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Supporting Information

High diversity on simple substrates: 1,4-dihalo-2-butenes and other difunctionalized allylic halides for Cu-catalyzed SN2' reactions

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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). IR spectra were recorded on Perkin-Elmer FT-IR Spectrometer. 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 or He as vector gas) with the stated column. 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 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 room temperature 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* **6a**
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(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 (–).

(–)-*(R)-(3-(Chloromethyl)pent-4-enyl)benzene* **7a**
SiO_2, pentane, R_F = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$) : 7.29 (m, 5H), 5.71 (ddd, *J*=8.3 Hz, *J*= 10.3 Hz, *J*= 17.2 Hz, 1H), 5.21 (d, *J*= 10.3 Hz, 1H), 5.16 (d, *J*= 17.2 Hz, 1H), 3.52 (d, *J*= 5.8 Hz, 2H), 2-73-2.53 (m, 2H), 2.45-2.37 (m, 1H), 1.73-1.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) : 142.0, 138.9, 128.5, 126.1, 117.6, 48.8, 45.4, 33.7, 33.1. MS (EI mode) *m/z* (%) : 194(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 73% 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 (–).

(–)-*(R)-3-(Chloromethyl)hept-1-ene* **9a**
^{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 (–).

(–)-*(R)-3-(Chloromethyl)-7-methylocta-1,6-diene* **10a**
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}. ^{1}H 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 (–).

(–)-*(R)-7-tert-Butoxy-3-(chloromethyl)hept-1-ene* **11a**
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 (–).

(–)-*(S)-(1-Bromobut-3-en-2-yl)cyclohexane* **6b**
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}. ^{1}H 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*-**6b**. Ee was measured by chiral GC with a Chirasil-Dex CB, Helium flow (program: 100-0-1-170) R_T: 35.53 (+), 36.20 (–).

(–)-*(R)-(3-(Bromomethyl)pent-4-enyl)benzene* **7b**
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*-**7b**. 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 (–).

(–)-*(R)-3-(Bromomethyl)hept-1-ene* **9b**
^{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*-**9b**. 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 (–).

(–)-*(R)-3-(Bromomethyl)-7-methylocta-1,6-diene* **10b**
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}. ^{1}H 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 (–).

(–)-*(R)-7-tert-Butoxy-3-(bromomethyl)hept-1-ene* **11b**
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}.
^{1}H 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 (–).

(R)-3-(bromomethyl)-5-methylhex-1-ene **12b**
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}. ^{1}H 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 (–).

(S)-(1-chlorobut-3-en-2-yl)benzene **13**
SiO_2, pentane, R_F = 0.88. ^{1}H NMR (400 MHz, $CDCl_3$) : 7.37-7.32 (m, 2H), 7.29-7.23 (m, 3H), 6.02 (ddd, *J*= 7.3 Hz, *J*= 10.4 Hz, *J*= 17.4 Hz, 1H), 5.23 (d, *J*= 10.3 Hz, 1H), 5.17 (d, *J*= 17.2 Hz, 1H), 3.79 (d, *J*=2.0 Hz, 1H), 3.77 (s, 1H), 3.70-3.65 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) : 140.8, 138.1, 128.8, 128.8, 127.9, 127.9, 127.3, 117.2, 52.0, 47.9. Ee was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 70-0-1-170) R_T: 38.30 (–), 40.98 (+).

(–)-*(S)-2-methyl-4-phenylbutan-1-ol* **18**
A solution of olefin (+)-**13** (0.86 mmol) in dry CH_2Cl_2 (30 mL) was cooled to –78°C, and ozone was passed through until a blue persisting color appeared (~10 min). After completion of the reaction, the excess ozone was removed by purging with O_2 and N_2. Cooling the system with an ice-bath, sodium borohydride (1.72 mmol) and methanol (5 mL) were added to the reaction. The resulting mixture was permitted to warm to RT and stirred overnight. More $NaBH_4$ (1.72 mmol) was added at 0°C (and more). After 7 days, reaction was hydrolyzed with H_2O (15 mL) and extracted with Et_2O, dried over Na_2SO_4. Crude product was then chromatographied on Silica gel (eluent pentane/Et_2O 75:25). One obtains the alcohol as slightly yellow oil (0.33 mmol) with 38% yield. ^{1}H

NMR (400 MHz, $CDCl_3$) : : 7.29-7.26 (m, 2H), 7.20-7.16 (m, 3H), 3.51 (dd, *J*= 38.1 Hz, *J*= 5.8 Hz, 1H), 3.51 (dd, *J*= 17.2 Hz, *J*= 5.8 Hz, 1H), 2.75-2.56 (m, 2H), 1.81-1.63 (m, 2H), 1.49-1.38 (m, 2H), 0.99 (d, *J*= 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) : 128.5, 125.9, 68.3, 35.5, 35.1, 33.4, 16.6. $[\alpha]_D^{22}$= –10.21 (*c* 0.89, $CHCl_3$) for 63% *ee*. (Litt $[\alpha]_D^{22}$= +20.0 (*c* 1.5, $CHCl_3$) for 99% *ee* (*R*))[1]

(+)-(S)-Hepta-1,6-dien-3-ylcyclohexane **19**
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).

(S)-but-3-en-2-ylcyclohexane **20**[2]
SiO_2, pentane, R_F = 0.97. ^{1}H-NMR ($CDCl_3$, 400 MHz) : 5.52 (ddd, 1H, J_1 = 17.60, J_2 = 9.6, J_3 = 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*).

(R)-7-tert-butoxy-3-(iodomethyl)hept-1-ene **21**[3]
A saturated solution of sodium iodide in acetone was added to a solution of the homoallylic bromide (**44**) or chloride (**36**) and left stirring overnight at room temperature or reflux until complete conversion. After precipitation of the salts, the solution is filtered and evaporated *in vacuo*. The crude is used without further purification (>98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) : 5.60-5.51 (m, 1H), 5.13-5.04 (m, 2H), 3.32 (t, *J*= 6.8Hz, 2H), 3.20-3.16 (m, 2H), 2.15-2.10 (m, 1H), 1.57-1.28 (m, 6H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) : 140.7, 116.5, 72.6, 61.4, 45.4, 34.6, 30.6, 27.7(3), 23.8, 13.8. MS (EI mode) *m/z* (%) : 295 (4), 181 (6), 109 (51), 67 (30), 59 (28), 57 (100), 55 (22). Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 110-33-0.5-115-25-20-170) R_T: 70.25 (major), 70.43 (minor).

(S)-(6-tert-Butoxy-2-vinylhexyl)(phenyl)sulfane **22**
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 **23**
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(+).

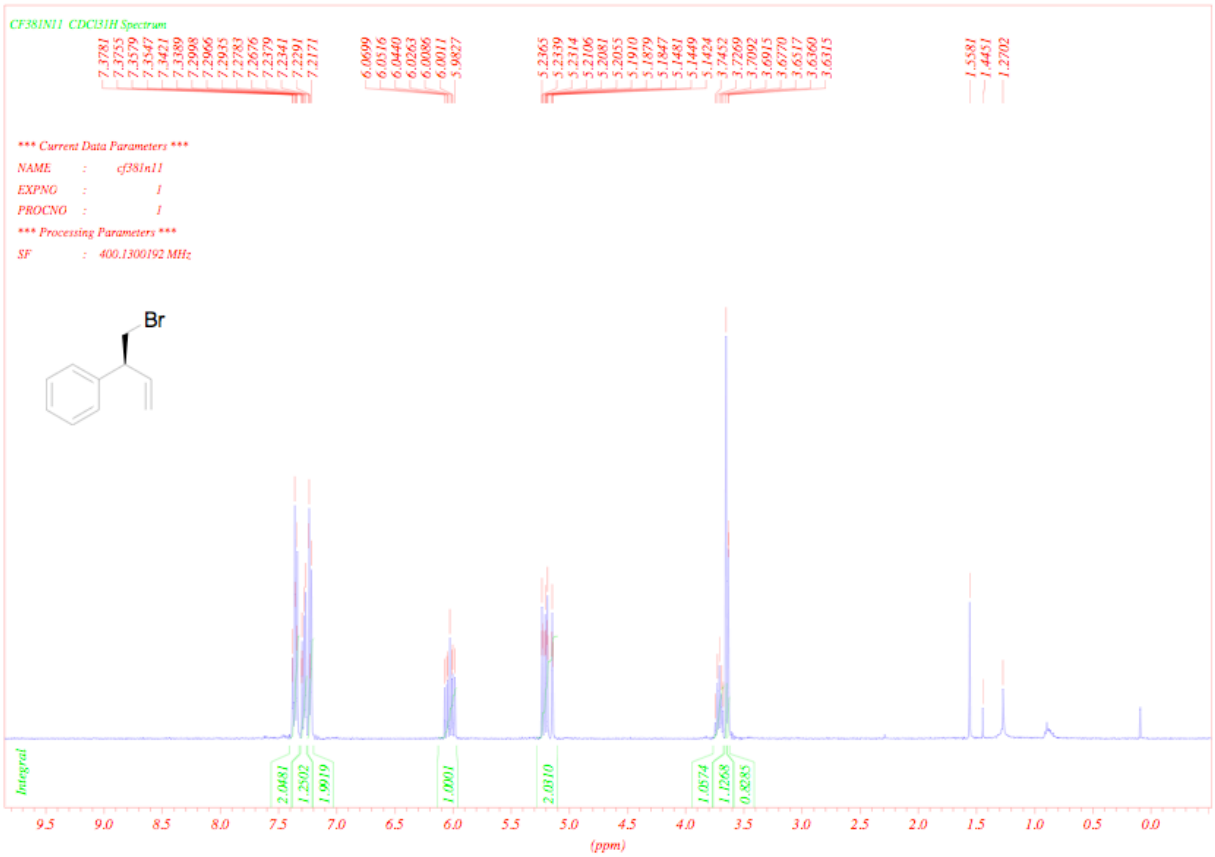
(+)-(R)-7-tert-butoxy-3-vinylheptanal **24**
SiO_2, pentane/diethyl ether 97.5:2.5, R_F = 0.23. IR (neat): 3071(w), 2974(m), 2935(m), 2865(m), 2718(w), 1725(s), 1641(w), 1477(w), 1461(w), 1391(m), 1362(s), 1253(w), 1198(s), 1081(s), 995(m), 915(m), 878(m), 751(br), 676(br) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 500 MHz) : 9.71 (*t*, *J*= 2.2Hz, 1H), 5.65 (*ddd*, J_1= 8.2 Hz, J_2= 9.8 Hz,

