

Advanced
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Supporting Information

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SUPPLEMENTARY MATERIAL

β - and γ -disubstituted olefins for copper-catalyzed asymmetric allylic substitution

Caroline A. Falciola, Karine Tissot-Croset, Hugo Reyneri, Alexandre Alexakis*

Department of Organic Chemistry, University of Geneva
30 quai E. Ansermet, 1211 Geneva 4 (Switzerland)
E-mail: alexandre.alexakis@chiorg.unige.ch

Experimental Data :

General remarks: ^1H (400 MHz), ^{13}C (100 MHz) NMR spectra were recorded on a Bruker 400FTNMR in CDCl_3 unless otherwise stated, and chemical shift (δ) are given in ppm relative to residual CHCl_3 . Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet). Coupling constants are reported in Hertz (Hz). IR spectra were recorded on a FT-IR Spectrometer. Evolution of reaction was followed by TLC and GC-MS (EI mode) on an HP6890. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter at 20°C in a 10 cm cell in the stated solvent; $[\alpha]_D$ values are given in $10^{-1} \text{ deg.cm}^2 \text{ g}^{-1}$ (concentration c given as g/100 mL). Enantiomeric excesses were determined by chiral GC measurement either on a HP6890 (H_2 as vector gas) or HP6850 (H_2 or He as vector gas) with the stated column. Temperature programs are described as follows: initial temperature ($^\circ\text{C}$) - initial time (min) - temperature gradient ($^\circ\text{C}/\text{min}$) - final temperature ($^\circ\text{C}$); retention times (R_T) are given in min. In some cases, enantiomeric excess were determined by chiral SFC measurement on a Berger SFC with the stated column. Gradient programs are described as follows: initial methanol concentration (%) - initial time (min) - percent gradient of methanol ($\%/ \text{min}$) - final methanol concentration (%). Flash chromatography was performed using silicagel 32-63 μm , 60 \AA . THF, DMSO, diethylether and dichloromethane were dried by filtration over alumina (activated at 350°C under nitrogen atmosphere for 12 h). Copper (I) thiophenecarboxylate (CuTC) was purchased from Frontier Scientific. All chiral ligands **L1**–**L13** were prepared according to the literature procedure.^[1]

Typical procedure for the enantioselective copper catalyzed allylic substitution with Grignard reagents: CuTC (1 mol%) and chiral ligand (1.1 mol%) are charged in a dried Schlenk tube, under inert gas, and suspended in dichloromethane (2 mL). The mixture is stirred at room temperature for 30 min, followed by the addition of the allylic halide (1 mmol) at room temperature before cooling the mixture to -78°C in an ethanol-dry ice cold bath. The Grignard (3 M in diethyl ether, 1.2 eq) diluted in CH_2Cl_2 (0.6 mL) is added over 60 min *via* a syringe pump. Upon completion of the addition, the reaction mixture is left a further 4h at -78°C . The reaction is quenched by addition of aqueous HCl (1N, 2 mL) and then Et_2O (10 mL). Aqueous phase is separated and further extracted with Et_2O (3 x 3mL). The combined organic fractions are washed with brine (5 mL), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The oily residue is purified by flash column chromatography. Gas Chromatography on a chiral stationary phase shows the enantiomeric excess of the S_N2' product.

(3-Chloro-2-methyl-propenyl)-benzene **1**^[2]

^1H NMR (400 MHz, CDCl_3): 7.33 (m, 5H), 6.60 (s, 1H), 4.20 (s, 2H), 2.00 (d, 3H, $J = 1.31$ Hz). ^{13}C NMR (100 MHz, CDCl_3): 136.7, 134.1, 129.7, 128.9, 128.2, 127.0, 52.8, 15.9. MS (EI mode) m/z (%): 166 (20), 131 (74) 115 (21), 91 (27), 18 (100).

(3-Chloro-1-methyl-propenyl)-benzene **2**^[3]

¹ a) K. Tissot-Croset, D. Polet, S. Gille, C. Hawner, A. Alexakis, *Synthesis* **2004**, 2586-2590; b) A. Alexakis, S. Gille, F. Prian, S. Rosset, K. Ditrich, *Tetrahedron Lett.* **2004**, 45, 1449-1451.

² Murai, T.; Yamamoto, M.; Kondo, S.; Kato, S. *J. Org. Chem.* **1993**, 58, 7440-7445.

³ Kraus, G. A.; Thomas, P. J.; Bougie, D.; Chen, L. *J. Org. Chem.* **1990**, 55, 1624-1627.

¹H NMR (400 MHz, CDCl₃) : 7.44-7.26 (m, 5H), 6.00 (dt, 1H, *J*₁ = 8.00, *J*₂ = 1.47 Hz), 4.30 (d, 2H, *J* = 8.00 Hz), 2.16 (d, 3H, *J* = 1.31 Hz). ¹³C NMR (100 MHz, CDCl₃) : 142.2, 140.9, 128.3, 127.7, 125.9, 122.7, 41.1, 15.8. MS (EI mode) *m/z* (%) : 166 (24), 131 (100), 115 (35), 91 (36), 18 (100).

3-(chloromethyl)-1,2-dihydronaphthalene **8**

In flame dried glassware and under Ar, dimethylsulfide (19.4 mmol; 1.43 mL) was added to a solution of N-chlorosuccinimide (17.8 mmol; 2.377 g) suspended in 80 mL of dry dichloromethane, resulting in a white precipitate. Then (3,4-dihydronaphthalen-2-yl)methanol (16 mmol),⁴ solubilised in dry dichloromethane (20 mL), is added dropwise over a 10 min period. Reaction is left stirring overnight at RT. After quenching with brine, the mixture was extracted with diethyl ether and washed with water before drying with anhydrous magnesium sulphate. After filtration of the clear yellow solution over SiO₂, one recuperates the chloride **11**, a clear liquid, with 54 % yield. SiO₂, 100% pentane, *R*_F = 0.46. IR (neat) : 3017 (s), 2933 (m), 2887 (s), 2831 (s), 1485 (s), 1436 (m), 1257 (s), 1154 (m), 755 (s), 677 (m). ¹H NMR (400 MHz, CDCl₃) : δ 2.44 (t, 2 H, *J* = 8.36 Hz), 2.90 (t, 2 H, *J* = 8.6 Hz), δ 4.24 (s, 2 H), 6.54 (s, 1 H), 7.05-7.08 (m, 2H), 7.14-7.26 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) : δ 136.3, 135.0, 127.7, 127.5, 126.9, 126.6, 49.5, 28.0, 25.1. MS (EI mode) *m/z* (%) : 180(39), 179(15), 178(78), 144(46), 143(100), 142(32), 141(63), 139(12), 129(64), 128(82), 127(27), 119(12), 117(13), 115(58), 115m(13), 91(11), 71(13).

(*E*)-1-(chloromethyl)cyclopent-1-ene **21**

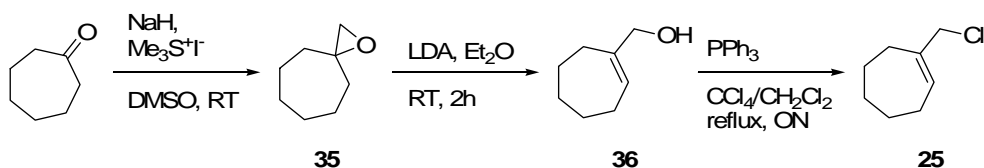
With method used for **25**, after distillation, 50% yield (b.p. 60°C/ 23 torr). ¹H NMR (400 MHz, CDCl₃) : 5.74 (s, 1H), 4.15 (s, 2H), 2.41-2.35 (m, 4H), 1.98-1.91 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) : 140.4, 130.3, 43.7, 33.0, 32.7, 23.6. MS (EI mode) *m/z* (%) : 116 (21), 81 (30), 79 (18), 67 (100), 53 (12).

(*E*)-1-(chloromethyl)cyclohex-1-ene **22**

With method used for **25**, after distillation 56% yield (b.p. 65°C/15 torr). ¹H NMR (400 MHz, CDCl₃) : 5.81 (s, 1H), 3.99 (s, 2H), 2.10-2.03 (m, 4H), 2.68-1.56 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) : 134.5, 127.7, 50.9, 26.0, 25.4, 22.5, 22.1. MS (EI mode) *m/z* (%) : 130 (22), 95 (24), 83 (16), 82 (13), 81 (100), 79 (31), 77 (12), 67 (25), 55 (19), 54 (10), 53 (18).

(+)-(*R*)-4-(2-methylenecyclopentyl)butyl 2,2,2-trifluoroacetate **23g**^[5]

SiO₂, pentane/diethyl ether 95:5, *R*_F = 0.97. ¹H-NMR (CDCl₃, 400 MHz) : 4.88 (s, 1H), 4.76 (s, 1H), 4.38-4.33 (m, 2H), 2.36-2.21 (m, 2H), 2.11-2.06 (m, 1H), 1.94-1.60 (m, 4H), 1.53-1.19 (m, 6H). MS (EI mode) *m/z* (%) : 250 (M⁺, 16), 95 (83), 93 (10), 82 (41), 81 (100), 79 (18), 67 (56), 55 (16), 53 (11). HR-MS (EI mode): calc. mass= 250.1181, mass found= 250.1183. Ee was measured by chiral GC with a Lipodex G column, Hydrogen flow (program: 70-40-1-170), *R*_T: 57.16(minor), 57.74(major).



1-Oxaspiro[2.6]nonane **35**^[6]

To a suspension of NaH (0.22 mmol; 1 eq) in dry DMSO (250 mL) at room temperature was added trimethylsulfonium salt (0.23 mmol; 1.05 eq) over a period of 15 min. The mixture was allowed to stir at room temperature over 45 min. A solution of cycloheptanone (0.20 mmol; 0.9 eq) in DMSO (5mL) was added via a dropping funnel to the mixture. After a 15 min stirring at room temperature, the reaction was heated at 65°C for 80 min. Water was then added to the reaction and further extracted with Et₂O (x4). Combined organic fractions were then washed with water and brine and dried over Na₂SO₄. Solvent was removed *in vacuo*. Crude product was distilled (81°C/ 43 torr) and afforded 56%

⁴ a) J. Verbel, R. Carrié, *Bull. Soc. Chim.*, **1982**, N° 3-4, 116-124; b) J. A. Murphy, C. W. Patterson, *J. Chem. Soc. Perkin Trans.*, **1993**, 405-410

⁵ H.-J. Gais, H. Mueller, J. Bund, M. Scommoda, J. Brandt, G. Raabe, *J. Am. Chem. Soc.* **1995**, *117*, 2453-2466.

⁶ E. J. Corey, M. Chaykovsky, *Organic Syntheses* **1973**, Coll. Vol. 5, p. 755.; **1969**, Vol. 49, p.48.

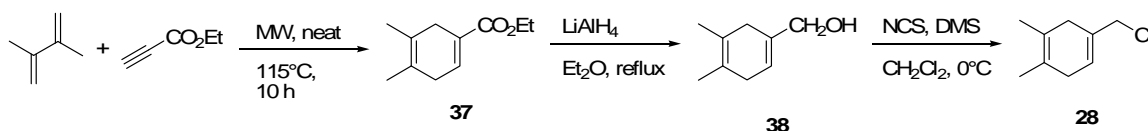
yield of epoxide. ^1H NMR (400 MHz, CDCl_3) : 2.57 (s, 2H), 1.67-1.51 (m, 12H). ^{13}C NMR (100 MHz, CDCl_3) : 60.6, 55.8, 36.0, 29.0, 24.7.

(E)-cycloheptenylmethanol 36

n-BuLi (60mmol; 2.4 eq) was added dropwise to diisopropylamine (60mmol; 2.4 eq), as the LDA gel is formed, dry Et₂O (50 mL) was added. Then the epoxide **35** (30 mmol) in Et₂O (25 mL) was added to the reaction mixture *via* syringe over a period of five minutes. After two hours at room temperature, the reaction was complete and poured into water (150 mL), extracted with Et₂O (x3). The combined organic extracts were washed with brine, dried over MgSO₄, concentrated and purified by flash chromatography (eluent *c*Hex/AcOEt 95:5) with 91% yield. SiO₂, *c*Hex/AcOEt 95:5, R_F = 0.13. IR (neat): 3310 (br), 2915 (s), 2847 (s), 2684 (w), 1663 (w), 1446 (m), 1023 (m), 994 (s), 845 (m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃) : 5.78 (t, *J*= 6.32 Hz, 1 H), 3.95 (s, 2H), 2.12 (m, 4H), 1.74 (m, 2H), 1.67 (s, 1 H), 1.48 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) : 144.0, 127.5, 68.8, 32.5, 30.2, 28.3, 27.1. MS (EI mode) *m/z* (%) : 126(19), 108(34), 93(100), 79(79), 67(58), 55(39).

(E)-1-(chloromethyl)cyclohept-1-ene 25

PPh₃ (1.2 eq; 28 mmol) was added to a solution of allylic alcohol **36** (1 eq; 23 mmol) in CCl₄ (7 mL) and CH₂Cl₂ (7 mL). The reaction was refluxed overnight. There is formation of the phosphine oxide precipitate. The reaction mixture was poured in pentane and filtered over celite/silica gel, and evaporated *in vacuo*. The latter procedure was repeated twice in order to remove all the phosphine oxide present. After filtration on silica gel, 76% yield. SiO₂, pentane, R_F = 0.93. IR (neat): 2920 (s), 2850 (m), 2690 (w), 1662 (w), 1445 (m), 1277 (w), 1256 (s), 680 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃) : 5.94 (t, *J*=6.6 Hz, 1H), 4.01 (s, 2H), 2.26-2.223 (m, 2H), 2.13 (dd, *J*=6.3 Hz, *J*=11.1 Hz, 2H), 1.78-1.72 (m, 2H), 1.58-1.47 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) : 140.6, 132.5, 53.0, 32.3, 31.0, 28.4, 26.8, 26.7. MS (EI mode) *m/z* (%) : 144 (15), 109 (19), 108 (12), 95 (100), 93 (45), 91 (35), 80 (17), 79 (54), 77 (37), 67 (78), 65 (21), 55 (19), 54 (16), 53 (23), 51 (18).



Ethyl 4,5-dimethylcyclohexa-1,4-dienecarboxylate 37

2,3-Dimethyl-1,3-butadiene (78.9 mmol; 4 eq) and ethyl propiolate (19.7 mmol; 1 eq) were heated in a MW vessel to 115°C for 10 hours. The remaining butadiene was removed *in vacuo*, affording clean crude product as a translucent oil with >98% yield. ¹H NMR (400 MHz, CDCl₃) : 6.95-6.93 (m, 1H), 4.21 (q, *J*= 7.08 Hz, 2H), 2.83-2.82 (m, 4H), 1.69 (s, 3H), 1.66 (s, 3H), 1.31 (t, *J*= 7.08 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) : 167.2, 136.6, 128.3, 123.5, 121.4, 60.4, 34.1, 31.9, 18.6, 18.2, 14.4. MS (EI mode) *m/z* (%) : 180(45), 165(29), 151(19), 137(20), 135(29), 133(27), 119(11), 107(100), 105(21), 93(23), 91(49), 79(13), 77(13), 39(10), 29(41), 27(14).

(4,5-dimethylcyclohexa-1,4-dienyl)methanol 38

LiAlH₄ (0.6 eq ; 7.2 mmol) was suspended in dry Et₂O (10 mL) followed by a dropwise addition of the ester **37** (1 eq; 12.1 mmol) allowing the reaction to go to reflux. After letting the reaction stir overnight at room temperature, the reaction was then quenched with water and extracted with Et₂O (x3). Combined organic fractions were washed with brine and dried over Na₂SO₄, and evaporated *in vacuo*. Crude alcohol was further purified by flash chromatography on silica gel (eluent pentane/diethyl ether 7:3) to yield a clear liquid with 98% yield. SiO₂, pentane/Et₂O 7:3, R_F = 0.31. ¹H NMR (400 MHz, CDCl₃) : 5.55-5.52 (m, 1H), 3.80 (s, 2H), 2.54-2.52 (m, 2H), 2.47-2.43 (m, 2H), 1.55-1.54 (m, 6H), 0.95 (br s, 1H). ¹³C NMR (100 MHz, CDCl₃) : 135.8, 123.0, 122.9, 119.8, 66.8, 33.8, 33.7, 18.6, 18.4.

4-(chloromethyl)-1,2-dimethylcyclohexa-1,4-diene 28

Similar procedure as the one used for **8**. Clean crude with 96% yield. ¹H NMR (400 MHz, C₆D₆) : 5.42 (s, 1H), 3.68 (s, 2H), 2.53-2.49 (m, 2H), 2.38-2.37 (m, 2H), 1.47 (s, 3H), 1.45 (s, 3H). ¹³C NMR (100 MHz, C₆D₆) : 132.1, 124.9, 122.8, 122.1, 49.5, 33.9, 33.7, 18.4, 18.1. MS (EI mode) *m/z* (%) : 158(15), 156(48), 121(57), 119(34), 108(10), 107(100), 106(11), 105(53), 93(16), 91(41), 79(20), 77(20), 65(10), 53(11), 51(17), 43(10), 41(23), 39(29), 29(11), 27(21). HRMS (EI) mass calculated for C₉H₁₃Cl = 156.0703, mass found = 156.0706. HR-MS : mass calculated for C₉H₁₃Cl = 137.1331, mass found = 137.1330.

(E)-1,4-dibromo-2-methylbut-2-ene **32**^[7]

Isoprene was distilled over NaBH₄ under nitrogen (b.p. 34°C/1 atm). To 30 mL of *n*-hexane were added consecutively isoprene (60 mmol; 1 eq) and K₂CO₃ (6 mmol; 10%), the resulting mixture was cooled to -50°C before a dropwise addition of bromine (30 mmol; 0.5 eq). After a complete addition, the reaction was left stirring overnight at -30°C. The reaction was then hydrolyzed with water, followed by extraction with Et₂O (x3). Combined organic layers were then rinsed with brine and dried over Na₂SO₄. Crude product was obtained with 95% yield (*E*:*Z* = 92:8). ¹H NMR (400 MHz, CDCl₃) : 5.90 (t, *J* = 8.1 Hz, 1H), 3.98 (s, 1H), 3.95 (s, 3H), 1.87 (s, 3H). ¹³C NMR (100 MHz, C₆D₆) : 138.0, 125.8, 39.1, 27.4, 14.2. MS (EI mode) *m/z* (%) : 228 (2), 145 (75), 147 (77), 119 (10), 68 (35), 67 (100), 65 (24), 53 (26), 51 (15).

(+)-2-Methyl-3-phenyl-1-pentene **3a**

¹H NMR (400 MHz, CDCl₃) : 7.36-7.23 (m, 5H), 4.97 (d, 1H, *J* = 0.8 Hz), 4.89 (t, 1H, *J* = 1.5 Hz), 3.15 (t, 1H, *J* = 7.6 Hz), 1.92 (m, 1H), 1.79 (m, 1H), 1.63 (s, 3H), 0.92 (t, 3H, *J* = 7.3 Hz). ¹³C NMR (100 MHz, CDCl₃) : 148.1, 143.8, 128.2, 127.9, 126.1, 110.3, 54.8, 25.9, 20.9, 12.5. MS (EI mode) *m/z* (%) : 160 (17), 131 (100), 115 (24), 91 (42). $[\alpha]_D^{22} = +39.6$ (*c* 0.9, CHCl₃) for 96% ee. Ee was measured by chiral GC with a Chirasil-Dex CB column, Helium flow (program: 85-30-1-170) R_T: 25.70 (+), 26.53 (-).

