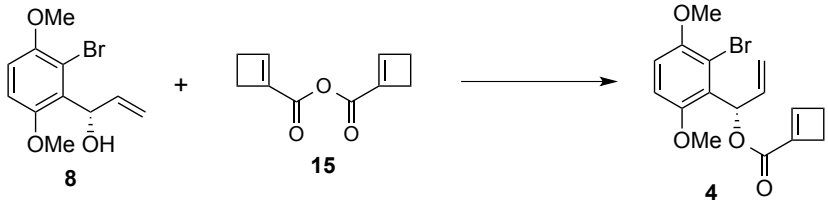
Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.3, 56.8, 75.1, 110.7, 110.9, 113.8, 114.4, 131.3, 138.6, 150.7, 152.0; HRMS calcd for $C_{11}H_{13}O_3Br$ (M^+) *m/z* 272.0048, found 272.0048.

Mixture of (1*S*)-1-(2-Bromo-3,6-dimethoxyphenyl)prop-2-en-1-yl (2*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (14R) and its diastereomer (*ent*-14S).



To a cooled (0 °C) stirred solution of **8** (36% ee, 6.6 mg, 24 μmol) in CH_2Cl_2 (1 mL) were added (*R*)-MTPA (11.4 mg, 48.7 μmol), DCC (15.4 mg, 74.6 μmol) and DMAP (5.8 mg, 47 μmol). The mixture was stirred at room temperature for 2.5 h, and (*R*)-MTPA (12.2 mg, 52.0 μmol), DCC (16.2 mg, 78.5 μmol) and DMAP (6.5 mg, 53 μmol) were added. After being stirred for 2 h, the mixture was diluted with EtOAc (2 mL). The precipitated solids were removed by filtration through a pad of Celite and washed well with EtOAc. The combined filtrate and washings were washed with saturated brine (15 mL), dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:30) to provide 9.0 mg (76%) of a mixture of **14R** and *ent*-**14S** (**14R**/*ent*-**14S** = ca. 2:1) as white solids: TLC R_f 0.51 (EtOAc/hexane, 1:2); ^{1}H NMR (500 MHz, $CDCl_3$) for compound **14R** δ 3.57 (s, 3H), 3.846 (s, 3H), 3.851 (s, 3H), 5.25 (dt, 1H, *J* = 10.3, 1.2 Hz), 5.43 (dt, 1H, *J* = 17.4, 1.2 Hz), 6.36 (ddd, 1H, *J* = 17.4, 10.3, 6.9 Hz), 6.75 (d, 1H, *J* = 9.0 Hz), 6.84 (d, 1H, *J* = 9.0 Hz), 7.11 (d, 1H, *J* = 6.9 Hz), 7.31–7.57 (m, 5H); for compound *ent*-**14S** δ 3.50 (s, 3H), 3.846 (s, 3H), 3.851 (s, 3H), 5.21 (dt, 1H, *J* = 10.5, 1.2 Hz), 5.35 (dt, 1H, *J* = 17.5, 1.2 Hz), 6.26 (ddd, 1H, *J* = 17.5, 10.5, 6.5 Hz), 6.83 (d, 1H, *J* = 9.20 Hz), 6.87 (d, 1H, *J* = 9.2 Hz), 7.17 (d, 1H, *J* = 6.5 Hz), 7.31–7.57 (m, 5H).

(1*S*)-1-(2-Bromo-3,6-dimethoxyphenyl)prop-2-en-1-yl cyclobut-1-encarboxylate (4).

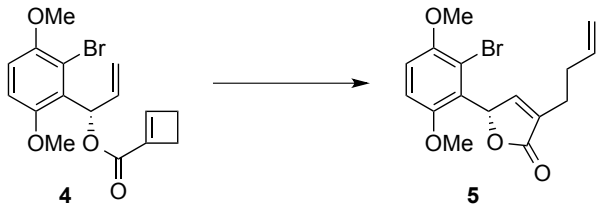


Anhydride **15** was prepared by the following method. To a cooled (0 °C) stirred solution of cyclobutenecarboxylic acid (**9**) (1.46 g, 14.9 mmol) were added Et_3N (2.5 mL, 18 mmol) and triphosgene (894 mg, 3.01 mmol). The mixture was stirred at 0 °C for 10 min and at room temperature for 40 min. Then argon was bubbled through the mixture for 10 min. The mixture

was concentrated under reduced pressure and diluted with THF. The precipitated solids were removed by filtration and washed well with THF. The combined filtrate and washings were concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 1.18 g (88%) of **15** as a colorless oil, which was used immediately in the next step.

The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of *i*Pr_2NH (0.63 mL, 4.5 mmol) in THF (4 mL) was added *n*BuLi (2.69 M solution in hexane, 1.7 mL, 4.6 mmol). The mixture was stirred at 0 °C for 30 min and cooled to –78 °C. A solution of **8** (814 mg, 2.98 mmol) in THF (4 mL) was added and the mixture was stirred at –78 °C for 30 min. Then a solution of **15** (1.14 g, 6.41 mmol) in THF (4 mL) was added. After being stirred at –78 °C for 45 min and at 0 °C for 5 min, the mixture was quenched with saturated aqueous NH_4Cl (30 mL), diluted with H_2O (15 mL) and extracted with EtOAc (30 mL × 3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (30 mL) and saturated brine (30 mL), respectively, dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:50) to provide 892 mg (85%) of **4** as a colorless oil: TLC R_f 0.50 (EtOAc/hexane, 1:2); $[\alpha]^{25}_D$ +36.8 (*c* 0.920, $CHCl_3$); IR (KBr) 2963, 1704, 1572 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.45 (t, 2H, *J* = 3.0 Hz), 2.73 (t, 2H, *J* = 3.0 Hz), 3.83 (s, 3H), 3.84 (s, 3H), 5.22 (d, 1H, *J* = 10.4 Hz), 5.32 (d, 1H, *J* = 16.9 Hz), 6.30 (ddd, 1H, *J* = 16.9, 10.4, 6.2 Hz), 6.81 (s, 1H), 6.83 (d, 1H, *J* = 9.1 Hz), 6.86 (d, 1H, *J* = 9.1 Hz), 7.00 (d, 1H, *J* = 6.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.1, 29.1, 56.9, 57.1, 72.8, 111.8, 112.0, 114.3, 117.3, 128.5, 134.4, 138.7, 146.8, 150.7, 152.8, 161.3; HRMS calcd for $C_{16}H_{17}O_4Br$ (M^+) *m/z* 352.0310, found 352.0308.

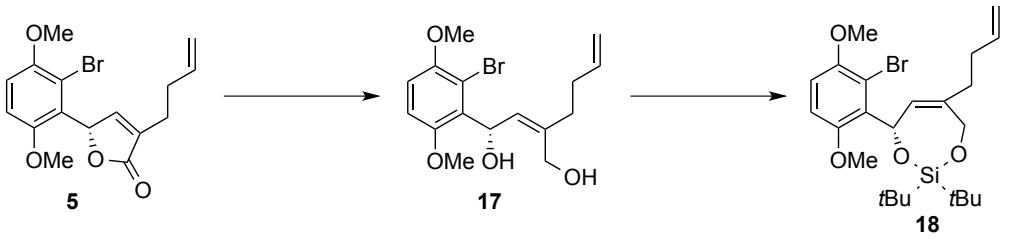
(5*S*)-5-(2-Bromo-3,6-dimethoxyphenyl)-3-(but-3-en-1-yl)-5*H*-furan-2-one (5).



To a heated (80 °C) stirred solution of **4** (892 mg, 2.53 mmol) in degassed toluene (130 mL) was added a solution of Grubbs catalyst 1st generation (208 mg, 0.253 mmol) in degassed toluene (100 mL) using syringe pump over a period of 5 h with bubbling Ar. While the Grubbs catalyst was added, a solution of 2,6-dichloro-1,4-benzoquinone (**16**) (22 mg × 10, 0.12 mmol × 10) in degassed toluene (2 mL × 10) was also added every 30 min. After completion of the addition, a solution of Grubbs catalyst 2nd generation (114 mg, 0.134 mmol) in degassed toluene (11 mL) was added. The mixture was stirred under atmospheric ethylene at 80 °C for 1 h and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel

(EtOAc/hexane, 1:10) to provide 675 mg (76%) of **5** as white crystals: mp 42–45 °C; TLC R_f 0.35 (EtOAc/hexane, 1:2); $[\alpha]^{26}_{D}$ –120 (*c* 0.970, $CHCl_3$); IR (neat) 2938, 1756, 1578 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.32–2.49 (m, 4H), 3.69 (s, 3H), 3.86 (s, 3H), 5.02 (dq, 1H, *J* = 10.4, 1.5 Hz), 5.09 (dd, 1H, *J* = 17.0, 1.5 Hz), 5.85 (ddt, 1H, *J* = 17.0, 10.4, 6.4 Hz), 6.63 (q, 1H, *J* = 1.7 Hz), 6.81 (d, 1H, *J* = 8.9 Hz), 6.89 (d, 1H, *J* = 8.9 Hz), 7.02 (q, 1H, *J* = 1.7 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 24.6, 31.4, 56.6, 57.0, 80.5, 111.5, 112.9, 115.2, 115.6, 122.8, 133.7, 137.1, 145.8, 150.5, 153.6, 174.6; HRMS calcd for $C_{16}H_{17}O_4Br$ (M^+) *m/z* 352.0310, found 352.0307.

(4*S*)-4-(2-Bromo-3,6-dimethoxyphenyl)-6-(but-3-en-1-yl)-2,2-di-*tert*-butyl-4,7-dihydro-1,3,2-dioxasilepine (18).

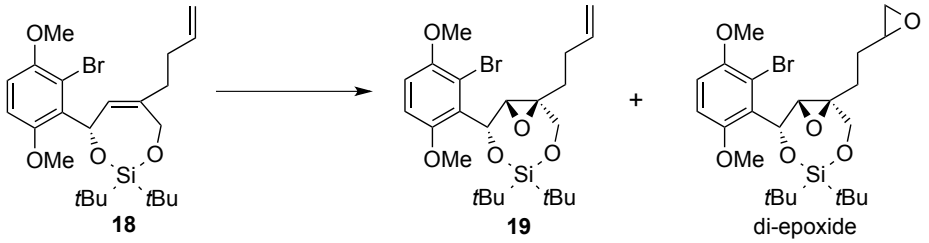


The following reaction was carried out under Ar. To a cooled (–78 °C) stirred solution of **5** (103 mg, 0.291 mmol) in THF (3 mL) was added DIBAL-H (1.0 M solution in toluene, 0.58 mL, 0.58 mmol). The mixture was stirred at –78 °C for 2 h and at 0 °C for 1.5 h, and DIBAL-H (1.0 M solution in toluene, 0.58 mL, 0.58 mmol) was added at –78 °C. The mixture was stirred at –78 °C for 30 min and at 0 °C for 1.5 h, and DIBAL-H (1.0 M solution in toluene, 0.58 mL, 0.58 mmol) was added at –78 °C. The mixture was stirred at –78 °C for 1 h and at 0 °C for 1.5 h, and DIBAL-H (1.0 M solution in toluene, 0.58 mL, 0.58 mmol) was added at –78 °C. After being stirred at –78 °C for 30 min, at 0 °C for 30 min and at room temperature for 30 min, the mixture was quenched with H_2O (5 mL). The precipitated solids were removed by filtration through a pad of Celite and washed well with CH_2Cl_2. The combined filtrate and washings were concentrated under reduced pressure to provide crude **17** (134 mg), which was used in the next step without further purification.

The following reaction was carried out under Ar. To a cooled (–78 °C) stirred solution of crude **17** (134 mg) obtained above in CH_2Cl_2 (3 mL) were added pyridine (0.14 mL, 1.7 mmol) and tBu$_2$Si(OTf)$_2$ (0.19 mL, 0.59 mmol). After being stirred at –78 °C for 20 min, at 0 °C for 15 min and at room temperature for 15 min, the mixture was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 92.5 mg (65% for 2 steps) of **18** as a colorless oil: TLC R_f 0.76 (EtOAc/hexane, 1:2); $[\alpha]^{27}_{D}$ +16.5 (*c* 0.460, $CHCl_3$); IR (neat) 2934, 1576 cm^{-1}; ^1H NMR (500 MHz,

$CDCl_3$) δ 1.05 (s, 9H), 1.06 (s, 9H), 2.04–2.05 (m, 2H), 2.15–2.19 (m, 2H), 3.78 (s, 3H), 3.86 (s, 3H), 4.56 (d, 1H, *J* = 14.9 Hz), 4.69 (d, 1H, *J* = 14.9 Hz), 4.93 (dd, 1H, *J* = 10.3, 1.7 Hz), 5.00 (dd, 1H, *J* = 16.9, 1.7 Hz), 5.60 (br s, 1H), 5.81 (ddt, 1H, *J* =16.9, 10.3, 6.5 Hz), 6.63 (br s, 1H), 6.81 (d, 1H, *J* = 9.0 Hz), 6.84 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$, 50 °C) δ 21.1, 21.5, 27.8 (3C), 27.9 (3C), 32.5, 36.2, 56.5, 57.0 (2C), 66.8, 111.2, 111.5, 114.6, 114.8, 129.2, 133.2, 138.2, 141.2, 150.8, 151.3; HRMS calcd for $C_{24}H_{37}O_4BrSi$ (M^+) *m/z* 496.1644, found 496.1640.

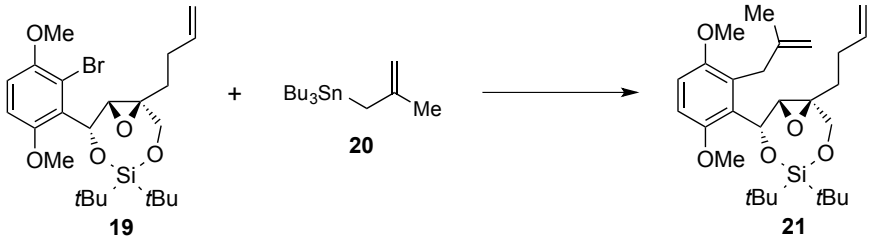
(4*R*,5*R*,6*S*)-4-(2-Bromo-3,6-dimethoxyphenyl)-6-(but-3-en-1-yl)-2,2-di-*tert*-butyl-5,6-epoxy-1,3,2-dioxasilepane (19).



To a cooled (0 °C) stirred solution of **18** (85.2 mg, 0.171 mmol) in CH_2Cl_2 (4 mL) was added mCPBA (65%, 44.0 mg, 0.166 mmol). The mixture was stirred at 0 °C for 3 h and at room temperature for 3.5 h, and mCPBA (65%, 12.6 mg, 0.0475 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 30 min and at room temperature for 1 h, and mCPBA (65%, 15.0 mg, 0.0565 mmol) was added at 0 °C. After being stirred at 0 °C for 30 min and at room temperature for 1 h, the mixture was quenched with 10 wt% aqueous $Na_2S_2O_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:20) to provide 44.7 mg (51%) of **19** and 29.6 mg (33%) of di-epoxide. Compound **19** was obtained as a colorless oil: TLC R_f 0.68 (EtOAc/hexane, 1:2); $[\alpha]^{24}_D$ +42.2 (*c* 1.37, $CHCl_3$); IR (neat) 2936, 1577 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.06 (s, 9H), 1.66 (m, 1H), 2.14–2.20 (m, 3H), 3.75 (d, 1H, *J* = 7.3 Hz), 3.82 (s, 3H), 3.86 (s, 3H), 4.16 (d, 1H, *J* = 12.2 Hz), 4.36 (d, 1H, *J* = 12.2 Hz), 4.96 (dd, 1H, *J* = 10.1, 1.6 Hz), 5.03 (dd, 1H, *J* = 16.9, 1.6 Hz), 5.81 (d, 1H, *J* = 7.3 Hz), 5.82 (ddt, 1H, *J* =16.9, 10.1, 6.2 Hz), 6.86 (d, 1H, *J* = 9.2 Hz), 6.88 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 22.7, 27.1 (3C), 27.8 (3C), 28.1, 33.2, 56.3, 57.0 (2C), 63.2, 64.0, 67.5, 111.1, 111.9, 114.8 (2C), 129.9, 138.0, 150.4, 153.1; HRMS calcd for $C_{20}H_{28}O_5BrSi$ (M^+–*t*-C_4H_9) *m/z* 455.0889, found 455.0887. Di-epoxide (ca. 1:1 diastereomeric mixture) was obtained as white crystals: mp 87–90 °C; TLC R_f 0.50 (EtOAc/hexane, 1:2); IR (neat) 2936, 1577 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.05 (s, 9H), 1.58–1.79 (m, 4H), 2.46–2.48 (m, 1H), 2.73–2.76 (m, 1H), 2.92–2.96 (m, 1H), 3.745 (d, 1H × 1/2, *J* = 7.2 Hz), 3.752 (d, 1H × 1/2, *J* = 7.2 Hz), 3.82 (s, 3H), 3.86 (s, 3H), 4.16 (d, 1H × 1/2, *J* = 12.2 Hz), 4.17 (d, 1H × 1/2, *J* = 12.2 Hz), 4.34 (d, 1H × 1/2, *J* =

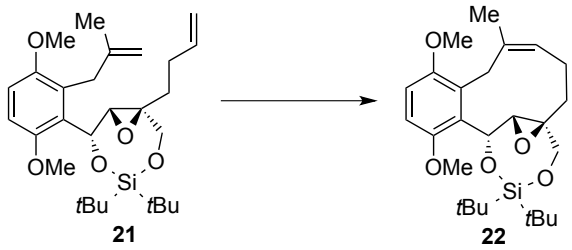
12.2 Hz), 4.35 (d, 1H × 1/2, J = 12.2 Hz), 5.80 (d, 1H × 1/2, J = 7.2 Hz), 5.81 (d, 1H × 1/2, J = 7.2 Hz), 6.86 (d, 1H, J = 9.2 Hz), 6.88 (d, 1H, J = 9.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 22.7, 27.1 (3C), 27.8 (3C), 29.9 (1/2C), 30.0 (1/2C), 47.1 (1/2C), 47.3 (1/2C), 51.9, 56.3, 57.0 (2C), 63.3 (1/2C), 63.4 (1/2C), 63.7 (1/2C), 63.8 (1/2C), 67.3, 67.5, 111.2, 112.0 (2C), 129.8, 150.4, 153.1; HRMS calcd for $C_{24}H_{37}O_6BrSi$ (M^+) m/z 528.1543, found 528.1541.

(4*R*,5*R*,6*S*)-6-(But-3-en-1-yl)-2,2-di-*tert*-butyl-4-[3,6-dimethoxy-2-(2-methylprop-2-en-1-yl)phenyl]-5,6-epoxy-1,3,2-dioxasilepane (21).



