ELECTRONIC SUPPLEMENTARY INFORMATION

Stereoselective synthesis of *syn* and *anti* 1,2-hydroxyalkyl moieties by Cu-catalyzed asymmetric allylic alkylation

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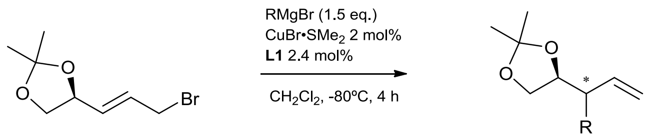
General Procedures:

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and cerium/molybdenum staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on a AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR300 (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Carbon assignments are based on APT ^{13}C-NMR experiments. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL).

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. CH_2Cl_2 was dried and distilled over calcium hydride. Substrate **4** was prepared according to literature procedures.[1] CuBr•SMe_2, Grubbs 2nd generation and Hoveyda-Grubbs 2nd generation catalysts, ligands **L1-4** and commercially available reagents were purchased from Aldrich, and used without further purification. Grignard reagents were purchased from Aldrich (MeMgBr, EtMgBr, *n*-HexMgBr, *c*-C_5H_9MgBr) or prepared from the corresponding alkyl bromides and magnesium turnings in Et_2O following standard procedures ($PhCH_2CH_2MgBr$). Grignard reagents were titrated using *s*-BuOH and catalytic amounts of 1,10-phenanthroline.

General procedure for the stereoselective Cu-catalyzed synthesis of 1,2-hydroxyalkyl compounds 5



4 **5**

In a Schlenk tube equipped with septum and stirring bar, CuBr•SMe_2 (10 μmol, 2.06 mg) and ligand **L1** (12 μmol, 8.24 mg) were dissolved in CH_2Cl_2 (2 mL) and stirred under nitrogen at room temperature for 15 min. The mixture was cooled to -80 °C and the

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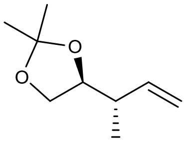
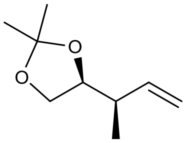
[1] (*a*) J. A. Marshall, J. D. Trometer, D. G. Cleary, *Tetrahedron*, 1989, **45**, 391; (*b*) A. R. Ellwood, A. J. P. Mortimer, D. A. Tocher, M. J. Porter, *Synlett*, 2008, 2199.

corresponding Grignard reagent (solution in Et_2O, 0.75 mmol) was added dropwise. Allyl bromide **4** (0.5 mmol, 110 mg) was then added dropwise as a solution in CH_2Cl_2 (0.8 mL) at that temperature over 1 h *via* a syringe pump. Once the addition was complete the resulting mixture was further stirred at -80 °C for 4 h. The reaction was quenched by addition of MeOH (0.5 mL) and the mixture was allowed to reach rt. Then, saturated aqueous NH_4Cl solution (2 mL) was added to the mixture. The organic phase was separated, and the resulting aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by flash chromatography on silica gel using a mixture of pentane:Et_2O as eluent to yield the corresponding 1,2-hydroxyalkyl compound **5**.

Note: GC analysis was carried out on a sample obtained after aqueous extraction with Et_2O, which has been passed through a short plug of silica gel to remove transition metal residues.



(-)-(*S*)-4-((*S*)-but-3-en-2-yl)-2,2-dimethyl-1,3-dioxolane (*anti*-5a): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded ***anti*-5a** (71 mg, 91%) as a colourless oil. $[\alpha]_D^{20}$ = - 2.8 (c = 0.5 in $CHCl_3$) [lit.[2] $[\alpha]_D^{20}$ = - 2.5 (c = 1.21 in $CHCl_3$)]. ^{1}H NMR (400 MHz, $CDCL_3$) δ 5.87 – 5.78 (m, 1H), 5.09 – 5.04 (m, 2H), 4.00 – 3.94 (m, 2H), 3.65 – 3.60 (m, 1H), 2.33 (sext., *J* = 6.5 Hz, 1H),1.40 (s, 3H), 1.35 (s, 3H), 1.00 (dd, *J* = 6.8, 1.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 115.2, 109.2, 79.5, 67.6, 41.0, 26.8, 25.7, 15.7. HRMS (APCI+, *m/z*): calculated for $C_9H_{17}O_2$ [M+H$^+$]: 157.1223, found: 157.1219.



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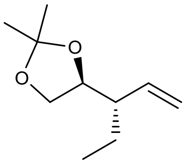
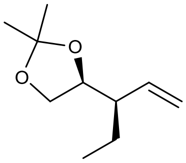
[2] R. W. Hoffmann, W. Helbig, *Chem. Ber.* 1981, **114**, 2802.

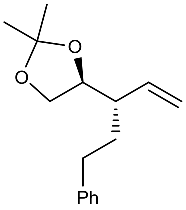
(+)-(*S*)-4-((*R*)-but-3-en-2-yl)-2,2-dimethyl-1,3-dioxolane (*syn*-5a): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded ***syn*-5a** (66 mg, 85%) as a colourless oil. $[\alpha]_D^{20}$ = + 7.6 (c = 0.65 in $CHCl_3$). ^1H NMR (400 MHz, $CDCL_3$) δ 5.74 – 5.65 (m, 1H), 5.08 (d, *J* = 17.4 Hz, 1H), 5.04 (d, *J* = 10.3 Hz, 1H), 3.97 – 3.87 (m, 2H), 3.64 (t, *J* = 7.3 Hz, 1H), 2.32 (sext., *J* = 6.8 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H), 1.09 (d, *J* = 6.7, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 115.6, 109.2, 79.6, 67.9, 41.9, 26.9, 25.7, 16.6. HRMS (APCI+, *m/z*): calculated for $C_9H_{17}O_2$ [M+H$^+$]: 157.1223, found: 157.1220.



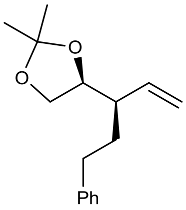
(+)-(*S*)-2,2-dimethyl-4-((*S*)-pent-1-en-3-yl)-1,3-dioxolane (*anti*-5b): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded ***anti*-5b** (76 mg, 89%) as a colourless oil. $[\alpha]_D^{20}$ = + 6.0 (c = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 – 5.58 (m, 1H), 5.13 (dd, *J* = 10.3, 0.6 Hz, 1H), 5.05 (dd, *J* = 17.2, 0.6 Hz, 1H), 4.06 – 3.96 (m, 2H), 3.63 (t, *J* = 7.4 Hz, 1H), 2.04 – 1.97 (m, 1H), 1.47 – 1.40 (m, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 1.32 – 1.20 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 117.3, 108.9, 78.5, 67.7, 49.3, 26.7, 25.7, 23.9, 11.9. HRMS (ESI+, *m/z*): calculated for $C_{10}H_{19}O_2$ [M+H$^+$]: 171.1370, found: 171.1379.



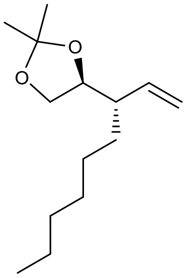
(+)-(*S*)-2,2-dimethyl-4-((*R*)-pent-1-en-3-yl)-1,3-dioxolane (*syn*-5b): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded ***syn*-5b** (68 mg, 80%) as a colourless oil. $[\alpha]_D^{20}$ = + 3.0 (c = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.42 (m, 1H), 5.12 – 5.00 (m, 2H), 3.95 – 3.90 (m, 2H), 3.61 (t, *J* = 10.2 Hz, 1H), 2.08 – 1.99 (m, 1H), 1.80 – 1.71 (m, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 1.32 – 1.18 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 117.5, 109.2, 78.5, 68.3, 50.3, 27.0, 25.9, 24.1, 11.5. HRMS (ESI+, *m/z*): calculated for $C_{10}H_{19}O_2$ [M+H$^+$]: 171.1370, found: 171.1378.



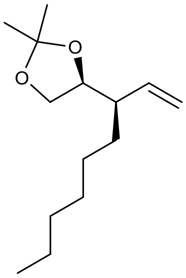
(+)-(*S*)-2,2-dimethyl-4-((*S*)-5-phenylpent-1-en-3-yl)-1,3-dioxolane (*anti*-5c): Purification by column chromatography (SiO$_2$, pentane/Et$_2$O 20:1) afforded ***anti*-5c** (103 mg, 84%) as a colourless oil. $[\alpha]_D^{20}$ = + 25.4 (c = 1.0 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 5.78 – 5.69 (m, 1H), 5.25 (d, *J* = 10.2 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 4.08 (dd, *J* = 12.5, 6.4 Hz, 1H), 4.01 – 3.97 (m, 1H), 3.64 (t, *J* = 7.6 Hz, 1H), 2.77 – 2.70 (m, 1H), 2.57 – 2.49 (m, 1H), 2.22 – 2.15 (m, 1H), 1.79 – 1.64 (m, 2H), 1.41 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.4, 138.1, 128.7, 128.6, 126.0, 118.0, 109.1, 78.7, 67.6, 47.0, 33.6, 32.9, 26.7, 25.7. HRMS (APCI+, *m/z*): calculated for $C_{16}H_{23}O_2$ [M+H$^+$]: 247.1693, found: 247.1690.



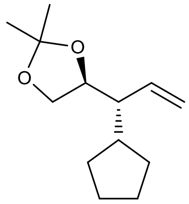
(-)-(*S*)-2,2-dimethyl-4-((*R*)-5-phenylpent-1-en-3-yl)-1,3-dioxolane (*syn*-5c): Purification by column chromatography (SiO$_2$, pentane/Et$_2$O 25:1) afforded ***syn*-5c** (89 mg, 72%) as a colourless oil. $[\alpha]_D^{20}$ = - 1.4 (c = 1.0 in CHCl$_3$). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.26 m, 2H), 7.23 – 7.10 (m, 3H), 5.63 – 5.54 (m, 1H), 5.18 – 5.12 (m, 2H), 3.98 – 3.92 (m, 2H), 3.67 – 3.62 (m, 1H), 2.77 – 2.70 (m, 1H), 2.57 – 2.49 (m, 1H), 2.23 – 2.15 (m, 1H), 2.13 – 2.05 (m, 1H), 1.62 – 1.53 (m, 1H), 1.38 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 142.5, 138.1, 128.7, 128.5, 125.9, 118.0, 109.3, 78.6, 68.2, 48.2, 33.3, 32.8, 27.0, 25.9. HRMS (APCI+, *m/z*): calculated for $C_{16}H_{23}O_2$ [M+H$^+$]: 247.1693, found: 247.1691.



(+)-(*S*)-2,2-dimethyl-4-((*S*)-non-1-en-3-yl)-1,3-dioxolane (*anti*-5d): Purification by column chromatography (SiO_2, pentane/Et_2O 40:1) afforded ***anti*-5d** (99 mg, 87%) as a colourless oil. $[\alpha]_D^{20}$ = + 33.8 (c = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.64 (dt, *J* = 17.2, 10.2 Hz, 1H), 5.12 (dd, *J* = 10.2, 1.1 Hz, 1H), 5.04 (dd, *J* = 17.2, 1.1 Hz, 1H), 4.05 – 3.97 (m, 2H), 3.63 (t, *J* = 7.2 Hz, 1H), 2.15 – 2.05 (m, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 1.33 – 1.18 (m, 10H), 0.87 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 117.1, 109.0, 78.8, 67.7, 47.6, 32.0, 31.0, 29.5, 27.3, 26.7, 25.7, 22.8, 14.3. HRMS (APCI+, *m/z*): calculated for $C_{14}H_{27}O_2$ [M+H$^+$]: 227.2006, found: 227.2005.

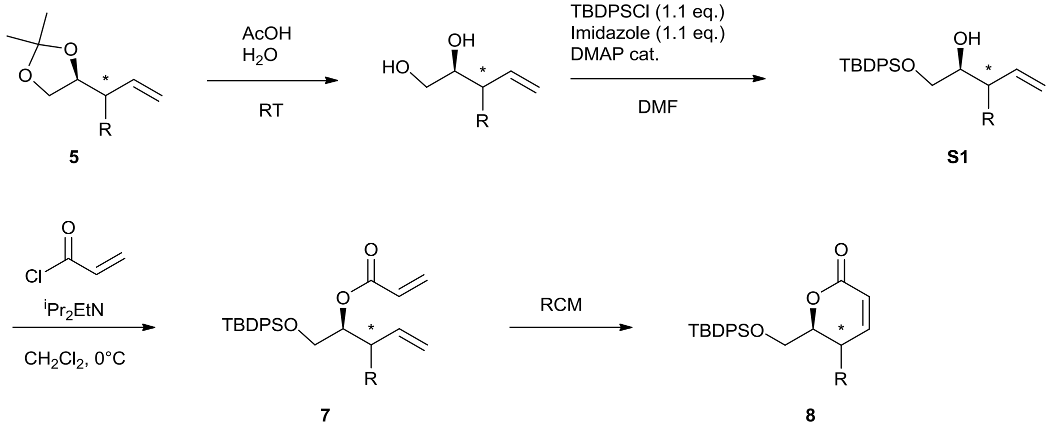


(+)-(*S*)-2,2-dimethyl-4-((*R*)-non-1-en-3-yl)-1,3-dioxolane (*syn*-5d): Purification by column chromatography (SiO_2, pentane/Et_2O 40:1) afforded ***syn*-5d** (88 mg, 79%) as a colourless oil. $[\alpha]_D^{20}$ = + 2.0 (c = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.54 – 5.45 (m, 1H), 5.09 – 5.02 (m, 2H), 3.94 – 3.88 (m, 2H), 3.65 – 3.60 (m, 1H), 2.16 – 2.07 (m, 1H), 1.72 – 1.64 (m, 1H), 1.40 (s, 3H), 1.35 (s, 3H), 1.33 – 1.18 (m, 9H), 0.87 (t, *J* = 6.8, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 117.3, 109.2, 78.7, 68.2, 48.7, 32.0, 31.2, 29.5, 27.1, 25.9, 22.9, 14.3. HRMS (APCI+, *m/z*): calculated for $C_{14}H_{27}O_2$ [M+H$^+$]: 227.2006, found: 227.2005.



