Supporting Information for:

The Enantioselective Tsuji Allylation

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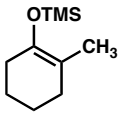
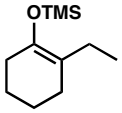
Materials and Methods. Unless otherwise stated, reactions were performed in flame-dried glassware under an argon atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Tetrabutylammonium triphenyldifluorosilicate (TBAT) was purchased from Sigma-Aldrich Chemical Company and azeotropically dried five times from acetonitrile prior to use. Trimethylsilyl chloride (TMSCl) and triethyl amine (TEA) were distilled from sodium hydride immediately prior to use. Sodium iodide was dried by heating at 90 °C (2 torr) for 12 h. (*R,R*)-Trost Ligand (**3**), (*R*)-Binap (**4**), (*R,R*)-Me-Duphos (**5**), (*R,R*)-Diop (**6**), (*R*)-Mop (**7**), (*R*)-Quinap (**8**), (*R*)-*i*-Pr-PHOX (**11**), and Tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) were purchased from Strem and stored in a glove box until immediately before use. (*R*)-Ph-PHOX (**9**), (*S*)-Bn-PHOX (**10**), and (*S*)-*t*-Bu-PHOX (**12**) were prepared by known methods.[1] Allyl chloroformate, and diallyl carbonate and dimethallyl carbonate were used as received. Methallyl chloroformate was prepared by the method of Kirby.[2] Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, anisaldehyde, or CAM staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing chiralcel AD, OD-H, or OJ columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd with visualization at 254 nm. Analytical chiral GC was performed with an Agilent 6850 GC utilizing a G-TA (30 m x 0.25cm) column (1.0 mL/min carrier gas flow). Analytical achiral GC was performed with an Agilent 6850 GC utilizing a DB-WAX (30m x 0.25 mm) column (1.0 mL/min carrier gas flow). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz and 75 MHz respectively), and are reported relative to Me_4Si (δ 0.0). Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Data for ^{13}C NMR spectra are reported in terms of chemical shift relative to Me_4Si (δ 0.0). IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High resolution mass spectra were obtained from the Caltech Mass Spectral Facility. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number.

General Procedure for the Synthesis of Silyl Enol Ethers.

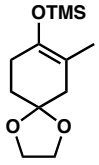
Table 3 Entry 2. Substrate:[3,4] To a solution of sodium iodide (15.0 g, 100 mmol, 1.25 equiv) in ACN (125 mL) were added 2-ethylcyclohexanone (10.1 g, 80 mmol, 1.0 equiv), TEA (14.0 mL, 100 mmol, 1.25 equiv), and finally TMSCl (11.6 mL, 91.2 mmol, 1.14 equiv) in a dropwise fashion. After 1 h, pentane (75 mL) was added, the biphasic mixture was stirred for 2 min, and the pentane decanted. After additional pentane extractions (5 x 75 mL), the combined pentane fractions were washed with water (2 x 50 mL), brine (1 x 50 mL), and dried (Na_2SO_4). Evaporation under reduced pressure gave the crude silyl enol ether (12.0 g) as an 80 : 20 mixture (NMR) of regioisomers favoring the tetrasubstituted silyl enol ether. An oxygen balloon was affixed to a flask containing a solution of the crude silyl enol ether (6.0 g) and palladium (II) diacetate (338.9 mg, 1.51 mmol) in DMSO (250 mL). The reaction mixture darkened and became heterogeneous. After 48 h, ^{1}H NMR analysis of an aliquot indicated less than 2% of the undesired isomer, and the reaction mixture was poured into a separatory funnel containing pentane (300 mL), water (300 mL), and ice (200 g). The layers were separated and the aqueous layer extracted with pentane (3 x 200 mL). The pentane fractions were washed with water (2 x 100 mL), brine (100 mL), and dried (Na_2SO_4). Evaporation and chromatography (2 % Et_2O in Hexanes on SiO_2) afforded the pure silyl enol ether (3.21 g, 40.5 % yield).
84.2 %



84.2 % yield of a ~10 : 1 mixture favoring the tetrasubstituted isomer was isolated after simple distillation. The minor isomer was removed by fractional distillation with a spinning band column.[5] ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (m, 2H), 1.94 (m, 2H), 1.64 (m, 2H), 1.58-1.49 (m, 5H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 111.8, 30.3, 30.1, 23.8, 23.0, 16.3, 0.7; IR (Neat Film NaCl) 2930, 1688, 1252, 1185, 843 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{20}OSi$ $[M]^+$: 184.1284, found 184.1275.

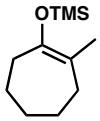


40.5 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08-1.90 (m, 6H), 1.62 (m, 2H), 1.54 (m, 2H), 0.92 (t, J = 7.8 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 117.4, 30.4, 27.0, 23.7, 23.1, 22.9, 12.2, 0.7; IR (Neat Film NaCl) 2961, 2933, 1680, 1252, 922, 843 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{22}OSi$ $[M]^+$: 198.1440, found 198.1436.

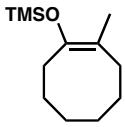


51.1 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (m, 4H), 2.21 (m, 4H), 1.79 (app. t, J = 6.9 Hz, 2H), 1.54 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 108.9, 108.0, 64.4,

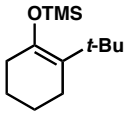
39.9, 31.7, 28.7, 16.2, 0.69; IR (Neat Film NaCl) 2956, 1691, 1252 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{22}O_3Si$ $[M]^+$: 242.1338, found 242.1334.



38.5 % yield. ^1H NMR (300 MHz, $CDCl_3$) δ 2.23 (app. t, J = 5.4 Hz, 2H), 2.01 (app. t, J = 5.1 Hz, 2H), 1.66 (m, 2H), 1.59 (s, 3H), 1.56-1.45 (m, 4H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 116.9, 35.1, 32.7, 31.6, 26.5, 25.5, 18.7, 0.6; IR (Neat Film NaCl) 2921, 1678, 1251, 1171, 892, 842 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{22}OSi$ [M]+: 198.1440, found 198.1439.



29.4 % yield. Pyridine was substituted for TEA. ^1H NMR (300 MHz, $CDCl_3$) δ 2.21 (m, 2H), 2.05 (m, 2H), 1.61-1.44 (m, 8H), 1.57 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 113.5, 31.7, 28.9, 28.8, 26.7, 26.3, 15.8, 0.8; IR (Neat Film NaCl) 2924, 1678, 1251 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{24}OSi$ [M]+: 212.1597, found 212.1590.



24.6 % yield. ^1H NMR (300 MHz, $CDCl_3$) δ 2.09-1.99 (m, 4H), 1.63-1.44 (m, 4H), 1.11 (s, 9H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 120.7, 34.1, 32.1, 29.6, 26.1, 23.7, 23.4, 1.3; IR (Neat Film NaCl) 2931, 1653, 1253, 1188, 931, 842 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{24}OSi$ [M]+: 226.1753, found 226.1743.

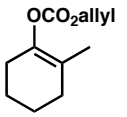
General Procedures for the Synthesis of Allyl Enol Carbonates.

Method A. Table 2 Entry 1. Substrate:[6] To a solution of potassium *t*-butoxide (5.88 g, 52.5 mmol, 1.05 equiv) in DMF (100 mL) was added 2-methylcyclohexanone (6.13 mL, 50 mmol, 1.0 equiv). After 12 h, the reaction mixture was cooled in an ice bath and allyl chloroformate (6.4 mL, 60 mmol, 1.2 equiv) was added in a dropwise fashion. After an additional 30 min in the ice bath and 15 min at 25 °C, the reaction mixture was quenched into water (250 mL), extracted with DCM / hexanes 2 / 1 (4 x 125 mL), dried ($MgSO_4$), and evaporated. Chromatography (2.5 → 4 % Et_2O in Hexanes on SiO_2) afforded the allyl enol carbonate (4.49 g, 45.7 % yield).

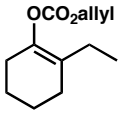
Method B. Table 2 Entry 4. Substrate:[7] To a solution of (2-ethylcyclohex-1-enyloxy)trimethylsilane (Table 3 Entry 2 Substrate) (1.50 g, 7.56 mmol, 1.0 equiv) in THF (14 mL) cooled to -78 °C was added a solution of potassium *t*-butoxide (0.933 g, 8.32 mmol, 1.1 equiv) in THF (8 mL) in a dropwise fashion over 2 min. The reaction mixture was maintained at -60 °C for 2.5 h, at which time allyl chloroformate (847 μL, 7.93 mmol, 1.05 equiv) in THF (3

mL) was added. After 1 h at -50 °C, the reaction mixture was poured into a mixture of DCM (20 mL) and half saturated aqueous NH_4Cl (20 mL). The layers were separated and the aqueous layer extracted with DCM (3 x 10 mL). The organic fractions were washed with water (50 mL), brine (50 mL), and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure followed by chromatography on (2 % Et_2O in Hexanes on SiO_2) and heating (rt → 105 °C) at 2 torr in a kugelrohr distillation apparatus afforded the allyl enol carbonate (0.944 g, 59.4 % yield).

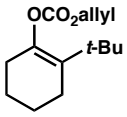
Method C. Table 2 Entry 12. Substrate:[8] To a cooled (0 °C) solution of LiHMDS (17.16 mmol, 1.1 equiv) in THF (37 mL) was added 2-methyl-1-tetralone (2.37 mL, 15.6 mmol, 1.0 equiv) in a dropwise manner over 15 min. After an additional 1.5 h at 0 °C, the enolate solution was added dropwise over 15 min to a -78 °C solution of allyl chloroformate (2.0 mL, 18.7 mmol, 1.2 equiv) in THF (80 mL). The reaction mixture was allowed to warm to 25 °C in a Dewar vessel over 8 h. At which time, the reaction was quenched into DCM (100 mL) and half saturated aqueous NH_4Cl (100 mL). The layers were separated and the aqueous layer extracted with DCM (2 x 50 mL). The organic fractions were washed with brine (100 mL), and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure, and chromatography (2 → 5 % Et_2O in Hexanes on SiO_2) afforded the allyl enol carbonate (3.34 g, 87.7 % yield).



45.7 % yield. Prepared by Method A: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (ddt, *J* = 17.4, 10.5, 5.6 Hz, 1H), 5.36 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.2, 1.2 Hz, 1H), 4.63 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.13 (m, 2H), 2.02 (m, 2H), 1.70 (m, 2H), 1.59 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.2, 131.5, 120.8, 118.8, 68.5, 30.0, 26.6, 23.1, 22.3, 15.7; IR (Neat Film NaCl) 3936, 1755, 1275, 1239, 1037 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{16}O_3$ $[M]^+$: 196.1100, found 196.1092.

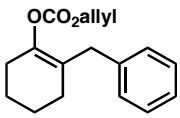


59.4 % yield. Prepared by Method B: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.4, 10.5, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.64 (dt, *J* = 5.7, 1.5 Hz, 2H), 2.16 (m, 2H), 2.05 (m, 2H), 1.99 (q, *J* = 7.8, 2H), 1.70 (m, 2H), 1.61 (m, 2H), 0.4 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.7, 131.5, 126.3, 118.8, 68.5, 27.2, 26.6, 23.0, 22.9, 22.3, 11.9; IR (Neat Film NaCl) 2936, 1754, 1239 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1255.

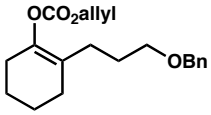


17.5 % yield. Prepared by Method B: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 5.65 (app. dt, *J* = 5.7, 1.2 Hz, 2H), 2.19 (m, 2H), 2.10 (m, 2H), 1.63 (m, 4H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ

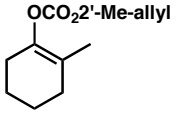
153.1, 142.1, 131.6, 130.7, 118.9, 68.4, 34.8, 29.4, 28.1, 26.4, 23.1, 22.7; IR (Neat Film NaCl) 2926, 1754, 1241 cm^{-1}; HRMS *m/z* calc'd for $C_{14}H_{22}O_3$ $[M]^+$: 238.1569, found 238.1566.



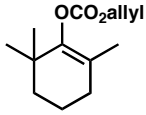
51.6 % yield. Prepared by Method A: ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.16 (m, 5H), 5.95 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.38 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.2,1.2 Hz, 1H), 4.66 (app. dt, *J* = 5.7, 1.2 Hz, 2H), 3.35 (s, 2H), 2.27 (app. t, *J* = 6.3 Hz, 2H), 1.95 (m, 2H), 1.73 (m, 2H), 1.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 143.1, 139.3, 131.4, 128.8, 128.3, 126.0, 123.9, 119.0, 68.6, 36.0, 27.5, 26.7, 23.0, 22.2; IR (Neat Film NaCl) 2937, 1754, 1702, 1648, 1600, 1239 cm^{-1}; HRMS *m/z* calc'd for $C_{17}H_{20}O_3$ $[M]^+$: 272.1413, found 272.1416.



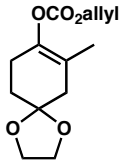
47.6 % yield. Prepared by Method A: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 5.92 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.35 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.25 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.60 (app. dt, *J* = 5.7, 0.9 Hz, 2H), 4.49 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.11 (m, 6H), 1.64 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 142.6, 138.7, 131.5, 128.3, 127.6, 127.4, 124.3, 118.8, 72.7, 70.0, 68.5, 27.7, 27.3, 26.6, 26.5, 23.0, 22.3; IR (Neat Film NaCl) 2924, 1754, 1240 cm^{-1}; HRMS *m/z* calc'd for $C_{20}H_{27}O_4$ $[M+H]^+$: 331.1909, found 331.1907.



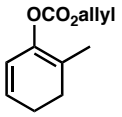
16.1 % yield. Prepared by Method B: ^1H NMR (300 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.96 (s, 1H), 4.57 (s, 2H), 2.16 (m, 2H), 2.034 (bs, 2H), 1.79 (s, 3H), 1.77-1.58 (m, 4H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 142.2, 139.4, 120.9, 113.4, 71.1, 30.1, 26.6, 23.1, 22.3, 19.3, 15.8; IR (Neat Film NaCl) 2926, 1755, 1236 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1259.



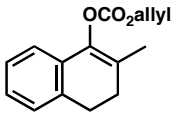
58.6 % yield. Prepared by Method C: ^1H NMR (300 MHz, $CDCl_3$) δ 5.96 (m, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 6.9 Hz, 2H), 2.05 (t, *J* = 5.4 Hz, 2H), 1.56 (m, 4H), 1.49 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 147.9, 131.6, 120.7, 118.8, 68.5, 39.2, 34.9, 31.1, 26.7, 19.1, 16.5; IR (Neat Film NaCl) 2935, 1759, 1238 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{20}O_3$ $[M]^+$: 224.1413, found 224.1418.



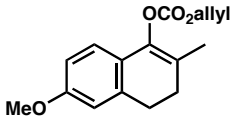
30.9 % yield. Prepared by Method B: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.41 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.65 (app. dt, *J* = 5.7, 1.5 Hz, 2H), 3.97 (m, 4H), 2.37 (m, 2H), 2.30 (bs, 2H), 1.87 (app. t, *J* = 6.6 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 141.3, 131.4, 119.0, 118.5, 107.3, 68.6, 64.5, 39.9, 31.3, 25.3, 15.8; IR (Neat Film NaCl) 2919, 1756, 1250 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{19}O_5$ $[M+H]^+$: 255.1232, found 255.1227.



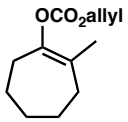
44.8 % yield. Prepared by Method C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.75 (m, 2H), 5.39 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.29 (d, *J* = 10.5, 1.2 Hz, 1H), 4.67 (app. dt, *J* = 5.7, 1.5 Hz, 2H), 2.42 (bs, 4H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 140.4, 131.3, 126.1, 122.7, 120.0, 119.1, 68.8, 28.2, 22.4, 15.7; IR (Neat Film NaCl) 2933, 1760, 1260 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{14}O_3$ $[M]^+$: 194.0943, found 194.0938.



87.7 % yield. Prepared by Method C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.08 (m, 4H), 6.01 (ddt, *J* = 17.7, 10.4, 5.6 Hz 1H), 5.41 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.32 (dd, *J* = 10.2, 1.0 Hz, 1H), 4.72 (dt, *J* = 6.3, 1.4 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 140.6, 135.2, 131.3, 130.8, 127.3, 127.0, 126.4, 124.4, 119.9, 119.1, 68.9, 28.8, 27.4, 16.5; IR (Neat Film NaCl) 2935, 2833, 1760, 1239 cm^{-1}; HRMS *m/z* calc'd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1100, found 244.1098.

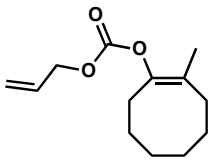


88.1 % yield. Prepared by Method C: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (m, 1H), 6.70 (m, 2H), 5.98 (ddt, *J* = 17.1, 10.4, 5.7 Hz 1H), 5.42 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.32 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.71 (dt, *J* = 5.7, 1.2 Hz, 2H), 3.78 (s, 3H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.38 (t, *J* = 8.1 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 153.1, 140.4, 137.2, 131.3, 123.9, 121.4, 121.1, 119.1, 113.7, 110.9, 68.9, 55.2, 28.8, 27.8, 16.3; IR (Neat Film NaCl) 2933, 1758, 1237 cm^{-1}; HRMS *m/z* calc'd for $C_{16}H_{18}O_4$ $[M]^+$: 274.1205, found 274.1213.



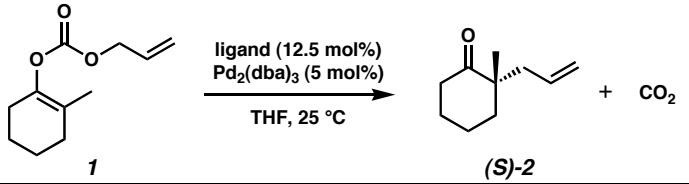
35.7 % yield. Prepared by Method B: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.5, 5.7 Hz 1H), 5.37 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.65 (app. dt, *J* =

6.0, 1.5 Hz, 2H), 2.33 (m, 2H), 2.10 (m, 2H), 1.70-1.54 (m, 6H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 146.2, 131.5, 125.5, 118.8, 68.5, 32.8, 32.5, 31.0, 25.7, 25.3, 18.3; IR (Neat Film NaCl) 2925, 1753, 1255, 1226 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1253.



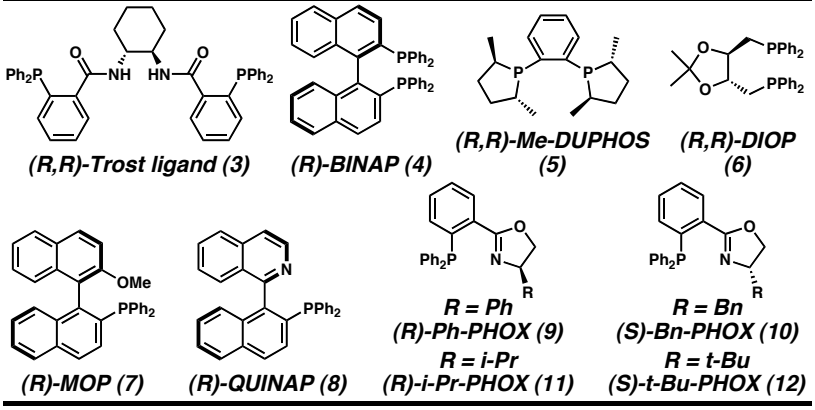
27.8 % yield. Prepared by Method B: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (m, 1H), 5.39 (d, *J* = 16.5 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 5.4 Hz, 2H), 2.34 (app. t, *J* = 5.7 Hz, 2H), 2.15 (app. t, *J* = 5.4 Hz, 2H), 1.59 (s, 3H), 1.64-1.48 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 143.7, 131.5, 123.0, 118.8, 68.5, 31.4, 29.7, 28.7, 28.4, 26.6, 25.6, 15.5; IR (Neat Film NaCl) 2927, 1754, 1227 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{20}O_3$ $[M]^+$: 224.1413, found 224.1419.

Table 1. *Ligand Screen.*



1 *(S)-2*

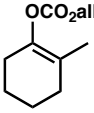
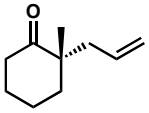
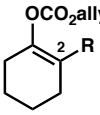
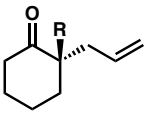
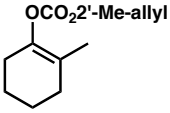
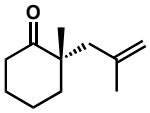
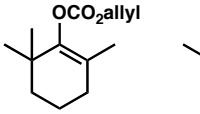
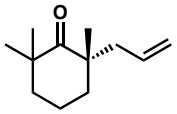
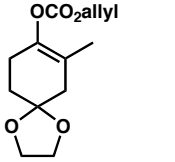
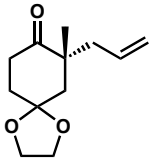
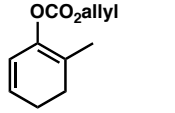
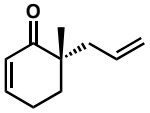
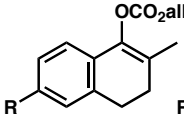
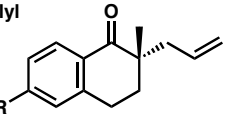
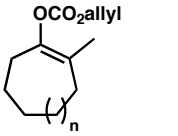
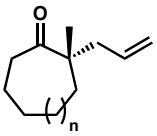
entry	ligand	time (h)	% yield[a]	% ee[b]
1	*(R,R)-Trost ligand (3)*	5	92	64[c]
2	*(R)-BINAP (4)*	5	76	2[c]
3	*(R,R)-Me-DUPHOS (5)*	5	66	0
4	*(R,R)-DIOP (6)*	2	59	2[c]
5	*(R)-MOP (7)*	3	47	13
6	*(R)-QUINAP (8)*	2	97	61
7	*(R)-Ph-PHOX (9)*	2	95	65[c]
8	*(S)-Bn-PHOX (10)*	5	94	63
9	*(R)-i-Pr-PHOX (11)*	2	95	83[c]
10	*(S)-t-Bu-PHOX (12)*	2	96	88



[a] GC yield relative to an internal standard (tridecane). [b] Enantiomeric excess measured by chiral GC. [c] (*R*)-**2** produced as the major product.

General Procedure for the Asymmetric Tsuji Allylation of Allyl Enol Carbonate (1) to produce Ketone (2). Ligand and Solvent Screening Trials. A 1 dram vial equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.05 equiv) and ligand (0.0125 mmol, 0.125 equiv) were added. After the flask was flushed with argon, THF (3.0 mL) was added, the contents were stirred at 25 °C for 30 min, at which time tridecane (12.25 μL) and allyl enol carbonate **1** (19.6 mg, 0.1 mmol, 1.0 equiv) were added by syringe. When the reaction was complete by TLC, the reaction mixture was diluted with hexanes (5 mL), filtered through a small plug of silica gel and analyzed by GC. GC yield determined on DB-WAX column (70 °C initial temp, 5 °C/min ramp to 180 °C), tridecane Ret. Time = 7.000 min, Ketone **2** Ret. Time = 12.309 min

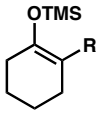
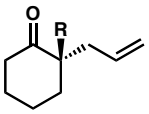
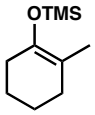
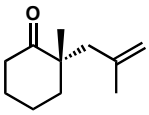
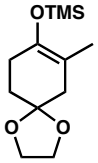
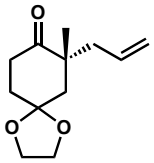
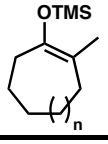
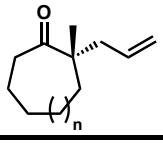
Table 2. *The Enantioselective Tsuji Enol-Carbonate Allylation.*[a]

entry	substrate	product		time (h)	% yield[b]	% ee[c]
1				2	85	87
2[d]				5	85	88 (96)[e]
3[f]				9	90	89
	1	***2***				
4			R = CH_2CH_3	2	96	92
5[g]			R = *t*-Bu	10	55[h]	81
6			R = CH_2Ph	2	96	85
7			R = $(CH_2)_3OBn$	2	87	88
8[g]				8	89	91
9				1	94	92
10				1	87	86
11				1	91	89
12[i]			R = H	2	87	91
13[i]			R = OCH_3	8	94	91
14			n = 1	6	81	87
15			n = 2	2	90	79

[a] Reactions were performed using 1.0 mmol of substrate in THF (0.033 M in substrate) at 25 °C with $Pd_2(dba)_3$ (2.5 mol%), **12** (6.25 mol%), unless stated otherwise. [b] Isolated yields. [c] Measured by chiral GC or HPLC. [d] Performed on 5.1 mmol scale. [e] In parentheses is the % ee after one recrystallization of the corresponding semicarbazone. [f] Reaction performed at 12 °C (GC yield). [g] Performed with 5 mol% $Pd_2(dba)_3$ and 12.5 mol% **12**. [h] Isolated yield after conversion to the corresponding diketone via Wacker oxidation. [i] Performed at 10 °C.

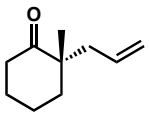
General Procedure for the Asymmetric Tsuji Allylation of Allyl Enol Carbonates: Preparative Runs (1.0 mmol) in Table 2. A 50 mL rb flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv) and *(S)*-*t*-Bu-PHOX (24.2 mg, 0.0625 mmol, 0.0625 equiv) were added. After the flask was flushed with argon, THF (30 mL) was added and the contents were stirred at 25 °C for 30 min, at which time allyl enol carbonate **1** (196.2 mg, 1.0 mmol, 1.0 equiv) was added by syringe in one portion. When the reaction was complete by TLC, the reaction mixture was evaporated under reduced pressure and the residue chromatographed (2 → 3 % Et_2O in Pentane on SiO_2) to afford ketone **2** (129.6 mg, 85.1% yield).

Table 3. *The Enantioselective Tsuji Enol-Silane Allylation.*[a]

entry	substrate	product		time (h)	% yield[b]	% ee[c]
1			R = CH_3	2	95	87
2			R = CH_2CH_3	3	96	92
3[d]				4	79	91
4				2	99	81
5			n = 1	2	94	86
6			n = 2	3	96	79

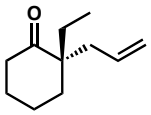
[a] Reactions were performed using 1.0 mmol of substrate in THF (0.033 M in substrate) at 25 °C with $Pd_2(dba)_3$ (2.5 mol%), **12** (6.25 mol%), diallyl carbonate (1.05 equiv), TBAT (35 mol%) unless stated otherwise. [b] Isolated yields. [c] Measured by chiral GC or HPLC. [d] Reaction performed with dimethallyl carbonate (1.05 equiv).

General Procedure for the Asymmetric Tsuji Allylation of Silyl Enol Ethers: Preparative Runs (1.0 mmol) in Table 3. A 50 mL rb flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv), *(S)-t*-Bu-PHOX (24.2 mg, 0.0625 mmol, 0.0625 equiv), and TBAT (189 mg, 0.35 mmol, 0.35 equiv) were added. After the flask was flushed with argon, THF (30 mL) was added, the contents were stirred at 25 °C for 30 min, at which time diallyl carbonate (150.6 _ L, 1.05 mmol, 1.05 equiv) and then (2-methylcyclohex-1-enyloxy)trimethylsilane (184.35 mg, 1.0 mmol, 1.0 equiv) were added by syringe in one portion. When the reaction was complete by TLC, the reaction mixture evaporated under reduced pressure and the residue chromatographed (2 → 3 % Et_2O in Pentane on SiO_2) to afford ketone **2** (144.3 mg, 94.8 % yield).

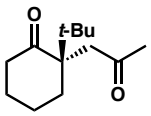


2

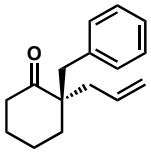
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75-5.61 (m, 1H), 5.05 (s, 1H), 5.01 (m, 1H), 2.40-2.31 (m, 3H), 2.21 (dd, *J* = 13.8, 7.5 Hz, 1H), 1.78 (m, 5H), 1.56 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 133.7, 117.9, 48.4, 41.9, 38.8, 38.5, 27.4, 22.6, 21.0; IR (Neat Film NaCl) 2934, 2865, 1707, 1451, 912 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{16}O$ $[M]^+$: 152.1201, found 152.1204; $[\alpha]_D^{28}$ -22.90° (*c* 2.09, hexane, 98 % ee).



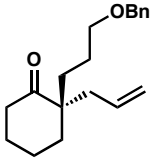
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (m, 1H), 5.02 (m, 2H), 2.47-2.18 (m, 4H), 1.90-1.60 (m, 7H), 1.46 (ddd, *J* = 21.6, 15.0, 7.2 Hz, 1H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 134.2, 117.6, 51.6, 39.2, 38.5, 36.0, 27.2, 27.1, 20.7, 7.8; IR (Neat Film NaCl) 2937, 1703 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{18}O$ $[M]^+$: 166.1358, found 166.1362; $[\alpha]_D^{28}$ +28.58° (*c* 1.51, hexane, 92 % ee).



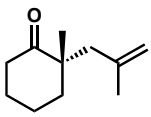
^{1}H NMR (300 MHz, $CDCl_3$) δ 3.29 (d, *J* = 18.0 Hz, 1H), 2.58 (app. dt, *J* = 16.2, 4.8 Hz, 1H), 2.34 (d, *J* = 17.7 Hz, 1H), 2.23 (dd, *J* = 11.1, 6.0 Hz, 1H), 2.18-2.00 (m, 2H), 2.07 (s, 3H), 1.92-1.60 (m, 4H), 0.94 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 207.6, 53.0, 51.3, 43.2, 36.6, 31.6, 30.5, 27.7, 24.0, 23.9; IR (Neat Film NaCl) 2955, 1716, 1692, 1372, 1171 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{22}O_2$ $[M]^+$: 210.1620, found 210.1615; $[\alpha]_D^{28}$ +132.01° (*c* 1.38, hexane, 81 % ee).



