Supporting Information for *Angew. Chem. Int. Ed.* Z **18047**

A Boronic Ester Annulation Strategy for Diversity-Oriented Organic Synthesis

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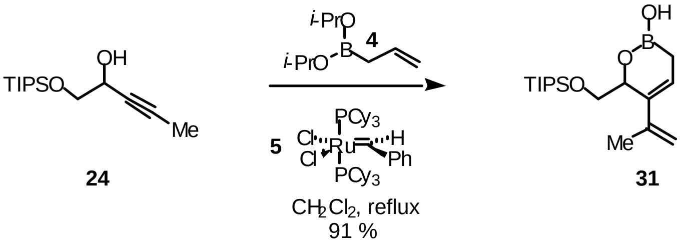
Materials and Methods. Except as otherwise noted, reactions were carried out under nitrogen with dry, freshly purified solvents. Solvents were purified by passage through a solvent column prior to use.[1] NMR spectra were recorded at either 500 MHz or 300 MHz using a Varian I-500 or a Varian M-300 instrument respectively. ^{1}H NMR chemical shifts are reported relative to residual $CHCl_3$ (7.26 ppm). ^{13}C NMR data were recorded at 125 MHz using a Varian I-500 instrument. ^{13}C chemical shifts are reported relative to the central line of $CDCl_3$ (77.0 ppm). ^{11}B NMR data were recorded at 96 MHz using a Varian M-300 instrument. Infrared spectra were recorded using a Nicolet 5PC FT-IR spectrometer (thin film). Mass spectra were obtained with JEOL AX 505, JEOL SX-102 and Micromass ESI-LCT spectrometers.



2-Hydroxy-5-(propen-2'-yl)-6-triisopropylsilanyloxymethyl-1,2-oxaborole (31): To a rt solution of the diisopropoxyallylboronic ester **4** (1.01 g, 5.94 mmol) and the propargylic alcohol **24** (514 mg, 2.00 mmol) was added 10 mL of CH_2Cl_2 followed by

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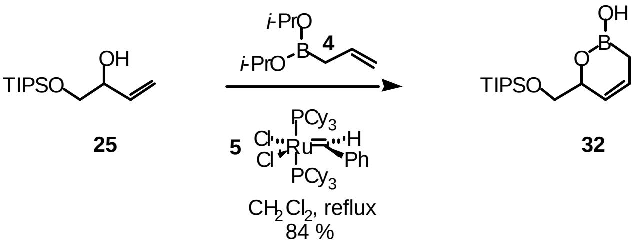
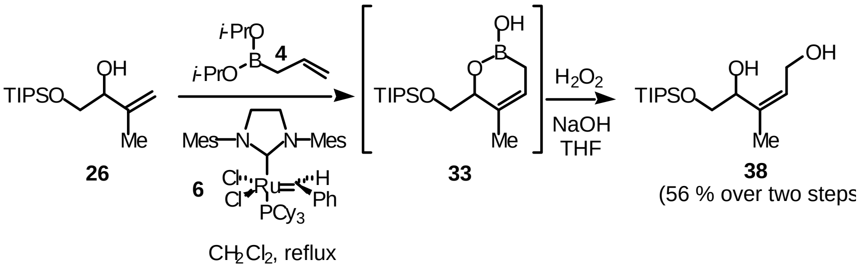
[1] The solvent columns are composed of activated alumina (A-2) and supported copper redox catalyst (Q-5 reactant). See: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

$(Cy_3P)_2Cl_2RuCHPh$ (340 mg, 0.4 mmol). The solution was then heated to reflux under N_2 for 24 h, after which time the solution was cooled to rt, diluted with EtOAc and washed with $NaHCO_3$ (sat) containing 0.5 mL Et_3N, then $KHSO_4$ (1N) (2x), then $NaHCO_3$ (sat), and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated to afford a crude oil which was purified by flash column chromatography [100 g SiO_2; eluted with 18 : 1 hexanes : EtOAc (1 L)] to afford 630 mg of the cyclic dienylic boronic acid **31** contaminated with 6 wt% 2-methyl-1-propanol (91% adjusted). A fraction of the impure material was repurified by flash column chromatography to obtain an enriched sample of **31**: ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 5.93 (dd, J = 5.6, 3.2 Hz, 1 H), 4.88 (s, 1 H), 4.74 (s, 1 H), 4.67 (s, 1 H), 3.73 (dd, J = 10.3, 2.9 Hz, 1 H), 3.62 (dd, J = 10.0, 3.2 Hz, 1.73 (s, 3 H), 1.41-1.29 (m, 2 H), 0.92-0.82 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 140.7, 135.7, 125.8, 109.9, 75.0, 66.0, 21.2, 17.44, 17.41, 11.7; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.6; IR (thin film) 3418, 3091, 2943, 2866, 1639, 1606, 1462, 1384, 1303, 1263, 1120, 1068, 1010 cm^{-1}.



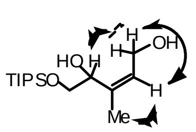
2-Hydroxy-6-triisopropylsilanyloxymethyl-1,2-oxaborole (32): To a rt solution of the diisopropoxyallylboronic ester **4** (250 mg, 1.47 mmol) and the allylic alcohol **25** (125mg, 0.51 mmol) was added 1.5 mL of CH_2Cl_2 followed by $(Cy_3P)_2Cl_2RuCHPh$ (35mg, 0.04 mmol). The solution was then heated to reflux under N_2 for 16 h, after which time the solution was cooled to rt, diluted with EtOAc and washed with $NaHCO_3$ (sat) containing 0.5 mL Et_3N, then $KHSO_4$ (1N) 2x, then $NaHCO_3$ (sat), and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated to afford a crude oil which was purified by flash column chromatography [60 g SiO_2; eluted with 18 : 1 hexanes : EtOAc (500 mL); 9 : 1 hexanes : EtOAc (500 mL)] to afford 122 mg of the cyclic allylboronic acid **32** (84%): ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 5.75-5.71 (m, 1 H), 5.49 (ddd, J = 10.1, 4.8, 2.1 Hz, 1 H), 4.50-4.46 (m, 1 H), 3.61-3.59 (m, 2 H), 1.22 (app dd, J = 7.3, 5.6 Hz, 2 H), 0.96-0.87 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 126.3, 125.9, 75.0, 66.9, 17.5, 11.7; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 30.9; IR (thin film) 3422, 3028, 2943, 2866, 1464, 1390, 1276, 1126, 1069, 1014 cm^{-1}.

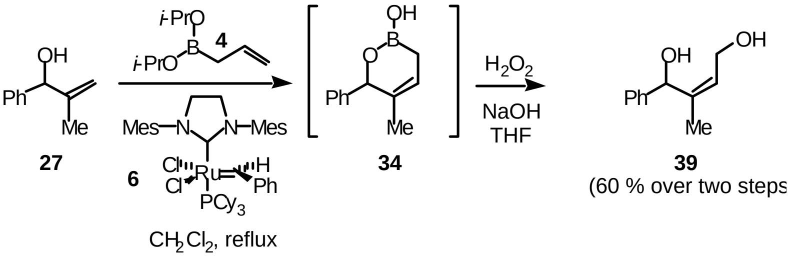


(*Z*)-5-triisopropylsilanyloxy-3-methyl-2-ene-1,4-diol (38): To a rt solution of the diisopropoxyallylboronic ester **4** (340 mg, 2.00 mmol) and the allylic alcohol **26** (148 mg, 1.00 mmol) was added 5 mL of CH_2Cl_2 followed by $(Cy_3P)(C_{21}H_{26}N_2)Cl_2RuCHPh$ (102 mg, 0.12 mmol). The solution was then heated to reflux under N_2 for 17 h, after which time the solution was cooled to rt. The reaction mixture was concentrated and purified by flash column chromatography [80 g SiO_2; eluted with 1L 14 : 1 hexanes : EtOAc (1 L)] to afford 205 mg of an impure oil which was used in the subsequent oxidation without further purification.

To a rt solution of the crude allylboronic acid **33** in THF (5 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with Et_2O and washed with $NaHCO_3$ (sat) (2x), diluted further with EtOAc and washed with brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (375 mL); 1 : 1 hexanes : EtOAc (500 mL)], affording 156 mg of the allylic alcohol **38** (54% over two steps): ^1H NMR (500 MHz, $CDCl_3$) δ 5.64 (dd, *J* = 7.1, 7.1 Hz, 1 H), 4.55 (dd, *J* = 6.3, 6.3 Hz, 1 H), 4.17-4.08 (m, 2 H), 3.65 (m, 2 H), 3.2-2.6 (br s, 1 H), 2.5-2.0 (br s, 1 H), 1.75 (s, 3 H), 1.12-1.06 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 127.8, 71.3, 65.5, 58.0, 19.2, 17.9, 11.8; IR (thin film) 3360, 2943, 2867, 1463, 1383, 1247, 1117, 1063, 1015 cm^{-1}; HRMS (TOF ES) calcd for $C_{15}H_{33}O_3Si$, 289.2199 *m/z* $(M+H)^+$; observed 289.2205 *m/z*.

Observed nOe's for **38**:



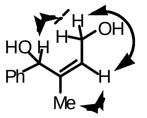


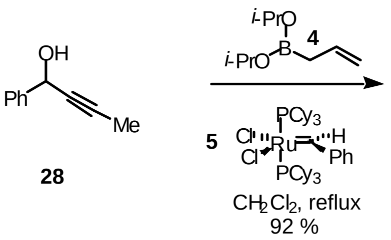
(*Z*)-5-phenyl-3-methyl-2-ene-1,4-diol (39): To a rt solution of the diisopropoxyallylboronic ester **4** (375 mg, 2.20 mmol) and the allylic alcohol **27** (165 mg, 1.11 mmol) was added 5 mL of CH_2Cl_2 followed by $(Cy_3P)(C_{21}H_{26}N_2)Cl_2RuCHPh$ (68 mg, 0.08

mmol). The solution was then heated to reflux under N_2 for 17 h, after which time the solution was cooled to rt. The reaction mixture was concentrated and purified by flash column chromatography [80 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (1 L)] to afford 152 mg of an impure oil which was used in the subsequent oxidation without further purification.

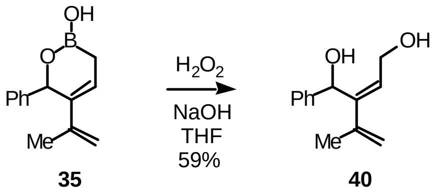
To a rt solution of the crude allylboronic acid **34** in THF (5 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with Et_2O and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (375 mL); 1 : 1 hexanes : EtOAc (400 mL)], affording 120 mg of the allylic alcohol **39** (60% over two steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.24 (m, 5 H), 5.68 (s, 1 H), 5.63 (dd, *J* = 7.1, 7.1 Hz, 1 H), 4.42 (dd, *J* = 12.2, 8.3 Hz, 1 H), 4.19 (dd, *J* 12.2, 5.9 Hz, 1 H), 3.45 (br s, 1 H), 2.89 (br s, 1 H), 1.61 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 141.4, 128.3, 127.2, 126.2, 125.7, 71.3, 58.1, 18.4; IR (thin film) 3342, 3028, 2921, 1665, 1603, 1494, 1450, 1377, 1323, 1245, 1173, 1084, 1009 cm^{-1}; HRMS (CI, NH_3) calcd for $C_{11}H_{18}NO_2$, 196.1338 *m/z* $(M+NH_4)^+$; observed 196.1332.

Observed nOe's for **39**:



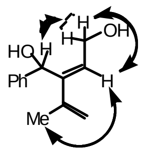


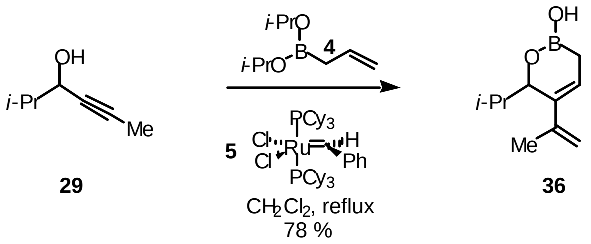
2-Hydroxy-5-(propen-2'-yl)-6-phenyl-1,2-oxaborole (35): To a rt solution of the diisopropoxyallylboronic ester **4** (350 mg, 2.06 mmol) and the propargylic alcohol **28** (150 mg, 1.03 mmol) was added 5 mL of CH_2Cl_2 followed by $(Cy_3P)_2Cl_2RuCHPh$ (70 mg, 0.09 mmol). The solution was then heated to reflux under N_2 for 38 h, after which time the solution was cooled to rt. The reaction mixture was then concentrated and purified by flash column chromatography [80 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (1 L); 4 : 1 hexanes : EtOAc (500 mL)] to afford 217 mg of the cyclic dienylic boronic acid **35** contaminated with 6 wt% 2-methyl-1-propanol (92% adjusted): ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 7.18-7.10 (m, 5 H), 6.10 (dd, *J* = 6.1, 0.5 Hz, 1 H), 5.77 (s, 1 H), 4.66 (s, 1 H), 4.55 (s, 1 H), 1.75 (s, 3 H), 1.48 (app dd, *J* = 21.0, 6.3 Hz, 1 H), 1.35 (app d, *J* = 21.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 141.7, 140.3, 138.3, 128.2, 127.6, 127.0, 124.5, 111.8, 76.6, 21.0, 17.4; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.3; IR (thin film) 3224, 2926, 1493, 1379, 1295, 1262, 1019 cm^{-1}; LRMS (ApCI) calcd for $C_{13}H_{16}BO_2$, 215.1 *m/z* $(M+H)^+$; observed 215.0.



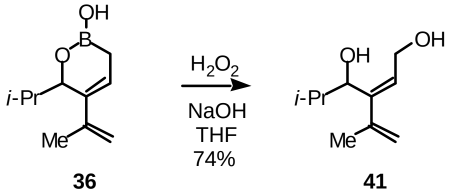
(*Z*)-5-phenyl-3-(propen-2’yl)-2-ene-1,4-diol (40): To a rt solution of the dienylic boronic acid **35** (215 mg. 1.00 mmol) in THF (5 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with Et_2O and washed with $NaHCO_3$ (sat), then diluted further with EtOAc and washed with brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (375 mL); 3 : 2 hexanes : EtOAc (500 mL)], affording 120 mg of the allylic alcohol **40** (59%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.23 (m, 5 H), 5.99 (dd, *J* = 6.6, 6.6 Hz, 1 H), 5.78 (s, 1 H), 4.96 (app s, 2 H), 4.30-4.22 (m, 2 H), 3.70-3.30 (br s, 1 H), 3.10-2.60 (br s, 1 H), 1.87 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 142.5, 142.4, 129.0, 128.3, 127.1, 125.7, 114.9, 71.1, 58.9, 22.4; IR (thin film) 3353, 3086, 3061, 3028, 2921, 1604, 1493, 1449, 1379, 1322, 1257, 1190, 1125, 1056, 1026 cm^{-1}; HRMS (CI, NH_3) calcd for $C_{13}H_{20}NO_2$, 222.1494 *m/z* $(M+NH_4)^+$; observed 222.1492.

Observed nOe's for **40**:



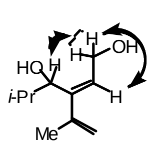


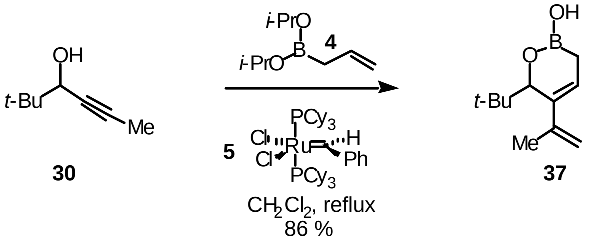
2-Hydroxy-5-(propen-2’-yl)-6-(propyl-2’’yl)-1,2-oxaborole (36): To a rt solution of the diisopropoxyallylboronic ester **4** (350 mg, 2.06 mmol) and the propargylic alcohol **29** (114 mg, 1.02 mmol) was added 5 mL of CH_2Cl_2 followed by $(Cy_3P)_2Cl_2RuCHPh$ (63 mg, 0.08 mmol). The solution was then heated to reflux under N_2 for 20 h, after which time the solution was cooled to rt. The reaction mixture was then concentrated and purified by flash column chromatography [90 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (1 L)] to afford 157 mg of the cyclic dienylic boronic acid **36** contaminated with 9 wt% 2-methyl-1-propanol (78 % adjusted): ^1H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 5.83 (m, 1 H), 4.71 (s, 1 H), 4.71-4.70 (m, 1 H), 4.67 (s, 1 H), 1.87-1.79 (m, 1 H), 1.71 (s, 3 H), 1.34-1.24 (m, 2 H), 0.89 (d, *J* = 7.3 Hz, 3 H), 0.54 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 141.4, 139.0, 123.3, 110.6, 78.9, 32.9, 21.3, 19.5, 14.3; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 30.9; IR (thin film) 3415, 3091, 2966, 2930, 2873, 1636, 1606, 1418, 1384, 1334, 1296, 1269, 1220, 1179, 1140, 1068, 1017 cm^{-1}.



(*Z*)-5-methyl-3-(propen-2'yl)-2-hexene-1,4-diol (41): To a rt solution of the dienylic boronic acid **36** (100mg, 0.56 mmol) in THF (5 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with Et_2O and washed with $NaHCO_3$ (sat), then diluted further with EtOAc and washed with brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (375 mL); 3 : 2 hexanes : EtOAc (500 mL)], affording 70 mg of the allylic alcohol **41** (74 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.80 (dd, *J* = 6.8, 6.8 Hz, 1 H), 5.09 (s, 1 H), 4.97 (m, 1 H), 4.31 (app ddd, *J* = 26.3, 13.2, 6.8 Hz, 2 H), 4.21 (d, *J* = 8.8 Hz, 1 H), 2.81 (app s, 2H), 1.99-1.91 (m, 1 H), 1.91 (s, 3 H), 1.02 (d, *J* = 6.3 Hz, 3 H), 0.77 (d, *J* 6.8 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl3) δ 145.1, 143.6, 128.5, 114.3, 76.2, 58.8, 32.8, 23.0, 19.4, 19.1; IR (thin film) 3359, 2959, 2871, 1626, 1605, 1468, 1452, 1382, 1263, 1112, 1014 cm^{-1}; HRMS (CI, NH_3) calcd for $C_{10}H_{22}NO_2$, 188.1651 *m/z* $(M+NH_4)^+$; observed 188.1652.

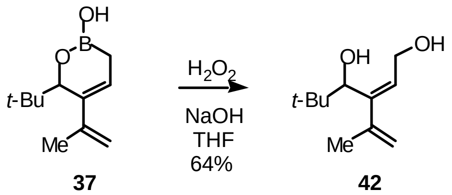
Observed nOe's for **41**:





2-Hydroxy-5-(propen-2'-methyl-2'-yl)-6-(propyl-2''yl)-1,2-oxaborole (37): To a rt solution of the diisopropoxyallylboronic ester **4** (352 mg, 2.07 mmol) and the propargylic alcohol **30** (127 mg, 1.01 mmol) was added 5 mL of CH_2Cl_2 followed by $(Cy_3P)_2Cl_2RuCHPh$ (65 mg, 0.08 mmol). The solution was then heated to reflux under

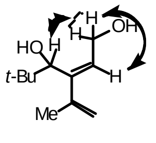
N_2 for 19 h, after which time the solution was cooled to rt. The reaction mixture was then concentrated and purified by flash column chromatography [90 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (1 L)] to afford 182 mg of the cyclic dienylic boronic acid **37** contaminated with 9 wt% 2-methyl-1-propanol (86 % adjusted). An enriched sample of **37** was obtained from a central fraction from the purification process: ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 5.85 (dd, *J* = 5.4, 3.4 Hz, 1 H), 4.76 (s, 1 H), 4.65 (s, 1 H), 4.51 (dd, *J* = 1.7, 1.7 Hz, 1 H), 1.73 (s, 3 H), 1.32-1.22 (m, 2 H), 0.72 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 144.5, 140.2, 124.4, 110.7, 81.8, 39.2, 25.9, 21.6; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.0; IR (thin film) 3405, 3232, 3087, 2954, 2871, 1638, 1479, 1465, 1374, 1310, 1263, 1216, 1190, 1127, 1102, 1033, 1008 cm^{-1}.

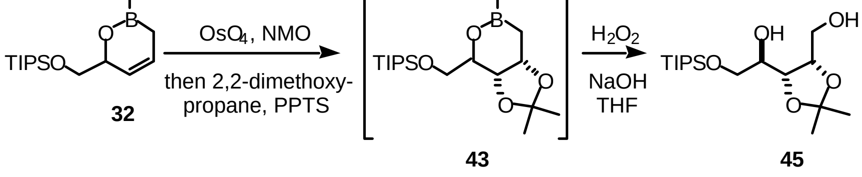


37 **42**

(*Z*)-5,5-dimethyl)-3-(propen-2'yl)-2-hexene-1,4-diol (42): To a rt solution of the dienylic boronic acid **37** (169 mg, 0.87 mmol) in THF (5 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with Et_2O and washed with $NaHCO_3$ (sat), then diluted further with EtOAc and washed with brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (375 mL); 3 : 2 hexanes : EtOAc (500 mL)], affording 102 mg of the allylic alcohol **42** (64 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.78 (dd, *J* = 7.1, 7.1 Hz, 1 H), 4.99 (s, 1 H), 4.86 (s, 1 H), 4.48 (app dd, *J* = 12.7, 7.3 Hz, 1 H), 4.36 (s, 3 H), 4.16 (app dd, *J* = 12.9, 7.1 Hz, 1 H), 3.07 (br s, 2 H), 1.92 (s, 3 H), 0.90 (s, 9 H); ^{13}C NMR (125 MHz, CDCl3) δ 146.9, 144.7, 129.2, 113.7, 78.8, 59.4, 36.8, 26.5, 23.4; IR (thin film) 3388, 3082, 2955, 2871, 1610, 1481, 1465, 1392, 1363, 1301, 1236, 1218, 1185, 1126, 1066, 1006 cm^{-1}; HRMS (CI, NH_3) calcd $C_{11}H_{24}NO_2$ 202.1807 *m/z* $(M+NH_4)^+$; observed 202.1805.