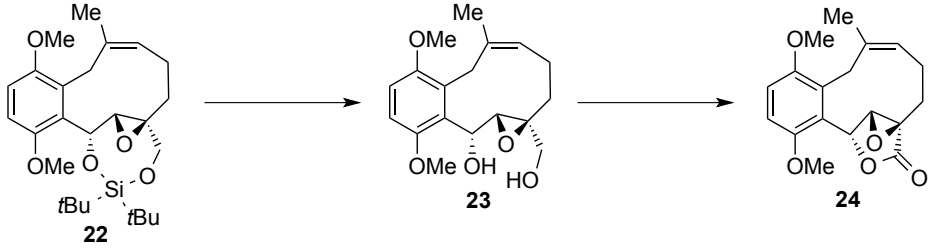
The following reaction was carried out under Ar. To a stirred solution of **19** (196 mg, 0.381 mmol) and CuCl (38.9 mg, 0.393 mmol) in degassed 1,4-dioxane (3 mL) were added a solution of $Pd(PPh_3)_4$ (88.5 mg, 0.0766 mmol) in degassed 1,4-dioxane (6 mL) and a solution of **20** (546 mg, 1.58 mmol) in degassed 1,4-dioxane (3 mL). The mixture was stirred at 80 °C for 1 h and at 100 °C for 20 h, diluted with 1 M aqueous KF (50 mL) and extracted with EtOAc (30 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 123 mg (66%) of **21** as a colorless oil: TLC R_f 0.70 (EtOAc/hexane, 1:4); $[\alpha]^{25}_D$ +37.2 (c 0.285, $CHCl_3$); IR (neat) 2935, 1597 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.05 (s, 9H), 1.62 (m, 1H), 1.82 (s, 3H), 2.04–2.17 (m, 3H), 3.49 (d, 1H, J = 16.9 Hz), 3.55 (d, 1H, J = 7.2 Hz), 3.63 (d, 1H, J = 16.9 Hz), 3.76 (s, 3H), 3.79 (s, 3H), 4.09 (d, 1H, J = 12.3 Hz), 4.31 (s, 1H), 4.32 (d, 1H, J = 12.3 Hz), 4.75 (s, 1H), 4.95 (dd, 1H, J = 10.3, 1.4 Hz), 5.02 (dd, 1H, J = 16.9, 1.4 Hz), 5.47 (br, 1H), 5.81 (ddt, 1H, J =16.9, 10.3, 6.0 Hz), 6.80 (d, 1H, J = 9.0 Hz), 6.83 (d, 1H, J = 9.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4, 22.7, 23.6, 27.1 (3C), 27.8 (3C), 28.0, 33.2, 34.0, 56.0, 56.4 (2C), 64.1, 64.2, 67.6, 109.9, 110.6, 111.0, 114.8, 128.7, 129.3, 138.0, 144.6, 152.1, 152.2; HRMS calcd for $C_{28}H_{44}O_5Si$ (M^+) m/z 488.2958, found 488.2961.

(5*R*,6*R*,7*S*,10*Z*)-14,14-Di-*tert*-butyl-6,7-epoxy-1,4-dimethoxy-11-methyl-5,6,7,8,9,12-hexahydro-5,7-(epoxysilanooxymethano)benzo[10]annulene (22).



The following reaction was carried out with bubbling Ar. To a heated (80 °C) stirred solution of **21** (115 mg, 0.236 mmol) in degassed toluene (130 mL) was added a solution of Grubbs catalyst 2nd generation (41.5 mg, 0.0489 mmol) in degassed toluene (100 mL) using syringe pump over a period of 11 h. While the Grubbs catalyst was added, a solution of 2,6-dichloro-1,4-benzoquinone (**16**) (4.4 mg × 4, 0.025 mmol × 4) in degassed toluene (2 mL × 4) was also added every 1 h. After completion of the addition, the mixture was stirred at 80 °C for further 7 h and concentrated under reduced pressure. The residue was diluted with 10wt% aqueous $Na_2S_2O_3$ (80 mL) and extracted with EtOAc (40 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:100) to provide 75.3 mg (69%) of **22** as a yellow oil: TLC R_f 0.74 (EtOAc/hexane, 1:4); $[\alpha]^{26}_{D}$ +111 (*c* 1.97, $CHCl_3$); IR (neat) 2936, 1596 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 0.99 (s, 9H), 1.10 (s, 9H), 1.53 (s, 3H), 1.58 (m, 1H), 1.90 (m, 1H), 2.02 (m, 1H), 2.31 (m, 1H), 3.64 (br d, 1H, *J* = 14.6 Hz), 3.70 (s, 1H), 3.78 (s, 3H), 3.79 (s, 3H), 3.96 (d, 1H, *J* = 14.6 Hz), 4.17 (d, 1H, *J* = 13.8 Hz), 4.79 (d, 1H, *J* = 13.8 Hz), 5.25 (t, 1H, *J* = 8.3 Hz), 6.36 (s, 1H), 6.77 (d, 1H, *J* = 8.9 Hz), 6.81 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.0, 21.3, 22.4, 23.8, 27.8, 28.3 (3C), 28.4 (3C), 35.2, 55.3, 56.1, 63.5, 64.9, 66.17, 66.19, 109.3, 110.0, 124.8, 128.3, 132.3, 136.0, 150.8, 152.9; HRMS calcd for $C_{26}H_{40}O_5Si$ (M^+) *m/z* 460.2645, found 460.2645.

Dimethyl ether of (+)-clavilactone A (24).

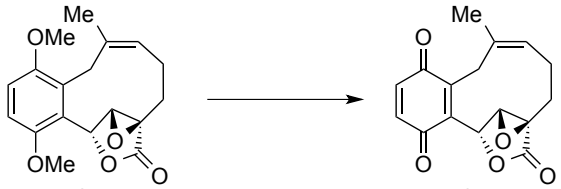


To a cooled (0 °C) stirred solution of **22** (73.4 mg, 0.159 mmol) in THF (3 mL) was added TBAF (1.0 M solution in THF, 0.80 mL, 0.80 mmol). The mixture was stirred at room temperature for 4.5 h, and TBAF (1.0 M solution in THF, 0.80 mL, 0.80 mmol) was added. After being stirred for further 17 h, the mixture was diluted with H_2O (5 mL) and extracted with CH_2Cl_2 (5 mL × 3). The combined extracts were washed with saturated brine (10 mL), dried and

concentrated under reduced pressure to provide crude **23** (127 mg), which was used in the next step without further purification.

The following reaction was carried out under Ar. To a cooled (0 °C) stirred solution of crude **23** (127 mg) obtained above in MeCN (3 mL) were added molecular sieves 4A powder (66.3 mg), NMO (58.8 mg, 0.502 mmol) and TPAP (8.9 mg, 0.025 mmol). The mixture was stirred at room temperature for 1 h, and NMO (54.0 mg, 0.461 mmol) and TPAP (8.5 mg, 0.024 mmol) were added at 0 °C. After being stirred at room temperature for 10 min, the mixture was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:40) to provide 33.3 mg (66% for 2 steps) of **24** as white crystals: mp 167–170 °C (lit.[1] 168–172 °C); TLC R_f 0.37 (EtOAc/hexane, 1:4); $[\alpha]^{26}_{D}$ +107 (*c* 1.57, MeOH) (lit.[1] +111 (*c* 0.1, MeOH); lit.[2] –105 (*c* 0.1, MeOH) for *ent*-**24**); IR (neat) 2940, 1776, 1595 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.27 (m, 1H), 1.49 (s, 3H), 2.17 (m, 1H), 2.48 (m, 1H), 2.72 (m, 1H), 3.02 (d, 1H, *J* = 15.2 Hz), 3.76 (br d, 1H, *J* = 15.2 Hz), 3.79 (s, 3H), 3.81 (s, 3H), 4.01 (br s, 1H), 5.25 (t, 1H, *J* = 7.9 Hz), 6.38 (d, 1H, *J* = 0.6 Hz), 6.83 (d, 1H, *J* = 9.0 Hz), 6.93 (d, 1H, *J* = 9.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.3, 22.5, 25.1, 27.3, 55.9, 56.6, 61.6, 63.7, 74.4, 110.2, 112.9, 121.9, 122.2, 130.3, 137.9, 152.5, 152.9, 172.3; HRMS calcd for $C_{18}H_{20}O_5$ (M^+) *m/z* 316.1311, found 316.1311.

(–)-Clavilactone B (2).

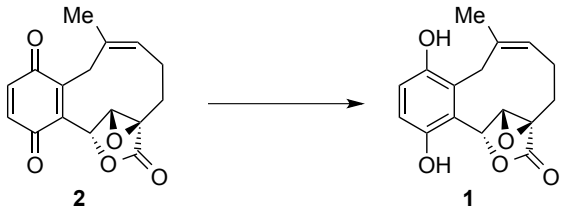


To a cooled (0 °C) stirred solution of **24** (14.1 mg, 44.6 μmol) in MeCN (1 mL) was added a solution of CAN (75.7 mg, 138 μmol) in H_2O (0.5 mL). The mixture was stirred at room temperature for 10 min, and a solution of CAN (25.0 mg, 45.6 μmol) in H_2O (0.2 mL) was added at 0 °C. After being stirred at room temperature for 10 min, the mixture was diluted with H_2O (5 mL) and extracted with CH_2Cl_2 (10 mL × 4). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10) to provide 11.1 mg (87%) of **2** as yellow amorphous solids: TLC R_f 0.21 (EtOAc/hexane, 1:4); $[\alpha]^{26}_{D}$ –42.6 (*c* 1.11, $CHCl_3$) (lit.[1] –55 (*c* 0.15, $CHCl_3$); lit.[2] +42 (*c* 0.77, $CHCl_3$) for *ent*-**2**); IR (neat) 2937, 1783, 1658, 1602 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.29 (m,

(1) Arnone, A.; Cardillo, R.; Meille, S. V.; Nasini, G.; Tolazzi, M. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2165–2168.
(2) Larrosa, I.; Da Silva, M. I.; Gómez, P. M.; Hannen, P.; Ko, E.; Lenger, S. R.; Linke, S. R.; White, A. J. P.; Wilton, D.; Barrett, A. G. M. *J. Am. Chem. Soc.* **2006**, *128*, 14042–14043.

1H), 1.49 (s, 3H), 2.26 (m, 1H), 2.39 (m, 1H), 2.72 (m, 1H), 2.96 (d, 1H, *J* = 13.8 Hz), 3.63 (d, 1H, *J* = 13.8 Hz), 3.97 (s, 1H), 5.35 (m, 1H), 6.06 (s, 1H), 6.92 (d, 1H, *J* = 10.0 Hz), 6.95 (d, 1H, *J* = 10.0 Hz); ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 1.36 (m, 1H), 1.56 (br s, 3H), 2.30 (m, 1H), 2.38 (m, 1H), 2.63 (m, 1H), 2.96 (br d, 1H, *J* = 13.9 Hz), 3.64 (br d, 1H, *J* = 13.9 Hz), 4.44 (br s, 1H), 5.42 (m, 1H), 5.97 (br s, 1H), 7.05 (d, 1H, *J* = 10.1 Hz), 7.08 (d, 1H, *J* = 10.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 22.7, 22.8, 24.6, 26.8, 60.4, 62.6, 71.6, 124.2, 134.7, 136.3, 136.7, 136.8, 149.1, 171.2, 184.7, 186.4; HRMS calcd for $C_{16}H_{14}O_5$ (M^+) *m/z* 286.0841, found 286.0842.

(+)-Clavilactone A (1).

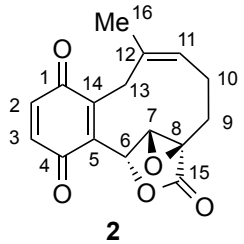


2 **1**

To a cooled (0 °C) stirred solution of **2** (11.6 mg, 40.5 μmol) in MeOH/H_2O (5:1, 1 mL) was added $NaBH_4$ (1.8 mg, 48 μmol). The mixture was stirred at room temperature for 10 min, diluted with 1 M aqueous HCl (2 mL) and extracted with CH_2Cl_2 (10 mL × 3). The combined extracts were dried and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5) to provide 9.2 mg (79%) of **1** as yellow crystals: mp 179–182 °C (lit.[1] 176 °C); TLC R_f 0.33 (EtOAc/hexane, 1:1); $[\alpha]^{25}_D$ +100 (*c* 0.46, MeOH) (lit.[1] +81 (*c* 0.2, MeOH)); IR (KBr) 3461, 3419, 2933, 1722 cm^{-1}; ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ 1.29 (m, 1H), 1.60 (s, 3H), 2.18 (m, 1H), 2.42 (m, 1H), 2.60 (m, 1H), 3.03 (d, 1H, *J* = 15.0 Hz), 3.70 (d, 1H, *J* = 15.0 Hz), 4.20 (s, 1H), 5.30 (t, 1H, *J* = 7.9 Hz), 6.30 (s, 1H), 6.79 (d, 1H, *J* = 8.8 Hz), 6.89 (d, 1H, *J* = 8.8 Hz), 8.14 (s, 1H, OH), 8.43 (s, 1H, OH); ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ 21.7, 23.1, 25.8, 28.0, 62.1, 64.3, 75.9, 115.4, 118.4, 121.0, 122.5, 127.9, 139.0, 150.40, 150.43, 173.1; HRMS calcd for $C_{16}H_{16}O_5$ (M^+) *m/z* 288.0998, found 288.0997.

2. Natural product NMR comparison tables for clavilactones A (1) and B (2)

Clavilactone B (2).

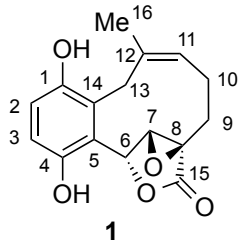


2

Proton	^{1}H NMR ($CDCl_3$)		^{1}H NMR ($(CD_3)_2CO$)	
	Synthetic (500 MHz)	Barrett's data[2] (400 MHz)	Synthetic (500 MHz)	Natural[1] (250 MHz)
2	6.95 (d, *J*=10.0 Hz)	6.95 (d, *J*=10.0 Hz)	7.08 (d, *J*=10.1 Hz)	7.04 (d, *J*=10.0 Hz)
3	6.92 (d, *J*=10.0 Hz)	6.91 (d, *J*=10.0 Hz)	7.05 (d, *J*=10.1 Hz)	7.01 (d, *J*=10.0 Hz)
6	6.06 (s)	6.05 (s)	5.97 (br s)	5.92 (br s)
7	3.97 (s)	3.97 (s)	4.44 (br s)	4.40 (br s)
9	1.29 (m)	1.29 (m)	1.36 (m)	1.34 (m)
9'	2.72 (m)	2.74 (m)	2.63 (m)	2.59 (m)
10	2.26 (m)	2.20–2.50 (m, 2H)	2.30 (m)	2.28 (m)
10'	2.39 (m)		2.38 (m)	2.35 (m)
11	5.35 (m)	5.34 (m)	5.42 (m)	5.38 (m)
13	2.96 (d, *J*=13.8 Hz)	2.95 (d, *J*=14.0 Hz)	2.96 (br d, *J*=13.9 Hz)	2.93 (br d, *J*=12.5 Hz)
13'	3.63 (d, *J*=13.8 Hz)	3.62 (d, *J*=14.0 Hz)	3.64 (br d, *J*=13.9 Hz)	3.62 (br d, *J*=12.5 Hz)
16	1.49 (s, 3H)	1.48 (s, 3H)	1.56 (br s, 3H)	1.51 (br s, 3H)

Carbon	^{13}C NMR ($CDCl_3$)	
	Synthetic (125 MHz)	Barrett's data[2] (100 MHz)
1	186.4	186.4
2	136.7	136.7
3	136.3	136.4
4	184.7	184.7
5	149.1	149.2
6	71.6	71.7
7	62.6	62.6
8	60.4	60.6
9	24.6	24.6
10	22.8	22.9
11	124.2	124.0
12	134.7	134.7
13	26.8	26.9
14	136.8	136.8
15	171.2	171.3
16	22.7	22.7

Clavilactone A (1).