^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (m, 3H), 7.12 (m, 2H), 5.74 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.12-5.03 (m, 2H), 2.91 (s, 2H), 2.46 (m, 2H), 2.28 (d, *J* = 7.2 Hz, 2H), 1.86-1.65 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 137.5, 133.7, 130.6, 127.9, 126.3, 118.2, 52.5, 40.8, 39.6, 39.2, 35.5, 26.8, 20.8; IR (Neat Film NaCl) 2937, 1704, 1638, 1602 cm^{-1}; HRMS *m/z* calc'd for $C_{16}H_{20}O$ $[M]^+$: 228.1514, found 228.1514; $[\alpha]_D^{28}$ -12.34° (*c* 2.07, hexane, 85 % ee).

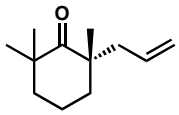


^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 5.68 (m, 1H), 5.06 (s, 1H), 5.01 (m, 1H), 4.84 (s, 2H), 3.44 (app. t, *J* = 6.3 Hz, 2H), 2.32 (m, 4H), 1.88-1.24 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8, 138.5, 133.9, 128.3, 127.5, 127.5, 117.8, 72.8, 70.5, 51.2, 39.2, 39.0, 36.4, 31.2, 27.1, 23.8, 20.7; IR (Neat Film NaCl) 2926, 1703, 1102 cm^{-1}; HRMS *m/z* calc'd for $C_{19}H_{27}O_2$ $[M+H]^+$: 287.2011, found 287.2001; $[\alpha]_D^{27}$ +24.19° (*c* 2.73, hexane, 88 % ee).

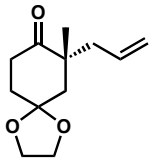


^{1}H NMR (300 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.64 (s, 1H), 2.52 (m, 1H), 2.48 (d, *J* = 13.5 Hz, 1H), 2.36 (app. dt, *J* = 14.7, 6.0 Hz, 1H), 2.25 (d, *J* = 13.8 Hz, 1H), 1.94-1.53 (m, 6H), 1.65 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.8, 142.2, 114.7, 48.7, 45.4, 40.0, 38.9,

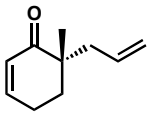
27.6, 24.3, 23.3, 21.1; IR (neat) 2927, 1707 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{18}O$ $[M]^+$: 166.1358, found 166.1358; $[\alpha]_D^{27}$ -26.42° (*c* 1.85, hexane, 90 % ee).



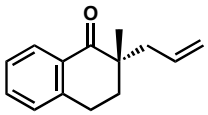
^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (m, 1H), 5.01 (m, 2H), 2.33 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.18 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.82-1.53 (m, 6H), 1.11 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.8, 134.6, 117.9, 47.6, 44.4, 43.9, 39.7, 36.8, 27.8, 27.2, 25.5, 17.7; IR (Neat Film NaCl) 2933, 1697, 1463 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{20}O$ $[M]^+$: 180.1514, found 180.1521; $[\alpha]_D^{27}$ -35.69° (*c* 2.15, hexane, 92 % ee).



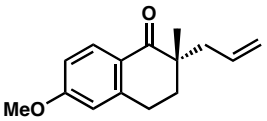
^1H NMR (300 MHz, $CDCl_3$) δ 5.67 (ddt, *J* = 17.1, 10.5, 7.2 Hz, 1H), 5.07 (bs, 1H), 5.02 (app. d, *J* = 9.3 Hz, 1H), 3.99 (app. d, *J* = 1.5 Hz, 4H), 2.57 (app. t, *J* = 6.3 Hz, 1H), 2.42 (m, 2H), 2.00 (d, *J* = 13.8 Hz, 1H), 1.98 (app. t, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 14.1 Hz, 1H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.9, 133.7, 118.4, 107.6, 64.4, 64.3, 47.5, 44.3, 42.7, 35.7, 34.5, 23.9; IR (Neat Film NaCl) 2964, 1710, 1116 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1255; $[\alpha]_D^{29}$ -7.99° (*c* 2.41, hexane, 86 % ee).



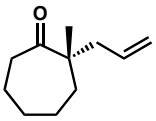
^1H NMR (300 MHz, $CDCl_3$) δ 6.87 (app. dt, *J* = 10.2, 4.2 Hz, 1H), 5.91 (app. dt, *J* = 10.2, 2.1 Hz, 1H), 5.72 (m, 1H), 5.07 (m, 1H), 5.02 (d, *J* = 9.3 Hz, 1H), 2.35 (m, 3H), 2.16 (dd, *J* = 13.8, 7.5, Hz, 1H), 1.91 (dt, *J* = 13.8, 6.0 Hz, 1H), 1.74 (dt, *J* = 13.8, 6.0 Hz, 1H), 1.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 148.8, 134.0, 128.4, 118.0, 44.4, 40.9, 32.9, 23.1, 21.6; IR (Neat Film NaCl) 2927, 1673 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{14}O$ $[M]^+$: 150.1045, found 150.1039; $[\alpha]_D^{26}$ +14.62° (*c* 1.56, hexane, 89 % ee).



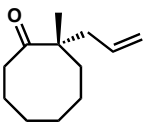
^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.29 (app. t, *J* = 7.2 Hz, 1H), 7.21 (app. d, *J* = 7.5 Hz, 1H), 5.85-5.71 (m, 1H), 5.10 (s, 1H), 5.05 (s, 1H), 2.97 (t, *J* = 6.3 Hz, 2H), 2.46 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.27 (ddt, *J* = 14.0, 7.5, 1.2 Hz, 1H), 2.07 (ddd, *J* = 13.4, 7.2, 6.0 Hz 1H), 1.89 (ddd, *J* = 14.0, 6.9, 5.7 1H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 143.2, 133.9, 133.0, 131.5, 128.6, 127.9, 126.5, 118.1, 44.5, 41.0, 33.2, 25.3, 21.8; IR (Neat Film NaCl) 3073, 2930, 1682, 1455, 1220, 916, 742 cm^{-1}; HRMS *m/z* calc'd for $C_{14}H_{16}O$ $[M]^+$: 200.1201, found 200.1194; $[\alpha]_D^{27}$ -18.59° (*c* 2.08, hexane, 88 % ee).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.78 (m, 1H), 5.09 (s, 1H), 5.04 (m, 1H), 3.84 (s, 3H), 3.93 (app. t, *J* = 6 Hz, 2H), 2.45 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.25 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.05 (m, 1H), 1.87 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 163.3, 145.7, 134.1, 130.4, 125.1, 118.0, 113.2, 112.2, 55.4, 44.3, 41.3, 33.4, 25.7, 22.0; IR (Neat Film NaCl) 2931, 1672, 1601, 1256 cm^{-1}; HRMS *m/z* calc'd for $C_{15}H_{18}O_2$ $[M]^+$: 230.1307, found 230.1313; $[\alpha]_D^{26}$ -13.71° (*c* 1.5, hexane, 89 % ee).

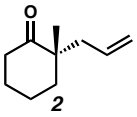
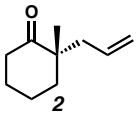
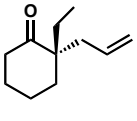
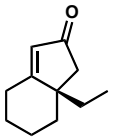
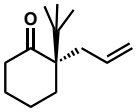
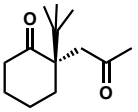
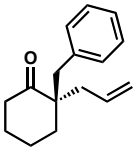
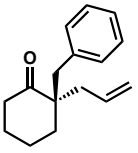
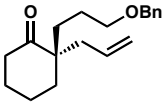
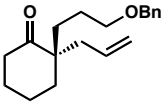
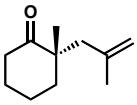
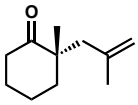
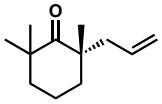
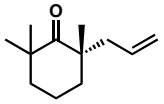
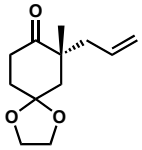
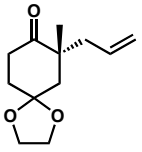


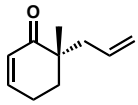
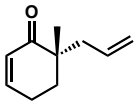
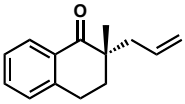
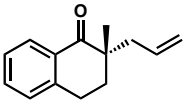
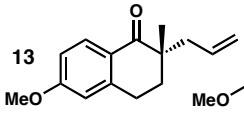
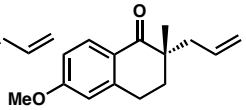
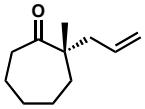
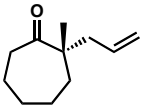
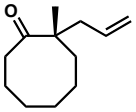
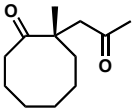
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (ddt, *J* = 16.8, 10.2, 7.5, 1H), 5.02 (m, 2H), 2.59 (app. td, *J* = 11.1, 2.7 Hz, 1H), 2.42 (app. t, *J* = 9.0 Hz, 1H), 2.24 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.16 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.78-1.30 (m, 8H), 1.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.4, 133.8, 117.9, 50.8, 43.6, 40.6, 36.6, 30.6, 26.4, 24.4, 22.3; IR (Neat Film NaCl) 2930, 1702, 1458 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{18}O$ $[M]^+$: 166.1358, found 166.1360; $[\alpha]_D^{28}$ -34.70° (*c* 1.52, hexane, 87 % ee).



^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (m, 1H), 5.04 (app. d, *J* = 1.2 Hz, 1H), 5.00 (app. d, *J* = 8.1 Hz, 1H), 2.59 (m, 1H), 2.29 (m, 2H), 2.12 (dd, *J* = 14.1, 7.7 Hz, 1H), 2.01 (m, 1H), 1.83-1.70 (m, 3H), 1.61-1.32 (m, 5H), 1.18 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.3, 133.9, 117.8, 50.1, 42.0, 36.8, 33.5, 30.4, 25.9, 24.8, 24.3, 19.8; IR (Neat Film NaCl) 2929, 1699 cm^{-1}; HRMS *m/z* calc'd for $C_{12}H_{20}O$ $[M]^+$: 180.1514, found 180.1508; $[\alpha]_D^{26}$ -21.22° (*c* 1.56, hexane, 79 % ee).

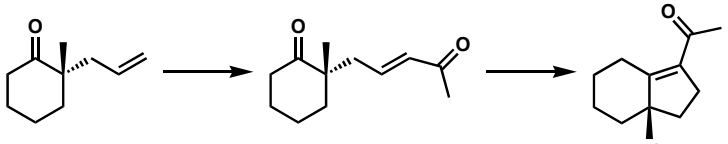
Table 4. *Methods utilized for the determination of enantiomeric excess.*

Entry	Product	Compound Assayed	ee Assay	Conditions	Retention time of (*S*) (major) isomer (min)	Retention time of (*R*) (minor) isomer (min)	% ee
1			GC G-TA	100 °C Isotherm	10.76	12.80	87
4[a]			GC G-TA	100 °C Isotherm	14.52	13.35	92
5[a]			GC G-TA	110 °C Isotherm	63.65	62.01	82
6			HPLC Chiralcel OJ	4 %EtOH in Hexane, isocratic 1.0 ml/min	17.76	11.90	85
7			HPLC Chiralcel AD	0.75 % IPA in Hexane, isocratic 1.0 ml/min	11.95	13.80	88
8			GC G-TA	100 °C Isotherm	17.84	20.44	91
9			GC G-TA	80 °C Isotherm	25.48	27.90	92
10			GC G-TA	120 °C Isotherm	26.74	28.46	86

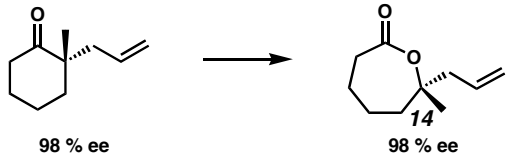
Entry	Product	Compound Assayed	ee Assay	Conditions	Retention time of (*S*) (major) isomer (min)	Retention time of (*R*) (minor) isomer (min)	% ee
11			GC G-TA	100 °C Isotherm	14.66	17.52	89
12			HPLC Chiralcel OD-H	0.1 % IPA in Heptane, isocratic 0.70 ml/min	21.60	23.19	91
13			HPLC Chiralcel OJ	1.0% EtOH in Hexane, isocratic 1.0 ml/min	11.38	10.16	91
14			GC G-TA	110 °C Isotherm	9.88	10.68	87
15[a]			GC G-TA	110 °C Isotherm	63.25	61.94	79

[a] Derivative made in an analogous manner to enone **16**

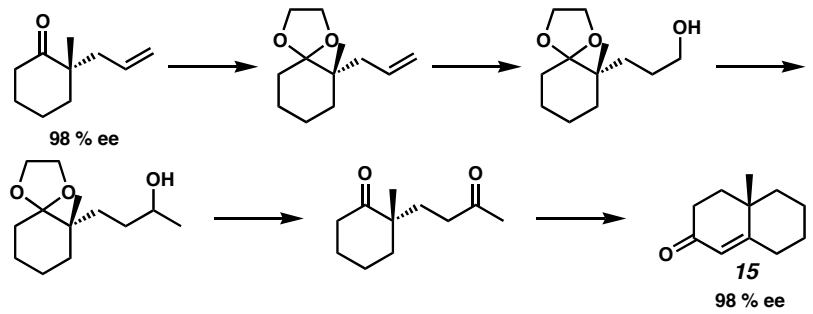
Representative Derivative Compounds:



Enone 13:[9] To a solution of ketone **2** (152.2 mg, 1.0 mmol, 1.0 equiv) and methyl vinyl ketone (208.1 _ L, 2.5 mmol, 2.5 equiv) in DCM (5 mL) was added Grubbs' 2nd generation catalyst (42.4 mg, 0.05 mmol, 0.05 equiv). The reaction mixture was heated at 40 °C for 18 h, cooled to 25 °C, and concentrated. Chromatography (20 % EtOAc in Hexanes on SiO_2) gave the enone (152.1 mg 78.3 % yield), which was dissolved in EtOAc (12 mL) and treated with 10 % Pd/C (30 mg) under an atmosphere of hydrogen gas for 12 h. The system was purged with argon, filtered through a small pad of silica gel, and concentrated. To a solution of the crude diketone in EtOH (12 mL) was added KOH (2.0 mL of a 50 mg/mL ethanolic solution). The reaction mixture was heated to 65 °C for 8 h, cooled to 25 °C, concentrated, and the residue partitioned between EtOAc (10 mL) and 1 M HCl (10 mL) The layers were separated, the aqueous layer extracted with Et_2O (3 x 25 mL), and the combined organics were washed with saturated $NaHCO_3$ (25 mL) then brine (25 mL), dried ($MgSO_4$) and concentrated. Chromatography (10→15 % Et_2O in Hexanes on SiO_2) gave enone **13** (112.4 mg, 80.5 % yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (d, *J* = 14.7 Hz, 1H), 2.59 (m, 2H), 2.23 (s, 3H), 2.01 (app. t, *J* = 13.5 Hz, 1H), 1.82 (m, 3H), 1.59 (m, 3H), 1.43-1.23 (m, 2H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 162.2, 131.9, 48.6, 41.5, 39.0, 30.9, 30.5, 27.1, 25.2, 22.9, 22.0; IR (Neat Film NaCl) 2931, 1678, 1654, 1614, 1357 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{18}O$ $[M]^+$: 178.1358, found 178.1355; $[\alpha]_D^{27}$ +82.91° (*c* = 3.26 , hexane, 98 % ee).



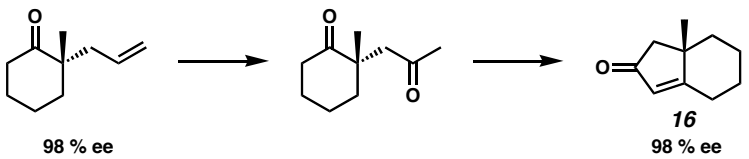
Lactone 14:[10] To a cooled (0 °C) solution of ketone **2** (152.2 mg, 1.0 mmol, 1.0 equiv) in DCM (20 mL) was added Na_2CO_3 (593.6 mg, 5.6 mmol, 5.6 equiv) and peracetic acid (800 _ L of 32 % solution in dilute acetic acid). The reaction mixture was maintained at 0 °C for 9 h, then allowed to warm to 25 °C for an additional 12 h, diluted with saturated $NaHCO_3$, and the organic layer dried (Na_2SO_4). Chromatography (5→20 % EtOAc in Hexanes on SiO_2) afforded lactone **14** (125.6 mg, 74.6 % yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (m, 1H), 5.15 (m, 1H), 5.11 (app. d, *J* = 8.4 Hz, 1H), 2.78-2.61 (m, 2H), 2.51 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.42 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.86-1.62 (m, 6H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 132.8, 119.0, 82.7, 46.7, 38.4, 37.3, 24.8, 23.8, 23.3; IR (Neat Film NaCl) 2936, 1717, 1172 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{16}O_2$ $[M]^+$: 168.1150, found 168.1154; $[\alpha]_D^{27}$ +20.58° (*c* = 3.46, hexane, 98 % ee).



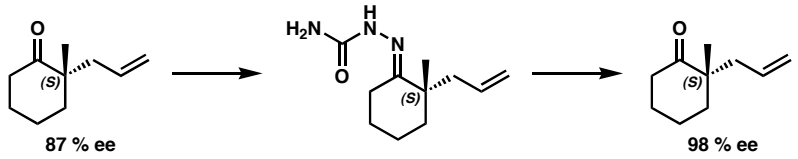
Enone 15: A solution of ketone **2** (1.23 g, 8.11 mmol, 1.0 equiv), ethylene glycol (1.8 mL), pyridinium tosylate (0.6 g) and benzene (45 mL) was refluxed for 22 h in a Dean-Stark apparatus. The reaction mixture was cooled, poured into in saturated $NaHCO_3$ (50 mL), the aqueous layer extracted with hexanes / Et_2O (1/1) (2 x 20 mL), and washed with brine (2 x 15 mL). The combined organics were dried ($MgSO_4$), concentrated, and chromatographed to give the ketal (1.59 g). The ketal in THF (15 mL) was added dropwise to a cooled (-25 °C) solution of BH_3•THF (20.3 mmol, 2.5 equiv) in THF (100 mL), and after 4 h was allowed to warm to 25 °C overnight. The reaction mixture was then cooled to -10 °C, water (25 mL) was slowly added, followed by $NaBO_3$•$4H_2O$ (4.99 g, 32.4 mmol, 4.0 equiv), and the reaction mixture was allowed to warm to 25 °C. After 48 h, the reaction mixture was partitioned between water (100 mL) and EtOAc (100 mL), the layers separated, the aqueous layer extracted with EtOAc (5 x 75 mL), and the organic fractions were dried (Na_2SO_4). Evaporation of the solvents under reduced pressure, and chromatography (20→40 % EtOAc in Hexanes on SiO_2) gave the primary alcohol (1.50 g, 86.5 % yield).

To a cooled (-78 °C) solution of DMSO (479.0 _ L, 6.72 mmol, 1.6 equiv) in DCM (45 mL) was added oxalyl chloride (475.2 _ L, 5.45mmol, 1.3 equiv). After 45 min, the primary alcohol (900 mg, 4.19 mmol, 1.0 equiv) in DCM (5 mL) was added in a dropwise manner. After an additional 30 min, TEA (2.32 mL, 16.8 mmol, 4.0 equiv) was added, the reaction mixture warmed to 25 °C, and quenched with half saturated aq. $NaHCO_3$. The aqueous layer was extracted with DCM (3 x 30 mL), the combined organics dried ($MgSO_4$), and solvents evaporated. This crude aldehyde in THF (45 mL) was cooled to -10 °C, treated with methyl magnesium bromide 3 M in Et_2O (8.40 mmol, 2.0 equiv), quenched with water (20 mL) and saturated aq. NH_4Cl (20 mL), extracted DCM (4 x 20 mL), dried ($MgSO_4$), and solvents evaporated. The resulting crude secondary alcohol was resubmitted to the Swern oxidation conditions described above to give a crude methyl ketone. A solution of the methyl ketone in acetone (45 mL) and water (0.7 mL) was treated with TsOH•H_2O (60 mg), and heated at 50 °C for 4 h. The reaction mixture was then concentrated, and chromatographed (7.5→20 % EtOAc in Hexanes on SiO_2) to give the diketone (515.8 mg, 67.5 % yield for 4 steps).

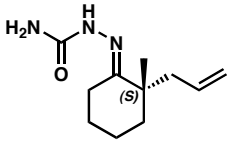
To a solution of KOH (300mg 5.36 mmol, 1.91 equiv) in EtOH (40 mL) was added the diketone (510.0 mg, 2.80 mmol, 1.0 eq) dissolved in EtOH (15 mL), and the reaction mixture heated at 60 °C for 4 h. The reaction was quenched with acetic acid (306 _ L, 5.36 mmol, 1.91 equiv), concentrated and chromatographed (5→20 % Et_2O in Hexanes on SiO_2) to give enone **15** (334.2 mg, 72.7 % yield, 42.4 % overall yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (s, 1H), 2.56-2.22 (m, 4H), 1.92-1.64 (m, 6H), 1.44-1.30 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 170.5, 124.1, 41.5, 38.0, 35.9, 34.0, 32.7, 27.1, 22.0, 21.7; IR (Neat Film NaCl) 2930, 1678 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{16}O$ $[M]^+$: 164.1201, found 164.1196; $[\alpha]_D^{28}$ +216.15° (*c* = 1.05, ethanol, 98 % ee).[11]



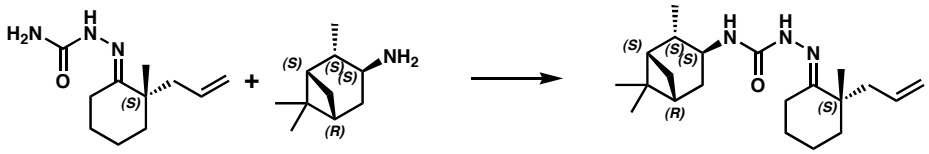
Enone 16:[12] To a solution of ketone **2** (304.4 mg, 2.0 mmol, 2.0 equiv) in dimethylacetamide (2.8 mL) and water (0.4 mL) was added palladium (II) chloride (53.1 mg, 1.2 mmol, 0.15 equiv), copper (II) acetate hydrate (217.9 mg, 1.20 mmol, 0.60 equiv), and an oxygen balloon. After 24 h of vigorous stirring at 25 °C the reaction mixture was chromatographed (5→25 % EtOAc in Hexanes on SiO_2). To a solution of the resulting diketone in EtOH (30 mL) was added KOH (3.4 mL of a 50 mg/mL ethanolic solution), and the reaction mixture was heated at 60 °C for 6 h. The temperature was increased to 80 °C and additional KOH (200 mg) was added. After 4 h the reaction was cooled and concentrated. The resulting residue was partitioned between EtOAc (30 mL) and water (20 mL) and acidified to pH = 2 with HCl (3 M). The layers were separated, and aqueous layer extracted with EtOAc (3 x 20 mL). The combined organics were washed with brine (30 mL), dried (Na_2SO_4), and concentrated. Chromatography (10→30% Et_2O in Pentane on SiO_2) afforded enone **16** (219.1 mg, 72.9% overall yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (s, 1H), 2.62 (bd, *J* = 12.0 Hz, 1H), 2.35 (td, *J* = 13.5, 5.4 Hz, 1H), 2.27 (dd, *J* = 18.3, 0.9 Hz, 1H), 2.17 (d, *J* = 18.6 Hz, 1H), 2.26-1.88 (m, 2H), 1.64 (m, 2H), 1.36 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2, 188.6, 126.0, 52.1, 43.1, 40.6, 27.9, 27.8, 24.0, 21.8; IR (Neat Film NaCl) 2934, 1713, 1622, 1221 cm^{-1}; HRMS *m/z* calc'd for $C_{10}H_{14}O$ $[M]^+$: 150.1045, found 150.1041; $[\alpha]_D^{27}$ -44.86° (*c* = 3.55, hexane, 98 % ee).



Procedure for Increasing Enantiomeric Excess of Ketone Products: To a solution of ketone **2** (661.4 mg, 4.34 mmol, 1.0 equiv) of 88 % ee in pyridine (1.22 mL), water (3.0 mL), and MeOH (8.0 mL) was added semicarbazide•HCl (848.1 mg, 7.60 mmol, 1.75 equiv). The reaction mixture was heated at 105 °C for 15 min, cooled, diluted with water (10 mL), filtered, and dried to give the semicarbazone (763 mg, 84.0 % yield). The semicarbazone (3.10 g, 14.8 mmol, 87 % ee) was suspended in EtOH / water (35/65 v/v 355 mL) and warmed to 90 °C. When all the material had dissolved, heating was discontinued, and the flask allowed to cool in the heating bath. After 8 h, crystals were filtered and dried giving the enantioenriched semicarbazone (1.894 g, 61.1 % yield, 95 % ee). Recrystalization of this material in EtOH / water (30/70 v/v 175 mL) by the same procedure gave semicarbazone (1.692 g, 89.3 % yield, 98 % ee). To a biphasic mixture of Et_2O (30 mL) and 3 M HCl (3.0 mL) was added the enriched semicarbazone (1.00g, 4.77mmol, 1.0 equiv). The reaction mixture was stirred vigorously for 2 h and then quenched with saturated $NaHCO_3$ (40 mL). The layers were separated, and aqueous layer extracted with Et_2O (4 x 30 mL). The combined organics were washed with brine (30 mL), dried ($MgSO_4$), and concentrated to give ketone **2** (718.2 mg, 98.9 % yield).

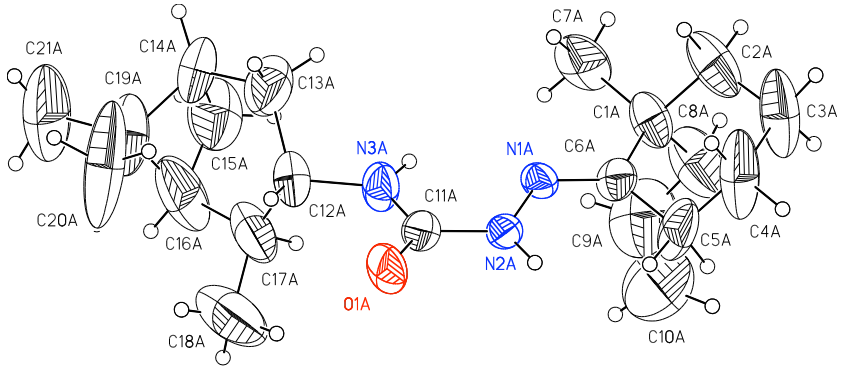


m.p. 188-189 °C from EtOH / water; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (bs, 1H), 5.73 (m, 1H), 5.05 (s, 1H), 5.00 (app. d, J = 3.3 Hz, 1H), 2.40-2.11 (m, 4H), 1.71-1.44 (m, 6H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 156.8, 134.6, 117.2, 42.9, 41.5, 38.6, 25.9, 24.5, 22.5, 21.0; IR (Neat Film NaCl) 3465, 3195, 1693, 1567, 1478 cm^{-1}; HRMS *m/z* calc'd for $C_{11}H_{20}N_3O$ $[M+H]^+$: 210.1606, found 210.1599; $[\alpha]_D^{28}$ -50.35° (*c* = 2.60, methanol).



SI1

(isopinocamphenylamine)-semicarbazone (*SI1*): To a solution of the semicarbazone (100 mg, 0.43 mmol, 1.0 equiv) in xylenes (1.0 mL) was added (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheylamine (76.2 μL, 0.45 mmol, 1.05 equiv). The reaction mixture was refluxed for 2 h, cooled, and concentrated. Chromatography (10→50 % EtOAc in Hexanes on SiO_2) afforded the (isopinocamphenylamine)-semicarbazone **SI1** (130.5 mg, 87.8 % yield): m.p. 131-133° from acetone; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (bs, 1H), 6.08 (bd, J = 8.7 Hz, 1H), 5.77 (m, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.18 (m, 1H), 2.63 (app. tdd, J = 9.9, 3.6, 2.4 Hz, 1H), 2.45-2.13 (m, 4H), 1.96 (m, 1H), 1.82 (m, 2H), 1.74-1.41 (m, 8H), 1.23 (s, 3H), 1.15 (d, J = 7.2 Hz, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 0.89 (d, J = 9.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 155.5, 134.9, 117.0, 48.0, 47.8, 46.8, 43.0, 41.6, 41.5, 38.5, 38.3, 37.8, 35.3, 28.0, 25.9, 24.5, 23.4, 22.4, 21.0, 20.8; IR (Neat Film NaCl) 3400, 3189, 3074, 2929, 1672, 1526 cm^{-1}; HRMS *m/z* calc'd for $C_{21}H_{36}N_3O$ $[M+H]^+$: 346.2858, found 346.2874; $[\alpha]_D^{27}$ -18.92° (*c* = 0.53, hexane).
The semicarbazone was recrystallized from EtOH/H_2O to provide suitable crystals for X-ray analysis.



Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 246585.

Table 5. Crystal data and structure refinement for DCB26 (CCDC 246585).

Empirical formula	$C_{21}H_{35}N_3O$
Formula weight	345.52
Crystallization Solvent	Ethanol/water
Crystal Habit	Fragment
Crystal size	0.41 x 0.37 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 7110 reflections used in lattice determination	2.31 to 24.12°
Unit cell dimensions	a = 23.1170(16) Å b = 13.6467(9) Å β= 90.396(2)° c = 13.2060(9) Å
Volume	4166.0(5) $Å^3$
Z	8
Crystal system	Monoclinic
Space group	C2
Density (calculated)	1.102 Mg/m^3
F(000)	1520
θ range for data collection	1.73 to 33.55°
Completeness to θ = 33.55°	81.9 %
Index ranges	$-29 \le h \le 34$, $-20 \le k \le 20$, $-18 \le l \le 17$
Data collection scan type	ω scans at 4 ϕ settings
Reflections collected	30377
Independent reflections	12571 [R_{int}= 0.0616]
Absorption coefficient	0.068 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9838 and 0.9726

Table 5 (cont.)