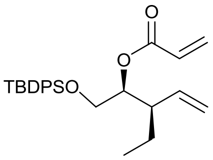
(+)-(*S*)-4-((*R*)-1-cyclopentylallyl)-2,2-dimethyl-1,3-dioxolane (*anti*-5e): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded ***anti*-5e** (84 mg, 80%) as a colourless oil. $[\alpha]_D^{20}$ = + 13.8 (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 – 5.70 (m, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.23 – 4.17 (m, 1H), 3.97 (t, *J* = 7.0 Hz, 1H), 3.63 (t, *J* = 7.7 Hz, 1H), 1.93 – 1.79 (m, 3H), 1.66 – 1.48 (m, 4H), 1.37 (s, 3H), 1.34 (s, 3H), 1.23 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 117.4, 108.8, 77.4, 67.9, 52.3, 41.5, 30.9, 30.8, 26.6, 25.7, 25.2, 25.1. HRMS (ESI+, *m/z*): calculated for $C_{13}H_{23}O_2$ [M+H$^+$]: 211.1693, found: 211.1690.

General procedure for the synthesis of compounds 7 and α,β-unsaturated δ-lactones 8.

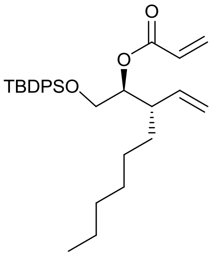


To a solution of **5** (1 mmol) in water (2 mL) at room temperature was added AcOH (5 mL). The solution was stirred at this temperature during 16 h. After some coevaporations with toluene (4 x 10 mL), the residue was dissolved in DMF (2 mL) and imidazole (75 mg, 1.1 mmol), DMAP (1 mg, 0.08 mmol) and *tert*-butyl(chloro)diphenylsilane (0.29 mL, 1.1 mmol) were added at 0 °C. The mixture was warmed to room temperature and was stirred during 16 h. Then it was poured into water (5 mL) and extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with water and brine and dried over Na_2SO_4. The resulting product **S1** was used in the next step without further purification.

To a solution of **S1** (1 mmol) and DIPEA (0.34 mL, 2 mmol) in CH_2Cl_2 (5 mL), acryloyl chloride (0.13 mL, 1.5 mmol) was added at 0 °C. The mixture was stirred at this temperature for 2 h. Then it was quenched with saturated aqueous solution of $NaHCO_3$ (2 mL), extracted with CH_2Cl_2 (3 x 5 mL) and dried over Na_2SO_4. The product was purified by flash chromatography on silica gel using a mixture of Pentane:Et_2O as eluent to yield the corresponding compound **7**.



(-)-(2*S*,3*R*)-1-((*tert*-butyldiphenylsilyl)oxy)-3-ethylpent-4-en-2-yl acrylate (7a): Purification by column chromatography (SiO_2, pentane/Et_2O 30:1) afforded **7a** (337 mg, 80%, over 3 steps) as a colourless oil. $[\alpha]_D^{20}$ = - 25.8 (c = 1.0 in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 4H), 7.45 – 7.34 (m, 6H), 6.43 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.17 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.85 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.55 – 5.46 (m, 1H), 5.10 – 5.00 (m, 3H), 3.80 – 3.72 (m, 2H), 2.40 (ddd, *J* = 18.3, 9.4, 3.5 Hz, 1H), 1.59 – 1.49 (m, 1H), 1.28 – 1.17 (m, 1H), 1.03 (s, 9H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 137.6, 135.6, 135.5, 133.4, 133.4, 130.5, 129.6, 129.6, 128.8, 127.6, 117.5, 76.4, 63.6, 46.6, 26.7, 22.9, 19.2, 11.4. HRMS (ESI+, *m/z*): calculated for $C_{26}H_{34}O_3SiNa$ $[M+Na^+]$: 445.2169, found: 445.2178.

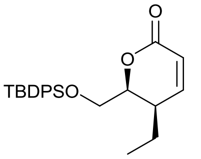


(+)-(2*S*,3*S*)-1-((*tert*-butyldiphenylsilyl)oxy)-3-vinylnonan-2-yl acrylate (7b): Purification by column chromatography (SiO_2, pentane/Et_2O 40:1) afforded **7b** (85%, over 3 steps) as a colourless oil. $[\alpha]_D^{20}$ = + 9.0 (c = 0.98 in $CHCl_3$). ^1H NMR (400 MHz,

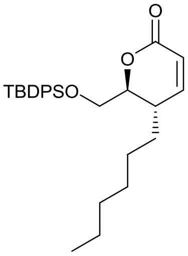
$CDCl_3$) δ 7.67 – 7.64 (m, 4H), 7.45 – 7.34 (m, 6H), 6.38 (dd, *J* = 17.3, 1.5 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.81 (dd, *J* = 10.4, 1.5 Hz, 1H), 5.58 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.12 (q, *J* = 5.1 Hz, 1H), 5.06 – 4.98 (m, 2H), 3.75 (dd, *J* = 10.8, 6.3 Hz, 1H), 3.68 (dd, *J* = 10.8, 4.8 Hz, 1H), 2.47 – 2.40 (m, 1H), 1.45 – 1.38 (m, 1H), 1.33 – 1.18 (m, 9H), 1.02 (s, 9H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 137.8, 135.6, 135.53, 133.4, 133.4, 130.4, 129.6, 129.6, 128.8, 127.6, 127.6, 117.2, 76.0, 63.5, 44.9, 31.7, 30.7, 29.1, 27.0, 26.7, 22.6, 19.2, 14.1. HRMS (ESI+, *m/z*): calculated for $C_{30}H_{43}O_3Si$ [M+H$^+$]: 479.2976, found: 479.2969.

General procedure for the RCM

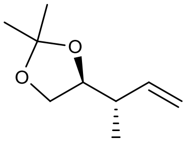
Grubbs 2nd generation catalyst (4.3 mg, 0.005 mmol) was added to a degassed solution of **7** (0.1 mmol) in CH_2Cl_2 (10 mL), and the mixture was refluxed during 14 h. The solvent was removed and the residue was purified by by flash chromatography on silica gel using a 5:1 mixture of Pentane:Et_2O as eluent to yield the corresponding compound **8**.



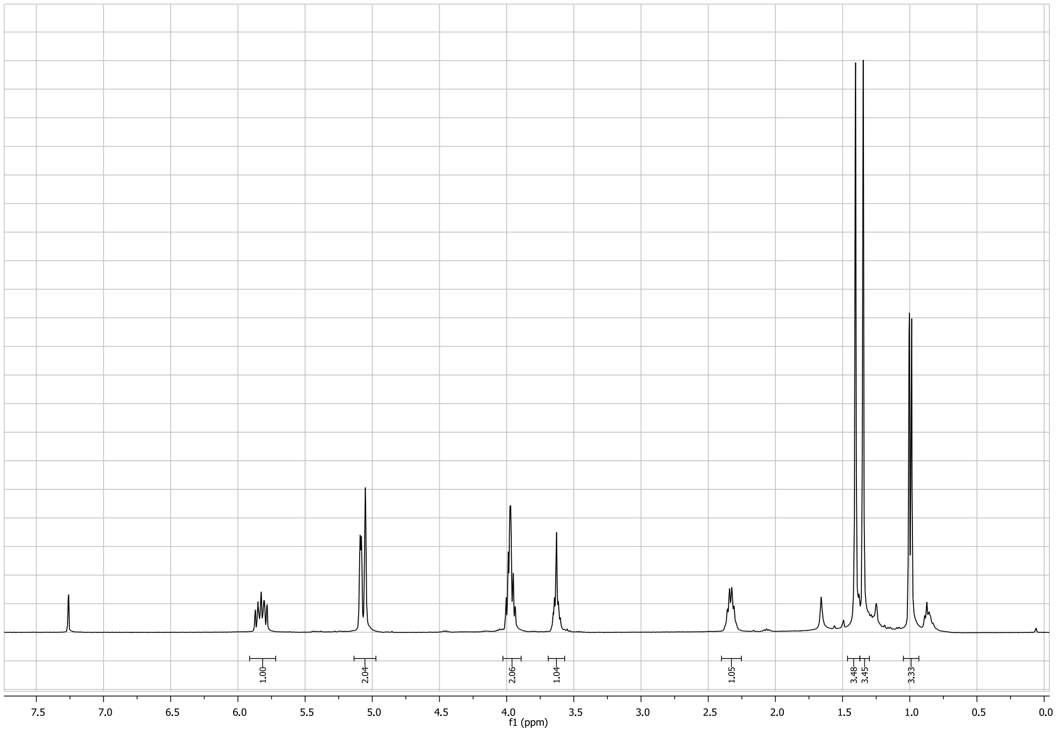
(-)-(5*R*,6*S*)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-ethyl-5,6-dihydro-2*H*-pyran-2-one (8a): Purification by column chromatography (SiO_2, pentane/Et_2O 5:1) afforded **8a** (39 mg, 97%) as a colourless oil. $[\alpha]_D^{20}$ = - 136.2 (c = 1.0 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 4H), 7.47 – 7.37 (m, 6H), 7.04 (dd, *J* = 9.8, 6.0 Hz, 1H), 6.03 (dd, *J* = 9.8, 0.9 Hz, 1H), 4.56 (ddd, *J* = 8.0, 5.9, 3.8 Hz, 1H), 3.92 (dd, *J* = 10.6, 5.9 Hz, 1H), 3.81 (dd, *J* = 10.6, 8.0 Hz, 1H), 2.56 – 2.50 (m, 1H), 1.69 – 1.59 (m, 1H), 1.45 (ddq, *J* = 14.7, 9.8, 7.5 Hz, 1H), 1.07 (s, 9H), 0.94 (t, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 150.3, 135.5, 132.9, 132.8, 129.9, 127.8, 120.9, 79.5, 62.1, 36.1, 26.8, 20.5, 19.2, 11.0. HRMS (ESI+, *m/z*): calculated for $C_{24}H_{30}O_3SiNa$ [M+Na$^+$]: 417.1856, found: 417.1863.



(+)-(5*S*,6*S*)-6-(((*tert*-butyldiphenylsilyl)oxy)methyl)-5-hexyl-5,6-dihydro-2*H*-pyran-2-one (8b): Purification by column chromatography (SiO_2, pentane/Et_2O 5:1) afforded **8b** (38 mg, 84%) as a colourless oil. $[\alpha]_D^{20}$ = + 84.2 (c = 0.92 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 4H), 7.46 – 7.37 (m, 6H), 6.73 (dd, *J* = 9.9, 4.0 Hz, 1H), 5.93 (dd, *J* = 9.9, 1.8 Hz, 1H), 4.32 – 4.28 (m, 1H), 3.86 (dd, *J* = 11.0, 4.9 Hz, 1H), 3.83 (dd, *J* = 11.0, 4.2 Hz, 1H), 2.77– 2.70 (m, 1H), 1.58 – 1.50 (m, 1H), 1.46 – 1.26 (m, 9H), 1.07 (s, 9H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 149.0, 135.6, 135.5, 132.9, 132.7, 129.9, 129.9, 127.8, 127.8, 119.9, 81.4, 63.4, 34.0, 31.6, 31.2, 29.2, 26.8, 26.3, 22.6, 19.2, 14.0. HRMS (ESI+, *m/z*): calculated for $C_{28}H_{38}O_3SiNa$ [$M+Na^+$]: 473.2482, found: 473.2459.


O
O

***anti*-5a**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3.33
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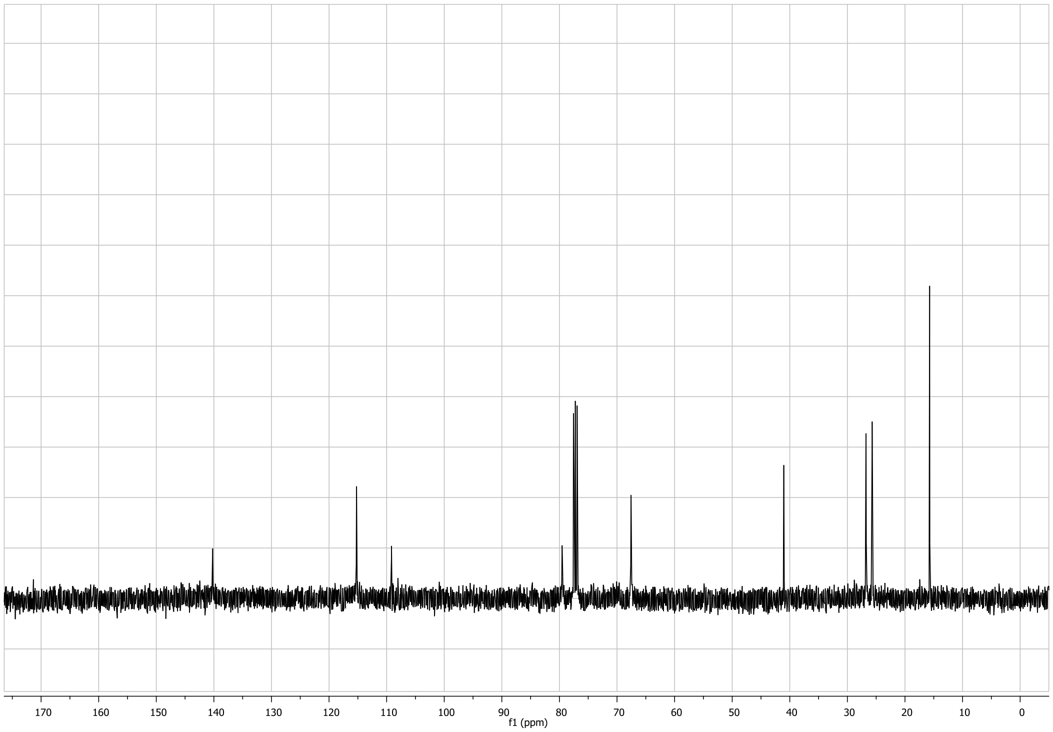
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170
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100
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50
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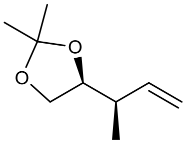
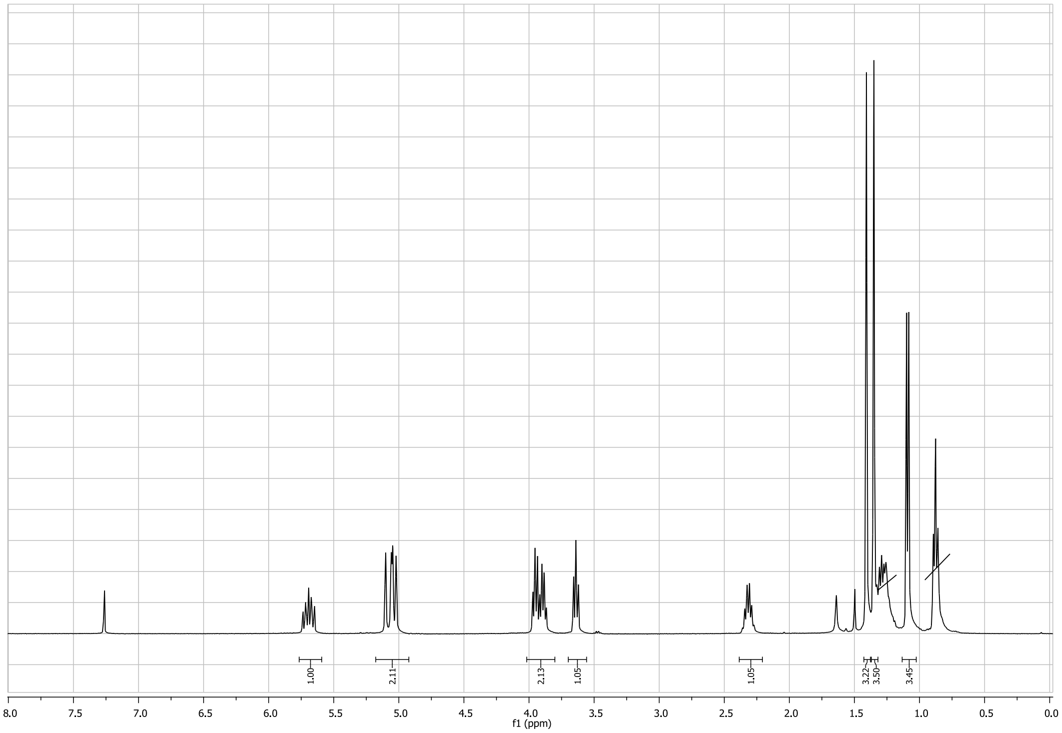
20
10
0
f1 (ppm)


O
O

***syn*-5a**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3.45
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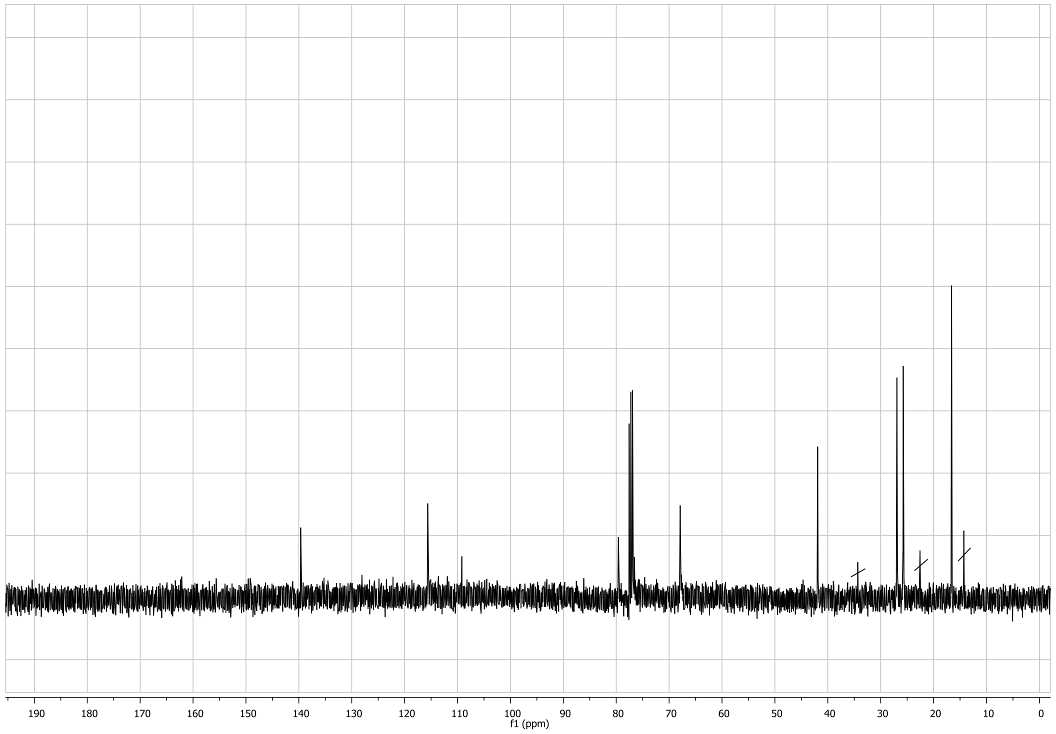
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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110
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90
80
70
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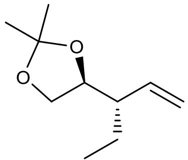
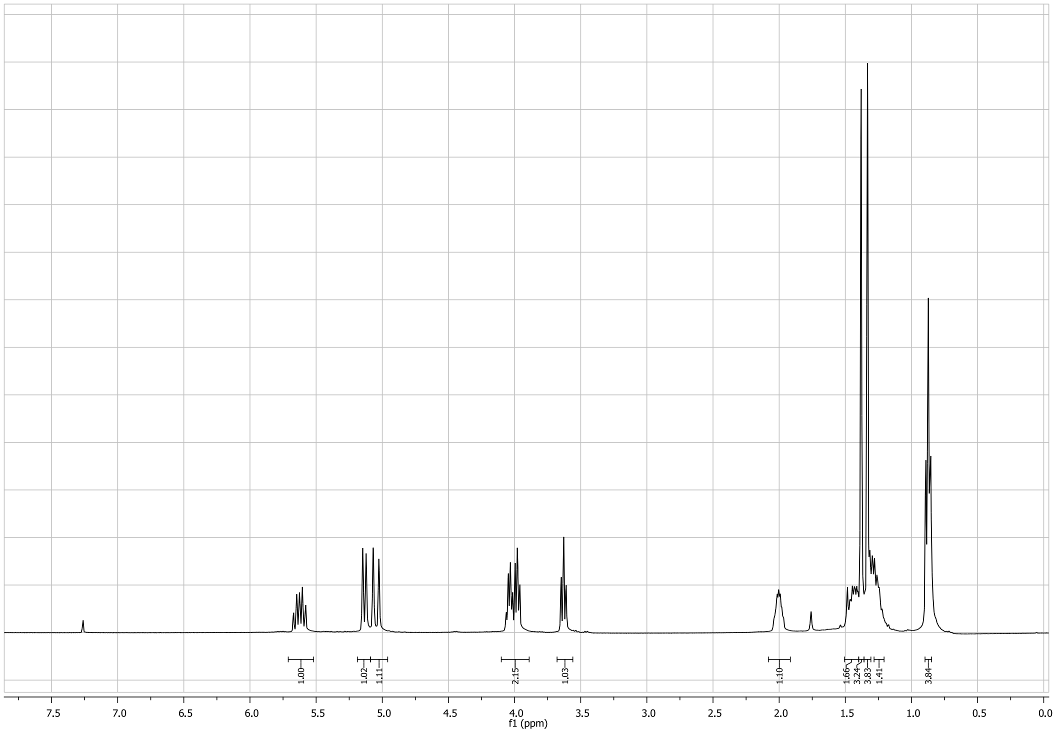
40
30
20
10
0
f1 (ppm)


O
O

***anti*-5b**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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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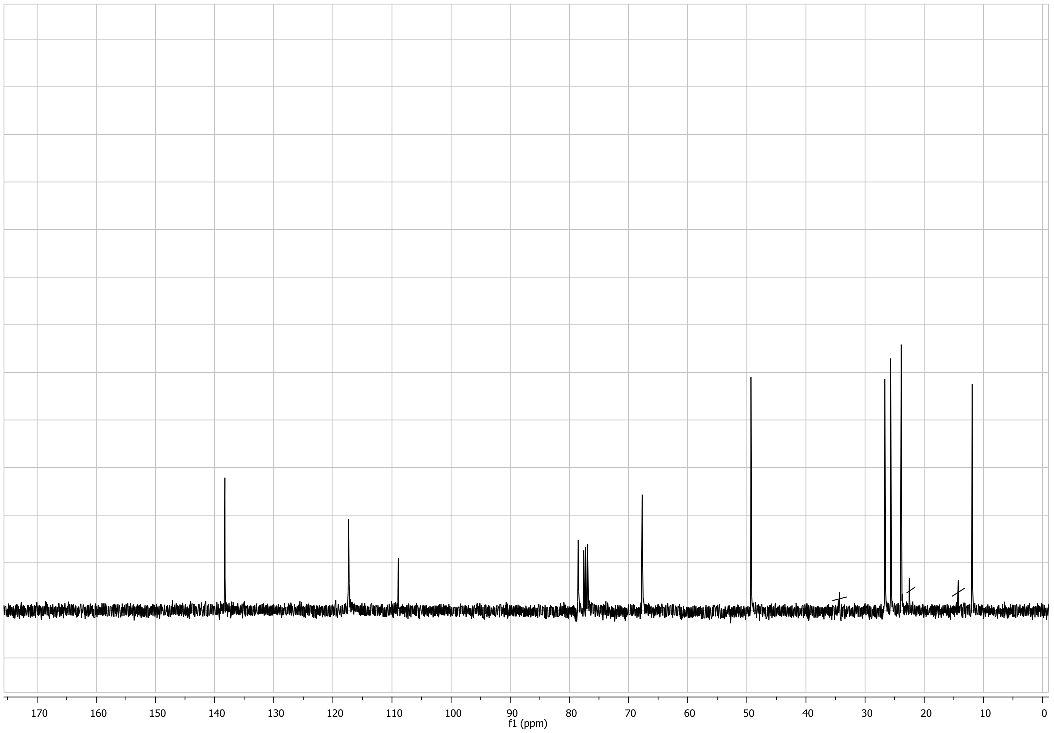
0.0
f1 (ppm)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120
110
100
90
80
70
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50
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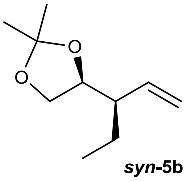
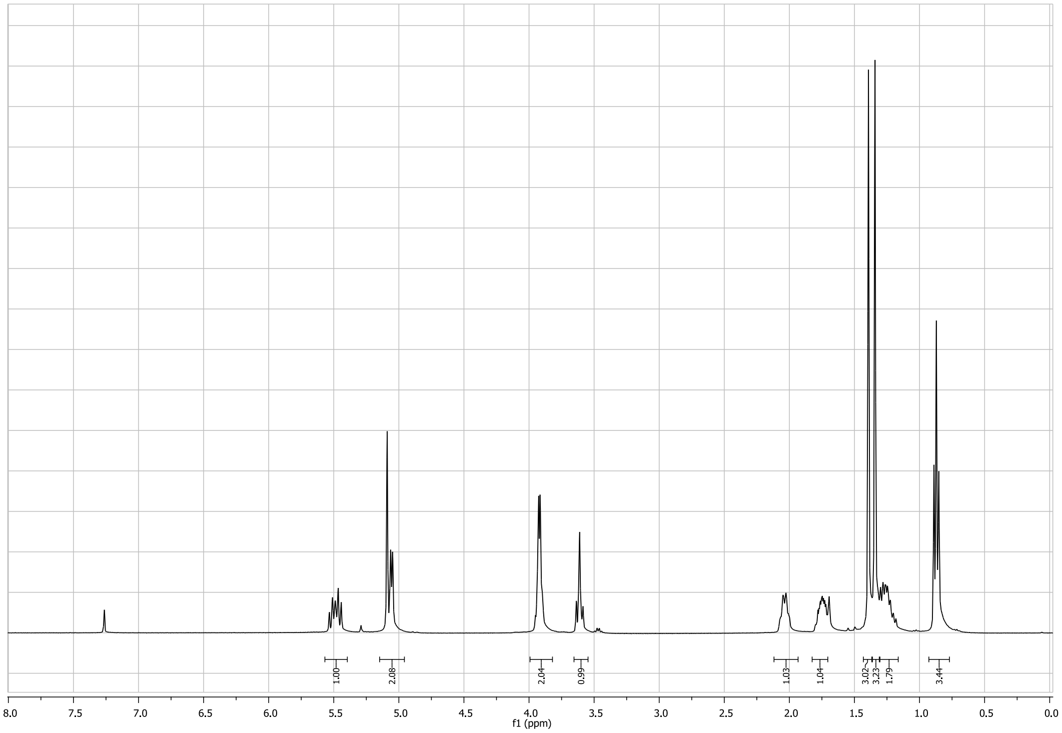
30
20
10
0
f1 (ppm)


