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Supporting Information

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A *trans*-Selective Hydroboration of Internal Alkynes**

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SUPPORTING INFORMATION

Crystallographic Summary

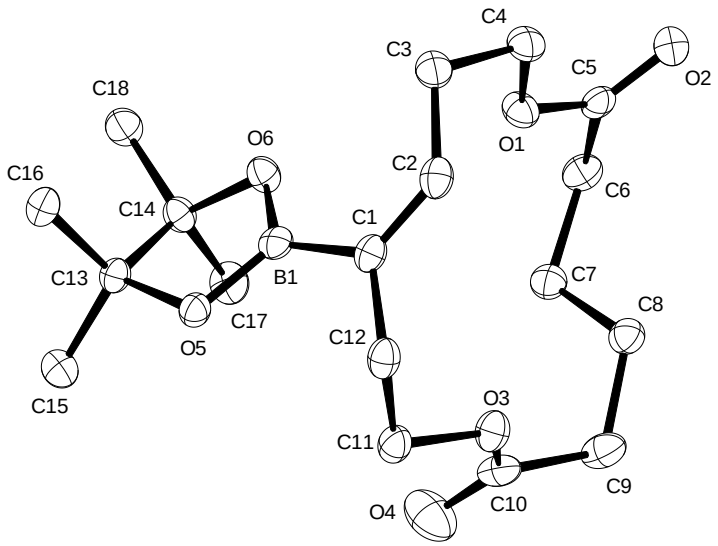

Figure S-1 Structure of compound *E*-**2** in the solid state. The anisotropic displacement parameters are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis of *E*-**2**: $C_{18}H_{29}BO_6$, M_r = 352.22 g · mol^{-1}, colorless, crystal size 0.36 x 0.25 x 0.09 mm, monoclinic, space group $P2_1/c$, a = 15.6802(9) Å, b = 9.8444(6) Å, c = 12.7099(8) Å, β = 106.896(2)°, V = 1877.2(2) Å^3, T = 100 K, Z = 4, D_{calc} = 1.246 g ·cm^3, λ = 1.54178 Å, $\mu(Cu\text{-}K_\alpha)$ = 0.746 mm^{-1}, empirical absorption correction (T_{min} = 0.77, T_{max} = 0.94), Bruker AXS X8 Proteum diffractometer, 2.945 < θ < 59.186, 37119 measured reflections, 2698 independent reflections, 2412 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.030 [$I > 2\sigma(I)$], wR_2 = 0.076, 230 parameters, H atoms riding, S = 1.087, residual electron density +0.2 / -0.2 e Å^{-3}.

CCDC-951785 contains the supplementary crystallographic data for this paper. This information can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General: Unless stated otherwise, all reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents under Ar: THF, Et_2O (Mg/anthracene), CH_2Cl_2, CH_3CN (CaH_2), hexane, toluene (Na/K), EtOH, MeOH (Mg). Flash chromatography (FC): Merck silica gel 60 (40-63 µm) and 60 (15-43 µm). NMR: Spectra were recorded on Bruker DPX 300, AMX 300, AV 400 or AVIII 600 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. ^{11}B NMR were recorded on a Bruker DPX 300 operating at 96 MHz, or a Bruker AV 400 at 128 MHz. ^{2}H NMR were recorded on a Bruker AVIII 600 spectrometer operating at 92 MHz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.0 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 53.8 ppm; residual $CHDCl_2$ in CD_2Cl_2: δ_H = 5.32 ppm); proton and carbon assignments were established using nOe, HSQC, and HMBC experiments. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker). Accurate mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). Unless stated otherwise, all commercially available compounds (Fluka, Aldrich) were used as received.

$[Cp^*Ru(CH_3CN)_3]PF_6$,[1] $[Cp^*RuCl_2]_2$,[2] and $[Cp^*Ru(\mu\text{-}H)_2]_2$ [3] were prepared on multigram scale according the literature procedures and were kept and transferred under Ar. ***Note***: Samples of $[Cp^*Ru(CH_3CN)_3]PF_6$ purchased from different commercial suppliers had largely different qualities and a potential user is advised to check this aspect carefully. The cited procedure for the preparation of this complex gave samples of excellent purity and is therefore recommended.

[Cp*Ru(cod)Cl] was purchased from Strem and stored under Ar.

Commercial AgOTf was dried under vacuum (10^{-3} bar) and stored and manipulated under Ar.

Deuterated pinacolborane (pin-D) was prepared according to a literature procedure.[4]

All alkynes were prepared according to literature procedures.[5]

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1 a) M. D. Mbaye, B. Demerseman, J.–L. Renaud, L. Toupet, C. Bruneau, *Adv. Synth. Catal*. **2004**, *346*, 835-841.

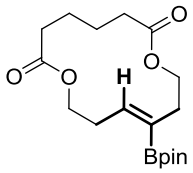
2 T. D. Tilley, R. H. Grubbs, E. J. Bercaw, *Organometallics*, **1984**, *3*, 274-278.

3 a) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, Y. Moro-oka, *Organometallics* **1988**, *7*, 2243-2245; b) H. Suzuki, H. Omori, D. H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka, Y. Moro-oka, *Organometallics* **1994**, *13*, 1129-1146.

4 J. Y. Wu, B. Moreau, T. Ritter, *J. Am. Chem. Soc.* **2009**, *131*, 12915-12917.

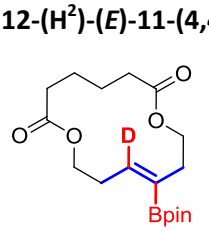
5 J. Heppekausen, R. Stade, R. Goddard, A. Fürstner, *J. Am. Chem. Soc*. **2010**, *132*, 11045-11057.

Representative procedure for the *trans*-hydroboration of alkynes: (*E*)-11-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,8-dioxacyclotetradec-11-ene-2,7-dione (*E*-2): A flame-dried 10 mL Schlenk tube was charged under Ar with [Cp*Ru(CH_3CN)$_3$]PF_6 (75.6 mg, 0.15 mmol) and CH_2Cl_2 (5 mL) and the resulting solution was cooled to 0°C with an ice bath. Pinacolborane (872 µL, 6 mmol) and alkyne **1** (1.12 g, 5 mmol) were successively added, the ice bath was removed and the solution stirred for 4 h at ambient temperature. For workup, the solvent was evaporated and the residue passed through a short column of silica, eluting with EtOAc/hexanes (1/4), to give alkenylboronate *E*-**2** as a white crystalline solid (1.61 g, 91%, *E/Z* ≥ 98:2). When the same reaction performed at 0.2 mmol scale, the product was isolated in 96% yield. Mp = 66.7-70.4°C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06 (1H, t, *J* = 7.0 Hz), 4.18 (2H, t, *J* = 5.5 Hz), 4.12 (2H, t, *J* = 5.5 Hz), 2.71 (2H, dt, *J* = 5.5, 7.1 Hz), 2.41 (2H, t, *J* = 5.0 Hz), 2.34-2.24 (4H, m), 1.65-1.55 (4H, m), 1.22 (s, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.2, 173.1, 145.8, 83.0, 64.2, 63.2, 36.1, 34.9, 34.8, 30.0, 24.7, 24.5, 24.5 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.6; IR (thin film): 2965, 1720, 1644, 1265, 1134, 861, 708 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{29}BO_6Na$ [M$^+$+Na]: 375.1947; found: 375.1949.

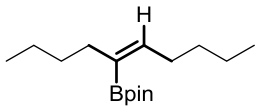


The corresponding stereoisomer *Z*-**2** was prepared for comparison according to a literature procedure.[6]

12-(H^2)-(*E*)-11-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,8-dioxacyclotetradec-11-ene-2,7-dione [D]-***E*-2:** White solid (62 mg, 88%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.19 (2H, t, *J* = 5.3 Hz), 4.13 (2H, t, *J* = 5.5 Hz), 2.71 (2H, t, *J* = 5.4 Hz), 2.42 (2H, t, *J* = 5.3 Hz), 2.35-2.23 (4H, m), 1.66-1.54 (4H, m), 1.23 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.0, 172.8, 145.2 (t, *J* = 23.42 Hz), 82.7, 64.0, 63.0, 35.8, 34.6, 34.5, 29.6, 24.4, 24.3, 24.2 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{2}H NMR (CH_2Cl_2, 92 MHz, 22°C): δ 6.1; ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.6; HRMS (ESI): *m/z* calcd for $C_{18}H_{28}BO_6DNa$ [M$^+$+Na]: 376.2010; found: 376.2012.



(*E*)-2-(Dec-5-en-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: Colorless oil (237 mg, 89%); reaction time = 1 h; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.97 (1H, t, *J* = 7.5 Hz), 2.29 (2H, q, *J* = 7.1, 14.2 Hz), 2.07 (2H, t, *J* = 6.9 Hz), 1.40-1.28 (m, 8H), 1.25 (12H, s), 0.93-0.81 (6H, m); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 146.4, 83.0, 37.0, 33.0, 32.7, 31.2, 25.1, 22.7, 22.6, 14.4, 14.3 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 96 MHz): δ 30.6; HRMS (ESI): *m/z* calcd for $C_{16}H_{31}BO_2Na$ [M$^+$+Na]: 289.2322; found: 289.2322.



[6] M. J. Hesse, C. P. Butts, C. L. Willis, V. K. Aggarwal., *Angew. Chem.* **2012**, *124*, 12612-12616; *Angew. Chem. Int. Ed.*, **2012**, *51*, 12444-12448.

(*E*)-2-(1,6-Bis(benzyloxy)hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: Colorless oil, (65 mg, 83%); reaction time = 2 h 30 min; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.12 (10H, m), 6.09 (1H, t, J = 7.3 Hz), 4.44 (2H, s), 4.42 (2H, s), 3.41 (4H, q, J = 7.0, 15.0 Hz), 2.61 (2H, q, J = 7.10, 14.2 Hz), 2.36 (2H, t, J = 7.1 Hz), 1.14 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.3, 143.3, 138.8, 138.6, 128.3, 128.2, 127.6, 127.4, 127.3, 82.9, 72.6 (2C), 70.7, 70.2, 37.1, 31.6, 24.7 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.9; HRMS (ESI): m/z calcd for $C_{26}H_{35}BO_4Na$ [M^++Na]: 445.2532; found: 445.2536.

(*E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-ene-1,6-diylbis(4-methylbenzene-sulfonate): Colorless oil (40 mg, 73%); reaction time = 2 h 30 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ =7.82-7.72 (4H, m), 7.38-7.28 (4H, m), 5.92 (1H, t, J = 7.3 Hz), 4.06-3.93 (4H, m), 2.68 (2H, q, J = 6.8, 13.9 Hz), 2.44 (3H, s), 2.43 (3H, s), 2.35 (2H, t, J = 6.8 Hz), 1.16 (12H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.6, 144.5, 144.0, 133.4, 133.2, 129.8, 129.7, 127.9 (2C), 83.3, 70.2, 70.0, 36.2, 30.5, 24.7, 21.56, 21.55 (the C-atom directly attached to boron is broadened and could not be precisely localized); HRMS (ESI): m/z calcd for $C_{26}H_{35}BO_8Na$ [M^++Na]: 573.1770; found: 573.1773.

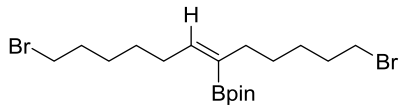
(*E*)-2-(1,6-Bis((tetrahydro-2*H*-pyran-2-yl)oxy)hex-3-en-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxa borolane: Colorless oil (42 mg, 61%); reaction time = 2 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.16 (1H, t, J = 7.5 Hz), 4.62-4.55 (2H, m), 3.92-3.80 (2H, m), 3.77-3.64 (2H, m), 3.52-3.35 (4H, m), 2.71-2.57 (2H, m), 2.39 (2H, t, J = 7.4 Hz), 1.91-1.75 (2H, m), 1.74-1.62 (2H, m), 1.62-1.42 (8H, m), 1.24 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.8, 98.4 (2C), 82.9, 67.7, 67.3, 62.1, 62.0, 37.0, 31.6, 30.7 (2C), 25.5 (2C), 24.8, 19.5 (2C) (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.7; HRMS (ESI): m/z calcd for $C_{26}H_{39}BO_6Na$ [M^++Na]: 433.2734; found: 433.2731.

(*E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-ene-1,6-diylbis(4-chlorobenzoate): White solid (73 mg, 94%); reaction time = 140 min; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.97-7.86 (4H, m), 7.40-7.29 (4H, m), 6.24 (1H, t, J = 7.5 Hz), 4.40-4.26 (4H, m), 2.83 (2H, q, J = 6.4, 13.6 Hz), 2.57 (2H, t, J = 6.6 Hz), 1.24 (12H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 165.60, 165.55, 144.9, 139.2, 139.1, 130.9, 130.8, 129.0, 128.9, 128.53, 128.52, 83.2, 65.0, 64.8, 36.1, 30.6, 24.7 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.7; HRMS (ESI): m/z calcd for $C_{26}H_{29}BCl_2O_6Na$ [M^++Na]: 541.1338; found: 541.1338.

(*E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-ene-1,6-diyl bis(4-methoxybenzoate): Colorless oil (40 mg, 75%); reaction time = 1 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (2H, d, J = 3.5 Hz), 7.87 (2H, d, J = 3.5 Hz), 6.87 (2H, d, J = 8.8 Hz), 6.84 (2H, d, J = 8.8 Hz), 6.28 (1H, t, J =

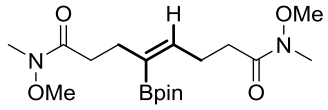
7.3 Hz), 4.36-4.25 (4H, m), 3.84 (3H, s), 3.82 (3H, s), 2.83 (2H, q, *J* = 6.8, 13.6 Hz), 2.56 (2H, t, *J* = 6.6 Hz), 1.24 (12H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.30, 166.25, 163.2, 163.1, 145.1, 131.54, 131.45, 123.1, 123.0, 113.47, 113.45, 83.2, 64.5, 64.4, 55.32, 55.31, 36.2, 30.8, 24.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 29.7; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{35}BO_8Na$ [M^++Na]: 533.2330; found: 533.2333.

(*E*)-2-(1,12-Dibromododec-6-en-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: Colorless oil,



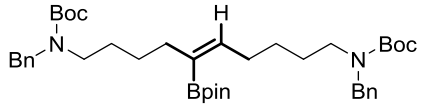
(77 mg, 85%); reaction time = 4 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.97 (1H, t, *J* = 7.5 Hz), 3.39 (4H, t, *J* = 6.9 Hz), 2.31 (2H, q, *J* = 7.4, 14.5 Hz), 2.07 (2H, t, *J* = 6.7 Hz), 1.92-1.78 (4H, m), 1.48-1.31 (8H, m), 1.26 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.0, 82.8, 36.5, 34.0, 33.9, 32.7, 32.6, 30.7, 29.3, 28.9, 27.7, 27.5, 24.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.1; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{33}BBr_2O_2Na$ [M^++Na]: 473.0842; found: 473.0832.

(*E*)-N^1,N^8-Dimethoxy-N^1,N^8-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-ene-



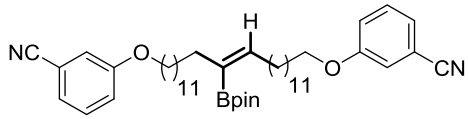
diamide: Colorless oil (39 mg, 85%); reaction time = 5 h; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.09 (1H, t, *J* = 7.3 Hz), 3.65 (3H, s), 3.64 (3H, s), 3.15 (3H, s), 3.14 (3H, s), 2.61 (2H, q, *J* = 7.2, 14.8 Hz), 2.54-2.31 (6H, m), 1.24 (12H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 174.4 (2C), 145.7, 83.0, 61.1 (2C), 32.7, 32.3, 32.2 (2C), 26.28, 26.25, 24.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 96 MHz): δ 29.6; HRMS (ESI): *m*/*z* calcd for $C_{18}H_{33}BN_2O_6Na$ [M^++Na]: 407.2331; found: 407.2337.

(*E*)-Di-*tert*-butyl(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-5-ene-1,10-diyl)bis(benzyl



carbamate): Colorless oil (87 mg, 82%); reaction time = 23 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.08 (10H, m), 5.85 (1H, t, *J* = 7.4 Hz), 4.43-4.25 (4H, m), 3.22-2.94 (4H, m), 2.20 (2H, q, *J* = 7.3, 14.6 Hz), 1.97 (2H, t, *J* = 7.3 Hz), 1.53-1.27 (22H, m), 1.26-1.16 (4H, m), 1.15 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.8, 155.3, 145.7, 138.3, 132.5, 128.1 (3C), 127.3, 126.7, 115.1, 82.7, 79.1 (2C), 50.0, 49.6, 46.2, 36.3, 36.2, 30.4, 28.1, 27.1 (2C), 27.0, 24.44, 24.39, 24.2 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 96 MHz): δ 31.1; HRMS (ESI): *m*/*z* calcd for $C_{40}H_{61}BN_2O_6Na$ [M^++Na]: 699.4521; found: 699.4514.

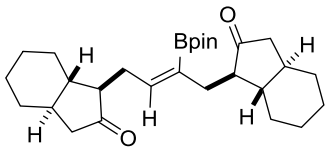
(*E*)-3,3'-((13-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexacos-13-ene-1,26-diyl)bis(oxy))-



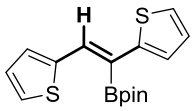
dibenzonitrile: White solid (53 mg, 87%); reaction time = 4 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47-7.30 (3H, m), 7.24-7.18 (2H, m), 7.12 (3H, m), 5.97 (1H, t, *J* = 7.3 Hz), 3.95 (4H, t, *J* = 6.5 Hz), 2.28 (2H, q, *J* = 6.8 Hz), 2.13 (1H, t, *J* = 6.0 Hz), 2.06 (2H, t, *J* = 6.9 Hz), 1.85-1.73 (4H, m), 1.51-1.39 (6H, m), 1.39-1.20 (41H, m); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 159.1, 145.9, 135.2, 134.9, 130.2, 130.0, 127.9, 124.2,

119.8, 118.8, 117.3, 113.1, 82.9, 80.2, 68.4, 53.4, 36.9, 31.1, 30.3, 30.14, 30.04, 29.62, 29.60, 29.58, 29.56, 29.55, 29.51, 29.46, 29.29, 29.24, 29.14, 29.13, 29.0, 28.8, 28.5, 25.9, 24.8, 18.7 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 77 MHz): δ 31.0; HRMS (ESI): *m*/*z* calcd for $C_{46}H_{69}BN_2O_4Na$ [M^++Na]: 747.5264; found: 747.5261.

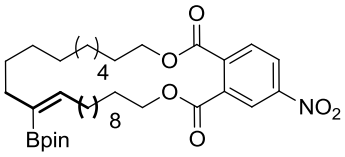
1,1'-((*E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-ene-1,4-diyl)bis(hexahydro-1*H*-inden-2(3*H*)-one): Colorless oil (52 mg, 75%); reaction time = 20 h; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.00 (1H, t, *J* = 8.0 Hz), 2.74-2.61 (1H, m), 2.60-2.50 (2H, m), 2.30 (2H, ddd, *J* = 6.5 Hz), 2.16-1.88 (6H, m), 1.87-1.70 (9H, m), 1.58-1.22 (6H, m), 1.18 (12H, s), 1.13-0.98 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 219.3, 219.2, 145.4, 82.9, 55.6, 55.5, 48.9, 48.5, 48.2, 44.9, 44.6, 41.7, 41.5, 35.51, 35.49, 31.43, 31.38, 30.7, 29.0, 26.3, 26.2, 26.1, 24.9 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.6; HRMS (ESI): *m*/*z* calcd for $C_{28}H_{43}BO_4Na$ [M^++Na]: 477.3149; found: 477.3146.



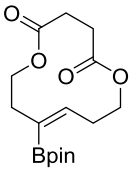
(*E*)-2-(1,2-Di(thiophen-2-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: The reaction was performed for 24 h at ambient temperature, after which an additional 5 mol% of the ruthenium catalyst was added and stirring was continued at 50°C for 48 h; pale yellow oil (49 mg, 59%), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61 (1H, s), 7.37 (1H, dd, *J* = 1.2, 5.0 Hz), 7.21 -7.18 (1H, m), 7.12–7.09 (1H, m), 7.09-7.05 (1H, m), 6.93-6.89 (2H, m), 1.30 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.6, 139.2, 138.8, 131.5, 128.8, 127.4, 126.16, 126.15, 125.8, 83.9, 24.7 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.3; HRMS (ESI): *m*/*z* calcd for $C_{16}H_{19}BO_2S_2Na$ [M^++Na]: 341.0815; found: 341.0811.



(*E*)-29-Nitro-13-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4,5,6,7,8,9,10,11,12,15,16,17,18,19,20,21,22,23,24-icosahydrobenzo[c][1,6]dioxacyclooctacosine-1,26-dione: White solid (48 mg, 77%); reaction time = 4 h; although the presence of the nitro group renders the compound unsymmetrical and two regioisomers are to be expected, only one data set was recorded: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.60 (1H, d, *J* = 2.27 Hz), 8.37 (1H, 2d, *J* = 2.2 Hz), 7.84 (1H, d, *J* = 8.3 Hz), 5.93 (1H, t, *J* = 7.4 Hz), 4.40-4.26 (4H, m), 2.33 (2H, q, *J* = 6.5, 13.3 Hz), 2.09 (2H, t, *J* = 6.3 Hz), 1.82-1.67 (4H, q, *J* = 7.0, 14.1 Hz), 1.46-1.13 (40H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.3, 165.2, 148.7, 147.1, 138.2, 133.2, 130.1, 125.8, 124.4, 82.6, 66.6, 36.2, 30.49, 30.47, 29.6, 29.5, 29.4, 29.32, 29.28, 29.2, 28.5, 28.43, 28.39, 28.37, 28.26, 28.21, 28.04, 27.96, 25.70, 25.65, 24.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.0; HRMS (ESI): *m*/*z* calcd for $C_{36}H_{56}BNO_8Na$ [M^++Na]: 664.4007; found: 664.4009.

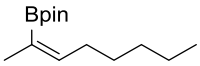


(*E*)-9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dioxacyclododec-9-ene-2,5-dione:



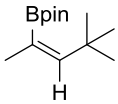
White solid (27 mg, 54%); reaction time = 20 min; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.95 (1H, t, J = 6.4 Hz), 4.36-4.21 (4H, m), 2.75 (2H, q, J = 6.1, 13.0 Hz), 2.55 (4H, m), 2.40 (2H, t, J = 5.6 Hz), 1.27 (12H, s); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.84, 171.83, 146.0, 83.0, 62.78, 62.76, 37.5, 30.6, 30.3, 30.2, 24.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): 30.4; HRMS (ESI): m/z calcd for $C_{16}H_{25}B_1O_6Na$ [M^++Na]: 347.1633; found: 347.1636.

(*E*)-4,4,5,5-Tetramethyl-2-(oct-2-en-2-yl)-1,3,2-dioxaborolane: Colorless oil (163 mg, 68%);



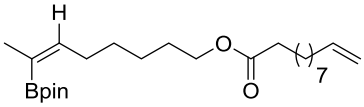
reaction time = 3 h; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.05 (1H, t, J = 7.0 Hz), 2.29 (2H, q, J = 6.9 Hz), 1.77-1.71 (2H, m), 1.42-1.15 (19H, m), 0.87 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.4, 82.7, 31.4, 30.9, 29.6, 24.8, 22.5, 22.3, 14.0 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.3; HRMS (ESI): m/z calcd for $C_{14}H_{27}BO_2Na$ [M^++Na]: 261.1999; found: 261.1996.

(*E*)-2-(4,4-Dimethylpent-2-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: Colorless oil (758



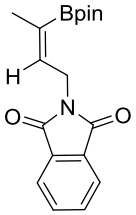
mg, 67%); reaction time = 1 h; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.27 (1H, d, J = 1.6 Hz), 1.79 (3H, d, J = 1.6 Hz), 1.24 (12H, s), 1.13 (9H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.0, 83.1, 34.2, 30.3, 24.8, 14.8 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 31.1; HRMS (ESI): m/z calcd for $C_{13}H_{25}BO_2Na$ [M^++Na]: 247.1837; found: 247.1839.

(*E*)-7-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oct-6-en-1-yl undec-10-enoate: Colorless oil



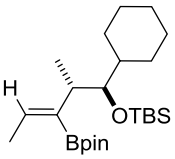
(49 mg, 60%); reaction time = 3 h; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.017 (1H, m), 5.78-5.72 (1H, m), 4.96-4.87 (2H, m), 4.02 (2H, m), 2.36-2.30 (2H, m), 2-30-2.25 (2H, m), 2.05-2.00 (2H, m), 1.72 (3H, s), 1.59-1.54 (4H, m), 1.33-1.26 (8H, m), 1.26-1.24 (6H, m), 1.25 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 174.0, 146.9, 139.2, 114.1, 82.8, 64.4, 30.7, 34.5, 33.8, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.4, 25.3, 25.0, 24.8, 22.3 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.1; HRMS (ESI): m/z calcd for $C_{25}H_{45}BO_4Na$ [M^++Na]: 443.3315; found: 443.3319.

(*E*)-2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)isoindoline-1,3-dione:

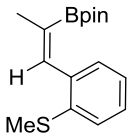


Colorless oil (143 mg, 88%); reaction time = 2 h; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87-7.74 (2H, m), 7.73-7.58 (2H, m), 5.97 (1H, t, J = 6.4 Hz), 4.62 (2H, d, J = 6.6 Hz), 1.75 (3H. s), 1.31 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.0, 139.0, 133.7, 132.3, 123.0, 83.4, 38.4, 24.9, 16.9 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.6; HRMS (ESI): m/z calcd for $C_{18}H_{22}BO_4NNa$ [M^+]: 327.1641; found: 327.1641.

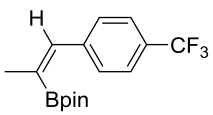
tert*-Butyl (((1*R*,2*S*,*E*)-1-cyclohexyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-1-yl)oxy)dimethylsilane:** Colorless oil (106 mg, 70%); reaction time = 2 h; spectroscopic data of the ***major isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.26 (1H, q, J = 1.5, 3.2 Hz), 3.26-3.22 (1H, m), 2.79-2.68 (1H, m), 1.64 (3H, d, J = 1.7 Hz), 1.22-1.20 (18H, m), 0.89-0.87 (14H, m), 0.85 (9H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.4, 82.6, 80.4, 42.0, 36.8, 30.9, 28.6, 26.8, 26.6, 26.3, 25.0, 24.8, 22.7, 17.5, −3.3 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 30.9; HRMS (ESI): m/z calcd for $C_{24}H_{47}BO_3SiNa$ [M^++Na]: 445.3276; found: 445.3279.



(*E*)-4,4,5,5-Tetramethyl-2-(1-(2-(methylthio)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane: Colorless oil, (54 mg, 91%); reaction time = 160 min; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (1H, bs), 7.16-7.13 (2H, m), 7.13-7.11 (1H, m), 7.05-7.03 (1H, m), 2.35 (3H, s), 1.76 (3H, d, J = 1.8 Hz), 1.23 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.3, 139.2, 135.4, 128.4, 126.6, 124.2, 123.1, 82.4, 23.8, 14.8, 14.6 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 77 MHz): δ 31.1; HRMS (ESI): m/z calcd for $C_{16}H_{23}BO_2SNa$ [M^++Na]: 313.1404; found: 313.1404.



(*E*)-Methyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)benzoate: Colorless oil, (106 mg, 70%); reaction time = 3 h; spectroscopic data of the ***major isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85-7.83 (2H, m), 7.30-7.26 (2H, m), 6.84 (1H, s), 3.81 (s, 3H), 1.92 (3H, d, J = 1.7 Hz), 1.18 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.0, 143.5, 139.7, 129.1, 127.9, 83.6, 24.6, 23.5 (the C-atom directly attached to boron is broadened and could not be precisely localized); spectroscopic data of the ***minor isomer***: ^{1}HNMR ($CDCl_3$, 400 MHz): δ 7.88-7.86 (2H, m), 7.32-7.26 (2H, m), 6.48 (1H, q, J = 7.0, 14.1 Hz), 3.80 (3H, s), 1.99 (3H, d, J = 1.7 Hz), 1.24 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.1, 148.2, 144.5, 129.4, 127.0, 83.5, 51.9, 24.7, 17.9 (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): 31.5; HRMS (ESI): m/z calcd for $C_{17}H_{23}BO_4Na$ [M^++Na]: 325.1580; found: 325.1581.

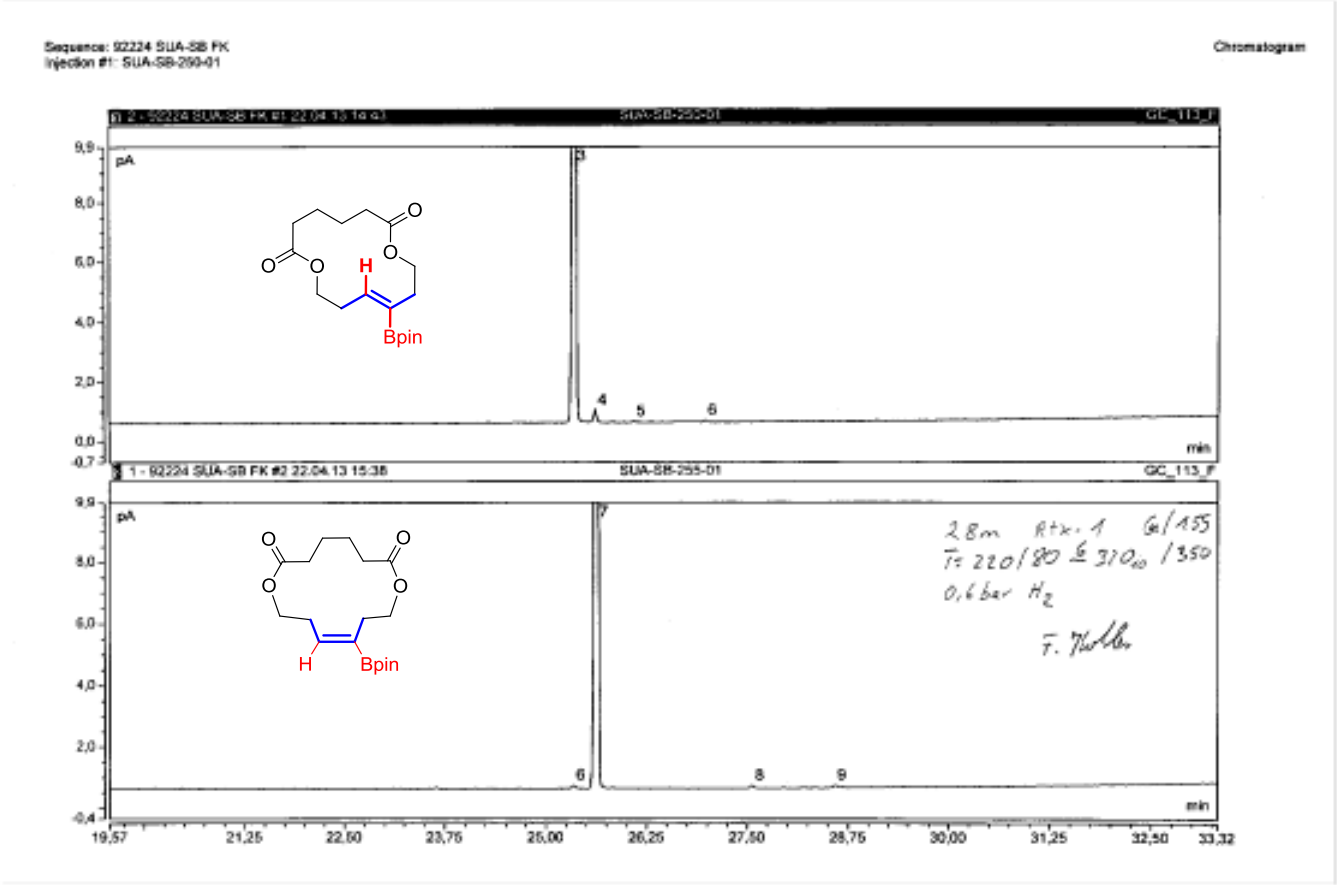


(*E*)-4,4,5,5-Tetramethyl-2-(1-(4-(trifluoromethyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane: Yellow oil (100 mg, 64%); reaction time = 80 min; spectroscopic data of the ***major isomer***:^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.50 (2H, m), 7.48-7.40 (2H, m), 6.94 (1H, s), 2.02 (3H, d, J = 1.5 Hz), 1.27 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.1, 139.1, 128.0 (2C), 124.4 (q), 83.3, 24.3, 23.2 (the C-atom directly attached to boron is broadened and could not be precisely localized); spectroscopic data of the ***minor isomer***: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.50 (2H, m), 7.47-7.39 (2H, m), 6.56 (1H, q, J = 7.0, 14.1 Hz), 2.11 (3H, d, J = 7.0 Hz), 1.34 (12H, s); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.9, 144.8, 127.1 (2C), 124.6 (q), 83.4, 24.5, 17.6; (the C-atom directly attached to boron is broadened and could not be precisely localized); ^{11}B NMR ($CDCl_3$, 128 MHz): δ 29.7; HRMS (ESI): m/z calcd for $C_{16}H_{20}BO_2F_3Na$ [M^+]: 312.1511; found: 312.1508.

