[Supporting Information]

Synthetic Study of the C’D’E’ Ring System of Maitotoxin via Furan Based Strategy

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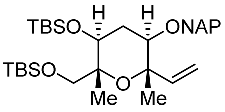
Abbreviations

Ac	acetyl
acac	acetylacetonate
AD	asymmetric dihydroxylation
aq	aqueous
9-BBN	9-borabicyclo[3.3.1]nonane
Bn	benzyl
Bu	butyl
calcd	calculated
cat	catalytic or catalyst
COD	1,5-cyclooctadiene
COSY	correlation spectroscopy
Cp*	pentamethylcyclopentadienyl
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
$(DHQ)_2PHAL$	hydroquinine 1,4-phthalazinediyl diether
DMAP	4-(*N*,*N*-dimethylamino)pyridine
DMDO	dimethyldioxirane
DMF	*N,N*-dimethylformamide
dqf-COSY	double quantum filtered correlation spectroscopy
dr	diastereomer ratio
dtbpy	4,4’-di-*tert*-butyl-2,2’-bipyridine
ee	enantiomeric excess
eq	equivalent(s)
ESI	electrospray ionization
Et	ethyl
HMBC	heteronuclear multiple bond correlation
HMQC	heteronuclear multiple quantum coherence
HRMS	high-resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
i	iso
IR	infrared
M	molar
MCPBA	*meta*-chloroperbenzoic acid

Me	methyl
MS	mass spectrometry
MS4A	molecular sieves 4 angstrom
n	normal
NAP	2-naphtylmethyl
NBS	*N*-bromosuccinimide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
NOESY	nuclear Overhauser effect spectroscopy
p	para
pin	pinacolate
Ph	phenyl
PPTS	pyridinium *para*-toluenesulfonate
quant	quantitative
rt	room temperature
t	tertiary
TBAF	tetra-*n*-butylammonium fluoride
TBHP	*tert*-butyl hydroperoxide
TBS	*tert*-butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidin-1-oxyl
TES	triethylsilyl
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl

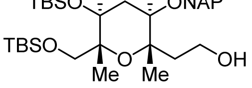
General methods for organic syntheses. All reactions sensitive to air or moisture were performed under argon atmosphere with dry glassware unless otherwise noted. The dehydrated solvents, CH_2Cl_2, tetrahydrofuran (THF), toluene, *N*,*N*-dimethylformamide (DMF) were used without further dehydration. TMSCl, pyridine, and 2,6-lutidine were distilled before use. Molecular sieves 4A (MS4A) were preactivated by heating in vacuo. PPTS and $CuCO_3 \cdot Cu(OH)_2$ were prepared according to the literature.[1] All other chemicals were obtained from local venders, and used as supplied unless otherwise stated. Thin-layer chromatography (TLC) was performed using precoated TLC glass plates (silica gel 60 F_{254}, 0.25-mm thickness) for the reaction analyses. For normal phase column chromatography, silica gel 60N (Kanto Chemical Co., Ltd., spherical, neutral, 100–210 μm) was used. For normal phase flash column chromatography, silica gel 60N (Kanto Chemical Co., Ltd., spherical, neutral, 40–50 μm) was used. Optical rotations were recorded on a JASCO P-1010 polarimeter. IR spectra were recorded on a FT/IR-4000 pectrometer (JASCO). ^1H NMR spectra were recorded on JNM ECA-600 or JNM ECS-400 spectrometer (JEOL) in 600 or 400 MHz, and ^{13}C NMR spectra were recorded at 150 or 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane (TMS) with reference to internal residual solvent [^1H NMR: $CHCl_3$ (7.26), C_6D_5H (7.16); ^{13}C NMR: $CDCl_3$ (77.16), C_6D_6 (128.06)]. The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High resolution mass spectra (HRMS) were recorded on micrOTOF II (Bruker) ESI-TOF equipment.



2

Bis-TBS ether 2. Imidazole (1.02 g, 14.9 mmol) and TBSCl (2.02 g, 13.4 mmol) were added to a solution of diol **1**[2] (2.02 g, 5.90 mmol) in DMF (6 mL) at 0 °C under argon atmosphere. The mixture was stirred at rt for 12 h. Additional imidazole (1.00 g, 15.9 mmol) and TBSCl (1.96 g, 13.0 mmol) were added to the mixture, and after stirring for 4 h, further imidazole (1.09 g, 16.0 mmol) and TBSCl (2.67 g, 17.7 mmol) were added. After stirring at rt for 2 h, the reaction mixture was warmed to 70 °C, stirred for 2 h, then warmed to 90 °C. The mixture was stirred for 50 min at 90 °C, quenched with MeOH, saturated aqueous NH_4Cl, and H_2O, diluted with EtOAc, and extracted with Et_2O. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography to give bis-TBS ether **2** (3.43 g, 6.16 mmol, quant).

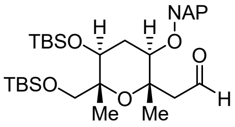
2: $[\alpha]_D^{15}$ +2.5 (*c* 1.16, $CHCl_3$); R_f = 0.77 (hexane/EtOAc = 10/1); IR (neat) 3724, 3057, 2953, 2928, 2885, 2857, 2360, 1123, 1098, 853, 836 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86–7.84 (m, 3H), 7.79 (s, 1H), 7.52–7.46 (m, 3H), 6.03 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.39 (dd, *J* = 17.4, 1.8 Hz, 1H), 5.09 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.70 (*J* = 11.7 Hz, 1H), 3.99 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.47 (d, *J* = 10.5 Hz, 1H), 3.44 (d, *J* = 10.5 Hz, 1H), 3.33 (dd, *J* = 11.9, 4.1 Hz, 1H), 1.99 (ddd, *J* = 11.9, 4.6, 4.1 Hz, 1H), 1.84 (ddd, *J* = 11.9, 11.9, 11.9, 1H), 1.43 (s, 3H), 1.12 (s, 3H), 0.93 (m, 9H), 0.88 (m, 9H), 0.09 (s, 3H), 0.08 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 136.2, 133.4, 133.1, 128.2, 128.0, 127.8, 126.3, 126.2, 125.9 (×2), 112.7, 80.5, 78.1, 76.1, 72.2, 68.0, 67.0, 31.2, 26.1, 25.8, 20.4, 18.41, 18.35, 18.0, −4.1, −4.95, −4.97, −5.2; HRESIMS *m*/*z* $[M + Na]^+$ calcd for $C_{33}H_{54}O_4Si_2Na^+$ 593.3453, fond 593.3465.



3

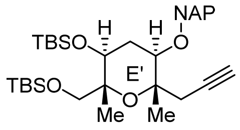
Alcohol 3. A solution of bisTBS ether **2** (1.86 g, 3.27 mmol) in THF (6.0 mL) was added to a solution of 9-BBN dimer (1.68 g, 6.94 mmol) in THF (18 mL) at 0 °C under argon atmosphere and washed with THF (4.0 mL + 5.0 mL). The mixture was stirred at rt for 3 h, then cooled to 0 °C. Saturated aqueous $NaHCO_3$ (10 mL) and 30% aqueous H_2O_2 (7.0 mL, 68.6 mmol) were added to reaction solution. The resulting mixture was stirred at rt for 30 min, quenched with saturated aqueous $Na_2S_2O_3$, and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give alcohol **3** (1.81 g, 3.08 mmol, 94%).

3: $[\alpha]_D^{20}$ −12.2 (*c* 1.10, $CHCl_3$); R_f = 0.67 (hexane/EtOAc = 10/1); IR (neat) 3501, 2952, 2928, 2885, 2856, 1123, 1089, 850, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 3H), 7.75 (s, 1H), 7.51–7.42 (m, 3H), 4.77 (d, *J* = 11.7 Hz, 1H), 4.64 (d, *J* = 11.7 Hz, 1H), 3.81 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.72–3.70 (m, 2H), 3.47 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.40 (d, *J* = 10.1, 1H), 3.36 (d, *J* = 10.1 Hz, 1H), 2.02 (ddd, *J* = 12.2, 4.6, 4.1 Hz, 1H), 1.89 (ddd, *J* = 15.4, 6.4, 4.1 Hz, 1H), 1.83–1.73 (m, 2H), 1.34 (s, 3H), 1.10 (s, 3H), 0.90 (m, 9H), 0.84 (m, 9H), 0.04 (s, 3H), 0.04 (s, 3H), 0.00 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.3, 133.1, 128.3, 128.0, 127.8, 126.5, 126.3, 126.1, 125.9, 78.7, 78.2 (×2), 71.7, 68.3, 67.7, 59.3, 42.3, 30.4, 26.2, 25.8, 21.5, 18.4, 18.1, 17.9, −3.7, −4.8, −5.3, −5.4; HRESIMS *m/z* $[M + Na]^+$ calcd for $C_{33}H_{56}O_5Si_2Na^+$ 611.3558, found 611.3572.



4

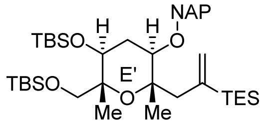
Aldehyde 4. TEMPO (26.7 mg, 171 mmol), 0.5 M aqueous KBr (1.2 mL, 0.6 mmol) were added to the solution of alcohol **3** (1.76g, 3.00 mmol) in CH_2Cl_2 (38 mL) at 0 °C. A aqueous solution of $NaOCl$-$NaHCO_3$ (8.8 mL, prepared from $NaOCl{\cdot}5H_2O$ (2.14 g, 13.0 mmol), H_2O (7.2 mL), and saturated aqueous $NaHCO_3$ (31 mL)) was added to the reaction mixture. The mixture was stirred at 0 °C for 1 h. Additional aqueous solution of $NaOCl$-$NaHCO_3$ (0.8 mL) was added to the reaction mixture, and after stirring for 15 min, the solution (0.6 mL) was added at 0 °C. The reaction mixture was stirred for 15 min, quenched with saturated aqueous $Na_2S_2O_3$, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude aldehyde **4** (1.72 g) which was used for the next reaction without further purification.



5

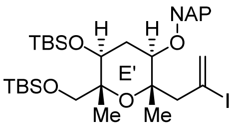
Alkyne 5. *n*-BuLi (1.6 M in hexane, 11.0 mL, 17.6 mmol) was added to a solution of TMS diazomethane (2.0 M solution in hexane, 9.0 mL, 18.0 mmol) in THF (10 mL) at −78 °C under argon atmosphere. The solution was stirred for 35 min. A solution of crude aldehyde **4** (1.72 g) in THF (5 mL) was added to the solution via canula and washed with THF (5 + 5 + 5 mL). The reaction mixture was stirred at −78 °C for 40 min, warmed to 0 °C. The mixture was stirred for 1 h, quenched with saturated aqueous NH_4Cl, and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give alkyne **5** (1.44 g, 2.47 mmol, 82%, 2 steps).

5: $[\alpha]_D^{19}$ −4.8 (*c* 1.13, $CHCl_3$); R_f = 0.83 (hexane/EtOAc = 7/1); IR (neat) 3312, 2953, 2928, 2885, 2856, 1125, 1099, 852, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 3H), 7.79 (s, 1H), 7.52–7.47 (m, 3H), 4.81 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 11.7 Hz, 1H), 3.88 (dd, *J* = 11.9, 4.6 Hz, 1H), 3.46 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.42 (s, 2H), 2.56 (dd, *J* = 16.6, 2.4 Hz, 1H), 2.35 (dd, *J* = 16.6, 2.4 Hz, 1H), 2.03–1.97 (m, 2H), 1.77 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.36 (s, 3H), 1.08 (s, 3H), 0.90 (m, 9H), 0.87 (m, 9H), 0.07 (s, 3H), 0.07 (s, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 133.4, 133.1, 128.3, 128.0, 127.8, 126.5, 126.2, 125.99, 125.96, 81.9, 79.0, 78.2, 75.5, 71.6, 70.3, 68.3, 67.2, 32.5, 30.6, 26.2, 25.8, 20.9, 18.6, 17.9, 17.8, −4.2, −4.9, −5.0, −5.2; HRESIMS *m/z* $[M + Na]^+$ calcd for $C_{34}H_{54}O_4Si_2Na^+$ 605.3453, found 605.3453.



6

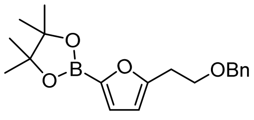
Alkene 6. $[Cp^*Ru(MeCN)_3]PF_6$ (135 mg, 0.267 mmol) and Et_3SiH (3.1 mL, 19.5 mmol) were added to a solution of alkyne **5** (1.44 g, 2.47 mmol) in CH_2Cl_2 (25 mL) at 0 °C. After the reaction mixture was stirred at rt for 3 h, $[Cp^*Ru(MeCN)_3]PF_6$ (39.7 mg, 78.7 μmol) was added to the mixture. The mixture was stirred for 30 min, and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to give a crude alkene **6** (1.91 g) which was used for the next reaction without further purification.



7

Iodide 7. 2,6-lutidine (2.0 mL, 17.3 mmol) and I_2 (6.37 g, 25.1 mmol) were added to a solution of crude alkene **6** (1.91 g) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was stirred at rt for 2 h. Additional I_2 (10. 6 g, 41.6 mmol) was added to the mixture. The mixture was stirred at rt for 1.5 h, quenched with saturated aqueous $Na_2S_2O_3$/Et_3N, extracted with EtOAc, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give iodide **7** (1.36 g, 1.91 mmol, 77%, 2 steps).

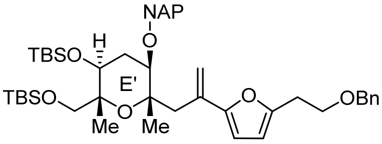
7: $[\alpha]_D^{18}$ −2.6 (*c* 1.23, $CHCl_3$); IR (neat) 2952, 2927, 2885, 2856, 1122, 1100, 1086, 852, 836, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84–7.82 (m, 3H), 7.78 (s, 1H), 7.49–7.46 (m, 3H), 6.37 (d, *J* = 1.4 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 3.84 (dd, *J* = 11.9, 4.7 Hz, 1H), 3.38 (s, 2H), 3.33 (*J* = 11.9, 4.3 Hz, 1H) 2.89 (d, *J* = 15.1 Hz, 1H), 2.65 (d, *J* = 15.1 Hz, 1H) 2.00 (ddd, *J* = 11.9, 4.7, 4.3 Hz, 1H), 1.75 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.34 (s, 3H), 1.06 (s, 3H), 0.87 (m, 9H), 0.83 (m, 9H), 0.02 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 133.4, 133.1, 130.7, 128.3, 128.0, 127.8, 126.4, 126.2, 126.0, 125.9, 103.3, 79.1, 78.2, 77.3, 71.3, 68.4, 67.2, 55.6, 30.3, 26.1, 25.8, 20.5, 18.4, 18.1, 18.0, −3.9, −4.9, −5.0, −5.1; HRESIMS *m*/*z* $[M + Na]^+$ calcd for $C_{34}H_{55}IO_4Si_2Na^+$ 733.2576, found 733.2610.



9

Furanylborate 9. A solution of furan **8**[3] (421 mg, 2.08 mmol) in octane (1.0 mL) was added to a solution of $[IrCl(COD)]_2$ (21.9 mg, 32.6 μmol), dtbpy (17.3 mg, 64.5 μmol), and B_2pin_2 (809 mg, 3.19 mmol) in octane (2.0 mL) under argon atmosphere and washed with octane (1.0 + 1.0 mL). The mixture was stirred at 80 °C for 18 h and purified by silica gel column chromatography to give furanylborate **9** (481 mg, 1.47 mmol, 70%).

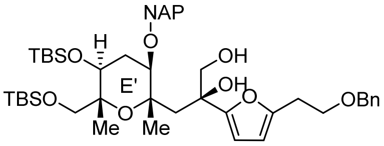
9: IR (neat) 2978, 2928, 2863 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 7.01 (d, *J* = 3.2 Hz, 1H), 6.15 (d, *J* = 3.2 Hz, 1H), 4.52 (s, 2H), 3.75 (t, *J* = 7.1 Hz, 2H), 3.03 (*J* = 7.1 Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 138.4, 128.5, 127.8, 127.7, 124.9, 107.4, 84.2, 73.1, 68.2, 29.3, 24.9 ; HRESIMS *m/z* $[M + Na]^+$ calcd for $C_{19}H_{25}BO_4Na^+$ 351.1738, found 351.1744.



10

Olefin 10. Na_2CO_3 (4.4 mg, 41.5 μmol) and $Pd(PPh_3)_2Cl_2$ (4.0 mg, 5.70 μmol) were added to a solution of iodide **7** (20.8 mg, 29.3 μmol) and furanylborate **9** (13.6 mg, 41.4 μmol) in DMF (degassed, 1.20 mL) and H_2O (degassed, 0.24 mL) at rt under argon atmosphere. The mixture was stirred for 30 min, warmed to 95 °C. After stirring for 3 h, the mixture was diluted with Et_2O, extracted with Et_2O dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give olefin **10** (17.5 mg, 22.3 μmol, 76%).