O
O

***syn*-5b**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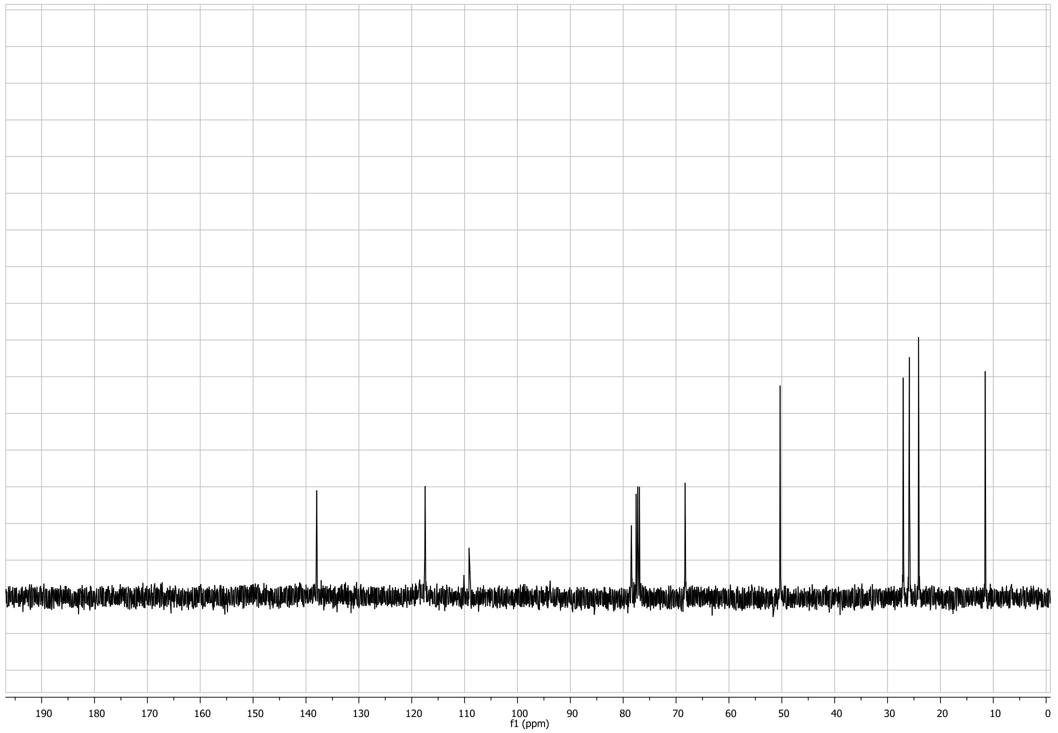
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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50
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30
20
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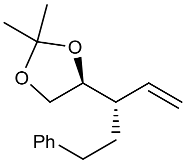
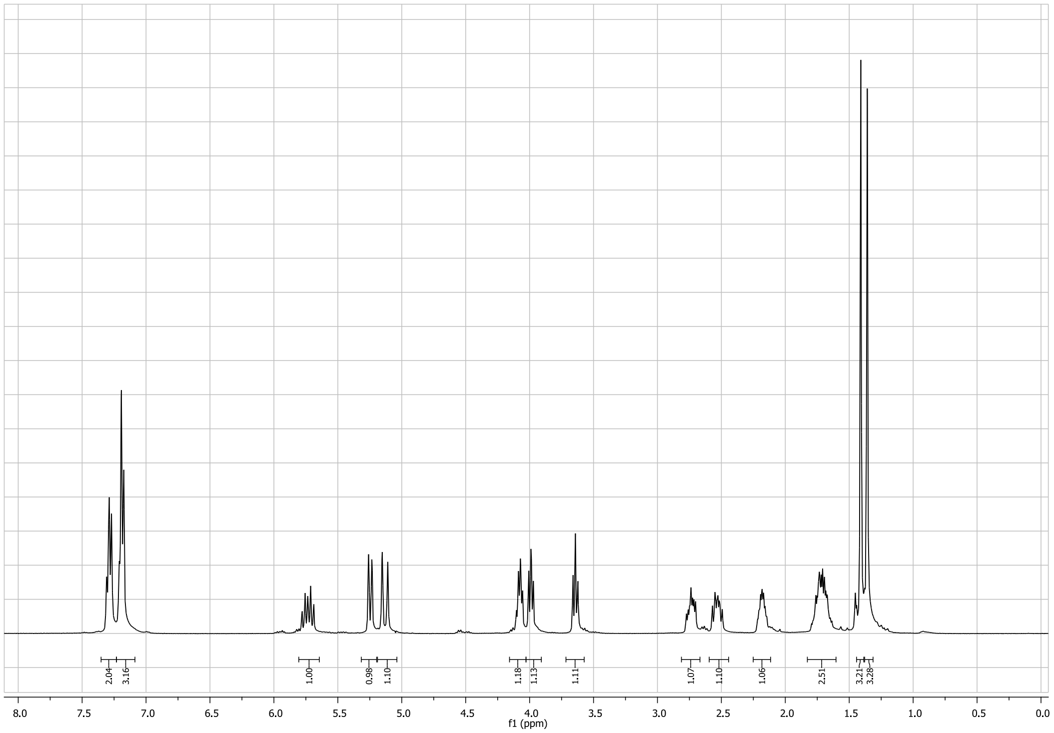
f1 (ppm)


O
O
Ph

***anti*-5c**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1.06
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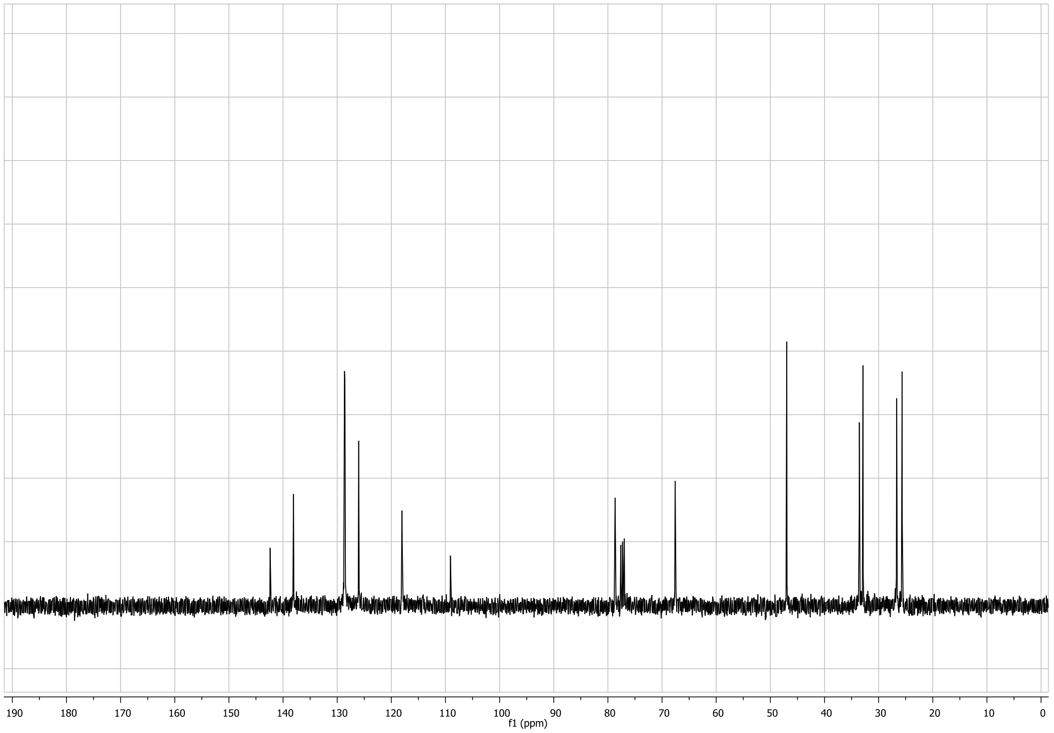
3.21
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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70
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30
20
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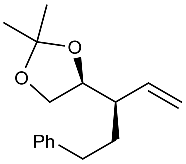
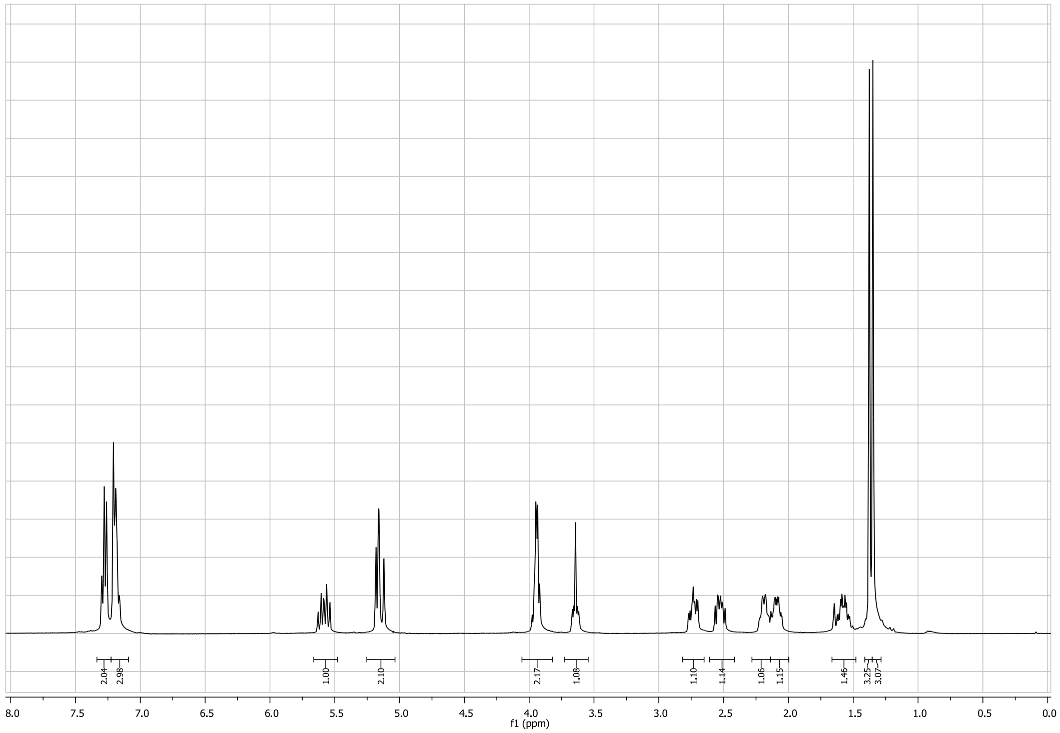
f1 (ppm)


O
O
Ph

***syn*-5c**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1.46
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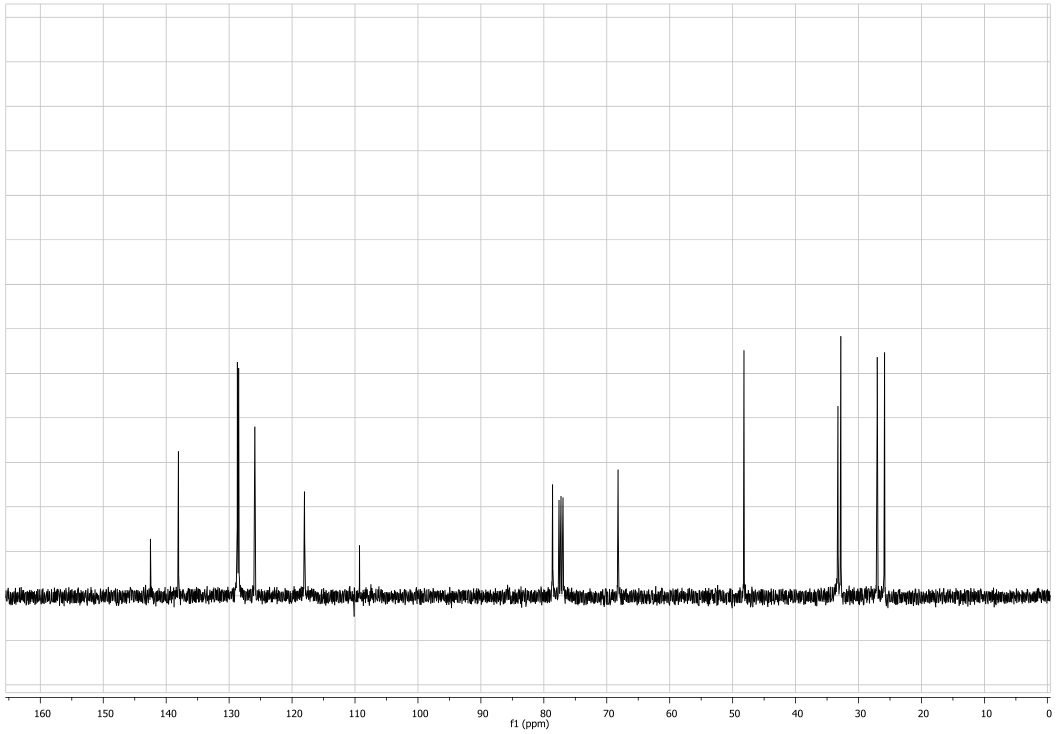
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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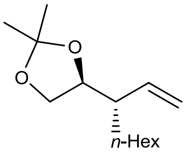
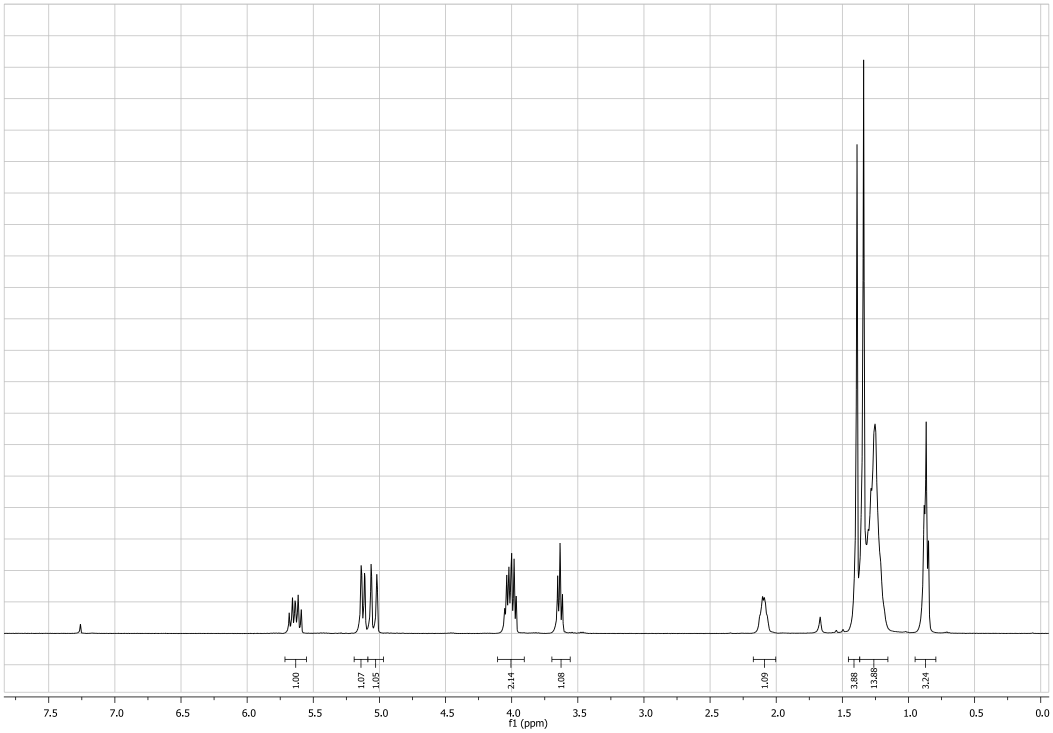
0
f1 (ppm)