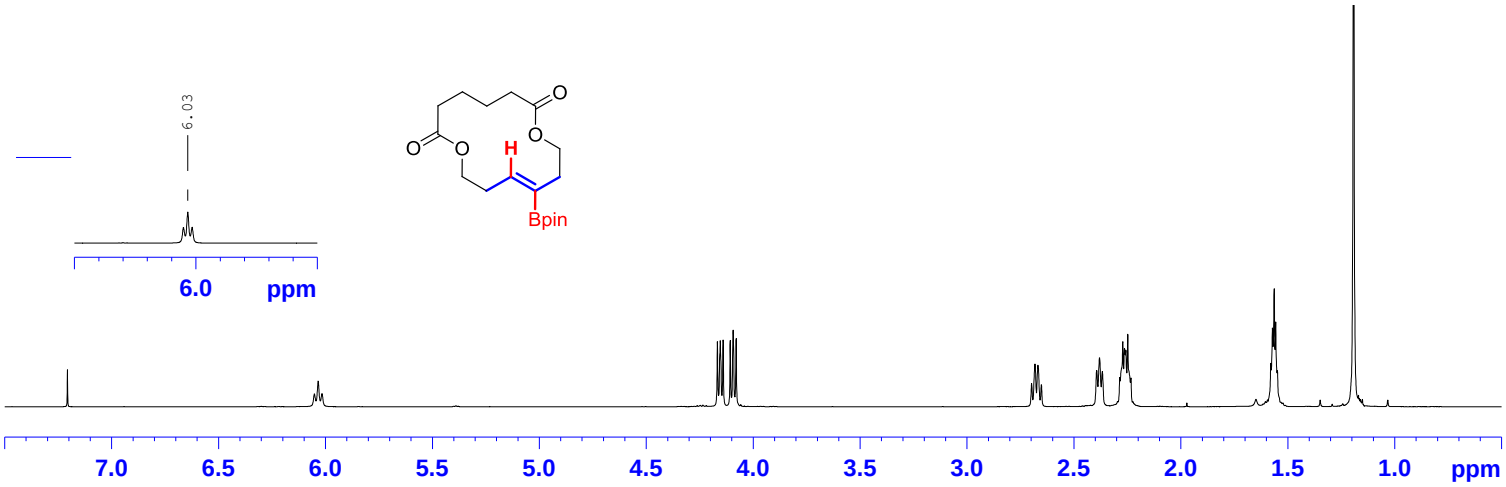
(*E*)-11-Methyl-1,8-dioxacyclotetradec-11-ene-2,7-dione: Iodomethane (10.6 µL, 0.170 mmol) and KOH (24 mg, 0.426 mmol) were added to a solution of $Pd(dba)_2$ (4.08 mg, 0.007 mmol, 5 mol%), $[HCy_3P]BF_4$ (7.84 mg, 0.021 mmol, 15 mol%) and alkenyl boronate *E*-**2** (50 mg, 0.142 mmol) in THF (1 mL) under argon. After stirring for 12 h at ambient temperature, the mixture was poured into diethyl ether (20 mL) before it was filtered through a pad of silica, which was carefully rinsed with diethyl ether (3 x 5 mL). Evaporation of the combined filtrates followed by flash chromatography (EtOAc/Hex, 4:1) gave the title compound as a colorless oil (18 mg, 53%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.20 (1H, t, J = 7.0, 14.1 Hz), 4.20 (2H, t, J = 5.4 Hz), 4.13 (2H, t, J = 5.5 Hz), 2.44-2.25 (8H, m), 1.64 (3H, s), 1.63 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.3, 173.1, 132.2, 123.7, 64.0, 60.9, 38.5, 35.0, 34.9, 27.2, 24.8, 24.6, 15.2; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}O_4Na$ [M^++Na]: 263.1251; found: 263.1253.

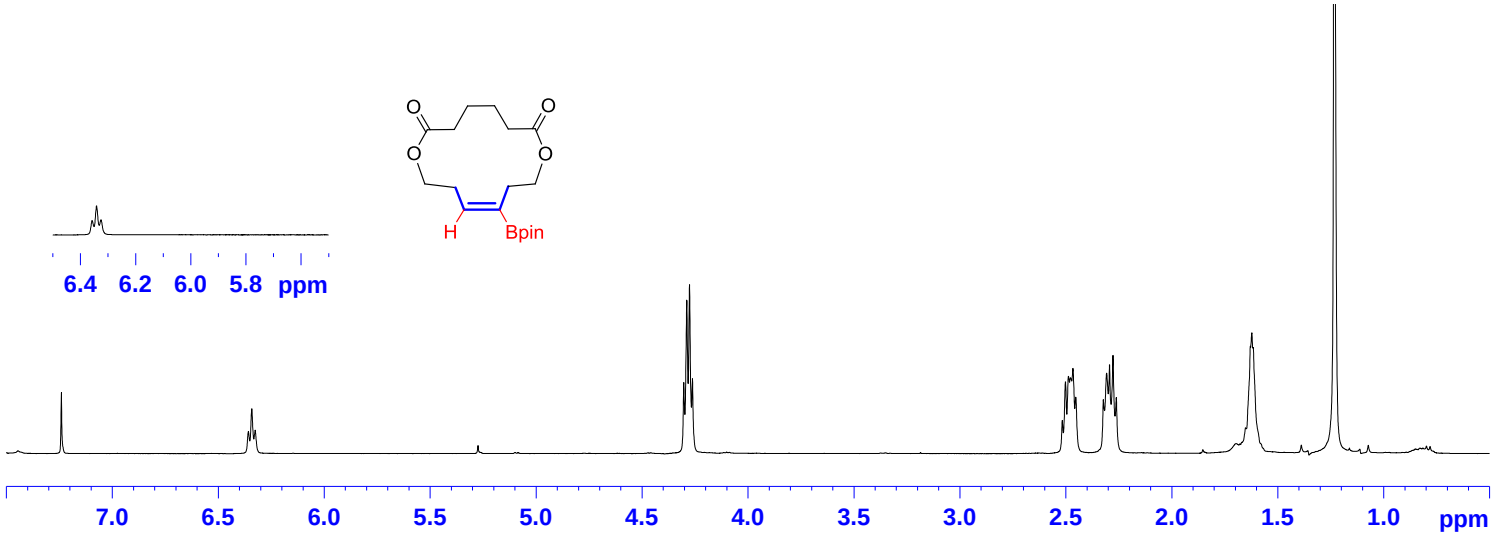
(*E*)-1,8-Dioxacyclotetradec-11-ene-2,7-dione: AgF (21.6 mg, 0.170 mmol) was added to a solution of *E*-**2** (30 mg, 0.08 mmol) in THF/MeOH/H_2O (10:9:1) (1 mL) under argon and the resulting mixture was stirred for 3 h in the dark. Insoluble materials were filtered off and carefully washed with Et_2O and EtOAc (3mL each), the combined filtrates were evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 4:1) to give the title compound as a colorless oil (15 mg, 78%; *E/Z* = 98:2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.47-5.43 (2H, m), 4.18-4.09 (4H, m), 2.44-2.24 (8H, m), 1.69-1.57 (4H, m); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 173.2, 129.2, 63.1, 35.0, 31.9, 24.7; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}O_4Na$ [M^++Na]: 249.1095; found: 249.1097.

COMPARISON of the GC CHROMATOGRAMS of the crude products formed by Ru-CATALYZED *trans*-HYDROBORATION (top) with the products formed by Cu-CATALYZED *cis* -HYDROBORATION (bottom)

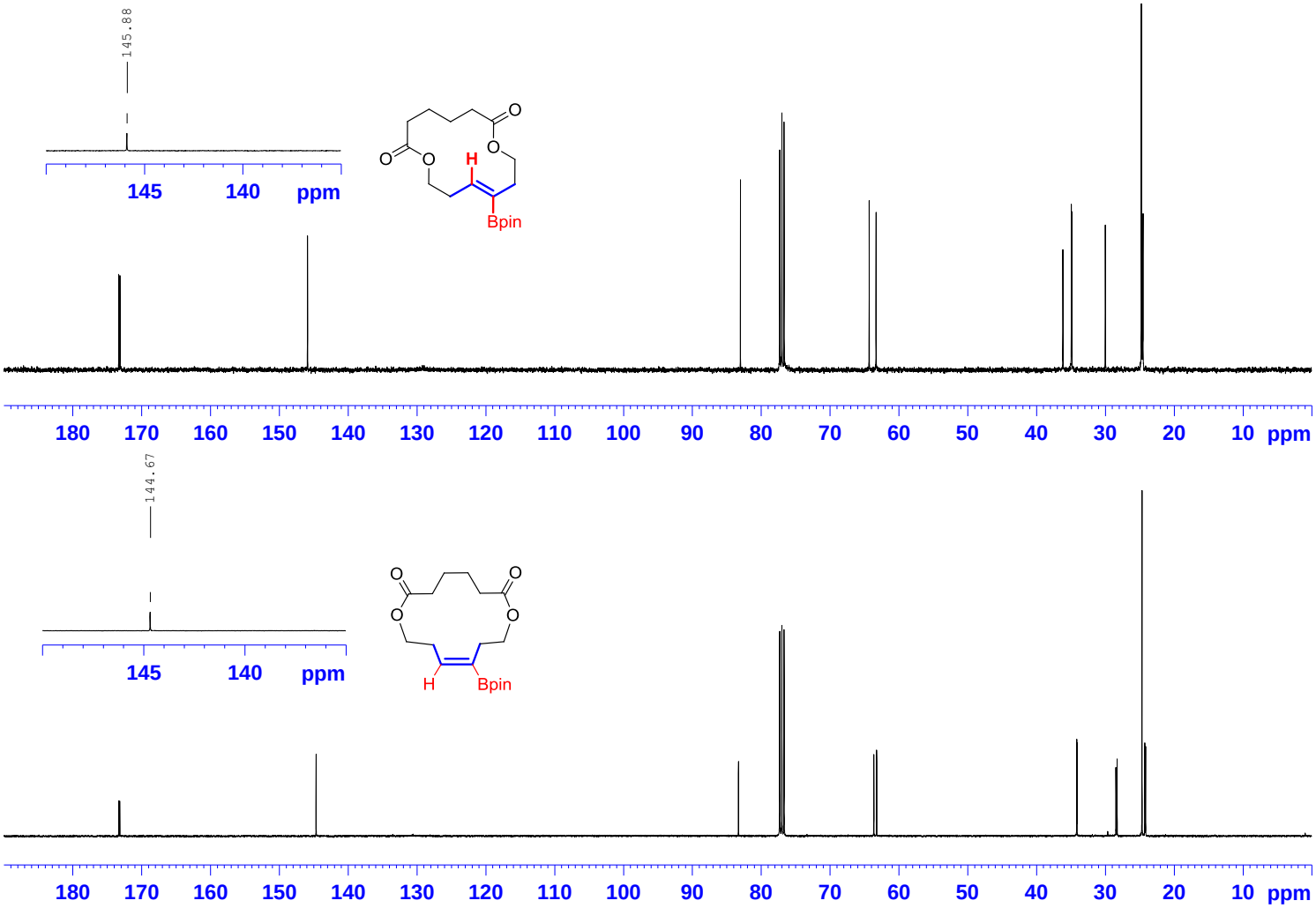


COMPARISON of the ^{1}H NMR SPECTRA of the product formed by Ru-CATALYZED *trans*-HYDROBORATION (top) with the product formed by Cu-CATALYZED *cis* -HYDROBORATION (bottom)

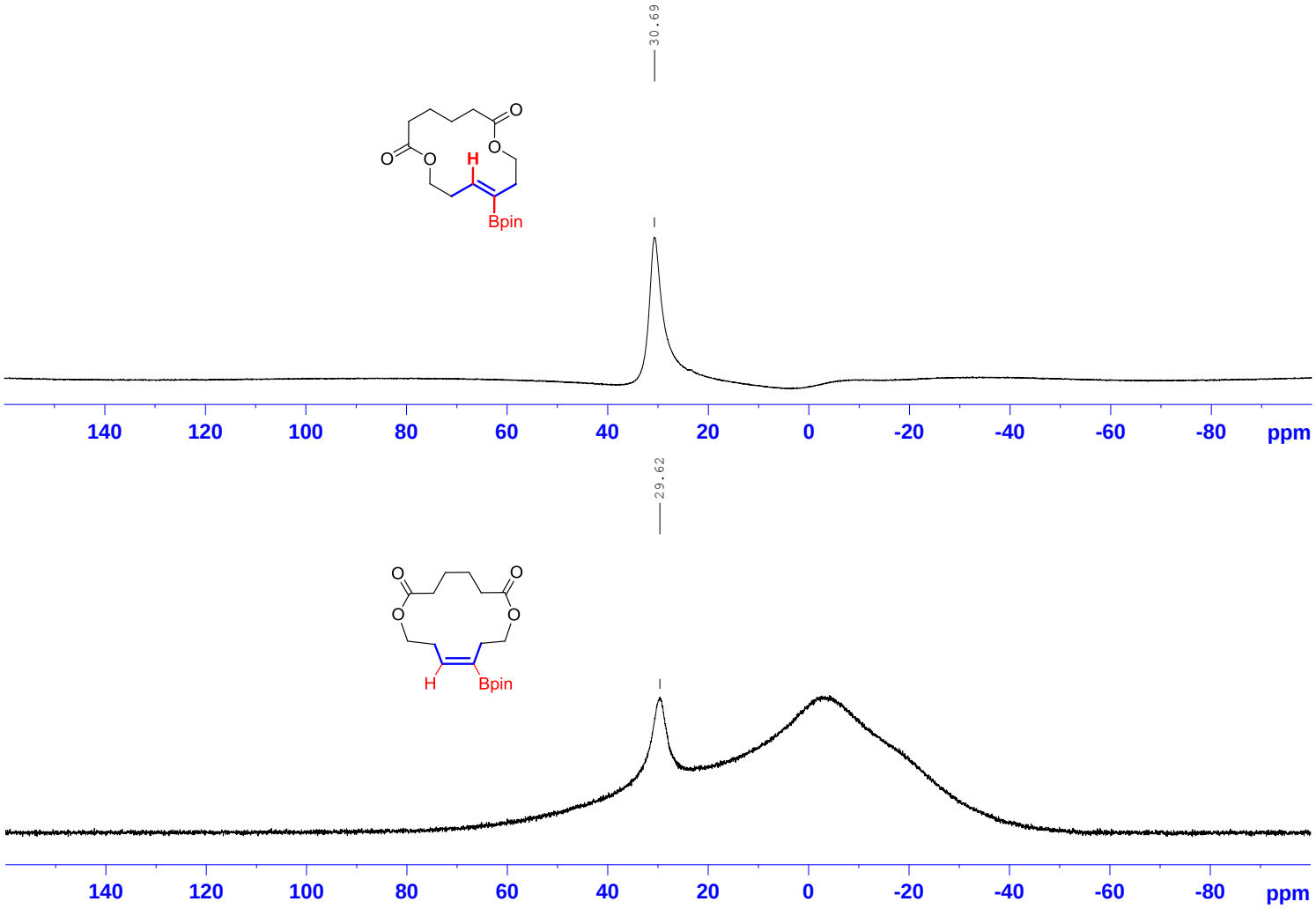




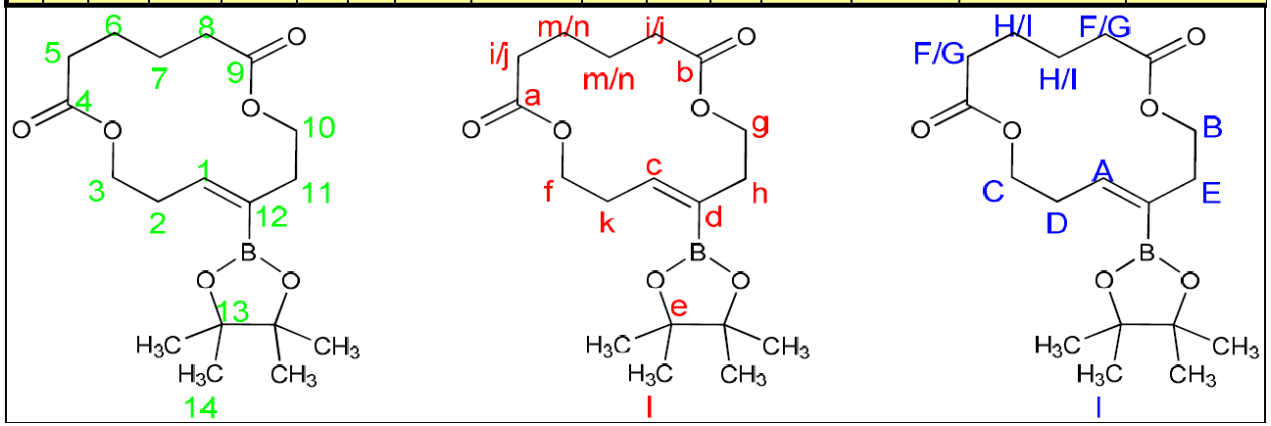
COMPARISON of the ^{13}C NMR SPECTRA of the product formed by Ru-CATALYZED *trans*-HYDROBORATION (top) with the products formed by Cu-CATALYZED *cis* -HYDROBORATION (bottom)



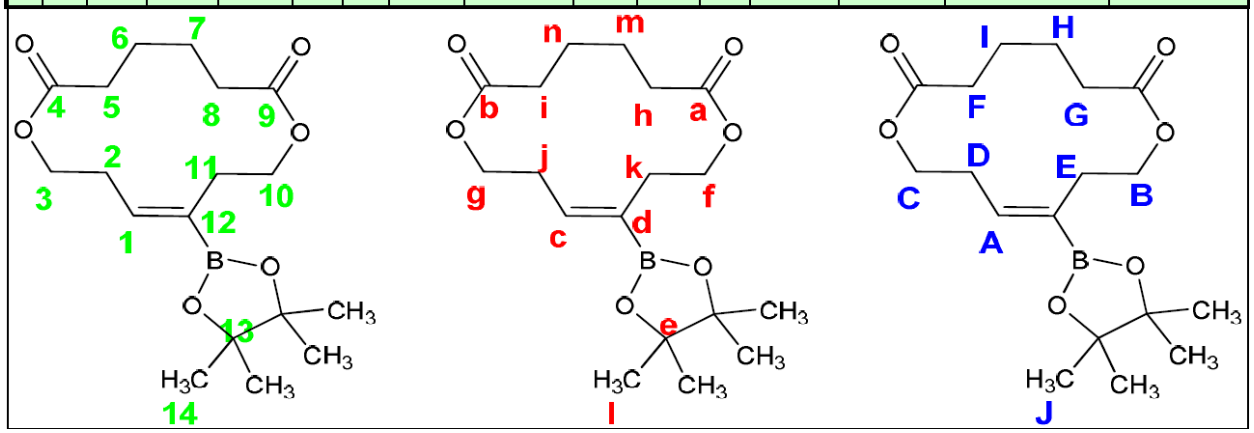
COMPARISON of the ^{11}B NMR SPECTRA of the product formed by Ru-CATALYZED *trans*-HYDROBORATION (top) with the products formed by Cu-CATALYZED *cis* -HYDROBORATION (bottom)

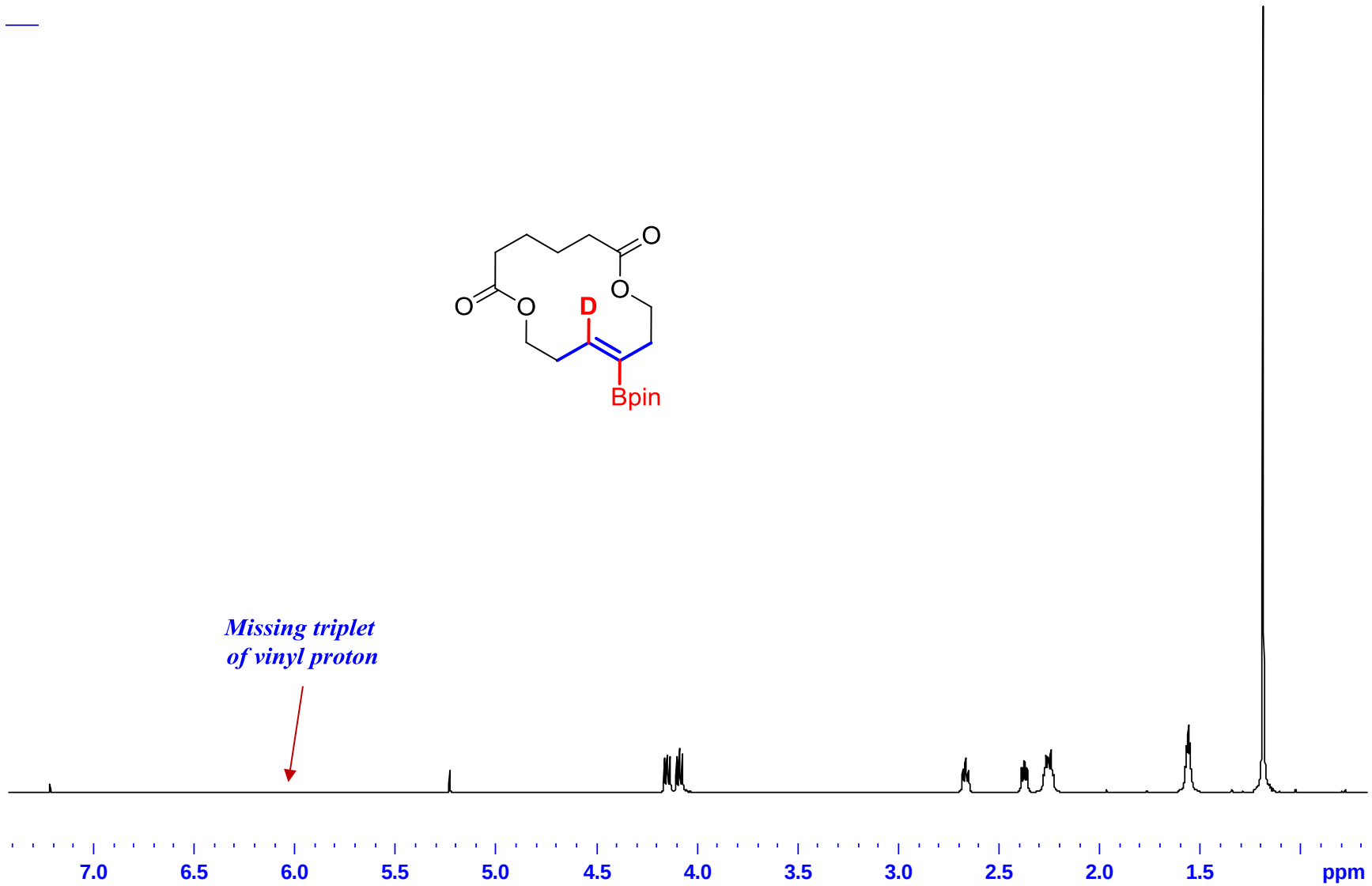


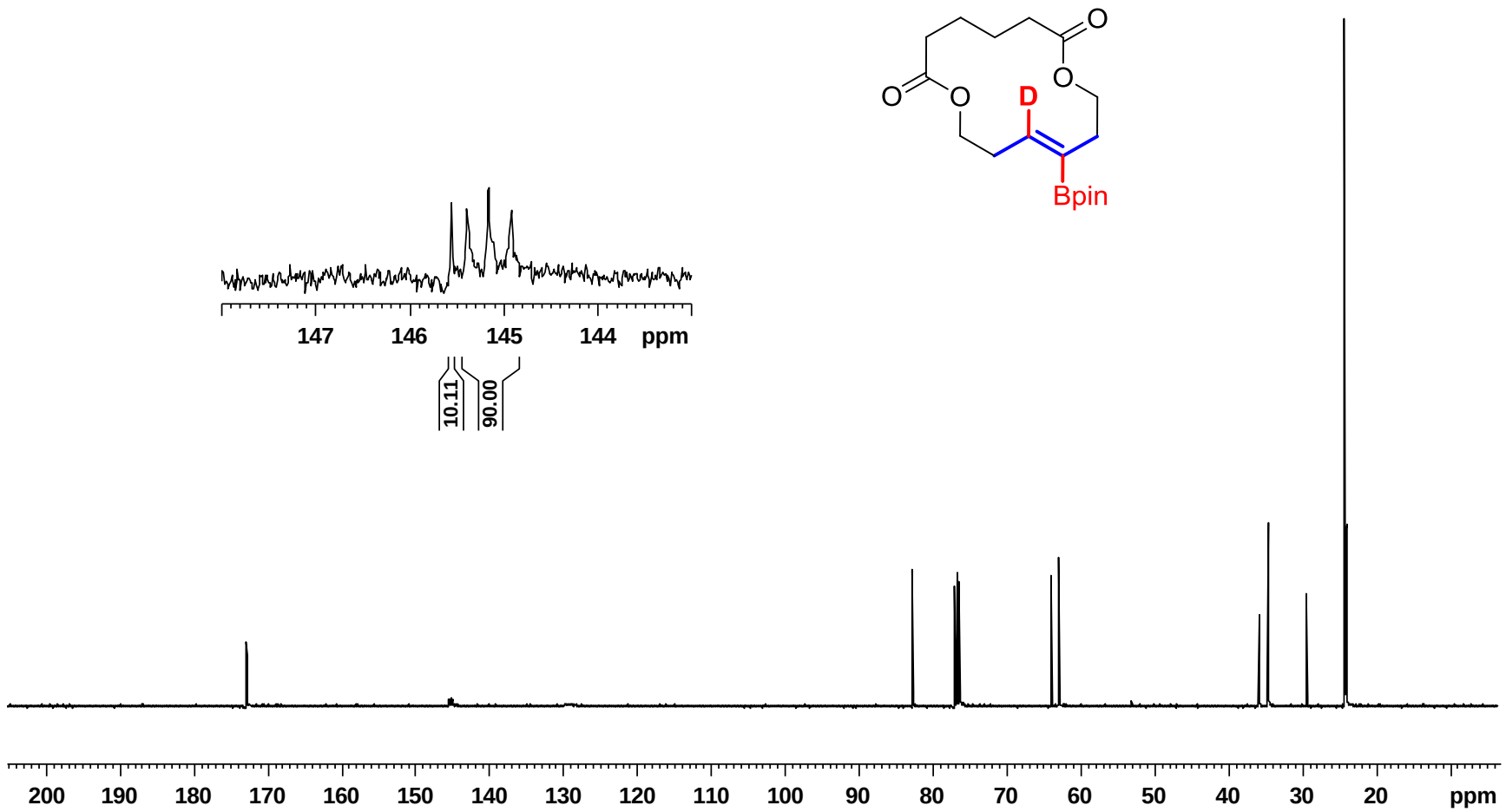
	mol	labe	assign	13C	mult	rel. i	HSQC	label	1H	int	mult	J	COSY	NOESY	HMBC
		a	4	172.33	s										
		b	9	172.16	s										
		c	1	144.93	d		<——>	A	6.026	1	t	7.1	A-D,(E)	A-C,D,**E!**,(H/I),(B)	A-f,h,k
		d	12	128.78	br										
		e	13	82.05	s										
		f	3	63.34	t		<——>	C	4.093	2	t	5.5	C-D	C-A,D,(J)	C-a,c,k
		g	10	62.34	t		<——>	B	4.154	2	t	5.4	B-E	B-E,(J)	B-b,h
		h	11	35.22	t		<——>	E	2.38	2	t	5.2	E-B,(A),(D)	E-**A!**,B,J	E-c,g,
		i	5/8	33.98	t		<——>	F	2.289	4(G)	m		F/G-HI	F/G-H/I	F/G-a/b,m,n
		j	5/8	33.90	t		<——>	G	2.26	4(H)	m		F/G-HI	F/G-H/I	F/G-a/b,m,n
		k	2	29.04	t		<——>	D	2.677	2	dt	7.1,5.5	D-C,(E)	D-A,C,**J!**	D-a,f
		l	14	23.81	q		<——>	J	1.193	12			--	J-**D!**,(C),(B),E	J-e
		m	6/7	23.62	t		<——>	H	1.565	4 (I)	m		H/I-F/G	H/I-F/G	H/I-a/b,i/j,l/H
		n	6/7	23.56	t		<——>	I	1.558	4(H)	m		H/I-F/G	H/I-F/G	H/I-a/b,i/j,l/H
		CDCl3		76.09				CHCl3	7.24						
Other nuclei				11B									Coupling to		
				29.70	~400Hz wide								A,E		

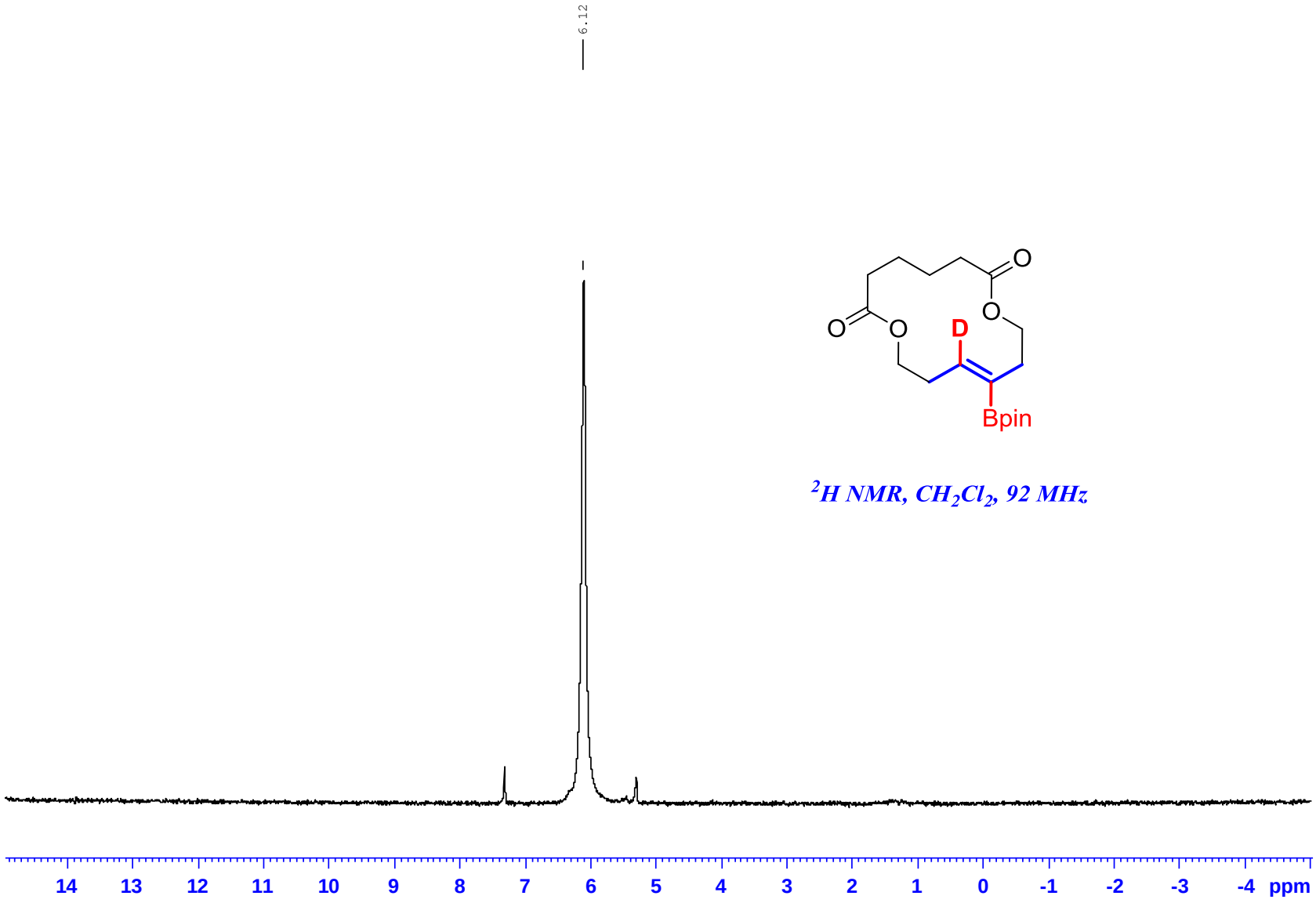


	mol	labe	assign	13C	mult	rel. i	HSQC	label	1H	int	mult	J	COSY	NOESY	HMBC
		a	9	173.32	s										
		b	4	173.16	s										
		c	1	144.67	d		<——>	A	6.342	1	t	6.5	A-D	A-B/C,D/E,**J!**,(H/I)	A-g,k
		d	12	130.50	br										
		e	13	83.31	s										
		f	10	63.65	t		<——>	B	4.289	2	t	5.4	B-E	B-E,(J),A	B-a,k
		g	3	63.24	t		<——>	C	4.278	2	t	5.1	C-D	C-D,A	C-b,c,j
		h	8	34.17	t		<——>	G	2.277	2	t	6.4	G-H		G-a
		i	5	34.12	t		<——>	F	2.3	2	t	6.2	F-I,G	F/G-H/I	F-b
		j	2	28.48	t		<——>	D	2.496	2	td	6.5,5.1	D-A,C	D/E-A,B/C	D-g
		k	11	28.31	t		<——>	E	2.466	2	t	5.4	E-B	D/E-A,B/C	E-f
		l	14	24.69	q		<——>	J	1.233	12				J-**A!**,B/C,H/I	
		m	7	24.28	t		<——>	H	1.617	2	m		H-G	H/I-F/G	H-a
		n	6	24.17	t		<——>	I	1.623	2	m		I-F	H/I-F/G	I-b
		CDCl3		77.00				CHCl3	7.24						
Other nuclei				11B									Coupling to		
				29.70	~400Hz wide								A,E		