(+)-3-(4-Methylphenyl)-2-methyl-1-pentene **9a**

¹H NMR (400 MHz, CDCl₃) : 7.14 (s, 4H), 4.94 (s, 1H), 4.86 (s, 1H), 3.10 (t, 1H, *J* = 6.8 Hz), 2.37 (s, 3H), 1.88 (m, 1H), 1.77 (m, 1H), 1.61 (s, 3H), 0.90 (t, 3H, *J* = 7.0 Hz). ¹³C NMR (100 MHz, CDCl₃) : 148.3, 140.8, 135.5, 128.9, 127.8, 110.1, 54.4, 25.9, 21.1, 20.9, 12.6. MS (EI mode) *m/z* (%) : 174 (20), 159 (8), 145 (100), 146 (12), 130 (22), 129 (17), 128 (14), 117 (10), 115 (17), 105 (28), 91 (11). $[\alpha]_D^{22} = +25.9$ (*c* 0.54, CHCl₃) for 96% ee. Ee was measured by chiral GC with a Hydrodex B6-TBDM column, Hydrogen flow (program: 100-0-1-170) R_T: 11.60 (+), 12.08 (-).

(+)-3-(4-Chlorophenyl)-2-methyl-1-pentene **10a**

¹H NMR (400 MHz, CDCl₃) : 7.29 (d, 2H, *J* = 8.4 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 4.93 (t, 1H, *J* = 0.9 Hz), 4.88 (d, 1H, *J* = 1.6 Hz), 3.10 (t, 1H, *J* = 7.6 Hz), 1.87 (m, 1H), 1.74 (m, 1H), 1.47 (s, 3H), 0.88 (t, 3H, *J* = 7.3 Hz). ¹³C NMR (100 MHz, CDCl₃) : 147.6, 142.3, 129.3, 128.3, 110.7, 54.1, 27.0, 25.8, 20.9, 12.4. MS (EI mode) *m/z* (%) : 194 (16), 167 (33), 165 (100), 159 (19), 130 (64), 129 (48), 128 (26), 127 (21), 125 (33), 115 (35). $[\alpha]_D^{22} = +36.0$ (*c* 0.58, CHCl₃) for 96% ee. Ee was measured by chiral GC with a Hydrodex B6-TBDM column, Hydrogen flow (program: 130-0-1-170) R_T: 8.14 (+), 8.47 (-).

(+)-2-Ethyl-3-phenyl-1-pentene **11a**

¹H NMR (400 MHz, CDCl₃) : 7.37-7.24 (m, 5H), 5.05 (s, 1H), 4.96 (d, 1H, *J* = 1.2 Hz), 3.18 (t, 1H, *J* = 7.3 Hz), 1.94 (m, 3H), 1.81 (m, 1H), 1.04 (t, 3H, *J* = 7.5 Hz), 0.93 (t, 3H, *J* = 7.3 Hz). ¹³C NMR (100 MHz, CDCl₃) : 153.8, 144.2, 128.2, 128.1, 126.1, 107.6, 53.9, 27.6, 26.8, 12.6, 12.3. MS (EI mode) *m/z* (%) : 174 (22), 146 (13), 145 (100), 130 (13), 129 (12), 128 (10), 117 (35), 115 (23), 105 (10), 91 (42). $[\alpha]_D^{22} = +66.2$ (*c* 1.09, CHCl₃) for 92% ee. Ee was measured by chiral GC with a Hydrodex B6-TBDM column, Hydrogen flow (program: 90-0-1-170) R_T: 13.67 (+), 14.07 (-).

(+)-(*R*)-1-ethyl-2-methylene-1,2,3,4-tetrahydronaphthalene **12a**

SiO₂, pentane, R_F = 0.7 IR (neat) : 3069 (s), 2958 (s), 2928 (s), 2871 (s), 1652 (s), 1487 (s), 1451 (s), 889 (s), 740 (s), 675 (s). ¹H NMR (400 MHz, CDCl₃) : 0.94 (t, 3 H, *J* = 7.32 Hz), 1.52-1.66 (m, 1 H), 1.72-1.82 (m, 1 H), 2.37-2.41 (m, 1 H), 2.46-2.54 (m, 1 H), 2.79-2.87 (m, 1 H), 2.93-2.97 (m, 1 H), 3.20 (dd, 1 H, *J* = 4.28 Hz, *J* = 10.12 Hz), 4.83 (s, 1 H), δ 4.91 (s, 1 H), 7.09-7.18 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) : 147.6, 141.6, 136.4, 128.9, 128.7, 126.0, 125.8, 109.5, 49.1, 31.5, 31.3, 28.8, 12.5. MS (EI mode) *m/z* (%) : 172(53), 144(26), 143(100), 141(18), 129(25), 128(68), 127(13), 115(23), 91(11). $[\alpha]_D^{22} = +95.07$ (*c* 0.95, CHCl₃) for 98% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 70-0-1-170-5) R_T : 45.22 (S), 46.22 (R).

(+)-2-Methyl-3-phenyl-1-hexene **13a**

⁷ U.S. Pat. Appl. Publ., 2002107422, 08 Aug 2002.

SiO₂, pentane, R_F = 0.69. ¹H NMR (400 MHz, CDCl₃) : 7.31-7.20 (m, 5H), 4.92 (m, 1H), 4.83 (m, 1H), 3.22 (t, 1H, *J* = 7.7 Hz), 1.88-1.58 (m, 2H), 1.58 (s, 3H), 1.30-1.22 (m, 2H), 0.91 (t, 3H, *J* = 7.3 Hz). ¹³C NMR (100 MHz, CDCl₃) : 148.2, 143.9, 128.1, 127.8, 126.0, 110.1, 52.4, 35.1, 20.9, 20.8, 14.1. MS (EI mode) *m/z* (%) : 174 (15), 131 (100), 115 (15), 91 (40). [α]_D²² = +34.0 (*c* 0.93, CHCl₃) for 97% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 50-10-1-170) R_T: 49.58 (+), 50.63 (-).

(+)-2-Methyl-3-phenyl-1-octene 14a

¹H NMR (400 MHz, CDCl₃) : 7.34-7.24 (m, 5H), 4.96 (d, 1H, *J* = 0.8 Hz), 4.88 (s, 1H), 3.25 (t, 1H, *J* = 7.6 Hz), 1.90-1.71 (m, 2H), 1.63 (s, 3H), 1.39-1.22 (m, 6H), 0.93 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) : 148.4, 144.0, 128.2, 127.9, 126.1, 110.2, 52.9, 32.9, 32.0, 27.5, 22.6, 20.9, 14.2. MS (EI mode) *m/z* (%) : 202 (7), 131 (100), 115 (13), 91 (34). [α]_D²² = +34.4 (*c* 1.13, CHCl₃) for 96% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 50-10-1-170) R_T: 73.79 (+), 74.66 (-).

(+)-2-Methyl-3-phenyl-1,6-heptadiene 15a

¹H NMR (400 MHz, CDCl₃) : 7.34-7.25 (m, 5H), 5.90-5.83 (m, 1H), 5.07-4.97 (m, 3H), 4.90 (s, 1H), 3.28 (t, 1H, *J* = 7.2 Hz), 2.04-1.86 (m, 4H), 1.62 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) : 147.9, 143.6, 138.7, 128.3, 127.9, 126.2, 114.7, 110.4, 52.0, 32.2, 31.9, 21.0. MS (EI mode) *m/z* (%) : 186 (3), 158 (15), 143 (100), 131 (82), 117 (36), 104 (15), 91 (78). [α]_D²² = +49.5 (*c* 0.88, CHCl₃) for 95% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 80-0-1-170) R_T: 26.38 (+), 27.15 (-).

(+)-2-Methyl-3-phenyl-1,7-octadiene 16a

¹H NMR (400 MHz, CDCl₃) : 7.36-7.25 (m, 5H), 5.88-5.79 (m, 1H), 5.07-4.97 (m, 3H), 4.89 (s, 1H), 3.28 (m, 1H), 2.11 (m, 2H), 1.91 (m, 1H), 1.80 (m, 1H), 1.63 (s, 3H), 1.43-1.35 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) : 148.1, 143.8, 138.9, 128.2, 127.9, 126.2, 114.5, 110.3, 52.7, 33.9, 32.4, 27.2, 21.0. MS (EI mode) *m/z* (%) : 200 (3), 172 (14), 157 (12), 131 (100), 115 (22), 91 (50). [α]_D²² = +36.0 (*c* 1.02, CHCl₃) for 93% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 90-0-1-170) R_T: 26.73 (+), 29.33 (-).

(+)-(R)-1-butyl-2-methylene-1,2,3,4-tetrahydronaphthalene 17a^[8]

SiO₂, pentane, R_F = 0.71. IR (neat) : 3069 (s), 2955 (s), 2927 (s), 2856 (s), 1652 (s), 1487 (s), 1452 (s), 888 (s), 742 (s), 676 (s), 612 (s). ¹H NMR (400 MHz, CDCl₃) : 0.90 (t, 3 H, *J* = 6.32), 1.22-1.45 (m, 6 H), 2.37-2.40 (m, 1 H), δ 2.47-2.55 (m, 1 H), 2.78-2.86 (m, 1 H), δ 2.93-2.9 (m, 1 H), 3.28 (dd, 1 H, *J* = 4.56 Hz, *J* = 10.12 Hz), 4.81 (s, 1 H), δ 4.88 (s, 1 H), δ 7.08-7.19 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) : 148.1, 128.8, 128.7, 125.7, 125.4, 122.1, 109.3, 47.4, 38.3, 31.7, 30.1, 28.6, 22.7, 14.2. MS (EI mode) *m/z* (%) : 201(10), 200(60), 144(44), 143(100), 142(12), 141(20), 129(36), 128(58), 127(11), 115(16). [α]_D²² = +100.01 (*c* 0.86, CHCl₃) for 98% ee; Lit.¹¹ [α]_D²² = +62.8 (*c* 2.08, THF) for 66% ee (*R*)-enantiomer. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 90-0-1-170-5) R_T : 40.98 (*S*), 42.40 (*R*).

(+)-(R)-2-methylene-1-phenethyl-1,2,3,4-tetrahydronaphthalene 18a

SiO₂, pentane, R_F = 0.41. IR (neat) : 3063 (s), 2927 (s), 2856 (s), 1652 (s), 1602 (s), 1495 (s), 1452 (s), 888 (s), 742 (s), 697 (s), 676 (s), 613 (s). ¹H NMR (400 MHz, CDCl₃) : δ 1.78-1.94 (m, 1 H), δ 1.95-2.03 (m, 1 H), δ 2.37-2.42 (m, 1 H), δ 2.49-2.71 (m, 3 H), δ 2.74-2.84 (m, 1 H), δ 2.90-2.96 (m, 1 H), δ 3.31 (dd, 1 H, *J* = 4.52 Hz, *J* = 10.36 Hz), δ 4.85 (s, 1 H), δ 4.93 (s, 1 H), δ 7.04-7.17 (m, 6 H), δ 7.22-7.27 (m, 3 H). ¹³C NMR (100 MHz, CDCl₃) : δ 147.6, 142.4, 141.3, 128.8, 128.7, 128.6, 128.5, 128.4, 126.1, 125.9, 125.8, 122.6, 110.0, 46.9, 39.9, 33.9, 31.5, 28.8. MS (EI mode) *m/z* (%) : 249(14), 248(68), 157(28), 144(50), 143(100), 142(12), 141(16), 129(27), 128(52), 115(14), 105(23), 91(21). [α]_D²² = + 115.22 (*c* 0.81, CHCl₃) for 96.4% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 90-0-1-170-5) R_T : 40.25 (*S*), 41.69 (*R*).

(+)-2 Methyl-3-phenylcyclopentene 19^[9]

⁸ M. Scommoda, H.-J. Gais, S. Bosshammer, G. Raabe, *J. Org. Chem.* **1996**, *61*, 4379-4390.

⁹ Heck, R. F. *J. Am. Chem. Soc.* **1971**, *93*, 6896-6901.

^1H NMR (400 MHz, CDCl_3) : 7.34-7.19 (m, 5H), 5.60 (m, 1H), 3.67 (m, 1H), 2.51-2.41 (m, 3H), 1.88 (m, 1H), 1.58 (d, 3H, $J = 1.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3) : 145.9, 142.7, 128.4, 127.6, 126.3, 126.0, 55.2, 34.6, 31.6, 15.2. MS (EI mode) m/z (%) : 158 (81), 143 (100), 128 (50), 115 (28), 91 (13). $[\alpha]_D^{22} = +172.8$ (c 0.78, CHCl_3) for 97% ee. Ee was measured by chiral GC with a Lipodex E column, Hydrogen flow (program: iso 60) R_T : 16.23 (+), 17.36 (-).

(+)-2-Methyl-3-phenylcyclohexene 20^[10]

^1H NMR (400 MHz, CDCl_3) : 7.36-7.23 (m, 5H), 5.74 (m, 1H), 3.31 (m, 1H), 2.14 (m, 2H), 2.03 (m, 1H), 1.71 (m, 1H), 1.57 (d, 3H, $J = 1.8$ Hz), 1.63-1.49 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) : 145.6, 134.7, 128.5, 128.2, 125.9, 124.4, 45.9, 32.8, 25.6, 22.8, 18.9. MS (EI mode) m/z (%) : 172 (100), 157 (36), 143 (52), 129 (80), 115 (29), 104 (48), 91 (41), 79 (14). $[\alpha]_D^{22} = +140.8$ (c 1.02, CHCl_3) for 96% ee. Ee was measured by chiral GC with a Hydrodex B-3P column, Hydrogen flow (program: 90-0-1-170) R_T : 22.96 (-), 23.49 (+).

(+)-(S)-1-butyl-2-methylenecyclopentane 23a^[11]

MS (EI mode) m/z (%) : 138 (4), 96 (16), 95 (30), 82 (75), 81 (100), 79 (37), 77 (10), 68 (10), 67 (78), 55 (21), 53 (24). $[\alpha]_D^{25} = +31$ (c 0.30, CHCl_3) for 98% ee. Ee was measured by chiral GC with a Lipodex G column, Hydrogen flow (program: 50-0-1-170), R_T : 13.03 (-), 13.61 (+).

(+)-(S)-1-hexyl-2-methylenecyclopentane 23b

SiO_2 , pentane, $R_F = 0.95$. ^1H -NMR (CDCl_3 , 400 MHz) : 4.85 (s, 1H), 4.77 (s, 1H), 2.35-2.26 (m, 3H), 1.89-1.85 (m, 1H), 1.75-1.65 (m, 1H), 1.61-1.46 (m, 2H), 1.31-1.28 (m, 10H), 0.89 (t, $J=7.1$ Hz, 3H). ^{13}C -NMR (CDCl_3 , 100 MHz) : 157.5, 104.0, 44.2, 34.7, 33.4, 32.9, 32.1, 29.7, 28.0, 24.4, 22.8, 14.3. MS (EI mode) m/z (%) : 166(M^+ , 6), 109(10), 96(34), 95(42), 83(13), 82(100), 81(95), 80(14), 79(21), 68(18), 67(81), 57(11), 55(28), 54(12), 53(17). $[\alpha]_D^{25} = +73.2$ (c 1.23, CHCl_3) for 98% ee. Ee was measured by chiral GC with a Heptakis-(2,3-O-diglykol-6-O-tert-butylidimethylsilyl)- β -cyclodextrin column, Helium flow, R_T : 196.99 (-), 200.36 (+).

(+)-(R)-1-(4-tert-butoxybutyl)-2-methylenecyclopentane 23c

SiO_2 , pentane/diethyl ether 97.5:2.5, $R_F = 0.41$. ^1H -NMR (CDCl_3 , 400 MHz) : 4.86 (m, 1H), 4.77 (m, 1H), 3.34 (t, $J = 6.6$ Hz, 2H), 2.32-2.23 (m, 3H), 1.94-1.86 (m, 1H), 1.76-1.22 (m, 9H), 1.19 (s, 9H). ^{13}C -NMR (CDCl_3 , 100 MHz) : 157.4, 104.1, 72.6, 61.7, 44.1, 34.5, 33.4, 32.9, 31.0, 27.7, 24.7, 24.4. MS (EI mode) m/z (%) : 154 (49), 153 (28), 137 (10), 136 (11), 135 (52), 121 (20), 109 (13), 108 (20), 107 (20), 95 (67), 94 (22), 93 (30), 82 (45), 18 (86), 80 (13), 79 (36), 77 (11), 71 (14), 69 (14), 67 (49), 59 (20), 58 (12), 57 (100), 55 (38), 53 (18). $[\alpha]_D^{25} = +63.93$ (c 1.22, CHCl_3) for 96% ee. Ee was measured by chiral GC analysis of **23g**.

(+)-(R)-(2-(2-Methylenecyclopentyl)ethyl)benzene 23d^[11]

SiO_2 , pentane, $R_F = 0.7$. ^1H -NMR (CDCl_3 , 400 MHz) : 7.30-7.17 (m, 5H), 4.89 (s, 1H), 4.80 (s, 1H), 2.76-2.58 (m, 2H), 2.43-2.29 (m, 3H), 2.02-1.90 (m, 2H), 1.88-1.70 (m, 1H), 1.61-1.49 (m, 2H), 1.39-1.30 (m, 1H). ^{13}C -NMR (CDCl_3 , 100 MHz) : 156.9, 142.9, 128.5, 128.5, 128.4, 128.4, 125.8, 104.4, 43.7, 36.5, 34.3, 33.4, 32.9, 24.3. MS (EI mode) m/z (%) : 186 (M^+ , 8), 105 (36), 104 (100), 95 (58), 94 (11), 92 (26), 91 (53), 82 (40), 81 (37), 80 (16), 67 (44), 65 (15), 55 (10), 53 (11). $[\alpha]_D^{25} = +77.3$ (c 0.62, CHCl_3) for 98% ee. Ee was measured by chiral GC with a Hydrodex-B-3P column, Hydrogen flow (program: 80-250-1-170), R_T : 272.16(+), 273.91(-).

(R)-1-methylene-2-(4-methylpent-3-enyl)cyclopentane 23f

SiO_2 , pentane, $R_F = 0.81$. IR (neat): 2965 (s), 2924 (s), 2855 (s), 2722 (w), 1652 (m), 1448 (br s), 1376 (m), 1105 (w), 976 (m), 877 (s), 833 (m), 731 (w) cm^{-1} . ^1H -NMR (CDCl_3 , 400 MHz) : 5.14-5.12 (m, 1H), 4.86 (s, 1H), 4.77 (s, 1H), 2.30-2.27 (m, 1H), 2.04-1.94 (m, 4H), 1.68-1.58 (m, 6H), 1.38-1.27 (m, 6H). ^{13}C -NMR (CDCl_3 , 100 MHz) : 157.3, 131.5, 124.9, 104.1, 43.8, 34.8, 33.4, 32.9, 26.5, 24.4, 22.5, 17.8. MS (EI mode) m/z (%) : 164 (5), 149 (12), 121 (25), 108 (14), 107 (12), 95 (51), 94 (29), 93 (42), 91 (24), 82 (100), 81 (36), 79 (75), 77 (31), 69 (36), 67 (96), 65 (15), 55 (54), 53 (40), 51 (11). Ee was measured by chiral GC with a Hydrodex B-3P column, Hydrogen flow (program: iso 80°C), R_T : 39.99 (minor), 40.86 (major).