Structure solution and Refinement

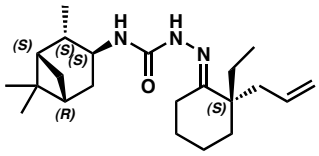
Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	12571 / 64 / 486
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.972
Final R indices [I>2σ(I), 5761 reflections]	R1 = 0.0873, *w*R2 = 0.1490
R indices (all data)	R1 = 0.1657, *w*R2 = 0.1573
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	0.4(16)
Largest diff. peak and hole	0.630 and -0.361 e.Å^{-3}

Special Refinement Details

The data are weak and the structure is disordered, in the allyl of molecule B. These two factors combine to produce a final structure that falls short of the desired quality. Nevertheless, the quality is sufficient to determine the relative stereochemistry around C1 and, given the known stereochemistry of another chiral center, the absolute conformation can be deduced. The allylic fragments were restrained to have similar geometry and the anisotropic displacement factors of the B molecule allyl fragment (only) were restrained to tend towards isotropic behavior.

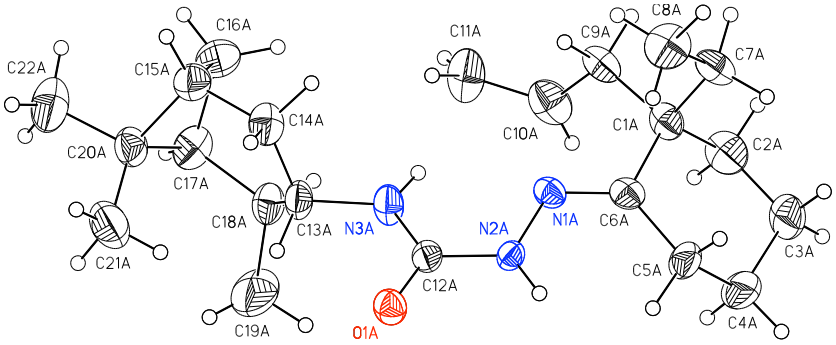
Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.



SI2

(isopinocamphenylamine)-semicarbazone (*SI2*): Prepared in an analogous manner to **SI1**: m.p. 145-146° from acetone; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (db, *J* = 21.3 Hz, 1H), 6.07 (db, *J* = 4.4 Hz, 1H), 5.86-5.72 (m, 1H), 5.08-5.04 (m, 1H), 5.00 (s, 1H), 4.23-4.12 (m, 1H), 2.68-2.55 (m, 1H), 2.46-2.34 (m, 2H), 2.30 (d, *J* = 7.5 Hz, 2H), 2.12-2.00 (m, 1H), 1.98-1.90 (m, 1H), 1.88-1.40 (m, 11H), 1.22 (s, 3H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.05 (s, 3H), 0.88 (d, *J* = 9.6 Hz, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 154.4, 135.3, 116.7, 48.0, 47.9, 46.8, 44.2, 41.7, 39.9, 38.3, 37.9, 35.6, 35.3, 28.1, 28.0, 25.6, 23.4, 22.6, 20.8, 20.7, 7.8; IR (Neat Film NaCl) 3402, 3194, 3074, 2930, 1672, 1526 cm^{-1}; HRMS *m/z* calc'd for $C_{22}H_{37}N_3O$ $[M]^+$: 359.2937, found 359.2940; $[\alpha]_D^{29}$ -4.43° (*c* = 0.38, hexane).
The semicarbazone was recrystallized from acetone to provide suitable crystals for X-ray analysis.



Note: Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 248956.

Table 6. Crystal data and structure refinement for DCB27 (CCDC 248956).

Empirical formula	$C_{22}H_{37}N_3O$
Formula weight	359.55
Crystallization Solvent	Acetone
Crystal Habit	Fragment
Crystal size	0.39 x 0.37 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 13615 reflections used in lattice determination	2.25 to 21.58°
Unit cell dimensions	a = 13.4105(11) Å b = 13.4433(11) Å c = 24.353(2) Å
Volume	4390.4(6) $Å^3$
Z	8
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.088 Mg/m^3
F(000)	1584
θ range for data collection	1.67 to 28.34°
Completeness to θ = 28.34°	94.5 %
Index ranges	$-17 \le h \le 17$, $-17 \le k \le 17$, $-32 \le l \le 30$
Data collection scan type	ω scans at 5 ϕ settings
Reflections collected	63444
Independent reflections	10086 [R_{int}= 0.0909]
Absorption coefficient	0.067 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9841 and 0.9744

Table 6 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	10086 / 447 / 570
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.208
Final R indices [I>2σ(I), 6214 reflections]	R1 = 0.0842, *w*R2 = 0.1195
R indices (all data)	R1 = 0.1330, *w*R2 = 0.1224
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.6(17)
Largest diff. peak and hole	0.271 and -0.287 e.Å^{-3}

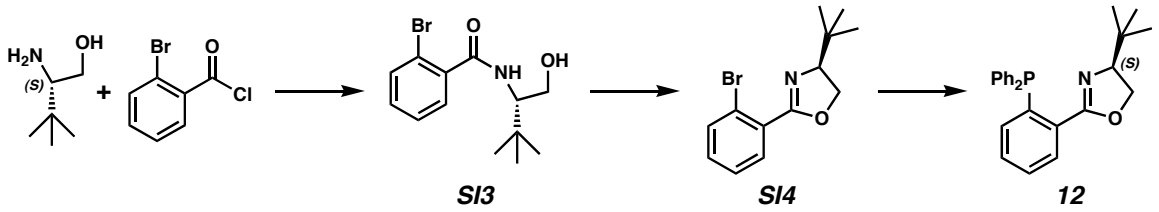
Special Refinement Details

The diffraction intensities fall off sharply past 2θ=40º, presumably because the structure is disordered. The asymmetric unit contains two molecules (hydrogen bonded to each other and of the same configuration) disordered in different ways. Molecule A is disordered about the terminal carbon (C11) of the allyl moiety. Both orientations were modeled, including riding hydrogen atoms, with the only restraint being a total occupancy of 1.0 for C11A and C11C. Molecule B is disordered in the camphene moiety, C13B-C22B. The disorder manifests as a rotation of the camphene around the N3B-C13B bond. Both orientations were restrained to have geometry similar to the corresponding part of the A molecule, using the SAME command. Additional restraints were imposed in this portion of molecule B as follows; 1) SIMU – to restrained bonded atoms to have similar displacement parameters and 2) ISOR – to restrain the anisotropic displacement parameters, U_{ij}, to approximate isotropic behavior without placing restraint on the refined value of the isotropic U.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Improved Synthesis of *(S)-t*-Bu-PHOX Ligand.



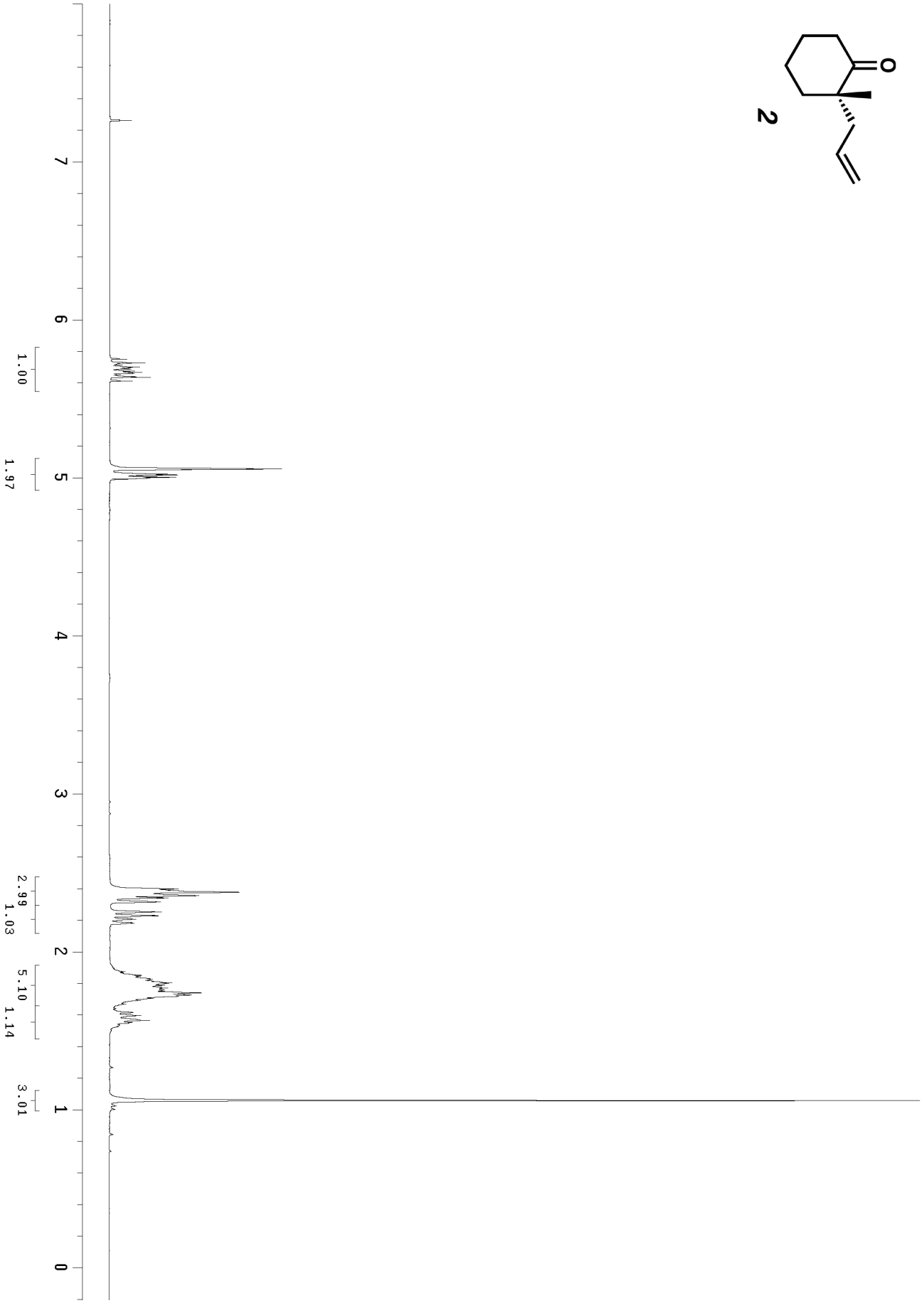
SI3 ***SI4*** ***12***

amide (*SI3*): To a solution of *(S)-t*-leucinol[13] (3.57 g, 30.5 mmol, 1.0 equiv) in DCM (100 mL) was added a solution of Na_2CO_3 (9.70 g, 91.5 mmol, 3.0 equiv) in water (75.0 mL). To the vigorously stirred biphasic mixture was added 2-bromobenzoyl chloride (4.58 mL, 35.1 mmol, 1.15 equiv) in a dropwise manner. After 12 h ambient temperature, the layers were separated, and aqueous layer extracted with DCM (2 x 50 mL). The combined organics were treated with KOH (15 mL of a 1 M methanolic solution) for 15 min, neutralized with 3 M HCl, and water (50 mL) was added. The layers were separated, and aqueous layer extracted with DCM (2 x 50 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (25→35 % Acetone in Hexanes on SiO_2) to give amide ***SI3*** (8.19 g, 89.5 % yield): m.p. 50.0-51.0° from acetone / hexanes; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 (app. dt, *J* = 7.4, 1.1 Hz, 1H), 7.26 (app. dt, *J* = 7.7, 1.8 Hz, 1H), 6.24 (bd, *J* = 8.1 Hz, 1H), 4.05 (m, 1H), 3.93 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.66 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.68 (bs, 1H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 137.9, 133.3, 131.2, 129.7, 127.6, 119.0, 62.9, 60.2, 33.8, 27.1; IR (Neat Film NaCl) 3245, 3070, 2963, 1640, 1557 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{19}NO_2Br$ $[M+H]^+$: 300.0599, found 300.0590; $[\alpha]_D^{29}$ +20.19° (*c* = 2.38, methanol, 100 % ee).

phenyloxazoline (SI4):[1] A solution of amide ***SI3*** (8.10 g, 27.0 mmol, 1.0 equiv), tosyl chloride (6.69 g, 35.1 mmol, 1.3 equiv), triethylamine (18.7 mL, 135.0 mmol, 5.0 equiv) in DCM (200 mL) in a rb flask equipped with a reflux condenser was heated at 55 °C for 22 h. At which time, water (28 mL) was added and heating continued at 75 °C for 2 h. The reaction mixture was cooled, the layers separated, and the aqueous layer extracted with DCM (2 x 25 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (5 % EtOAc in Hexanes on SiO_2) to give phenyloxazoline ***SI4*** (6.19 g, 81.2 % yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (app. dt, *J* = 8.7, 1.7 Hz, 2H), 7.33 (app. dt, *J* = 7.7, 1.5 Hz, 1H), 7.26 (m, 1H), 4.38 (dd, *J* = 10.5, 8.9 Hz, 1H), 4.25 (app. t, *J* = 8.3 Hz, 1H), 4.10 (dd, *J* = 10.2, 8.1 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 133.6, 131.4, 131.2, 130.2, 127.0, 121.8, 76.6, 69.0, 34.0, 25.9; IR (Neat Film NaCl) 2956, 1661, 1478, 1354, 1099, 1022, 963 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{17}NOBr$ $[M+H]^+$: 282.0493, found 282.0488; $[\alpha]_D^{29}$ -48.32° (*c* = 3.77, hexane, 100 % ee).

(S)-t*-Bu-PHOX (12):**[14] A mixture of copper(I) iodide (338.3 mg, 1.77 mmol, 0.125 equiv), diphenylphosphine (4.64 mL, 26.7 mmol, 1.88 equiv), N,N'-dimethylethylenediamine (1.32 mL, 12.4 mmol, 0.875 equiv) in toluene (60 mL) was stirred for 20 min a ambient temperature. At which point, phenyloxazoline ***SI4 (4.00 g, 14.2 mmol, 1.0 equiv), cesium carbonate (17.4 g, 53.3 mmol, 3.75 equiv), and toluene (60 mL) were added, the flask sealed and heated to 110 °C with stirring. A the reaction mixture became deep red after ~15 min of heating. After 6 h, the reaction mixture was allowed to cool to ambient temperature, filtered, and washed with DCM (2 x 50 mL). Evaporation of the solvent and chromatography (3→7 % EtO_2 in Hexanes on SiO_2) afforded the known[1] *(S)-t*-Bu-PHOX **12** (4.48 g, 81.4 % yield).