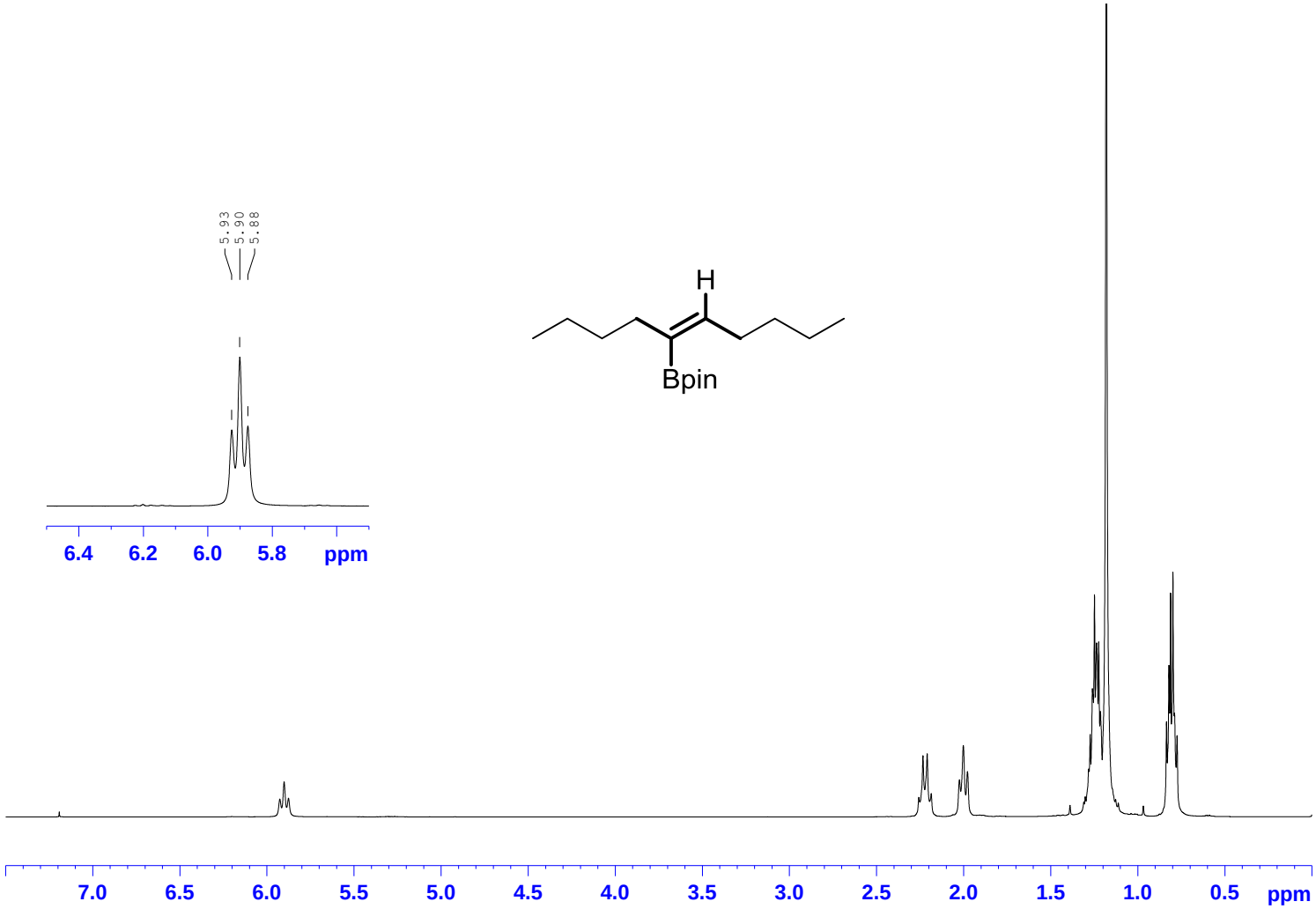


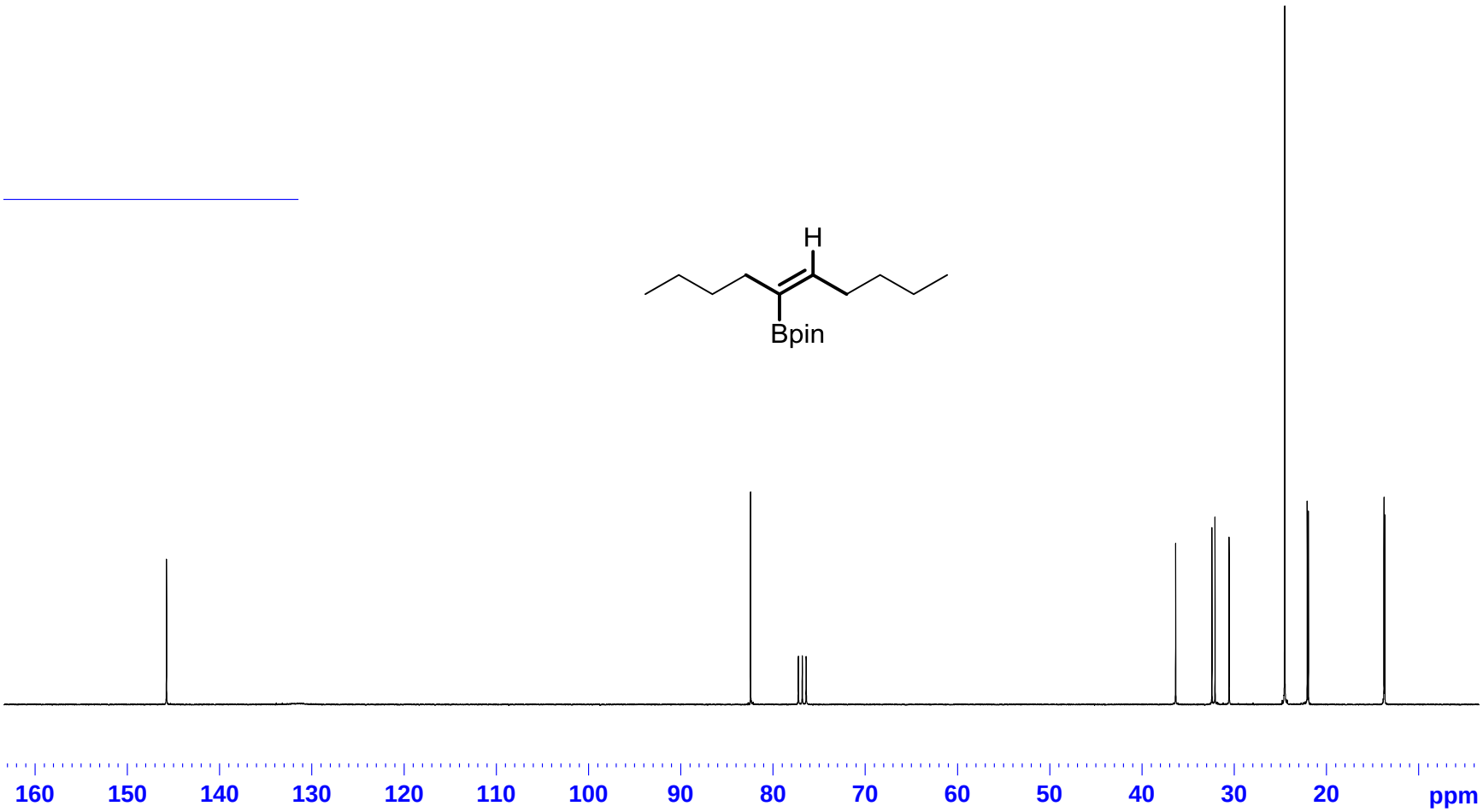

O
O
O
O
D
Bpin
Missing triplet
of vinyl proton
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm

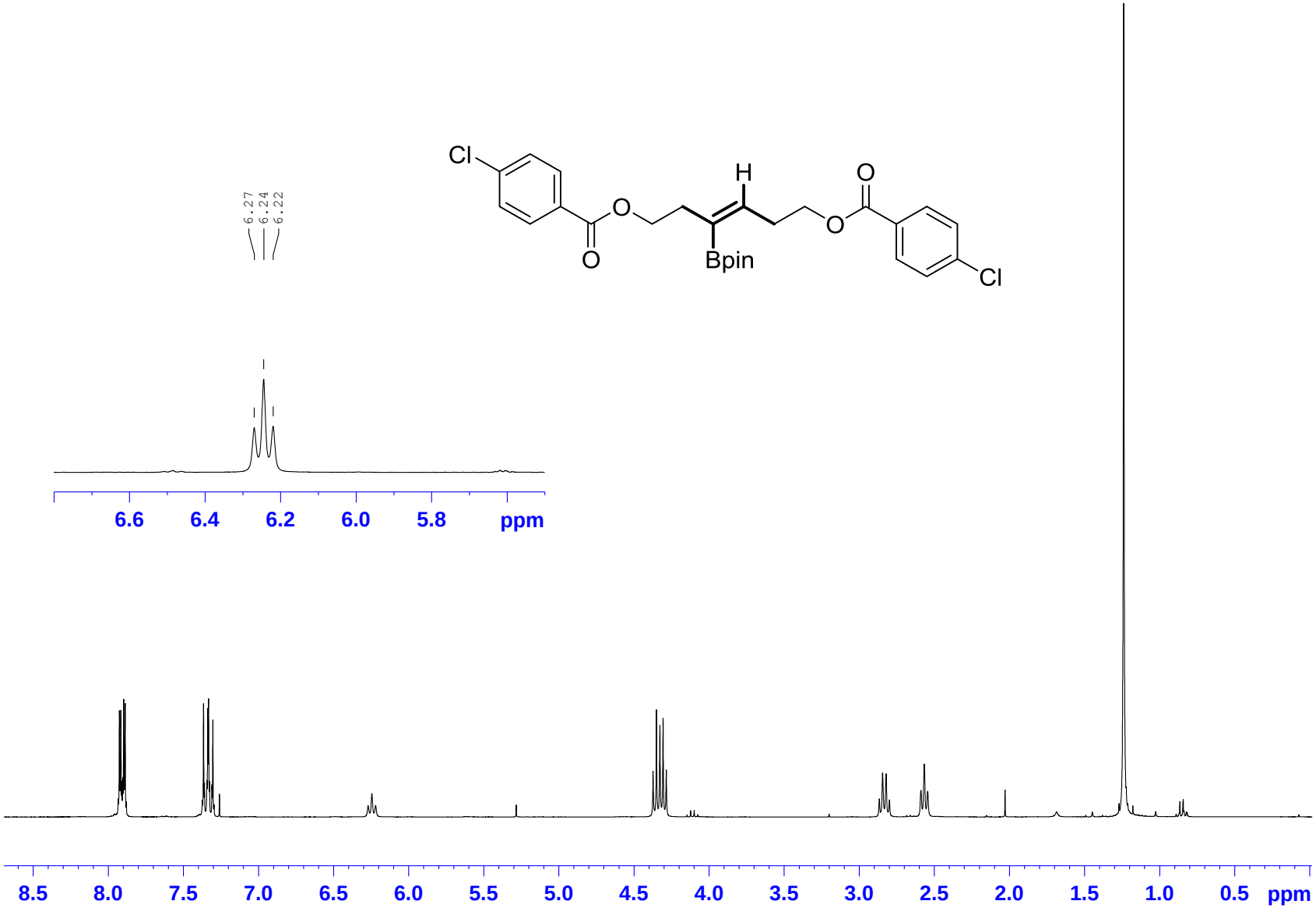

O
O
O
O
D
Bpin
147
146
145
144
ppm
10.11
90.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

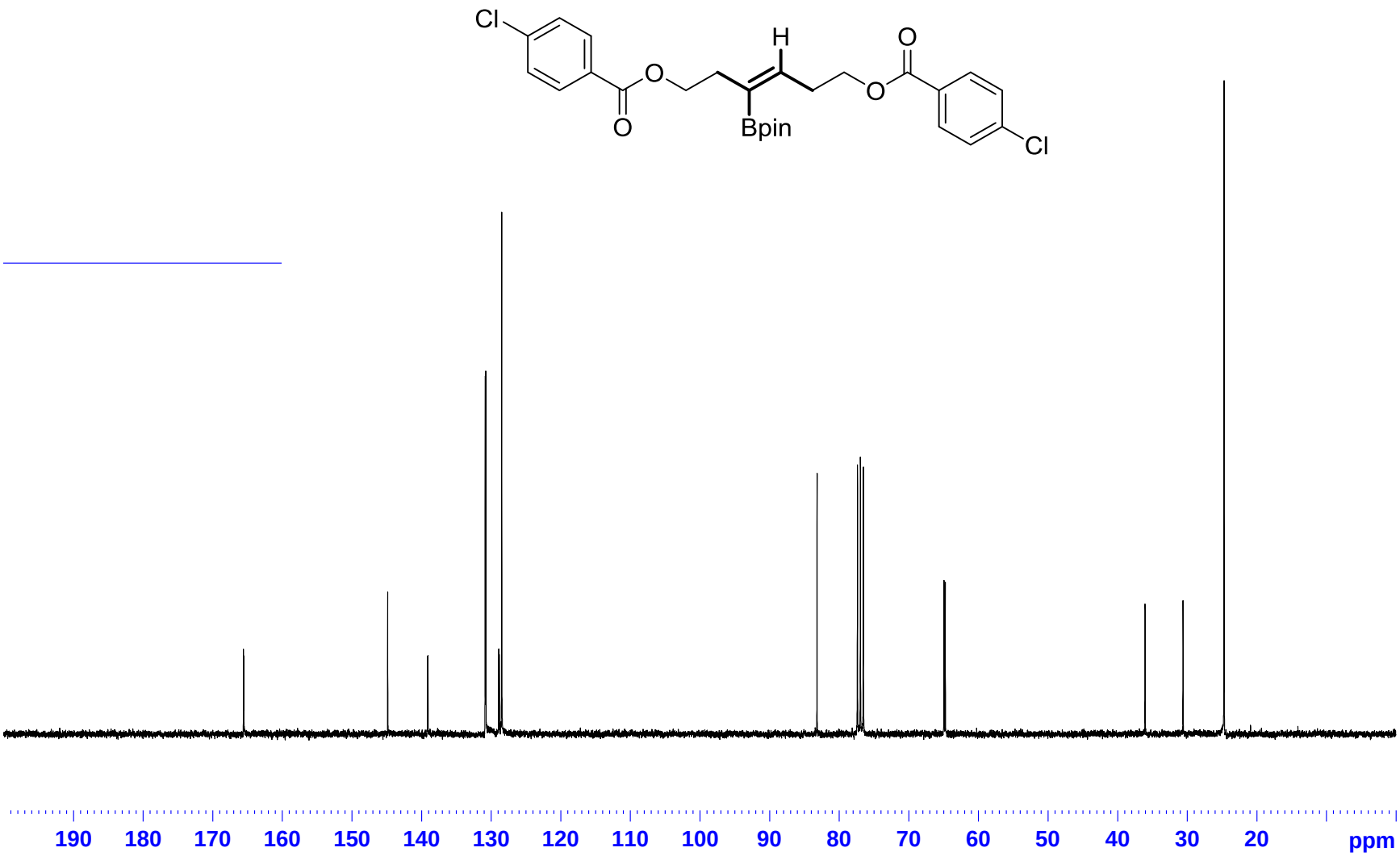


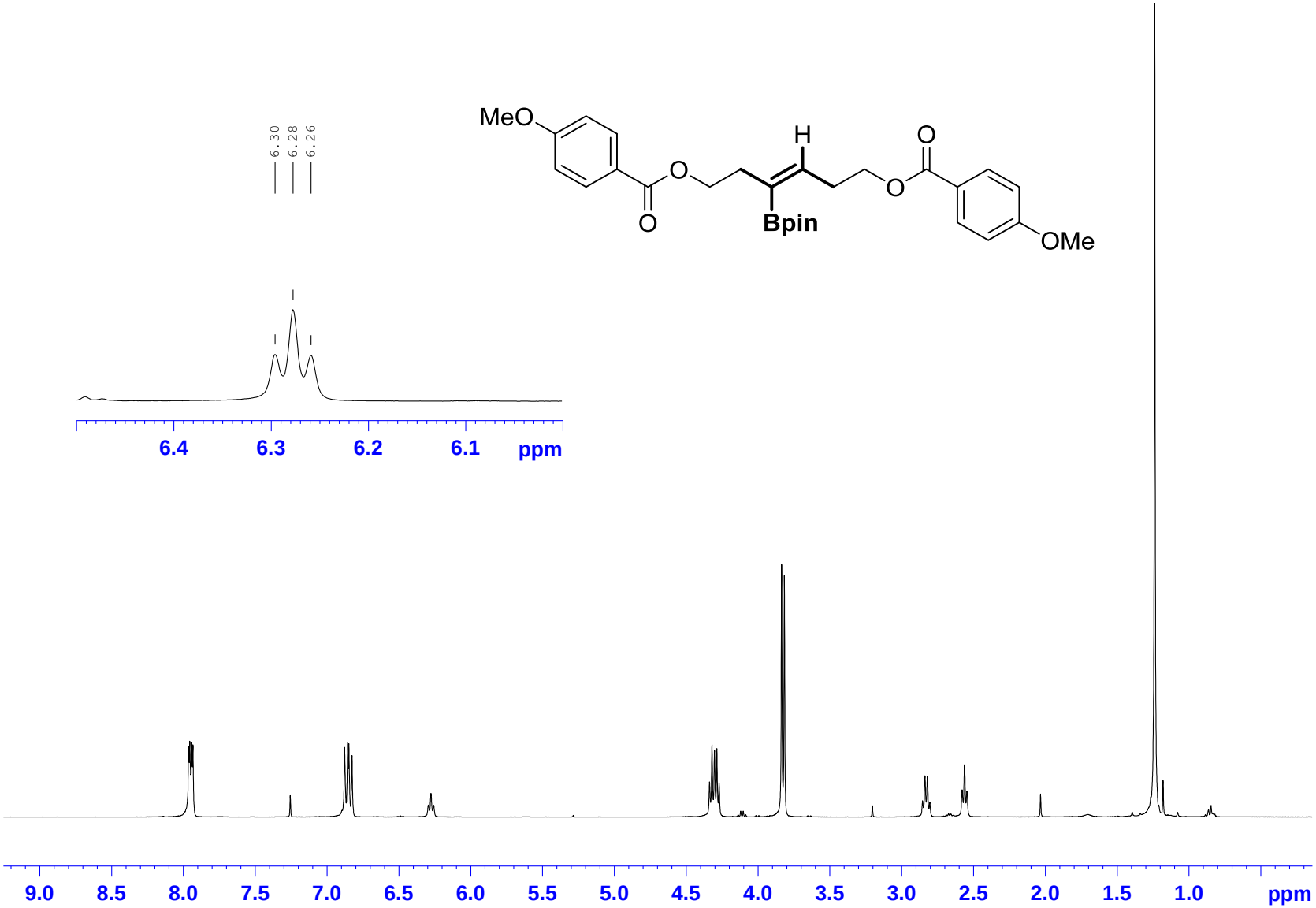
^{2}H NMR, CH_2Cl_2, 92 MHz

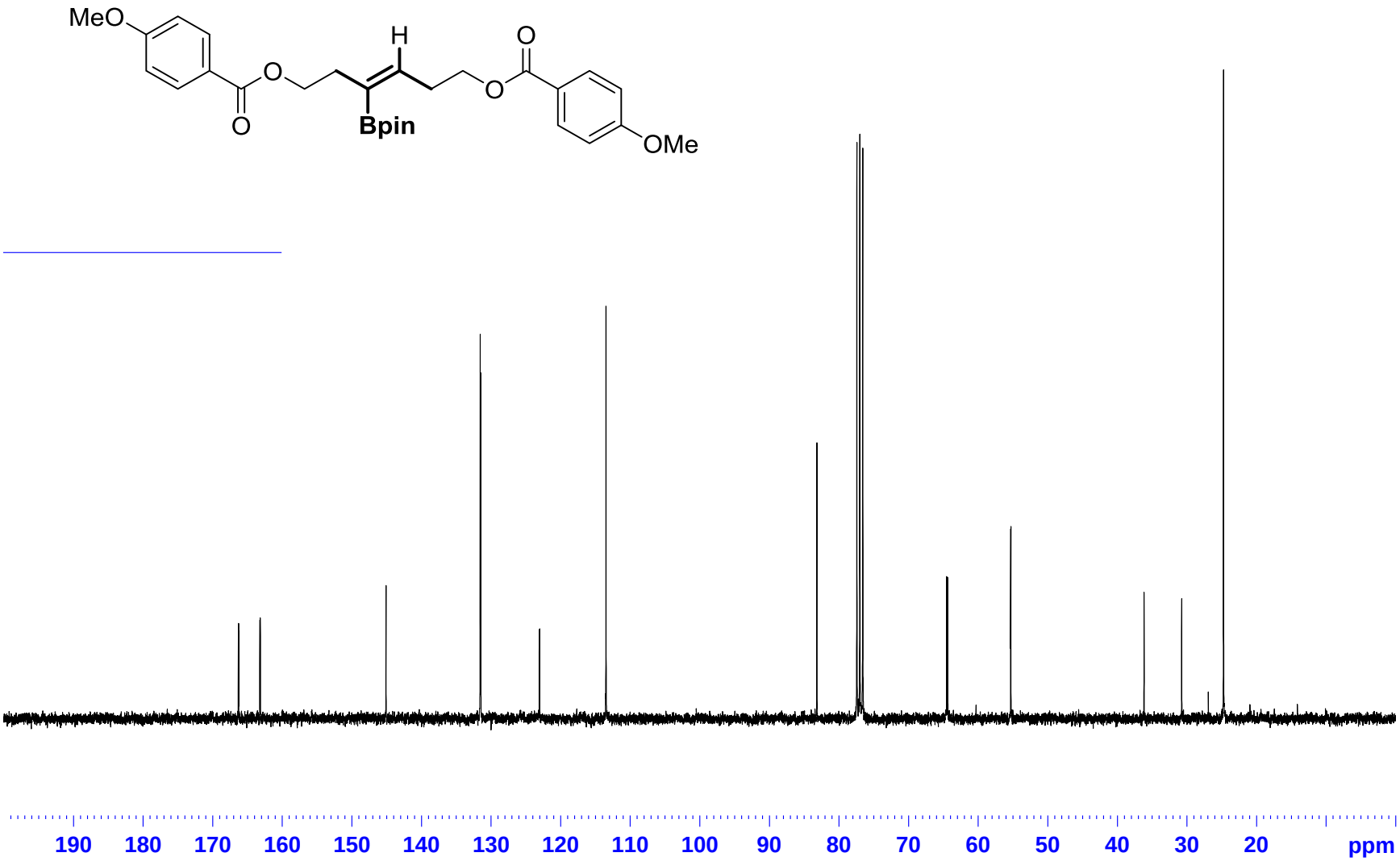

5.93
5.90
5.88
6.4
6.2
6.0
5.8
ppm
H
Bpin
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

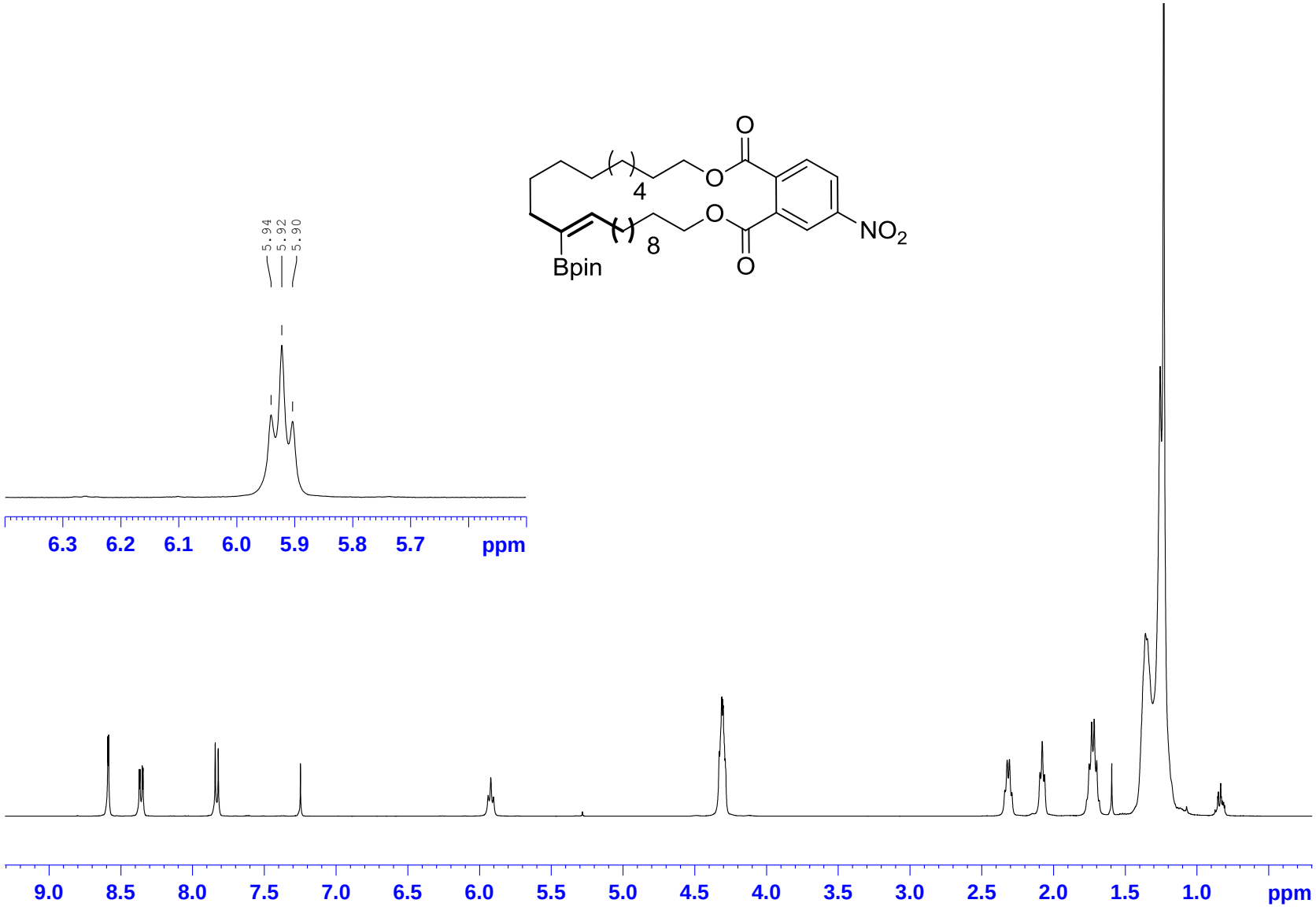

H
Bpin
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

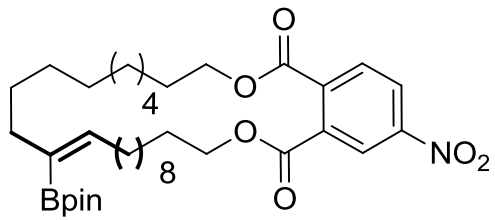

6.27
6.24
6.22
Cl
O
O
H
Bpin
O
O
Cl
6.6
6.4
6.2
6.0
5.8
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

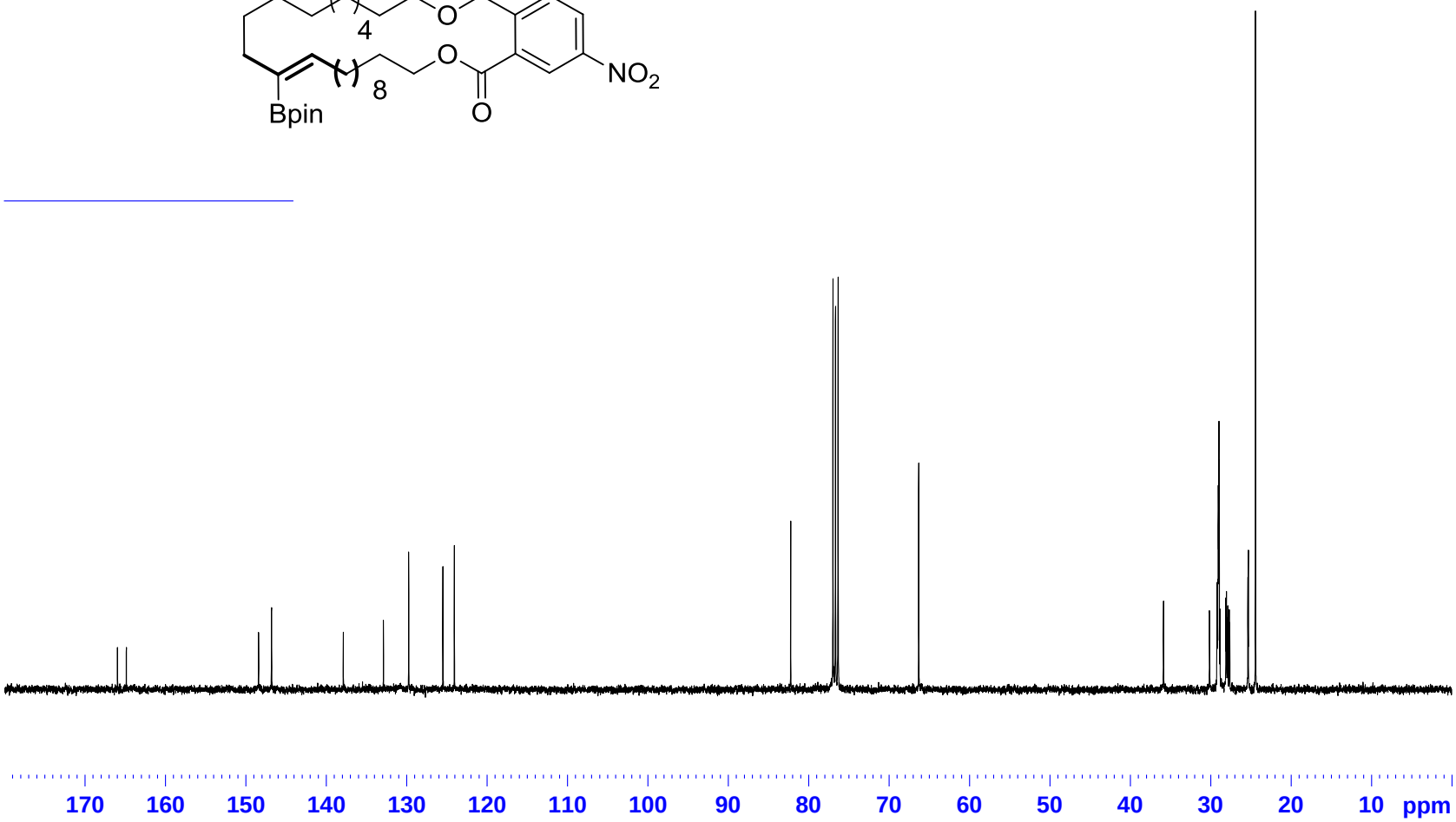

Cl
O
O
H
Bpin
O
O
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

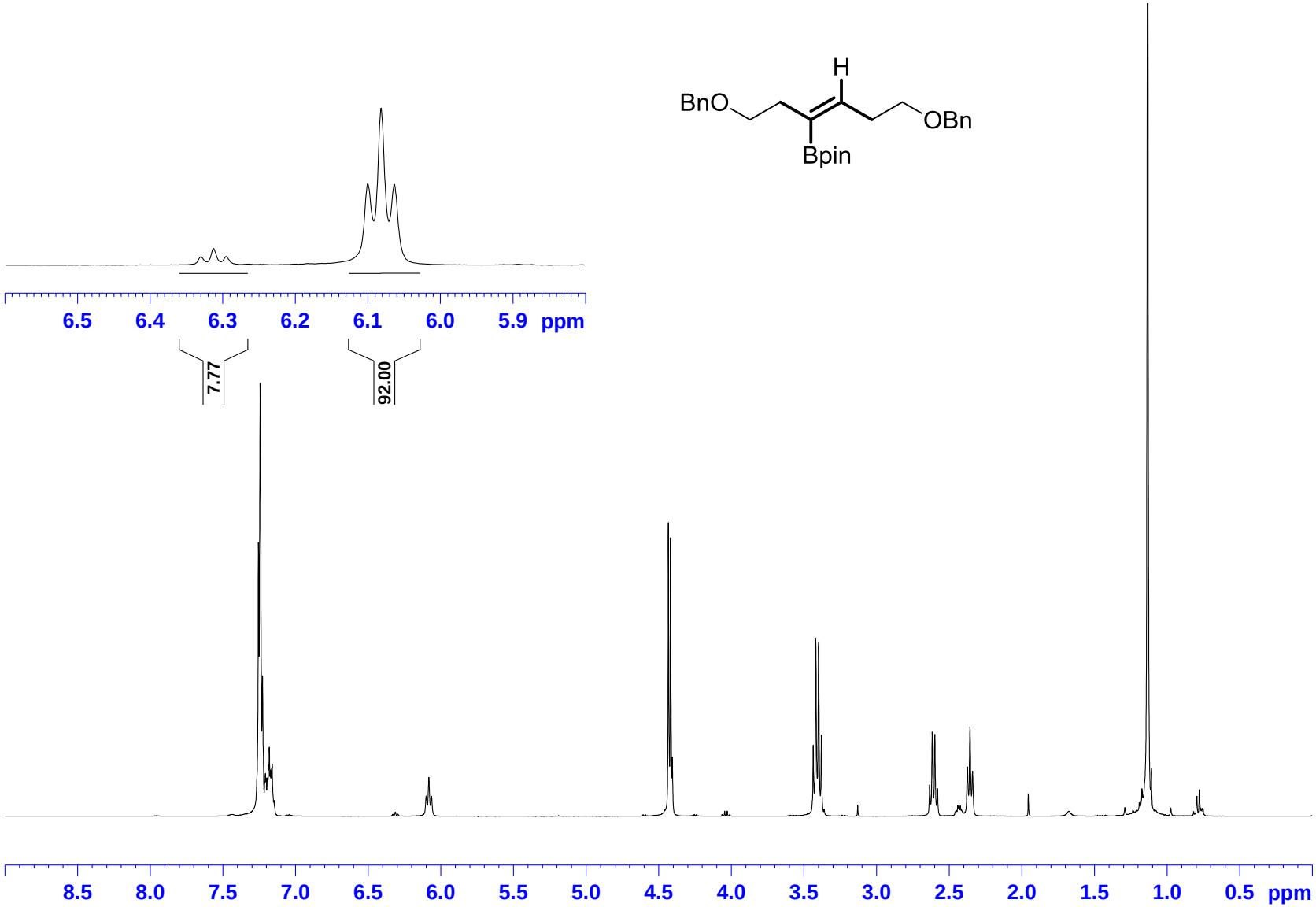

6.30
6.28
6.26
MeO
H
O
O
O
O
Bpin
OMe
6.4
6.3
6.2
6.1
ppm
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