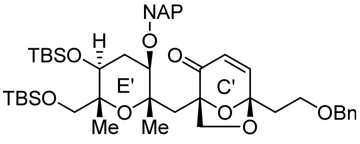
10: $[\alpha]_D^{17}$ −1.8 (*c* 1.23, $CHCl_3$); IR (neat) 2952, 2927, 2884, 2856, 1119, 1100, 853, 775 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 7.73–7.64 (m, 4H), 7.43–7.41 (m, 1H), 7.32–7.08 (m, 7H), 6.55 (d, *J* = 3.0 Hz, 1H), 6.07 (s, 1H), 6.02 (d, *J* = 3.0 Hz, 1H), 5.50 (s, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.35 (d, *J* = 11.9 Hz, 1H), 4.22 (s, 2H), 3.99 (dd, *J* = 11.9, 4.1 Hz, 1H), 3.53–3.45 (m, 5H), 3.01(d, *J* = 14.2 Hz, 1H), 2.80 (t, *J* = 6.9 Hz, 2H), 2.71 (d, *J* = 14.2 Hz, 1H), 2.09 (ddd, *J* = 11.9, 4.6, 4.1 Hz, 1H), 1.86 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.47 (s, 3H), 1.17 (s, 3H), 1.06 (m, 9H), 0.94 (m, 9H), 0.19 (s, 3H), 0.15 (s, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 155.2, 153.1, 139.2, 137.0, 134.2, 133.9, 133.5, 128.6, 128.5, 127.7, 127.6, 126.4, 126.1, 126.0, 112.9, 108.9, 108.3, 80.0, 78.3, 77.3, 72.9, 71.2, 69.1, 68.6, 68.2, 44.8, 31.0, 29.5, 26.3, 25.9, 20.7, 18.7, 18.3, 18.1, −3.8, −4.8, −5.0 (×2). The ^{13}C NMR signals of **10** is partially overlapped with the signal of C_6D_6; HRESIMS *m*/*z* $[M + Na]^+$ calcd for $C_{47}H_{68}O_6Si_2Na^+$ 807.4447, found 807.4463.



11

Diol 11. K_2CO_3 (127 mg, 0.915 mmol), $K_3Fe(CN)_6$ (302 mg, 0.917 mmol), $(DHQD)_2PHAL$ (46.7 mg, 60.0 μmol), $MeSO_2NH_2$ (21.8 mg, 0.229 mmol), and $K_2OsO_4{\cdot}2H_2O$ (8.9 mg, 24.2 μmol) were dissolved in *t*-BuOH (3.8 mL) and H_2O (3.8 mL). The suspension was stirred at rt for 30 min then cooled to 0 °C. Olefine **10** (120 mg, 0.153 mmol) in *t*-BuOMe (2.0 mL) was added to the suspension and washed with *t*-BuOMe (2.0 + 2.0 + 1.6 mL). The mixture was stirred at rt for 2 h, quenched with solid $Na_2S_2O_3$, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give diol **11** (113 mg, 0.138 mmol, 90%, dr > 20:1).

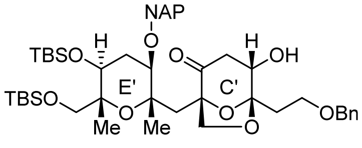
11: $[\alpha]_D^{21}$ +41.3 (*c* 1.03, C_6H_6); IR (neat) 3405, 2953, 2928, 2884, 2857, 1120, 1091, 838, 777 cm^{-1}; ^{1}H NMR (600 MHz, C_6D_6) δ 7.72 (s, 1H), 7.70–7.63 (m, 3H), 7.45–7.44 (m, 1H), 7.29–7.23 (m, 2H), 7.17–7.13 (m, 5H), 6.58 (d, *J* = 3.1 Hz, 1H), 6.00 (d, *J* = 3.1 Hz, 1H), 5.96 (s, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.26 (d, *J* = 12.0 Hz, 1H), 4.11 (s, 2H), 4.05 (ddd, *J* = 12.0, 4.8, 4.1 Hz, 1H), 3.87 (ddd, *J* = 12.0, 4.8, 4.1 Hz, 1H), 3.83–3.81 (m, 2H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.49 (d, *J* = 10.0 Hz, 1H), 3.38–3.31 (m, 2H), 2.66 (d, *J* = 12.4 Hz, 1H), 2.65 (d, *J* = 12.4 Hz, 1H), 2.60 (d, *J* = 15.1 Hz, 1H), 2.61–2.56 (m, 1H), 2.50 (d, *J* = 15.1 Hz, 1H), 2.00 (ddd, *J* = 12.0, 4.8, 4.1 Hz, 1H), 1.72 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.35 (s, 3H), 1.09 (m, 9H), 1.08 (s, 3H), 0.88 (m, 9H), 0.23 (s, 3H), 0.20 (s, 3H), 0.03 (s, 3H), −0.08 (s, 3H); ^{13}C NMR (150 MHz, C_6D_6) δ 158.3, 152.8, 139.1, 137.4, 133.9, 133.5, 128.6, 128.5, 128.40, 128.35, 127.7, 127.6, 126.4, 126.0, 125.9, 125.8, 107.4, 107.1, 79.8, 79.0, 76.9, 74.4, 72.8, 71.22, 71.17, 68.4, 68.2, 67.4, 42.4, 31.3, 29.2, 26.6, 25.9, 24.1, 18.9, 18.4, 18.0, −3.6, −4.8, −5.0, −5.1; HRESIMS *m*/*z* [M + Na]$^+$ calcd for $C_{47}H_{70}O_8Si_2Na^+$ 841.4501, found 841.4536.



12

Enone 12. 0.132 M aqueous Oxone (0.65 mL, 85.9 μmol) was added to a solution of diol **11** (28.2 mg, 34.4 μmol) and $NaHCO_3$ (29.3 mg, 0.3488 mmol) in acetone (2.2 mL) at 0 °C. The mixture was stirred at rt for 3 h. Aqueous Oxone (0.32 mL, 42.3 μmol) was added to the reaction mixture. After stirring for 25 min, further aqueous Oxone (0.32 mL, 42.3 μmol) was added. The resulting mixture was stirred at rt for 1 h, extracted with EtOAc, washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. PPTS (67.8 mg, 0.2698 mmol) was added to a solution of the residue (31.6 mg) in CH_2Cl_2 (3.0 mL) at 0 °C. The mixture was stirred for 1 h, quenched with saturated aqueous $NaHCO_3$, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give enone **12** (20.9 mg, 74%, 2 steps).

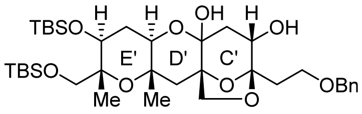
12: $[\alpha]_D^{16}$ −25.1 (*c* 0.95, $CHCl_3$); IR (neat) 3058, 2954, 2928, 2883, 2856, 1119, 1100, 853, 837, 776cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79 (m, 3H), 7.75 (s, 1H), 7.47–7.43 (m, 3H), 7.36–7.28 (m, 5H), 6.96 (d, *J* = 9.8 Hz, 1H), 5.93 (d, *J* = 9.8 Hz, 1H), 4.92 (d, *J* = 8.7 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.64 (d, *J* = 11.9 Hz, 1H), 4.43 (s, 2H),3.72−3.59 (m, 4H), 3.45 (m, 1H), 3.44 (d, *J* = 9.8 Hz, 1H), 3.38 (d, *J* = 9.8 Hz, 1H), 2.45 (d, *J* = 15.1 Hz, 1H), 2.30−2.19 (m, 2H), 2.15 (d, *J* = 15.1 Hz, 1H), 1.99 (ddd, *J* = 12.4, 4.6, 4.1 Hz, 1H), 1.75 (ddd, *J* = 12.4, 12.4, 12.4 Hz, 1H), 1.33 (s, 3H), 1.10 (s, 3H), 0.89 (s, 9H), 0.85 (s, 9H), 0.03 (s, 6H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 148.6, 138.2, 136.4, 133.4, 133.1, 131.0, 128.5, 128.2, 128.0, 127.8, 127.7, 126.3, 126.1, 125.95, 125.87, 103.4, 86.8, 78.4, 78.3, 76.4, 73.3, 71.3, 69.7, 68.5, 66.0, 65.7, 38.1, 35.9, 30.7, 26.2, 25.8, 22.9, 18.6, 18.01, 17.96, −3.7, −4.8, −5.1, −5.2. The one ^{13}C NMR signal of **12** overlapped in the aromatic region; HRESIMS *m*/*z* [M + Na]$^+$ calcd for $C_{47}H_{68}O_8Si_2Na^+$ 839.4345, found 839.4374.



14

Hydroxyketone 14. B_2pin_2 (29.1 mg, 0.115 mmol), PPh_3 (28.7 mg, 0.109 mmol), $CuCO_3\cdot Cu(OH)_2$ (9.6 mg, 43.4 μmol) were added to a solution of enone **12** (29.0 mg, 35.5 μmol) in THF (0.50 mL) and H_2O (0.50 mL) at 0 °C. The mixture was stirred at rt for 2.5 h. Saturated aqueous $NaHCO_3$ (0.60 mL, 0.68 mmol) and 30% aqueous H_2O_2 (0.20 mL, 1.96 mmol) were added to the reaction mixture at 0 °C. The resulting mixture was stirred at rt for 20 min, quenched with saturated aqueous NH_4Cl and saturated aqueous $Na_2S_2O_3$, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give hydroxyketone **14** (28.1 mg, 336 μmol, 95%).

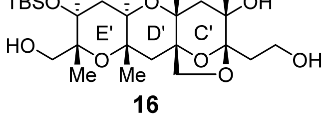
14: $[\alpha]_D^{23}$ −2.4 (*c* 1.33, $CHCl_3$); IR (neat) 3471, 3058, 2953, 2928, 2883, 2856, 1732, 1104, 1089, 854, 837, 775 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.84–7.82 (m, 3H), 7.77 (s, 1H), 7.49–7.45 (m, 3H), 7.37–7.29 (m, 5H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.66 (d, *J* = 11.7 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 3.90–3.88 (m, 1H), 3.80 (s, 2H), 3.74 (td, *J* = 9.6, 2.8 Hz, 1H), 3.70–3.67 (m, 1H), 3.56 (dd, *J* = 12.0, 4.1 Hz, 1H), 3.39 (d, *J* = 10.0 Hz, 1H), 3.35 (dd, *J* = 12.0, 3.8 Hz, 1H), 3.29 (d, *J* = 10.0 Hz, 1H), 2.81 (dd, *J* = 15.1, 5.50 Hz, 1H), 2.74 (dd, *J* = 15.1, 6.9 Hz, 1H), 2.51 (ddd, *J* = 14.7, 10.0, 4.5 Hz, 1H), 2.28 (d, *J* = 14.1 Hz, 1H), 2.02 (d, *J* = 14.1 Hz, 1H), 1.95–1.90 (m, 2H), 1.74 (ddd, *J* = 12.0, 12.0, 12.0 Hz, 1H), 1.37 (s, 3H), 1.09 (s, 3H), 0.91 (s, 9H), 0.83 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H), −0.04 (s, 3H), −0.04 (s, 3H) ; ^{13}C NMR (150 MHz, $CDCl_3$) δ 208.7, 137.4, 136.2, 133.4, 133.1, 128.7, 128.3, 128.1, 128.0, 127.9, 127.8, 126.5, 126.2, 126.01, 125.97, 109.4, 87.6, 81.5, 78.9, 75.9, 73.7, 72.3, 72.2, 71.8, 69.8, 68.8, 65.9, 42.9, 41.4, 34.7, 30.6, 26.3, 25.8, 21.6, 18.6, 17.9, 17.8, −3.8, −4.9, −5.1, −5.2 ; HRESIMS *m*/*z* $[M + Na]^+$ calcd for $C_{47}H_{70}O_9Si_2Na^+$ 857.4451, found 857.4450.



15

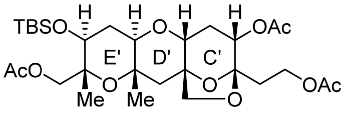
Hemiacetal 15. DDQ (19.5 mg, 85.7 μmol) was added to a solution of ketone **14** (35.8 mg, 42.9 μmol) in CH_2Cl_2 (1.42 mL) and pH 7 buffer (0.72 mL) at 0 °C. The mixture was stirred at rt for 35 min, quenched with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$, extracted with EtOAc, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give hemiacetal **15** (24.8 mg, 35.7 μmol, 83%).

15: $[\alpha]_D^{19}$ +26.1 (*c* 1.20, $CHCl_3$); IR (neat) 3384, 2953, 2929, 2894, 2857, 1099, 1037, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.29 (m, 5H), 4.54 (s, 2H), 4.45 (brs, 1H), 4.20 (dd, *J* = 8.0, 5.7 Hz, 1H), 4.12 (d, *J* = 7.8 Hz, 1H), 4.10 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.83 (m, 1H), 3.76 (ddd, *J* = 10.0, 7.8, 3.4 Hz, 1H), 3.61 (ddd, *J* = 10.0, 6.9, 3.7 Hz, 1H), 3.51 (d, *J* = 7.8 Hz, 1H), 3.34 (s, 2H), 2.36 (d, *J* = 11.9 Hz, 1H), 2.20–2.07 (m, 3H), 1.92–1.86 (m, 2H), 1.79–1.71 (m, 2H), 1.18 (s, 3H), 1.10 (s, 3H), 0.91 (s, 9H), 0.85 (s, 9H), 0.07 (s, 6H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 128.7, 128.2, 128.1, 107.1, 94.4, 82.7, 79.0, 73.6, 73.1, 72.2, 70.4, 70.1, 68.6, 68.4, 65.7, 41.8, 36.4, 35.8, 30.7, 26.1, 25.8, 20.8, 19.1, 18.5, 18.0, −3.9, −4.7, −5.1, −5.2; HRESIMS *m/z* $[M + Na]^+$ calcd for $C_{36}H_{62}O_9Si_2Na^+$ 717.3825, found 717.3860.



16

Triol 16. Et_3SiH (0.27 mL, 1.69 mmol) and $TiCl_4$ (50 μL, 0.456 mmol) were added to a solution of hemiacetal **15** (19.4 mg, 27.9 μmol) in CH_2Cl_2 (5.4 mL) at −40 °C under argon atmosphere. The mixture was stirred for 25 min, warmed to 0 °C, then stirred for 50 min. After warming to rt, the mixture was stirred for 1 h, quenched with saturated aqueous $NaHCO_3$, filtered through a thin Celite® pad. The filtrate was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude triol **16** (12.8 mg) which was used for the next reaction without further purification.



17

Triacetate 17. DMAP (8.6 mg, 70.4 µmol) and Ac_2O (0.20 mL, 2.12 mmol) were added to a solution of crude triol **16** (12.8 mg, 27.9 µmol) in pyridine (2.5 mL) at 0 °C under argon atmosphere. The mixture was stirred at rt for 3 h, concentrated under reduced pressure. The reside was purified by silica gel column chromatography to give triacetate **17** (7.0 mg, 11.7 µmol, 42%, 2 steps).

17: $[\alpha]_D^{24}$ +76.8 (*c* 1.28, $CHCl_3$); IR (neat) 2954, 2929, 2887, 2857, 1740, 1372, 1248, 1100, 1073, 1051 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.59 (dd, *J* = 4.8, 1.5 Hz, 1H), 4.31 (ddd, *J* = 11.0, 7.9, 5.8 Hz, 1H), 4.20 (d, *J* = 11.3 Hz, 1H), 4.16 (ddd, *J* = 11.0, 7.8, 6.6 Hz, 1H), 4.06 (dd, *J* = 12.3, 3.7 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.7 Hz, 1H), 3.73 (d, *J* = 7.8 Hz, 1H), 3.70 (d, *J* = 11.3 Hz, 1H), 3.64 (dd, *J* = 4.8, 1.5 Hz, 1H), 3.36 (d, *J* = 7.8 Hz, 1H), 2.18 (ddd, *J* = 14.0, 7.8, 5.8 Hz, 1H), 2.13–2.07 (m, 7H), 2.06–1.99 (m, 4H), 1.97 (ddd, *J* = 15.9, 1.5, 1.5 Hz, 1H), 1.90 (m, 2H), 1.84 (d, *J* = 14.9 Hz, 1H), 1.74 (ddd, *J* = 11.9, 11.9, 11.9 Hz, 1H), 1.31 (s, 3H), 1.17 (s, 3H), 0.86 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.2, 171.1, 170.5, 107.2, 81.4, 77.5, 72.6, 71.4, 70.9, 69.1, 68.9, 68.4, 67.5, 59.3, 44.9, 32.6, 31.3, 29.4, 25.8, 24.3, 21.3, 21.2, 21.1, 18.7, 17.9, −4.0, −5.0; HRESIMS *m/z* $[M + Na]^+$ calcd for $C_{29}H_{48}O_{11}SiNa^+$ 623.2858, found 623.2884.