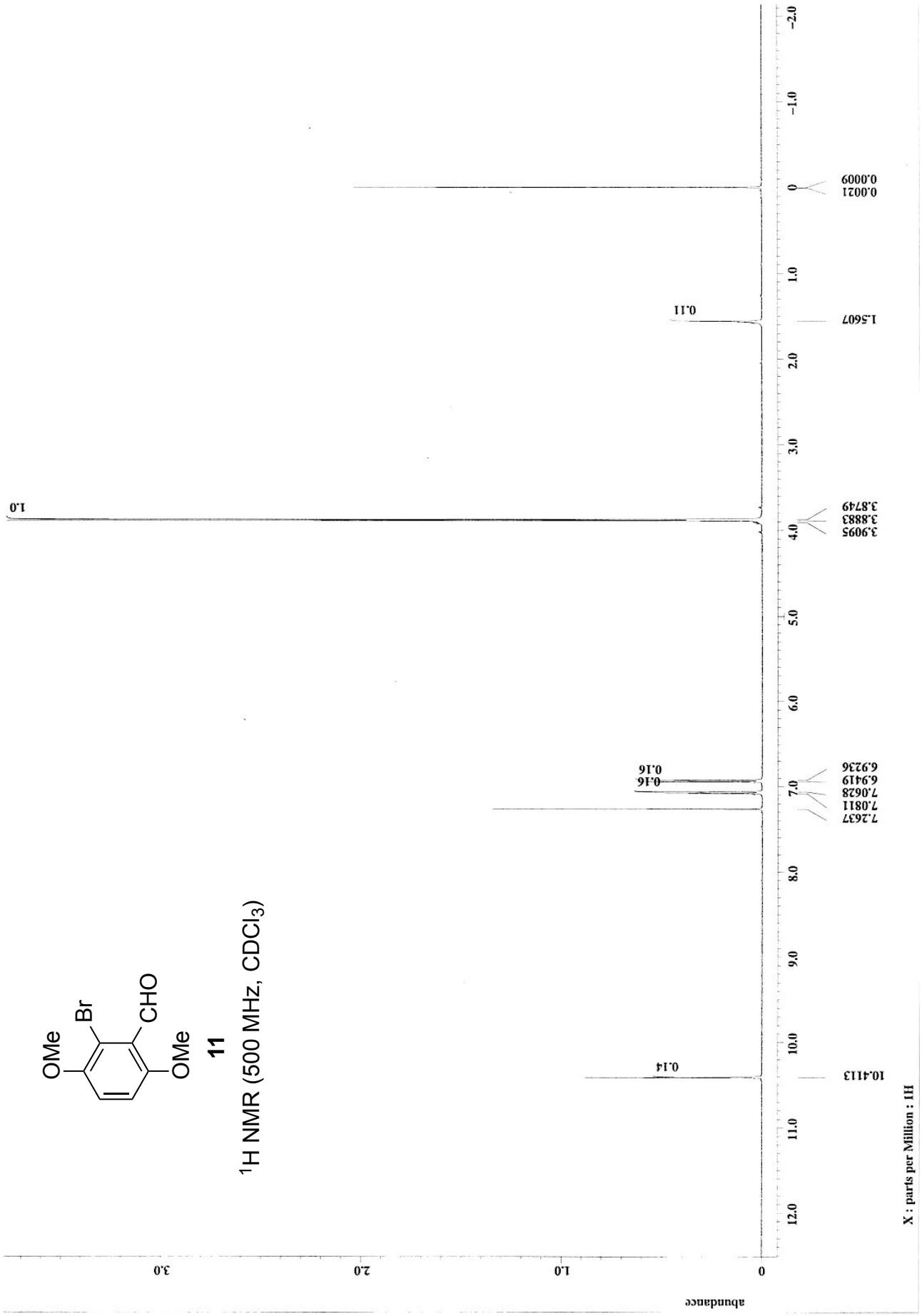


1

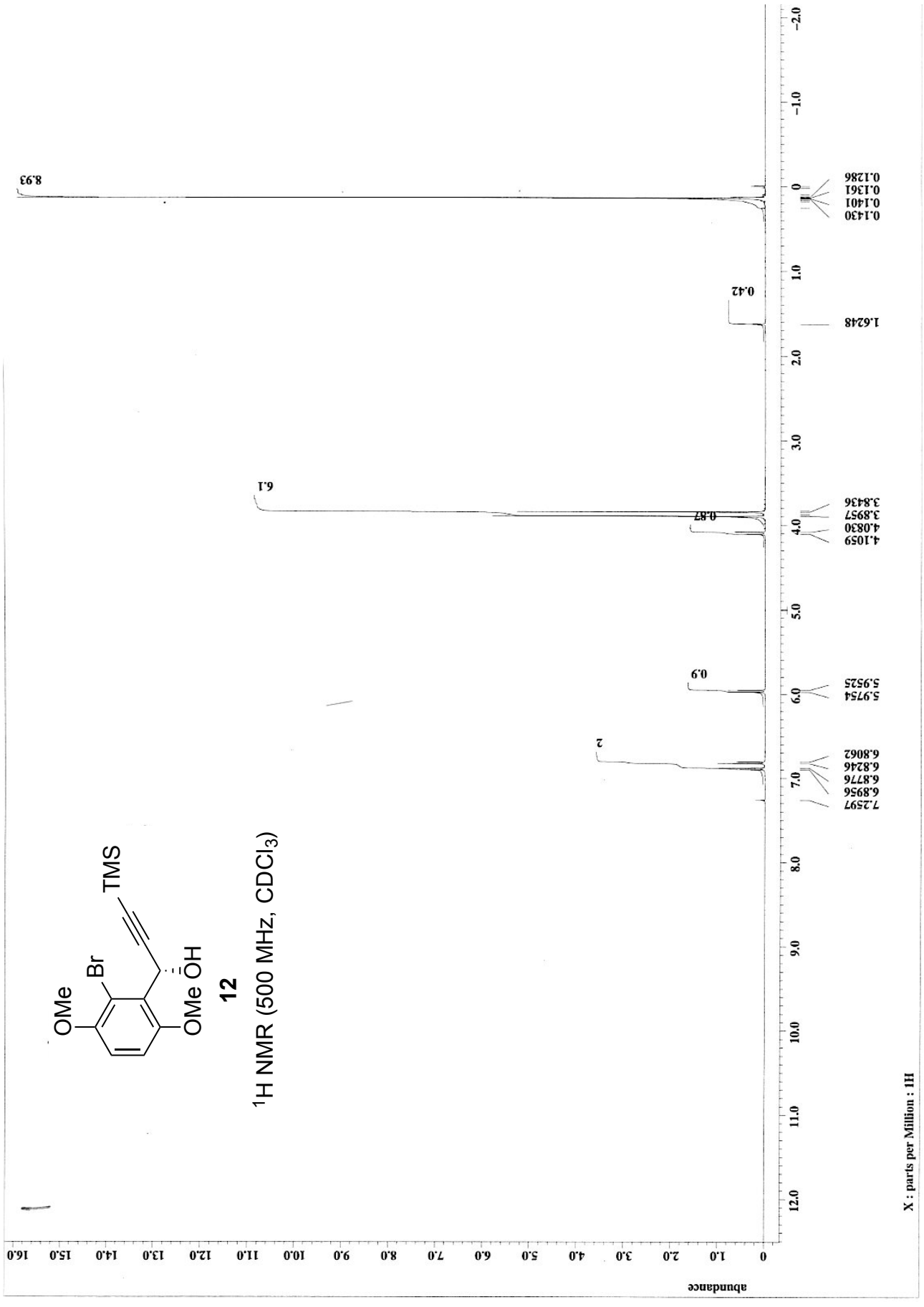
Proton	^{1}H NMR ($(CD_3)_2CO$)	
	Synthetic (500 MHz)	Natural[1] (250 MHz)
2	6.89 (d, *J*=8.8 Hz)	6.88 (d, *J*=8.7 Hz)
3	6.79 (d, *J*=8.8 Hz)	6.79 (d, *J*=8.7 Hz)
6	6.30 (s)	6.30 (d, *J*=1.0 Hz)
7	4.20 (s)	4.20 (d, *J*=0.7 Hz)
9	1.29 (m)	1.29 (m)
9’	2.60 (m)	2.60 (m)
10	2.18 (m)	2.17 (m)
10’	2.42 (m)	2.42 (m)
11	5.30 (t, *J*=7.9 Hz)	5.29 (m)
13	3.03 (d, *J*=15.0 Hz)	3.02 (d, *J*=15.2 Hz)
13’	3.70 (d, *J*=15.0 Hz)	3.70 (d, *J*=15.2 Hz)
16	1.60 (s, 3H)	1.60 (s, 3H)
1-OH	8.14 (s)	8.19 (s)
4-OH	8.43 (s)	8.49 (s)

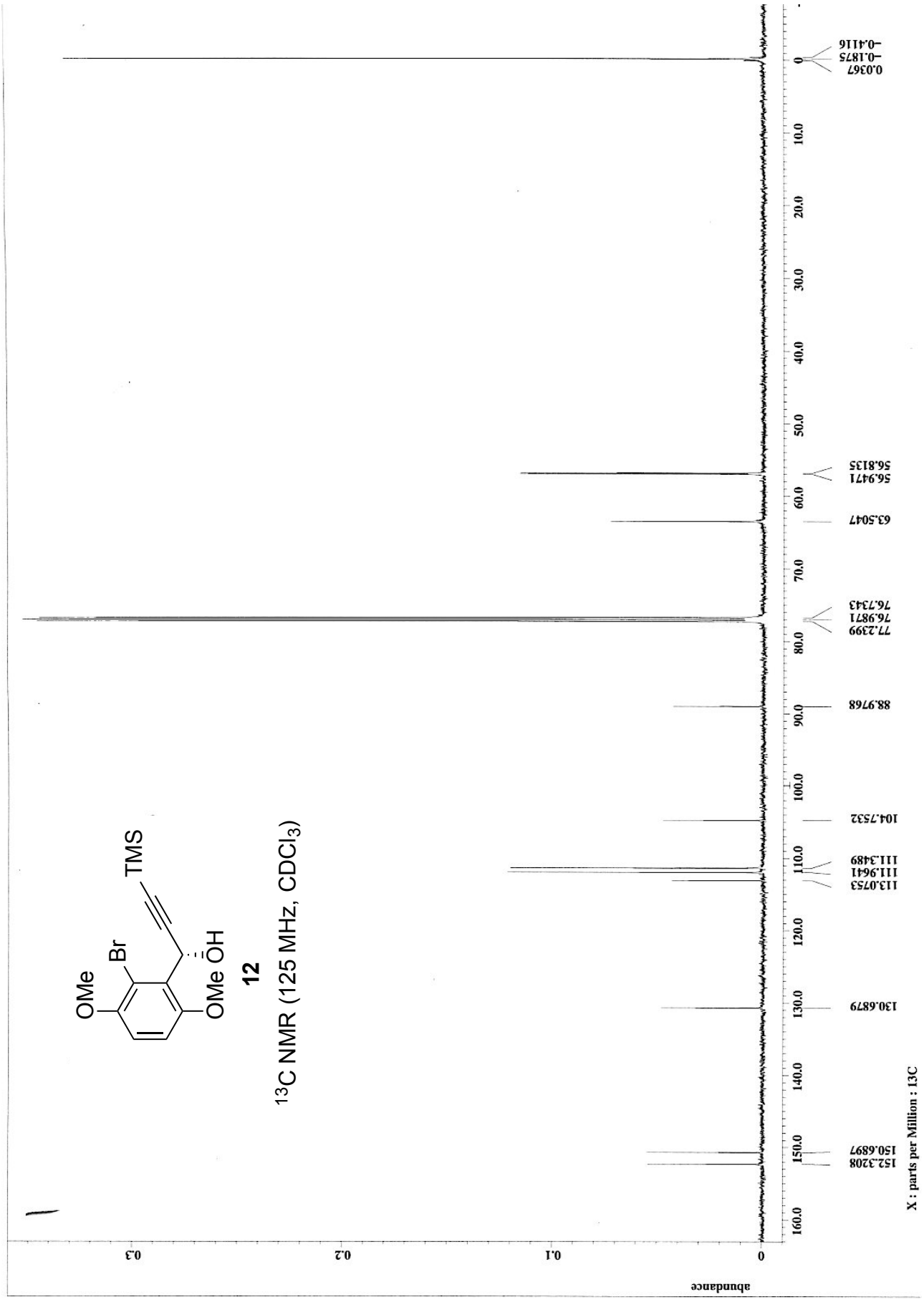
Carbon	^{13}C NMR ($(CD_3)_2CO$)	
	Synthetic (125 MHz)	Natural[1] (62.5 MHz)
1	150.4	150.3
2	118.4	118.4
3	115.4	115.3
4	150.4	150.3
5	121.0	120.9
6	75.9	75.9
7	64.3	64.3
8	62.1	62.1
9	25.8	26.0
10	23.1	23.1
11	122.5	122.4
12	139.0	138.9
13	28.0	28.0
14	127.9	127.8
15	173.1	173.1
16	21.7	21.6

3. ^{1}H and ^{13}C NMR spectra of new compounds



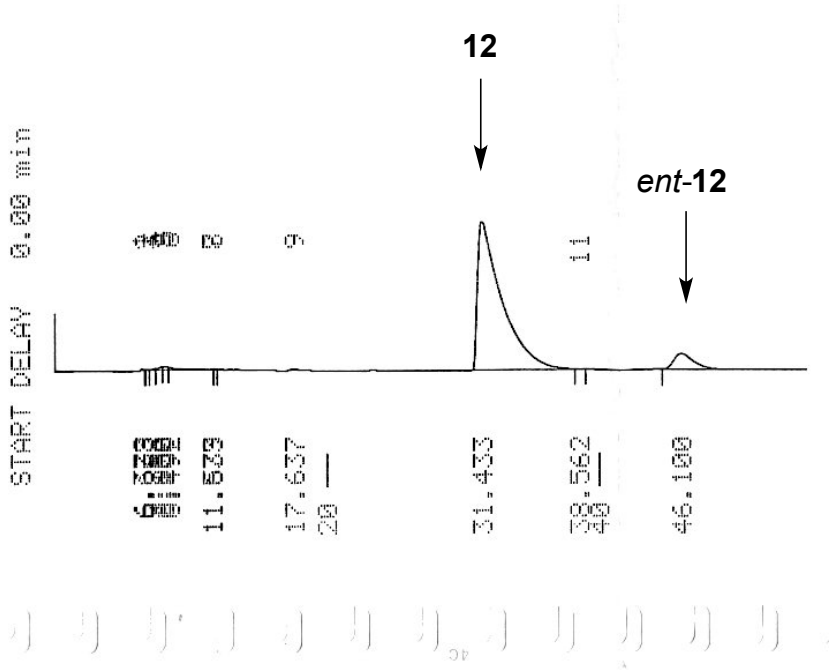
OMe
Br
CHO
OMe
11
^{13}C NMR (125 MHz, $CDCl_3$)
190.9044
155.4075
117.1207
111.4597
77.3936
77.2552
77.0025
76.7497
57.1962
56.6048
X : parts per Million : 13C
abundance


TMS
Br
OMe
OMe
OH
12
1H NMR (500 MHz, CDCl3)
abundance
X : parts per Million : 1H
8.93
6.1
2
0.9
0.87
0.42
1.6248
7.2597
6.8956
6.8776
6.8246
6.8062
5.9754
5.9525
4.1059
4.0830
3.8957
3.8436
0.1430
0.1401
0.1361
0.1286

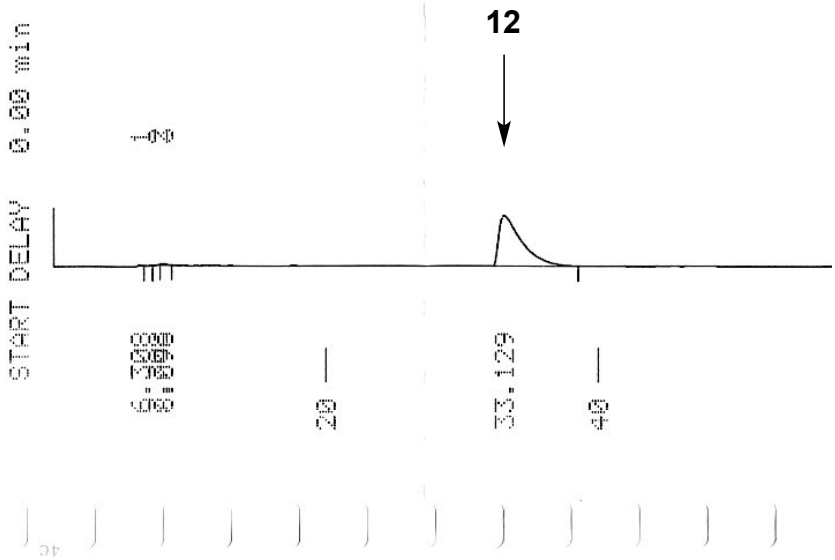

TMS
Br
OMe
OMe
OH
12
^{13}C NMR (125 MHz, CDCl$_3$)
X : parts per Million : 13C
abundance
0.03671
-0.18751
-0.41161
152.3208
150.6897
130.6879
113.0753
111.9641
111.3489
104.7532
88.9768
77.2399
76.9871
76.7343
63.5047
56.9471
56.8135

