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Supporting Information

69451 Weinheim, Germany

1,4-Dichloro and 1,4-dibromo-2-butene as substrates for Cu-catalyzed asymmetric allylic substitution

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Experimental Data :

General Remarks:

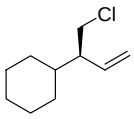
^{1}H (400 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400FTNMR in $CDCl_3$ unless otherwise stated, and chemical shift (δ) are given in ppm relative to residual $CHCl_3$. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet). Coupling constants are reported in Hertz (Hz). Evolution of reaction was followed by TLC and GC-MS (EI mode) on an HP6890. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 20°C in a 10 cm cell in the stated solvent ; $[\alpha]_D$ values are given in 10-1 deg.cm^2 g^{-1} (concentration c given as g/100 mL). Enantiomeric excesses were determined by chiral GC measurement either on a HP6890 (H_2 as vector gas) or HP6850 (H_2 as vector gas) with the stated column or. Temperature programs are described as follows: initial temperature (°C) - initial time (min) - temperature gradient (°C/min) - final temperature (°C); retention times (R_T) are given in min. In some cases, enantiomeric excess were determined by chiral SFC measurement on a Berger SFC with the stated column. Gradient programs are described as follows: initial methanol concentration (%) - initial time (min) – percent gradient of methanol (%/min) – final methanol concentration (%).

Flash chromatography was performed using silicagel 32-63 μm, 60 Å. THF, diethylether, *n*-hexane and dichloromethane were dried by filtration over alumina (activated at 350 °C under nitrogen atmosphere for 12 h). Copper (I) thiophenecarboxylate (CuTC) was purchased from Frontier Scientific. *Trans*-1,4-dichloro-2-butene and *trans*-1,4-dibromo-2-butene were purchased from Fluka, and *cis*-1,4-dichloro-2-butene was purchased from Aldrich.

Typical procedure for the enantioselective copper catalyzed allylic substitution with Grignard reagents:

CuTC (1 mol%) and chiral ligand (1.1 mol%) are charged in a dried Schlenk tube, under inert gas, and suspended in dichloromethane (2 mL). The mixture is stirred at room temperature for 30 min, followed by the addition of the allylic halide (1 mmol) at r.t. before cooling the mixture to –78°C in an ethanol-dry ice cold bath. The Grignard (3 M in diethyl ether, 1.2 eq) diluted in CH_2Cl_2 (0.6 mL) is added over 60 min *via* a syringe pump. Upon completion of the addition, the reaction mixture is left a further 4h at -78°C. The reaction is quenched by addition of aqueous HCl (1N, 2 mL) and then Et_2O (10 mL). Aqueous phase is separated and further extracted with Et_2O (3 x 3mL). The combined organic fractions are washed with brine (5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The oily residue is purified by flash column chromatography. Gas Chromatography on a chiral stationary phase shows the enantiomeric excess of the S_N2' product.

(-)-*(S)-(1-Chlorobut-3-en-2-yl)cyclohexane* 3a



SiO_2, pentane, R_F = 0.80.

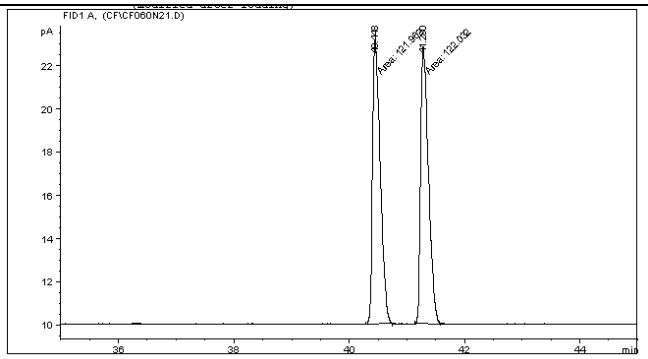
^{1}H NMR (400 MHz, $CDCl_3$) : 5.71-5.63 (*m*, 1H), 5.15-5.04 (*m*, 2H), 3.62-3.52 (*m*, 2H), 2.19-2.13 (*m*, 1H), 1.75-1.63 (*m*, 6H), 1.32-0.87 (*m*, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) : 137.9, 117.6, 51.9, 47.1, 38.8, 31.0, 29.5, 26.6, 26.5, 26.5.

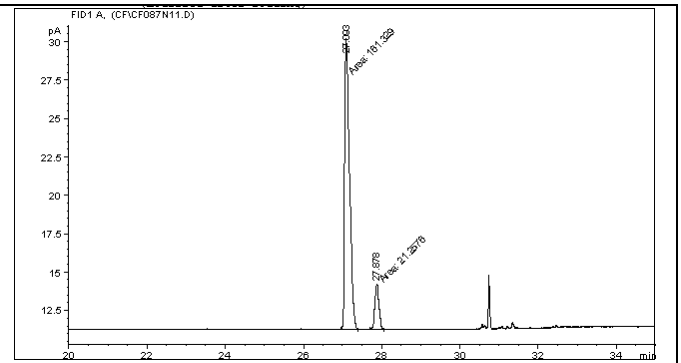
MS (EI mode) *m/z* (%) : 172(M+, 1), 136(1), 123(1), 116(2), 109(2), 96(3), 91(3), 83(67), 67(19), 54(100).

$[\alpha]_D^{22}$ = - 34.9 (*c* 1.1, $CHCl_3$) for 75% ee.

Ee was measured by chiral GC with a Chirasil-Dex CB column, Helium flow (program: 85-0-1-170) R_T: 27.65 (+), 28.53 (-).

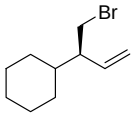


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.448	MM	0.1544	121.96193	13.16786	49.98559
2	41.280	MM	0.1584	122.03226	12.83858	50.01441



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	27.093	MM	0.1426	161.32893	18.86064	88.35750
2	27.878	MM	0.1213	21.25764	2.92099	11.64250

(-)-(S)-(1-Bromobut-3-en-2-yl)cyclohexane **3b**



SiO_2, pentane, R_F = 0.79.

IR (neat): 3077(w), 2923(s), 2852(m), 1640(w), 1449(m), 1435(m), 1279(m), 1236(w), 994(m), 916(s), 705(m), 655(m) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) : 5.69-5.60 (*m*, 1H), 5.15-5.03 (*m*, 2H), 3.50-3.40 (*m*, 2H), 2.20-2.13 (*m*, 1H), 1.75-1.63 (*m*, 5H), 1.54-1.45 (*m*, 1H), 1.31-0.86 (*m*, 5H).

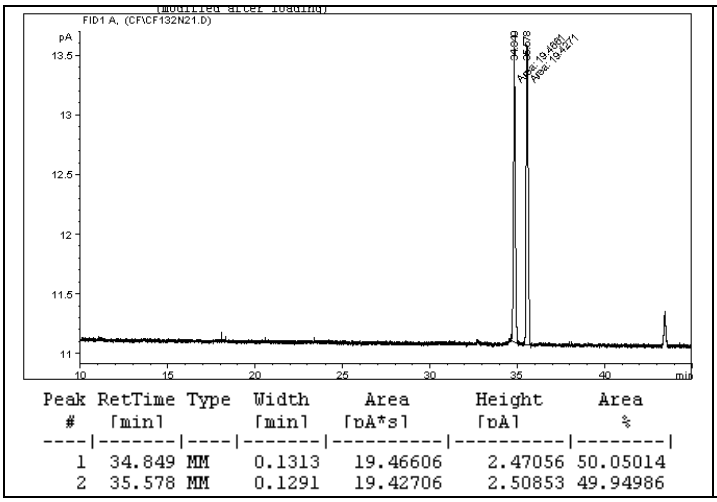
^{13}C NMR (100 MHz, $CDCl_3$) : 138.3, 117.5, 51.5, 39.7, 36.9, 30.9, 29.4, 26.5, 26.5, 26.4.

MS (EI mode) *m/z* (%) : 137(4), 83(68), 82(24), 81(18), 67(21), 55(94), 54(100), 53(15).

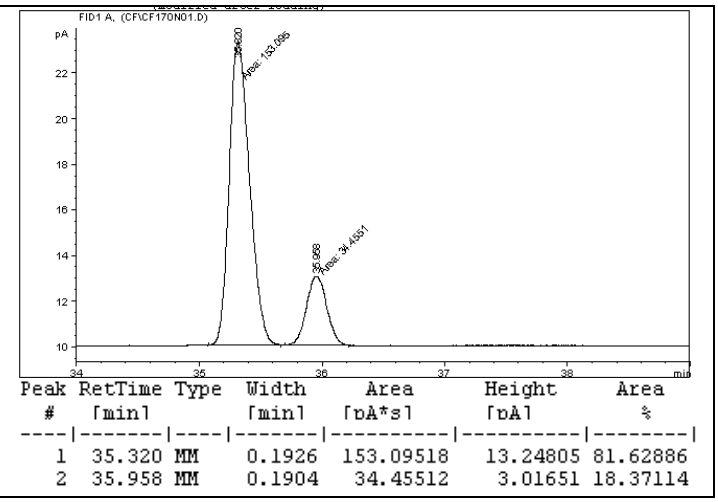
HR-MS : calc. mass= 137.1331, mass found= 137.1330.

$[\alpha]_D^{22}$ = + 2.27 (*c* 1.24, $CHCl_3$) for 52% ee on *ent*-**3b**.

Ee was measured by chiral GC with a Chirasil- Dex CB, Helium flow (program: 100-0-1-170) R_T: 35.53 (+), 36.20 (-).

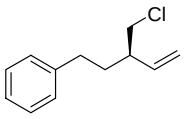


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	34.849	MM	0.1313	19.46606	2.47056	50.05014
2	35.578	MM	0.1291	19.42706	2.50853	49.94986



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	35.320	MM	0.1926	153.09518	13.24805	81.62886
2	35.958	MM	0.1904	34.45512	3.01651	18.37114

(-)-(R)-(3-(Chloromethyl)pent-4-enyl)benzene **6a**



SiO_2, pentane, R_F = 0.38.

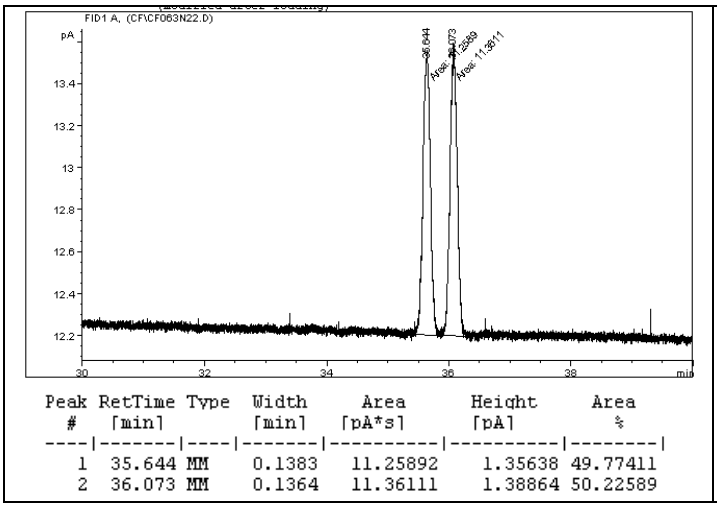
^1H NMR (400 MHz, $CDCl_3$) : 7.33-7.28 (*m*, 2H), 7.23-7.18 (*m*, 3H), 5.73 (*ddd*, J=8.3 Hz, J=10.3 Hz, J=17.2 Hz, 1H), 5.23 (*d*, J=10.3 Hz, 1H), 5.18 (*d*, J=17.2 Hz, 1H), 3.54 (*d*, J=5.8 Hz, 2H), 2.75-2.55 (*m*, 2H), 2.47-2.39 (*m*, 1H), 1.99-1.90 (*m*, 1H), 1.75-1.65 (*m*, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) : 142.0, 138.8, 128.5, 128.5, 128.3, 128.3, 126.0, 117.6, 48.8, 45.4, 33.6, 33.1.

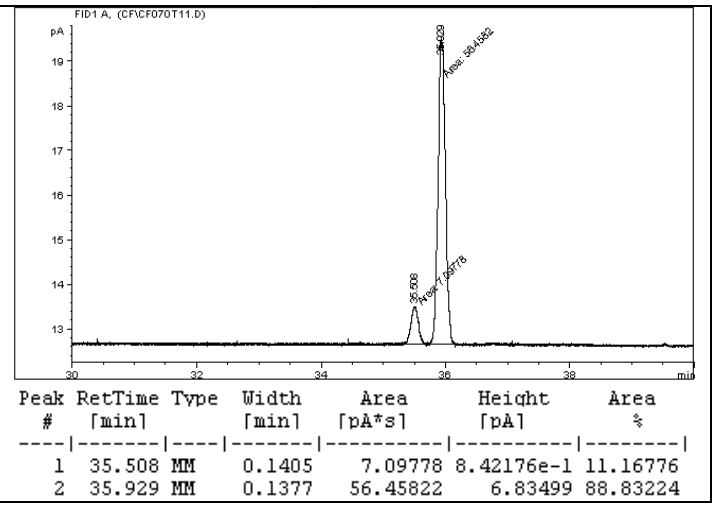
MS (EI mode) *m/z* (%) : 194 (M+, 2), 179(2), 158(11), 143(11), 129(20), 117(7), 104(83), 91(100), 77(11), 65(14), 51(7).

$[\alpha]_D^{22}$ = - 6.13 (*c* 0.62, $CHCl_3$) for 77% ee.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 90-0-1-170) R_T: 35.50 (+), 35.94 (-).

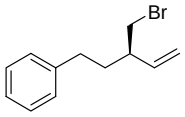


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	35.644	MM	0.1383	11.25892	1.35638	49.77411
2	36.073	MM	0.1364	11.36111	1.38864	50.22589



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	35.508	MM	0.1405	7.09778	8.42176e-1	11.16776
2	35.929	MM	0.1377	56.45822	6.83499	88.83224

(-)-(R)-(3-(Bromomethyl)pent-4-enyl)benzene **6b**



SiO_2, pentane, R_F = 0.47.

IR (neat): 3063(w), 3026(w), 2926(br), 2857(w), 1641(w), 1603(m), 1496(m), 1454(m), 1258(br), 1222(br), 1030(m), 992(m), 919(s), 745(s), 697(s) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) : 7.30-7.26 (*m*, 2H), 7.21-7.17 (*m*, 3H), 5.68 (*ddd*, J_1= 8.3 Hz, J_2= 10.4 Hz, J_3= 17.2 Hz, 1H), 5.20 (*dd*, J_1= 10.4 Hz, J_2= 1.5 Hz, 1H), 5.15 (*ddd*, J_1= 17.2 Hz, J_2= 1.5 Hz, 1H), 3.40 (*d*, *J*= 5.8 Hz, 2H), 2.71-2.53 (*m*, 2H), 2.45-2.36 (*m*, 1H), 1.97-1.88 (*m*, 1H), 1.73-1.64 (*m*, 1H).

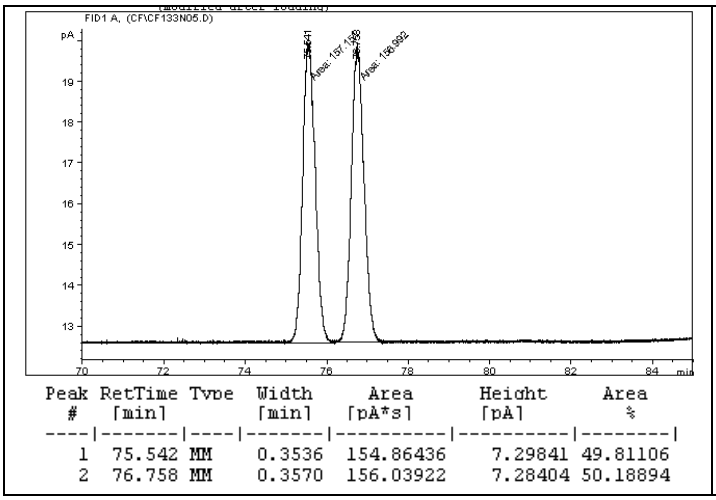
^{13}C NMR (100 MHz, $CDCl_3$) : 141.9, 139.3, 128.7, 128.5, 128.3, 126.0, 125.8, 117.5, 45.0, 38.2, 34.7, 33.2.

MS (EI mode) *m/z* (%) : 159(7), 158(17), 143(7), 129(15), 117(10), 105(30), 104(60), 92(18), 91(100), 77(10), 65(13).

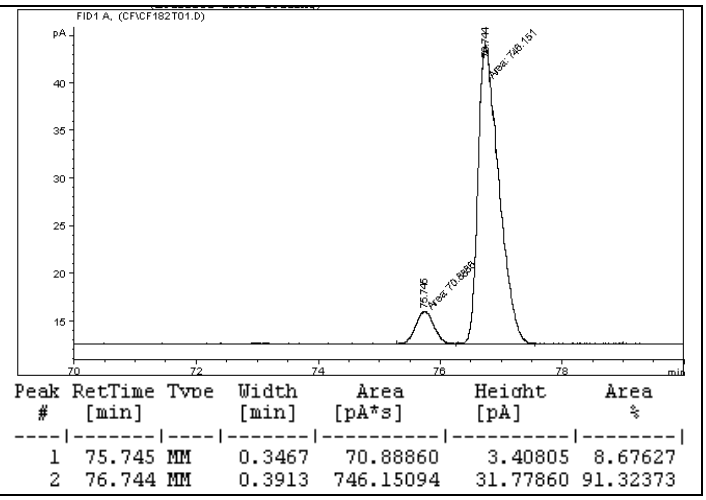
HR-MS : (-HBr, -81) calc. mass= 158.1096, mass found= 158.1095.

