Supporting Information

Convergent Synthesis of the [5-7-6-3] Tetracyclic Core of Premyrsinane Diterpenes

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General Remarks

Dehydrated tetrahydrofuran, dichloromethane and methanol were purchased from FUJIFILM Wako Pure Chemical Co.. N,N-Dimethylformamide, diethyl ether, and toluene were purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS4A. Acetonitrile was purchased from FUJIFILM Wako Pure Chemical Co. and stored over activated MS3A. 2-(2-(tert-butyldimethylsilyl)ethyl)cyclopent-2-en-1-one (**1**)[1], (1*S*,4*R*,6*R*)-4-chloro-7,7-dimethylbicyclo[4.1.0]heptan-3-one (**13**)[2] and 3-(prop-2-yn-1-yloxy)prop-1-ene (**20**)[3] were prepared according to the literatures.

All other reagents were purchased at the commercial grade and were used as received, without further purification. Reactions were performed in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. Reactions that require heating were conducted in an oil bath unless otherwise noted. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Preparative TLC separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F254. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical, 40-100 mesh) unless otherwise noted.

Optical rotations were measured on a JASCO P-2200 Polarimeter at room temperature using the sodium D line.

Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrophotometer and were reported in wavenumbers (cm^{-1}).

Nuclear magnetic resonance (^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz)) spectra were determined on JEOL-ECS400 or JEOL-ECZ400 instrument unless otherwise noted. Chemical shifts were reported in δ (ppm) using residual solvent as the internal standard (δ 7.26 for $CDCl_3$ in ^{1}H NMR, δ 77.16 for $CDCl_3$ in ^{13}C NMR). Coupling constants were reported as *J* values in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad.

High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics compact in positive electrospray ionization (ESI) method using ESI tuning mix as the internal standard.

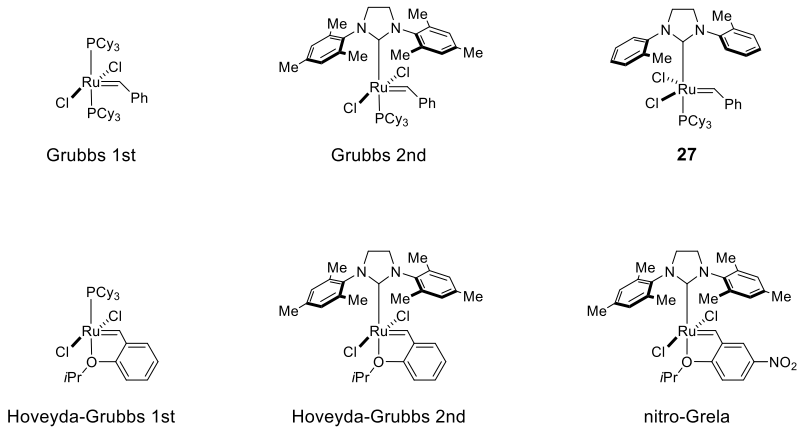
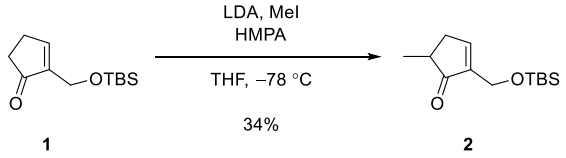


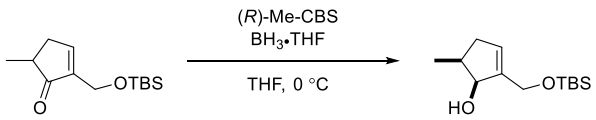
Figure S1. Catalysts used in the metathesis reactions.

Experimental Procedures



To a solution of diisopropylamine (29.5 ml, 210 mmol, 1.21 equiv) in THF (174 mL) was added *n*-BuLi (2.64 M in hexane, 79.2 mL, 209 mmol, 1.2 equiv) dropwise at −78 °C over a period of 10 min. After 20 minutes of stirring at 0 °C, the mixture was cooled at −78 °C and a solution of enone **1** (39.3 g, 174 mmol) in THF (174 mL) cooled at 0 °C was added slowly via a cannula to the mixture over 30 min. After stirring the mixture at −78 °C for 1 h, hexamethylphosphoric triamide (109 ml, 626 mmol, 3.6 equiv) and methyl iodide (54.2 mL, 870 mmol, 5 equiv) were added to the reaction mixture, which was stirred for 6 h at −78 °C. The reaction was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc three times. The combined organic layer was washed with aqueous LiCl solution (1 M) and brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:40 to 1:30 EtOAc/hexane) to afford enone **2** (14.4 g, 59.9 mmol, 34%) as a colorless oil.

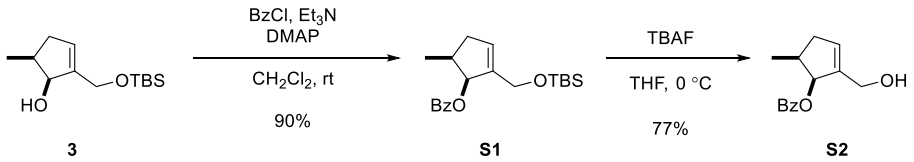
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48-7.44 (m, 1H), 4.38 (d, J = 16.0 Hz, 1H), 4.34 (d, J = 16.0 Hz, 1H), 2.86 (tddd, J = 2.8, 2.8, 6.7, 19.0 Hz, 1H), 2.44 (ddq, J = 2.5, 6.7, 7.3 Hz, 1H), 2.19 (ddtd, J = 2.5, 2.8, 2.8, 19.0 Hz, 1H), 1.18 (d, J = 7.3 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 211.1 (C), 156.3 (CH), 145.2 (C), 58.5 (CH_2), 41.0 (CH), 35.9 (CH_2), 26.0 (CH_3), 18.4 (C), 16.3 (CH_3), −5.32 (CH_3)
IR (film, cm^{-1}): 2956, 2929, 2885, 2857, 1704, 1256, 1119, 838, 777
HRMS (ESI): m/z $[M+Na]^+$ Calcd for $C_{13}H_{24}NaO_2Si$ 263.1438; Found 263.1440



2 3

Under argon atmosphere, (*R*)-(+)-2-methyl-CBS-oxazaborolidine (1.66 g, 5.99 mmol, 10 mol%) and enone **2** (14.4 g, 59.9 mmol) were dissolved in THF (666 mL) and the solution was cooled at 0 ºC. BH_3•THF (1.0 M solution in THF, 30.0 ml, 30.0 mmol, 0.5 equiv) was dropwisely added and the reaction mixture was kept stirring for 30 min at 0 ºC. After the solution was quenched with saturated aqueous NH_4Cl solution, the resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:40 to 1:30 EtOAc/hexane) to afford alcohol **3** (6.37 g, 26.3 mmol, 44%) as a colorless oil. The enantiomeric excess of **3** was determined after transformation into alcohol **S2**.

$[\alpha]_D^{26}$: −25.3º (*c* 4.02, $CHCl_3$)
^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.75 (br s, 1H), 4.52 (t, *J* = 4.6 Hz, 1H), 4.33 (q, *J* = 1.8 Hz, 2H), 2.24-2.36 (m, 1H), 2.34 (qddd, *J* = 7.1, 7.2, 7.2, 7.2 Hz, 1H), 2.10-2.03 (m, 1H), 2.02 (d, *J* = 4.6 Hz, 1H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.9 (C), 129.7 (CH), 78.3 (CH), 61.8 (CH_2), 38.5 (CH_2), 37.8 (CH), 26.0 (CH_3), 18.4 (C), 13.9 (CH_3), −5.3 (CH_3)
IR (film, cm^{-1}): 3366, 2956, 2928, 2900, 2856, 1471, 1462, 1254, 1084, 1054, 838, 776
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{13}H_{26}NaO_2Si$ 265.1594; Found 265.1607



To a solution of alcohol **3** (42.2 mg, 0.174 mmol) in CH_2Cl_2 (1.74 mL) at 25 °C were sequentially added Et_3N (96 μL, 0.696 mmol, 4 equiv), BzCl (41 μL, 0.35 mmol, 2 equiv) and 4-DMAP (21 mg, 0.174 mmol, 1 equiv). The resulting mixture was stirred for 10 h and quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:15 EtOAc/hexane) to afford benzoate **S1** (53.9 mg, 0.156 mmol, 90%) as a colorless oil. To a solution of benzoate **S1** (43.4 mg, 0.125 mmol) in THF (0.46 mL) at 0 °C was added tetrabutylammonium fluoride (1.0 M in THF, 0.188 mL, 0.188 mmol, 1.5 equiv). The reaction mixture was stirred for 2 h at 0 °C and quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:3 EtOAc/hexane) to afford alcohol **S2** (22.4 mg, 96.4 μmol, 77%) as a colorless oil. The enantiomeric excess was determined by HPLC analysis with a chiral HPLC column (DAICEL CHIRALCEL OD-H, *n*-hexane:2-propanol = 99:1 to 95:5 (0.0 to 15.0 min) to 90:10 (15.0 to 25.0 min), 1.0 mL/min at 25 °C, UV 230 nm).

$[\alpha]_D^{24}$: −130° (*c* 1.14, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.07-8.01 (m, 2H), 7.57 (tt, *J* = 1.4, 7.3 Hz, 1H), 7.47-7.40 (m, 2H), 5.96 (s, 1H), 5.89 (dd, *J* = 1.4, 6.9 Hz, 1H), 4.22 (d, *J* = 14.2 Hz, 1H), 4.16 (d, *J* = 14.2 Hz, 1H), 2.68 (dddq, *J* = 6.9, 6.9, 6.9, 6.9 Hz, 1H), 2.64-2.52 (m, 2H), 2.24-2.14 (m, 1H), 1.14 (d, *J* = 6.9 Hz, 3H)

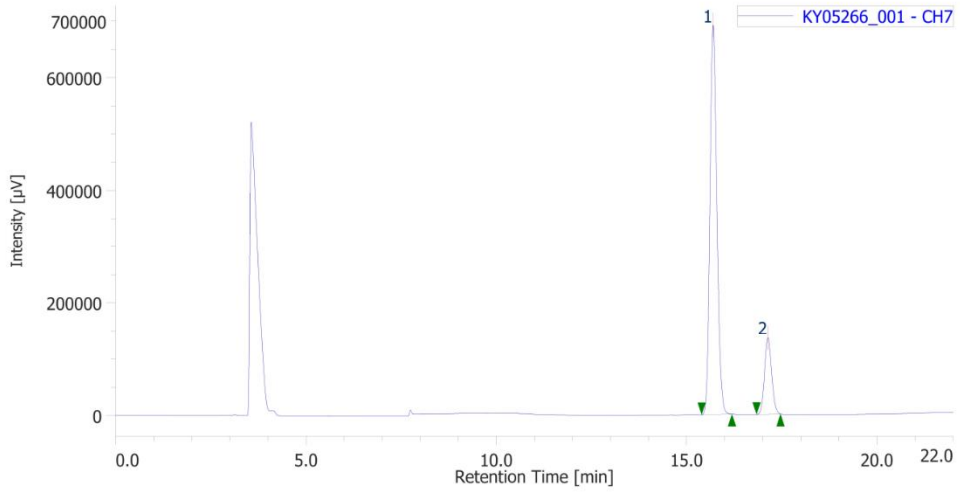
^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.5 (C), 142.6 (C), 133.2 (CH), 132.5 (CH), 130.3 (C), 129.8 (CH), 128.5 (CH), 80.4 (CH), 60.0 (CH_2), 38.9 (CH_2), 36.6 (CH), 14.7 (CH_3)

IR (film, cm^{-1}): 3420, 2966, 2930, 2874, 2849, 1713, 1274, 1112, 713

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{14}H_{16}NaO_3$ 255.0992; Found 255.1004

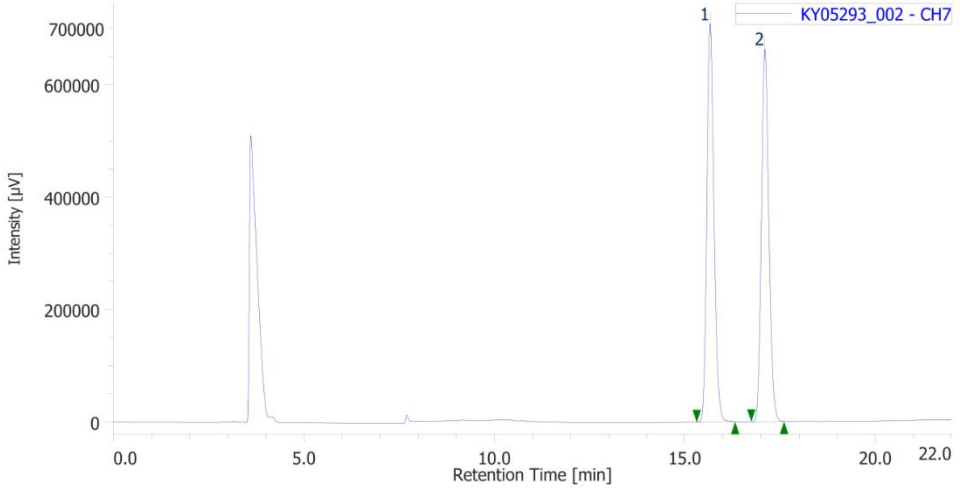
Chiral HPLC chart of S2

DAICEL CHIRALCEL OD-H *n*-hexane:2-propanol = 99:1 to 95:5 (0.0 to 15.0 min) to 90:10 (15.0 to 25.0 min), 1.0 mL/min, 25 °C, UV 230 nm

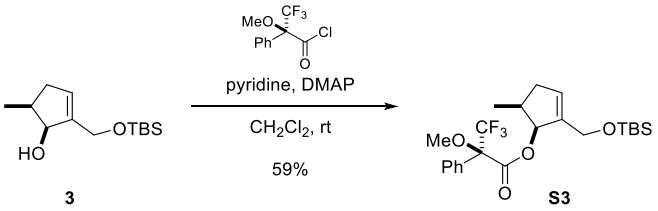


No.	tR	Area	Height	Area (%)
1	15.697	8762161	691046	83.635
2	17.133	1754394	135222	16.365

Chiral HPLC chart of S2 (racemate)



No.	tR	Area	Height	Area (%)
1	15.663	9143711	708214	50.456
2	17.097	8978456	662654	49.544



To a solution of alcohol **3** (26.0 mg, 0.107 mmol) in CH_2Cl_2 (2.0 mL) at 25 °C were sequentially added pyridine (25.9 μL, 0.321 mmol, 3 equiv), (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (30.1 μL, 0.161 mmol, 1.5 equiv) and 4-DMAP (2.61 mg, 21.4 μmol, 20 mol%). The resulting mixture was stirred for 10 h and quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:15 EtOAc/hexane) to afford **S3** (29.1 mg, 0.0635 mmol, 59%) as a colorless oil.

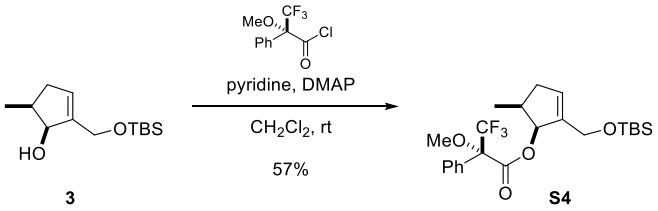
$[\alpha]_D^{26}$: −19.3° (*c* 1.18, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.51 (m, 2H), 7.45-7.36 (m, 3H), 5.95 (dd, *J* = 1.8, 2.3 Hz, 1H), 5.83 (dd, *J* = 1.4, 6.7 Hz, 1H), 4.09 (dddd, J = 2.3, 2.3, 2.3, 14.6 Hz, 1H), 4.05-3.97 (m, 1H), 3.53 (q, *J* = 0.9 Hz, 3H), 2.61 (dddq, *J* = 6.7, 6.9, 6.9, 7.1 Hz, 1H), 2.54-2.43 (m, 1H), 2.14-2.02 (m, 1H), 1.00 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.9 (C), 142.1 (C), 132.2 (C), 132.0 (CH), 129.7 (CH), 128.5 (CH), 127.7 (CH), 123.5 (q, *J* = 287.0 Hz, C), 84.9 (q, *J* = 27.7 Hz, C), 82.9 (CH), 60.5 (CH_2), 55.5 (CH_3), 38.6 (CH_2), 37.1 (CH), 26.0 (CH_3), 18.5 (C), 14.7 (CH_3), −5.3 (CH_3), −5.4 (CH_3)

IR (film, cm^{-1}): 2954, 2931, 2856, 1743, 1462, 1254, 1170, 839

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{23}H_{33}F_3NaO_3Si$ 481.1992; Found 481.1994



To a solution of alcohol **3** (50.0 mg, 0.206 mmol) in CH_2Cl_2 (4.1 mL) at 25 °C were sequentially added pyridine (49.8 μL, 0.618 mmol, 3 equiv), (*R*)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (57.8 μL, 0.309 mmol, 1.5 equiv) and 4-DMAP (5.03 mg, 41.2 μmol, 20 mol%). The resulting mixture was stirred for 10 h and quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:15 EtOAc/hexane) to afford benzoate **S4** (53.5 mg, 0.117 mmol, 57%) as a colorless oil.

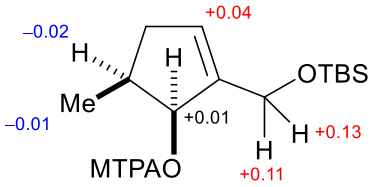
$[\alpha]_D^{26}$: −52.3° (*c* 2.68, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.51 (m, 2H), 7.47-7.34 (m, 3H), 5.99 (s, 1H), 5.84 (d, *J* = 6.6 Hz, 1H), 4.20 (dd, *J* = 2.3, 14.2 Hz, 1H), 4.14 (d, *J* = 14.2 Hz, 1H), 3.55 (s, 3H), 2.59 (dddq, *J* = 6.6, 6.9, 6.9, 7.3 Hz, 1H), 2.53-2.42 (m, 1H), 2.16-2.02 (m, 1H), 0.90 (d, *J* = 7.3 Hz, 3H), 0.88 (s,9H), 0.04 (s, 3H), 0.02 (s, 3H)

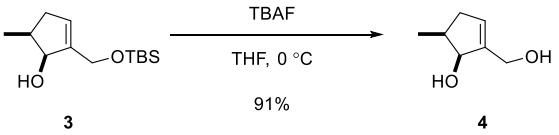
^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.8 (C), 142.0 (C), 132.6 (C), 132.5 (CH), 129.7 (CH), 128.5 (CH), 127.5 (CH), 123.6 (q, *J* = 287.0 Hz, C), 84.6 (q, *J* = 27.7 Hz, C), 82.7 (CH), 60.6 (CH_2), 55.5 (CH_3), 38.6 (CH_2), 37.3 (CH), 26.0 (CH_3), 18.5 (C), 14.2 (CH_3), −5.30 (CH_3), −5.34 (CH_3)

IR (film, cm^{-1}): 2954, 2931, 2856, 1743, 1462, 1254, 1170, 839

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{23}H_{33}F_3NaO_3Si$ 481.1992; Found 481.2015



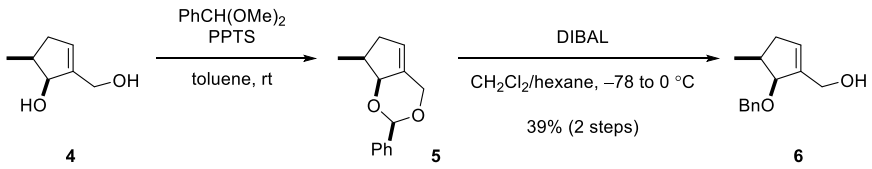
$\Delta\delta_H$ values [δ_H of (*S*)-MTPA ester **S4** − δ_H of (*R*)-MTPA ester **S3**]



3 4

To a solution of alcohol **3** (4.02 g, 16.6 mmol) in THF (99.4 mL) at 0 °C was added tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 19.9 mL, 19.9 mmol, 1.2 equiv). The reaction mixture was stirred for 1 h at 0 °C and quenched with NH_4Cl (1.07 g, 19.9 mmol, 1.2 equiv). The resulting mixture was filtered through a short plug of Celite and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (1:1 EtOAc/hexane to EtOAc only) to afford diol **4** (1.94 g, 15.1 mmol, 91%) as a colorless oil.

$[\alpha]_D^{26}$: –32.9° (*c* 2.79, $CHCl_3$)
^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.82 (s, 1H), 4.60 (dd, *J* = 5.0, 5.9 Hz, 1H), 4.32 (s, 2H), 2.48-2.40 (m, 1H), 2.38 (qddd, *J* = 6.9, 7.0, 7.0, 7.0 Hz, 1H), 2.11-2.02 (m, 1H), 2.00 (br s, 1H), 1.74 (d, *J* = 5.9 Hz, 1H), 1.08 (d, *J* = 6.9 Hz, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.9 (C), 130.5 (CH), 78.1 (CH), 60.5 (CH_2), 38.4 (CH_2), 37.5 (CH), 14.0 (CH_3)
IR (film, cm^{-1}): 3334, 2962, 2924, 2873, 2847, 1655, 1455, 1055, 1031, 977, 693
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_7H_{12}NaO_2$ 151.0730; Found 151.0731



4 5 6

To a solution of diol **4** (1.94 g, 15.1 mmol) in toluene (252 mL) at room temperature were added $PhCH(OMe)_2$ (9.19 mL, 60.4 mmol, 4 equiv) and pyridinium *p*-toluenesulfonate (759 mg, 3.02 mmol, 20 mol%). After stirring for 2.5 h at ambient temperature, the reaction mixture was concentrated and the residue was roughly purified by column chromatography (1:20 EtOAc/hexane) to afford a mixture containing acetal **5**, $PhCH(OMe)_2$ and benzaldehyde. To a solution of the mixture containing acetal **5** in CH_2Cl_2 (75.5 mL) at −78 ºC was added, diisobutylaluminium hydride (1.0 M in hexane, 60.4 mL, 60.4 mmol, 4 equiv) and the resulting mixture was warmed to 0 ºC. After stirring for 15 min, the reaction was quenched with 30% aqueous Rochelle solution, and the resulting mixture was extracted with CH_2Cl_2 and Et_2O. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. To the residue was added H_2O (400 mL) and evaporated to remove benzyl alcohol. The residue was purified by column chromatography (1:7 to 1:2 EtOAc/hexane) to afford ether **6** (1.29 g, 5.91 mmol, 39%, 2 steps) as a pale-yellow oil.

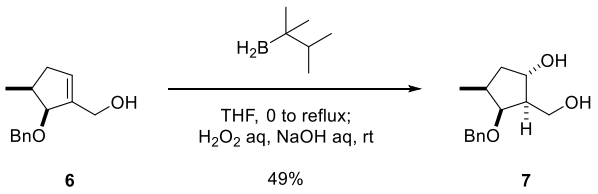
$[\alpha]_D^{26}$: +15.9º (*c* 1.14, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.27 (m, 5 H), 5.74 (ddddd, *J* = 1.4, 1.6, 1.6, 2.3, 2.3 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 6.9 Hz, 1H), 4.48 (d, *J* = 11.5 Hz, 1H), 4.23 (d, *J* = 13.1 Hz, 1H), 4.17 (d, *J* = 13.1 Hz, 1H), 2.61-2.50 (m, 1H), 2.44 (dtddd, *J* = 1.6, 1.8, 1.8, 7.3, 16.3 Hz, 1H), 2.10 (br s, 1H), 2.05 (dtddd, *J* = 1.6, 1.8, 1.8, 4.1, 16.3 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9 (C), 138.6 (C), 129.0 (CH), 128.6 (CH), 128.0 (CH), 127.9 (CH), 86.2 (CH), 72.8 (CH_2), 60.9 (CH_2), 38.7 (CH_2), 36.3 (CH), 14.8 (CH_3)

IR (film, cm^{-1}): 3388, 2961, 2924, 2870, 2848, 1454, 1098, 1066, 1028, 992, 736, 698

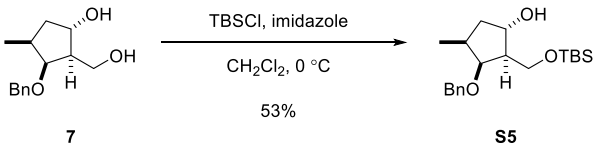
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{14}H_{18}NaO_2$ 241.1199; Found 241.1206



6 49% 7

A solution of thexylboran (0.891 M solution in THF, 138 ml, 123 mmol, 3 equiv) was added to a flask charged with alcohol **6** (8.95 g, 41.0 mmol) via a cannula at 0 ºC. The reaction mixture was warmed to reflux and stirred for 30 min. After cooling to 0 ºC, the reaction was quenched with hydrogen peroxide solution (30.0-35.5%, 16 mL, 2.5 M) and 3.0 M aqueous NaOH solution (16 mL, 2.5 M) and the reaction mixture was stirred for another 1 h at room temperature. The resulting mixture was extracted with Et_2O three times and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:1 EtOAc/hexane to EA gradiently) to afford diol **7** (4.74 g, 20.1 mmol, 49%) as a pale-yellow oil.

$[\alpha]_D^{26}$: +41.1º (*c* 3.68, $CHCl_3$)
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.27 (m, 5H), 4.63 (d, *J* = 11.4 Hz, 1H), 4.46 (d, *J* = 11.4 Hz, 1H), 4.39 (ddd, *J* = 4.1, 6.6, 7.6 Hz, 1H), 4.00 (dd, *J* = 5.0, 5.7 Hz, 1H), 3.86 (dd, *J* = 5.7, 11.0 Hz, 1H), 3.81 (dd, *J* = 5.9, 11.0 Hz, 1H), 2.46-2.26 (m, 1H), 2.07 (dddd, *J* = 5.6, 5.7, 5.7, 5.9 Hz, 1H), 1.86 (ddd, *J* = 7.6, 9.6, 13.1 Hz, 1H), 1.70 (ddd, *J* = 4.1, 8.2, 13.1 Hz, 1H), 1.64 (br s, 1H), 1.08 (d, *J* = 6.9 Hz, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.4 (C), 128.6 (CH), 127.93 (CH), 127.90 (CH), 84.9 (CH), 74.1 (CH_2), 73.8 (CH), 61.8 (CH_2), 55.8 (CH), 40.9 (CH), 37.4 (CH), 14.8 (CH_3)
IR (film, cm^{-1}): 3364, 2954, 2928, 2873, 1454, 1346, 1068, 1045, 1027, 735, 699
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{14}H_{20}NaO_3$ 259.1305; Found 259.1317



7 S5

To a solution of diol **7** (4.67 g, 19.8 mmol) in CH_2Cl_2 (99 mL) at 0 °C were sequentially added imidazole (4.04 g, 59.4 mmol, 3 equiv) and TBSCl (4.48 g, 29.7 mmol, 1.5 equiv). The resulting mixture was stirred at the same temperature for 1.5 h and quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with CH_2Cl_2 twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:5 EtOAc/hexane) to afford alcohol **S5** (3.64 g, 10.4 mmol, 53%) as a pale-yellow oil.

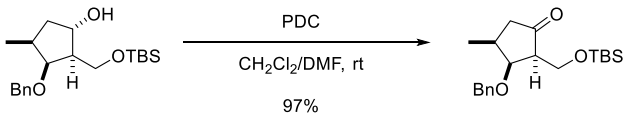
$[\alpha]_D^{26}$: +31.8° (*c* 1.77, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.24 (m, 5H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.44 (d, *J* = 11.9 Hz, 1H), 4.26 (ddd, *J* = 4.1, 8.0, 8.7 Hz, 1H), 3.86-3.74 (m, 3H), 2.40-2.27 (m, 1H), 2.24 (s, 1H), 2.05 (dddd, *J* = 4.1, 7.8, 7.8, 8.0 Hz, 1H), 1.87 (ddd, *J* = 8.7, 9.6, 13.7 Hz, 1H), 1.72 (ddd, *J* = 4.1, 9.6, 13.7 Hz, 1H), 1.03 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.0 (C), 128.4 (CH), 127.9 (CH), 127.7 (CH), 83.9 (CH), 76.3 (CH), 74.1 (CH_2), 63.3 (CH_2), 56.9 (CH), 40.1 (CH_2), 37.6 (CH), 26.1 (CH_3), 18.3 (C), 15.0 (CH_3), –5.29 (CH_3), –5.32 (CH_3)

IR (film, cm^{-1}): 3364, 2953, 2928, 2883, 2857, 1255, 1093, 1072, 837, 776

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{20}H_{34}NaO_3Si$ 373.2169; Found 373.2173



S5 **8**

To a solution of alcohol **S5** (3.61 g, 10.3 mmol) in CH_2Cl_2 (68 mL) and DMF (34 mL) at 0 ºC were added pyridinium dichromate (5.83 g, 15.5 mmol, 1.5 equiv) and Celite (5.83 g). The resulting mixture was stirred at room temperature for 4 h and then purified by column chromatography (1:5 EtOAc/hexane) to afford ketone **8** (3.49 g, 10.0 mmol, 97%) as a colorless oil.

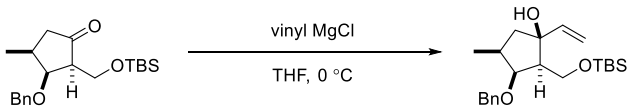
$[\alpha]_D^{26}$: +74.8º (*c* 1.71, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.15 (m, 5H), 4.68 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 11.4 Hz, 1H), 4.12 (dd, *J* = 3.2, 4.3 Hz, 1H), 3.94 (dd, *J* = 4.8, 10.5 Hz, 1H), 3.78 (dd, *J* = 10.1, 10.5 Hz, 1H), 2.53 (ddd, *J* = 4.3, 4.8, 10.1 Hz, 1H), 2.26 (dd, *J* = 7.8, 16.7 Hz, 1H), 2.26-2.13 (m, 1H), 2.11 (dd, *J* = 6.4, 16.7 Hz, 1H), 1.10 (d, *J* = 6.4 Hz, 3H), 0.85 (s, 9H), −0.006 (s, 3H), −0.005 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 216.7 (C), 138.8 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 80.7 (CH), 74.3 (CH_2), 60.6 (CH), 58.2 (CH_2), 43.4 (CH_2), 35.5 (CH), 26.0 (CH), 18.3 (C), 15.0 (CH_3), −5.2 (CH_3), −5.3 (CH_3)

IR (film, cm^{-1}): 2955, 2928, 2883, 2856, 1742, 1704, 1252, 1095, 838, 776, 704

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{20}H_{32}NaO_3Si$ 371.2013; Found 371.2010



8 **9**

To a solution of ketone **8** (1.29 g, 3.70 mmol) in THF (18 mL) at 0 ºC was added vinyl magnesium chloride (1.38 M in THF, 11.3 mL, 4.2 equiv). The resulting mixture was stirred at ambient temperature for 1 h and quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:40 to 1:30 EtOAc/hexane) to afford olefin **9** (1.08 g, 2.87 mmol, 78%) as a colorless oil.

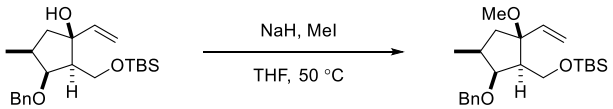
$[\alpha]_D^{26}$: +25.7º (*c* 3.26, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.27 (m, 5H), 5.81 (ddd, *J* = 0.9, 10.5, 17.2 Hz, 1H), 5.25 (dd, *J* = 1.6, 17.2 Hz, 1H), 5.04 (dd, *J* = 1.6, 10.5 Hz, 1H), 4.69 (d, *J* = 11.2 Hz, 1H), 4.65 (d, *J* = 11.2 Hz, 1H), 4.06 (dd, *J* = 3.6, 4.1 Hz, 1H), 3.93 (dd, *J* = 10.1, 10.5 Hz, 1H), 3.73 (dd, *J* = 4.6, 10.5 Hz, 1H), 3.47 (d, *J* = 0.9 Hz, 1H), 2.27 (dd, *J* = 10.1, 14.2 Hz, 1H), 2.16-2.04 (m, 1H), 1.93 (ddd, *J* = 3.6, 4.6, 10.1 Hz, 1H), 1.62 (dd, *J* = 8.7, 14.2 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 3H), 0.92 (s, 9H), 0.063 (s, 3H), 0.057 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.9 (CH), 138.6 (C), 128.5 (CH), 127.9 (CH), 127.8 (CH), 111.8 (CH_2), 84.7 (CH), 81.7 (C), 74.6 (CH_2), 58.3 (CH_2), 57.0 (CH_2), 49.5 (CH_2), 37.7 (CH), 26.1 (CH_3), 18.3 (C), 15.6 (CH_3), –5.19 (CH_3), –5.24 (CH_3)

IR (film, cm^{-1}): 3525, 2954, 2928, 2883, 2856, 1255, 1091, 1065, 837, 775

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{22}H_{36}NaO_3Si$ 399.2326; Found 399.2338



9 **10**

To a suspension of NaH (55% oil dispersion, 204 mg, 4.68 mmol, 3 equiv) in THF (7.0 mL) at 0 °C were sequentially added a solution of olefin **9** (588 mg, 1.56 mmol) in THF (0.8 mL) and MeI (0.388 mL, 6.24 mmol, 4 equiv). The resulting mixture was warmed to 50 °C and stirred for 1 h. After cooling to 0 °C, the reaction was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:40 to 1:30 EtOAc/hexane) to afford ether **10** (551 mg, 1.41 mmol, 90%) as a colorless oil.

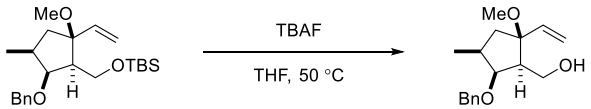
$[\alpha]_D^{26}$: −16.3° (*c* 1.86, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* = 7.32 Hz, 2H), 7.36-7.30 (m, 2H), 7.29-7.23 (m, 1H), 5.89 (dd, *J* = 11.0, 17.4 Hz, 1H), 5.12 (dd, *J* = 1.4, 17.4 Hz, 1H), 5.07 (dd, *J* = 1.4, 11.0 Hz, 1H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.61 (d, *J* = 11.9 Hz, 1H), 3.92 (dd, *J* = 9.4, 10.1 Hz, 1H), 3.84 (dd, *J* = 3.6, 4.4 Hz, 1H), 3.80 (dd, *J* = 4.8, 10.1 Hz, 1H), 3.09 (s, 3H), 2.02 (dd, *J* = 5.0, 11.4 Hz, 1H), 1.99 (ddd, *J* = 4.4, 4.8, 9.4 Hz, 1H), 1.95-1.80 (m, 2H), 1.04 (d, *J* = 6.4 Hz, 3H), 0.91 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.8 (CH), 139.8 (C), 128.2 (CH), 128.0 (CH), 127.3 (CH), 111.9 (CH_2), 85.4 (C), 83.1 (CH), 73.9 (CH_2), 59.0 (CH), 58.5 (CH_2), 51.1 (CH_3), 40.5 (CH_2), 38.1 (CH), 26.1 (CH_3), 18.3 (C), 14.7 (CH_3), −5.15 (CH_3), −5.20 (CH_3)

IR (film, cm^{-1}): 2954, 2929, 2883, 2956, 1082, 1062, 836, 774

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{23}H_{38}NaO_3Si$ 413.2482; Found 413.2496



10 **11**

To a solution of ether **10** (516 mg, 1.32 mmol) in THF (5.0 mL) at 0 ºC was added tetrabutylammonium fluoride (1.0 M in THF, 1.98 mL, 1.89 mmol, 1.5 equiv). The resulting mixture was warmed to 50 ºC and stirred for 2 h. After cooling to 0 ºC, the reaction was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with Et_2O twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:4 EtOAc/hexane) to afford alcohol **11** (346 mg, 1.25 mmol, 95%) as a pale-yellow oil.

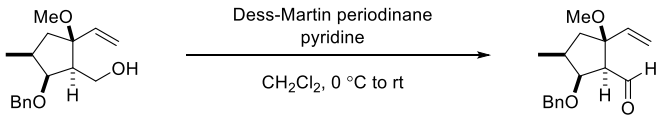
$[\alpha]_D^{26}$: –5.35º (*c* 2.34, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.16 (m, 5H), 5.74 (ddd, *J* = 0.9, 10.5, 18.1 Hz, 1H), 5.07 (dd, *J* = 0.9, 10.5 Hz, 1H), 5.05 (dd, *J* = 0.9, 18.1 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 3.89 (dd, *J* = 8.2, 11.4 Hz, 1H), 3.74 (dd, *J* = 5.5, 5.9 Hz, 1H), 3.69 (dd, *J* = 6.0, 11.4 Hz, 1H), 3.05 (s, 3H), 2.53 (br s, 1H), 2.16 (ddd, *J* = 5.9, 6.0, 8.2 Hz, 1H), 2.04 (dd, *J* = 7.3, 11.9 Hz, 1H), 2.05-1.91 (m, 1H), 1.72 (ddd, *J* = 0.9, 11.4, 11.9 Hz, 1H), 1.01 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.3 (CH), 138.8 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 113.6 (CH_2), 85.6 (C), 81.9 (CH), 73.5 (CH_2), 60.3 (CH_2), 55.7 (CH), 51.3 (CH_3), 39.0 (CH_2), 36.6 (CH), 15.4 (CH_3)

IR (film, cm^{-1}): 3436, 2956, 2933, 2904, 2826, 1455, 1084, 1075, 699

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{17}H_{24}NaO_3$ 299.1618; Found 299.1621



11 **12**

To a solution of alcohol **11** (100 mg, 0.362 mmol) in CH_2Cl_2 (3.6 mL) at 0 ºC were sequentially added pyridine (87.8 μL, 1.09 mmol, 3 equiv) and Dess-Martin periodinane (230 mg, 0.543 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 2 h and then purified by neutral silica gel column chromatography (1:7 EtOAc/hexane) to afford aldehyde **12** (85.5 mg, 0.312 mmol, 86%) as a colorless oil.

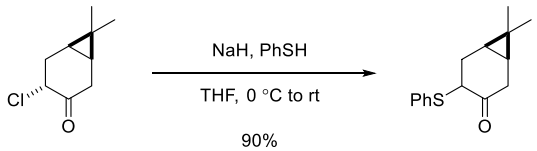
$[\alpha]_D^{26}$: +5.31º (*c* 2.05, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.86 (d, *J* = 5.0 Hz, 1H), 7.36-7.24 (m, 5H), 5.78 (dd, *J* = 10.3, 17.7 Hz, 1H), 5.25 (d, *J* = 10.3 Hz, 1H), 5.17 (d, *J* = 17.7 Hz, 1H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 4.04 (dd, *J* = 6.6, 6.9 Hz, 1H), 3.12 (s, 3H), 2.89 (dd, *J* = 5.0, 6.6 Hz, 1H), 2.29-2.07 (m, 3H), 1.16 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.7 (CH), 140.6 (CH), 138.2 (C), 128.4 (CH), 127.8 (CH), 127.7 (CH), 115.5 (CH_2), 86.0 (C), 82.3 (CH), 73.3 (CH_2), 63.4 (CH), 51.8 (CH_3), 41.2 (CH_2), 36.6 (CH), 14.8 (CH_3)

IR (film, cm^{-1}): 2961, 2935, 2873, 2829, 1719, 1455, 1075, 737, 698

HRMS (ESI): *m/z* $[M+Na]^+$ Calcd for $C_{17}H_{22}NaO_3$ 297.1461; Found 297.1465



13 **14**

To a suspension of NaH (55% oil dispersion, 3.37 g, 77.2 mmol, 1.2 equiv) in THF (300 mL) at 0 °C was added PhSH (6.58 mL, 64.3 mmol, 1 equiv). After stirring for 15 min, a solution of chloride **13** (11.1 g, 64.3 mmol) in THF (22 mL) was added at 0 °C. After stirring for 30 min at room temperature, the reaction mixture was cooled at 0 °C and quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with EtOAc twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:15 EtOAc/hexane) to afford sulfide **14** (14.3 g, 58.0 mmol, 90%, a mixture of diastereomers) as a pale-yellow solid.