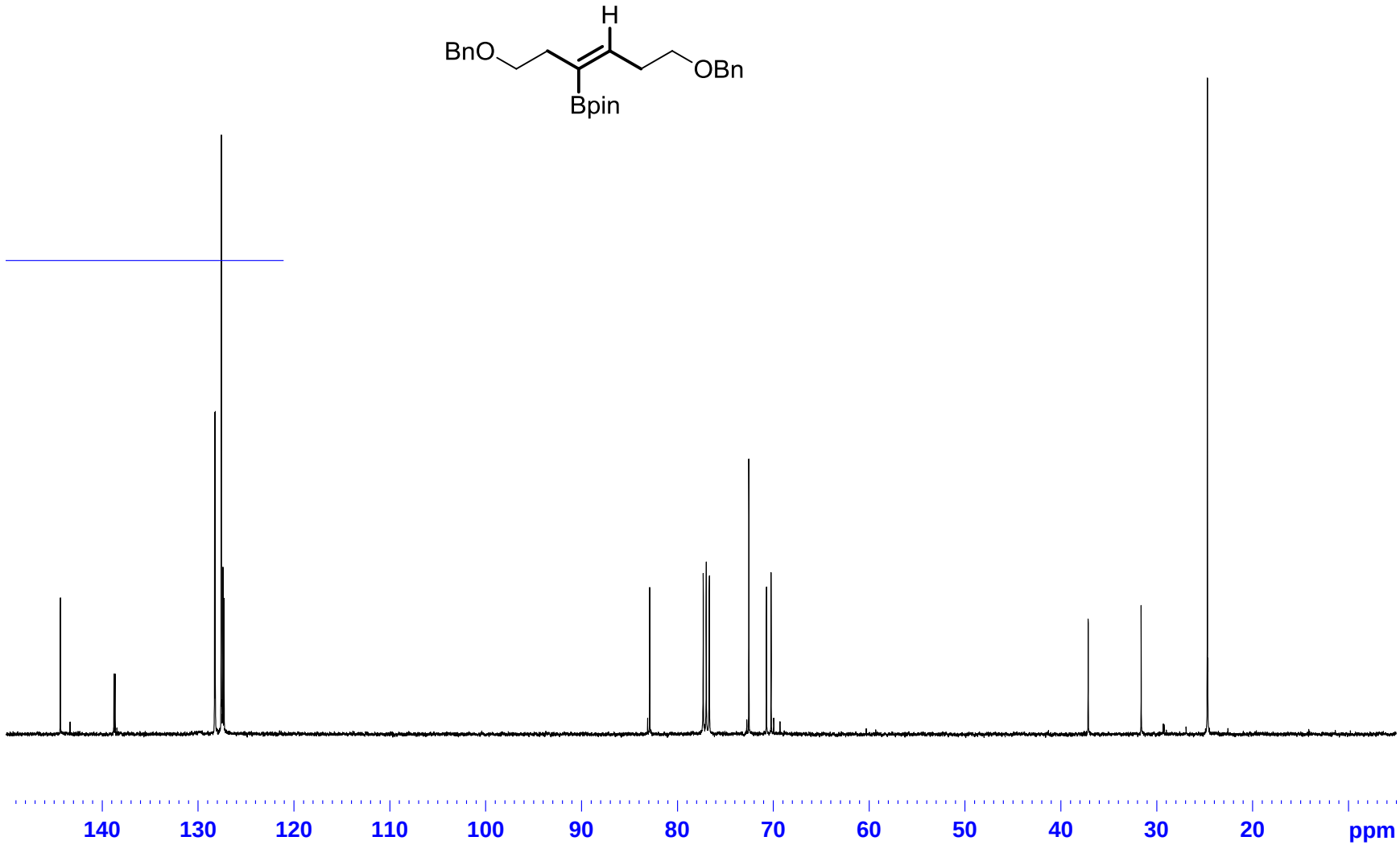

MeO
O
O
H
Bpin
O
O
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

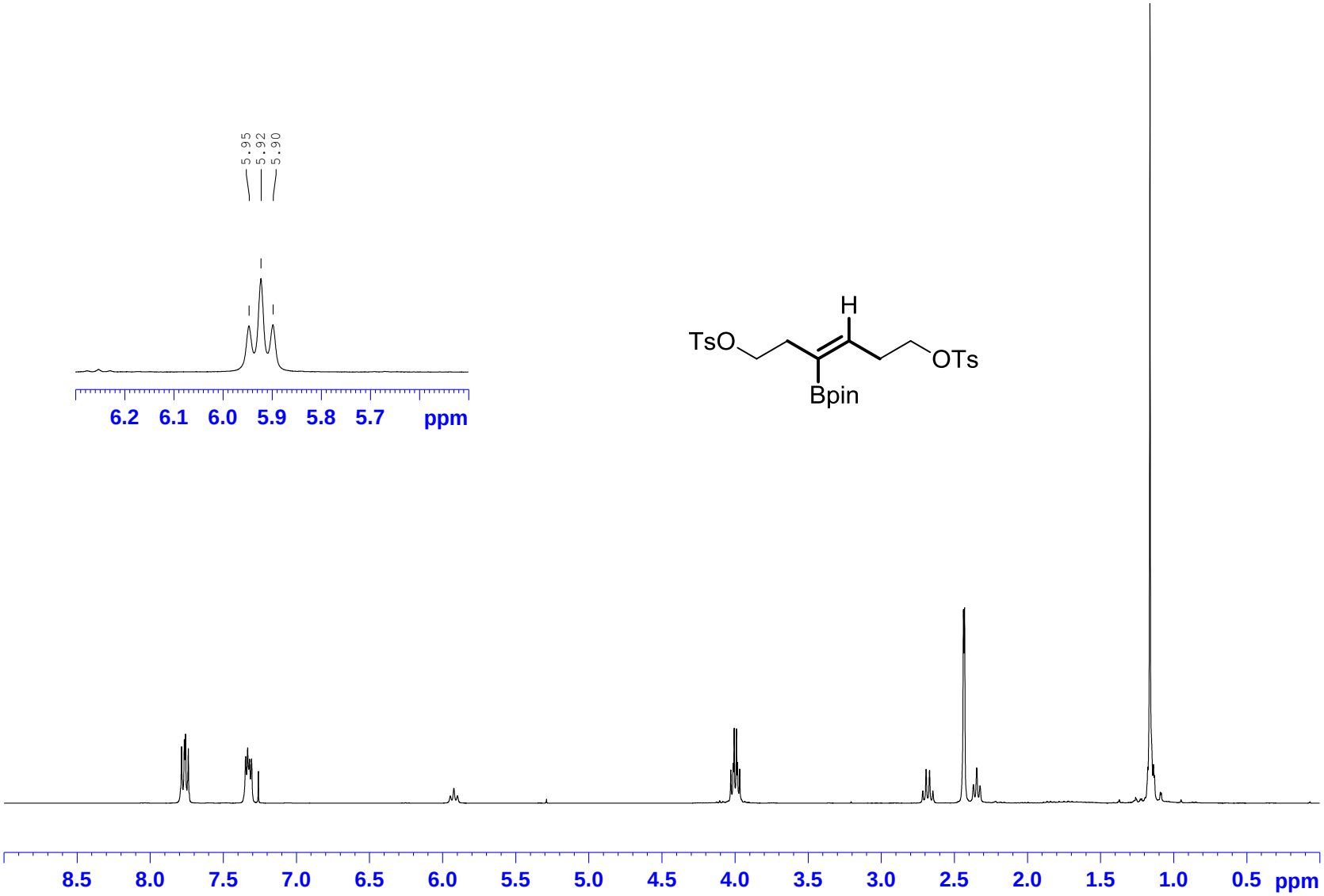

5.94
5.92
5.90
6.3
6.2
6.1
6.0
5.9
5.8
5.7
ppm
O
O
O
O
4
8
Bpin
NO2
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

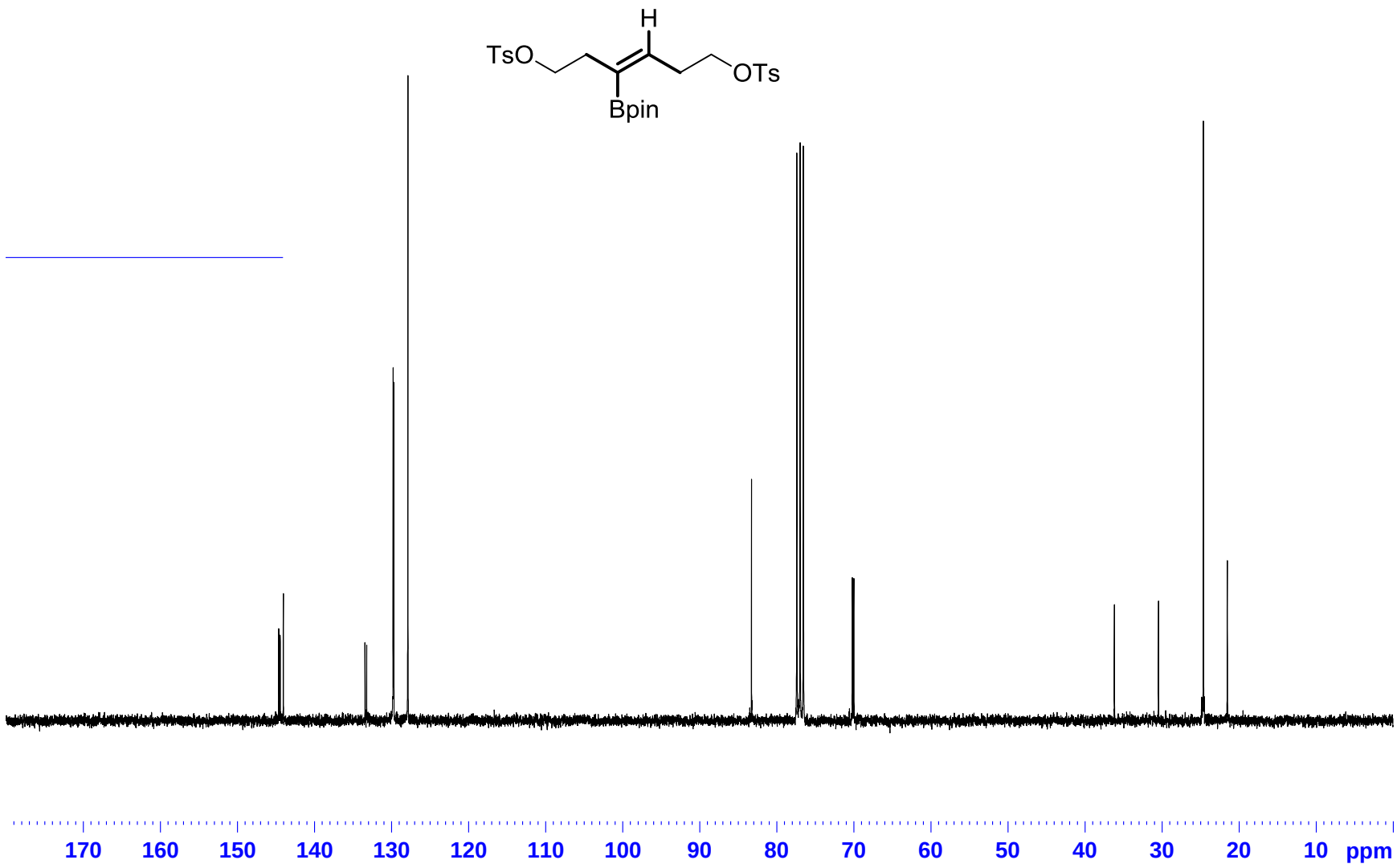

O
O
O
O
4
8
Bpin
NO2

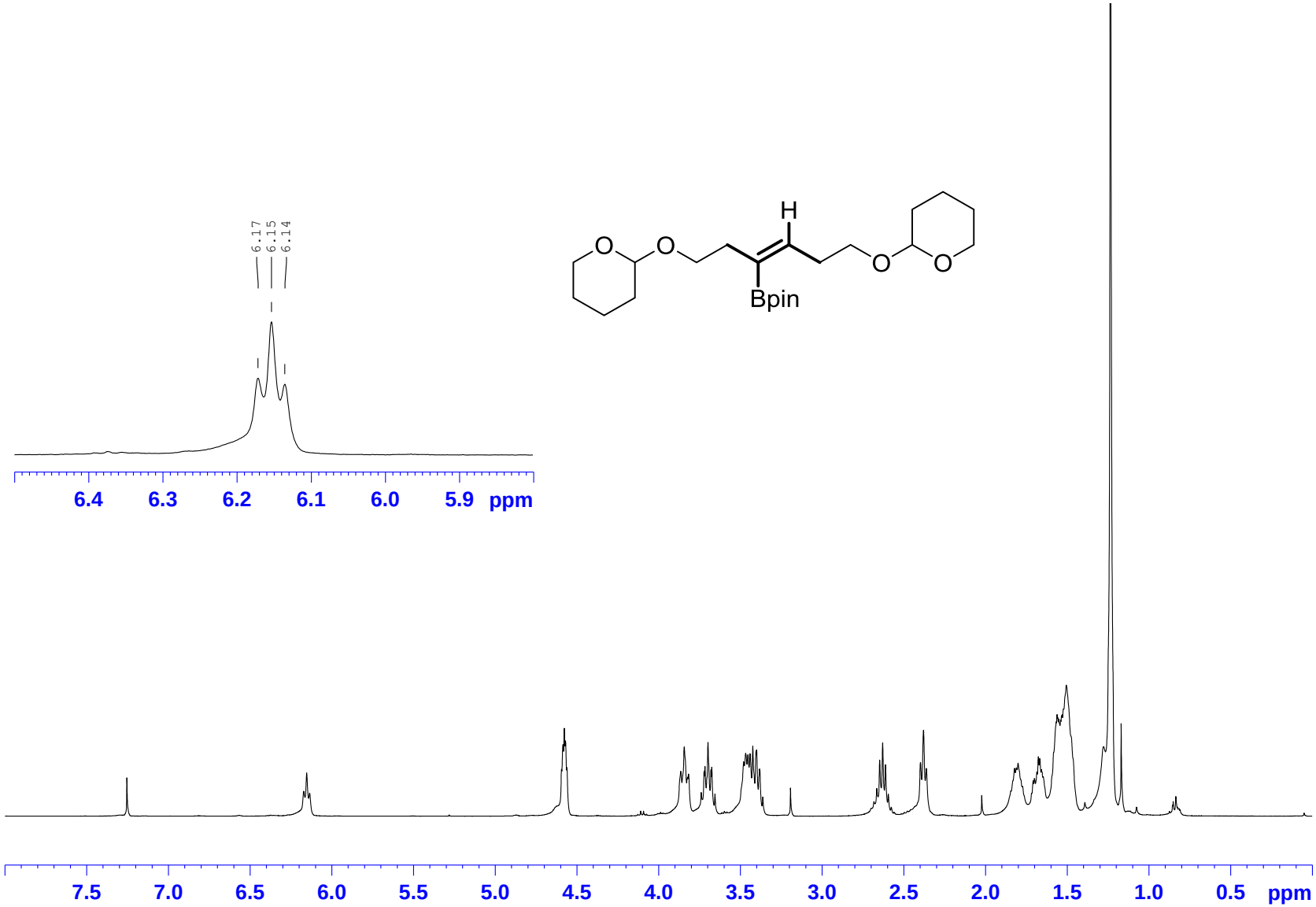

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

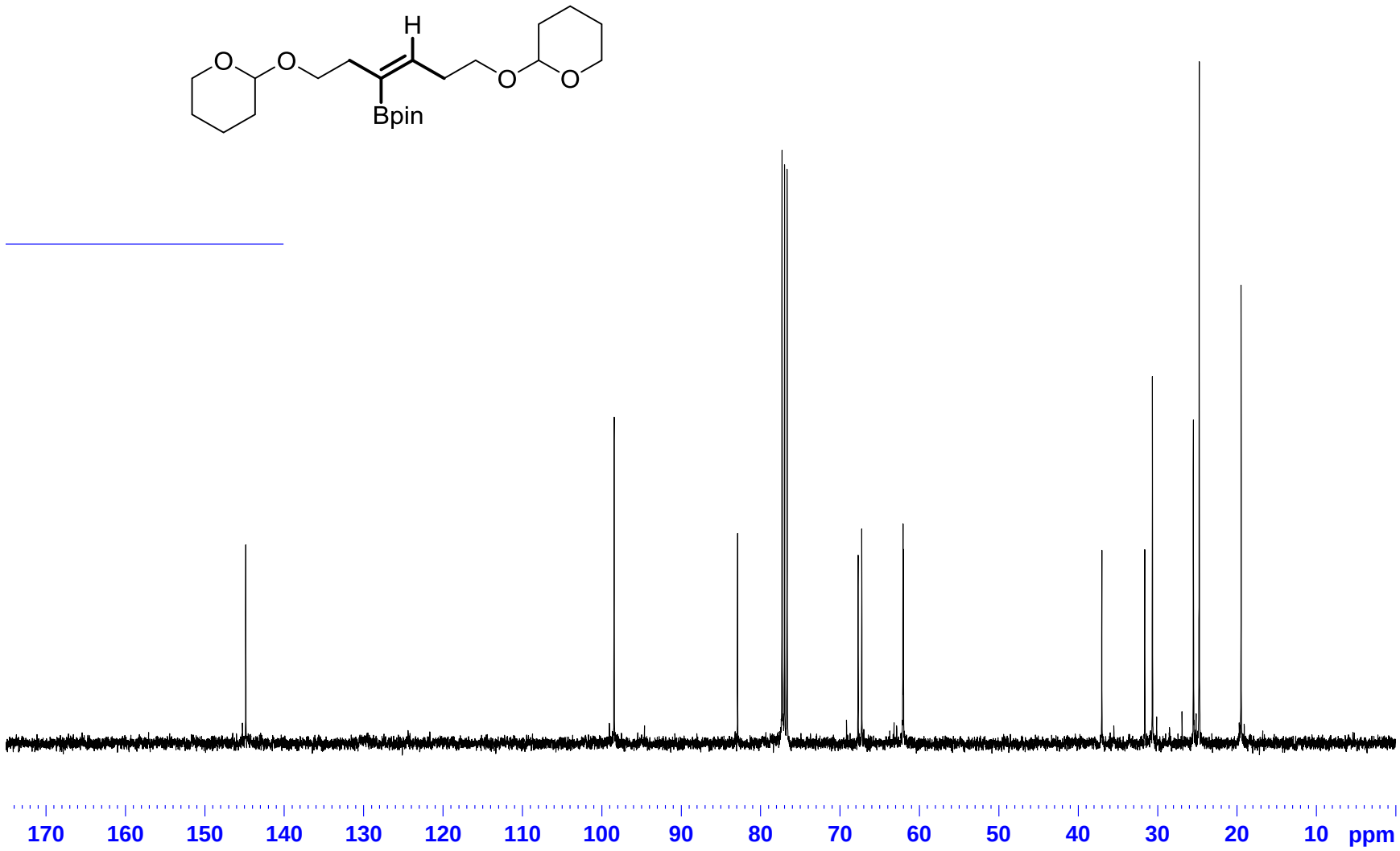

H
BnO
OBn
Bpin
6.5
6.4
6.3
6.2
6.1
6.0
5.9
ppm
7.77
92.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

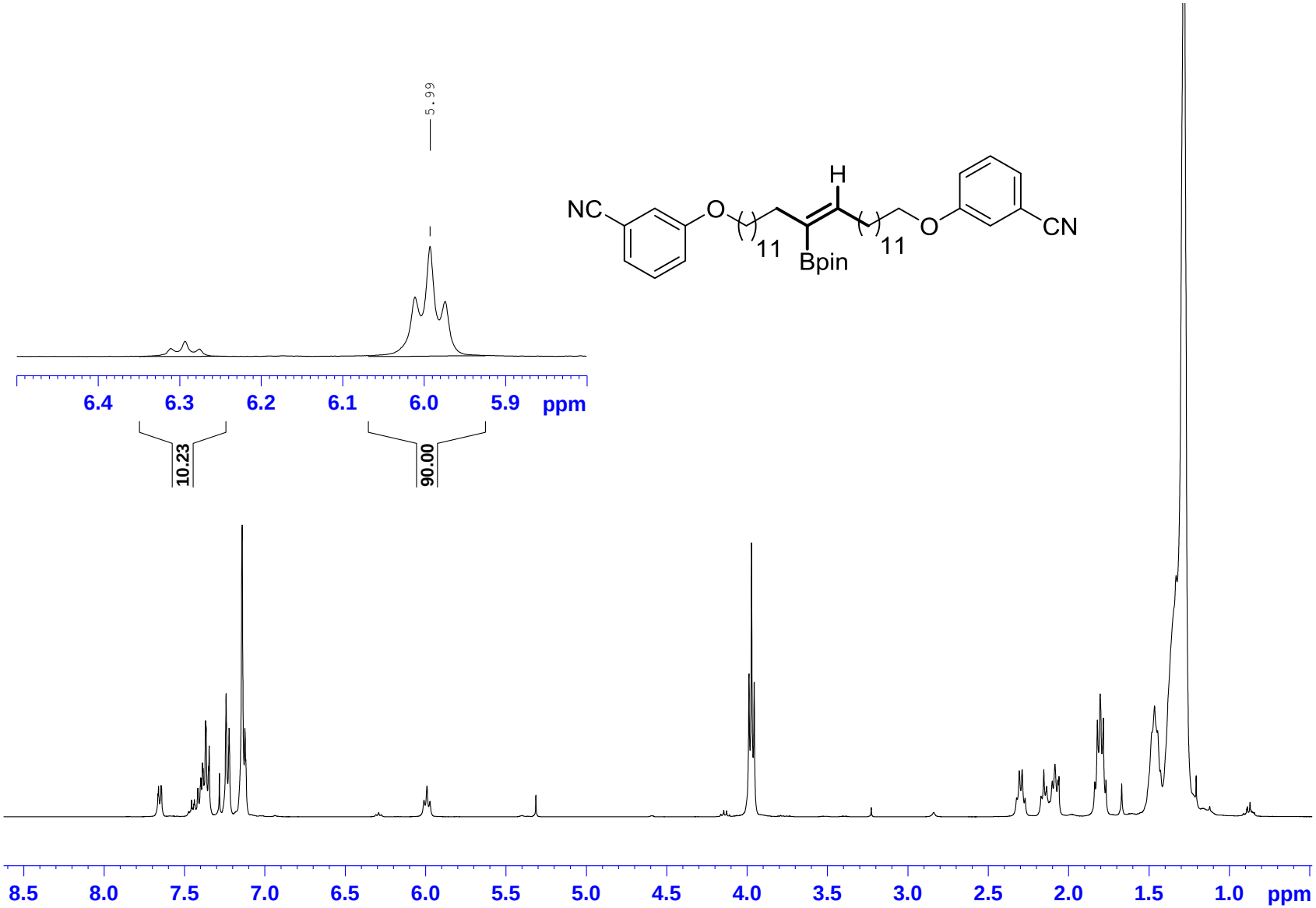

H
BnO
OBn
Bpin
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

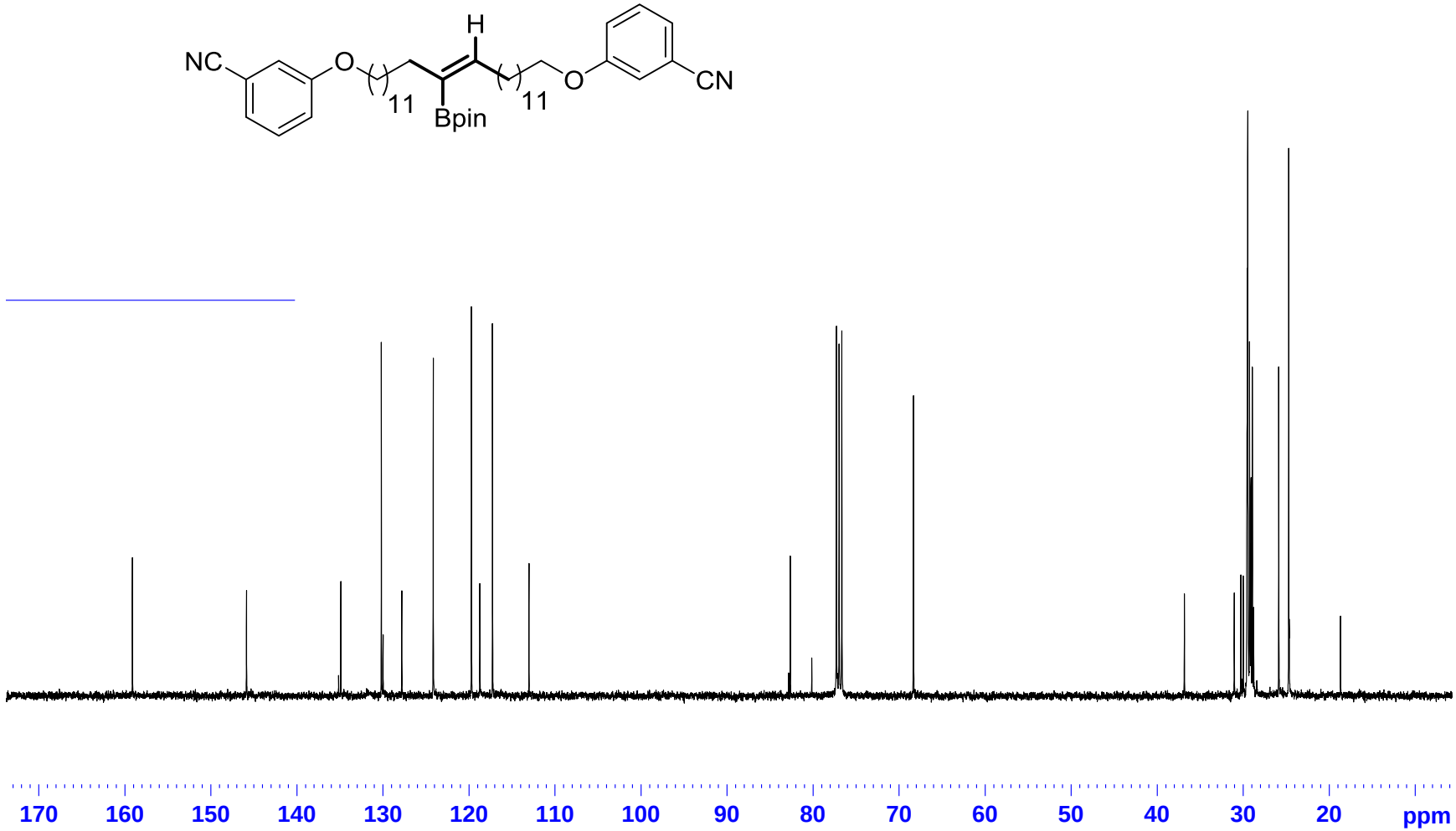

5.95
5.92
5.90
6.2 6.1 6.0 5.9 5.8 5.7 ppm
H
TsO
OTs
Bpin
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

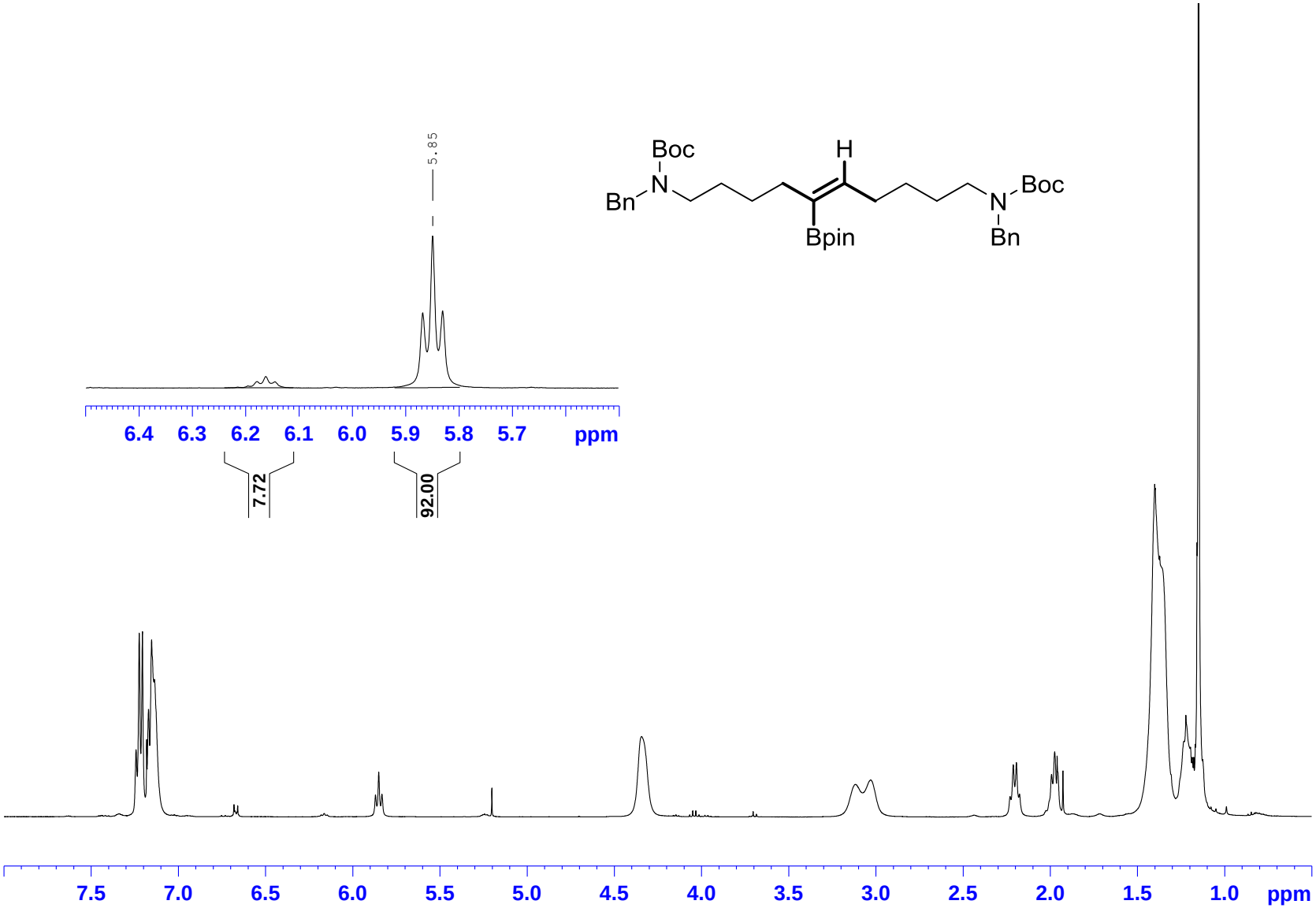

H
TsO
OTs
Bpin
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

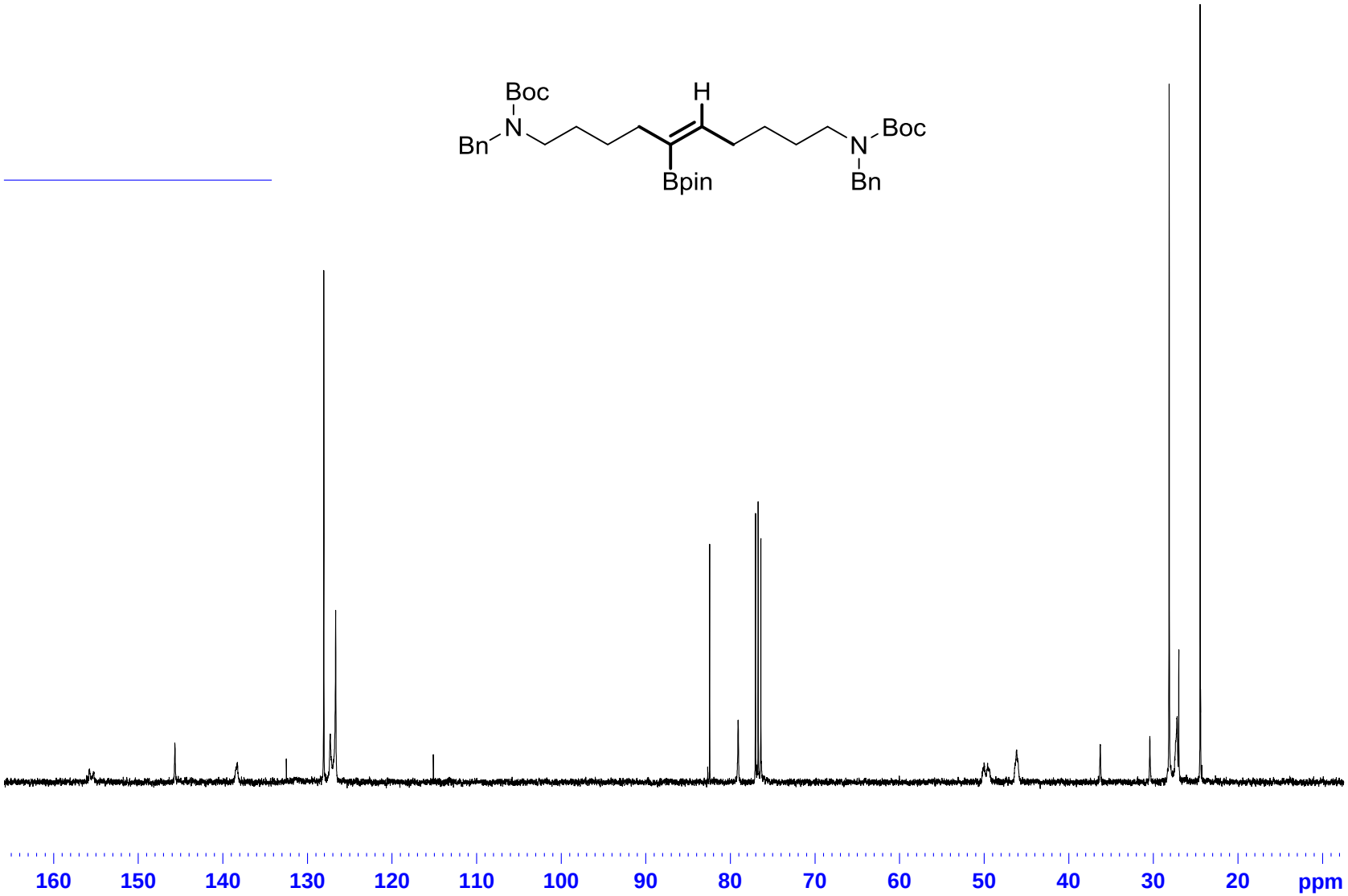

6.17
6.15
6.14
6.4
6.3
6.2
6.1
6.0
5.9
ppm
H
O
O
O
O
Bpin
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