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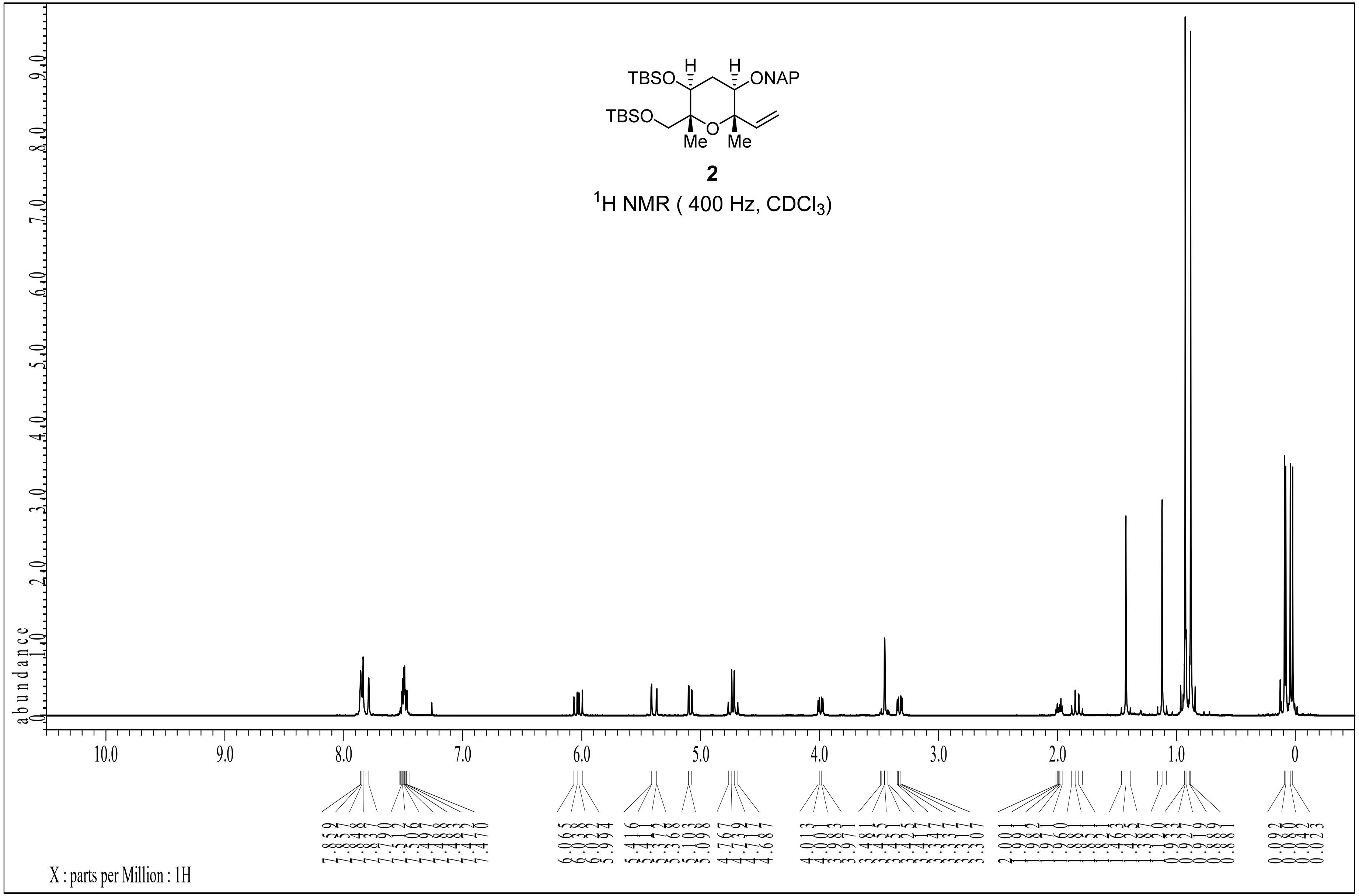
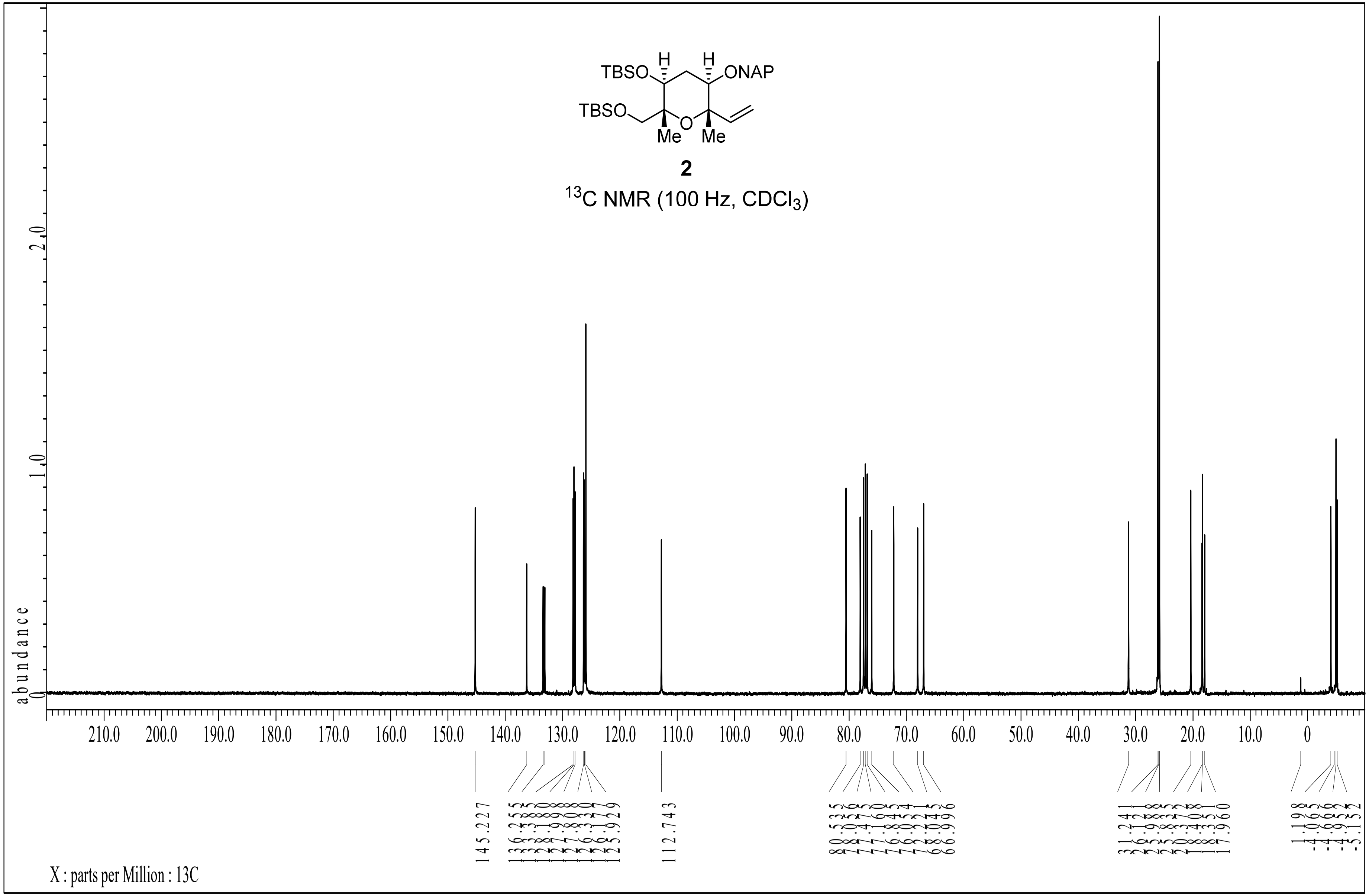


2

^{1}H NMR (400 Hz, CDCl$_3$)



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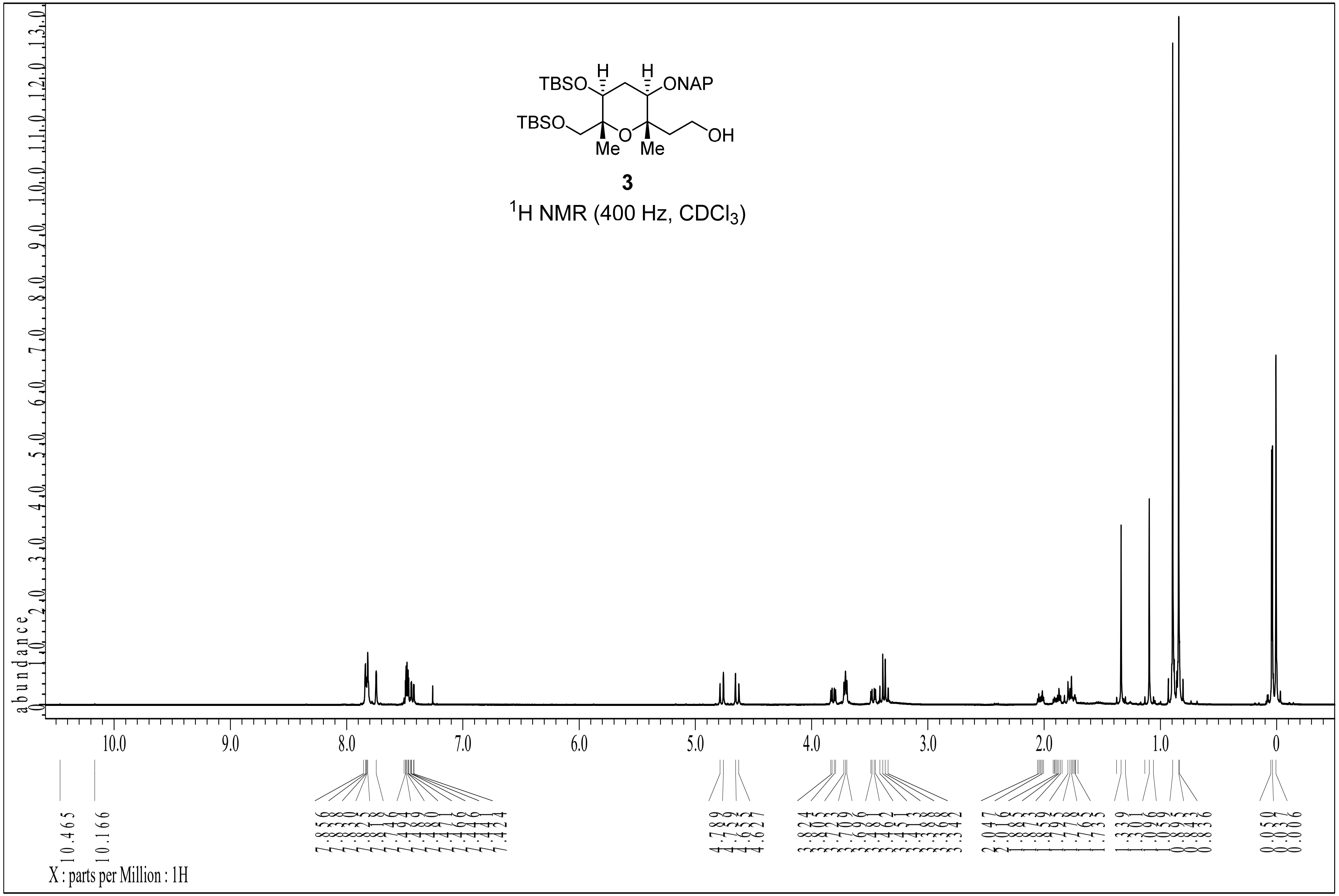
^{13}C NMR (100 Hz, CDCl$_3$)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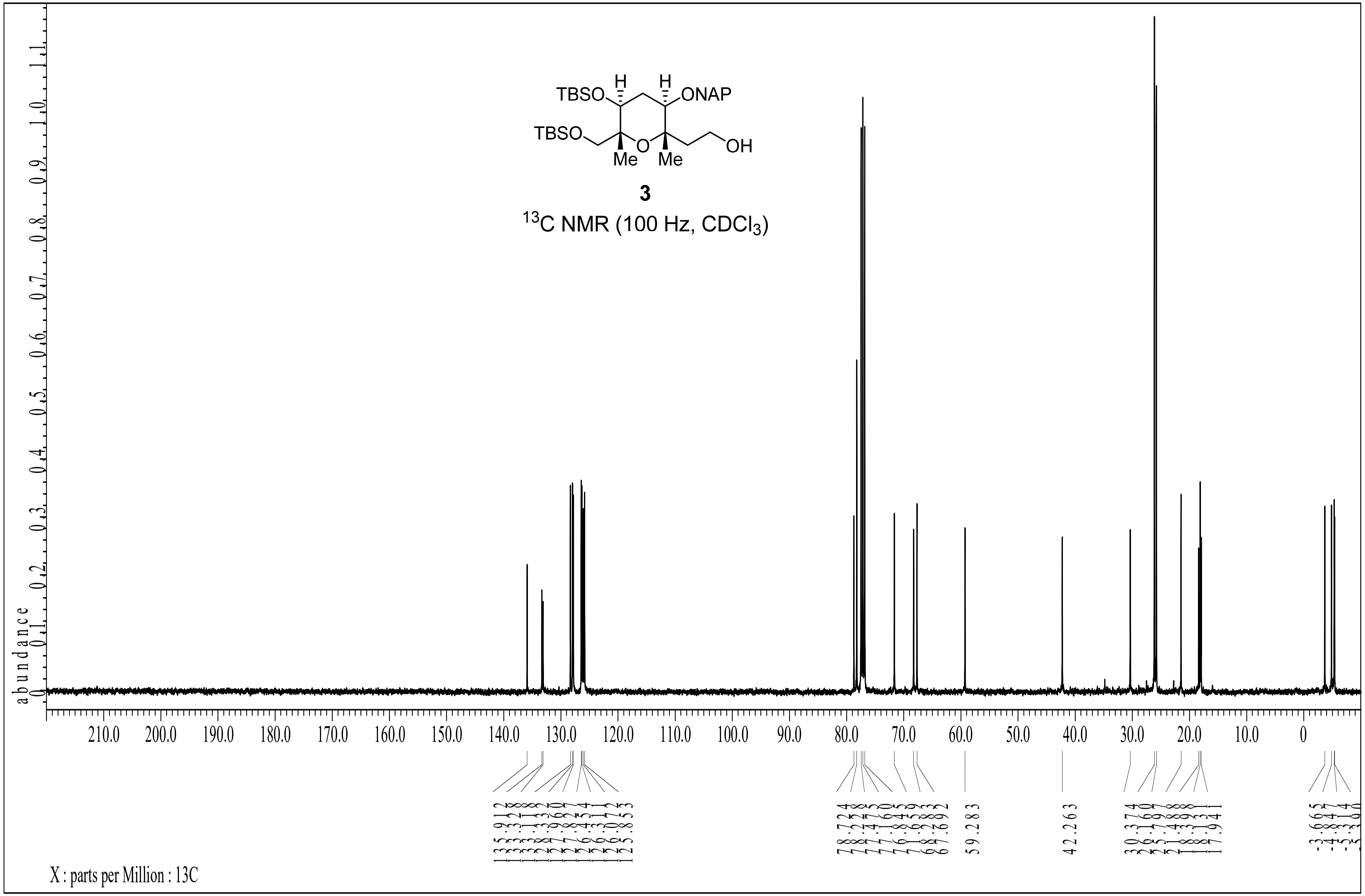