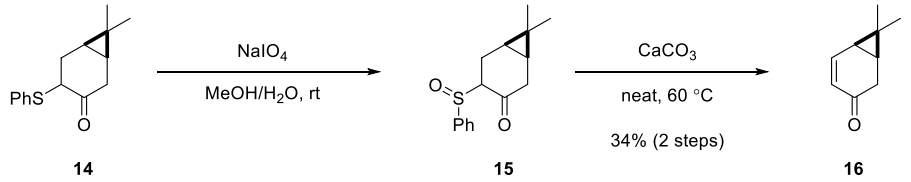
$[\alpha]_D^{26}$: +65.0° (*c* 3.35, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz, mixture of diastereomers): δ 7.45-7.36 (m, 2H), 7.32-7.20 (m, 3H), [3.93 (dd, *J* = 6.4, 13.3 Hz), 3.49 (dd, *J* = 2.7, 4.6 Hz), *all sum to* 1H], [3.02 (dd, *J* = 9.2, 18.8 Hz), 2.71-2.62 (m), *all sum to* 1H], [2.62-2.55 (m), 2.52 (ddd, *J* = 6.4, 9.2, 14.7 Hz), *all sum to* 1H], [2.38 (dd, *J* = 3.0, 17.8 Hz), 2.20 (d, *J* = 18.8 Hz), *all sum to* 1H], [2.04 (ddd, *J* = 4.6, 5.7, 16.0 Hz), 1.59 (ddd, *J* = 6.0, 13.3, 14.7 Hz), *all sum to* 1H], [1.25 (ddd, *J* = 1.8, 9.2, 8.9 Hz), 1.08 (ddd, *J* = 3.0, 8.2, 8.9 Hz), *all sum to* 1H], [1.08 (s), 1.03 (s), *all sum to* 3H], 0.96 (ddd, *J* = 5.6, 8.9, 9.2 Hz, 1H), [0.89 (s), 0.87(s), *all sum to* 3H]

^{13}C NMR ($CDCl_3$, 100 MHz): δ 210.5 (C), 209.8 (C), 134.2 (C), 133.7 (C), 132.8 (CH), 131.1 (CH), 129.2 (CH), 129.0 (CH), 127.5 (CH), 127.4 (CH), 55.4 (CH), 52.2 (CH), 37.3 (CH_2), 32.9 (CH_2), 29.2 (CH_2), 27.85 (CH_3), 27.81 (CH_3), 26.6 (CH_2), 23.0 (CH), 22.6 (CH), 20.8 (CH), 20.3 (C), 20.0 (C), 16.4 (CH), 15.1 (CH_3), 14.9 (CH_3)

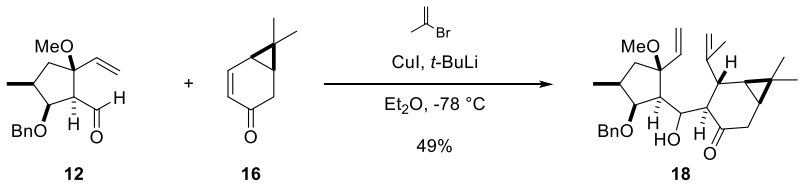
IR (film, cm^{-1}): 3006, 2944, 2866, 1710, 1481, 1439, 741, 691

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{15}H_{18}NaOS$ 269.0971; Found 269.0983



To a solution of sulfide **14** (14.3 g, 58.0 mmol) in MeOH (174 mL) and H_2O (58 mL) at room temperature was added $NaIO_4$ (14.9 g, 69.6 mmol, 1.2 equiv). After stirring for 4 h at ambient temperature, the reaction mixture was extracted with EtOAc twice, and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:5 to 1:1 EtOAc/hexane) to afford a mixture of sulfoxide **15** and a trace amount of enone **16**. To the mixture containing sulfoxide **15** was added $CaCO_3$ (581 mg, 5.80 mmol, 10 mol%) and the resulting mixture was warmed to 60 °C. After stirring for 5 h, the reaction mixture was filtrated through a short plug of Celite eluting with EtOAc and the filtrate was concentrated. The residue was distilled under reduced pressure (2.4 Torr) at 50 °C to afford enone **16** (2.69 g, 19.8 mmol, 34%, 2 steps) as a pale-yellow oil.

$[\alpha]_D^{26}$: –311° (*c* 1.72, $CHCl_3$)
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.04 (dd, *J* = 5.7, 10.1 Hz, 1H), 5.95 (d, *J* = 10.1 Hz, 1H), 2.62 (dd, *J* = 7.4, 19.7 Hz, 1H), 2.57-2.49 (m, 1H), 1.44 (ddd, *J* = 1.4, 5.7, 7.6 Hz, 1H), 1.37 (ddd, *J* = 1.4, 7.4, 7.6 Hz, 1H), 1.25 (s, 3H), 0.88 (s, 3H)
^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.2 (C), 149.3 (CH), 126.9 (CH), 32.9 (CH_2), 27.7 (CH_3), 25.9 (C), 24.2 (CH), 14.0 (CH), 13.2 (CH_3)
IR (film, cm^{-1}): 3012, 2949, 1664, 1399, 976, 810
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_9H_{12}NaO$ 159.0780; Found 159.0785



To a solution of 2-bromopropene (26.9 μL, 0.309 mmol, 8.5 equiv) in Et_2O (0.9 mL) cooled at –78 °C was added *t*-BuLi (1.39 M in pentane, 0.445 mL, 0.619 mmol, 17 equiv) dropwise over 5 min. The light-yellow mixture was stirred at –78 °C for 30 min, and then at room temperature for another 20 min. The resulting mixture was added to a flask charged with CuI (29.1 mg, 0.153 mmol, 4.2 equiv) via a cannula. After stirring for 15 min at room temperature, the resulting suspension was cooled to –78 °C and stirred for 5 min. To this mixture was added a solution of enone **16** (19.9 mg, 0.146 mmol, 4 equiv) in Et_2O (0.36 mL) dropwise. After stirring the yellow mixture at –78 °C for 1 h, a solution of aldehyde **12** (10.0 mg, 36.4 μmol) in Et_2O (0.36 mL) was added dropwise over 3 min. The reaction mixture was stirred at –78 °C for 20 min to produce a bright orange suspension, which was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with Et_2O three times and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (1:4 EtOAc/hexane) to afford diene **18** (8.1 mg, 18 μmol, 49%) as a colorless oil.

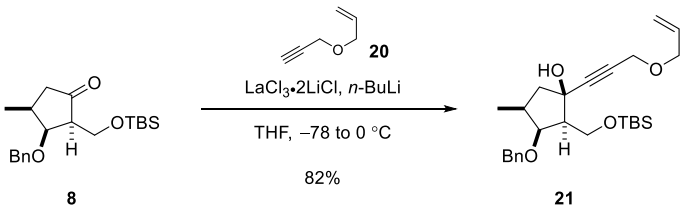
$[\alpha]_D^{26}$: +27.2° (*c* 0.430, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.22 (m, 5H), 5.67 (dd, *J* = 10.8, 17.4 Hz, 1H), 5.02 (dd, *J* = 1.4, 17.4 Hz, 1H), 4.96 (dd, *J* = 1.4, 10.8 Hz, 1H), 4.92 (d, *J* = 1.8 Hz, 1H), 4.80 (dd, *J* = 1.4, 1.8 Hz, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.03 (ddd, *J* = 1.4, 10.5, 11.0 Hz, 1H), 3.92 (dd, *J* = 3.2, 3.9 Hz, 1H), 3.13 (s, 3H), 3.00 (d, *J* = 11.9 Hz, 1H), 2.91 (d, *J* = 11.0 Hz, 1H), 2.84 (dd, *J* = 4.3, 11.9 Hz, 1H), 2.51 (dd, *J* = 8.2, 16.0 Hz, 1H), 2.42 (dd, *J* = 3.9, 10.5 Hz, 1H), 2.31 (d, *J* = 16.0 Hz, 1H), 2.08-1.95 (m, 1H), 1.88 (s, 3H), 1.87-1.77 (m, 2H), 1.14-1.08 (m, 1H), 1.04 (s, 3H), 1.03 (d, *J* = 6.4 Hz, 3H), 0.90 (s, 3H), 0.85 (dd, *J* = 4.3, 9.2 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 221.1 (C), 146.4 (C), 143.9 (CH), 140.0 (C), 128.2 (CH), 128.1 (CH), 127.2 (CH), 113.2 (CH_2), 110.7 (CH_2), 85.0 (C), 84.8 (CH), 74.4 (CH_2), 66.6 (CH), 58.7 (CH), 50.9 (CH_3), 50.5 (CH), 46.1 (CH), 42.1 (CH_2), 39.3 (CH_2), 37.8 (CH), 28.7 (CH_3), 25.7 (CH), 24.3 (CH), 20.2 (C), 17.8 (CH_3), 15.3 (CH_3), 14.4 (CH_3)

IR (film, cm^{-1}): 3530, 2929, 2872, 1693, 1455, 1085, 697

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{29}H_{40}NaO_4$ 475.2819; Found 475.2823



To a mixture of *n*-butyllithium (2.64 M in hexane, 11.3 mL, 29.7 mmol, 3 equiv) and THF (150 mL) was added a solution of alkyne **20** (2.86 g, 29.7 mmol, 3 equiv) in THF (15 mL) dropwise at −78 °C over a period of 10 min. After stirring for 1 h at −78 °C, the reaction mixture was warmed to 0 °C and a solution of $LaCl_3$·2LiCl (0.6 M in THF, 16.5 mL, 9.90 mmol, 1 equiv) was added. After stirring for another 15 min, a solution of ketone **8** (3.45 g, 9.90 mmol) in THF (99 mL) was added via a cannula. After stirring for 30 min at ambient temperature, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, and the resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:10 EtOAc/hexane) to afford enyne **21** (3.63 g, 8.16 mmol, 82%) as a yellow oil.

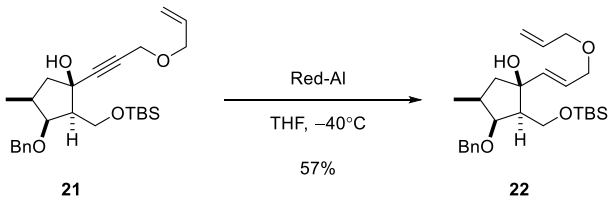
$[\alpha]_D^{26}$: +32.7° (*c* 4.40, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.25 (m, 5H), 5.89 (tdd, *J* = 5.5, 10.5, 17.4 Hz, 1H), 5.29 (dtd, *J* = 1.4, 1.6, 17.4 Hz, 1H), 5.19 (dtd, *J* = 1.4, 1.4, 10.5 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 4.18 (s, 2H), 4.04 (ddd, *J* = 1.4, 1.6, 5.5 Hz, 2H), 4.02-3.94 (m, 3H), 3.48 (s, 1H), 2.55 (dd, *J* = 9.6, 14.2 Hz, 1H), 2.26 (ddd, *J* = 3.6, 6.0, 9.6 Hz, 1H), 2.22-2.10 (m, 1H), 1.84 (dd, *J* = 9.2, 14.2 Hz, 1H), 1.08 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.3 (C), 134.2 (CH), 128.5 (CH), 128.0 (CH), 127.9 (CH), 117.7 (CH_2), 89.5 (C), 83.7 (CH), 78.5 (C), 75.0 (C), 74.6 (CH_2), 70.5 (CH_2), 58.9 (CH), 58.7 (CH_2), 57.6 (CH_2), 50.6 (CH_2), 37.6 (CH), 26.0 (CH_3), 18.3 (C), 15.2 (CH_3), −5.2 (CH_3), −5.3 (CH_3)

IR (film, cm^{-1}): 3495, 2954, 2929, 2882, 2856, 1470, 1462, 1456, 1350, 1254, 1089, 838, 776

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{26}H_{40}NaO_4Si$ 467.2588; Found 467.2577



21 22

To a stirred solution of enyne **21** (3.54 g, 7.96 mmol) in THF (70 mL) was added Red-Al (3.3 M in toluene, 4.82 mL, 15.9 mmol, 2 equiv) at −40 °C. After stirring for 2 h at −40 °C, the mixture was quenched with saturated aqueous Rochel salt at −40 °C and allowed to warm to room temperature with stirring. The resulting mixture was extracted with Et_2O twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1:10 to 1:2 EtOAc/hexane) to afford diene **22** (2.03 g, 4.54 mmol, 57%) as a pale-yellow oil.

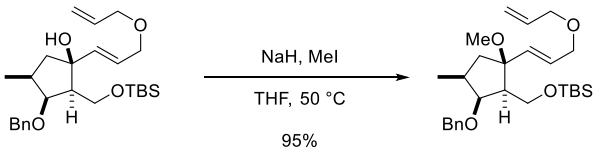
$[\alpha]_D^{26}$: +28.8° (*c* 2.52, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.27 (m, 5H), 5.92 (tdd, *J* = 5.5, 10.5, 17.4 Hz, 1H), 5.78 (dt, *J* = 5.5, 15.6 Hz, 1H), 5.68 (d, *J* = 15.6 Hz, 1H), 5.23 (tdd, *J* = 1.4, 3.4, 17.4 Hz, 1H), 5.17 (tdd, *J* = 1.4, 3.4, 10.5 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.63 (d, *J* = 11.2 Hz, 1H), 4.05 (dd, *J* = 3.7, 4.1 Hz, 1H), 4.03-3.99 (m, 2H), 3.98 (d, *J* = 5.5 Hz, 2H), 3.92 (dd, *J* = 10.1, 10.3 Hz, 1H), 3.72 (dd, *J* = 4.4, 10.3 Hz, 1H), 3.46 (s, 1H), 2.28 (dd, *J* = 10.5, 14.2 Hz, 1H), 2.14-2.03 (m, 1H), 1.93 (ddd, *J* = 3.7, 4.4, 10.1 Hz, 1H), 1.61 (dd, *J* = 8.7, 14.2 Hz, 1H), 1.12 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.6 (C), 137.8 (CH), 135.0 (CH), 128.5 (CH), 127.9 (CH), 127.8 (CH), 123.9 (CH), 116.9 (CH_2), 84.7 (CH), 81.2 (C), 74.6 (CH_2), 70.9 (CH_2), 70.4 (CH_2), 58.3 (CH_2), 57.2 (CH), 49.6 (CH_2), 37.7 (CH), 26.1 (CH_3), 18.3 (C), 15.6 (CH_3), −5.2 (CH_3), −5.2 (CH_3)

IR (film, cm^{-1}): 3520, 2953, 2928, 2882, 2856, 1254, 1088, 837, 776

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{26}H_{42}NaO_4Si$ 469.2745; Found 469.2745



22 **S6**

A suspension of NaH (55%, 153 mg, 3.50 mmol, 1.5 equiv) in THF (10 mL) was added a solution of diene **22** (1.04 g, 2.33 mmol) in THF (2 mL) at 0 °C. After stirring for 10 min at 0 °C, methyl iodide (0.290 mL, 4.66 mmol, 2 equiv) was added and the resulting mixture was heated at 50 °C for 2 h. The reaction was quenched with saturated NH_4Cl aq at 0 °C. The resulting mixture was extracted with Et_2O twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (1:9 EtOAc/hexane) to afford ether **S6** (1.02 g, 2.21 mmol, 95%) as a pale-yellow oil.

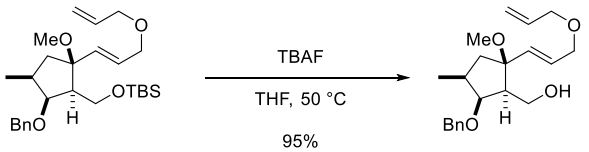
$[\alpha]_D^{26}$: −7.21° (*c* 2.17, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39-7.22 (m, 5H), 5.92 (tdd, *J* = 5.7, 10.5, 17.4 Hz, 1H), 5.77 (d, *J* = 15.8 Hz, 1H), 5.65 (td, *J* = 5.7, 15.8 Hz, 1H), 5.28 (tdd, *J* = 1.4, 1.6, 17.4 Hz, 1H), 5.19 (tdd, *J* = 1.4, 1.6, 10.5 Hz, 1H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 4.0 (dd, *J* = 0.9, 5.7 Hz, 2H), 3.98 (ddd, *J* = 1.4, 1.4, 5.7 Hz, 2H), 3.88 (dd, *J* = 9.4, 10.1 Hz, 1H), 3.82 (dd, *J* = 4.1, 4.1 Hz, 1H), 3.79 (dd, *J* = 5.0, 10.1 Hz, 1H), 3.08 (s, 3H), 2.01 (dd, *J* = 4.6, 5.5 Hz, 1H), 1.99 (ddd, *J* = 5.0, 9.4, 9.6 Hz, 1H), 1.93-1.82 (m, 2H), 1.02 (d, 3H), 0.89 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.8 (C), 138.1 (CH), 134.9 (CH), 128.2 (CH), 128.0 (CH), 127.3 (CH), 124.1 (CH), 117.2 (CH_2), 84.8 (C), 83.1 (CH), 73.9 (CH_2), 71.1 (CH_2), 70.6 (CH_2), 59.2 (CH), 58.5 (CH_2), 51.2 (CH_3), 41.0 (CH_2), 38.0 (CH), 26.1 (CH_3), 18.3 (C), 14.7 (CH_3), −5.2 (CH_3), −5.2 (CH_3)

IR (film, cm^{-1}): 2954, 2929, 2882, 2855, 1254, 1082, 837, 774

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{27}H_{44}NaO_4Si$ 483.2901; Found 483.2889



S6 **23**

To a solution of ether **S6** (981 mg, 2.13 mmol) in THF (21 mL) at 0 °C was added tetrabutylammonium fluoride (1.0 M in THF, 3.20 mL, 3.20 mmol, 1.5 equiv). The resulting mixture was warmed to 50 °C with stirring for 2 h. After cooling to 0 °C, the reaction was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with Et_2O twice and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:3 EtOAc/hexane) to afford alcohol **23** (705 mg, 2.03 mmol, 95%) as a colorless oil.

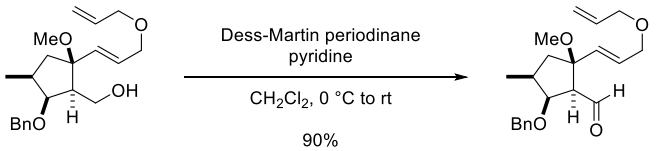
$[\alpha]_D^{25}$: +1.79° (*c* 1.97, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.25 (m, 5H), 5.91 (ddt, *J* = 5.5, 10.5, 17.4 Hz, 1H), 5.72 (d, *J* = 16.0 Hz, 1H), 5.66 (dd, *J* = 5.2, 16.0 Hz, 1H), 5.27 (dtd, *J* = 1.4, 1.8, 17.4 Hz, 1H), 5.19 (dtd, *J* = 1.4, 1.8, 10.5 Hz, 1H), 4.57 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.01 (d, *J* = 5.24 Hz, 2H), 3.99-3.94 (m, 1H), 3.97 (ddd, *J* = 1.4, 1.4, 5.5 Hz, 2H), 3.82 (dd, *J* = 5.5, 5.7 Hz, 1H), 3.80-3.70 (m, 1H), 3.14 (s, 3H), 2.64-2.50 (s, 1H), 2.25 (ddd, *J* = 5.7, 6.0, 8.2 Hz, 1H), 2.10 (dd, *J* = 7.3, 11.4 Hz, 1H), 2.14-2.01 (m, 1H), 1.83 (dd, *J* = 10.5, 11.4 Hz, 1H), 1.09 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.8 (C), 137.2 (CH), 134.7 (CH), 128.5 (CH), 127.9 (CH), 127.7 (CH), 125.8 (CH), 117.3 (CH_2), 85.2 (C), 81.9 (CH), 73.6 (CH_2), 71.3 (CH_2), 70.4 (CH_2), 60.3 (CH_2), 56.1 (CH), 51.4 (CH_3), 39.7 (CH_2), 36.7 (CH), 15.3 (CH_3)

IR (film, cm^{-1}): 3464, 2932, 2900, 2873, 1454, 1352, 1075, 735, 698

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{21}H_{30}NaO_4$ 369.2036; Found 369.2031



23 **24**

To a solution of alcohol **23** (511 mg, 1.47 mmol) in CH_2Cl_2 (14.7 mL) at 0 ºC were sequentially added pyridine (0.355 mL, 4.41 mmol, 3 equiv) and Dess-Martin periodinane (937 mg, 2.21 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 2 h and purified by neutral silica gel column chromatography (1:7 EtOAc/hexane) to afford aldehyde **24** (458 mg, 1.33 mmol, 90%) as a colorless oil.

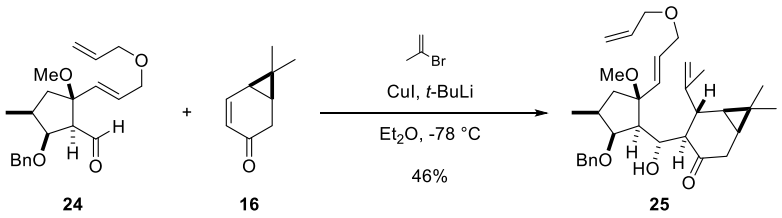
$[\alpha]_D^{25}$: +13.9º (*c* 2.74, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.84 (d, *J* = 5.0 Hz, 1H), 7.40-7.24 (m, 5H), 5.91 (tdd, *J* = 6.0, 10.3, 17.2 Hz, 1H), 5.71 (dd, *J* = 4.1, 15.8 Hz, 1H), 5.66 (d, *J* = 15.8 Hz, 1H), 5.30 (tdd, *J* = 1.1, 1.4, 17.2 Hz, 1H), 5.20 (tdd, *J* = 1.4, 1.4, 10.3 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.43 (d, *J* = 11.7 Hz, 1H), 4.04 (dd, *J* = 6.0, 6.2 Hz, 1H), 4.02 (d, *J* = 4.12 Hz, 2H), 3.97 (ddd, *J* = 1.1, 1.4, 6.0 Hz, 2H), 3.12 (s, 3H), 2.87 (dd, *J* = 5.0, 6.2 Hz, 1H), 2.27-2.10 (m, 3H), 1.15 (d, *J* = 6.4 Hz, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 202.4 (CH), 138.1 (C), 135.0 (CH), 134.6 (CH), 128.4 (CH), 127.8 (CH), 127.7 (CH), 127.7 (CH), 117.3 (CH_2), 85.5 (C), 82.3 (CH), 73.2 (CH_2), 71.4 (CH_2), 70.0 (CH_2), 63.8 (CH), 51.7 (CH_3), 41.5 (CH_2), 36.7 (CH), 14.7 (CH_3)

IR (film, cm^{-1}): 2959, 2934, 2905, 2871, 1715, 1454, 1072, 980, 738, 699

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{21}H_{28}NaO_4$ 367.1880; Found 367.1886



To a solution of 2-bromopropene (1.31 mL, 15.0 mmol, 8.5 equiv) in Et_2O (44 mL) was added *t*-BuLi (1.39 M in pentane, 21.5 mL, 29.9 mmol, 17 equiv) dropwise at –78 °C over 5 min. After stirring the light-yellow mixture at –78 °C for 30 min, the mixture was warmed to room temperature and stirred for another 20 min. The resulting mixture was transferred into a flask containing CuI (1.41 g, 7.39 mmol, 4.2 equiv) via a cannula and the resulting mixture was stirred for 15 min at room temperature. The suspension was cooled to –78 °C, and stirred for 5 min. To the mixture was added a solution of enone **16** (959 mg, 7.04 mmol, 4 equiv) in Et_2O (18 mL) dropwise. The yellow reaction mixture was stirred at –78 °C for 1 h, and then a solution of aldehyde **24** (605 mg, 1.76 mmol) in Et_2O (18 mL) was added dropwise over 5 min. The reaction mixture was stirred at –78 °C for 20 min to produce a bright orange suspension, which was quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with Et_2O three times and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (1:4 EtOAc/hexane) to afford triene **25** (425 mg, 0.813 mmol, 46%) as a pale-yellow oil.

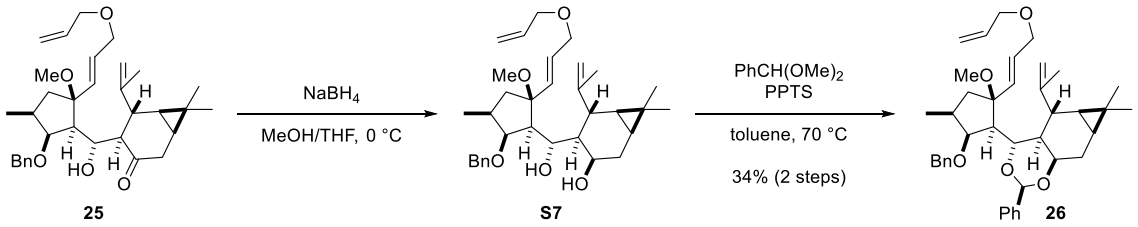
$[\alpha]_D^{26}$: +64.1° (*c* 2.63, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (d, *J* = 6.9 Hz, 2H), 7.30 (dd, *J* = 6.9, 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 5.91 (tdd, *J* = 5.7, 10.3, 17.2 Hz, 1H), 5.57-5.55 (m, 2H), 5.28 (dtd, *J* = 1.4, 1.6, 17.2 Hz, 1H), 7.35 (dd, *J* = 1.4, 10.3 Hz, 1H), 4.92 (d, *J* = 1.8 Hz, 1H), 4.80 (s, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.58 (d, *J* = 11.5 Hz, 1H), 4.02 (dd, *J* = 10.5, 10.8 Hz, 1H), 3.96 (dd, *J* = 1.6, 5.7 Hz, 2H), 3.94-3.89 (m, 3H), 3.12 (s, 3H), 2.99 (d, *J* = 12.4 Hz, 1H), 2.94 (d, *J* = 10.8 Hz, 1H), 2.84 (dd, *J* = 8.7, 16.5 Hz, 1H), 2.42 (dd, *J* = 4.1, 10.5 Hz, 1H), 2.29 (d, *J* = 16.5 Hz, 1H), 2.05-1.98 (m, 1H), 1.87 (s, 3H), 1.85-1.79 (m, 2H), 1.11 (dd, *J* = 8.7, 8.9 Hz, 1H), 1.04 (s, 3H), 1.03 (d, *J* = 8.2 Hz, 3H), 0.90 (s, 3H), 0.85 (dd, *J* = 4.6, 8.9 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 221.1 (C), 146.4 (C), 140.0 (C), 138.7 (CH), 134.8 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 122.9 (CH), 117.2 (CH_2), 113.2 (CH_2), 84.8 (CH), 84.4 (C), 74.4 (CH_2), 71.4 (CH_2), 70.6 (CH_2), 66.5 (CH), 58.9 (CH), 50.9 (CH_3), 50.5 (CH), 46.2 (CH), 42.5 (CH_2), 39.4 (CH_2), 37.7 (CH), 28.6 (CH_3), 25.7 (CH), 24.3 (CH), 20.2 (C), 17.8 (CH_3), 15.3 (CH_3), 14.4 (CH_3)

IR (film, cm^{-1}): 3528, 2929, 2871, 1692, 1083, 740, 698

HRMS (ESI): *m/z* $[M+Na]^+$ Calcd for $C_{33}H_{46}NaO_5$ 545.3237; Found 545.3239



To a solution of ketone **25** (111 mg, 0.212 mmol) in MeOH (1.1 mL) and THF (2.1 mL) at 0 °C were added $NaBH_4$ (160 mg, 4.24 mmol, 20 equiv). The resulting mixture was stirred at room temperature for 1 h and quenched with saturated aqueous NH_4Cl solution. The resulting mixture was extracted with Et_2O three times and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue containing diol **S7** was dissolved in toluene (2.2 mL), and to this solution were added $PhCH(OMe)_2$ (63.3 μL, 0.424 mmol, 2 equiv) and pyridinium *p*-toluenesulfonate (10.7 mg, 42.2 μmol, 20 mol%) at room temperature. After stirring for 2.5 h at 70 °C, the residue was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (1:5 EtOAc/hexane) to afford acetal **26** (44.2 mg, 72.1 μmol, 34%) as a colorless oil.

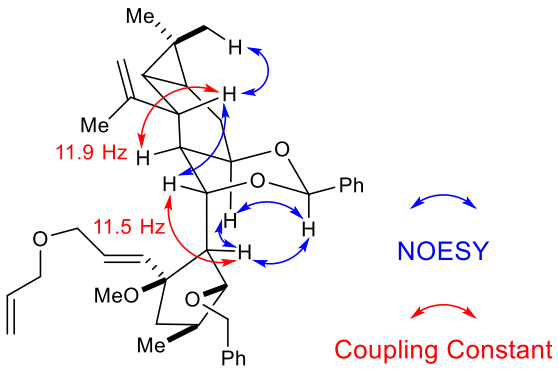
$[\alpha]_D^{26}$: −8.59° (*c* 0.470, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45-7.40 (m, 2H), 7.35-7.28 (m, 3H), 7.25-7.19 (m, 5H), 5.95 (tdd, *J* = 5.5, 10.5, 17.2 Hz, 1H), 5.78 (d, *J* = 16.0 Hz, 1H), 5.74 (s, 1H), 5.68 (td, *J* = 5.0, 16.0 Hz, 1H), 5.31 (dtd, *J* = 1.4, 1.8, 17.2 Hz, 1H), 5.22 (dtd, *J* = 1.4, 1.4, 10.5 Hz, 1H), 4.97 (d, *J* = 2.3 Hz, 1H), 4.85 (dd, *J* = 1.4, 2.3 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.25 (dd, *J* = 1.4, 8.5 Hz, 1H), 4.05-3.99 (m, 4H), 3.73 (dd, *J* = 3.2, 3.9 Hz, 1H), 3.10 (s, 3H), 2.91 (dd, *J* = 3.9, 11.5 Hz, 1H), 2.73 (dd, *J* = 6.4, 11.9 Hz, 1H), 2.22 (ddd, *J* = 8.5, 9.2, 16.7 Hz, 1H), 2.08-1.87 (m, 3H), 1.85 (s, 3H), 1.72 (dd, *J* = 1.4, 11.9 Hz, 1H), 1.71 (d, *J* = 16.7 Hz, 1H), 1.13 (s, 3H), 1.03 (s, 3H), 1.02 (d, *J* = 6.4 Hz, 3H), 0.78 (dd, *J* = 6.4, 9.6 Hz, 1H), 0.47 (ddd, *J* = 0.9, 9.2, 9.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1 (C), 140.0 (C), 139.6 (C), 138.9 (CH), 134.8 (CH), 128.7 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 127.3 (CH), 126.5 (CH), 124.0 (CH), 117.3 (CH_2), 113.0 (CH_2), 95.1 (CH), 84.8 (C), 84.8 (CH), 74.4 (CH_2), 71.5 (CH_2), 71.1 (CH), 70.5 (CH_2), 70.3 (CH), 53.2 (CH), 50.8 (CH_3), 42.7 (CH_2), 38.3 (CH), 37.4 (CH), 34.7 (CH), 29.4 (CH_3), 27.1 (CH), 25.7 (CH_2), 18.5 (CH_3), 17.8 (CH), 17.7 (C), 15.5 (CH_3), 14.4 (CH_3)

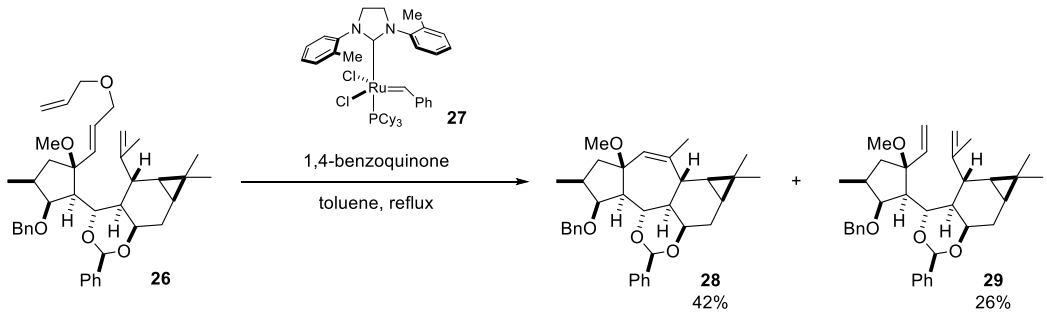
IR (film, cm^{-1}): 2924, 2868, 1089, 1065, 697

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{40}H_{52}NaO_5$ 635.3707; Found 635.3707



26

Selected NOESY correlations and coupling constants of **26**



To a solution of acetal **26** (4.0 mg, 6.5 μmol) and 1,4-benzoquinone (0.70 mg, 6.5 μmol, 1 equiv) in toluene (6 mL) at 110 ºC was added a solution of [1,3-bis(2-methylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium(II) (**27**, 1.0 mg, 1.3 μmol, 20 mol%) in toluene (0.5 mL). The reaction mixture was stirred at same temperature for 15 min. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (1:5 EtOAc/hexane) to afford compound **28** (1.4 mg, 2.7 μmol, 42%) as a colorless oil and diene **29** (0.90 mg, 1.7 μmol, 26%) as a colorless oil.

Compound 28

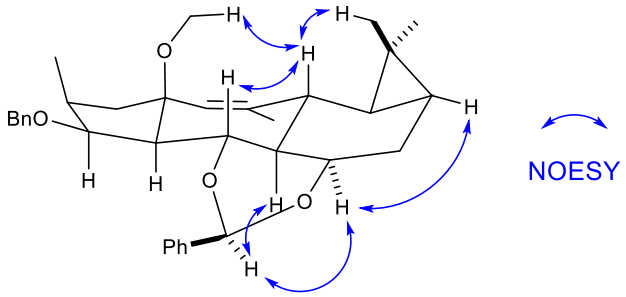
$[\alpha]_D^{26}$: +47.2º (*c* 0.595, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.49-7.42 (m, 2H), 7.32-7.12 (m, 8H), 5.82 (s, 1H), 5.49 (s, 1H), 4.79 (dd, *J* = 10.5, 10.6 Hz, 1H), 4.57 (d, *J* = 12.6 Hz, 1H), 4.40 (d, *J* = 12.6 Hz, 1H), 4.2 (ddd, *J* = 4.6, 9.1, 12.8 Hz, 1H), 3.91 (dd, *J* = 4.1, 4.6 Hz, 1H), 3.05 (s, 3H), 2.84 (dd, *J* = 9.6, 10.1 Hz, 1H), 2.09-1.76 (m, 5H), 1.85 (s, 3H), 1.25 (s, 1H), 1.32-1.16 (m, 1H), 1.08 (s, 3H), 1.06 (s, 3H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.72 (dd, *J* = 9.6, 19.0 Hz, 1H), 0.68 (ddd, *J* = 6.9, 9.2, 19.0 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.7 (C), 140.4 (C), 131.4 (CH), 128.7 (CH), 128.3 (CH), 127.9 (CH), 127.7 (CH), 126.8 (CH), 126.5 (CH), 97.6 (CH), 84.2 (C), 82.9 (CH), 76.5 (CH), 73.4 (CH_2), 68.6 (CH), 59.0 (CH), 50.0 (CH_3), 45.6 (CH_2), 42.9 (CH), 37.5 (CH), 31.4 (CH), 28.4 (CH_3), 23.4 (CH_3), 23.3 (CH_2), 21.2 (CH), 21.0 (CH), 18.3 (C), 15.8 (CH_3), 15.1 (CH_3), One quarterly carbon of a phenyl group was not observed perhaps due to overlapping.

IR (film, cm^{-1}): 2927, 2877, 1455, 1155, 1127, 1111, 1075, 1062, 1027, 698

HRMS (ESI): *m/z* $[M+Na]^+$ Calcd for $C_{34}H_{42}NaO_4$ 537.2975; Found 537.2981



28

Selected NOESY correlations of **28**

Diene 29

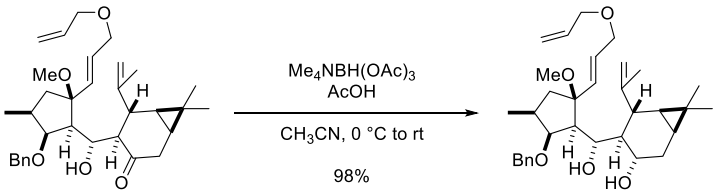
$[\alpha]_D^{26}$: –8.14° (*c* 0.530, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 (dd, *J* = 1.8, 7.6 Hz, 2H), 7.35-7.28 (m, 3H), 7.27-7.17 (m, 5H), 5.90 (dd, *J* = 11.0, 17.6 Hz, 1H), 5.74 (s, 1H), 5.14 (dd, *J* = 0.9, 17.6 Hz, 1H), 5.09 (d, *J* = 0.9, 11.0 Hz, 1H), 4.98 (d, *J* = 2.5 Hz, 1H), 4.85 (dd, *J* = 1.4, 2.5 Hz, 1H), 4.69 (d, *J* = 11.4 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 4.39 (d, *J* = 10.8 Hz, 1H), 4.27 (dd, *J* = 1.4, 8.2 Hz, 1H), 3.74 (dd, *J* = 3.6, 3.9 Hz, 1H), 3.09 (s, 3H), 2.90 (dd, *J* = 3.9, 11.4 Hz, 1H), 2.73 (dd, *J* = 6.2, 11.3 Hz, 1H), 2.23 (ddd, *J* = 8.2, 9.6, 16.7 Hz, 1H), 2.06-1.95 (m, 2H), 1.94-1.88 (m, 1H), 1.85 (s, 3H), 1.72 (d, *J* = 16.7 Hz, 1H), 1.71 (dd, *J* = 1.4, 11.3 Hz, 1H), 1.14 (s, 3H), 1.034 (d, *J* = 5.0 Hz, 3H), 1.027 (s, 3H), 0.78 (dd, *J* = 6.2, 9.6 Hz, 1H), 0.47 (ddd, *J* = 1.4, 9.6, 9.6 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1 (C), 144.3 (CH), 140.0 (C), 139.6 (C), 128.7 (CH), 128.6 (CH), 128.2 (CH), 128.0 (CH), 127.2 (CH), 126.5 (CH), 113.0 (CH_2), 111.8 (CH_2), 95.2 (CH), 85.3 (C), 83.4 (CH), 74.4 (CH_2), 71.1 (CH), 70.3 (CH), 53.1 (CH), 50.7 (CH_3), 42.2 (CH_2), 38.3 (CH), 37.4 (CH), 34.7 (CH), 29.4 (CH_3), 27.1 (CH), 25.7 (CH_2), 18.5 (CH_3), 17.7 (CH), 15.5 (CH_3), 14.4 (CH_3), One quaternary carbon of cyclopropane ring was not observed perhaps due to overlapping.

IR (film, cm^{-1}): 2924, 2871, 1455, 1090, 1064, 697

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{36}H_{46}NaO_4$ 565.3288; Found 565.3299



25 **30**

To a suspension of $Me_4NBH(OAc)_3$ (1.16 g, 4.41 mmol, 10 equiv) and AcOH (0.635 mL, 11.1 mmol, 25 equiv) in CH_3CN (4 mL) was added a solution of ketone **25** (231 mg, 0.442 mmol) in CH_3CN (4 mL) at 0 ºC. After stirring for 5 min, the mixture was warmed to room temperature and stirred for 6 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with Et_2O three times and the combined organic layer was washed with brine, dried over anhydrous sodium sulphate and concentrated under reduced pressure. The residue was purified by column chromatography (1:5 to 1:3 EtOAc/hexane) to afford diol **30** (227 mg, 0.433 mmol, 98%) as a colorless oil.

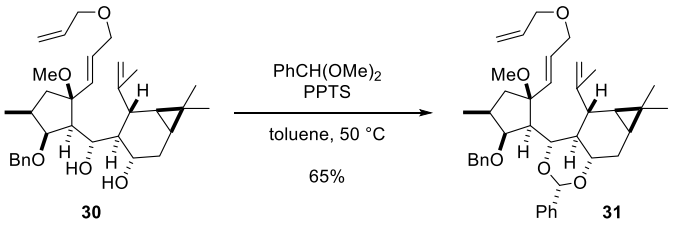
$[\alpha]_D^{26}$: +37.4º (*c* 1.82, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38-7.23 (m, 5H), 5.99 (d, *J* = 16.0 Hz, 1H), 5.92 (tdd, *J* = 6.0, 10.3, 17.2 Hz, 1H), 5.67 (td, *J* = 6.0, 16.0 Hz, 1H), 5.28 (tdd, *J* = 1.4, 1.8, 17.2 Hz, 1H), 5.19 (tdd, *J* = 1.4, 1.8, 10.3 Hz, 1H), 4.79 (d, *J* = 12.1 Hz, 1H), 4.78 (d, *J* = 2.1 Hz, 1H), 4.75 (d, *J* = 2.1 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.12-4.07 (m, 1H), 4.04-3.96 (m, 1H), 3.99 (d, *J* = 6.0 Hz, 2H), 3.98 (d, *J* = 6.0 Hz, 2H), 3.92 (dd, *J* = 3.7, 4.4 Hz, 1H), 3.13 (s, 3H), 2.23 (br s, 1H), 2.18 (dd, *J* = 4.4, 8.7 Hz, 1H), 2.05-1.91 (m, 3H), 1.86-1.69 (m, 4H), 1.77 (s, 3H), 1.27-1.17 (m, 1H), 1.16 (d, *J* = 6.0 Hz, 3H), 1.02 (s, 3H), 0.99 (s, 3H), 0.72 (ddd, *J* = 7.3, 7.3, 8.2 Hz, 1H), 0.60 (dd, *J* = 7.3, 9.2 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.4 (C), 139.9 (CH), 139.3 (C), 134.8 (CH), 128.7 (CH), 127.8 (CH), 127.6 (CH), 124.0 (CH), 117.3 (CH_2), 111.7 (CH_2), 85.0 (CH), 84.8 (C), 74.0 (CH_2), 71.6 (CH_2), 70.4 (CH_2), 68.5 (CH), 68.4 (CH), 59.1 (CH), 51.0 (CH_3), 45.9 (CH), 41.9 (CH_2), 41.8 (CH), 38.3 (CH), 29.0 (CH_3), 28.3 (CH_2), 25.6 (CH), 19.0 (CH_3), 18.5 (CH), 18.0 (C), 15.2 (CH_3), 15.1 (CH_3)

IR (film, cm^{-1}): 3595, 3474, 2932, 2871, 1454, 1146, 1077, 736, 698

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{33}H_{48}NaO_5$ 547.3394; Found 547.3403



To a solution of diol **30** (102 mg, 0.194 mmol) in toluene (3.2 mL) were added $PhCH(OMe)_2$ (0.107 mL, 0.388 mmol, 2 equiv) and pyridinium *p*-toluenesulfonate (9.75 mg, 38.8 μmol, 20 mol%) at room temperature. After stirring for 1.5 h at 50 °C, the reaction mixture was concentrated under reduced pressure. The residue was purified by column chromatography (1:15 EtOAc/hexane) to afford acetal **31** (78.1 mg, 0.127 mmol, 65%) as a colorless oil.