O
O
n-Hex

***anti*-5d**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13.88
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6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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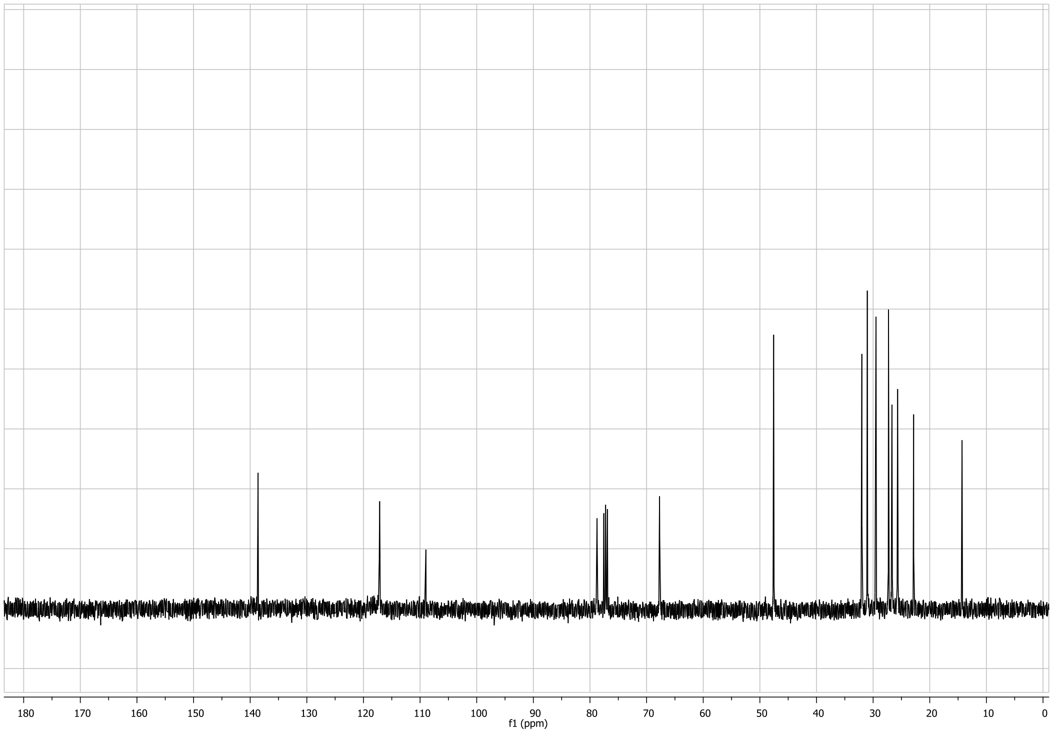
1.0
0.5
0.0
f1 (ppm)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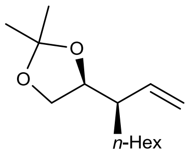
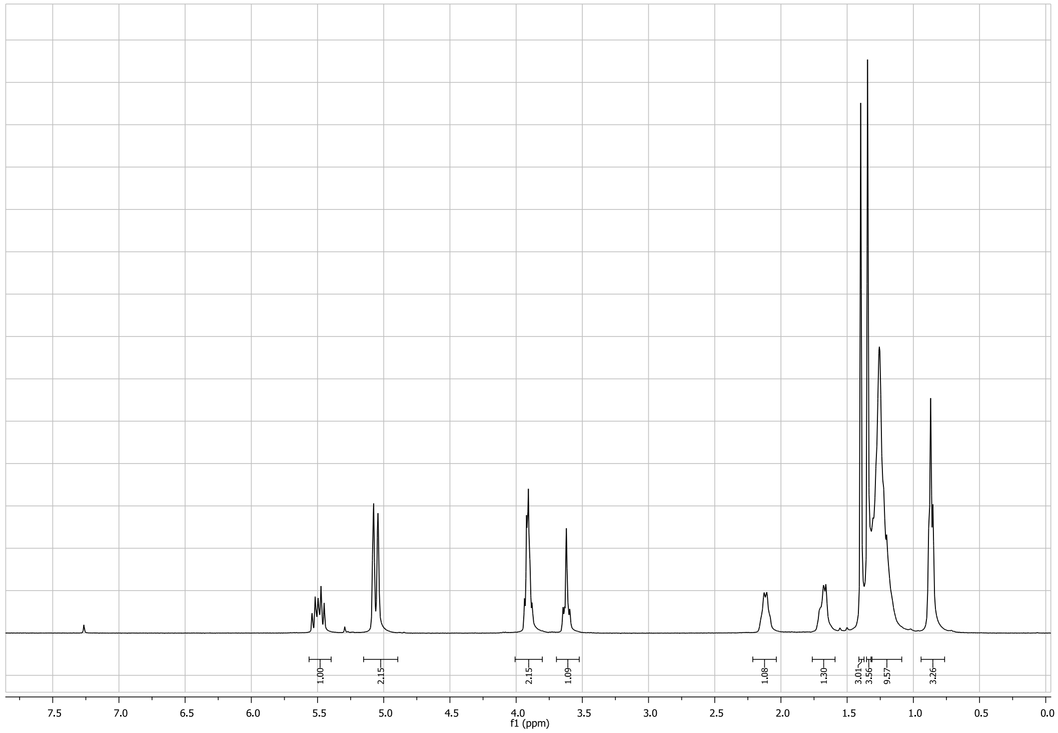
f1 (ppm)


O
O
n-Hex

***syn*-5d**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6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
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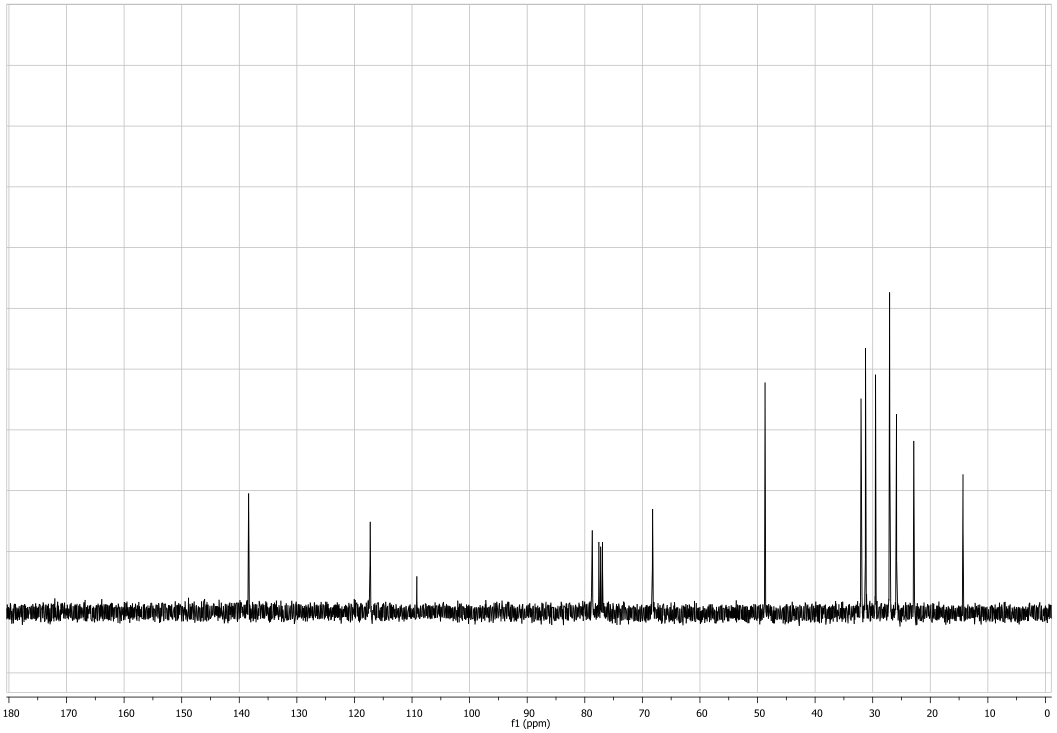
1.0
0.5
0.0
f1 (ppm)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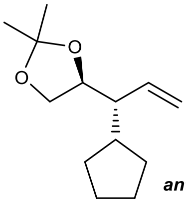
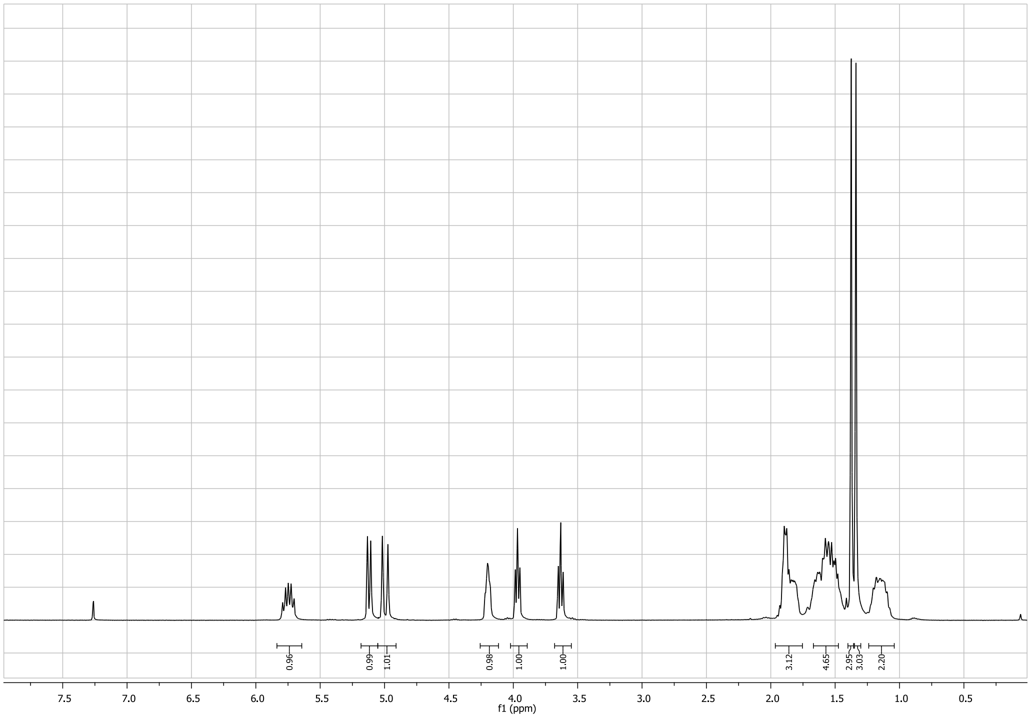
f1 (ppm)



***anti*-5e**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6.5
6.0
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3.0
2.5
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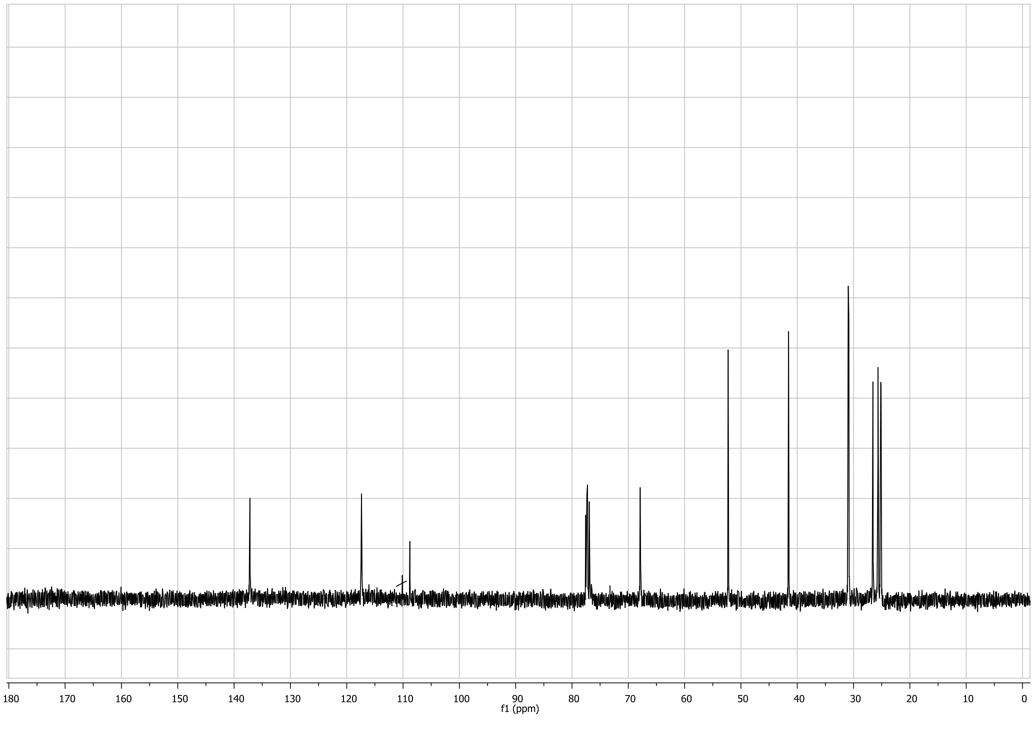
f1 (ppm)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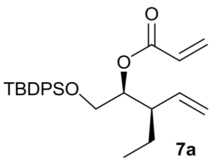
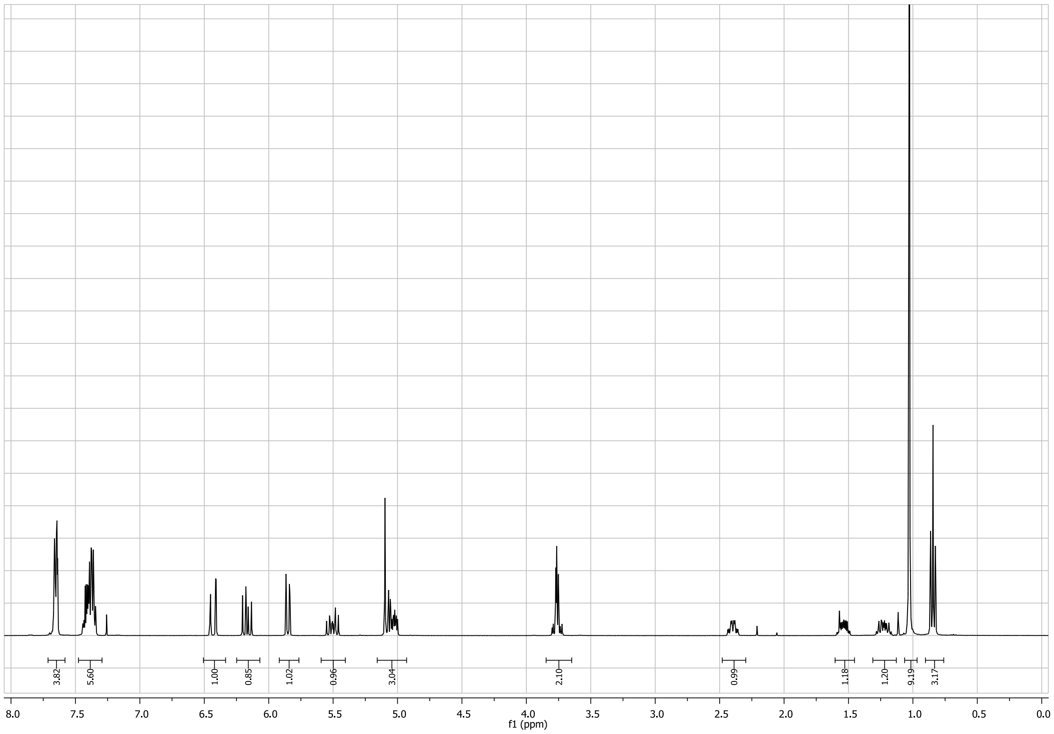
f1 (ppm)


O
O
TBDPSO

7a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0.96
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2.10
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1.20
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3.17
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
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1.0
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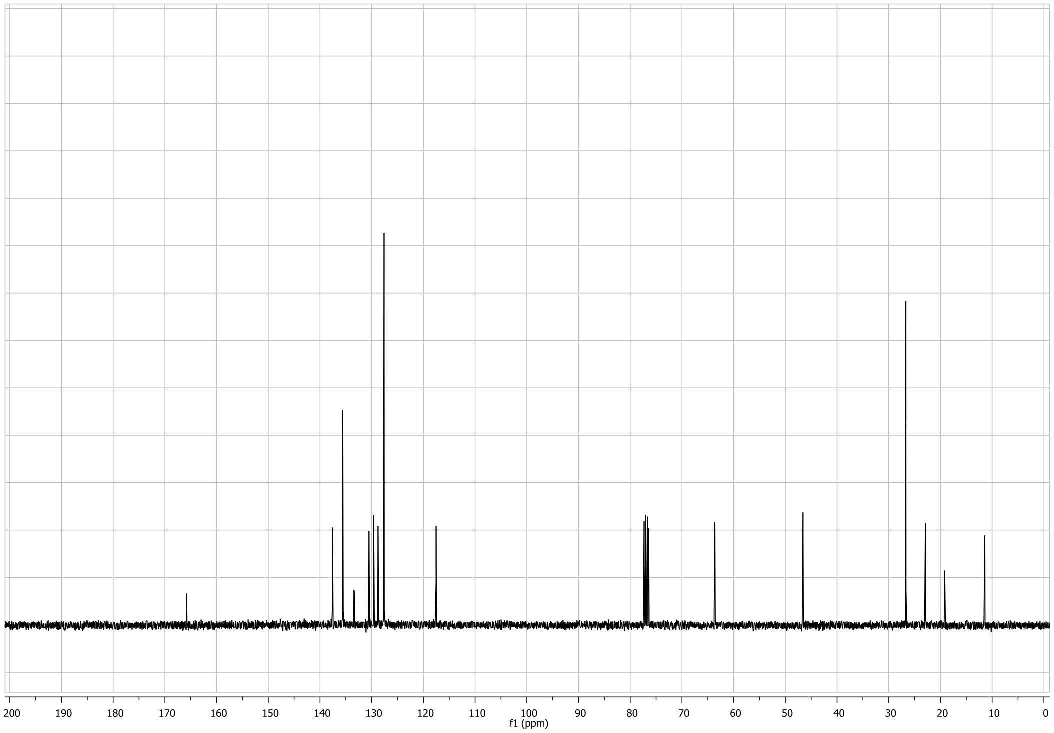
0.0
f1 (ppm)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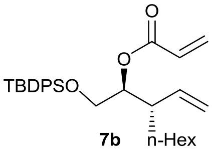
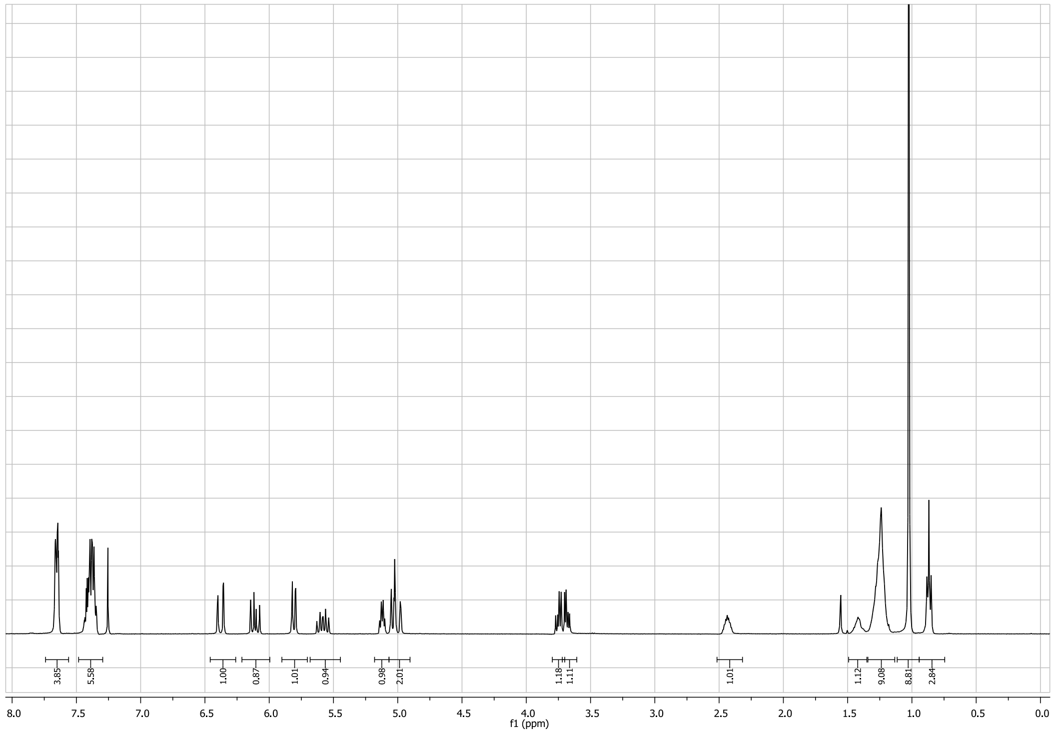
50
40
30
20
10
0
f1 (ppm)


O
O
TBDPSO
n-Hex

7b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1.11
1.01
1.12
9.08
8.81
2.84
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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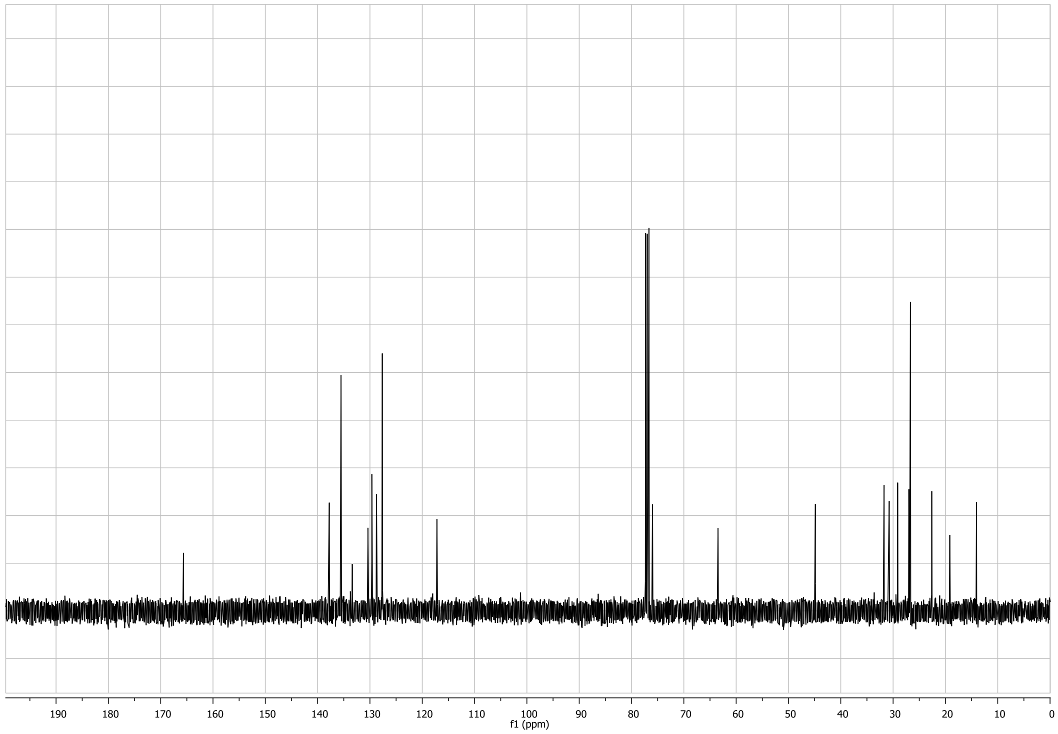
0.0
f1 (ppm)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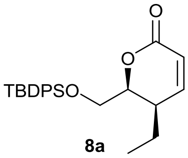
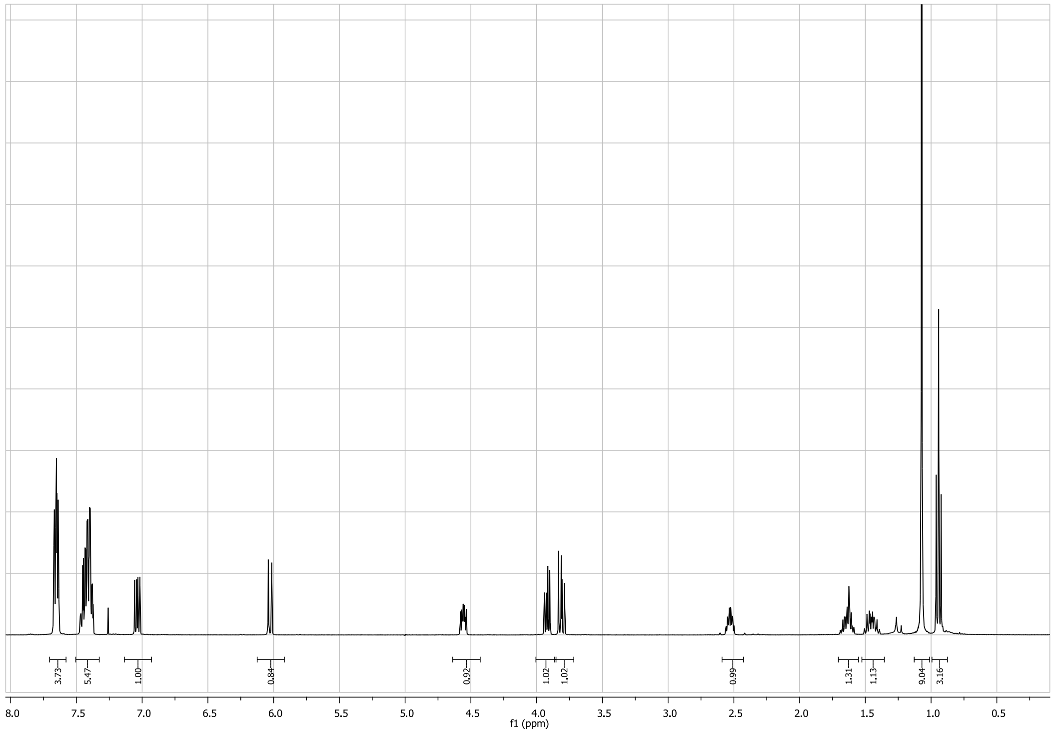
30
20
10
0
f1 (ppm)


O
O
TBDPSO

8a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0.99
1.31
1.13
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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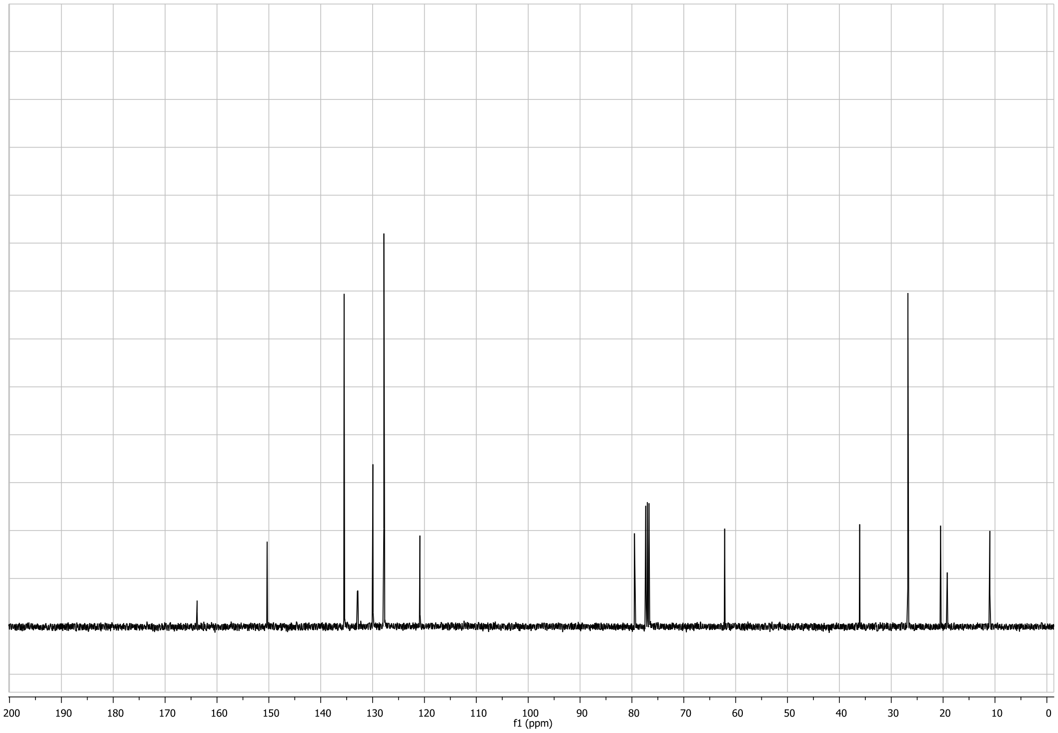
0.5
f1 (ppm)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110
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90
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70
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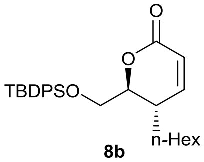
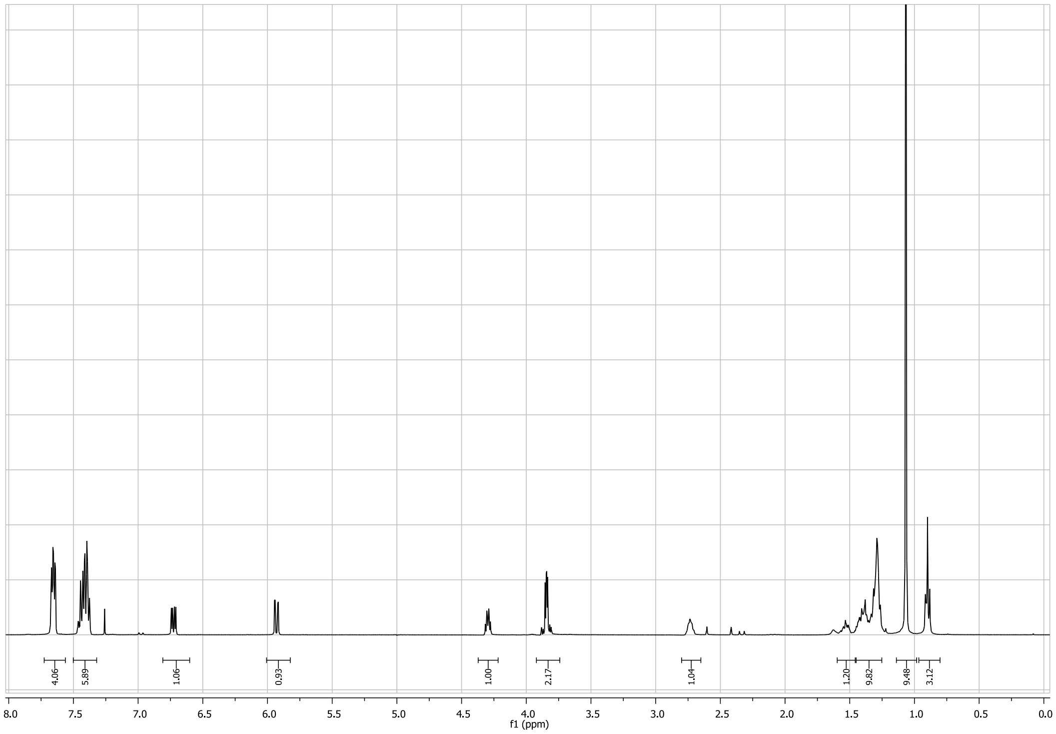
50
40
30
20
10
0
f1 (ppm)


O
O
TBDPSO
n-Hex

8b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1.04
1.20
9.82
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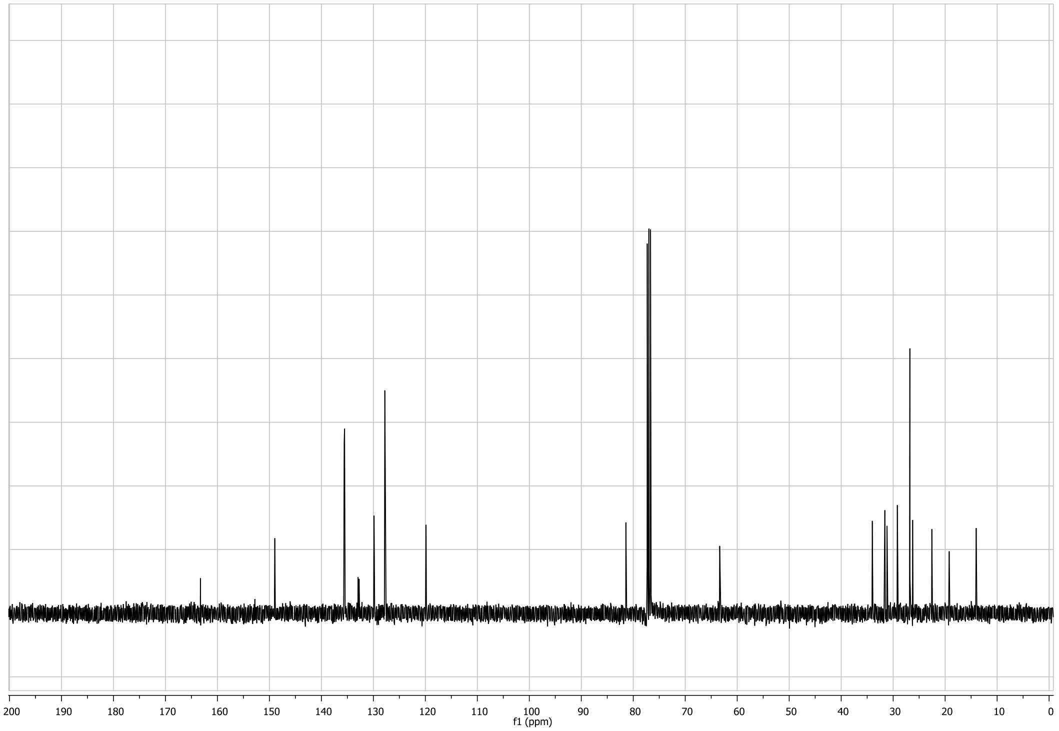
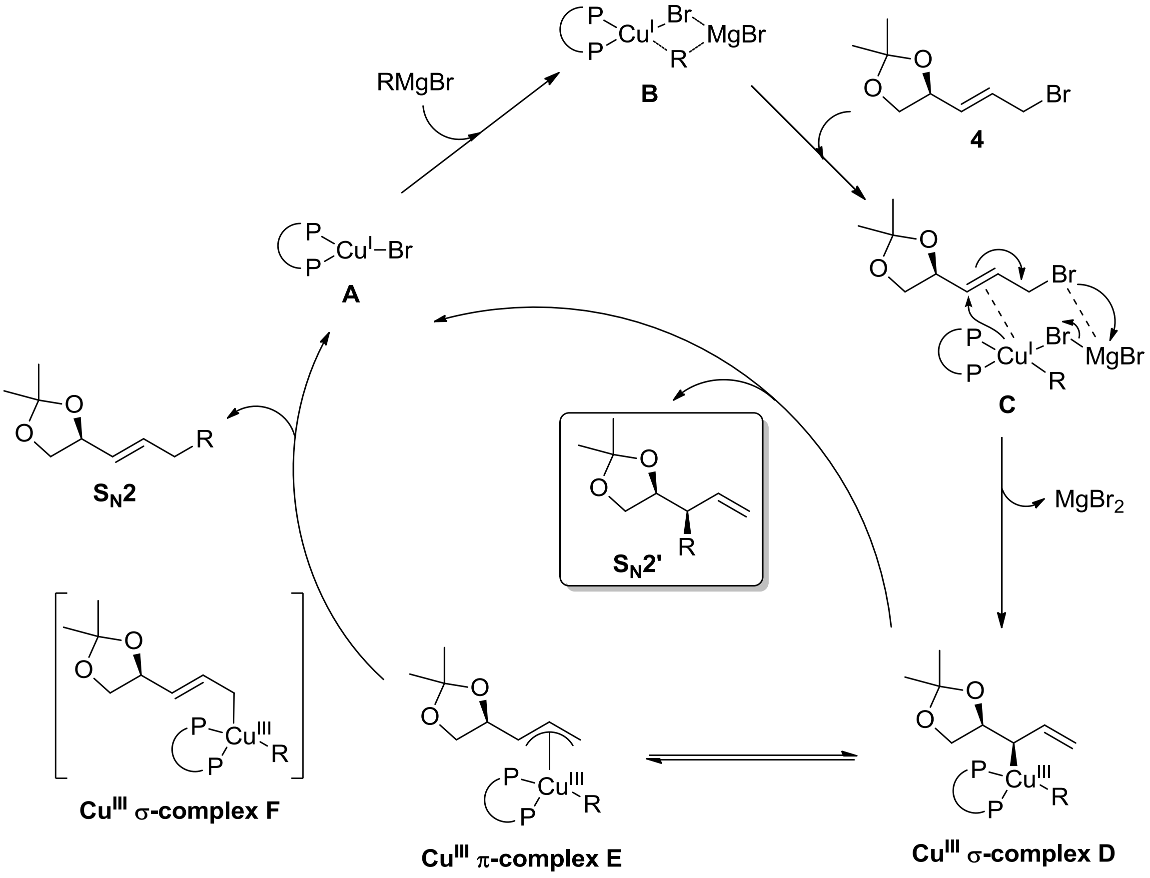
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Proposed mechanism for the copper-catalyzed AAA of allyl bromide 4 with Grignard reagents



In analogy with the proposed mechanism by Goering and co-workers,[3] the catalytic cycle depicted above can be proposed for the Cu-taniaphos catalyzed AAA of allyl bromide **4**. In this mechanism the precatalyst **A** and the Grignard reagent form the active catalyst **B**.[4] Subsequently, the interaction with allyl bromide **4** forms the Cu^I π-complex **C**. Oxidative addition and allylic rearrangement from **C** gives the Cu^{III} σ-complex **D** which leads to the S_N2' product via reductive elimination.

The formation of the competing S_N2 product can be explained through an isomerization of the Cu^{III} σ-complex **D** into the Cu^{III} π-complex **E**. It has been shown that this conversion of the Cu^{III} σ-complex into the Cu^{III} π-complex is faster at higher

---

[3] C. C. Tseng, S. D. Paisley, H. L. Goering, *J. Org. Chem.* 1986, **51**, 2884.