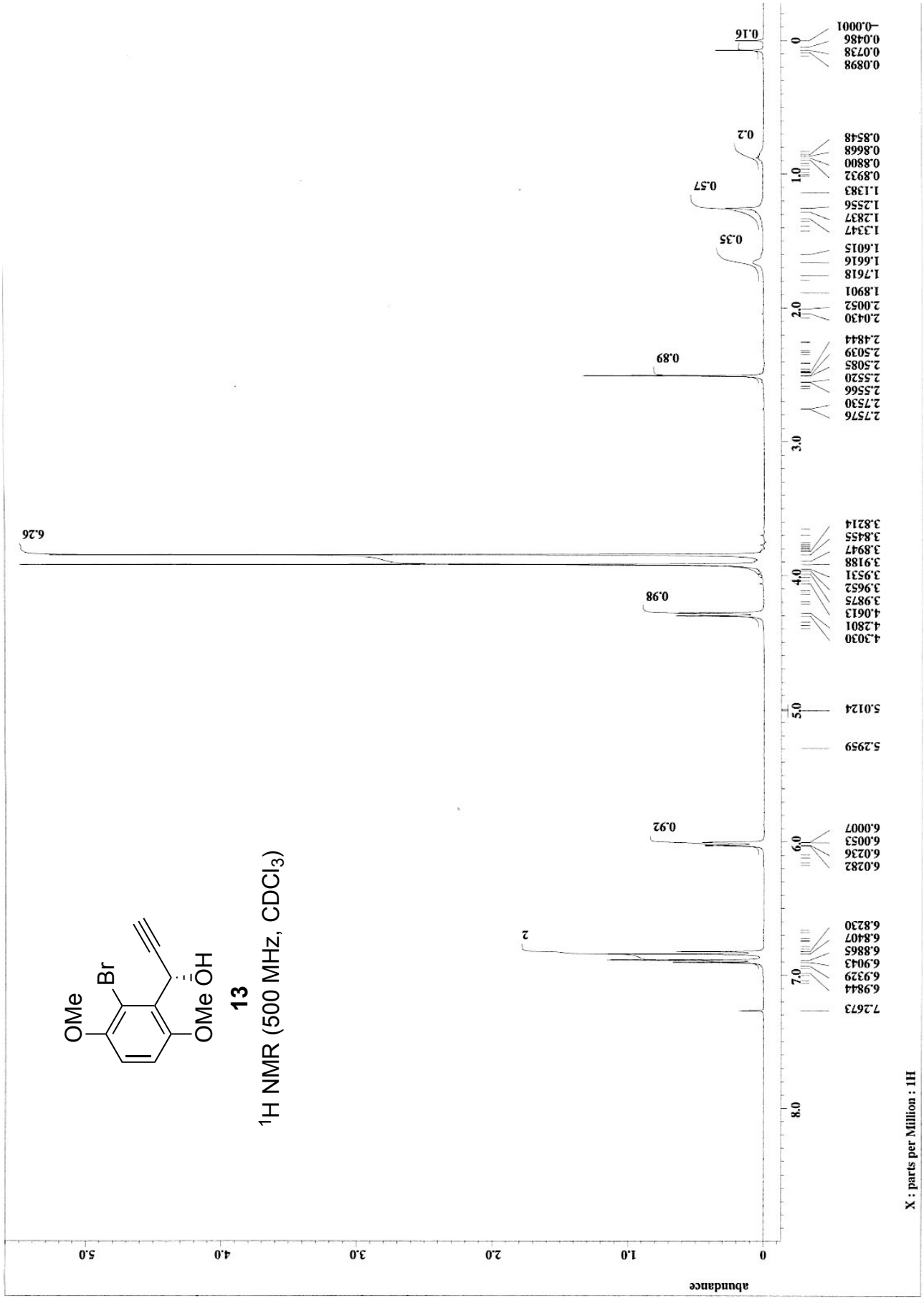
HPLC spectra of compound **12**

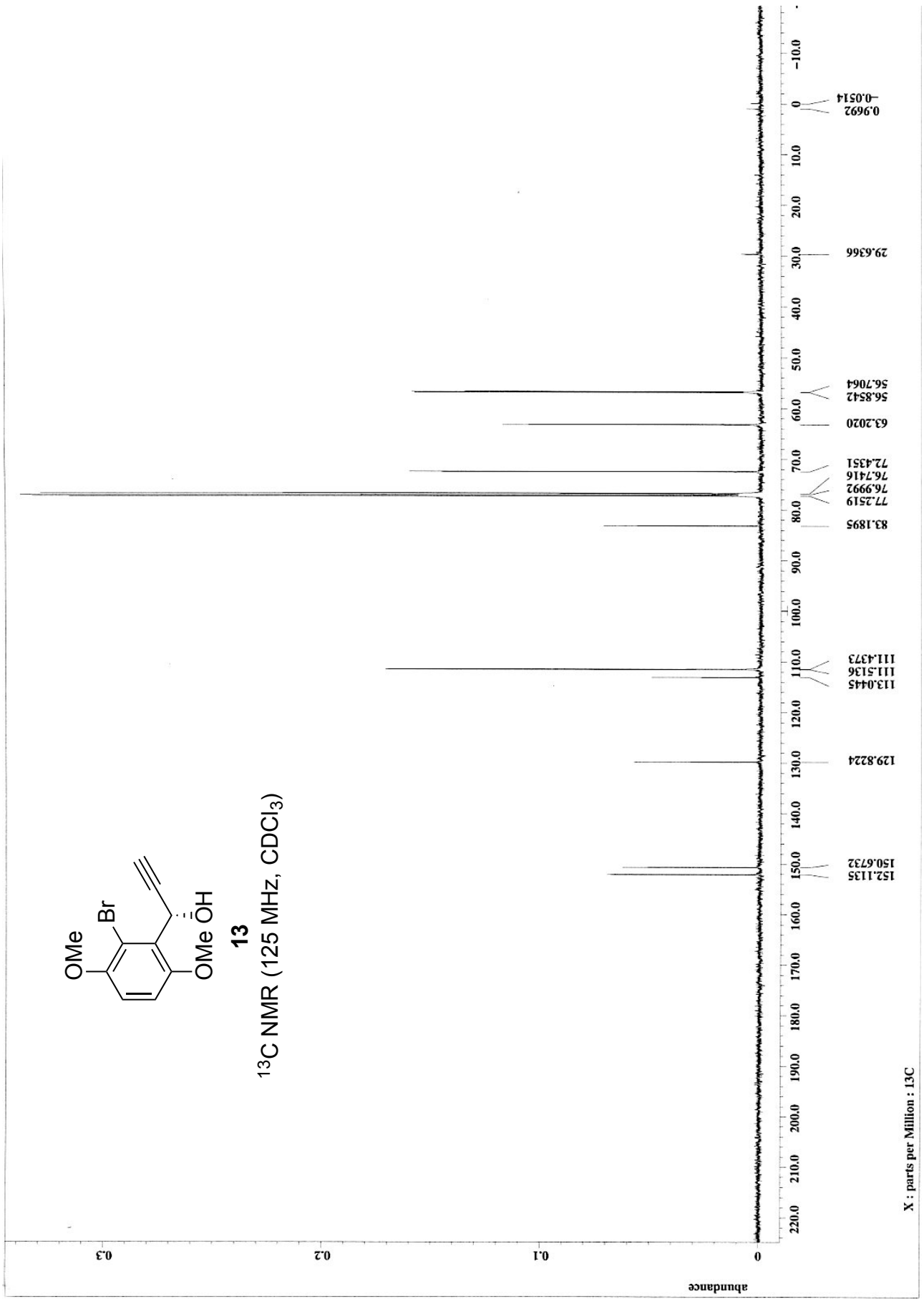
Before recrystallization

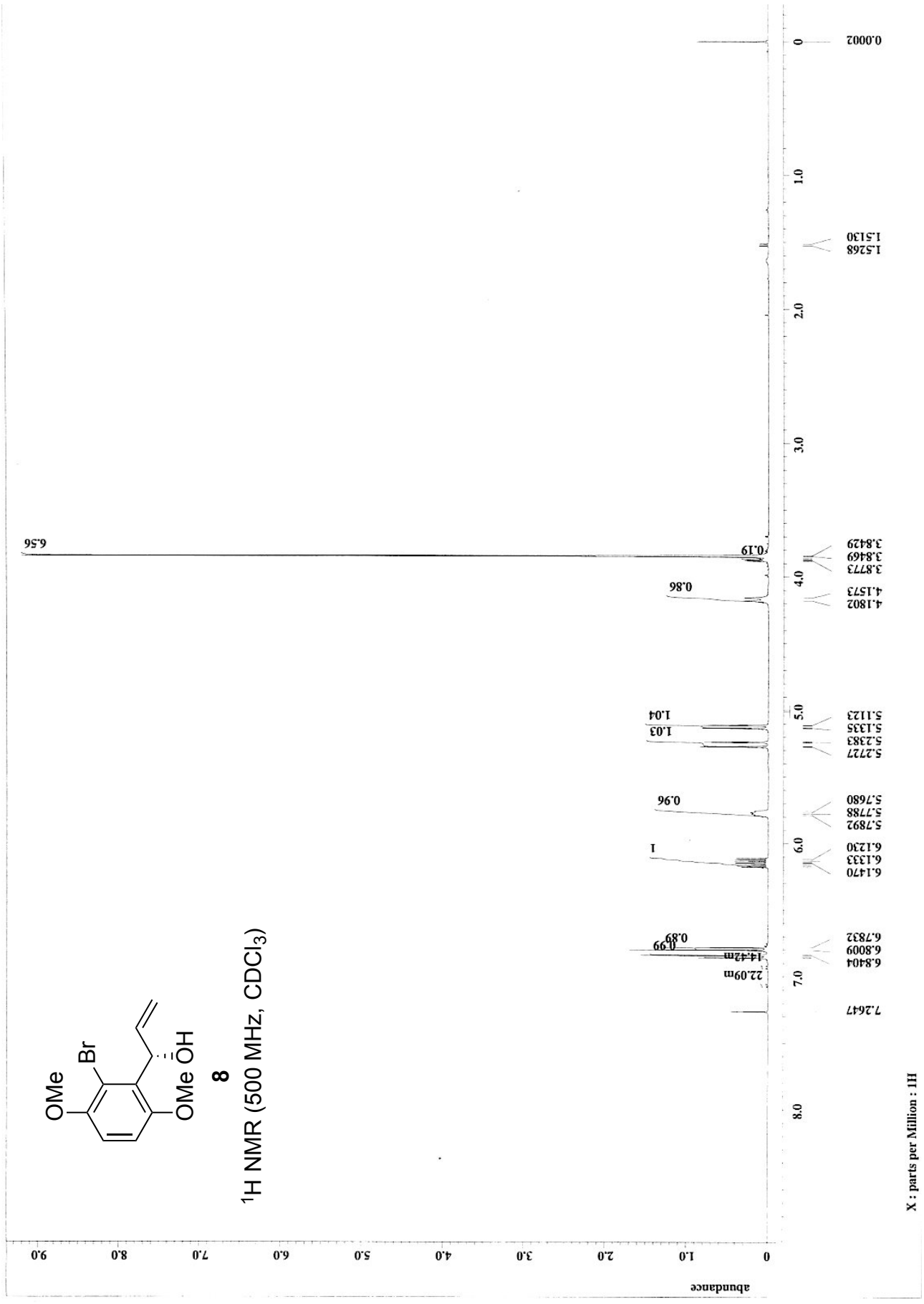


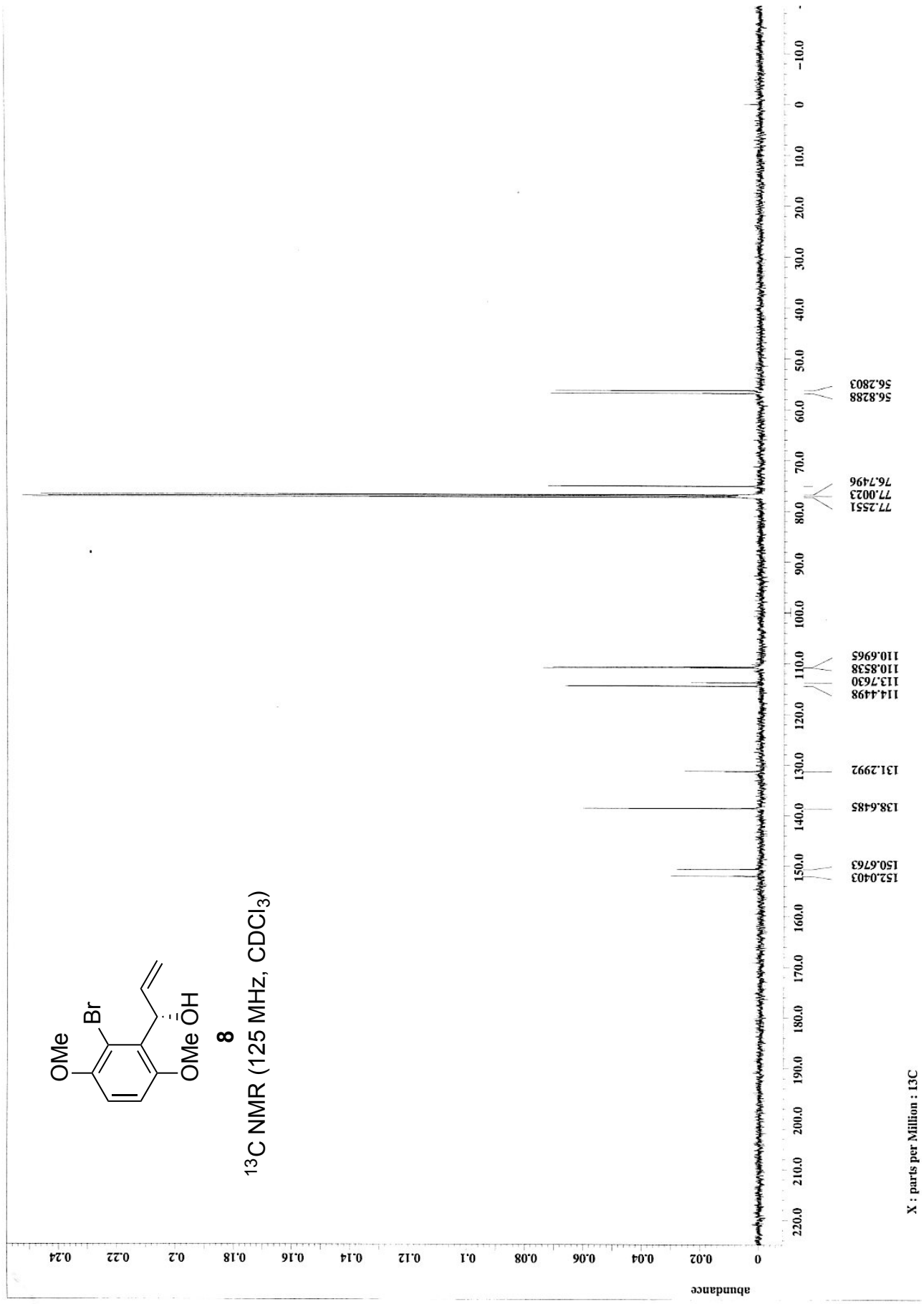
After recrystallization

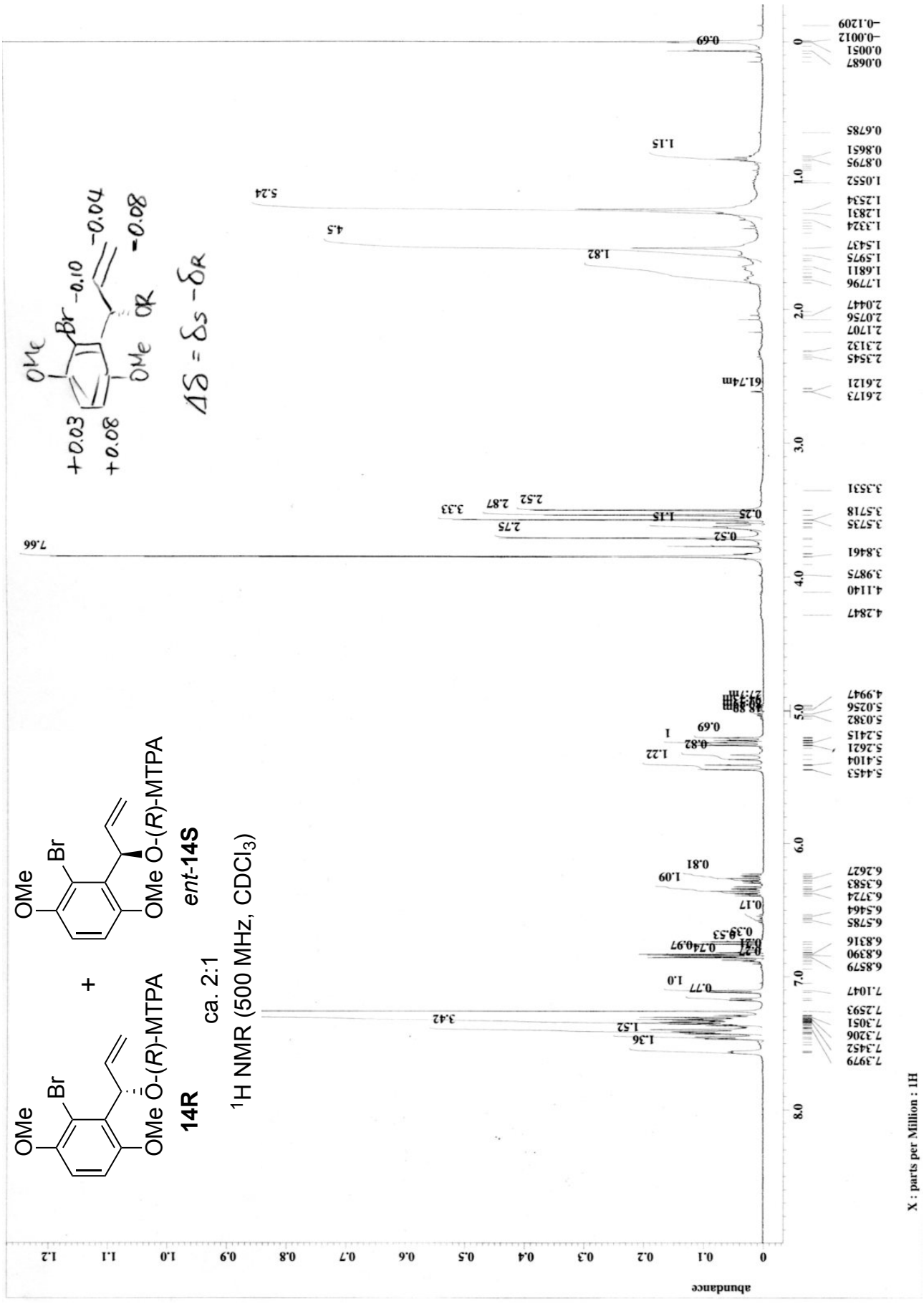


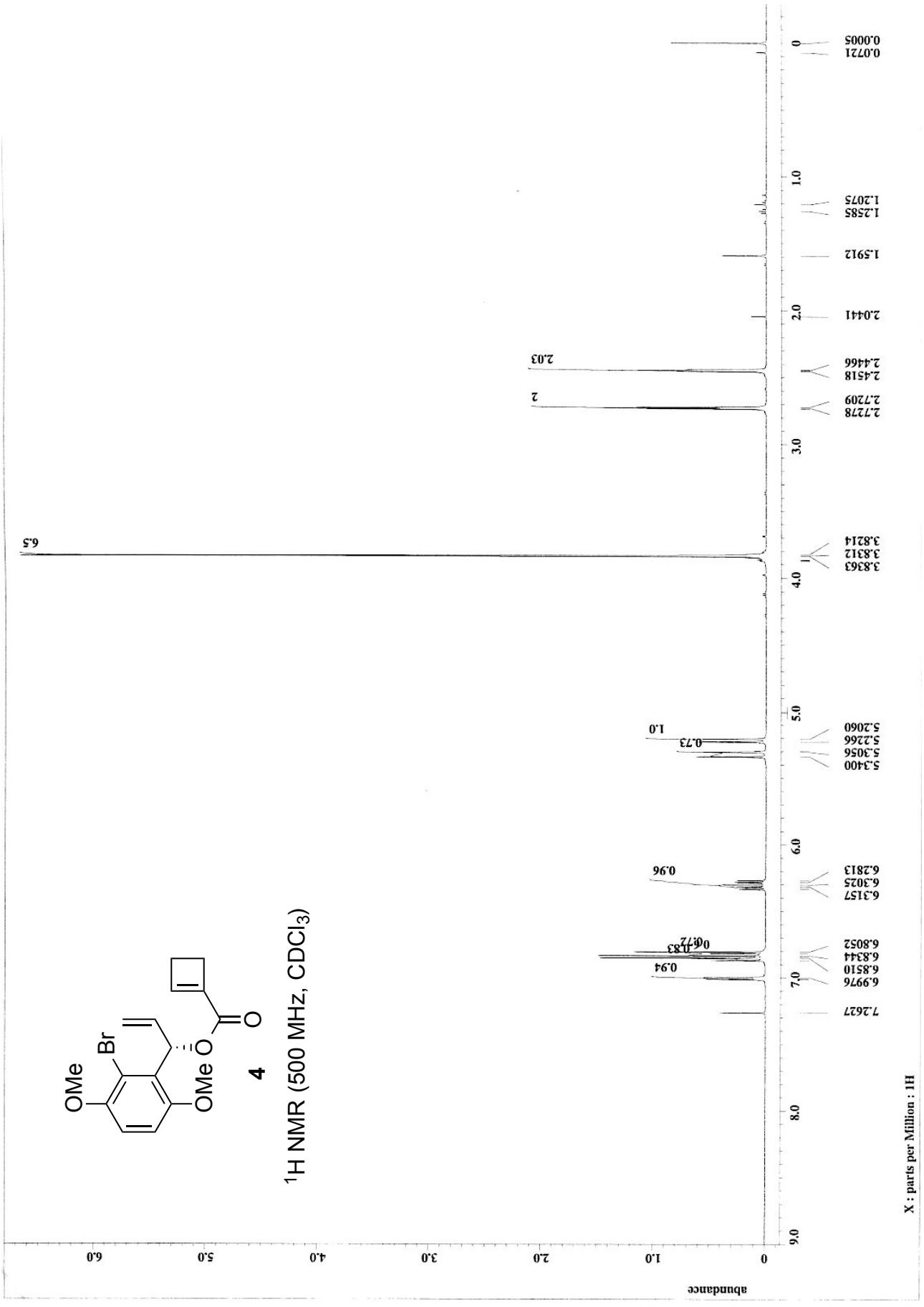

OMe
Br
OMe
OH
13
1H NMR (500 MHz, CDCl3)
abundance
X : parts per Million : 1H

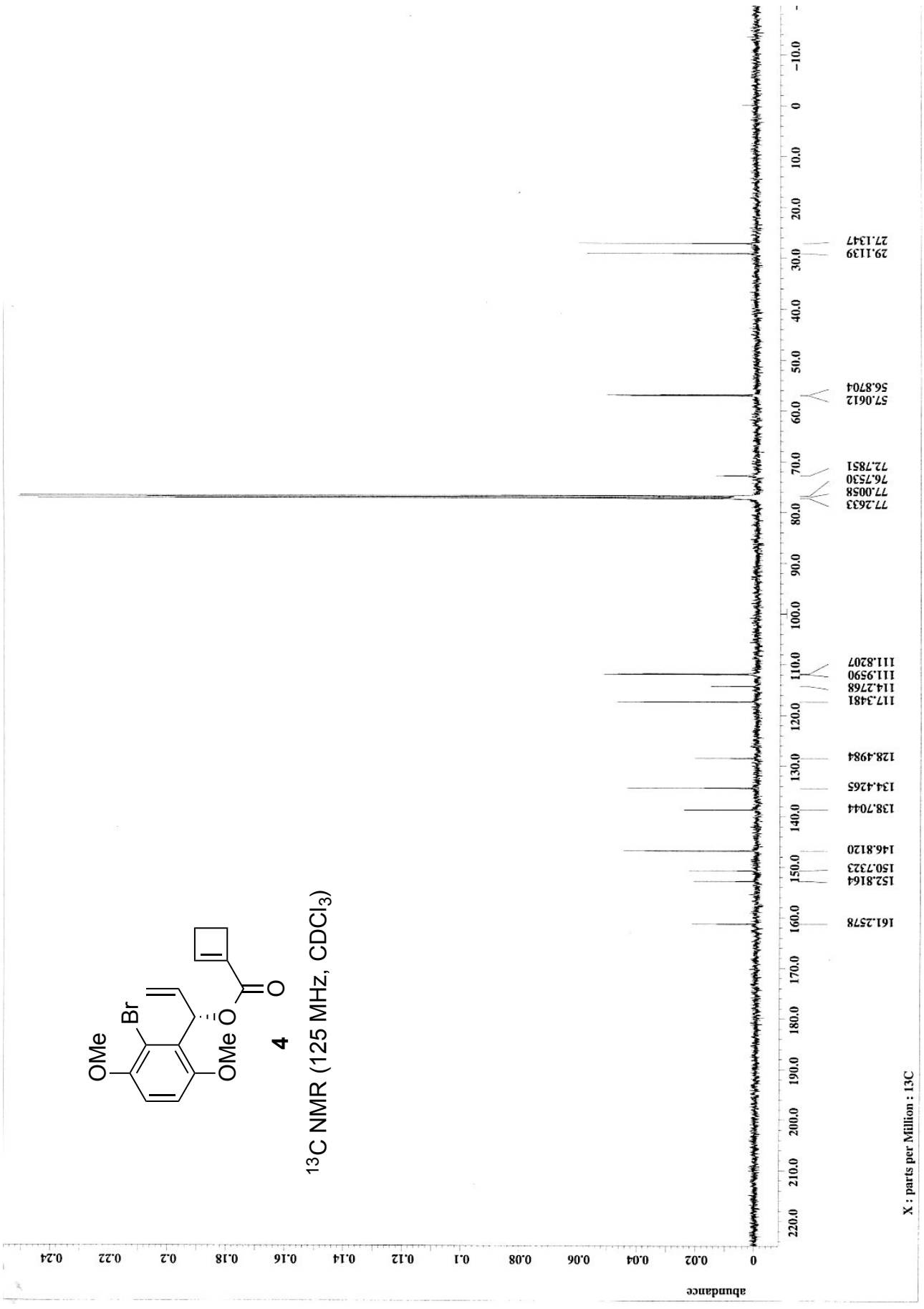

OMe
Br
OMe
OH
13
13C NMR (125 MHz, CDCl3)
abundance
X : parts per Million : 13C
152.1135
150.6732
129.8224
113.0445
111.5136
111.4373
83.1895
77.2519
76.9992
76.7416
72.4351
63.2020
56.8542
56.7064
29.6366
0.9692
-0.0514

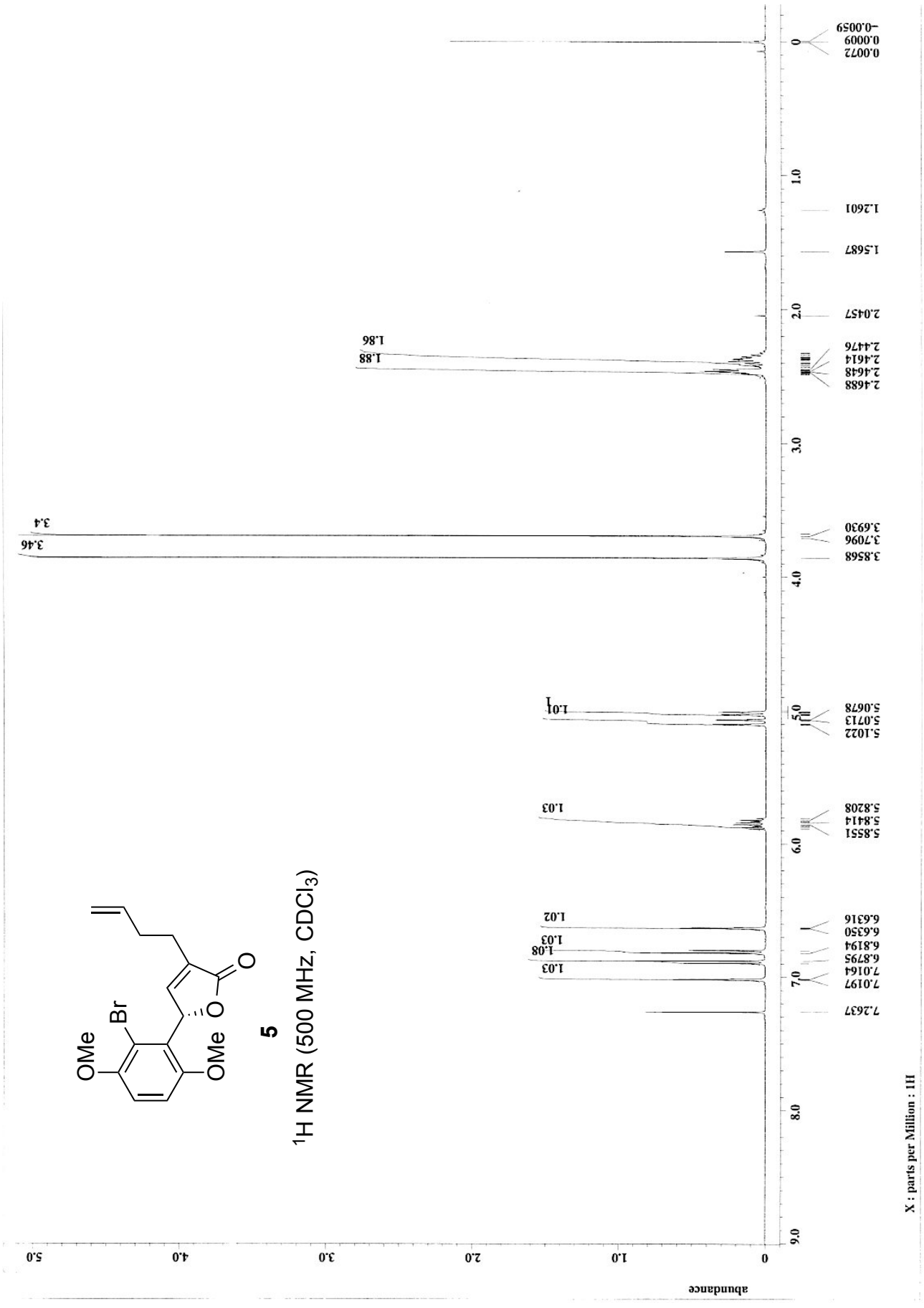

OMe
Br
OMe
OH
8
^{1}H NMR (500 MHz, $CDCl_3$)
abundance
X : parts per Million : 1H
7.2647
6.8404
6.8009
6.7832
6.1470
6.1333
6.1230
5.7892
5.7788
5.7680
5.2727
5.2383
5.1335
5.1123