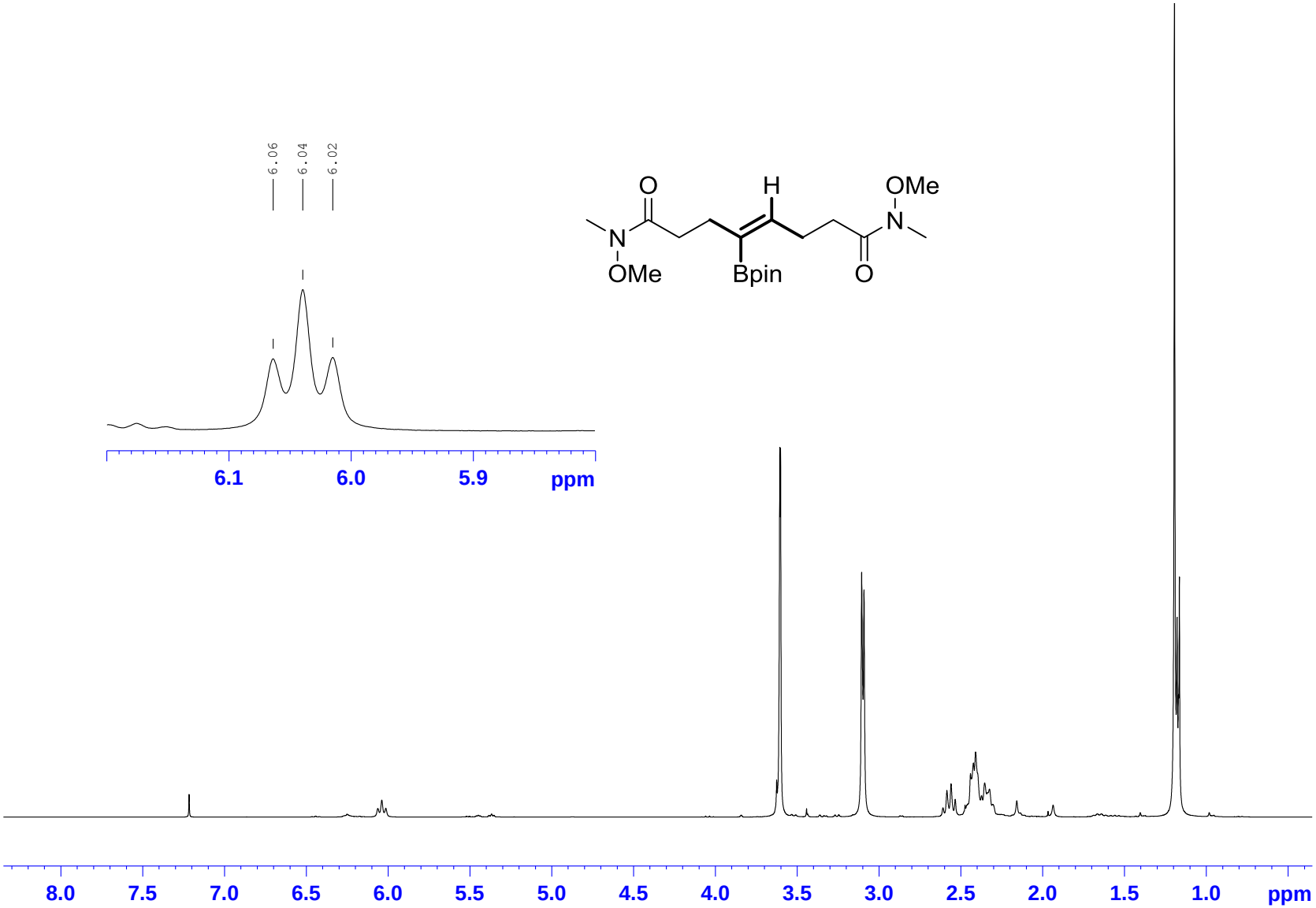

H
O
O
O
O
Bpin
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

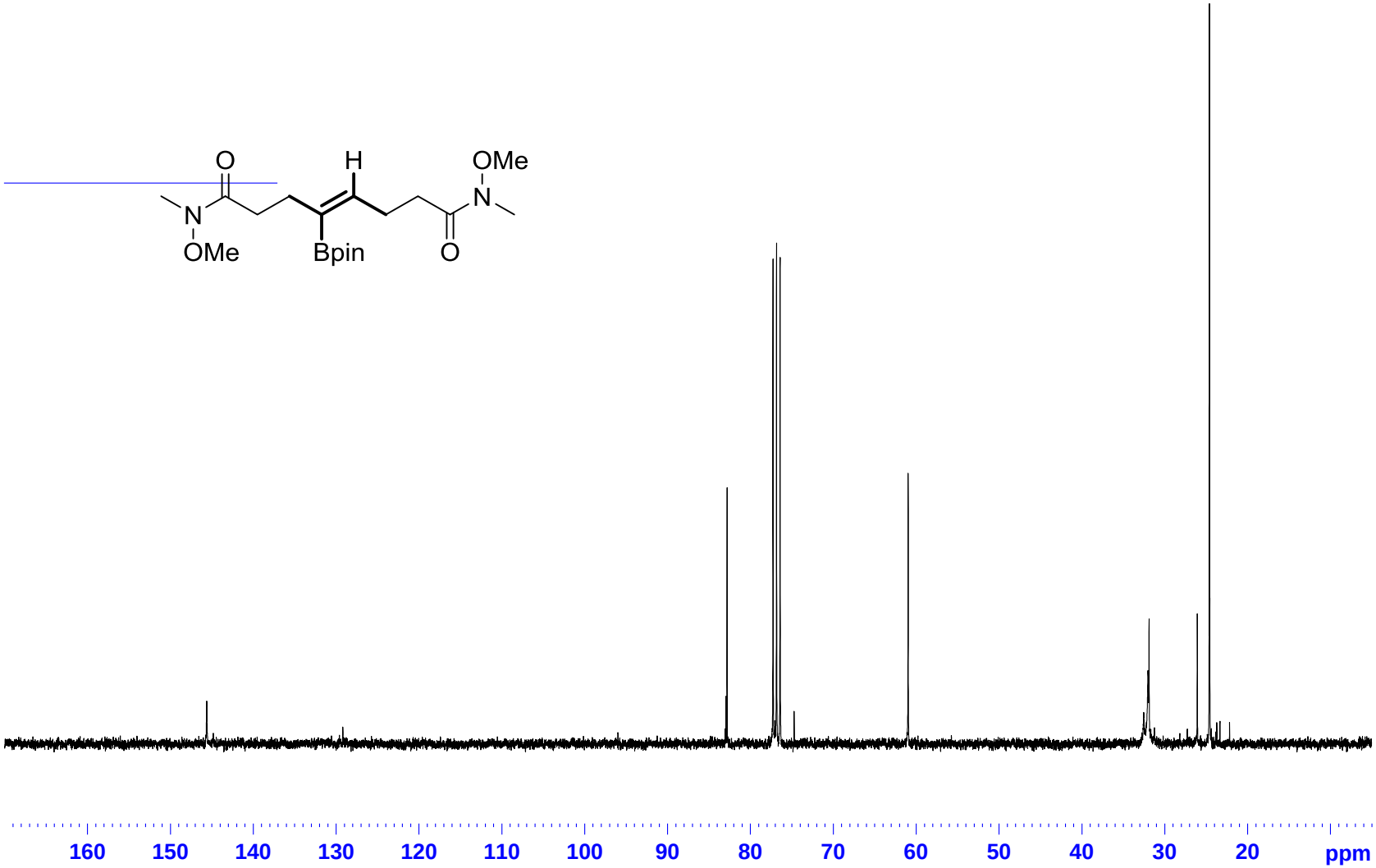

5.99
6.4
6.3
6.2
6.1
6.0
5.9
ppm
10.23
90.00
NC
O
11
H
Bpin
11
O
CN
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

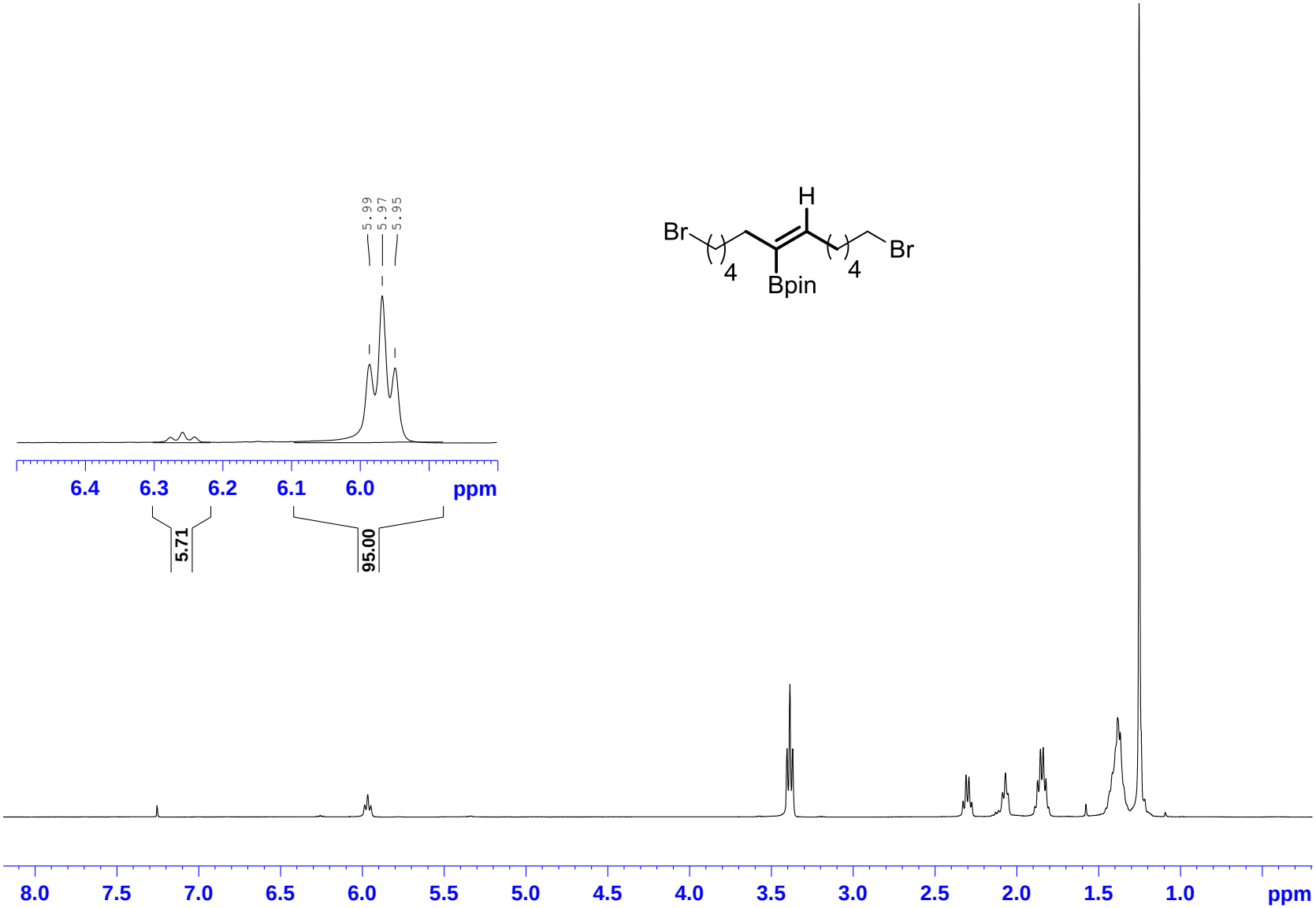

NC
O
11
Bpin
H
11
O
CN
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

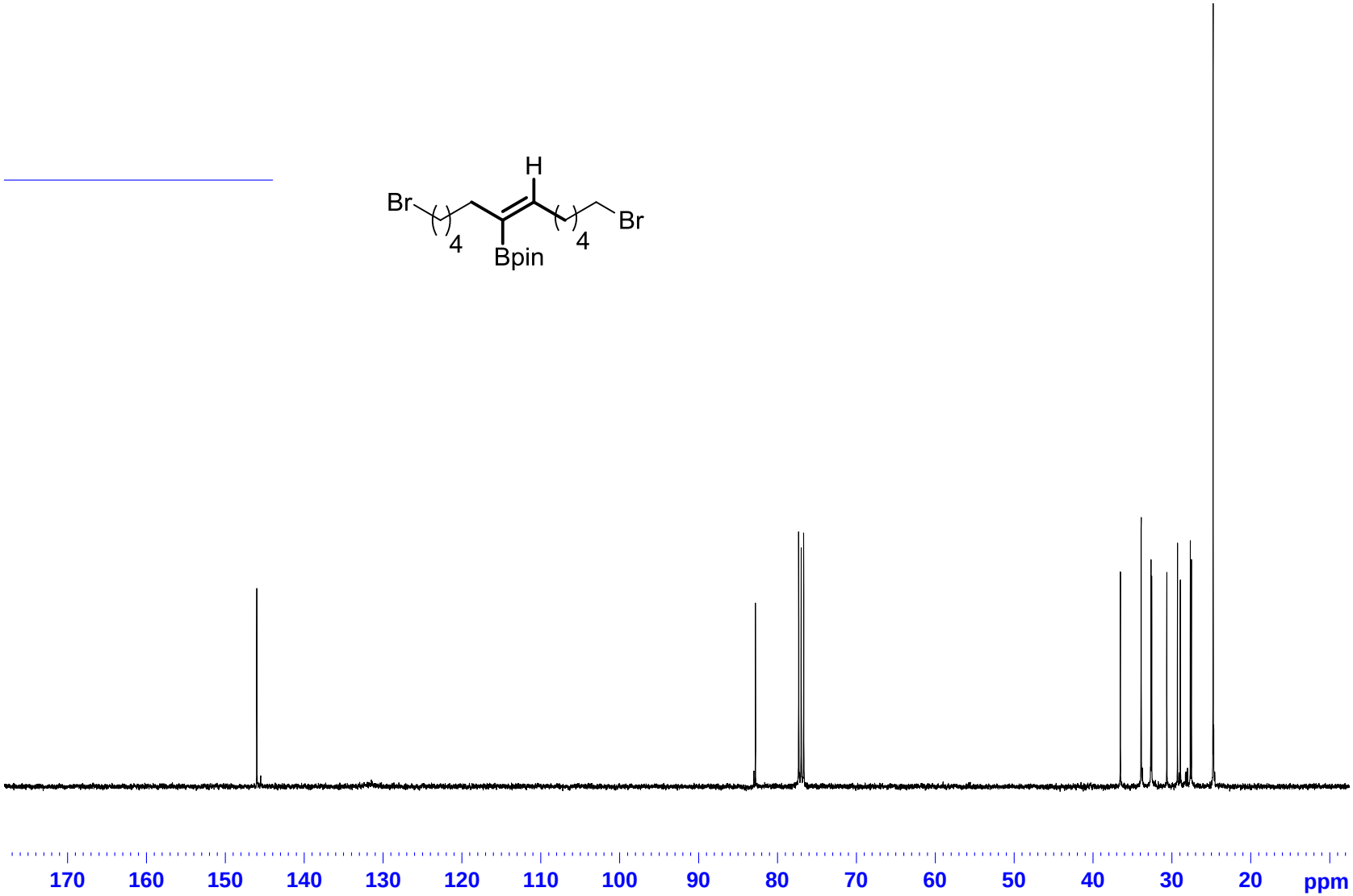

5.85
6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 ppm
7.72
92.00
Boc
H
Bn
N
Boc
N
Bpin
Bn
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

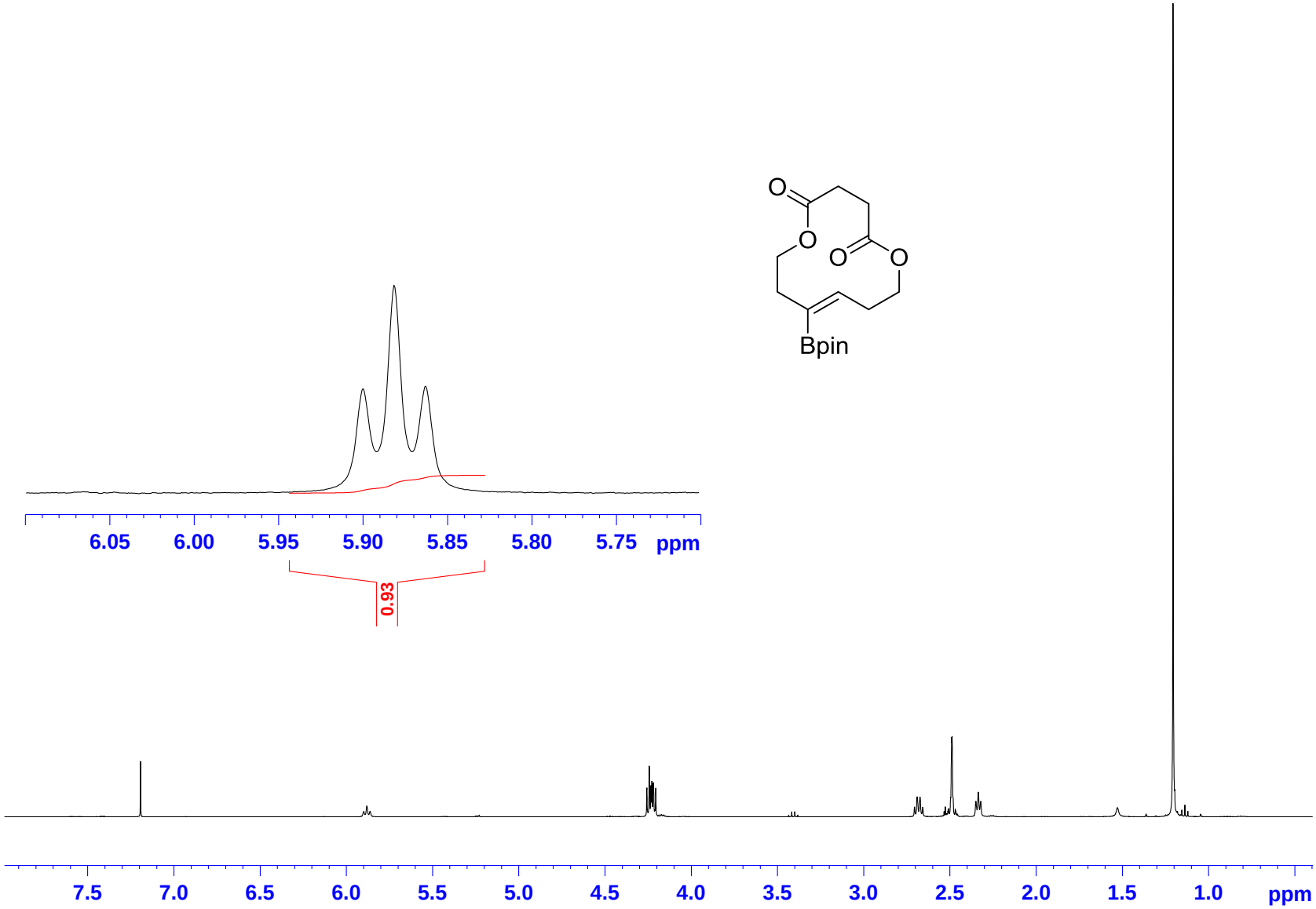

Boc
N
Bn
H
Bpin
N
Boc
Bn
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

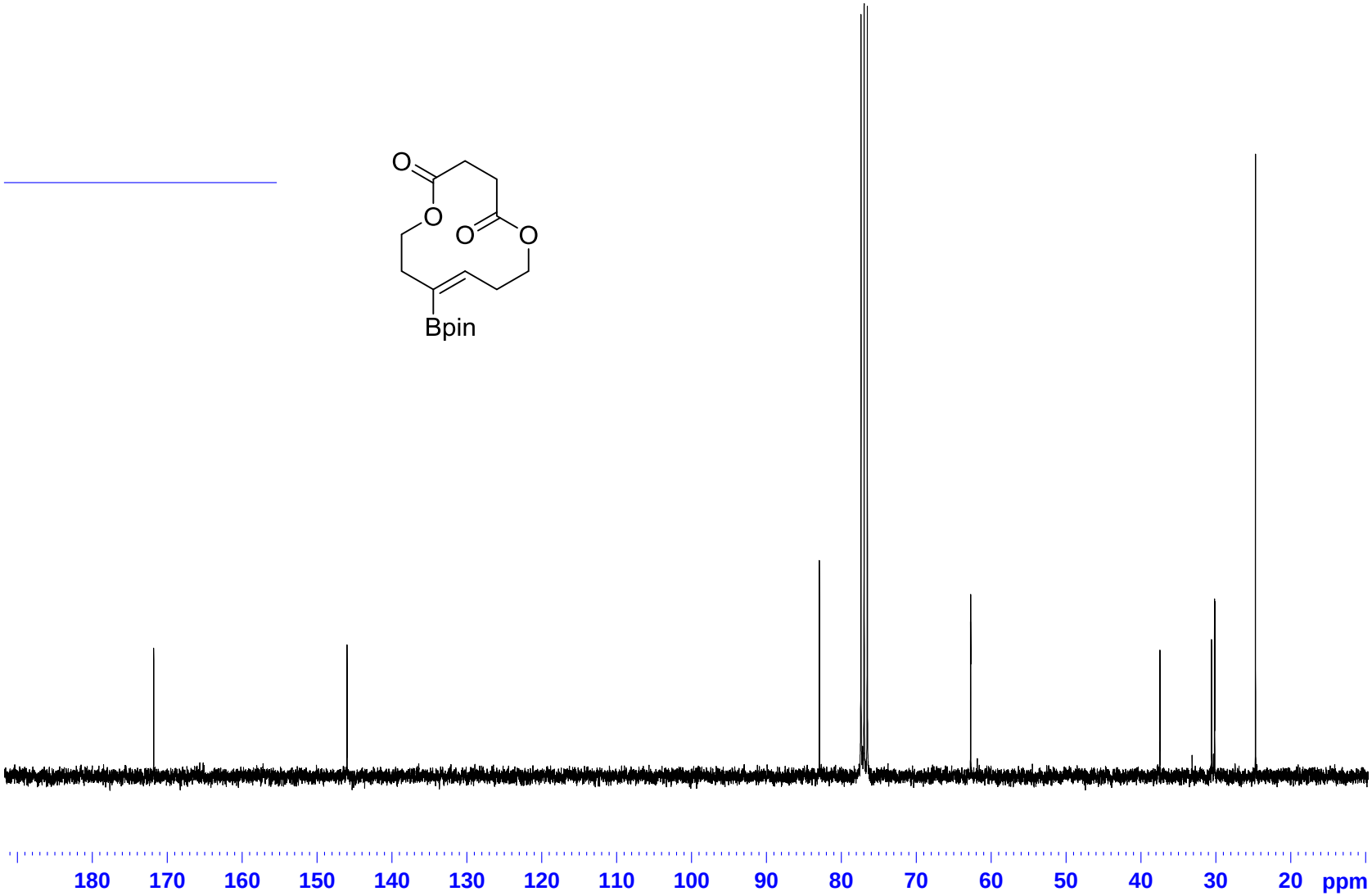

6.06
6.04
6.02
6.1
6.0
5.9
ppm
O
H
OMe
N
N
OMe
Bpin
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

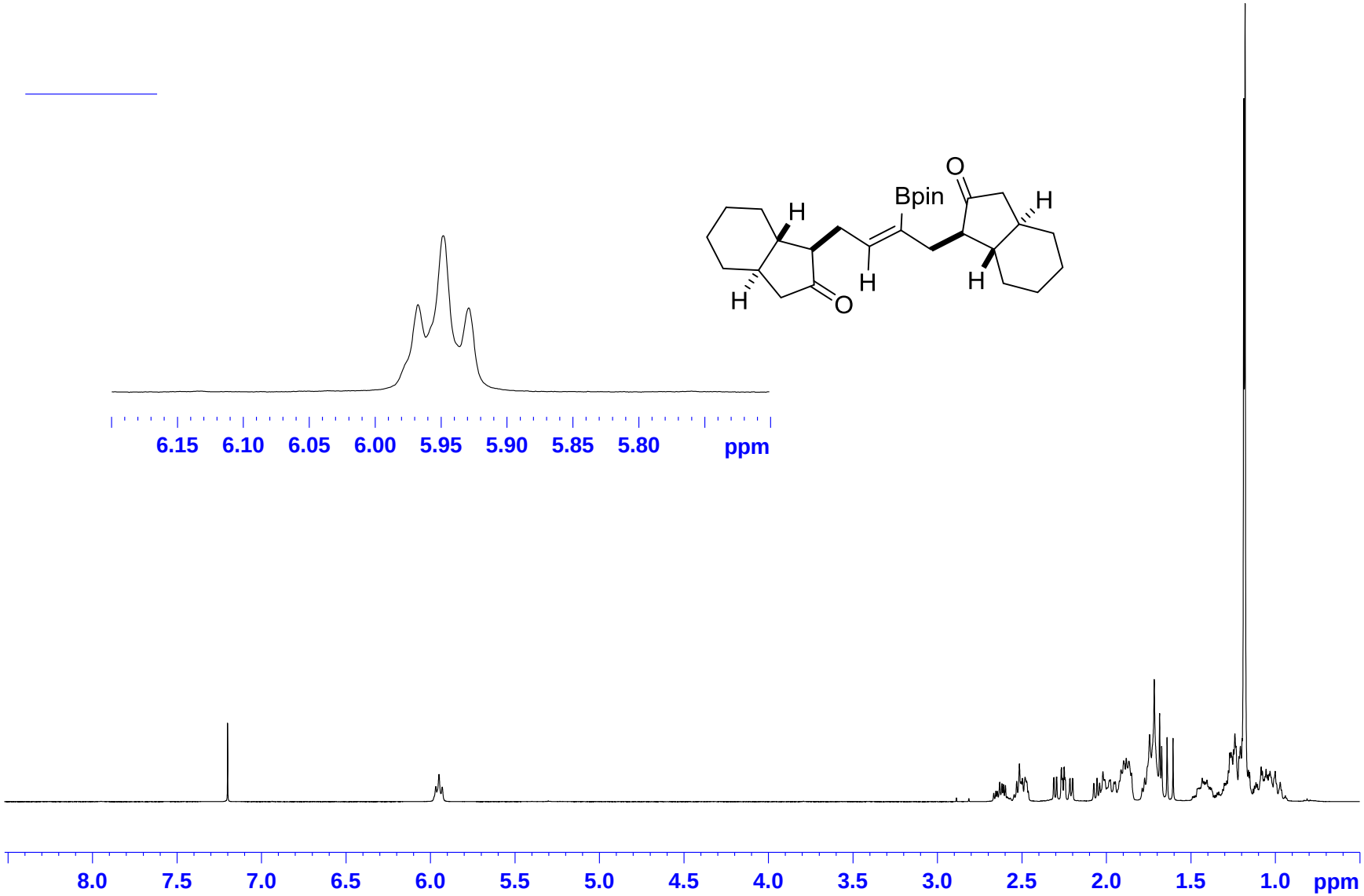

O
H
OMe
N
N
OMe
Bpin
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

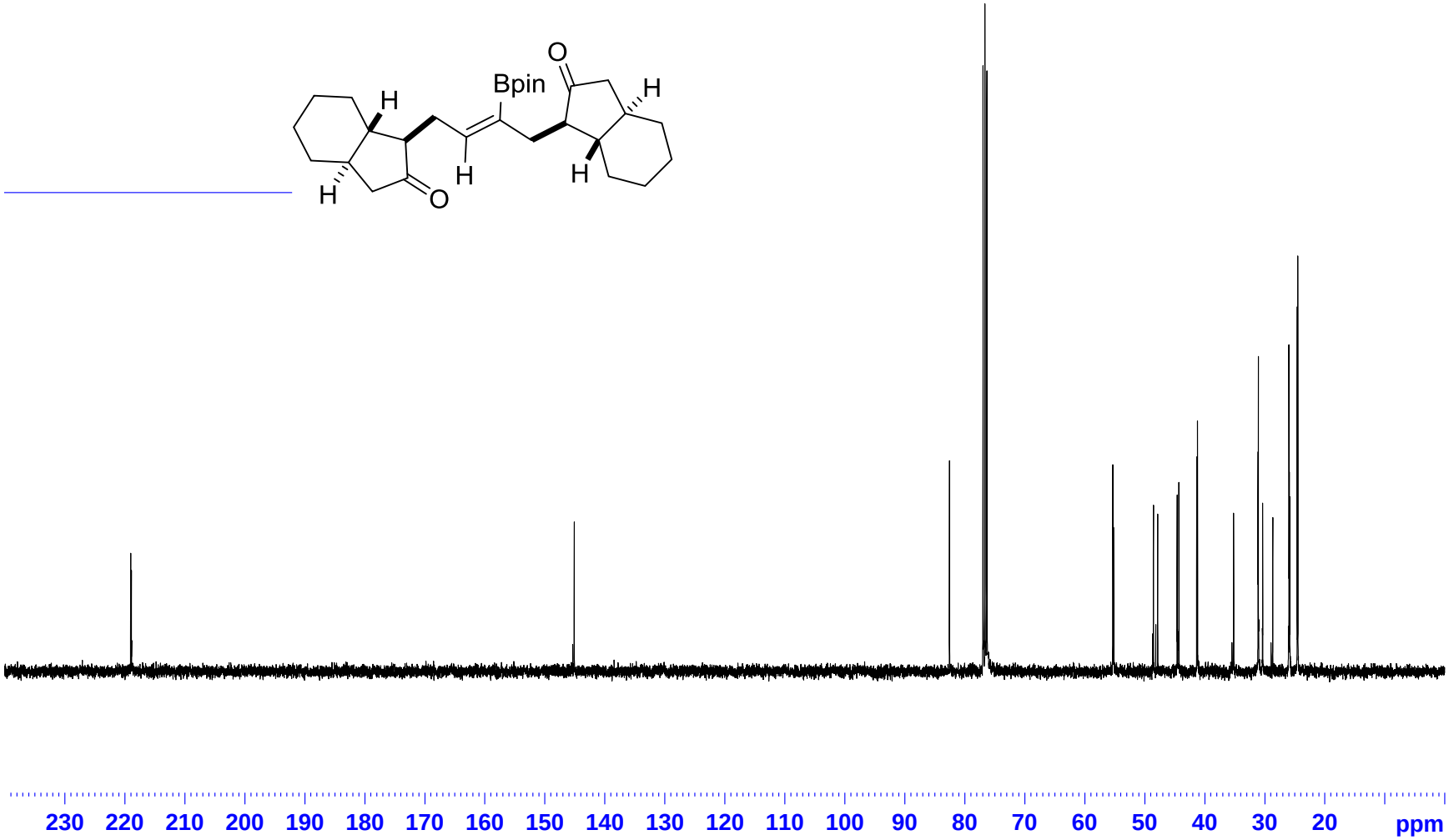

5.99
5.97
5.95
6.4
6.3
6.2
6.1
6.0
ppm
5.71
95.00
H
Br
4
Bpin
4
Br
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