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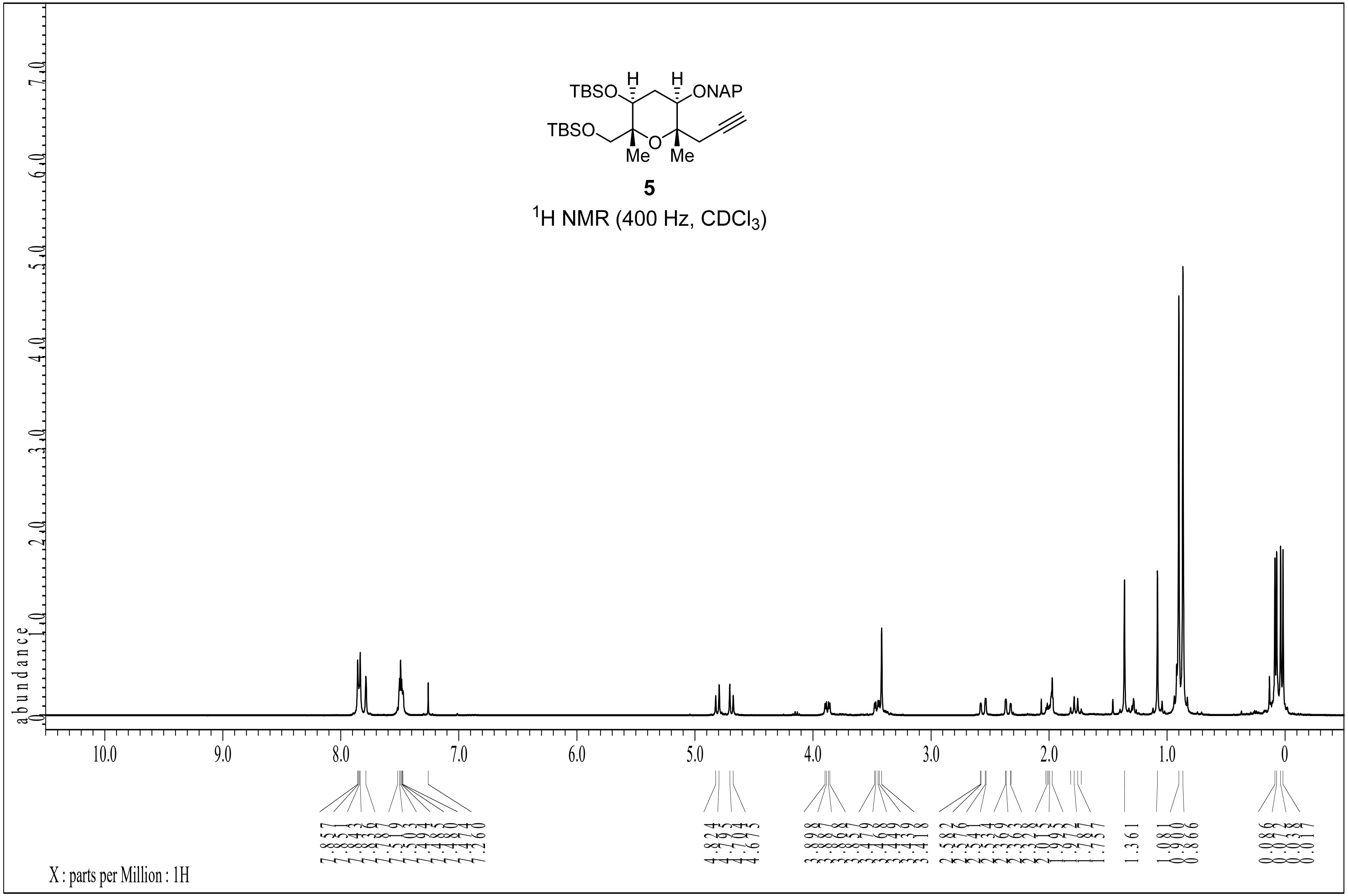
^{13}C NMR (100 Hz, CDCl$_3$)



5

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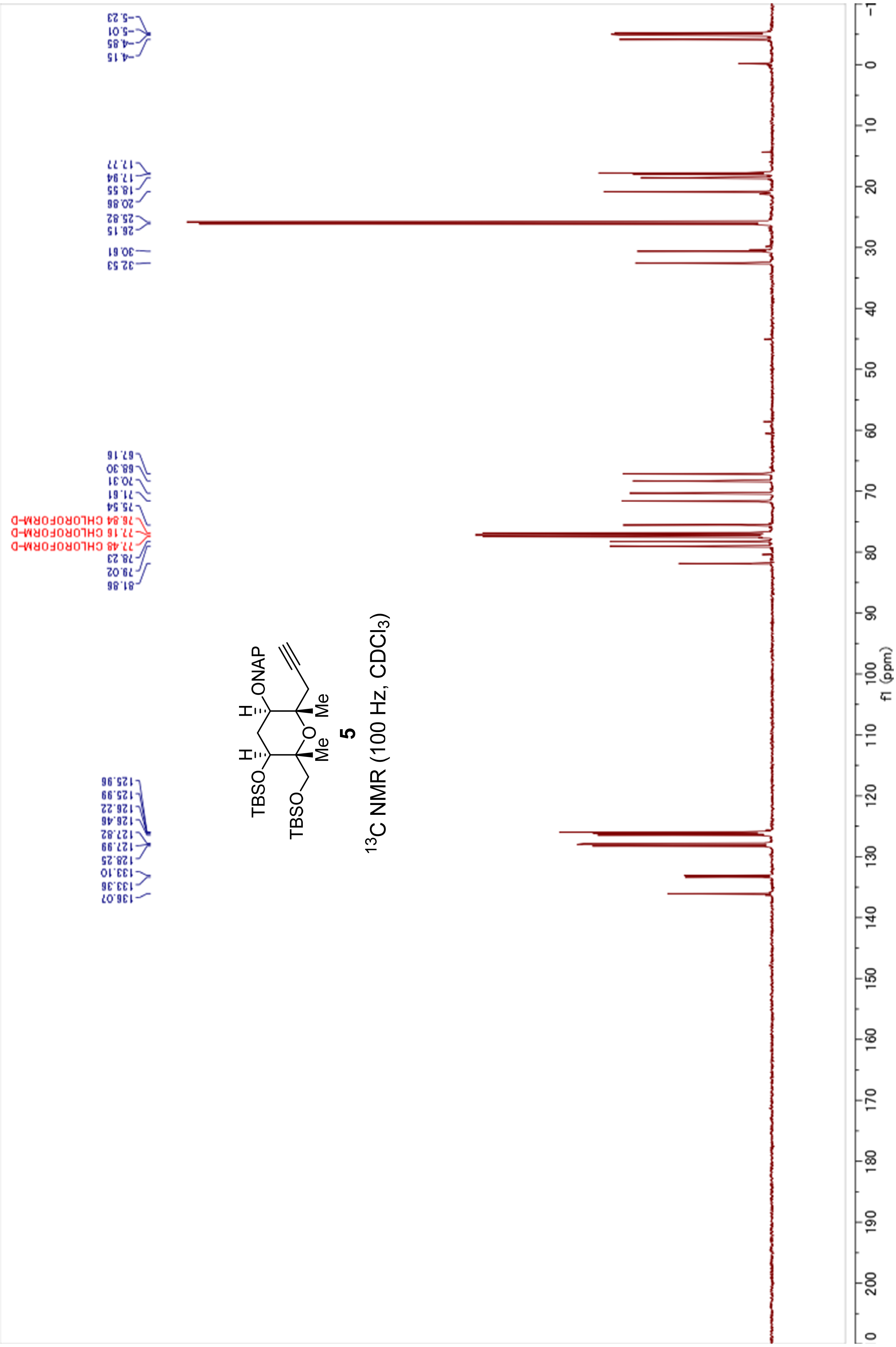

5

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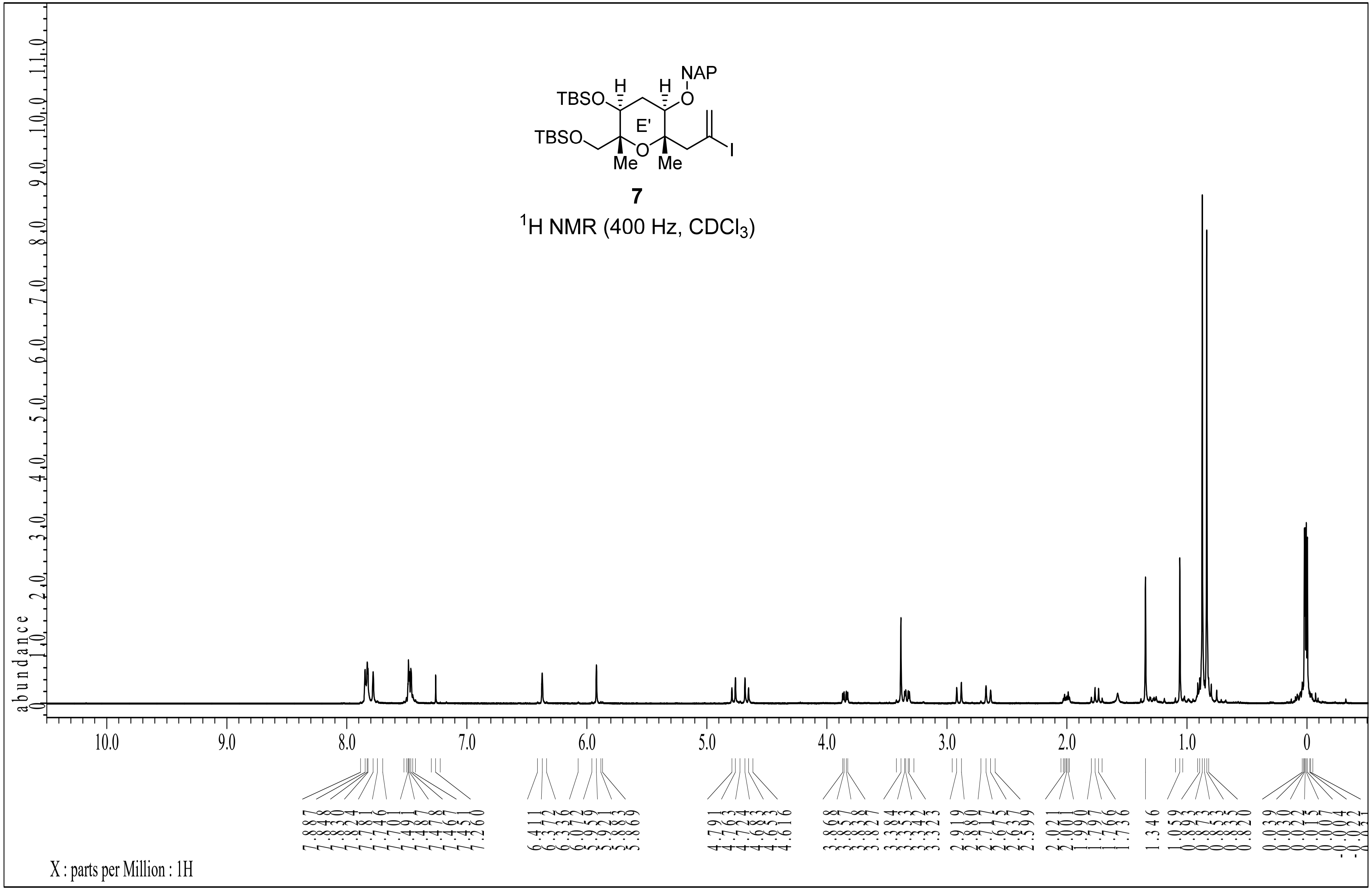

7

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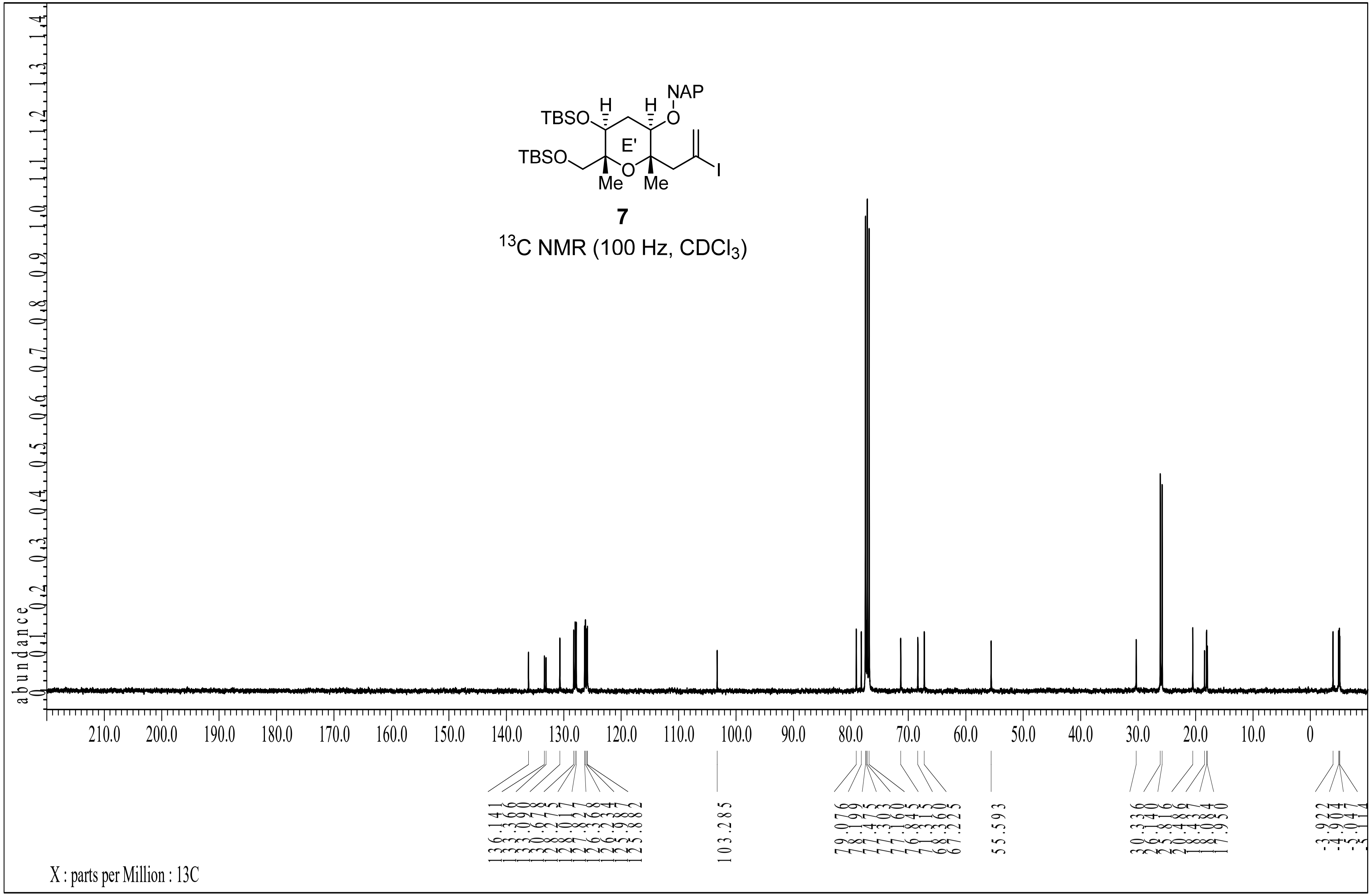
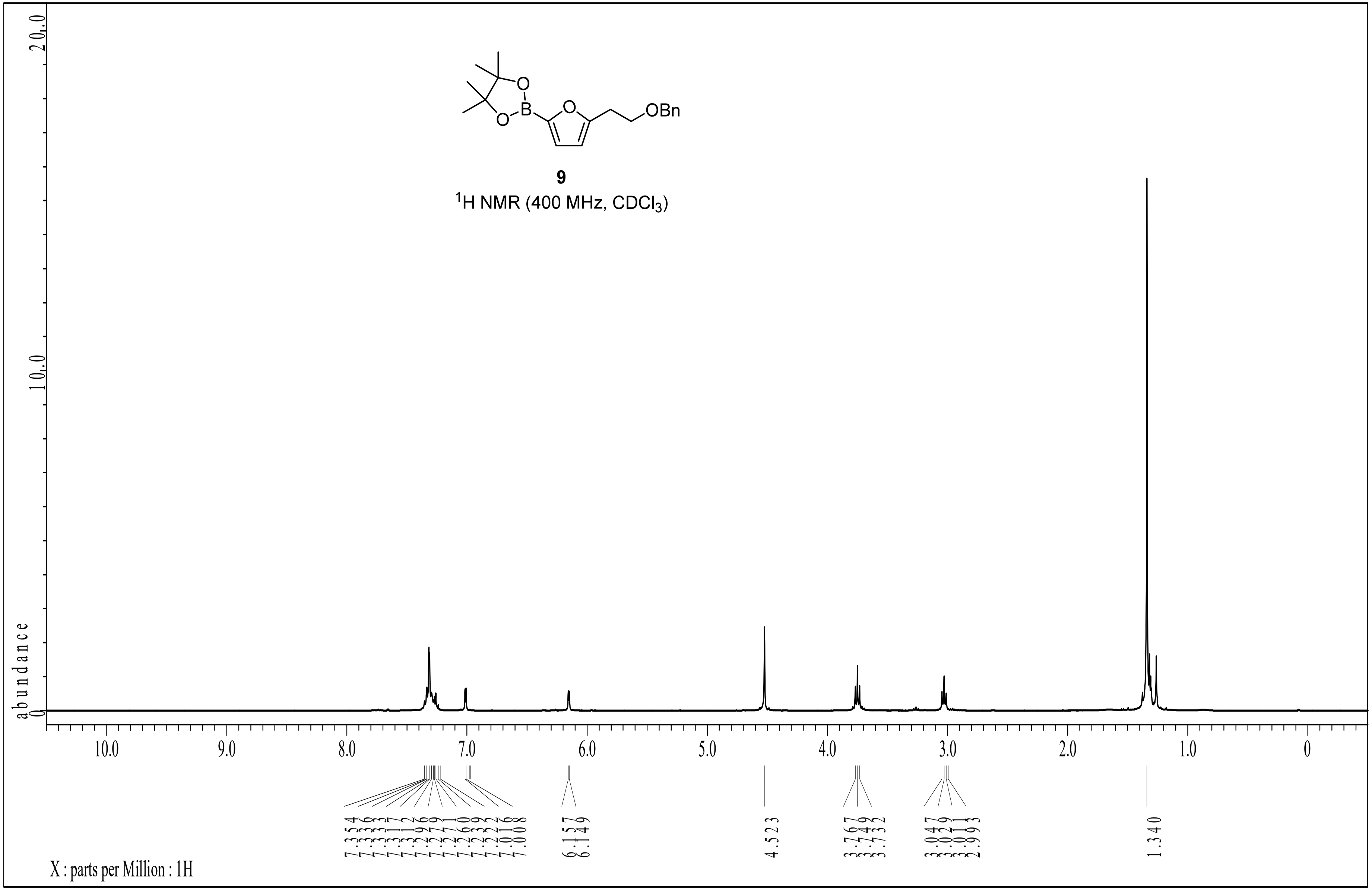