4.1802
4.1573
3.8773
3.8469
3.8429
1.5268
1.5130
0.0002
6.56
0.19
0.86
1.03
1.04
0.96
1
0.89
0.99
14.42m
22.09m

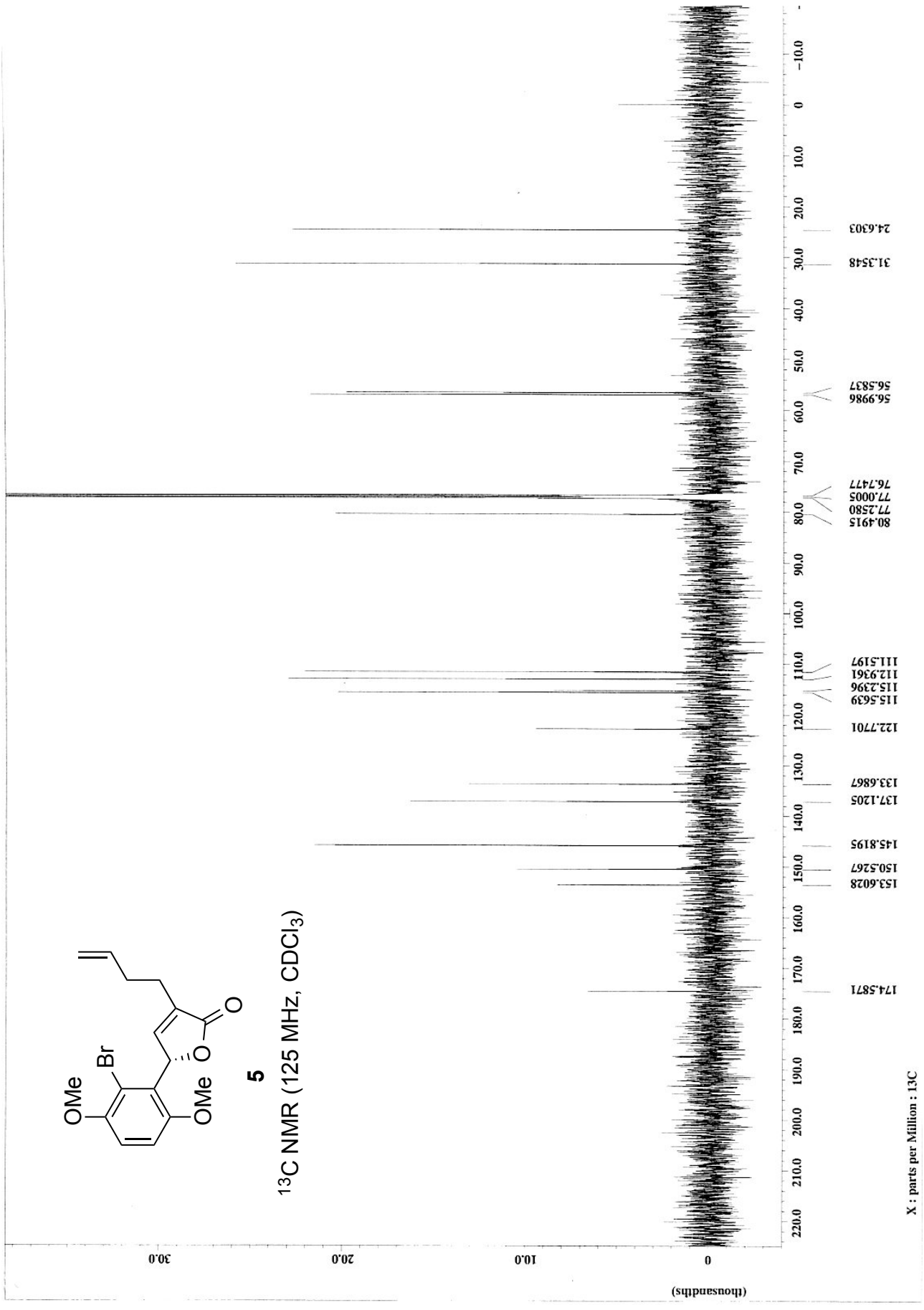

OMe
Br
OMe
OH
8
13C NMR (125 MHz, CDCl3)
152.0403
150.6763
138.6485
131.2992
114.4498
113.7630
110.8538
110.6965
77.2551
77.0023
76.7496
56.8288
56.2803
abundance
X : parts per Million : 13C

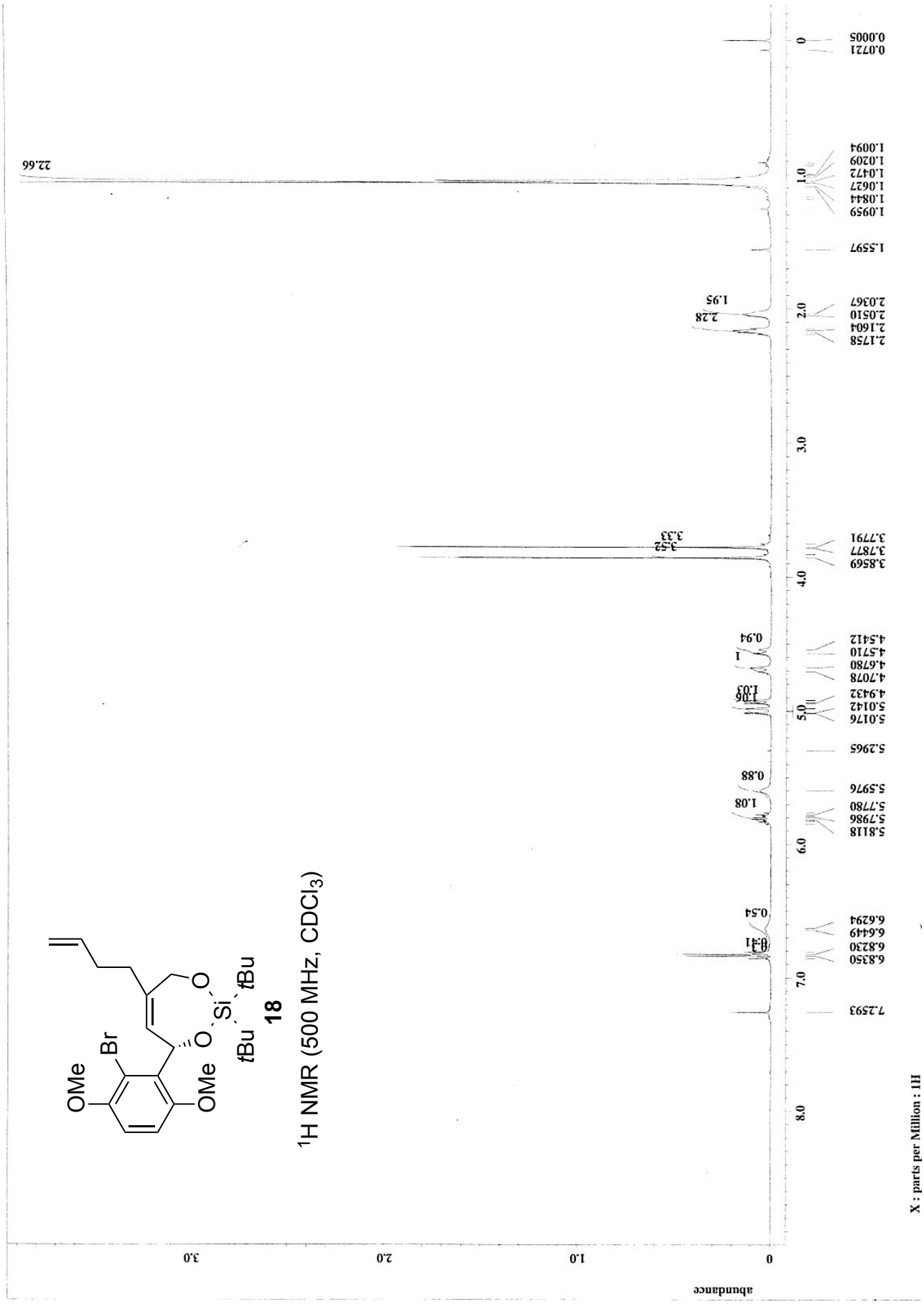

OMe
Br
OMe O-(R)-MTPA
14R
+
OMe
Br
OMe O-(R)-MTPA
ent-14S
ca. 2:1
1H NMR (500 MHz, CDCl3)
ΔδS = δS - δR
+0.03
+0.08
-0.10
-0.04
-0.08
abundance
X : parts per Million : 1H

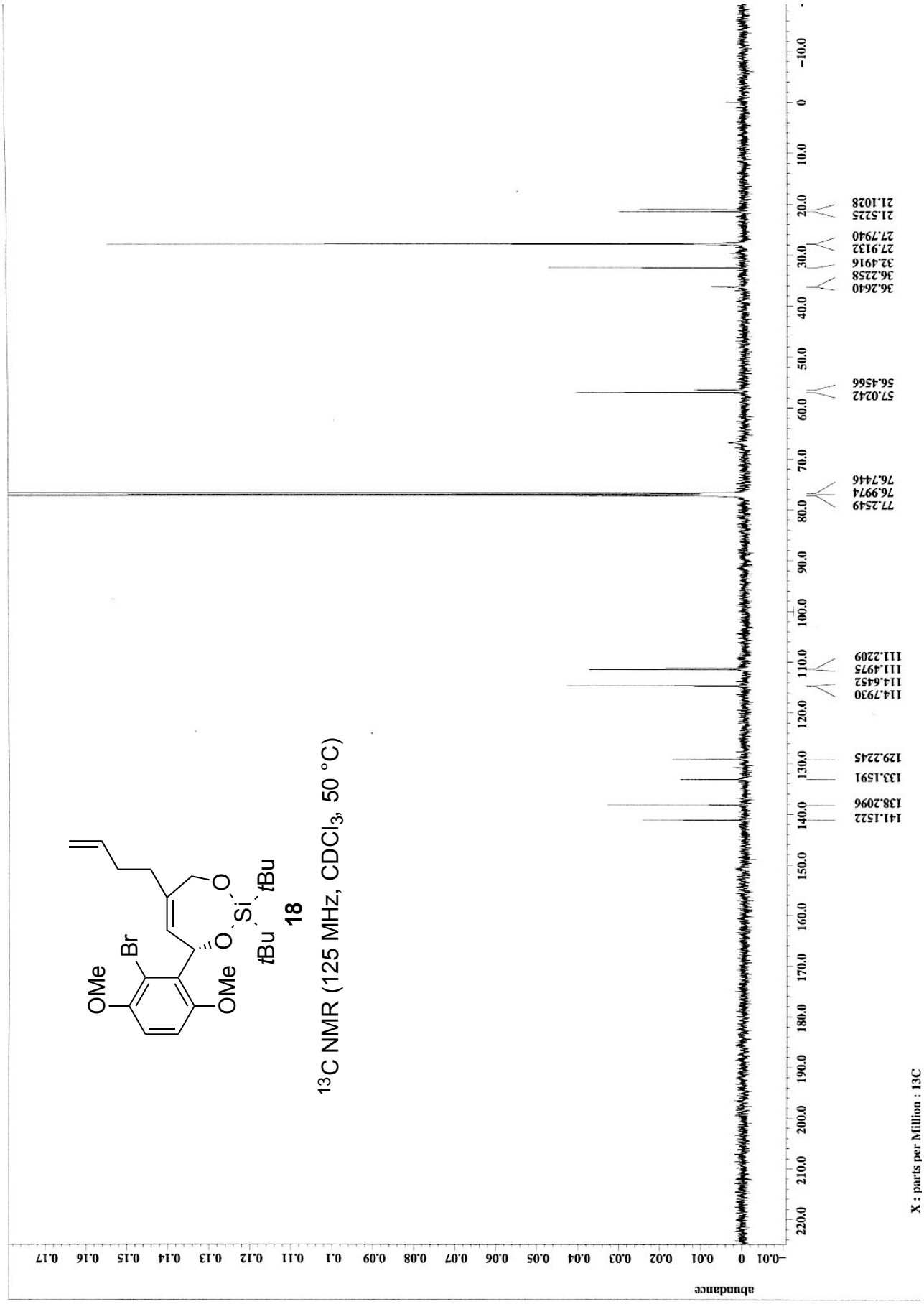

OMe
Br
OMe
O
O
4
^{1}H NMR (500 MHz, CDCl$_3$)
abundance
X : parts per Million : 1H
6.5
2.03
2
1.0
0.96
0.94
0.83
0.72
0.73
7.2627
6.9976
6.8510
6.8344
6.8052
6.3157
6.3025
6.2813
5.3400
5.3056
5.2266
5.2060
3.8363
3.8312
3.8214
2.7278
2.7209
2.4518
2.4466
2.0441
1.5912
1.2585
1.2075
0.0721
0.0005