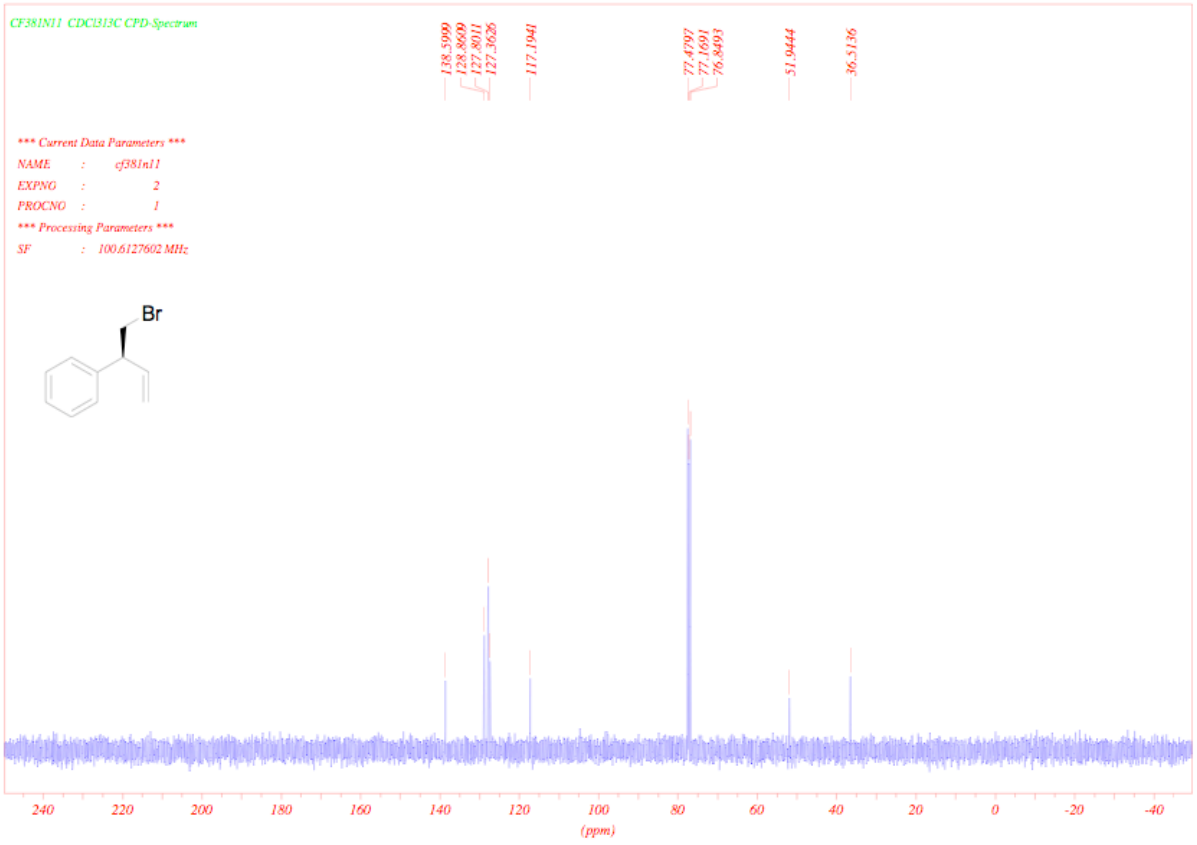
[1] Z. Huang, Z. Tan, T. Novak, G. Zhu,E. Negishi, *Adv. Synth. Catal*. **2007**, *349*, 539 – 545
[2] a) S. E. Denmark, L. K. Marble, *J. Org. Chem*. **1990**, *55*, 1984; b) K. Tissot-Croset, A. Alexakis, *Tetrahedron Letters* **2004**, *45*, 7375; c) M. A. Kacprzynski, A. H. Hoveyda, *J. Am. Chem. Soc*. **2004**, *126*, 10676.
[3] T. W. Baughman, J. C. Sworen, K. B. Wagener, *Tetrahedron* **2004**, *60*, 10943.

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(-).

(–)-*(R)-cyclopent-2-enylcyclohexane* **25**
SiO_2, pentane, R_F = 0.99. ^{1}H-NMR ($CDCl_3$, 400 MHz) : 5.74 (s, 2H), 2.47-0.92 (7m, 16H). ^{13}C-NMR ($CDCl_3$, 100 MHz) : 133.5, 130.6, 51.8, 43.0, 32.2, 31.2, 31.1, 27.4, 26.8, 26.6, 26.6. MS (EI mode) *m/z* (%) : 150 (34), 109 (15), 82 (45), 67 (100), 55 (44). $[\alpha]_D^{22}$= -88.2 (*c* 1.03, CHCl3) for 73% 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).

(R)-3-(bromomethyl)-2-methylhept-1-ene **27a**
SiO_2, pentane, R_F = 0.95. ^{1}H NMR (400 MHz, $CDCl_3$) : 4.89 (s, 1H), 4.78 (s, 1H), 3.38 (d, *J*= 6.6 Hz, 2H), 2.40 (quint, *J*= 7.1 Hz, 1H), 1.66 (s, 3H), 1.59-1.50 (m, 1H), 1.45-1.19 (m, 5H), 0.89 (t, *J*= 7.1 Hz, 3H). MS (EI mode) *m/z* (%) : 150(7), 148(7), 95(5), 91(5), 83(6), 79(6), 69(100), 68(14), 67(36), 55(29), 53(15). Ee was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 70-0-1-170) R_T: 21.41 (minor), 21.93 (major). [for **28a**: Ee was measured by chiral GC with a Hydrodex B3P, Hydrogen flow (program: 80-0-1-170) R_T: 16.38 (major), 16.66 (minor)].

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36.5136
*** Current Data Parameters ***
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EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
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120
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60
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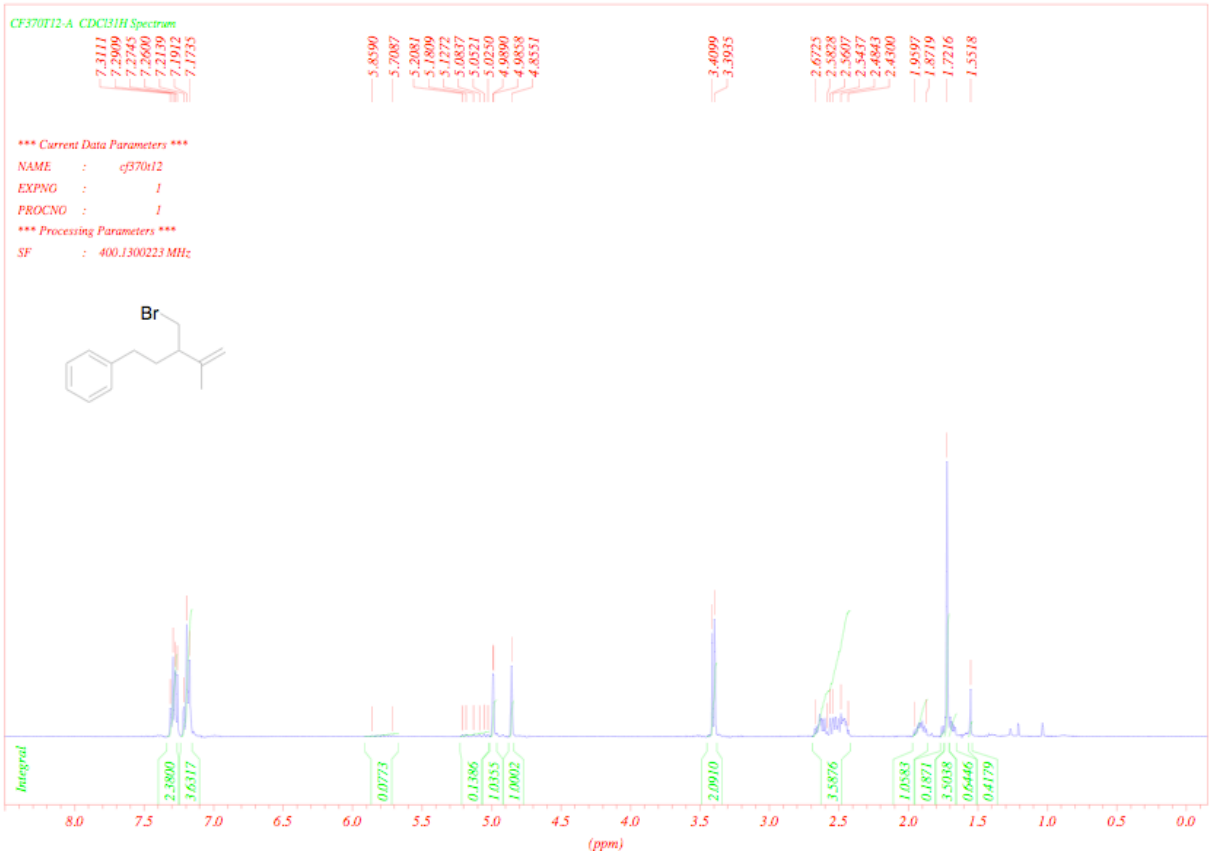
(ppm)


