Copper-Catalyzed Enantioselective Synthesis of Axially Chiral Allenes

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Supporting Information

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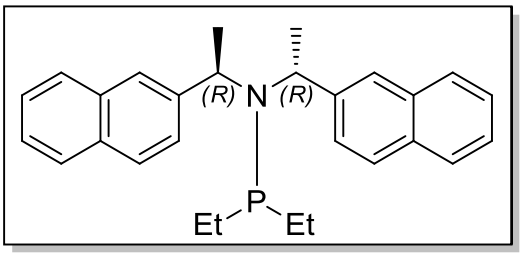
I) General remarks

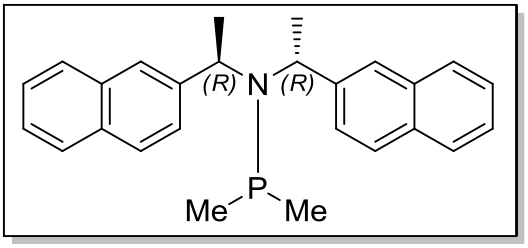
All reactions were carried out under argon atmosphere with flame-dried glassware. Solvents were dried by filtration over alumina previously activated at 350 °C during 12 hours under nitrogen before use. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{31}P (162 MHz) and ^{19}F (376 MHz) NMR spectra were recorded on a Bruker 400FTNMR in $CDCl_3$, 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), ddd (doublet of doublet of doublet), brs (broad singlet). Coupling constants are reported in Hertz (Hz). Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 25 °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. Temperature programs are described as follows: initial temperature (°C) - initial time (min) – temperature gradient (°C/min) - final temperature (°C); retention times (RT) are given in minute. Flash chromatography was performed using silicagel 32-63 µm, 60 Å. All chiral phosphoramidite ligands were prepared according to the litterature procedure.[1] The Simplephos ligands were prepared according to the literature procedure.[2] CuTC was purchased from FrontierScientific and used as received. CuBr and CuI was purchased from Sigma-Aldrich and used as received.

II) Experimental part

A) Preparation of Simplephos ligands.
For the details of preparation procedure, see references. [2]



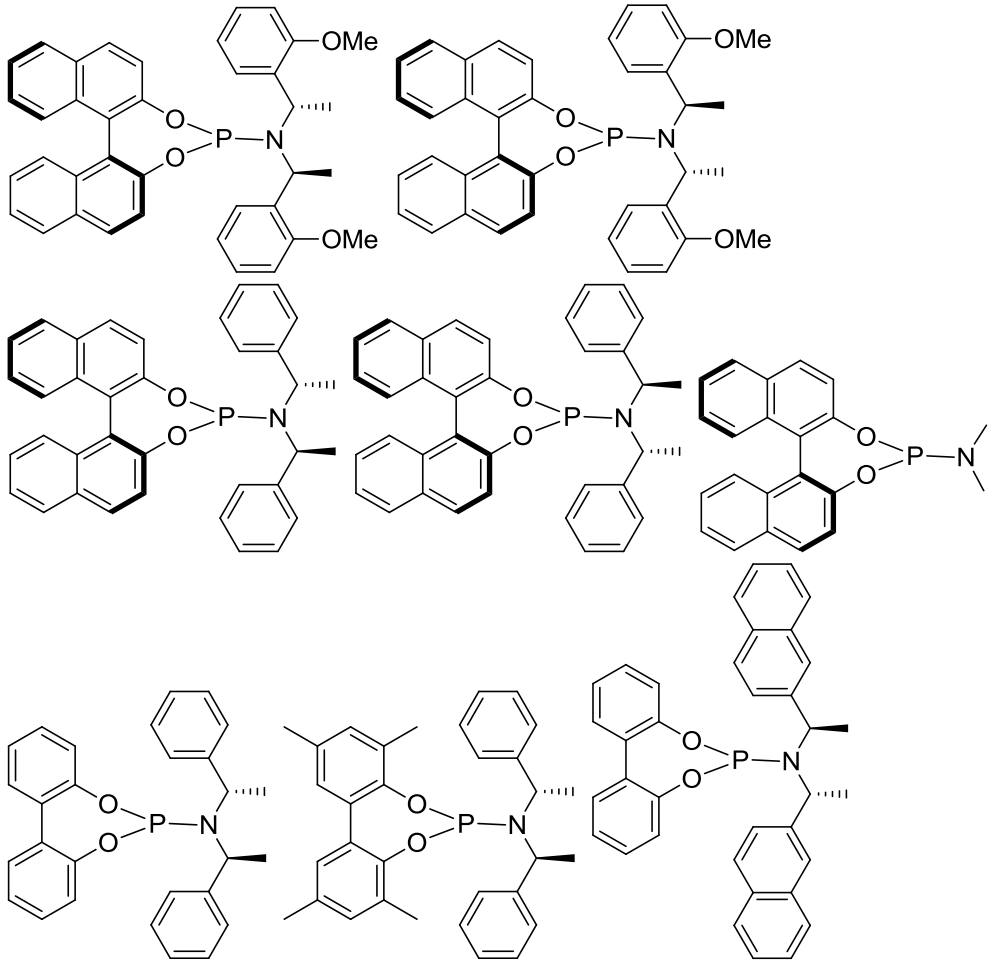
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2H), 7.57-7.51 (m, 4H), 7.43-7.36 (m, 6H), 7.10-7.07 (m, 2H), 4.58-4.50 (m, 2H), 1.84-1.78 (m, 1H), 1.75 (d, *J* = 6.9 Hz), 1.64-1.62 (m, 1H), 1.52-1.39 (m, 2H), 1.25 (dt, *J* = 15.8, 7.6 Hz), 0.64 (dt, *J* = 17.2, 7.6 Hz).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.1, 133.1, 132.3 128.0, 127.4, 127.3, 127.1, 126.2, 125.6, 125.4, 53.7 (d, *J* = 6.8 Hz), 22.0 (d, *J* =34.1 Hz), 21.8 (d, *J* =29.9 Hz), 21.7, 10.7 (d, *J* = 20.1 Hz), 9.7 (d, *J*=19.7 Hz)
^{31}P NMR (162 MHz, $CDCl_3$) δ 41.55.

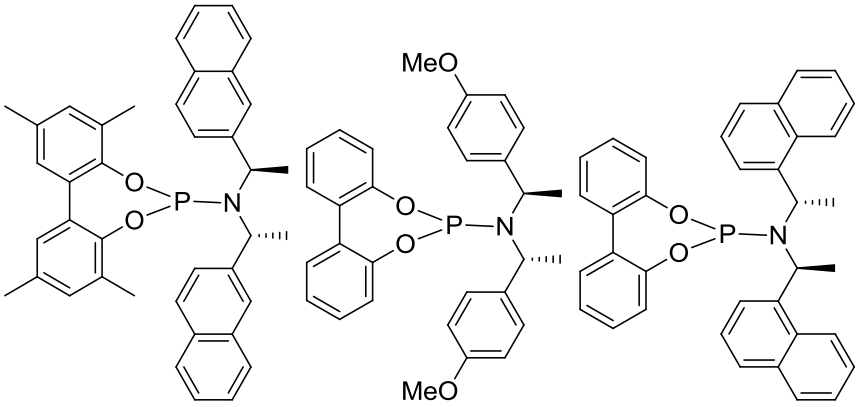


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.58-7.55 (m, 4H), 7.44-7.37 (m, 6H), 7.15 (dd, *J* = 8.6, 1.8 Hz, 2H), 4.58-4.50 (m, 2H), 1.76 (d, *J* = 6.9 Hz, 6H), 1.33 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 5.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 133.2, 132.4, 128.0, 127.5, 127.3, 127.2, 126.0, 125.7, 125.5, 53.5 (d, *J* = 6.5 Hz), 21.5 (d, *J* = 9.1 Hz), 17.7 (d, *J* = 18.2 Hz), 17.1 (d, *J* = 14.5 Hz).
^{31}P NMR (162 MHz, $CDCl_3$) δ 13.47.

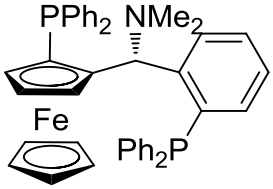
B) Chiral ligands list.

<u>Phosphoramidite ligands.</u>

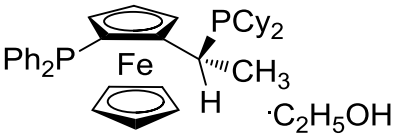




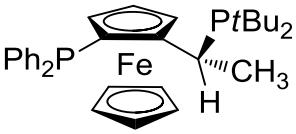
Ferrocene-based phosphorous ligands.



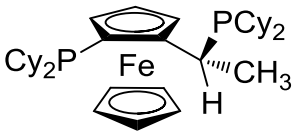
Taniaphos
T001-1



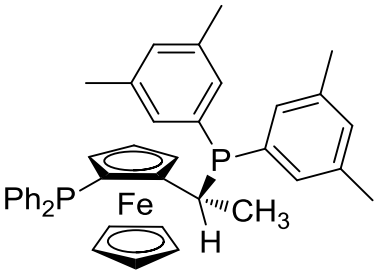
Josiphos
J001-1



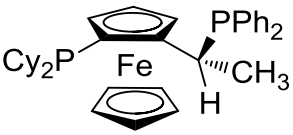
Josiphos
J002-1



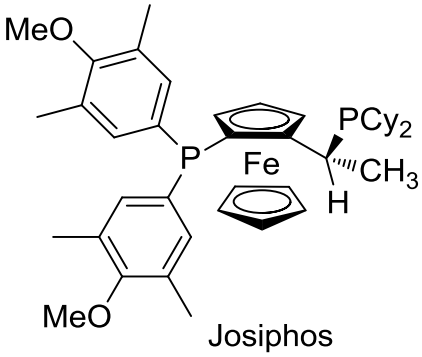
Josiphos
J003-1



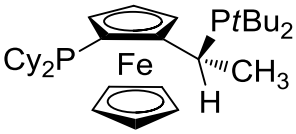
Josiphos
J005-1



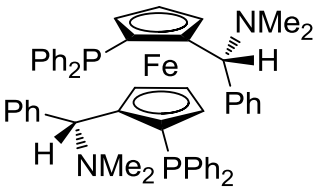
Josiphos
J004-1



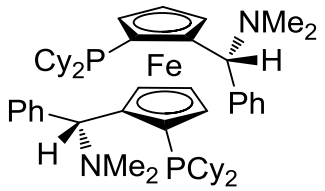
Josiphos
J007-1



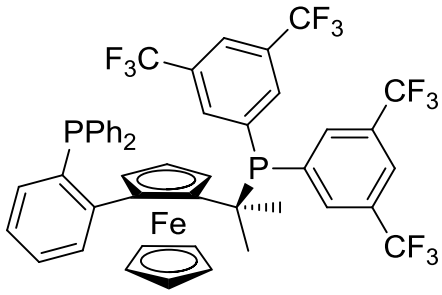
Josiphos
J009-1



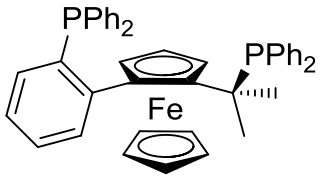
Mandyphos
M001-1



Mandyphos
M002-1

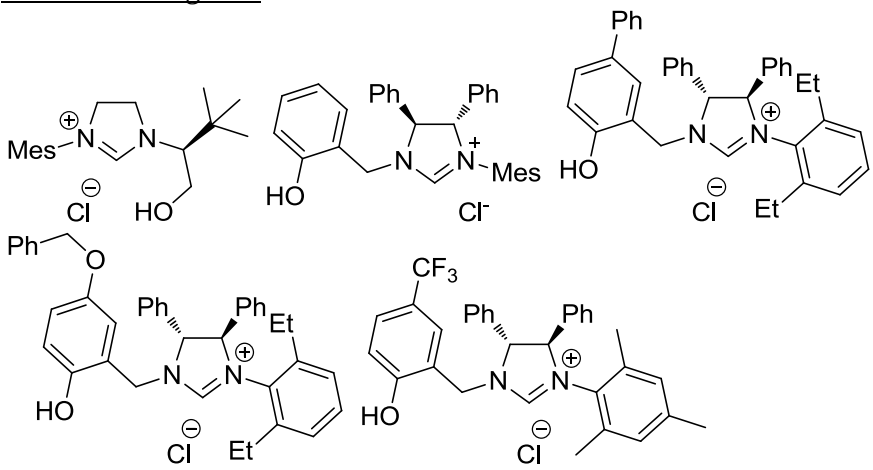


Walphos
W001-1

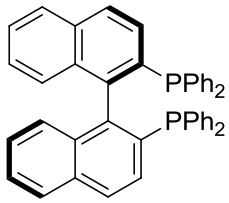


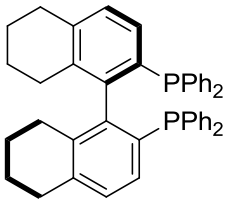
Walphos
W002-1

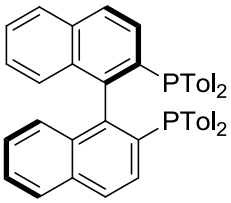
NHC carbene ligands.

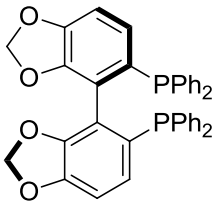


BINAP type ligands and derivatives.

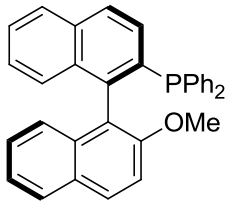


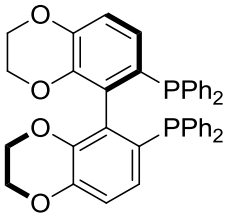


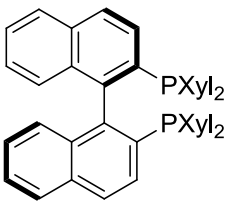




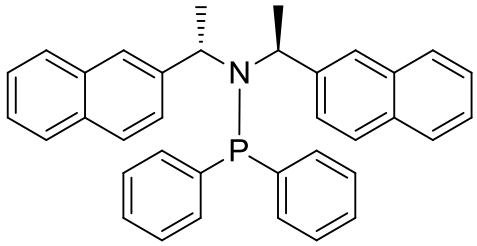
SEGPHOS

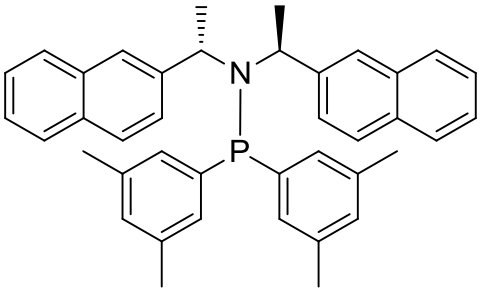


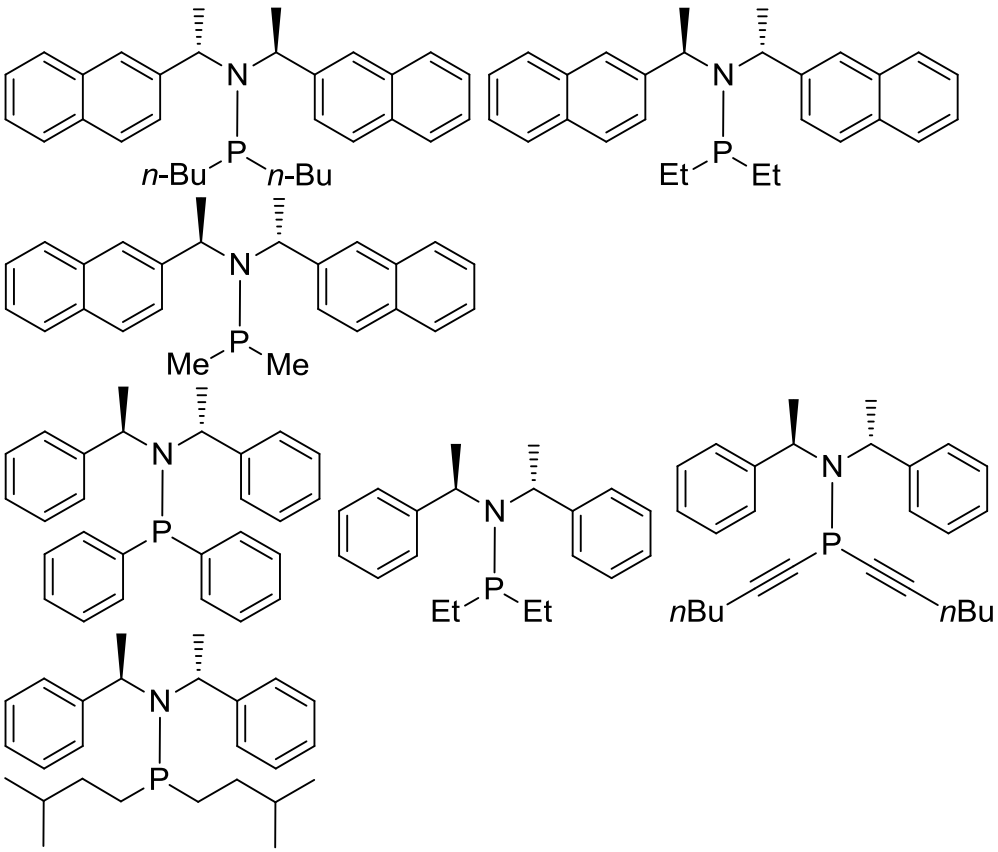




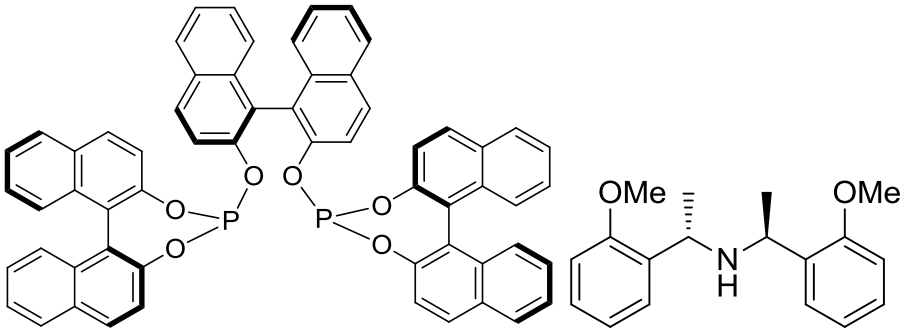
Simplephos ligands.







Other ligands.



C) Preparation of dichloro alkyne substrates.

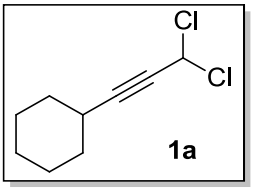
Representative procedure for 1,1-dichloro substrates ((3,3-dichloroprop-1-yn-1-yl)cyclohexane **1a**): [3], [4]

To a solution of alkyne (2.61mL, 20 mmol) in Et_2O (16 mL) at -40 ℃ was added dropwise 1.6M *n*-BuLi (12.5 mL, 20 mmol) followed by the addition of anhydrous DMF (2.4 mL, 30 mmol) in one portion. The clear reaction mixture was allowed to warmed up to room temperature and stirred for 30 min. The solution was then poured into a biphasic mixture of 100mL 10% KH_2PO_4 aqueous solution and ether (80 mL) at 0 ℃. The mixture was stirred vigorously, and layers were partitioned. The aqueous layer was extracted with ether (3 x 50 mL). The organic layers were collected, combined, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product obtained was used in the following chloration step without further purification.

The crude product was dissolved in dry CH_2Cl_2 (40 mL) and cooled to -20 ℃. Then, PCl_5 (6.2 g, 30 mmol) was added portion wise and the reaction mixture was stirred overnight. It was quenched by the addition of solid $NaHCO_3$ (8.4 g, 100mmol) at - 20 ℃ followed by water. The mixture allowed to warm back to 25 ℃. Additional $NaHCO_3$ was added to

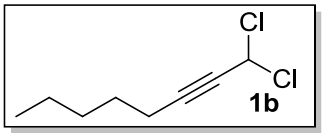
completely neutralize the solution. The aqueous phase was extracted by CH_2Cl_2 3 times, the organic phases were collected, dried over Na_2SO_4, concentrated under reduced pressure. Purification by column chromatography on silica gel (eluant: pentane, Rf=0.83) provided the desired compound 3.01 g as slightly yellow liquid. (79% yield over 2 steps)

(3,3-dichloroprop-1-yn-1-yl)cyclohexane **1a**



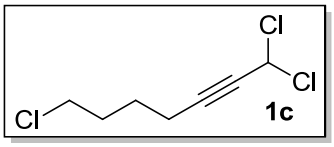
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (d, *J* = 1.8 Hz, 1H), 2.54-2.48 (m, 1H), 1.84-1.77 (m, 2H), 1.74-1.66 (m, 2H), 1.54-1.43 (m, 3H), 1.38-1.29 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 96.2, 76.6, 56.3, 31.9, 29.2, 25.8, 24.8.
HRMS (EI) calcd for $C_9H_{12}Cl_2$ $[M]^+$ 190.0311, found 190.0306

1,1-dichlorooct-2-yne **1b**



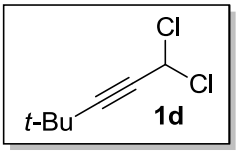
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (t, *J* = 2.0 Hz, 1H), 2.31 (td, *J* = 7.2, 2.0 Hz, 2H), 1.55 (p, *J* = 7.2 Hz, 2H), 1.41-1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 92.7, 76.5, 56.2, 31.1, 27.7, 22.3, 19.0, 14.1.
HRMS (EI) calcd for $C_8H_{12}Cl$ $[M\text{-}Cl]^+$ 143.0622, found 143.0621

1,1,7-trichlorohept-2-yne **1c**



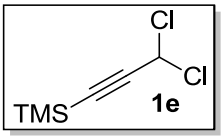
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (t, *J* = 1.9 Hz, 1H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.38 (td, *J* = 7.0, 2.0 Hz, 2H), 1.93-1.85 (m, 2H), 1.76-1.68 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 91.4, 77.1, 56.0, 44.4, 31.5, 25.2, 18.3.
HRMS (EI) calcd for $C_7H_9Cl_2$ $[M\text{-}Cl]^+$ 163.0076, found 163.0076

1,1-dichloro-4,4-dimethylpent-2-yne **1d**



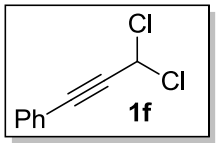
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 1.25 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 99.8, 75.3, 56.3, 30.4, 27.8.
HRMS (EI) calcd for $C_6H_7Cl_2$ $[M\text{-}CH_3]^+$ 148.9919, found 148.9918

(3,3-dichloroprop-1-yn-1-yl)trimethylsilane **1e**



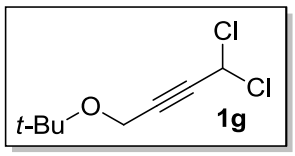
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (s, 1H), 0.22 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 98.9, 96.2, 55.2, -0.5.
HRMS (EI) calcd for $C_5H_7Cl_2Si$ $[M-CH_3]^+$ 164.9689, found 164.9687

(3,3-dichloroprop-1-yn-1-yl)benzene **1f**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.43-7.34 (m, 3H), 6.50 (S, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1, 130.0, 128.6, 120.7, 90.0, 84.2, 56.1.
HRMS (EI) calcd for $C_9H_6Cl_2$ $[M]^+$ 183.9841, found 183.9840

4-(*tert*-butoxy)-1,1-dichlorobut-2-yne **1g**



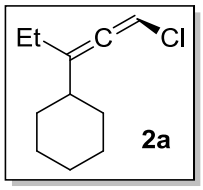
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 ((t, *J* = 1.7 Hz, 1H), 4.20 (d, *J* = 1.7 Hz, 2H), 1.25 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 88.8, 80.1, 75.1, 55.6, 50.6, 27.6.
HRMS (EI) calcd for $C_7H_9OCl_2$ $[M-CH_3]^+$ 179.0025, found 179.0026

D) Copper-catalyzed 1,3-substituion on 1,1-dichloro alkynes.

Representative procedure.

A dried Schlenk tube was charged with copper salt (5 mol%) and the chiral ligand (5.5 mol%). Tolene (2 mL) was added and the mixture was stirred at room temperature for 10 min. The 1,1-dichloro alkyne **1a** (0.25 mmol) was introduced dropwise and the reaction mixture was stirred at room temperature for a further 5 min before being cooled to –78 ℃ in an ethanol-dry ice cold bath. The ethyl Grignard reagent (3M in diethyl ether, 1.2 eq) was added manually during 20min. Once the addition was complete the reaction mixture was stirred at –78 ℃ for 2 hours. The reaction was quenched by adding aqueous solution of saturated NH_4Cl. Diethyl ether (5 mL) was added and the aqueous phase was separated and extracted with diethyl ether (3 x 2mL). The combined organic fractions were washed with brine (3 mL), dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel using pentane as eluant, and the desired product **2a** 0.039g was recovered as colorless oil. (84% yield)

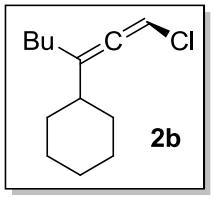
(1-chloropenta-1,2-dien-3-yl)cyclohexane **2a**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08-6.06 (m, 1H), 2.13-2.06 (m, 2H), 1.90-1.73 (m, 5H), 1.67-1.63 (m, 1H), 1.31-1.10 (m, 5H), 1.03 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 124.8, 90.0, 41.7, 32.1, 32.0, 26.46, 26.42, 26.3, 24.6, 12.1.
HRMS (EI) calcd for $C_{11}H_{17}Cl$ $[M]^+$ 184.1013, found 184.1011

$[\alpha]_D^{20}$= -86.3 (c=0.50 in $CHCl_3$, 92% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method: 60-0-1-110-0-20-170-5) RT= 48.20, 49.14min)

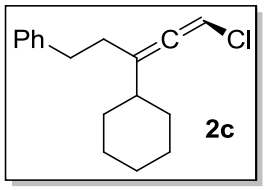
(1-chlorohepta-1,2-dien-3-yl)cyclohexane **2b**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (q, *J* = 2.1 Hz, 1H), 2.08 (td, *J* = 8.0, 7.4, 2.3 Hz, 2H), 1.89-1.74 (m, 5H), 1.68-1.64 (m, 1H), 1.46-1.09 (m, 9H), 0.91 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 123.0, 89.5, 41.7, 32.1, 32.0, 31.2, 29.7, 26.5, 26.4, 26.3, 22.5, 14.1.
HRMS (EI) calcd for $C_{13}H_{21}Cl$ $[M]^+$ 212.1326, found 212.1324

$[\alpha]_D^{20}$= -47.5 (c=0.48 in $CHCl_3$, 94% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P; method: 60-0-1-130-0-20-170-5) RT= 62.33, 63.18 min

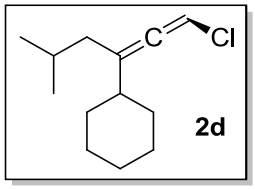
(5-chloro-3-cyclohexylpenta-3,4-dien-1-yl)benzene **2c**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 2H), 7.21-7.17 (m, 3H), 6.08 (q, *J* = 2.2 Hz, 1H), 2.76 (dd, *J* = 8.7, 7.3 Hz, 2H), 2.42-2.39 (m,2H), 1.93-1.75 (m, 5H), 1.68-1.65 (m,1H), 1.32-1.09 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 141.8, 128.52, 128.49, 126.1, 122.4, 90.2, 41.9, 33.9, 33.2, 32.02, 31.97, 26.43, 26.40, 26.29.
HRMS (EI) calcd for $C_{17}H_{21}Cl$ $[M]^+$ 260.1326, found 260.1327

$[\alpha]_D^{20}$= -3.7 (c=0.50 in $CHCl_3$, 90% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P; method: 60-0-1-170-5) RT= 113.16, 113.72min

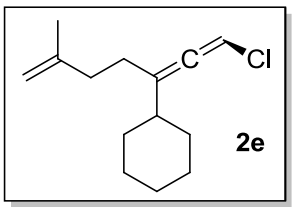
(1-chloro-5-methylhexa-1,2-dien-3-yl)cyclohexane **2d**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (q, *J* = 1.9 Hz, 1H), 1.97-1.94 (m, 2H), 1.86-1.74 (m, 6H), 1.67-1.63 (m, 1H), 1.29-1.09 (m, 5H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* =6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 121.7, 89.2, 41.7, 41.0, 32.1, 32.0, 26.7, 26.5, 26.4, 26.3, 22.8, 22.7.
HRMS (EI) calcd for $C_{13}H_{21}Cl$ $[M]^+$ 212.1326, found 212.1322

$[\alpha]_D^{20}$= -54.7 (c=0.53 in $CHCl_3$, 93% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method 60-0-1-120-0-20-170-5) RT= 56.91, 57.17min

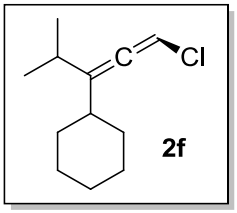
(1-chloro-6-methylhepta-1,2,6-trien-3-yl)cyclohexane **2e**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (q, *J* = 2.1 Hz, 1H), 4.75-4.73 (m, 1H), 4.70-4.68 (m, 1H), 2.25-2.19 (m, 2H), 2.16-2.13 (m, 2H), 1.92-1.72 (m, 8H), 1.68-1.65 (m, 1H), 1.33-1.08 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 145.2, 122.5, 110.3, 89.9, 41.8, 35.5, 32.1, 32.0, 29.6, 26.45, 26.41, 26.3, 22.8.
HRMS (EI) calcd for $C_{14}H_{21}Cl$ $[M]^+$ 224.1326, found 224.1327

$[\alpha]_D^{20}$= -24.7 (c=0.50 in $CHCl_3$, 94% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method: 60-0-1-150-0-20-170-5) RT= 71.01, 71.85 min.

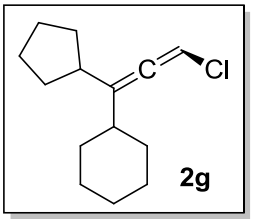
(1-chloro-4-methylpenta-1,2-dien-3-yl)cyclohexane **2f**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (dd, *J* = 1.5, 1.5Hz, 1H), 2.32-2.24 (m, 1H), 1.95-1.74 (m, 5H), 1.68-1.64 (m, 1H), 1.33-1.10 (m, 5H), 1.08-1.03 (m, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 129.6, 90.4, 40.5, 32.7, 32.65, 30.7, 26.6, 26.5, 26.3, 22.1, 22.0.
HRMS (EI) calcd for $C_{12}H_{19}$ $[M\text{-}Cl]^+$ 163.1481, found 163.1481

$[\alpha]_D^{20}$= -63.9 (c=0.51 in $CHCl_3$, 96% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (Hydrodex β-3P, method: 60-0-1-110-0-20-170-5) RT= 46.15, 50.10min.

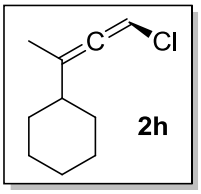
(3-chloro-1-cyclopentylpropa-1,2-dien-1-yl)cyclohexane **2g**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05-6.04 (m, 1H), 2.51-2.43 (m, 1H), 1.93-1.74 (m, 7H), 1.70-1.62 (m,3H), 1.60-1.51 (m, 2H), 1.48-1.36 (m, 2H), 1.29-1.05 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6 , 127.7, 90.0, 41.8, 41.3, 32.6, 32.5, 32.3, 32.29, 26.6, 26.5, 26.3, 25.1, 25.0.

$[\alpha]_D^{20}$= -4.6 (c=0.54 in $CHCl_3$, 96% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (Hydrodex β-3P, method: 60-0-1-140-0-20-170-5) RT= 77.52, 78.46min.

(4-chlorobuta-2,3-dien-2-yl)cyclohexane **2h**

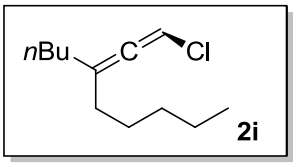


^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96 (q, *J* = 2.0 Hz, 1H), 1.97-1.74 (m, 8H), 1.68-1.63 (m, 1H), 1.33-1.06 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 117.6, 87.7, 42.4, 31.64, 31.61, 26.35, 26.29, 18.0.
HRMS (EI) calcd for $C_{10}H_{15}Cl$ $[M]^+$ 170.0857, found 170.0853

$[\alpha]_D^{20}$= -141.6 (c=0.51 in $CHCl_3$, 91% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (Hydrodex β-3P, method: 60-0-1-110-0-20-170-5) RT= 40.89, 42.27min.

Scale-up reaction on 2mmol substrate provided the desired product **2h** 0.324g (95% yield) with 90% *ee*.

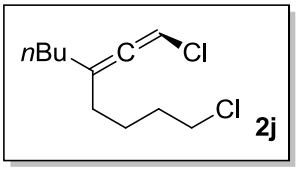
5-(2-chlorovinylidene)decane **2i**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (p, *J* = 2.2 Hz, 1H), 2.07-2.02 (m, 4H), 1.49-1.40 (m, 4H), 1.38-1.26 (m, 6H), 0.91 (t, *J*= 7.3 Hz, 3H), 0.89 (t, *J*= 7.2 Hz, 3H)
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 117.7, 88.7, 33.2, 33.0, 31.5, 29.5, 27.0, 22.6, 22.4, 14.20, 14.19, 14.1.
HRMS (EI) calcd for $C_{12}H_{21}Cl$ $[M]^+$ 200.1326, found 200.1324

$[\alpha]_D^{20}$= -4.5 (c=0.50 in $CHCl_3$, 92% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Hydrodex β-3P: method 60-0-1-110-0-20-170-5) RT= 45.23, 45.90min.

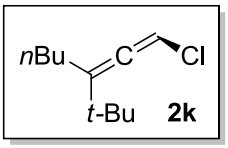
1-chloro-5-(2-chlorovinylidene)nonane **2j**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (p, *J* = 2.2 Hz, 1H), 3.55 (td, *J* = 6.6, 0.8 Hz, 2H), 2.11-2.04 (m, 4H), 1.87-1.74 (m, 2H), 1.67-1.56 (m, 2H), 1.78-1.29 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 116.9, 89.2, 45.0, 32.9, 32.4, 32.0, 29.5, 24.5, 22.4, 14.1.
HRMS (EI) calcd for $C_{11}H_{18}Cl$ $[M-Cl]^+$ 185.1092, found 185.1091

$[\alpha]_D^{20}$= -9.6 (c=0.54 in $CHCl_3$, 89% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Dex CB: method 60-0-1-140-0-20-170-5, showed the retention time of the 2 enantioisomers: 77.82, 78.10min

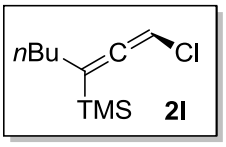
3-(tert-butyl)-1-chlorohepta-1,2-diene **2k**



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.04 (t, *J* = 2.5 Hz, 1H), 2.12-1.99 (m, 2H), 1.46-1.29 (m, 4H), 1.08 (s, 9H), 0.92 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 126.7, 89.9, 34.9, 30.1, 29.1, 27.6, 22.6, 14.2
HRMS (EI) calcd for $C_8H_{13}Cl$ $[M-C_3H_6]^+$ 144.0700, found 144.0697

$[\alpha]_D^{20}$= +23.2 (c=0.52 in $CHCl_3$, 84% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Hydrodex β-3P method: 60-0-1-90-0-20-170-5) RT= 25.62, 28.54 min

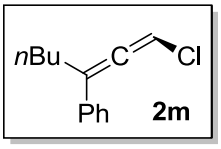
(1-chlorohepta-1,2-dien-3-yl)trimethylsilane **2l**



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (t, *J* = 2.3 Hz, 1H), 2.15-2.02 (m, 2H), 1.51-1.30 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.14 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 111.4, 86.2, 30.9, 29.6, 22.4, 14.1, -1.7.
HRMS (EI) calcd for $C_{10}H_{19}ClSi$ $[M]^+$ 202.0939, found 202.0939

$[\alpha]_D^{20}$= -39.6 (c=0.49 in $CHCl_3$, 85% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method: 60-0-1-90-0-20-170-5) RT= 23.64, 24.90min.

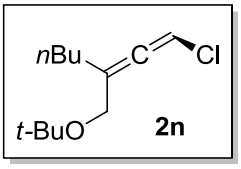
(1-chlorohepta-1,2-dien-3-yl)benzene **2m**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.42 (m, 2H), 7.39-7.34 (m, 2H), 7.31-7.26 (m, 1H), 6.37 (t, *J* = 2.4 Hz, 1H), 2.61-2.49 (m, 2H), 1.62-1.54 (m, 2H), 1.48-1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 135.1, 128.7, 128.4, 126.9, 116.9, 90.7, 30.2, 29.8, 22.5, 14.1.
HRMS (EI) calcd for $C_{13}H_{15}Cl$ $[M]^+$ 206.0857, found 206.0857

$[\alpha]_D^{20}$= -208.7 (c=0.50 in $CHCl_3$, 64% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method: 60-0-1-140-0-20-170-5) RT= 73.43, 74.76min.

3-(tert-butoxymethyl)-1-chlorohepta-1,2-diene **2n**



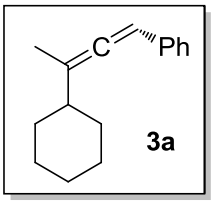
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (t, *J* = 2.0 Hz, 1H), 3.98-3.91 (m, 2H), 2.12 (ddd, *J* = 8.5, 5.9, 1.9 Hz, 2H), 1.49-1.31 (m, 4H), 1.21 (s, 9H), 0.91 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 115.9, 89.3, 74.0, 62.8, 29.5, 29.4, 27.7, 22.4, 14.1.
HRMS (EI) calcd for $C_8H_{13}OCl$ $[M-C_4H_8]^+$ 160.0649, found 160.0647

$[\alpha]_D^{20}$= -3.4 (c=0.47 in $CHCl_3$, 62% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-3P, method: 60-0-1-110-0-20-170-5) RT= 43.89, 44.33min

E) Copper-catalyzed substitution on chloroallenes.

Representative procedure of copper-catalyzed 1,1-substituion on chloroallene.[4]
A dried argon-flushed Schlenk tube was charged with CuCN 15mol% and the chloroallene **2g** (36.9mg, 0.2mmol) in 2mL THF at -20℃. PhMgBr (1M in THF, 0.4mmol, 0.4mL) was added dropwise to the solution. The reaction mixture was allowed to warm back to room temperature to provide the full conversion of the starting material. Then the reaction mixture was quenched by saturated NH_4Cl aqueous solution, the mixture was extracted twice by ether, the combined organic phases was dried over Na_2SO_4, concentrated under reduced pressure, and purified on flash chromatography over silica gel using pentane as eluant. (Rf=0.69) 0.0385g (85% yield) product was obtained as colorless oil.

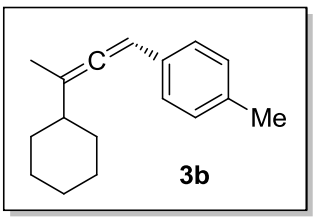
(3-cyclohexylbuta-1,2-dien-1-yl)benzene **3a**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (m, 4H), 7.20-7.14 (m, 1H), 6.08 (p, *J* = 2.8 Hz, 1H), 1.94-1.85 (m, 3H), 1.82 (d, *J* = 2.8 Hz, 3H), 1.77-1.73 (m, 2H), 1.69-1.63 (m, 1H), 1.35-1.11 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.4, 136.3, 128.63, 128.61, 126.47, 126.43, 109.1, 94.6, 42.3, 32.3, 32.1, 26.6, 26.4, 17.4.
HRMS (EI) calcd for $C_{16}H_{20}$ $[M]^+$ 212.1560, found 212.1560

$[\alpha]_D^{20}$= +233.3 (c=0.53 in $CHCl_3$, 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-6-TBDMS, method: 60-0-1-170-5) RT= 86.81, 87.19min

1-(3-cyclohexylbuta-1,2-dien-1-yl)-4-methylbenzene **3b**

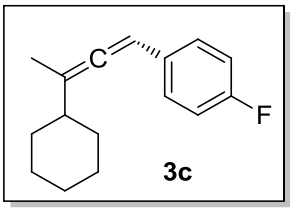


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 6.06 (t, *J* = 2.7 Hz, 1H), 2.33 (s, 3H), 1.93-1.85 (m, 3H), 1.81 (d, *J* = 2.8 Hz, 3H), 1.78-1.72 (m, 2H), 1.68-1.63 (m, 1H), 1.34-1.10 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 136.1, 133.3, 129.4, 126.4, 109.0, 94.4, 42.4, 32.3, 32.2, 26.6, 26.5, 21.3, 17.4.
HRMS (EI) calcd for $C_{17}H_{22}$ $[M]^+$ 226.1716, found 226.1713

$[\alpha]_D^{20}$= +211.1 (c=0.52 in $CHCl_3$ 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-6-TBDMS: method 60-0-1-170-5) RT= 109.16, 109.64min.

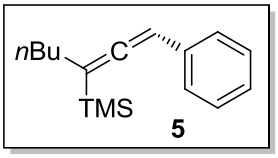
1-(3-cyclohexylbuta-1,2-dien-1-yl)-4-fluorobenzene **3c**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.19 (m, 2H), 7.00-6.94 (m, 2H), 6.04 (p, *J* = 2.7 Hz, 1H), 1.91-1.86 (m, 3H), 1.81 (d, *J* = 2.9 Hz, 3H), 1.78-1.73 (m, 2H), 1.68-1.64 (m, 1H), 1.34-1.09 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.1, 161.7 (d, *J* = 245.2 Hz), 132.3, 127.8 (d, *J* = 7.5 Hz), 115.5 (d, *J* = 21.9 Hz), 109.4, 93.7, 42.3, 32.3, 32.1, 26.6, 26.4, 17.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ -116.50.
HRMS (EI) calcd for $C_{16}H_{19}F$ $[M]^+$ 230.1465, found 230.1466

$[\alpha]_D^{20}$= +244.9 (c=0.52 in $CHCl_3$ 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: hydrodex β-6-TBDMS: method 60-0-1-170-5) RT= 99.93, 100.46min

trimethyl(1-phenylhepta-1,2-dien-3-yl)silane **5**

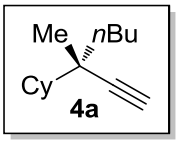


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.26 (m, 2H), 7.24-7.21 (m, 2H), 7.15-7.11 (m, 1H), 5.88 (t, *J* = 3.1 Hz, 1H), 2.14-2.08 (m, 2H), 1.53-1.46 (m, 2H), 1.41-1.33 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H), 0.16 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 136.5, 128.6, 125.9, 125.8, 101.3, 90.0, 31.6, 29.4, 22.7, 14.1, -1.2.

$[\alpha]_D^{20}$= +119.5 (c=0.92 in $CHCl_3$ 83% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Dex CB: method 60-0-1-140-0-20-170-5) RT= 78.98, 79.29min

Representative procedure of copper-catalyzed 1,3-substituion on chloroallene.
A dried argon-flushed Schlenk tube was charged with CuCN 15mol% and the chloroallene **2g** (36.9mg, 0.2mmol) in 2mL dichloromethane at 0 ℃. *n*BuMgBr (3.9M in Et_2O, 0.4mmol, 0.1mL) was added dropwise to the solution. The reaction mixture was allowed to warm back to room temperature to provide the full conversion of the starting material. Then the reaction mixture was quenched by saturated NH_4Cl aqueous solution, the mixture was extracted twice by ether, the combined organic phases was dried over Na_2SO_4, concentrated under reduced pressure, and purified on flash chromatography over silica gel using pentane as eluant. 0.0342g (89% yield) product was obtained as colorless oil.

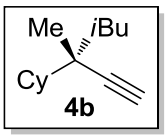
(3-methylhept-1-yn-3-yl)cyclohexane **4a**



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (s, 1H), 1.93-1.89 (m, 1H), 1.80-1.76 (m, 3H), 1.68-1.63 (m, 1H), 1.49-1.05 (m, 15H), 0.92 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 91.4, 69.1, 45.6, 38.8, 38.3, 28.2, 27.4, 27.0, 26.98, 26.9, 26.7, 23.5, 23.46, 14.3.
HRMS (EI) calcd for $C_{11}H_{17}$ $[M-C_3H_7]^+$ 149.1325, found 149.1323

$[\alpha]_D^{20}$= +2.7 (c=0.49 in $CHCl_3$, 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Hydrodex β-6-TBDMS: method 60-0-1-110-0-20-170-5) RT= 47.34, 47.86min

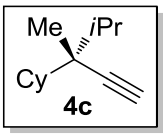
(3,5-dimethylhex-1-yn-3-yl)cyclohexane **4b**



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 1H), 1.95-1.91 (m, 1H), 1.87-1.75 (m, 4H), 1.68-1.63 (m, 1H), 1.47-1.42 (m, 1H), 1.27-1.04 (m, 10H), 0.97 (t, *J* = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 91.6, 69.5, 47.3, 46.8, 38.1, 28.2, 27.5, 27.1, 27.0, 26.7, 25.2, 25.1, 24.9, 24.1.
HRMS (EI) calcd for $C_{14}H_{24}$ $[M]^+$ 192.1873, found 192.1873

$[\alpha]_D^{20}$= +6.1 (c=0.59 in $CHCl_3$, 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Hydrodex β-6-TBDMS: method 60-0-1-110-0-20-170-5) RT= 43.77, 44.09min

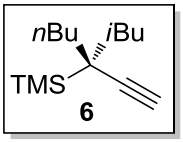
(3,4-dimethylpent-1-yn-3-yl)cyclohexane **4c**



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.06 (s, 1H), 1.95-1.91 (m, 1H), 1.84-1.65 (m, 5H), 1.45-1.38 (m, 1H), 1.26-1.06 (m, 5H), 1.02 (s, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 89.9, 69.9, 43.4, 42.2, 32.5, 28.5, 27.1, 27.0, 26.8, 18.8, 18.5, 17.3.

$[\alpha]_D^{20}$= -0.7 (c=0.54 in $CHCl_3$, 90% *ee* (S)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Hydrodex β-6-TBDMS: method 60-0-1-110-0-20-170-5) RT= 43.77, 44.09min

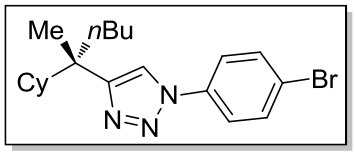
(4-ethynyl-2-methyloctan-4-yl)trimethylsilane **6**



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 1H), 1.90-1.83 (m, 1H), 1.36-1.31 (m, 8H), 1.01-0.89 (m, 9H), 0.09 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 90.4, 70.3, 42.7, 35.6, 28.4, 26.3, 25.6, 25.0, 24.6, 23.7, 14.2, -3.0.