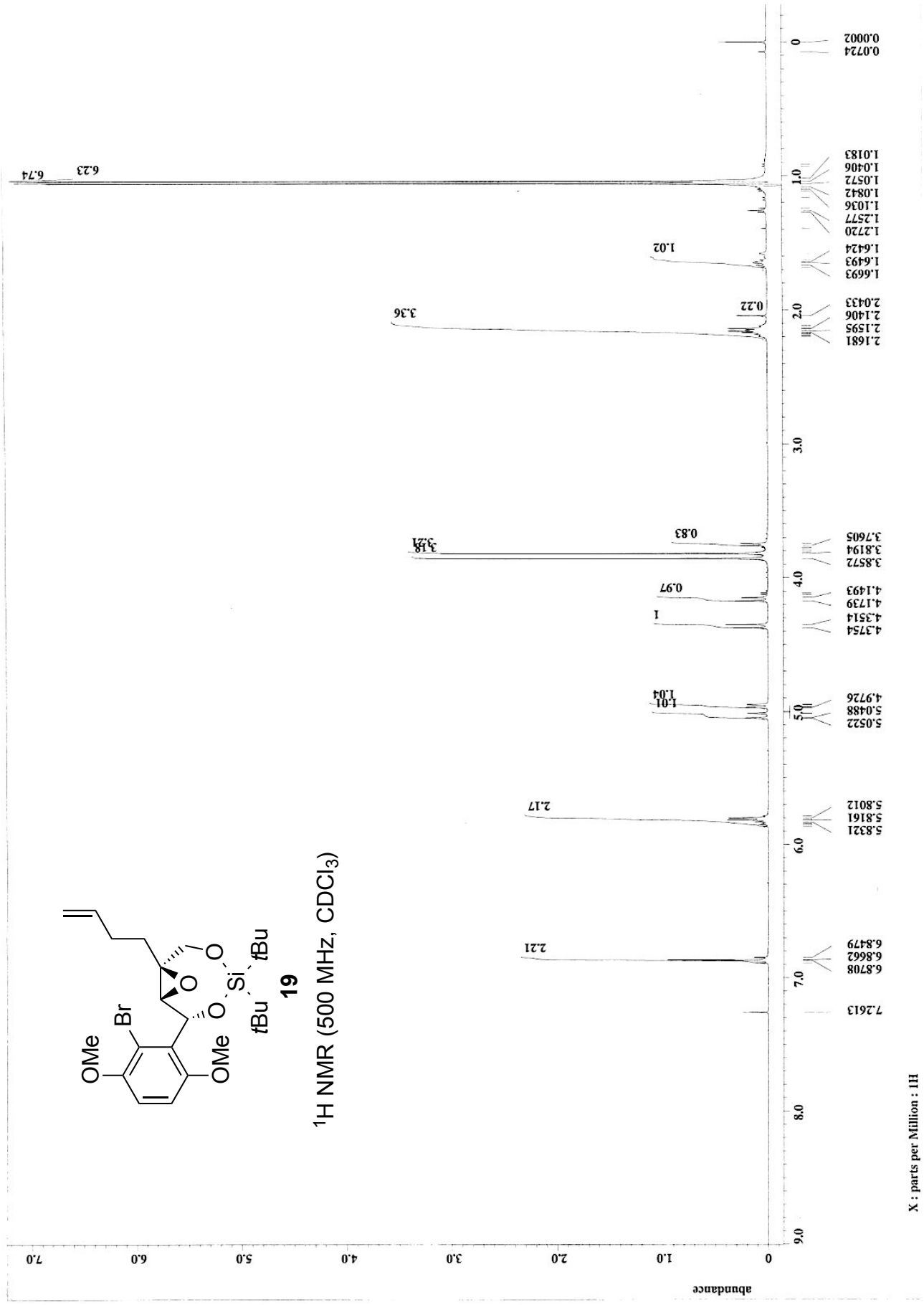

OMe
Br
OMe
O
O
4
^{13}C NMR (125 MHz, CDCl$_3$)
X : parts per Million : 13C
abundance
161.2578
152.8164
150.7323
146.8120
138.7044
134.4265
128.4984
117.3481
114.2768
111.9590
111.8207
77.2633
77.0058
76.7530
72.7851
57.0612
56.8704
29.1139
27.1347

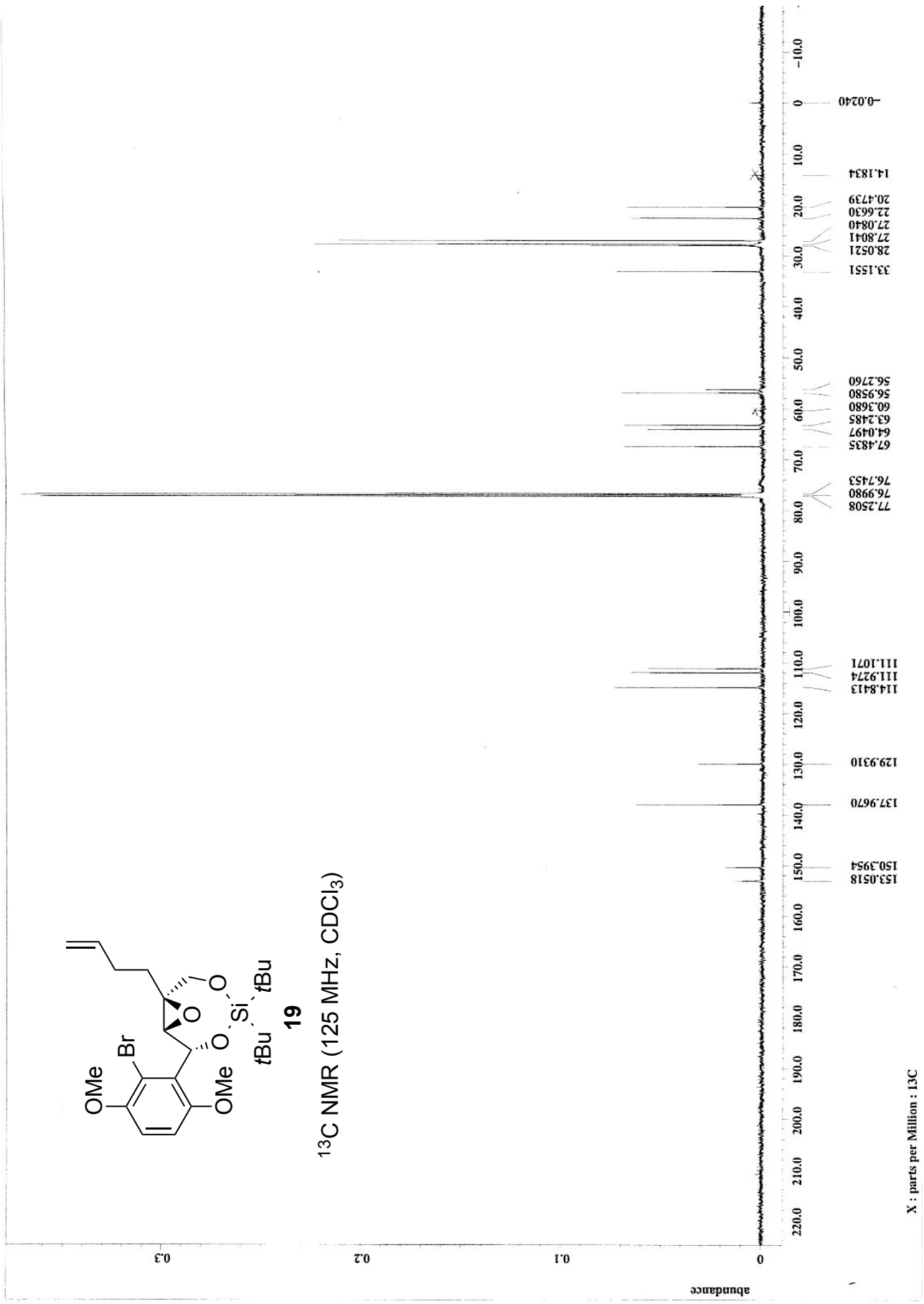

5
1H NMR (500 MHz, CDCl3)
OMe
Br
OMe
O
O
O
abundance
X : parts per Million : 1H
0.0072
0.0009
-0.0059
1.2601
1.5687
2.0457
2.4688
2.4648
2.4614
2.4476
1.88
1.86
3.8568
3.7096
3.6930
3.46
3.4
5.1022
5.0713
5.0678
1.01
5.8551
5.8414
5.8208
1.03
6.6316
6.6350
6.8194
6.8795
7.0164
7.0197
1.02
1.03
1.08
1.03
7.2637

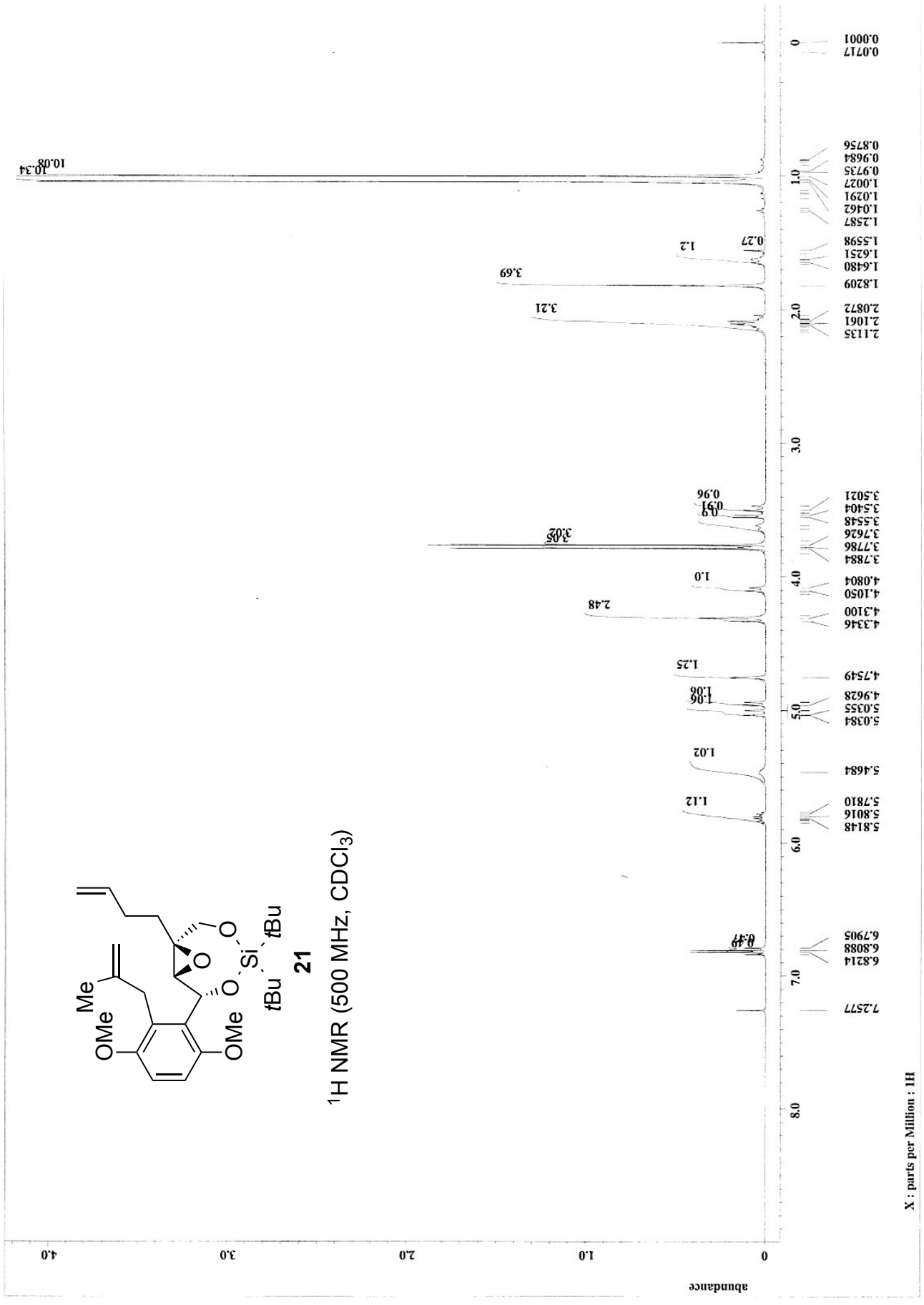

OMe
Br
OMe
O
O
O
5
^{13}C NMR (125 MHz, CDCl$_3$)
(thousandths)
X : parts per Million : 13C
174.5871
153.6028
150.5267
145.8195
137.1205
133.6867
122.7701
115.5639
115.2396
112.9361
111.5197
80.4915
77.2580
77.0005
76.7477
56.9986
56.5837
31.3548
24.6303

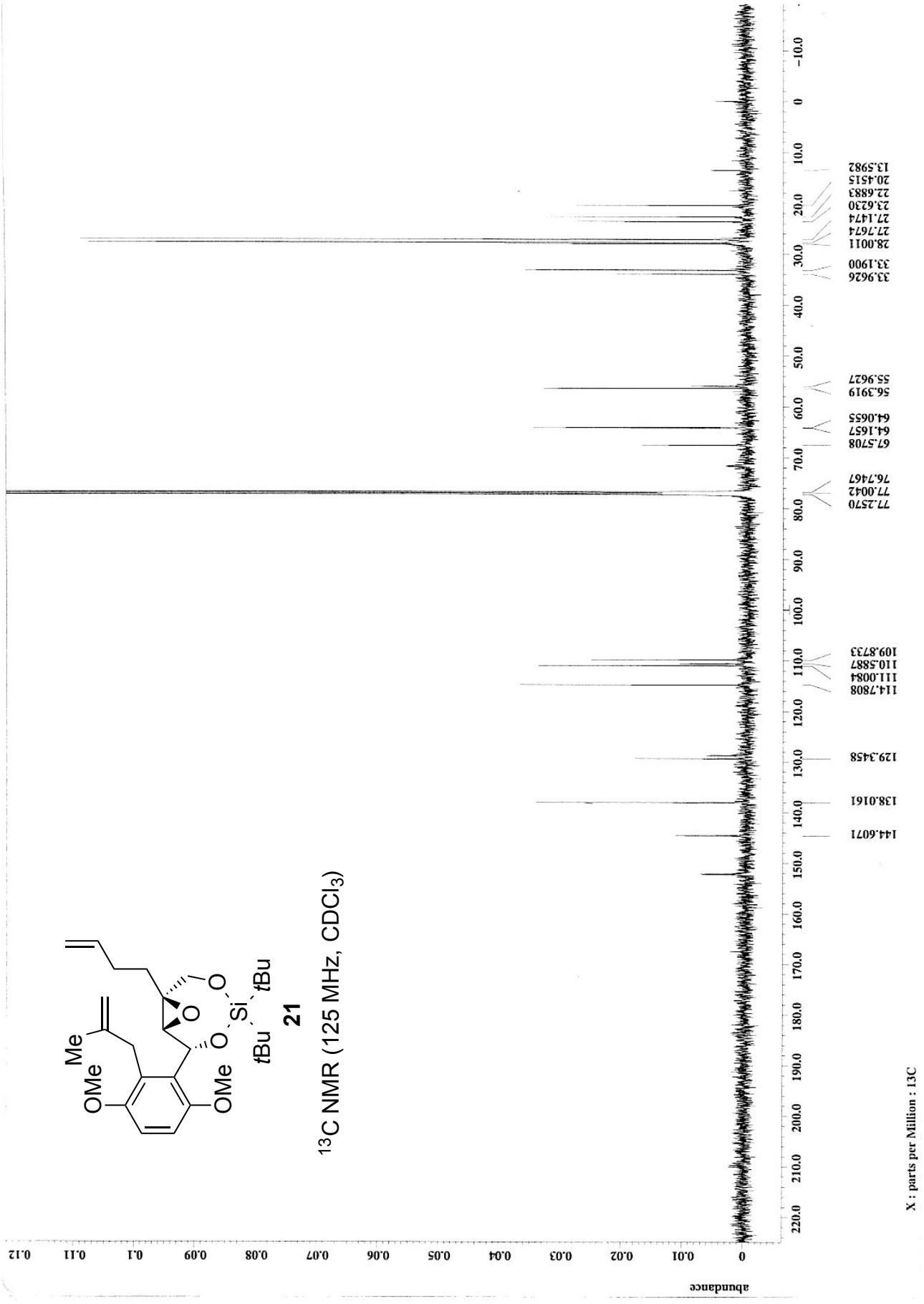

OMe
Br
OMe
O
Si
tBu
tBu
18
1H NMR (500 MHz, CDCl3)
X : parts per Million : 1H
abundance