^{1}H NMR of Product Ketones: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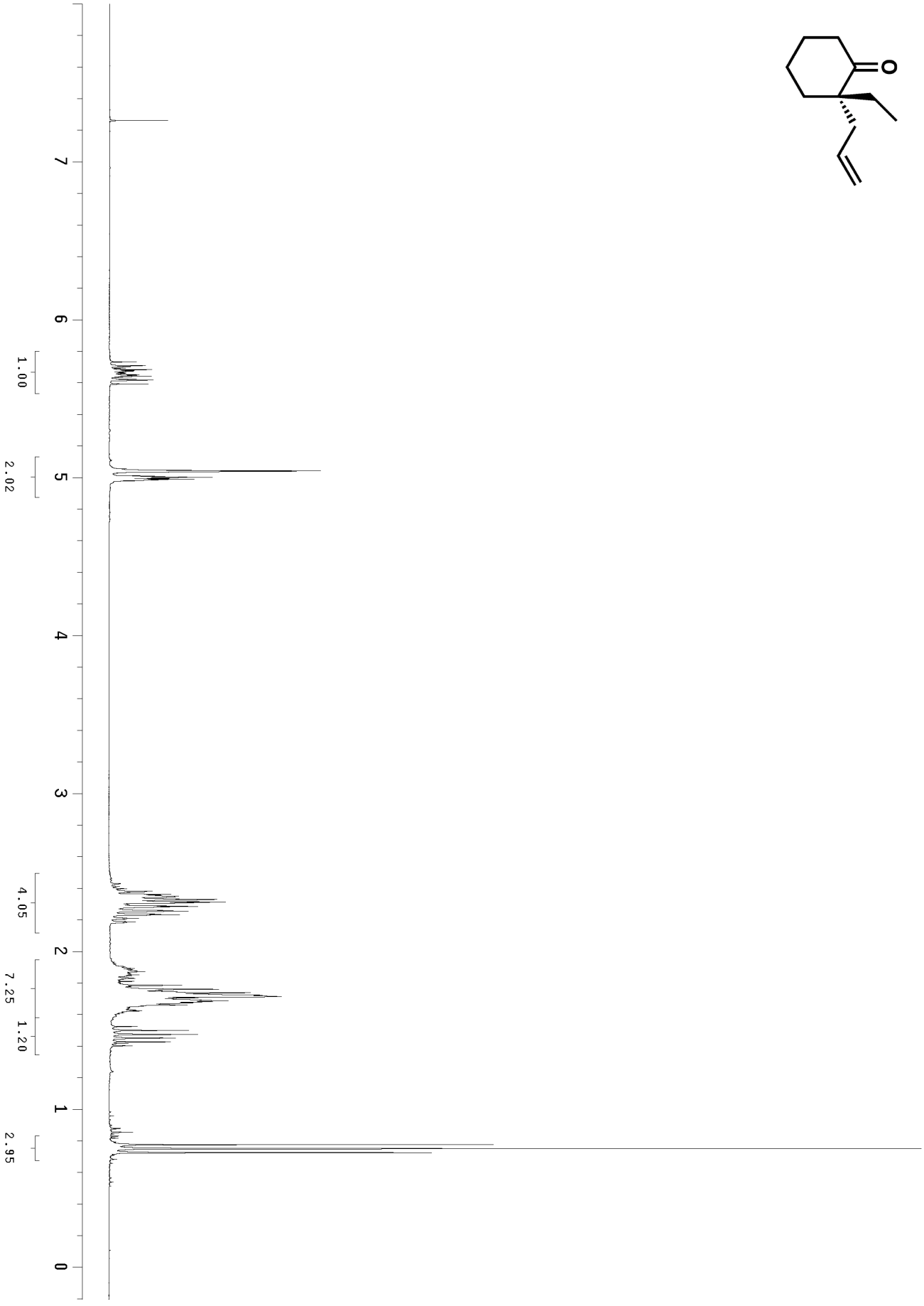
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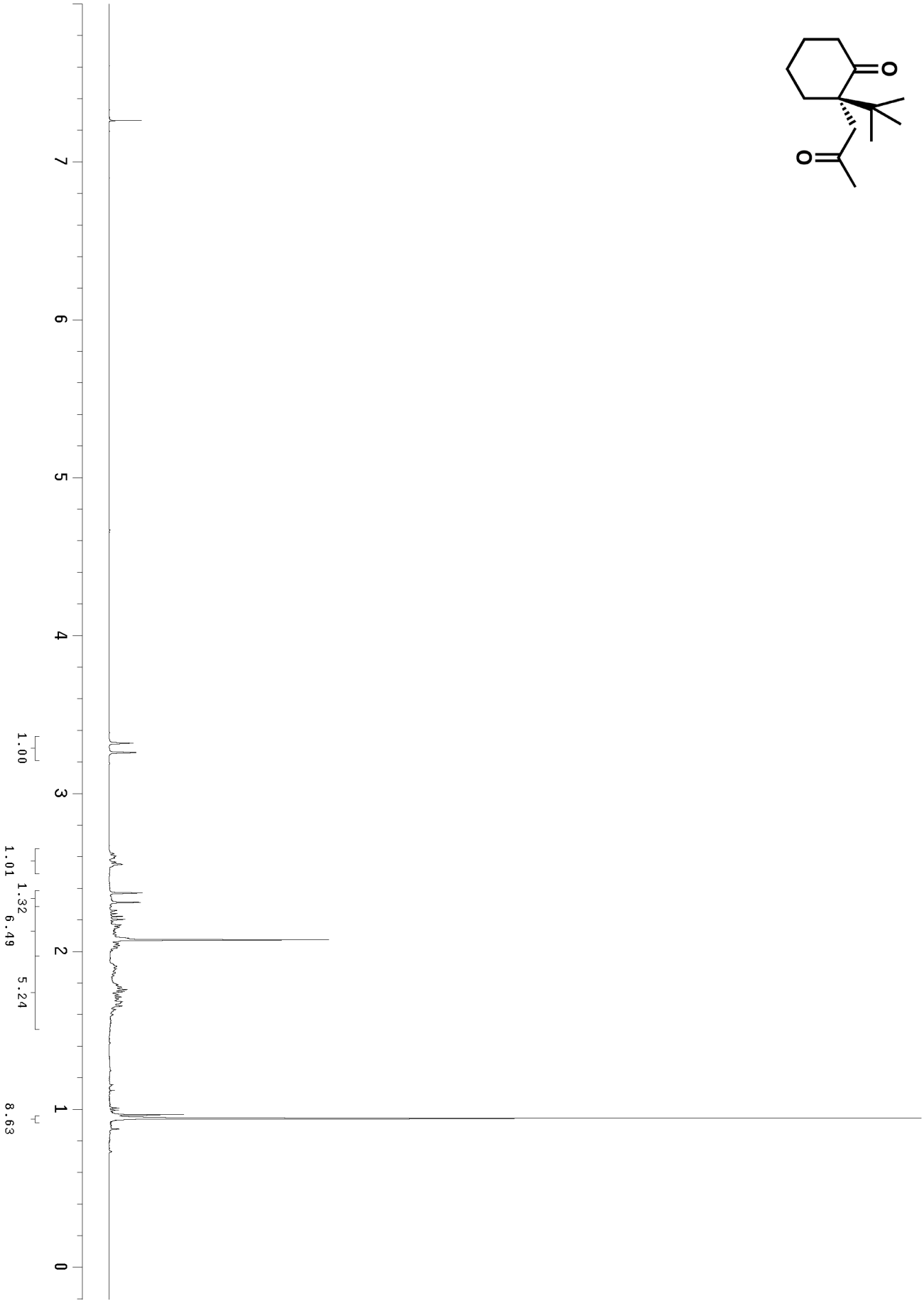
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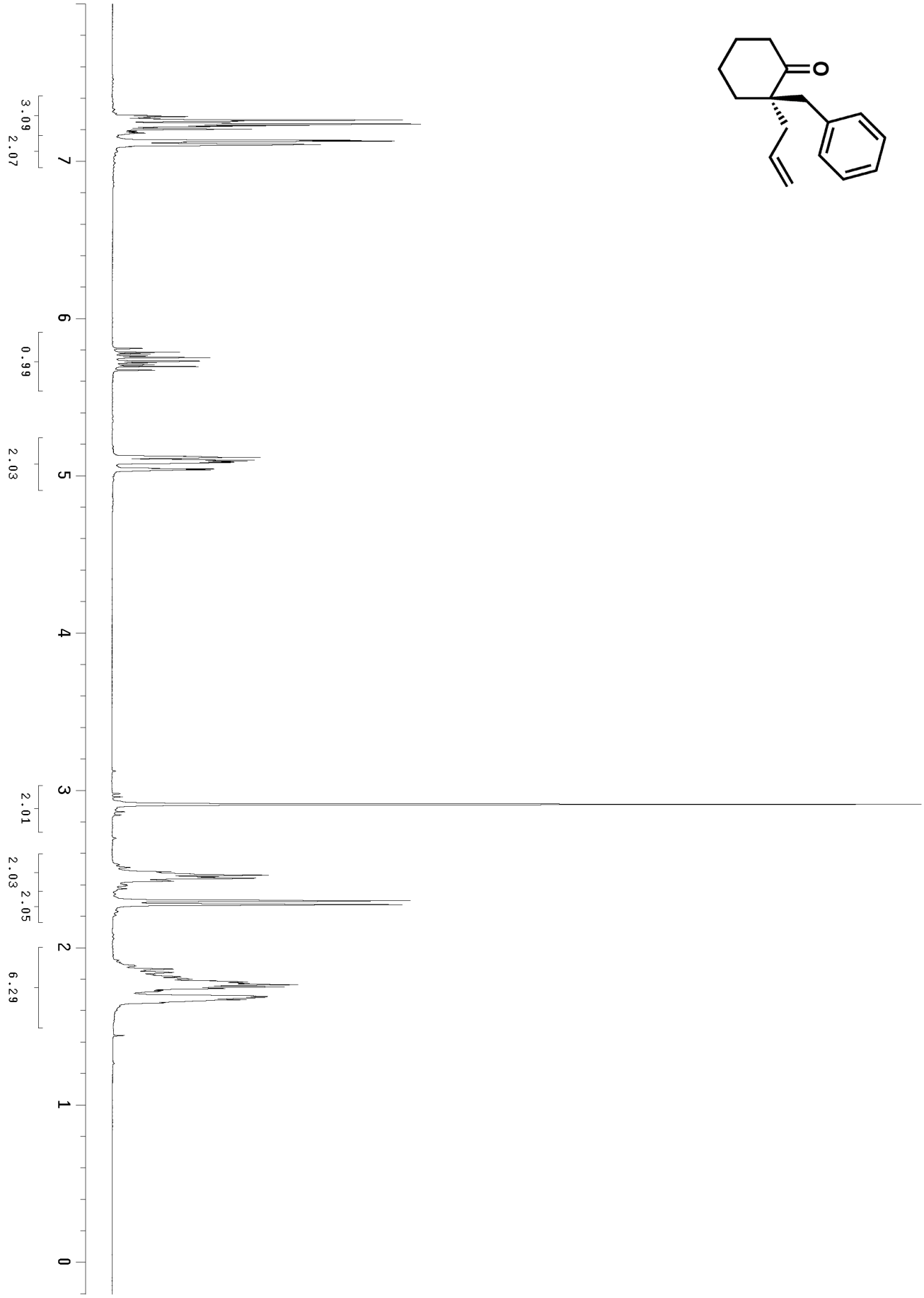
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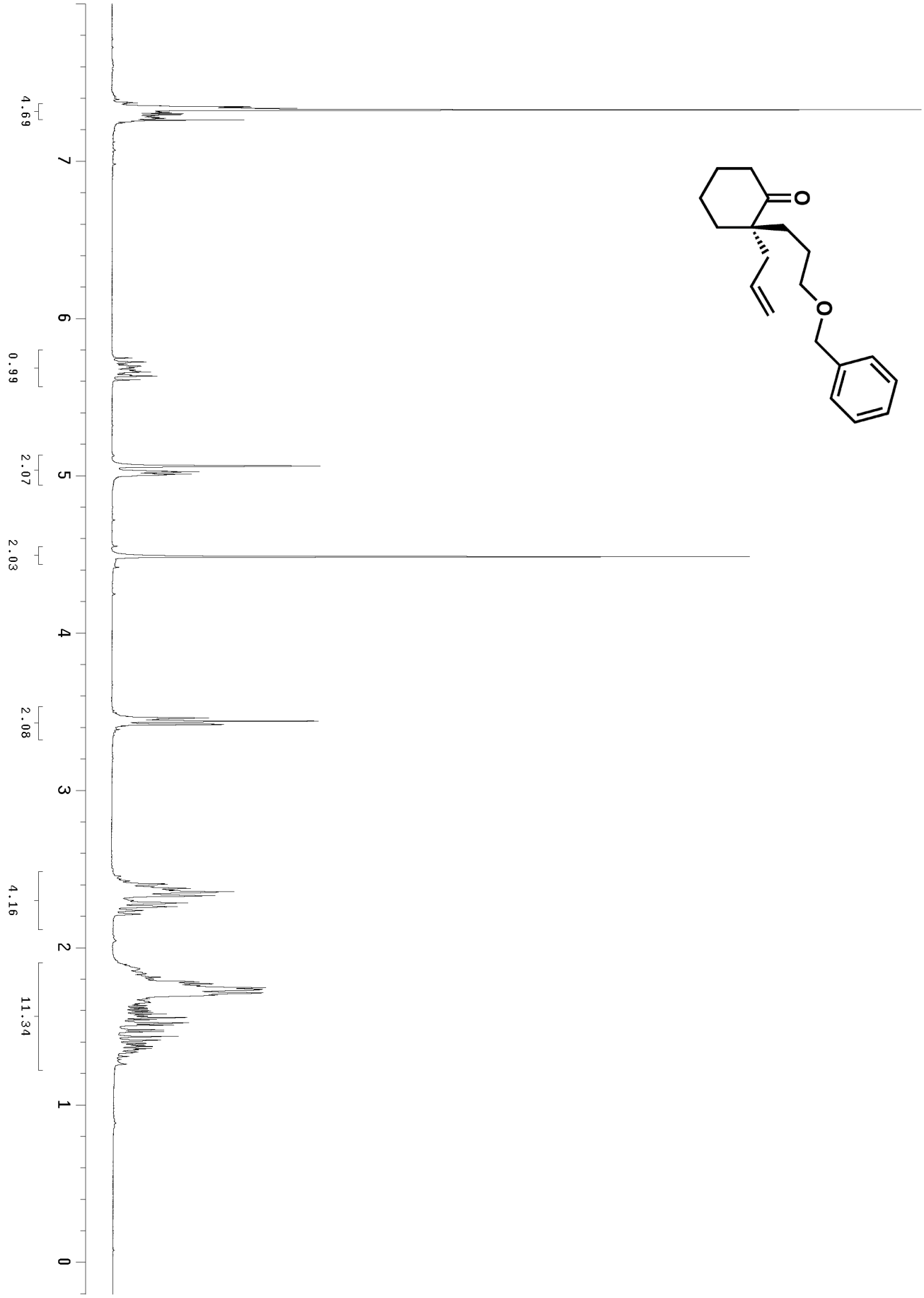
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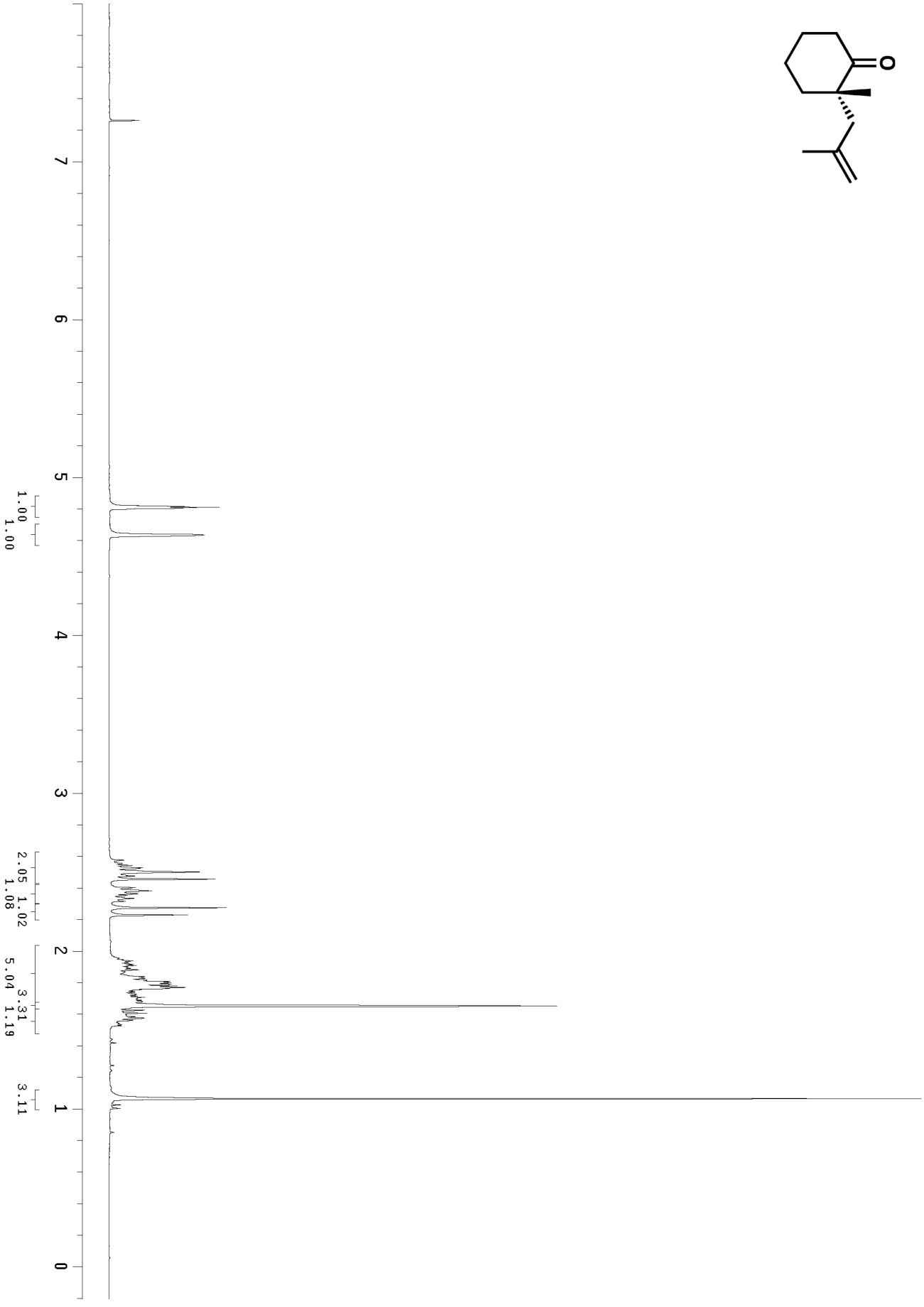
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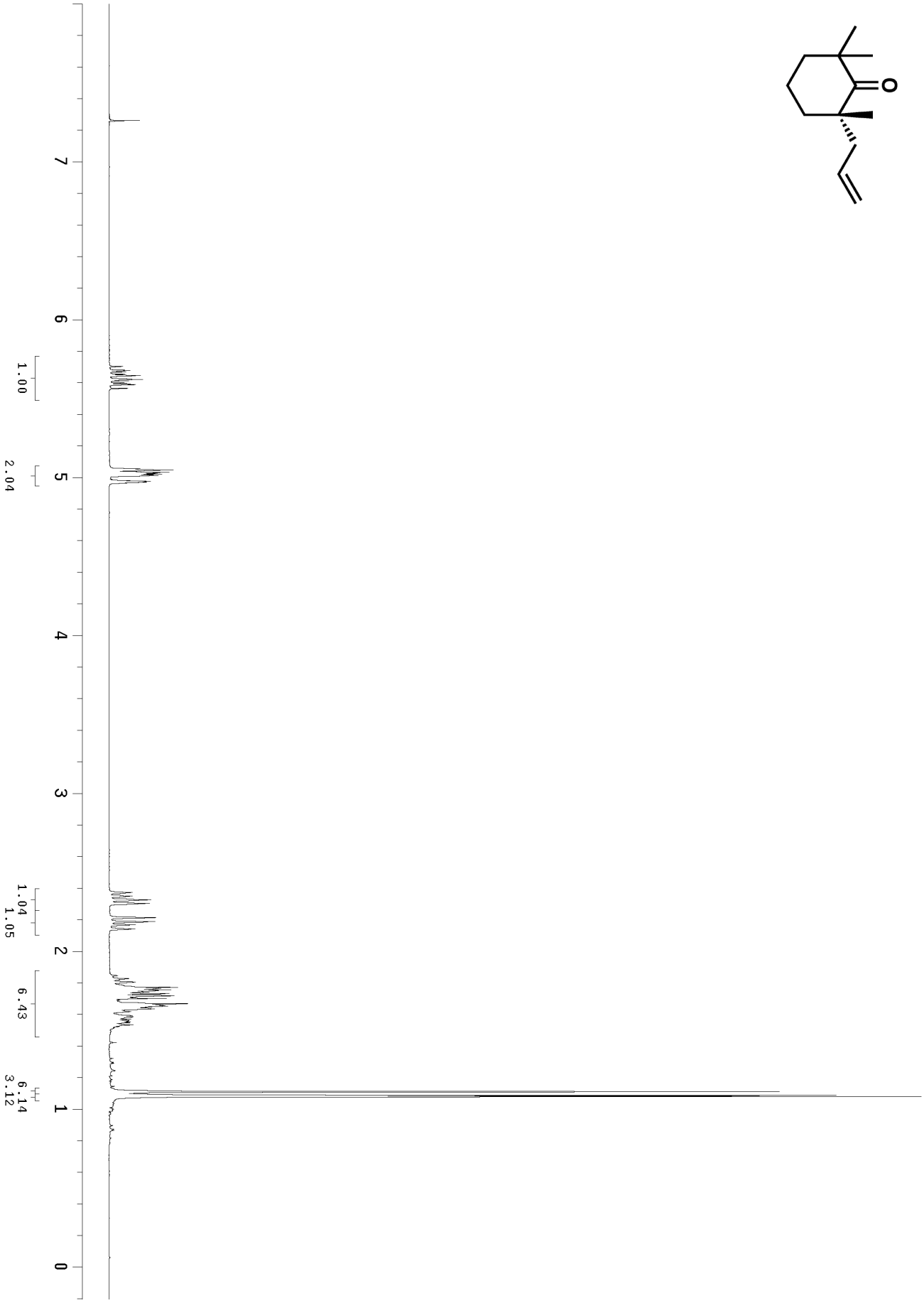
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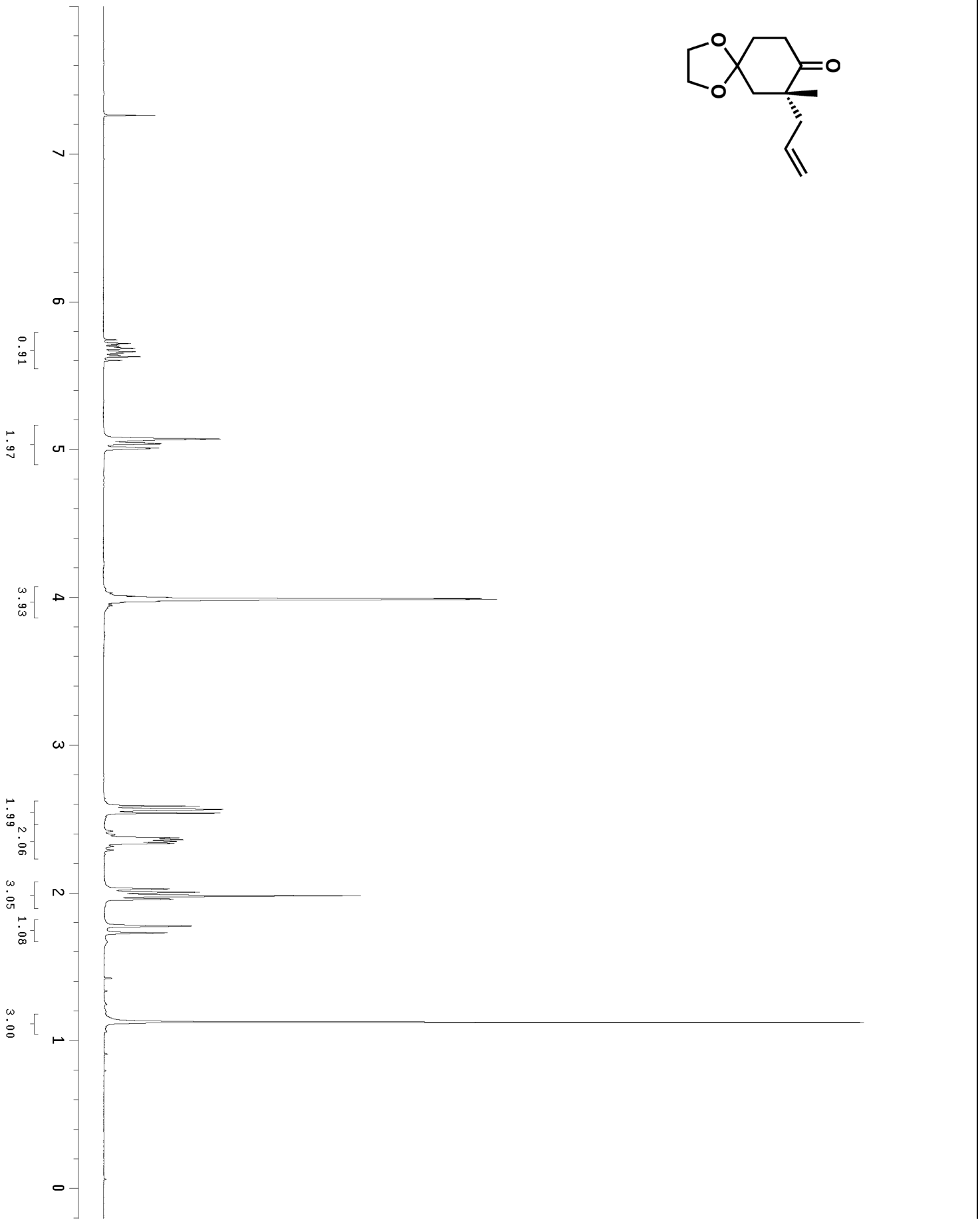
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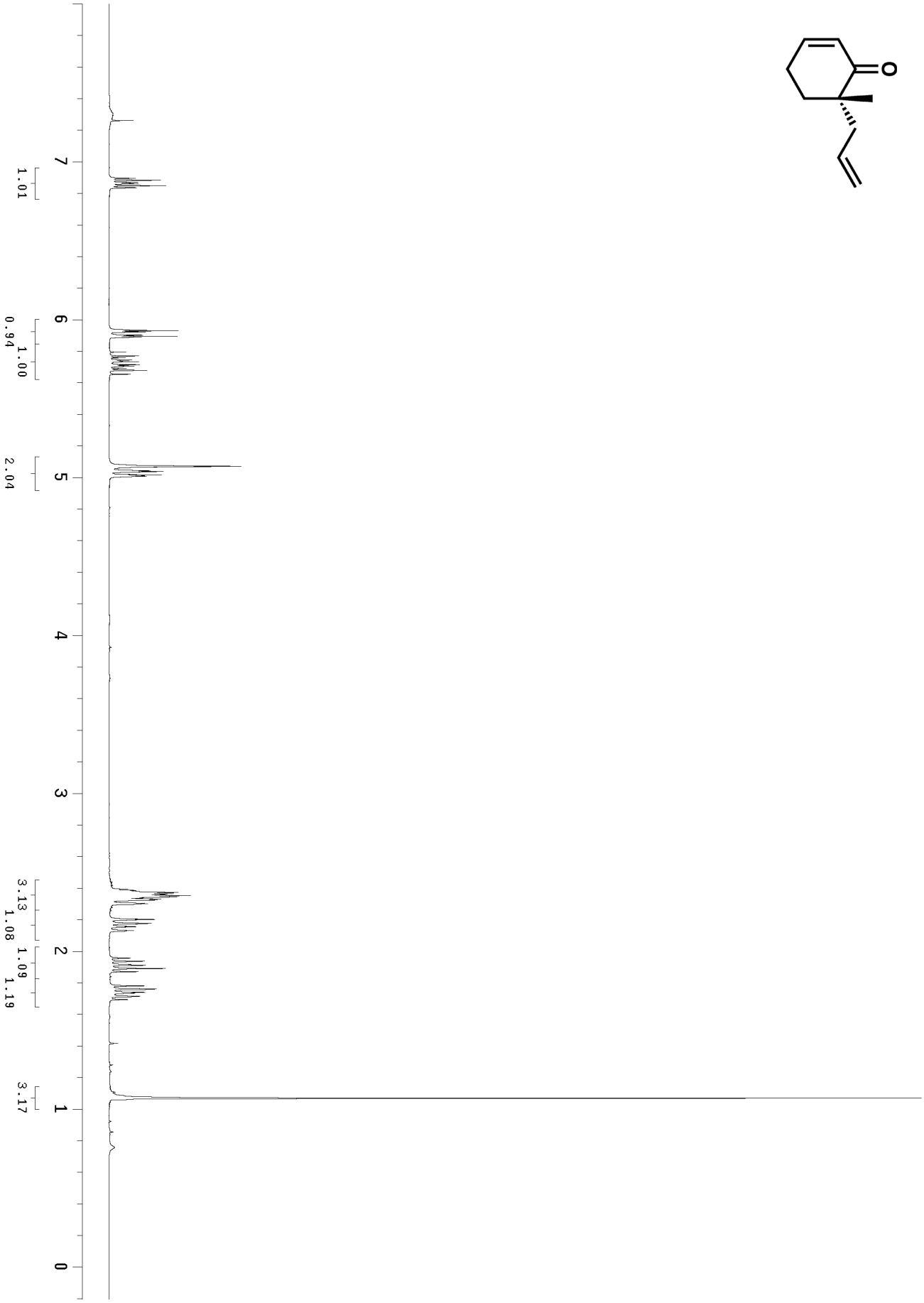
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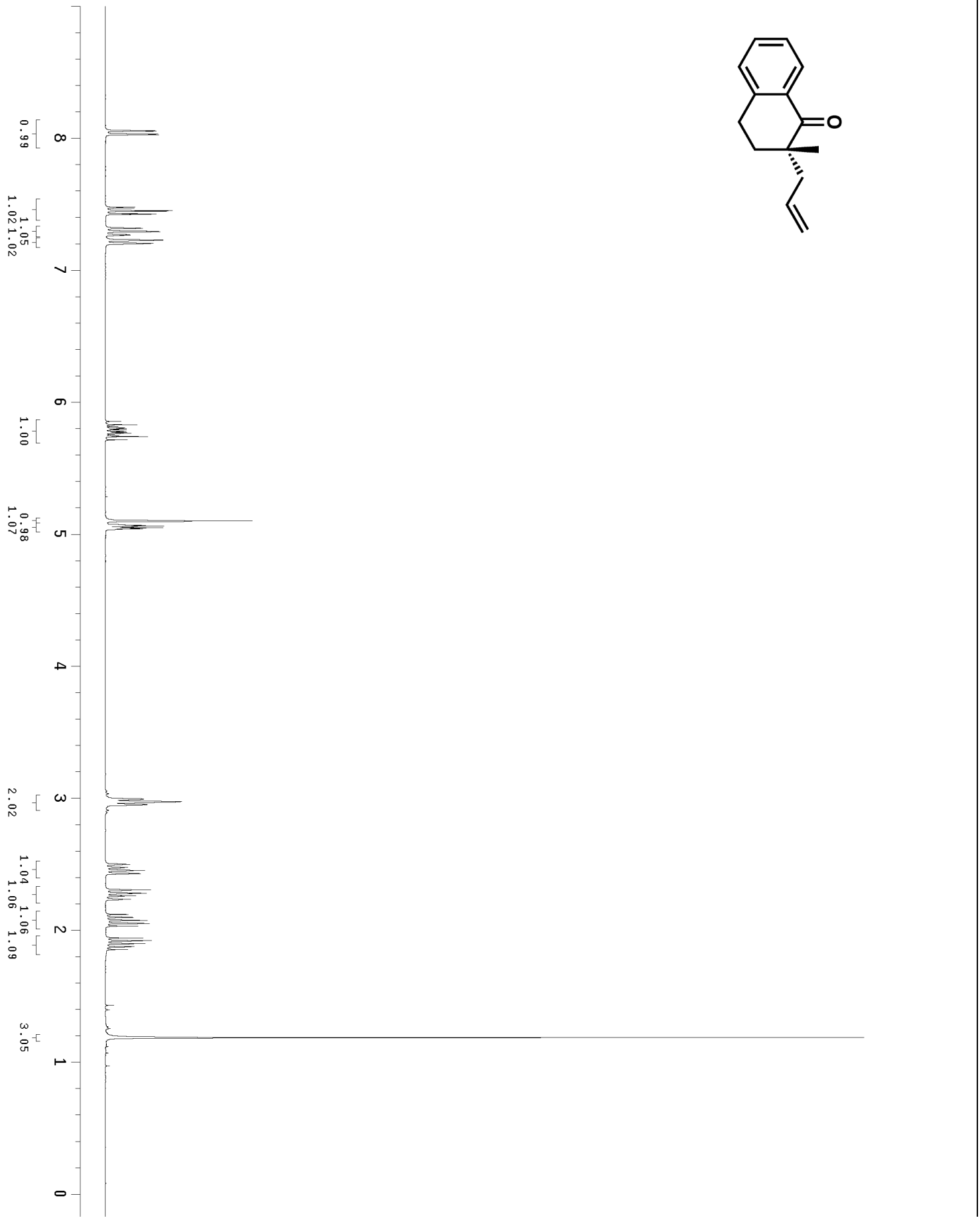
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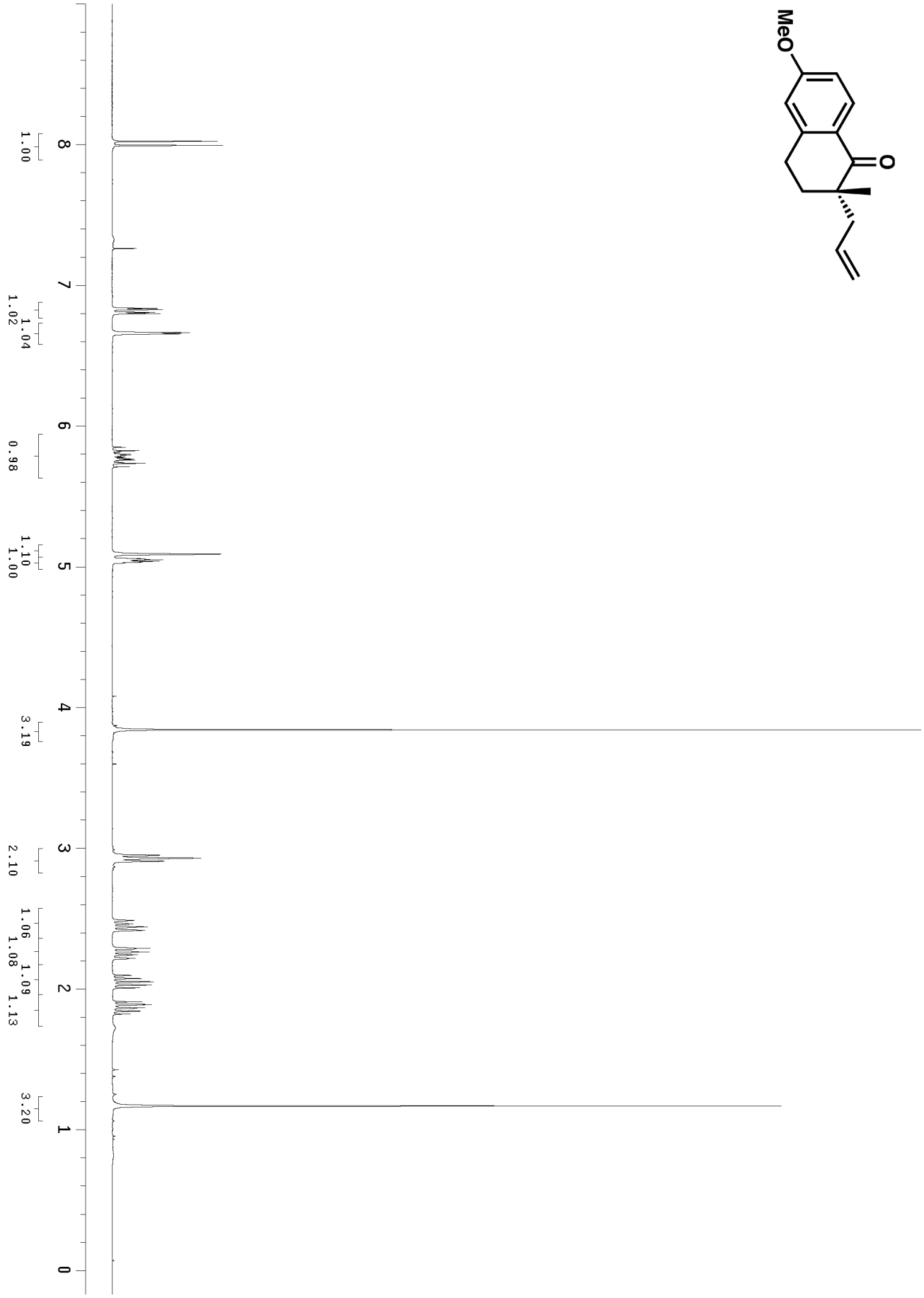
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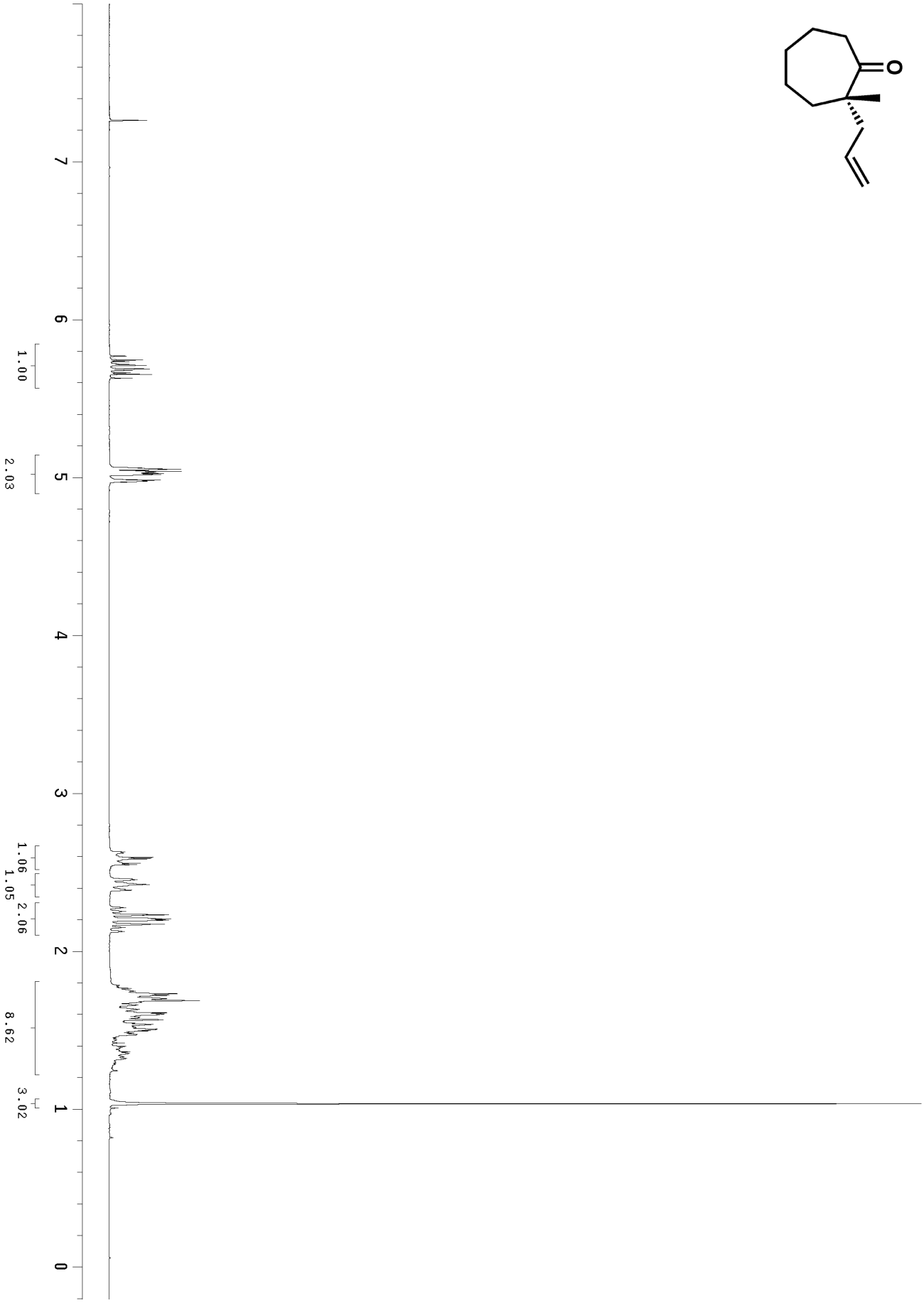
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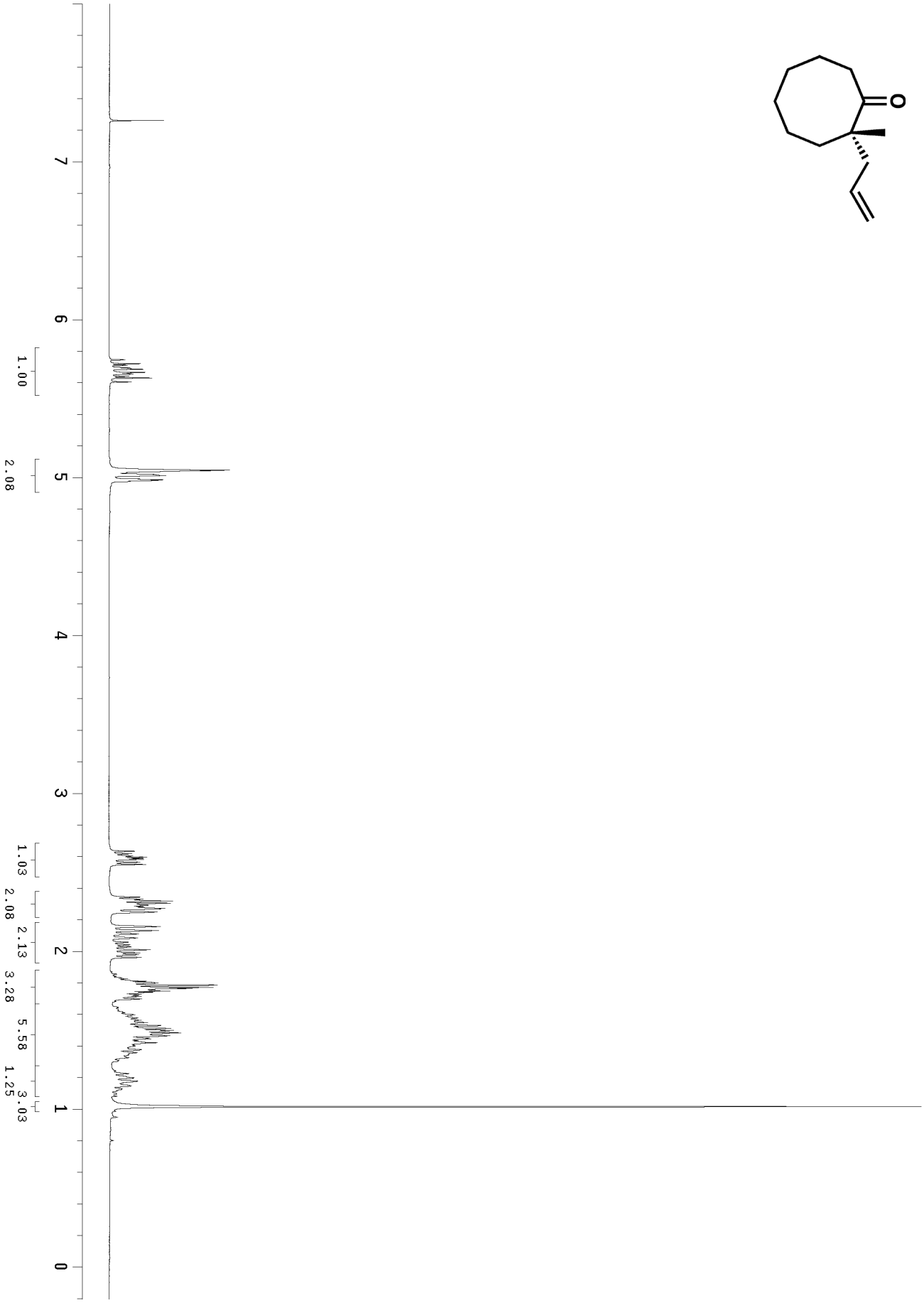
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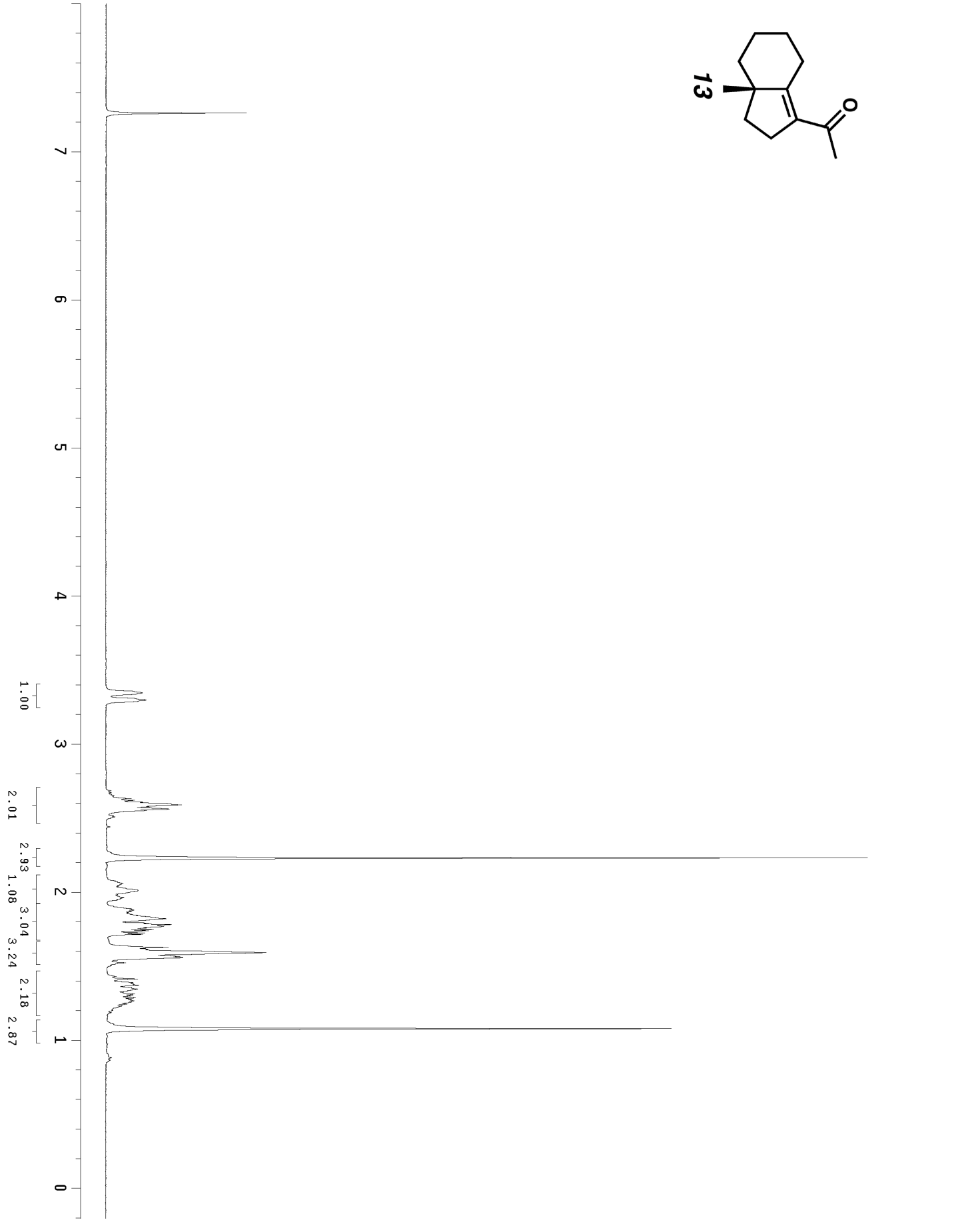
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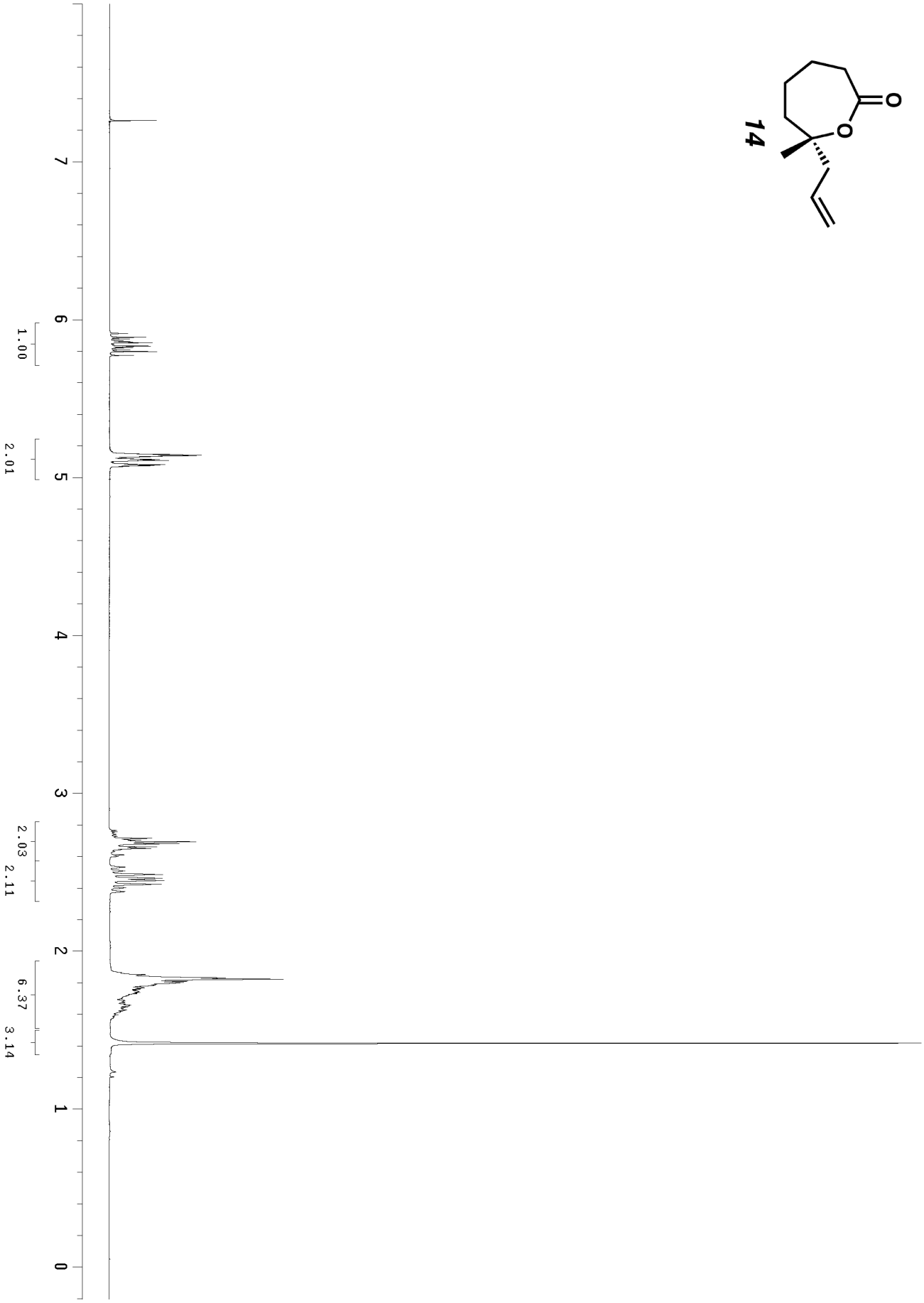
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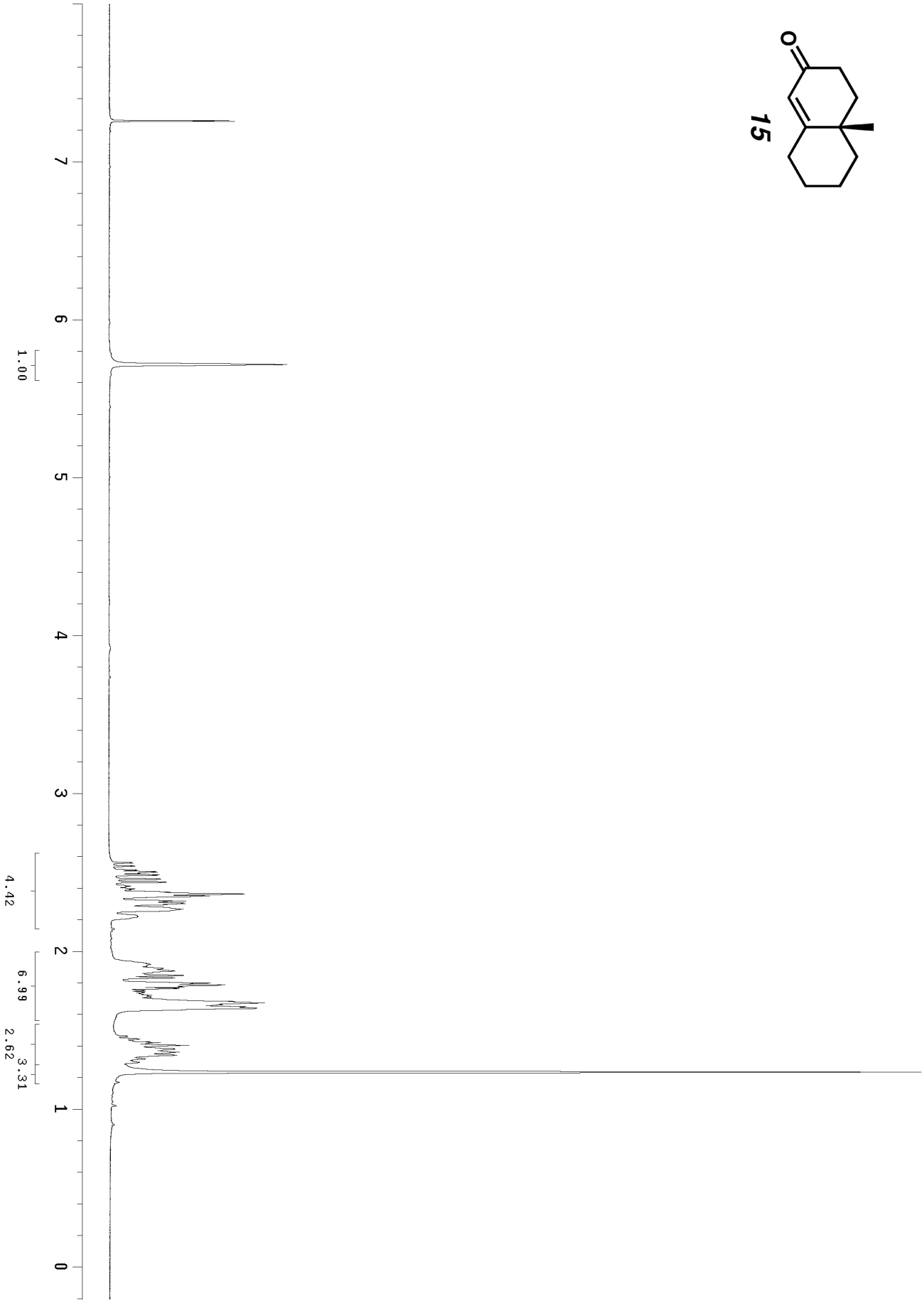
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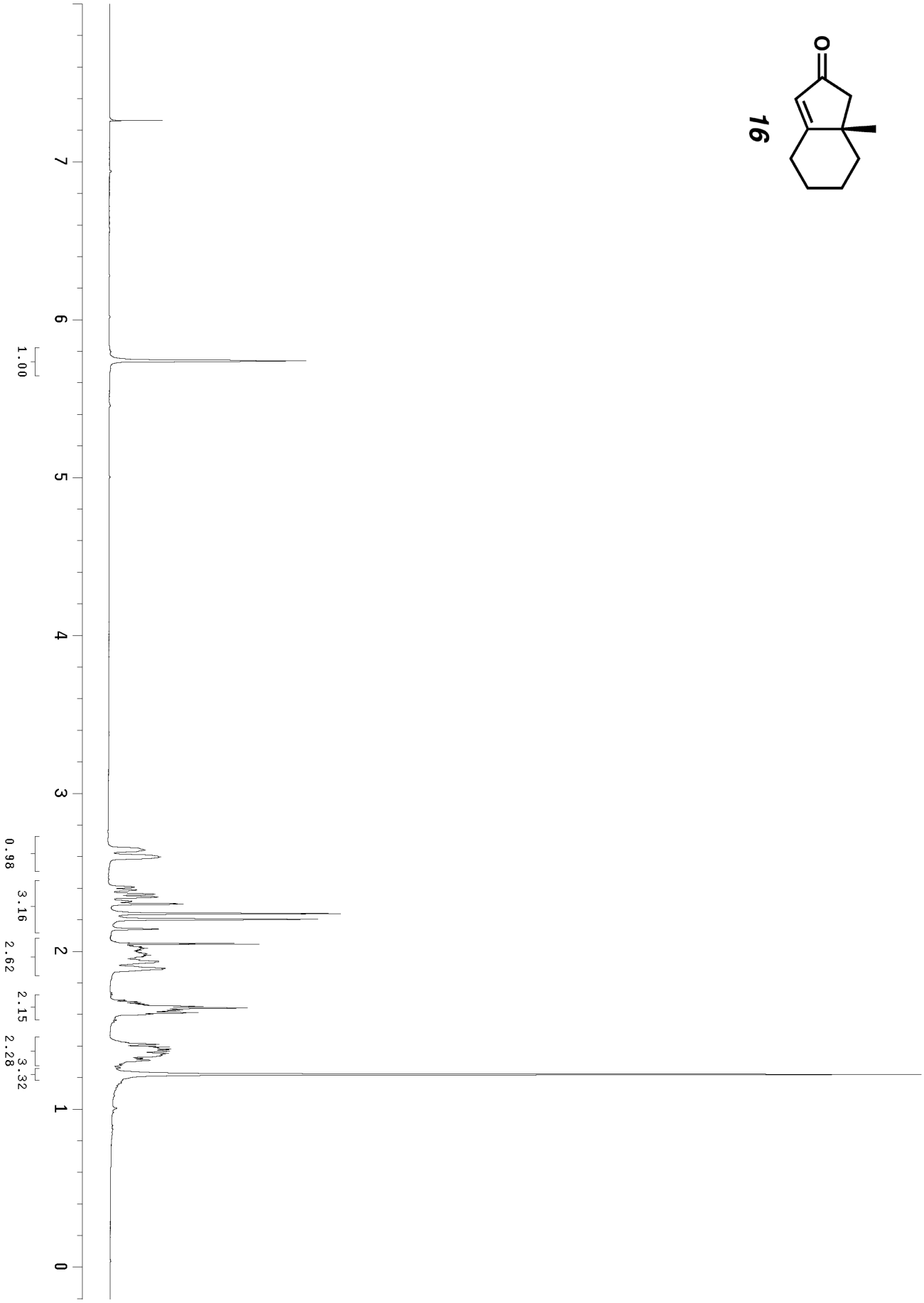
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Representative GC and HPLC Traces of Product Ketones:

