Electronic Supplementary Information

Synthesis of Biologically Active Natural Products, Aspergillides A and B, Entirely from Biomass-Derived Platform Chemicals

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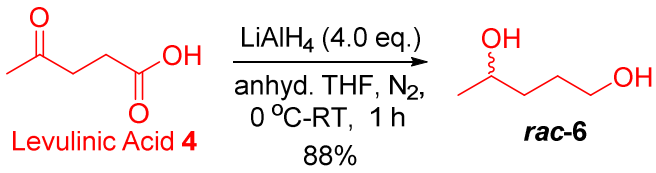
1. General Methods

All reagents were commercially purchased and were used as received for the reactions. All reactions were carried out in oven-dried glassware while THF was freshly distilled from Na/Benzophenone ketyl and DCM was freshly distilled from Calcium Hydride. Thin-layer chromatography (TLC) was conducted with Merck 60 F254 precoated silica gel plate (0.2 mm thickness) and visualized under UV, by potassium permanganate or ceric ammonium molybdate stain. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. ^{1}H-NMR spectra were performed on a Bruker Avance 300, Bruker Avance 400 or Bruker Avance 500 NMR spectrometer and are reported in ppm downfield from $SiMe_4$ (δ 0.0), relative to the signal of chloroform-d (δ = 7.26, singlet) or methanol-d_4 (δ = 3.31, quintet). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad; coupling constant(s) in Hz; integration. Proton-decoupled ^{13}C-NMR spectra were recorded on Bruker Avance 300 (75 MHz) or Bruker Avance 400 (100MHz) or Bruker Avance 500 (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 77.16 ppm or CD_2Cl_2 at 53.84 ppm). IR spectra were recorded using nujol mull technique for solids and recorded neat (or a concentrated solution of $CHCl_3$) for liquids on NaCl plates on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer were reported in frequency of absorption (cm^{-1}). High-resolution mass spectral analysis (HRMS) was performed on Q-Tof Premier mass spectrometer (Waters Corporation).

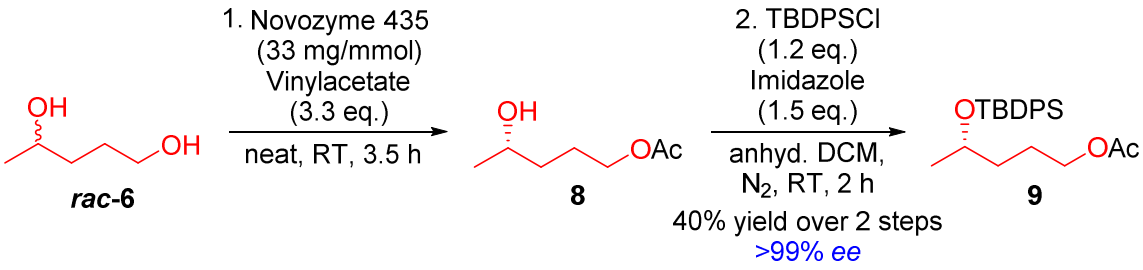
2. Synthesis and characterization of compounds



Pentane-1,4-diol (*rac*-6)[1]

To an oven-dried, vacuum cooled 250 mL round-bottom flask equipped with a stir bar was added levulinic acid **4** (2.0 mL, 2.29 g, 19.7 mmol, 1.0 equiv.) and anhydrous THF (20 mL) under N_2 atmosphere. The solution was cooled down to 0 ^{o}C before $LiAlH_4$ (39.5 mL, 2.0 M solution in THF, 79 mmol, 4.0 equiv.) was slowly added dropwise to give initial effervescence and then a white suspension. After addition, the mixture was allowed to warm to room temperature and allowed to stir at RT for an additional 1 h to give an almost clear solution. The mixture was cooled down to 0 ^{o}C and H_2O (3.1 mL) was slowly added dropwise, followed by addition of aqueous NaOH (3.1 mL, 15 wt%, 3.75 M) and finally H_2O (9.2 mL) to give a white suspension after stirring at room temperature for another 1 h. The suspension was filtered through a pad of celite, washed with ethyl acetate and dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: ethyl acetate) afforded ***rac*-6** as a colourless oil (1.81 g, 17.4 mmol, 88%). TLC (ethyl acetate): R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.90-3.82 (m, 1H), 3.73-3.63 (m, 2H), 2.48 (bs, 1H), 2.36 (bs, 1H), 1.69-1.47 (m, 4H), 1.22 (d, J = 6.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 68.1, 63.1, 36.4, 29.3, 23.8; FTIR (neat, NaCl, cm^{-1}): 3306, 2932, 1454, 1373, 1134; HRMS (ESI) *m/z* Calcd for $C_5H_{13}O_2$ $[M+H]^+$: 105.0916; found: 105.0921.

[1] (*R*)-pentan-1,4-diol: J. C. Killen, L. C. Axford, S. E. Newberry, T. J. Simpson and C. L. Willis, *Org. Lett.*, 2012, **14**, 4194-4197.



(*S*)-4-hydroxypentyl acetate (8)

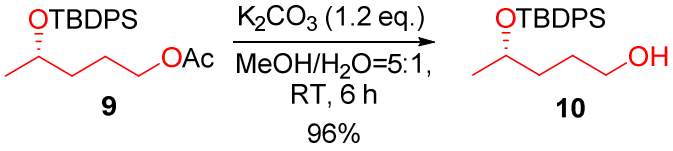
To a 25 mL round-bottom flask equipped with a stir bar was added pentane-1,4-diol ***rac*-6** (1.80 g, 17.3 mmol, 1.0 equiv.) and vinylacetate (5.3 mL, 4.91 g, 57.1 mmol, 3.3 equiv.) before Novozyme 435 (571 mg, 33 mg/mmol) was added. The suspension was allowed to stir at RT for 3.5 h before filtering through a pad of celite, washed with ethyl acetate and concentrated under reduced pressure to afford a crude mixture which is immediately used in the subsequent step without further purification.

Alternatively the crude mixture can be purified using silica gel chromatography (eluent: hexanes/ethyl acetate = 2:1) to afford **8** as a colourless oil. TLC (hexanes/ethyl acetate = 2:1): R_f = 0.13; $[\alpha]^{23}_D$ = +13.4 (c = 1.49, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.09 (t, *J* = 6.6 Hz, 2H), 3.84 (sextet, *J* = 6.2 Hz, 1H), 2.05 (s, 3H), 1.78-1.67 (m, 3H), 1.54-1.48 (m, 2H), 1.21 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.4, 67.5, 64.6, 35.4, 25.0, 23.6, 21.0; FTIR (neat, NaCl, cm^{-1}): 3426, 2967, 1736, 1454, 1368, 1140; HRMS (ESI) *m/z* Calcd for $C_7H_{15}O_3$ $[M+H]^+$: 147.1021; found: 147.1017.

(*S*)-4-((*tert*-butyldiphenylsilyl)oxy)pentyl acetate (9)

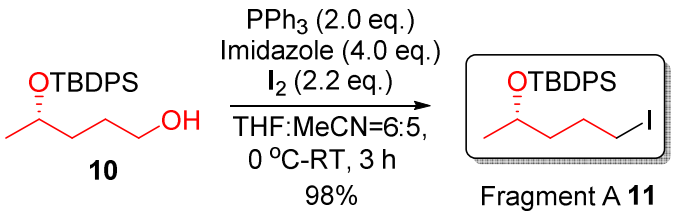
To the crude mixture obtained above in a 50 mL round-bottom flask equipped with a stir bar was added anhydrous CH_2Cl_2 (18 mL) under N_2 atmosphere. Imidazole (882 mg, 13.0 mmol, 1.5 equiv. with respect to 50% conversion) was then added at RT and stirred to achieve complete dissolution before *tert*-butyl(chloro)diphenylsilane (2.7 mL, 2.85 g, 10.4 mmol, 1.2 equiv. with respect to 50% conversion) was added. The mixture was allowed to stir at room temperature for 2 h before saturated aqueous NH_4Cl (10 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (10 mL x 3) and the combined organic phase washed with brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 50:1) to afford **9** as a colourless oil (2.66 g, 6.92 mmol, 40% over 2 steps out the theoretical maximum of 50%), *ee* = >99%. The *ee* was determined on Chiralcel OJ column with hexane/2-propanol = 100:0, flow = 0.5 mL/min, wavelength = 220 nm. Retention times: 10.1 min [(*R*)-enantiomer], 17.4 min [(*S*)-enantiomer]. TLC (hexanes/ethyl acetate = 2:1): R_f = 0.69; $[\alpha]^{21}_D$ = -12.9 (c = 2.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68-7.66 (m, 4H), 7.44-7.35 (m, 6H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.88 (sextet, *J* = 5.9 Hz, 1H), 2.01 (s, 3H), 1.65-1.61 (m, 2H), 1.50-1.46 (m, 2H), 1.06 (d, *J* = 6.2 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 171.3, 136.0, 136.0, 134.9, 134.5, 129.7, 129.6, 127.7, 127.6, 69.2, 64.8, 35.7. 27.2, 24.4, 23.2, 21.1, 19.4; FTIR (neat,

NaCl, cm^{-1}): 3071, 2961, 1740, 1589, 1427, 1363, 1111;HRMS (ESI) *m/z* Calcd for $C_{23}H_{32}NaO_3Si$ $[M+Na]^+$: 407.2018; found: 407.2023.



(*S*)-4-((*tert*-butyldiphenylsilyl)oxy)pentan-1-ol (10)[2]

To (*S*)-4-((*tert*-butyldiphenylsilyl)oxy)pentyl acetate **9** (2.60 g, 6.77 mmol, 1.0 equiv.) in a 25 mL round-bottom flask equipped with a stir bar was added MeOH (15 mL) and H_2O (3 mL) before solid K_2CO_3 (1.12 g, 8.12 mmol, 1.2 equiv.) was added in one portion. The mixture was allowed to stir at RT for 6 h before saturated aqueous NH_4Cl (10 mL) and H_2O (10 mL) were added, extracted with ethyl acetate (25 mL x 4), the combined organic phase washed with brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1 to 2:1) to afford **10** as a colourless oil (2.22 g, 6.50 mmol, 96%). TLC (hexanes/ ethyl acetate = 2:1): R_f = 0.59; $[\alpha]^{20}_D$ = -9.3 (c = 0.45, MeOH), (Lit.[2]: $[\alpha]_D$ = -50.1 (c = 0.0051, MeOH); $[\alpha]^{21}_D$ = -6.5 (c = 1.00, $CHCl_3$), (Lit. (enantiomer)[3]: $[\alpha]^{22}_D$ = +5.4 (c = 2.10, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.68-7.67 (m, 4H), 7.42-7.41 (m, 2H), 7.41-7.35 (m, 4H), 3.91 (sextet, *J* = 6.0 Hz, 1H), 3.55-3.53 (m, 2H), 1.60-1.56 (m, 3H), 1.52-1.50 (m, 2H), 1.07 (d, *J* = 6.2 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 136.0, 136.0, 134.8, 134.5, 129.7, 129.7, 127.7, 127.6, 69.4, 63.2, 35.7, 28.4, 27.2, 23.0, 19.4; FTIR (neat, NaCl, cm^{-1}): 3361, 3070, 2932, 1589, 1427, 1367, 1111; HRMS (ESI) *m/z* Calcd for $C_{21}H_{31}O_2Si$ $[M+H]^+$: 343.2093; found: 343.2104.

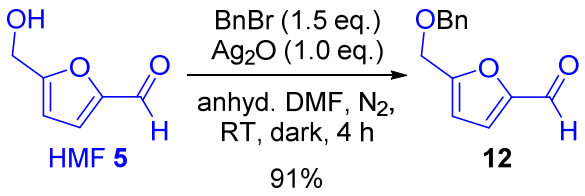


(*S*)-*tert*-butyl((5-iodopentan-2-yl)oxy)diphenylsilane (11)[3]

To a 250 mL round-bottom flask equipped with a stir bar was added PPh_3 (3.13 g, 11.9 mmol, 2.0 equiv.) and imidazole (1.62 g, 23.8 mmol, 4.0 equiv.) before THF/MeCN (6:5) (15 mL) was added and cooled down to 0 °C to give a brown solution. I_2 (3.33 g, 13.1 mmol, 2.2

[2] G. B. Jones, G. Hynd, J. M. Wright and A. Sharma, *J. Org. Chem.*, 1999, **65**, 263-265.
[3] (*R*)-*tert*-butyl((5-iodopentan-2-yl)oxy)diphenylsilane (enantiomer): T. Motozaki, K. Sawamura, A. Suzuki, K. Yoshida, T. Ueki, A. Ohara, R. Munakata, K.-i. Takao and K.-i. Tadano, *Org. Lett.*, 2005, **7**, 2265-2267.

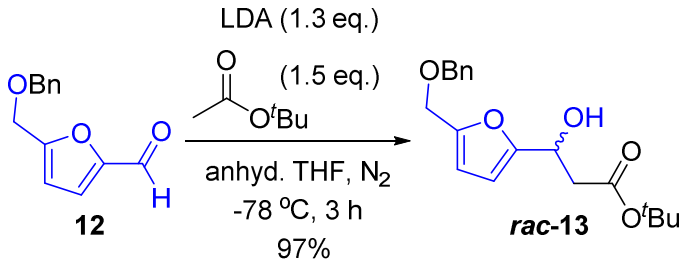
equiv.) was then added in one portion to the stirring mixture at 0 °C and allowed to stirred at 0 °C for 1 h to give a brown suspension. (*S*)-4-((*tert*-butyldiphenylsilyl)oxy)pentan-1-ol **10** (2.04 g, 5.96 mmol, 1.0 equiv.) dissolved in THF (15 mL) was then added to the suspension was allowed to stir at room temperature for 3 h before saturated aqueous $Na_2S_2O_3$ (10 mL) was added and concentrated under reduced pressure. Ethyl acetate (30 mL) was added to dilute the mixture and the layers were separated, the aqueous phase extracted with EA (30 mL x 3), the combined organic phase washed with brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 50:1) to afford **11** as a pale yellow oil (2.63 g, 5.82 mmol, 98%). TLC (hexanes/ethyl acetate = 20:1): R_f = 0.76; $[\alpha]^{20}_D$ = -20.2 (c = 2.17, $CHCl_3$), (Lit.(enantiomer)[3]: $[\alpha]^{22}_D$ = +20.5 (c = 1.93, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.68-7.66 (m, 4H), 7.43-7.35 (m, 6H), 3.87 (sextet, *J* = 5.9 Hz, 1H), 3.11-3.04 (m, 2H), 1.87-1.82 (m, 2H), 1.56-1.49 (m, 2H), 1.06 (d, *J* = 6.2 Hz, 3H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 136.0, 136.0, 134.8, 134.4, 129.7, 129.7, 127.7, 127.6, 68.7, 40.3, 29.5, 27.2, 23.4, 19.4, 7.4; FTIR (neat, NaCl, cm^{-1}): 3071, 2961, 1589, 1427, 1377, 1111; HRMS (ESI) *m/z* Calcd for $C_{21}H_{29}NaOSiI$ $[M+Na]^+$: 475.0930; found: 475.0946.



5-((benzyloxy)methyl)furan-2-carbaldehyde (12)[4]

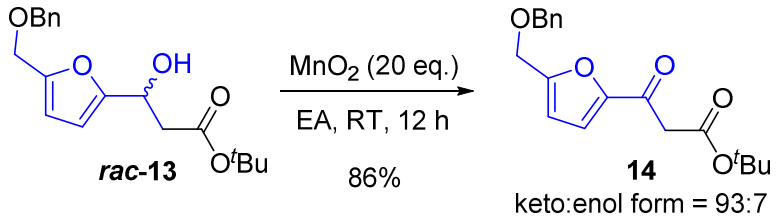
To an oven-dried, vacuum cooled 250 mL round-bottom flask equipped with a stir bar was added 5-(hydroxymethyl)furan-2-carbaldehyde **5** (6.11 g, 48.5 mmol, 1.0 equiv.) and anhydrous DMF (35 mL) under N_2 atmosphere before benzyl bromide (8.6 mL, 12.4 g, 72.7 mmol, 1.5 equiv.) and silver oxide (11.3 g, 48.5 mmol, 1.0 equiv.) were added. The round-bottom flask was covered with aluminium foil to exclude light and the suspension was allowed to stir at room temperature for 4 h. The suspension was diluted with ethyl acetate (30 mL) and filtered through a pad of celite, washed with ethyl acetate and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 30:1) to afford **12** as a yellow oil (9.53 g, 44.1 mmol, 91%). TLC (hexanes/ethyl acetate = 2:1): R_f = 0.50; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.63 (s, 1H), 7.36-7.30 (m, 5H), 7.21 (d, *J* = 3.5 Hz, 1H), 6.54 (d, *J* = 3.5 Hz, 1H), 4.61 (s, 2H), 4.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.9, 158.6, 152.8, 137.4, 128.7, 128.2, 128.1, 122.0, 111.4, 73.1, 64.3; FTIR (neat, NaCl, cm^{-1}): 3062, 3032, 2859, 1678, 1524, 1454, 1192; HRMS (ESI) *m/z* Calcd for $C_{13}H_{13}O_3$ $[M+H]^+$: 217.0865; found: 217.0863.

[4] L. Cottier, G. Descotes, L. Eymard and K. Rapp, *Synthesis*, 1995, 303-306.



tert-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-hydroxypropanoate (_rac_-13)

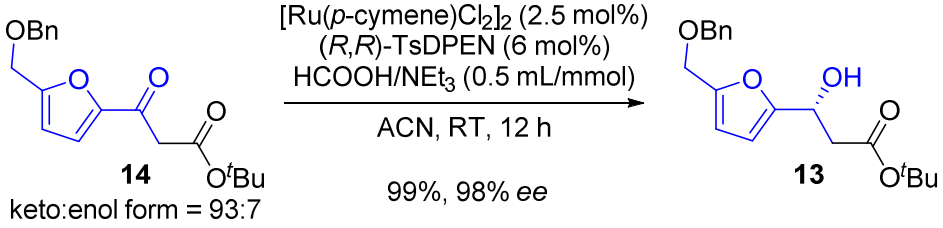
To an oven-dried, vacuum cooled 250 mL round-bottom flask equipped with a stir bar was added diisopropylamine (9.2 mL, 6.60 g, 65.4 mmol, 1.5 equiv.) and anhydrous THF (15 mL) under N_2 atmosphere before cooling down to 0 ^{o}C. *n*-Butyllithium (35.4 mL, 1.6 m in hexanes, 56.7 mmol, 1.3 equiv.) was slowly added dropwise at 0 ^{o}C and stirred for 30 min before cooling down to -78 ^{o}C. *tert*-Butyl acetate (8.8 mL, 7.6 g, 65.4 mmol, 1.5 equiv.) dissolved in anhydrous THF (20 mL) was then slowly added dropwise to the mixture at -78 ^{o}C and stirred for 30 min. 5-((benzyloxy)methyl)furan-2-carbaldehyde **12** (9.41 g, 43.6 mmol, 1.0 equiv.) dissolved in anhydrous THF (45 mL) was then slowly added dropwise to the mixture at -78 ^{o}C and allowed to stir at -78 ^{o}C for an additional 3 h. Saturated aqueous NH_4Cl (20 mL) was slowly added to quench the reaction and the mixture was concentrated under reduced pressure before diluting with ethyl acetate (50 mL) and H_2O (50 mL). The layers were separated, the aqueous phase extracted with ethyl acetate (50 mL x 4), the combined organic phase washed with brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 6:1 to 2:1) to afford ***rac*-13** as a pale yellow oil (14.0 g, 42.3 mmol, 97%). TLC (hexanes/ethyl acetate = 2:1): R_f = 0.45; ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.35-7.30 (m, 5H), 6.27 (d, *J* = 3.2 Hz, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 5.10- 5.04 (m, 1H), 4.54 (s, 2H), 4.45 (s, 2H), 3.38 (d, *J* = 5.0 Hz, 1H), 2.82 (dd, *J* = 16.5 Hz, 7.6 Hz, 1H), 2.75 (dd, *J* = 16.4 Hz, 4.8 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.5, 155.4, 151.2, 138.0, 128.5, 128.0, 127.9, 110.3, 107.0, 81.8, 72.1, 64.6, 64.1, 40.9, 28.2; FTIR (neat, NaCl, cm^{-1}): 3443, 3060, 2980, 2929.9, 1726, 1454, 1151; HRMS (ESI) *m/z* Calcd for $C_{19}H_{25}O_5$ $[M+H]^+$: 333.1702; found: 333.1691.



tert-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-oxopropanoate (14)

To *tert*-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-hydroxypropanoate (***rac*-13**) (6.66 g, 20.1 mmol, 1.0 equiv.) in a 100 mL round-bottom flask equipped with a stir bar was added ethyl acetate (40 mL) and manganese dioxide (34.9 g, 401 mmol, 20 equiv.). The black

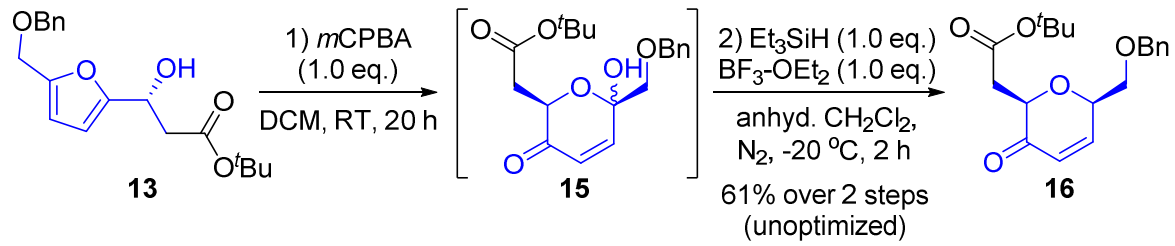
suspension was allowed to stir at room temperature for 12 h before being filtered through a pad of celite, washed with ethyl acetate and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1 to 2:1) to afford **14** (keto form : enol form = 93:7) as a pale yellow oil which solidified at -30 ^{o}C to give a pale yellow solid (5.69 g, 17.3 mmol, 86%). mp = 53-54 ^{o}C; TLC (hexanes/ethyl acetate = 2:1): R_f = 0.65; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.30 (m, 5H), 7.21 (d, *J* = 3.6 Hz, 1H, keto), 6.85 (d, *J* = 3.4 Hz, 1H, enol), 6.49 (d, *J* = 3.2 Hz, 1H, keto), 6.41 (d, *J* = 3.4 Hz, 1H, enol), 5.56 (s, 1H, enol), 4.59 (s, 2H, keto), 4.56 (s, 2H, enol), 4.54 (s, 2H, keto), 4.49 (s, 2H, enol), 3.74 (s, 2H), 1.52 (s, 9H, enol), 1.44 (s, 9H, keto); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 181.6, 166.3, 157.1, 151.9, 137.4, 128.6, 128.1, 128.0, 119.0, 111.6, 82.2, 72.8, 64.2, 46.9, 28.0 (enol peaks not depicted); FTIR (Nujol, NaCl, cm^{-1}): 3117, 2953, 2922, 2852, 1732, 1667, 1454, 1138; HRMS (ESI) *m/z* Calcd for $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1545; found: 333.1547.



(*R*)-*tert*-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-hydroxypropanoate (13)

To a 50 mL round-bottom flask equipped with a stir bar was added dichloro(*p*-cymene)ruthenium(II) dimer (263 mg, 0.43 mmol, 2.5 mol%), (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine[5] (376 mg, 1.03 mmol, 6 mol%) and MeCN (34 mL) before triethylamine (356 μL, 260 mg, 2.57 mmol, 15 mol%) was added. The mixture was allowed to stir at room temperature for 1 h to give a dark orange solution before $5HCOOH{\cdot}2NEt_3$ azeotrope (8.6 mL) was added. The mixture was then transferred to another 50 mL round-bottom flask equipped with a stir bar containing *tert*-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-oxopropanoate **14** (5.66 g, 17.2 mmol, 1.0 equiv.) and allowed to stir at room temperature for 12 h. The mixture was concentrated under reduced pressure and purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 4:1) to afford **13** as a pale yellow oil (5.66 g, 17.0 mmol, 99%, *ee* = 98%). The *ee* was determined on Chiralcel OB-H column with hexane/2-propanol = 90:10, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 10.8 min [(*S*)-enantiomer], 15.4 min [(*R*)-enantiomer]. $[\alpha]^{22}_{D}$ = +21.9 (c = 2.05, $CHCl_3$), see ***rac*-13** for the rest of the characterization data.

[5] Lutz F. Tietze, Y. Zhou and E. Töpken, *Eur. J. Org. Chem.*, 2000, 2247-2252.



tert-butyl (_R_)-2-(6-((benzyloxy)methyl)-6-hydroxy-3-oxo-3,6-dihydro-2_H_-pyran-2-yl) acetate (15)

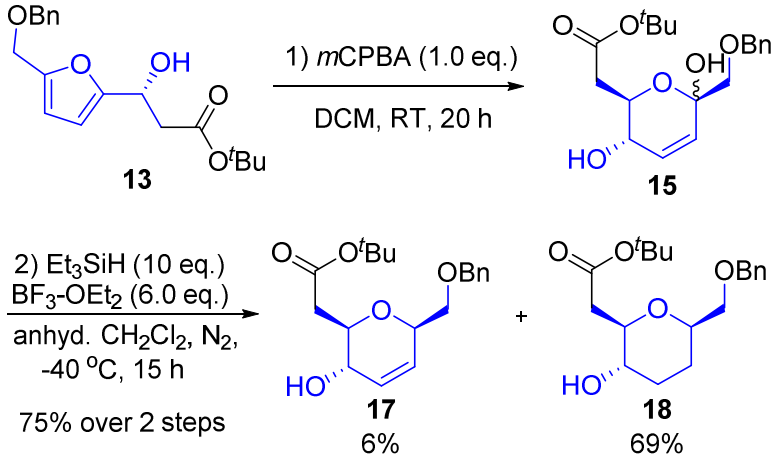
To (*R*)-*tert*-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-hydroxypropanoate (**13**) (445 mg, 1.34 mmol, 1.0 equiv.) in a 25 mL round-bottom flask equipped with a stir bar was added CH_2Cl_2 (4.5 mL) and then *meta*-chloroperoxybenzoic acid (329 mg, ~70 wt. %, 1.34 mmol, 1.0 equiv.) in one portion. The mixture was allowed to stir at room temperature for 15 h to give a white suspension before saturated aqueous $NaHCO_3$ (5 mL) was added. The layers were separated, the aqueous phase extracted with CH_2Cl_2 (5 mL x 3), the combined organic phase washed with water (5 mL), brine (5 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure to afford crude **15** as a mixture of isomers (major:minor = 91:9) which is immediately used in the subsequent step without further purification.

Alternatively, the crude mixture can be purified using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1 to 1:1) to afford **15** as a mixture of isomers (major:minor = 91:9) as a pale yellow oil. TLC (hexanes/ethyl acetate = 2:1): R_f = 0.38; $[\alpha]^{22}_D$ = +41.0 (c = 3.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.36-7.32 (m, 5H), 6.89 (d, *J* = 10.4 Hz, 1H, minor), 6.81 (d, *J* = 10.3 Hz, 1H, major), 6.19 (d, *J* = 10.4 Hz, 1H, minor), 6.13 (d, *J* = 10.3 Hz, 1H, major), 4.94 (dd, *J* = 6.9 Hz, 4.4 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.43 (bs, 1H, minor), 4.01 (bs, 1H, major), 3.62 (d, *J* = 10.3 Hz, 1H), 3.57 (d, *J* = 10.3 Hz, 1H), 2.88 (dd, *J* = 16.5 Hz, 4.4 Hz, 1H), 2.71 (dd, *J* = 16.5 Hz, 6.9 Hz, 1H), 1.44 (s, 9H, minor), 1.42 (s, 9H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.4, 194.9 (minor), 169.8, 147.5 (minor), 145.2, 137.4, 128.7, 128.2, 128.1, 128.0, 127.9 (minor), 127.9 (minor), 93.9 (minor), 93.2, 81.8 (minor), 81.3, 75.1 (minor), 74.3, 74.1, 74.0 (minor), 73.0 (minor), 71.8, 39.3 (minor), 36.7, 28.2; FTIR (neat, NaCl, cm^{-1}): 3401, 3067, 3030, 2978, 2932, 2868, 1730, 1694, 1632; HRMS (ESI) *m/z* Calcd for $C_{19}H_{25}O_6$ $[M+H]^+$: 349.1651; found: 349.1643.

tert-butyl 2-((2_R_,6_R_)-6-((benzyloxy)methyl)-3-oxo-3,6-dihydro-2_H_-pyran-2-yl)acetate (16)

To the crude mixture of **15** obtained above in a 25 mL round-bottom flask equipped with a stir bar was added anhydrous CH_2Cl_2 (6.7 mL) under N_2 atmosphere. Triethylsilane (195 μL, 142 mg, 1.34 mmol, 1.0 equiv.) was added and cooled down to -20 °C before boron trifluoride diethyl etherate (165 μL, 190 mg, 1.34 mmol, 1.0 equiv.) was slowly added dropwise and stirred at -20 °C for another 2 h. The reaction was quenched with saturated aqueous NH_4Cl (5 mL) and H_2O (2 mL) before warming to room temperature. The layers

were separated, the aqueous phase extracted with CH_2Cl_2 (5 mL x 4), the combined organic phase washed with water (5 mL), brine (5 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1 to 2:1) to afford **16** (271 mg, 0.82 mmol, 61% over 2 steps) as a yellow oil. TLC (hexanes/ethyl acetate = 2:1): R_f = 0.50; $[\alpha]^{22}_D$ = +70.4 (c = 2.21, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.36-7.30 (m, 5H), 7.07 (dd, *J* = 10.4 Hz, 1.5 Hz, 1H), 6.18 (dd, *J* = 10.4 Hz, 2.5 Hz, 1H), 4.64-4.56 (m, 3H), 4.45 (ddd, *J* = 7.1 Hz, 4.6 Hz, 2.2 Hz, 1H), 3.71 (dd, *J* = 10.0 Hz, 5.6 Hz, 1H), 3.58 (dd, *J* = 10.0 Hz, 5.9 Hz, 1H), 2.93 (dd, *J* = 16.5 Hz, 4.5 Hz, 1H), 2.62 (dd, *J* = 16.4 Hz, 7.2 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.1, 170.0, 148.9, 137.8, 128.6, 128.0, 127.9, 127.4, 81.1, 77.7, 74.0, 73.8, 71.2, 36.8, 28.2; FTIR (neat, NaCl, cm^{-1}): 3057, 3034, 2982, 2934, 2874, 1728, 1628; HRMS (ESI) *m/z* Calcd for $C_{19}H_{25}O_5$ $[M+H]^+$: 333.1702; found: 333.1705.



***tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-hydroxy-3,6-dihydro-2*H*-pyran-2-yl) acetate (17)**

***tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-hydroxytetrahydro-2*H*-pyran-2-yl) acetate (18)**

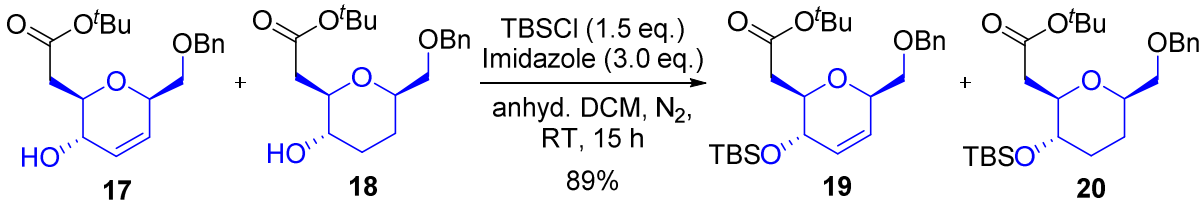
To (*R*)-*tert*-butyl 3-(5-((benzyloxy)methyl)furan-2-yl)-3-hydroxypropanoate (**13**) (5.66 g, 17.1 mmol, 1.0 equiv.) in a 100 mL round-bottom flask equipped with a stir bar was added CH_2Cl_2 (40 mL) and then *meta*-chloroperoxybenzoic acid (4.19 g, ~70 wt. %, 17.1 mmol, 1.0 equiv.) in one portion. The mixture was allowed to stir at room temperature for 20 h to give a white suspension before saturated aqueous $NaHCO_3$ (80 mL) was added. The layers were separated, the aqueous phase extracted with CH_2Cl_2 (80 mL x 3), the combined organic phase washed with water (50 mL), brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure to afford crude **15** as a mixture of isomers (major:minor = 91:9) which is immediately used in the subsequent step without further purification.

To the crude mixture of **15** obtained above in a 100 mL round-bottom flask equipped with a stir bar was added anhydrous CH_2Cl_2 (85 mL) under N_2 atmosphere. Triethylsilane (24.8 mL,

18.1 g, 170 mmol, 10 equiv.) was added and cooled down to -40 ^{o}C before boron trifluoride diethyl etherate (12.6 mL, 14.5 g, 102 mmol, 6.0 equiv.) was slowly added *via* a syringe pump over 30 min and stirred at -40 ^{o}C for another 15 h. The reaction was quenched with saturated aqueous NH_4Cl (50 mL) and H_2O (20 mL) before warming to room temperature. The layers were separated, the aqueous phase extracted with CH_2Cl_2 (50 mL x 4), the combined organic phase washed with water (50 mL), brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1 to 2:1) to afford **17** (343 mg, 1.03 mmol, 6% over 2 steps) and **18** (3.96 g, 11.8 mmol, 69% over 2 steps) separately as pale yellow oils. Total yield: 75% over 2 steps.

17: TLC (hexanes/ethyl acetate = 2:1): R_f = 0.30; $[\alpha]^{22}_D$ = +70.1 (c = 0.72, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.34-7.30 (m, 5H), 5.86 (d, *J* = 10.5 Hz, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 4.57 (s, 2H), 4.34 (m, 1H), 4.05 (m, 1H), 3.71-3.64 (m, 1H), 3.51 (dd, *J* = 10.2 Hz, 6.0 Hz, 1H), 3.46 (dd, *J* = 10.1 Hz, 5.1 Hz, 1H), 2.75 (dd, *J* = 15.5 Hz, 5.7 Hz, 1H), 2.59 (dd, *J* = 15.5 Hz, 6.8 Hz, 1H), 2.37 (bs, 1H), 1.46 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.6, 138.3, 130.3, 128.8, 128.5, 127.9, 127.8, 81.3, 76.1, 74.7, 73.5, 72.4, 68.2, 40.4, 28.2; FTIR (neat, NaCl, cm^{-1}): 3424, 3060, 2978, 2930, 2868, 1732, 1620; HRMS (ESI) *m/z* Calcd for $C_{19}H_{27}O_5$ $[M+H]^+$: 335.1858; found: 335.1854.