¹⁰ Mehta, G.; Singh, B. P. *Tetrahedron* **1974**, *30*, 2409-2412.

(+)-(S)-1-butyl-2-methylenecyclohexane **24a**

¹H-NMR (CDCl₃, 400 MHz): 4.63 (s, 1H), 4.56 (s, 1H), 2.24-2.19 (m, 1H), 2.03-1.89 (m, 2H), 1.78-1.20 (m, 12H), 0.91-0.87 (m, 3H). ¹³C-NMR (CDCl₃, 100 MHz): 153.5, 105.4, 43.3, 35.0, 34.0, 32.0, 29.9, 29.1, 24.4, 23.1, 14.3. MS (EI mode) *m/z* (%): 152 (5), 130 (7), 109 (10), 96 (80), 95 (56), 91 (12), 83 (14), 82 (20), 81 (100), 79 (20), 77 (11), 68 (18), 67 (50), 55 (32), 54 (13), 53 (18). [α]_D²⁵ = +50.68 (c 0.58, CHCl₃) for 97% *ee*. *Ee* was measured by chiral GC with a Chirasil-Dex CB column, Helium flow (program: iso 55°C), R_T: 108.9 (+), 112.0 (-).

(+)-1-hexyl-2-methylenecyclohexane **24b**

SiO₂, pentane, R_F = 0.85. ¹H-NMR (CDCl₃, 300 MHz): 4.63 (s, 1H), 4.56 (s, 1H), 2.26-2.18 (m, 1), 2.05-1.96 (m, 2H), 1.79-1.38 (m, 6H), 1.28-1.21 (m, 10H), 0.88 (t, *J*=9.4 Hz, 3H). ¹³C-NMR (CDCl₃, 75 MHz): 153.4, 105.3, 43.2, 34.8, 33.9, 32.2, 31.9, 29.6, 28.9, 27.5, 24.3, 22.7, 14.2. MS (EI mode) *m/z* (%): 180 (4), 109(13), 97(11), 96(100), 95(52), 82(14), 81(54), 68(15), 67(31), 55(19). [α]_D²⁵ = +33.3 (c 1.11, CHCl₃) for 98% *ee*. *Ee* was measured by chiral GC with a Hydrodex B6-TBDM column, Hydrogen flow (program: iso 95°C), R_T: 29.95 (-), 31.06 (+).

(+)-1-(4-tert-butoxybutyl)-2-methylenecyclohexane **24c**

SiO₂, pentane/diethyl ether 97.5:2.5, R_F = 0.33. ¹H-NMR (CDCl₃, 400 MHz): 4.63 (s, 1H), 4.56 (s, 1H), 3.34-3.30 (m, 2H), 2.22-2.19 (m, 1H), 2.04-1.99 (m, 2H), 1.90-1.21 (m, 12H), 1.18 (s, 9H). ¹³C-NMR (CDCl₃, 100 MHz): 153.3, 105.5, 72.6, 61.8, 43.2, 35.0, 34.0, 32.1, 31.0, 29.0, 27.8, 27.7 (x3), 24.4, 24.3. MS (EI mode) *m/z* (%): 168 (60), 167 (17), 150 (14), 149 (61), 135 (18), 122 (11), 121 (17), 109 (39), 108 (16), 107 (20), 97 (10), 96 (63), 95 (84), 94 (13), 93 (29), 91 (10), 83 (30), 82 (14), 81 (73), 80 (10), 79 (32), 77 (14), 71 (27), 69 (27), 68 (17), 67 (69), 59 (29), 58 (16), 57 (100), 56 (13), 55 (65), 54 (11), 53 (24). [α]_D²⁵ = -14.89 (c 1.07, CHCl₃) for 74% *ee* for *ent*-**23c**. *Ee* was measured by chiral GC with a Hydrodex B6 TBDM column, Hydrogen flow (program: iso 110°C), R_T: 44.71 (-), 46.26 (+).

(+)-(R)-(2-(2-methylenecyclohexyl)ethyl)benzene **24d**

SiO₂, pentane, R_F = 0.61. ¹H-NMR (CDCl₃, 300 MHz): 7.31-7.27 (m, 2H), 7.21-7.16 (m, 3H), 4.70 (s, 1H), 4.62 (s, 1H), 2.64-2.56 (m, 2H), 2.30-2.21 (m, 1H), 2.14-1.41 (m, 9H), 1.36-1.26 (m, 1H). ¹³C-NMR (CDCl₃, 80 MHz): 152.8, 143.1, 128.6, 128.6, 128.4, 128.4, 125.7, 106.0, 42.9, 34.8, 34.3, 34.1, 33.9, 29.0, 24.3. MS (EI mode) *m/z* (%): 200(4), 109(23), 105(27), 104(100), 96(67), 95(25), 94(14), 92(15), 91(42), 81(43), 79(13), 77(12), 68(10), 67(31), 65(12), 55(16). [α]_D²⁵ = -17.87 (c 1.50, CHCl₃) for 87% *ee* for *ent*-**23d**. *Ee* was measured by chiral GC with a Hydrodex B6 TBDM column, Hydrogen flow (program: iso 110°C), R_T: 93.3 (-), 95.8 (+).

(+)-1-(but-3-enyl)-2-methylenecyclohexane **24e**

SiO₂, pentane, R_F = 0.93. ¹H-NMR (CDCl₃, 400 MHz): 5.83 (*ddt*, *J*=10.1 Hz, *J*=16.9 Hz, *J*= 6.6Hz, 1H), 5.01 (*dq*, *J*=16.9 Hz, *J*=1.5 Hz, 1H), 4.95 (*dt*, *J*=10.1 Hz, *J*=1.0 Hz, 1H), 4.66 (s, 1H), 4.57 (s, 1H), 2.25-2.19 (m, 1H), 2.08-1.98 (m, 4H), 1.79-1.32 (m, 7H), 1.30-1.22 (m, 1H). ¹³C-NMR (CDCl₃, 100 MHz): 152.9, 139.3, 114.3, 105.8, 42.6, 34.8, 33.9, 31.8, 31.4, 29.0, 24.3. MS (EI mode) *m/z* (%): 150 (14), 135 (25), 122 (21), 121 (35), 109 (21), 108 (33), 107 (20), 96 (46), 95 (49), 94 (27), 93 (40), 91 (12), 83 (12), 82 (15), 81 (100), 80 (24), 79 (44), 77 (14), 69 (11), 68 (34), 67 (90), 55 (60), 54 (21), 53 (24). [α]_D²⁵ = +37.3 (c 1.24, CHCl₃) for 99.2% *ee*. *Ee* was measured by chiral GC with a Chirasil-Dex CB, Helium flow (program: 60-0-1-170), R_T: 29.1 (+), 29.5 (-).

(+)-(S)-1-butyl-2-methylenecycloheptane **26**

52% yield. SiO₂, pentane, R_F = 0.93. ¹H NMR (400 MHz, CDCl₃): 4.76 (*d*, *J*= 2.0Hz, 1H), 4.65 (*d*, *J*= 2.2Hz, 1H), 2.20-2.15 (m, 2H), 2.02-1.92 (m, 1H), 1.88-1.81 (m, 2H), 1.79-1.62 (m, 2H), 1.29-1.07 (m, 10H), 0.89-0.86 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): 155.5, 111.3, 46.2, 36.2, 34.5, 33.4, 31.4, 30.6, 29.9, 26.6, 23.0, 14.3. MS (EI mode) *m/z* (%): 166 (8), 123 (10), 110 (67), 111 (40), 96 (18), 95 (63), 93 (13), 91 (18), 82 (59), 81 (93), 79 (39), 77 (21), 69 (19), 68 (32), 67 (100), 65 (14), 55 (49), 54 (12), 53 (25). [α]_D²² = +79.26 (c 0.35, CHCl₃) for 96% *ee*; Lit.¹¹ [α]_D²² = +35.7 (c 0.85, THF) for 60% *ee*. *Ee* was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 60-20-1-170) R_T: 44.60 (+), 47.70(-).

¹¹ a) J. Bund, H. J. Gais, I. Erdelmeier, *J. Am. Chem. Soc.* **1991**, *113*, 1442; b) H.-J. Gais, H. Mueller, J. Bund, M. Scommoda, J. Brandt, G. Raabe, *J. Am. Chem. Soc.* **1995**, *117*, 2453.

(+)-(R)-1-methylene-2-phenethylcycloheptane 27

SiO₂, pentane, R_F = 0.85. IR (neat): 3064(w), 3026(w), 2921(s), 2851(m), 1637(w), 1603(w), 1496(m), 1453(m), 1342(w), 1030(w), 886(s), 746(m), 696(s), 655(m) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.29-7.26 (m, 2H), 7.19-7.15 (m, 3H), 4.84 (s, 1H), 4.72 (s, 1H), 2.68-2.50 (m, 2H), 2.29-2.19 (m, 2H), 2.09-2.00 (m, 1H), 1.93-1.81 (m, 4H), 1.38-1.14 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): 154.8, 143.2, 128.6, 128.6, 128.5, 128.5, 125.8, 45.9, 38.1, 34.7, 34.0, 33.6, 31.4, 30.6, 26.7. MS (EI mode) *m/z* (%): 214 (10), 129 (16), 128 (15), 123 (20), 117 (19), 115 (18), 110 (70), 105 (17), 104 (47), 95 (37), 92 (15), 91 (100), 82 (33), 81 (93), 79 (31), 77 (29), 68 (15), 67 (57), 65 (34), 55 (27), 53 (17), 51 (11). $[\alpha]_D^{22} = +69.70$ (c 0.89, CHCl₃) for 97% *ee*. *Ee* was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 90-0-1-170) R_T: 61.04 (+), 62.02(-).

(+)-(2-(3,4-dimethyl-6-methylenecyclohex-3-enyl)ethyl)benzene 29

SiO₂, pentane, R_F = 0.6. IR (neat): 3064 (w), 3026 (w), 2982 (w), 2912 (m), 2857 (m), 1650 (m), 1496 (m), 1453 (m), 1382 (w), 1030 (w), 883 (s), 749 (m), 697 (s) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 7.30-7.28 (m, 2H), 7.20-7.16 (m, 3H), 4.77 (s, 1H), 4.72 (s, 1H), 2.68 (s, 2H), 2.61 (t, *J* = 8.1 Hz, 2H), 2.32-2.29 (m, 2H), 1.93-1.83 (m, 2H), 1.65-1.58 (m, 7H). ¹³C NMR (100 MHz, CDCl₃): 149.4, 143.0, 128.6, 128.4, 125.8, 124.6, 124.5, 106.3, 40.9, 40.6, 39.4, 34.3, 33.9, 19.1, 18.7. MS (EI mode) *m/z* (%): 226(9), 135(15), 123(12), 122(100), 121(55), 120(9), 107(83), 105(23), 93(14), 91(41), 79(13), 77(13), 41(14). HR-MS: mass calculated for C₁₀H₁₇ = 137.1331, mass found = 137.1330. $[\alpha]_D^{22} = +51.82$ (c 0.69, CHCl₃) for 72% *ee*. *Ee* was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 110-0-1-170-10) R_T: 46.54 (+), 47.00(-) and by SFC on OJ-column (200 bars, 2%-2-1-15%, 30°C) R_T: 3.54 (+), 4.64(-)

4-butyl-1,2-dimethyl-5-methylenecyclohex-1-ene 30

SiO₂, pentane, R_F = 0.95. ¹H NMR (400 MHz, CDCl₃): 4.72 (s, 1H), 4.67 (s, 1H), 2.65 (br s, 2H), 2.26-2.20 (m, 2H), 1.64-1.53 (m, 6H), 1.43-1.26 (m, 6H), 0.91-0.87 (m, 3H). ¹³C NMR (100 MHz, CDCl₃): 150.1, 124.8, 124.5, 105.7, 41.3, 40.6, 39.5, 31.8, 29.9, 23.0, 19.1, 18.7, 14.2. MS (EI mode) *m/z* (%): 178 (10), 133 (40), 122 (55), 121 (48), 119 (15), 107 (100), 105 (36), 93 (27), 91 (45), 79 (24), 77 (25), 65 (10), 55 (10), 53 (10). *Ee* was measured by chiral GC with a Hydrodex B-3P, Hydrogen flow (program: 80-0-1-170) R_T: 23.80 (major), 25.29 (minor).

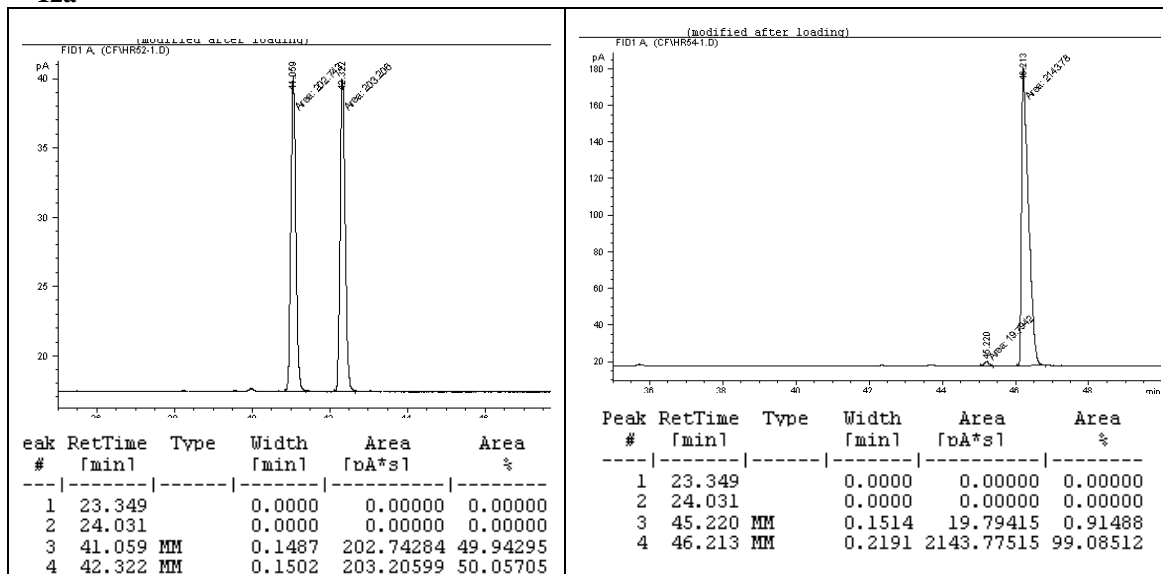
(+)-4-(4-tert-butoxybutyl)-1,2-dimethyl-5-methylenecyclohex-1-ene 31

SiO₂, 98:2 pentane/Et₂O, R_F = 0.39. ¹H NMR (400 MHz, CDCl₃): 4.71 (s, 1H), 4.66 (s, 1H), 3.34-3.30 (m, 2H), 2.65 (br s, 2H), 2.27-2.23 (m, 1H), 1.98-1.94 (m, 1H), 1.81-1.75 (m, 1H), 1.64-1.61 (m, 6H), 1.49-1.25 (m, 6H), 1.18 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): 150.0, 124.7, 124.5, 105.7, 72.6, 61.7, 41.2, 40.5, 39.4, 32.2, 30.8, 27.7, 24.3, 19.0, 18.7. MS (EI mode) *m/z* (%): 250(6), 194(12), 176(12), 175(72), 133(66), 122(12), 121(56), 120(16), 119(100), 107(50), 105(23), 95(16), 93(12), 91(19), 79(10), 69(10), 57(94), 55(15). HR-MS: mass calculated for C₁₇H₃₀ONa = 273.2194, mass found = 273.2195. $[\alpha]_D^{22} = +33.36$ (c 0.79 in CHCl₃) for 84% *ee*. *Ee* was measured by chiral GC with a Chirasil Dex CB, Helium flow (program: 100-0-1-170-5) R_T: 45.39 (+), 45.85(-).

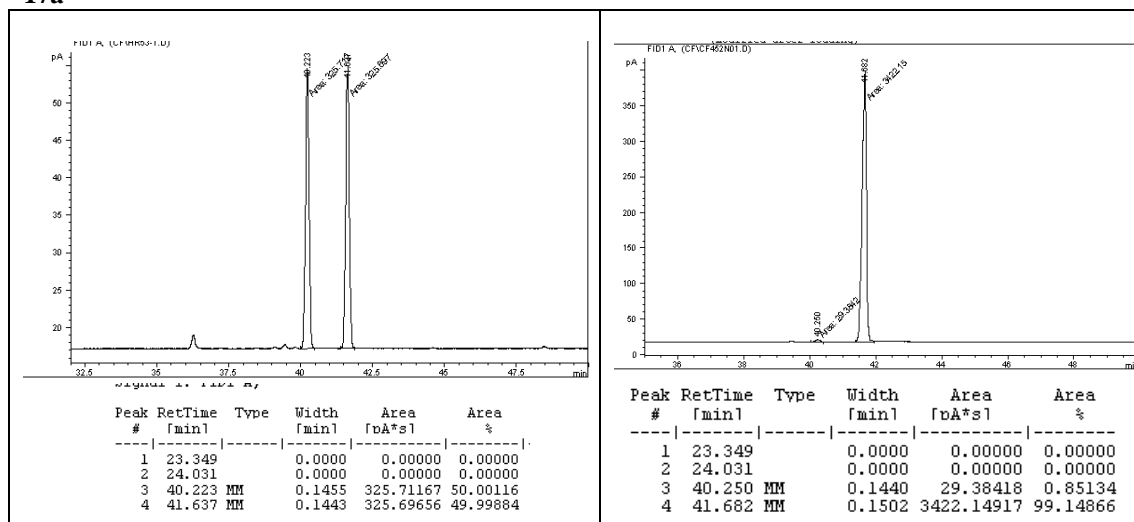
3-(bromomethyl)-2-methylhept-1-ene 33

SiO₂, pentane, R_F = 0.95. ¹H NMR (400 MHz, CDCl₃): 4.89 (s, 1H), 4.78 (s, 1H), 3.38 (d, *J* = 6.6 Hz, 2H), 2.40 (quint, *J* = 7.1 Hz, 1H), 1.66 (s, 3H), 1.59-1.50 (m, 1H), 1.45-1.19 (m, 5H), 0.89 (t, *J* = 7.1 Hz, 3H). MS (EI mode) *m/z* (%): 150(7), 148(7), 95(5), 91(5), 83(6), 79(6), 69(100), 68(14), 67(36), 55(29), 53(15). *Ee* was measured by chiral GC with a Hydrodex B6-TBDM, Hydrogen flow (program: 70-0-1-170) R_T: 21.41 (minor), 21.93 (major). [for **34**: *Ee* was measured by chiral GC with a Hydrodex B3P, Hydrogen flow (program: 80-0-1-170) R_T: 16.38 (major), 16.66 (minor)].

