Supporting Information

Total Synthesis of (+)-Brasilenyne *via* Concise Construction of Oxonane Framework Containing 1,3-*cis*,*cis*-Diene

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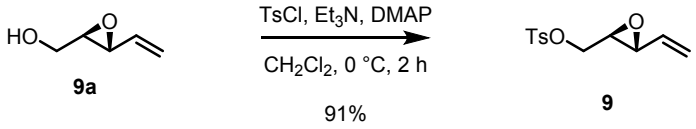
I. General Experimental

Unless noted otherwise, all starting materials and reagents were obtained from commercial suppliers and were used without further purification. Tetrahydrofuran and Et_2O were distilled from sodium benzophenone `. Dichloromethane, chloroform, triethylamine, acetonitrile and pyridine were freshly distilled from calcium hydride. All solvents used for routine isolation of products and chromatography were reagent grade and glass distilled. Reaction flasks were dried at 100 °C. Air and moisture sensitive reactions were performed under argon atmosphere. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck) with the indicated solvents. Thin-layer chromatography was performed using 0.25 mm silica gel plates (Merck). Optical rotations were measured with JASCO P-2000 digital polarimeter at ambient temperature using 100 mm cell of 2 mL capacity. Infrared spectra were recorded on a JASCO FT-IR-4200 spectrometer. High resolution mass spectra were obtained with JEOL JMS-700 instrument and Agilent Q TOF 6530. ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-ECA-600, JEOL JNM-LA 300, BRUKER AVANCE-500, BRUKER AVANCE-400, and BRUKER AVANCE-800. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane and are referenced to the deuterated solvent ($CHCl_3$). ^{1}H-NMR data were reported in the order of chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet and/or multiple resonances), number of protons, and coupling constant in hertz (Hz).

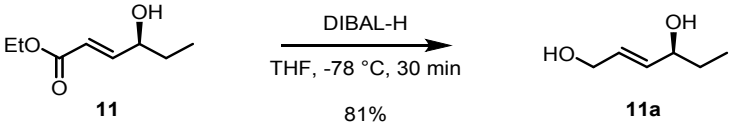
II. Experimental procedures

((2*R*,3*R*)-3-Vinyloxiran-2-yl)methyl 4-methylbenzenesulfonate (9)



To a cooled (0 °C) solution of known alcohol[1] **9a** (3.4 g, 34.0 mmol) in CH_2Cl_2 (170 mL) were added Et_3N (9.5 mL, 68.2 mmol) and 4-toluenesulfonyl chloride (7.8 g, 40.8 mmol). The mixture was stirred for 2 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 7.8 g (91%) of **9** as an amorphous powder. $[\alpha]_D^{20}$ = +32.76 (*c* 1.00, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.49 (ddd, *J* = 17.2, 9.8, 7.1 Hz, 1H), 5.45 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.30 (dd, *J* = 9.5, 2.0 Hz, 1H), 4.22 (dd, *J* = 11.4, 3.7 Hz, 1H), 4.00 (dd, *J* = 11.5, 5.7Hz, 1H), 3.21(dd, *J* = 7.0, 2.0 Hz, 1H), 3.09 (ddd, *J* = 5.7, 3.7, 2.1 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 145.1, 133.6, 132.6, 129.9, 128.0, 120.8, 69.4, 56.4 56.3, 21.6; IR (thin film, thin film, neat) ν_{max} 3090, 2990, 2926, 1598, 1455, 1364, 1190, 1097, 963, 816, 762 cm^{-1}; HR-MS (ESI+) calcd for $C_{12}H_{14}NaO_4S$ (M + Na^+) 277.0505, found 277.0511.

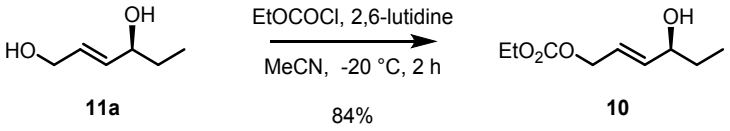
(*S*,*E*)-Hex-2-ene-1,4-diol (11a)



To a cooled (-78 °C) solution of known ester[2] **11** (16.5 g, 104.0 mmol) in THF (500 mL) was added DIBAL-H (1 M in toluene, 208 mL, 208.0 mmol). The mixture was stirred for 30 min at the same temperature, quenched with saturated Rochelle's solution (500 mL), extracted with *i*PrOH/$CHCl_3$ (1:4).

The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:3 to EtOAc only) to provide 9.8 g (81%) of **11a** as a colorless oil. $[\alpha]_D^{20}$ = +11.96 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (dt, *J* = 15.6, 5.0 Hz, 1H), 5.69 (dd, *J* = 15.6, 6.2 Hz, 1H), 4.11 (d, *J* = 5.1 Hz, 2H), 4.02 (q, *J* = 6.4 Hz, 1H), 2.22 (br s, 2H), 1.61-1.46 (m, 2H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.2, 129.9, 73.6, 63.0, 30.1, 9.7; IR (thin film, neat) ν_{max} 3315, 2959, 2926, 2856, 1731, 1463, 1378, 1286, 1123, 1075, 967, 799, 742 cm^{-1}; HR-MS (ESI+) calcd for $C_6H_{12}NaO_2$ (M + Na^+) 139.0730, found 139.0727.

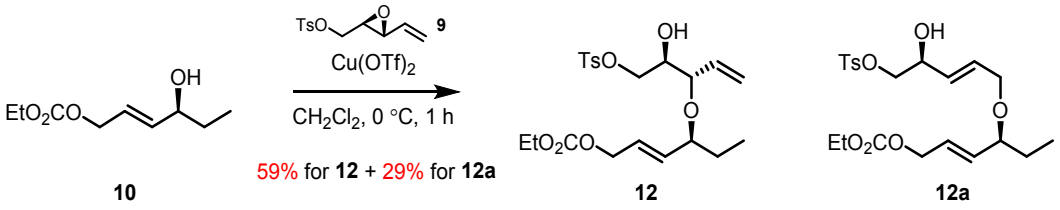
(*S*,*E*)-Ethyl (4-hydroxyhex-2-en-1-yl) carbonate (10)



11a **10**

To a cooled (-20 °C) solution of diol **11a** (9.0 g, 77.5 mmol) in MeCN (390 mL) was added 2,6-lutidine (18.1 mL, 155.4 mmol). The mixture was stirred for 30 min at the same temperature, and a solution of ethyl chloroformate (8.2 mL, 85.8 mmol) in MeCN (77.5 mL) was slowly added for 30 min. The mixture was stirred for 1 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 12.3 g (84%) of **10** as a colorless oil. $[\alpha]_D^{20}$ = +5.93 (*c* 1.00, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 5.81 (dd, *J* = 15.6, 5.4 Hz, 1H), 5.78 (dt, *J* = 15.7, 5.2 Hz, 1H), 4.60 (d, *J* = 4.8 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.06-4.05 (m, 1H), 1.60 (s, 1H), 1.57-1.52 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 154.9, 137.8, 124.0, 73.3, 67.4, 64.0, 29.9, 14.2, 9.6; IR (thin film, neat) ν_{max} 3428, 2968, 2936, 2878, 1680, 1465, 1382, 1118, 1061, 918, 792, 734 cm^{-1}; HR-MS (ESI+) calcd for $C_9H_{16}NaO_4$ (M + Na^+) 211.0941, found 211.0936.

(2*R*,3*S*)-3-(((*S*,*E*)-6-((Ethoxycarbonyl)oxy)hex-4-en-3-yl)oxy)-2-hydroxypent-4-en-1-yl 4-methylbenzenesulfonate (12)

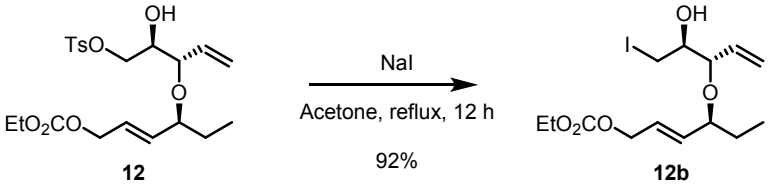


To a cooled (0 °C) solution of alcohol **10** (5.8 g, 30.7 mmol) and epoxide **9** (2.6 g, 10.2 mmol) in CH_2Cl_2 (20 mL) was added copper(II) trifluoromethanesulfonate (0.4 g, 1.0 mmol). The mixture was stirred for 1 h at the same temperature, quenched with saturated $NaHCO_3$ solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 2.7 g (59%) of **12** as a colorless oil, 1.3 g (29%) of regioisomer **12a** as a colorless oil, and 4.0 g of remained alcohol **10**. $[\alpha]_D^{20}$ = +10.52 (*c* 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.70-5.62 (m, 3H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.22 (d, *J* = 17.6 Hz, 1H), 4.56 (d, *J* = 5.3 Hz, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 4.11 (dd, *J* = 10.3, 3.8 Hz, 1H), 4.07 (dd, *J* = 10.4, 6.1 Hz, 1H), 3.87-3.84 (m, 1H), 3.81-3.79 (m, 1H), 3.77 (q, *J* = 6.2 Hz, 1H), 2.43 (s, 3H), 2.20 (d, *J* = 4.1 Hz, 1H), 1.54 (dqd, *J* = 13.5, 7.2, 6.0 Hz,1H), 1.44 (d quint, *J* = 13.9, 7.0 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 145.0, 135.6, 135.0, 132.7, 129.9, 128.0, 125.2, 119.6, 79.7, 78.9, 71.3, 70.4, 67.4, 64.0, 27.3, 21.6, 14.3, 9.2; IR (thin film, neat) ν_{max} 3525, 2966, 2931, 2878, 1746, 1598, 1457, 1400, 1363, 1257, 1177, 982, 917, 871, 816, 732 cm^{-1}; HR-MS (ESI+) calcd for $C_{21}H_{30}NaO_8S$ (M + Na^+) 465.1554, found 465.1572.

(*S*,*E*)-5-(((*S*,*E*)-6-((Ethoxycarbonyl)oxy)hex-4-en-3-yl)oxy)-2-hydroxypent-3-en-1-yl 4-methylbenzenesulfonate (12a): $[\alpha]_D^{20}$ = +6.57 (*c* 1.00, $CHCl_3$); ^{1}H NMR (300 MHz, CDCl3) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 5.85 (dtd, *J* = 15.6, 5.3, 1.3 Hz, 1H), 5.71 (dt, *J* = 15.7, 5.6 Hz, 1H), 5.61 (d, *J* = 16.5 Hz, 1H), 5.59 (d, *J* = 15.6 Hz, 1H), 4.60 (d, *J* = 5.5 Hz, 2H), 4.39 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.03 (dd, *J* = 10.1, 3.4 Hz, 1H), 3.94 (dd, *J* = 13.2, 5.1 Hz, 1H), 3.88 (dd,

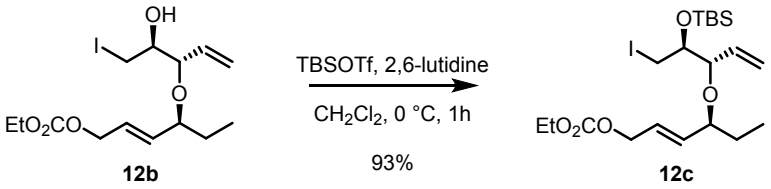
J = 7.6, 10.2 Hz, 1H), 3.80 (dd, *J* = 13.2, 5.5 Hz, 1H), 3.60 (dt, *J* = 6.8, 6.6 Hz, 1H), 2.43 (s, 3H), 1.64-1.40 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 3H) ; ^{13}C NMR (200 MHz, $CDCl_3$) δ 154.9, 145.1, 135.5, 132.6, 131.0, 129.9, 128.0, 128.0, 126.1, 81.0, 73.0, 69.8, 67.9, 67.4, 64.1, 28.2, 21.6, 14.2, 9.6; IR (thin film, neat) ν_{max} 3525, 2967, 2936, 2876, 1813, 1746, 1454, 1363, 1257, 1177, 1097, 975, 816, 792, 756 cm^{-1}; HR-MS (ESI+) calcd for $C_{21}H_{30}NaO_8S$ (M + Na^+) 465.1554, found 465.1558.

ethyl ((*S*,*E*)-4-(((3*S*,4*S*)-4-Hydroxy-5-iodopent-1-en-3-yl)oxy)hex-2-en-1-yl) carbonate (12b)



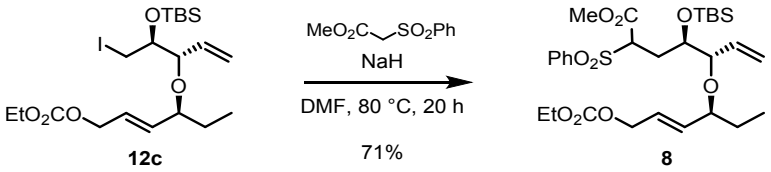
To a refluxing solution of tosylate **12** (5.1 g, 11.5 mmol) in acetone (57 mL) was added sodium iodide (17.3 g, 115.2 mmol). After refluxing for 12 h, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. The reaction mixture was diluted with water and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:10 to 1:6) to provide 4.2 g (92%) of **12b** as a colorless oil. $[\alpha]_D^{20}$ = -10.79 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77-5.68 (m, 2H), 5.65 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.30 (d, *J* = 11.5 Hz, 1H), 5.29 (d, *J* = 16.3 Hz, 1H), 4.58 (d, *J* = 5.5 Hz, 2H), 4,18 (td, *J* = 7.4, 6.8 Hz, 2H), 3.88-3.85 (m, 1H), 3.84 (td, *J* = 6.4, 5.9 Hz, 1H), 3.57 (dq, *J* = 5.3, 4.8 Hz,1H) 3.31 (d, *J* = 5.5 Hz, 2H), 2,24 (d, *J* = 4.1 Hz, 1H), 1.61 (dqd, *J* = 13.7, 7.8, 6.0 Hz, 1H), 1.52 (d quint, *J* = 14.7, 6.4 Hz, 1H), 1.29 (t, *J* = 7.4 Hz, 3H), 0.86 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 135.8, 135.1, 125.2, 119.9, 81.0, 79.4, 72.6, 67.4, 64.0, 27.4, 14.3, 9.8, 9.3; IR (thin film, neat) ν_{max} 3502, 3078, 2967, 2933, 2877, 1746, 1644, 1464, 1382, 1259, 1062, 975, 930, 873, 792, 732 cm^{-1}; HR-MS (ESI+) calcd for $C_{14}H_{24}IO_5$ (M + H^+) 399.0663, found 399.0667.

(*S*,*E*)-4-(((3*S*,4*S*)-4-((*tert*-Butyldimethylsilyl)oxy)-5-iodopent-1-en-3-yl)oxy)hex-2-en-1-yl ethyl carbonate (12c)



To a cooled (0 °C) solution of iodide **12b** (3.9 g, 9.8 mmol) in CH_2Cl_2 (48 mL) were slowly added 2,6-lutidine (2.3 mL, 19.8 mmol) and *t*-butyldimehtylsilyl trifluoromethanesulfonate (3.4 mL, 14.8 mmol). The mixture was stirred for 1 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:20 to 1:10) to provide 4.7 g (93%) of **12c** as a colorless oil. $[\alpha]_D^{20}$ = -56.04 (*c* 1.00, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.72 (ddd, *J* = 17.4, 10.6, 7.3 Hz, 1H), 5.68 (dt, *J* = 15,6, 6.0 Hz, 1H), 5.64 (dd, *J* = 15.6, 6.4 Hz, 1H), 5.21(d, *J* = 16.7 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 5.5 Hz, 2H), 4.18 (q, *J* = 7.3 Hz, 2H), 3.91-3.89 (m, 1H), 3.85 (td, *J* = 6.4, 6.0 Hz, 1H), 3.80 (td, *J* = 5.0, 4.6 Hz, 1H), 3.62 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.51 (dd, *J* = 11.5, 4.1 Hz, 1H), 1.60 (dqd, *J* = 13.7, 7.3, 5.5 Hz, 1H), 1.51 (d quint, *J* = 14.2, 6.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 9H), 0.85 (t, *J* = 7.6 Hz, 3H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 136.3, 136.3, 125.0, 118.3, 79.6, 79.6, 75.0, 67.6, 64.0, 46.3, 27.4, 25.8, 18.1, 14.3, 9.2, -4.4, -4.6; IR (thin film, neat) ν_{max} 2961, 2932, 2886, 2858, 1749, 1465, 1366, 1257, 1118, 1007, 930, 876, 838, 793, 704 cm^{-1}; HR-MS (ESI+) calcd for $C_{20}H_{37}INaO_5Si$ ($M + Na^+$) 535.1347, found 535.1354.

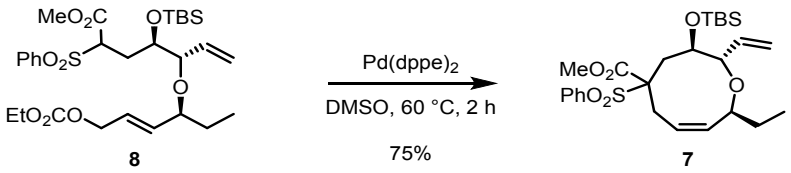
Methyl (4*R*,5*S*)-4-((*tert*-butyldimethylsilyl)oxy)-5-(((*S*,*E*)-6-((ethoxycarbonyl)oxy)hex-4-en-3-yl)oxy)-2-(phenylsulfonyl)hept-6-enoate (8)



To a cooled (0 °C) suspension of 60% sodium hydride (0.73 g, 32.1 mmol) in DMF (16 mL) was added methyl phenylsulfonylacetate (5.27 mL, 32.1 mmol). The mixture was stirred for 1 h at room temperature, and a solution of iodide **12c** (4.11 g, 8.0 mmol) in DMF (16 mL) was added. The reaction mixture was stirred for 20 h at 80 °C, cooled to room temperature, quenched with saturated NH_4Cl solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 3.41g (71%, 1.5:1 mixture of inseparable two diastereomers) of **8** as a colorless oil. ^{1}H NMR (800 MHz, $CDCl_3$, mixture of diastereomers) δ 7.84-7.82 (m, 2H for each isomer, mixture of two isomers), 7.66-7.64 (m, 1H for each isomer, mixture of two isomers), 7.54 (t, J = 7.8 Hz, 2H for each isomer, mixture of two isomers), 5.65-5.56 (m, 3H for each isomer, mixture of two isomers), 5.15-5.08 (m, 2H for each isomer, mixture of two isomers), 4.56 (d, J = 5.4 Hz, 2H, major isomer), 4.55 (d, J = 5.7 Hz, 2H, minor isomer), 4.31 (dd, J = 11.7, 2.4 Hz, 1H, major isomer), 4.28 (dd, J = 8.5, 4.6 Hz, 1H, minor isomer), 4.18 (q, J = 7.1 Hz, 2H, major isomer), 4.17 (q, J = 7.1 Hz, 2H, minor isomer), 3.80 (td, J = 6.4, 5.9 Hz, 1H, major isomer), 3.78-3.76 (m, 2H, minor isomer), 3.72-3.71 (m, 1H, major isomer), 3.69 (dd, J = 6.9, 3.8 Hz, 1H, minor isomer), 3.65 (s, 3H, major isomer), 3.61 (s, 3H, minor isomer), 3.58 (dt, J = 8.6, 2.8 Hz, 1H, major isomer), 2.25-2.17 (m, 1H for major isomer, 2H for minor isomer, mixture of two isomers), 2.10 (ddd, J = 13.9, 11.8, 2.9 Hz, 1H, major isomer), 1.61-1.54 (m, 1H for each isomer, mixture of two isomers), 1.44 (d quint, J = 13.9, 7.0 Hz, 1H, major isomer), 1.41 (d quint, J = 13.7, 7.2 Hz, 1H, minor isomer), 1.29(t, J = 7.1 Hz, major isomer), 1.29(t, J = 7.1 Hz, minor isomer), 0.85 (s, 9H, minor isomer), 0.82 (s, 9H, major isomer), 0.80 (t, J = 7.4 Hz, 3H, major isomer), 0.80 (t, J = 7.4 Hz, 3H, minor isomer), 0.06 (s, 3H, minor isomer), 0.03 (s, 3H, minor isomer), 0.01 (s, 3H, major isomer), -0.06 (s, 3H, major isomer); ^{13}C NMR (200 MHz, $CDCl_3$, mixture of diastereomers) δ 166.6, 166.3, 154.9, 137.6, 137.2, 136.4, 136.3, 136.3, 135.7, 134.1, 134.1,

129.3, 129.1, 129.0, 129.0, 124.9, 124.9, 118.2, 118.1, 82.6, 82.3, 80.3, 80.2, 72.4, 72.3, 67.5, 67.5, 67.5, 67.3, 64.0, 52.8, 30.4, 29.7, 27.6, 27.4, 25.9, 25.9, 18.1, 18.0, 14.3, 9.3, 9.3, -3.8, -4.4, -4.8, -5.4; IR (thin film, neat) ν_{max} 3069, 2956, 2930, 2857, 1747, 1464, 1366, 1329, 1259, 1196, 1149, 1085, 1004, 937, 837, 810, 780, 723 cm^{-1}; HR-MS (ESI+) calcd for $C_{29}H_{46}KO_9SSi$ ($M + K^+$) 637.2263, found 637.2273.

Methyl (2*S*,3*R*,9*S*,*Z*)-3-((*tert*-butyldimethylsilyl)oxy)-9-ethyl-5-(phenylsulfonyl)-2-vinyl-2,3,4,5,6,9-hexahydrooxonine-5-carboxylate (7)



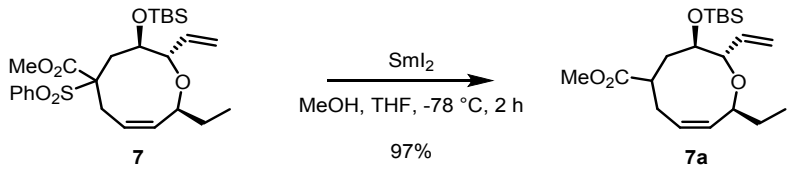
To a heated (60 °C) solution of allylic carbonate **8** (1.95 g, 3.3 mmol) in DMSO (32.6 mL) was added $Pd(dppe)_2$ (0.59 g, 0.7 mmol). The reaction mixture was stirred for 2 h at the same temperature, quenched with water, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 0.63 g (38%) of a diastereomer (top spot of TLC) of **7** as a colorless oil and 0.61 g (37%) of other diastereomer (bottom spot of TLC) of **7** as a white gum.

Top diastereomer: $[\alpha]_D^{20}$ = -11.36 (*c* 1.00, $CHCl_3$); ^1H NMR (800 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.9 Hz, 2H), 6.03 (td, *J* = 10.1, 5.3 Hz, 1H), 5.73 (dd, *J* = 10.4, 3.7 Hz, 1H), 5.70 (ddd, *J* = 17.3, 10.3, 7.5 Hz, 1H), 5.14 (dd, *J* = 17.3, 1.0, 1H), 5.06 (dd, *J* = 10.4, 1.4, 1H), 4.29-4.27 (m, 1H), 3.76 (t, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 3.46 (dd, *J* = 14.8, 11.8 Hz, 1H), 3.27 (t, *J* = 8.9 Hz, 1H), 3.05 (dd, *J* = 15.0, 5.3 Hz, 1H), 2.44 (dd, *J* = 14.2, 9.6 Hz, 1H), 2.28 (d, *J* = 14.2 Hz, 1H), 1.71 (d quint, *J* = 13.8, 7.4 Hz, 1H), 1.42 (d quint, *J* = 13,8, 7.3 Hz, 1H), 0.86 (t, *J* = 7.3 Hz, 3H), 0.71 (s, 9H), -0.16 (s, 3H), -0.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1, 140.2, 136.1, 135.2, 134.1, 132.3, 130.8, 128.7, 116.8, 78.9, 76.9, 76.2, 72.4, 52.9, 39.0, 29.9, 27.1, 25.8, 17.9, 10.7,

-4.7, -4.9; IR (thin film, neat) ν_{max} 3032, 2956, 2856, 1735, 1645, 1584, 1447, 1321, 1252, 1206, 1146, 1081, 1019, 863, 837, 778, 721 cm^{-1}; HR-MS (ESI+) calcd for $C_{26}H_{40}NaO_6SSi$ ($M + Na^+$) 531.2207, found 531.2196.

Bottom diastereomer: $[\alpha]_D^{20}$ = +24.05 (*c* 1.00, $CHCl_3$); ^1H NMR (800 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.9 Hz, 2H), 5.87 (ddd, *J* = 17.3, 10.4, 7.4 Hz, 1H), 5.61 (ddd, *J* = 10.4, 3.2, 1.0 Hz, 1H), 5.38 (dtd, *J* = 10.9, 5.0, 2.4 Hz, 1H), 5.17 (dd, *J* = 17.2, 0.6 Hz, 1H), 5.08 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.37-4.34 (m, 2H), 3.79 (t, *J* = 11.9 Hz, 1H), 3.76 (t, *J* = 7.5 Hz, 1H), 3.59 (s, 3H), 2.98 (d, *J* = 15.8 Hz, 1H), 2.53 (dd, *J* = 11.0, 3.3 Hz, 1H), 2.34 (dd, *J* = 15.8, 9.8 Hz, 1H), 1.75 (d quint, *J* = 13.8, 7.4 Hz, 1H), 1.41 (d quint, *J* = 13.8, 7.4 Hz, 1H), 0.88 (t, *J* = 7.4 Hz, 3H), 0.86 (s, 9H), 0.22 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 168.5, 140.5, 136.6, 136.0, 134.0, 130.2, 129.4, 128.6, 115.9, 80.5, 76.5, 75.8, 71.0, 53.2, 38.9, 31.2, 27.1, 26.1, 18.1, 10.8, -4.1, -4.5; IR (thin film, neat) ν_{max} 3071, 2930, 2856, 1736, 1645, 1585, 1462, 1310, 1250, 1146, 1068, 1008, 921, 838, 781, 721, 689 cm^{-1}; HR-MS (ESI+) calcd for $C_{26}H_{40}NaO_6SSi$ ($M + Na^+$) 531.2207, found 531.2197.

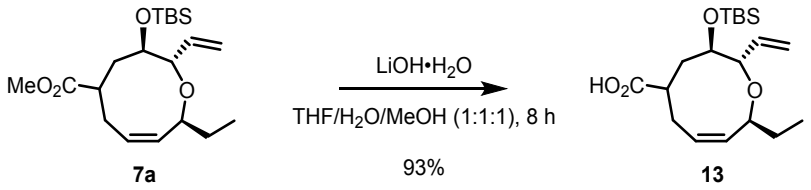
Methyl (2*S*,3*R*,9*S*,*Z*)-3-((*tert*-butyldimethylsilyl)oxy)-9-ethyl-2-vinyl-2,3,4,5,6,9-hexahydrooxonine-5-carboxylate (7a)



To a cooled (-78 °C) solution of cyclic ether **7** (714 mg, 1.4 mmol) in MeOH (14 mL) was added a solution of SmI_2 in THF (0.1 M in THF, 42 ml, 4.2 mmol). The mixture was stirred for 30 min at the same temperature, quenched with saturated $NaHCO_3$ solution, filtered through a pad of Celite, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:10) to provide 502 mg (97%, 3:1 mixture of inseparable two diastereomers) of **7a** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$, mixture of diastereomers) δ 5.88-5.78 (m, 2H for major isomer, 1H for minor isomer, mixture of two isomers), 5.71-5.66 (m, 1H, minor isomer), 5.61 (dd, J = 10.8, 4.8 Hz, 1H, minor isomer), 5.43 (dd, J = 10.5, 5.5 Hz, 1H, major isomer), 5.20 (d, J = 17.4 Hz, 1H, minor isomer), 5.16(d, J = 17.5 Hz, 1H, major isomer), 5.15 (dd, J = 10.1, 1.8 Hz, 1H, minor isomer), 5.05 (dd, J = 10.3, 1.2 Hz, major isomer), 4.34 (dt, J = 6.8, 6.4 Hz, 1H, major isomer), 4.17 (td, J = 6.4, 6.0 Hz, 1H, minor isomer), 3.82 (t, J = 8.3 Hz, 1H, minor isomer), 3.76 (t, J = 7.8 Hz, 1H, major isomer), 3.66 (s, 3H, minor isomer), 3.65 (s, 3H, major isomer), 3.63-3.58 (m, 1H for each isomer, mixture of two isomers), 2.79-2.75 (m, 2H, minor isomer), 2.65-2.56 (m, 2H, major isomer), 2.47 (qd, J = 7.8, 4.6 Hz, 1H, minor isomer), 2.44-2.40 (m, 1H, major isomer), 2.26 (ddd, J = 14.6, 11.5, 7.8 Hz, 1H, minor isomer), 2,15 (ddd, J = 15.1, 5.9, 2.3 Hz, 1H, major isomer), 2.06 (ddd, J = 15.1, 6.9, 1.8 Hz, 1H, major isomer), 1.89 (d, J = 15.1 Hz, 1H, minor isomer), 1.70 (d quint, J = 13.7, 7.3 Hz, 1H, major isomer), 1.68 (d quint, J = 13.7, 7.4 Hz, 1H, minor isomer), 1.46 (d quint, J = 13.8, 7.3 Hz, 1H, minor isomer), 1.44 (d quint, J = 13.8, 7.3 Hz, 1H, major isomer), 0.87 (t, J = 7.4 Hz, 3H, major isomer), 0.85 (t, J = 7.4 Hz, 3H, minor isomer), 0.82 (s, 9H for each isomer, mixture of two isomers), 0.01 (s, 3H, minor isomer), -0.02 (s, 3H, major isomer), -0.03 (s, 3H, minor isomer), -0.05 (s, 3H, major isomer); ^{13}C NMR (150 MHz, $CDCl_3$, mixture of diastereomers) δ 176.8, 176.1, 140.1, 139.1, 134.5, 134.3, 132.0, 131.9, 117.6, 115.9, 81.1, 76.6, 75.7, 74.3, 73.6, 72.9, 51.7, 51.6, 42.3, 38.8, 38.3, 38.2, 31.8, 29.1, 28.7, 28.2, 25.9, 25.8, 17.9, 10.6, 10.4, -4.3, -4.5; IR (thin film, neat) ν_{max} 3015, 2957, 2930, 2882, 2857, 1739, 1644, 1471, 1436, 1361, 1255, 1193, 1169, 1091, 921, 837, 776 cm^{-1}; HR-MS (ESI+) calcd for $C_{20}H_{37}O_4Si$ (M + H$^+$) 369.2456, found 369.2448.

(2*S*,3*R*,9*S*,*Z*)-3-((*tert*-Butyldimethylsilyl)oxy)-9-ethyl-2-vinyl-2,3,4,5,6,9-hexahydrooxonine-5-carboxylic acid (13)



7a **13**

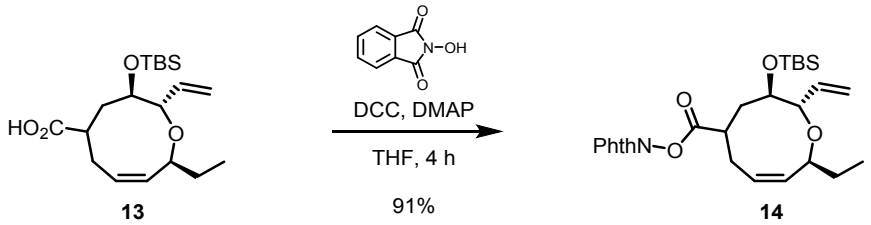
To a solution of ester **7a** (347 mg, 0.9 mmol) in a mixture of THF, H_2O, and MeOH (1:1:1, 9 mL) was added $LiOH{\cdot}H_2O$ (119 mg, 2.8 mmol) at room temperature. The mixture was stirred for 8 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6 to 1:3 to 1:1) to provide 232 mg (70%) of major diastereomer (top spot of TLC) of **13** as a colorless oil and 77 mg (23%) of minor diastereomer (bottom spot of TLC) of **13** as a colorless oil.

Top (major) diastereomer: $[\alpha]_D^{20}$ = +4.46 (*c* 0.50, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 5.88-5.84 (m, 1H), 5.84 (ddd, *J* = 17.2, 10.3, 7.0 Hz, 1H), 5.46 (dd, *J* = 10.5, 5.4 Hz, 1H), 5.17 (d, J = 17.2 Hz, 1H), 5.07 (dd, *J* = 10.4, 1.0 Hz, 1H), 4.35 (q, *J* = 6.4 Hz, 1H), 3.78 (t, *J* = 7.7 Hz, 1H), 3.64 (td, *J* = 7.3, 1.4 Hz, 1H), 2.69-2.67 (m, 1H), 2.62 (dt, *J* = 12,8, 10.1 Hz, 1H), 2,49 (ddd, *J* = 13.1, 7.1, 2.8 Hz, 1H), 2.19 (ddd, *J* = 15.1, 6.3, 2.1 Hz, 1H), 2.08 (ddd, *J* = 15.1, 7.0, 1.5 Hz, 1H), 1.71 (d quint, *J* = 13,6, 7.4 Hz, 1H), 1.45 (d quint, *J* = 13,7, 7.3 Hz, 1H), 0.87 (t, *J* = 7.4, 3H), 0.82 (s, 9H), 0.00 (s, 3H), -0.04(s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 181.3, 140.1, 133.9, 132.2, 116.1, 76.9, 75.8, 72.7, 38.2, 38.0, 31.5, 28.6, 25.8, 17.9, 10.4, -4.4, -4.5; IR (thin film, neat) ν_{max} 3077, 3016, 2882, 2857, 2310, 1705, 1543, 1472, 1417, 1299, 1253, 1090, 922, 837, 784 cm^{-1}; HR-MS (ESI+) calcd for $C_{19}H_{35}O_4Si$ ($M + H^+$) 355.2299, found 355.2301.