Observed nOe's for **42**:





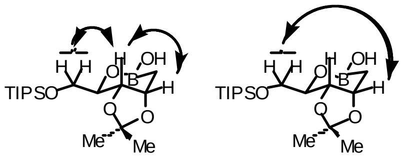
32

43
(d.s. >13:1)

45
44%
(3 steps)

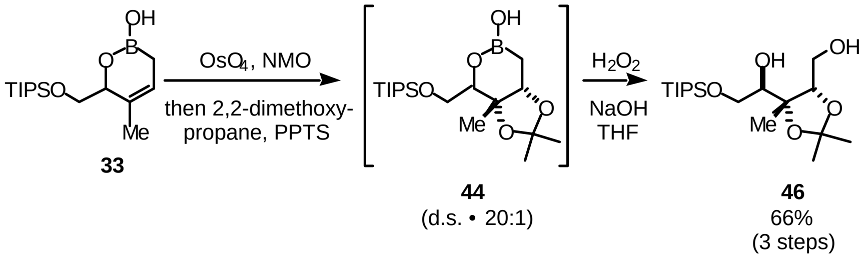
4-Hydroxymethyl-5-(2'-triisopropylsilanyloxy-1'-hydroxy-1'-ethyl)-1,3-dioxolane (45): To a rt solution of the cyclic allylboronic acid **32** (67 mg, 0.24 mmol) in acetone (1.5 mL) and pH 7 buffer (0.5 mL) was added OsO_4 (50 µL, 2.5 wt. % in 2-methyl-2-propanol) followed by *N*-methylmorpholine-*N*-oxide (50 wt. % in H_2O). The solution was stirred at rt for 3 h, then 1 mL of 0.5 M $Na_2S_2O_3$ was added, and the solution was stirred an additional 15 min. The solution was diluted with EtOAc and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4, filtered and concentrated to afford a crude oil which was used in the next step without further purification.

To a rt solution of the crude diol in CH_2Cl_2 (3 mL) was added 2,2-dimethoxypropane (500 µL) followed by PPTS (25 mg). The solution was stirred at rt for 1 h, then diluted with EtOAc and washed with $NaHCO_3$ (sat) followed by brine. The organic phase was dried over Na_2SO_4, filtered and concentrated to afford 67 mg of the crude bicyclic boronic acid **43** (79 %; d.s. >13 : 1): ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 4.30 (dd, *J* = 12.7, 7.3 Hz, 1 H), 3.90 (dd, *J* = 6.6, 6.6 Hz, 1 H), 3.79-3.73 (m, 2 H), 3.66 (dd, *J* = 10.5, 8.3 Hz, 1 H), 1.26 (s, 3 H), 1.26-1.18 (m, 2 H), 1.15 (s, 3 H), 0.96-0.84 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 108.0, 75.2, 74.0, 71.8, 64.3, 27.0, 24.4, 18.4, 17.5, 11.6; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.3; IR (thin film) 3415, 2942, 2893, 2867, 1463, 1407, 1381, 1331, 1261, 1214, 1129, 1097, 1061, 1015 cm^{-1}.



Observed nOe's for **43**:

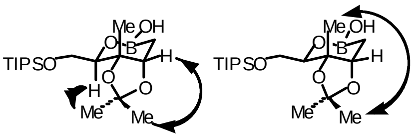
To a rt solution of the crude bicyclic boronic acid **43** (67 mg) in THF (3 mL) was simultaneously added NaOH (1 mL, 1N) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with EtOAc and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 4 : 1 hexanes : EtOAc (500 mL)], affording 38 mg of the xylitol derivative **45** (44 % over three steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.37 (ddd, *J* = 8.1, 5.5, 5.5 Hz, 1 H), 4.09 (dd, *J* = 9.8, 5.9 Hz, 1 H), 3.94 (dd, *J* = 9.8, 2.9 Hz, 1 H), 3.91-3.86 (m, 1 H), 3.83-3.76 (m, 1 H), 3.74 (dd, *J* = 9.8, 6.3 Hz, 1 H), 3.24 (dd, *J* = 9.0, 4.6 Hz, 1 H), 3.15 (d, *J* = 4.4 Hz, 1 H), 1.39 (s, 3 H), 1.33 (s, 3 H), 1.25-1.06 (m, 21 H); ^{13}C NMR (125 MHz, CDCl3) δ 108.5, 77.6, 76.5, 69.5, 64.5, 60.8, 27.8, 25.2, 17.89, 17.88, 11.8; IR (thin film) 3413, 2942, 2892, 2867, 1463, 1381, 1370, 1248, 1219, 1168, 1113, 1065 cm^{-1}; HRMS (TOF ES) calcd $C_{17}H_{37}O_5Si$ 349.2410 *m/z* $(M+H)^+$; observed 349.2390.



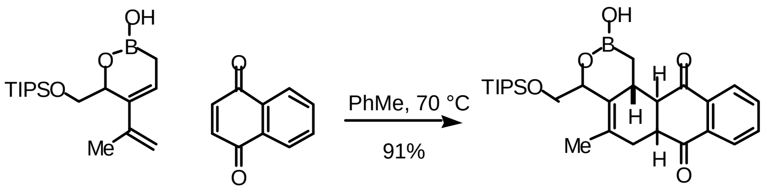
4-Hydroxymethyl-5-(2'-triisopropylsilanyloxy-1'-hydroxy-1'-ethyl)-5-methyl-1,3-dioxolane (46): To a rt solution of the cyclic allylboronic acid **33** (61 mg, 0.21 mmol) in acetone (1.5 mL) and pH 7 buffer (0.5 mL) was added OsO_4 (50 µL, 2.5 wt. % in 2-methyl-2-propanol) followed by *N*-methylmorpholine-*N*-oxide (50 wt. % in H_2O). The solution was stirred at rt for 3 h, then 1 mL of 0.5 M $Na_2S_2O_3$ was added, and the solution was stirred an additional 15 min. The solution was diluted with EtOAc and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4, filtered and concentrated to afford a crude oil which was used in the next step without further purification.

To a rt solution of the crude diol in CH_2Cl_2 (3 mL) was added 2,2-dimethoxypropane (500 µL) followed by PPTS (25 mg). The solution was stirred at rt for 1 h, then diluted with EtOAc and washed with $NaHCO_3$ (sat) followed by brine. The organic phase was dried over Na_2SO_4, filtered and concentrated to afford 69 mg of the crude bicyclic boronic acid **44** (91 %; d.s. >20 : 1): ^{1}H NMR (500 MHz, C_6D_6/CD_3OD (3/1)) δ 4.10 (d, *J* = 11.2 Hz, 1 H), 3.94 (app d, *J* = 7.3 Hz, 1 H), 3.86 (app dd, *J* = 10.3, 7.3 Hz, 1 H), 3.74 (dd, *J* = 8.3, 3.9 Hz, 1 H), 1.41-1.35 (m, 1 H), 1.35 (s, 3 H), 1.19 (s, 3 H), 1.08-1.02 (m, 22 H), 0.98 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 107.8, 80.2, 78.9, 77.3, 63.3, 27.8, 26.0, 18.1, 17.51, 17.49, 11.7; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.7; IR (thin film) 3406, 2943, 2867, 1463, 1406, 1379, 1291, 1257, 1215, 1087, 1018 cm^{-1}.

Observed nOe's for **44**:



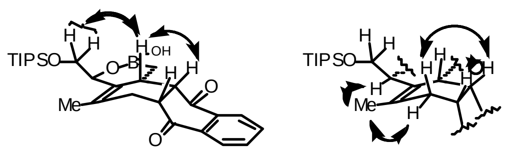
To a rt solution of the crude bicyclic boronic acid **44** (69 mg) in THF (3 mL) was simultaneously added 1N NaOH (1 mL) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with EtOAc and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 5.3 : 1 hexanes : EtOAc (475mL); 3 :1 hexanes : EtOAc (400 mL)], affording 48 mg of the substituted xylitol derivative **46** (66 % over three steps): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97-3.89 (m, 4 H), 3.85 (ddd, *J* = 8.9, 3.3, 1.6 Hz, 1 H), 3.72 (dd, *J* = 9.3, 9.3 Hz, 1 H), 3.37 (dd, *J* = 7.3, 7.3 Hz, 1 H), 3.28 (d, *J* = 1.5 Hz, 1 H), 1.37 (s, 3 H), 1.36 (s, 3 H), 1.33 (s, 3 H), 1.15-1.06 (m, 21 H); ^{13}C NMR (125 MHz, CDCl3) δ 107.8, 83.5, 82.2, 71.1, 62.8, 60.6, 28.3, 26.4, 19.8, 17.9, 11.8; IR (thin film) 3454, 2943, 2867, 1462, 1379, 1257, 1217, 1192, 1096, 1061, 1014 cm^{-1}; HRMS (TOF ES) calcd $C_{18}H_{39}O_5Si$ 363.2567 *m/z* (M+H)$^+$; observed 363.2559.



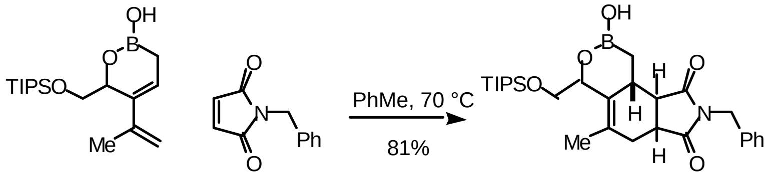
31 **47**
(d.s. • 13:1)

Tetracyclic boronic acid 47: A solution of the dienylic boronic acid **31** (55 mg, 0.17 mmol) and naphthoquinone (56 mg, 0.35 mmol) in toluene (2 mL) was heated at 70 °C for 36 h. The reaction mixture was concentrated and purified by flash column chromatography [60 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (500 mL); 6 :1 hexanes : EtOAc (1 L)], affording 75 mg of the tetracyclic boronic acid **47** (91%): ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 7.92-7.88 (m, 1 H), 7.83-7.79 (m, 1 H), 7.59-7.56 (m, 2 H), 4.83 (dd, *J* = 5.6, 5.6 Hz, 1 H), 3.66-3.59 (m, 2 H), 3.31-3.26 (m, 2 H), 2.03 (d, *J* = 18.1, 6.8 Hz, 1 H), 1.65 (s, 3 H), 0.97-0.84 (m, 21 H), 0.26 (dd, *J* = 15.6, 4.9 Hz, 1 H), 0.08 (dd, *J* = 15.6, 13.7 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 199.3, 198.0, 135.9, 135.4, 134.2, 133.8, 128.6, 127.6, 126.3, 125.8, 73.9, 66.1, 50.6, 44.3, 30.9, 28.5, 18.6, 17.5, 11.6; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 30.5; IR (thin film) 3453, 2943, 1692, 1594, 1464, 1380, 1332, 1282, 1254, 1207, 1119, 1069 cm^{-1}; LRMS (ApCI) calcd $C_{27}H_{39}BO_5Si$ 482.3 *m/z* (M)$^-$; observed 482.3.

Observed nOe's for **47**:

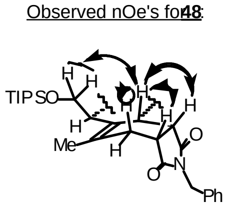


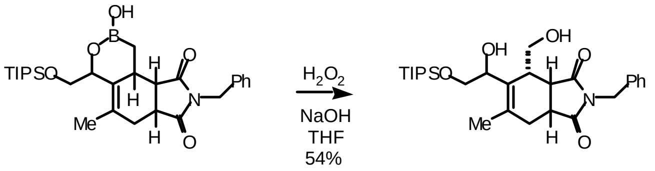
in C_6D_6/CD_3OD (3/1)



31 **48**
(d.s. >20:1)

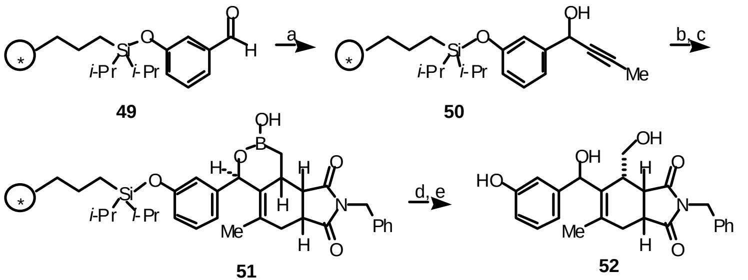
Tricyclic boronic acid (48): A solution of the dienylic boronic acid **31** (56 mg, 0.17 mmol) and *N*-benzylmaleimide (70 mg, 0.37 mmol) in toluene (2 mL) was heated at 70 °C for 36 h. The reaction mixture was concentrated and purified by flash column chromatography [60 g SiO_2; eluted with 9 : 1 hexanes : EtOAc (500 mL); 3 : 2 hexanes : EtOAc (500 mL); 1 : 1 hexanes : EtOAc (500 mL)], affording 71 mg of the tricyclic boronic acid **48** (81%): ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 7.13-7.07 (m, 5 H), 4.47-4.45 (m, 1 H), 4.46 (A of AB, *J* = 13.7 Hz, 1 H), 4.30 (B of AB, *J* = 14.2 Hz, 1 H), 3.54-3.47 (m, 2 H), 2.93-2.90 (m, 1 H), 2.82 (dd, *J* = 8.5, 5.1 Hz, 1 H), 2.54 (m, 1 H), 2.28 (dd, *J* = 14.7, 1.5 Hz, 1 H), 2.04 (dd, *J* = 14.7, 6.8 Hz, 1 H), 1.23 (s, 3 H), 1.18-1.15 (m, 2 H), 0.90-0.85 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 179.7, 178.9, 135.6, 130.8, 129.9, 128.1, 128.0, 127.4, 73.1, 67.0, 46.2, 41.8, 39.8, 31.9, 31.7, 18.4, 17.42, 17.39, 11.6; ^{11}B NMR (96 MHz, $CDCl_3/CD_3OD$ (3/1)) δ 31.0; IR (thin film) 3450, 3033, 2943, 2865, 1772, 1697, 1497, 1433, 1402, 1330, 1294, 1248, 1178, 1149, 1119, 1067 cm^{-1}.





48 **53**

2-Benzyl-5-methyl-6-(2’-triisopropylsilanyloxy-1’-hydroxy-eth-1’-yl)-7-hydroxymethyl-3a,4,7,7a-tetrahydro-isoindole-1,3-dione (53): To a rt solution of the tricyclic boronic acid **48** (35 mg, 0.07 mmol) in THF (3 mL) was simultaneously added 1 N NaOH (1 mL) and 500 µL H_2O_2 (30% in H_2O). The solution was stirred for 5 min. at rt, then diluted with EtOAc and washed with $NaHCO_3$ (sat) then brine. The organic phase was dried over Na_2SO_4 and purified via flash column chromatography [40 g SiO_2; eluted with 2.3 : 1 hexanes : EtOAc (300 mL); 2 :1 hexanes : EtOAc (300 mL)], affording 19 mg of the diol **49** (54 %): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2 H), 7.32-7.27 (m, 3 H), 4.74 (dd, *J* = 8.8, 4.4 Hz, 1 H), 4.64 (app s, 2 H), 3.57 (dd, *J* = 9.8, 4.9 Hz, 1 H), 3.51 (app dd, *J* = 9.3, 9.3 Hz, 1 H), 3.39-3.37 (m, 1 H), 3.32 (s, 1 H), 32.8-3.21 (m, 2 H), 2.99 (dd, *J* = 18.8, 9.5 Hz, 1 H), 2.91 (dd, *J* = 9.8, 6.3 Hz, 1 H), 2.88 (br s, 1 H), 2.53-2.44 (m, 2 H), 1.82 (s, 3 H), 1.13-1.05 (m, 21 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 179.4, 177.7, 135.6, 133.2, 131.0, 128.9, 128.6, 128.0, 70.1, 65.2, 60.9, 42.9, 42.3, 38.7, 37.0, 29.2, 19.8, 17.9, 11.8; IR (thin film) 3390, 2942, 2865, 1772, 1704, 1496, 1458, 1432, 1397, 1346, 1169, 1115, 1061 cm^{-1}; LRMS (TOF ES) calcd $C_{28}H_{44}NO_5Si$ 502.3 *m/z* $(M+H)^+$; observed 502.2.



49 **50** **51** **52**

ca. 90 nmol compound/bead
10 µL of 9 mM stock solution/bea

(a) 1-propynylmagnesium bromide, THF, 0°C to rt; (b) **4** (10 eq), **5** (15 mol %), CH_2Cl_2, 40 °C; (c) *N*-benzylmaleimide (8 eq), PhMe, 80 °C; (d) H_2O_2, NaOH, THF; (e) HF•pyr/pyr, THF.

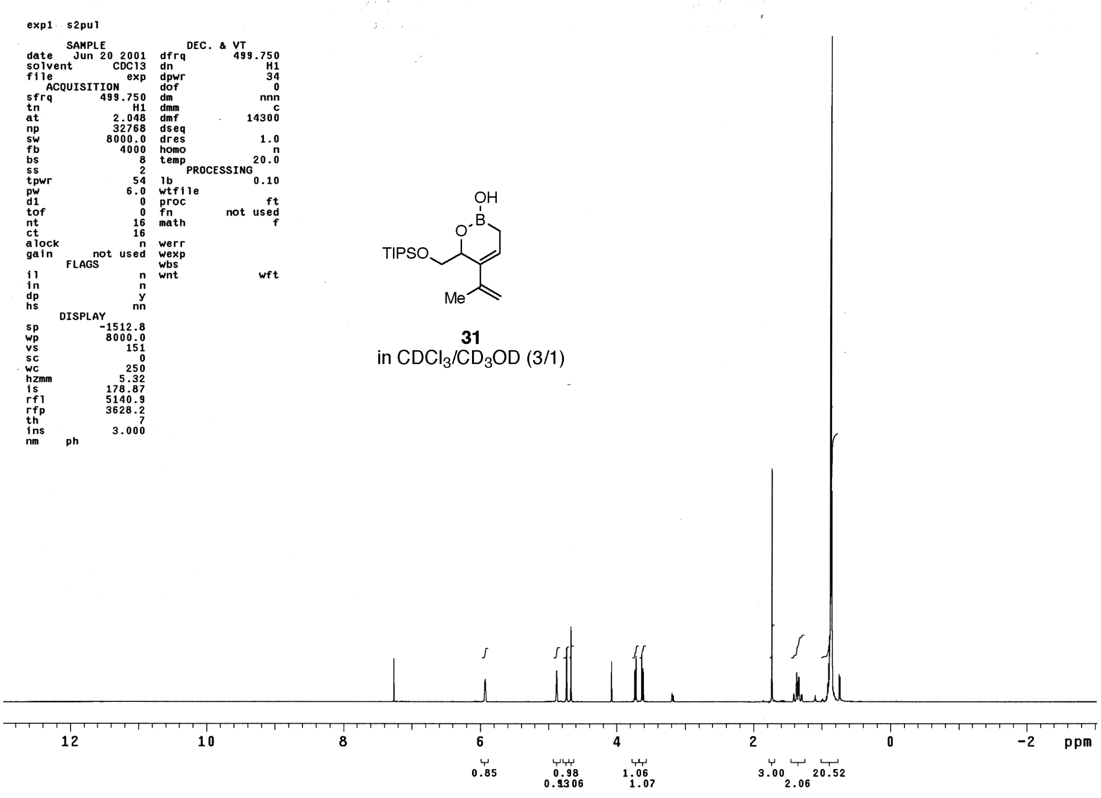
(a) To a 0 °C solution of the resin bound aldehyde **49** (400 mg @ ca. 1.4 mmol/g) in 2 mL THF was added 1-propynylmagnesium bromide (4 mL, 0.5 M solution in THF). The solution was allowed to warm to rt overnight, then remained at rt for an additional 10 h. To the rt solution was added NH_4Cl (sat), then the beads were washed successively with THF (2x), THF : *i*-PrOH (3 : 1) (1x); THF : H2O (2 : 1) (1x), then THF (tumbled overnight). The solid was then dried under reduced pressure for 12 h.

(b) The resin bound propargylic alcohol **50** (crude from (a)) was diluted with CH_2Cl_2 (3.5 mL). After 15 min, the diisopropoxyallylboronic ester **4** was added (1 mL) followed by $(Cy_3P)_2(Cl)_2Ru{=}CHPh$ (67 mg). The reaction vessel was flushed with argon, then sealed (screw cap vial) and heated at 40 °C. After 5 min, the vial was vented and flushed with argon. The vial was then sealed again and heated at 40 °C for 19h. The vessel was cooled to rt, the beads were removed and washed successively with CH_2Cl_2 (1x), THF (1x), THF : *i*-PrOH (3 : 1) (1x), THF (1x), then CH_2Cl_2 (1x). The solid was dried overnight under a stream of nitrogen, then via reduced pressure for 24 h.

(c) A solution of the resin bound diene (via (b)) and *N*-benzylmaleimide (800 mg, 4.3 mmol) in 2.5 mL of toluene was heated at 75 °C for 63 h. The resin was then washed successively with THF (2x), THF : *i*-PrOH (3 : 1) (1x), then THF (2x). The solid was then dried overnight under a stream of N2, then via reduced pressure for 6 h (providing 555 mg of crude **51**).

