Dynamic kinetic asymmetric transformation in copper catalyzed allylic alkylation

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Supporting Information

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) and ^{13}C (100 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), qd (quartet of doublet), brs (broad singlet). Coupling constants are reported in Hertz (Hz). Evolution of reaction was followed by GC-MS (EI mode) on an HP6890. 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 (R_T) are given in min. Enantiomeric excesses were in some cases determined by chiral-SFC measurement on a Berger SFC with the stated column. Gradient programs are described as follows: initial methanol concentration (%) - initial time (min) - percent gradient of methanol (%/min) - final methanol concentration (%); retention times (R_T) are given in min. Flash chromatography was performed using silicagel 32-63 µm, 60 Å.
All chiral ligands were prepared according to the litterature procedure (for ligands **L1**-**L6**, see reference 1, for ligand **L7**, see reference 2, ligand **L8** was a gift from Solvias, for ligand **L9,** see reference 3). CuTC was purchased from FrontierScientific and used as received.
Substrates were prepared according to the literature (for substrate **5**, **8** and **9** see reference 4, for substrate **10**, see references 5 and 6). Substrate **8** is very light and air sensitive so it is used directly after its distillation. Epoxides were prepared according to the literature (see reference 7).

II) Additional datas

Table 1. Influence of the nature of the copper source[a].

Entry	Cu salt	Conversion [%][b]	*ee* [%][c]
1	CuTC	>99	86 (*S*)
2	$CuBr.SMe_2$	>99	80 (*S*)
3	CuBr	>99	82 (*S*)
4	CuCl	>99	82 (*S*)
5	$Cu(OAc)_2$	>99	82 (*S*)
6	$Cu(OTf)_2$	>99	56 (*S*)
7	CuCN	>99	28 (*S*)

[a] Reaction conditions: Racemic substrate **5** (0.5 mmol) was added to a solution of Cu salt (5 mol%) and **L1** (5.5 mol%) in dry DCM (4 ml). Reaction mixture was cooled to -78ºC and Grignard reagent (1 M in Et_2O, 1.5 equiv) was added dropwise.[b] Conversion determined by GC-MS.[c] Determined by GC on a chiral stationary phase.

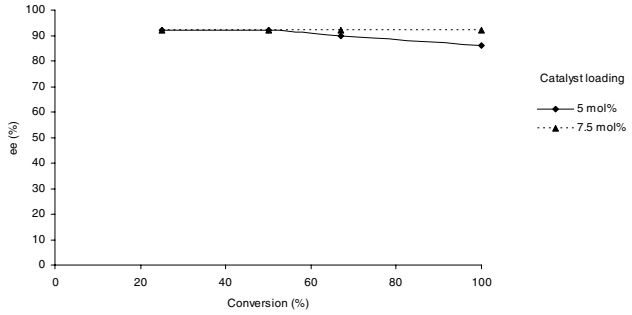
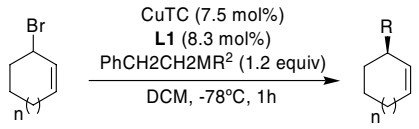


Figure 1. Enantiomeric excess of the product **7** as a function of the conversion of the reaction.

Table 2. Influence of the organometallic reagent[a].



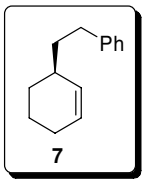
Entry	Substrate	$PhCH_2CH_2MR$	Conversion [%][b]	*ee* [%][d]
1	**5**	$PhCH_2CH_2MgBr$	>99	92 (*S*)
2	**5**	$(PhCH_2CH_2)_2Zn$	>99[c]	90 (*S*)
3	**9**	$PhCH_2CH_2MgBr$	>99	38 (*S*)
4	**9**	$(PhCH_2CH_2)_2Zn$	>99[c]	38 (*S*)

[a] Reaction conditions: Organometallic reagent (1.2 eq) was added dropwise, at -78ºC, to a solution containing the substrate, the Cu salt and the ligand. [b] Yield of isolated product. [c] Organozinc reagent was prepared by addition of two equivalents of Grignard reagent to $ZnBr_2$ in DCM. [d] Determined by GC on a chiral stationary phase after derivatisation of a sample of the isolated product into the corresponding epoxides.

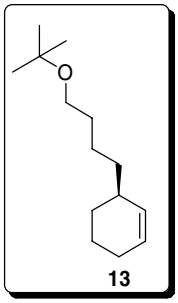
III) General procedure for copper catalyzed asymmetric allylic alkylation

In a flame-dried Schlenk tube under argon atmosphere, CuTC (7.2 mg, 0.038 mmol, 0.075 eq) and **L1** (22.2 mg, 0.041 mmol, 0.083 eq) were dissolved in dry DCM (4 ml) and the solution was stirred for 10 min at room temperature. Then the substrate (0.5 mmol) was added and the solution was cooled to -78°C. After 10 min at this temperature, the alkylmagnesium bromide

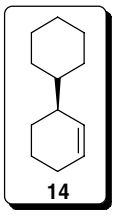
solution 1M in Et_2O (0.6 ml, 0.6 mmol, 1.2 eq) was added dropwise and the reaction mixture was stirred for 1h. The reaction was quenched with a aqueous solution of HCl 1M (15 ml) and extracted with Et_2O (15 ml). Organic layer was washed with HCl 1M (15 ml) and brine (15 ml), dried over Na_2SO_4, filtered and concentrated on vacuo. Crude mixture was purified on silica gel chromatography column (pentane). Desired product was recovered as a colorless liquid. A sample of the isolated product was treated with *m*cpba and Na_2HPO_4 in DCM. After 1h, Et_2O (10 ml) was added and the reaction was quenched with an aqueous solution of saturated $Na_2S_2O_3$. Organic layer was washed two times with an aqueous solution of NaOH 1M, dried over Na_2SO_4, filtered and concentrated on vacuo. The crude mixture of two diastereoisomeric epoxides was directly analyzed in chiral GC.



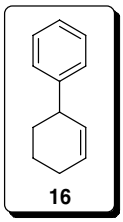
(*S*)-(2-(cyclohex-2-enyl)ethyl)benzene 7: prepared from **cyclohex-1-enyl-3-bromide 5**. Yield = 95 %. The enantiomeric excess was determined by GC on a chiral stationary phase (Hydrodex B3P column, Method: 60-30-1-140-20-170-5, R_T: 102.17 (*S*), 102.76 (*R*) min). The enantiomeric excess was also determined after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 97.99, 99.01, 102.71, 104.25 min). $[\alpha]^{25}_D$ = -104.4 (c = 1.2 in $CHCl_3$, 92 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.34-1.37 (m, 1H), 1.59-1.81 (m, 4H, 1.89 (m, 1H), 2.06 (m, 2H), 2.18 (m, 1H), 2.74 (m, 2H), 5.71-5.76 (m, 2H), 7.25-7.35 ppm (m, 5H); ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 21.6, 25.5, 29.2, 33.4, 34.9, 38.4, 125.8, 127.3, 128.4, 128.5, 131.9, 143 ppm. IR ($CHCl_3$): 71.9, 1453, 1493, 2856, 2923, 3023 cm^{-1}. MS (EI mode) *m*/z %: 186 (28), 143 (4), 129 (4), 104 (26), 91 (100), 65 (34), 53 (22). HRMS (ESI) calcd for $C_{14}H_{18}$ [M^+] 186.1407, found 186.1409.



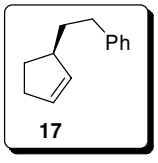
(*S*)-3-(4-*tert*-butoxybutyl)cyclohex-1-ene 13: prepared from **cyclohex-1-enyl-3-bromide 5**. Yield = 91 %. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 87.43, 88.95, 91.50, 93.15 min). $[\alpha]^{25}_D$ = -145.8 (c = 1.8 in $CHCl_3$, 90 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.17 (s, 9H), 1.35-1.37 (m, 5H), 1.49 (m, 2H), 1.94-2.03 (m, 3H), 3.32 (t, 2H, J = 6.6 Hz), 5.57-5.63 ppm (m, 2H); ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 21.6, 23.7, 25.5, 27.7, 29.2, 31, 35.3, 36.4, 61.7, 72.5, 126.8, 132.4 ppm. IR ($CHCl_3$): 1083.7, 1198.7, 1361.6, 2860.9, 2929.4, 2973.2 cm^{-1}. MS (EI mode) *m*/z %: 226 (8), 207 (10), 163 (2), 147 (2), 135 (12), 93 (8), 71 (12), 57 (100). HRMS (ESI) calcd for corresponding epoxide $C_{14}H_{26}O_2$ [M^+] 226.1933, found 226.1927.



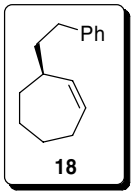
(*S*)-3-cyclohexylcyclohex-1-ene 14: prepared from **cyclohex-1-enyl-3-bromide 5**.Yield = 98 %. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 71.96, 72.42, 79.05, 80.11 min). $[\alpha]^{25}_D$ = -42 (c = 1.0 in $CHCl_3$, 70 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.02-1.34 (m, 7H), 1.49 (m, 1H), 1.72 (m, 7H), 1.94 (m, 3H), 5.62-5.67 ppm (m, 2H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 22.4, 25.6, 25.9, 26.9, 30, 30.4, 41.1, 42.8, 127.3, 131.2 ppm. IR ($CHCl_3$): 721.2, 1448, 2851.8, 2933.3, 3022.9 cm^{-1}. MS (EI mode) *m*/z %: 164 (30), 149 (4), 135 (6), 121 (6), 97 (8), 82 (100), 81 (65), 55 (90), 53 (26). HRMS (ESI) calcd for $C_{12}H_{20}$ [M^+] 164.1564, found 164.1565.



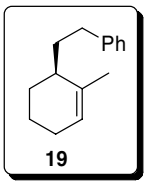
Cyclohex-2-enylbenzene 16: prepared from **cyclohex-1-enyl-3-bromide 5**.Yield = 97 %. The enantiomeric excess was determined by SFC on a chiral stationary phase after derivatisation in corresponding epoxides (Chiracel OJ column, Method: MeOH 2%-2-1-15%, R_T: 4.57 (*S*), 4.97 (*R*) min). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.51 (m, 2H), 1.69 (m, 1H), 1.96-2.04 (m, 3H), 3.35 (m, 1H), 5.68 (m, 1H), 5.82 (m, 1H), 7.14-7.25 ppm (m, 5H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 21.3, 25.2, 32.8, 42, 126.1, 127.9, 128.4, 128.5, 130.3, 146.8 ppm. IR ($CHCl_3$): 701, 723.6, 755.2, 1075.2, 1451.6, 1491.6, 1738.9, 2836.6, 2931.5, 3022.9 cm^{-1}. MS (EI mode) *m*/z %: 158 (100), 143 (52), 129 (92), 115 (66), 104 (20), 77 (30), 65 (18), 63 (14), 51 (32). HRMS (ESI) calcd for $C_{12}H_{14}$ [M^+] 158.1095, found 158.1096.



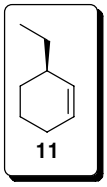
(*S*)-(2-(cyclopent-2-enyl)ethyl)benzene 17: prepared from **cyclopent-1-enyl-3-bromide 8** directly after its distillation. Yield = 93 %. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 86.75, 87.23, 94.06, 95.54 min). $[\alpha]^{25}_D$ = -117 (c = 1.5 in $CHCl_3$, 44 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.51 (m, 3H), 2.14 (m, 1H), 2.37 (m, 2H), 2.71 (m, 3H), 5.76 (m, 2H), 7.22-7.32 ppm (m, 5H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 29.9, 32.1, 34.4, 45.3, 125.7, 128.4, 128.5, 130.6, 135, 142.9 ppm. IR ($CHCl_3$): 697.7, 717.5, 748.6, 772.2, 1362.2, 1454.2, 1496, 1739.1, 2850.5, 2929.9, 30.26.9, 3050.9 cm^{-1}. MS (EI mode) *m*/z %: 172 (28), 152 (2), 144 (8), 129 (4), 115 (4), 104 (36), 92 (88), 81 (44), 67 (100), 53 (14), 51 (18). HRMS (ESI) calcd for $C_{13}H_{16}$ [M^+] 172.1249, found 172.1252.



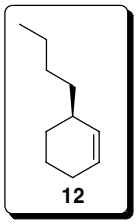
(*S*)-(2-(cyclohept-2-enyl)ethyl)benzene 18: prepared from **cyclohept-1-enyl-3-bromide 9**. Yield = 98 %. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 107.43, 109.05, 109.87, 110.70 min). $[\alpha]^{25}_D$ = -18 (c = 1.0 in $CHCl_3$, 38 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.25 (m, 2H), 1.32-1.35 (m, 5H), 1.95 (m, 1H), 2.15 (m, 2H), 2.26 (m, 1H), 2.65 (m, 2H), 5.67 (m, 1H), 5.80 (m, 1H), 7.19-7.29 ppm (m, 5H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 27.1, 28.9, 30.7, 33.5, 33.8, 39, 39.3, 125.7, 128.4, 128.5, 131.6, 137.8, 143 ppm. IR ($CHCl_3$): 697.6, 747.7, 1217.2, 1365.9, 1453.5, 1496.2, 1738.2, 2850.1, 2933.3, 3024.7 cm^{-1}. MS (EI mode) *m*/z %: 200 (14), 172 (2), 143 (6), 129 (4), 104 (32), 91 (100), 67 (62), 55 (30). HRMS (ESI) calcd for $C_{15}H_{20}$ [M^+] 200.1565, found 200.1565.



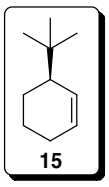
(*S*)-(2-(2-methylcyclohex-2-enyl)ethyl)benzene 19: prepared from **1-methylcyclohex-1-enyl-6-bromide 10**. Yield = 95 %. The enantiomeric excess was determined by GC on a chiral stationary phase after derivatisation in corresponding epoxides (Hydrodex TBDM column, Method: 60-0-1-170-5, R_T: 93.90, 96.29, 98.94, 100.37 min). $[\alpha]^{25}_D$ = -7.5 (c = 1.25 in $CHCl_3$, 18 % ee). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 1.56-1.70 (m, 5H), 1.68 (s, 3H), 1.99 (m, 4H), 2.55-2.75 (m, 2H), 5.45 (s, 1H), 7.23-7.31 ppm (m, 5H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 19.9, 22.3, 25.7, 27.5, 33.7, 34.7, 38.4, 122.8, 125.7, 128.4, 128.5, 137.1, 143.1 ppm. IR ($CHCl_3$): 697.9, 748.2, 1217.1, 1377.1, 1453.5, 1496.1, 1739.2, 2858.3, 2929.8, 3026.3). MS (EI mode) *m*/z %:. HRMS (ESI) calcd for $C_{15}H_{20}$ [M^+] 200.1565, found 200.1566.



(*R*)-3-ethylcyclohex-1-ene 11: prepared from **cyclohex-1-enyl-3-bromide 5**. Highly volatile product isolated after derivatisation in corresponding epoxides. After treatment with mcpba, **2-ethyl-7-oxa-bicyclo[4.1.0]heptane** is isolated as a mixture of diastereoisomeric epoxides with a ratio 1/1. Yield = 79 % (after two steps). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 0.82 (m, 1H), 0.98 (m, 6H), 1.22 (m, 2H), 1.36-1.83 (m, 13H), 2.05 (m, 2H), 2.85 (m, 1H), 3.12 ppm (m, 3H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 11.8, 17.4, 20.2, 24.1, 25, 26.3, 27, 27.1, 36.1, 36.9, 52.9, 55.7, 56.4 ppm. IR ($CHCl_3$): 1217, 1259.9, 1364.8, 1419, 1738.1, 2936.6 cm^{-1}. MS (EI mode) *m*/z %: 126 (8), 111 (30), 97 (56), 82 (42), 67 (100), 55 (96), 51 (10). HRMS (ESI) calcd for $C_8H_{14}O$ [M^+] 126.1044, found 126.1045.