CF370T12-A CDCl3 1H Spectrum
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7.2745
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7.1912
7.1735
5.8590
5.7087
5.2081
5.1809
5.1272
5.0837
5.0521
5.0250
4.9890
4.9658
4.8551
3.4099
3.3935
2.6725
2.5828
2.5607
2.5437
2.4843
2.4300
1.9597
1.8719
1.7216
1.5518
*** Current Data Parameters ***
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PROCNO : 1
*** Processing Parameters ***
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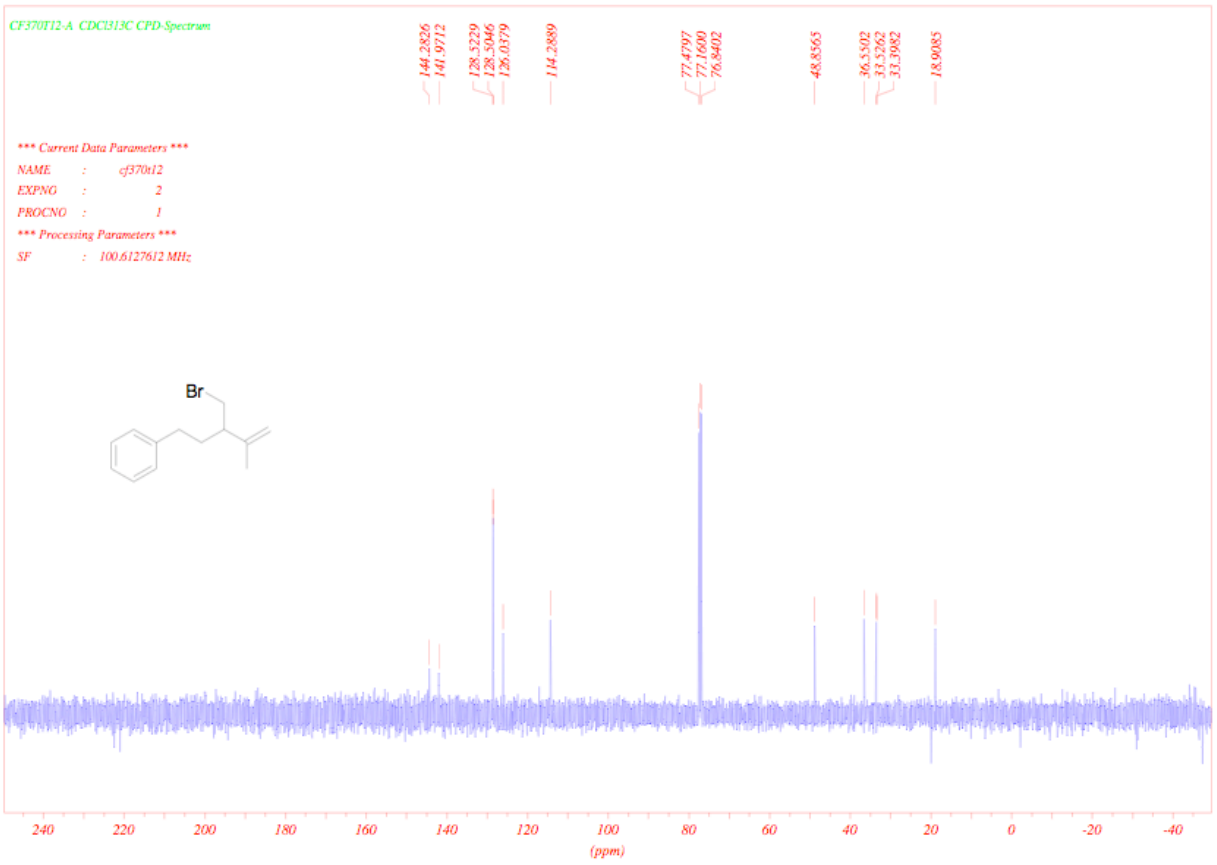
0.0773
0.1386
1.0355
1.0002
2.0910
3.5876
1.0583
0.1871
3.5038
0.6446
0.4179
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)


CF370T12-A CDCl313C CPD-Spectrum
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128.5229
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77.4797
77.1600
76.8402
48.8565
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PROCNO : 1
*** Processing Parameters ***
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60
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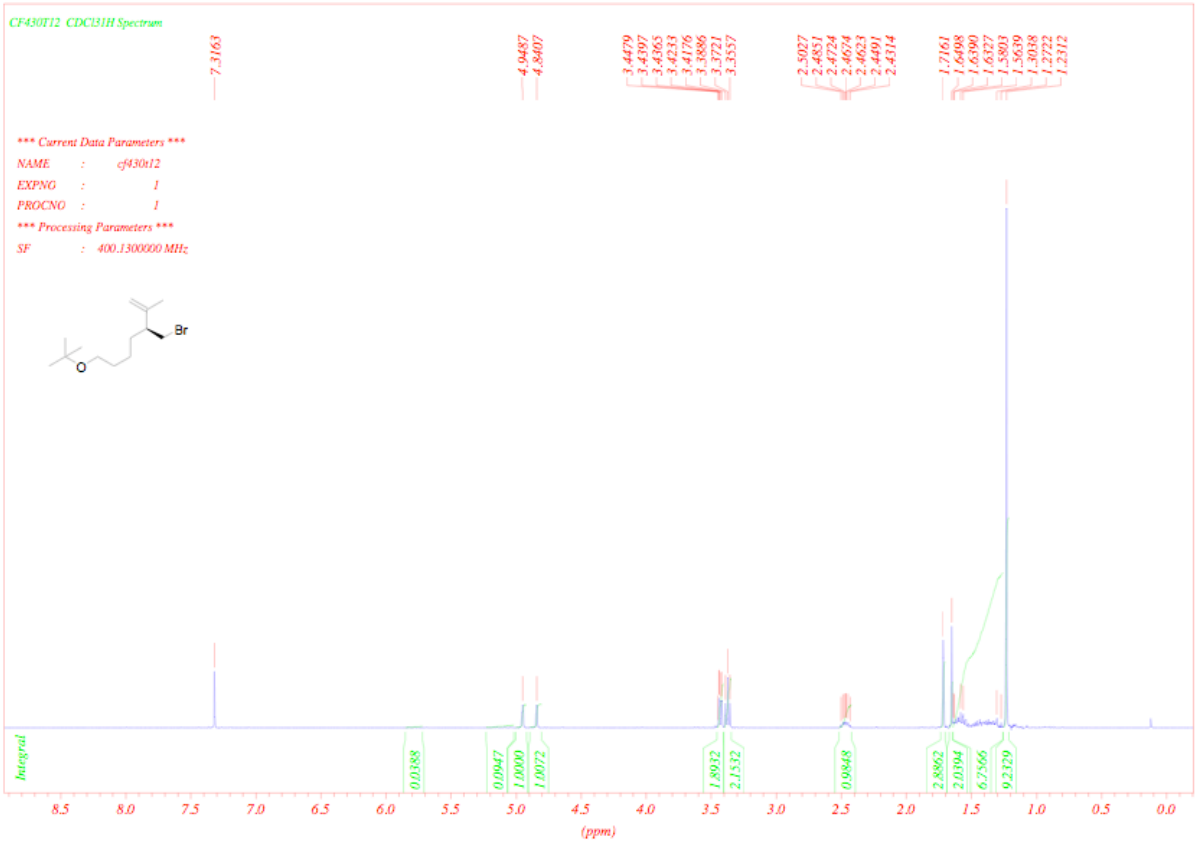
(ppm)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3.3721
3.3557
2.5027
2.4851
2.4724
2.4674
2.4623
2.4491
2.4314
1.7161
1.6498
1.6390
1.6327
1.5803
1.5639
1.3038
1.2722
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PROCNO : 1
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O
Integral
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2.1532
0.9848
2.8862
2.0394
6.7566
9.2329
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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2.0
1.5
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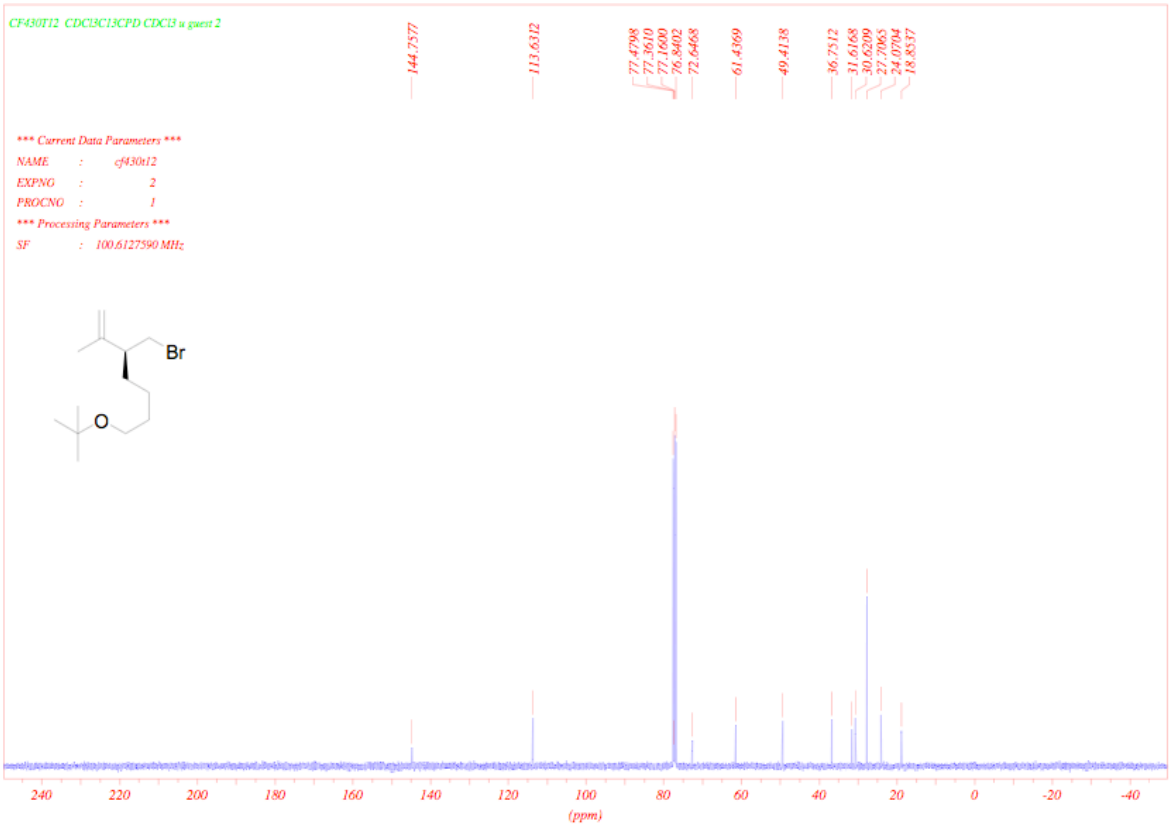
0.0
(ppm)