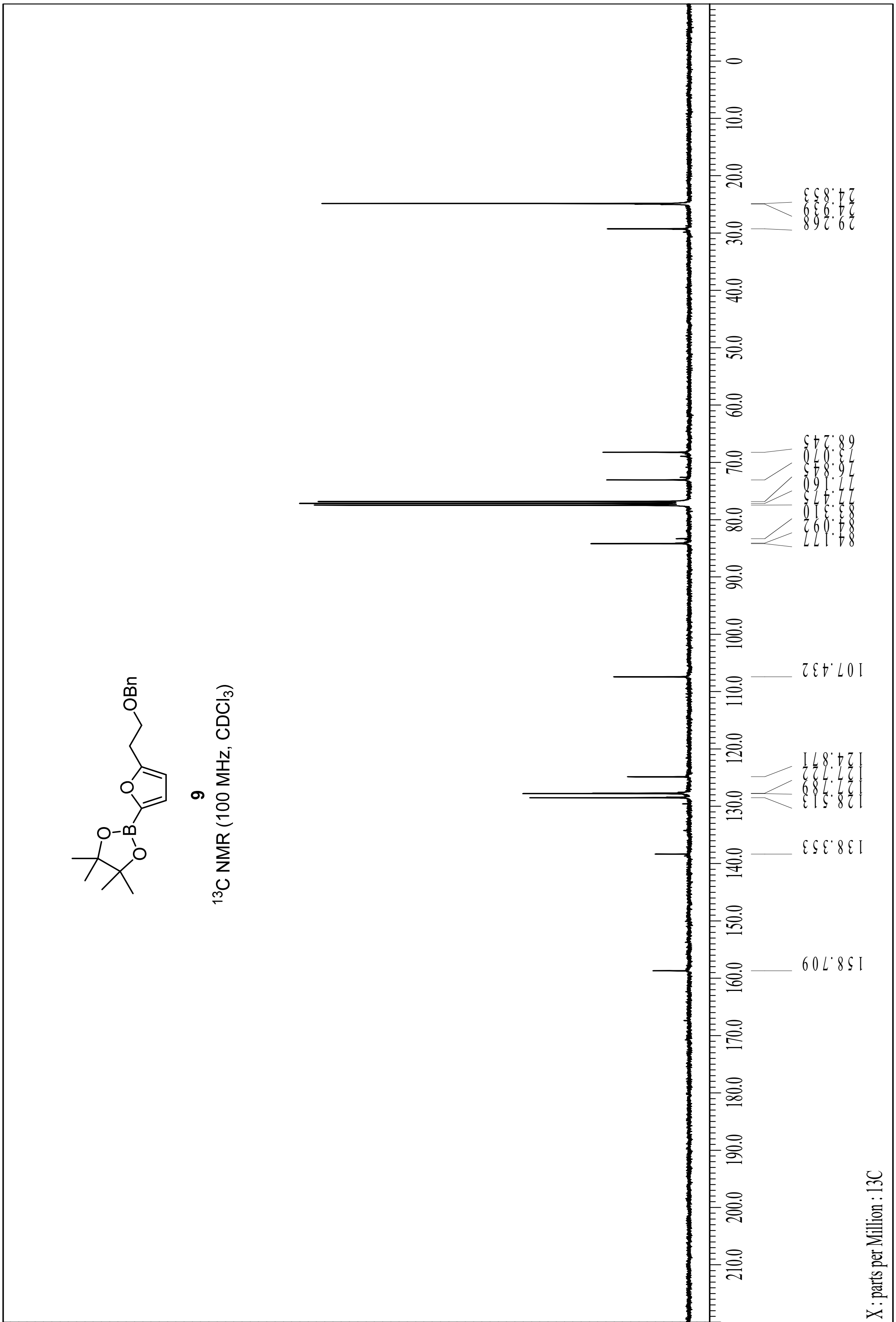
7

^{13}C NMR (100 Hz, CDCl$_3$)



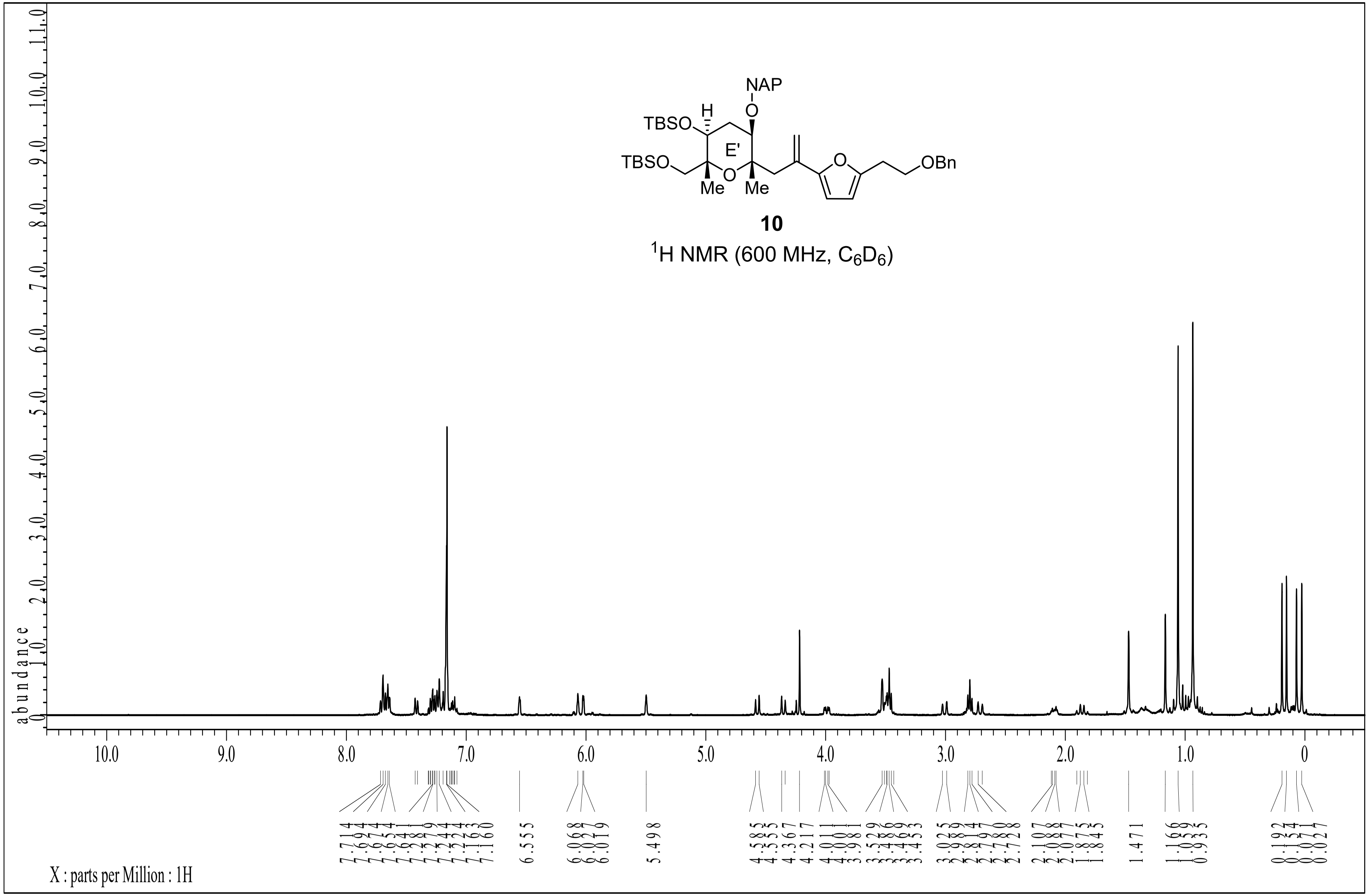
9

^{1}H NMR (400 MHz, CDCl$_3$)



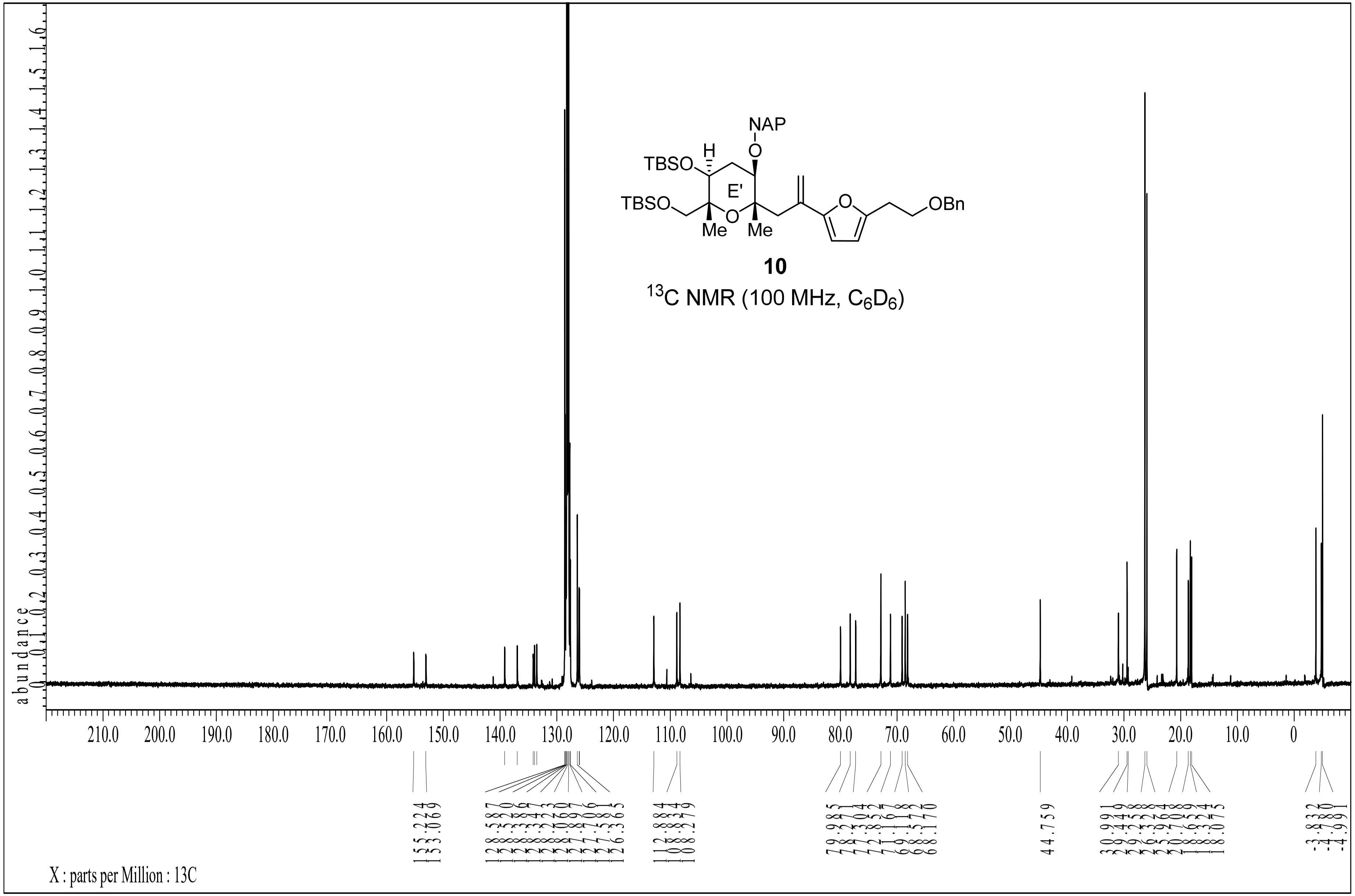
9

^{13}C NMR (100 MHz, CDCl$_3$)



10

^{1}H NMR (600 MHz, C_6D_6)



10

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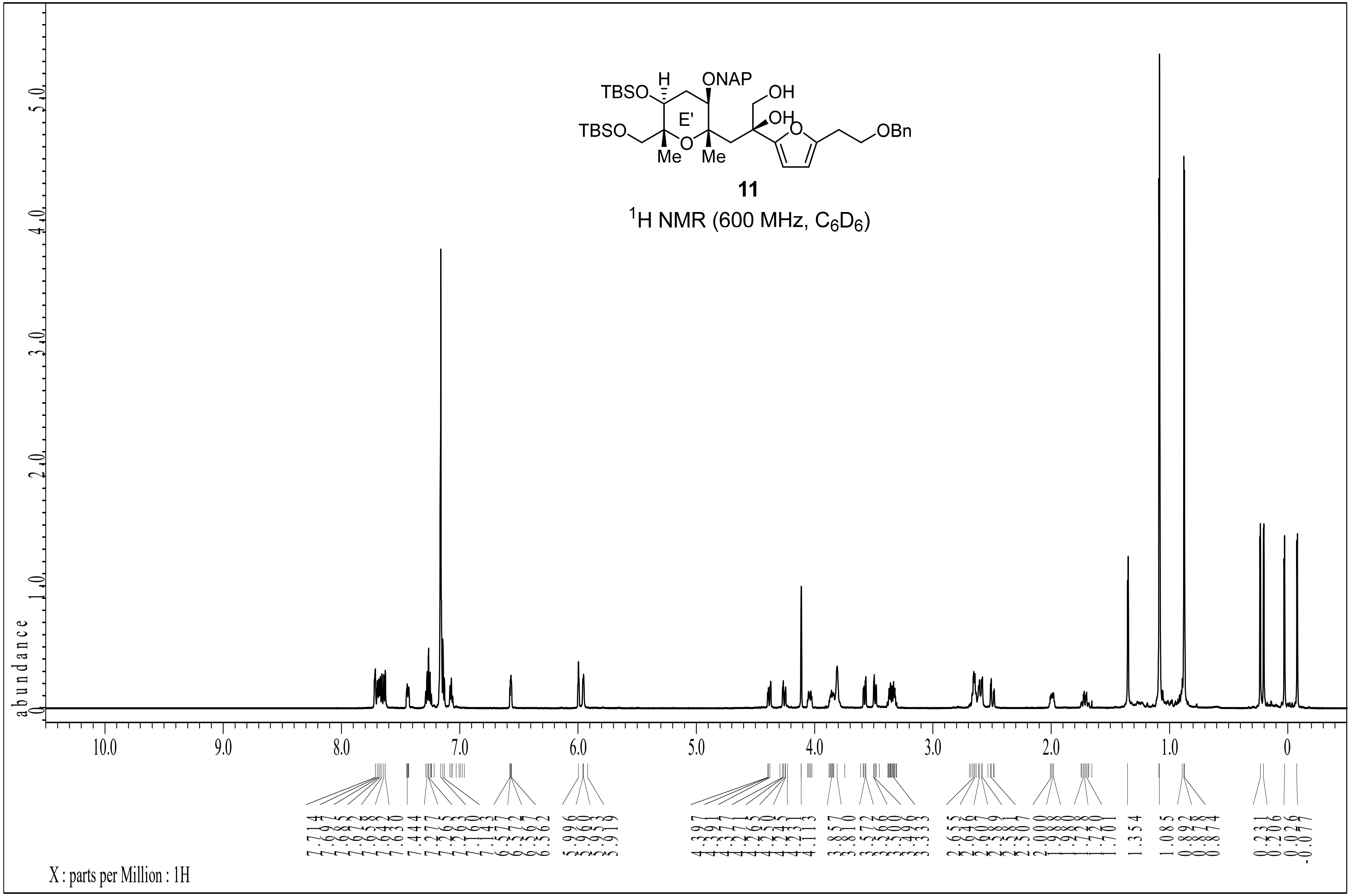