(d) To a rt solution of the resin bound tricycle **51** (52 mg) in 500 µL of THF was added NaOH (250 µL of a 1.0N solution) followed by H_2O_2 (30 % in H_2O). The vessel was sealed and tumbled for 30 min. The beads were then washed with THF (1x), THF : H_2O (3 : 1) (1x), then THF. The solid was then dried overnight under a stream of nitrogen, then under reduced pressure for 5 h.

(e) To a rt solution of the resin bound diol (100 beads) in THF was added 200 µL HF•pyr•pyr in THF (5% HF•pyr +5% pyr). The solution was agitated via shaking for 1 h, after which time TMSOMe (200 µL) was added. The solution was agitated via shaking for an additional 30 min, then solution was filtered through a plug of glass wool and the beads were washed successively with THF (2x), MeOH (2x), then CH_2Cl_2 (2x). The combined organics were combined and concentrated to afford 5.5 mg of **52** (>70 % pure by inspection of the ^{1}H NMR spectra; corresponds to ca. 90 nmol/bead).



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bs                8   temp            20.0
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tpwr             54   lb              0.10
pw              6.0   wtfile
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tof               0   fn          not used
nt               16   math               f
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alock             n   werr
gain       not used   wexp
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nm     ph
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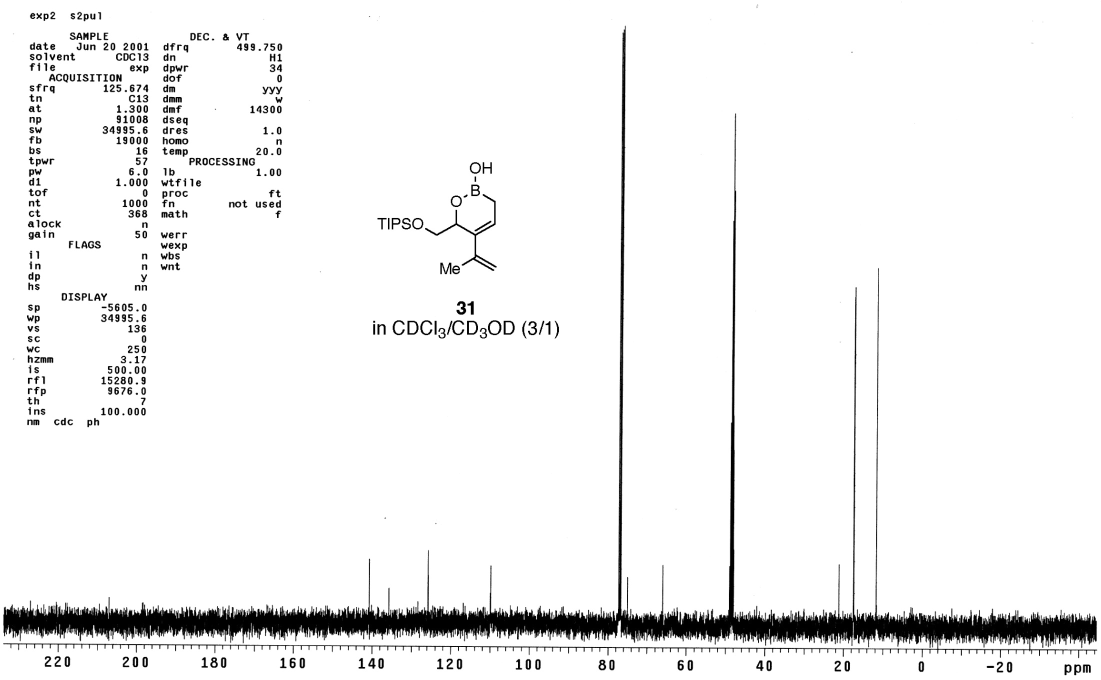
31
in $CDCl_3/CD_3OD$ (3/1)



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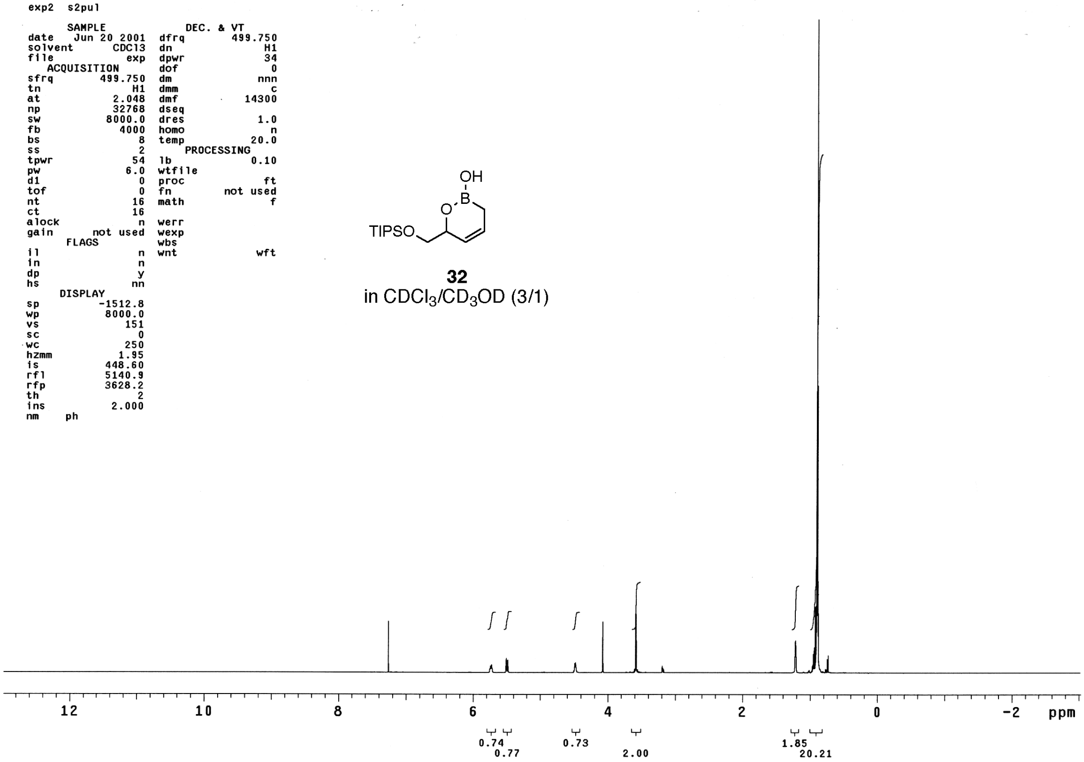
31
in $CDCl_3/CD_3OD$ (3/1)



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tn              H1  dmm              c
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np           32768  dseq
sw          8000.0  dres           1.0
fb            4000  homo             n
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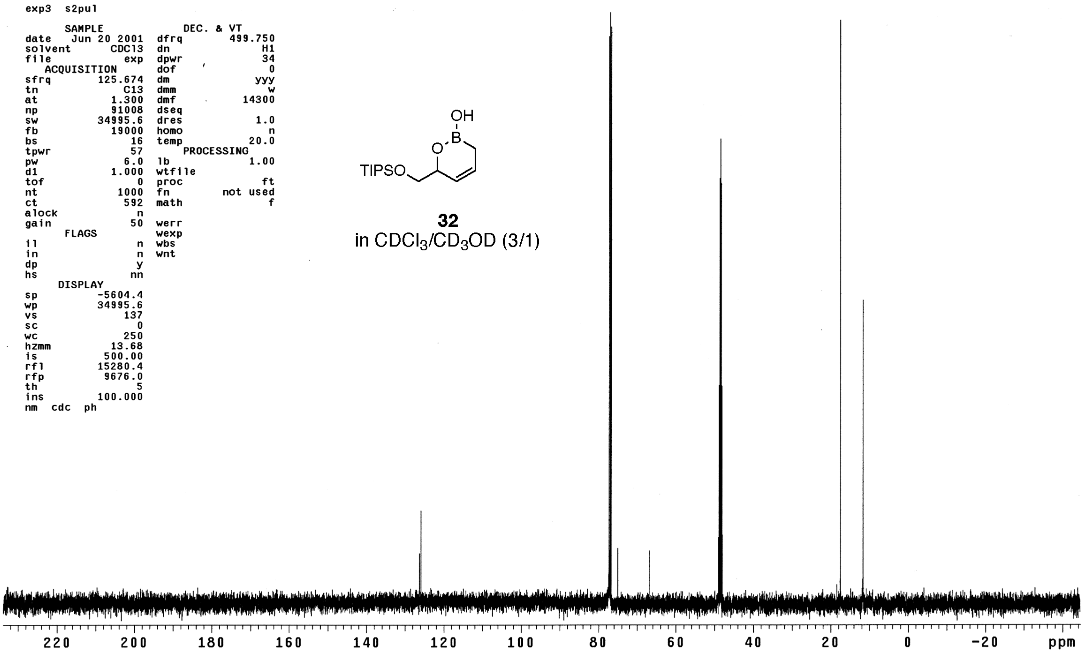
32
in $CDCl_3/CD_3OD$ (3/1)



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file           exp  dpwr            34
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tn             C13  dmm              w
at           1.300  dmf          14300
np           91008  dseq
sw         34995.6  dres           1.0
fb           19000  homo             n
bs              16  temp          20.0
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d1           1.000  wtfile
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nm  cdc  ph
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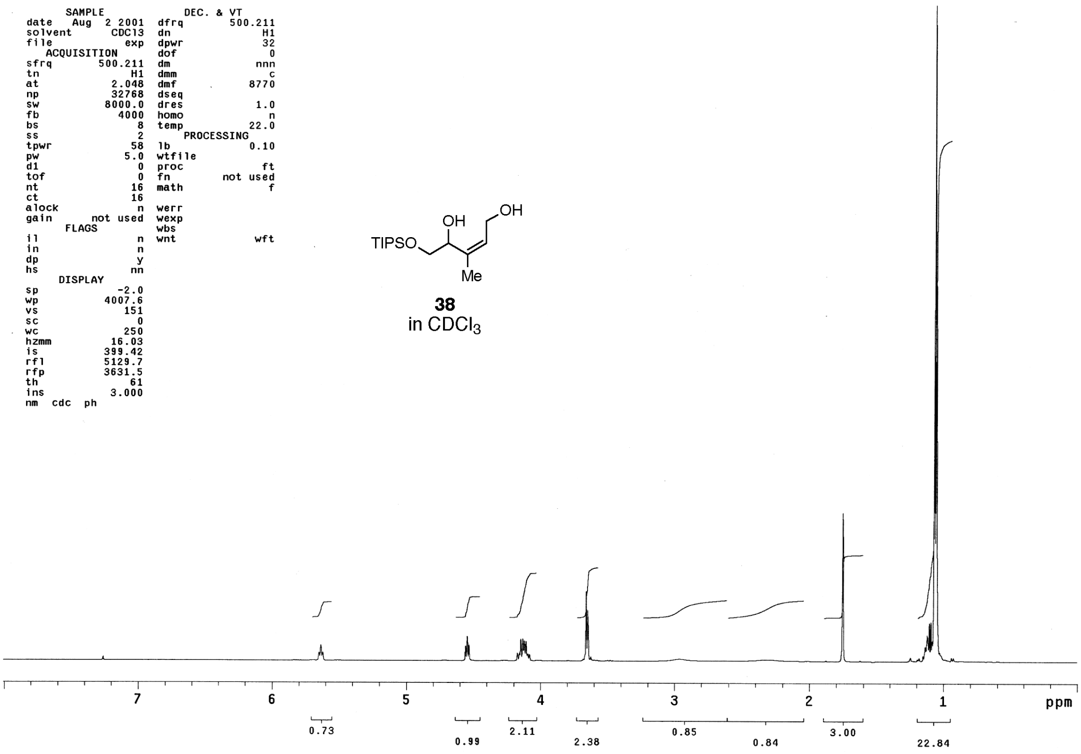
32
in $CDCl_3/CD_3OD$ (3/1)



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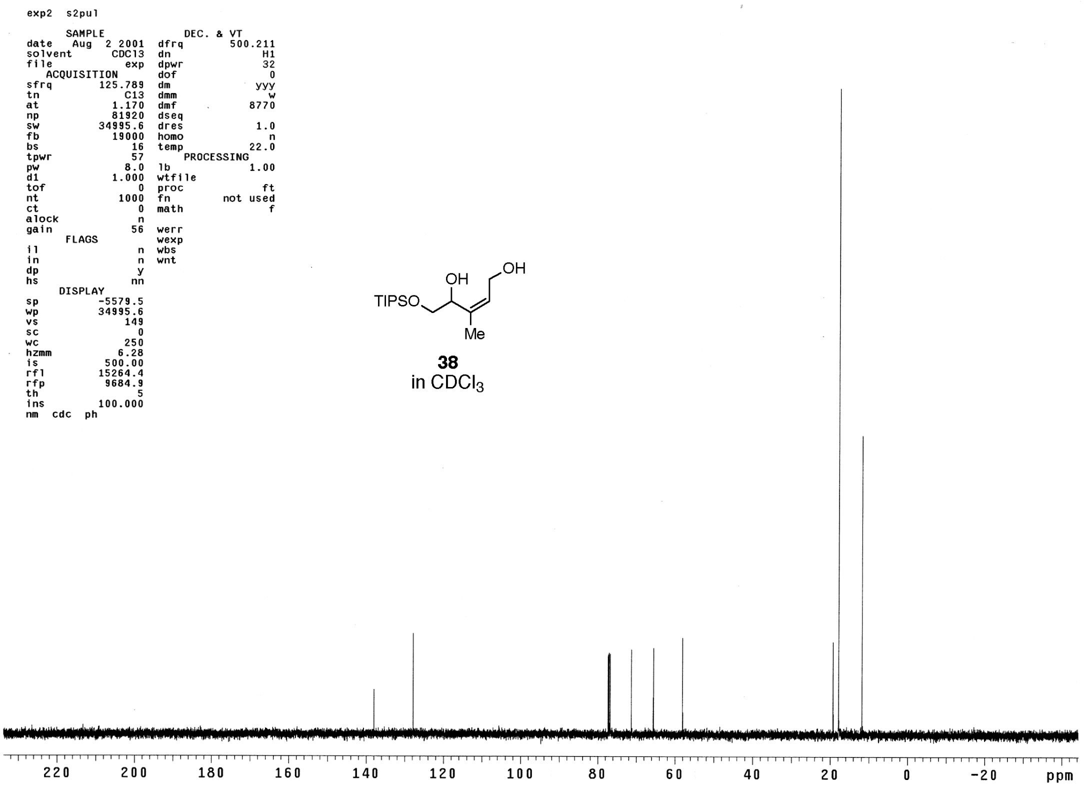
   ACQUISITION       dof               0
sfrq        500.211  dm              nnn
tn               H1  dmm               c
at            2.048  dmf            8770
np            32768  dseq
sw           8000.0  dres            1.0
fb             4000  homo              n
bs                8  temp           22.0
ss                2      PROCESSING
tpwr             58  lb             0.10
pw              5.0  wtfile
d1                0  proc             ft
tof               0  fn         not used
nt               16  math              f
ct               16
alock             n  werr
gain       not used  wexp
      FLAGS          wbs
il                n  wnt             wft
in                n
dp                y
hs               nn
     DISPLAY
sp             -2.0
wp           4007.6
vs              151
sc                0
wc              250
hzmm          16.03
is           399.42
rfl          5129.7
rfp          3631.5
th               61
ins           3.000
nm  cdc  ph
```

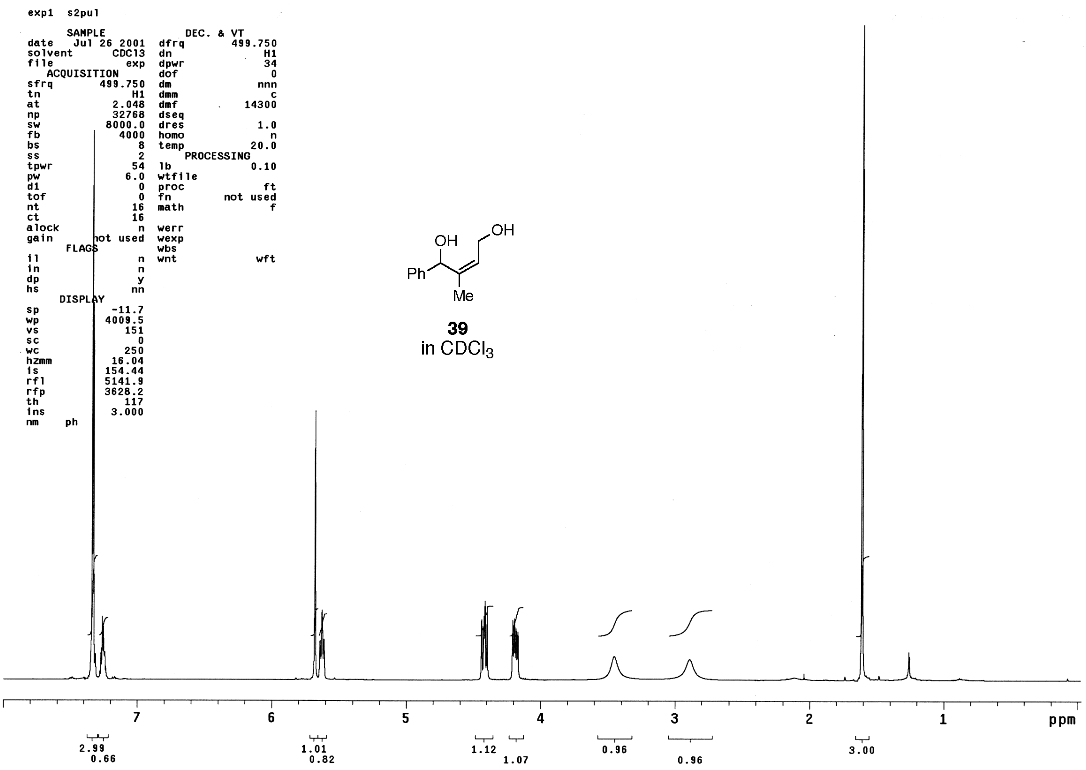
38
in CDCl$_3$



```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Aug  2 2001  dfrq         500.211
solvent       CDC13  dn               H1
file            exp  dpwr             32
   ACQUISITION       dof               0
sfrq        125.789  dm              yyy
tn              C13  dmm               w
at            1.170  dmf            8770
np            81920  dseq
sw          34995.6  dres            1.0
fb            19000  homo              n
bs               16  temp           22.0
tpwr             57      PROCESSING
pw              8.0  lb             1.00
d1            1.000  wtfile
tof               0  proc             ft
nt             1000  fn         not used
ct                0  math              f
alock             n
gain             56  werr
      FLAGS          wexp
il                n  wbs
in                n  wnt
dp                y
hs               nn
     DISPLAY
sp          -5579.5
wp          34995.6
vs              149
sc                0
wc              250
hzmm           6.28
is           500.00
rfl         15264.4
rfp          9684.9
th                5
ins         100.000
nm  cdc  ph
```

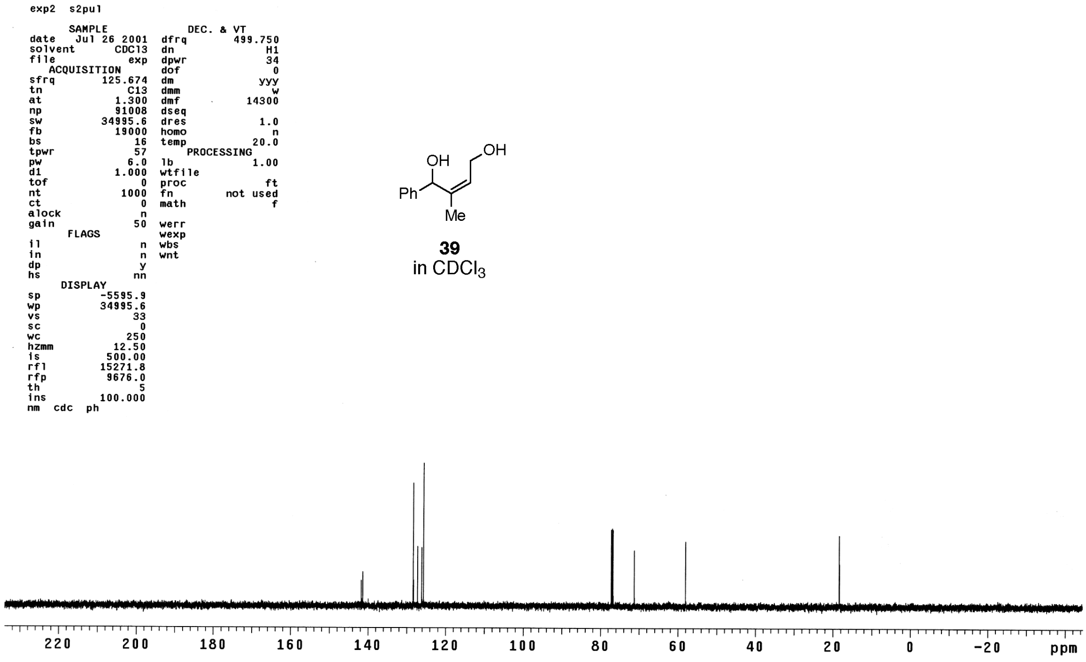
38
in CDCl$_3$