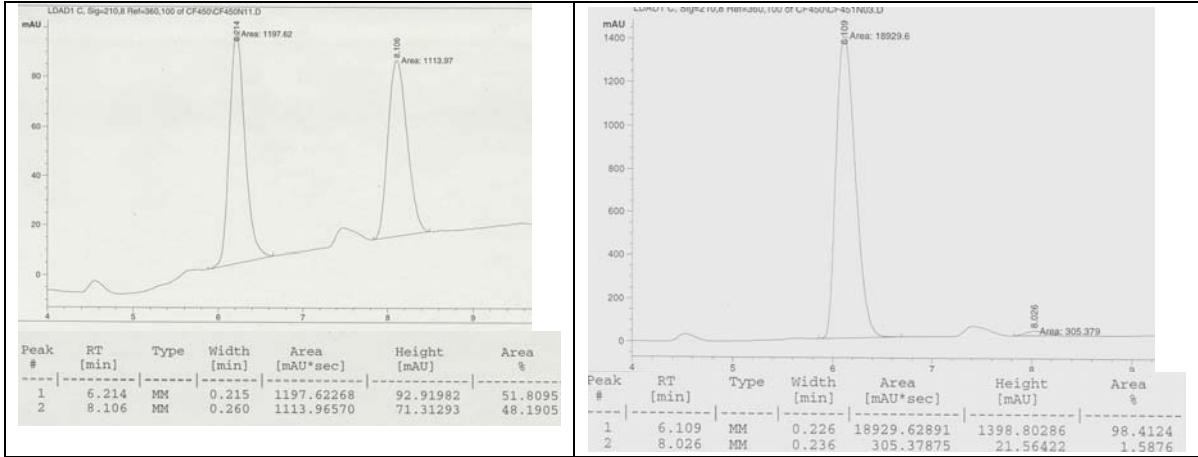
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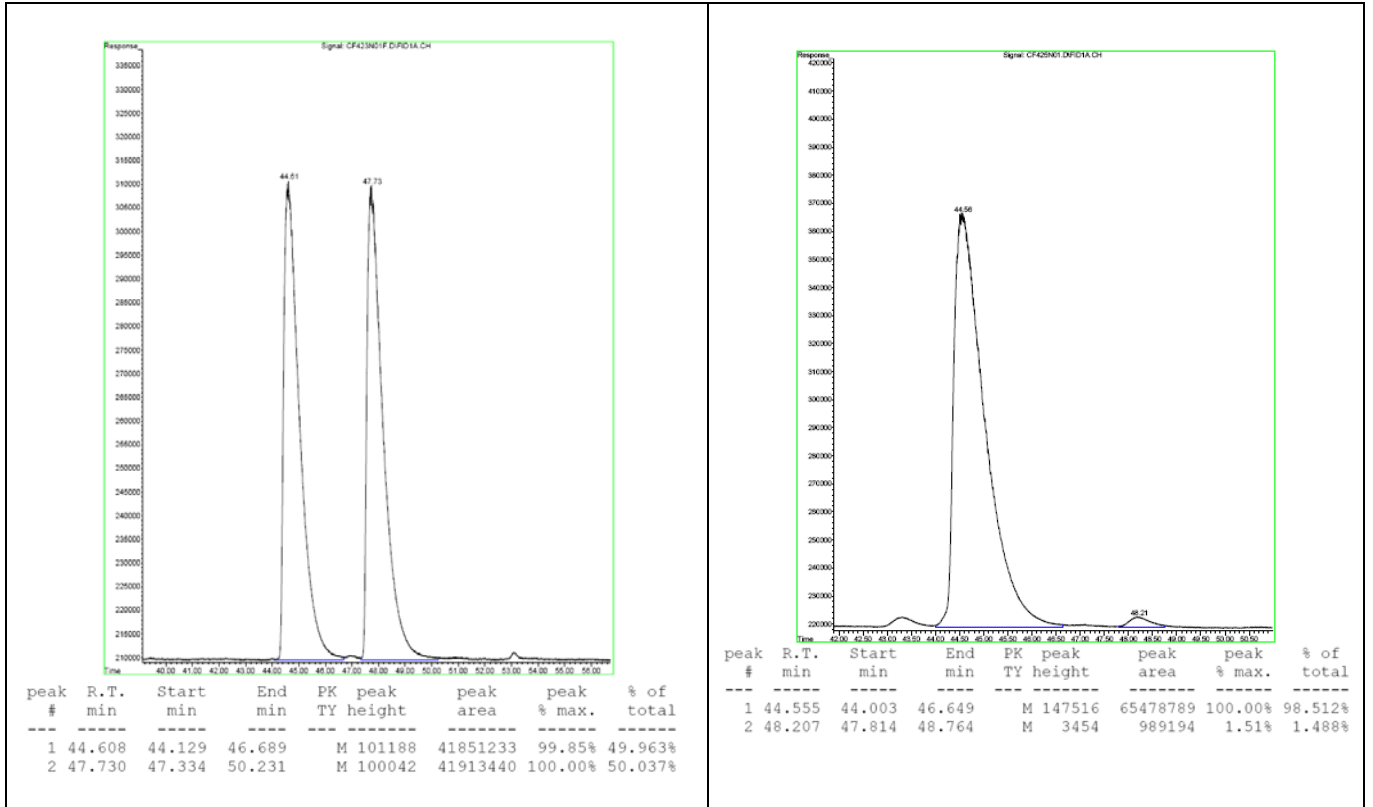
17a



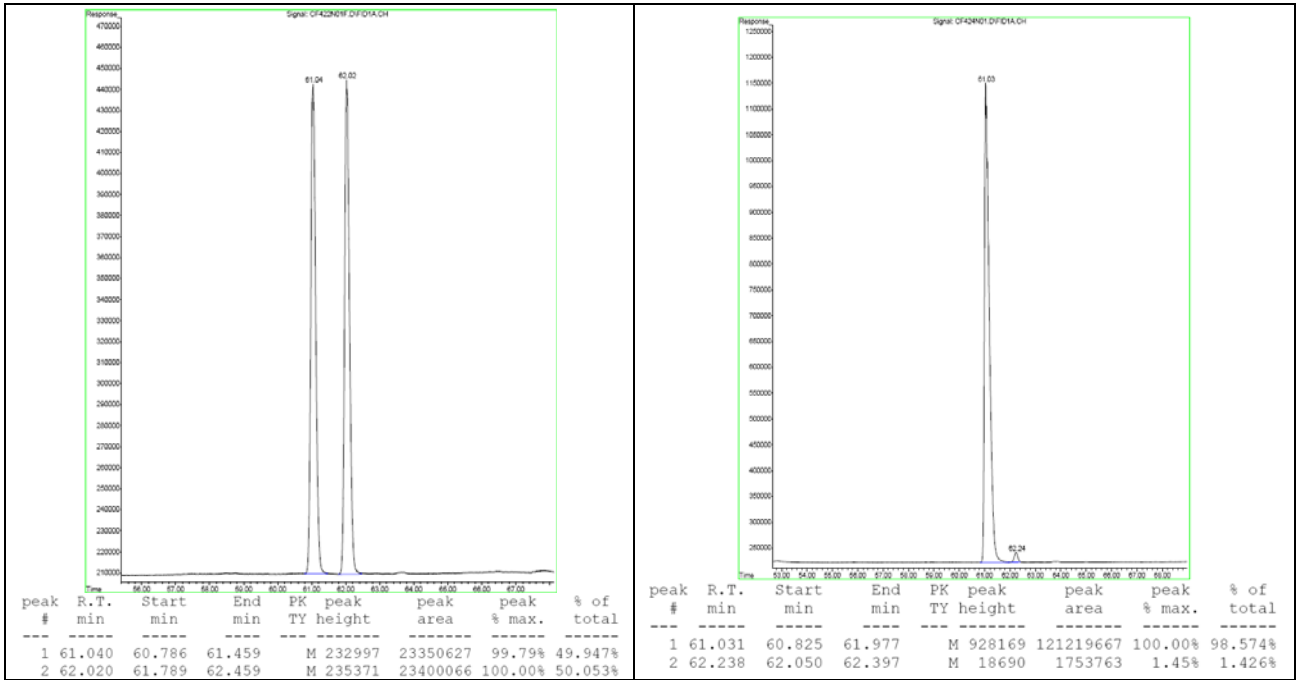
18a



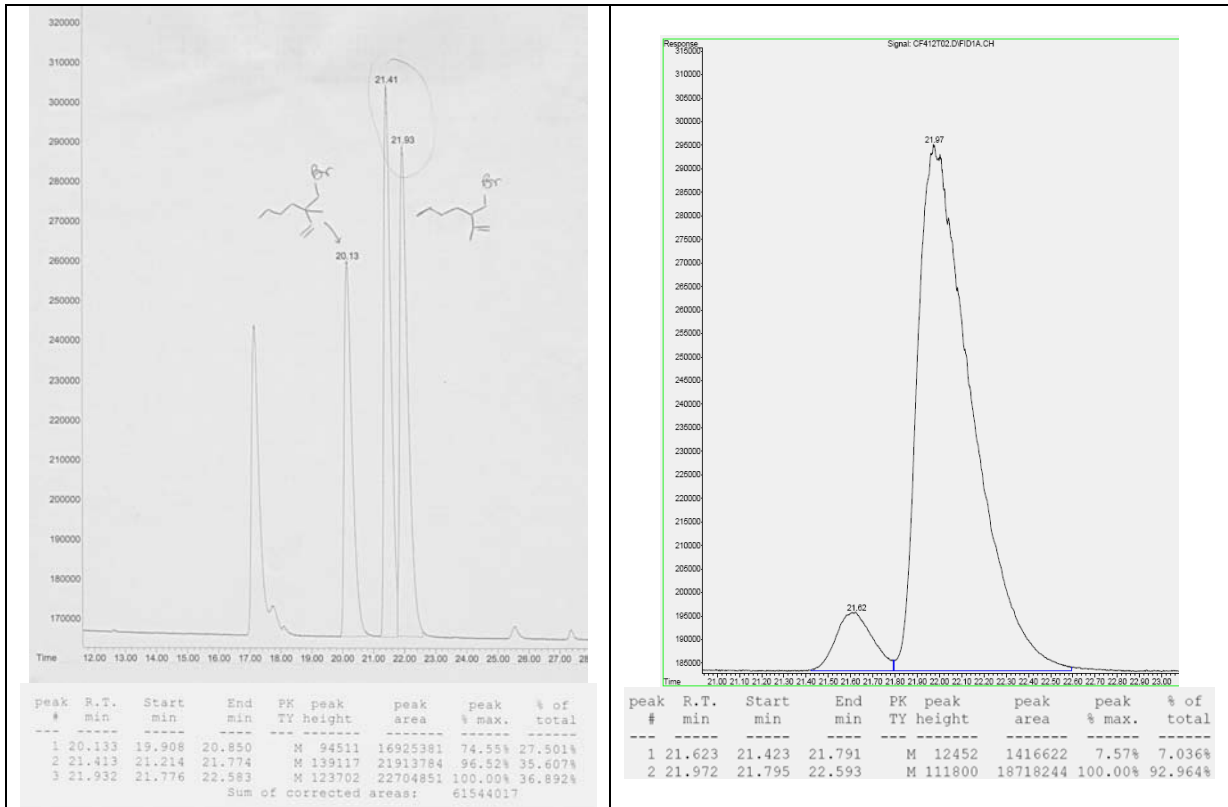
26

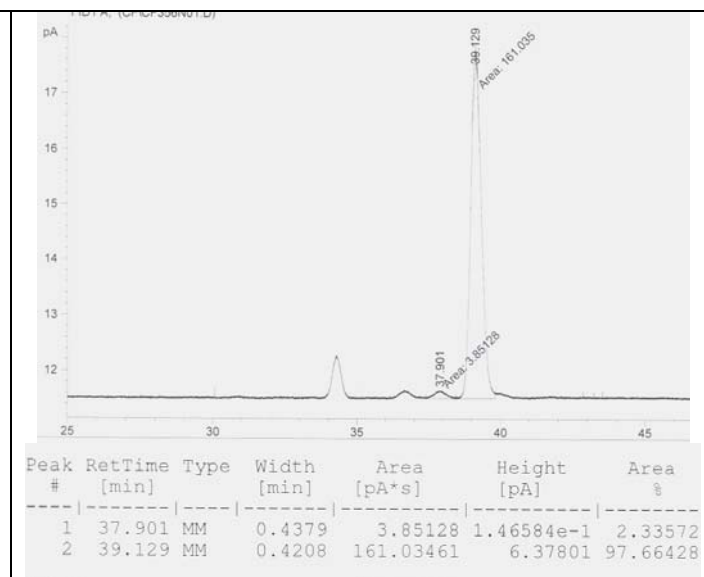
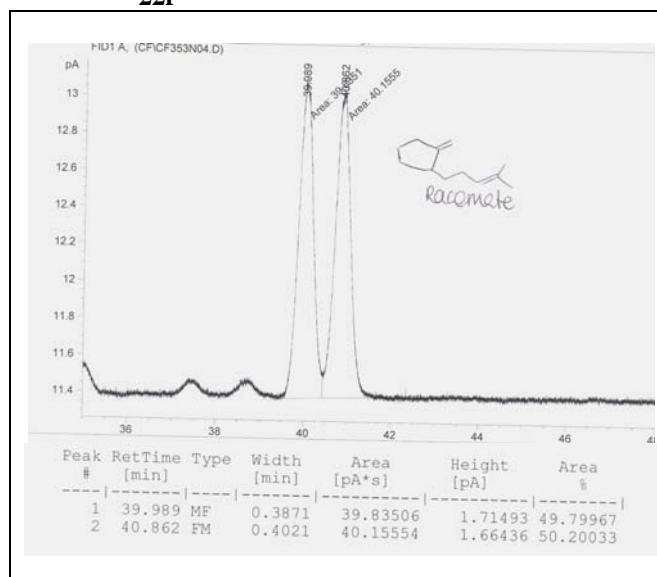
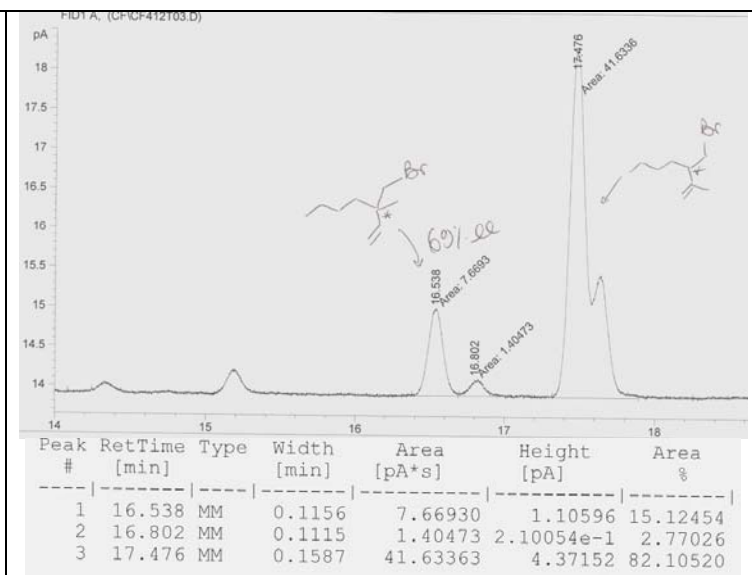
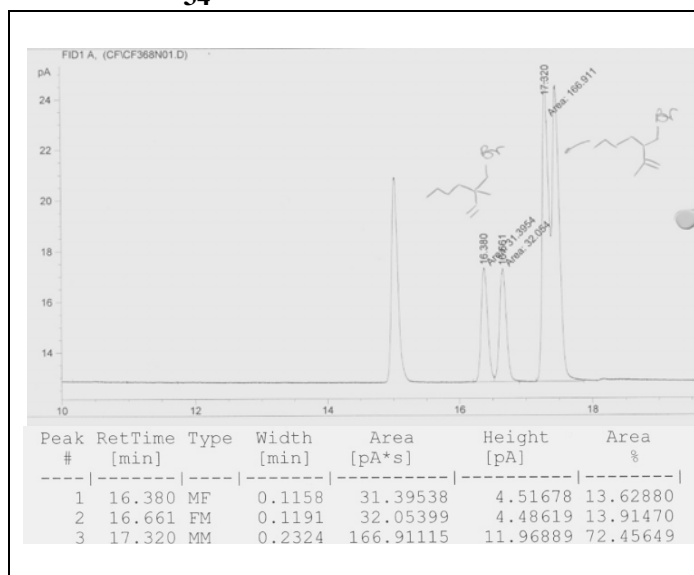


27

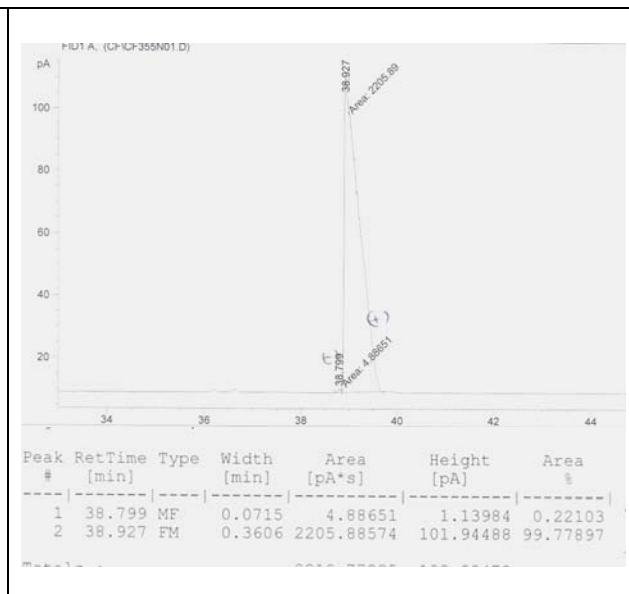
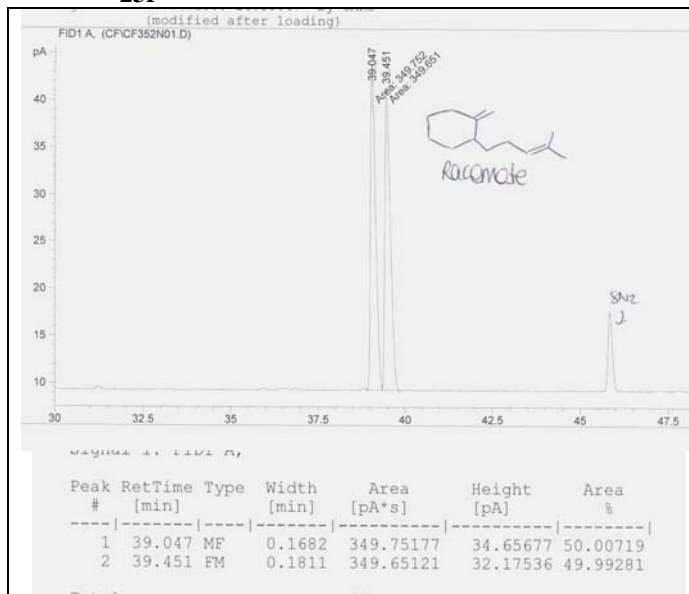