$[\alpha]_D^{22}$ = + 6.91 (*c* 0.91, $CHCl_3$) for 76% ee on *ent*-**5b**.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 110-65-1-170) R_T: 75.74 (+), 76.74 (-).

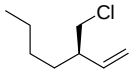


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	75.542	MM	0.3536	154.86436	7.29841	49.81106
2	76.758	MM	0.3570	156.03922	7.28404	50.18894



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	75.745	MM	0.3467	70.88860	3.40805	8.67627
2	76.744	MM	0.3913	746.15094	31.77860	91.32373

(-)-(R)-3-(Chloromethyl)hept-1-ene **7a**



SiO_2, pentane, R_F = .

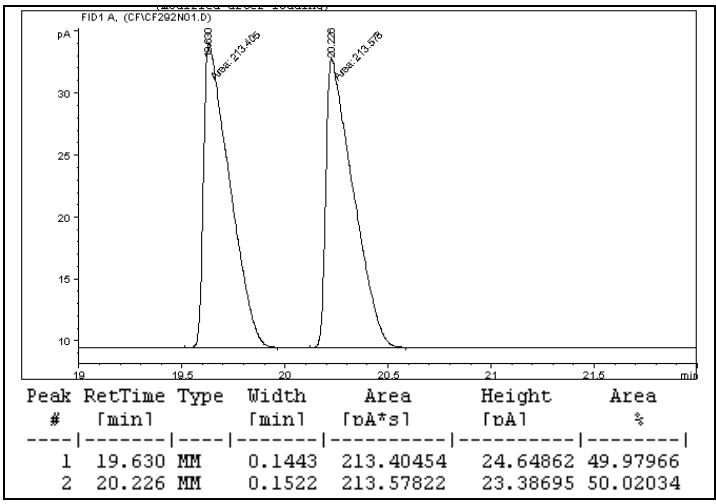
^{1}H NMR (500 MHz, $CDCl_3$) : 5.64 (*ddd*, J_1= 8.5 Hz, J_2= 10.4 Hz, J_3= 17.0 Hz, 1H), 5.13-5.08 (*m*, 2H), 3.49 (*dd*, J_1= 1.6 Hz, J_2= 6.0 Hz, 2H), 2.38-2.31 (*m*, 1H), 1-60-1.53 (*m*, 1H), 1.37-1.21 (*m*, 5H), 0.90 (*t*, *J*= 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) : 139.4, 116.8, 48.9, 46.0, 31.7, 29.1, 22.8, 14.1.

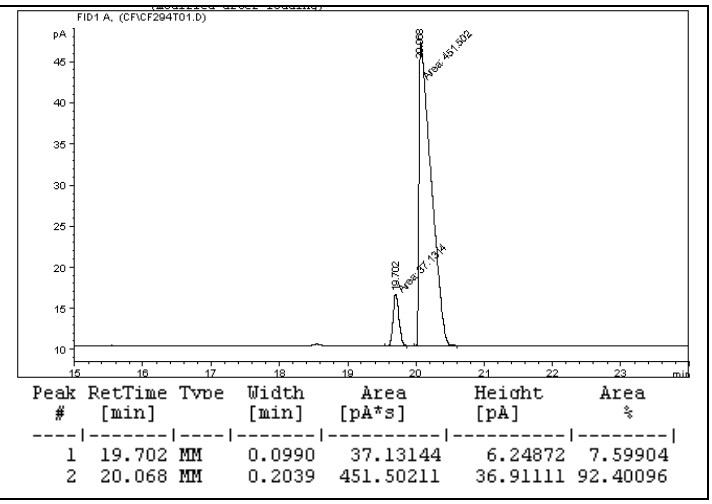
MS (EI mode) *m/z* (%) : 197(13), 95(47), 69(10), 59(30), 57(100), 55(22), 43(11), 41(22), 32(13), 31(18), 29(15).

$[\alpha]_D^{22}$ = - 10.2 (*c* 1.33, $CHCl_3$) for 85% *ee*.

Ee was measured by chiral GC with a Chirasil Dex-CB column, Helium flow (program: 60-0-1-170) R_T: 19.51 (+), 20.14 (-).

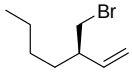


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.630	MM	0.1443	213.40454	24.64862	49.97966
2	20.226	MM	0.1522	213.57822	23.38695	50.02034



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.702	MM	0.0990	37.13144	6.24872	7.59904
2	20.068	MM	0.2039	451.50211	36.91111	92.40096

(-)-(R)-3-(Bromomethyl)hept-1-ene **7b**



SiO_2, pentane, R_F = .

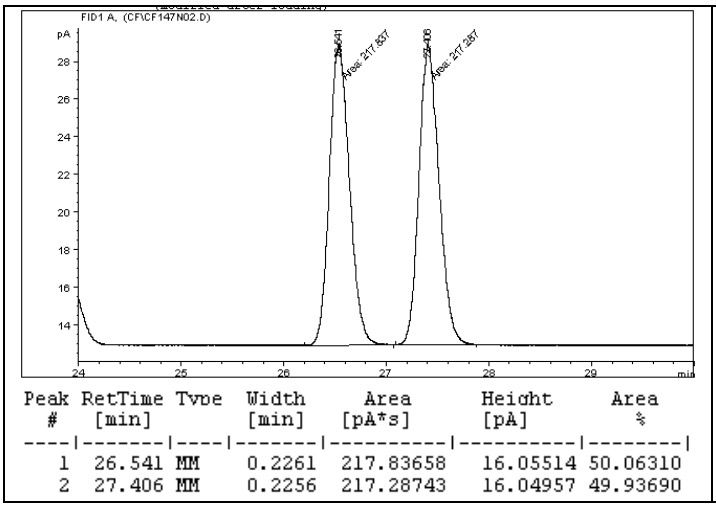
^{1}H NMR (400 MHz, $CDCl_3$) : 5.68-5.56 (*m*, 1H), 5.14-5.06 (*m*, 2H), 3.38 (*d*, *J*=8.3Hz, 2H), 2.36-2.30 (*m*, 1H), 1.36-1.25 (*m*, 6H), 0.90 (*t*, *J*=8.4Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) : 139.9, 116.7, 45.7, 38.5, 32.8, 29.2, 22.7, 14.1.

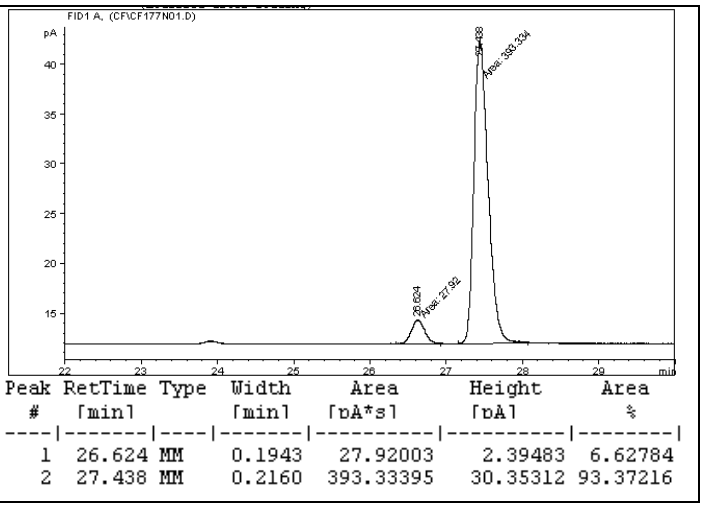
MS (EI mode) *m/z* (%) : 150(4), 148(4), 136(9), 134(9), 111(5), 95(5), 83(8), 81(8), 69(76), 67(18), 57(13), 56(12), 55(100), 54(39), 53(34), 51(8).

$[\alpha]_D^{22}$ = + 25.81 (*c* 1.36, $CHCl_3$) for 82% ee on *ent*-**6b**.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 60-0-1-170) R_T: 26.5 (+), 27.4 (-).

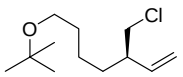


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.541	MM	0.2261	217.83658	16.05514	50.06310
2	27.406	MM	0.2256	217.28743	16.04957	49.93690



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.624	MM	0.1943	27.92003	2.39483	6.62784
2	27.438	MM	0.2160	393.33395	30.35312	93.37216

(-)-(R)-7-tert-Butoxy-3-(chloromethyl)hept-1-ene **8a**



SiO_2, pentane/ Et_2O 97.5:2.5, R_F = 0.40.

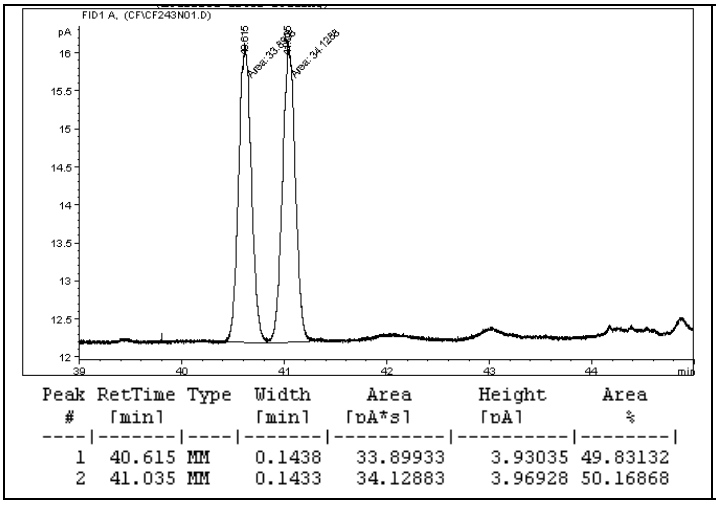
^{1}H NMR (400 MHz, $CDCl_3$) : 5.68-5.59 (*m*, 1H), 5.13-5.08 (*m*, 2H), 3.48 (*d*, *J*=6.3Hz, 2H), 3.32 (*t*, *J*=6.6Hz, 2H), 2.40-2.32 (*m*, 1H), 1.63-1.46 (*m*, 3H), 1.43-1.25 (*m*, 3H), 1.18 (*s*, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) : 139.2, 116.9, 72.6, 61.4, 48.8, 46.0, 31.8, 30.7, 27.7(3), 23.6.

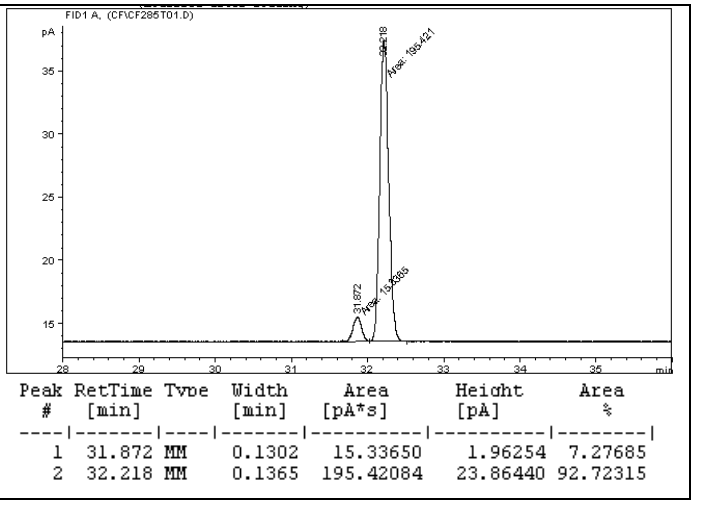
MS (EI mode) *m/z* (%) : 205(15), 203(45), 109(52), 67(23), 59(79), 57(100), 56(12), 55(22).

$[\alpha]_D^{22}$ = - 5.34 (*c* 1.22, $CHCl_3$) for 79% ee.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 80-0-1-170) R_T: 40.61 (+), 50.08 (-).

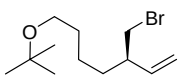


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.615	MM	0.1438	33.89933	3.93035	49.83132
2	41.035	MM	0.1433	34.12883	3.96928	50.16868



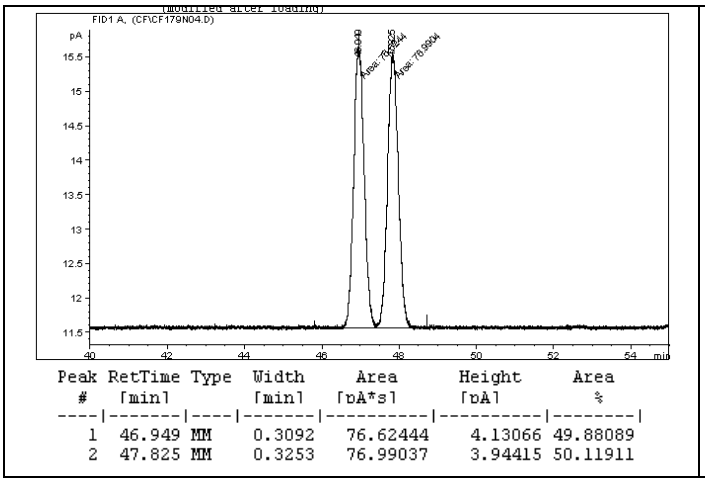
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.872	MM	0.1302	15.33650	1.96254	7.27685
2	32.218	MM	0.1365	195.42084	23.86440	92.72315

(-)-(R)-7-tert-Butoxy-3-(bromomethyl)hept-1-ene **8b**

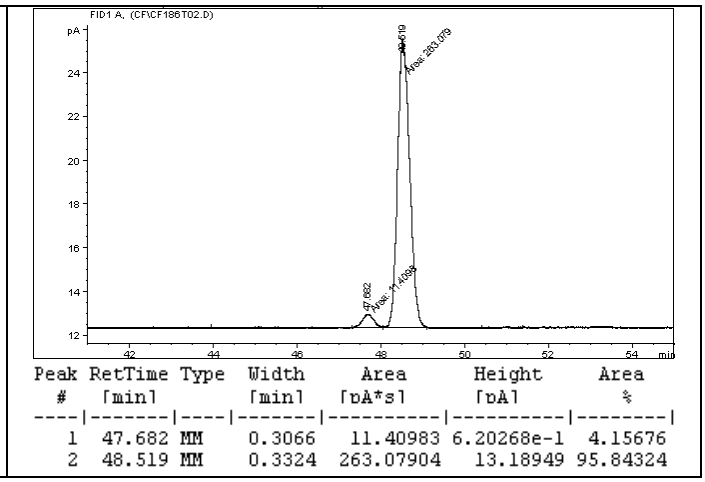


SiO_2, pentane/Et_2O 97.5:2.5, R_F = 0.31.
IR (neat): 3071(w), 2973(m), 2935(m), 2864(m), 1642(w), 1459(br), 1390(w), 1362(m), 1197(s), 1082(s), 992(m), 917(s), 877(br), 751(w), 695(m), 653(m) cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) : 5.66-5.57 (*m*, 1H), 5.13-5.07 (*m*, 2H), 3.37 (*dd*, J_1=1.8Hz, J_2=6.0Hz 2H), 3.32 (*t*, *J*=6.8Hz, 2H), 2.39-2.34 (*m*, 1H), 1.60-1.21 (*m*, 6H), 1.17 (*s*, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) : 139.7, 116.8, 72.6, 61.5, 45.7, 38.4, 32.9, 30.6, 27.7(3), 23.7.
MS (EI mode) *m/z* (%) : 250(2), 249(15), 247(15), 135(6), 133(6), 110(5), 109(57), 108(5), 81(6), 69(7), 67(30), 59(70), 58(7), 57(100), 56(15), 55(28), 54(6), 53(12).
HR-MS : (-O, -16) calc. mass= 247.0698, mass found= 247.0698.
$[\alpha]_D^{22}$ = - 5.50 (*c* 1.07, $CHCl_3$) for 92% ee.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 110-33-0.5-115-10-20-170) R_T: 47.70 (+), 48.52 (-).