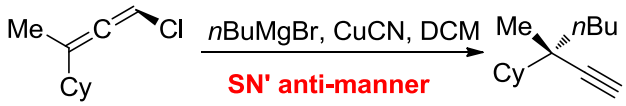
$[\alpha]_D^{20}$= +2.5 (c=0.98 in $CHCl_3$, 83% *ee* (R)). The enantiomeric excess was determined by GC on a chiral stationary phase (column: Dex CB: method 60-0-1-100-0-20-170-5) RT= 38.31, 38.64min

F) Click chemistry [5]:
General procedure:
The alkyne substrate (3-methylhept-1-yn-3-yl)cyclohexane (19.2mg, 0.1mmol, 1eq.) and 1-azido-4-bromobenzene (19.8mg, 0.1mmol) were suspended in a 1:1 mixture of water and *t*BuOH (0.8mL). Sodium ascorbate (2.0mg, 0.01mol, 0.1eq. freshly dissolved in 0.01mL H_2O) was added, followed by $CuSO_4$ (0.16mg, 0.01eq.). The heterogeneous mixture was stirred vigorously overnight. The reaction mixture was diluted with water, cooled in ice, and the precipitate was collected by filtration. The product was purified by flash chromatography on silica gel (eluant: pentane/ether 9/1 Rf=0.33) to provide the slightly yellow solid 0.0299g. (77% yield)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.60 (m, 5H), 1.85-1.78 (m, 2H), 1.75-1.73 (m, 1H), 1.70-1.62 (m, 3H), 1.46-1.43 (m, 1H), 1.28-0.92 (m, 13H), 0.84 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 156.2, 136.4, 132.9, 121.8, 121.7, 118.7, 46.8, 40.2, 39.0, 28.2, 27.4, 27.1, 27.1, 26.8, 26.6, 23.6, 20.3, 14.3.
HRMS (ESI positif) calcd for $C_{20}H_{29}N_3Br$ $[M+H]^+$ 390.1539, found 390.1543

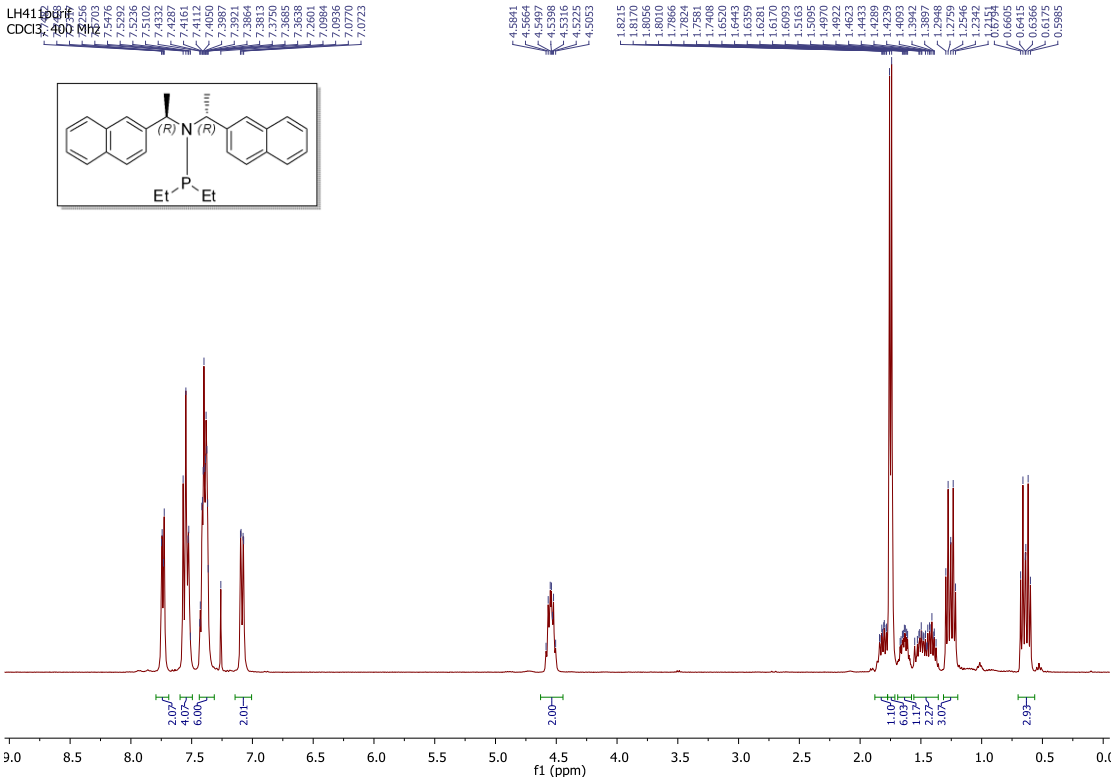
G) Proof of Absolute Stereochemistry:
In order to gain more insight of these products, alkyne **4a** was subjected to "click" reaction conditions with p-bromo phenyl azide. [5] X-ray diffraction on the resulting crystalline product allowed the determination of the absolute configuration. According to the previous work of Corey [6] and Caporusso [7] on the substitution reactions of bromoallenes, we presumed that, in our case, the nucleophilic attack still follows the reported S_N' *anti* manner, and in this way, we have attributed the absolute configuration of the axially chiral chloroallene compounds. Knowing also that aryl nucleophiles have a preference for *anti* S_N2 type substitution, we presumed that the aryl allenes **3a-c** have the shown stereochemistry (which is also in accordance with presumptions from Lowe's extension of Breswster's rules. [8]).
Absolute configurations alkyne **4a** was established by the X-ray analysis of (S)-1-(4-bromophenyl)-4-(2-cyclohexylhexan-2-yl)-1H-1,2,3-triazole as mentioned above. See V) X-ray data for details. The absolute stereochemistry for the corresponding enantiomerically enriched allene **2h** was presumed according to *anti* mechanism reported by Corey and Caporusso and the absolute stereochemistry for all the other chiral allene compounds were assigned by inference.

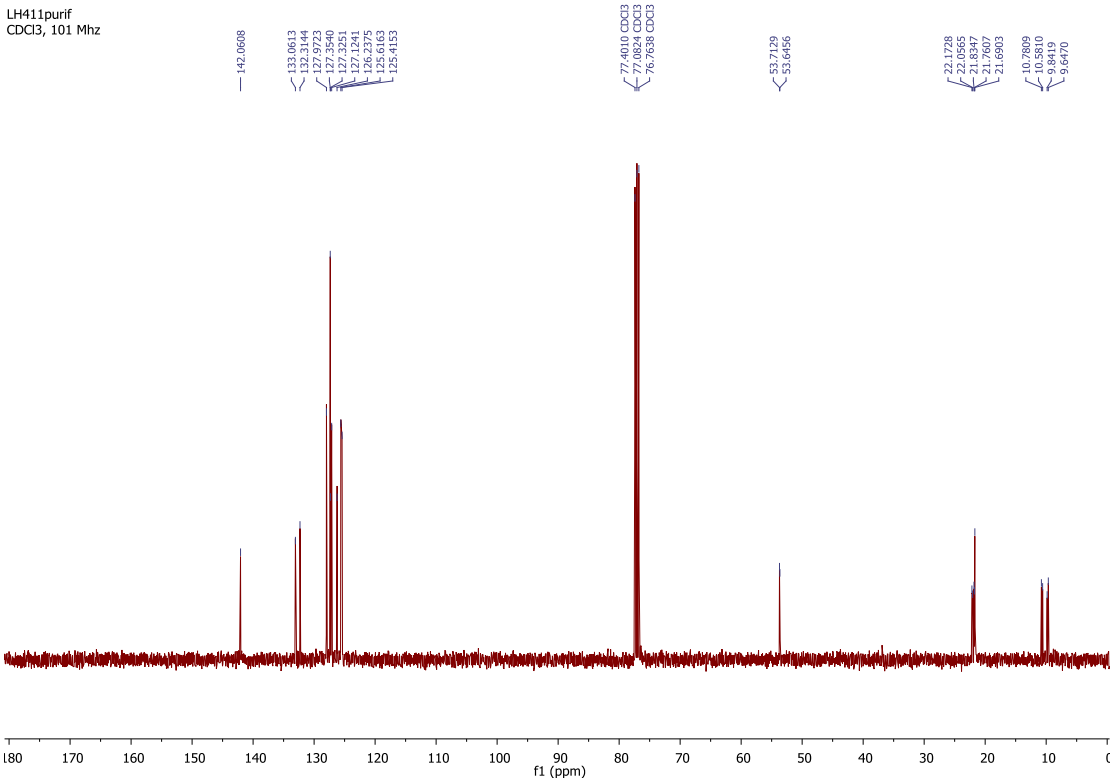


III) References

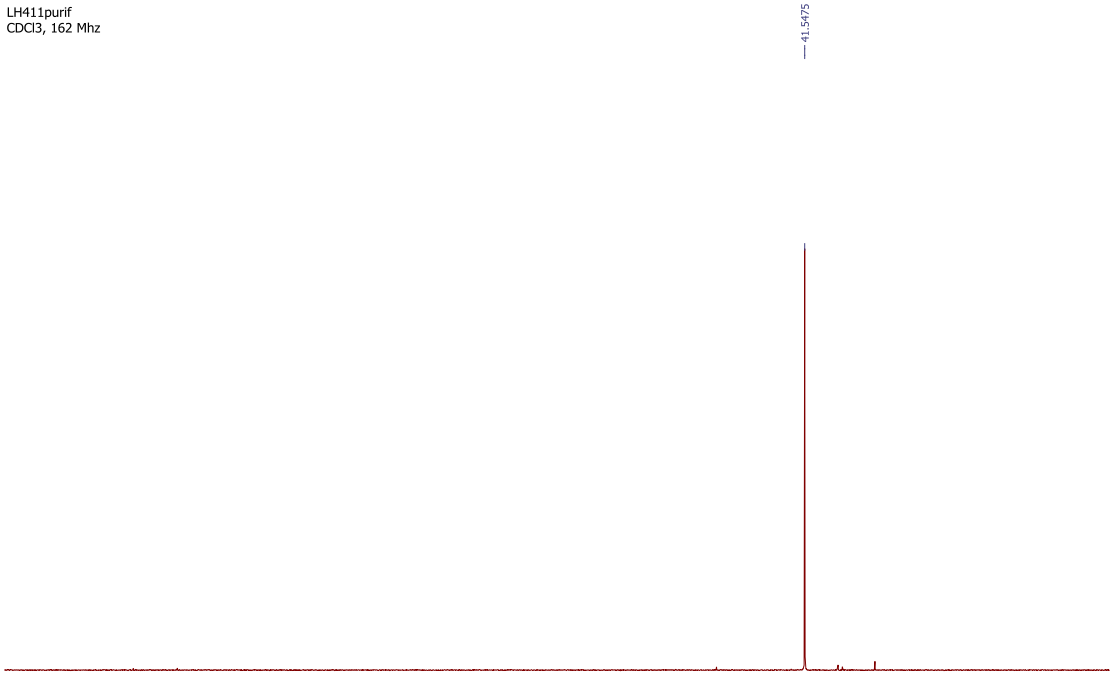
[1] a) A. Alexakis, D. Polet, S. Rosset, S. March, *J. Org. Chem*. **2004**, *69*, 5660-5667; b) K. Tissot-Croset, D. Polet, A. Alexakis, *Angew. Chem. Int. Ed.* **2004**, *43*, 2426-2428.
[2] a) D. Müller, M. Tissot, A. Alexakis, *Org. Lett.* **2011**, *13*, 3040-3043; b) C. Bournaud, C. Falciola, T. Lecourt, S. Rosset, A. Alexakis, L. Micouin *Org. Lett.* **2006**, *8*, 3581-3584.
[3] S. Belot, K. A. Vogt, C. Besnard, N. Krause, A. Alexakis, *Angew. Chem. Int. Ed.* **2009**, *48*, 8923-8926.
[4] M. A. Schade, S. Yamada, P. Knochel, *Chem. Eur. J.* **2011**, *17*, 4232-4237.
[5] V. V. Rostovstev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596-2599.
[6] E. J. Corey, N. W. Boaz, *Tetrahedron Lett.* **1984**, *25*, 3059-3062.
[7] a) A. M. Caporusso, C. Polizzi, L. Lardicci, *Tetrahedron Lett.* **1987**, *28*, 6073-6076 ; b) A. M. Caporusso, C. Polizzi, L. Lardicci, *J. Org. Chem.* **1987**, *52*, 3920-3923; c) C. Polizzi, C. Consoloni, L. Lardicci, A. M. Caporusso, *J. Organomet. Chem.* **1991**, *417*, 289-304; d) A. M. Caporusso, S. Filippi, F. Barontini, P. Salvadori, *Tetrahedron Lett.* **2000**, *41*, 1227-1230; e) A. M. Caporusso, L. A. Aronica, R. Geri, M. Gori, *J. Organomet. Chem.* **2002**, *648*, 109-118; f) A. M. Caporusso, A. Zampieri, L. A. Aronica, D. Banti, *J. Org. Chem.* **2006**, *71*, 1902-1910.
[8] a) J. H. Brewster, *J. Am. Chem. Soc.* **1959**, *81*, 5475-5483; b) G. Lowe, *Chem. Commun*. **1965**, 411.

IV) Spectroscopic and chromatographic data

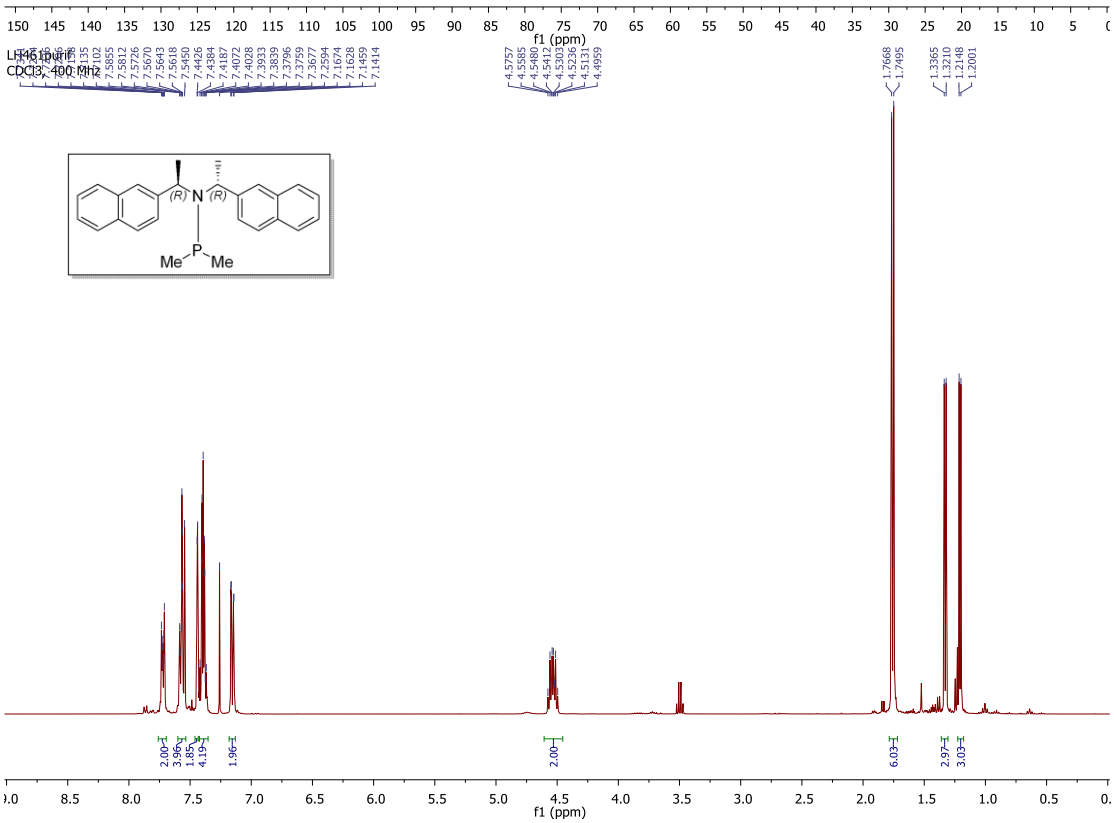




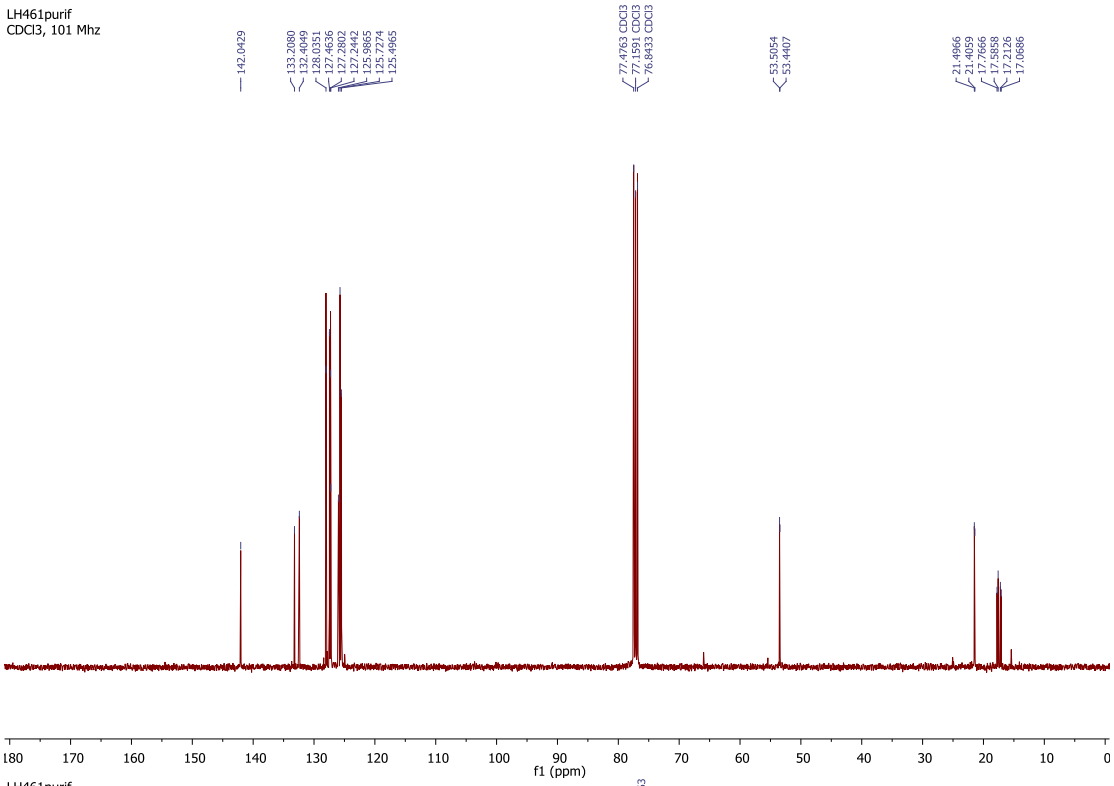
LH411purif
CDCl3, 162 Mhz



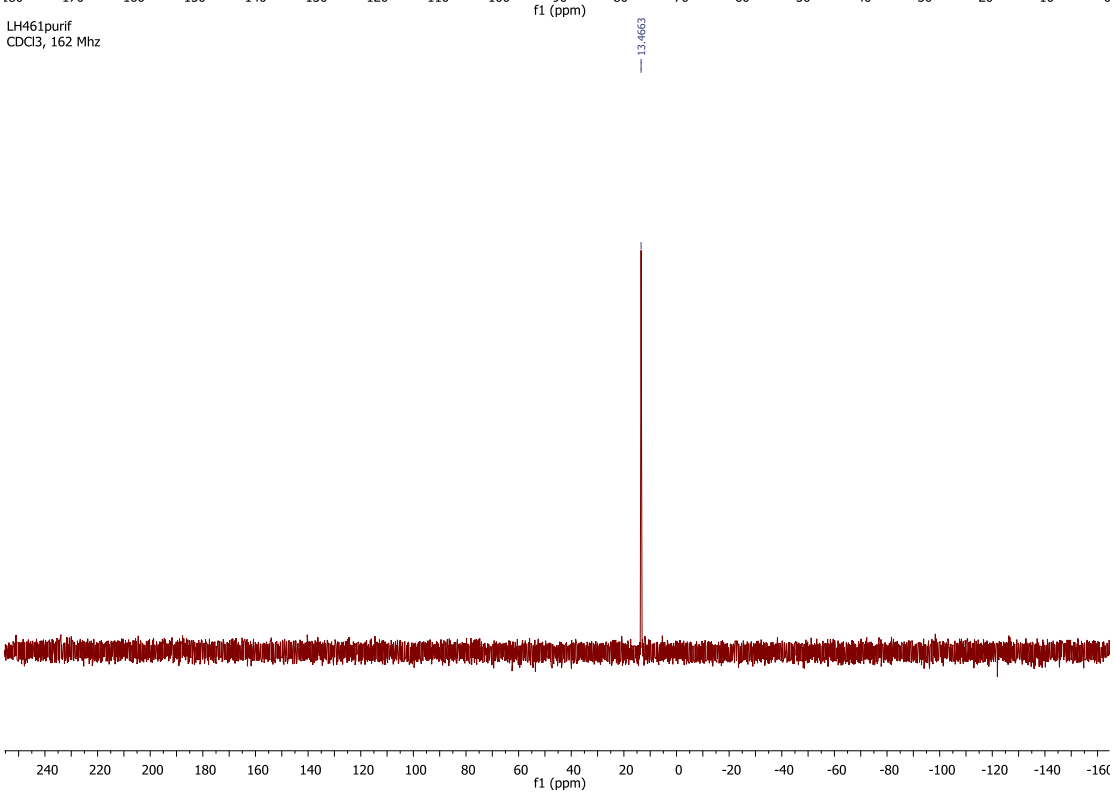
LH411purif
CDCl3, 400 Mhz

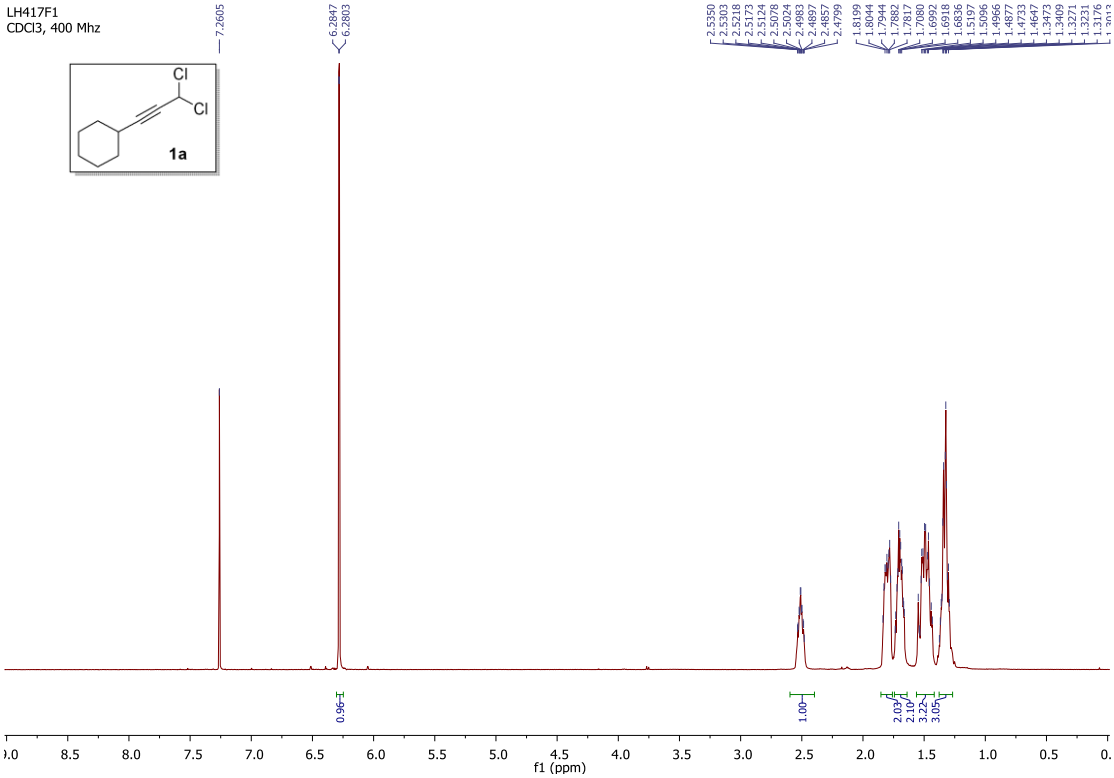


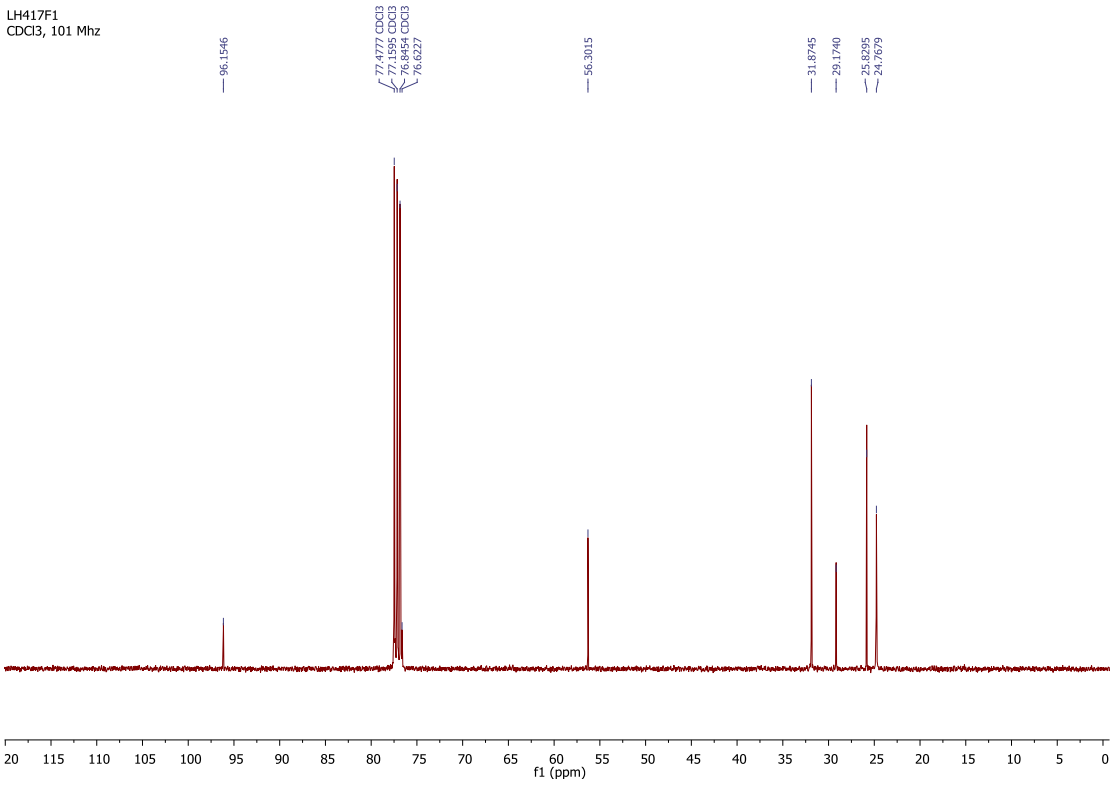
LH461purif
CDCl3, 101 Mhz



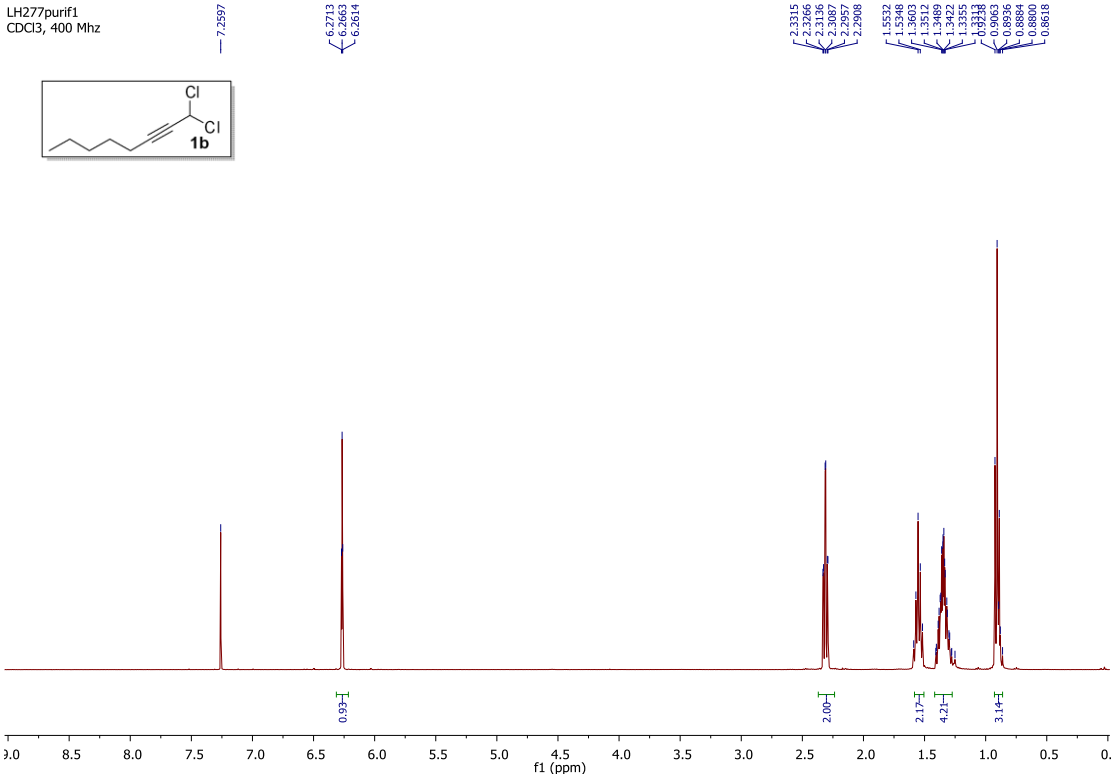
LH461purif
CDCl3, 162 Mhz



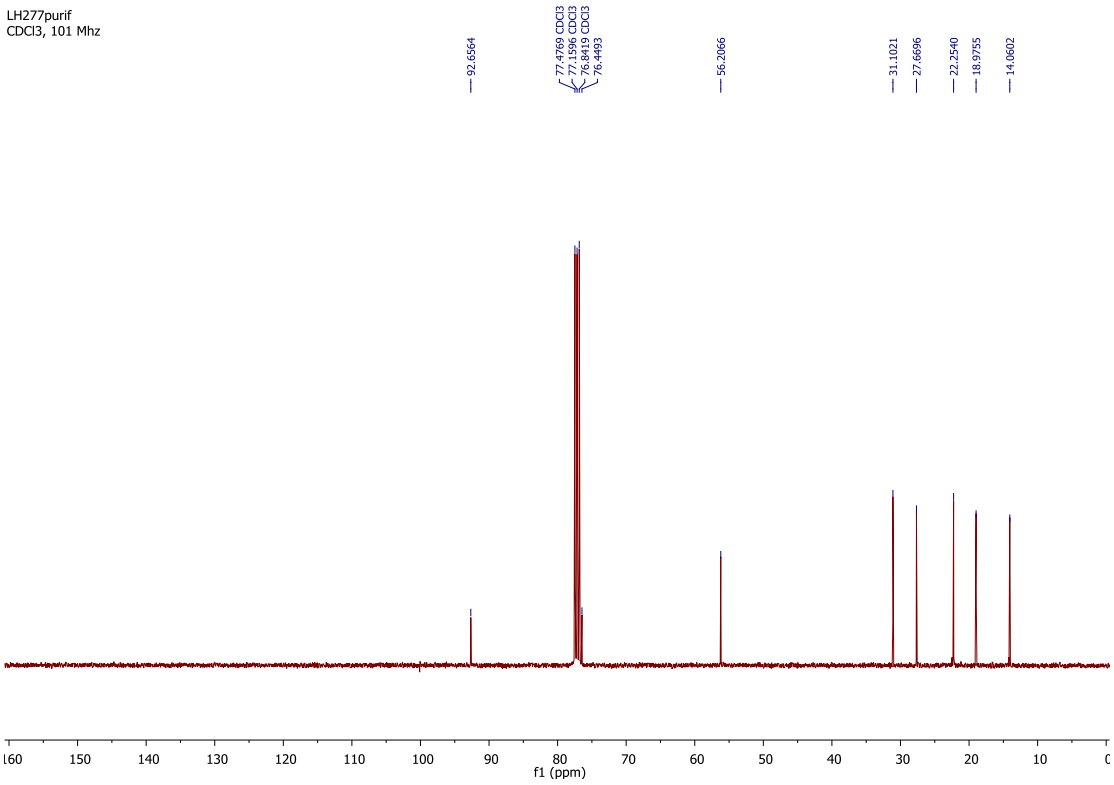

LH417F1
CDCl3, 400 Mhz
Cl
Cl
1a
7.2605
6.2847
6.2803
0.96
1.00
2.03
2.10
3.22
3.05
f1 (ppm)

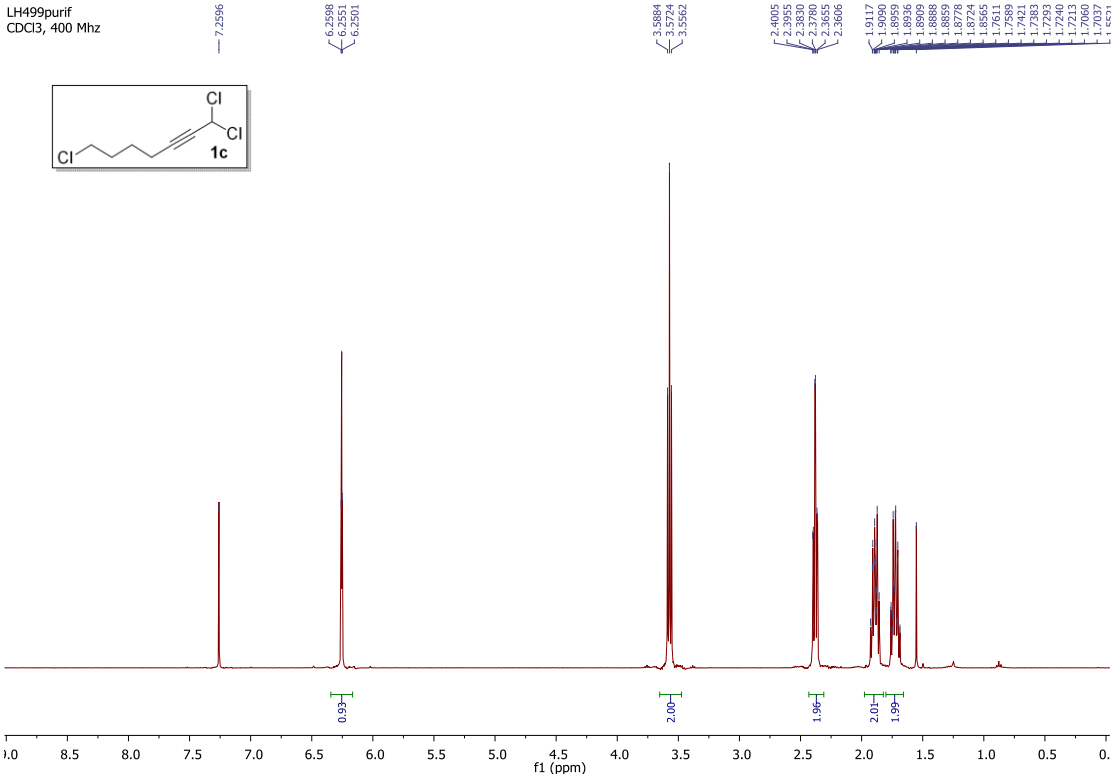

LH417F1
CDCl3, 101 Mhz
96.1546
77.4777 CDCl3
77.1595 CDCl3
76.8454 CDCl3
76.6227
56.3015
31.8745
29.1740
25.8295
24.7679
f1 (ppm)

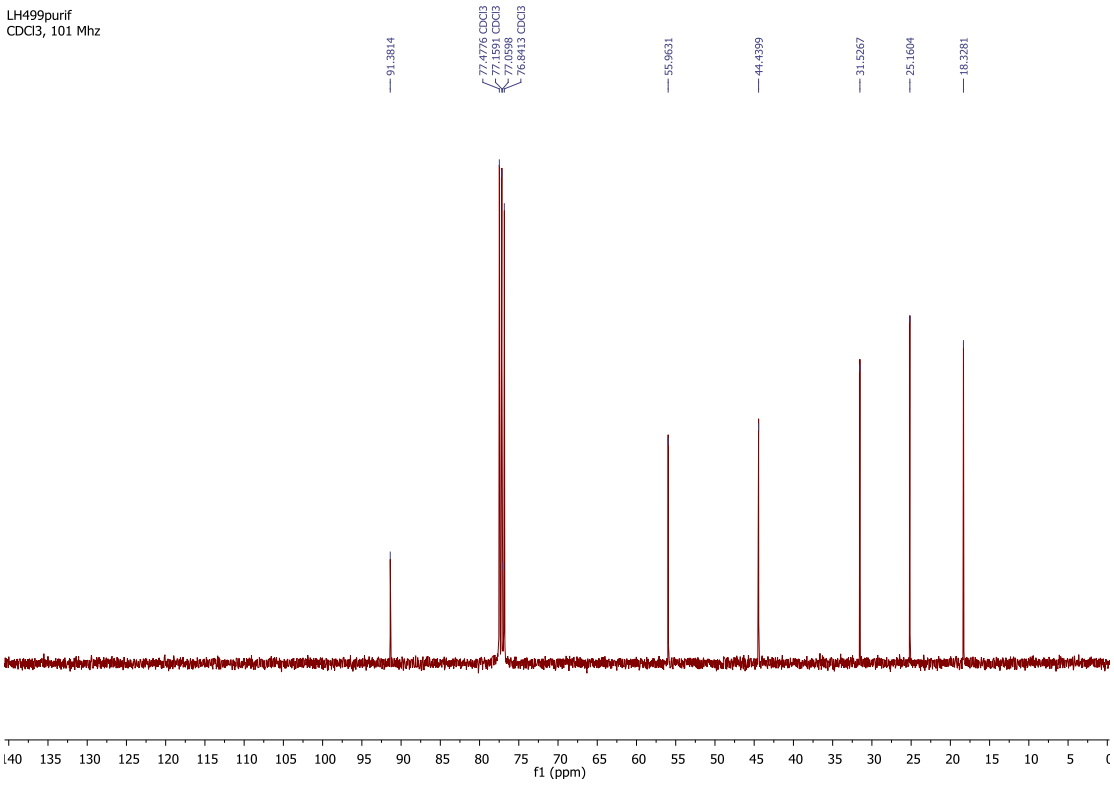
LH277purif1
CDCl3, 400 Mhz



LH277purif
CDCl3, 101 Mhz




LH499purif
CDCl3, 400 Mhz
7.2596
6.2598
6.2551
6.2501
3.5884
3.5724
3.5562
2.4005
2.3955
2.3930
2.3780
2.3655
2.3606
1.9117
1.9090
1.8959
1.8936
1.8909
1.8888
1.8859
1.8778
1.8724
1.8565
1.7651
1.7589
1.7421
1.7383
1.7293
1.7240
1.7213
1.7060
1.7037
Cl
Cl
Cl
1c
0.93
2.00
1.96
2.01
1.99
f1 (ppm)


LH499purif
CDCl3, 101 Mhz
91.3814
77.4776 CDCl3
77.1591 CDCl3
77.0598
76.8413 CDCl3
55.9631
44.4399
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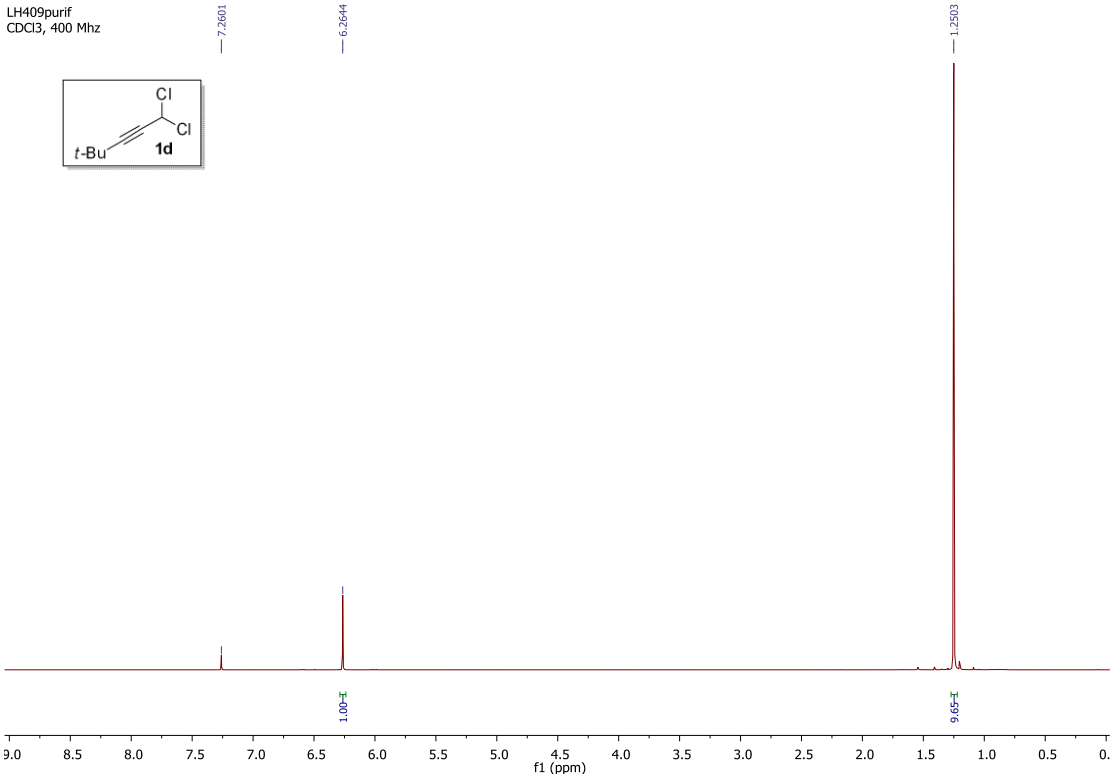
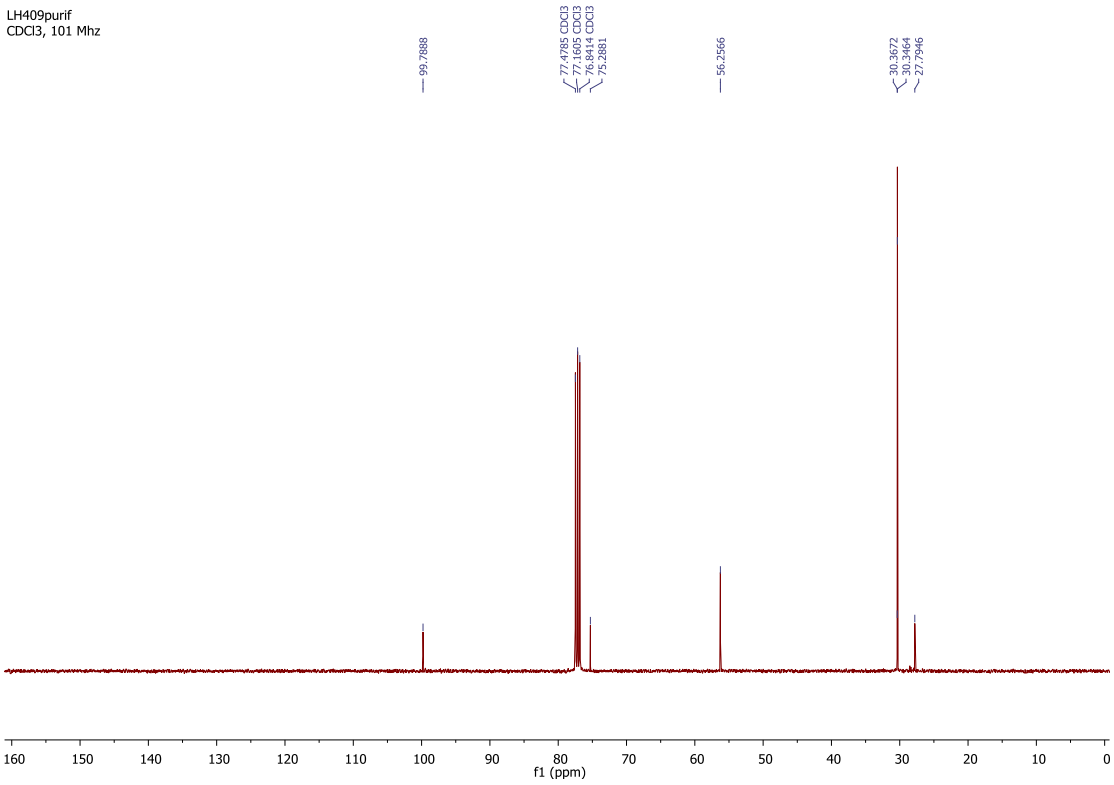
18.3281
f1 (ppm)


LH409purif
CDCl3, 400 Mhz
7.2601
6.2644
1.2503
Cl
Cl
t-Bu
1d
1.00
9.65
f1 (ppm)


