Supporting Information

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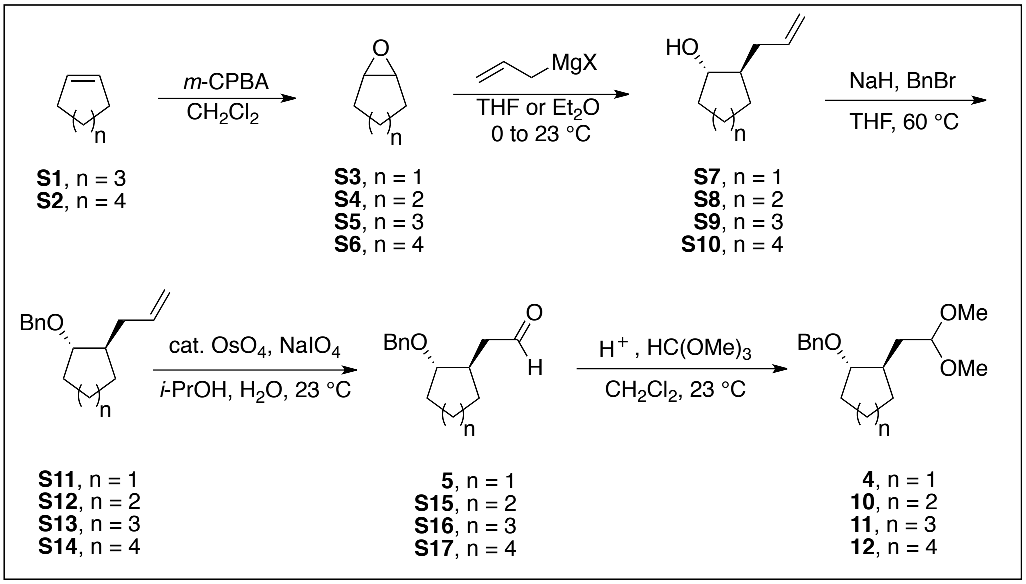
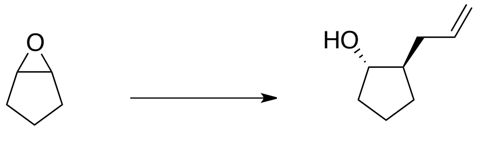
I. General Experimental

^{1}H and ^{13}C NMR spectra were acquired at ambient temperature using Bruker AV–400 (400 and 100 MHz, respectively), AV–500 (500 and 125 MHz, respectively), or AVIII–600 (600 and 150 MHz, respectively) spectrometers, as indicated. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane or referenced to residual solvent (^{1}H NMR: C_6D_6 δ 7.16; $CDCl_3$ δ 7.26. ^{13}C NMR: C_6D_6 δ 128.06; $CDCl_3$ δ 77.16) on the δ scale, multiplicity (appar = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were obtained using a Thermo Nicolet *AVATAR* 360 FT-IR 5000 spectrometer using either attenuated total reflectance (ATR) or a thin film on a salt plate, as indicated. High-resolution mass spectra (HRMS) were acquired on an Agilent 6224 Accurate-Mass time-of-flight spectrometer. Microanalyses were performed by Atlantic Microlab Inc., Norcross, GA. Analytical thin layer chromatography was performed on Silicycle silica gel 60 Å F_{254} plates. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Silicycle silica gel (SiO_2) 60 (230-400 mesh). THF, CH_2Cl_2, and Et_2O were dried by filtration through alumina according to the method of Grubbs.[1] All reactions using THF, CH_2Cl_2, and Et_2O as solvents were run under an atmosphere of nitrogen in glassware that was flame-dried under vacuum and cooled under a stream of nitrogen unless otherwise stated.

II. Synthesis of Substrates

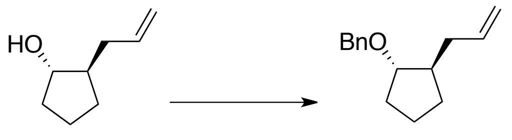
A. 1,2-Acetals





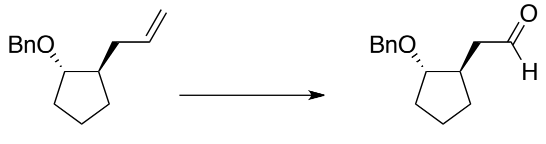
S3 **S7**

Alcohol S7. A procedure reported by Hegedus and McKearin[2] was used to prepare alcohol **S7**. To a cooled (0 °C) solution of cyclopentene oxide (1.0 mL, 12 mmol) in THF (25 mL) was added allylmagnesium chloride (9.3 mL, 2.0 M in THF, 19.0 mmol). The reaction mixture was stirred for 3 h at 0 °C. Saturated aqueous NH_4Cl (25 mL) and Et_2O (50 mL) were added, the layers were separated, and the aqueous layer was extracted with Et_2O (2 x 50 mL). The combined organic layers were washed with H_2O (100 mL) then brine (100 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (20:80 EtOAc:hexanes) afforded alcohol **S7** as a colorless oil (1.36 g, 87%). The spectral data are consistent with the data reported (^{1}H NMR and IR spectra):[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.1, 10.1, 7.0, 1H), 5.06 (ddt, *J* = 17.1, 2.1, 1.5, 1H), 4.99 (ddt, *J* = 10.2, 2.1, 1.1, 1H), 3.89–3.84 (m, 1H), 2.18 (quint of t, *J* = 7.0, 1.2, 1H), 2.07–2.00 (m, 1H), 1.96–1.86 (m, 2H), 1.84–1.68 (m, 2H), 1.65–1.51 (m, 2H), 1.47–1.46 (m, 1H), 1.22 (dq, *J* = 12.6, 7.9, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.8 (CH), 115.8 (CH_2), 78.9 (CH), 47.8 (CH), 38.2 (CH_2), 34.5 (CH_2), 29.8 (CH_2), 21.8 (CH_2); IR (ATR) 3325, 2955, 2873, 1641, 993, 908 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_8H_{15}O$ $(M+H)^+$ 127.1117, found 127.1112. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.94; H, 11.42.



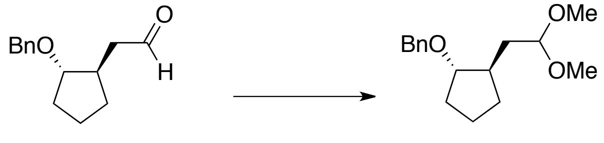
S7 **S11**

Representative procedure for the benzylation of alcohols (Benzyl ether S11). To a solution of alcohol **S7** (0.209 g, 1.66 mmol) in THF (3.3 mL) was added NaH (0.200 g, 60% dispersion in mineral oil, 5.0 mmol), followed by BnBr (0.24 mL, 2.0 mmol) and the reaction mixture was heated to 60 °C. After 14 h, saturated aqueous NH_4Cl (5 mL) and Et_2O (10 mL) were added, the layers were separated, and the aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic layers were washed with brine (60 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (2:98 EtOAc:hexanes) afforded benzyl ether **S11** as a colorless oil (0.276 g, 77%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.31 (m, 4H), 7.28–7.24 (m, 1H), 5.80 (ddt, *J* = 17.1, 10.2, 6.9, 1H), 5.00 (ddt, *J* = 17.1, 2.2, 1.5, 1H), 4.97 (ddt, *J* = 10.1, 2.2, 1.1, 1H), 4.52 (d, *J* = 11.9, 1H), 4.44 (d, *J* = 11.9, 1H), 3.59 (dt, *J* = 6.4, 4.5, 1H), 2.25–2.20 (m, 1H), 2.04–2.00 (m, 1H), 1.99–1.94 (m, 1H), 1.90–1.85 (m, 1H), 1.84–1.78 (m, 1H), 1.74–1.66 (m, 2H), 1.61–1.54 (m, 1H), 1.23–1.17 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1 (C), 137.7 (CH), 128.4 (CH), 127.8 (CH), 127.5 (CH), 115.5 (CH_2), 85.5 (CH), 71.2 (CH_2), 45.2 (CH), 38.4 (CH_2), 31.4 (CH_2), 29.9 (CH_2), 22.7 (CH_2); IR (ATR) 1640, 1024, 1067 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{15}H_{21}O$ $(M+H)^+$ 217.1587, found 217.1590. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.51; H, 9.49.



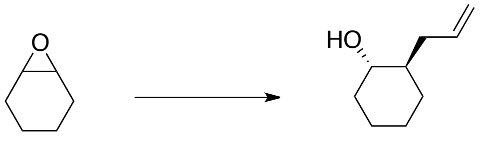
S11 **5**

Representative procedure for the preparation of aldehydes from alkenes (Aldehyde 5). To a solution of benzyl ether **S11** (0.110 g, 0.508 mmol) and $NaIO_4$ (0.270 g, 1.27 mmol) in *i*-PrOH:H_2O (2:1, 5 mL) was added OsO_4 (0.080 mL, 0.16 M in H_2O, 13.0 µmol). After 13 h, H_2O (5 mL) and EtOAc (10 mL) were added, the layers were separated, and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc: hexanes) afforded aldehyde **5** as a colorless oil (0.073 g, 75%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.75 (t, *J* = 2.3, 1H), 7.35–7.30 (m, 4H), 7.29–7.25 (m, 1H), 4.54 (d, *J* = 11.7, 1H), 4.43 (d, *J* = 11.8, 1H), 3.63–3.59 (m, 1H), 2.55 (ddd, *J* = 15.6, 6.1, 2.4, 1H), 2.44–2.38 (m, 1H), 2.35 (ddd, *J* = 15.6, 7.9, 2.2, 1H), 2.02–1.96 (m, 1H), 1.94–1.86 (m, 1H), 1.81–1.74 (m, 1H), 1.69–1.59 (m, 2H), 1.23–1.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.5 (CH), 138.7 (C), 128.5 (CH), 127.9 (CH), 127.7 (CH), 85.3 (CH), 71.6 (CH_2), 48.1 (CH_2), 40.3 (CH), 30.7 (CH_2), 29.7 (CH_2), 22.1 (CH_2); IR (ATR) 2951, 2869, 1720, 1205, 1065 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{14}H_{18}NaO_2$ $(M+Na)^+$ 241.1199, found 241.1216.



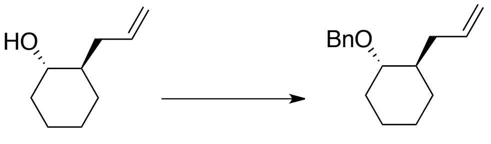
5 **4**

Representative procedure for the preparation of dimethyl acetals catalyzed by H_2SO_4 (Dimethyl acetal 4). To a solution of aldehyde **5** (0.055 g, 0.25 mmol) and $HC(OMe)_3$ (0.28 mL, 2.5 mmol) and MeOH (2.5 mL) was added H_2SO_4 (3 drops). After 4 h, saturated aqueous $NaHCO_3$ (3 mL) and CH_2Cl_2 (10 mL) were added. The layers were separated and the organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (1:10:89 Et_3N:EtOAc:hexanes) afforded dimethyl acetal **4** as a colorless oil (0.051 g, 76%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35–7.31 (m, 4H), 7.28–7.25 (m, 1H), 4.54 (d, *J* = 11.9, 1H), 4.44 (d, *J* = 12.2, 1H and m, 1H), 3.59–3.57 (m, 1H), 3.31 (s, 3H), 3.30 (s, 3H), 2.01 (ddt, *J* = 16.2, 8.1, 5.9, 1H), 1.96–1.91 (m, 1H), 1.86–1.79 (m, 2H), 1.75–1.64 (m, 2H), 1.63–1.57 (m, 1H), 1.48 (ddd, *J* = 13.9, 8.4, 5.6, 1H), 1.19 (dq, *J* = 12.6, 8.1, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1 (C), 128.5 (CH), 127.8 (CH), 127.5 (CH), 103.8 (CH), 85.9 (CH), 71.3 (CH_2), 53.2 (CH_3), 52.3 (CH_3), 41.7 (CH), 36.9 (CH_2), 31.1 (CH_2), 30.4 (CH_2), 22.5 (CH_2); IR (ATR) 2828, 1193, 1124, 1051 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{24}NaO_3$ $(M+Na)^+$ 287.1618, found 287.1616. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.47; H, 8.93.



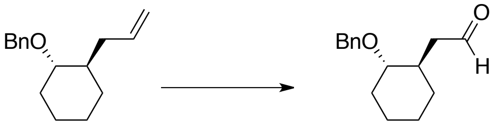
S4 **S8**

Alcohol S8. A procedure reported by Hegedus and McKearin[2] was used to prepare alcohol **S8**. To a cooled (0 °C) solution of cyclohexene oxide (1.44 mL, 14.3 mmol) in Et_2O (29 mL) was added allylmagnesium bromide (20.0 mL, 1.0 M in Et_2O, 20 mmol). The reaction mixture was stirred for 1 h at 0 °C. Saturated aqueous NH_4Cl (30 mL) and Et_2O (60 mL) were added, the layers were separated, and the aqueous layer was extracted with Et_2O (2 x 60 mL). The combined organic layers were washed with H_2O (120 mL) then brine (120 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (10:90 EtOAc:hexanes) afforded alcohol **S8** as a colorless oil (1.86 g, 93%). The spectral data are consistent with the data reported (^{1}H NMR and IR spectra):[3] ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.90–5.83 (m, 1H), 5.08–5.05 (m, 1H), 5.02 (ddt, *J* = 10.1, 2.2, 1.1, 1H), 3.27 (td, *J* = 9.8, 4.5, 1H), 2.45 (dddt, *J* = 14.0, 6.8, 4.7, 1.3, 1H), 2.01–1.94 (m, 2H), 1.79–1.72 (m, 2H), 1.65–1.61 (m, 2H), 1.36–1.29 (m, 1H), 1.28–1.23 (m, 2H), 1.22–1.13 (m, 1H), 0.99–0.92 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.7 (CH), 116.2 (CH_2), 74.8 (CH), 45.1 (CH), 37.6 (CH_2), 35.7 (CH_2), 30.5 (CH_2), 25.7 (CH_2), 25.0 (CH_2); IR (ATR) 3334, 2924, 2855, 1640, 1036, 994, 907 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_9H_{17}O$ $(M+H)^+$ 141.1274, found 141.1264.



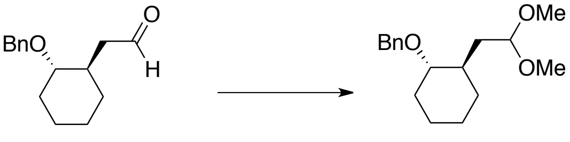
S8 **S12**

Benzyl ether S12. Benzyl ether **S12** was prepared using the representative procedure for the benzylation of alcohols using alcohol **S8** (4.35 g, 31.0 mmol), NaH (3.72 g, 60% dispersion in mineral oil, 93.0 mmol) and BnBr (4.4 mL, 37.0 mmol) in THF (62 mL). Purification by flash chromatography (3:97 EtOAc:hexanes) afforded benzyl ether **S12** as a colorless oil (5.12 g, 72%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H), 7.29–7.24 (m, 1H), 5.77 (dddd, *J* = 16.9, 10.4, 8.3, 6.4, 1H), 5.03–4.98 (m, 1H), 4.98–4.96 (m, 1H), 4.64 (d, *J* = 11.5, 1H), 4.42 (d, *J* = 11.5, 1H), 3.02 (td, *J* = 9.7, 4.2, 1H), 2.61–2.54 (m, 1H), 2.18–2.14 (m, 1H), 1.93 (dt, *J* = 13.7, 8.4, 1H), 1.84–1.74 (m, 2H), 1.65–1.59 (m, 1H), 1.52–1.44 (m, 1H), 1.29–1.13 (m, 3H), 1.00–0.88 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3 (C), 137.5 (CH), 128.5 (CH), 127.9 (CH), 127.6 (CH), 115.9 (CH_2), 81.4 (CH), 70.7 (CH_2), 43.1 (CH), 37.0 (CH_2), 31.2 (CH_2), 30.3 (CH_2), 25.6 (CH_2), 24.9 (CH_2); IR (ATR) 1640, 1204, 1073 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{22}NaO$ $(M+Na)^+$ 253.1563, found 253.1570. Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.24; H, 9.76.



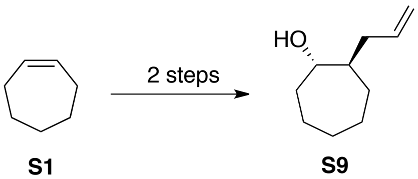
S12 **S15**

Aldehyde S15. Aldehyde **S15** was prepared using the representative procedure for the preparation of aldehydes from alkenes using **S12** (3.19 g, 13.8 mmol), $NaIO_4$ (7.40 g, 34.6 mmol) and OsO_4 (0.87 mL, 0.16 M in H_2O, 0.14 mmol) in *i*-PrOH:H_2O (2:1, 120 mL). Purification by flash chromatography (5:95 EtOAc:hexanes) afforded aldehyde **S15** as a colorless oil that could not be further purified (1.91 g, 59% unpurified yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (dd, *J* = 3.3, 1.9, 1H), 7.36–7.24 (m, 5H), 4.57 (d, *J* = 11.4, 1H), 4.36 (d, *J* = 11.4, 1H), 2.99 (td, *J* = 10.0, 4.3, 1H), 2.58 (ddd, *J* = 15.9, 7.1, 3.3, 1H), 2.19 (ddd, *J* = 15.8, 6.2, 1.9, 1H and m, 1H), 2.09–1.99 (m, 1H), 1.81–1.76 (m, 2H), 1.68–1.60 (m, 1H), 1.31–1.19 (m, 3H), 1.13–1.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6 (CH), 138.6 (C), 128.5 (CH), 128.1 (CH), 127.8 (CH), 81.8 (CH), 70.6 (CH_2), 48.7 (CH_2), 40.0 (CH), 32.1 (CH_2), 31.2 (CH_2), 25.6 (CH_2), 24.8 (CH_2); HRMS (TOF MS ES+) *m / z* calcd for $C_{15}H_{20}NaO_2$ $(M+Na)^+$ 255.1356, found 255.1358.



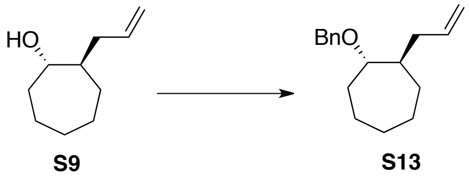
S15 **10**

Dimethyl Acetal 10. Dimethyl acetal **10** was prepared using the representative procedure for the preparation of dimethyl acetals catalyzed by H_2SO_4, using aldehyde **S15** (1.91 g, 8.22 mmol), $HC(OMe)_3$ (9.0 mL, 82.0 mmol), H_2SO_4 (4 drops), and MeOH (35 mL). Purification by flash chromatography (1:5:94 Et_3N:EtOAc:hexanes) afforded dimethyl acetal **10** as a colorless oil (2.23 g, 58% over two steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.34 (m, 4H), 7.32–7.24 (m, 1H), 4.64 (d, *J* = 11.7, 1H), 4.55 (dd, *J* = 6.8, 5.4, 1H), 4.42 (d, *J* = 11.6, 1H), 3.31 (s, 3H), 3.26 (s, 3H), 3.02–2.97 (m, 1H), 2.15 (ddd, *J* = 14.0, 6.8, 4.1, 2H), 1.91–1.87 (m, 1H), 1.78–1.75 (m, 1H), 1.67–1.58 (m, 1H), 1.59–1.49 (m, 1H), 1.35–1.16 (m, 4H), 1.06–0.95 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.2 (C), 128.4 (CH), 127.8 (CH), 127.5 (CH), 103.3 (CH), 82.1 (CH), 70.6 (CH_2), 53.3 (CH_3), 51.5 (CH_3), 39.3 (CH), 35.6 (CH_2), 31.4 (CH_2), 31.1 (CH_2), 25.5 (CH_2), 24.7 (CH_2); IR (ATR) 2855, 1051, 1027 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{17}H_{26}NaO_3$ $(M+Na)^+$ 301.1775, found 301.1775. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.34; H, 9.41. Found: C, 73.07; H, 9.42.

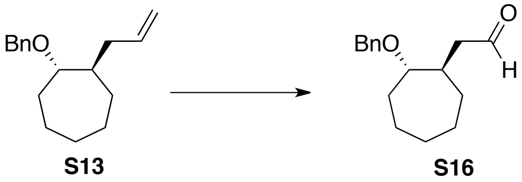


Alcohol S9. To a solution of cycloheptene (4.13 mL, 35.7 mmol) in 27.4 mL of CH_2Cl_2 was slowly added *m*-CPBA (12.1 g, 72% with water, 50.6 mmol) in 116 mL CH_2Cl_2 at 0 °C. The reaction mixture was left to stir at 23 °C. After 36 h, saturated $Na_2S_2O_3$ (15 mL) was added, followed by saturated $NaHCO_3$ (60 mL) and brine (60 mL), and the mixture was left to stir for 30 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (120 mL). The combined organic layers were washed with saturated $NaHCO_3$ (2 x 240 mL), brine (240 mL), then dried over $MgSO_4$ and concentrated. The epoxide was carried forward without further purification (3.10 g, 78% unpurified yield). The spectral data for cycloheptene oxide (**S5**) are consistent with the data reported for the commercially available product (^{1}H NMR and ^{13}C NMR spectra).[4]

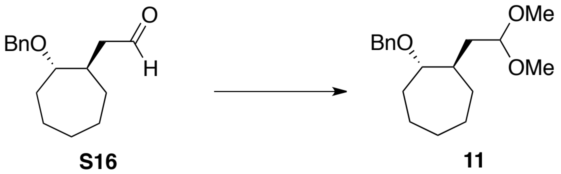
To a solution of cycloheptene oxide (**S5**, 3.10 g, 27.6 mmol) in THF (55.3 mL) was added a solution of allylmagnesium chloride (20.7 mL, 2 M in THF, 41.5 mmol) dropwise at 0 °C. The reaction mixture was stirred at 23 °C for 8 days. Excess reagents were quenched with a saturated aqueous solution of NH_4Cl (20 mL) and H_2O (60 mL). The aqueous layer was extracted with Et_2O (2 x 140 mL). The combined organic layers were washed with H_2O (280 mL) and brine (280 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (10:90 Et_2O:hexanes) afforded alcohol **S9** as a yellow oil (3.03 g, 55%, over two steps). The spectral data are consistent with the data reported (^{1}H NMR and ^{13}C NMR).[5]



Benzyl ether S13. Benzyl ether **S13** was prepared using the representative procedure for the benzylation of alcohols using alcohol **S9** (0.465 g, 3.01 mmol), NaH (0.362 g, 60% dispersion in mineral oil, 9.04 mmol) and BnBr (0.430 mL, 3.62 mmol) in THF (6 mL). The reaction mixture was stirred at 60 °C for 24 h. Purification by flash chromatography with 100% hexanes afforded benzyl ether **S13** as a colorless oil (0.252 g, 34%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37–7.33 (m, 4H), 7.29–7.26 (m, 1H), 5.78 (dddd, *J* = 16.6, 10.6, 8.1, 6.1, 1H), 5.00–4.98 (m, 1H), 4.98–4.95 (m, 1H), 4.59 (d, *J* = 11.4, 1H), 4.37 (d, *J* = 11.5, 1H), 3.24–3.21 (m, 1H), 2.39–2.35 (m, 1H), 2.02–1.97 (m, 1H), 1.91–1.86 (m, 1H), 1.76–1.60 (m, 6H), 1.47–1.38 (m, 3H), 1.26–1.20 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2 (C), 137.9 (CH), 128.5 (CH), 128.0 (CH), 127.5 (CH), 116.0 (CH_2), 83.7 (CH), 70.9 (CH_2), 45.0 (CH), 39.0 (CH_2), 30.8 (CH_2), 29.7 (CH_2), 28.9 (CH_2), 27.1 (CH_2), 22.7 (CH_2); IR (ATR) 1638, 1205, 1065 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{17}H_{25}O$ $(M+H)^+$ 245.1905, found 245.1900. Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.57; H, 9.97.



Aldehyde S16. Aldehyde **S16** was prepared using the representative procedure for the preparation of aldehydes from alkenes using **S13** (1.30 g, 5.32 mmol), $NaIO_4$ (2.85 g, 13.3 mmol) and OsO_4 (0.832 mL, 0.16 M in H_2O, 0.133 mmol) in an *i*-PrOH:H_2O (2:1, 76.1 mL) mixture. Purification by flash chromatography (5:95 EtOAc:hexanes) afforded aldehyde **S16** (0.650 g, 50%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (dd, *J* = 3.3, 1.8, 1H), 7.36–7.29 (m, 4H), 7.28–7.25 (m, 1H), 4.51 (d, *J* = 11.2, 1H), 4.28 (d, *J* = 11.2, 1H), 3.15 (ddd, *J* = 8.8, 7.1, 3.4, 1H), 2.52 (ddd, *J* = 15.3, 7.0, 3.4, 1H), 2.30 (ddd, *J* = 15.2, 6.4, 1.9, 1H), 2.26–2.19 (m, 1H), 1.92–1.83 (m, 1H), 1.82–1.61 (m, 4H), 1.60–1.55 (m, 1H), 1.53–1.40 (m, 3H), 1.37–1.27 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.4 (CH), 138.5 (C), 128.5 (CH), 128.2 (CH), 127.7 (CH), 84.4 (CH), 70.7 (CH_2), 50.2 (CH_2), 41.5 (CH), 30.9 (CH_2), 30.7 (CH_2), 28.7 (CH_2), 26.5 (CH_2), 22.7 (CH_2); IR (ATR) 2925, 2856, 1717, 1206, 1067 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{16}H_{22}NaO_2$ $(M+Na)^+$ 269.1517, found 269.1512.[a]



Representative procedure for the preparation of dimethyl acetals catalyzed by PPTS (Dimethyl acetal 11). To aldehyde **S16** (0.637 g, 2.58 mmol) in CH_2Cl_2 (43.1 mL) was added $HC(OMe)_3$ (4.24 mL, 38.8 mmol) and pyridinium *p*-toluenesulfonate (0.078 g, 0.310 mmol). After 2 days, saturated aqueous $NaHCO_3$ (40 mL) was added. The layers

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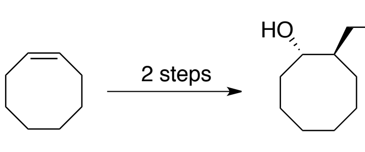
[a] Attempt at combustion analysis yielded unsatisfactory results.

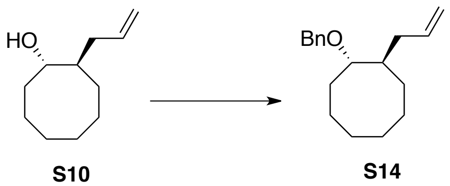
were separated and the aqueous phase was extracted with CH_2Cl_2 (40 mL). The combined organic layers were washed with brine (80 mL), dried over Na_2SO_4, and concentrated *in vacuo*. Acetal **11** was used without further purification (0.735 g, 97% unpurified yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 4H), 7.28–7.23 (m, 1H), 4.59 (d, *J* = 11.6, 1H), 4.48 (dd, *J* = 4.6, 3.2, 1H), 4.38 (d, *J* = 11.6, 1H), 3.30 (s, 3H), 3.26 (s, 3H), 3.20 (ddd, *J* = 5.2, 4.4, 1.6, 1H), 1.90 (ddd, *J* = 9.3, 4.6, 2.7, 1H), 1.88–1.82 (m, 1H), 1.80–1.61 (m, 6H), 1.50–1.39 (m, 4H), 1.33–1.26 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.2 (C), 128.4 (CH), 127.9 (CH), 127.5 (CH), 103.4 (CH), 84.5 (CH), 70.9 (CH_2), 53.5 (CH_3), 51.3 (CH_3), 41.0 (CH), 37.0 (CH_2), 30.4 (CH_2), 29.54 (CH_2), 29.49 (CH_2), 26.3 (CH_2), 22.8 (CH_2); IR (ATR) 2924, 2855, 1191, 1124, 1054 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{18}H_{28}NaO_3$ $(M+Na)^+$ 315.1936, found 315.1931. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 74.16; H, 9.57.



S2 **S10**

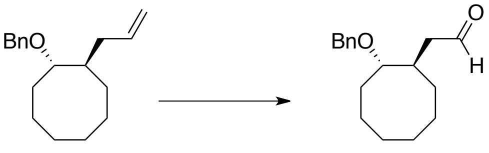
Alcohol S10. To a solution of cyclooctene (2.62 mL, 20.0 mmol) in 15.4 mL of CH_2Cl_2 is slowly added *m*-CPBA (6.81 g, 72% with water, 28.4 mmol) in 65.3 mL CH_2Cl_2 at 0 °C. The reaction mixture was then left to stir at 23 °C. After 19 h, saturated $Na_2S_2O_3$ (10 mL) was added, followed by saturated $NaHCO_3$ (80 mL) and brine (80 mL) and the mixture was left to stir for 30 min. The layers were then separated and the aqueous layer was extracted with CH_2Cl_2 (160 mL). The combined organic layers were washed with saturated $NaHCO_3$ (2 x 240 mL), brine (240 mL), then dried over $MgSO_4$ and concentrated *in vacuo*. The epoxide was carried forward without further purification (2.47 g, 98% unpurified yield). The spectral data for cyclooctene oxide (**S6**) are consistent with the data reported for the commercially available product (^{1}H NMR and ^{13}C NMR spectra).[4]

To a solution of cyclooctene oxide (**S6**, 2.47 g, 19.6 mmol) in Et_2O (39.2 mL) was added a solution of allylmagnesium bromide (29.4 mL, 1 M in ether, 29.4 mmol) dropwise at 0 °C. The reaction mixture was stirred at 23 °C for 7.5 days. Excess reagents were quenched with a saturated aqueous solution of NH_4Cl (30 mL) and H_2O (50 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (80 mL). The combined organic layers were washed with H_2O (150 mL) and brine (150 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc:hexanes) afforded alcohol **S10** as a yellow oil (1.80 g, 58%, over two steps): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.79 (m, 1H), 5.10–5.02 (m, 2H), 3.54–3.53 (m, 1H), 2.47–2.44 (m, 1H), 2.00 (m, 1H), 1.91–1.85 (m, 1H), 1.79–1.75 (m, 2H), 1.69–1.55 (m, 5H), 1.53–1.44 (m, 3H), 1.40–1.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0 (CH), 116.2 (CH_2), 76.0 (CH), 43.8 (CH), 38.9 (CH_2), 33.8 (CH_2), 27.9 (CH_2), 27.2 (CH_2), 26.8 (CH_2), 25.6 (CH_2), 23.8 (CH_2); IR (ATR) 3339, 2916, 2853, 1649, 993, 907 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{11}H_{20}NaO$ $(M+Na)^+$ 191.1412, found 191.1406. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.63; H, 12.04.



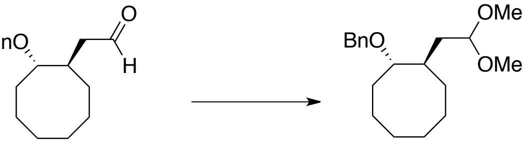
S10 **S14**

Benzyl ether S14. Benzyl ether **S14** was prepared using the representative procedure for the benzylation of alcohols using alcohol **S10** (1.21 g, 7.84 mmol), NaH (0.942 g, 60% dispersion in mineral oil, 23.5 mmol) and BnBr (1.12 mL, 9.41 mmol) in THF (15.7 mL). The reaction mixture was stirred at 60 °C for 45 h. Purification by flash chromatography (1:99 EtOAc:hexanes) afforded benzyl ether **S14** as a yellow oil (1.84 g, 91%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39–7.34 (m, 4H), 7.31–7.27 (m, 1H), 5.79 (dddd, *J* = 16.9, 10.1, 8.6, 5.6, 1H), 5.03–4.99 (m, 2H), 4.61 (d, *J* = 11.3, 1H), 4.36 (d, *J* = 11.3, 1H), 3.24 (ddd, *J* = 9.7, 6.6, 1.7, 1H), 2.56–2.52 (m, 1H), 1.96–1.90 (m, 2H), 1.89–1.86 (m, 1H), 1.85–1.80 (m, 1H), 1.77–1.71 (m, 1H), 1.69–1.62 (m, 4H), 1.51–1.40 (m, 2H), 1.39–1.31 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1 (C), 138.1 (CH), 128.5 (CH), 128.1 (CH), 127.6 (CH), 115.8 (CH_2), 83.3 (CH), 71.0 (CH_2), 42.4 (CH), 38.2 (CH_2), 28.1 (CH_2), 27.3 (CH_2), 26.9 (CH_2), 26.5 (CH_2), 25.9 (CH_2), 24.7 (CH_2); IR (ATR) 2920, 1638, 1453, 1204, 1065 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{18}H_{27}O$ $(M+H)^+$ 259.2062, found 259.2056. Anal. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14. Found: C, 83.94; H, 9.96.



S14 **S17**

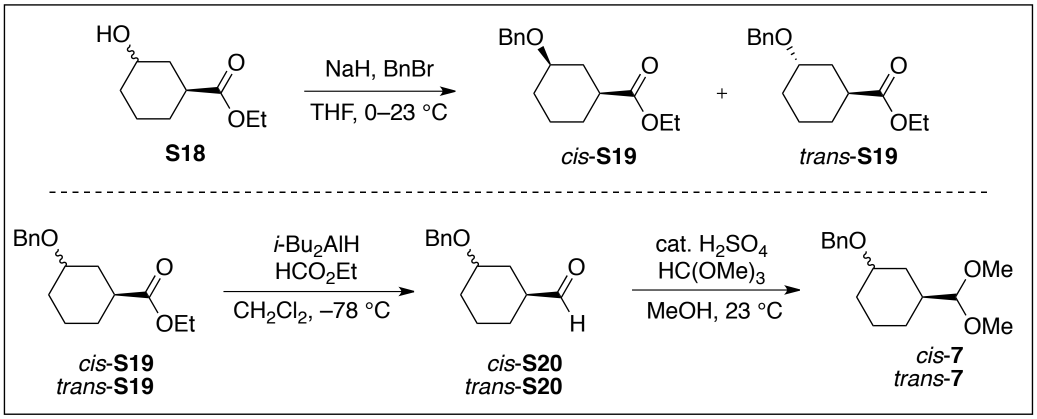
Aldehyde S17. Aldehyde **S17** was prepared using the representative procedure for the preparation of aldehydes from alkenes using **S14** (1.54 g, 5.97 mmol), $NaIO_4$ (2.68 g, 12.5 mmol) and OsO_4 (0.934 mL, 0.16 M in H_2O, 0.149 mmol) in an *i*-PrOH:H_2O (2:1, 85.2 mL) mixture. The reaction mixture was stirred at room temperature for 20 h. Purification by flash chromatography (5:95 EtOAc:hexanes) afforded aldehyde **S17** (0.943 g, 61%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (dd, *J* = 3.6, 1.8, 1H), 7.36–7.25 (m, 5H), 4.49 (d, *J* = 11.2, 1H), 4.26 (d, *J* = 11.1, 1H), 3.25–3.21 (m, 1H), 2.56 (ddd, *J* = 14.8, 6.8, 3.5, 1H), 2.37–2.29 (m, 1H), 2.26 (ddd, *J* = 14.9, 6.2, 1.8, 1H), 1.91–1.86 (m, 2H), 1.85–1.78 (m, 1H), 1.74–1.59 (m, 4H), 1.52–1.41 (m, 4H), 1.39–1.30 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.4 (CH), 138.4 (C), 128.5 (CH), 128.3 (CH), 127.8 (CH), 83.4 (CH), 70.6 (CH_2), 49.6 (CH_2), 38.8 (CH), 29.0 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 25.8 (CH_2), 25.1 (CH_2); IR (ATR) 2921, 2854, 1717, 1467, 1206, 1060 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{17}H_{24}NaO_2$ $(M+Na)^+$ 283.1674, found 283.1669. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.41; H, 9.30.

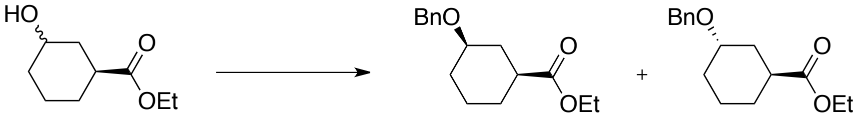


S17 **12**

Dimethyl acetal 12. Dimethyl acetal **12** was prepared using the representative procedure for the preparation of dimethyl acetals catalyzed by PPTS, using aldehyde **S17** (0.943 g, 3.62 mmol), CH_2Cl_2 (60.4 mL), $HC(OMe)_3$ (5.94 mL, 54.3 mmol), and pyridinium *p*-toluenesulfonate (0.109 g, 0.435 mmol). Acetal **12** was used without further purification (1.04 g, 94% unpurified yield): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.27–7.25 (m, 1H), 4.60 (d, *J* = 11.4, 1H), 4.52 (dd, *J* = 7.4, 4.6, 1H), 4.34 (d, *J* = 11.5, 1H), 3.31 (s, 3H), 3.26 (s, 3H), 3.23–3.20 (m, 1H), 2.07 (ddd, *J* = 13.9, 7.4, 3.5, 1H), 1.89–1.80 (m, 3H), 1.78–1.74 (m, 1H), 1.73–1.61 (m, 4H), 1.46–1.36 (m, 5H), 1.32–1.26 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.1 (C), 128.4 (CH), 128.0 (CH), 127.5 (CH), 103.4 (CH), 84.1 (CH), 71.0 (CH_2), 53.6 (CH_3), 51.1 (CH_3), 38.8 (CH), 35.9 (CH_2), 28.9 (CH_2), 27.2 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.1 (CH_2), 25.7 (CH_2); IR (ATR) 2921, 1453, 1120, 1061, 1028 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{19}H_{30}NaO_3$ $(M+Na)^+$ 329.2093, found 329.2087. Anal. Calcd for $C_{19}H_{30}O_3$: C, 74.47; H, 9.87. Found: C, 74.33; H, 9.69.

B. 1,3-Acetals (Substrates *cis*-16 and *trans*-16)

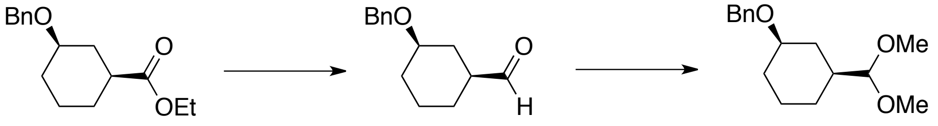




S18 *cis*-**S19** *trans*-**S19**

Esters *cis*-S19 and *trans*-S19. To a cooled (0 °C) mixture of NaH (3.62 g, 90.5 mmol) in THF (115 mL) was added ethyl 3-hydroxycyclohexane-1-carboxylate (4.60 mL, 28.5

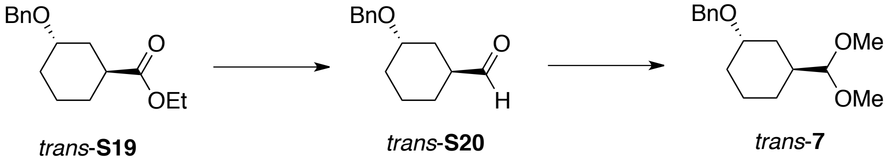
mmol) dropwise over 5 min. BnBr (5.25 mL, 44.1 mmol) was then added dropwise over 6 min. The reaction mixture was allowed to warm to room temperature over 12 h. After 28 h, the mixture was cooled to 0 °C, and saturated aqueous NH_4Cl (250 mL) was added over 10 min. The resulting solution was extracted with CH_2Cl_2 (4 x 500 mL). The combined organic layers were washed with brine (100 mL), dried over $MgSO_4$, and concentrated *in vacuo,* yielding a clear yellow oil. Separation by silica gel column chromatography (10:90 EtOAc:hexanes) afforded the desired products *cis*-**S19** (0.971 g, 13%) and *trans*-**S19** (1.17 g, 16%) both as clear pale yellow oils: c*is*-**S19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 4.59 (d, *J* = 11.9, 1H), 4.55 (d, *J* = 11.9, 1H), 4.13 (q, *J* = 7.1, 2H), 3.35 (tt, *J* = 10.6, 4.1, 1H), 2.39–2.24 (m, 2H), 2.10–2.05 (m, 1H), 1.93–1.84 (m, 2H), 1.44 (dt, *J* = 10.9, 12.1, 1H), 1.41–1.22 (m, 3H), 1.25 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1 (C), 139.1 (C), 128.5 (CH), 127.7 (CH), 127.6 (CH), 76.7 (CH), 70.0 (CH_2), 60.5 (CH_2), 42.2 (CH), 34.8 (CH_2), 32.0 (CH_2), 28.4 (CH_2), 23.6 (CH_2), 14.4 (CH_3); IR (thin film) 2938, 2862, 1728, 1177, 1093, 1042 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{22}NaO_3$ $(M+Na)^+$ 285.1467, found 285.1469. *trans*-**S19**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.24 (m, 5H), 4.52 (s, 2H), 4.11 (q, *J* = 7.1, 2H), 3.74 (tt, *J* = 4.7, 2.8, 1H), 2.76 (tt, *J* = 10.5, 3.8, 1H), 2.09–2.01 (m, 1H), 1.91–1.78 (m, 2H), 1.76–1.65 (m, 2H), 1.58–1.42 (m, 3H), 1.24 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2 (C), 139.3 (C), 128.5 (CH), 127.52 (CH), 127.49 (CH), 72.9 (CH), 70.0 (CH_2), 60.3 (CH_2), 38.3 (CH), 32.7 (CH_2), 29.9 (CH_2), 28.6 (CH_2), 20.3 (CH_2), 14.4 (CH_3); IR (ATR) 2935, 2861, 1728, 1175, 1122, 1066 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{22}NaO_3$ $(M+Na)^+$ 285.1467, found 285.1471.



cis-**S19** *cis*-**S20** *cis*-**7**

Dimethyl Acetal *cis*-7. To a cooled (–78 °C) mixture of ester *cis*-**S19** (1.14 g, 4.36 mmol) in CH_2Cl_2 (20 mL) was added DIBAL (5.6 mL, 5.6 mmol, 1 M solution in hexanes) dropwise over 26 min. The reaction mixture was allowed to stir at –78 °C. After 4 h, ethyl formate (7 mL) was added dropwise over 9 min. After stirring at –78 °C for an additional 40 min, the reaction mixture was allowed to warm to room temperature. Saturated aqueous Rochelle's salt (15 mL) was added and the reaction mixture was allowed to stir overnight at room temperature before being poured into Et_2O (100 mL). The layers were partitioned and the aqueous layer was extracted with Et_2O (4 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo,* yielding a clear yellow oil. Purification by silica gel column chromatography (5:95 EtOAc:hexanes) afforded the desired product *cis*-**S20** (0.368 g, 39% yield) as a clear colorless oil.

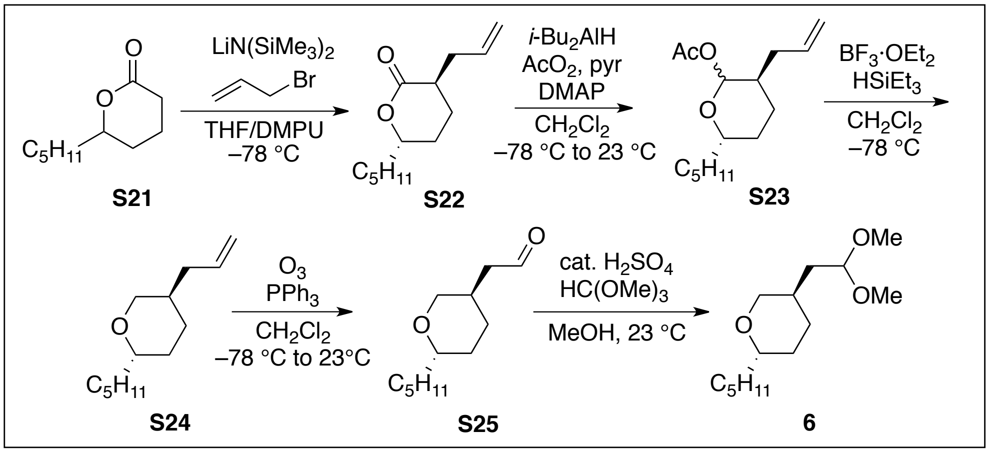
To a mixture of aldehyde *cis*-**S20** (0.355 g, 1.63 mmol) in MeOH (7.5 mL) was added $HC(OCH_3)_3$ (2.00 mL, 18.3 mmol) and concentrated H_2SO_4 (3 drops). After 30 min, the reaction mixture was diluted with CH_2Cl_2 (75 mL) and poured into saturated aqueous $NaHCO_3$ (75 mL). The layers were partitioned and the aqueous layer was extracted with CH_2Cl_2 (3 x 75 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo* (using oven-dried glassware pre-treated with NH_4OH), yielding the desired product *cis*-**7** (0.416 g, 97%) as a clear colorless oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.28–7.24 (m, 1H), 4.59 (d, *J* = 11.9, 1H), 4.55 (d, *J* = 11.9, 1H), 4.04 (d, *J* = 7.1, 1H), 3.36 (s, 3H), 3.34 (s, 3H), 3.36–3.29 (m, 1H), 2.21 (dtt, *J* = 11.6, 4.0, 2.0, 1H), 2.10–2.04 (m, 1H), 1.85–1.80 (m, 1H), 1.73 (d, *J* = 13.0, 1H), 1.65 (tdt, *J* = 12.0, 7.0, 3.5, 1H), 1.27–1.15 (m, 2H), 1.03 (q, *J* = 11.8, 1H), 0.94 (qd, *J* = 12.5, 3.8, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.3 (C), 128.5 (CH), 127.7 (CH), 127.5 (CH), 108.4 (CH), 77.4 (CH), 70.0 (CH_2), 54.3 (CH_3), 53.8 (CH_3), 39.4 (CH), 34.2 (CH_2), 32.6 (CH_2), 27.3 (CH_2), 23.7 (CH_2); IR (ATR) 2933, 2858, 1127, 1068, 1053, 973 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{24}NaO_3$ $(M+Na)^+$ 287.1623, found 287.1619. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.86; H, 9.22.