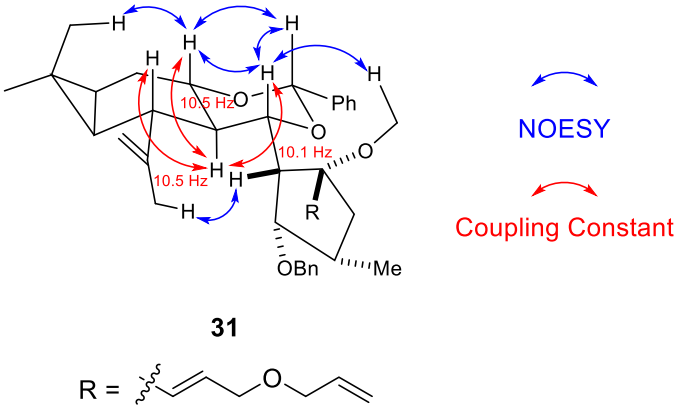
$[\alpha]_D^{26}$: +44.5° (*c* 1.06, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, *J* = 7.3 Hz, 1H), 7.51 (d, *J* = 6.0 Hz, 1H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.33 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.28-7.22 (m, 4H), 5.95 (tdd, *J* = 5.5, 10.3, 17.1 Hz, 1H), 5.67 (td, *J* = 5.5, 17.2 Hz, 1H), 5.52 (d, *J* = 17.2 Hz, 1H), 5.50 (s, 1H), 5.31 (tdd, *J* = 1.4, 1.6, 17.1 Hz, 1H), 5.22 (tdd, *J* = 1.4, 1.6, 10.3 Hz, 1H), 4.81 (br s, 1H), 4.67 (br s, 1H), 4.55 (s, 2H), 4.04 (dd, *J* = 0.9, 5.5 Hz, 2H), 4.00 (ddd, *J* = 1.4, 1.4, 5.5 Hz, 2H), 4.10-3.99 (m, 1H), 3.97 (d, *J* = 10.1 Hz, 1H), 3.44 (ddd, *J* = 6.4, 6.4, 10.5 Hz, 1H), 3.14 (s, 3H), 2.83 (br s, 1H), 2.24 (ddd, *J* = 10.1, 10.5, 10.5 Hz, 1H), 2.13 (dd, *J* = 6.4, 14.2 Hz, 1H), 2.04 (br s, 1H), 1.92-1.82 (m, 4H), 1.79 (s, 3H), 1.06 (s, 3H), 0.98 (s, 3H), 0.79 (d, *J* = 6.8 Hz, 3H), 0.71 (dd, *J* = 8.2, 8.9 Hz, 1H), 0.42 (dd, *J* = 3.6, 8.9 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 150.3 (C), 139.6 (C), 139.3 (C), 138.0 (CH), 134.9 (CH), 128.4 (CH), 128.1 (CH), 128.0 (CH), 127.0 (CH), 126.9 (CH), 126.2 (CH), 117.1 (CH_2), 112.2 (CH_2), 101.3 (CH), 82.9 (C), 81.6 (CH), 80.0 (CH), 79.0 (CH), 72.8 (CH_2), 71.0 (CH_2), 70.6 (CH_2), 51.9 (CH_3), 49.5 (CH), 44.5 (CH), 41.3 (CH_2), 39.5 (CH), 34.4 (CH), 30.0 (CH_3), 27.3 (CH_2), 26.8 (C), 20.4 (CH), 18.3 (CH_3), 17.8 (C), 16.4 (CH_3), 14.2 (CH_3), One CH peak of a phenyl group was not observed perhaps due to overlapping.

IR (film, cm^{-1}): 2932, 2896, 2864, 1454, 1359, 1115, 1095, 1029, 698

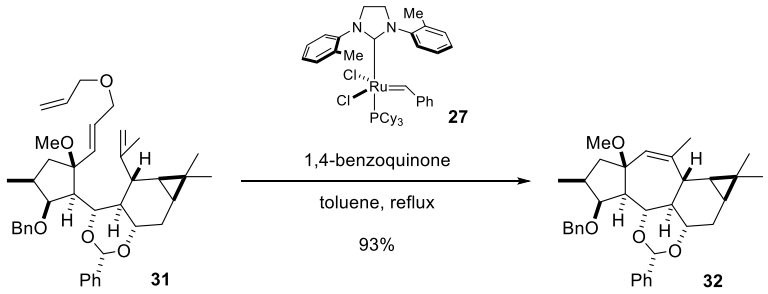
HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{40}H_{52}NaO_5$ 635.3707; Found 635.3723



31

R =

Selected NOESY correlations and coupling constants of **31**



To a solution of acetal **31** (10.0 mg, 16.3 μmol) and 1,4-benzoquinone (4.43 mg, 40.8 μmol, 2.5 equiv) in toluene (33 mL) at 110 ºC was added a solution of [1,3-Bis(2-methylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)-ruthenium(II) (**27**, 6.5 mg, 8.2 μmol, 50 mol%) in toluene (0.5 mL). The mixture was stirred at same temperature for 15 min. After cooling to room temperature, the mixture was concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography (1:5 EtOAc/hexane) to afford compound **32** (7.8 mg, 15.2 μmol, 93%) as a colorless oil.

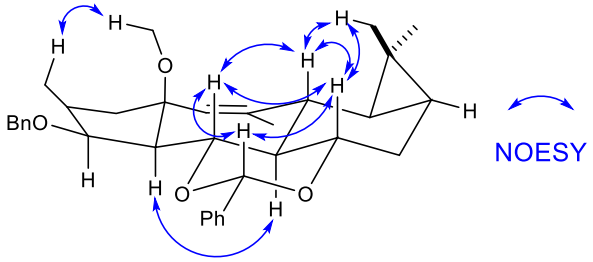
$[\alpha]_D^{26}$: +84.4º (*c* 0.105, $CHCl_3$)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55-7.15 (m, 10H), 5.62 (s, 1H), 5.49 (s, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.49 (d, *J* = 12.4 Hz, 1H), 4.49 (dd, *J* = 9.2, 10.8 Hz, 1H), 4.00 (dd, *J* = 4.8, 5.0 Hz, 1H), 3.77 (ddd, *J* = 6.2, 10.5, 11.0 Hz, 1H), 3.14 (s, 3H), 3.07 (d, *J* = 11.5 Hz, 1H), 2.16 (dd, *J* = 6.2, 13.7 Hz, 1H), 2.12-2.06 (m, 1H), 2.05 (dd, *J* = 4.8, 10.8 Hz, 1H), 2.00-1.90 (m, 1H), 1.93 (s, 3H),1.90-1.75 (m, 2H), 1.79 (dd, *J* = 10.1, 13.7 Hz, 1H), 1.29 (ddd, *J* = 9.2, 10.5, 11.5 Hz, 1H), 1.09 (s, 3H), 1.08 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.87-0.81 (m, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5 (C), 140.0 (C), 139.1 (C), 131.0 (CH), 128.7 (CH), 128.3 (CH), 128.1 (CH), 128.0 (CH), 127.1 (CH), 126.4 (CH), 101.3 (CH), 84.5 (C), 83.4 (CH), 79.9 (CH), 78.3 (CH), 74.2 (CH_2), 58.1 (CH), 50.3 (CH_3), 45.1 (CH), 44.9 (CH_2), 37.1 (CH), 30.9 (CH), 30.8 (CH_3), 26.5 (CH_2), 23.7 (CH_3), 21.5 (CH), 21.0 (CH), 17.2 (C), 16.7 (CH_3), 16.1 (CH_3)

IR (film, cm^{-1}): 2925, 2871, 1454, 1352, 1108, 734, 698

HRMS (ESI): *m*/*z* $[M+Na]^+$ Calcd for $C_{34}H_{42}NaO_4$ 537.2975; Found 537.2987



32

Selected NOESY correlations of **32**

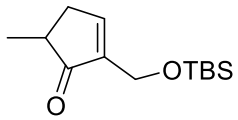
References for Supporting Information

1) S. Bonazzi, M. Binaghi, C. Fellay, J. Y. Wach, K. Gademann, *Synthesis*, 2010, 631.

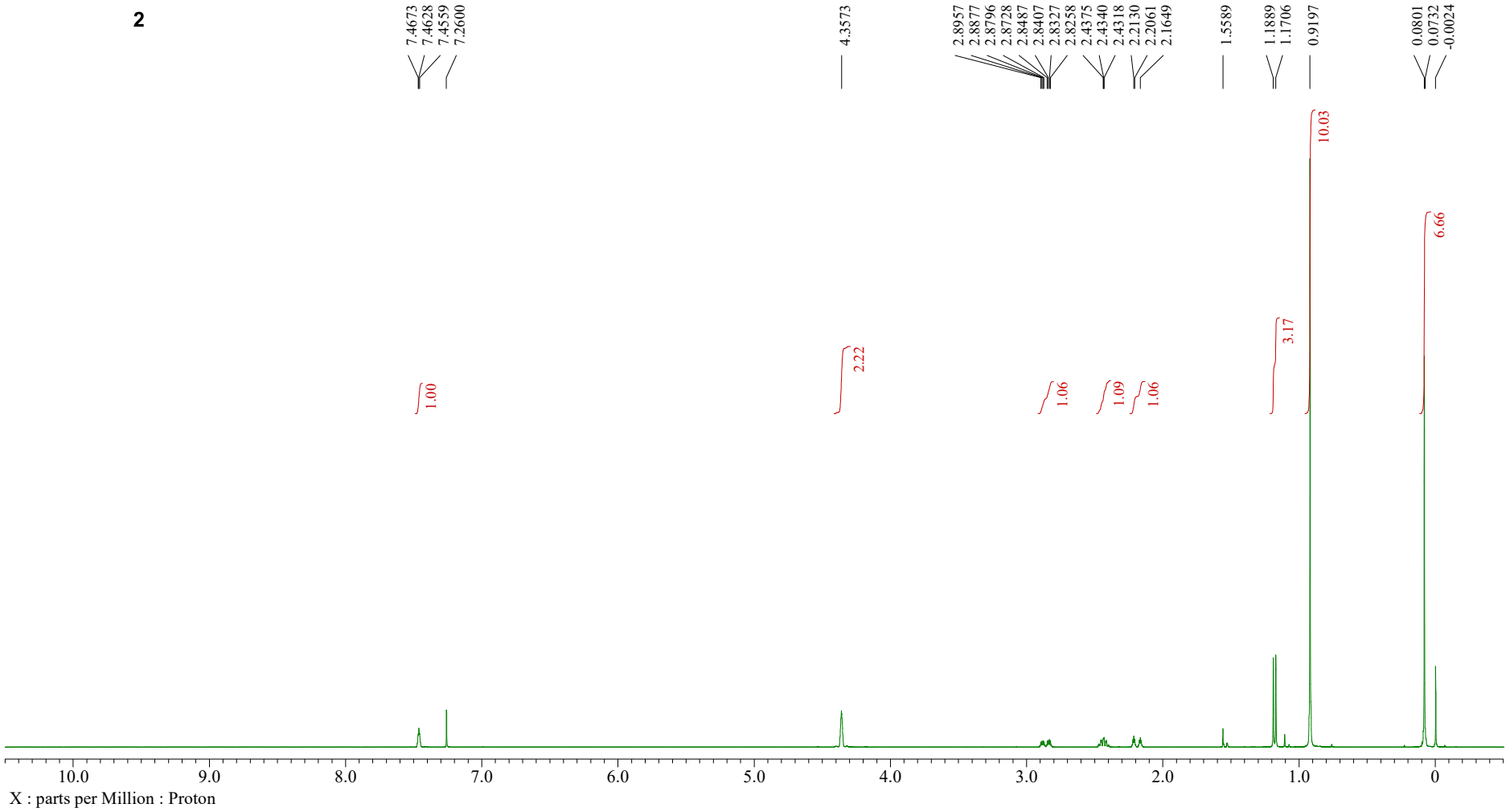
2) S. J. McKerrall, L. Jørgensen, C. A. Kuttruff, F. Ungeheuer and P. S. Baran, *J. Am. Chem. Soc.*, 2014, **136**, 5799.

3) A. A. Kejani, H. Khosravi, F. Rominger, S. Balalaie, B. Breit, *Org. Lett.*, 2021, **23**, 1291.

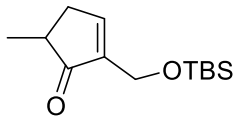
^{1}H NMR (400 MHz, $CDCl_3$)



2



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



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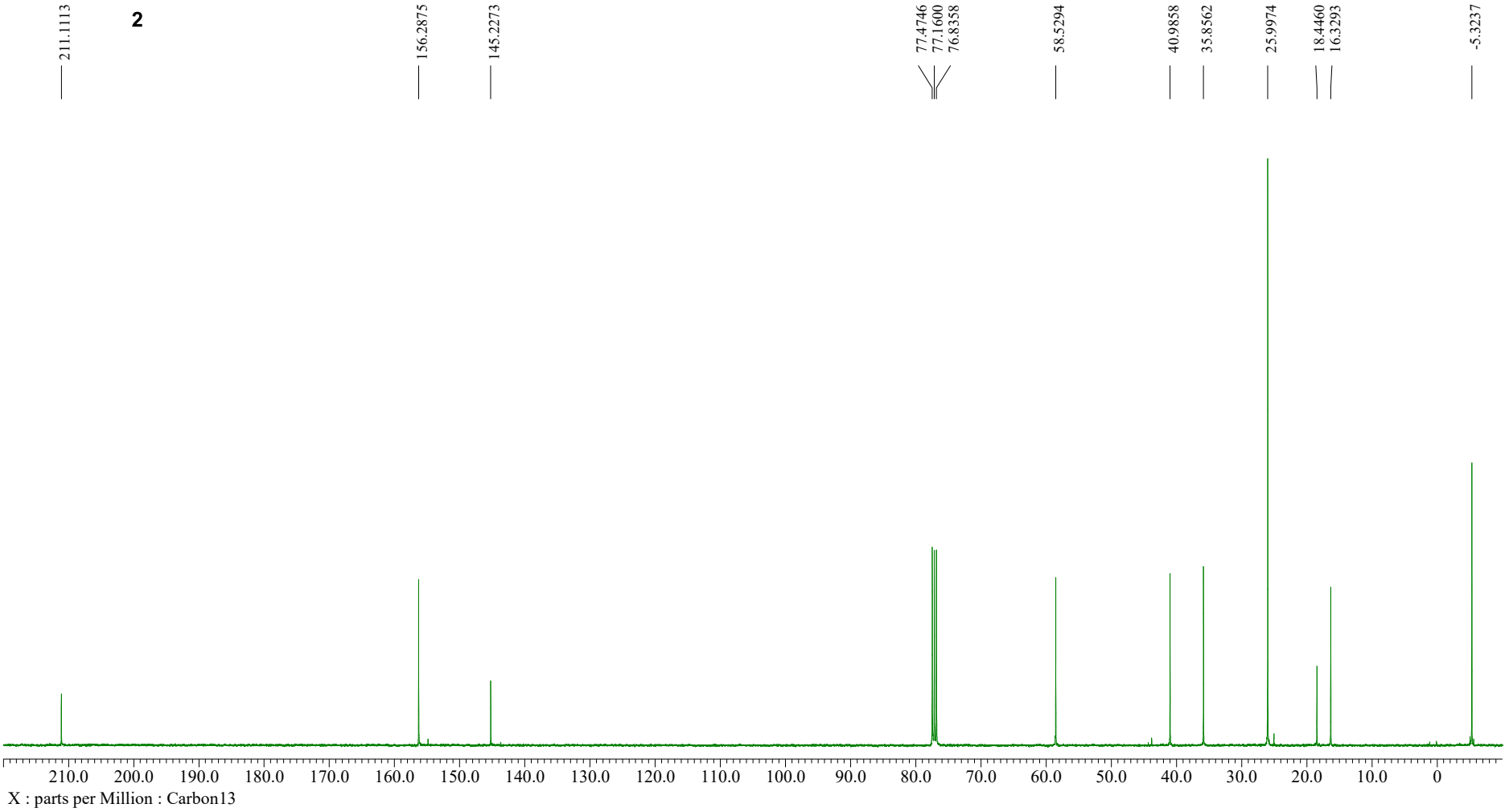
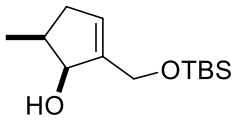
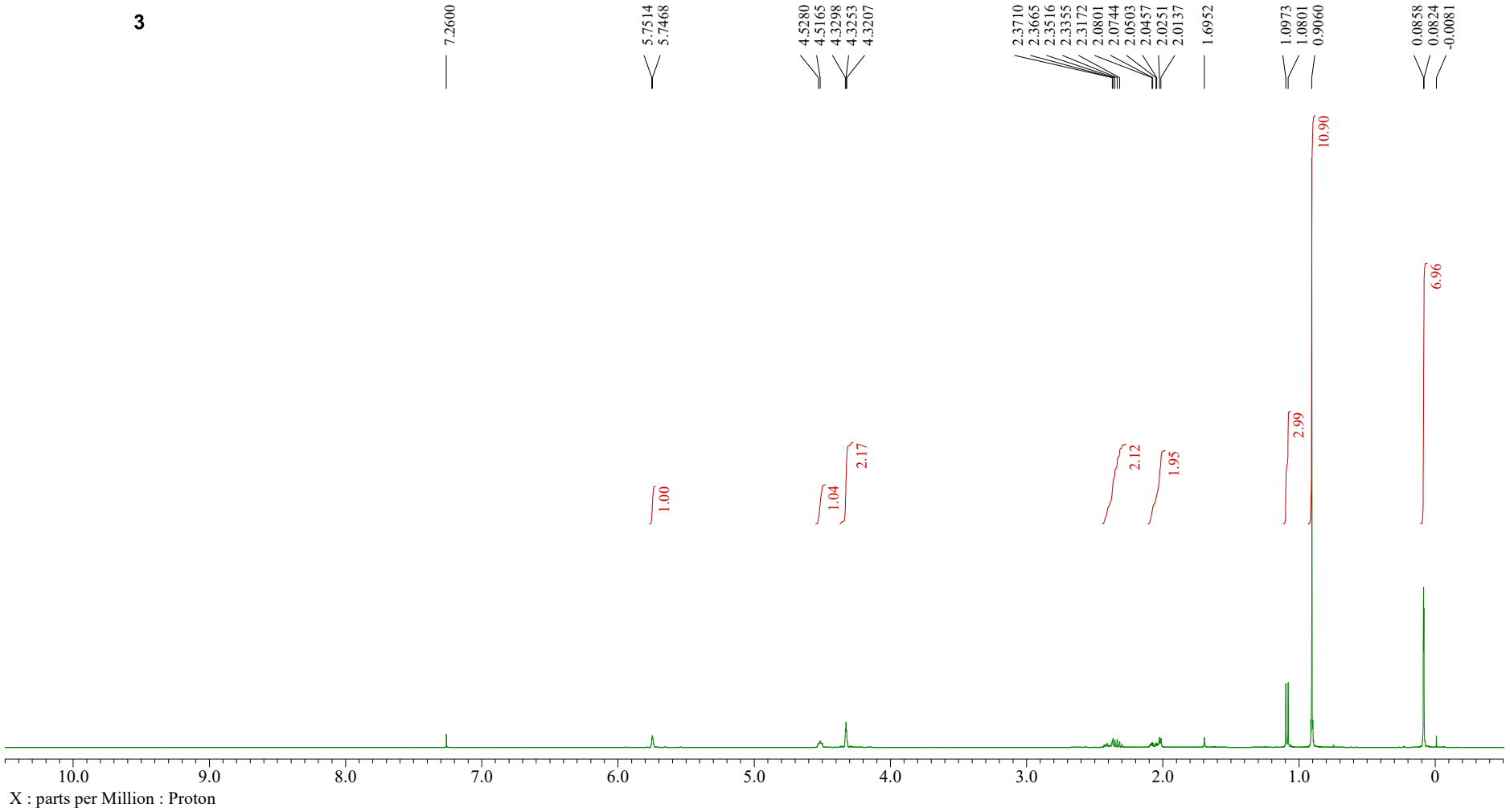


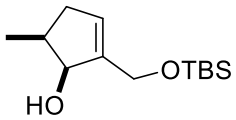
^{1}H NMR (400 MHz, $CDCl_3$)



3



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



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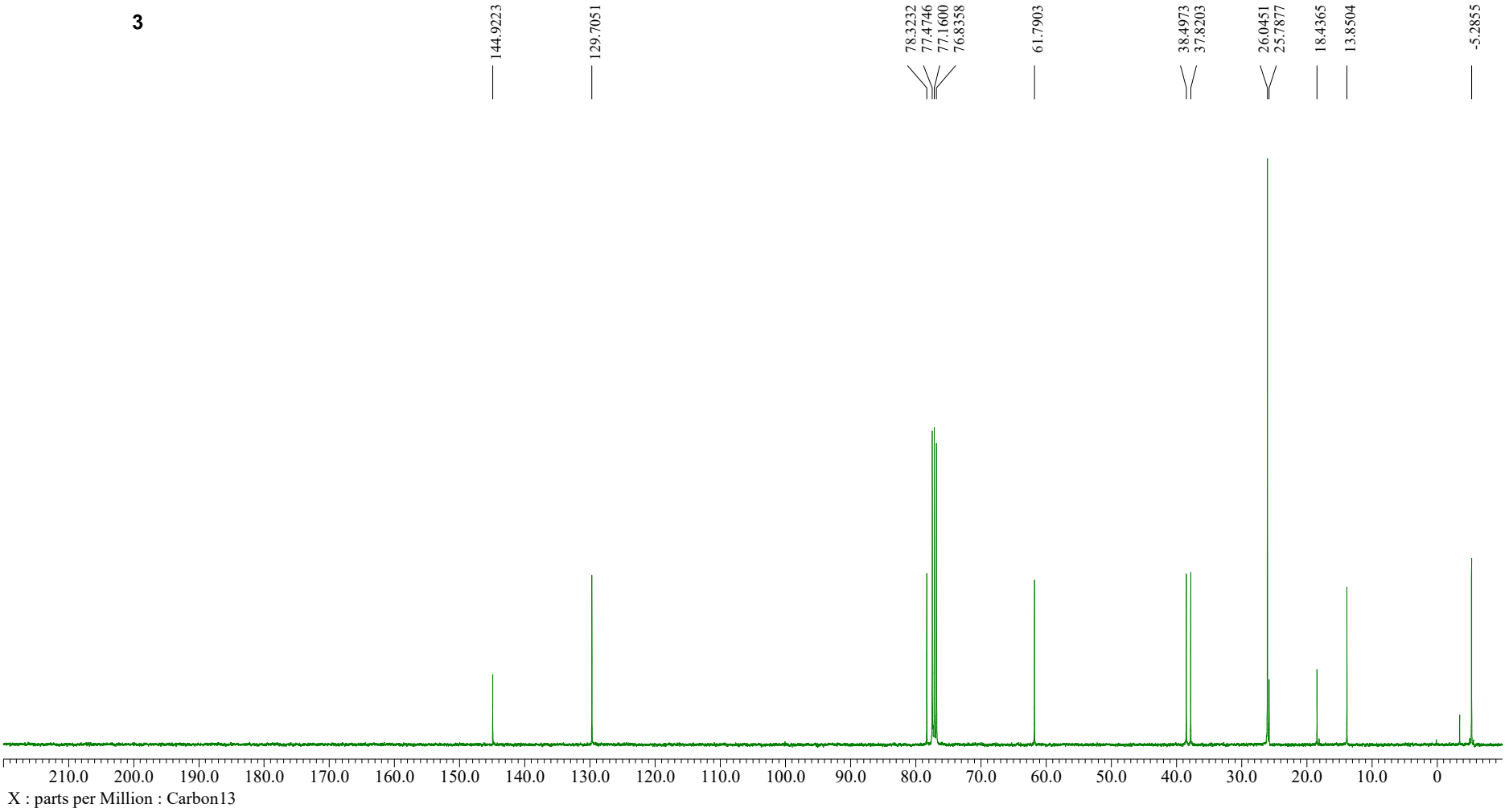
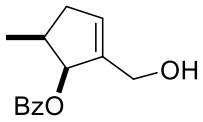
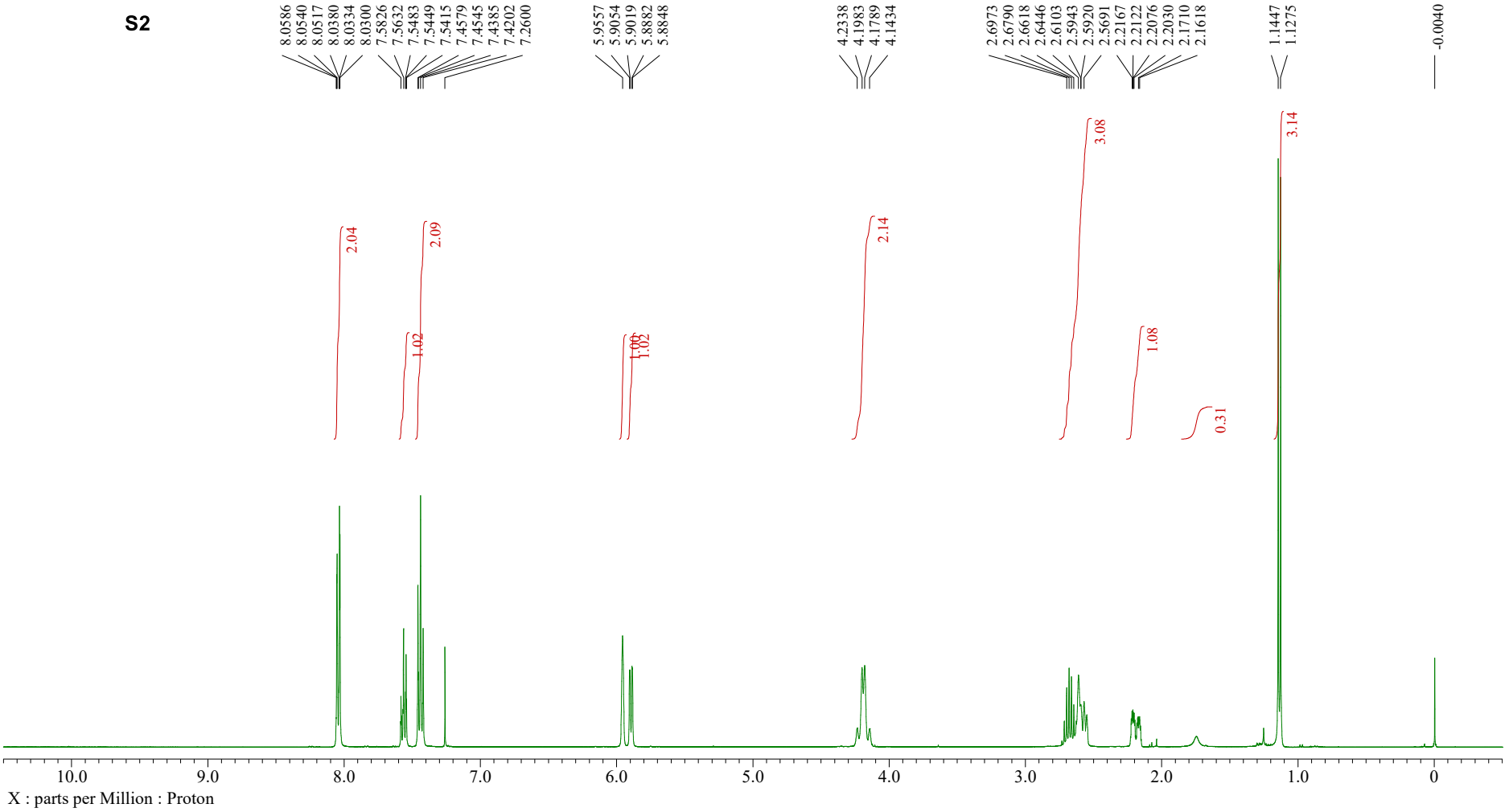


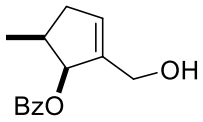
^{1}H NMR (400 MHz, $CDCl_3$)



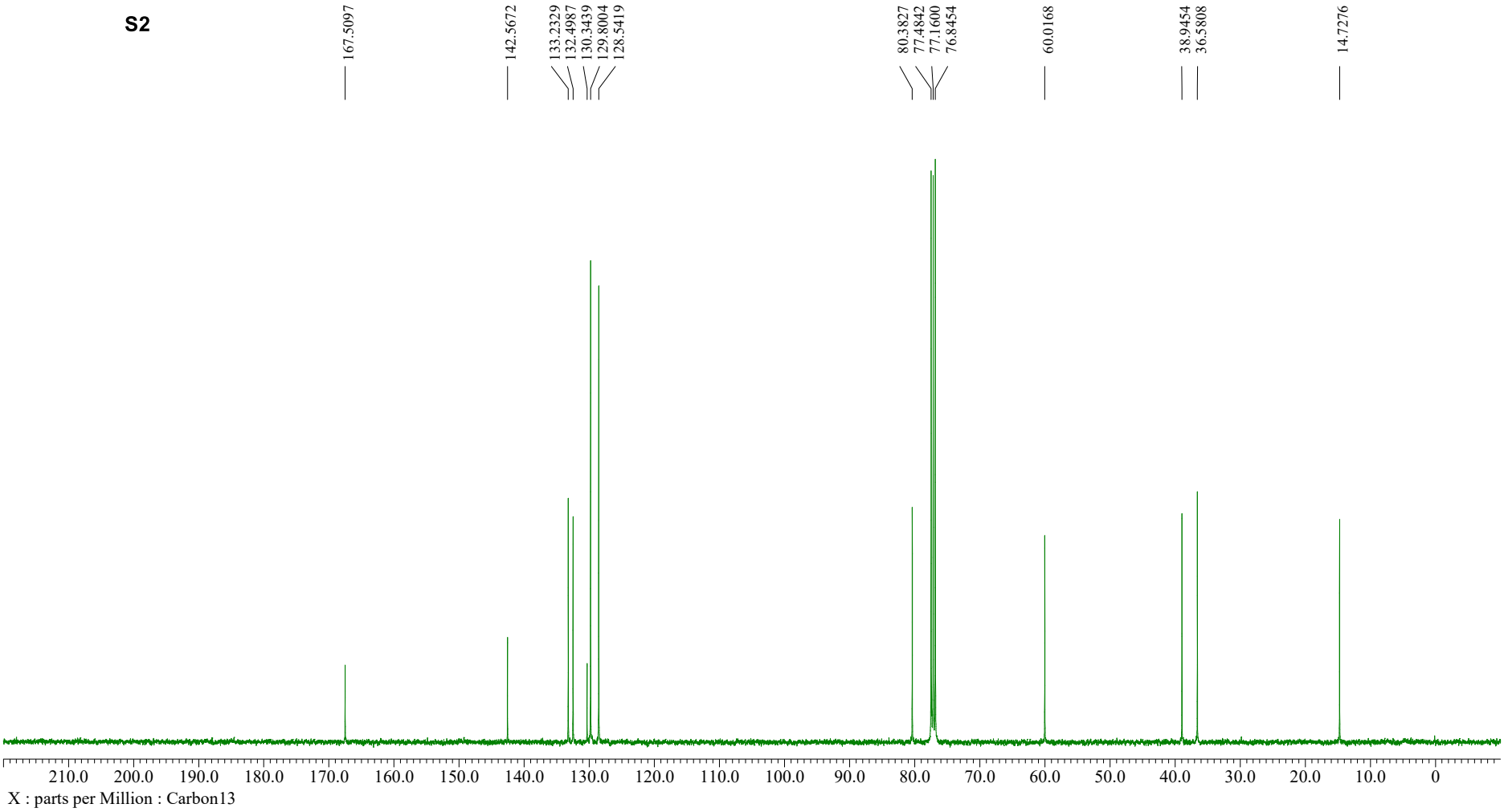
S2



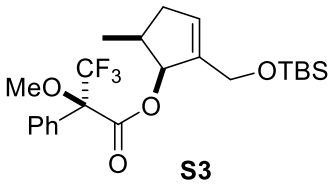
^{13}C NMR (100 MHz, $CDCl_3$)



S2



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



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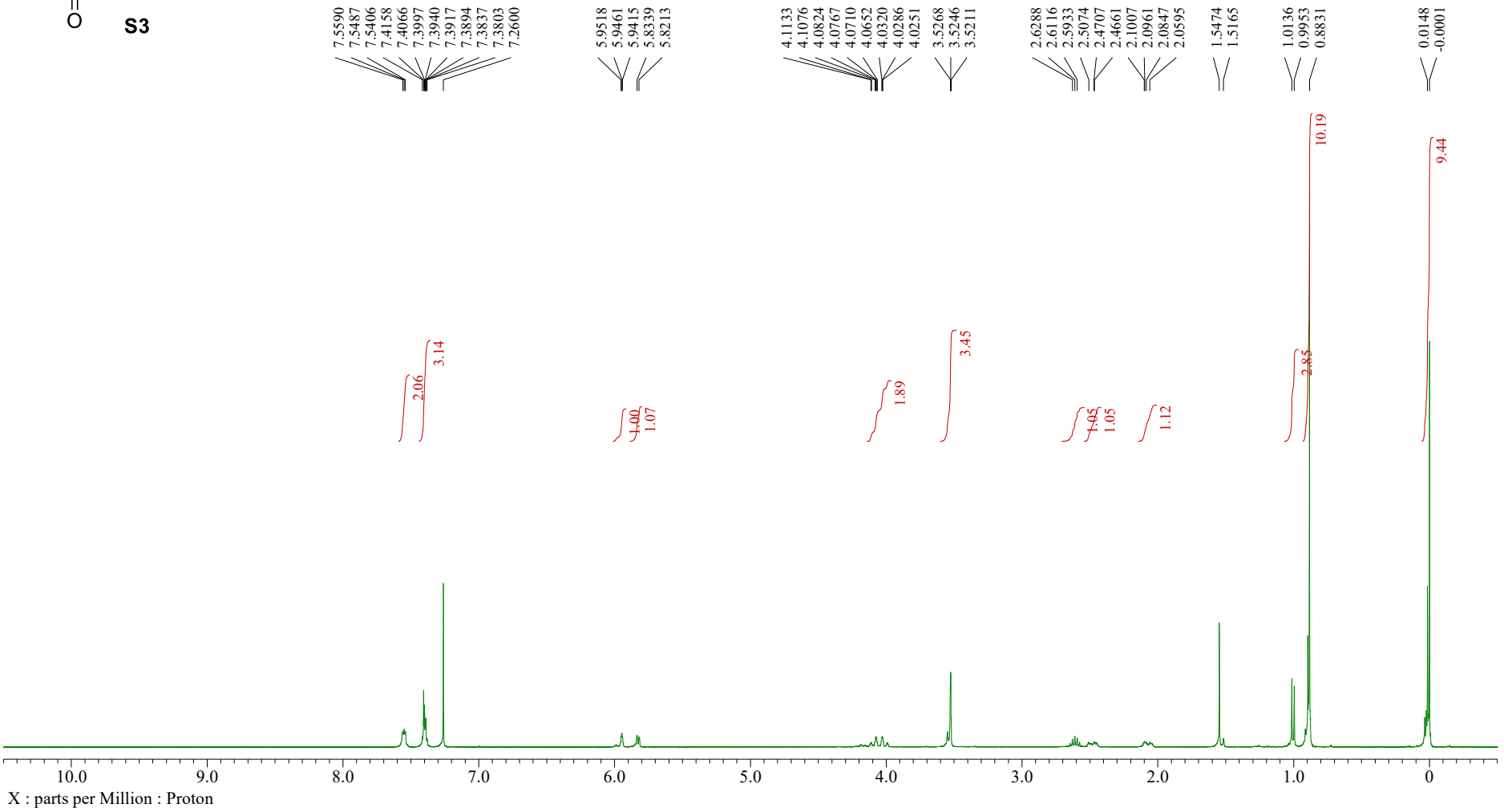
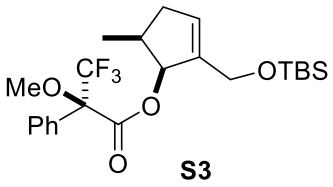


^{13}C NMR (100 MHz, $CDCl_3$)



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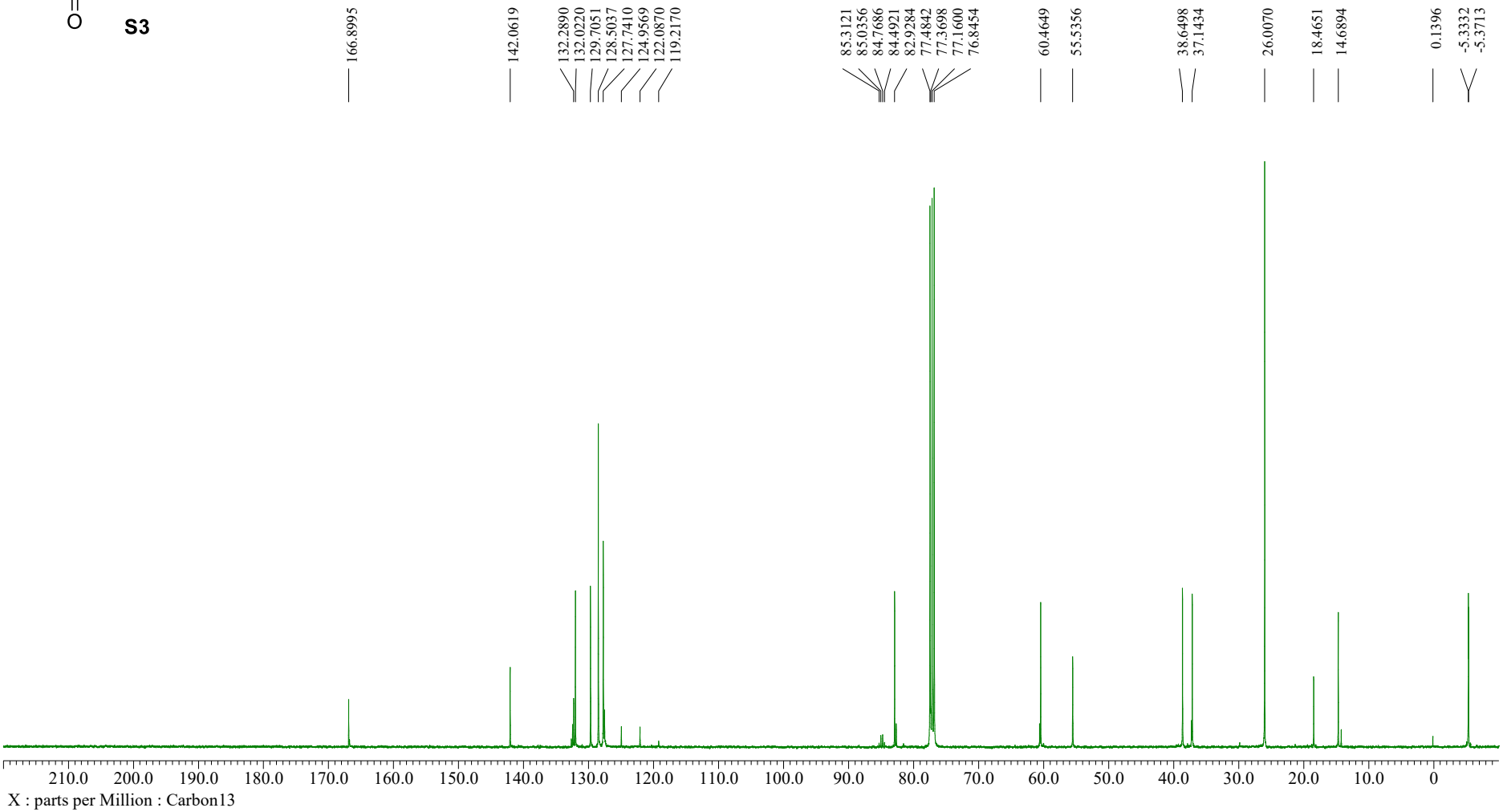

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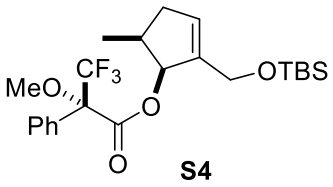