LH409purif
CDCl3, 101 Mhz
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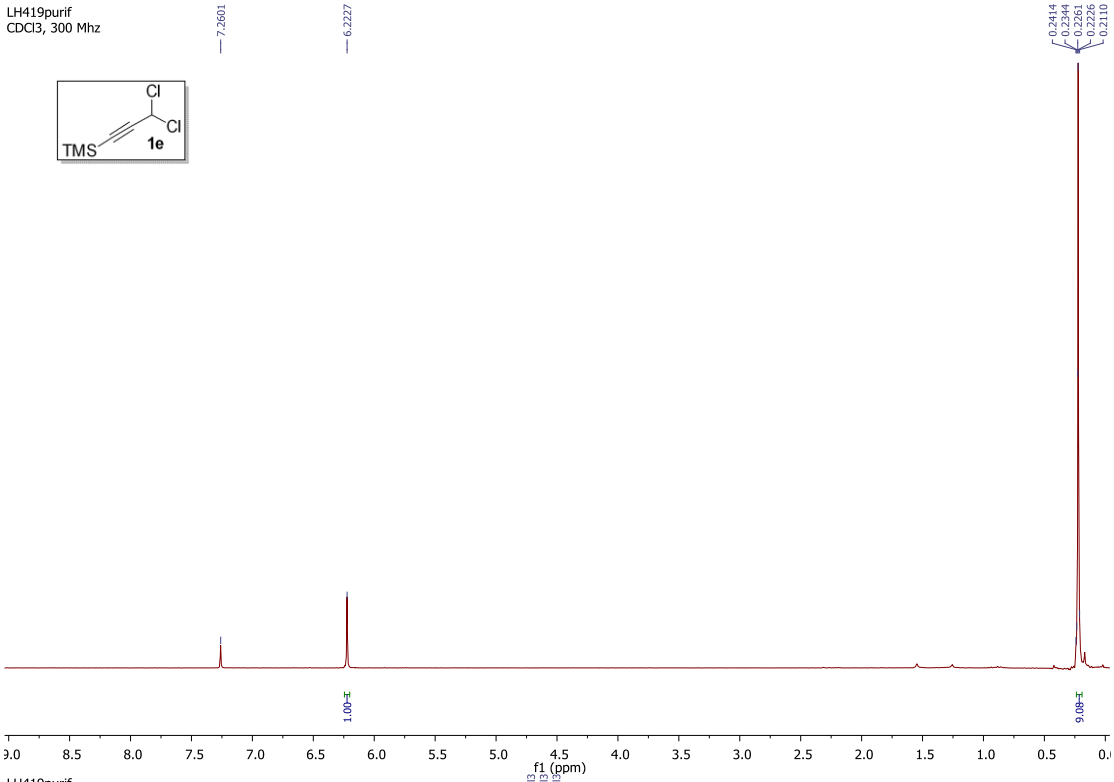
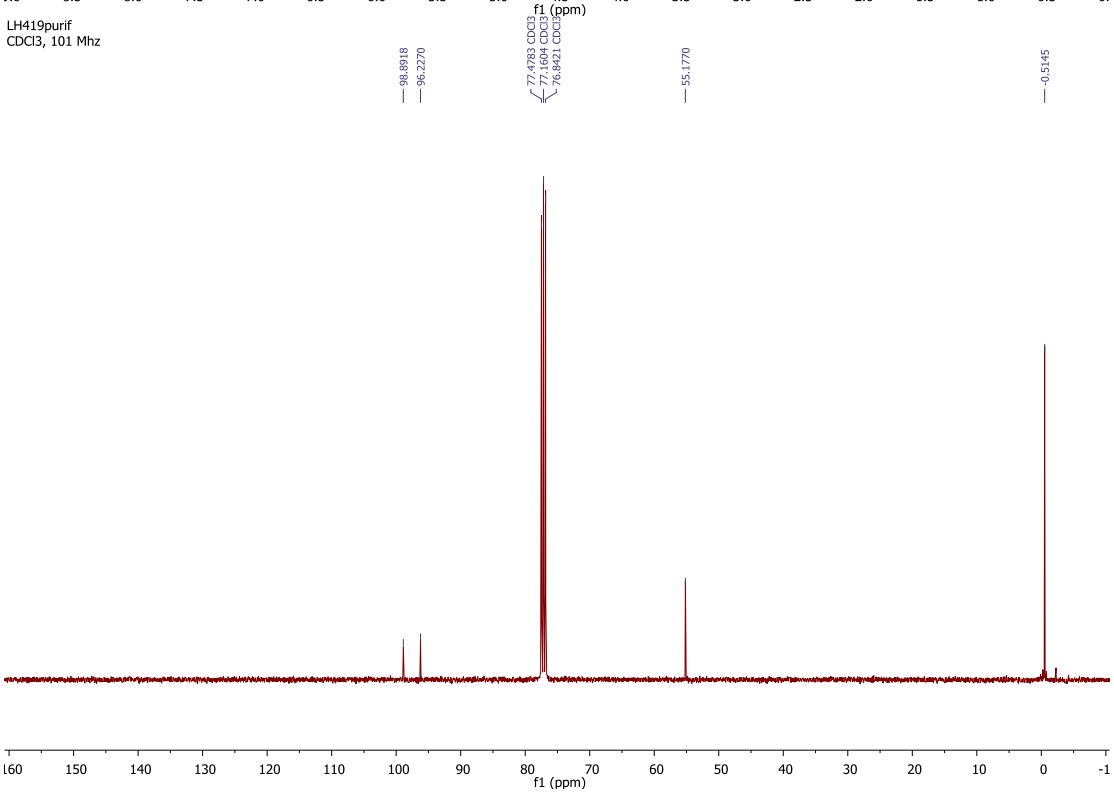
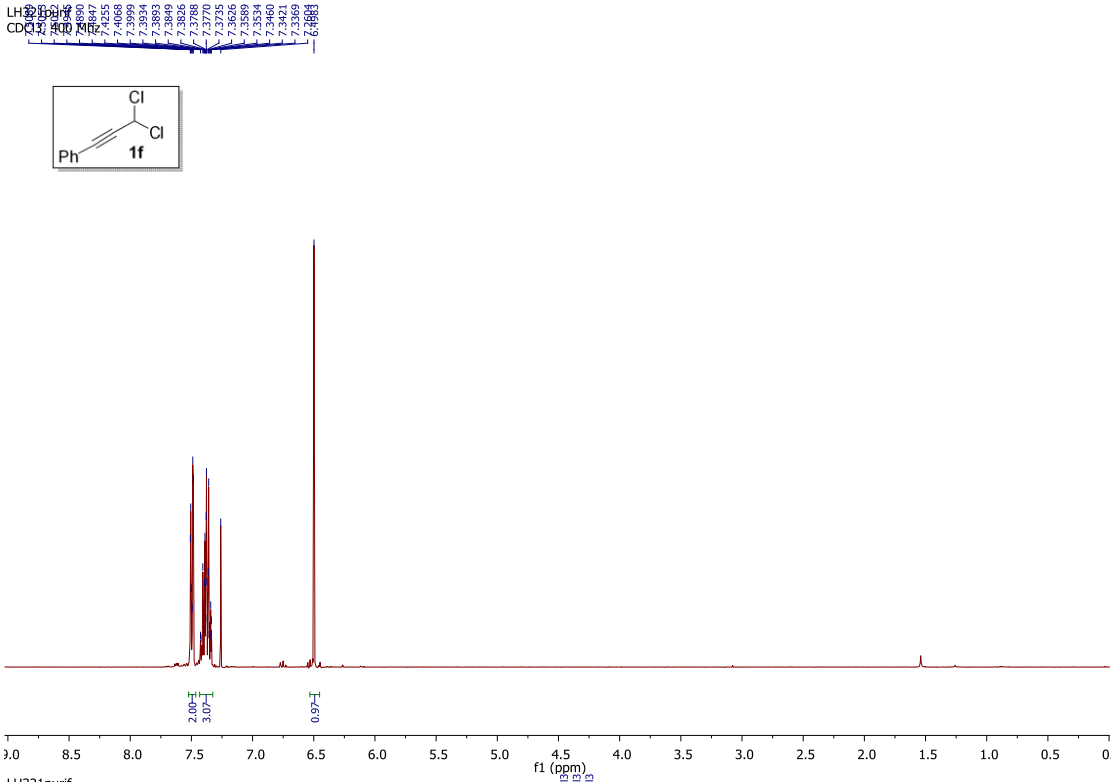
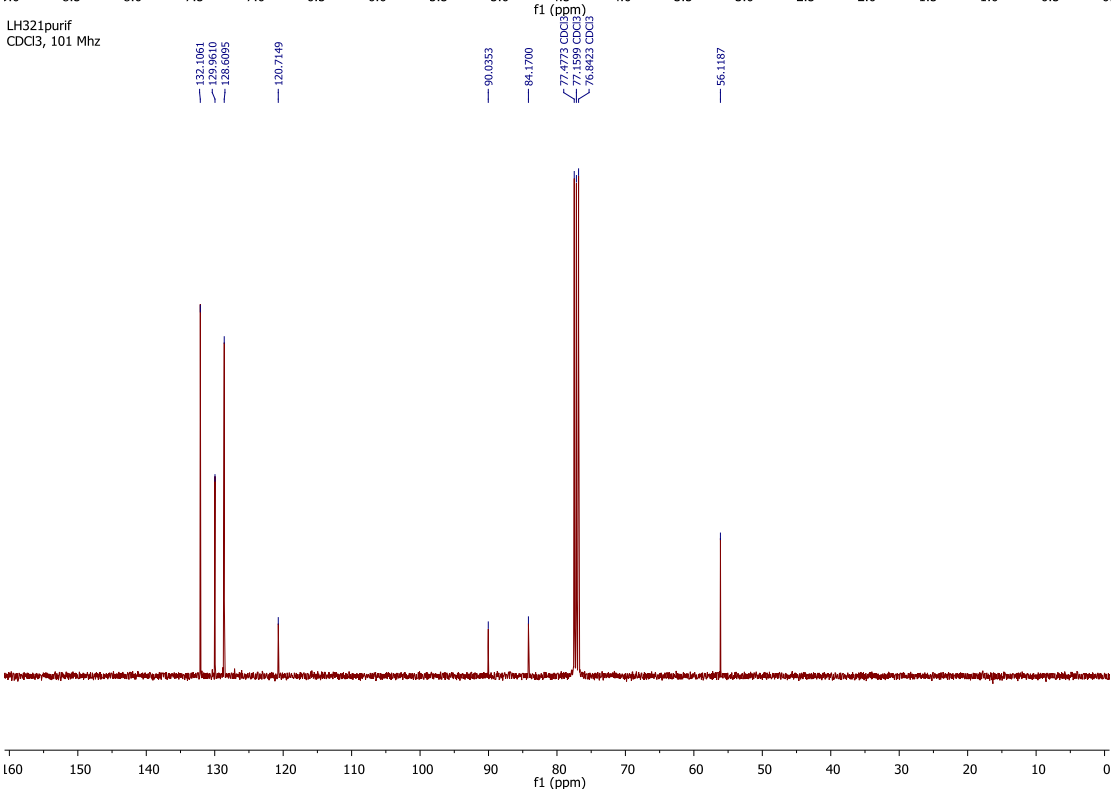
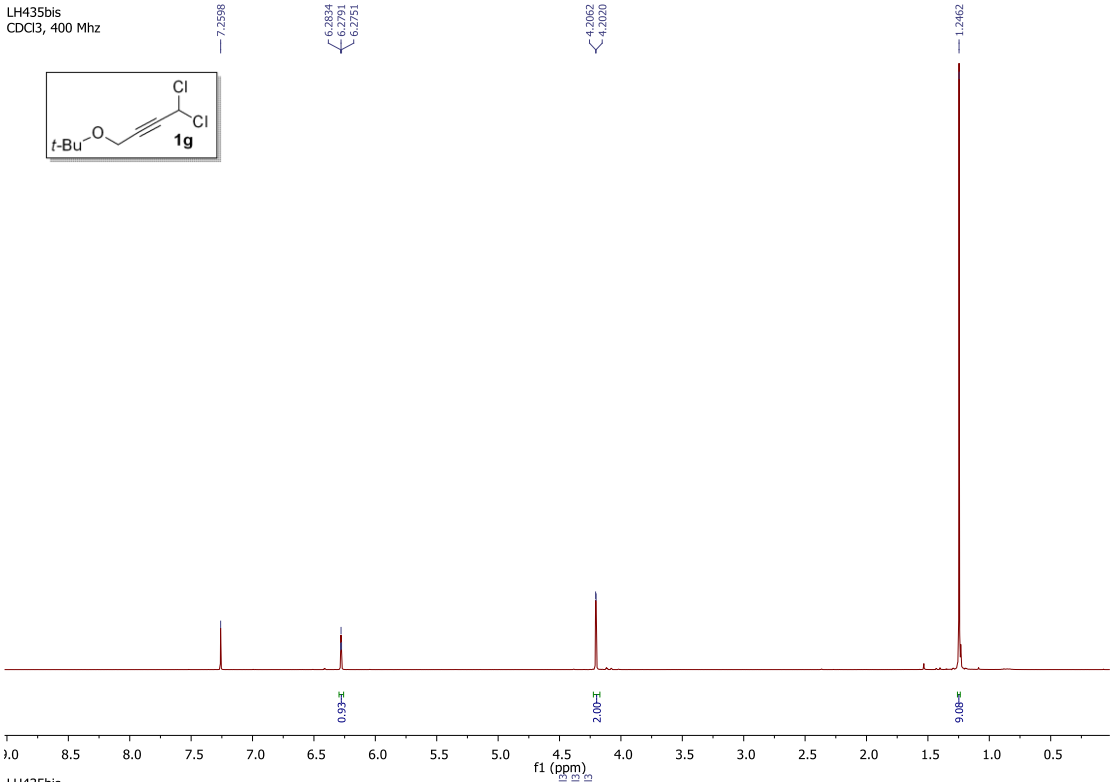
27.7946
f1 (ppm)

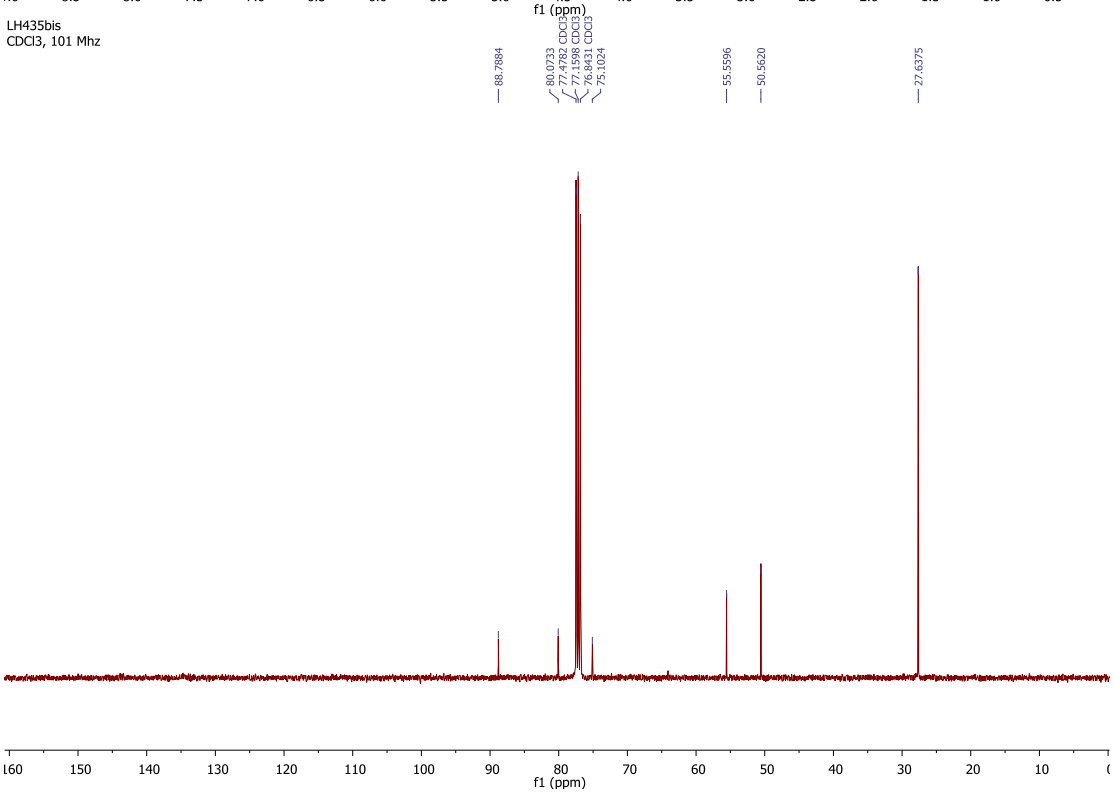

LH419purif
CDCl3, 300 Mhz
7.2601
6.2227
0.2414
0.2344
0.2261
0.2226
0.2110
Cl
Cl
TMS
1e
1.00
9.08
f1 (ppm)

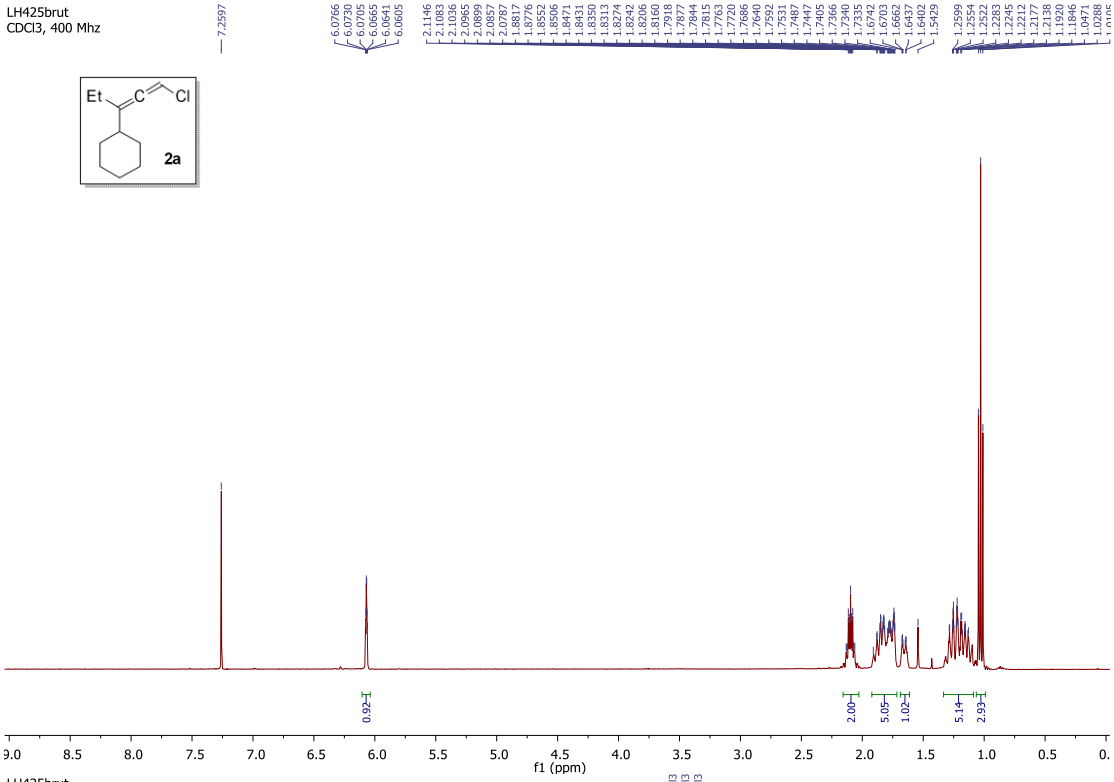

LH419purif
CDCl3, 101 Mhz
98.8918
96.2270
77.4783 CDCl3
77.1604 CDCl3
76.8421 CDCl3
55.1770
-0.5145
f1 (ppm)

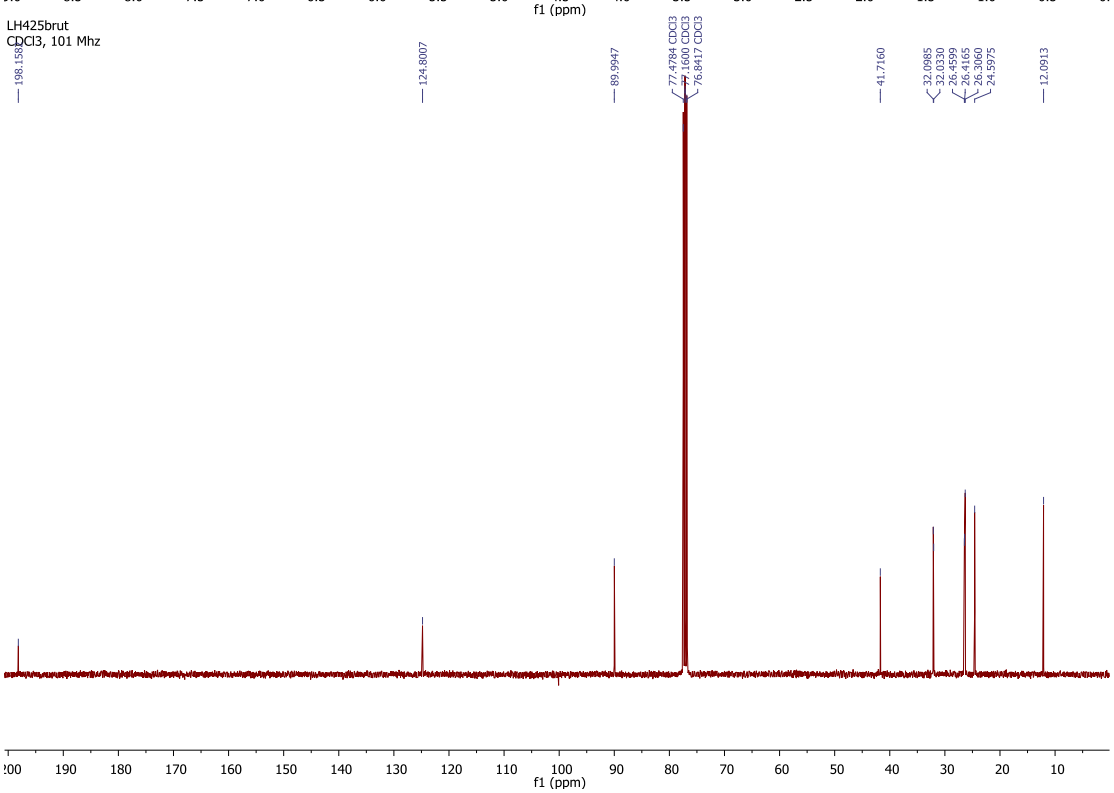

LH321purif
CDCl3, 400 MHz
Cl
Cl
Ph
1f
2.00
3.07
0.97
f1 (ppm)

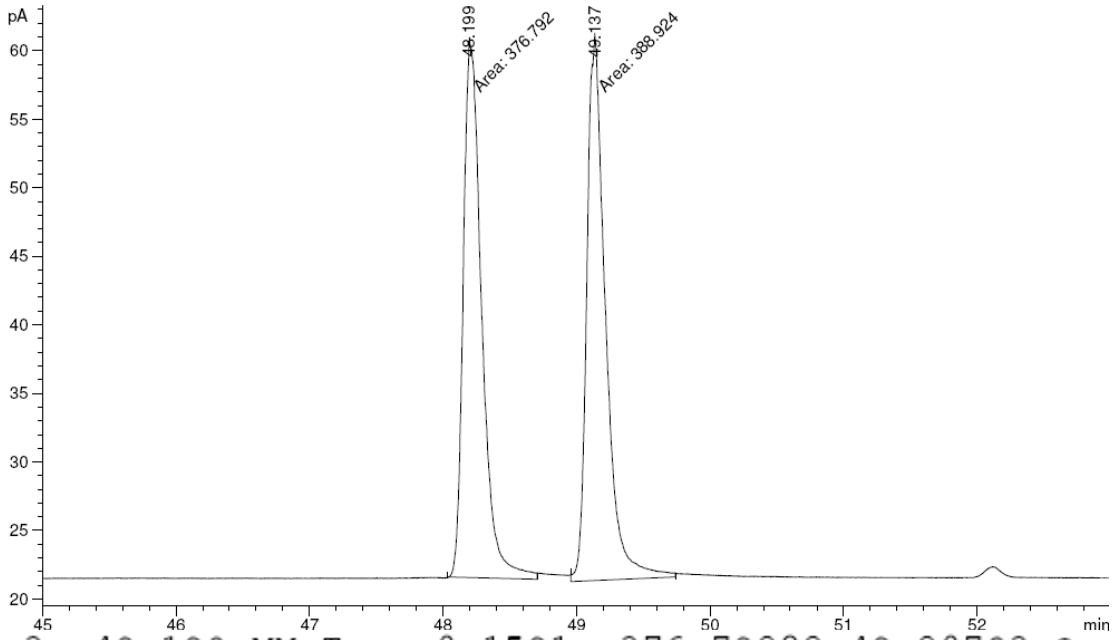

LH321purif
CDCl3, 101 Mhz
132.1061
129.9610
128.6095
120.7149
90.0353
84.1700
77.4773 CDCl3
77.1599 CDCl3
76.8423 CDCl3
56.1187
f1 (ppm)


LH435bis
CDCl3, 400 Mhz
7.2598
6.2834
6.2791
6.2751
4.2062
4.2020
1.2462
Cl
Cl
t-Bu
O
1g
0.93
2.00
9.08
f1 (ppm)

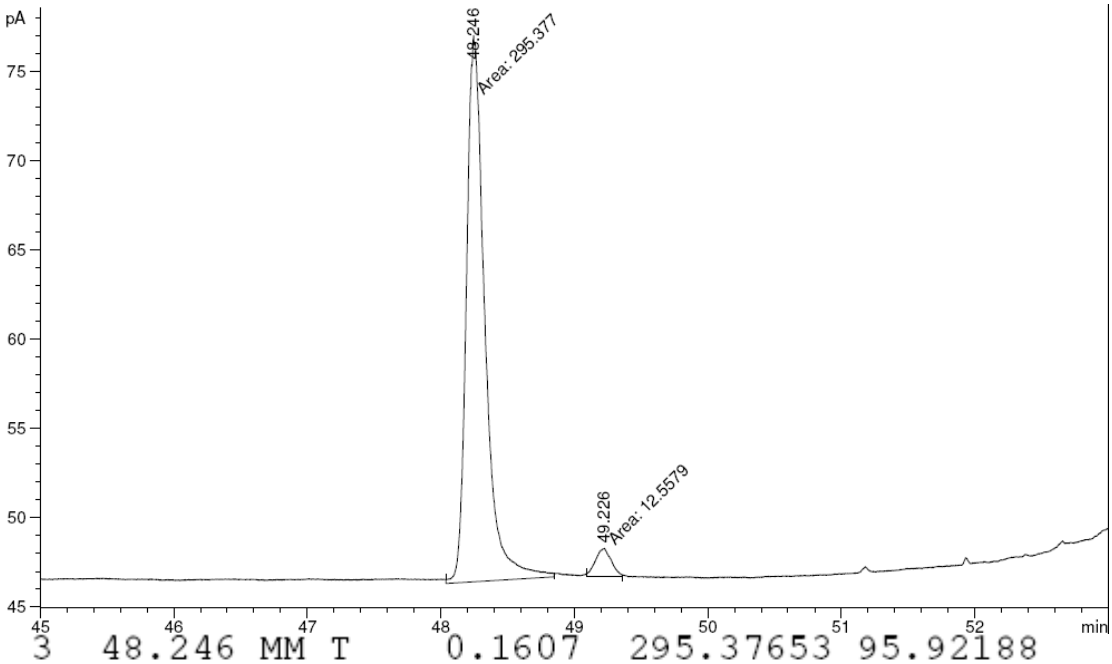

LH435bis
CDCl3, 101 Mhz
88.7884
80.0733
77.4782 CDCl3
77.1598 CDCl3
76.8431 CDCl3
75.1024
55.5596
50.5620
27.6375
f1 (ppm)


LH425brut
CDCl3, 400 Mhz
Et
C
Cl
2a
7.2597
6.0766
6.0730
6.0705
6.0665
6.0641
6.0605
2.1146
2.1083
2.1036
2.0965
2.0899
2.0857
2.0787
1.8817
1.8776
1.8552
1.8506
1.8471
1.8431
1.8350
1.8313
1.8274
1.8242
1.8206
1.8160
1.7918
1.7877
1.7844
1.7815
1.7763
1.7720
1.7686
1.7640
1.7592
1.7531
1.7487
1.7447
1.7405
1.7366
1.7340
1.7335
1.6742
1.6703
1.6662
1.6437
1.6402
1.5429
1.2599
1.2554
1.2522
1.2283
1.2245
1.2217
1.2177
1.2138
1.1920
1.1846
1.0471
1.0288
0.92
2.00
5.05
1.02
5.14
2.93
f1 (ppm)

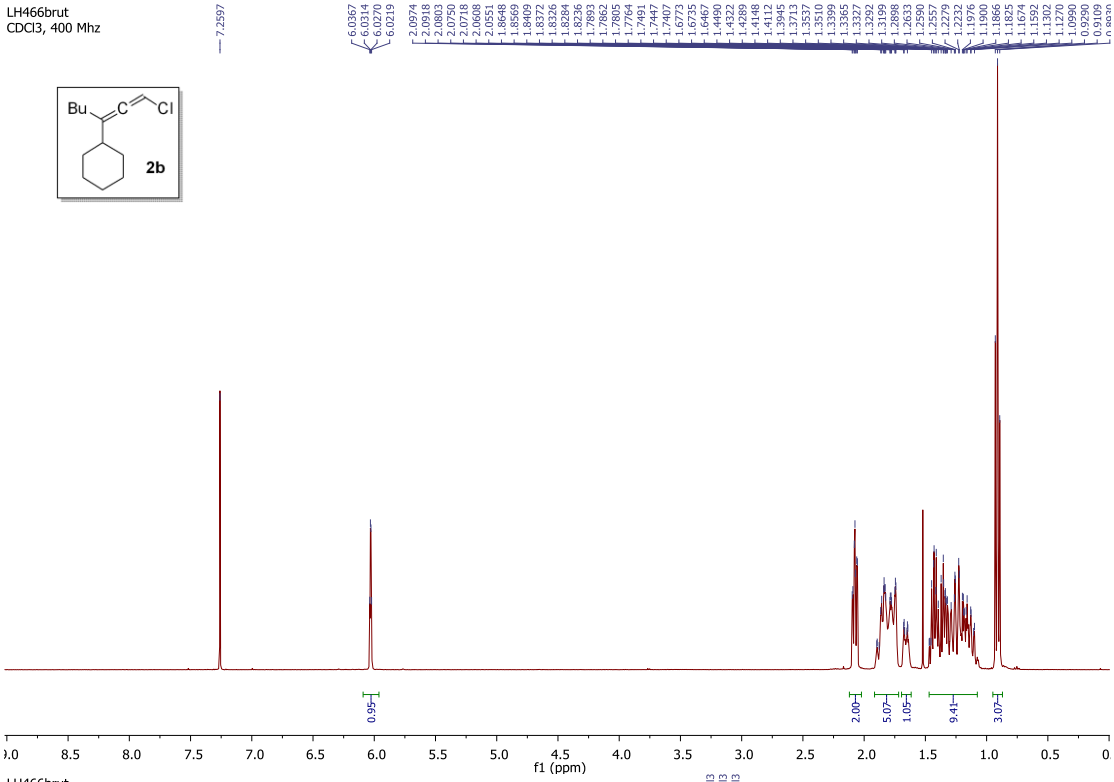

LH425brut
CDCl3, 101 Mhz
198.158
124.8007
89.9947
77.4784 CDCl3
77.1600 CDCl3
76.8417 CDCl3
41.7160
32.0985
32.0370
26.4599
26.4165
26.3060
24.5975
12.0913
f1 (ppm)

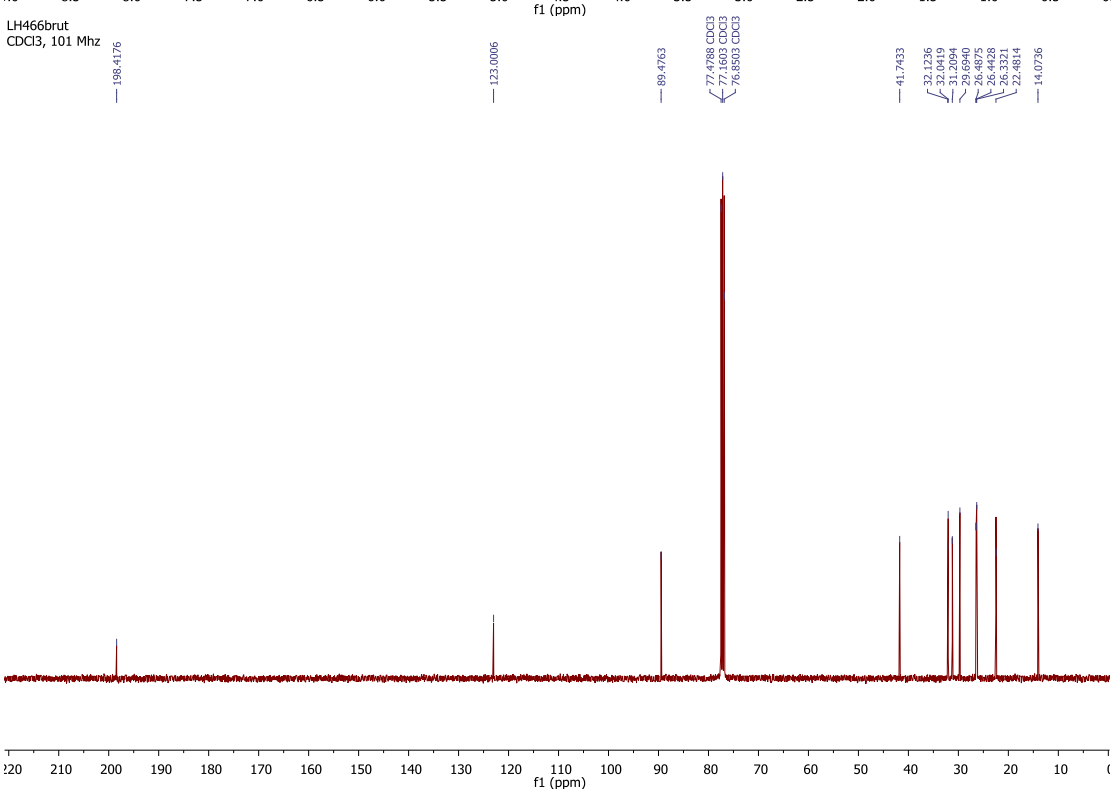


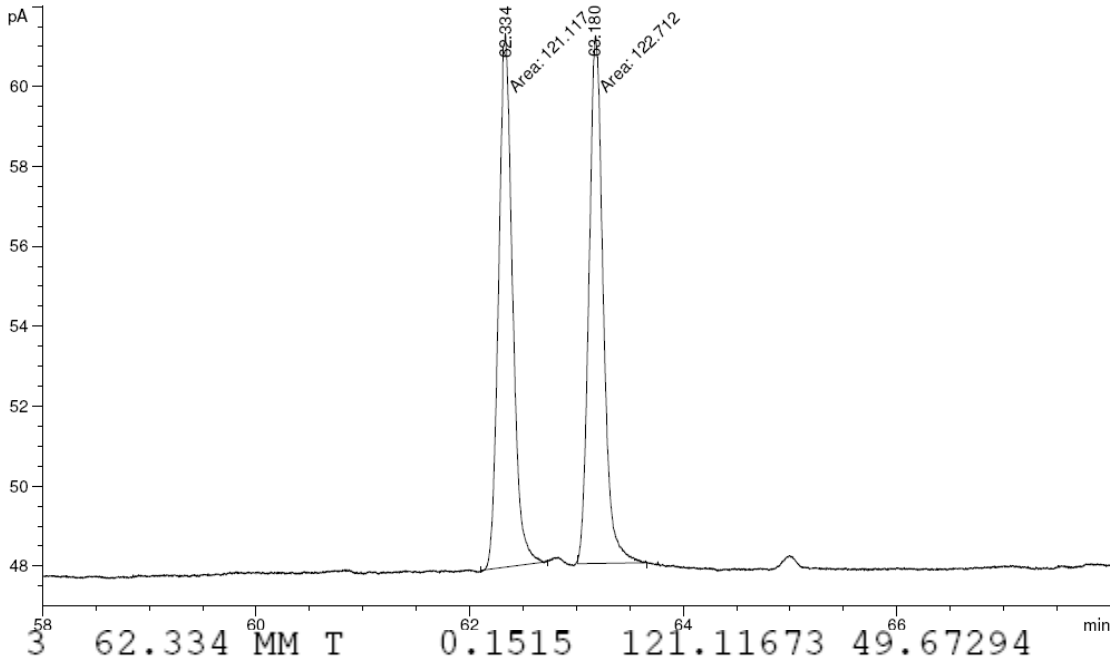
3	48.199	MM	T	0.1591	376.79202	49.20783 ?
4	49.137	MM	T	0.1630	388.92358	50.79217 ?



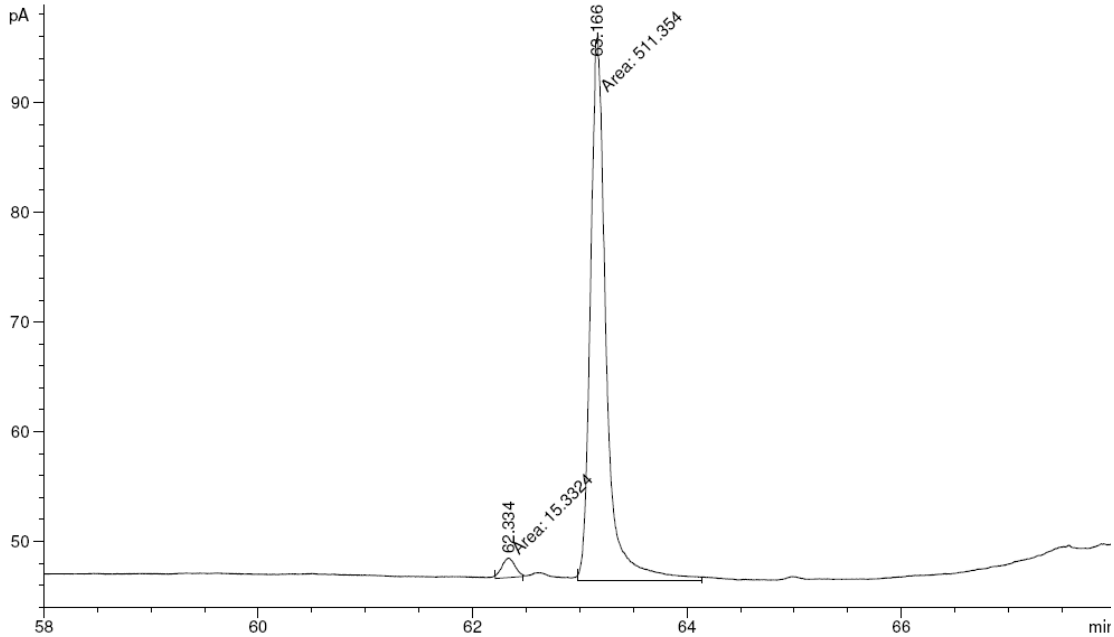
3	48.246	MM	T	0.1607	295.37653	95.92188
4	49.226	MM	T	0.1340	12.55793	4.07812


LH466brut
CDCl3, 400 Mhz
Bu
C
Cl
2b
7.2597
6.0367
6.0314
6.0270
6.0219
0.95
2.00
5.07
1.05
9.41
3.07
f1 (ppm)

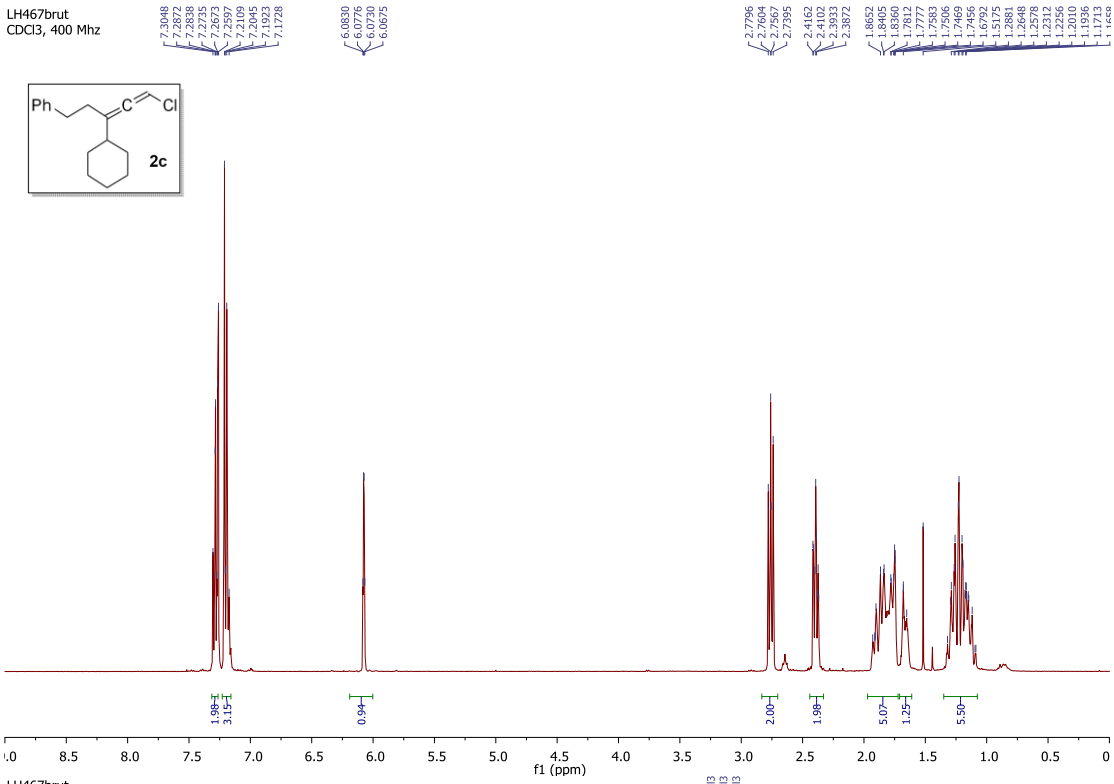

LH466brut
CDCl3, 101 Mhz
198.4176
123.0006
89.4763
77.4788 CDCl3
77.1603 CDCl3
76.8503 CDCl3
41.7433
32.1236
32.0459
31.7094
29.6940
26.4875
26.4428
26.3321
22.4814
14.0736
f1 (ppm)

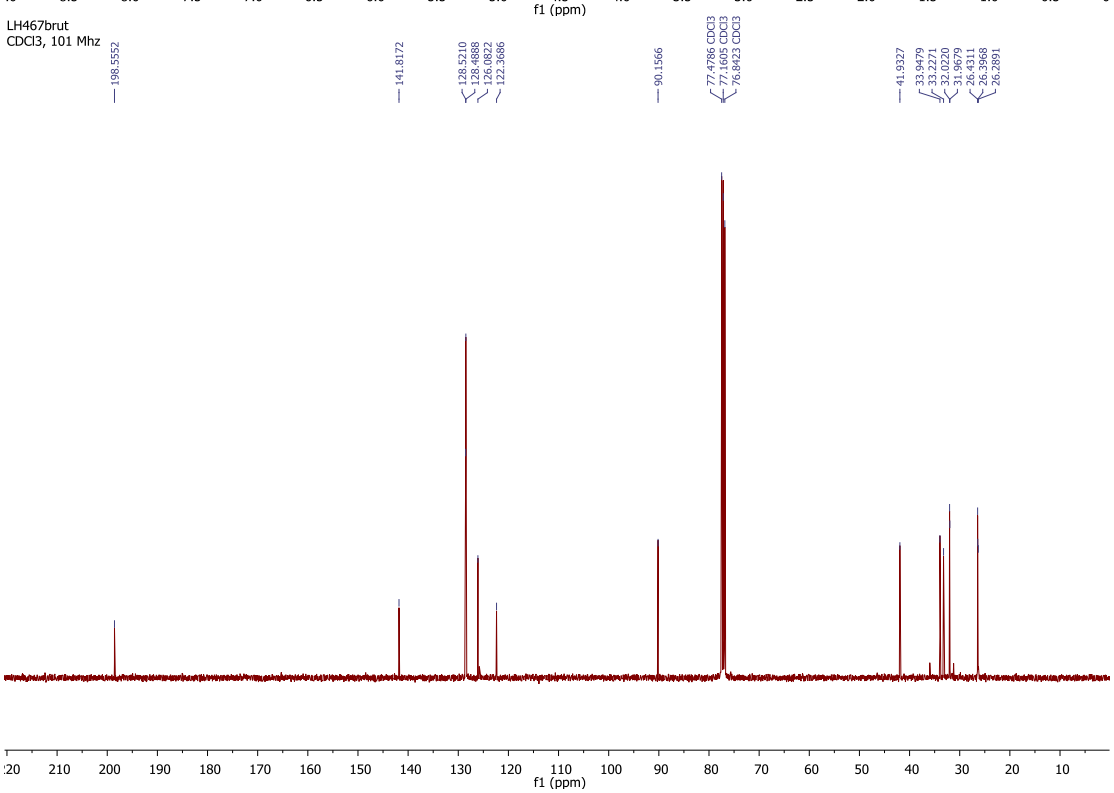


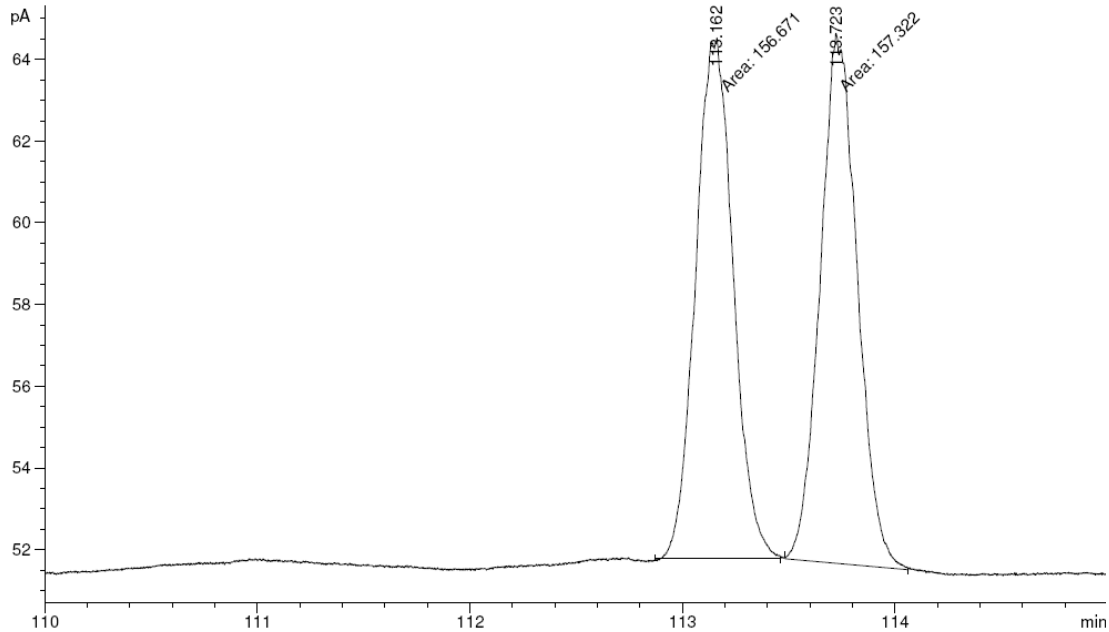
3	62.334	MM	T	0.1515	121.11673	49.67294
4	63.180	MM	T	0.1550	122.71167	50.32706