(*R*)-3-butylcyclohex-1-ene 12: prepared from **cyclohex-1-enyl-3-bromide 5**. Highly volatile product isolated after derivatisation in corresponding epoxides. After treatment with mcpba, **2-butyl-7-oxa-bicyclo[4.1.0]heptane** is isolated as a mixture of diastereoisomeric epoxides with a ratio 1/1. Yield = 81 % (after two steps). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 0.81 (m, 1H), 0.89 (m, 6H), 1.11-1.82 (m, 24H), 2.06 (m, 1H), 2.84 (m, 1H), 3.06-3.14 ppm (m, 3H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 14.1, 14.2, 17.4, 20.2, 22.9, 23, 24.1, 25.1, 25.4, 27.4, 29.4, 33.1, 33.8, 33.8, 34.3, 35.1, 52.9, 53, 55.9, 56.6 ppm. IR ($CHCl_3$): 769.9, 825.6, 1217, 1259.7, 1377.4, 1456.2, 1738.6, 2858, 2933 cm^{-1}. MS (EI mode) *m*/z %: 154 (6), 139 (2), 136 (2), 125 (4), 111 (64), 97 (38), 81 (56), 68 (68), 55 (100), 51 (8). HRMS (ESI) calcd for $C_{10}H_{18}O$ [M^+] 154.1357, found 154.1358.



(*R*)-3-*tert*-butylcyclohex-1-ene 15: prepared from **cyclohex-1-enyl-3-bromide 5**. Highly volatile product isolated after derivatisation in corresponding epoxides. After treatment with mcpba, **2-*tert*-butyl-7-oxa-bicyclo[4.1.0]heptane** is isolated as a mixture of diastereoisomeric epoxides with a ratio 1/9. Yield = 80 % (after two steps). ^{1}H NMR (400 MHZ, $CDCl_3$, 25°C): δ = 0.97 (m, 8H), 1.25-1.42 (m, 4H), 1.55-1.60 (m, 4H), 1.87 (m, 1H), 2.11 (m, 1H), 3.03 (m, 1H), 3.15-3.20 ppm (m, 1H). ^{13}C NMR (100 MHZ, $CDCl_3$, 25°C): δ = 17.6, 17.7, 17.9, 19.9, 20.3, 22.8, 25.1, 25.2, 27.4, 28.3, 32.7, 38.3, 44.8, 53, 53.1, 53.3, 54.3, 54.6, 55.4 ppm. IR ($CHCl_3$): 703.7, 751.2, 786.3, 831.2, 842.1, 960.7, 1016.1, 1091.9, 1216.9, 1259.1, 1366.5, 1456.4, 1721.1, 2868.3, 2933 cm^{-1}. MS (EI mode) *m*/z %:. HRMS (ESI) calcd for $C_{10}H_{18}O$ [M^+] 154.1352, found 154.1358.

IV) References

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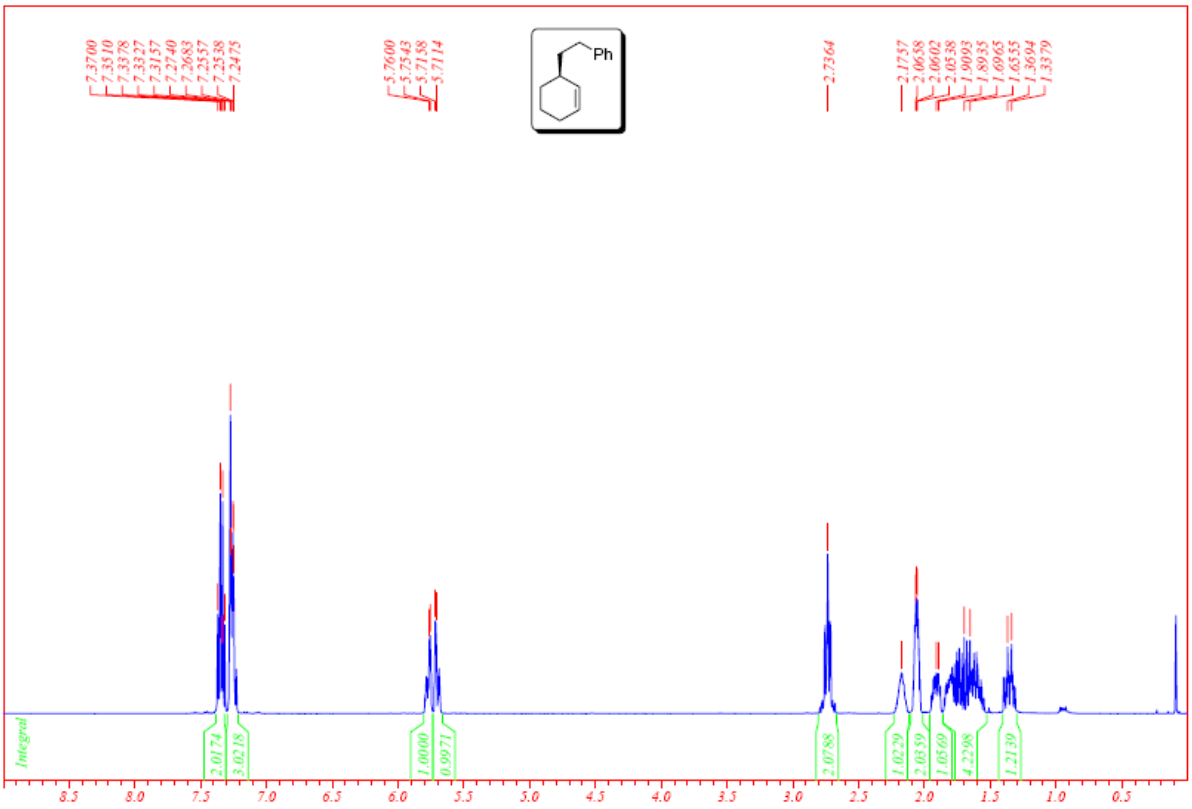
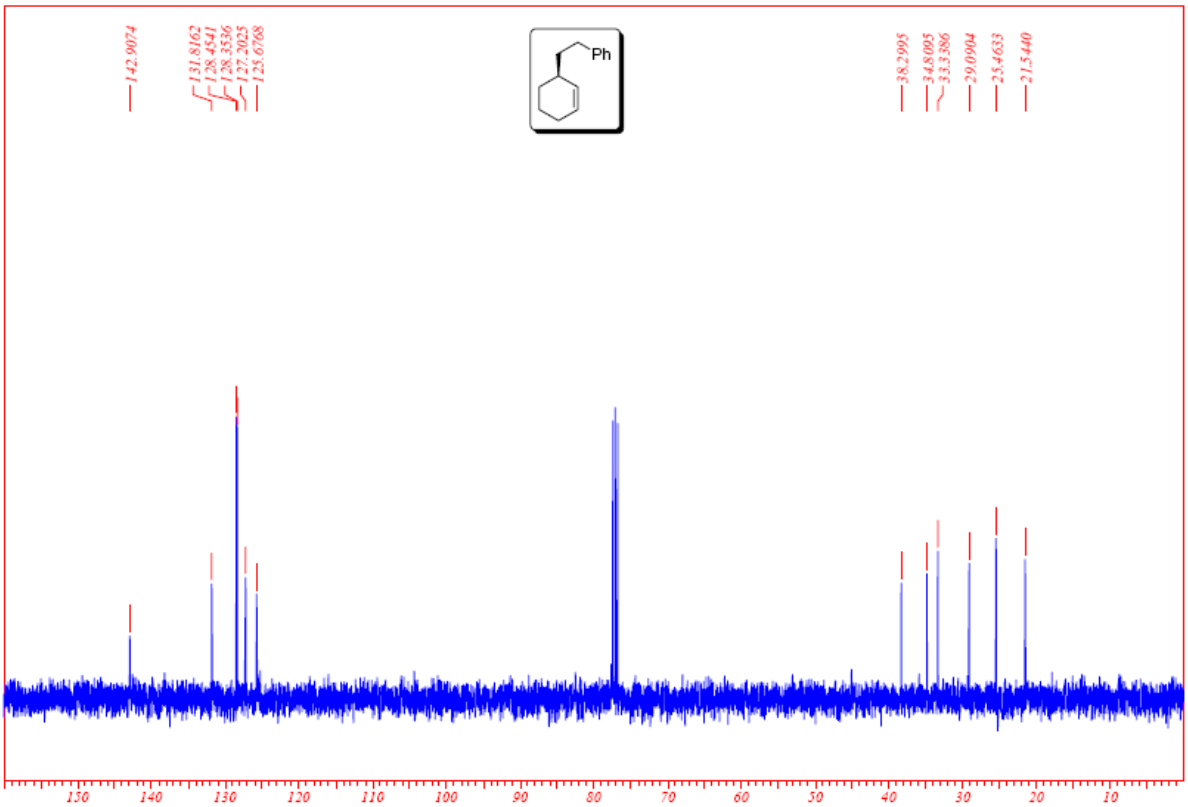
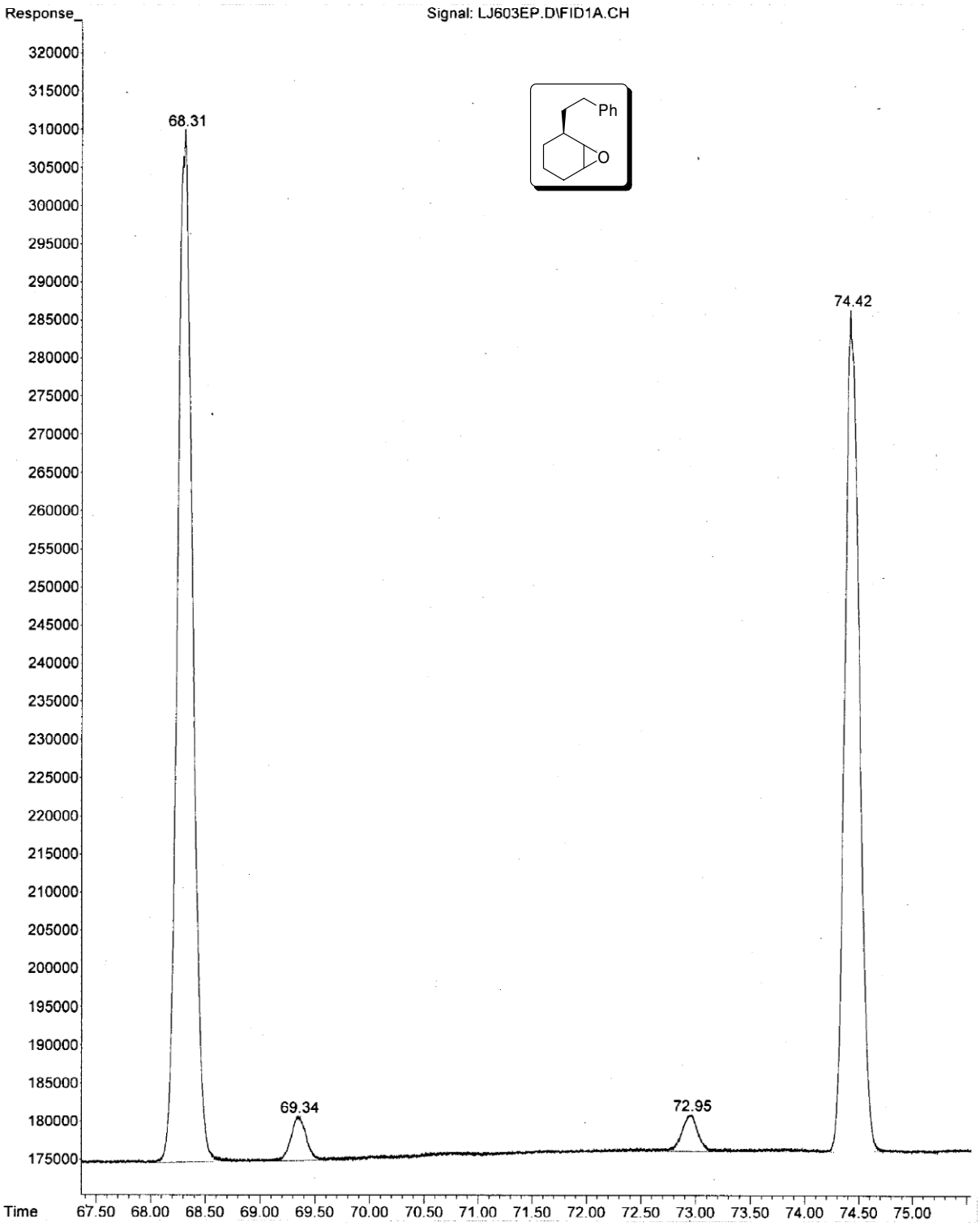
V) Spectroscopic datas