Bottom (minor) diastereomer: $[\alpha]_D^{20}$ = -48.27 (*c* 0.50, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 5.82 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 1H), 5.71 (dtd, *J* = 10.2, 7.2, 1.3 Hz, 1H), 5.63 (dd, *J* = 10.6, 4.8 Hz, 1H), 5.21 (d, *J* = 17.3 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.19 (td, *J* = 6.4, 6.1 Hz, 1H) 3.84 (t, *J* = 8.1 Hz, 1H), 3.62 (td, *J* = 8.1, 1.3 Hz, 1H), 2.83-2.79 (m, 2H), 2.55-2.51 (m, 1H), 2.28 (ddd, *J* = 14.8, 11.4, 7.6 Hz, 1H), 1.96 (d, *J* = 14.9 Hz, 1H), 1.69 (d quint, *J* = 13.6, 7.3 Hz, 1H), 1.46 (d quint, *J* = 13.6, 7.4

Hz, 1H), 0.86 (t, J = 7.4 Hz, 3H), 0.82 (s, 9H), 0.03 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 180.4, 139.0, 134.6, 131.7, 117.7, 81.0, 74.4, 73.7, 42.0, 38.4, 29.0, 28.2, 25.8, 17.9, 10.6, -4.3, -4.5; IR (thin film, neat) ν_{max} 3078, 3021, 2958, 2884, 2857, 1705, 1471, 1417, 1361, 1297, 1255, 1074, 927, 836, 776 cm^{-1}; HR-MS (ESI+) calcd for $C_{19}H_{35}O_4Si$ ($M + H^+$) 355.2299, found 355.2303.

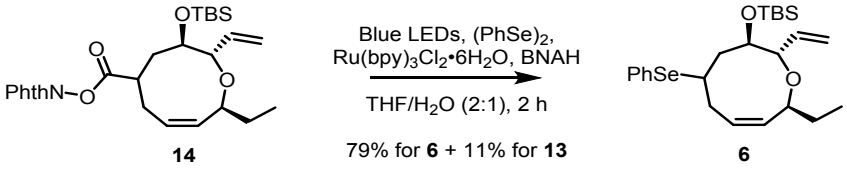
1,3-Dioxoisoindolin-2-yl (2*S*,3*R*,9*S*,*Z*)-3-((*tert*-butyldimethylsilyl)oxy)-9-ethyl-2-vinyl-2,3,4,5,6,9-hexahydrooxonine-5-carboxylate (14)



To a solution of acid **13** (281 mg, 0.8 mmol) in THF (8 mL) were added *N*,*N*′-dicyclohexylcarbodiimide (254 mg, 1.2 mmol), *N*-hydroxyphthalimide (194 mg, 1.2 mmol) and 4-dimethylaminopyridine (5 mg, 0.1 mmol) at room temperature. The mixture was stirred for 4 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:10 to 1:6) to provide 362 mg (91%, 3:1 mixture of inseparable two diastereomers) of **14** as a colorless oil. ^{1}H NMR (800 MHz, $CDCl_3$, mixture of diastereomers) δ 7.86 (dd, J = 5.4, 3.0 Hz, 2H for each isomer, mixture of two isomers), 7.76 (dd, J = 5.4, 3.0 Hz, 2H for each isomer, mixture of two isomers), 5.98 (dtd, J = 10.3, 7.7, 1.7 Hz, 1H, major isomer), 5.86 (ddd, J = 17.2, 10.3, 6.9 Hz, 1H, major isomer), 5.84 (ddd, J = 17.2, 10.4, 7.4 Hz, 1H, minor isomer), 5.79 (tdd, J = 10.2, 7.2, 1.6 Hz, 1H, minor isomer), 5.70 (dd, J = 10.7, 4.6 Hz, 1H, minor isomer), 5.49 (dd, J = 10.5, 5.8 Hz, 1H, major isomer), 5.23 (d, J = 17.1 Hz, 1H, minor isomer), 5.20 (ddd, J = 17.3, 1.7, 1.1 Hz, 1H, major isomer), 5.17 (dd, J = 10.4, 1.3 Hz, 1H, minor isomer), 5.09 (ddd, J = 10.3, 1.8, 0.7 Hz, 1H, major isomer), 4.37 (dt, J = 7.0, 6.2 Hz, 1H, major isomer), 4.23 (dt, J = 6.6,

6.0 Hz, 1H, minor isomer), 3.86 (t, *J* = 8.1 Hz, 1H, minor isomer), 3.81 (t, *J* = 8.1 Hz, 1H, major isomer), 3.73 (ddd, J = 8.4, 5.4, 1.8 Hz, 1H, major isomer), 3.64 (td, *J* = 8.3, 1.4 Hz, 1H, minor isomer), 3.23-3.20 (m, 1H, minor isomer), 3.01-2.97 (m, 1H for each isomer, mixture of two isomers), 2.74 (ddd, *J* = 13.5, 7.8, 2.1 Hz, 1H, major isomer), 2.64 (dt, *J* = 13.4, 9.6 Hz, 1H, major isomer), 2.64-2.61 (m, 1H, minor isomer), 2.40 (ddd, *J* = 14.9, 11.5, 8.2 Hz, 1H, minor isomer), 2.34 (ddd, *J* = 15.1, 5.3, 1.6 Hz, 1H, major isomer), 2.24 (ddd, *J* = 15.2 7.8, 1.9 Hz, 1H, major isomer), 2.12 (dt, *J* = 14.8, 1.8 Hz, 1H, minor isomer), 1.72 (d quint, *J* = 13.5, 7.4 Hz, 1H, major isomer), 1.71 (d quint, *J* = 13.5, 7.3 Hz, 1H, minor isomer), 1.48 (d quint, *J* = 13.7, 7.3 Hz, 1H, major isomer), 1.48 (d quint, *J* = 13.7, 7.3 Hz, 1H, minor isomer), 0.89 (t, *J* = 7.4 Hz, 3H, major isomer), 0.87 (t, *J* = 7.4 Hz, 3H, minor isomer), 0.85 (s, 9H, major isomer), 0.84 (s, 9H, minor isomer), 0.07 (s, 3H, minor isomer), 0.05 (s, 3H, major isomer), 0.00 (s, 3H, minor isomer), -0.02 (s, 3H, major isomer); ^{13}C NMR (200 MHz, $CDCl_3$, mixture of diastereomers) δ 172.7, 171.9, 162.0, 139.7, 139.1, 135.4, 134.7, 134.7, 133.1, 132.5, 131.1, 129.0, 129.0, 123.9, 117.5, 116.5, 80.6, 76.1, 75.6, 74.8, 73.7, 72.7, 39.7, 38.6, 38.1, 35.0, 32.3, 29.0, 27.9, 25.8, 25.8, 17.9, 17.9, 10.6, 10.3, -4.3, -4.5, -4.6, -4.6; IR (thin film, neat) ν_{max} 3518, 3076, 3019, 2930, 2857, 1813, 1615, 1469, 1362, 1255, 1187, 1122, 1082, 991, 904, 878, 837, 777 cm^{-1}; HR-MS (ESI+) calcd for $C_{27}H_{38}NO_6Si$ (M + H$^+$) 500.2463, found 500.2461.

***tert*-butyl(((2*S*,3*R*,9*S*,*Z*)-9-Ethyl-5-(phenylselanyl)-2-vinyl-2,3,4,5,6,9-hexahydrooxonin-3-yl)oxy)dimethylsilane (6)**



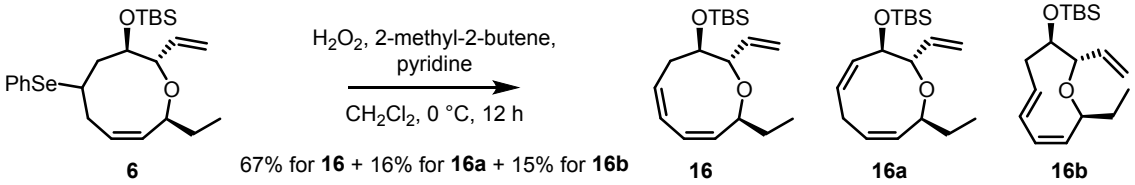
To a solution of ester **14** (143 mg, 0.3 mmol) in a mixture of THF and H_2O (2:1, 6 mL) were added 1-benzyl-1,4-dihydronicotinamide (128 mg, 0.4 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (11 mg, 0.01 mmol) and diphenyldiselenide (144 mg, 0.4 mmol) at room temperature. After stirring for 10 min, the reaction

mixture was placed in the center of 8 Blue LEDs (5 W, 460-470 nm, 55-75 lm) loop (circumference: 30 cm). The reaction mixture was irradiated for 2 h and concentrated *in vacuo*. The reaction mixture was diluted with water and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (pentane only to Et_2O/pentane = 1:6) to provide 105 mg (79%, 1.5:1 mixture of inseparable two diastereomers) of **6** as a colorless oil and 11 mg (11%) of acid **13**. ^{1}H NMR (800 MHz, $CDCl_3$, mixture of diastereomers) δ 7.58-7.57 (m, 2H, minor isomer), 7.53-7.52 (m, 2H, major isomer), 7.27-7.24 (m, 3H for each isomer, mixture of two isomers), 5.85 (ddd, *J* = 17.2, 10.4, 7.1 Hz, 1H, major isomer), 5. 78 (ddd, *J* = 17.2, 10.3, 7.8 Hz, 1H, minor isomer), 5.74 (dtd, *J* = 10.4, 7.0, 1.4 Hz, 1H, minor isomer), 5.65 (dtd, *J* = 10.5, 7.0, 1.9 Hz, 1H, major isomer), 5.64 (dd, *J* = 10.6, 5.0 Hz, 1H, minor isomer), 5.44 (dd, *J* = 10.6, 5.1 Hz, 1H, major isomer), 5.18 (ddd, *J* = 17.1, 1.7, 0.7 Hz, 1H, minor isomer), 5.17 (ddd, *J* = 17.2, 1.8, 1.0 Hz, 1H, major isomer), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H, minor isomer), 5.07 (ddd, *J* = 10.4, 1.7, 0.6 Hz, 1H, major isomer), 4.31 (td, *J* = 6.6, 6.2 Hz, 1H, major isomer), 4.16 (td, *J* = 6.6, 6.0 Hz, 1H, minor isomer), 3.84 (t, *J* = 7.7 Hz, 1H, major isomer), 3.82 (t, *J* = 8.2 Hz, 1H, minor isomer), 3.66 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, major isomer), 3.63 (dtd, *J* = 12.4, 4.4, 3.6 Hz, 1H, minor isomer), 3.59 (dddd, *J* = 10.6, 6.4, 3.4, 2.5 Hz, 1H, major isomer), 3.56 (ddd, *J* = 8.6, 7.3, 1.3 Hz, 1H, minor isomer), 3.00 (ddd, *J* = 13.5, 10.1, 4.1 Hz, 1H, minor isomer), 2.82 (dt, *J* = 13.0, 10.6 Hz, 1H, major isomer), 2.48-2.44 (m, 1H for each isomer, mixture of two isomers), 2.41 (ddd, *J* = 14.6, 12.4, 7.3 Hz, 1H, minor isomer), 2.29 (ddd, *J* = 15.0, 7.0, 2.2 Hz, 1H, major isomer), 2.16 (ddd, *J* = 15.0, 7.1, 1.5 Hz, 1H, major isomer), 1.90 (dd, *J* = 14.6, 2.2 Hz, 1H, minor isomer), 1.69 (d quint, *J* = 13.6, 7.4 Hz, 1H, major isomer), 1.68 (d quint, *J* = 13.7, 7.3 Hz, 1H, minor isomer), 1.46 (d quint, *J* = 13.8, 7.4 Hz, 1H, minor isomer), 1.43 (d quint, *J* = 13.7, 7.4 Hz, 1H, major isomer), 0.86 (t, *J* = 7,4 Hz, 3H, major isomer), 0.84 (t, *J* = 7.4 Hz, 3H, minor isomer), 0.83 (s, 9H, major isomer), 0.72 (s, 9H, minor isomer), -0.01 (s, 3H, major isomer), -0.02 (s, 3H, major isomer), -0.13 (s, 3H, minor isomer), -0.23 (s, 3H, minor isomer); ^{13}C NMR (200 MHz, $CDCl_3$, mixture of diastereomers) δ 140.2, 139.0, 135.6, 134.6, 134.5, 133.9, 132.3, 131.6, 130.9, 129.6, 129.1, 129.0, 127.8, 127.2, 117.7, 116.1, 81.6, 77.6, 75.8, 74.3, 74.0, 73.2, 43.8, 42.3, 42.0, 38.4, 36.9, 32.9, 28.3, 25.9, 25.7, 18.0, 17.8, 10.6, 10.5, -

4.1, -4.4, -4.6, 4.6; IR (thin film, neat) ν_{max} 3072, 3014, 2957, 2928, 2856, 1735, 1644, 1579, 1473, 1361, 1300, 1254, 1189, 1127, 1006, 921, 813, 776, 739 cm^{-1}; HR-MS (ESI+) calcd for $C_{24}H_{39}O_2SeSi$ ($M + H^+$) 467.1880, found 467.1884.

Reaction Apparatus

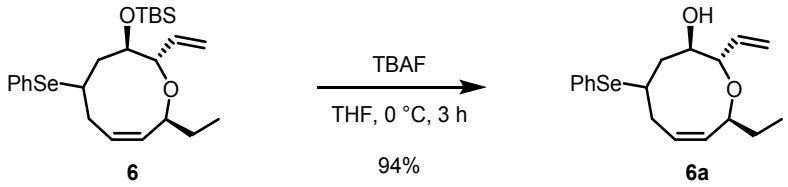
***tert*-Butyl(((2*S*,3*R*,5*Z*,7*Z*,9*S*)-9-ethyl-2-vinyl-2,3,4,9-tetrahydrooxonin-3-yl)oxy)dimethylsilane (16)**



To a cooled (0 °C) solution of phenylselenide **6** (35 mg, 0.1 mmol) in CH_2Cl_2 (2 mL) were added pyridine (0.1 mL, 1.2 mmol), 2-methyl-2-butene (0.1 mL, 0.9 mmol), and hydrogen peroxide (0.1 mL, 0.9 mmol). The mixture was stirred for 12 h at the same temperature, quenched with saturated $Na_2S_2O_3 \cdot 5H_2O$ solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (pentane only to Et_2O/pentane. 1:40) to provide 15.7 mg (0.051 mmol, 67%) of **16** as a colorless oil, 3.8 mg (16%) of regioisomer **16a** as a colorless oil, and 4 mg (15%) of (*E*)-olefinic isomer **16b** as a colorless oil. $[\alpha]_D^{20}$ = +94.93 (*c* 0.30, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.11 (d,

J = 11.5 Hz, 1H), 5.92 (d, J = 10.1 Hz, 1H), 5.90 (ddd, J = 17.4, 10.5, 7.3 Hz, 1H), 5.76 (td, J = 9.6, 7.3 Hz, 1H), 5.58 (ddd, J = 11.5, 5.0, 1.4 Hz, 1H), 5.19 (d, J = 16.9 Hz, 1H), 5.09 (d, J = 10.6 Hz, 1H), 4.09-4.05 (m, 1H), 4.06 (dt, J = 8.5, 7.3 Hz, 1H), 3.51 (td, J = 8.7, 2.3 Hz, 1H), 2.65 (dt, J = 13.3, 9.4 Hz, 1H), 2.21 (dd, J = 13.3, 7.4 Hz, 1H), 1.69 (d quint, J = 13.3, 7.4 Hz, 1H), 1.46 (d quint, J = 13.7, 7.3 Hz, 1H) 0.84 (s, 9H), 0.84 (t, J = 7.3 Hz, 3H), 0.03 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 139.9, 134.6, 132.5, 130.0, 127.3, 116.0, 81.3, 76.1, 72.2, 37.8, 28.1, 25.8, 18.0, 10.5, -4.5, -4.5; IR (thin film, neat) ν_{max} 3005, 2958, 2857, 1741, 1644, 1463, 1378, 1257, 1188, 1086, 1021, 921, 837, 737 cm^{-1}; HR-MS (ESI+) calcd for $C_{18}H_{33}O_2Si$ ($M + H^+$) 309.2244, found 309.2246.

(2*S*,3*R*,9*S*,*Z*)-9-Ethyl-5-(phenylselanyl)-2-vinyl-2,3,4,5,6,9-hexahydrooxonin-3-ol (6a)



6 **6a**

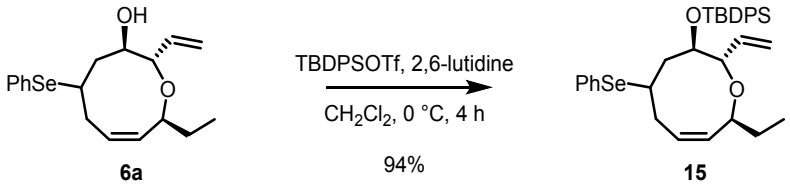
To a cooled (0 °C) solution of phenylselenide **6** (68 mg, 0.2 mmol) in THF (3 mL) was added TBAF (1M in THF, 0.3 mL, 0.3 mmol). The mixture was stirred for 3 h at the same temperature, quenched with water, and extracted with EtOAc. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (EtOAc/Hexane = 1:6) to provide 29 mg (56%) of major diastereomer (top spot of TLC) of **6a** as a colorless oil and 20 mg (38%) of minor diastereomer (bottom spot of TLC) of **6a** as a white gum.

Top (major) diastereomer: $[\alpha]_D^{20}$ = -56.16 (*c* 1.00, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.27-7.24 (m, 3H), 5.94 (ddd, J = 17,9, 9.8, 8.0 Hz, 1H), 5.58 (dtd, J = 10.6, 6.5, 1.4 Hz, 1H), 5.52 (dd, J = 10.6, 5.8 Hz, 1H), 5.31 (d, J = 16.8 Hz, 1H), 5.30 (d, J = 11.4 Hz, 1H), 4.23 (q, J = 6.7 Hz, 1H), 3.91 (ddt, J = 8.8, 6.2, 2.6 Hz, 1H), 3.83 (t, J = 8.5 Hz, 1H), 3.55 (dtd, J = 11.8, 4.7, 3.0 Hz, 1H), 2.83 (q, J = 11.7 Hz, 1H), 2.48 (ddd, J = 12.3, 6.0, 2.8 Hz, 1H), 2.45 (ddd, J = 12.4, 5.8, 5.4 Hz, 1H), 1.95 (ddd, J = 15.4, 5.2, 2.2 Hz, 1H), 1.66 (d quint, J = 13.8, 7.3 Hz, 1H), 1.57 (d, J = 2.9 Hz, 1H),

1.45 (d quint, J = 13.7, 7.4 Hz, 1H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 138.4, 134.7, 133.8, 132.2, 129.6, 129.1, 127.6, 119.0, 80.2, 73.6, 69.4, 40.6, 38.0, 34.0, 28.5, 10.3; IR (thin film, neat) ν_{max} 3356, 2959, 2875, 1578, 1477, 1428, 1377, 1293, 1270, 1231, 1166, 1046, 934, 915, 879, 754 cm^{-1}; HR-MS (ESI+) calcd for $C_{18}H_{25}O_2Se$ (M + H$^+$) 353.1015, found 353.1018.

Bottom (minor) diastereomer: $[\alpha]_D^{20}$ = -9.28 (*c* 0.70, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.27-7.26 (m, 3H), 5.87 (ddd, J = 17.4, 10.3, 8.3 Hz, 1H), 5.80 (dtd, J = 10.6, 6.5, 1.6 Hz, 1H), 5.63 (dd, J = 10.8, 4.8 Hz, 1H), 5.33 (dd, J = 10.4, 1.0 Hz, 1H), 5.29 (dd, J = 17.4, 1.4 Hz, 1H), 4.18 (q, J = 6.4 Hz, 1H), 3.80 (t, J = 8.6 Hz, 1H), 3.73 (dtd, J = 12.4, 4.0, 3.7 Hz, 1H), 3.57 (tt, J = 8.0, 2.1 Hz, 1H), 3.07 (ddd, J = 13.6, 10.6, 4.4 Hz, 1H), 2.38 (ddd, J = 13.3, 5.7, 4.7 Hz, 1H), 2.30 (ddd, J = 14.4, 12.4, 7.4 Hz, 1H), 2.10 (d, J = 14.4 Hz, 1H), 1.66 (d quint, J = 13.8, 7.4 Hz, 1H), 1.47 (d quint, J = 13.8,7.3 Hz, 1H), 1.44 (d, J = 2.6 Hz, 1H), 0.86 (t, J = 7.4 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 138.3, 134.7, 134.3, 131.8, 129.9, 129.1, 127.6, 119.8, 81.2, 74.6, 72.1, 41.8, 40.9, 32.5, 28.2, 10.5; IR (thin film, neat) ν_{max} 3323, 3006, 2963, 2875, 1579, 1509, 1479, 1437, 1300, 1220, 1149, 1042, 989, 927, 878, 738 cm^{-1}; HR-MS (ESI+) calcd for $C_{18}H_{25}O_2Se$ (M + H$^+$) 353.1015, found 353.1022.

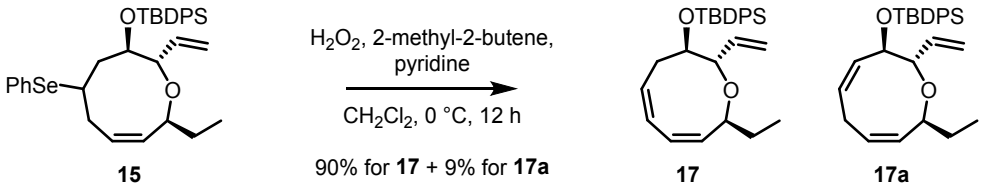
***tert*-Butyl(((2*S*,3*R*,9*S*,*Z*)-9-ethyl-5-(phenylselanyl)-2-vinyl-2,3,4,5,6,9-hexahydrooxonin-3-yl)oxy)diphenylsilane (15)**



To a cooled (0 °C) solution of alcohol **6a** (46 mg, 0.1 mmol) in CH_2Cl_2 (1.3 mL) were added 2,6-lutidine (0.91 mL, 0.8 mmol) and *t*-butyldiphenylsilyl trifluoromethanesulfonate (152 mg, 0.4 mmol). The mixture was stirred for 4 h at the same temperature, quenched with saturated NH_4Cl solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (Et_2O/pentane = 1:20)

to provide 68 mg (88%, 1.5:1 mixture of inseparable two diastereomers along with trace amount of tirene **17**) of **15** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$, mixture of diastereomers) δ 7.68 (dd, J = 8.2, 1.4 Hz, 2H, major isomer), 7.61 (dd, J = 7.8, 1.4 Hz, 2H, major isomer), 7.59 (dd, J = 8.0, 1.4 Hz, 2H, minor isomer), 7.54 (dd, J = 7.8, 1.4 Hz, 2H, minor isomer), 7.45 (dd, J = 8.0, 1.6 Hz, 2H, major isomer), 7.42-7.27 (m, 6H for major isomer, 8H for minor isomer, mixture of two isomers), 7.25-7.19 (m, 3H for major isomer, 1H for minor isomer, mixture of two isomers), 7.14 (t, J = 7.6 Hz, 2H, minor isomer), 5.72-5.66 (m, 1H for each isomer, mixture of two isomers), 5.64 (td, J = 10.1, 8.7 Hz, 1H, major isomer), 5.51-5.49 (m, 2H, minor isomer), 5.47 (dd, J = 11.0, 5.0 Hz, 1H, major isomer), 5.27 (dd, J = 17.5, 1.4 Hz, 1H, minor isomer), 5.18 (dd, J = 10.0, 1.9 Hz, 1H, minor isomer), 4.96 (d, J = 11.0 Hz, 1H, major isomer), 4.96 (d, J = 17.0 Hz, 1H, major isomer), 4.12 (q, J = 6.4 Hz, 1H, major isomer), 3.98-3.91 (m, 1H for major isomer, 2H for minor isomer, mixture of two isomers), 3.88-3.85 (m, 1H, minor isomer), 3.78 (td, J = 6.9, 1.4 Hz, 1H, major isomer), 3.74-3.71 (m, 1H, major isomer), 2.93-2.90 (m, 1H, major isomer), 2.75 (dddd, J = 12.5, 9.1, 6.5, 3.5 Hz, 1H, minor isomer), 2.49 (dt, J = 13.7, 8.4 Hz, 1H for each isomer, mixture of two isomers), 2.35 (ddd, J = 14.7, 12.8, 6.2 Hz, 1H, minor isomer), 2.27-2.23 (m, 1H, minor isomer), 2.14 (ddd, J = 14.7, 7.8, 2.8 Hz, 1H, major isomer), 2.06-2.01 (m, 1H for each isomer, mixture of two isomers), 1.61 (d quint, J = 13.7, 7.8 Hz, 1H, major isomer), 1.60 (d quint, J = 13.7, 7.3 Hz, 1H, minor isomer), 1.45 (d quint, J = 13.7, 7.3 Hz, 1H, major isomer), 1.41 (d quint, J = 13.7, 7.3 Hz, minor isomer), 1.02 (s, 9H, major isomer), 0.93 (s, 9H, minor isomer), 0.84 (t, J = 7.4 Hz, 3H, major isomer), 0.77 (t, J = 7.3 Hz, 3H, minor isomer); IR (thin film, neat) ν_{max} 3439, 3071, 3012, 2959, 2930, 2857, 1730, 1692, 1578, 1473, 1462, 1437, 1362, 1111, 1065, 934, 822, 740 cm^{-1}; HR-MS (ESI+) calcd for $C_{34}H_{43}O_2SeSi$ (M + H$^+$) 591.2195, found 591.2208.

***tert*-Butyl(((2*S*,3*R*,5*Z*,7*Z*,9*S*)-9-ethyl-2-vinyl-2,3,4,9-tetrahydrooxonin-3-yl)oxy)diphenylsilane (17)**

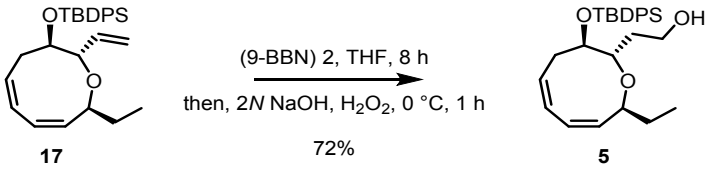


To a cooled (0 °C) solution of phenylselenide **15** (61 mg, 0.1 mmol) in CH_2Cl_2 (3 mL) were added pyridine (0.1 mL, 1.2 mmol), 2-methyl-2-butene (0.1 mL, 0.9 mmol) and hydrogen peroxide (0.1 mL, 0.9 mmol). The mixture was stirred for 12 h at the same temperature, quenched with saturated $Na_2S_2O_3 \cdot 5H_2O$ solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (pentane only to Et_2O/pentane = 1:40) to provide 40 mg (90%) of **17** as a colorless oil and 4 mg (9%) of regioisomer **17a** as a colorless oil. $[\alpha]_D^{20}$ = +80.09 (*c* 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 4H), 7.41-7.38 (m, 2H), 7.34 (dt, *J* = 7.2, 6.9 Hz, 4H), 6.02 (dd, *J* = 11.3, 1.1 Hz, 1H), 5.94 (ddd, *J* = 17.2, 10.3, 7.4 Hz, 1H), 5.73 (d, *J* = 11.0 Hz, 1H), 5.54 (ddd, *J* = 11.3, 5.5, 1.0 Hz, 1H), 5.25 (td, *J* = 10.5, 6.8 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.10 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.19 (t, *J* = 7.6 Hz, 1H), 3.97 (td, *J* = 6.6, 6.3 Hz, 1H), 3.67 (td, *J* = 8.4, 2.1 Hz, 1H), 2.57 (dt, *J* = 13.2, 9.4 Hz, 1H), 2.07 (dd, *J* = 13.2, 7.2 Hz, 1H), 1.67 (d quint, *J* = 13.6, 7.2 Hz, 1H), 1.44 (d quint, *J* = 13.6, 7.3 Hz, 1H), 1.00 (s, 9H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.7, 136.1, 136.0, 134.7, 134.4, 133.5, 132.4, 130.1, 129.6, 129.5, 127.5, 127.4, 126.9, 116.5, 82.2, 75.7, 73.4, 37.4, 28.3, 27.0, 19.4, 10.4; IR (thin film, neat) ν_{max} 3071, 3002, 2961, 2858, 1641, 1589, 1472, 1428, 1362, 1304, 1246, 1189, 1110, 997, 922, 790, 739 cm^{-1}; HR-MS (ESI+) calcd for $C_{28}H_{37}O_2Si$ (M + H^+) 433.2557, found 433.2564.

***tert*-Butyl(((2*S*,3*R*,4*Z*,7*Z*,9*S*)-9-ethyl-2-vinyl-2,3,6,9-tetrahydrooxonin-3-yl)oxy)diphenylsilane (17a)**: $[\alpha]_D^{20}$ = +38.50 (*c* 0.50, $CHCl_3$); ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.8 Hz, 2H), 7.63 (d, *J* = 6.7 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 5.87 (ddd, *J* = 17.2, 10.2, 8.3 Hz, 1H), 5.70 (td, *J* = 10.0, 7.8 Hz, 1H), 5.46-5.41 (m, 2H), 5.29 (d, *J* = 17.0 Hz, 1H), 5.22-5.19 (m, 2H), 5.13 (t, *J* = 7.0 Hz, 1H), 4.15 (td, *J* = 8.0, 4.2 Hz, 1H), 4.11 (t, *J* = 7.8 Hz, 1H), 2.79 (dt, *J* = 12.8, 9.4 Hz, 1H), 2.23-2.19 (m, 1H), 1.56 (dqd, *J* = 13.1, 7.5, 4.2

Hz, 1H), 1.41 (d quint, J = 13.0, 7.4 Hz, 1H), 1.02 (s, 9H), 0.72 (t, J = 7.5 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 136.9, 136.2, 136.1, 134.3, 133.8, 133.2, 132.4, 132.2, 129.6, 129.5, 127.9, 127.4, 127.3, 119.1, 84.2, 69.3, 69.2, 29.3, 27.0, 26.8, 19.3, 9.2; IR (thin film, neat) ν_{max} 3071, 3015, 2961, 2930, 2857, 1737, 1589, 1462, 1427, 1362, 1260, 1191, 1111, 960, 918, 821, 740 cm^{-1}; HR-MS (ESI+) calcd for $C_{28}H_{36}NaO_2Si$ (M + Na^+) 455.2377, found 455.2374.

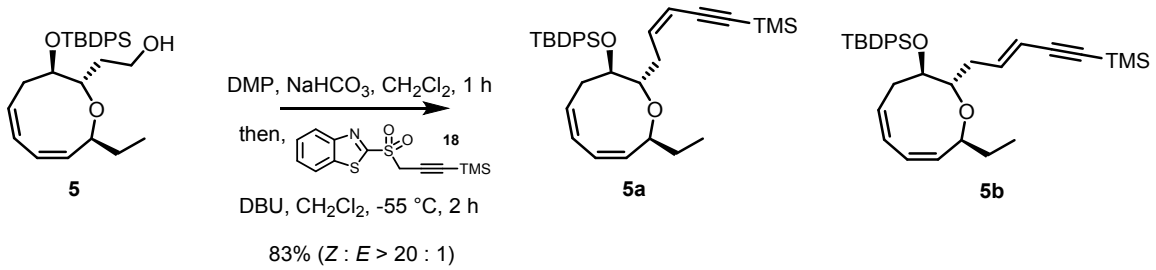
2-((2*S*,3*R*,5*Z*,7*Z*,9*S*)-3-((*tert*-Butyldiphenylsilyl)oxy)-9-ethyl-2,3,4,9-tetrahydrooxonin-2-yl)ethan-1-ol (5)



To a solution of 9-borabicyclo[3.3.1]nonane dimer (21 mg, 0.1 mmol) in THF (0.2 mL) was added a solution of triene **17** (33 mg, 0.1 mmol) in THF (0.5 mL) at room temperature. The mixture was stirred for 8 h at room temperature, and aqueous 2*N* NaOH (0.4 mL) and hydrogen peroxide (0.2 mL) were added at 0 °C. The resulting mixture was stirred for 30 min at the same temperature, quenched with saturated $Na_2S_2O_3{\cdot}5H_2O$ solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (Et_2O/pentane = 1:10 to 1:6 to 1:3) to provide 25 mg (72%) of **5** as a colorless oil. $[\alpha]_D^{20}$ = +85.94 (*c* 0.70, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67-7.65 (m, 4H), 7.44-7.40 (m, 2H), 7.38-7.35 (m, 4H), 5.99 (dd, J = 11.5, 2.3 Hz, 1H), 5.64 (dd, J = 11.2, 3.0 Hz, 1H), 5.38(dd, J = 11.0, 7.8 Hz, 1H), 5.05 (dt, J = 11.0, 8.5 Hz, 1H), 4.09 (td, J = 7.8, 3.2 Hz, 1H), 3.92 (td, J = 7.8, 5.9 Hz, 1H), 3.79-3.75 (m, 2H), 3.73-3.69 (m, 1H), 2.56-2.51 (m, 2H), 2.11 (dd, J = 14.2, 7.8 Hz, 1H), 2.01 (dddd, J = 14.7, 7.3, 4.6, 2.8 Hz, 1H), 1.95-1.89 (m, 1H), 1.64 (dqd, J = 13.3, 7.4, 5.5 Hz, 1H), 1.48 (d quint, J = 13.7, 7.6 Hz, 1H), 1.03 (s, 9H), 0.80 (t, J = 7.6 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 136.0, 135.9, 134.3, 133.2, 132.8, 132.1, 129.8, 129.7, 129.6, 127.7, 127.6, 127.0, 83.2, 74.0, 73.6, 61.6, 37.8,

34.6, 29.1, 27.0, 19.4, 9.8; IR (thin film, neat) ν_{max} 3430, 3071, 3004, 2960, 2857, 1726, 1636, 1589, 1463, 1427, 1361, 1260, 1188, 1110, 1008, 939, 823, 741 cm^{-1}; HR-MS (ESI+) calcd for $C_{28}H_{38}NaO_3Si$ ($M + Na^+$) 473.2482, found 473.2491.