CF430T12 CDCl3C13CPD CDCl3 u guest 2
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113.6312
77.4798
77.3610
77.1600
76.8402
72.6468
61.4369
49.4138
36.7512
31.6168
30.6200
27.7065
24.0704
18.8337
*** Current Data Parameters ***
NAME : cf430t12
EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
SF : 100.6127590 MHz
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O
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220
200
180
160
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40
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-20
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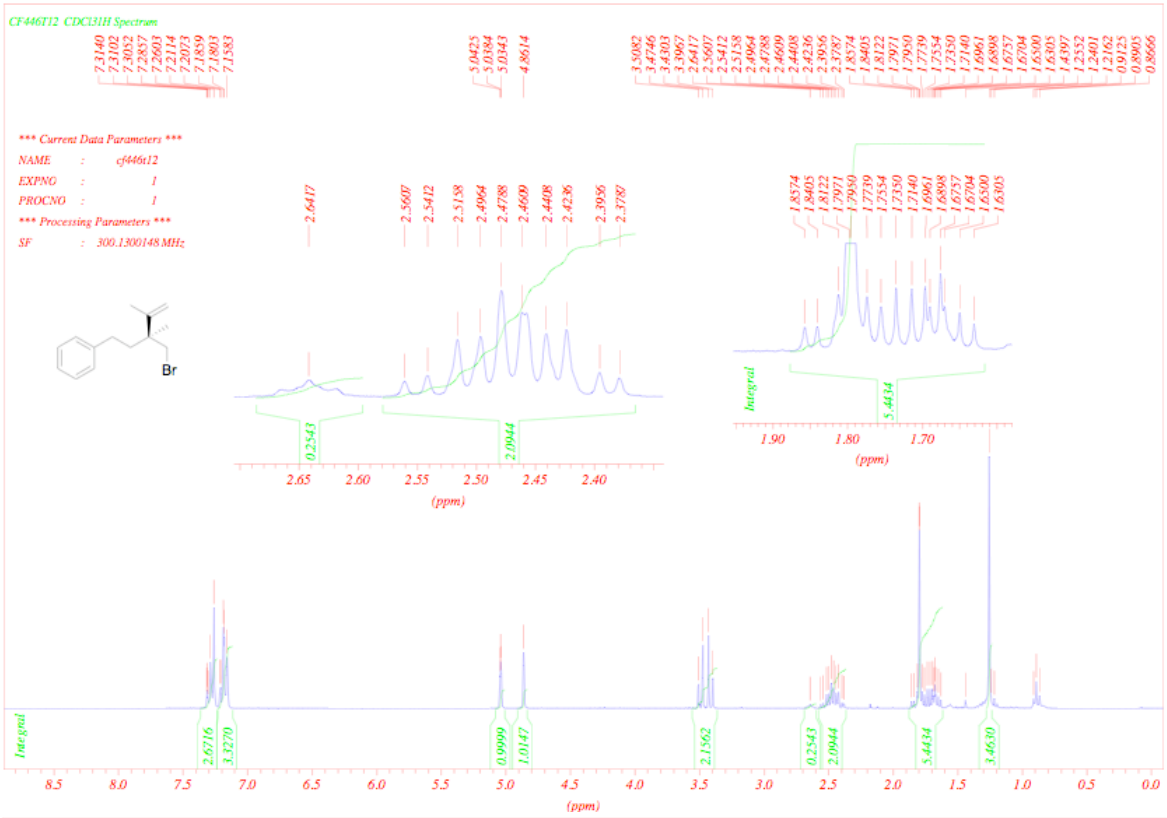
(ppm)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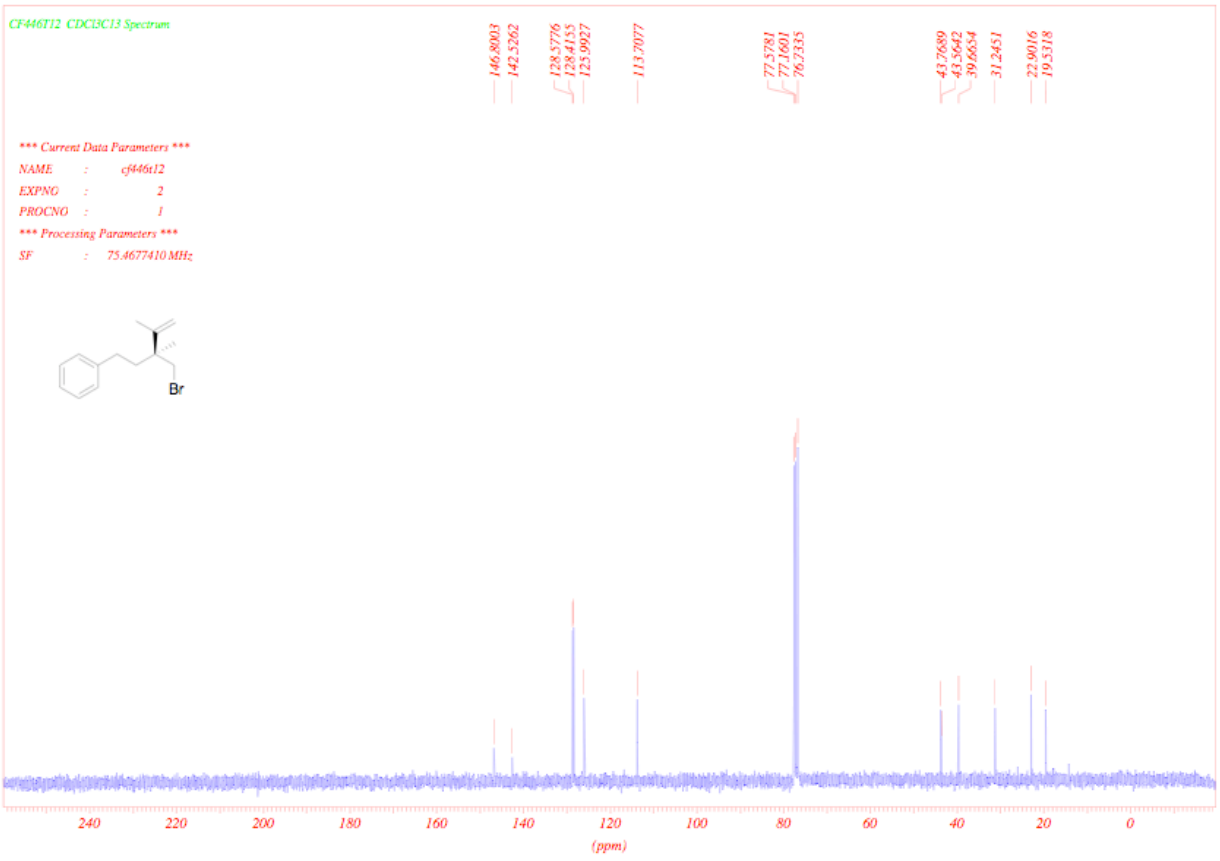
Br
Integral
(ppm)