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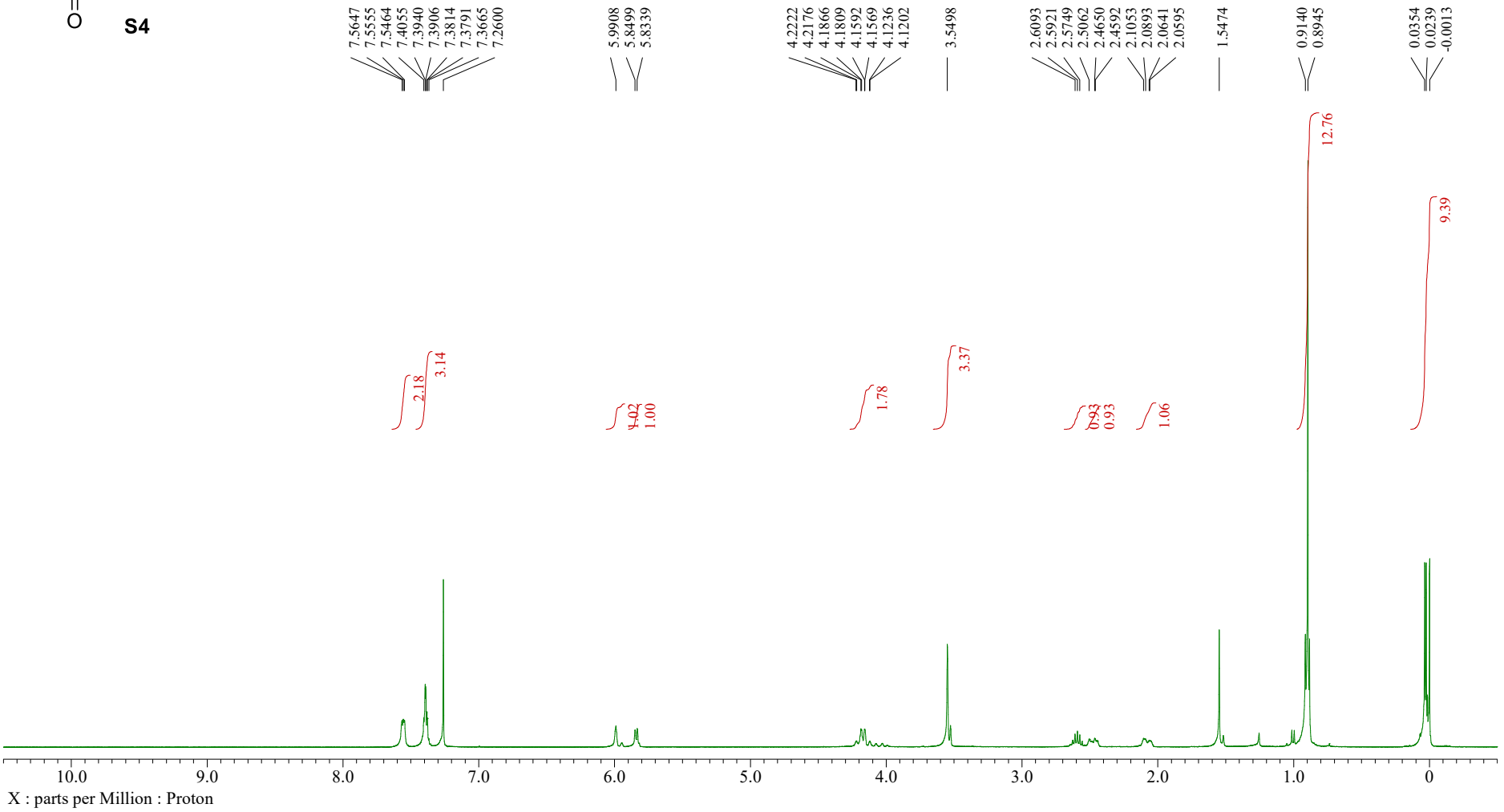
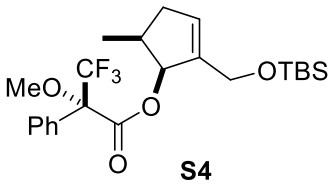


^{13}C NMR (100 MHz, $CDCl_3$)



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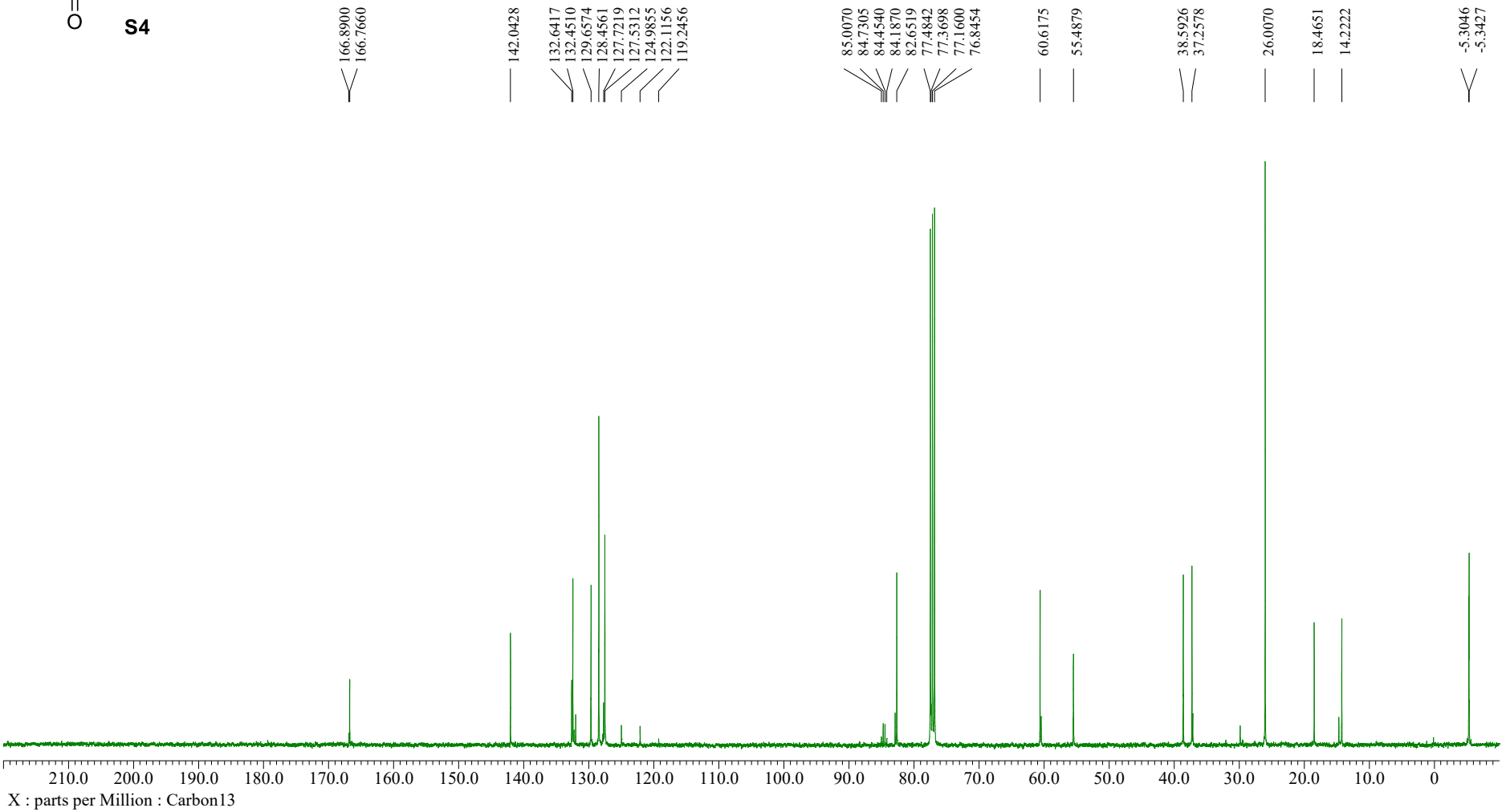
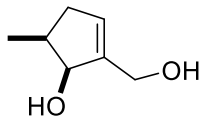


^{1}H NMR (400 MHz, $CDCl_3$)



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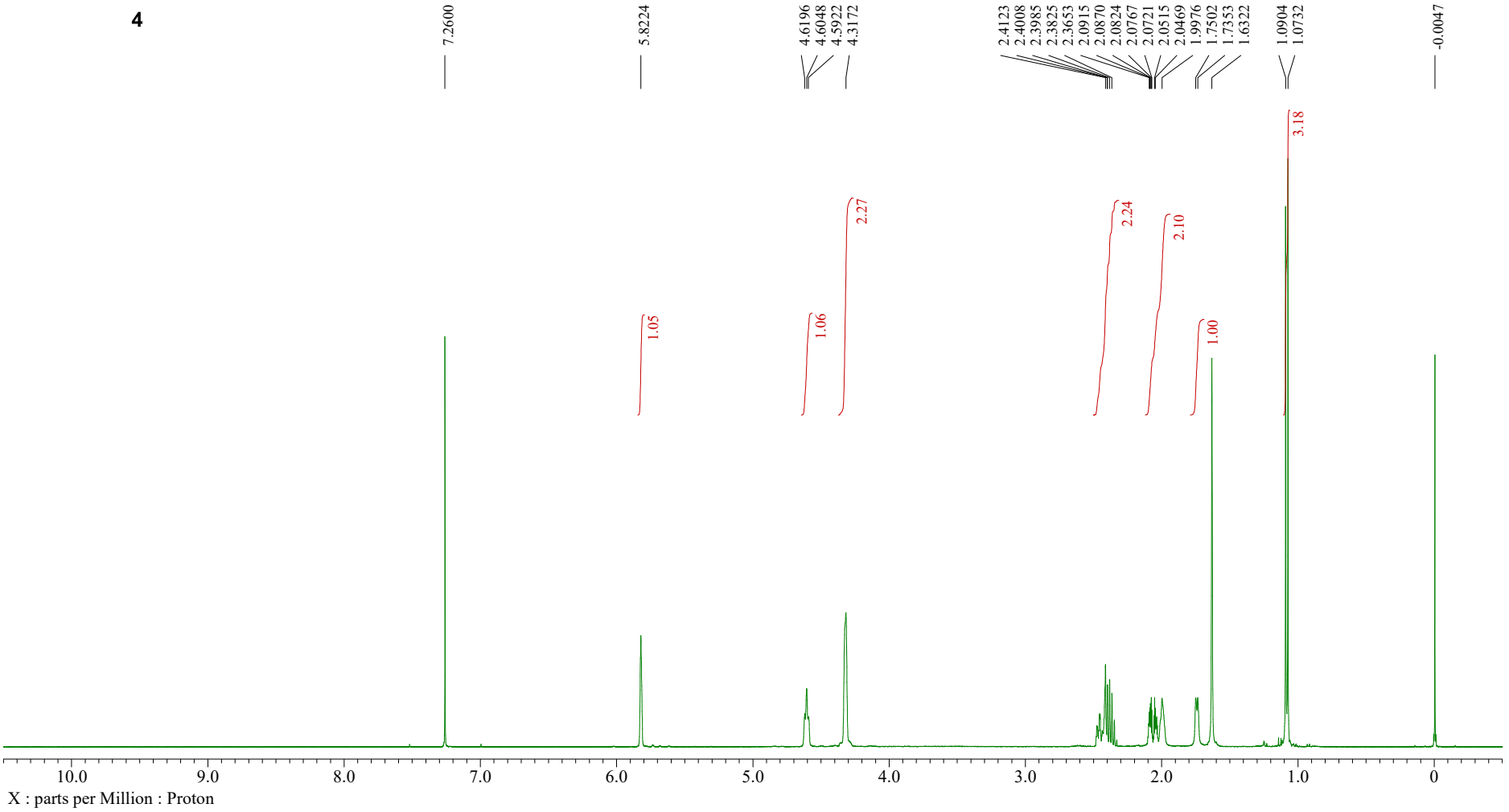
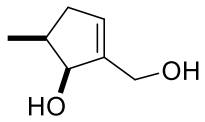


^{13}C NMR (100 MHz, $CDCl_3$)



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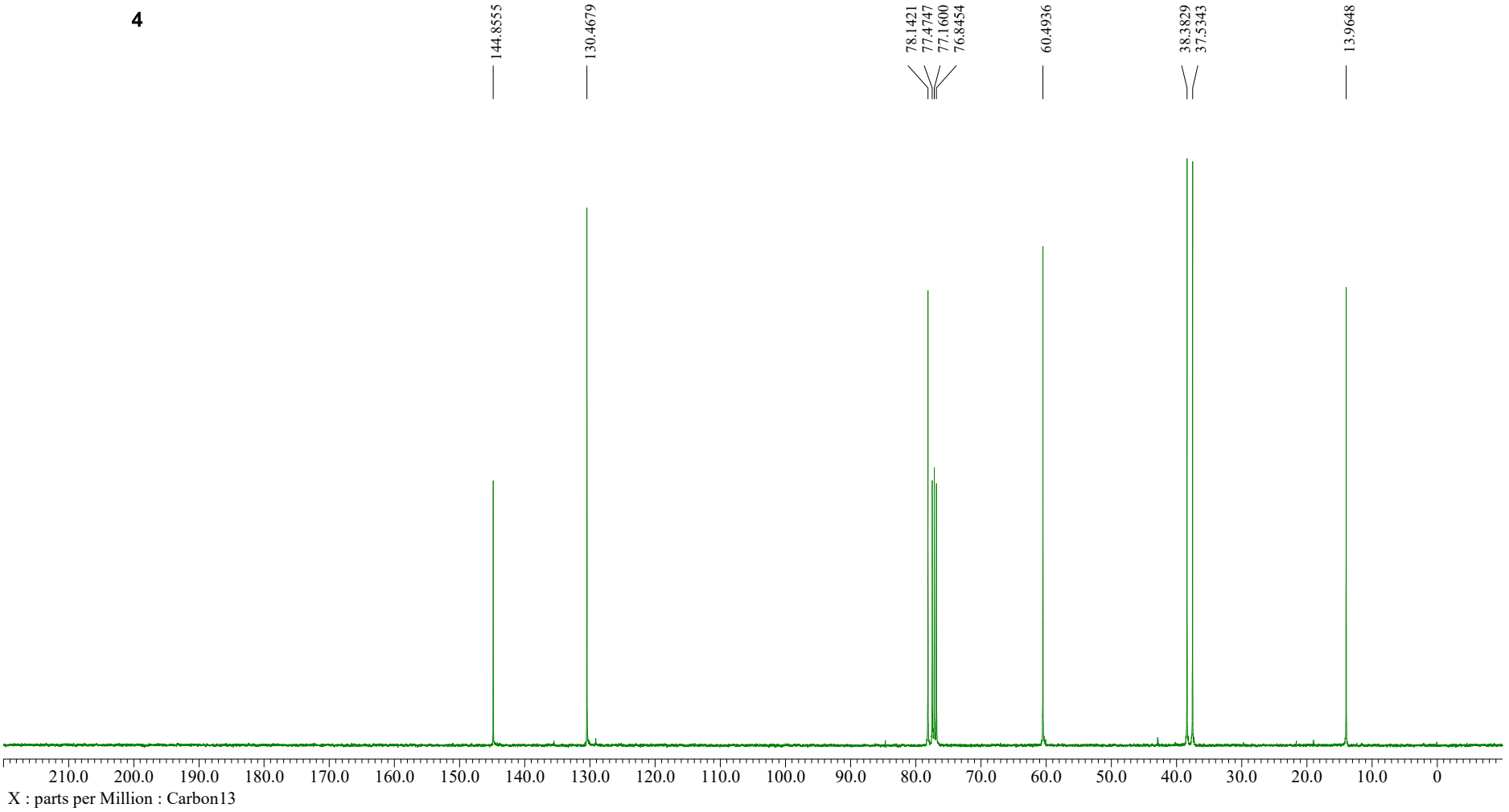
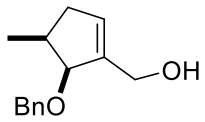


^{1}H NMR (400 MHz, $CDCl_3$)



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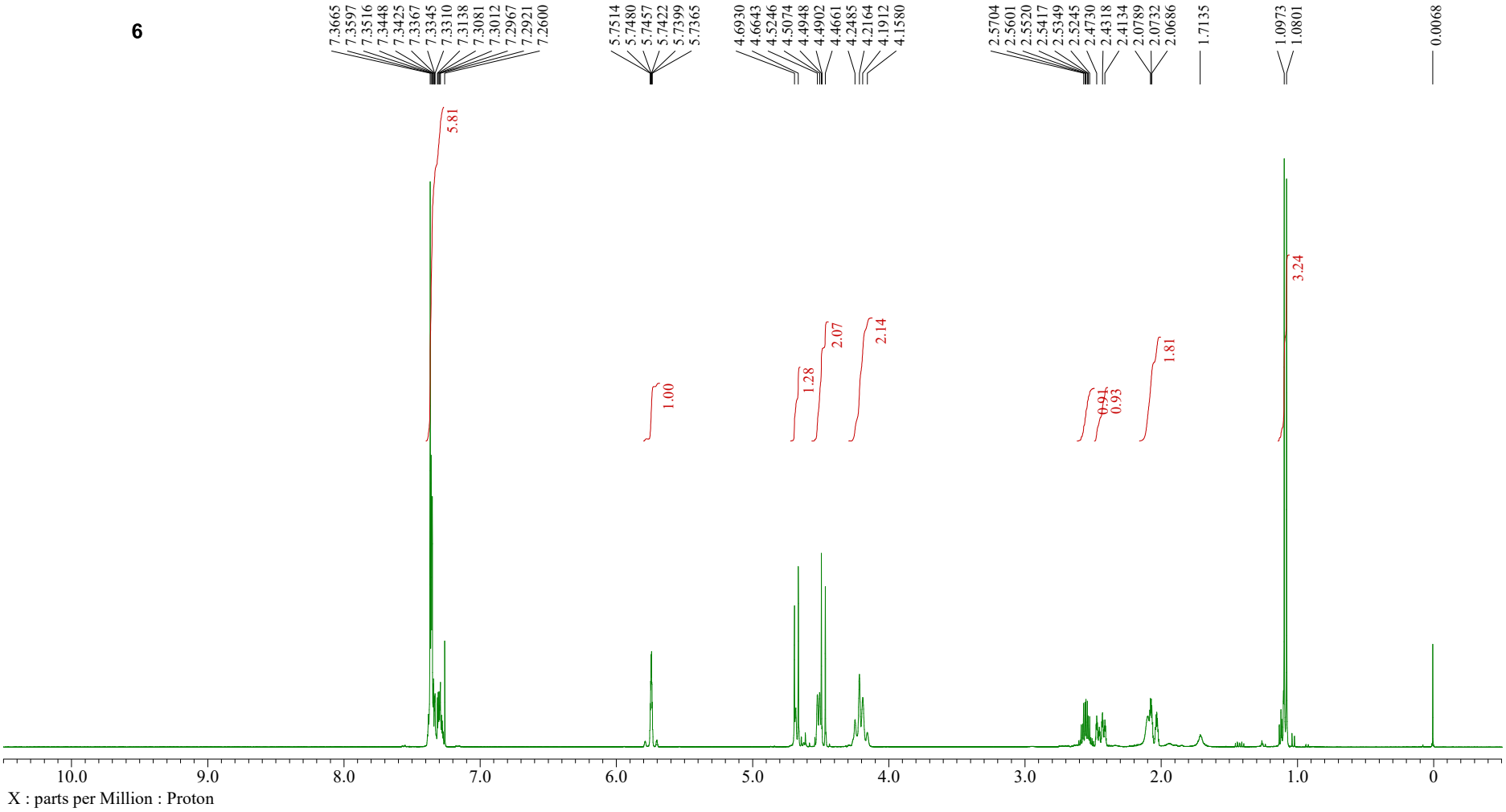

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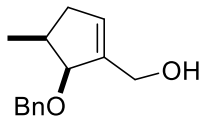

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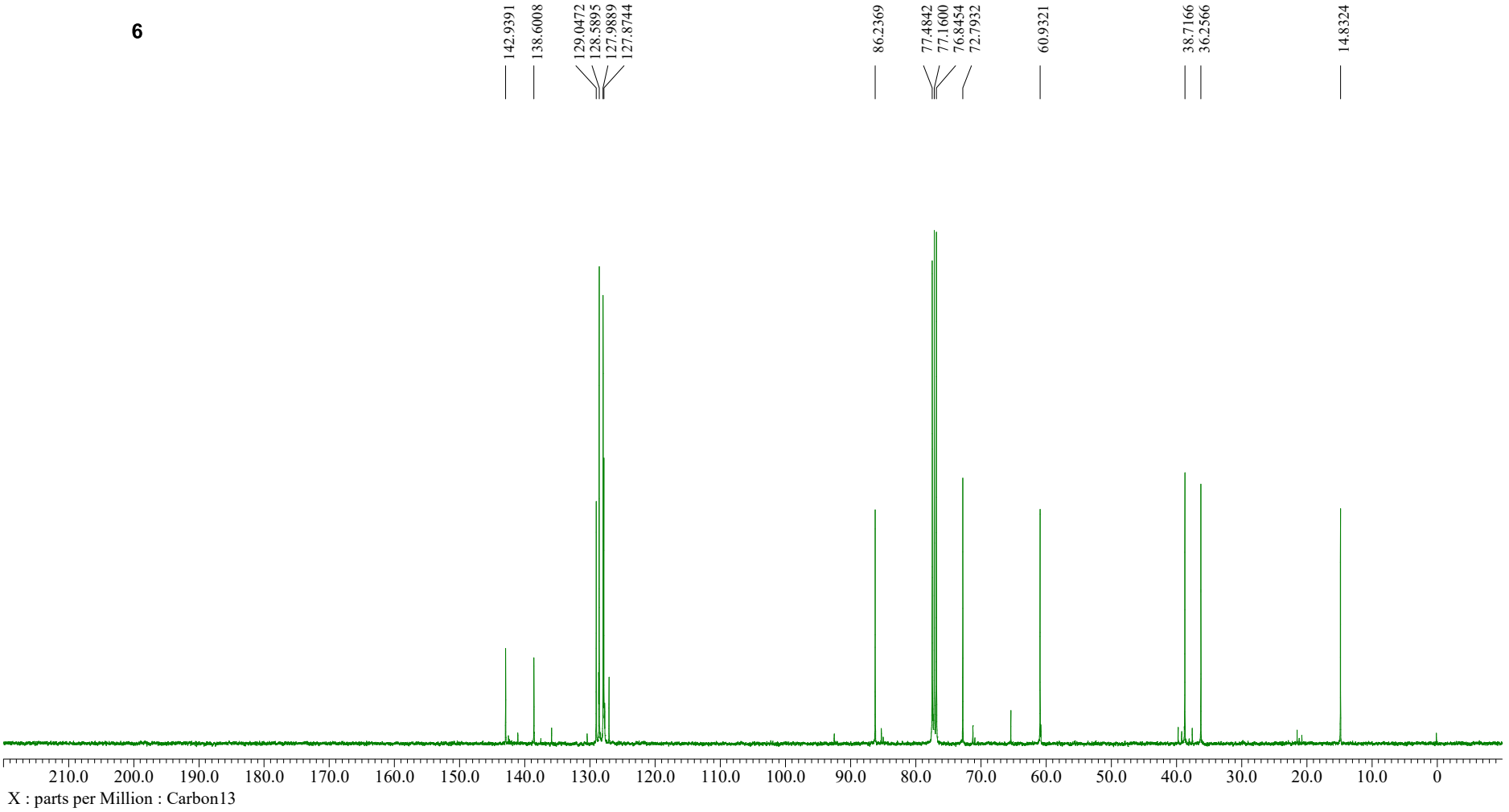

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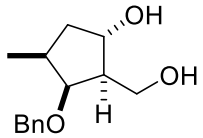

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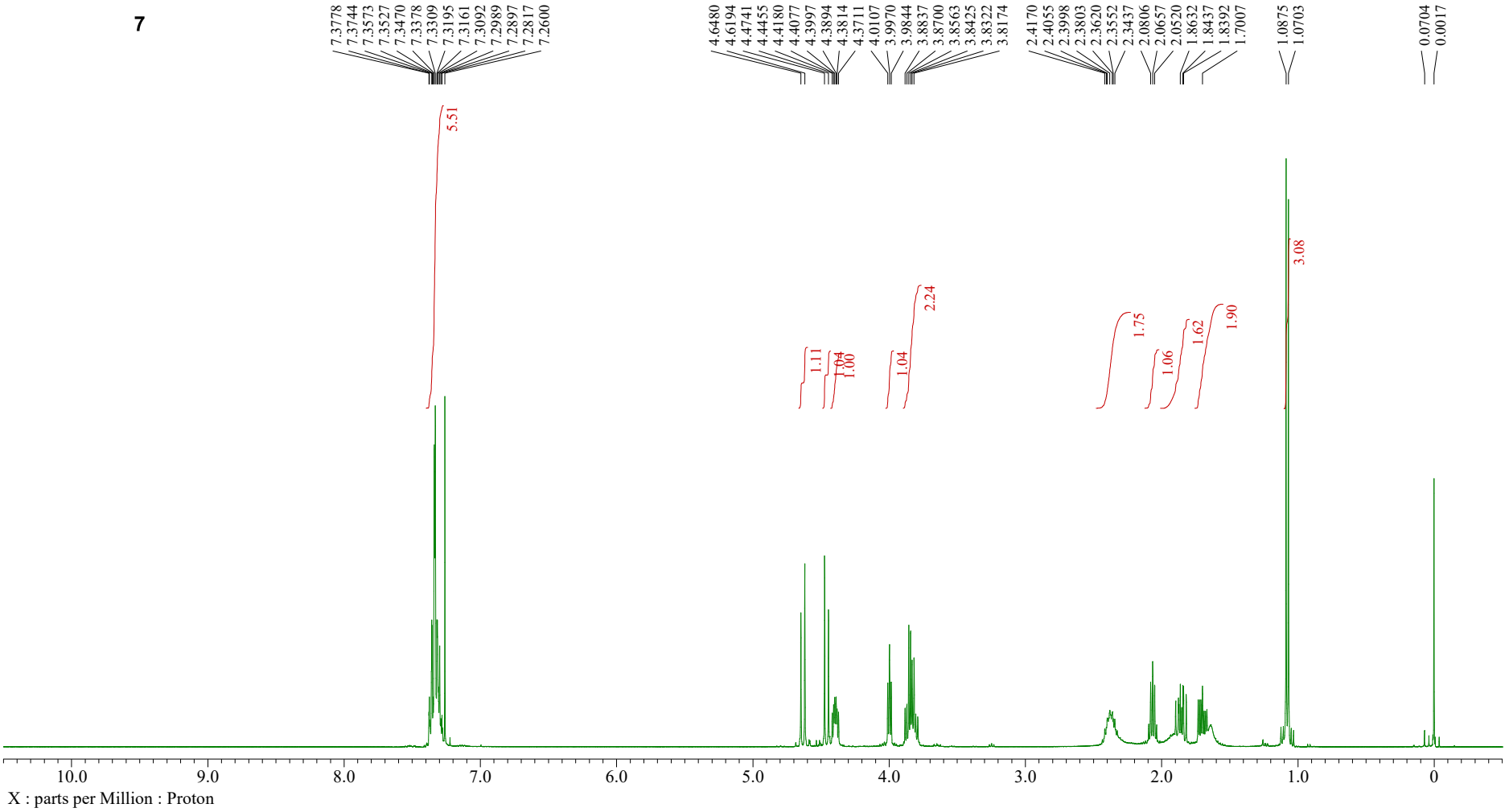
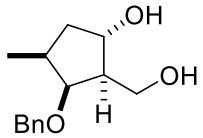


^{13}C NMR (100 MHz, $CDCl_3$)



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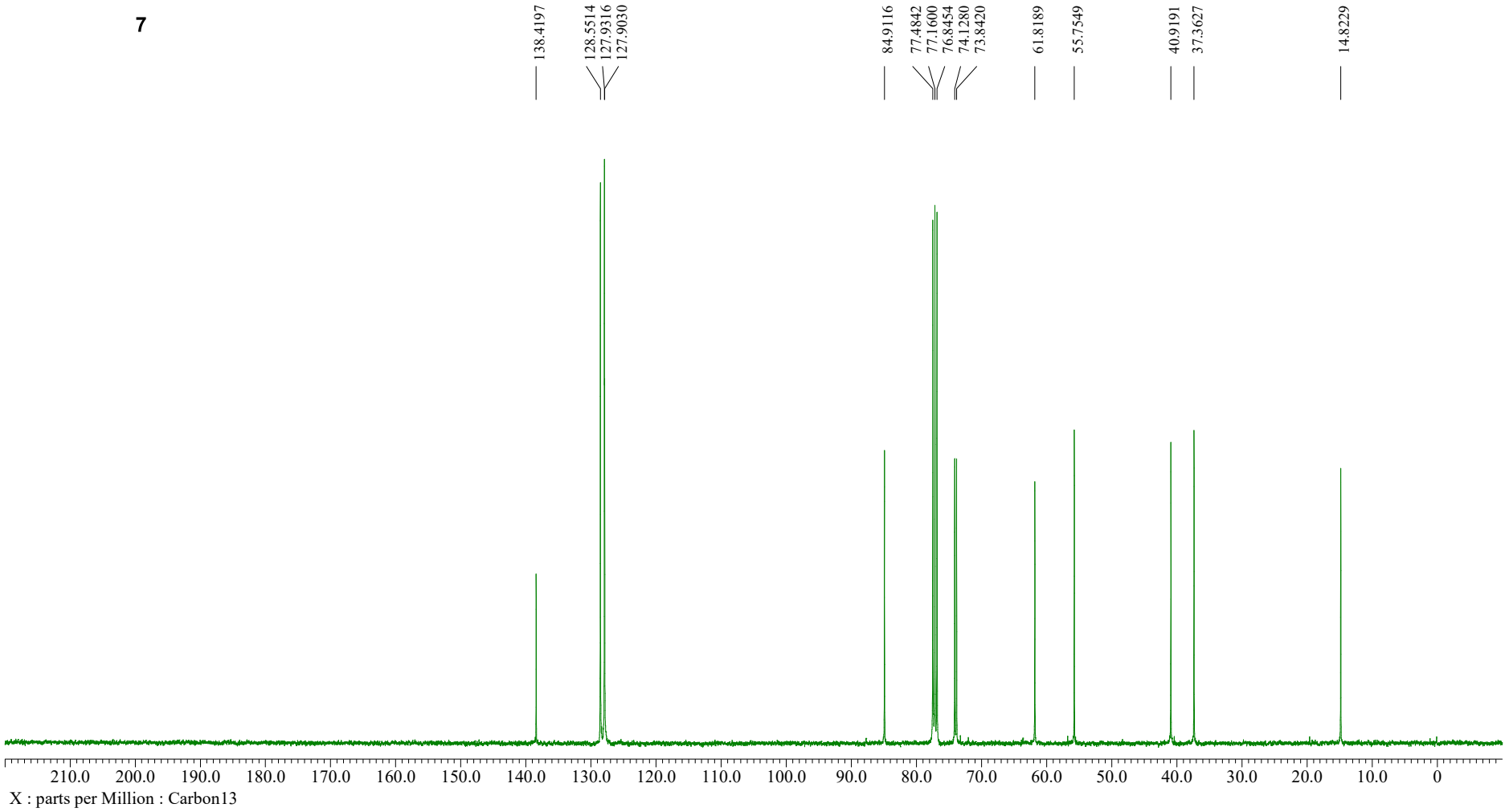

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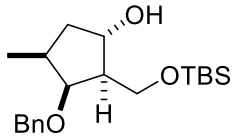
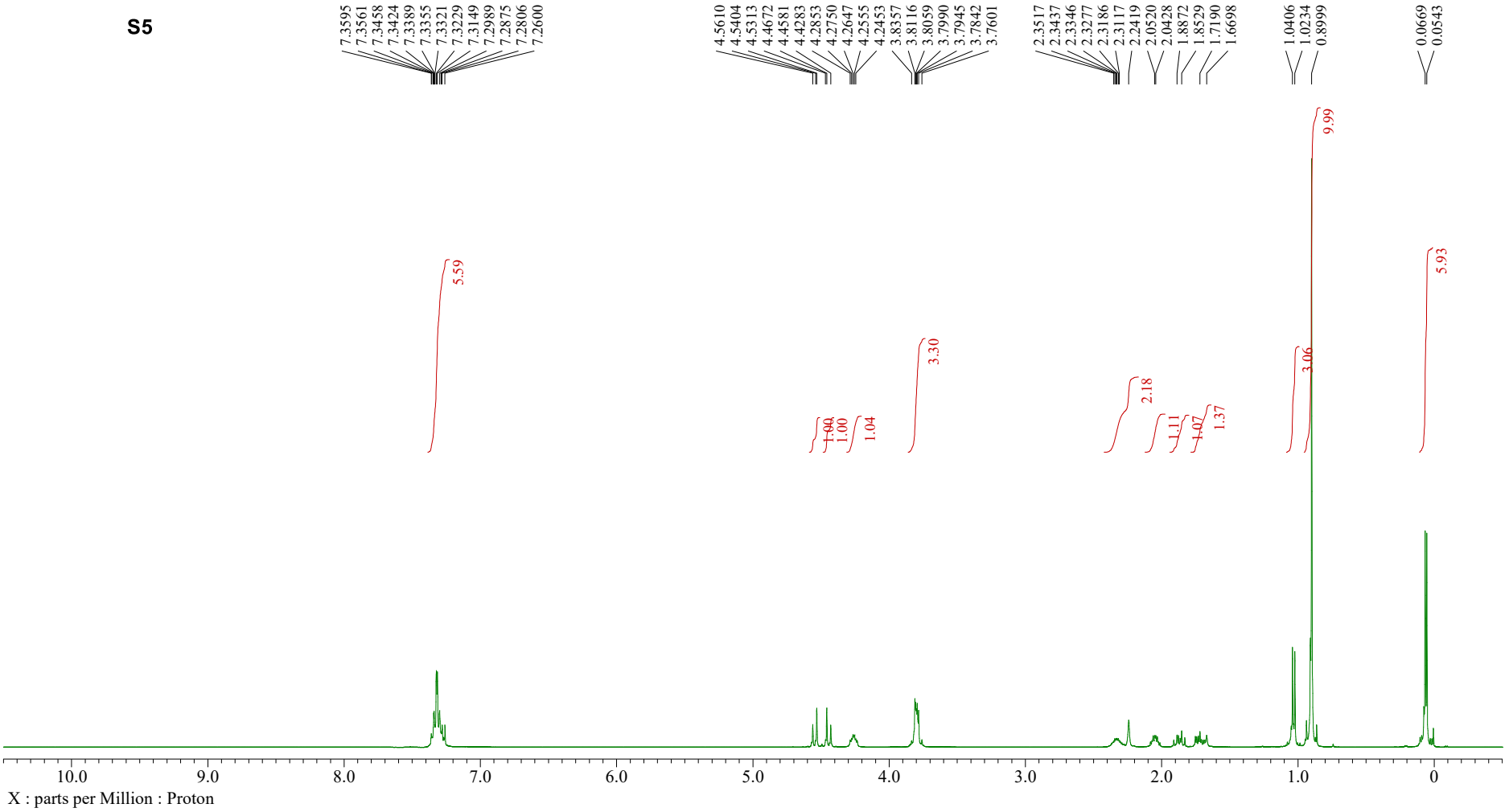


S5



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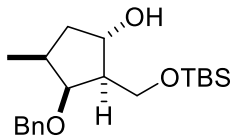

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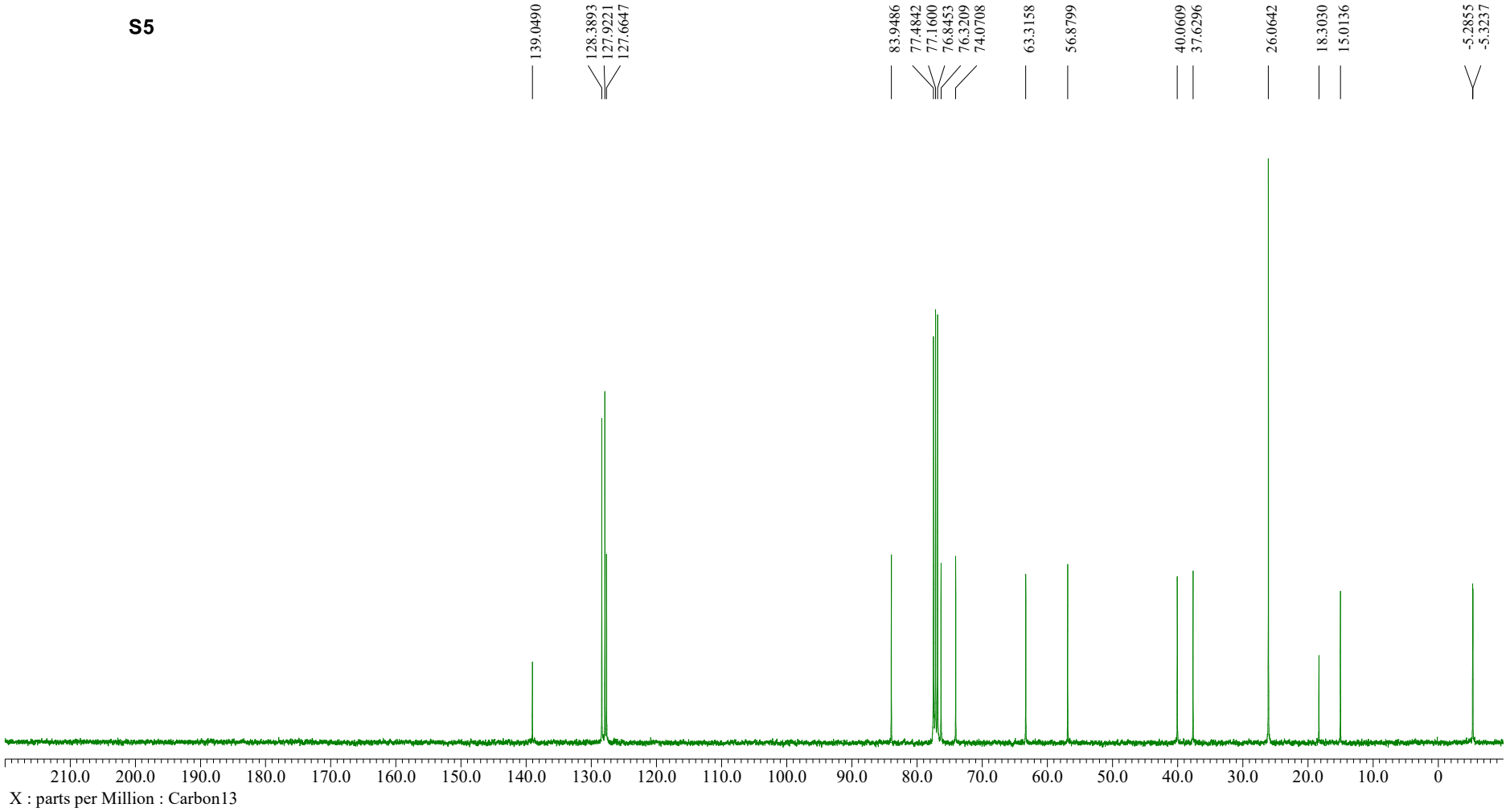

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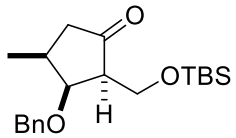

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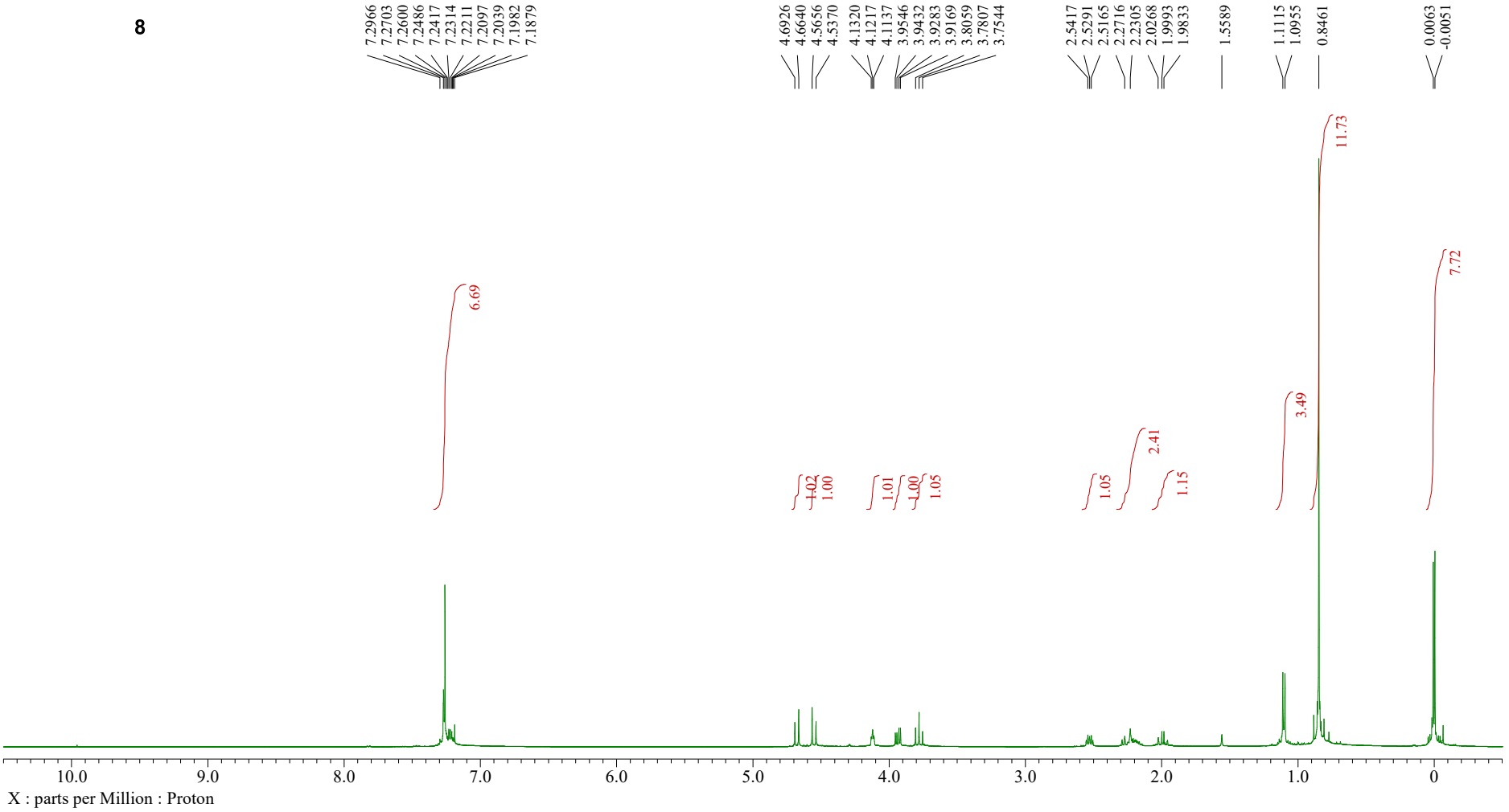

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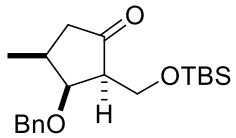