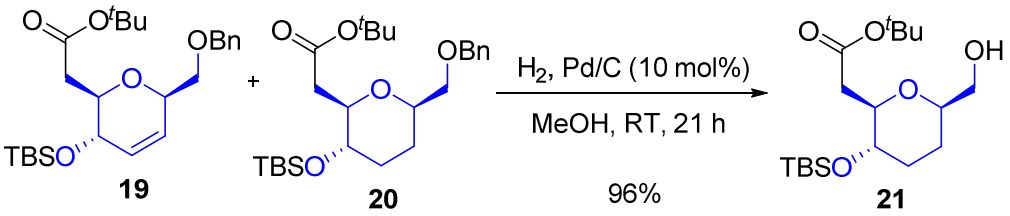
18: TLC (hexanes/ethyl acetate = 2:1): R_f = 0.23; $[\alpha]^{23}_D$ = +24.1 (c = 2.37, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.33-1.28 (m, 5H), 4.57 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 3.58-3.57 (m, 1H), 3.58-3.57 (m, 1H), 3.53-3.51 (m, 1H), 3.50-3.46 (m, 1H), 3.41 (dd, *J* = 10.1 Hz, 4.4 Hz, 1H), 3.36 (m, 1H), 2.72 (dd, *J* = 15.2 Hz, 5.5 Hz, 1H), 2.50 (dd, *J* = 15.3 Hz, 6.5 Hz, 1H), 2.23 (bs, 1H), 2.14-2.12 (m, 1H), 1.76-1.73 (m, 1H), 1.47 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.8, 138.5, 128.5, 127.8, 127.7, 81.1, 78.9, 77.0, 73.5, 72.9, 71.0, 40.5, 32.8, 28.2, 28.0; FTIR (neat, NaCl, cm^{-1}): 3443, 3060, 2978, 2934, 2868, 1732, 1603; HRMS (ESI) *m/z* Calcd for $C_{19}H_{29}O_5$ $[M+H]^+$: 337.2015; found: 337.2011.



tert-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-((_tert_-butyldimethylsilyl)oxy)-3,6-dihydro-2*H*-pyran-2-yl)acetate (19)

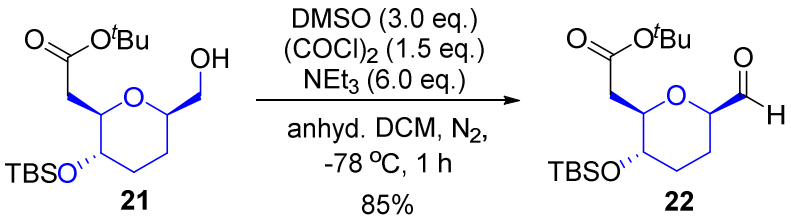
tert-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-((_tert_-butyldimethylsilyl)oxy) tetrahydro-2*H*-pyran-2-yl)acetate (20)

To a mixture of *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-hydroxy-3,6-dihydro-2*H*-pyran-2-yl)acetate **17** (343 mg, 1.03 mmol) and *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-hydroxytetrahydro-2*H*-pyran-2-yl)acetate **18** (3.96 g, 11.8 mmol) in a 50 mL round-bottom flask equipped with a stir bar was added anhydrous CH_2Cl_2 (26 mL) under N_2 atmosphere. Imidazole (2.62 g, 38.5 mmol, 3.0 equiv. w.r.t combined amount of both reactants) was then added at RT and stirred to achieve complete dissolution before *tert*-butyl(chloro)dimethylsilane (2.90 g, 19.2 mmol, 1.5 equiv. w.r.t combined amount of both reactants) was added. The mixture was allowed to stir at room temperature for 15 h before saturated aqueous NH_4Cl (10 mL) and H_2O (5 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (10 mL x 3) and the combined organic phase washed with H_2O (5 mL) and brine (5 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 40:1 to 20:1) to afford **19** and **20** as an inseparable mixture (colourless oil) (5.14 g, 11.4 mmol, 89%). TLC (hexanes/ethyl acetate = 10:1): R_f = 0.39; $[\alpha]^{23}_D$ = +48.5 (c = 1.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33-7.27 (m, 5H), 5.76 (m, 2H, **19**), 4.58-4.52 (m, 2H), 4.35 (m, 1H, **19**), 4.08-4.05 (m, 1H, **19**), 3.75 (m, 1H, **19**), 3.59-3.55 (m, 2H), 3.50-3.47 (m, 1H), 3.43-3.32 (m, 2H), 2.78-2.74 (m, 1H), 2.38-2.33 (m, 1H, **19**), 2.24 (dd, *J* = 14.8 Hz, 9.7 Hz, 1H), 2.01 (m, 1H), 1.76-1.73 (m, 1H), 1.44 (m, 11H), 0.06 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.3, 138.6, 128.4, 127.8, 127.6, 80.4, 79.8, 76.8, 73.4, 72.9, 70.9 , 39.5, 33.2, 28.3, 28.1, 25.9, 18.1, -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 3061, 3030, 2953, 2930, 2857, 1732; HRMS (ESI) *m/z* Calcd for $C_{25}H_{43}O_5Si$ $[M+H]^+$: 451.2880; found: 451.2887.



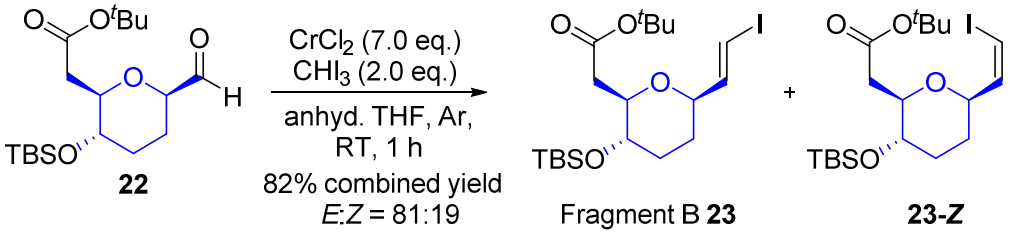
tert-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)acetate (21)

To a mixture of *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-((*tert*-butyldimethyl silyl)oxy)-3,6-dihydro-2*H*-pyran-2-yl)acetate **(19)** and *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((benzyloxy)methyl)-3-((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)acetate **(20)** **(**5.00 g, 11.1 mmol, 1.0 equiv.) in a 100 mL round-bottom flask equipped with a stir bar was added MeOH (30 mL) and palladium on carbon (1.18 g, 10 wt. %, 1.11 mmol, 10 mol%). The round-bottom flask was evacuated and backfilled with H_2 (balloon) thrice and allowed to stir at RT for 21 h, filtered through a short plug of silica gel, washed with ethyl acetate and concentrated to afford *tert*-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl)acetate **21** as a colourless oil (3.84 g, 10.7 mmol, 96%). TLC (hexanes/ethyl acetate = 2:1): R_f = 0.43; $[\alpha]^{23}_D$ = +42.8 (c = 1.90, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.58-3.54 (m, 2H), 3.48-3.43 (m, 2H), 3.32 (td, *J* = 9.6 Hz, 4.2 Hz, 1H), 2.77 (dd, *J* = 14.8 Hz, 2.8 Hz, 1H), 2.20 (dd, *J* = 14.8 Hz, 9.9 Hz, 1H), 2.02-1.99 (m, 1H), 1.70 (bs, 1H), 1.61-1.48 (m, 3H), 1.45 (s, 9H), 1.42-1.41 (m, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.2, 80.6, 79.6, 77.8, 70.9, 65.7, 39.6, 32.9, 28.3, 26.8, 25.9, 18.0 , -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 3466, 2953, 2930, 2857, 1728; HRMS (ESI) *m/z* Calcd for $C_{18}H_{37}O_5Si$ $[M+H]^+$: 361.2410; found: 361.2417.



tert-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-formyltetrahydro-2*H*-pyran-2-yl)acetate (22)

To an oven-dried, vacuum cooled 250 mL round-bottom flask equipped with a stir bar was added anhydrous DMSO (2.2 mL, 2.40 g, 30.8 mmol, 3.0 equiv.) and anhydrous CH_2Cl_2 (20 mL) under N_2 atmosphere before cooling down to -78 ^oC. Oxalyl chloride (1.3 mL, 1.95 g, 15.4 mmol, 1.5 equiv.) was slowly added dropwise at -78 ^oC and stirred for 15 min. *tert*-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yl) acetate **21** (3.69 g, 10.3 mmol, 1.0 equiv.) dissolved in anhydrous CH_2Cl_2 (50 mL) was then slowly added dropwise to the mixture at -78 ^oC and stirred for 1 h. Triethylamine (8.5 mL, 6.21 g, 61.5 mmol, 6.0 equiv.) was then added in portion to the mixture at -78 ^oC and allowed to stir at -78 ^oC for an additional 15 min before warming to room temperature and stirred for another 30 min. Saturated aqueous NH_4Cl (20 mL) and H_2O (5 mL) was added to the mixture and the layers were separated, the aqueous phase extracted with CH_2Cl_2 (30 mL x 3), the combined organic phase washed with H_2O (10 mL), brine (10 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 30:1) to afford **22** as a pale yellow oil (3.12 g, 8.71 mmol, 85%). The aldehyde product is not very stable and should be stored a low temperature or used immediately in the subsequent step. TLC (hexanes/ethyl acetate = 2:1): R_f = 0.55; $[\alpha]^{22}_D$ = +84.4 (c = 1.72, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 9.59 (s, 1H), 3.78 (dd, *J* = 11.5 Hz, 2.4 Hz, 1H), 3.64 (td, *J* = 9.4 Hz, 2.7 Hz, 1H), 3.36 (td, *J* = 9.6 Hz, 4.2 Hz, 1H), 2.79 (dd, *J* = 15.1 Hz, 2.8 Hz, 1H), 2.30 (dd, *J* = 15.2 Hz, 9.6 Hz, 1H), 2.10-2.07 (m, 1H), 1.95-1.92 (m, 1H), 1.57-.50 (m, 2H), 1.46 (s, 9H), 0.87 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 201.5, 171.0, 81.1, 80.8, 79.8, 70.2, 39.2, 32.7, 28.3, 26.0, 25.9, 18.0, -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 2955, 2930, 2859, 1738, 1732, 1368; HRMS (ESI) *m/z* Calcd for $C_{18}H_{35}O_5Si$ $[M+H]^+$: 359.2254; found: 359.2247.



tert-butyl 2-((2*R*,3*S*,6*R*)-3-((_tert_-butyldimethylsilyl)oxy)-6-((*E*)-2-iodovinyl)tetrahydro-2*H*-pyran-2-yl)acetate (23)

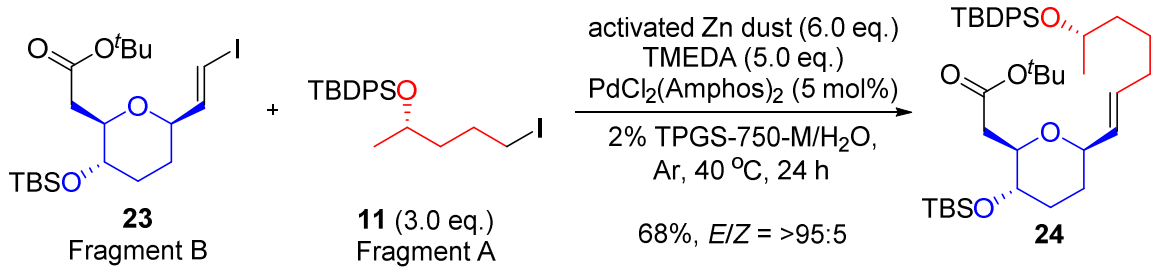
tert-butyl 2-((2*R*,3*S*,6*R*)-3-((_tert_-butyldimethylsilyl)oxy)-6-((*Z*)-2-iodovinyl)tetrahydro-2*H*-pyran-2-yl)acetate (23-*Z*)

To an oven-dried, vacuum-cooled 100 mL round-bottom flask equipped with a stir bar was added anhydrous chromium(II) chloride (5.39 g, 43.8 mmol, 7.0 equiv.) under Ar atmosphere and cooled down to 0 ^{o}C before anhydrous THF (26 mL) was slowly added at 0 ^{o}C to give a grey suspension. The mixture was allowed to warm to room temperature and a mixture containing *tert*-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-formyltetrahydro-2*H*-pyran-2-yl)acetate **(22)** (2.24 g, 6.26 mmol, 1.0 equiv.) and iodoform (4.93 g, 12.5 mmol, 2.0 equiv.) dissolved in anhydrous THF (13 mL) was slowly added dropwise at room temperature to the stirring suspension and allowed to stir for another 1 h to give a brown solution. H_2O (50 mL) and ethyl acetate (30 mL) was added and the layers were separated. The aqueous phase was extracted with ethyl acetate (50 mL x 3) and the combined organic phase washed with saturated aqueous $NaHCO_3$ (50 mL), saturated aqueous $Na_2S_2O_3$ (50 mL) and brine (30 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered through a pad of silica gel and concentrated under reduced pressure. Purification using silica gel chromatography in the dark (eluent: hexanes/ethyl acetate = 100:1) to afford **23** as the major product (colourless oil) (1.99 g, 4.13 mmol, 66%) and **23-*Z*** as the minor product (colourless oil) (481 mg, 1.00 mmol, 16%). The products were stored under Ar, in the absence of light at -20 ^{o}C and **23** was used in the subsequent step within a few days.

23: TLC (hexanes/ethyl acetate = 10:1): R_f = 0.54; $[\alpha]^{22}_D$ = +47.4 (c = 1.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.50 (dd, *J* = 14.5 Hz, 4.6 Hz, 1H), 6.31 (dd, *J* = 14.5 Hz, 1.5 Hz, 1H), 3.83-3.80 (m, 1H), 3.57 (td, *J* = 9.3 Hz, 2.9 Hz, 1H), 3.33 (td, *J* = 9.5 Hz, 4.4 Hz, 1H), 2.73 (dd, *J* = 14.8 Hz, 3.0 Hz, 1H), 2.23 (dd, *J* = 14.8 Hz, 9.7 Hz, 1H), 2.02-1.98 (m, 1H), 1.78-.174 (m, 1H), 1.44 (m, 11H), 0.87 (s, 9H) 0.05 (s, 3H), 0.05 (s,3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.2, 145.6, 80.6, 79.8, 78.9, 77.3, 70.5, 39.5, 33.2, 30.8, 28.3, 25.9, 18.1, -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 3053, 2953, 2930, 2857, 1730, 1612; HRMS (ESI) *m/z* Calcd for $C_{19}H_{36}IO_4Si$ $[M+H]^+$: 483.1428; found: 483.1425. ***rac*-23**: mp = 53-54 ^{o}C.

23-*Z*: mp = 71-72 ^{o}C; TLC (hexanes/ethyl acetate = 10:1): R_f = 0.46; $[\alpha]^{22}_D$ = +7.8 (c = 1.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.27-6.19 (m, 2H), 4.08 (dd, *J* = 8.8 Hz, 8.3 Hz, 1H), 3.60 (td, *J* = 9.3 Hz, 2.5 Hz, 1H), 3.35 (td, *J* = 9.7 Hz, 4.5 Hz, 1H), 2.76-2.71 (m, 1H), 2.19 (dd, *J* = 14.8 Hz, 9.5 Hz, 1H), 2.04-2.00 (m, 1H), 1.84-1.80 (m, 1H), 1.64-1.54

(m, 1H), 1.48-1.38 (m, 10H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s,3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm): 171.2, 142.0, 81.9, 80.7, 80.5, 80.0, 70.6, 39.8, 33.5, 29.9, 28.3, 26.0, 18.2, -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 3053, 2953, 2930, 2857, 1730, 1620; HRMS (ESI) *m/z* Calcd for $C_{19}H_{36}IO_4Si$ [M+H]$^+$: 483.1428; found: 483.1429. ***rac*-23-*Z***: mp = 71-72 °C.

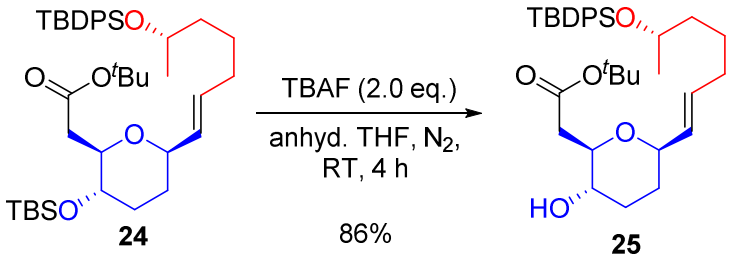


tert-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-((*S*,*E*)-6-((tert-butyldiphenyl silyl)oxy)hept-1-en-1-yl)tetrahydro-2*H*-pyran-2-yl)acetate (24)

To a 4 mL sample vial wrapped in aluminium foil containing *tert*-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-((*E*)-2-iodovinyl)tetrahydro-2*H*-pyran-2-yl)acetate **23** (300 mg, 0.62 mmol, 1.0 equiv.) and (*S*)-*tert*-butyl((5-iodopentan-2-yl)oxy)diphenylsilane **11** (844 mg, 1.87 mmol, 3.0 equiv.) was added 2% TPGS-750-M solution (1.2 mL) under Ar. Tetramethylethylenediamine (465 μL, 361 mg, 3.11 mmol, 5.0 equiv.) was then added with stirring. $PdCl_2Amphos_2$ (22 mg, 0.031 mmol, 5 mol%) and activated zinc dust[6] (244 mg, 3.73, 6.0 equiv.) were then added together, and the sample vial was sealed under Ar. The mixture was allowed to stir vigorously in the dark, in a pre-heated oil bath at 40 °C for 24 h and allowed to cool to room temperature. The mixture was filtered through a short pad of silica gel (washed with ethyl acetate) and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes to hexanes/ethyl acetate = 100:1) followed by Preparative Thin Layer Chromatography (eluent: hexanes/ethyl acetate = 100:1) afforded **24** as a pale yellow oil (286 mg, 0.42 mmol, 68%) as a mixture of *E*/*Z* isomers in the ratio >95/5. TLC (hexanes/ethyl acetate = 20:1): R_f = 0.53; $[\alpha]^{22}_D$ = +18.5 (c = 1.19, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 (dd, *J* = 7.9 Hz, 1.4 Hz, 4H), 7.43-7.34 (m, 6H), 5.57 (dt, *J* = 15.5 Hz, 7.2 Hz, 1H), 5.36 (dd, *J* = 15.5 Hz, 5.5 Hz, 1H), 3.84-3.75 (m, 2H), 3.58 (td, *J* = 9.3 Hz, 2.9 Hz, 1H), 3.33 (td, *J* = 9.6 Hz, 4.3 Hz, 1H), 2.74 (dd, *J* = 14.8 Hz, 3.0 Hz, 1H), 2.23 (dd, *J* = 14.8 Hz, 9.7 Hz, 1H), 2.01-1.97 (m, 1H), 1.91-1.86 (m, 2H), 1.71-1.68 (m, 1H), 1.43 (s, 9H), 1.47-1.33 (m, 6H), 1.04 (s, 9H), 1.02 (d, *J* = 6.2 Hz, 3H), 0.88 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.5, 136.0, 136.0, 135.1, 134.7, 131.8, 130.3, 129.6, 129.5, 127.6, 127.5, 80.3, 79.8, 77.7, 70.9, 69.6, 39.6, 39.1, 33.6, 32.5, 31.5, 28.3, 27.2, 25.9, 24.8, 23.3, 19.4, 18.1, -3.9, -4.6; FTIR (neat, NaCl, cm^{-1}): 3071,

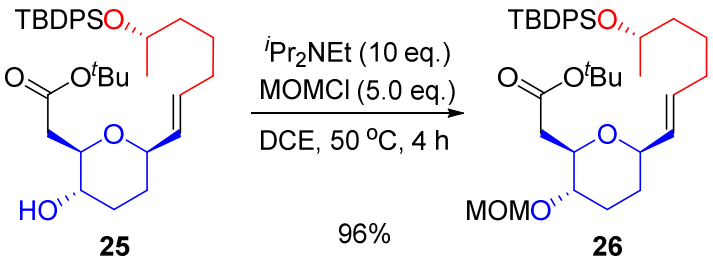
[6] Activated zinc dust was prepared using a modified procedure from: S. Yamamura, M. Toda and Y. Hirata, *Org. Synth.*, 1973, **53**, 86. Zinc dust was stirred in 1M HCl for 30 min, quickly washed with H_2O, filtered and washed with ethanol, acetone, diethyl ether sequentially, dried between filter paper and used immediately.

2930, 2867, 1960, 1890, 1825, 1730, 1589; HRMS (ESI) *m/z* Calcd for $C_{40}H_{64}O_5Si_2Na$ $[M+Na]^+$: 703.4190; found: 703.4187.



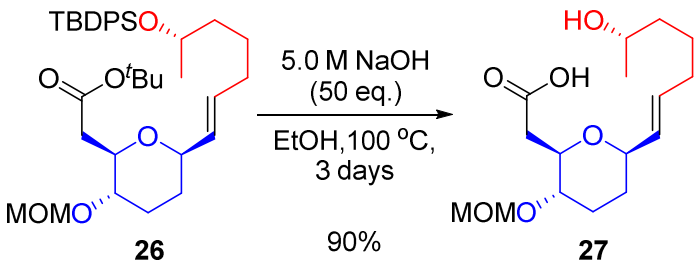
tert-butyl 2-((2*R*,3*S*,6*R*)-6-((*S*,*E*)-6-((_tert_-butyldiphenylsilyl)oxy)hept-1-en-1-yl)-3-hydroxytetrahydro-2*H*-pyran-2-yl)acetate (25)

To *tert*-butyl 2-((2*R*,3*S*,6*R*)-3-((*tert*-butyldimethylsilyl)oxy)-6-((*S*,*E*)-6-((tert-butyldiphenyl silyl)oxy)hept-1-en-1-yl)tetrahydro-2*H*-pyran-2-yl)acetate **24** (139 mg, 0.205 mmol, 1.0 equiv.) in a 4 mL sample vial equipped with a stir bar, was added anhydrous THF (2.0 mL) before tetrabutylammonium fluoride (0.41 mL, 1.0 M solution in THF, 0.41 mmol, 2.0 equiv.) was added under N_2. The mixture was allowed to stir at RT for 4 h before saturated aqueous NH_4Cl (5 mL) was added to the mixture and the layers were separated, the aqueous phase extracted with EA (10 mL x 3), the combined organic phase washed with, brine (5 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 5:1) to afford **25** as a pale yellow oil (99.7 mg, 0.176 mmol, 86%). TLC (hexanes/ethyl acetate = 2:1): R_f = 0.48; $[\alpha]^{22}_D$ = +2.5 (c = 0.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.68-7.66 (m, 4H), 7.41-7.34 (m, 6H), 5.59 (dt, *J* = 15.5 Hz, 7.2 Hz, 1H), 5.37 (dd, *J* = 15.5 Hz, 5.9 Hz, 1H), 3.85-3.75 (m, 2H), 3.53 (dt, *J* = 9.0 Hz, 6.0 Hz, 1H), 3.39-3.33 (m, 1H), 2.71 (dd, *J* = 15.1 Hz, 5.6 Hz, 1H), 2.49 (dd, *J* = 15.1 Hz, 6.4 Hz, 1H), 2.18 (bs, 1H), 2.16-2.11 (m, 1H), 1.92-1.87 (m, 2H), 1.73-1.70 (m, 1H), 1.45 (s, 9H), 1.45-1.32 (m, 6H), 1.04 (s, 9H), 1.03 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.9, 136.0, 136.0, 135.1, 134.7, 132.3, 130.1, 129.6, 129.5, 127.6, 127.5, 81.1, 78.9, 78.0, 71.0, 69.6, 40.5, 39.1, 33.1, 32.4, 31.5, 28.2, 27.2, 24.8, 23.3, 19.4; FTIR (neat, NaCl, cm^{-1}): 3418, 3071, 2932, 2857, 1960, 1892, 1823, 1730, 1589; HRMS (ESI) *m/z* Calcd for $C_{34}H_{50}O_5SiNa$ $[M+Na]^+$: 589.3325; found: 589.3319.



tert-butyl 2-((2*R*,3*S*,6*R*)-6-((*S*,*E*)-6-((_tert_-butyldiphenylsilyl)oxy)hept-1-en-1-yl)-3-(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl)acetate (26)

To *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((*S*,*E*)-6-((*tert*-butyldiphenylsilyl)oxy)hept-1-en-1-yl)-3-hydroxytetrahydro-2*H*-pyran-2-yl)acetate **25** (96.1 mg, 0.17 mmol, 1.0 equiv.) in a 4 mL sample vial equipped with a stir bar was added 1,2-dichloroethane (1.7 mL) before *N*,*N*-diisopropylethylamine (296 μL, 219 mg, 1.7 mmol, 10 equiv.) was added followed by chloromethyl methyl ether (65 μL, 68.3 mg, 0.85 mmol, 5.0 equiv.). The mixture was allowed to stir at 50 ^{o}C for 4 h before being concentrated under reduced pressure. Purification using silica gel chromatography (eluent: hexanes/ethyl acetate = 10:1) to afford **26** as a pale yellow oil (99.6 mg, 0.163 mmol, 96%). TLC (hexanes/ethyl acetate = 2:1): R_f = 0.68; $[\alpha]^{22}_D$ = +15.8 (c = 0.62, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.67 (dd, *J* = 7.9 Hz, 1.4 Hz, 4H), 7.41-7.34 (m, 6H), 5.58 (dt, *J* = 15.5 Hz, 7.2 Hz, 1H), 5.36 (dd, *J* = 15.5 Hz, 5.7 Hz, 1H), 4.71 (d, *J* = 6.8 Hz, 1H), 4.59 (d, *J* = 6.8 Hz, 1H), 3.84-3.77 (m, 2H), 3.68 (td, *J* = 8.8 Hz, 4.4 Hz, 1H), 3.36 (s, 3H), 3.29 (td, *J* = 9.8 Hz, 4.3 Hz, 1H), 2.71 (dd, *J* = 14.9 Hz, 4.2 Hz, 1H), 2.36 (dd, *J* = 14.9 Hz, 8.2 Hz, 1H), 2.24-2.20 (m, 1H), 1.92-1.86 (m, 2H), 1.74-1.70 (m, 1H), 1.48-1.32 (m, 6H), 1.44 (s, 9H), 1.04 (s, 9H), 1.03 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.0, 136.0, 136.0, 135.1, 134.7, 132.2, 130.2, 129.6, 129.5, 127.6, 127.5, 95.3, 80.4, 77.9, 77.8, 75.6, 69.6, 55.7, 39.9, 39.1, 32.4, 31.2, 30.2, 28.3, 27.2, 24.8, 23.3, 19.4; FTIR (neat, NaCl, cm^{-1}): 3049, 2932, 2857, 1960, 1900, 1827, 1726, 1589; HRMS (ESI) *m/z* Calcd for $C_{36}H_{55}O_6Si$ $[M+H]^+$: 611.3768; found: 611.3776.

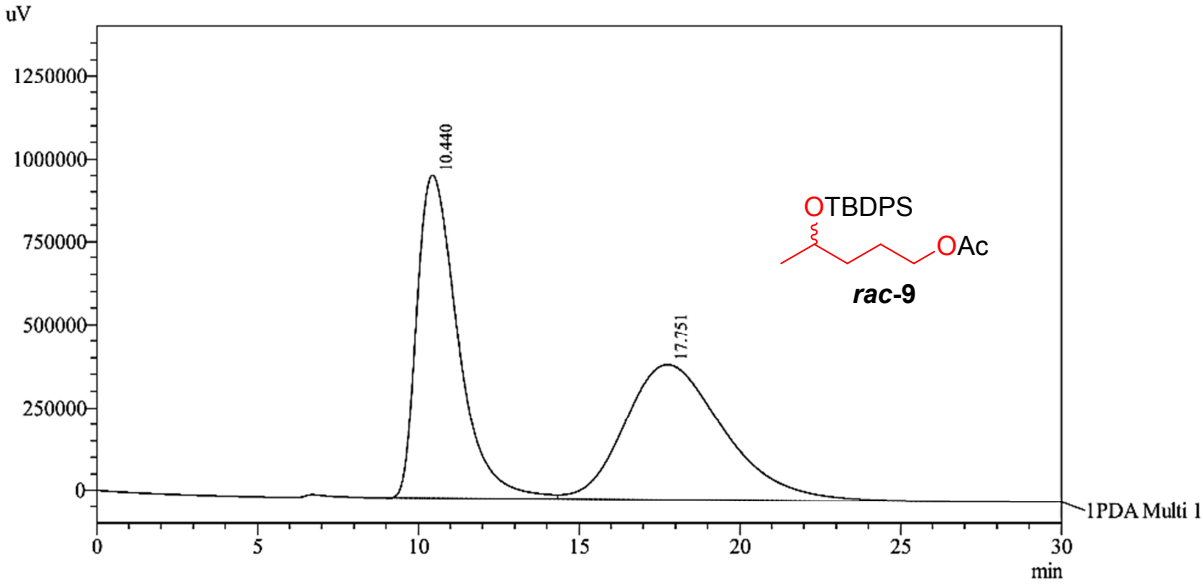


2-((2*R*,3*S*,6*R*)-6-((*S*,*E*)-6-hydroxyhept-1-en-1-yl)-3-(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl)acetic acid (27)[7]

To *tert*-butyl 2-((2*R*,3*S*,6*R*)-6-((*S*,*E*)-6-((*tert*-butyldiphenylsilyl)oxy)hept-1-en-1-yl)-3-(methoxymethoxy)tetrahydro-2*H*-pyran-2-yl)acetate **26** (89.7 mg, 0.147 mmol, 1.0 equiv.) in a 4 mL vial equipped with a stir bar was added ethanol (1.5 mL) before aqueous NaOH (1.5 mL, 5.0 M, 7.5 mmol, 50 equiv.) was added and allowed to stir at 100 °C for 3 days. The mixture was acidified with 3 M HCl (4 mL), extracted with chloroform (12 mL x 4), washed with brine (5 mL), dried over anhydrous $MgSO_4$ before being filtered and concentrated under reduced pressure. Purification using silica gel chromatography (eluent: DCM/MeOH = 20:1 to 10:1) to afford **27** as a colourless oil (41.7 mg, 0.132 mmol, 90%). TLC (DCM/MeOH = 10:1): R_f = 0.27; $[\alpha]^{22}_D$ = +38.9 (c = 0.83, $CHCl_3$). (Lit[7]: $[\alpha]^{28}_D$ = +59.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.67 (dt, *J* = 15.5 Hz, 7.2 Hz, 1H), 5.45 (dd, *J* = 15.5 Hz, 6.1 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 4.60 (d, *J* = 6.8 Hz, 1H), 3.89-3.86 (m, 1H), 3.82-3.76 (m, 1H), 3.70 (td, *J* = 8.6 Hz, 3.4 Hz, 1H), 3.34 (s, 3H), 3.33-3.28 (m, 1H), 2.87 (dd, *J* = 15.5 Hz, 3.2 Hz, 1H), 2.53 (dd, *J* = 15.4 Hz, 8.2 Hz, 1H), 2.26-2.24 (m, 1H), 2.04-2.03 (m, 2H), 1.79-1.76 (m, 1H), 1.58-1.38 (m, 6H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.7, 132.6, 130.2, 95.3, 78.2, 77.4, 75.2, 68.2, 55.8, 38.7, 38.2, 32.3, 31.1, 29.9, 25.2, 23.5; FTIR (neat, NaCl, cm^{-1}): 3433, 2936, 1715, 1103, 1036; HRMS (ESI) *m/z* Calcd for $C_{16}H_{28}O_6Na$ $[M+Na]^+$: 339.1784; found: 339.1770.

[7] H. Fuwa, H. Yamaguchi and M. Sasaki, *Tetrahedron*, 2010, **66**, 7492-7503.