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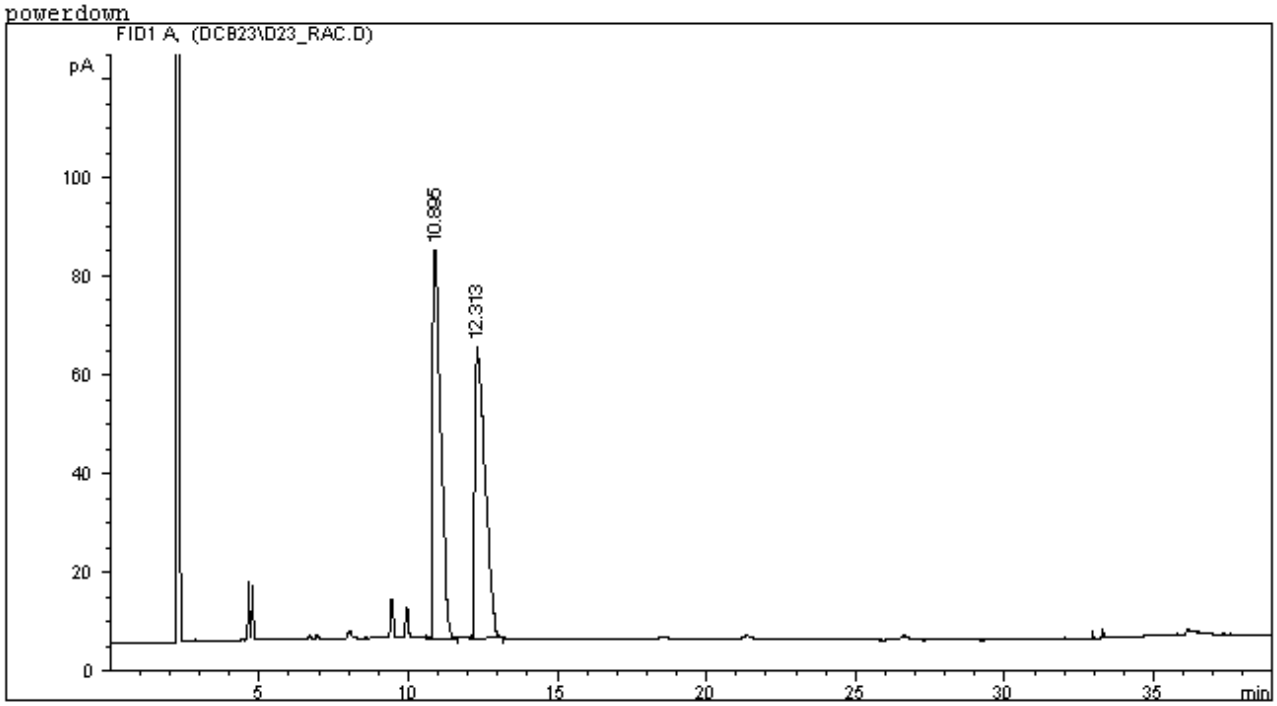


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


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   2  12.313 PB    0.3214 1428.09216   59.21593 49.84511

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 Results obtained with enhanced integrator!
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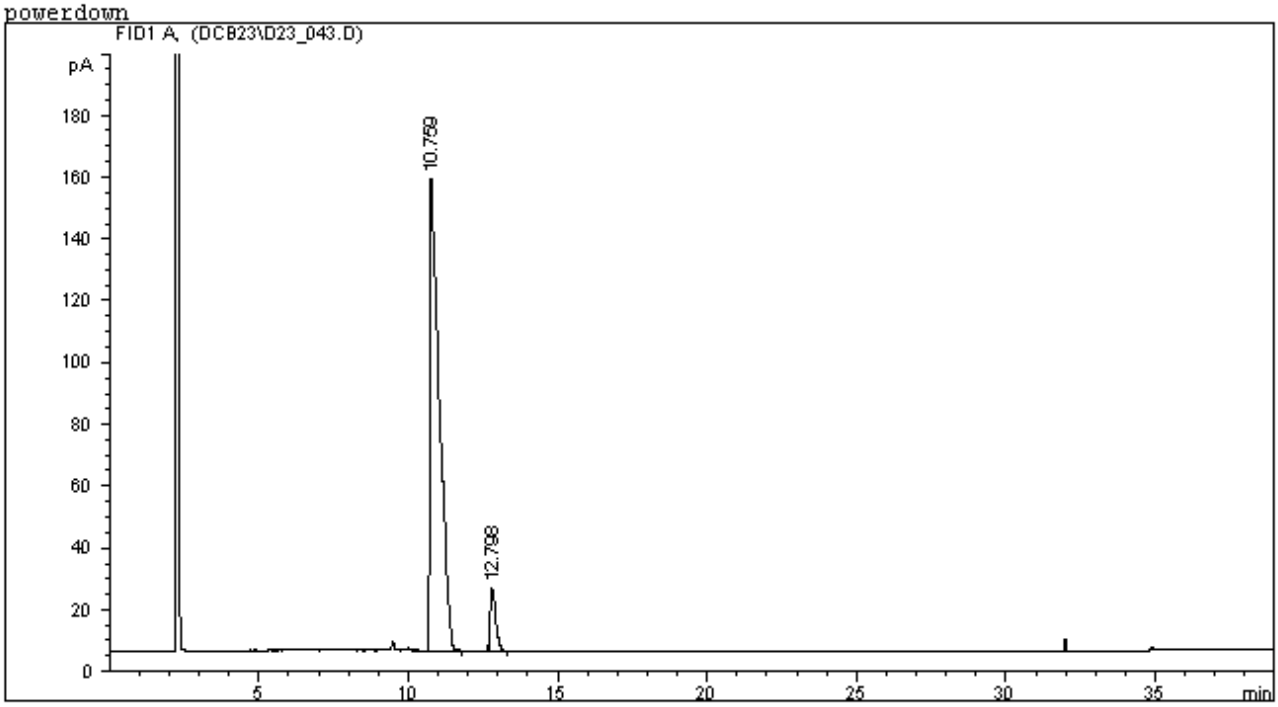


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Use Multiplier & Dilution Factor with ISTDs


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 Results obtained with enhanced integrator!
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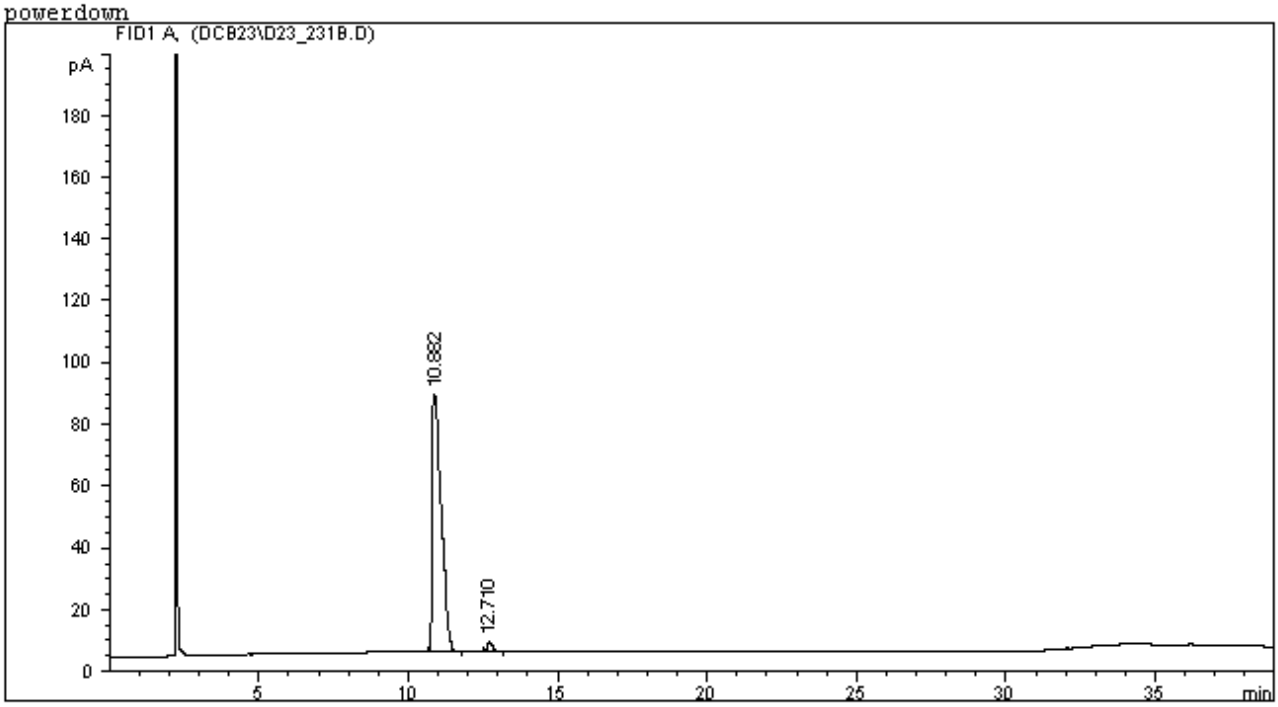
Data File E:\HPCHEM\1\DATA\DCB23\D23_231B.D Sample Name: dcb23_2312ndBlcr

```
==========================================================================
Injection Date  : 9/5/04 12:33:37 PM            Seq. Line :   2
Sample Name     : dcb23 2312ndBlcr               Location : Vial 2
Acq. Operator   : DCB                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\DB100IS0.M
Last changed    : 2/19/03 5:36:15 PM by pnc
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 9:50:56 AM by JTM
                  (modified after loading)
powerdown
```

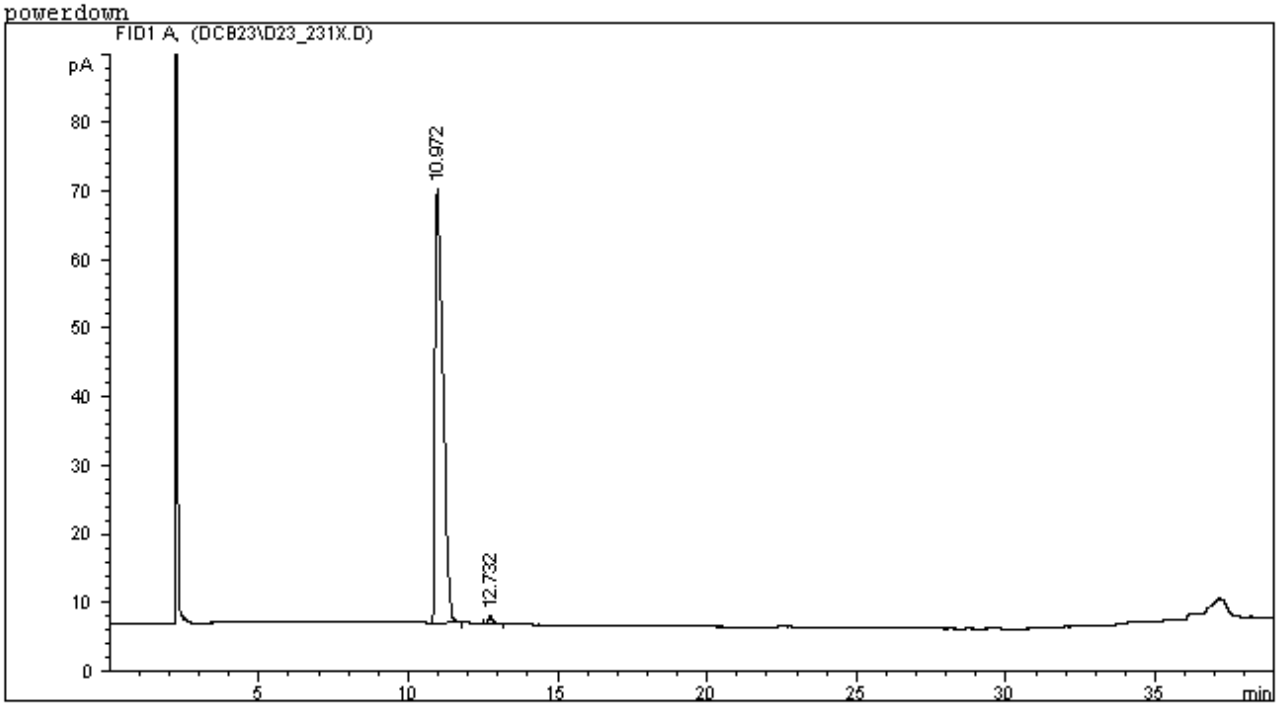



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  10.882 PB    0.2975 1768.95886   83.37096 97.80504
   2  12.710 BB    0.1823   39.69930    3.44913  2.19496

Totals :                  1808.65816   86.82009

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Ketone ***2*** Two Recrystalizations:

Data File E:\HPCHEM\1\DATA\DCB23\D23_231X.D Sample Name: 2ndxstal2ndBatch

```
==========================================================================
Injection Date  : 9/9/04 9:02:13 PM              Seq. Line :   3
Sample Name     : 2ndxstal2ndBatch                Location : Vial 2
Acq. Operator   : DCB                                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\DB100IS0.M
Last changed    : 2/19/03 5:36:15 PM by pnc
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 9:57:00 AM by JTM
                  (modified after loading)
powerdown
```

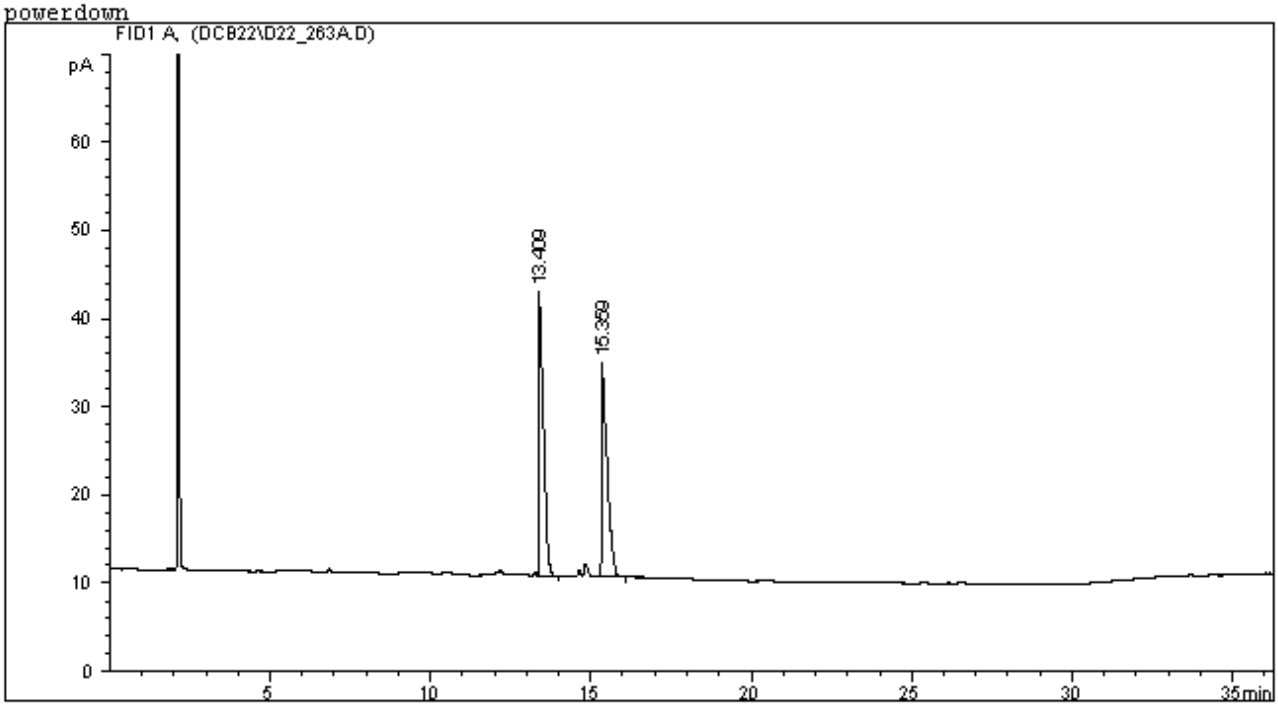



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  10.972 PB    0.2601 1146.78455   63.09054 98.91424
   2  12.732 BP    0.1613   12.58796    1.17246  1.08576