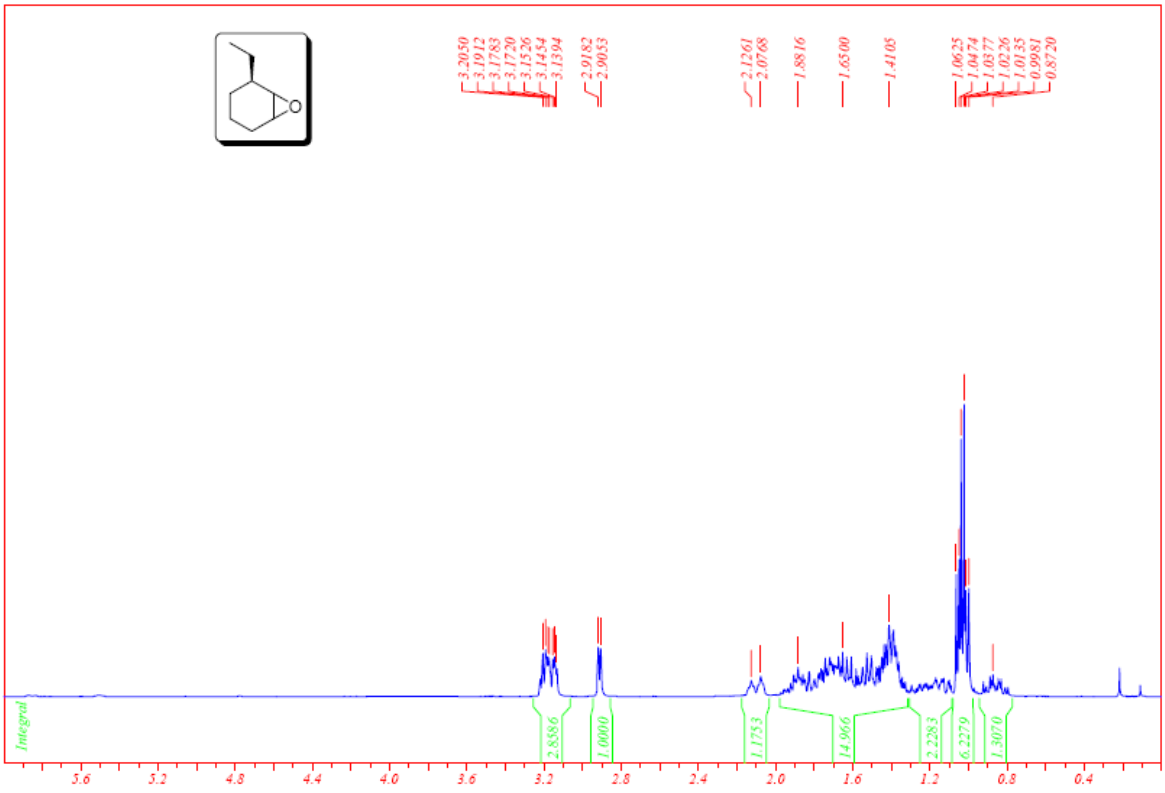


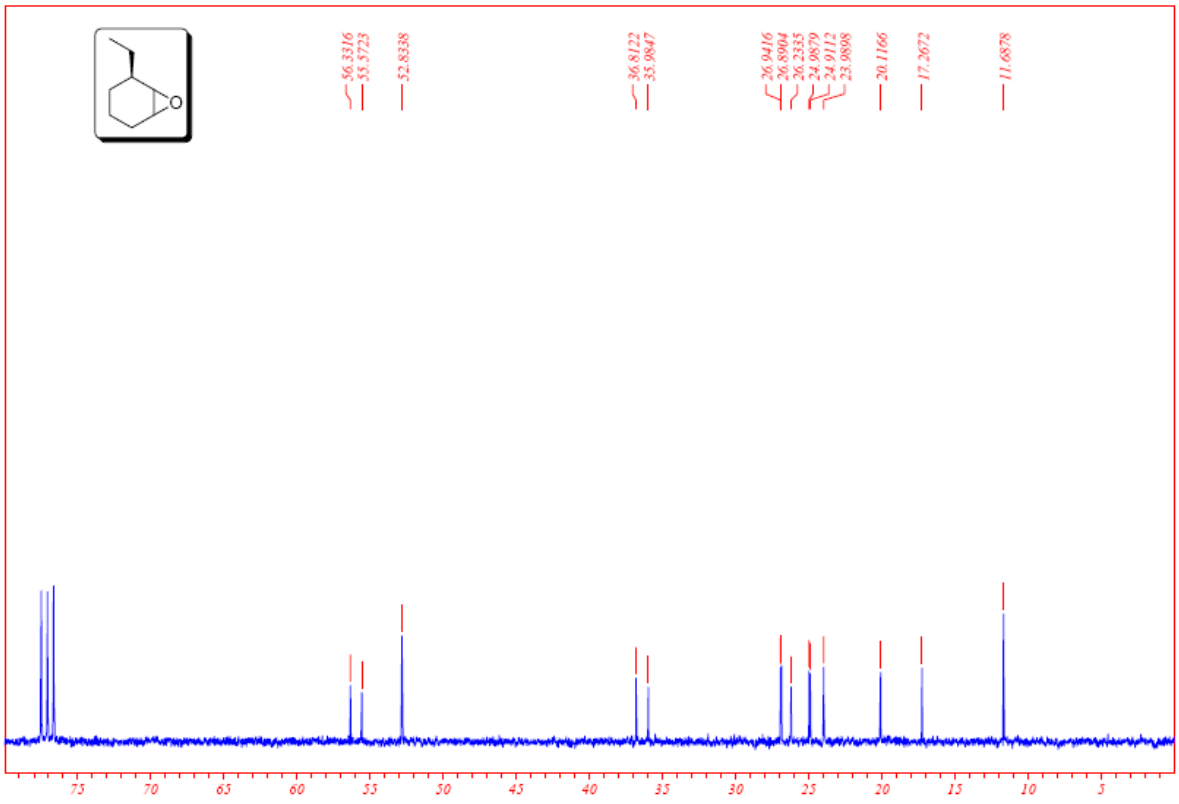


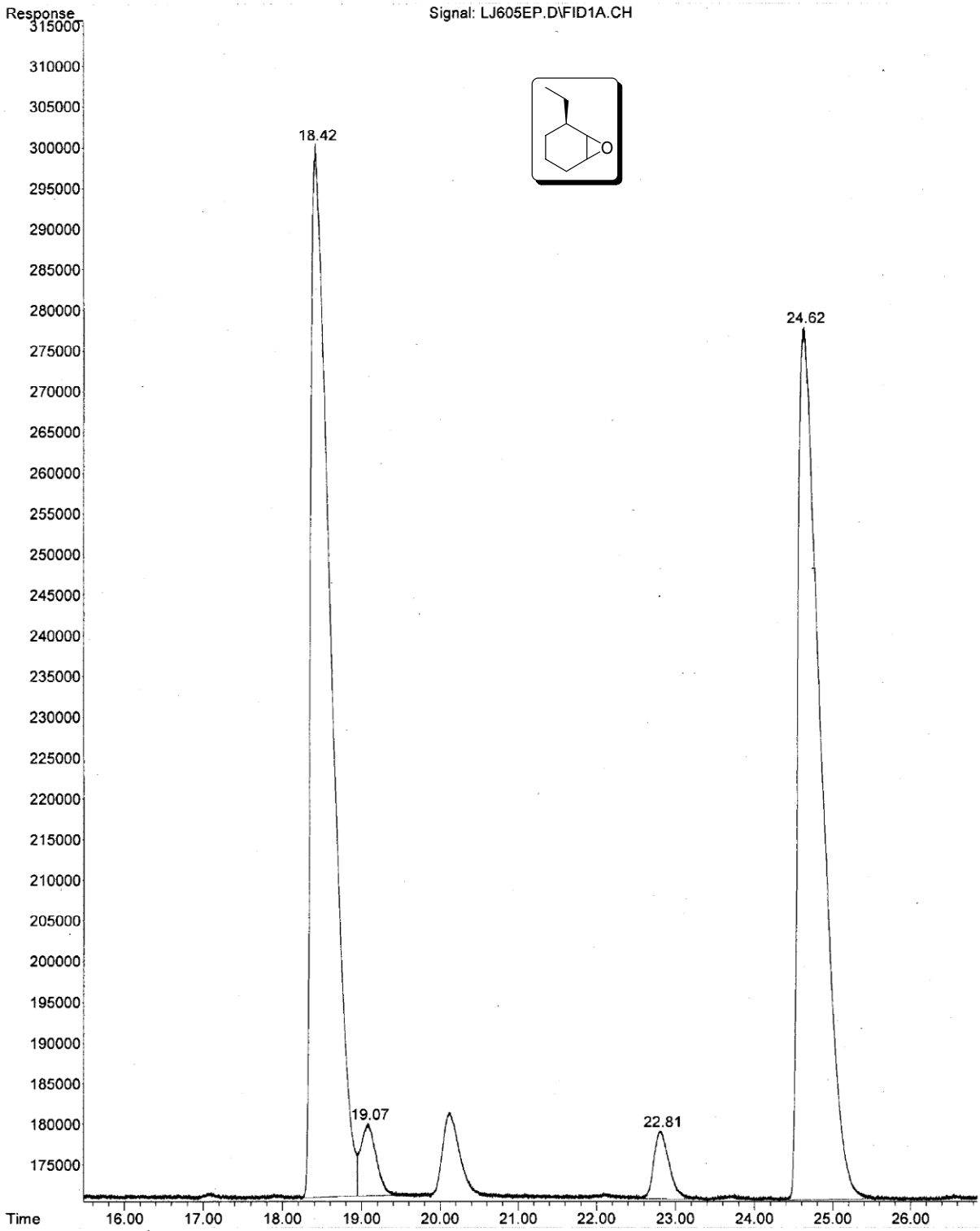


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	68.311	68.011	68.621	M	135379	13127825	100.00%	53.361%
2	69.339	69.143	69.547	M	5822	545450	4.15%	2.217%
3	72.947	72.730	73.157	M	4849	478043	3.64%	1.943%
4	74.419	74.178	74.722	M	110278	10450381	79.60%	42.478%

Sum of corrected areas: 24601698

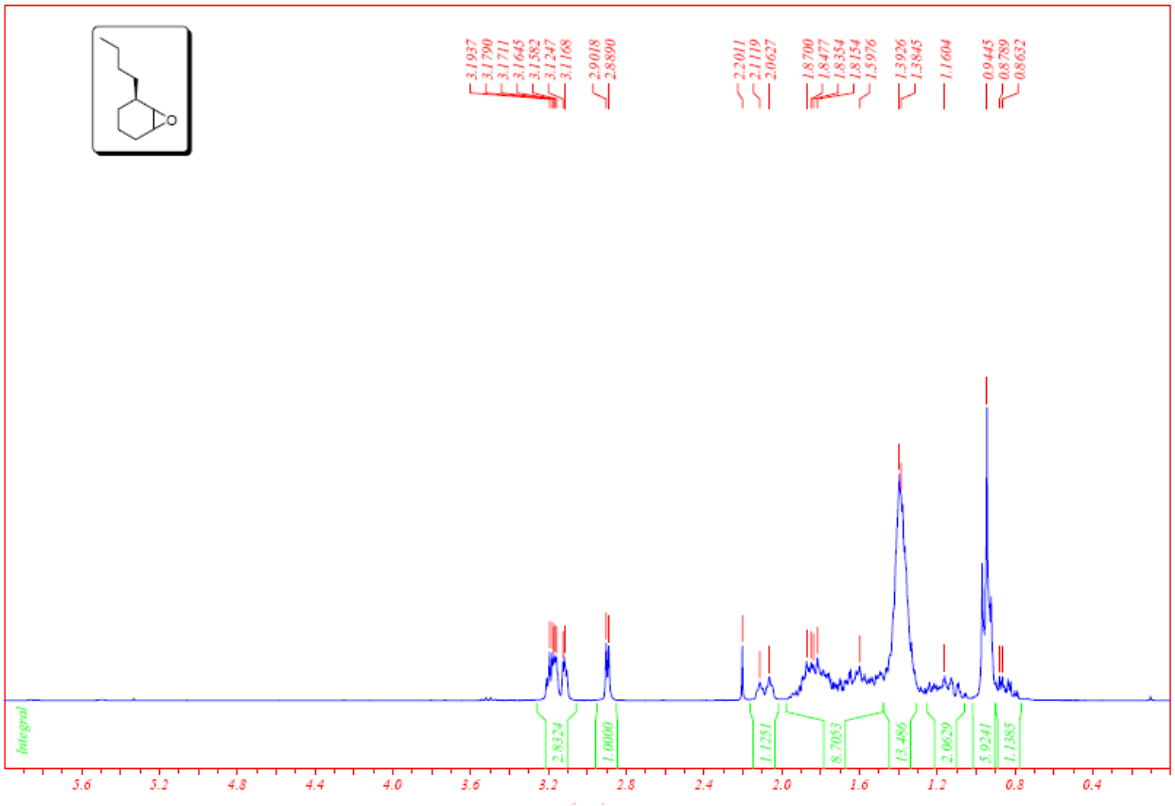

3.2050
3.1912
3.1783
3.1720
3.1526
3.1454
3.1394
2.9182
2.9053
2.1261
2.0768
1.8816
1.6500
1.4105
1.0625
1.0474
1.0377
1.0226
1.0135
0.9981
0.8720
Integral
2.8586
1.0000
1.1753
14.9666
2.2283
6.2279
1.3070
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

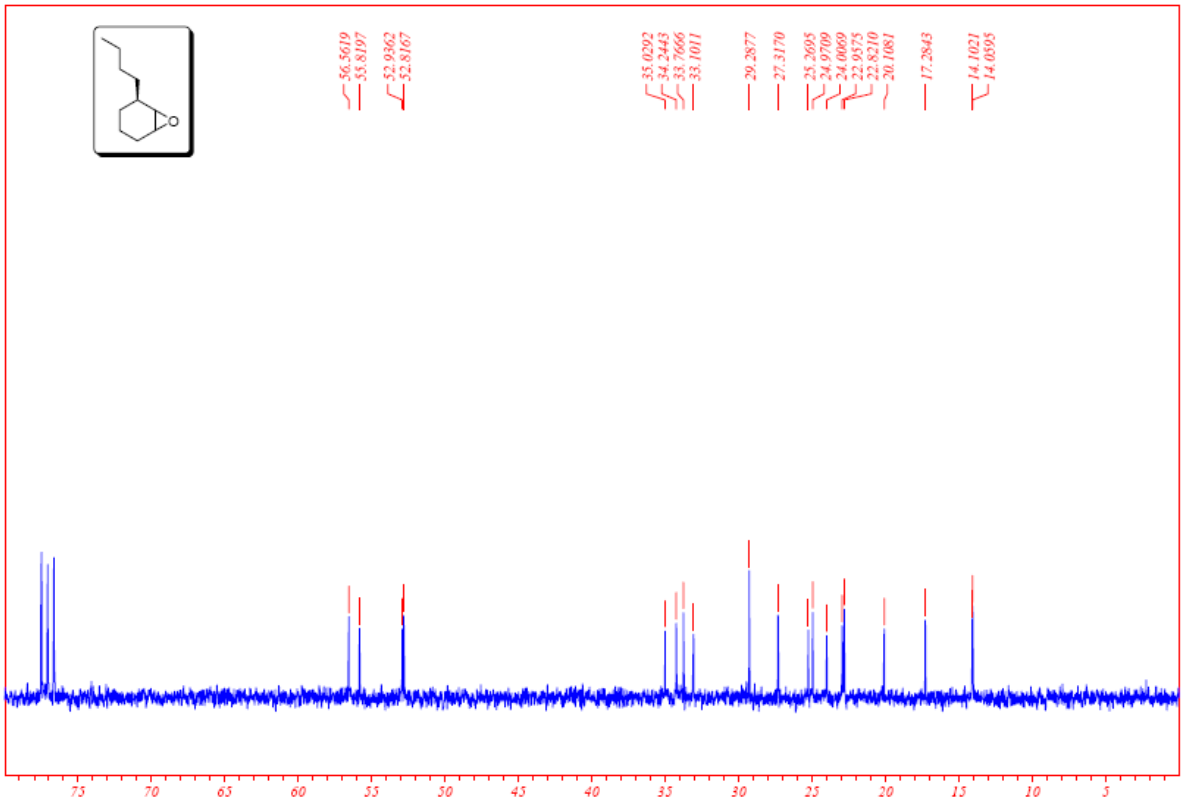

56.3316
55.5723
52.8338
36.8122
35.9847
26.9416
26.8904
26.2335
24.9879
24.9112
23.9898
20.1166
17.2672
11.6878
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	18.416	18.249	18.942	M	129418	22559894	100.00%	48.639%
2	19.074	18.946	19.385	M	8952	1199827	5.32%	2.587%
3	22.811	22.585	23.195	M	8333	1098250	4.87%	2.368%
4	24.619	24.402	25.479	M	107170	21524560	95.41%	46.407%