33

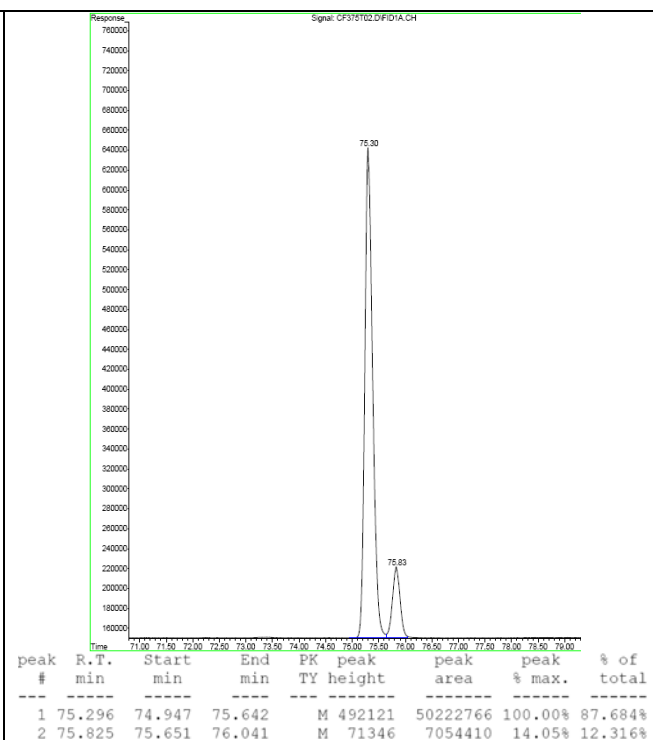
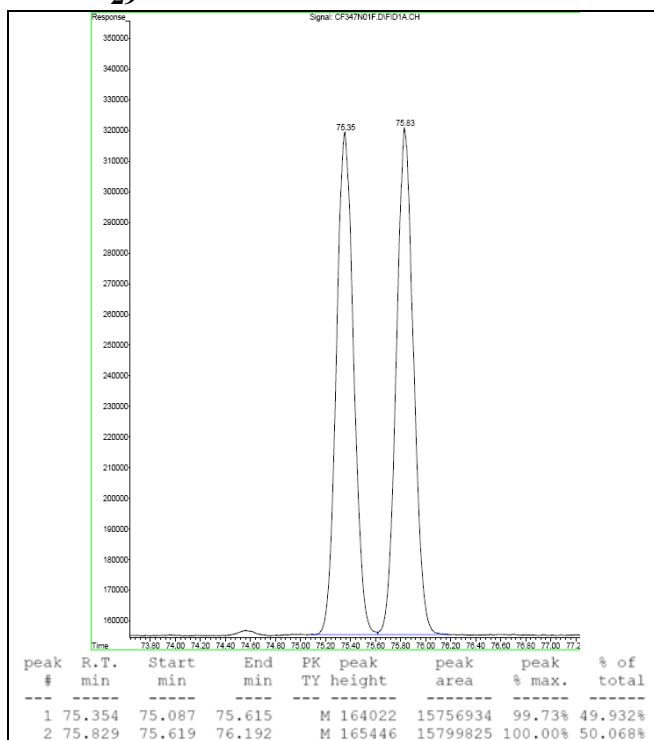


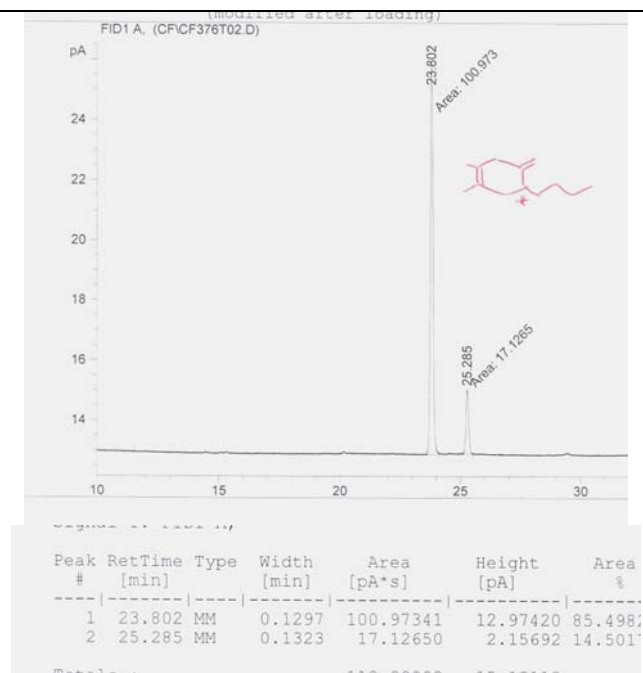
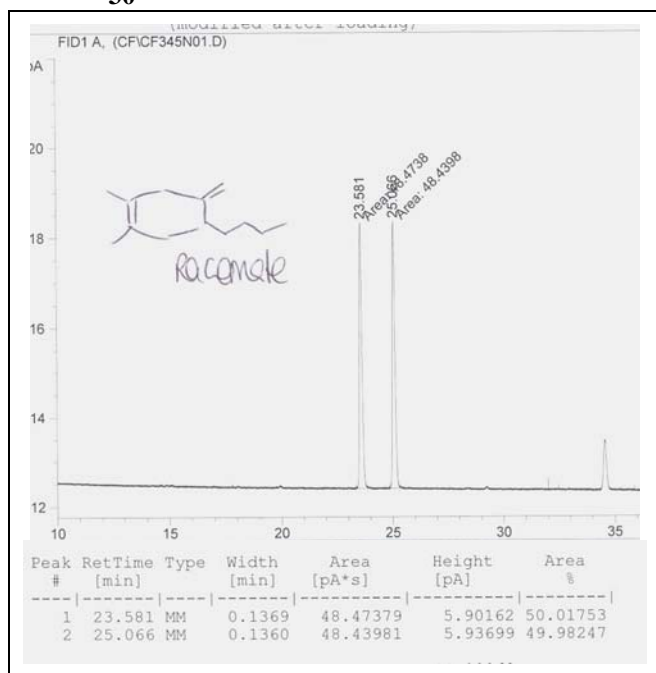
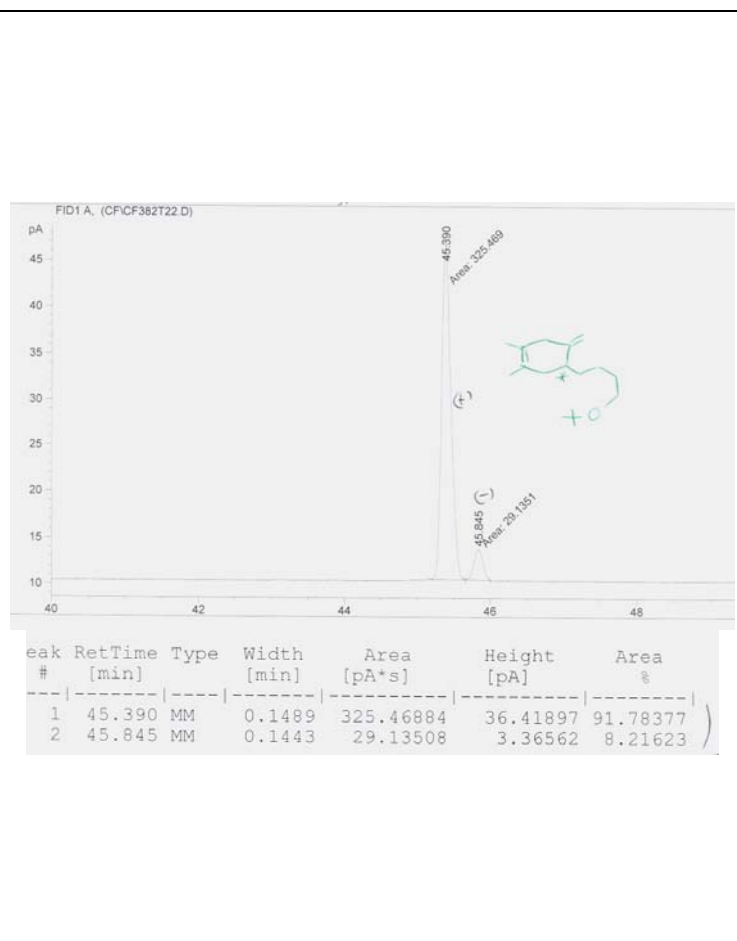
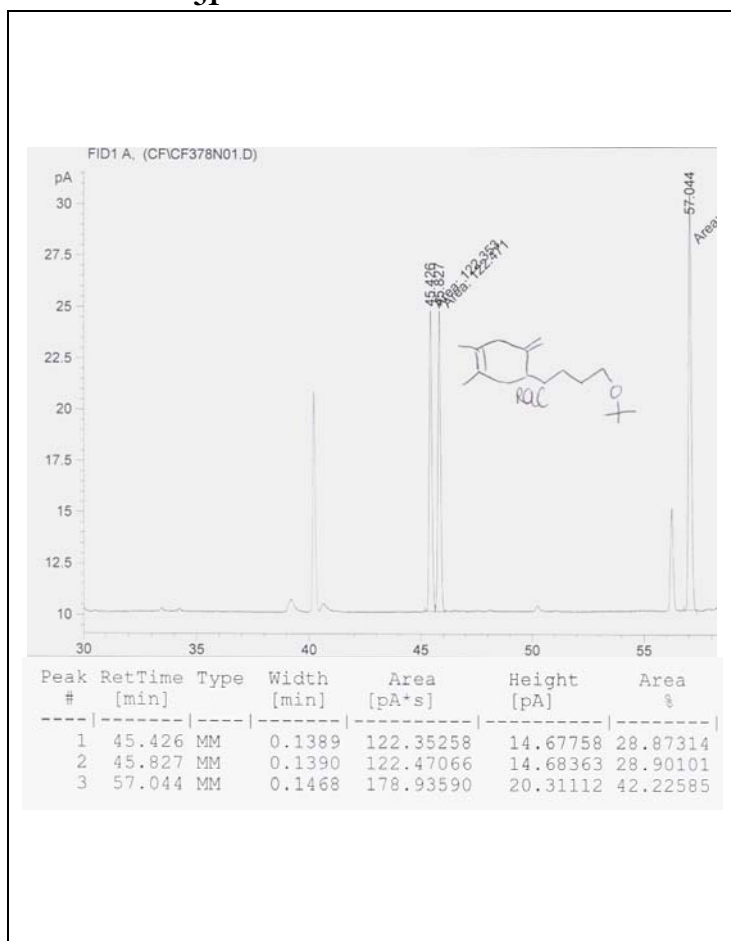


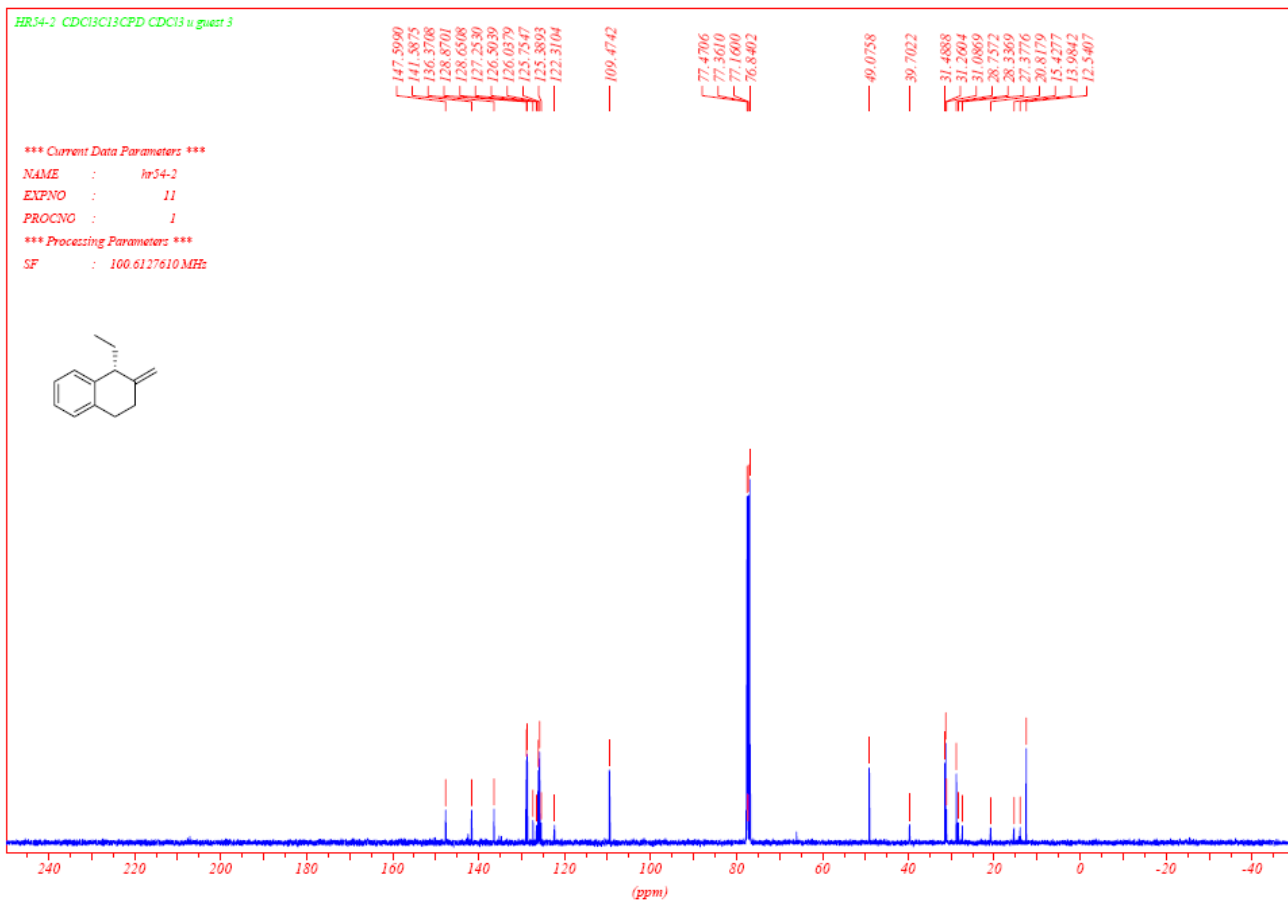
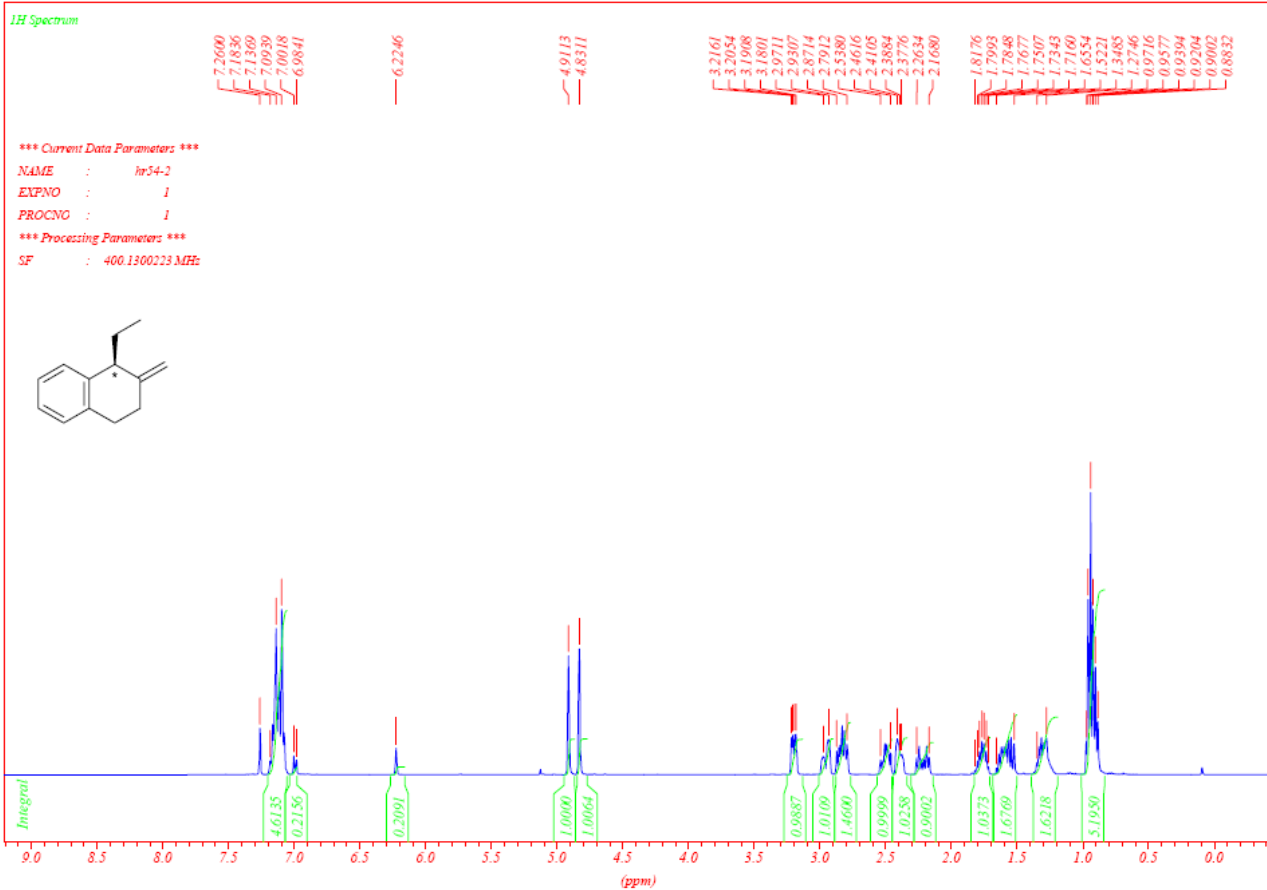
23f



29







CF452N11 CDC13PROTON CDC13 ii guest 1

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7.0952
7.0037
6.9834

6.2240

5.3154

4.8943

4.8274

3.3153
3.3039
3.2900
3.2793
2.9895
2.9813
2.9497
2.9408
2.8752
2.7944

2.5027
2.4863
2.4118
2.4048
2.3971
2.3769
2.3708
2.1933

1.7141
1.6806
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*** Current Data Parameters ***

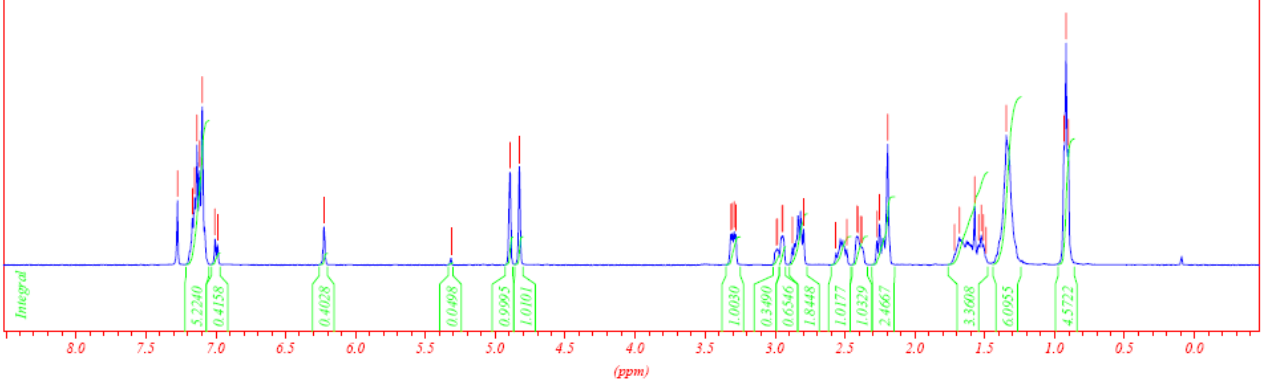
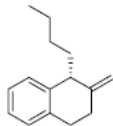
NAME : c452n11