11

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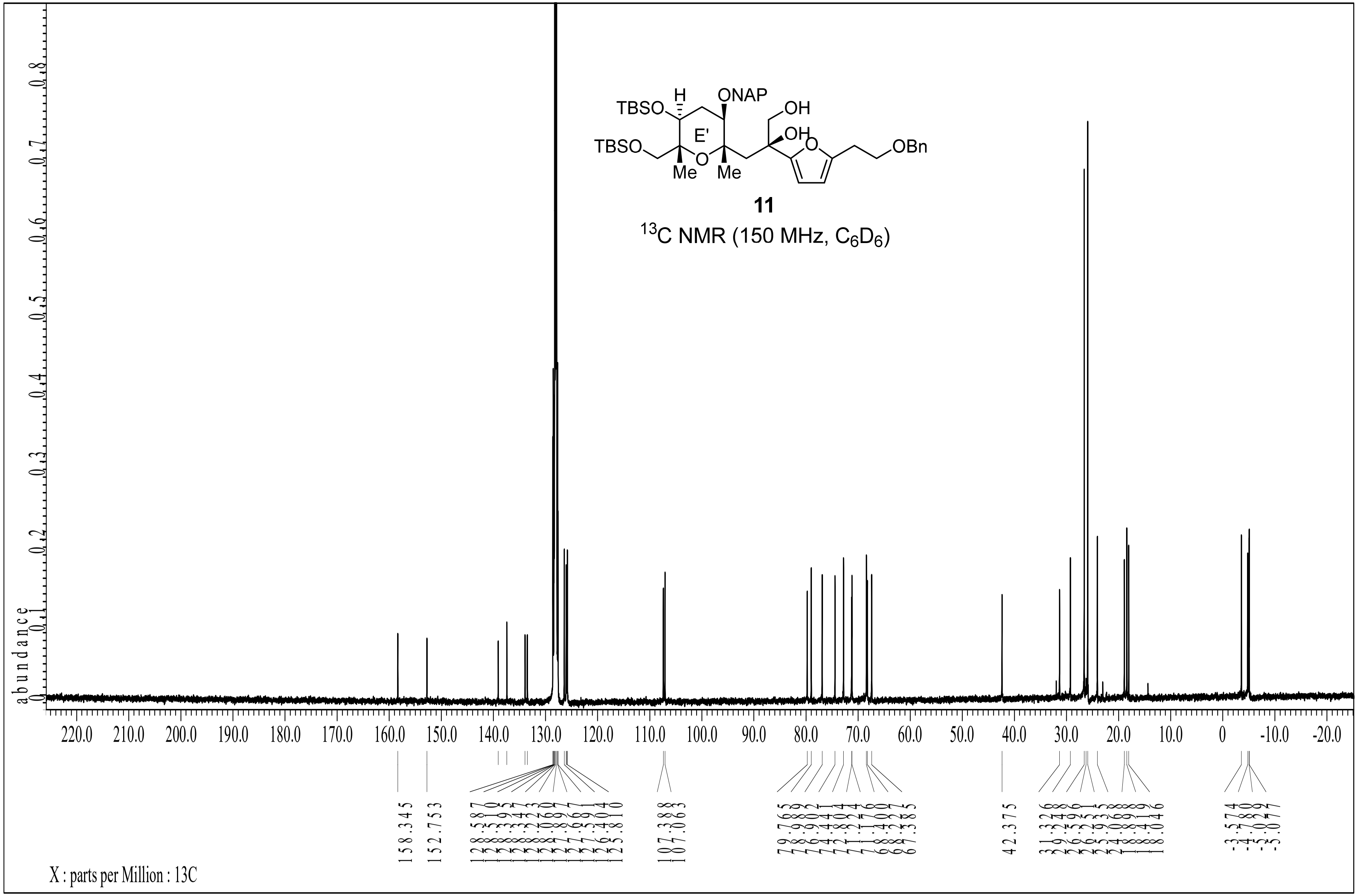
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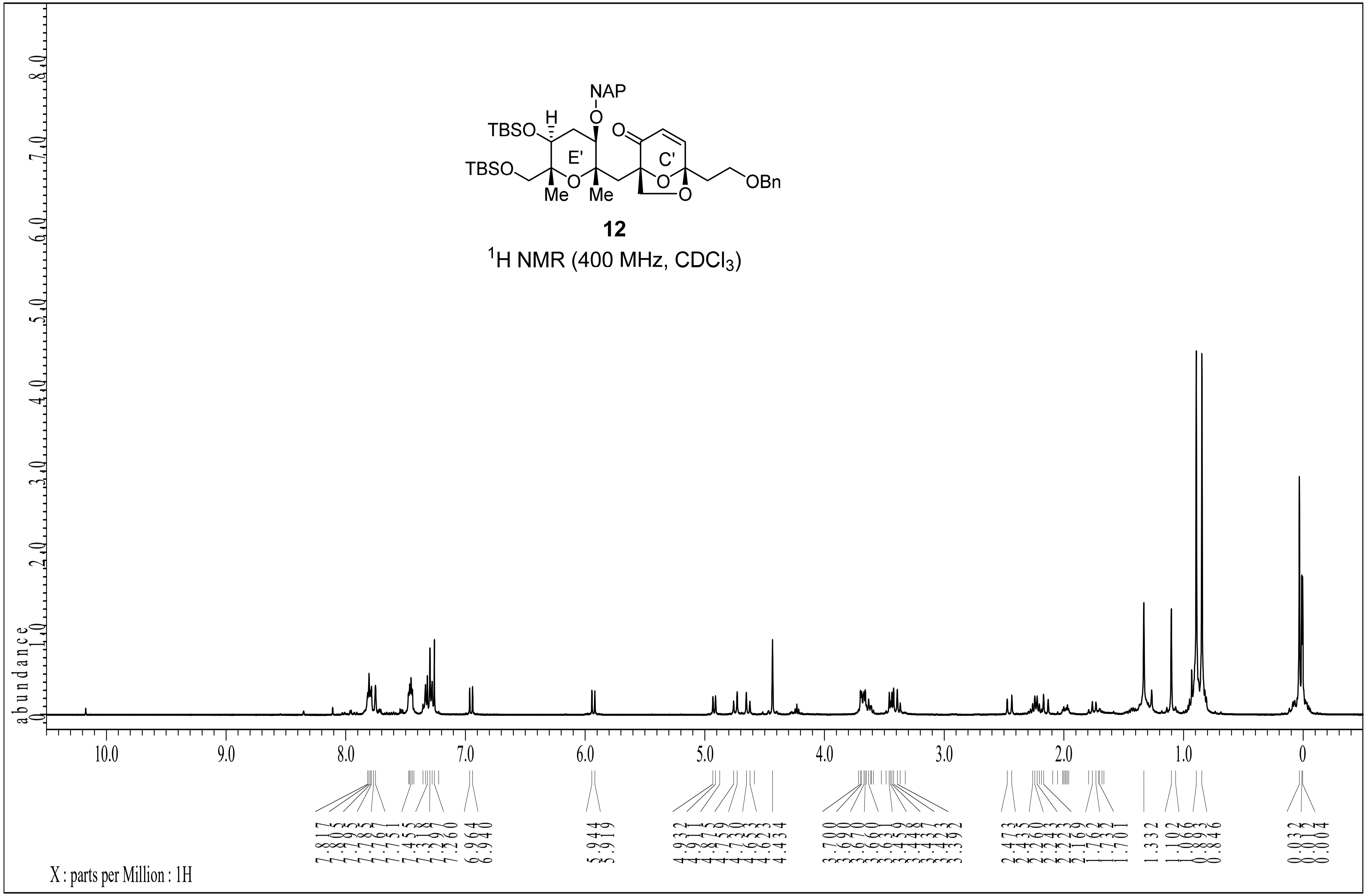
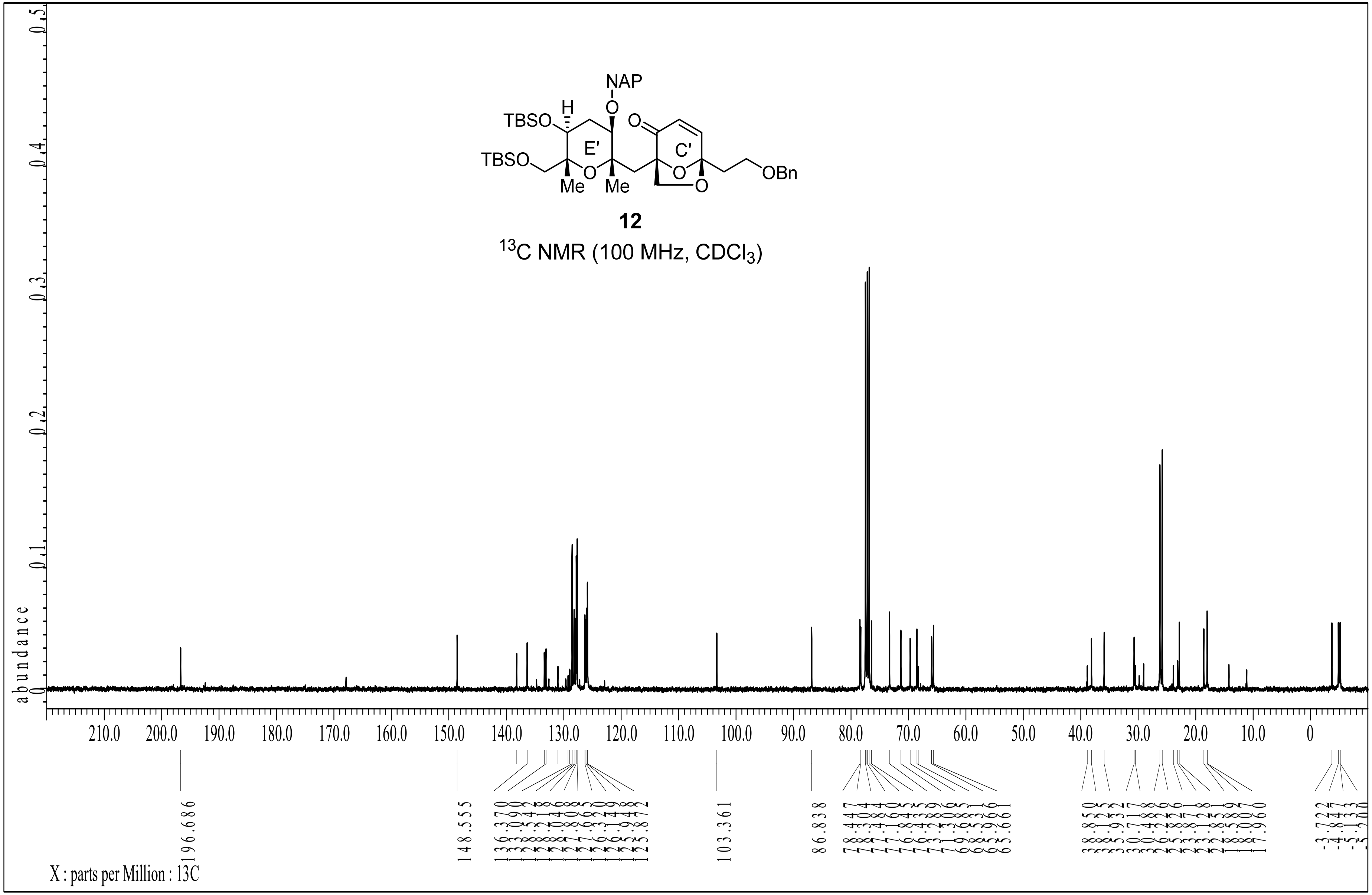


12

^{1}H NMR (400 MHz, $CDCl_3$)



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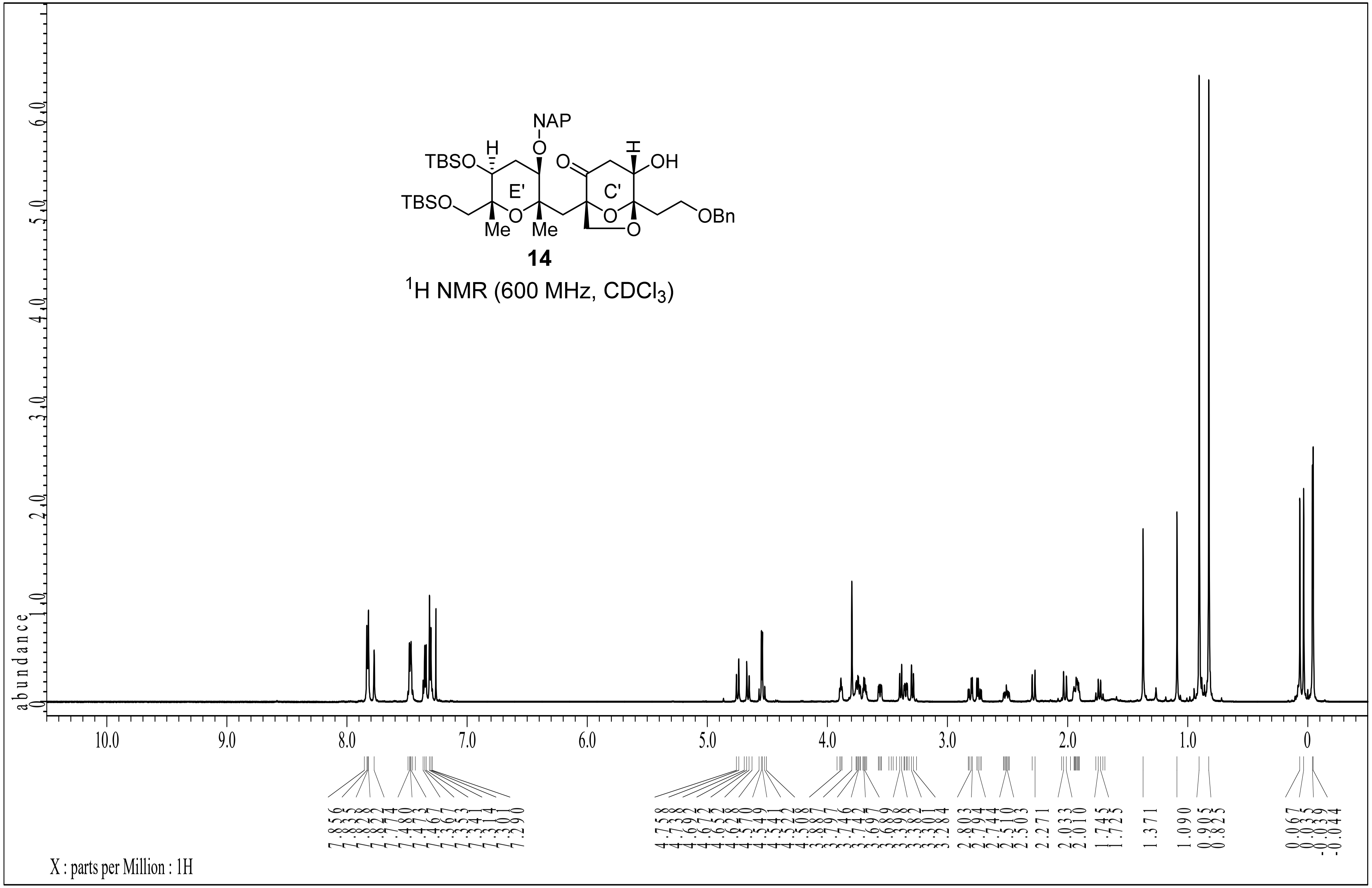

14

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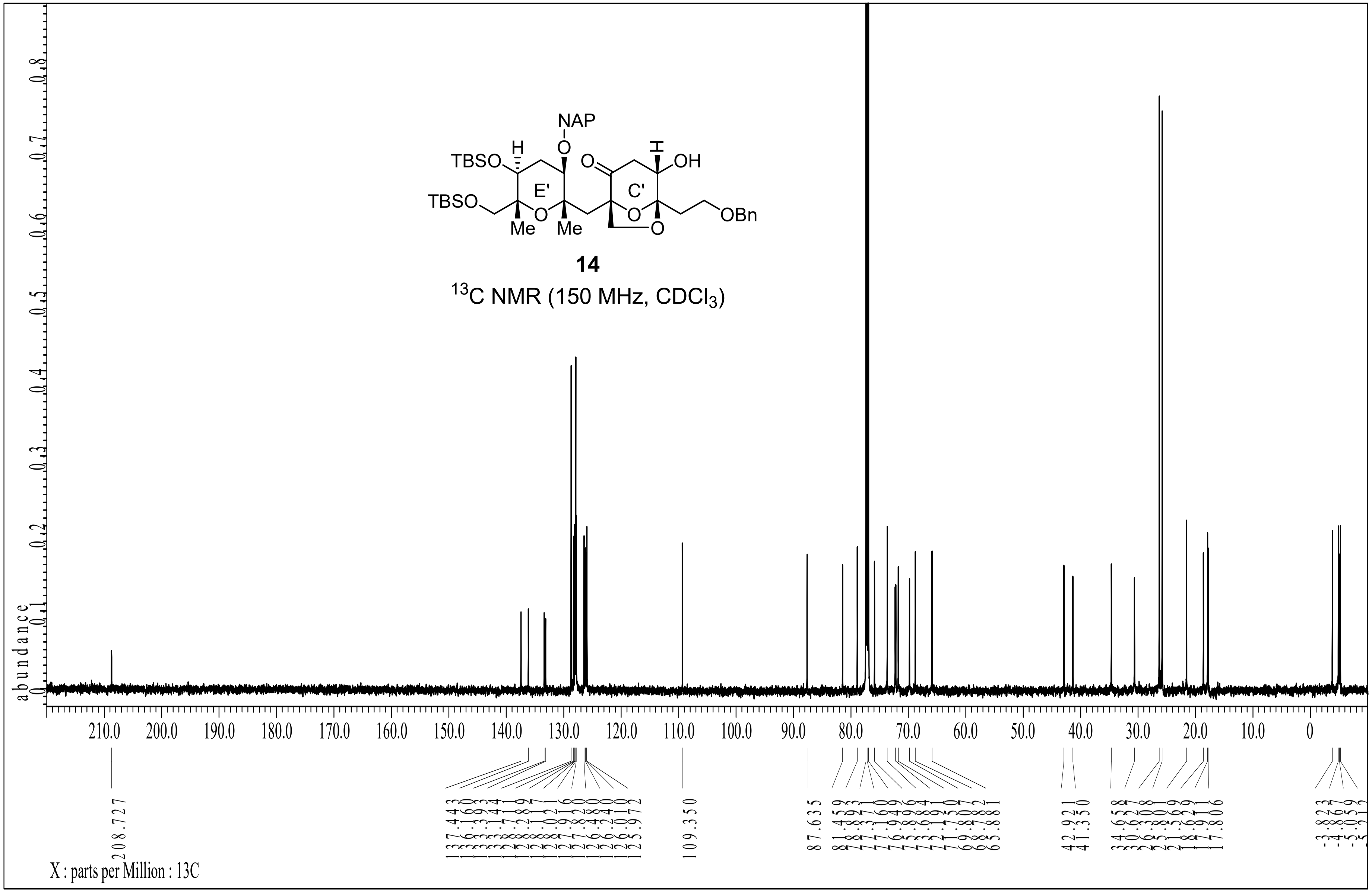