Sum of corrected areas: 46382531


3.1937
3.1790
3.1711
3.1645
3.1582
3.1247
3.1168
2.9018
2.8890
2.2011
2.1119
2.0627
1.8700
1.8477
1.8354
1.8154
1.5976
1.3926
1.3845
1.1604
0.9445
0.8789
0.8632
Integral
2.8324
1.0000
1.1251
8.7053
13.466
2.0629
3.9241
1.1385
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4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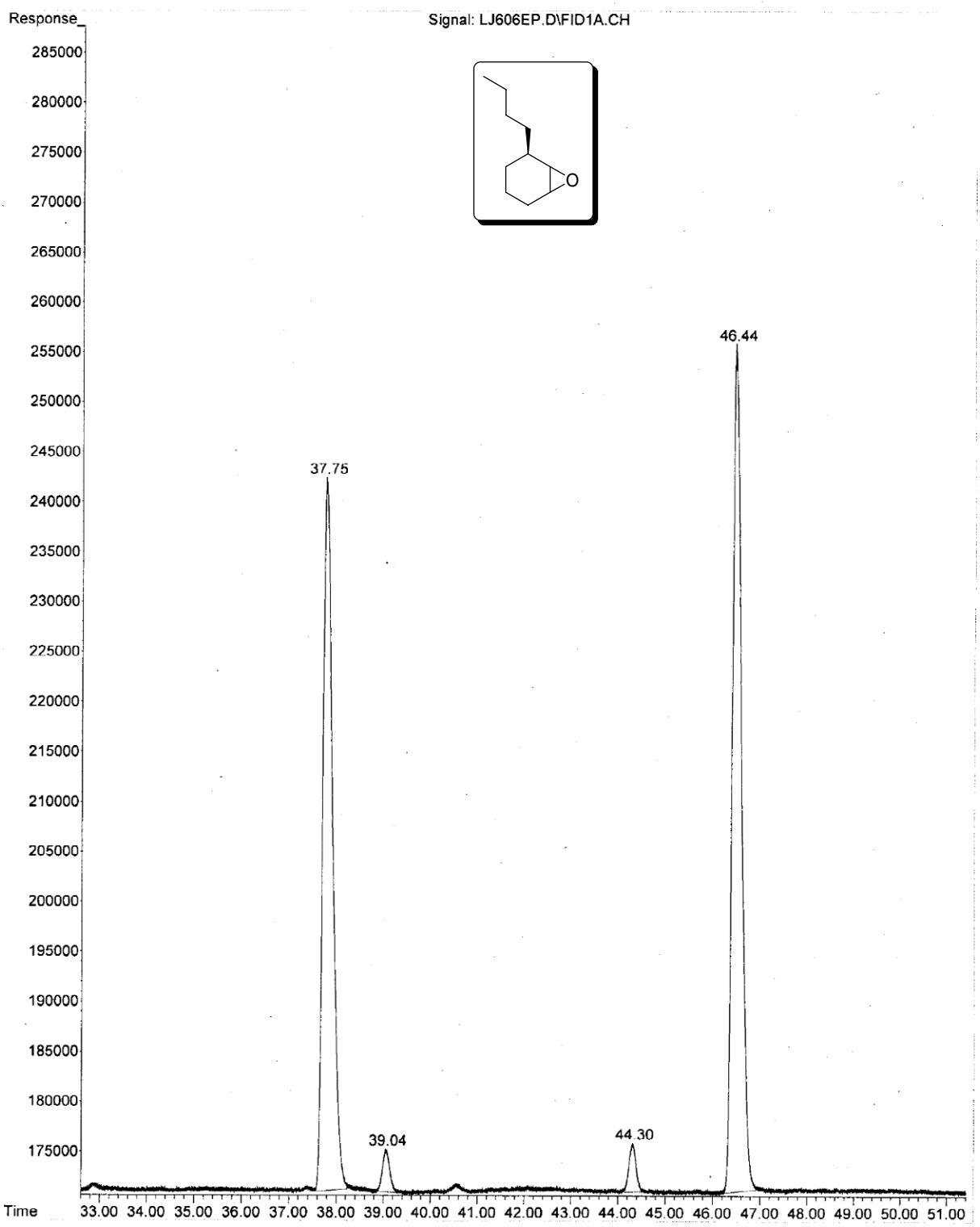
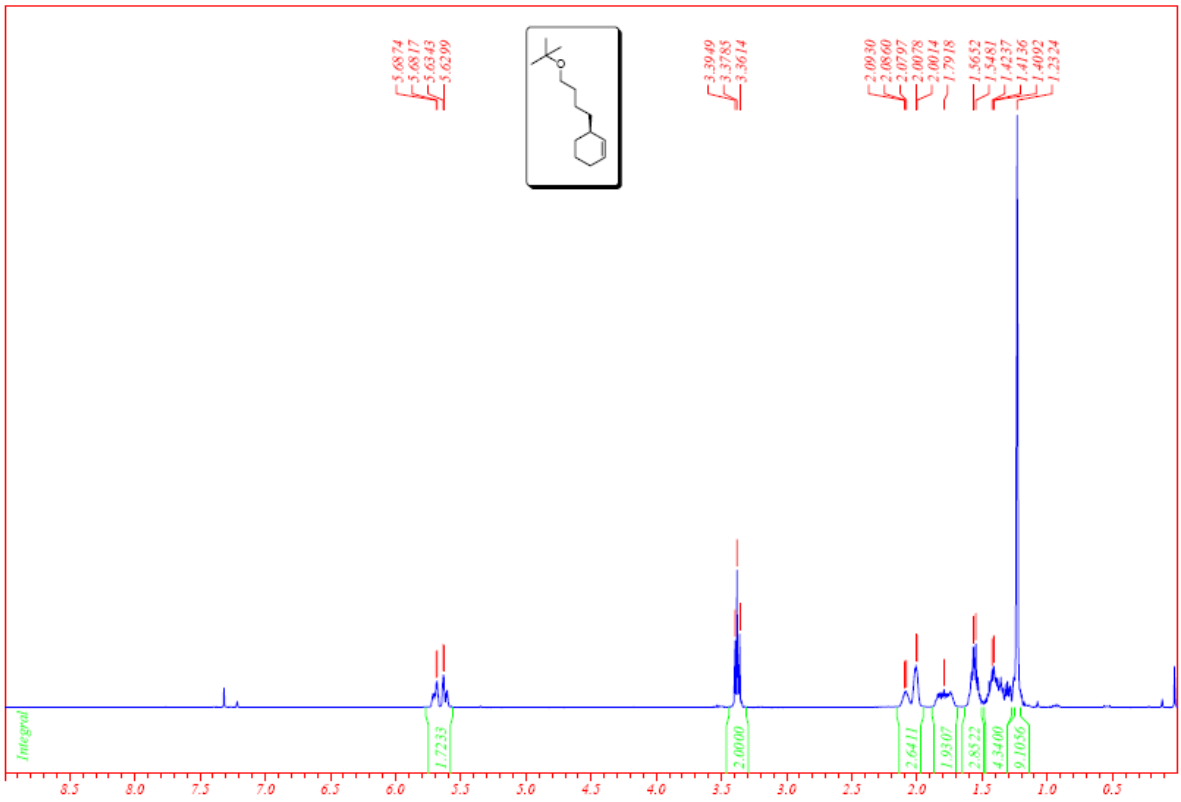
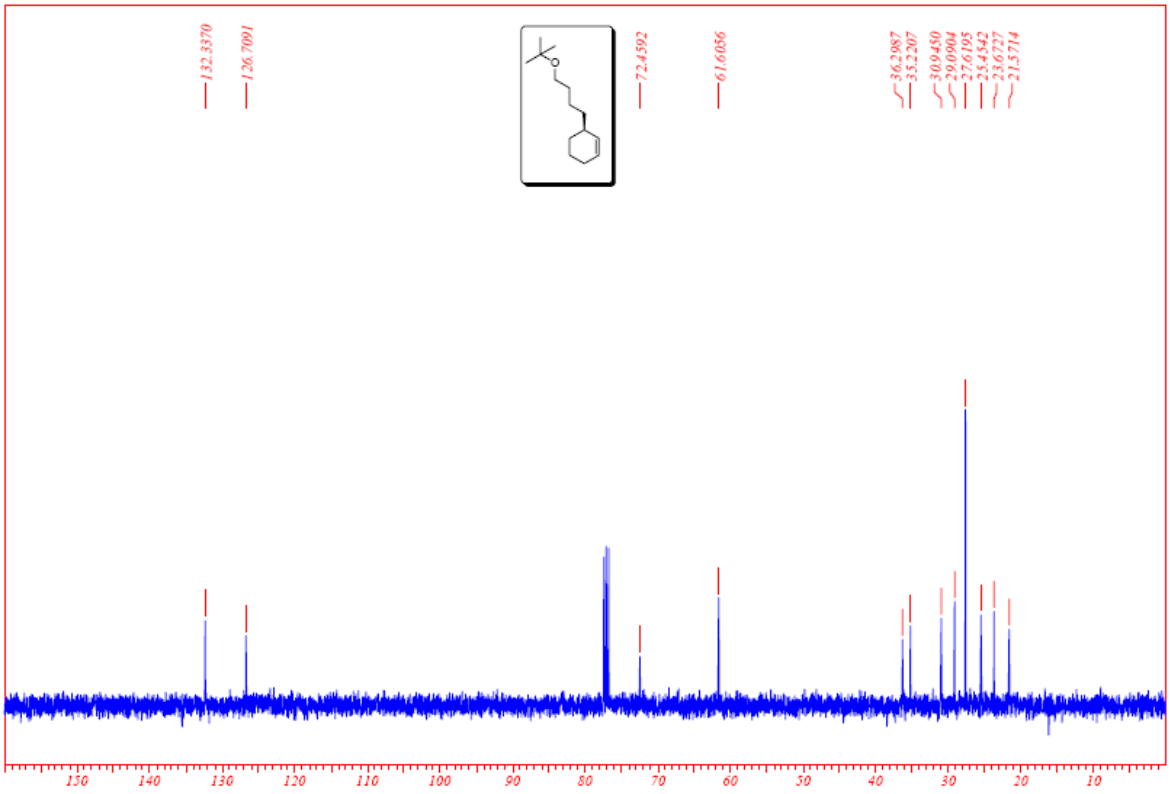
52.9362
52.8167
35.0292
34.2443
33.7666
33.1011
29.2877
27.3170
25.2695
24.9709
24.0069
22.9575
22.8210
20.1081
17.2843
14.1021
14.0595
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	37.749	37.566	38.228	M	71406	10098033	88.85%	45.062%
2	39.038	38.880	39.250	M	4313	446423	3.93%	1.992%
3	44.302	44.116	44.505	M	4908	498982	4.39%	2.227%
4	46.441	46.231	46.930	M	84936	11365831	100.00%	50.719%

Sum of corrected areas: 22409268


5.6874
5.6817
5.6343
5.6299
3.3949
3.3785
3.3614
2.0930
2.0660
2.0797
2.0078
2.0014
1.7918
1.5652
1.5481
1.4237
1.4136
1.4092
1.2324
Integral
1.7235
2.0000
2.6411
1.9307
2.8522
4.3400
9.1036
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


132.3370
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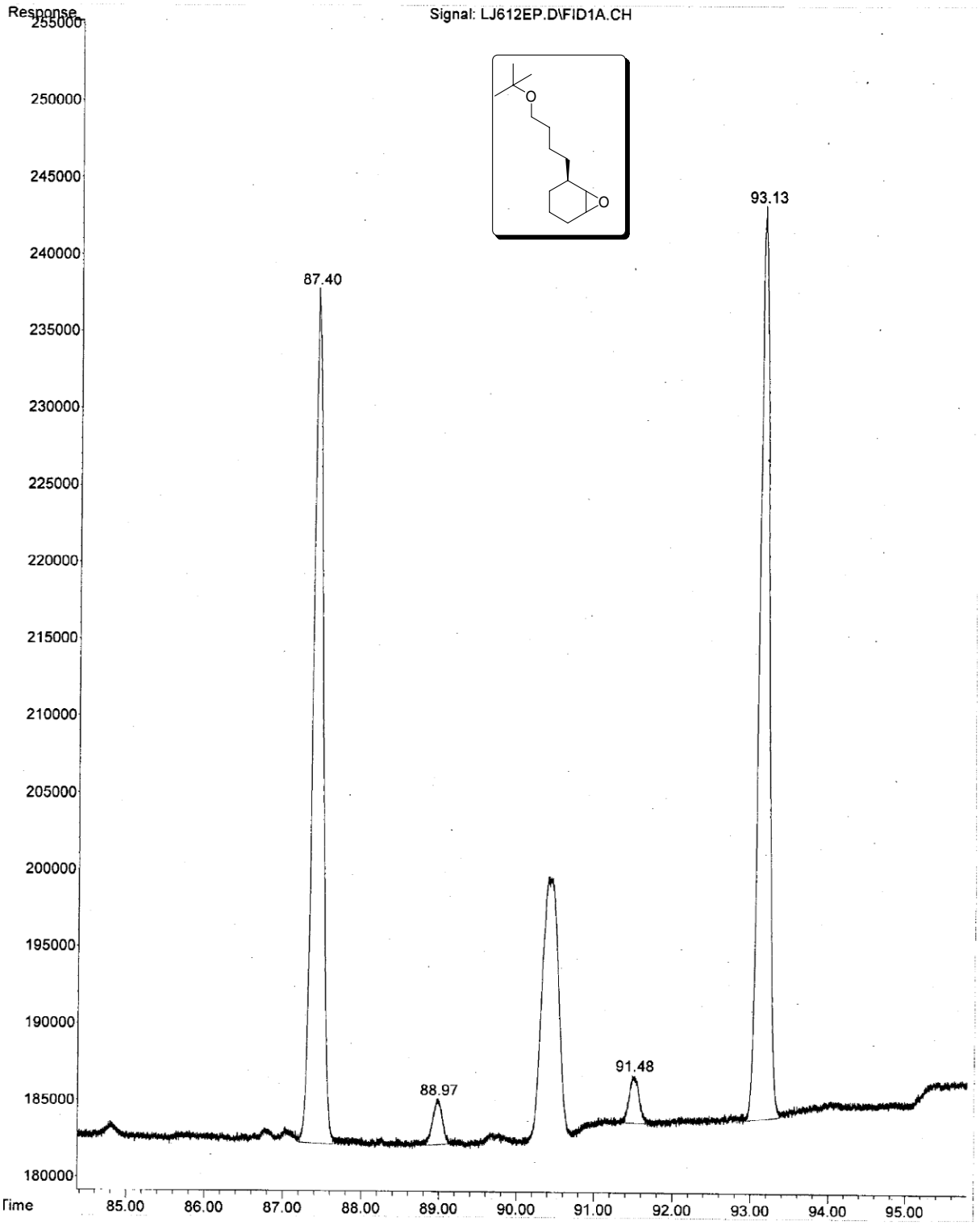
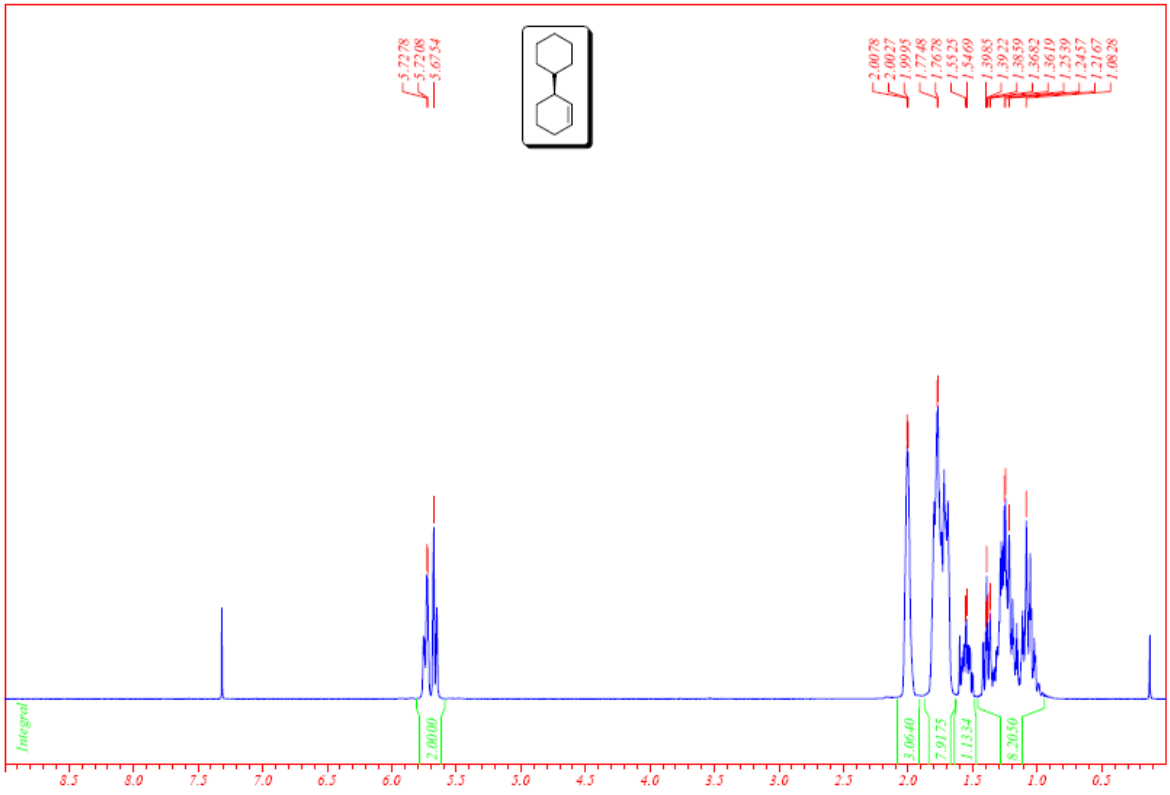
72.4592
61.6056
36.2987
35.2207
30.9450
29.0904
27.6195
25.4542
23.6727
21.5714
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	87.397	87.177	87.630	M	55555	4894857	94.23%	46.143%
2	88.968	88.826	89.114	M	3012	249724	4.81%	2.354%
3	91.484	91.354	91.676	M	3127	269145	5.18%	2.537%
4	93.133	92.929	93.360	M	59301	5194347	100.00%	48.966%