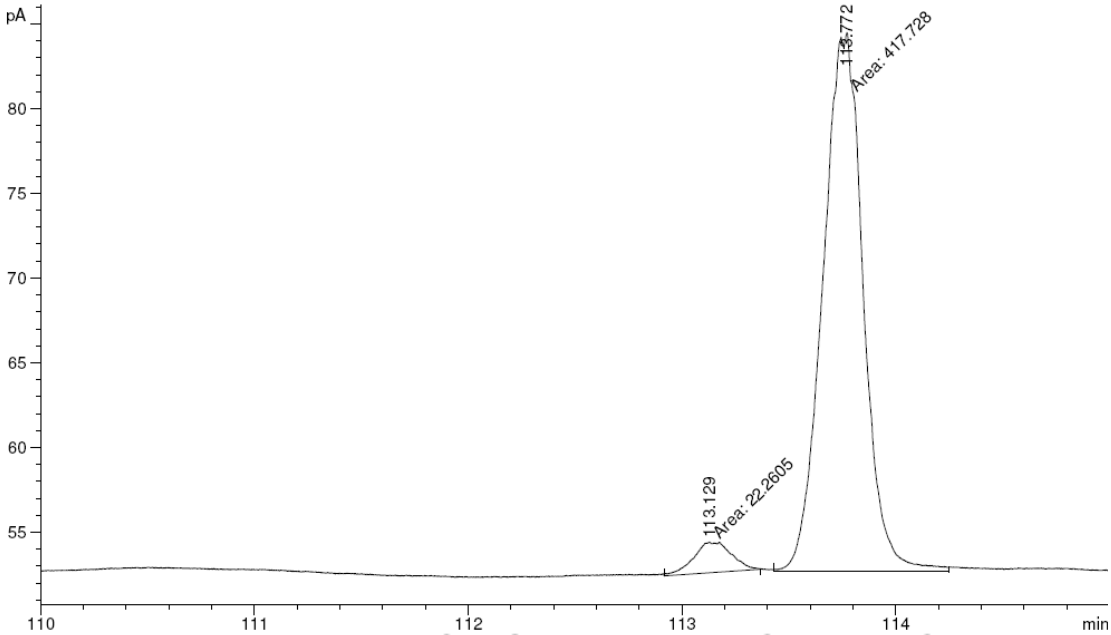
3	62.334	MM	T	0.1445	15.33242	2.91111
4	63.166	MM	T	0.1706	511.35431	97.08889


LH467brut
CDCl3, 400 Mhz
Ph
C
Cl
2c
f1 (ppm)

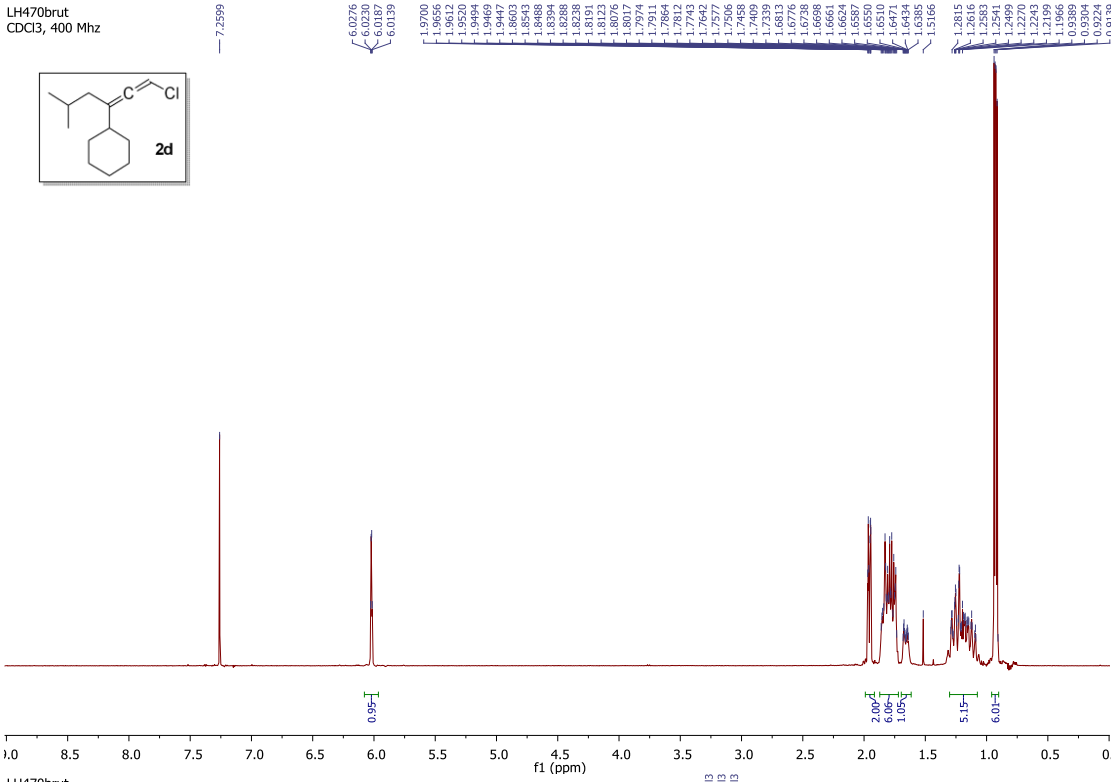

LH467brut
CDCl3, 101 Mhz
198.5552
141.8172
128.5210
128.4888
126.0822
122.3686
90.1566
77.4786 CDCl3
77.1605 CDCl3
76.8423 CDCl3
41.9327
33.9479
33.2271
32.0220
31.9679
26.4311
26.3968
26.2891
f1 (ppm)

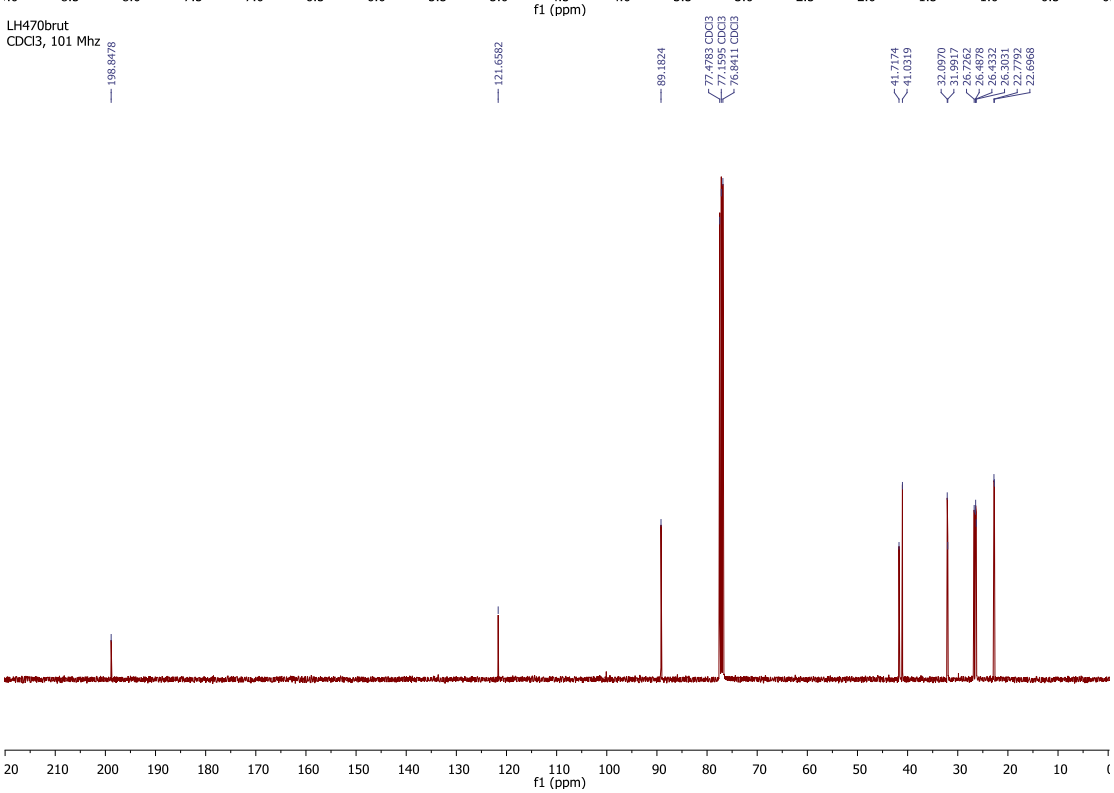


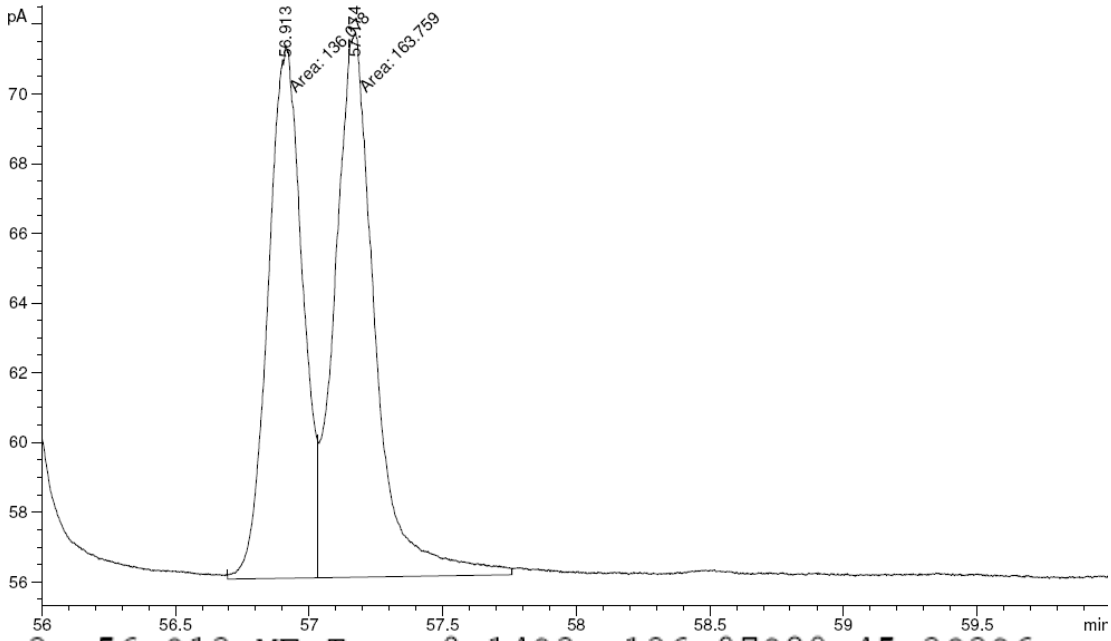
3	113.162	MM	T	0.2048	156.67085	49.89637
4	113.723	MM	T	0.2021	157.32164	50.10363



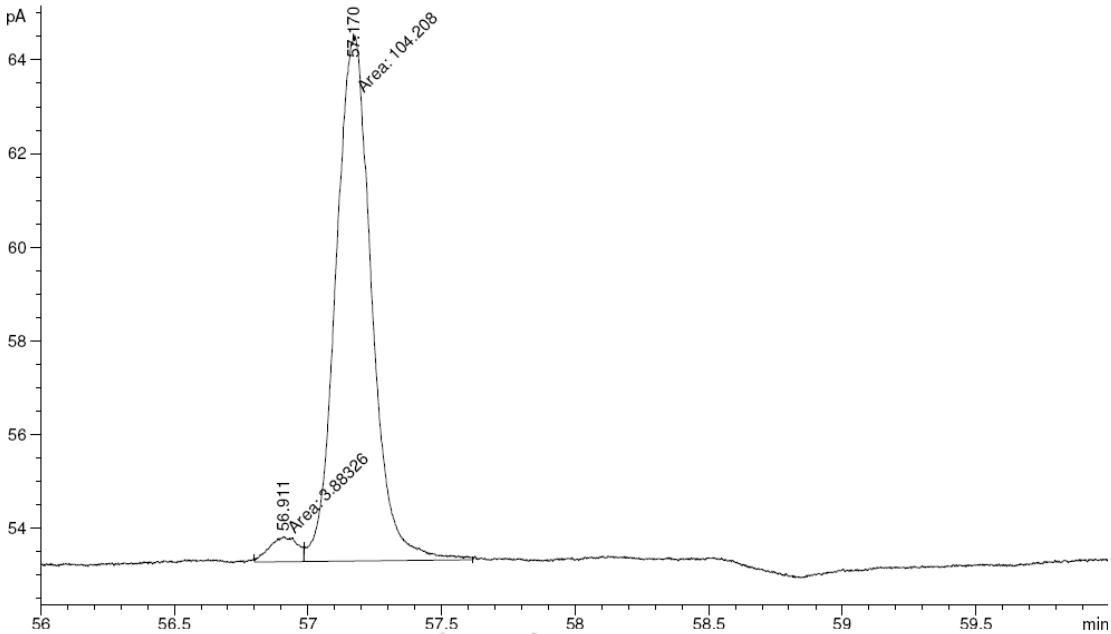
3	113.129	MM	T	0.2037	22.26052	5.05934
4	113.772	MM	T	0.2189	417.72797	94.94066


LH470brut
CDCl3, 400 Mhz
2d
f1 (ppm)

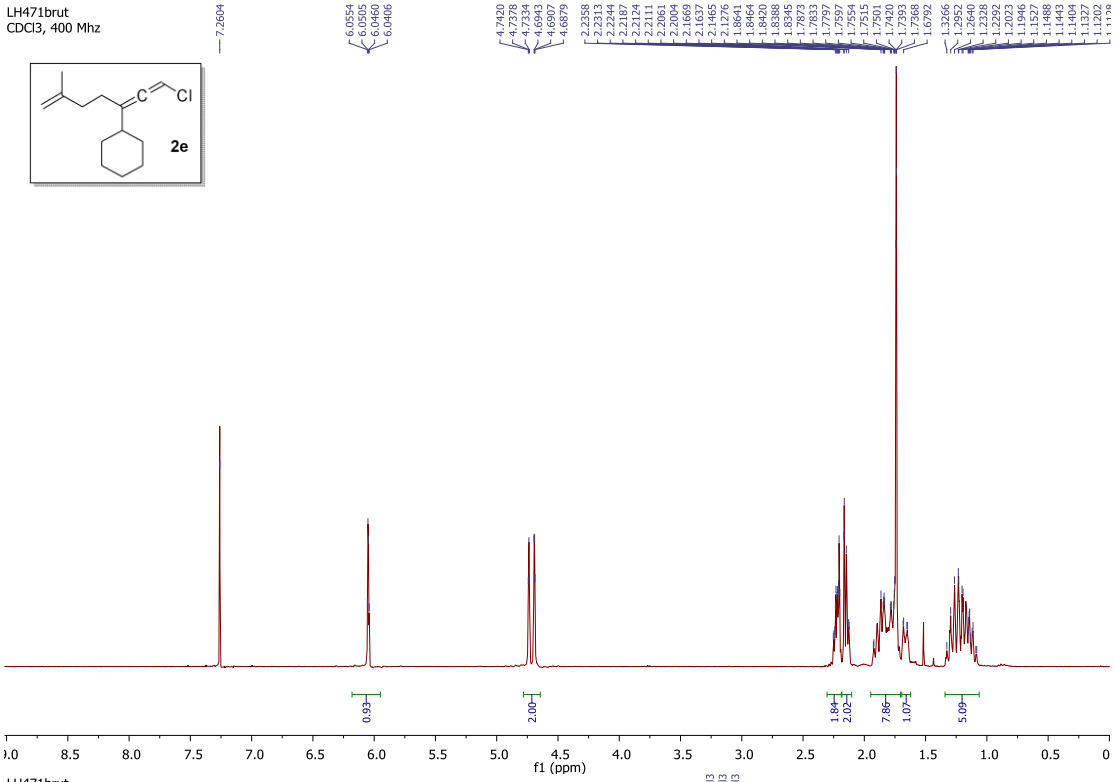

LH470brut
CDCl3, 101 Mhz
198.8478
121.6582
89.1824
77.4783 CDCl3
77.1595 CDCl3
76.8411 CDCl3
41.7174
41.0319
32.0970
31.9927
26.7262
26.4878
26.4332
26.3031
22.7792
22.6968
f1 (ppm)

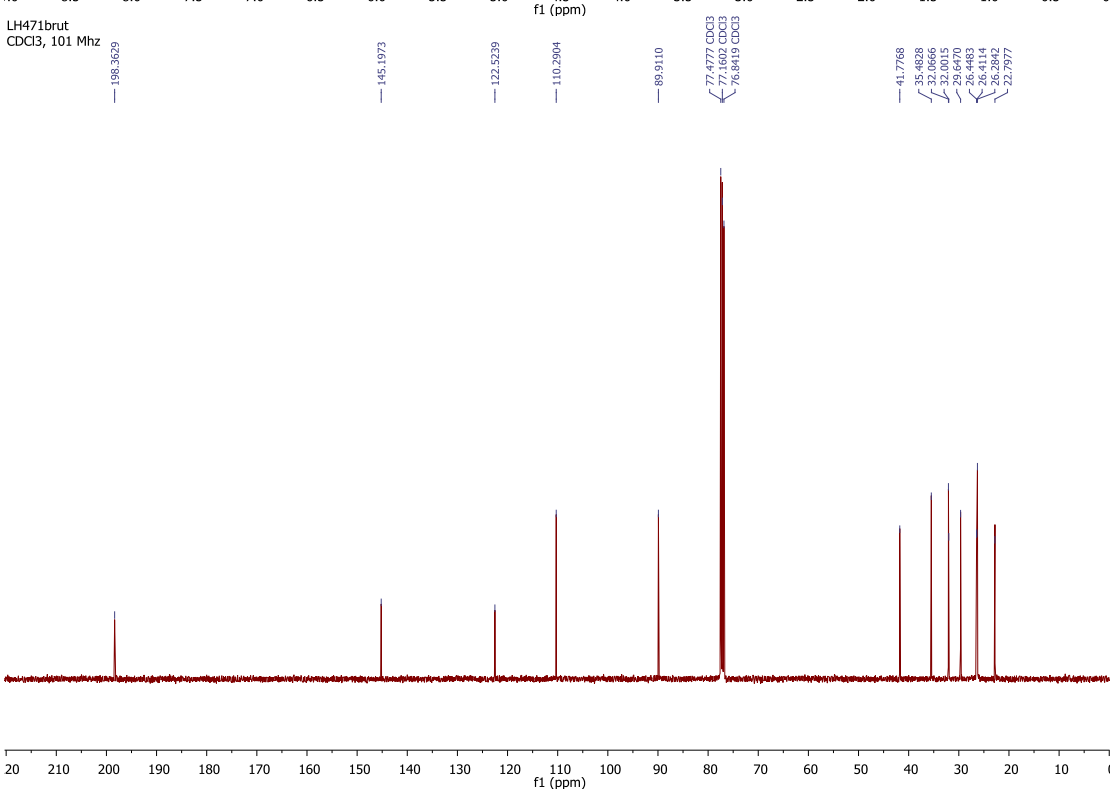


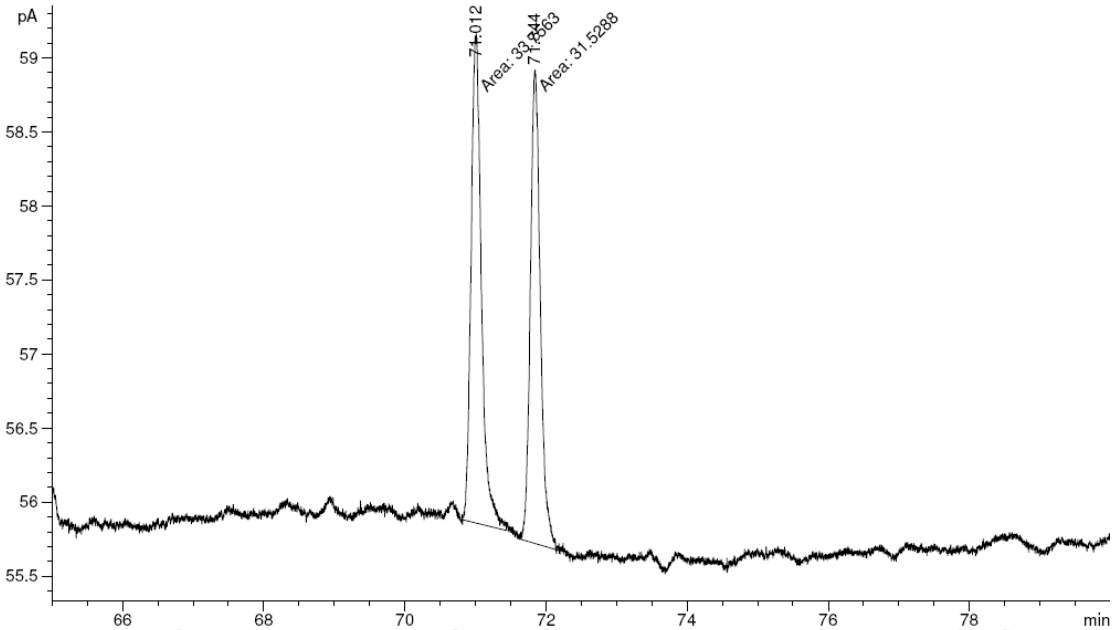
3	56.913	MF	T	0.1483	136.07800	45.38396
4	57.174	FM	T	0.1749	163.75922	54.61604



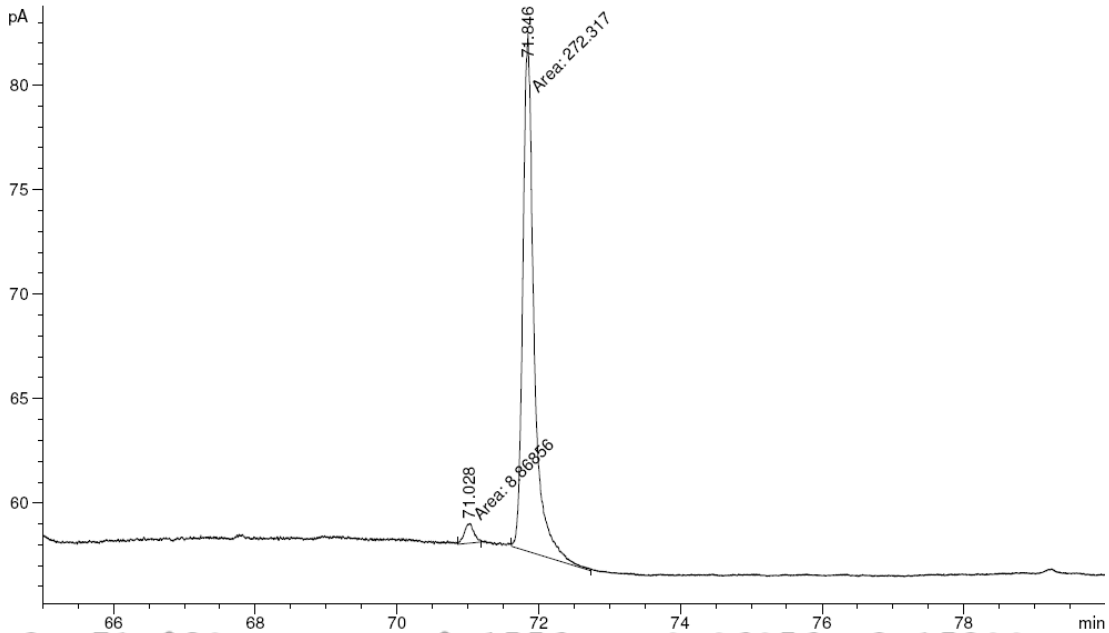
3	56.911	MF	T	0.1203	3.88326	3.59256
4	57.170	FM	T	0.1541	104.20831	96.40744


LH471brut
CDCl3, 400 Mhz
2e
f1 (ppm)

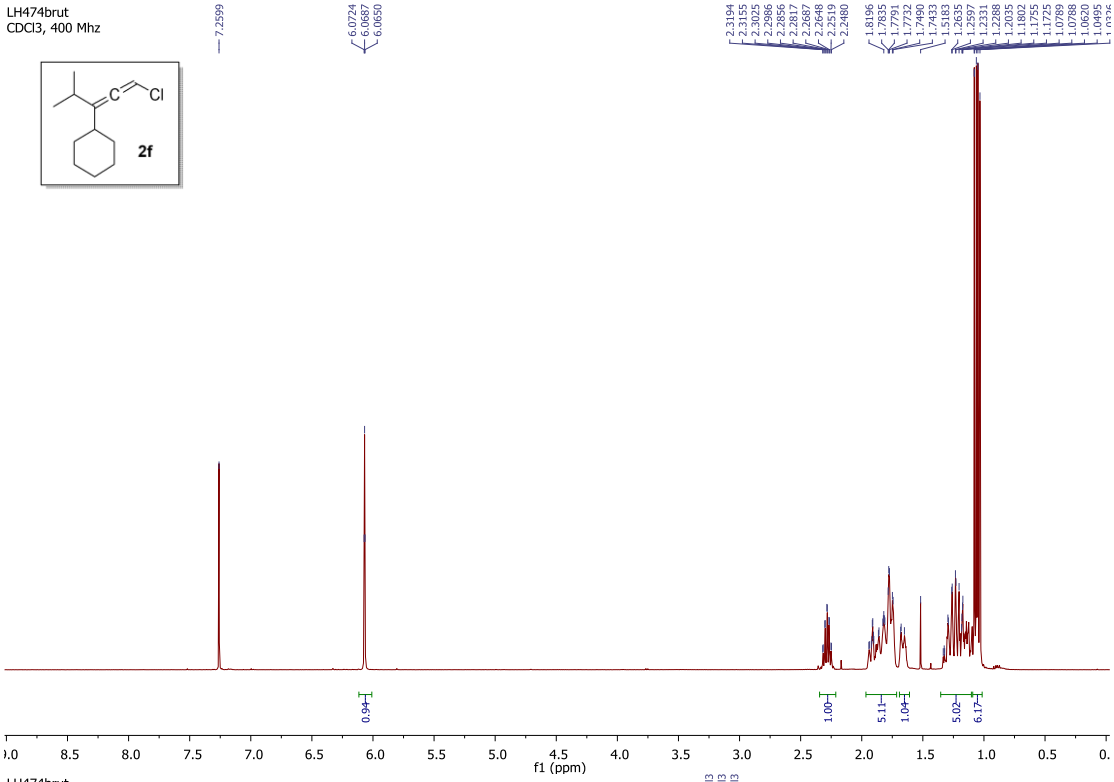

LH471brut
CDCl3, 101 Mhz
f1 (ppm)

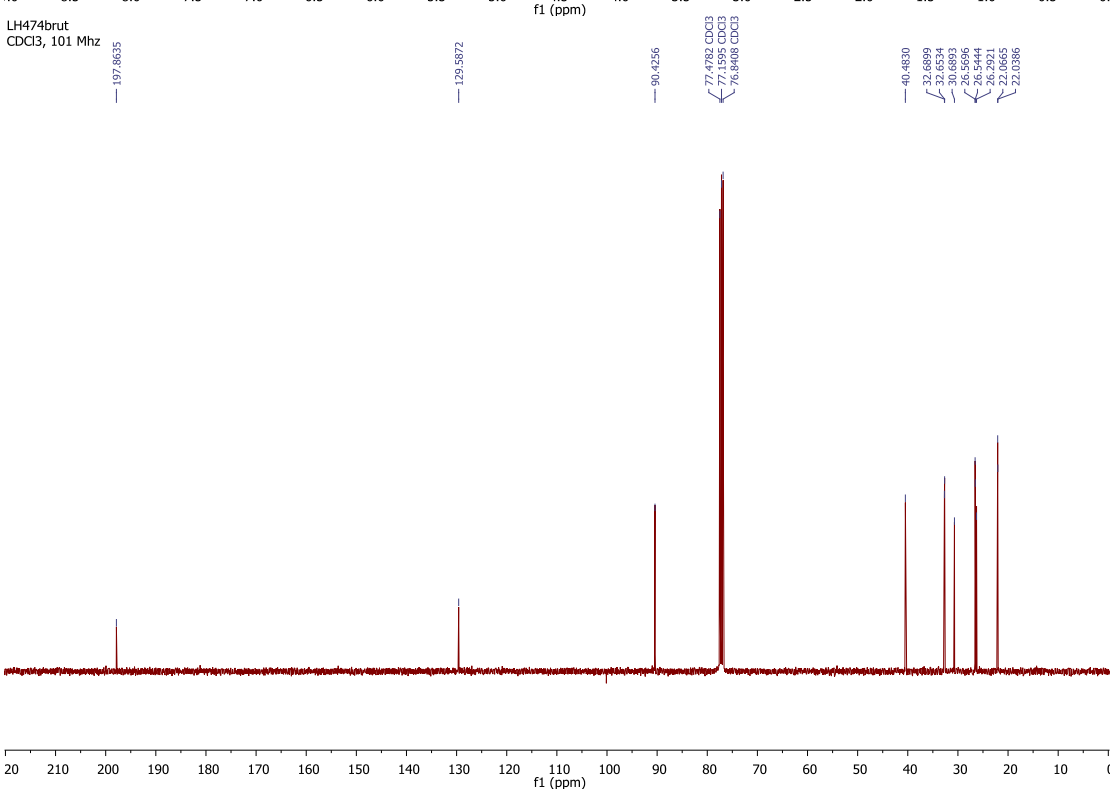


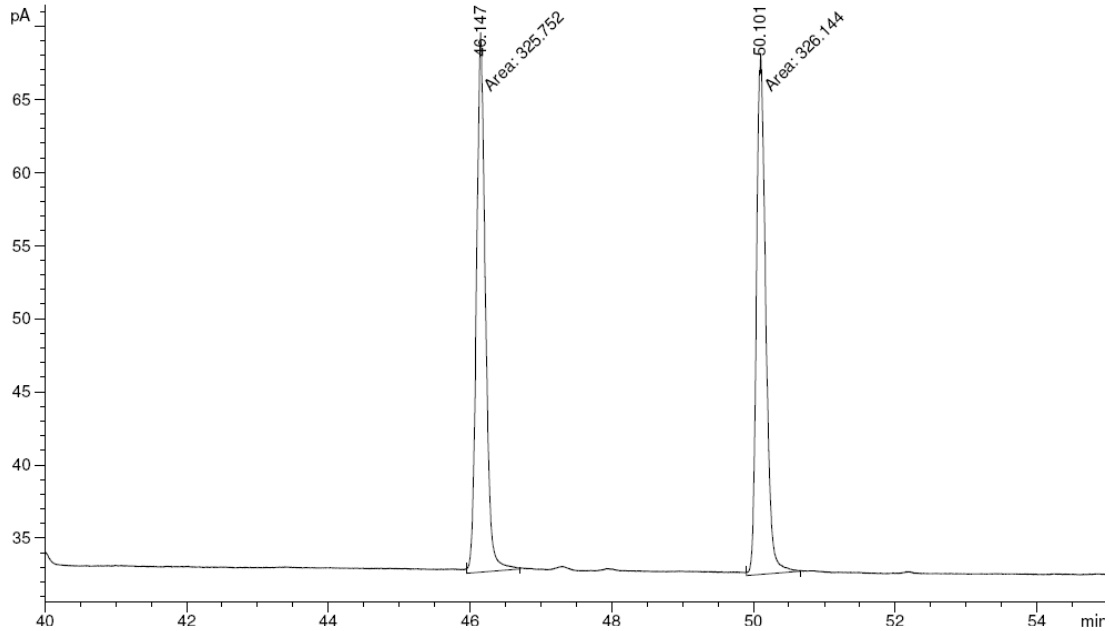
3	71.012	MM	T	0.1707	33.75630	51.70602
4	71.844	MM	T	0.1642	31.52875	48.29398



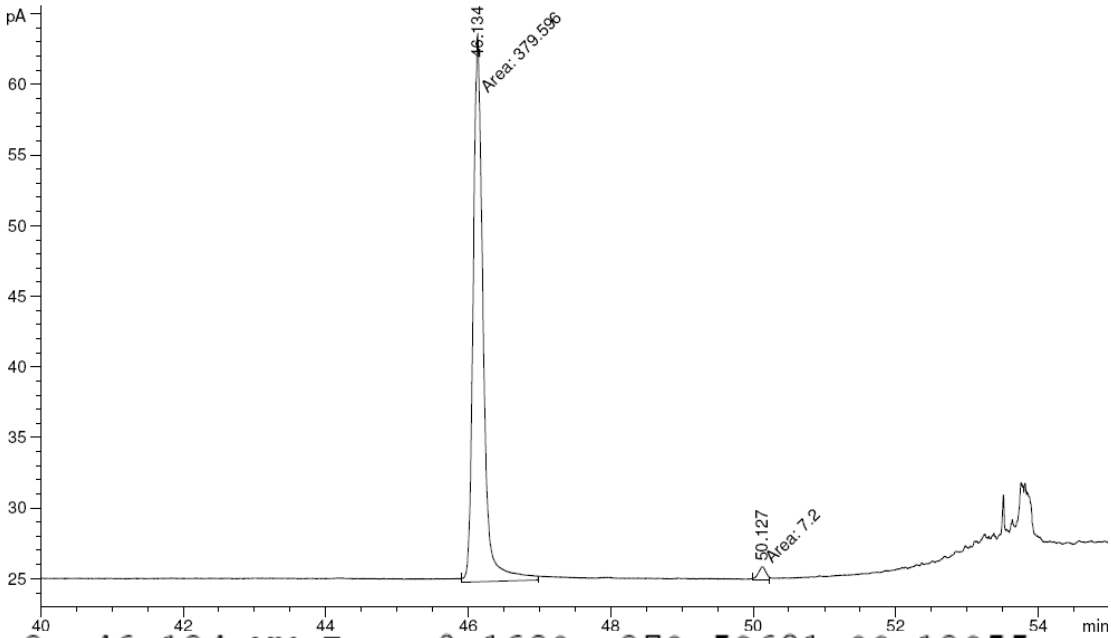
3	71.028	MM	T	0.1556	8.86856	3.15399
4	71.846	MM	T	0.1831	272.31677	96.84601


LH474brut
CDCl3, 400 Mhz
2f
f1 (ppm)


LH474brut
CDCl3, 101 Mhz
f1 (ppm)

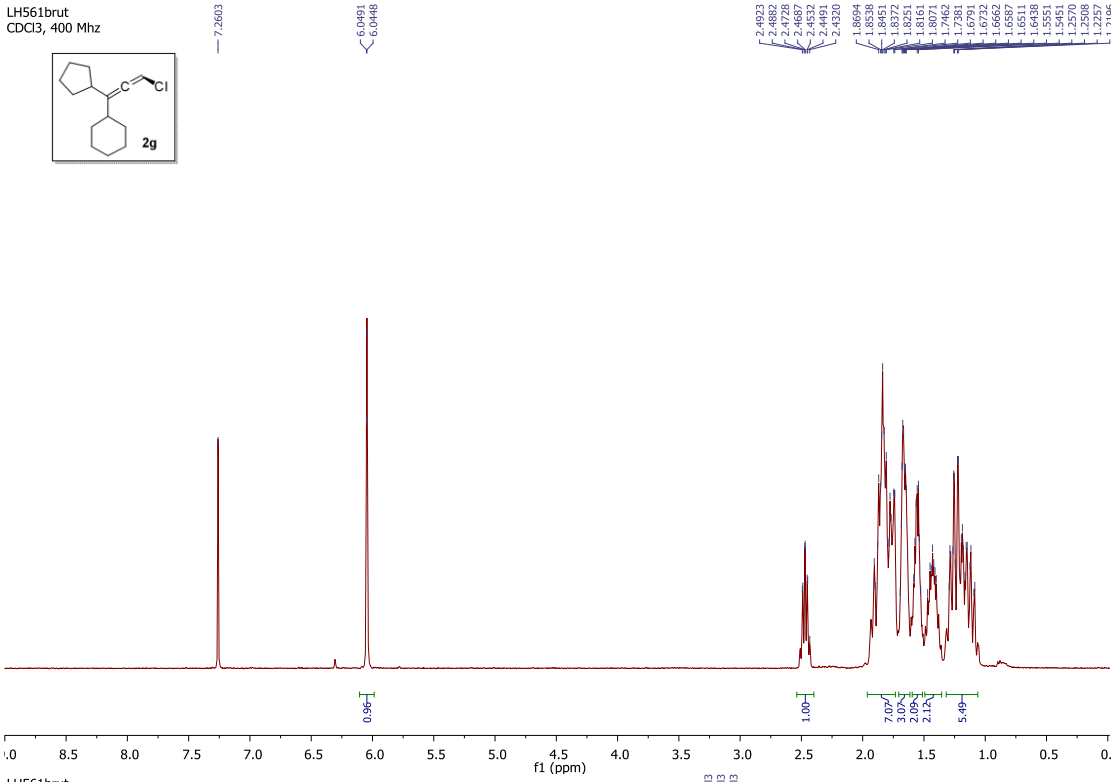


3	46.147	MM	T	0.1473	325.75153	49.96991
4	50.101	MM	T	0.1524	326.14380	50.03009

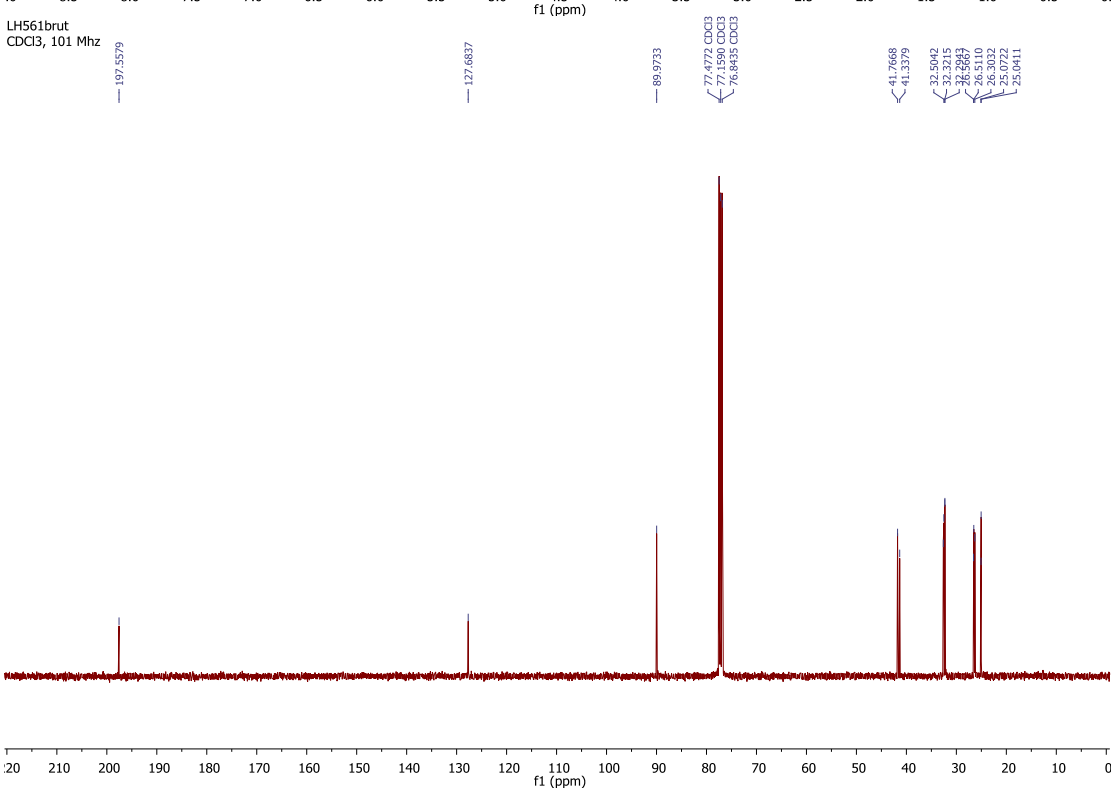


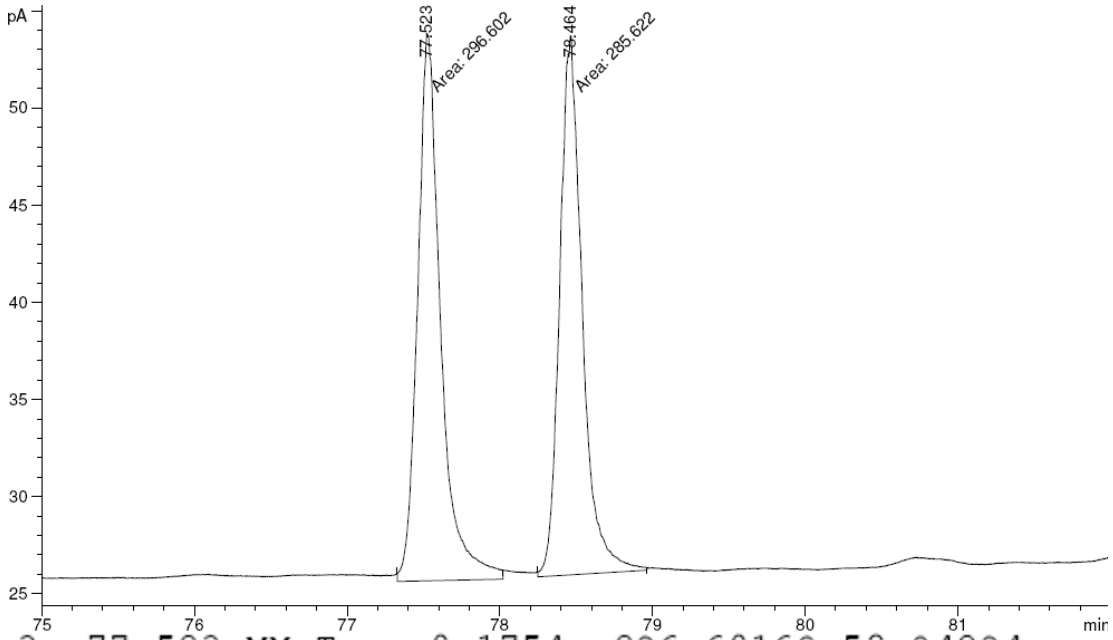
3	46.134	MM	T	0.1629	379.59601	98.13855
4	50.127	MM	T	0.1255	7.20000	1.86145