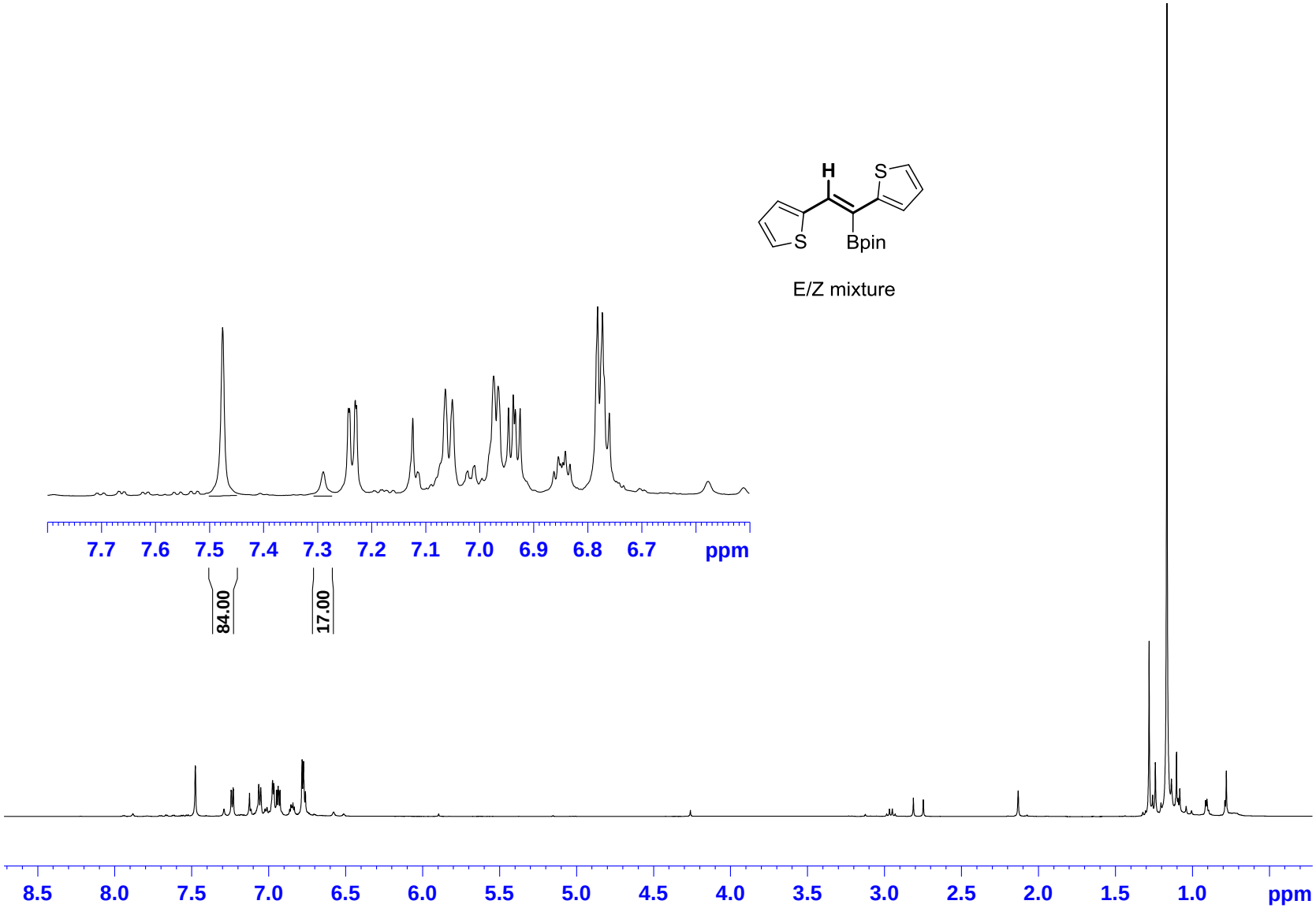

H
Br
4
Bpin
4
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
O
O
O
Bpin
6.05
6.00
5.95
5.90
5.85
5.80
5.75
ppm
0.93
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
ppm

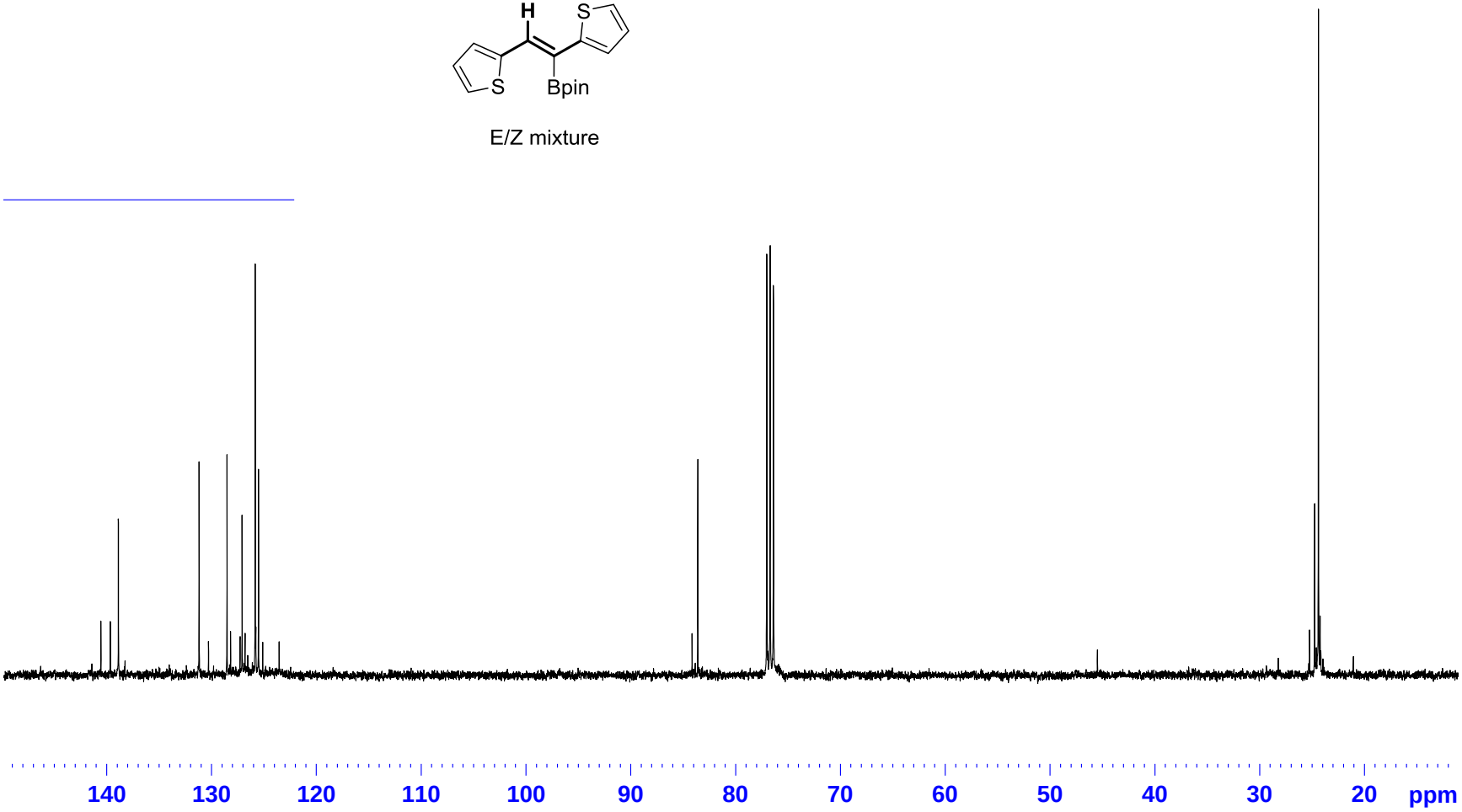

O
O
O
O
Bpin
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

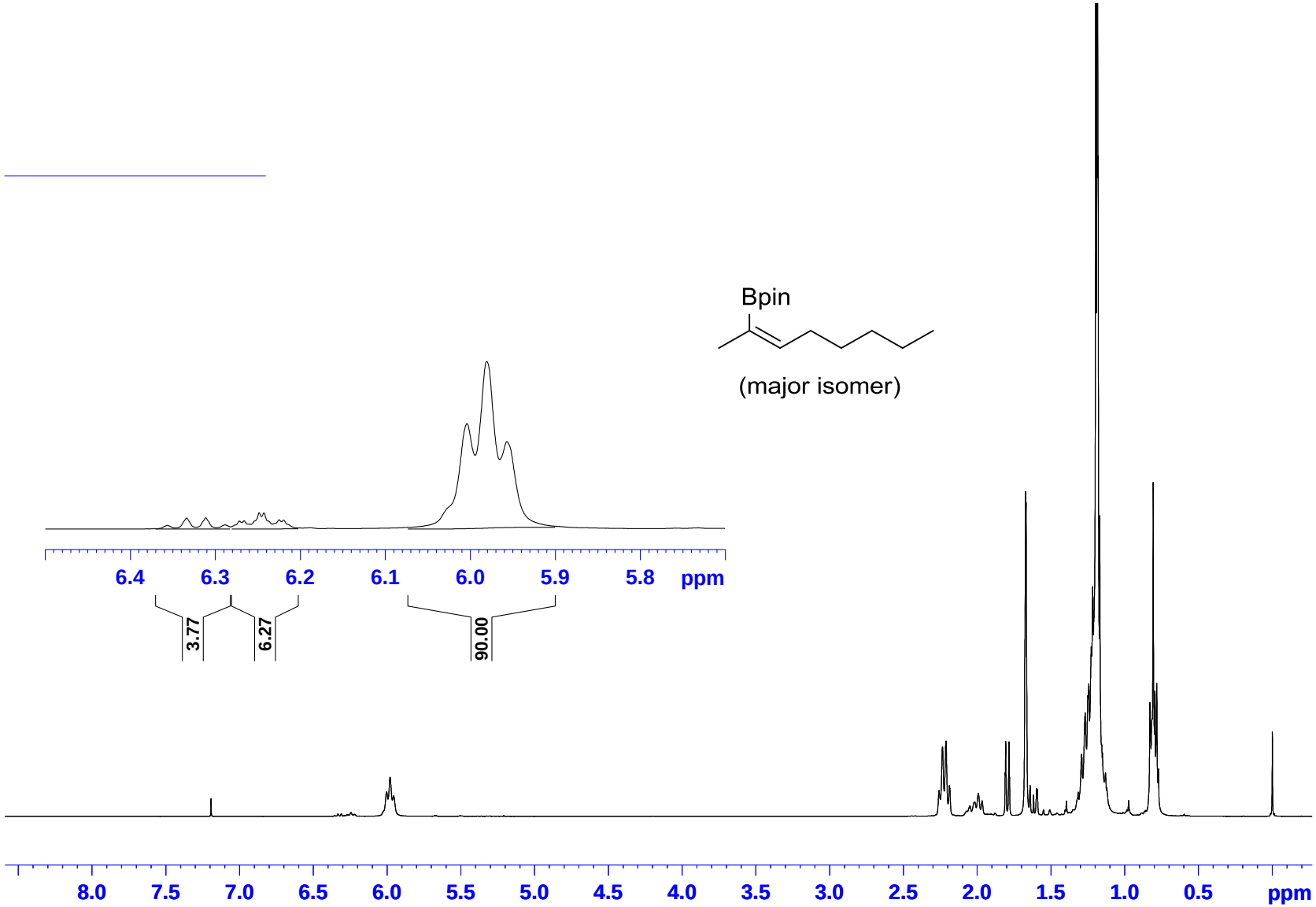

Bpin
O
H
H
H
H
H
O
6.15
6.10
6.05
6.00
5.95
5.90
5.85
5.80
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

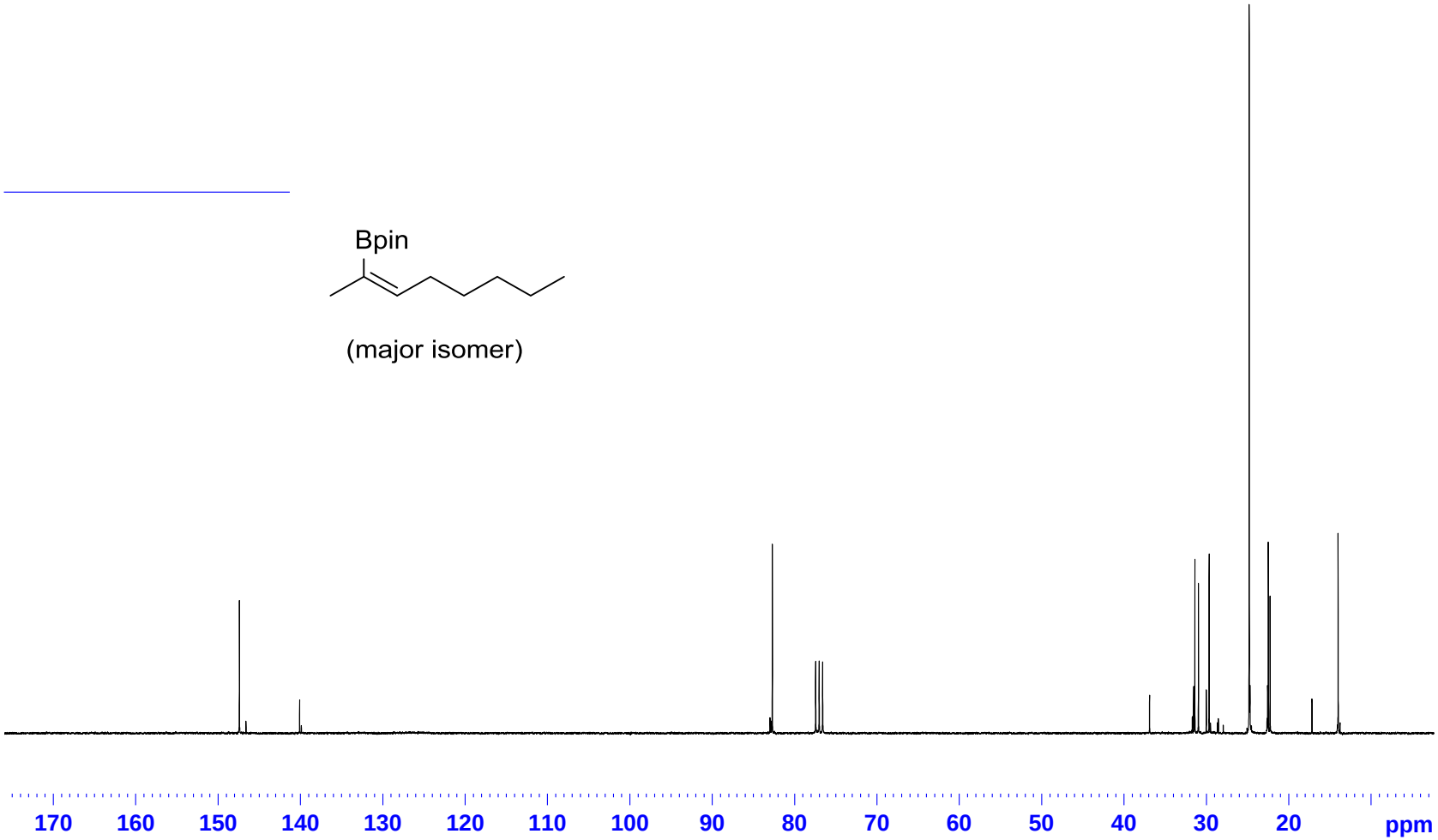

O
Bpin
H
H
H
H
H
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

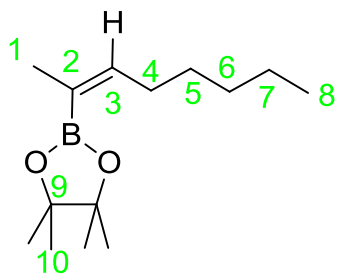

H
S
S
Bpin
E/Z mixture
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
84.00
17.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm

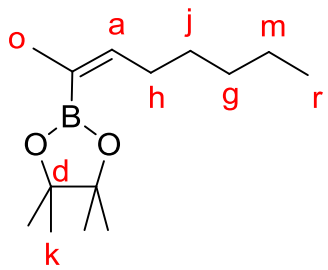
E/Z mixture

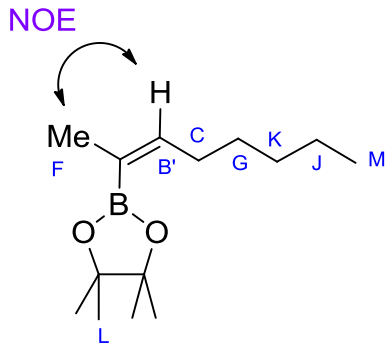



Bpin
(major isomer)
6.4
6.3
6.2
6.1
6.0
5.9
5.8
ppm
3.77
6.27
90.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

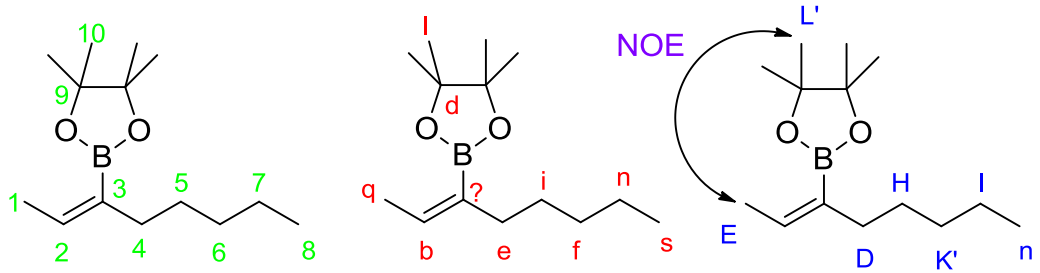

Bpin
(major isomer)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



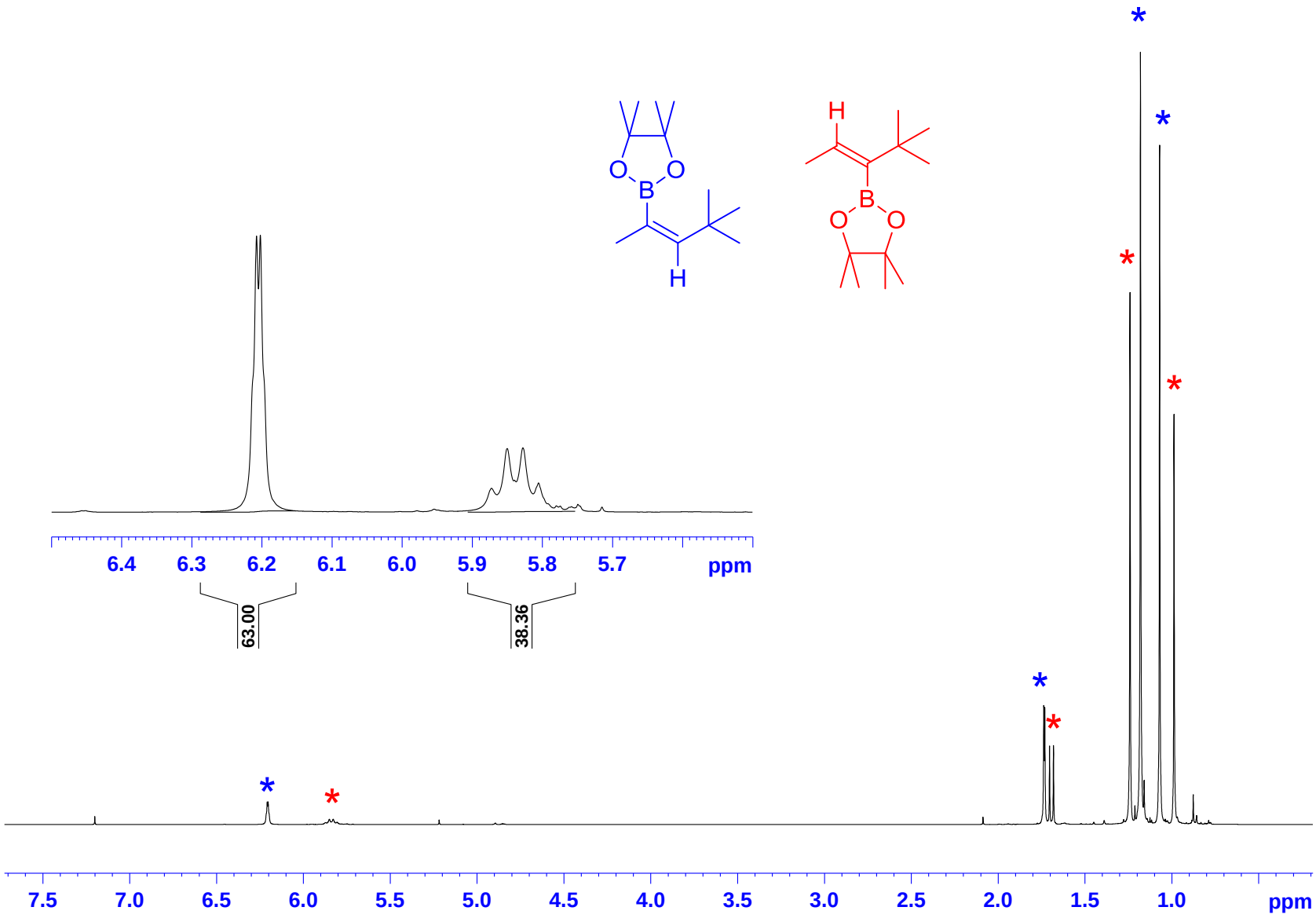


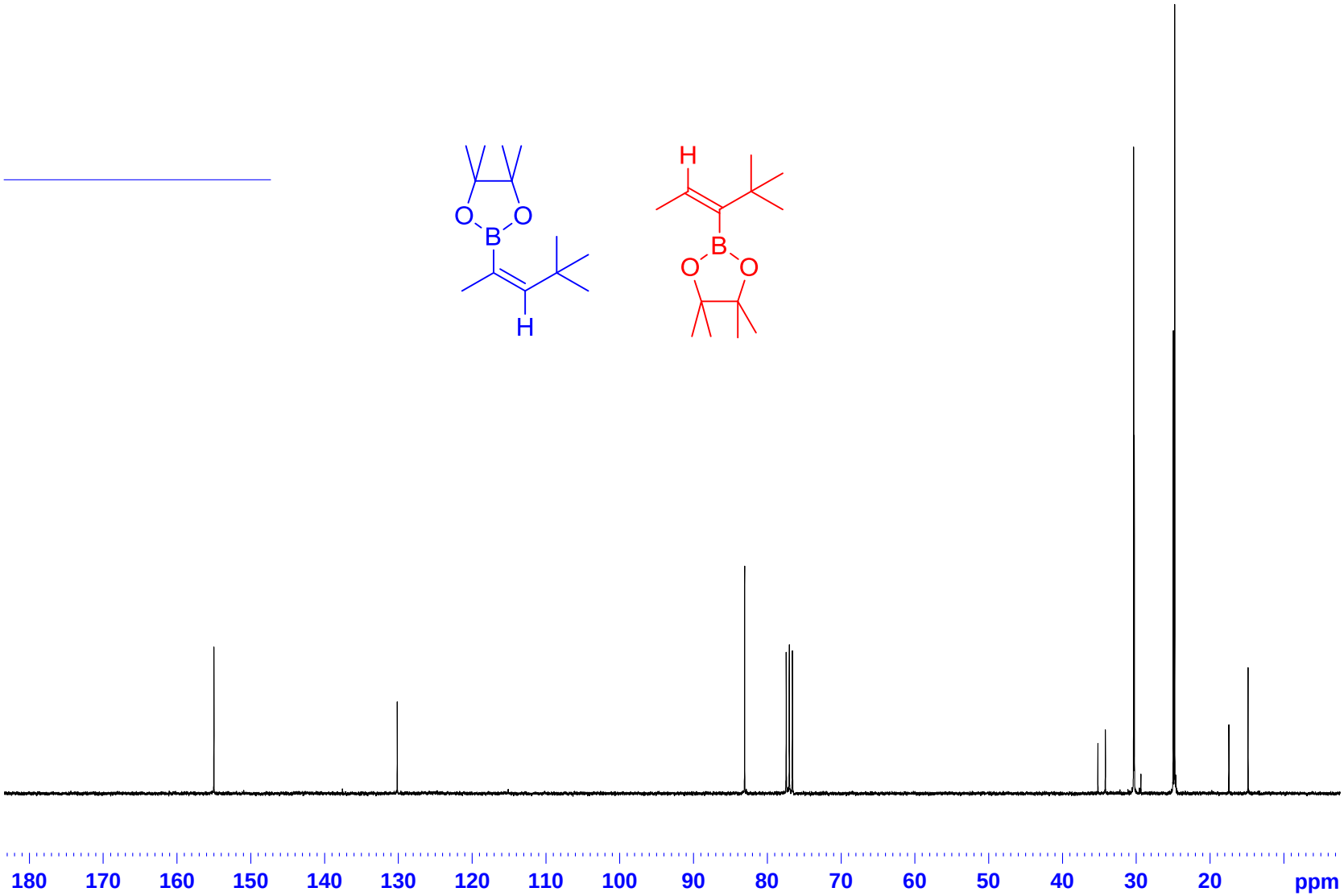


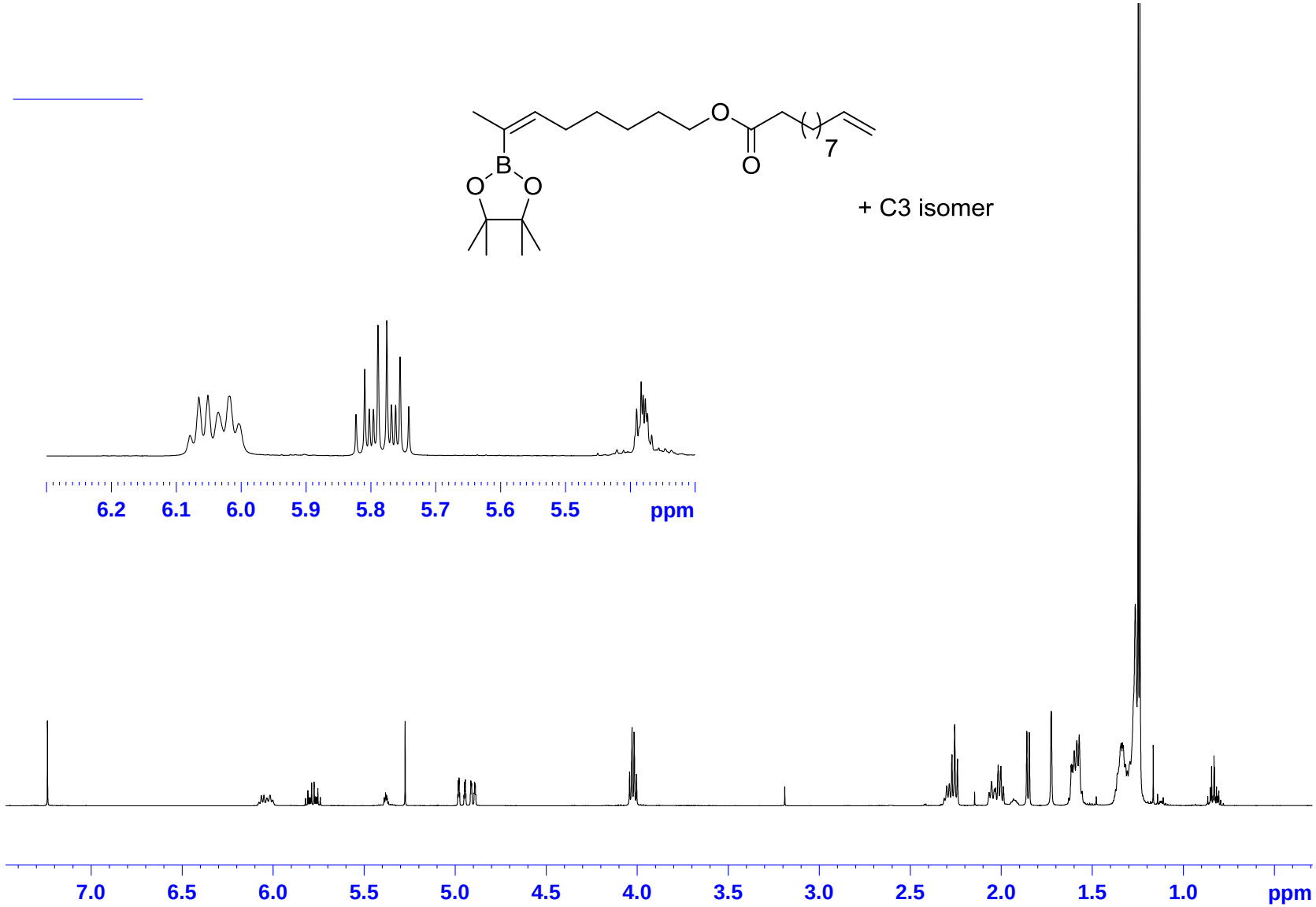
	mol	labe	assign	13C	mult	rel. int	HSQC		label	1H	int	mult	J	COSY	NOESY	HMBC
	b	a	3	147.44	d		<——>		B	6.031		ol		B-C		B-h,p
	b	d	9	82.71	s											
	b	g	6	31.37	t		<——>		K	1.2484						
	b	h	4	30.95	t		<——>		C	2.2738		dt		C-B,G		C-a,g
	b	j	5	29.63	t		<——>		G	1.3138				G-C,K		G-g
	b	k	10	24.79	q		<——>		L	1.2467				K-G,J		L-d
	b	m	7	22.56	t		<——>		J	1.2657				J-K,M		
	b	o	1	22.31	q		<——>		F	1.7263		s(q)!			F-B!	F-a
	b	r	8	14.023	q		<——>		M	0.8584						M-g,m

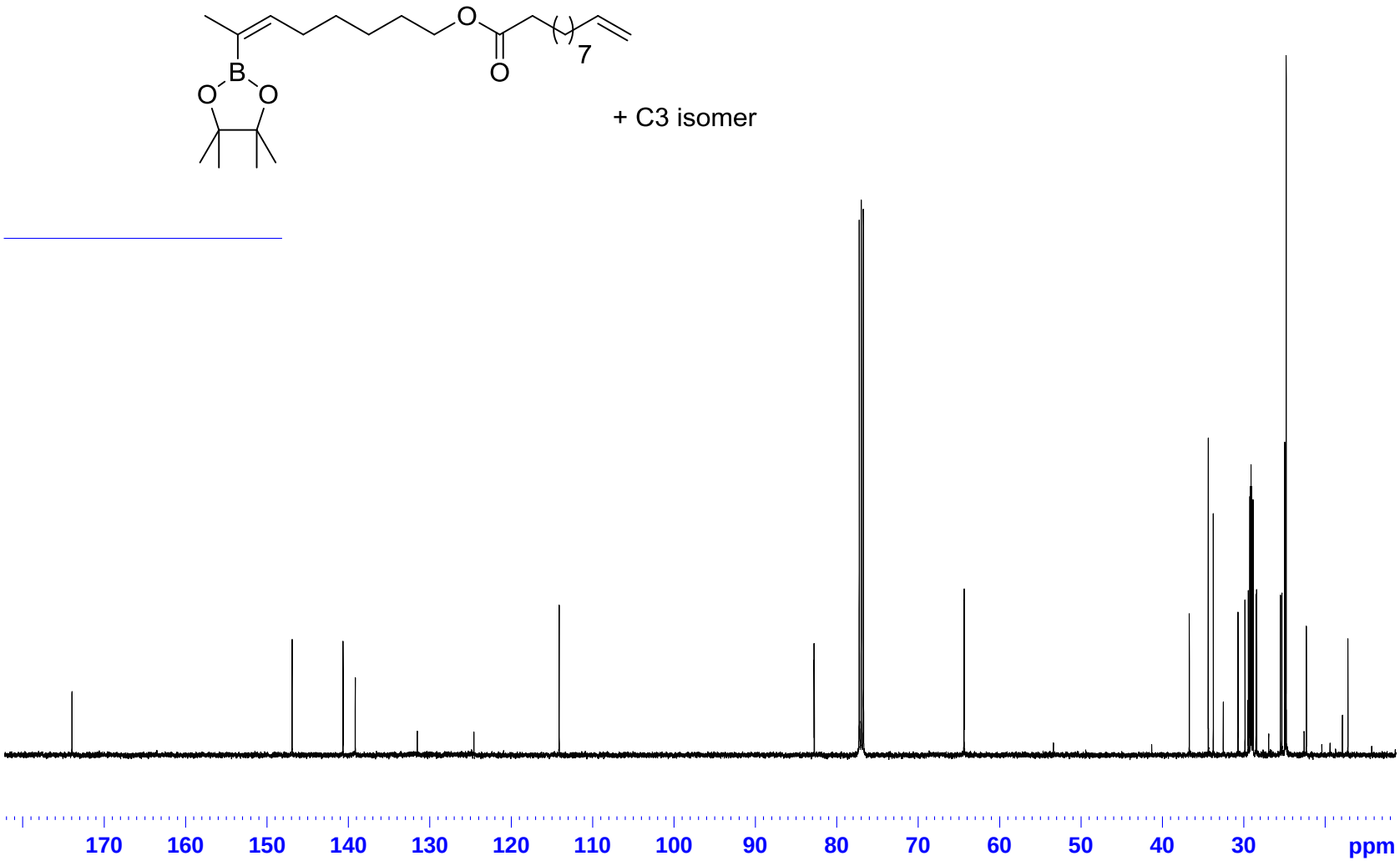


	mol	labe	assign	13C	mult	rel. int	HSQC		label	1H	int	mult	J	COSY	NOESY	HMBC
	s	b	2	140.09	d		<——>		A	6.0472		ol		A-E		A-e,q
	s	c	9	82.74	s											
	s	e	4	36.90	t		<——>		D	2.041		t		D-H		
	s	f	6	31.52	t		<——>		K'	1.2484				K'-H,I		
	s	i	5	29.99	t		<——>		H	1.3127				H-K',D		H-e
	s	l	10	24.78	q		<——>		L'	1.2467						L'-c
	s	n	7	22.47	t		<——>		I	1.2693				I-K',N		
	s	q	1	17.20	q		<——>		E	1.8478		d(t)!	6.7	E-A	E-L'	E-e,
	s	s	8	14.01	q		<——>		N	0.8475				N-I		N-f,n