***tert*-Butyl(((2*S*,3*R*,5*Z*,7*Z*,9*S*)-9-ethyl-2-((*Z*)-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)-2,3,4,9-tetrahydrooxonin-3-yl)oxy)diphenylsilane (5a)**

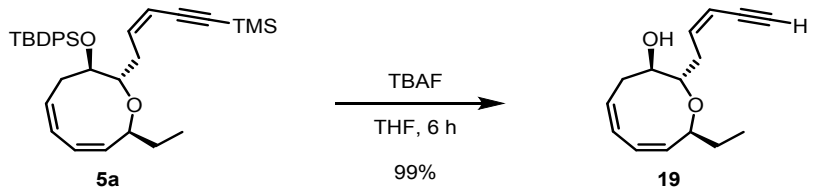


To a solution of alcohol **5** (20 mg, 0.05 mmol) in CH_2Cl_2 (1 mL) were added $NaHCO_3$ (8 mg, 0.1 mmol) and Dess-Martin Periodinane (29 mg, 0.1 mmol) at room temperature. The mixture was stirred for 1 h at the same temperature, and benzothiazolyl sulfone **18** (42 mg, 0.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene(0.04 mL, 0.3 mmol) were added at -55 °C. The reaction mixture was stirred for 2 h at the same temperature, quenched with saturated $NaHCO_3$ solution, and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (Et_2O/pentane = 1:40) to provide 20 mg (83% isolated yield) of **5a** as a colorless oil and (*E*)-isomer **5b** (*Z*/*E* > 20:1 by ^1H NMR analysis) as a colorless oil. $[\alpha]_D^{20}$ = +78.45 (*c* 0.20, $CHCl_3$); ^1H NMR (800 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.42-7.40 (m, 2H), 7.37 (td, *J* = 7.1, 5.8 Hz, 4H), 5.99 (dt, *J* = 11.0, 6.7 Hz, 1H), 5.90 (d, *J* = 11.2 Hz, 1H), 5.61 (dd, *J* = 11.0, 2.2 Hz, 1H), 5.52 (d, *J* = 11.0 Hz, 1H), 5.44 (dd, *J* = 11.2, 7.0 Hz, 1H), 5.06 (td, *J* = 10.2, 7.5 Hz, 1H), 4.00 (td, *J* = 7.6, 4.1 Hz, 1H), 3.87 (td, *J* = 7.2, 5.8 Hz, 1H), 3.80 (td, *J* = 7.5, 1.7 Hz, 1H), 2.83-2.80 (m, 1H), 2.71 (ddd, *J* = 13.7, 8.4, 8.0 Hz, 1H), 2.68 (d quint, *J* = 16.2, 8.0 Hz, 1H), 2.05 (dd, *J* = 13.5, 7.1 Hz, 1H), 1.64 (dqd, *J* = 13.3, 7.3, 5.5 Hz, 1H), 1.47 (d quint, *J* = 13.4, 7.6 Hz, 1H) 1.02 (s, 9H), 0.77 (t, *J* = 7.4 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 142.5, 136.0, 135.9,

134.5, 133.8, 133.2, 131.1, 130.1, 129.8, 129.6, 127.8, 127.5, 126.7, 110.3, 102.3, 98.9, 83.2, 73.7, 73.3, 36.7, 34.3, 29.1, 27.1, 19.4, 9.8, 0.1; IR (thin film, neat) ν_{max} 3071, 3049, 2960, 2858, 2148, 1730, 1590, 1463, 1428, 1250, 1220, 1110, 1044, 940, 844, 772, 741 cm^{-1}; HR-MS (ESI+) calcd for $C_{34}H_{47}O_2Si_2$ (M + H^+) 543.3109, found 543.3106.

***tert*-Butyl(((2*S*,3*R*,5*Z*,7*Z*,9*S*)-9-ethyl-2-((*E*)-5-(trimethylsilyl)pent-2-en-4-yn-1-yl)-2,3,4,9-tetrahydrooxonin-3-yl)oxy)diphenylsilane (5b)**: $[\alpha]_D^{20}$ = +28.21 (*c* 0.10, $CHCl_3$); ^1H NMR (800 MHz, $CDCl_3$) δ 7.66-7.65 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.38-7.35 (m, 4H), 6.24 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.91 (dd, *J* = 11.3, 1.9 Hz, 1H), 5.63 (dd, *J* = 11.2, 2.9 Hz, 1H), 5.48 (dt, *J* = 16.0, 1.4 Hz, 1H), 5.43 (dd, *J* = 11.2, 6.9 Hz, 1H), 5.11 (td, *J* = 10.2, 7.5 Hz, 1H), 3.90 (td, *J* = 7.8, 3.4 Hz, 1H), 3.86 (q, *J* = 6.7 Hz, 1H), 3.70 (td, *J* = 7.7, 2.0 Hz, 1H), 2.70 (ddd, *J* = 13.8, 9.4, 7.7 Hz, 1H), 2.49 (dddd, *J* = 15.1, 7.3, 3.5, 1.6 Hz, 1H), 2.40 (dtd, *J* = 15.2, 7.2, 1.5 Hz, 1H), 2.09 (dd, *J* = 13.4, 7.3 Hz, 1H), 1.57 (dqd, *J* = 13.3, 7.5, 5.8 Hz, 1H), 1.47 (d quint, *J* = 13.4, 7.6 Hz, 1H) 1.01 (s, 9H), 0.78 (t, *J* = 7.4 Hz, 3H), 0.17 (s, 9H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.2, 136.0, 134.2, 133.7, 133.2, 131.1, 130.2, 129.8, 129.6, 127.8, 127.5, 126.7, 111.4, 104.2, 92.7, 82.9, 73.6, 73.6, 36.7, 36.5, 29.2, 27.0, 19.3, 9.8, 0.0; IR (thin film, neat) ν_{max} 3071, 3049, 2961, 2927, 2856, 2148, 1738, 1463, 1428, 1377, 1261, 1098, 1029, 843, 756, 741 cm^{-1}; HR-MS (ESI+) calcd for $C_{34}H_{47}O_2Si_2$ (M + H^+) 543.3109, found 543.3104.

(2*S*,3*R*,5*Z*,7*Z*,9*S*)-9-Ethyl-2-((*Z*)-pent-2-en-4-yn-1-yl)-2,3,4,9-tetrahydrooxonin-3-ol (19)

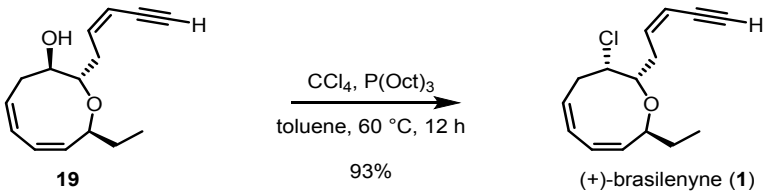


5a **19**

To a solution of enyne **5a** (13 mg, 0.02 mmol) in THF (1 mL) was added TBAF (1M in THF, 0.1 mL, 0.1 mmol) at room temperature. The mixture was stirred for 6 h at the same temperature, quenched with water, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography

(Et_2O/pentane = 1:6) to provide 6 mg (99%) of **19** as a white solid.[3] mp. 48-49 °C; $[\alpha]_D^{20}$ = +368.20 (*c* 0.20, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.24 (dddd, *J* = 11.0, 9.2, 5.9, 0.9 Hz, 1H), 6.12 (ddd, *J* = 11.5, 3.2, 1.4 Hz, 1H), 5.92 (d, *J* = 11.0 Hz, 1H), 5.79 (td, *J* = 9.6, 7.3 Hz, 1H), 5.58 (d, *J* = 11.0 Hz, 1H), 5.54 (ddd, *J* = 11.2, 5.7, 1.1 Hz, 1H), 4.06 (q, *J* = 6.4 Hz, 1H), 3.86 (dt, *J* = 8.3, 5.0 Hz, 1H), 3.60 (tdd, *J* = 8.7, 5.0, 2.8 Hz, 1H), 3.13 (d, *J* = 2.3 Hz, 1H), 2.87 (ddd, *J* = 15.1, 9.2, 5.0 Hz, 1H), 2.68 (dt, *J* = 13.3, 9.2 Hz, 1H), 2.57 (dtd, *J* = 14.7, 5.5, 1.7 Hz, 1H), 2.28 (dd, *J* = 13.3, 6.9 Hz, 1H), 1.92 (d, *J* = 5.1 Hz, 1H), 1.70 (d quint, *J* = 13.7, 7.4 Hz, 1H), 1.55 (d quint, *J* = 13.3, 7.4 Hz, 1H), 0.89 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (200 MHz, $CDCl_3$) δ 142.5, 134.1, 132.7, 130.0, 127.5, 109.8, 82.2, 80.6, 79.6, 75.0, 70.9, 36.6, 34.6, 29.0, 10.2; IR (thin film, neat) ν_{max} 3423, 3311, 3006, 2960, 2926, 2874. 2096, 1727, 1637, 1442, 1378, 1232, 1122, 1063, 891, 860, 752 cm^{-1}; HR-MS (ESI+) calcd for $C_{15}H_{20}NaO_2$ (M + Na^+) 255.1356, found 255.1350.

(+)-Brasilenyne (1)[3,4]



19 (+)-brasilenyne (**1**)

To a solution of alcohol **19** (4.4 mg, 0.02 mmol) in toluene (0.5 mL) were added carbon tetrachloride (0.01 mL, 0.1 mmol) and (*n*-Oct)$_3$P (0.08 mL, 0.2 mmol). The mixture was stirred for 30 min at room temperature and then was warmed to 60 °C. The reaction mixture was stirred for 12 h, quenched with saturated Na_2SO_3 solution, and extracted with Et_2O. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography (Et_2O/pentane = 1:50) to provide 4.2 mg (93%) of (+)-brasilenyne (**1**) as a white solid.[3,4] mp. 37-38 °C; $[\alpha]_D^{20}$ = +224.47 (*c* 0.35, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.21 (d, *J* = 11.5 Hz, 1H), 6.05 (d, *J* = 11.5 Hz, 1H), 6.03 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.79 (dt, *J* = 11.0, 7.8 Hz, 1H), 5.55 (dd, *J* = 11.0, 1.4 Hz, 1H), 5.53 (d, J = 11.0 Hz, 1H), 4.27 (q, *J* = 6.9 Hz, 1H), 4.07 (d, *J* = 8.2 Hz,

1H), 3.89 (t, J = 6.9 Hz, 1H), 3.11 (d, J = 2.0 Hz, 1H), 2.70 (dt, J = 14.2, 7.8 Hz, 1H), 2.65 (dt, J = 13.7, 7.6 Hz, 1H), 2.60 (dt, J = 13.3, 7.1 Hz, 1H), 2.46 (dd, J = 13.5, 8.0 Hz, 1H), 1.70 (d quint, J = 13.7, 7.3 Hz, 1H), 1.51 (d quint, J = 13.7, 7.3 Hz, 1H), 0.89 (t, J = 7.3 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.4, 134.3, 133.5, 129.7, 128.7, 110.5, 82.2, 80.2, 75.7, 75.6, 63.0, 36.5, 36.0, 28.7, 10.1; IR (thin film, neat) ν_{max} 3296, 3007, 2962, 2930, 2875, 2096, 1731, 1624, 1463, 1435, 1379, 1353, 1328, 1261, 1121, 1089, 1026, 860, 750; HR-MS (ESI+) calcd for $C_{15}H_{19}ClNaO$ ($M + Na^+$) 273.1017, found 273.1027.

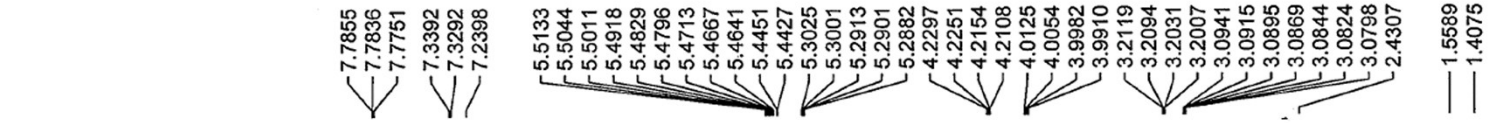
Table 1. ^{1}H NMR Data of Natural and Synthetic (+)-Brasilenyne (**2**)

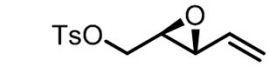
Carbon No.	Natural **2** Solvent: CCl_4 (220 MHz) Ref. peak: TMS	Denmark's Synthetic **2** Solvent: $CDCl_3$ (500 MHz) Ref. peak: $CHCl_3$ (δ 7.26 ppm)	Synthetic **2** Solvent: $CDCl_3$ (600 MHz) Ref. peak: $CHCl_3$ (δ 7.24 ppm)
7	6.24 (ddd, *J* = 10.0, 2.0, 1.0 Hz)	6.23 (ddd, *J* = 11.0, 2.5, 1.5 Hz)	6.21 (d, *J* = 11.5 Hz)
6	~ 6.0 (dd, *J* = 11.0, 2.0 Hz)	6.07 (br d, *J* = 11.5 Hz)	6.05 (d, *J* = 11.5 Hz)
2'	~ 6.09 (m)	6.04 (dddd, *J* = 11.0, 8.0, 7.0, 1.0 Hz)	6.03 (dt, *J* = 11.5, 7.6 Hz)
5	5.82 (ddd, *J* = 11.0, 8.0, 8.0 Hz)	5.81 (dddd, *J* = 11.0, 7.5, 7.5, 1.0 Hz)	5.79 (dt, *J* = 11.0, 7.8 Hz)
8	~ 5.55 (dd, *J* = 10.0, 8.0 Hz)	5.55 (ddd, *J* = 11.0, 7.0, 1.0 Hz)	5.55 (dd, *J* = 11.0, 1.4 Hz)
3'	~ 5.55 (dd, *J* = 11.0, 2.0 Hz)	5.54 (dd, *J* = 11.0, 1.0)	5.53 (d, *J* = 11.0 Hz)
9	4.29 (dddd, *J* = 8.0, 7.0, 7.0,1.0 Hz)	4.29 (ddd, *J* = 7.0, 7.0, 7.0 Hz)	4.27 (q, *J* = 6.9 Hz)
3	4.09 (ddd, *J* = 8.0, 3.0, 1.0 Hz)	4.08 (br d, *J* = 8.0 Hz)	4.07 (d, *J* = 8.2 Hz)
2	3.91 (ddd, *J* = 7.0, 7.0, 1.0 Hz)	3.90 (ddd, *J* = 8.5, 6.5, 1.0 Hz)	3.89 (t, *J* = 6.9 Hz)
5'	3.14 (d, *J* = 2.0)	3.13 (d, *J* = 2.0)	3.11 (d, *J* = 2.0 Hz)
1'	~ 2.7 (m)	2.72 (dddd, *J* = 14.0, 8.0, 8.0, 1.0 Hz)	2.70 (dt, *J* = 14.2, 7.8 Hz)
4	~2.7 (m)	2.67 (dddd, *J* = 13.5, 7.5, 7.5, 1.0 Hz)	2.65 (dt, *J* = 13.7, 7.6 Hz)
1'	~ 2.60 (ddd, *J* = 14.0, 8.0, 8.0 Hz)	2.61 (dddd, *J* = 14.0, 7.0, 6.5, 1.0 Hz)	2.60 (dt, *J* = 13.3, 7.1 Hz)
4	2.50 (ddd, *J* = 14.0, 8.0, 3.0 Hz)	2.48 (dd, *J* = 13.5, 8.0 Hz)	2.46 (dd, *J* = 13.5, 8.0 Hz)
10	1.73 (dddd, *J* = 14.0, 7.0, 7.0, 7.0 Hz)	1.72 (ddq, *J* = 14.5, 7.5, 7.5 Hz)	1.70 (d quint, *J* = 13.7, 7.3 Hz)
10	1.55 (dddd, *J* = 14.0, 7.0, 7.0,7.0 Hz)	1.53 (ddq, *J* = 14.5, 7.5, 7.5 Hz)	1.51 (d quint, *J* = 13.7, 7.3 Hz)
11	0.91 (dd, *J* = 7.0, 7.0)	0.91 (dd, *J* = 7.5, 7.5 Hz)	0.89 (t, *J* = 7.3 Hz)

Table 2. ^{13}C NMR Data of Natural and Synthetic (+)-Brasilenyne (**2**)

Carbon No.	Natural **2** Solvent: CCl_4 (55 MHz) Ref. peak: TMS	Denmark's Synthetic **2** Solvent: $CDCl_3$ (125 MHz) Ref. peak: $CDCl_3$ (δ 77.0 ppm)	Synthetic **2** Solvent: $CDCl_3$ (150 MHz) Ref. peak: $CDCl_3$ (δ 77.0 ppm)	Δ δ (Natural **2**/ Denmark's Synthetic **2)**
2'	141.2	141.4	141.4	+0.2/0
8	134.2	134.3	134.3	+0.1/0
7	133.3	133.5	133.5	+0.2/0
6	129.5	129.7	129.7	+0.2/0
5	128.6	128.7	128.7	+0.1/0
3'	110.4	110.7	110.5	+0.1/-0.2
5'	82.0	82.2	82.2	+0.2/0
4'	80.1	80.2	80.2	+0.1/0
2	76.0	75.7	75.7	-0.3/0
9	75.6	75.5	75.6	0/+0.1
3	62.9	63.0	63.0	+0.1/0
1'	36.3	36.4	36.5	+0.2/+0.1
4	35.9	36.0	36.0	+0.1/0
10	28.5	28.6	28.7	+0.2/+0.1
11	9.9	10.1	10.1	+0.2/0

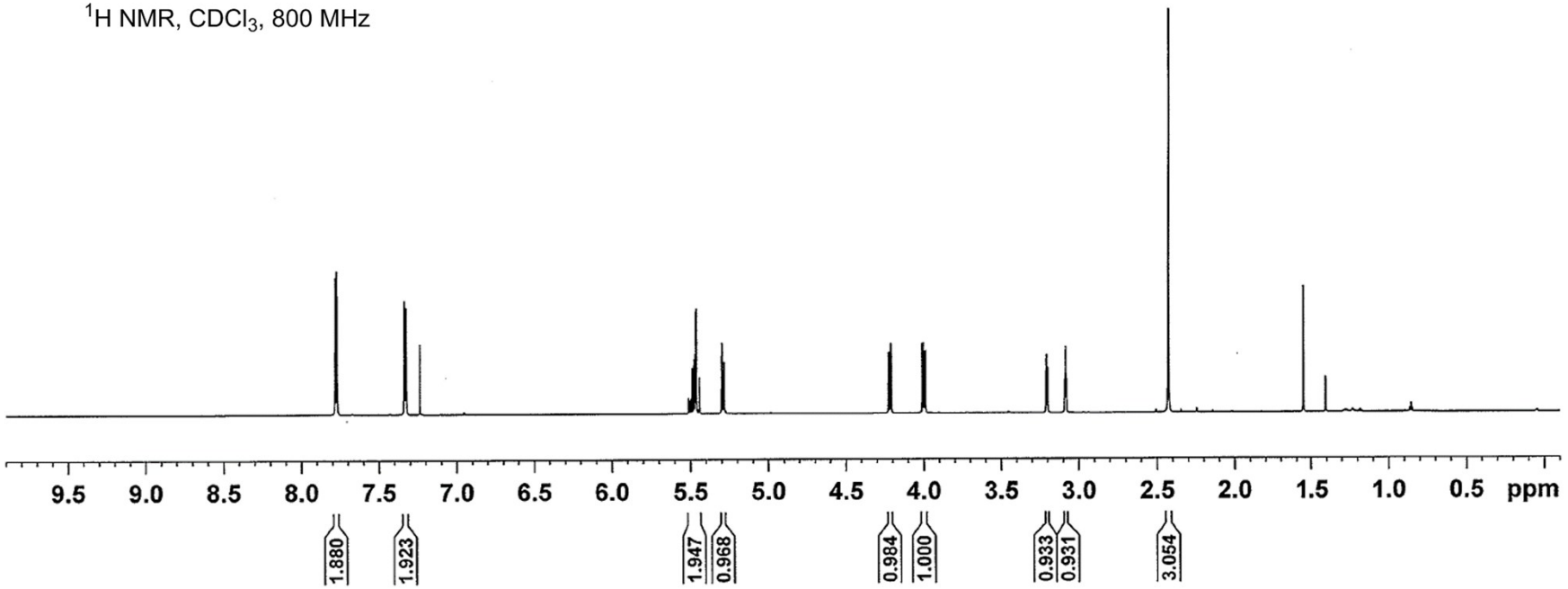
III. ^{1}H- and ^{13}C-NMR Spectra

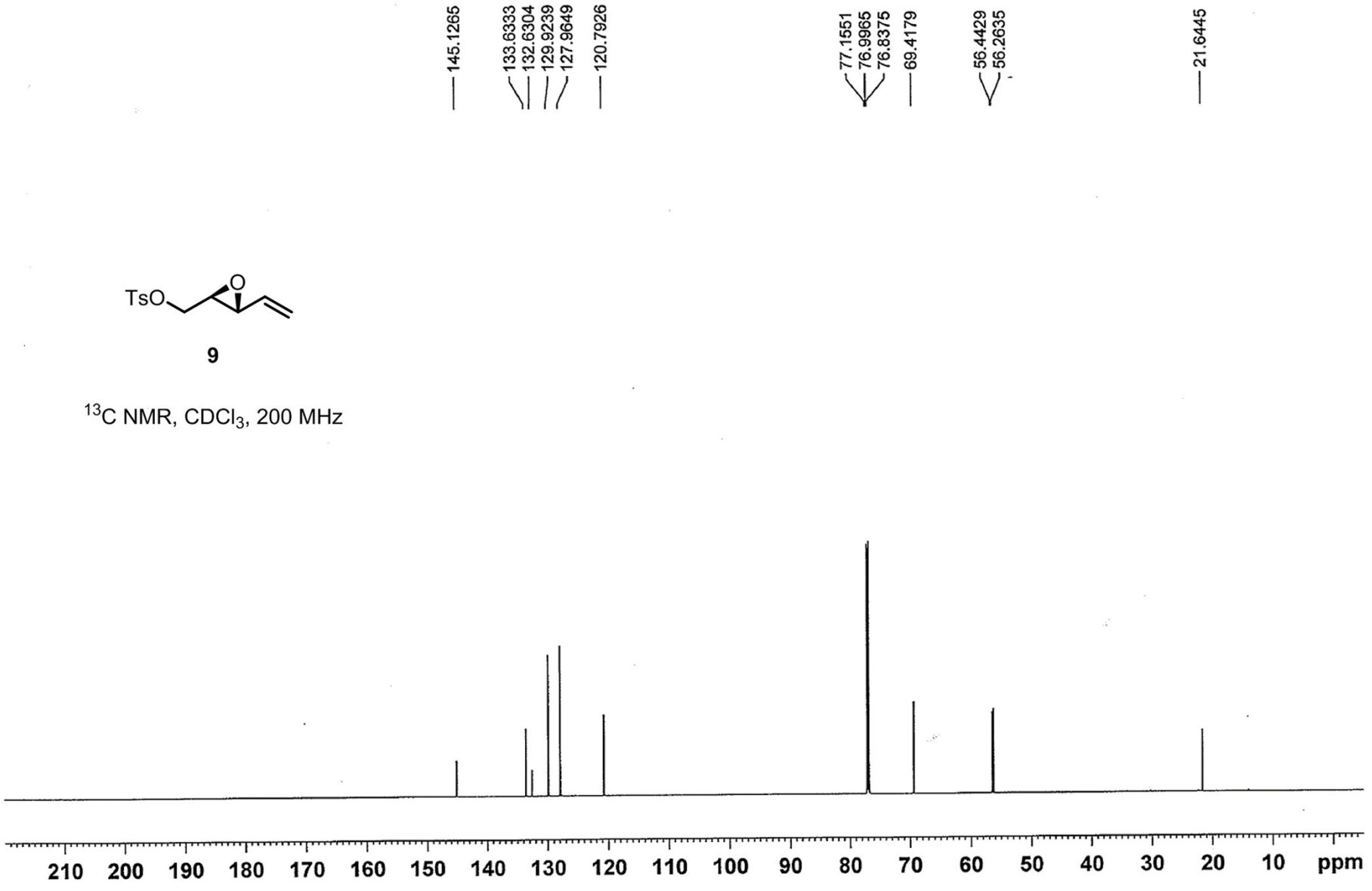


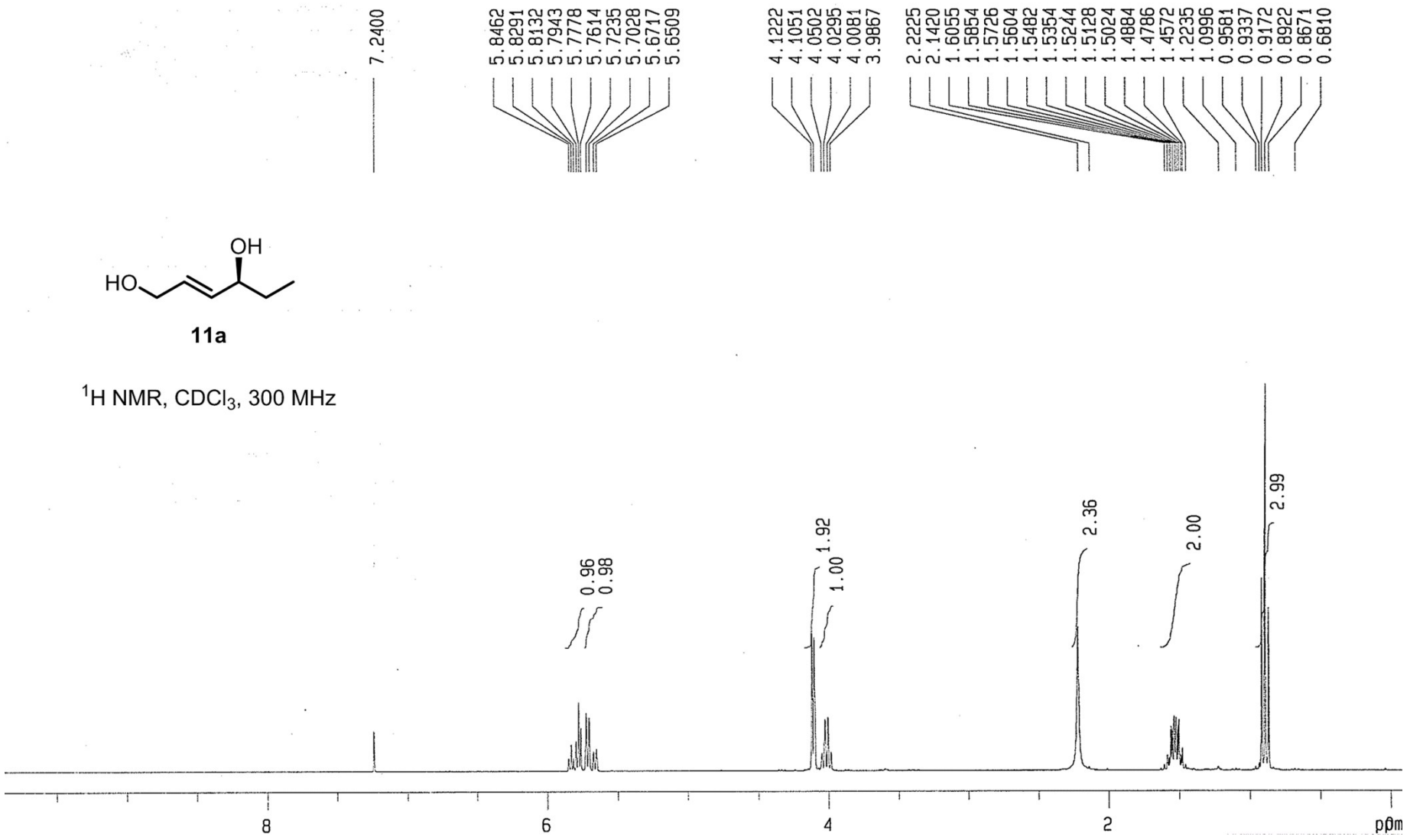


9

^{1}H NMR, $CDCl_3$, 800 MHz




145.1265
133.6333
132.6304
129.9239
127.9649
120.7926
77.1551
76.9965
76.8375
69.4179
56.4429
56.2635
21.6445
TsO
O
9
^{13}C NMR, $CDCl_3$, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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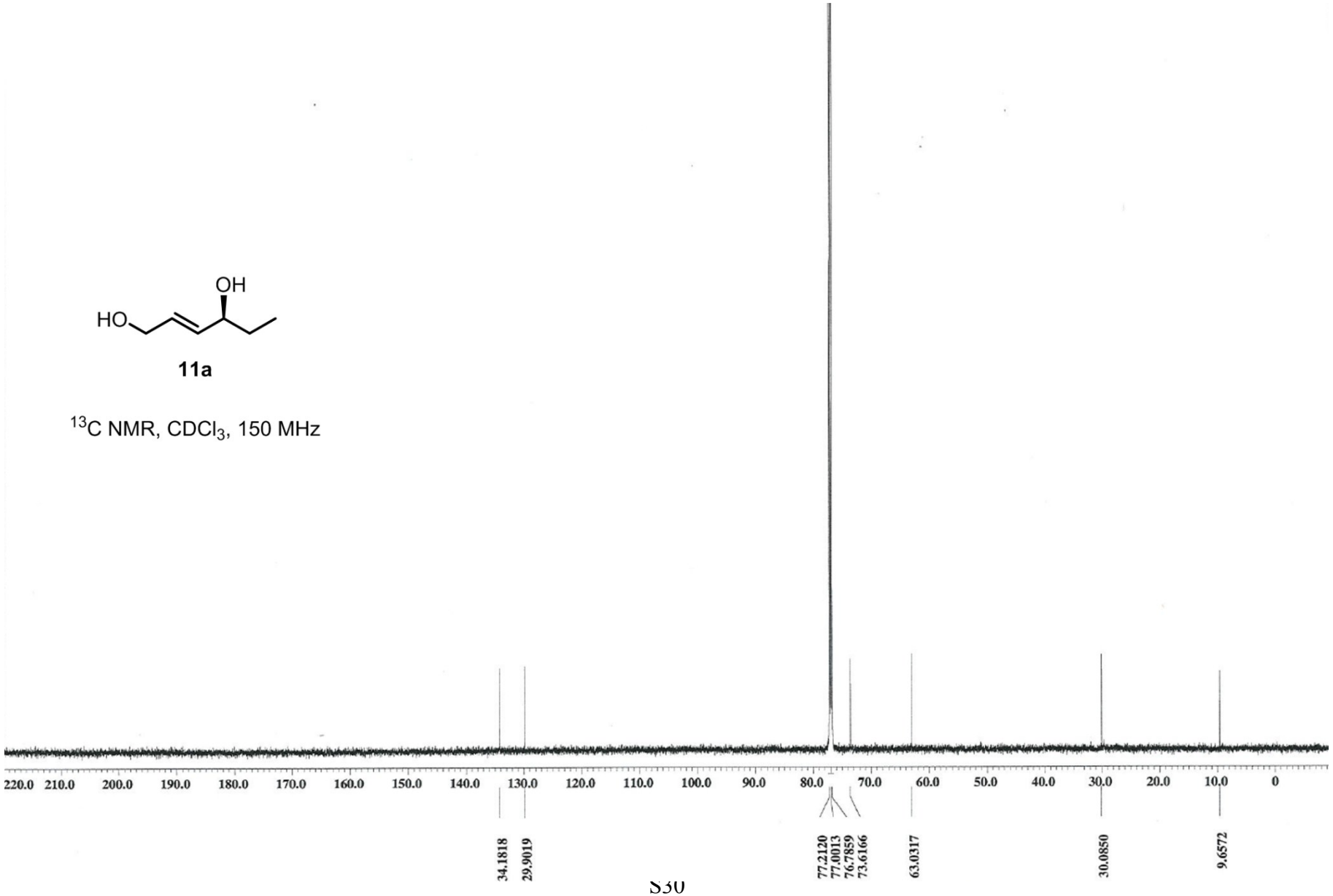
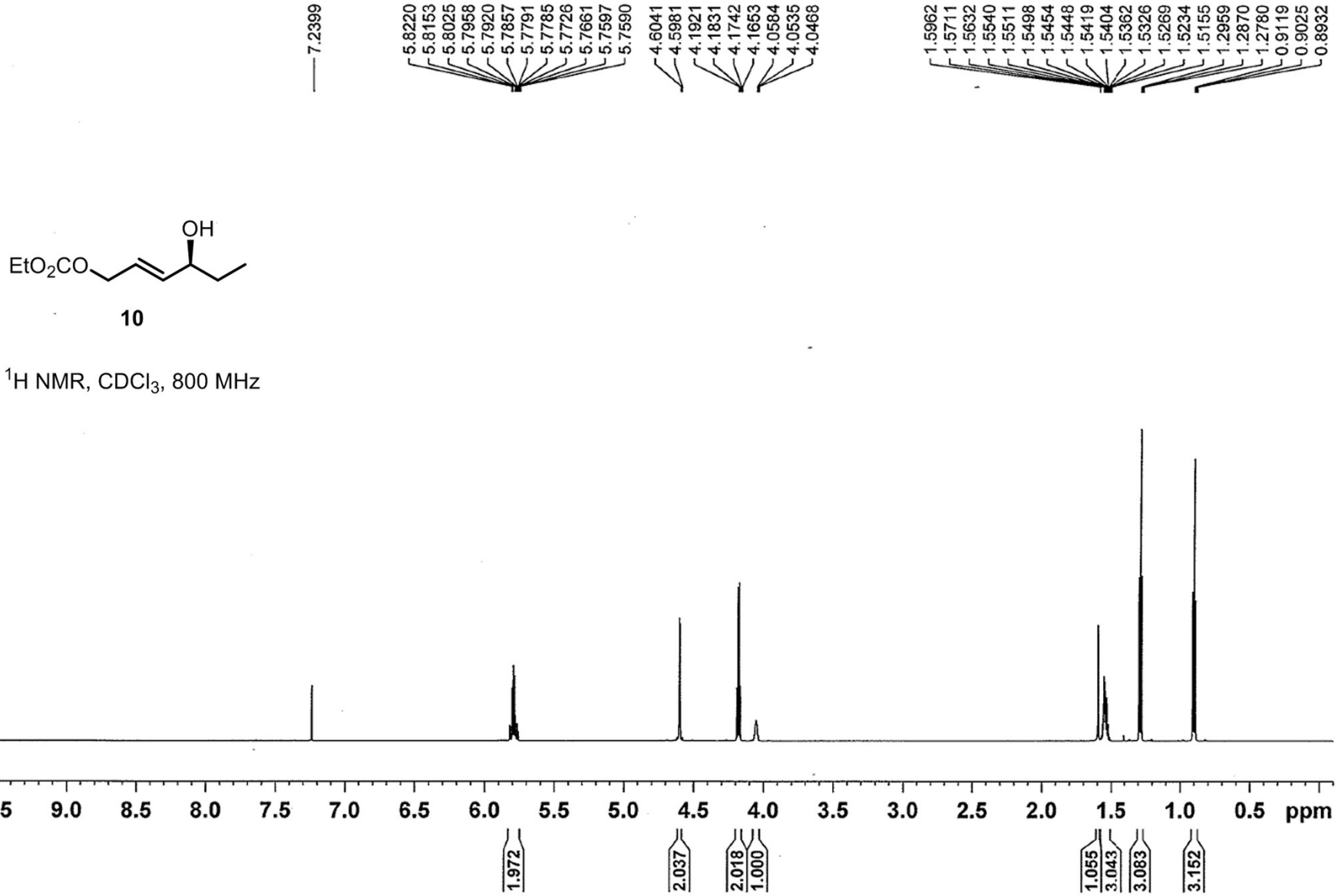
5.8462
5.8291
5.8132
5.7943
5.7778
5.7614
5.7235
5.7028
5.6717
5.6509
4.1222
4.1051
4.0502
4.0295
4.0081
3.9867
2.2225
2.1420
1.6055
1.5854
1.5726
1.5604
1.5482
1.5354
1.5244
1.5128
1.5024
1.4884
1.4786
1.4572
1.2235
1.0996
0.9581
0.9337
0.9172
0.8922
0.8671
0.6810
OH
HO
11a
1H NMR, CDCl3, 300 MHz
0.96
0.98
1.92
1.00
2.36
2.00
2.99
8
6
4
2
0
ppm