EXPNO : 10

PROCNO : 1

*** Processing Parameters ***

SF : 400.1300172 MHz



CF452N11 CDC1313CPD CDC13 ii guest 1

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128.0874
127.2622
126.3130
126.0471
125.7564
125.3895
122.1277

109.2550

77.4798
77.3610
77.1600
76.8402

47.4130

38.2861
37.5917
31.7081
31.5071
30.0636
28.6749
28.3552
27.4324
27.3302
22.7274
22.6725
14.2217

*** Current Data Parameters ***

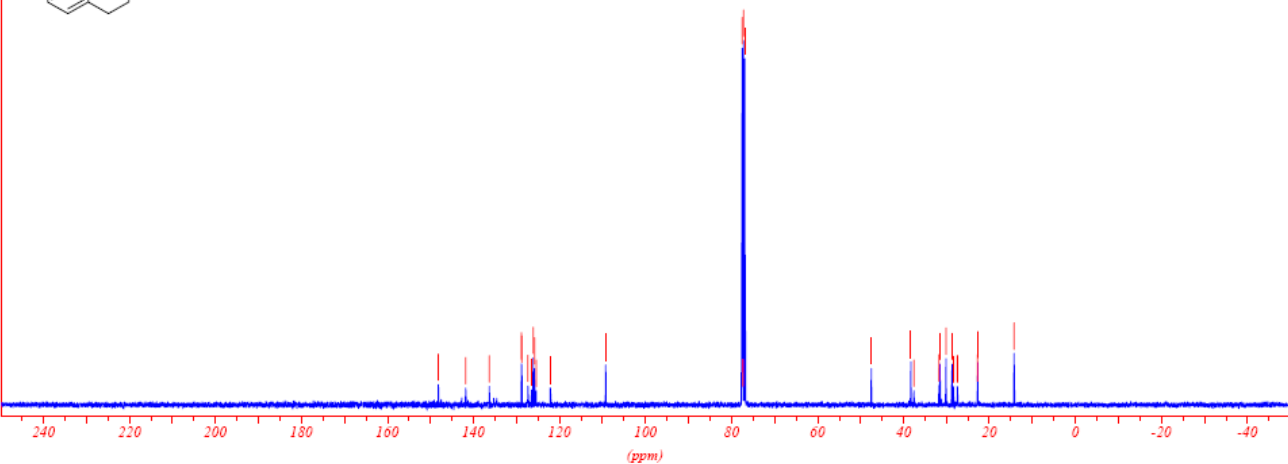
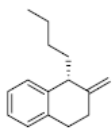
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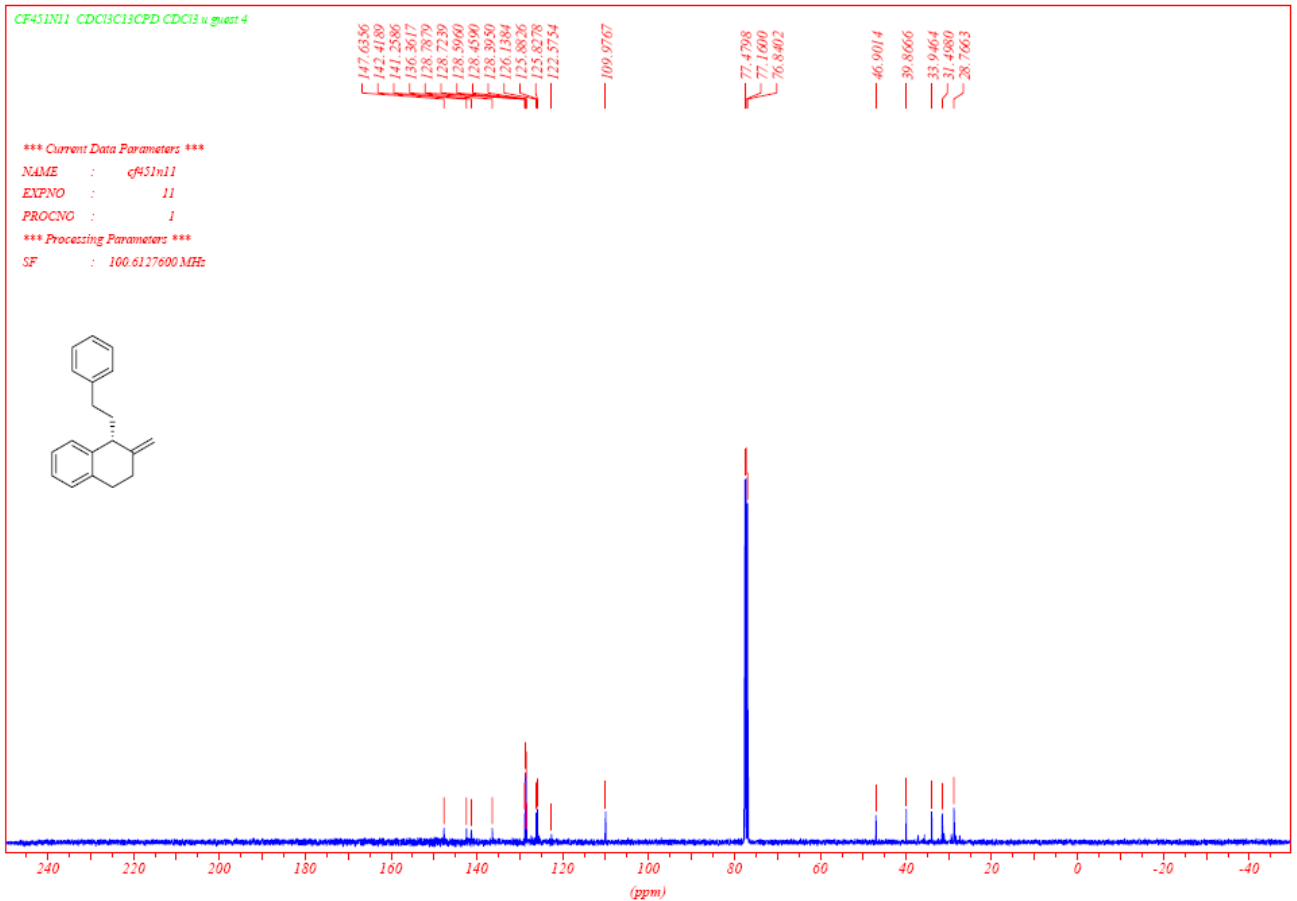
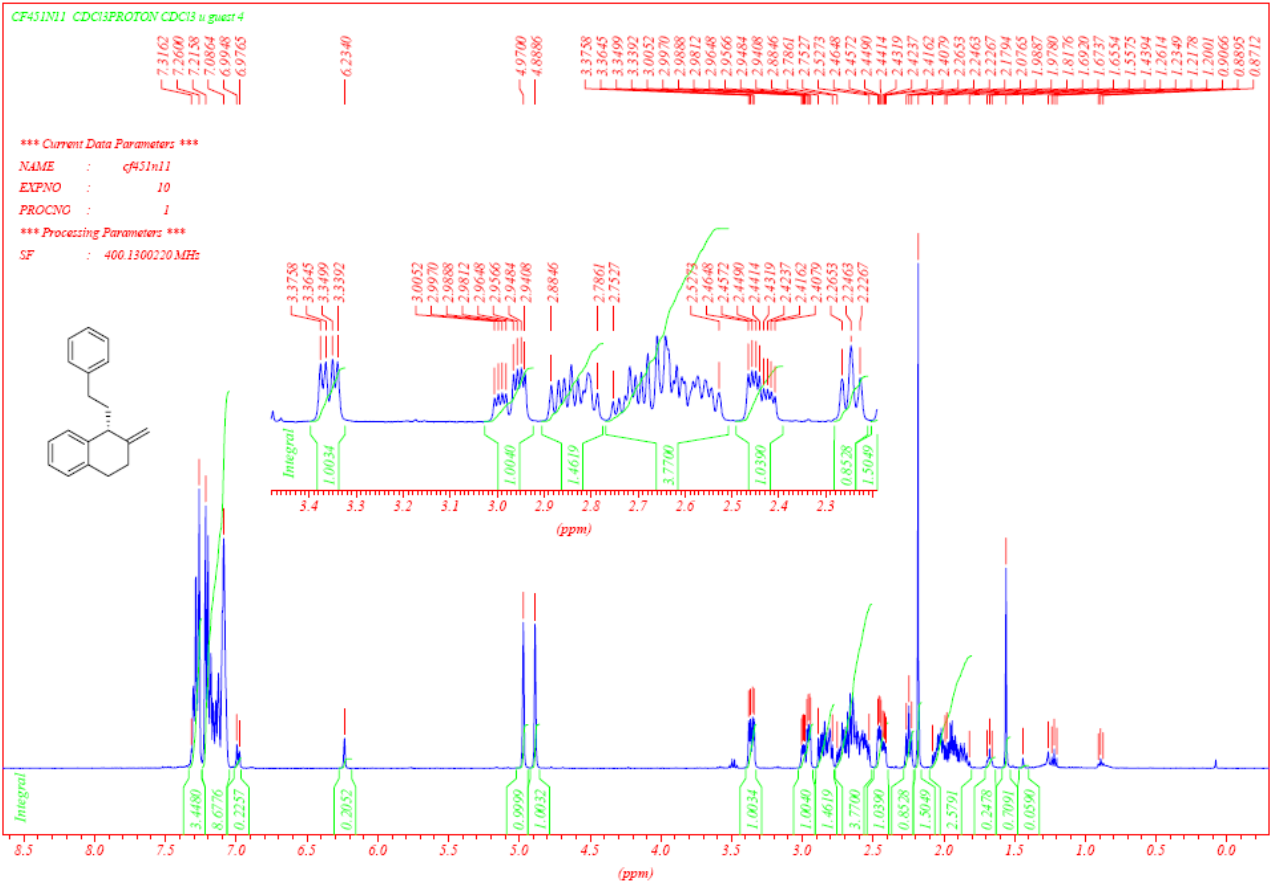
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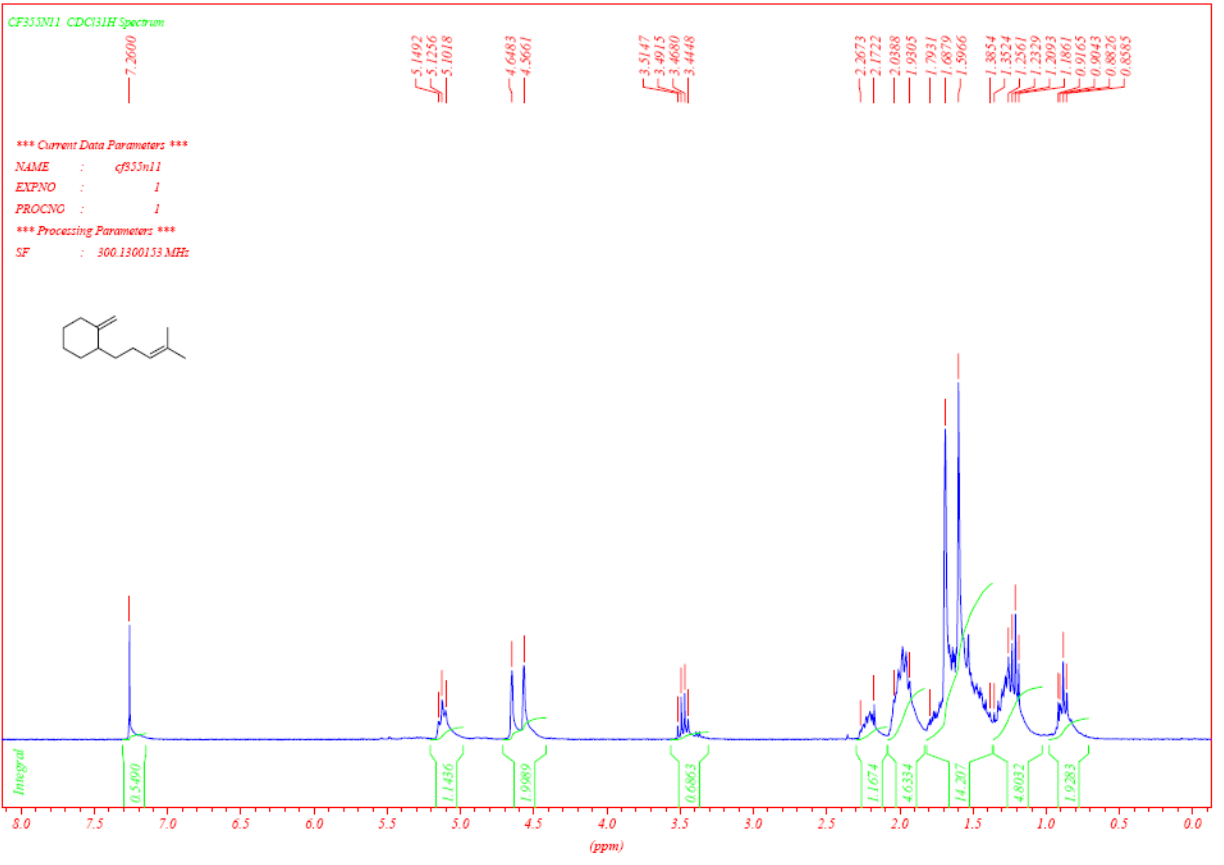
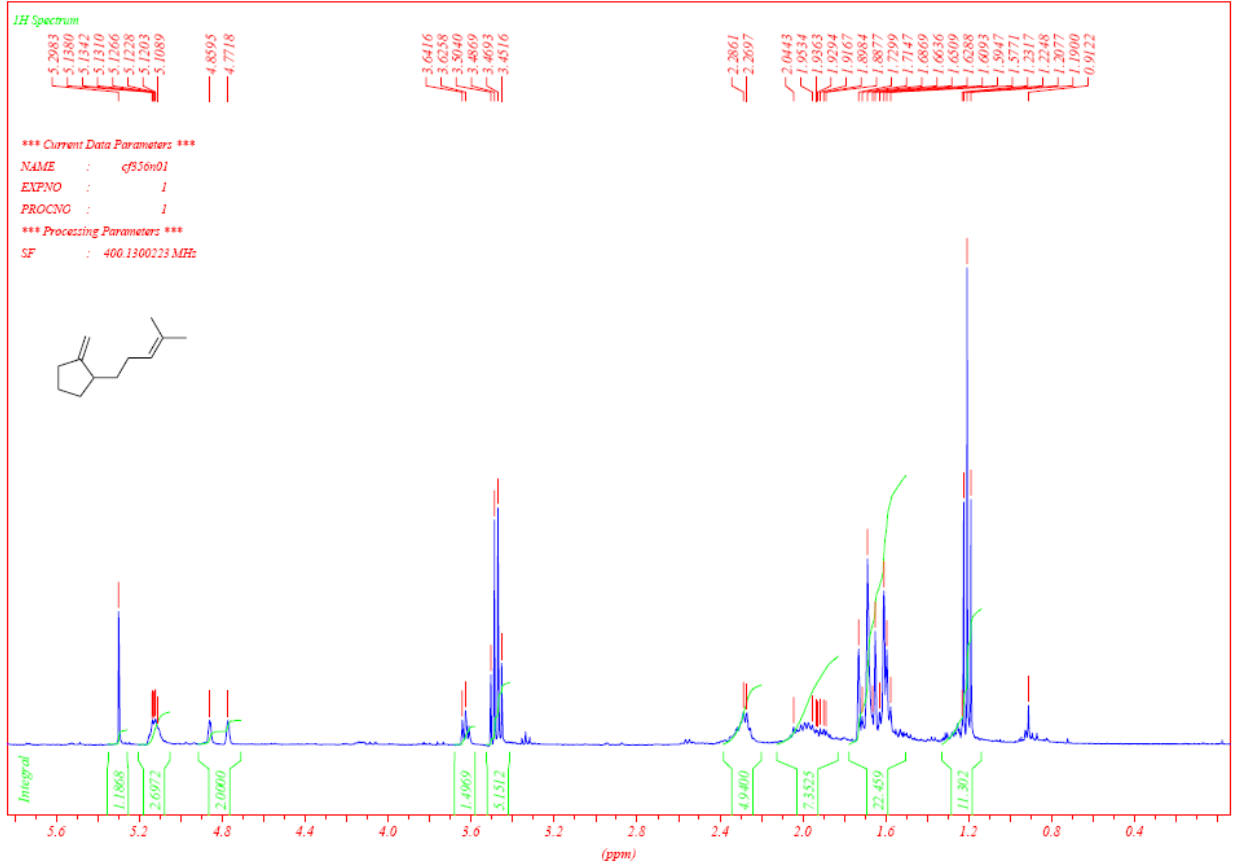
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*** Processing Parameters ***