```
exp1  s2pul

        SAMPLE              DEC. & VT
date    Jul 26 2001   dfrq        499.750
solvent       CDCl3   dn               H1
file            exp   dpwr             34
   ACQUISITION        dof               0
sfrq        499.750   dm              nnn
tn               H1   dmm               c
at            2.048   dmf           14300
np            32768   dseq
sw           8000.0   dres            1.0
fb             4000   homo              n
bs                8   temp           20.0
ss                2      PROCESSING
tpwr             54   lb             0.10
pw              6.0   wtfile
d1                0   proc             ft
tof               0   fn         not used
nt               16   math              f
ct               16
alock             n   werr
gain       not used   wexp
       FLAGS          wbs
il                n   wnt             wft
in                n
dp                y
hs               nn
      DISPLAY
sp            -11.7
wp           4009.5
vs              151
sc                0
wc              250
hzmm          16.04
is           154.44
rfl          5141.9
rfp          3628.2
th              117
ins           3.000
nm    ph
```

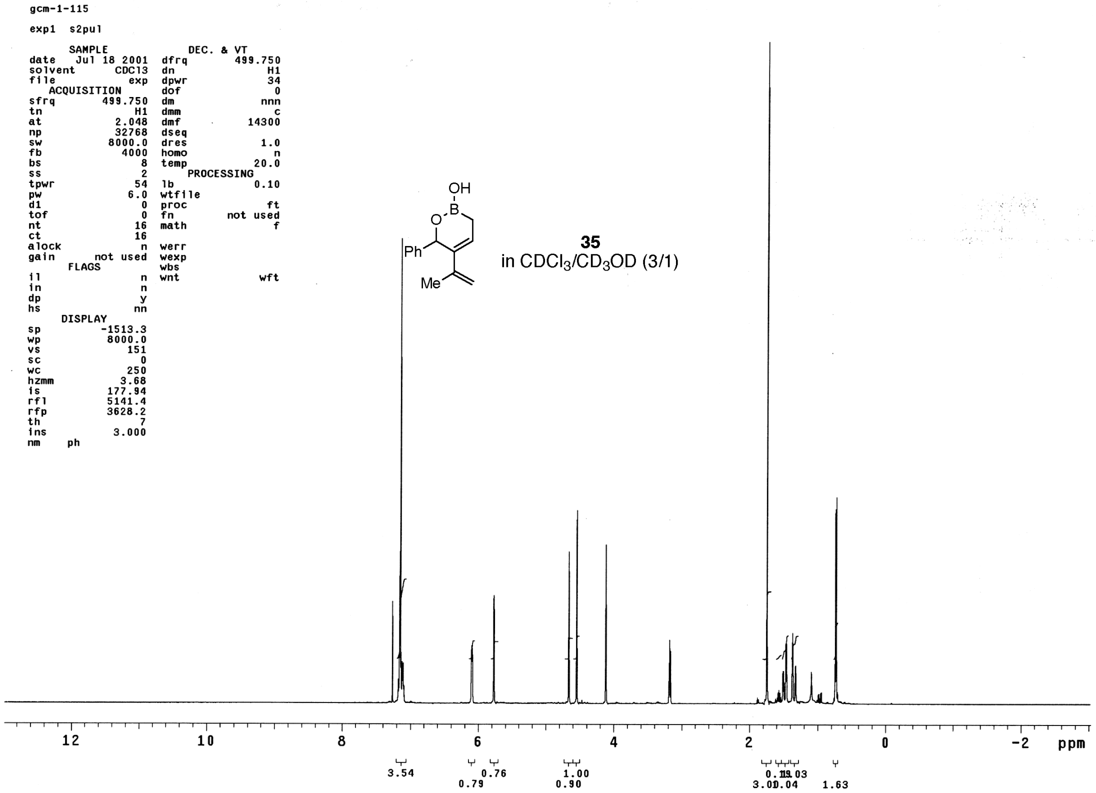
39
in $CDCl_3$



```
exp2  s2pul

        SAMPLE              DEC. & VT
date    Jul 26 2001   dfrq        499.750
solvent       CDCl3   dn               H1
file            exp   dpwr             34
   ACQUISITION        dof               0
sfrq        125.674   dm              yyy
tn              C13   dmm               w
at            1.300   dmf           14300
np            91008   dseq
sw          34995.6   dres            1.0
fb            19000   homo              n
bs               16   temp           20.0
tpwr             57      PROCESSING
pw              6.0   lb             1.00
d1            1.000   wtfile
tof               0   proc             ft
nt             1000   fn         not used
ct                0   math              f
alock             n
gain             50   werr
       FLAGS          wexp
il                n   wbs
in                n   wnt
dp                y
hs               nn
      DISPLAY
sp          -5595.9
wp          34995.6
vs               33
sc                0
wc              250
hzmm          12.50
is           500.00
rfl         15271.8
rfp          9676.0
th                5
ins         100.000
nm   cdc   ph
```

39
in $CDCl_3$



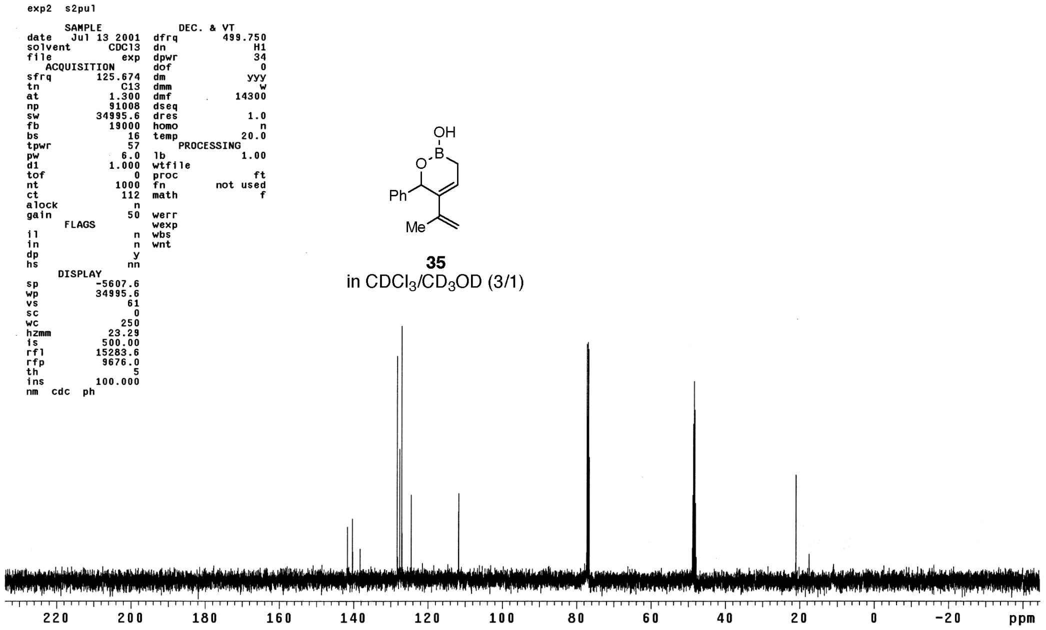
```
gcm-1-115

exp1  s2pul

      SAMPLE              DEC. & VT
date   Jul 18 2001   dfrq        499.750
solvent      CDCl3   dn               H1
file           exp   dpwr             34
   ACQUISITION       dof               0
sfrq       499.750   dm              nnn
tn              H1   dmm               c
at           2.048   dmf           14300
np           32768   dseq
sw          8000.0   dres            1.0
fb            4000   homo              n
bs               8   temp           20.0
ss               2        PROCESSING
tpwr            54   lb             0.10
pw             6.0   wtfile
d1               0   proc             ft
tof              0   fn         not used
nt              16   math              f
ct              16
alock            n   werr
gain      not used   wexp
      FLAGS          wbs
il               n   wnt             wft
in               n
dp               y
hs              nn
      DISPLAY
sp         -1513.3
wp          8000.0
vs             151
sc               0
wc             250
hzmm          3.68
is          177.94
rfl         5141.4
rfp         3628.2
th               7
ins          3.000
nm    ph
```

35

in $CDCl_3/CD_3OD$ (3/1)

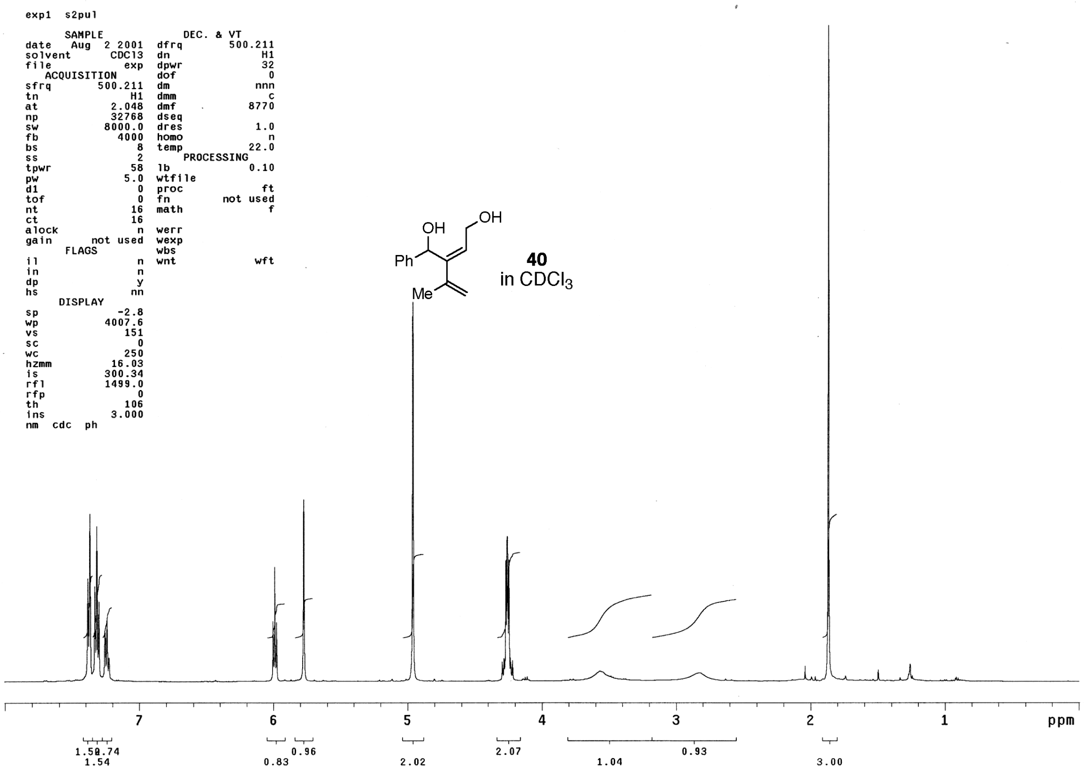


```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Jul 13 2001   dfrq        499.750
solvent      CDCl3   dn               H1
file           exp   dpwr             34
   ACQUISITION       dof               0
sfrq       125.674   dm              yyy
tn             C13   dmm               w
at           1.300   dmf           14300
np           91008   dseq
sw         34995.6   dres            1.0
fb           19000   homo              n
bs              16   temp           20.0
tpwr            57        PROCESSING
pw             6.0   lb             1.00
d1           1.000   wtfile
tof              0   proc             ft
nt            1000   fn         not used
ct             112   math              f
alock            n
gain            50   werr
      FLAGS          wexp
il               n   wbs
in               n   wnt
dp               y
hs              nn
      DISPLAY
sp         -5607.6
wp         34995.6
vs              61
sc               0
wc             250
hzmm         23.29
is          500.00
rfl        15283.6
rfp         9676.0
th               5
ins        100.000
nm  cdc  ph
```

35

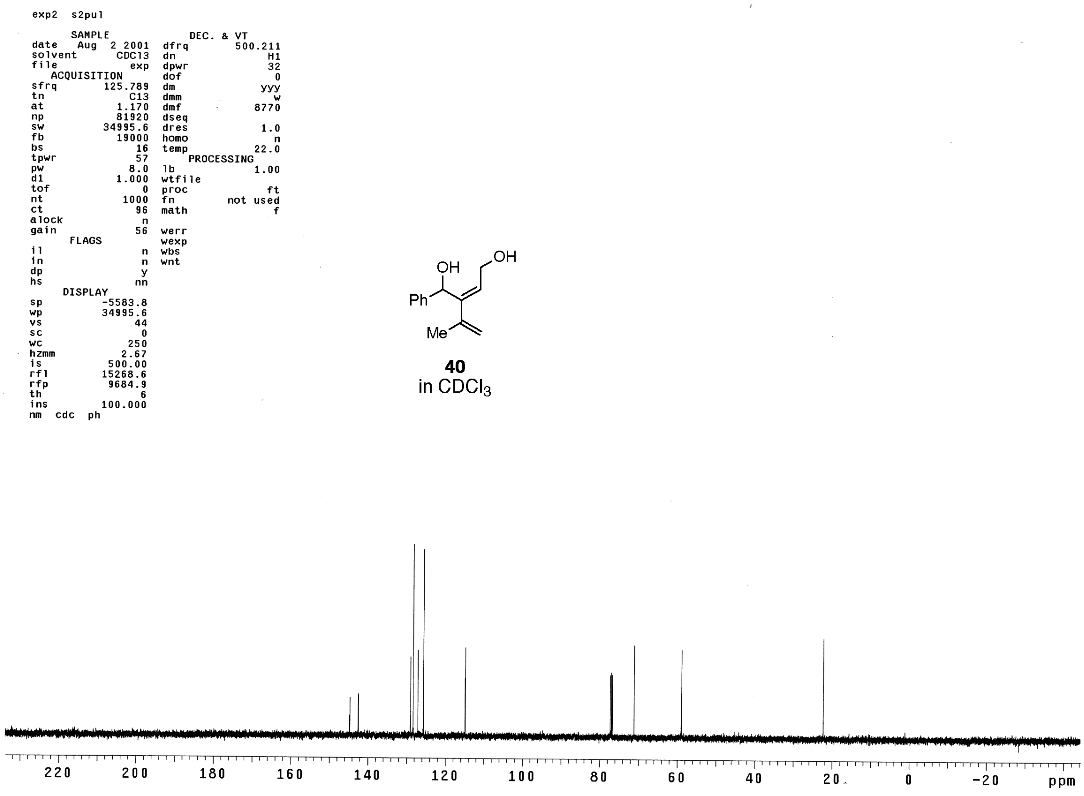
in $CDCl_3/CD_3OD$ (3/1)



```
exp1  s2pul

      SAMPLE             DEC. & VT
date   Aug  2 2001  dfrq        500.211
solvent      CDCl3  dn               H1
file           exp  dpwr             32
   ACQUISITION      dof               0
sfrq       500.211  dm              nnn
tn              H1  dmm               c
at           2.048  dmf            8770
np           32768  dseq
sw          8000.0  dres            1.0
fb            4000  homo              n
bs               8  temp           22.0
ss               2       PROCESSING
tpwr            58  lb             0.10
pw             5.0  wtfile
d1               0  proc             ft
tof              0  fn         not used
nt              16  math              f
ct              16
alock            n  werr
gain      not used  wexp
      FLAGS         wbs
il               n  wnt             wft
in               n
dp               y
hs              nn
     DISPLAY
sp            -2.8
wp          4007.6
vs             151
sc               0
wc             250
hzmm         16.03
is          300.34
rfl         1499.0
rfp              0
th             106
ins          3.000
nm  cdc  ph
```

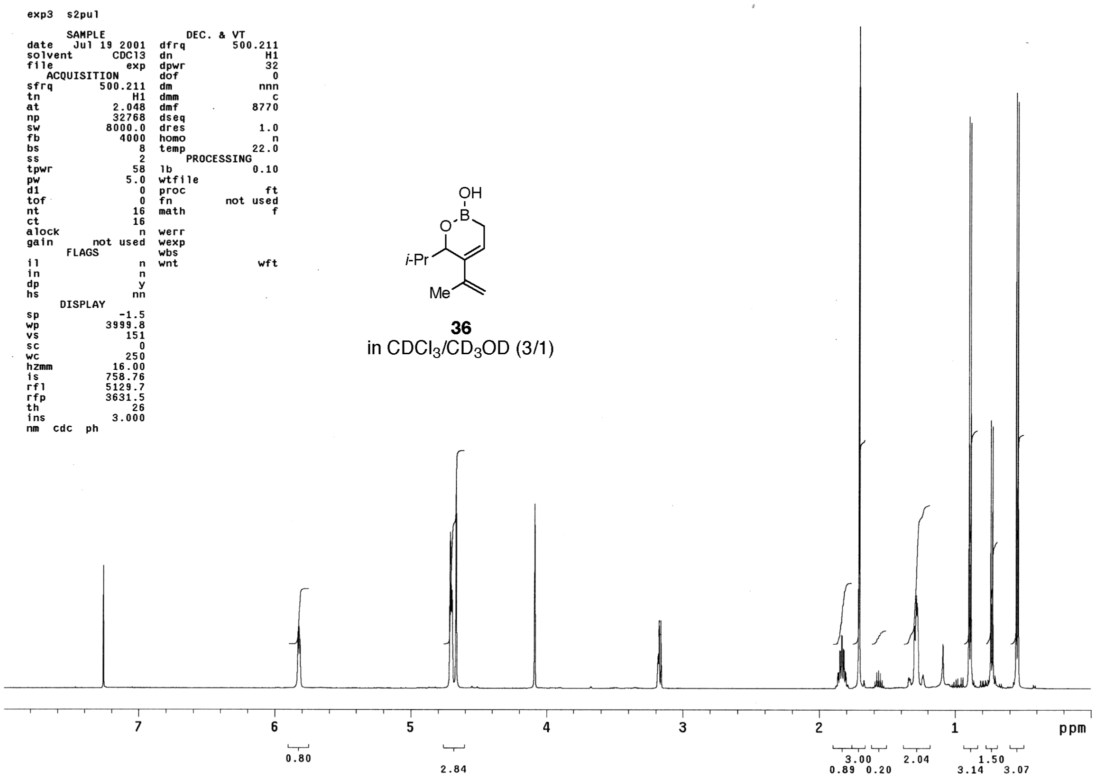
40
in $CDCl_3$



```
exp2  s2pul

      SAMPLE             DEC. & VT
date   Aug  2 2001  dfrq        500.211
solvent      CDCl3  dn               H1
file           exp  dpwr             32
   ACQUISITION      dof               0
sfrq       125.789  dm              yyy
tn             C13  dmm               w
at           1.170  dmf            8770
np           81920  dseq
sw         34995.6  dres            1.0
fb           19000  homo              n
bs              16  temp           22.0
tpwr            57       PROCESSING
pw             8.0  lb             1.00
d1           1.000  wtfile
tof              0  proc             ft
nt            1000  fn         not used
ct              96  math              f
alock            n
gain            56  werr
      FLAGS         wexp
il               n  wbs
in               n  wnt
dp               y
hs              nn
     DISPLAY
sp         -5583.8
wp         34995.6
vs              44
sc               0
wc             250
hzmm          2.67
is          500.00
rfl        15268.6
rfp         9684.9
th               6
ins        100.000
nm  cdc  ph
```

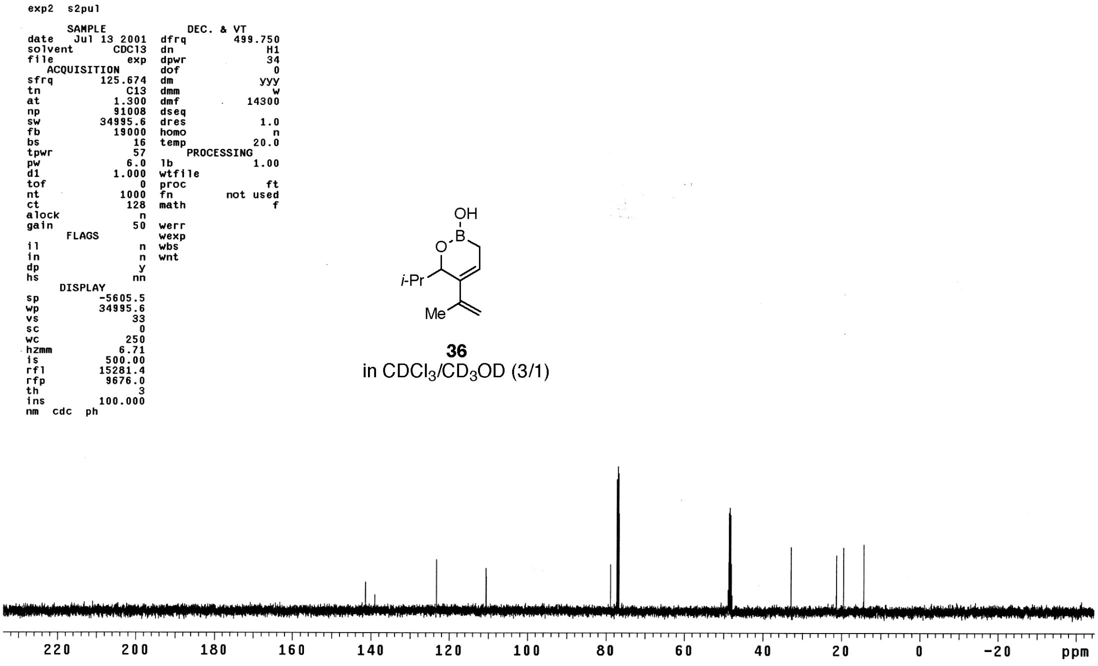
40
in $CDCl_3$