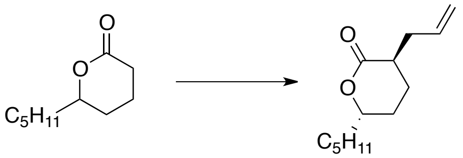


Dimethyl Acetal *trans*-7. To a cooled (–78 °C) mixture of ester *trans*-**S19** (0.948 g, 3.62 mmol) in CH_2Cl_2 (20 mL) was added DIBAL (4 mL, 4 mmol, 1 M solution in hexanes) dropwise over 21 min. The reaction mixture was allowed to stir at –78 °C. After 1 h, ethyl formate (7 mL) was added dropwise over 12 min. After stirring for an additional 40 min, the reaction mixture was allowed to warm to room temperature. Saturated aqueous Rochelle's salt (15 mL) was added and the reaction mixture was allowed to stir overnight at room temperature before being poured into Et_2O (100 mL). The layers were partitioned and the aqueous layer was extracted with Et_2O (4 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo,* yielding a clear colorless oil. Purification by silica gel column chromatography (5:95 EtOAc:hexanes) afforded the desired product *trans*-**S20** (0.631 g, 80%) as a clear colorless oil: IR (ATR) 2937, 2864, 1701, 1278, 1121, 1067 cm^{-1}.

To a mixture of aldehyde *trans*-**S20** (0.612 g, 2.80 mmol) in MeOH (13 mL) was added $HC(OCH_3)_3$ (4.5 mL, 41.1 mmol) and concentrated H_2SO_4 (3 drops). After 30 min, the reaction mixture was diluted with CH_2Cl_2 (100 mL) and poured into saturated aqueous $NaHCO_3$ (100 mL). The layers were partitioned and the aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo,* (using oven-dried glassware pre-treated with NH_4OH), yielding the desired product *trans*-**7** (0.746 g, 99% yield) as a clear colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.22 (m, 5H), 4.53 (ABq, $\Delta\delta_{AB}$ = 0.04, J_{AB} = 11.2, 2H), 4.02 (d, *J* = 6.9, 1H), 3.73 (quint, *J* = 3.5, 1H), 3.34 (s, 3H), 3.33 (s, 3H), 2.10 (tdt, *J* = 10.9, 7.0, 3.6, 1H), 2.01 (dtt, *J* = 11.4, 3.8, 1.9, 1H), 1.89 (m, 1H), 1.75 (m, 1H), 1.66 (tt, *J* = 12.7, 3.7, 1H), 1.51 (m, 1H), 1.35 (dddd, *J* = 12.9, 13.4, 4.1, 2.8, 1H), 1.21 (ddd, *J* = 14.0, 11.7, 2.7, 1H), 1.08 (qd, *J* = 12.1, 3.9, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6 (C), 128.4 (CH), 127.4 (CH), 127.3 (CH), 108.5 (CH), 73.0 (CH), 69.8 (CH_2), 53.9 (CH_3), 53.7 (CH_3), 34.4 (CH), 31.5 (CH_2), 30.2 (CH_2), 27.4 (CH_2), 20.1 (CH_2); IR (ATR) 2930, 2860, 1136, 1064, 979 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{16}H_{24}NaO_3$ $(M+Na)^+$ 287.1623, found 287.1618. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.66; H, 9.26.

C. Tetrahydropyran acetal (Acetal **6** was prepared as a mixture of cis and trans-isomers and hydrolysis experiments were performed using the mixture of isomers.)

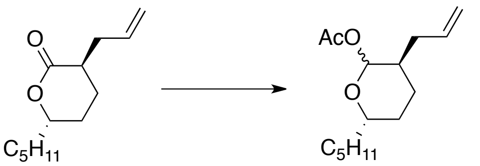




S21 **S22**

(+ *cis*-isomer)

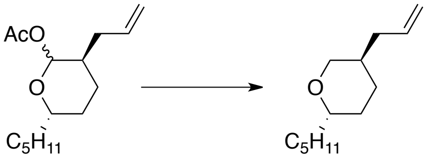
Lactone S22. To a cooled (–78 °C) solution of $HN(SiMe_3)_2$ (0.58 mL, 2.7 mmol) in THF (3 mL) was added *n*-BuLi (1.4 mL, 2.3 M in hexanes, 2.9 mmol). After 30 min, δ-decanolactone (**S21**, 0.35 mL, 2.0 mmol) in THF (5 mL) was added dropwise over 30 min. The reaction mixture was maintained at –78 °C for 1 h and 1,3-dimethyl-2-imizolidine (0.35 mL, 3.1 mmol) was added, followed by allyl bromide (0.25 mL, 2.9 mmol). After 1.5 h, saturated aqueous NH_4Cl (5 mL) and EtOAc (10 mL) were added. The layers were separated and the organic layer was washed with saturated aqueous $NaHCO_3$ (15 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (5:95 EtOAc:hexanes) afforded lactone **S22** as a colorless oil (0.118 g, 28%). ^{1}H NMR spectroscopic analysis showed the product was a mixture of diastereomers in a 62:38 ratio: ^{1}H NMR (600 MHz, C_6D_6) δ 5.84–5.77 (m, 0.6H), 5.74–5.67 (m, 1.0H), 5.02–5.00 (m, 1.7H), 4.99–4.97 (m, 1.7H), 3.73–3.68 (m, 1.0H), 3.62–3.58 (m, 0.7H), 2.62–2.57 (m, 1.8H), 2.36–2.31 (m, 1.1H), 2.13–2.08 (m, 0.7H), 2.03–1.94 (m, 1.7H), 1.46–1.29 (m, 6.3H), 1.28–1.09 (m, 13.4H), 1.08–1.01 (m, 2.5H), 1.00–0.93 (m, 1.2H), 0.92–0.83 (m, 6.1H); ^{13}C NMR (150 MHz, C_6D_6) δ 173.6 (C), 171.3 (C), 136.3 (CH), 136.0 (CH), 117.3 (CH_2), 116.9 (CH_2), 80.7 (CH), 76.9 (CH), 40.7 (CH), 37.8 (CH), 36.7 (CH_2), 36.5 (CH_2), 35.64 (CH_2), 35.62 (CH_2), 32.0 (CH_2), 29.1 (CH_2), 28.3 (CH_2), 26.8 (CH_2), 25.5 (CH_2), 25.2 (CH_2), 25.0 (CH_2), 23.2 (CH_2), 22.9 (CH_2), 22.8 (CH_2), 14.4 (CH_3), 14.3 (CH_3); IR (ATR) 1726, 1641, 1183, 1112 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{13}H_{22}NaO_2$ $(M+Na)^+$ 233.1512, found 233.1520. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.42; H, 10.60.



S22 (+ *cis*-isomer)

S23 (+ *cis*-isomer)

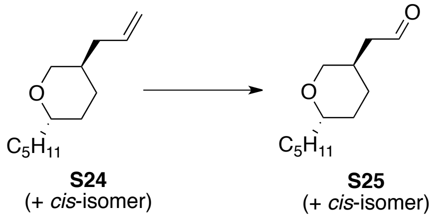
Tetrahydropyran Acetal S23. To a cooled (–78 °C) solution of lactone **S22** (0.112 g, 0.531 mmol) in CH_2Cl_2 (5.3 mL) was added DIBAL (0.64 mL, 1.0 M in hexanes, 0.640 mmol) dropwise over 3 min. The reaction mixture was maintained at –78 °C for 4 h, then Ac_2O (0.25 mL, 2.7 mmol), pyridine (0.17 mL, 2.10 mmol) and DMAP (0.100 g, 0.800 mmol) were added. The reaction mixture was warmed to room temperature and, after 24 h, saturated aqueous NH_4Cl (10 mL) was added. The mixture was concentrated *in vacuo* and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were washed with saturated aqueous potassium sodium tartrate (20 mL) then brine (20 mL), dried over $MgSO_4$, and concentrated *in vacuo*. Purification by flash chromatography (5:95 Et_2O:hexanes) afforded tetrahydropyran acetal **S23** (0.092 g, 68%). ^1H NMR spectroscopic analysis showed the product was a mixture of diastereomers in a 65:35 ratio: ^1H NMR (600 MHz, C_6D_6) δ 5.93 (d, *J* = 2.3, 0.5H), 5.73–5.61 (m, 1.5H), 5.57 (d, *J* = 8.8, 1.0H), 5.07–5.03 (m, 0.5H), 5.03–5.00 (m, 0.6H), 4.99–4.97 (m, 1.1H), 4.97–4.95 (m, 1.1H), 3.42–3.37 (m, 0.5H), 3.32–3.26 (m, 1.0H), 2.57–2.49 (m, 0.6H), 2.27–2.21 (m, 0.5H), 2.21–2.14 (m, 1.1H), 1.79–1.70 (m, 1.5H), 1.67 (s, 3.0H), 1.65 (s, 2.1H), 1.65–1.53 (m, 4.7H), 1.49–1.39 (m, 2.0H), 1.39–1.28 (m, 4.2H), 1.28–1.14 (m, 8.9H), 1.12–1.02 (m, 1.6H), 0.98–0.89 (m, 1.1H), 0.89–0.83 (m, 5.1H); ^{13}C NMR (150 MHz, C_6D_6) δ 169.1 (C), 168.7 (C), 137.5 (CH), 136.2 (CH), 116.4 (CH_2), 116.1 (CH_2), 97.5 (CH), 95.7 (CH), 76.92 (CH), 76.91 (CH), 39.6 (CH), 36.7 (CH), 36.20 (CH_2), 36.16 (CH_2), 35.7 (CH_2), 32.2 (CH_2), 31.7 (CH_2), 30.6 (CH_2), 28.3 (CH_2), 25.9 (CH_2), 25.6 (CH_2), 25.5 (CH_2), 24.7 (CH_2), 23.03 (CH_2), 23.02 (CH_2), 20.8 (CH_3), 20.7 (CH_3), 14.3 (CH_3); IR (ATR) 2859, 1753, 1641, 1221, 1041 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{15}H_{26}NaO_3$ $(M+Na)^+$ 277.1774, found 277.1780. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 70.93; H, 10.16.



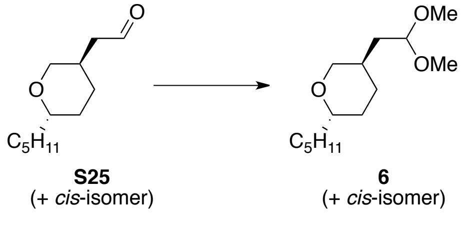
S23 (+ *cis*-isomer)

S24 (+ *cis*-isomer)

Cyclic Ether S24. To a cooled (–78 °C) solution of tetrahydropyran acetal **S23** (6.03 g, 23.7 mmol) and triethylsilane (30.3 mL, 190 mmol) in CH_2Cl_2 (120 mL) was added $BF_3 \cdot OEt_2$ (6.0 mL, 47 mmol). After 2 h, a solution of CH_2Cl_2:Et_3N:MeOH (1:1:1, 120 mL) was added followed by saturated aqueous $NaHCO_3$ (150 mL). The layers were separated and the organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (3:97 EtOAc:hexanes) afforded cyclic ether **S24** as a colorless oil (4.30 g, 93%). ^1H NMR spectroscopic analysis showed the product was a mixture of diastereomers in a 29:71 trans:cis ratio (assigned by coupling constants of the methylene hydrogen's next to the oxygen): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.81–5.71 (m, 1.5H), 5.07–5.03 (m, 1.0H), 5.02–4.97 (m, 1.9H), 3.93 (ddd, *J* = 11.2, 4.2, 2.2, 0.4H), 3.76–3.74 (m, 1.0H), 3.56 (dd, *J* = 11.4, 4.2, 1.0H), 3.29–3.24 (m, 1.0H), 3.18–3.14 (m, 0.4H), 3.02 (t, *J* = 11.2, 0.4H), 2.33–2.28 (m, 1.0H), 2.22–2.17 (m, 1.0H), 1.91–1.83 (m, 1.3H), 1.68–1.59 (m, 2.9H), 1.57–1.46 (m, 2.6H), 1.43–1.35 (m, 4.9H), 1.34–1.22 (m, 8.1H), 1.14–1.07 (m, 0.5H), 0.90–0.87 (m, 4.5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.7 (CH),136.4 (CH), 116.1 (CH_2), 116.0 (CH_2), 78.03 (CH), 78.01 (CH), 73.5 (CH_2), 70.7 (CH_2), 37.2 (CH_2), 36.5 (CH_2), 36.1 (CH_2), 35.9 (CH), 35.0 (CH_2), 33.8 (CH), 32.1 (CH_2), 31.0 (CH_2), 30.4 (CH_2), 27.2 (CH_2), 26.9 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 22.80 (CH_2), 22.78 (CH_2), 14.2 (CH_3); IR (ATR) 1641, 1095 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{13}H_{25}O$ $(M+H)^+$ 197.1900, found 197.1901. Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.41; H, 12.36.



Aldehyde S25. Ozone was bubbled into a cooled (–78 °C) solution of cyclic ether **S24** (1.11 g, 5.66 mmol) in CH_2Cl_2 (28 mL) for 1 h. After stirring for 1 h at –78 °C, triphenylphosphine (2.97 g, 11.3 mmol) was added and the reaction mixture was brought to room temperature. After 14 h, the reaction mixture was concentrated *in vacuo*. The unpurified aldehyde was passed through a plug of silica (5:95 EtOAc:hexanes) and used without further purification (2.28 g, yellow oil). ^{1}H NMR spectroscopic analysis showed the product was a mixture of diastereomers in a 39:61 trans:cis ratio: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.5, 1.0H), 9.75 (t, *J* = 2.0, 0.5H), 3.93 (ddd, *J* = 11.1, 4.0, 2.4, 0.6H), 3.75 (dt, *J* = 11.6, 2.0, 1.0H), 3.53 (ddd, *J* = 11.1, 4.0, 2.4, 1.0H), 3.28–3.24 (m, 1.0H), 3.21–3.17 (m, 0.6H), 3.08 (t, *J* = 11.0, 0.7H), 2.81 (ddd, *J* = 17.7, 7.4, 1.3, 1.0H), 2.57 (dddd, *J* = 17.7, 6.6, 1.7, 0.7, 1.0H), 2.26–2.12 (m, 3.1H), 1.93–1.89 (m, 0.7H), 1.78 (tt, *J* = 13.4, 4.6, 1.0H), 1.66–1.62 (m, 1.8H), 1.54–1.44 (m, 3.1H), 1.42–1.38 (m, 4.6H), 1.36–1.24 (m, 9.7H), 1.23–1.17 (m, 1.0H), 0.92–0.87 (m, 5.4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.2 (CH), 201.3 (CH), 78.2 (CH), 77.9 (CH), 72.6 (CH_2), 71.2 (CH_2), 46.7 (CH_2), 45.2 (CH_2), 36.34 (CH_2), 36.28 (CH_2), 32.1 (CH_2), 31.6 (CH_2), 31.2 (CH), 30.5 (CH_2), 28.1 (CH), 27.6 (CH_2), 27.2 (CH_2), 25.4 (CH_2), 25.3 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 14.2 (CH_3); IR (ATR) 1723, 1093 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{12}H_{23}O_2$ $(M+H)^+$ 199.1693, found 199.1701.



Dimethyl Acetal 6. Dimethyl acetal **6** was prepared using the representative procedure for the preparation of dimethyl acetals catalyzed by H_2SO_4, using aldehyde **S25** (2.28 g, 5.66 mmol), $HC(OMe)_3$ (6.2 mL, 57 mmol), H_2SO_4 (8 drops) and MeOH (11 mL). Purification by flash chromatography (1:5:94 Et_3N:EtOAc:hexanes) afforded dimethyl acetal **6** as a colorless oil (1.12 g, 81% over two steps). ^1H NMR spectroscopic analysis showed the product was a mixture of diastereomers in a 39:61 trans:cis ratio: ^1H NMR (600 MHz, $CDCl_3$) δ 4.47–4.45 (m, 1.0H), 4.15 (t, *J* = 5.9, 0.7H), 3.95 (ddd, *J* = 11.2, 4.3, 2.3, 0.6H), 3.76 (dt, *J* = 11.5, 2.1, 1.0H), 3.55 (dd, *J* = 11.5, 2.3, 1.0H), 3.32 (s, 3.0H), 3.31 (s, 1.8H and s, 3.0H), 3.29 (s, 1.9H), 3.28–3.24 (m, 1.3H), 3.19–3.15 (m, 0.8H), 3.04 (t, *J* = 11.2, 0.7H), 1.93–1.87 (m, 1.6H), 1.72–1.60 (m, 5.3H), 1.54–1.45 (m, 1.7H), 1.45–1.34 (m, 6.5H), 1.34–1.23 (m, 9.0H), 1.18–1.11 (m, 0.9H), 0.89–0.87 (m, 5.0H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 103.5 (CH), 102.9 (CH), 78.1 (CH), 78.0 (CH), 73.5 (CH_2), 71.3 (CH_2), 53.0 (CH_3), 52.9 (CH_3), 52.5 (CH_3), 52.4 (CH_3), 36.5 (CH_2), 36.2 (CH_2), 35.6 (CH_2), 33.1 (CH_2), 32.7 (CH), 32.1 (CH_2), 31.9 (CH_2), 30.9 (CH_2), 30.0 (CH), 27.8 (CH_2), 27.3 (CH_2), 25.44 (CH_2), 25.38 (CH_2), 22.80 (CH_2), 22.78 (CH_2), 14.0 (CH_3); IR (ATR) 2856, 1123, 1052 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{14}H_{28}NaO_3$ $(M+Na)^+$ 267.1931, found 267.1931. Anal. Calcd for $C_{14}H_{28}O_3$: C, 68.81; H, 11.55. Found: C, 68.91; H, 11.67.

III. Hydrolysis of Acetals

A. General Procedure

A stock solution (1.0 mL, 0.2 M) of starting acetal (200 μmol) and 1,4-dimethoxybenzene (75 μmol) in acetone-d_6 was prepared along with a stock solution of DCl in D_2O (1.0 mL, 0.01 M). The 0.01 M acid solution was prepared from a 35% DCl in D_2O solution. In some cases, a higher concentration of DCl in D_2O was used to perform the rate experiment (for acetals *cis*-**7**, *trans*-**7**, and **9**), a 0.0625 M solution of DCl in D_2O (1.0 mL) was prepared.

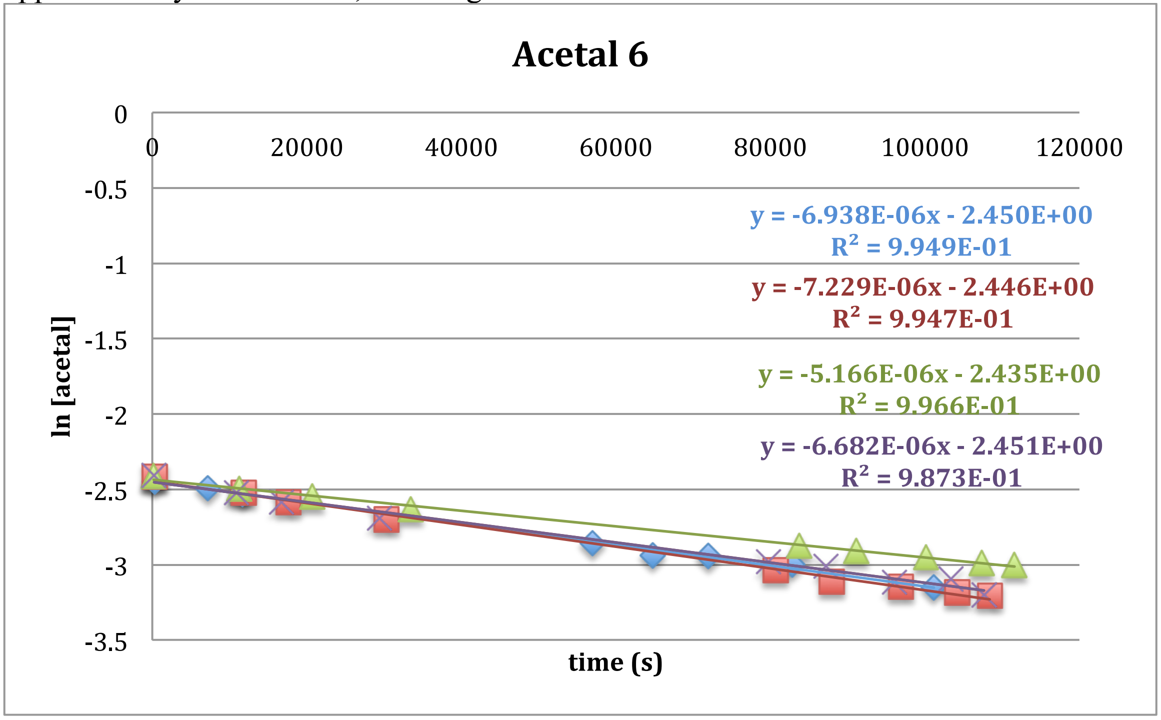
B. Rate Data Collection

The stock solution containing the starting acetal and 1,4-dimethoxybenzene in acetone-d_6 (500 uL, 0.2 M) was added to an NMR tube and a ^1H single-pulse NMR spectrum was acquired. The stock solution of DCl in D_2O (125 uL, 0.01 M) was then added to the NMR tube and a second ^1H single-pulse experiment was performed. Monitoring was continued by ^1H NMR spectroscopy with the sample removed from the probe between time points to allow for the reaction to proceed at room temperature. For samples with faster rates, the sample was allowed to remain within the probe and the temperature in the probe was maintained at 25 °C. Rates were calculated by following the decrease in starting material and plotting ln [starting material] versus t (s).

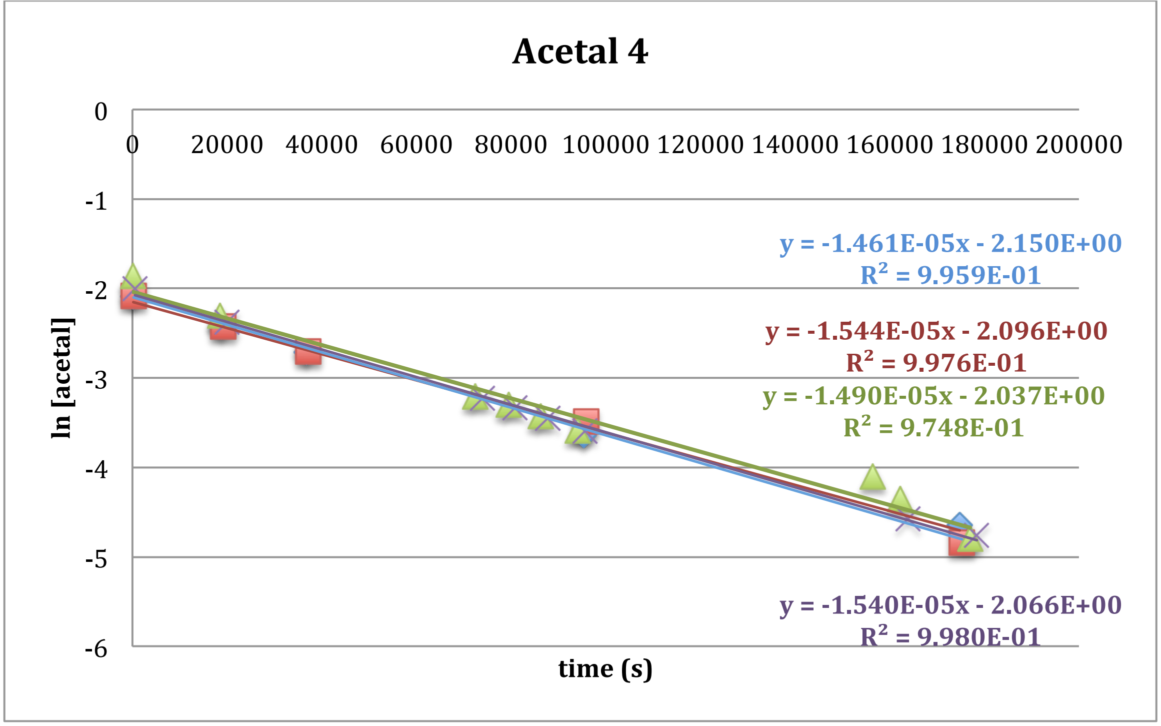
C. The Kinetic Data

The following kinetic plots were used to determine the rate constants in Chart 1 for acetals **4** and **6-12**. Multiple runs for each substrate were performed and the average rate of all runs was used. Each run is represented by one trendline displaying k_{obs}. $k_{obs} = k[HCl]$, therefore $k = k_{obs}/[HCl]$ and the final rate values are displayed in the caption above the graph.

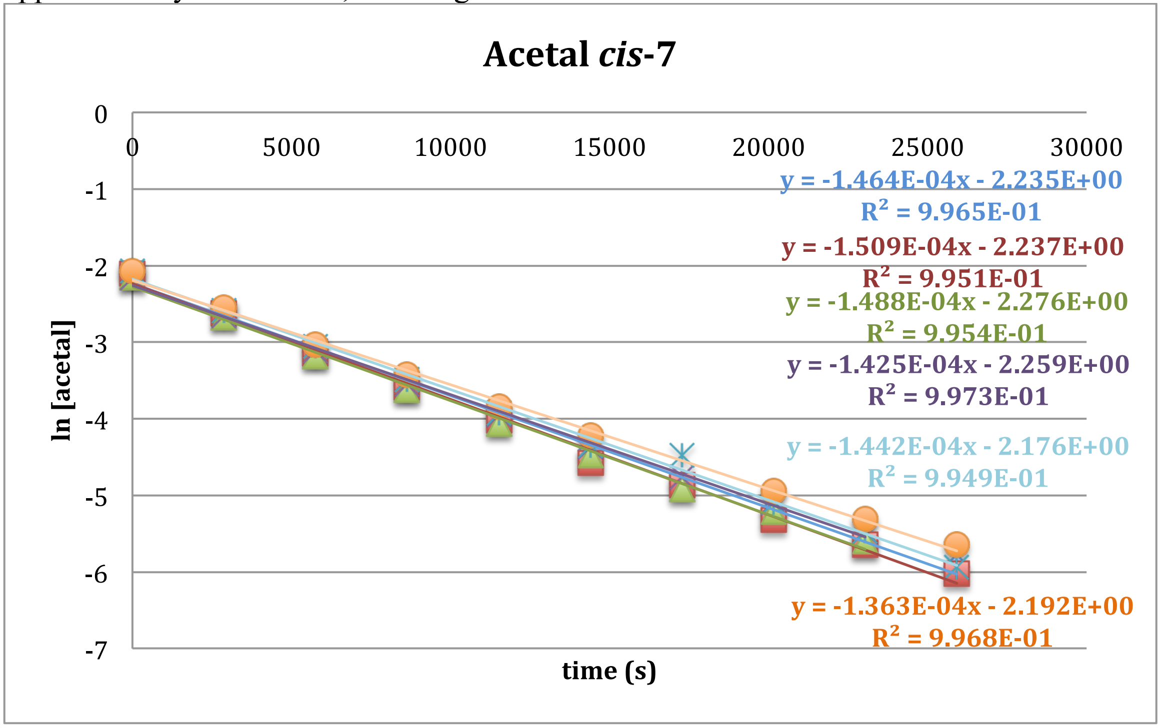
Graph S1. Rate of hydrolysis of acetal **6** plotted as ln [acetal] versus t (s) over approximately one half-life, resulting in $k = 6.50 \times 10^{-4}$.



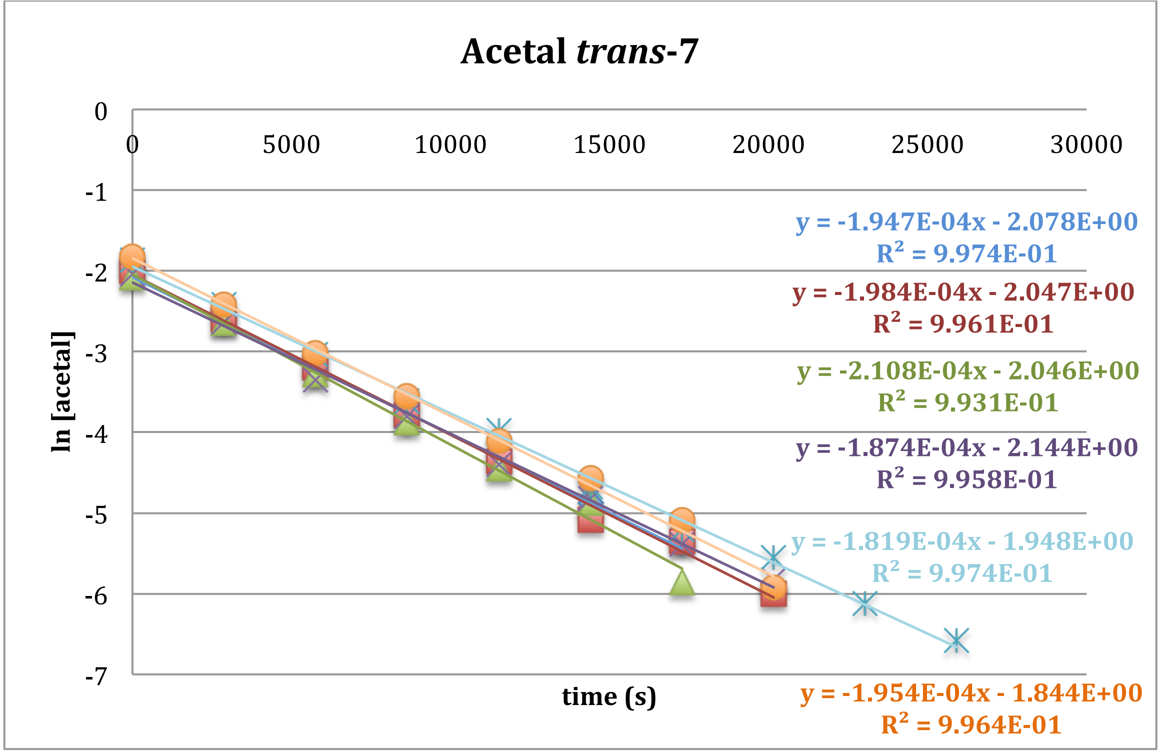
Graph S2. Rate of hydrolysis of acetal **4** plotted as ln [acetal] versus t (s) over approximately 3.8 half-lives, resulting in *k* = 1.51 x 10^{-3}.



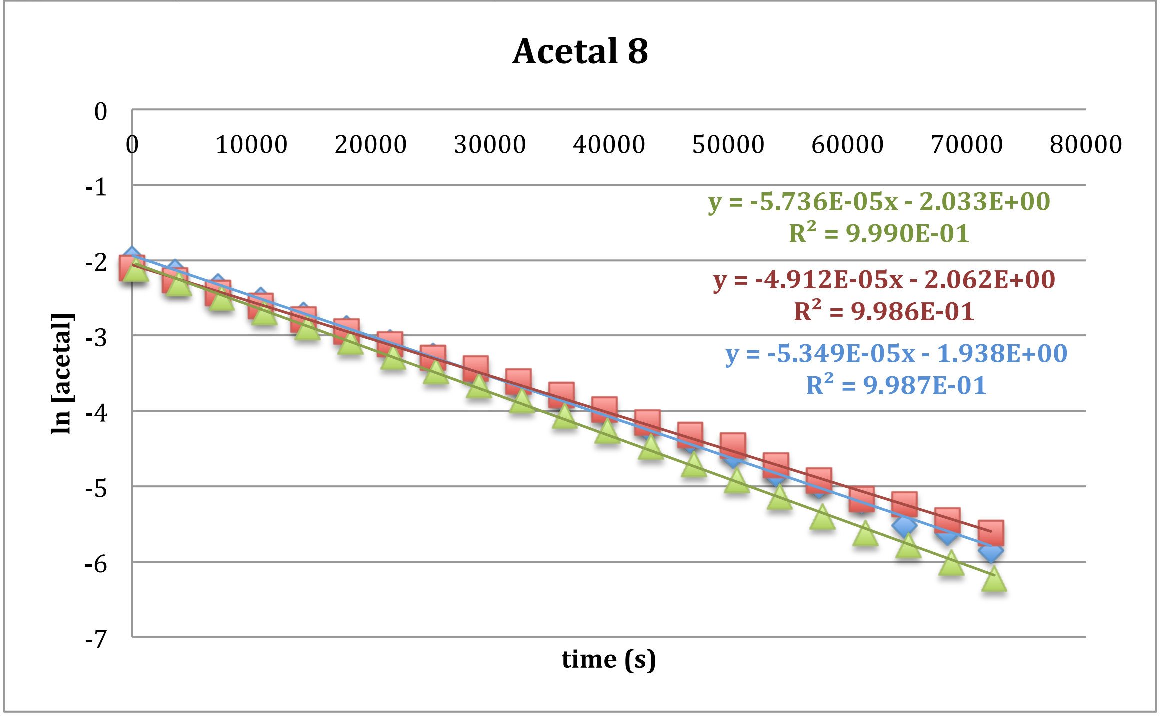
Graph S3. Rate of hydrolysis of acetal *cis*-**7** plotted as ln [acetal] versus t (s) over approximately 5 half-lives, resulting in *k* = 2.32 x 10^{-3}.



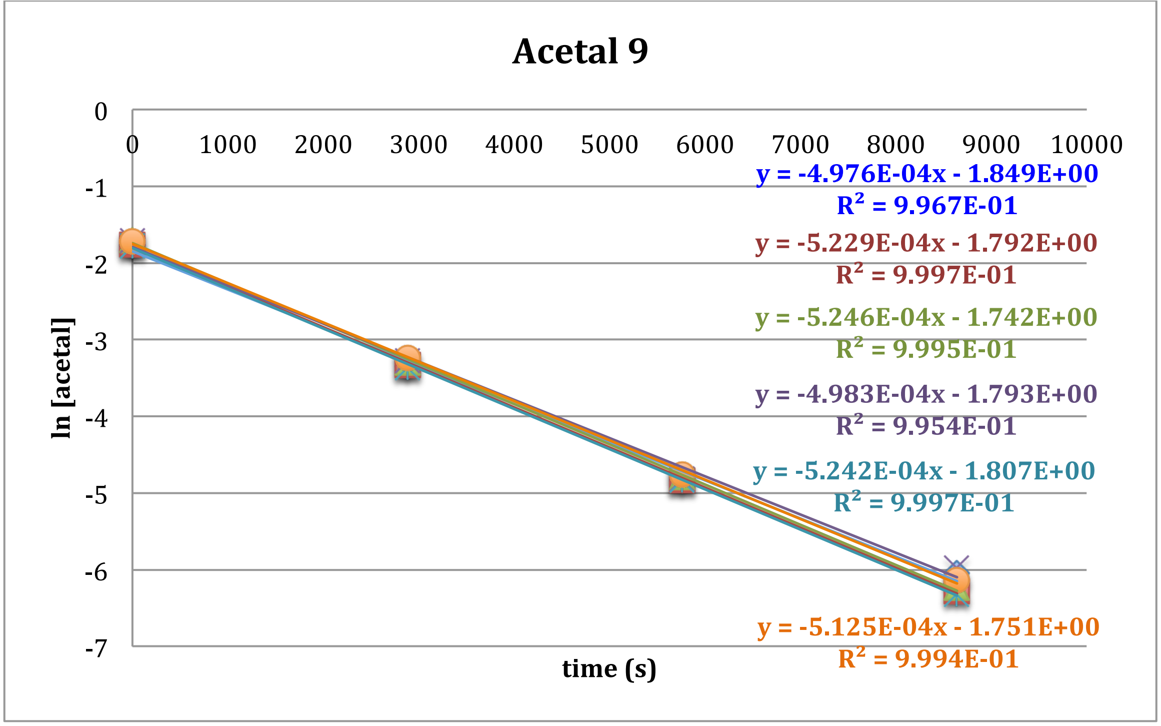
Graph S4. Rate of hydrolysis of acetal *trans*-**7** plotted as ln [acetal] versus t (s) over approximately 5 half-lives, resulting in $k = 3.12 \times 10^{-3}$.



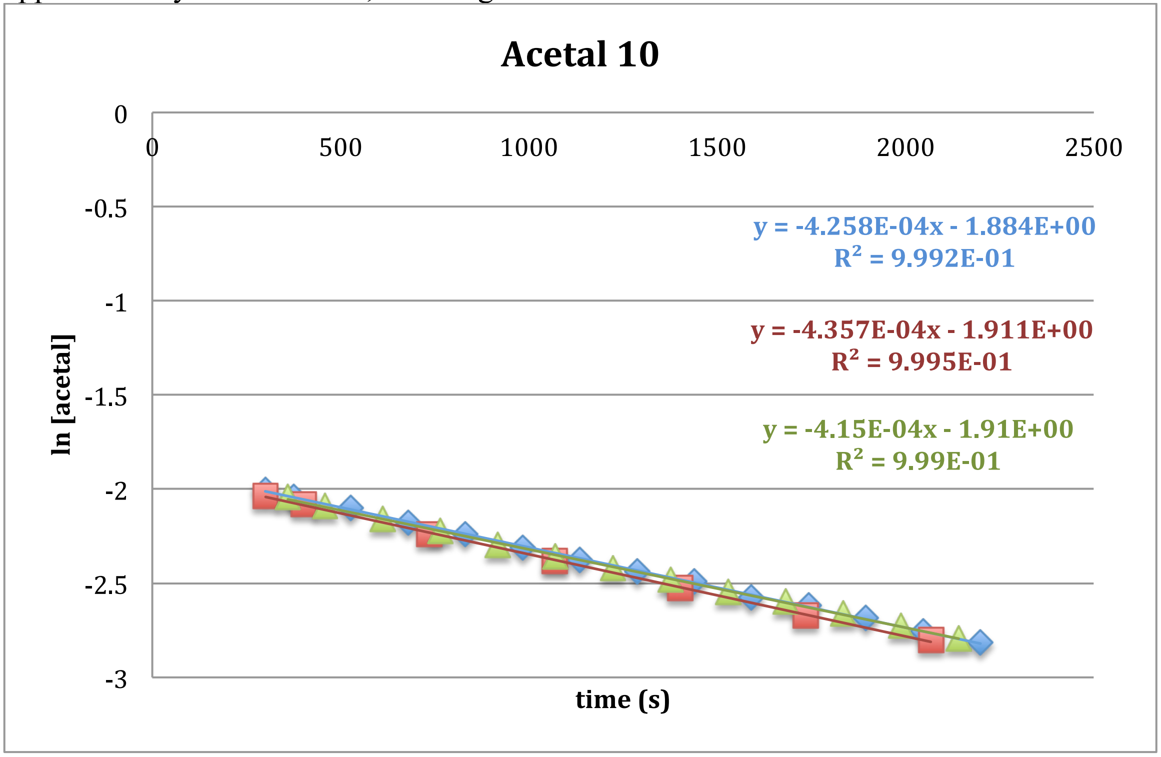
Graph S5. Rate of hydrolysis of acetal **8** plotted as ln [acetal] versus t (s) over approximately five half-lives, resulting in $k = 5.33 \times 10^{-3}$.



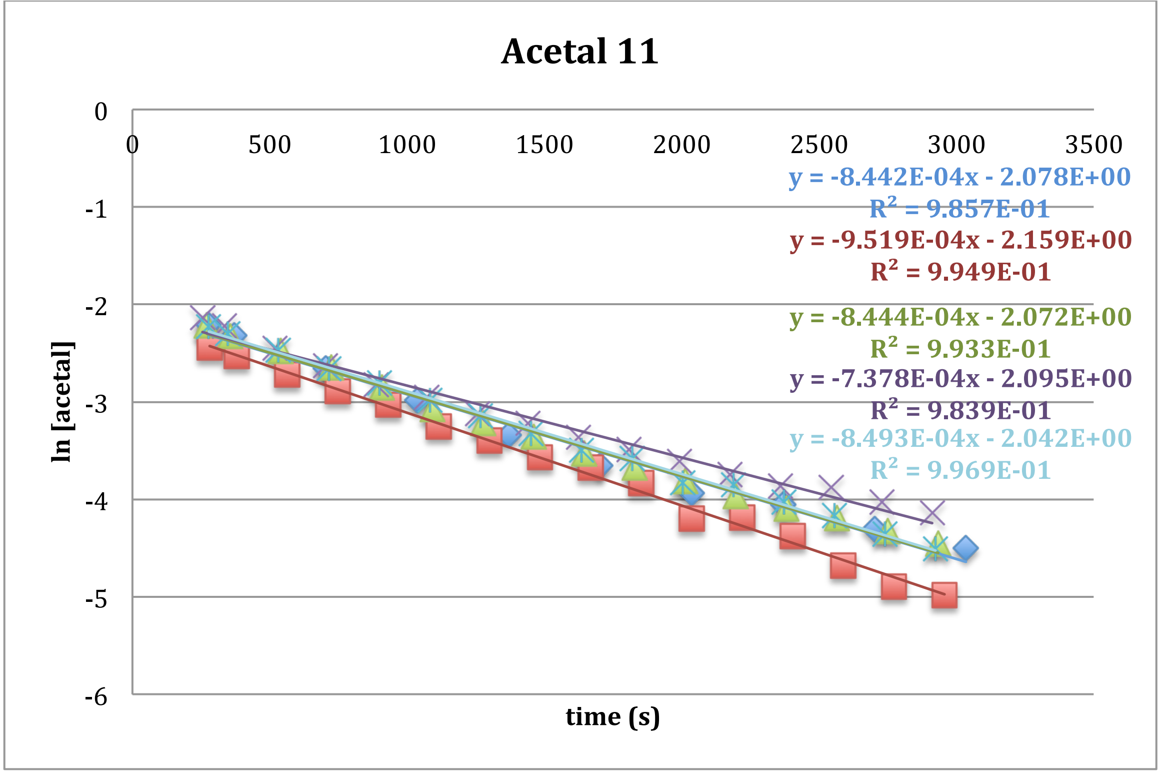
Graph S6. Rate of hydrolysis of acetal **9** plotted as ln [acetal] versus t (s) over approximately 6 half-lives, resulting in *k* = 8.21 x 10^{-3}.



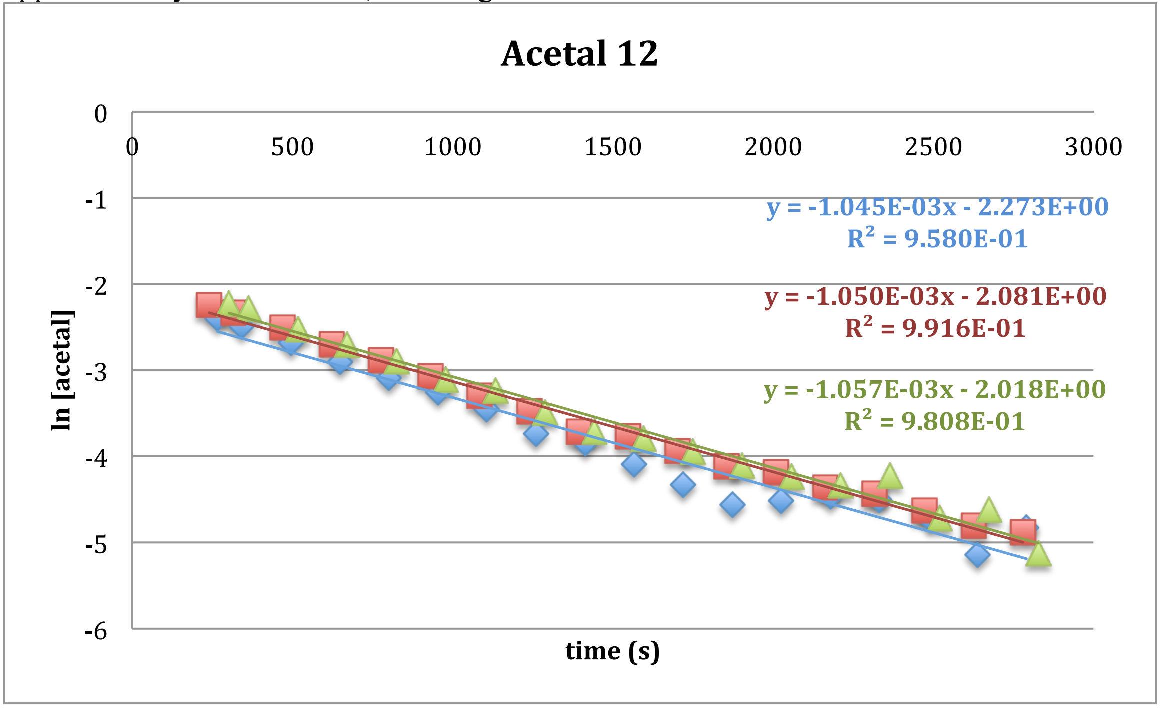
Graph S7. Rate of hydrolysis of acetal **10** plotted as ln [acetal] versus t (s) over approximately 1.3 half-lives, resulting in *k* = 4.26 x 10^{-2}.