Totals :                  1159.37251   64.26300

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 4 Enone Derivative Racemic:

Data File E:\HPCHEM\1\DATA\DCB22\D22_263A.D Sample Name: dcb22_263

```
==================================================================
Injection Date  : 7/2/04 10:52:43 AM            Seq. Line :   3
Sample Name     : dcb22 263                      Location : Vial 1
Acq. Operator   : DCB                               Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\140IS030.M
Last changed    : 6/6/04 2:33:48 PM by dcvb
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 10:02:01 AM by JTM
                  (modified after loading)
powerdown
```

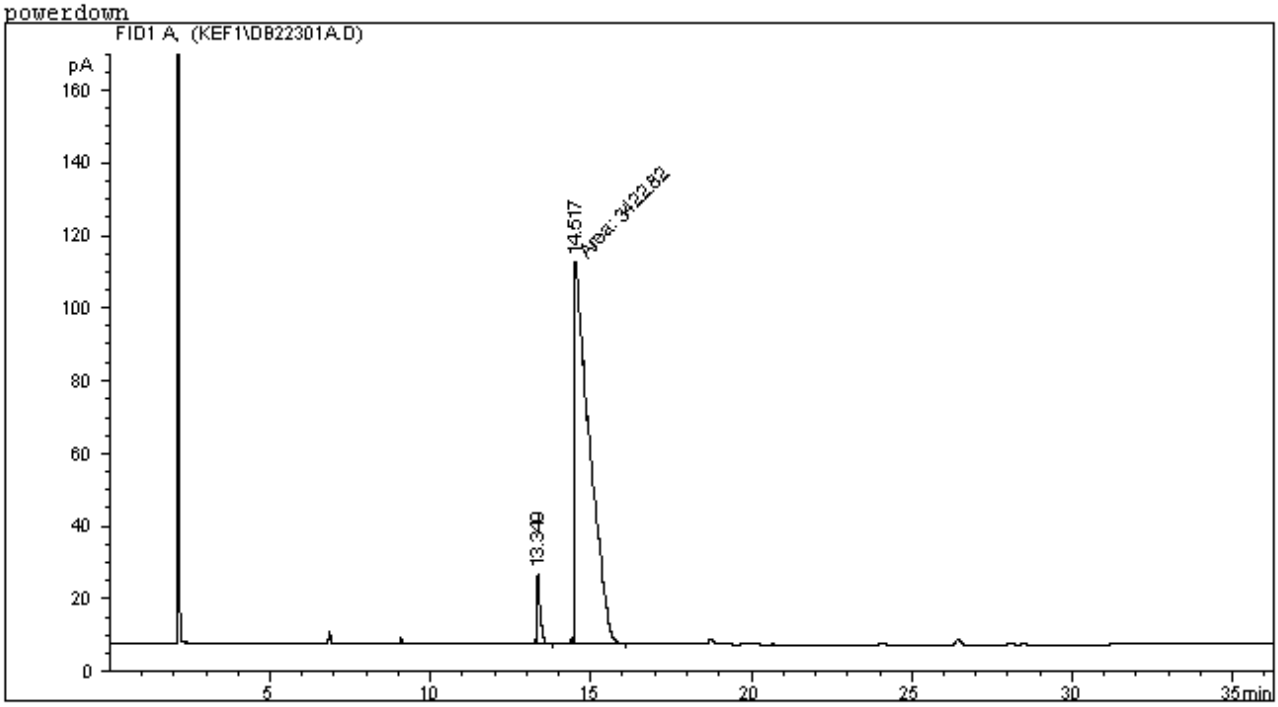



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  13.409 VP    0.1254  306.60608   32.10103 49.99098
   2  15.359 PP    0.1699  306.71667   24.20015 50.00902

Totals :                   613.32275   56.30118

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```

Table 2 Entry 4 Enone Derivative 92 % ee:

Data File E:\HPCHEM\1\DATA\KEF1\DB22301A.D Sample Name: dcb22_301

```
==================================================================
Injection Date  : 7/9/04 10:26:07 PM            Seq. Line :  11
Sample Name     : dcb22 301                      Location : Vial 3
Acq. Operator   : kristin                            Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\140IS030.M
Last changed    : 6/6/04 2:33:48 PM by dcvb
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 10:05:02 AM by JTM
                  (modified after loading)
powerdown
```

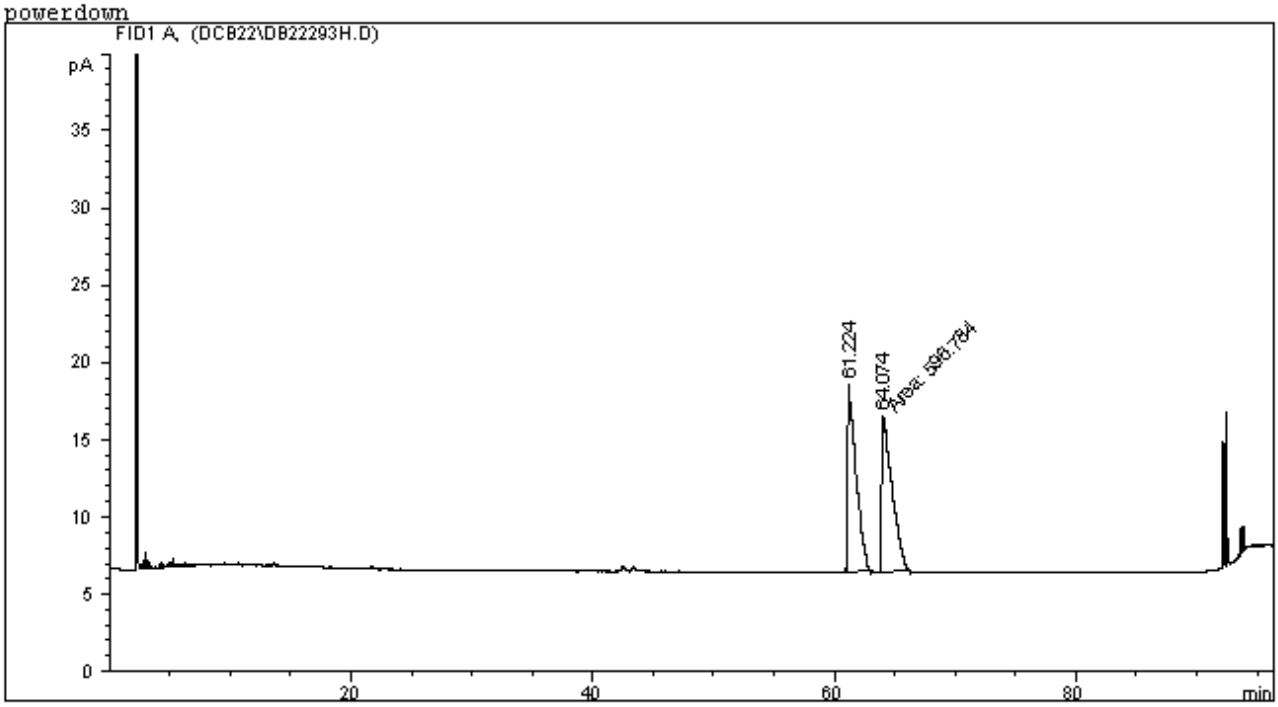



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  13.349 VB    0.1073  139.93250   19.14288  3.92765
   2  14.517 MM    0.5429 3422.81885  105.07720 96.07235

Totals :                  3562.75134  124.22008

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 5 Diketone Derivative Racemic:

Data File E:\HPCHEM\1\DATA\DCB22\DB22293H.D Sample Name: dcb22_293

```
==================================================================
Injection Date  : 7/10/04 9:56:28 PM          Seq. Line :   3
Sample Name     : dcb22 293                    Location : Vial 3
Acq. Operator   : DCB                             Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110S090.M
Last changed    : 7/10/04 7:44:46 PM by kefl
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 10:21:45 AM by JTM
                  (modified after loading)
powerdown
```

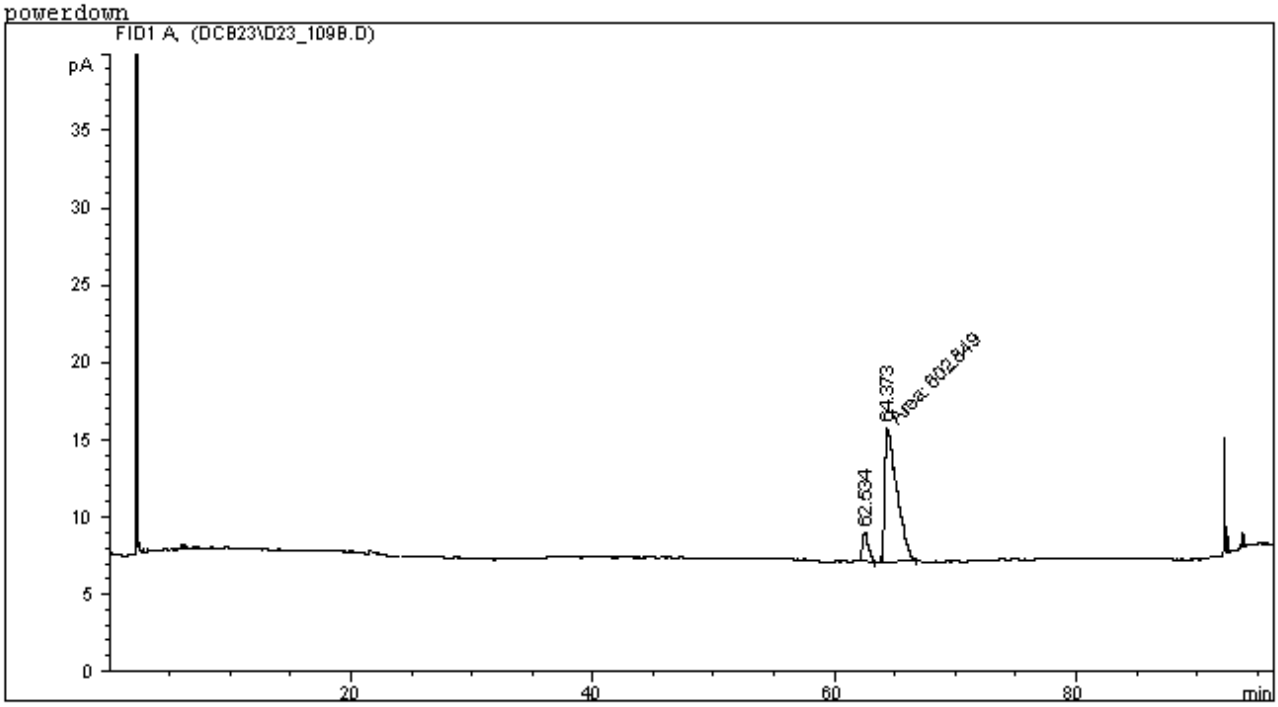



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  61.224 PB    0.5760  595.49561   12.14650 49.94596
   2  64.074 MM    0.9878  596.78430   10.06973 50.05404

Totals :                  1192.27991   22.21623

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 5 Enone Derivative 82 % ee:

Data File E:\HPCHEM\1\DATA\DCB23\D23_109B.D Sample Name: DCB23_109

```
==================================================================
Injection Date  : 8/5/04 5:34:52 PM             Seq. Line :   4
Sample Name     : DCB23 109                      Location : Vial 1
Acq. Operator   : dcb                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110S090.M
Last changed    : 7/10/04 7:44:46 PM by kefl
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 10:18:39 AM by JTM
                  (modified after loading)
powerdown
```

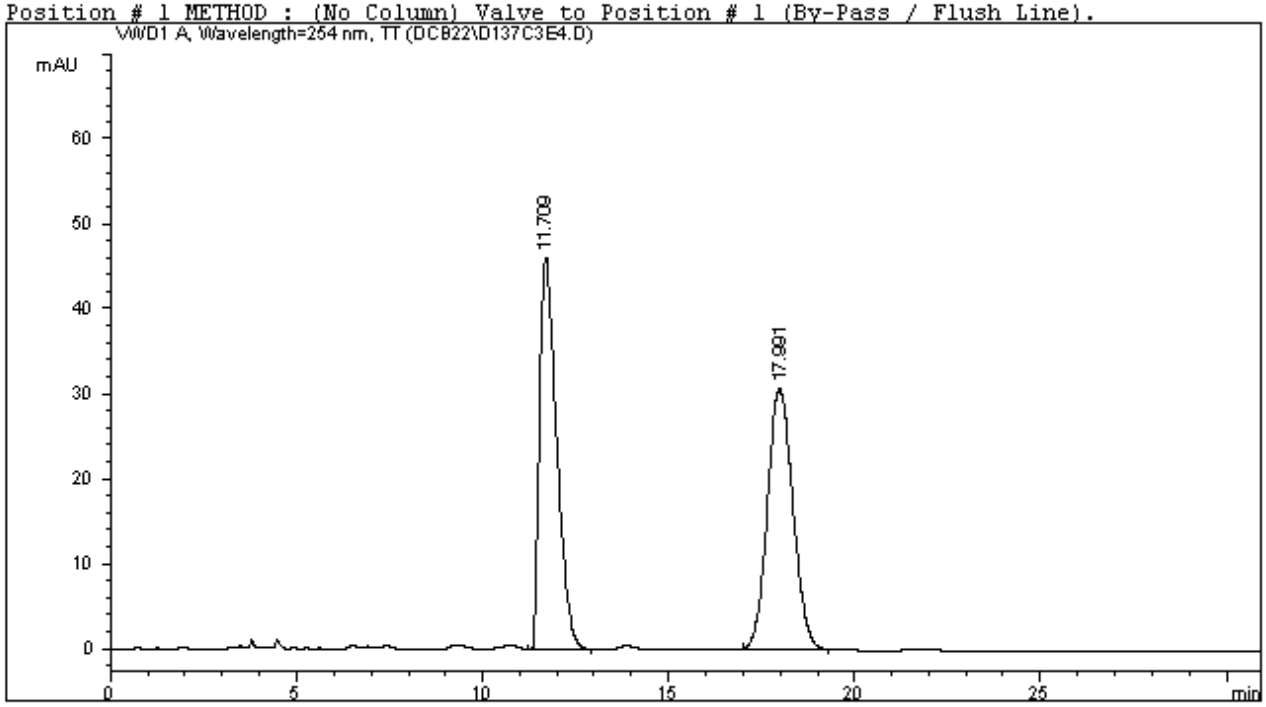



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  62.534 BB    0.3972   60.73349    1.80201  9.15237
   2  64.373 MM    1.1678  602.84882    8.60358 90.84763

Totals :                   663.58231   10.40559

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```

Table 2 Entry 6 Racemic:

Data File C:\HPCHEM\2\DATA\DCB22\D137C3E4.D Sample Name: dcb22_137

```
==========================================================================
Injection Date  : 5/25/2004 4:43:07 PM          Seq. Line :  14
Sample Name     : dcb22 137                      Location : Vial 61
Acq. Operator   : DCB                               Inj :  1
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\4-EOH30.M
Last changed    : 3/31/2004 3:41:22 PM by mike
Analysis Method : C:\HPCHEM\2\METHODS\BYPASS.M
Last changed    : 10/8/2004 10:24:52 AM by dra
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

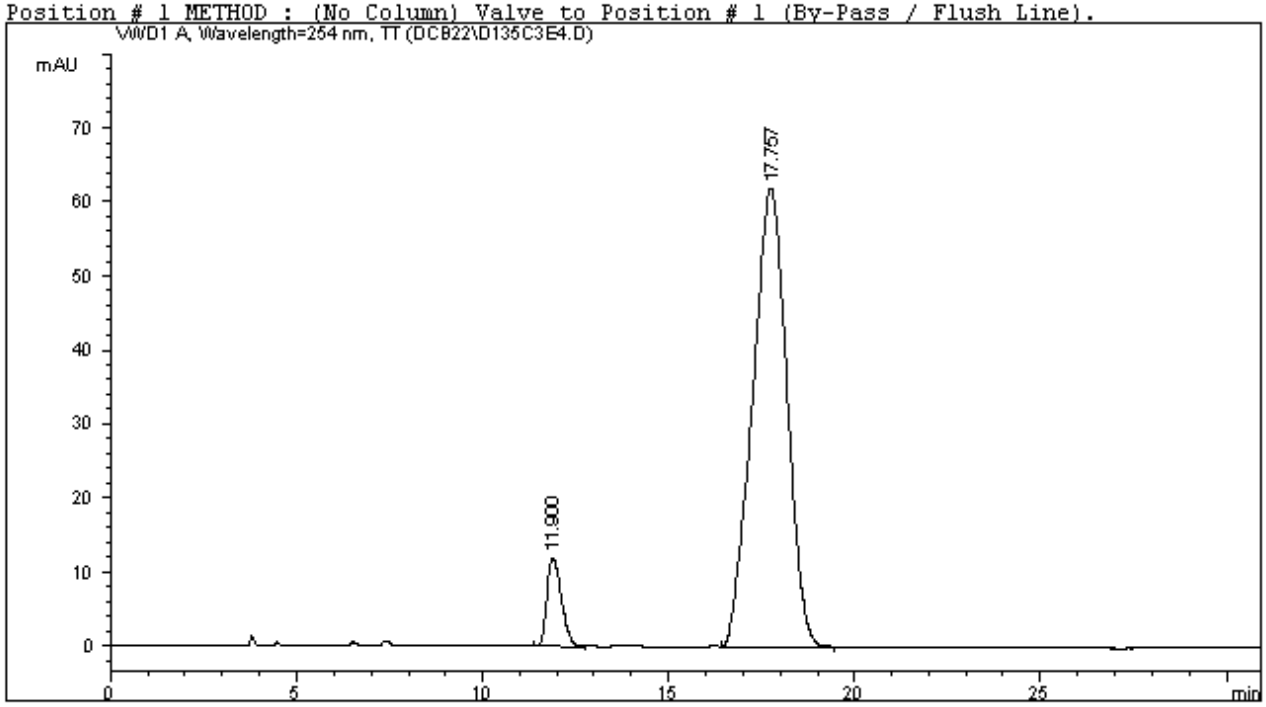



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.709 VB    0.4984 1464.16248   46.13335  50.0769
   2  17.991 BP    0.7385 1459.66443   30.68317  49.9231

Totals :                  2923.82690   76.81651

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 6 85 % ee:

Data File C:\HPCHEM\2\DATA\DCB22\D135C3E4.D Sample Name: dcb22_135

```
==================================================================
Injection Date  : 5/26/2004 12:17:20 AM          Seq. Line :  16
Sample Name     : dcb22 135                       Location : Vial 62
Acq. Operator   : DCB                                 Inj :  1
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\4-EOH30.M
Last changed    : 3/31/2004 3:41:22 PM by mike
Analysis Method : C:\HPCHEM\2\METHODS\BYPASS.M
Last changed    : 10/8/2004 10:27:45 AM by dra
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

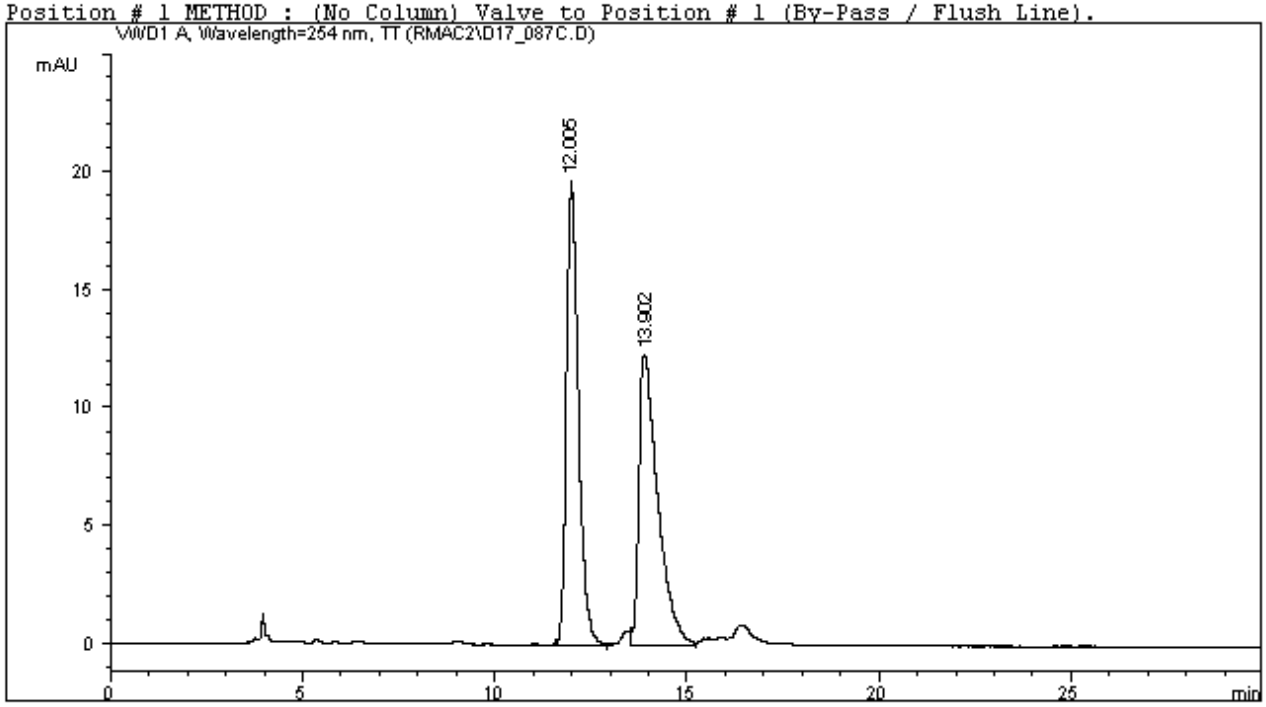



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.900 PB    0.4318  325.66907   11.93796   7.5503
   2  17.757 BB    0.9816 3987.63940   61.90025  92.4497

Totals :                  4313.30847   73.83821

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 7 Racemic:

Data File C:\HPCHEM\3\DATA\RMAC2\D17_087C.D Sample Name: dcb17_87

```
==========================================================================
Injection Date  : 6/23/2004 11:33:30 AM          Seq. Line :  11
Sample Name     : dcb17 87                        Location : Vial 11
Acq. Operator   : rmm                                Inj :   1
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\15D30.M
Last changed    : 6/23/2004 9:30:17 AM by rmm
Analysis Method : C:\HPCHEM\3\METHODS\BYPASS.M
Last changed    : 10/8/2004 10:33:25 AM by jmb
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

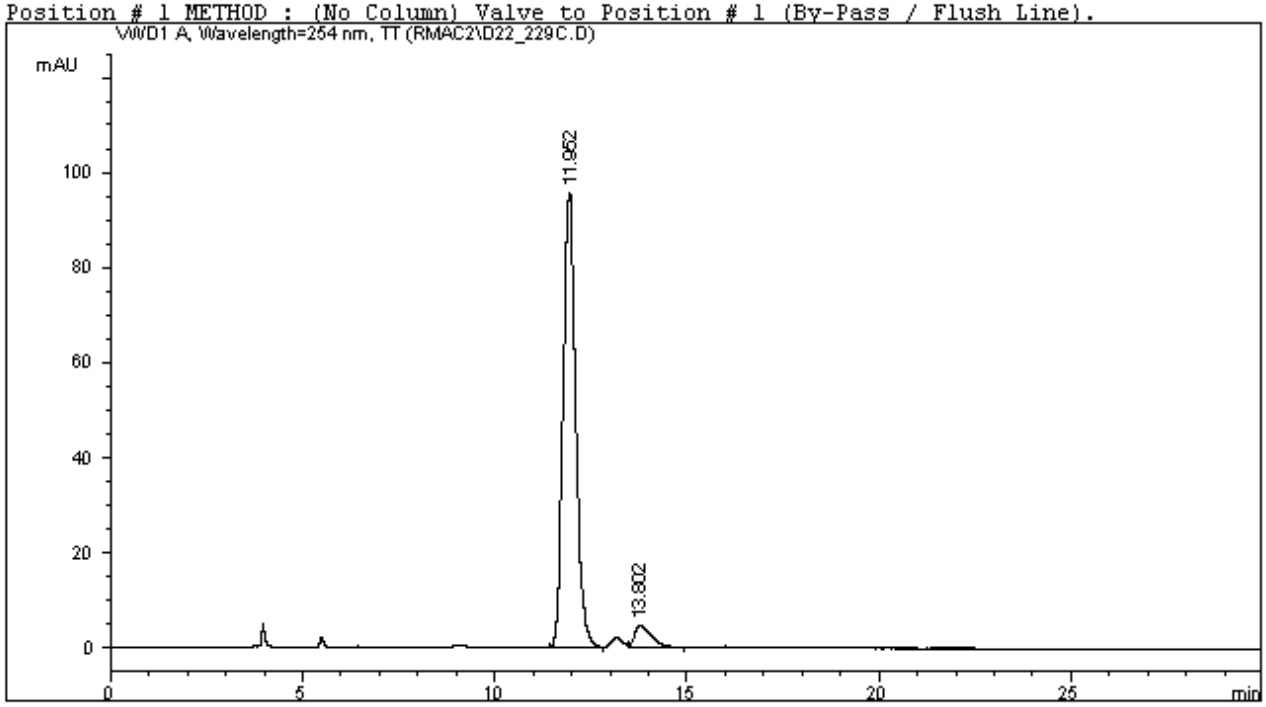



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  12.005 BB    0.3254  421.15051   19.67632  50.3042
   2  13.902 VB    0.4822  416.05701   12.29345  49.6958

Totals :                   837.20752   31.96977

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 7 88 % ee:

Data File C:\HPCHEM\3\DATA\RMAC2\D22_229C.D Sample Name: DCB22_229

```
==========================================================================
Injection Date  : 6/23/2004 10:52:08 AM          Seq. Line :   9
Sample Name     : DCB22 229                      Location : Vial 12
Acq. Operator   : rmm                               Inj :   1
                                                 Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\15D30.M
Last changed    : 6/23/2004 9:30:17 AM by rmm
Analysis Method : C:\HPCHEM\3\METHODS\BYPASS.M
Last changed    : 10/8/2004 10:36:42 AM by jmb
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

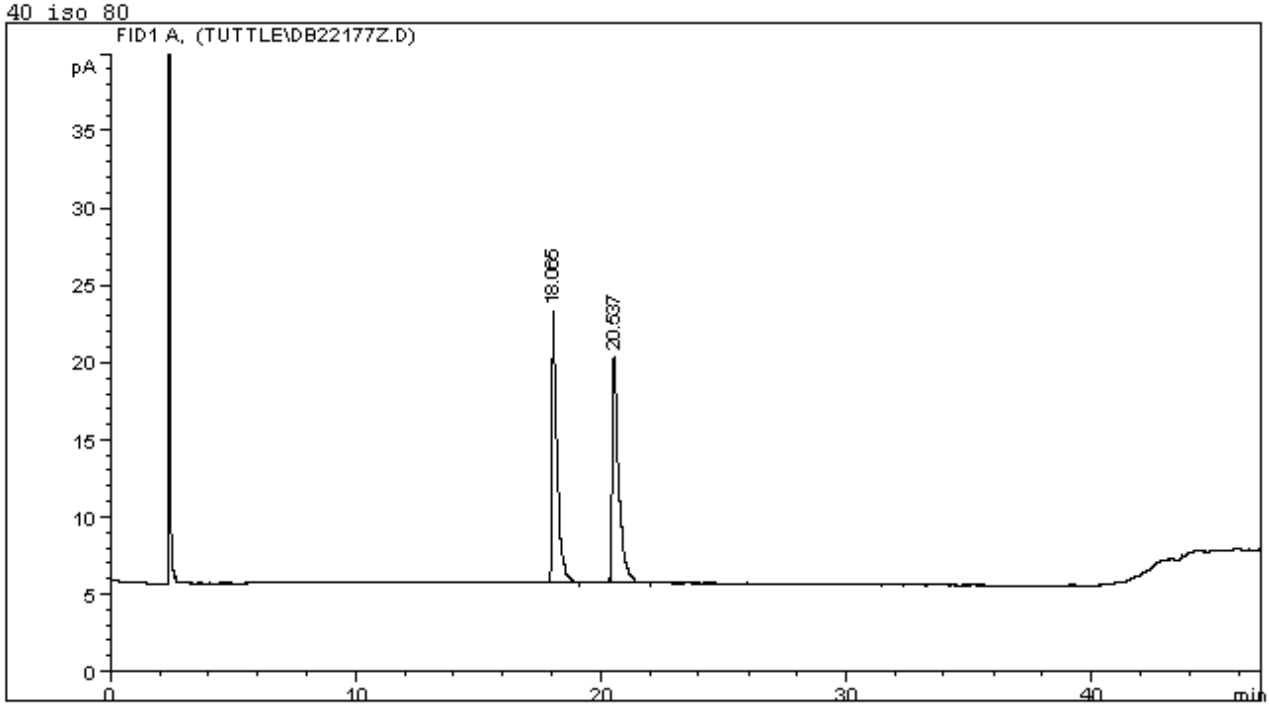



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  11.952 BV    0.3543 2189.22803   95.67223  93.7334
   2  13.802 VB    0.4552  146.36189    4.75447   6.2666