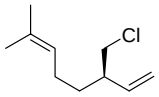


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.949	MM	0.3092	76.62444	4.13066	49.88089
2	47.825	MM	0.3253	76.99037	3.94415	50.11911



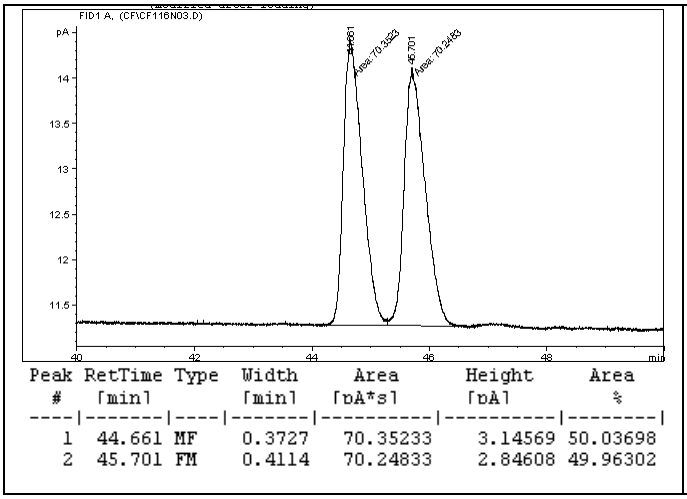
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	47.682	MM	0.3066	11.40983	6.20268e-1	4.15676
2	48.519	MM	0.3324	263.07904	13.18949	95.84324

(-)-(R)-3-(Chloromethyl)-7-methylocta-1,6-diene **9a**

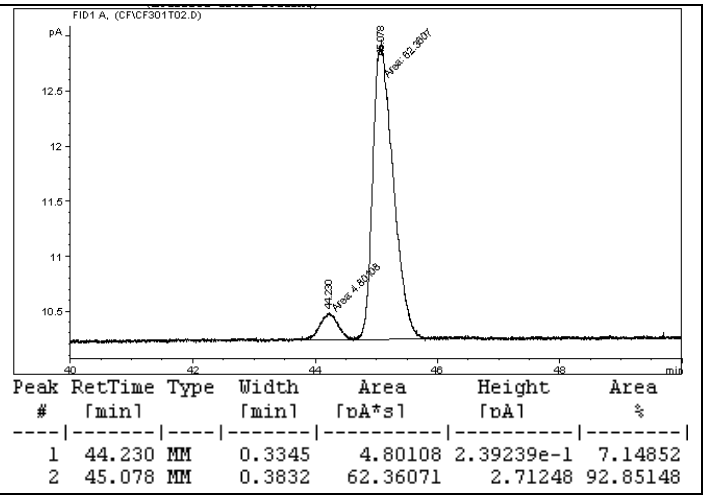


SiO_2, pentane, R_F = 0.79.
IR (neat): 3073(w), 2967(m), 2918(s), 2856(m), 2722(w), 1641(w), 1441(br), 1377(m), 1105(br), 992(s), 919(s), 831(br), 742(s) cm^{-1}.
^1H NMR (500 MHz, $CDCl_3$) : 5.65 (*ddd*, J_1= 8.6 Hz, J_2= 10.4 Hz, J_3= 17.4 Hz, 1H), 5.15-5.07 (*m*, 3H), 3.50 (*dd*, J_1= 2.2 Hz, J_2= 6.0 Hz, 2H), 2.41-2.34 (*m*, 1H), 2.06-1.91 (*m*, 2H), 1.69 (*s*, 3H), 1.59 (*s*, 3H), 1.43-1.39 (*m*, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) : 139.2, 132.2, 124.0, 117.0, 48.8, 45.5, 32.1, 25.9, 25.4, 17.9.
MS (EI mode) *m/z* (%) : 174(3), 172(M^+, 9), 159(2), 157(7), 129(19), 123(22), 121(8), 107(5), 102(7), 95(13), 93(44), 91(13), 83(19), 82(69), 81(40), 80(12), 79(29), 77(14), 70(11), 69(100), 68(20), 67(81), 65(12), 56(16), 55(95), 54(18), 53(44), 51(13).
$[\alpha]_D^{22}$ = - 2.75 (*c* 0.76, $CHCl_3$) for 85% ee.

Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 50-10-1-170) R_T: 49.58 (+), 50.63 (-).

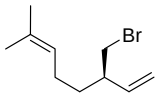


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.661	MF	0.3727	70.35233	3.14569	50.03698
2	45.701	FM	0.4114	70.24833	2.84608	49.96302



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.230	MM	0.3345	4.80108	2.39239e-1	7.14852
2	45.078	MM	0.3832	62.36071	2.71248	92.85148

(-)-(R)-3-(Bromomethyl)-7-methylocta-1,6-diene **9b**



SiO_2, pentane, R_F = 0.67.

IR (neat): 3076(w), 2967(m), 2916(s), 2855(m), 1642(w), 1437(br), 1377(m), 1280(w), 1221(w), 1106(br), 992(s), 919(s), 844(br), 740(w), 695(m), 655(w) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$) : 5.63 (*ddd*, J_1= 8.5 Hz, J_2= 10.4 Hz, J_3= 17.4 Hz, 1H), 5.15-5.07 (*m*, 3H), 3.38 (*dd*, J_1= 4.1 Hz, J_2= 5.7 Hz, 2H), 2.41-2.34 (*m*, 1H), 2.05-1.92 (*m*, 2H), 1.69 (*s*, 3H), 1.59 (*s*, 3H), 1.43-1.35 (*m*, 2H).

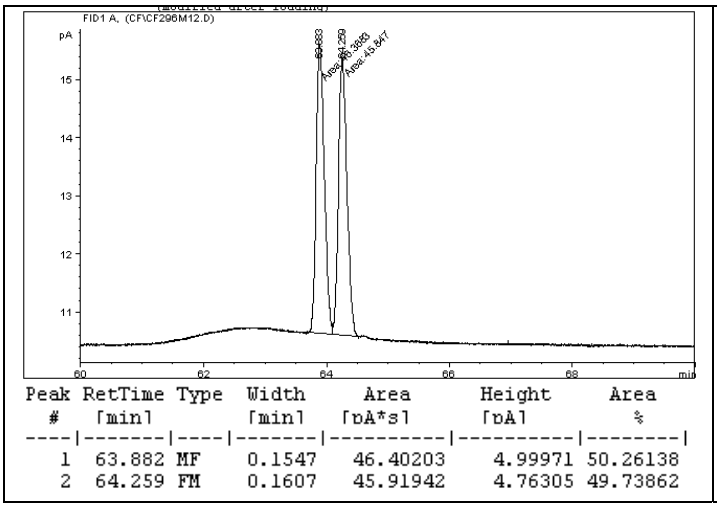
^{13}C NMR (125 MHz, $CDCl_3$) : 139.6, 132.2, 123.9, 117.0, 45.1, 38.4, 33.2, 25.9, 25.4, 17.9.

MS (EI mode) *m/z* (%) : 218(6), 216(6), 203(3), 201(3), 175(8), 173(7), 137(19), 123(11), 95(31), 93(25), 83(22), 82(53), 81(49), 79(8), 69(100), 68(10), 67(42), 56(11), 55(69), 53(21), 43(14), 41(89), 39(20), 32(40), 31(53), 29(10), 29(19), 28(20), 27(17).

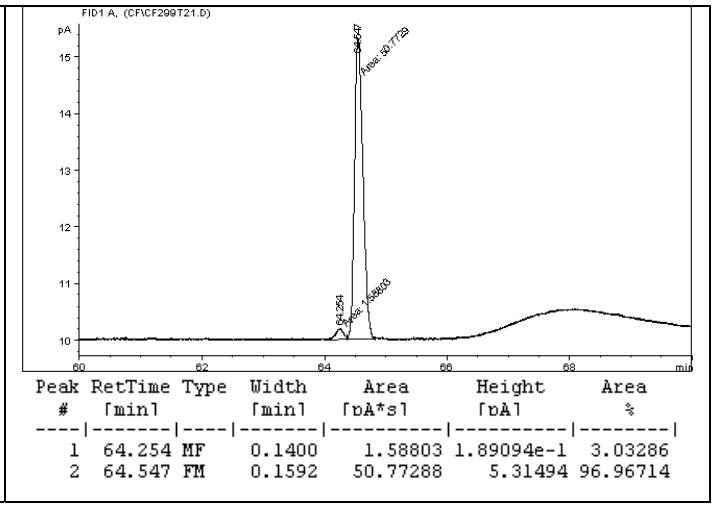
HR-MS (EI mode): calc. mass= 216.0514, mass found= 216.0513.

$[\alpha]_D^{22}$ = - 1.83 (*c* 0.77, $CHCl_3$) for 94% ee.

Ee was measured by chiral GC with a Chirasil Dex CB column, Helium flow (program: 70-30-1-170) R_T: 64.18 (+), 64.39 (-).

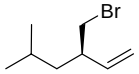


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	63.882	MF	0.1547	46.40203	4.99971	50.26138
2	64.259	FM	0.1607	45.91942	4.76305	49.73862



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	64.254	MF	0.1400	1.58803	1.89094e-1	3.03286
2	64.547	FM	0.1592	50.77288	5.31494	96.96714

(R)-3-(bromomethyl)-5-methylhex-1-ene **10b**[1]



SiO_2, pentane, R_F = 0.78.

IR (neat): 3080(w), 2956(s), 2925(m), 2870(w), 1840(br), 1642(w), 1467(m), 1434(w), 1418(w), 1385(w), 1367(m), 1268(w), 1221(m), 1170(br), 993(s), 917(s), 861(br), 797(br), 697(s), 649(m), 611(m) cm^{-1}.

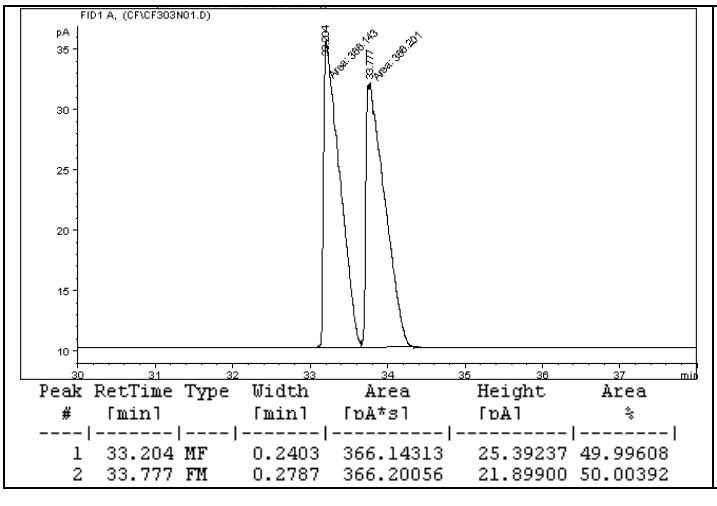
^1H NMR (400 MHz, $CDCl_3$) : 5.59 (*ddd*, J_1= 8.6 Hz, J_2= 10.6 Hz, J_3= 16.9 Hz, 1H), 5.13-5.08 (*m*, 2H), 3.39-3.31 (*m*, 2H), 2.49-2.41 (*m*, 1H), 1.66-1.57 (*m*, 1H), 1.38-1.24 (*m*, 2H), 0.91-0.86 (*m*, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) : 139.9, 116.8, 43.7, 42.4, 38.9, 25.4, 23.5, 21.9.

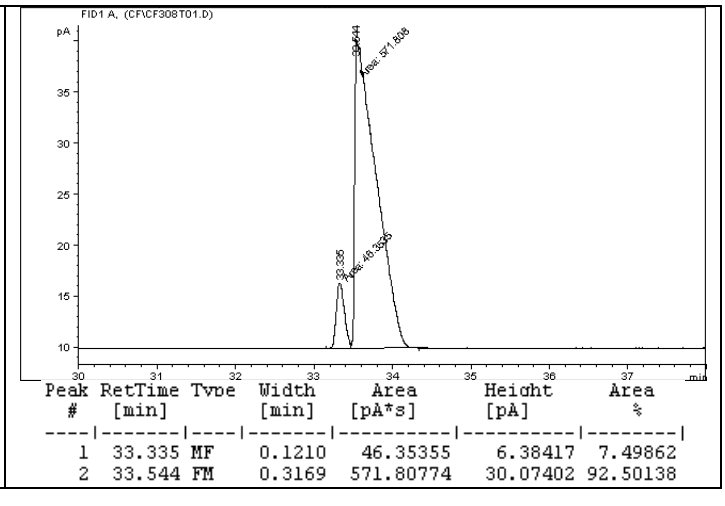
MS (EI mode) *m/z* (%) : 177(1), 163(1), 161(1), 150(2), 148(3), 135(6), 111(26), 97(13), 95(6), 69(47), 67(10), 57(46), 56(59), 55(67), 54(24), 53(13), 43(33), 41(45), 39(16), 32(76), 31(100), 29(21), 29(38), 28(16), 27(16).

$[\alpha]_D^{26}$= - 24.30 (*c* 0.88, $CHCl_3$) for 84% *ee*.

Ee was measured by chiral GC with a Chirasil Dex CB column, Helium flow (program: 60-15-1-170) R_T: 33.20 (+), 33.78 (-).



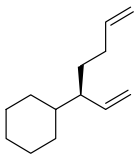
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.204	MF	0.2403	366.14313	25.39237	49.99608
2	33.777	FM	0.2787	366.20056	21.89900	50.00392



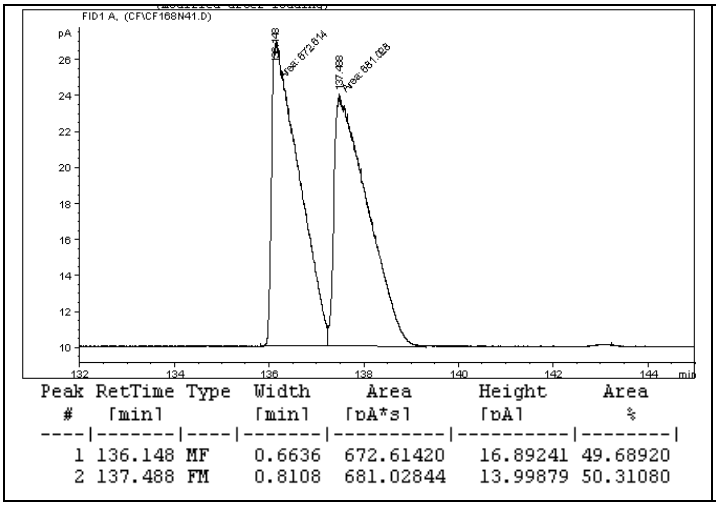
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.335	MF	0.1210	46.35355	6.38417	7.49862
2	33.544	FM	0.3169	571.80774	30.07402	92.50138

[1] C. Jennings-White, R. G. Almquist, *Tet. Lett.* **1982**, *23*, 2533.

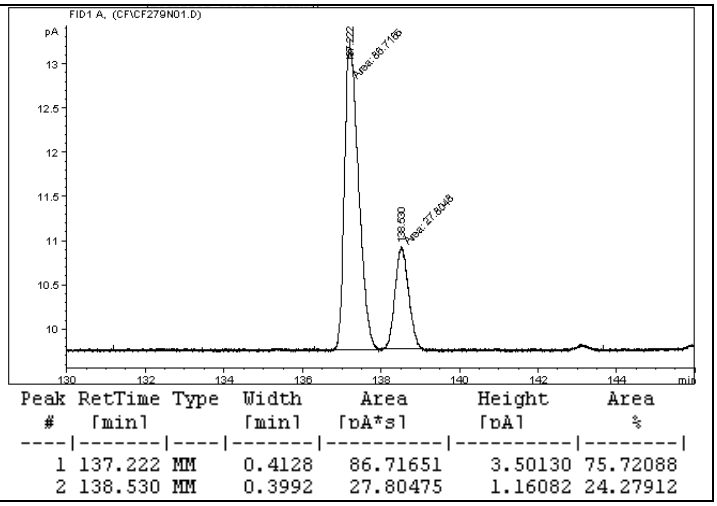
(+)-(S)-Hepta-1,6-dien-3-ylcyclohexane **11**



SiO_2, pentane, R_F = 0.97.
^{1}H-NMR ($CDCl_3$, 400 MHz) : 5.80 (*m*, 1H), 5.54 (*m*, 1H), 4.95 (*m*, 4H), 2.05-0.89 (*m*, 18H).
^{13}C-NMR ($CDCl_3$, 100 MHz) : 141.6, 139.2, 114.9, 50.1, 41.8, 33.9, 31.2, 29.7, 26.9, 26.8, 26.7, 26.7.
MS (EI mode) *m/z* (%) : 192(1), 164(14), 109(20), 95(17), 83(66), 67(63), 55(100).
$[\alpha]_D^{22}$= +6.81 (*c* 1.35, $CHCl_3$) for 78% *ee*.
Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 60-80-0.5-85-15-20-170), R_T: 137.22(major), 138.53(minor).

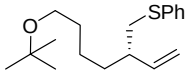


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	136.148	MF	0.6636	672.61420	16.89241	49.68920
2	137.488	FM	0.8108	681.02844	13.99879	50.31080



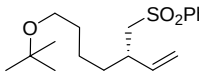
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	137.222	MM	0.4128	86.71651	3.50130	75.72088
2	138.530	MM	0.3992	27.80475	1.16082	24.27912

(S)-(6-tert-Butoxy-2-vinylhexyl)(phenyl)sulfane **13**

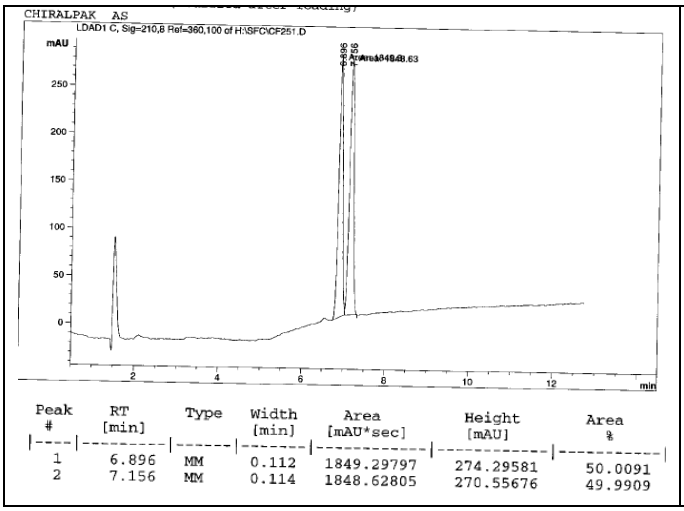


SiO_2, pentane/diethyl ether 97.5:2.5, R_F = 0.35.
^{1}H-NMR ($CDCl_3$, 400 MHz) : 7.34-7.26 (*m*, 4H), 7.17 (*tt*, J_1= 1.2 Hz, J_2= 7.3 Hz, 1H), 5.65 (*ddd*, J_1= 8.8 Hz, J_2= 10.3 Hz, J_3= 17.2 Hz, 1H), 5.10-5.04 (*m*, 2H), 3.32 (*t*, *J*= 6.8 Hz, 2H), 2.99-2.90 (*m*, 2H), 2.35-2.26 (*m*, 1H), 1.67-1.59 (*m*, 1H), 1.56-1.23 (*m*, 5H), 1.19 (*s*, 9H).
^{13}C-NMR ($CDCl_3$, 100 MHz) : 141.1, 137.3, 129.0(2), 129.0(2), 125.8, 116.0, 72.6, 61.5, 43.6, 39.1, 34.0, 30.7, 27.7(3), 23.8.
MS (EI mode) *m/z* (%) : 292(M^+, 25), 236(15), 235(71), 219(32), 127(23), 125(19), 124(25), 123(100), 110(71), 109(38), 109(20), 108(14), 107(17), 81(13), 79(15), 77(11), 71(10), 67(31), 65(10), 59(10), 57(88), 55(27), 54(10), 45(34).
Ee could not be determined by SFC or chiral GC.