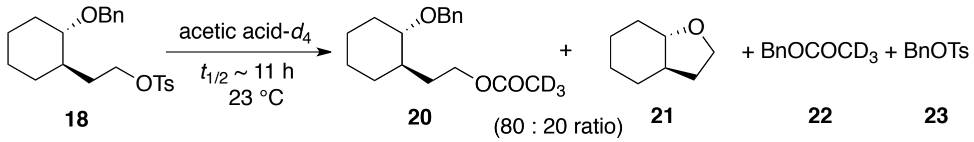
Graph S8. Rate of hydrolysis of acetal **11** plotted as ln [acetal] versus t (s) over approximately 3.6 half-lives, resulting in *k* = 8.45 x 10^{-2}.



Graph S9. Rate of hydrolysis of acetal **12** plotted as ln [acetal] versus t (s) over approximately 4.2 half-lives, resulting in *k* = 1.05 x 10^{-1}.



IV. Solvolysis Studies

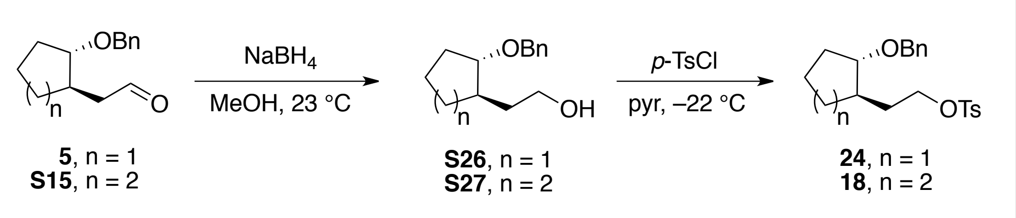


Ratio and product analysis was determined by ^{1}H NMR spectroscopy with acetic acid-d_4. Product characterization was performed on un-deuterated compounds after reacting tosylates with protic acetic acid.

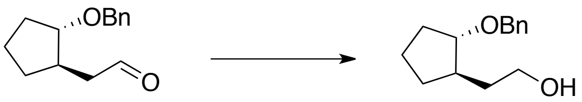
A. General Procedure for ^{1}H NMR spectroscopy studies

The tosylate starting material was added to a standard NMR tube containing 1,4-dimethoxybenzene as an internal standard. Acetic acid-d_4 was added to the NMR tube and the tube was inverted. An NMR spectrum was obtained at 25 °C at given time points until there was no observance of starting material. The decrease of starting material/tosylate was measured to determine the rate, by plotting ln (c_0/c) versus time (s).

B. Synthesis of Tosylates

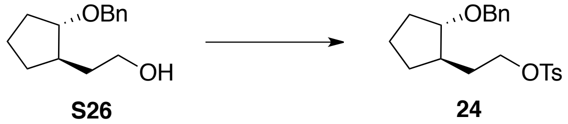


*Synthesis of aldehyde previously stated in section II.A.

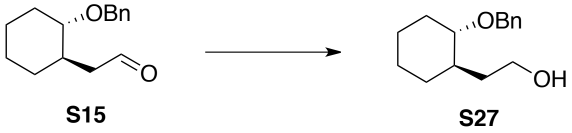


5 **S26**

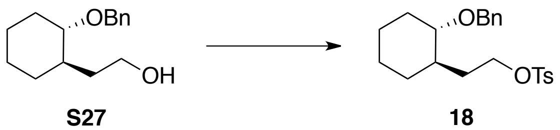
Alcohol S26. **Representative procedure for alcohol S26 by reduction of the aldehyde.** To a solution of aldehyde **5** (0.667 g, 3.06 mmol) in anhydrous MeOH (30.6 mL) was added NaBH$_4$ (0.462 g, 12.2 mmol) in portions at 0 °C. After addition, the reaction mixture was stirred at room temperature (23 °C) overnight (24 h). H$_2$O (30 mL) and Et$_2$O (60 mL) were added. The layers were separated and the organic phase was washed with H$_2$O (3 x 60 mL), dried over MgSO$_4$, filtered, and concentrated *in vacuo*. The product was purified by flash chromatography (15:85 EtOAc:hexanes) to afford alcohol **S26** as a yellow oil (0.379 g, 48% over three steps from alcohol **S7**): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37–7.33 (m, 4H), 7.32–7.27 (m, 1H), 4.57 (d, J = 11.4, 1H), 4.44 (d, J = 11.4, 1H), 3.73–3.61 (m, 3H), 2.68 (br s, 1H), 2.02–1.85 (m, 3H), 1.77–1.55 (m, 5H), 1.22 (dq, *J* = 11.8, 8.2, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2 (C), 128.6 (CH), 128.1 (CH), 127.9 (CH), 86.1 (CH), 71.8 (CH_2), 62.2 (CH_2), 43.8 (CH), 37.2 (CH_2), 31.1 (CH_2), 30.9 (CH_2), 22.1 (CH_2); IR (ATR) 3371, 3030, 1351, 1064, 1028 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{14}H_{20}NaO_2$ $(M+Na)^+$ 243.1361, found 243.1356. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.28; H, 9.09.



Tosylate 24. Representative procedure for the tosylation of alcohols.[6] To a cooled (0 °C) solution of alcohol **S26** (0.520 g, 2.36 mmol) in pyridine (4.1 mL) was added *p*-TsCl (0.901 g, 4.72 mmol). The solids were dissolved and the reaction mixture was stored in the freezer (–22 °C). After two days, needles were filtered off and the filtrate solution was poured into ice water. Et_2O (10 mL) was added and the layers were separated. The aqueous phase was extracted with Et_2O (2 x 10 mL) and the combined organic layers were washed with H_2O (30 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo.* The product was purified by flash chromatography (5:95 EtOAc:hexanes) to afford tosylate **24** as a colorless oil (0.372 g, 29%, over three steps from alkene **S11**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 8.3, 1.8, 2H), 7.35–7.26 (m, 7H), 4.49 (d, *J* = 11.7, 1H), 4.37 (d, *J* = 11.8, 1H), 4.07 (t, *J* = 6.8, 2H), 3.50 (dd, *J* = 11.9, 5.5, 1H), 2.43 (s, 3H), 1.92–1.78 (m, 4H), 1.71–1.54 (m, 4H), 1.10 (dq, *J* = 12.4, 8.0, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.7 (C), 138.7 (C), 133.3 (C), 129.9 (CH), 128.5 (CH), 128.0 (CH), 127.8 (CH), 127.6 (CH), 85.8 (CH), 71.4 (CH_2), 69.9 (CH_2), 42.2 (CH), 33.3 (CH_2), 31.0 (CH_2), 29.9 (CH_2), 22.3 (CH_2), 21.7 (CH_3); IR (ATR) 1598, 1356, 1188, 1174 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{21}H_{26}NaO_4S$ $(M+Na)^+$ 397.1449, found 397.1457. Anal. Calcd for $C_{21}H_{26}O_4S$: C, 67.35; H, 7.00. Found: C, 67.29; H, 7.02.



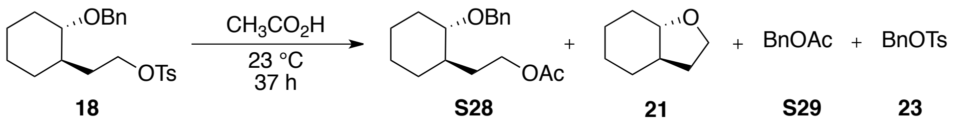
Alcohol S27. Alcohol **S27** was prepared using the representative procedure for the reduction of aldehydes, using aldehyde **S15** (1.00 g, 4.31 mmol), $NaBH_4$ (0.490 g, 12.9 mmol) and anhydrous MeOH (43.1 mL). The product was purified by flash chromatography (15:85 EtOAc:hexanes) to afford the alcohol as a yellow oil (0.582 g, 55%, over two steps from alkene **S12**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 4H), 7.33–7.27 (m, 1H), 4.68 (d, *J* = 11.4, 1H), 4.44 (d, *J* = 11.4, 1H), 3.74–3.65 (m, 1H), 3.64–3.57 (m, 1H), 3.06–3.00 (m, 1H), 2.47 (br s, 1H), 2.24–2.19 (m, 1H), 1.90–1.83 (m, 1H), 1.82–1.77 (m, 2H), 1.67–1.62 (m, 1H), 1.55–1.40 (m, 2H), 1.27–1.17 (m, 3H), 1.10–1.00 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.5 (C), 128.5 (CH), 128.1 (CH), 127.8 (CH), 82.4 (CH), 70.5 (CH_2), 61.8 (CH_2), 41.4 (CH), 37.3 (CH_2), 32.5 (CH_2), 31.1 (CH_2), 25.7 (CH_2), 24.7 (CH_2); IR (ATR) 3377, 1351, 1090, 1061 cm^{-1}; HRMS (TOF MS ES+) *m / z* calcd for $C_{15}H_{22}NaO_2$ $(M+Na)^+$ 257.1517, found 257.1512. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.77; H, 9.32.



Tosylate 18. Tosylate **18** was prepared using the representative procedure for tosylation of alcohols, using alcohol **S27** (0.371 g, 1.58 mmol) and *p*-TsCl (0.603 g, 3.16 mmol) in pyridine (2.7 mL).[6] The product was purified by flash chromatography (5:95 EtOAc:hexanes) to afford tosylate **18** as a colorless oil (0.349 g, 57%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (dt, *J* = 8.3, 1.8, 2H), 7.34–7.31 (m, 2H), 7.30–7.26 (m, 5H), 4.58 (d, *J* = 11.5, 1H), 4.33 (d, *J* = 11.5, 1H), 4.15–4.11 (m, 1H), 4.09–4.05 (m, 1H), 2.96–2.92 (m, 1H), 2.42 (s, 3H), 2.15–2.06 (m, 2H), 1.76–1.72 (m, 1H), 1.71–1.68 (m, 1H), 1.61–1.55 (m, 1H), 1.49–1.39 (m, 2H), 1.18–1.10 (m, 3H), 0.97–0.90 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6 (C), 138.9 (C), 133.4 (C), 129.9 (CH), 128.5 (CH), 128.0 (CH), 127.9 (CH), 127.6 (CH), 81.9 (CH), 70.4 (CH_2), 69.9 (CH_2), 40.2 (CH), 32.5 (CH_2), 31.09 (CH_2), 31.06 (CH_2), 25.4 (CH_2), 24.6 (CH_2), 21.8 (CH_3); IR (ATR) 1598, 1356, 1188, 1174 cm^{-1}; HRMS (TOF MS ES+) *m* / *z* calcd for $C_{22}H_{28}NaO_4S$ $(M+Na)^+$ 411.1606, found 411.1601.[b]

C. Characterization of Solvolysis Products

General Procedure: Approximately 180 mg of tosylate starting material was dissolved in approximately 2 mL of protic acetic acid and the reaction mixture was left to sit at room temperature (23 °C) until full consumption of the starting material. CH_2Cl_2 (2 mL) and saturated aqueous $NaHCO_3$ (2 mL) were added. The layers were separated and the organic layer was washed with saturated $NaHCO_3$ (2 x 2 mL), H_2O (2 mL), dried over $MgSO_4$, and concentrated. In the case of tosylate **24**, only traces of decomposition were observed after a total of four months at 23 °C.



^{1}H NMR spectroscopic analysis of the unpurified reaction mixture showed a 4:1 ratio of **S28** to cyclic ether **21**. The product was purified by flash chromatography (5:95 EtOAc:hexanes) in an effort to isolate **21**. ^{1}H NMR data for **21** was obtained from a sample also containing benzyl acetate. A crude mixture containing **S28**, **21**, benzyl tosylate (**23**) and benzyl acetate (**S29**) was used for the remaining data. **Cyclic ether 21**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89–3.86 (m, 2H), 2.96 (td, *J* = 10.4, 3.7, 1H), 2.13–2.08 (m, 1H), 2.02–1.94 (m, 2H), 1.84–1.80 (m, 1H), 1.75–1.70 (m, 1H), 1.36–1.17 (m, 5H), 1.14–1.05 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 83.5 (CH), 66.5 (CH_2), 45.3 (CH), 31.3 (CH_2), 31.0 (CH_2), 29.2 (CH_2), 25.9 (CH_2), 24.5 (CH_2); HRMS (TOF MS ES+) *m* / *z* calcd for $C_8H_{15}O$ $(M+H)^+$ 127.1123, found 127.1117. **Acetate S28**: The spectral data (^{1}H

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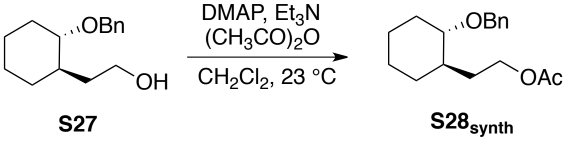
[b] Attempt at combustion analysis yielded unsatisfactory results.

NMR and ^{13}C NMR) are consistent with the data reported for the authentic acetate **S28$_{synth}$**. HRMS (TOF MS ES+) *m / z* calcd for $C_{17}H_{24}NaO_3$ $(M+H)^+$ 299.1623, found 299.1618. The spectral data for benzyl acetate (**S29**) and benzyl tosylate (**23**) are consistent with the data reported (^{1}H NMR and ^{13}C NMR).[7,8]

D. Synthesis of Acetates for Solvolysis Characterization



Acetate S28$_{synth}$. To a solution of alcohol **S27** (0.258 g, 1.10 mmol) in CH_2Cl_2 (5.5 mL), were added 4-(dimethylamino)pyridine (0.067 g, 0.551 mmol), triethylamine (0.614 mL, 4.40 mmol), and acetic anhydride (0.125 mL, 1.32 mmol) and the mixture was stirred at room temperature (23 °C) for 7 h. The reaction mixture was concentrated *in vacuo* and purified by flash chromatography (5:95 EtOAc:hexanes) to afford acetate **S28$_{synth}$** as a colorless oil (0.163 g, 54%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36–7.32 (m, 4H), 7.29–7.26 (m, 1H), 4.64 (d, *J* = 11.6, 1H), 4.43 (d, *J* = 11.5, 1H), 4.15–4.09 (m, 2H), 3.03–2.99 (m, 1H), 2.18–2.12 (m, 2H), 2.03 (s, 3H), 1.86–1.83 (m, 1H), 1.79–1.77 (m, 1H), 1.66–1.62 (m, 1H), 1.55–1.49 (m, 1H), 1.45–1.39 (m, 1H), 1.26–1.18 (m, 3H), 1.03–0.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4 (C), 139.1 (C), 128.5 (CH), 127.9 (CH), 127.6 (CH), 81.8 (CH), 70.6 (CH_2), 63.3 (CH_2), 40.5 (CH), 31.6 (CH_2), 31.2 (CH_2), 30.8 (CH_2), 25.5 (CH_2), 24.8 (CH_2), 21.3 (CH_3); IR (ATR) 1735, 1363, 1234, 1092, 1070; HRMS (TOF MS ES+) *m / z* calcd for $C_{17}H_{24}NaO_3$ $(M+Na)^+$ 299.1623, found 299.1618. Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.86; H, 8.65.

V. References

[1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* **1996**, *15*, 1518-1520.
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[6] C. V. Magatti, J. J. Kaminski, I. Rothberg, *J. Org. Chem.* **1991**, *56*, 3102-3108.
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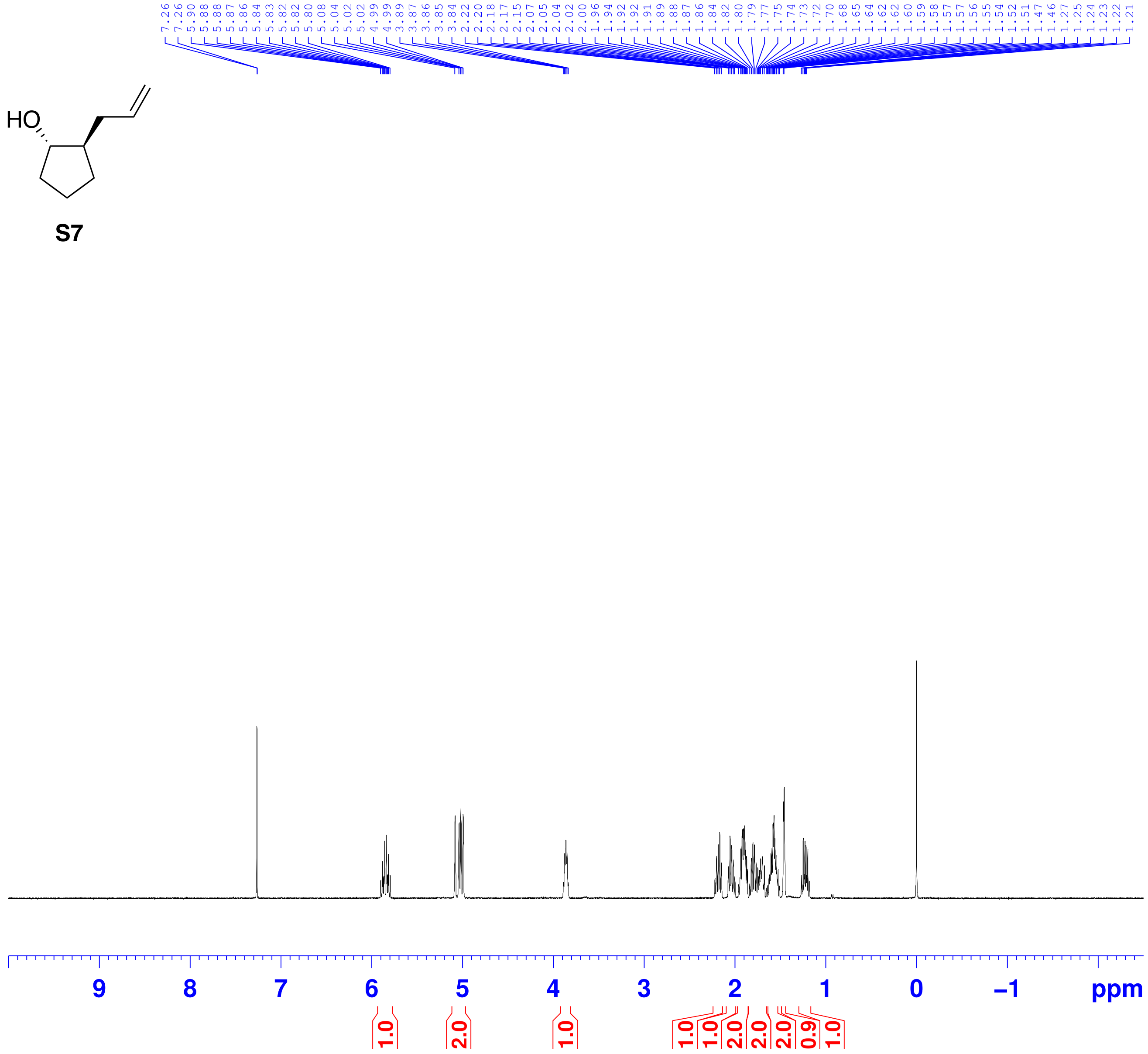
VI. Analytical Data

S7



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PROCNO                  1

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FIDRES           0.126314 Hz
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RG                    256
DW                 60.400 usec
DE                   6.50 usec
TE                  298.3 K
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TD0                     1

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F2 - Processing parameters
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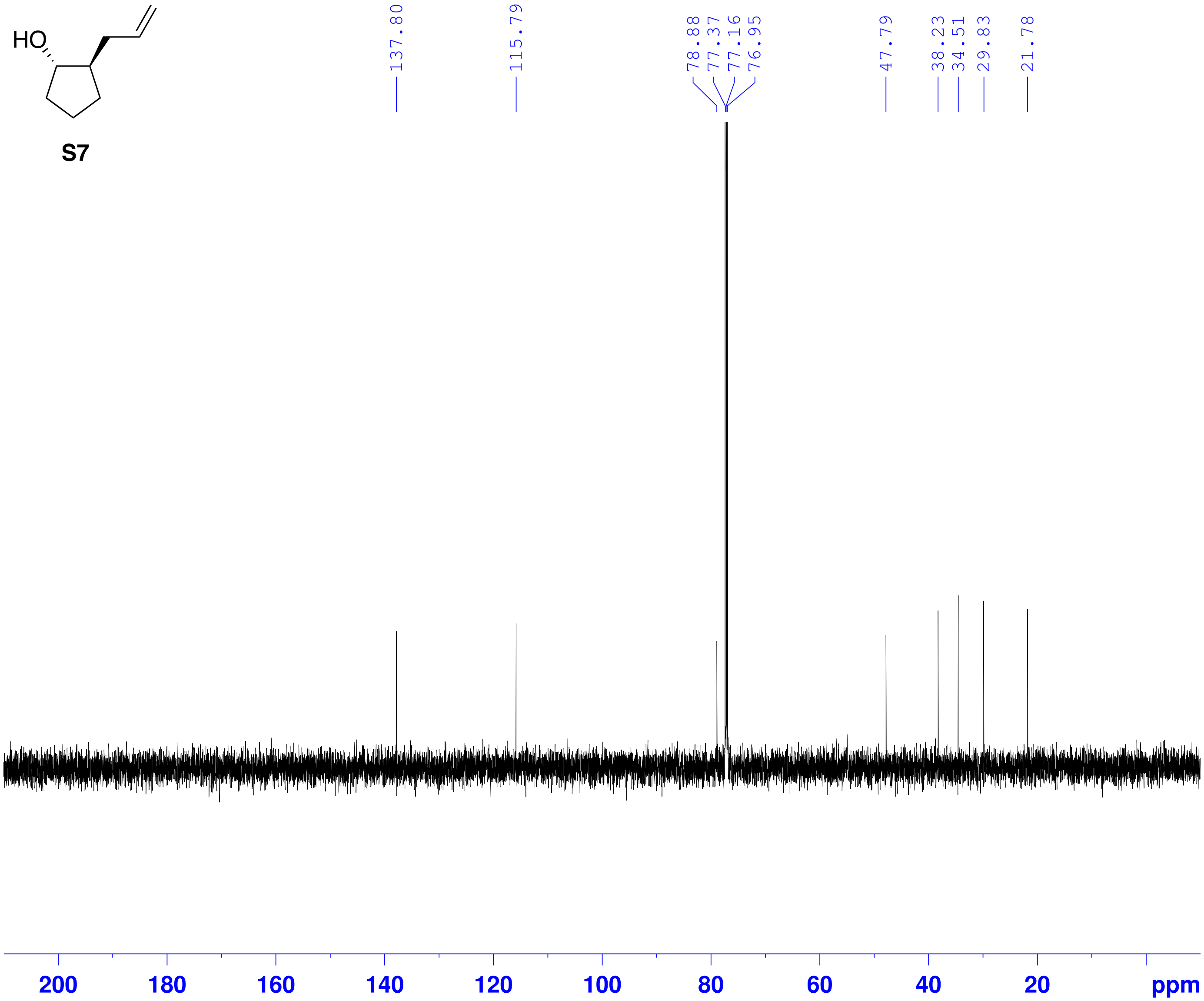

S7

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SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.50000000 sec
D11           0.03000000 sec
TD0                    1

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NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz

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NUC2                  1H
PCPD2              70.00 usec
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PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
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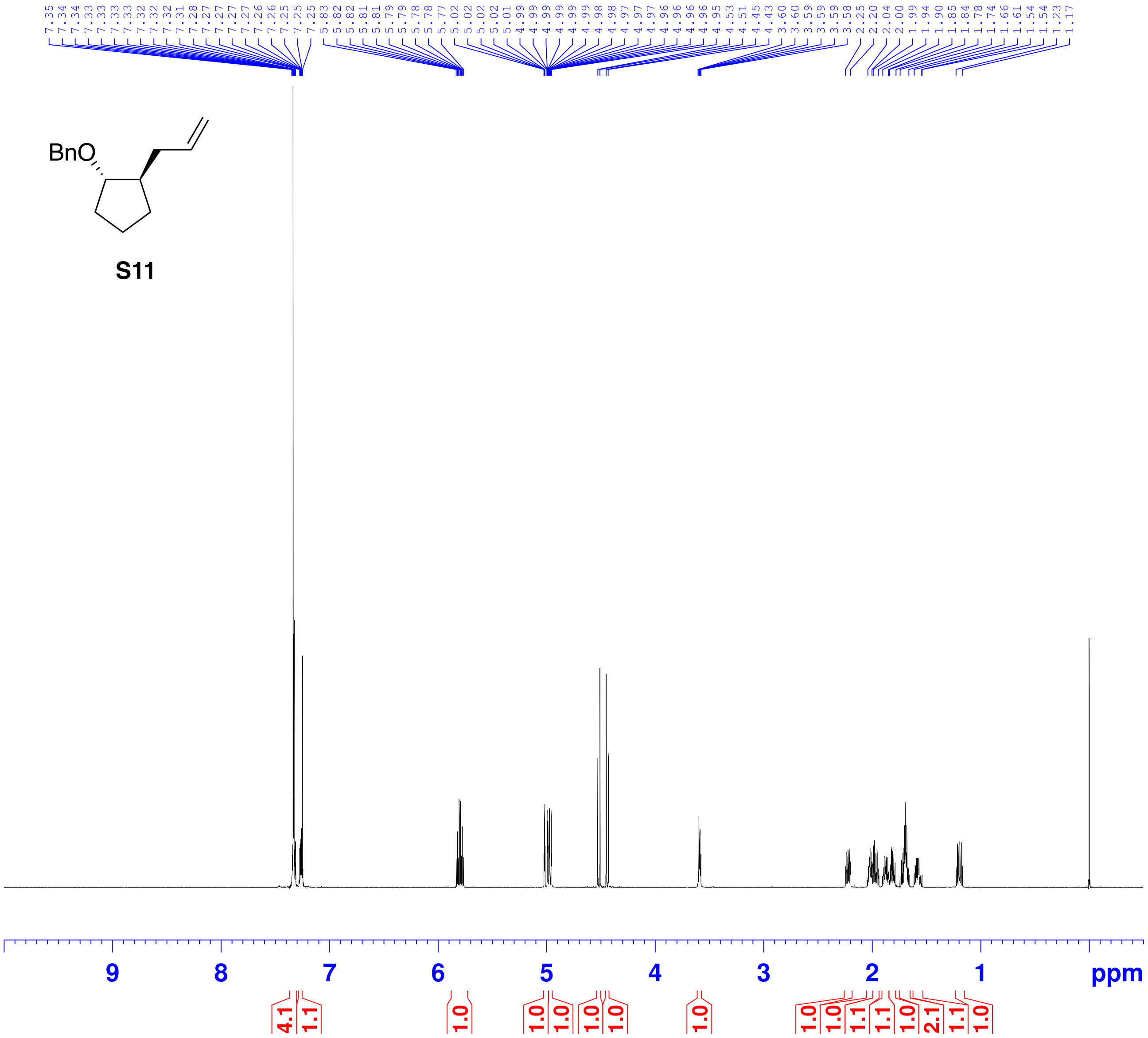
S11



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SOLVENT              CDCl3
NS                       8
DS                       0
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FIDRES         0.188225 Hz
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TE                 298.1 K
D1          1.00000000 sec
TD0                      1

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P1                9.79 usec
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SFO1       600.1937064 MHz

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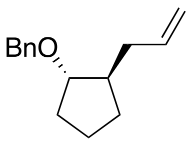
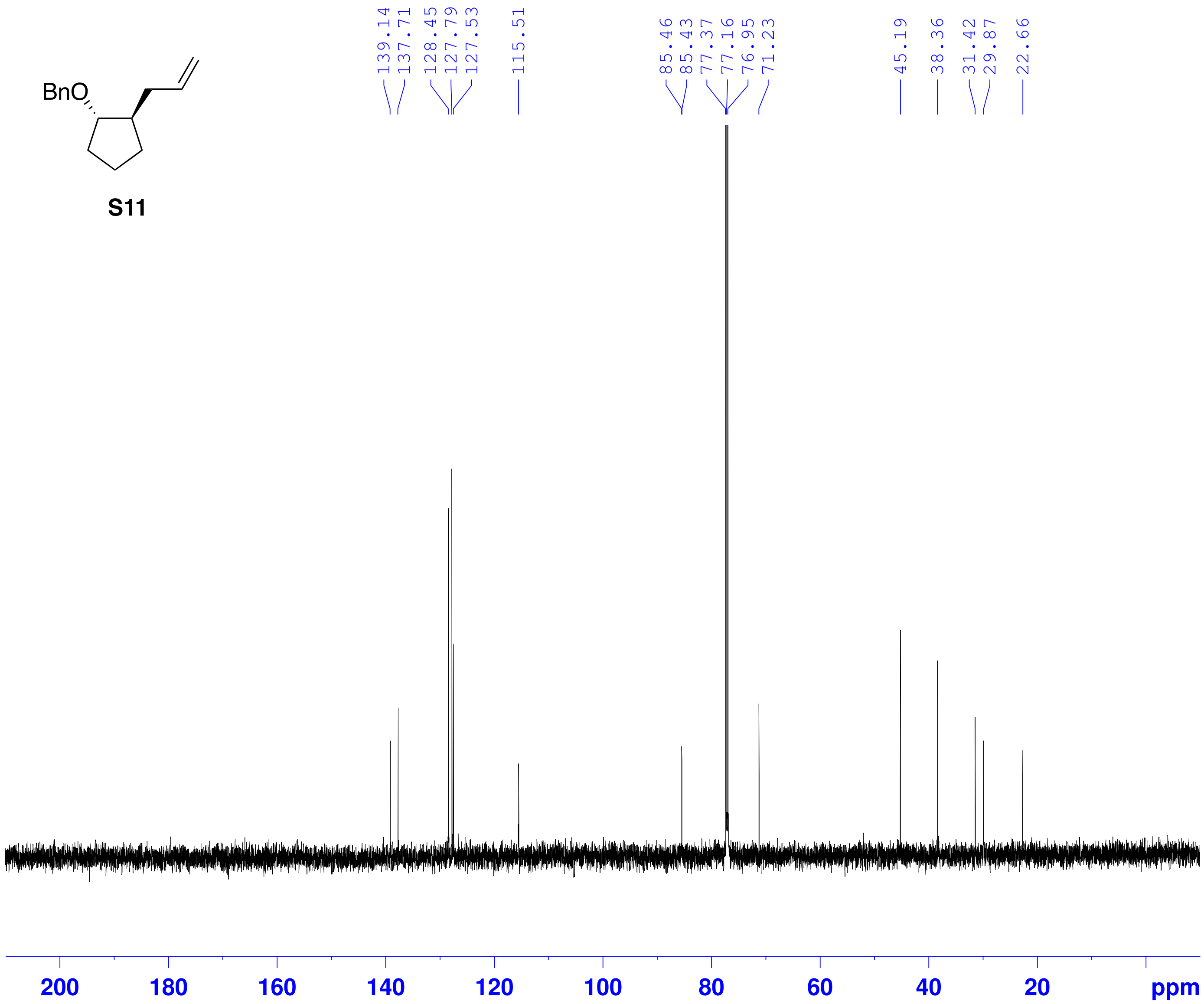


S11



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FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG              184.65
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DE                6.50 usec
TE               298.2 K
D1          2.50000000 sec
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TD0                   1

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SFO1       150.9329866 MHz

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PLW13        0.08913500 W
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F2 - Processing parameters
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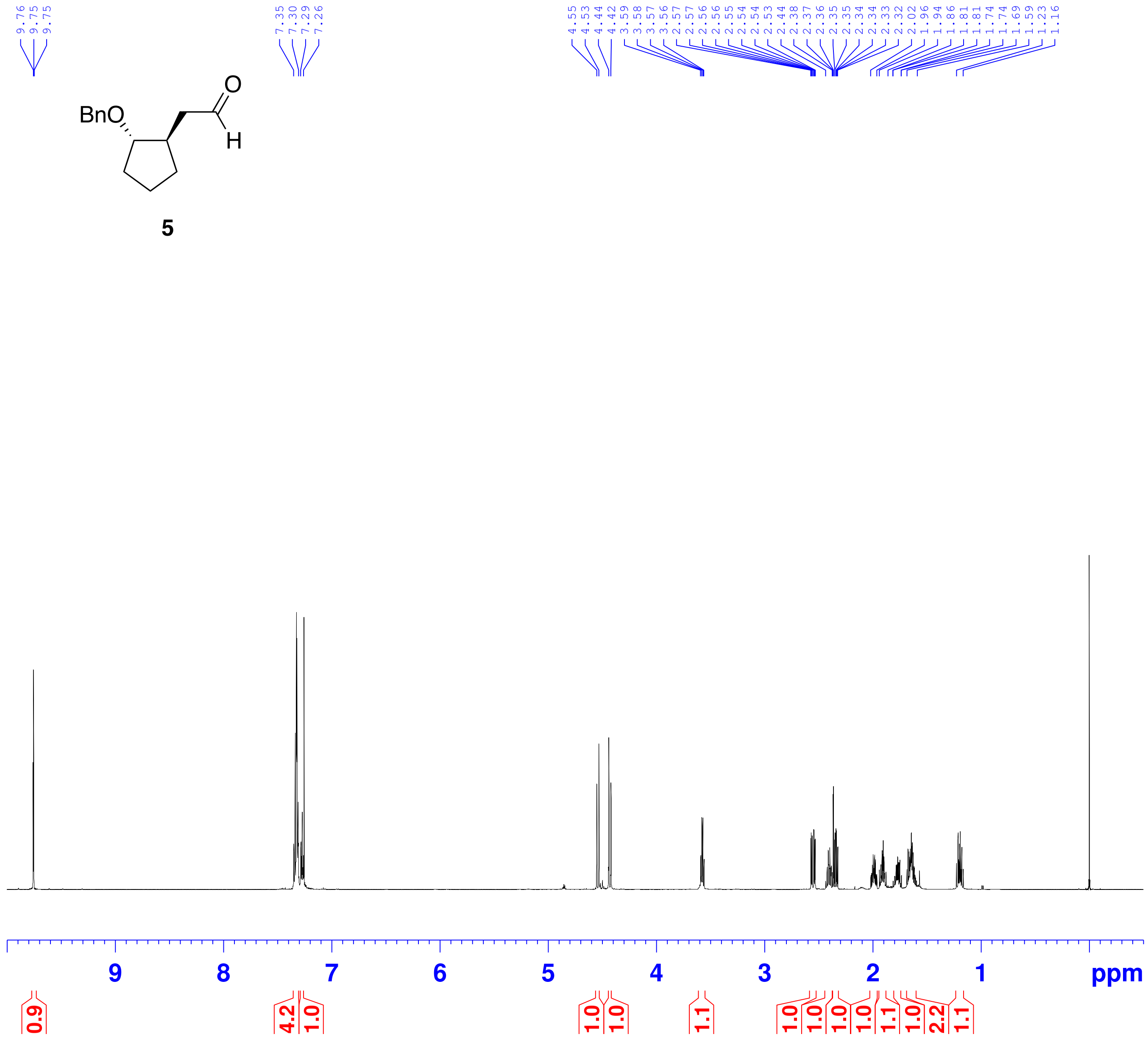

5

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NS                       8
DS                       0
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                   85.84
DW                  40.533 usec
DE                    6.50 usec
TE                   298.2 K
D1             1.00000000 sec
TD0                      1

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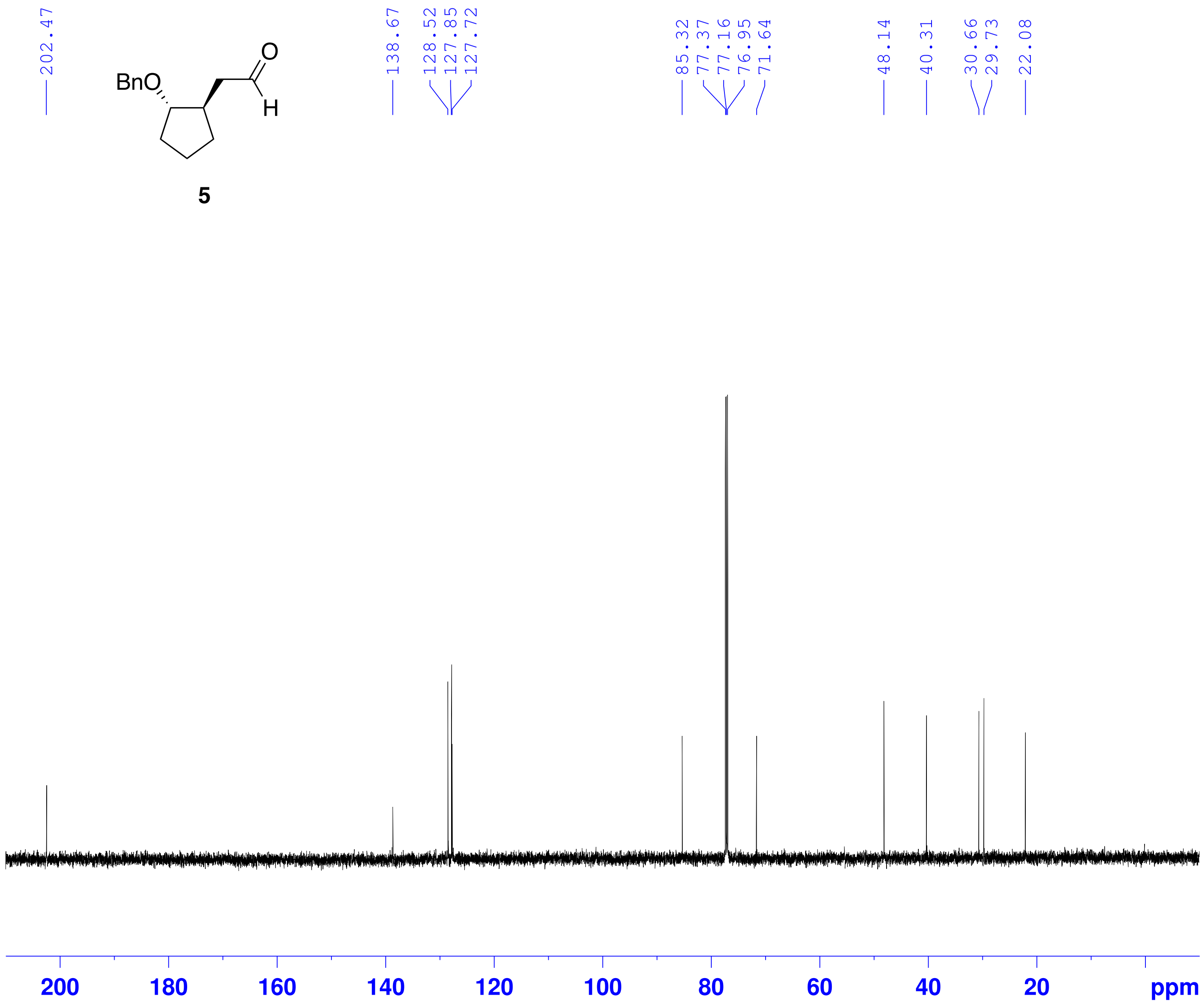
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PROCNO                  1

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SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                 184.65
DW                 13.867 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
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P1                  15.00 usec
PLW1         106.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
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NUC2                   1H
PCPD2               70.00 usec
PLW2           9.30000019 W
PLW12          0.18190999 W
PLW13          0.08913500 W
SFO2         600.1924008 MHz

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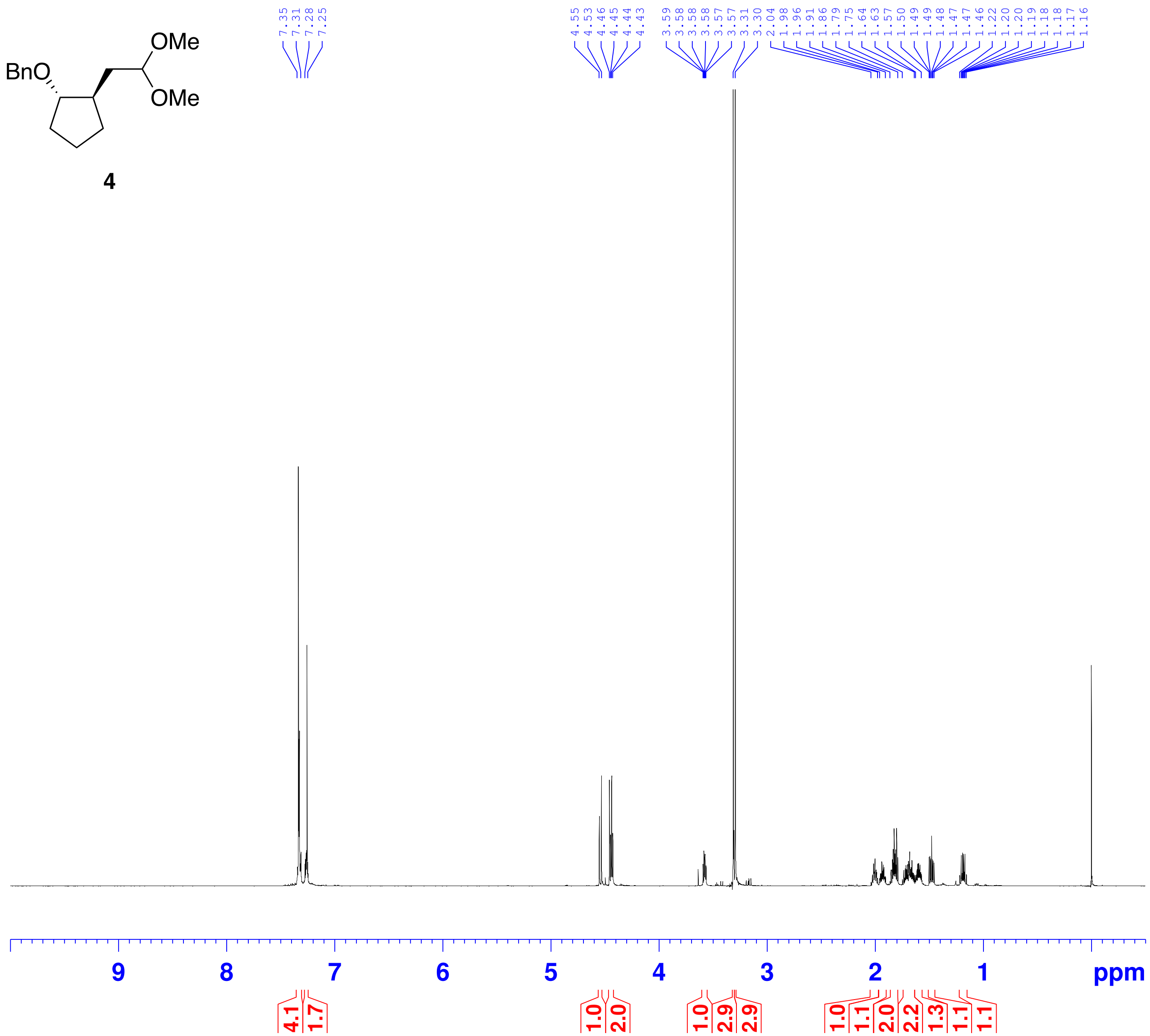

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FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                   85.84
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DE                    6.50 usec
TE                   298.2 K
D1          1.00000000 sec
TD0                      1