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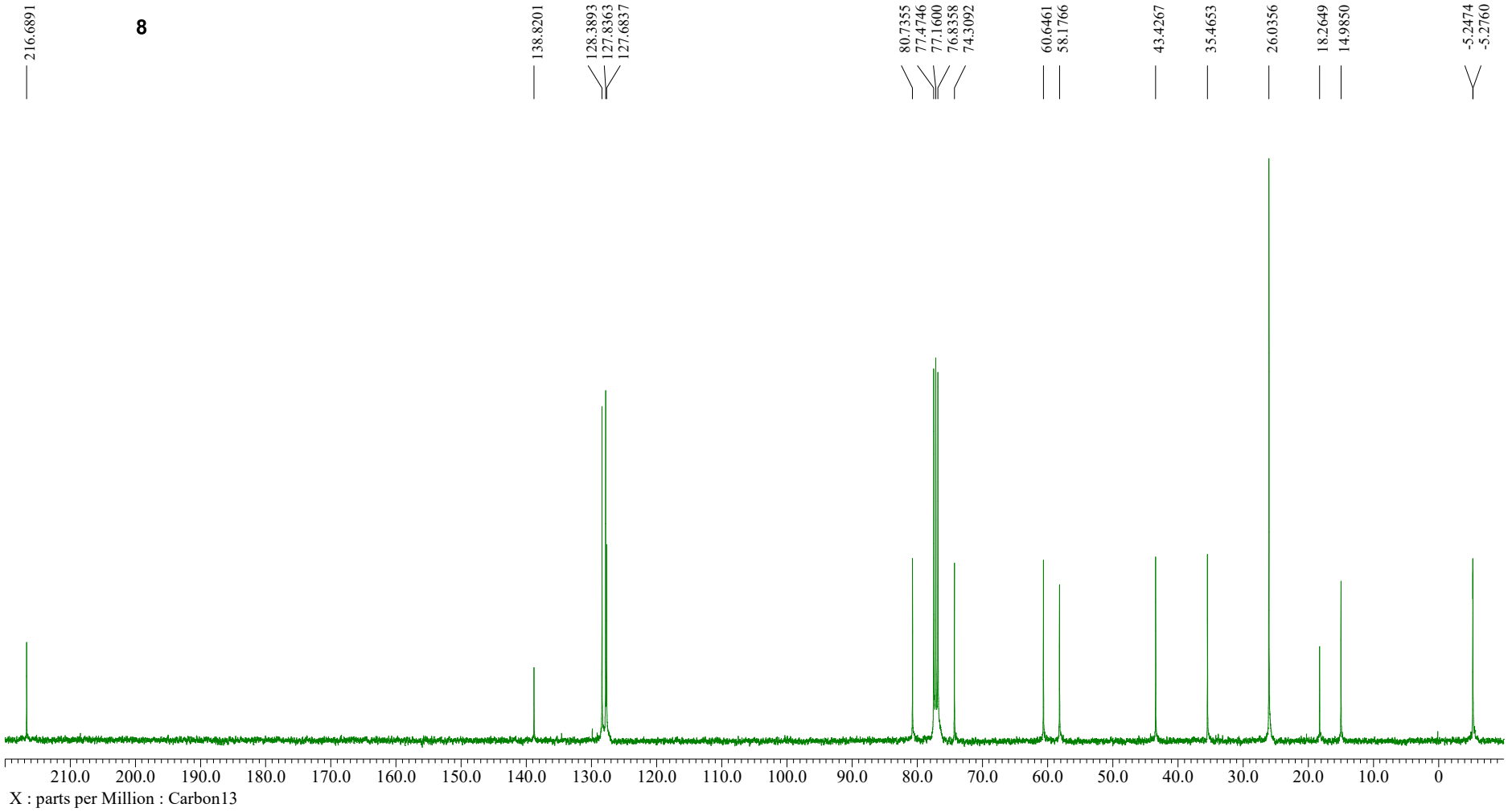

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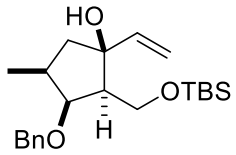

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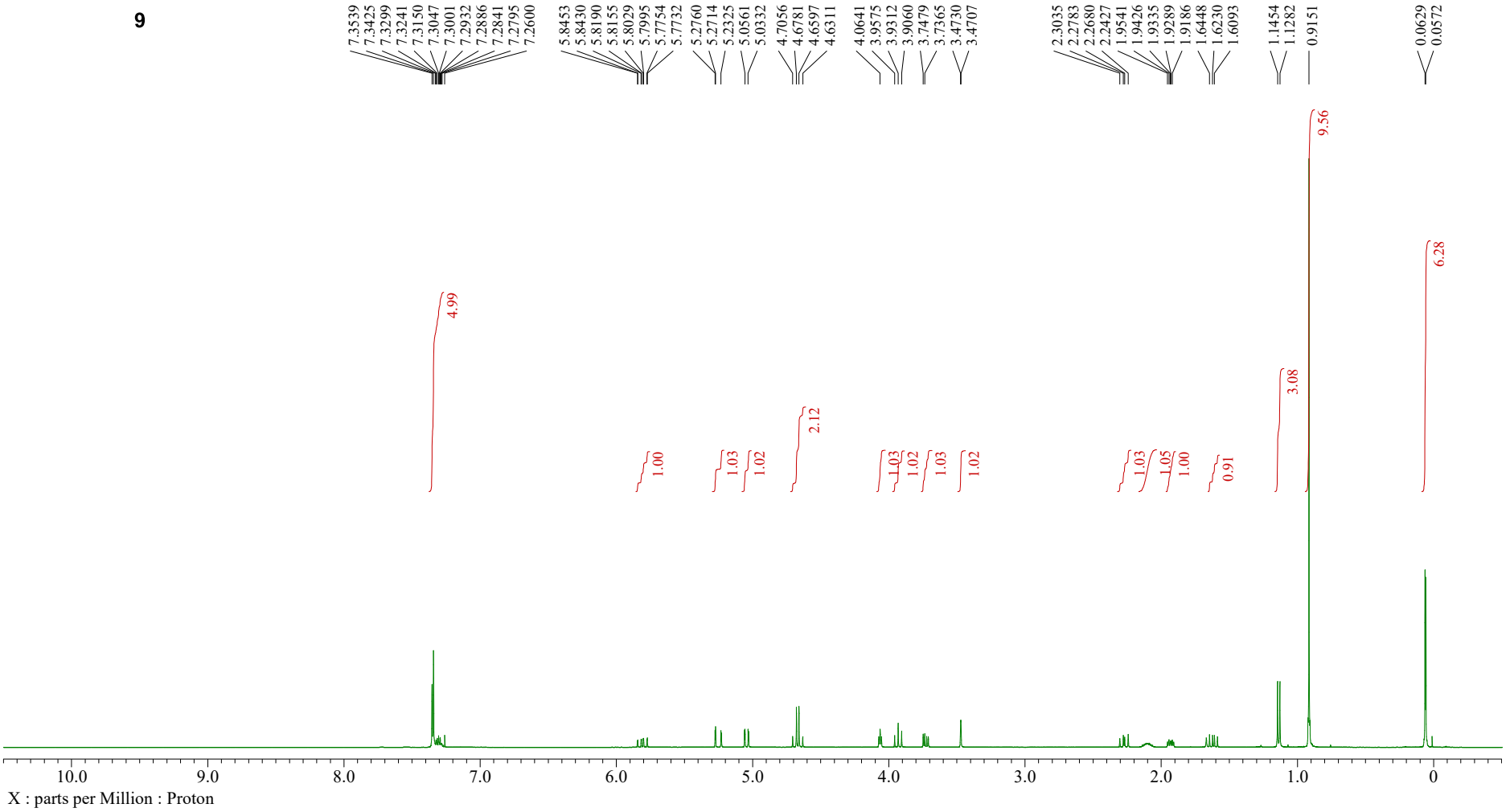

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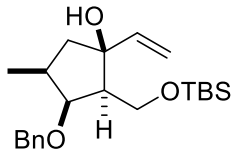

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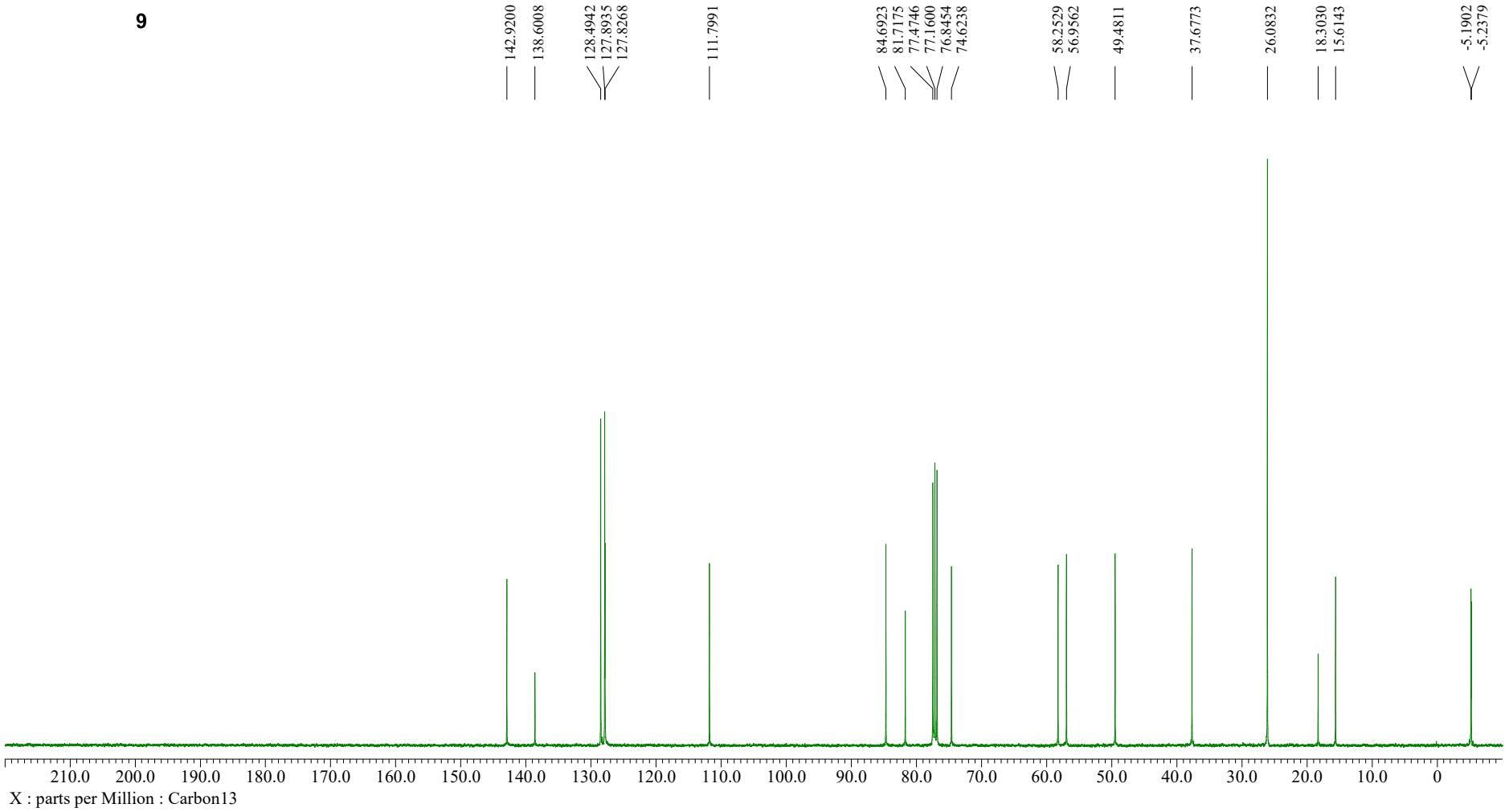

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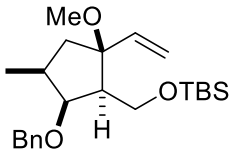

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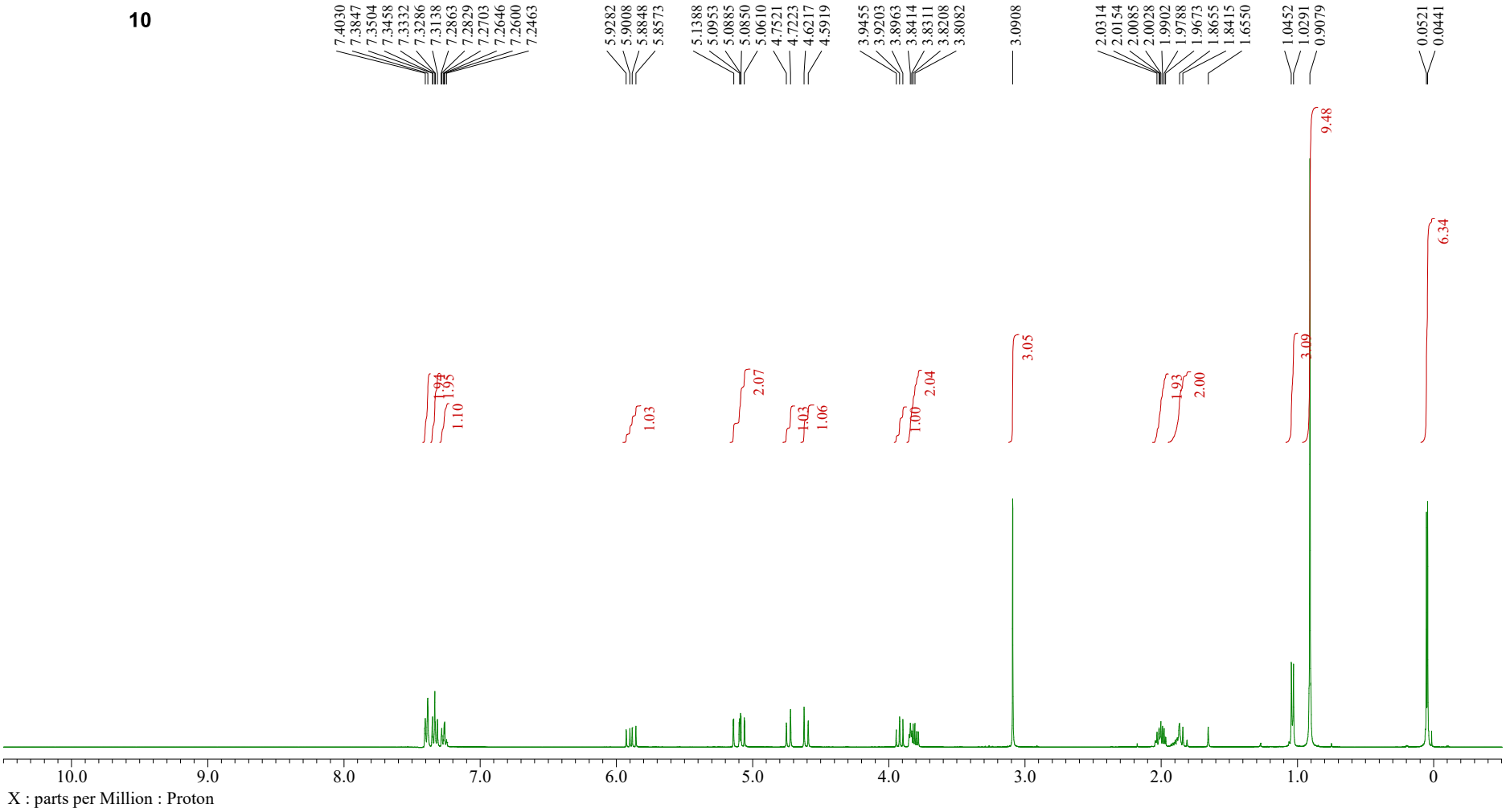
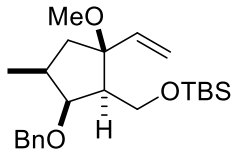


^{13}C NMR (100 MHz, $CDCl_3$)



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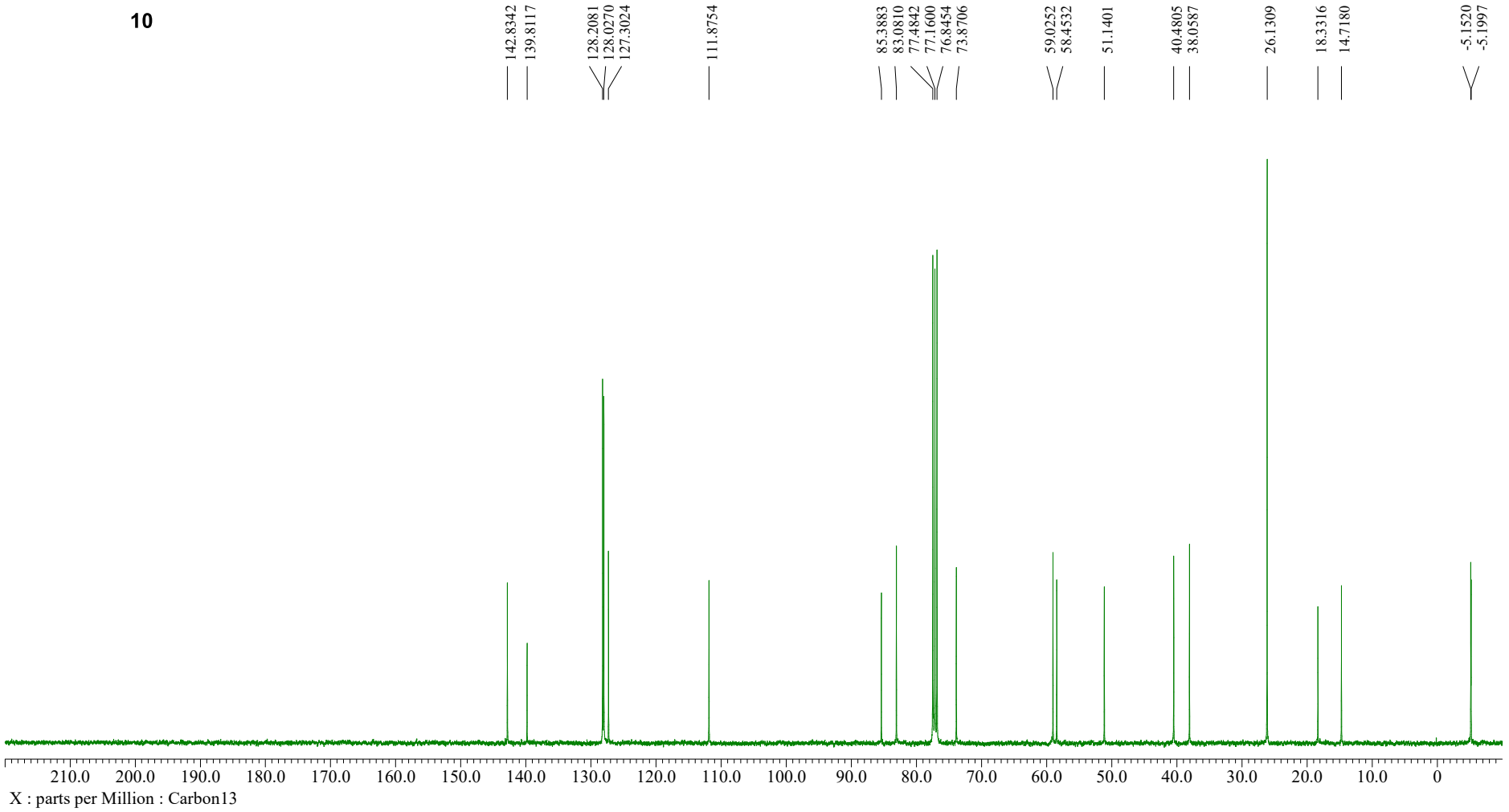

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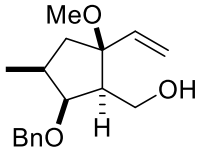

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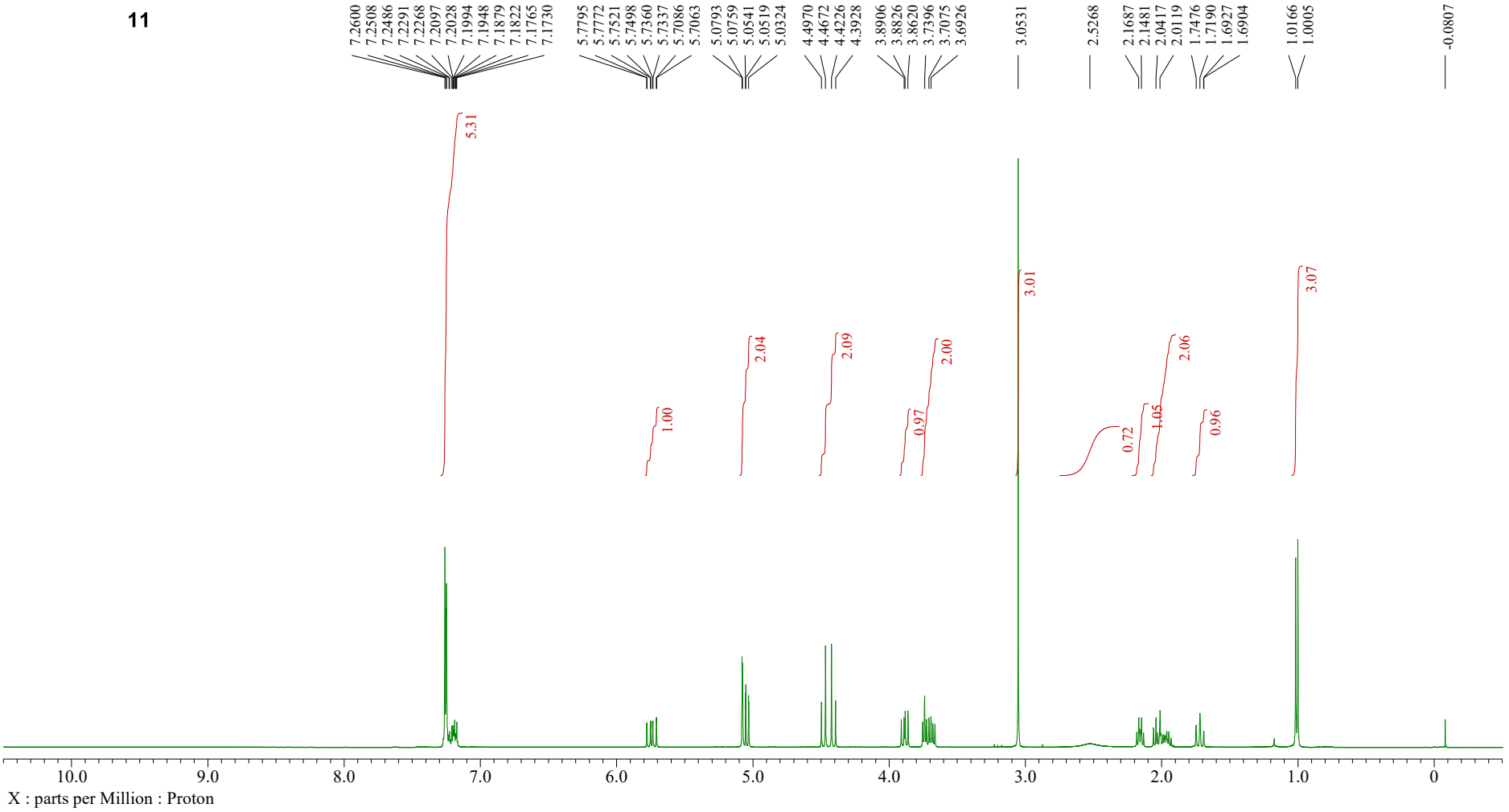

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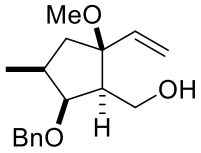

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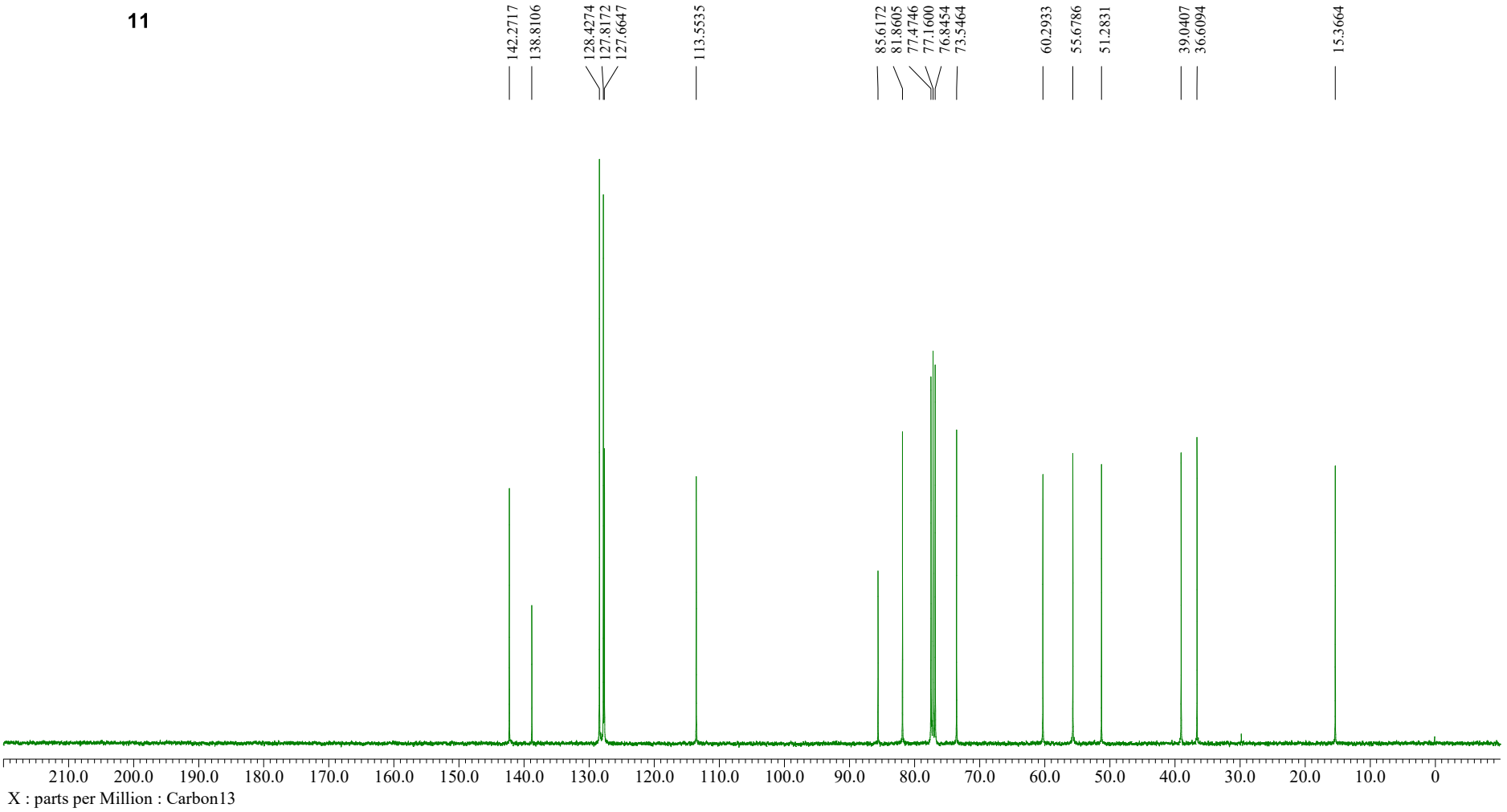

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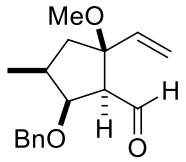

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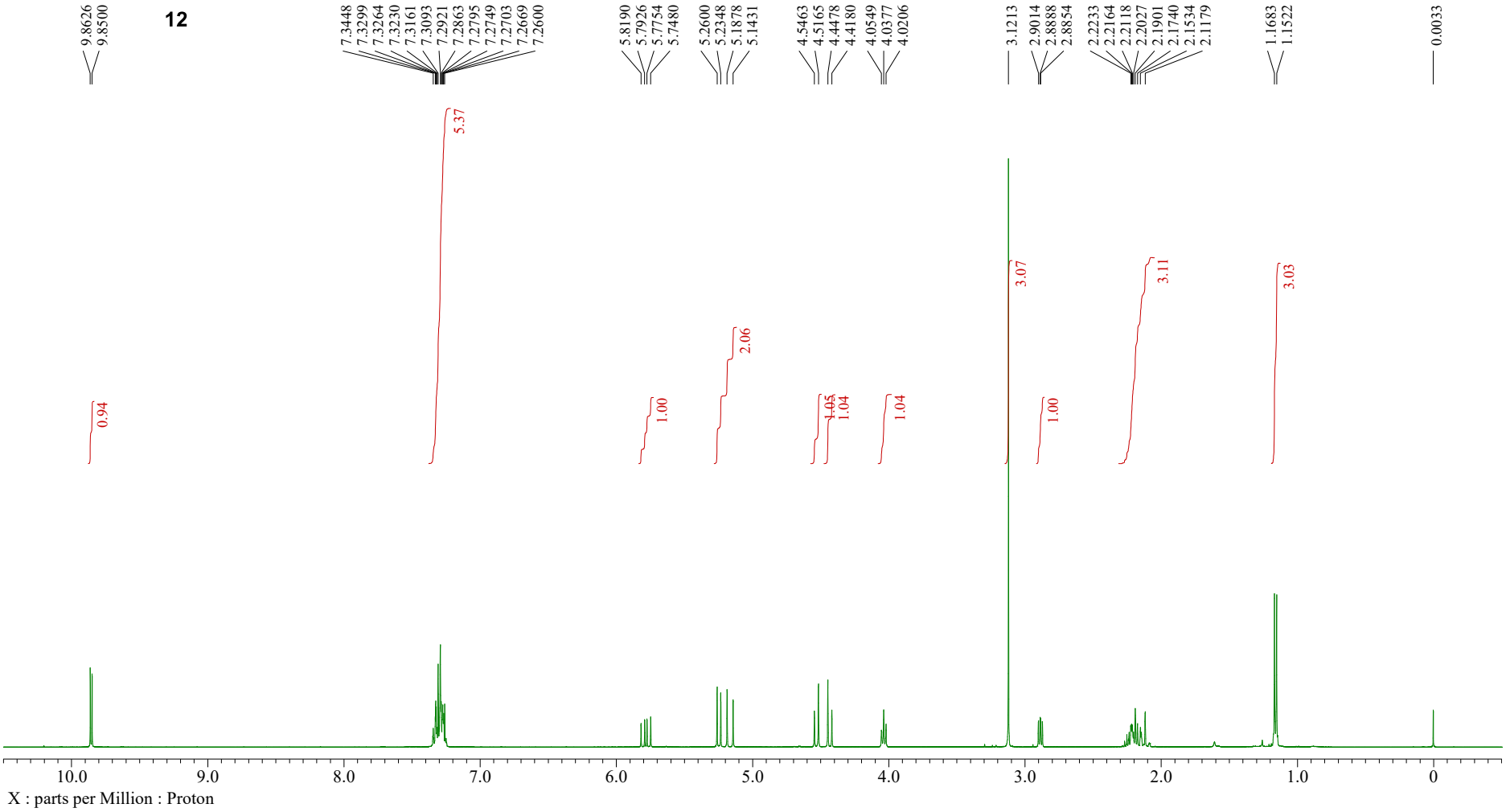

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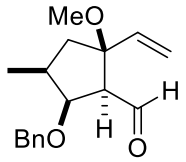

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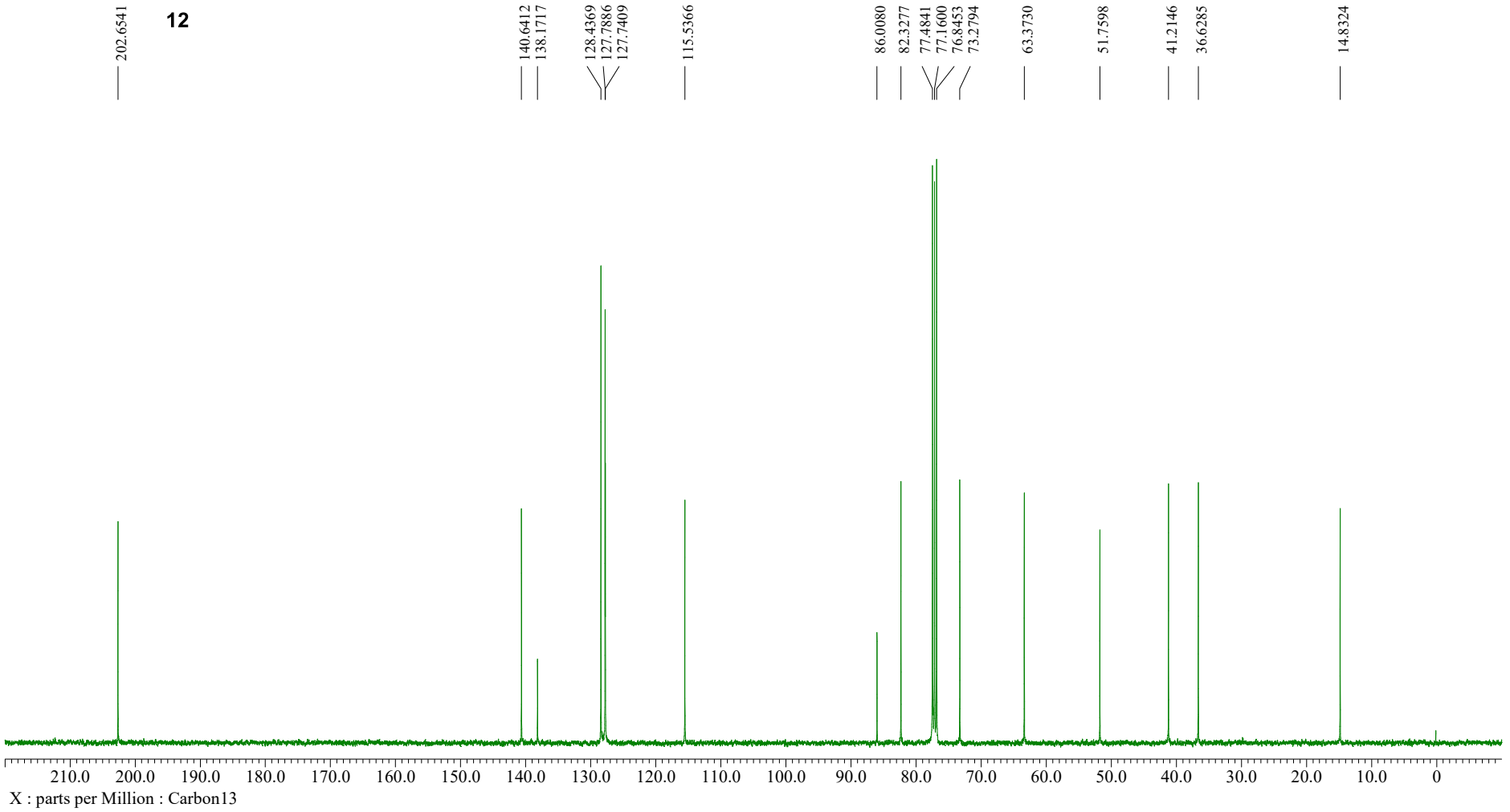
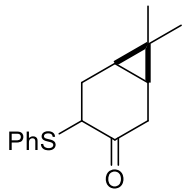


^{1}H NMR (400 MHz, $CDCl_3$)



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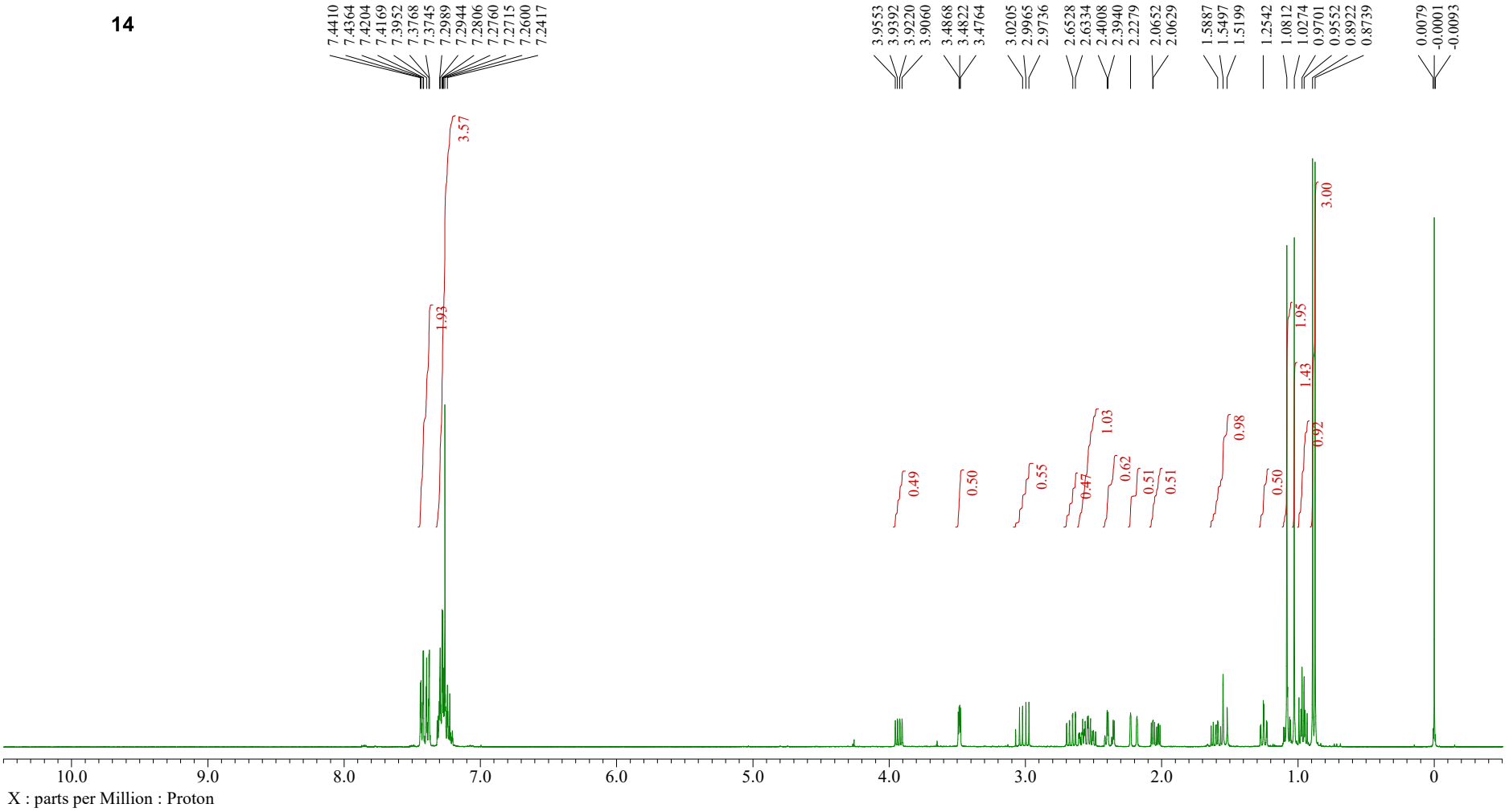

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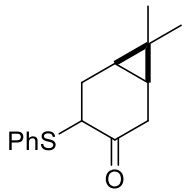

14

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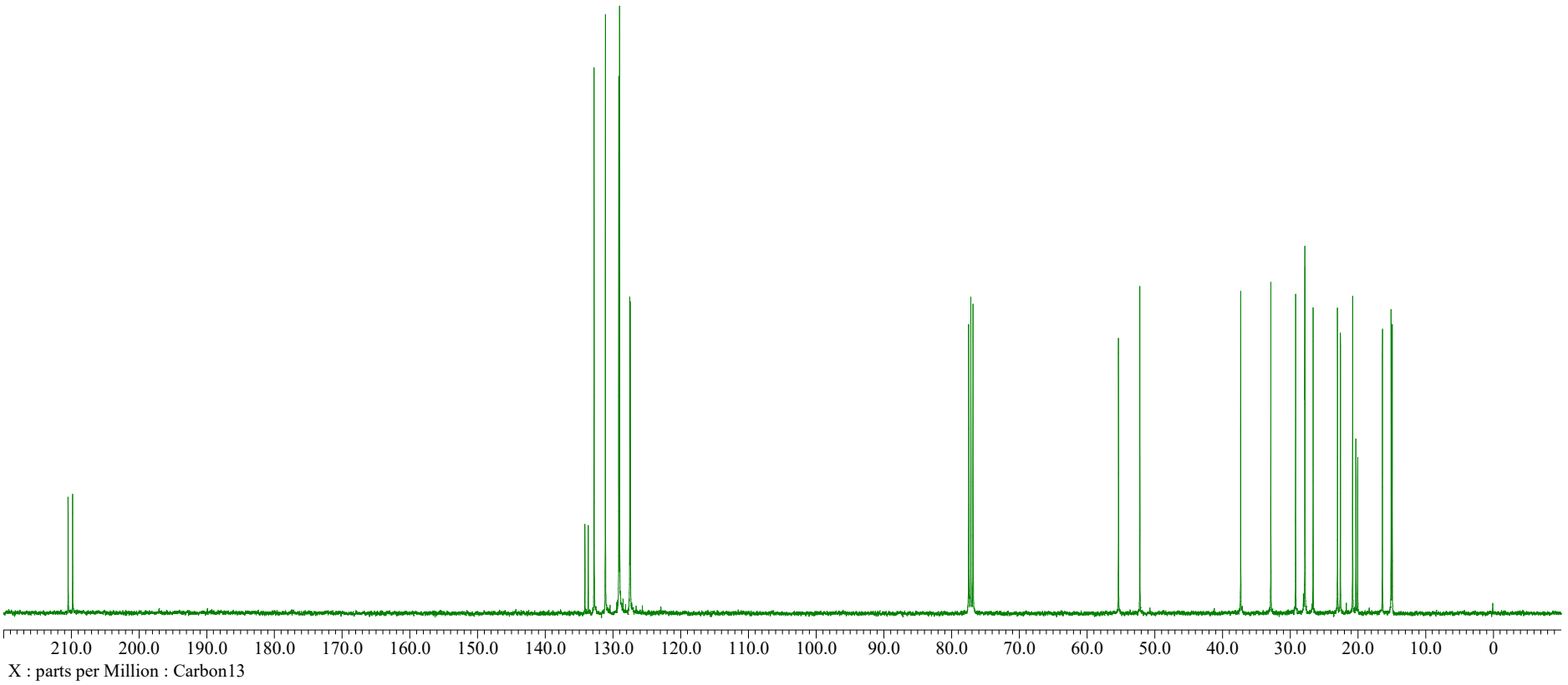