OH
HO
11a
^{13}C NMR, $CDCl_3$, 150 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
34.1818
29.9019
77.2120
77.0013
76.7859
73.6166
63.0317
30.0850
9.6572


7.2399
5.8220
5.8153
5.8025
5.7958
5.7920
5.7857
5.7791
5.7785
5.7726
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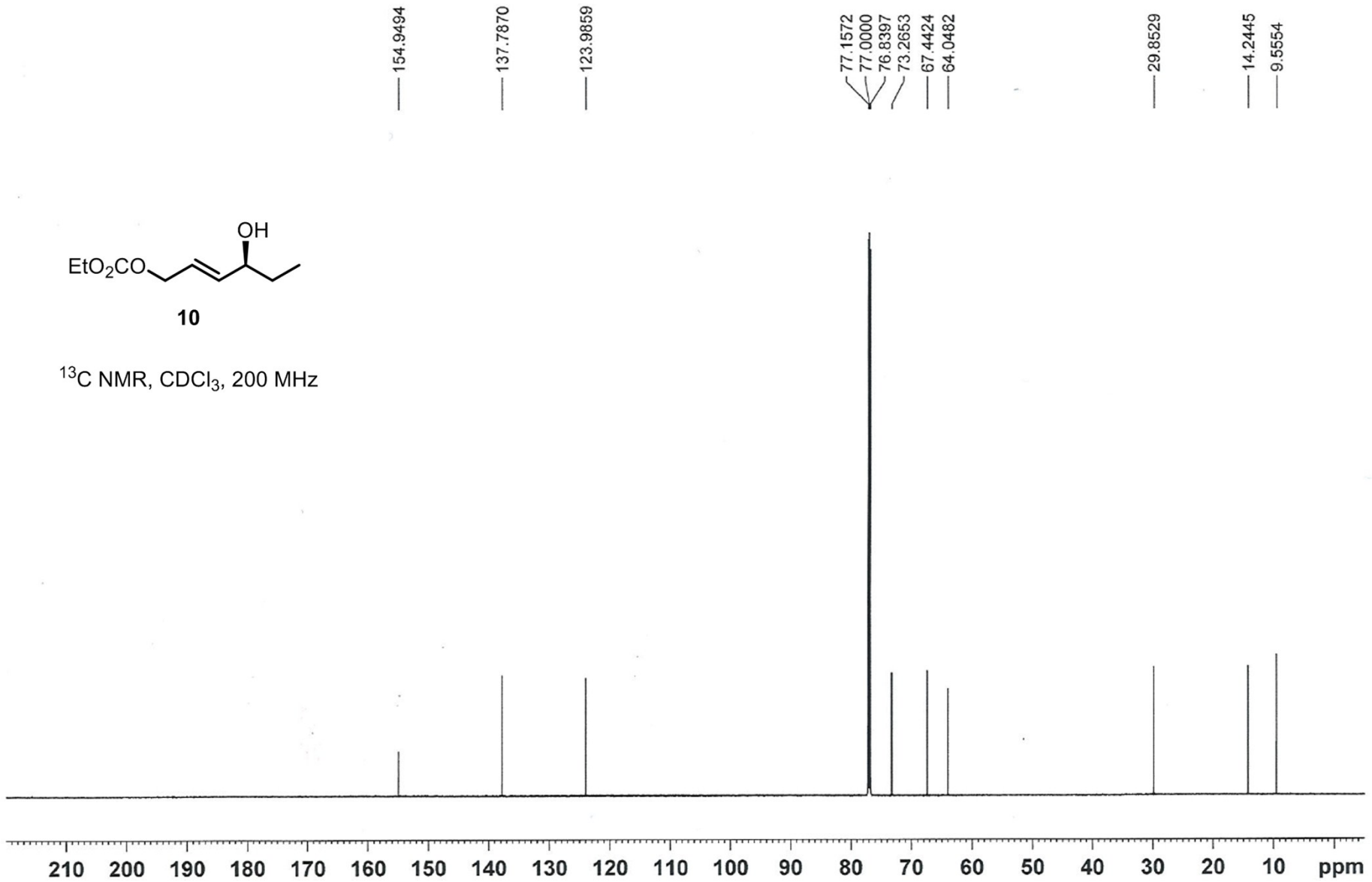
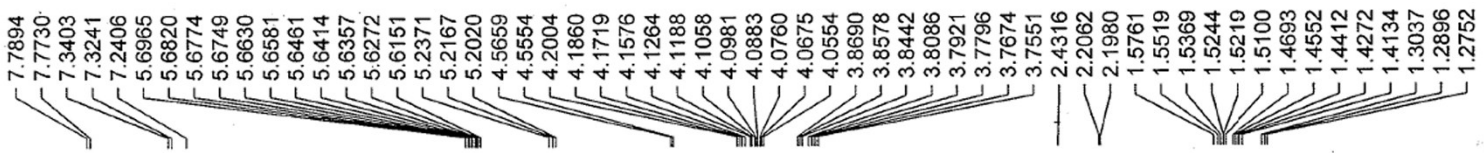
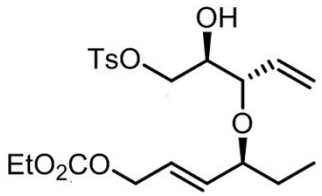
5.7597
5.7590
4.6041
4.5981
4.1921
4.1831
4.1742
4.1653
4.0584
4.0535
4.0468
1.5962
1.5711
1.5632
1.5540
1.5511
1.5498
1.5454
1.5448
1.5419
1.5404
1.5362
1.5326
1.5269
1.5234
1.5155
1.2959
1.2870
1.2780
0.9119
0.9025
0.8932
OH
EtO2CO
10
1H NMR, CDCl3, 800 MHz
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.972
2.037
2.018
1.000
1.055
3.043
3.083
3.152

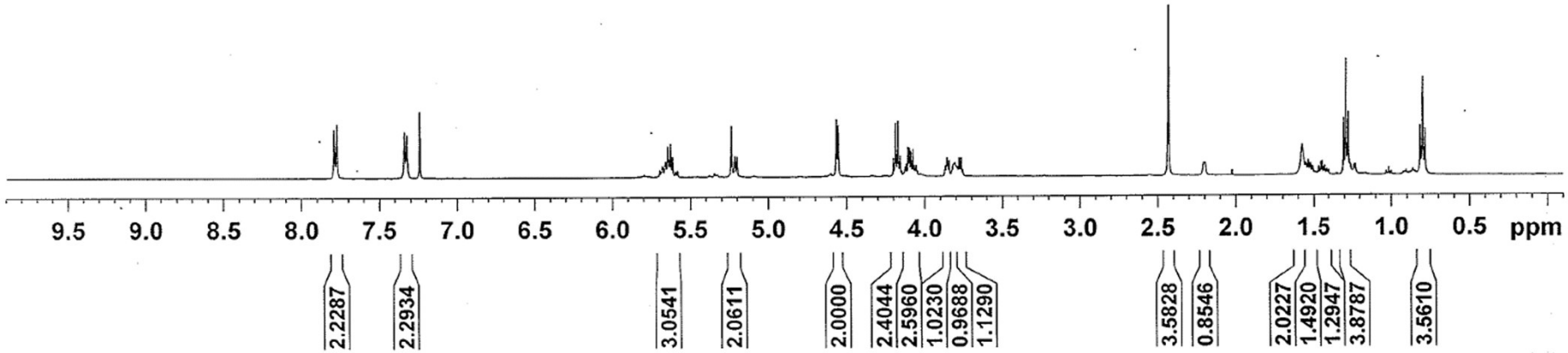

154.9494
137.7870
123.9859
77.1572
77.0000
76.8397
73.2653
67.4424
64.0482
29.8529
14.2445
9.5554
OH
EtO2CO
10
13C NMR, CDCl3, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

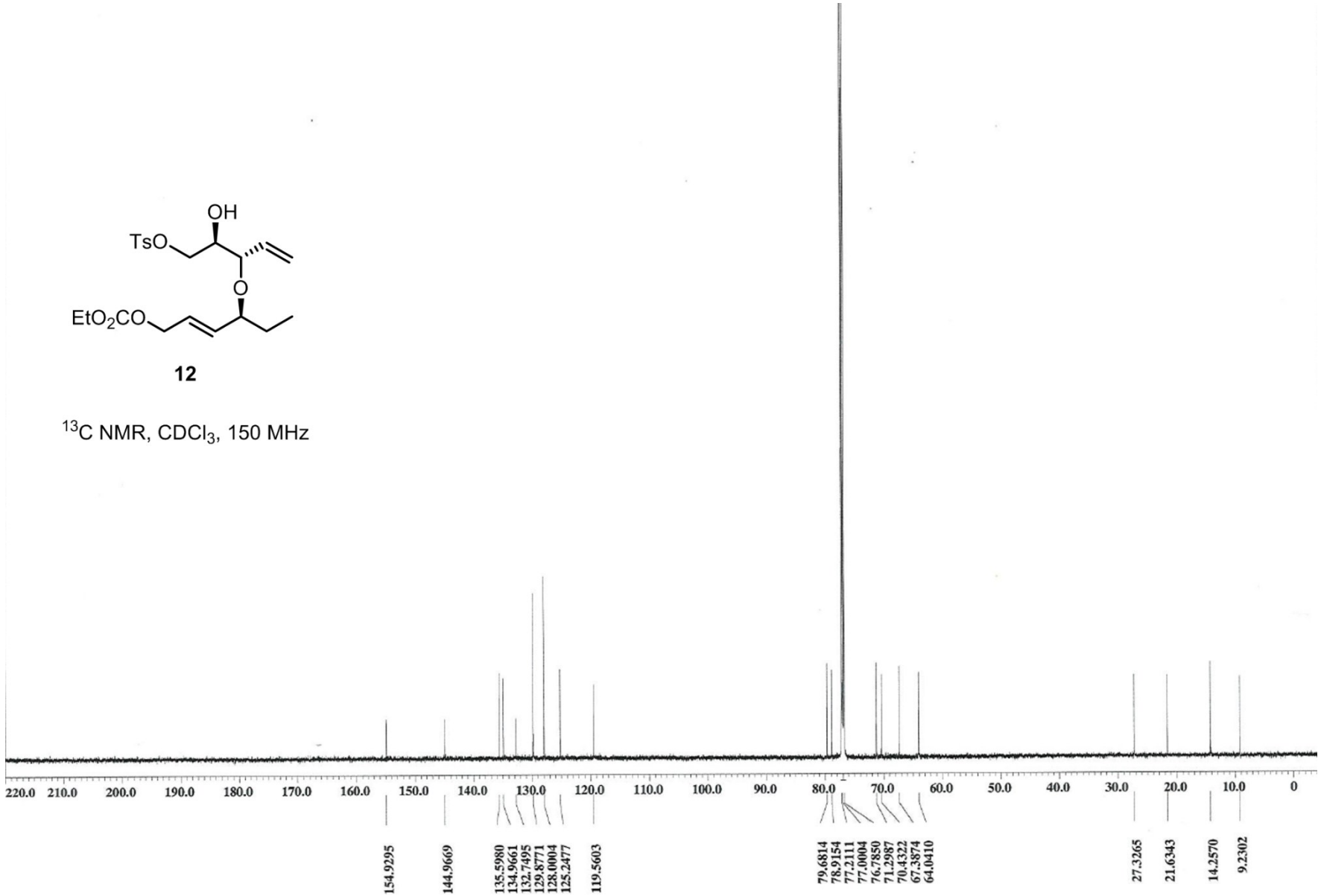


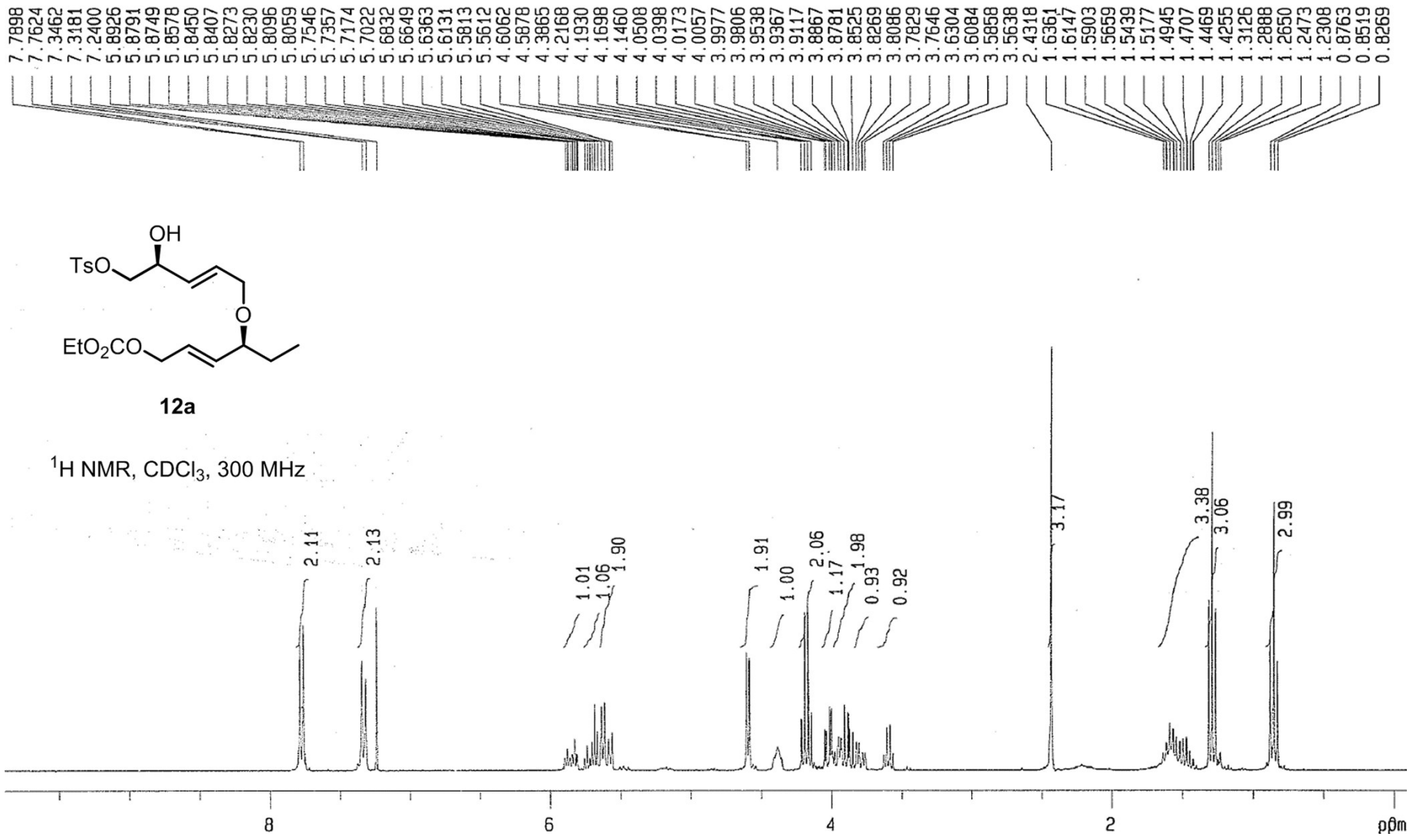


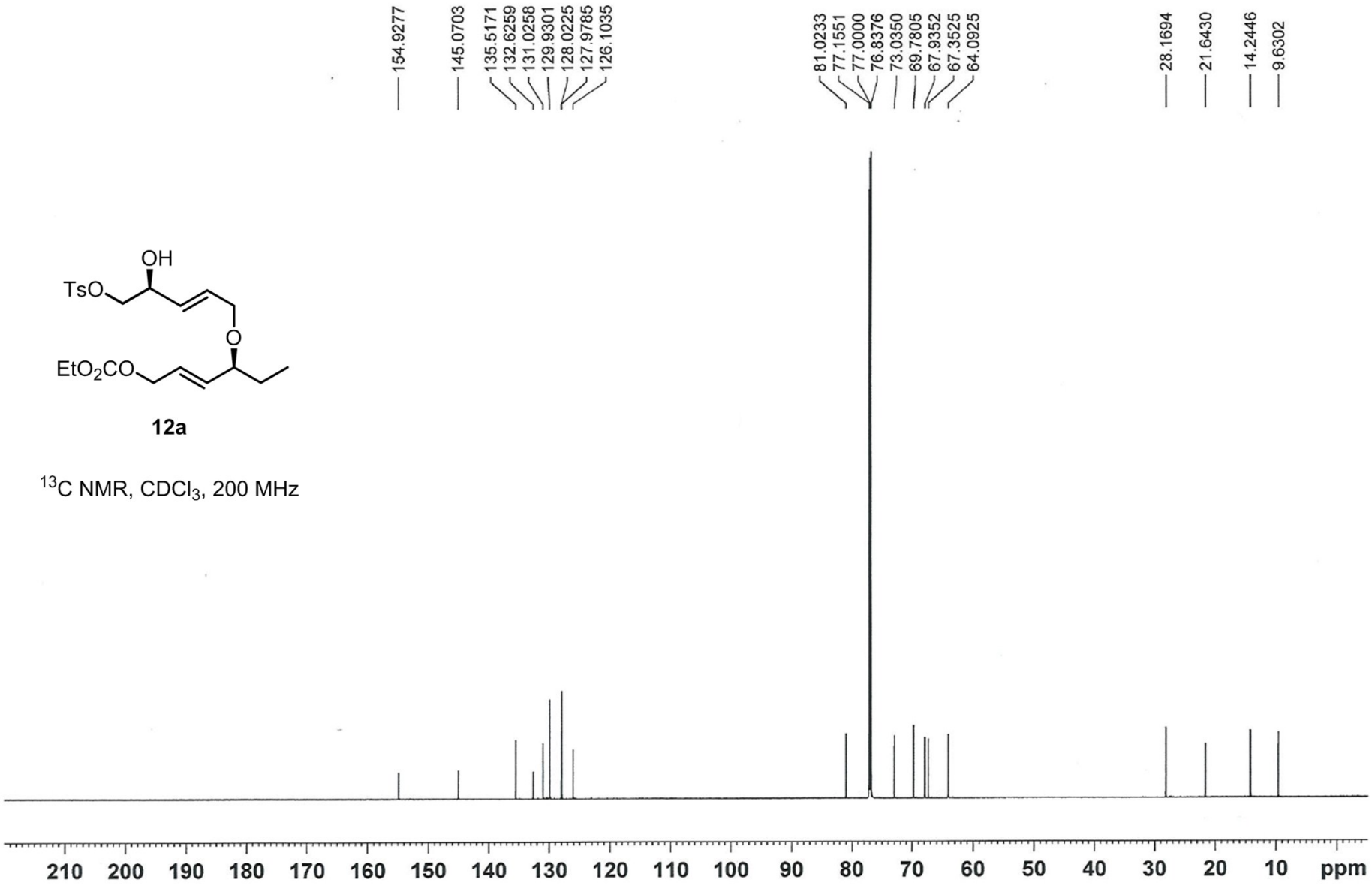
12

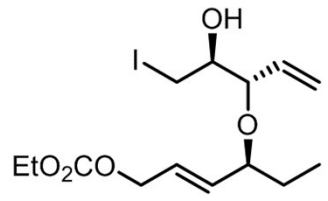
^{1}H NMR, $CDCl_3$, 500 MHz




OH
TsO
O
EtO2CO
12
13C NMR, CDCl3, 150 MHz
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
154.9295
144.9669
135.5980
134.9661
132.7495
129.8771
128.0004
125.2477
119.5603
79.6814
78.9154
77.2111
77.0004
76.7850
71.2987
70.4322
67.3874
64.0410
27.3265
21.6343
14.2570
9.2302

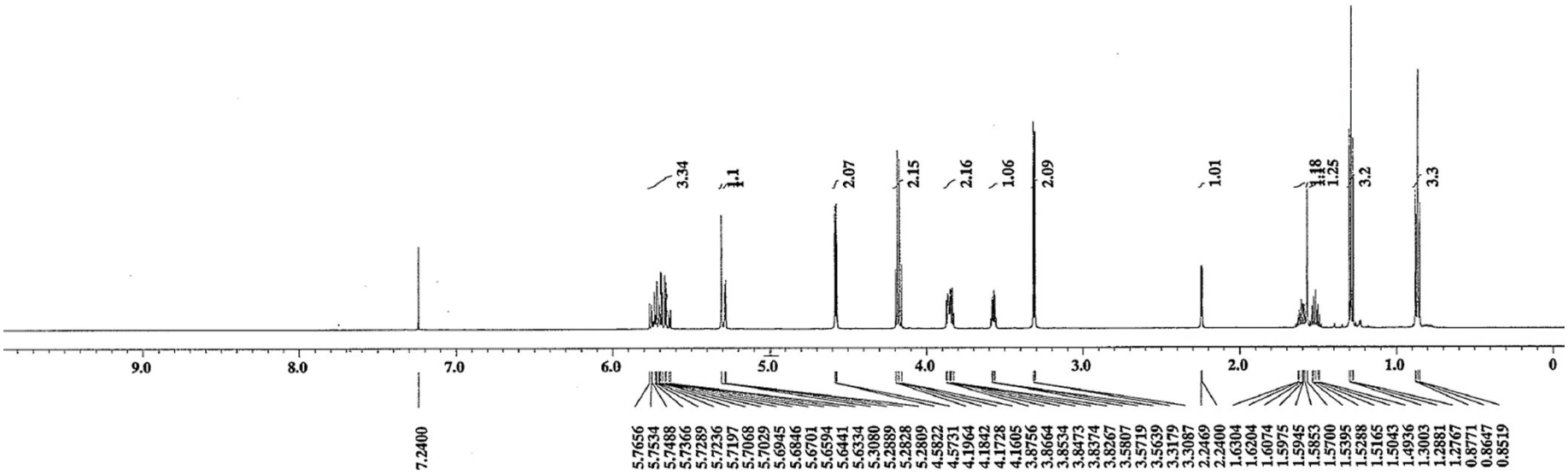

7.7898
7.7624
7.3462
7.3181
7.2400
5.8926
5.8791
5.8749
5.8578
5.8450
5.8407
5.8273
5.8230
5.8096
5.8059
5.7546
5.7357
5.7174
5.7022
5.6832
5.6649
5.6363
5.6131
5.5813
5.5612
4.6062
4.5878
4.3865
4.2168
4.1930
4.1698
4.1460
4.0508
4.0398
4.0173
4.0057
3.9977
3.9806
3.9538
3.9367
3.9117
3.8867
3.8781
3.8525
3.8269
3.8086
3.7829
3.7646
3.6304
3.6084
3.5858
3.5638
2.4318
1.6361
1.6147
1.5903
1.5659
1.5439
1.5177
1.4945
1.4707
1.4469
1.4255
1.3126
1.2888
1.2650
1.2473
1.2308
0.8763
0.8519
0.8269
OH
TsO
O
EtO2CO
12a
1H NMR, CDCl3, 300 MHz
2.11
2.13
1.01
1.06
1.90
1.91
1.00
2.06
1.17
1.98
0.93
0.92
3.17
3.38
3.06
2.99
8
6
4
2
ppm

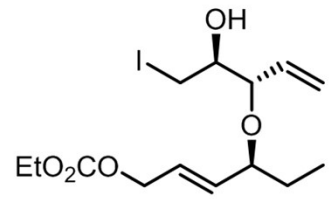

154.9277
145.0703
135.5171
132.6259
131.0258
129.9301
128.0225
127.9785
126.1035
81.0233
77.1551
77.0000
76.8376
73.0350
69.7805
67.9352
67.3525
64.0925
28.1694
21.6430
14.2446
9.6302
OH
TsO
O
EtO2CO
12a
13C NMR, CDCl3, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