CF446T12 CDCl3C13 Spectrum
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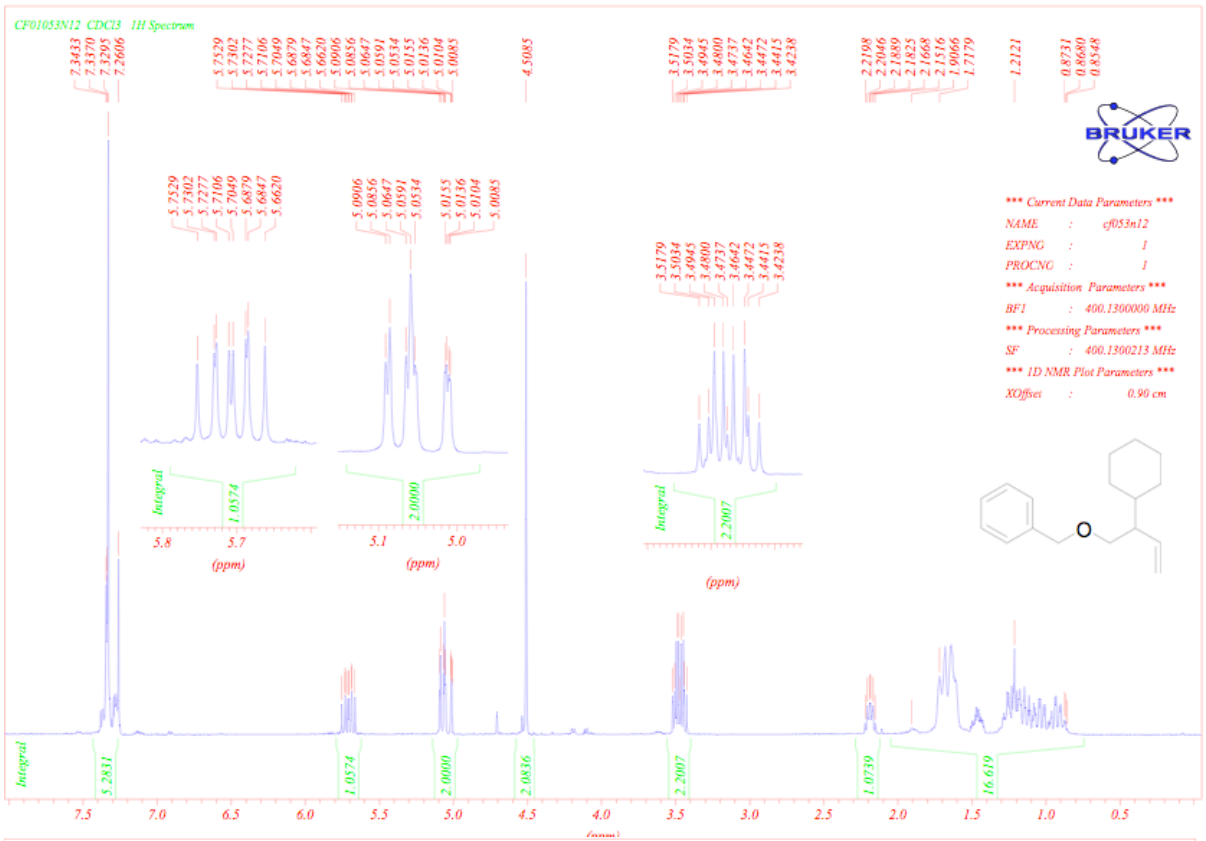
Br
(ppm)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BRUKER
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*** 1D NMR Plot Parameters ***
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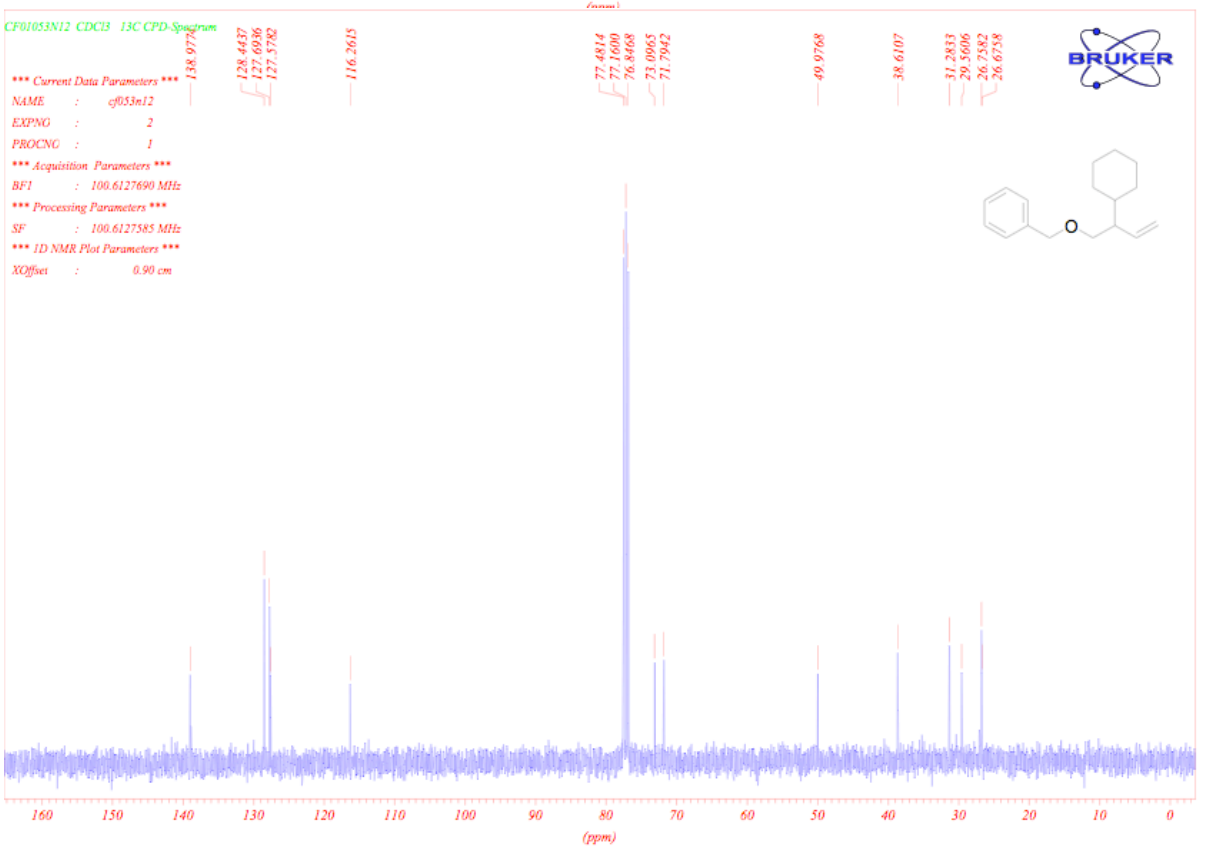
16.619
(ppm)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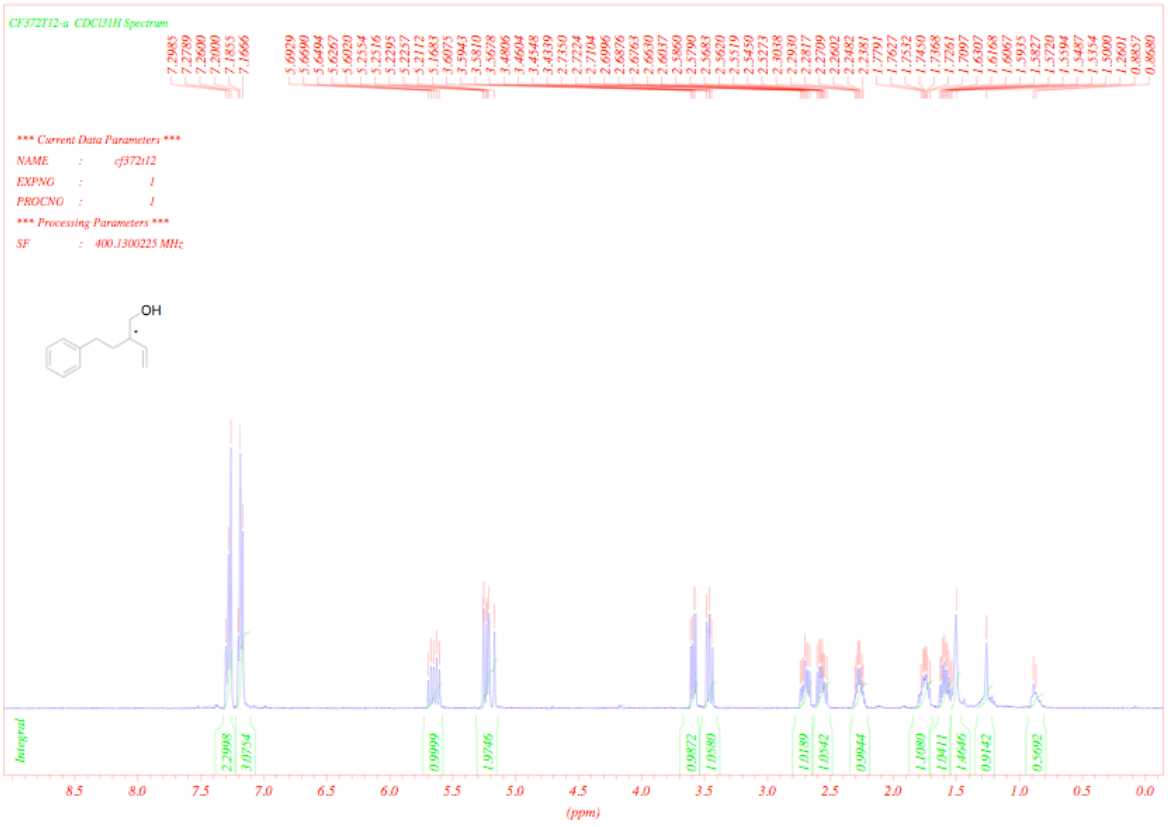
CF372T12-a CDCl3 1H Spectrum
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*** Processing Parameters ***
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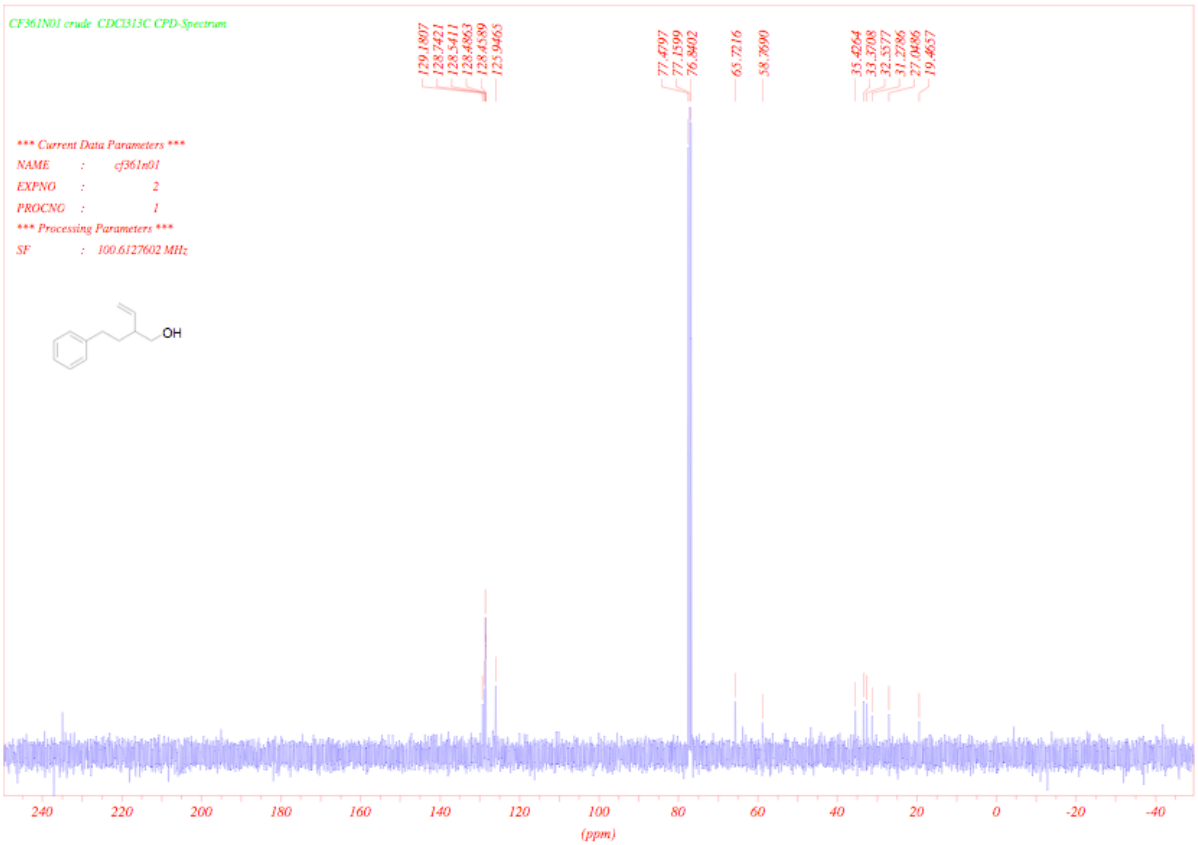
Integral
(ppm)


CF361N01 crude CDCl3 13C CPD-Spectrum
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EXPNO : 2
PROCNO : 1
*** Processing Parameters ***
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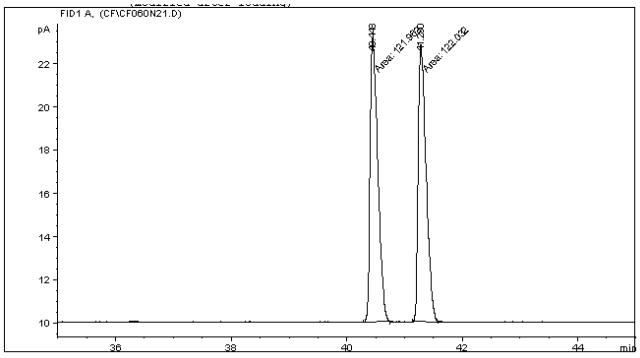
(ppm)

6a



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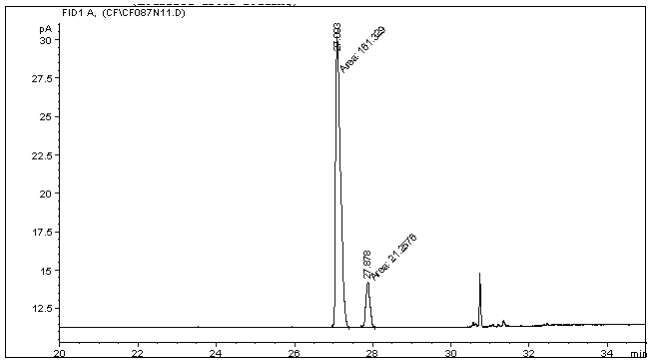

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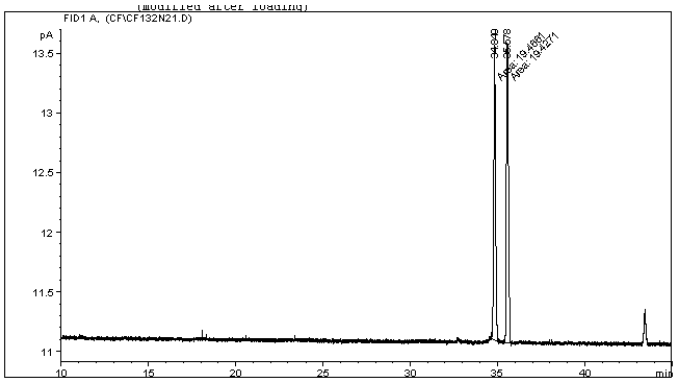
6b