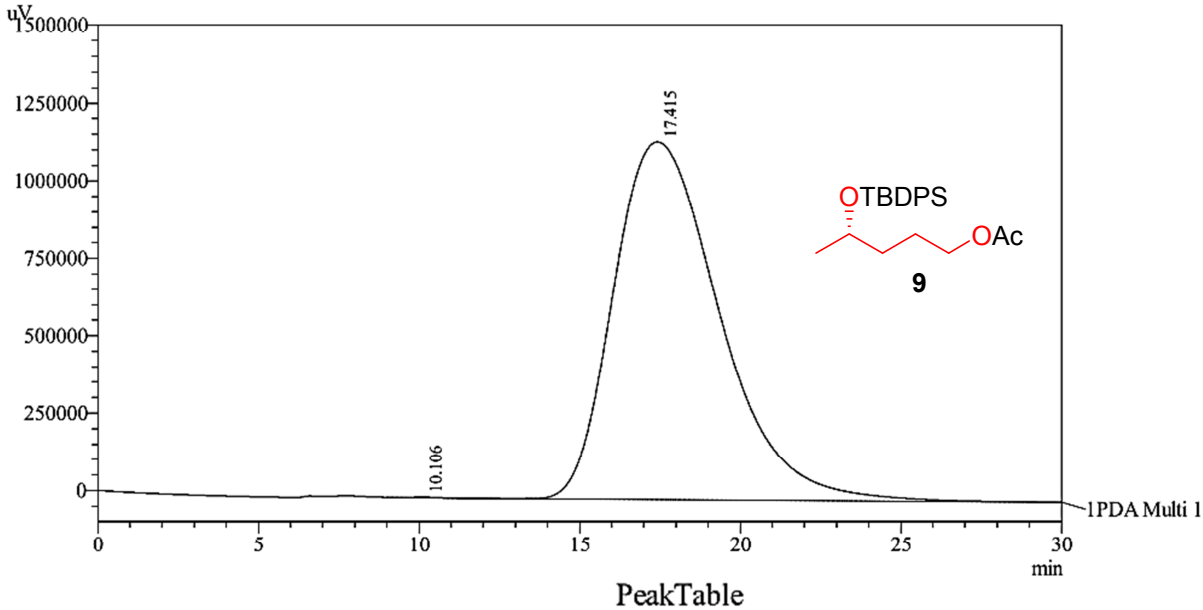
3.1 Determination of enantiomeric excess by HPLC for 9:



PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.440	86820408	973805	49.727	70.491
2	17.751	87773940	407648	50.273	29.509
Total		174594348	1381453	100.000	100.000



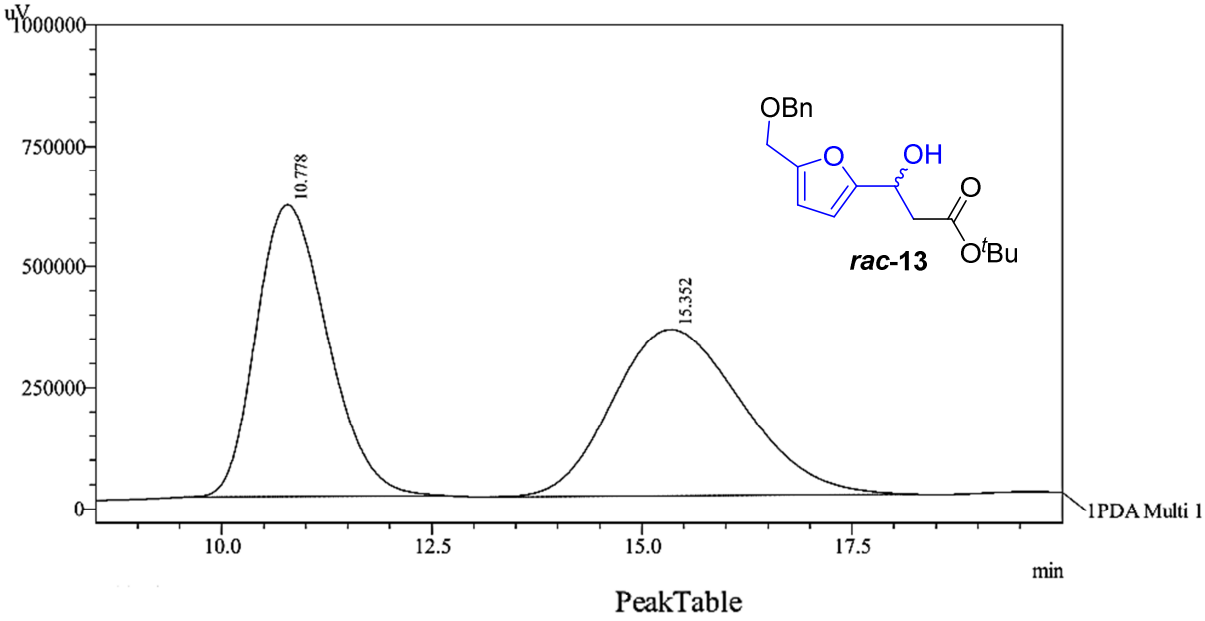
PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.106	50412	2129	0.019	0.184
2	17.415	265144799	1154354	99.981	99.816
Total		265195211	1156483	100.000	100.000

HPLC trace of **9** (Chiralcel OJ, hexanes/2-propanol = 100:0, 0.5 mL/min, 220 nm)

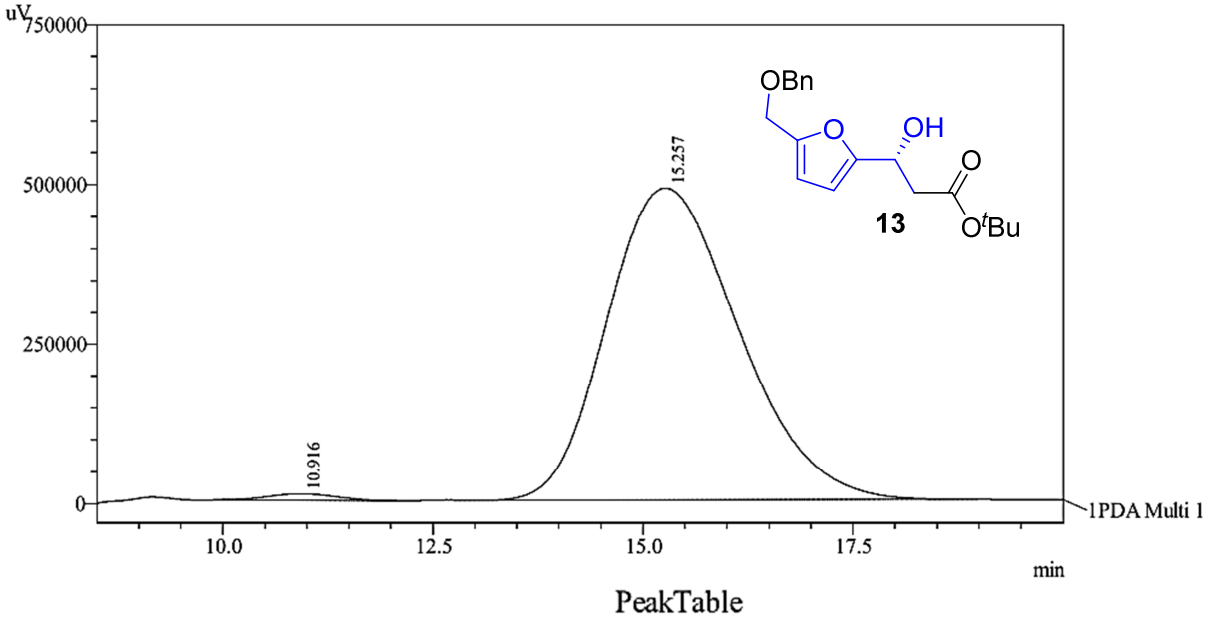
3.2 Determination of enantiomeric excess by HPLC for 13:



PeakTable

PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.778	35718382	603334	49.170	63.756
2	15.352	36924915	342977	50.830	36.244
Total		72643297	946311	100.000	100.000



PeakTable

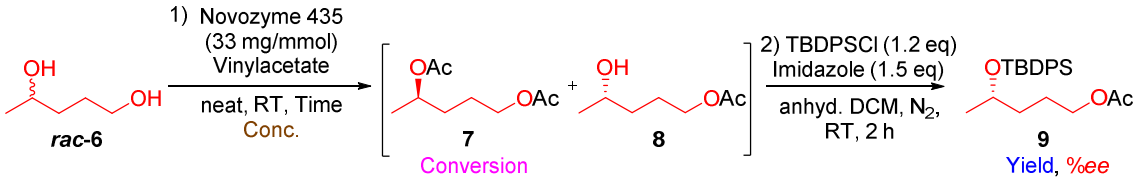
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.916	587066	10336	1.086	2.070
2	15.257	53474427	489091	98.914	97.930
Total		54061493	499428	100.000	100.000

HPLC trace of **13** (Chiralcel OB-H, hexanes/2-propanol = 90:10, 1.0 mL/min, 220 nm)

4. Optimization Tables:

4.1 Enzymatic kinetic resolution optimization



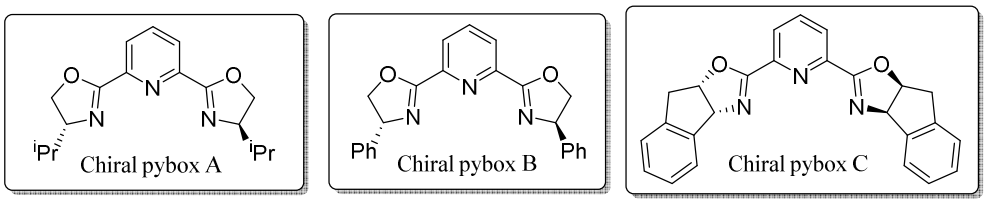
Entry	Conc.	Time	Conv.[1]	Yield[2]	%ee
1	3.3 M	5 h	62%	29%[3]	>99%
2	1.0 M	3 h	50%	46%	95%
3	3.3 M	3 h	50%	45%	94%
4	3.3 M	3.5 h	54%	42%	>99%
5	3.3 M	4 h	57%	40%	>99%

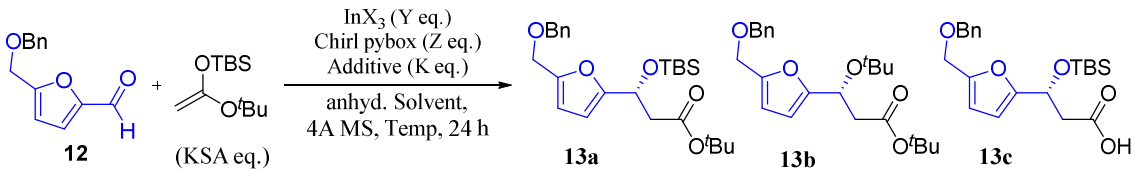
[1] Determined using NMR based on ratio of products
[2] Isolated yield over 2 steps [3] With isolation of **8**

References:

a) Review: A. Ghanem, *Tetrahedron*, 2007, **63**, 1721-1754. b) F. Felluga, C. Forzato, F. Ghelfi, P. Nitti, G. Pitacco, U. M. Pagnoni and F. Roncaglia, *Tetrahedron: Asymmetry*, 2007, **18**, 527-536.

4.2 Mukaiyama Aldol optimization



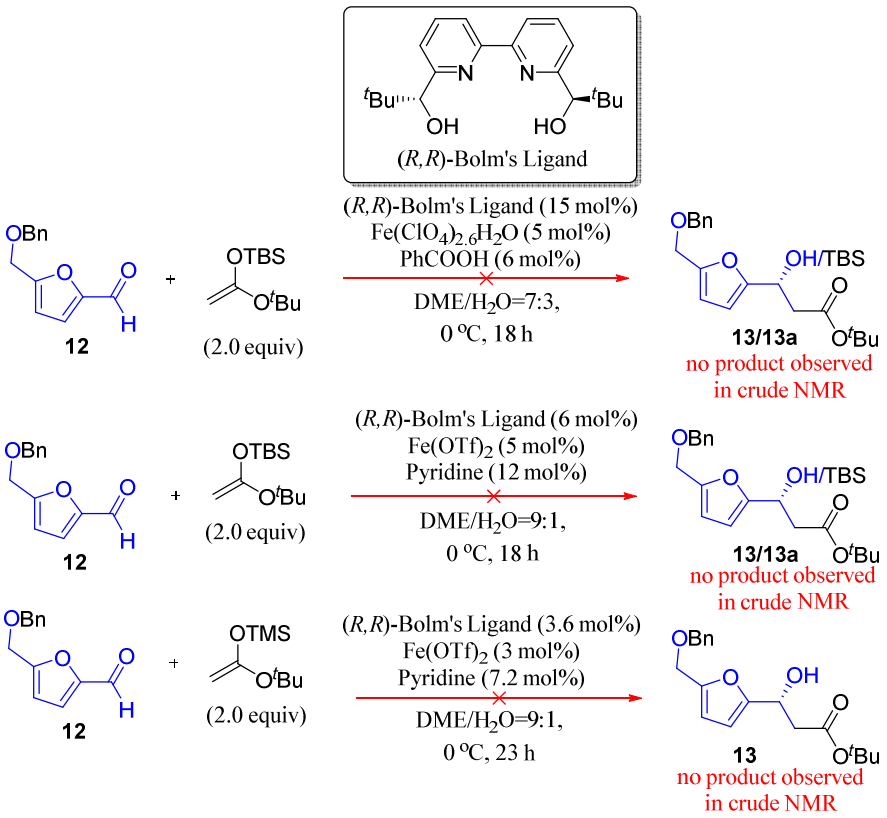


Entry	KSA	InX_3	Y eq.	Pybox	Z eq.	Additive	K eq.	Solvent	Temp	SM[1]	**13a**[1]	**13b**[1]	**13c**[1]
1	1.2	$In(OTf)_3$	0.20	A	0.22	-	-	DCM	-40 °C	40%	25%	6%	15%
2	1.2	$In(OTf)_3$	0.20	B	0.22	-	-	DCM	-40 °C	37%	30%	7%	16%
3	1.2	$In(OTf)_3$	0.20	C	0.22	-	-	DCM	-40 °C	48%	23%	6%	14%
4	1.5	$InBr_3$	0.05	A	0.06	$AgSbF_6$	0.05	MeCN	-20 °C	87%	1%	-	-
5	1.5	$InBr_3$	0.05	B	0.06	$AgSbF_6$	0.05	MeCN	-20 °C	100%	-	-	-
6	1.5	$InBr_3$	0.05	C	0.06	$AgSbF_6$	0.05	MeCN	-20 °C	90%	-	-	-

[1] Isolated yields

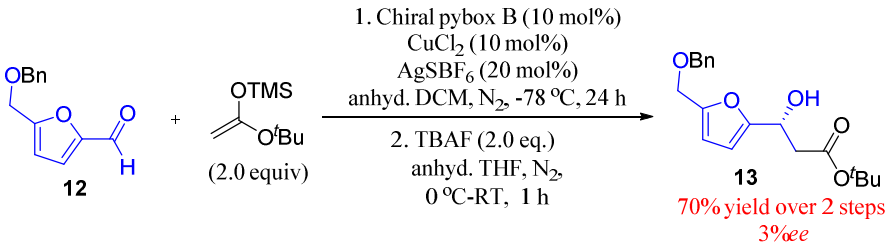
References:

a. F. Fu, Y.-C. Teo and T.-P. Loh, *Tetrahedron Lett.*, 2006, **47**, 4267-4269.
b. J.-F. Zhao, B.-H. Tan and T.-P. Loh, *Chem. Sci.*, 2011, **2**, 349-352.



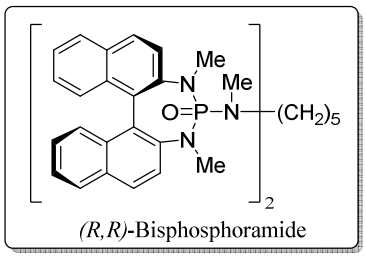
References:

a. T. Ollevier and B. Plancq, *Chem. Commun.*, 2012, **48**, 2289-2291.
b. T. Kitanosono, T. Ollevier and S. Kobayashi, *Chem. Asian J.*, 2013, **8**, 3051-3062.

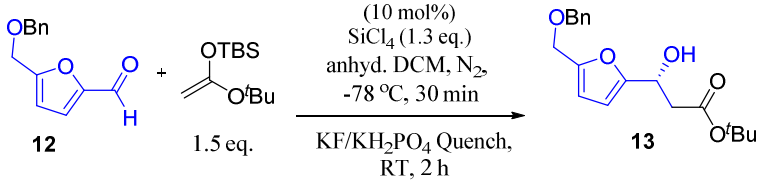


References:

a. D. A. Evans, J. A. Murry and M. C. Kozlowski, *J. Am. Chem. Soc.*, 1996, **118**, 5814-5815.



(R,R)-Bisphosphoramide



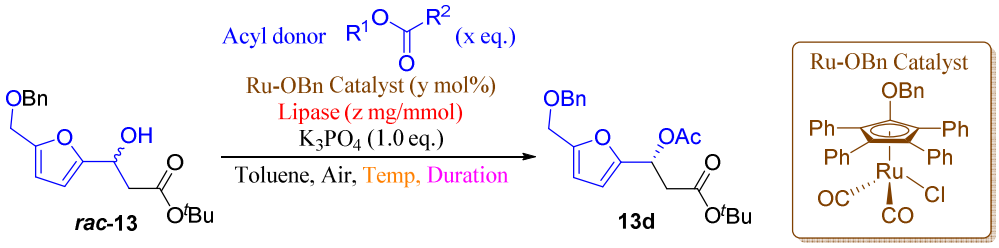
Entry	change from above	SM[1]	**13** Yield[2]	**13** %*ee*
1	as shown above	none	67%	71%
2	O-TMS KSA	none	84%	59%
3	with TBAI (20 mol%)	4%	67%	73%
4	anhyd. THF	6%	76%	22%
5	anhyd. ether	25%	58%	22%
6	anhyd. toluene	12%	62%	0%

[1]NMR yield based on internal standard [2]Isolated yield

References:

a. S. E. Denmark, T. Wynn and G. L. Beutner, *J. Am. Chem. Soc.*, 2002, **124**, 13405-13407.

4.3 Dynamic enzymatic kinetic resolution optimization



Entry	Acyl donor (x)	(y)	Lipase (z)	Temp	Duration	Pdt Yield[1]	Pdt %ee	SM Yield[1]
1	IPA (1.5)	4	N435 (8)	RT	109 h	(2%)	N.D.[4]	(95%)
2	IPA (1.5)	4	CAL-B (8)	RT	109 h	(3%)	N.D.[4]	(97%)
3	IPA (1.5)	4	N435 (32)	RT	109 h	(6%)	N.D.[4]	(94%)
4	IPA (1.5)	4	CAL-B (32)	RT	109 h	(8%)	N.D.[4]	(92%)
5	IPA (1.5)	-[2]	N435 (8)	RT	72 h	(1%)	N.D.[4]	(99%)
6	IPA (1.5)	-[2]	CAL-B (8)	RT	72 h	(1%)	N.D.[4]	(99%)
7	IPA (1.5)	4	N435 (200)	RT	69 h	7%	40%	86%
8	IPA (1.5)	4	CAL-B(200)	RT	69 h	10%	40%	81%
9	IPA (1.5)	4	N435 (200)	60 °C	69 h	30%	36%	59%
10	IPA (1.5)	4	CAL-B(200)	60 °C	69 h	27%	36%	58%
11	VB (1.5)	4	N435 (200)	RT	120 h	(1%)	N.D.[4]	(97%)
12	VA (1.5)	4	N435 (200)	RT	120 h	(1%)	N.D.[4]	(97%)
13	VB (5.0)	4	N435 (200)	RT	120 h	(1%)	N.D.[4]	(98%)
14	VB (1.5)	4[3]	N435 (200)	RT	120 h	(1%)	N.D.[4]	(97%)
15	VB (1.5)	15	N435 (200)	RT	120 h	(1%)	N.D.[4]	(96%)
16	VA (1.5)	4	Lipase PS (200)	RT	70 h	(5%)	36%	(95%)
17	IPA (1.5)	4	Lipase PS (200)	RT	70 h	(7%)	N.D.[4]	(93%)
18	VB (5.0)	4	Lipase PS (200)	RT	70 h	(3%)	N.D.[4]	(97%)
19	CPA (1.5)	4	Lipase PS (200)	RT	70 h	80%	3%	(1%)
20	VB (1.5)	4	Lipase PS (200)	70 °C	70 h	(15%)	N.D.[4]	(79%)
21	CPA (1.5)	4	Lipase PS (200)	70 °C	70 h	68%	0%	(14%)

[1] Isolated Yields, NMR Yields shown in parenthesis using NO_2Ph as internal standard [2] No Ru catalyst and K_3PO_4, reaction in TBME [3] 2.0 eq. of K_3PO_4 used

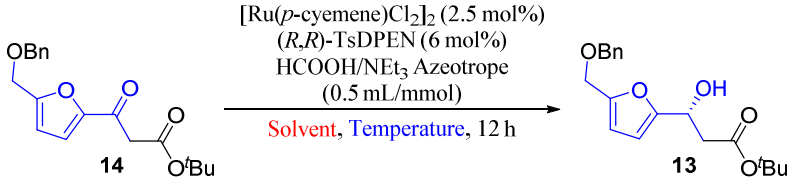
Vinyl Acetate (VA): R^1 = Vinyl, R^2 = Me
Isopropenyl Acetate (IPA): R^1 = Isopropenyl, R^2 = Me
Vinyl Butyrate (VB): R^1 = Vinyl, R^2 = ^{n}Pr
p-Chlorophenyl Acetate (CPA): R^1 = *p*-Cl-phenyl, R^2 = Me

N435: Novozyme 435
CAL-B: Lipase from Candida antarctica immobilised on acrylic resin
Lipase PS: Lipase from Pseudomonas Cepacia

References:

a. N. Kim, S.-B. Ko, M. S. Kwon, M.-J. Kim and J. Park, *Org. Lett.*, 2005, **7**, 4523-4526.
b. J. Brem, A. Liljeblad, C. Paizs, M. I. Toşa, F.-D. Irimie and L. T. Kanerva, *Tetrahedron: Asymmetry*, 2011, **22**, 315-322.
c. P. Hoyos, V. Pace and A. R. Alcántara, *Adv. Synth. Catal.*, 2012, **354**, 2585-2611.
d. B. A. Persson, A. L. E. Larsson, M. Le Ray and J.-E. Bäckvall, *J. Am. Chem. Soc.*, 1999, **121**, 1645-1650.

4.4 Asymmetric transfer hydrogenation optimization

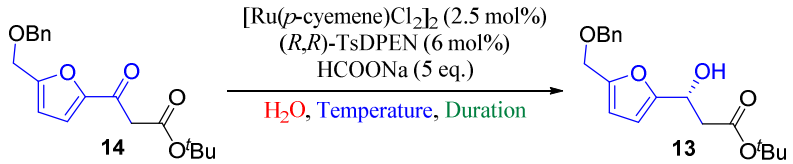


Entry	Solvent	Temperature	Yield[1]	%*ee*
1	DCM	RT	89%[2]	97%
2	ACN	RT	99%	98%
3	DCM	40 °C	99%	94%
4	ACN	40 °C	98%	96%
5[3]	ACN	RT	98%	98%

[1] Isolated Yields [2] 10% SM remaining [3] Inert conditions

References:

a. A. Fujii, S. Hashiguchi, N. Uematsu, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 2521-2522.
b. R. Noyori and S. Hashiguchi, *Acc. Chem. Res.*, 1997, **30**, 97-102.
c. Lutz F. Tietze, Y. Zhou and E. Töpken, *Eur. J. Org. Chem.*, 2000, 2247-2252.
d. P. N. Liu, P. M. Gu, F. Wang and Y. Q. Tu, *Org. Lett.*, 2003, **6**, 169-172.
e. K. Everaere, A. Mortreux and J.-F. Carpentier, *Adv. Synth. Catal.*, 2003, **345**, 67-77.
f. S. Gladiali and E. Alberico, *Chem. Soc. Rev.*, 2006, **35**, 226-236.



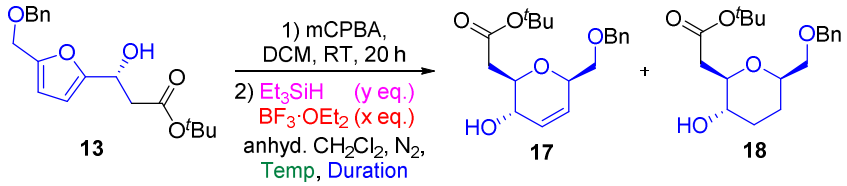
Entry	Temperature	Duration	Yield[1]	%*ee*
1	RT	17 h	87%	91%
2	40 °C	5 h	92%	89%
3[2]	40 °C	2 h	97%	93%

[1] Isolated Yields. [2] $[Cp^*RhCl_2]_2$ was used instead.

References:

a. X. Wu, X. Li, A. Zanotti-Gerosa, A. Pettman, J. Liu, A. J. Mills and J. Xiao, *Chem. Eur. J.*, 2008, **14**, 2209-2222.
b. X. Wu, X. Li, W. Hems, F. King and J. Xiao, *Org. Biomol. Chem.*, 2004, **2**, 1818-1821.

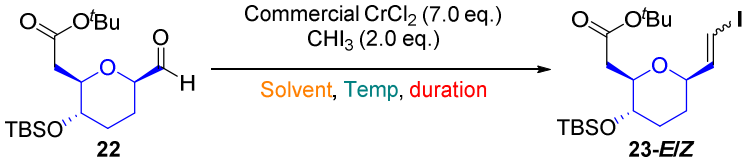
4.5 Triple reduction optimization



Entry	x	y	Conc.	Temp	Duration	Yield[1] of **17**	Yield[1] of **18**
1	3.0	6.0	0.2 M	-20 °C	43 h	6%	41%
2	4.0	6.0	1.0 M	-20 °C	20 h	5%	31%
3	4.0	6.0	1.0 M	-78 -> -40 °C	70 h	5%	50%
4	4.0	6.0	0.2 M	-40 °C	36 h	2%	62%
5	6.0	10.0	0.2 M	-40 °C	15 h	8%	67%

[1] Isolated yield

4.6 Takai iodo-olefination optimization



Entry	Solvent[1]	Temp	Duration	Yield[2]	SM[3]	*E*/*Z*[3]
1	THF	RT	1 h	82%	-	81:19
2	THF	0 °C	3 h	67%	5%	86:14
3	Dioxane/THF=6:1	RT	3 h	63%	1%	88:12
4	Dioxane/THF=6:1	0 °C	21 h	64%	-	89:11

[1] Anhydrous solvents [2] Combined Isolated yields [3] Determined from crude NMR

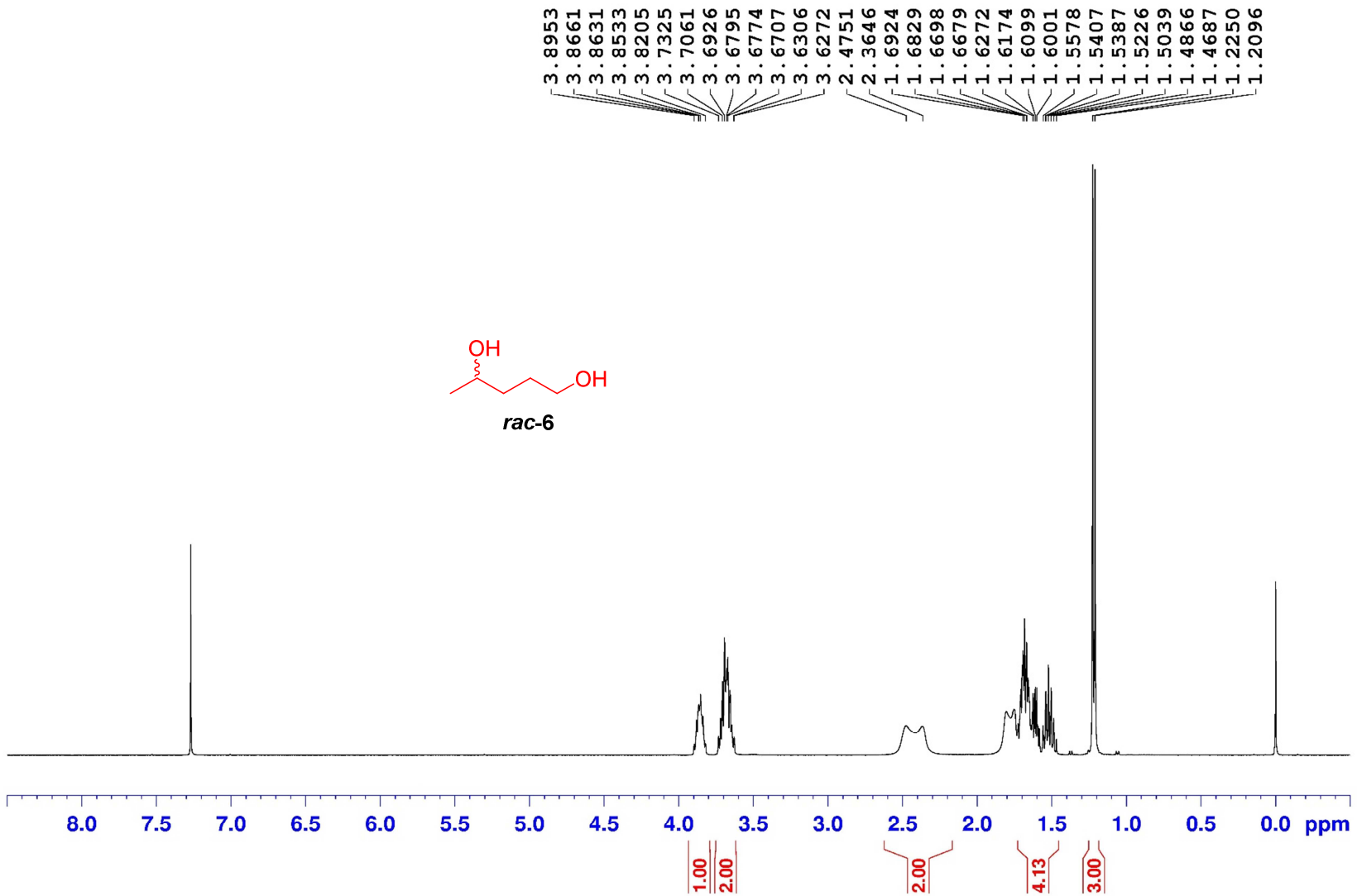
4.7 Negishi coupling optimization

Entry	x	y	z	Temp.	Conc.	Conv.	Yield[1] of **24**	*E*/*Z* of **24**	Yield[2] of **23-*H***
1	6.0	4.0	0.10	RT	0.3 M	15%	0%	-	N.D[4]
2	3.0	5.0	0.15	40 °C	0.1 M	100%	74%	58:42	8%
3	3.0	5.0	0.15	40 °C	0.2 M	100%	76%	91:9	6%
4	6.0	5.0	0.15	40 °C	0.1 M	100%	79%	73:27	2%
5	6.0	5.0	0.15	RT	0.2 M	31%	9%	N.D[4]	11%
6	6.0	5.0	0.15	40 °C	0.5 M	100%	74%	91:9	11%
7	6.0	5.0	0.05	40 °C	0.5 M	100%	68%	>95:5	14%
8	4.0	5.0	0.05	40 °C	0.5 M	88%	59%	>95:5	17%
9	3.0	2.0	0.01	40 °C	0.5 M	68%	45%	>95:5	11%

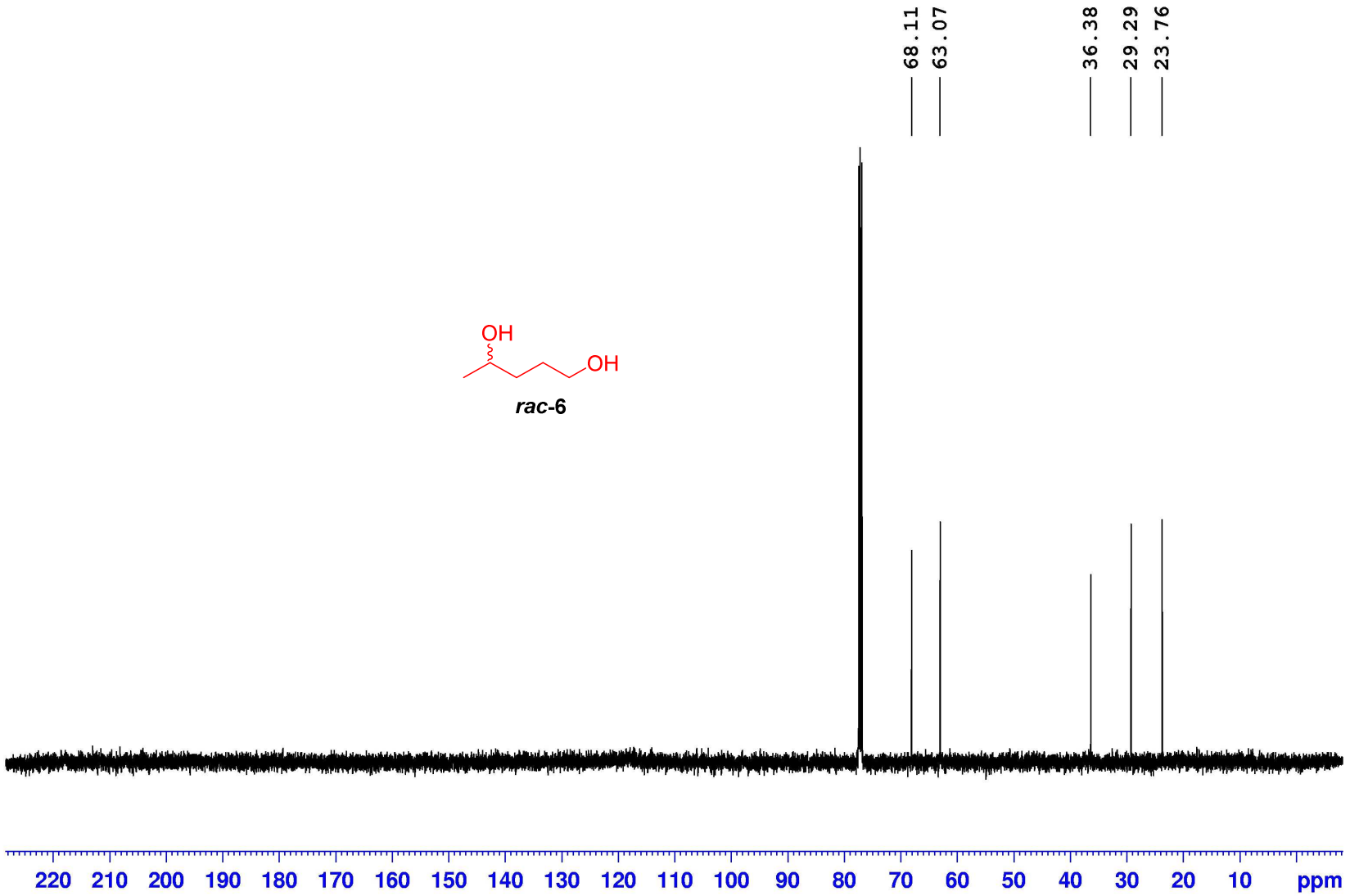
[1]Isolated yields [2]Determined from crude NMR [3]Unactivated Zn dust [4]Not determined