14

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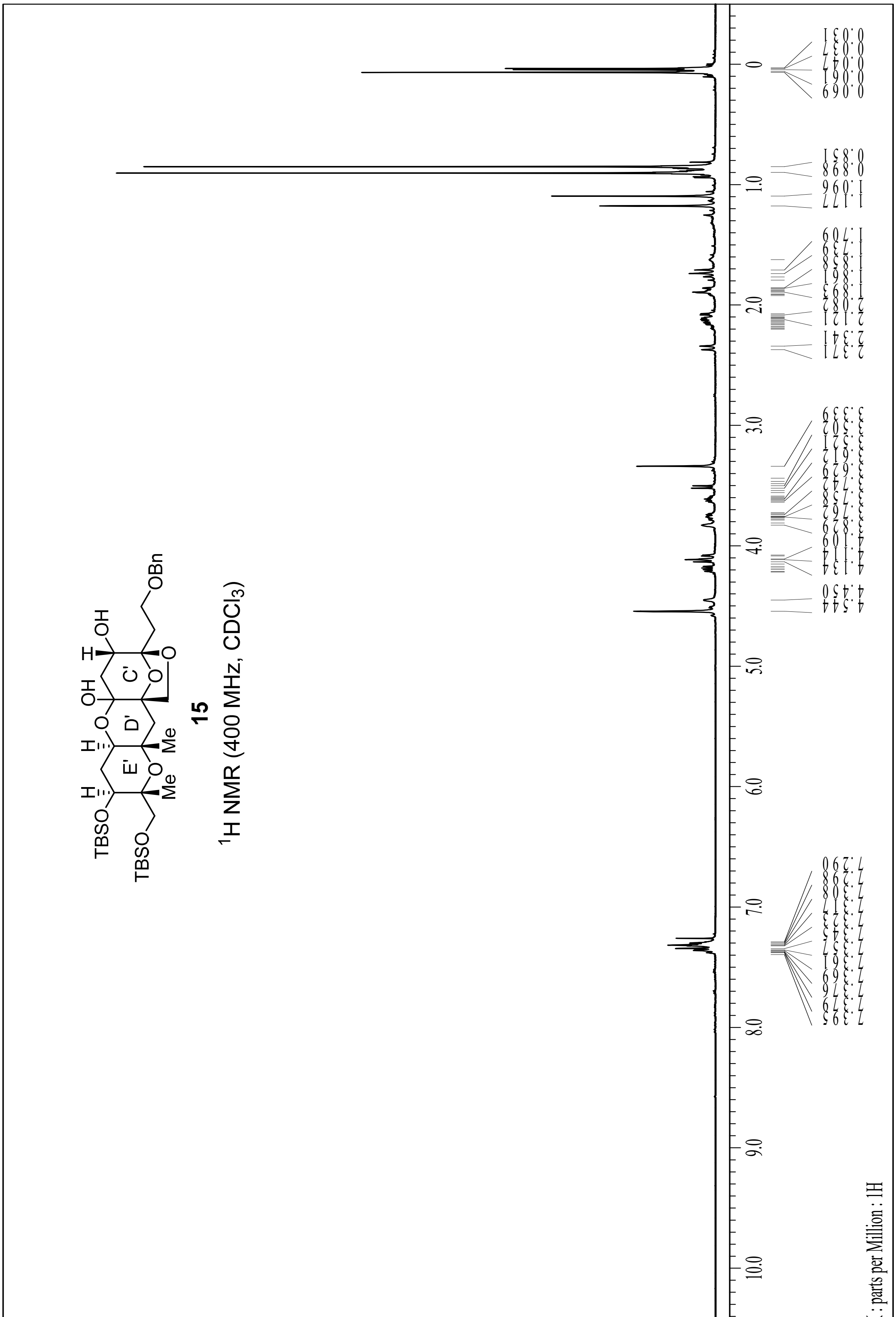TBSO
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OH
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OH
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D'
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O
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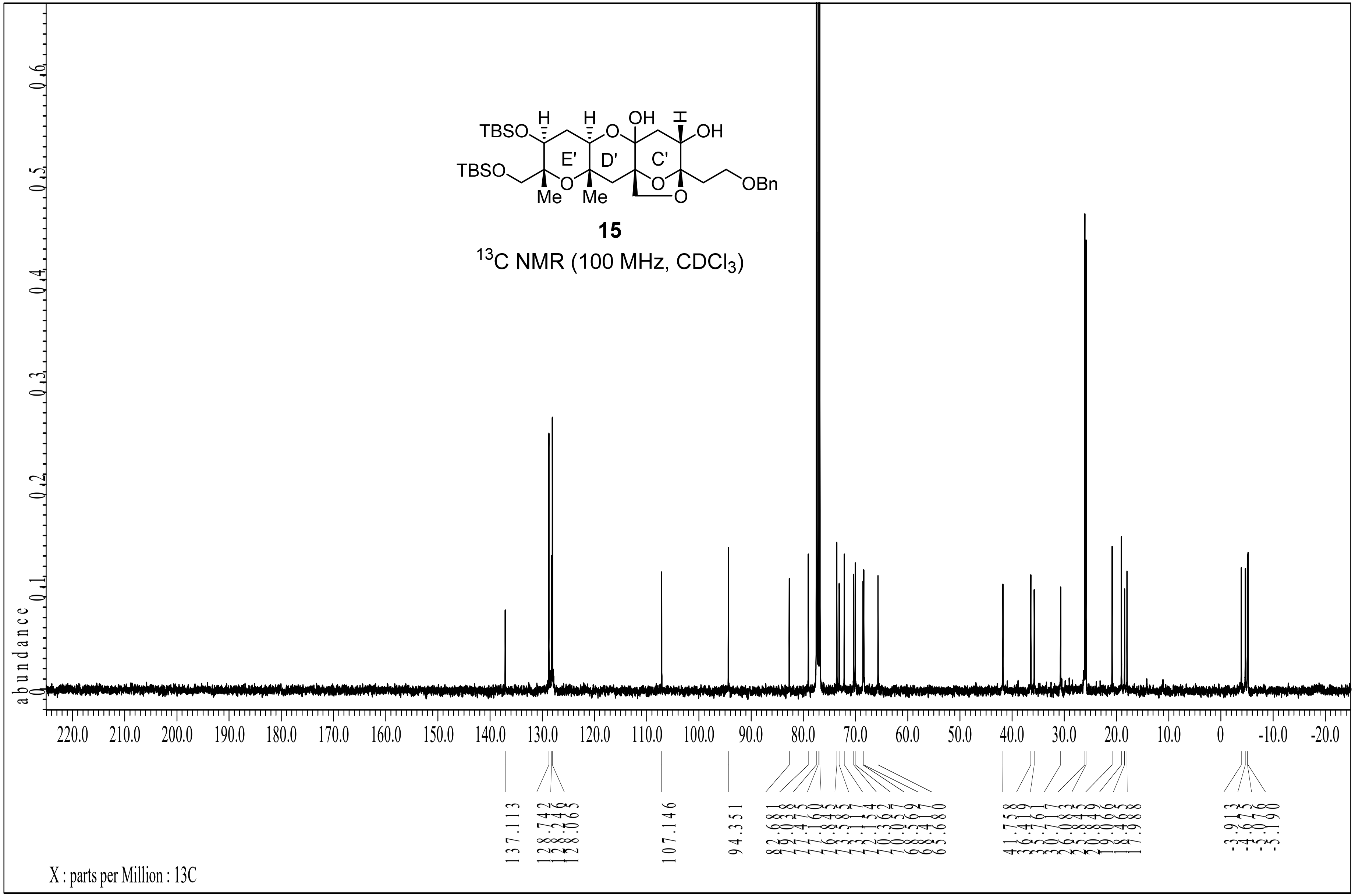
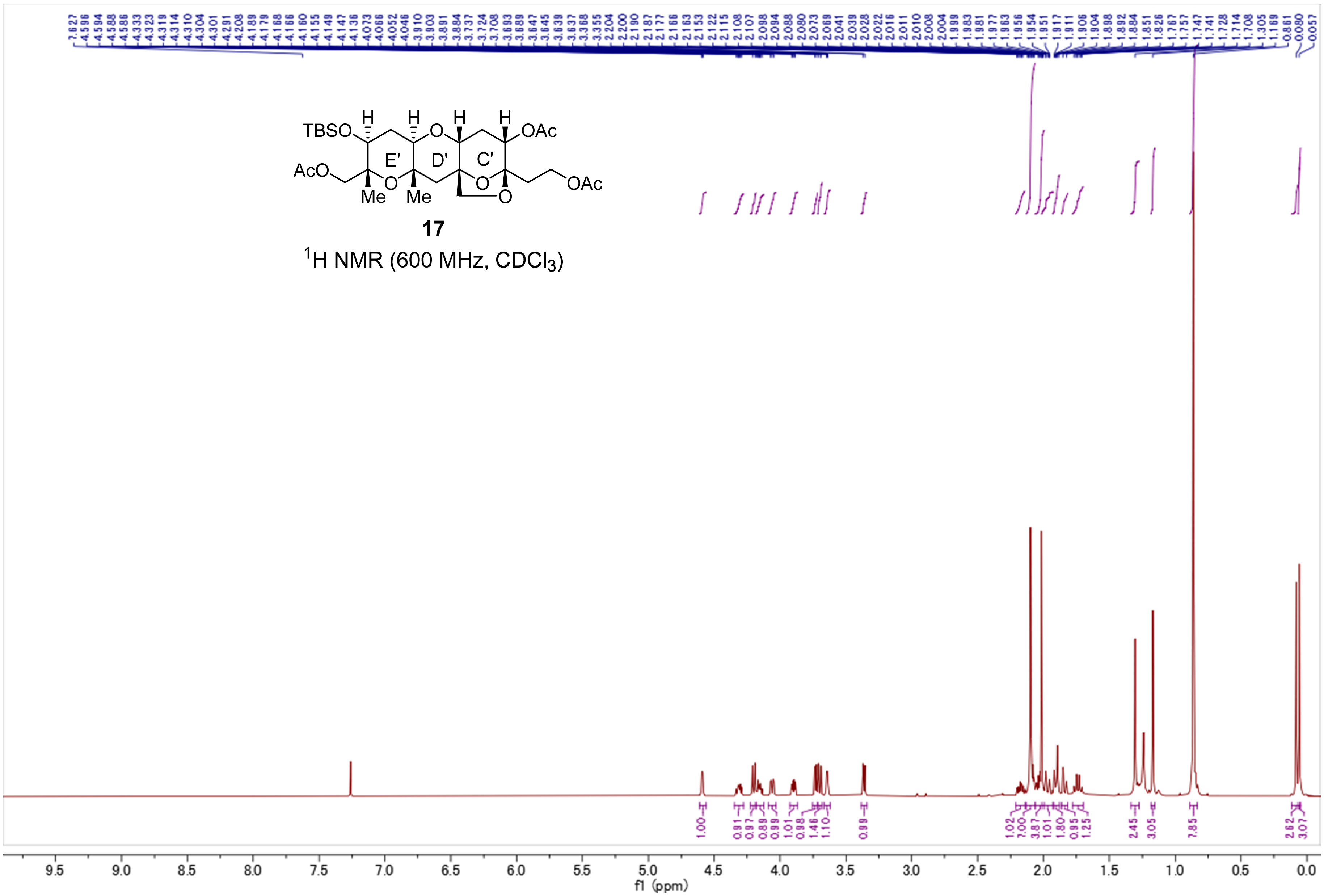
Me
Me
OBn
15
^{1}H NMR (400 MHz, CDCl$_3$)
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
X : parts per Million : 1H
0.031
0.037
0.047
0.061
0.069
0.851
0.898
1.096
1.177
1.709
1.739
1.858
1.861
1.893
2.082
2.121
2.341
2.371
3.339
3.502
3.521
3.612
3.629
3.742
3.758
3.762
3.829
4.109
4.114
4.134
4.450
4.544
7.290
7.298
7.308
7.317
7.325
7.343
7.357
7.361
7.369
7.376
7.379
7.395



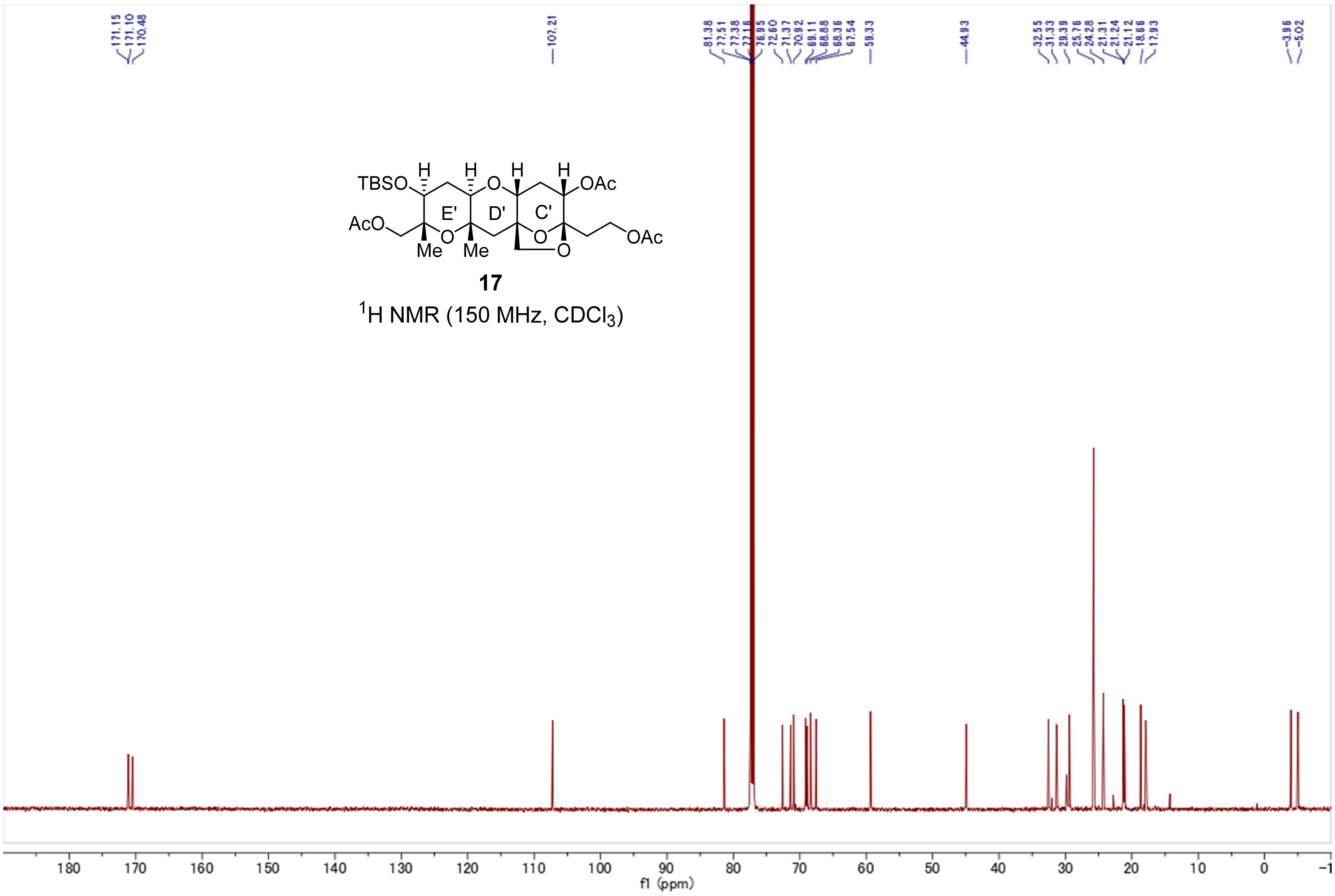
15

^{13}C NMR (100 MHz, $CDCl_3$)



17

^{1}H NMR (600 MHz, $CDCl_3$)