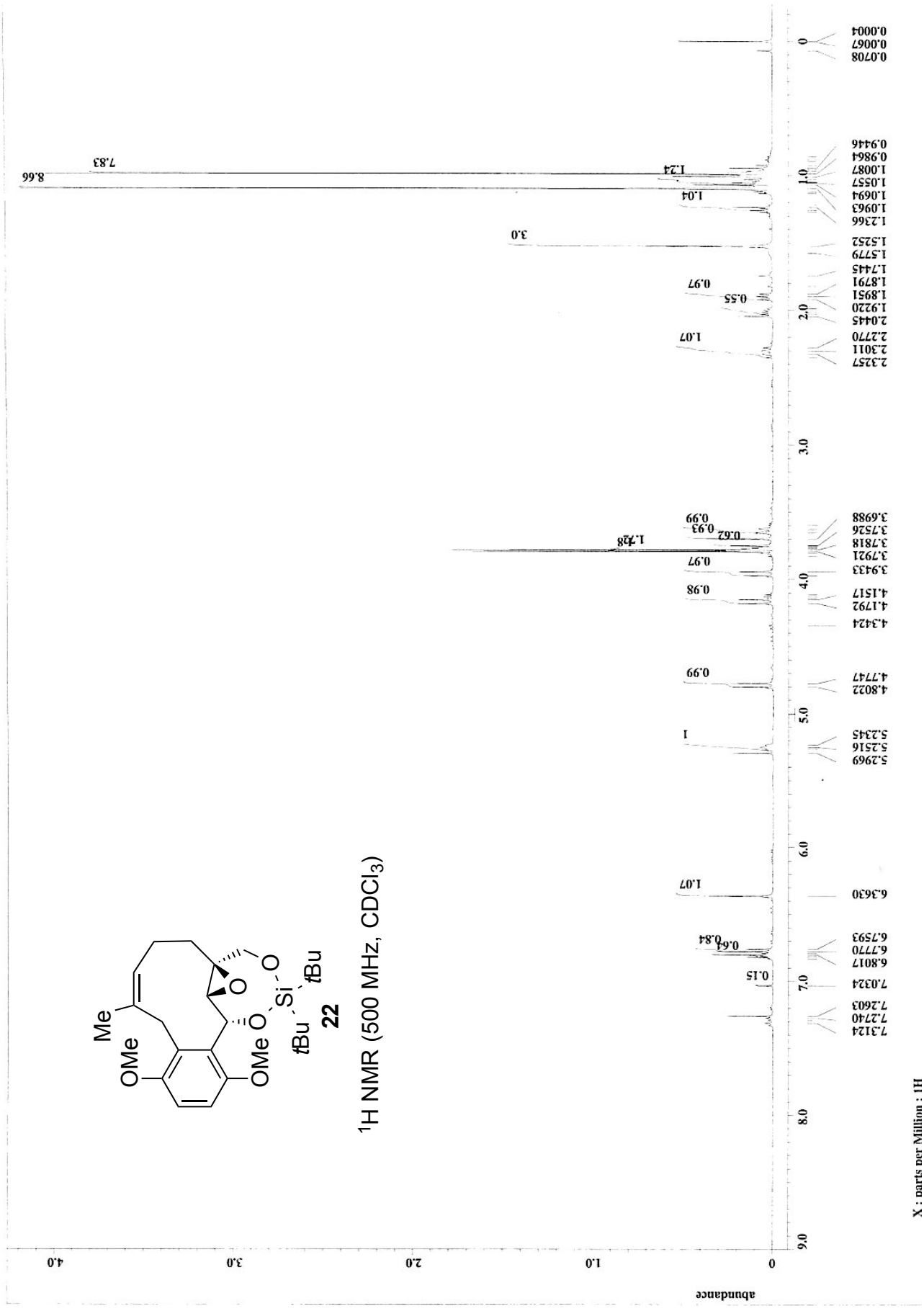

OMe
Br
OMe
O
Si
tBu
tBu
18
^{13}C NMR (125 MHz, $CDCl_3$, 50 °C)
141.1522
138.2096
133.1591
129.2245
114.7930
114.6452
111.4975
111.2209
77.2549
76.9974
76.7446
57.0242
56.4566
36.2640
36.2258
32.4916
27.9132
27.7940
21.5225
21.1028
abundance
X : parts per Million : 13C

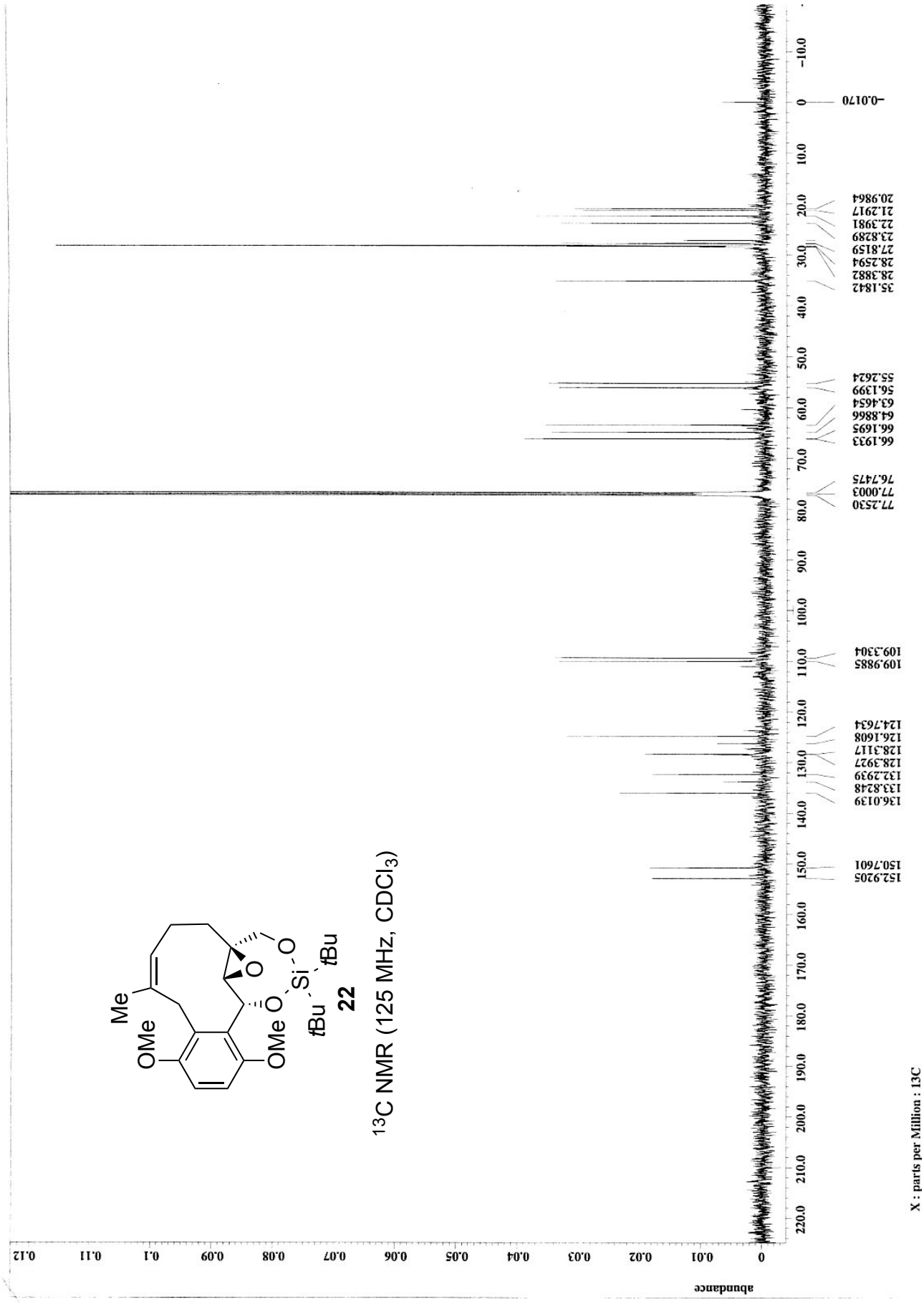

OMe
Br
OMe
O
O
O
Si
tBu
tBu
19
1H NMR (500 MHz, CDCl3)
abundance
X : parts per Million : 1H

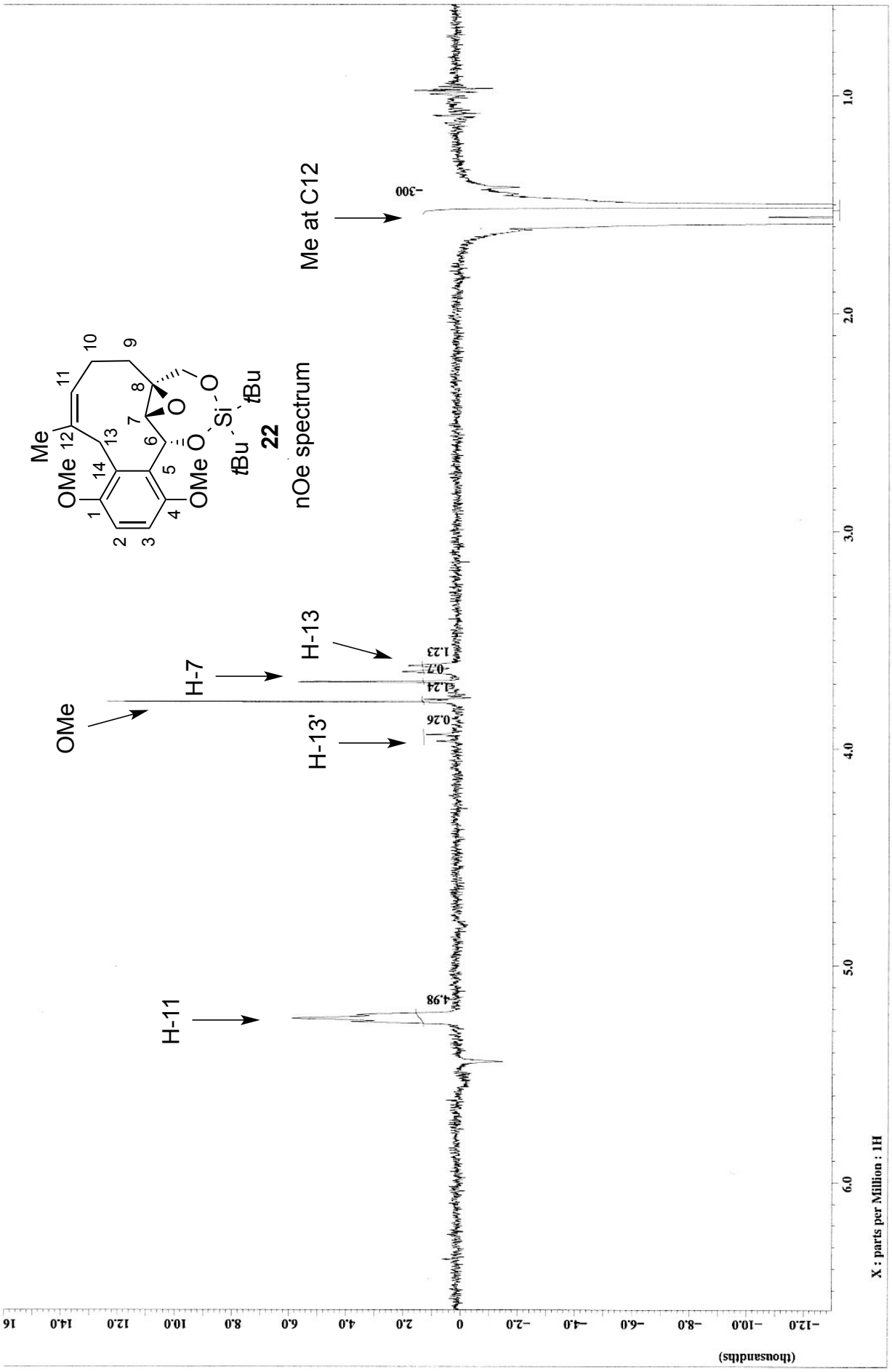

OMe
Br
OMe
O
O
Si
tBu
tBu
19
13C NMR (125 MHz, CDCl3)
153.0518
150.3954
137.9670
129.9310
114.8413
111.9274
111.1071
77.2508
76.9980
76.7453
67.4835
64.0497
63.2485
60.3680
56.9580
56.2760
33.1551
28.0521
27.8041
27.0840
22.6630
20.4739
14.1834
-0.0240
abundance
X : parts per Million : 13C

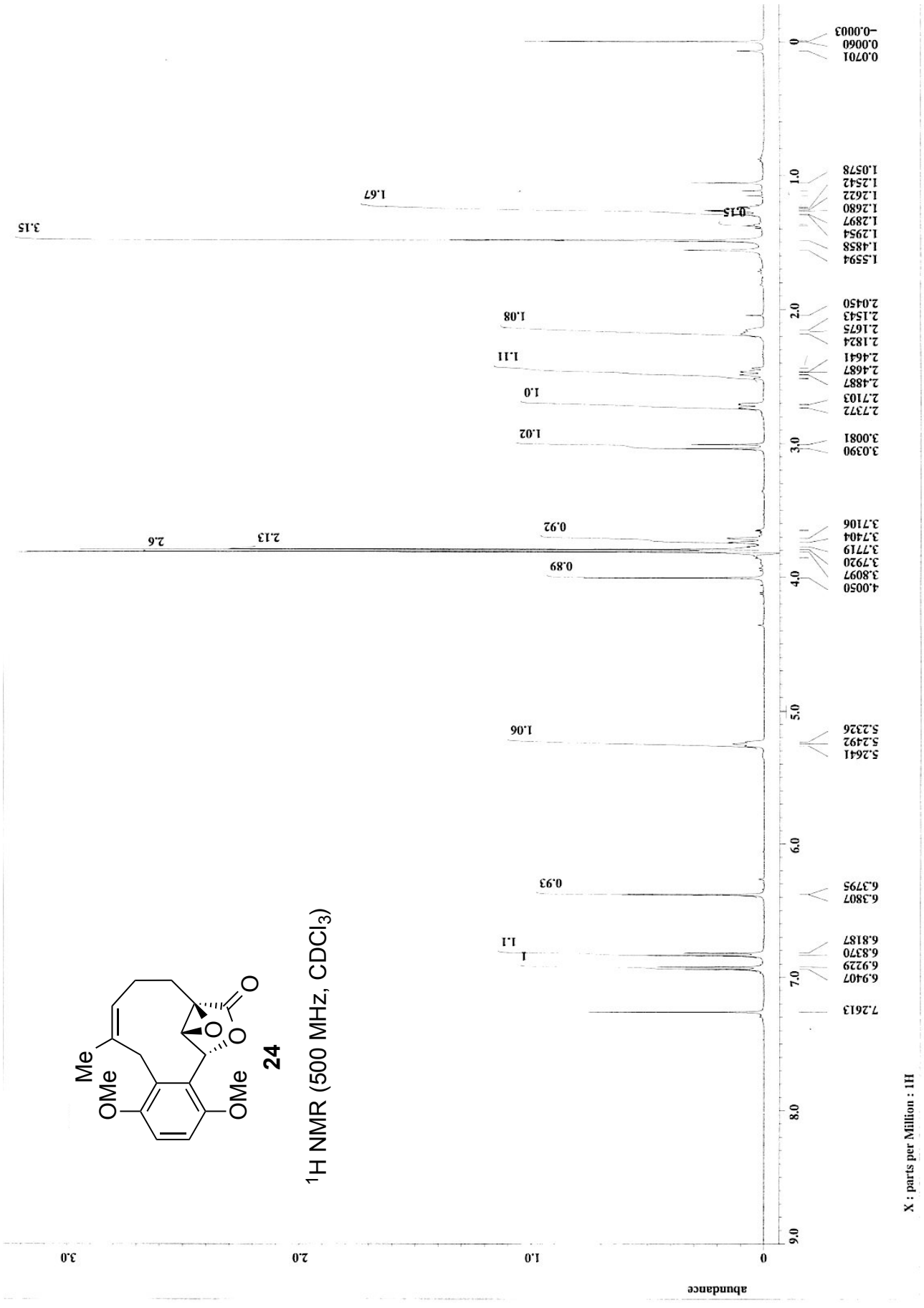

21
^{1}H NMR (500 MHz, CDCl$_3$)
Me
OMe
OMe
O
O
Si
tBu
tBu
abundance
X : parts per Million : 1H

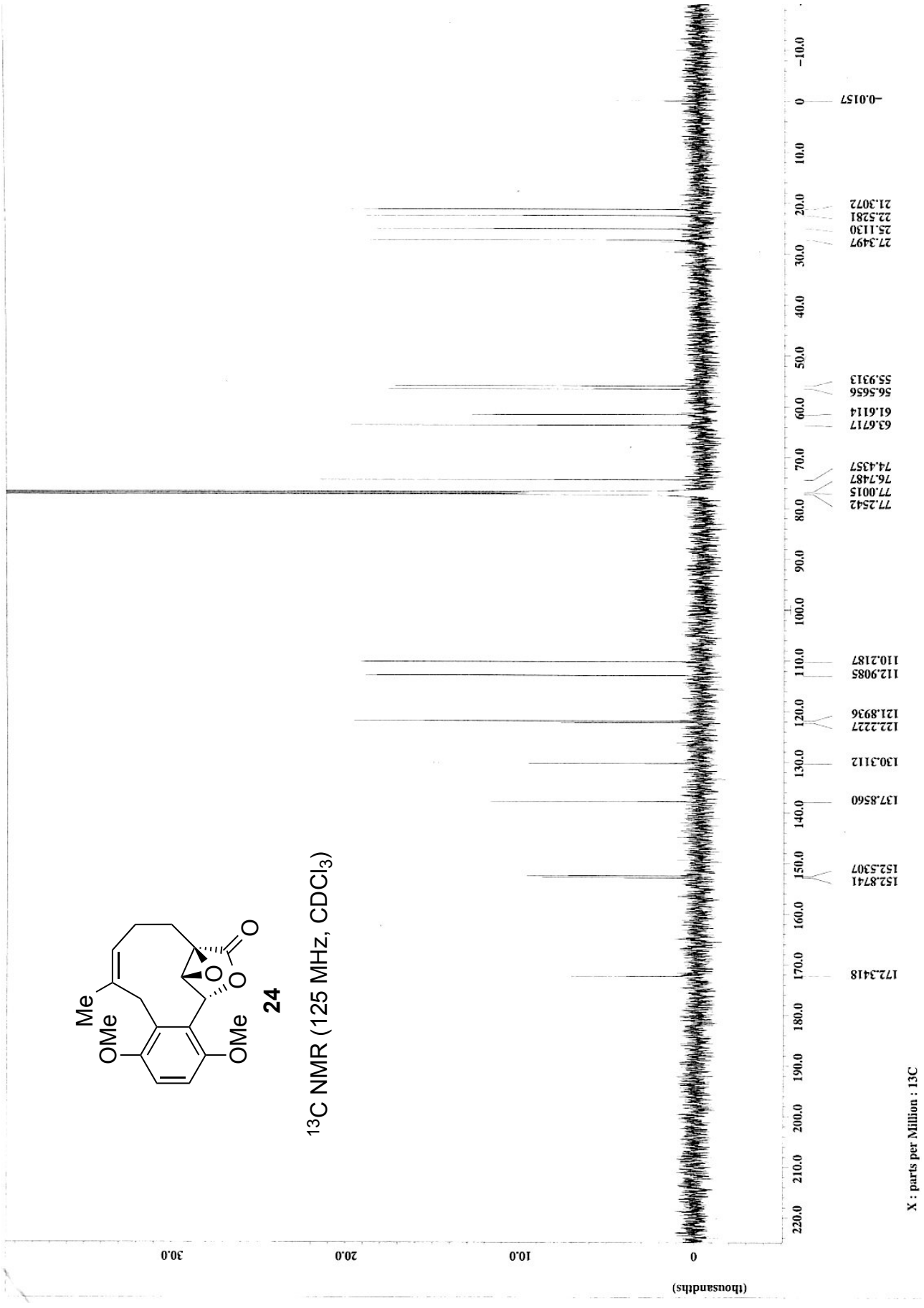

13.5982
20.4515
22.6883
23.6230
27.1474
27.7674
28.0011
33.1900
33.9626
55.9627
56.3919
64.0655
64.1657
67.5708
76.7467
77.0042
77.2570
109.8733
110.5887
111.0084
114.7808
129.3458
138.0161
144.6071
X : parts per Million : 13C
abundance
21
^{13}C NMR (125 MHz, CDCl$_3$)
Me
OMe
OMe
O
O
O
Si
tBu
tBu