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SFO1       600.1937064 MHz

F2 - Processing parameters
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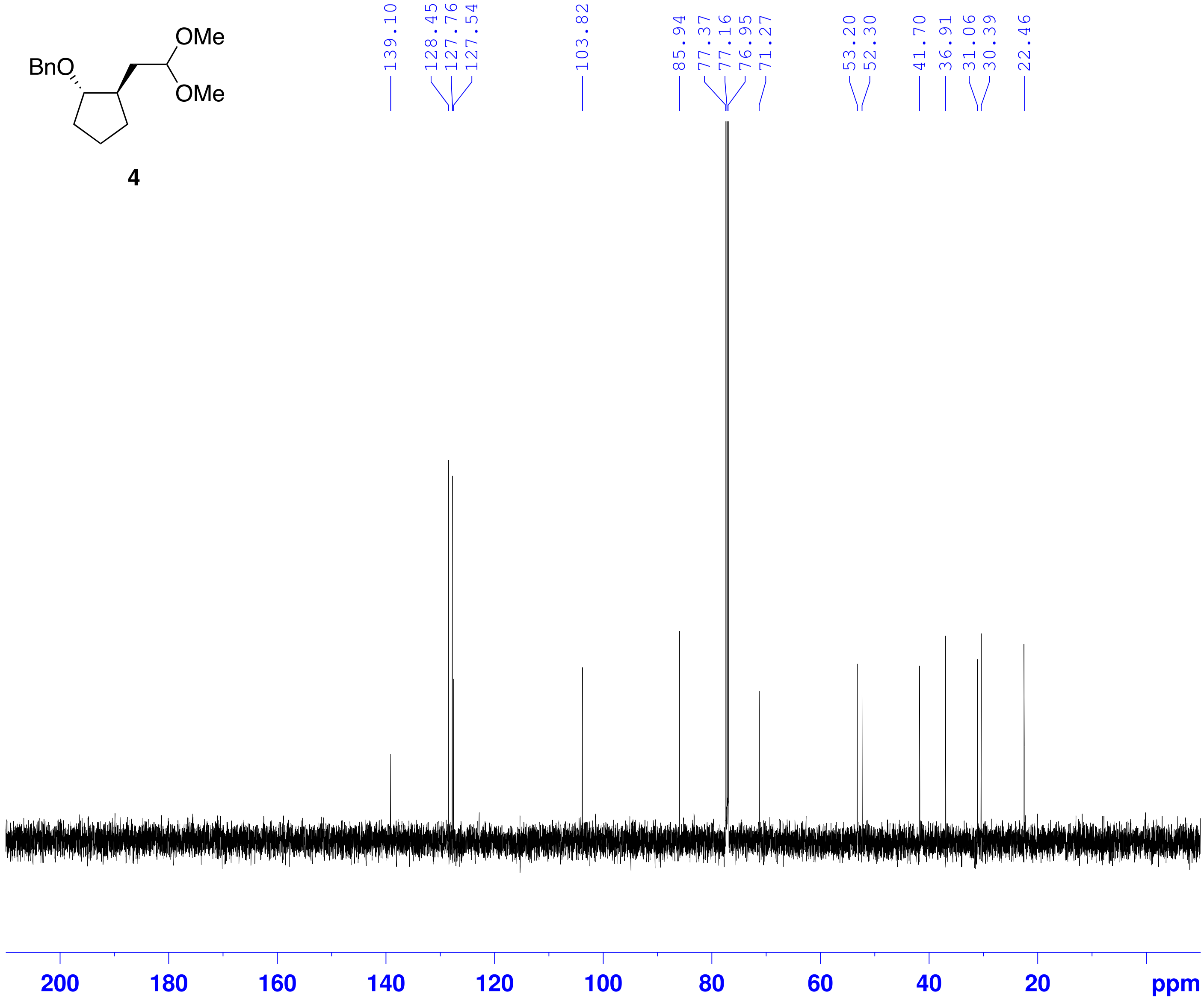
PC                    1.00
```

4



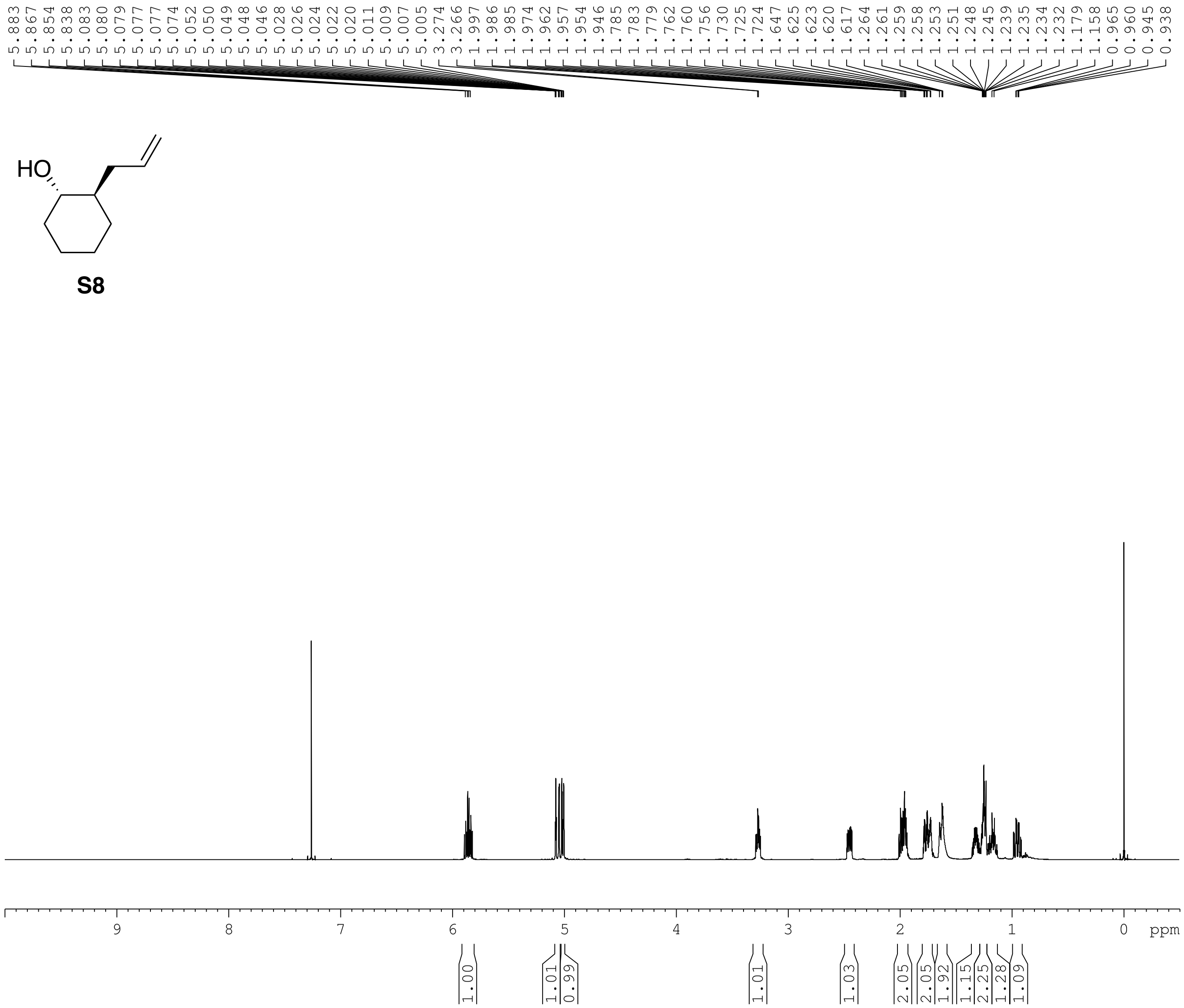
```
Current Data Parameters
NAME              II-133-P
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20130317
Time                 18.46
INSTRUM              spect
PROBHD   5 mm PABBO BB/
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                      32
DS                       0
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                  184.65
DW                  13.867 usec
DE                    6.50 usec
TE                   298.2 K
D1              2.50000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   10.65 usec
PLW1          104.00000000 W
SFO1           150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                    1H
PCPD2                70.00 usec
PLW2           26.50000000 W
PLW12           0.65438998 W
PLW13           0.32065001 W
SFO2           600.1924008 MHz

F2 - Processing parameters
SI                   32768
SF             150.9178746 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```



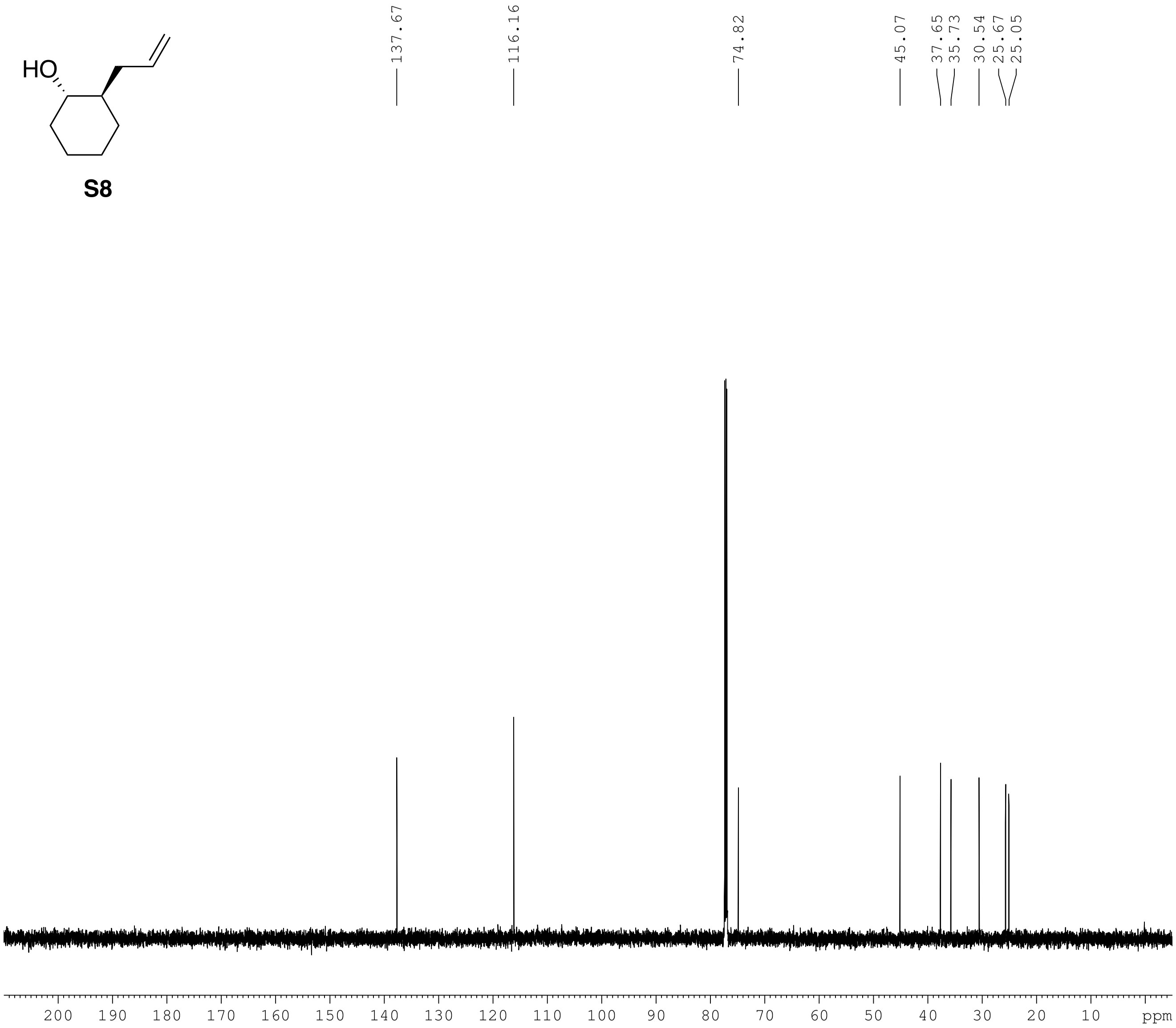
S8

```
Current Data Parameters
NAME             II-29-P
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121120
Time               16.38
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH          12335.526 Hz
FIDRES        0.188225 Hz
AQ           2.6564426 sec
RG                 85.84
DW                40.533 usec
DE                  6.50 usec
TE                 298.1 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.79 usec
PLW1          9.30000019 W
SFO1        600.1937064 MHz

F2 - Processing parameters
SI                 65536
SF          600.1900136 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



S8

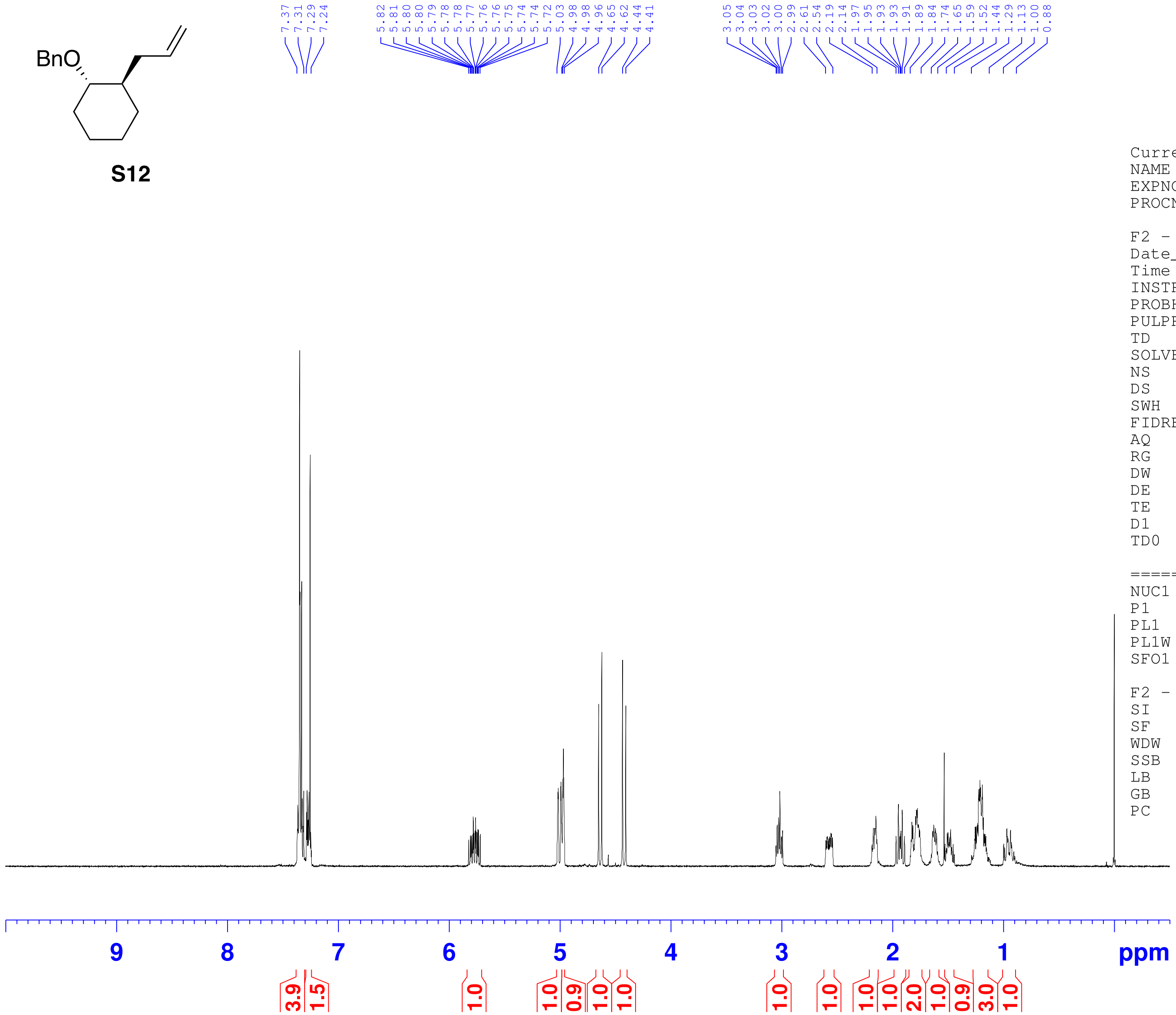
```
Current Data Parameters
NAME             II-29-P
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20121120
Time               16.45
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     0
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.50000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178746 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



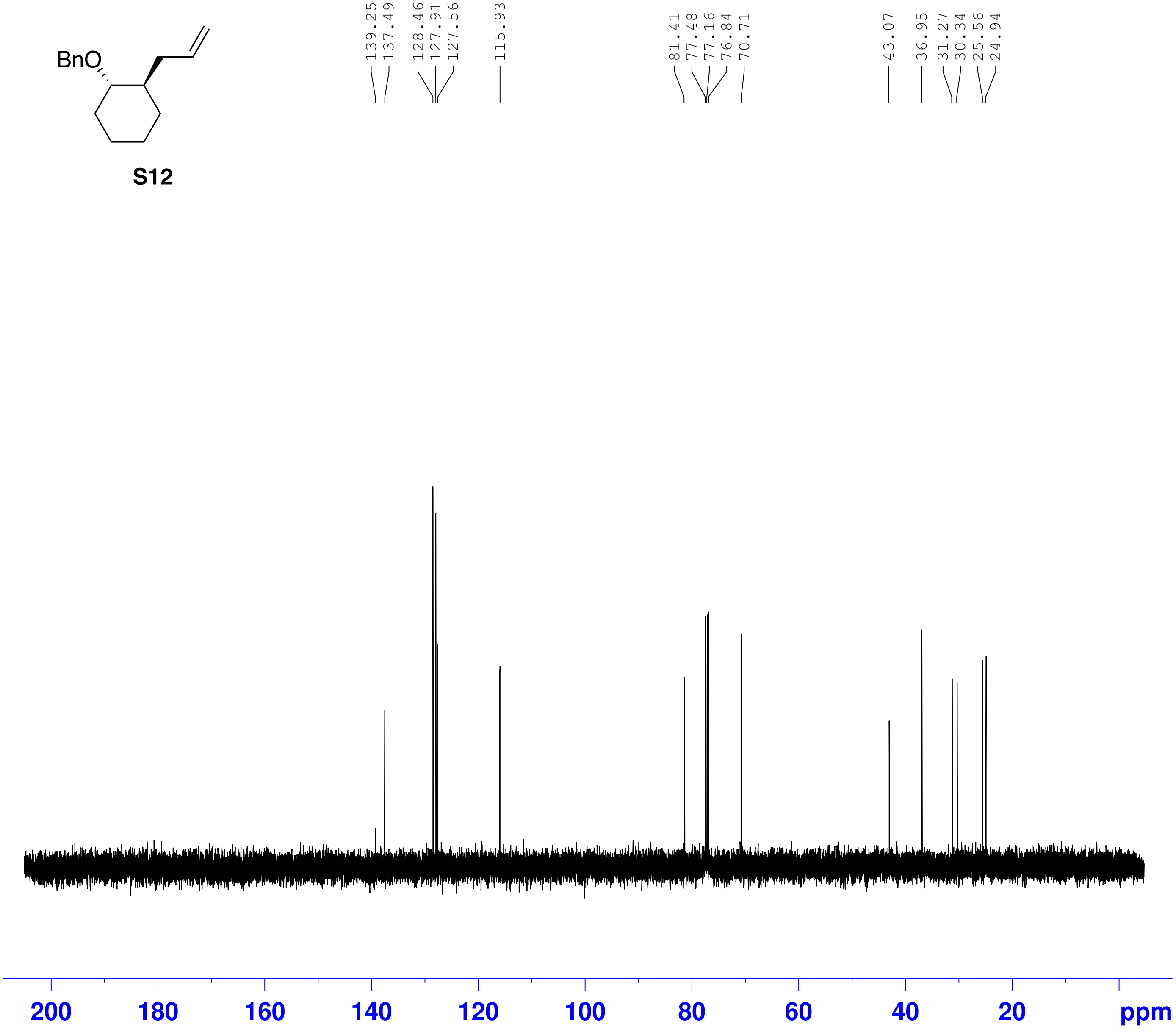
S12

```
Current Data Parameters
NAME              I-92-36
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120524
Time                20.42
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    256
DW                 60.400 usec
DE                   6.50 usec
TE                  298.5 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.75 usec
PL1                 -5.00 dB
PL1W          31.77312851 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300113 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



S12

```
Current Data Parameters
NAME              I-92-36
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120524
Time                20.48
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zgpg
TD                  65536
SOLVENT             CDCl3
NS                     69
DS                      4
SWH             21097.047 Hz
FIDRES           0.321915 Hz
AQ              1.5532532 sec
RG                 5792.6
DW                 23.700 usec
DE                   6.00 usec
TE                  299.1 K
D1             2.50000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.60 usec
PL1                 -4.00 dB
PL1W          25.23829460 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                 -5.00 dB
PL12                13.84 dB
PL13                13.84 dB
PL2W          31.77312851 W
PL12W          0.41501135 W
PL13W          0.41501135 W
SFO2          400.1316005 MHz

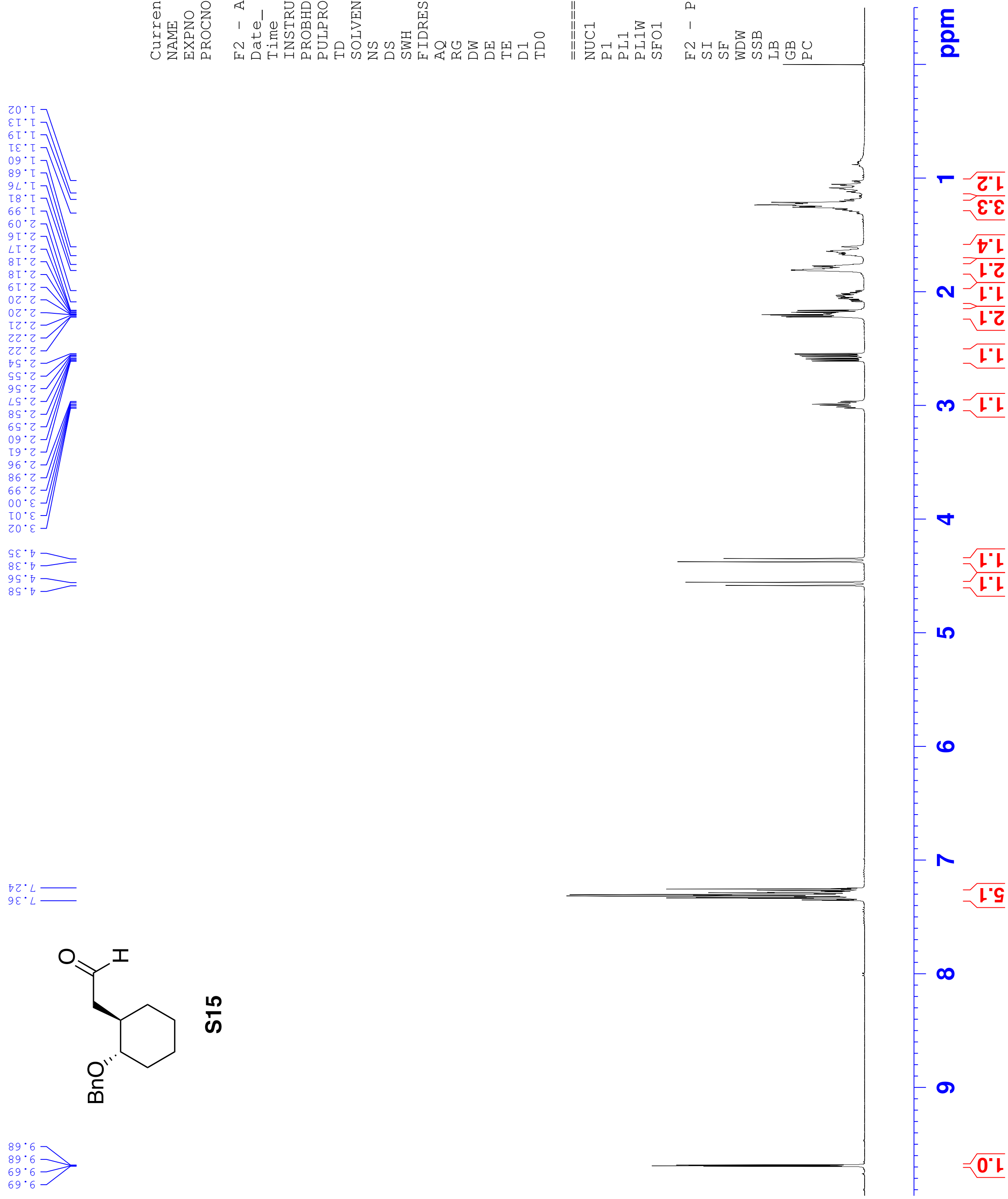
F2 - Processing parameters
SI                 131072
SF            100.6127548 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.40
```

```
Current Data Parameters
NAME          I-97-31
EXPNO               1
PROCNO              1

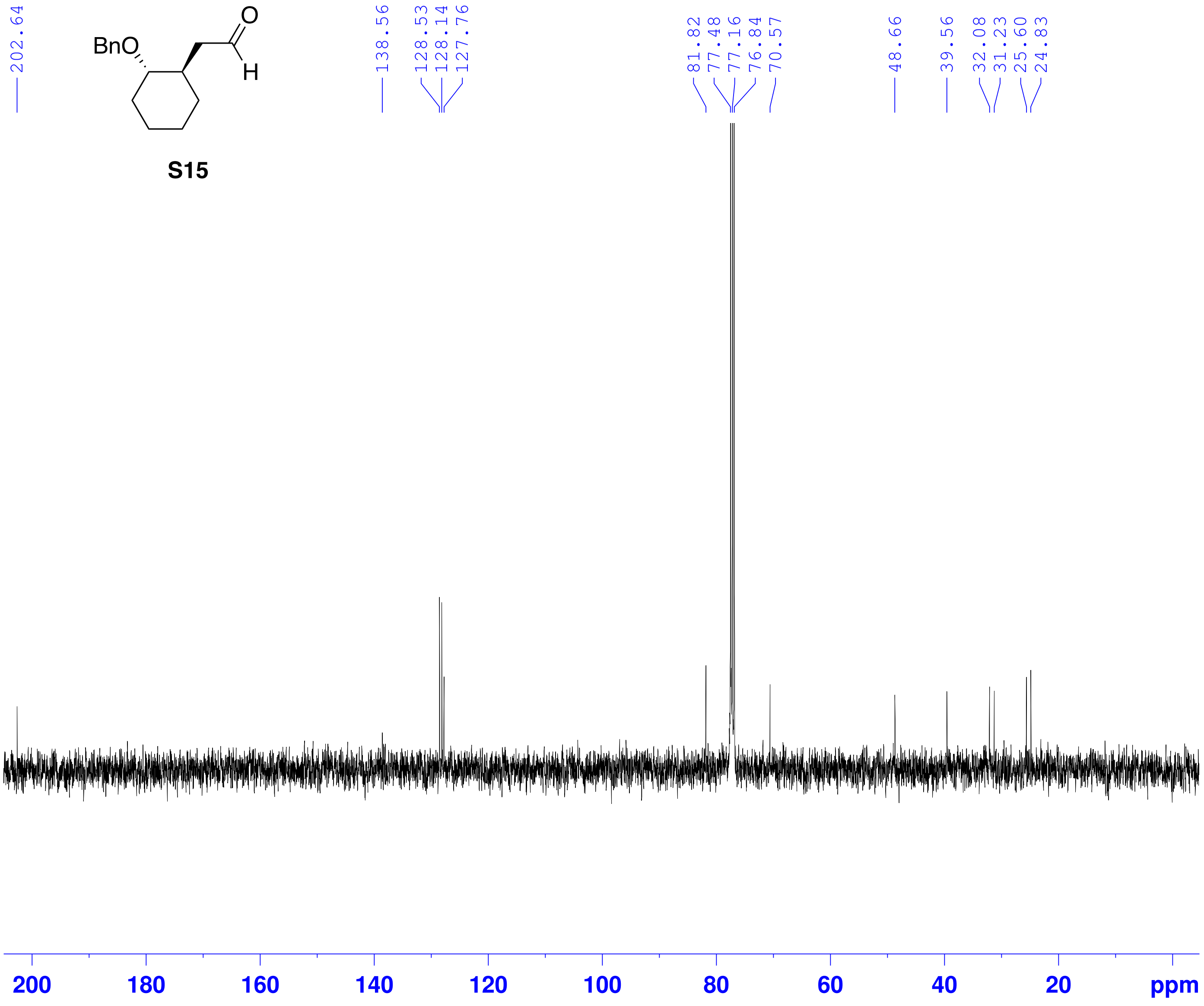
F2 - Acquisition Parameters
Date_          20120527
Time              18.03
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   13
DS                    2
SWH            8278.146 Hz
FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                 90.5
DW               60.400 usec
DE                 6.50 usec
TE                298.9 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                 7.75 usec
PL1               -5.00 dB
PL1W        31.77312851 W
SFO1        400.1324710 MHz

F2 - Processing parameters
SI                32768
SF          400.1300109 MHz
WDW                  no
SSB      0
LB       0 Hz
GB       0
PC                 1.00
```



S15



```
Current Data Parameters
NAME              I-97-31
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120527
Time                19.41
INSTRUM             spect
PROBHD    5 mm BBO BB-1H
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    128
DS                      4
SWH            23980.814 Hz
FIDRES          0.365918 Hz
AQ             1.3664756 sec
RG               20642.5
DW                20.850 usec
DE                  6.50 usec
TE                 299.5 K
D1            2.50000000 sec
D11           0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                   6.60 usec
PL1                 -4.00 dB
PL1W          25.23829460 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PL2                 -5.00 dB
PL12                13.84 dB
PL13                13.84 dB
PL2W          31.77312851 W
PL12W          0.41501135 W
PL13W          0.41501135 W
SFO2          400.1316005 MHz

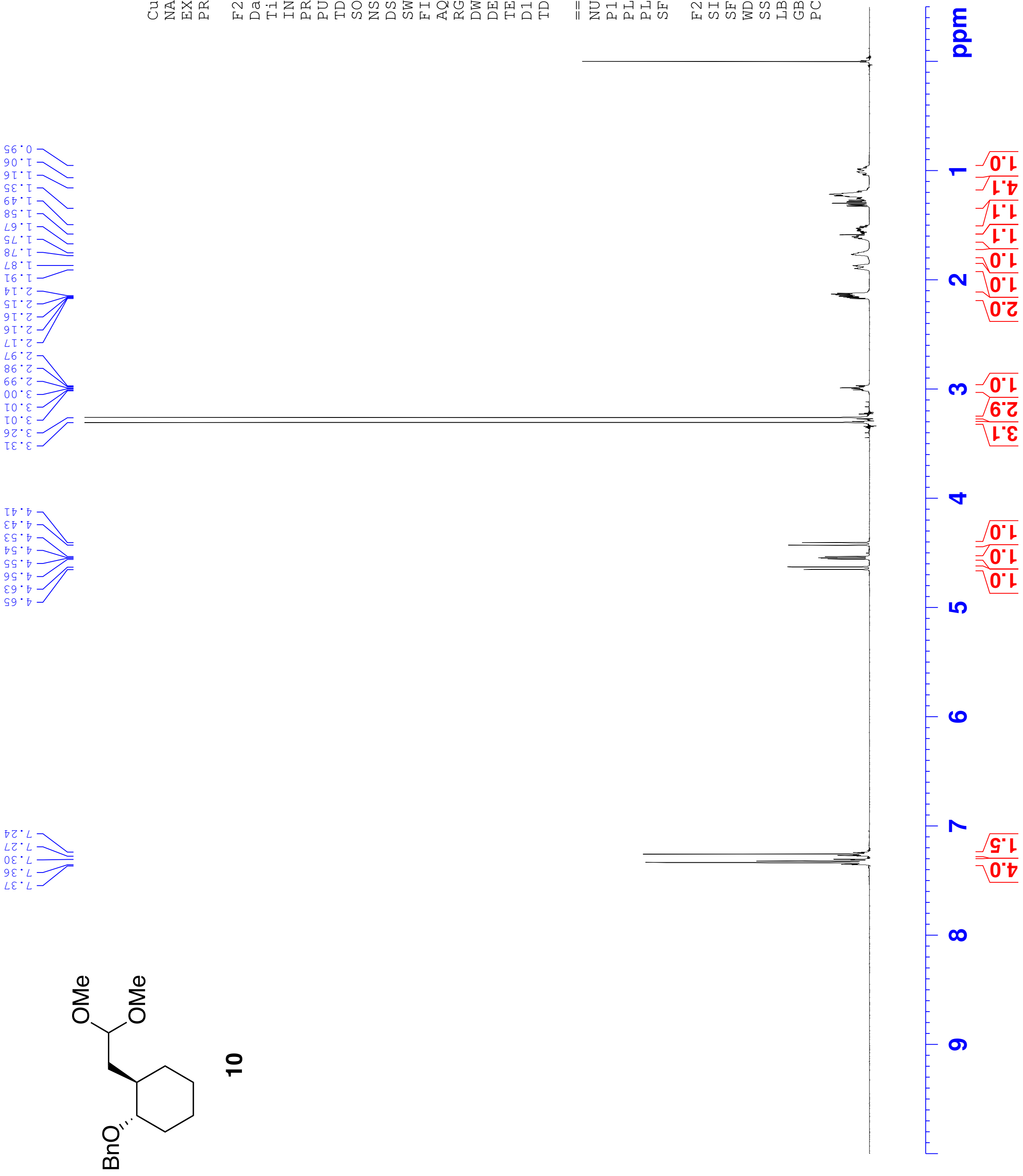
F2 - Processing parameters
SI                  32768
SF            100.6127537 MHz
WDW                    EM
SSB      0
LB                   2.00 Hz
GB       0
PC                   1.40
```

```
Current Data Parameters
NAME               III-4-P
EXPNO                   12
PROCNO                   1

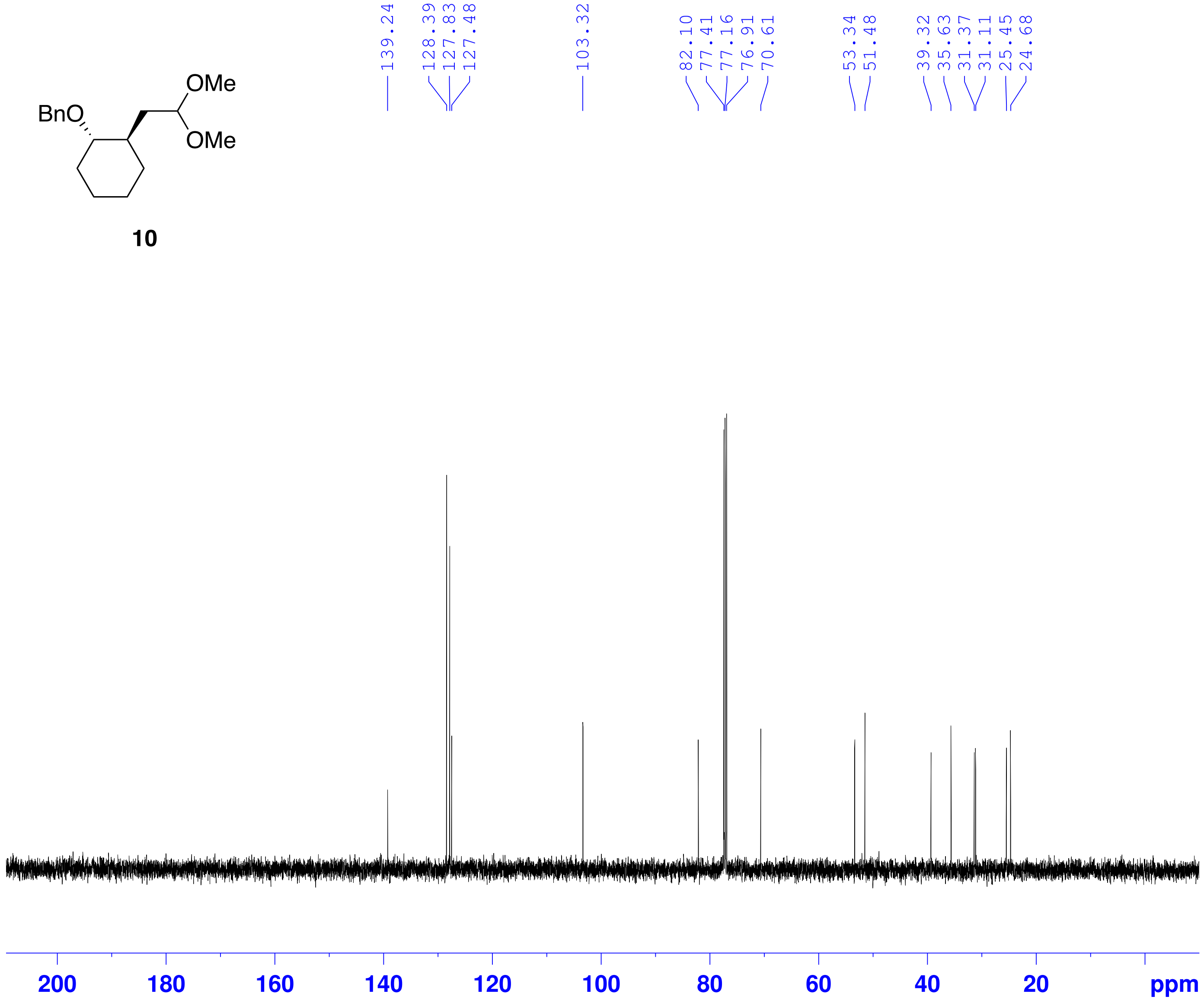
F2 - Acquisition Parameters
Date_             20130725
Time                 11.02
INSTRUM              spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ              3.1719923 sec
RG                   228.1
DW                  48.400 usec
DE                    6.50 usec
TE                   298.2 K
D1             2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    9.72 usec
PL1                  -3.00 dB
PL1W           37.58904266 W
SFO1           500.2020889 MHz

F2 - Processing parameters
SI                   32768
SF             500.1990157 MHz
WDW                     no
SSB      0
LB       0 Hz
GB       0
PC                    1.00
```



10



10

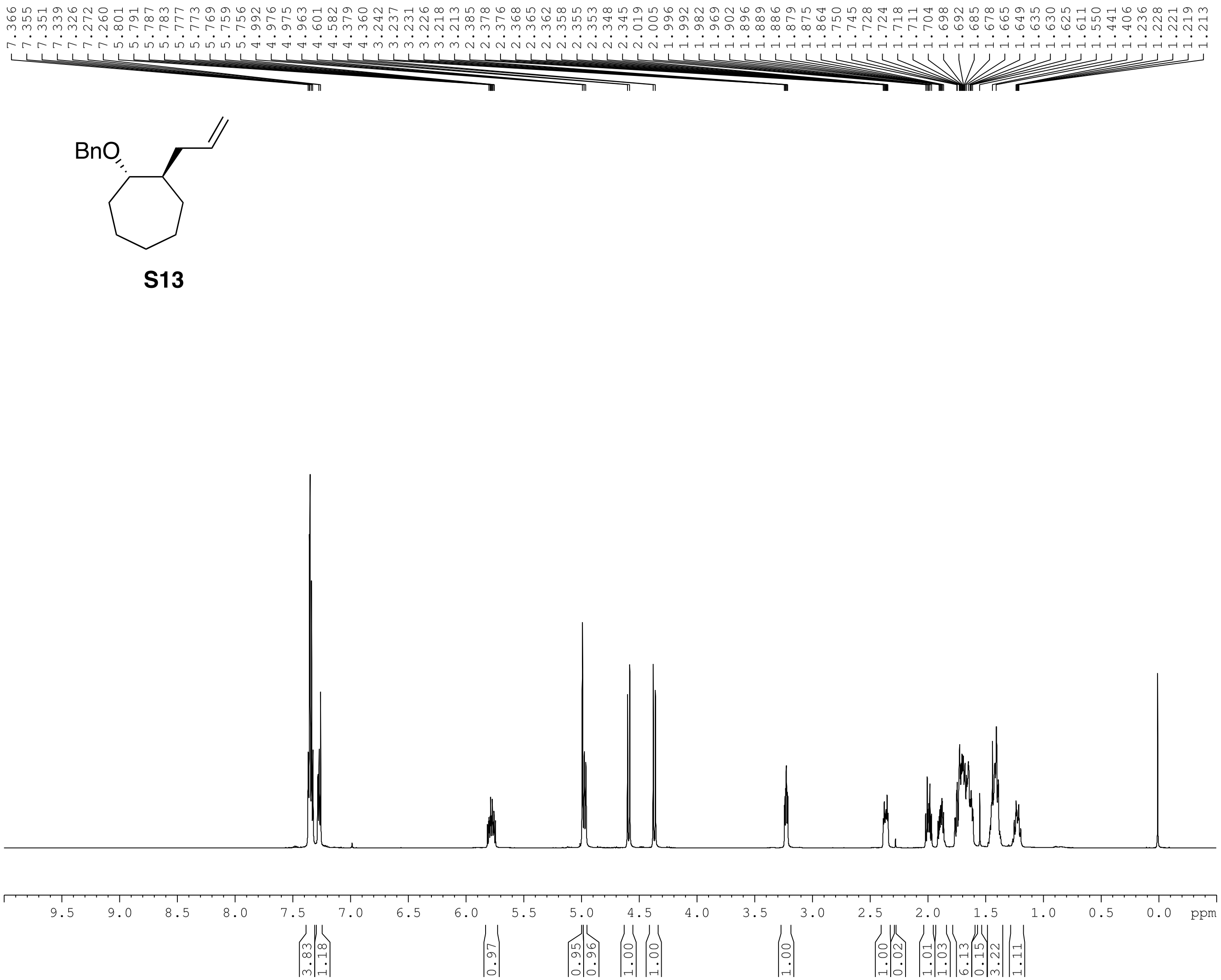
```
Current Data Parameters
NAME              III-4-P
EXPNO                  11
PROCNO                  1

F2 - Acquisition Parameters
Date_           20130619
Time               12.45
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   64
DS                    0
SWH          30030.029 Hz
FIDRES        0.458222 Hz
AQ           1.0912244 sec
RG                 8192
DW               16.650 usec
DE                 6.50 usec
TE                298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 9.75 usec
PL1                2.00 dB
PL1W        49.29017639 W
SFO1        125.7877161 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -3.00 dB
PL12              13.50 dB
PL13              13.50 dB
PL2W        37.58904266 W
PL12W        0.84151381 W
PL13W        0.84151381 W
SFO2        500.2010008 MHz

F2 - Processing parameters
SI                32768
SF          125.7751239 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```