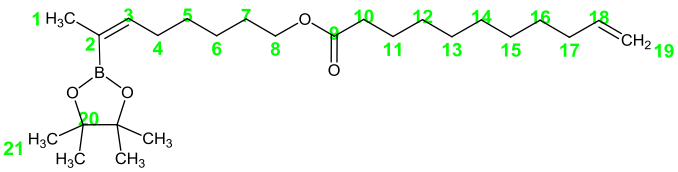

O
B
O
H
H
B
O
O
6.4
6.3
6.2
6.1
6.0
5.9
5.8
5.7
ppm
63.00
38.36
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

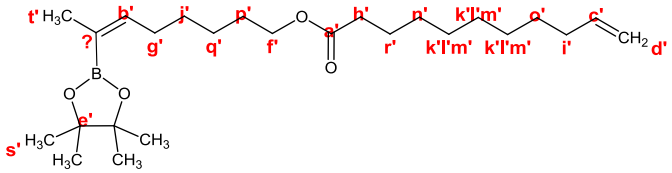

O
B
O
H
H
B
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


B
O
O
O
O
7
+ C3 isomer
6.2
6.1
6.0
5.9
5.8
5.7
5.6
5.5
ppm
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
ppm

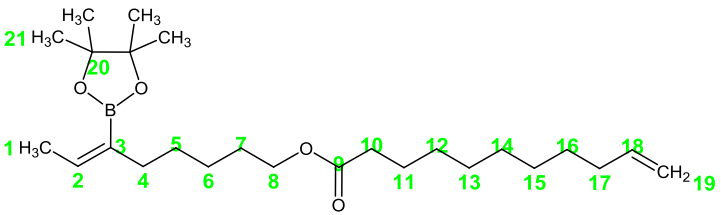

O
O
7
B
O
O
+ C3 isomer
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

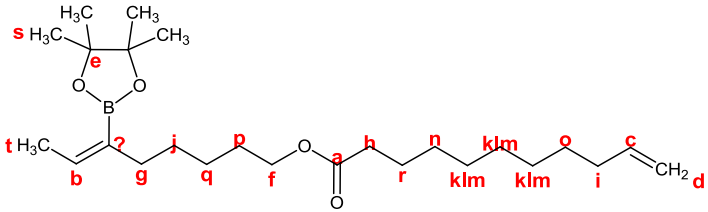
mol	label	assign	13C	mult	rel. int	HSQC		label	1H	int
	a/a'	9	173.98/173.96	s	0,35		1			
	b'	3	146,93	d		<——>	2	A'	6,017	1.25(A')
	c/c'	18	139.18/139.16	d	0,54	<——>	3	B/B'	5,782	1,00
	d/d'	19	114,12	t	0,73	<——>	4	C/C'	4,961	1,04
						<——>	5	D/D'	4,901	1,07
	e/e'	20	82.80/82.77	s	0,76		6			
	f/f'	8	64.41/64.37	t	1,44	<——>	7	E/E'	4,024	2,86
	g'	4	30,73	t	0,64	<——>	8	G'	2,293	4.2(F/F')
	h/h'	10	34,39	t	1,27	<——>	9	F/F'	2,254	4.2(G')
	i/i'	17	33,77	t	0,86	<——>	10	H/H'	2,010	3,76
	j'	5	29.88/29.46	t	0,64	<——>	11	M/M'	1,333	*
	k/k'	13/14/15/	29,28	t	1,00	<——>	12	R/R'	1,252	*
	l/l'	13/14/15/	29,19	t	1,05	<——>	13	Q/Q'	1,252	*
	m/m'	13/14/15/	29,13	t	1,10	<——>	14	P/P'	1,260	*
	n/n'	12	29,04	t	1,04	<——>	15	O/O'	1,260	*
	o/o'	16	28,88	t	0,95	<——>	16	L/L'	1,339	*
	p/p'	7	28.52/28.43	t	0,68	<——>	17	J/J'	1,586	7.52 (K)
	q'	6	25,34	t	0,69	<——>	18	N/N'	1,289	*
	r/r'	11	24,99	t	1,40	<——>	19	K/K'	1,581	7.52 (J)
	s'	21	24,80	q	5,20	<——>	20	S'	1,249	*
	t'	1	22,33	q			21	I'	1,726	2,13

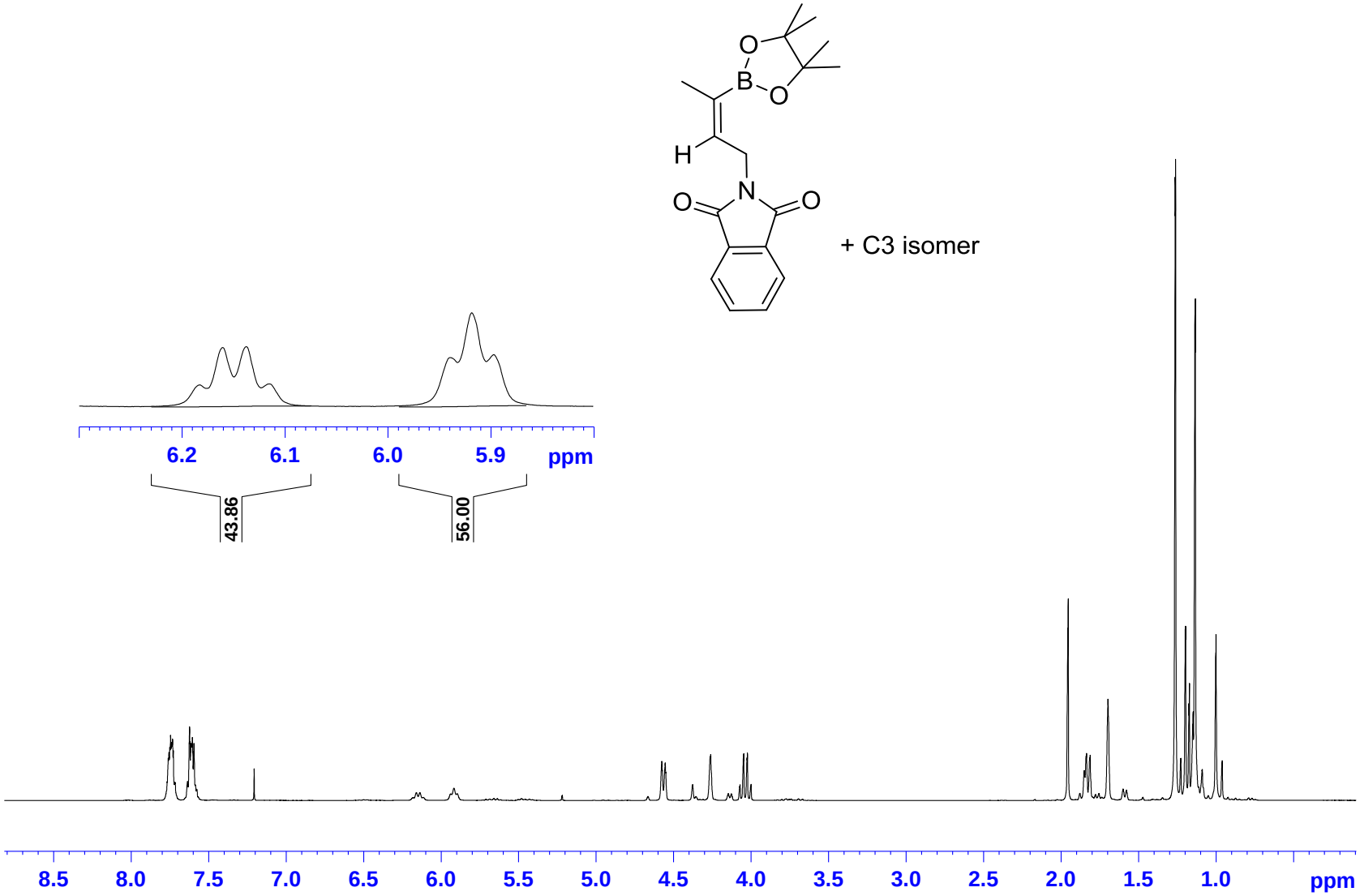


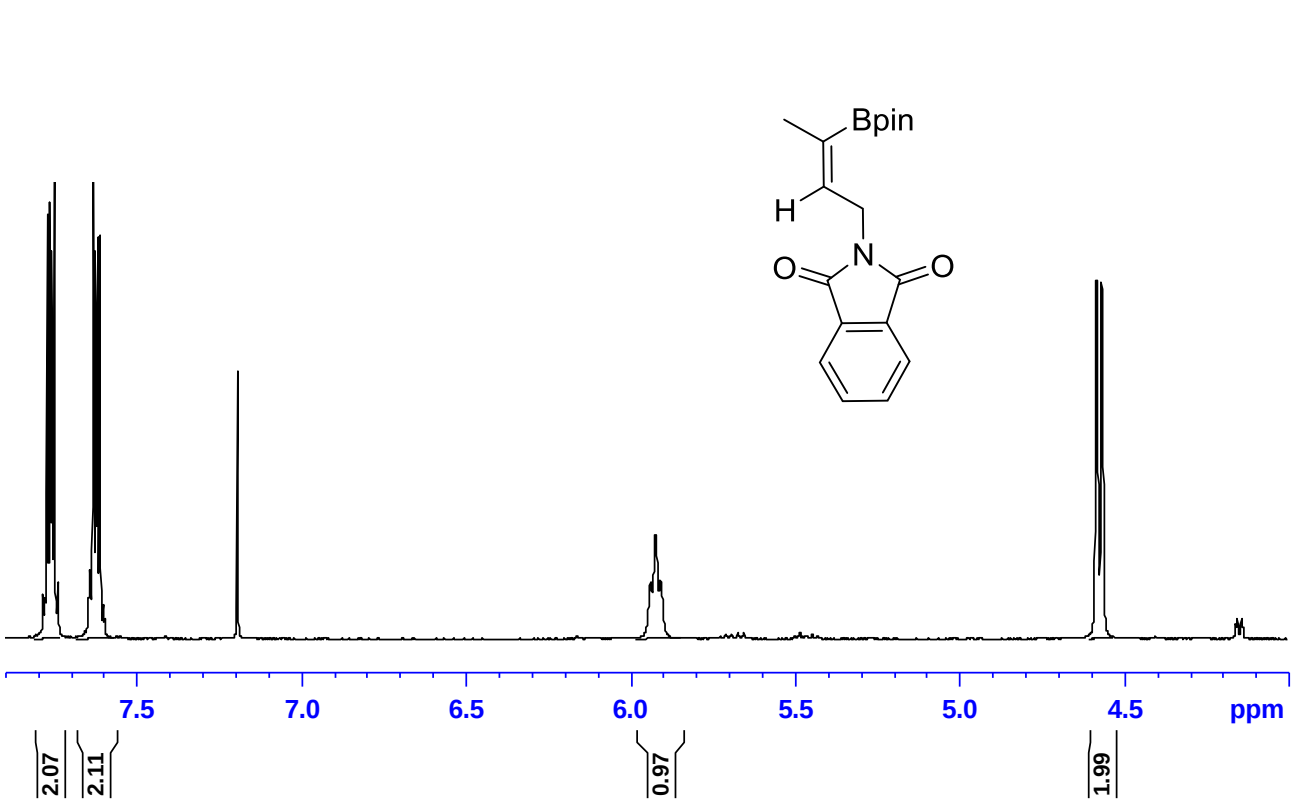


mol	label	assign	13C	mult	rel. int	HSQC		label	1H	int
	a/a'	9	173.98/173.96	s	0,35		1			
	b	2	140,67	d	0,57	<——>	2	A	6,058	1.25(A')
	c/c'	18	139.18/139.16	d	0,54	<——>	3	B/B'	5,782	1,00
	d/d'	19	114,12	t	0,73	<——>	4	C/C'	4,961	1,04
						<——>	5	D/D'	4,901	1,07
	e/e'	20	82.80/82.77	s	0,76		6			
	f/f'	8	64.41/64.37	t	1,44	<——>	7	E/E'	4,024	2,86
	g	4	36,72	t	0,65	<——>	8	G	2,054	3.76(H)
	h/h'	10	34,39	t	1,27	<——>	9	F/F'	2,254	4.2(G')
	i/i'	17	33,77	t	0,86	<——>	10	H/H'	2,010	3.76(G)
	j	5	29,46	t	0,64	<——>	11	M/M'	1,333	*
	k/k'	13/14/15/	29,28	t	1,00	<——>	12	R/R'	1,252	*
	l/l'	13/14/15/	29,19	t	1,05	<——>	13	Q/Q'	1,252	*
	m/m'	13/14/15/	29,13	t	1,10	<——>	14	P/P'	1,260	*
	n/n'	12	29,04	t	1,04	<——>	15	O/O'	1,260	*
	o/o'	16	28,88	t	0,95	<——>	16	L/L'	1,339	*
	p/p'	7	28.52/28.43	t	0,68	<——>	17	J/J'	1,586	7.52 (K)
	q	6	25,52	t	0,69	<——>	18	N/N'	1,289	*
	r/r'	11	24,99	t	1,40	<——>	19	K/K'	1,581	7.52 (J)
	s	21	24,82	q	5,20	<——>	20	S	1,239	*
	t	1	17,23	q	0,48	<——>	21	I	1,853	2,00

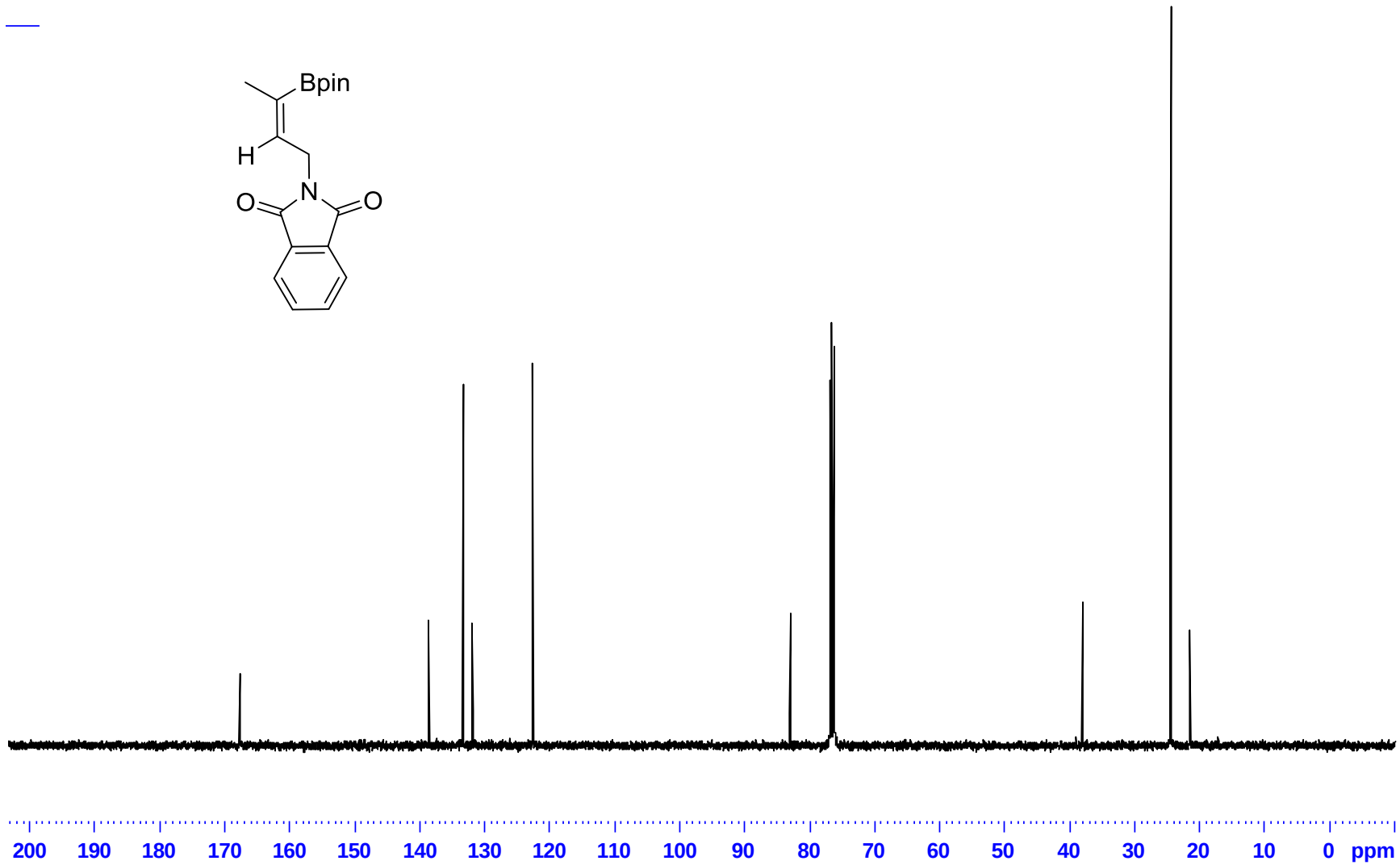


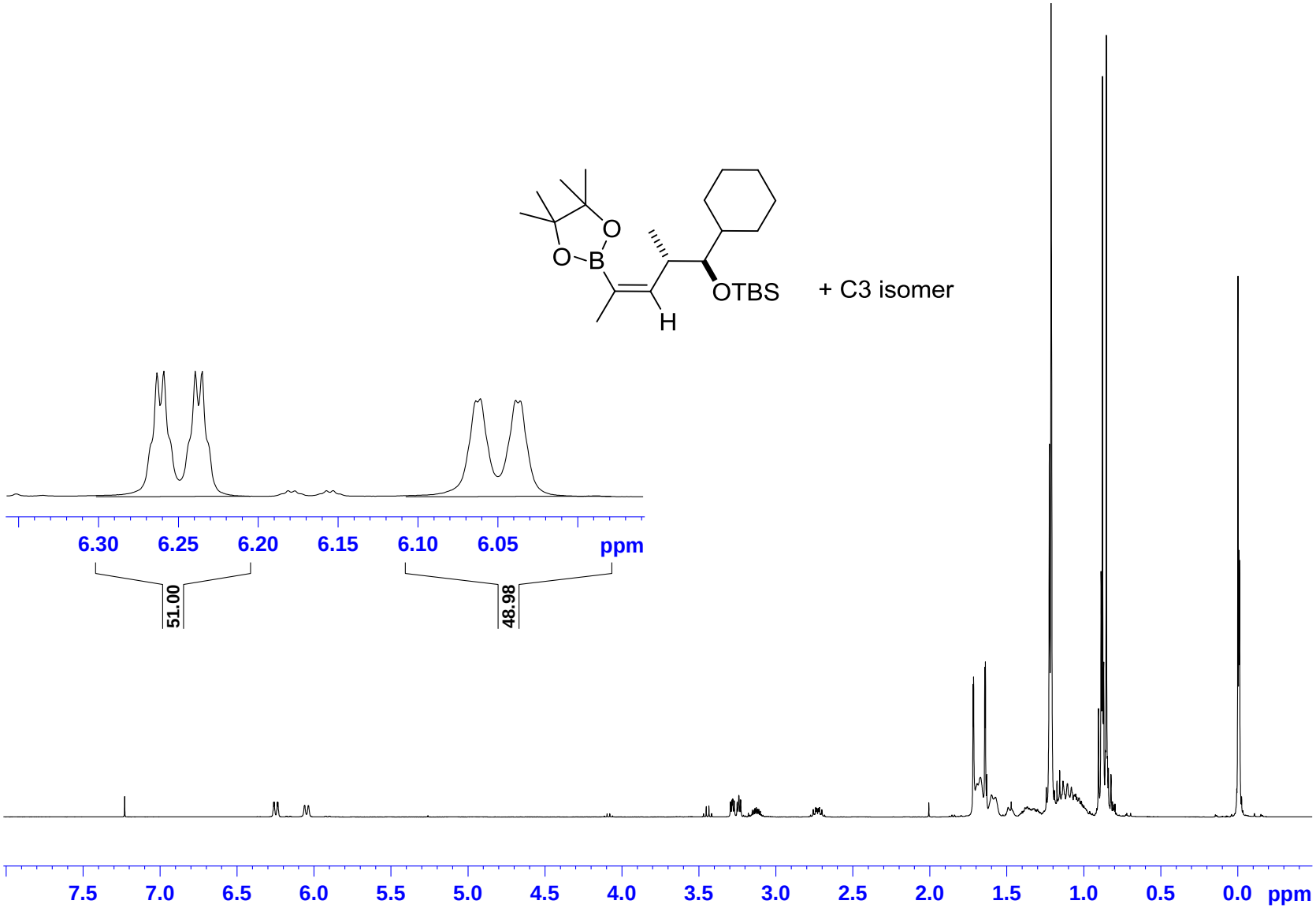


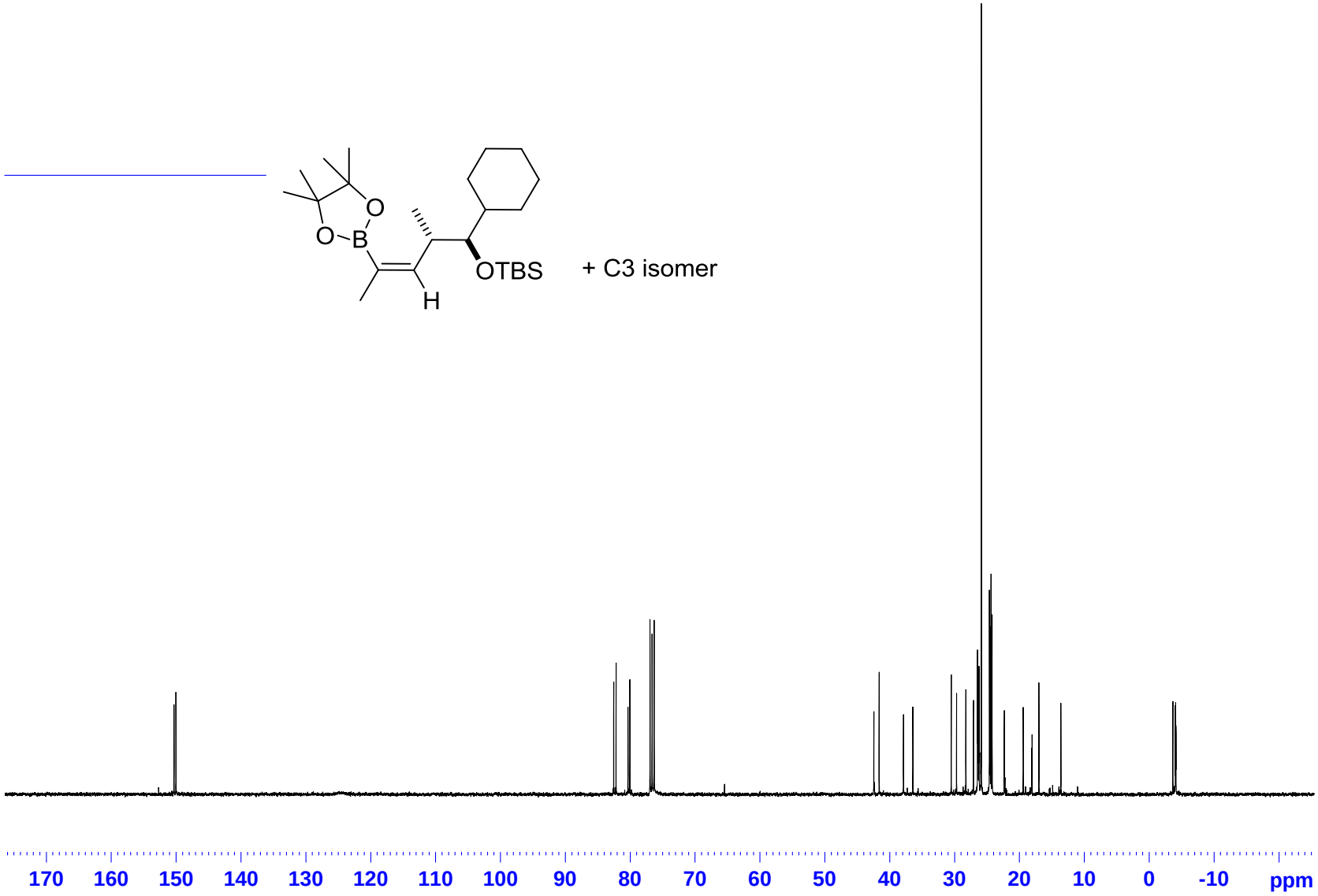

O
B
O
H
N
O
O
+ C3 isomer
6.2
6.1
6.0
5.9
ppm
43.86
56.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

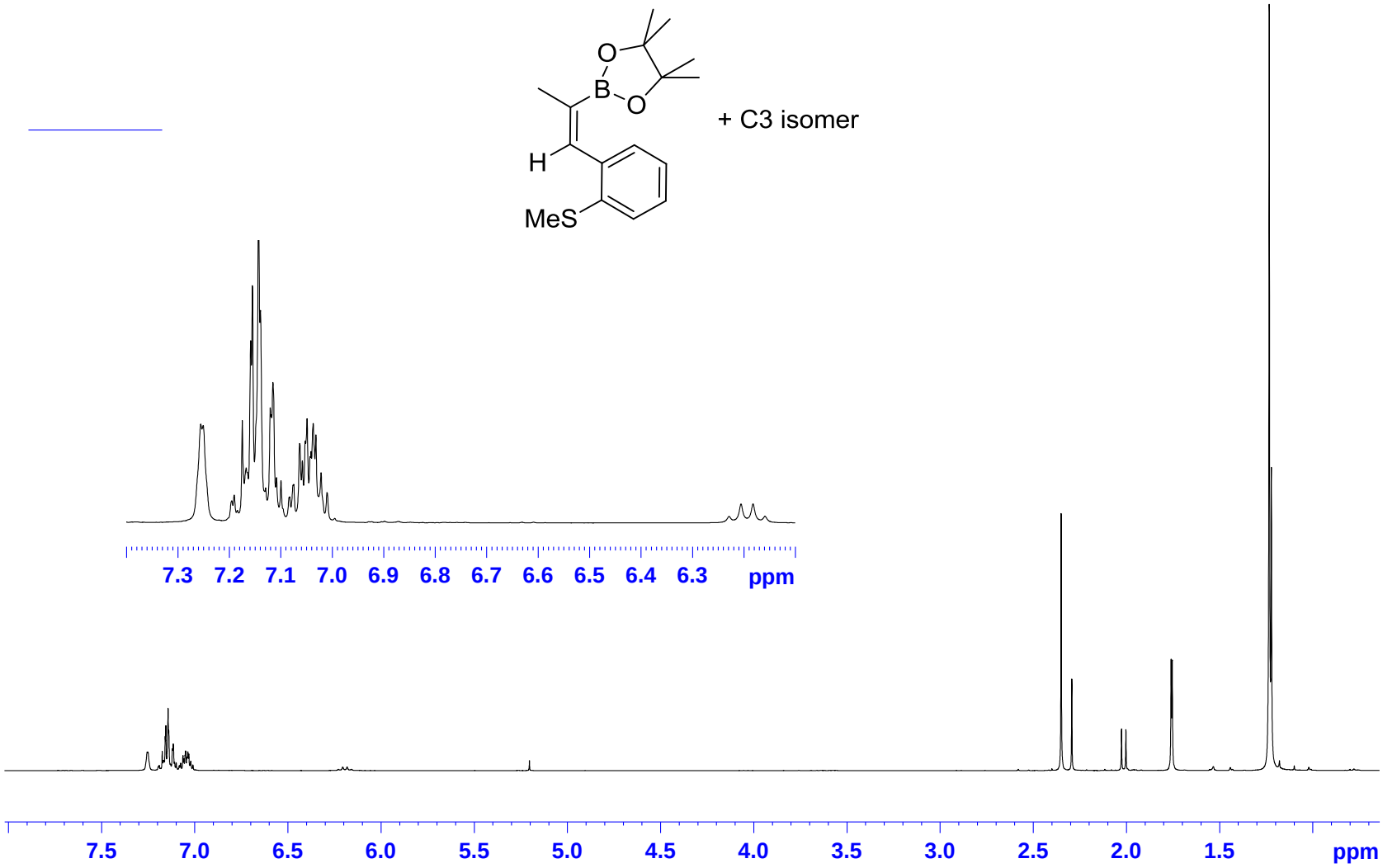

Bpin
H
N
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
ppm
2.07
2.11
0.97
1.99

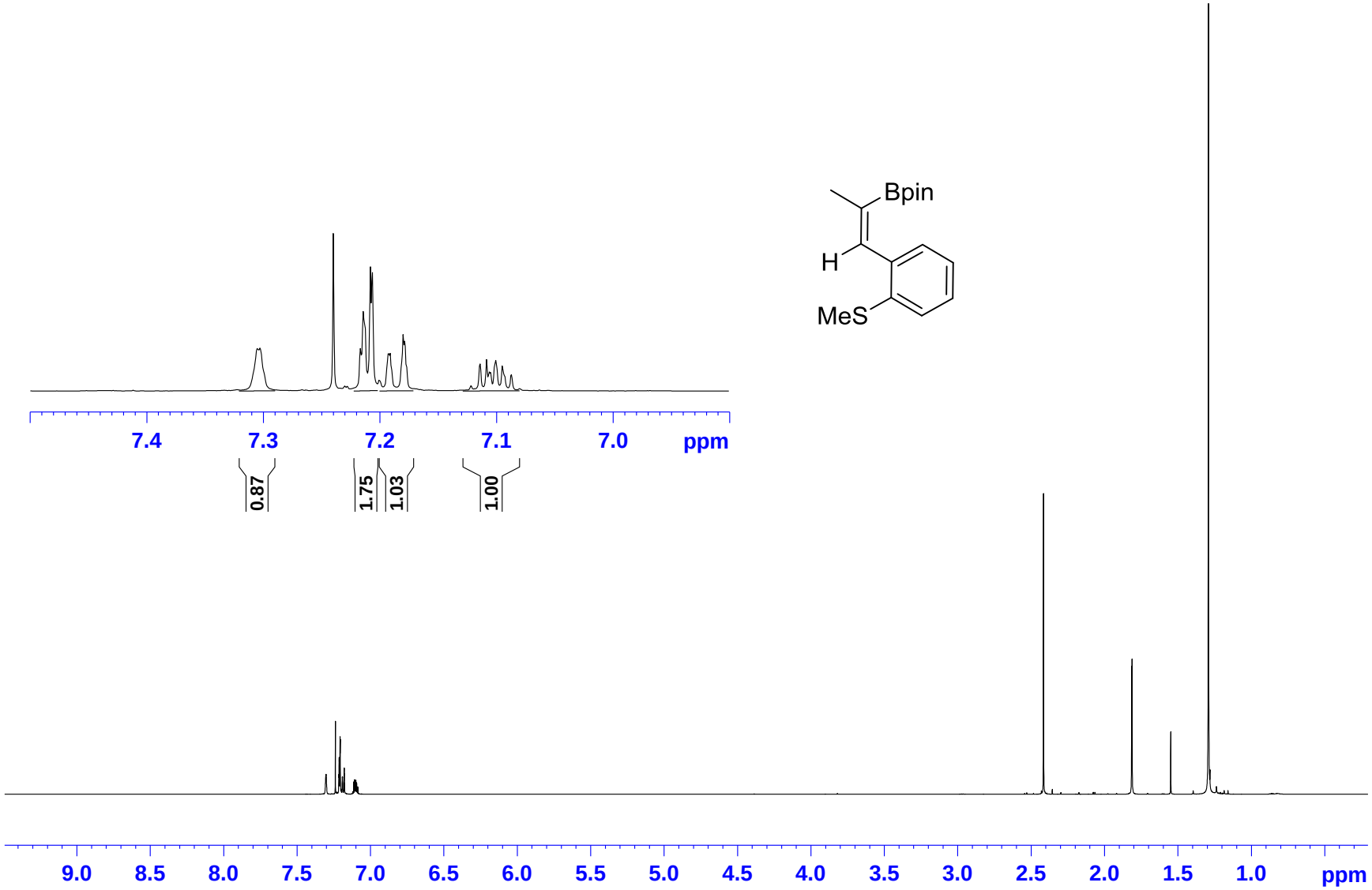
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

