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# Supporting Information



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# A Diels-Alder Approach to (-)-Ovalicin

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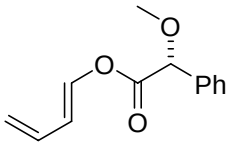
General:

All reactions were carried out in oven or flame-dried glassware under an argon atmosphere, unless otherwise stated. Anhydrous tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were freshly distilled from sodium/benzophenone under argon; anhydrous dichloromethane (DCM) was freshly distilled from $CaH_2$ under argon. All other solvents were HPLC grade. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with E. Merck silica gel 60-F254 plates. Flash column chromatography was performed with Merck silica gel (0.04-0.063 mm, 240-400 mesh) under pressure. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. NMR spectra were recorded on either Bruker Avance DRX 400 or DRX 600 MHz spectrometer. Unless otherwise stated, all NMR spectra were measured in CDCl3 solutions and referenced to the residual $CHCl_3$ signal ($^1H$, $\delta = 7.26$; $^{13}C$, $\delta = 77.16$). All $^1H$ and $^{13}C$ shifts are given in ppm (s = singlet; d = doublet; t = triplet; q = quadruplet; m = multiplet; b = broad signal). Coupling constants *J* are given in Hz. Assignments of proton resonances were confirmed, when possible, by correlated spectroscopy. Optical rotations were measured on a P 341 Perkin- Elmer polarimeter. Mass spectra were measured on a Micro mass, trio 200 Fisions Instruments. High resolution mass spectra (HRMS) were performed with a Finnigan MAT 8230 with a resolution of 10000.

Experimental Procedures:

(S)-Methoxyphenylacetic acid (E)-buta-1,3-dienyl ester (**10**)




To a solution of (*R*)-methoxyphenylacetic acid[1] (2.15 g, 12.9 mmol) in DCM (67 mL) was added (diethylamino)sulphur trifluoride (2.92 g, 18.1 mmol) at room temperature. After stirring for 50 min. the solution was washed with cold water and brine. , The organic layer was dried over magnesium sulfate, filtered and the solvent removed under reduced pressure (20 mbar, 45 °C) to yield a yellow oil (2.21 g), which was employed without further purification for the next step.
The crude acid fluoride was dissolved in THF (17.5 mL) and cooled to 0 °C. After the addition of (Trimethylsiloxy)butadiene[2] (*E*:*Z* ≥ 10:1; 1.67 g, 11.7 mmol) and TBAF (1.0 M in THF; 0.59 mL) the resulting solution was stirred for 2 h at 0°C. Silica gel (10 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (100 g silica gel) using hexane:ethylacetate = 20:1 to 10:1 as an eluent yielded diene **10** (*E*:*Z* ≥ 10:1; 2.38 g, 93 %).

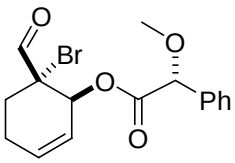
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.34 (m, 6H), 6.24 (dt, J = 16.9, 10.6 Hz, 1H), 6.06 (dd, J = 11.7, 11.7 Hz, 1H), 5.20 (bd, J =16.6 Hz, 1H), 5.09 (bd, J = 10.4 Hz, 1H), 4.84 (s, 1H), 3.44 (s, 3H)

[1] Bulman Page, P. C.; Chan, Y.; Heaney, H.; McGrath, M. J.; Moreno, E. *Synlett* **2004**, 2606; Jones, L. H.; Badger, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 3126. (purification of the crude carboxylic acid by extraction with saturated $NaHCO_3$ solution was sufficient)

[2] Commercially available. Preparation from crotonaldehyde: Gaonac'h, O.; Maddaluno, J.; Chauvin, J.; Duhamel, L. *J. Org. Chem.* **1991**, *56*, 4045.

**$^{13}$C NMR** (100 MHz, CDCl3) δ 167.8 (C), 138.4 (CH), 135.6 (C), 131.4 (CH), 129.2 (CH), 128.9 (CH, 2C), 127.5 (CH, 2C), 118.0 ($CH_2$), 117.3 (CH), 82.4 (CH), 57.6 ($CH_3$).
**IR** [$cm^{-1}$]: 3089, 2931, 1765, 1657, 1455, 1235, 1149, 1113, 994, 924.
**HRMS**(EI) calcd. for $C_{13}H_{14}O_3$: 218,0943, found: 218.0940.
**$[\alpha]_D^{20}$** = +5.9 (c = 1.20, DCM).

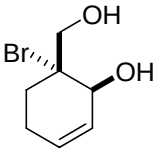
(1'*S*, 2*S*, 6'*S*)-Methoxyphenylacetic acid 6'-bromo-6'-formylcyclohex-2'-en-1'-yl ester (**11**)




To a solution of diene **10** (1.84 g, 8.43 mmol) in DCM (42 mL) was added 2-bromoacrolein[3] (2.28 g, 16.9 mmol) at – 78°C. After stirring for 10 min at this temperature $BF_3.OEt_2$ (350 µL, 2.77 mmol) was added. The reaction was quenched after 5 h by addition of saturated $NaHCO_3$ solution (20 mL). After the emulsion reached room temperature the organic phase was separated and the aqueous layer was extracted 3 times with DCM. The combined organic phases were washed with saturated $NaHCO_3$ solution, dried over magnesium sulfate, filtered, silica gel (20 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (240 g silica gel) using hexane:ethylacetate = 10:1 to 5:1 as an eluent yielded aldehyde **11** (2.23 g, 75 %).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.39-7.32 (m, 5H), 5.98 (dt, J = 9.4, 3.6 Hz, 1H), 5.70-5.67 (m, 1H), 5.64-5.58 (m, 1H), 4.72 (s, 1H), 3.39 (s, 3H), 2.36-2.26 (m, 2H), 2.21-2.14 (m, 2H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 190.0 (CH), 169.9 (C), 135.7 (C), 133.9 (CH), 129.1 (CH), 128.8 (CH, 2C), 127.2 (CH, 2C), 120.6 (CH), 82.5 (CH), 70.6 (CH), 65.7 (C), 57.6 ($CH_3$), 25.8 ($CH_2$), 23.4 ($CH_2$).
**IR** [$cm^{-1}$]: 3035, 2930, 1751, 1730, 1456, 1232, 1197, 1164, 1144, 1103, 1030, 997, 920.
**HRMS**(EI) calcd. for $C_{16}H_{17}O_4Br$: 352.0310, found: 352.0301.
**$[\alpha]_D^{20}$** = +199 (c = 1.24, DCM).

(1*S*, 6*R*)-6-Bromo-6-hydroxymethyl-cyclohex-2-en-1-ol (**12**)

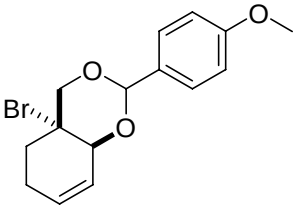



To a solution of aldehyde **11** (2.06 g, 5.83 mmol) in regular $Et_2O$ (50 mL) was added $BH_3.NH_3$ (198 mg, 6.41 mmol) at room temperature and stirred for 2.5 h. After quenching by addition of 1N HCl (20 mL) and stirring for additional 30 min the phases were separated. Sodium chloride was added to the aqueous layer which was subsequently extracted 5 times with $Et_2O$. The combined organic phases were dried over magnesium sulfate, filtered, silica gel (10 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (120 g silica gel) using pentane:$Et_2O$ = 1:1 to 0:1 as an eluent yielded diol **12** (1.07 g, 89 %) and (*R*)-2-Methoxy-2-phenylethanol (801 mg, 90%).

[3] Corey, E.J.; Loh, T.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8966.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.98-5.91 (m, 1H), 5.83-5.75 (m, 1H), 4.53-4.47 (m, 1H), 4.06-3.98 (m, 1H), 3.92-3.85 (m, 1H), 2.57 (d, J = 6.0 Hz, 1H), 2.51 (dd, J = 9.5, 5.8 Hz, 1H), 2.39-2.27 (m, 1H), 2.26-2.15 (m, 1H), 2.10-2.00 (m, 1H), 1.99-1.91 (m, 1H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 131.1 (CH), 125.9 (CH), 75.3 (C), 71.0 (CH), 69.5 ($CH_2$), 28.8 ($CH_2$), 24.2 ($CH_2$).
**IR** [$cm^{-1}$]: 3383, 2922, 1426, 1401, 1068, 1053, 1035, 1010, 978.
**HRMS**(EI) calcd. for $C_7H_9OBr$ (M-$H_2O$): 187.9837,found: 187.9832.
**$[\alpha]_D^{20}$** = +82.0(c = 1.23, DCM)

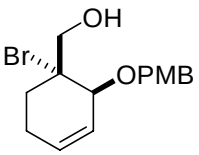
(4a*R*, 8a*S*)- 4a-Bromo-2-(4'-methoxyphenyl)-4a,5,6,8a-tetrahydro-4*H*-benzo[1,3]dioxine




To a solution of diol **12** (1.03 g, 4.97 mmol) in DCM (56 mL) was added anisaldehyde dimethyl acetal (1.13g, 6.22 mmol) and (±)-campher-10-sulfonic acid (46mg, 0.20 mmol). After stirring for 3 h at room temperature additional anisaldehyde dimethyl acetal (180 mg, 0.99 mmol) was added. After 30 min. the reaction was quenched by addition of saturated $NaHCO_3$ solution (5 mL) and water (50 mL). The organic phase was separated and the aqueous layer was extracted 3 times with DCM. The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed under vacuum. Purification by column chromatography (80 g silica gel) using hexane:ethylacetate = 10:1 as an eluent yielded title acetal (1.44 g, 89 %) as a white solid.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.37 (m, 2H), 6.91-6.85 (m, 2H), 6.07-6.00 (m, 1H), 5.82-5.76 (m, 1H), 5.63 (s, 1H), 4.44 (bd, J = 5.1 Hz, 1H), 4.39 (d, J = 11.4 Hz, 1H), 4.24 (d, J = 11.4 Hz, 1H), 3.79 (s, 3H), 2.85-2.76 (m, 1H), 2.52-2.39 (m, 1H), 2.37-2.26 (m, 1H), 1.92-1.83 (m, 1H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 160.4 (C), 132.8 (CH), 130.1 (C), 127.7 (CH, 2C), 122.3 (CH), 113.9 (CH, 2C), 102.3 (CH), 77.6 ($CH_2$), 76.5 (CH), 61.3 (C), 55.5 ($CH_3$), 28.5 ($CH_2$), 24.6 ($CH_2$).
**IR** [$cm^{-1}$]: 1615, 1520, 1256, 1171, 1084, 1021, 1001..
**HRMS**(EI) calcd. for $C_{15}H_{18}O_3Br$: 324.0361, found: 324.0366.
**$[\alpha]_D^{20}$** = +124 (c = 1.00, DCM)

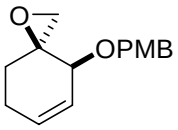
(1*R*, 2*S*)- [1-Bromo-2-(4'-methoxybenzyloxy)-cyclohex-3-en-1-yl]-methanol (**13**)




A solution of (4a*R*, 8a*S*)- 4a-Bromo-2-(4'-methoxyphenyl)-4a,5,6,8a-tetrahydro-4*H*-benzo[1,3]dioxine (1.09 g, 3.35 mmol) in DCM (42 mL) was cooled to -10 °C using a sodium chloride/ice cooling bath. DIBAL-H in toluene (1.19 M; 8.45 mL, 10.1 mmol) was added slowly and the resulting solution allowed to reach 0°C within 2.5 h. After stirring was continued for 1h at 0°C, the reaction was quenched by addition of saturated KNa-tartrate solution. Stirring was continued for 45 min. The organic phase was separated and the aqueous layer was extracted 3 times with $Et_2O$. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered and the solvent was removed under vacuum. Purification by column chromatography (90 g silica gel) using hexane:ethylacetate = 5:1 as an eluent yielded alcohol **13** (1.04 g, 94 %).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 6.91-6.86 (m, 2H), 5.98-5.91 (m, 1H), 5.81-5.75 (m, 1H), 4.66 (d, J = 11.1 Hz, 1H), 4.59 (d, J = 11.1 Hz, 1H), 4.23 (bd, J = 4.3 Hz, 1H), 4.01 (dd, J = 12.3, 8.2 Hz, 1H), 3.86 (dd, J = 12.1, 6.1 Hz, 1H), 3.81 (s, 3H), 2.51 (dd, J = 8.2, 5.9 Hz, 1H), 2.37-2.13 (m, 3H), 2.01-1.93 (m, 1H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 159.6 (C), 130.9 (CH), 130.2 (C), 129.8 (CH, 2C), 123.9 (CH), 114.1 (CH, 2C), 77.2 (CH), 73.9 (C), 71.9 ($CH_2$), 69.3 ($CH_2$), 55.4 ($CH_3$), 29.2 ($CH_2$), 24.2 ($CH_2$).
**IR** [$cm^{-1}$]: 2924, 2867, 1612, 1513, 1465, 1453, 1437, 1424, 1388, 1302, 1249, 1207, 1174, 1110, 1035. .
**HRMS**(EI) calcd. for $C_{15}H_{19}O_3Br$: 326.0518, found: 326.0512.
**$[\alpha]_D^{20}$** = +145 (c = 1.07, DCM)