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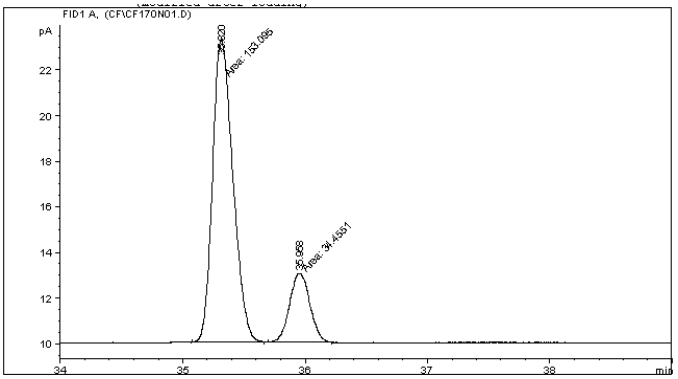

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1	35.320	MM	0.1926	153.09518	13.24805	81.62886
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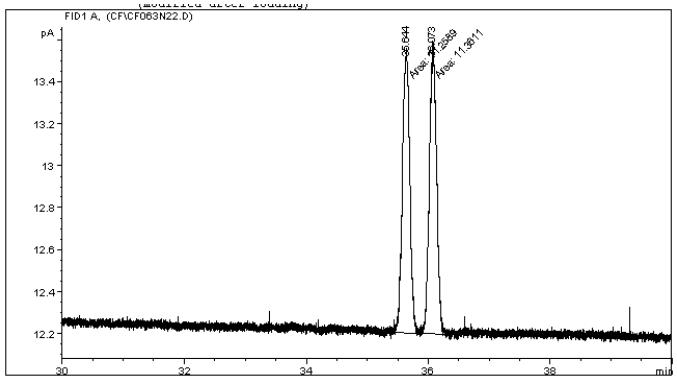
7a



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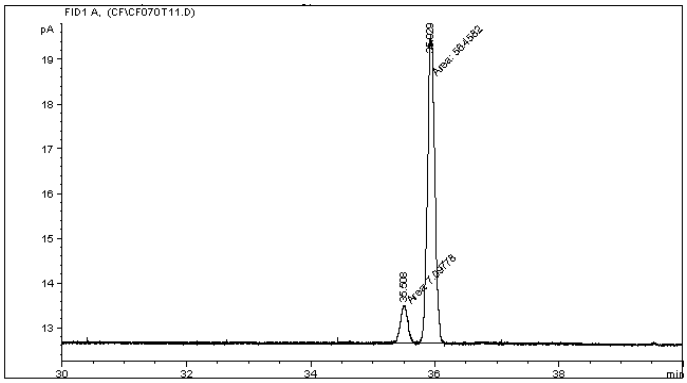

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
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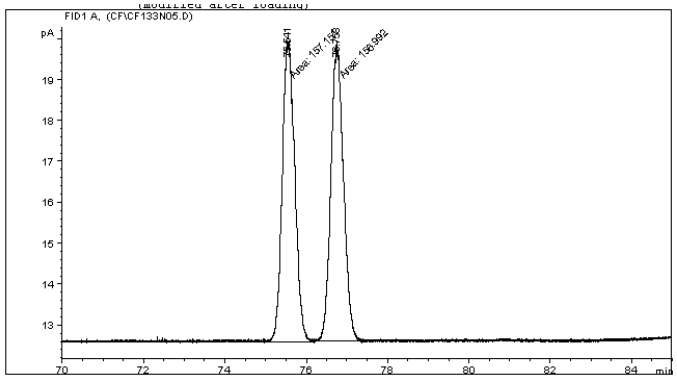
7b



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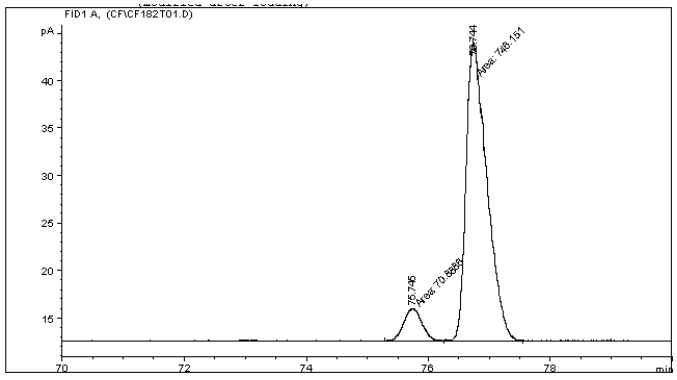

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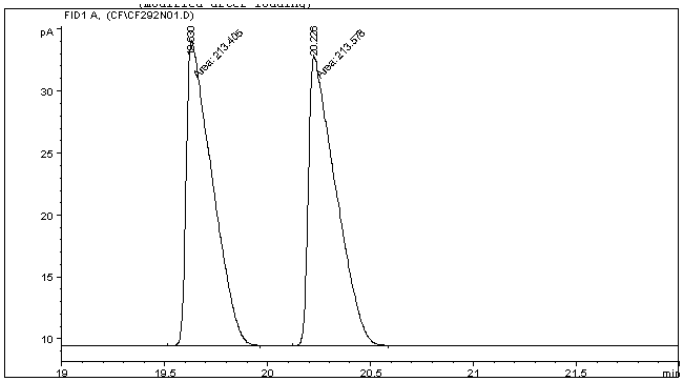
9a



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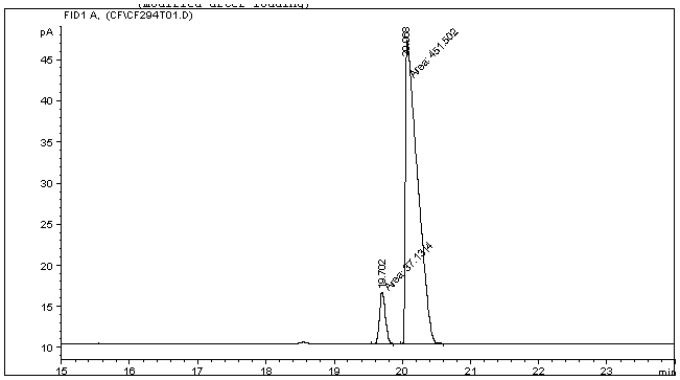

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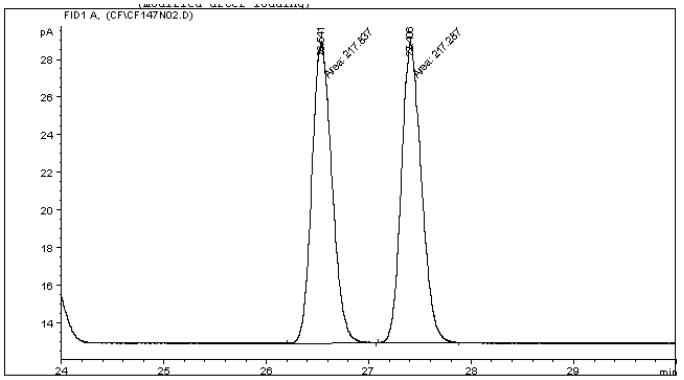
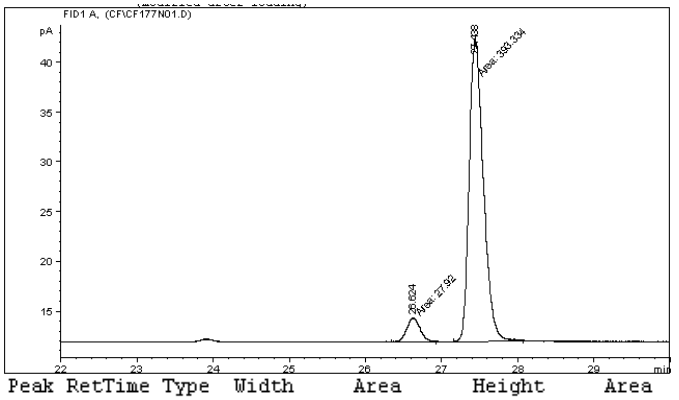
2	20.068	MM	0.2039	451.50211	36.91111	92.40096

9b

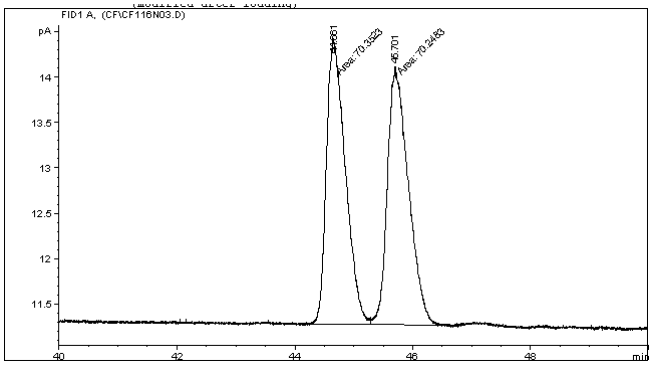


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.541	MM	0.2261	217.83658	16.05514	50.06310
2	27.406	MM	0.2256	217.28743	16.04957	49.93690

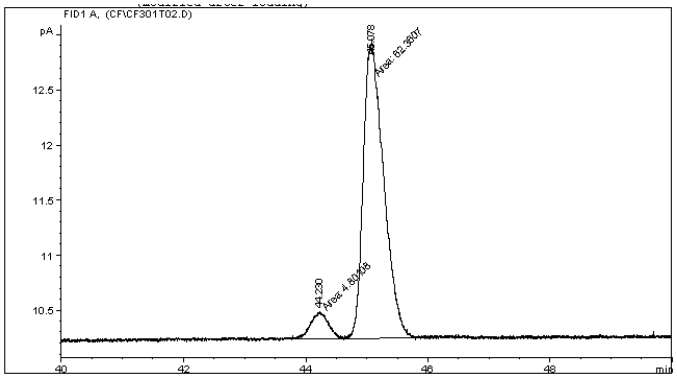


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	26.624	MM	0.1943	27.92003	2.39483	6.62784
2	27.438	MM	0.2160	393.33395	30.35312	93.37216