Sum of corrected areas: 10608073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5.7208
5.6754
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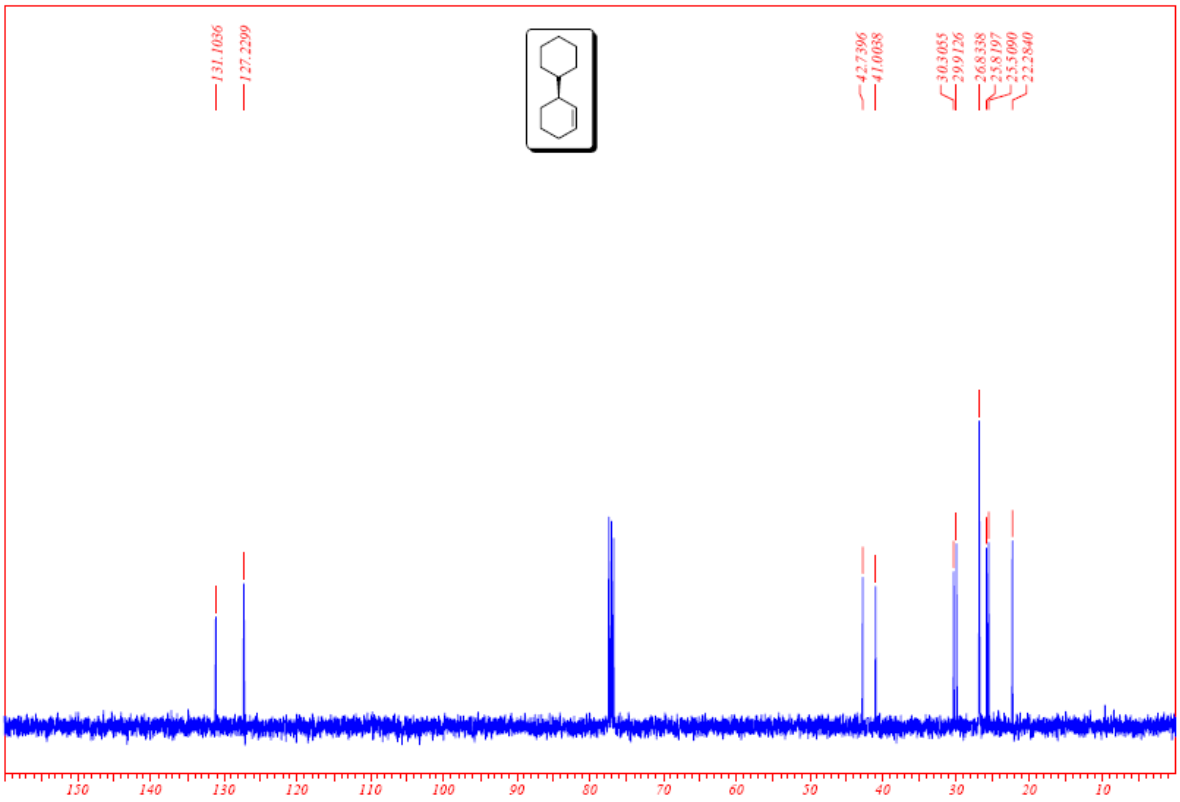
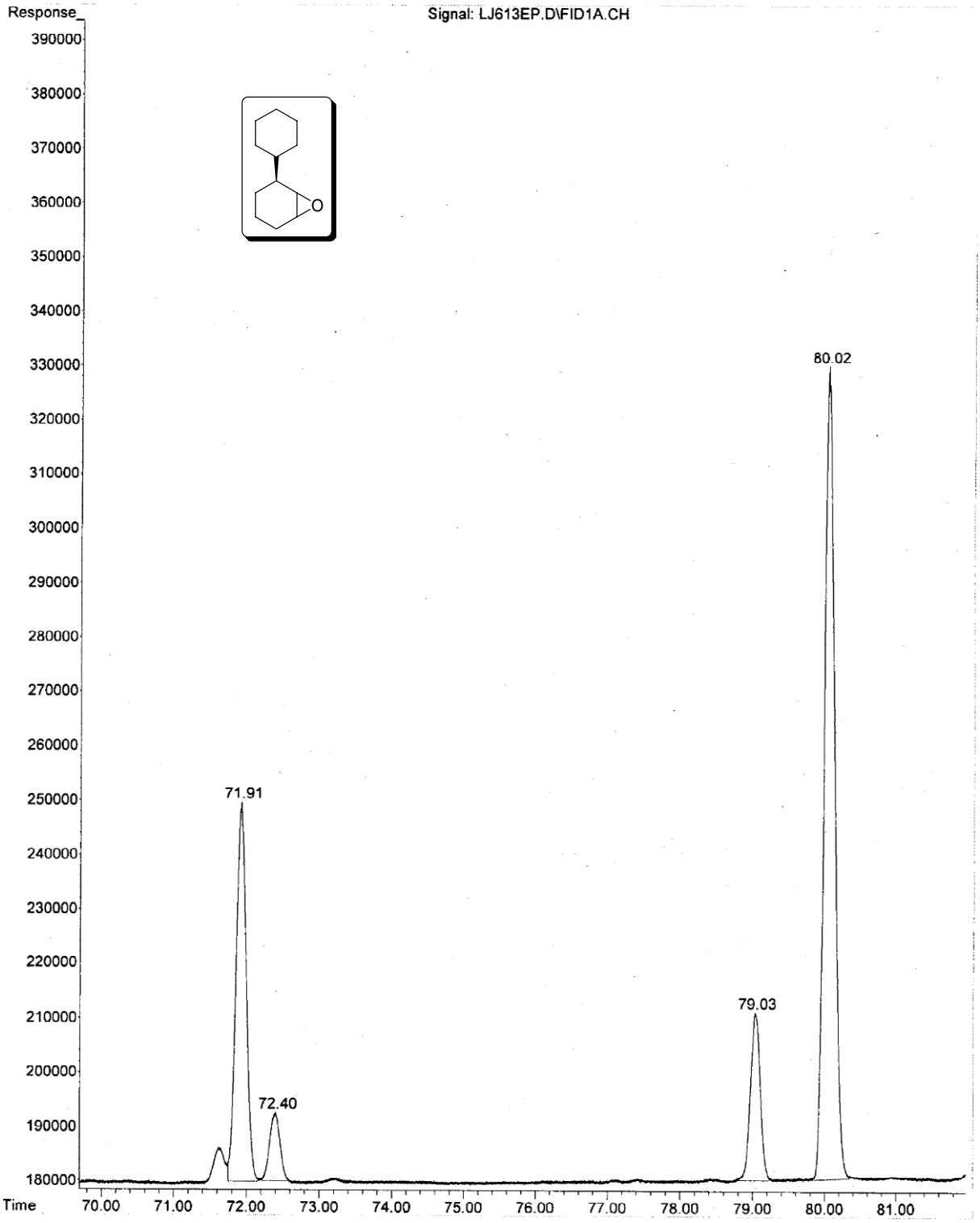
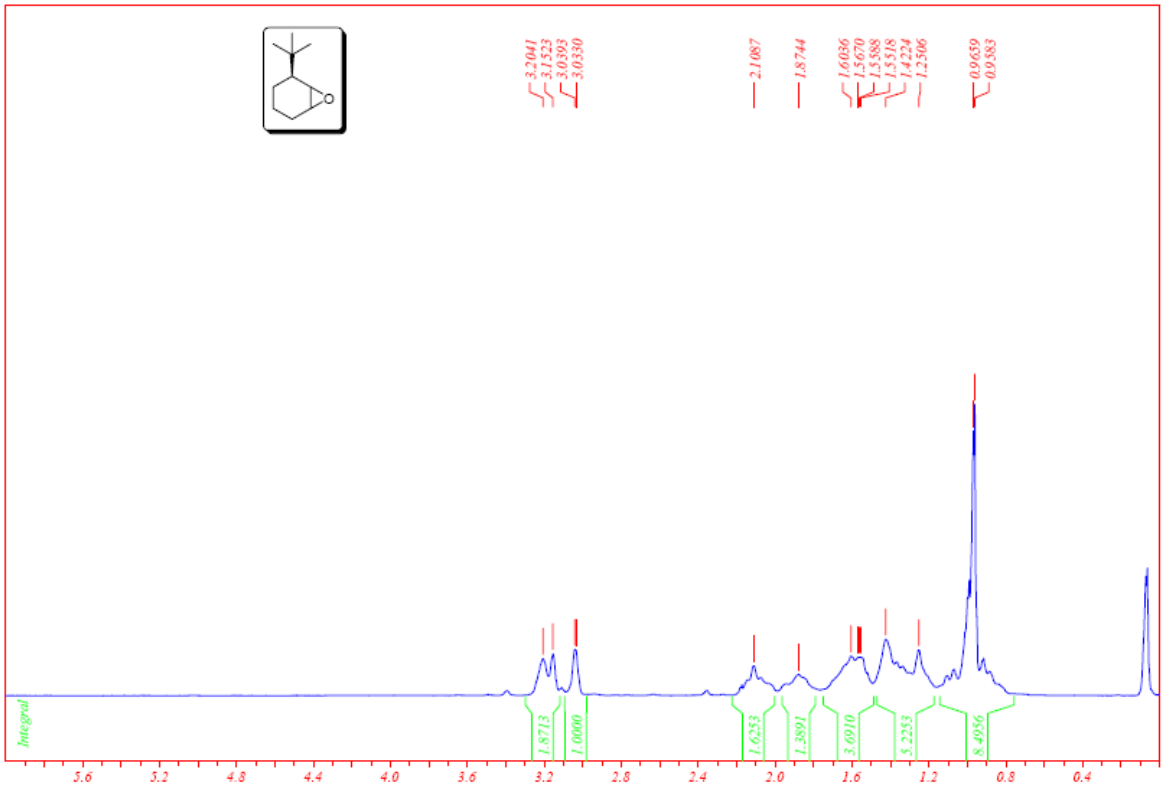
2.0027
1.9995
1.7748
1.7678
1.5525
1.5469
1.3985
1.3922
1.3859
1.3682
1.3619
1.2539
1.2457
1.2167
1.0828
Integral
2.0000
3.0640
7.9175
1.1334
8.2050
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

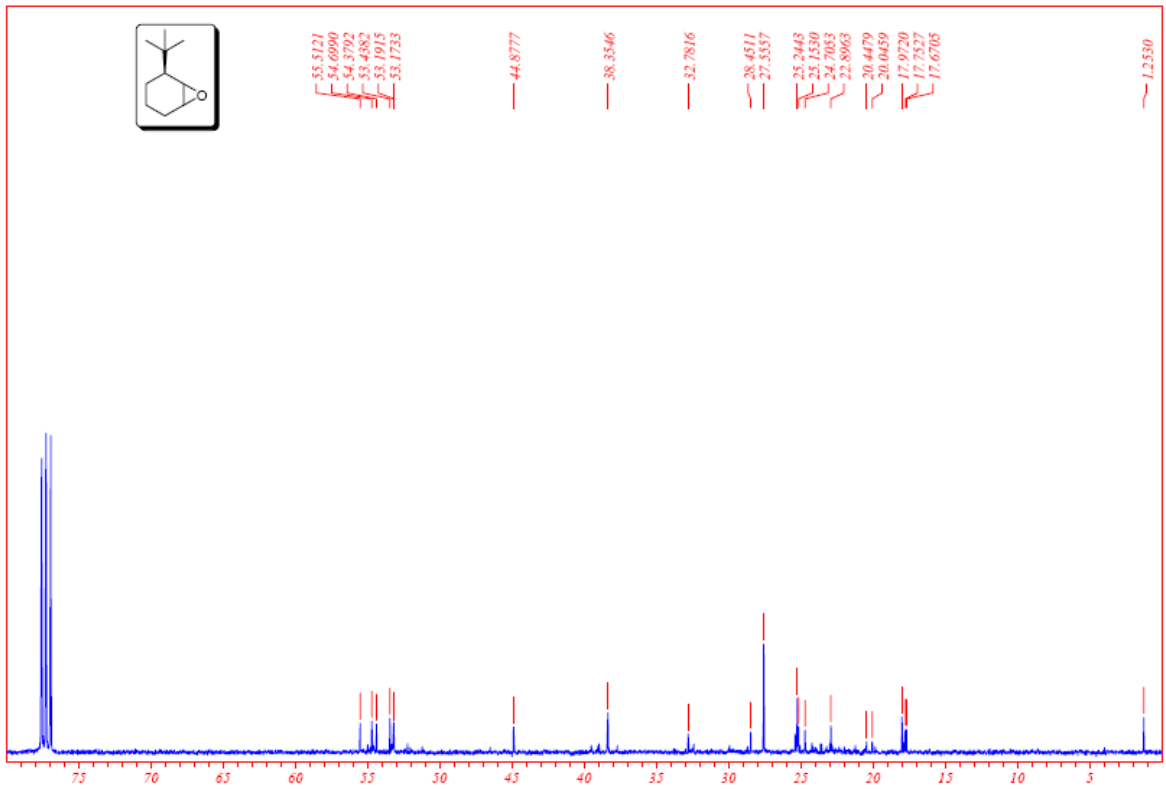

131.1036
127.2299
42.7396
41.0038
30.3055
29.9126
26.8338
25.8197
25.5090
22.2840
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