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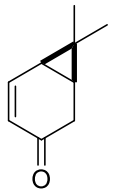
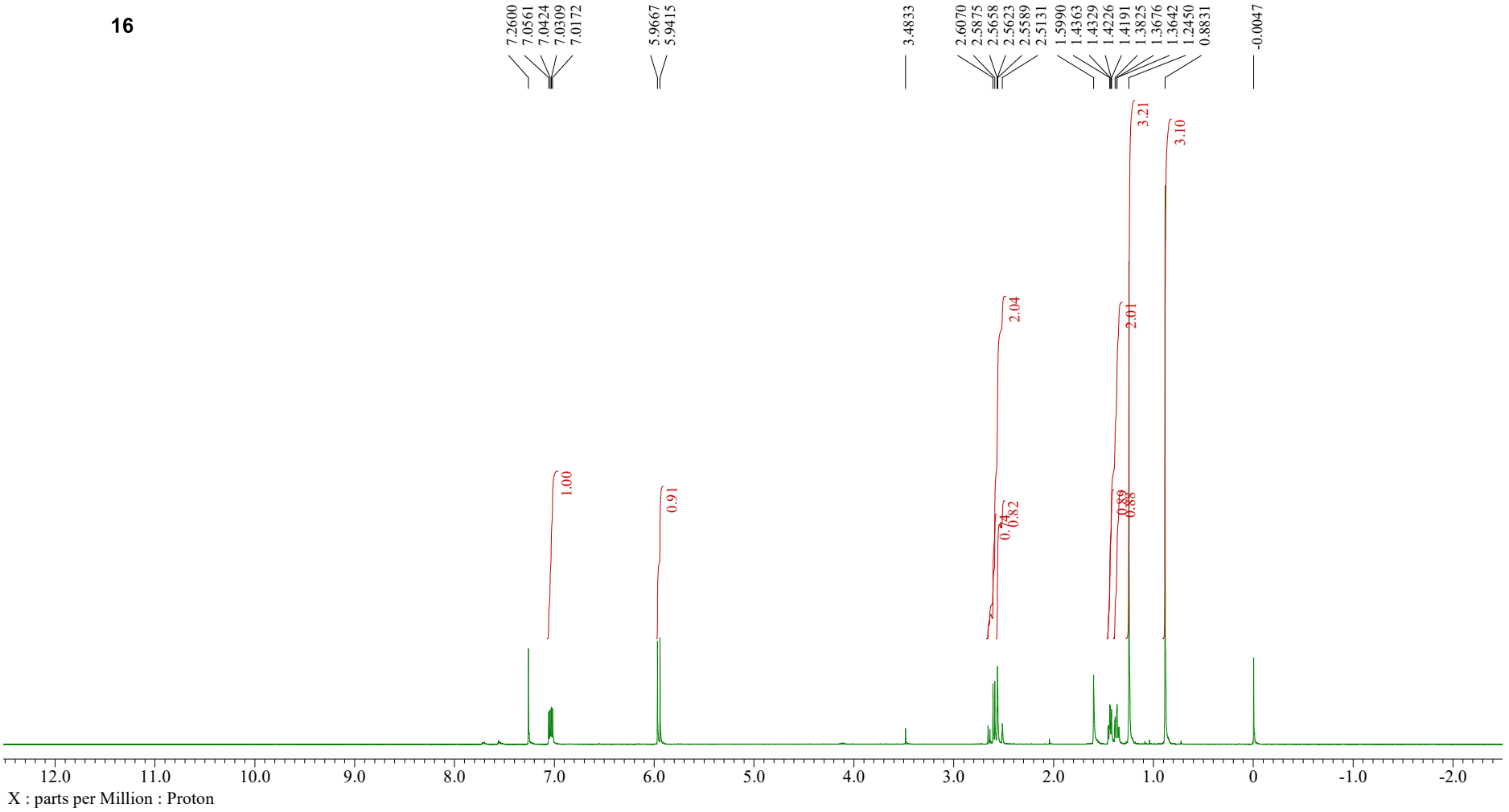
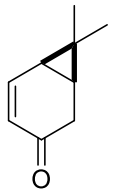


16



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



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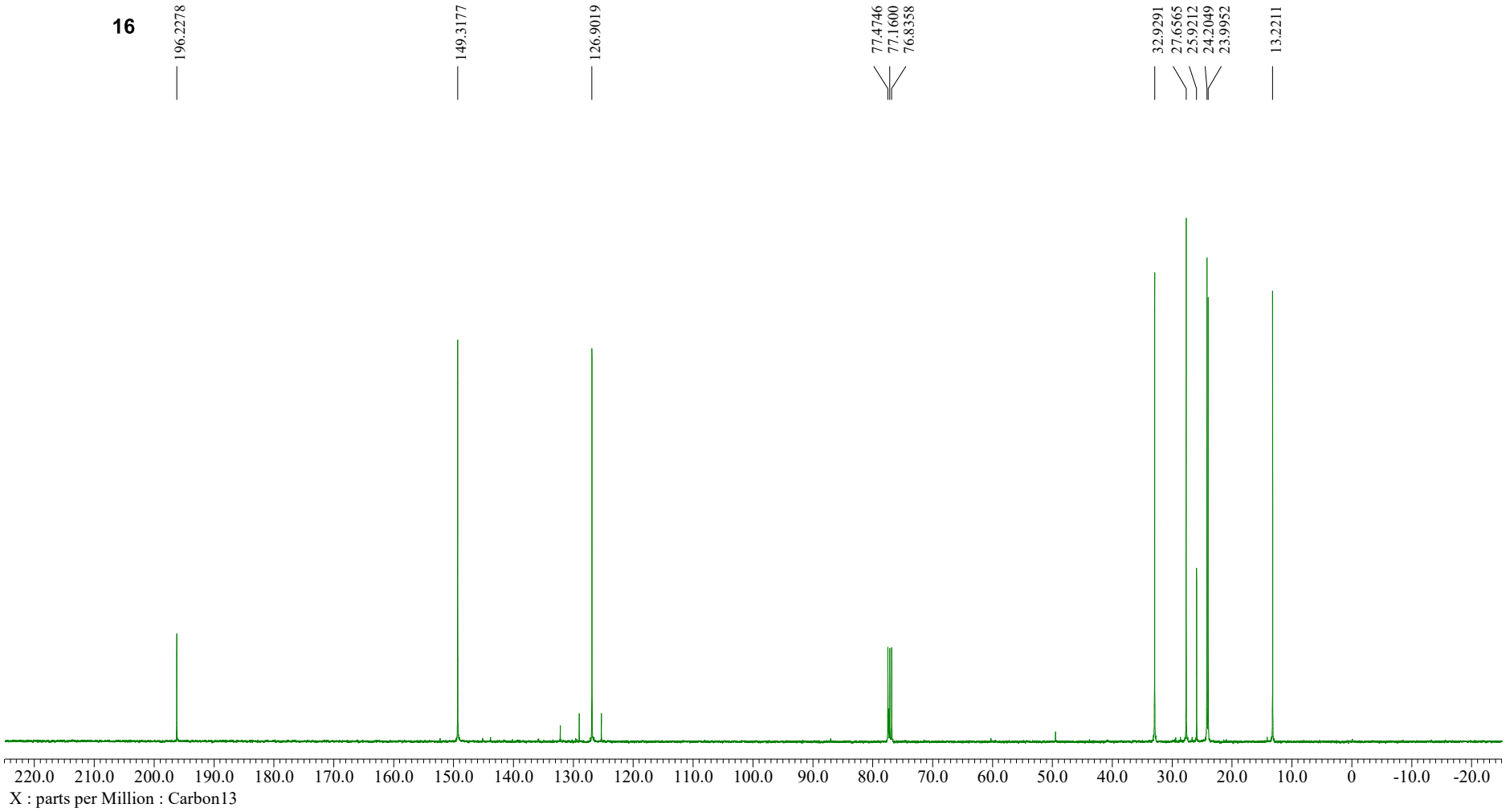
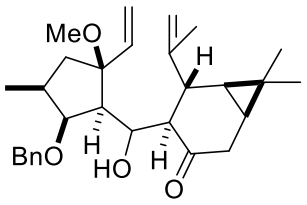


^{1}H NMR (400 MHz, $CDCl_3$)



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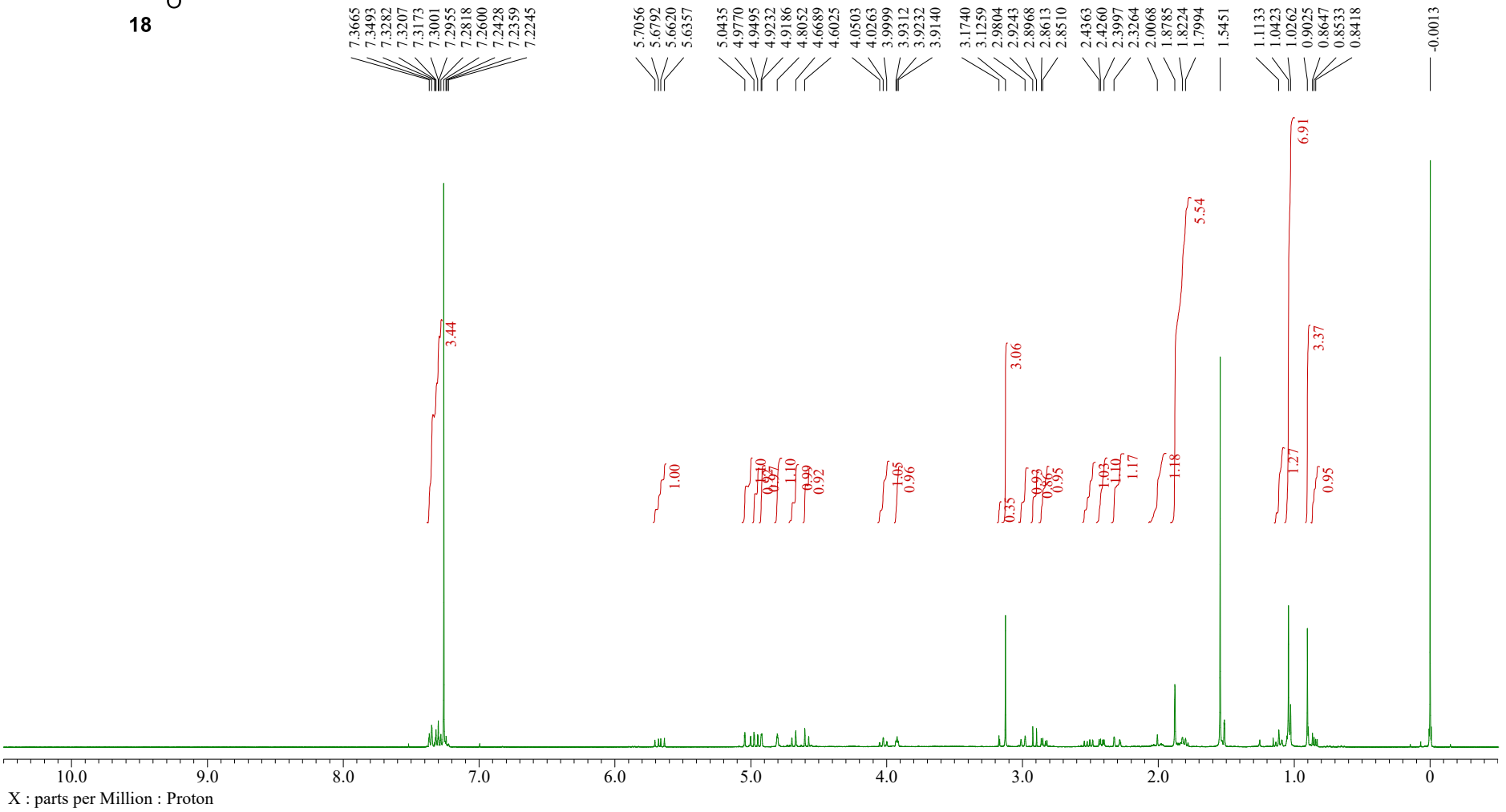
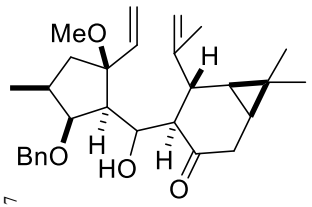


^{13}C NMR (100 MHz, $CDCl_3$)



18

221.1417
146.4383
143.9116
140.0310
128.1509
128.0556
127.2070
113.2103
110.6550
85.0356
84.7972
77.4842
77.1600
76.8454
74.4140
66.5766
58.6915
50.8541
50.5204
46.1345
42.1395
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37.7536
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25.7209
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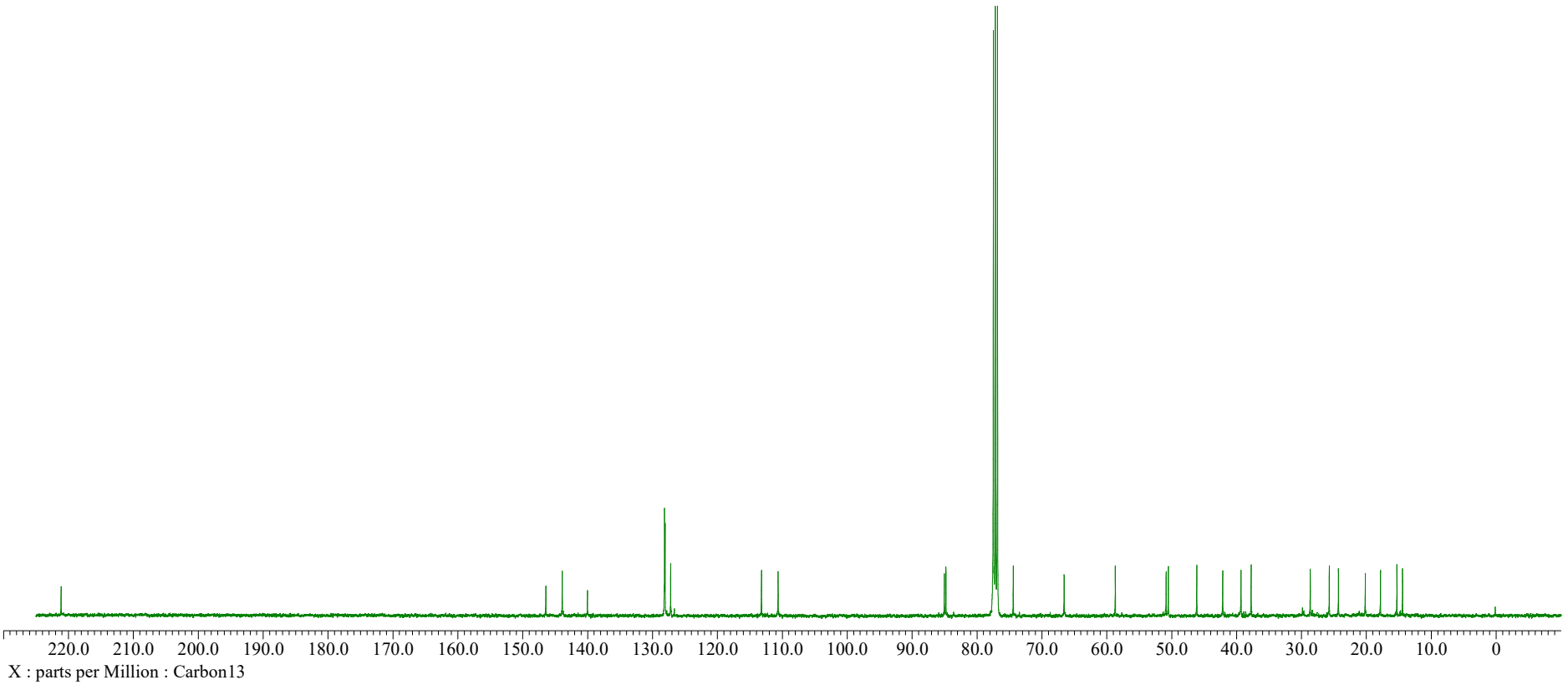
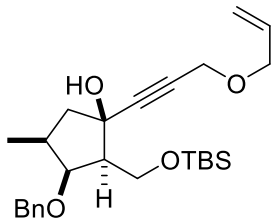
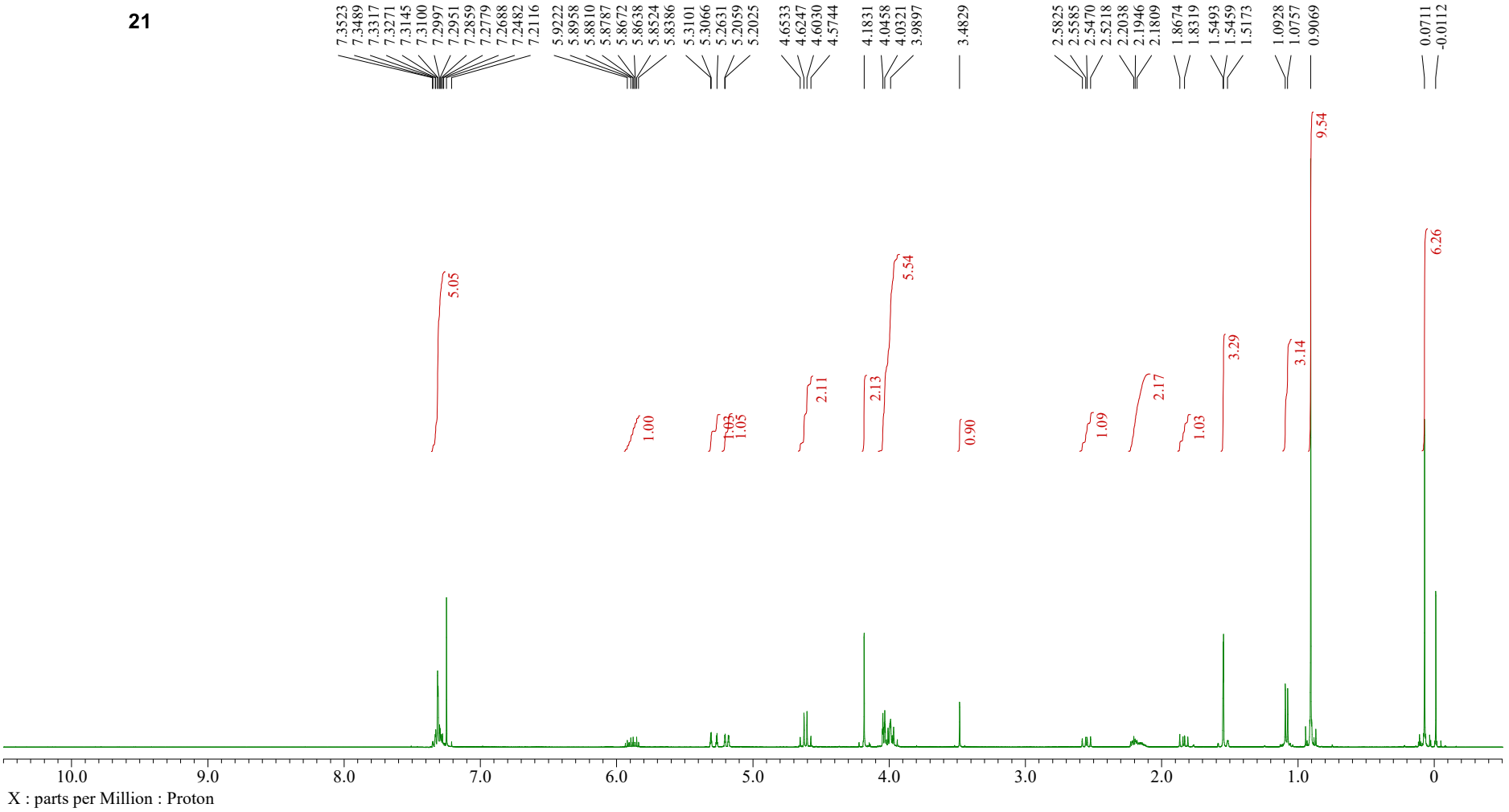
15.2996
14.4320

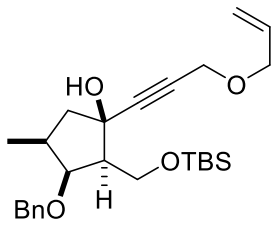




21

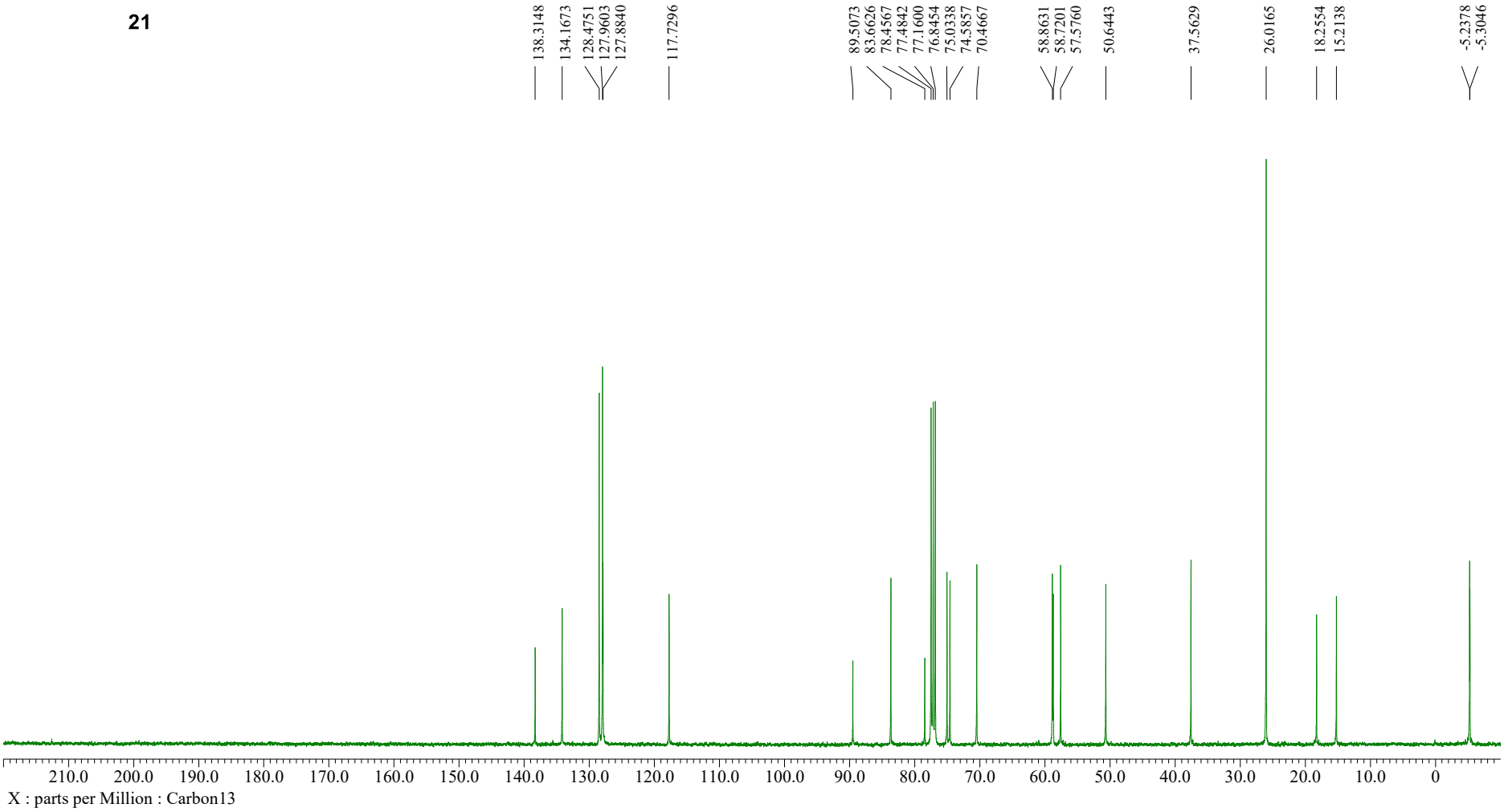
^{1}H NMR (400 MHz, $CDCl_3$)



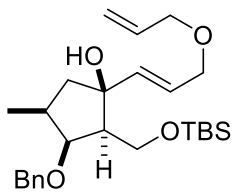


21

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



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



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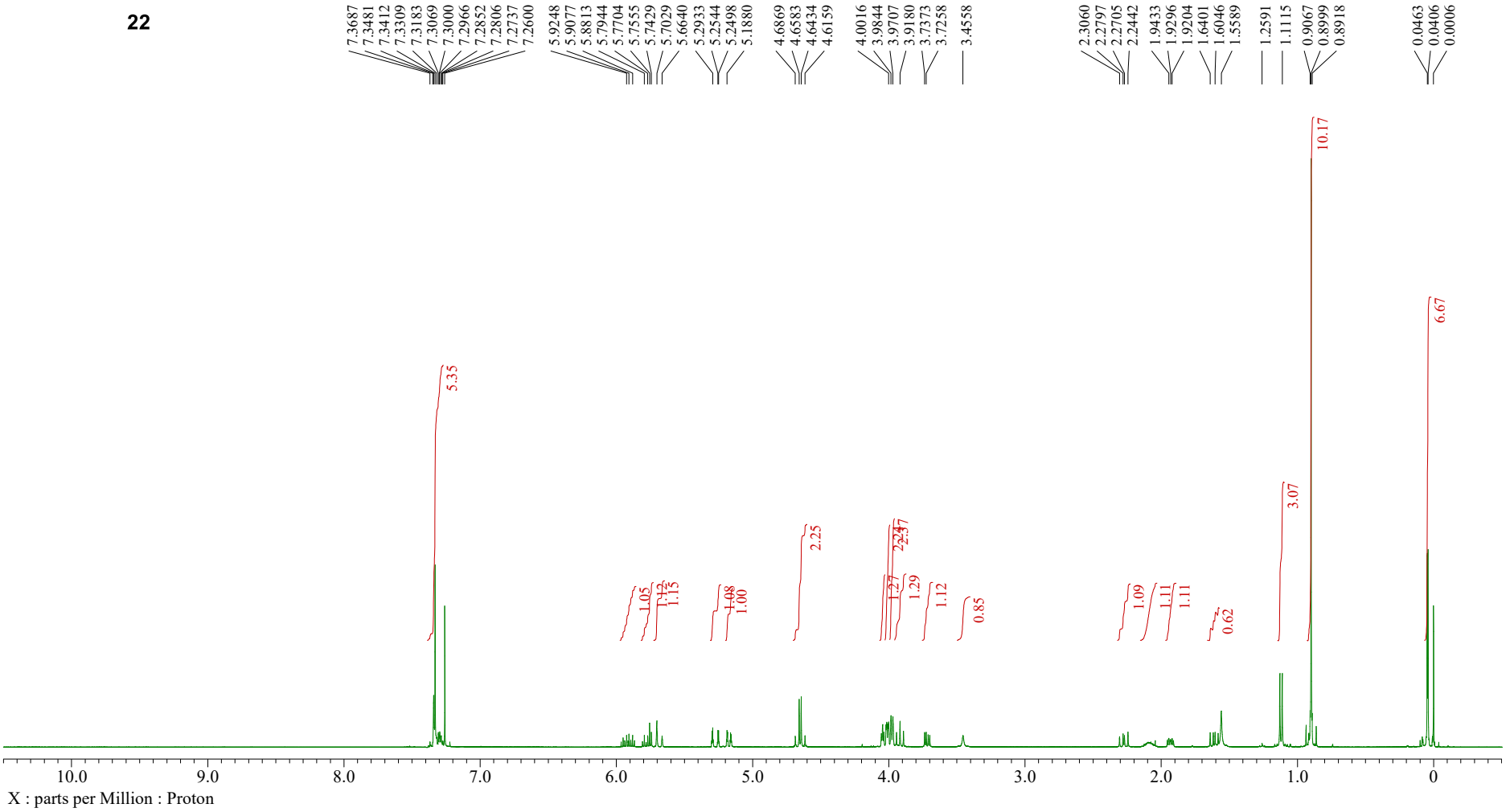
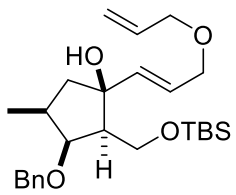


^{13}C NMR (100 MHz, $CDCl_3$)



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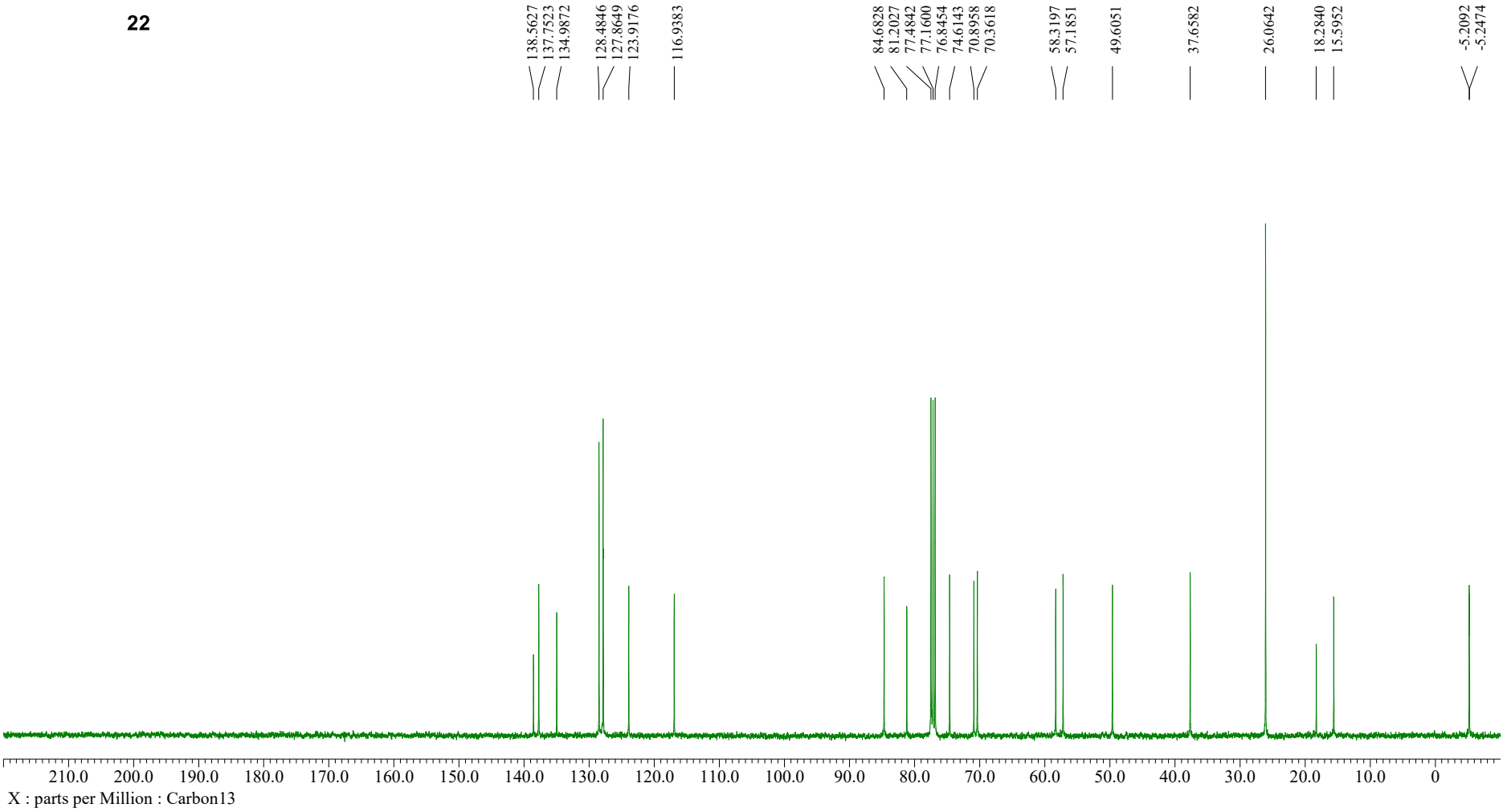
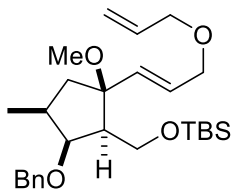
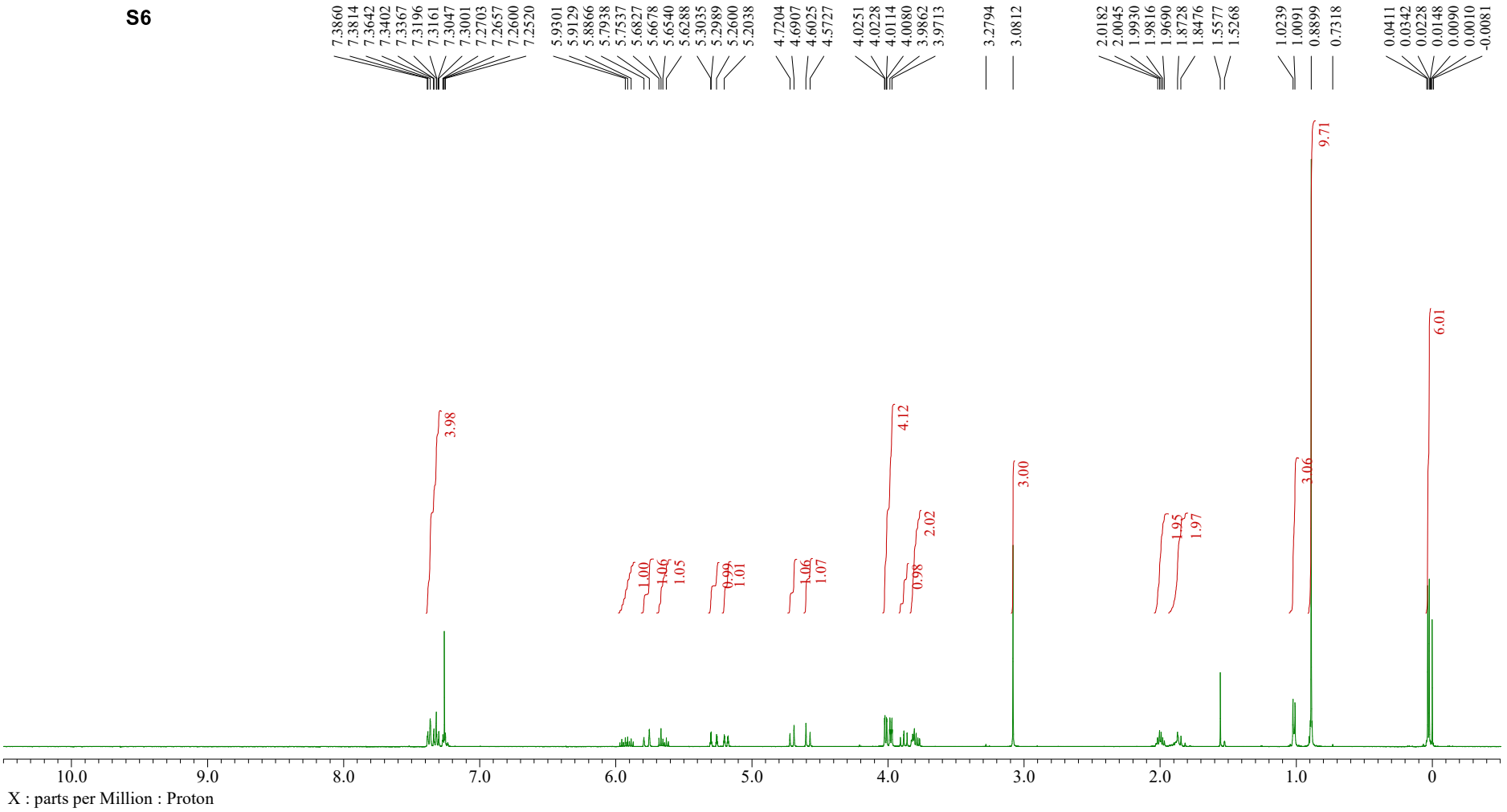


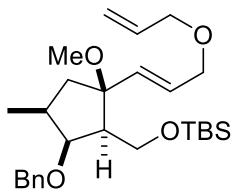
^{1}H NMR (400 MHz, $CDCl_3$)



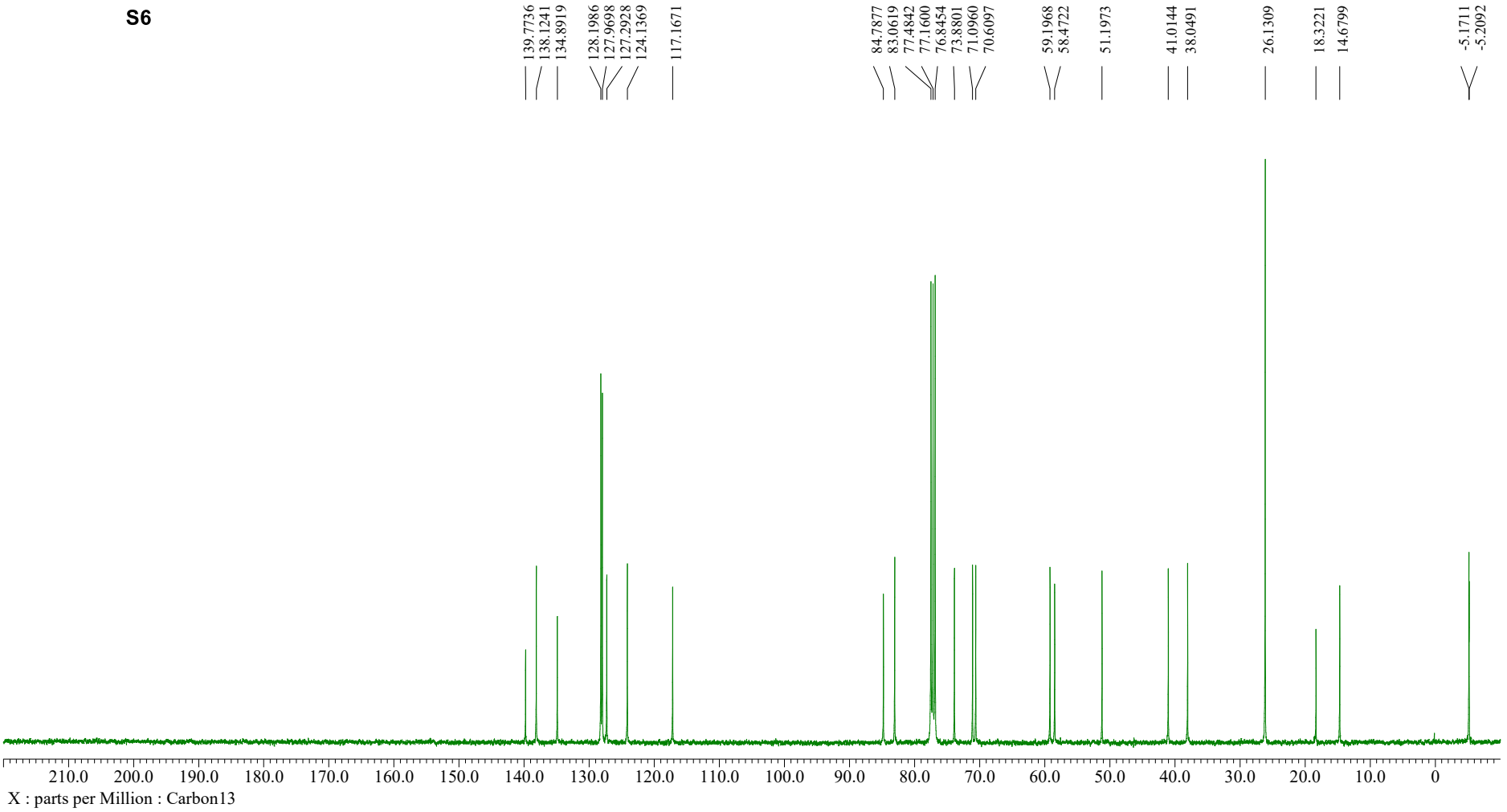
S6



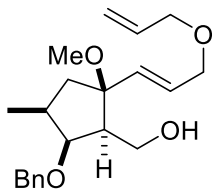
^{13}C NMR (100 MHz, $CDCl_3$)



S6



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



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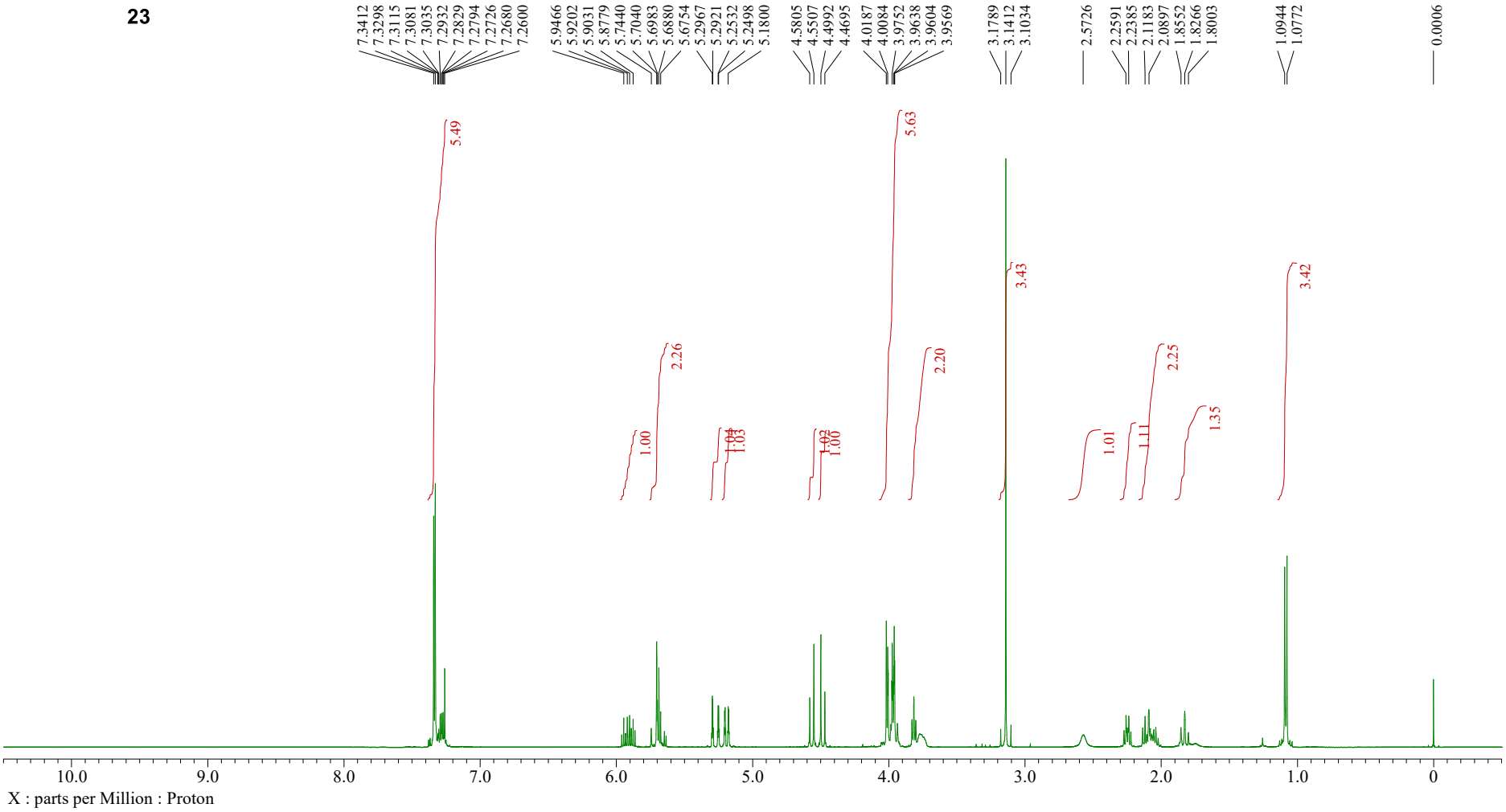
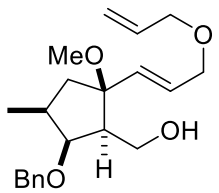


^{13}C NMR (100 MHz, $CDCl_3$)



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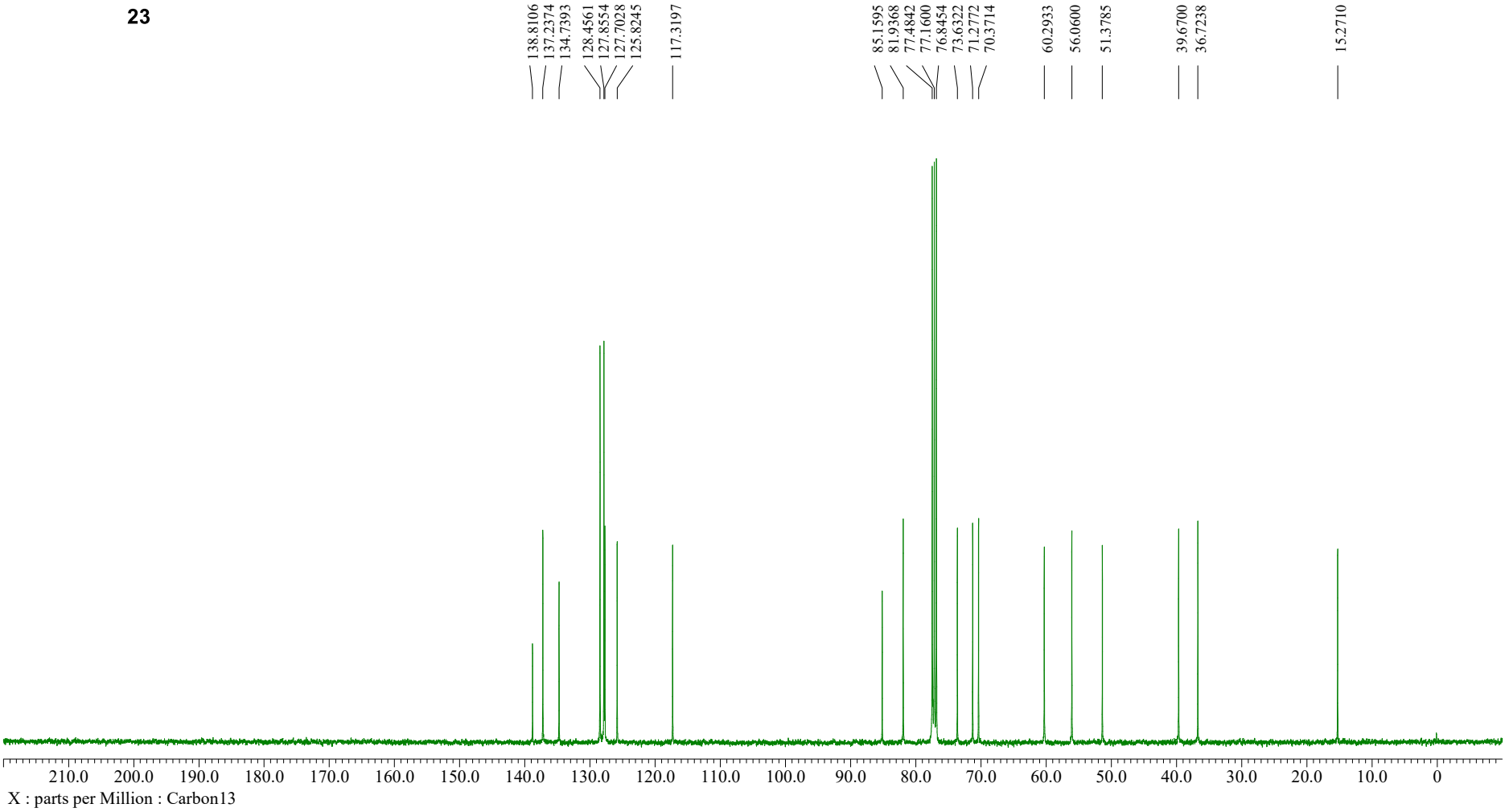
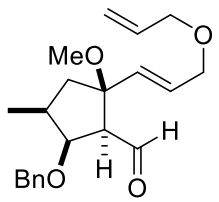
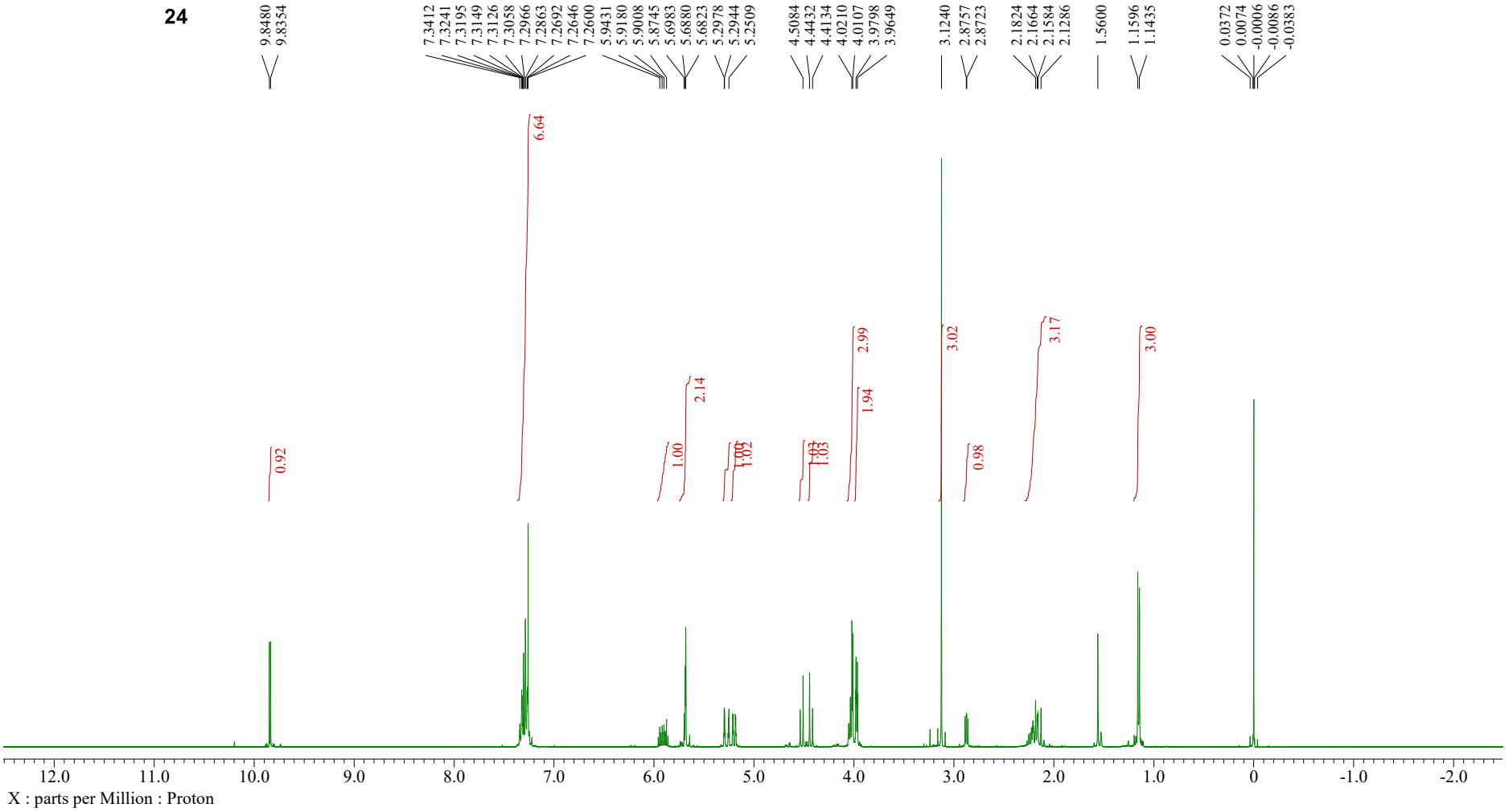


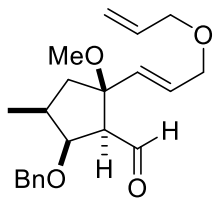
^{1}H NMR (400 MHz, $CDCl_3$)



24

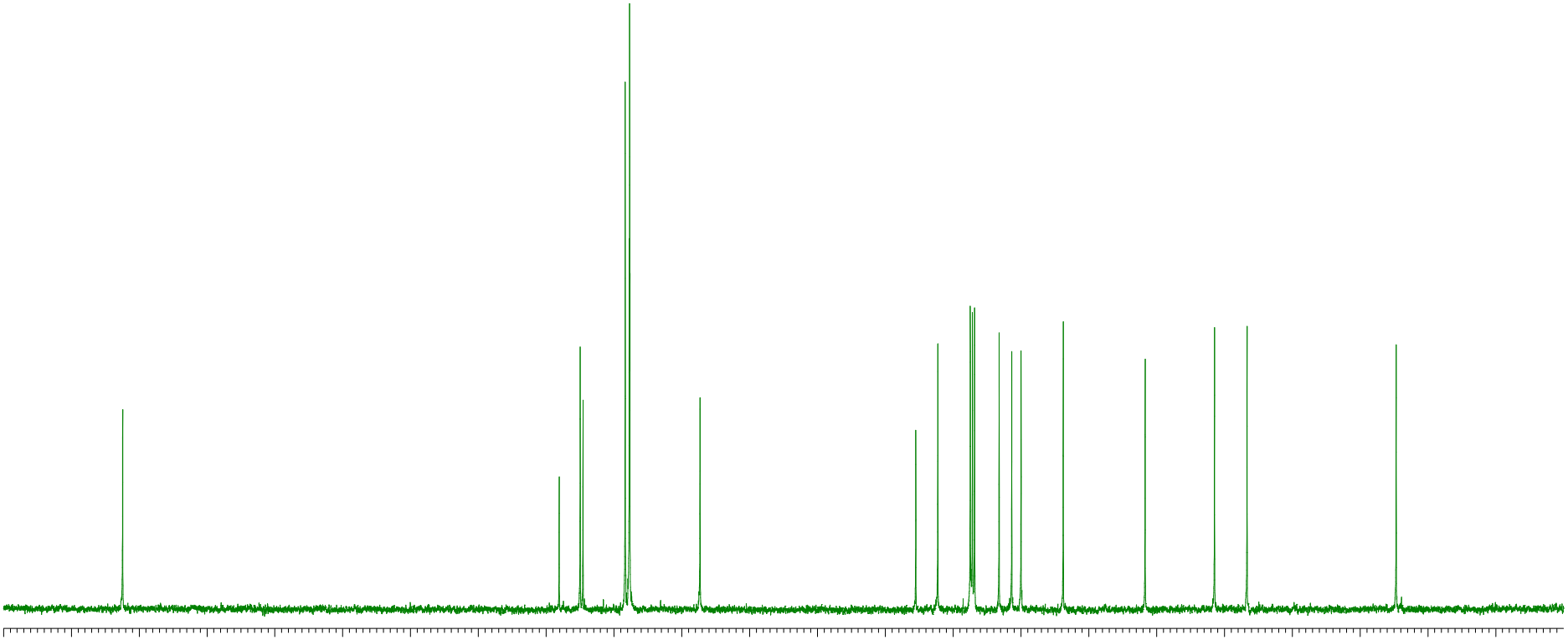


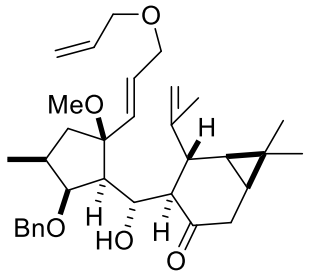
^{13}C NMR (100 MHz, $CDCl_3$)



24

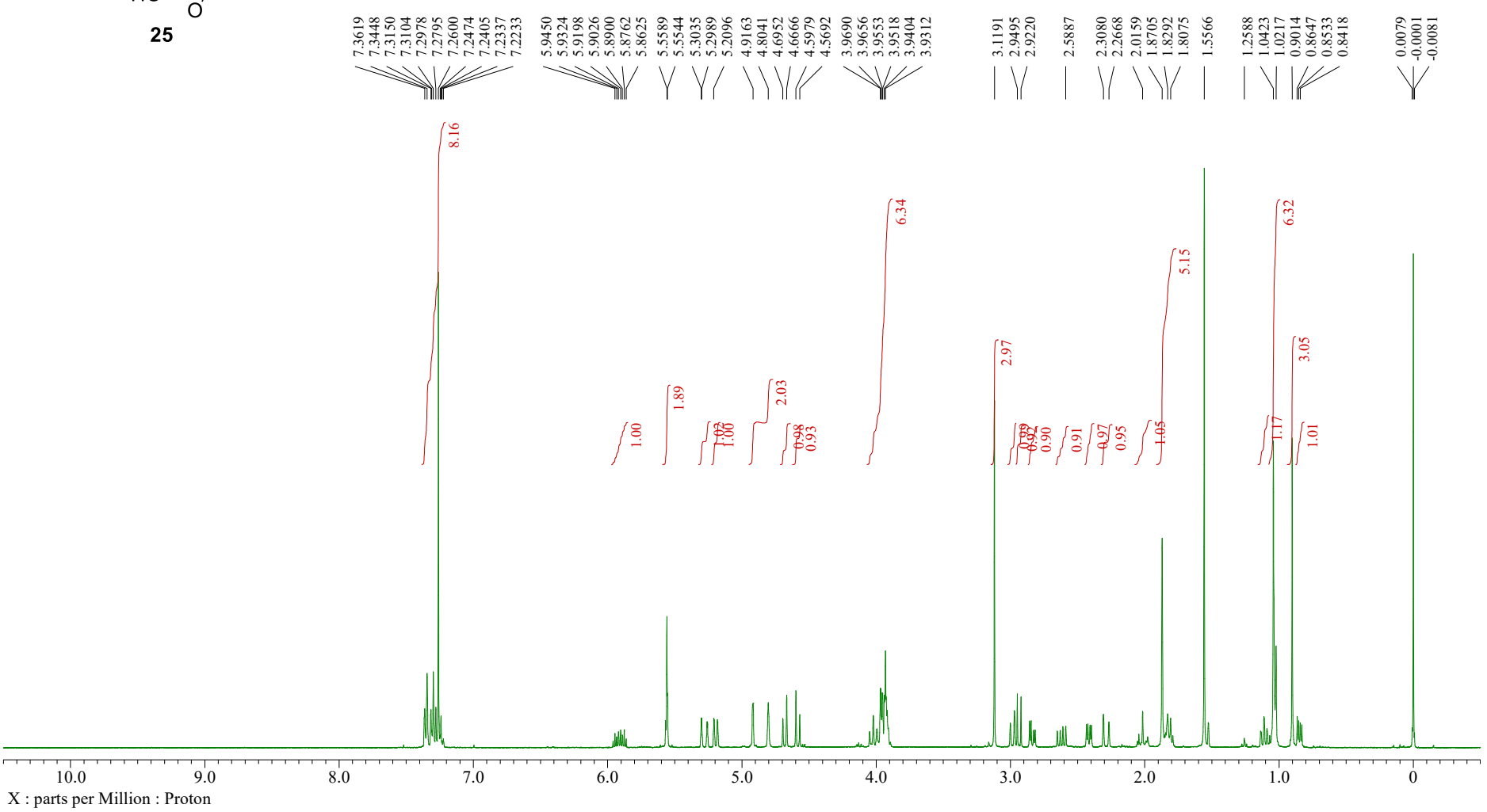
202.4349
138.0860
134.9872
134.5677
128.3512
127.7505
127.7028
127.6551
117.3101
85.5028
82.2515
77.4746
77.1600
76.8358
73.2222
71.3534
69.9805
63.7639
51.6931
41.4625
36.6666
14.6799

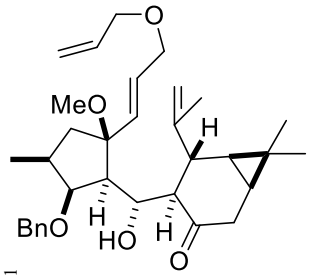




25

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

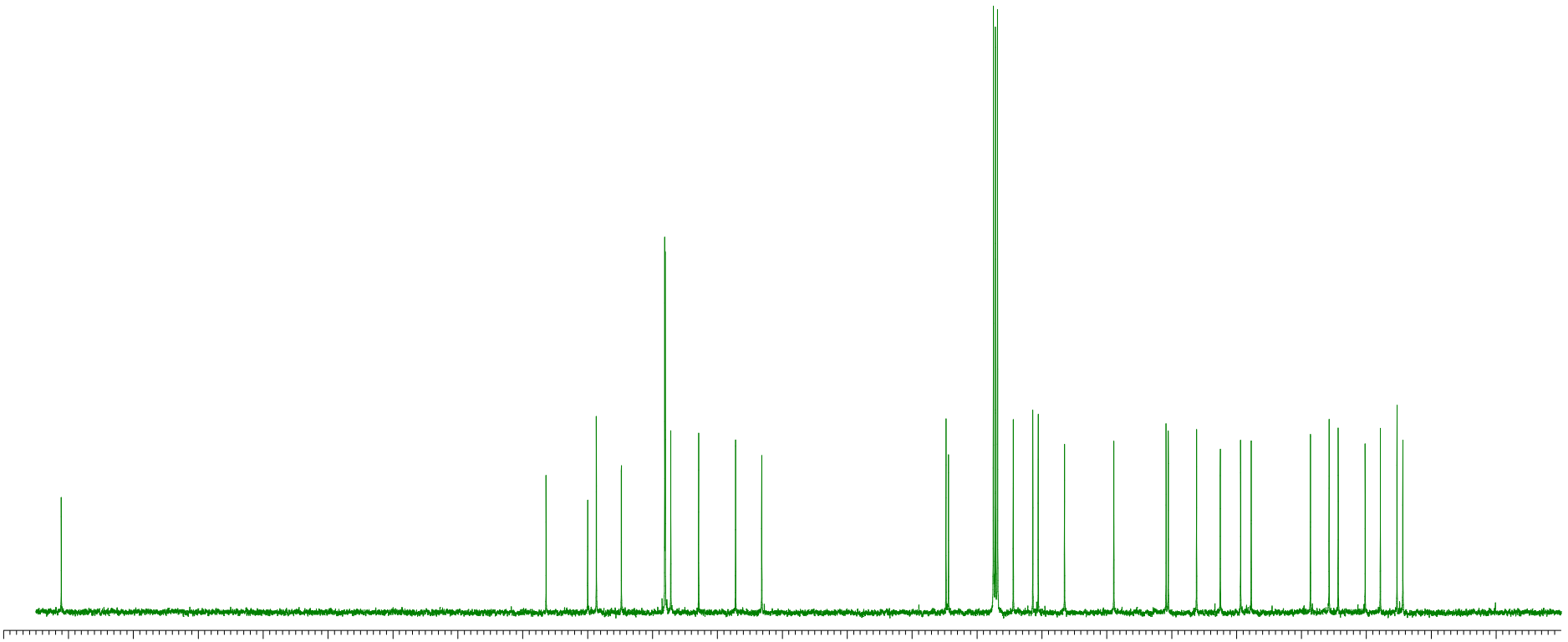




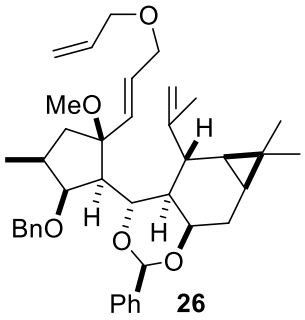
25

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

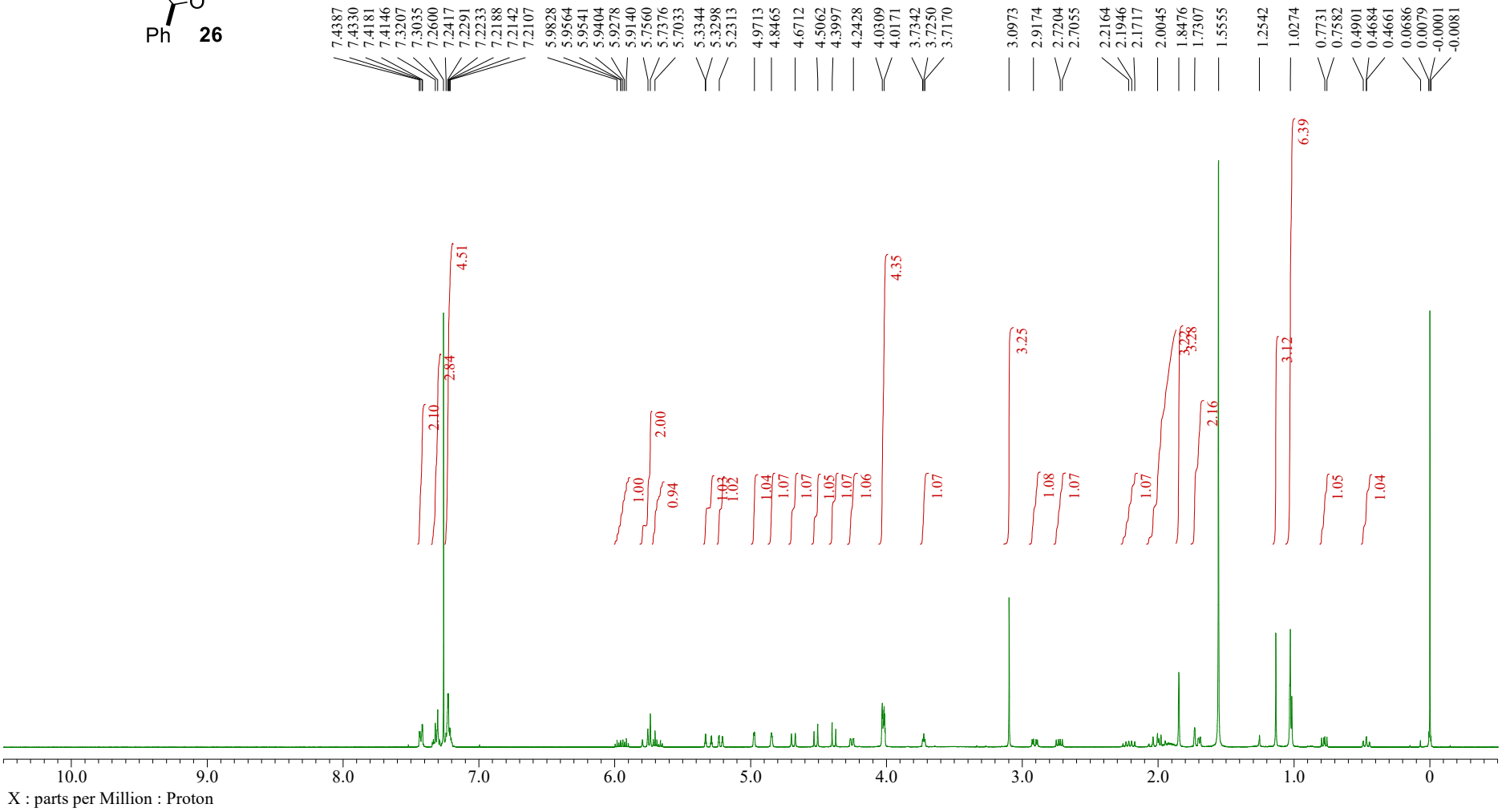
221.1131
146.4097
139.9929
138.6581
134.7965
128.1223
128.0461
127.1880
122.8974
117.2052
113.1721
84.7781
84.3967
77.4746
77.1600
76.8358
74.4140
71.4011
70.5716
66.5194
58.9203
50.8636
50.5299
46.1726
42.5113
39.3840
37.7440
28.6290
25.7495
24.3480
20.1909
17.8454
15.2806
14.3843

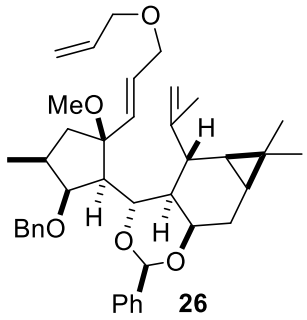


X : parts per Million : Carbon13



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





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

148.1163
140.0215
139.5829
138.8583
134.7775
128.7230
128.2558
127.9793
126.5396
117.3197
112.9719
95.1232
84.7877
83.7579
74.4236
71.5060
71.1055
70.5144
70.2951
53.2377
50.7873
42.7402
38.2780
37.4103
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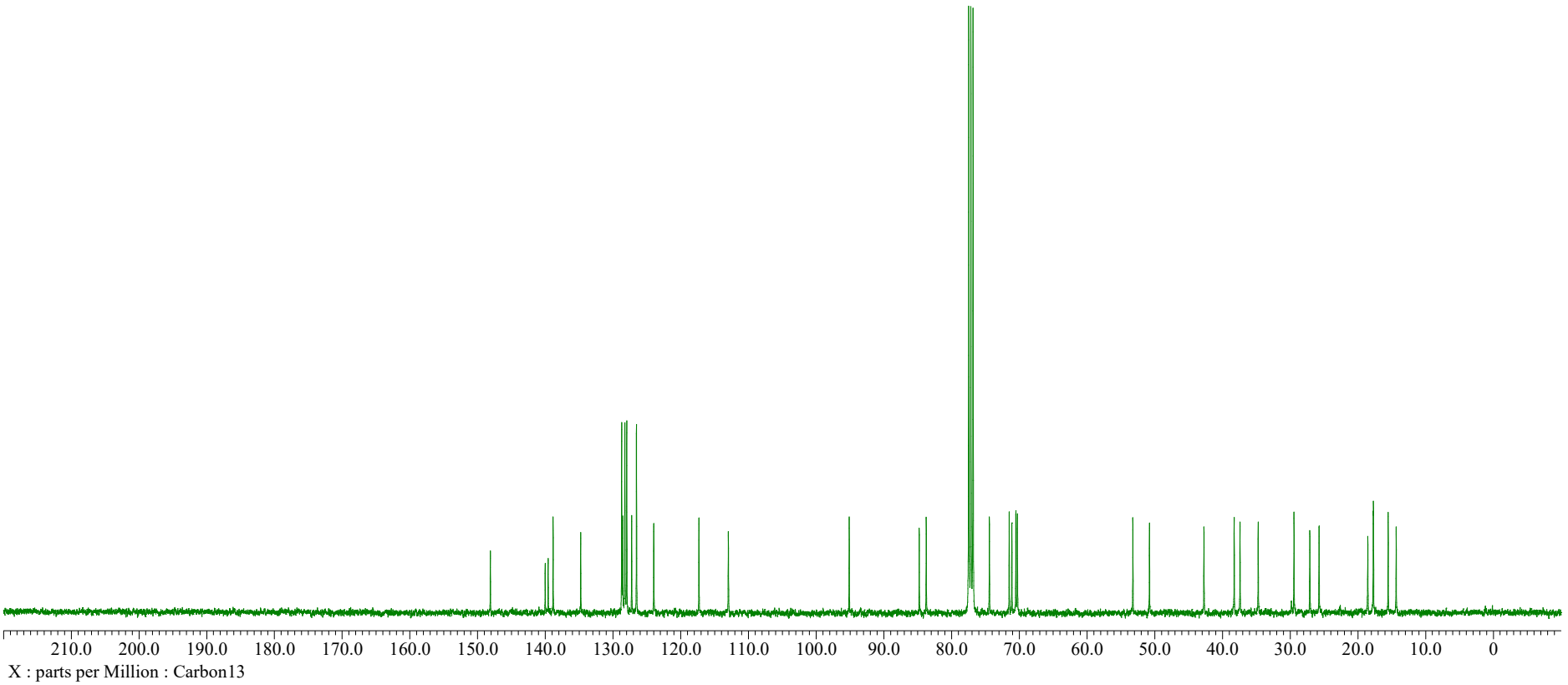
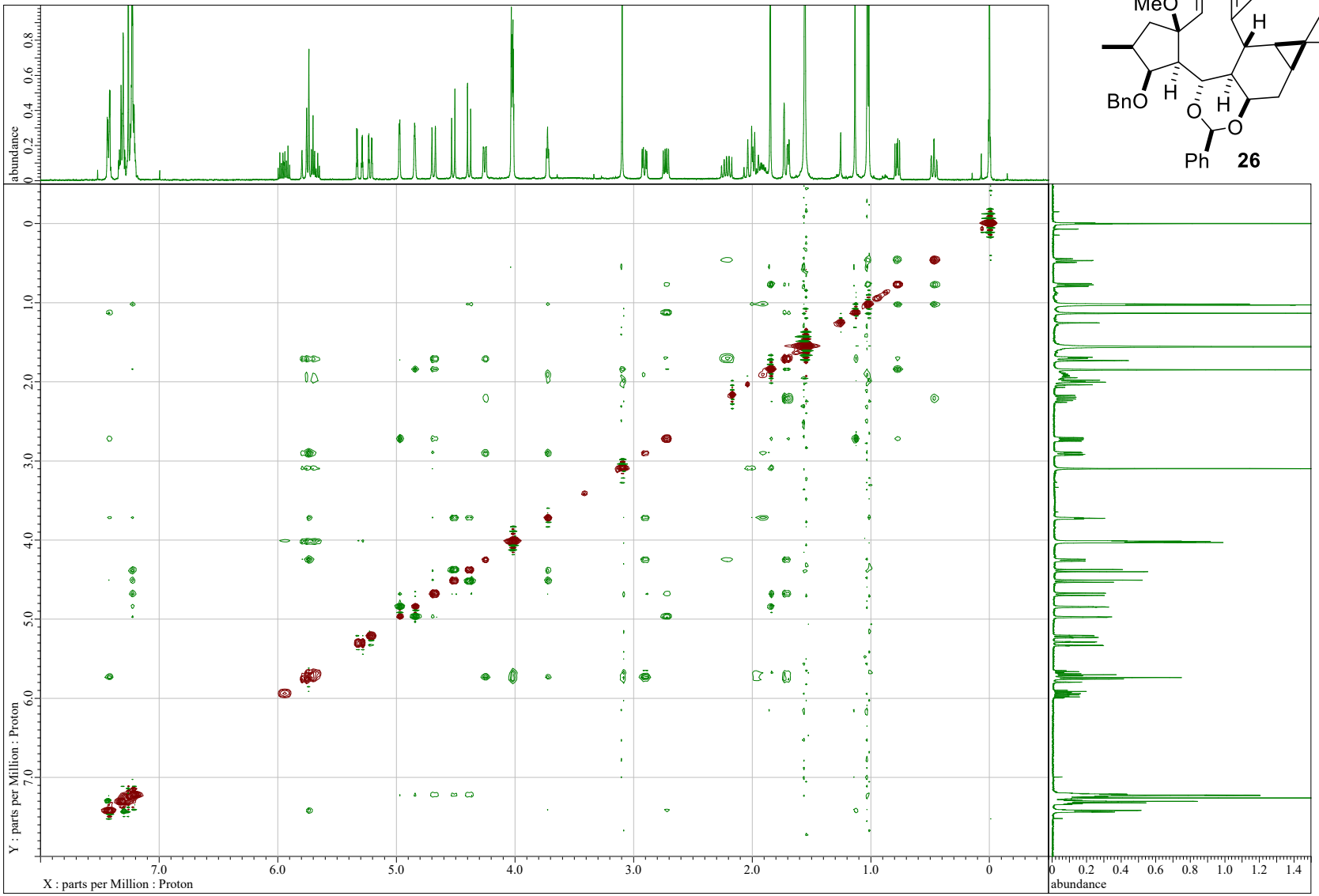
18.5414
17.7500
17.7119
15.5380
14.3557

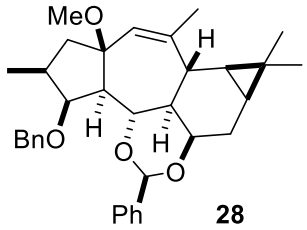


NOESY ($CDCl_3$)

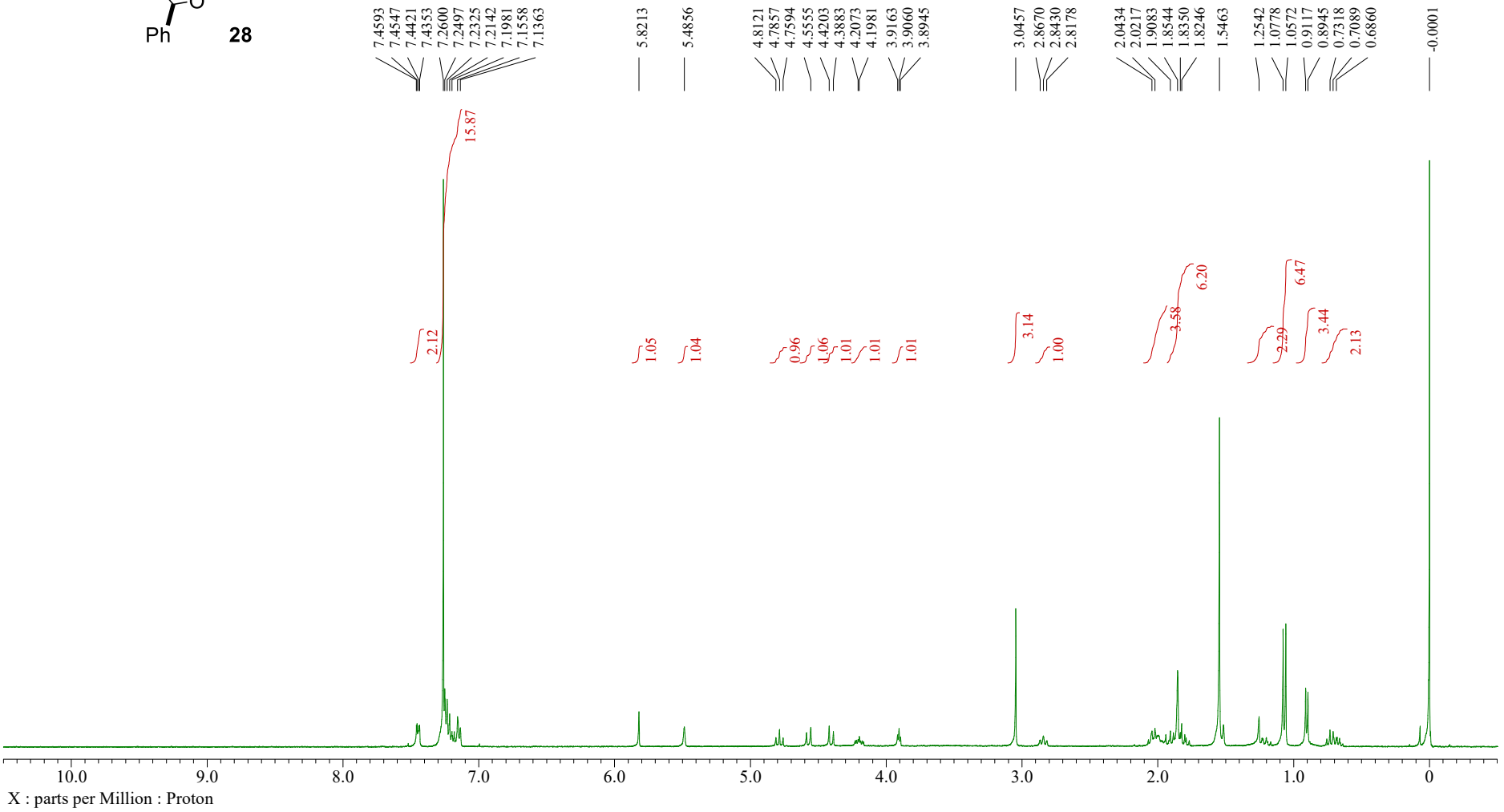


26

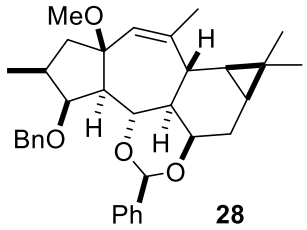
^{1}H NMR (400 MHz, $CDCl_3$)



28



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



28

143.6923
140.3552
131.4213
129.1711
128.7230
128.2749
127.9126
127.7028
126.7780
126.5301
97.5831
84.1775
82.9380
77.4842
77.1600
76.8454
76.5498
73.4129
68.6456
59.0443
50.0341
45.5624
42.8736
37.4675
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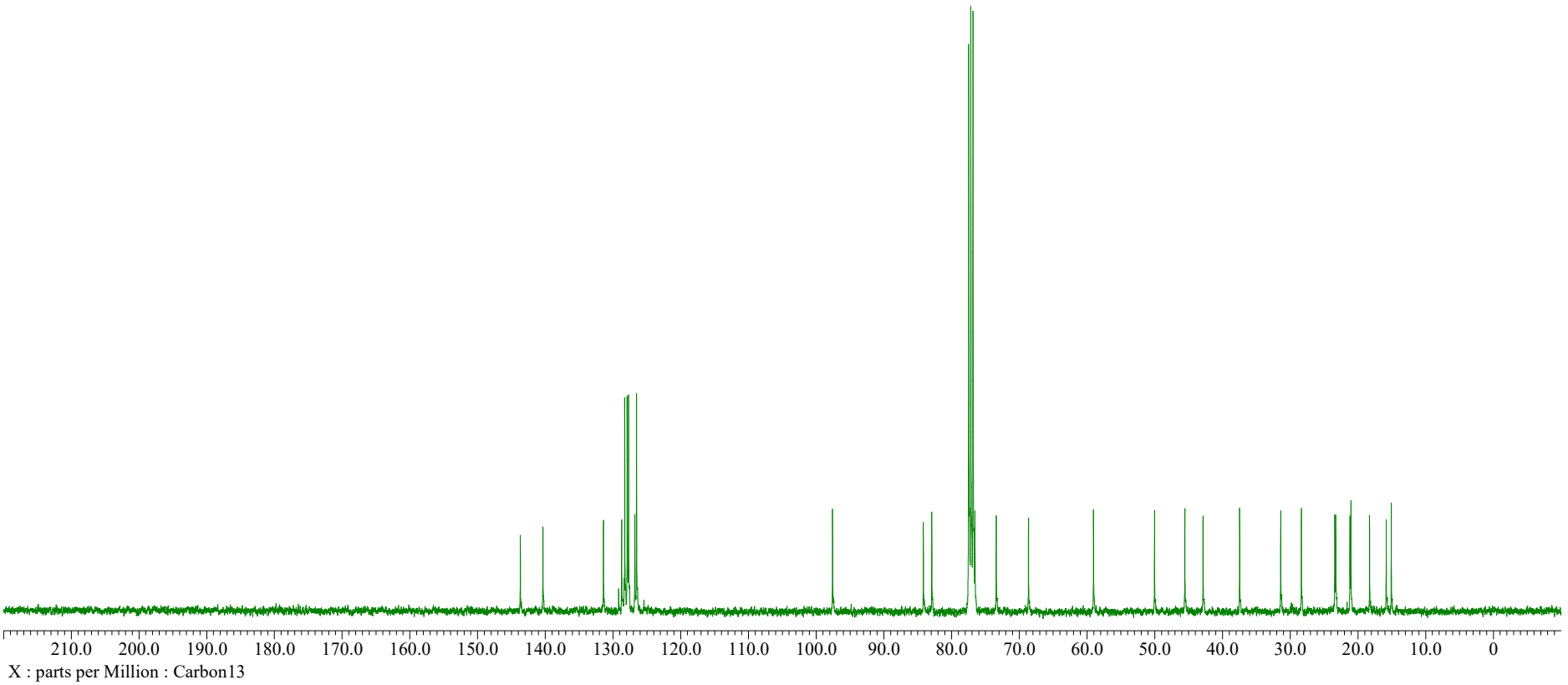
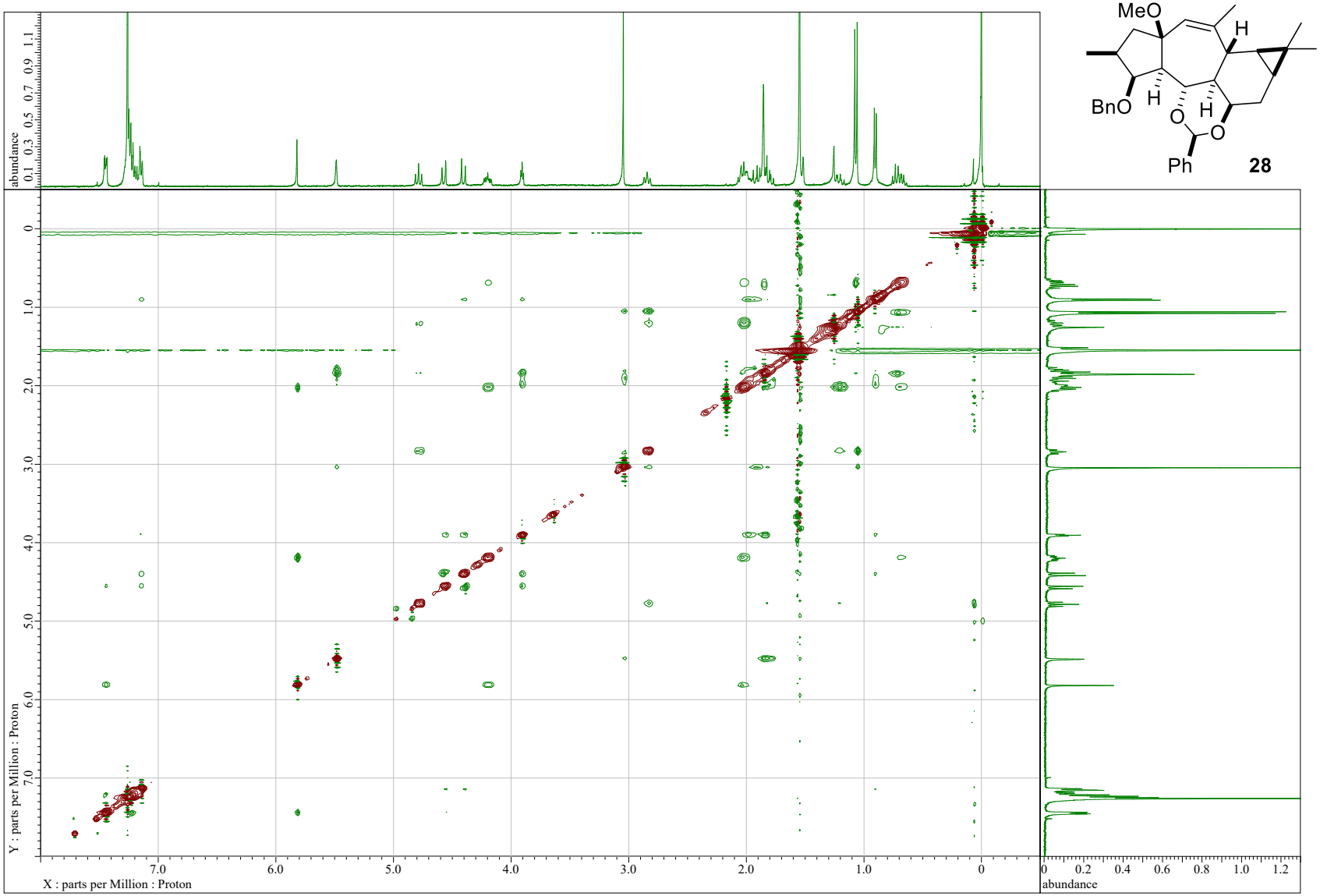
23.2705
21.1825
21.0395
18.2840
15.8240
15.0803

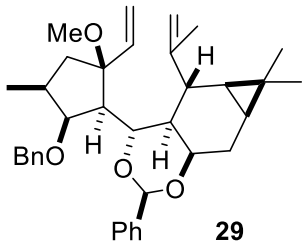


NOESY ($CDCl_3$)

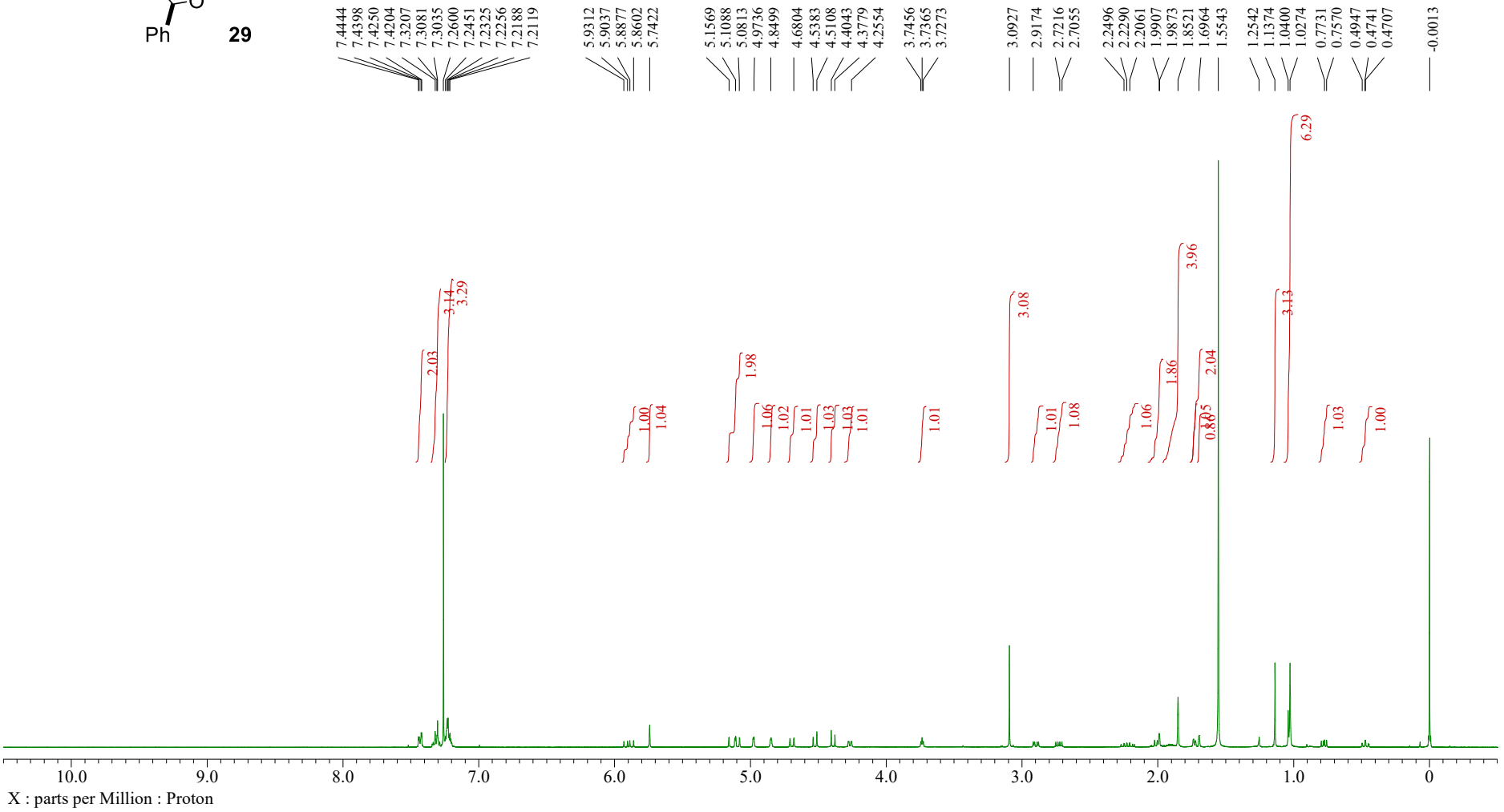


28

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

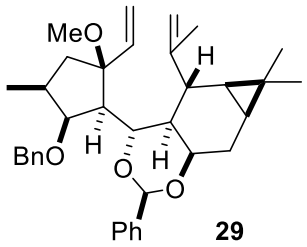


29



X : parts per Million : Proton

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



29

148.1450
144.2644
140.0406
139.6210
128.7325
128.5705
128.2463
127.9698
126.5491
112.9624
111.7991
95.1518
85.3407
83.8819
77.4746
77.1600
76.8358
74.4236
71.1341
70.2856
53.1233
50.7206
42.2444
38.3352
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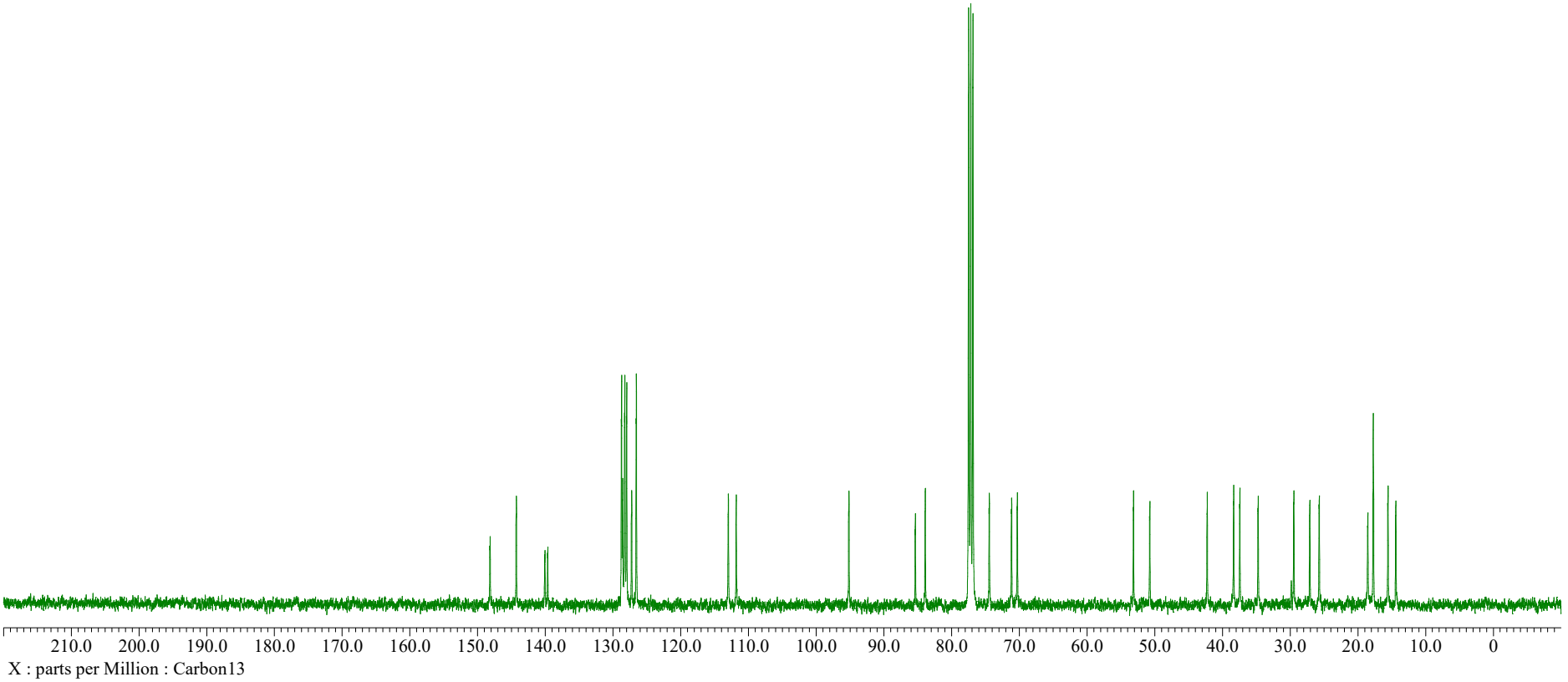
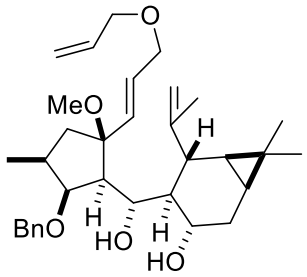
25.7019
18.5319
17.7310
15.5475
14.3939

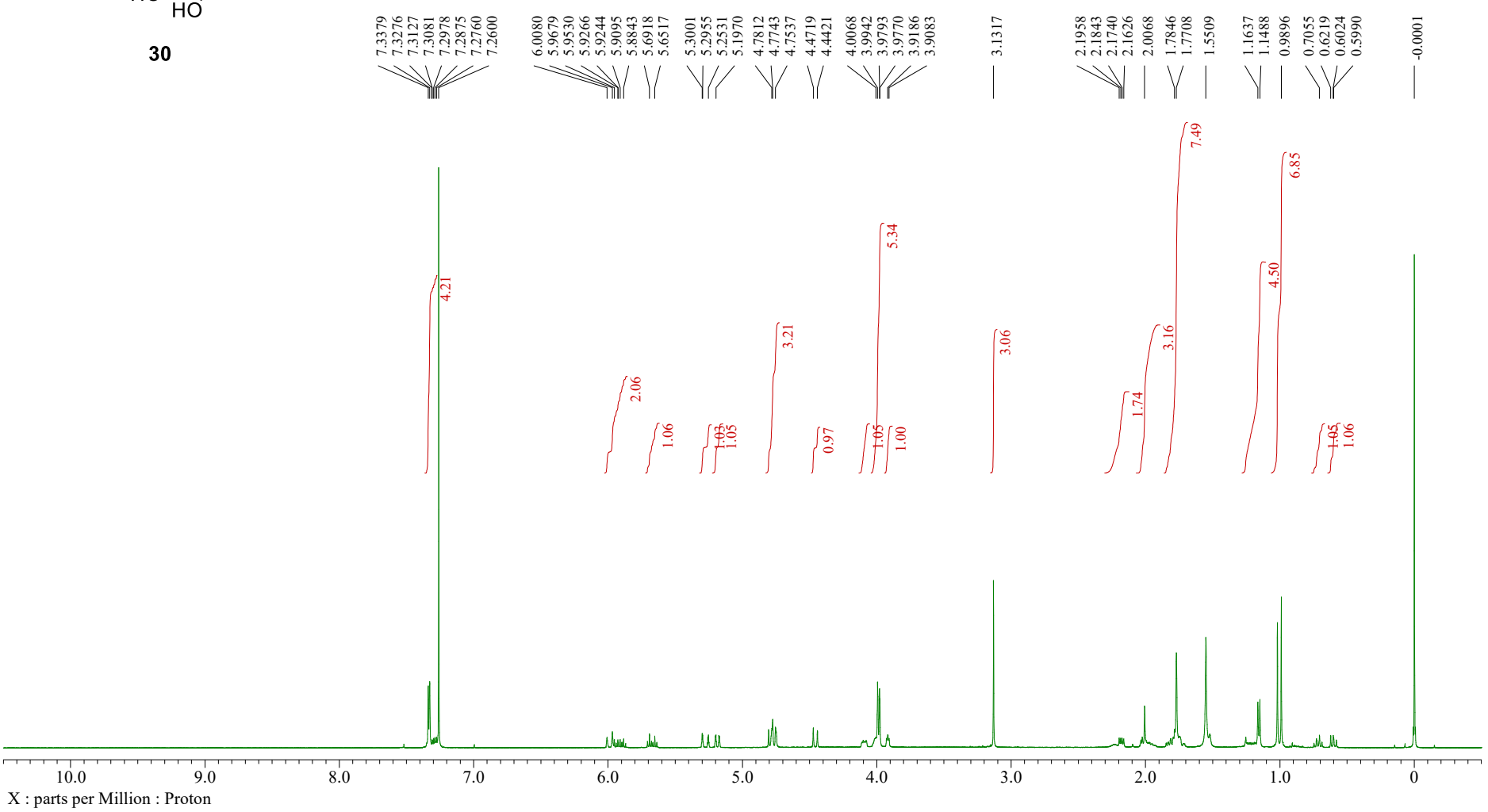


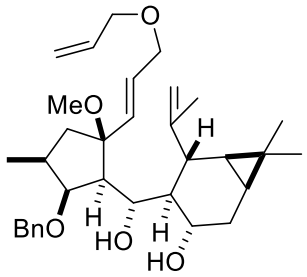
X : parts per Million : Carbon13



30

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

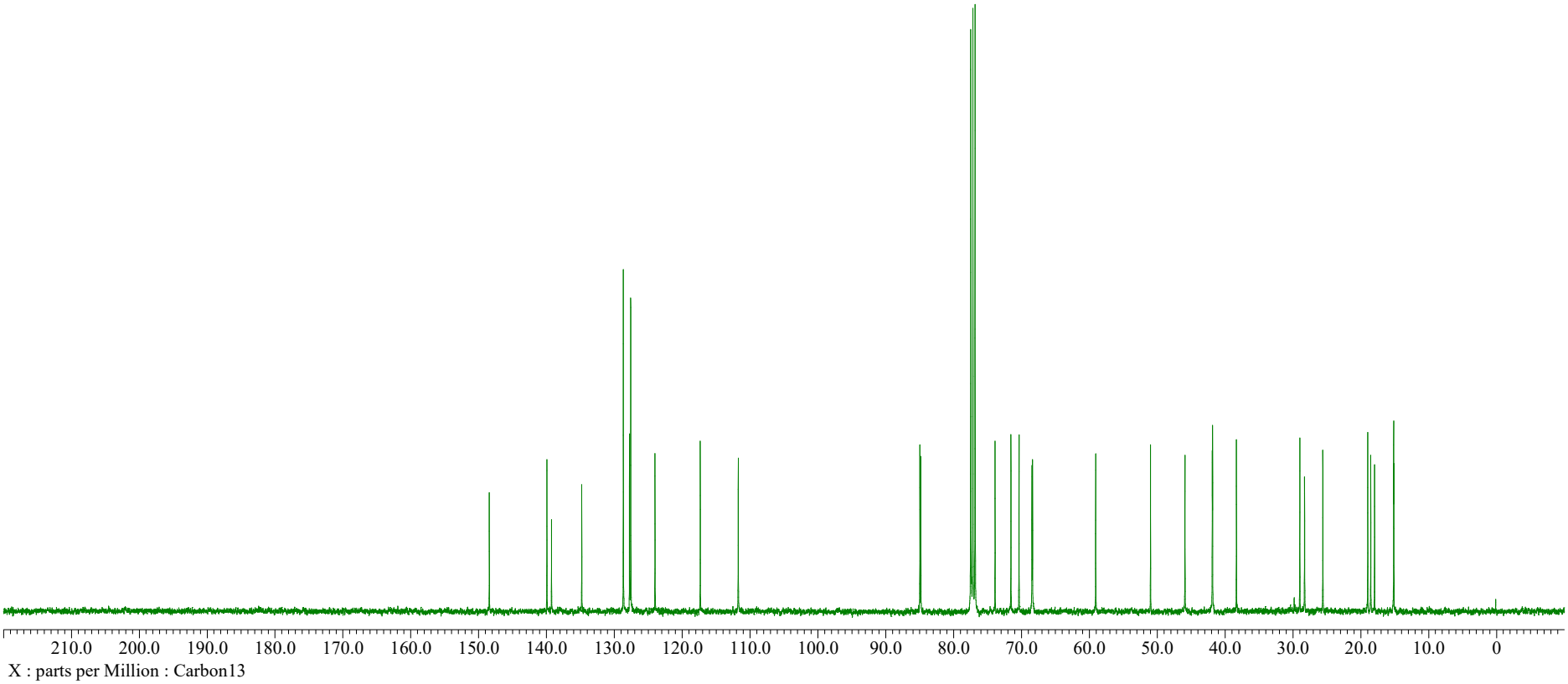


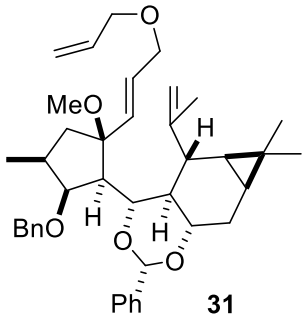


30

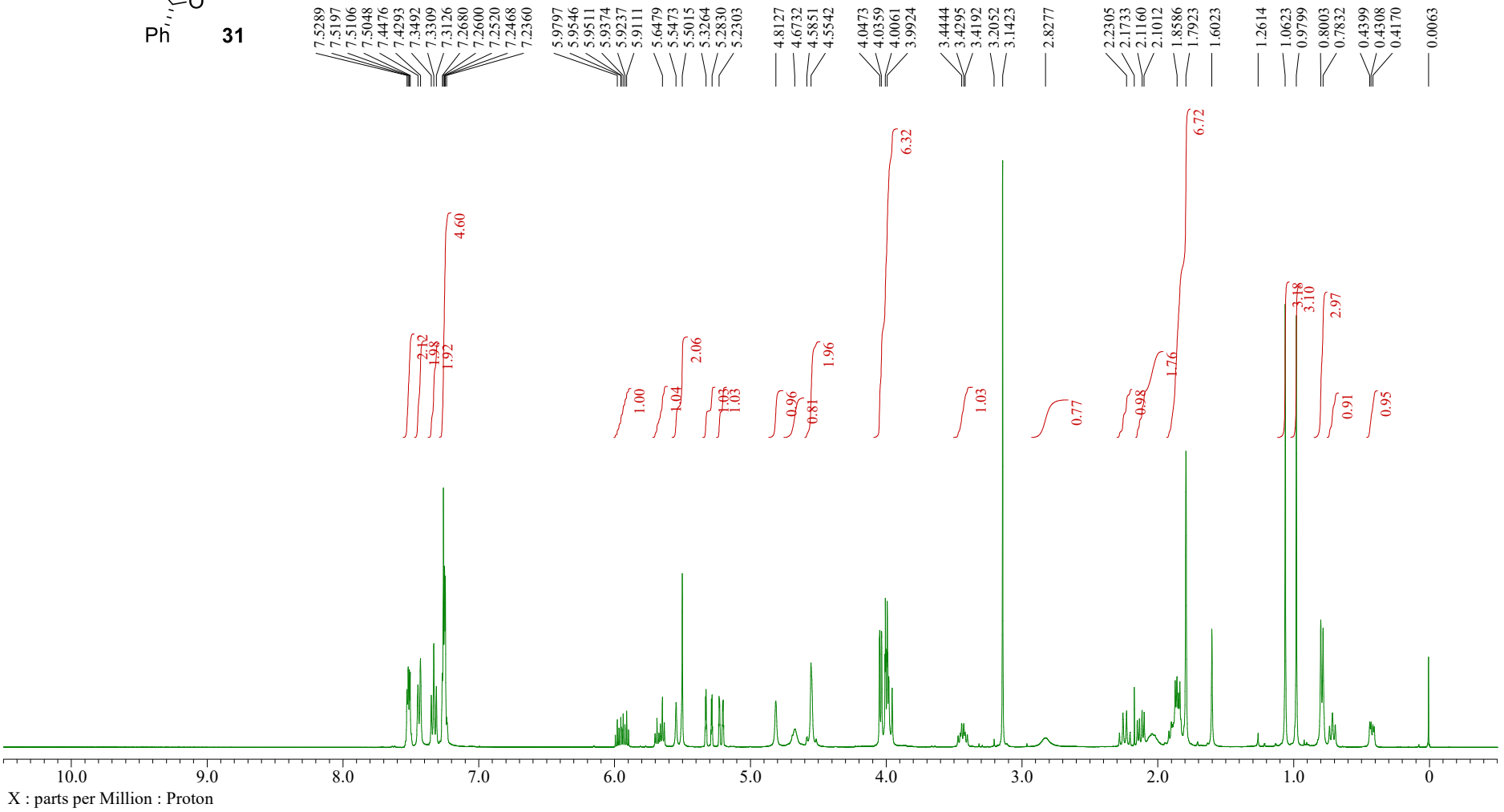
^{13}C NMR (100 MHz, $CDCl_3$)

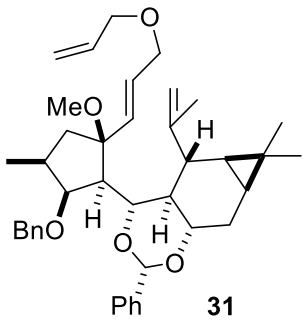
148.4310
139.9357
139.2587
134.8061
128.6753
127.7600
127.5884
124.0129
117.3387
111.7419
84.9784
84.8353
77.4842
77.1600
76.8454
73.8992
71.5632
70.3714
68.3786
59.0634
50.9876
45.9152
41.8820
41.8439
38.3352
28.9913
28.2857
25.5970
18.9800
18.5414
17.9789
15.1566
15.1280





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





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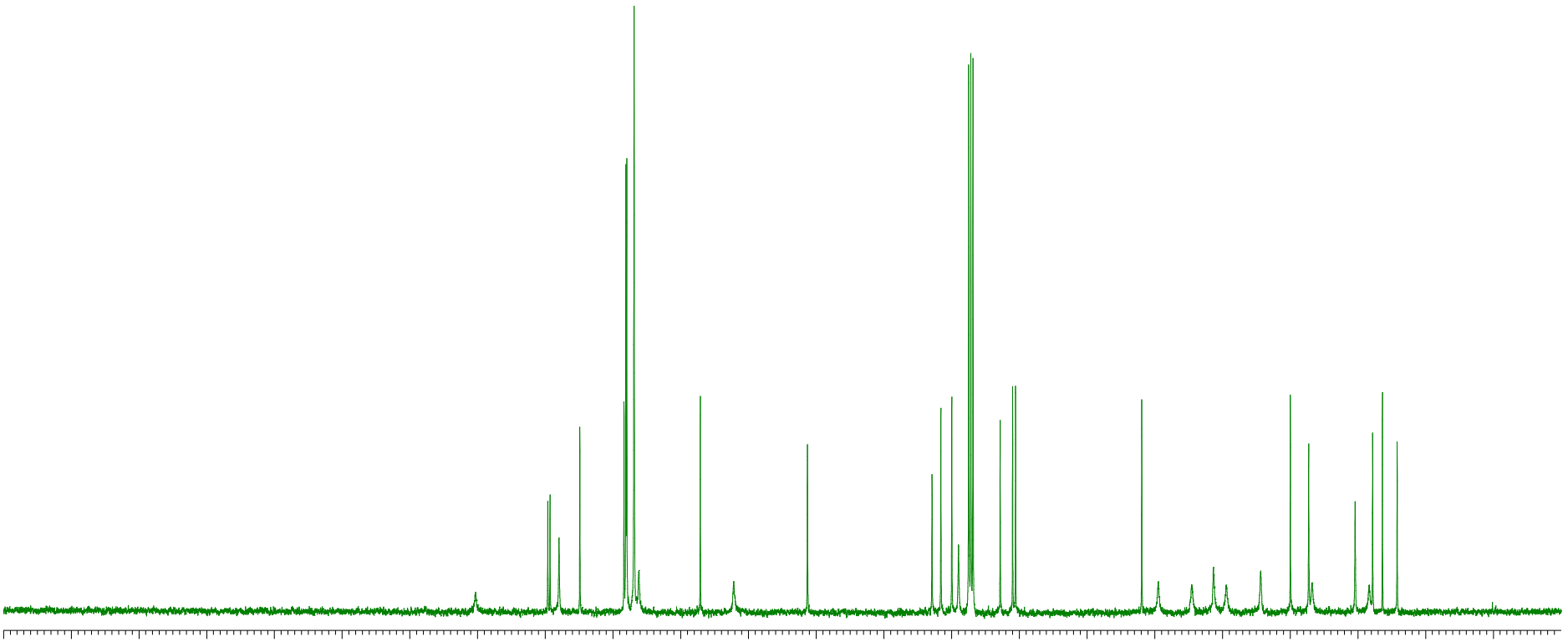
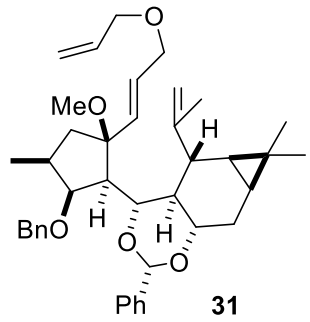
^{13}C NMR (100 MHz, $CDCl_3$)

150.2903
139.6306
139.3064
137.9811
134.9014
128.3798
128.1128
127.9698
126.8829
117.1194
112.1615
101.2920
82.8903
81.5840
79.9727
78.9811
77.4842
77.1600
76.8454
72.8313
70.9911
70.5525
51.9220
49.4716
41.3386
39.3649
34.3593
29.9734
27.2655
26.7697
20.4197
18.3221
17.8263
16.3770
14.2127



X : parts per Million : Carbon13

NOESY ($CDCl_3$)



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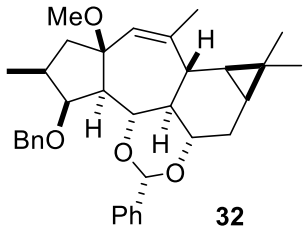
^{1}H NMR (400 MHz, $CDCl_3$)



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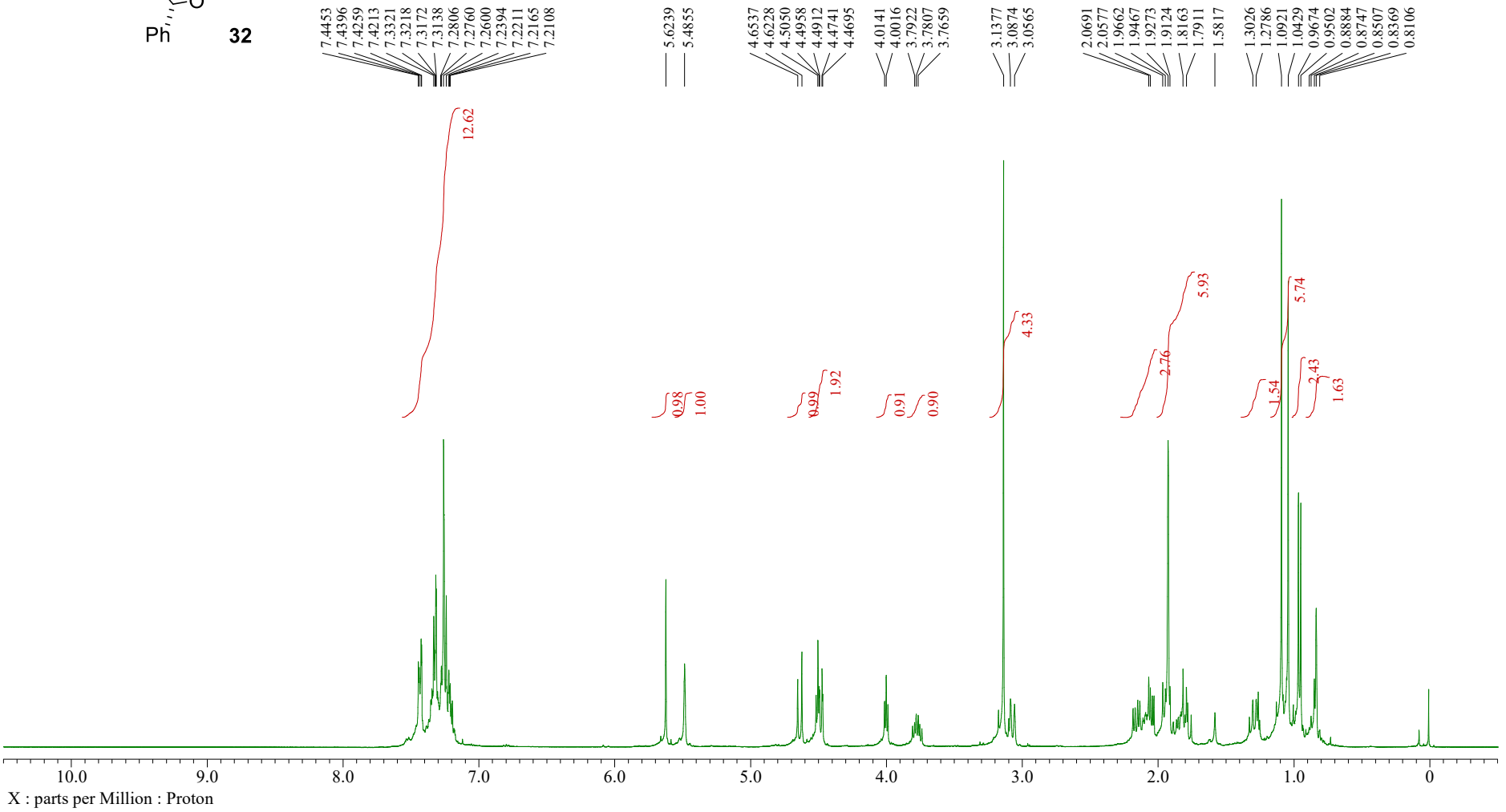
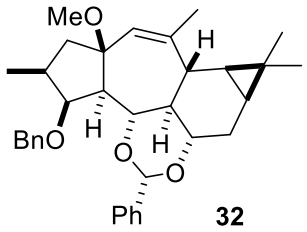


^{13}C NMR (100 MHz, $CDCl_3$)



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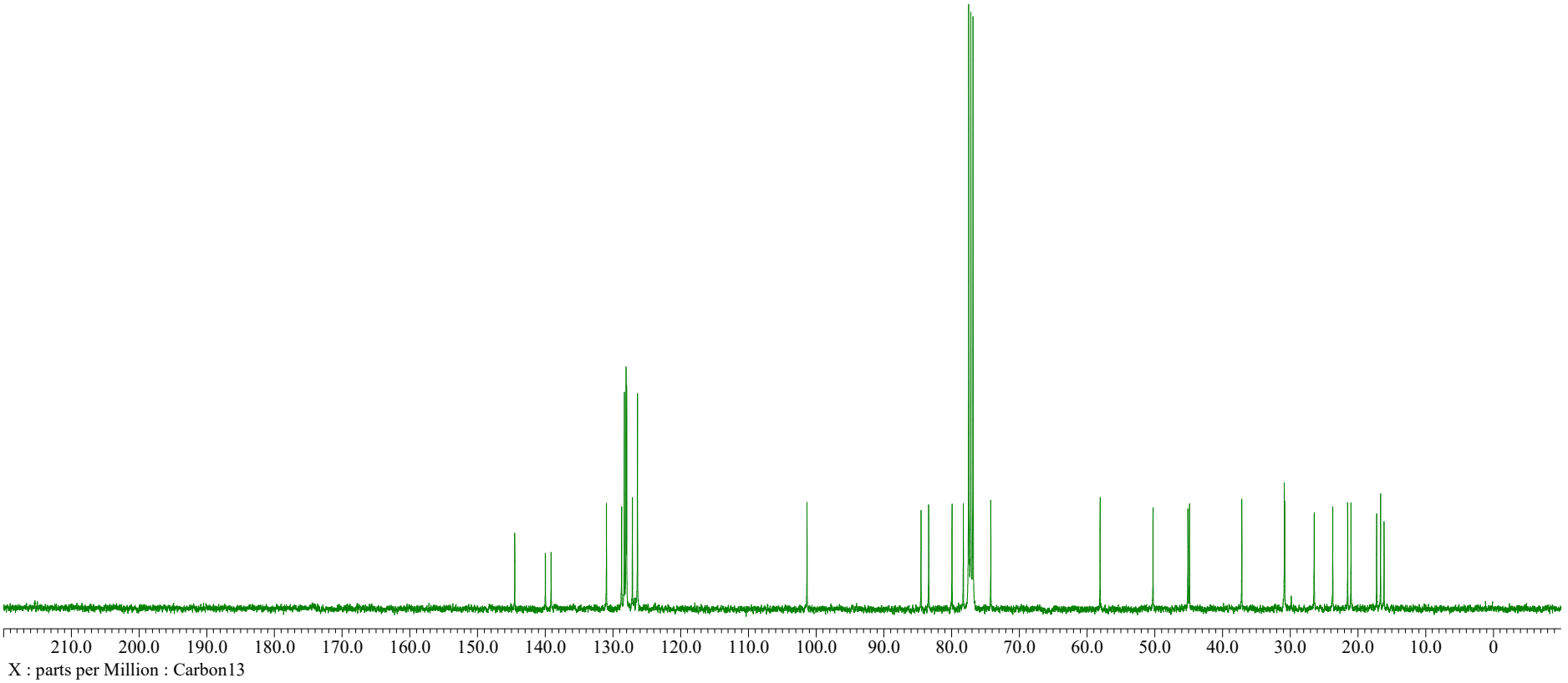
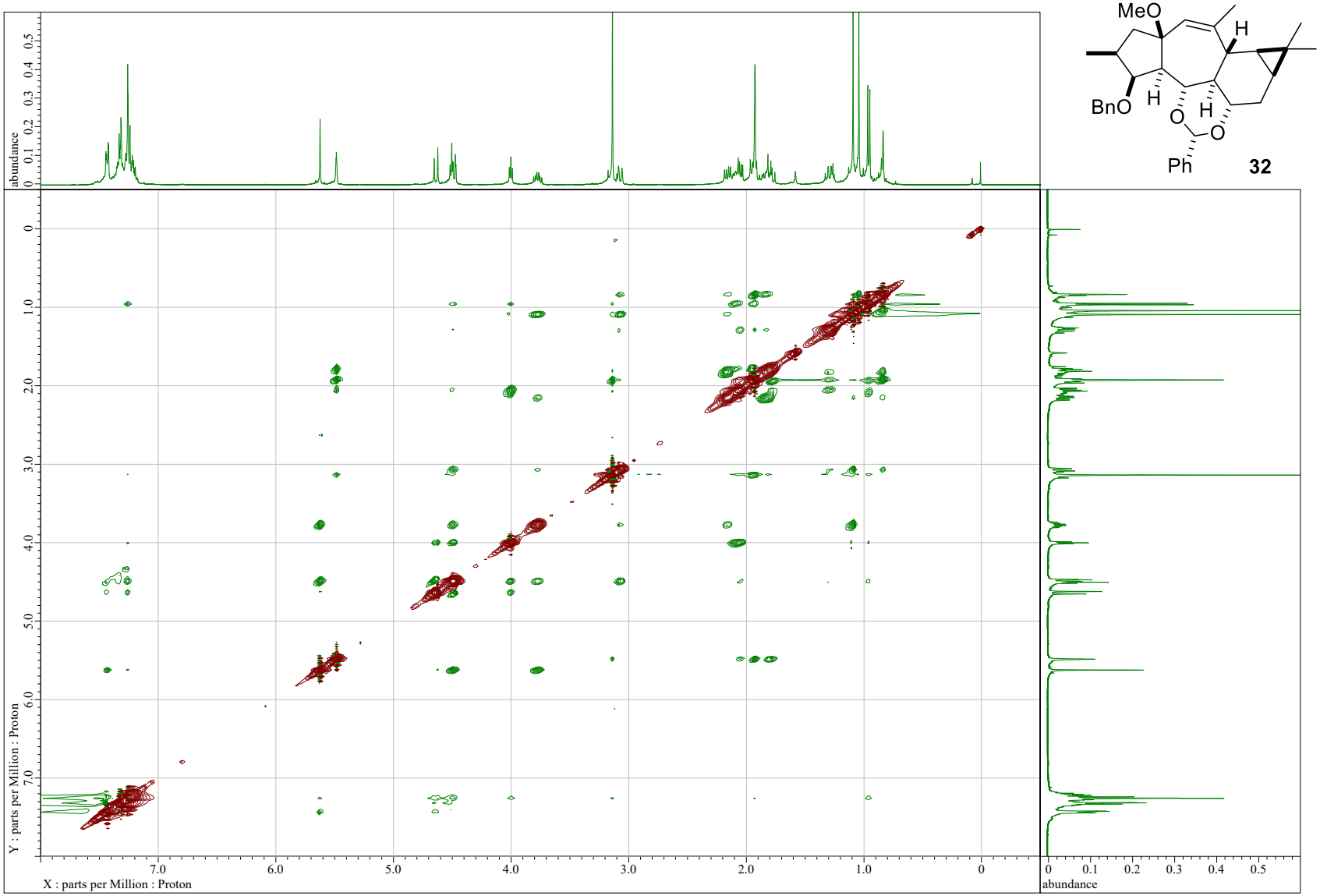
144.5123
139.9929
139.1443
130.9732
128.7325
128.3226
128.0842
127.9889
127.1403
126.3870
101.3492
84.5207
83.3861
79.9441
78.2755
77.4746
77.1600
76.8358
74.2138
58.0718
50.2534
45.1047
44.8664
37.1434
30.8696
30.8124
26.4551
23.7187
21.5162
21.0204
17.2352
16.6535
16.1387



NOESY ($CDCl_3$)



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