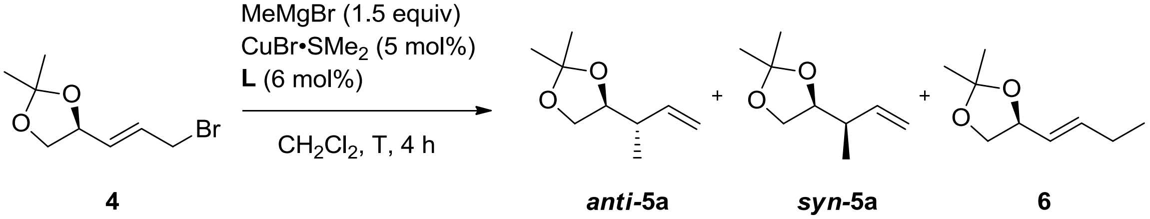
[4] S. Harutyunyan, F. López, W. R. Brown, A. Correa, D. Peña, R. Badorrey, A. Meetsma, A. J. Minnaard, B. L. Feringa, *J. Am. Chem. Soc.* 2006, **128**, 9103.

temperatures.[5] Intermediate **E** would evolve to the S_N2 product via reductive elimination (initially Goering and co-workers[ref1] proposed the formation of a **F** type Cu^{III} σ-complex before the reductive elimination can take place). Recent calculations by Nakamura and co-workers have shown that reductive elimination will proceed directly from the π-complex.[6]

GC traces for the temperature-depending experiments for the AAA of allyl bromide 4 with MeMgBr catalyzed by Cu-TaniaPhos (Table 1).

Product ratio was determined by GC analysis of the reaction crude, (GC, HP6890: MS HP5973) with an HP5 column, initial temp. 50°C then 10 °C/min to 270 °C (hold for 3 min, final temp).

Retention times (min): 4.2 (***syn*-5a**), 4.4 (***anti*-5a**); and 5.3 (**6**).



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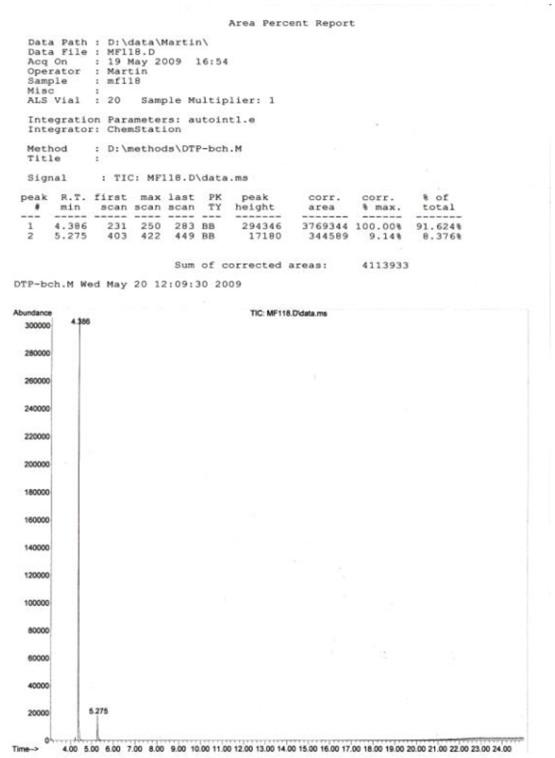
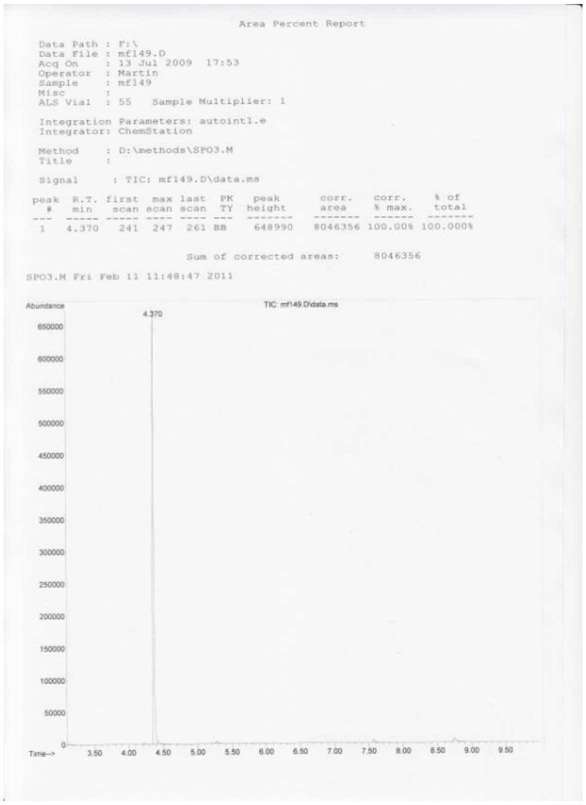
[5] E. R. Bartholomew, S. H. Bertz, S. Cope, M. Murphy, C. A. Ogle, *J. Am. Chem. Soc.* 2008, **130**, 11244.
[6] M. Yamanaka, S. Kato, E. Nakamura, *J. A. Chem. Soc.* 2004, **126**, 6287.

- L = (***R*,*R***)-(+)-taniaphos, T = -75 ^{o}C (Table 1, entry 1):



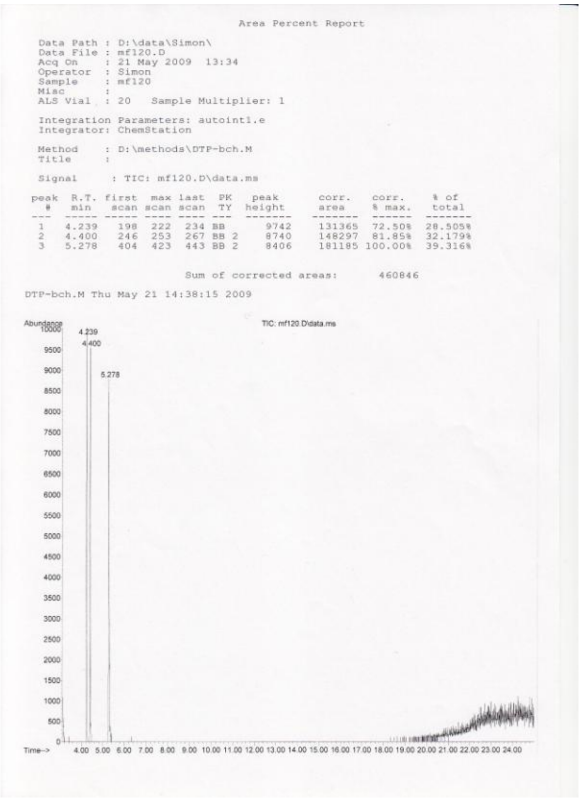
```
                              Area Percent Report

  Data Path : D:\data\Martin\
  Data File : MF118.D
  Acq On    : 19 May 2009  16:54
  Operator  : Martin
  Sample    : mf118
  Misc      :
  ALS Vial  : 20   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\methods\DTP-bch.M
  Title     :

  Signal     : TIC: MF118.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- ---  -------  ------- ------  -------
 1   4.386   231  250  283 BB    294346  3769344 100.00%  91.624%
 2   5.275   403  422  449 BB     17180   344589   9.14%   8.376%

                        Sum of corrected areas:     4113933

DTP-bch.M Wed May 20 12:09:30 2009
```

- L = (***R*,*R***)-(+)-taniaphos, T = -80 ^{o}C (Table 1, entry 11):



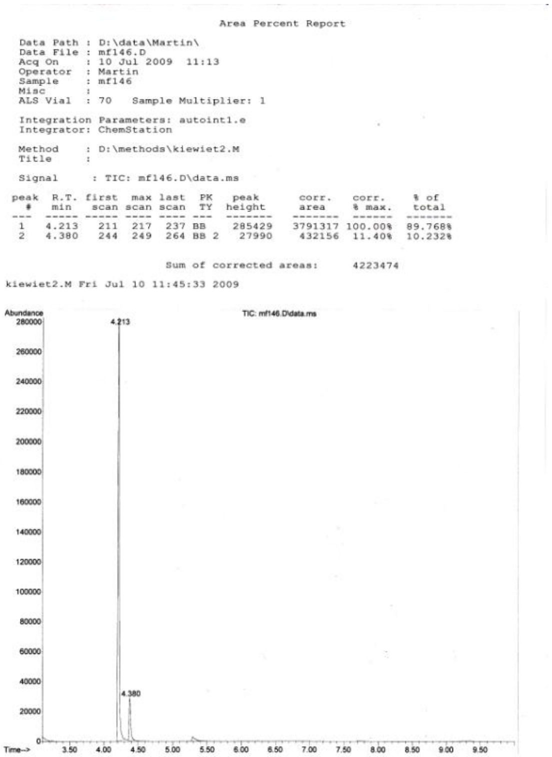
```
                              Area Percent Report

  Data Path : F:\
  Data File : mf149.D
  Acq On    : 13 Jul 2009  17:53
  Operator  : Martin
  Sample    : mf149
  Misc      :
  ALS Vial  : 55   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\methods\SPO3.M
  Title     :

  Signal     : TIC: mf149.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #   min   scan scan scan  TY  height     area    % max.   total
---  ----- ----- ---- ---- ---  -------  ------- ------  -------
 1   4.370   241  247  261 BB    648990  8046356 100.00% 100.000%

                        Sum of corrected areas:     8046356

SPO3.M Fri Feb 11 11:48:47 2011
```

- L = (*S*,*S*)-(-)-taniaphos, T = -75 $^{\mathrm{o}}$C (Table 1, entry 2):



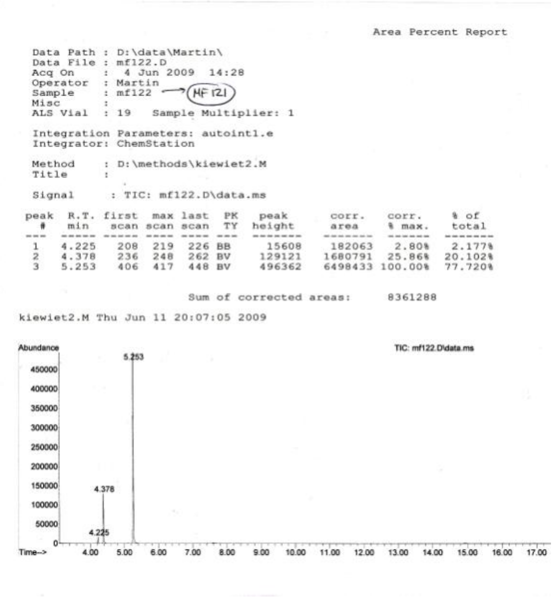
```
                         Area Percent Report

 Data Path : D:\data\Simon\
 Data File : mf120.D
 Acq On    : 21 May 2009  13:34
 Operator  : Simon
 Sample    : mf120
 Misc      :
 ALS Vial  : 20   Sample Multiplier: 1

 Integration Parameters: autoint1.e
 Integrator: ChemStation

 Method    : D:\methods\DTP-bch.M
 Title     :

 Signal     : TIC: mf120.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #    min  scan scan scan  TY  height     area   % max.   total
---  ----- ----- ---- ---- ---  -------   ------- ------  -------
 1   4.239   198  222  234 BB      9742    131365  72.50%  28.505%
 2   4.400   246  253  267 BB 2    8740    148297  81.85%  32.179%
 3   5.278   404  423  443 BB 2    8406    181185 100.00%  39.316%

                  Sum of corrected areas:      460846

DTP-bch.M Thu May 21 14:38:15 2009
```

- L = (*S*,*S*)-(-)-taniaphos, T = -80 $^{\mathrm{o}}$C (Table 1, entry 12):



```
                         Area Percent Report

 Data Path : D:\data\Martin\
 Data File : mf146.D
 Acq On    : 10 Jul 2009  11:13
 Operator  : Martin
 Sample    : mf146
 Misc      :
 ALS Vial  : 70   Sample Multiplier: 1

 Integration Parameters: autoint1.e
 Integrator: ChemStation

 Method    : D:\methods\kiewiet2.M
 Title     :

 Signal     : TIC: mf146.D\data.ms

peak  R.T. first  max last  PK   peak      corr.   corr.    % of
  #    min  scan scan scan  TY  height     area   % max.   total
---  ----- ----- ---- ---- ---  -------   ------- ------  -------
 1   4.213   211  217  237 BB    285429   3791317 100.00%  89.768%
 2   4.380   244  249  264 BB 2   27990    432156  11.40%  10.232%

                  Sum of corrected areas:     4223474

kiewiet2.M Fri Jul 10 11:45:33 2009
```

- L = (*S*,*S*)-(-)-taniaphos, T = -50 ^{o}C:



```
                                                   Area Percent Report

  Data Path : D:\data\Martin\
  Data File : mf122.D
  Acq On    :  4 Jun 2009  14:28
  Operator  : Martin
  Sample    : mf122 → MF 121
  Misc      :
  ALS Vial  : 19   Sample Multiplier: 1

  Integration Parameters: autoint1.e
  Integrator: ChemStation

  Method    : D:\methods\kiewiet2.M
  Title     :

  Signal     : TIC: mf122.D\data.ms

 peak  R.T. first  max last  PK   peak      corr.   corr.    % of
   #   min   scan scan scan  TY  height     area    % max.   total
 ---  ----- ----- ---- ---- ---  -------  ------- ------  -------
   1  4.225   208  219  226 BB     15608   182063   2.80%   2.177%
   2  4.378   236  248  262 BV    129121  1680791  25.86%  20.102%
   3  5.253   406  417  448 BV    496362  6498433 100.00%  77.720%

                          Sum of corrected areas:     8361288

kiewiet2.M Thu Jun 11 20:07:05 2009
```