10a

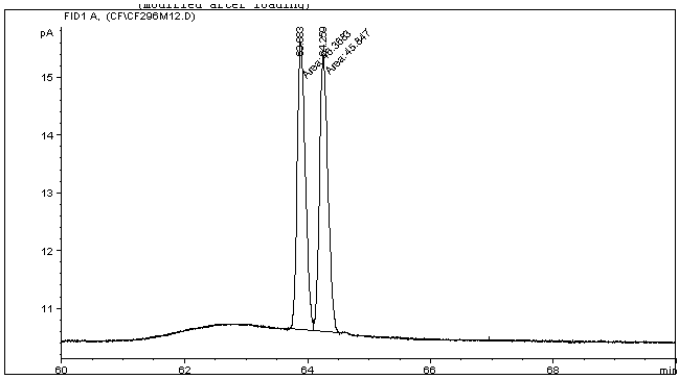


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.661	MF	0.3727	70.35233	3.14569	50.03698
2	45.701	FM	0.4114	70.24833	2.84608	49.96302

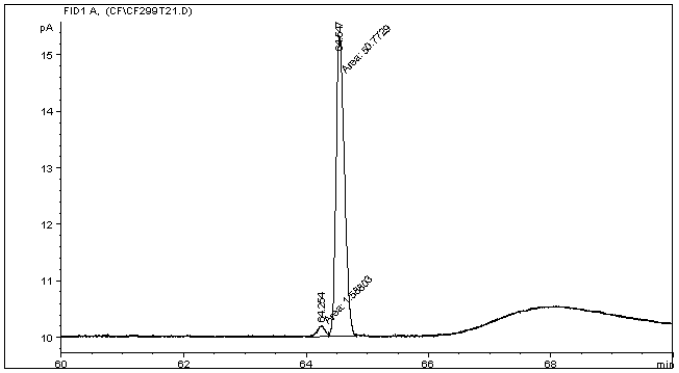


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	44.230	MM	0.3345	4.80108	2.39239e-1	7.14852
2	45.078	MM	0.3832	62.36071	2.71248	92.85148

10b

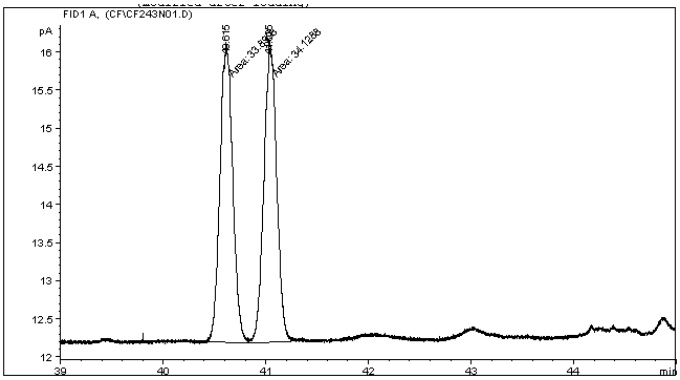


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	63.882	MF	0.1547	46.40203	4.99971	50.26138
2	64.259	FM	0.1607	45.91942	4.76305	49.73862

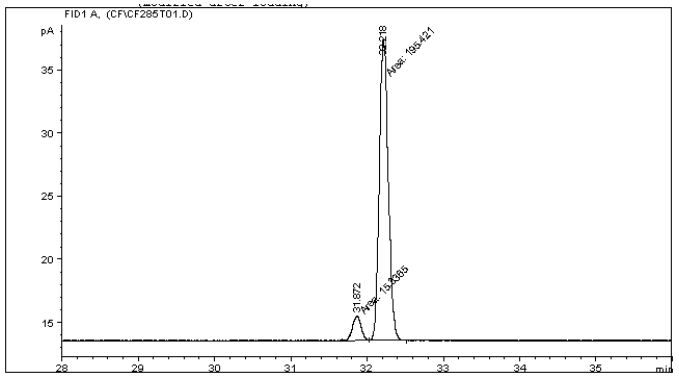


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	64.254	MF	0.1400	1.58803	1.89094e-1	3.03286
2	64.547	FM	0.1592	50.77288	5.31494	96.96714

11a

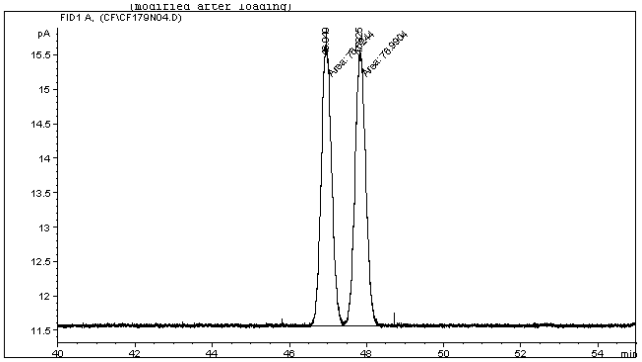


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	40.615	MM	0.1438	33.89933	3.93035	49.83132
2	41.035	MM	0.1433	34.12883	3.96928	50.16868

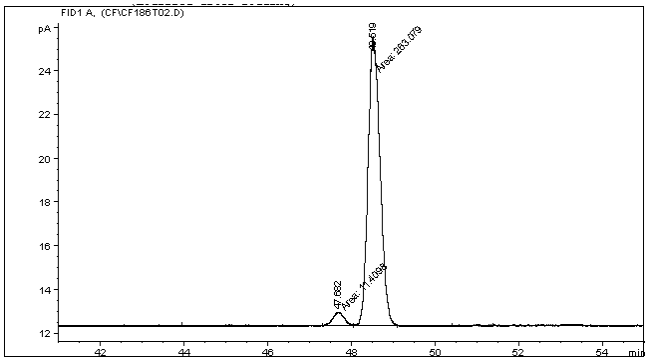


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	31.872	MM	0.1302	15.33650	1.96254	7.27685
2	32.218	MM	0.1365	195.42084	23.86440	92.72315

11b

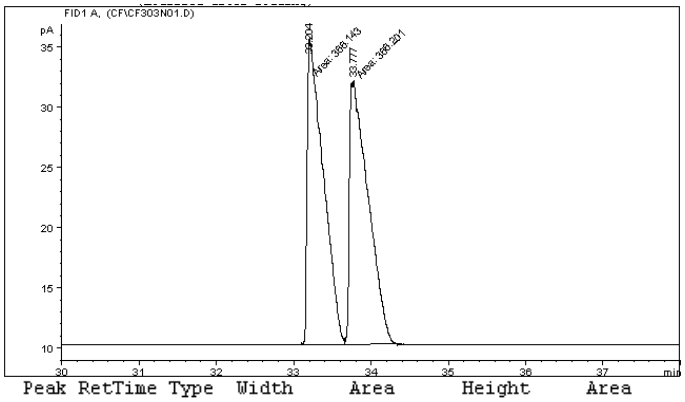


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	46.949	MM	0.3092	76.62444	4.13066	49.88089
2	47.825	MM	0.3253	76.99037	3.94415	50.11911

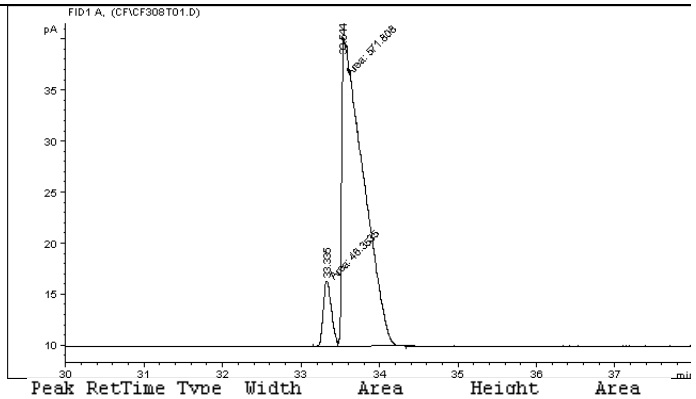


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	47.682	MM	0.3066	11.40983	6.20268e-1	4.15676
2	48.519	MM	0.3324	263.07904	13.18949	95.84324

12b

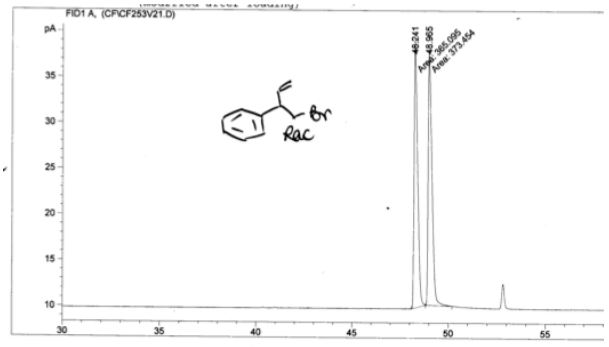


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.204	MF	0.2403	366.14313	25.39237	49.99608
2	33.777	FM	0.2787	366.20056	21.89900	50.00392

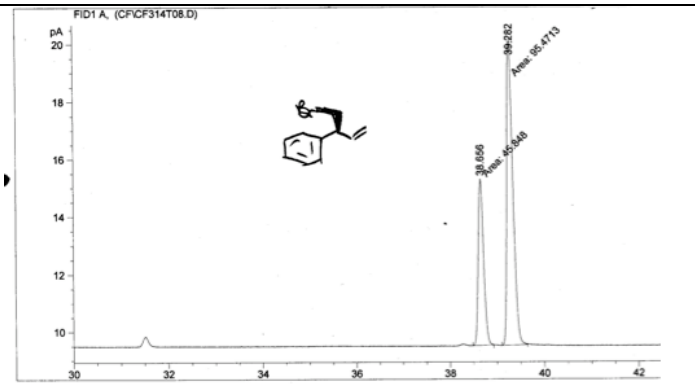


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	33.335	MF	0.1210	46.35355	6.38417	7.49862
2	33.544	FM	0.3169	571.80774	30.07402	92.50138

15

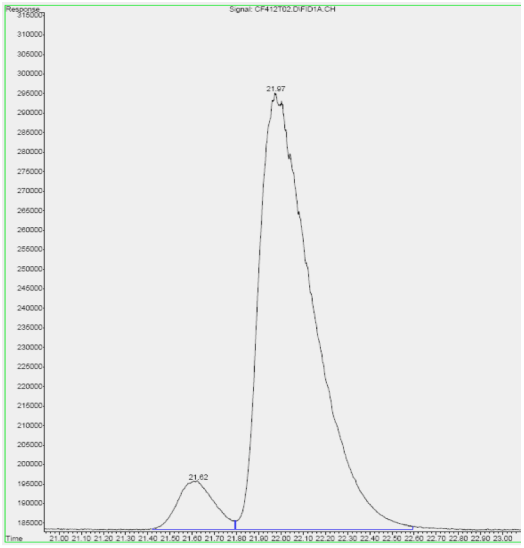


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	48.241	MM	0.2079	365.09497	29.27159	49.43412
2	48.965	MM	0.2251	373.45358	27.65007	50.56588