```
exp3  s2pul

      SAMPLE               DEC. & VT
date   Jul 19 2001  dfrq        500.211
solvent      CDCl3  dn               H1
file           exp  dpwr             32
   ACQUISITION      dof               0
sfrq       500.211  dm              nnn
tn              H1  dmm               c
at           2.048  dmf            8770
np           32768  dseq
sw          8000.0  dres            1.0
fb            4000  homo              n
bs               8  temp           22.0
ss               2      PROCESSING
tpwr            58  lb             0.10
pw             5.0  wtfile
d1               0  proc             ft
tof              0  fn         not used
nt              16  math              f
ct              16
alock            n  werr
gain      not used  wexp
      FLAGS         wbs
il               n  wnt             wft
in               n
dp               y
hs              nn
     DISPLAY
sp            -1.5
wp          3999.8
vs             151
sc               0
wc             250
hzmm         16.00
is          758.76
rfl         5129.7
rfp         3631.5
th              26
ins          3.000
nm  cdc  ph
```

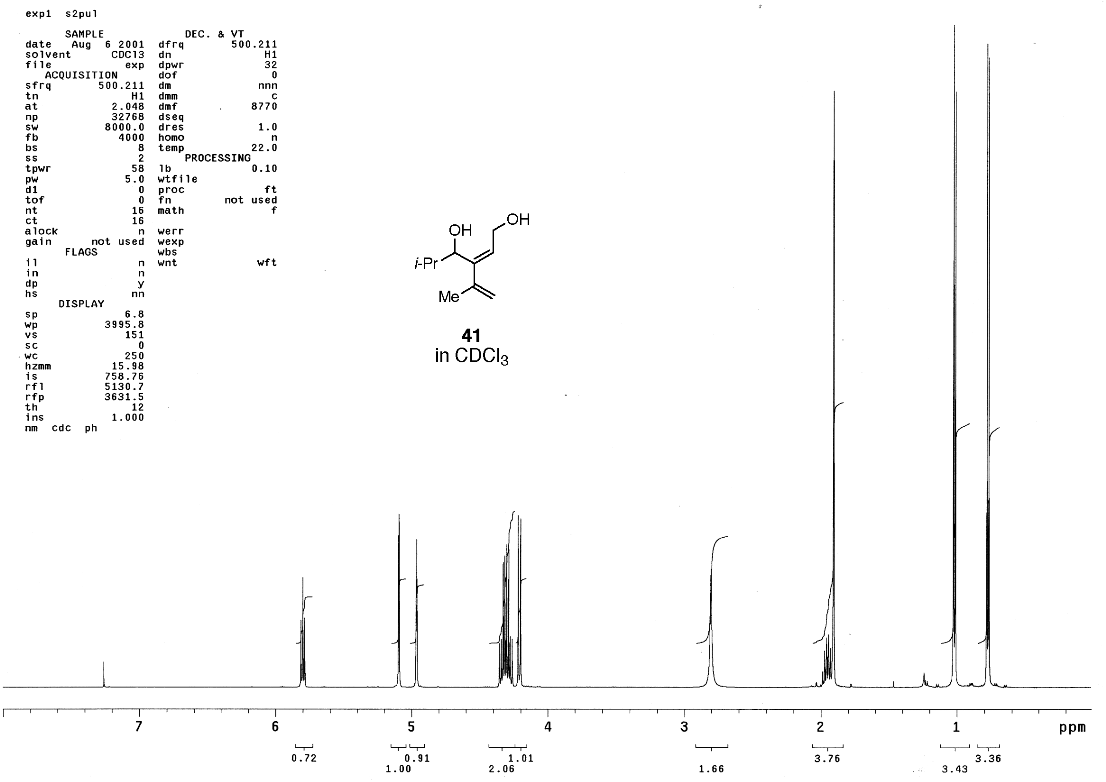
36
in $CDCl_3/CD_3OD$ (3/1)



```
exp2  s2pul

      SAMPLE               DEC. & VT
date   Jul 13 2001  dfrq        499.750
solvent      CDCl3  dn               H1
file           exp  dpwr             34
   ACQUISITION      dof               0
sfrq       125.674  dm              yyy
tn             C13  dmm               w
at           1.300  dmf           14300
np           91008  dseq
sw         34995.6  dres            1.0
fb           19000  homo              n
bs              16  temp           20.0
tpwr            57      PROCESSING
pw             6.0  lb             1.00
d1           1.000  wtfile
tof              0  proc             ft
nt            1000  fn         not used
ct             128  math              f
alock            n
gain            50  werr
      FLAGS         wexp
il               n  wbs
in               n  wnt
dp               y
hs              nn
     DISPLAY
sp         -5605.5
wp         34995.6
vs              33
sc               0
wc             250
hzmm          6.71
is          500.00
rfl        15281.4
rfp         9676.0
th               3
ins        100.000
nm  cdc  ph
```

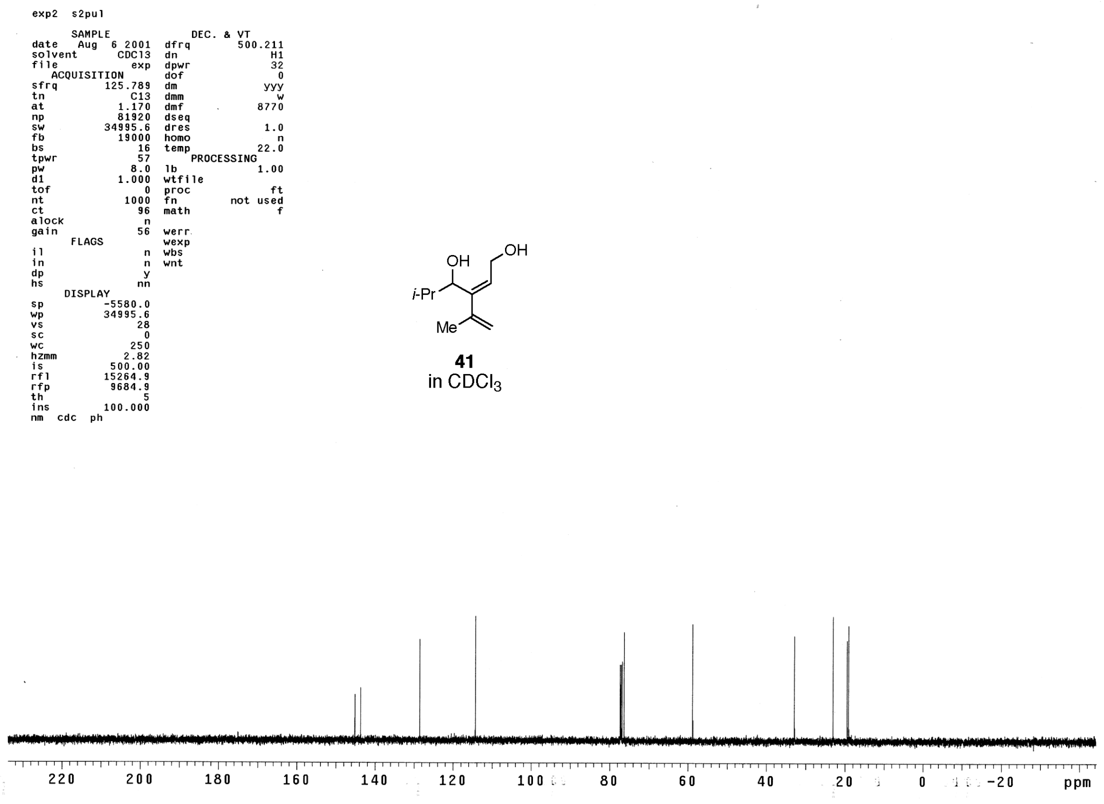
36
in $CDCl_3/CD_3OD$ (3/1)



```
exp1  s2pul

       SAMPLE              DEC. & VT
date   Aug  6 2001   dfrq        500.211
solvent       CDCl3   dn               H1
file            exp   dpwr             32
   ACQUISITION        dof               0
sfrq        500.211   dm              nnn
tn               H1   dmm               c
at            2.048   dmf            8770
np            32768   dseq
sw           8000.0   dres            1.0
fb             4000   homo              n
bs                8   temp           22.0
ss                2       PROCESSING
tpwr             58   lb             0.10
pw              5.0   wtfile
d1                0   proc             ft
tof               0   fn         not used
nt               16   math              f
ct               16
alock             n   werr
gain       not used   wexp
       FLAGS          wbs
il                n   wnt             wft
in                n
dp                y
hs               nn
      DISPLAY
sp              6.8
wp           3995.8
vs              151
sc                0
wc              250
hzmm          15.98
is           758.76
rfl          5130.7
rfp          3631.5
th               12
ins           1.000
nm  cdc  ph
```

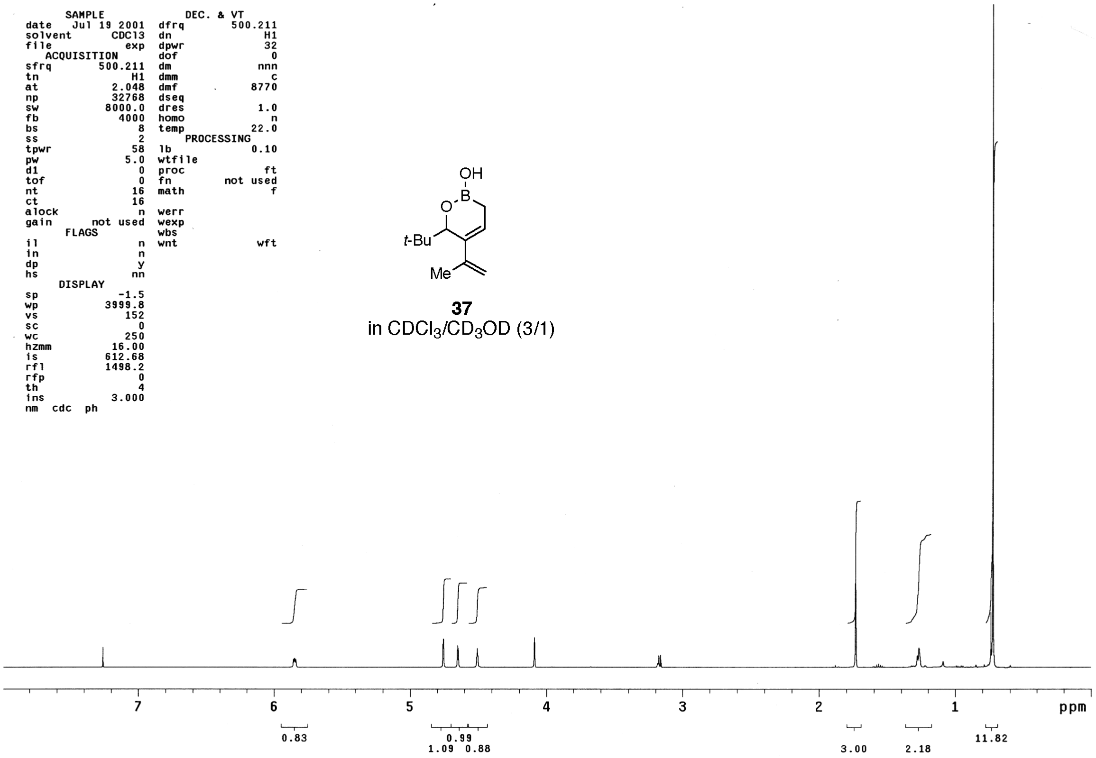
41
in $CDCl_3$



```
exp2  s2pul

       SAMPLE              DEC. & VT
date   Aug  6 2001   dfrq        500.211
solvent       CDCl3   dn               H1
file            exp   dpwr             32
   ACQUISITION        dof               0
sfrq        125.789   dm              yyy
tn              C13   dmm               w
at            1.170   dmf            8770
np            81920   dseq
sw          34995.6   dres            1.0
fb            19000   homo              n
bs               16   temp           22.0
tpwr             57       PROCESSING
pw              8.0   lb             1.00
d1            1.000   wtfile
tof               0   proc             ft
nt             1000   fn         not used
ct               96   math              f
alock             n
gain             56   werr
       FLAGS          wexp
il                n   wbs
in                n   wnt
dp                y
hs               nn
      DISPLAY
sp          -5580.0
wp          34995.6
vs               28
sc                0
wc              250
hzmm           2.82
is           500.00
rfl         15264.9
rfp          9684.9
th                5
ins         100.000
nm  cdc  ph
```

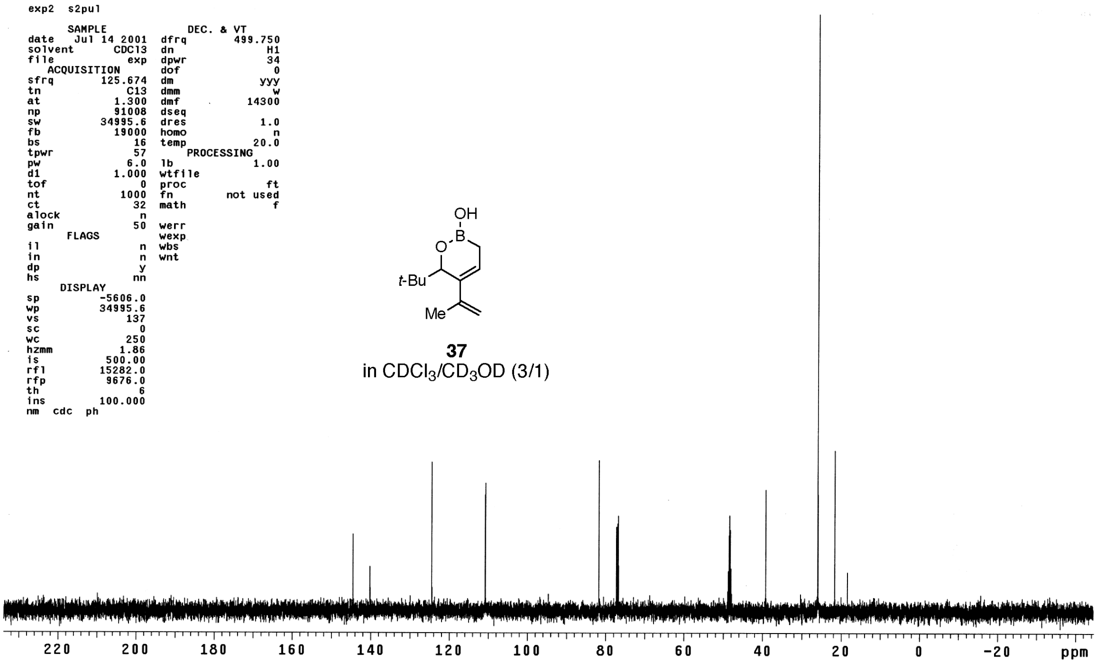
41
in $CDCl_3$



```
exp3  s2pul

       SAMPLE              DEC. & VT
date   Jul 19 2001    dfrq        500.211
solvent      CDC13    dn               H1
file           exp    dpwr             32
   ACQUISITION        dof               0
sfrq       500.211    dm              nnn
tn              H1    dmm               c
at           2.048    dmf            8770
np           32768    dseq
sw          8000.0    dres            1.0
fb            4000    homo              n
bs               8    temp           22.0
ss               2        PROCESSING
tpwr            58    lb             0.10
pw             5.0    wtfile
d1               0    proc             ft
tof              0    fn         not used
nt              16    math              f
ct              16
alock            n    werr
gain      not used    wexp
       FLAGS          wbs
il               n    wnt             wft
in               n
dp               y
hs              nn
      DISPLAY
sp            -1.5
wp          3999.8
vs             152
sc               0
wc             250
hzmm         16.00
is          612.68
rfl         1498.2
rfp              0
th               4
ins          3.000
nm  cdc  ph
```

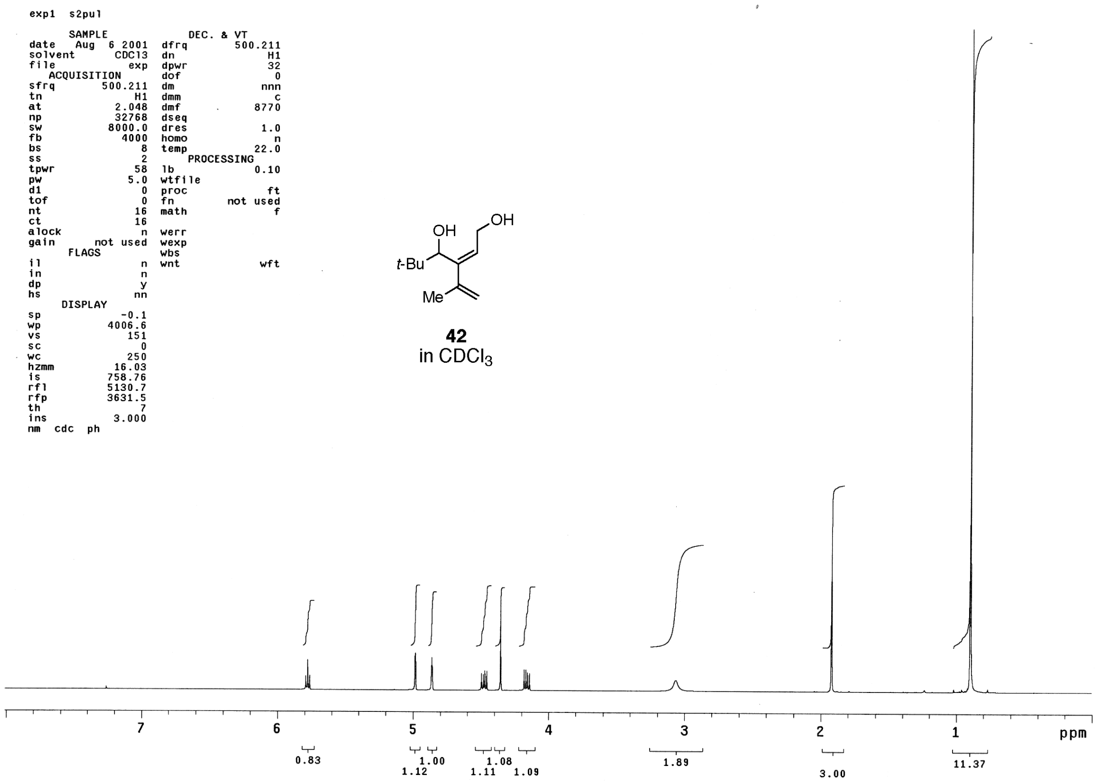
37
in CDCl$_3$/CD$_3$OD (3/1)



```
exp2  s2pul

       SAMPLE              DEC. & VT
date   Jul 14 2001    dfrq        499.750
solvent      CDC13    dn               H1
file           exp    dpwr             34
   ACQUISITION        dof               0
sfrq       125.674    dm              yyy
tn             C13    dmm               w
at           1.300    dmf           14300
np           91008    dseq
sw         34995.6    dres            1.0
fb           19000    homo              n
bs              16    temp           20.0
tpwr            57        PROCESSING
pw             6.0    lb             1.00
d1           1.000    wtfile
tof              0    proc             ft
nt            1000    fn         not used
ct              32    math              f
alock            n
gain            50    werr
       FLAGS          wexp
il               n    wbs
in               n    wnt
dp               y
hs              nn
      DISPLAY
sp         -5606.0
wp         34995.6
vs             137
sc               0
wc             250
hzmm          1.86
is          500.00
rfl        15282.0
rfp         9676.0
th               6
ins        100.000
nm  cdc  ph
```

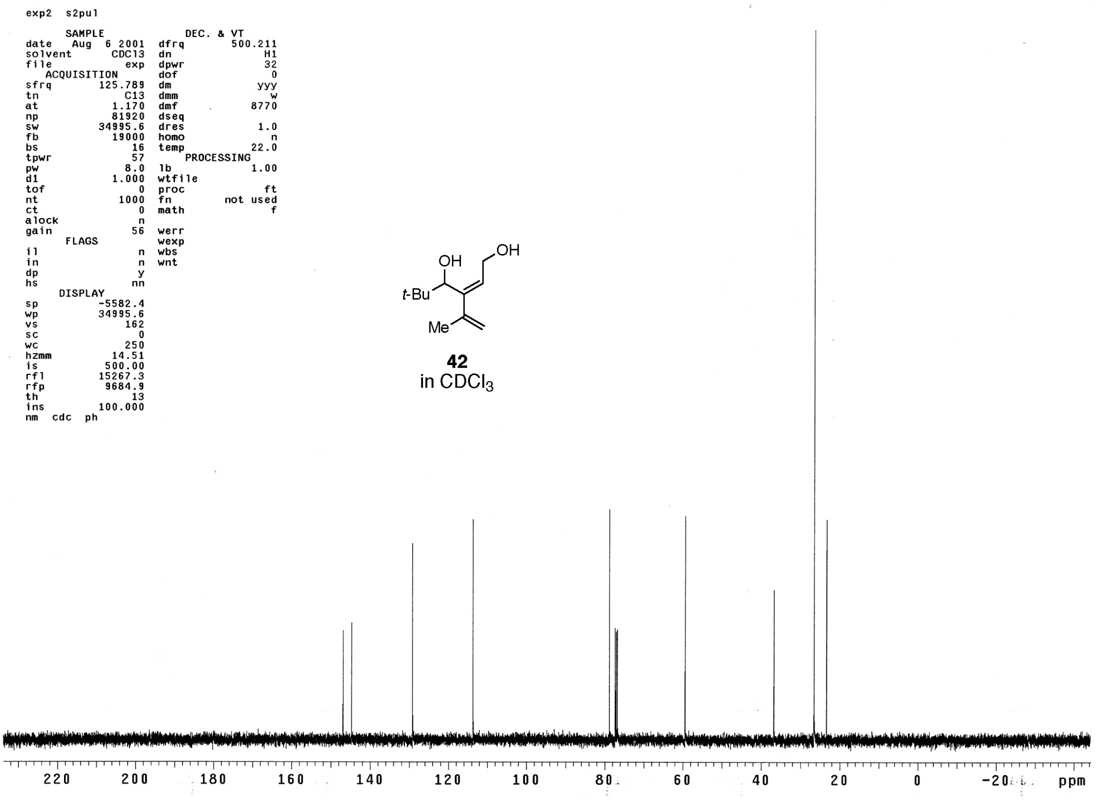
37
in CDCl$_3$/CD$_3$OD (3/1)



```
exp1  s2pul

      SAMPLE              DEC. & VT
date   Aug  6 2001   dfrq       500.211
solvent       CDCl3   dn              H1
file            exp   dpwr            32
   ACQUISITION        dof              0
sfrq        500.211   dm             nnn
tn               H1   dmm              c
at            2.048   dmf           8770
np            32768   dseq
sw           8000.0   dres           1.0
fb             4000   homo             n
bs                8   temp          22.0
ss                2       PROCESSING
tpwr             58   lb            0.10
pw              5.0   wtfile
d1                0   proc            ft
tof               0   fn        not used
nt               16   math             f
ct               16
alock             n   werr
gain       not used   wexp
      FLAGS           wbs
il                n   wnt            wft
in                n
dp                y
hs               nn
     DISPLAY
sp             -0.1
wp           4006.6
vs              151
sc                0
wc              250
hzmm          16.03
is           758.76
rfl          5130.7
rfp          3631.5
th                7
ins           3.000
nm  cdc  ph
```

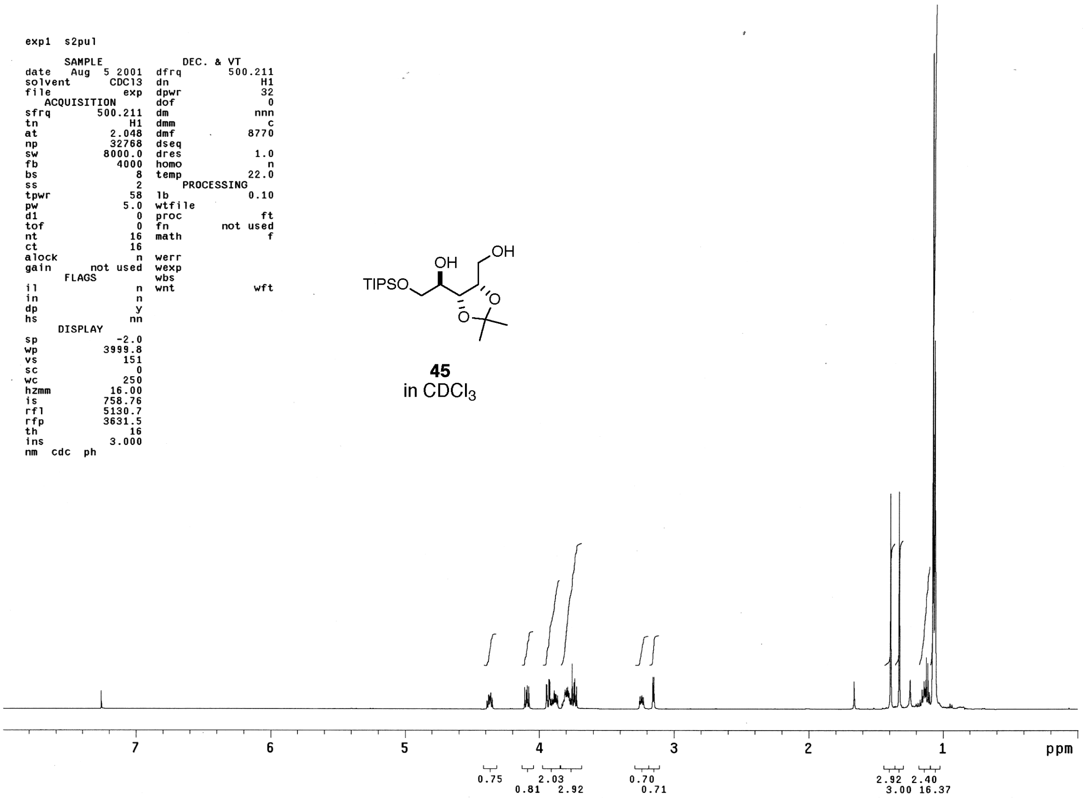
42
in $CDCl_3$



```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Aug  6 2001   dfrq       500.211
solvent       CDCl3   dn              H1
file            exp   dpwr            32
   ACQUISITION        dof              0
sfrq        125.789   dm             yyy
tn              C13   dmm              w
at            1.170   dmf           8770
np            81920   dseq
sw          34995.6   dres           1.0
fb            19000   homo             n
bs               16   temp          22.0
tpwr             57       PROCESSING
pw              8.0   lb            1.00
d1            1.000   wtfile
tof               0   proc            ft
nt             1000   fn        not used
ct                0   math             f
alock             n
gain             56   werr
      FLAGS           wexp
il                n   wbs
in                n   wnt
dp                y
hs               nn
     DISPLAY
sp          -5582.4
wp          34995.6
vs              162
sc                0
wc              250
hzmm          14.51
is           500.00
rfl         15267.3
rfp          9684.9
th               13
ins         100.000
nm  cdc  ph
```

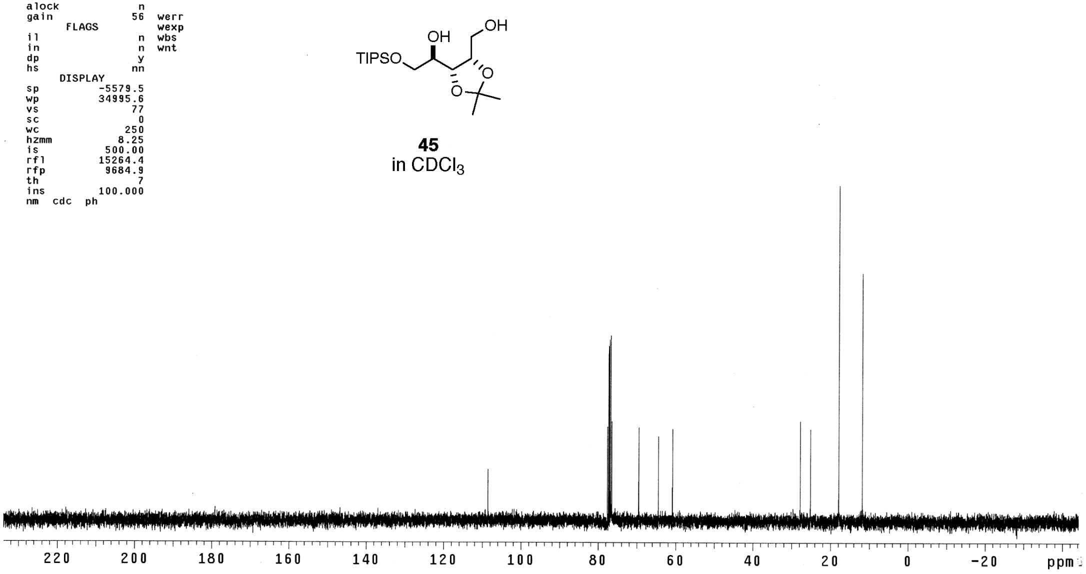
42
in $CDCl_3$



45
in $CDCl_3$

```
exp1  s2pul

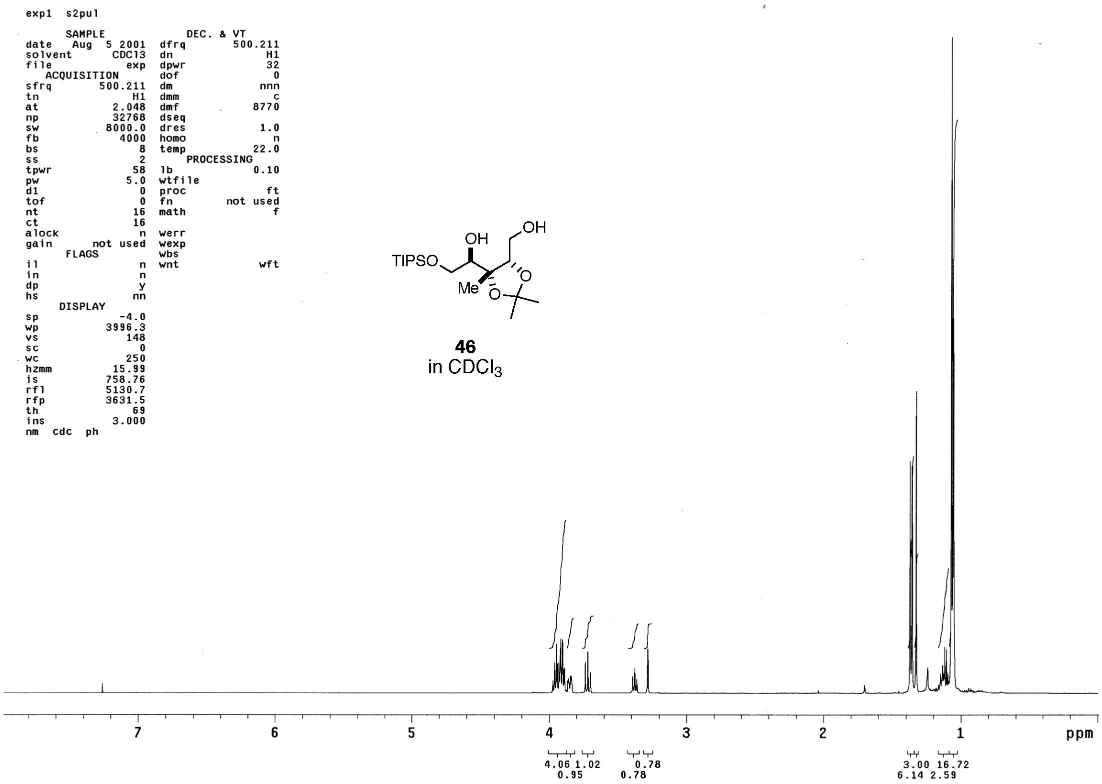
      SAMPLE            DEC. & VT
date   Aug  5 2001   dfrq       500.211
solvent      CDC13   dn              H1
file           exp   dpwr            32
   ACQUISITION       dof              0
sfrq       500.211   dm             nnn
tn              H1   dmm              c
at           2.048   dmf           8770
np           32768   dseq
sw          8000.0   dres           1.0
fb            4000   homo             n
bs               8   temp          22.0
ss               2       PROCESSING
tpwr            58   lb            0.10
pw             5.0   wtfile
d1               0   proc            ft
tof              0   fn        not used
nt              16   math             f
ct              16
alock            n   werr
gain      not used   wexp
      FLAGS          wbs
il               n   wnt            wft
in               n
dp               y
hs              nn
     DISPLAY
sp            -2.0
wp          3999.8
vs             151
sc               0
wc             250
hzmm         16.00
is          758.76
rfl         5130.7
rfp         3631.5
th              16
ins          3.000
nm  cdc  ph
```



45
in $CDCl_3$

```
exp2  s2pul

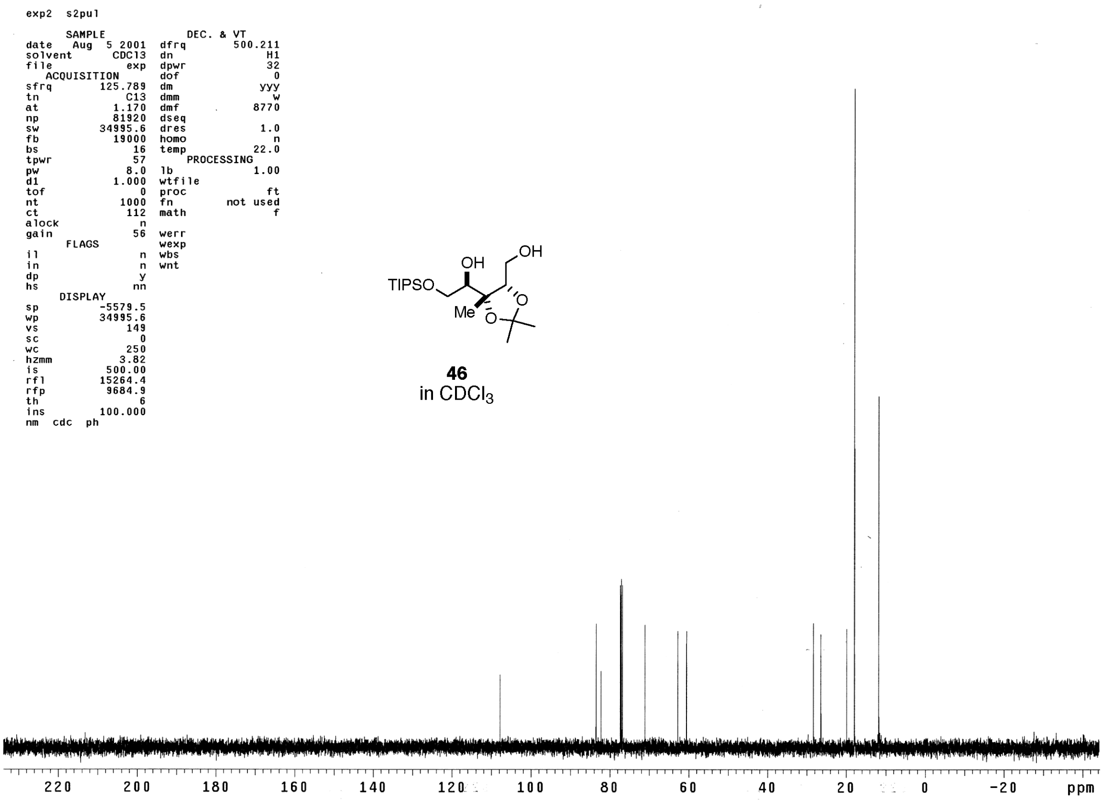
      SAMPLE            DEC. & VT
date   Aug  5 2001   dfrq       500.211
solvent      CDC13   dn              H1
file           exp   dpwr            32
   ACQUISITION       dof              0
sfrq       125.789   dm             yyy
tn             C13   dmm              w
at           1.170   dmf           8770
np           81920   dseq
sw         34995.6   dres           1.0
fb           19000   homo             n
bs              16   temp          22.0
tpwr            57       PROCESSING
pw             8.0   lb            1.00
d1           1.000   wtfile
tof              0   proc            ft
nt            1000   fn        not used
ct             144   math             f
alock            n
gain            56   werr
      FLAGS          wexp
il               n   wbs
in               n   wnt
dp               y
hs              nn
     DISPLAY
sp         -5579.5
wp         34995.6
vs              77
sc               0
wc             250
hzmm          8.25
is          500.00
rfl        15264.4
rfp         9684.9
th               7
ins        100.000
nm  cdc  ph
```



```
exp1  s2pul

      SAMPLE              DEC. & VT
date   Aug  5 2001  dfrq       500.211
solvent       CDC13  dn               H1
file            exp  dpwr             32
   ACQUISITION       dof               0
sfrq        500.211  dm              nnn
tn               H1  dmm               c
at            2.048  dmf            8770
np            32768  dseq
sw           8000.0  dres            1.0
fb             4000  homo              n
bs                8  temp           22.0
ss                2        PROCESSING
tpwr             58  lb             0.10
pw              5.0  wtfile
d1                0  proc             ft
tof               0  fn         not used
nt               16  math              f
ct               16
alock             n  werr
gain       not used  wexp
      FLAGS          wbs
il                n  wnt             wft
in                n
dp                y
hs               nn
     DISPLAY
sp             -4.0
wp           3996.3
vs              148
sc                0
wc              250
hzmm          15.99
is           758.76
rfl          5130.7
rfp          3631.5
th               69
ins           3.000
nm  cdc  ph
```

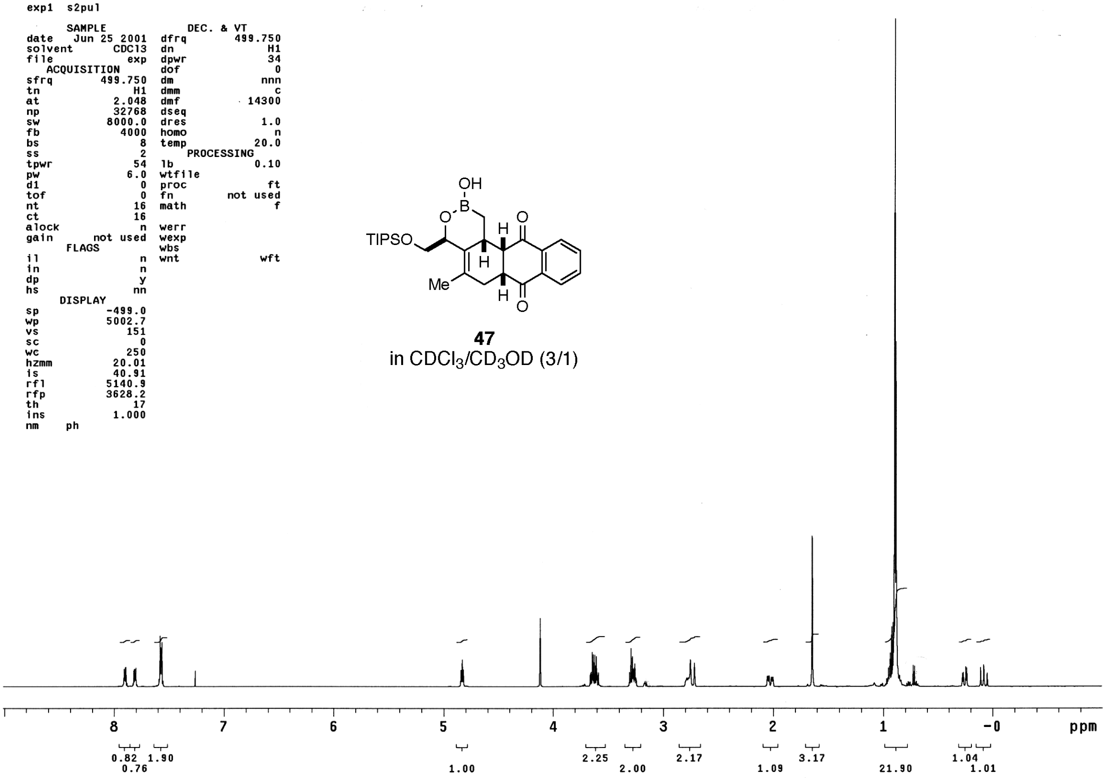
46
in CDCl$_3$



```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Aug  5 2001  dfrq       500.211
solvent       CDC13  dn               H1
file            exp  dpwr             32
   ACQUISITION       dof               0
sfrq        125.789  dm              yyy
tn              C13  dmm               w
at            1.170  dmf            8770
np            81920  dseq
sw          34995.6  dres            1.0
fb            19000  homo              n
bs               16  temp           22.0
tpwr             57        PROCESSING
pw              8.0  lb             1.00
d1            1.000  wtfile
tof               0  proc             ft
nt             1000  fn         not used
ct              112  math              f
alock             n
gain             56  werr
      FLAGS          wexp
il                n  wbs
in                n  wnt
dp                y
hs               nn
     DISPLAY
sp          -5579.5
wp          34995.6
vs              149
sc                0
wc              250
hzmm           3.82
is           500.00
rfl         15264.4
rfp          9684.9
th                6
ins         100.000
nm  cdc  ph
```

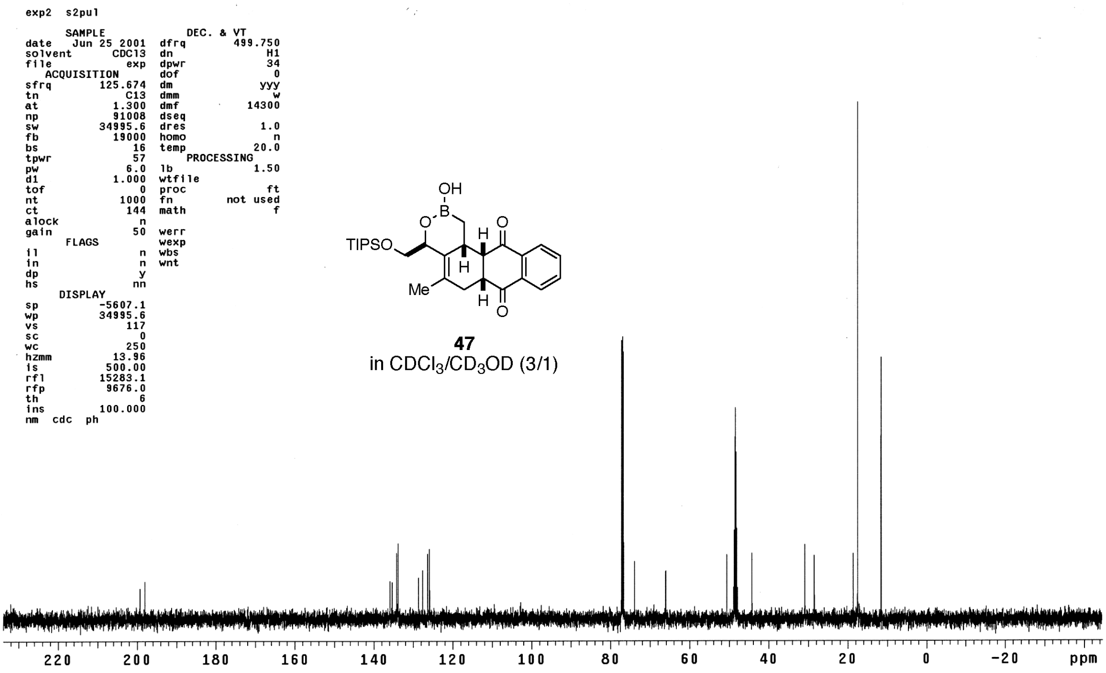
46
in CDCl$_3$



```
exp1  s2pul

      SAMPLE              DEC. & VT
date   Jun 25 2001  dfrq        499.750
solvent       CDC13  dn               H1
file            exp  dpwr             34
   ACQUISITION       dof               0
sfrq        499.750  dm              nnn
tn               H1  dmm               c
at            2.048  dmf           14300
np            32768  dseq
sw           8000.0  dres            1.0
fb             4000  homo              n
bs                8  temp           20.0
ss                2        PROCESSING
tpwr             54  lb             0.10
pw              6.0  wtfile
d1                0  proc             ft
tof               0  fn         not used
nt               16  math              f
ct               16
alock             n  werr
gain       not used  wexp
      FLAGS          wbs
il                n  wnt             wft
in                n
dp                y
hs               nn
     DISPLAY
sp           -499.0
wp           5002.7
vs              151
sc                0
wc              250
hzmm          20.01
is            40.91
rfl          5140.9
rfp          3628.2
th               17
ins           1.000
nm    ph
```

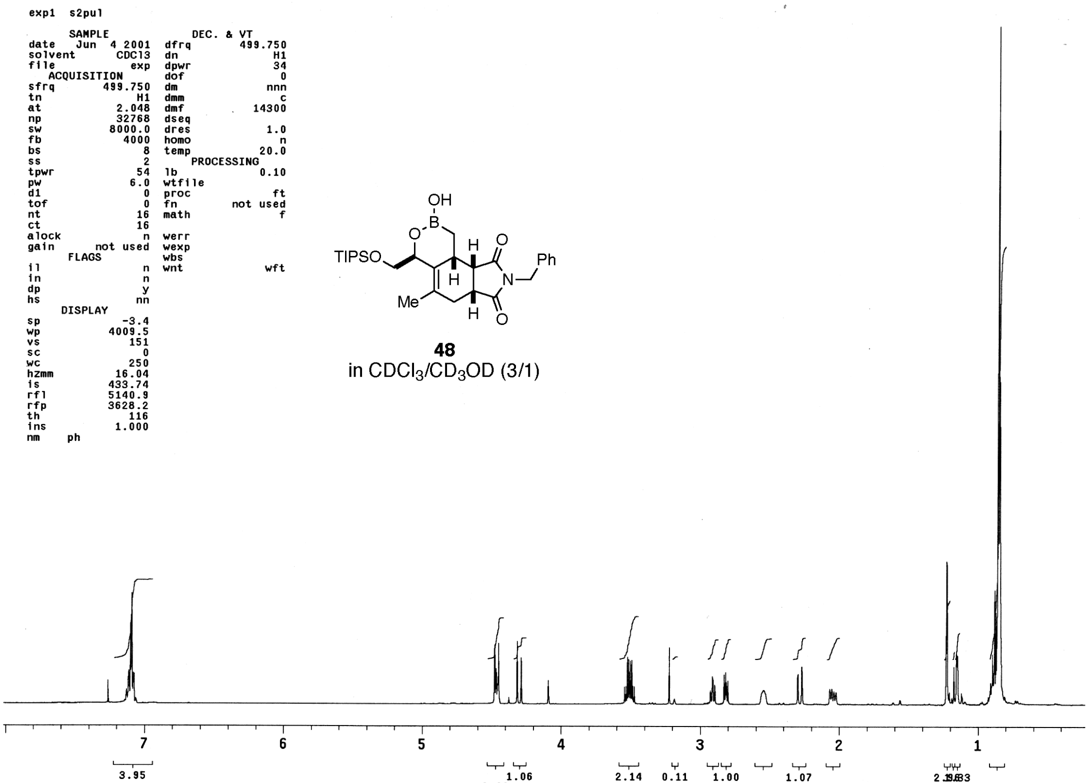
47
in $CDCl_3/CD_3OD$ (3/1)



```
exp2  s2pul

      SAMPLE              DEC. & VT
date   Jun 25 2001  dfrq        499.750
solvent       CDC13  dn               H1
file            exp  dpwr             34
   ACQUISITION       dof               0
sfrq        125.674  dm              yyy
tn              C13  dmm               w
at            1.300  dmf           14300
np            91008  dseq
sw          34995.6  dres            1.0
fb            19000  homo              n
bs               16  temp           20.0
tpwr             57        PROCESSING
pw              6.0  lb             1.50
d1            1.000  wtfile
tof               0  proc             ft
nt             1000  fn         not used
ct              144  math              f
alock             n
gain             50  werr
      FLAGS          wexp
il                n  wbs
in                n  wnt
dp                y
hs               nn
     DISPLAY
sp          -5607.1
wp          34995.6
vs              117
sc                0
wc              250
hzmm          13.96
is           500.00
rfl         15283.1
rfp          9676.0
th                6
ins         100.000
nm  cdc  ph
```

47
in $CDCl_3/CD_3OD$ (3/1)

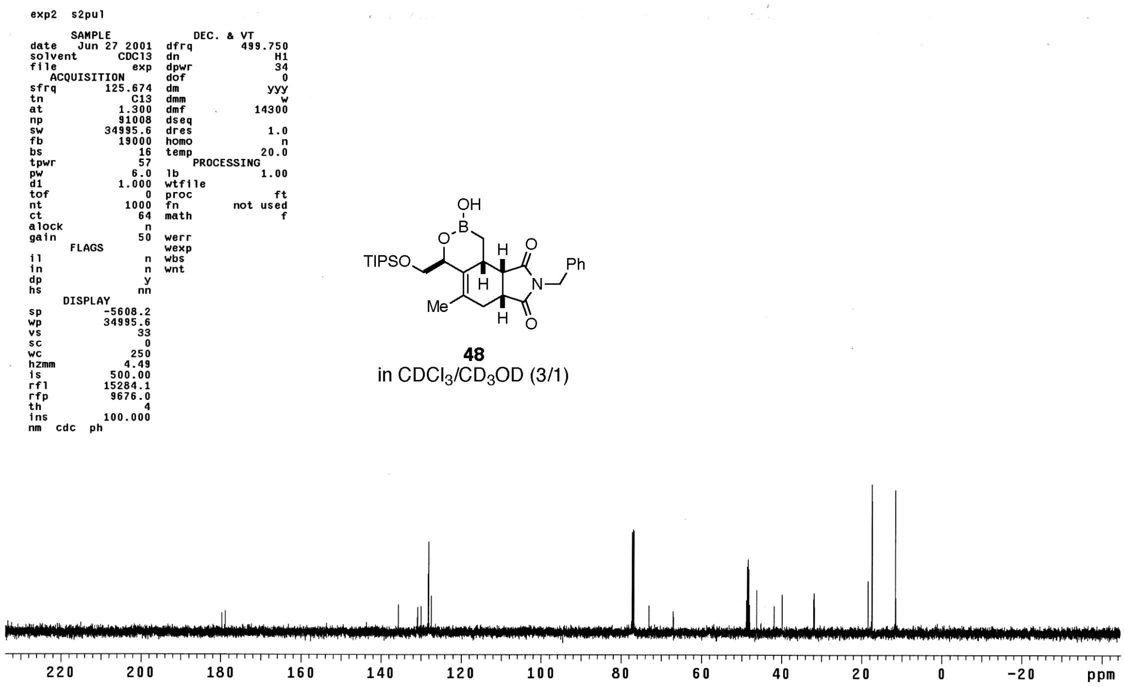


```
exp1  s2pul

     SAMPLE              DEC. & VT
date   Jun  4 2001   dfrq       499.750
solvent      CDCl3   dn              H1
file           exp   dpwr            34
   ACQUISITION       dof              0
sfrq       499.750   dm             nnn
tn              H1   dmm              c
at           2.048   dmf          14300
np           32768   dseq
sw          8000.0   dres           1.0
fb            4000   homo             n
bs               8   temp          20.0
ss               2      PROCESSING
tpwr            54   lb            0.10
pw             6.0   wtfile
d1               0   proc            ft
tof              0   fn        not used
nt              16   math             f
ct              16
alock            n   werr
gain      not used   wexp
      FLAGS          wbs
il               n   wnt            wft
in               n
dp               y
hs              nn
     DISPLAY
sp            -3.4
wp          4009.5
vs             151
sc               0
wc             250
hzmm         16.04
is          433.74
rfl         5140.9
rfp         3628.2
th             116
ins          1.000
nm    ph
```

48

in $CDCl_3/CD_3OD$ (3/1)

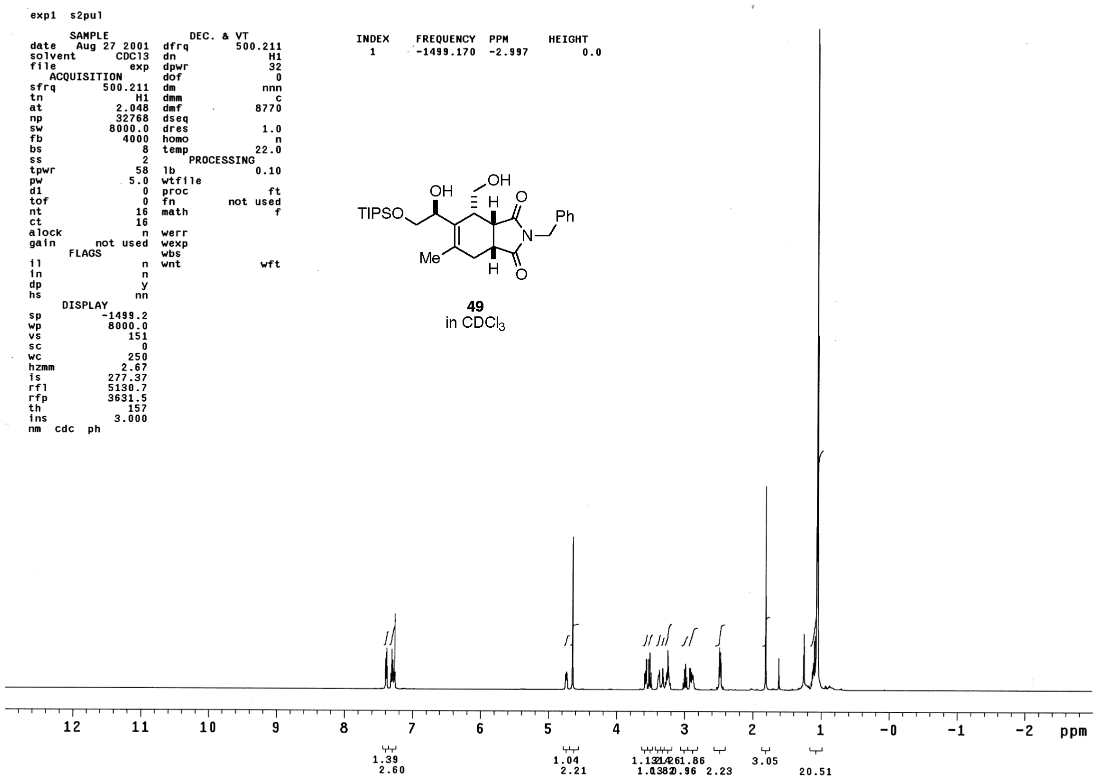


```
exp2  s2pul

     SAMPLE              DEC. & VT
date   Jun 27 2001   dfrq       499.750
solvent      CDCl3   dn              H1
file           exp   dpwr            34
   ACQUISITION       dof              0
sfrq       125.674   dm             yyy
tn             C13   dmm              w
at           1.300   dmf          14300
np           91008   dseq
sw         34995.6   dres           1.0
fb           19000   homo             n
bs              16   temp          20.0
tpwr            57      PROCESSING
pw             6.0   lb            1.00
d1           1.000   wtfile
tof              0   proc            ft
nt            1000   fn        not used
ct              64   math             f
alock            n
gain            50   werr
      FLAGS          wexp
il               n   wbs
in               n   wnt
dp               y
hs              nn
     DISPLAY
sp         -5608.2
wp         34995.6
vs              33
sc               0
wc             250
hzmm          4.49
is          500.00
rfl        15284.1
rfp         9676.0
th               4
ins        100.000
nm  cdc  ph
```

48

in $CDCl_3/CD_3OD$ (3/1)

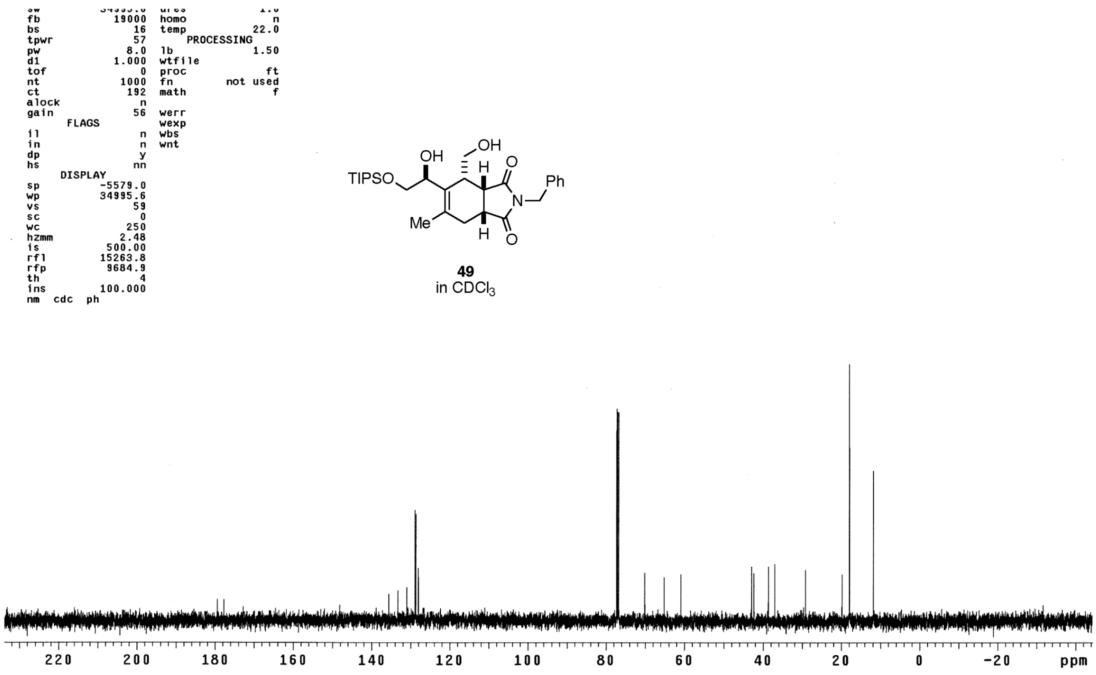


49
in $CDCl_3$

```
exp1  s2pul

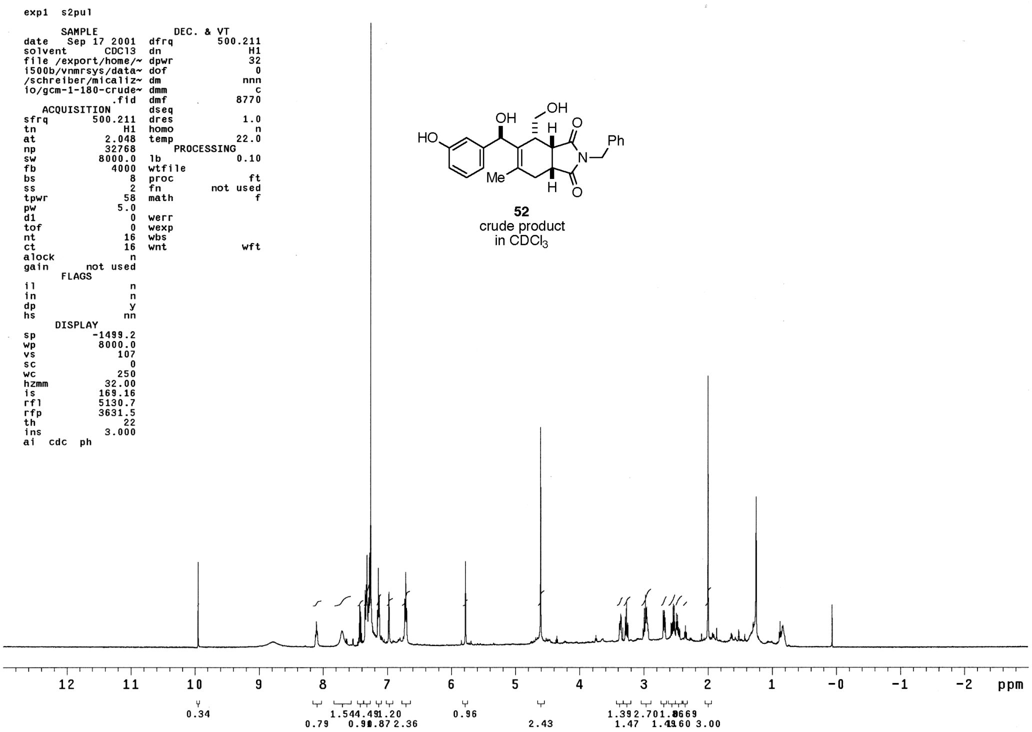
      SAMPLE                 DEC. & VT
date   Aug 27 2001   dfrq          500.211
solvent       CDC13  dn                 H1
file            exp  dpwr               32
   ACQUISITION       dof                 0
sfrq        500.211  dm                nnn
tn               H1  dmm                 c
at            2.048  dmf              8770
np            32768  dseq
sw           8000.0  dres              1.0
fb             4000  homo                n
bs                8  temp             22.0
ss                2      PROCESSING
tpwr             58  lb               0.10
pw              5.0  wtfile
d1                0  proc               ft
tof               0  fn           not used
nt               16  math                f
ct               16
alock             n  werr
gain       not used  wexp
      FLAGS          wbs
il                n  wnt               wft
in                n
dp                y
hs               nn
     DISPLAY
sp          -1499.2
wp           8000.0
vs              151
sc                0
wc              250
hzmm           2.67
is           277.37
rfl          5130.7
rfp          3631.5
th              157
ins           3.000
nm  cdc  ph
```

```
INDEX    FREQUENCY  PPM      HEIGHT
  1      -1499.170  -2.997       0.0
```



49
in $CDCl_3$

```
fb            19000  homo                n
bs               16  temp             22.0
tpwr             57      PROCESSING
pw              8.0  lb               1.50
d1            1.000  wtfile
tof               0  proc               ft
nt             1000  fn           not used
ct              192  math                f
alock             n
gain             56  werr
      FLAGS          wexp
il                n  wbs
in                n  wnt
dp                y
hs               nn
     DISPLAY
sp          -5579.0
wp          34995.6
vs               59
sc                0
wc              250
hzmm           2.48
is           500.00
rfl         15263.8
rfp          9684.9
th                4
ins         100.000
nm  cdc  ph
```