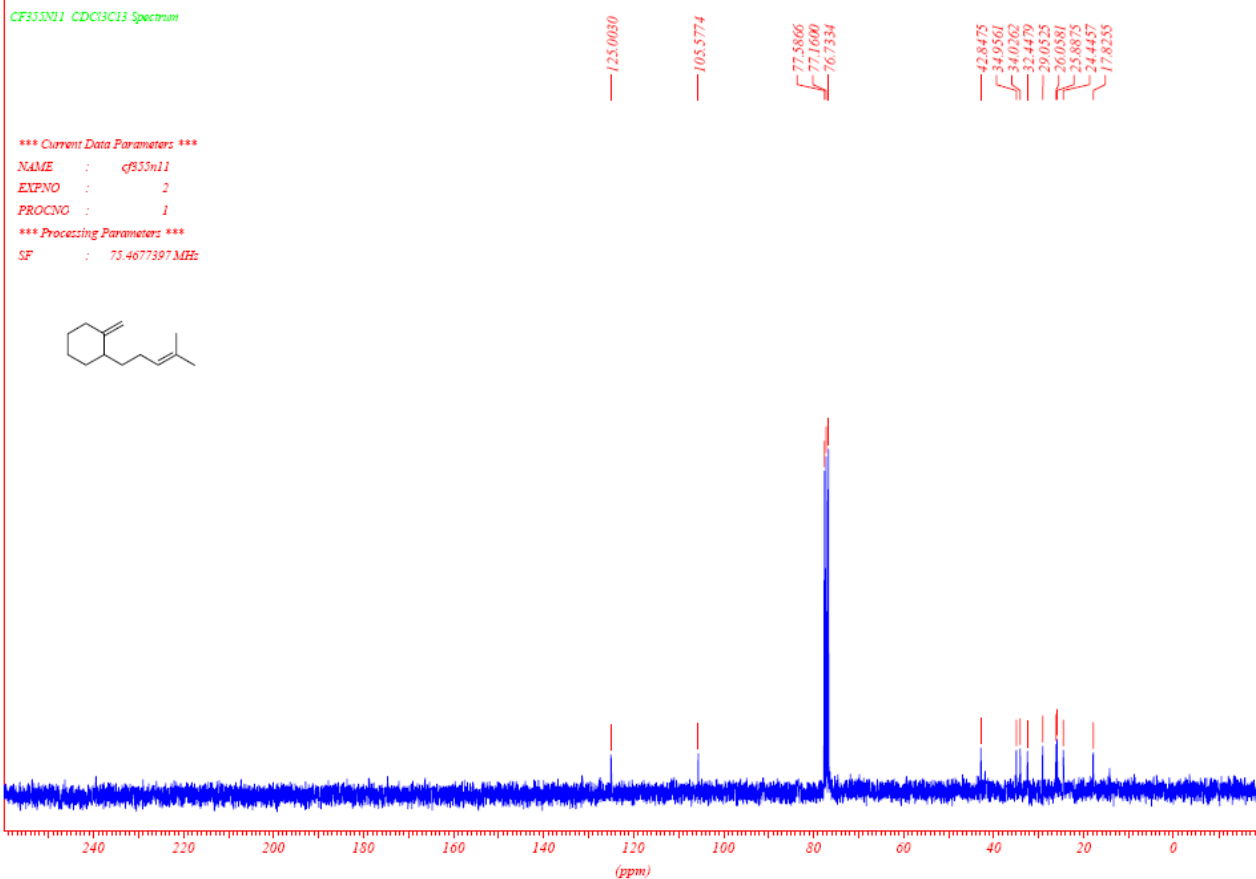
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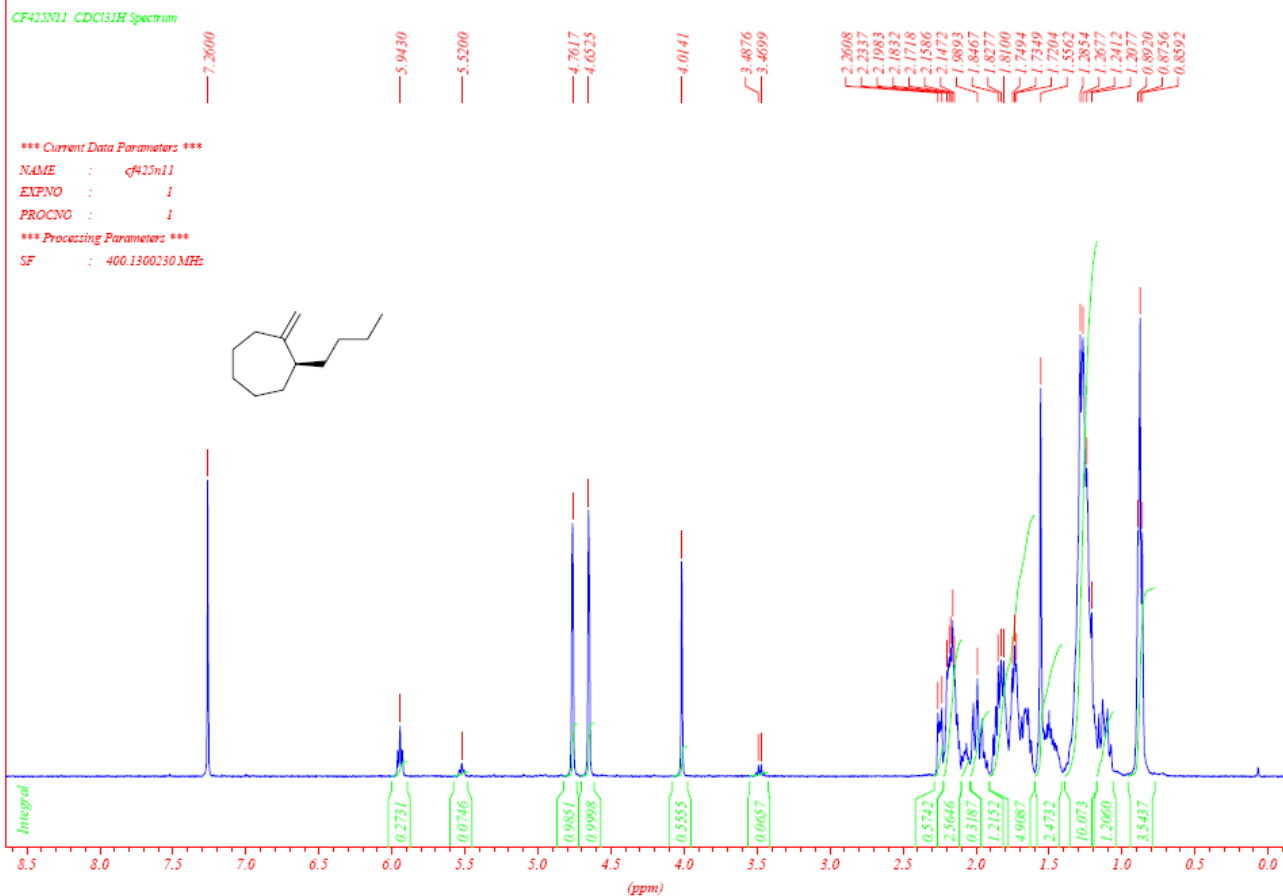


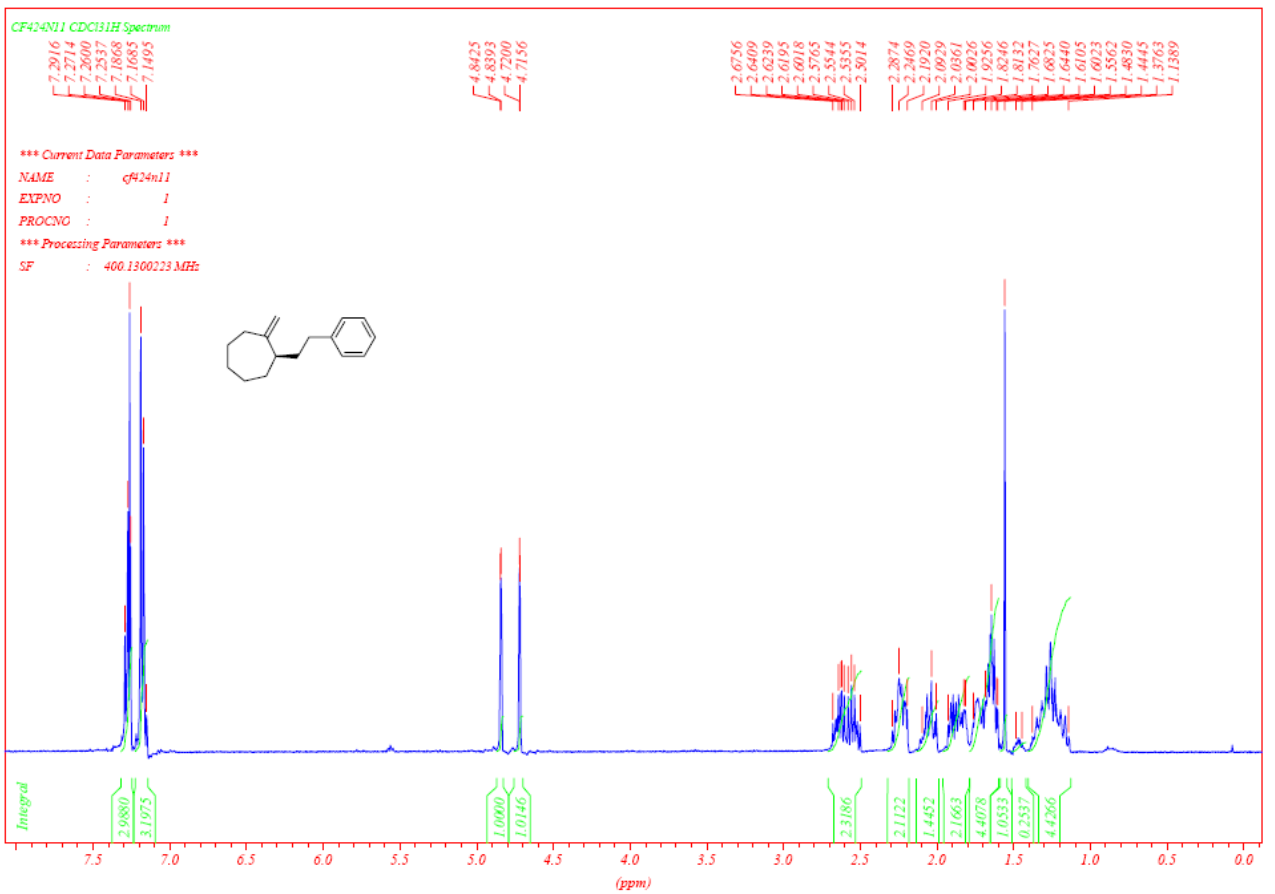
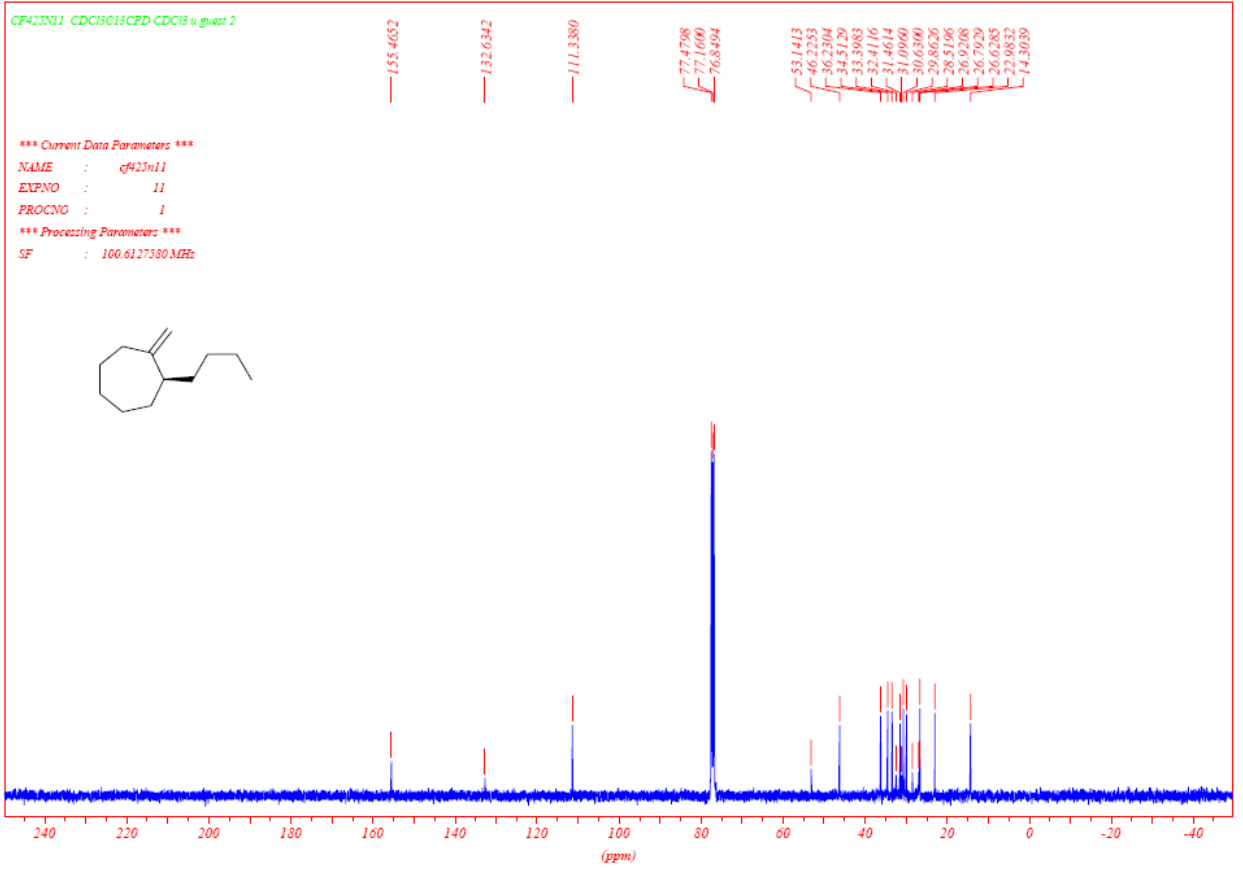


CF355N11 CDCl3C13 Spectrum



CF425N11 CDCl31H Spectrum





CF424N11 CDCl3(13CPD CDCl3 is guest 1

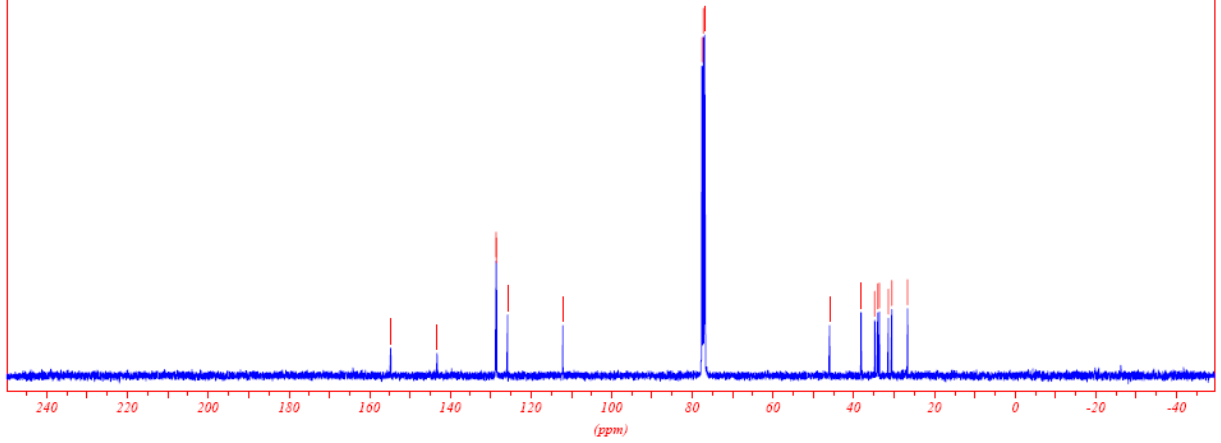
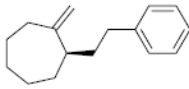
154.7571
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128.6462
128.4635
125.7501
112.0369
77.5574
77.2468
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38.1170
34.7001
33.9875
33.5673
31.4020
30.5015
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*** Current Data Parameters ***

NAME : qf124n11
EXPNO : 11
PROCNO : 1

*** Processing Parameters ***

SF : 100.6127506 MHz



CF354N11 CDCl3(1H Spectrum

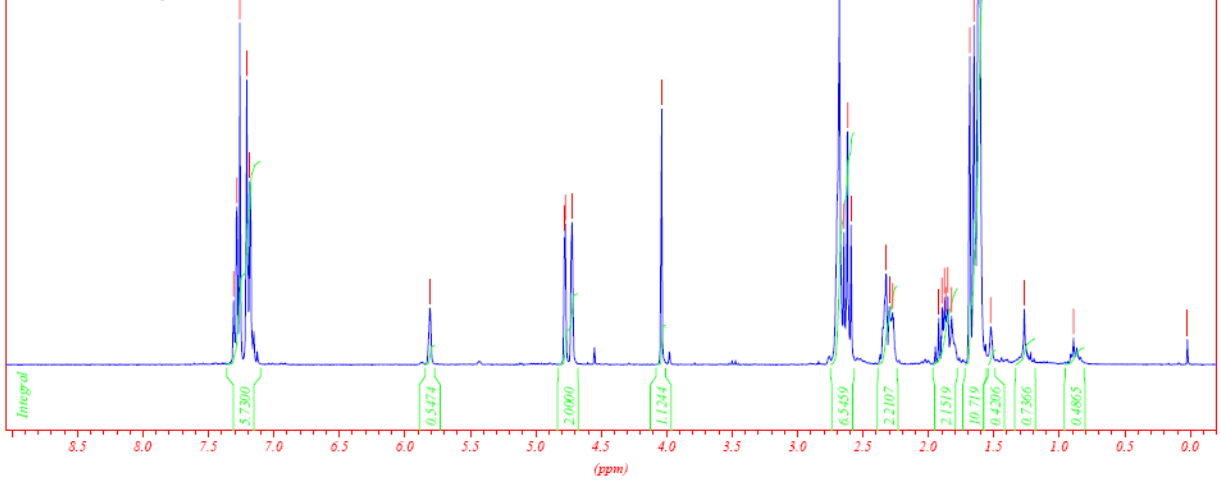
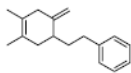
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7.3063
7.2063
7.1822
5.8066
4.7788
4.7741
4.7233
4.0373
2.6806
2.6445
2.6172
2.5908
2.3222
2.2880
2.2717
1.9195
1.8935
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*** Current Data Parameters ***

NAME : qf354n11
EXPNO : 1
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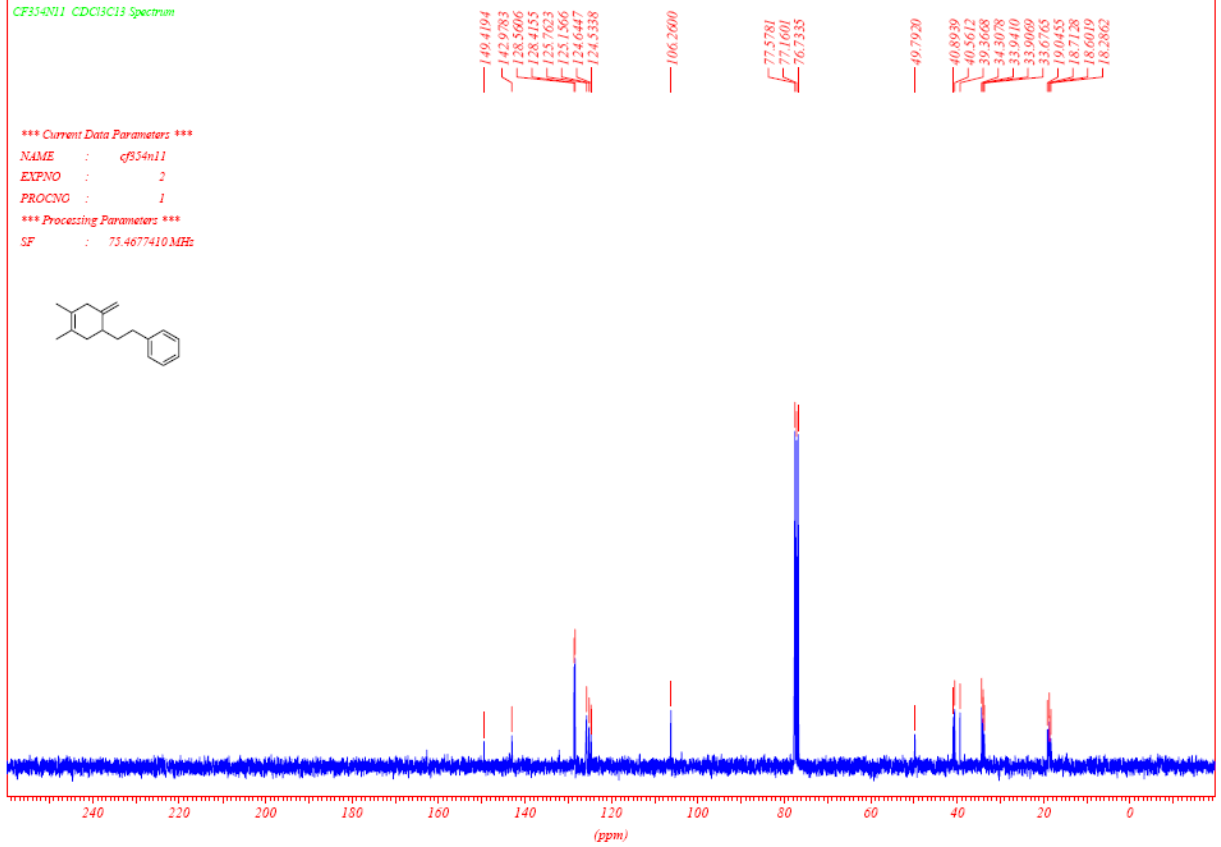
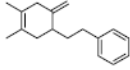
*** Processing Parameters ***