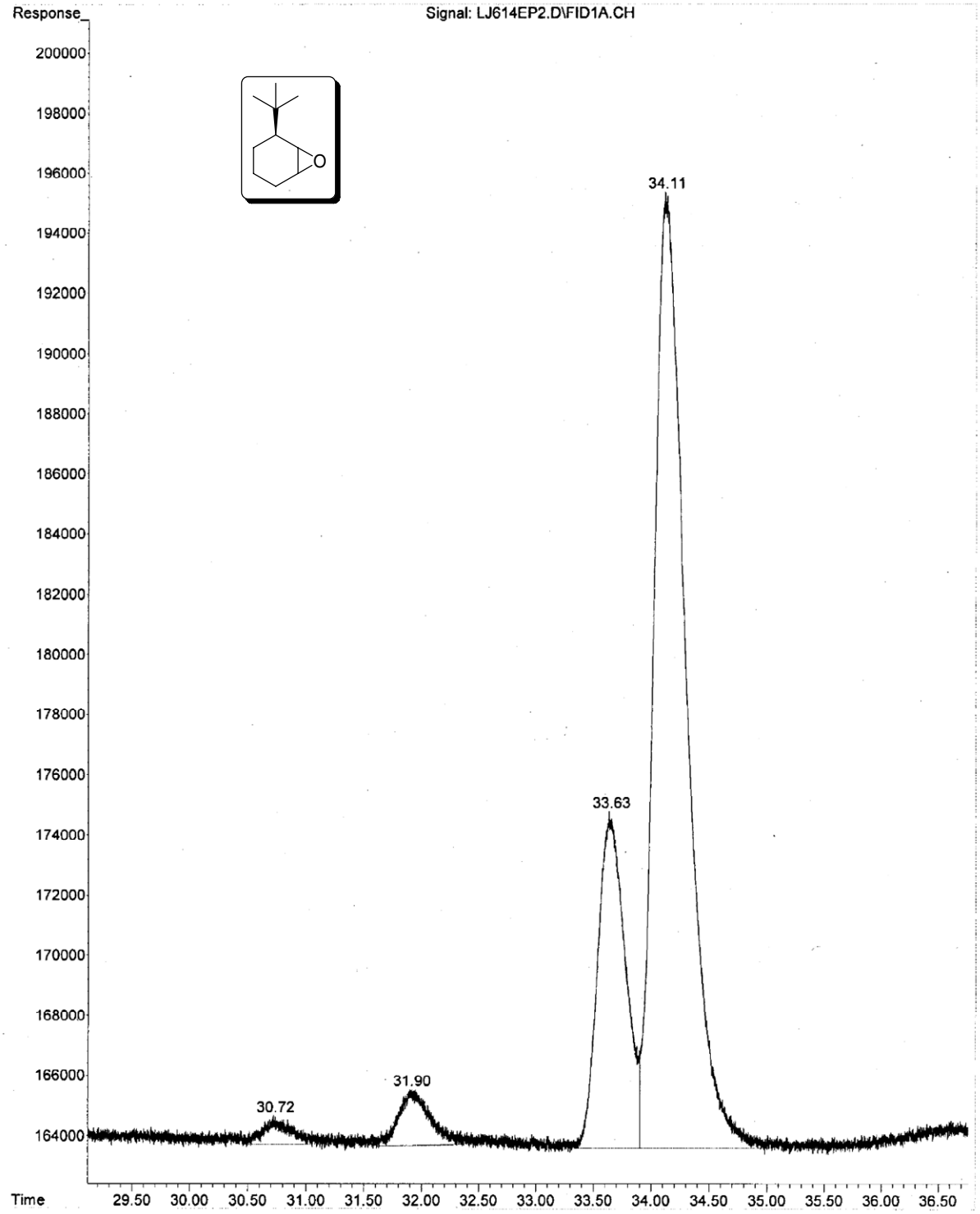


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	71.914	71.751	72.159	M	69802	6804854	45.82%	26.389%
2	72.399	72.215	72.568	M	12722	1227644	8.27%	4.761%
3	79.030	78.791	79.259	M	30894	2902718	19.55%	11.257%
4	80.023	79.835	80.347	M	149528	14851110	100.00%	57.593%

Sum of corrected areas: 25786327

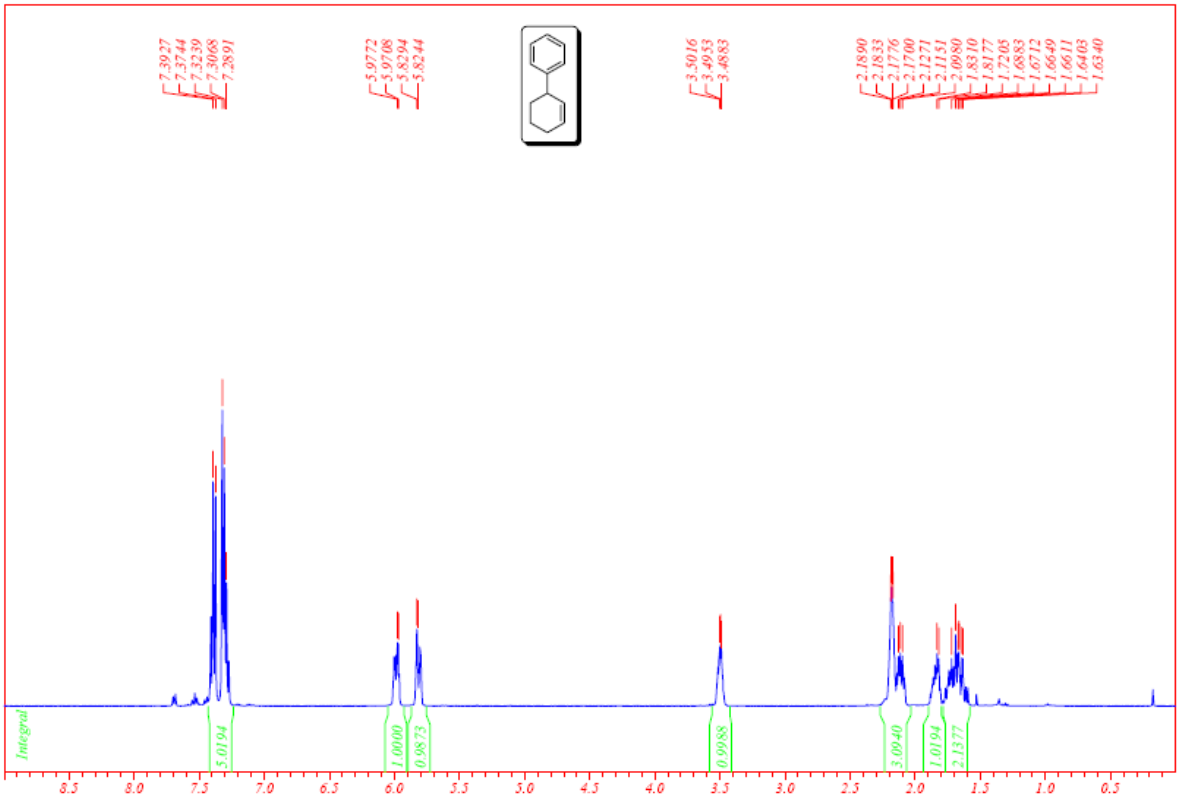

3.2041
3.1523
3.0393
3.0330
2.1087
1.8744
1.6086
1.5670
1.5588
1.5518
1.4224
1.2506
0.9659
0.9583
Integral
1.8713
1.0000
1.6253
1.3891
3.6910
5.2253
8.4956
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4

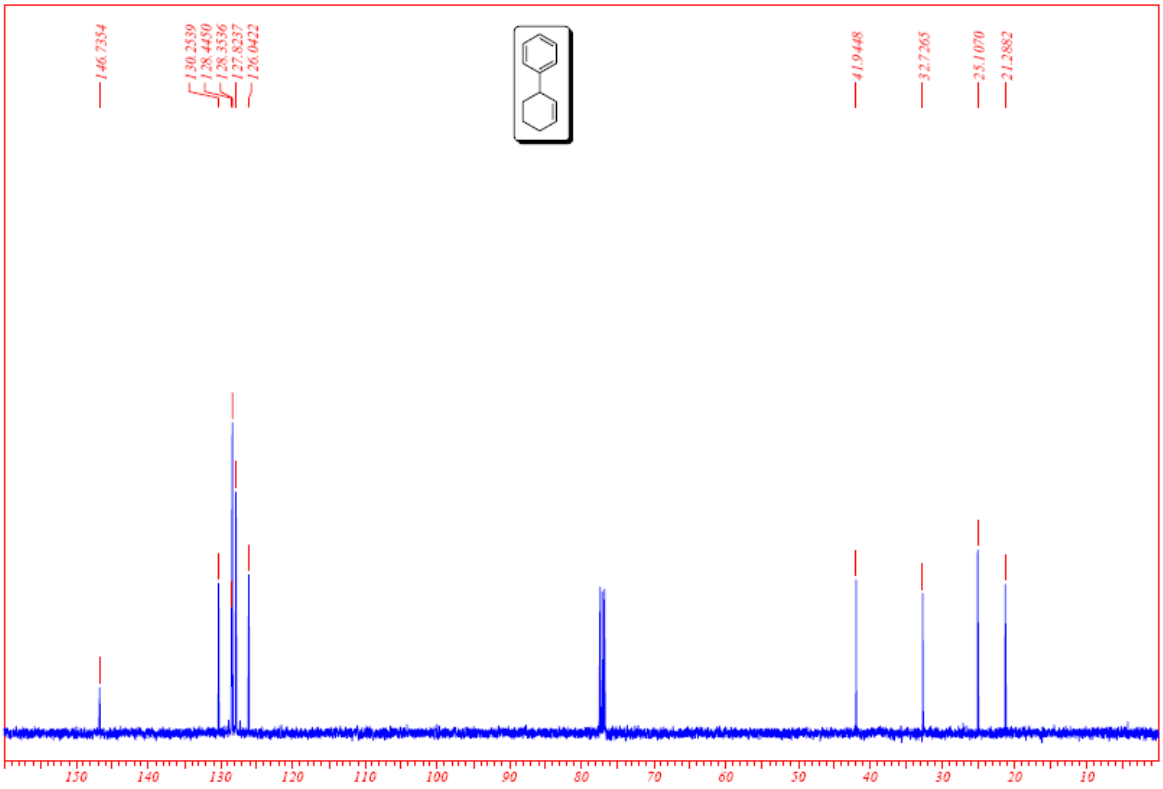

55.5121
54.6990
54.3792
53.4882
53.1915
53.1733
44.8777
38.3546
32.7816
28.4511
27.5557
25.2443
25.1530
24.7053
22.8963
20.4479
20.0459
17.9720
17.7527
17.6705
1.2530
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5

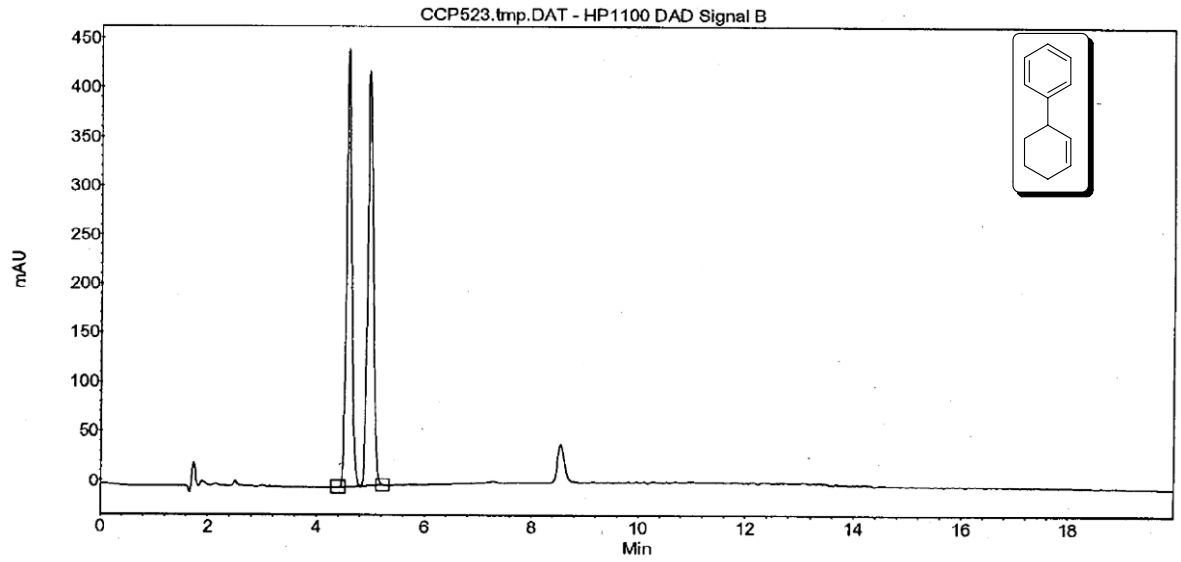


peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	30.722	30.500	31.058	M	967	138933	2.28%	1.650%
2	31.897	31.633	32.341	M	1879	340568	5.58%	4.043%
3	33.634	33.340	33.903	M	11192	1836288	30.07%	21.802%
4	34.114	33.903	34.954	M	31774	6106906	100.00%	72.505%

Sum of corrected areas: 8422695

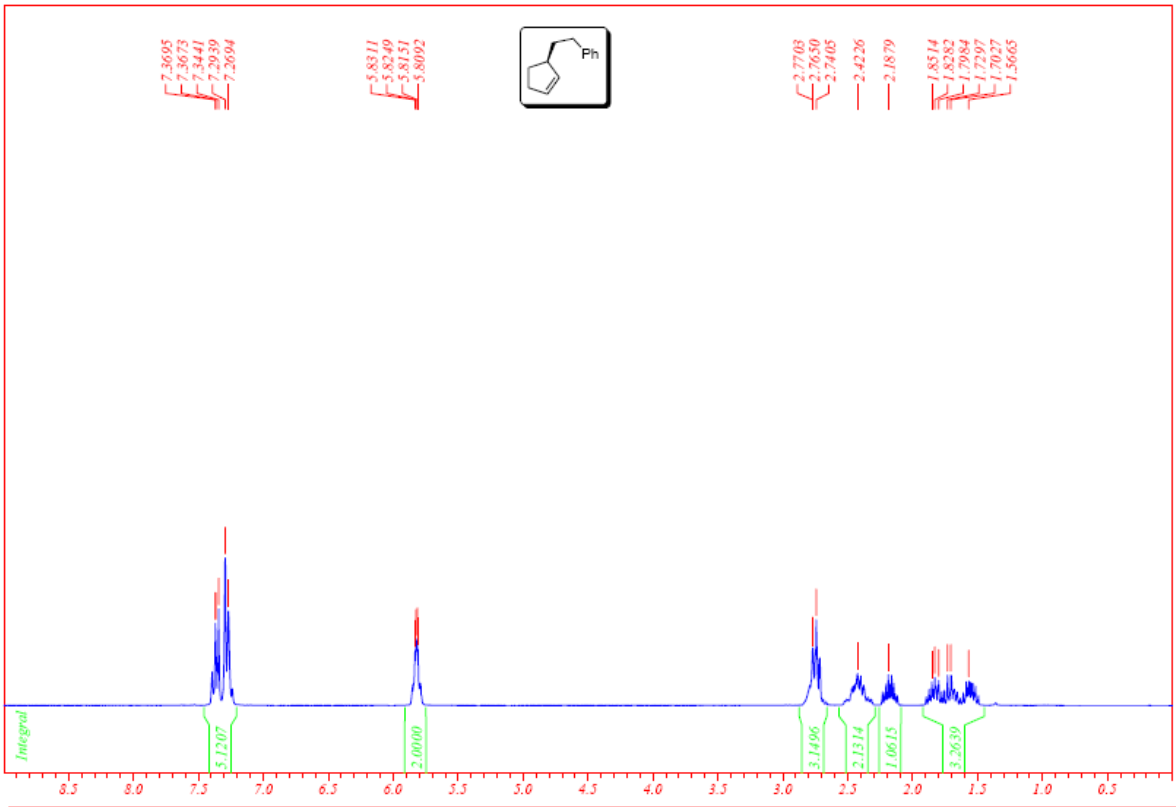

7.3927
7.3744
7.3239
7.3068
7.2891
5.9772
5.9708
5.8294
5.8244
3.5016
3.4953
3.4883
2.1890
2.1833
2.1776
2.1700
2.1271
2.1151
2.0980
1.8310
1.8177
1.7205
1.6883
1.6712
1.6649
1.6611
1.6403
1.6340
Integral
5.0194
1.0000
0.9873
0.9988
3.0940
1.0194
2.1377
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