LH561brut
CDCl3, 400 Mhz

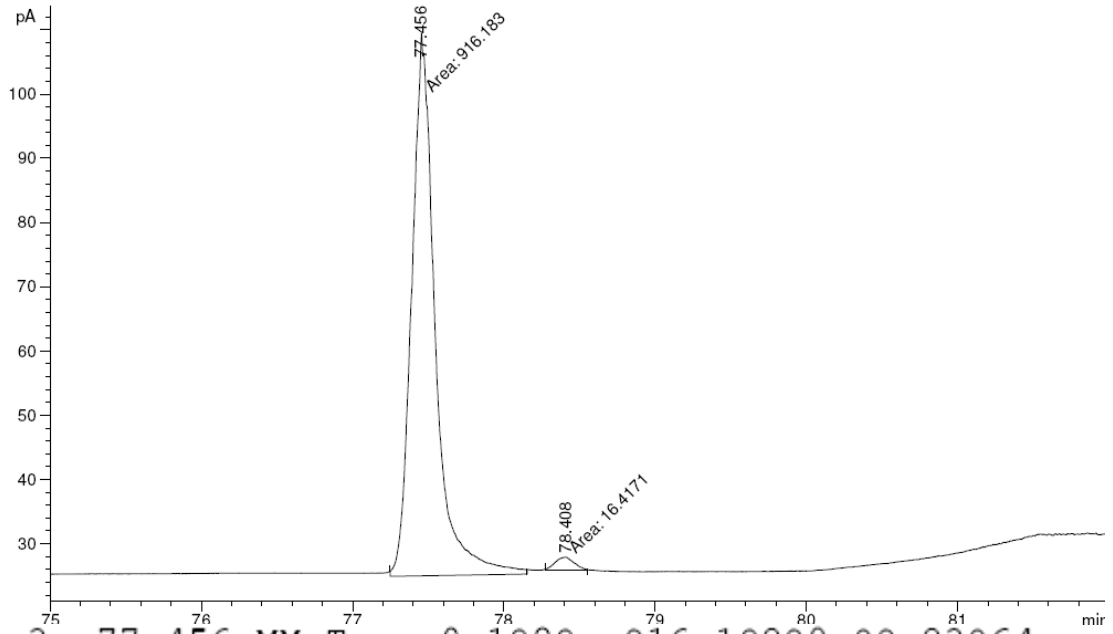


LH561brut
CDCl3, 101 Mhz

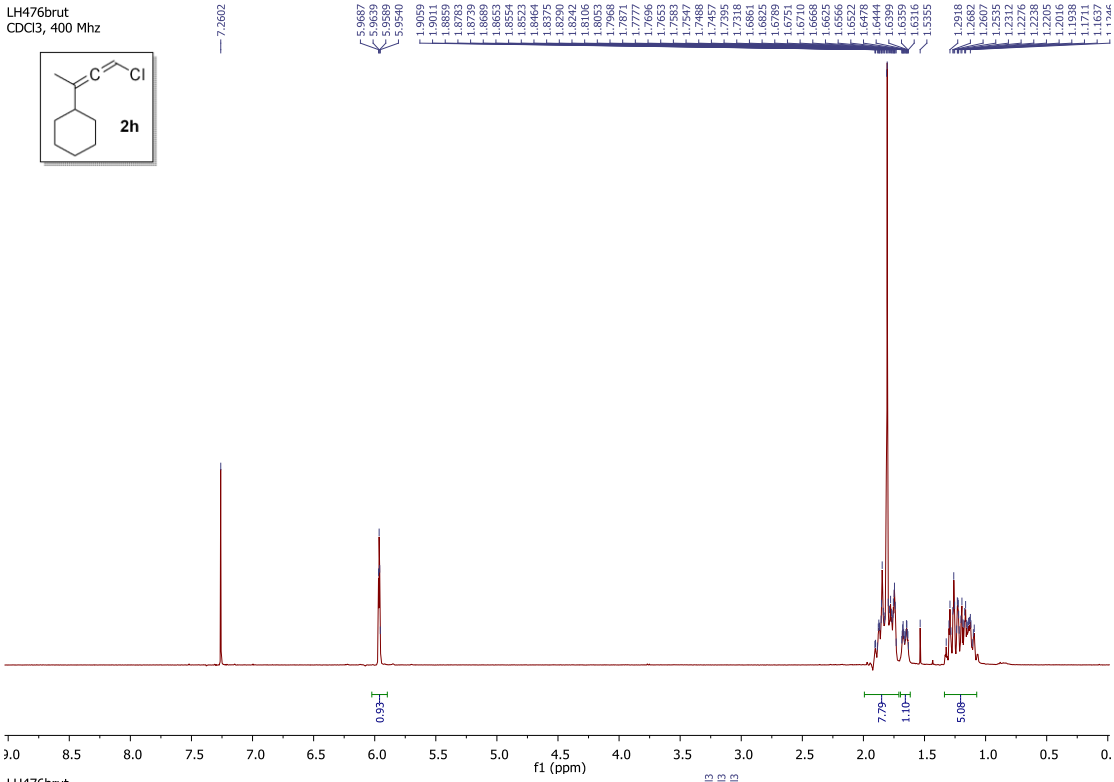




3	77.523	MM	T	0.1754	296.60168	50.94294
4	78.464	MM	T	0.1715	285.62164	49.05706



3	77.456	MM	T	0.1808	916.18280	98.23964
4	78.408	MM	T	0.1406	16.41711	1.76036


LH476brut
CDCl3, 400 Mhz
2h
7.2602
5.9687
5.9639
5.9589
5.9540
1.9059
1.9011
1.8859
1.8783
1.8739
1.8689
1.8653
1.8554
1.8523
1.8464
1.8375
1.8290
1.8242
1.8106
1.8053
1.7968
1.7871
1.7777
1.7696
1.7653
1.7592
1.7547
1.7488
1.7457
1.7395
1.7318
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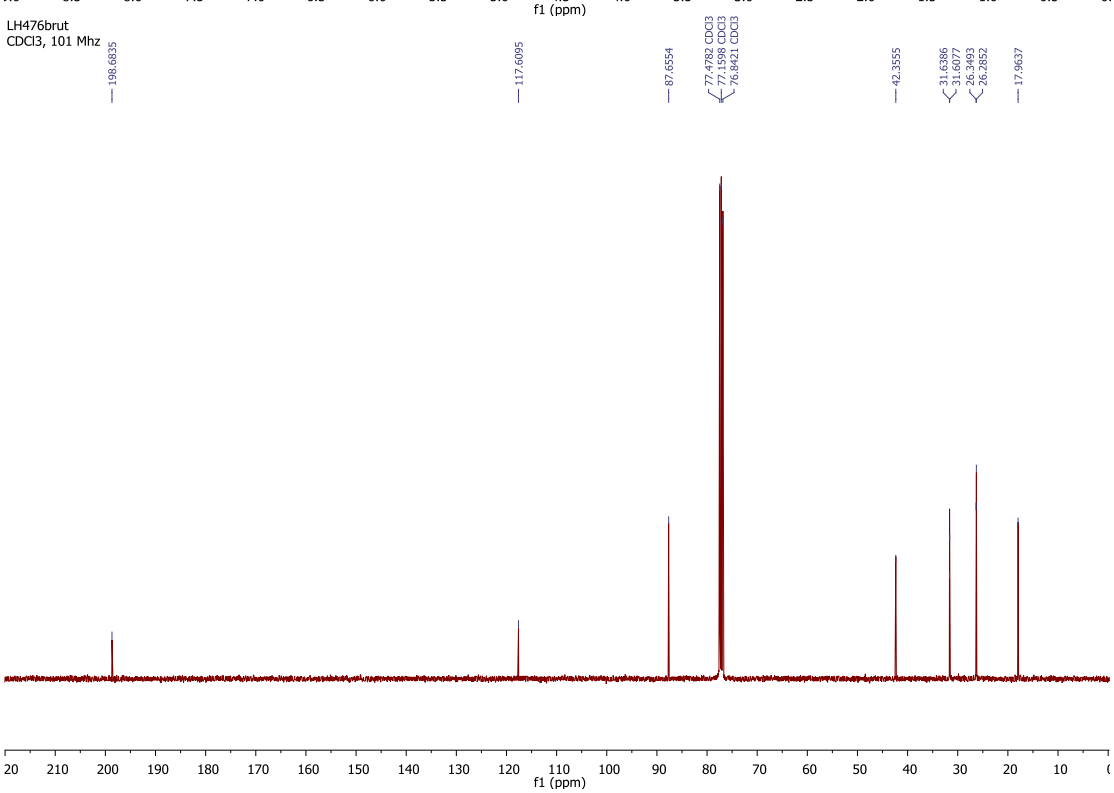
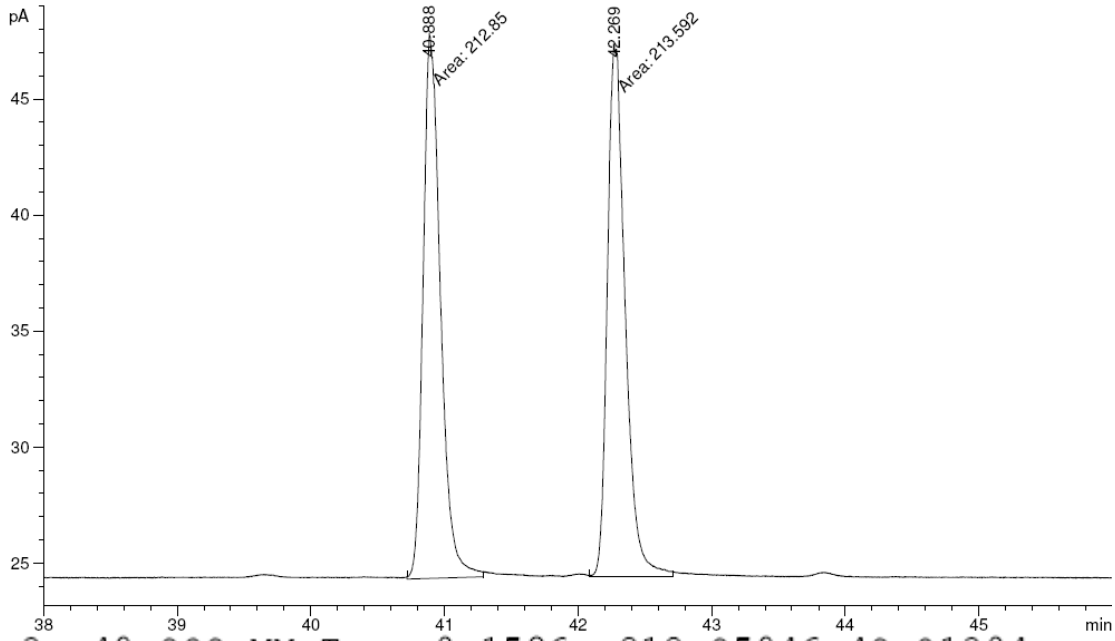
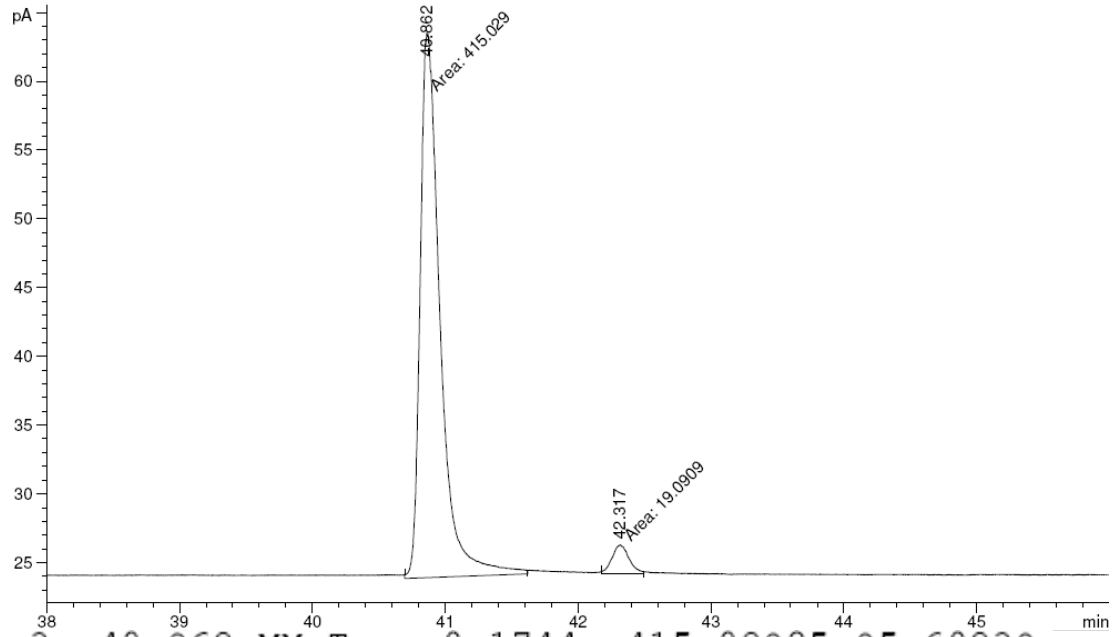
1.6825
1.6789
1.6751
1.6710
1.6668
1.6625
1.6566
1.6522
1.6478
1.6444
1.6399
1.6359
1.6316
1.5355
1.2918
1.2682
1.2607
1.2355
1.2312
1.2276
1.2238
1.2205
1.2016
1.1938
1.1711
1.1637
0.93
7.79
1.10
5.08
f1 (ppm)


LH476brut
CDCl3, 101 Mhz
198.6835
117.6095
87.6554
77.4782 CDCl3
77.1598 CDCl3
76.8421 CDCl3
42.3555
31.6386
31.6077
26.3493
26.2852
17.9637
f1 (ppm)

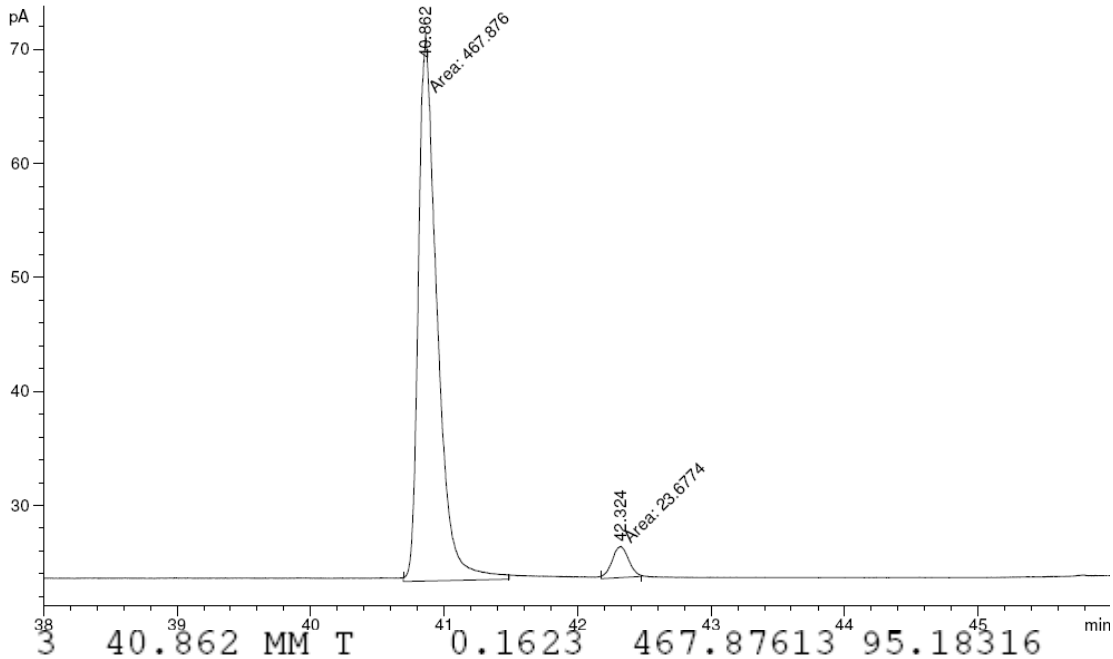


3	40.888	MM	T	0.1506	212.85046	49.91304
4	42.269	MM	T	0.1546	213.59215	50.08696

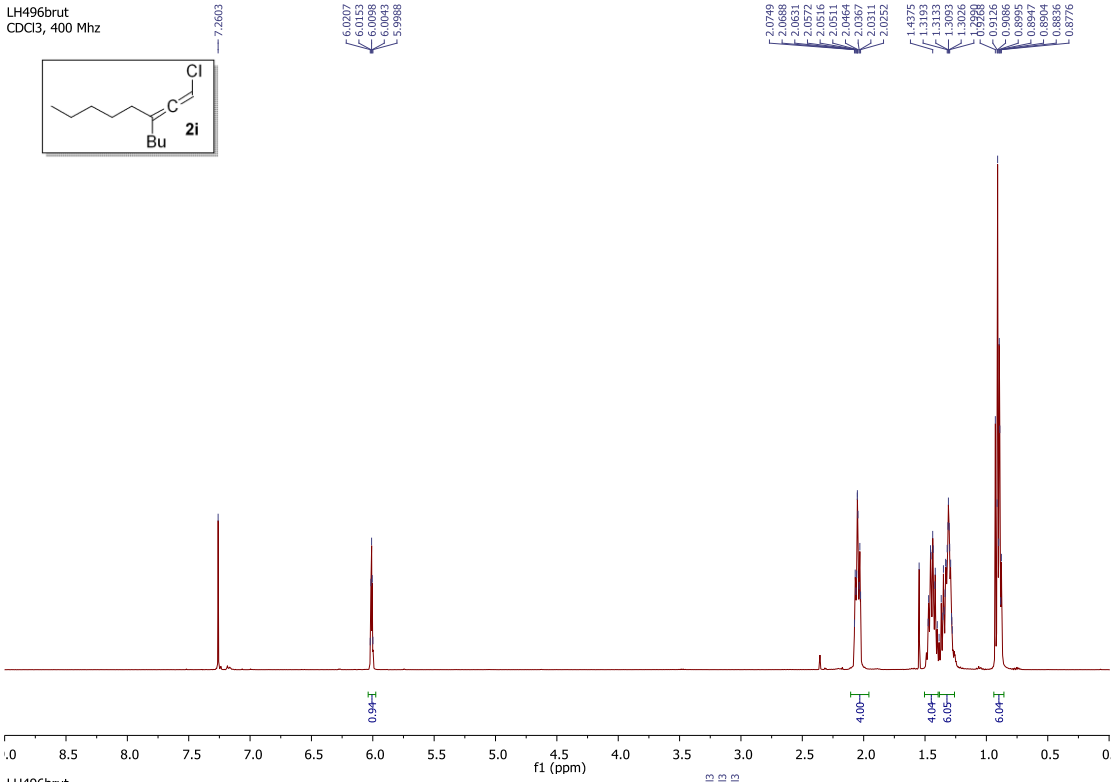


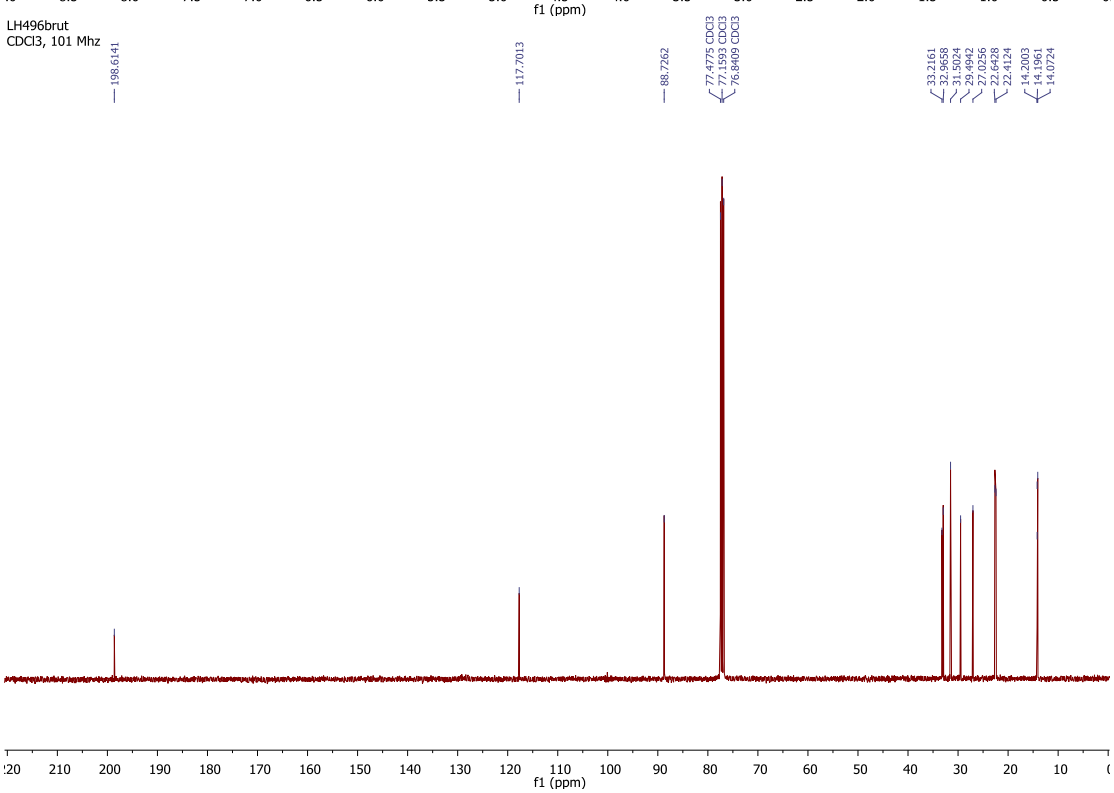
3	40.862	MM	T	0.1744	415.02905	95.60239
4	42.317	MM	T	0.1504	19.09088	4.39761

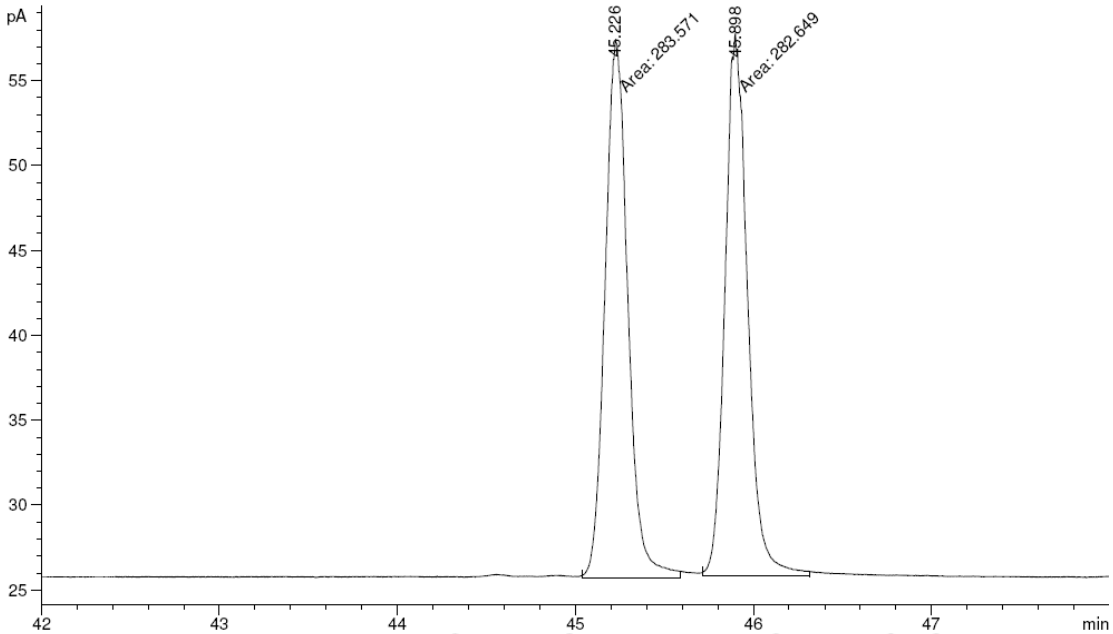
Scale up 2mmol substrate



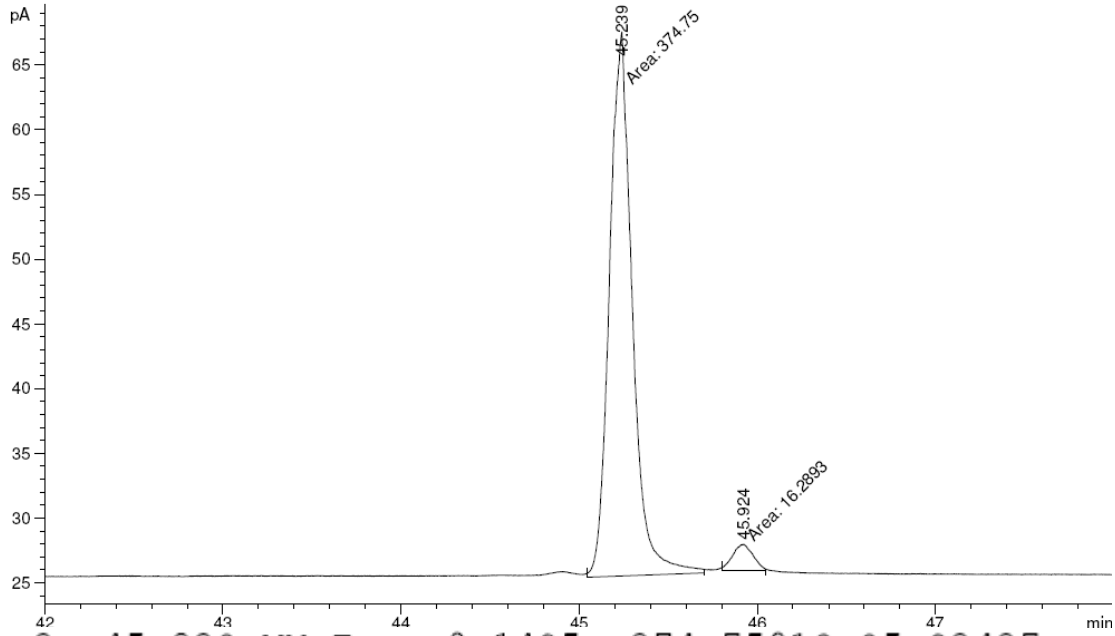
3	40.862	MM	T	0.1623	467.87613	95.18316
4	42.324	MM	T	0.1441	23.67735	4.81684


LH496brut
CDCl3, 400 Mhz
Cl
C
Bu
2i
7.2603
6.0207
6.0153
6.0098
6.0043
5.9988
2.0749
2.0688
2.0631
2.0572
2.0516
2.0511
2.0464
2.0367
2.0311
2.0252
1.4375
1.3193
1.3133
1.3093
1.3026
0.9126
0.9086
0.8995
0.8947
0.8904
0.8836
0.8776
0.94
4.00
4.04
6.05
6.04
f1 (ppm)

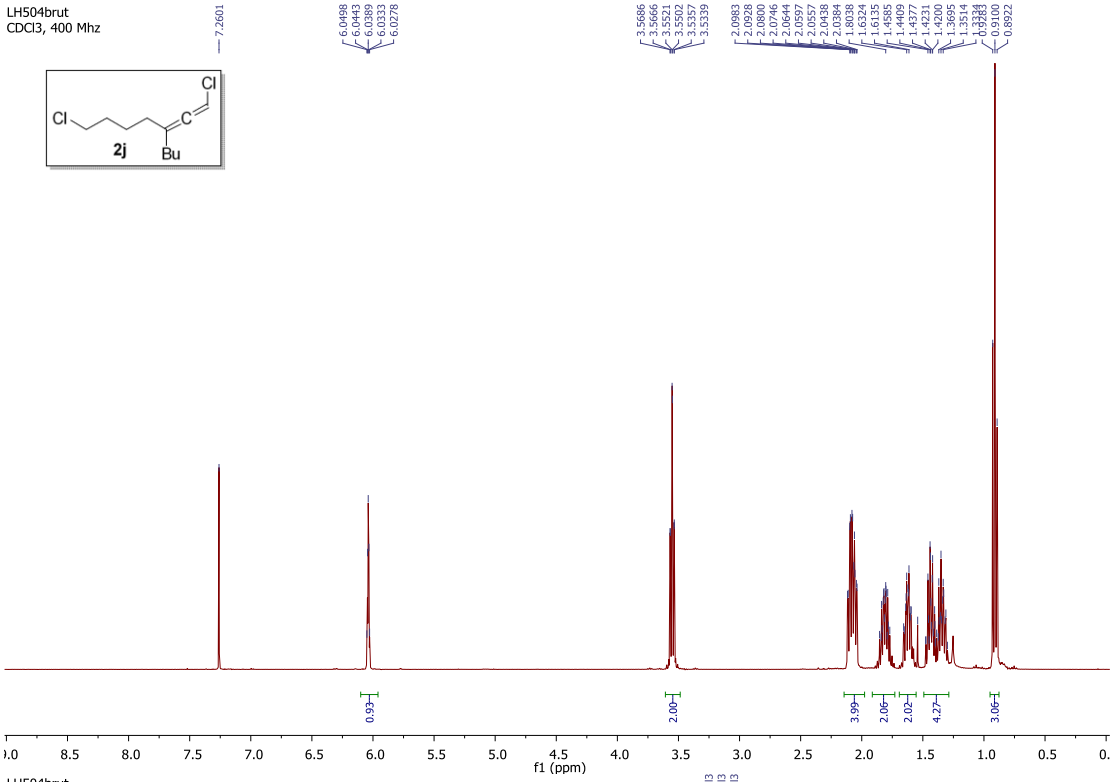

LH496brut
CDCl3, 101 Mhz
198.6141
117.7013
88.7262
77.4775 CDCl3
77.1593 CDCl3
76.8409 CDCl3
33.2161
32.9658
31.5024
29.4942
27.0455
22.6428
22.4124
14.2003
14.1951
14.0724
f1 (ppm)

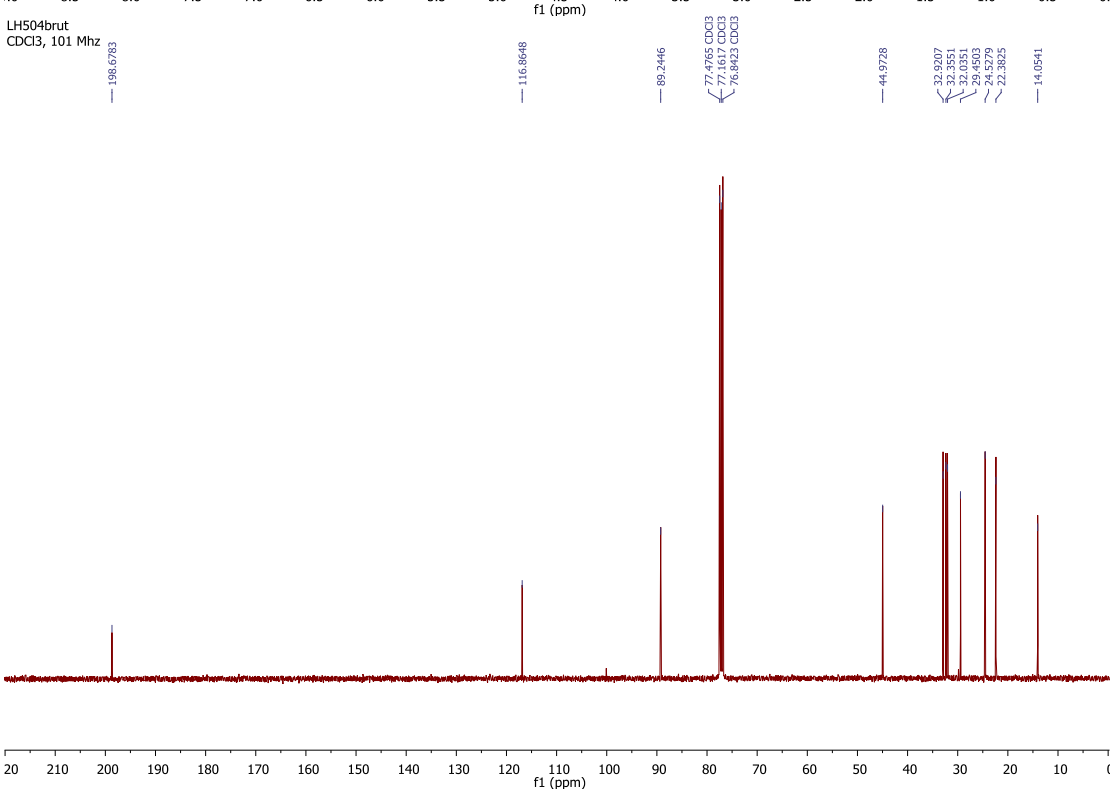


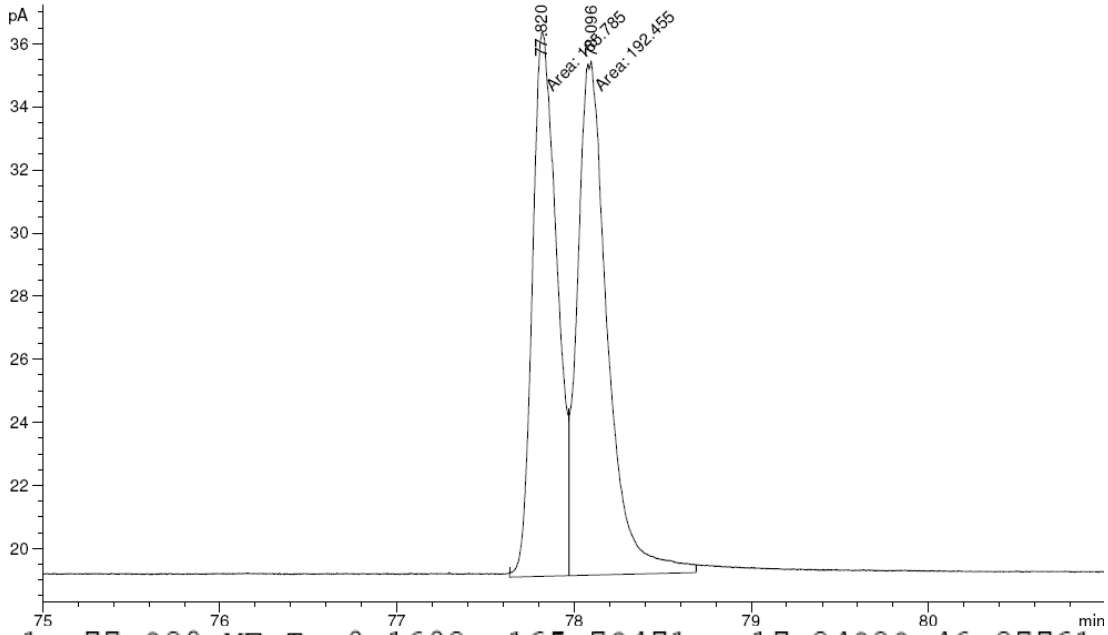
3	45.226	MM	T	0.1490	283.57059	50.08137
4	45.898	MM	T	0.1472	282.64914	49.91863



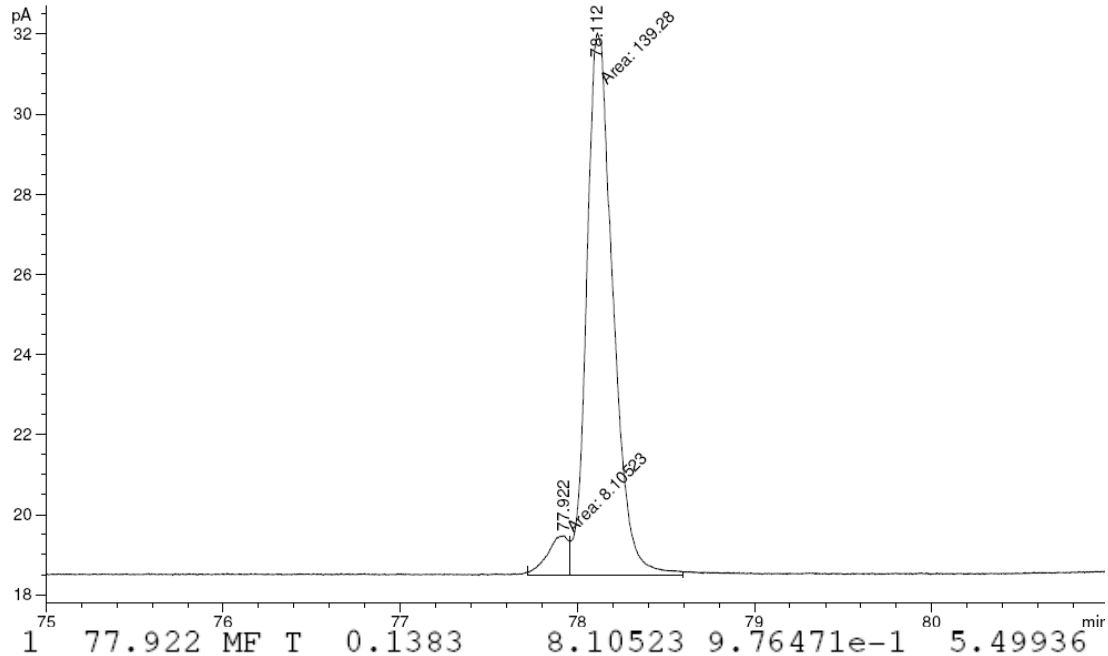
3	45.239	MM	T	0.1485	374.75018	95.83437
4	45.924	MM	T	0.1333	16.28926	4.16563


LH504brut
CDCl3, 400 Mhz
7.2601
6.0498
6.0443
6.0389
6.0333
6.0278
3.5686
3.5666
3.5521
3.5502
3.5357
3.5339
2.0983
2.0928
2.0800
2.0746
2.0644
2.0597
2.0557
2.0438
2.0384
1.8038
1.6324
1.6135
1.4585
1.4469
1.4377
1.4321
1.4200
1.3695
1.3514
1.3334
1.3284
0.9100
0.8922
Cl
Cl
C
2j
Bu
0.93
2.00
3.99
2.06
2.02
4.27
3.06
f1 (ppm)

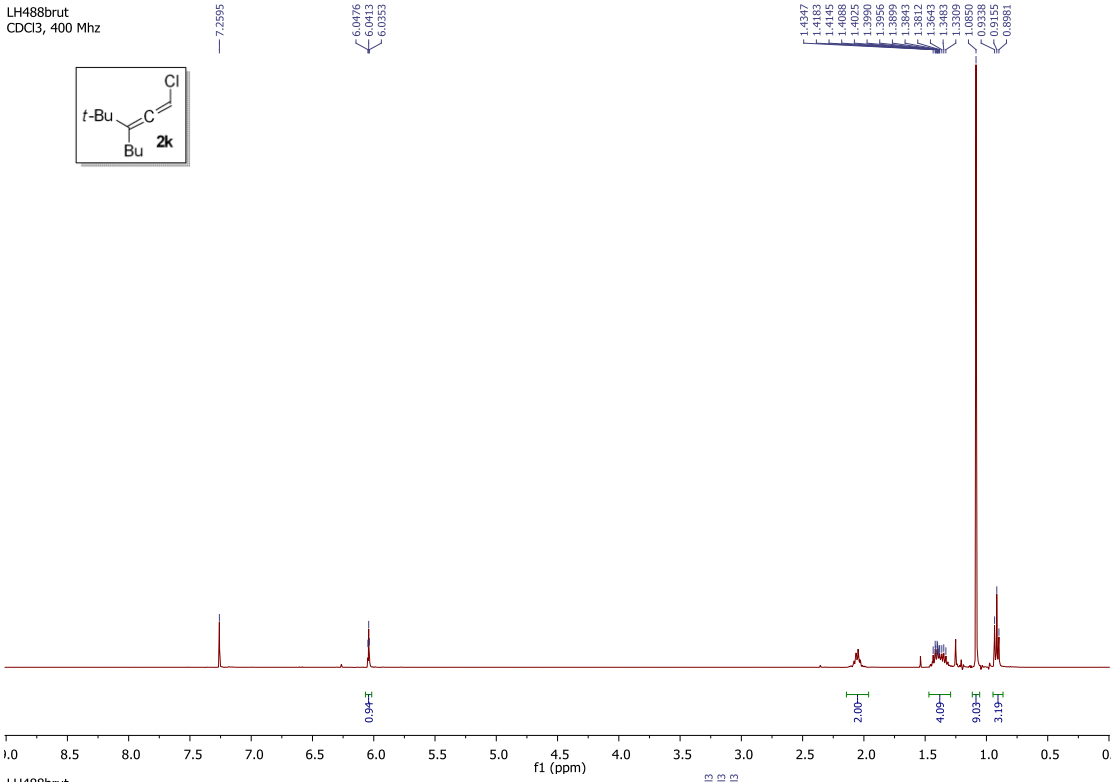

LH504brut
CDCl3, 101 Mhz
198.6783
116.8648
89.2446
77.4765 CDCl3
77.1617 CDCl3
76.8423 CDCl3
44.9728
32.9207
32.3551
32.0351
29.4503
24.5279
22.3825
14.0541
f1 (ppm)

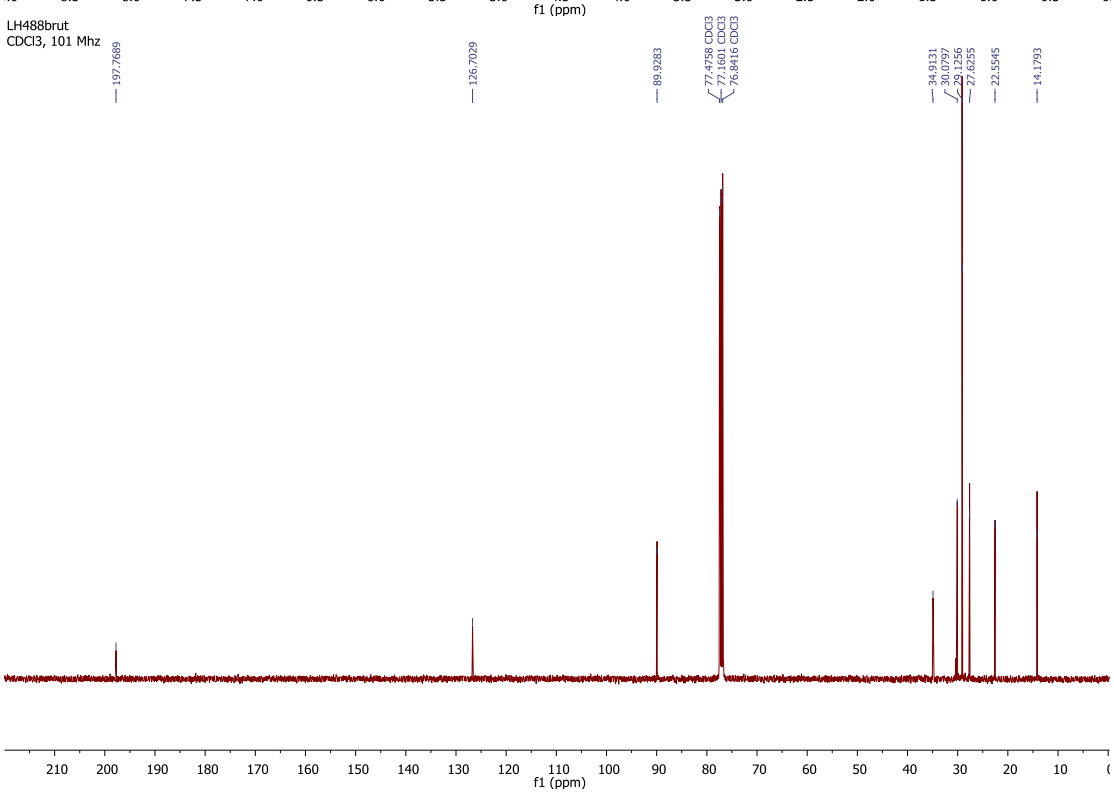


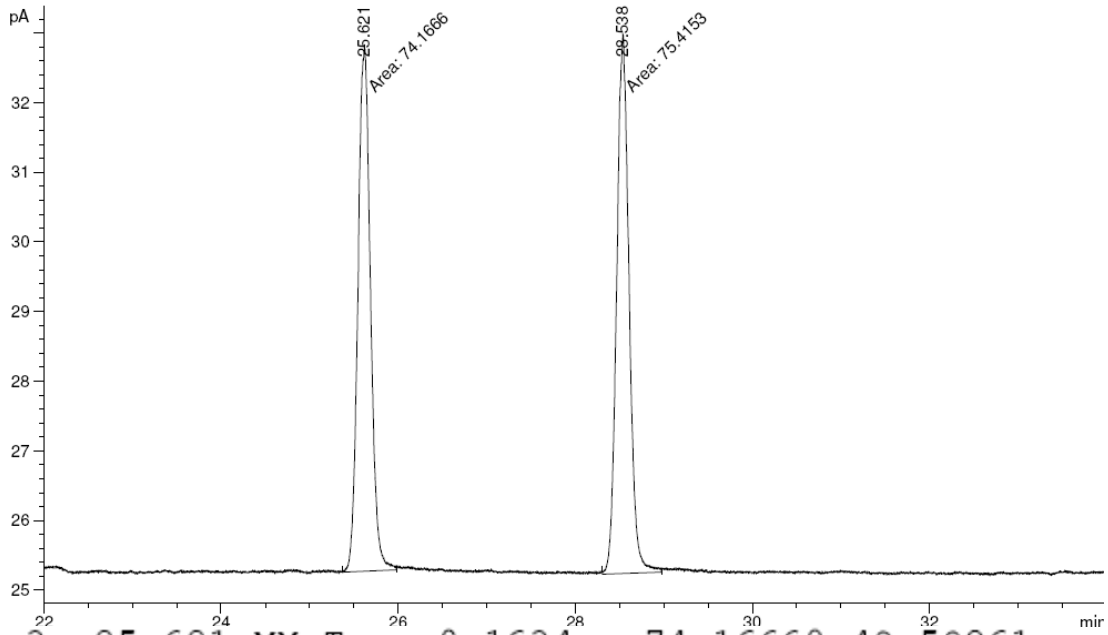
1	77.820	MF	T	0.1602	165.78471	17.24839	46.27761
2	78.096	FM	T	0.1965	192.45490	16.32036	53.72239



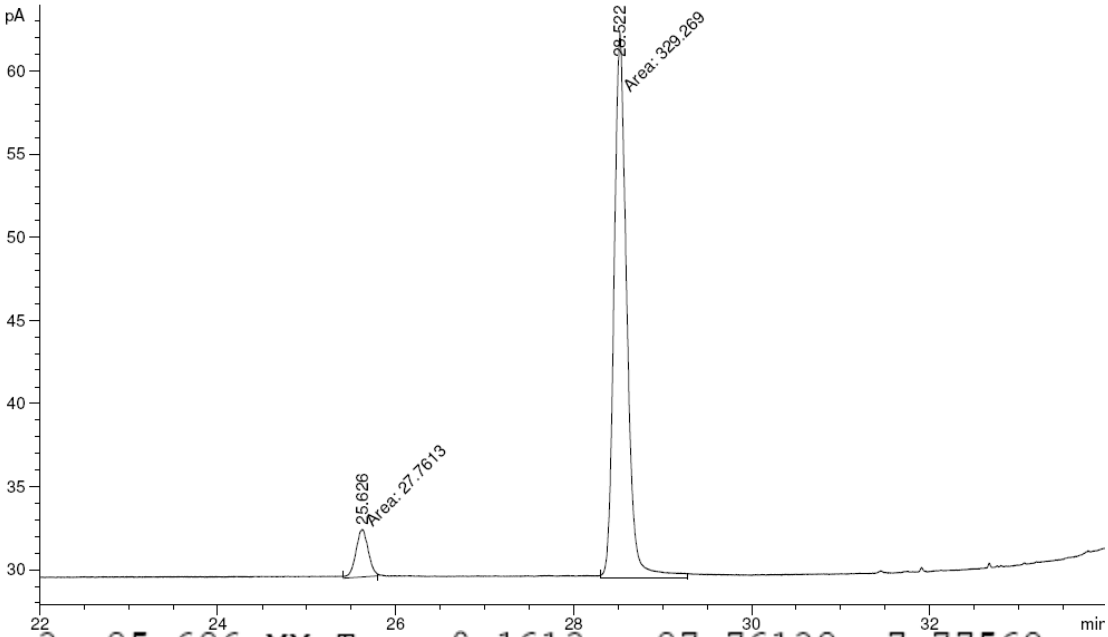
1	77.922	MF	T	0.1383	8.10523	9.76471e-1	5.49936
2	78.112	FM	T	0.1718	139.27986	13.51426	94.50064


LH488brut
CDCl3, 400 Mhz
7.2595
6.0476
6.0413
6.0353
1.4347
1.4183
1.4145
1.4098
1.4025
1.3990
1.3956
1.3899
1.3843
1.3812
1.3643
1.3483
1.3309
1.0850
0.9238
0.9155
0.8981
Cl
t-Bu
C
Bu
2k
0.94
2.00
4.09
9.03
3.19
f1 (ppm)

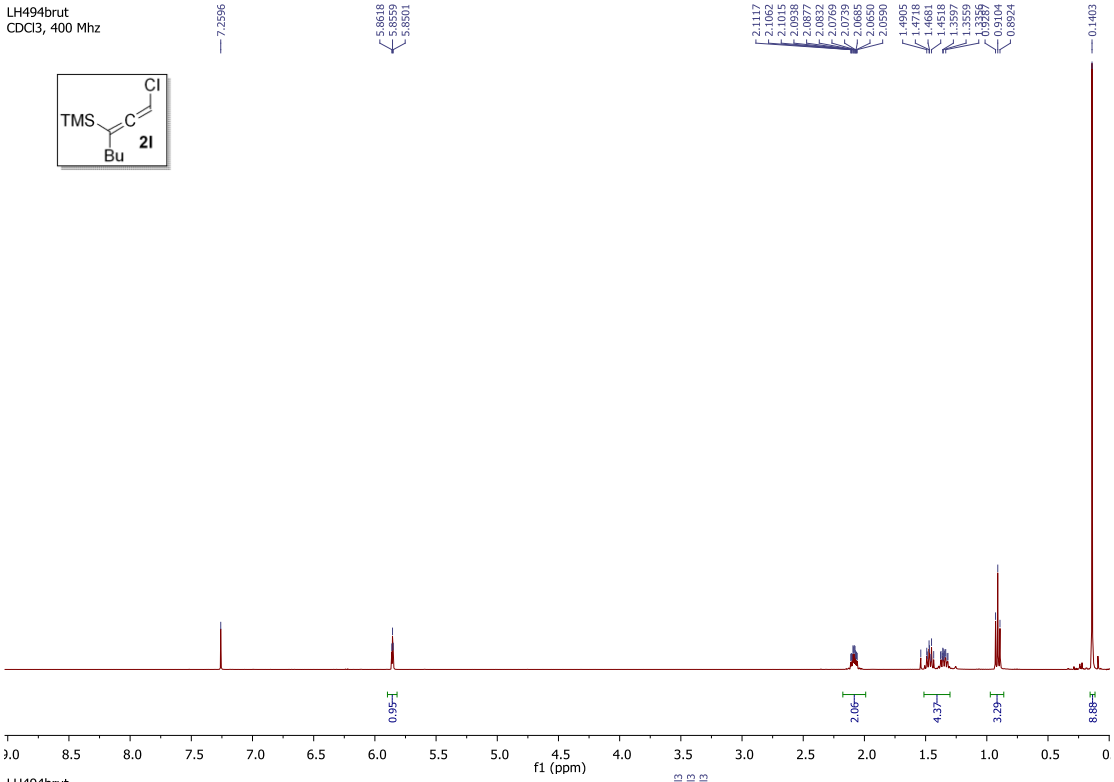

LH488brut
CDCl3, 101 Mhz
197.7689
126.7029
89.9283
77.4758 CDCl3
77.1601 CDCl3
76.8416 CDCl3
34.9131
30.0797
29.1256
27.6255
22.5545
14.1793
f1 (ppm)