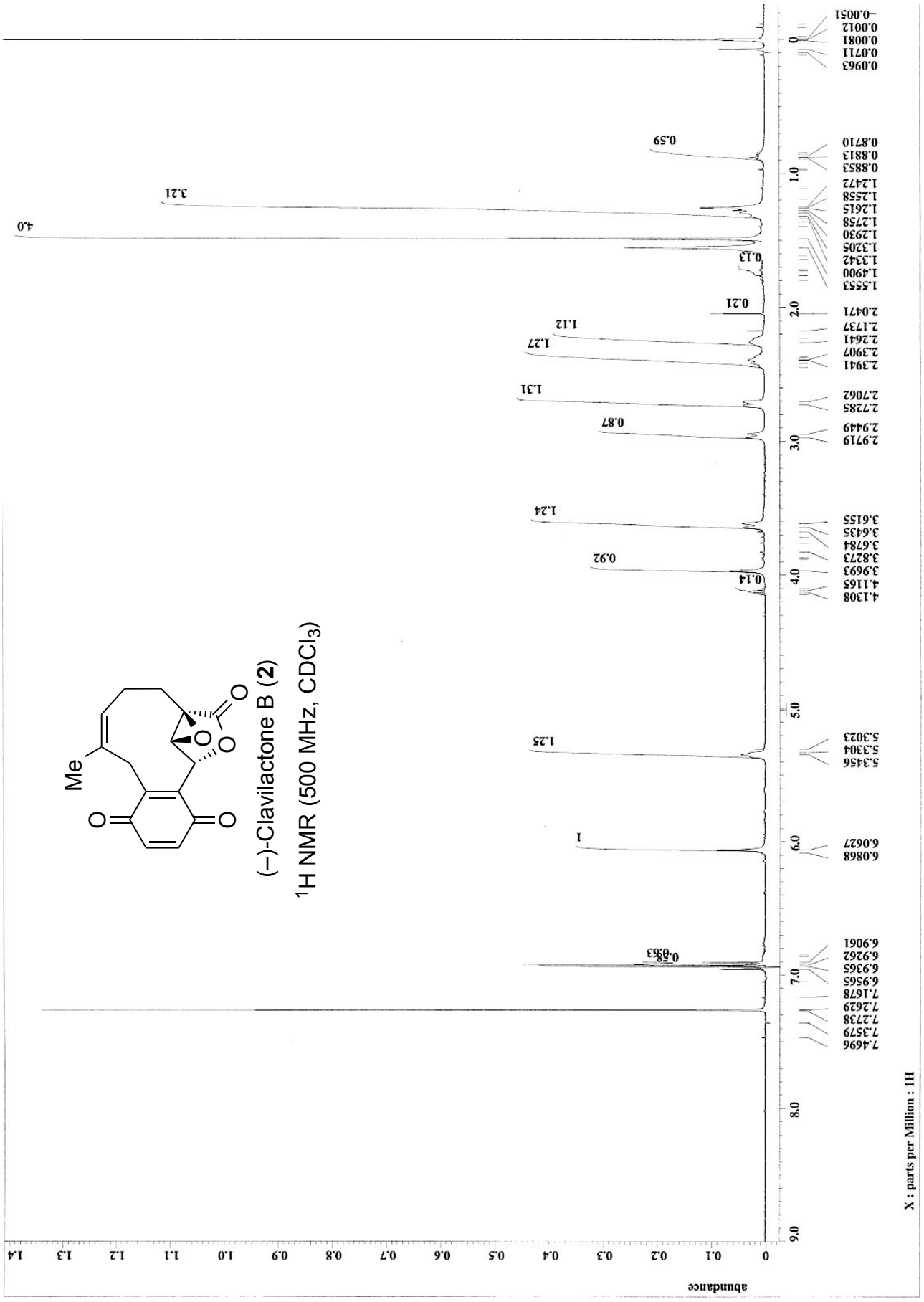

Me
OMe
OMe
O
O
Si
tBu
tBu
22
^{1}H NMR (500 MHz, CDCl$_3$)
abundance
X : parts per Million : 1H

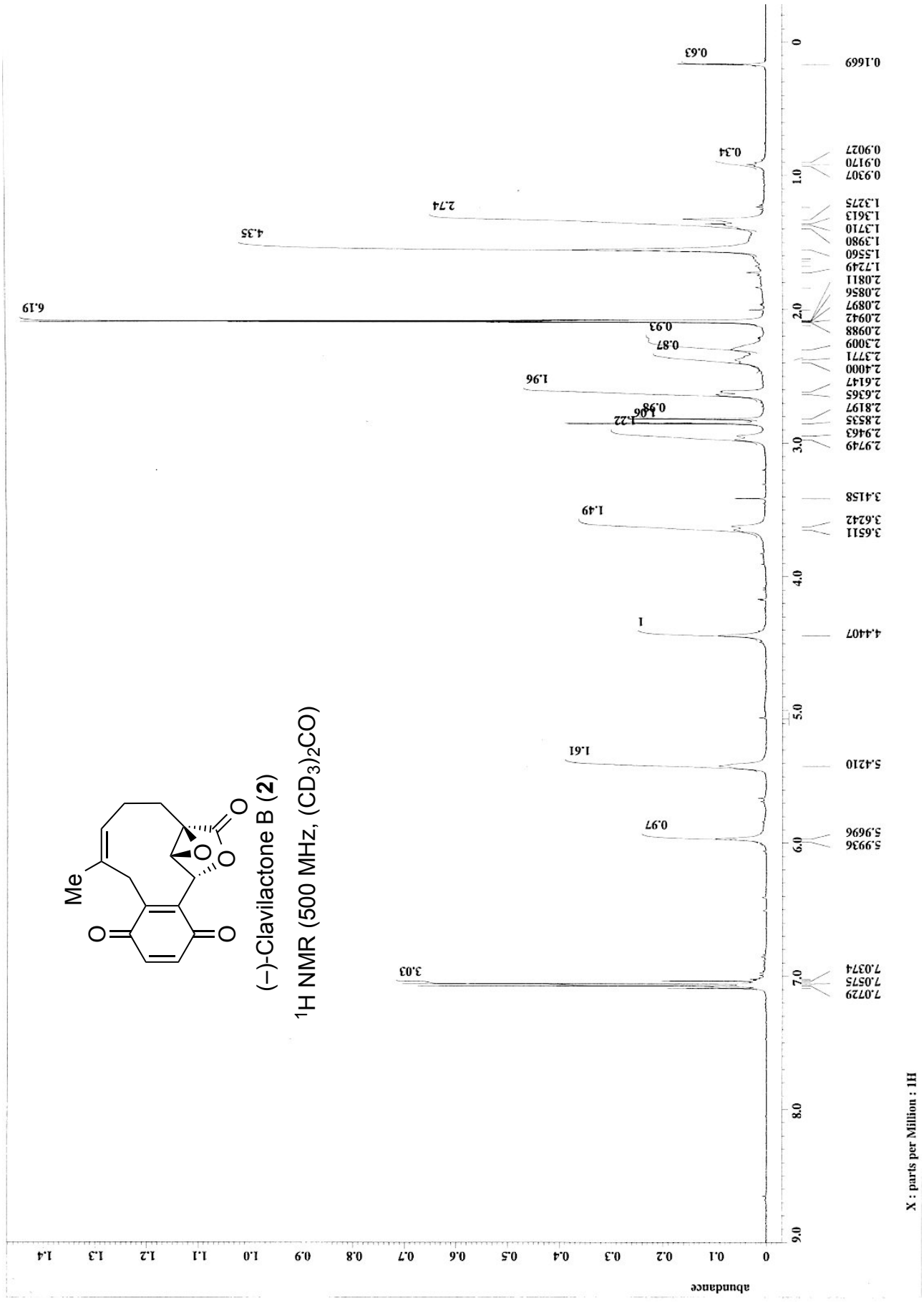

Me
OMe
OMe
O
O
Si
O
tBu
tBu
22
13C NMR (125 MHz, CDCl3)
abundance
X : parts per Million : 13C
-0.0170
20.9864
21.2917
22.3981
23.8289
27.8159
28.2594
28.3882
35.1842
55.2624
56.1399
63.4654
64.8866
66.1695
66.1933
76.7475
77.0003
77.2530
109.3304
109.9885
124.7634
126.1608
128.3117
128.3927
132.2939
133.8248
136.0139
150.7601
152.9205


Me at C12
nOe spectrum
22
OMe
H-7
H-13
H-13'
H-11
X : parts per Million : 1H
(thousandths)

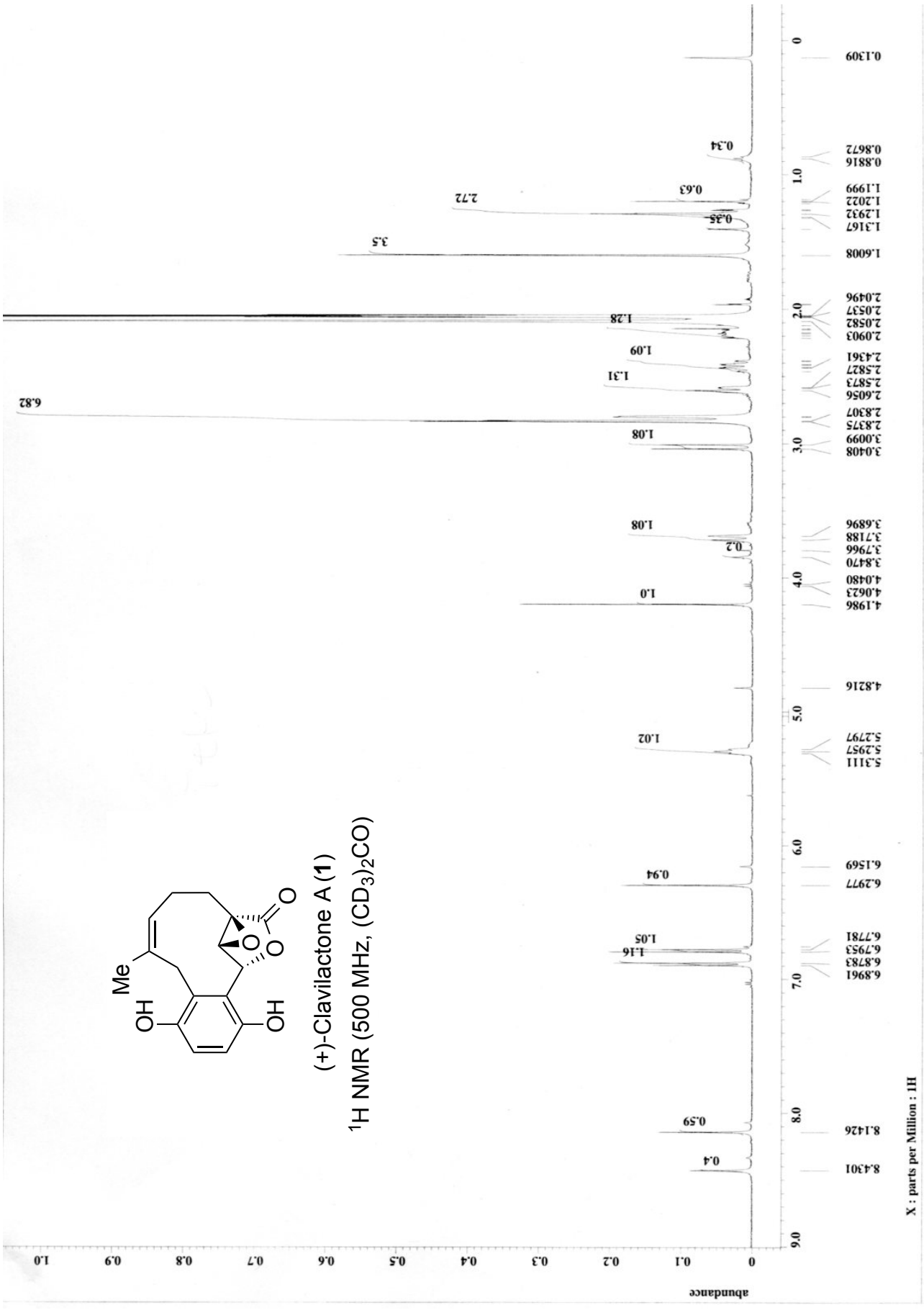

24
^{1}H NMR (500 MHz, CDCl$_3$)
Me
OMe
OMe
X : parts per Million : 1H
abundance

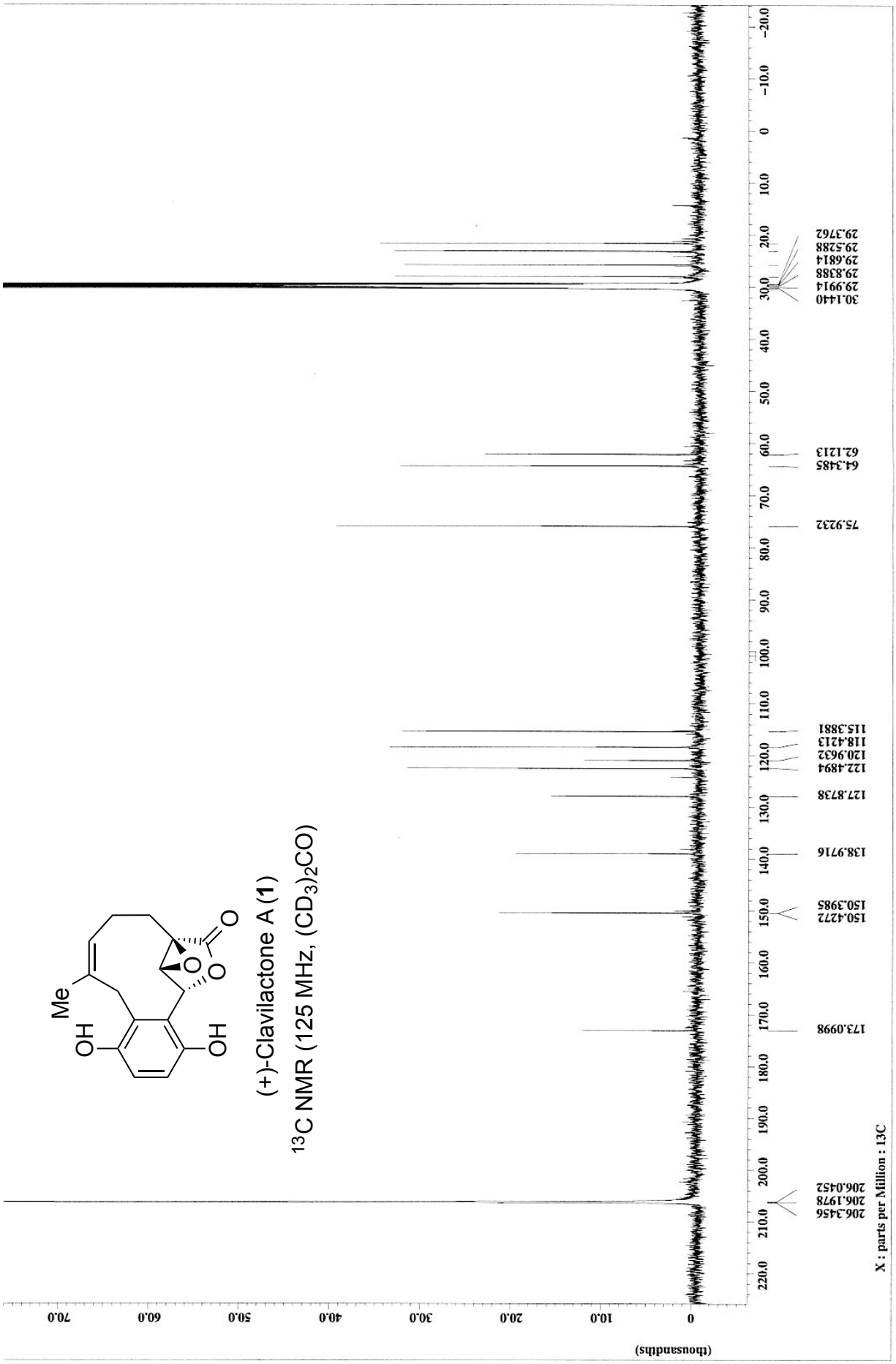

Me
OMe
OMe
O
O
O
24
^{13}C NMR (125 MHz, CDCl$_3$)
(thousandths)
0
10.0
20.0
30.0
X : parts per Million : 13C
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-0.0157
21.3072
22.5281
25.1130
27.3497
55.9313
56.5656
61.6114
63.6717
74.4357
76.7487
77.0015
77.2542
110.2187
112.9085
121.8936
122.2227
130.3112
137.8560
152.5307
152.8741
172.3418


(–)-Clavilactone B (2)
^{1}H NMR (500 MHz, CDCl$_3$)
Me
O
O
O
O
O
abundance
X : parts per Million : 1H


(–)-Clavilactone B (2)
^{1}H NMR (500 MHz, $(CD_3)_2CO$)
Me
O
O
O
O
O
abundance
X : parts per Million : 1H
6.19
4.35
3.03
2.74
1.96
1.61
1.49
1.22
1.06
1
0.98
0.97
0.93
0.87
0.63
0.34
7.0729
7.0575
7.0374
5.9936
5.9696
5.4210
4.4407
3.6511
3.6242
3.4158
2.9749
2.9463
2.8535
2.8197
2.6365
2.6147
2.4000
2.3771
2.3009
2.0988
2.0942
2.0897
2.0856
2.0811
1.7249
1.5560
1.3980
1.3710
1.3613
1.3275
0.9307
0.9170
0.9027
0.1669

(–)-Clavilactone B (2)
^{13}C NMR (125 MHz, $CDCl_3$)
Me
O
O
O
O
O
X : parts per Million : 13C
(thousandths)
186.3554
184.6957
136.8085
136.7227
136.3221
134.7244
124.1893
77.2512
76.9985
76.7457
71.6284
62.6099
26.8364
24.5520
22.8494
14.1886
-0.0187


(+)-Clavilactone A (1)
^{1}H NMR (500 MHz, $(CD_3)_2CO$)
Me
OH
OH
O
O
O
abundance
X : parts per Million : 1H


(+)-Clavilactone A (1)
^{13}C NMR (125 MHz, $(CD_3)_2CO$)
Me
OH
OH
O
O
O
X : parts per Million : 13C
(thousandths)
206.3456
206.1978
206.0452
173.0998
150.4272
150.3985
138.9716
127.8738
122.4894
120.9632
118.4213
115.3881
75.9232
64.3485
62.1213
30.1440
29.9914
29.8388
29.6814
29.5288
29.3762