S13

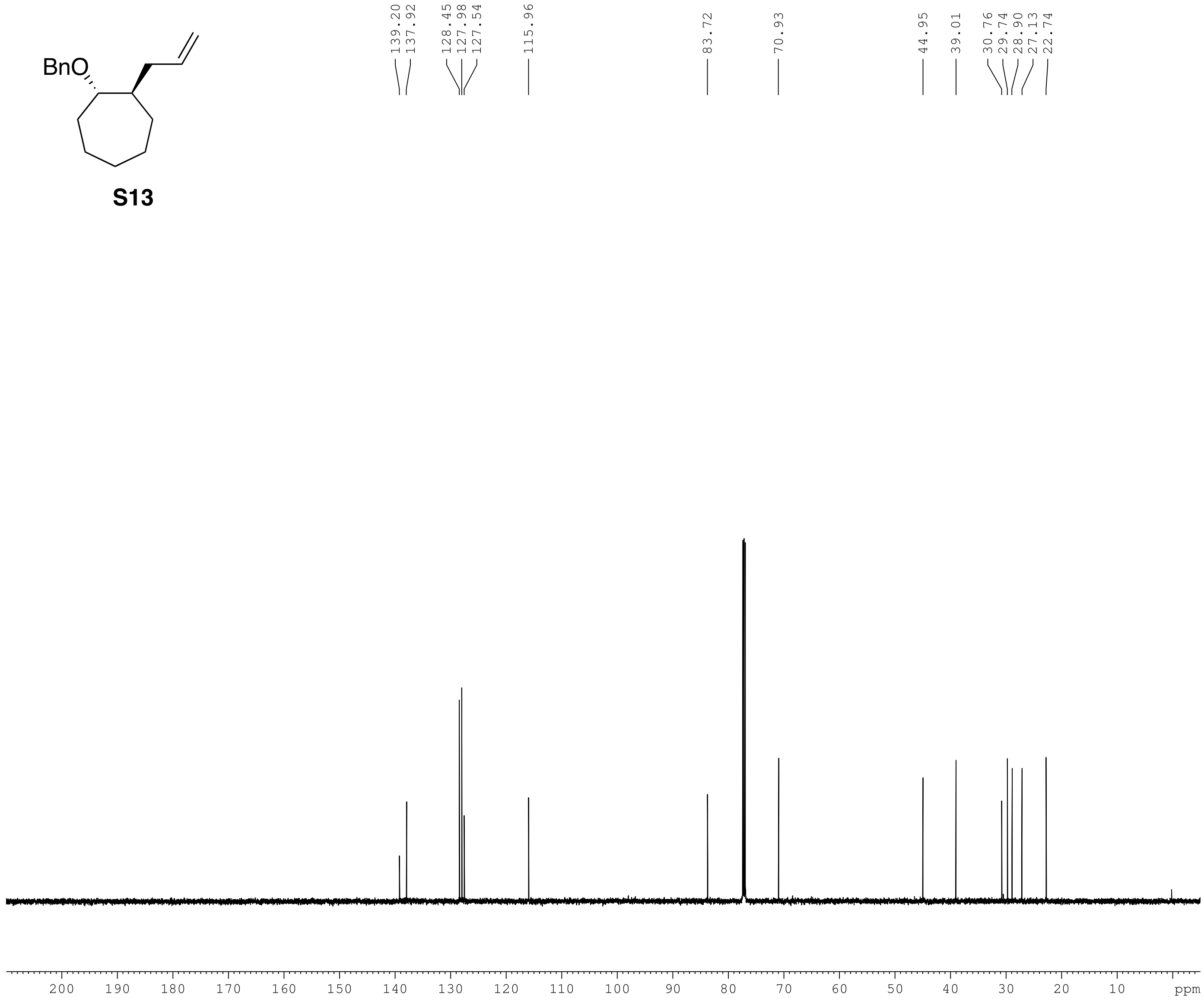
```
Current Data Parameters
NAME      AG-1-112-P_pub
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130325
Time               17.21
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                 59.15
DW                40.533 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 11.00 usec
PLW1         26.50000000 W
SFO1         600.1937064 MHz

F2 - Processing parameters
SI                 65536
SF           600.1900150 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

S13



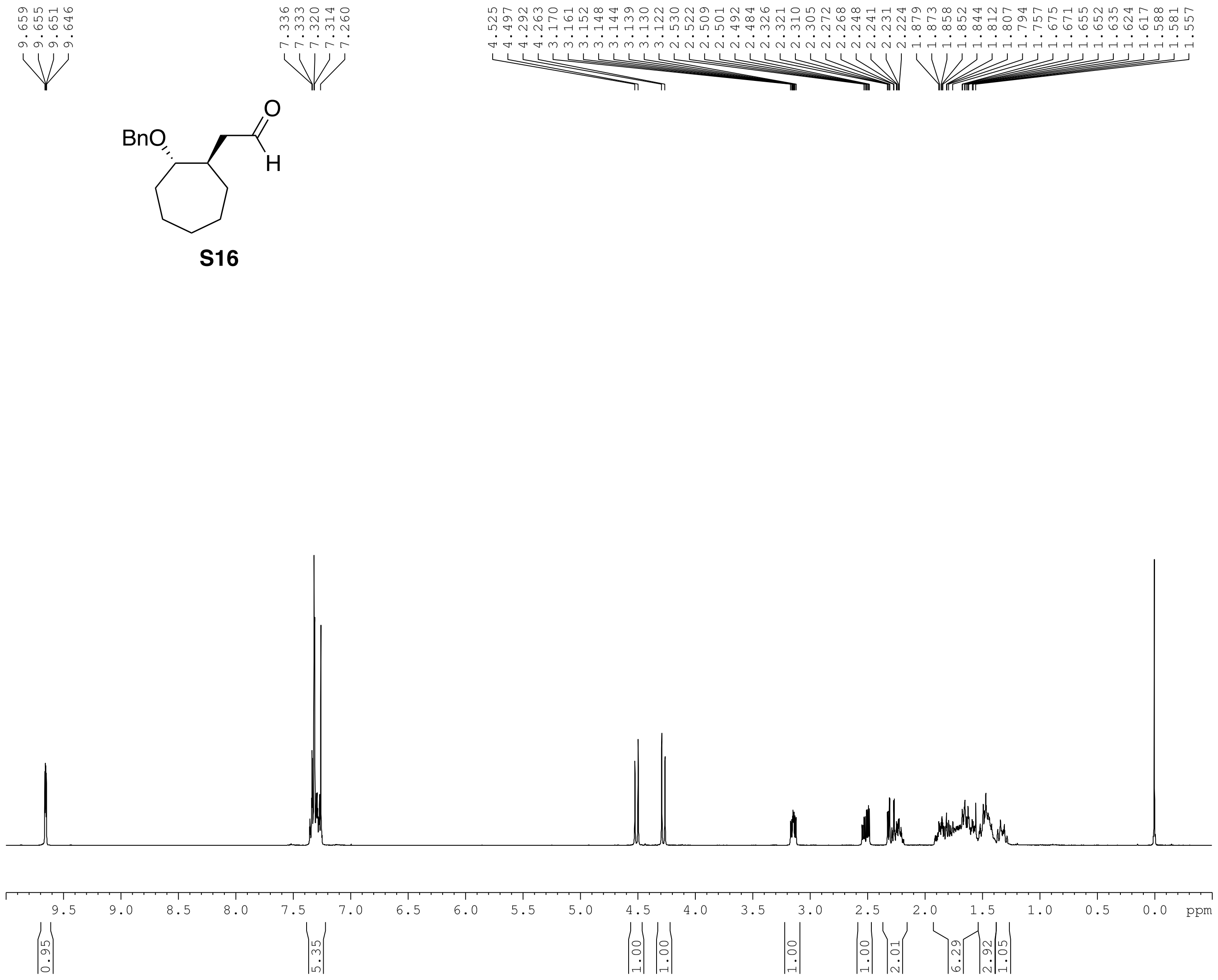
```
Current Data Parameters
NAME     AG-1-112-P-C13_pub
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130325
Time                  17.27
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      137
DS                        4
SWH              36057.691 Hz
FIDRES            0.550197 Hz
AQ               0.9088159 sec
RG                   184.65
DW                   13.867 usec
DE                     6.50 usec
TE                    298.2 K
D1               2.50000000 sec
D11              0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    10.65 usec
PLW1         104.00000000 W
SFO1          150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                 70.00 usec
PLW2          26.50000000 W
PLW12          0.65438998 W
PLW13          0.32065001 W
SFO2          600.1924008 MHz

F2 - Processing parameters
SI                    32768
SF            150.9178761 MHz
WDW                      EM
SSB      0
LB                     1.00 Hz
GB       0
PC                     1.40
```



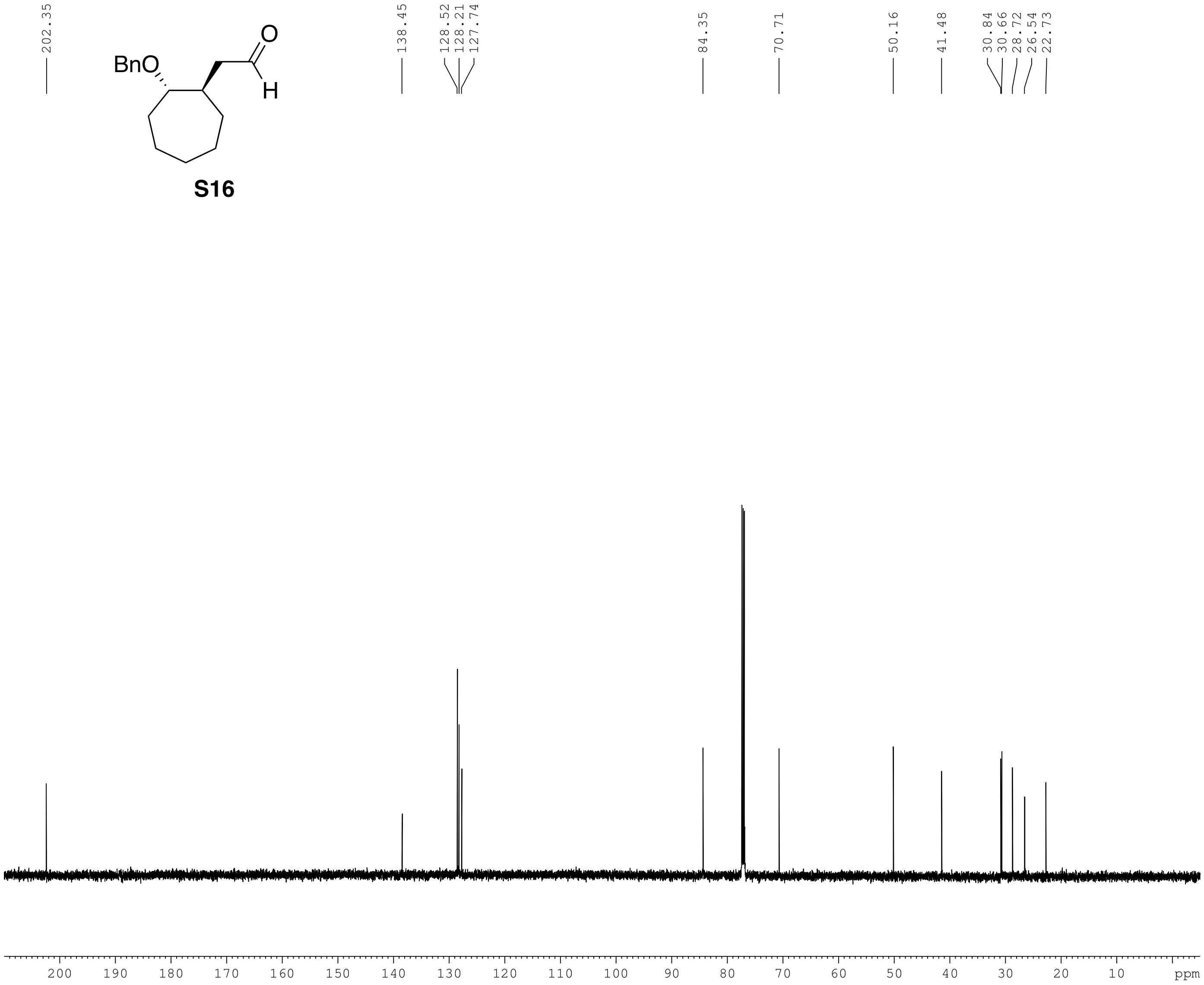
S16

```
Current Data Parameters
NAME          AG-1-159-P1
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130416
Time                19.04
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                  228.1
DW                 60.400 usec
DE                   6.50 usec
TE                  298.5 K
D1            2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.75 usec
PL1                 -5.00 dB
PL1W          31.77312851 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300098 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S16

```
Current Data Parameters
NAME     AG-1-159-P_C13
EXPNO                 1
PROCNO                1

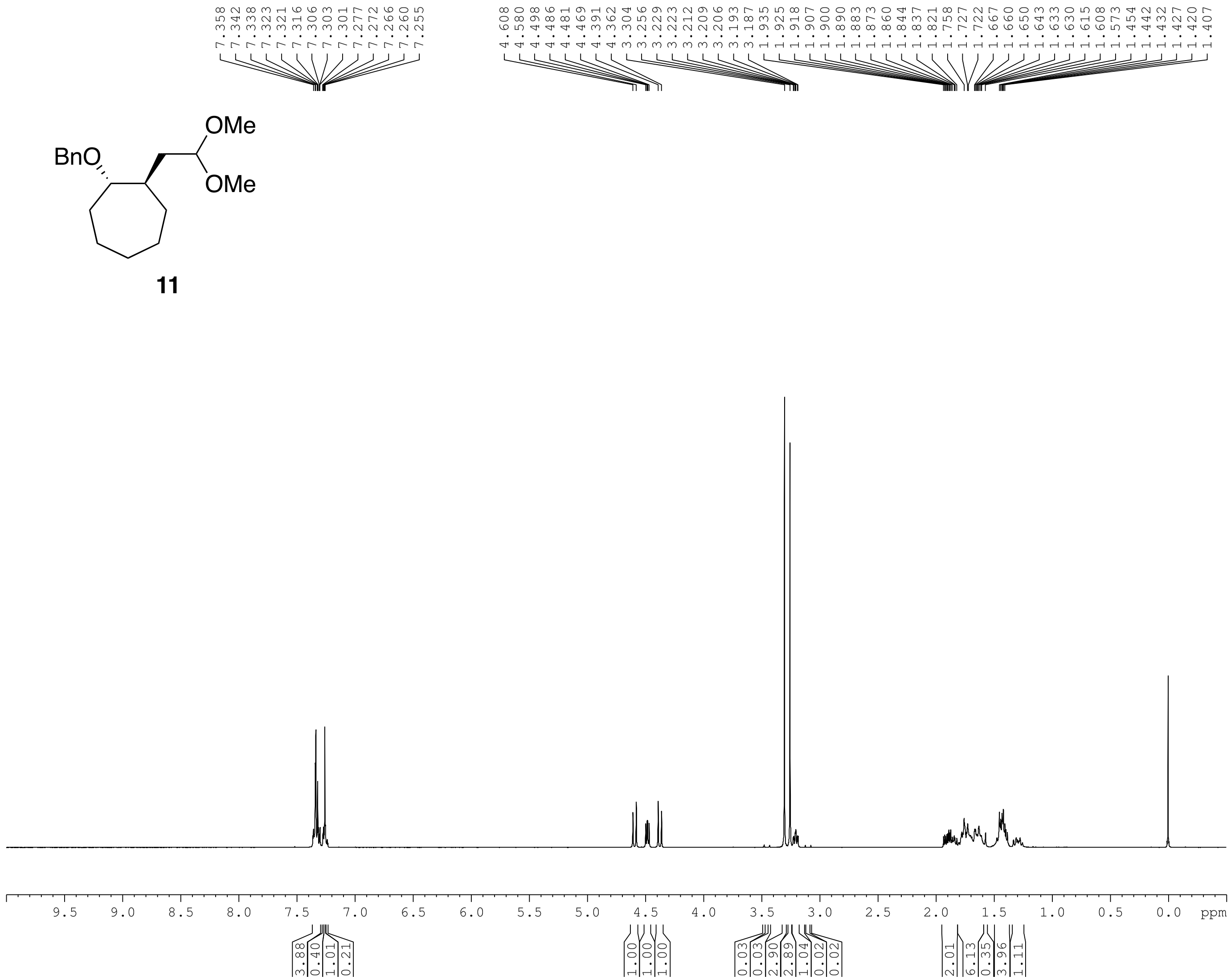
F2 - Acquisition Parameters
Date_          20130623
Time              12.51
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  173
DS                    4
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG               184.65
DW               13.867 usec
DE                 6.50 usec
TE                298.0 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PLW1       106.00000000 W
SFO1        150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                32768
SF          150.9178772 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

11

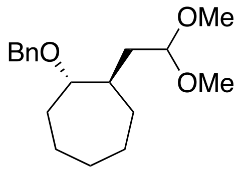


```
Current Data Parameters
NAME             AG-1-164
EXPNO                   1
PROCNO                  1

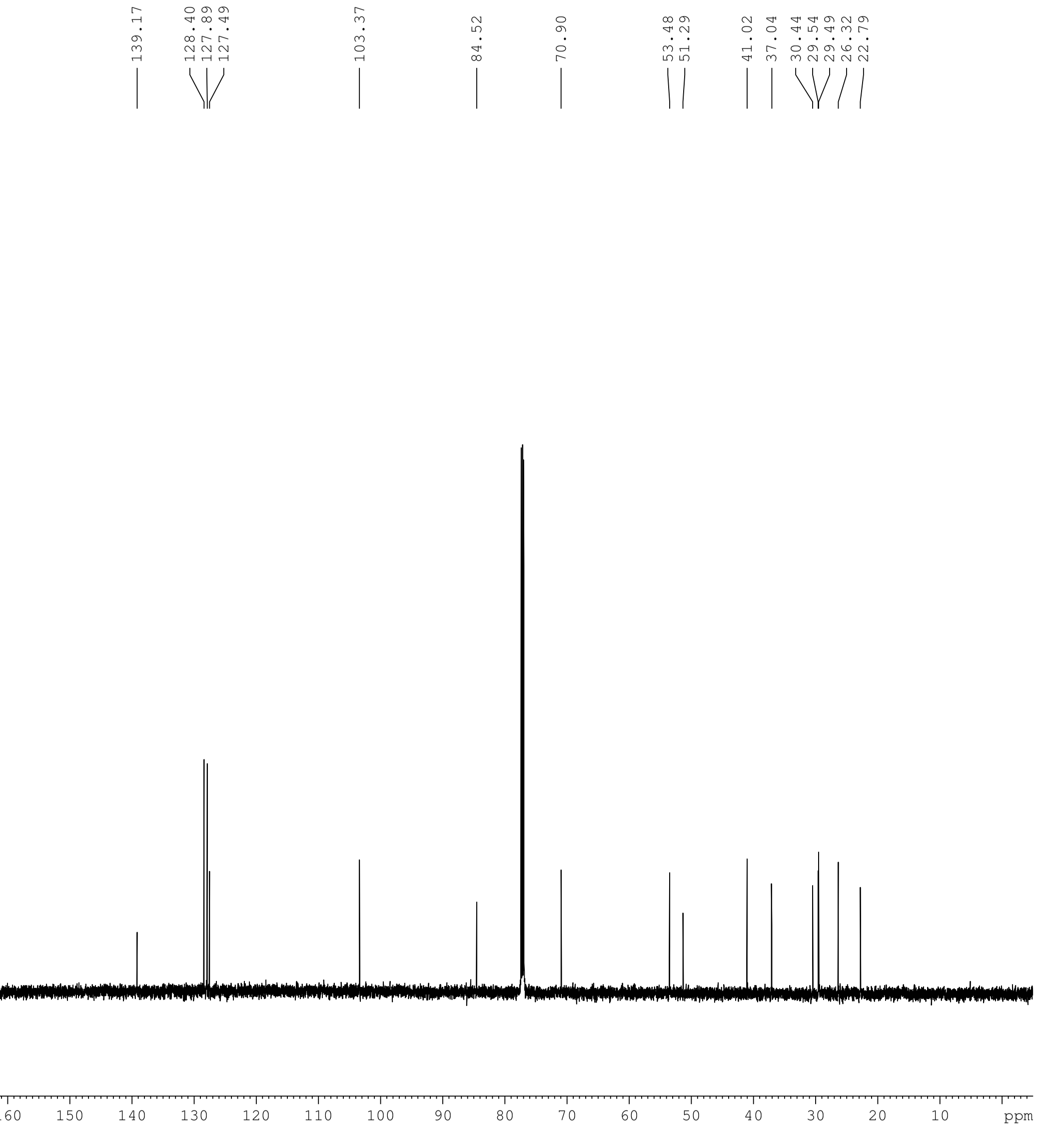
F2 - Acquisition Parameters
Date_            20130419
Time                19.26
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9584243 sec
RG                    181
DW                 60.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.75 usec
PL1                 -5.00 dB
PL1W          31.77312851 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300098 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



11



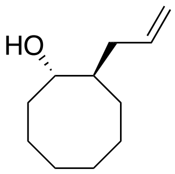
```
Current Data Parameters
NAME       AG-1-164_C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130623
Time              13.16
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  162
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9088159 sec
RG               184.65
DW               13.867 usec
DE                 6.50 usec
TE                298.0 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                   1

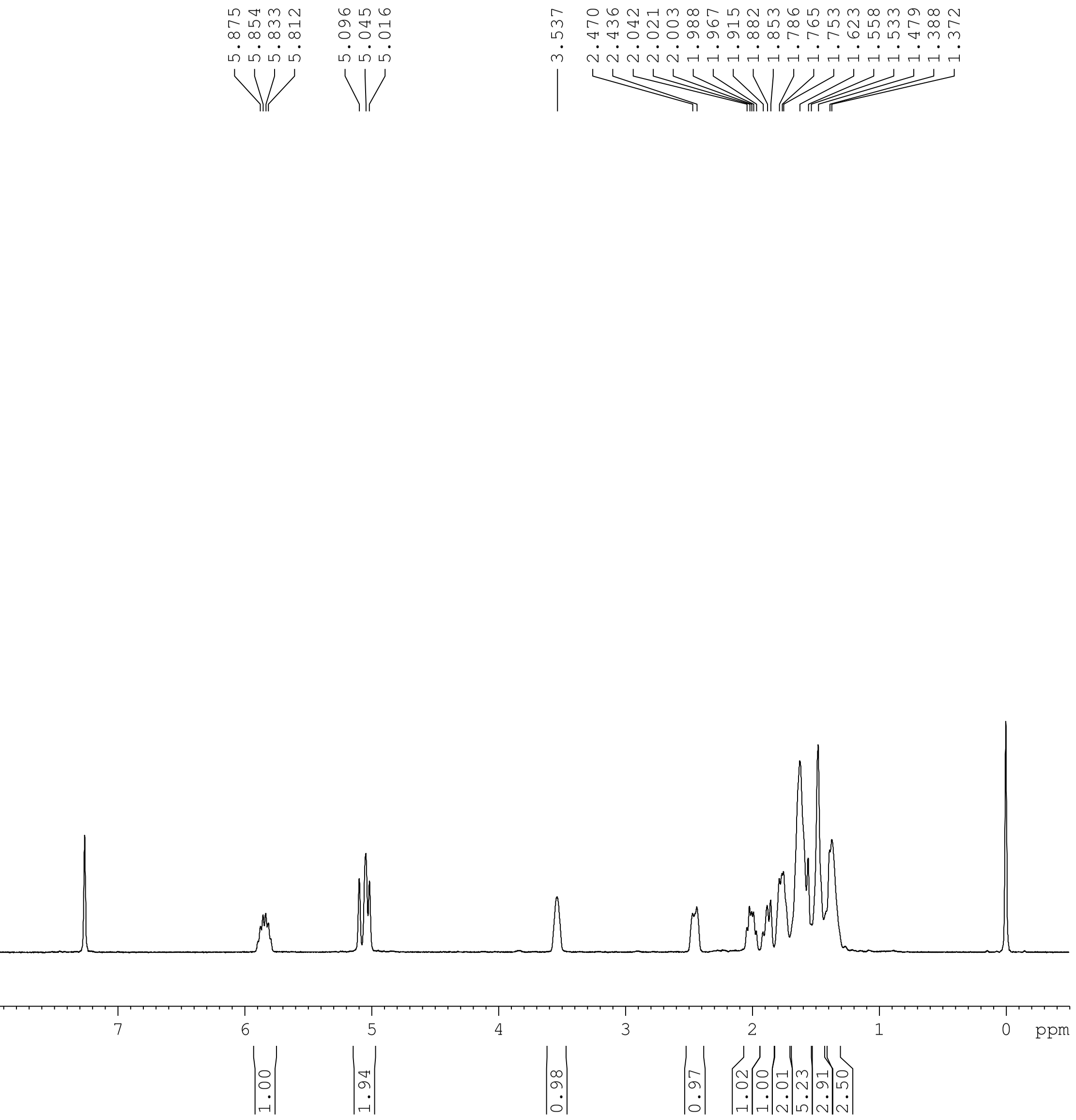
======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PLW1       106.00000000 W
SFO1        150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PLW2         9.30000019 W
PLW12        0.18190999 W
PLW13        0.08913500 W
SFO2        600.1924008 MHz

F2 - Processing parameters
SI                32768
SF          150.9178761 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



S10

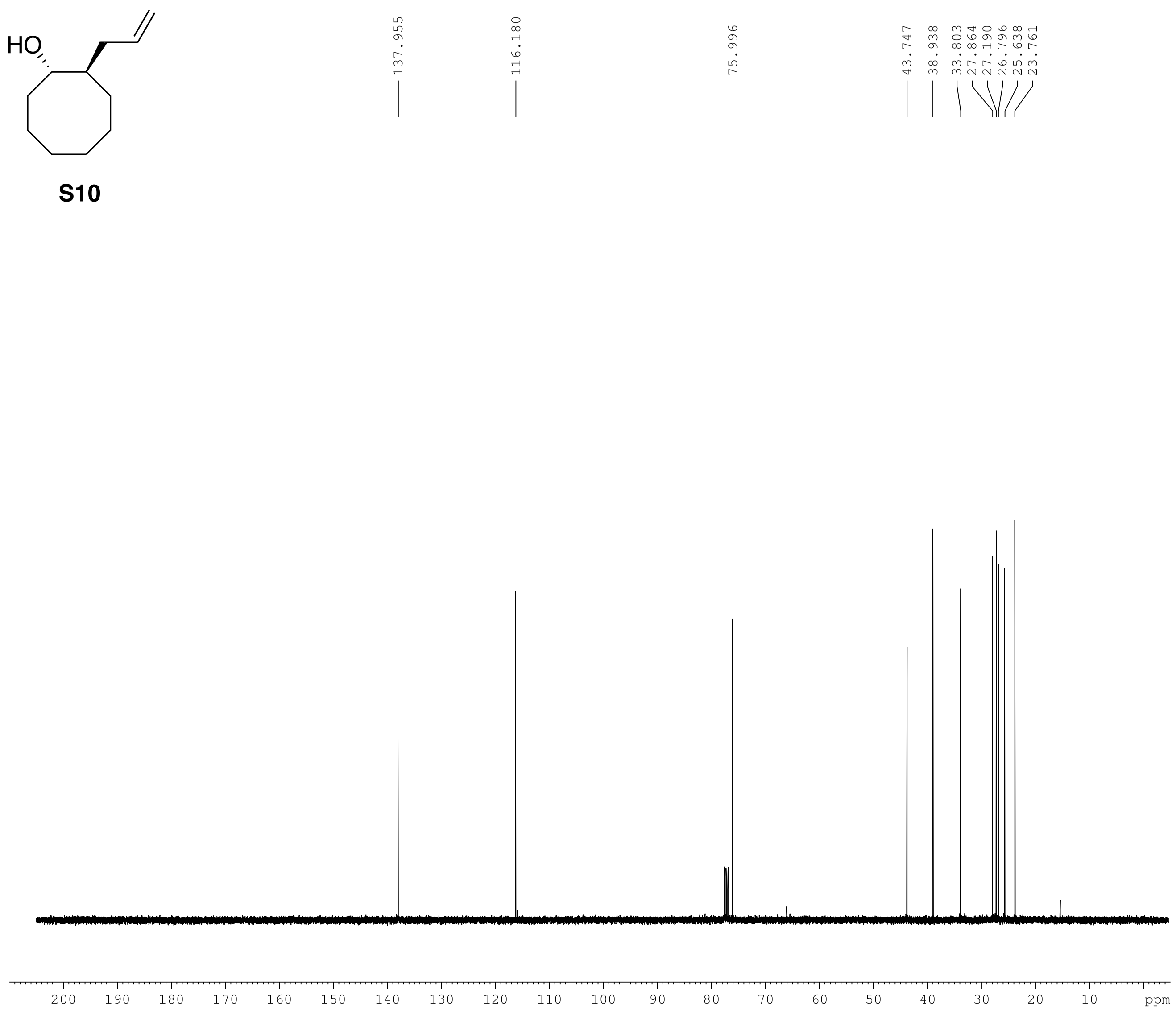


```
Current Data Parameters
NAME           AG-1-65-C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130103
Time               12.02
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                   256
DW                60.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.75 usec
PL1                -5.00 dB
PL1W         31.77312851 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300105 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



S10

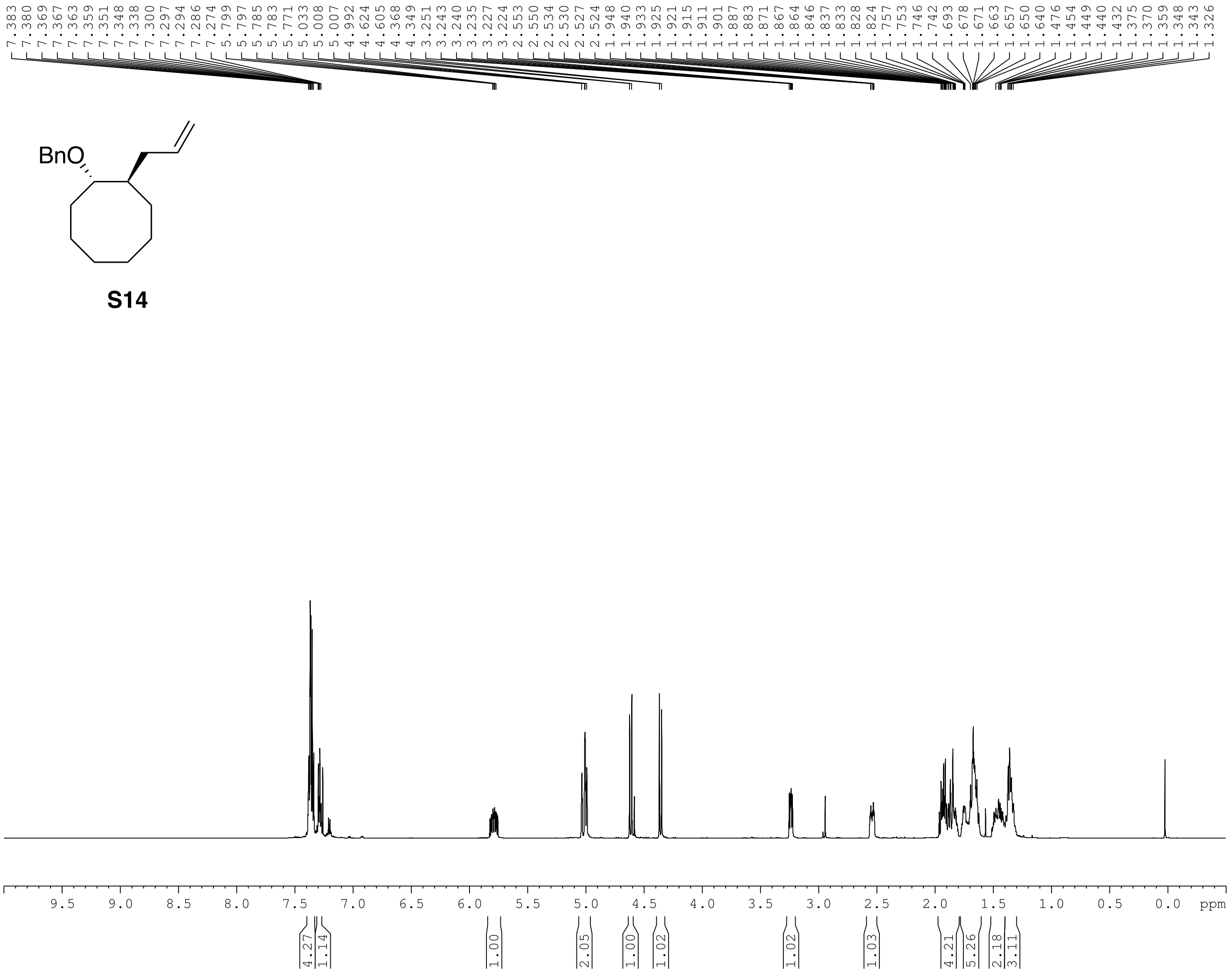
```
Current Data Parameters
NAME     AG-1-65-C13-Iv
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130103
Time              19.58
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG            zgpg
TD                65536
SOLVENT           CDCl3
NS                   73
DS                    4
SWH           21097.047 Hz
FIDRES         0.321915 Hz
AQ            1.5532532 sec
RG              20642.5
DW               23.700 usec
DE                 6.00 usec
TE                298.2 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                 6.60 usec
PL1               -4.00 dB
PL1W        25.23829460 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PL2               -5.00 dB
PL12              13.84 dB
PL13              13.84 dB
PL2W        31.77312851 W
PL12W        0.41501135 W
PL13W        0.41501135 W
SFO2        400.1316005 MHz

F2 - Processing parameters
SI               131072
SF          100.6127573 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.40
```



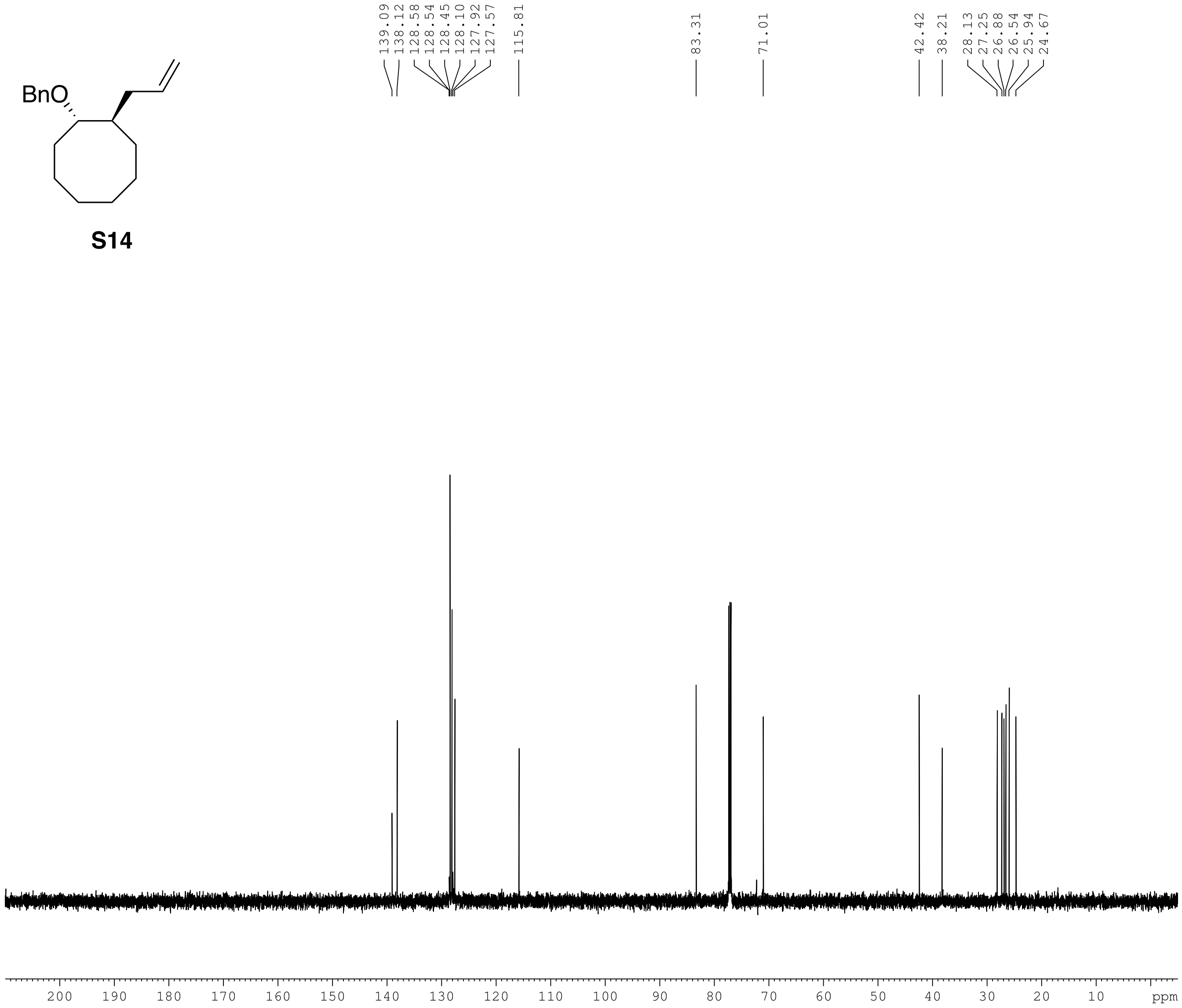
S14

```
Current Data Parameters
NAME     AG-1-133-P_11814
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140118
Time                16.14
INSTRUM             spect
PROBHD   5 mm PAQXI 1H/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                  33.59
DW                 40.533 use
DE                   6.50 use
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 =======
SFO1         600.1937064 MHz
NUC1                   1H
P1                   9.79 use
PLW1           9.30000019 W

F2 - Processing parameters
SI                  65536
SF            600.1900144 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```

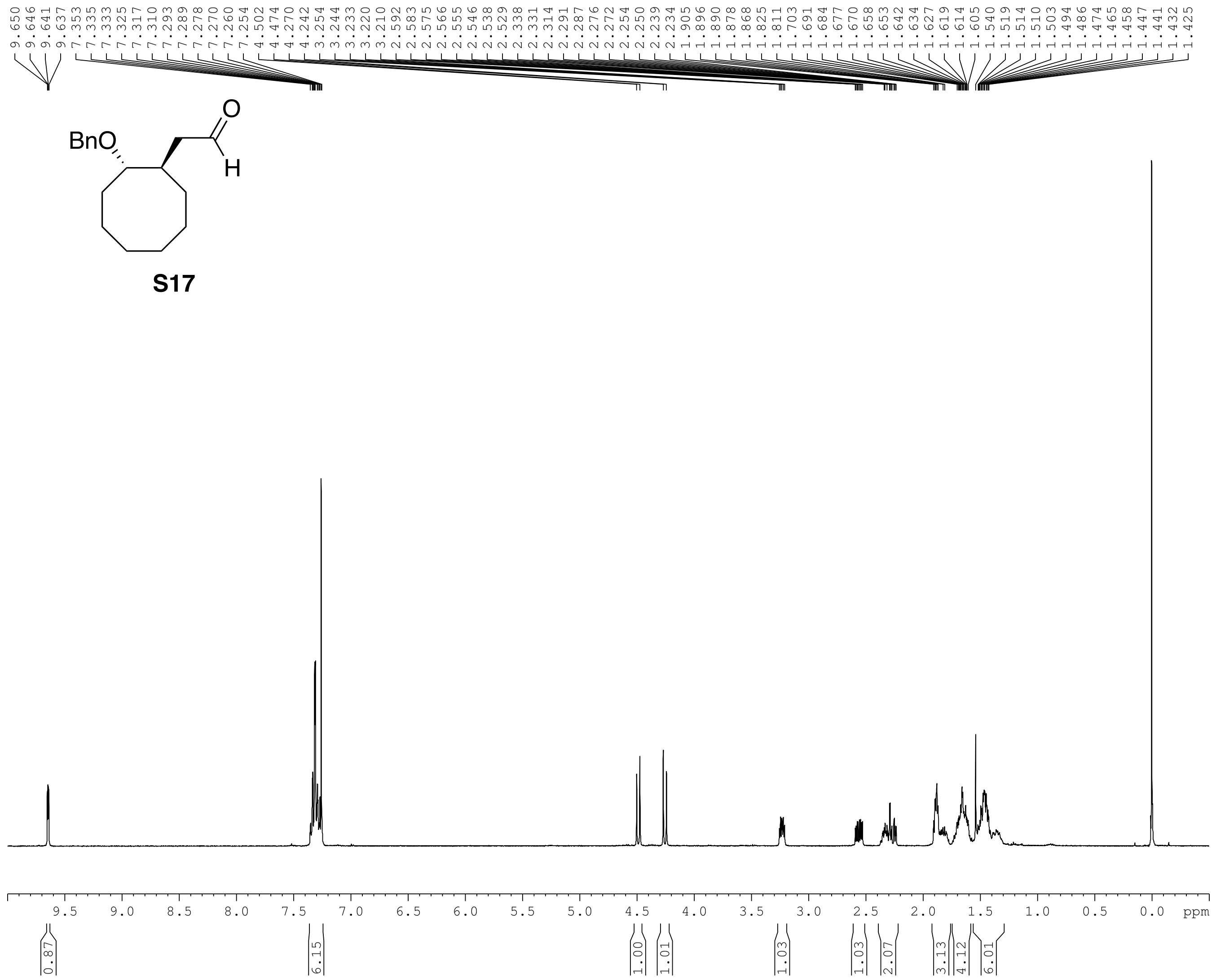


S14

```
Current Data Parameters
NAME     AG-1-133-P_C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140118
Time              16.29
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 371
DS                   4
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG              184.65
DW              13.867 usec
DE                6.50 usec
TE               298.1 K
D1          2.50000000 sec
d11         0.03000000 sec
DELTA       2.40000010 sec
TD0                  1
NUC1               13C
P1               15.00 usec
PLW1      106.00000000 W
SFO1       150.9329866 MHz
CPDPRG2
NUC2                1H
PLW2        9.30000019 W
PLW12       0.18190999 W
PLW13       0.08913500 W
SFO2       600.1924008 MHz

F2 - Processing parameters
SI               32768
SF         150.9178793 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```



S17

```
Current Data Parameters
NAME           AG-1-63-P
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130104
Time               16.58
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 322.5
DW                60.400 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  7.75 usec
PL1                -5.00 dB
PL1W         31.77312851 W
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300100 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

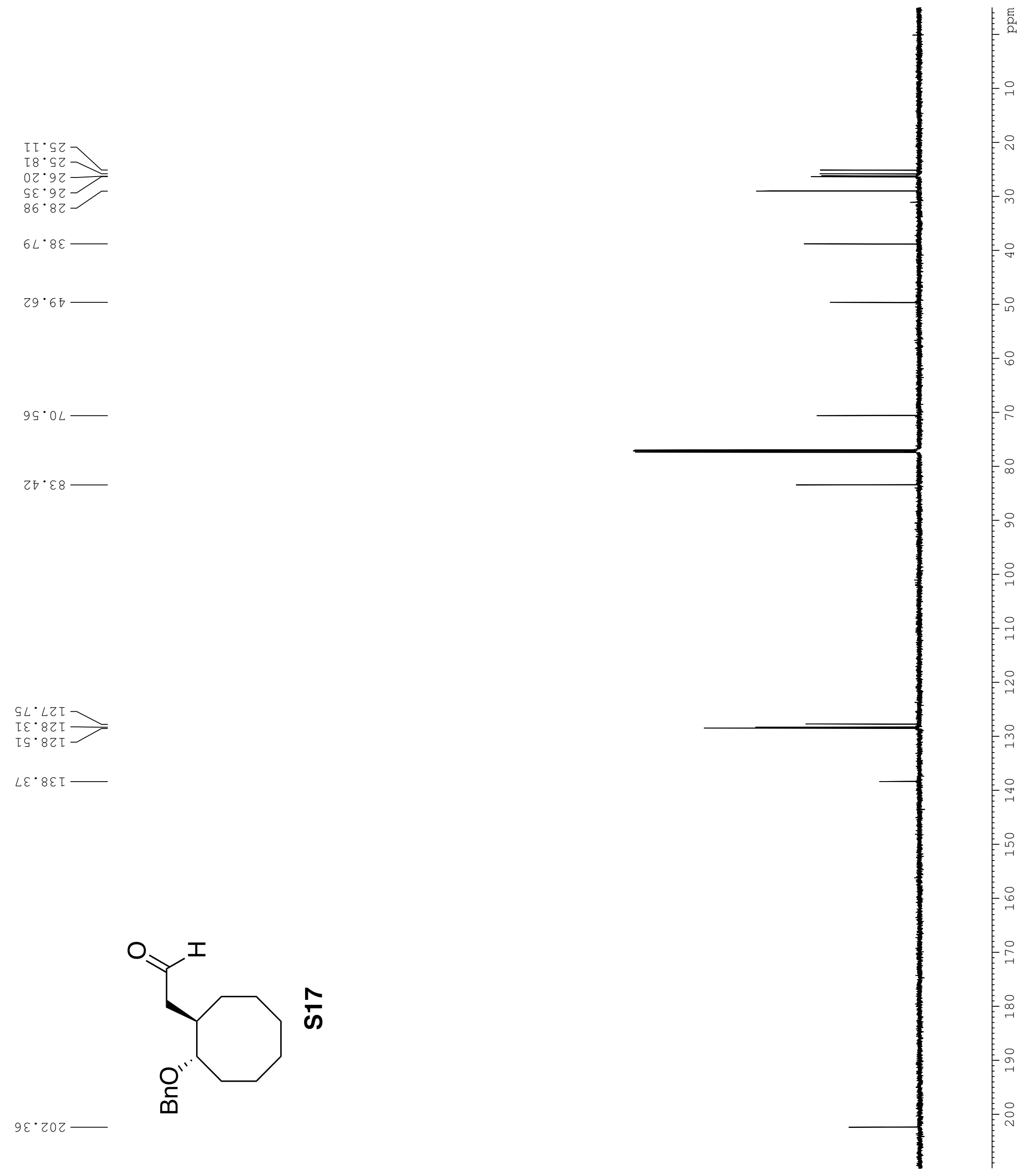
```
Current Data Parameters
NAME        AG-1-63-P-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20130104
Time              20.04
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 102
DS                   4
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG              184.65
DW              13.867 usec
DE                6.50 usec
TE               298.2 K
D1          2.50000000 sec
D11         0.03000000 sec
TD0                  1

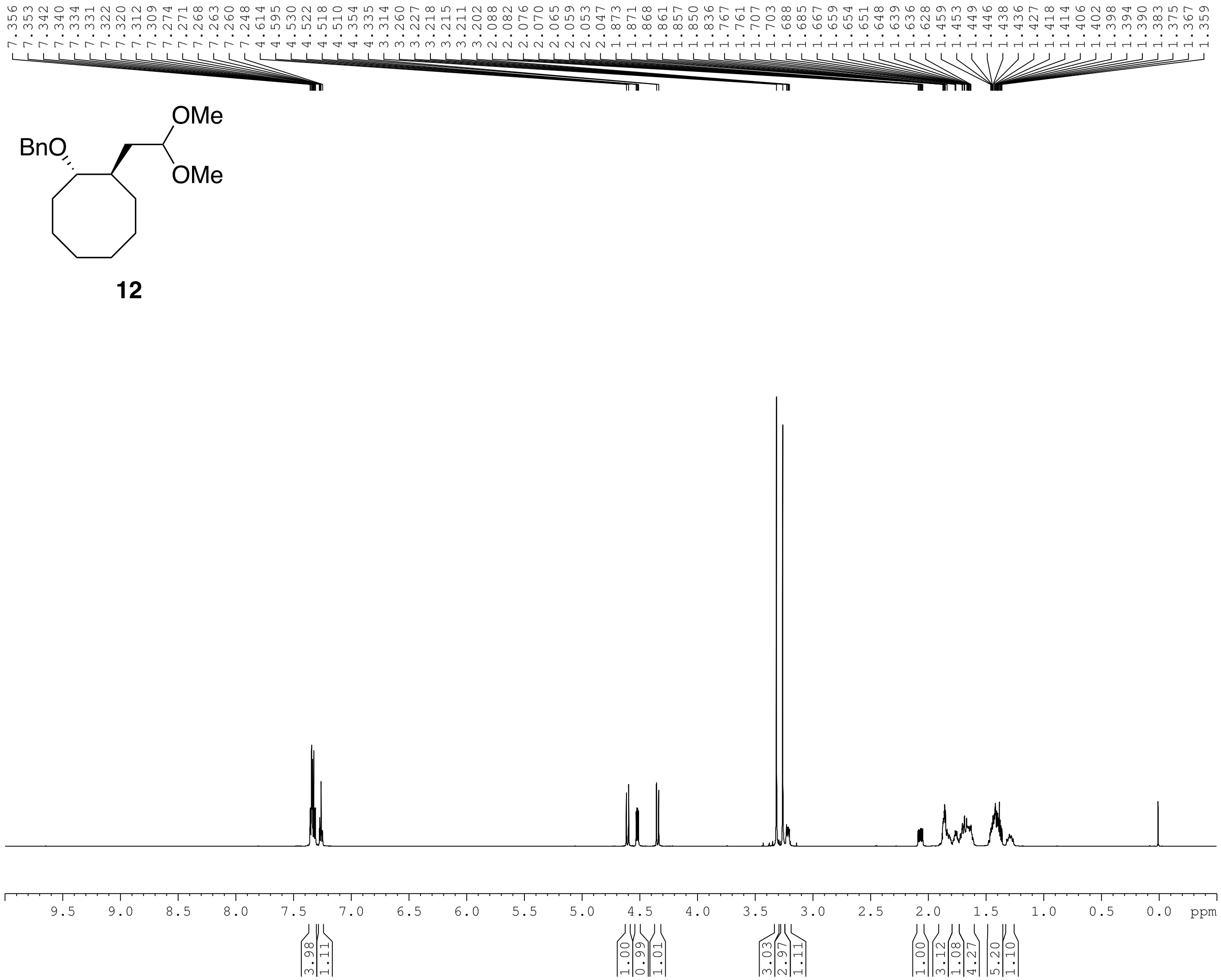
======== CHANNEL f1 ========
NUC1                13C
P1                10.65 usec
PLW1       104.00000000 W
SFO1        150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PLW2        26.50000000 W
PLW12        0.65438998 W
PLW13        0.32065001 W
SFO2        600.1924008 MHz

F2 - Processing parameters
SI                32768
SF          150.9178772 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



S17



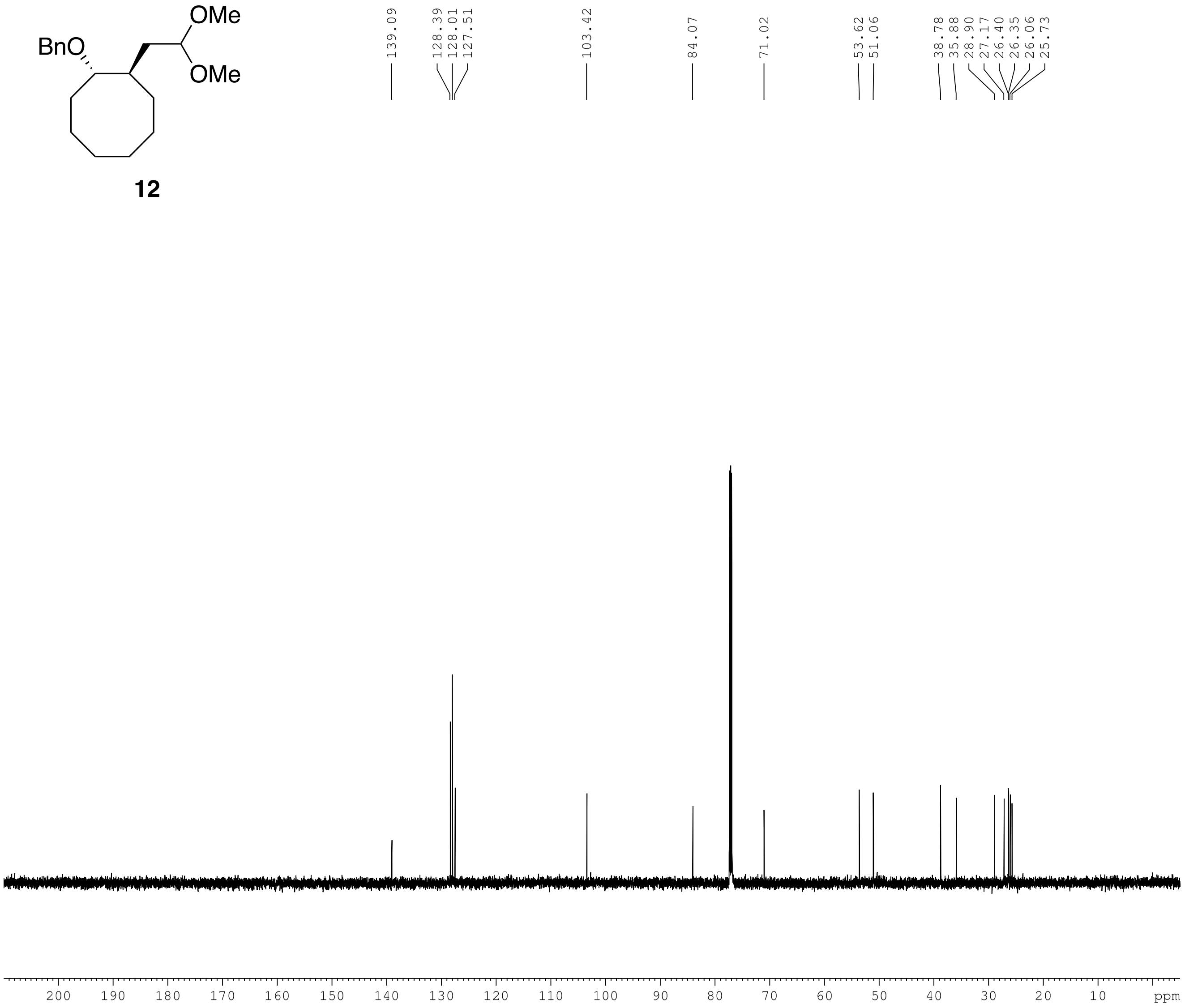
12

```
Current Data Parameters
NAME     AG-1-166_11814
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140118
Time              16.53
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                33.59
DW               40.533 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1937064 MHz
NUC1                 1H
P1                 9.79 usec
PLW1         9.30000019 W

F2 - Processing parameters
SI                65536
SF          600.1900144 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



12

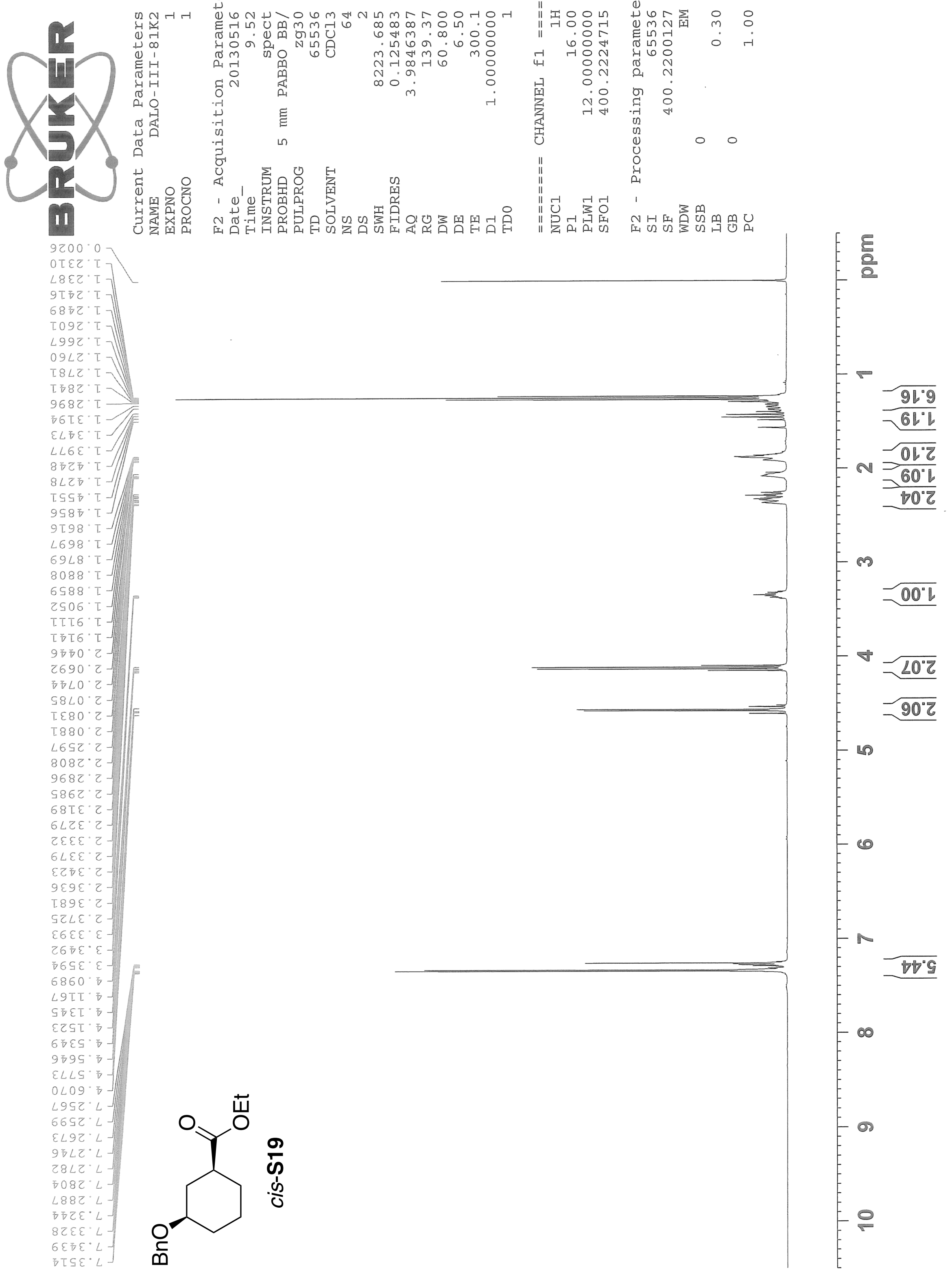
```
Current Data Parameters
NAME     AG-1-166ii_C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130623
Time              21.01
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  142
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9088159 sec
RG               184.65
DW               13.867 usec
DE                 6.50 usec
TE                298.0 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PLW1       106.00000000 W
SFO1        150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             70.00 usec
PLW2         9.30000019 W
PLW12        0.18190999 W
PLW13        0.08913500 W
SFO2        600.1924008 MHz

F2 - Processing parameters
SI                32768
SF          150.9178761 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



cis-**S19**

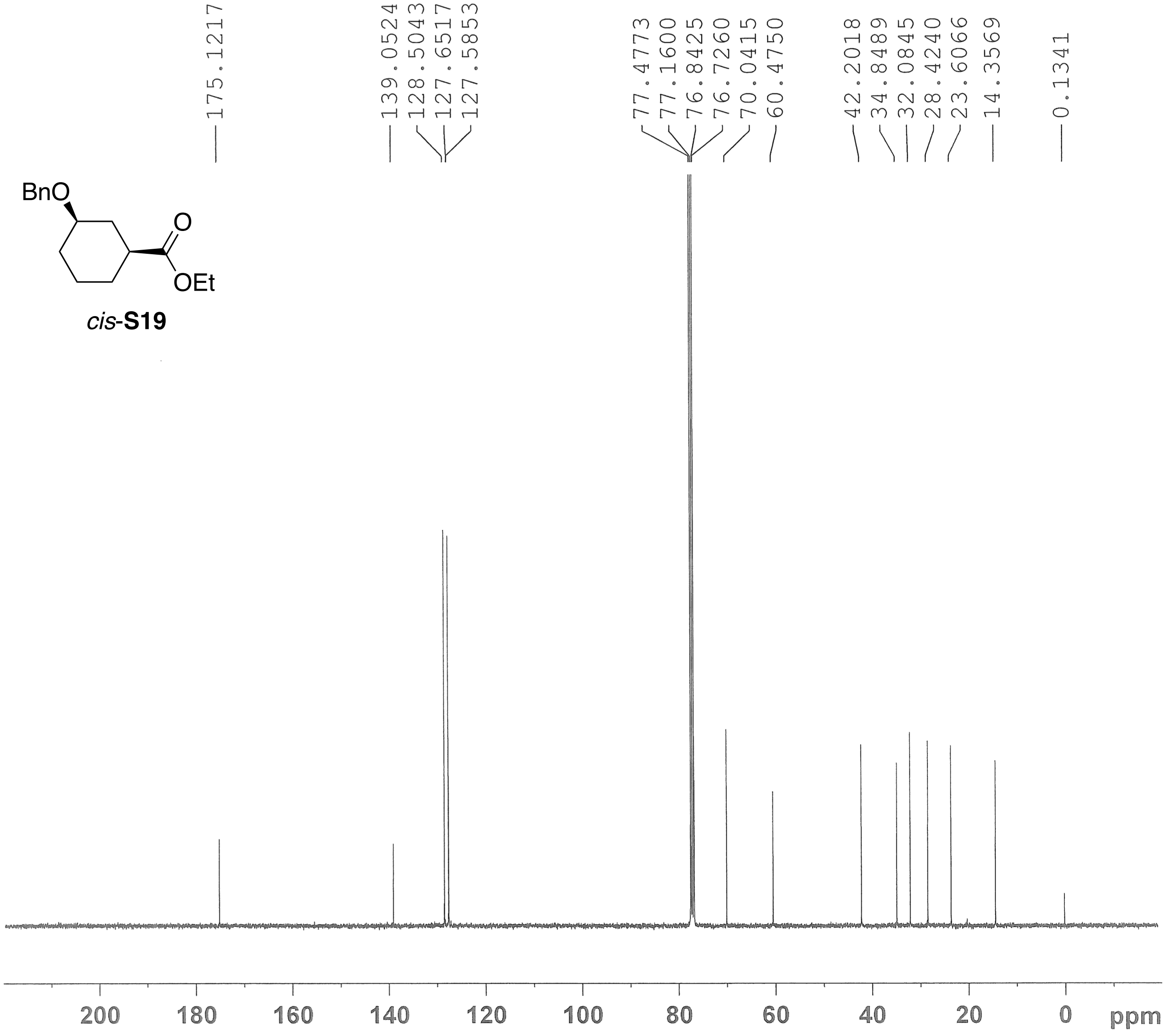
```
Current Data Parameters
NAME       DALO-III-81K2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130516
Time                9.52
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH            8223.685 Hz
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG                139.37
DW                60.800 usec
DE                  6.50 usec
TE                 300.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 16.00 usec
PLW1         12.00000000 W
SFO1         400.2224715 MHz

F2 - Processing parameters
SI                 65536
SF           400.2200127 MHz
WDW                   EM
SSB      0
LB       0          0.30 Hz
GB       0
PC                  1.00
```

cis-**S19**



BRUKER

```
Current Data Parameters
NAME        DALO-III-81K2
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130516
Time                11.51
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 301.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PLW1         54.00000000 W
SFO1         100.6454621 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.37926000 W
PLW13         0.30720001 W
SFO2         400.2216009 MHz

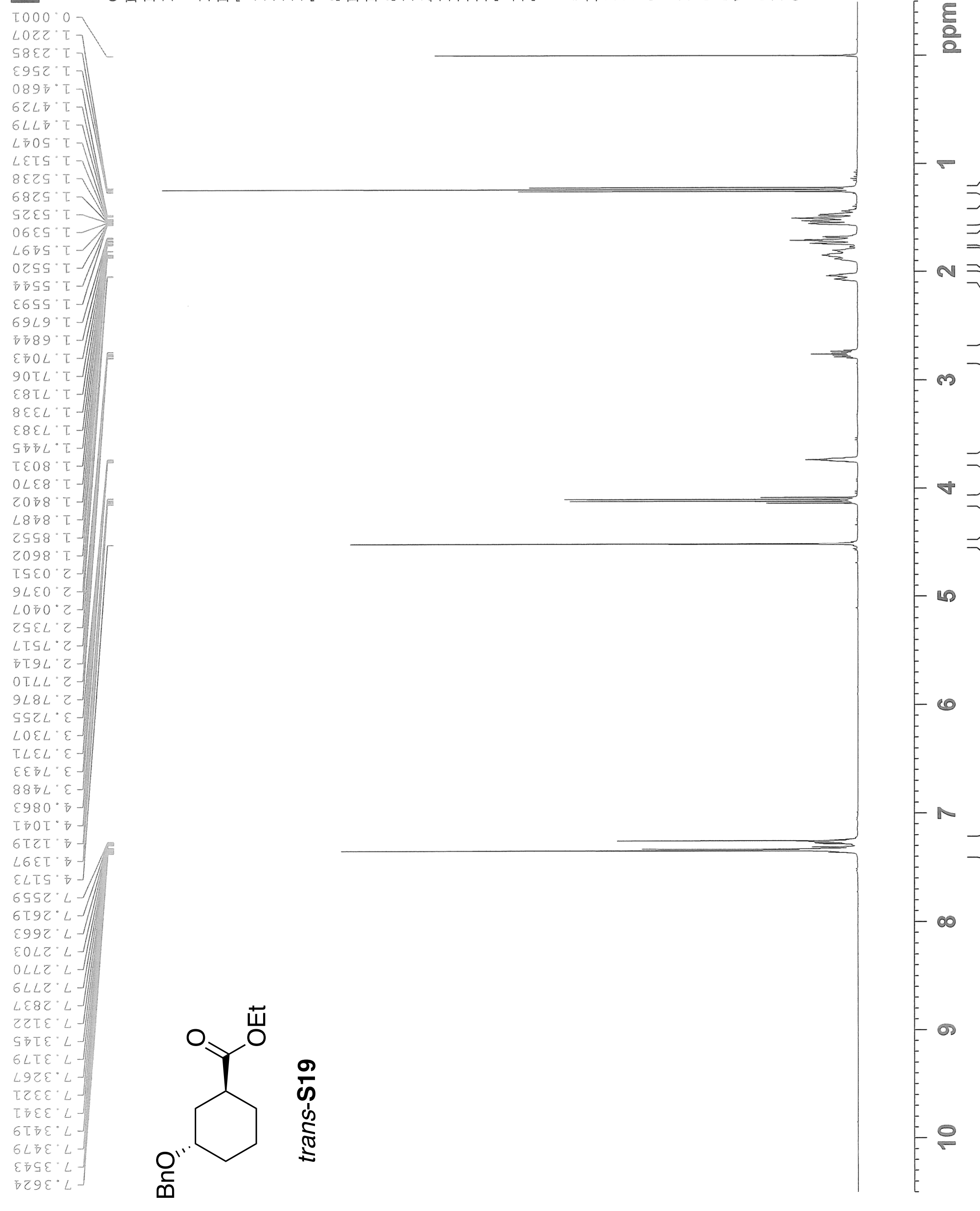
F2 - Processing parameters
SI                 32768
SF           100.6353855 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

```
Current Data Parameters
NAME       DALO-III-81K1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130516
Time               16.10
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    64
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                139.37
DW                60.800 usec
DE                  6.50 usec
TE                 301.9 K
D1            1.00000000 sec
TD0                    1

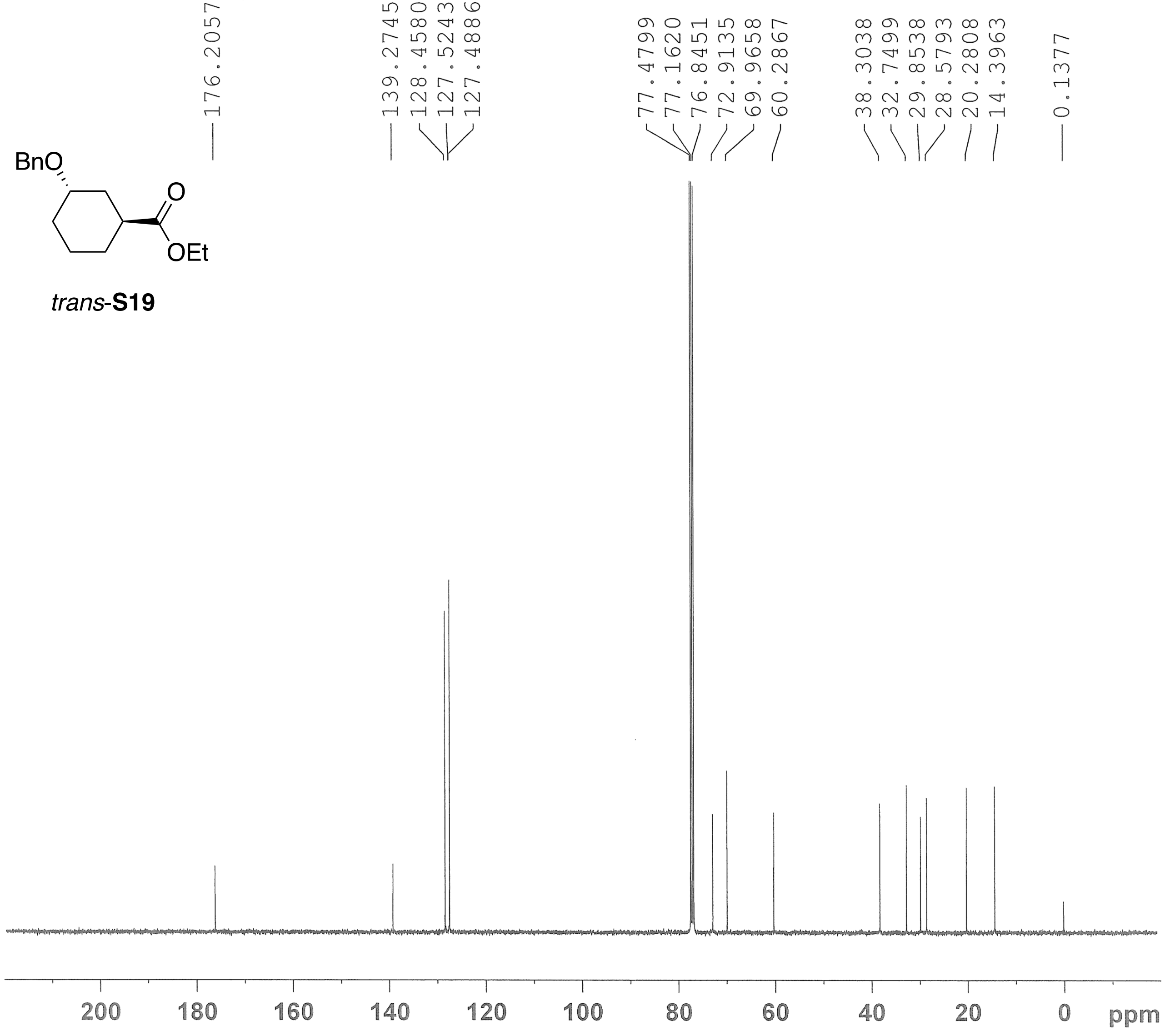
======== CHANNEL f1 ========
NUC1                  1H
P1                 16.00 usec
PLW1         12.00000000 W
SFO1         400.2224715 MHz

F2 - Processing parameters
SI                 65536
SF           400.2200139 MHz
WDW                   EM
SSB      0
LB       0          0.30 Hz
GB       0
PC                  1.00
```



trans-**S19**

DALO-III-81K1
C13CPD CDCl3 C:\\ nmr 81



trans-**S19**

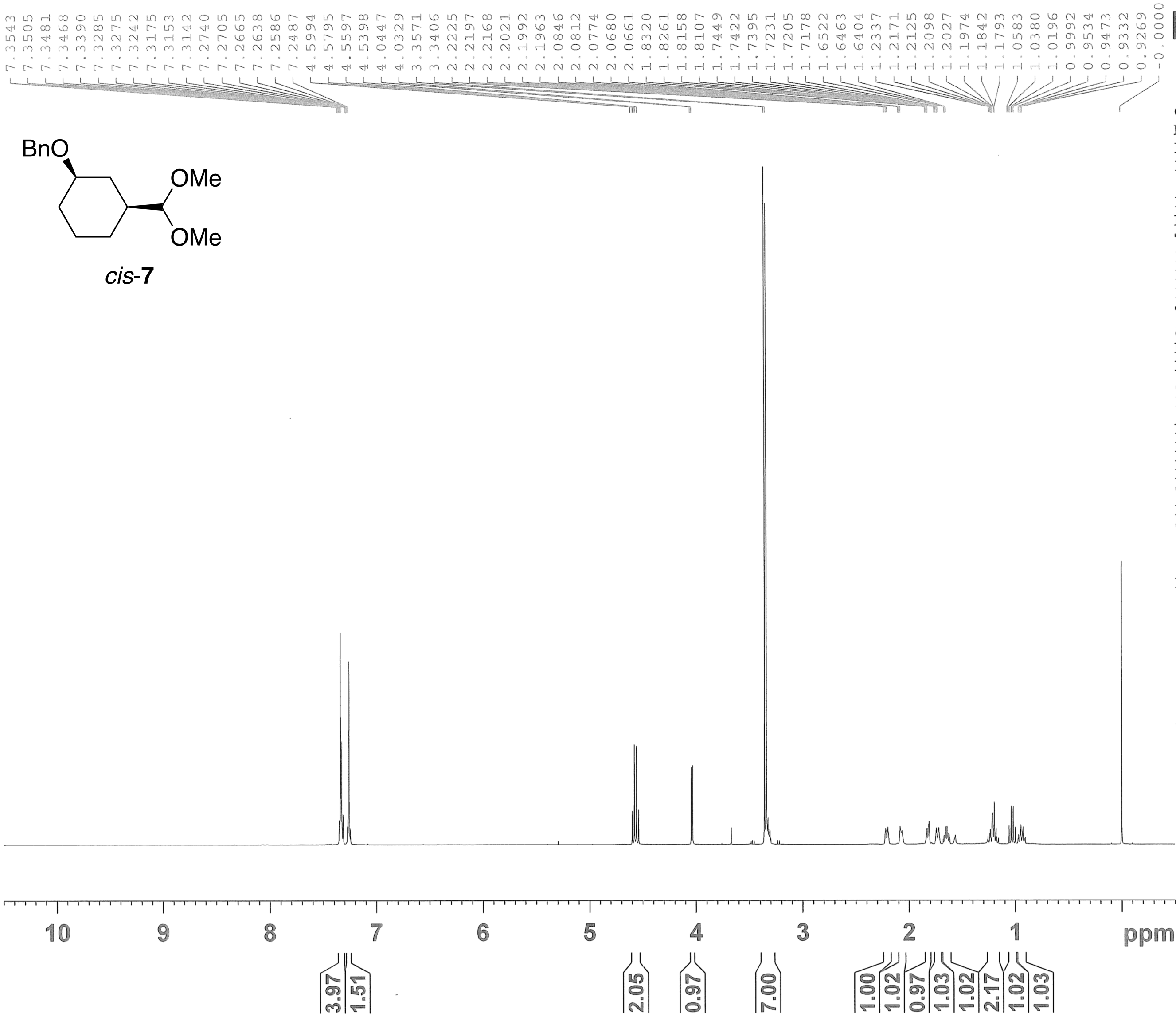
```
Current Data Parameters
NAME       DALO-III-81K1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130516
Time               16.12
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  2048
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 302.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PLW1         54.00000000 W
SFO1        100.6454621 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.37926000 W
PLW13         0.30720001 W
SFO2        400.2216009 MHz

F2 - Processing parameters
SI                 32768
SF          100.6353844 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



cis-**7**

```
Current Data Parameters
NAME     DALO-III-154K10
EXPNO                  1
PROCNO                 1

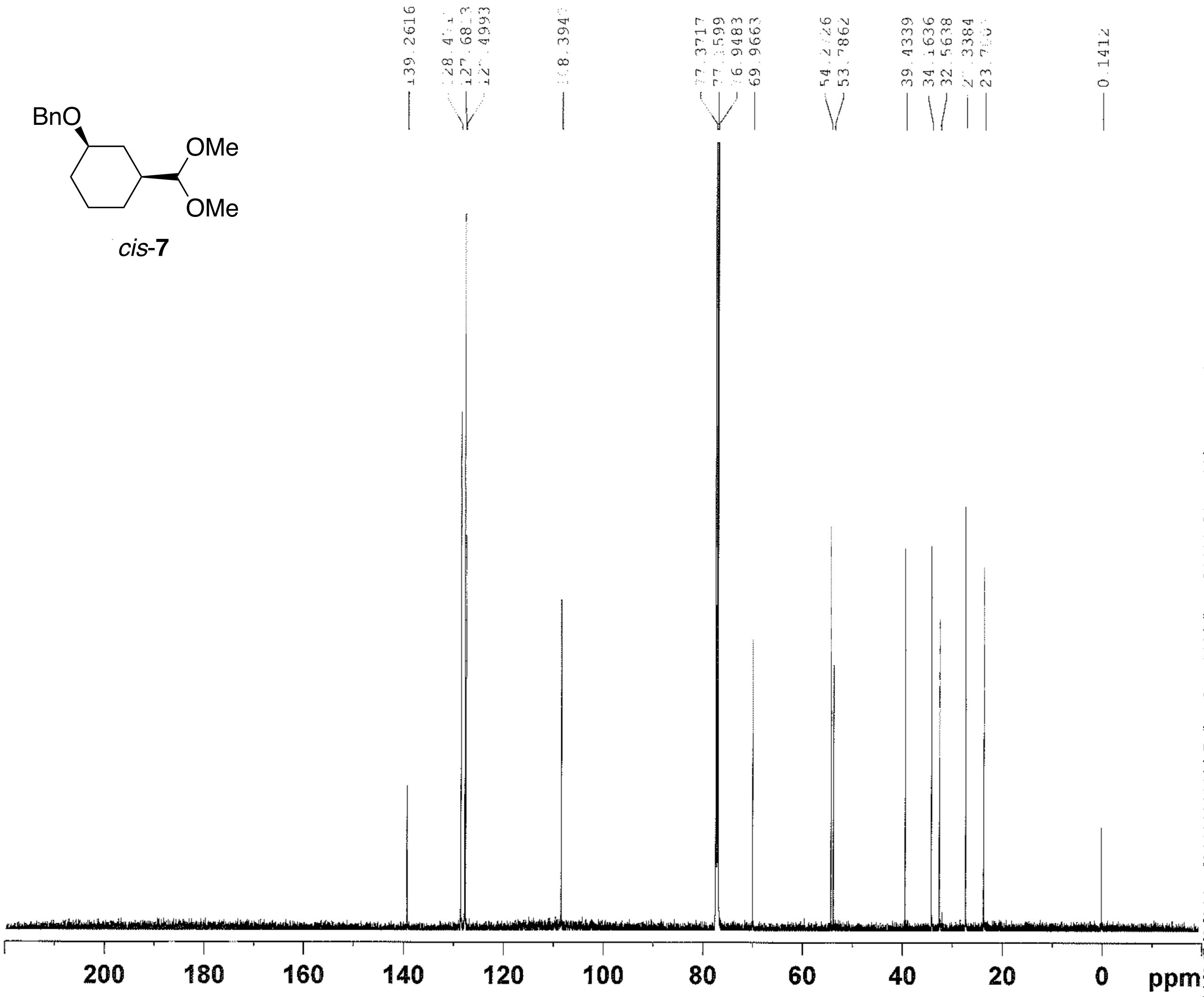
F2 - Acquisition Parameters
Date_           20130605
Time               20.02
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                104.51
DW                40.533 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.79 usec
PLW1          9.30000019 W
SFO1        600.1937064 MHz

F2 - Processing parameters
SI                 65536
SF          600.1900151 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```

DALO-III-154K10

cis-**7**



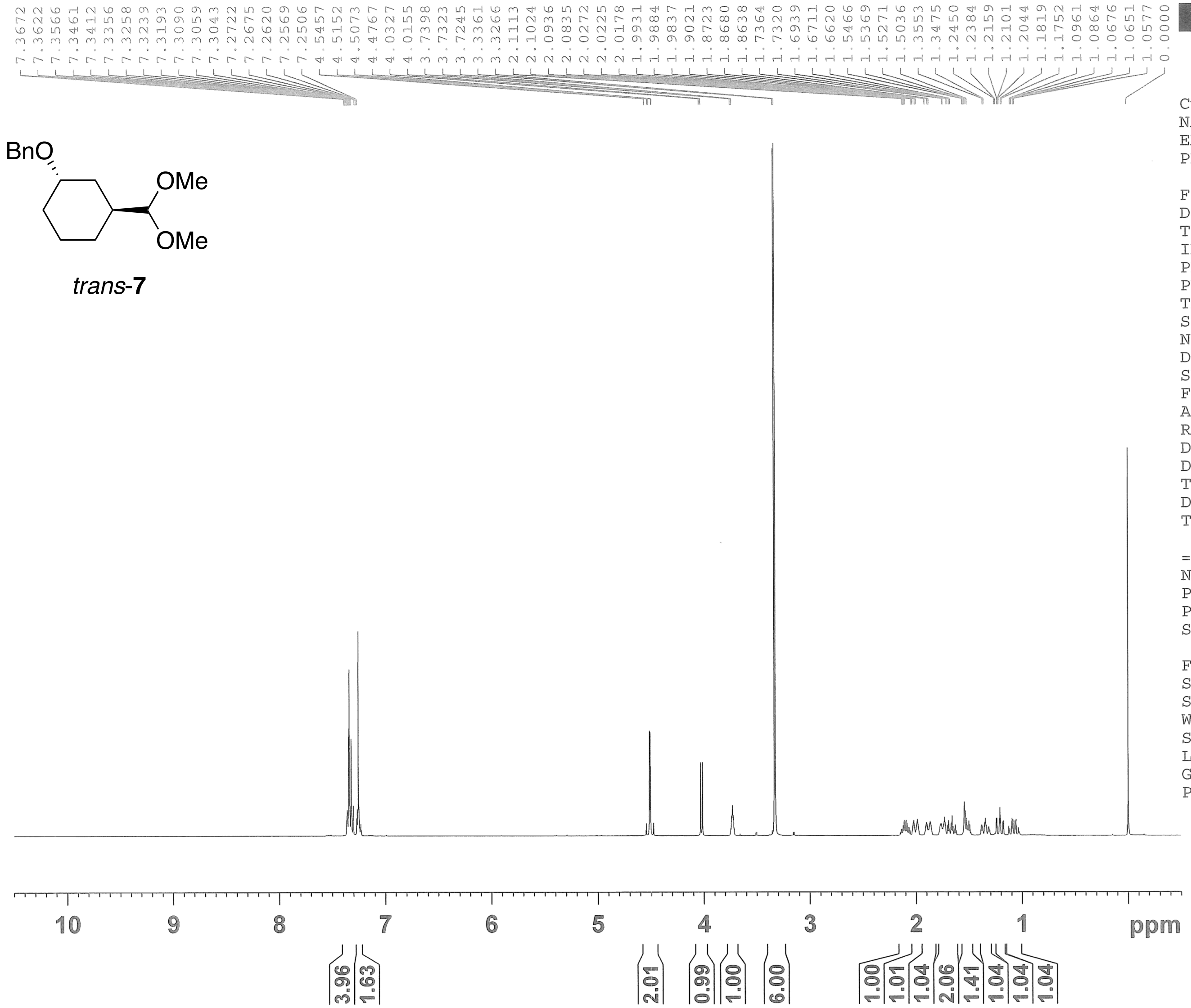
```
Current Data Parameters
NAME     DALO-III-154K10
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130605
Time               23.27
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 4096
DS                    4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9088159 sec
RG               184.65
DW               13.867 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                15.00 usec
PLW1       106.00000000 W
SFO1        150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             70.00 usec
PLW2         9.30000019 W
PLW12        0.18190999 W
PLW13        0.08913500 W
SFO2        600.1924008 MHz

F2 - Processing parameters
SI                32768
SF          150.9178750 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



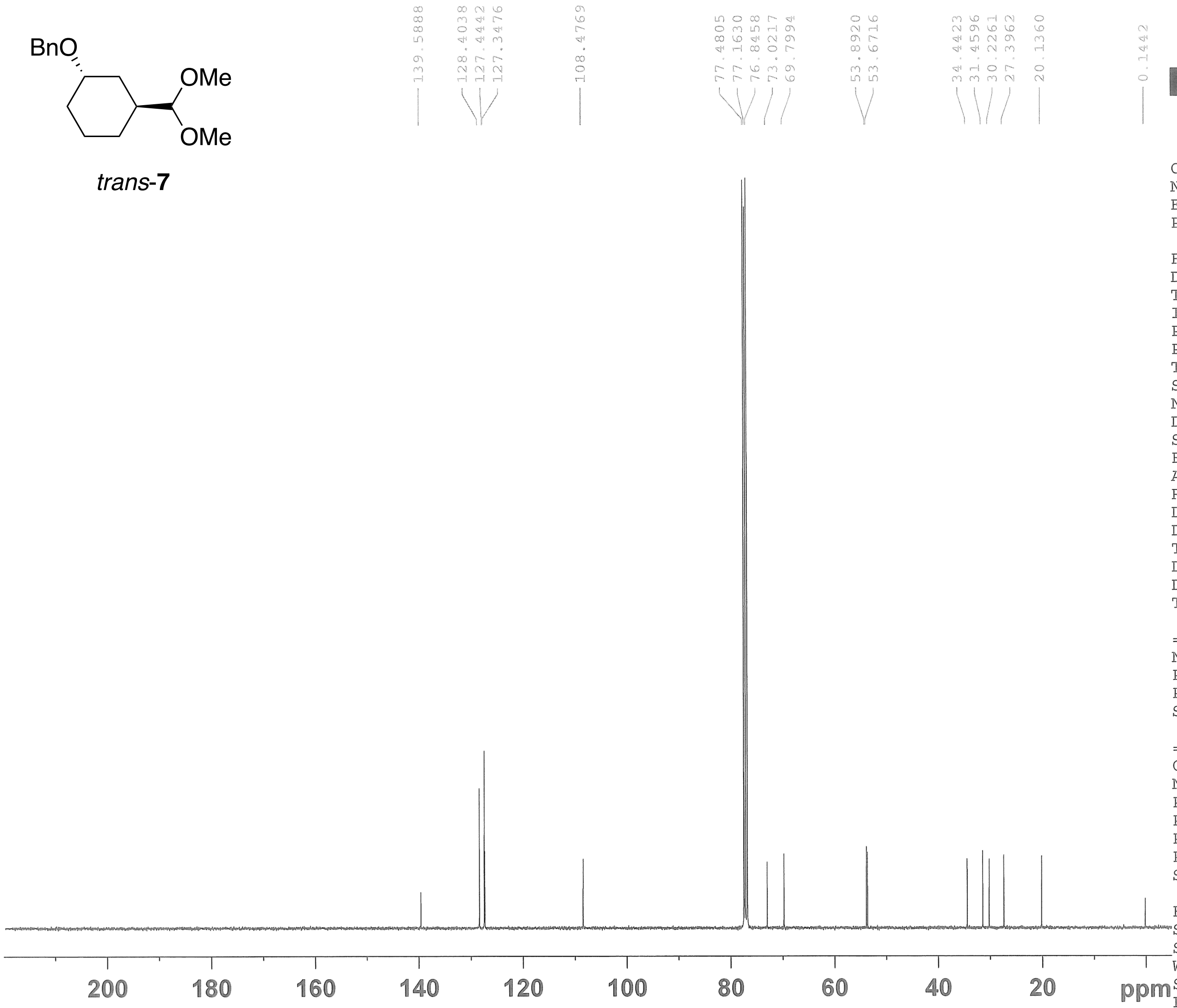
trans-**7**

```
Current Data Parameters
NAME     DALO-III-157K11
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130614
Time               16.53
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                   512
DS                     2
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                180.34
DW                60.800 usec
DE                  6.50 usec
TE                 301.5 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 16.00 usec
PLW1         12.00000000 W
SFO1         400.2224715 MHz

F2 - Processing parameters
SI                 65536
SF           400.2200135 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



trans-**7**

```
Current Data Parameters
NAME      DALO-III-157K11
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130614
Time                21.40
INSTRUM             spect
PROBHD    5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  4096
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631988 sec
RG                200.67
DW                20.800 usec
DE                  6.50 usec
TE                 303.5 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

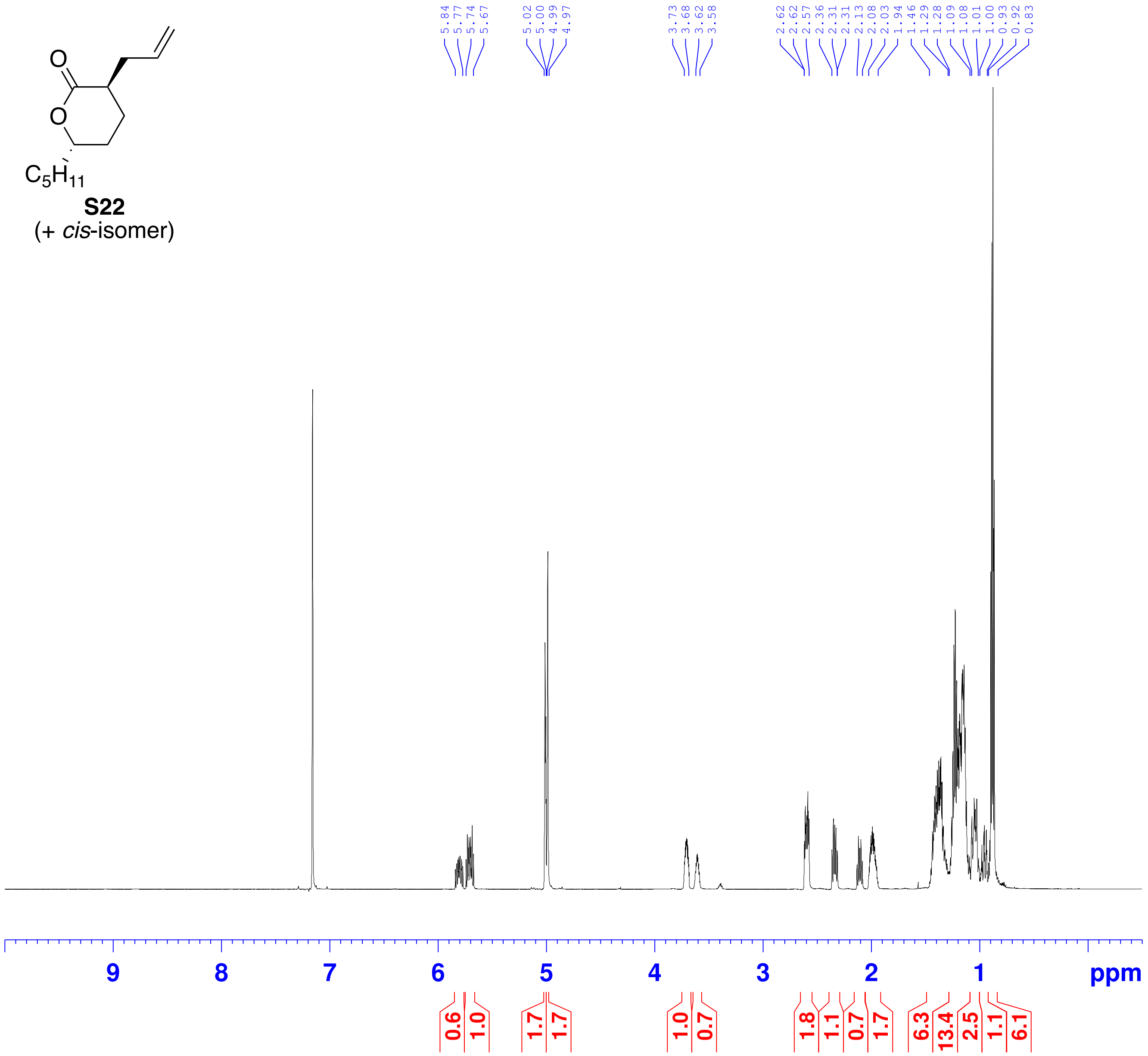
======== CHANNEL f1 ========
NUC1                 13C
P1                  9.40 usec
PLW1         54.00000000 W
SFO1         100.6454621 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              90.00 usec
PLW2         12.00000000 W
PLW12         0.37926000 W
PLW13         0.30720001 W
SFO2         400.2216009 MHz

F2 - Processing parameters
SI                 32768
SF           100.6353837 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

S22

(+ *cis*-isomer)

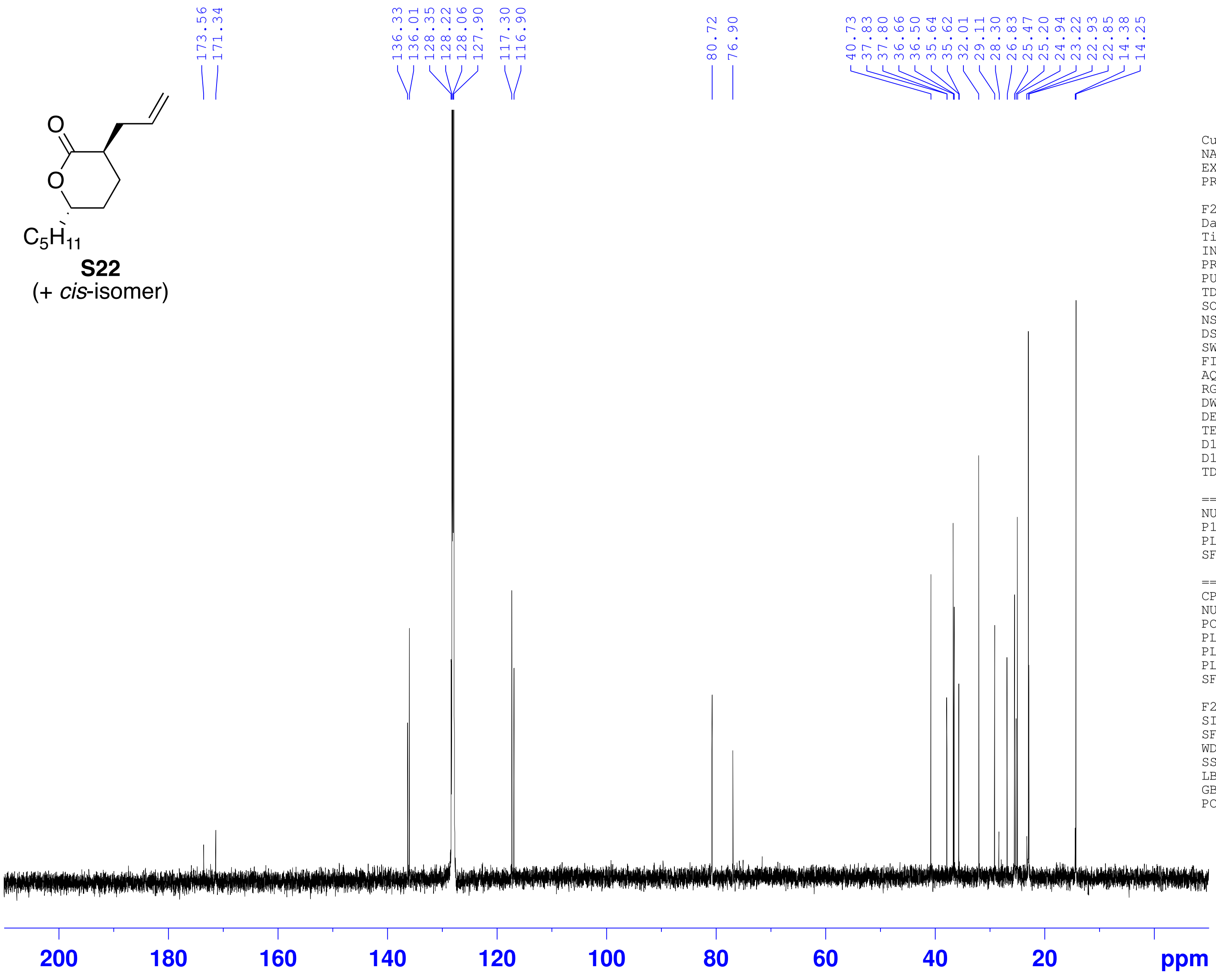


```
Current Data Parameters
NAME              II-79-P
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130128
Time                15.19
INSTRUM             spect
PROBHD    5 mm PAQXI 1H/
PULPROG              zg30
TD                  65536
SOLVENT              C6D6
NS                      8
DS                      0
SWH             12335.526 Hz
FIDRES           0.188225 Hz
AQ              2.6564426 sec
RG                  29.77
DW                 40.533 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   9.79 usec
PLW1           9.30000019 W
SFO1          600.1937064 MHz

F2 - Processing parameters
SI                  65536
SF            600.1899951 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



S22
(+ *cis*-isomer)

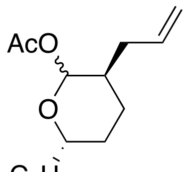
```
Current Data Parameters
NAME              II-79-P
EXPNO                   3
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130128
Time                15.35
INSTRUM             spect
PROBHD   5 mm PAQXI 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                   256
DS                     0
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

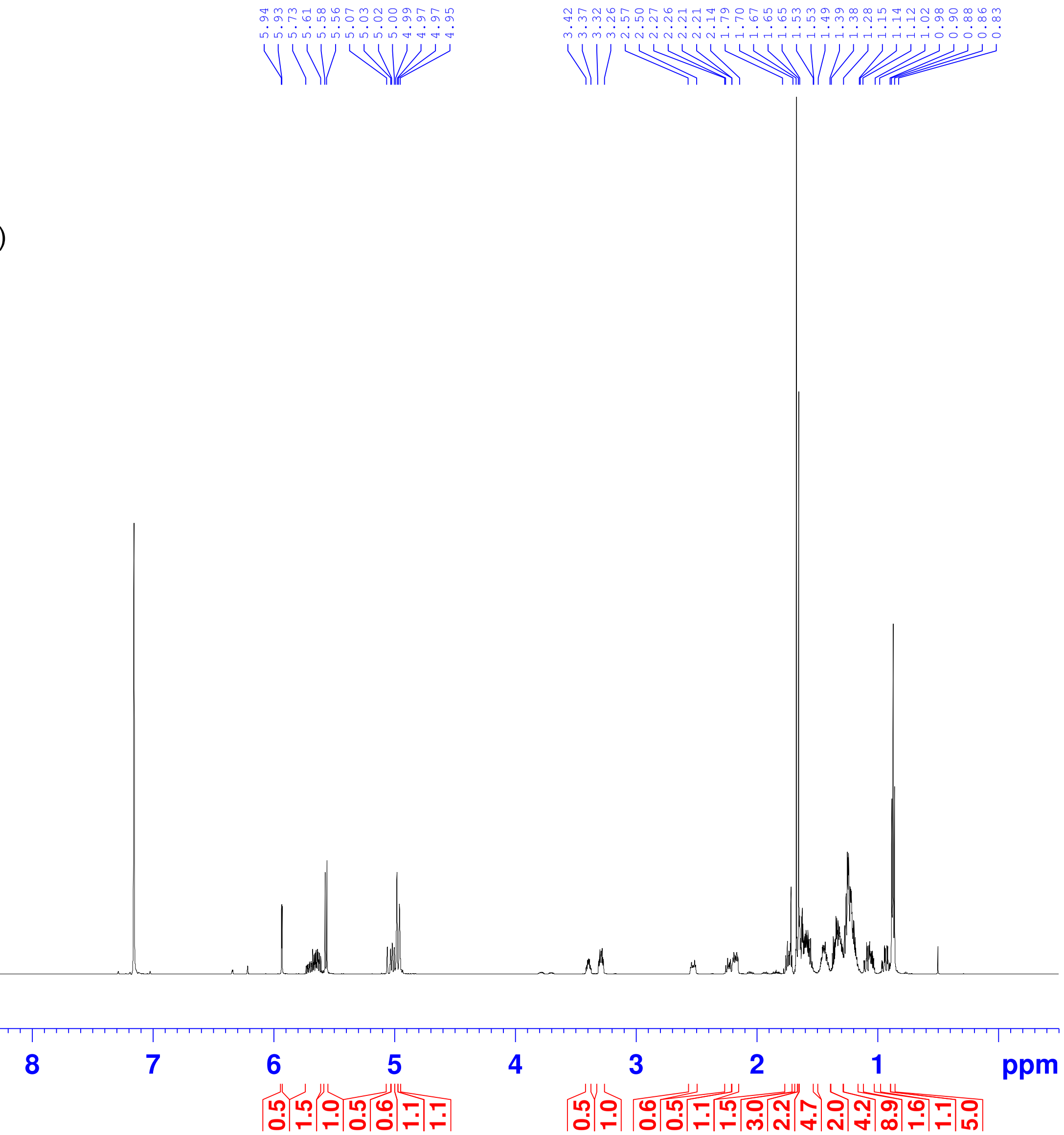
======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178387 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



S23
(+ *cis*-isomer)

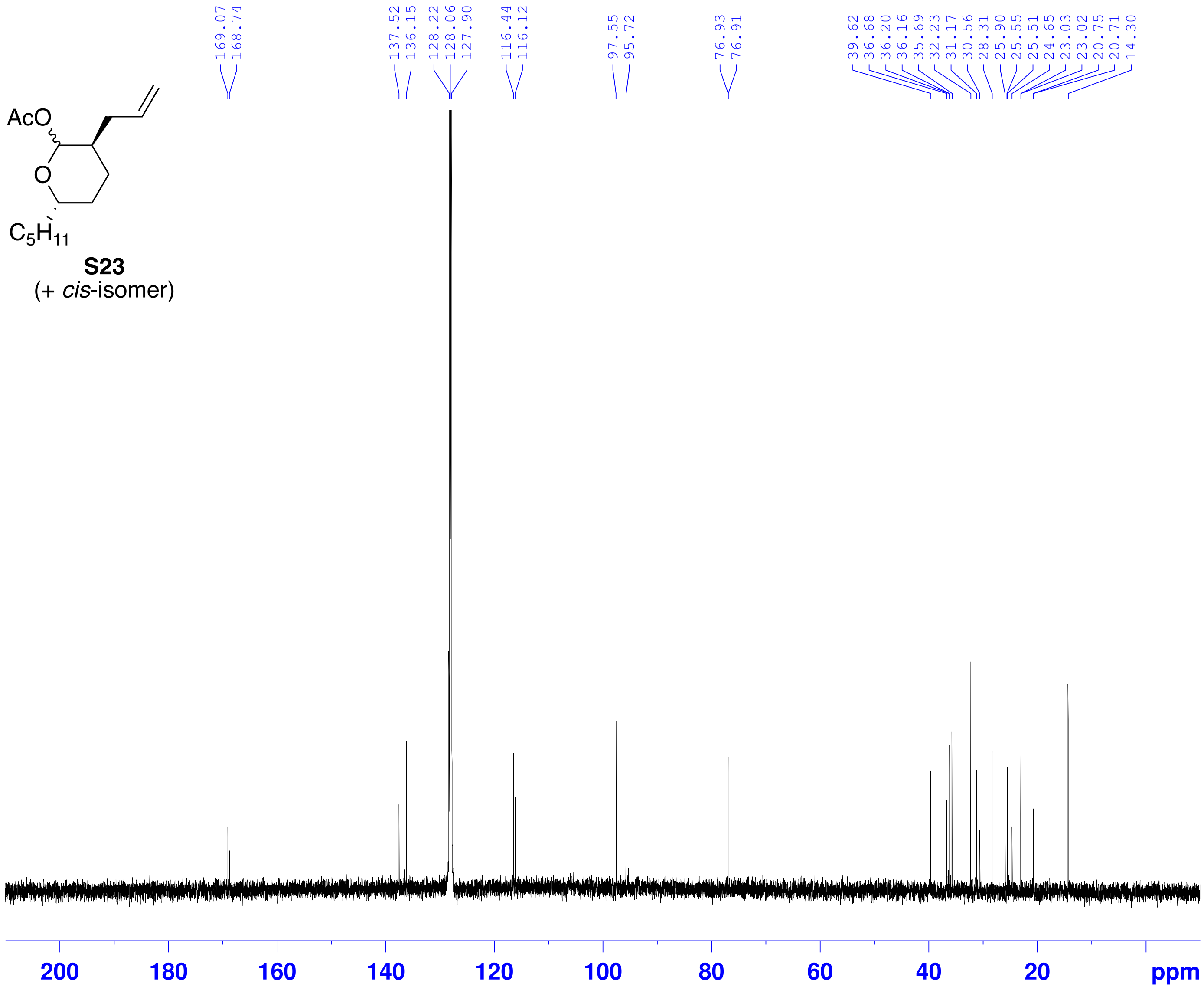


```
Current Data Parameters
NAME                II-84-P
EXPNO                     4
PROCNO                    1

F2 - Acquisition Parameters
Date_              20130131
Time                   9.43
INSTRUM               spect
PROBHD   5 mm PAQXI 1H/
PULPROG                zg30
TD                    65536
SOLVENT                C6D6
NS                        8
DS                        0
SWH              12335.526 Hz
FIDRES            0.188225 Hz
AQ               2.6564426 sec
RG                    68.89
DW                   40.533 usec
DE                     6.50 usec
TE                    298.1 K
D1              1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                     9.79 usec
PLW1             9.30000019 W
SFO1            600.1937064 MHz

F2 - Processing parameters
SI                    65536
SF              600.1899950 MHz
WDW                      no
SSB      0
LB       0 Hz
GB       0
PC                     1.00
```



S23
(+ *cis*-isomer)

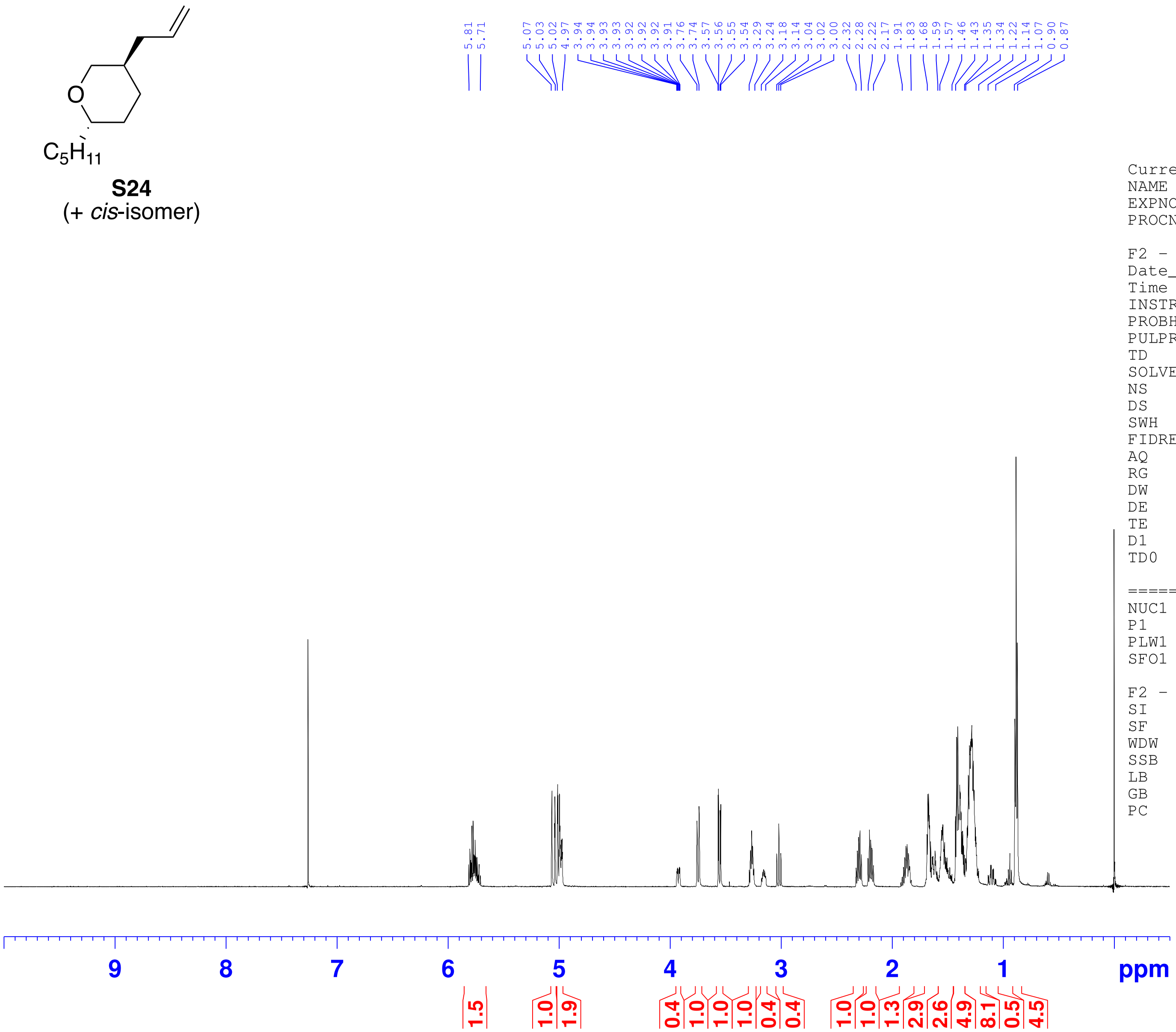
```
Current Data Parameters
NAME              II-84-P
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130131
Time                 9.55
INSTRUM             spect
PROBHD    5 mm PAQXI 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT             C6D6
NS                   256
DS                     0
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178389 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



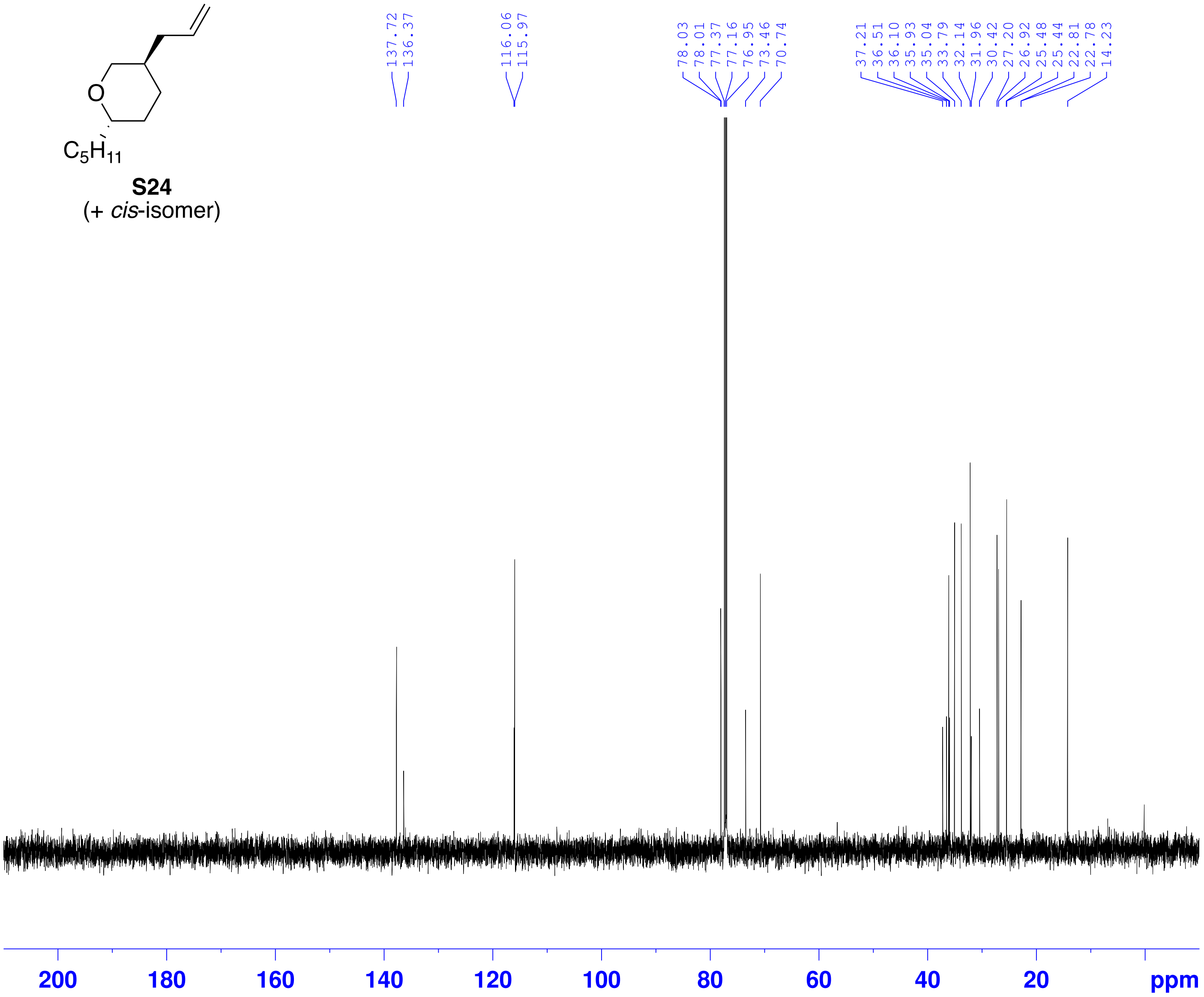
S24
(+ *cis*-isomer)

```
Current Data Parameters
NAME             II-149-P
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130330
Time                16.46
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ              1.8175818 sec
RG                  59.15
DW                 27.733 usec
DE                   6.50 usec
TE                  298.2 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PLW1          26.50000000 W
SFO1          600.1937064 MHz

F2 - Processing parameters
SI                  65536
SF            600.1900142 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



S24
(+ *cis*-isomer)

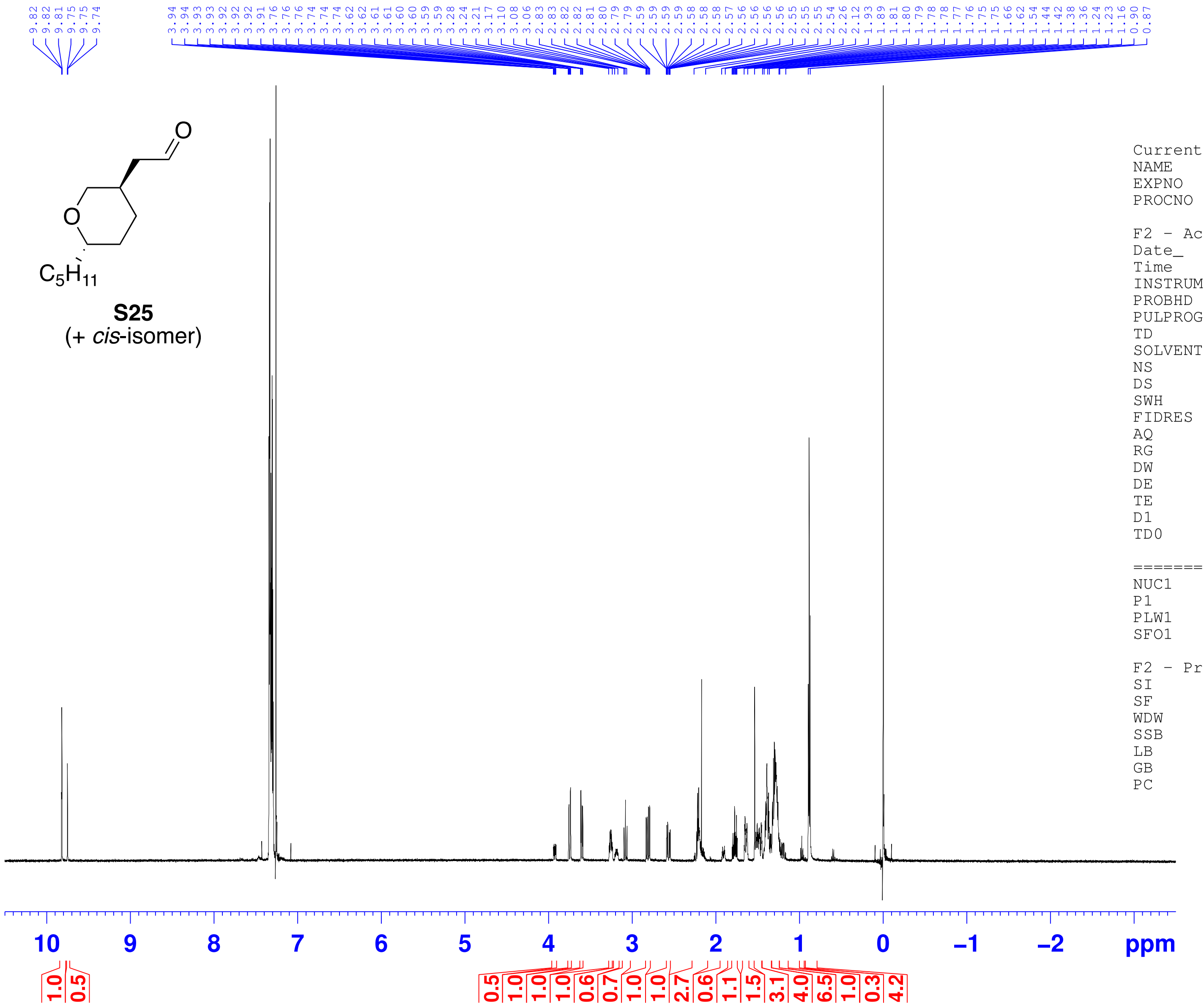
```
Current Data Parameters
NAME             II-149-P
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130330
Time                16.49
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                  65536
SOLVENT             CDCl3
NS                     64
DS                      0
SWH             36057.691 Hz
FIDRES           0.550197 Hz
AQ              0.9088159 sec
RG                 184.65
DW                 13.867 usec
DE                   6.50 usec
TE                  298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.65 usec
PLW1         104.00000000 W
SFO1          150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               70.00 usec
PLW2          26.50000000 W
PLW12          0.65438998 W
PLW13          0.32065001 W
SFO2          600.1924008 MHz

F2 - Processing parameters
SI                  32768
SF            150.9178738 MHz
WDW                    EM
SSB      0
LB                   1.00 Hz
GB       0
PC                   1.40
```



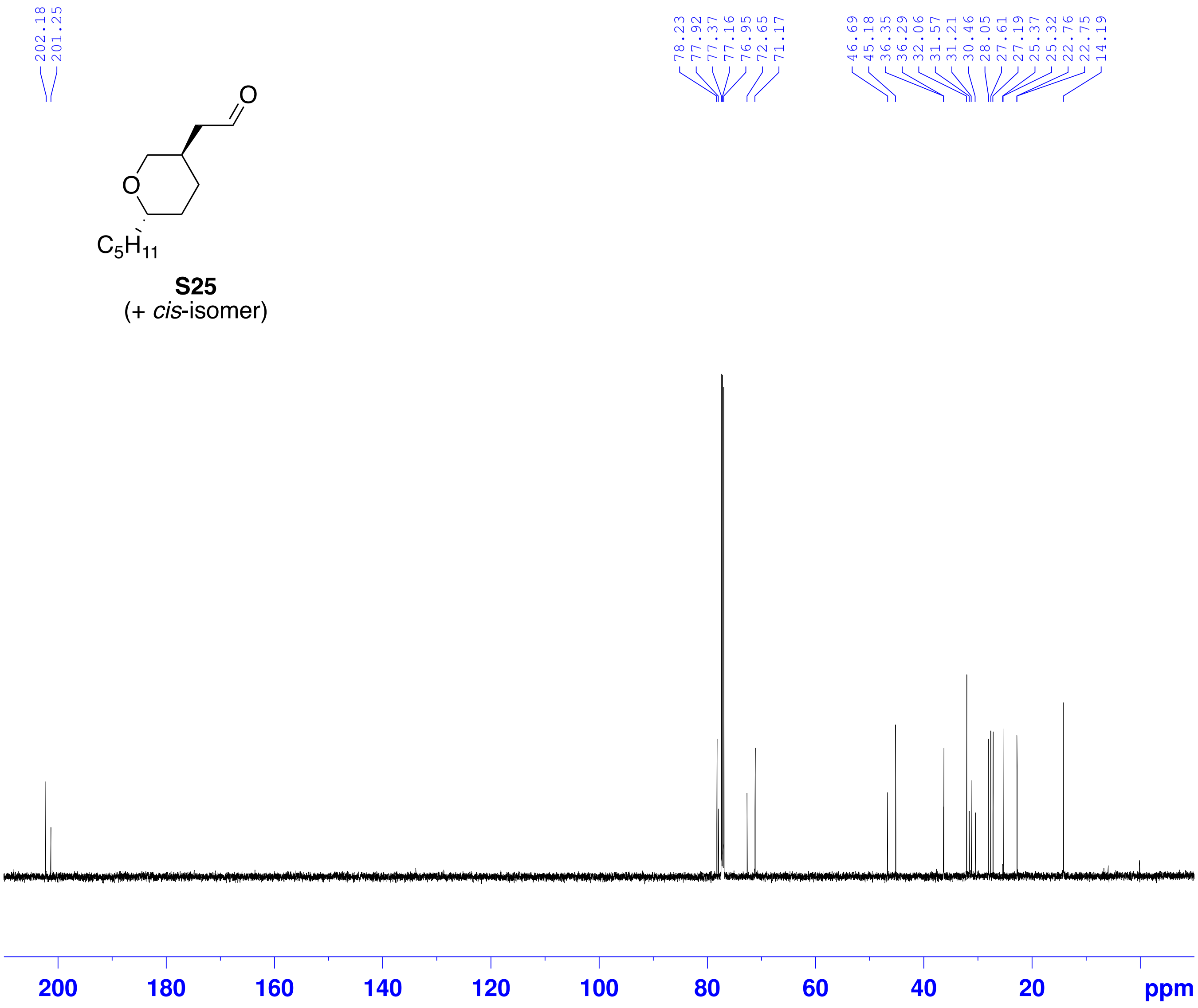
S25
(+ *cis*-isomer)

```
Current Data Parameters
NAME           II-156-CR
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130401
Time               15.19
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                 148.2
DW                40.533 use
DE                  6.50 use
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 =======
NUC1                  1H
P1                 11.00 use
PLW1         26.50000000 W
SFO1         600.1937064 MHz

F2 - Processing parameters
SI                 65536
SF           600.1900155 MHz
WDW                   no
SSB      0
LB       0 Hz
GB       0
PC                  1.00
```



S25
(+ *cis*-isomer)

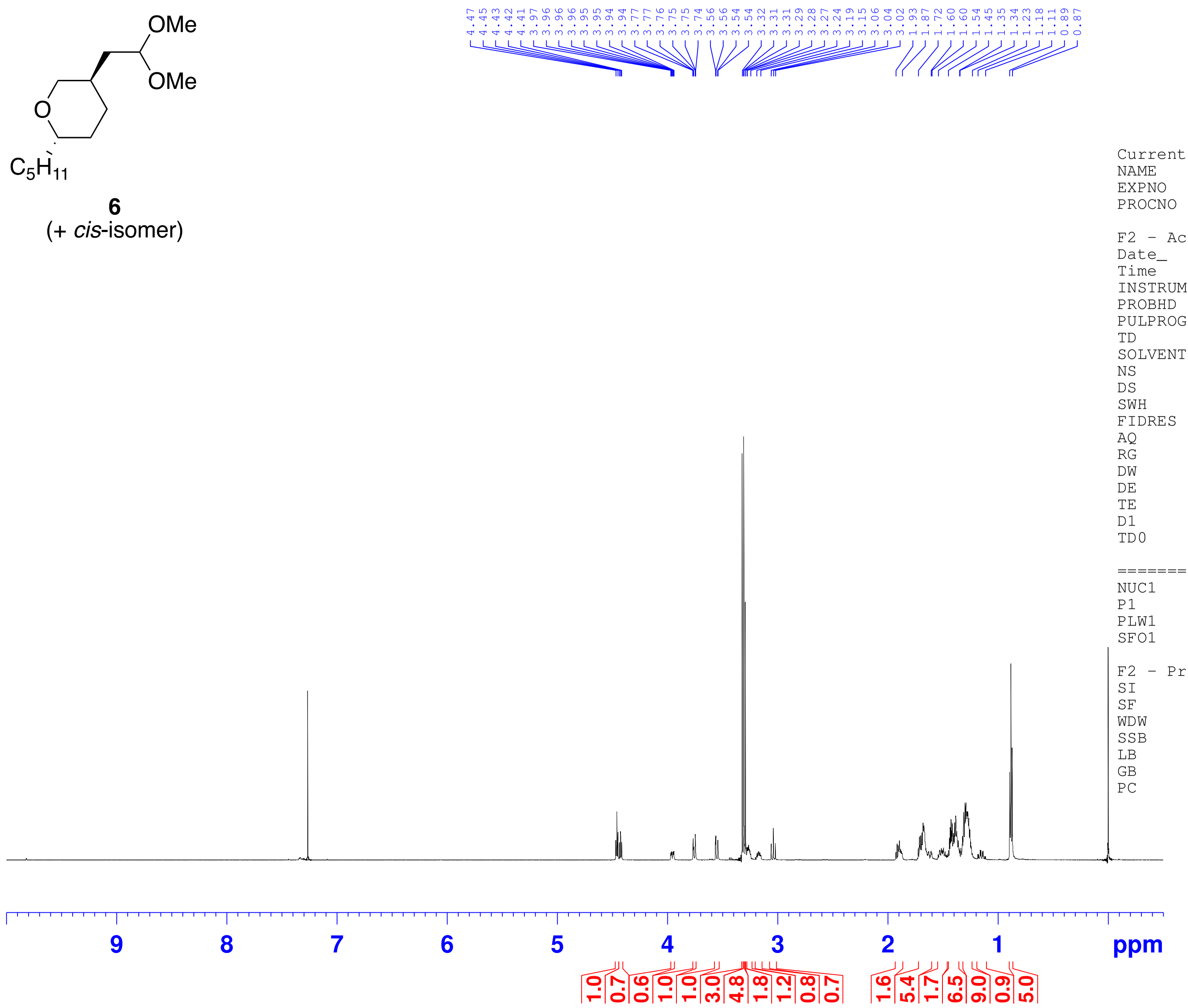
```
Current Data Parameters
NAME             II-151-P
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130328
Time                16.12
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     0
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.1 K
D1           2.50000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.65 usec
PLW1        104.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              70.00 usec
PLW2         26.50000000 W
PLW12         0.65438998 W
PLW13         0.32065001 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178761 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

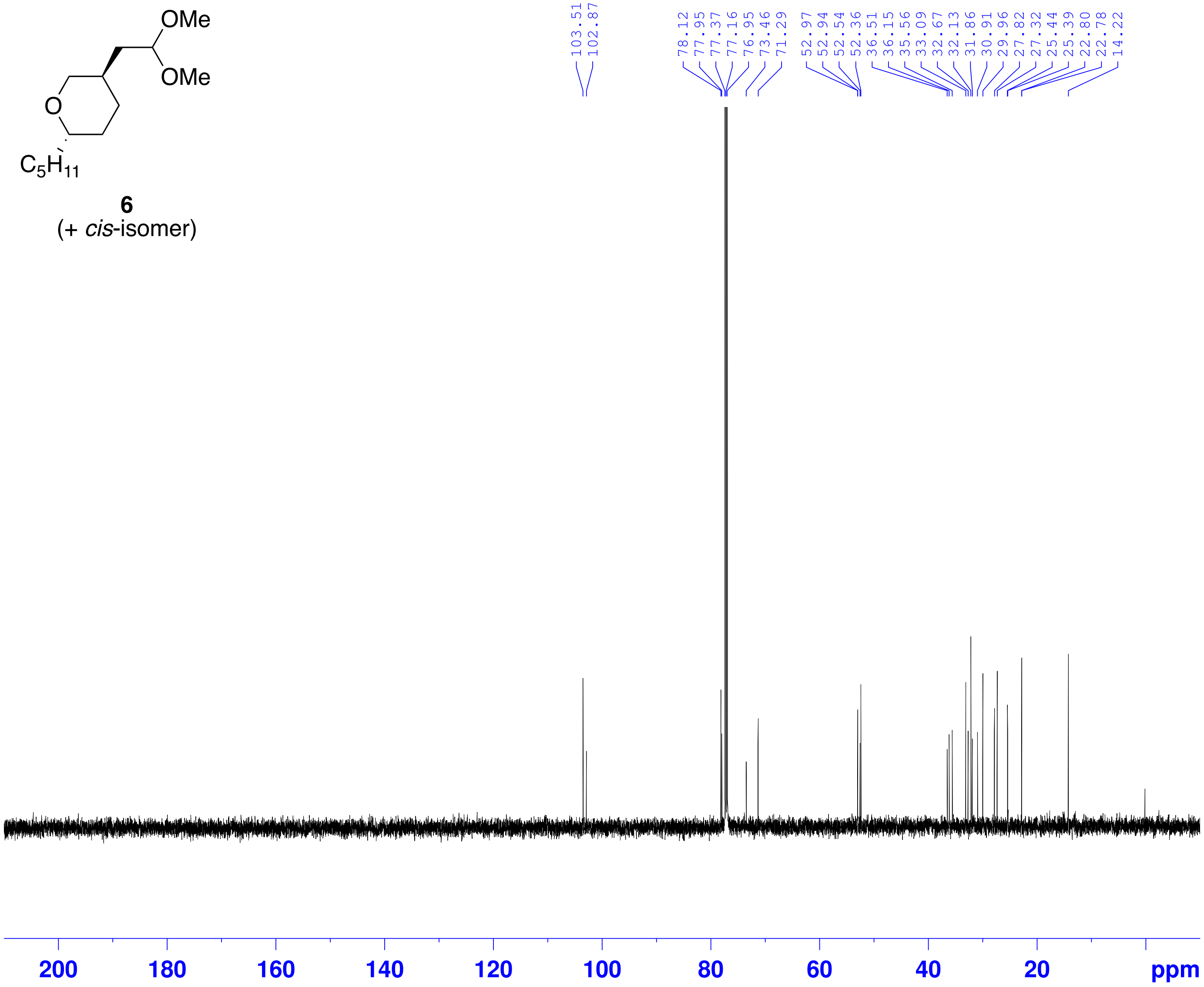


```
Current Data Parameters
NAME             II-153-P
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20130331
Time                11.43
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      1
DS                      0
SWH             18028.846 Hz
FIDRES           0.275098 Hz
AQ              1.8175818 sec
RG                  85.84
DW                 27.733 usec
DE                   6.50 usec
TE                  298.2 K
D1            30.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  11.00 usec
PLW1          26.50000000 W
SFO1          600.1937064 MHz

F2 - Processing parameters
SI                  65536
SF            600.1900129 MHz
WDW                    no
SSB      0
LB       0 Hz
GB       0
PC                   1.00
```



6
(+ *cis*-isomer)

```
Current Data Parameters
NAME             II-153-P
EXPNO                   2
PROCNO                  1

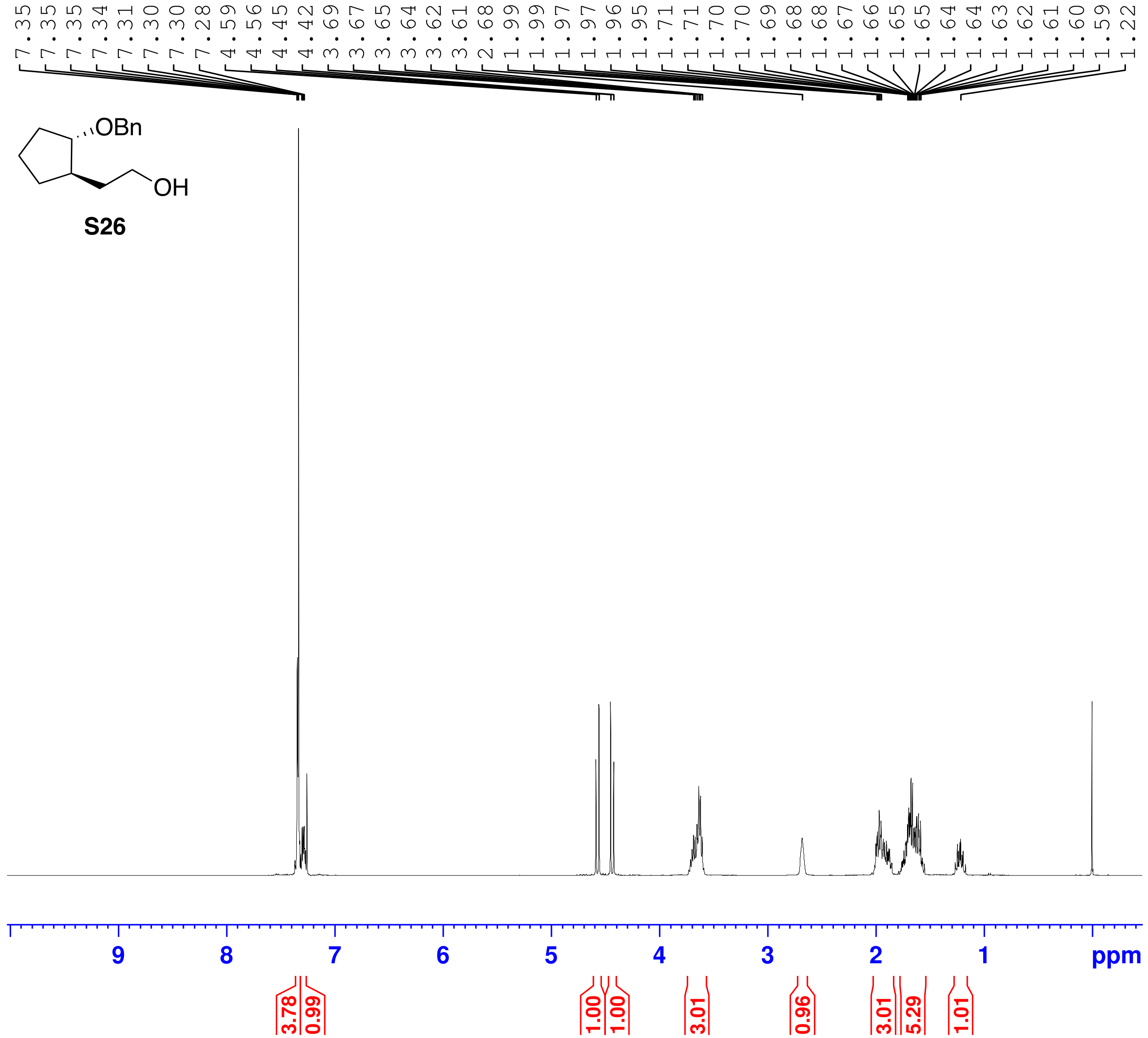
F2 - Acquisition Parameters
Date_            20130331
Time                11.49
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   128
DS                     0
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.65 usec
PLW1        104.00000000 W
SFO1         150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              70.00 usec
PLW2         26.50000000 W
PLW12         0.65438998 W
PLW13         0.32065001 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178738 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