Totals :                  2335.58992  100.42670

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 8 Racemic:

Data File C:\HPCHEM\3\DATA\TUTTLE\DB22177Z.D Sample Name: dcb22_177

```
==========================================================================
Injection Date  : 6/16/2004 10:49:27 PM          Seq. Line :  12
Sample Name     : dcb22 177                       Location : Vial 27
Acq. Operator   : jamie                               Inj :  1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\3\METHODS\100IS040.M
Last changed    : 6/10/2004 11:07:16 PM by nIKKI
Analysis Method : C:\HPCHEM\3\METHODS\45IS55F.M
Last changed    : 10/8/2004 11:03:01 AM by jbt
                  (modified after loading)
40 iso 80
```

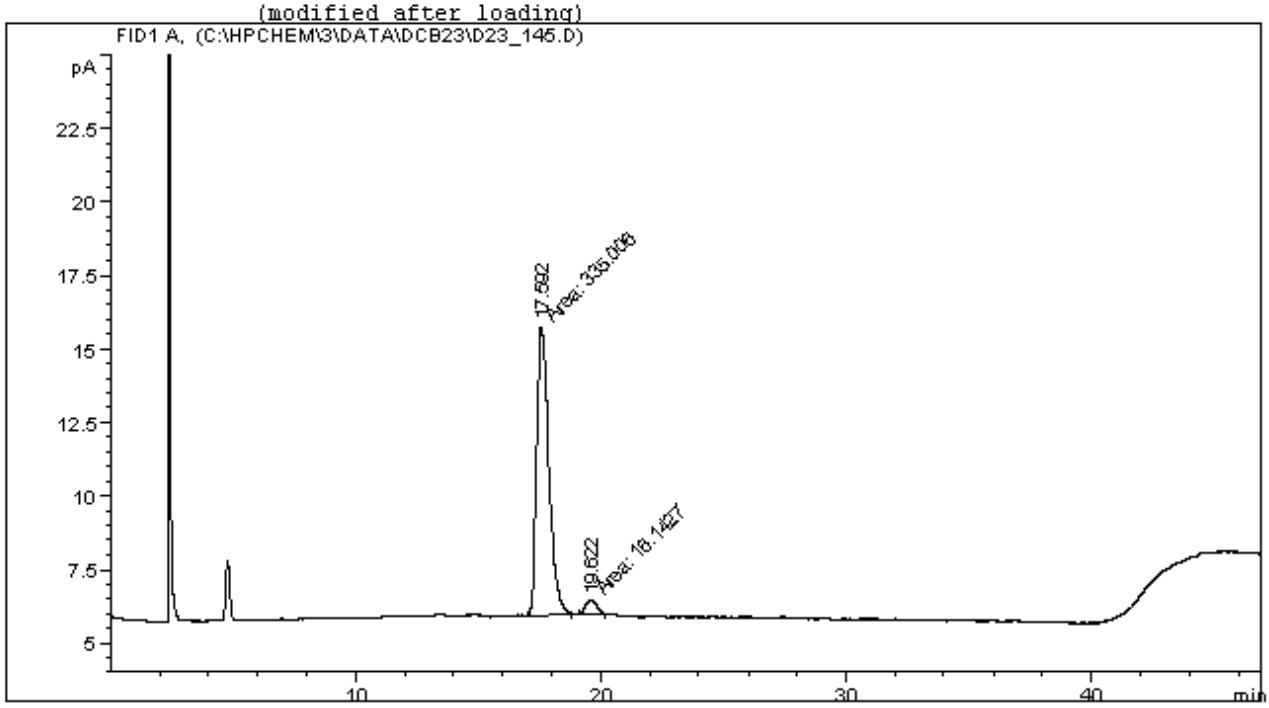



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  18.065 BB    0.2128  259.56442   17.52343 49.85883
   2  20.537 PB    0.2604  261.03427   14.61583 50.14117

Totals :                   520.59869   32.13926

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 8 91 % ee:

Data File C:\HPCHEM\3\DATA\DCB23\D23_145.D Sample Name: DCB23_145

```
==================================================================
Injection Date  : 8/10/2004 3:11:18 PM          Seq. Line :   2
Sample Name     : DCB23 145                      Location : Vial 6
Acq. Operator   : dcb                               Inj :   1
Acq. Instrument : Instrument 3                  Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\3\METHODS\100IS040.M
Last changed    : 6/10/2004 11:07:16 PM by nIKKI
Analysis Method : C:\HPCHEM\1\METHODS\150IS090.M
Last changed    : 10/8/2004 1:22:58 PM by ians
                  (modified after loading)
```

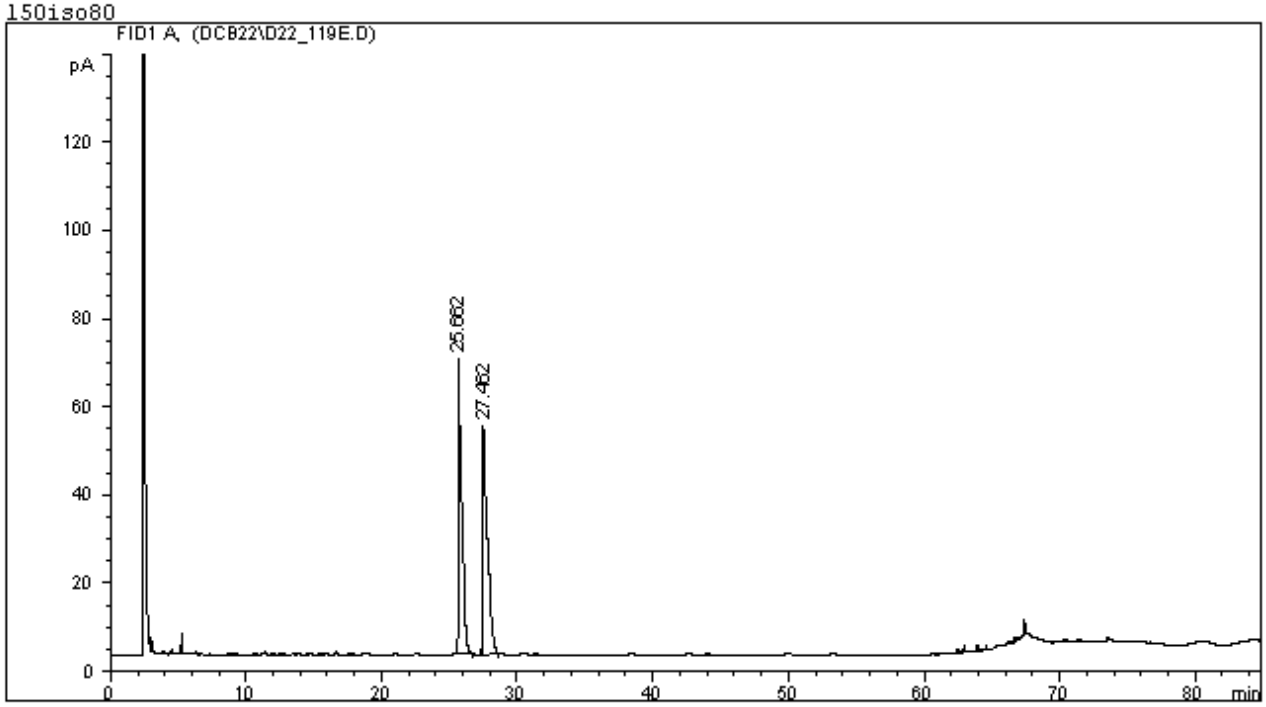



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  17.592 MM    0.5690  335.00635    9.81331 95.40288
   2  19.622 MM    0.5282   16.14274 5.09399e-1  4.59712

Totals :                   351.14909   10.32271

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```

Table 2 Entry 9 Racemic:

Data File C:\HPCHEM\2\DATA\DCB22\D22_119E.D Sample Name: dcb22_119

```
==================================================================
Injection Date  : 5/23/2004 11:44:31 AM          Seq. Line :   2
Sample Name     : dcb22 119                       Location : Vial 19
Acq. Operator   : DCB                                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\2\METHODS\80IS060.M
Last changed    : 4/26/2004 4:15:11 PM by yh
Analysis Method : C:\HPCHEM\2\METHODS\150IS80.M
Last changed    : 10/8/2004 11:28:36 AM by spb
                  (modified after loading)
150iso80
```

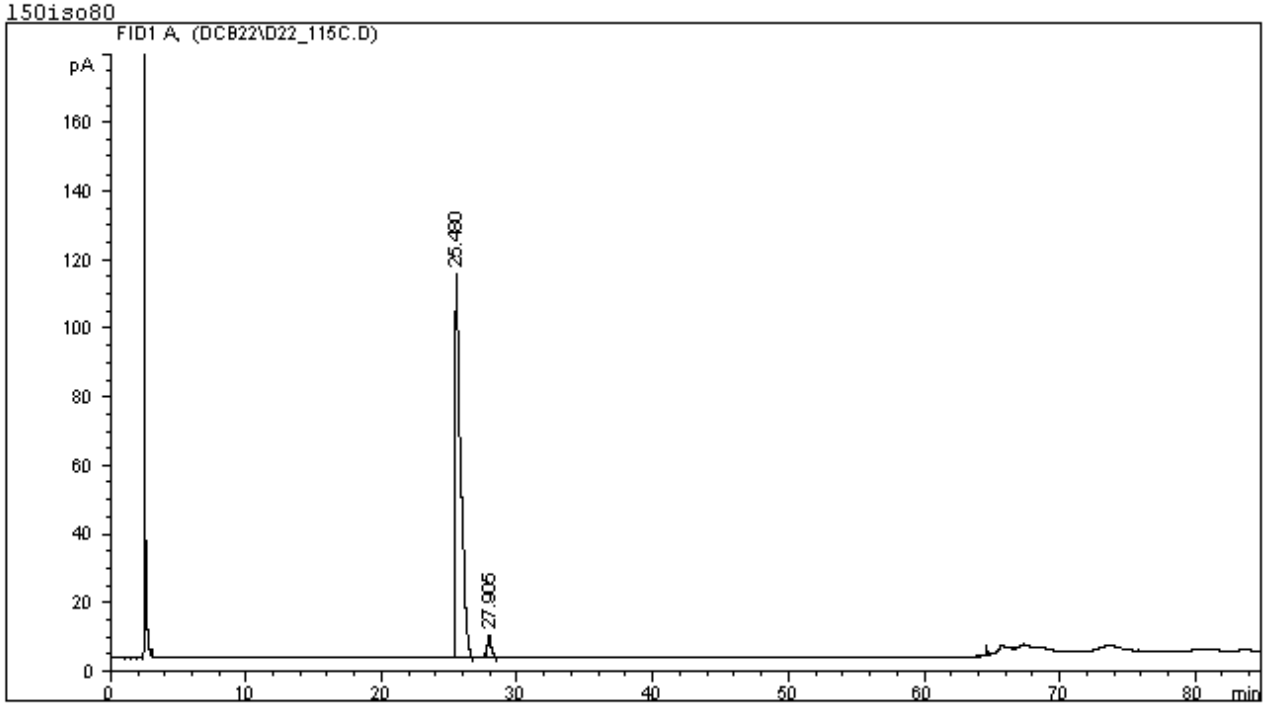



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  25.662 BB    0.2510 1326.54626   66.98425 49.97898
   2  27.462 PB    0.3171 1327.66199   51.79283 50.02102

Totals :                  2654.20825  118.77708

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 9 92 % ee:

Data File C:\HPCHEM\2\DATA\DCB22\D22_115C.D Sample Name: dcb22_115

```
==========================================================================
Injection Date  : 5/23/2004 3:43:31 PM          Seq. Line :   5
Sample Name     : dcb22 115                      Location : Vial 10
Acq. Operator   : DCB                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\2\METHODS\80IS060.M
Last changed    : 4/26/2004 4:15:11 PM by yh
Analysis Method : C:\HPCHEM\2\METHODS\150IS80.M
Last changed    : 10/8/2004 11:27:38 AM by spb
                  (modified after loading)
150iso80
```

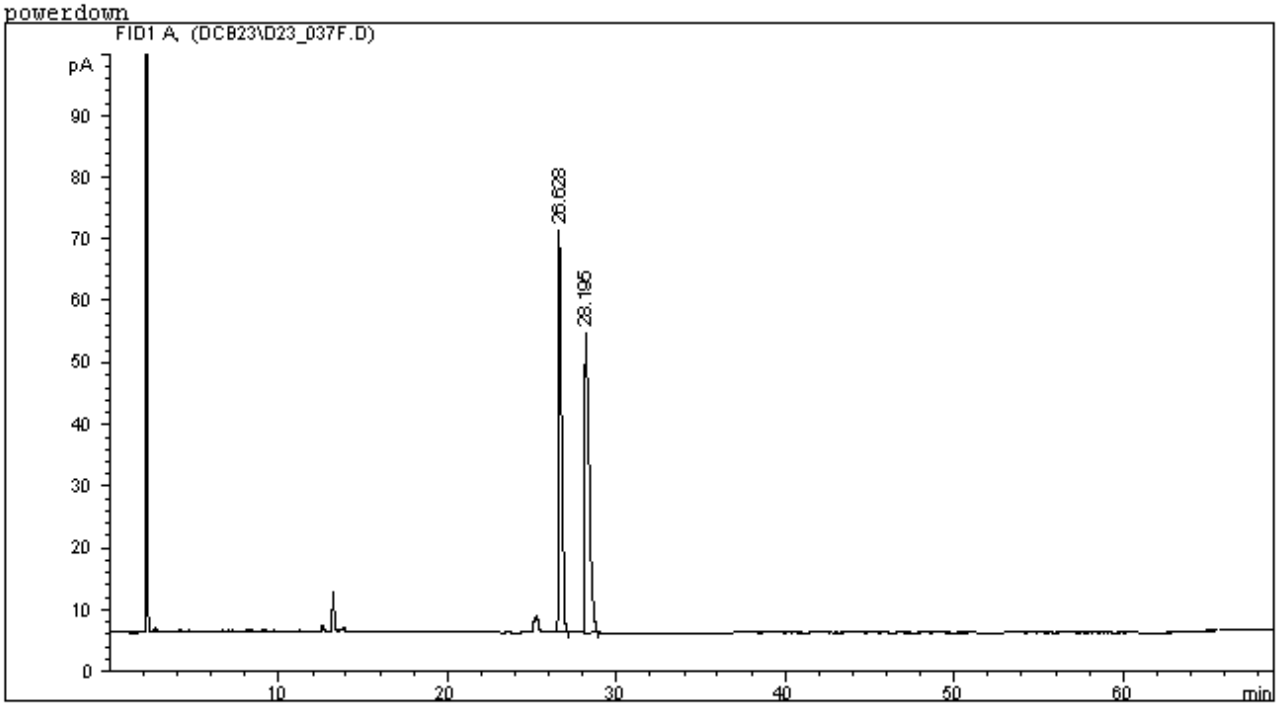



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  25.480 PB    0.3194 2897.96167  112.18385 95.77809
   2  27.905 BB    0.2384  127.74248    6.46859  4.22191

Totals :                  3025.70415  118.65245

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 10 Racemic:

Data File E:\HPCHEM\1\DATA\DCB23\D23_037F.D Sample Name: DCB23_037

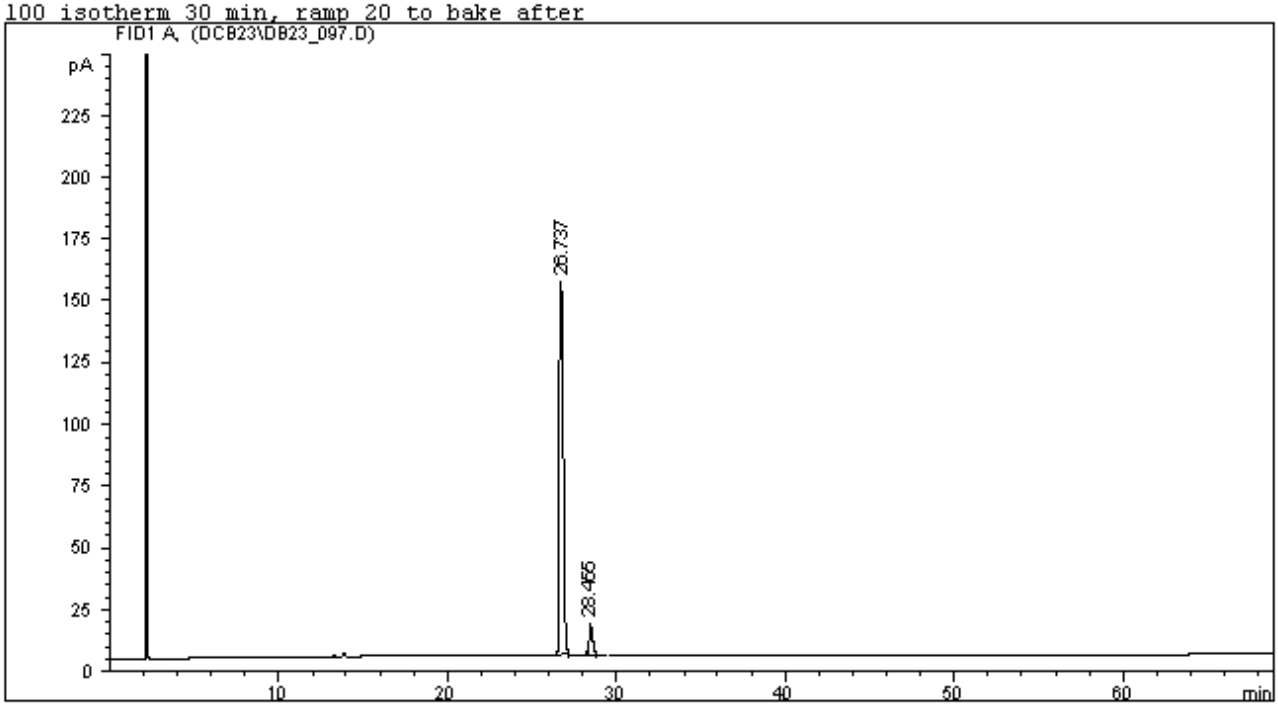
```
==========================================================================
Injection Date  : 7/13/04 8:08:33 PM            Seq. Line :   5
Sample Name     : DCB23 037                      Location : Vial 3
Acq. Operator   : DCB                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\120IS060.M
Last changed    : 8/6/03 10:48:34 PM by DCB
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 11:16:40 AM by JTM
                  (modified after loading)
powerdown
```




```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  26.628 PB    0.1795  847.58063   64.83565 50.13650
   2  28.195 BB    0.2247  842.96545   48.28147 49.86350

Totals :                  1690.54608  113.11712

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 10 86 % ee:

```
Data File E:\HPCHEM\1\DATA\DCB23\DB23_097.D                    Sample Name: DCB23_97

==========================================================================
Injection Date  : 7/30/04 5:57:53 PM            Seq. Line :   2
Sample Name     : DCB23 97                       Location : Vial 1
Acq. Operator   : DCB                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\120IS060.M
Last changed    : 8/6/03 10:48:34 PM by DCB
Analysis Method : C:\HPCHEM\1\METHODS\DB100IS0.M
Last changed    : 10/8/04 11:22:24 AM by JTM
                  (modified after loading)
100 isotherm 30 min, ramp 20 to bake after
```

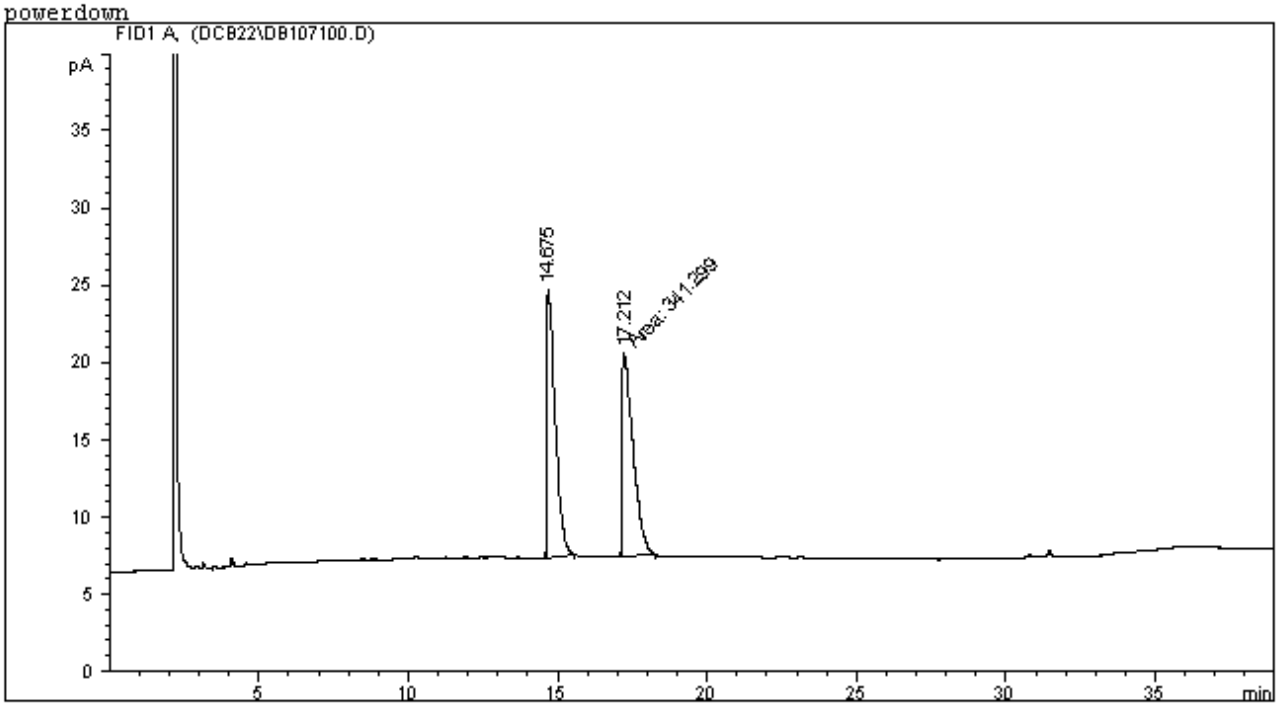



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  26.737 BB    0.1953 2448.60522  150.88455 93.03473
   2  28.455 BB    0.1954  183.32065   12.62448  6.96527

Totals :                  2631.92587  163.50903

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Table 2 Entry 11 Racemic:

Data File E:\HPCHEM\1\DATA\DCB22\DB107100.D Sample Name: dcb22_107

```
==========================================================================
Injection Date  : 5/12/04 10:20:31 AM            Seq. Line :   2
Sample Name     : dcb22 107                       Location : Vial 1
Acq. Operator   : DCB                                 Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\DB100ISO.M
Last changed    : 2/19/03 5:36:15 PM by pnc
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 11:26:21 AM by JTM
                  (modified after loading)
powerdown
```

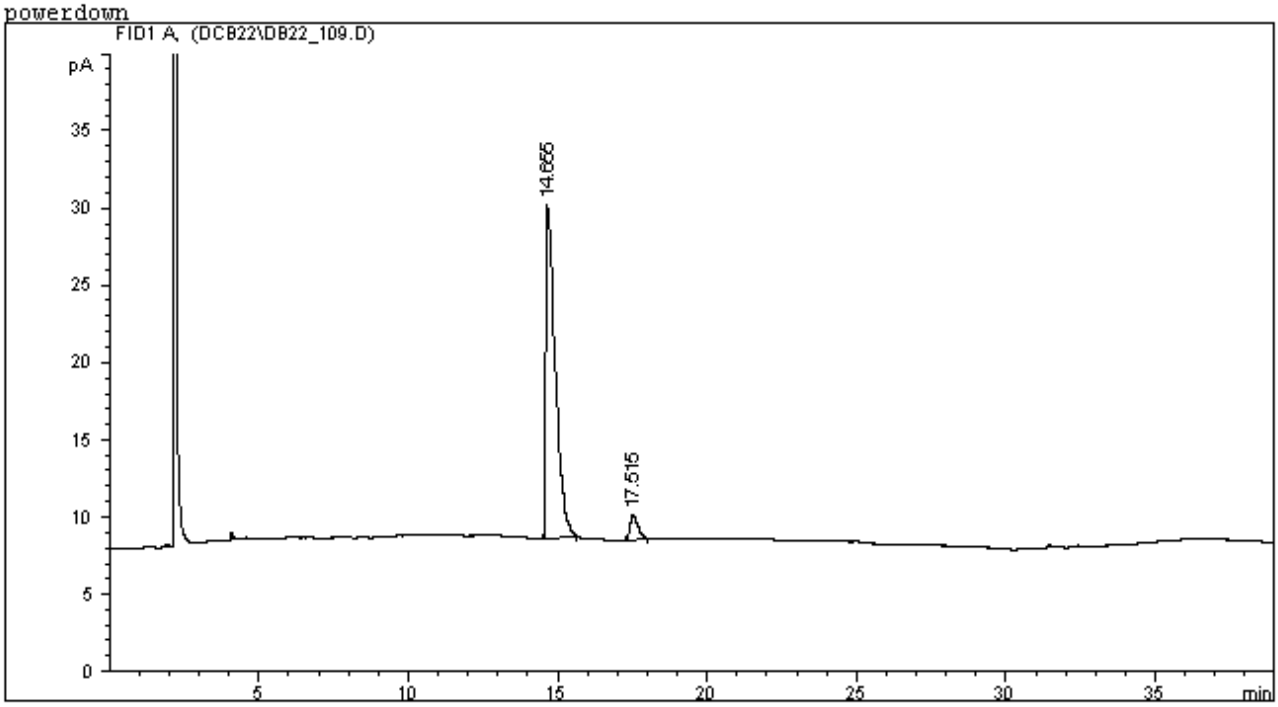



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.675 PB    0.2359  342.18802   17.29111 50.06505
   2  17.212 MM    0.4298  341.29883   13.23439 49.93495

Totals :                   683.48685   30.52550

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 11 89 % ee:

Data File E:\HPCHEM\1\DATA\DCB22\DB22_109.D Sample Name: dcb22_109

```
==========================================================================
Injection Date  : 5/13/04 12:47:55 AM          Seq. Line :   2
Sample Name     : dcb22 109                     Location : Vial 2
Acq. Operator   : DCB                              Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\DB100IS0.M
Last changed    : 2/19/03 5:36:15 PM by pnc
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 11:28:24 AM by JTM
                  (modified after loading)
powerdown
```

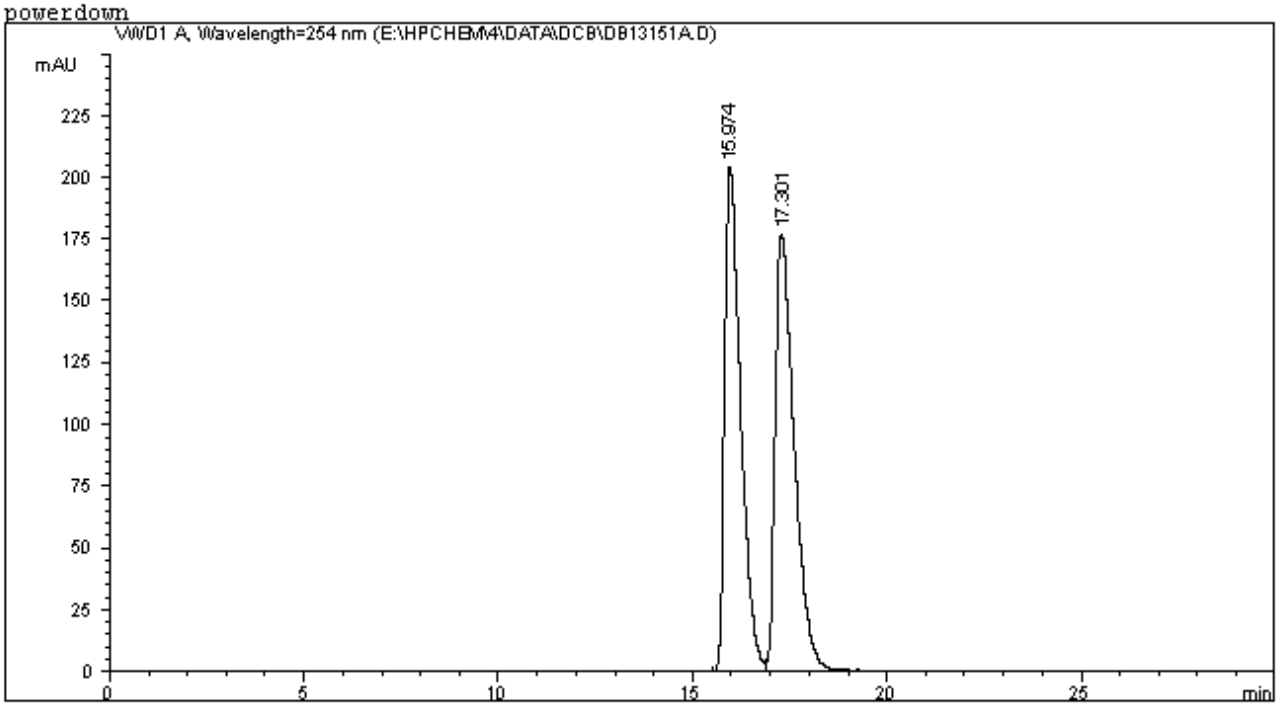



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  14.655 PB    0.2696  483.15540   21.54602 94.50080
   2  17.515 PB    0.2066   28.11581    1.63529  5.49920

Totals :                   511.27120   23.18131

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 12 Racemic:

Data File E:\HPCHEM\4\DATA\DCB\DB13151A.D Sample Name: db13_151