146.7354
130.2539
128.4450
128.3536
127.8237
126.0422
41.9448
32.7265
25.1070
21.2882
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



Peak results :

Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.40	4.57	4.80	0.00	49.57	446.0	50.1	49.567
2	UNKNOWN	4.80	4.97	5.22	0.00	50.43	422.5	51.0	50.433
Total						100.00	868.5	101.1	100.000


7.3695
7.3673
7.3441
7.2939
7.2694
5.8311
5.8249
5.8151
5.8092
Ph
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2.7650
2.7405
2.4226
2.1879
1.8514
1.8282
1.7984
1.7297
1.7027
1.5665
Integral
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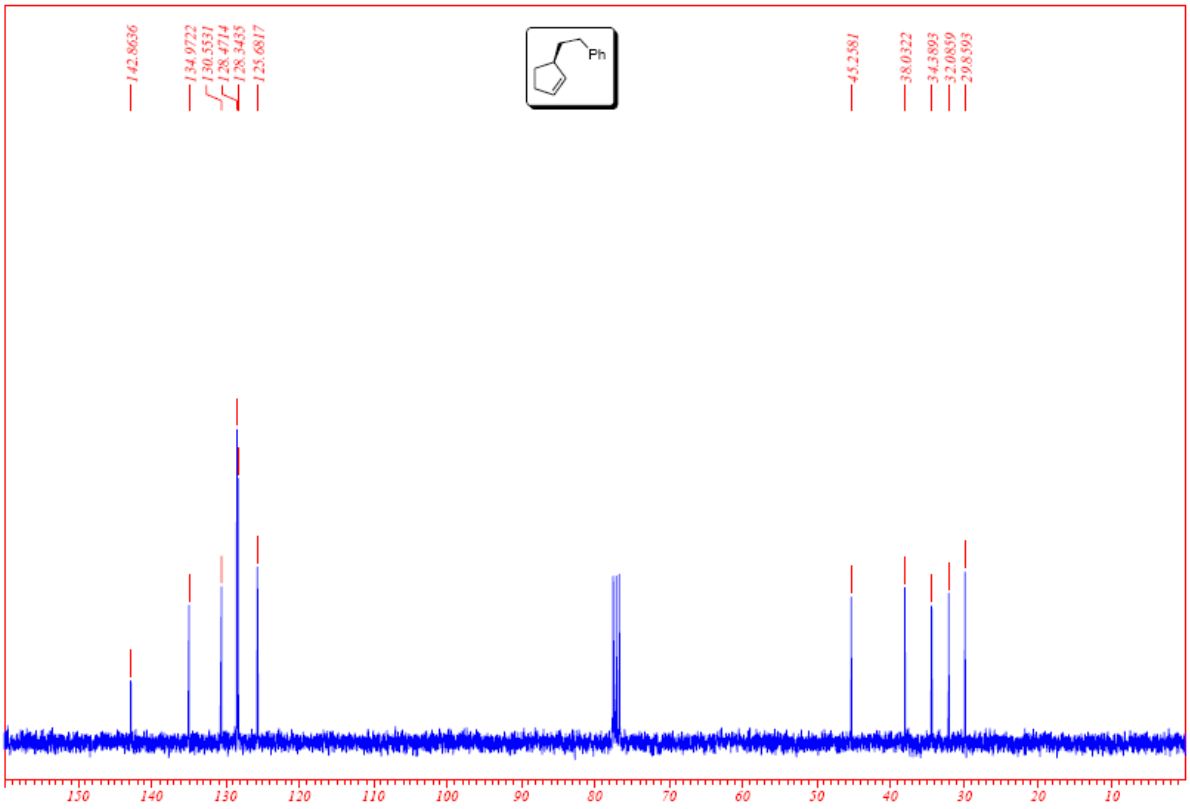
3.1496
2.1314
1.0615
3.2639


142.8636
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130.5531
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128.3435
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38.0322
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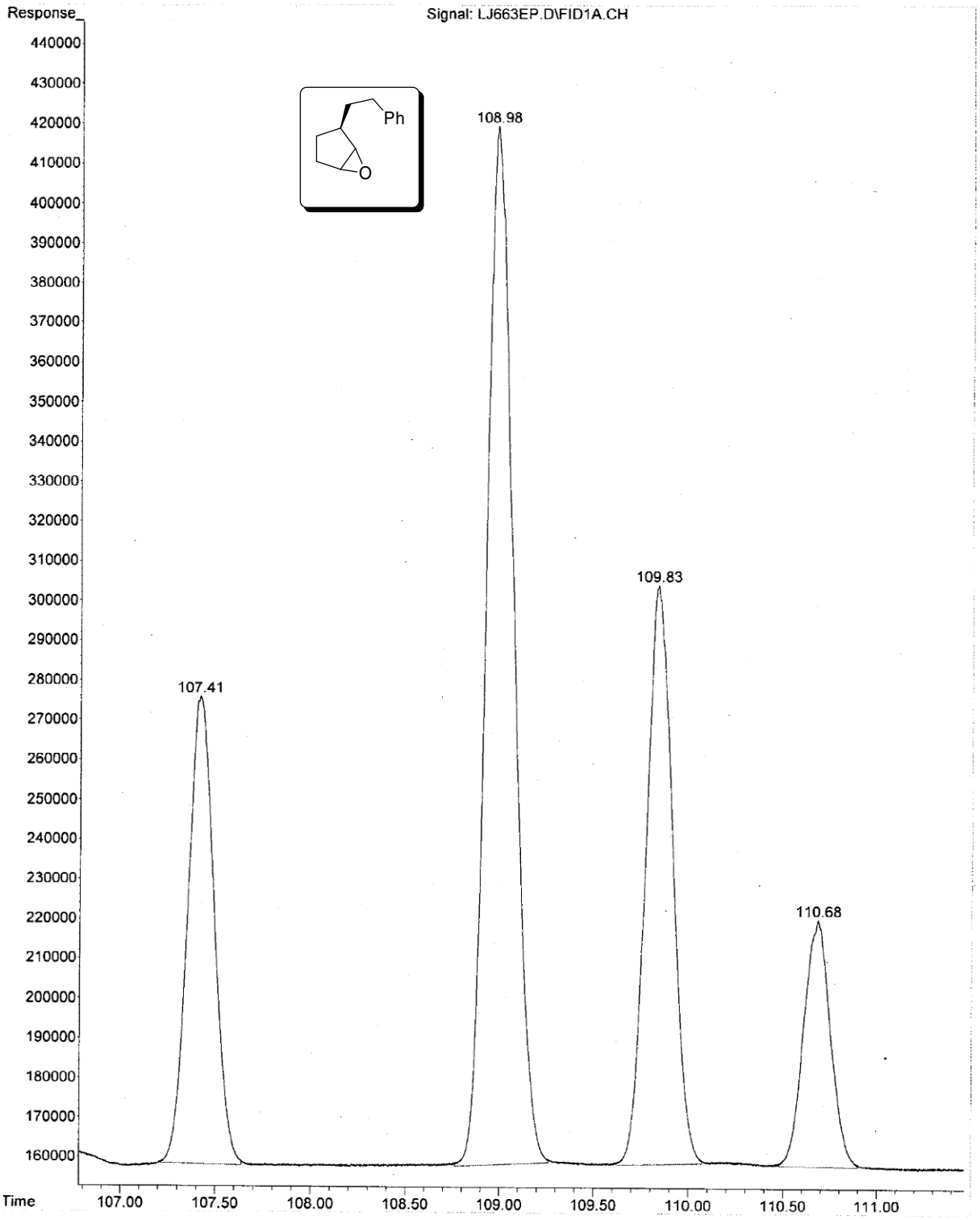
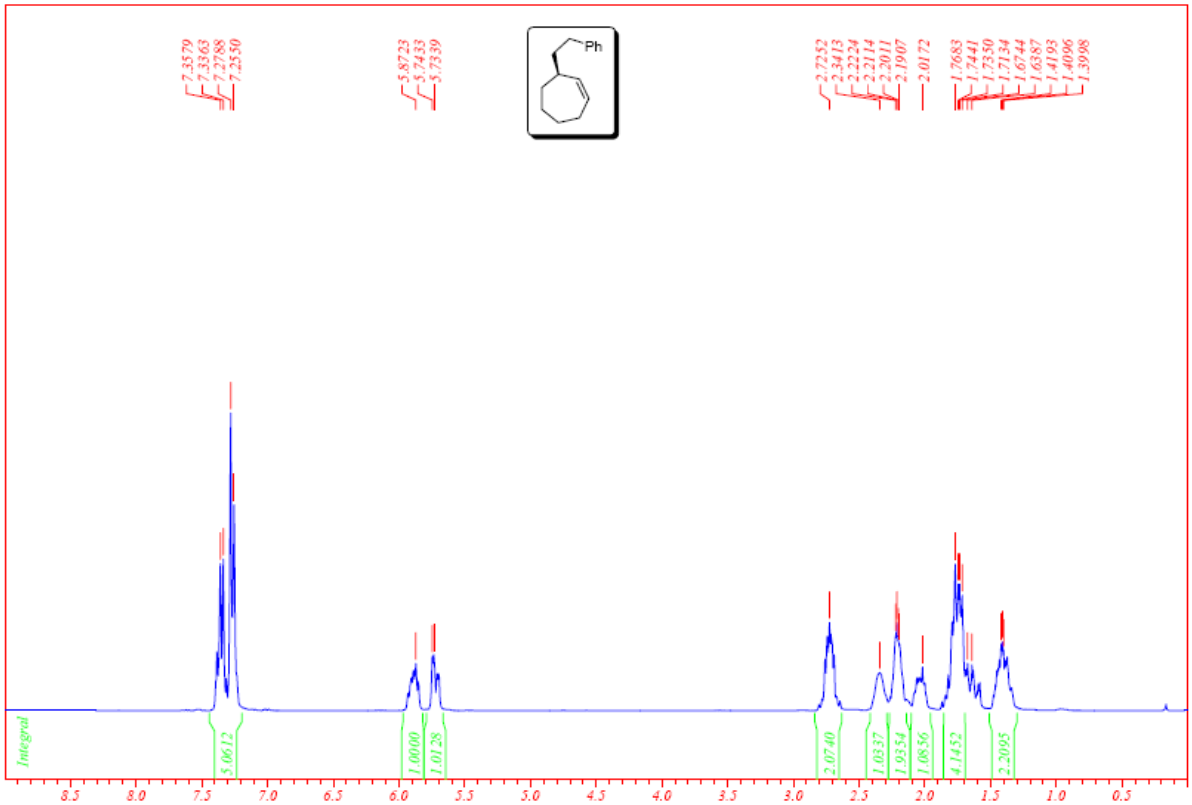
32.0859
29.8593



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	107.412	107.192	107.637	M	117719	11270350	42.88%	19.510%
2	108.976	108.765	109.263	M	260995	26285417	100.00%	45.503%
3	109.834	109.623	110.072	M	145441	14075967	53.55%	24.367%
4	110.684	110.480	110.898	M	62009	6134487	23.34%	10.620%