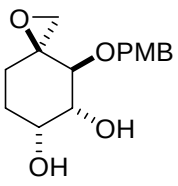
(3*S*, 4*S*)- 4-(4'-Methoxybenzyloxy)-1-oxaspiro[2.5]oct-5-ene




To a suspension of sodium hydride (washed with hexane, dried; 63mg, 2.63 mmol) in THF (25mL) was added alcohol **13** (660 mg, 2.02 mmol) in THF (9 mL) at 0°C. After addition of methanol (0.7 mL) the suspension was stirred for 10 min. at 0°C and 30 min. at room temperature. The reaction was quenched by addition of saturated $NH_4Cl$ solution (10 mL) and water (100mL). and extracted 4 times with $Et_2O$. The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed under vacuum yielding title compound as a slightly yellow oil (484 mg, 98%), which was employed without further purification for the next step.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 2H), 6.88-6.84 (m, 2H), 5.96-5.90 (m, 1H), 5.83-5.77 (m, 1H), 4.76 (d, J = 11.6 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 3.79 (s, 3H), 3.50 (bd, J = 4.3 Hz, 1H), 2.66 (dd, J = 4.9, 1.1 Hz, 1H), 2.62 (d, J = 4.9 Hz, 1H), 2.42-2.31 (m, 2H), 2.29-2.16 (m, 1H), 1.36-1.30 (m, 1H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 159.3 (C), 132.0 (CH), 131.1 (C), 129.6 (CH, 2C), 126.6 (CH), 113.9 (CH, 2C), 74.3 (CH), 71.7 ($CH_2$), 60.2 (C), 55.4 ($CH_3$), 50.5 ($CH_2$), 26.0 ($CH_2$), 25.8 ($CH_2$).
**IR** [$cm^{-1}$]: 2930, 2836, 1612, 1513, 1465, 1453, 1302, 1248, 1173, 1062, 1052, 1035.
**HRMS**(EI) calcd. for $C_{15}H_{18}O_3$: 246.1256, found: 246.1250.
**$[\alpha]_D^{20}$** = +162 (c = 1.00, DCM)

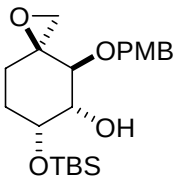
(3*S*, 4*S*, 5*R*, 6*R*)- 4-(4'-Methoxybenzyloxy)-1-oxaspiro[2.5]octane-5,6-diol (**14**)




To a solution of (3*S*, 4*S*)- 4-(4'-Methoxybenzyloxy)-1-oxaspiro[2.5]oct-5-ene (505 mg, 2.05 mmol) in acetone/water (9:1, 12mL) was added 4-methylmorpholine-4-oxide monohydrate (346 mg, 2.56 mmol) and osmium tetraoxide (2.5 % (w/w) solution in *t*-butanol; 260 µL, 0.02 mmol). After stirring for 20 h at room temperature 7.5 mL toluene were added and the solvent was removed under vacuum. The residue was dissolved in DCM, silica gel (5 g) was added and the solvent was carefully removed under reduced pressure. Purification of the adsorbed material by column chromatography (45 g silica gel) using hexane:ethylacetate = 1:3 to 0:1 as an eluent yielded diol **14** (527 mg, 92 %) as a white solid.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2H), 6.91-6.86 (m, 2H), 4.69 (d, J = 11.6 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 4.17-4.12 (m, 1H), 3.86-3.78 (m, 1H), 3.80 (s, 3H), 3.67 (d, J = 7.6 Hz, 1H), 2.89 (d, J = 4.8 Hz, 1H), 2.65 (d, J = 4.8 Hz, 1H), 2.37 (bs, 1H), 2.30 (bs, 1H), 1.95-1.75 (m, 3H), 1.60-1.52 (m, 1H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 159.6 (C), 130.2 (C), 129.7 (CH, 2C), 114.2 (CH, 2C), 77.9 (CH), 73.8 ($CH_2$), 73.7 (CH), 69.0 (CH), 59.0 (C), 55.4 ($CH_3$), 50.5 ($CH_2$), 27.0 ($CH_2$), 26.6 ($CH_2$).
**IR** [$cm^{-1}$]:3441, 2935, 1612, 1515, 1456, 1302, 1249, 1176, 1077, 1033, 1006.
**HRMS**(EI) calcd. for $C_{15}H_{20}O_5$: 280.1311, found: 280.1308.
**$[\alpha]_D^{20}$** = -57.3 (c = 0.78, DCM)

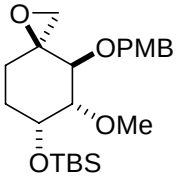
(3*S*, 4*S*, 5*S*, 6*R*)-6-(*tert*-Butyldimethylsilyloxy)-4-(4'-methoxybenzyloxy)-1-oxaspiro[2.5]octan-5-ol




To a solution of diol **14** (520 mg, 1.86 mmol) in DCM (34 mL) was added imidazol (379 mg, 5.57 mmol) and *t*-butyl dimethylsilylchloride (559 mg, 3.71 mmol) at room temperature. After stirring for 20 h the reaction mixture was washed with saturated $NH_4Cl$ solution and brine. The organic phase was dried over magnesium sulfate, filtered, silica gel (4 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (35 g silica gel) using hexane:ethylacetate = 5:1 as an eluent yielded title compound (651 mg, 89 %).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.20-7.14 (m, 2H), 6.80-6.75 (m, 2H), 4.62 (d, J = 11.6 Hz, 1H), 4.42 (d, J = 11.6 Hz, 1H), 4.05-3.99 (m, 1H), 3.74-3.68 (m, 1H), 3.70 (s, 3H), 3.35 (d, J = 5.6 Hz, 1H), 2.71 (dd, J = 4.8, 0.8 Hz, 1H), 2.52 (d, J = 4.8 Hz, 1H), 2.16 (d, J = 2.8 Hz, 1H), 1.88-1.77 (m, 1H), 1.76-1.59 (m, 2H), 1.41-1.31 (m, 1H), 0.79 (s, 9H), -0.02 (s, 6H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 159.4 (C), 130.7 (C), 129.6 (CH, 2C), 114.0 (CH, 2C), 79.0 (CH), 74.0 ($CH_3$), 72.7 ($CH_2$), 69.9 (CH), 58.8 (C), 55.4 (CH), 51.0 ($CH_2$), 28.3 ($CH_2$), 26.4 ($CH_2$), 25.9 ($CH_3$, 3C), 18.2 (C), -4.5 ($CH_3$), -4.7 ($CH_3$).
**IR** [$cm^{-1}$]: 2952, 2930, 1514, 1250, 1084, 1037, 1005.
**HRMS**(EI) calcd. for $C_{17}H_{25}O_5Si$ (M-$C_4H_9$): 337.1471, found: 337.1476.
**$[\alpha]_D^{20}$** = -25.5 (c = 0.95, DCM)

(3*S*, 4*S*, 5*S*, 6*R*)-*tert*-Butyl-[5-methoxy-4-(4'-methoxybenzyloxy)-1-oxaspiro[2.5]oct-6-yloxy]-dimethylsilane

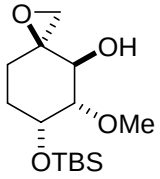



To a solution of (3*S*, 4*S*, 5*S*, 6*R*)-6-(*tert*-Butyldimethylsilyloxy)-4-(4'-methoxybenzyloxy)-1-oxaspiro[2.5]octan-5-ol (560 mg, 1.42 mmol) in THF (15 mL) was added sodium hydride (washed with hexane, dried; 102mg, 4.26 mmol) at 0 °C. After stirring for 20 min at 0°C methyl iodide (1.01g, 7.10 mmol) was added and the cooling bath removed. The reaction was quenched by the addition of saturated $NH_4Cl$ solution (15 mL) after 16 h. The organic layer was separated

and the aqueous phase extracted 3 times with $Et_2O$. The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed under vacuum yielding title compound as a slightly yellow oil (580 mg, 100%), which was employed without further purification for the next step.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 6.89-6.84 (m, 2H), 4.62 (bs, 2H), 4.24-4.19 (m, 1H), 3.80 (s, 3H), 3.63-3.55 (m, 1H), 3.44 (s, 3H), 3.38-3.32 (m, 1H), 2.81 (d, J=4.8 Hz, 1H), 2.54 (d, J = 4.8 Hz, 1H), 1.87-1.55 (m, 4H), 0.91 (s, 9H), 0.11 (s, 3H), 0.07 (s, 3H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 159.3 (C), 130.9 (C), 129.6 (CH, 2C), 113.8 (CH, 2C), 84.5 (CH), 76.9 (CH), 73.1 ($CH_2$), 69.2 (CH), 59.4 (C), 59.1 ($CH_3$), 55.4 ($CH_3$), 50.8 ($CH_2$), 28.7 ($CH_2$), 26.9 ($CH_2$), 26.0 ($CH_3$, 3C), 18.3 (C), -4.5 ($CH_3$), -4.7 ($CH_3$).
**IR** [$cm^{-1}$]: 2930, 2856, 1514, 1464, 1250, 1114, 1034.
**HRMS**(EI) calcd. for $C_{18}H_{27}O_5Si$ (M-$C_4H_9$): 351.1628 ,found: 351.1634.
**$[\alpha]_D^{20}$** = -13.5 (c = 1.09, DCM)

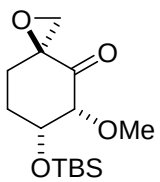
(3*S*, 4*S*, 5*S*, 6*R*)-6-(*tert*-Butyldimethylsilyloxy)-5-methoxy-1-oxaspiro[2.5]octan-4-ol (**15**)




DDQ (351 mg, 1.55 mmol) was added to a solution of (3*S*, 4*S*, 5*S*, 6*R*)-*tert*-Butyl-[5-methoxy-4-(4'-methoxybenzyloxy)-1-oxaspiro[2.5]oct-6-yloxy]-dimethylsilane (574 mg, 1.41 mmol) in DCM (21 mL) and water (1 mL). After stirring for 2 h saturated $NaHCO_3$ solution (17 mL) and $Et_2O$ (50 ml) were added and the layers separated. The aqueous phase was extracted 3 times with $Et_2O$. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered, silica gel (4 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material by column chromatography (40 g silica gel) using hexane:ethylacetate = 3:1 as an eluent yielded alcohol **15** (360 mg, 89 %) as a white solid.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.34-4.30 (m, 1H), 4.09 (dd, J = 9.5, 6.1 Hz, 1H), 3.43 (s, 3H), 3.12 (d, J = 5.1 Hz, 1H), 3.08 (dd, J = 9.5, 2.4 Hz, 1H), 2.61 (d, J = 5.1 Hz, 1H), 2.36-2.25 (m, 1H), 1.98 (d, J = 6.1 Hz, 1H), 1.81-1.66 (m, 2H), 1.26-1.18 (m, 1H), 0.90 (s, 9H), 0.25 (s, 3H), 0.21 (s, 3H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 85.5 (CH), 67.5 (CH), 66.9 (CH), 60.1 (C), 57.7 ($CH_3$), 50.1 ($CH_2$), 29.0 ($CH_2$), 26.4 ($CH_2$), 25.9 ($CH_3$, 3C), 18.3 (C), -4.5 ($CH_3$), -4.9 ($CH_3$).
**IR** [$cm^{-1}$]: 3677, 2952, 2929, 1120, 1094, 1025, 986.
**HRMS**(EI) calcd. for $C_{10}H_{19}O_4Si$ (M-$C_4H_9$): 231.1053, found: 231.1057.
**$[\alpha]_D^{20}$** = -65.0 (c = 1.03, DCM)

(3*S*, 5*R*, 6*R*)-6-(*tert*-Butyldimethylsilyloxy)-5-methoxy-1-oxaspiro[2.5]octan-4-one (**16**)