```
==================================================================
Injection Date  : 2/27/03 7:00:19 PM            Seq. Line :   5
Sample Name     : db13 151                       Location : Vial 1
Acq. Operator   : DCB                               Inj :   1
Acq. Instrument : Instrument 4
Acq. Method     : C:\HPCHEM\4\METHODS\1-IPA30.M
Last changed    : 4/19/02 2:20:48 PM by DCB
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 11:59:05 AM by JTM
                  (modified after loading)
powerdown
```

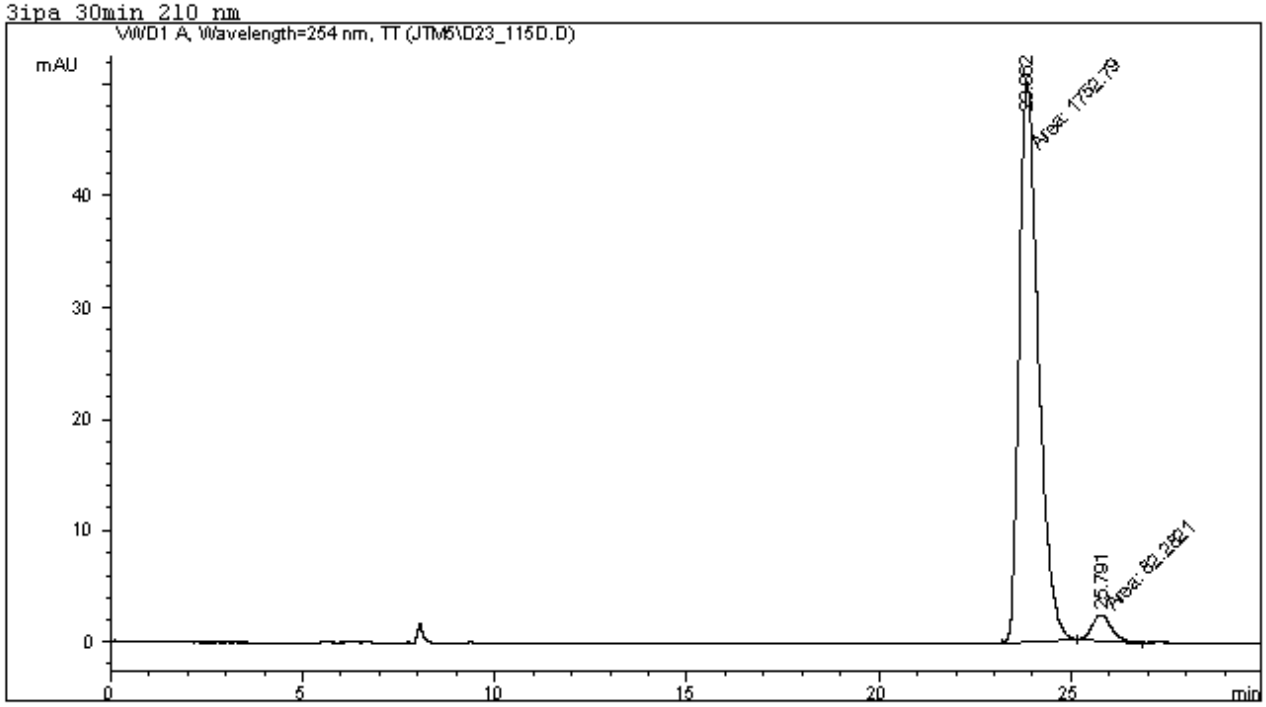



```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  15.974 BV    0.4351 5883.85937  204.26538 49.32317
   2  17.301 VB    0.5157 6045.33936  176.65131 50.67683

Totals :                  1.19292e4   380.91669

 Results obtained with enhanced integrator!
==================================================================
                      *** End of Report ***
```

Table 2 Entry 12 91 % ee:

Data File C:\HPCHEM\3\DATA\JTM5\D23_115D.D Sample Name: DCB23_115

```
==========================================================================
Injection Date  : 8/5/2004 6:41:49 AM            Seq. Line :  27
Sample Name     : DCB23 115                       Location : Vial 13
Acq. Operator   : JTM                                 Inj :  1
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\3\METHODS\DB30MIN.M
Last changed    : 2/27/2003 4:45:00 PM by rmm
Analysis Method : C:\HPCHEM\3\METHODS\3-IPA30J.M
Last changed    : 10/8/2004 11:42:11 AM by jmb
                  (modified after loading)
3ipa 30min 210 nm
```

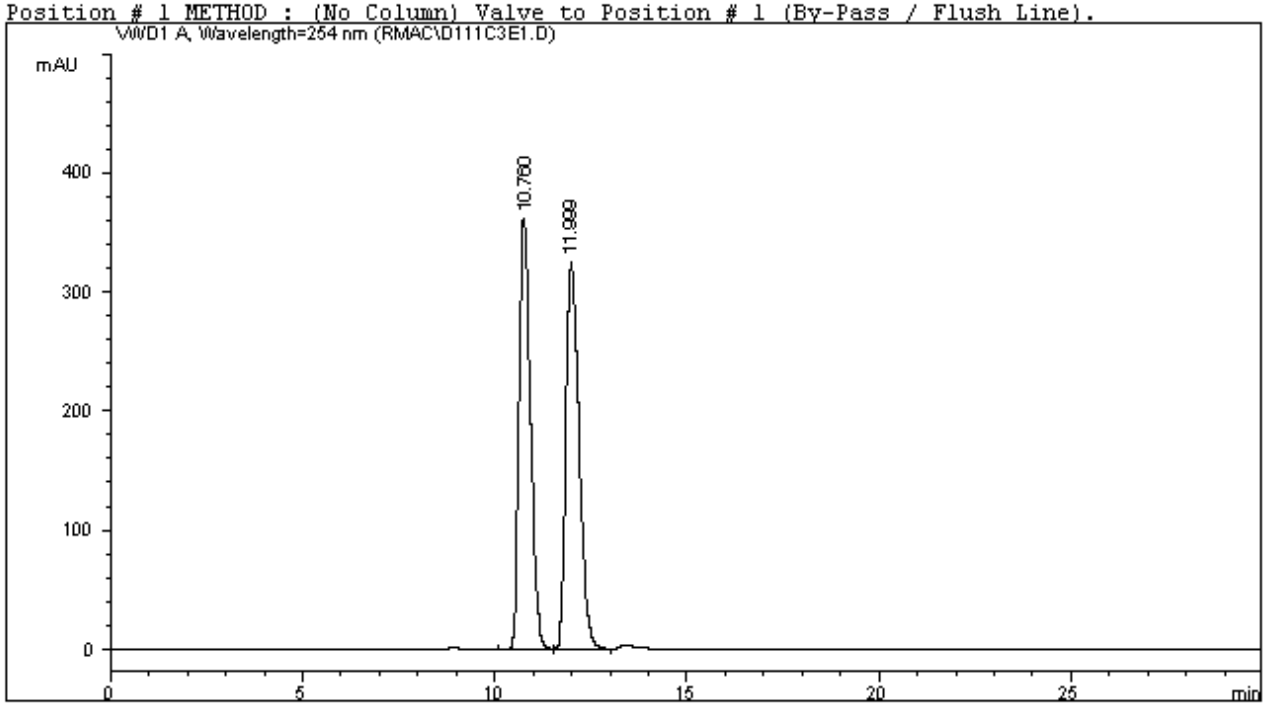



```
==========================================================================
                        Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  23.862 MM    0.5816 1752.78979   50.22748  95.5161
   2  25.791 MM    0.5942   82.28210    2.30773   4.4839

Totals :                  1835.07190   52.53521

 Results obtained with enhanced integrator!
==========================================================================
                        *** End of Report ***
```

Table 2 Entry 13 Racemic:

Data File C:\HPCHEM\2\DATA\RMAC\D111C3E1.D Sample Name: db22_111

```
==================================================================
Injection Date  : 5/19/2004 5:09:11 AM          Seq. Line :  25
Sample Name     : db22 111                       Location : Vial 10
Acq. Operator   : emf                                Inj :  1
                                                Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\1-EOH30.M
Last changed    : 4/14/2003 8:56:54 PM by Dan
Analysis Method : C:\HPCHEM\2\METHODS\BYPASS.M
Last changed    : 10/8/2004 12:04:02 PM by dra
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

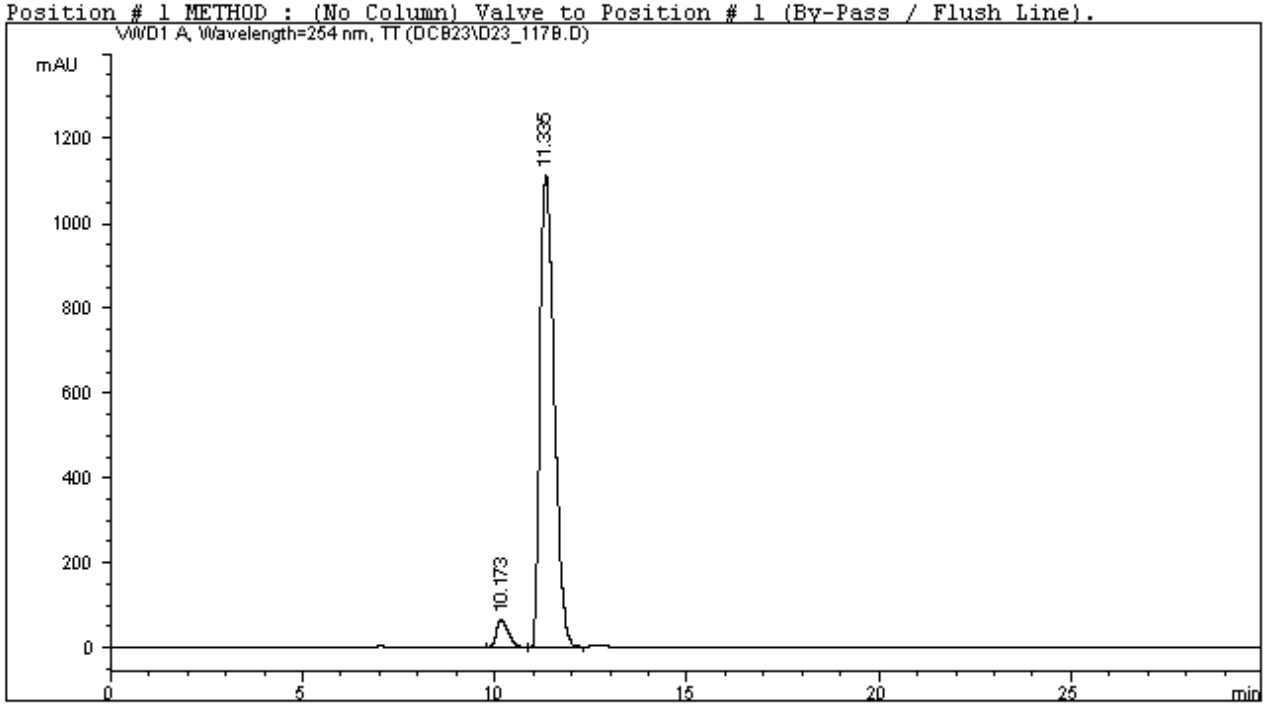



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.760 BV    0.3303 7619.01514  361.51328  49.5862
   2  11.999 VV    0.3706 7746.17480  325.71719  50.4138

Totals :                  1.53652e4   687.23047

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 13 91 % ee:

Data File C:\HPCHEM\2\DATA\DCB23\D23_117B.D Sample Name: dcb23_117

```
==================================================================
Injection Date  : 8/5/2004 1:29:50 AM          Seq. Line :   7
Sample Name     : dcb23 117                     Location : Vial 11
Acq. Operator   : DCB                              Inj :   1
                                               Inj Volume : 5 µl
Acq. Method     : C:\HPCHEM\2\METHODS\2 IPA30.M
Last changed    : 5/19/2004 9:40:10 AM by emf
Analysis Method : C:\HPCHEM\2\METHODS\BYPASS.M
Last changed    : 10/8/2004 12:01:33 PM by dra
                  (modified after loading)
Position # 1 METHOD : (No Column) Valve to Position # 1 (By-Pass / Flush Line).
```

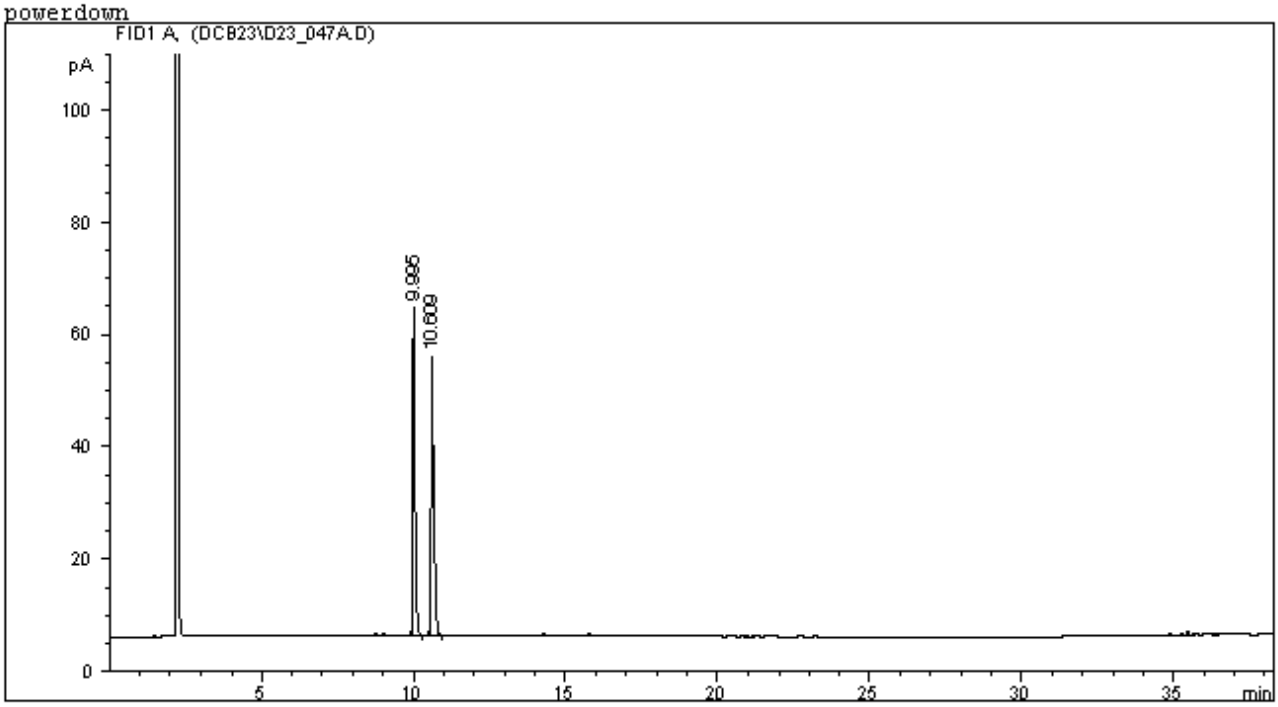



```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000


Signal 1: VWD1 A, Wavelength=254 nm, TT

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  10.173 BV    0.3325 1390.20593   65.00232   4.6564
   2  11.335 VV    0.4067 2.84657e4  1110.97388  95.3436

Totals :                  2.98559e4  1175.97620

 Results obtained with enhanced integrator!
==================================================================
                        *** End of Report ***
```

Table 2 Entry 14 Racemic:

Data File E:\HPCHEM\1\DATA\DCB23\D23_047A.D Sample Name: DCB23_047

```
==========================================================================
Injection Date  : 7/14/04 12:28:51 PM            Seq. Line :   2
Sample Name     : DCB23 047                       Location : Vial 6
Acq. Operator   : DCB                                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110IS030.M
Last changed    : 9/11/03 10:31:22 AM by JLS
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 12:09:54 PM by JTM
                  (modified after loading)
powerdown
```

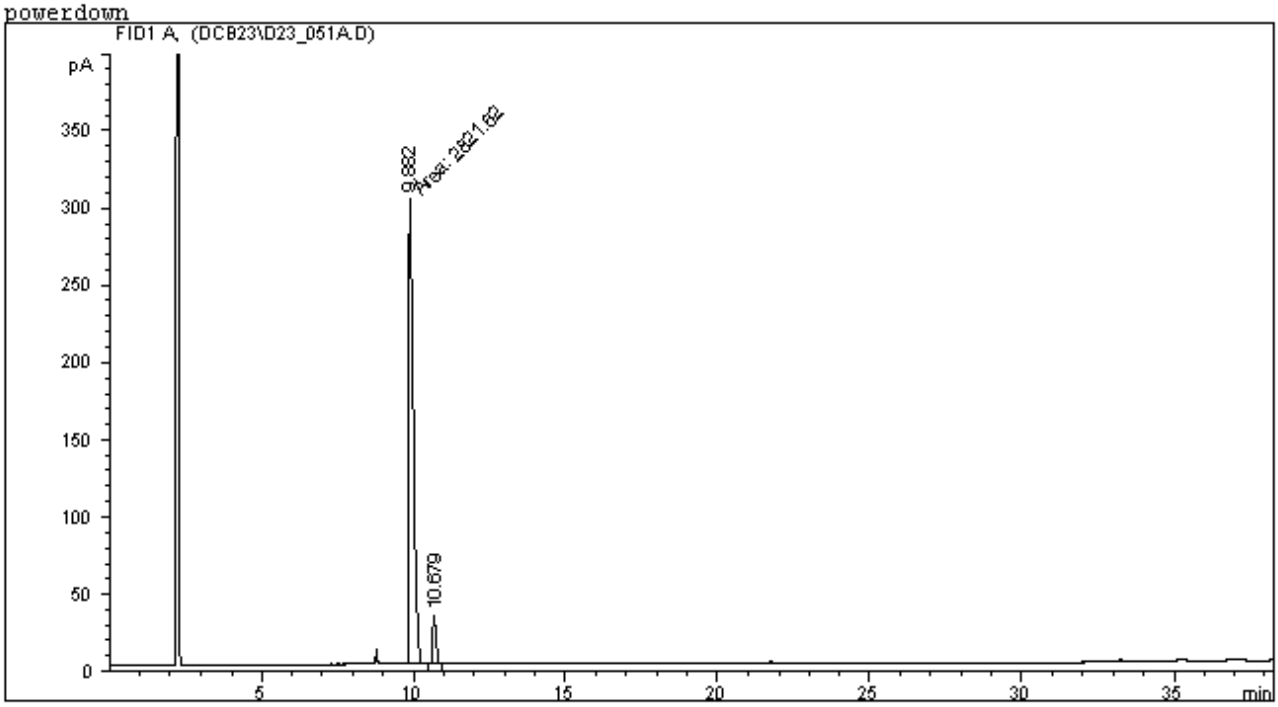



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   9.995 PB    0.0876  332.98715   58.30622 50.03587
   2  10.609 BB    0.1000  332.50970   49.75749 49.96413

Totals :                   665.49686  108.06371

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 14 87 % ee:

Data File E:\HPCHEM\1\DATA\DCB23\D23_051A.D Sample Name: DCB23_51

```
==========================================================================
Injection Date  : 7/15/04 12:21:12 PM            Seq. Line :   1
Sample Name     : DCB23 51                        Location : Vial 8
Acq. Operator   : DCB                                 Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110IS030.M
Last changed    : 9/11/03 10:31:22 AM by JLS
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 12:15:03 PM by JTM
                  (modified after loading)
powerdown
```

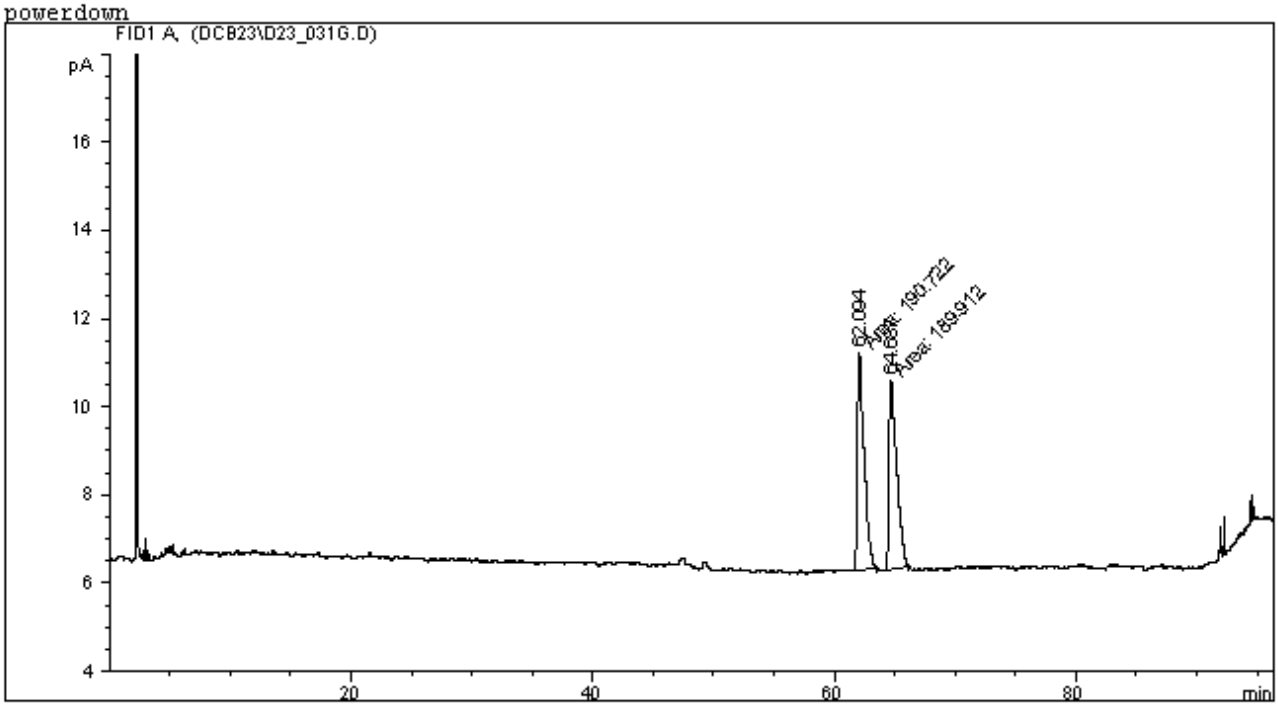



```
==========================================================================
                          Area Percent Report
==========================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   9.882 MM    0.1564 2821.61987  300.76633 93.26244
   2  10.679 PB    0.0995  203.84238   30.66639  6.73756

Totals :                  3025.46225  331.43271

 Results obtained with enhanced integrator!
==========================================================================
                          *** End of Report ***
```

Table 2 Entry 15 Diketone Derivative Racemic:

Data File E:\HPCHEM\1\DATA\DCB23\D23_031G.D Sample Name: DCB23_031

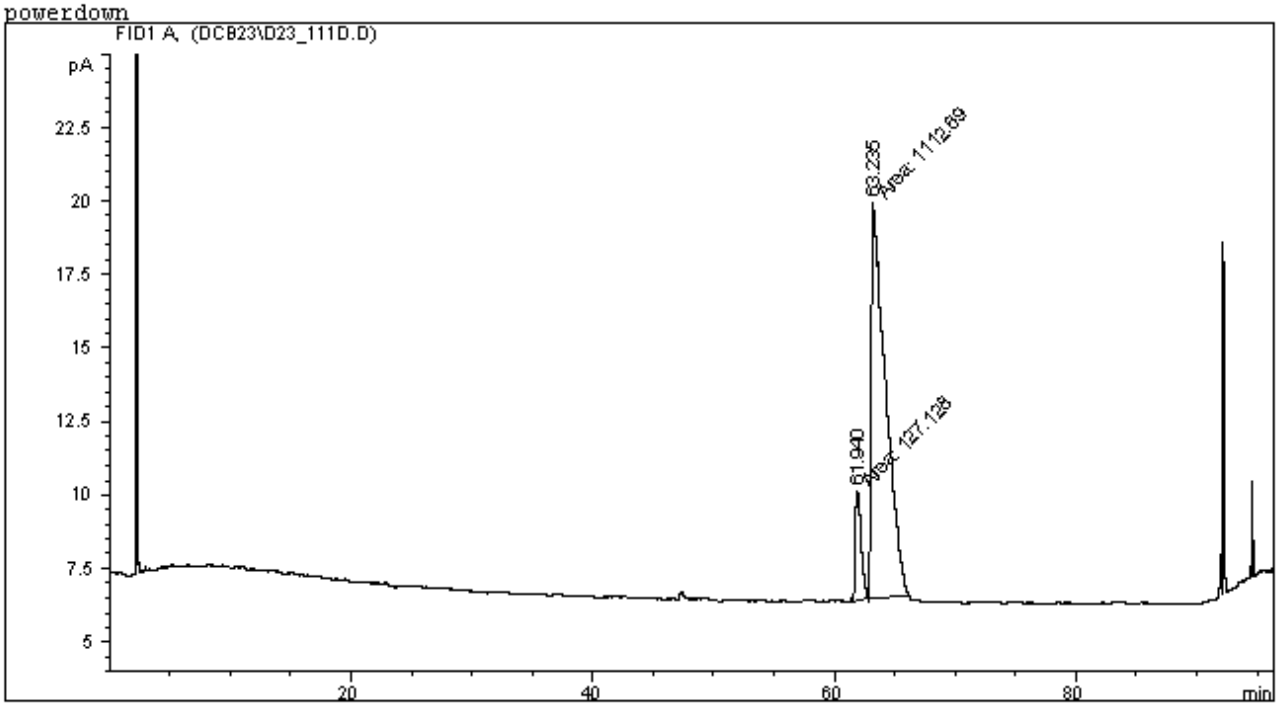
```
==================================================================
Injection Date  : 7/13/04 10:53:32 AM          Seq. Line :  10
Sample Name     : DCB23 031                     Location : Vial 2
Acq. Operator   : DCB                              Inj :   1
                                               Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110S090.M
Last changed    : 7/10/04 7:44:46 PM by kefl
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 12:18:09 PM by JTM
                  (modified after loading)
powerdown
```




```
==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  62.094 MM    0.6459  190.72234    4.92111 50.10648
   2  64.687 MM    0.7403  189.91176    4.27549 49.89352

Totals :                   380.63409    9.19660

 Results obtained with enhanced integrator!
==================================================================
                          *** End of Report ***
```

Table 2 Entry 15 Diketone Derivative 79 % ee:

```
Data File E:\HPCHEM\1\DATA\DCB23\D23_111D.D                    Sample Name: DCB23_111CONC

=====================================================================
Injection Date  : 8/5/04 10:30:41 AM            Seq. Line :   2
Sample Name     : DCB23 111CONC                  Location : Vial 1
Acq. Operator   : dcb                               Inj :   1
                                                Inj Volume : 1 µl
Acq. Method     : C:\HPCHEM\1\METHODS\110S090.M
Last changed    : 7/10/04 7:44:46 PM by kefl
Analysis Method : C:\HPCHEM\1\METHODS\PWRDOWN.M
Last changed    : 10/8/04 12:23:53 PM by JTM
                  (modified after loading)
powerdown
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A,

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1  61.940 MM    0.5693  127.12809    3.72197 10.25381
   2  63.235 MM    1.3796 1112.68542   13.44196 89.74619

Totals :                  1239.81351   17.16393

 Results obtained with enhanced integrator!
=====================================================================
                        *** End of Report ***
```

References:

1. Peer, M.; de Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahedron* **1996**, *52*, 7547-7583.

2. Kirby, G. W.; McGuigan, H.; McLean, D. *J. Chem. Soc., Perkin Trans. 1* **1985**, *9*, 1961-1966.

3. Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dungogues, J. *Tetrahedron* **1987**, *43*, 2075-2088.

4. Larock, R. C.; Hightower, T. R.; Kraus, G. A.; Hahn, P.; Zheng, D. *Tetrahedron Lett.* **1995**, *36*, 2423-2426.

5. House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, D. H. *J. Org. Chem.* **1969**, *34*, 2324-2336.

6. Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 1793-1796.

7. (a) Yu, W.; Jin, Z. *Tetrahedron Lett.* **2001**, *42*, 369-372. (b) Duhamel, P.; Cahard, D.; Quesnel, Y.; Poirier, J.-M. *J. Org. Chem.* **1996**, *61*, 2232-2235. (c) Duhamel, P.; Cahard, D.; Poirier, J.-M. *Chem. Soc., Perkin Trans. 1* **1993**, 2509-2511.

8. Aboulhoda, S. J.; Henin, F.; Muzart, J.; Thorey, C. *Tetrahedron Lett.* **1995**, *36*, 4795-4796.

9. Chatterjee, A. K.; Morgan, J. P.; Scholl, M.; Grubbs, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 3783-3784.

10. Buono, F.; Tenaglia, A. *J. Org. Chem.* **2000**, *65*, 3869-3874.

11. The optical rotation of enone **15** further corroborates the assignment of the absolute configuration of ketone **2** to be (*S*), as both (*S*)-(+) **15**: (a) Gratten, T. J.; White, J. S. *J. Chem. Soc., Chem. Commun.* **1988**, 43-44. $[\alpha]_D^{20}$ +198° (*c* = 0.8, ethanol) (b) Shimizu, I.; Matsumoto, Y.; Shoji, K.; Ono, T.; Satake, A.; Yamamoto, A. *Tetrahedron Lett.* **1996**, *37*, 7115-7118. $[\alpha]_D^{20}$ +206° (*c* = 1.0, ethanol) and (*R*)-(-) **15**: (a) Pfau, M.; Revial, G.; Guingant, A.; d'Angelo, J. *J. Am. Chem. Soc.* **1985**, *107*, 273-274. $[\alpha]_D^{24}$ -207° (*c* = 1.0, ethanol) (b) Doering, W. E.; Birladeanu, L.; Sarma, K.; Shao, L. S. *J. Am. Chem. Soc.* **1996**, *118*, 6660-6665. $[\alpha]_D^{20}$ -228° (*c* = 1.2, ethanol) (c) Doering, W. E.; He, J.; Shao, L. *J. Am. Chem. Soc.* **2001**, *123*, 9153-9161. $[\alpha]_D^{20}$ -229° (*c* = 1.1, ethanol)

12. Smith, A. B.; Cho, Y. S.; Friestad, G. K. *Tetrahedron Lett.* **1998**, *39*, 8765-8768.

13. McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. . *J. Org. Chem.* **1993**, *58*, 3568-3571.

14. Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett.* **2003**, *5*, 2315-2318.