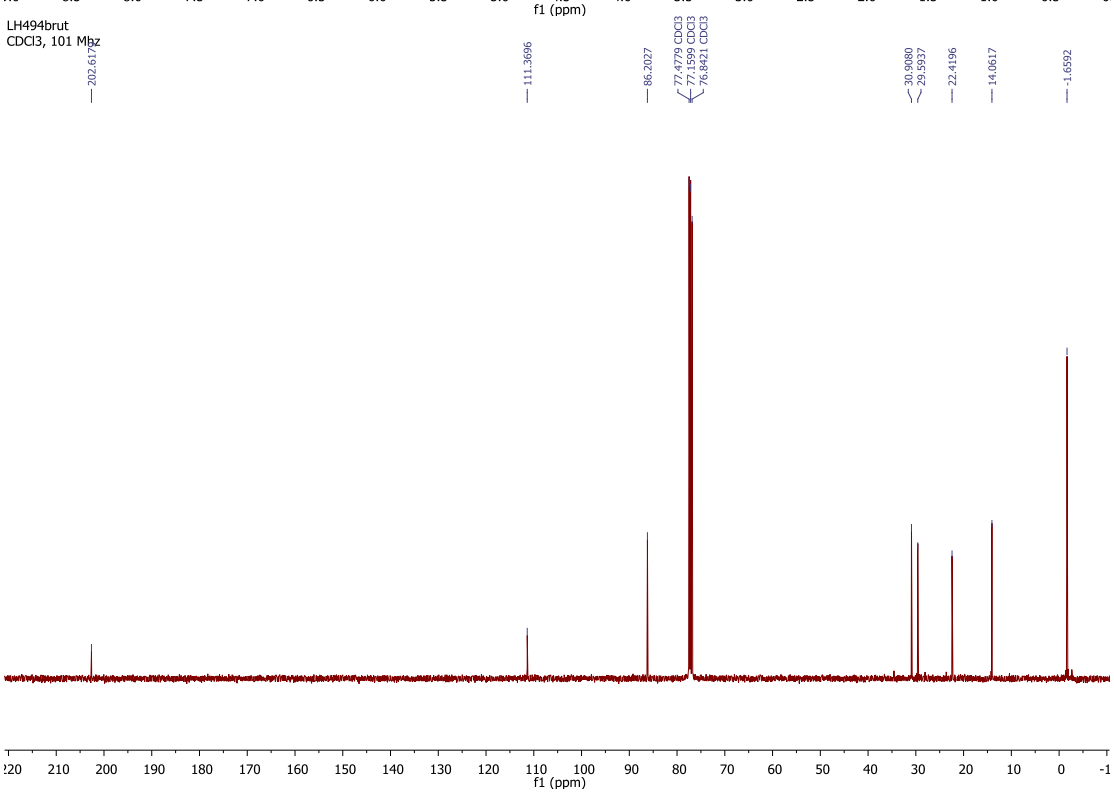


3	25.621	MM	T	0.1634	74.16660	49.58261
4	28.538	MM	T	0.1623	75.41527	50.41739



3	25.626	MM	T	0.1613	27.76132	7.77562
4	28.522	MM	T	0.1673	329.26901	92.22438


LH494brut
CDCl3, 400 Mhz
TMS
Cl
Bu
2l
7.2596
5.8618
5.8559
5.8501
2.1117
2.1062
2.1015
2.0938
2.0877
2.0832
2.0769
2.0739
2.0685
2.0650
2.0590
1.4905
1.4718
1.4681
1.4518
1.3597
1.3559
1.3356
0.9289
0.9104
0.8924
0.1403
0.95
2.06
4.37
3.29
8.88
f1 (ppm)


LH494brut
CDCl3, 101 Mhz
202.6175
111.3696
86.2027
77.4779 CDCl3
77.1599 CDCl3
76.8421 CDCl3
30.9080
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22.4196
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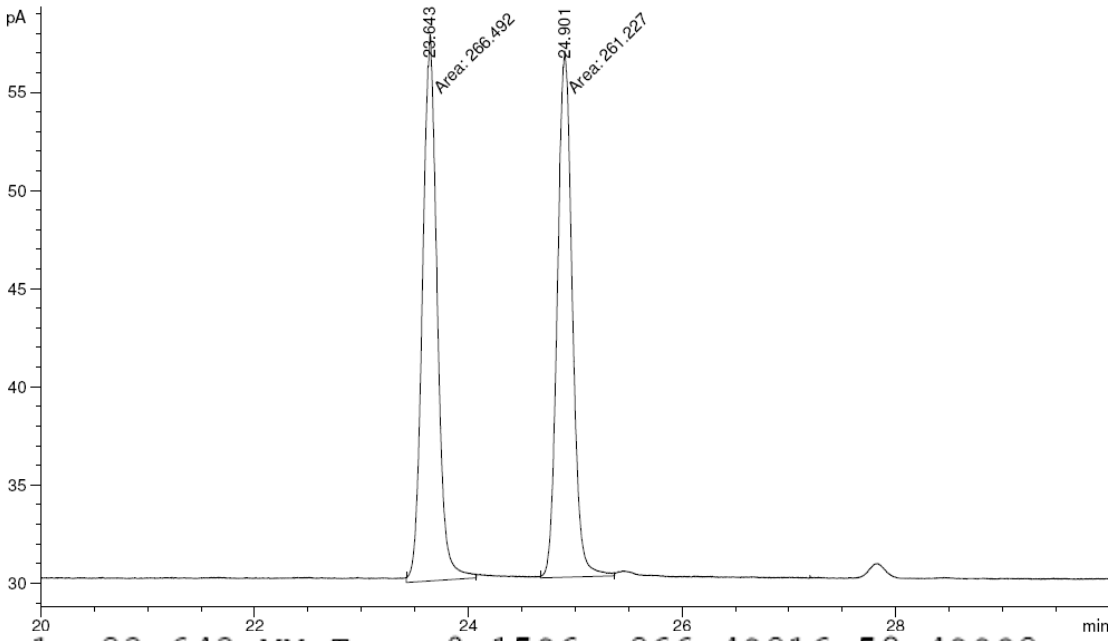
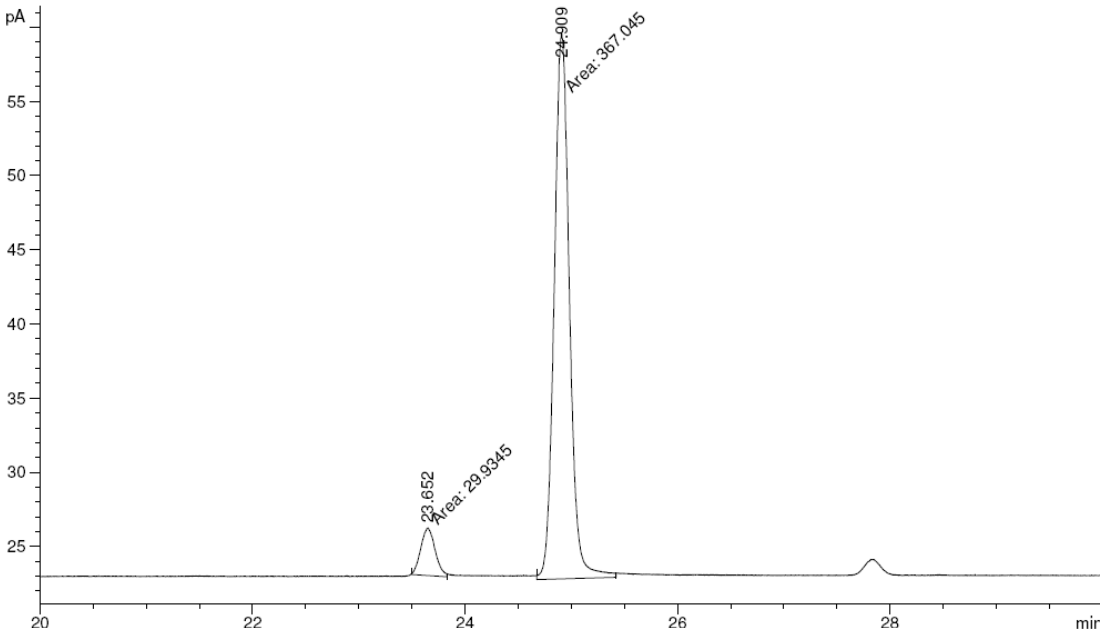
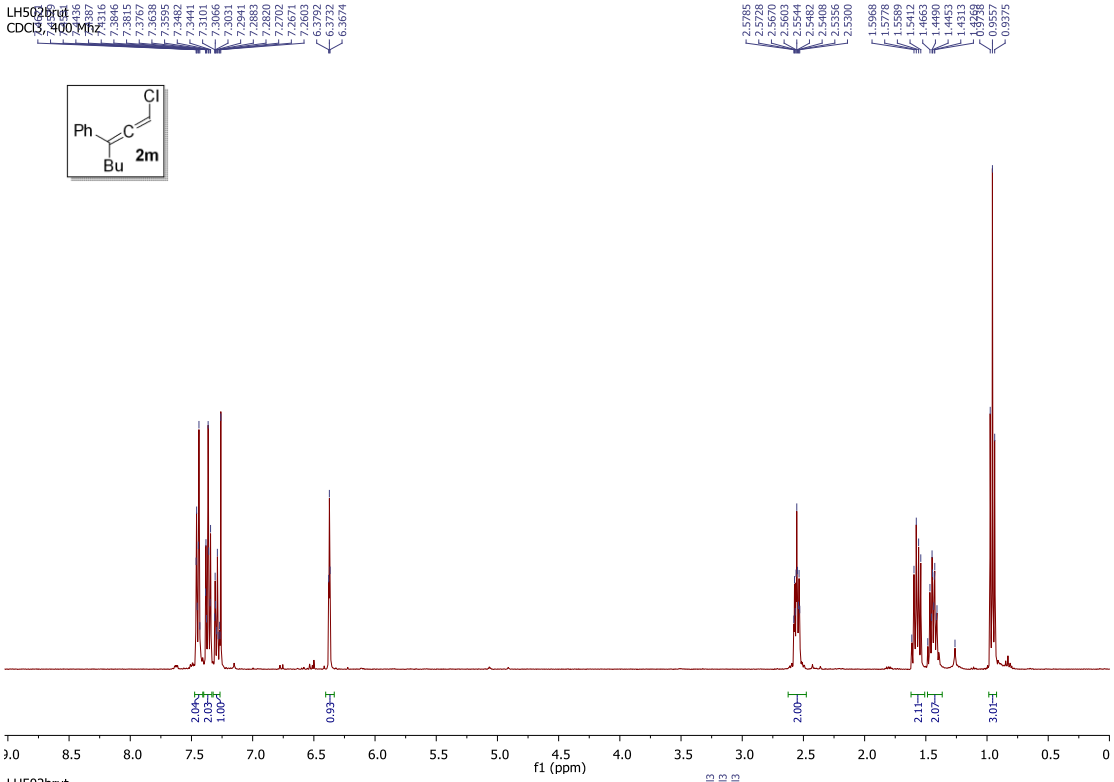
-1.6592
f1 (ppm)

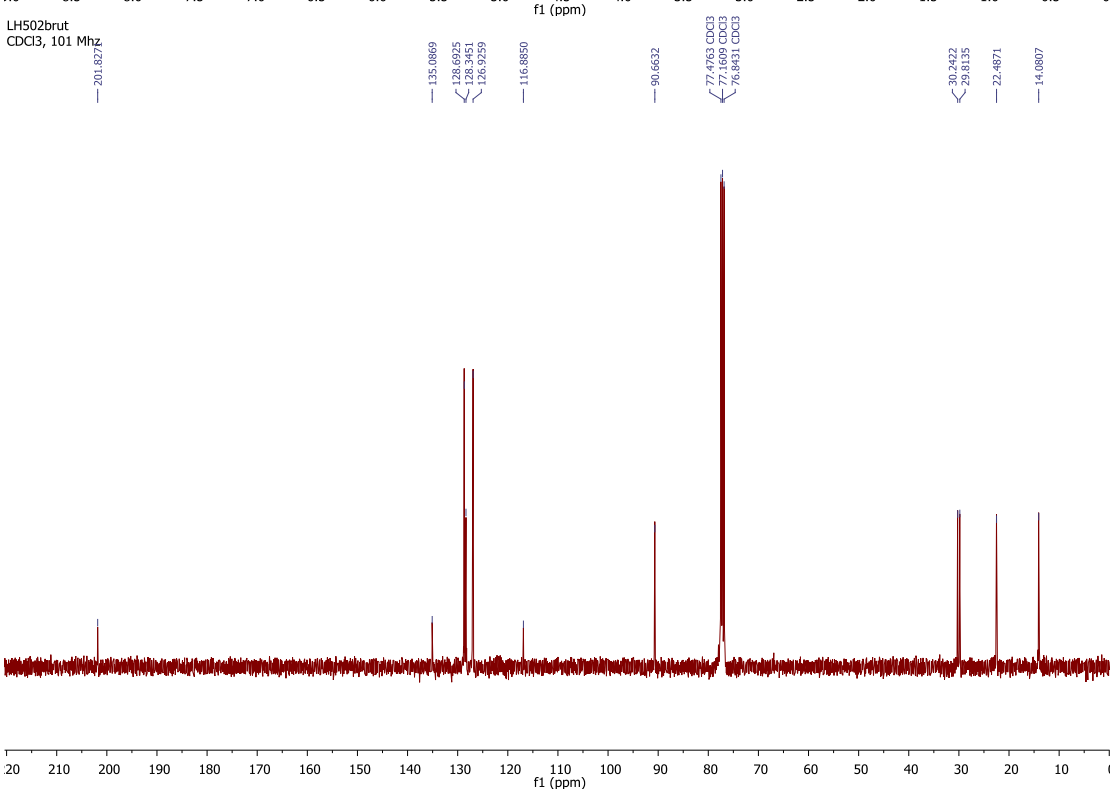


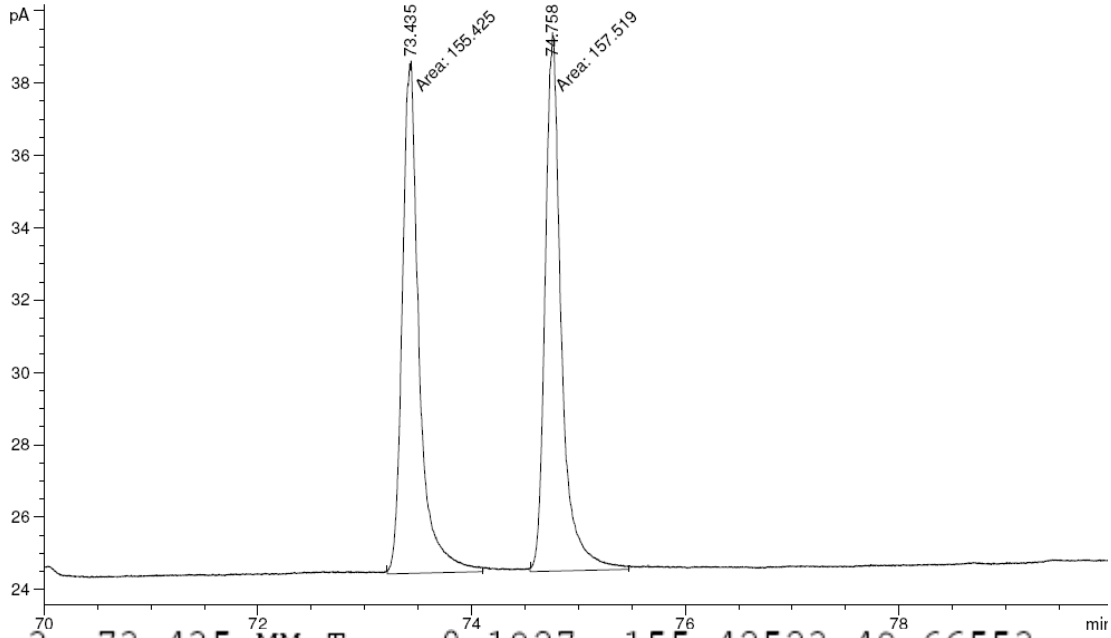
1	23.643	MM	T	0.1596	266.49216	50.49882
3	24.901	MM	T	0.1623	261.22739	49.50118



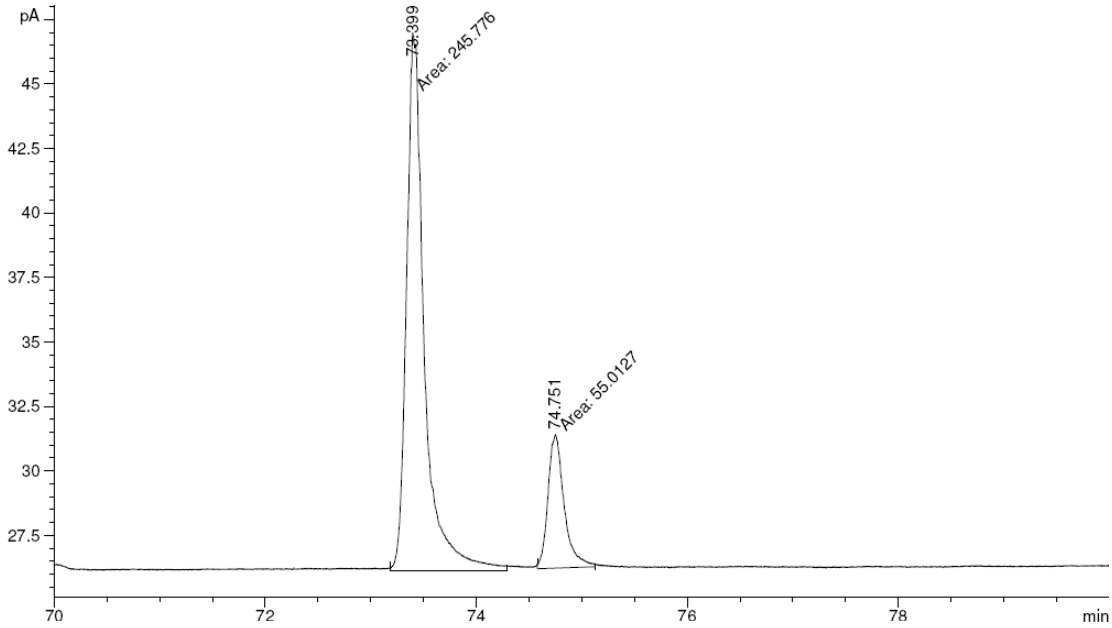
1	23.652	MM	T	0.1551	29.93448	7.54057
3	24.909	MM	T	0.1664	367.04468	92.45943


LH502brut
CDCl3, 400 Mhz
Ph
Cl
C
Bu
2m
f1 (ppm)

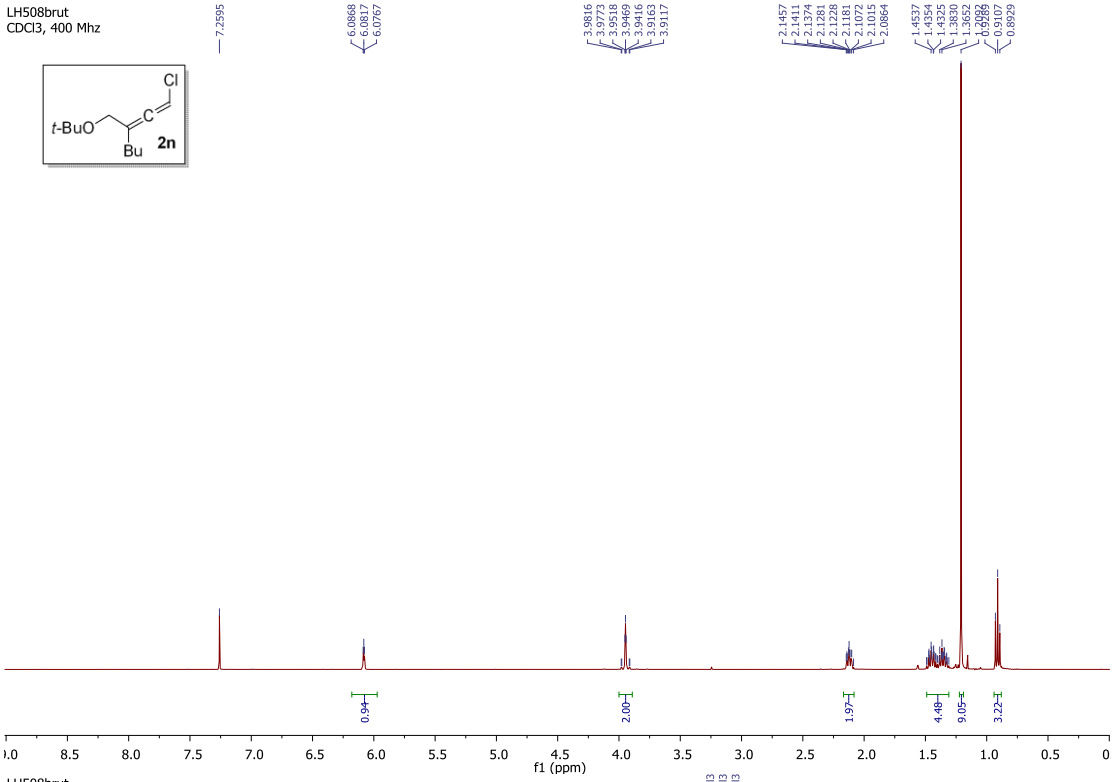

LH502brut
CDCl3, 101 Mhz
201.8277
135.0869
128.6925
128.3451
126.9259
116.8850
90.6632
77.4763 CDCl3
77.1609 CDCl3
76.8431 CDCl3
30.2422
29.8135
22.4871
14.0807
f1 (ppm)

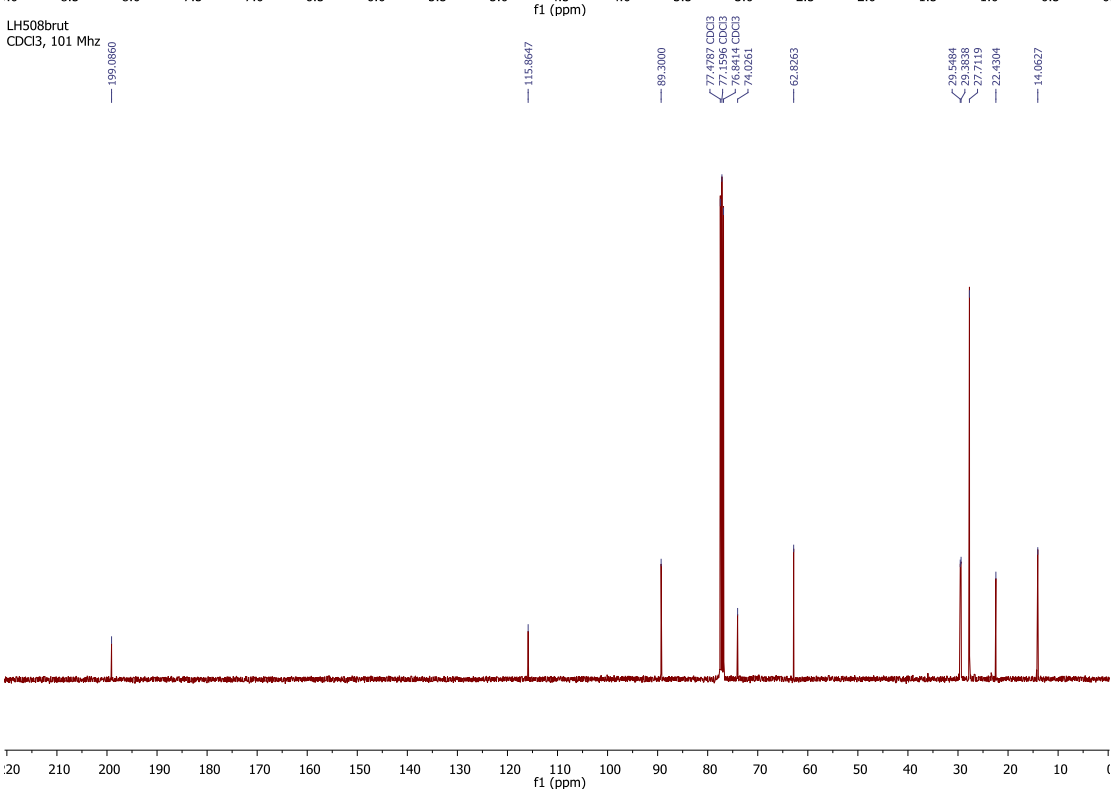


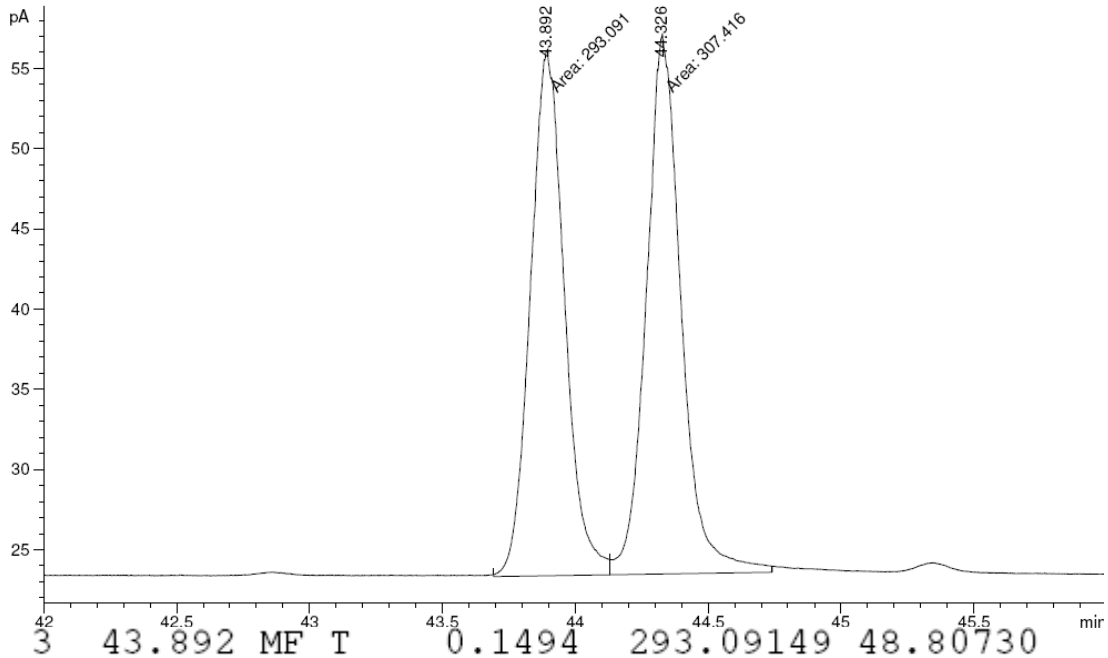
3	73.435	MM	T	0.1827	155.42523	49.66553
4	74.758	MM	T	0.1761	157.51863	50.33447



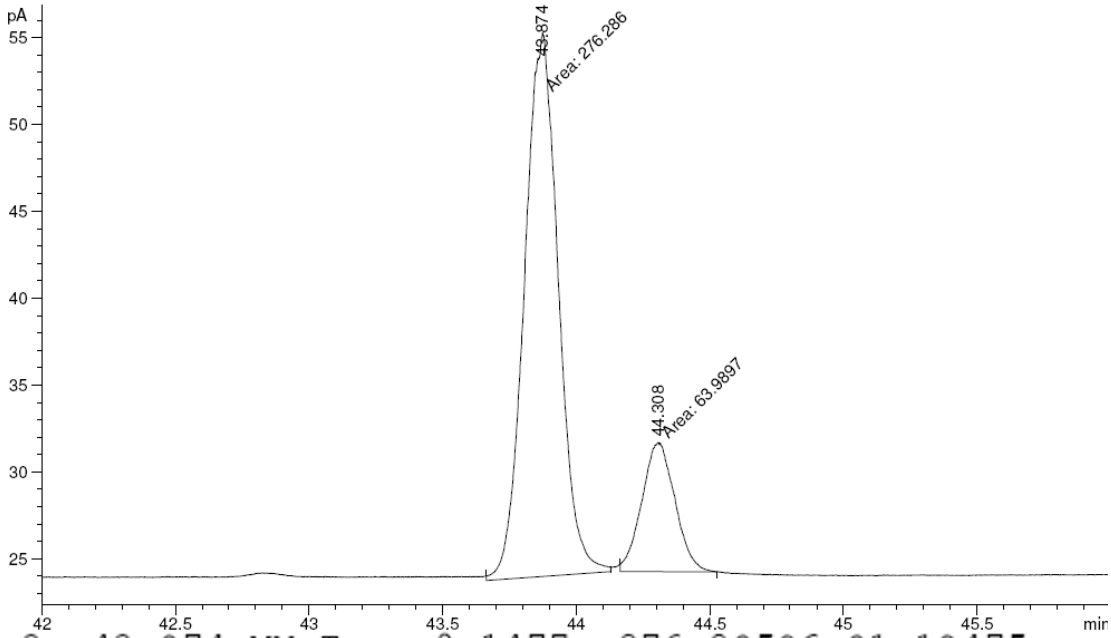
3	73.399	MM	T	0.1962	245.77557	81.71050
4	74.751	MM	T	0.1769	55.01265	18.28950


LH508brut
CDCl3, 400 Mhz
t-BuO
Cl
C
Bu
2n
7.2595
6.0868
6.0817
6.0767
3.9816
3.9773
3.9518
3.9469
3.9416
3.9163
3.9117
2.1457
2.1411
2.1374
2.1281
2.1228
2.1181
2.1072
2.1015
2.0864
1.4537
1.4354
1.4325
1.3920
1.3652
1.2089
0.9289
0.9107
0.8929
0.94
2.00
1.97
4.48
9.05
3.22
f1 (ppm)

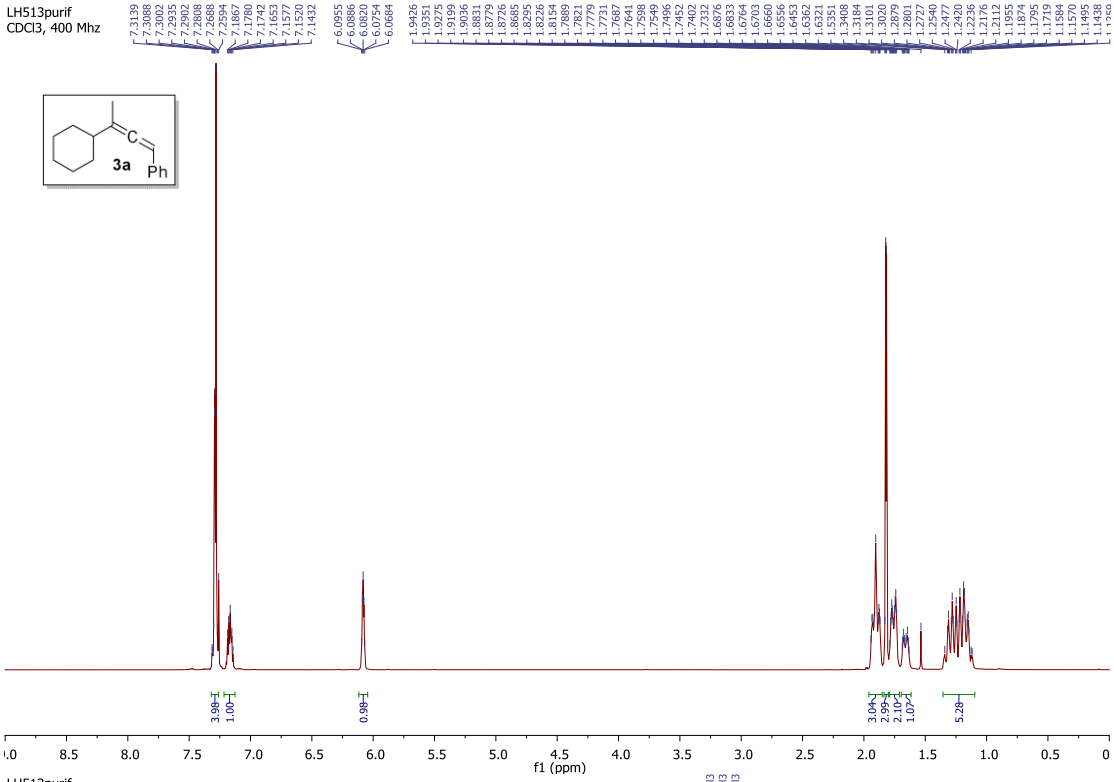

LH508brut
CDCl3, 101 Mhz
199.0860
115.8647
89.3000
77.4787 CDCl3
77.1596 CDCl3
76.8414 CDCl3
74.0261
62.8263
29.5484
29.3838
27.7119
22.4304
14.0627
f1 (ppm)

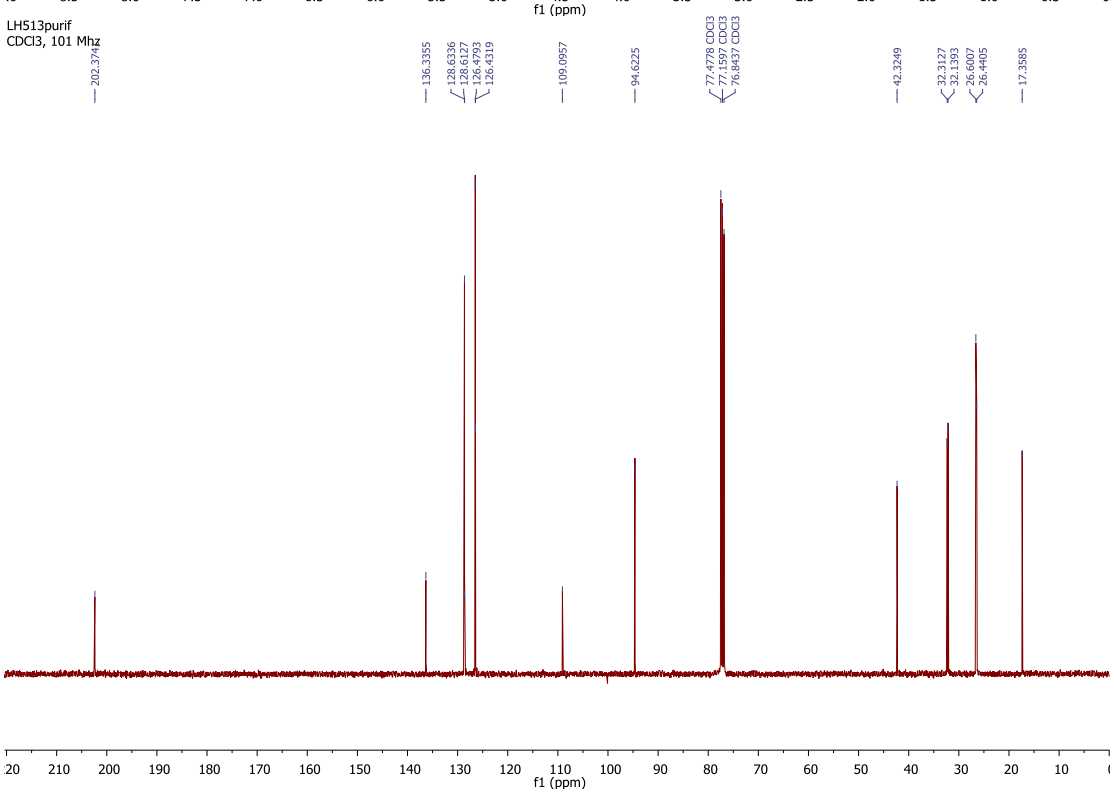


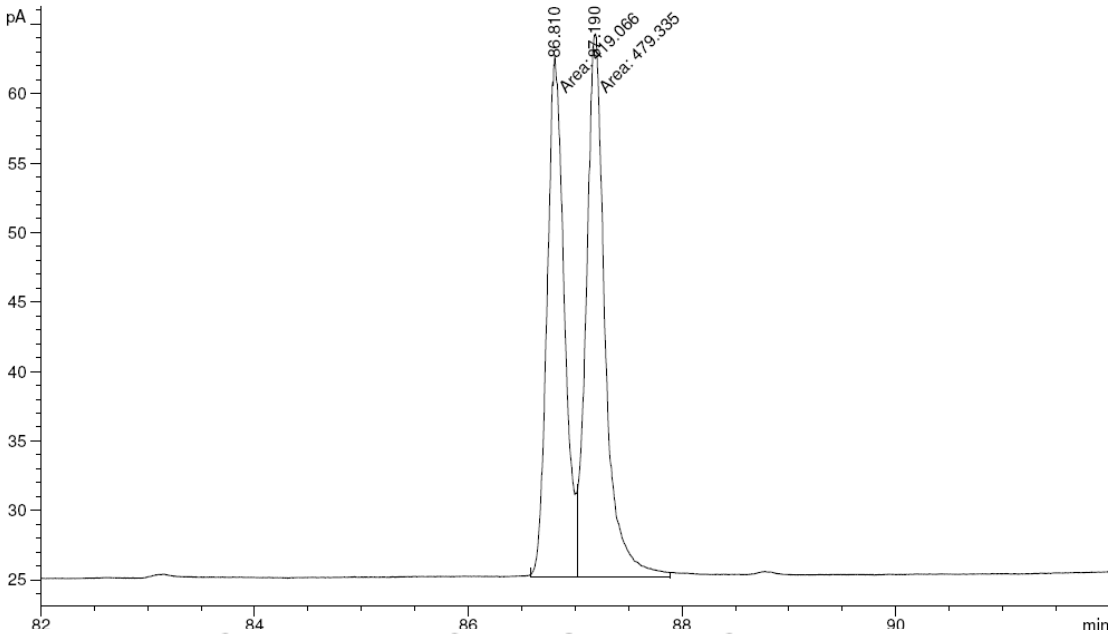
3	43.892	MF	T	0.1494	293.09149	48.80730
4	44.326	FM	T	0.1529	307.41605	51.19270



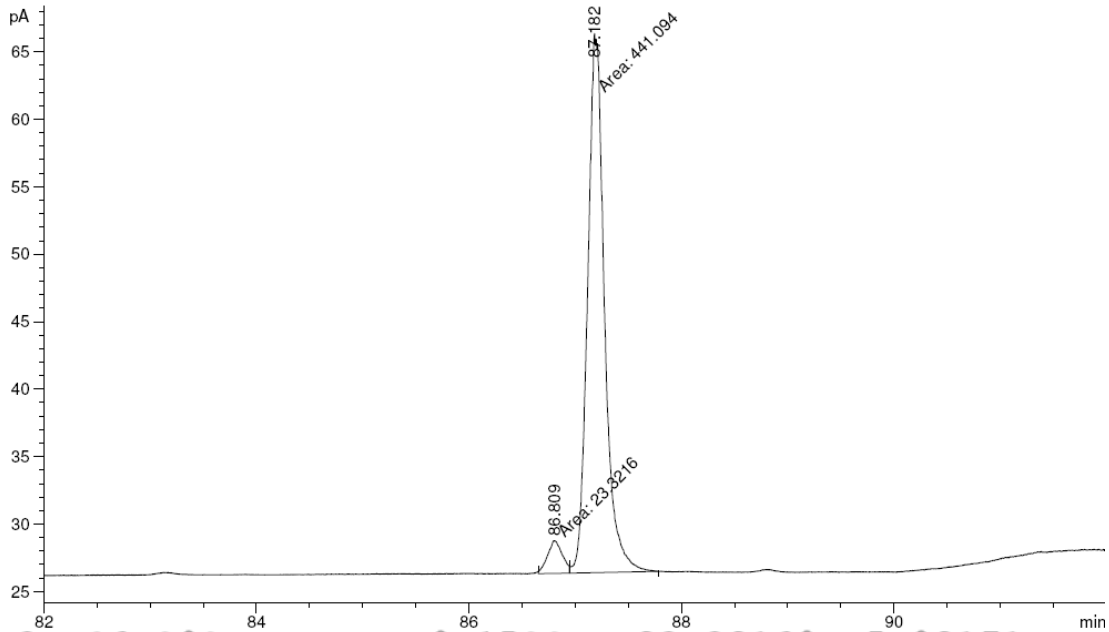
3	43.874	MM	T	0.1477	276.28586	81.19475
4	44.308	MM	T	0.1431	63.98967	18.80525


LH513purif
CDCl3, 400 Mhz
3a
Ph
f1 (ppm)

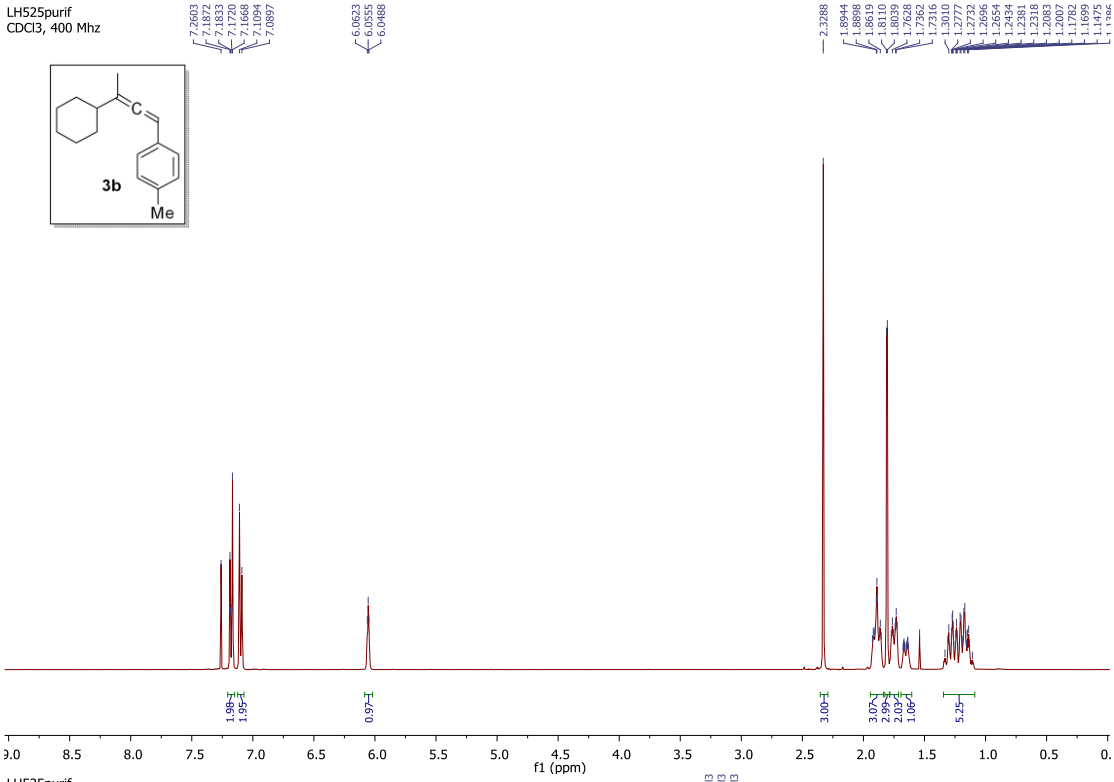

LH513purif
CDCl3, 101 Mhz
202.3741
136.3355
128.6336
126.5727
126.4793
126.4319
109.0957
94.6225
77.4778 CDCl3
77.1597 CDCl3
76.8437 CDCl3
42.3249
32.3127
32.1393
26.6007
26.4405
17.3585
f1 (ppm)

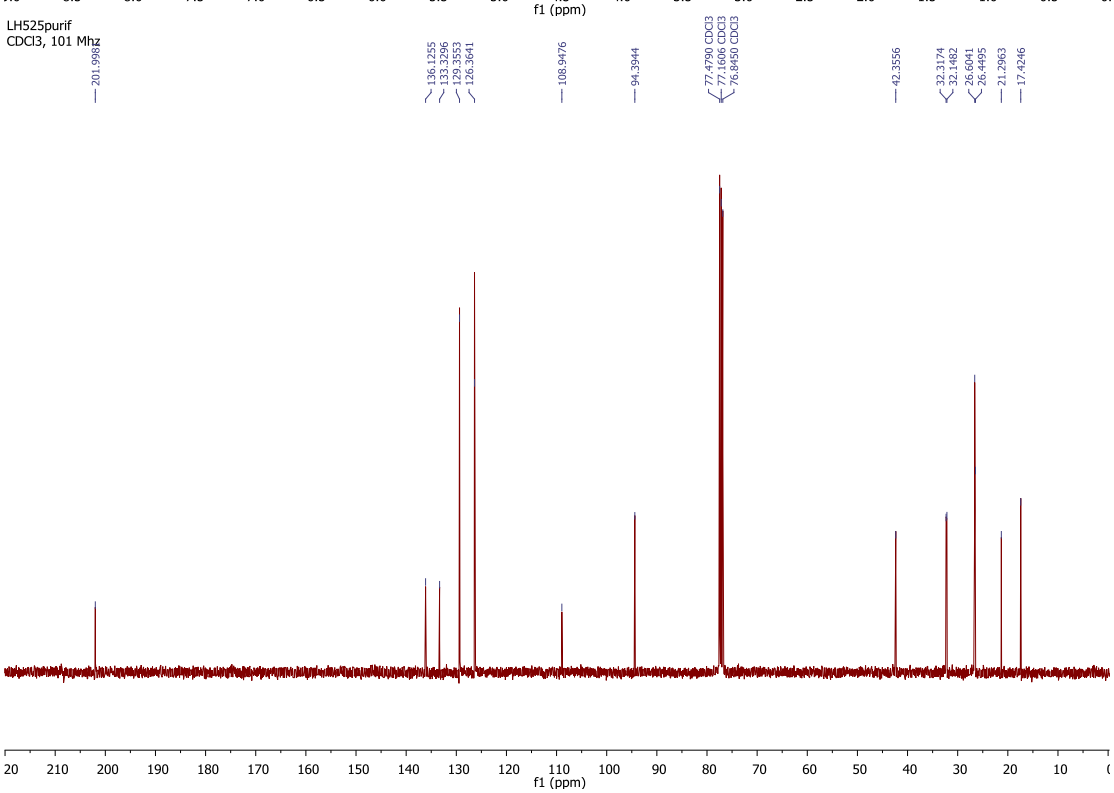


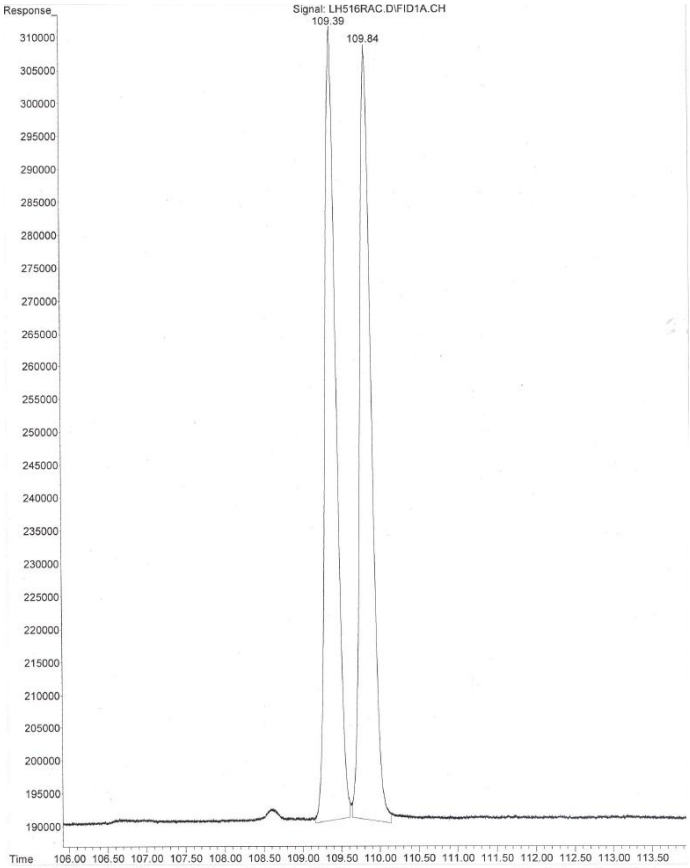
3	86.810	MF	T	0.1860	419.06589	46.64573
4	87.190	FM	T	0.2042	479.33545	53.35427