S26

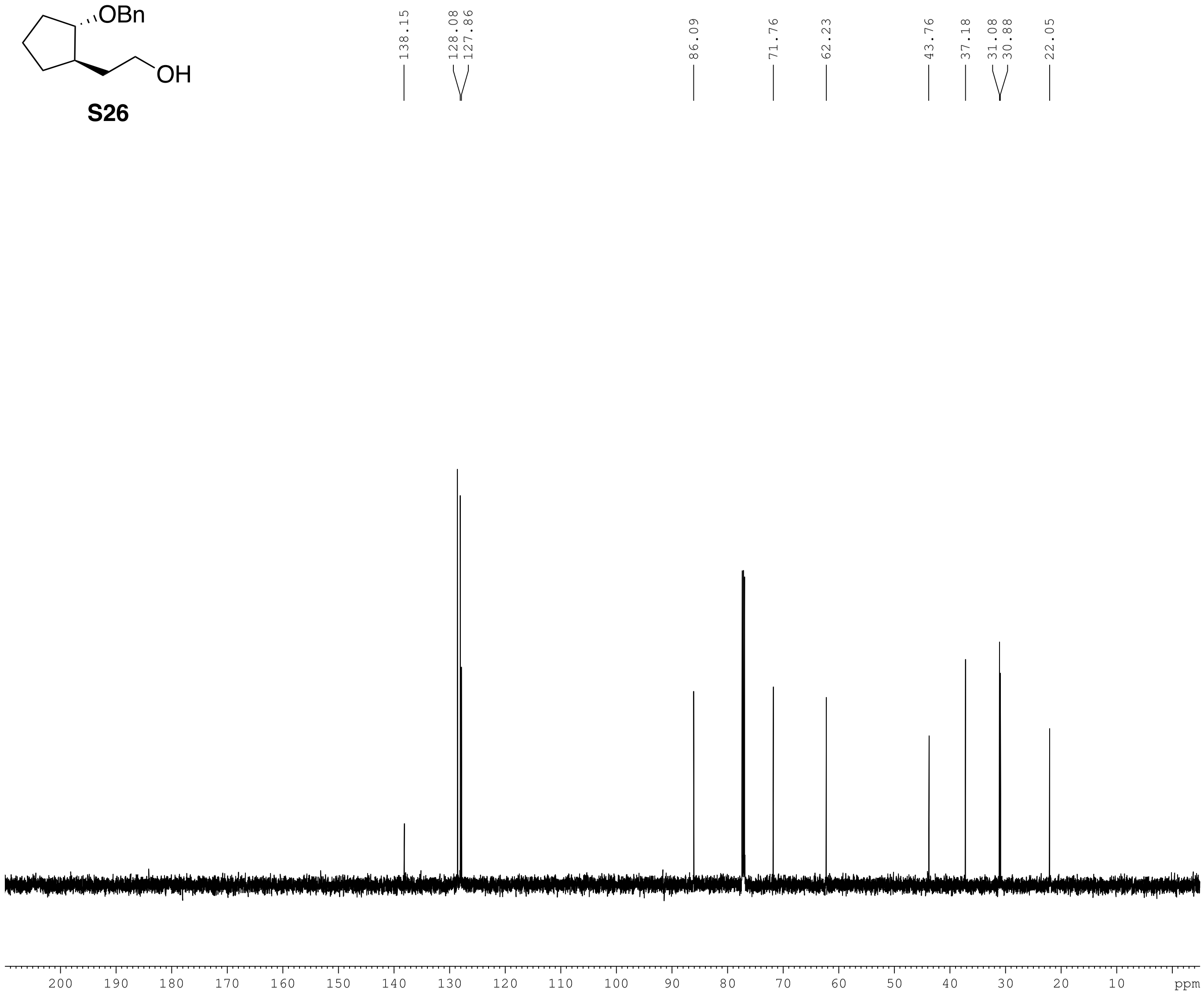


```
Current Data Parameters
NAME          AG-II-133-P
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20131009
Time                19.34
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                    128
DW                 60.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.75 usec
PL1                 -5.00 dB
PL1W          31.77312851 W
SFO1          400.1324710 MHz

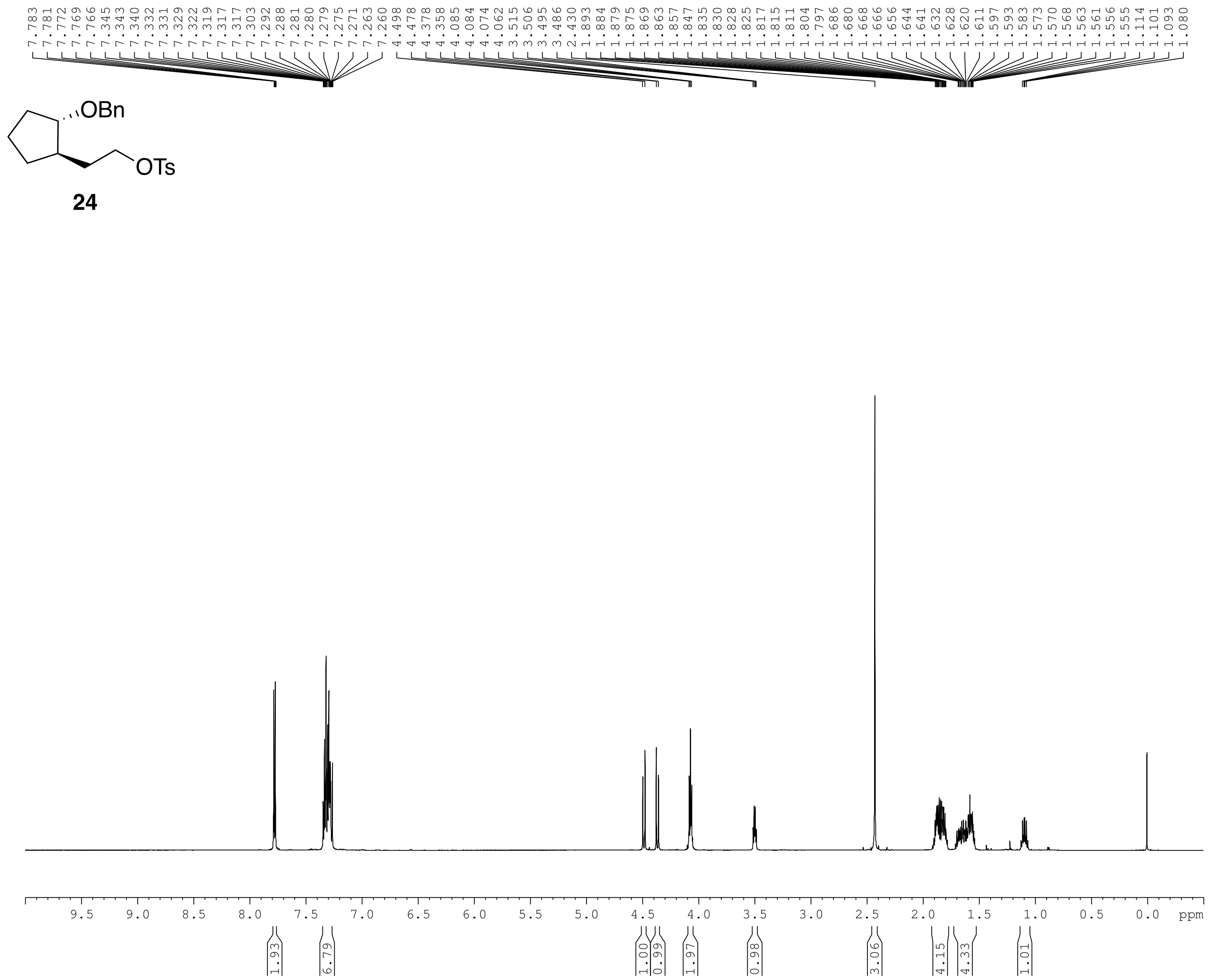
F2 - Processing parameters
SI                  32768
SF            400.1300095 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```


S26

```
Current Data Parameters
NAME     AG-II-133-P2_C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20140118
Time                15.50
INSTRUM             spect
PROBHD   5 mm PAQXI 1H/
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   367
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.50000000 sec
d11           0.03000000 sec
DELTA         2.40000010 sec
TD0                    1
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz
CPDPRG2
NUC2                  1H
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178817 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



24

```
Current Data Parameters
NAME      AG-II-23-P_1H
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20140118
Time              17.12
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                33.59
DW               40.533 usec
DE                 6.50 usec
TE                298.1 K
D1           2.00000000 sec
TD0                   1

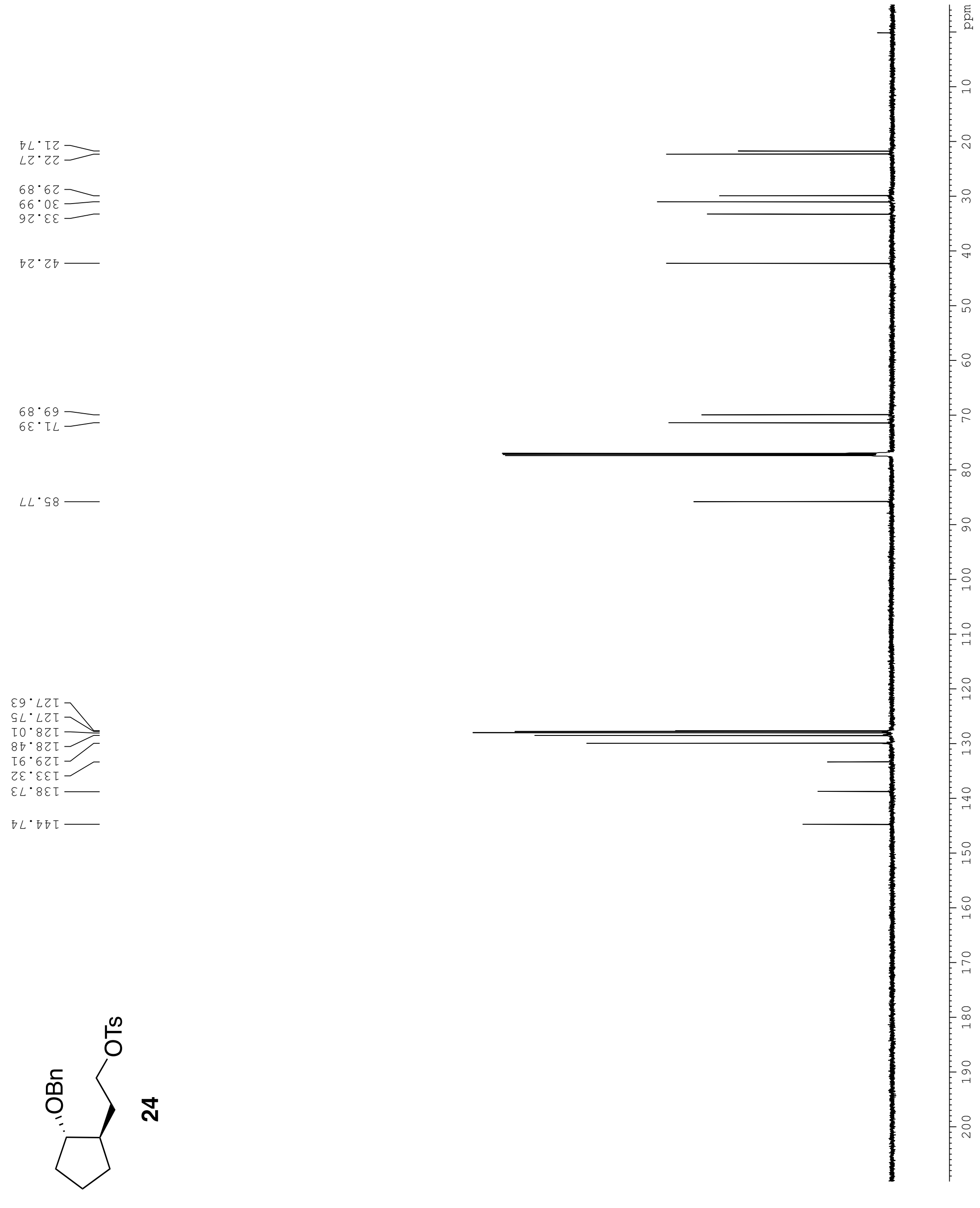
======== CHANNEL f1 ========
SFO1        600.1937064 MHz
NUC1                 1H
P1                 9.79 usec
PLW1         9.30000019 W

F2 - Processing parameters
SI                65536
SF          600.1900143 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```

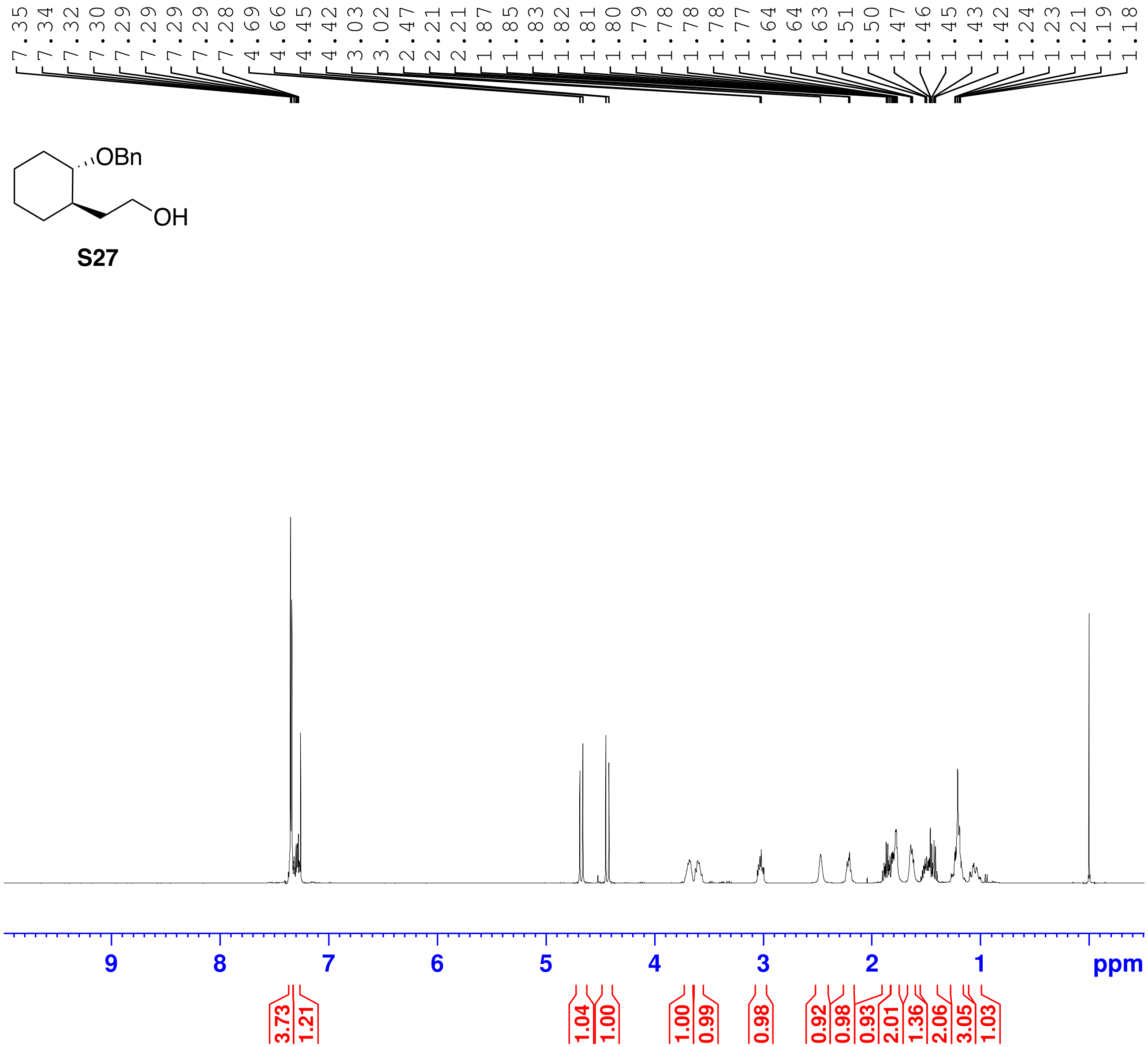
```
Current Data Parameters
NAME      AG-II-23-P_C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140118
Time               17.28
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   982
DS                     4
SWH            36057.691 Hz
FIDRES          0.550197 Hz
AQ             0.9088159 sec
RG                184.65
DW                13.867 usec
DE                  6.50 usec
TE                 298.1 K
D1            2.50000000 sec
d11           0.03000000 sec
DELTA         2.40000010 sec
TD0                    1
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz
CPDPRG2
NUC2                  1H
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

F2 - Processing parameters
SI                 32768
SF           150.9178799 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



24



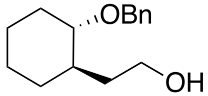
S27

```
Current Data Parameters
NAME           AG-II-47-P
EXPNO                   1
PROCNO                  1

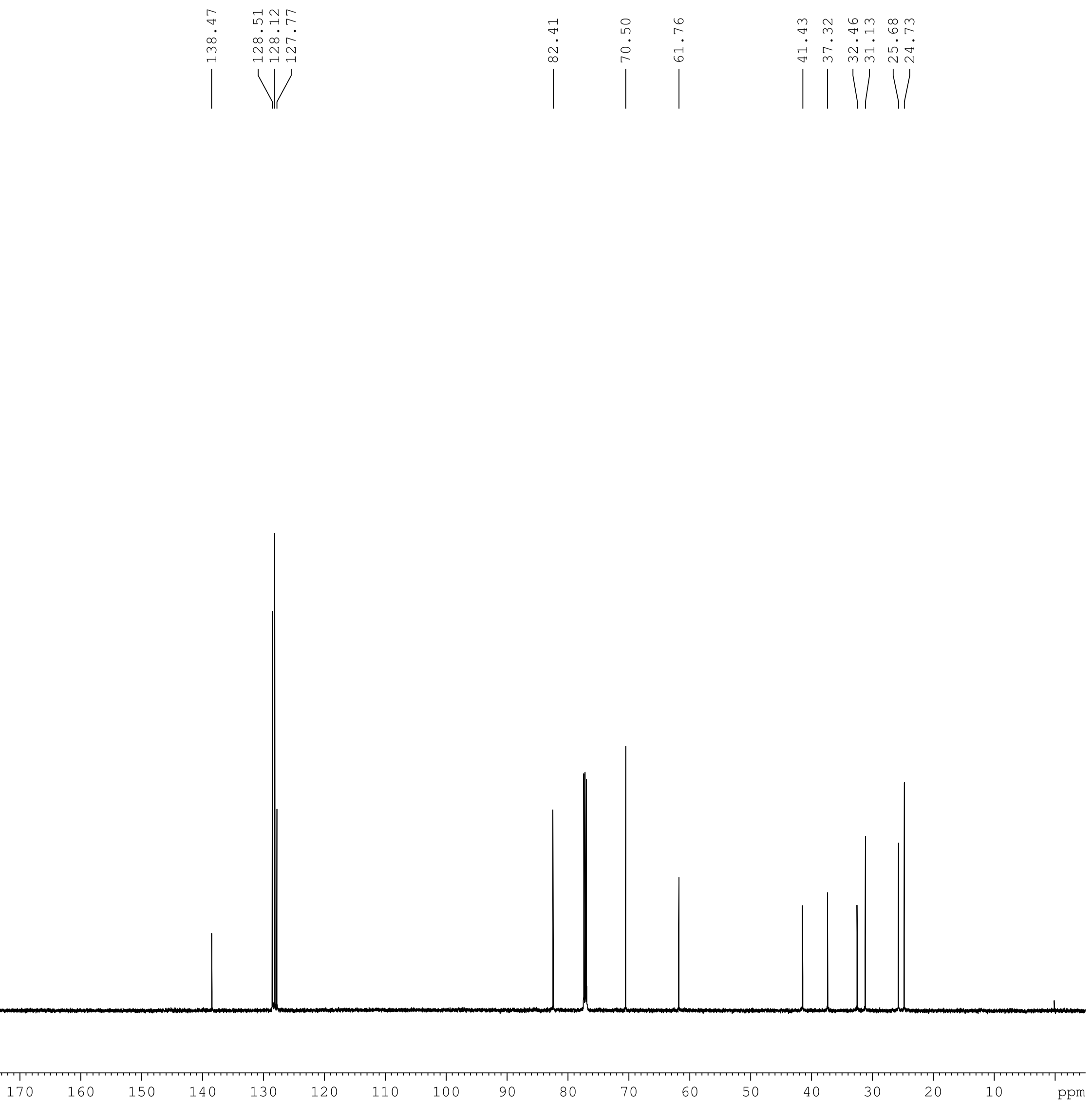
F2 - Acquisition Parameters
Date_            20130824
Time                20.51
INSTRUM             spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      0
SWH              8278.146 Hz
FIDRES           0.126314 Hz
AQ              3.9583745 sec
RG                    181
DW                 60.400 usec
DE                   6.50 usec
TE                  298.2 K
D1             2.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                   7.75 usec
PL1                 -5.00 dB
PL1W          31.77312851 W
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                  32768
SF            400.1300093 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



S27



```
Current Data Parameters
NAME     AG-II-47-P2_C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140118
Time               14.52
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   609
DS                     4
SWH           36057.691 Hz
FIDRES         0.550197 Hz
AQ            0.9088159 sec
RG               184.65
DW               13.867 usec
DE                 6.50 usec
TE                298.2 K
D1           2.50000000 sec
d11          0.03000000 sec
DELTA        2.40000010 sec
TD0                    1
NUC1                 13C
P1                 15.00 usec
PLW1        106.00000000 W
SFO1         150.9329866 MHz
CPDPRG2
NUC2                  1H
PLW2          9.30000019 W
PLW12         0.18190999 W
PLW13         0.08913500 W
SFO2         600.1924008 MHz

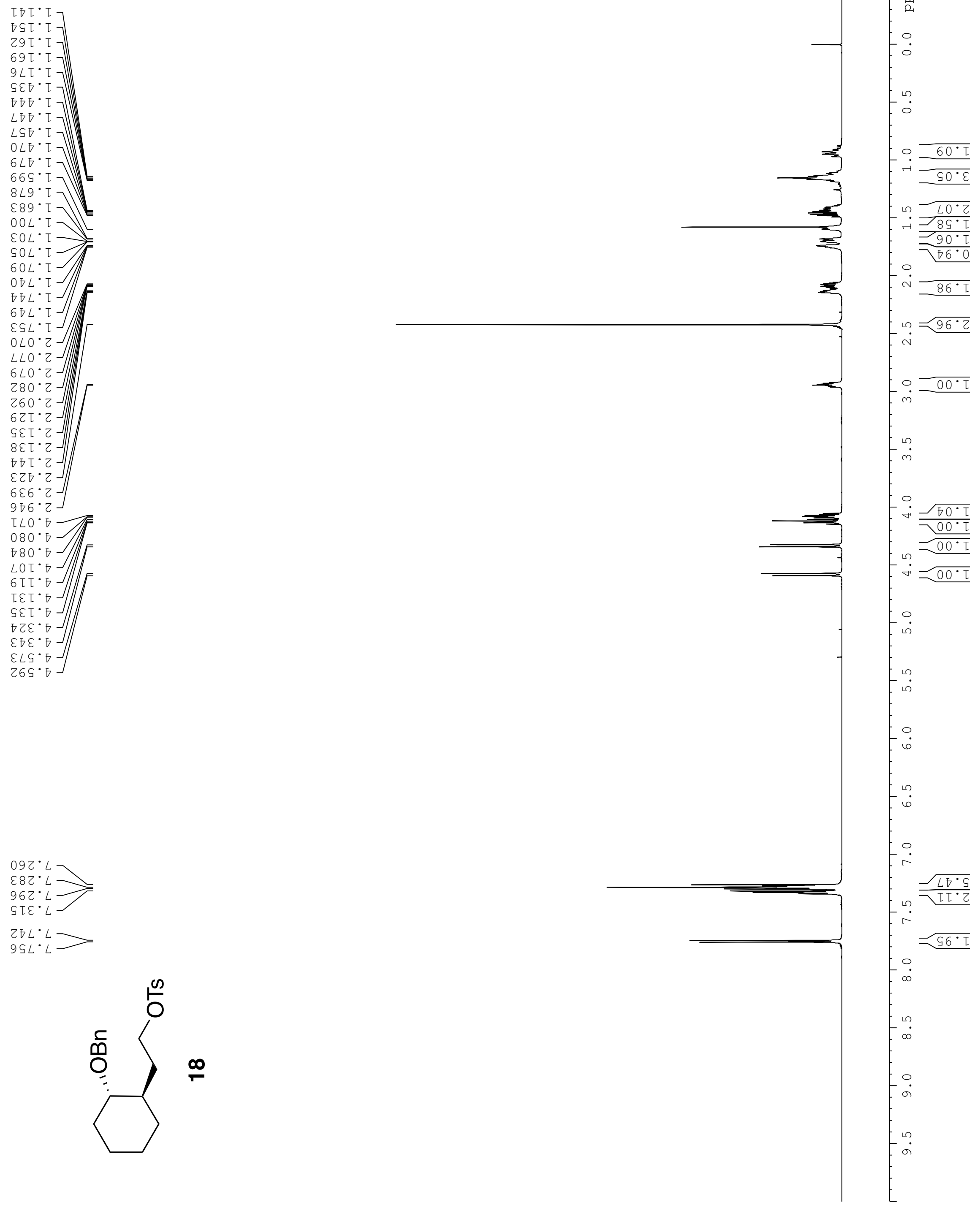
F2 - Processing parameters
SI                 32768
SF           150.9178823 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```

```
Current Data Parameters
NAME       AG-1-205-P_ii
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130623
Time               21.05
INSTRUM            spect
PROBHD   5 mm PAQXI 1H/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            12335.526 Hz
FIDRES          0.188225 Hz
AQ             2.6564426 sec
RG                164.46
DW                40.533 usec
DE                  6.50 usec
TE                 298.0 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                  9.79 usec
PLW1         9.30000019 W
SFO1        600.1937064 MHz

F2 - Processing parameters
SI                 65536
SF           600.1900144 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



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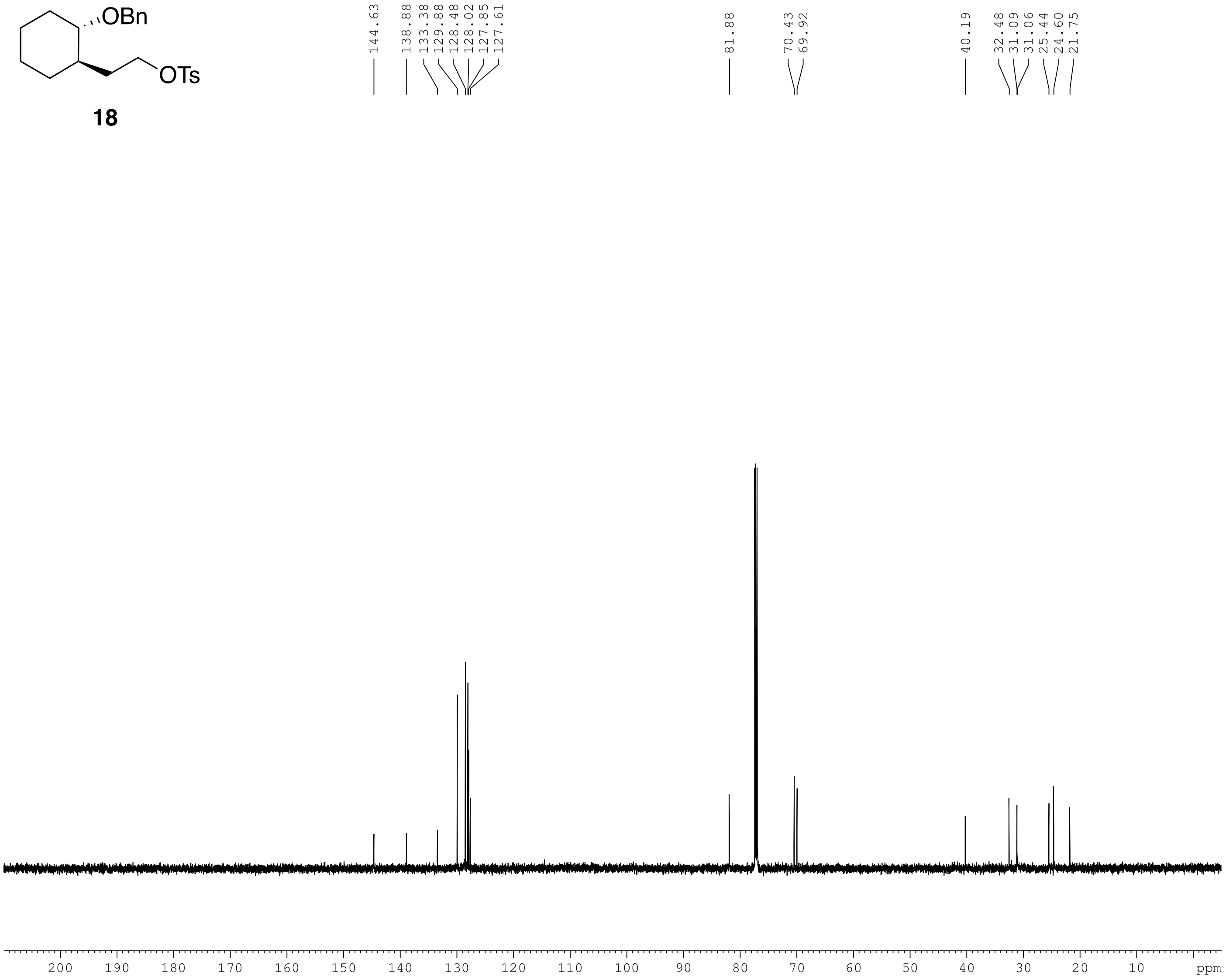


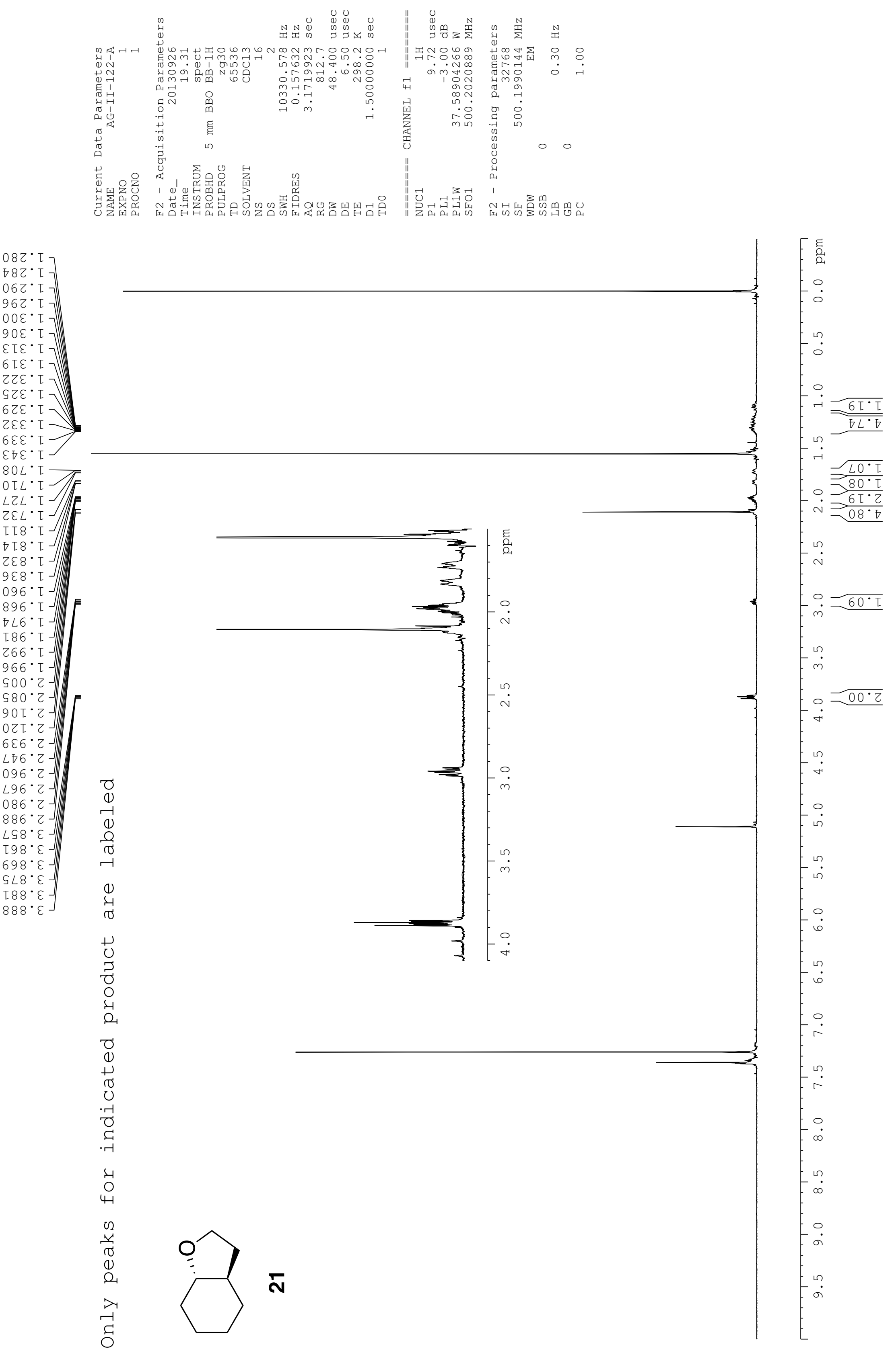
```
Current Data Parameters
NAME     AG-1-205-P_ii_C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130623
Time              21.10
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 232
DS                   4
SWH          36057.691 Hz
FIDRES        0.550197 Hz
AQ           0.9088159 sec
RG              184.65
DW              13.867 usec
DE                6.50 usec
TE               298.0 K
D1          2.50000000 sec
D11         0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1               15.00 usec
PLW1      106.00000000 W
SFO1       150.9329866 MHz

======== CHANNEL f2 ========
CPDPRG2        waltz16
NUC2                1H
PCPD2            70.00 usec
PLW2        9.30000019 W
PLW12       0.18190999 W
PLW13       0.08913500 W
SFO2       600.1924008 MHz

F2 - Processing parameters
SI               32768
SF         150.9178772 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```



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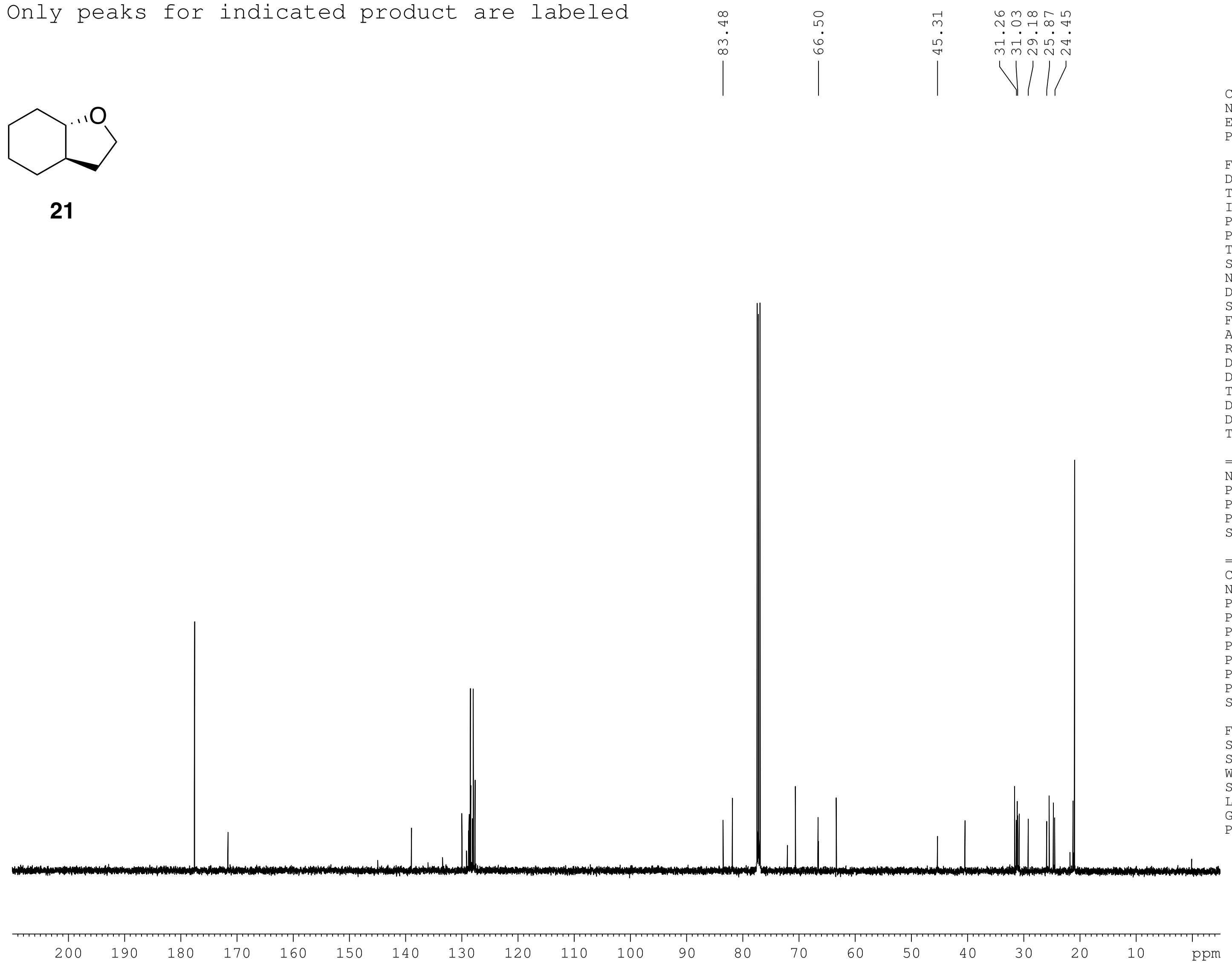
Only peaks for indicated product are labeled

Only peaks for indicated product are labeled



21

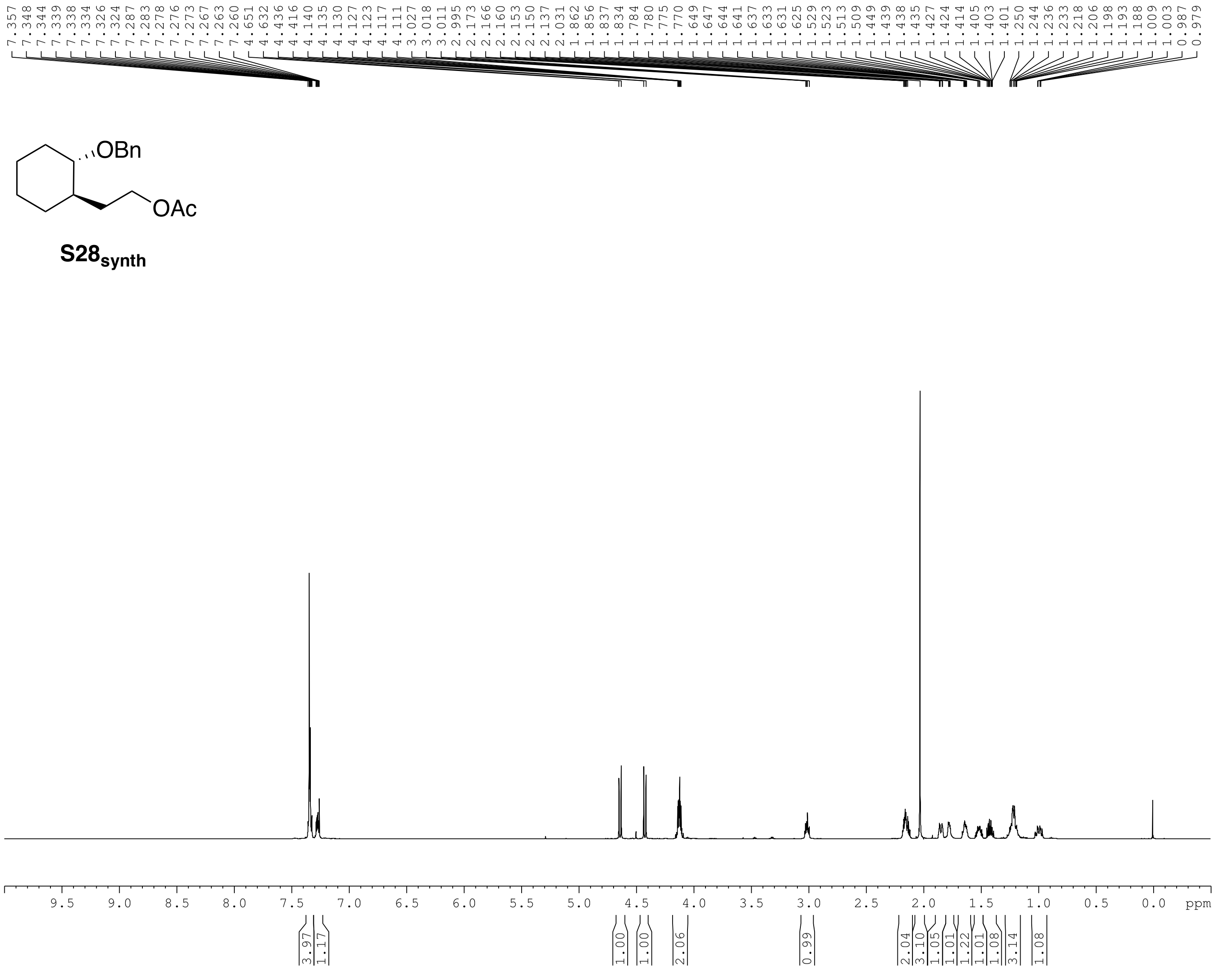
```
Current Data Parameters
NAME     AG-II-45_s1_C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20130805
Time               21.12
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  540
DS                    4
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912244 sec
RG              23170.5
DW               16.650 usec
DE                 6.50 usec
TE                298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1                 10.41 usec
PL1                 2.00 dB
PL1W         49.29017639 W
SFO1         125.7877161 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -3.00 dB
PL12               15.31 dB
PL13               18.31 dB
PL2W         37.58904266 W
PL12W         0.55470389 W
PL13W         0.27801058 W
SFO2         500.2010008 MHz

F2 - Processing parameters
SI                 32768
SF           125.7751245 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



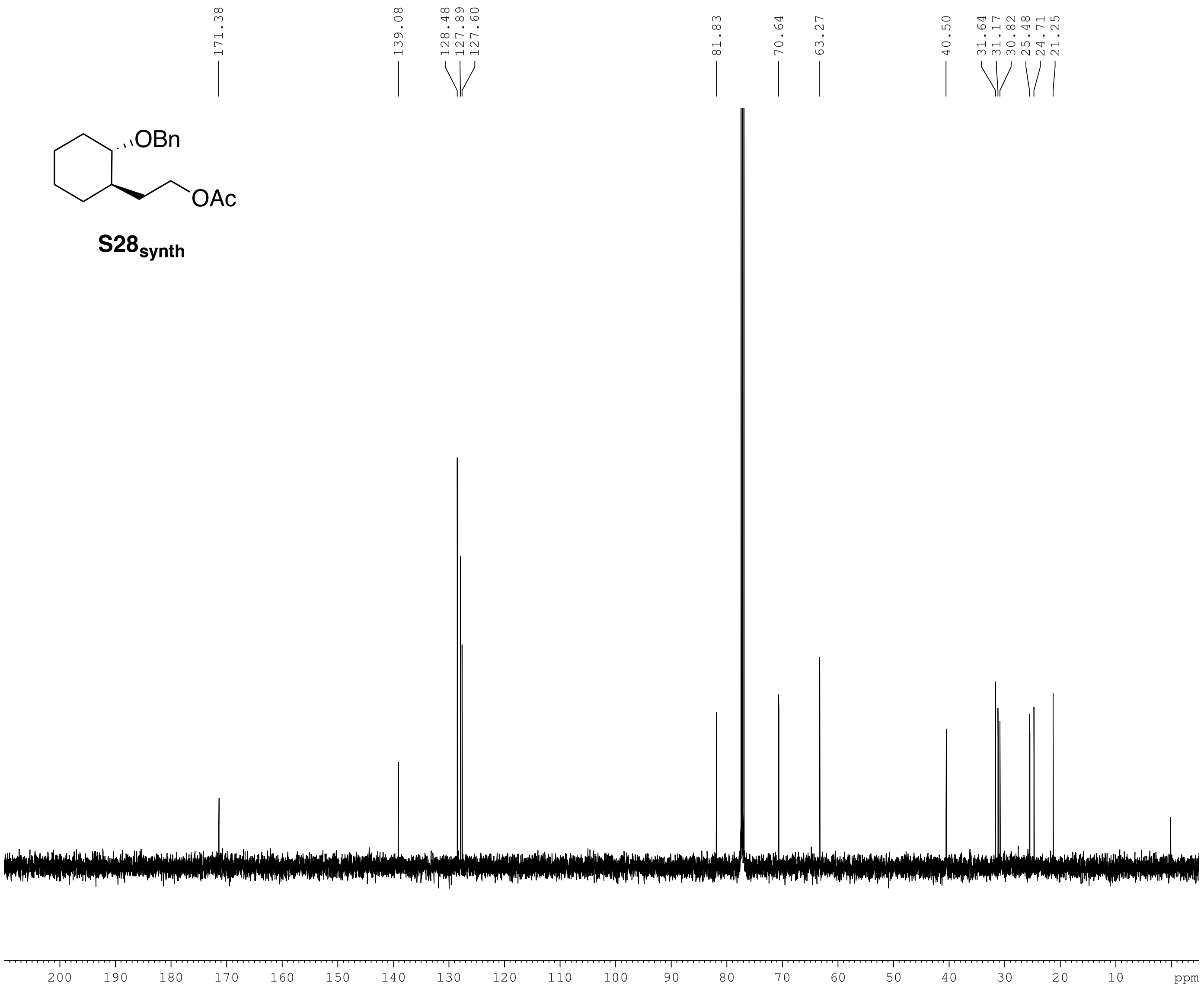
S28$_{synth}$

```
Current Data Parameters
NAME        AG-II-28-P2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130806
Time              20.37
INSTRUM           spect
PROBHD   5 mm PAQXI 1H/
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           12335.526 Hz
FIDRES         0.188225 Hz
AQ            2.6564426 sec
RG                33.59
DW               40.533 usec
DE                 6.50 usec
TE                298.1 K
D1          2.00000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        600.1937064 MHz
NUC1                 1H
P1                 9.79 usec
PLW1         9.30000019 W

F2 - Processing parameters
SI                65536
SF          600.1900141 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



S28$_{synth}$

```
Current Data Parameters
NAME     AG-II-28-P_C13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20130806
Time              17.20
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  202
DS                    4
SWH           30030.029 Hz
FIDRES         0.458222 Hz
AQ            1.0912244 sec
RG                16384
DW               16.650 usec
DE                 6.50 usec
TE                298.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                10.41 usec
PL1                2.00 dB
PL1W        49.29017639 W
SFO1        125.7877161 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PL2               -3.00 dB
PL12              15.31 dB
PL13              18.31 dB
PL2W        37.58904266 W
PL12W        0.55470389 W
PL13W        0.27801058 W
SFO2        500.2010008 MHz

F2 - Processing parameters
SI                32768
SF          125.7751223 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```