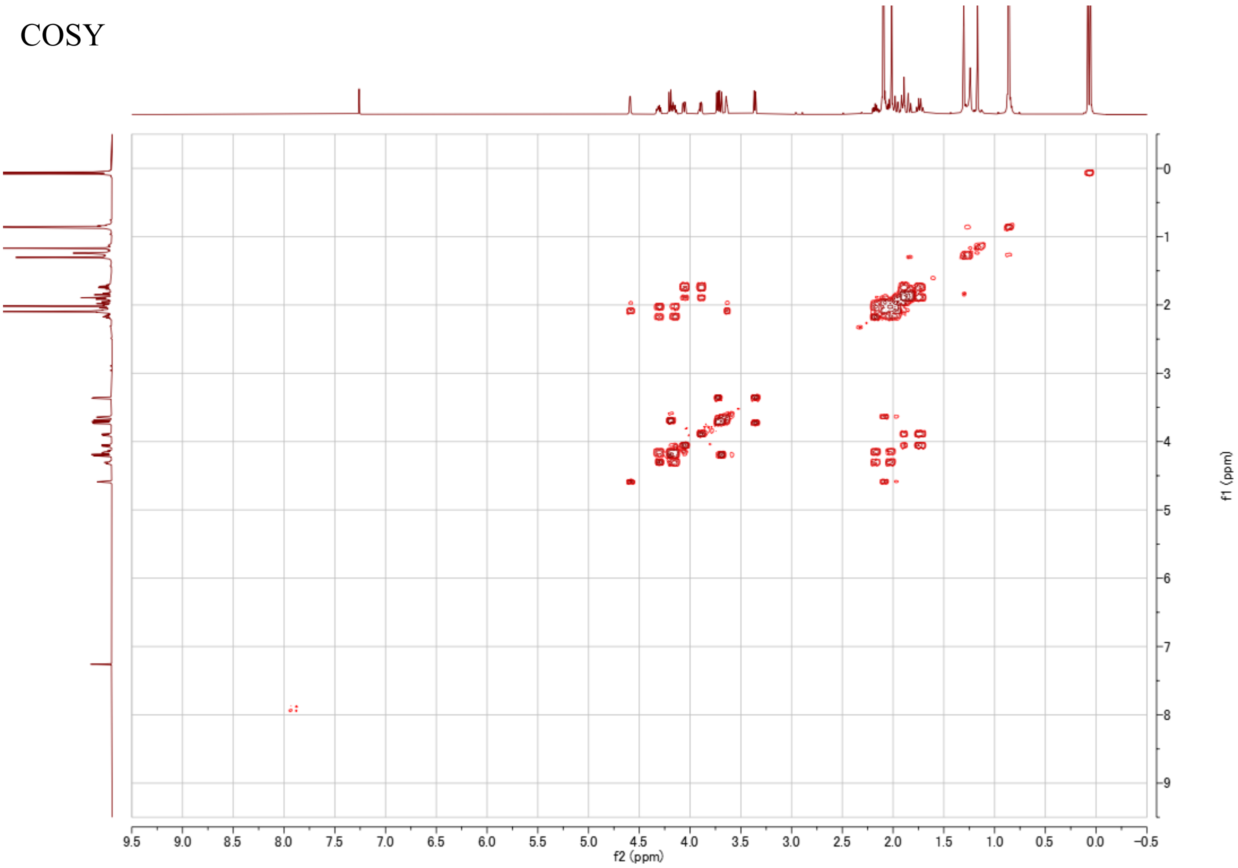


17

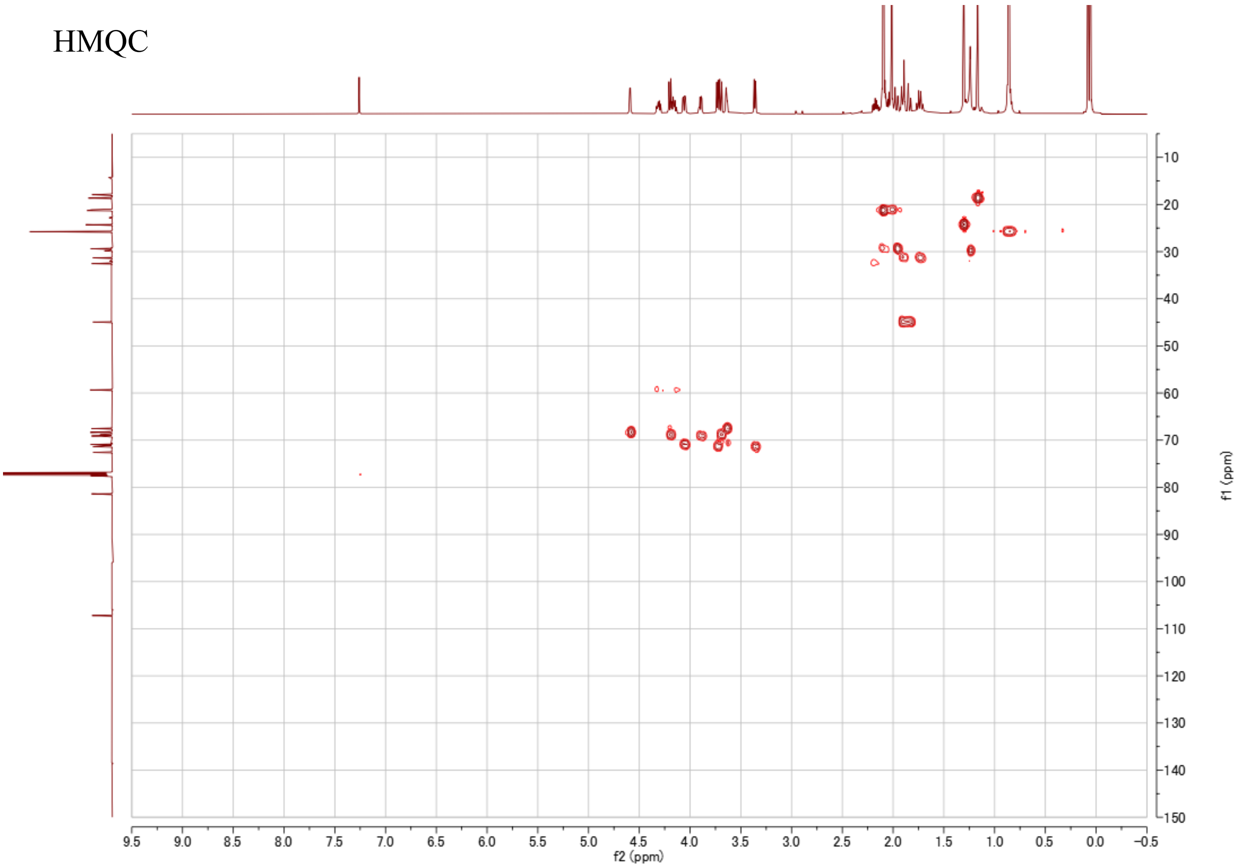
^{1}H NMR (150 MHz, CDCl$_3$)

1D and 2D NMR spectra of 17

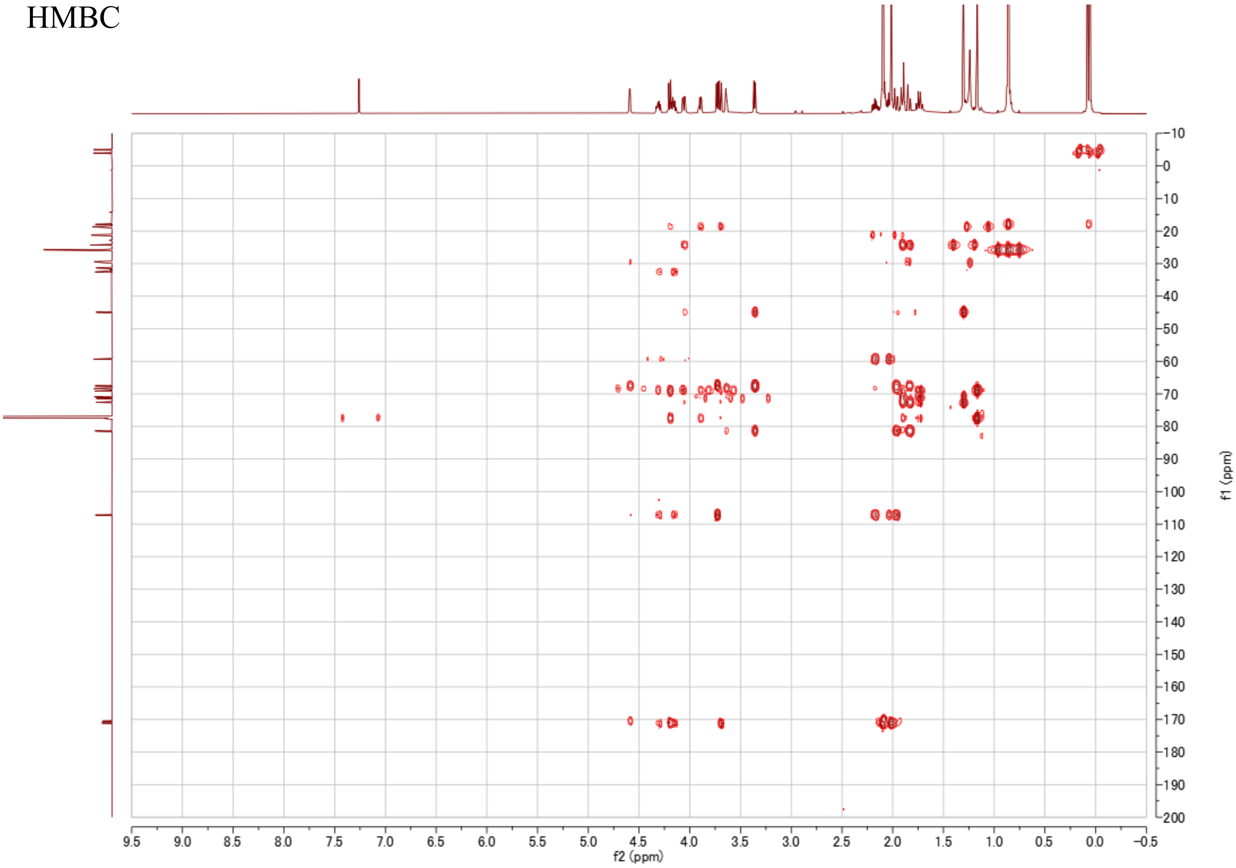
COSY



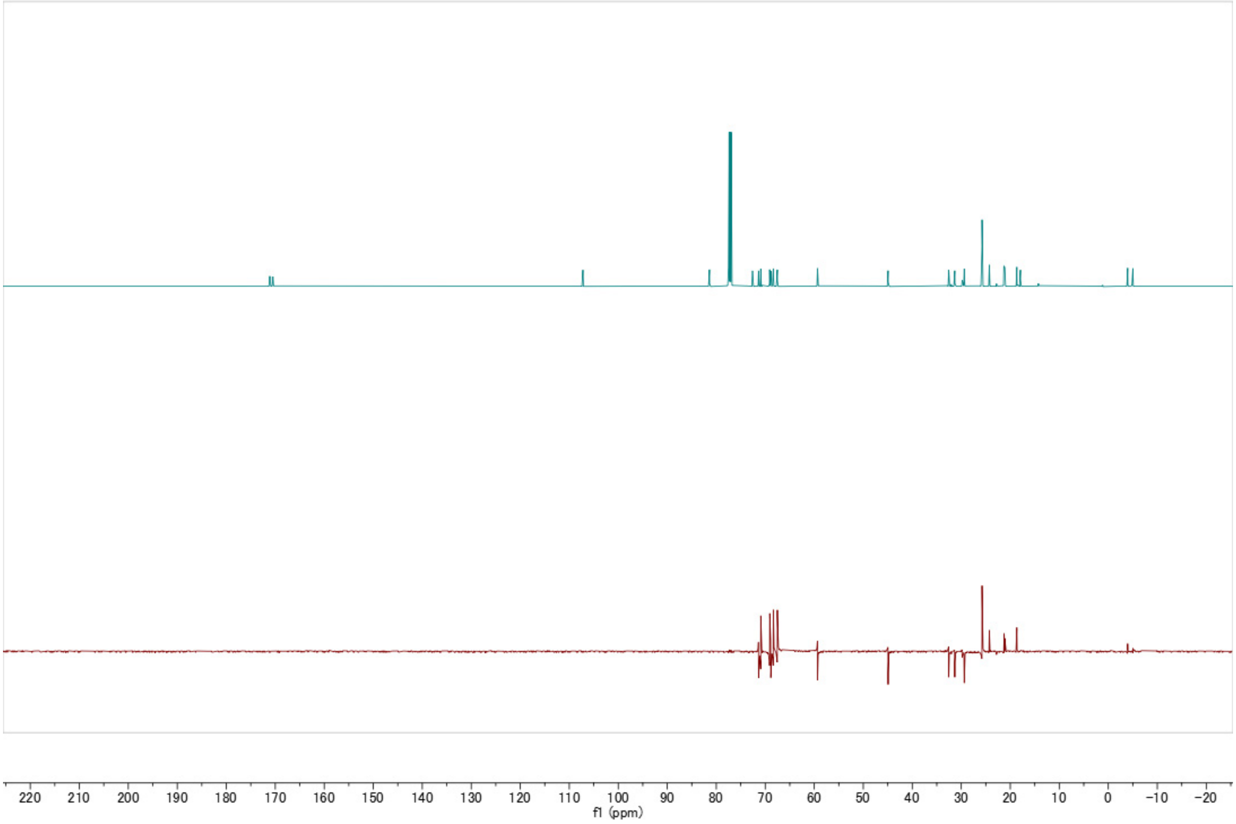
HMQC



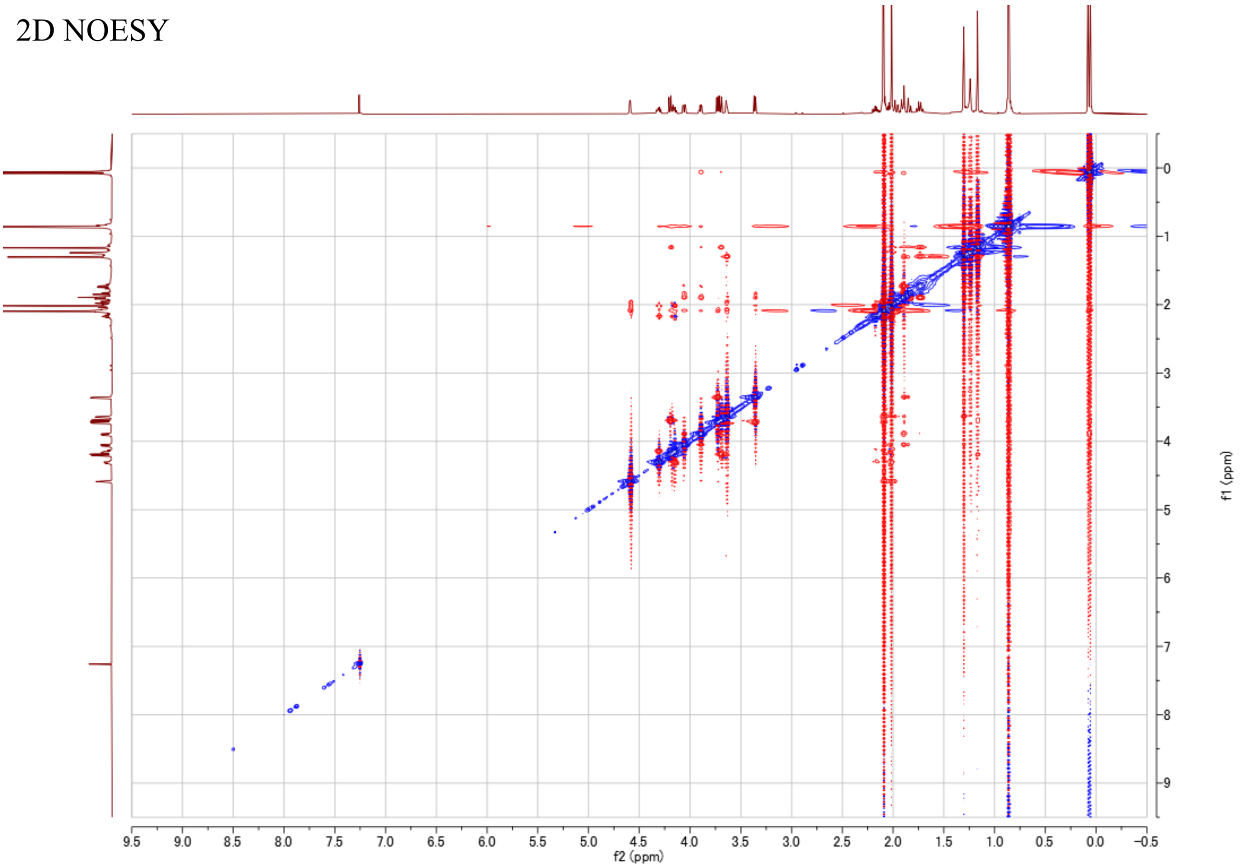
HMBC



^{13}C NMR (top) and DEPT135 (bottom)



2D NOESY



^{1}H NMR (top) and 1D NOESY (bottom, irradiation of H-124, 3.64 ppm)