```
exp1  s2pul

      SAMPLE              DEC. & VT
date   Sep 17 2001  dfrq        500.211
solvent      CDCl3  dn               H1
file /export/home/~ dpwr             32
i500b/vnmrsys/data~ dof               0
/schreiber/micaliz~ dm              nnn
io/gcm-1-180-crude~ dmm               c
               .fid dmf            8770
   ACQUISITION      dseq
sfrq        500.211 dres            1.0
tn               H1 homo              n
at            2.048 temp           22.0
np            32768     PROCESSING
sw           8000.0 lb             0.10
fb             4000 wtfile
bs                8 proc             ft
ss                2 fn         not used
tpwr             58 math              f
pw              5.0
d1                0 werr
tof               0 wexp
nt               16 wbs
ct               16 wnt             wft
alock             n
gain       not used
      FLAGS
il                n
in                n
dp                y
hs               nn
     DISPLAY
sp          -1499.2
wp           8000.0
vs              107
sc                0
wc              250
hzmm          32.00
is           169.16
rfl          5130.7
rfp          3631.5
th               22
ins           3.000
ai  cdc  ph
```

52
crude product
in $CDCl_3$

X-Ray Data For Compound 48

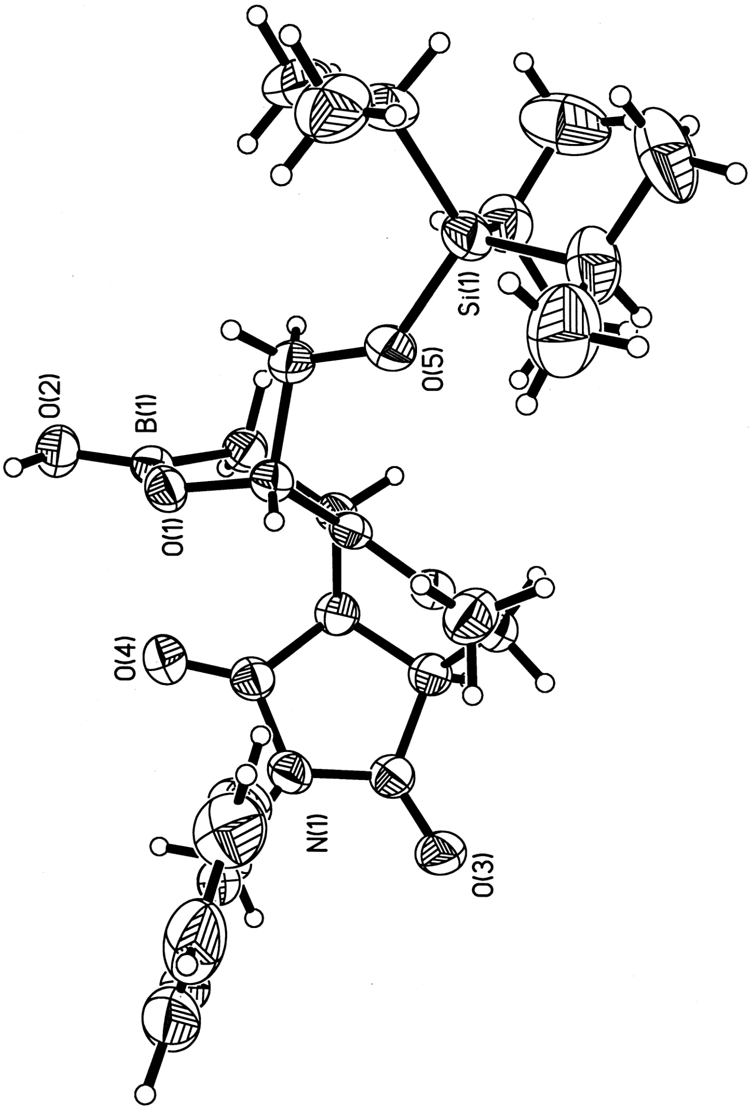
Data were collected using a Bruker APEX CCD (charge coupled device) based diffractometer equipped with an LT-3 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3 ° per frame for 30 seconds, such that a hemisphere was collected. A total of 1271 frames were collected with a maximum resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART[1] software and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software[2] which corrects for Lp and decay. The structures are solved by the direct method using the SHELXS-97[3] program and refined by least squares method on F^2, SHELXL-97, [4] incorporated in SHELXTL V5.10.[5]

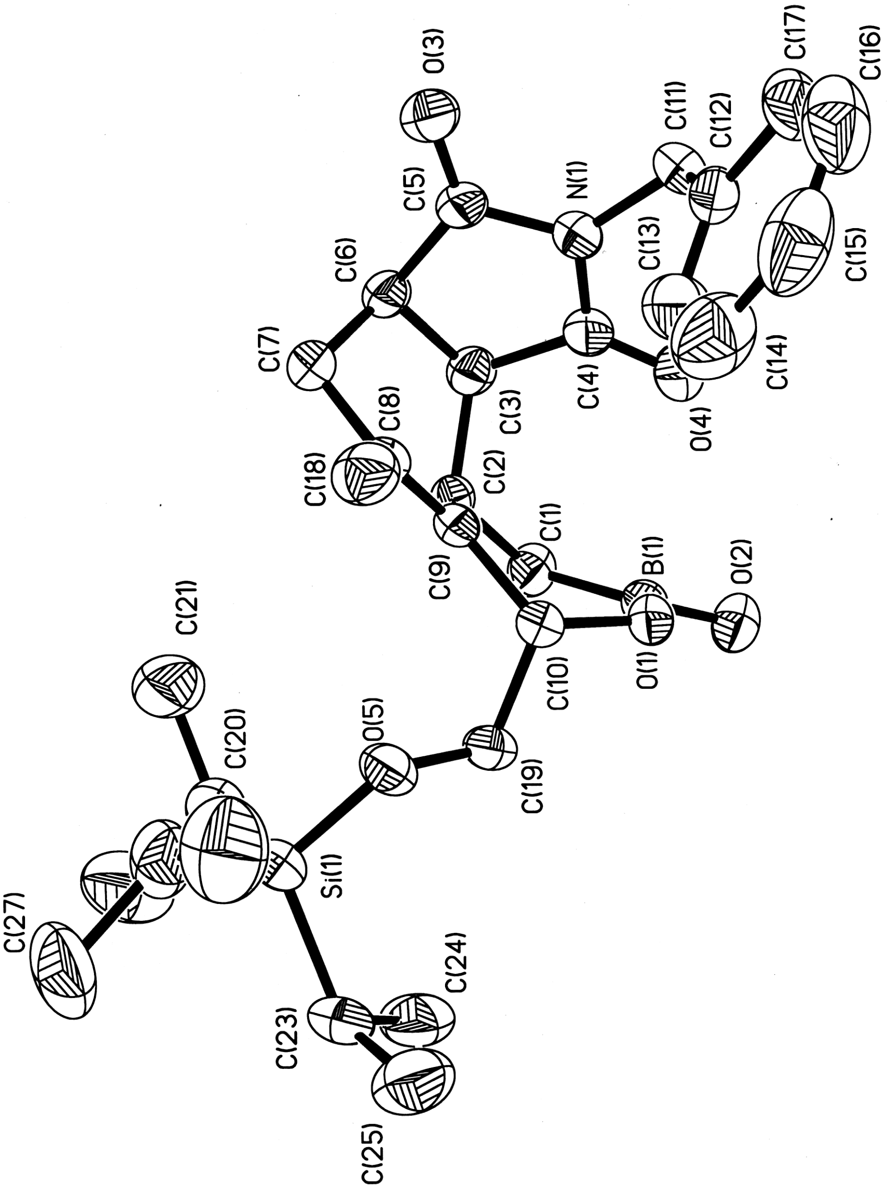
The structure was solved in the space group $P2_1/c$ (# 14) by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. All drawing are done at 50% ellipsiods.

Acknowledgement. The CCD based x-ray diffractometer at Harvard University was purchased through NIH grant (1S10RR11937-01).

References

1. SMART V 5.054 (NT) *Software for the CCD Detector System*; Bruker Analytical X-ray Systems, Madison, WI (1998).
2. SAINT V 6.02 (NT) *Software for the CCD Detector System* Bruker Analytical X-ray Systems, Madison, WI (2000).
3. Sheldrick, G. M. SHELXS-90, *Program for the Solution of Crystal Structure,* University of Göttingen, Germany, 1990.
4. Sheldrick, G. M. SHELXL-97, *Program for the Refinement of Crystal Structure,* University of Göttingen, Germany, 1997.
5. SHELXTL 6.10 (PC/NT-Version), *Program library for Structure Solution and Molecular Graphics*; Bruker Analytical X-ray Systems, Madison, WI (2000).


O(2)
B(1)
O(1)
O(5)
Si(1)
O(4)
N(1)
O(3)


O(3)
C(17)
C(16)
C(11)
C(12)
C(5)
N(1)
C(6)
C(13)
C(15)
C(7)
C(4)
C(3)
C(14)
O(4)
C(8)
C(18)
C(2)
C(1)
C(9)
B(1)
O(2)
C(21)
C(10)
O(1)
C(20)
O(5)
C(19)
Si(1)
C(27)
C(24)
C(23)
C(25)

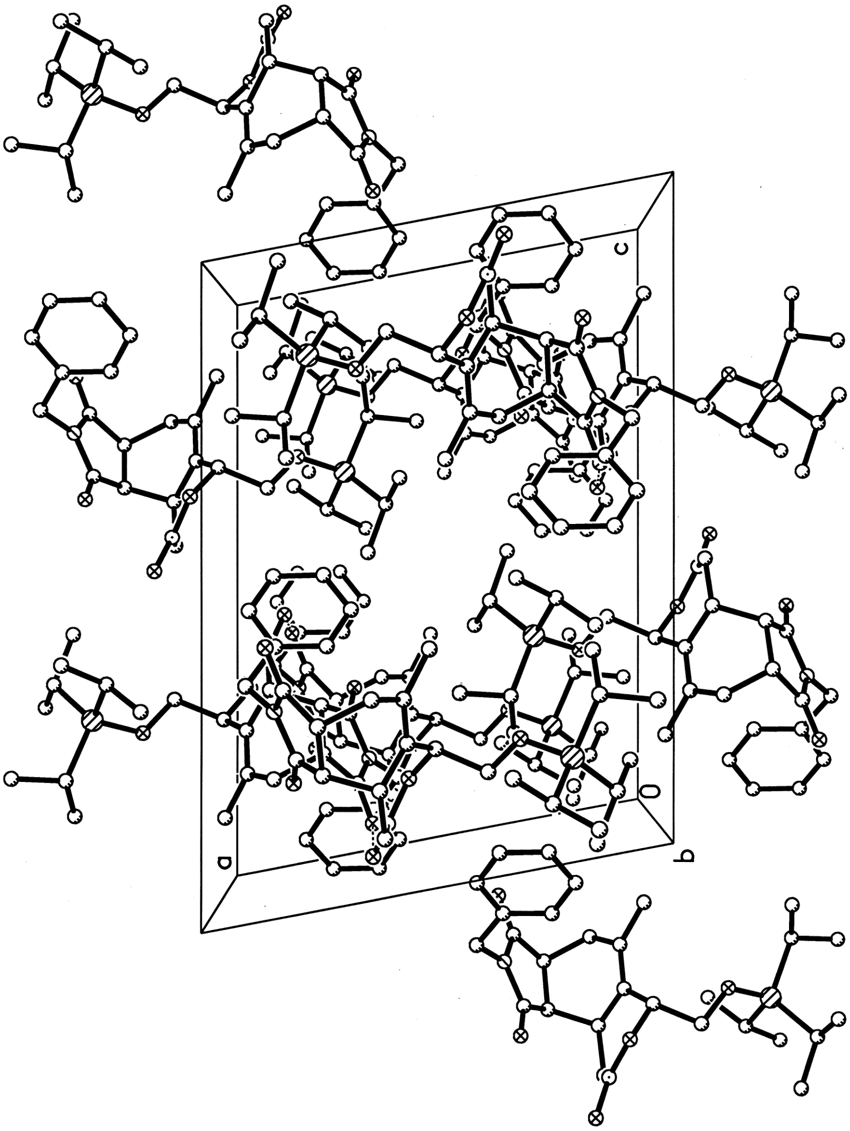

c
0
a
b

Table 1. Crystal data and structure refinement for sls62t.

Identification code	sls62t	
Empirical formula	C28 H42 B N O5 Si	
Formula weight	511.53	
Temperature	213(2) K	
Wavelength	0.71073 .	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.6782(14) .	α= 90..
	b = 13.0256(14) .	β= 101.022(2)..
	c = 17.613(2) .	γ = 90..
Volume	2855.0(5) .^{3}	
Z	4	
Density (calculated)	1.190 Mg/m^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	1104	
Crystal size	0.15 x 0.12 x 0.04 mm^3	
Theta range for data collection	1.96 to 28.30..	
Index ranges	-16<=h<=14, -11<=k<=17, -23<=l<=23	
Reflections collected	20380	
Independent reflections	7076 [R(int) = 0.0995]	
Completeness to theta = 28.30.	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7076 / 0 / 325	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1511	
R indices (all data)	R1 = 0.0647, wR2 = 0.1619	
Largest diff. peak and hole	0.371 and -0.323 e..$^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (.^{2}x 10^3) for sls62t. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	2188(1)	1060(1)	1627(1)	41(1)
B(1)	6058(1)	-598(1)	1049(1)	35(1)
O(1)	5615(1)	-977(1)	1649(1)	34(1)
O(2)	6391(1)	-1262(1)	554(1)	44(1)
O(3)	8548(1)	1663(1)	4093(1)	49(1)
O(4)	8067(1)	-329(1)	1948(1)	52(1)
O(5)	3252(1)	369(1)	2007(1)	45(1)
N(1)	8432(1)	512(1)	3107(1)	39(1)
C(1)	6097(1)	588(1)	920(1)	39(1)
C(2)	6199(1)	1205(1)	1675(1)	35(1)
C(3)	7376(1)	1410(1)	2071(1)	37(1)
C(4)	7975(1)	425(1)	2327(1)	38(1)
C(5)	8199(1)	1427(1)	3423(1)	38(1)
C(6)	7453(1)	2042(1)	2820(1)	38(1)
C(7)	6356(1)	2173(1)	3067(1)	42(1)
C(8)	5704(1)	1195(1)	2951(1)	37(1)
C(9)	5635(1)	714(1)	2271(1)	32(1)
C(10)	5041(1)	-282(1)	2062(1)	33(1)
C(11)	9094(1)	-284(1)	3544(1)	48(1)
C(12)	8506(1)	-924(1)	4039(1)	46(1)
C(13)	7397(2)	-1004(1)	3899(1)	58(1)
C(14)	6894(2)	-1613(2)	4371(1)	75(1)
C(15)	7515(3)	-2151(2)	4978(1)	82(1)
C(16)	8613(3)	-2089(2)	5106(1)	78(1)
C(17)	9104(2)	-1478(1)	4651(1)	61(1)
C(18)	5171(1)	885(1)	3603(1)	52(1)
C(19)	3919(1)	-147(1)	1574(1)	43(1)
C(20)	2638(1)	2158(1)	1076(1)	53(1)
C(21)	3472(2)	2828(2)	1592(2)	75(1)
C(22)	1736(2)	2821(2)	636(2)	93(1)
C(23)	1203(1)	254(1)	951(1)	54(1)

C(24)	1609(2)	−22(2)	205(1)	67(1)
C(25)	866(2)	−721(2)	1317(1)	74(1)
C(26)	1653(2)	1504(1)	2495(1)	63(1)
C(27)	499(2)	1922(2)	2278(2)	90(1)
C(28)	1750(2)	685(2)	3128(2)	93(1)

Table 3. Bond lengths [.] and angles [.] for sls62t.

Si(1)-O(5)	1.6529(10)
Si(1)-C(23)	1.8739(16)
Si(1)-C(20)	1.8766(18)
Si(1)-C(26)	1.8797(18)
B(1)-O(2)	1.3524(18)
B(1)-O(1)	1.3788(18)
B(1)-C(1)	1.564(2)
O(1)-C(10)	1.4430(15)
O(3)-C(5)	1.2171(17)
O(4)-C(4)	1.2052(17)
O(5)-C(19)	1.4133(17)
N(1)-C(5)	1.3715(18)
N(1)-C(4)	1.3899(18)
N(1)-C(11)	1.4586(18)
C(1)-C(2)	1.5380(19)
C(2)-C(9)	1.5190(18)
C(2)-C(3)	1.5455(18)
C(3)-C(4)	1.5150(19)
C(3)-C(6)	1.5414(19)
C(5)-C(6)	1.5096(19)
C(6)-C(7)	1.545(2)
C(7)-C(8)	1.5109(19)
C(8)-C(9)	1.3399(18)
C(8)-C(18)	1.494(2)
C(9)-C(10)	1.5098(17)
C(10)-C(19)	1.5239(18)
C(11)-C(12)	1.503(2)
C(12)-C(13)	1.384(2)
C(12)-C(17)	1.395(2)
C(13)-C(14)	1.389(3)
C(14)-C(15)	1.391(3)
C(15)-C(16)	1.370(4)
C(16)-C(17)	1.362(3)
C(20)-C(22)	1.522(3)

C(20)–C(21)	1.529(3)
C(23)–C(25)	1.522(3)
C(23)–C(24)	1.543(3)
C(26)–C(28)	1.530(3)
C(26)–C(27)	1.540(3)

O(5)–Si(1)–C(23)	110.22(7)
O(5)–Si(1)–C(20)	108.64(7)
C(23)–Si(1)–C(20)	109.29(8)
O(5)–Si(1)–C(26)	103.34(8)
C(23)–Si(1)–C(26)	112.88(8)
C(20)–Si(1)–C(26)	112.28(8)
O(2)–B(1)–O(1)	119.27(12)
O(2)–B(1)–C(1)	121.02(13)
O(1)–B(1)–C(1)	119.59(12)
B(1)–O(1)–C(10)	118.68(10)
C(19)–O(5)–Si(1)	124.48(9)
C(5)–N(1)–C(4)	113.05(11)
C(5)–N(1)–C(11)	123.36(12)
C(4)–N(1)–C(11)	123.59(12)
C(2)–C(1)–B(1)	113.00(11)
C(9)–C(2)–C(1)	113.85(11)
C(9)–C(2)–C(3)	107.61(10)
C(1)–C(2)–C(3)	113.22(12)
C(4)–C(3)–C(6)	104.59(11)
C(4)–C(3)–C(2)	111.95(10)
C(6)–C(3)–C(2)	112.10(11)
O(4)–C(4)–N(1)	123.20(13)
O(4)–C(4)–C(3)	128.47(13)
N(1)–C(4)–C(3)	108.33(11)
O(3)–C(5)–N(1)	123.15(13)
O(3)–C(5)–C(6)	127.63(13)
N(1)–C(5)–C(6)	109.22(11)
C(5)–C(6)–C(3)	104.36(11)
C(5)–C(6)–C(7)	109.68(12)
C(3)–C(6)–C(7)	112.76(11)

C(8)-C(7)-C(6)	111.55(11)
C(9)-C(8)-C(18)	126.77(13)
C(9)-C(8)-C(7)	117.11(13)
C(18)-C(8)-C(7)	116.09(12)
C(8)-C(9)-C(10)	124.35(12)
C(8)-C(9)-C(2)	117.51(11)
C(10)-C(9)-C(2)	118.15(11)
O(1)-C(10)-C(9)	112.72(10)
O(1)-C(10)-C(19)	107.10(10)
C(9)-C(10)-C(19)	114.02(11)
N(1)-C(11)-C(12)	113.70(12)
C(13)-C(12)-C(17)	118.89(18)
C(13)-C(12)-C(11)	122.54(13)
C(17)-C(12)-C(11)	118.54(16)
C(12)-C(13)-C(14)	120.20(18)
C(15)-C(14)-C(13)	119.4(2)
C(16)-C(15)-C(14)	120.3(2)
C(17)-C(16)-C(15)	120.19(19)
C(16)-C(17)-C(12)	121.0(2)
O(5)-C(19)-C(10)	109.91(11)
C(22)-C(20)-C(21)	110.20(17)
C(22)-C(20)-Si(1)	115.01(14)
C(21)-C(20)-Si(1)	111.82(14)
C(25)-C(23)-C(24)	109.47(16)
C(25)-C(23)-Si(1)	113.95(13)
C(24)-C(23)-Si(1)	112.37(11)
C(28)-C(26)-C(27)	111.62(19)
C(28)-C(26)-Si(1)	112.80(14)
C(27)-C(26)-Si(1)	112.31(17)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (.^{2}x 10^3) for sls62t. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	28(1)	45(1)	52(1)	-4(1)	8(1)	2(1)
B(1)	36(1)	32(1)	32(1)	2(1)	-2(1)	3(1)
O(1)	33(1)	28(1)	41(1)	1(1)	6(1)	2(1)
O(2)	58(1)	35(1)	38(1)	-1(1)	10(1)	3(1)
O(3)	51(1)	39(1)	49(1)	-3(1)	-9(1)	-1(1)
O(4)	47(1)	46(1)	59(1)	-11(1)	3(1)	11(1)
O(5)	30(1)	55(1)	47(1)	-9(1)	2(1)	6(1)
N(1)	32(1)	34(1)	49(1)	0(1)	-1(1)	2(1)
C(1)	51(1)	32(1)	32(1)	5(1)	1(1)	2(1)
C(2)	39(1)	25(1)	36(1)	4(1)	-2(1)	3(1)
C(3)	38(1)	31(1)	42(1)	2(1)	5(1)	-5(1)
C(4)	29(1)	36(1)	47(1)	-2(1)	4(1)	-2(1)
C(5)	33(1)	31(1)	46(1)	-2(1)	0(1)	-5(1)
C(6)	38(1)	26(1)	46(1)	-1(1)	-2(1)	-4(1)
C(7)	39(1)	35(1)	47(1)	-10(1)	-3(1)	4(1)
C(8)	29(1)	37(1)	39(1)	-4(1)	-2(1)	4(1)
C(9)	27(1)	29(1)	36(1)	1(1)	-3(1)	3(1)
C(10)	28(1)	32(1)	37(1)	-3(1)	1(1)	2(1)
C(11)	36(1)	42(1)	59(1)	-2(1)	-7(1)	9(1)
C(12)	55(1)	33(1)	44(1)	-7(1)	-6(1)	9(1)
C(13)	57(1)	45(1)	66(1)	11(1)	-3(1)	-4(1)
C(14)	87(1)	58(1)	80(1)	6(1)	15(1)	-17(1)
C(15)	143(3)	44(1)	62(1)	4(1)	29(1)	-2(1)
C(16)	126(2)	60(1)	46(1)	3(1)	7(1)	32(1)
C(17)	79(1)	54(1)	42(1)	-7(1)	-9(1)	25(1)
C(18)	49(1)	61(1)	46(1)	-12(1)	11(1)	-3(1)
C(19)	28(1)	49(1)	49(1)	-16(1)	-1(1)	3(1)
C(20)	48(1)	53(1)	59(1)	-2(1)	14(1)	-1(1)
C(21)	62(1)	52(1)	105(2)	4(1)	3(1)	-12(1)
C(22)	76(2)	93(2)	102(2)	44(1)	-6(1)	-4(1)
C(23)	28(1)	59(1)	71(1)	-3(1)	-3(1)	-3(1)

C(24)	50(1)	81(1)	62(1)	−13(1)	−9(1)	−10(1)
C(25)	64(1)	68(1)	87(1)	−6(1)	6(1)	−21(1)
C(26)	61(1)	53(1)	82(1)	−12(1)	36(1)	−2(1)
C(27)	75(1)	76(1)	134(2)	−5(1)	58(2)	20(1)
C(28)	110(2)	100(2)	78(2)	−9(1)	44(1)	7(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (.^{2}x 10 ^{3}) for sls62t.

	x	y	z	U(eq)
H(2A)	6372	-1856	721	65
H(1A)	6710	749	676	47
H(1B)	5442	800	565	47
H(2B)	5855	1880	1540	42
H(3A)	7748	1781	1708	45
H(6A)	7772	2723	2756	46
H(7A)	6473	2371	3614	50
H(7B)	5953	2725	2763	50
H(10A)	4960	-622	2550	40
H(11A)	9713	40	3876	57
H(11B)	9368	-736	3182	57
H(13A)	6983	-645	3483	70
H(14A)	6140	-1660	4281	90
H(15A)	7179	-2561	5302	98
H(16A)	9029	-2468	5509	94
H(17A)	9858	-1430	4750	73
H(18A)	4778	251	3471	77
H(18B)	4678	1420	3694	77
H(18C)	5712	783	4067	77
H(19A)	3963	250	1108	52
H(19B)	3612	-820	1412	52
H(20A)	3005	1850	683	63
H(21A)	3684	3386	1289	112
H(21B)	4097	2416	1802	112
H(21C)	3164	3106	2012	112
H(22A)	2039	3366	370	140
H(22B)	1331	3118	997	140
H(22C)	1263	2402	262	140
H(23A)	547	674	794	65
H(24A)	1074	-435	-127	100

H(24B)	2275	-405	336	100
H(24C)	1735	604	-64	100
H(25A)	359	-1100	935	111
H(25B)	529	-542	1749	111
H(25C)	1494	-1143	1498	111
H(26A)	2110	2086	2719	75
H(27A)	259	2147	2741	135
H(27B)	26	1385	2028	135
H(27C)	485	2497	1926	135
H(28A)	1466	953	3562	139
H(28B)	2500	503	3299	139
H(28C)	1346	81	2925	139