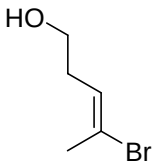



Compound **15** (182 mg, 631 µmol) was dissolved in regular DCM (8.0 mL) and cooled to 0 °C. After the addition of $NaHCO_3$ (530 mg, 6.31 mmol) and Dess-Martin periodinane (348 mg, 820 µmol) the cooling bath was removed and stirred for 2 h. Saturated $NaHCO_3$ solution (5 mL) and water (5 mL) were added, the layers separated and the aqueous phase extracted 3 times with $Et_2O$. The combined organic phases were dried over magnesium sulfate, filtered, silica gel (1 g) was added and the solvent was carefully removed under vacuum. Purification of the adsorbed material

by column chromatography (15 g silica gel) using hexane:ethylacetate = 10:1 as an eluent yielded ketone **16** (166 mg, 92 %).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 4.45-4.41 (m, 1H), 3.97 (d, J = 2.5 Hz, 1H), 3.43 (s, 3H), 3.28 (d, J = 4.8 Hz, 1H), 2.75 (d, J = 4.8 Hz, 1H), 2.54-2.45 (m, 1H), 2.13-1.95 (m, 2H), 1.55 (dt, J = 14.5, 4.4 Hz, 1H), 0.85 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 202.4 (C), 87.4 (CH), 72.3 (CH), 60.6 (C), 58.4 ($CH_3$), 51.3 ($CH_2$), 28.9 ($CH_2$), 27.0 ($CH_2$), 25.8 ($CH_3$, 3C), 18.3 (C), -4.5 ($CH_3$), -5.1 ($CH_3$).
**IR** [$cm^{-1}$]: 2953, 2929, 2856, 1745, 1253, 1097, 1066, 1021.
**HRMS**(EI) calcd. for $C_{10}H_{17}O_4Si$ (M-$C_4H_9$): 229.0896, found: 229.0902.
**$[\alpha]_D^{20}$** = -1.20 (c = 1.00, DCM)

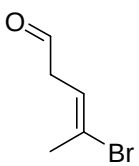
(E)-4-Bromopent-3-en-1-ol




To a stirred solution of (*E*)-4-(tri-n-butylstannyl)pent-3-en-1-ol (**19**) (1.00g, 2.66 mmol) in DCM (30 mL) was added N-bromosuccinimide (474 mg, 2.66 mmol) at 0 °C. After stirring the solution for 1 h at this temperature saturated $Na_2SO_3$ solution (20 mL) was added. The organic layer was separated and the aqueous phase extracted 2 times with DCM. The combined organic phases were dried over magnesium sulphate, filtered and the solvent was removed under vacuum (300 mbar, 45 °C) Purification by column chromatography (12 g silica gel) using pentane:$Et_2O$ = 1:1 as an eluent yielded, after removing solvent under vacuum (300 mbar, 45 °C) 578 mg of a clear liquid consisting of (*E*)-4-bromopent-3-en-1-ol (434 mg, 99 %) and $Et_2O$.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.91-5.85 (m, 1H), 3.67 (q, J = 6.1 Hz, 2H), 2.33-2.27 (m, 2H), 2.27-2.24 (m, 3H), 1.43 (t, J = 5.7 Hz, 1H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 128.3 (CH), 122.0 (C), 61.7 ($CH_2$), 33.2 ($CH_2$), 23.5 ($CH_3$).
**IR** [$cm^{-1}$]: 3351 (bs), 2953, 2923, 1429, 1380, 1051, 1012.
**HRMS**(EI) calcd. for $C_5H_9OBr$: 163.9837, found: 163.9839.

(E)-4-Bromopent-3-enal (**20**)

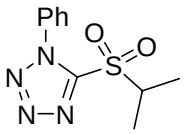



To a stirred solution of (*E*)-4-bromopent-3-en-1-ol (430 mg, 2.61 mmol) in regular DCM (24 mL) was added $NaHCO_3$ (2.19 g, 26.1 mmol) and Dess-Martin periodinane (1.33 mg, 3.13 mmol) at 0 °C. The cooling bath was removed and after stirring for 2.5 h additional Dess-Martin periodinane (330 mg, 0.78 mmol) was added. The stirring was continued until TLC showed complete consumption of the starting material (ca. 1 h) when saturated solution of $NaHCO_3$ (10 mL), saturated solution of $Na_2S_2O_3$ (10 mL) and water (20 mL) were added. After stirring for 15 min the layers were separated and the aqueous phase extracted 2 times with DCM. The combined organic phases were dried over magnesium sulphate, filtered and the solvent was removed under vacuum (300 mbar, 45 °C) yielding 680 mg of a yellow liquid consisting of aldehyde **20** (400 mg, 94 %) and DCM. It was used without further purification.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.65 (t, J = 1.6 Hz, 1H), 6.06 (qt, J = 7.4, 1.3 Hz, 1H), 3.17 (bd, J = 7.4 Hz, 2H), 2.24 (d, J = 1.1 Hz, 3H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 197.4 (CH), 124.0 (C), 121.3 (CH), 44.2 ($CH_2$), 23.8 ($CH_3$).
**IR** [$cm^{-1}$]: 2922, 2854, 1725, 1380, 1108, 1065.

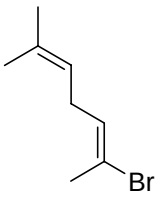
1-Phenyl-5-(propane-2-sulfonyl)-1*H*-tetrazole (**21**)



To a stirred solution of 2-propanol (5.00 g, 83.2 mmol), triphenyl phosphine (21.8 g, 83.2 mmol) and 1-phenyl-1H-tetrazole-5-thiol (14.8 g, 83.2 mmol) in anhydrous THF (300 mL) at 0°C was added DIAD (19.3 mL, 99.8 mmol) dropwise and stirred for 2 h. at 0°C. The mixture was diluted with Et2O (200 mL) and saturated aq. NaHCO3 solution (100 mL) and extracted with Et2O (3 x 100 mL), washed with brine (1 x 100 mL), dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was then treated with 1:1 hexanes:Et2O (500 mL) and stored at -20°C for a 2 h. period. The precipitate was filtered of, washed with 1:1 hexanes:$Et_2O$ (2 x 50 mL), silica gel (30 g) was added and the solvent carefully removed under vacuum. Purification of the adsorbed material by column chromatography (350 g silica gel) using hexanes:ethylacetate (10:1 to 3:1) as the mobile phase afforded 5-Isopropylsulfanyl-1-phenyl-1*H*-tetrazole as white solid (7.5 g g, 41%).
To a suspension of 5-Isopropylsulfanyl-1-phenyl-1*H*-tetrazole (6.75 g, 30.6 mmol) and sodium hydrogen carbonate (25.7g, 306 mmol) in DCM (550 mL), 77% mCPBA (34.3 g, 153 mmol) was added in portions and stirred for 16 h. Saturated aq. $NaHCO_3$ solution (200 mL) and saturated aq. $Na_2S_2O_3$ solution (200 mL) was added and stirred for 10 min. After extraction with DCM (4 x 150 mL), the combined organic layers were washed with brine (50 mL), dried over MgSO4, filtered, silica gel (20 g) was added and the solvent carefully removed under vacuum. Purification of the adsorbed material by column chromatography (200 g silica gel) using hexanes:ethyl acetate (3:1) as the mobile phase afforded 1-Phenyl-5-(propane-2-sulfonyl)-1*H*-tetrazole (**21**) as a pale yellow solid (6.59 g, 85%).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.56 (m, 5H), 4.02 (hept., J =6.9 Hz, 1H), 1.52 (d, J = 6.9 Hz, 6H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 152.8 (C), 133.3 (C), 131.6 (CH), 129.7 (CH, 2C), 125.5 (CH, 2C), 57.0 (CH), 15.2 ($CH_3$, 2C).
**IR** [$cm^{-1}$]: 2985, 2943, 1497, 1333, 1169, 1147, 1056.
**HRMS**(EI) calcd. for $C_{10}H_{12}O_2N_4S$: 252.0681, found: 252.0676.

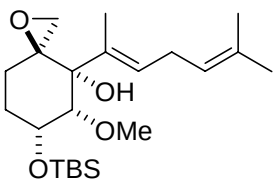
(E)-2-Bromo-6-methylhepta-2,5-diene (**17**)



To a solution of **21** in THF (19 mL) was added a 1.0M solution of LHMDS in hexane (2.70 mL, 2.70 mmol) slowly at -78 °C and stirred for 35 min. at this temperature. In a separate flask aldehyde **20** (400 mg, 2.45 mmol) in THF (9 mL) was cooled to -78 °C and dropwise added via double-ended needle. The reaction was allowed to warm to room temperature over night (16 h). After addition of $Et_2O$ (100 mL) and extraction with saturated aq. $NH_4Cl$ solution (20 mL), the organic phase was dried over MgSO4, filtered, silica gel (3 g) was added and the solvent carefully removed under vacuum. Purification of the adsorbed material by column chromatography (30 g silica gel) using pentane as the mobile phase and concentration under vaccum (300 mbar, 45 °C) yielded 430 mg of a colourless liquid consisting of **17** (325 mg, 70 %) and pentane.

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.83-5.77 (m, 1H), 5.11-5.04 (m, 1H), 2.73-2.66 (m, 2H), 2.24-2.23 (m, 3H), 1.71-1.68 (m, 3H), 1.62 (bs, 3H).
**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 133.2 (C), 131.0 (CH), 121.0 (CH), 119.3 (C), 28.8 ($CH_2$), 25.8 ($CH_3$), 23.3 ($CH_3$), 17.9 ($CH_3$).
**IR** [$cm^{-1}$]: 2970, 2924, 2854, 1448, 1430, 1378, 1106, 1083.
**HRMS**(EI) calcd. for $C_8H_{13}Br$: 188.0201, found: 188.0194.

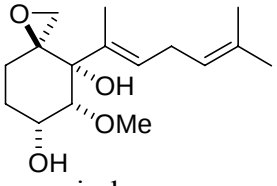
(3*S*, 4*R*, 5*R*, 6*R*)-6-(*tert*-Butyldimethylsilyloxy)-4-((E)-1',5'-dimethylhexa-1',4'-dienyl)-5-methoxy-1-oxaspiro[2.5]octan-4-ol (**22**)




To a solution of **17** (110 mg, 582 µmol) in $Et_2O$ (2.4 mL) was added dropwise a 1.5M solution of *t*-Butyllithium in pentane (0.77 mL, 1.16 mmol) at -78 °C. After stirring for 40 min. at this temperature, the cooling bath was removed for 1 min. A solution of **16** (128 mg, 447 µmol) in toluene (total 2 mL) was added slowly to the slightly yellow solution at -78 °C. After stirring at this temperature for 1 h the reaction was quenched by the addition of saturated $NH_4Cl$ solution (5 mL) and water (5 mL). The organic layer was separated and the aqueous phase extracted 3 times with $Et_2O$. The combined organic phases were washed with brine, dried over magnesium sulfate, filtered and the solvent was removed under vacuum Purification by column chromatography (18 g silica gel) using hexane:ethylacetate = 10:1 as an eluent yielded alcohol **22** (135 mg, 76 %).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.70 (bt, J = 7.1 Hz, 1H), 5.15-5.08 (m, 1H), 4.81 (bs, 1H), 4.47-4.41 (m, 1H), 3.50 (d, J = 2.5 Hz, 1H), 3.44 (s, 3H), 2.84-2.66 (m, 2H), 2.80 (d, J = 5.1 Hz, 1H), 2.57-2.44 (m, 1H), 2.42 (d, J = 5.1 Hz, 1H), 1.95-1.87 (m, 1H), 1.86-1.75 (m, 1H), 1.66 (s, 6H), 1.61 (s, 3H), 1.22-1.11 (m, 1H), 0.92 (s, 9H), 0.14 (s, 3H), 0.13 (s, 3H).
**$^{13}$C NMR** (100 MHz, CDCl3) δ 132.7 (C), 131.6 (C), 127.7 (CH), 123.0 (CH), 80.6 (CH), 79.2 (C), 68.6 (CH), 62.1 (C), 57.8 ($CH_3$), 50.6 ($CH_2$), 28.6 ($CH_2$), 27.3 ($CH_2$), 25.9 ($CH_3$, 3C), 25.8 ($CH_3$), 25.5 ($CH_2$), 18.0 (C), 17.9 ($CH_3$), 14.1 ($CH_3$), -4.7 ($CH_3$), -4.9 ($CH_3$).
**IR** [$cm^{-1}$]: 3467,2955, 2929, 2857, 1472, 1464, 1444, 1376, 1254, 1132, 1102, 1068.
**HRMS**(EI) calcd. for $C_{22}H_{40}O_4Si$: 396.2696, found: 396.2704.
**$[\alpha]_D^{20}$** = -74.0 (c = 1.04, DCM)

(3*S*, 4*R*, 5*R*, 6*R*)- 4-((E)-1', 5'-Dimethylhexa-1',4'-dienyl)-5-methoxy-1-oxaspiro[2.5]octane-4,6-diol (**23**)