SF : 300.1300146 MHz



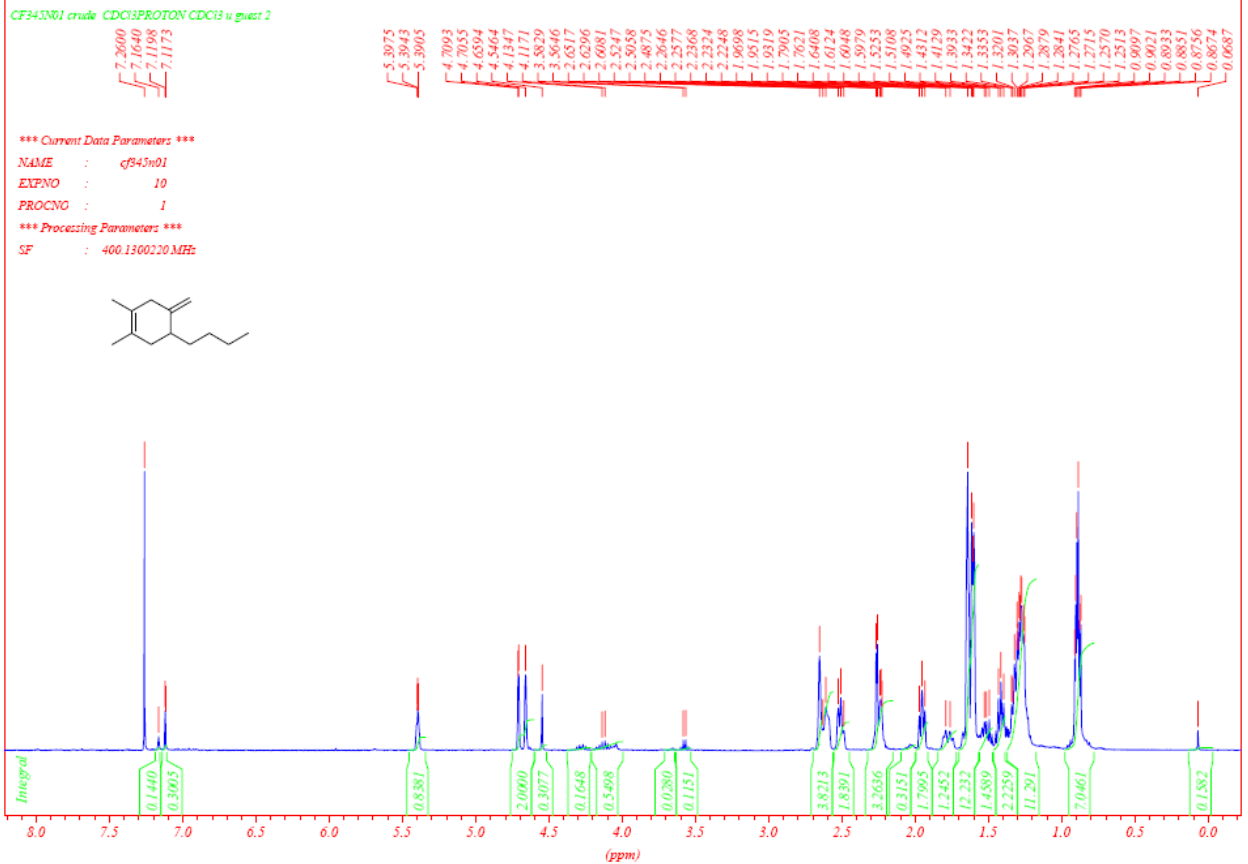
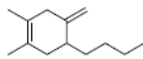
CF345N11 CDCl3C13 Spectrum

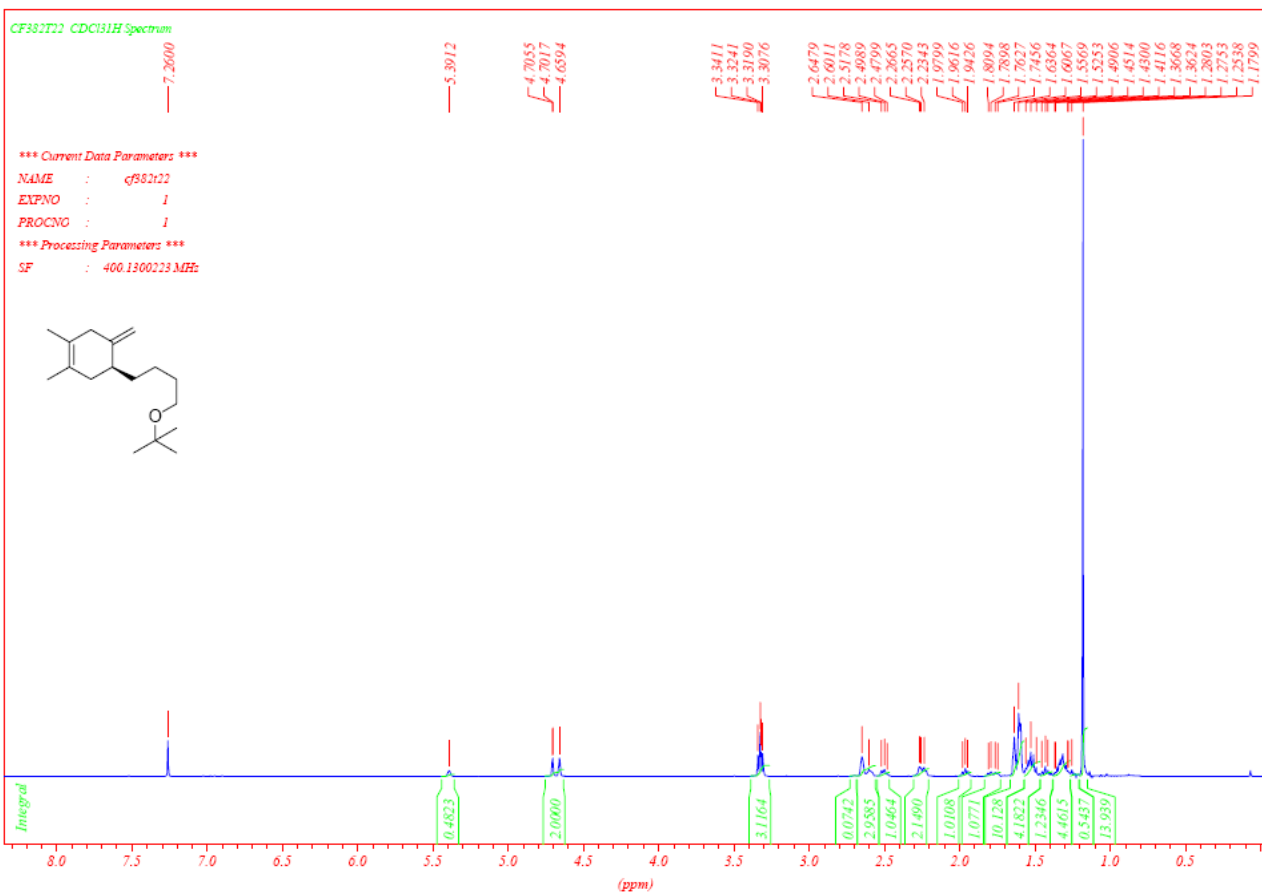
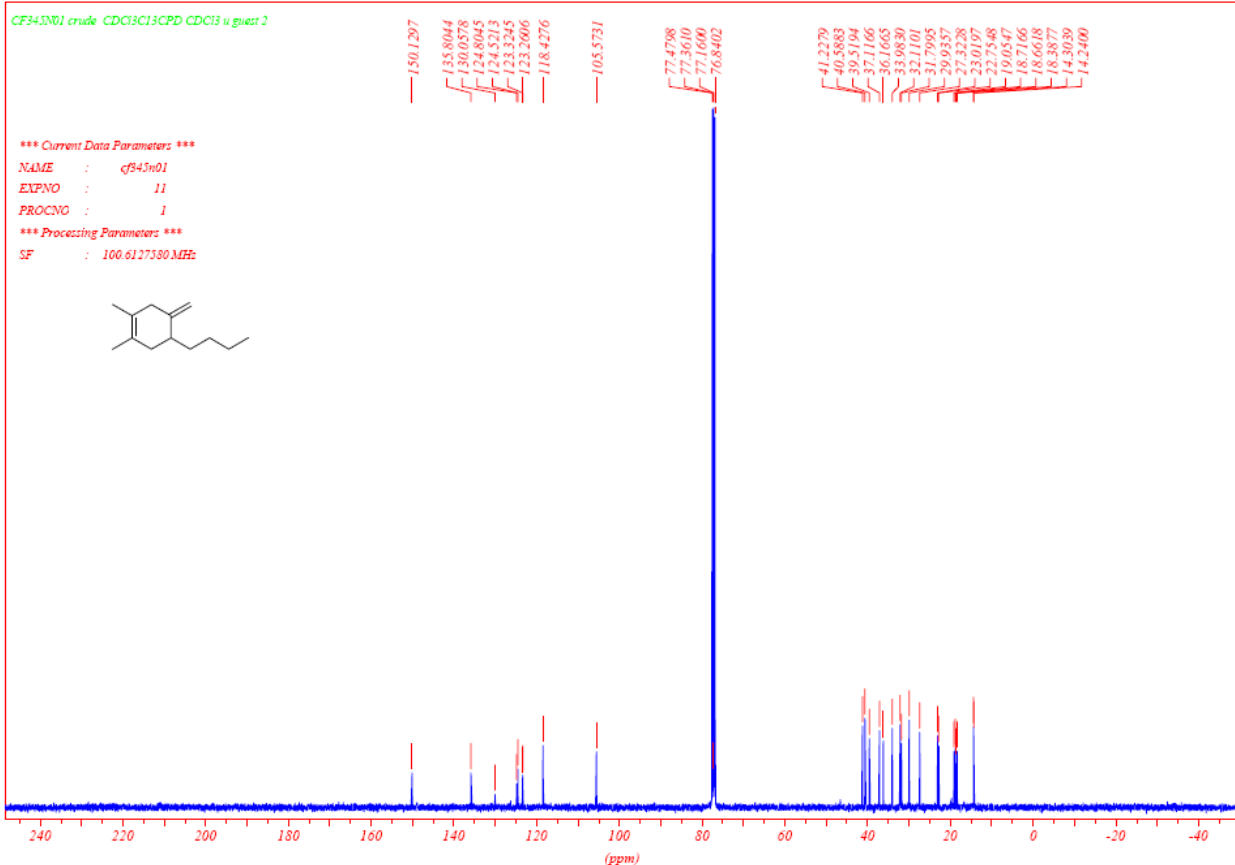
*** Current Data Parameters ***
 NAME : cf345n11
 EXPNO : 2
 PROCNO : 1
 *** Processing Parameters ***
 SF : 75.4677410 MHz



CF345N01 crude CDCl3PROTON CDCl3 u guest 2

*** Current Data Parameters ***
 NAME : cf345n01
 EXPNO : 10
 PROCNO : 1
 *** Processing Parameters ***
 SF : 400.1300220 MHz





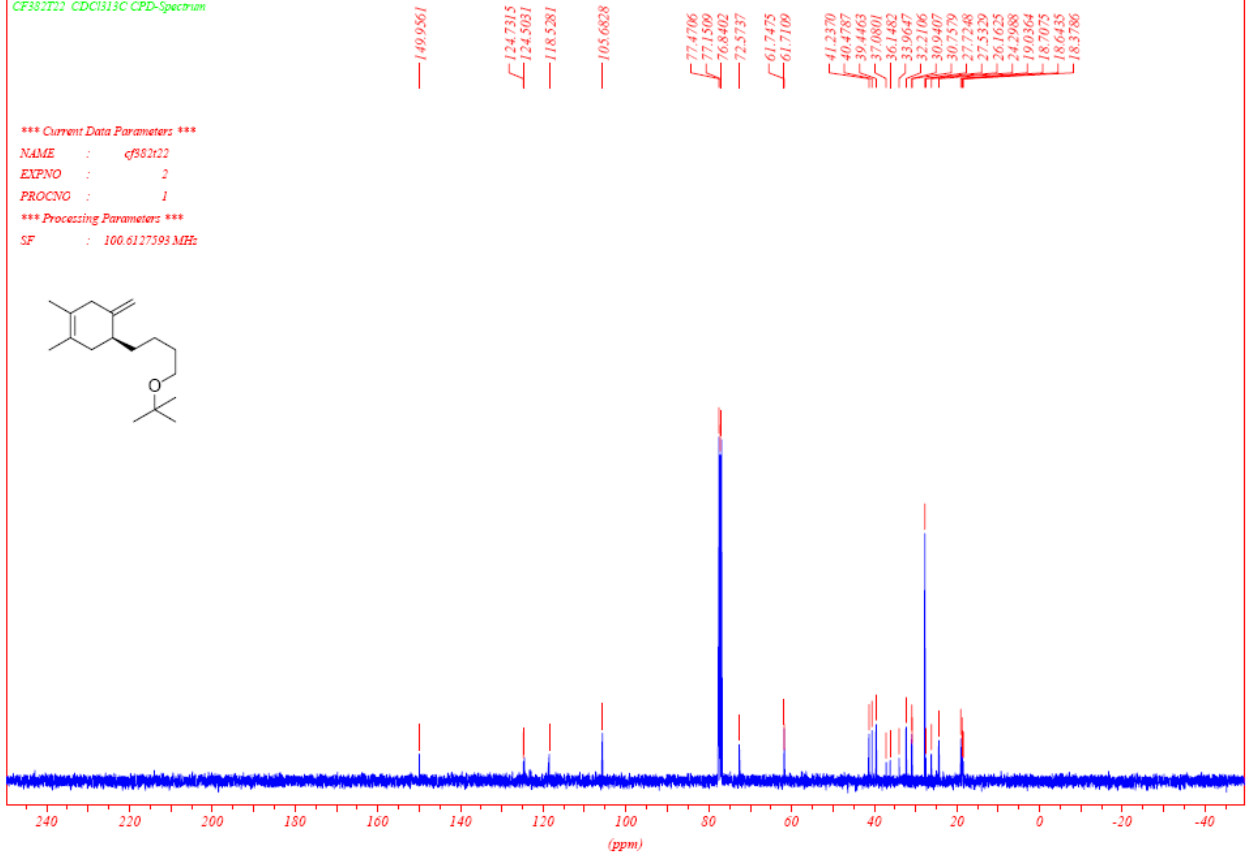
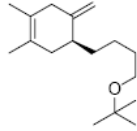
CF382T22 CDCl313C CPD-Spectrum

*** Current Data Parameters ***

NAME : cf382t22
 EXPNO : 2
 PROCNO : 1

*** Processing Parameters ***

SF : 100.6127393 MHz



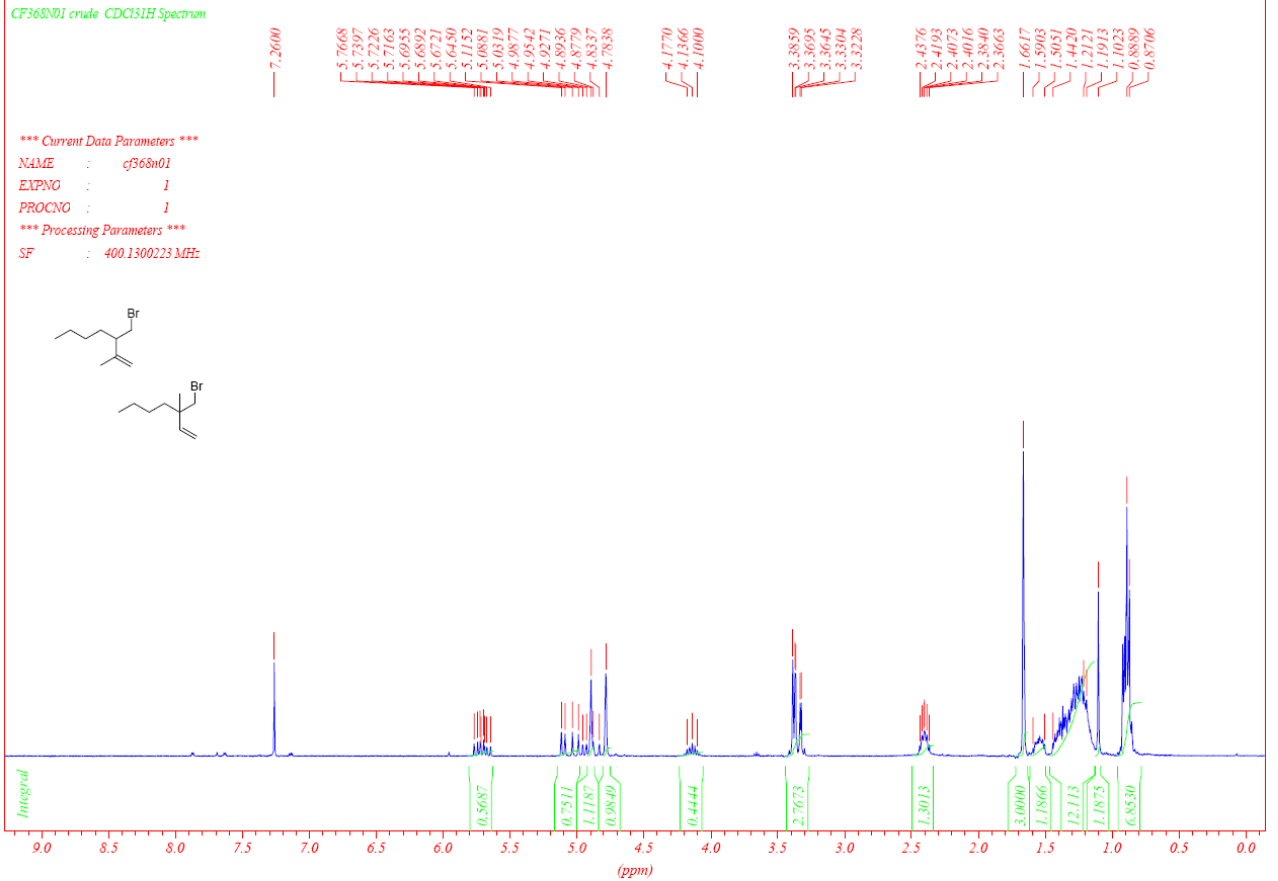
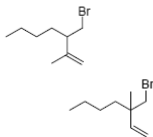
CF368N01 crude CDCl31H Spectrum

*** Current Data Parameters ***

NAME : cf368n01
 EXPNO : 1
 PROCNO : 1

*** Processing Parameters ***

SF : 400.1300223 MHz



CF368N01 crude CDCl3/13C CPD-Spectrum