12b

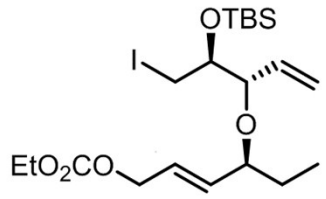
^{1}H NMR, $CDCl_3$, 600 MHz





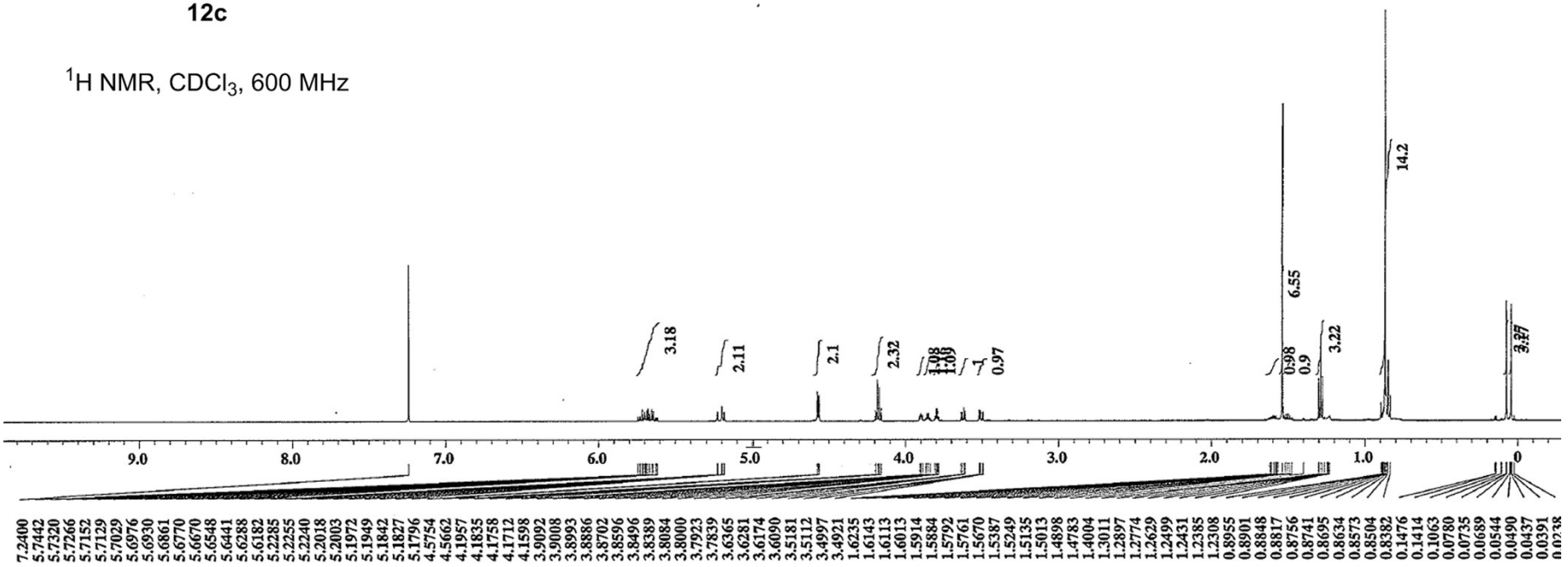
12b

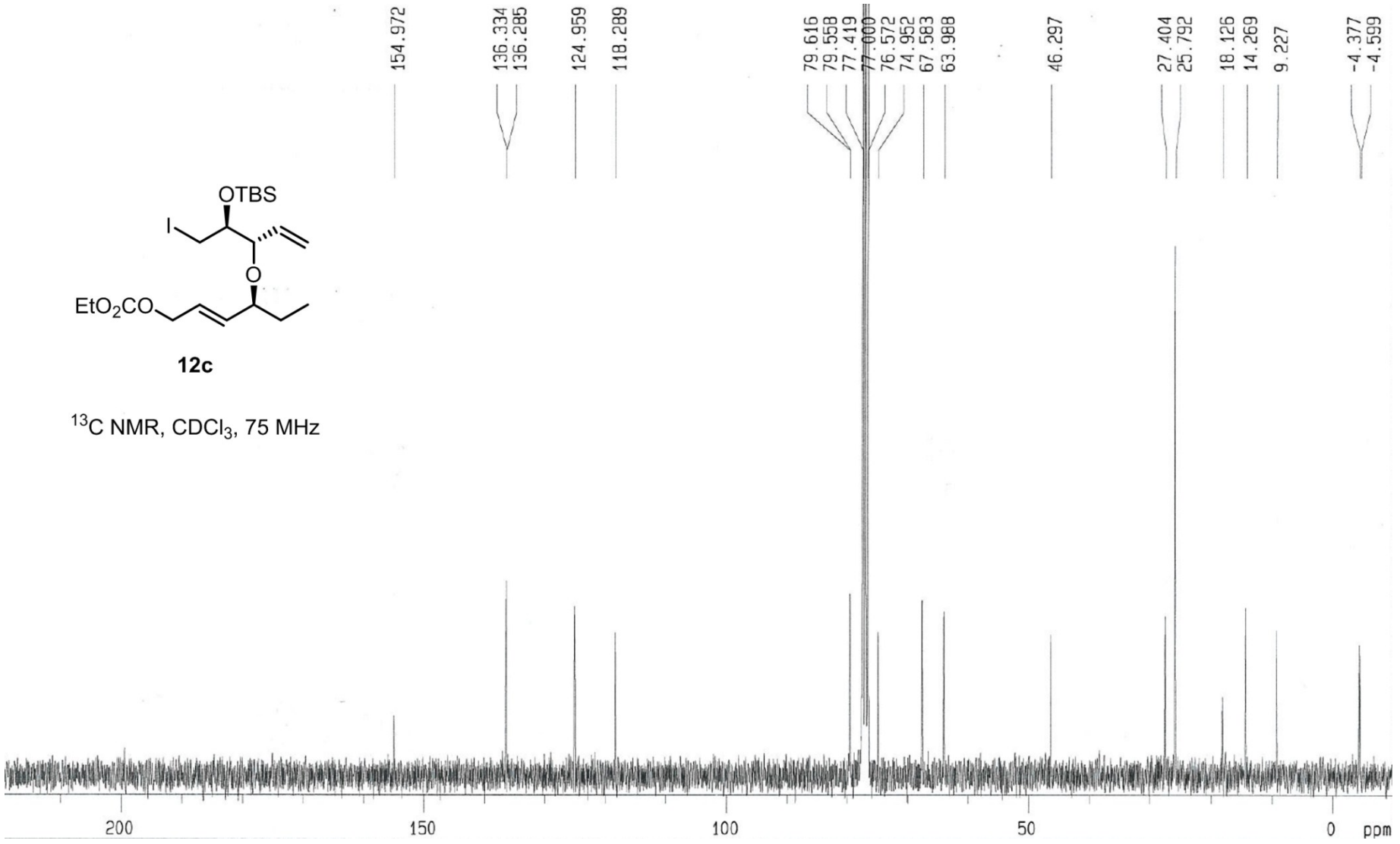
^{13}C NMR, $CDCl_3$, 150 MHz

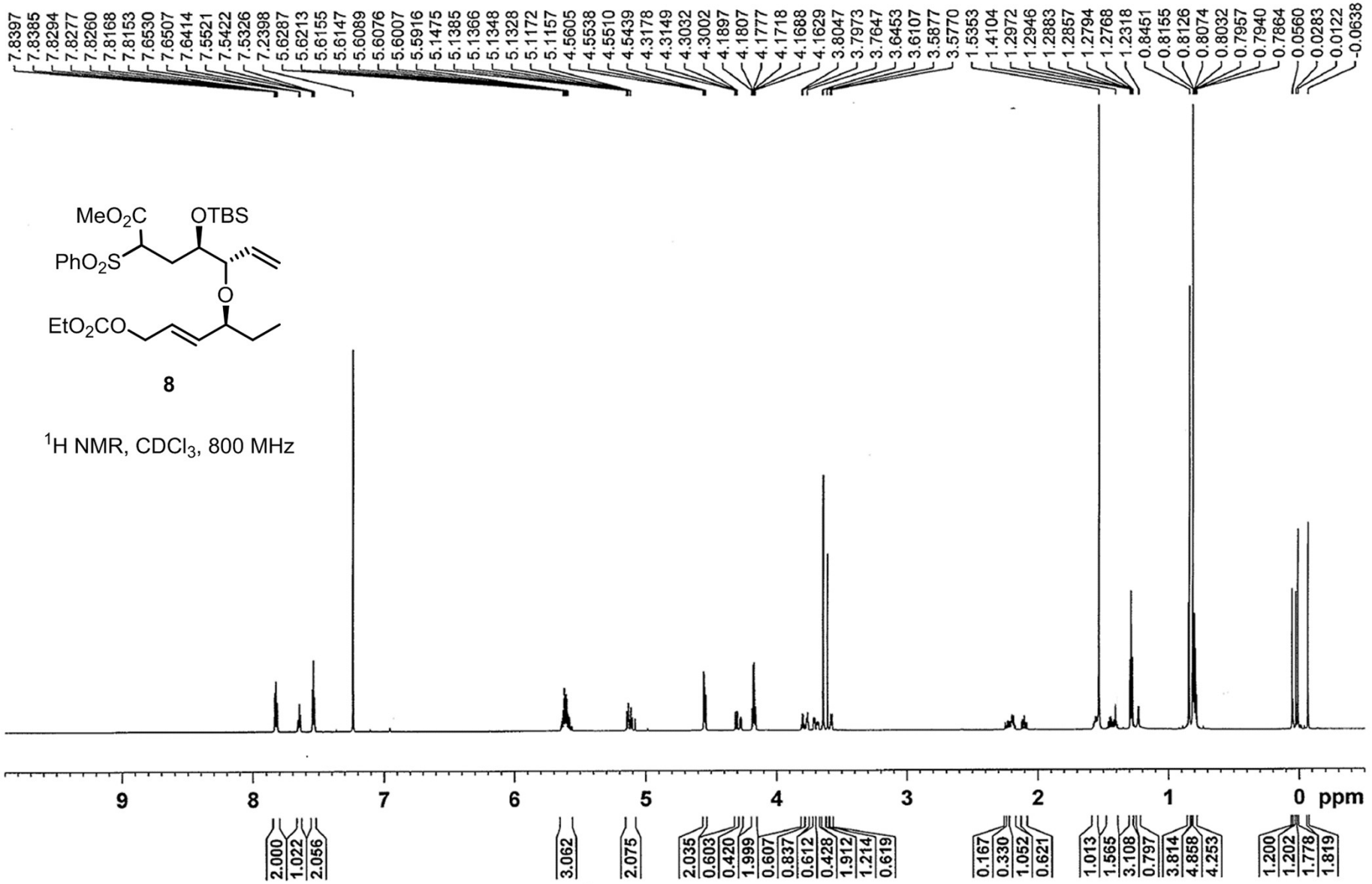


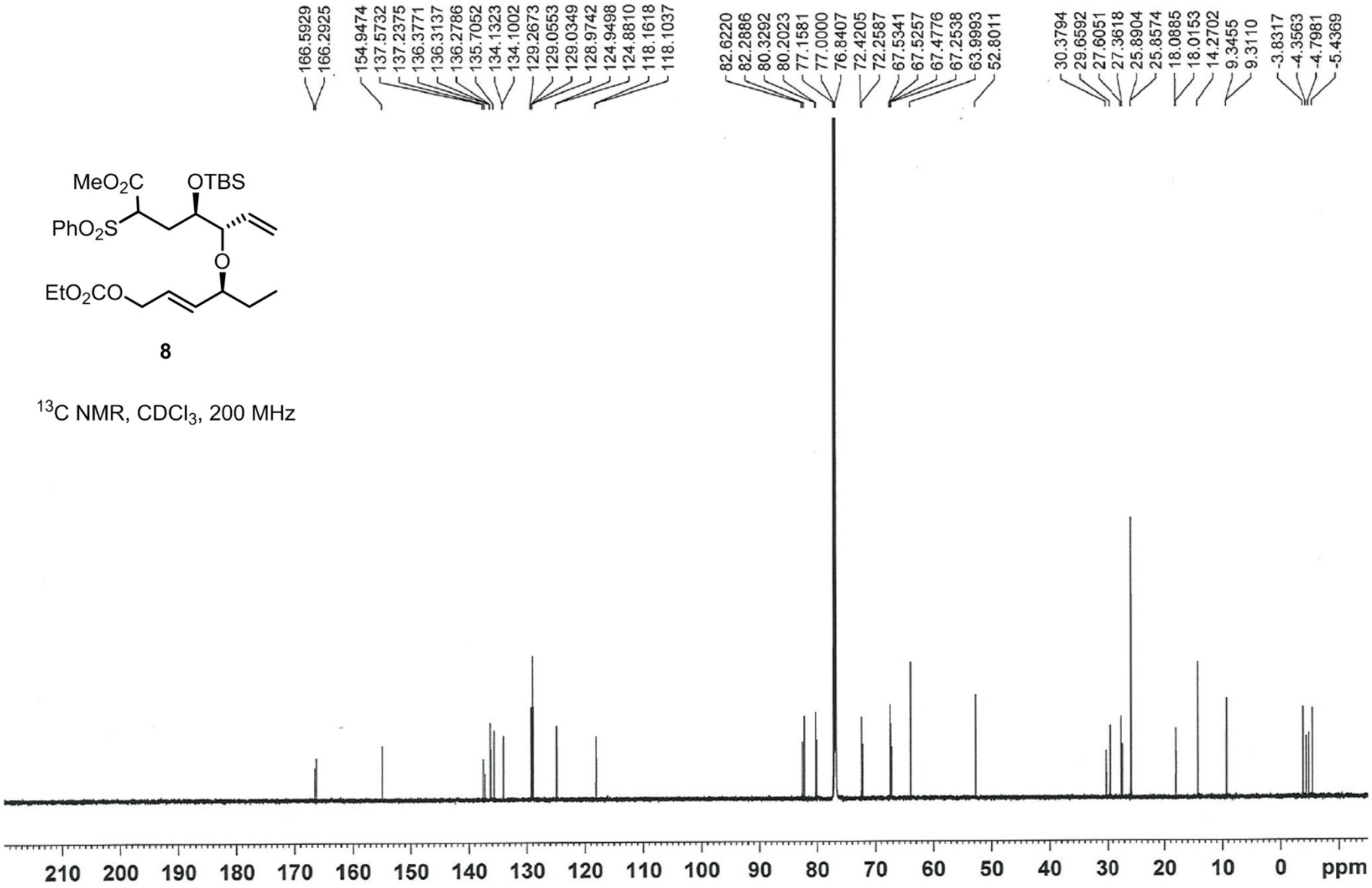
12c

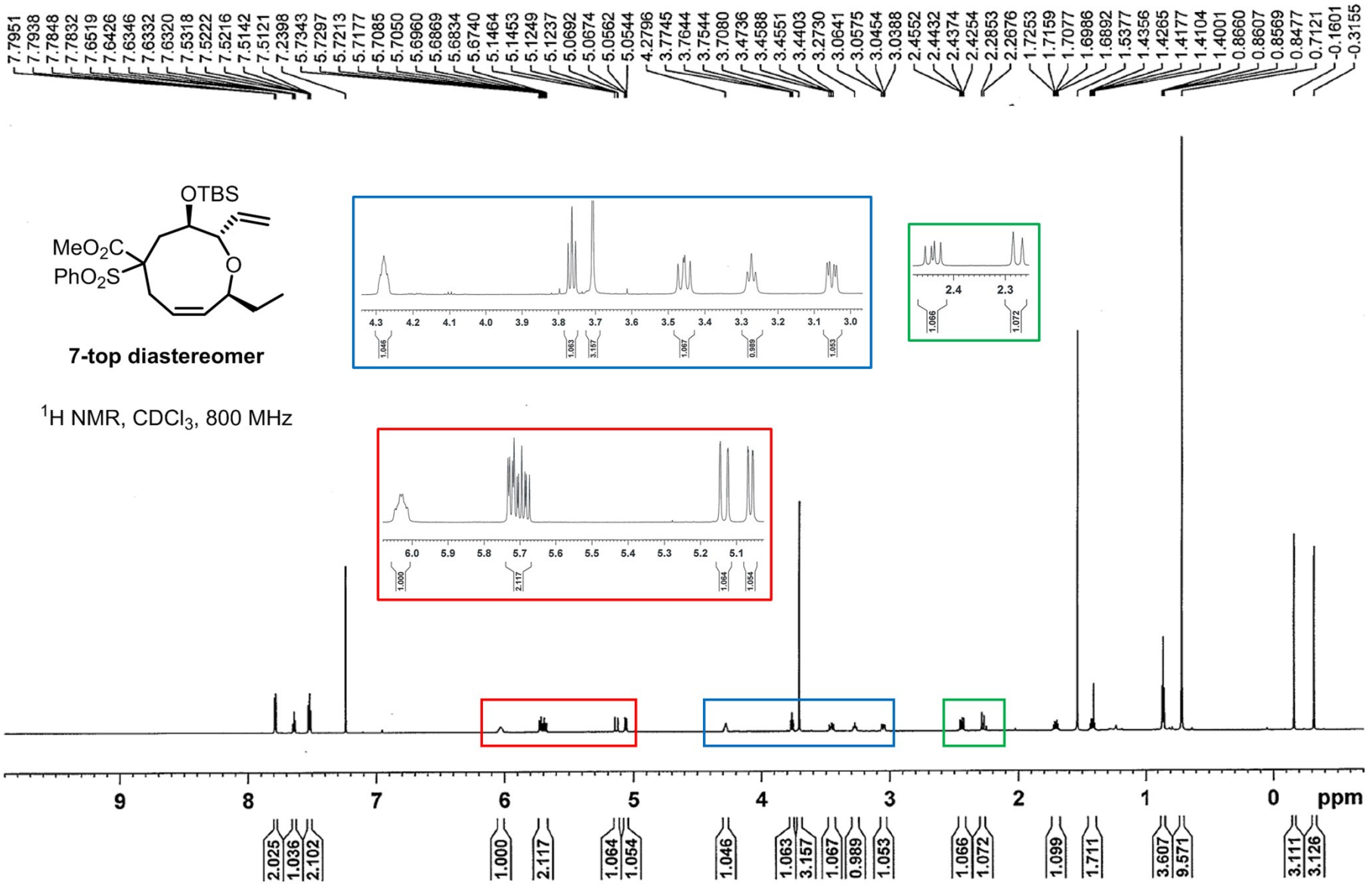
^{1}H NMR, $CDCl_3$, 600 MHz




154.972
136.334
136.285
124.959
118.289
79.616
79.558
77.419
77.000
76.572
74.952
67.583
63.988
46.297
27.404
25.792
18.126
14.269
9.227
-4.377
-4.599
OTBS
I
O
EtO2CO
12c
13C NMR, CDCl3, 75 MHz
200
150
100
50
0
ppm


7.8397
7.8385
7.8294
7.8277
7.8260
7.8168
7.8153
7.6530
7.6507
7.6414
7.5521
7.5422
7.5326
7.2398
5.6287
5.6213
5.6155
5.6147
5.6089
5.6076
5.6007
5.5916
5.1475
5.1385
5.1366
5.1348
5.1328
5.1172
5.1157
4.5605
4.5538
4.5510
4.5439
4.3178
4.3149
4.3032
4.3002
4.1897
4.1807
4.1777
4.1718
4.1688
4.1629
3.8047
3.7973
3.7647
3.6453
3.6107
3.5877
3.5770
1.5353
1.4104
1.2972
1.2946
1.2883
1.2857
1.2794
1.2768
1.2318
0.8451
0.8155
0.8126
0.8074
0.8032
0.7957
0.7940
0.7864
0.0560
0.0283
0.0122
-0.0638
MeO2C
OTBS
PhO2S
O
EtO2CO
8
1H NMR, CDCl3, 800 MHz
9
8
7
6
5
4
3
2
1
0 ppm
2.000
1.022
2.056
3.062
2.075
2.035
0.603
0.420
1.999
0.607
0.837
0.612
0.428
1.912
1.214
0.619
0.167
0.330
1.052
0.621
1.013
1.565
3.108
0.797
3.814
4.858
4.253
1.200
1.202
1.778
1.819


166.5929
166.2925
154.9474
137.5732
137.2375
136.3771
136.3137
136.2786
135.7052
134.1323
134.1002
129.2673
129.0553
129.0349
128.9742
124.9498
124.8810
118.1618
118.1037
82.6220
82.2886
80.3292
80.2023
77.1581
77.0000
76.8407
72.4205
72.2587
67.5341
67.5257
67.4776
67.2538
63.9993
52.8011
30.3794
29.6592
27.6051
27.3618
25.8904
25.8574
18.0885
18.0153
14.2702
9.3455
9.3110
-3.8317
-4.3563
-4.7981
-5.4369
MeO2C
OTBS
PhO2S
O
EtO2CO
8
13C NMR, CDCl3, 200 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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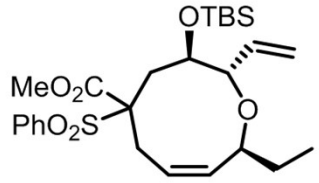
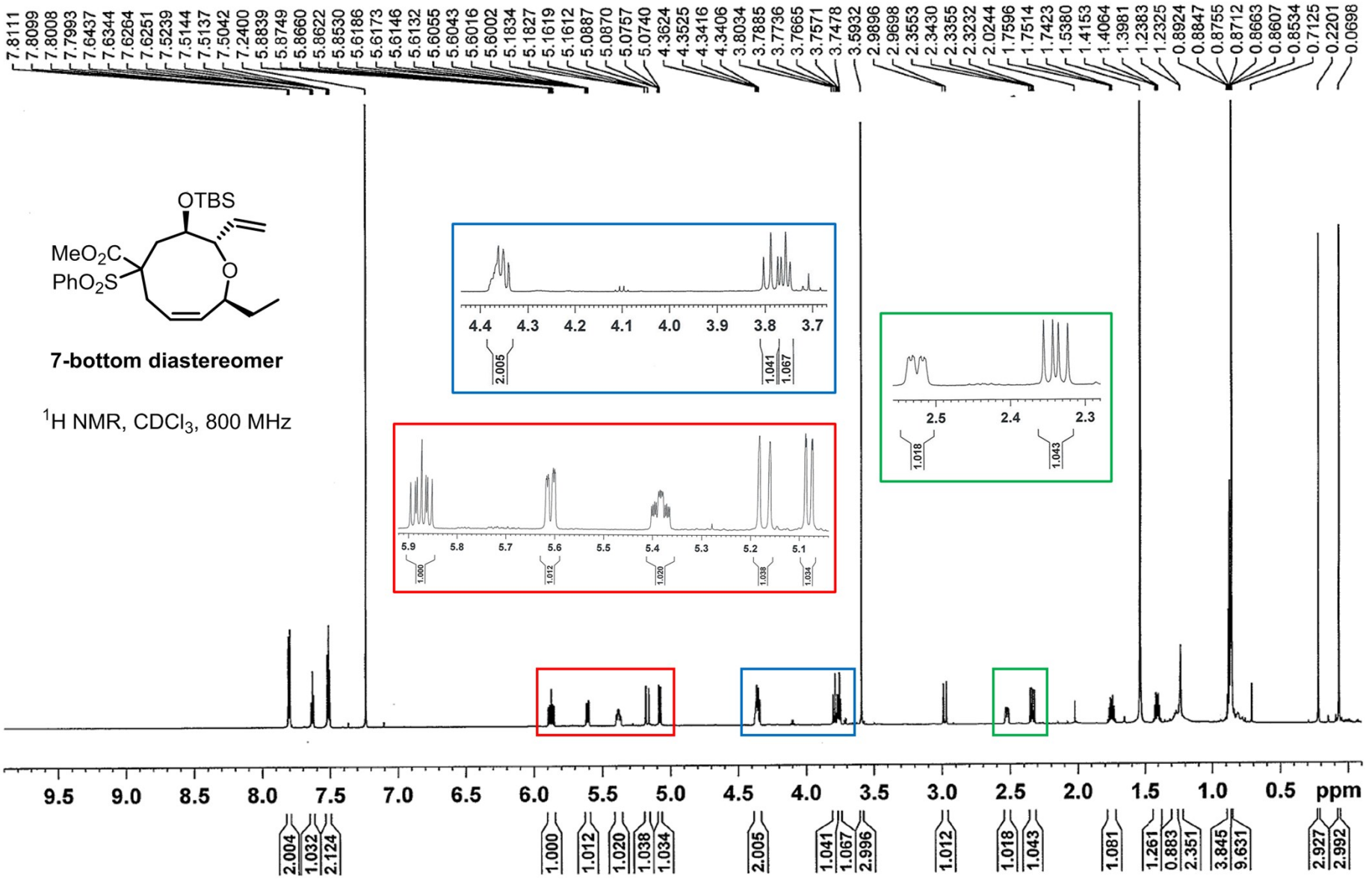
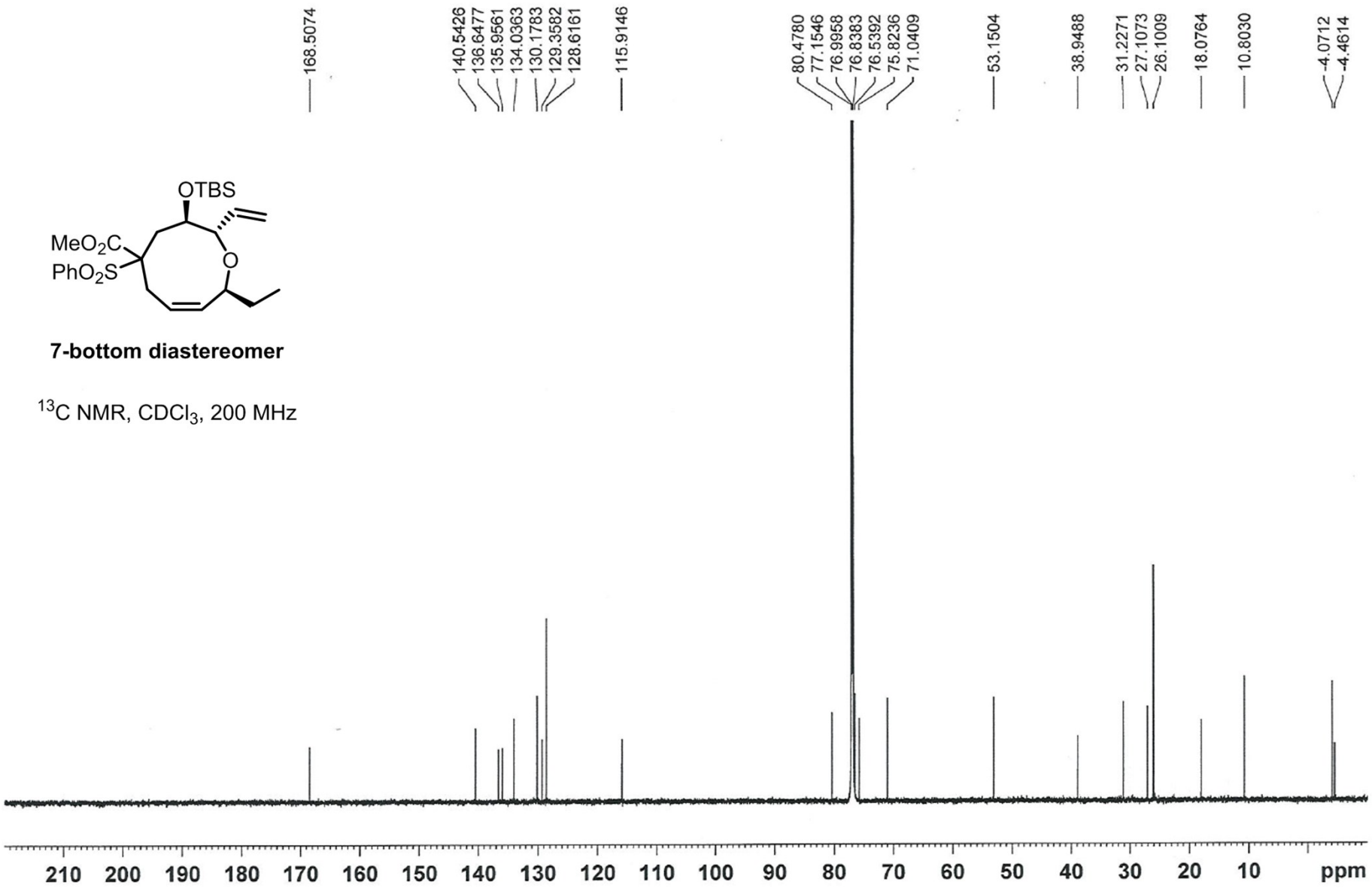
7.7938
7.7848
7.7832
7.6519
7.6426
7.6346
7.6332
7.6320
7.5318
7.5222
7.5216
7.5142
7.5121
7.2398
5.7343
5.7297
5.7213
5.7177
5.7085
5.7050
5.6960
5.6869
5.6834
5.6740
5.1464
5.1453
5.1249
5.1237
5.0692
5.0674
5.0562
5.0544
4.2796
3.7745
3.7644
3.7544
3.7080
3.4736
3.4588
3.4551
3.4403
3.2730
3.0641
3.0575
3.0454
3.0388
2.4552
2.4432
2.4374
2.4254
2.2853
2.2676
1.7253
1.7159
1.7077
1.6986
1.6892
1.5377
1.4356
1.4265
1.4177
1.4104
1.4001
0.8660
0.8607
0.8569
0.8477
0.7121
-0.1601
-0.3155
OTBS
MeO2C
PhO2S
O
7-top diastereomer
1H NMR, CDCl3, 800 MHz
ppm
2.025
1.036
2.102
1.000
2.117
1.064
1.054
1.046
1.063
3.157
1.067
0.989
1.053
1.066
1.072
1.099
1.711
3.607
9.571
3.111
3.126



7-top diastereomer

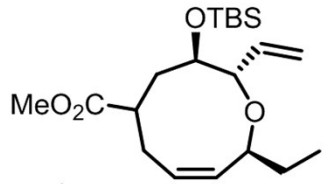
^{13}C NMR, $CDCl_3$, 150 MHz


OTBS
MeO2C
PhO2S
O
7-bottom diastereomer
1H NMR, CDCl3, 800 MHz
ppm



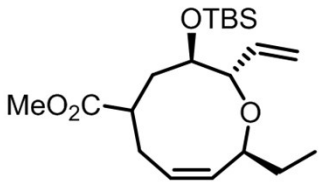
7-bottom diastereomer

^{13}C NMR, $CDCl_3$, 200 MHz



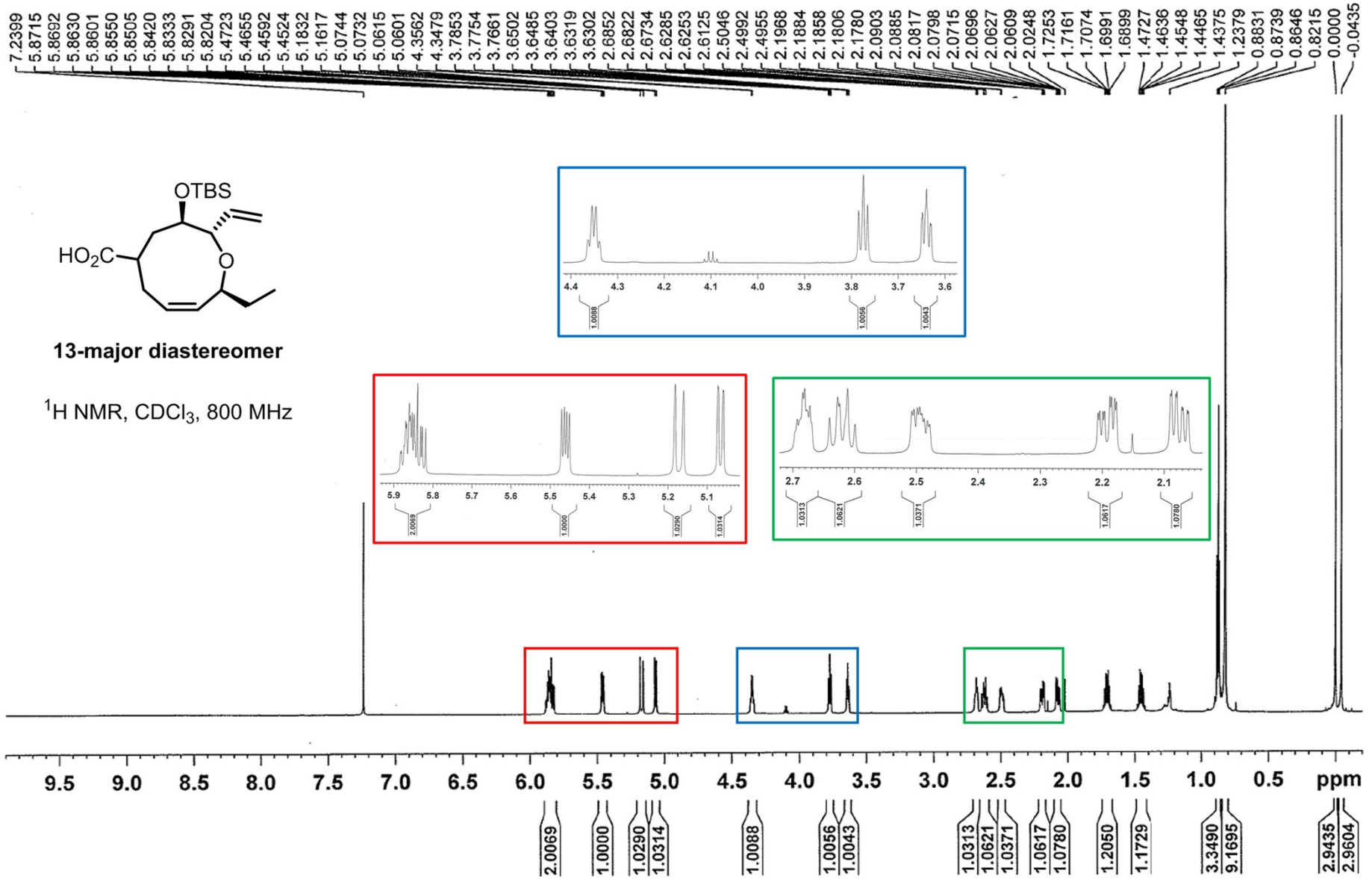
7a

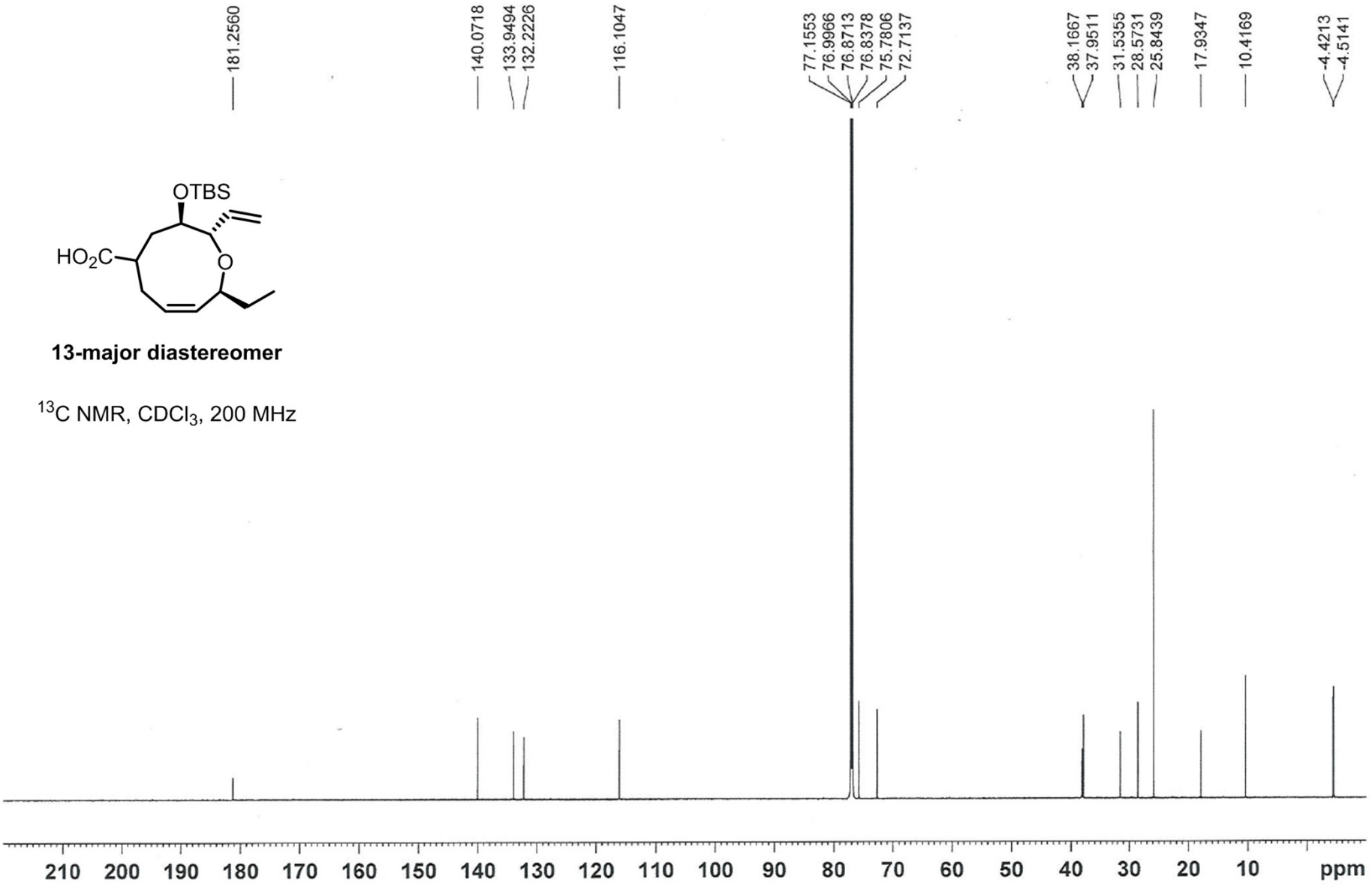
^{1}H NMR, $CDCl_3$, 600 MHz

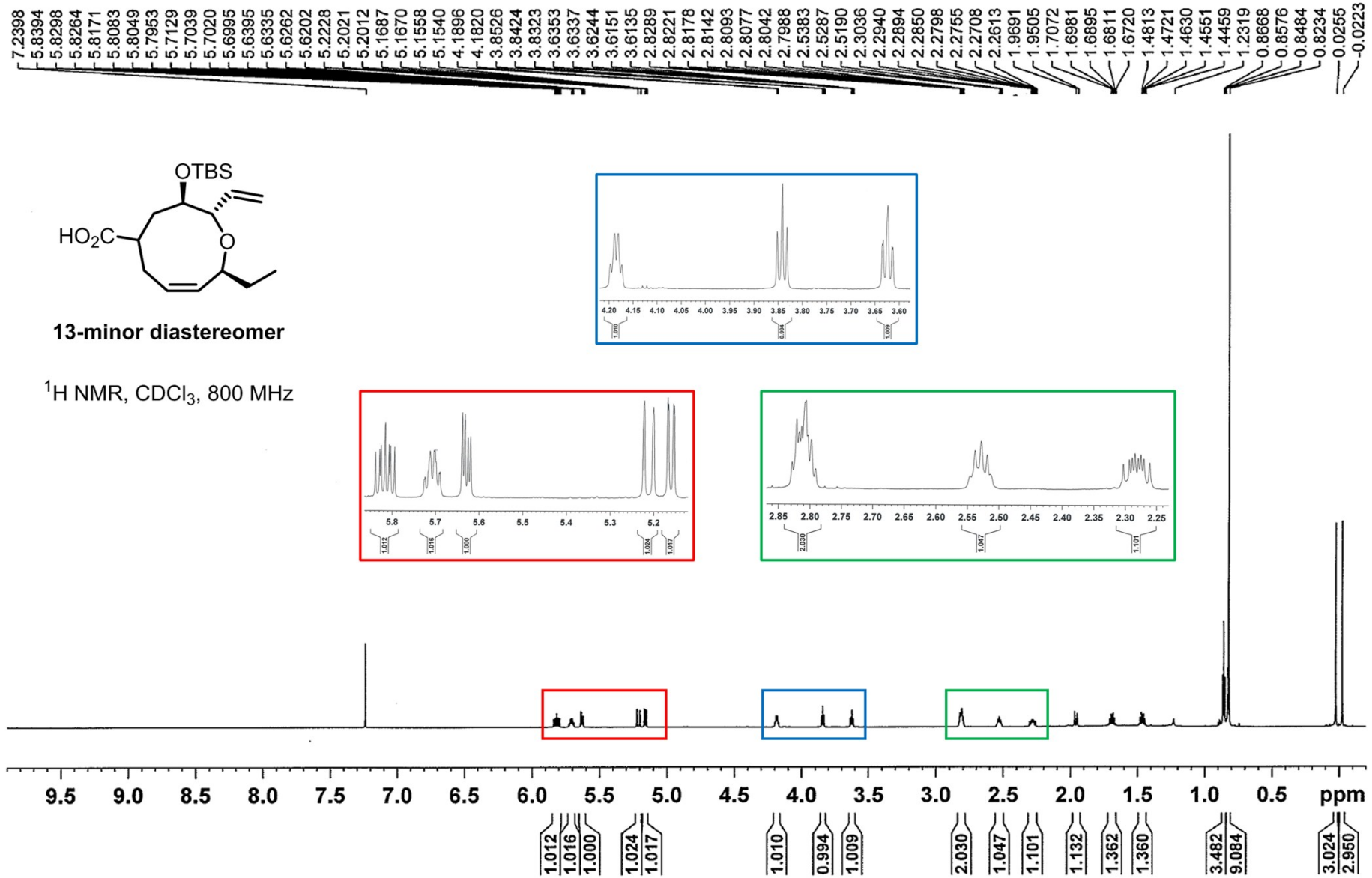


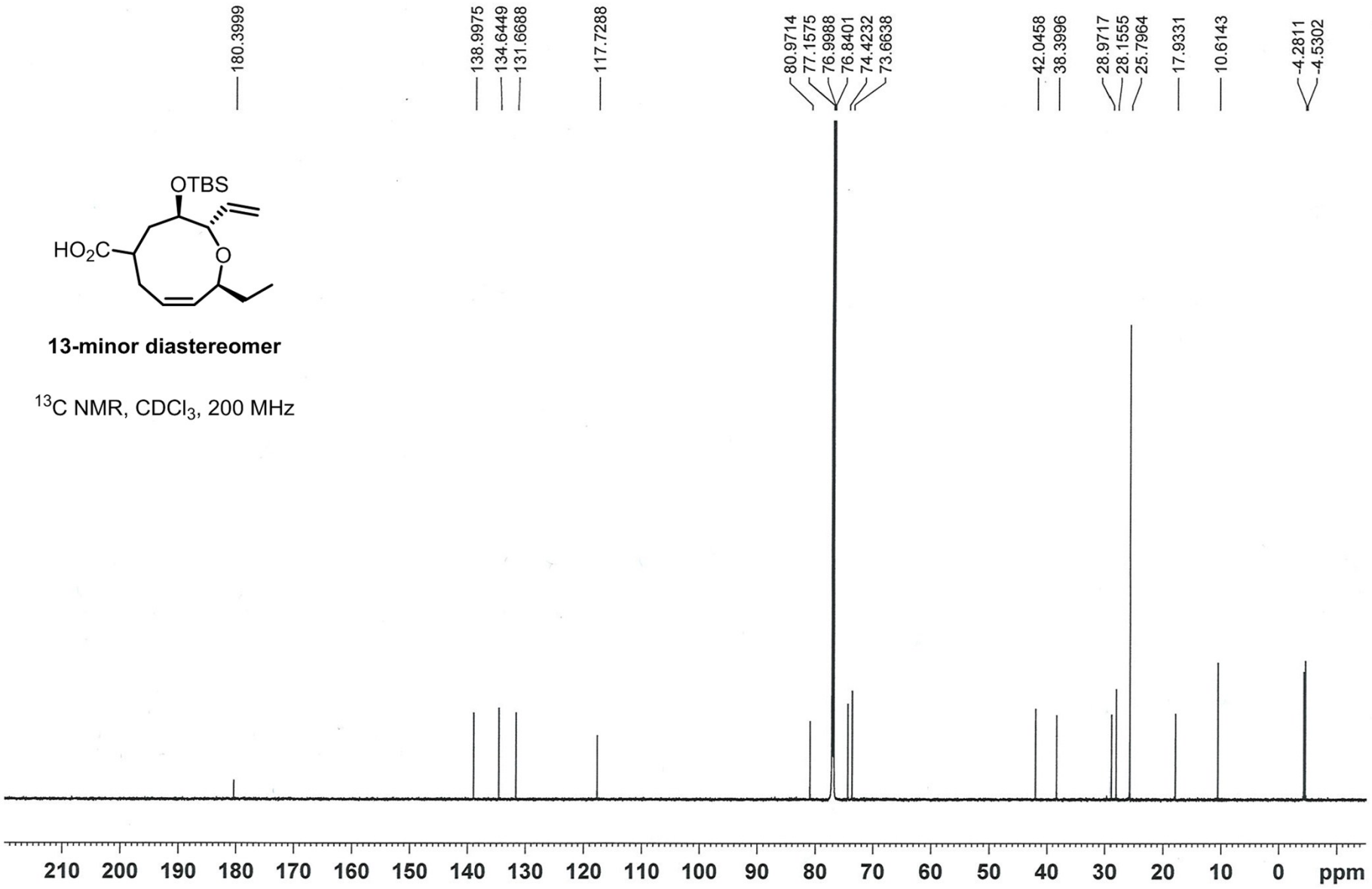
7a

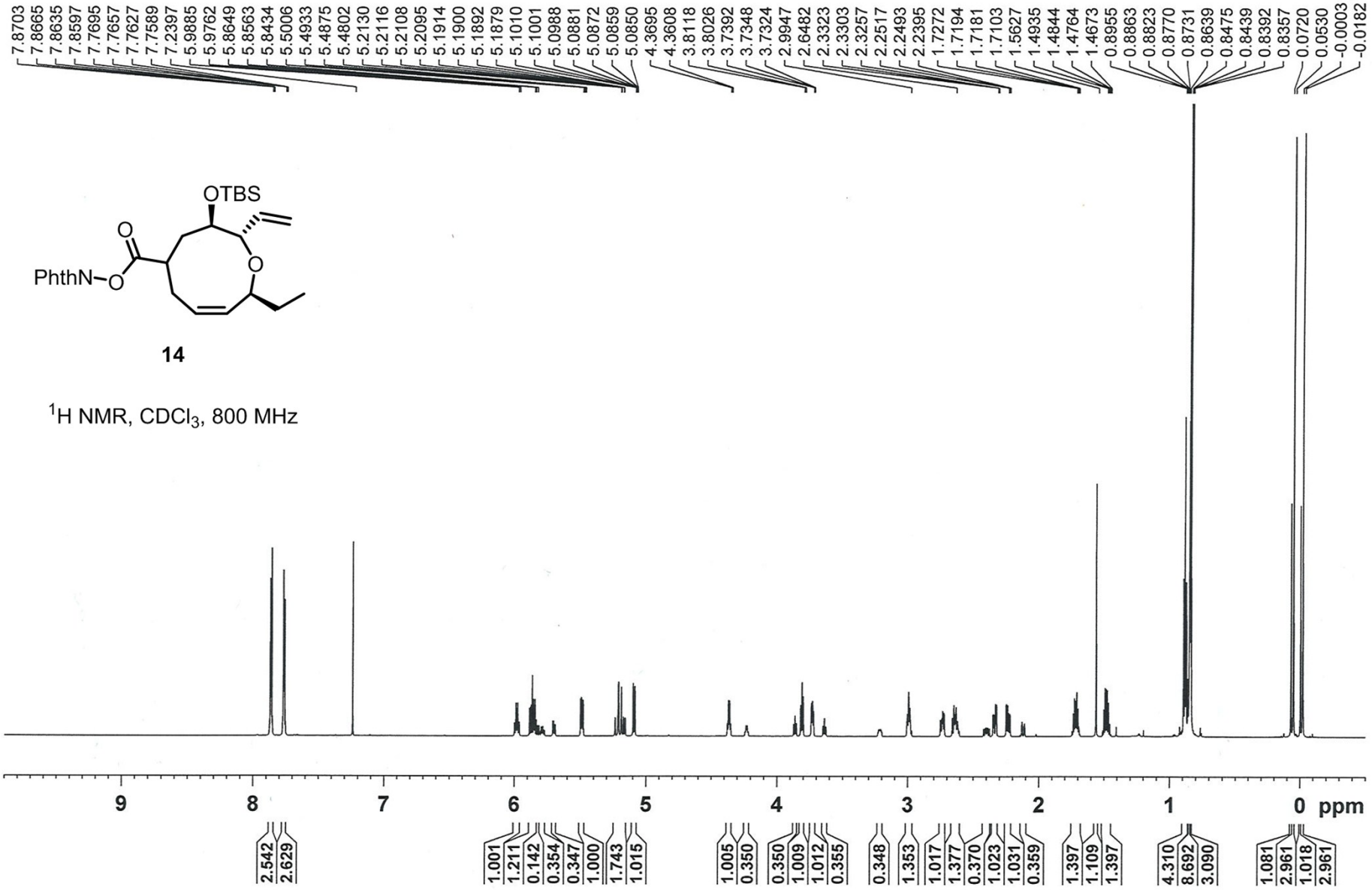
^{13}C NMR, $CDCl_3$, 150 MHz

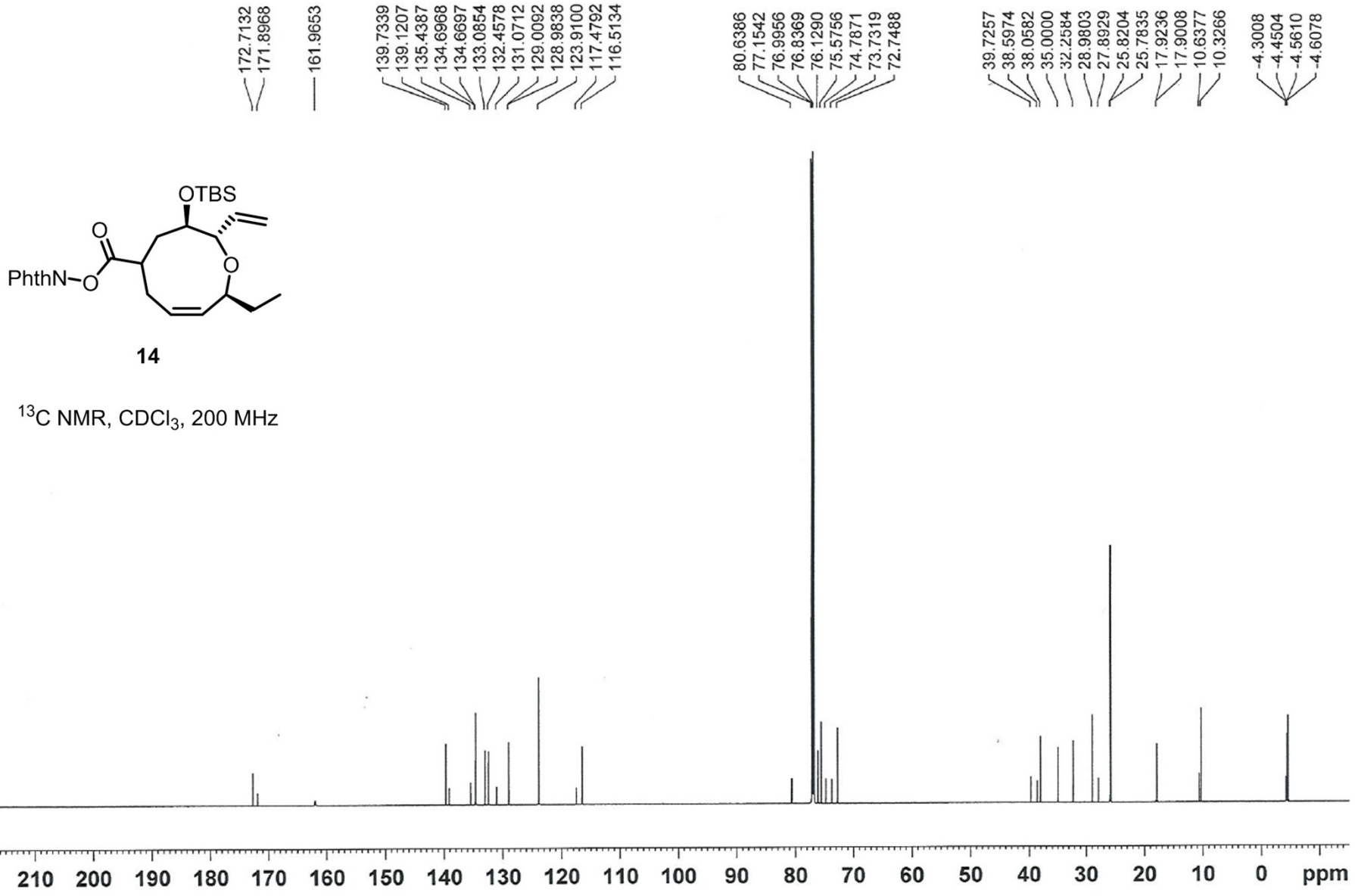

OTBS
HO2C
O
13-major diastereomer
1H NMR, CDCl3, 800 MHz
ppm

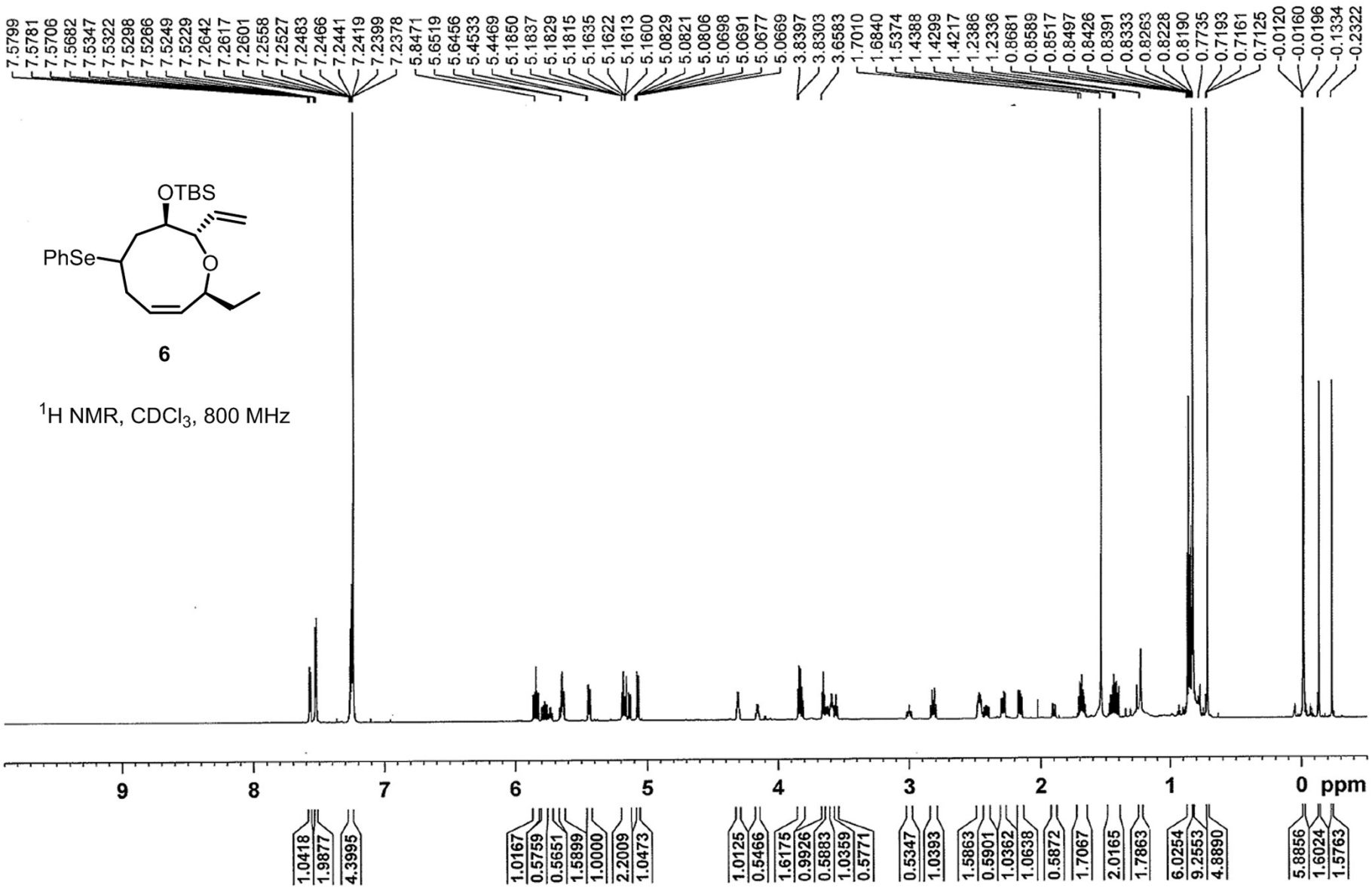

181.2560
140.0718
133.9494
132.2226
116.1047
77.1553
76.9966
76.8713
76.8378
75.7806
72.7137
38.1667
37.9511
31.5355
28.5731
25.8439
17.9347
10.4169
-4.4213
-4.5141
OTBS
HO2C
O
13-major diastereomer
13C NMR, CDCl3, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

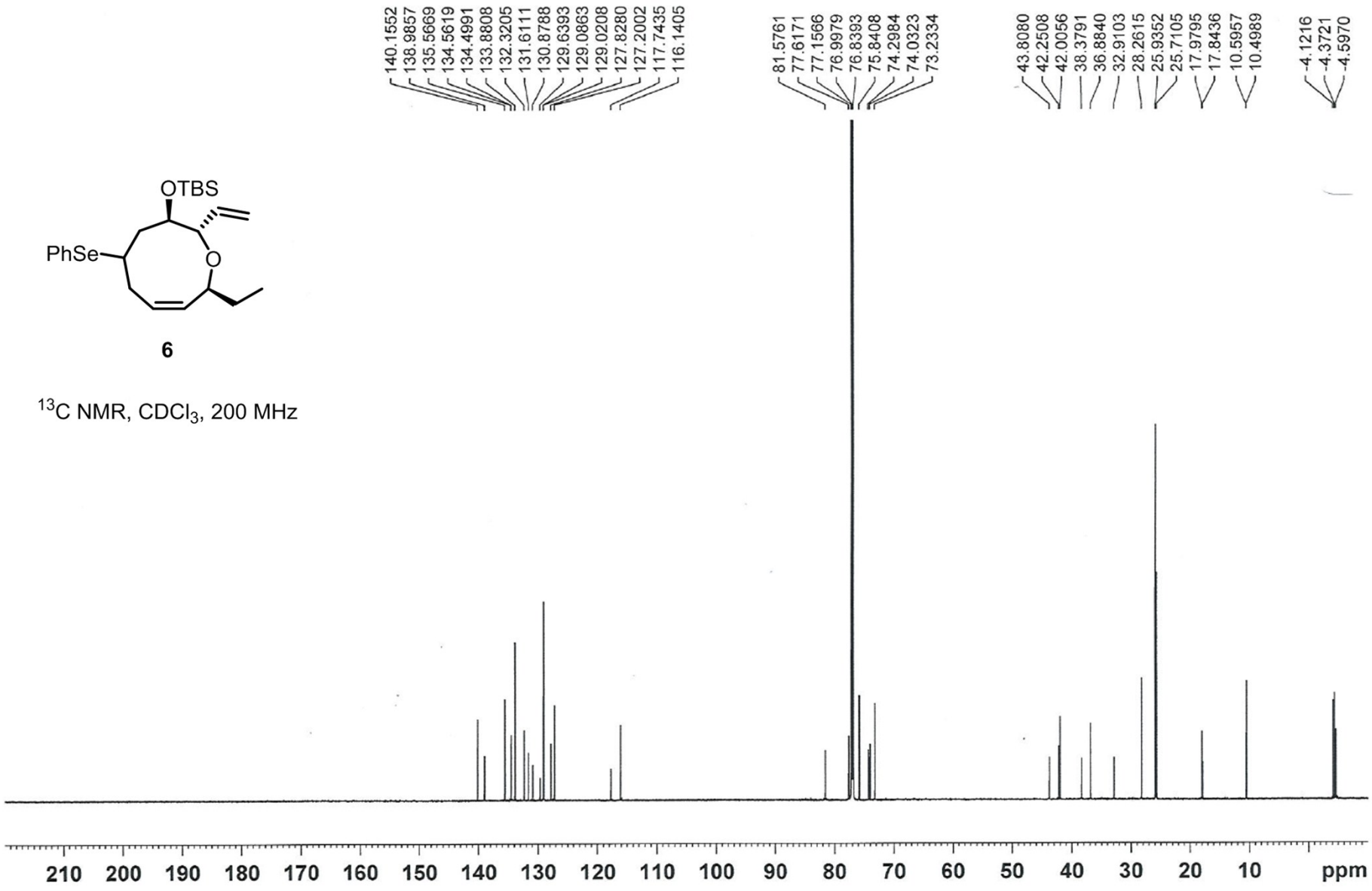

OTBS
HO2C
O
13-minor diastereomer
1H NMR, CDCl3, 800 MHz
ppm

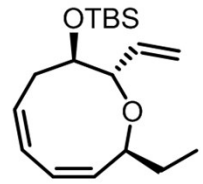

180.3999
138.9975
134.6449
131.6688
117.7288
80.9714
77.1575
76.9988
76.8401
74.4232
73.6638
42.0458
38.3996
28.9717
28.1555
25.7964
17.9331
10.6143
-4.2811
-4.5302
OTBS
HO2C
O
13-minor diastereomer
13C NMR, CDCl3, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.8703
7.8665
7.8635
7.8597
7.7695
7.7657
7.7627
7.7589
7.2397
5.9885
5.9762
5.8649
5.8563
5.8434
5.5006
5.4933
5.4875
5.4802
5.2130
5.2116
5.2108
5.2095
5.1914
5.1900
5.1892
5.1879
5.1010
5.1001
5.0988
5.0881
5.0872
5.0859
5.0850
4.3695
4.3608
3.8118
3.8026
3.7392
3.7348
3.7324
2.9947
2.6482
2.3323
2.3303
2.3257
2.2517
2.2493
2.2395
1.7272
1.7194
1.7181
1.7103
1.5627
1.4935
1.4844
1.4764
1.4673
0.8955
0.8863
0.8823
0.8770
0.8731
0.8639
0.8475
0.8439
0.8392
0.8357
0.0720
0.0530
-0.0003
-0.0182
OTBS
O
PhthN
O
O
14
1H NMR, CDCl3, 800 MHz
9
8
7
6
5
4
3
2
1
0 ppm
2.542
2.629
1.001
1.211
0.142
0.354
0.347
1.000
1.743
1.015
1.005
0.350
0.350
1.009
1.012
0.355
0.348
1.353
1.017
1.377
0.370
1.023
1.031
0.359
1.397
1.109
1.397
4.310
8.692
3.090
1.081
2.961
1.018
2.961


172.7132
171.8968
161.9653
139.7339
139.1207
135.4387
134.6968
134.6697
133.0854
132.4578
131.0712
129.0092
128.9838
123.9100
117.4792
116.5134
80.6386
77.1542
76.9956
76.8369
76.1290
75.5756
74.7871
73.7319
72.7488
39.7257
38.5974
38.0582
35.0000
32.2584
28.9803
27.8929
25.8204
25.7835
17.9236
17.9008
10.6377
10.3266
-4.3008
-4.4504
-4.5610
-4.6078
OTBS
O
PhthN
O
O
14
13C NMR, CDCl3, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

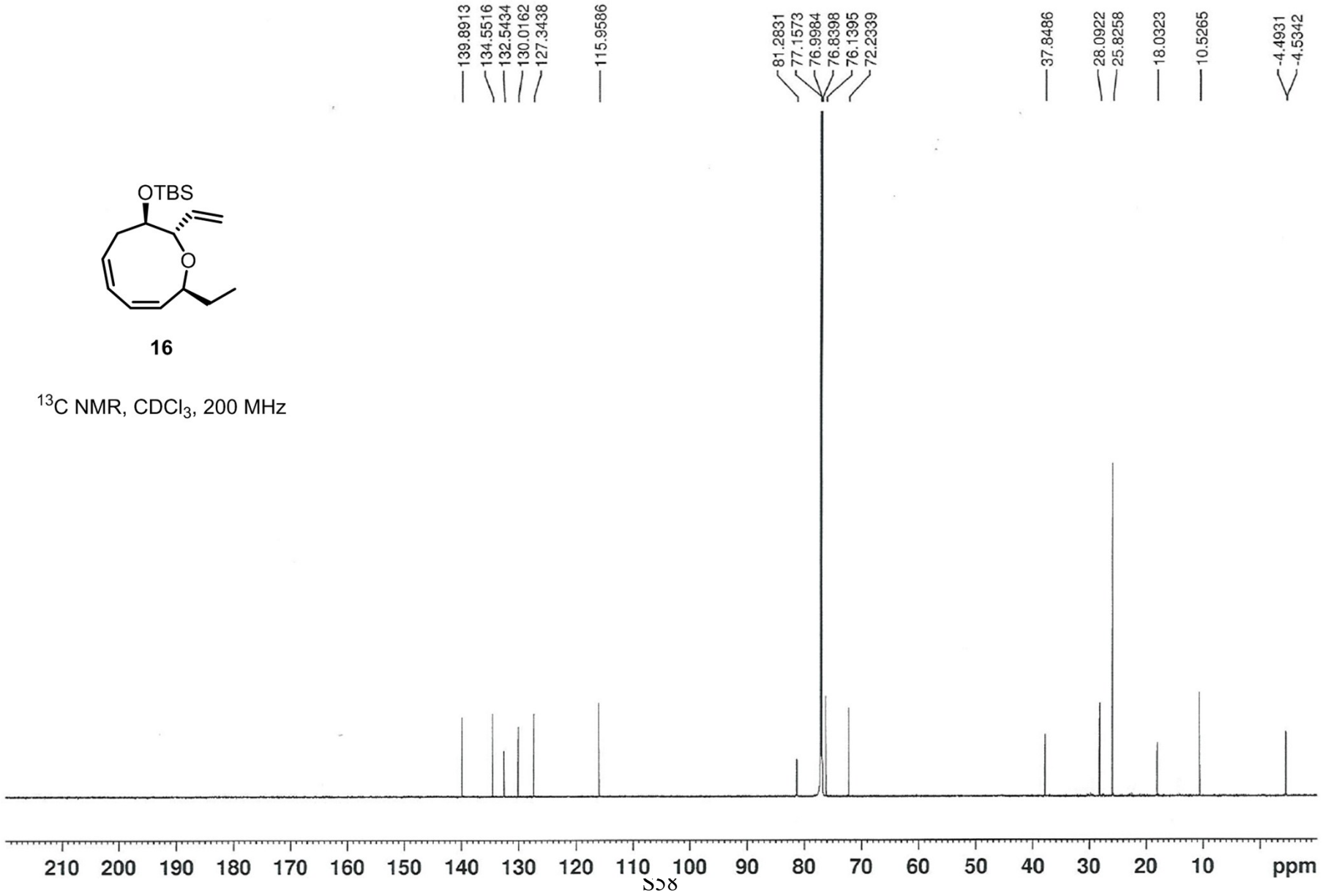

OTBS
PhSe
O
6
^{1}H NMR, $CDCl_3$, 800 MHz
9
8
7
6
5
4
3
2
1
0 ppm

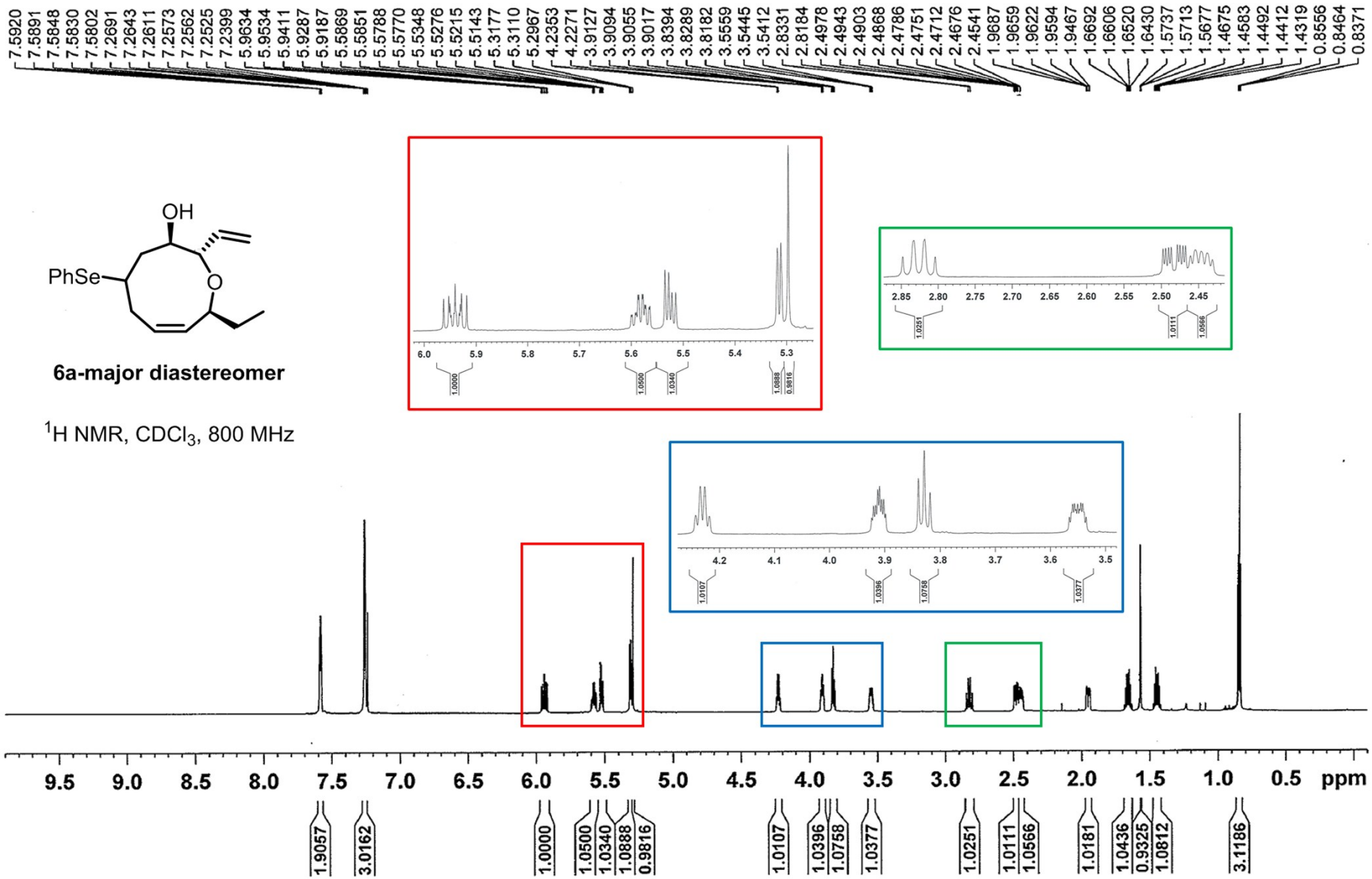

140.1552
138.9857
135.5669
134.5619
134.4991
133.8808
132.3205
131.6111
130.8788
129.6393
129.0863
129.0208
127.8280
127.2002
117.7435
116.1405
81.5761
77.6171
77.1566
76.9979
76.8393
75.8408
74.2984
74.0323
73.2334
43.8080
42.2508
42.0056
38.3791
36.8840
32.9103
28.2615
25.9352
25.7105
17.9795
17.8436
10.5957
10.4989
-4.1216
-4.3721
-4.5970
OTBS
PhSe
O
6
^{13}C NMR, $CDCl_3$, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



16

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


OTBS
O
16
13C NMR, CDCl3, 200 MHz
139.8913
134.5516
132.5434
130.0162
127.3438
115.9586
81.2831
77.1573
76.9984
76.8398
76.1395
72.2339
37.8486
28.0922
25.8258
18.0323
10.5265
-4.4931
-4.5342
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.5891
7.5848
7.5830
7.5802
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7.2643
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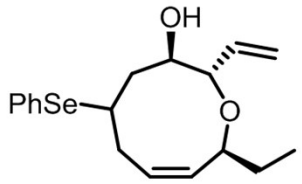
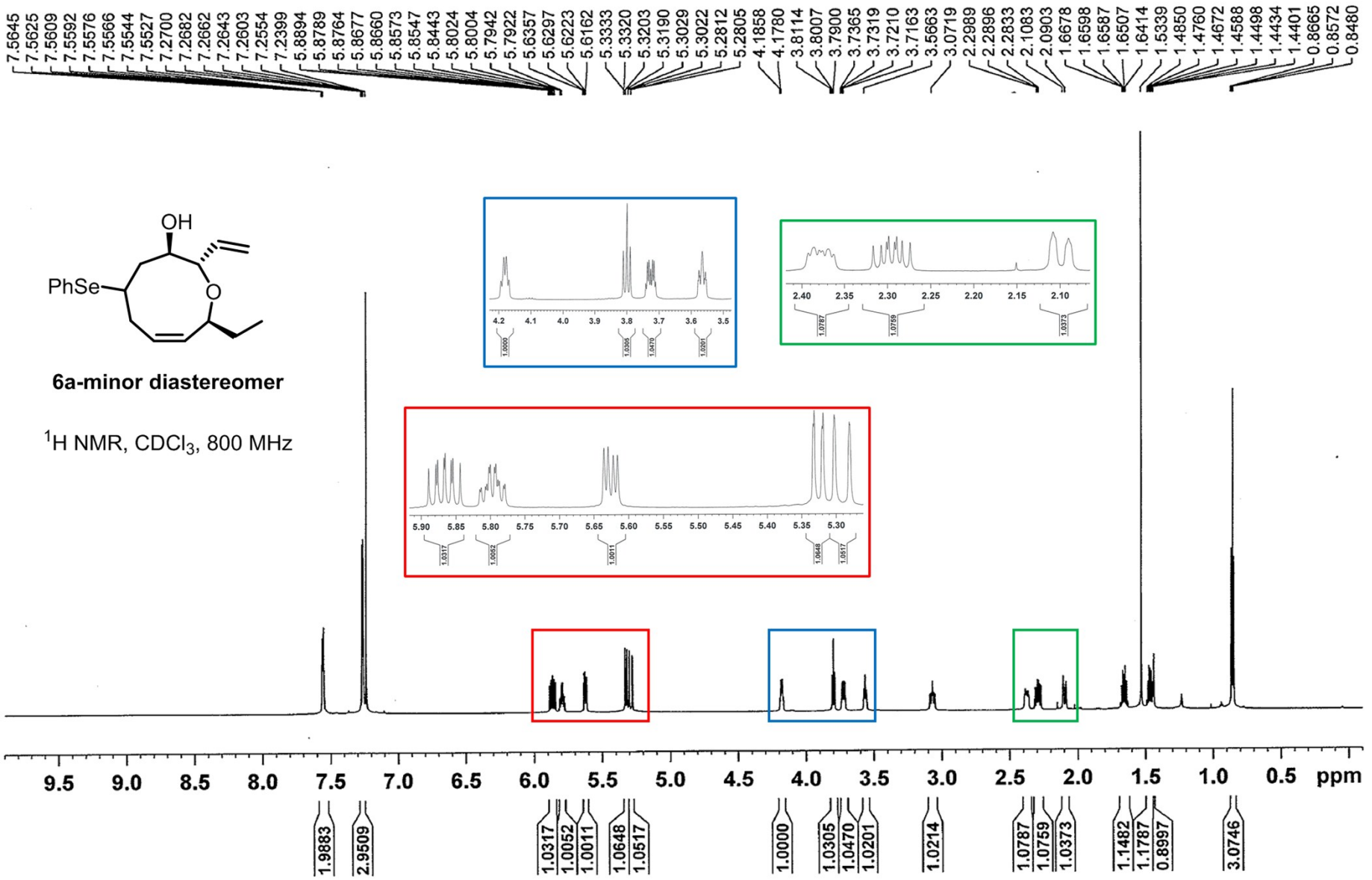
7.2573
7.2562
7.2525
7.2399
5.9634
5.9534
5.9411
5.9287
5.9187
5.5869
5.5851
5.5788
5.5770
5.5348
5.5276
5.5215
5.5143
5.3177
5.3110
5.2967
4.2353
4.2271
3.9127
3.9094
3.9055
3.9017
3.8394
3.8289
3.8182
3.5559
3.5445
3.5412
2.8331
2.8184
2.4978
2.4943
2.4903
2.4868
2.4786
2.4751
2.4712
2.4676
2.4541
1.9687
1.9659
1.9622
1.9594
1.9467
1.6692
1.6606
1.6520
1.6430
1.5737
1.5713
1.5677
1.4675
1.4583
1.4492
1.4412
1.4319
0.8556
0.8464
0.8371
OH
PhSe
O
6a-major diastereomer
1H NMR, CDCl3, 800 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.9057
3.0162
1.0000
1.0500
1.0340
1.0888
0.9816
1.0107
1.0396
1.0758
1.0377
1.0251
1.0111
1.0566
1.0181
1.0436
0.9325
1.0812
3.1186



6a-major diastereomer

^{13}C NMR, $CDCl_3$, 200 MHz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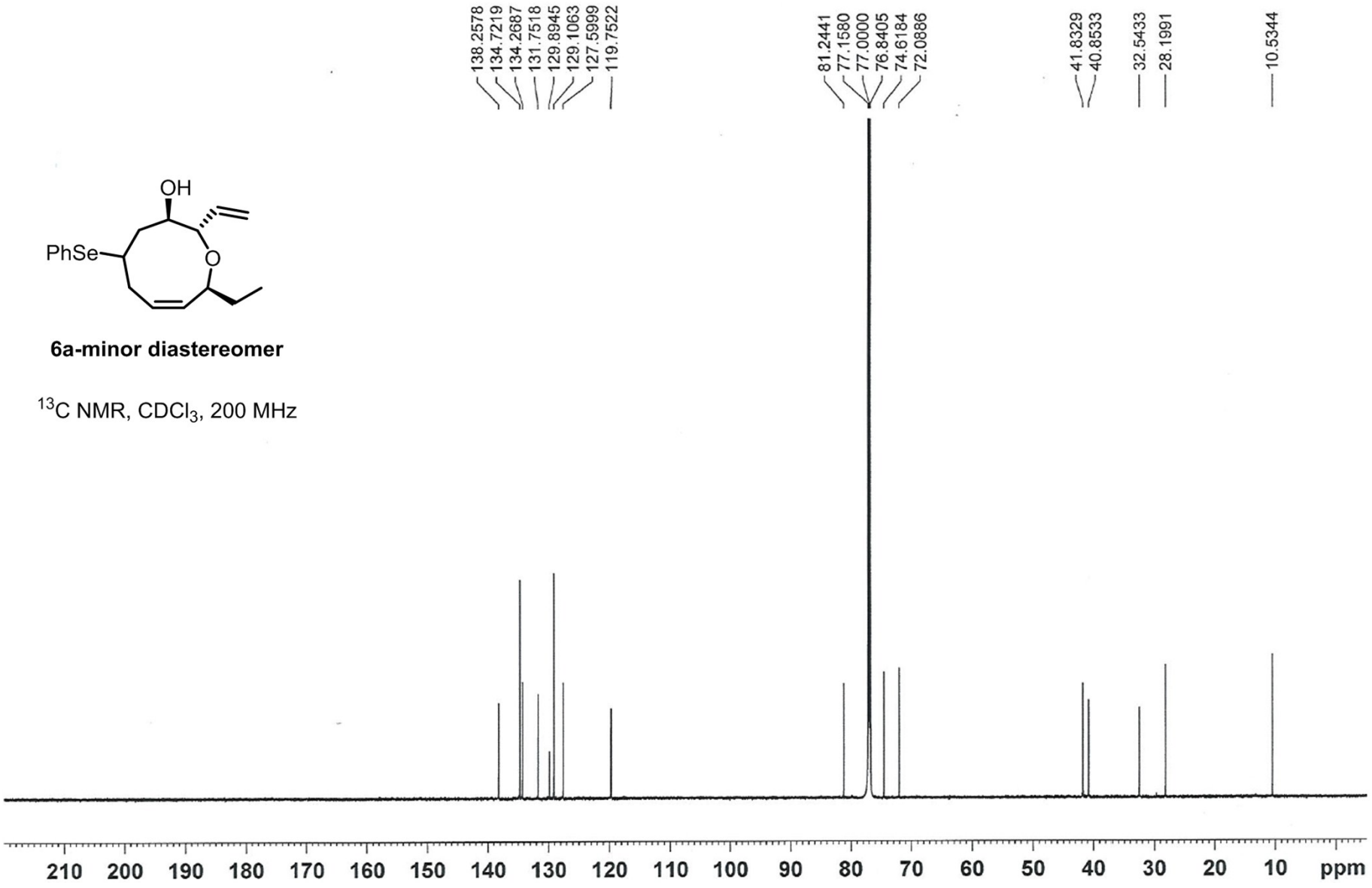
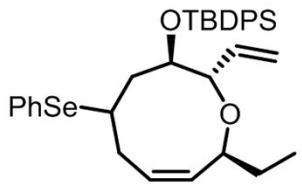
7.5625
7.5609
7.5592
7.5576
7.5566
7.5544
7.5527
7.2700
7.2682
7.2662
7.2643
7.2603
7.2554
7.2399
5.8894
5.8789
5.8764
5.8677
5.8660
5.8573
5.8547
5.8443
5.8024
5.8004
5.7942
5.7922
5.6357
5.6297
5.6223
5.6162
5.3333
5.3320
5.3203
5.3190
5.3029
5.3022
5.2812
5.2805
4.1858
4.1780
3.8114
3.8007
3.7900
3.7365
3.7319
3.7210
3.7163
3.5663
3.0719
2.2989
2.2896
2.2833
2.1083
2.0903
1.6678
1.6598
1.6587
1.6507
1.6414
1.5339
1.4850
1.4760
1.4672
1.4588
1.4498
1.4434
1.4401
0.8665
0.8572
0.8480
OH
PhSe
O
6a-minor diastereomer
1H NMR, CDCl3, 800 MHz
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.9883
2.9509
1.0317
1.0052
1.0011
1.0648
1.0517
1.0000
1.0305
1.0470
1.0201
1.0214
1.0787
1.0759
1.0373
1.1482
1.1787
0.8997
3.0746



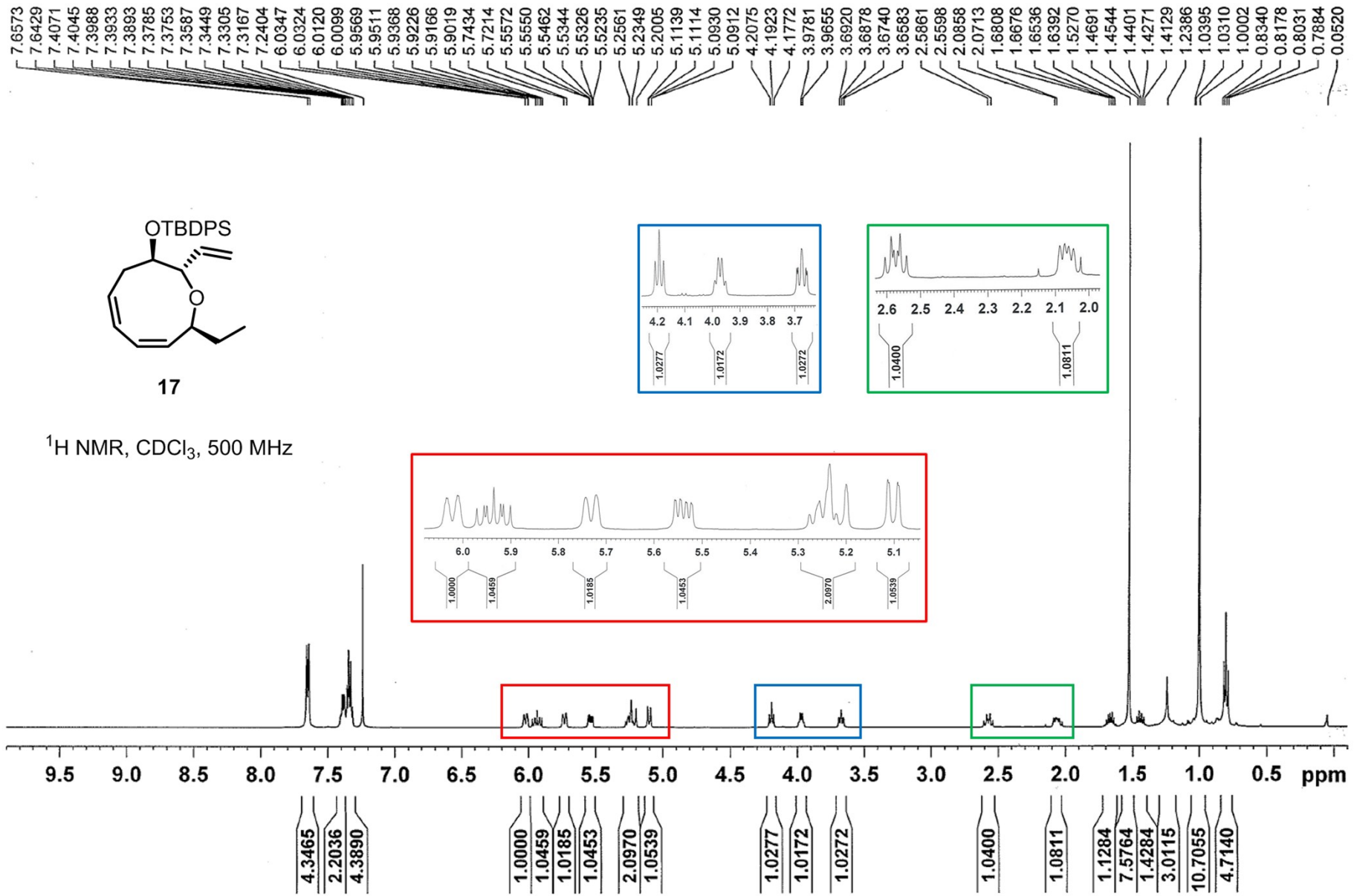
6a-minor diastereomer

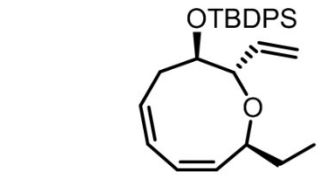
^{13}C NMR, $CDCl_3$, 200 MHz



15

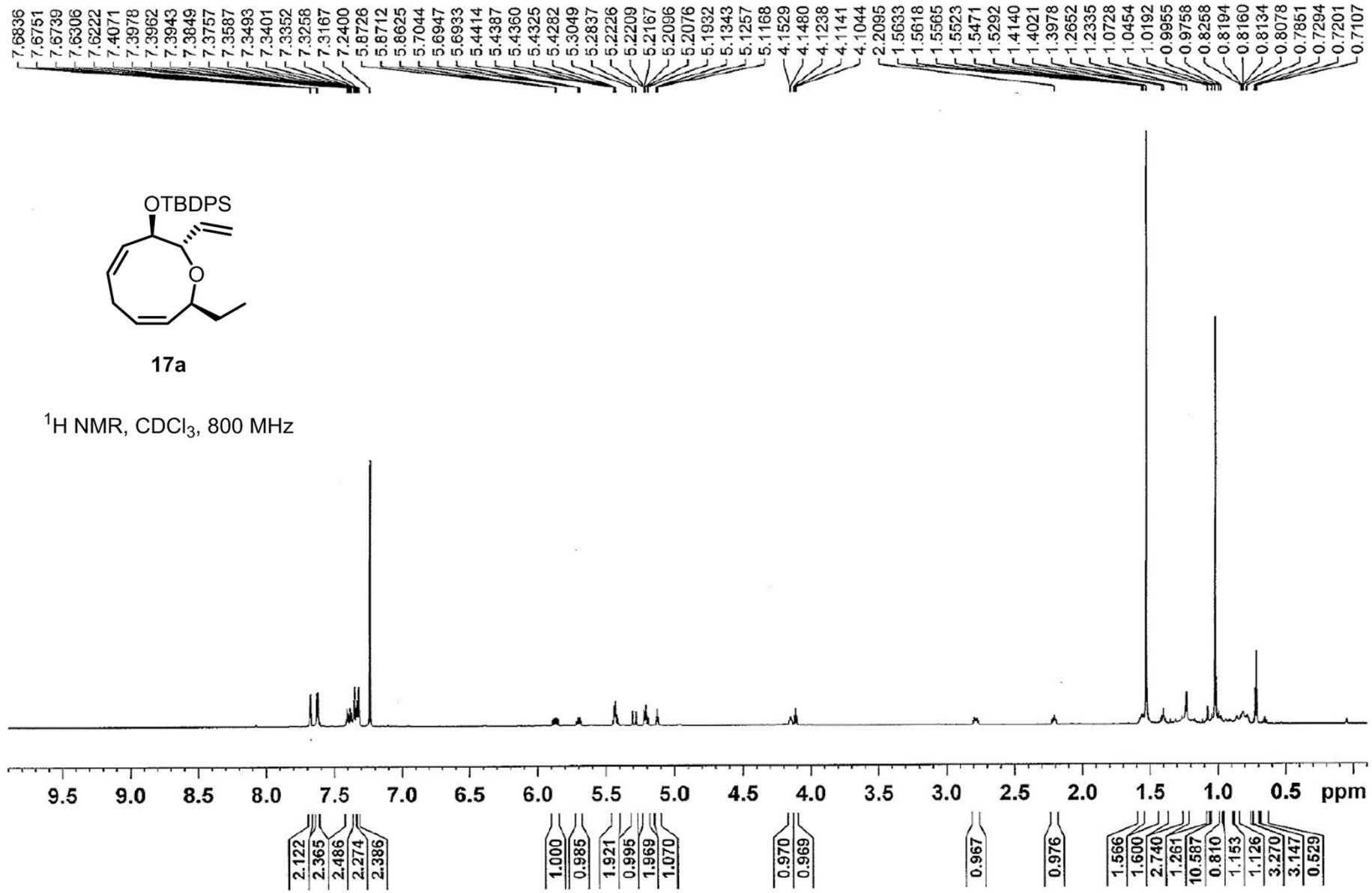
^{1}H NMR, $CDCl_3$, 600 MHz


OTBDPS
O
17
^{1}H NMR, $CDCl_3$, 500 MHz
7.6573 7.6429 7.4071 7.4045 7.3988 7.3933 7.3893 7.3785 7.3753 7.3587 7.3449 7.3305 7.3167 7.2404 6.0347 6.0324 6.0120 6.0099 5.9569 5.9511 5.9368 5.9226 5.9166 5.9019 5.7434 5.7214 5.5572 5.5550 5.5462 5.5344 5.5326 5.5235 5.2561 5.2349 5.2005 5.1139 5.1114 5.0930 5.0912 4.2075 4.1923 4.1772 3.9781 3.9655 3.6920 3.6878 3.6740 3.6583 2.5861 2.5598 2.0858 2.0713 1.6808 1.6676 1.6536 1.6392 1.5270 1.4691 1.4544 1.4401 1.4271 1.4129 1.2386 1.0395 1.0310 1.0002 0.8340 0.8178 0.8031 0.7884 0.0520
4.2 4.1 4.0 3.9 3.8 3.7
1.0277 1.0172 1.0272
2.6 2.5 2.4 2.3 2.2 2.1 2.0
1.0400 1.0811
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1
1.0000 1.0459 1.0185 1.0453 2.0970 1.0539
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.3465 2.2036 4.3890 1.0000 1.0459 1.0185 1.0453 2.0970 1.0539 1.0277 1.0172 1.0272 1.0400 1.0811 1.1284 7.5764 1.4284 3.0115 10.7055 4.7140



17

^{13}C NMR, $CDCl_3$, 150 MHz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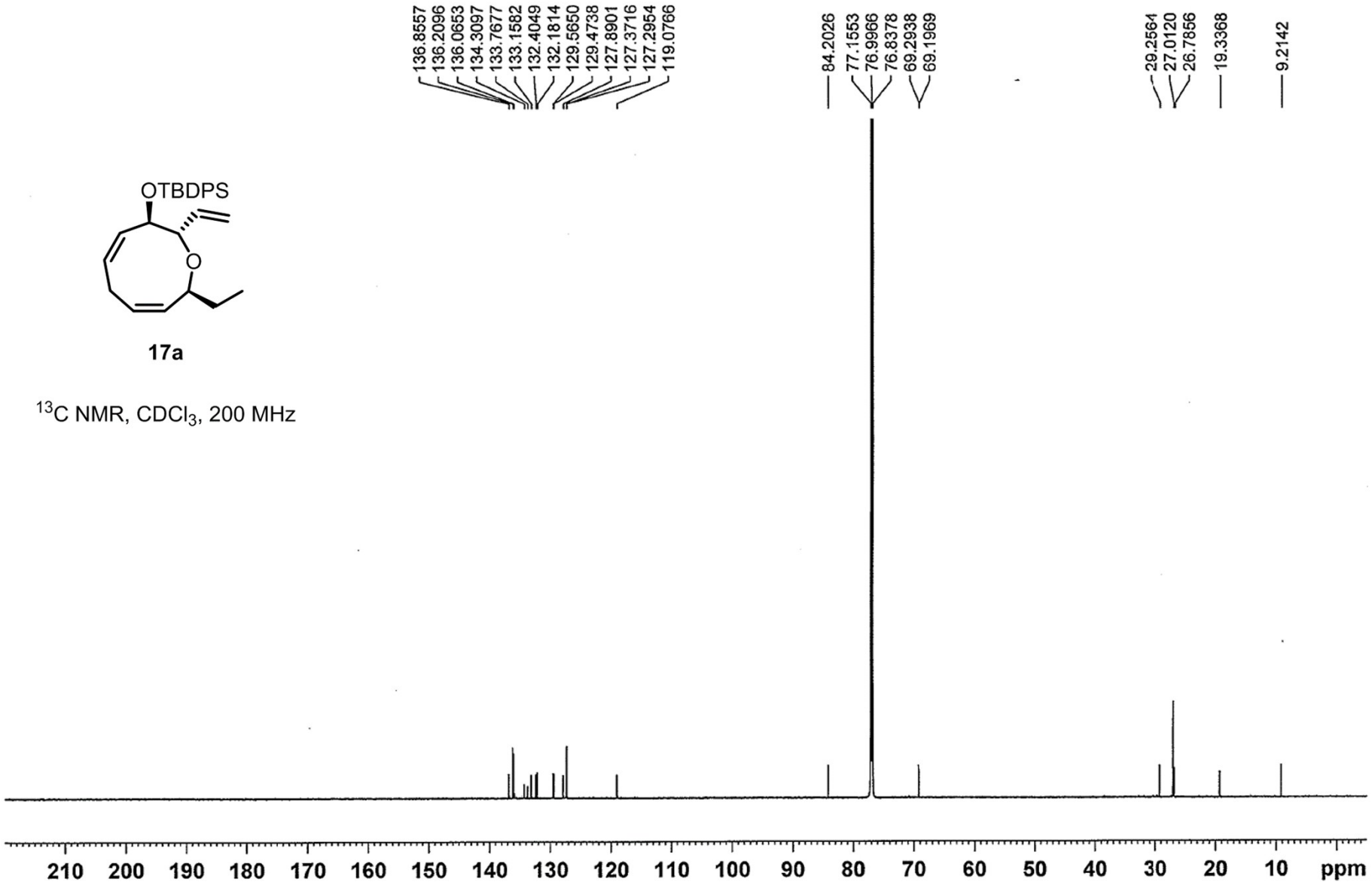
7.6751
7.6739
7.6306
7.6222
7.4071
7.3978
7.3962
7.3943
7.3849
7.3757
7.3587
7.3493
7.3401
7.3352
7.3258
7.3167
7.2400
5.8726
5.8712
5.8625
5.7044
5.6947
5.6933
5.4414
5.4387
5.4360
5.4325
5.4282
5.3049
5.2837
5.2226
5.2209
5.2167
5.2096
5.2076
5.1932
5.1343
5.1257
5.1168
4.1529
4.1480
4.1238
4.1141
4.1044
2.2095
1.5633
1.5618
1.5565
1.5523
1.5471
1.5292
1.4140
1.4021
1.3978
1.2652
1.2335
1.0728
1.0454
1.0192
0.9955
0.9758
0.8258
0.8194
0.8160
0.8134
0.8078
0.7851
0.7294
0.7201
0.7107
OTBDPS
O
17a
1H NMR, CDCl3, 800 MHz
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.122
2.365
2.486
2.274
2.386
1.000
0.985
1.921
0.995
1.969
1.070
0.970
0.969
0.967
0.976
1.566
1.600
2.740
1.261
10.587
0.810
1.153
1.126
3.270
3.147
0.529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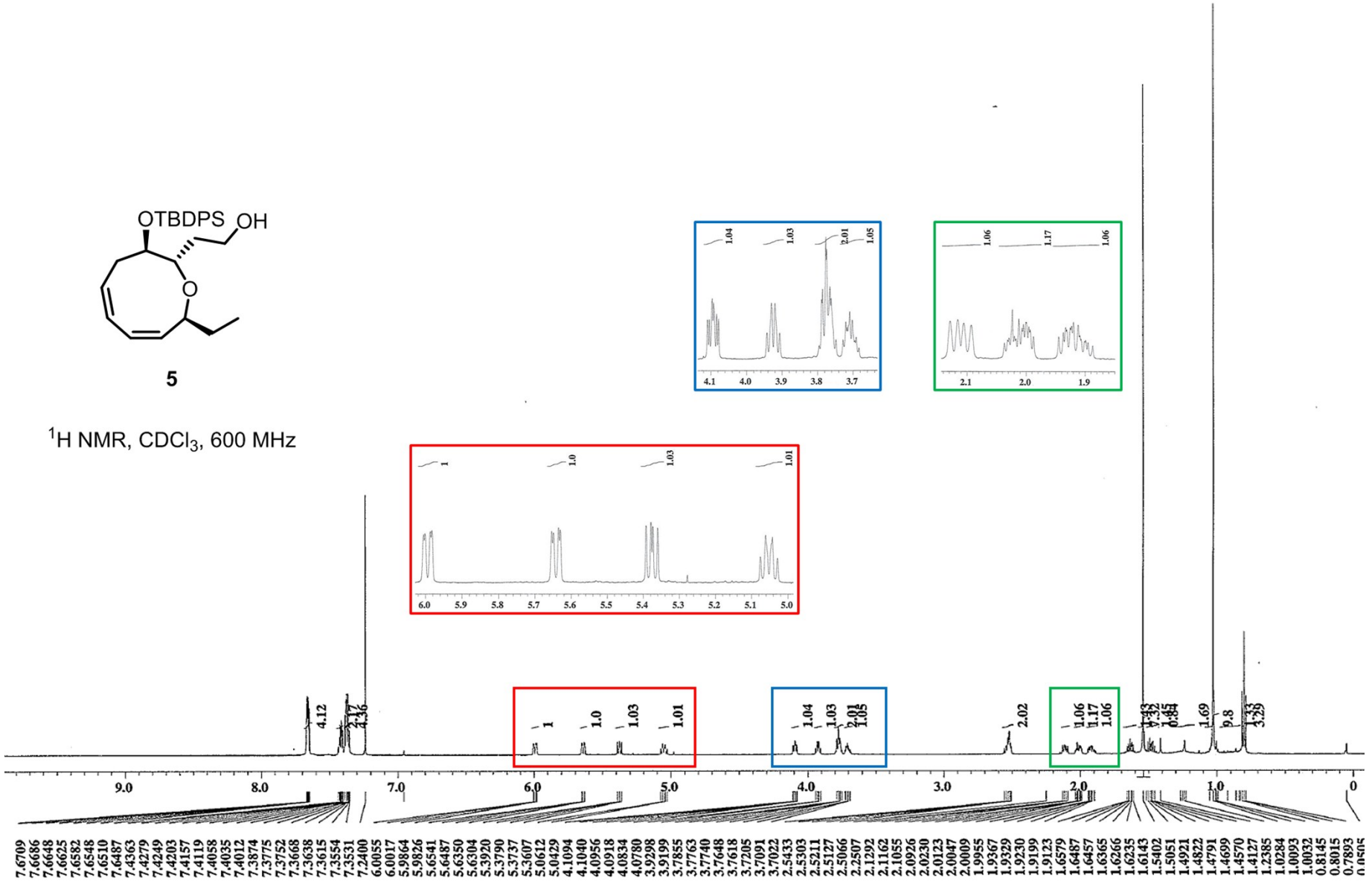
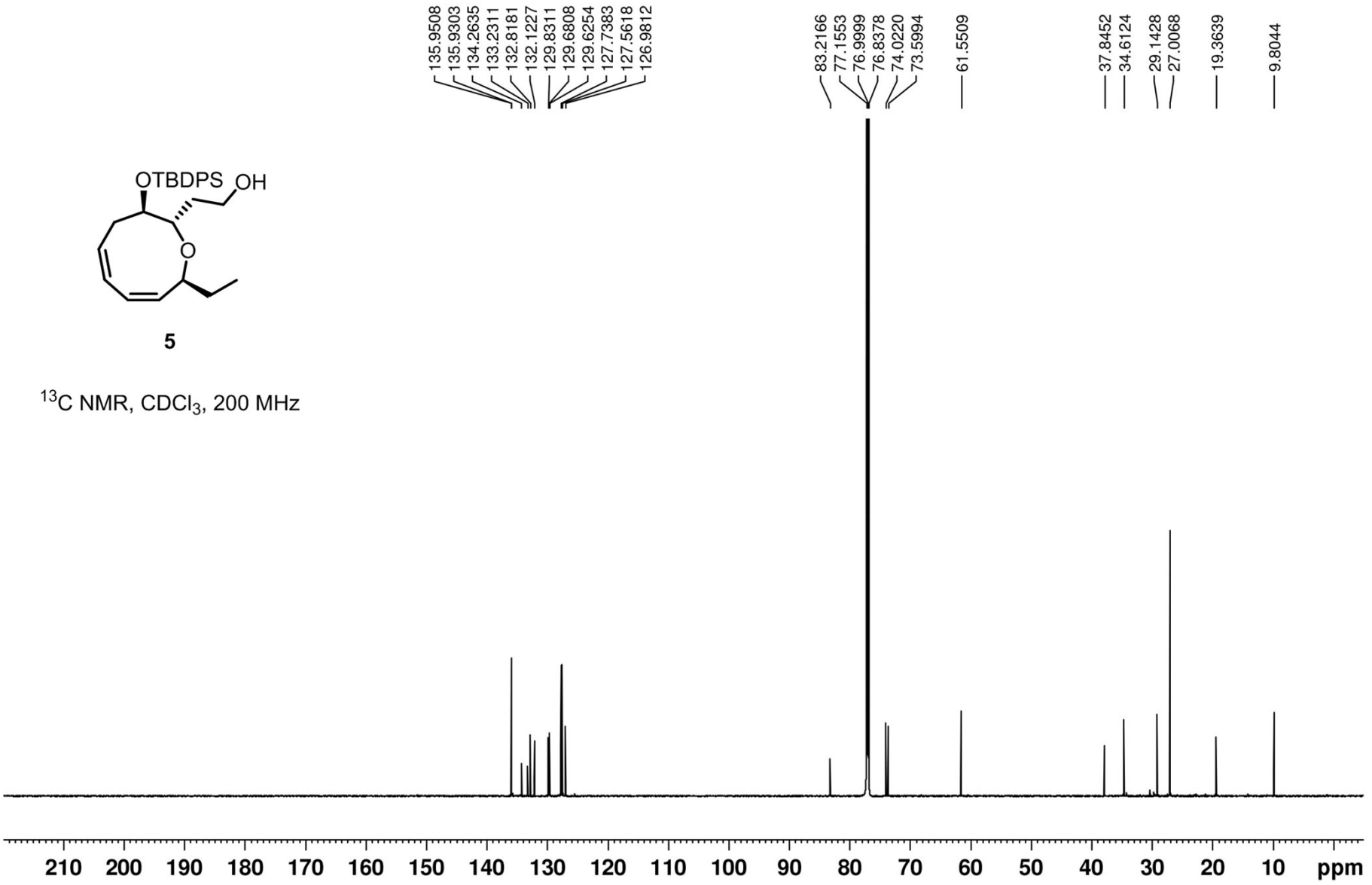
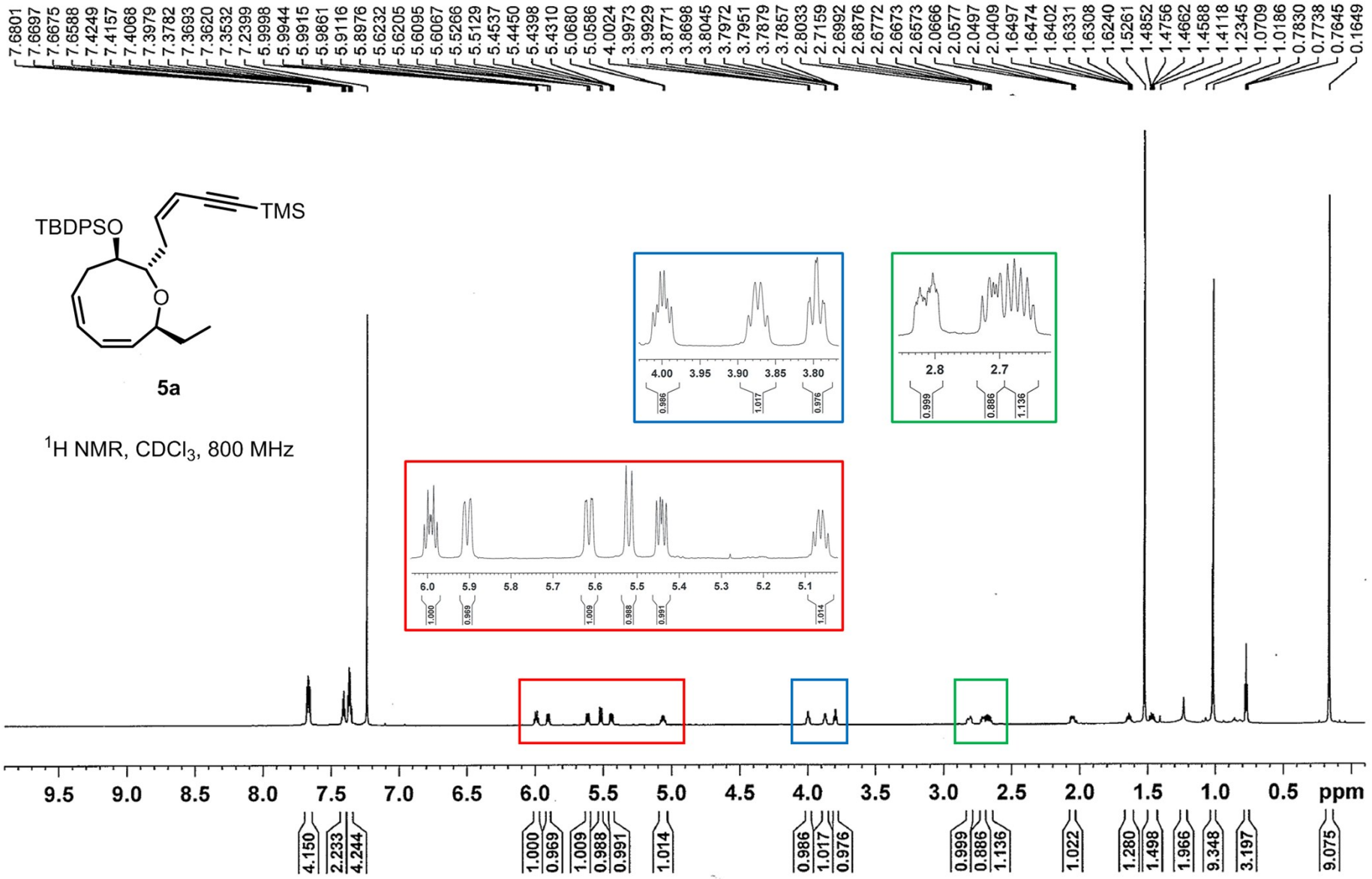
136.2096
136.0653
134.3097
133.7677
133.1582
132.4049
132.1814
129.5650
129.4738
127.8901
127.3716
127.2954
119.0766
84.2026
77.1553
76.9966
76.8378
69.2938
69.1969
29.2564
27.0120
26.7856
19.3368
9.2142
OTBDPS
O
17a
^{13}C NMR, $CDCl_3$, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


OTBDPS
OH
O
5
^{1}H NMR, $CDCl_3$, 600 MHz


135.9508
135.9303
134.2635
133.2311
132.8181
132.1227
129.8311
129.6808
129.6254
127.7383
127.5618
126.9812
83.2166
77.1553
76.9999
76.8378
74.0220
73.5994
61.5509
37.8452
34.6124
29.1428
27.0068
19.3639
9.8044
OTBDPS
OH
O
5
^{13}C NMR, $CDCl_3$, 200 MHz
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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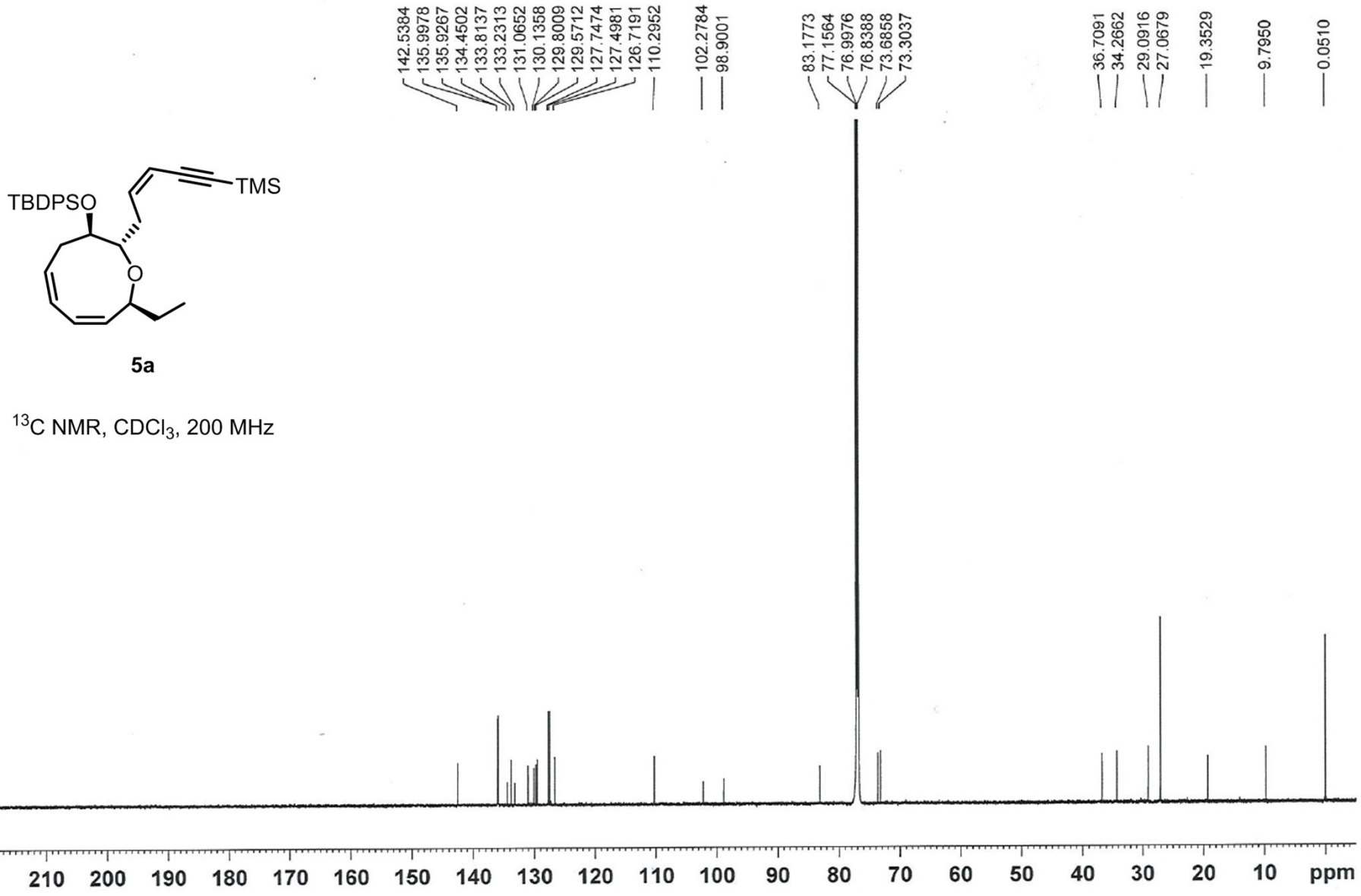
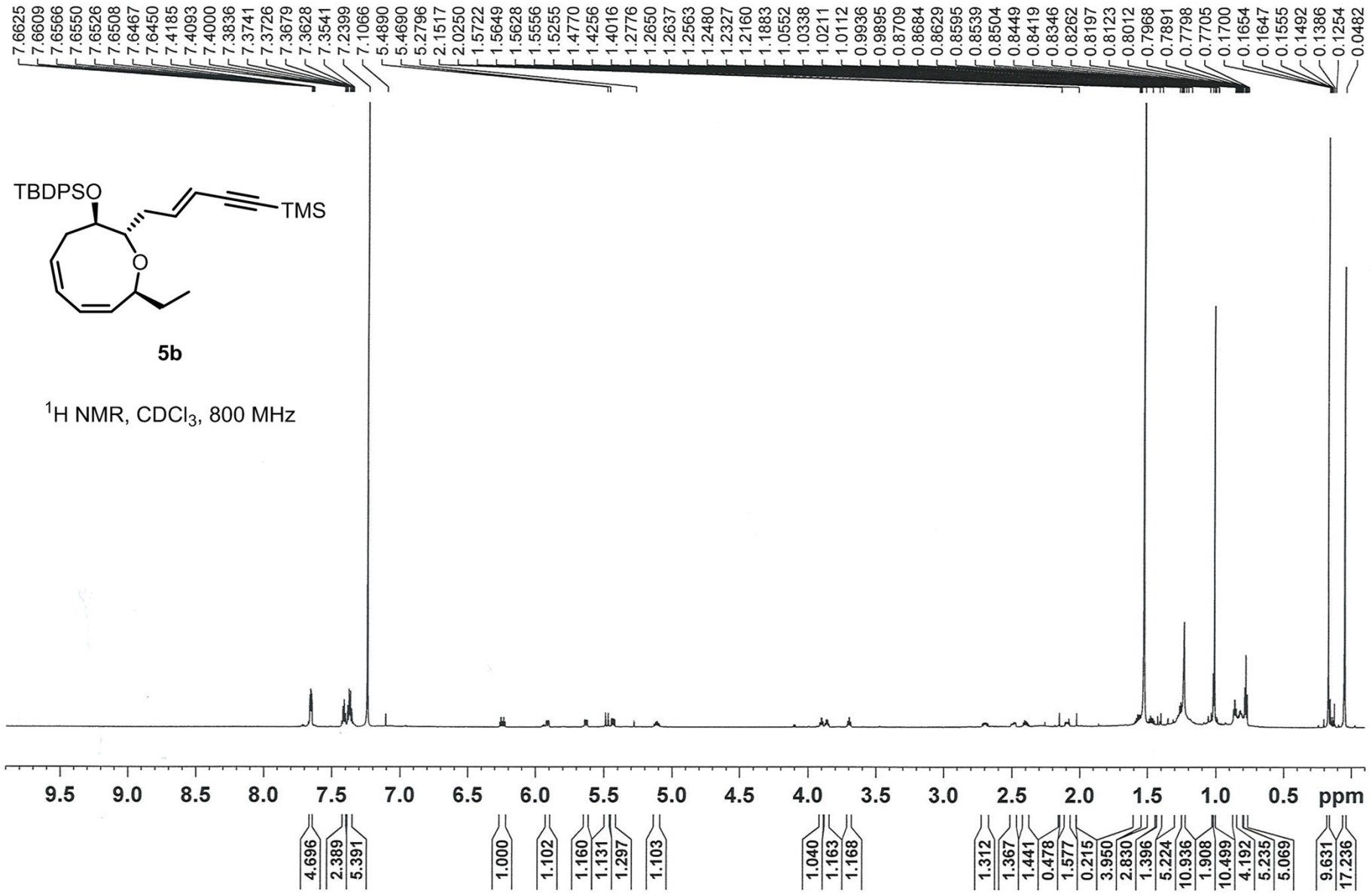
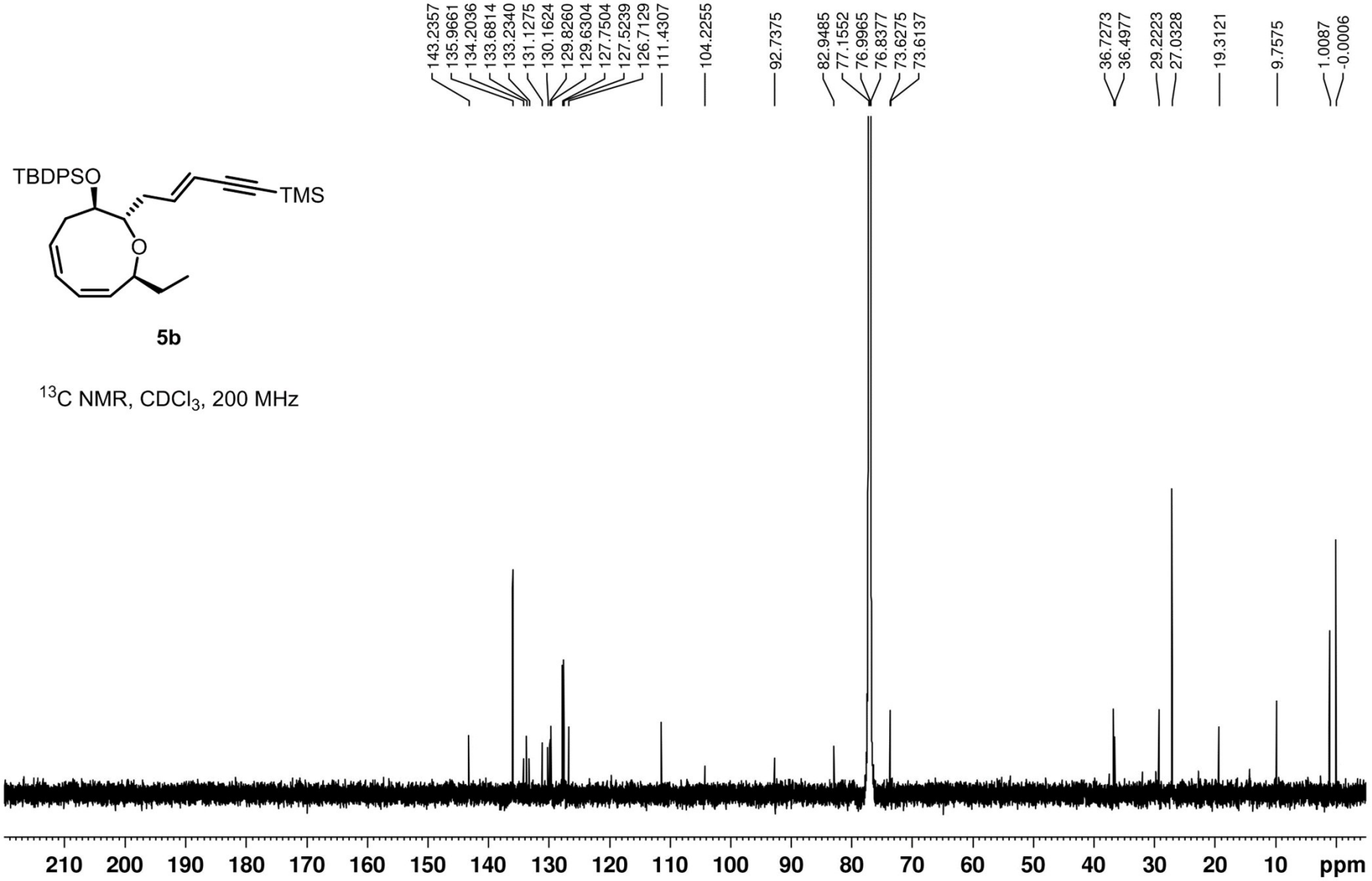
7.6697
7.6675
7.6588
7.4249
7.4157
7.4068
7.3979
7.3782
7.3693
7.3620
7.3532
7.2399
5.9998
5.9944
5.9915
5.9861
5.9116
5.8976
5.6232
5.6205
5.6095
5.6067
5.5266
5.5129
5.4537
5.4450
5.4398
5.4310
5.0680
5.0586
4.0024
3.9973
3.9929
3.8771
3.8698
3.8045
3.7972
3.7951
3.7879
3.7857
2.8033
2.7159
2.6992
2.6876
2.6772
2.6673
2.6573
2.0666
2.0577
2.0497
2.0409
1.6497
1.6474
1.6402
1.6331
1.6308
1.6240
1.5261
1.4852
1.4756
1.4662
1.4588
1.4118
1.2345
1.0709
1.0186
0.7830
0.7738
0.7645
0.1649
TBDPSO
TMS
O
5a
^{1}H NMR, $CDCl_3$, 800 MHz
4.00 3.95 3.90 3.85 3.80
0.966 1.017 0.976
2.8 2.7
0.999 0.886 1.136
6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1
1.000 0.969 1.009 0.988 0.991 1.014
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.150 2.233 4.244 1.000 0.969 1.009 0.988 0.991 1.014 0.986 1.017 0.976 0.999 0.886 1.136 1.022 1.280 1.498 1.966 9.348 3.197 9.075

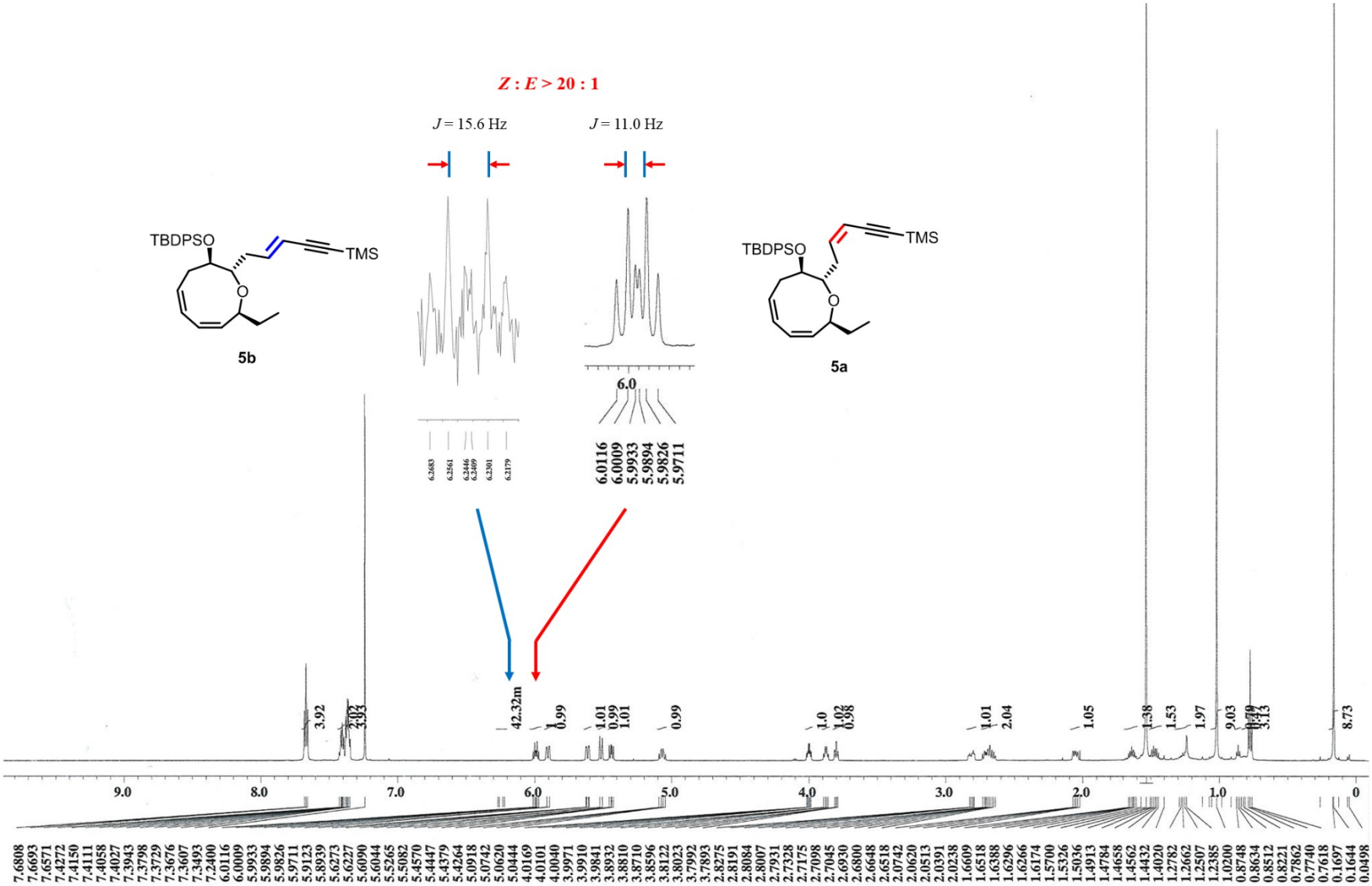


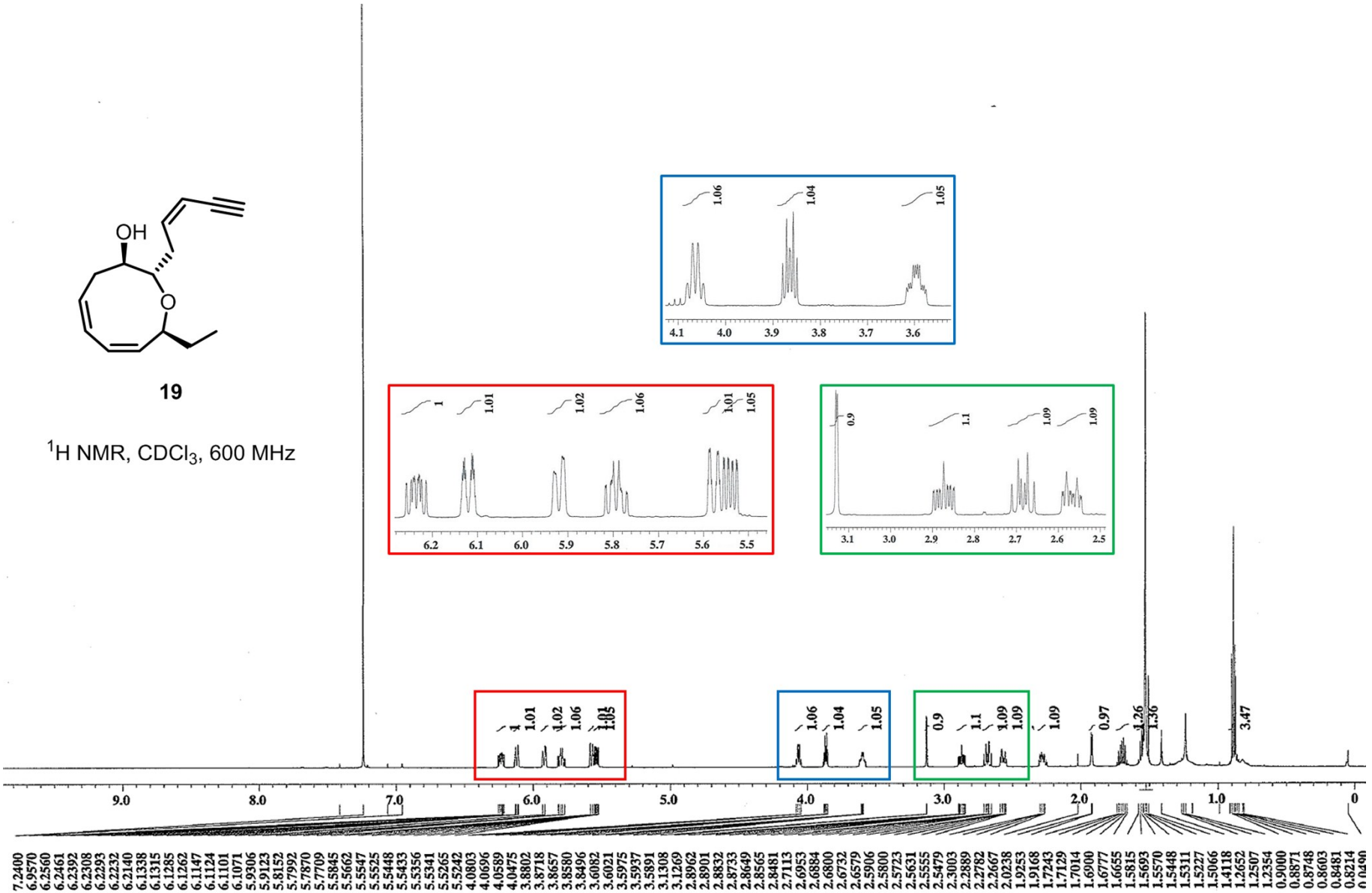
5a

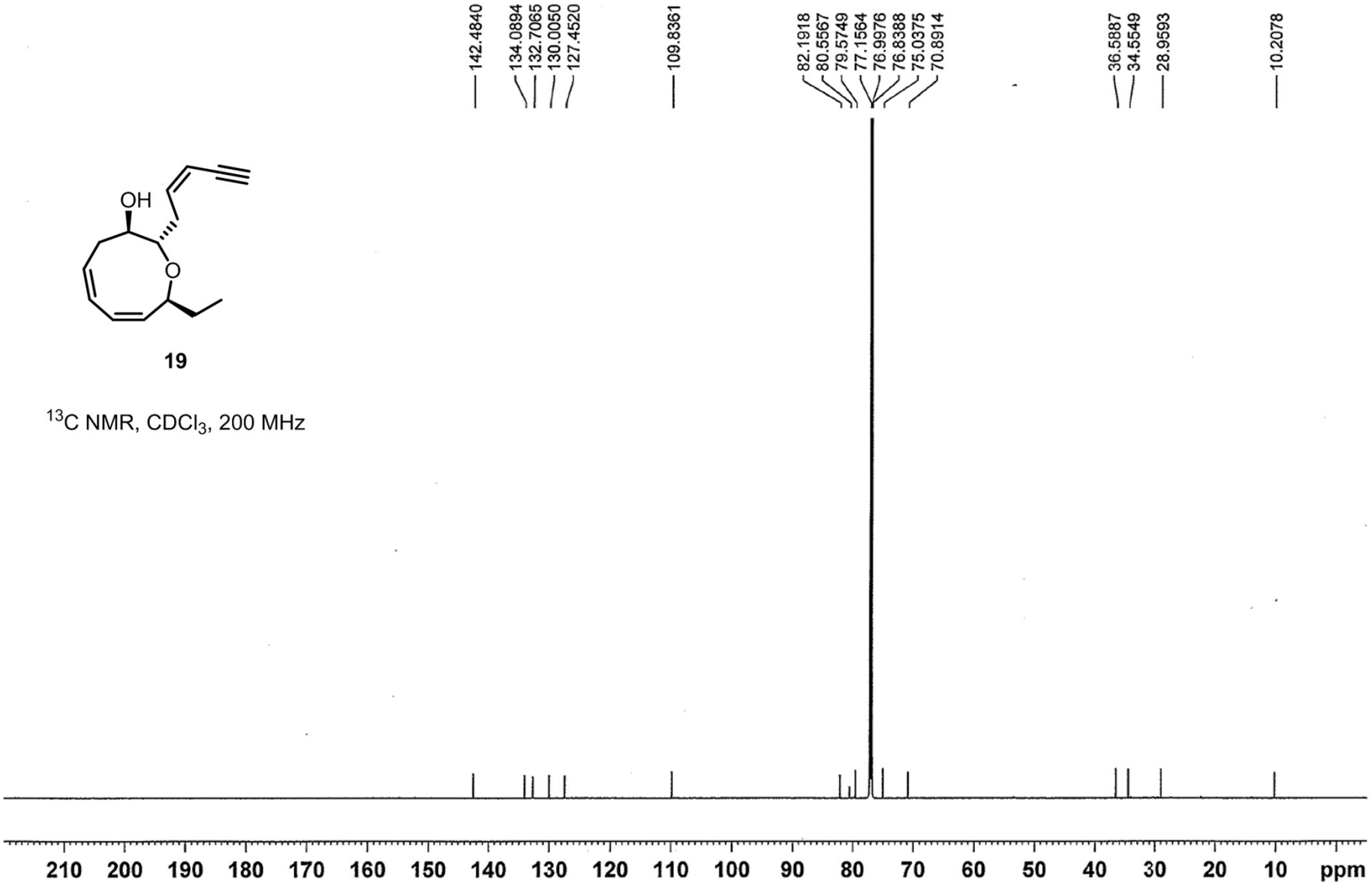
^{13}C NMR, $CDCl_3$, 200 MHz


TBDPSO
TMS
O
5b
^{1}H NMR, $CDCl_3$, 800 MHz
7.6625
7.6609
7.6566
7.6550
7.6526
7.6508
7.6467
7.6450
7.4185
7.4093
7.4000
7.3836
7.3741
7.3726
7.3679
7.3628
7.3541
7.2399
7.1066
5.4890
5.4690
5.2796
2.1517
2.0250
1.5722
1.5649
1.5628
1.5556
1.5255
1.4770
1.4256
1.4016
1.2776
1.2650
1.2637
1.2563
1.2480
1.2327
1.2160
1.1883
1.0552
1.0338
1.0211
1.0112
0.9936
0.9895
0.8709
0.8684
0.8629
0.8595
0.8539
0.8504
0.8449
0.8419
0.8346
0.8262
0.8197
0.8123
0.8012
0.7968
0.7891
0.7798
0.7705
0.1700
0.1654
0.1647
0.1555
0.1492
0.1386
0.1254
0.0482
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.696
2.389
5.391
1.000
1.102
1.160
1.131
1.297
1.103
1.040
1.163
1.168
1.312
1.367
1.441
0.478
1.577
0.215
3.950
2.830
1.396
5.224
10.936
1.908
10.499
4.192
5.235
5.069
9.631
17.236


143.2357
135.9661
134.2036
133.6814
133.2340
131.1275
130.1624
129.8260
129.6304
127.7504
127.5239
126.7129
111.4307
104.2255
92.7375
82.9485
77.1552
76.9965
76.8377
73.6275
73.6137
36.7273
36.4977
29.2223
27.0328
19.3121
9.7575
1.0087
-0.0006
TBDPSO
TMS
O
5b
^{13}C NMR, $CDCl_3$, 200 MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

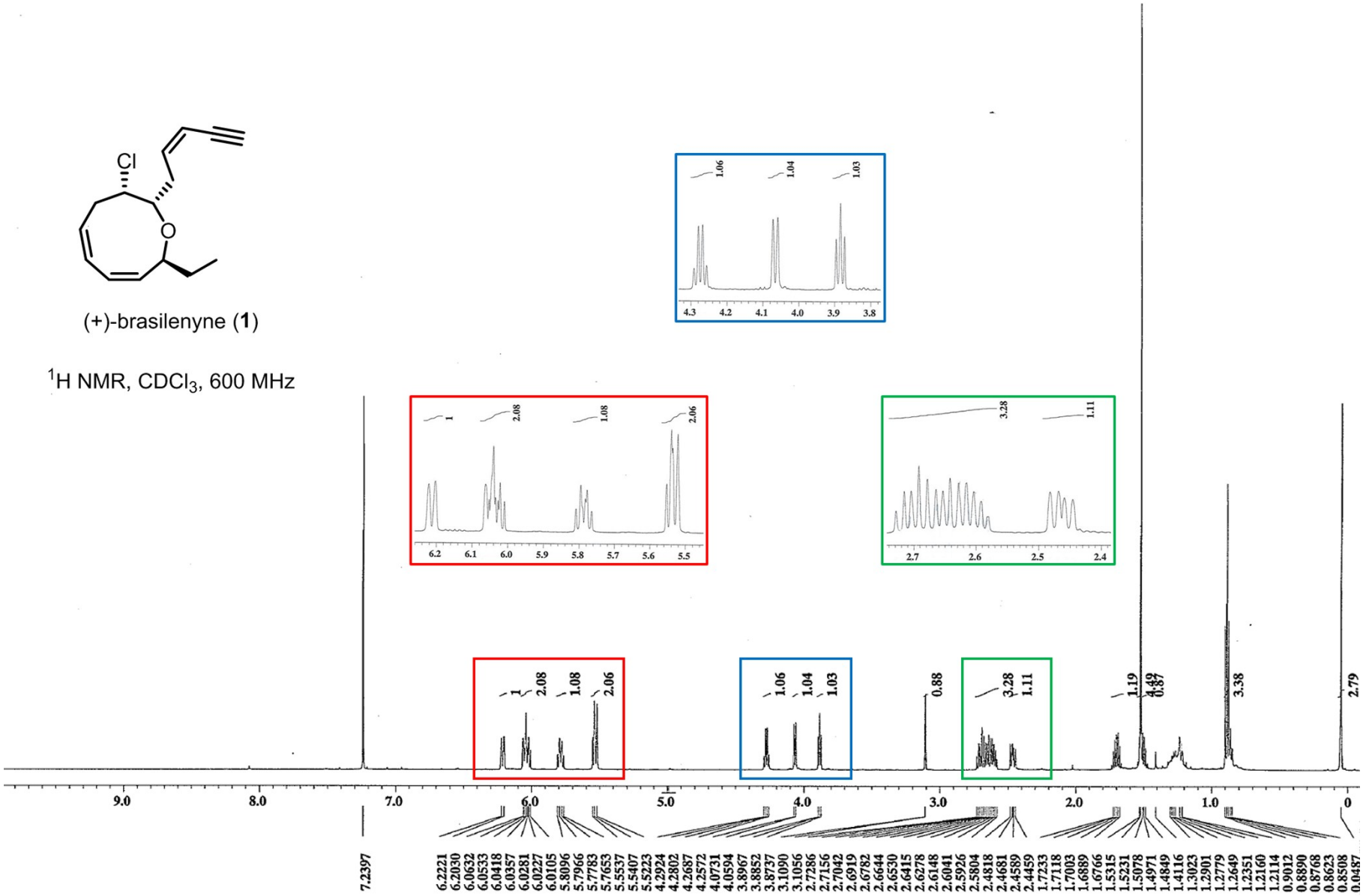

Z : E > 20 : 1
J = 15.6 Hz
J = 11.0 Hz
TBDPSO
TMS
5b
TBDPSO
TMS
5a
6.0
6.0116
6.0009
5.9933
5.9894
5.9826
5.9711
42.32m
3.92
1.38
1.53
1.97
9.03
8.73

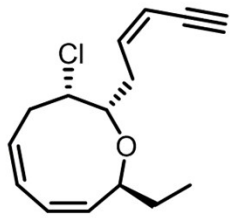

OH
O
19
^{1}H NMR, CDCl$_3$, 600 MHz



19

^{13}C NMR, $CDCl_3$, 200 MHz


Cl
O
(+)-brasilenyne (1)
1H NMR, CDCl3, 600 MHz



(+)-brasilenyne (**1**)

^{13}C NMR, $CDCl_3$, 150 MHz

IV. References

[1] S. Torssell, P. Somfai, *Org. Biomol. Chem.* **2004**, *2*, 1643-1646.

[2] a) H. Nagatomo, Y. Matsushita, K. Sugamoto, T. Matsui, *Tetrahedron: Asymmetry* **2003**, *14*, 2339-2350; b) K. S. Petersen, G. H. Posner, *Org. Lett.* **2008**, *10*, 4685-4687.

[3] a) S. E. Denmark, S. M. Yang, *J. Am. Chem. Soc.* **2002**, *124*, 15196-15197; b) S. E. Denmark, S. M. Yang, *J. Am. Chem. Soc.* **2004**, *126*, 12432-12440.

[4] R. B. Kinnel, R. K. Dieter, J. Meinwald, D. Vanengen, J. Clardy, T. Eisner, M. O. Stallard, W. Fenical, *Proc. Natl. Acad. Sci. USA* **1979**, *76*, 3576-3579.