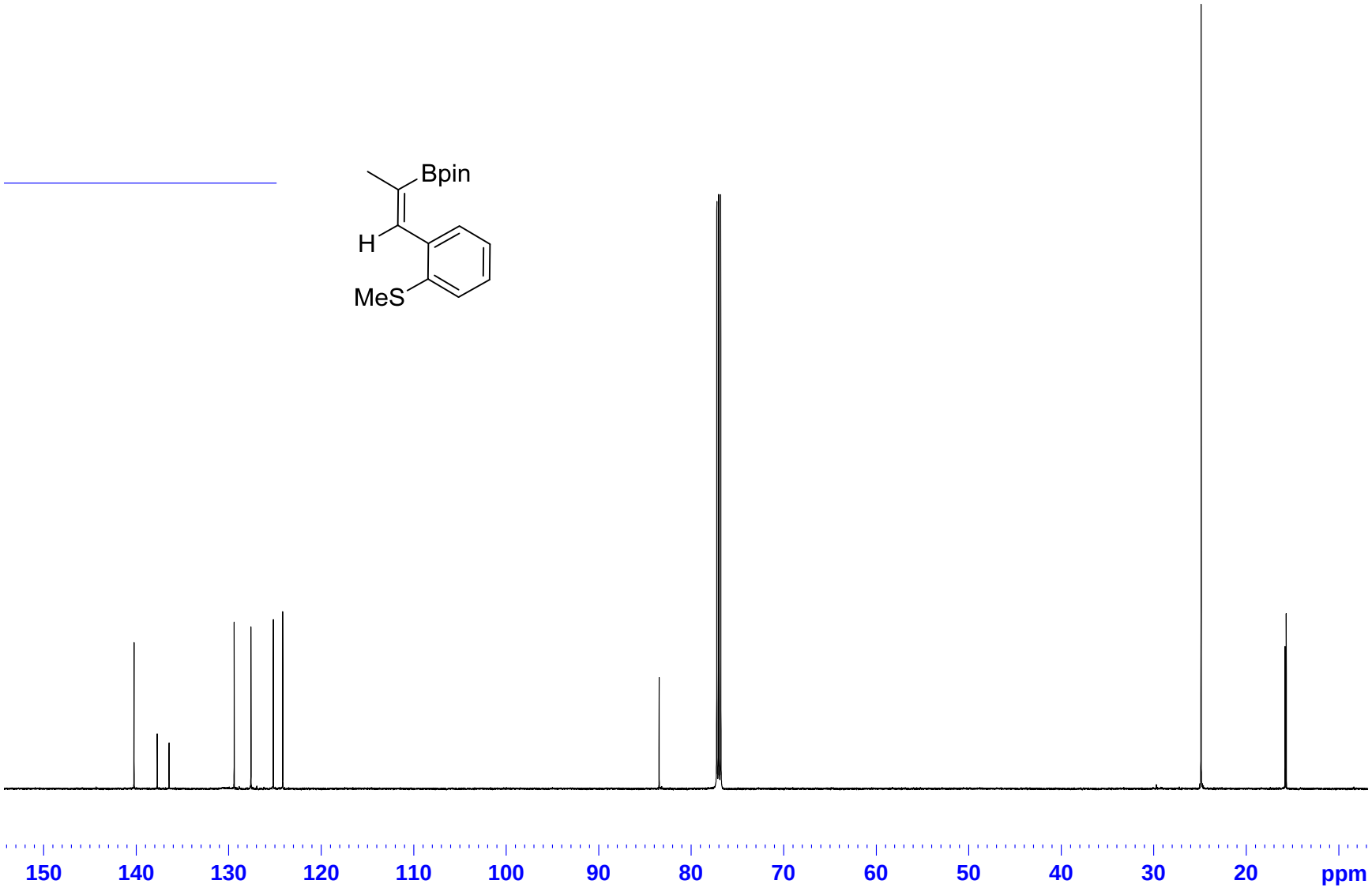

Bpin
H
N
O
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

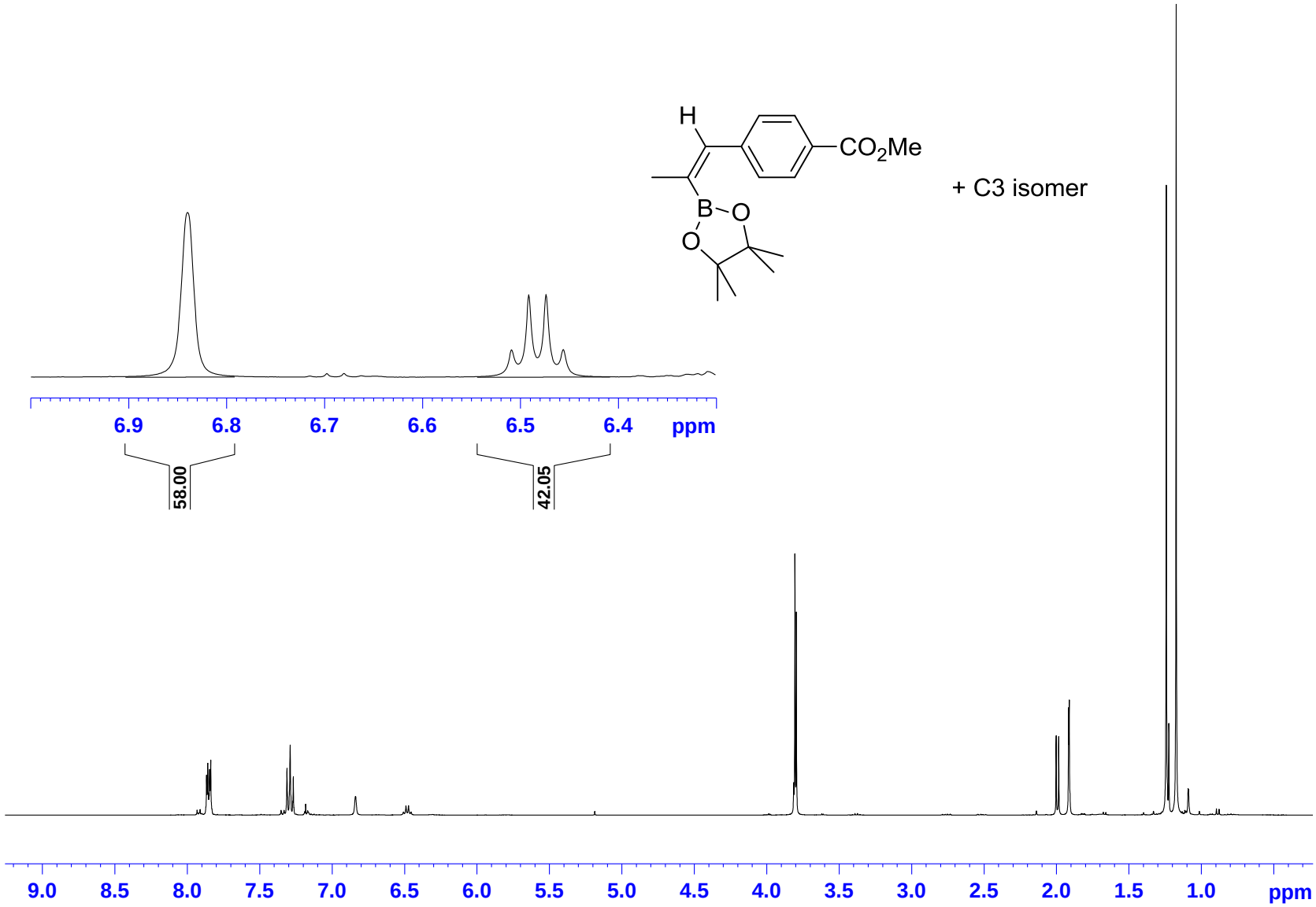

O
O
B
OTBS
H
+ C3 isomer
6.30
6.25
6.20
6.15
6.10
6.05
ppm
51.00
48.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

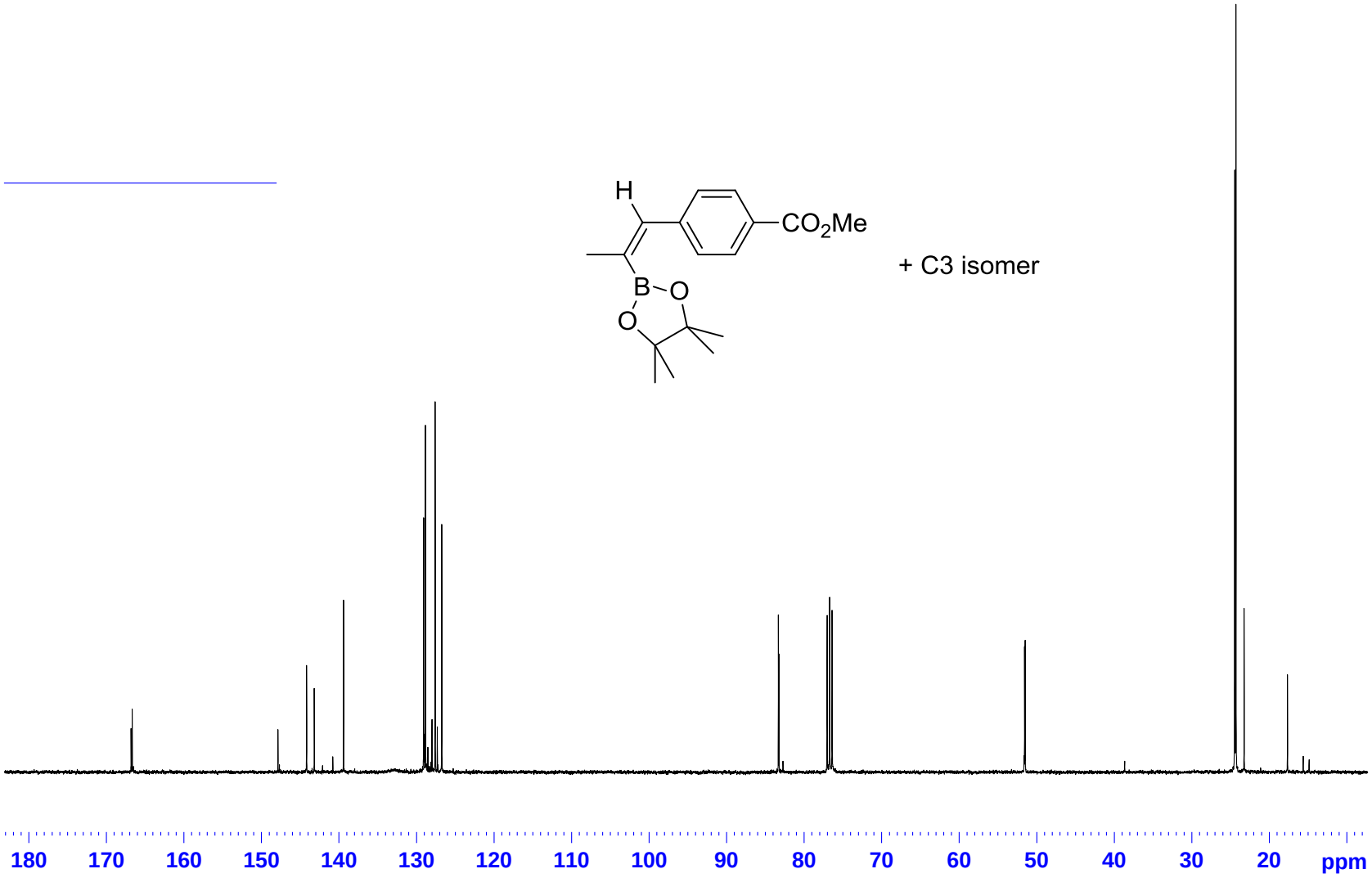

O
O
B
OTBS
H
+ C3 isomer
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

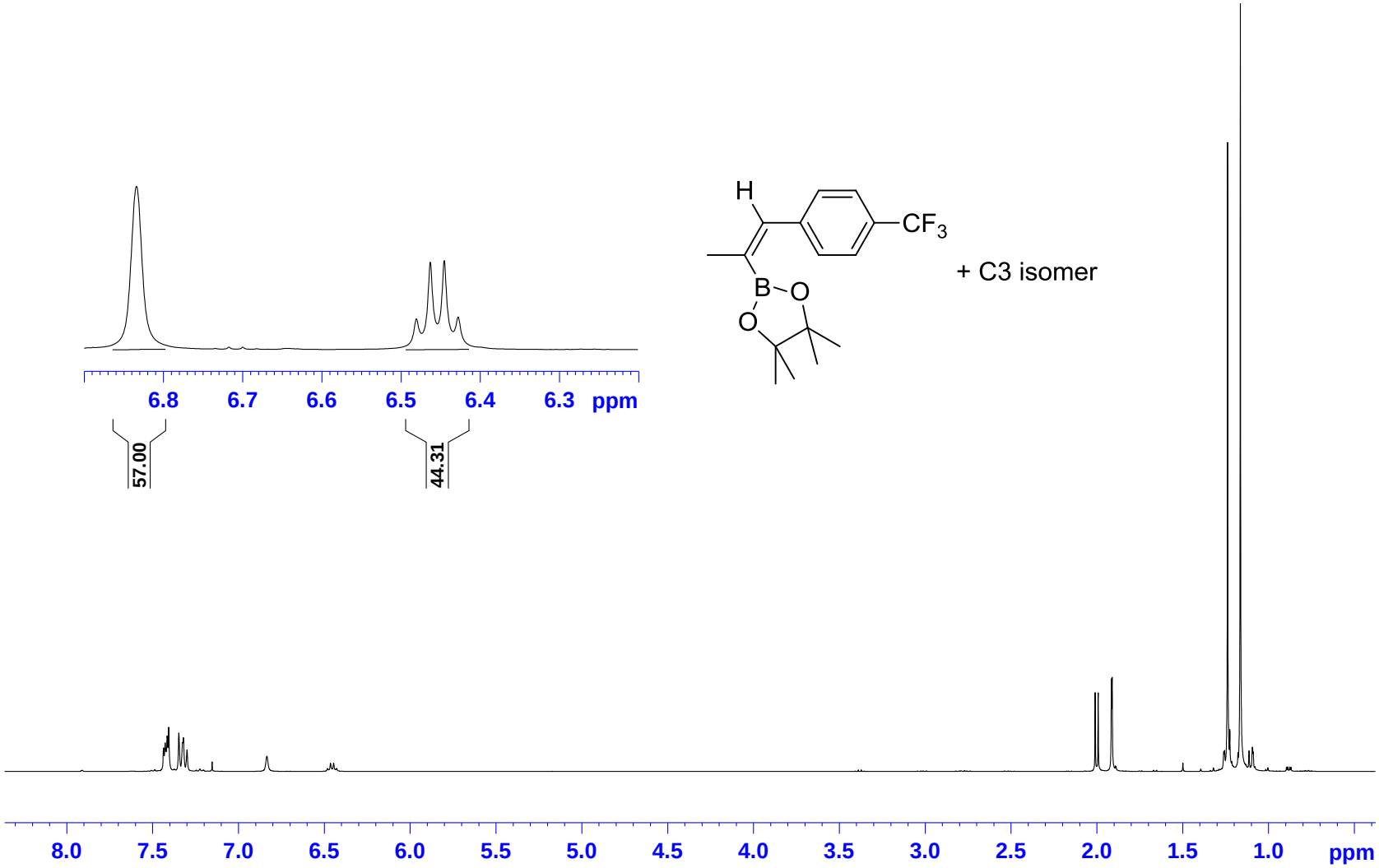

O
B
O
H
MeS
+ C3 isomer
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

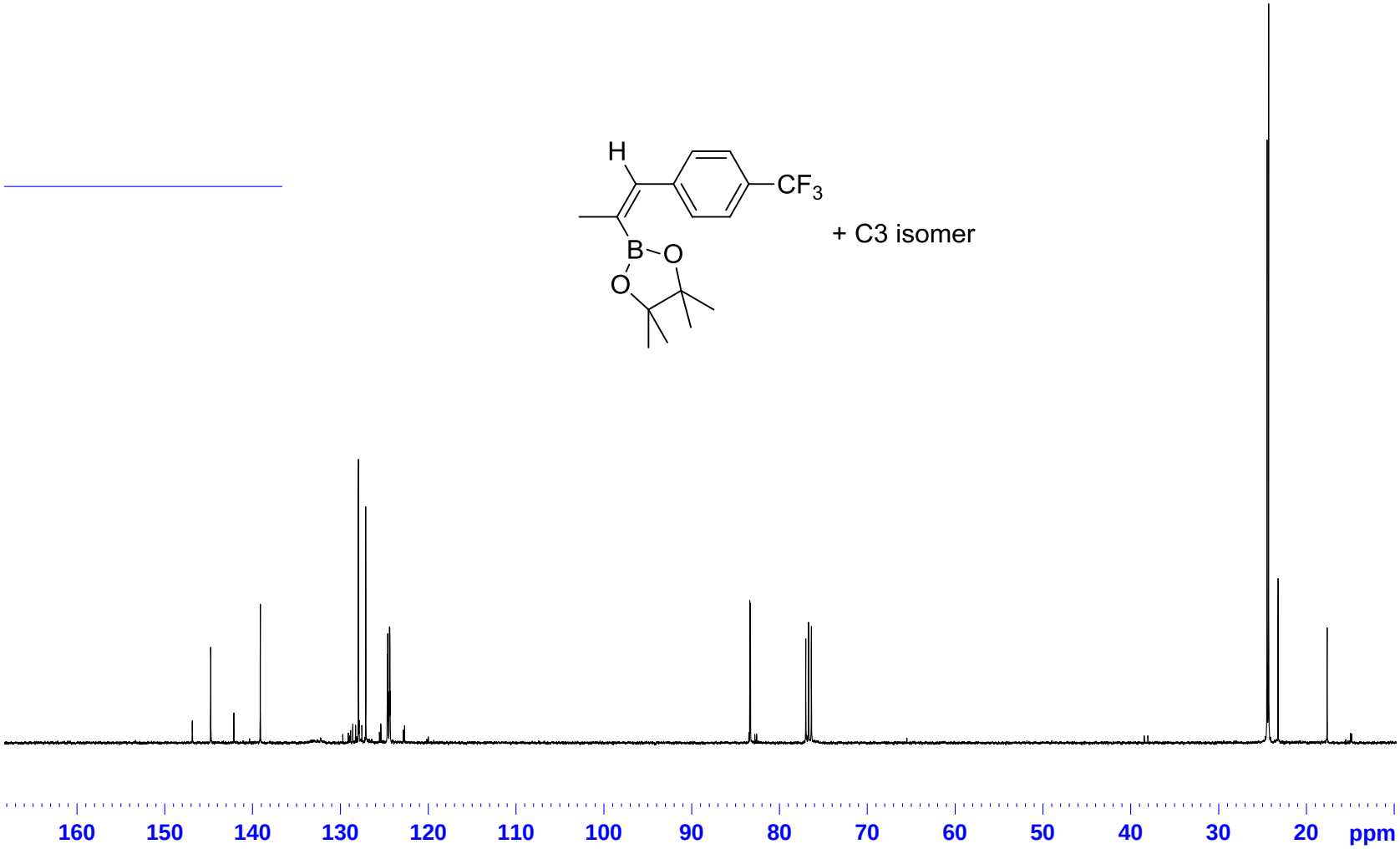

Bpin
H
MeS
7.4
7.3
7.2
7.1
7.0
ppm
0.87
1.75
1.03
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

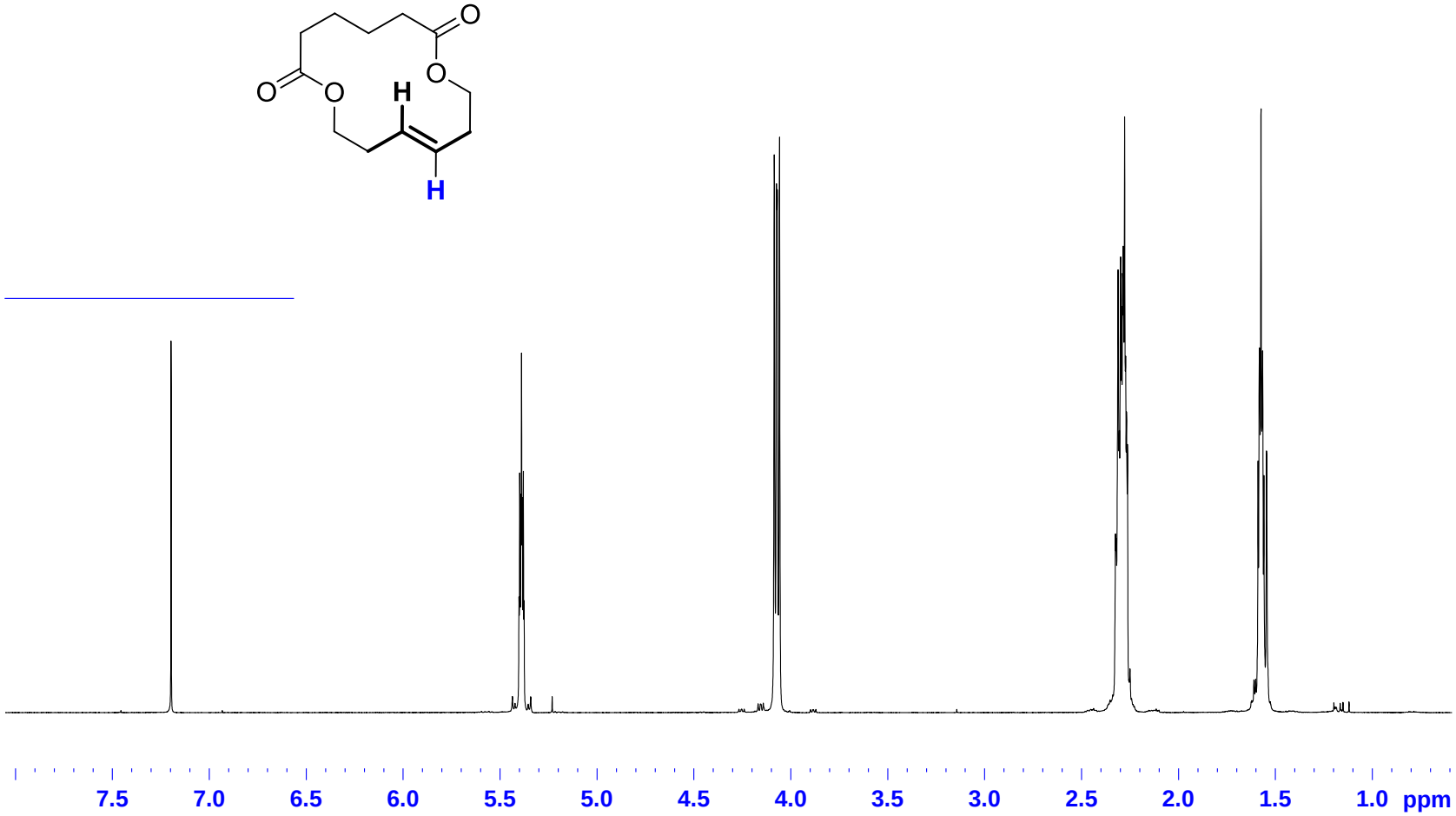

Bpin
H
MeS
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

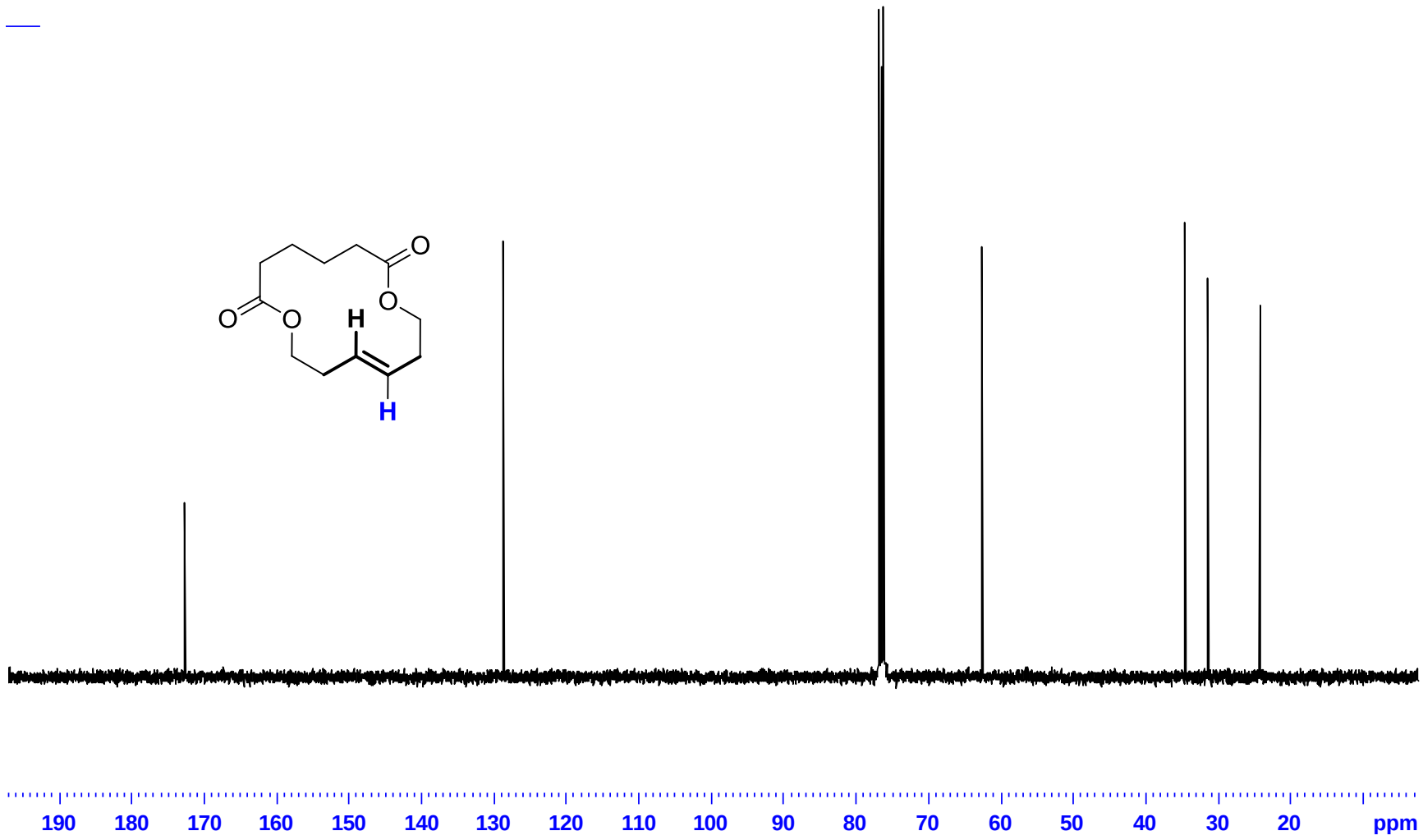

H
CO2Me
B
O
O
+ C3 isomer
6.9
6.8
6.7
6.6
6.5
6.4
ppm
58.00
42.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm


H
CO2Me
B
O
O
+ C3 isomer
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


H
CF3
B
O
O
+ C3 isomer
6.8
6.7
6.6
6.5
6.4
6.3
ppm
57.00
44.31
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
ppm


H
CF3
B
O
O
+ C3 isomer
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


O
O
O
O
H
H
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
ppm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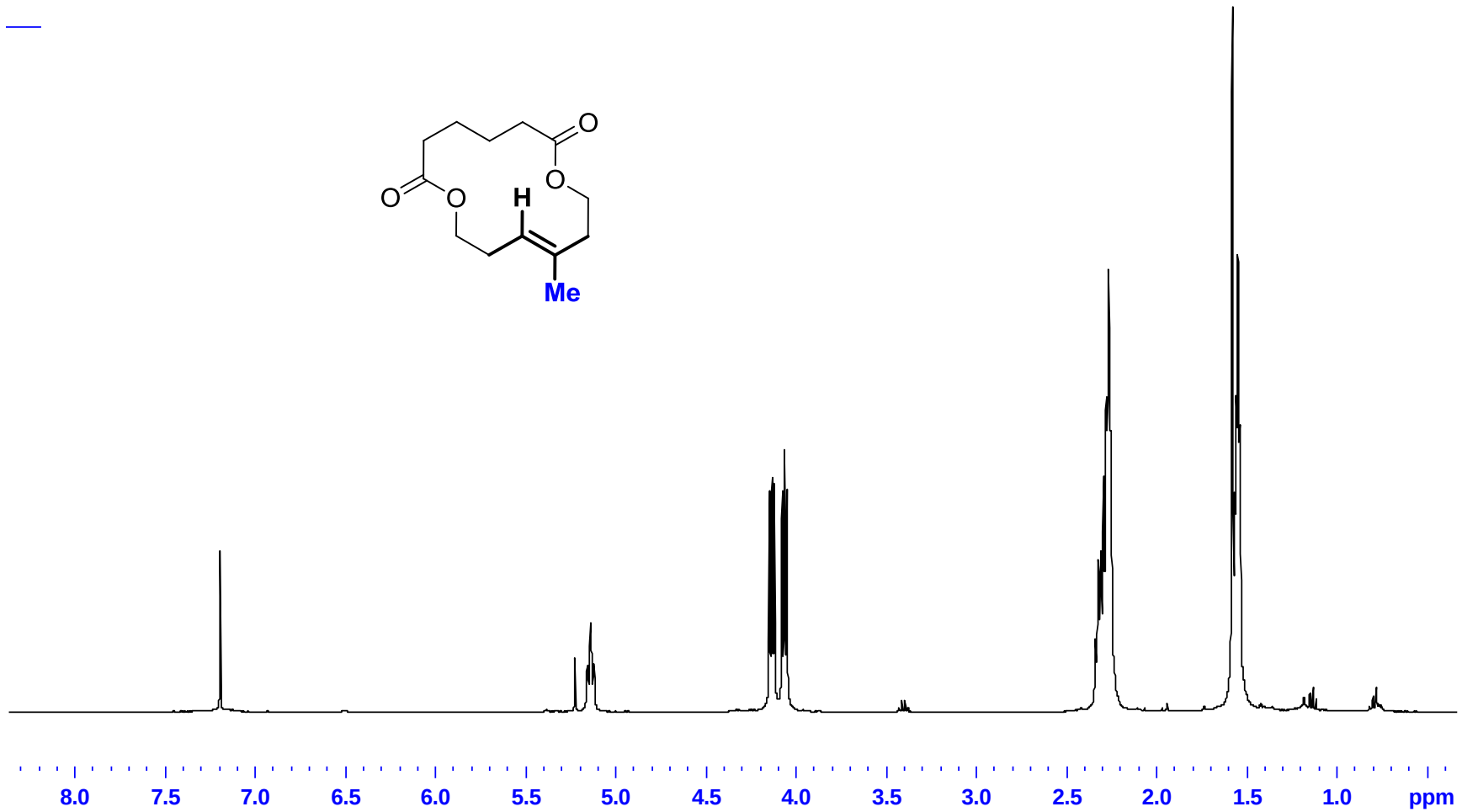
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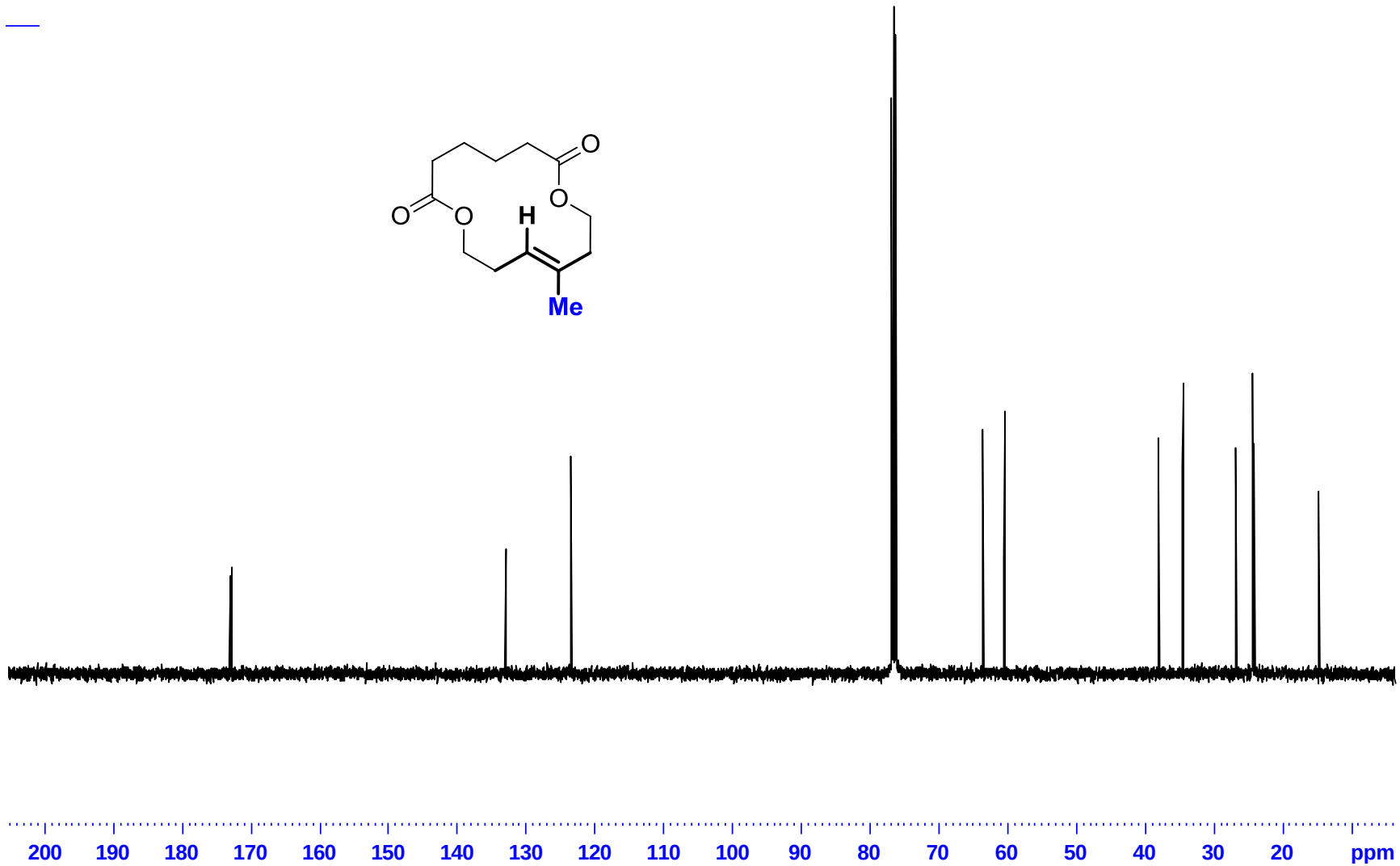
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20
ppm