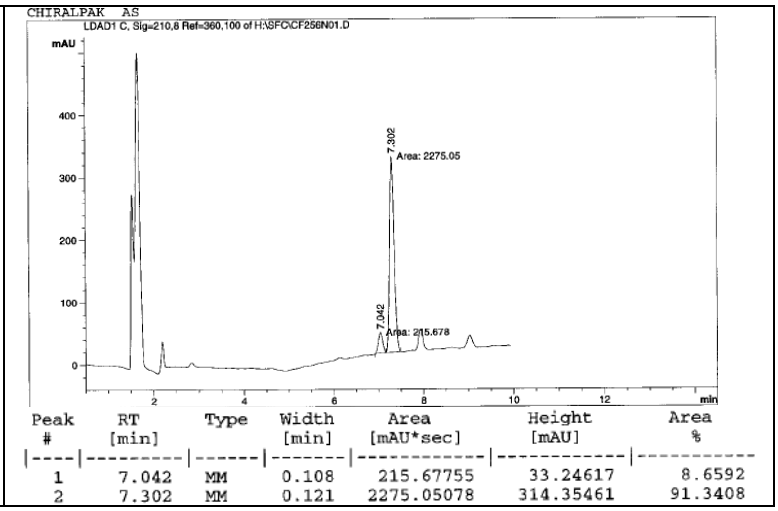
(+)-(S)-(6-tert-butoxy-2-vinylhexylsulfonyl)benzene **14**



SiO_2, pentane/diethyl ether 7:3, R_F = 0.26.
IR (neat): 2973(m), 2933(m), 2865(m), 1641(w), 1586(w), 1480(w), 1447(m), 1392(br), 1362(m), 1306(br), 1197(s), 1146(s), 1085(s), 1022(w), 998(w), 916(m), 747(s), 689(s) cm^{-1}.
^{1}H-NMR ($CDCl_3$, 500 MHz) : 7.90-7.88 (*m*, 2H), 7.66-7.62 (*m*, 1H), 7.57-7.53 (*m*, 2H), 5.52 (*ddd*, J_1= 8.6 Hz, J_2= 10.6 Hz, J_3= 16.9 Hz, 1H), 5.00-4.96 (*m*, 2H), 3.28 (*t*, *J*= 6.6 Hz, 2H), 3.13 (*d*, *J*= 6.3 Hz, 2H), 2.66-2.57 (*m*, 1H), 1.60-1.52 (*m*, 1H), 1.50-1.20 (*m*, 5H), 1.16 (*s*, 9H).
^{13}C-NMR ($CDCl_3$, 125 MHz) : 140.2, 139.2, 133.7, 129.3(2), 128.2(2), 116.5, 72.6, 61.4, 61.0, 38.8, 34.5, 30.5, 27.7(3), 23.4.
MS (EI mode) *m/z* (%) : 250 (M^+, 16), 95 (83), 93 (10), 82 (41), 81 (100), 79 (18), 67 (56), 55 (16), 53 (11).
HR-MS (EI mode): calc. mass= 250.1181, mass found= 250.1183.
$[\alpha]_D^{26}$= +7.54 (*c* 0.87, $CHCl_3$) for 82% *ee*
Ee was measured by chiral SFC with OD-H column (program: 2%-2-1-15%, 200 bars, 2mL/min, 30°C) R_T: 6.90(-), 7.16(+).

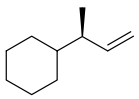


Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.896	MM	0.112	1849.29797	274.29581	50.0091
2	7.156	MM	0.114	1848.62805	270.55676	49.9909

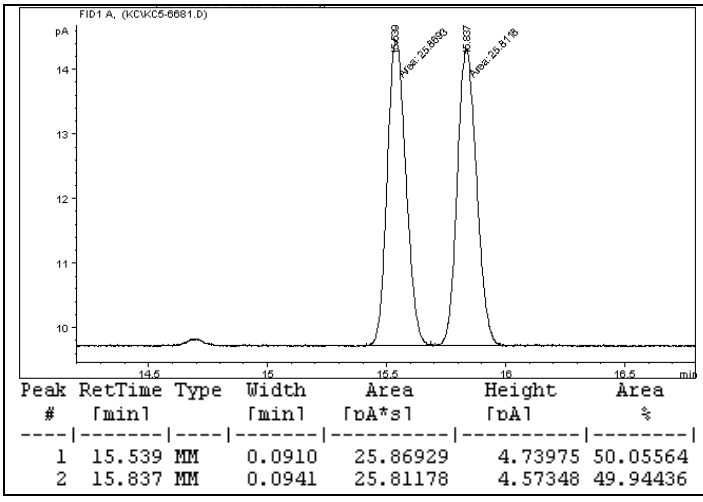


Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	7.042	MM	0.108	215.67755	33.24617	8.6592
2	7.302	MM	0.121	2275.05078	314.35461	91.3408

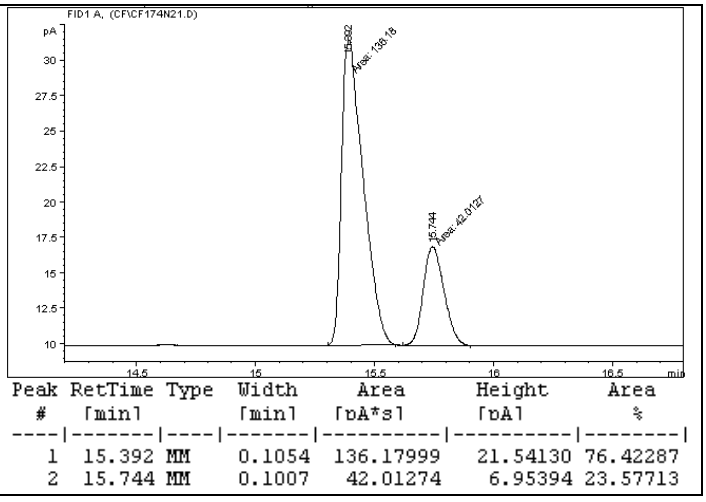
(S)-but-3-en-2-ylcyclohexane **15**[2]



SiO_2, pentane, R_F = 0.97.
^{1}H-NMR ($CDCl_3$, 400 MHz) : 5.52 (ddd, 1H, *J1* = 17.60, *J2* = 9.6, *J3* = 8.0 Hz), 4.92 (m, 2H), 1.95 (m, 1H), 1.74-1-60 (m, 5H), 1.26-1.01 (m, 4H), 0.96 (d, 3H, *J* = 6.80 Hz), 0.99-0.87 (m, 2H).
^{13}C-NMR ($CDCl_3$, 100 MHz) : 141143.8, 113.1, 43.7, 43.0, 30.5, 30.4, 26.8, 26.8, 17.2.
MS (EI mode) *m/z* (%) : 138 (2), 96 (9), 83 (55), 67 (39), 55 (100).
$[\alpha]_D^{22}$ = -8.3 (*c* = 1.13, CHCl3) for 72% *ee* ; Lit. $[\alpha]_D^{22}$= +13.6 (*c* 0.50, CHCl3) for 87% *ee* (*R*) enantiomer.
Ee was measured by chiral GC with a Chirasil-Dex CB column, Helium flow (program: 70-0-1-170), R_T: 15.54 (*R*), 15.84 (*S*).

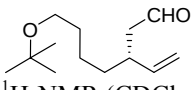


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.539	MM	0.0910	25.86929	4.73975	50.05564
2	15.837	MM	0.0941	25.81178	4.57348	49.94436



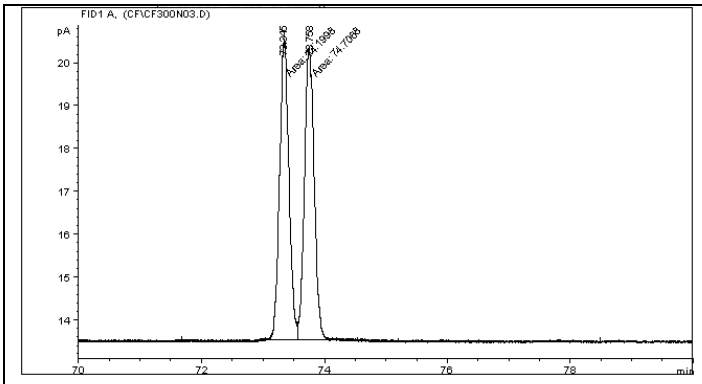
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	15.392	MM	0.1054	136.17999	21.54130	76.42287
2	15.744	MM	0.1007	42.01274	6.95394	23.57713

(+)-(R)-7-tert-butoxy-3-vinylheptanal **17**

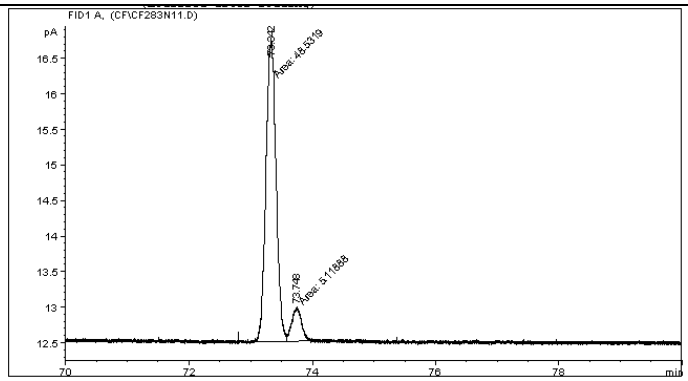


SiO_2, pentane/diethyl ether 97.5:2.5, R_F = 0.23.
IR (neat): 3071(w), 2974(m), 2935(m), 2865(m), 2718(w), 1725(s), 1641(w), 1477(w), 1461(w), 1391(m), 1362(s), 1253(w), 1198(s), 1081(s), 995(m), 915(m), 878(m), 751(br), 676(br) cm^{-1}.
^{1}H-NMR ($CDCl_3$, 500 MHz) : 9.71 (*t*, *J*= 2.2Hz, 1H), 5.65 (*ddd*, J_1= 8.2 Hz, J_2= 9.8 Hz, J_3= 17.7 Hz, 1H), 5.06-5.02 (*m*, 2H), 3.31 (*t*, *J*= 6.7Hz, 2H), 2.64-2.58 (*m*, 1H), 2.42 (*ddd*, , J_1= 2.2 Hz, J_2= J_3= 5.7 Hz, 2H), 1.55-1.47 (*m*, 2H), 1.44-1.29 (*m*, 4H), 1.17 (*s*, 9H).
^{13}C-NMR ($CDCl_3$, 125 MHz) : 202.6, 141.0, 115.5, 72.6, 61.5, 48.6, 38.5, 34.7, 30.7, 27.7(3), 23.8.
MS (EI mode) *m/z* (%) : 105(10), 97(29), 90(17), 70(16), 69(18), 68(11), 67(10), 57(17), 56(24), 55(100), 54(28), 53(12), 43(13), 41(40), 39(13), 32(15), 31(20), 29(25), 27(17).
$[\alpha]_D^{25}$= +1.39 (*c* 0.71, $CHCl_3$) for 81% *ee*.
Ee was measured by chiral GC with a Hydrodex B-3P column, Hydrogen flow (program: 90-40-1-170), R_T: 73.34(+), 73.76(-).

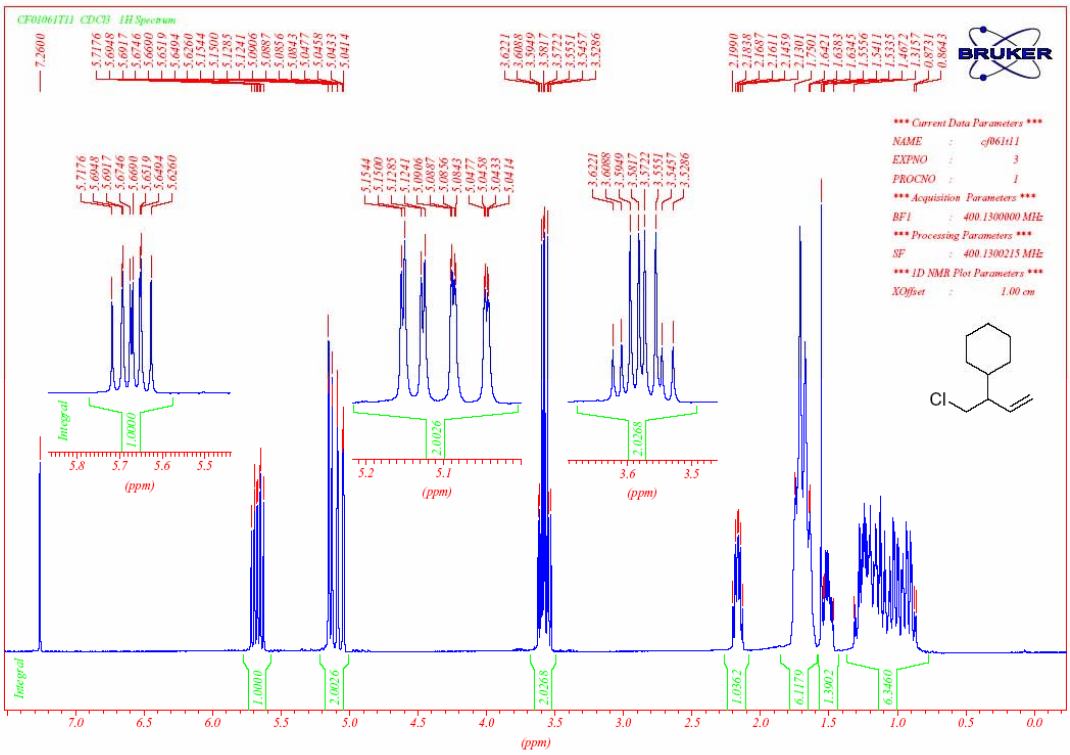
[2] a) S. E. Denmark, L. K. Marble, *J. Org. Chem.* **1990**, *55*, 1984; b) K. Tissot-Croset, A. Alexakis, *Tetrahedron Letters* **2004**, *45*, 7375; c) M. A. Kacprzynski, A. H. Hoveyda, *J. Am. Chem. Soc.* **2004**, *126*, 10676.

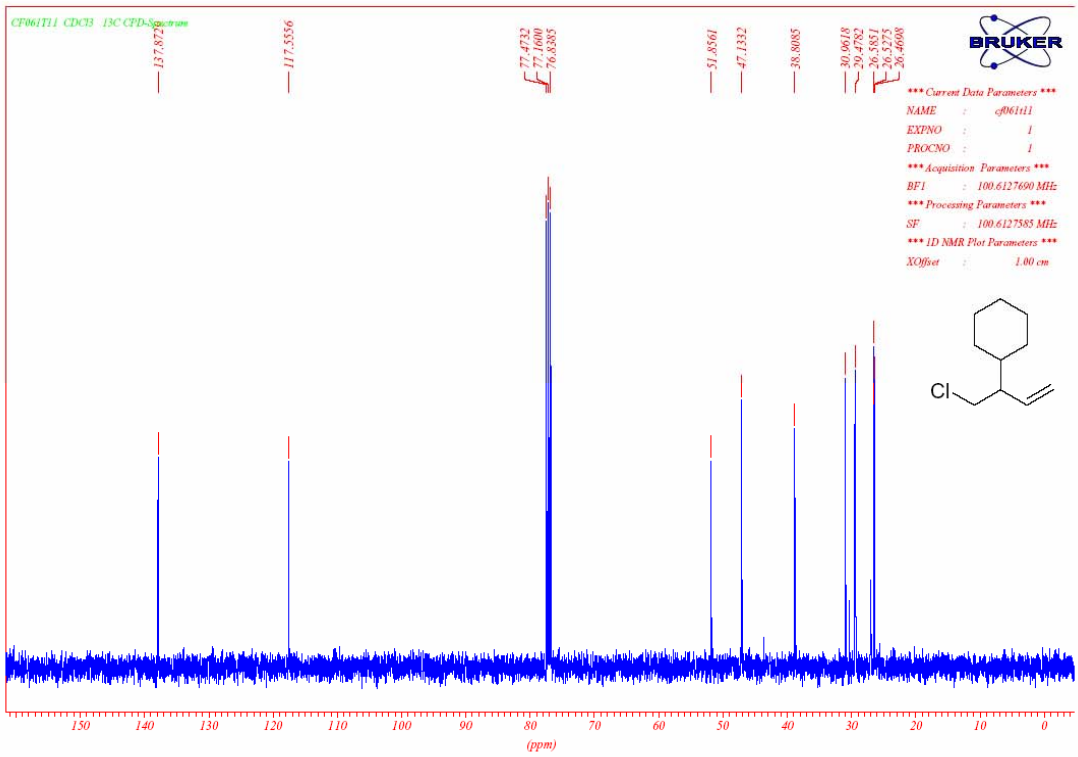


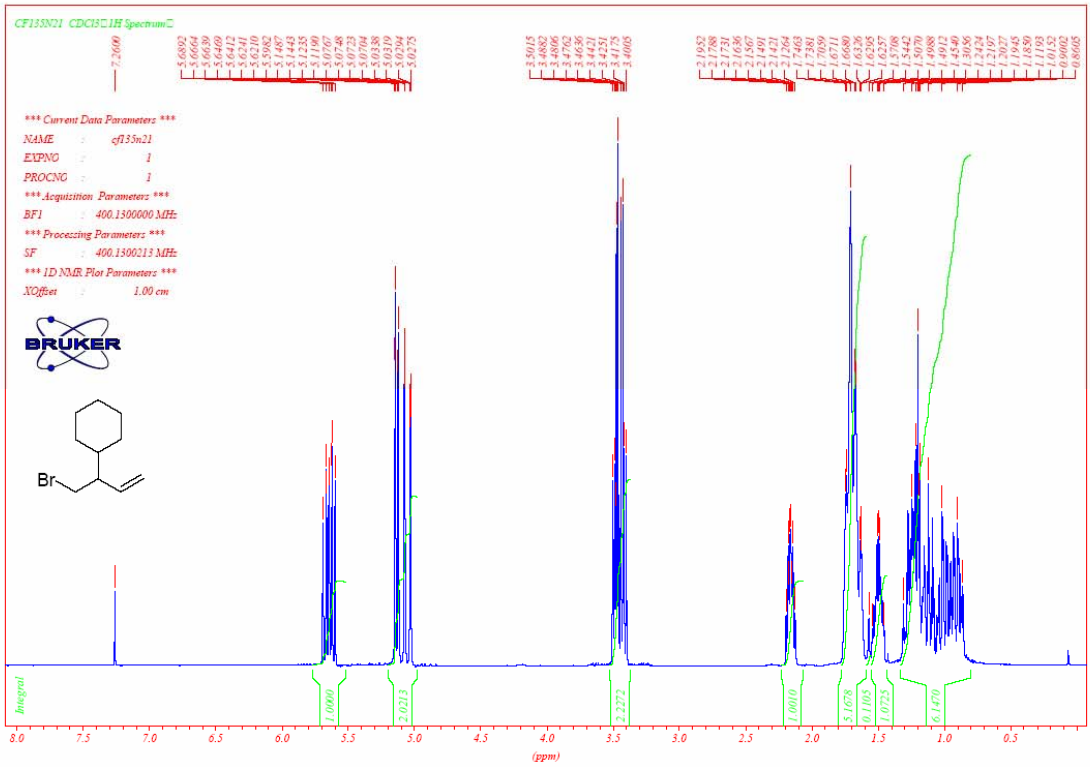
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	73.345	MF	0.1765	74.19975	7.00478	49.82973
2	73.758	FM	0.1816	74.70684	6.85618	50.17027

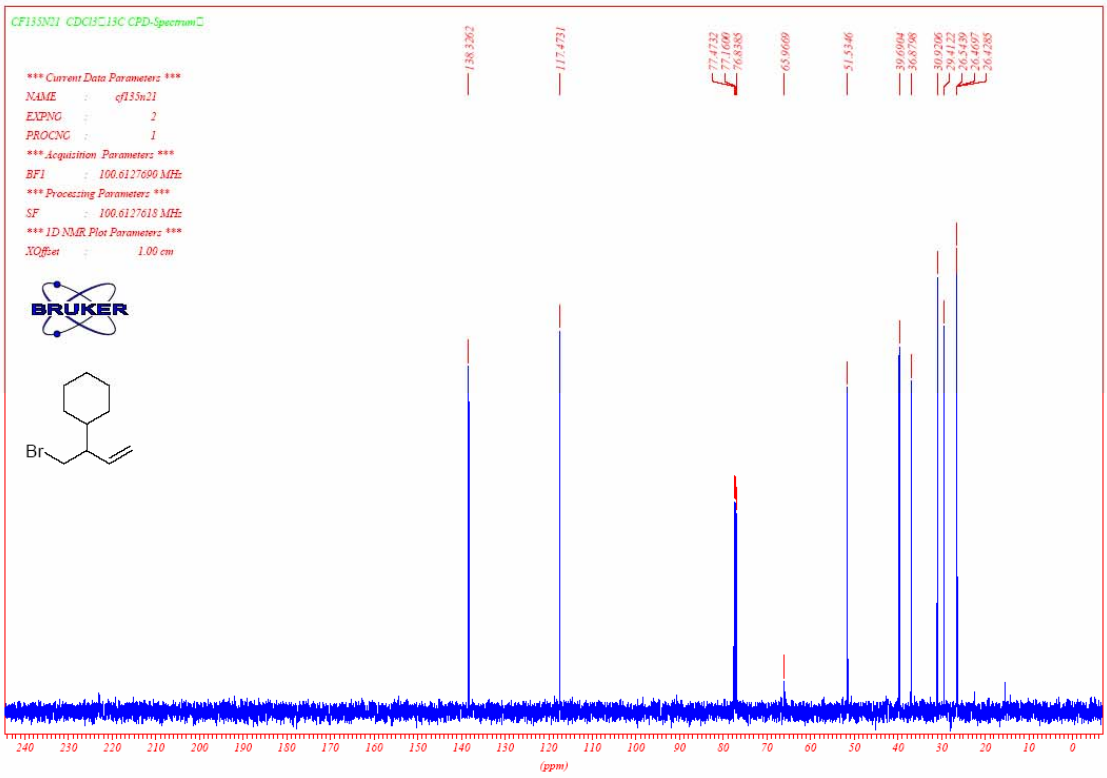


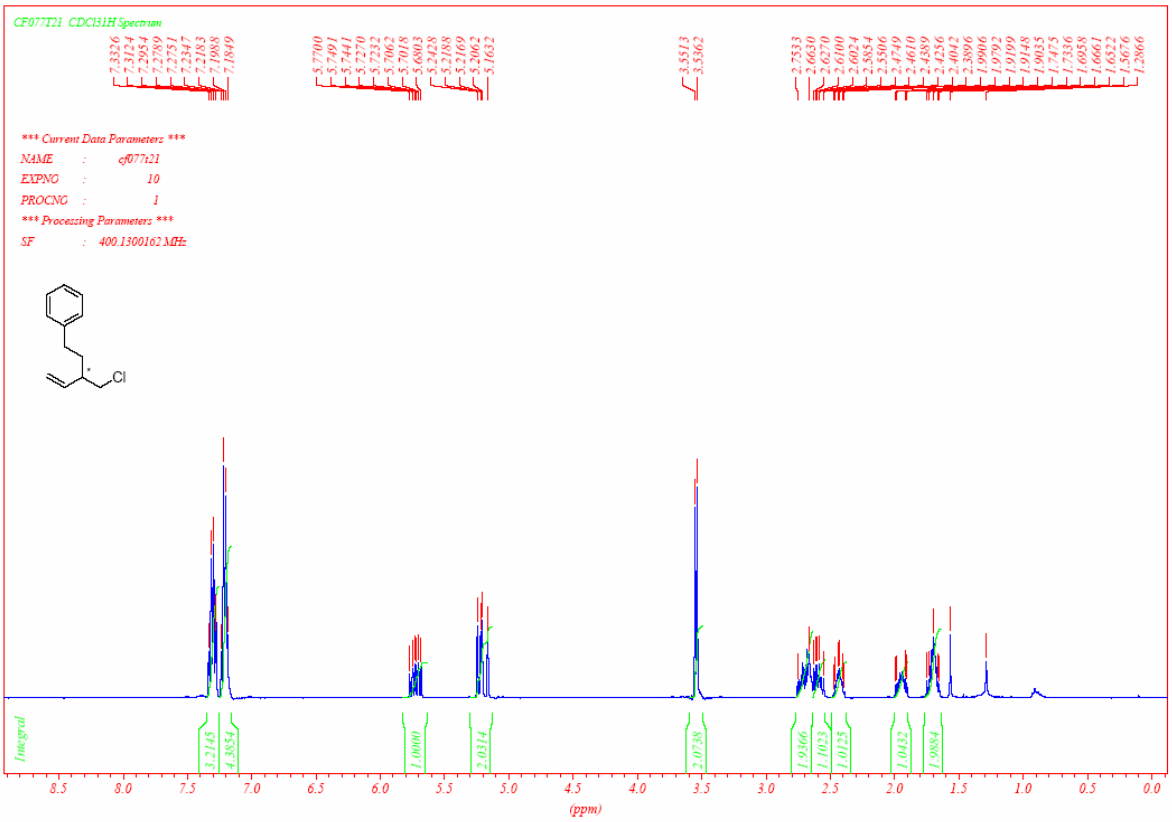
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	73.342	MF	0.1911	48.53194	4.23354	90.45890
2	73.748	FM	0.1751	5.11888	4.87139e-1	9.54110


CF01061T11 CDCl3 1H Spectrum
BRUKER
*** Current Data Parameters ***
NAME : cf061t11
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
*** Processing Parameters ***
SF : 400.1300215 MHz
*** 1D NMR Plot Parameters ***
XOffset : 1.00 cm
Cl
Integral
1.0000
2.0026
2.0268
1.0362
6.1179
1.3902
6.3460
(ppm)

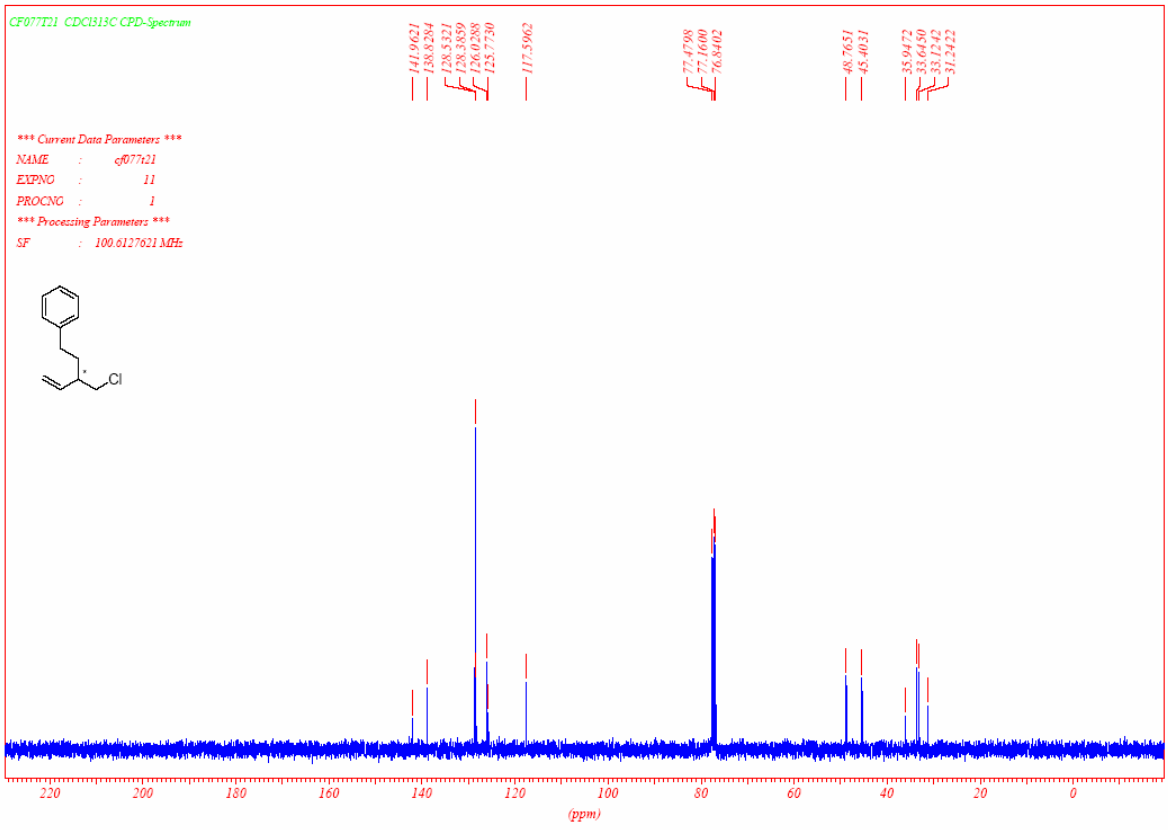

CF061T11 CDCl3 13C CPD-Spectrum
BRUKER
*** Current Data Parameters ***
NAME : cf061t11
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
*** Processing Parameters ***
SF : 100.6127585 MHz
*** 1D NMR Plot Parameters ***
XOffset : 1.00 cm
Cl
137.8724
117.5556
77.4732
77.1600
76.8385
51.8561
47.1332
38.8085
30.9618
29.4782
26.5851
26.5275
26.4698
(ppm)

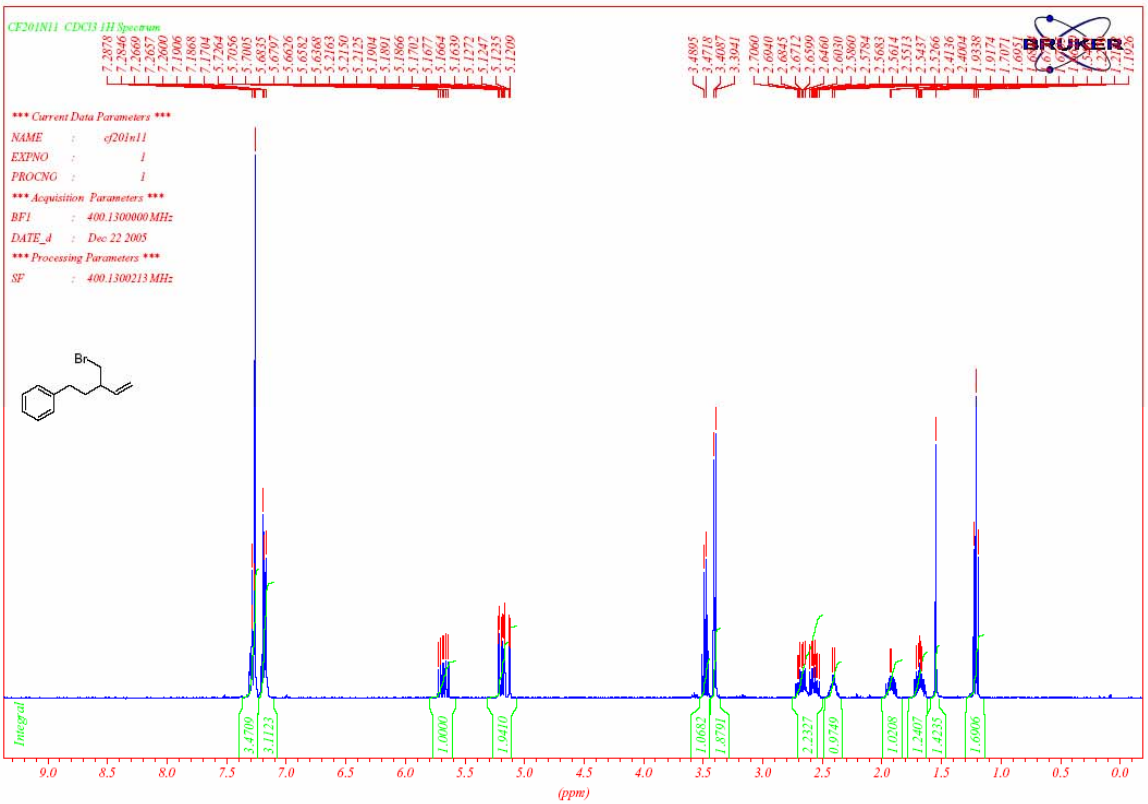

CF135N21 CDCl3□1H Spectrum□
*** Current Data Parameters ***
NAME : cf135n21
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
*** Processing Parameters ***
SF : 400.1300213 MHz
*** 1D NMR Plot Parameters ***
XOffset : 1.00 cm
BRUKER
Br
Integral
1.0000
2.0215
2.2272
1.0010
5.1678
0.1105
1.0725
6.1470
(ppm)

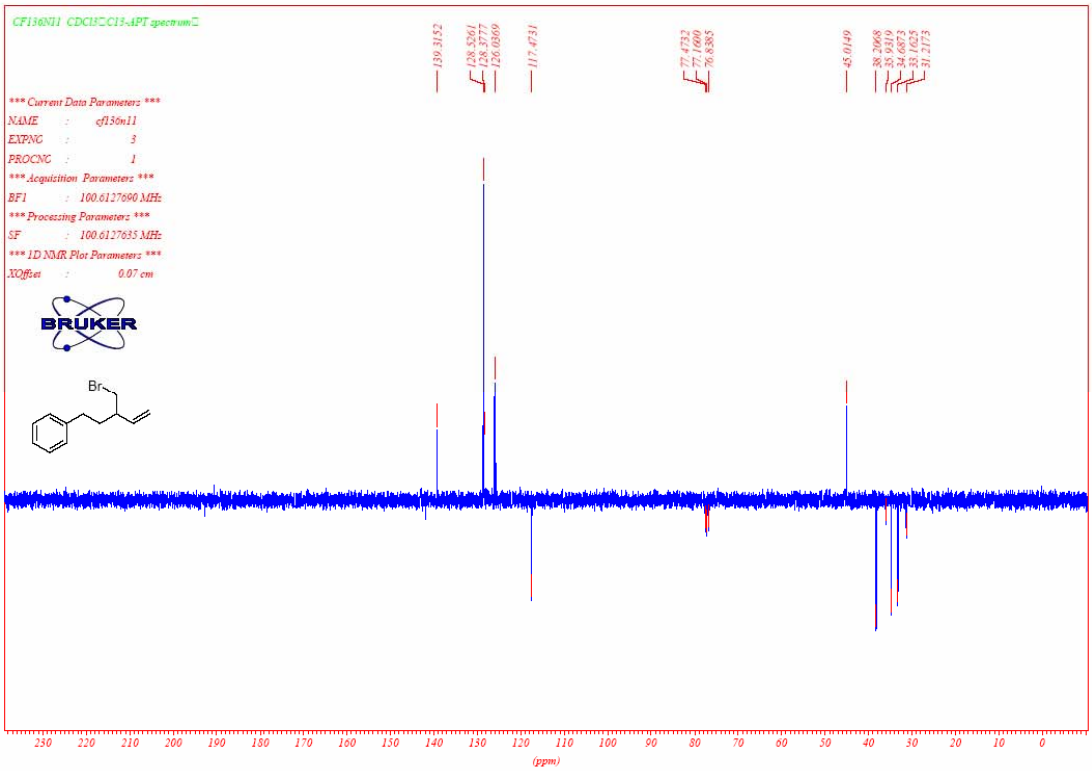

CF135N21 CDCl3□13C CPD-Spectrum□
*** Current Data Parameters ***
NAME : cf135n21
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
*** Processing Parameters ***
SF : 100.6127618 MHz
*** 1D NMR Plot Parameters ***
XOffset : 1.00 cm
BRUKER
Br
138.3362
117.4731
77.4732
77.1606
76.8385
65.9669
51.5346
39.6904
36.8786
30.9206
29.4122
26.5439
26.4495
26.4285
(ppm)

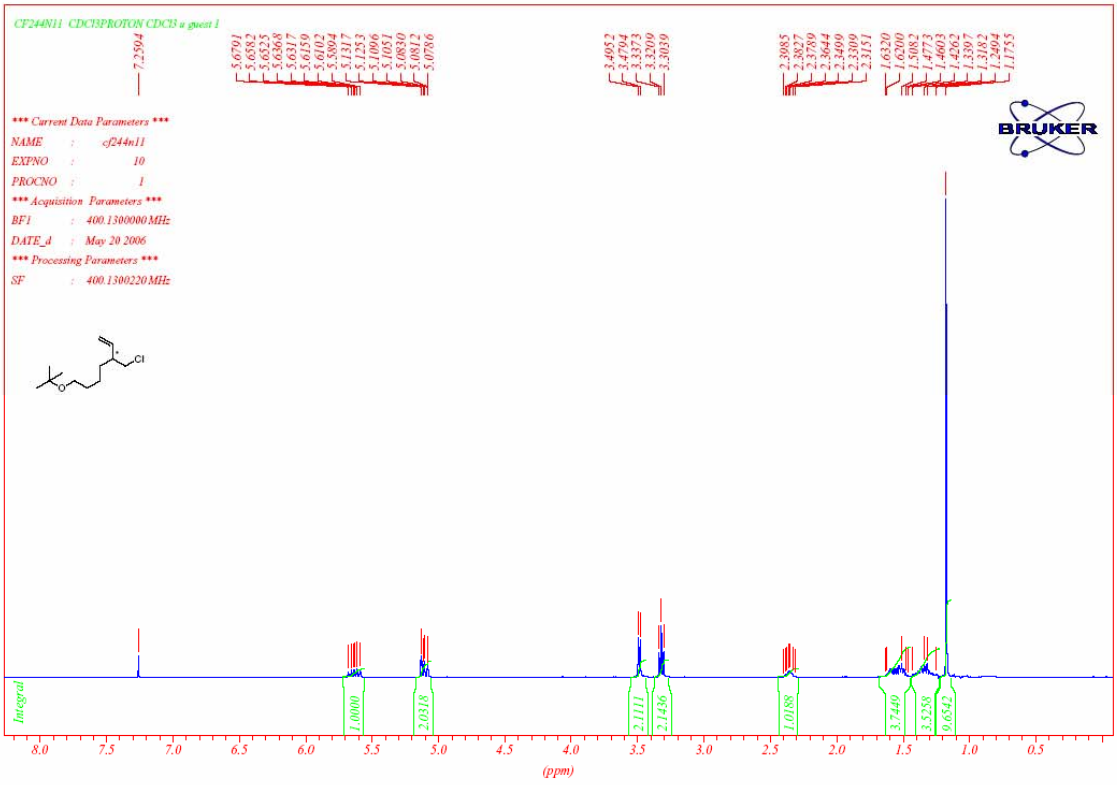


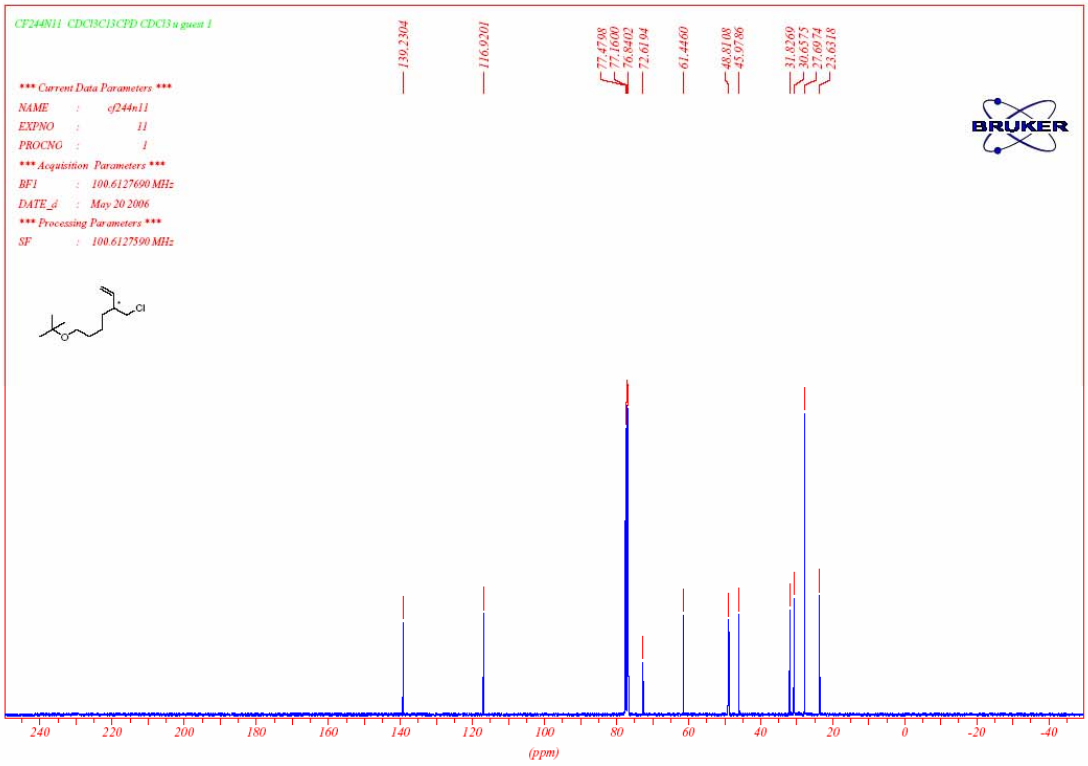
Contains as an impurity $Ph(CH_2)_4Ph$ (25%) resulting from the oxidative coupling of the organomagnesium reagent. ^{1}H NMR (400 MHz, $CDCl_3$) :7.33-7.28 (*m*, 2H), 7.23-7.18 (*m*, 3H), 2.75-2.55 (*m*, 4H), 1.75-1.65 (*m*, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) : 142.0, 128.5, 128.5, 128.3, 128.3, 125.8, 35.9, 31.2.

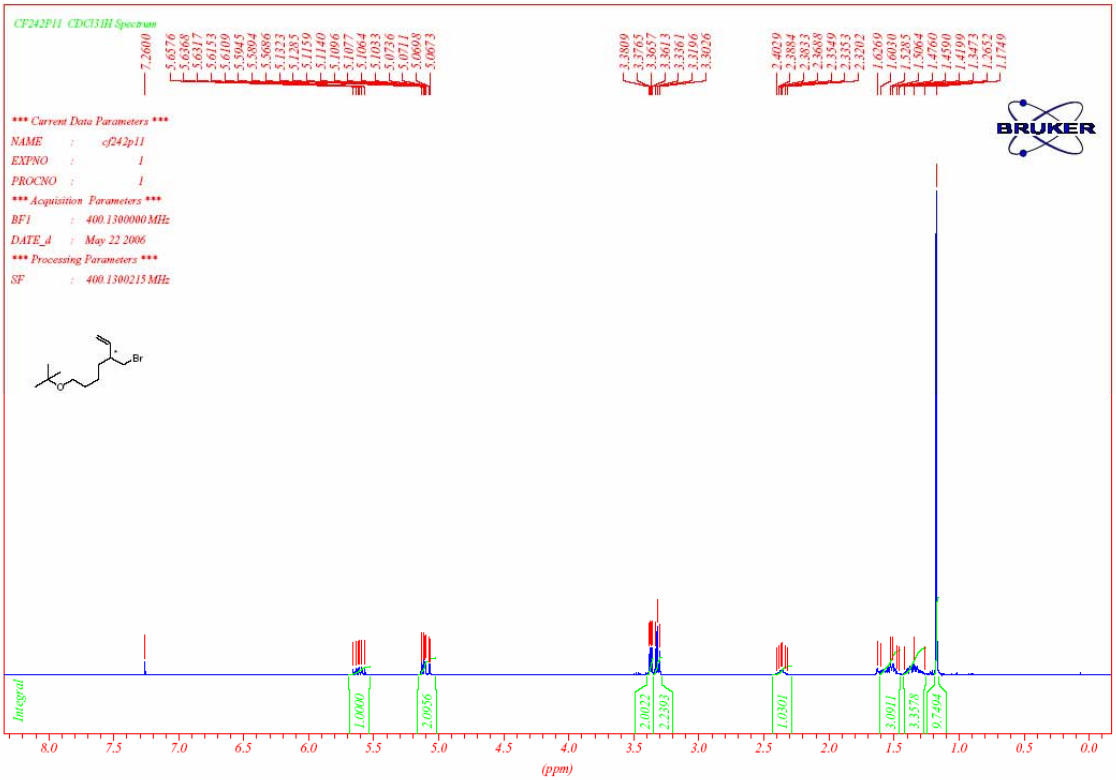


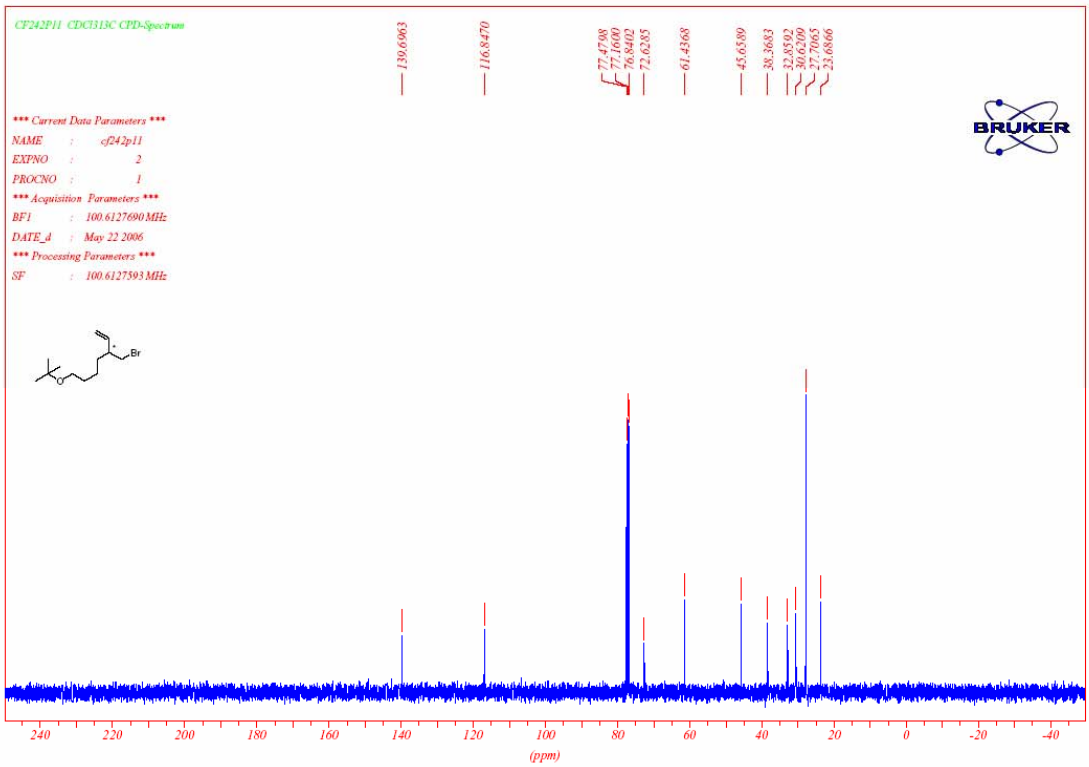

CF201N11 CDCl3 1H Spectrum
*** Current Data Parameters ***
NAME : cf201n11
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
DATE_d : Dec 22 2005
*** Processing Parameters ***
SF : 400.1300213 MHz
Br
Integral
3.4709
3.1123
1.0000
1.9410
1.0682
1.8791
2.2327
0.9749
1.0208
1.2407
1.4235
1.6906
(ppm)

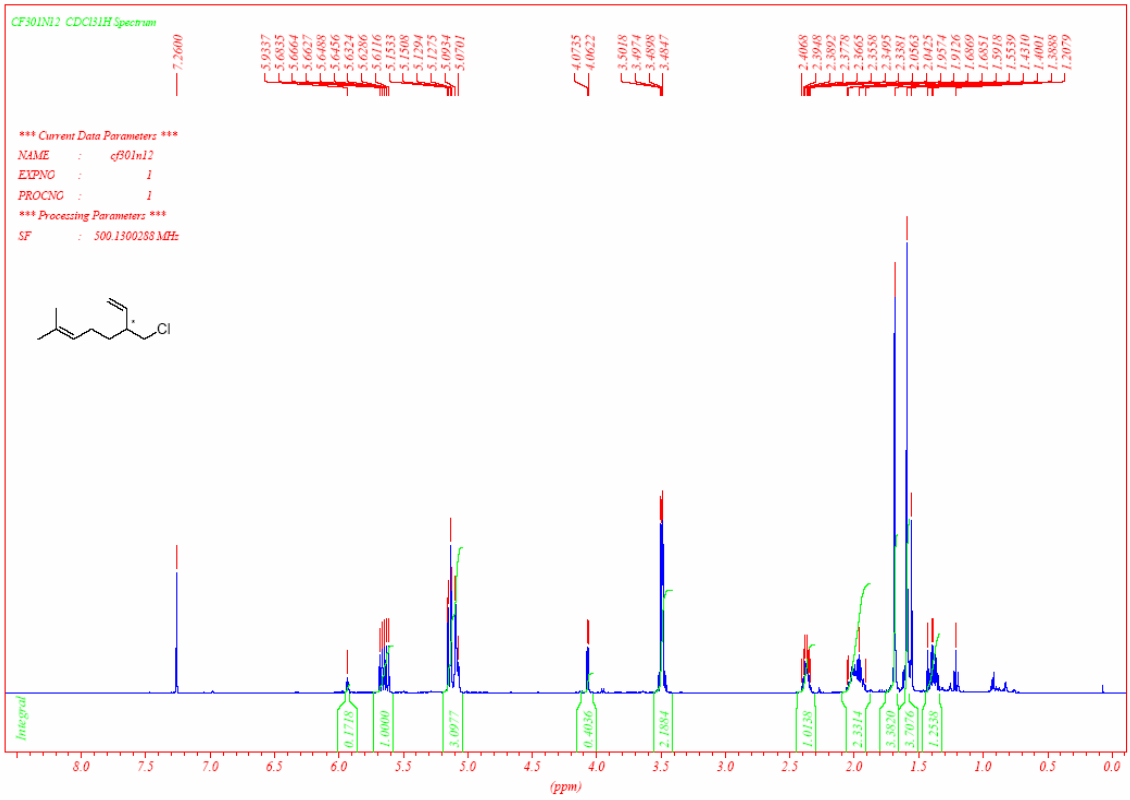

CF136N11 CDCl3□C13-APT spectrum□
*** Current Data Parameters ***
NAME : cf136n11
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
*** Processing Parameters ***
SF : 100.6127635 MHz
*** 1D NMR Plot Parameters ***
XOffset : 0.07 cm
BRUKER
Br
139.3152
128.5261
128.3777
126.0369
117.4731
77.4732
77.1600
76.8385
45.0149
38.2968
35.9319
34.6873
33.1625
31.2173
(ppm)

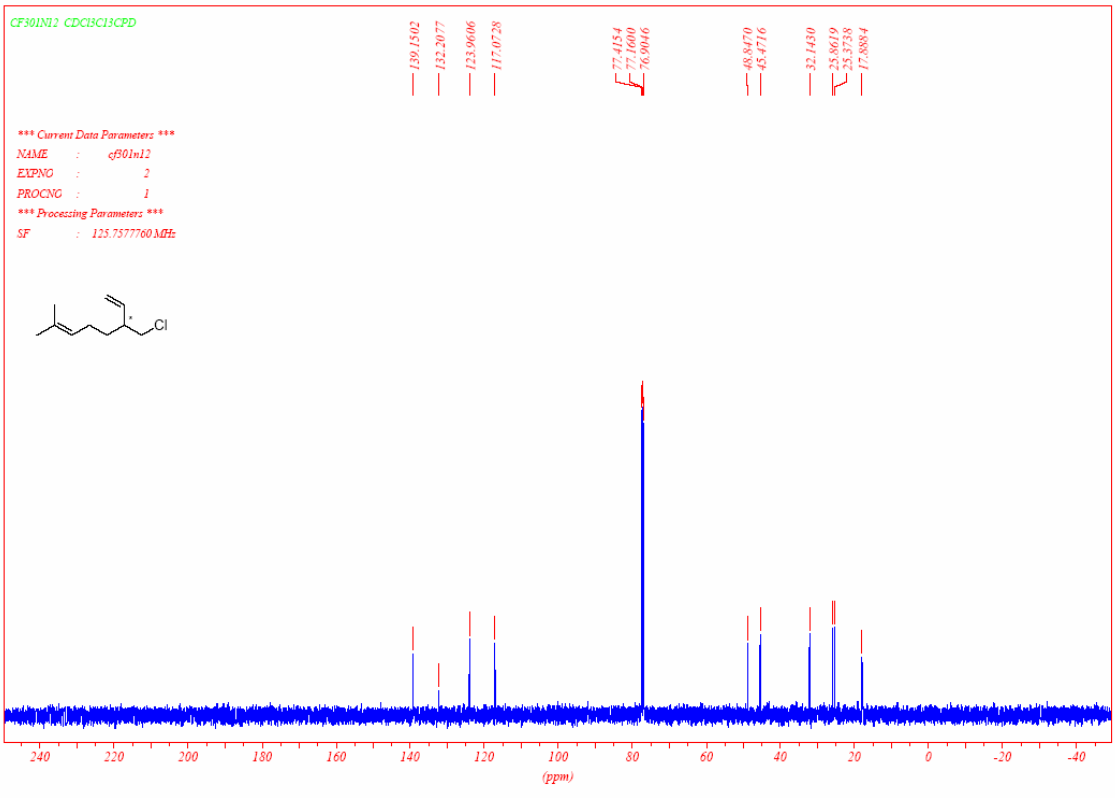

CF244N11 CDCl3PROTON CDCl3 u guest 1
*** Current Data Parameters ***
NAME : cf244n11
EXPNO : 10
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
DATE_d : May 20 2006
*** Processing Parameters ***
SF : 400.1300220 MHz
Integral
(ppm)

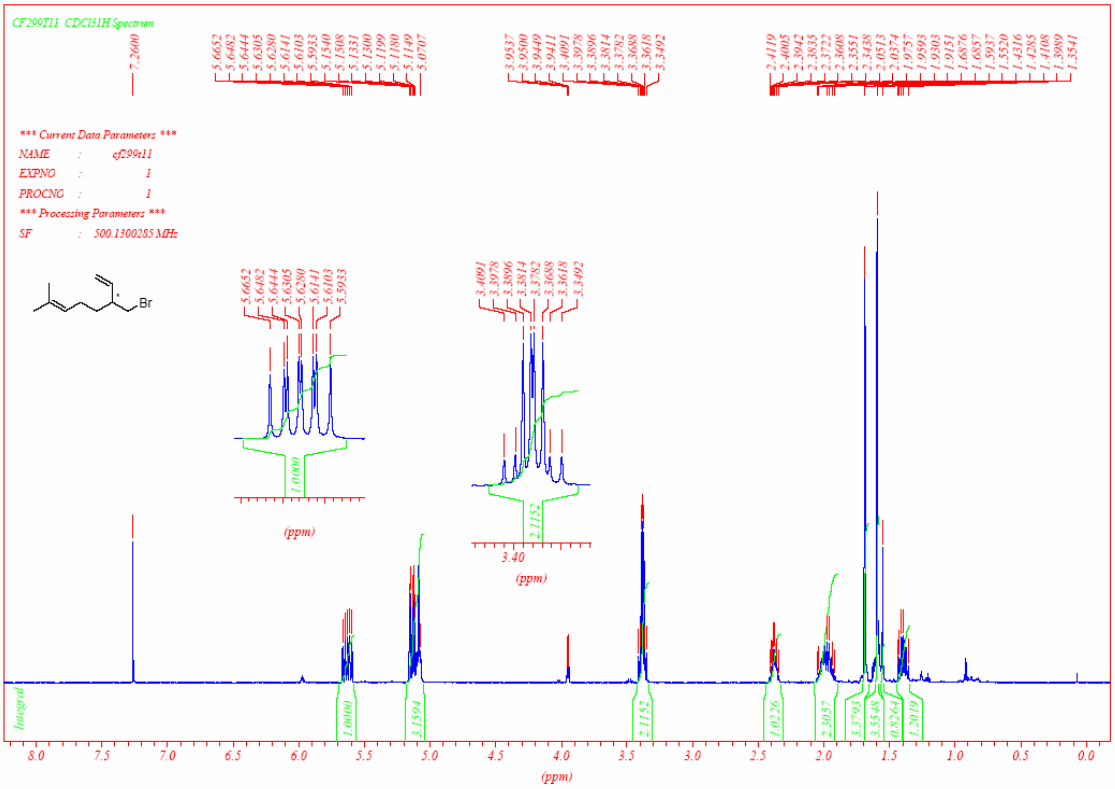

CF244N11 CDCl3C13CPD CDCl3 u guest 1
*** Current Data Parameters ***
NAME : cf244n11
EXPNO : 11
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
DATE_d : May 20 2006
*** Processing Parameters ***
SF : 100.6127590 MHz
(ppm)

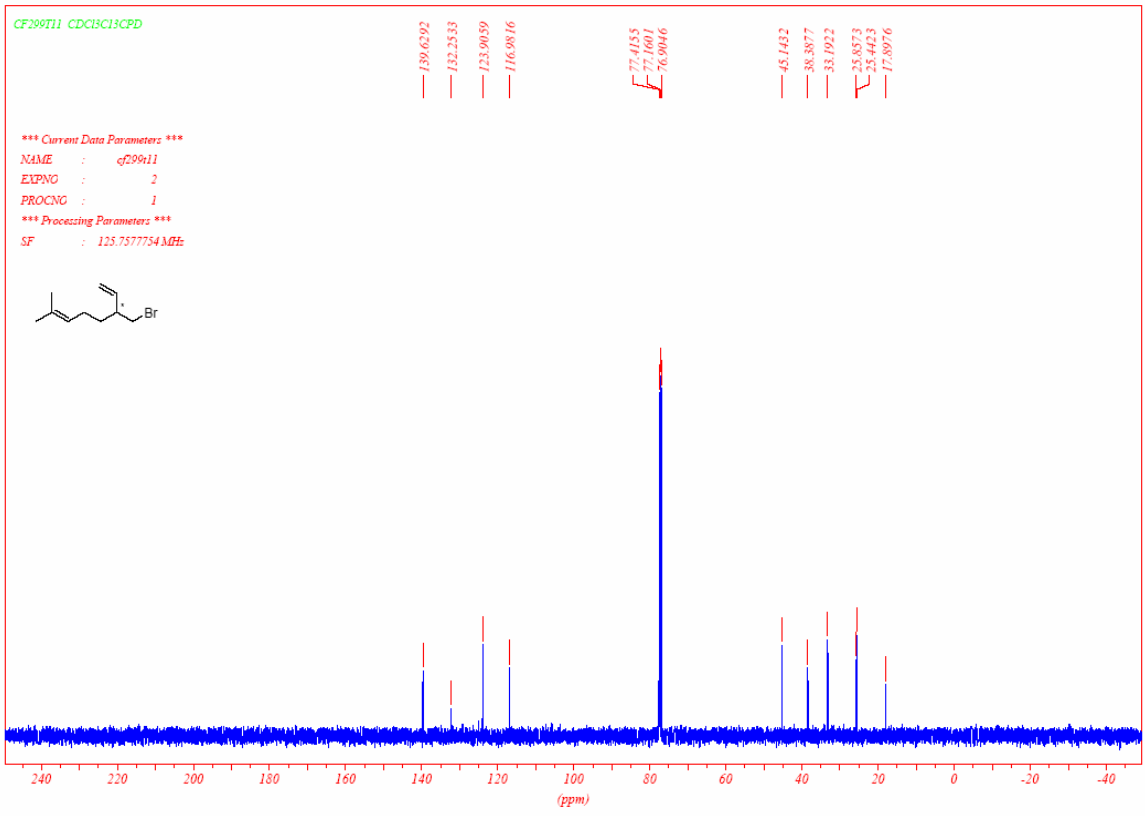

CF242P11 CDCl3 1H Spectrum
*** Current Data Parameters ***
NAME : cf242p11
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
DATE_d : May 22 2006
*** Processing Parameters ***
SF : 400.1300215 MHz
Br
Integral
1.0000
2.0056
2.0022
2.2393
1.0301
3.0911
3.3578
9.7404
(ppm)

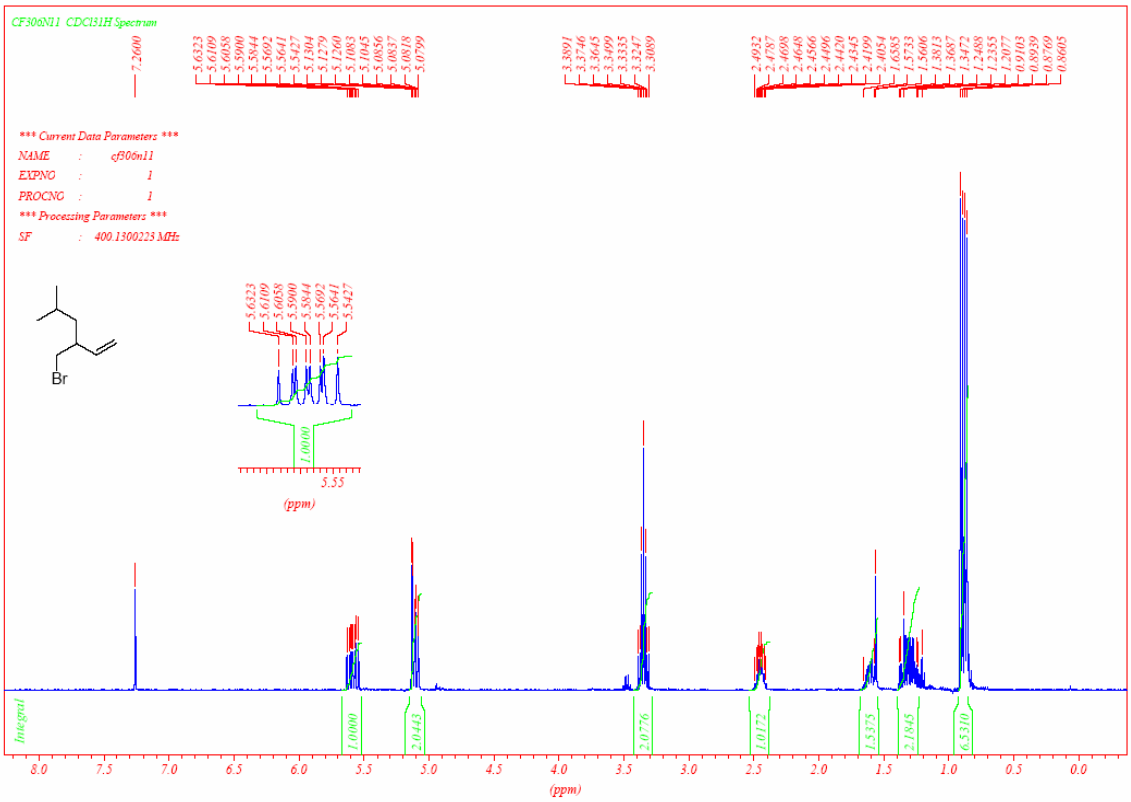

CF242P11 CDCl3 13C CPD-Spectrum
*** Current Data Parameters ***
NAME : cf242p11
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
DATE_d : May 22 2006
*** Processing Parameters ***
SF : 100.6127593 MHz
Br
(ppm)

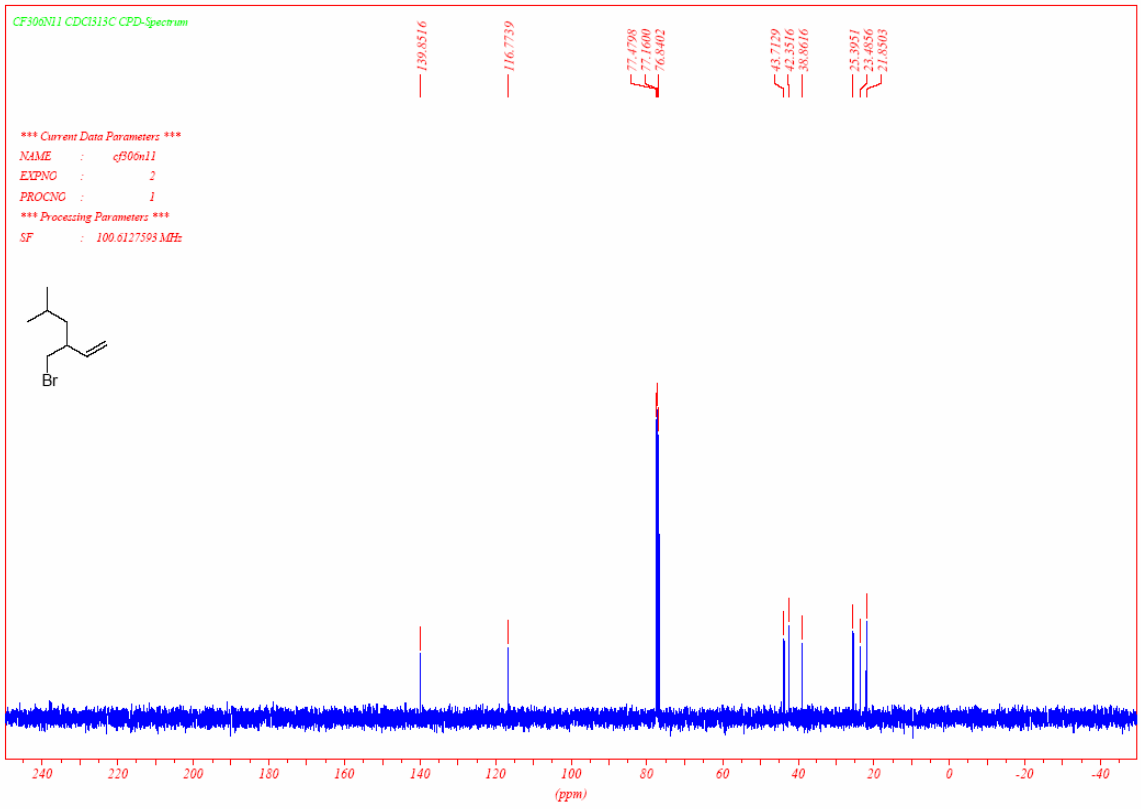

CF301N12 CDCl3 1H Spectrum
*** Current Data Parameters ***
NAME : cf301n12
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 500.1300288 MHz
Cl
Integral
(ppm)