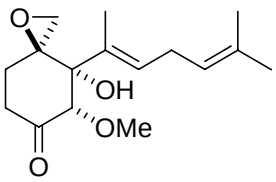



To a stirred solution of **22** (96 mg, 242 µmol) in THF (5.5 mL) was added a 1.0M solution of *n*-tetraburtyammonium fluoride ( 310 µL, 310 µmol) at 0 °C. After stirring for 25 min.at this temperature additional 1.0M solution of *n*-tetraburtyammonium fluoride ( 50 µL, 50 µmol) was added. After 5 min. the reaction was quenched by the addition of brine (18 mL). The organic layer was separated and the aqueous phase extracted 3 times with $Et_2O$. The combined organic phases were dried over magnesium sulfate, filtered and the solvent was removed under

vacuum Purification by column chromatography (6 g silica gel) using hexane:ethylacetate = 1:1 as an eluent yielded alcohol **23** (65 mg, 94 %).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.65 (bt, J = 7.1 Hz, 1H), 5.10 (tt, J = 7.0, 1.3 Hz, 1H), 4.37-4.32 (m, 1H), 3.61 (d, J = 3.3 Hz, 1H), 3.49 (s, 3H), 3.17 (bs, 1H), 3.07 (bs, 1H), 2.79 (d, J = 5.1 Hz, 1H), 2.79-2.69 (m, 2H), 2.45 (d, J = 5.1 Hz, 1H), 2.45-2.37 (m, 1H), 2.04-2.00 (m, 1H), 1.89-1.81 (m, 1H), 1.68 (s, 3H), 1.67 (s, 3H), 1.62 (s, 3H), 1.24-1.18 (m, 1H).
**$^{13}$C NMR** (150 MHz, CDCl3) δ 133.9 (C), 132.2 (C), 127.5 (CH), 122.5 (CH), 80.0 (CH), 79.8 (C), 67.0 (CH), 61.4 (C), 57.7 ($CH_3$), 50.3 ($CH_2$), 27.7 ($CH_2$), 27.2 ($CH_2$), 25.8 ($CH_3$), 25.1 ($CH_2$), 17.9 ($CH_3$), 14.3 ($CH_3$).
**IR** [$cm^{-1}$]: 3400 (bs), 2929, 1443, 1376, 1199, 1100, 1074, 1018..
**HRMS**(EI) calcd. for $C_{16}H_{26}O_4$: 282.1831, found: 282.1821.
**$[\alpha]_D^{20}$** = -53.2 (c = 0.70, DCM)

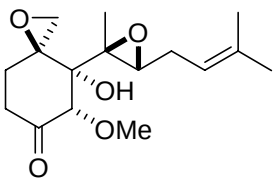
(3*S*, 4*R*, 5*S*)- 4-((E)-1',5'-Dimethylhexa-1',4'-dienyl)-4-hydroxy-5-methoxy-1-oxaspiro[2.5]octan-6-one (**24**)




Compound **23** (40 mg, 142 µmol) was dissolved in regular DCM (1.8 mL) and cooled to 0 °C. After the addition of $NaHCO_3$ (119 mg, 1.42 mmol) and Dess-Martin periodinane (78 mg, 184 µmol) the cooling bath was removed. After stirring for 1.5 h. additional Dess-Martin periodinane (24 mg, 57 µmol) was added. The stirring was continued until TLC showed complete consumption of the starting material (ca. 30 min). The reaction mixture was directly loaded onto a column and purified by column chromatography (6 g silica gel) using hexane:ethylacetate = 5:1 as an eluent yielded ketone **24** (36 mg, 90 %).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.66-5.62 (m, 1H), 5.10-5.06 (m, 1H), 4.26 (d, J = 1.1 Hz, 1H), 3.50 (s, 3H), 2.85 (d, J = 4.9 Hz, 1H), 2.80-2.62 (m, 4H), 2.61 (d, J = 4.9 Hz, 1H), 2.51-2.47 (m, 2H), 1.70-1.68 (m, 6H), 1.62 (s, 3H), 1.52-1.48 (m, 1H).
**$^{13}$C NMR** (150 MHz, CDCl3) δ 207.6 (C), 133.8 (C), 132.5 (C), 127.8 (CH), 122.3 (CH), 85.8 (CH), 83.0 (C), 61.0 (C), 59.6 ($CH_3$), 51.1 ($CH_2$), 37.0 ($CH_2$), 30.4 ($CH_2$), 27.1 ($CH_2$), 25.8 ($CH_3$), 17.9 ($CH_3$), 14.5 ($CH_3$).
**IR** [$cm^{-1}$]: 3418, 2964, 2924, 1732, 1439, 1379, 1259, 1112.
**HRMS**(EI) calcd. for $C_{16}H_{24}O_4$: 280.1675, found: 280.1669.
**$[\alpha]_D^{20}$** = -106 (c = 0.55, DCM)

(-)-Ovalicin (**1**)




Ketone **24** (33 mg, 118 µmol) was dissolved in benzene (0.5 mL) and the solvent removed under vacuum. After repeating this process once, the residue was dissolved in benzene (0.9 mL) and cooled in a water bath (5 °C). After the addition of vanadyl acetylacetonate ( 5.3 mg, 20 µmol) and a 5.5M solution of *t*-butyl hydroperoxide (36 mg, 236 µmol) the cooling bath was removed and the mixture stirred for 1.5 h. The reaction mixture was directly loaded

onto a column and purified by column chromatography (6 g silica gel) using hexane:ethylacetate = 6:1 as an eluent yielded (-)-ovalicin (**1**) (25 mg, 71 %).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.21-5.16 (m, 1H), 4.23 (s, 1H), 3.57 (s, 3H), 3.14 (s, 1H), 3.10 (d, J = 4.2 Hz, 1H), 2.90 (dd, J = 7.0 Hz, 6.2 Hz, 1H), 2.73 (d, J = 4.2 Hz, 1H), 2.71-2.61 (m, 2H), 2.51-2.47 (m, 1H), 2.45-2.39 (m, 1H), 2.18-2.12 (m, 1H), 1.75 (d, J = 1.1 Hz, 3 H), 1.66 (s, 3H), 1.45-1.41 (m, 1H), 1.37 (s, 3H).
**$^{13}$C NMR** (150 MHz, CDCl3) δ 206.8 (C), 135.6 (C), 118.1 (CH), 86.3 (CH), 78.7 (C), 60.7 (C), 60.5 (C), 59.4 ($CH_3$), 56.9 (CH), 51.4 ($CH_2$), 36.8 ($CH_2$), 30.5 ($CH_2$), 27.2 ($CH_2$), 25.9 ($CH_3$), 18.2 ($CH_3$), 14.5 ($CH_3$).
**IR** [$cm^{-1}$]: 3501, 2926, 1733, 1441, 1382, 1247, 1205, 1169, 1108, 1032.
**HRMS**(EI) calcd. for $C_{16}H_{24}O_5$: 296.1624, found: 296.1628.
**$\alpha_D^{20}$** = -115 (c = 0.10, $CHCl_3$) [Lit.[4]: $\alpha_D^{20}$ = -117 (c = 0.40, $CHCl_3$); Lit.[5]: $\alpha_D^{25}$ = -112.9 (c = 0.21, $CHCl_3$)]

[4] H. Sigg, H. Weber, *Helv. Chim. Acta* **1968**, *51*, 1395.
[5] S. Takahashi, N. Hishinuma, H. Koshino, T. Nakata, *J. Org. Chem.* **2005**, 70, 10162 (Supporting Information).

Crystal structure of (±)-15:

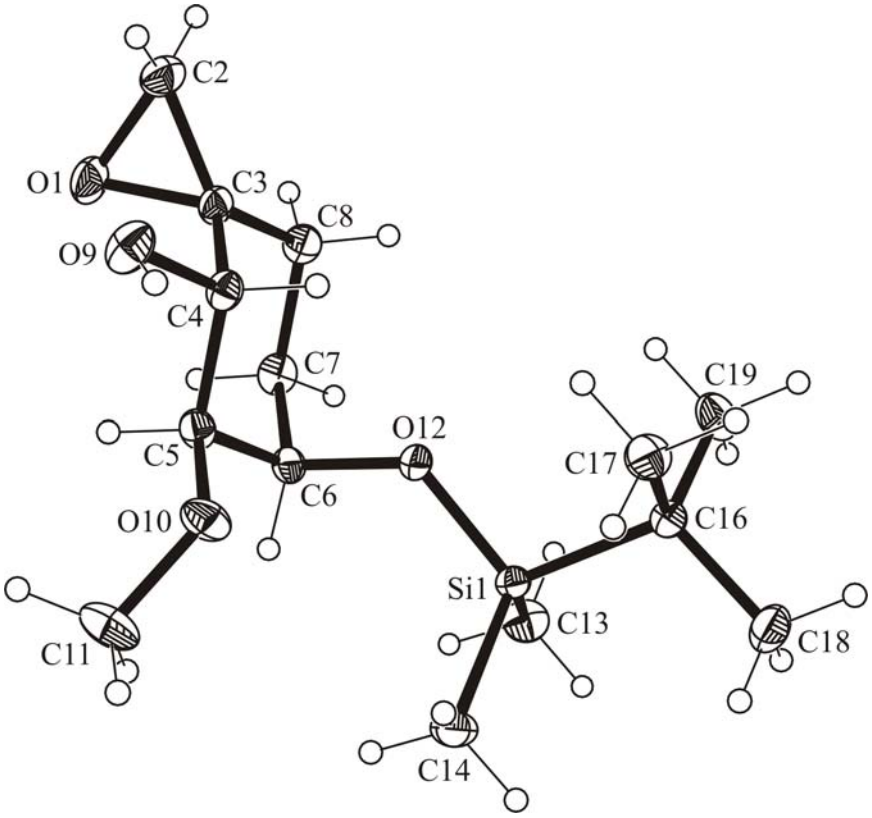
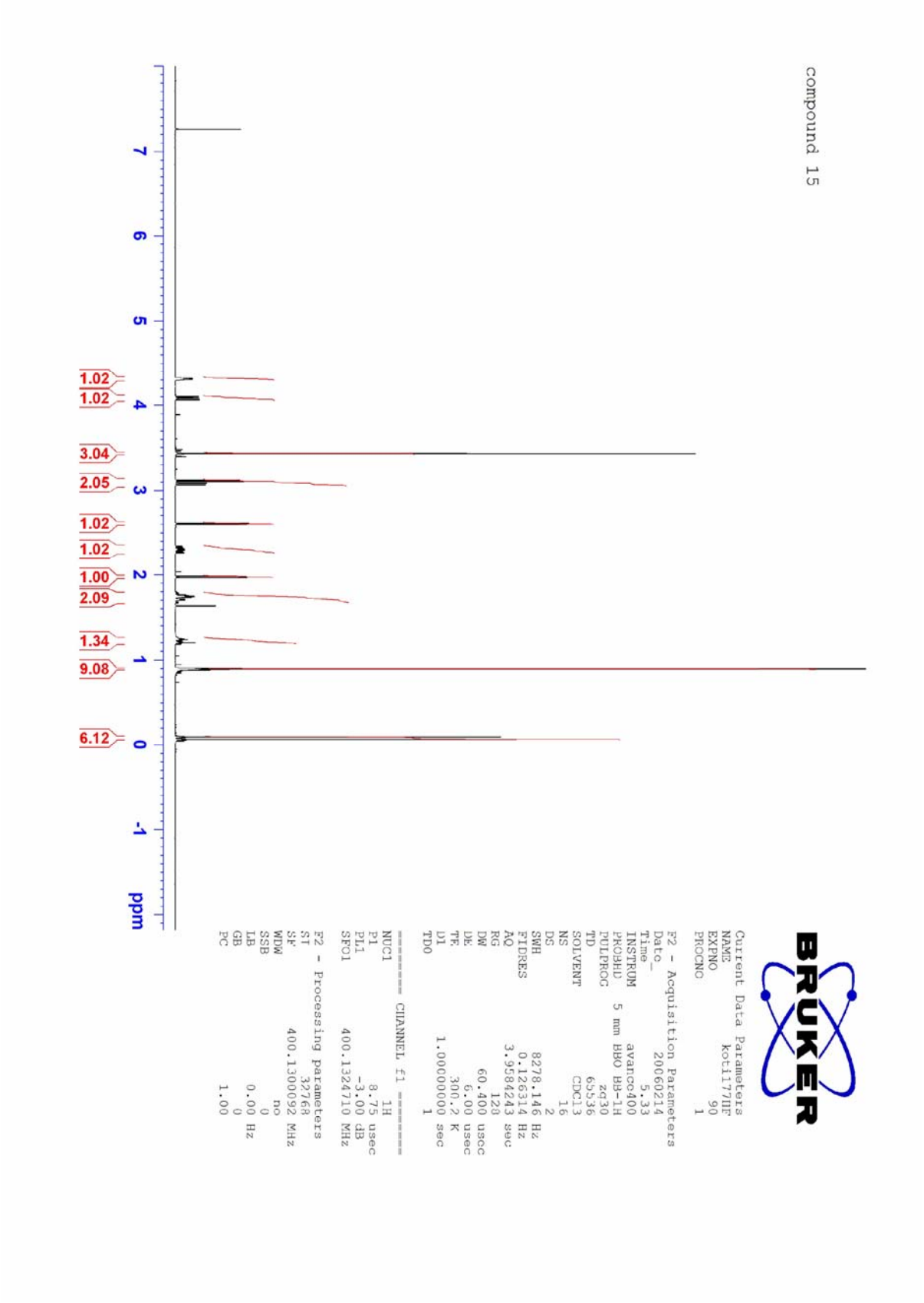
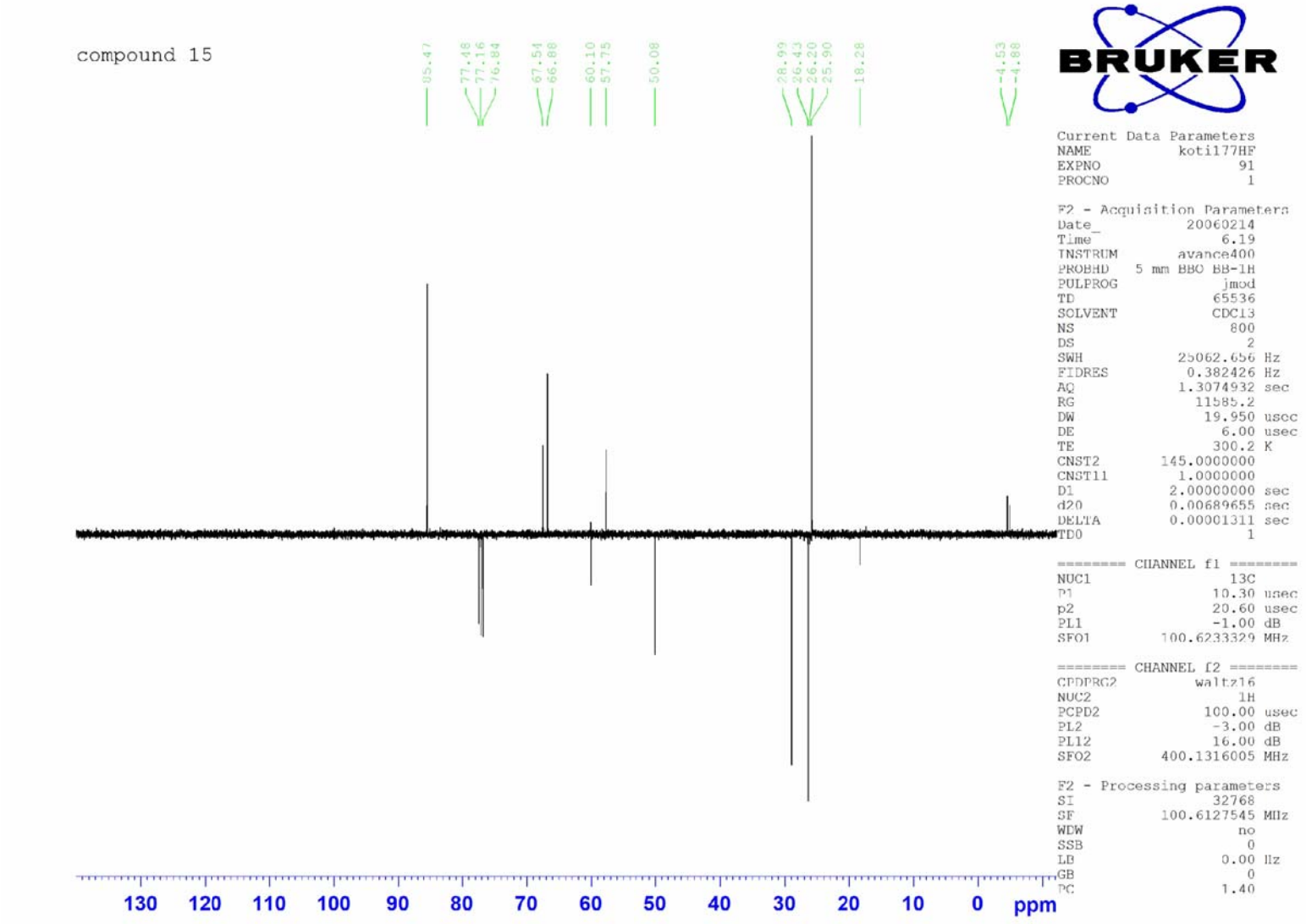



**Figure S1**. ORTEP view of one enantiomer in the crystal structure of (±)–**15** with labelling scheme. The thermal ellipsoids are drawn at 50% probability level.

NMR spectra of compounds 15, 16, 22, 23, 24, 1:






BRUKER

Current Data Parameters
NAME kotil77HF
EXPNO 91
PROCNO 1

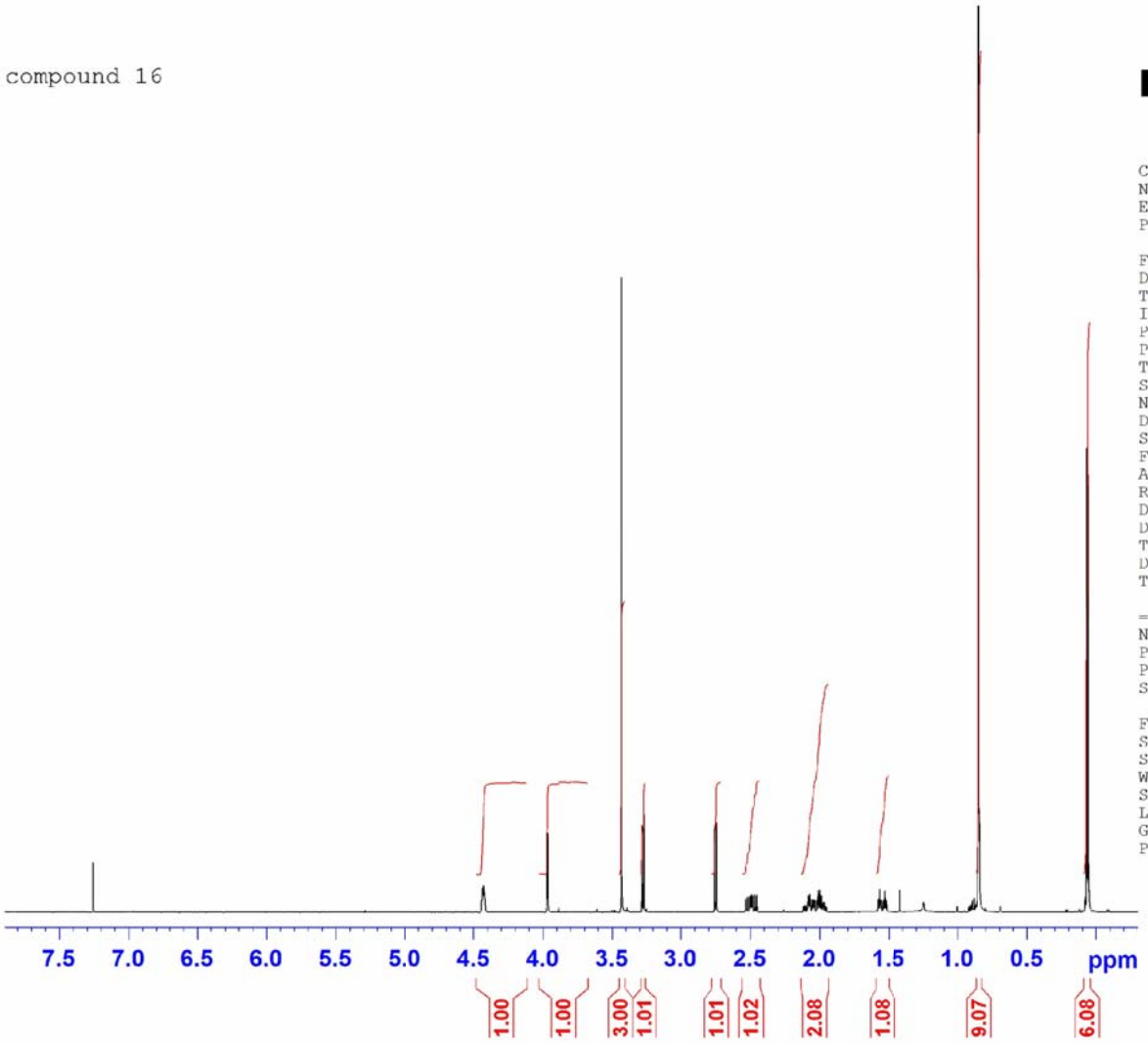
F2 - Acquisition Parameters
Date_ 20060214
Time 6.19
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 800
DS 2
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 11585.2
DW 19.950 usec
DE 6.00 usec
TE 300.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001311 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
p2 20.60 usec
PL1 -1.00 dB
SFO1 100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127545 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40

compound 16



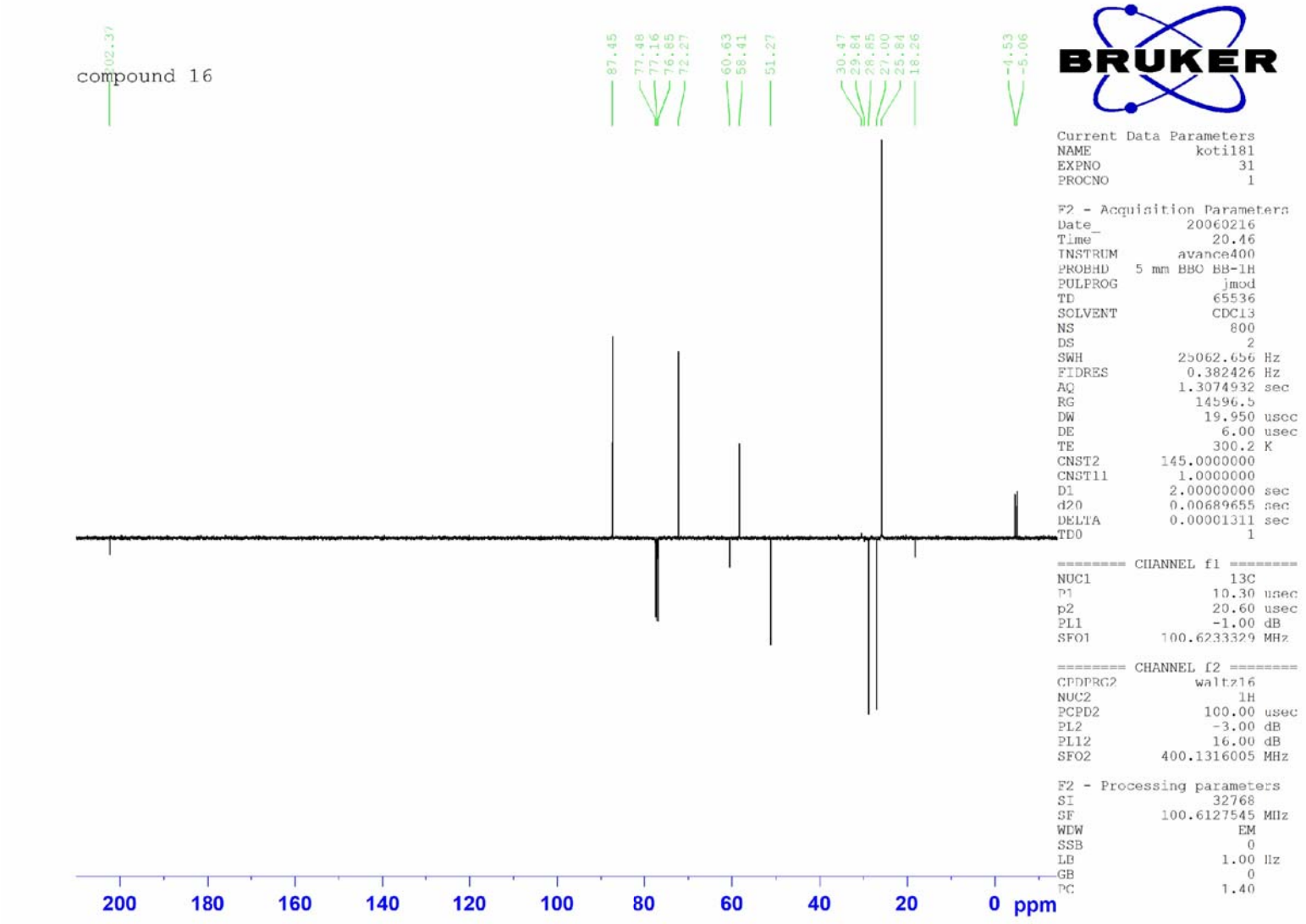

BRUKER

```
Current Data Parameters
NAME                 koti181
EXPNO                     30
PROCNO                     1

F2 - Acquisition Parameters
Date_              20060216
Time                  19.59
INSTRUM           avance400
PROBHD    5 mm BBO BB-1H
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8278.146 Hz
FIDRES            0.126314 Hz
AQ                3.9584243 sec
RG                      128
DW                   60.400 usec
DE                    6.00 usec
TE                   300.2 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     8.75 usec
PL1                   -3.00 dB
SFO1          400.1324710 MHz

F2 - Processing parameters
SI                     32768
SF            400.1300095 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.00
```




BRUKER

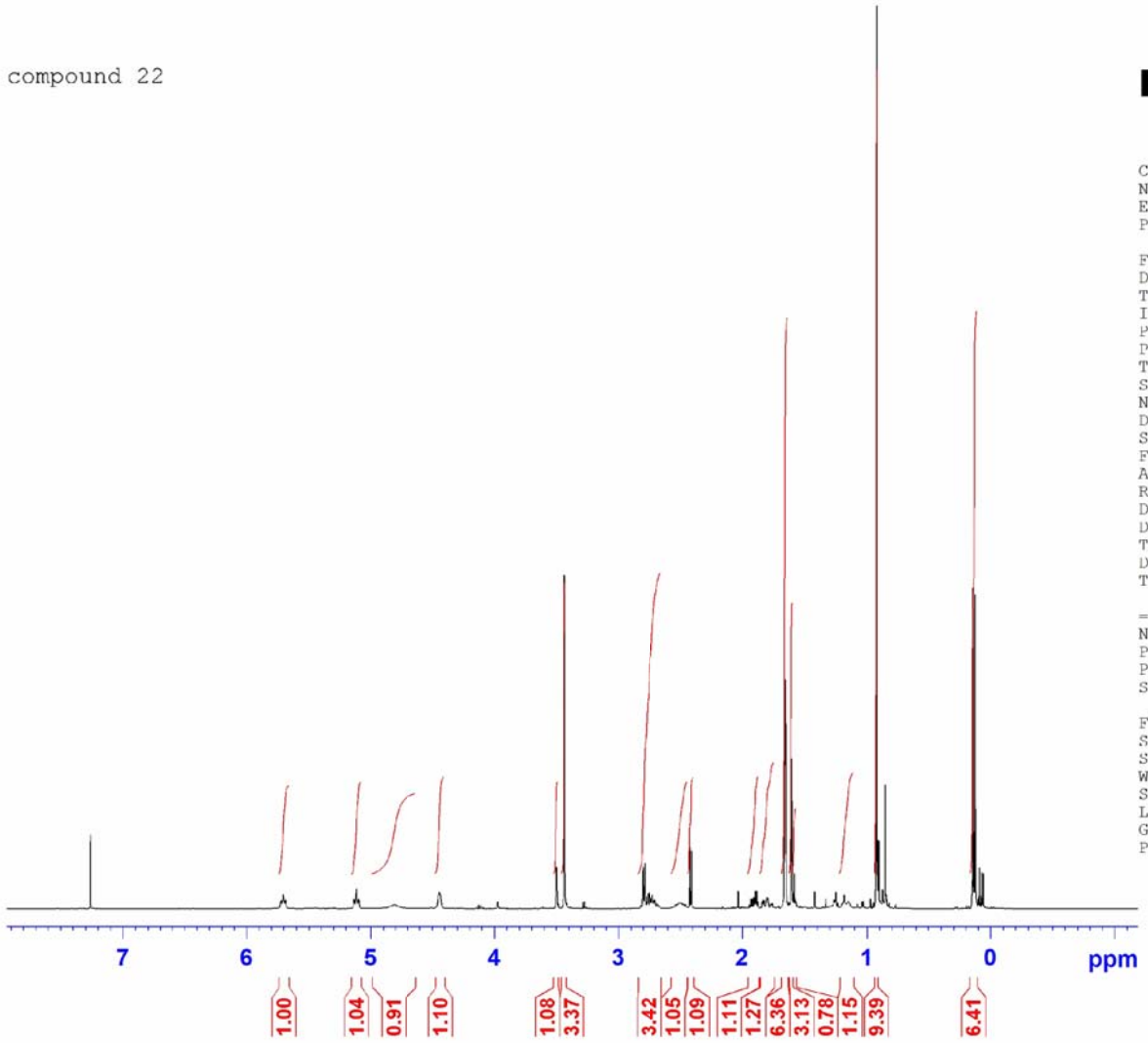
Current Data Parameters
NAME koti181
EXPNO 31
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060216
Time 20.46
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 800
DS 2
SWH 25062.656 Hz
FIDRES 0.382426 Hz
AQ 1.3074932 sec
RG 14596.5
DW 19.950 usec
DE 6.00 usec
TE 300.2 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001311 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 10.30 usec
p2 20.60 usec
PL1 -1.00 dB
SFO1 100.6233329 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 -3.00 dB
PL12 16.00 dB
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127545 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40




BRUKER

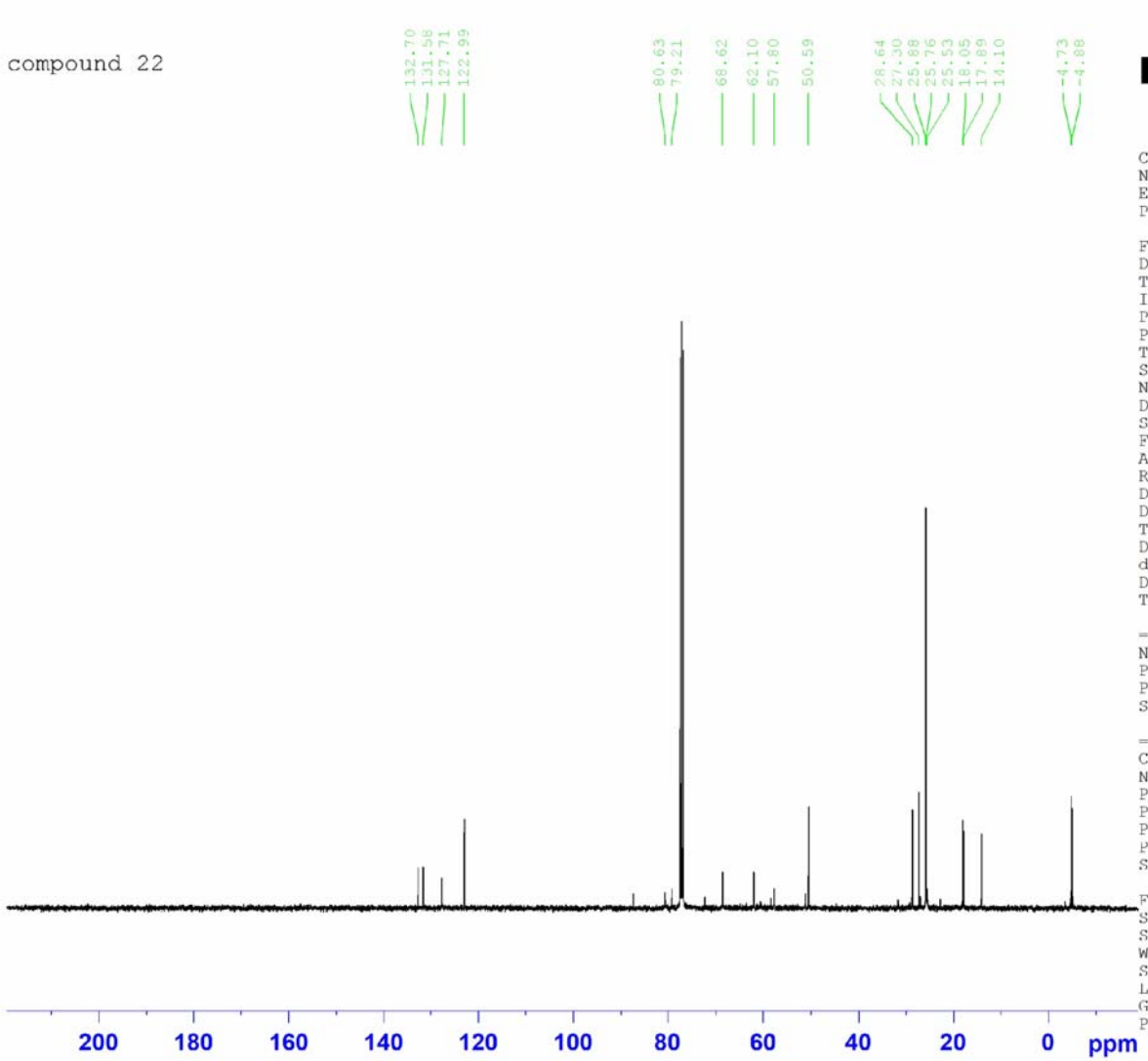
Current Data Parameters
NAME koti279
EXPNO 50
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060922
Time 9.44
INSTRUM avance400
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 114
DW 60.400 usec
DE 6.00 usec
TE 300.2 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 8.75 usec
PL1 -3.00 dB
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300094 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

compound 22




BRUKER

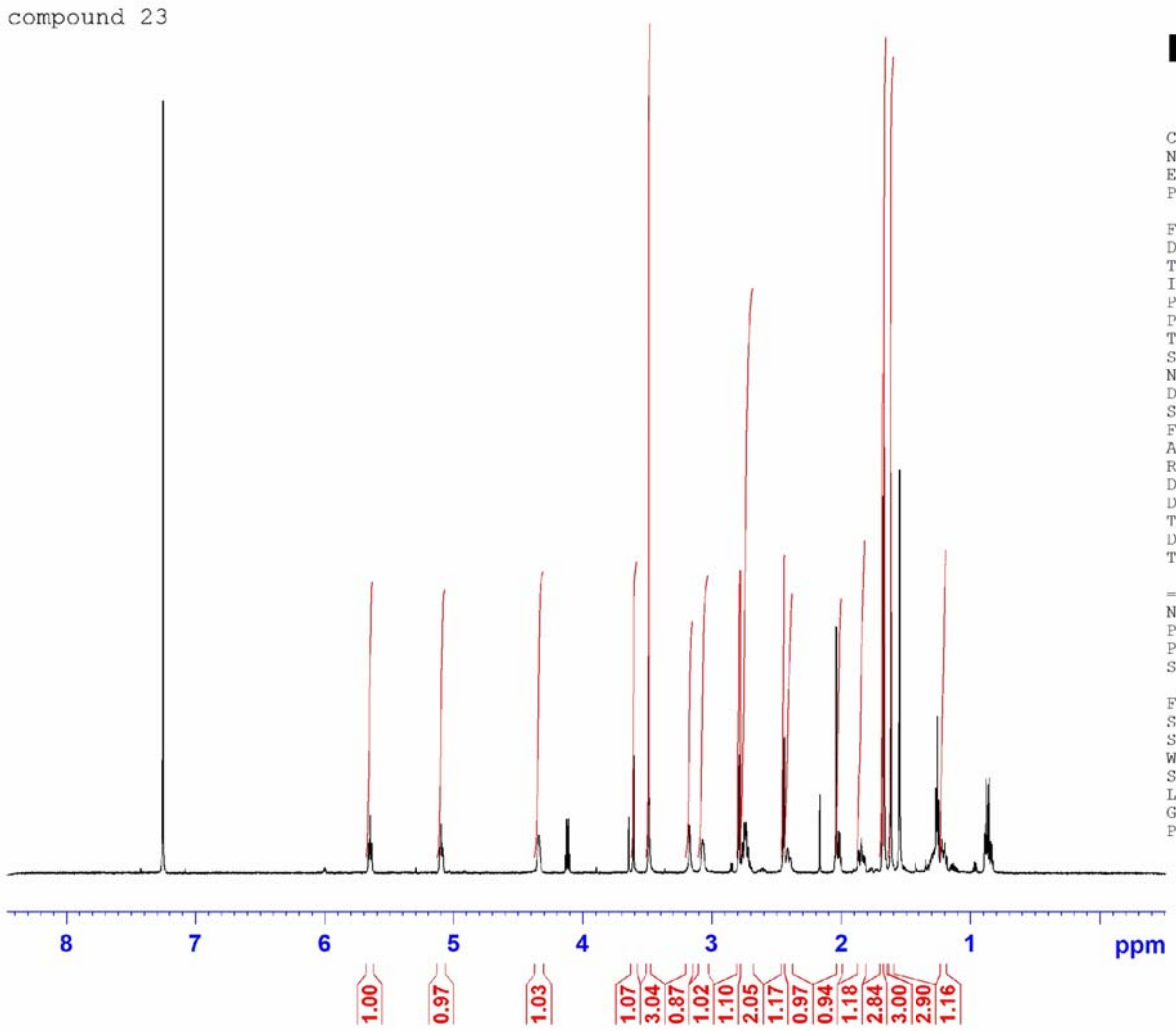
```
Current Data Parameters
NAME                 koti279
EXPNO                     51
PROCNO                     1

F2 - Acquisition Parameters
Date_               20060922
Time                   10.01
INSTRUM             avance400
PROBHD    5 mm BBO BB-1H
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                       1200
DS                          4
SWH                 23980.814 Hz
FIDRES                0.365918 Hz
AQ                    1.3664756 sec
RG                       5160.6
DW                       20.850 usec
DE                        6.00 usec
TE                       300.2 K
D1                  2.00000000 sec
d11                 0.03000000 sec
DELTA               1.89999998 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                       10.30 usec
PL1                      -1.00 dB
SFO1              100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                  100.00 usec
PL2                      -3.00 dB
PL12                     16.00 dB
PL13                     20.00 dB
SFO2              400.1316005 MHz

F2 - Processing parameters
SI                        32768
SF                100.6127543 MHz
WDW                          EM
SSB                           0
LB                       1.00 Hz
GB                            0
PC                        1.40
```




BRUKER

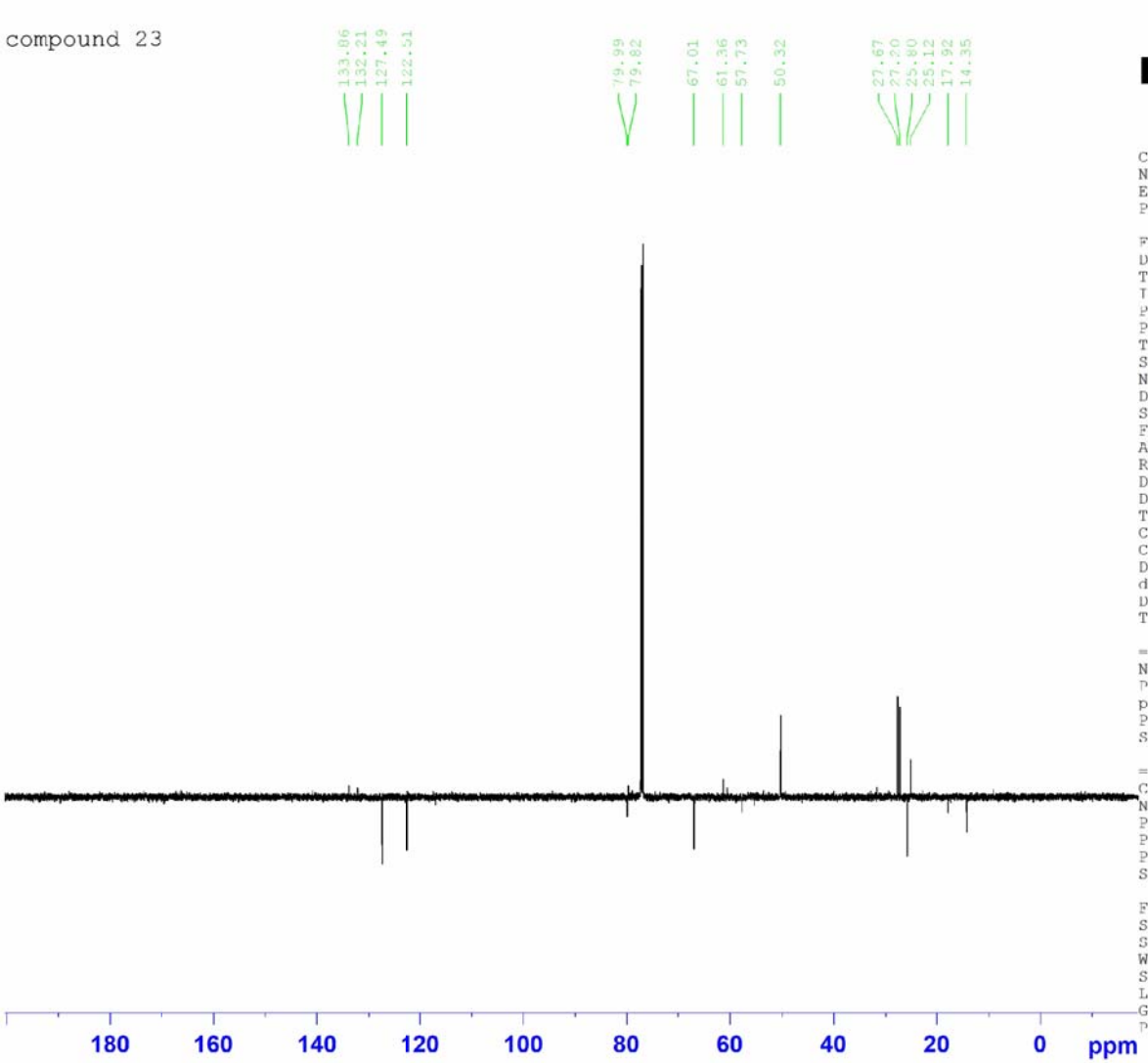
```
Current Data Parameters
NAME                 koti227
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20060528
Time                   18.32
INSTRUM             avance600
PROBHD    5 mm PAQNP Swi
PULPROG                zg30
TD                    32768
SOLVENT                CDCl3
NS                        32
DS                         2
SWH                5387.931 Hz
FIDRES            0.164427 Hz
AQ                3.0410132 sec
RG                       512
DW                  92.800 usec
DE                   6.00 usec
TE                   300.0 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    13.85 usec
PL1                   -6.00 dB
SFO1          600.1324005 MHz

F2 - Processing parameters
SI                        32768
SF            600.1300176 MHz
WDW                        no
SSB                         0
LB                    0.00 Hz
GB                          0
PC                     1.00
```

compound 23



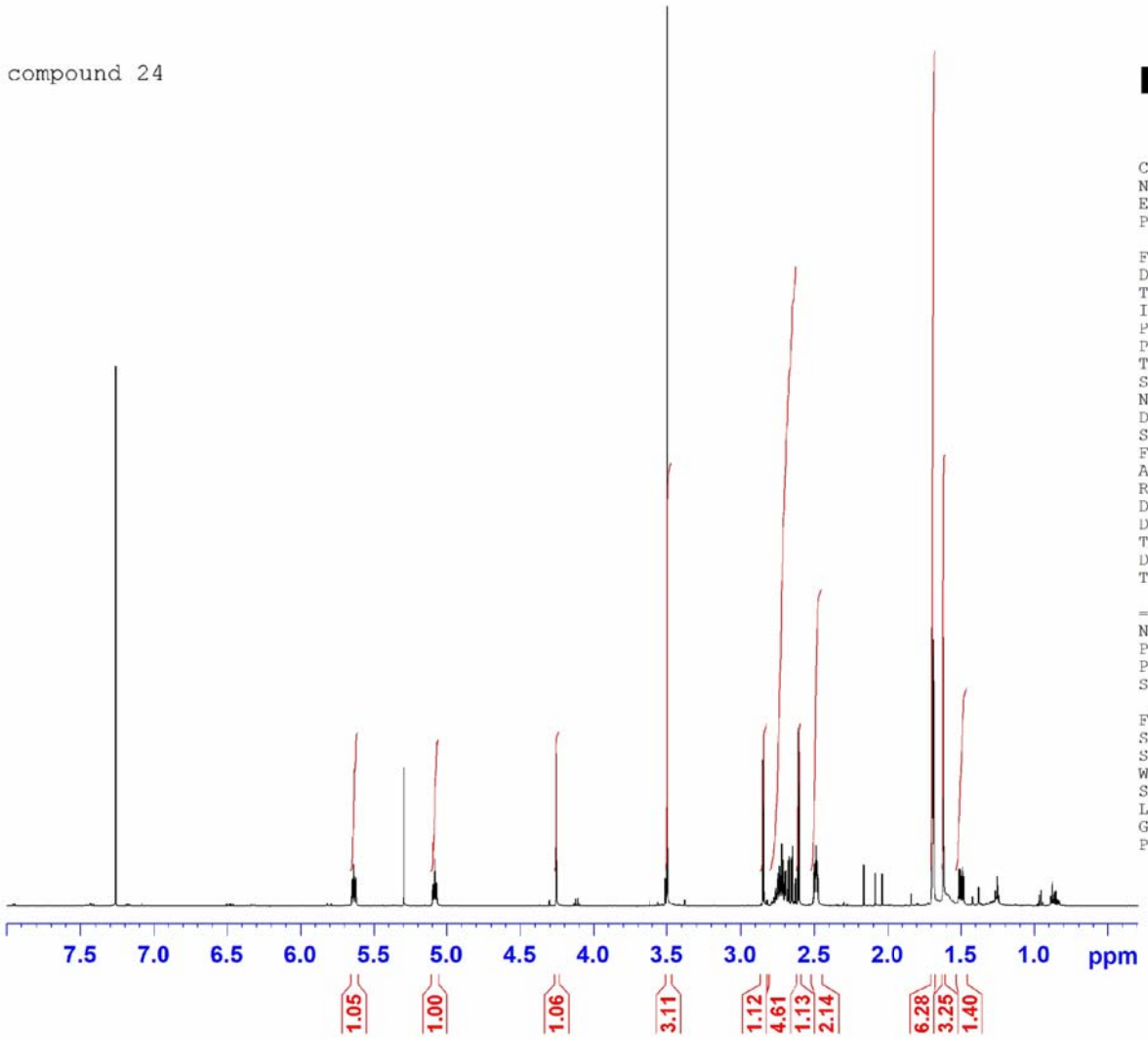

```
Current Data Parameters
NAME                  koti227
EXPNO                       8
PROCNO                      1

F2 - Acquisition Parameters
Date_                20060529
Time                     7.55
INSTRUM              avance600
PROBHD    5 mm PAQNP Swi
PULPROG                  jmod
TD                      65536
SOLVENT                 CDCl3
NS                       3072
DS                          4
SWH                 35971.223 Hz
FIDRES                0.548877 Hz
AQ                    0.9110143 sec
RG                       5160.6
DW                       13.900 usec
DE                        6.00 usec
TE                       300.0 K
CNST2               145.0000000
CNST11                1.0000000
D1                    2.00000000 sec
d20                   0.00689655 sec
DELTA                 0.00001019 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                        8.00 usec
p2                       16.00 usec
PL1                       0.00 dB
SFO1                150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                       1H
PCPD2                    80.00 usec
PL2                      -6.00 dB
PL12                     12.20 dB
SFO2                600.1324005 MHz

F2 - Processing parameters
SI                         32768
SF                  150.9027870 MHz
WDW                           EM
SSB                            0
LB                        1.00 Hz
GB                             0
PC                        1.40
```



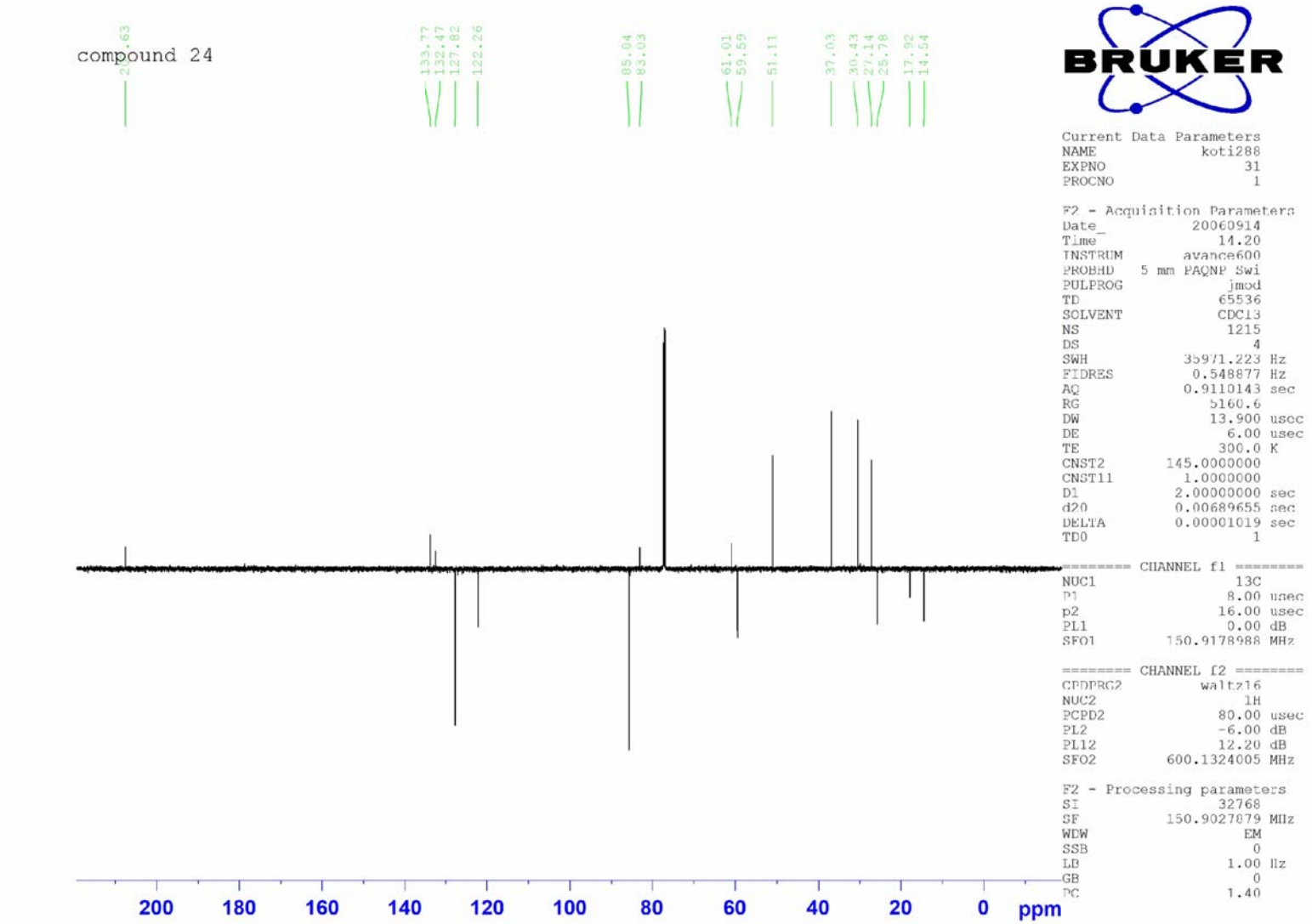

BRUKER

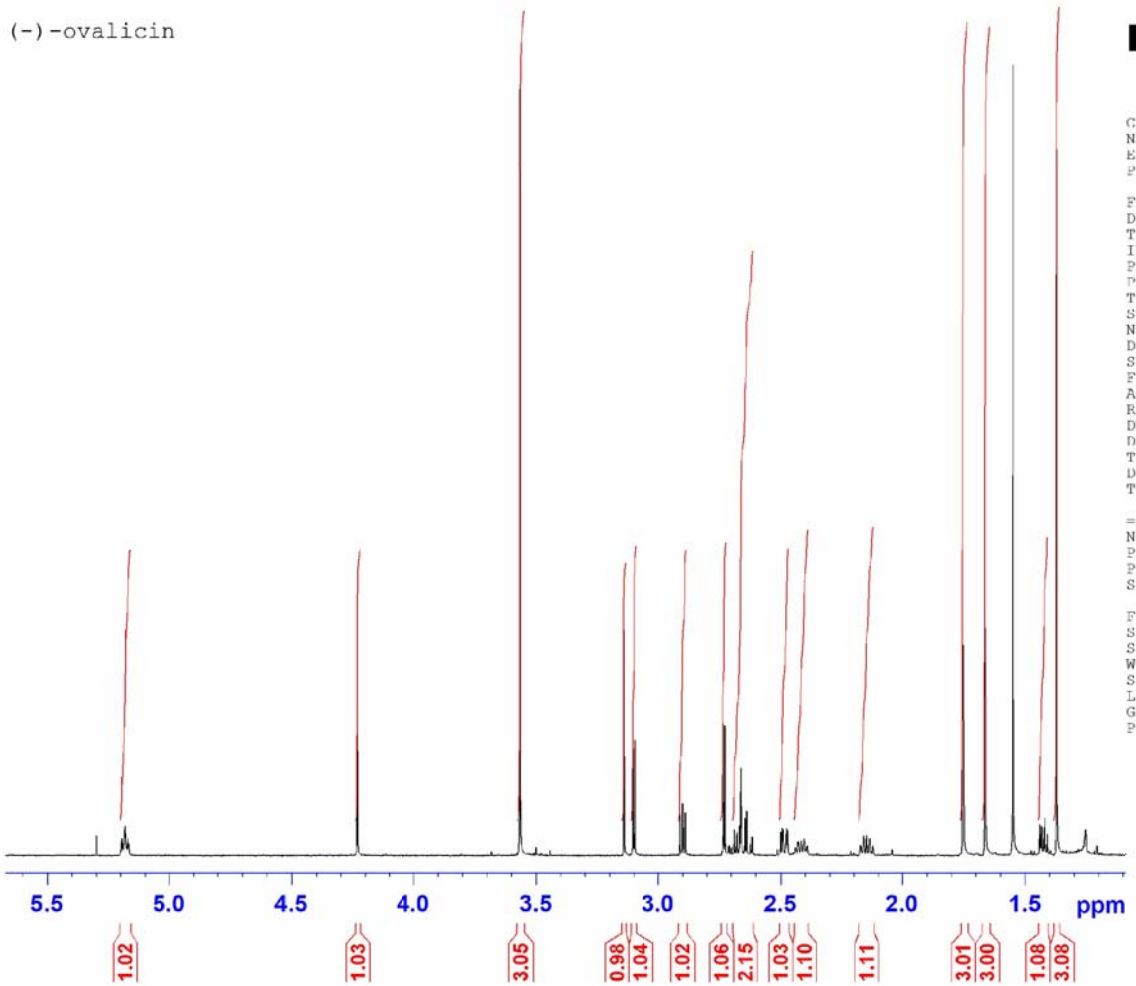
Current Data Parameters
NAME koti288
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060914
Time 13.19
INSTRUM avance600
PROBHD 5 mm PAQNP Swi
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6477449 sec
RG 406.4
DW 40.400 usec
DE 6.00 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 13.85 usec
PL1 -6.00 dB
SFO1 600.1337060 MHz

F2 - Processing parameters
SI 32768
SF 600.1300174 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.00


compound 24
20.63
133.77
132.47
127.82
122.26
85.04
83.03
61.01
59.59
51.11
37.03
30.43
27.14
25.78
17.92
14.54
200
180
160
140
120
100
80
60
40
20
0
ppm
BRUKER
Current Data Parameters
NAME koti288
EXPNO 31
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060914
Time 14.20
INSTRUM avance600
PROBHD 5 mm PAQNP Swi
PULPROG jmod
TD 65536
SOLVENT CDCl3
NS 1215
DS 4
SWH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 5160.6
DW 13.900 usec
DE 6.00 usec
TE 300.0 K
CNST2 145.0000000
CNST11 1.0000000
D1 2.00000000 sec
d20 0.00689655 sec
DELTA 0.00001019 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.00 usec
p2 16.00 usec
PL1 0.00 dB
SFO1 150.9178988 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -6.00 dB
PL12 12.20 dB
SFO2 600.1324005 MHz
F2 - Processing parameters
SI 32768
SF 150.9027879 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



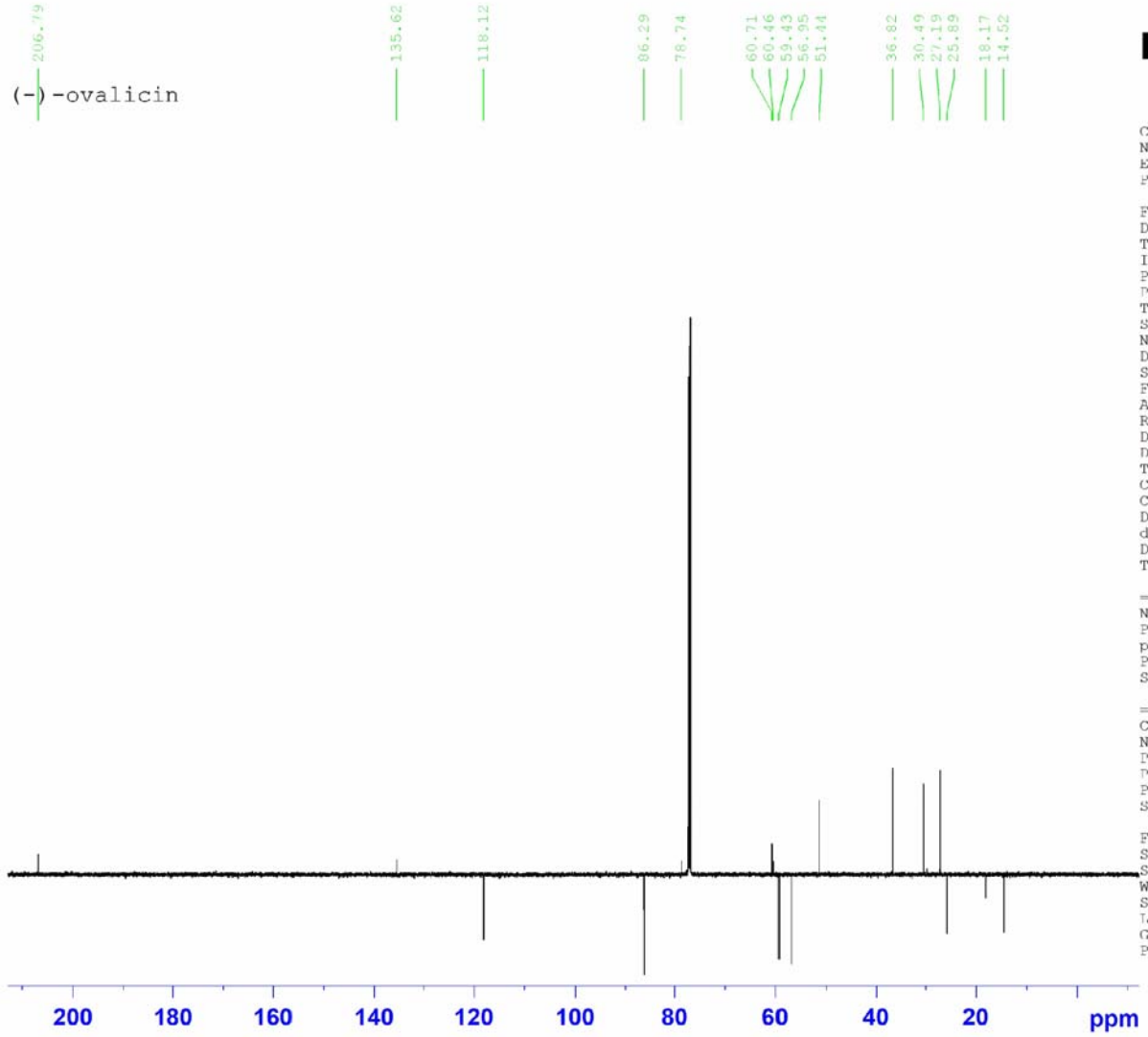

BRUKER

```
Current Data Parameters
NAME      koti290F2_Ovalicin_600
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060915
Time              16.07
INSTRUM         avance600
PROBHD    5 mm PAQNP Swi
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    32
DS                     2
SWH           12376.237 Hz
FIDRES         0.188846 Hz
AQ             2.6477449 sec
RG                 645.1
DW                40.400 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.85 usec
PL1                -6.00 dB
SFO1         600.1337060 MHz

F2 - Processing parameters
SI                 32768
SF           600.1300174 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```




BRUKER

```
Current Data Parameters
NAME      koti290F2_Ovalicin_600
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20060915
Time              23.33
INSTRUM         avance600
PROBHD   5 mm PAQNP Swi
PULPROG             jmod
TD                 65536
SOLVENT            CDCl3
NS                  9000
DS                     4
SWH            35971.223 Hz
FIDRES          0.548877 Hz
AQ             0.9110143 sec
RG                3649.1
DW                13.900 usec
DE                 6.00 usec
TE                300.0 K
CNST2         145.0000000
CNST11          1.0000000
D1              2.00000000 sec
d20             0.00689655 sec
DELTA           0.00001019 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                13C
P1                 8.00 usec
p2                16.00 usec
PL1                0.00 dB
SFO1         150.9178988 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2              80.00 usec
PL2                -6.00 dB
PL12               12.20 dB
SFO2         600.1324005 MHz

F2 - Processing parameters
SI                 32768
SF           150.9027871 MHz
WDW                EM
SSB                0
LB                 1.00 Hz
GB                 0
PC                 1.40
```