5. ^{1}H NMR and ^{13}C NMR Spectra

400 MHz



125 MHz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63.07
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29.29
23.76
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OH
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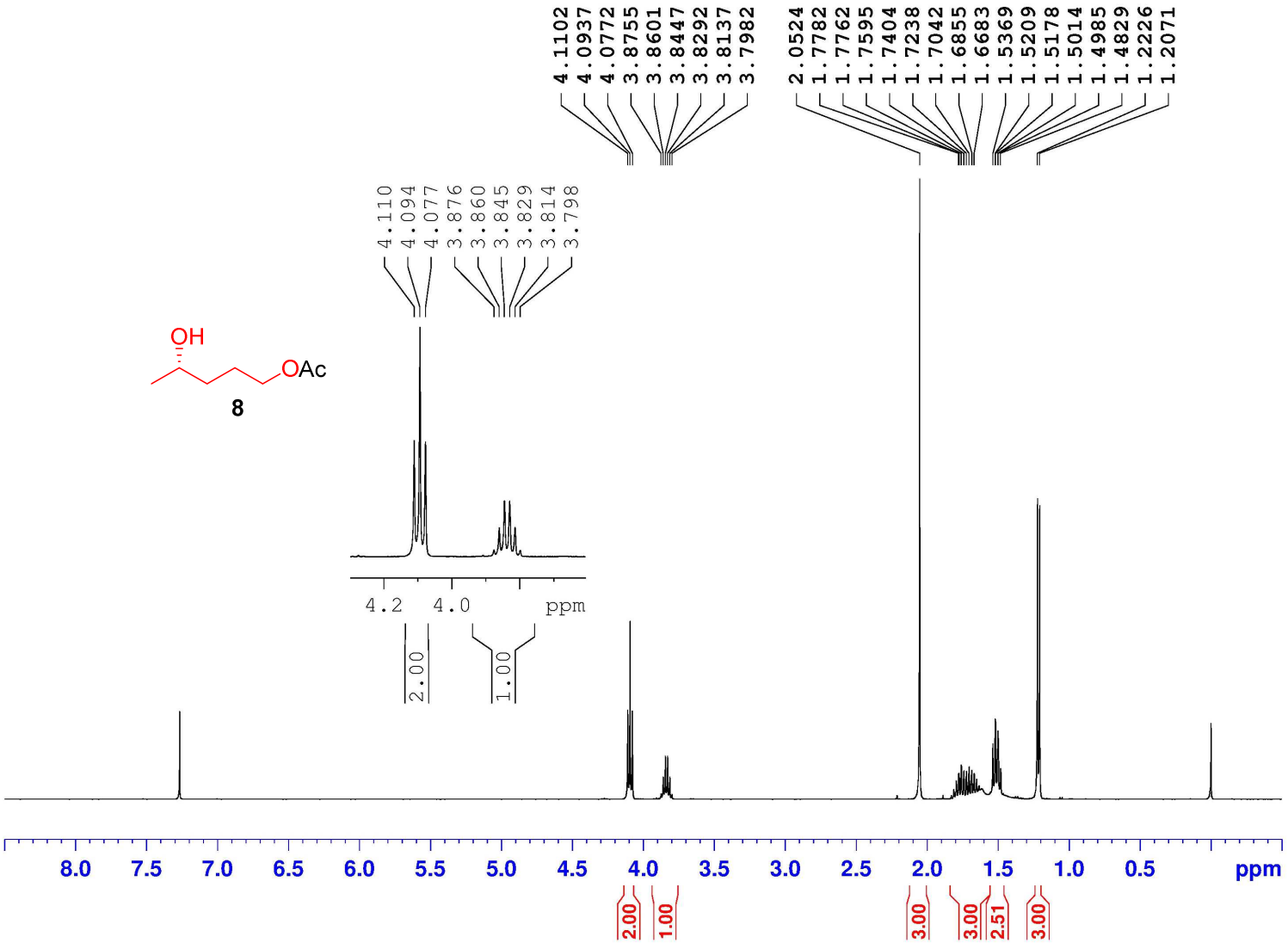
***rac*-6**

400 MHz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1.7782
1.7762
1.7595
1.7404
1.7238
1.7042
1.6855
1.6683
1.5369
1.5209
1.5178
1.5014
1.4985
1.4829
1.2226
1.2071
4.110
4.094
4.077
3.876
3.860
3.845
3.829
3.814
3.798
OH
OAc
8
4.2
4.0
ppm
2.00
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.0
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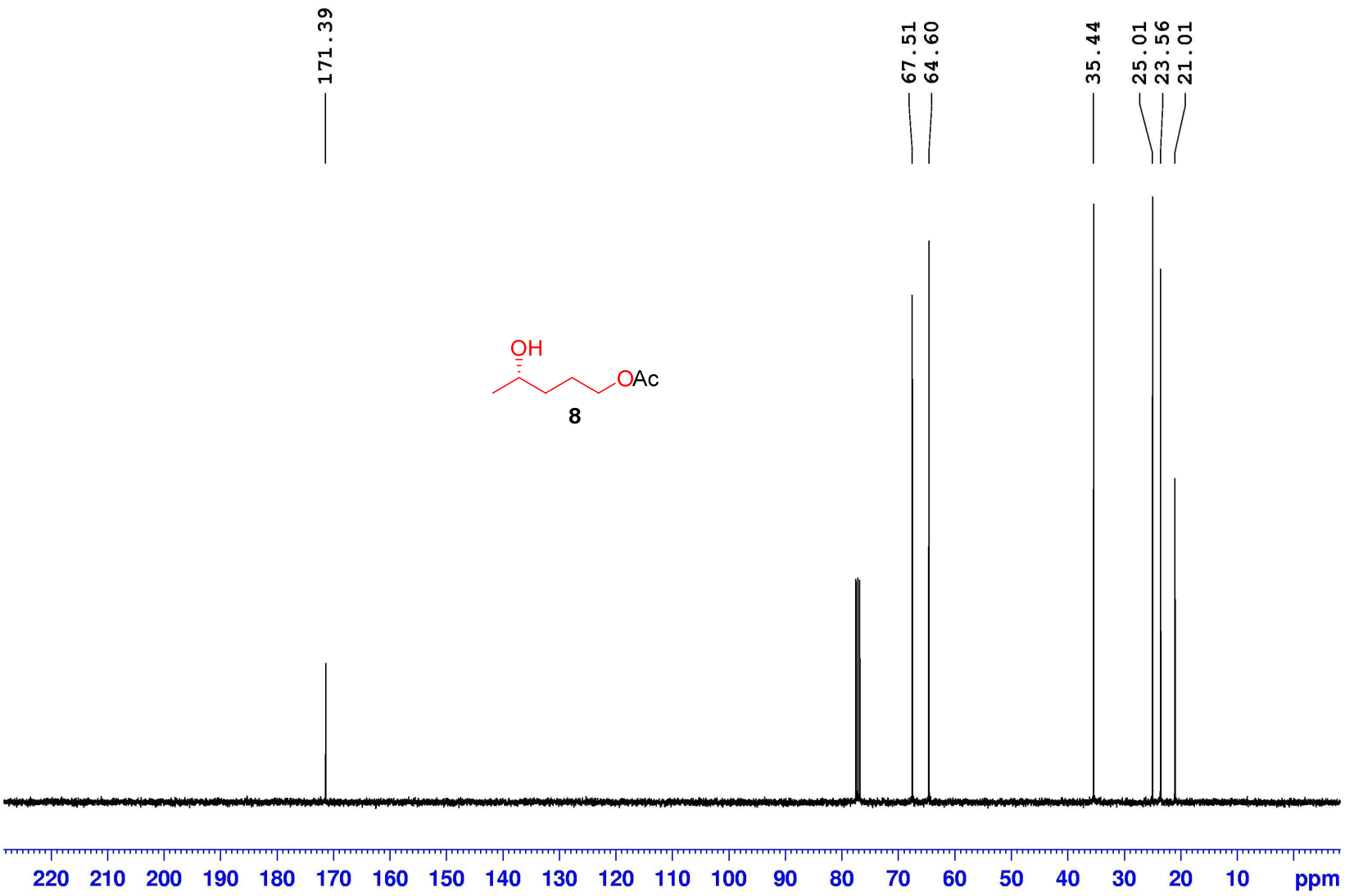
2.51
3.00

100 MHz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23.56
21.01
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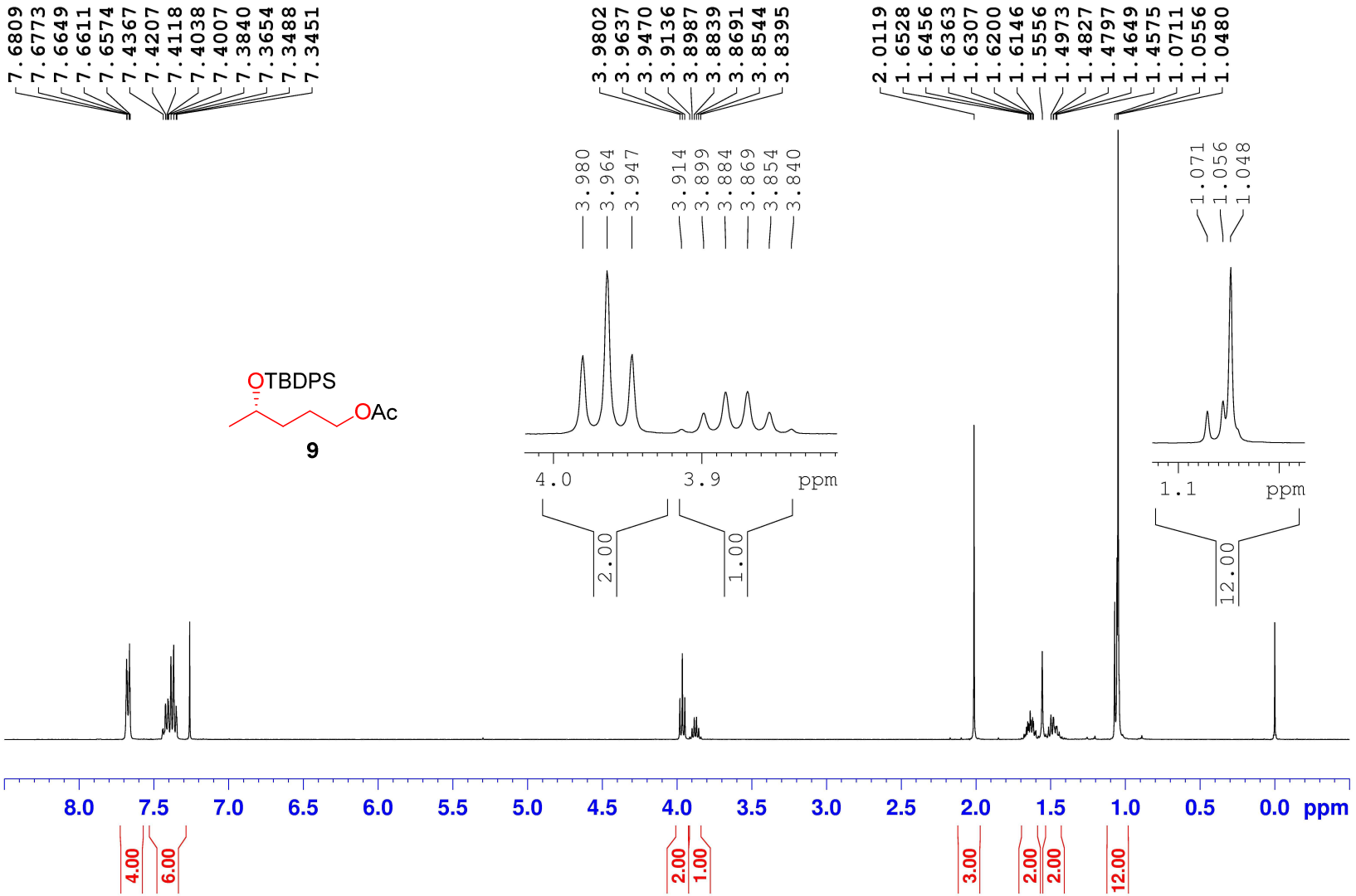
OAc
8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

400 MHz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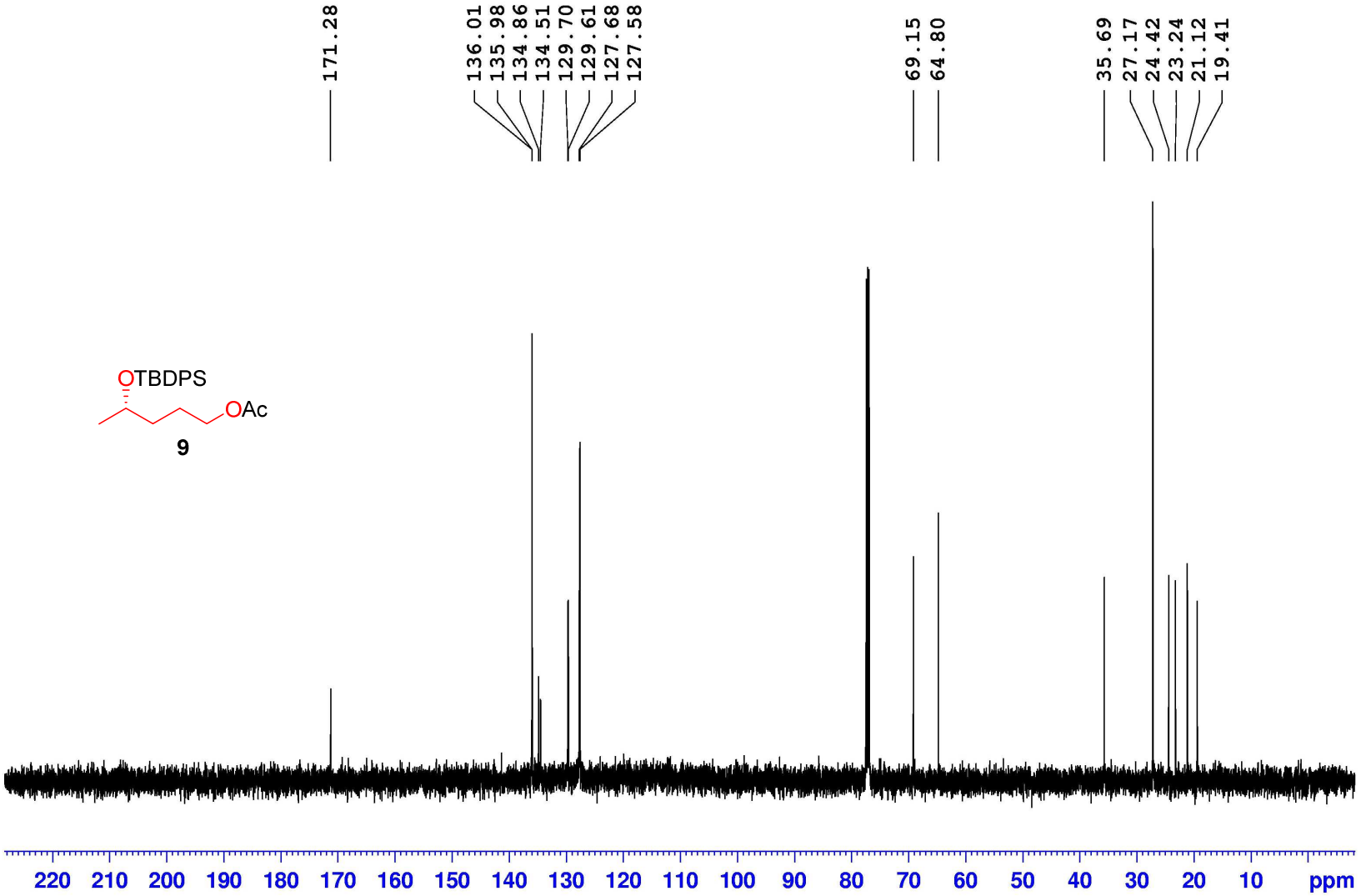
7.4207
7.4118
7.4038
7.4007
7.3840
7.3654
7.3488
7.3451
3.9802
3.9637
3.9470
3.9136
3.8987
3.8839
3.8691
3.8544
3.8395
2.0119
1.6528
1.6456
1.6363
1.6307
1.6200
1.6146
1.5556
1.4973
1.4827
1.4797
1.4649
1.4575
1.0711
1.0556
1.0480
3.980
3.964
3.947
3.914
3.899
3.884
3.869
3.854
3.840
1.071
1.056
1.048
OTBDPS
OAc
9
4.0
3.9
ppm
2.00
1.00
1.1
ppm
12.00
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
0.0
ppm
4.00
6.00
2.00
1.00
3.00
2.00
2.00
12.00

125 MHz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127.68
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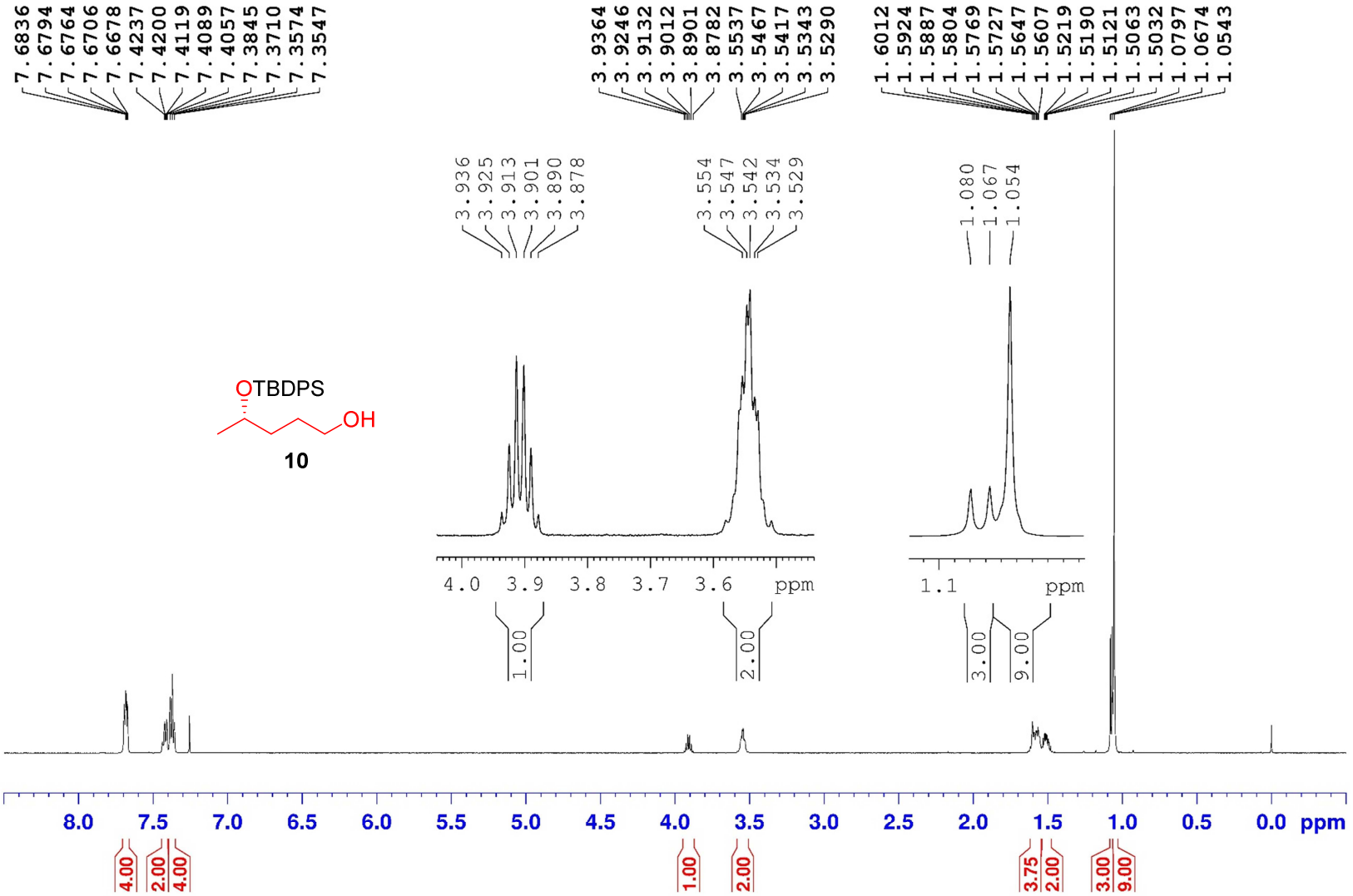
69.15
64.80
35.69
27.17
24.42
23.24
21.12
19.41
OTBDPS
OAc
9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

500 MHz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7.3710
7.3574
7.3547
3.9364
3.9246
3.9132
3.9012
3.8901
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3.5537
3.5467
3.5417
3.5343
3.5290
1.6012
1.5924
1.5887
1.5804
1.5769
1.5727
1.5647
1.5607
1.5219
1.5190
1.5121
1.5063
1.5032
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1.0674
1.0543
3.936
3.925
3.913
3.901
3.890
3.878
3.554
3.547
3.542
3.534
3.529
1.080
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1.054
OTBDPS
OH
10
4.0
3.9
3.8
3.7
3.6
ppm
1.1
ppm
1.00
2.00
3.00
9.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
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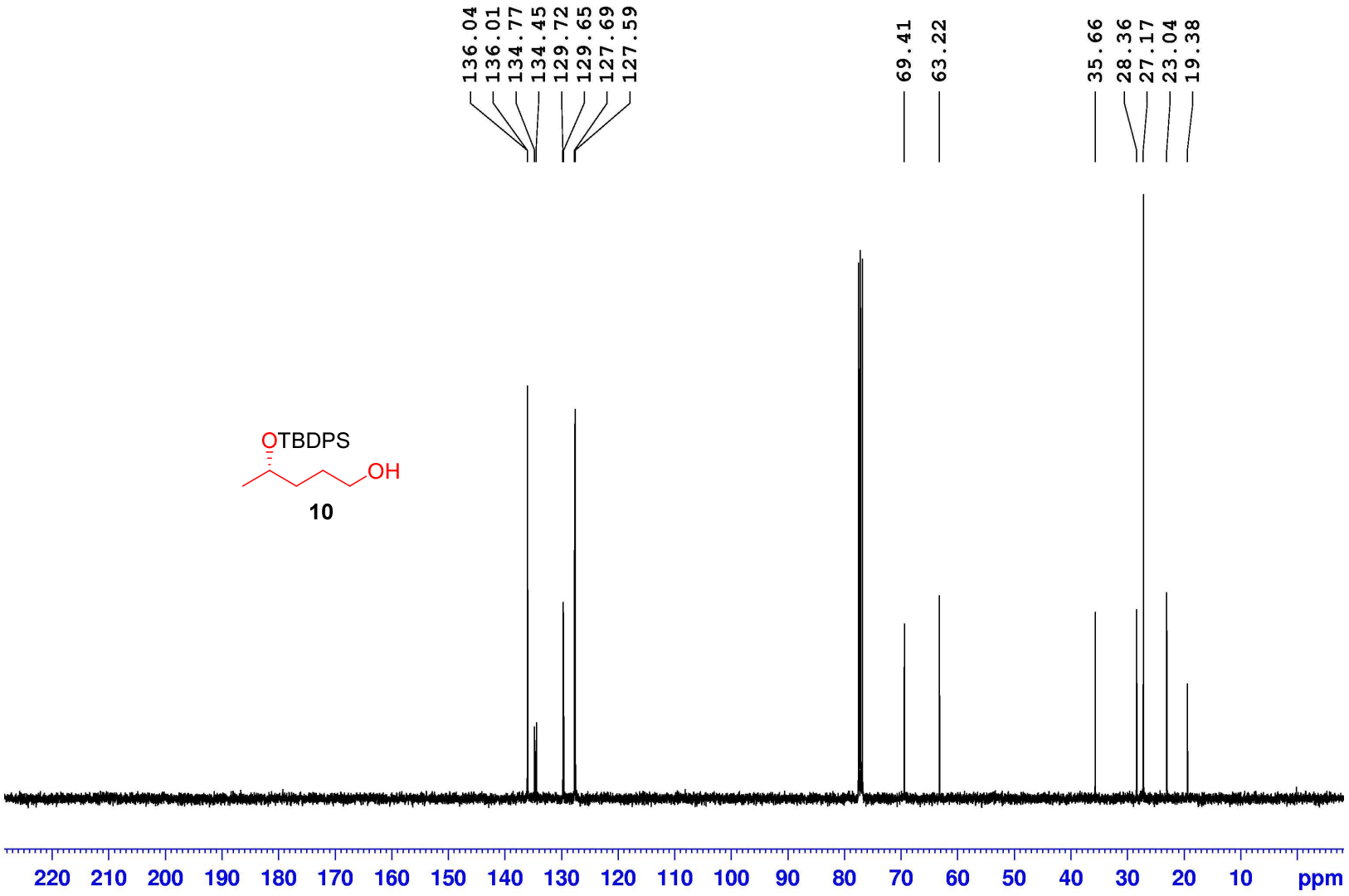
2.00
3.00
9.00

100 MHz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127.69
127.59
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63.22
35.66
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23.04
19.38
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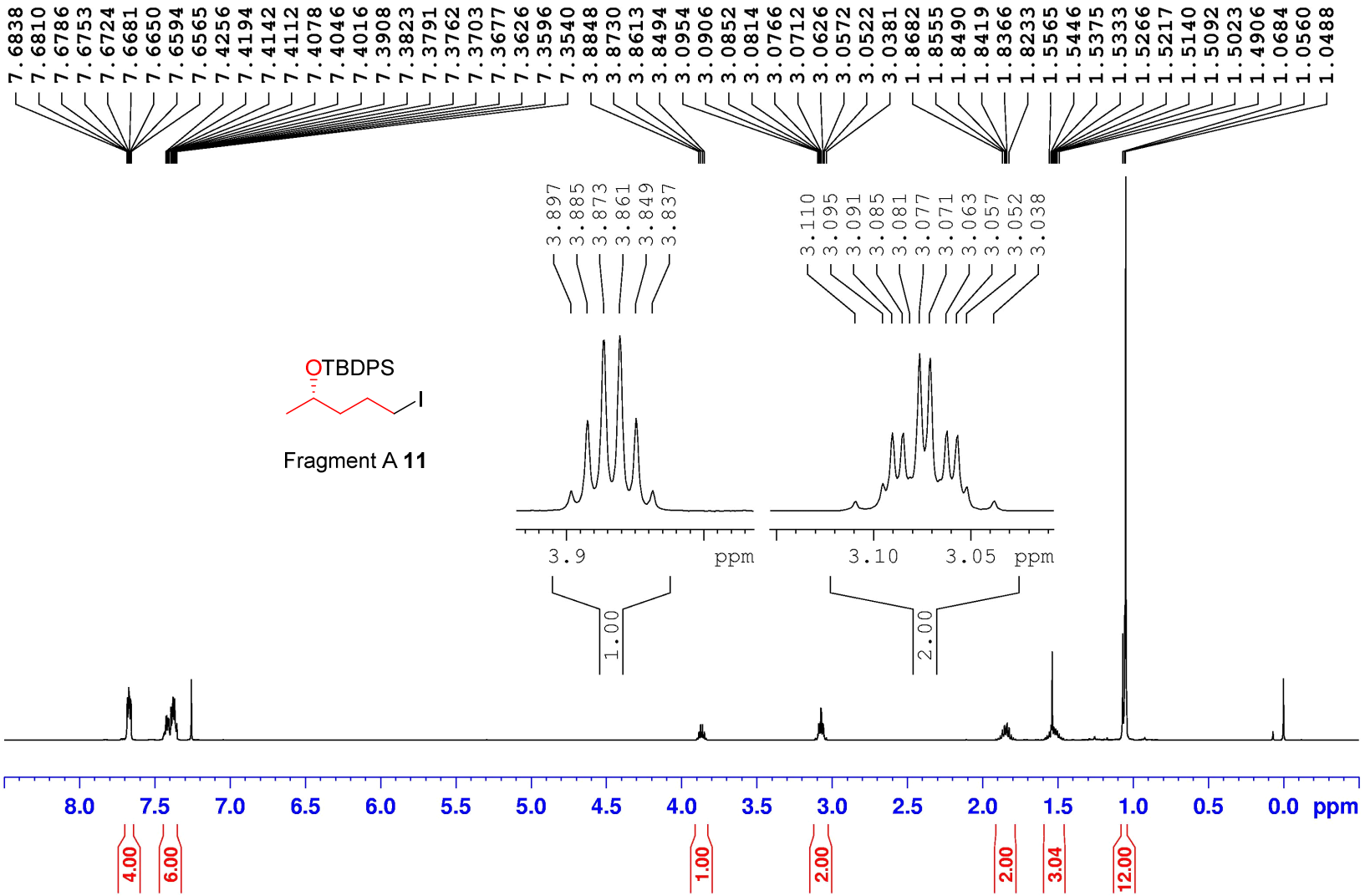
500 MHz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7.3626
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3.0766
3.0712
3.0626
3.0572
3.0522
3.0381
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3.038
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ppm
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3.5
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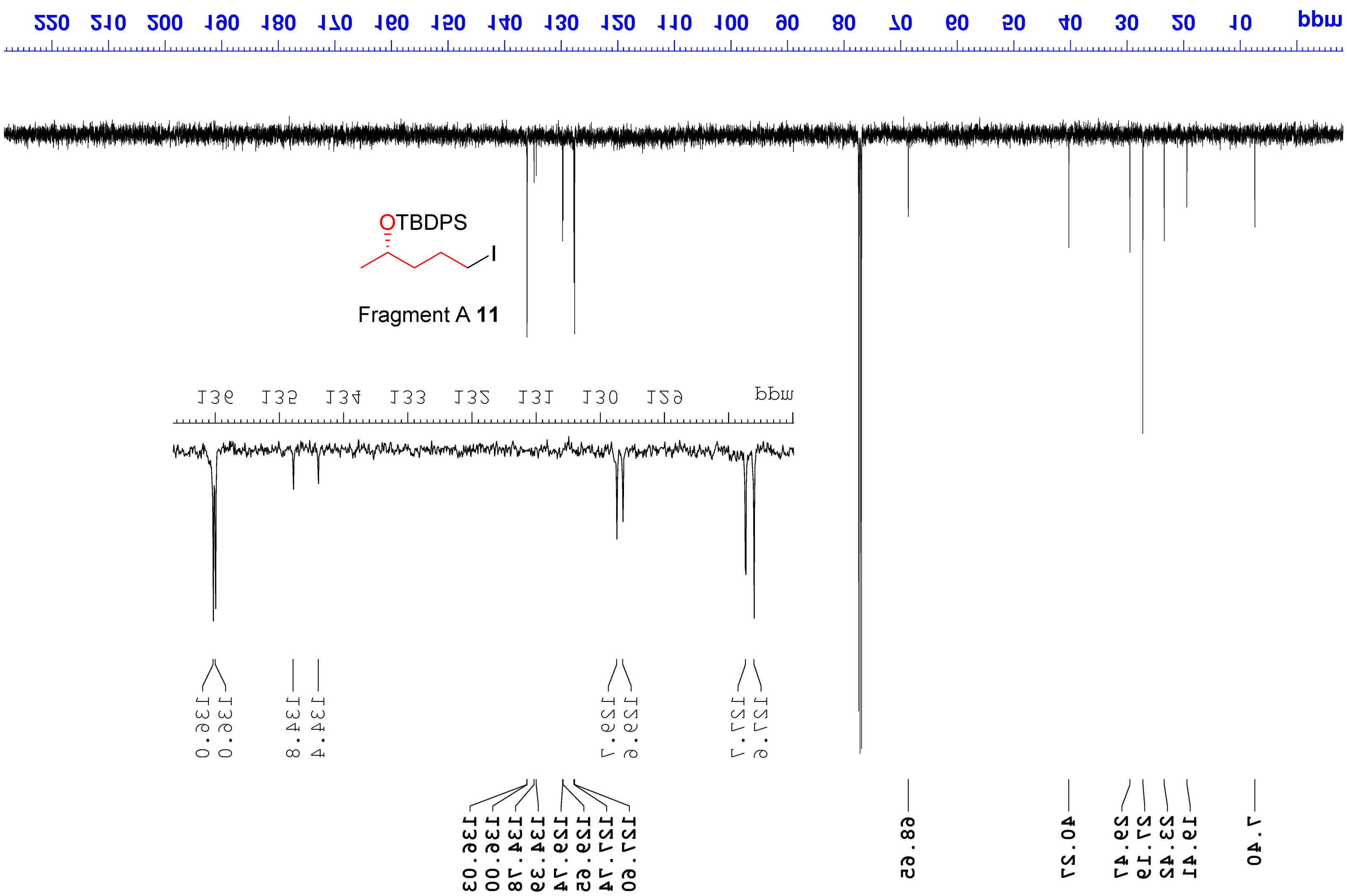
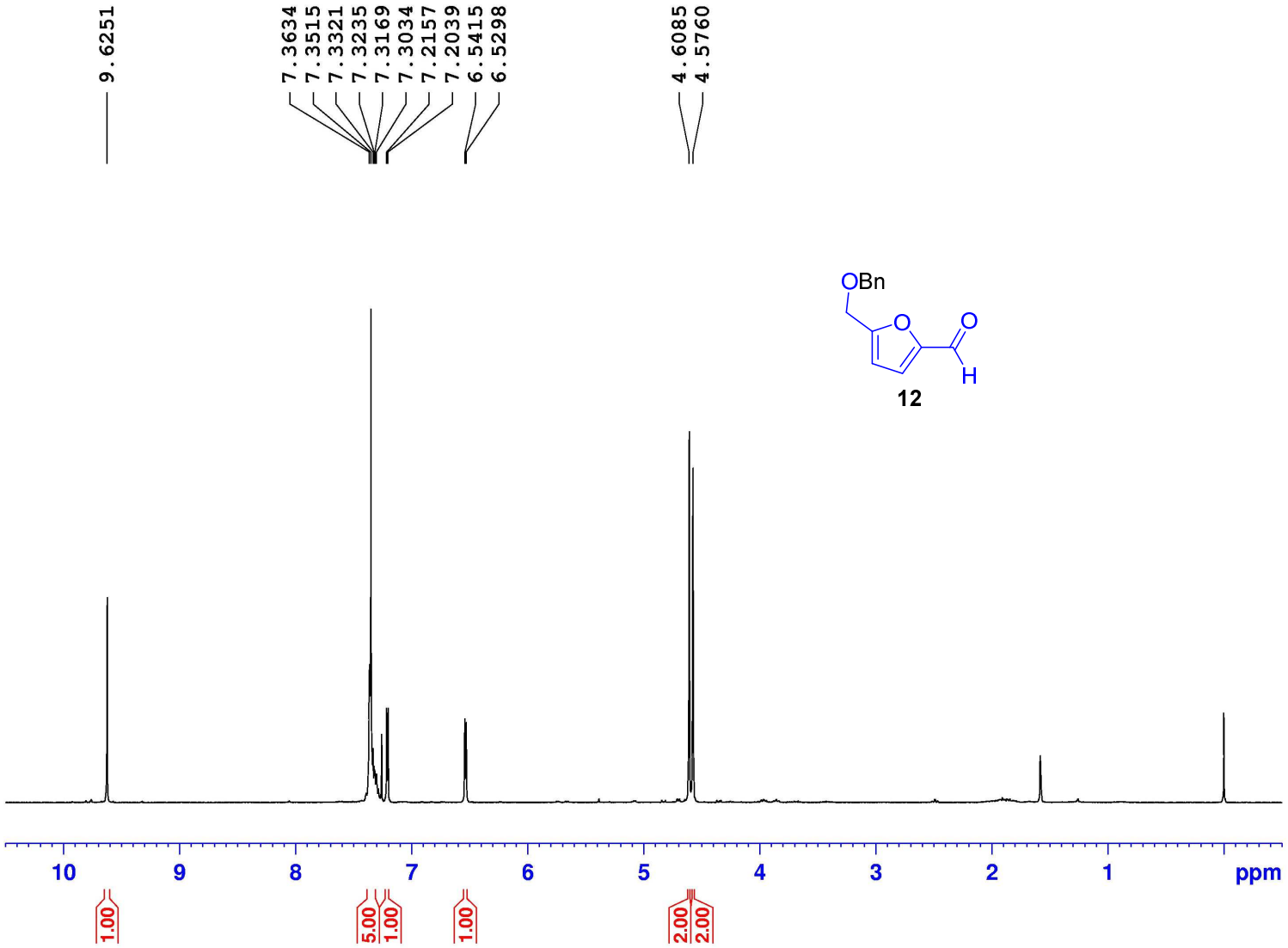
125 MHz