Sum of corrected areas: 57766221


7.3579
7.3363
7.2788
7.2550
5.8723
5.7433
5.7339
2.7252
2.3413
2.2224
2.2114
2.2011
2.1907
2.0172
1.7683
1.7441
1.7350
1.7134
1.6744
1.6387
1.4193
1.4096
1.3998
Ph
Integral
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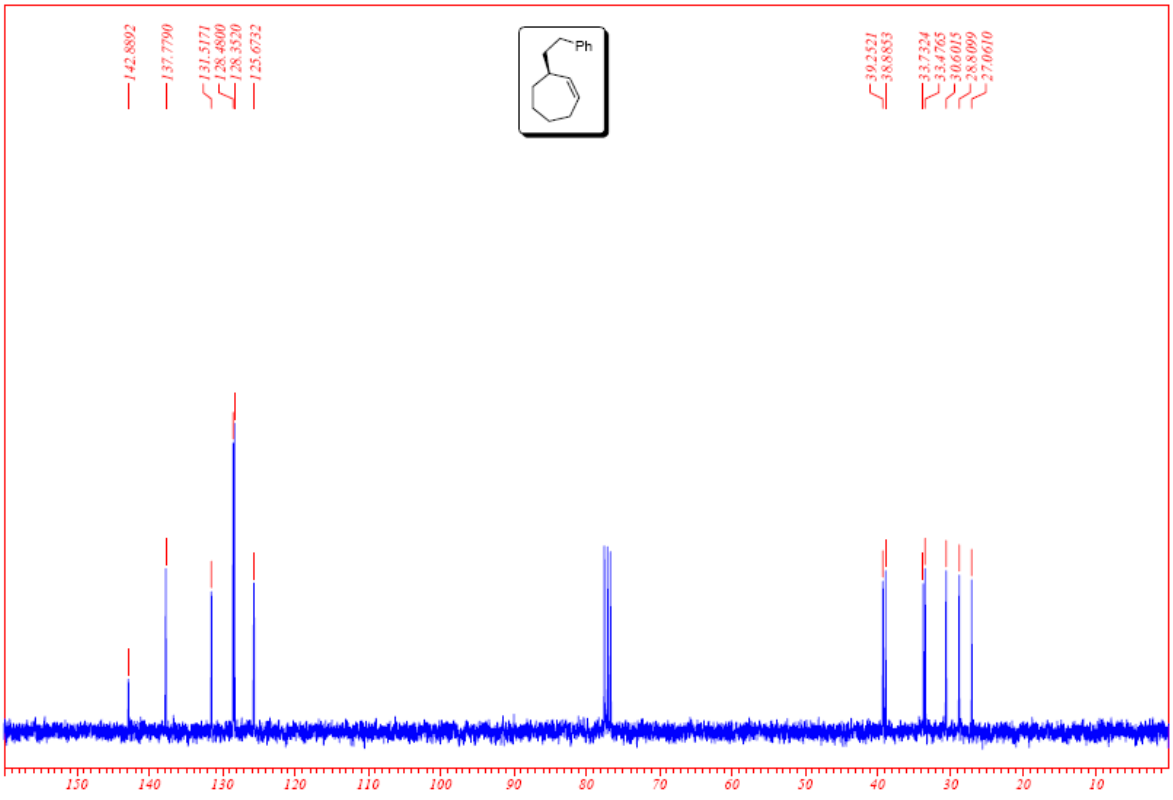
1.0000
1.0128
2.0740
1.0337
1.9354
1.0856
4.1452
2.2095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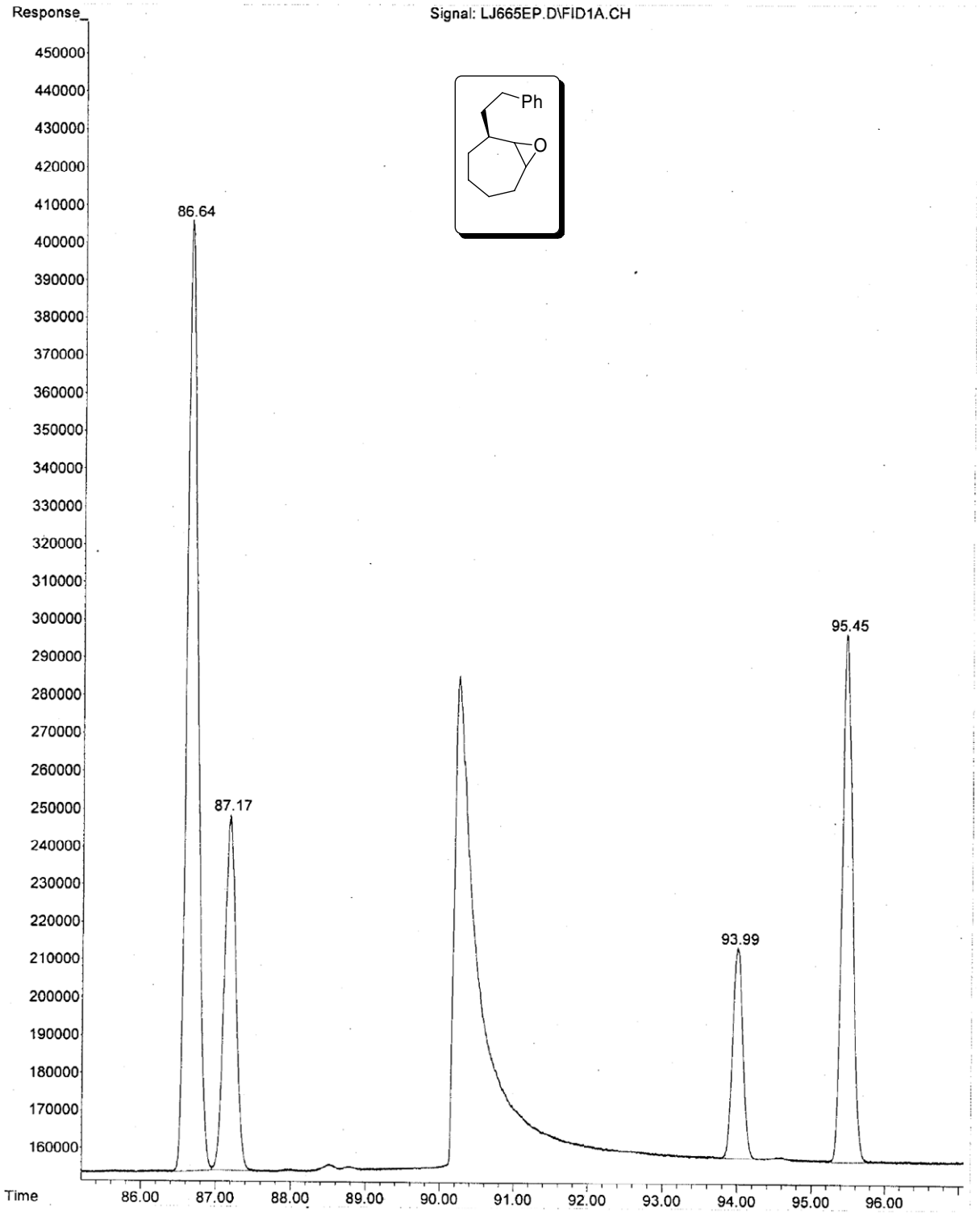
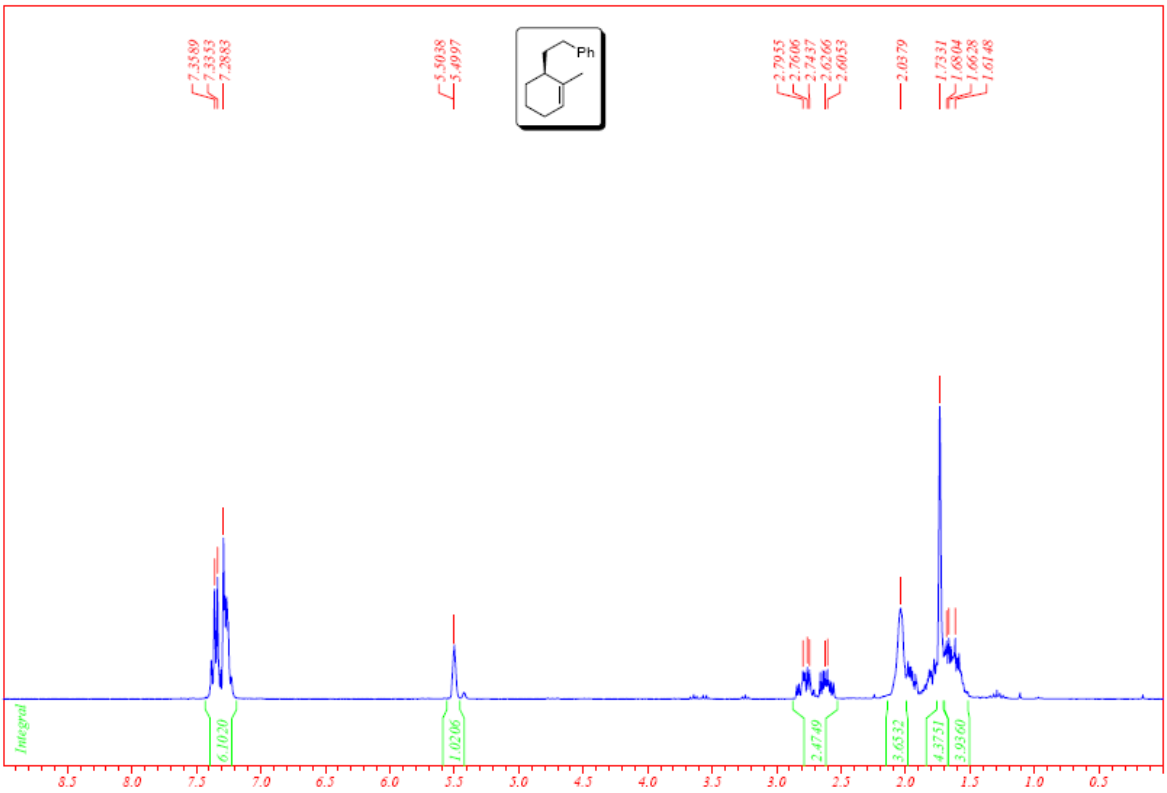
128.4800
128.3520
125.6732
39.2521
38.8853
33.7324
33.4765
30.6015
28.5099
27.0610
Ph



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	86.635	86.430	86.952	M	252134	25781898	100.00%	47.151%
2	87.174	86.952	87.491	M	94454	10061440	39.03%	18.401%
3	93.994	93.799	94.219	M	55804	5266005	20.43%	9.631%
4	95.449	95.275	95.736	M	139478	13569652	52.63%	24.817%

Sum of corrected areas: 54678994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7.2883
5.5038
5.4997
Ph
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2.7606
2.7437
2.6266
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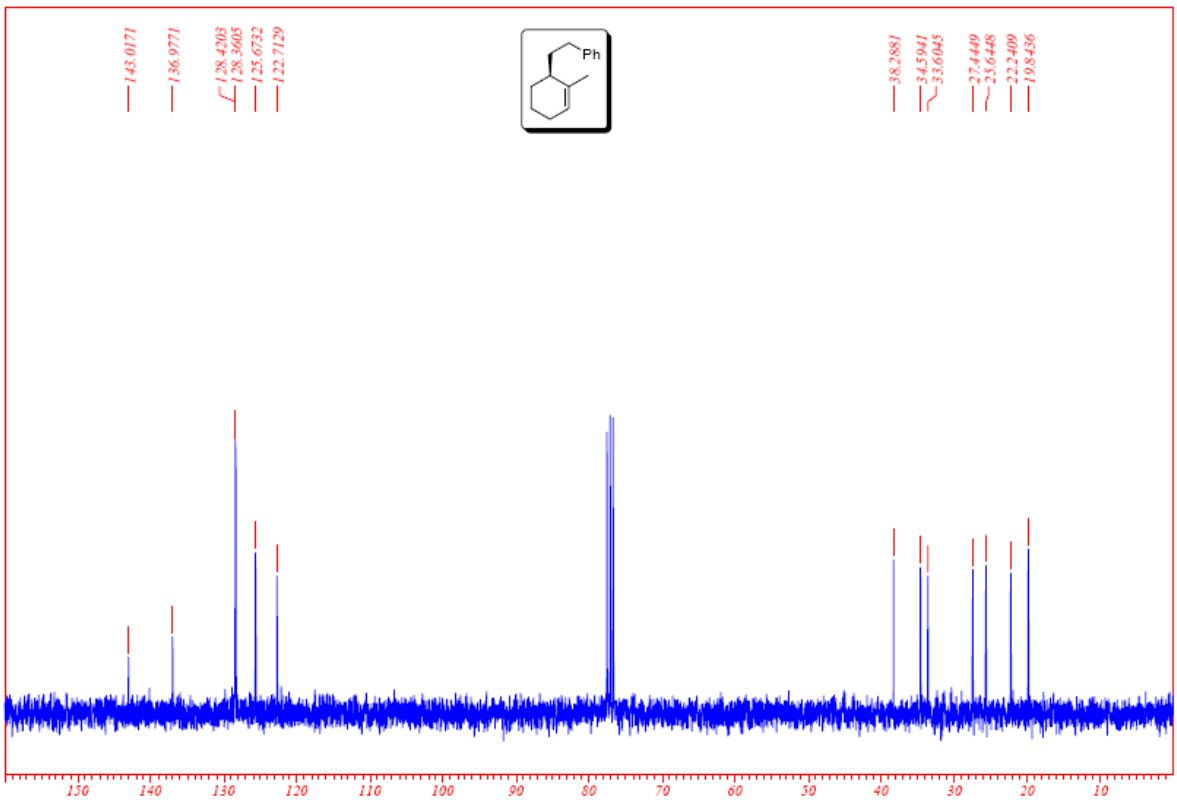
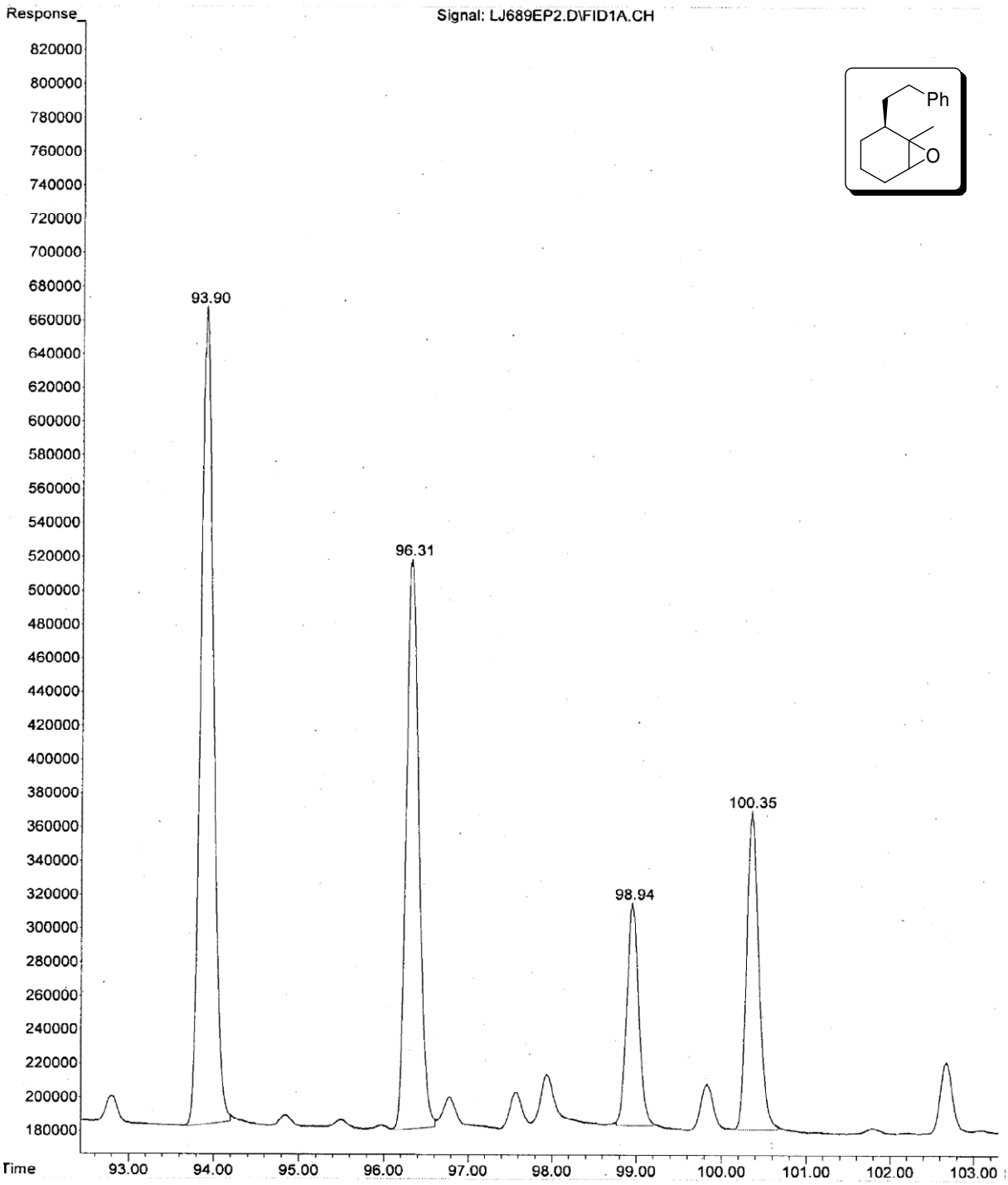
2.0379
1.7331
1.6804
1.6628
1.6148
Integral
6.1020
1.0206
2.4749
3.6532
4.3751
3.9360
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


143.0171
136.9771
128.4203
128.3605
125.6732
122.7129
Ph
38.2881
34.5941
33.6045
27.4449
25.6448
22.2409
19.8436
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10



peak #	R.T. min	Start min	End min	PK TY	peak height	peak area	peak % max.	% of total
1	93.896	93.678	94.199	M	484391	50922478	100.00%	43.064%
2	96.311	96.126	96.605	M	337581	35505607	69.72%	30.026%
3	98.944	98.761	99.198	M	132181	12915141	25.36%	10.922%
4	100.351	100.157	100.667	M	188724	18905946	37.13%	15.988%

Sum of corrected areas: 118249172