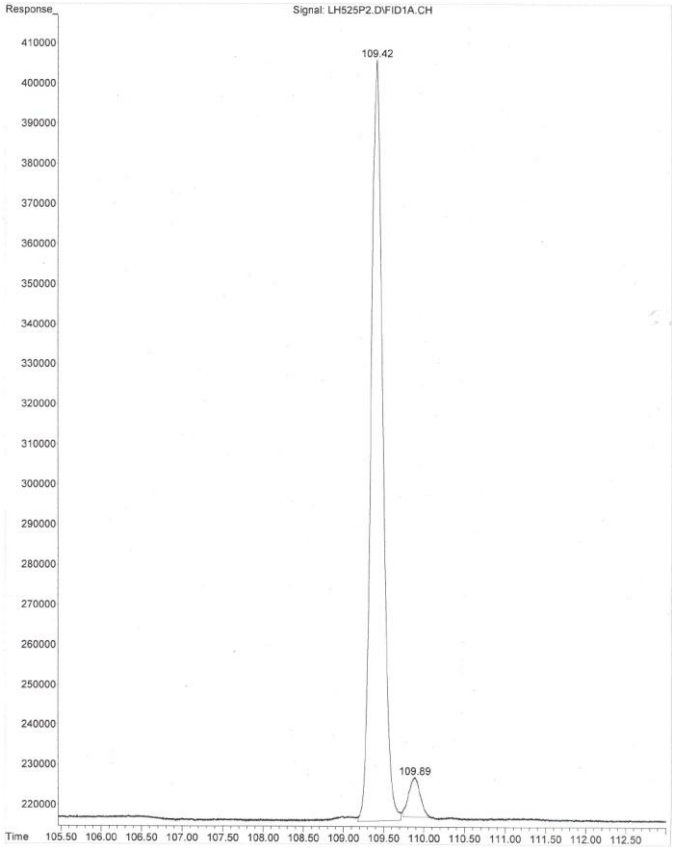
3	86.809	MF	T	0.1599	23.32160	5.02171
4	87.182	FM	T	0.1842	441.09412	94.97829


LH525purif
CDCl3, 400 Mhz
3b
Me
f1 (ppm)

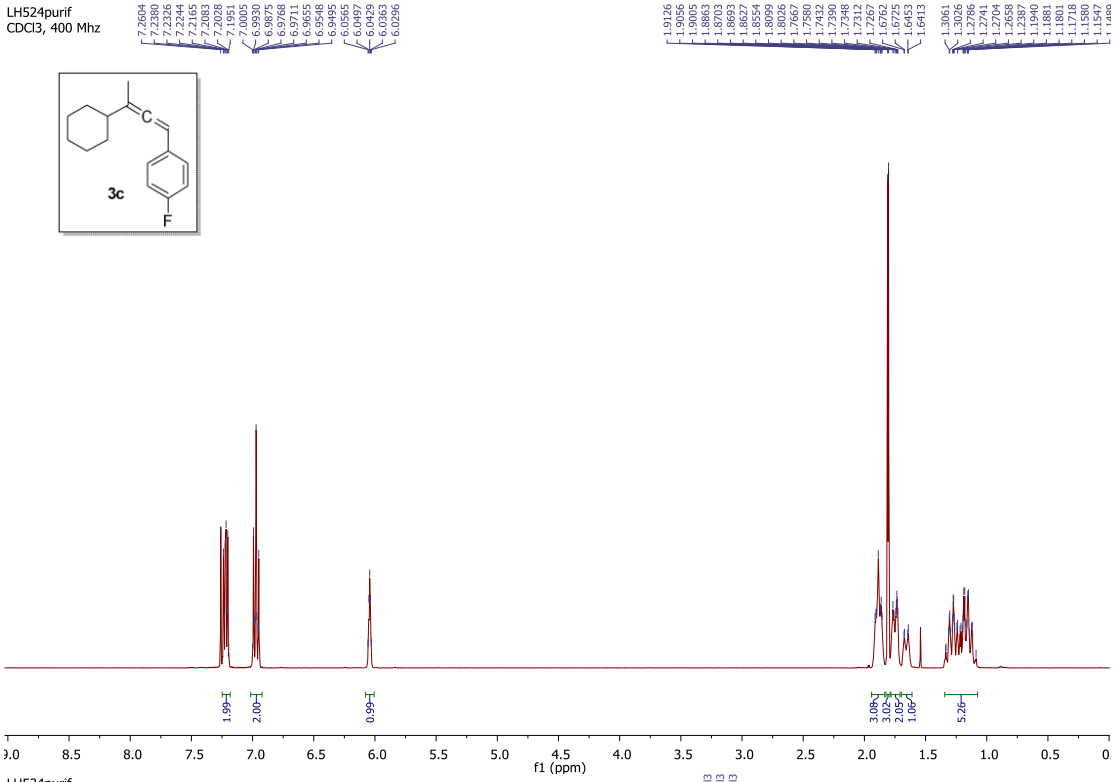

LH525purif
CDCl3, 101 Mhz
f1 (ppm)

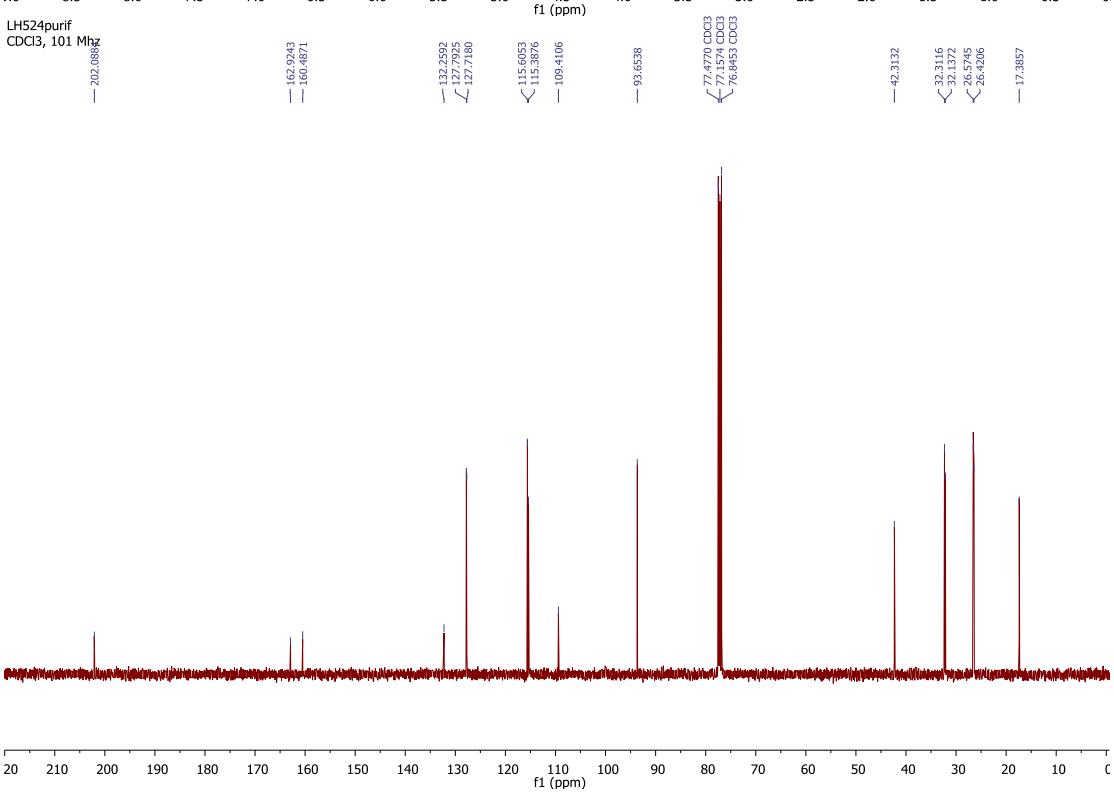


1	109.389	109.160	109.614	M	120602	12100475	98.72% 49.679%
2	109.836	109.637	110.144	M	117706	12256798	100.00% 50.321%

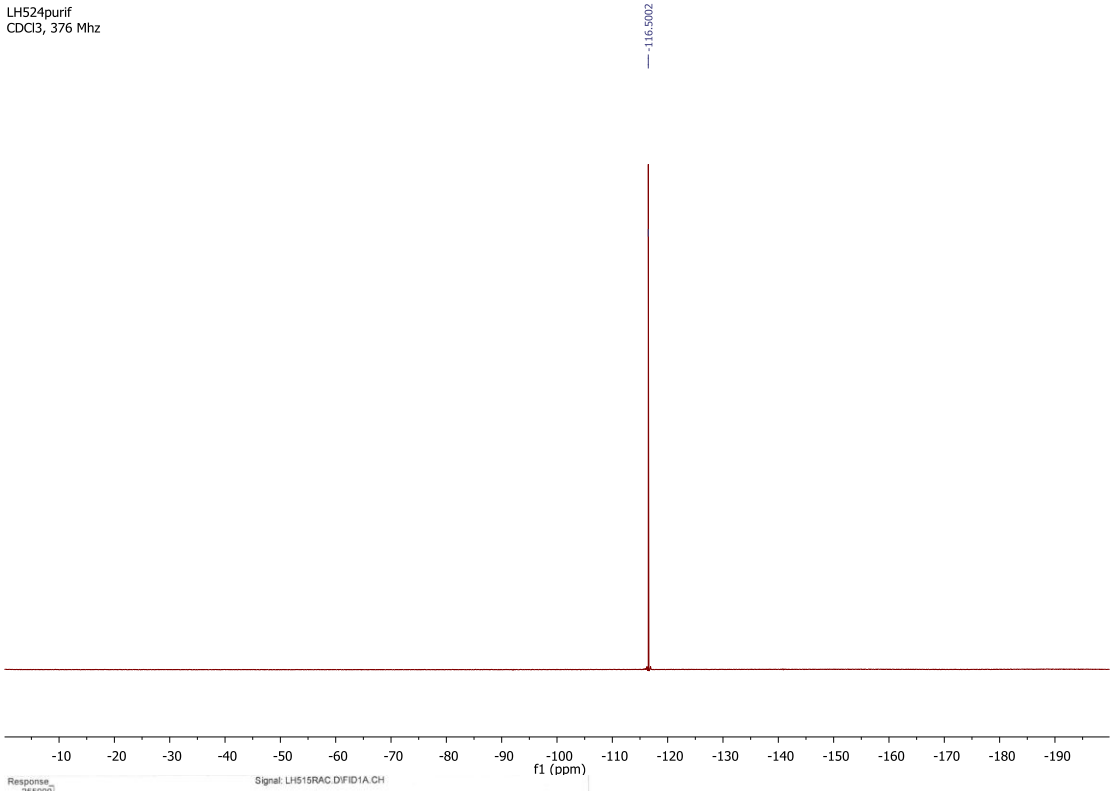


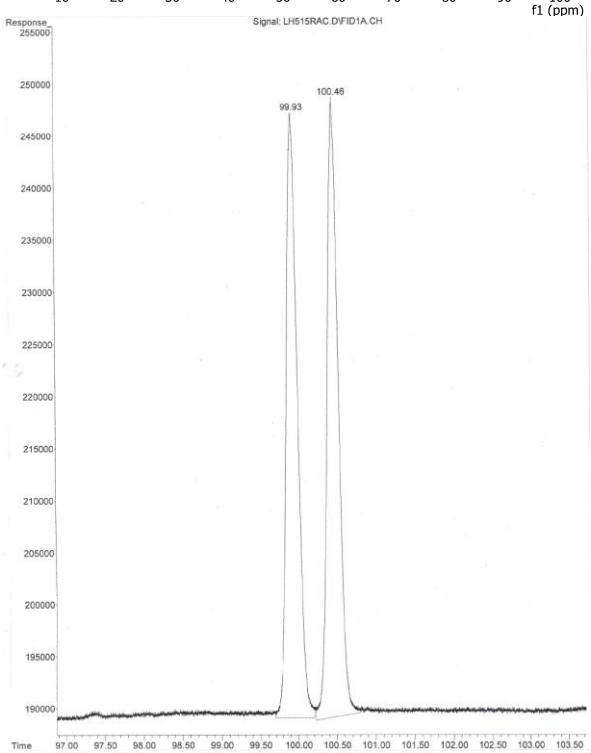
1	109.417	109.180	109.715	M	189883	19349334	100.00% 95.139%
2	109.887	109.737	110.113	M	9959	988530	5.11% 4.861%


LH524purif
CDCl3, 400 Mhz
3c
F
f1 (ppm)

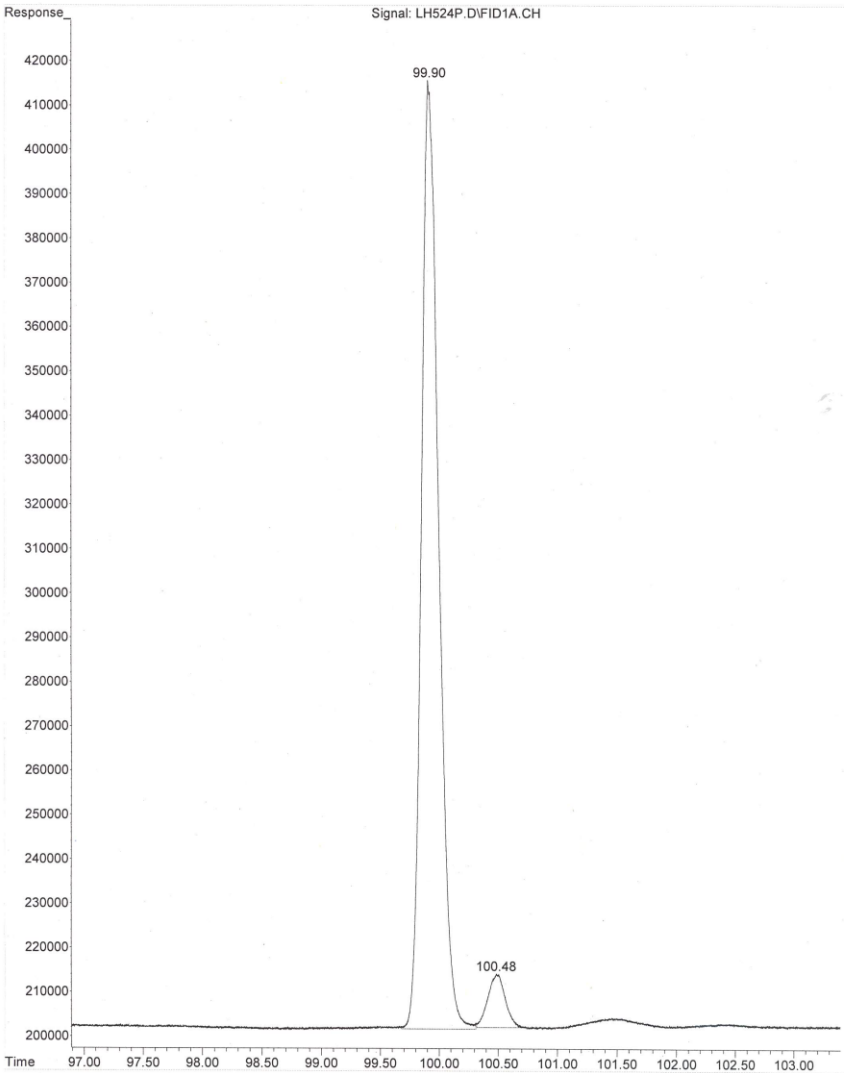

LH524purif
CDCl3, 101 Mhz
202.0886
162.9243
160.4871
132.2592
127.7925
127.7180
115.6053
115.3876
109.4106
93.6538
77.4770 CDCl3
77.1574 CDCl3
76.8453 CDCl3
42.3132
32.3116
32.1372
26.5745
26.4206
17.3857
f1 (ppm)

LH524purif
CDCl3, 376 Mhz

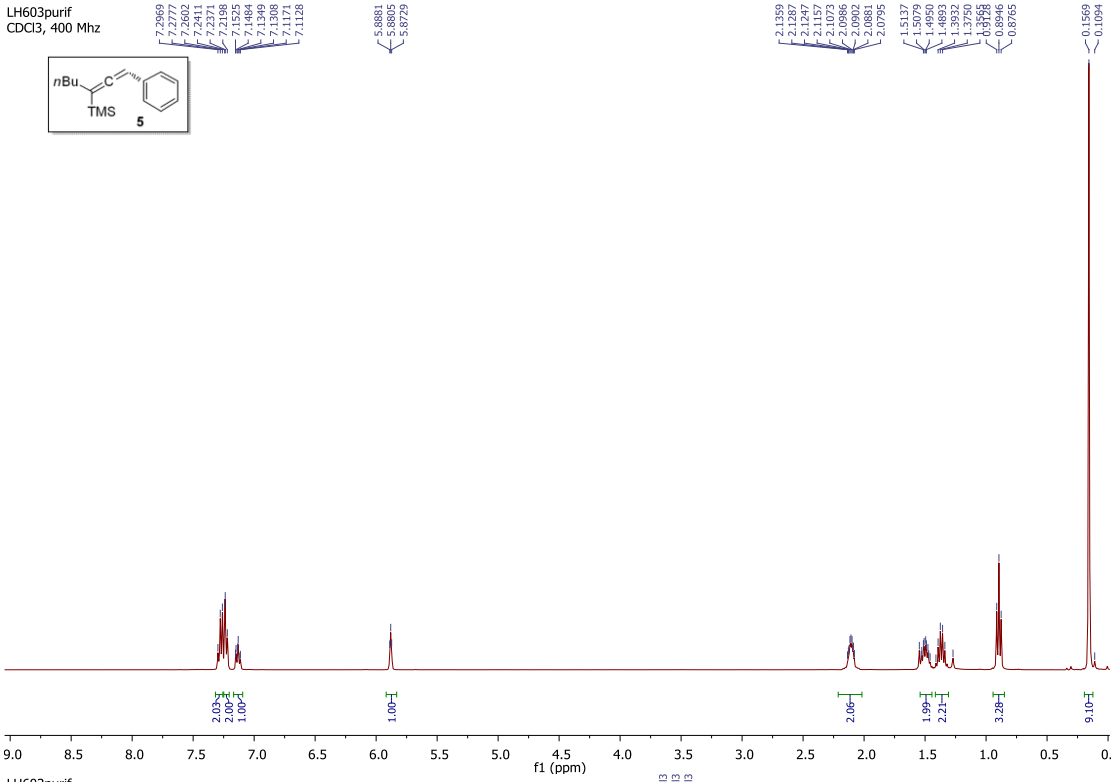


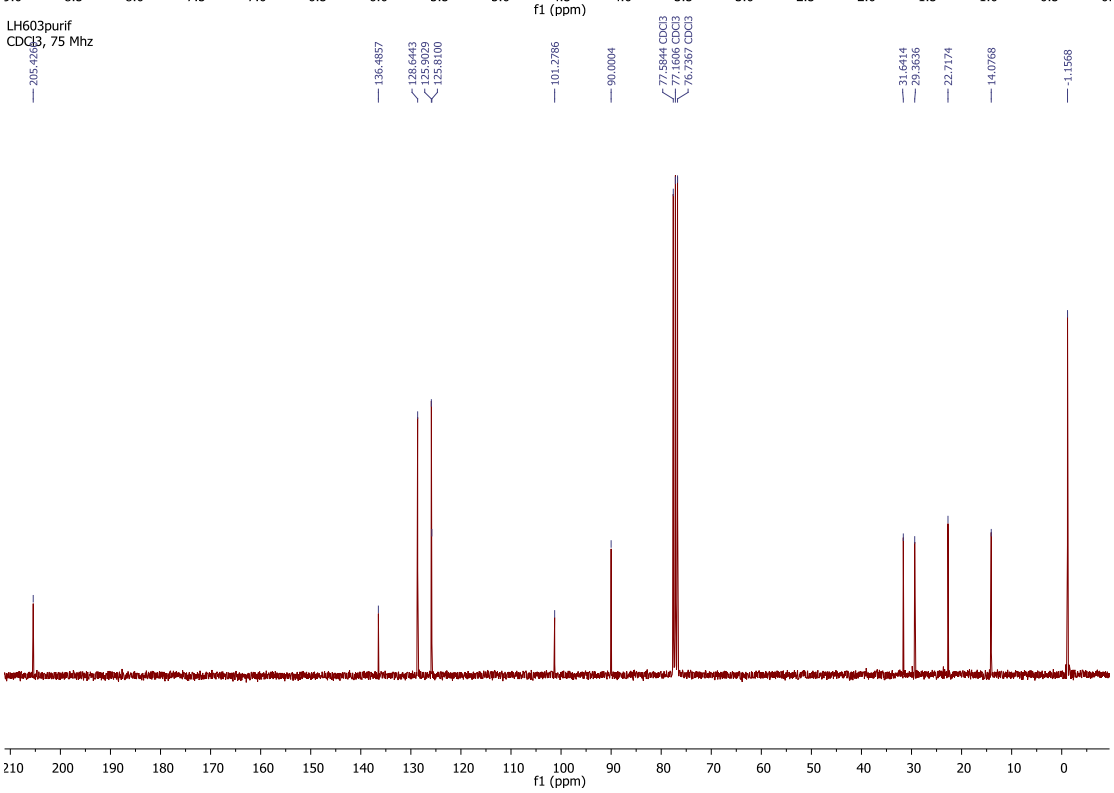


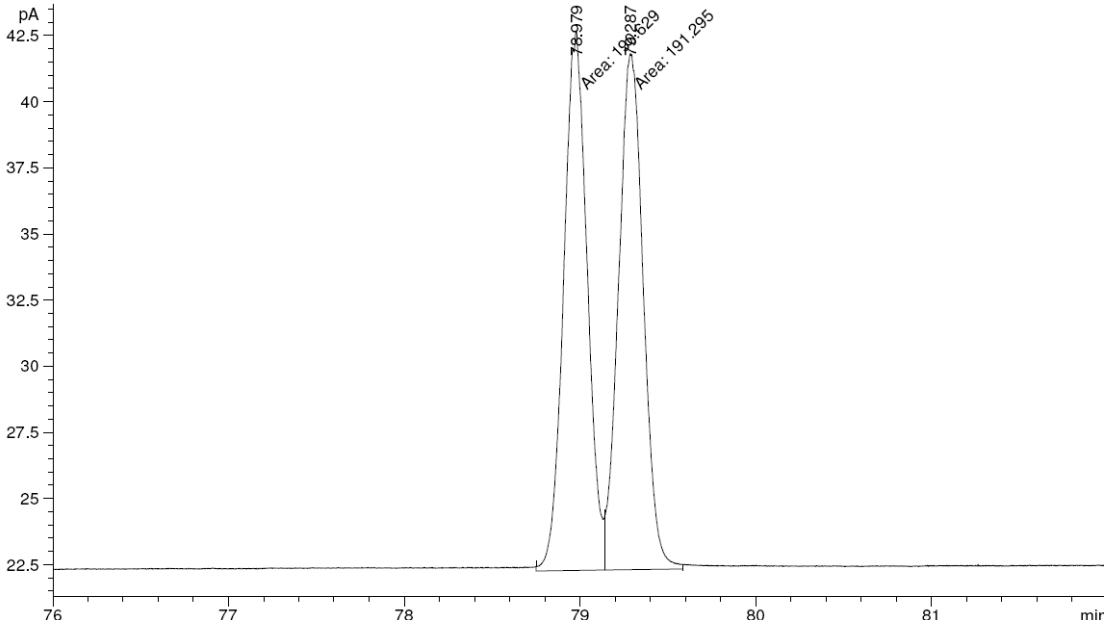
1	99.927	99.683	100.209	M	58179	5863197	98.78%	49.694%
2	100.462	100.222	100.806	M	59571	5935335	100.00%	50.306%



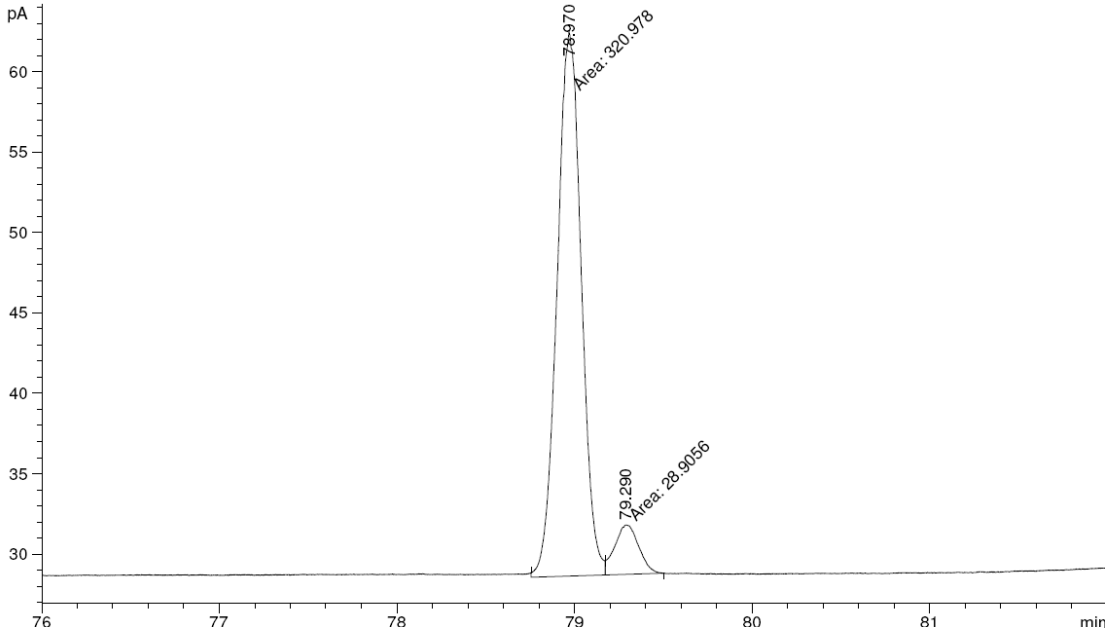
1	99.901	99.677	100.313	M	213948	21874961	100.00%	94.729%
2	100.483	100.319	100.699	M	12067	1217170	5.56%	5.271%


LH603purif
CDCl3, 400 Mhz
nBu
TMS
5
f1 (ppm)


LH603purif
CDCl3, 75 Mhz
f1 (ppm)

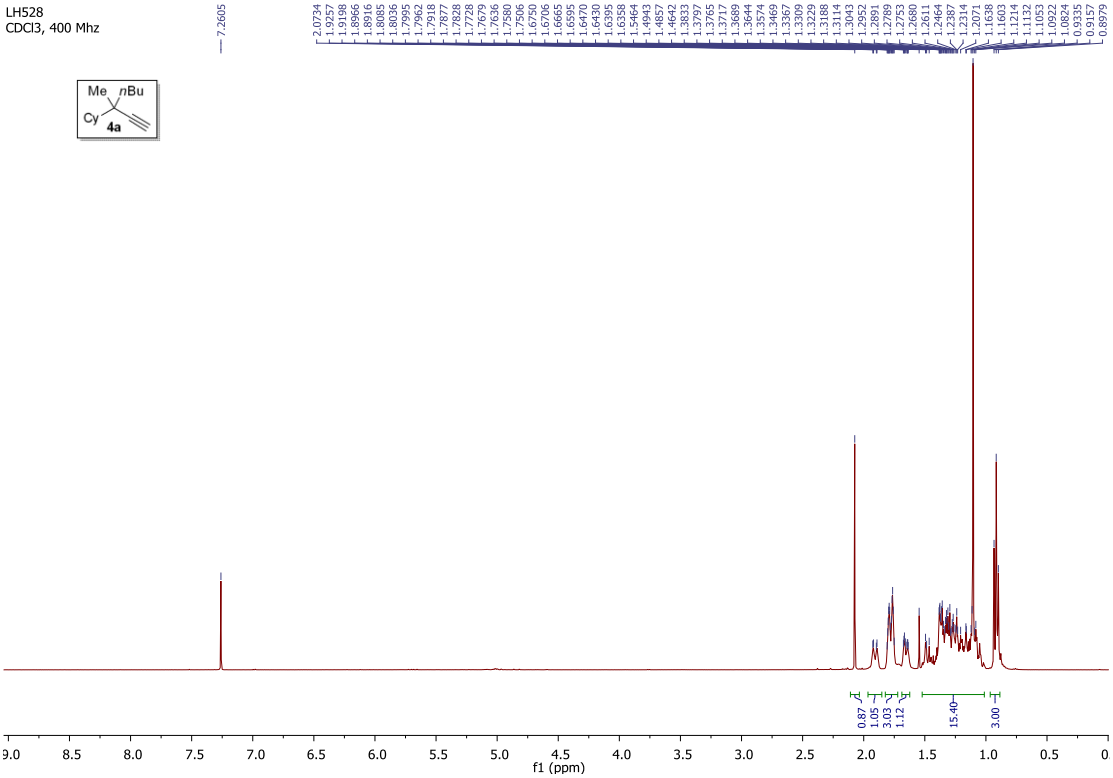


1	78.979	MF	T	0.1559	190.62891	20.38207	49.91284
2	79.287	FM	T	0.1634	191.29468	19.51563	50.08716

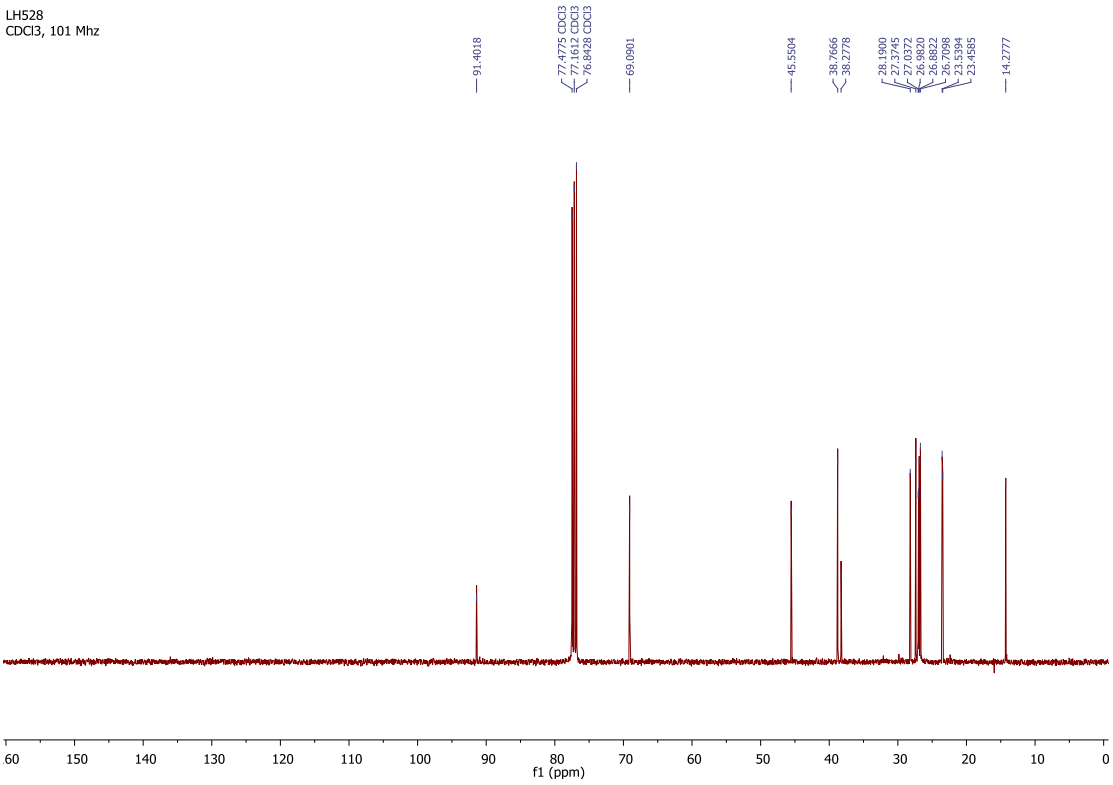


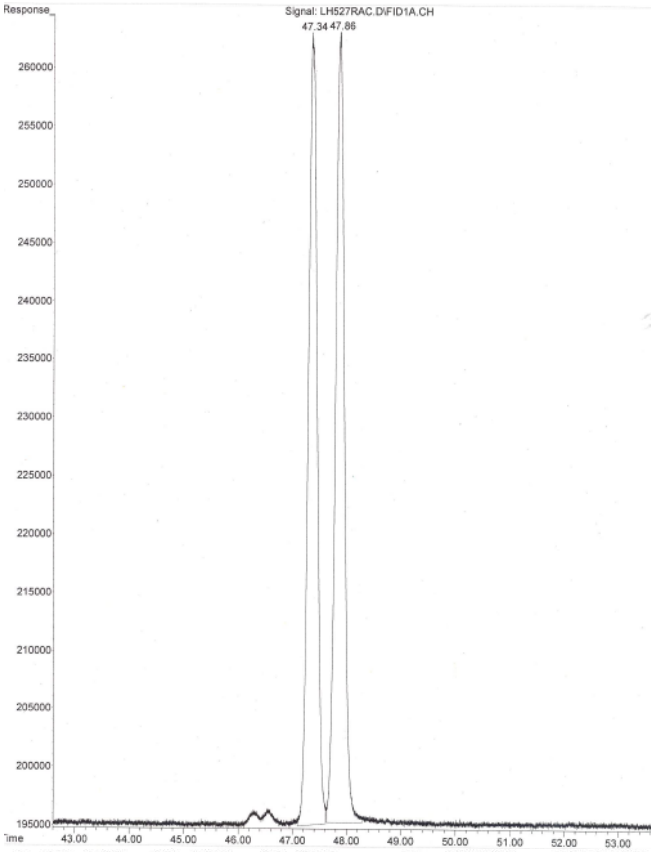
1	78.970	MF	T	0.1578	320.97775	33.90977	91.73851
2	79.290	FM	T	0.1563	28.90558	3.08322	8.26149

LH528
CDCl3, 400 Mhz

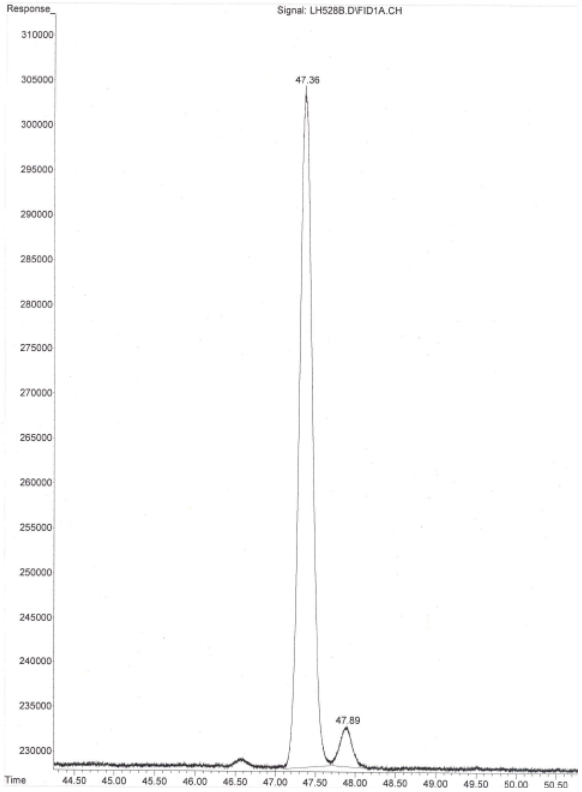


LH528
CDCl3, 101 Mhz



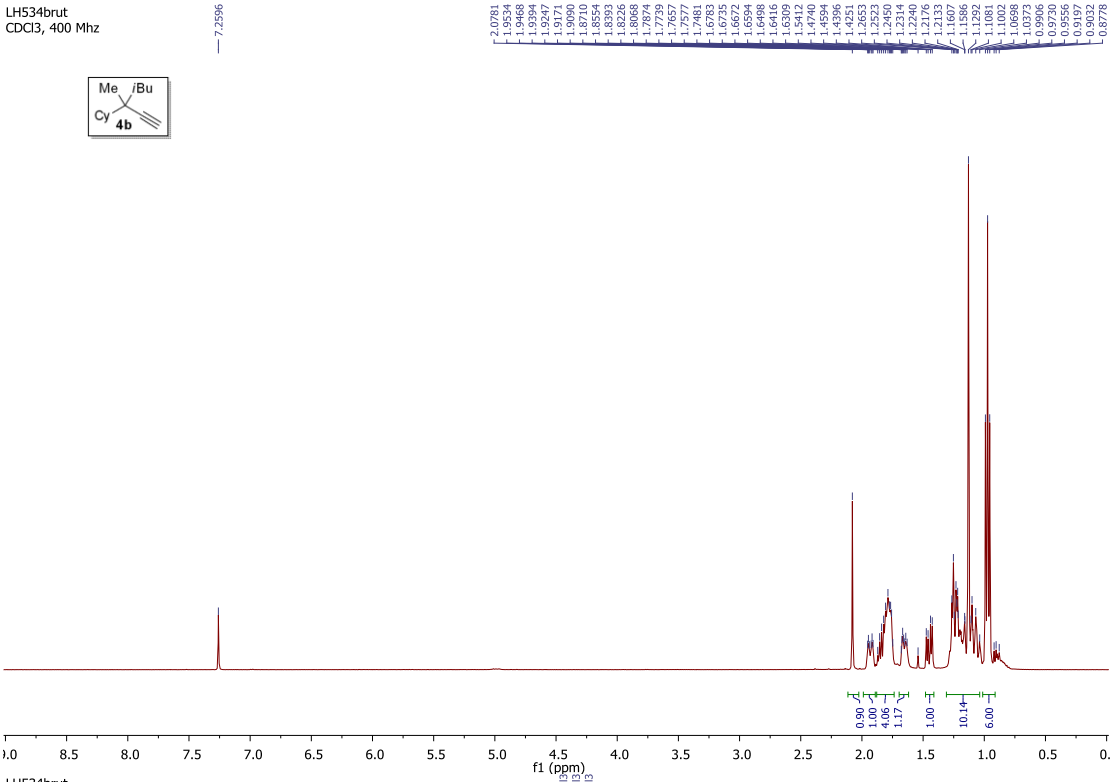


1	47.340	47.082	47.611	M	67799	7618321	97.91%	49.472%
2	47.859	47.618	48.279	M	67839	7780884	100.00%	50.528%

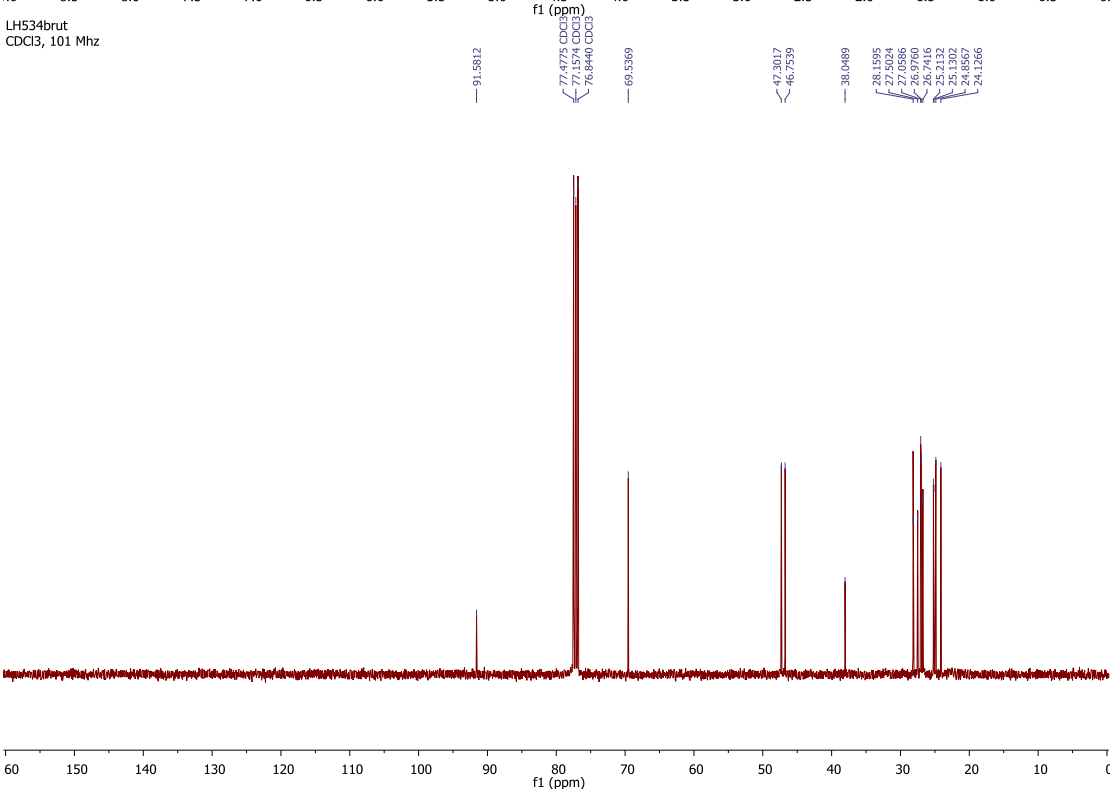


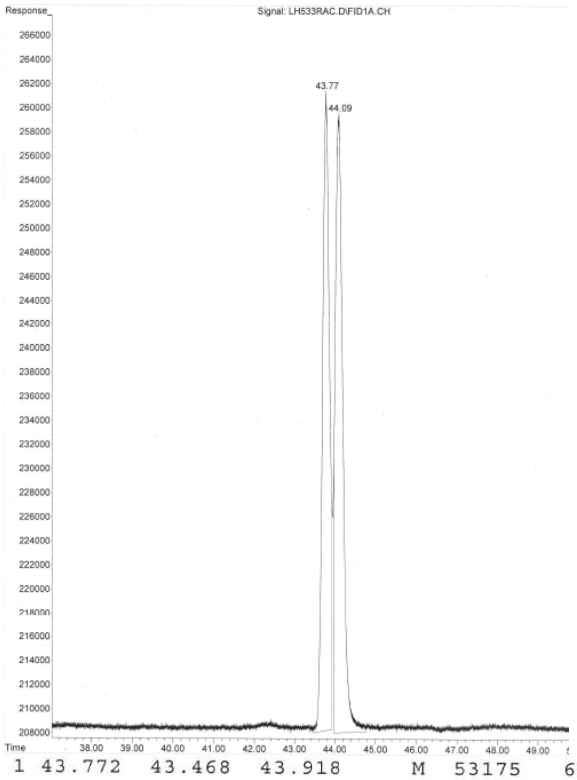
1	47.357	47.095	47.698	M	76154	8578164	100.00%	94.672%
2	47.889	47.718	48.124	M	4568	482728	5.63%	5.328%