300 MHz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6.5298
4.6085
4.5760
OBn
O
O
H
12
10
9
8
7
6
5
4
3
2
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ppm
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1.00
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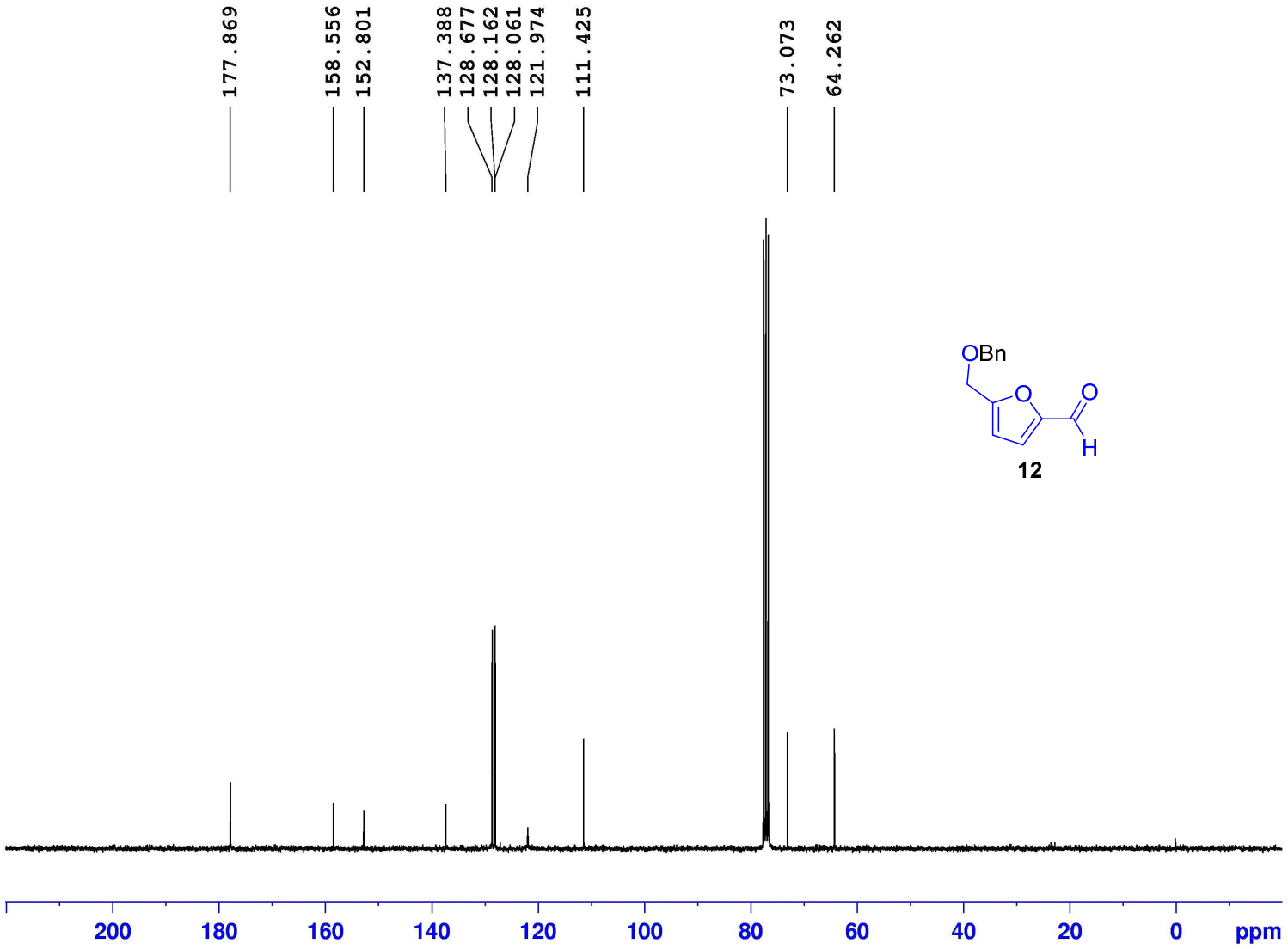
2.00
2.00

75 MHz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O
H
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160
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100
80
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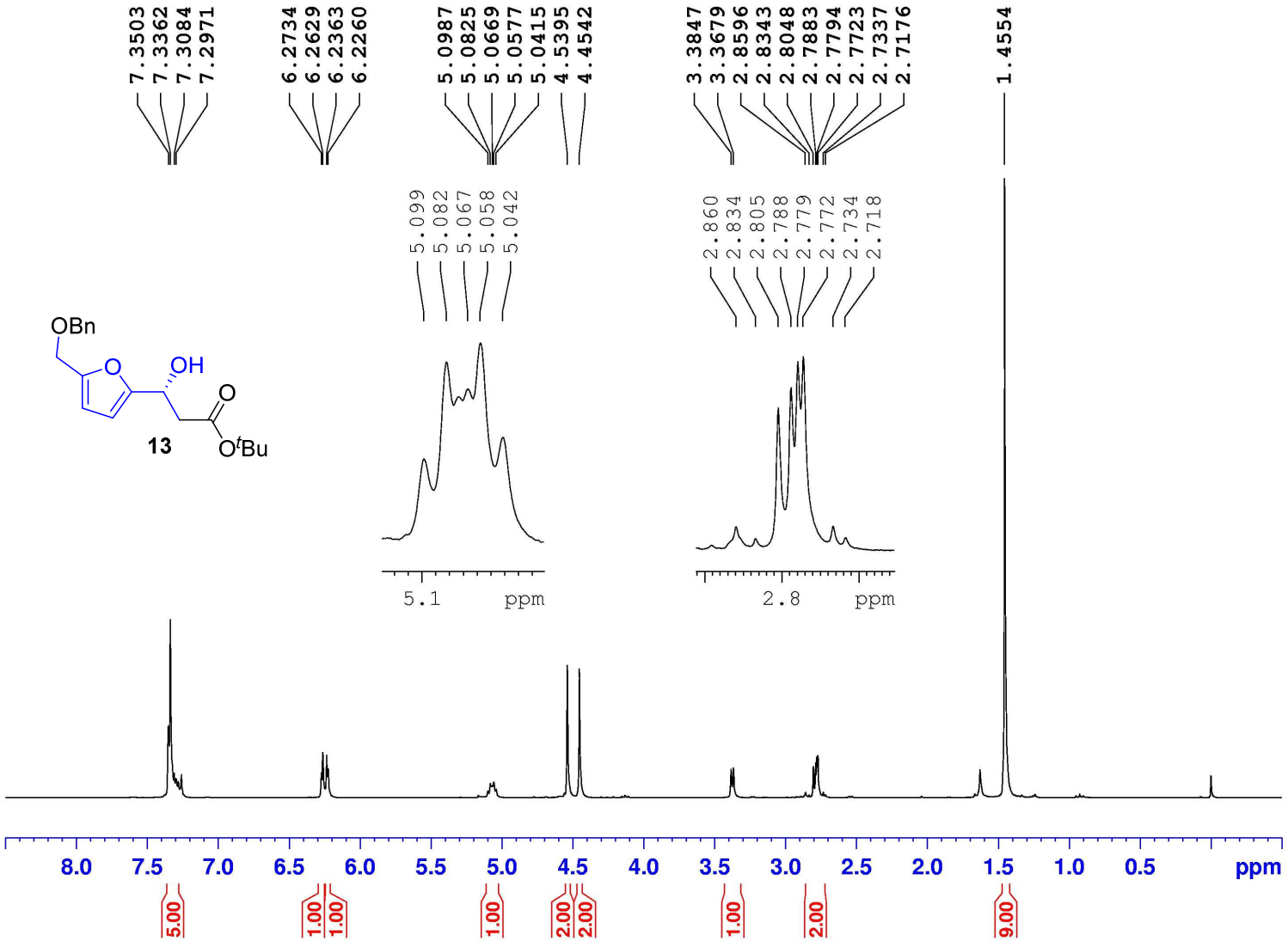
40
20
0
ppm

300 MHz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5.0577
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4.4542
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2.8343
2.8048
2.7883
2.7794
2.7723
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2.7176
1.4554
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5.082
5.067
5.058
5.042
2.860
2.834
2.805
2.788
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O
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O^{t}Bu
5.1
ppm
2.8
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
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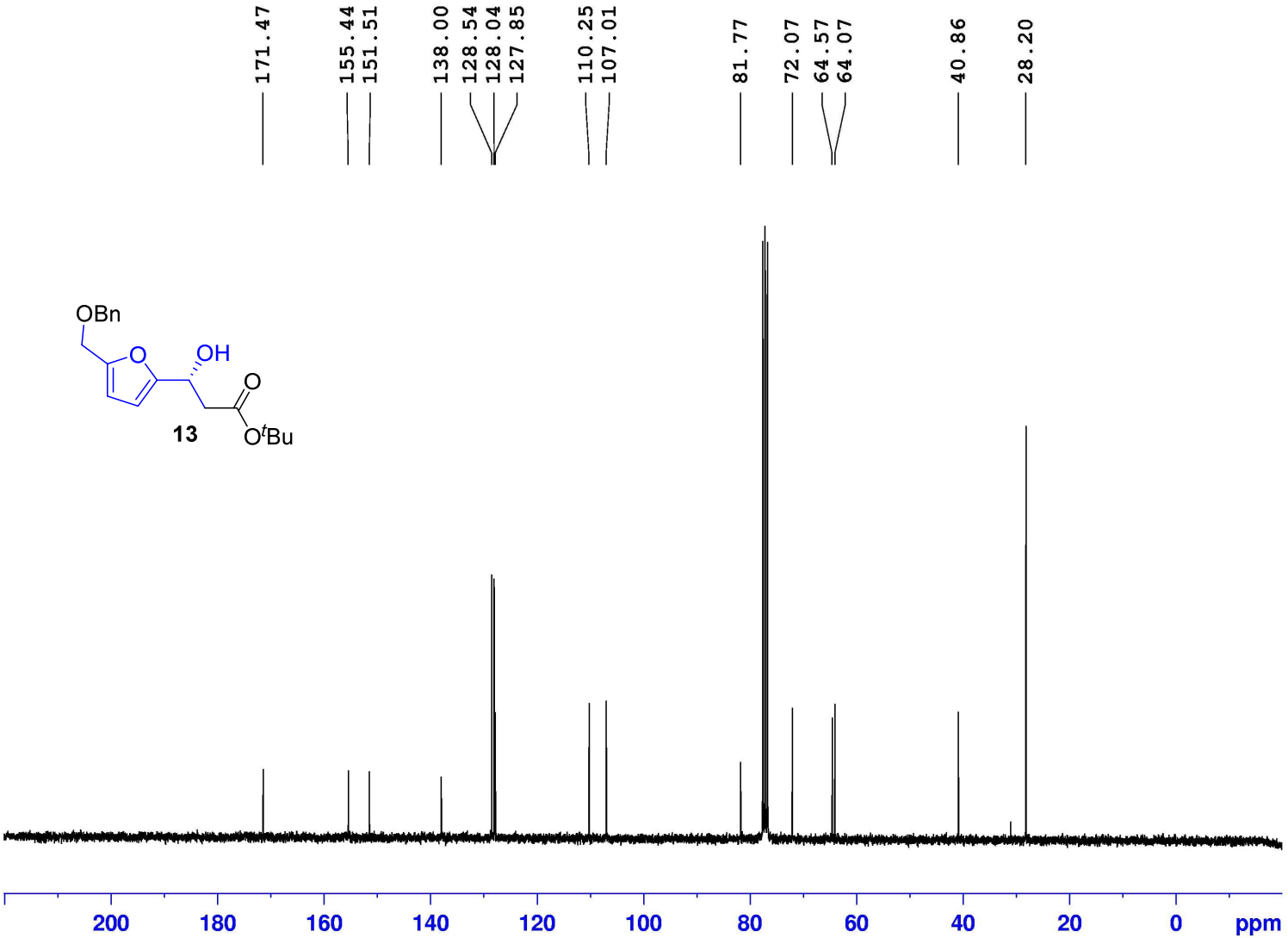
2.00
1.00
2.00
9.00

75 MHz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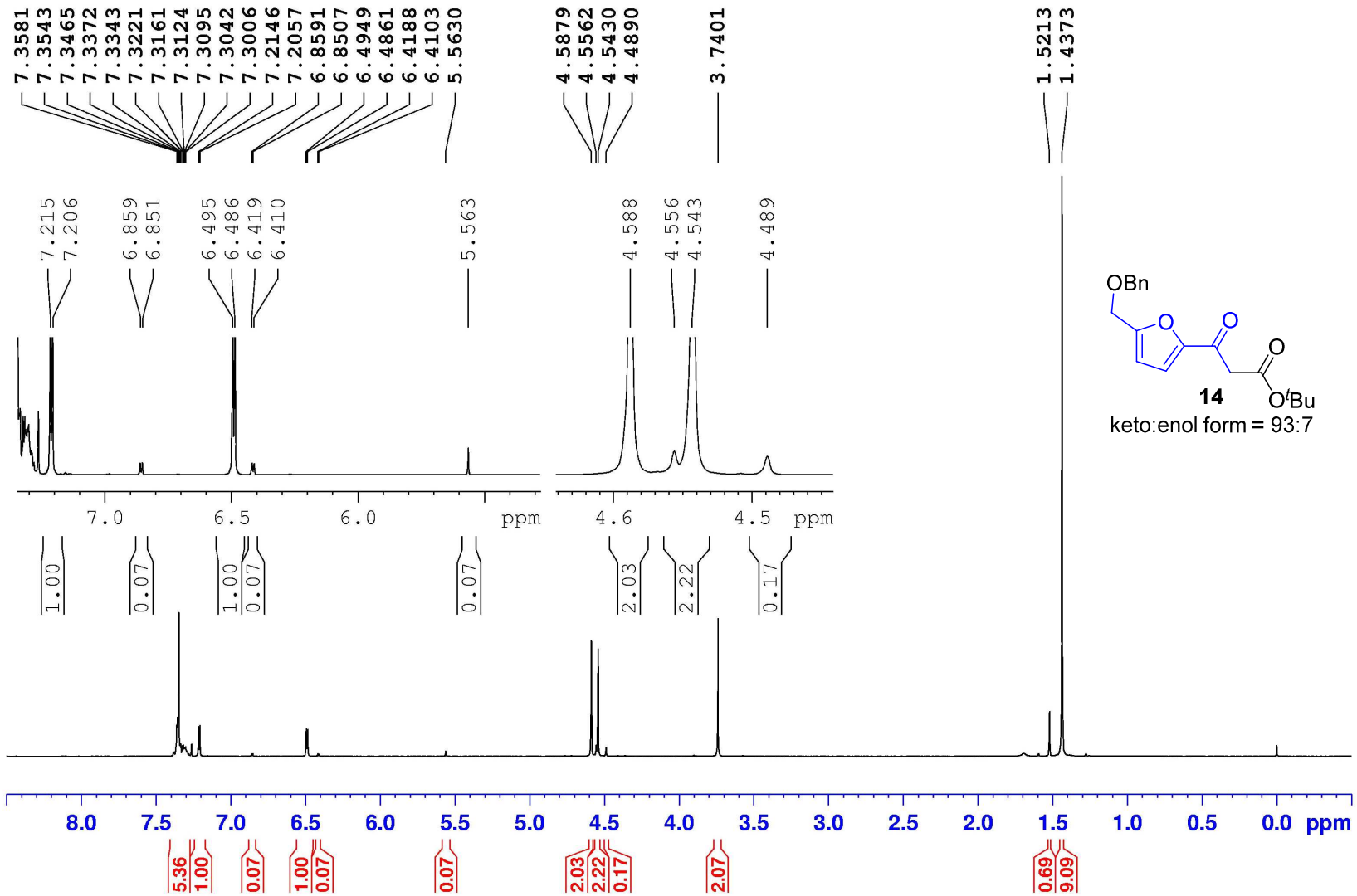
64.07
40.86
28.20
OBn
O
OH
O
O^{t}Bu
13
200
180
160
140
120
100
80
60
40
20
0
ppm

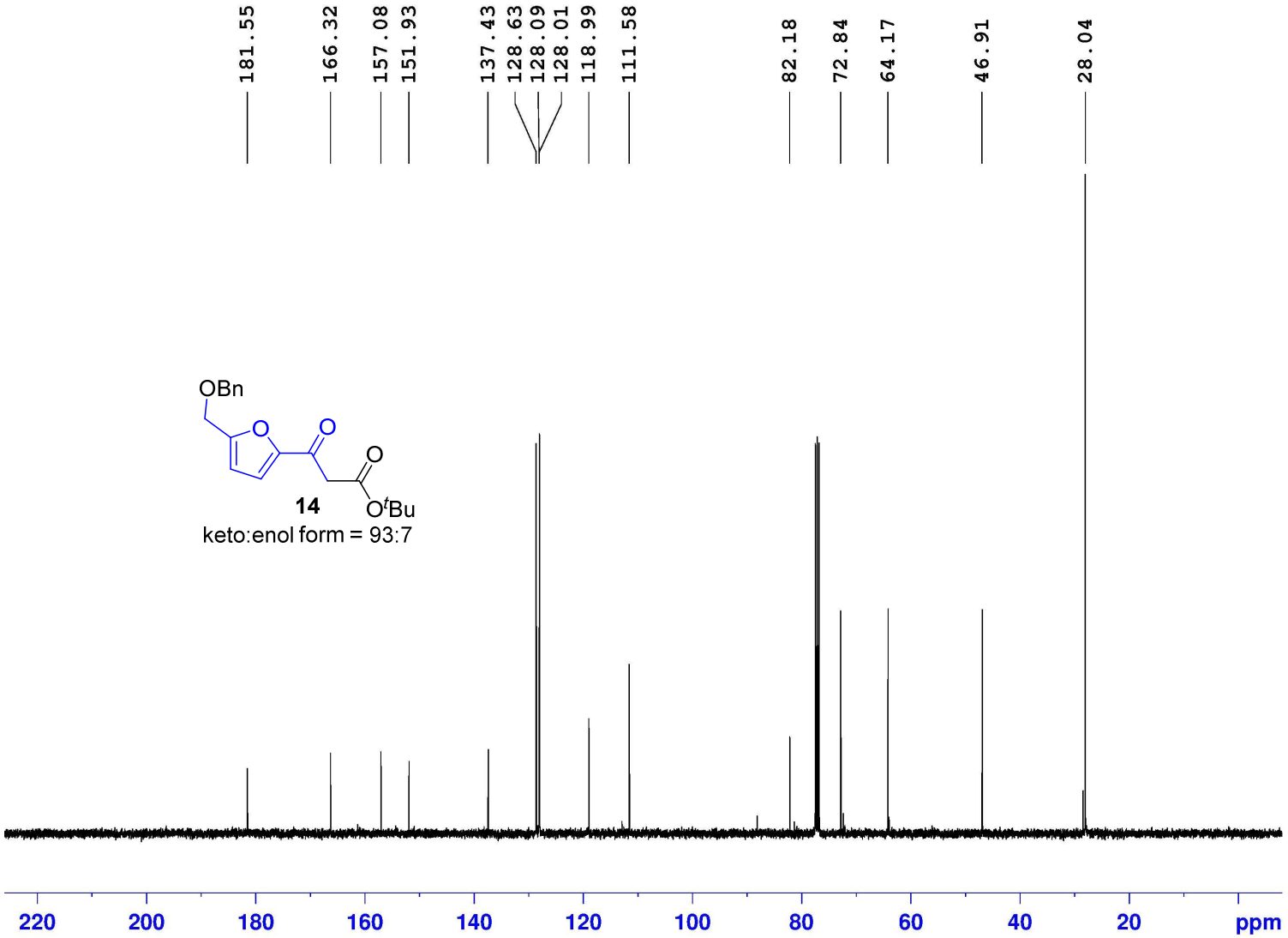
400 MHz



14

keto:enol form = 93:7

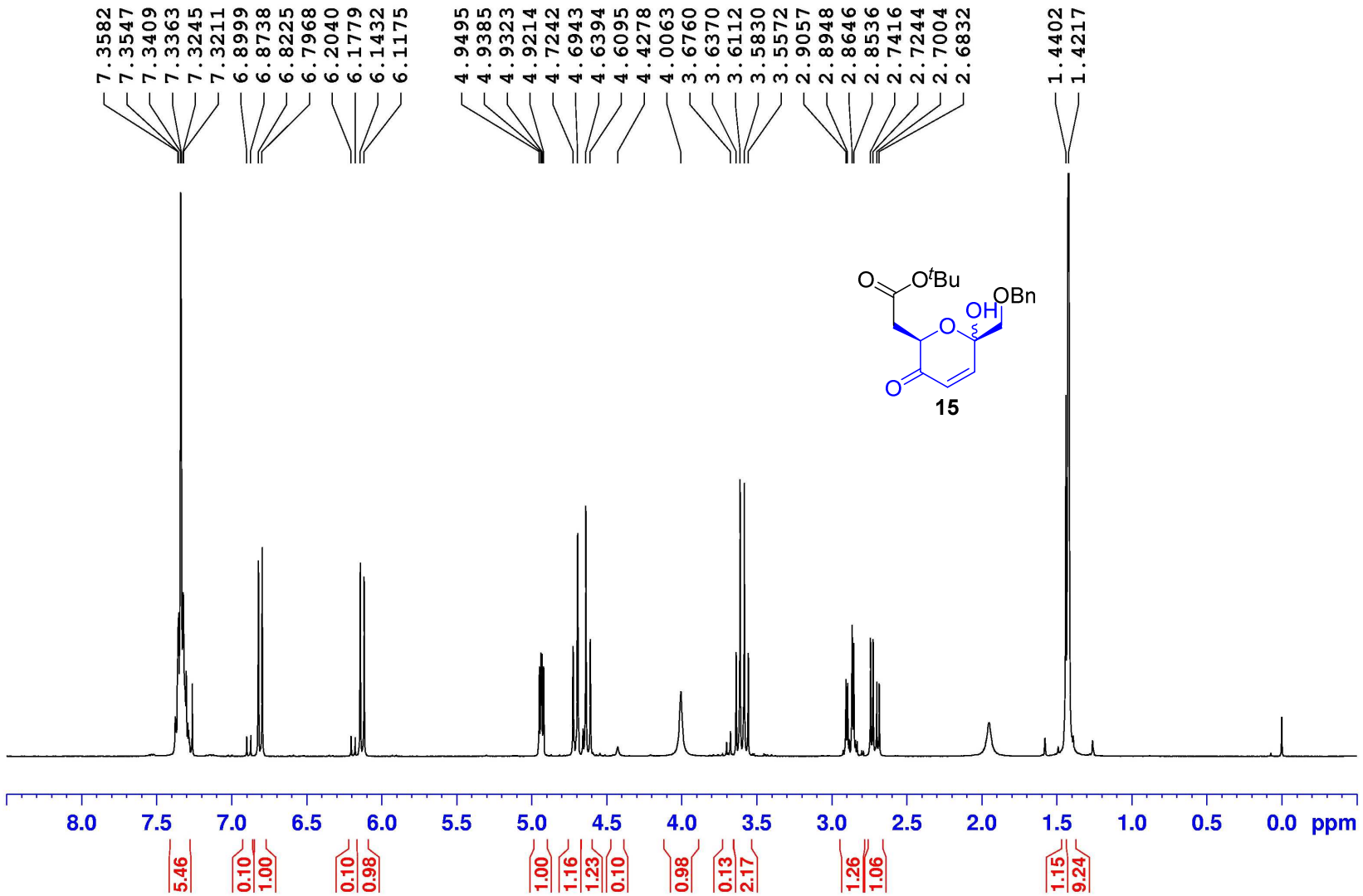
100 MHz



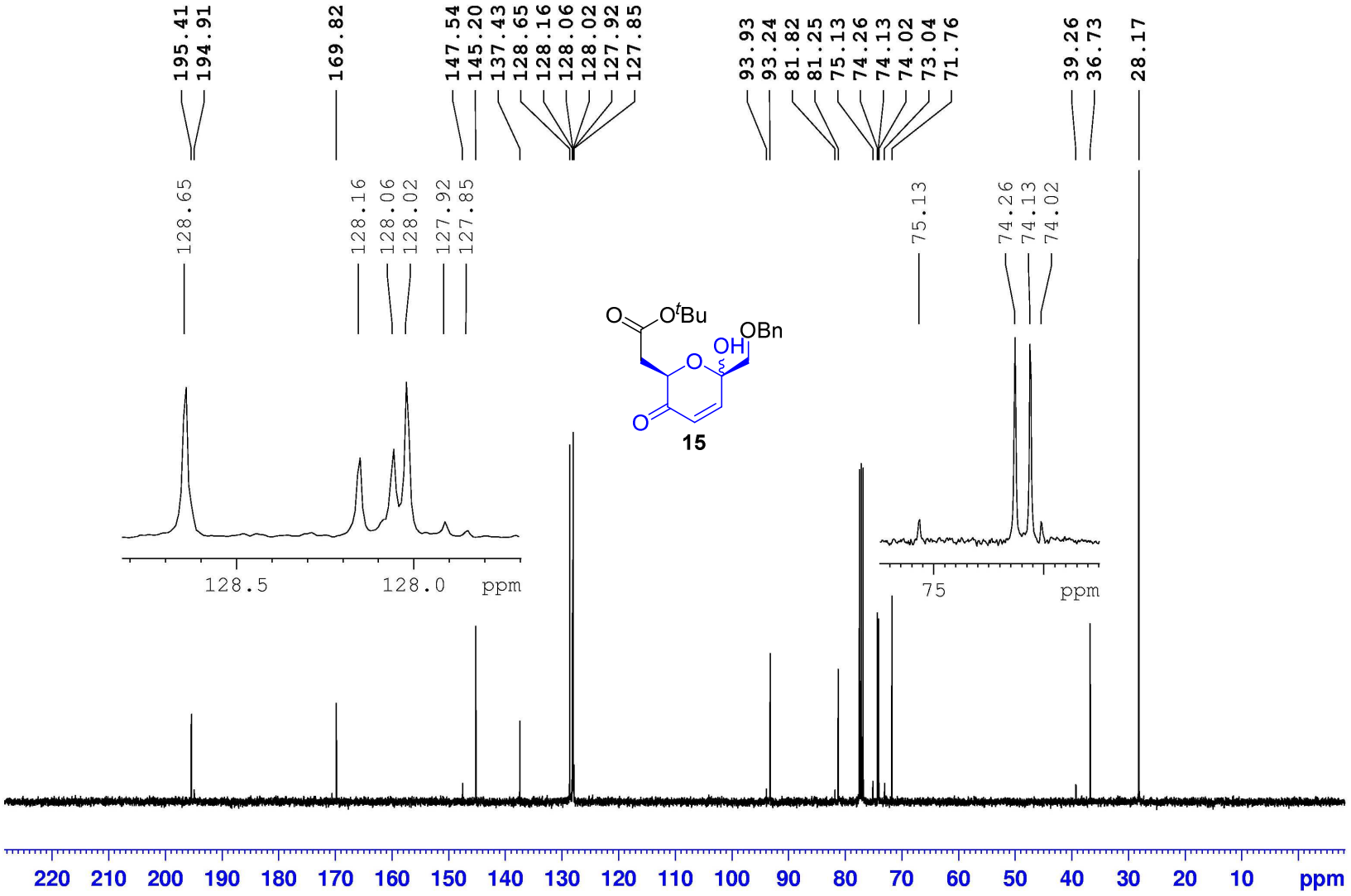
14

keto:enol form = 93:7

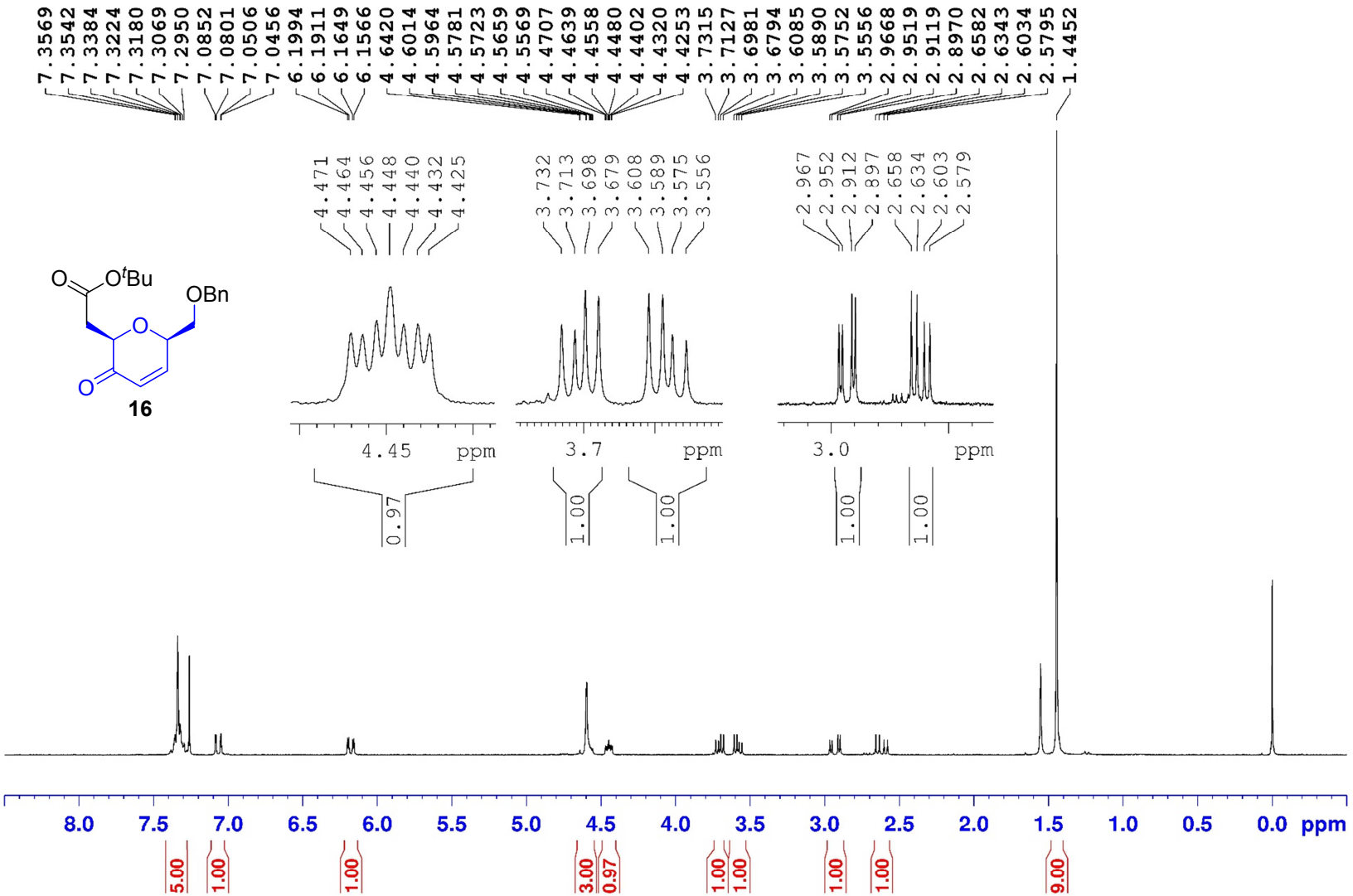
400 MHz


7.3582
7.3547
7.3409
7.3363
7.3245
7.3211
6.8999
6.8738
6.8225
6.7968
6.2040
6.1779
6.1432
6.1175
4.9495
4.9385
4.9323
4.9214
4.7242
4.6943
4.6394
4.6095
4.4278
4.0063
3.6760
3.6370
3.6112
3.5830
3.5572
2.9057
2.8948
2.8646
2.8536
2.7416
2.7244
2.7004
2.6832
1.4402
1.4217
O
O^{t}Bu
OBn
OH
O
O
15
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
0.0
ppm
5.46
0.10
1.00
0.10
0.98
1.00
1.16
1.23
0.10
0.98
0.13
2.17
1.26
1.06
1.15
9.24

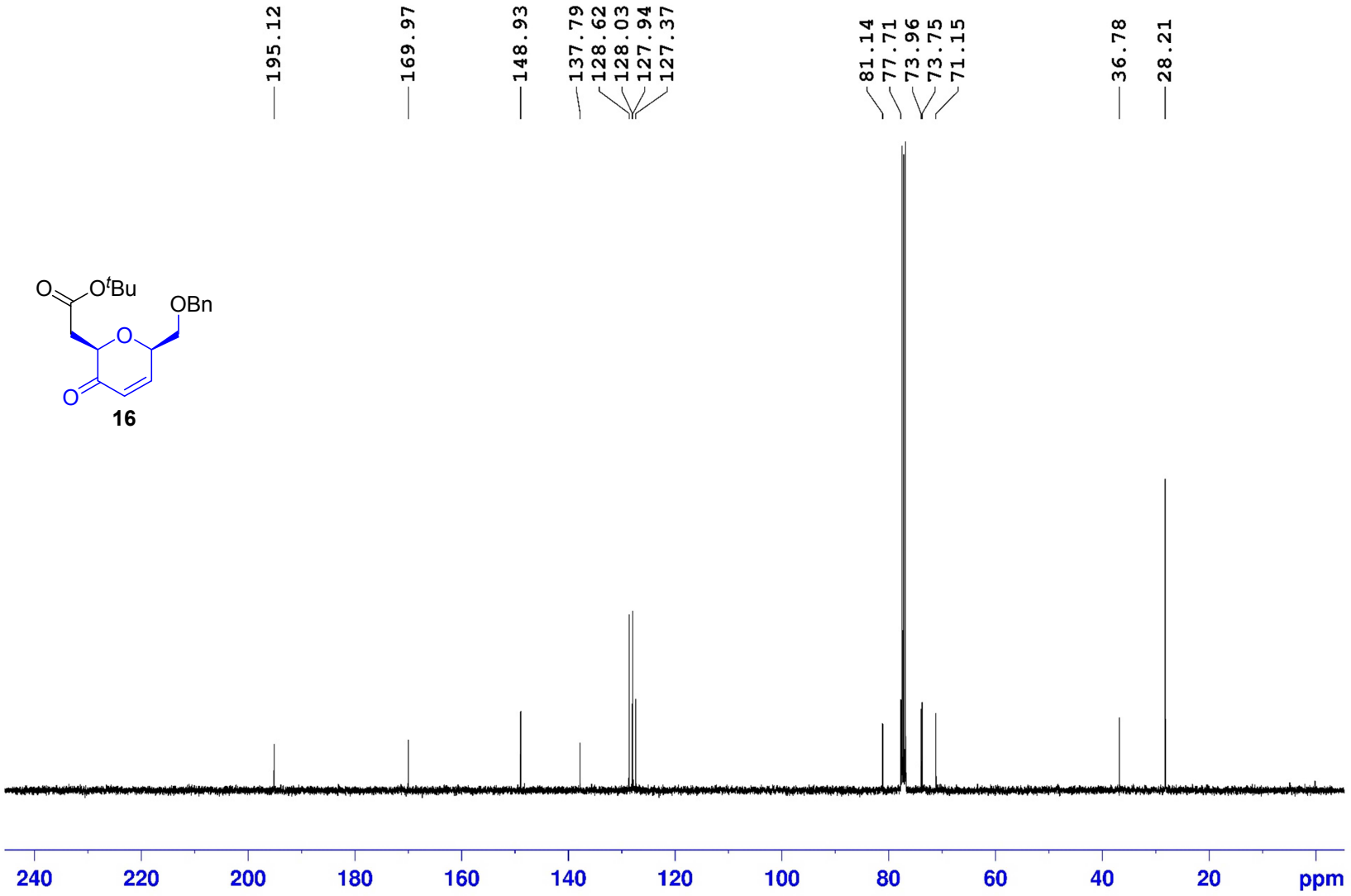
100 MHz


195.41
194.91
169.82
147.54
145.20
137.43
128.65
128.16
128.06
128.02
127.92
127.85
93.93
93.24
81.82
81.25
75.13
74.26
74.13
74.02
73.04
71.76
39.26
36.73
28.17
128.65
128.16
128.06
128.02
127.92
127.85
75.13
74.26
74.13
74.02
O
O^{t}Bu
OBn
OH
O
15
128.5
128.0
ppm
75
ppm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

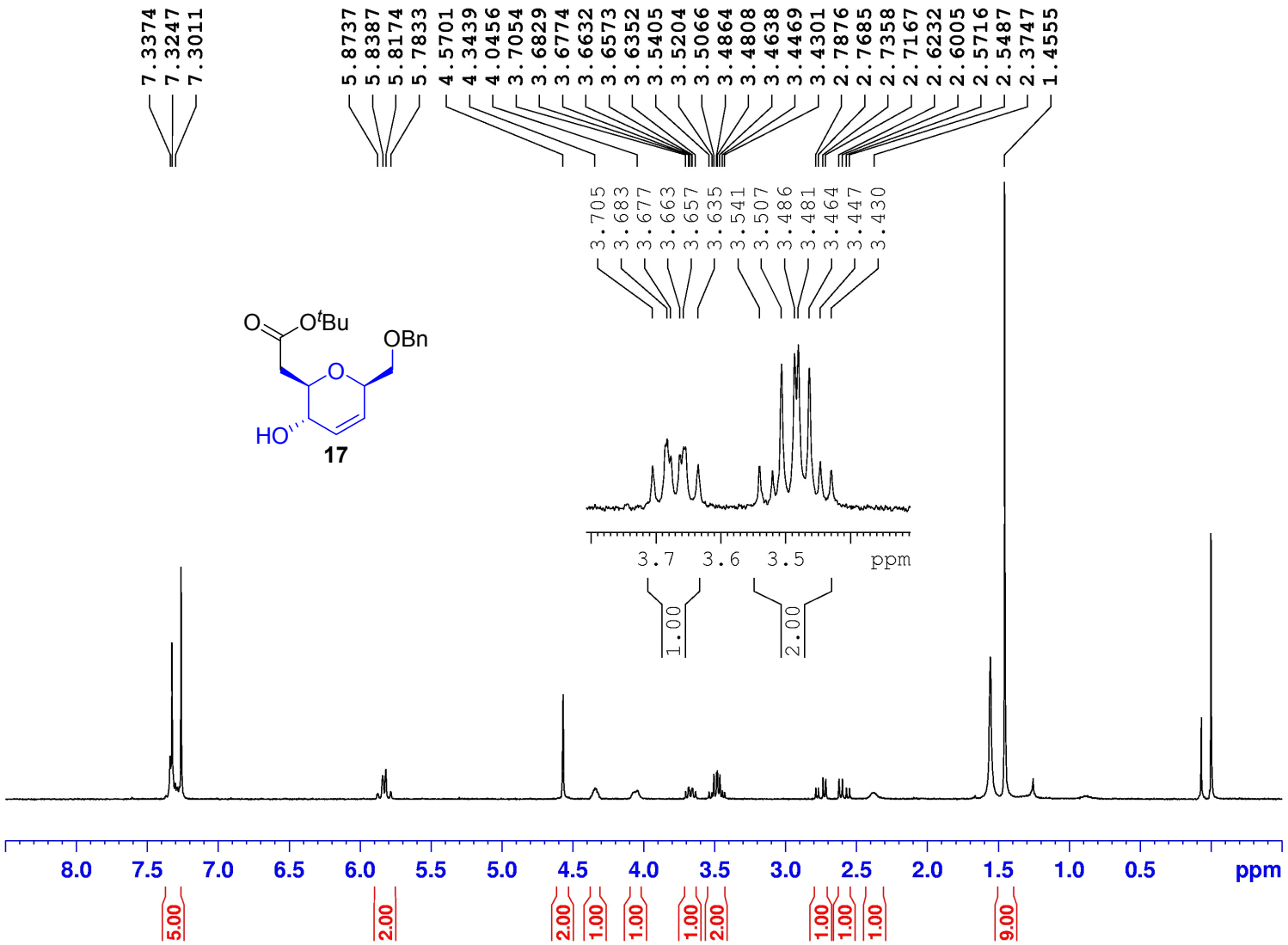
300 MHz


7.3569
7.3542
7.3384
7.3224
7.3180
7.3069
7.2950
7.0852
7.0801
7.0506
7.0456
6.1994
6.1911
6.1649
6.1566
4.6420
4.6014
4.5964
4.5781
4.5723
4.5659
4.5569
4.4707
4.4639
4.4558
4.4480
4.4402
4.4320
4.4253
3.7315
3.7127
3.6981
3.6794
3.6085
3.5890
3.5752
3.5556
2.9668
2.9519
2.9119
2.8970
2.6582
2.6343
2.6034
2.5795
1.4452
4.471
4.464
4.456
4.448
4.440
4.432
4.425
3.732
3.713
3.698
3.679
3.608
3.589
3.575
3.556
2.967
2.952
2.912
2.897
2.658
2.634
2.603
2.579
O
O^{t}Bu
OBn
O
O
16
4.45 ppm
3.7 ppm
3.0 ppm
0.97
1.00
1.00
1.00
1.00
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 0.0 ppm
5.00
1.00
1.00
3.00
0.97
1.00
1.00
1.00
1.00
9.00

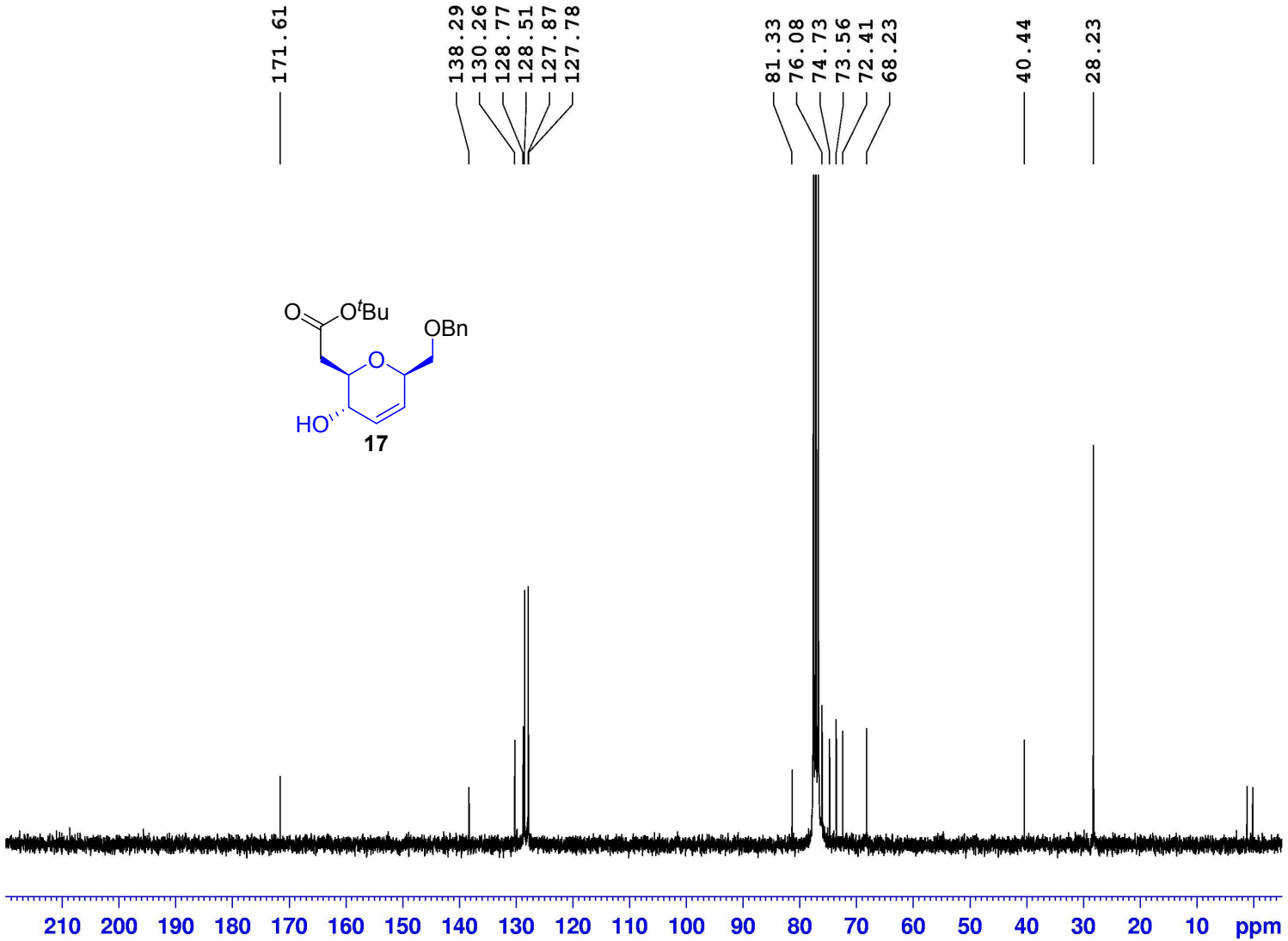
100 MHz


195.12
169.97
148.93
137.79
128.62
128.03
127.94
127.37
81.14
77.71
73.96
73.75
71.15
36.78
28.21
O
O^{t}Bu
OBn
O
O
16
240
220
200
180
160
140
120
100
80
60
40
20
ppm

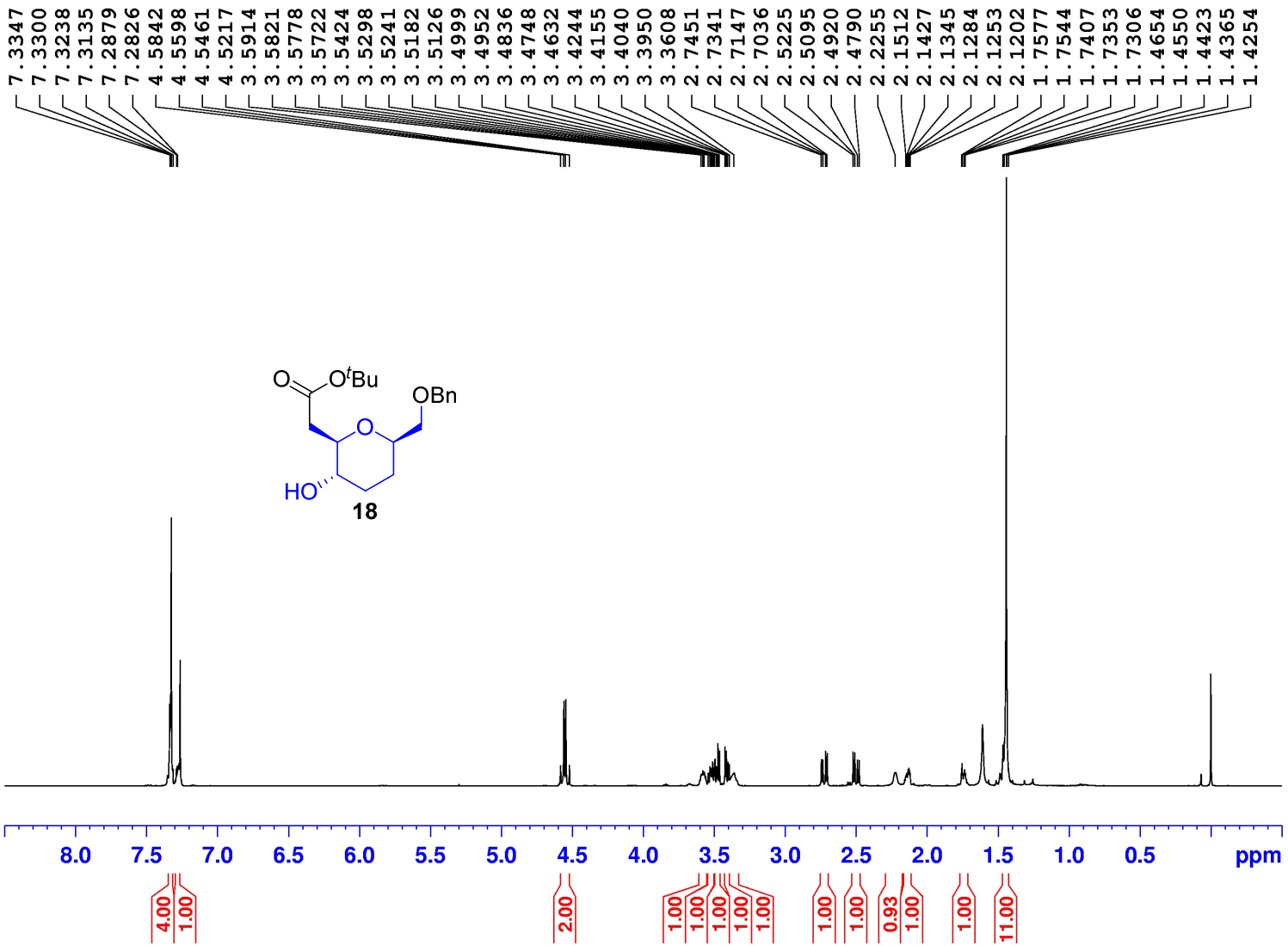
300 MHz


7.3374
7.3247
7.3011
5.8737
5.8387
5.8174
5.7833
4.5701
4.3439
4.0456
3.7054
3.6829
3.6774
3.6632
3.6573
3.6352
3.5405
3.5204
3.5066
3.4864
3.4808
3.4638
3.4469
3.4301
2.7876
2.7685
2.7358
2.7167
2.6232
2.6005
2.5716
2.5487
2.3747
1.4555
3.705
3.683
3.677
3.663
3.657
3.635
3.541
3.507
3.486
3.481
3.464
3.447
3.430
O
O^{t}Bu
OBn
O
HO
17
3.7
3.6
3.5
ppm
1.00
2.00
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
5.00
2.00
2.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
9.00

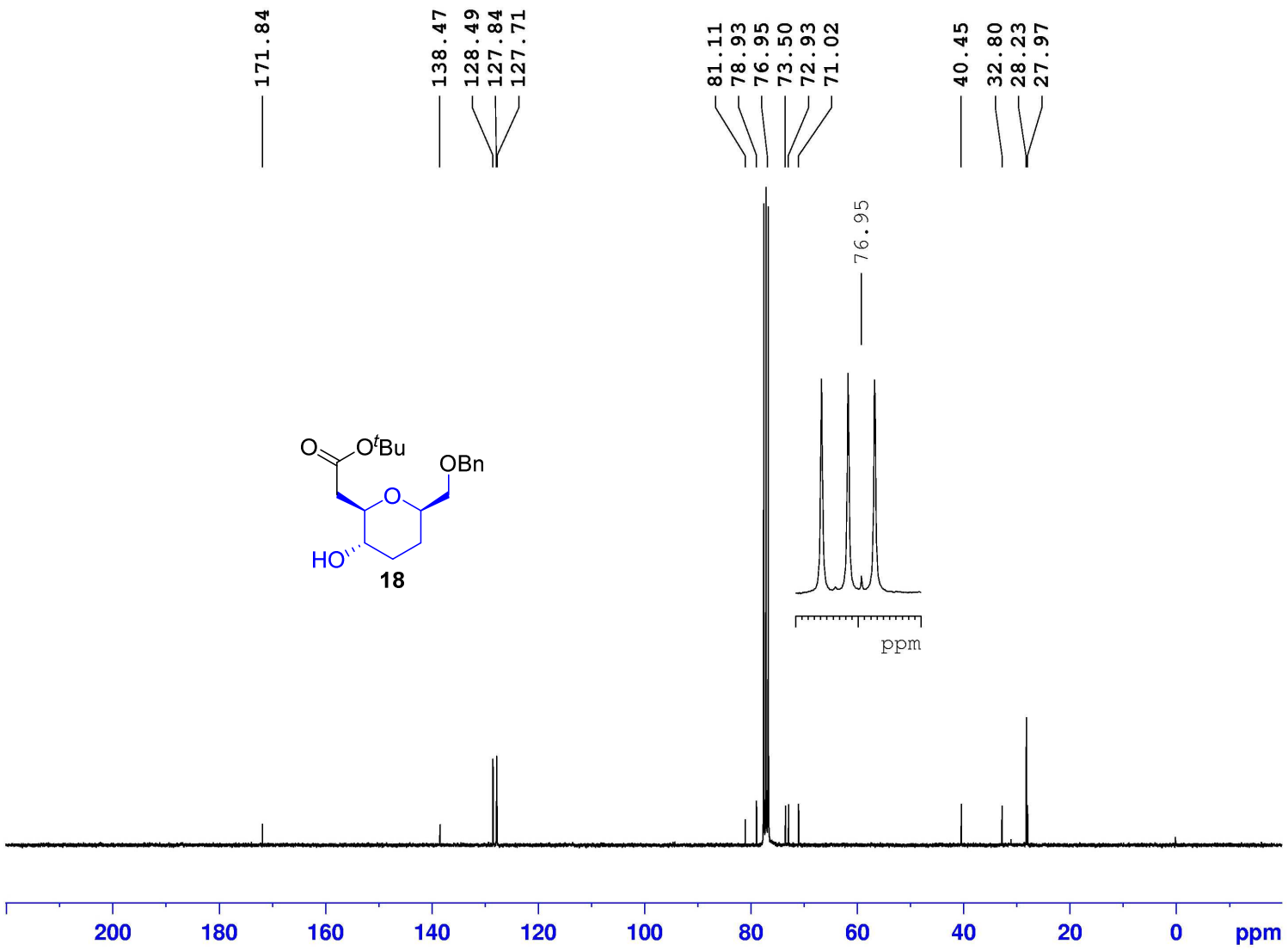
75 MHz


171.61
138.29
130.26
128.77
128.51
127.87
127.78
81.33
76.08
74.73
73.56
72.41
68.23
40.44
28.23
O
O^{t}Bu
OBn
O
HO
17
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

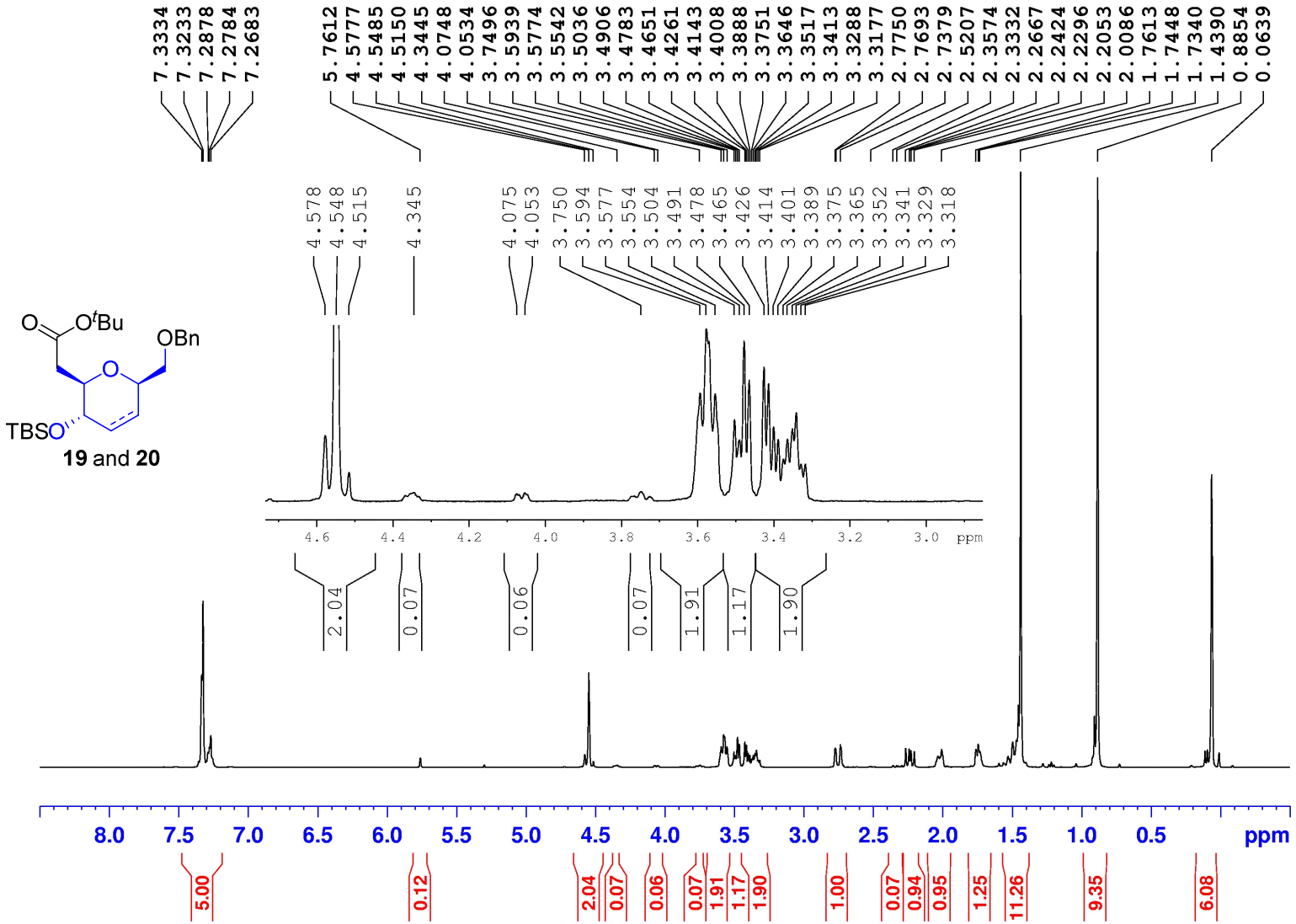
500 MHz


7.3347
7.3300
7.3238
7.3135
7.2879
7.2826
4.5842
4.5598
4.5461
4.5217
3.5914
3.5821
3.5778
3.5722
3.5424
3.5298
3.5241
3.5182
3.5126
3.4999
3.4952
3.4836
3.4748
3.4632
3.4244
3.4155
3.4040
3.3950
3.3608
2.7451
2.7341
2.7147
2.7036
2.5225
2.5095
2.4920
2.4790
2.2255
2.1512
2.1427
2.1345
2.1284
2.1253
2.1202
1.7577
1.7544
1.7407
1.7353
1.7306
1.4654
1.4550
1.4423
1.4365
1.4254
O
O^{t}Bu
OBn
O
HO
18
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
4.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
0.93
1.00
1.00
11.00

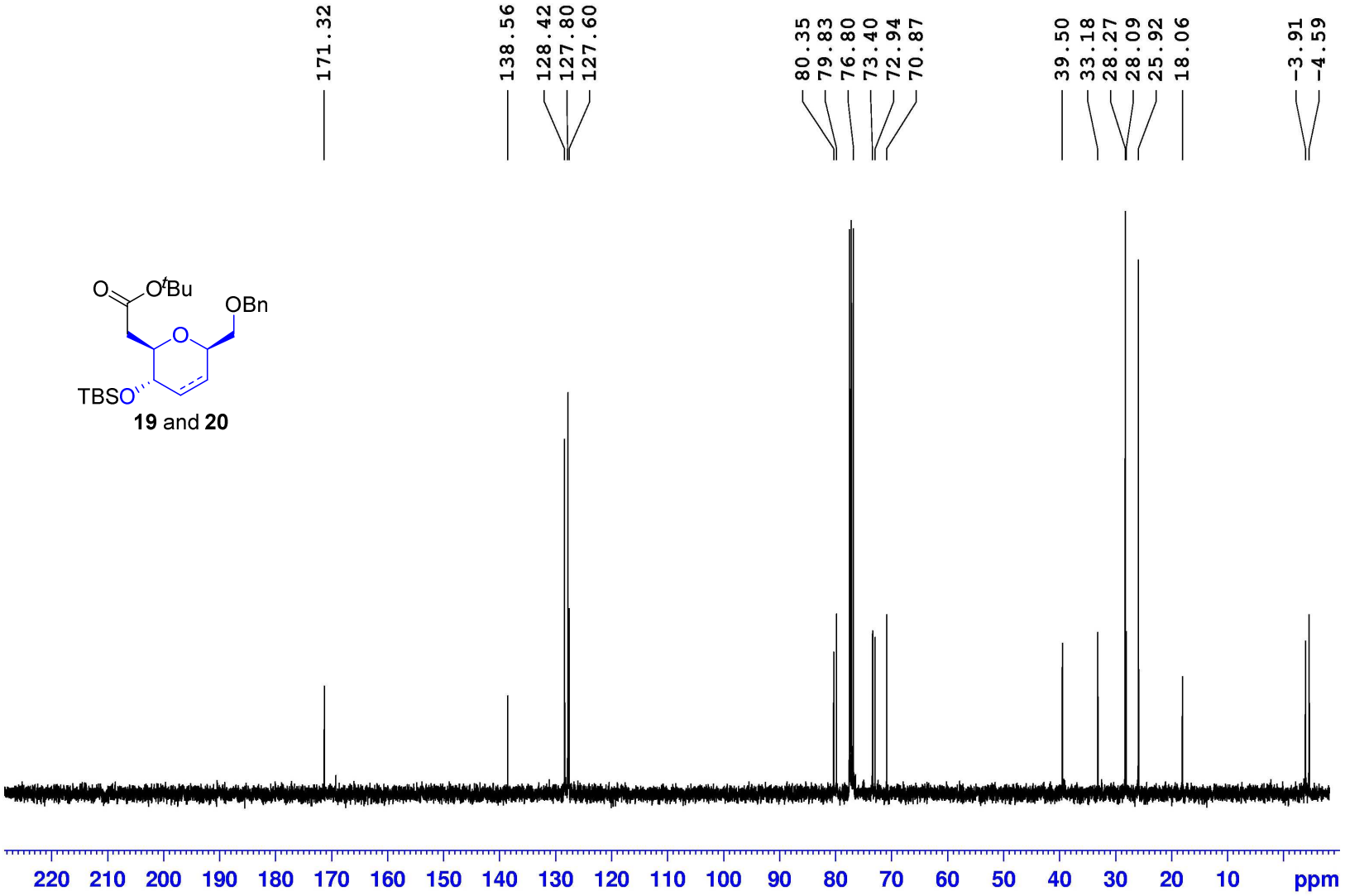
75 MHz


171.84
138.47
128.49
127.84
127.71
81.11
78.93
76.95
73.50
72.93
71.02
40.45
32.80
28.23
27.97
76.95
ppm
O
O^{t}Bu
OBn
O
HO
18
200
180
160
140
120
100
80
60
40
20
0
ppm

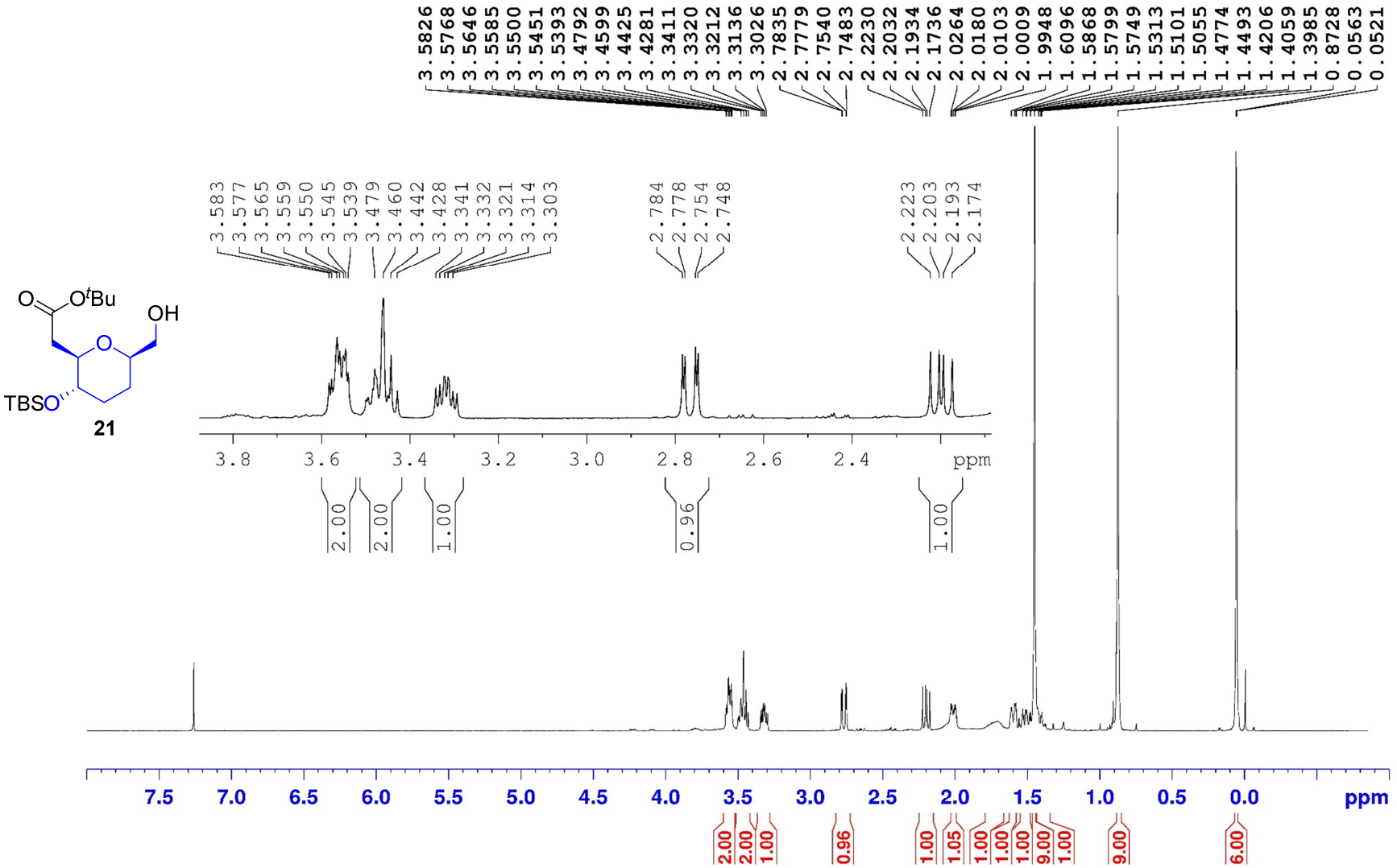
400 MHz


7.3334
7.3233
7.2878
7.2784
7.2683
5.7612
4.5777
4.5485
4.5150
4.3445
4.0748
4.0534
3.7496
3.5939
3.5774
3.5542
3.5036
3.4906
3.4783
3.4651
3.4261
3.4143
3.4008
3.3888
3.3751
3.3646
3.3517
3.3413
3.3288
3.3177
2.7750
2.7693
2.7379
2.5207
2.3574
2.3332
2.2667
2.2424
2.2296
2.2053
2.0086
1.7613
1.7448
1.7340
1.4390
0.8854
0.0639
4.578
4.548
4.515
4.345
4.075
4.053
3.750
3.594
3.577
3.554
3.504
3.491
3.478
3.465
3.426
3.414
3.401
3.389
3.375
3.365
3.352
3.341
3.329
3.318
O
O^{t}Bu
OBn
O
TBSO
19 and 20
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
ppm
2.04
0.07
0.06
0.07
1.91
1.17
1.90
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
5.00
0.12
2.04
0.07
0.06
0.07
1.91
1.17
1.90
1.00
0.07
0.94
0.95
1.25
11.26
9.35
6.08

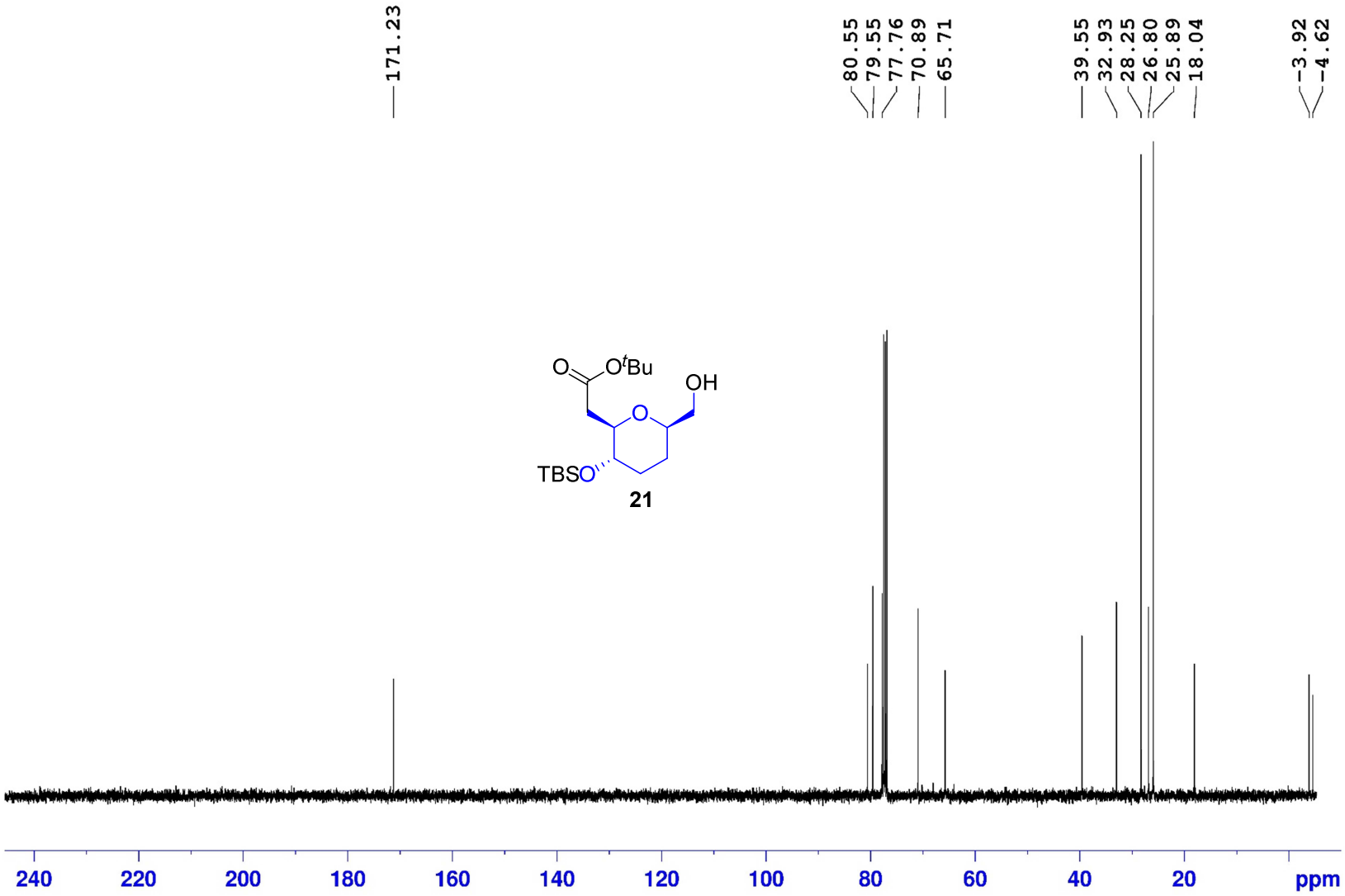
100 MHz


171.32
138.56
128.42
127.80
127.60
80.35
79.83
76.80
73.40
72.94
70.87
39.50
33.18
28.27
28.09
25.92
18.06
-3.91
-4.59
O
O
tBu
OBn
O
TBSO
19 and 20
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

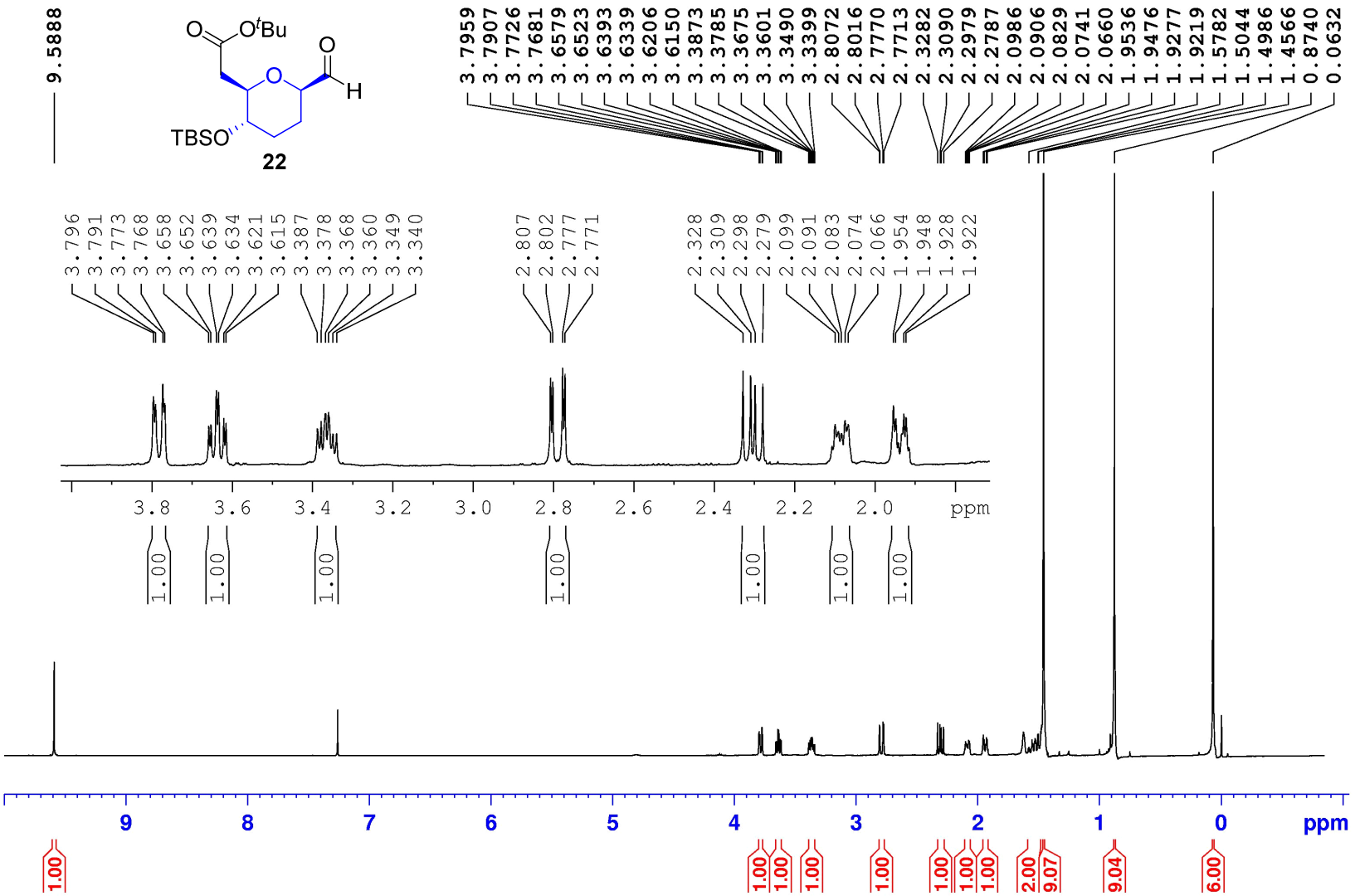
500 MHz


3.5826
3.5768
3.5646
3.5585
3.5500
3.5451
3.5393
3.4792
3.4599
3.4425
3.4281
3.3411
3.3320
3.3212
3.3136
3.3026
2.7835
2.7779
2.7540
2.7483
2.2230
2.2032
2.1934
2.1736
2.0264
2.0180
2.0103
2.0009
1.9948
1.6096
1.5868
1.5799
1.5749
1.5313
1.5101
1.5055
1.4774
1.4493
1.4206
1.4059
1.3985
0.8728
0.0563
0.0521
3.583
3.577
3.565
3.559
3.550
3.545
3.539
3.479
3.460
3.442
3.428
3.341
3.332
3.321
3.314
3.303
2.784
2.778
2.754
2.748
2.223
2.203
2.193
2.174
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
ppm
2.00
2.00
1.00
0.96
1.00
O
O
tBu
OH
O
TBSO
21
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
2.00
2.00
1.00
0.96
1.00
1.05
1.00
1.00
1.00
9.00
1.00
9.00
6.00

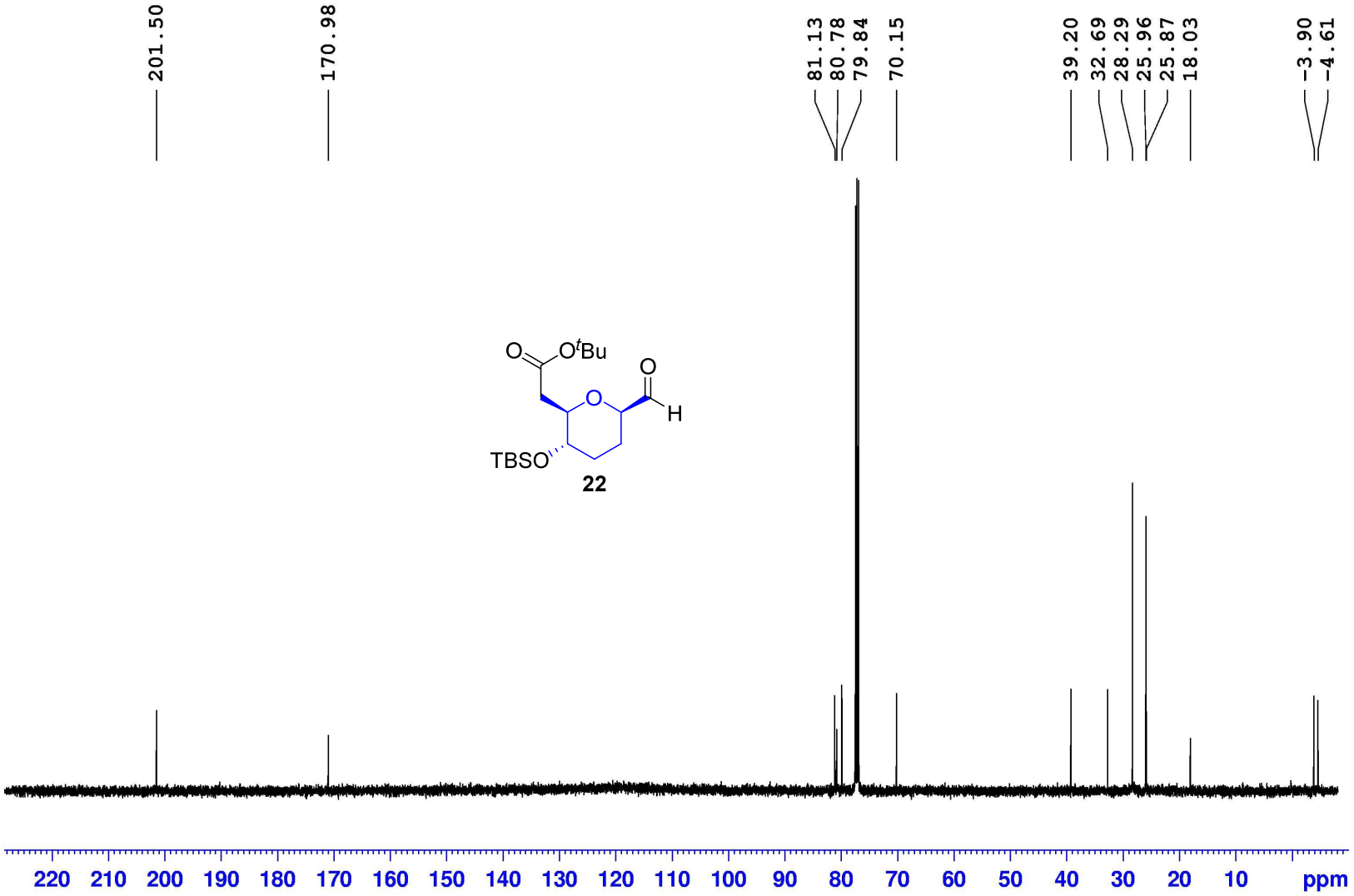
100 MHz


171.23
80.55
79.55
77.76
70.89
65.71
39.55
32.93
28.25
26.80
25.89
18.04
-3.92
-4.62
O
O^{t}Bu
OH
O
TBSO
21
240
220
200
180
160
140
120
100
80
60
40
20
ppm

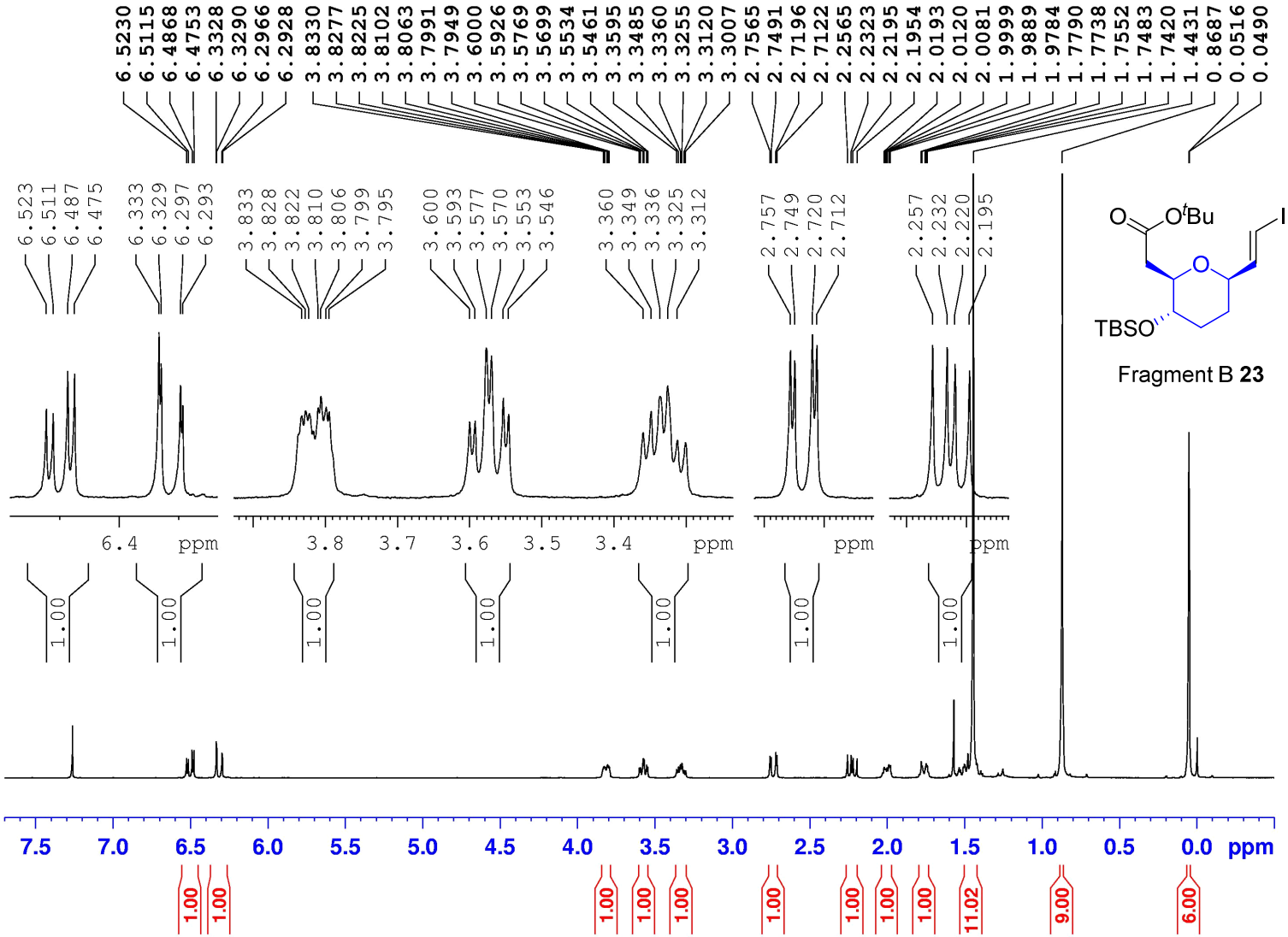
500 MHz


9.5888
O
O
tBu
O
O
H
TBSO
22
3.7959
3.7907
3.7726
3.7681
3.6579
3.6523
3.6393
3.6339
3.6206
3.6150
3.3873
3.3785
3.3675
3.3601
3.3490
3.3399
2.8072
2.8016
2.7770
2.7713
2.3282
2.3090
2.2979
2.2787
2.0986
2.0906
2.0829
2.0741
2.0660
1.9536
1.9476
1.9277
1.9219
1.5782
1.5044
1.4986
1.4566
0.8740
0.0632
3.796
3.791
3.773
3.768
3.658
3.652
3.639
3.634
3.621
3.615
3.387
3.378
3.368
3.360
3.349
3.340
2.807
2.802
2.777
2.771
2.328
2.309
2.298
2.279
2.099
2.091
2.083
2.074
2.066
1.954
1.948
1.928
1.922
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
ppm
1.00
1.00
1.00
1.00
1.00
1.00
1.00
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
9.07
9.04
6.00

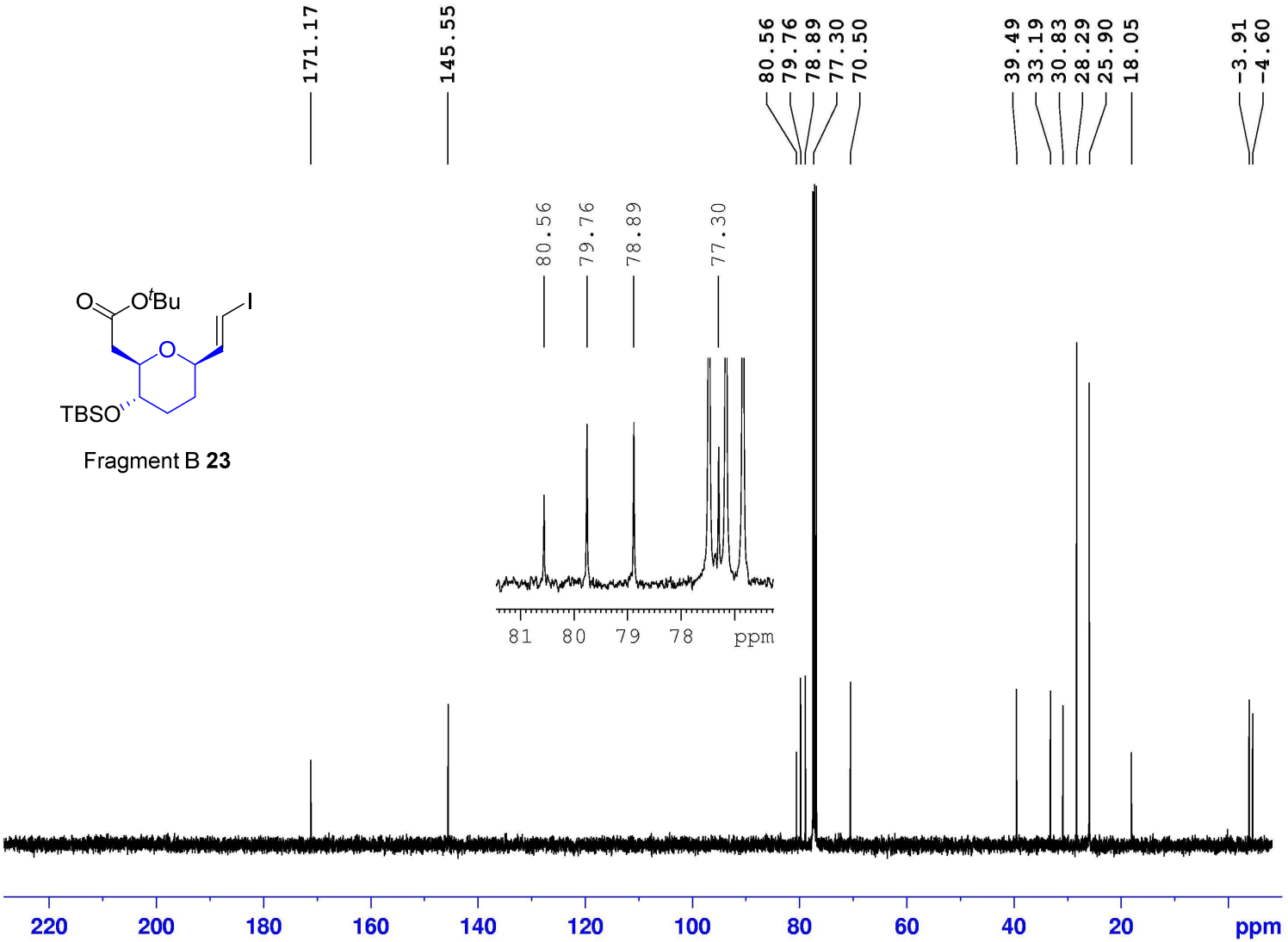
125 MHz


201.50
170.98
81.13
80.78
79.84
70.15
39.20
32.69
28.29
25.96
25.87
18.03
-3.90
-4.61
O
O
tBu
O
O
H
TBSO
22
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

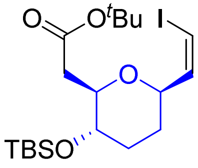
400 MHz


6.5230 6.5115 6.4868 6.4753 6.3328 6.3290 6.2966 6.2928
3.8330 3.8277 3.8225 3.8102 3.8063 3.7991 3.7949 3.6000 3.5926 3.5769 3.5699 3.5534 3.5461 3.3595 3.3485 3.3360 3.3255 3.3120 3.3007
2.7565 2.7491 2.7196 2.7122 2.2565 2.2323 2.2195 2.1954 2.0193 2.0120 2.0081 1.9999 1.9889 1.9784 1.7790 1.7738 1.7552 1.7483 1.7420 1.4431 0.8687 0.0516 0.0490
6.523 6.511 6.487 6.475
6.333 6.329 6.297 6.293
3.833 3.828 3.822 3.810 3.806 3.799 3.795
3.600 3.593 3.577 3.570 3.553 3.546
3.360 3.349 3.336 3.325 3.312
2.757 2.749 2.720 2.712
2.257 2.232 2.220 2.195
6.4 ppm
3.8 3.7 3.6 3.5 3.4 ppm
ppm
ppm
1.00
O
O
tBu
I
O
TBSO
Fragment B 23
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
1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 11.02 9.00 6.00

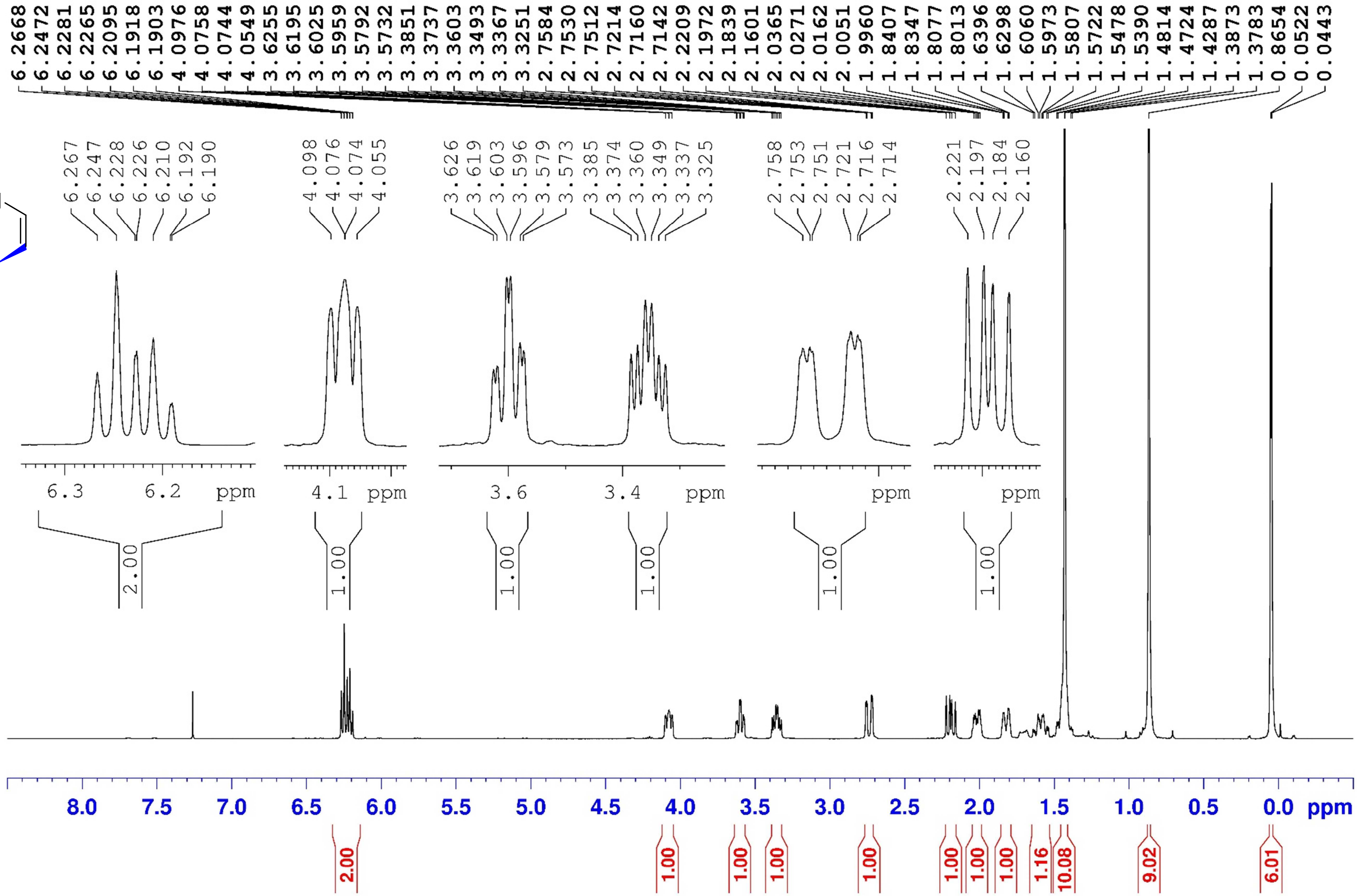
100 MHz


171.17
145.55
80.56
79.76
78.89
77.30
70.50
39.49
33.19
30.83
28.29
25.90
18.05
-3.91
-4.60
O
O^{t}Bu
I
O
TBSO
Fragment B **23**
81
80
79
78
ppm
220
200
180
160
140
120
100
80
60
40
20
ppm

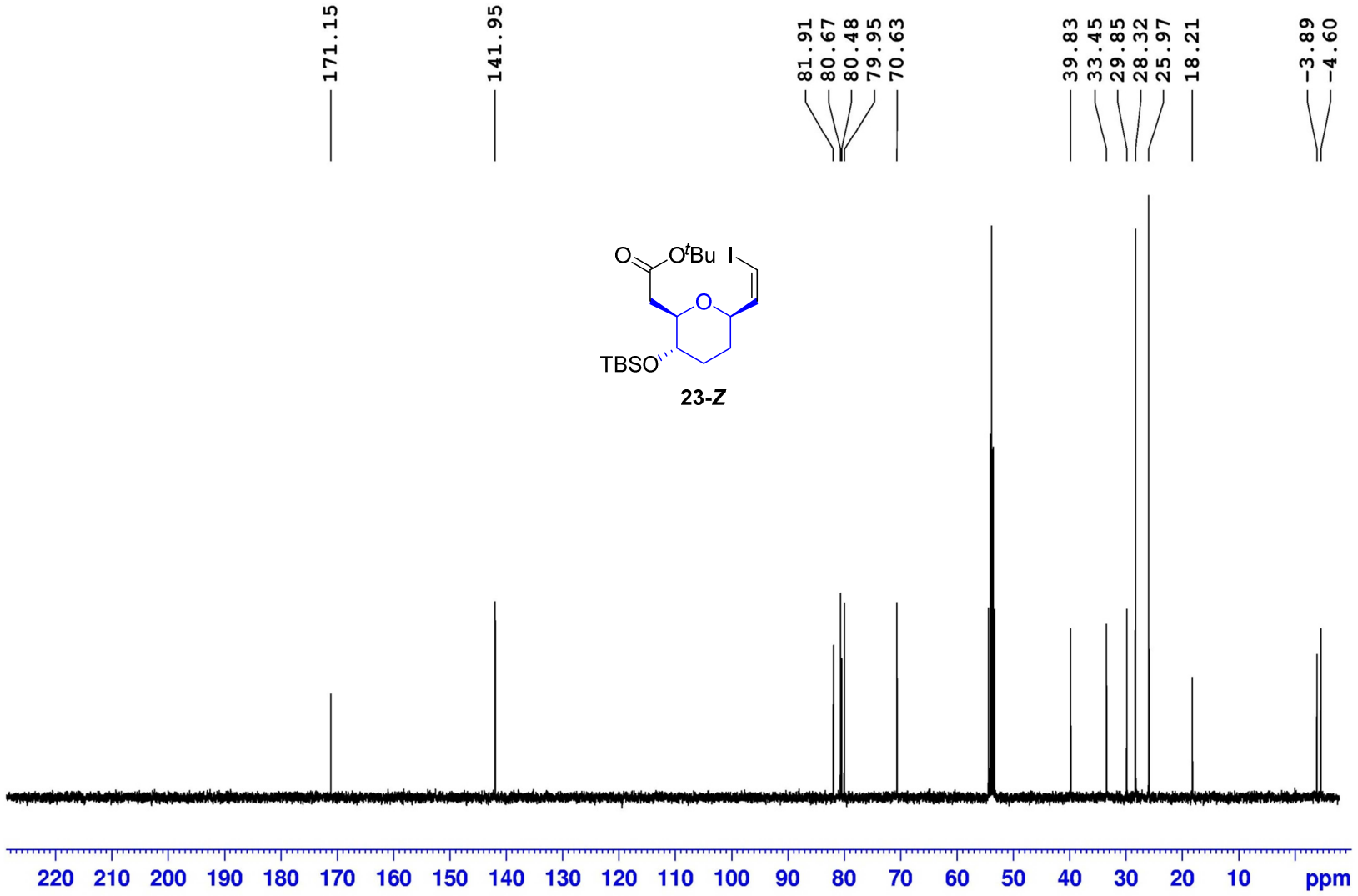
400 MHz


O
O^{t}Bu
I
O
TBSO

23-*Z*

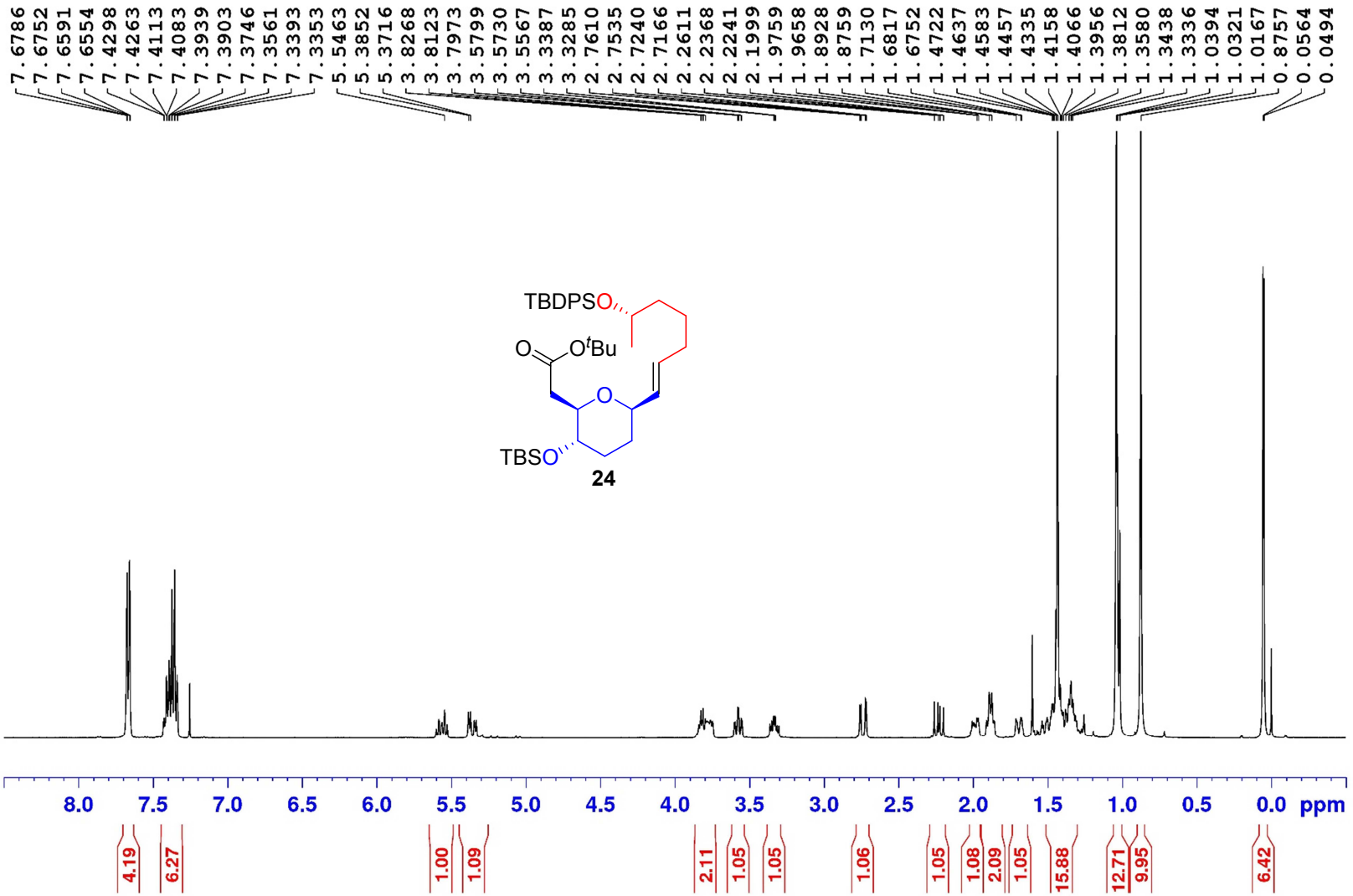

6.2668 6.2472 6.2281 6.2265 6.2095 6.1918 6.1903 4.0976 4.0758 4.0744 4.0549 3.6255 3.6195 3.6025 3.5959 3.5792 3.5732 3.3851 3.3737 3.3603 3.3493 3.3367 3.3251 2.7584 2.7530 2.7512 2.7214 2.7160 2.7142 2.2209 2.1972 2.1839 2.1601 2.0365 2.0271 2.0162 2.0051 1.9960 1.8407 1.8347 1.8077 1.8013 1.6396 1.6298 1.6060 1.5973 1.5807 1.5722 1.5478 1.5390 1.4814 1.4724 1.4287 1.3873 1.3783 0.8654 0.0522 0.0443
6.267 6.247 6.228 6.226 6.210 6.192 6.190
4.098 4.076 4.074 4.055
3.626 3.619 3.603 3.596 3.579 3.573
3.385 3.374 3.360 3.349 3.337 3.325
2.758 2.753 2.751 2.721 2.716 2.714
2.221 2.197 2.184 2.160
6.3 6.2 ppm
4.1 ppm
3.6 3.4 ppm
ppm
ppm
2.00
1.00
1.00
1.00
1.00
1.00
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 0.0 ppm
2.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.16 10.08 9.02 6.01

100 MHz, CD_2Cl_2



23-*Z*

400 MHz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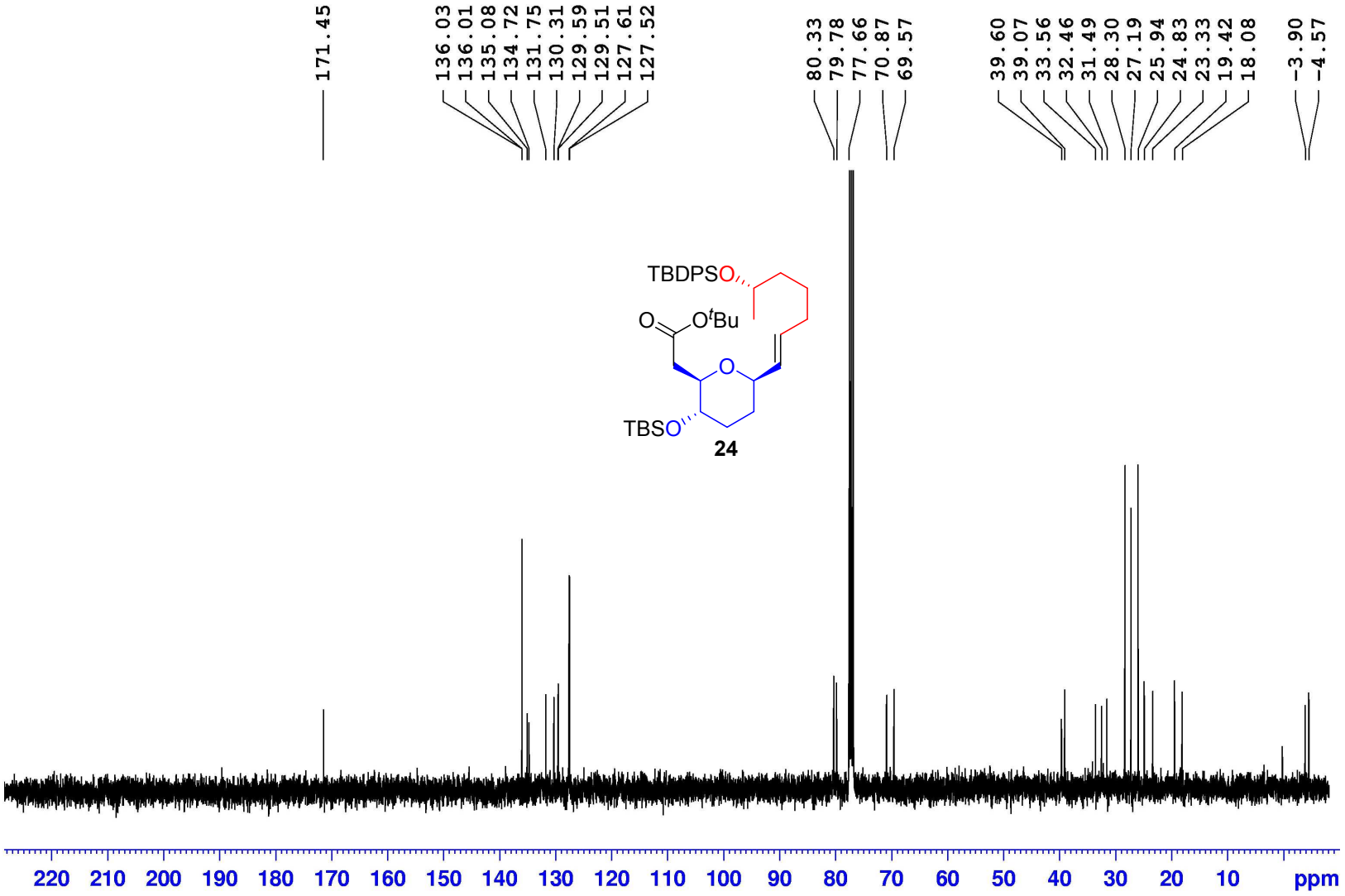
7.6752
7.6591
7.6554
7.4298
7.4263
7.4113
7.4083
7.3939
7.3903
7.3746
7.3561
7.3393
7.3353
5.5463
5.3852
5.3716
3.8268
3.8123
3.7973
3.5799
3.5730
3.5567
3.3387
3.3285
2.7610
2.7535
2.7240
2.7166
2.2611
2.2368
2.2241
2.1999
1.9759
1.9658
1.8928
1.8759
1.7130
1.6817
1.6752
1.4722
1.4637
1.4583
1.4457
1.4335
1.4158
1.4066
1.3956
1.3812
1.3580
1.3438
1.3336
1.0394
1.0321
1.0167
0.8757
0.0564
0.0494
TBDPSO
O
O^{t}Bu
O
TBSO
24
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
0.0
ppm
4.19
6.27
1.00
1.09
2.11
1.05
1.05
1.06
1.05
1.08
2.09
1.05
15.88
12.71
9.95
6.42

100 MHz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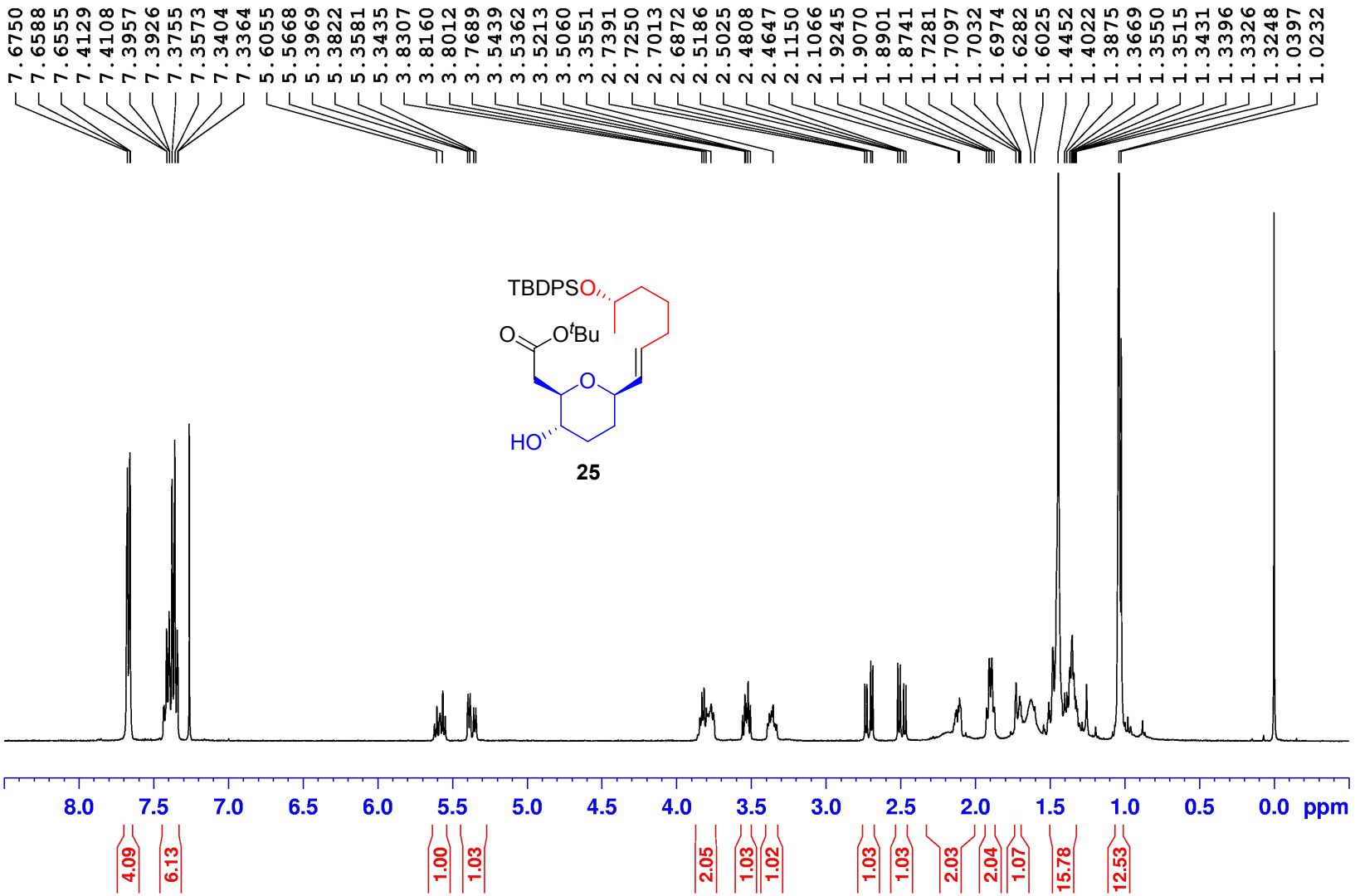
136.03
136.01
135.08
134.72
131.75
130.31
129.59
129.51
127.61
127.52
80.33
79.78
77.66
70.87
69.57
39.60
39.07
33.56
32.46
31.49
28.30
27.19
25.94
24.83
23.33
19.42
18.08
-3.90
-4.57
TBDPSO
O
O^{t}Bu
O
TBSO
24
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

400 MHz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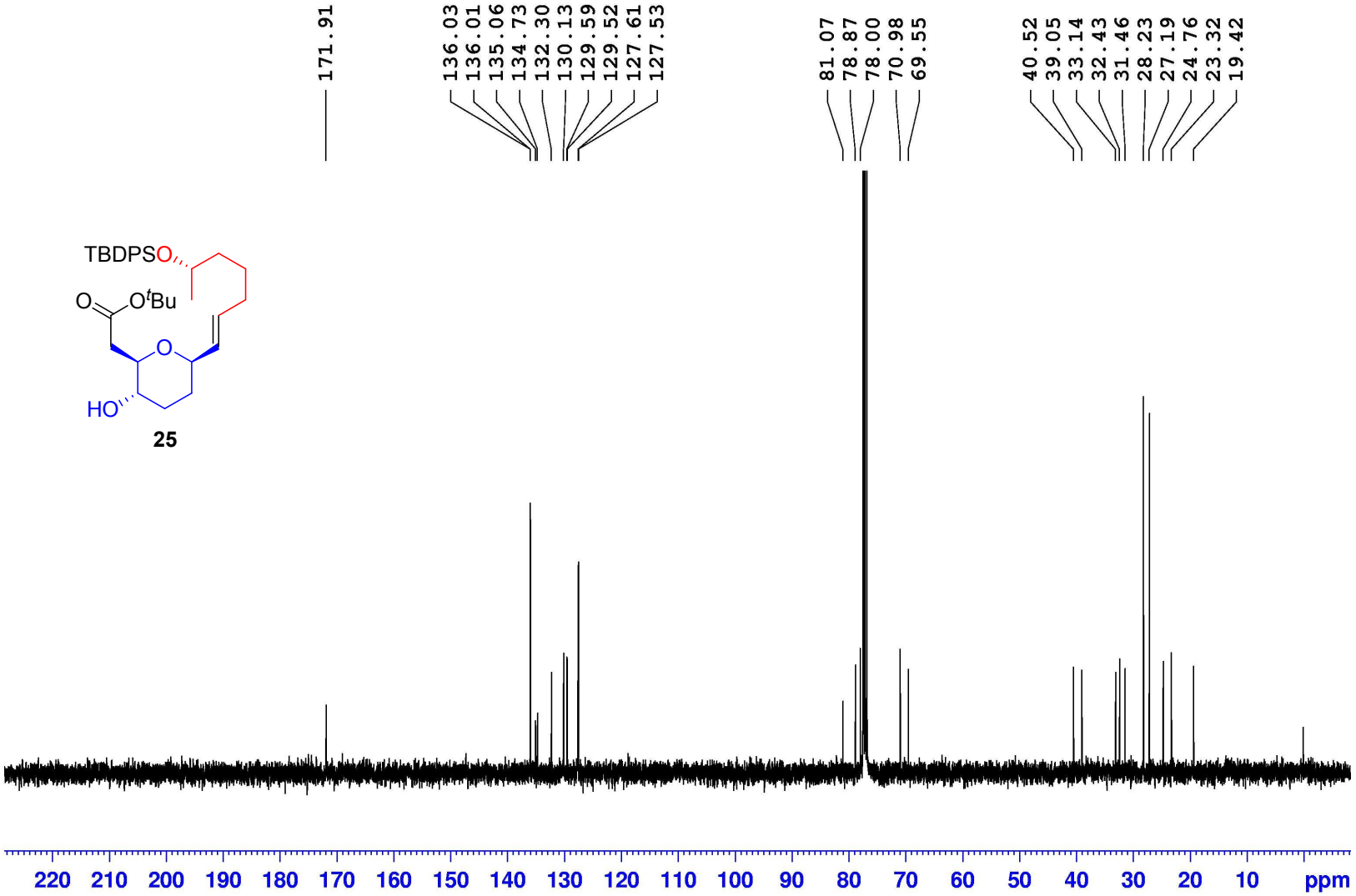
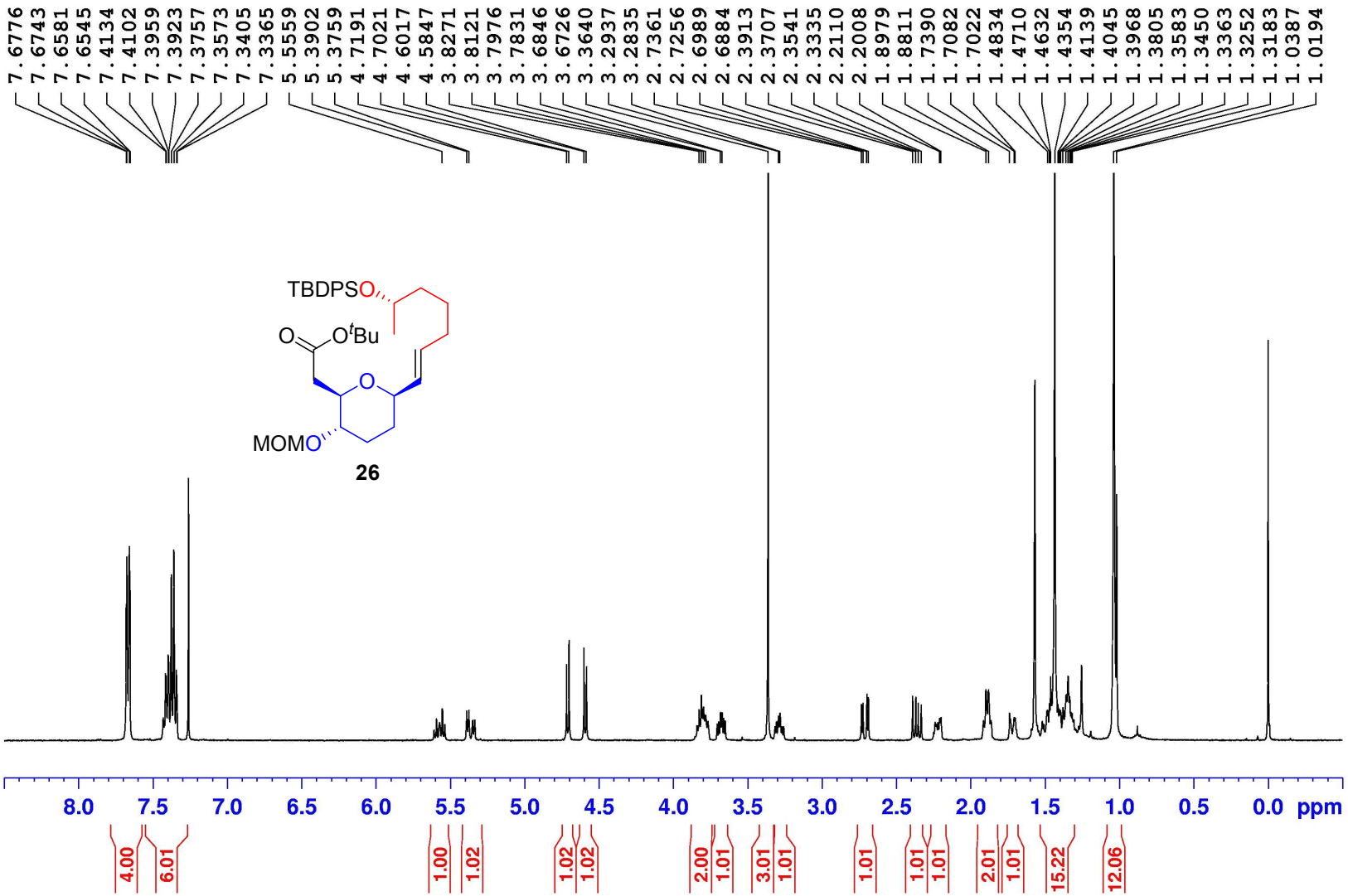
7.6588
7.6555
7.4129
7.4108
7.3957
7.3926
7.3755
7.3573
7.3404
7.3364
5.6055
5.5668
5.3969
5.3822
5.3581
5.3435
3.8307
3.8160
3.8012
3.7689
3.5439
3.5362
3.5213
3.5060
3.3551
2.7391
2.7250
2.7013
2.6872
2.5186
2.5025
2.4808
2.4647
2.1150
2.1066
1.9245
1.9070
1.8901
1.8741
1.7281
1.7097
1.7032
1.6974
1.6282
1.6025
1.4452
1.4022
1.3875
1.3669
1.3550
1.3515
1.3431
1.3396
1.3326
1.3248
1.0397
1.0232
TBDPSO
O
O^{t}Bu
O
HO
25
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
0.0
ppm
4.09
6.13
1.00
1.03
2.05
1.03
1.02
1.03
1.03
2.03
2.04
1.07
15.78
12.53

100 MHz


171.91
136.03
136.01
135.06
134.73
132.30
130.13
129.59
129.52
127.61
127.53
81.07
78.87
78.00
70.98
69.55
40.52
39.05
33.14
32.43
31.46
28.23
27.19
24.76
23.32
19.42
TBDPSO
O
O
tBu
O
HO
25
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

400 MHz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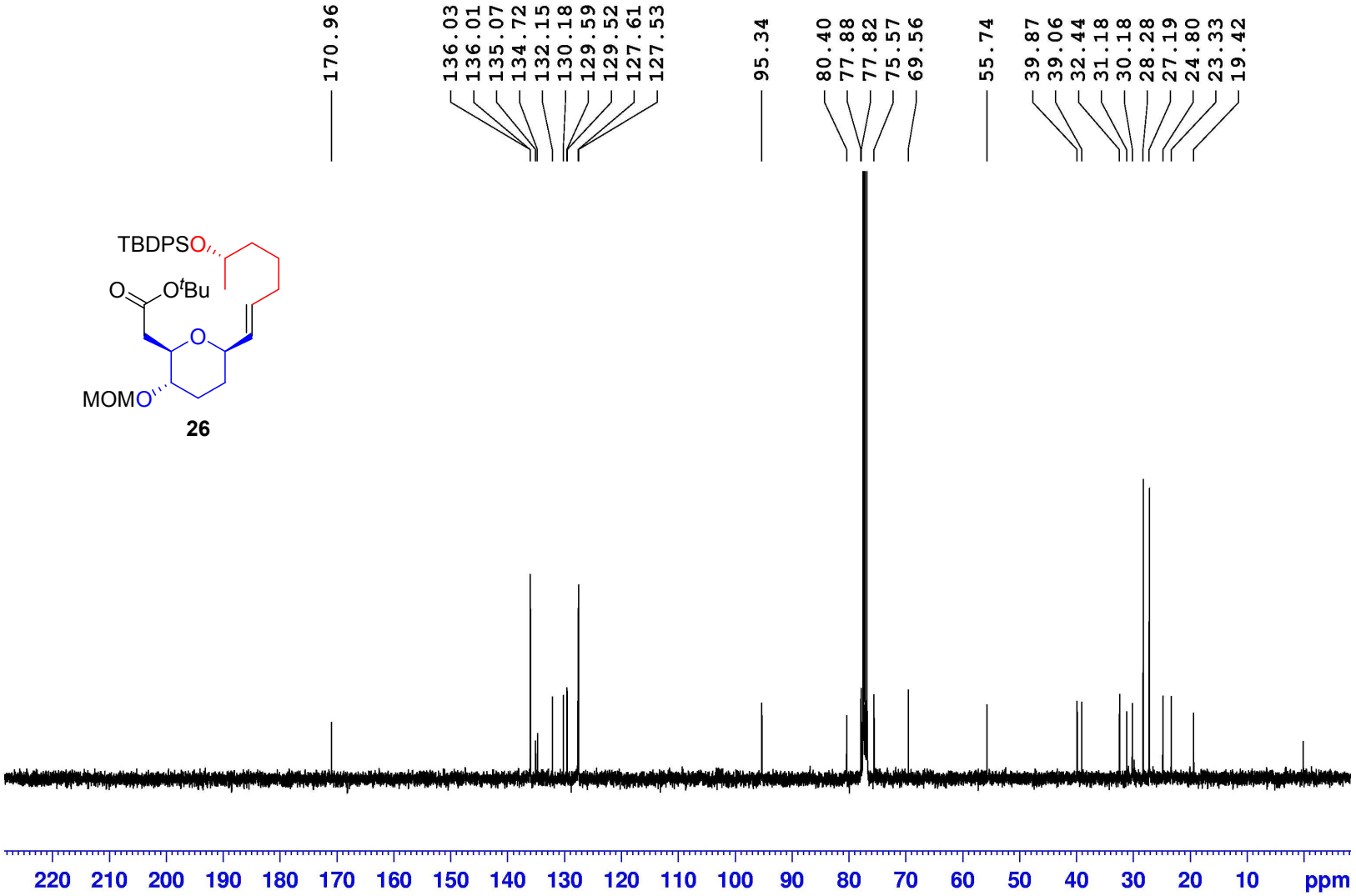
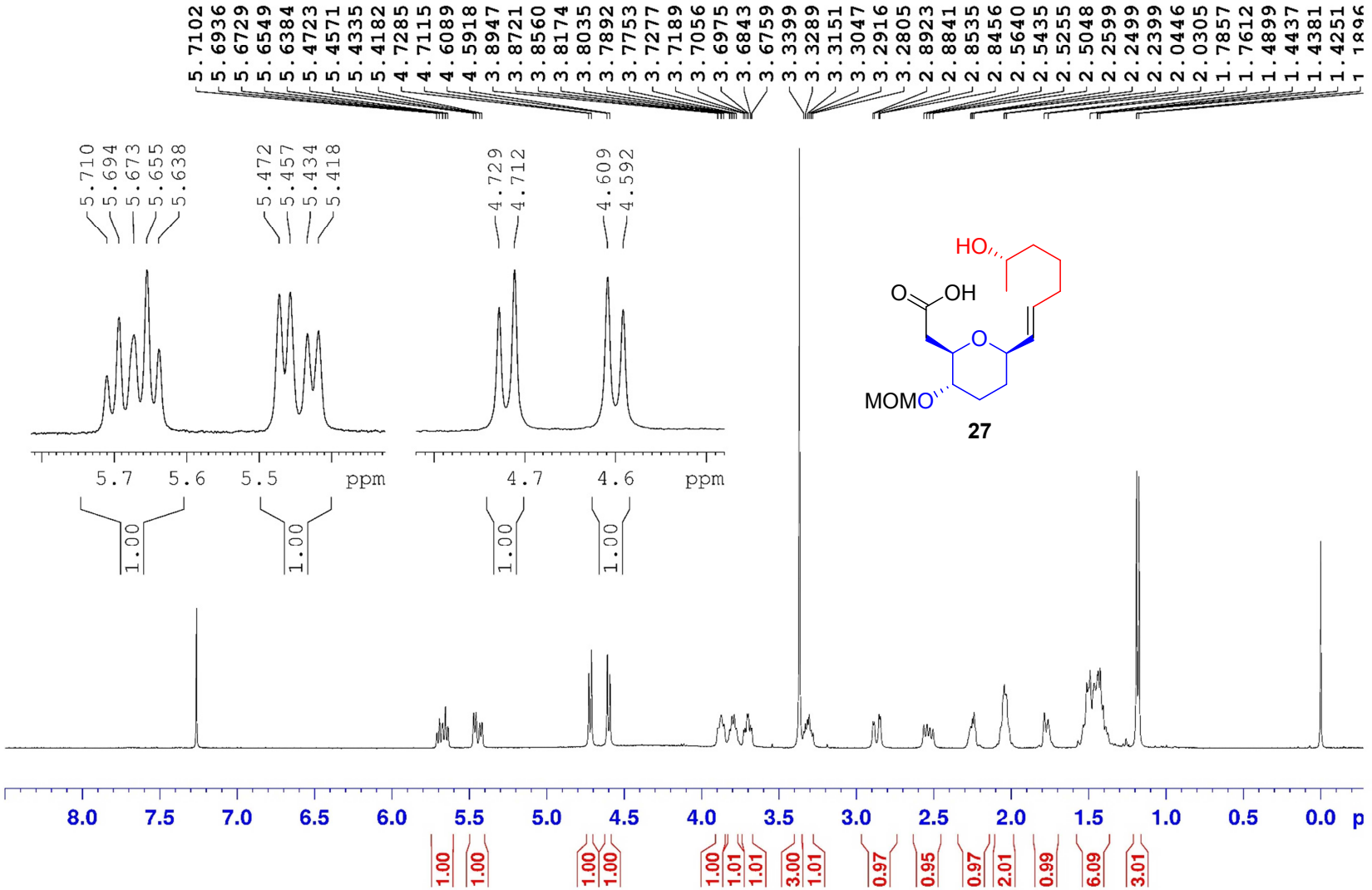
7.6743
7.6581
7.6545
7.4134
7.4102
7.3959
7.3923
7.3757
7.3573
7.3405
7.3365
5.5559
5.3902
5.3759
4.7191
4.7021
4.6017
4.5847
3.8271
3.8121
3.7976
3.7831
3.6846
3.6726
3.3640
3.2937
3.2835
2.7361
2.7256
2.6989
2.6884
2.3913
2.3707
2.3541
2.3335
2.2110
2.2008
1.8979
1.8811
1.7390
1.7082
1.7022
1.4834
1.4710
1.4632
1.4354
1.4139
1.4045
1.3968
1.3805
1.3583
1.3450
1.3363
1.3252
1.3183
1.0387
1.0194
TBDPSO
O
O^{t}Bu
O
MOMO
26
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
0.0
ppm
4.00
6.01
1.00
1.02
1.02
1.02
2.00
1.01
3.01
1.01
1.01
1.01
1.01
2.01
1.01
15.22
12.06

100 MHz


170.96
136.03
136.01
135.07
134.72
132.15
130.18
129.59
129.52
127.61
127.53
95.34
80.40
77.88
77.82
75.57
69.56
55.74
39.87
39.06
32.44
31.18
30.18
28.28
27.19
24.80
23.33
19.42
TBDPSO
O
O^{t}Bu
O
MOMO
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

26

400 MHz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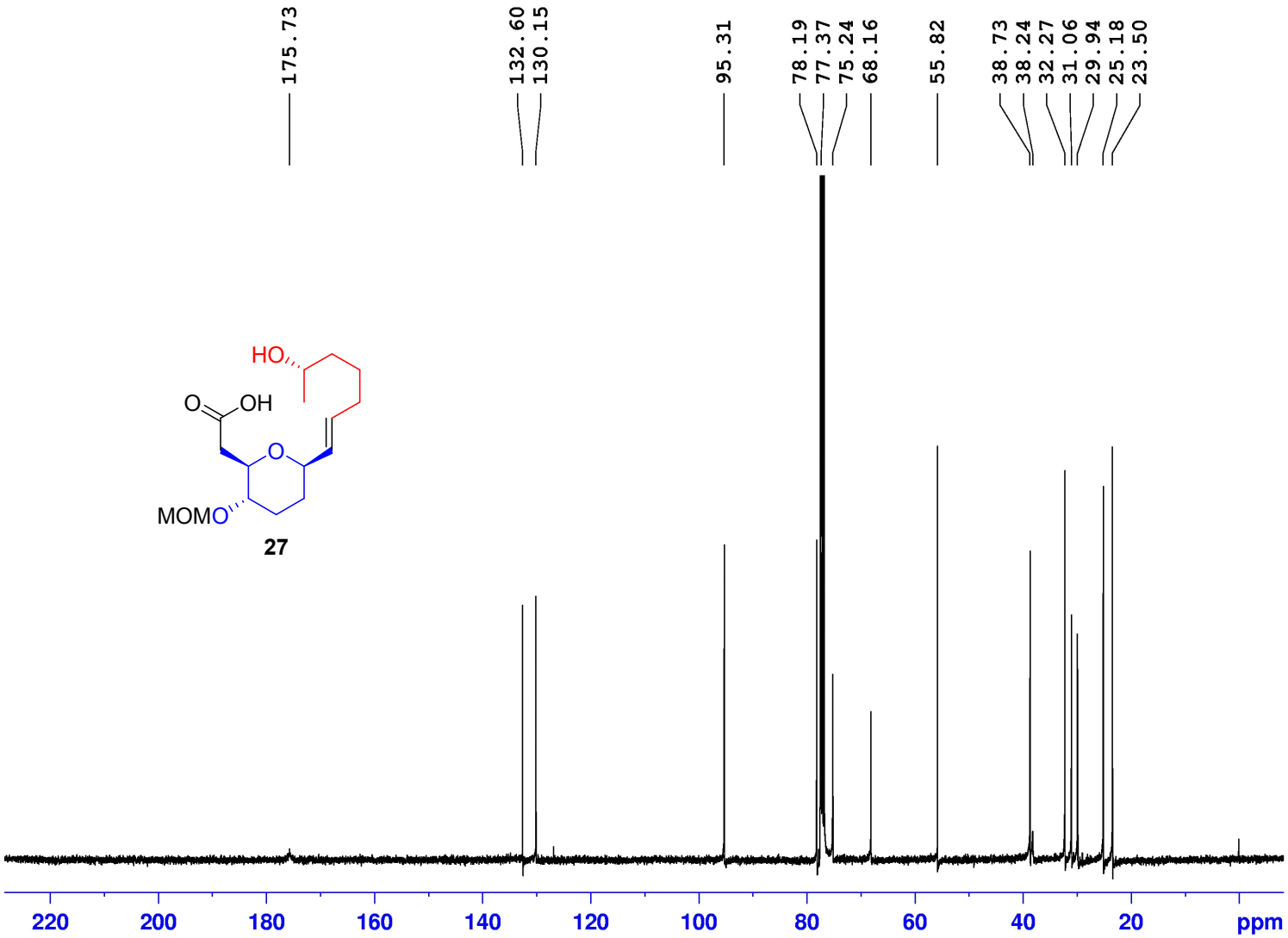
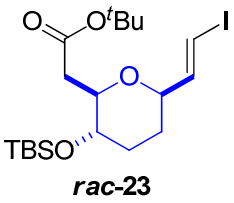
5.6729
5.6549
5.6384
5.4723
5.4571
5.4335
5.4182
4.7285
4.7115
4.6089
4.5918
3.8947
3.8721
3.8560
3.8174
3.8035
3.7892
3.7753
3.7277
3.7189
3.7056
3.6975
3.6843
3.6759
3.3399
3.3289
3.3151
3.3047
3.2916
3.2805
2.8923
2.8841
2.8535
2.8456
2.5640
2.5435
2.5255
2.5048
2.2599
2.2499
2.2399
2.0446
2.0305
1.7857
1.7612
1.4899
1.4437
1.4381
1.4251
5.710
5.694
5.673
5.655
5.638
5.472
5.457
5.434
5.418
4.729
4.712
4.609
4.592
5.7
5.6
5.5
ppm
4.7
4.6
ppm
1.00
1.00
1.00
1.00
HO
O
OH
O
MOMO
27
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
0.0
p
1.00
1.00
1.00
1.00
1.00
1.01
1.01
3.00
1.01
0.97
0.95
0.97
2.01
0.99
6.09
3.01

100 MHz


175.73
132.60
130.15
95.31
78.19
77.37
75.24
68.16
55.82
38.73
38.24
32.27
31.06
29.94
25.18
23.50
HO
O
OH
O
MOMO
27
220
200
180
160
140
120
100
80
60
40
20
ppm

6. X-Ray Structure for *rac*-23

Cambridge Crystallographic Data Centre Deposition Number: 1047243



***rac*-23**