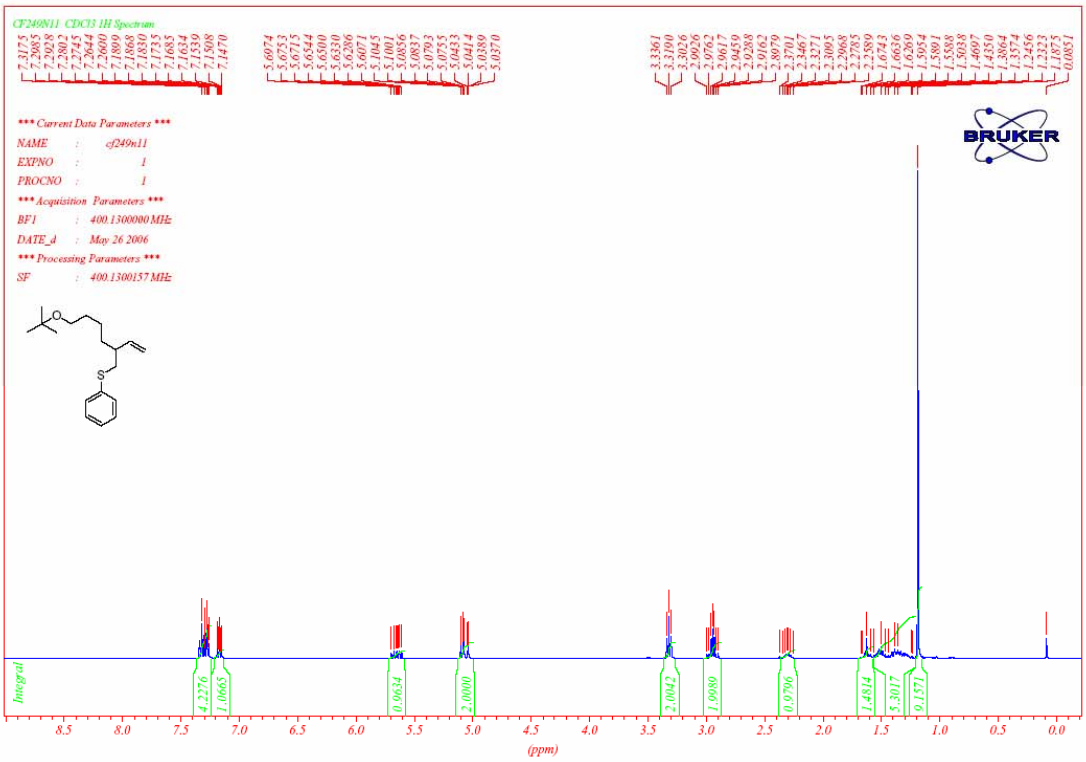

CF301N12 CDCl3C13CPD
*** Current Data Parameters ***
NAME : cf301n12
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577760 MHz
Cl
(ppm)

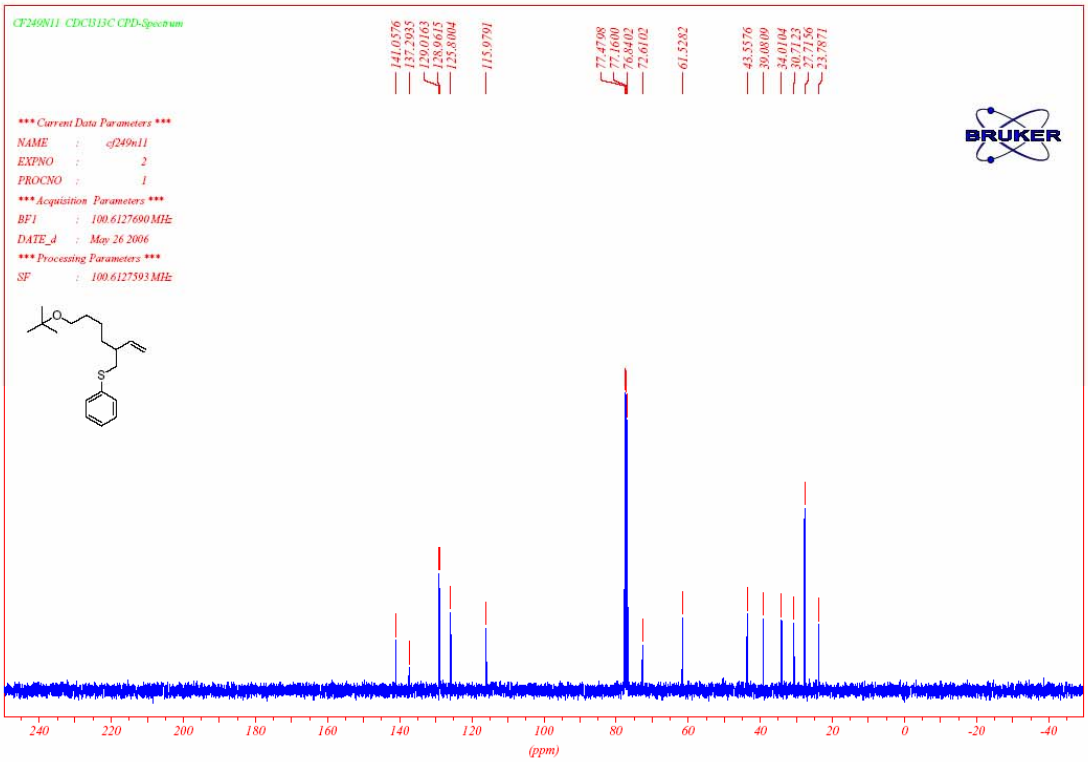

CF299T11 CDCl3 1H Spectrum
*** Current Data Parameters ***
NAME : cf299t11
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 500.1300285 MHz
Br
(ppm)
Integral

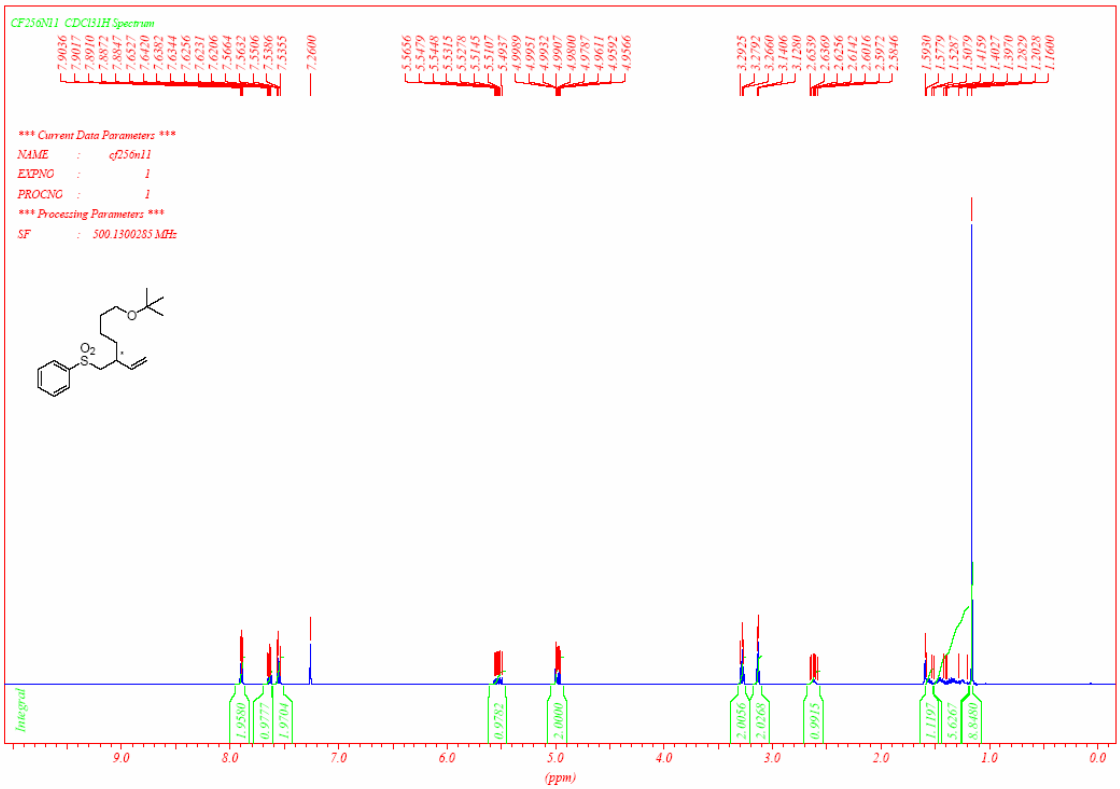

CF299T11 CDCl3 C13CPD
*** Current Data Parameters ***
NAME : cf299t11
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577754 MHz
Br
(ppm)

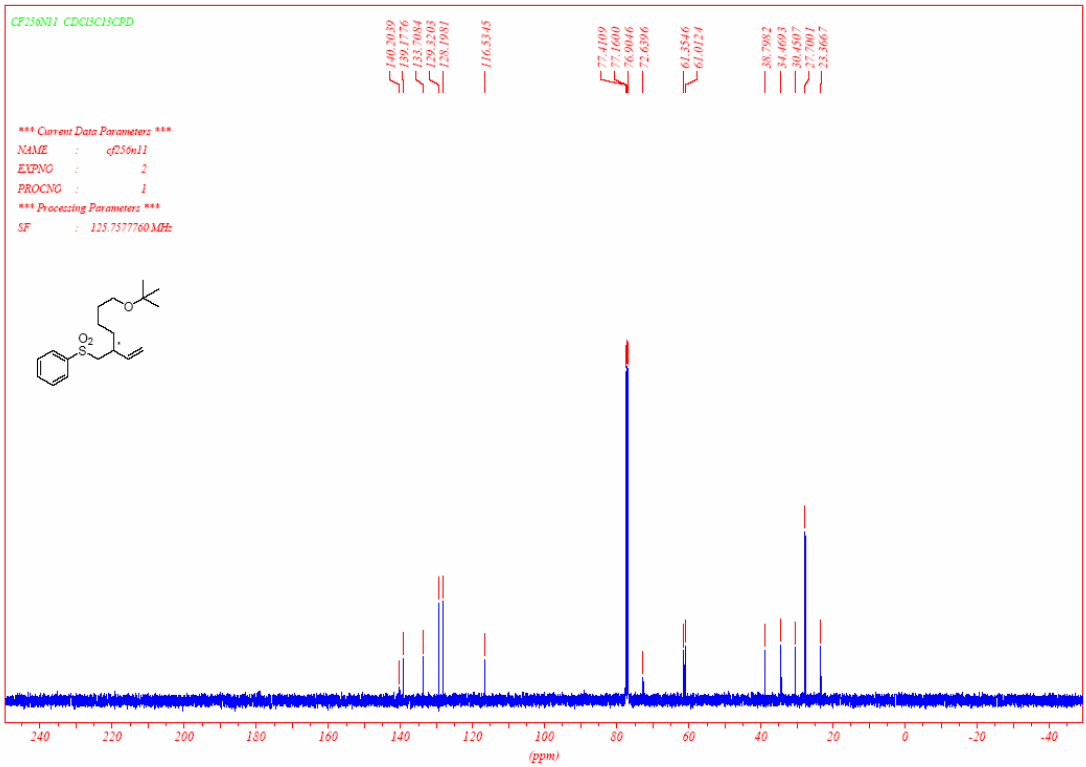

CF306N11 CDCl31H Spectrum
*** Current Data Parameters ***
NAME : cf306n11
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 400.1300223 MHz
Br
Integral
(ppm)

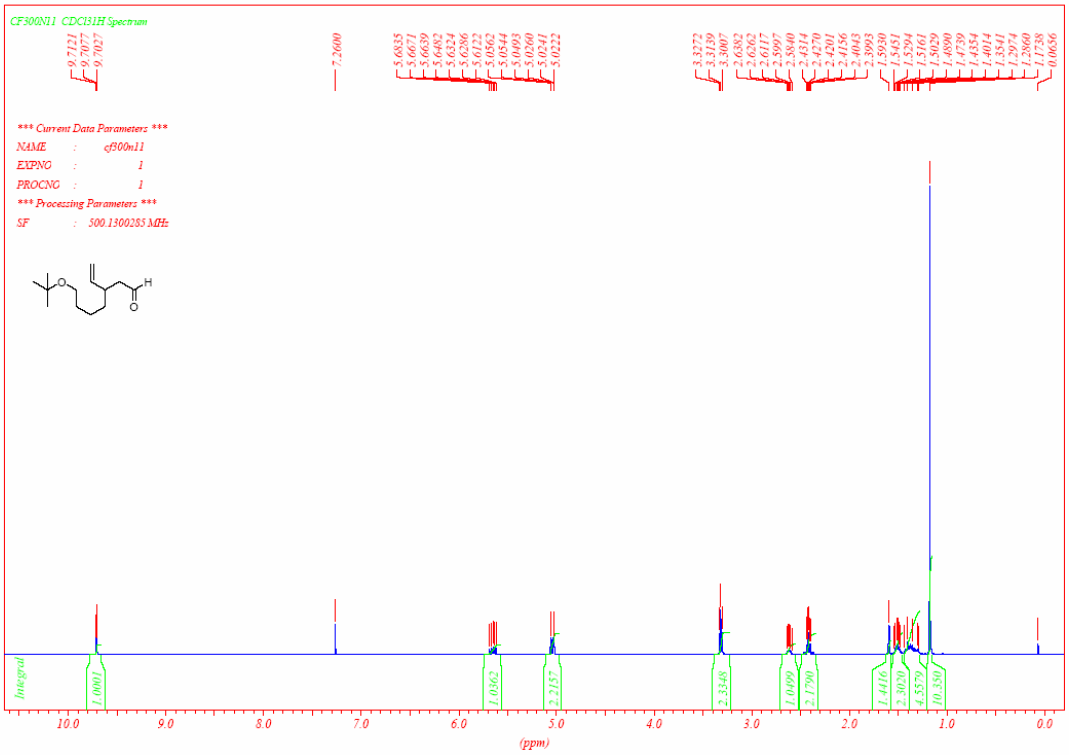

CF306N11 CDCl313C CPD-Spectrum
*** Current Data Parameters ***
NAME : cf306n11
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127598 MHz
Br
(ppm)

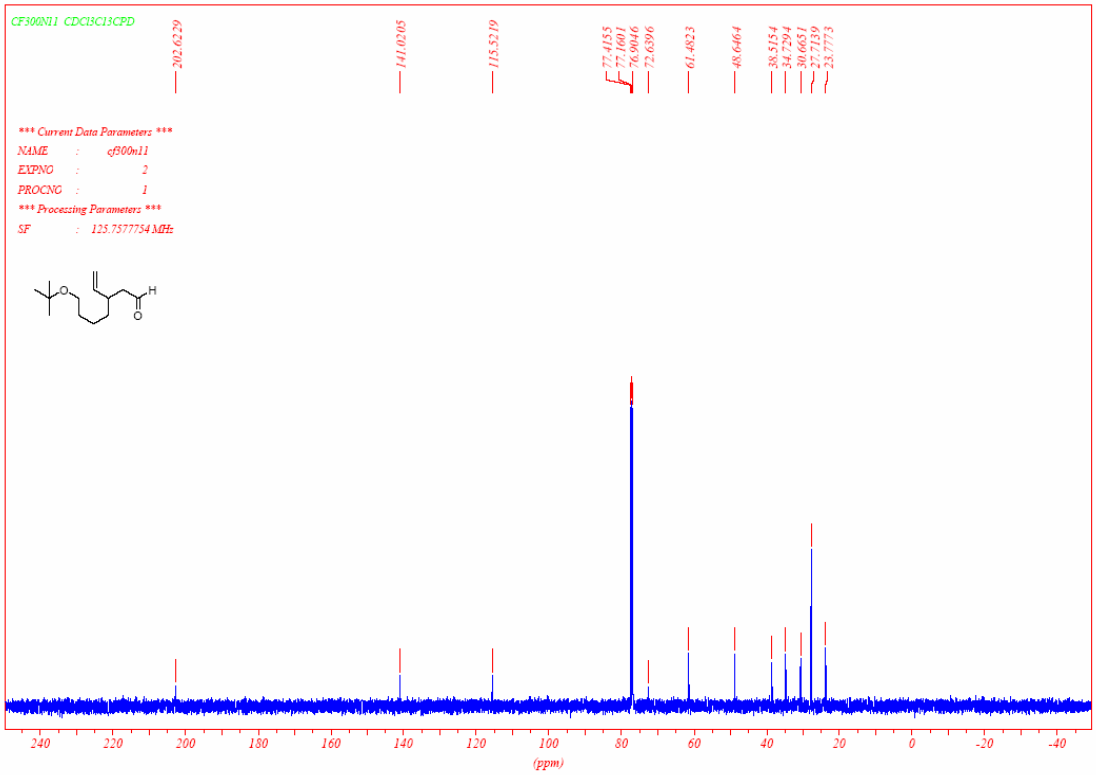

CF249N11 CDCl3 1H Spectrum
*** Current Data Parameters ***
NAME : cf249n11
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 400.1300000 MHz
DATE_d : May 26 2006
*** Processing Parameters ***
SF : 400.1300157 MHz
BRUKER
Integral
4.2276
1.0665
0.9634
2.0000
2.0042
1.9989
0.9706
1.4814
5.3017
9.1571
(ppm)


CF249N11 CDCl313C CPD-Spectrum
*** Current Data Parameters ***
NAME : cf249n11
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
BF1 : 100.6127690 MHz
DATE_d : May 26 2006
*** Processing Parameters ***
SF : 100.6127593 MHz
BRUKER
141.0576
137.2955
129.0163
128.9615
125.8004
115.9791
77.4798
77.1600
76.8402
72.6102
61.5282
43.5576
39.0809
34.0104
30.7123
27.7156
23.7871
(ppm)


CF256N11 CDCl31H Spectrum
*** Current Data Parameters ***
NAME : cf256n11
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 500.1300285 MHz
Integral
(ppm)


CF256N11 CDCl3C13CPD
*** Current Data Parameters ***
NAME : cf256n11
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577760 MHz
(ppm)


CF300N11 CDCl31H Spectrum
*** Current Data Parameters ***
NAME : cf300n11
EXPNO : 1
PROCNO : 1
*** Processing Parameters ***
SF : 500.1300285 MHz
Integral
(ppm)


CF300N11 CDCl3C13CPD
*** Current Data Parameters ***
NAME : cf300n11
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 125.7577754 MHz
(ppm)