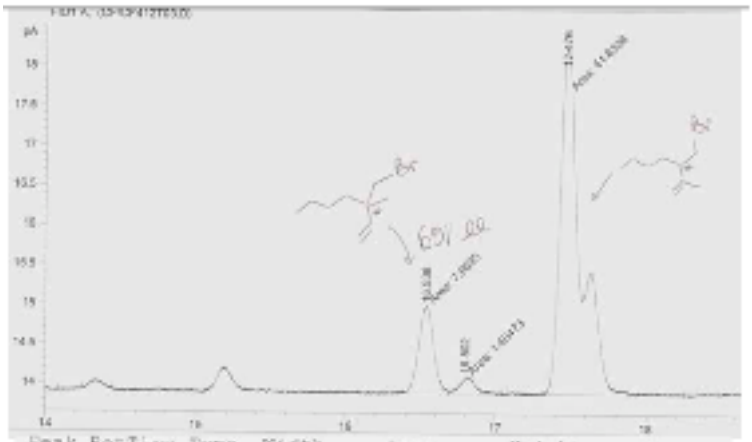
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	38.656	MM	0.1320	45.84803	5.78817	32.44286
2	39.282	MM	0.1497	95.47130	10.63162	67.55714

27a



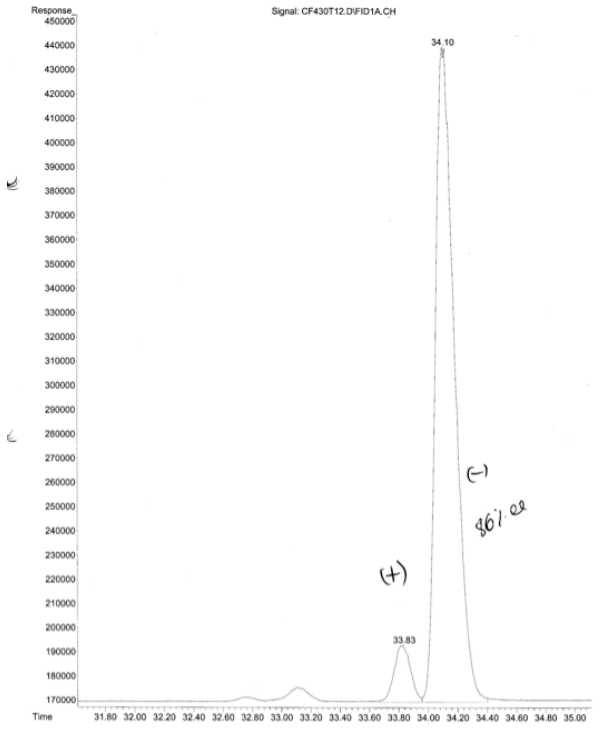
peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	21.623	21.423	21.791	M	12452	1416622	7.57%	7.036%
2	21.972	21.795	22.593	M	111800	18718244	100.00%	92.964%

28a



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.538	MM	0.1156	7.66930	1.10596	15.12454
2	16.802	MM	0.1115	1.40473	2.10054e-1	2.77026
3	17.476	MM	0.1587	41.63363	4.37152	82.10520

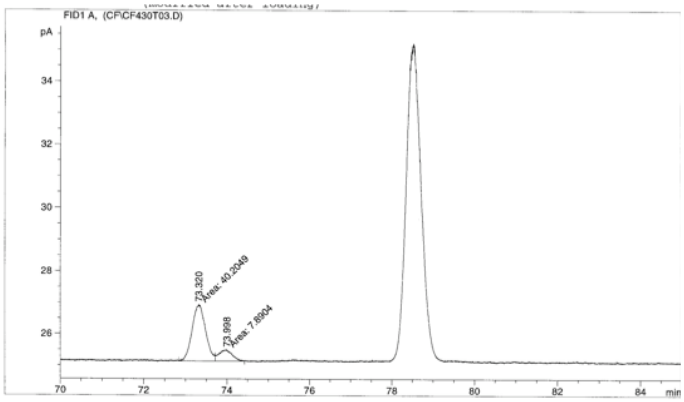
27c



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	33.829	33.667	33.954	M	23695	1850069	7.56%	7.027%
2	34.095	33.959	34.401	M	270337	24476526	100.00%	92.973%

Sum of corrected areas: 26326595

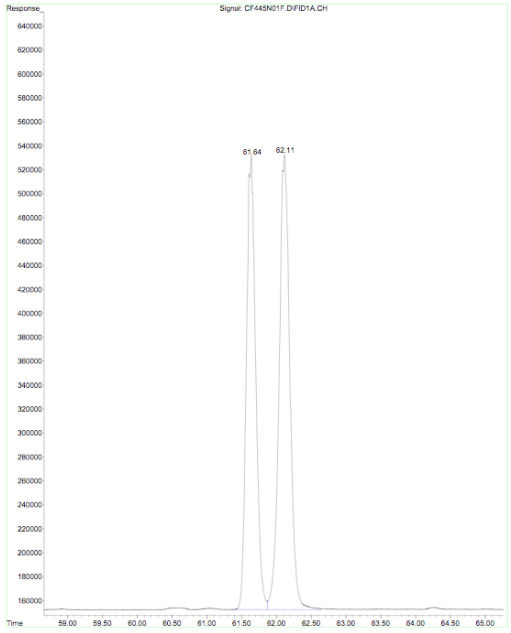
28c



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	73.320	MF	0.3703	40.20486	1.80973	83.59422
2	73.998	FM	0.3608	7.89040	3.64521e-1	16.40578
Totals :				48.09526	2.17425	

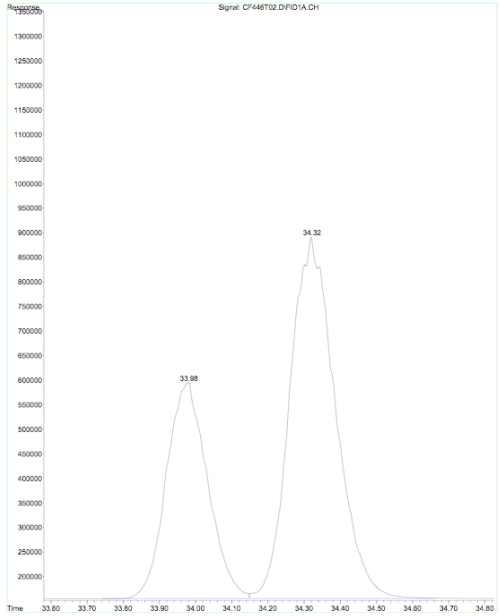
30

(program: 70-0-1-170)



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	61.639	61.349	61.869	M	379142	35259816	86.64%	46.420%
2	62.115	61.872	62.644	M	380575	40697712	100.00%	53.580%

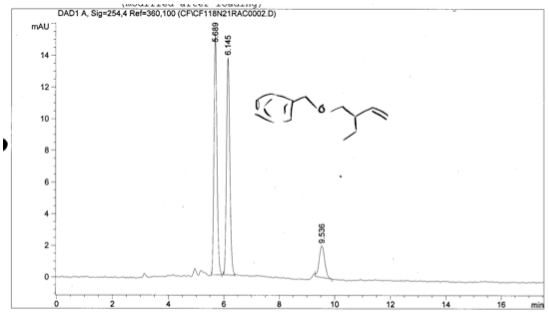
Sum of corrected areas: 75957529



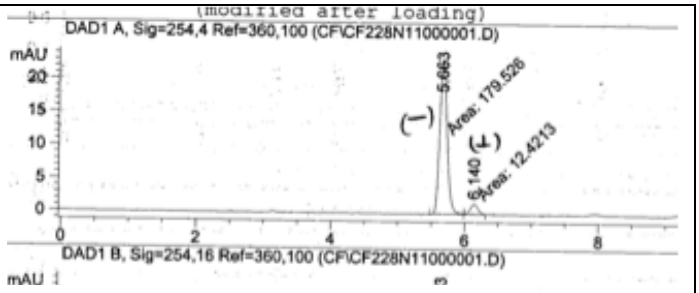
peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	33.979	33.742	34.147	M	440316	34785262	54.22%	35.157%
2	34.319	34.150	34.663	M	737416	64158530	100.00%	64.843%

Sum of corrected areas: 98943792

33

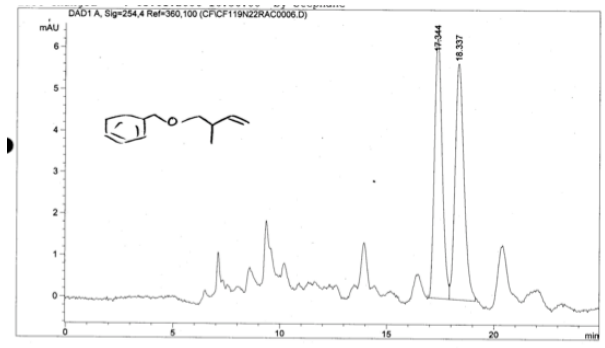


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.689	BB	0.1178	114.03793	15.15289	44.4034
2	6.145	BB	0.1295	114.84702	13.73886	44.7185

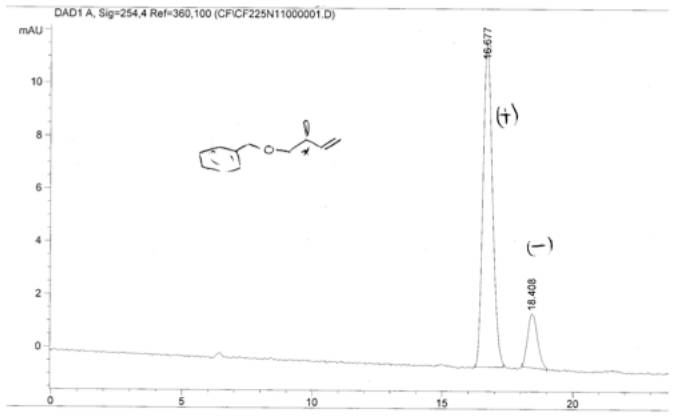


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.663	MM	0.1274	179.52573	23.48961	93.5288
2	6.140	MM	0.1320	12.42133	1.56826	6.4712

34



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.344	BV	0.3745	156.61659	6.24615	48.9917
2	18.337	VB	0.3974	163.06351	5.67139	51.0083



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.677	BB	0.3808	309.04266	12.23073	85.1101
2	18.408	BB	0.3207	54.06675	2.04360	14.8899