LH534brut
CDCl3, 400 Mhz

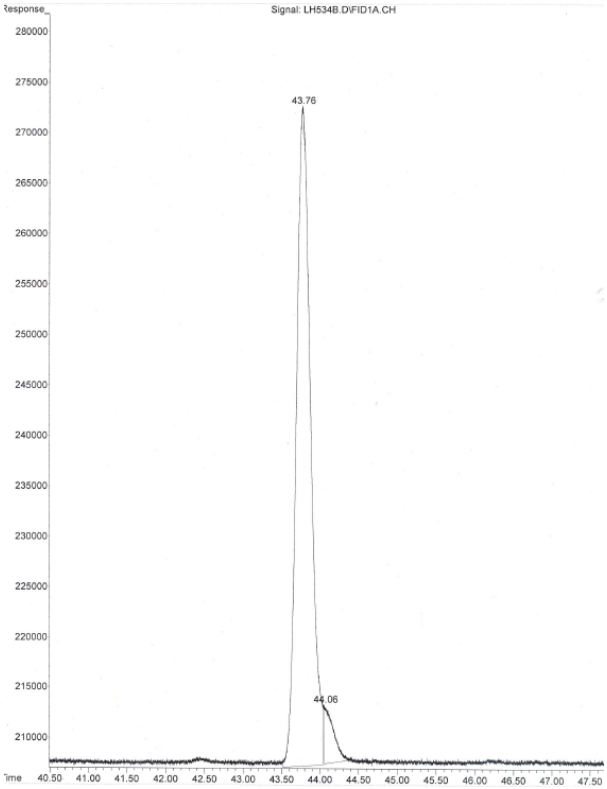


LH534brut
CDCl3, 101 Mhz



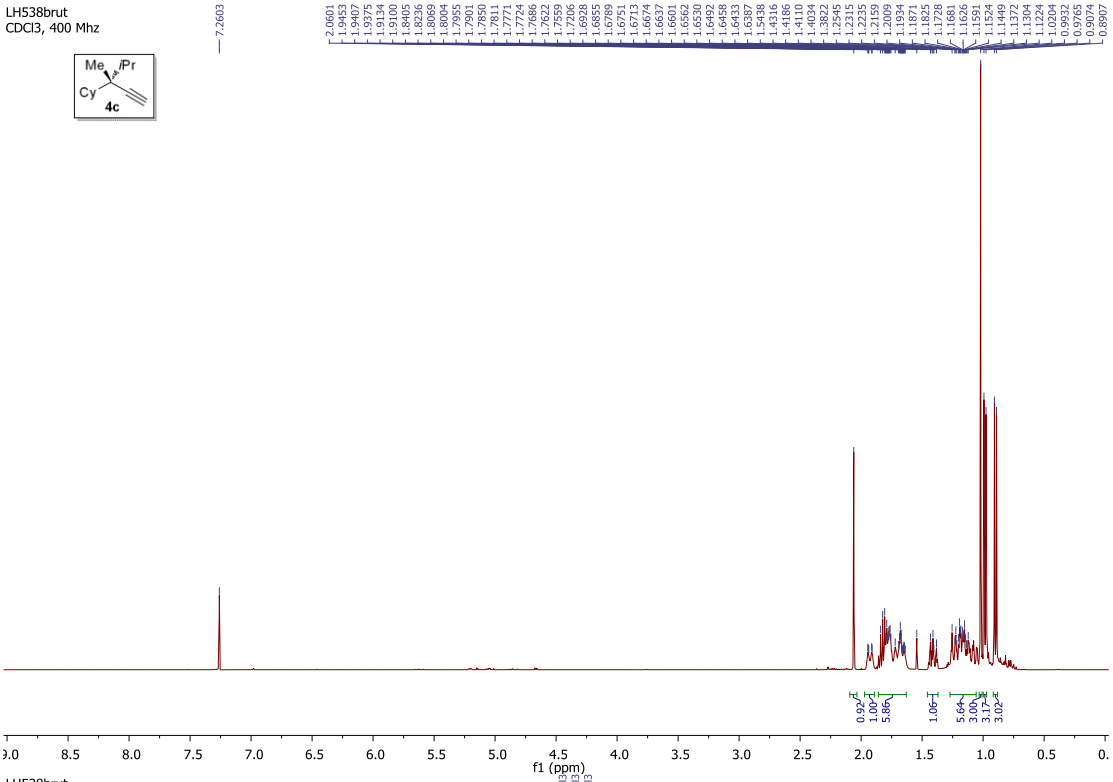


1	43.772	43.468	43.918	M	53175	6148904	93.15%	48.226%
2	44.091	43.969	44.766	M	51509	6601380	100.00%	51.774%

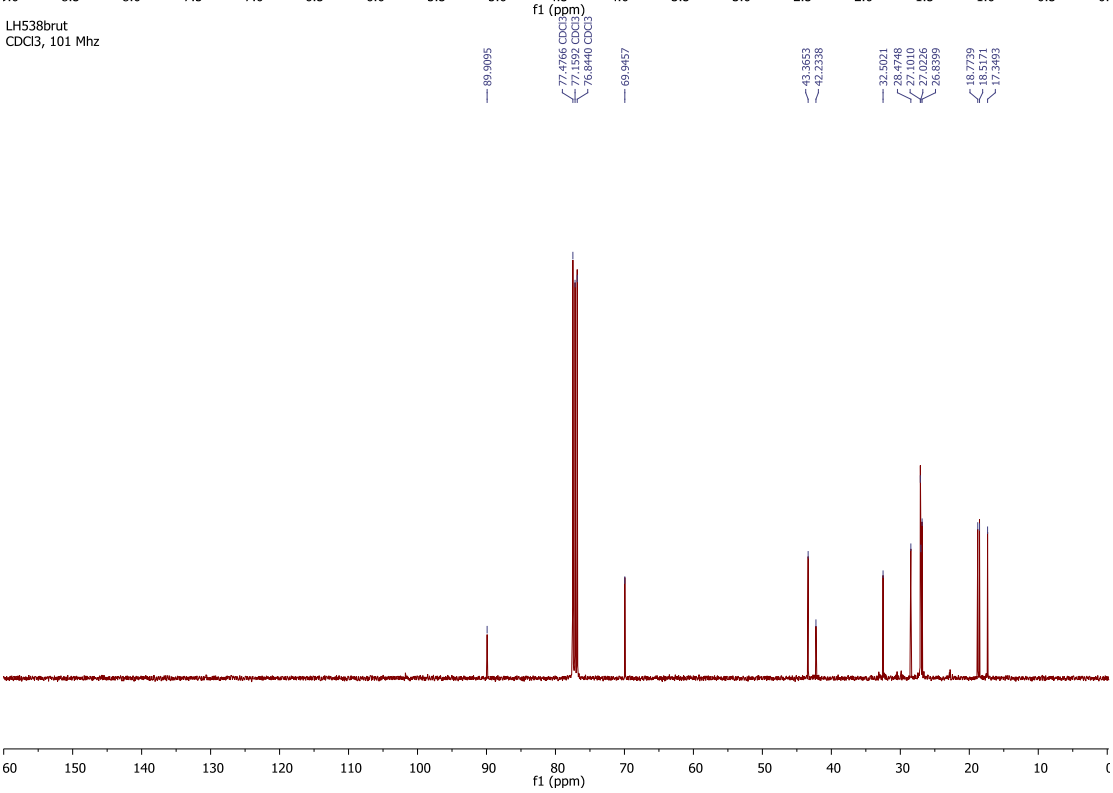


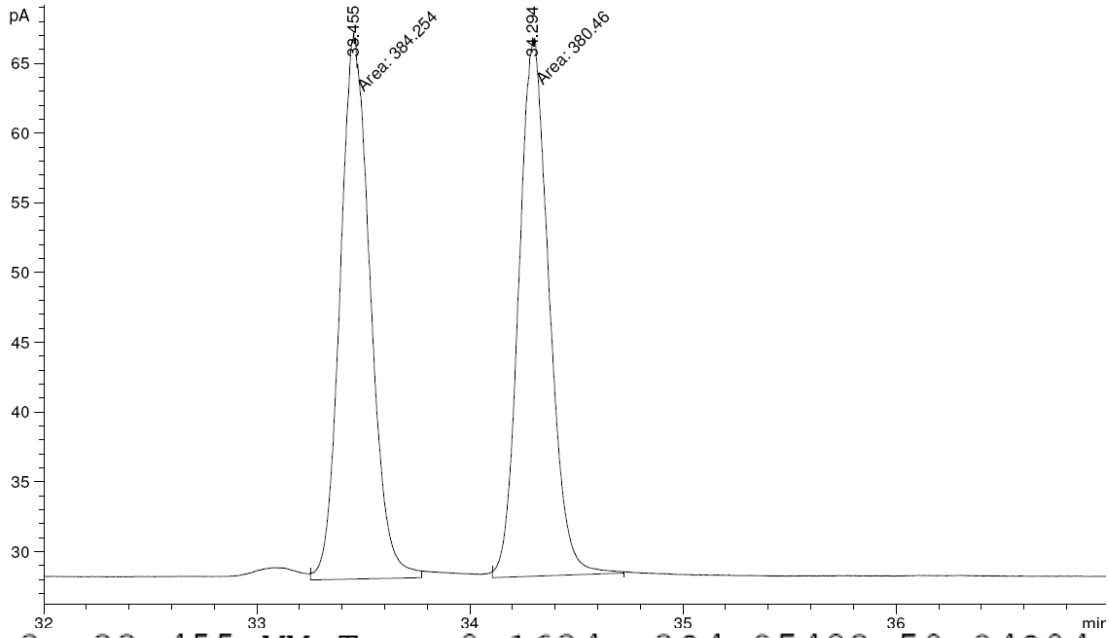
1	43.764	43.513	44.034	M	65422	8405569	100.00%	94.835%
2	44.056	44.055	44.366	M	5808	457755	5.45%	5.165%

LH538brut
CDCl3, 400 Mhz

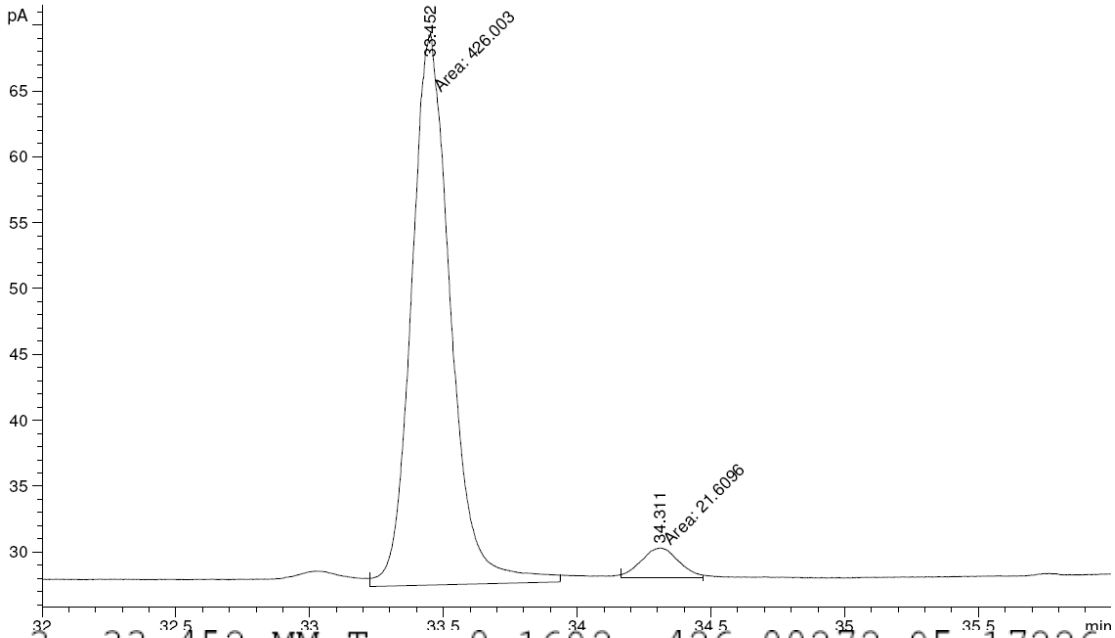


LH538brut
CDCl3, 101 Mhz



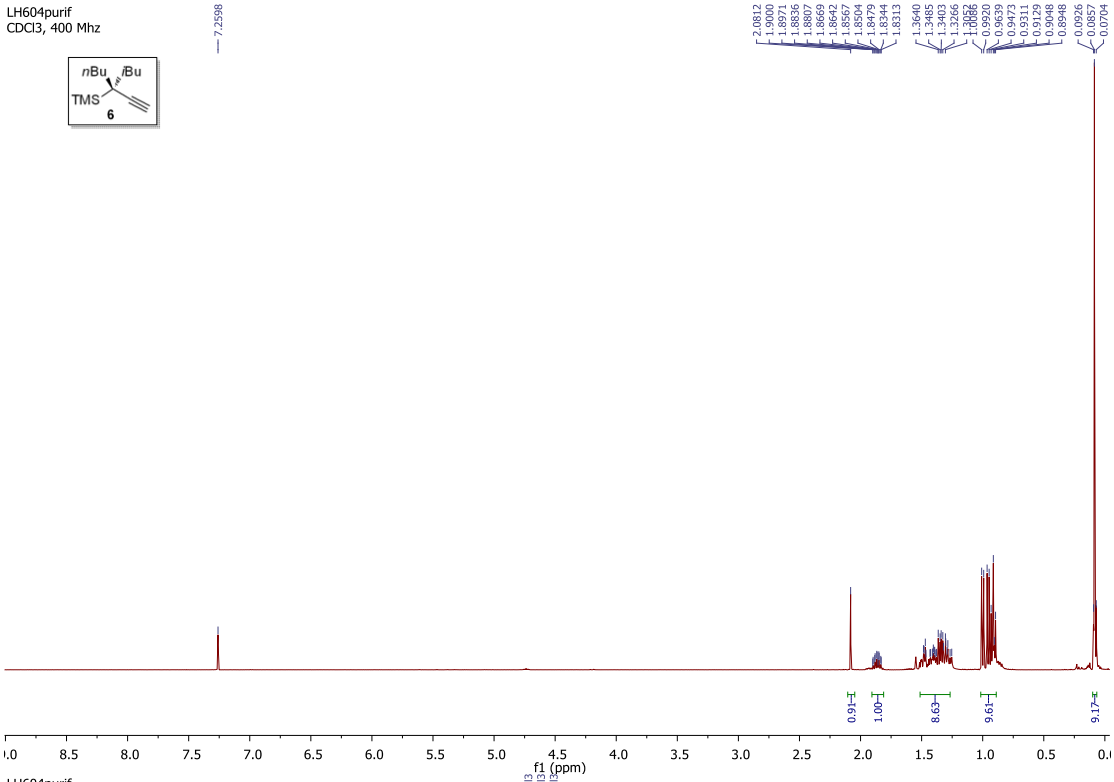


3	33.455	MM	T	0.1634	384.25403	50.24804
4	34.294	MM	T	0.1643	380.46036	49.75196

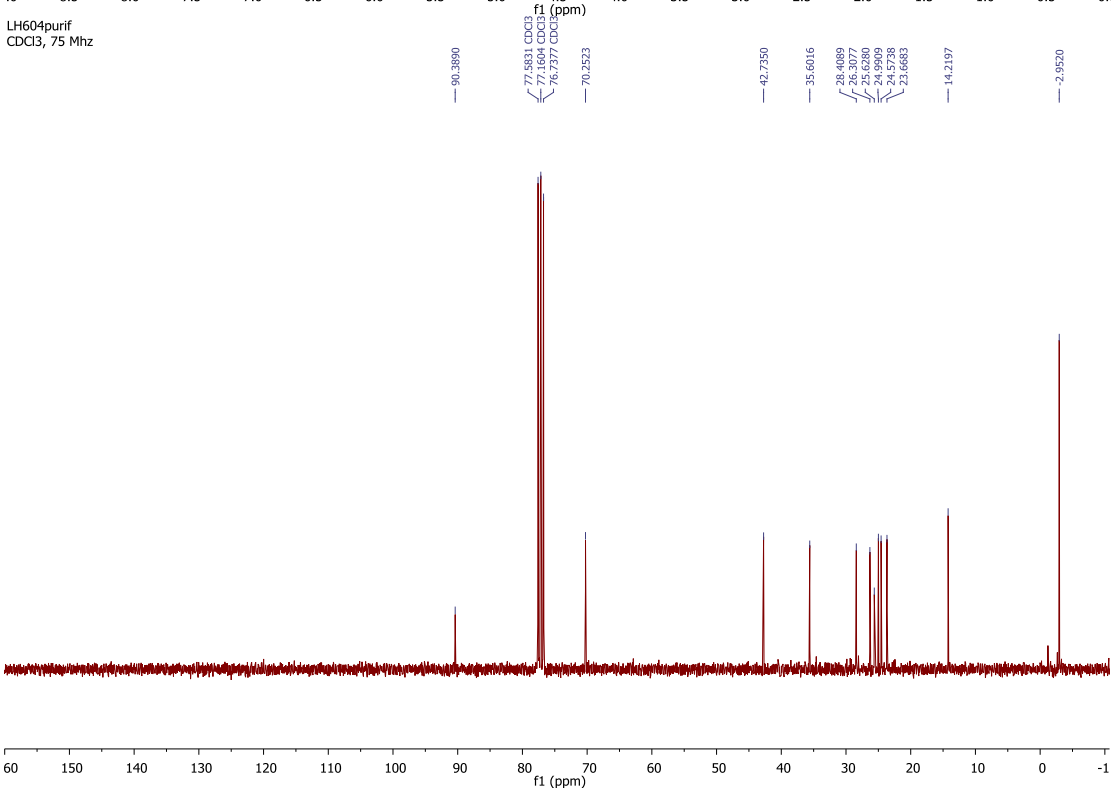


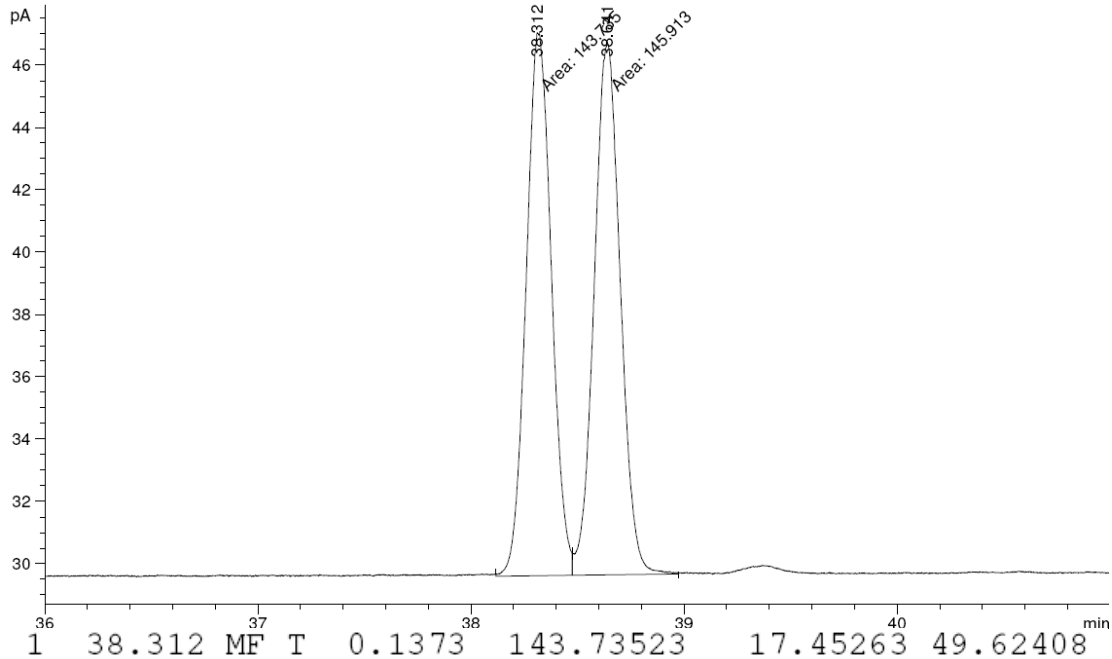
3	33.452	MM	T	0.1692	426.00272	95.17226
4	34.311	MM	T	0.1618	21.60957	4.82774

LH604purif
CDCl3, 400 Mhz

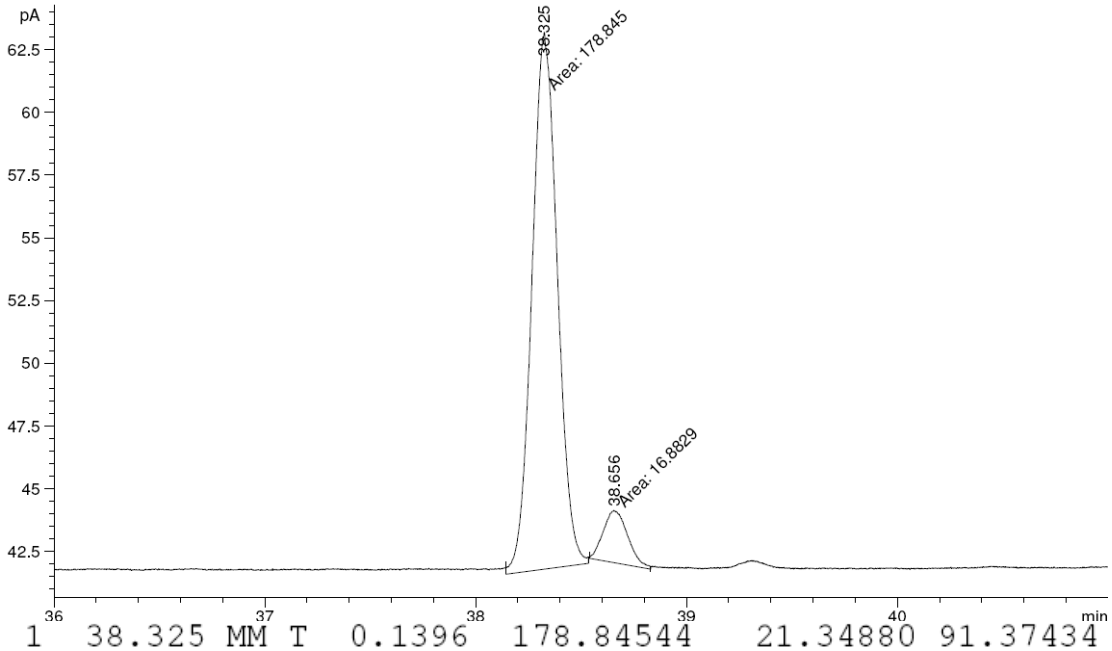


LH604purif
CDCl3, 75 Mhz



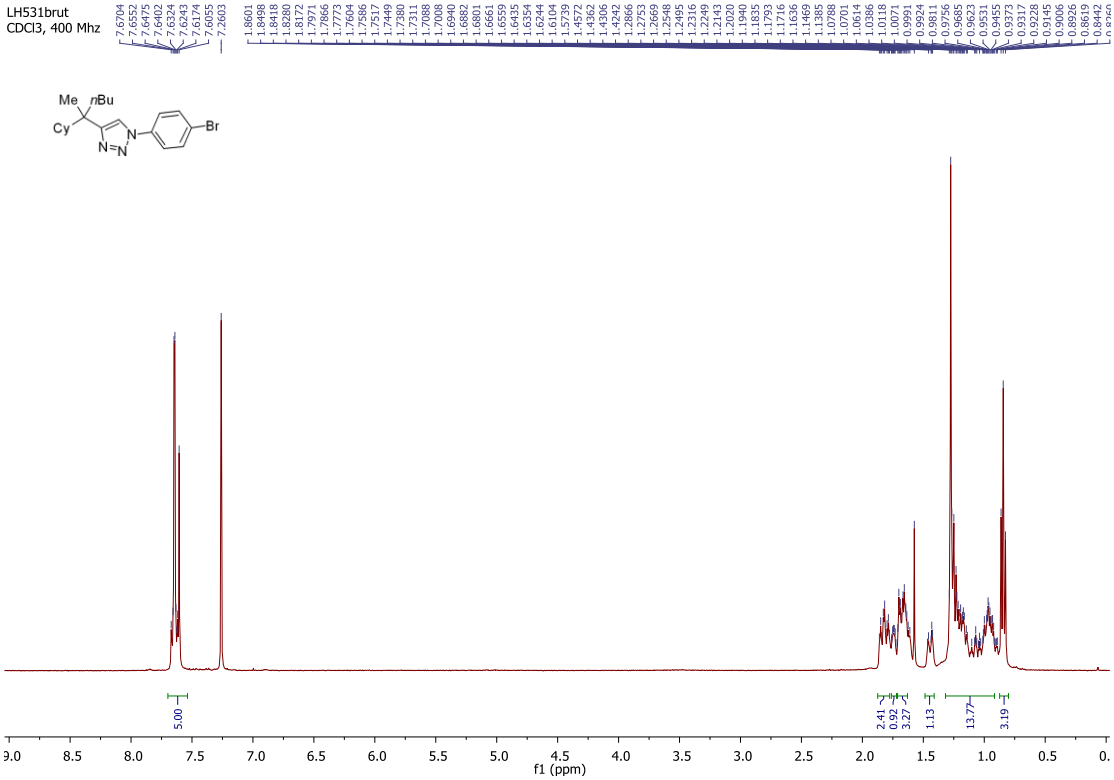


1	38.312	MF	T	0.1373	143.73523	17.45263	49.62408
2	38.641	FM	T	0.1423	145.91292	17.08403	50.37592

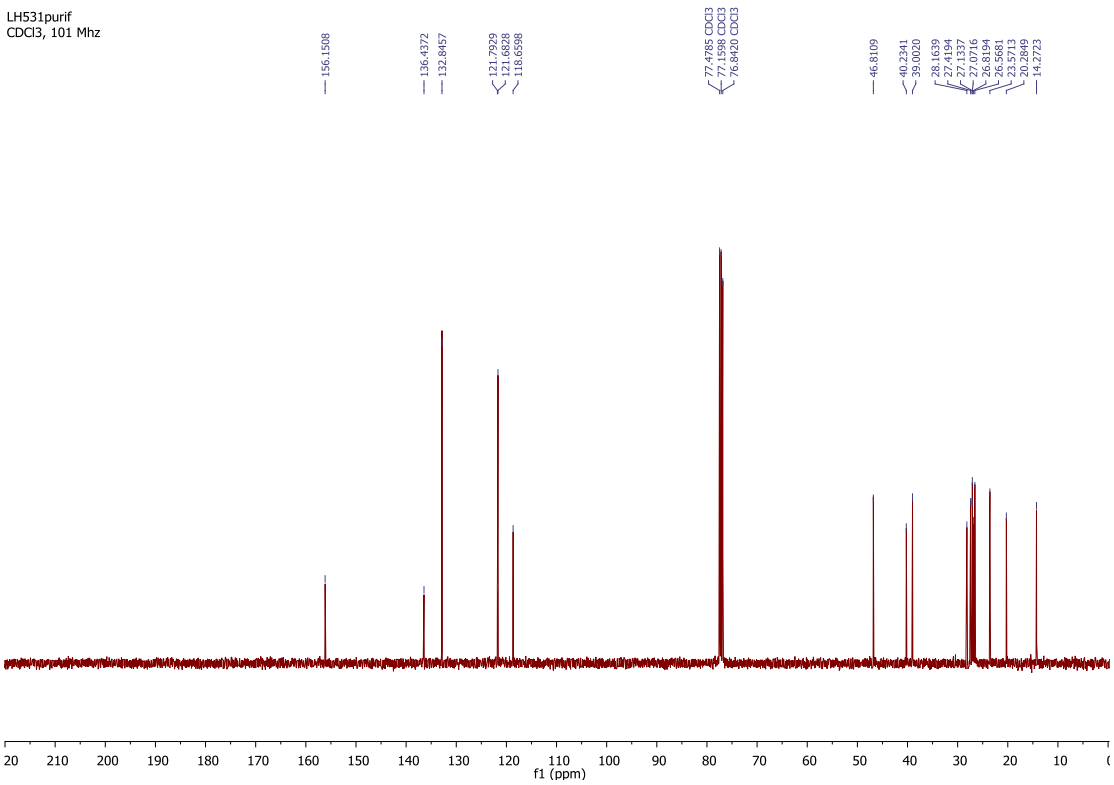


1	38.325	MM	T	0.1396	178.84544	21.34880	91.37434
2	38.656	MM	T	0.1353	16.88285	2.07944	8.62566

LH531brut
CDCl3, 400 Mhz



LH531purif
CDCl3, 101 Mhz



V) X-ray data

CCDC 886545 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

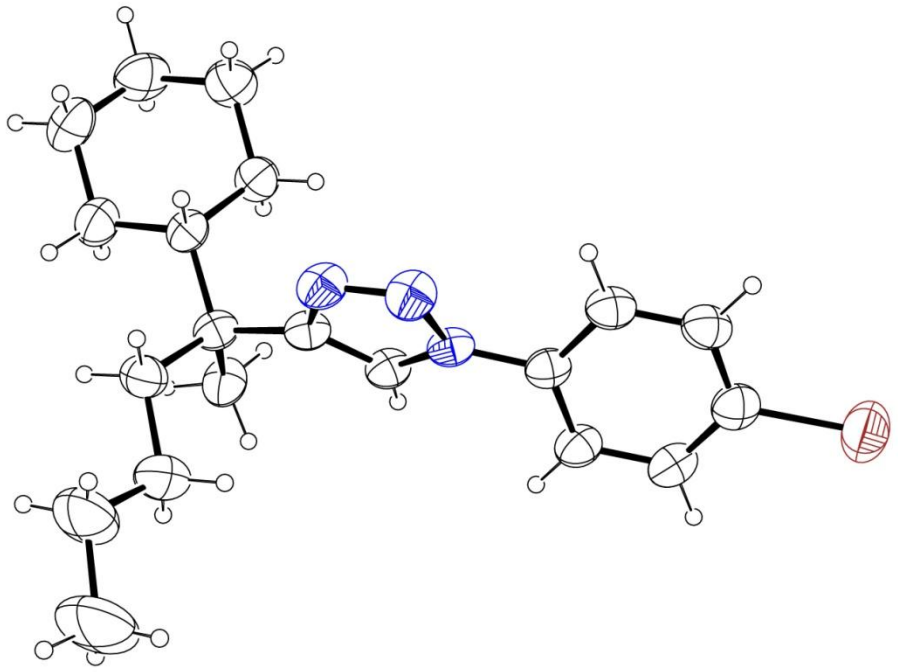


Figure Ortep (50% probability) of LH531.

Table 1. Crystal data and structure refinement for lh531_abs.

Identification code	shelxl	
Empirical formula	C20 H28 Br N3	
Formula weight	390.36	
Temperature	180(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2	
Unit cell dimensions	a = 39.7414(11) Å	α= 90 °.
	b = 5.82580(15) Å	β= 93.687(3) °.
	c = 17.3579(5) Å	γ = 90 °.
Volume	4010.48(19) $Å^3$	
Z	8	
Density (calculated)	1.293 Mg/m^3	
Absorption coefficient	2.820 mm^{-1}	
F(000)	1632	
Crystal size	0.3176 x 0.0656 x 0.0164 mm^3	
Theta range for data collection	3.28 to 73.71 °.	
Index ranges	-47<=h<=48, -6<=k<=7, -21<=l<=21	
Reflections collected	18119	
Independent reflections	7492 [R(int) = 0.0310]	
Completeness to theta = 67.00 °	99.9 %	
Absorption correction	Analytical	
Max. and min. transmission	0.955 and 0.633	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	7492 / 1 / 438
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.0969
R indices (all data)	R1 = 0.0484, wR2 = 0.1034
Absolute structure parameter	-0.022(17)
Largest diff. peak and hole	0.352 and -0.381 e.$Å^{-3}$

Table 2. Bond lengths [Å] and angles [ ] for lh531_abs.

Br(1)-C(2)	1.891(4)
N(8)-C(12)	1.352(4)
N(8)-N(9)	1.363(5)
N(8)-C(5)	1.429(5)
N(9)-N(10)	1.307(4)
N(10)-C(11)	1.374(5)
C(2)-C(7)	1.377(5)
C(2)-C(3)	1.393(6)
C(3)-C(4)	1.378(5)
C(3)-H(3)	0.9500
C(4)-C(5)	1.388(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.382(5)
C(6)-C(7)	1.399(5)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(11)-C(12)	1.370(5)
C(11)-C(13)	1.509(5)
C(12)-H(12)	0.9500
C(13)-C(20)	1.532(5)
C(13)-C(21)	1.540(5)
C(13)-C(14)	1.556(4)
C(14)-C(15)	1.535(5)

C(14)-C(19)	1.538(4)
C(14)-H(14)	1.0000
C(15)-C(16)	1.518(5)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.531(6)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.513(6)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.534(6)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.527(5)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.521(7)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900

C(23)-C(24)	1.542(7)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
Br(25)-C(26)	1.901(4)
N(32)-C(36)	1.355(4)
N(32)-N(33)	1.358(4)
N(32)-C(29)	1.420(4)
N(33)-N(34)	1.307(4)
N(34)-C(35)	1.364(5)
C(26)-C(27)	1.375(5)
C(26)-C(31)	1.380(6)
C(27)-C(28)	1.387(5)
C(27)-H(27)	0.9500
C(28)-C(29)	1.390(5)
C(28)-H(28)	0.9500
C(29)-C(30)	1.393(5)
C(30)-C(31)	1.385(5)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(35)-C(36)	1.362(5)
C(35)-C(37)	1.509(5)
C(36)-H(36)	0.9500

C(37)-C(44)	1.531(6)
C(37)-C(45)	1.534(5)
C(37)-C(38)	1.583(6)
C(38)-C(43)	1.487(6)
C(38)-C(39)	1.523(6)
C(38)-H(38)	1.0000
C(39)-C(40)	1.580(9)
C(39)-H(39A)	0.9900
C(39)-H(39B)	0.9900
C(40)-C(41)	1.453(8)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(42)	1.510(8)
C(41)-H(41A)	0.9900
C(41)-H(41B)	0.9900
C(42)-C(43)	1.557(8)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800
C(45)-C(46)	1.525(6)
C(45)-H(45A)	0.9900

C(45)-H(45B)	0.9900
C(46)-C(47)	1.535(7)
C(46)-H(46A)	0.9900
C(46)-H(46B)	0.9900
C(47)-C(48)	1.503(8)
C(47)-H(47A)	0.9900
C(47)-H(47B)	0.9900
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800

C(12)-N(8)-N(9)	110.7(3)
C(12)-N(8)-C(5)	129.0(3)
N(9)-N(8)-C(5)	120.3(3)
N(10)-N(9)-N(8)	106.8(3)
N(9)-N(10)-C(11)	109.5(3)
C(7)-C(2)-C(3)	121.3(4)
C(7)-C(2)-Br(1)	119.0(3)
C(3)-C(2)-Br(1)	119.7(3)
C(4)-C(3)-C(2)	119.2(3)
C(4)-C(3)-H(3)	120.4
C(2)-C(3)-H(3)	120.4
C(3)-C(4)-C(5)	119.7(3)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1

C(6)-C(5)-C(4)	121.2(3)
C(6)-C(5)-N(8)	119.6(3)
C(4)-C(5)-N(8)	119.2(3)
C(5)-C(6)-C(7)	119.1(3)
C(5)-C(6)-H(6)	120.4
C(7)-C(6)-H(6)	120.4
C(2)-C(7)-C(6)	119.4(3)
C(2)-C(7)-H(7)	120.3
C(6)-C(7)-H(7)	120.3
C(12)-C(11)-N(10)	108.0(3)
C(12)-C(11)-C(13)	130.4(3)
N(10)-C(11)-C(13)	121.6(3)
N(8)-C(12)-C(11)	105.0(3)
N(8)-C(12)-H(12)	127.5
C(11)-C(12)-H(12)	127.5
C(11)-C(13)-C(20)	108.8(3)
C(11)-C(13)-C(21)	108.6(3)
C(20)-C(13)-C(21)	110.3(3)
C(11)-C(13)-C(14)	108.6(3)
C(20)-C(13)-C(14)	111.5(3)
C(21)-C(13)-C(14)	109.1(3)
C(15)-C(14)-C(19)	108.6(3)
C(15)-C(14)-C(13)	113.5(3)
C(19)-C(14)-C(13)	114.2(3)
C(15)-C(14)-H(14)	106.7

C(19)-C(14)-H(14)	106.7
C(13)-C(14)-H(14)	106.7
C(16)-C(15)-C(14)	112.4(3)
C(16)-C(15)-H(15A)	109.1
C(14)-C(15)-H(15A)	109.1
C(16)-C(15)-H(15B)	109.1
C(14)-C(15)-H(15B)	109.1
H(15A)-C(15)-H(15B)	107.9
C(15)-C(16)-C(17)	111.2(3)
C(15)-C(16)-H(16A)	109.4
C(17)-C(16)-H(16A)	109.4
C(15)-C(16)-H(16B)	109.4
C(17)-C(16)-H(16B)	109.4
H(16A)-C(16)-H(16B)	108.0
C(18)-C(17)-C(16)	110.3(3)
C(18)-C(17)-H(17A)	109.6
C(16)-C(17)-H(17A)	109.6
C(18)-C(17)-H(17B)	109.6
C(16)-C(17)-H(17B)	109.6
H(17A)-C(17)-H(17B)	108.1
C(17)-C(18)-C(19)	111.7(4)
C(17)-C(18)-H(18A)	109.3
C(19)-C(18)-H(18A)	109.3
C(17)-C(18)-H(18B)	109.3
C(19)-C(18)-H(18B)	109.3

H(18A)-C(18)-H(18B)	107.9
C(18)-C(19)-C(14)	111.7(3)
C(18)-C(19)-H(19A)	109.3
C(14)-C(19)-H(19A)	109.3
C(18)-C(19)-H(19B)	109.3
C(14)-C(19)-H(19B)	109.3
H(19A)-C(19)-H(19B)	107.9
C(13)-C(20)-H(20A)	109.5
C(13)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(13)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(13)	116.8(3)
C(22)-C(21)-H(21A)	108.1
C(13)-C(21)-H(21A)	108.1
C(22)-C(21)-H(21B)	108.1
C(13)-C(21)-H(21B)	108.1
H(21A)-C(21)-H(21B)	107.3
C(23)-C(22)-C(21)	111.0(4)
C(23)-C(22)-H(22A)	109.4
C(21)-C(22)-H(22A)	109.4
C(23)-C(22)-H(22B)	109.4
C(21)-C(22)-H(22B)	109.4
H(22A)-C(22)-H(22B)	108.0

C(22)-C(23)-C(24)	112.0(6)
C(22)-C(23)-H(23A)	109.2
C(24)-C(23)-H(23A)	109.2
C(22)-C(23)-H(23B)	109.2
C(24)-C(23)-H(23B)	109.2
H(23A)-C(23)-H(23B)	107.9
C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(36)-N(32)-N(33)	110.0(3)
C(36)-N(32)-C(29)	129.6(3)
N(33)-N(32)-C(29)	120.3(3)
N(34)-N(33)-N(32)	107.1(3)
N(33)-N(34)-C(35)	109.4(3)
C(27)-C(26)-C(31)	122.0(3)
C(27)-C(26)-Br(25)	118.6(3)
C(31)-C(26)-Br(25)	119.4(3)
C(26)-C(27)-C(28)	119.7(3)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(27)-C(28)-C(29)	118.7(3)
C(27)-C(28)-H(28)	120.6

C(29)-C(28)-H(28)	120.6
C(28)-C(29)-C(30)	121.3(3)
C(28)-C(29)-N(32)	119.3(3)
C(30)-C(29)-N(32)	119.4(3)
C(31)-C(30)-C(29)	119.4(3)
C(31)-C(30)-H(30)	120.3
C(29)-C(30)-H(30)	120.3
C(26)-C(31)-C(30)	118.9(3)
C(26)-C(31)-H(31)	120.5
C(30)-C(31)-H(31)	120.5
C(36)-C(35)-N(34)	108.1(3)
C(36)-C(35)-C(37)	129.8(3)
N(34)-C(35)-C(37)	122.0(3)
N(32)-C(36)-C(35)	105.4(3)
N(32)-C(36)-H(36)	127.3
C(35)-C(36)-H(36)	127.3
C(35)-C(37)-C(44)	109.1(3)
C(35)-C(37)-C(45)	108.7(3)
C(44)-C(37)-C(45)	109.7(4)
C(35)-C(37)-C(38)	106.6(3)
C(44)-C(37)-C(38)	112.8(4)
C(45)-C(37)-C(38)	109.8(3)
C(43)-C(38)-C(39)	109.6(4)
C(43)-C(38)-C(37)	115.3(4)
C(39)-C(38)-C(37)	111.7(4)

C(43)-C(38)-H(38)	106.6
C(39)-C(38)-H(38)	106.6
C(37)-C(38)-H(38)	106.6
C(38)-C(39)-C(40)	109.9(5)
C(38)-C(39)-H(39A)	109.7
C(40)-C(39)-H(39A)	109.7
C(38)-C(39)-H(39B)	109.7
C(40)-C(39)-H(39B)	109.7
H(39A)-C(39)-H(39B)	108.2
C(41)-C(40)-C(39)	111.6(5)
C(41)-C(40)-H(40A)	109.3
C(39)-C(40)-H(40A)	109.3
C(41)-C(40)-H(40B)	109.3
C(39)-C(40)-H(40B)	109.3
H(40A)-C(40)-H(40B)	108.0
C(40)-C(41)-C(42)	110.4(5)
C(40)-C(41)-H(41A)	109.6
C(42)-C(41)-H(41A)	109.6
C(40)-C(41)-H(41B)	109.6
C(42)-C(41)-H(41B)	109.6
H(41A)-C(41)-H(41B)	108.1
C(41)-C(42)-C(43)	110.9(5)
C(41)-C(42)-H(42A)	109.4
C(43)-C(42)-H(42A)	109.4
C(41)-C(42)-H(42B)	109.4

C(43)-C(42)-H(42B)	109.4
H(42A)-C(42)-H(42B)	108.0
C(38)-C(43)-C(42)	110.6(4)
C(38)-C(43)-H(43A)	109.5
C(42)-C(43)-H(43A)	109.5
C(38)-C(43)-H(43B)	109.5
C(42)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	108.1
C(37)-C(44)-H(44A)	109.5
C(37)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
C(37)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(46)-C(45)-C(37)	115.9(3)
C(46)-C(45)-H(45A)	108.3
C(37)-C(45)-H(45A)	108.3
C(46)-C(45)-H(45B)	108.3
C(37)-C(45)-H(45B)	108.3
H(45A)-C(45)-H(45B)	107.4
C(45)-C(46)-C(47)	112.1(4)
C(45)-C(46)-H(46A)	109.2
C(47)-C(46)-H(46A)	109.2
C(45)-C(46)-H(46B)	109.2
C(47)-C(46)-H(46B)	109.2

H(46A)-C(46)-H(46B)	107.9
C(48)-C(47)-C(46)	111.4(6)
C(48)-C(47)-H(47A)	109.3
C(46)-C(47)-H(47A)	109.3
C(48)-C(47)-H(47B)	109.3
C(46)-C(47)-H(47B)	109.3
H(47A)-C(47)-H(47B)	108.0
C(47)-C(48)-H(48A)	109.5
C(47)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
C(47)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 3. Torsion angles [°] for lh531_abs.

C(12)-N(8)-N(9)-N(10)	0.3(4)
C(5)-N(8)-N(9)-N(10)	179.1(3)
N(8)-N(9)-N(10)-C(11)	-0.5(4)
C(7)-C(2)-C(3)-C(4)	-0.2(5)
Br(1)-C(2)-C(3)-C(4)	178.1(3)
C(2)-C(3)-C(4)-C(5)	-0.1(5)
C(3)-C(4)-C(5)-C(6)	0.3(5)
C(3)-C(4)-C(5)-N(8)	-178.9(3)
C(12)-N(8)-C(5)-C(6)	-28.3(5)
N(9)-N(8)-C(5)-C(6)	153.1(3)
C(12)-N(8)-C(5)-C(4)	151.0(3)
N(9)-N(8)-C(5)-C(4)	-27.7(5)
C(4)-C(5)-C(6)-C(7)	-0.2(5)
N(8)-C(5)-C(6)-C(7)	179.0(3)
C(3)-C(2)-C(7)-C(6)	0.3(5)
Br(1)-C(2)-C(7)-C(6)	-178.0(3)
C(5)-C(6)-C(7)-C(2)	-0.1(5)
N(9)-N(10)-C(11)-C(12)	0.5(4)
N(9)-N(10)-C(11)-C(13)	-179.3(3)
N(9)-N(8)-C(12)-C(11)	0.1(4)
C(5)-N(8)-C(12)-C(11)	-178.7(3)
N(10)-C(11)-C(12)-N(8)	-0.3(4)
C(13)-C(11)-C(12)-N(8)	179.4(3)

C(12)-C(11)-C(13)-C(20)	0.4(5)
N(10)-C(11)-C(13)-C(20)	-179.8(3)
C(12)-C(11)-C(13)-C(21)	120.5(4)
N(10)-C(11)-C(13)-C(21)	-59.8(4)
C(12)-C(11)-C(13)-C(14)	-121.1(4)
N(10)-C(11)-C(13)-C(14)	58.6(4)
C(11)-C(13)-C(14)-C(15)	55.9(4)
C(20)-C(13)-C(14)-C(15)	-63.9(4)
C(21)-C(13)-C(14)-C(15)	174.0(3)
C(11)-C(13)-C(14)-C(19)	-178.8(3)
C(20)-C(13)-C(14)-C(19)	61.4(4)
C(21)-C(13)-C(14)-C(19)	-60.7(4)
C(19)-C(14)-C(15)-C(16)	56.1(4)
C(13)-C(14)-C(15)-C(16)	-175.8(3)
C(14)-C(15)-C(16)-C(17)	-57.1(5)
C(15)-C(16)-C(17)-C(18)	55.6(5)
C(16)-C(17)-C(18)-C(19)	-55.6(5)
C(17)-C(18)-C(19)-C(14)	56.9(5)
C(15)-C(14)-C(19)-C(18)	-55.4(5)
C(13)-C(14)-C(19)-C(18)	176.8(3)
C(11)-C(13)-C(21)-C(22)	-59.4(4)
C(20)-C(13)-C(21)-C(22)	59.7(4)
C(14)-C(13)-C(21)-C(22)	-177.5(3)
C(13)-C(21)-C(22)-C(23)	175.8(4)
C(21)-C(22)-C(23)-C(24)	174.1(5)

C(36)-N(32)-N(33)-N(34)	-0.7(4)
C(29)-N(32)-N(33)-N(34)	176.8(3)
N(32)-N(33)-N(34)-C(35)	0.8(4)
C(31)-C(26)-C(27)-C(28)	0.2(5)
Br(25)-C(26)-C(27)-C(28)	-177.6(2)
C(26)-C(27)-C(28)-C(29)	-0.1(5)
C(27)-C(28)-C(29)-C(30)	0.4(5)
C(27)-C(28)-C(29)-N(32)	178.9(3)
C(36)-N(32)-C(29)-C(28)	-28.1(5)
N(33)-N(32)-C(29)-C(28)	154.9(3)
C(36)-N(32)-C(29)-C(30)	150.4(3)
N(33)-N(32)-C(29)-C(30)	-26.6(5)
C(28)-C(29)-C(30)-C(31)	-0.8(5)
N(32)-C(29)-C(30)-C(31)	-179.3(3)
C(27)-C(26)-C(31)-C(30)	-0.6(5)
Br(25)-C(26)-C(31)-C(30)	177.2(3)
C(29)-C(30)-C(31)-C(26)	0.9(5)
N(33)-N(34)-C(35)-C(36)	-0.5(4)
N(33)-N(34)-C(35)-C(37)	-177.6(3)
N(33)-N(32)-C(36)-C(35)	0.4(4)
C(29)-N(32)-C(36)-C(35)	-176.9(3)
N(34)-C(35)-C(36)-N(32)	0.0(4)
C(37)-C(35)-C(36)-N(32)	176.8(3)
C(36)-C(35)-C(37)-C(44)	9.3(6)
N(34)-C(35)-C(37)-C(44)	-174.3(4)

C(36)-C(35)-C(37)-C(45)	129.0(4)
N(34)-C(35)-C(37)-C(45)	-54.6(5)
C(36)-C(35)-C(37)-C(38)	-112.7(4)
N(34)-C(35)-C(37)-C(38)	63.7(4)
C(35)-C(37)-C(38)-C(43)	-171.4(4)
C(44)-C(37)-C(38)-C(43)	68.9(5)
C(45)-C(37)-C(38)-C(43)	-53.8(5)
C(35)-C(37)-C(38)-C(39)	62.6(5)
C(44)-C(37)-C(38)-C(39)	-57.1(5)
C(45)-C(37)-C(38)-C(39)	-179.8(4)
C(43)-C(38)-C(39)-C(40)	56.9(6)
C(37)-C(38)-C(39)-C(40)	-174.0(4)
C(38)-C(39)-C(40)-C(41)	-57.3(8)
C(39)-C(40)-C(41)-C(42)	56.9(10)
C(40)-C(41)-C(42)-C(43)	-57.2(9)
C(39)-C(38)-C(43)-C(42)	-58.0(6)
C(37)-C(38)-C(43)-C(42)	175.0(4)
C(41)-C(42)-C(43)-C(38)	58.0(7)
C(35)-C(37)-C(45)-C(46)	-51.3(5)
C(44)-C(37)-C(45)-C(46)	68.0(5)
C(38)-C(37)-C(45)-C(46)	-167.6(4)
C(37)-C(45)-C(46)-C(47)	179.9(4)
C(45)-C(46)-C(47)-C(48)	-179.8(5)

Symmetry transformations used to generate equivalent atoms: