Supporting Information

Efficient Synthetic Method of Allyl-Epoxides via Allylation of α-Haloketones or Esters with Allylmagnesium Bromide

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General Information

Metallic magnesium and all other chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Solvents were purchased from commercial source, without further purification before use. Petroleum ether (PE) used refers to the 60-90 ^{o}C boiling point fraction of petroleum. Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. The flash column chromatography was carried out on Merck silica gel (300-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 or 400 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.50 ppm). IR spectra were recorded on Varian F-1000 spectrometer in KBr with absorptions in cm^{-1}. HRMS were obtained with a GCT-TOF instrument.

Synthesis of allylmagnesium bromide and epoxides

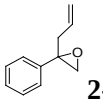
The preparation of allylmagnesium bromide and its concentration of calibration

Magnesium turnings (1.06g, 44mmol) and spiked with I_2 were added to a round-bottom flask assembled with a constant pressure funnel, which had been previously flame dried and allowed to cool under a stream of nitrogen. Freshly distilled THF (40 mL) mixed with allyl bromide (3.4mL, 40mmol) in the constant pressure funnel was slowly added to the flask. After several minutes, the reaction mixture turned from yellow to turbid gray. Then, the round-bottom flask was cooled to 0 °C with an ice bath. After dropping was finished, the reaction was stirred for 3 hours at the room temperature. The solvent transfers were made using standard cannulation techniqes. The concentration of Grignard reagent was determined by titration, using sodium hydroxide (0.10M) as titrant and phenolphthalein as indicator.

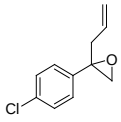
General procedure for the synthesis of epoxides

Allylmagnesium bromide (the amounts can be seen from the feet of the **table 1**, **2**) was added to α-haloketones or esters (0.5 mmol) in dry THF (5 mL) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 0.5 h (the reaction was monitored by TLC) and then was quenched with water. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded epoxides **3** or **5** (300–400 mesh, petroleum ether and ethyl acetate).

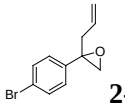
Analytical and spectral data for compounds



2-allyl-2-phenyloxirane (3a)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 94%; IR (KBr): 3060, 2918, 1648, 1490, 1407, 1001, 920, 777, 709 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.22–7.39 (m, 5H), 5.70–5.84 (m, 1H), 5.06–5.15 (m, 2H), 2.98 (d, J = 5.3 Hz, 1H), 2.88 (dd, J = 6.5, 15.0 Hz, 1H), 2.74 (d, J = 5.3 Hz, 1H), 2.64 (dd, J = 7.3, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.29, 133.02, 128.55, 127.77, 126.19, 118.71, 59.55, 55.03, 39.75. HRMS (EI^+) calcd for $C_{11}H_{12}O$ (M^+): 160.0888; found: 160.0885.

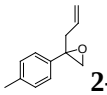


2-allyl-2-(4-chlorophenyl) oxirane (3b)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 95%; IR (KBr): 3068, 2915, 1642, 1492, 1410, 1004, 919, 820 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31 (s, 4H), 5.72–5.79 (m, 1H), 5.09–5.15 (m, 2H), 3.01 (d, J = 5.1 Hz, 1H), 2.88 (dd, J = 6.4, 15.0 Hz, 1H), 2.73 (d, J = 5.1 Hz, 1H), 2.61 (dd, J = 7.1, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.96, 133.79, 132.82, 128.91, 127.81, 119.22, 59.33, 55.36, 39.79. HRMS (EI^+) calcd for $C_{11}H_{11}{}^{35}ClO$ (M^+): 194.0498; found: 194.0499; $C_{11}H_{11}{}^{37}ClO$ (M^+-C_3H_5): 155.0078; found: 155.0475.

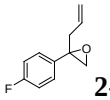


2-allyl-2-(4-bromophenyl) oxirane (3c)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 96%; IR (KBr): 3067, 2910, 1658, 1489, 1415, 999, 915, 823 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.45–7.47 (m, 2H), 7.24–7.26 (m, 2H), 5.70–5.80

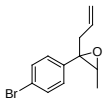
(m, 1H), 5.09–5.15 (m, 2H), 3.01 (d, J = 5.3 Hz, 1H), 2.85–2.90 (m, 1H), 2.72 (d, J = 5.3 Hz, 1H), 2.61 (dd, J = 7.3, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.35, 132.62, 131.66, 127.98, 121.74, 119.03, 59.14, 55.10, 39.51. HRMS (EI$^+$) calcd for $C_{11}H_{11}{}^{79}BrO$ (M^+): 237.9993; found: 237.9953; $C_{11}H_{11}{}^{81}BrO$ (M^+): 239.9973; found: 239.9969.



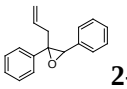
2-allyl-2-p-tolyloxirane (3d)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 81%; IR (KBr): 3050, 2965, 2869, 1670, 1487, 1405, 1000, 922, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 5.73–5.83 (m, 1H), 5.07–5.15 (m, 2H), 2.99 (d, J = 5.3 Hz, 1H), 2.88 (dd, J = 6.5, 15.0 Hz, 1H), 2.75 (d, J = 5.3 Hz, 1H), 2.64 (dd, J = 7.3, 14.9 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 137.67, 137.38, 133.31, 129.44, 126.29, 118.84, 59.67, 55.35, 39.98, 21.58. HRMS (EI$^+$) calcd for $C_{12}H_{14}O$ (M^+): 174.1045; found: 174.1043.



2-allyl-2-(4-fluorophenyl) oxirane (3e)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 94%; IR (KBr): 3064, 2923, 1640, 1505, 1421, 989, 915, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32–7.36 (m, 2H), 6.99–7.04 (m, 2H), 5.71–5.81 (m, 1H), 5.09–5.15 (m, 2H), 3.00 (d, J = 5.3 Hz, 1H), 2.86 (dd, J = 6.5, 15.0 Hz, 1H), 2.73 (d, J = 5.3 Hz, 1H), 2.63 (dd, J = 7.3, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.59 (^1J(C, F) = 244.5 Hz), 136.21 (^4J(C, F) = 3.0 Hz), 133.00, 128.17 (^3J(C, F) = 8.1 Hz), 119.14, 115.64 (^2J(C, F) = 21.4 Hz), 59.43, 55.31, 40.09. HRMS (EI$^+$) calcd for $C_{11}H_{11}OF$ (M^+): 178.0794; found: 178.0794.

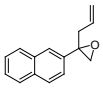


2-allyl-2-(4-bromophenyl)-3-methyloxirane (3f)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 95%; IR (KBr): 3067, 2950, 2855, 1657, 1476, 1395, 985, 923, 834 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43–7.48 (m, 2H), 7.18–7.24 (m, 2H), 5.66–5.80 (m, 1H), 5.04–5.11 (m, 2H), 3.21 (q, J = 5.4 Hz, 1H; cis), 2.96 (q, J = 5.5 Hz, 1H; trans), 2.78–2.85 (m, 1H; cis, trans), 2.56 (dd, J = 6.6, 15.3 Hz, 1H; trans), 2.47 (dd, J = 7.4, 14.7 Hz, 1H; cis), 1.46 (d, J = 5.5 Hz, 3H; trans), 0.99 (d, J = 5.4 Hz, 3H; cis). ^{13}C NMR ($CDCl_3$, 100 MHz): cis: δ 137.82, 132.90, 131.63, 129.30, 121.70, 119.05, 65.08, 59.86, 42.23, 14.88; trans: δ 140.77, 133.32, 131.76, 128.26, 121.66, 118.82, 63.12, 62.62, 36.25, 14.88. HRMS (EI$^+$) calcd for $C_{12}H_{13}{}^{79}BrO$ (M^+): 252.0150; found: 252.0153; $C_{12}H_{13}{}^{81}BrO$ (M^+): 254.0129; found: 254.0120.



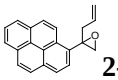
2-allyl-2,3-diphenyloxirane (3g)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 18%; IR (KBr): 3073, 2921, 1645, 1487, 1407, 977, 923, 791, 686 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): cis: δ 7.01–7.25 (m, 10H), 5.76–5.90 (m, 1H), 5.10–5.16 (m, 2H), 4.19 (s, 1H), 2.88 (dd, J = 6.5, 14.4 Hz, 1H), 2.69 (dd, J = 7.5, 14.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.09, 135.57, 132.73, 127.91, 127.86, 127.82, 127.56, 127.40, 126.74, 118.92, 68.58, 63.92, 43.32. HRMS (EI$^+$) calcd for $C_{17}H_{16}O$ (M^+): 236.1201; found: 236.1201.

2-allyl-3-methyl-2-phenyl-oxirane (3h)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 91%; IR (KBr): 3069, 2954, 2858, 1674, 1487, 1408, 976, 907, 765, 715 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25–7.36 (m, 5H), 5.68–5.79 (m, 1H), 5.03–5.08 (m, 2H), 3.21 (q, J = 5.4 Hz, 1H; cis), 3.01 (q, J = 5.5 Hz, 1H; trans), 2.84 (dd, J = 6.6, 14.6 Hz, 1H; cis, trans), 2.59 (dd, J = 6.6, 15.2 Hz, 1H; trans), 2.50 (dd, J = 7.5, 14.7 Hz, 1H; cis), 1.47 (d, J = 5.5 Hz, 3H; trans), 0.98 (d, J = 5.4 Hz, 3H; cis). ^{13}C NMR ($CDCl_3$, 100 MHz): cis: δ 138.69, 133.23, 128.42, 127.63, 127.43, 118.67, 65.45, 59.75, 42.43, 14.93; trans: δ 138.69, 133.23, 128.61, 127.72, 126.40, 118.42, 62.54, 62.27, 36.42, 14.93. HRMS (EI^+) calcd for $C_{12}H_{14}O$ (M^+): 174.1045; found: 174.1045.



2-allyl-2-(naphthalen-2-yl) oxirane (3i)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 94%; IR (KBr): 3053, 2899, 1632, 1489, 1356, 1001, 928, 818, 741 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81–7.86 (m, 4H), 7.47–7.49 (m, 3H), 5.77–5.87 (m, 1H), 5.09–5.18 (m, 2H), 3.09 (d, J = 5.2 Hz, 1H), 3.01 (dd, J = 6.4, 15.0 Hz, 1H), 2.85 (d, J = 5.2 Hz, 1H), 2.74 (dd, J = 7.2, 15.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.89, 133.53, 133.16, 128.50, 128.41, 128.07, 126.68, 126.46, 125.46, 124.23, 119.01, 60.02, 55.42, 40.00. HRMS (EI^+) calcd for $C_{15}H_{14}O$ (M^+): 210.1045; found: 210.1040.

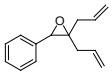
2-allyl-2-tert-butyloxirane (3j)[9] The title compound was obtained according to the general procedure. Colourless oil; Yield: 86% (**3ja**) and 80% (**3jb**); IR (KBr): 2960, 1640, 1474, 1371, 996, 914, 818 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz,): δ 5.63–5.73 (m, 1H), 5.03–5.07 (m, 2H), 2.71 (d, J = 4.3 Hz, 1H), 2.50–2.55 (m, 3H), 0.96 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz,): δ 134.48, 118.07, 63.59, 48.35, 35.01, 34.20, 26.54. HRMS (EI^+) calcd for $C_9H_{16}O$ (M^+-H_2O): 122.1096; found: 122.1096.



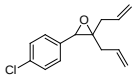
2-allyl-2-(pyren-1-yl) oxirane (3k)[10] The title compound was obtained according to the general procedure. Colourless oil; Yield: 75%; IR (KBr): 3073, 2904, 1647, 1496, 1370, 982, 899, 809, 729 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.32 (d, J = 9.0 Hz, 1H), 7.91–8.14 (m, 8H), 5.72–5.85 (m, 1H), 5.00–5.06 (m, 2H), 3.28 (d, J = 5.2 Hz, 1H), 3.02 (d, J = 5.2 Hz, 1H), 2.95 (dd, J = 6.6, 14.1 Hz, 1H), 2.84 (dd, J = 7.5, 14.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.02, 132.79, 131.48, 131.15, 130.91, 128.33, 128.17, 127.72, 127.62, 126.28, 125.85, 125.67, 125.55, 124.97, 124.83, 124.76, 123.72, 118.98, 61.03, 53.30, 42.31. HRMS (EI^+) calcd for $C_{21}H_{16}O$ (M^+): 284.1201; found: 284.1201.

6H-Indeno [1,2-b]oxirene, 1a,6a-dihydro-1a-allyl- (3l) The title compound was obtained according to the general procedure. Colourless oil; Yield: 80%; Compound purity: 99.40% (confirmed by HPLC); IR (KBr): 3074, 2977, 2918, 2851, 1639, 1609, 1476, 1436, 1343, 1253, 1152, 1065, 997, 920, 736cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.40–7.42 (m, 1H), 7.21–7.31 (m, 3H), 5.70–5.84 (m, 1H), 5.10–5.17 (m, 2H), 4.67–4.70 (t, 1H), 3.29–3.47 (m, 2H), 2.56–2.66 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.23, 139.77, 133.31, 129.23, 127.71, 125.13, 124.20,

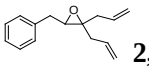
119.34, 81.80, 61.06, 42.05, 40.44. HRMS (EI^+) calcd for $C_9H_{16}O$ (M^+): 172.0888; found: 172.0890.



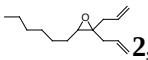
2,2-diallyl-3-phenyloxirane (5a) The title compound was obtained according to the general procedure. Colourless oil; Yield: 85% (**5aa**), 73% (**5ab**) and 23% (**5ac**); Compound purity: 99.12% (**5aa**), 99.85% (**5ab**), 99.54% (**5ac**) (confirmed by HPLC); IR (KBr): 3078, 2979, 2912, 2846, 1641, 1605, 1497, 1434, 1346, 1263, 1178, 1028, 971, 917, 859, 750, 700, 653 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.40 (m, 5H), 5.83–5.97 (m, 1H), 5.60–5.73 (m, 1H), 5.17–5.23 (m, 2H), 4.93–5.06 (m, 2H), 3.98 (s, 1H), 2.45–2.60 (m, 2H), 2.03–2.21 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.19, 133.20, 128.28, 127.70, 126.65, 118.69, 118.33, 65.03, 62.75, 39.45, 34.47. HRMS (EI^+) calcd for $C_{14}H_{16}O$ (M^+): 200.1201; found: 201.1205.



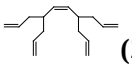
2,2-diallyl-3-(4-chlorophenyl) oxirane (5b) The title compound was obtained according to the general procedure. Colourless oil; Yield: 83%; Compound purity: 99.50% (confirmed by HPLC); IR (KBr): 3078, 2979, 2913, 2845, 1641, 1600, 1493, 1434, 1342, 1290, 1174, 1090, 972, 919, 838, 722, 684, 648 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.25–7.30 (m, 4H), 5.80–5.89 (m, 1H), 5.58–5.66 (m, 1H), 5.15–5.19 (m, 2H), 4.90–5.04 (m, 2H), 3.91 (s, 1H), 2.42–2.56 (m, 2H), 2.02–2.11 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 131.59, 130.37, 129.77, 129.70, 125.34, 124.85, 115.71, 115.37, 62.03, 58.93, 36.14, 31.29. HRMS (EI^+) calcd for $C_{14}H_{15}ClO$ (M^+): 234.0811; found: 235.0814.



2,2-diallyl-3-benzyloxirane (5c) The title compound was obtained according to the general procedure. Colourless oil; Yield: 78%; Compound purity: 99.17% (confirmed by HPLC); IR (KBr): 3078, 2978, 2916, 1641, 1605, 1495, 1454, 1308, 1031, 997, 917, 741, 699, 656 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.24–7.31 (m, 5H), 5.67–5.91 (m, 2H), 5.06–5.18 (m, 4H), 3.03–3.05 (m, 1H), 2.91–2.92 (m, 2H), 2.27–2.55 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.20, 133.40, 133.14, 128.99, 128.84, 126.77, 118.57, 62.99, 62.64, 39.75, 35.83, 35.09. HRMS (EI^+) calcd for $C_{15}H_{18}O$ (M^+): 214.1358; found: 215.1350.



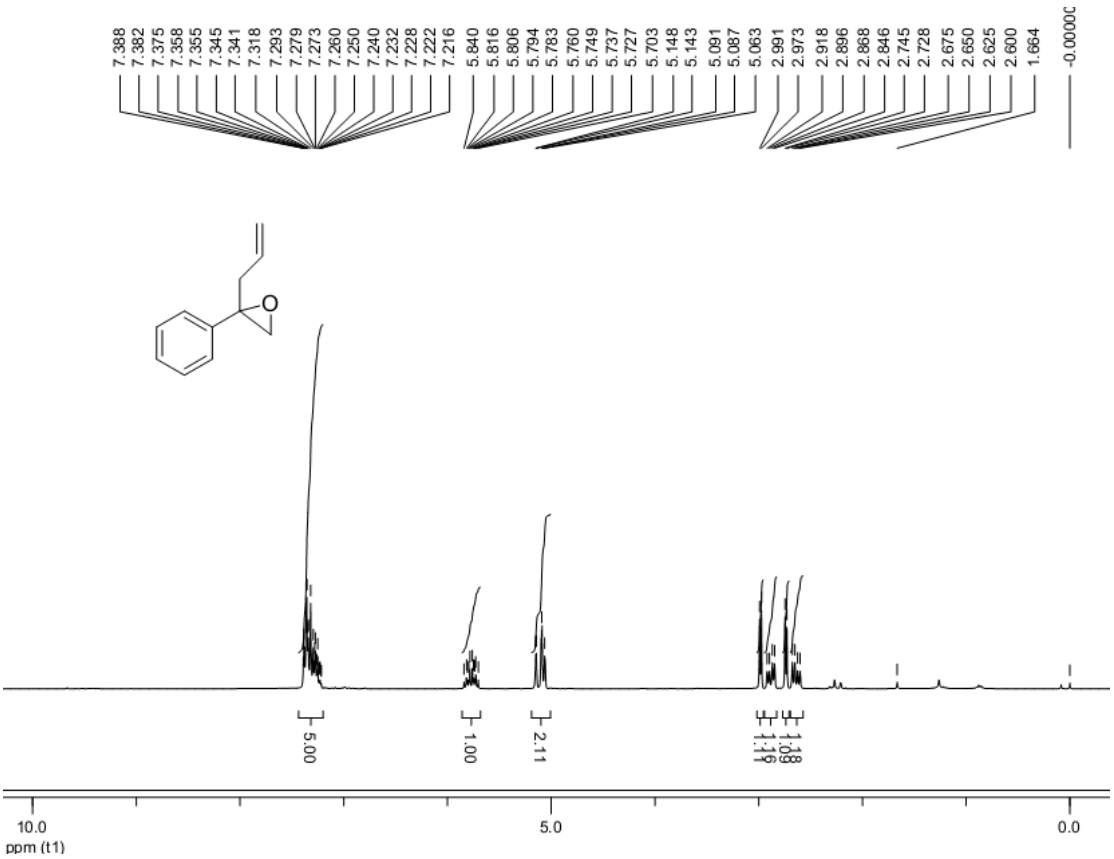
2,2-diallyl-3-hexyloxirane (5d) The title compound was obtained according to the general procedure. Light yellow oil; Yield: 75%; Compound purity: 99.60% (confirmed by HPLC); IR (KBr): 3079, 2957, 2858, 1641, 1353, 1112, 996, 915cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ 5.72–5.83 (m, 2H), 5.07–5.15 (m, 4H), 2.77–2.81 (t, 1H), 2.21–2.36 (m, 4H), 1.30–1.65 (m, 10H), 0.87–0.91 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.63, 133.43, 118.24, 118.16, 62.96, 62.25, 39.87, 35.62, 31.96, 29.38, 28.63, 26.85, 22.76, 14.25. HRMS (EI^+) calcd for $C_{14}H_{24}O$ (M^+): 208.1827; found: 209.1821.

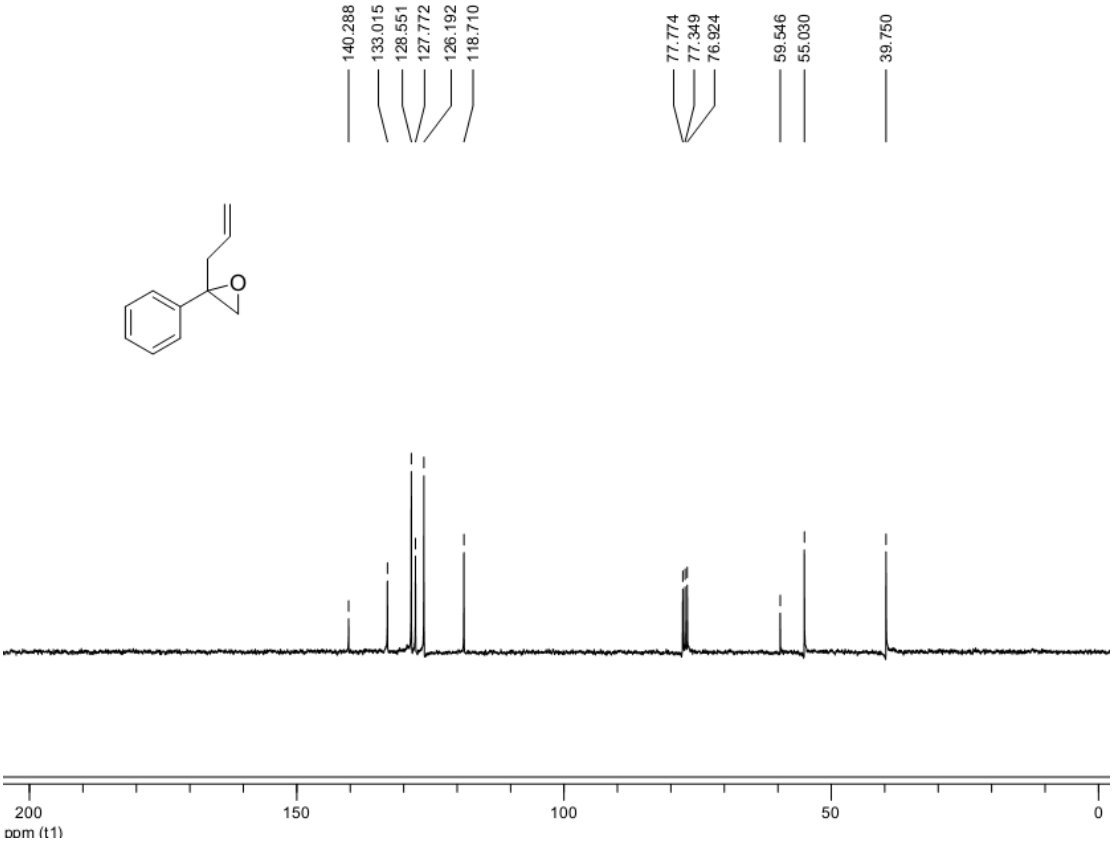


(Z)-4,7-diallyldeca-1,5,9-triene (5e) The title compound was obtained according to the general procedure. Light yellow oil; Yield: 43%; Compound purity: 99.99% (confirmed by HPLC); IR (KBr): 3076, 2979, 2839, 1639, 1222, 996, 915, 704cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 5.74–5.82 (m, 4H), 5.67 (s, 2H), 5.09–5.16 (m, 8H), 2.26–2.37 (m, 8H), 1.80 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.01, 131.47, 117.02, 71.56, 43.61. HRMS (EI^+) calcd for $C_{16}H_{24}O$ (M^+): 216.1878; found: 217.1876.

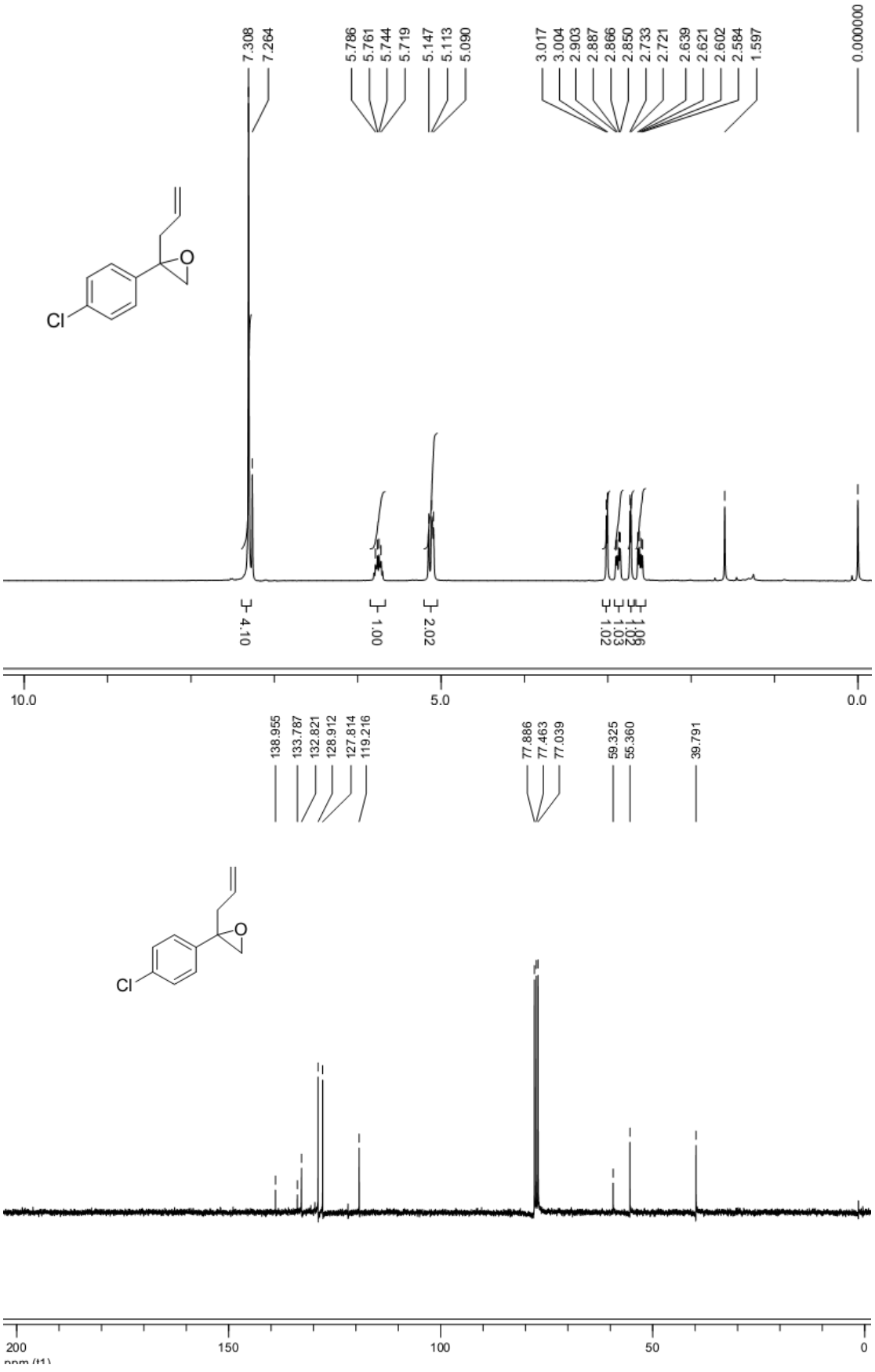
NMR spectrum of compounds

3a

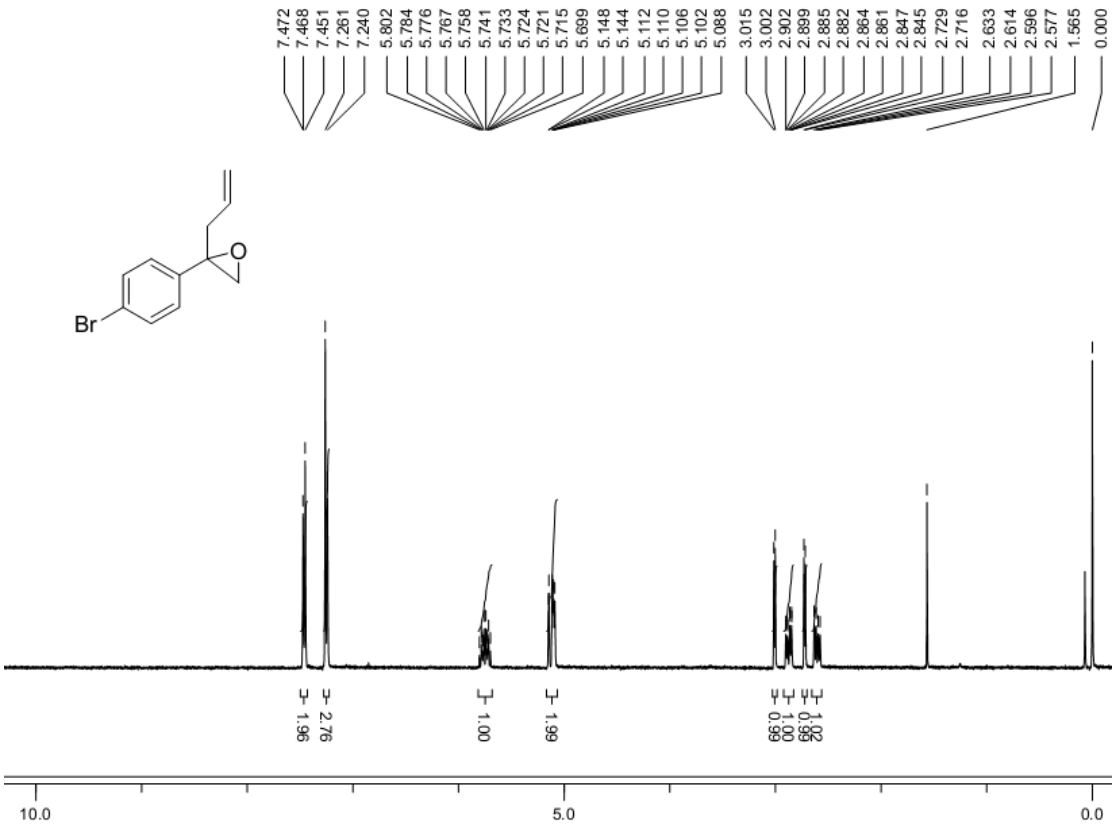


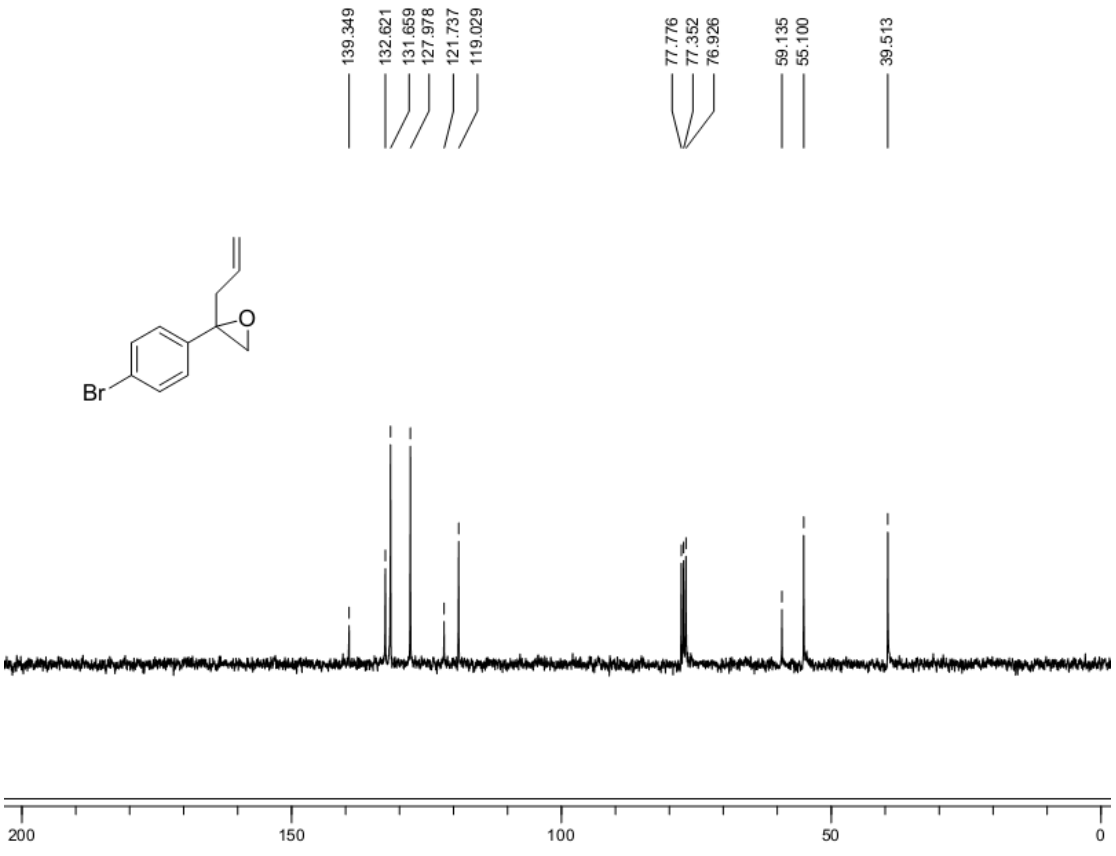


3b



3c





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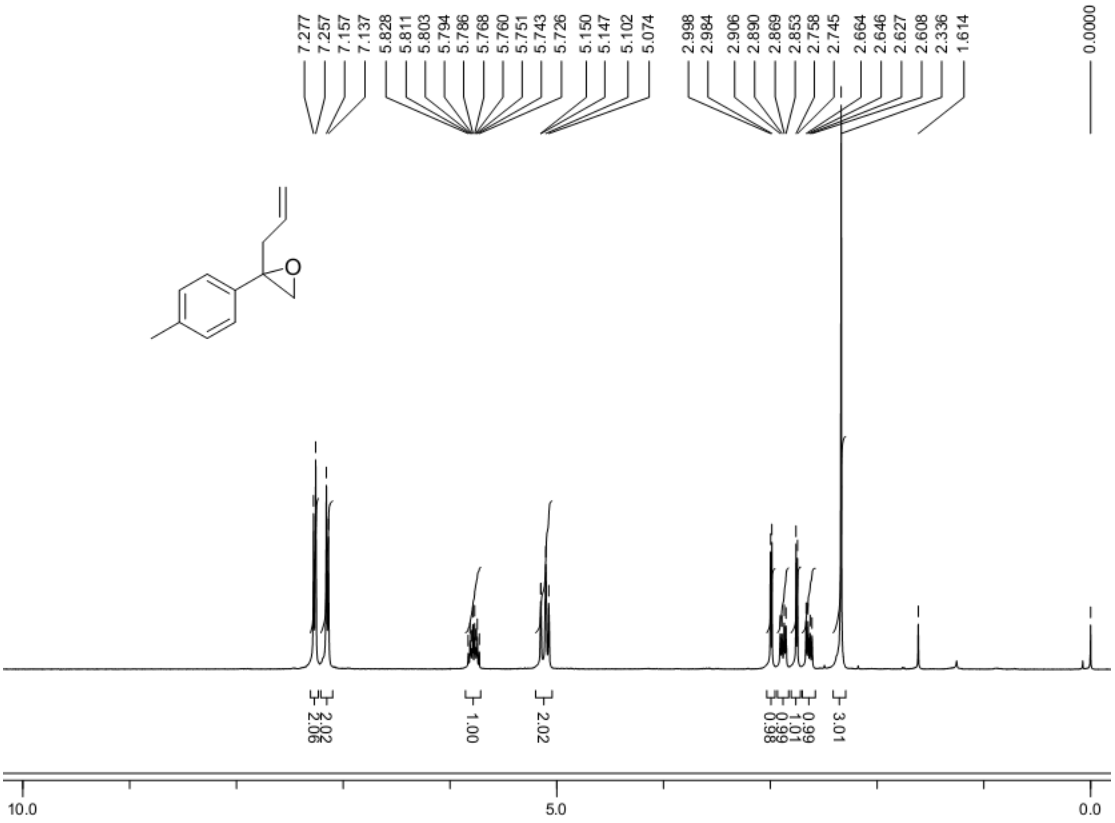
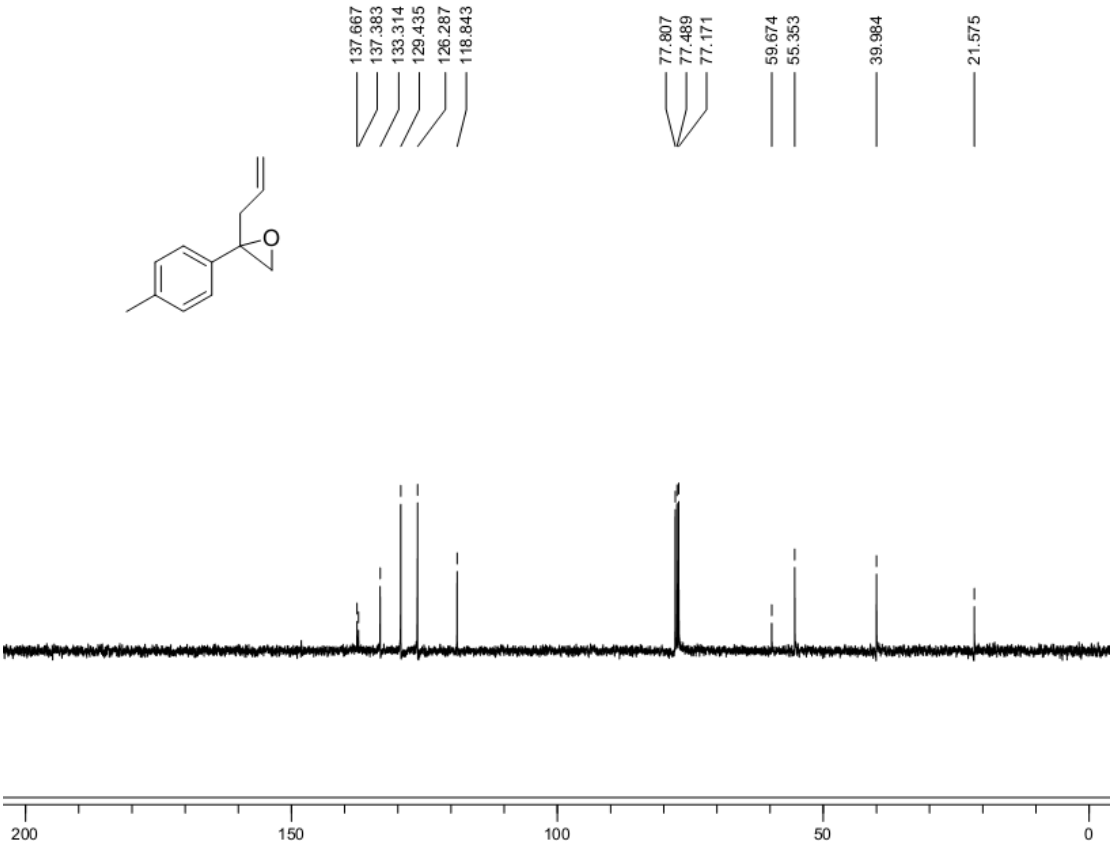
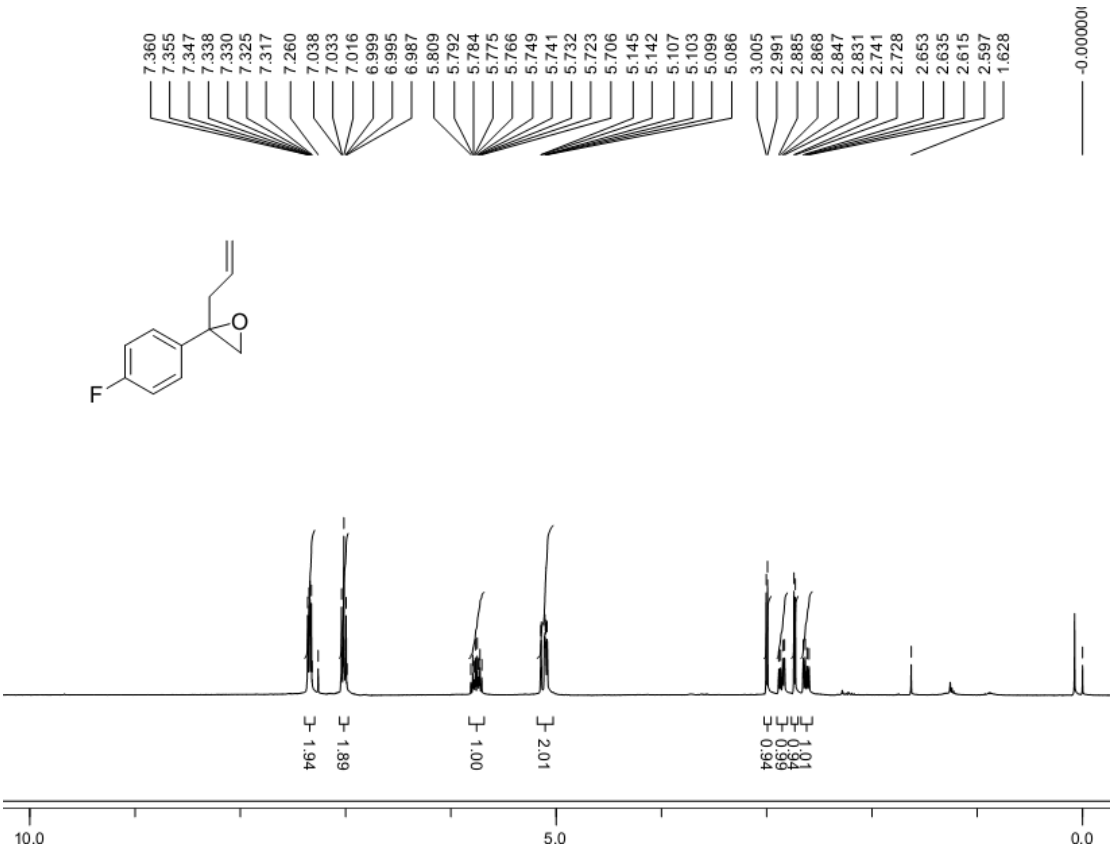
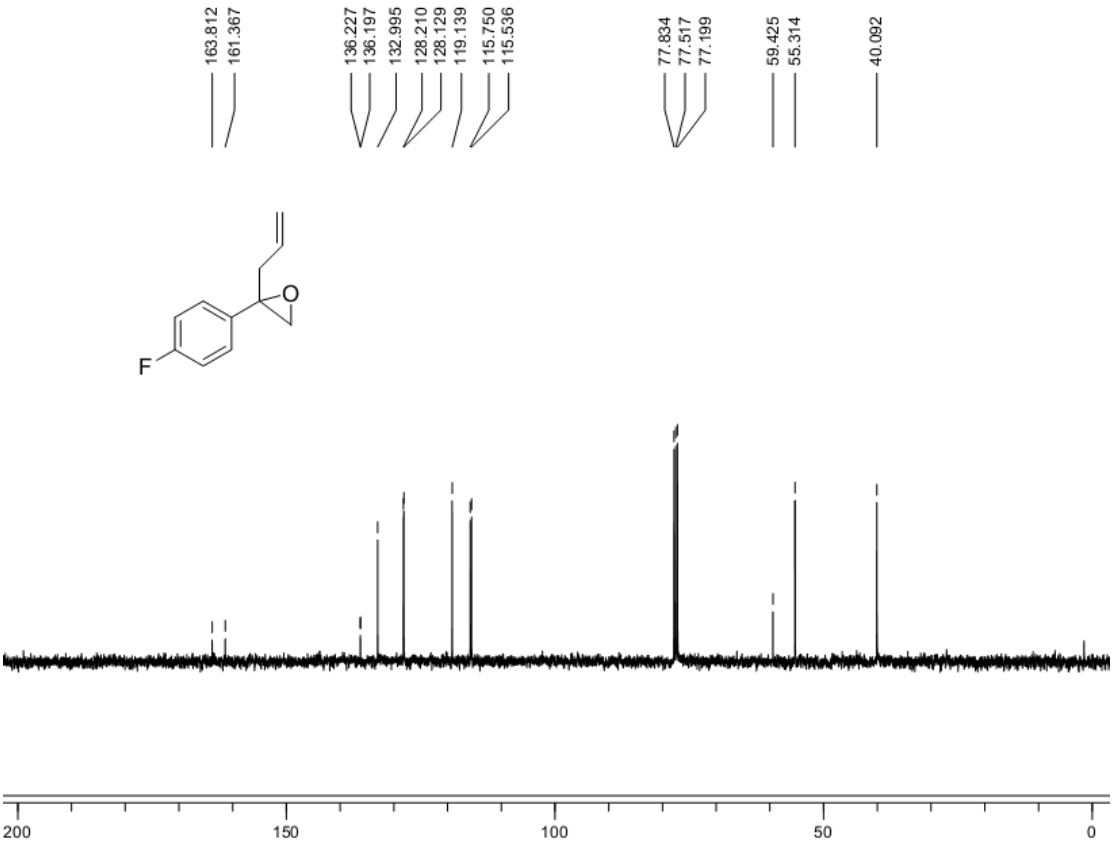


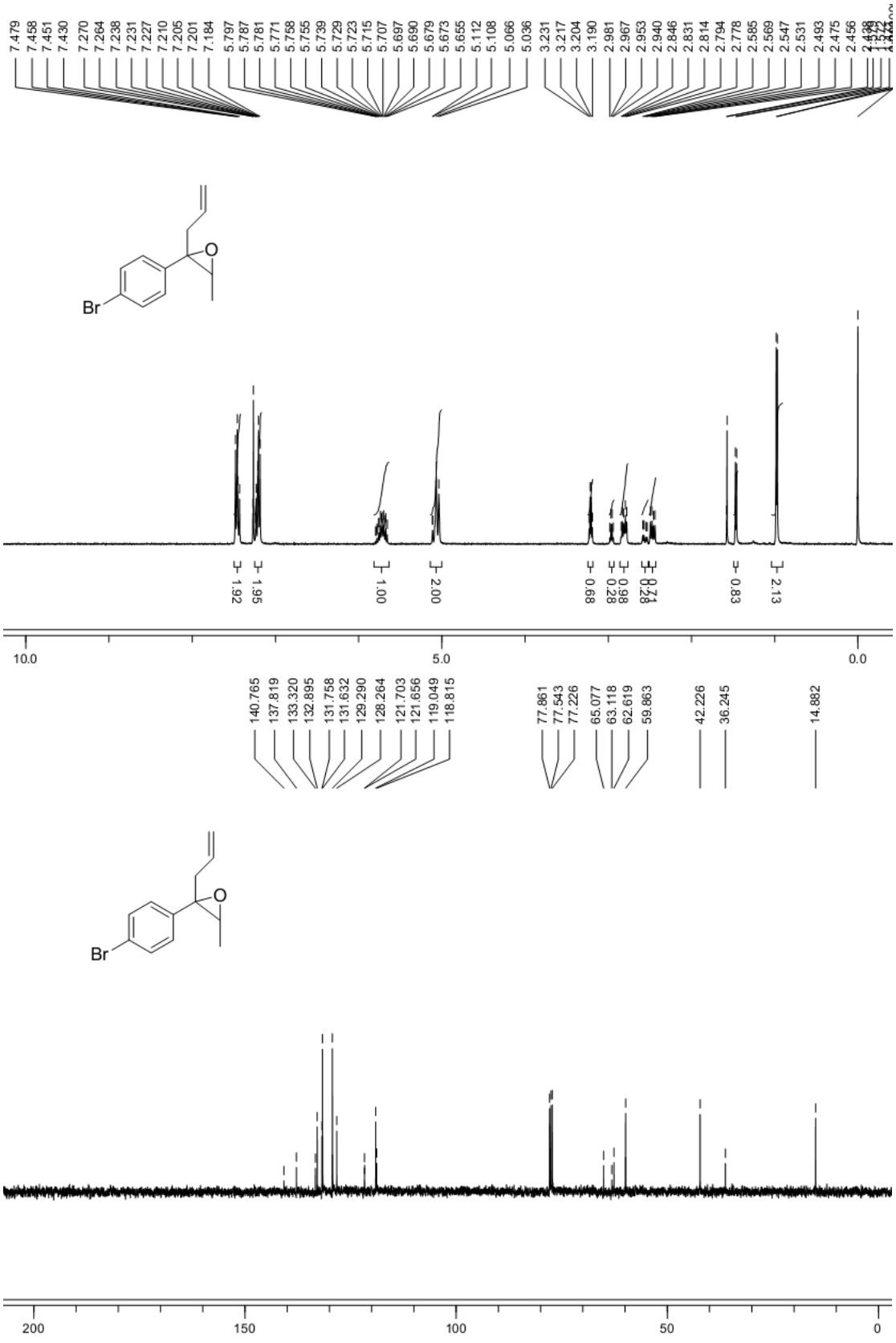


3e





3f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7.238
7.231
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7.210
7.205
7.201
7.184
5.797
5.787
5.781
5.771
5.758
5.755
5.739
5.729
5.723
5.715
5.707
5.697
5.690
5.679
5.673
5.655
5.112
5.108
5.066
5.036
3.231
3.217
3.204
3.190
2.981
2.967
2.953
2.940
2.846
2.831
2.814
2.794
2.778
2.585
2.569
2.547
2.531
2.493
2.475
2.456
Br
O
1.92
1.95
1.00
2.00
0.68
0.98
0.28
0.78
0.83
2.13
10.0
5.0
0.0
140.765
137.819
133.320
132.895
131.758
131.632
129.290
128.264
121.703
121.656
119.049
118.815
77.861
77.543
77.226
65.077
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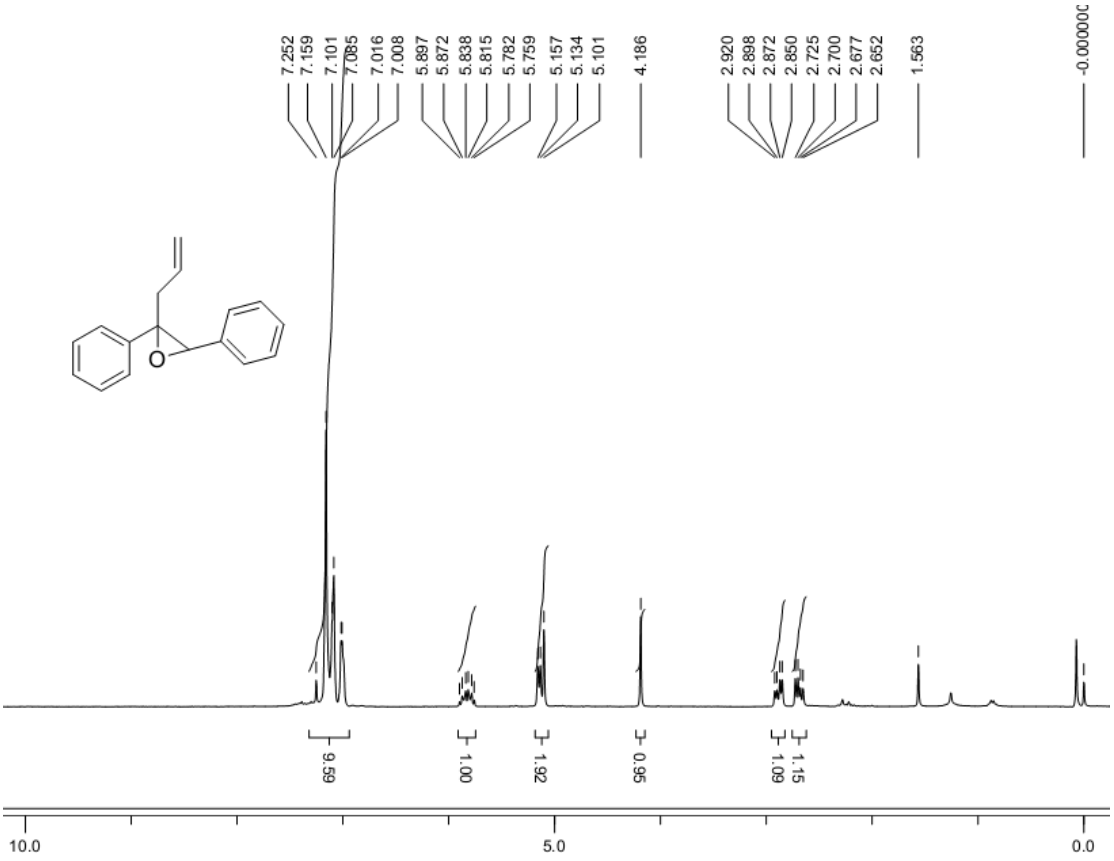
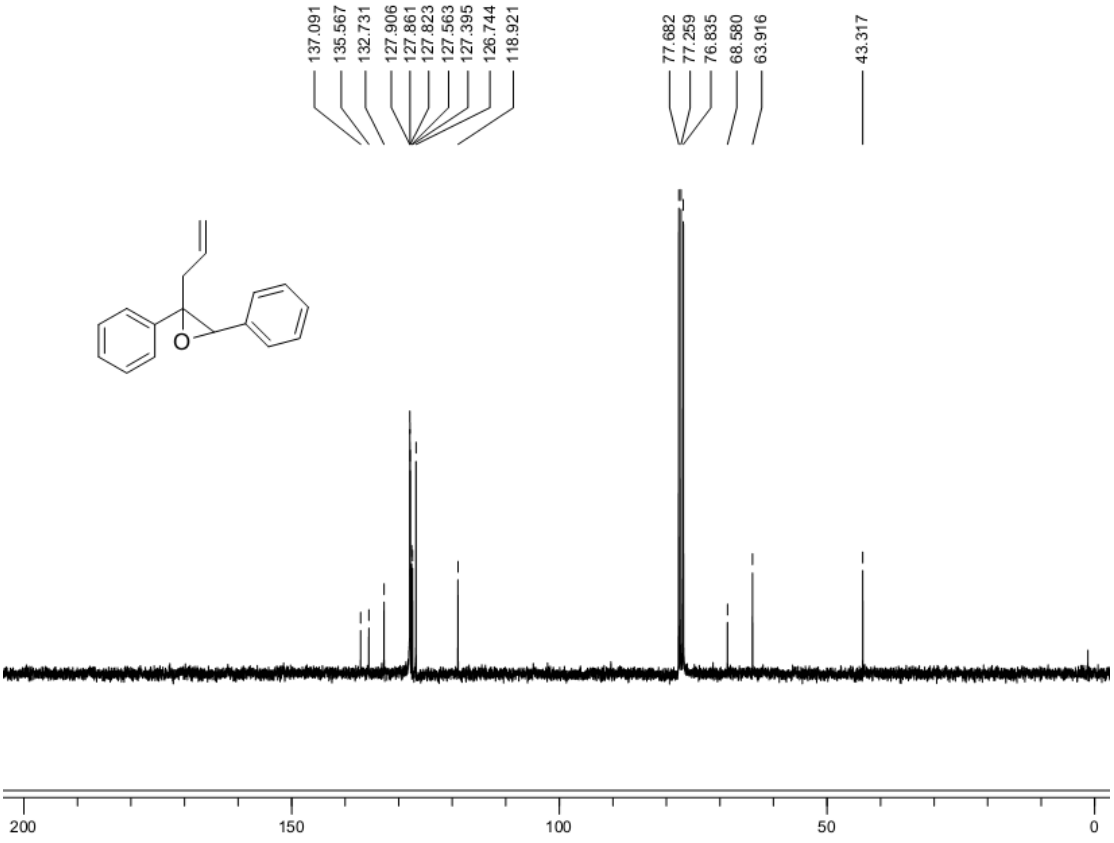
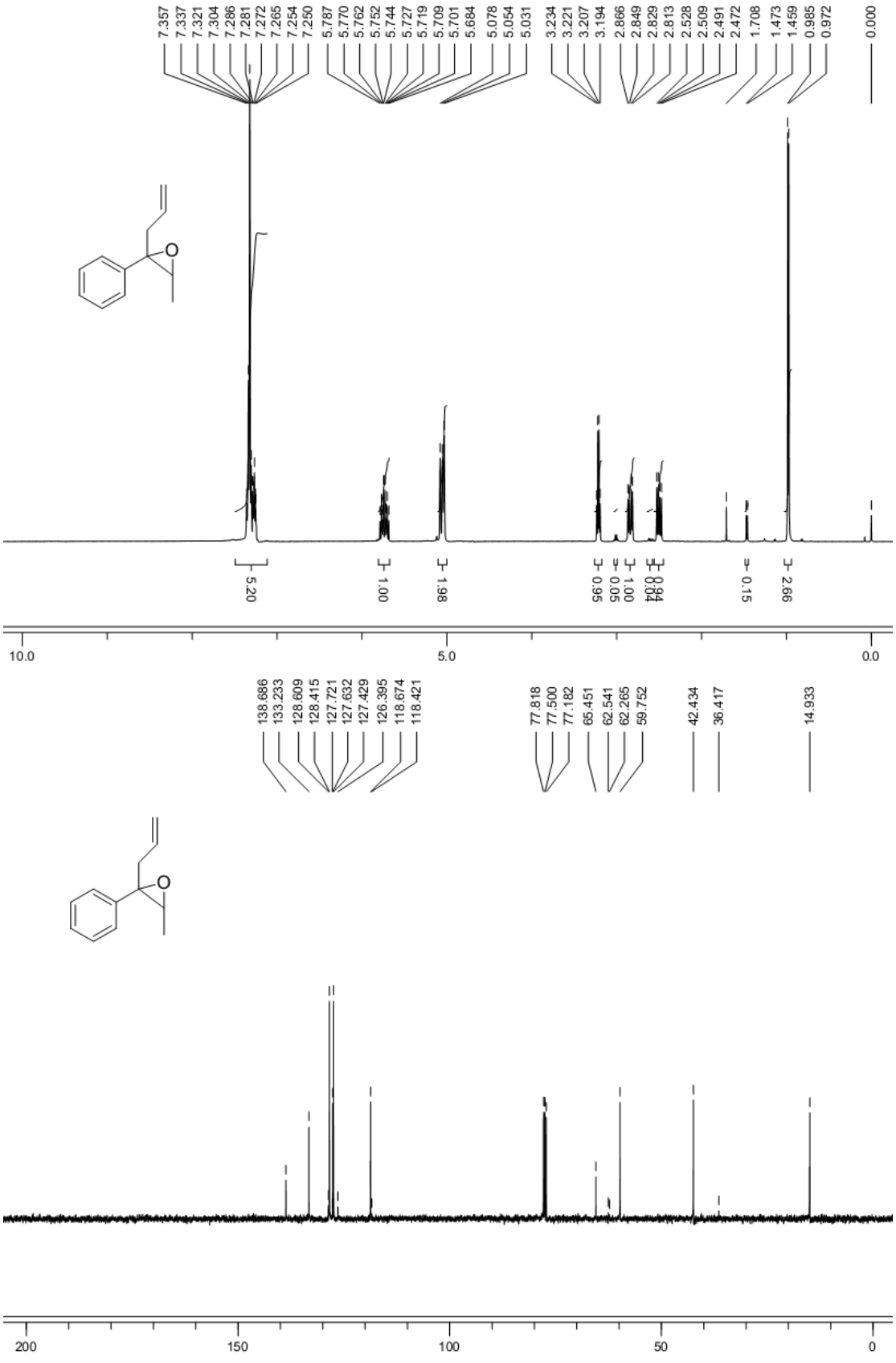
59.863
42.226
36.245
14.882
Br
O
200
150
100
50
0

3g

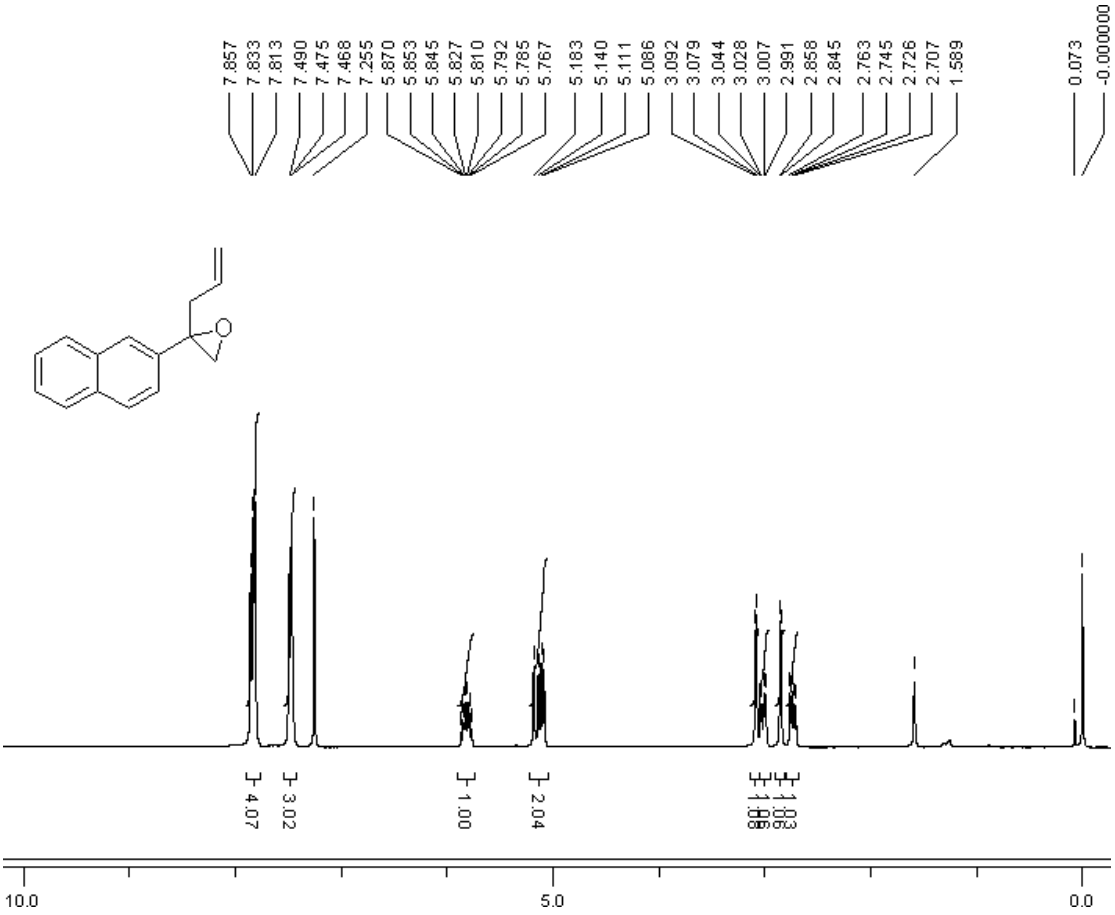


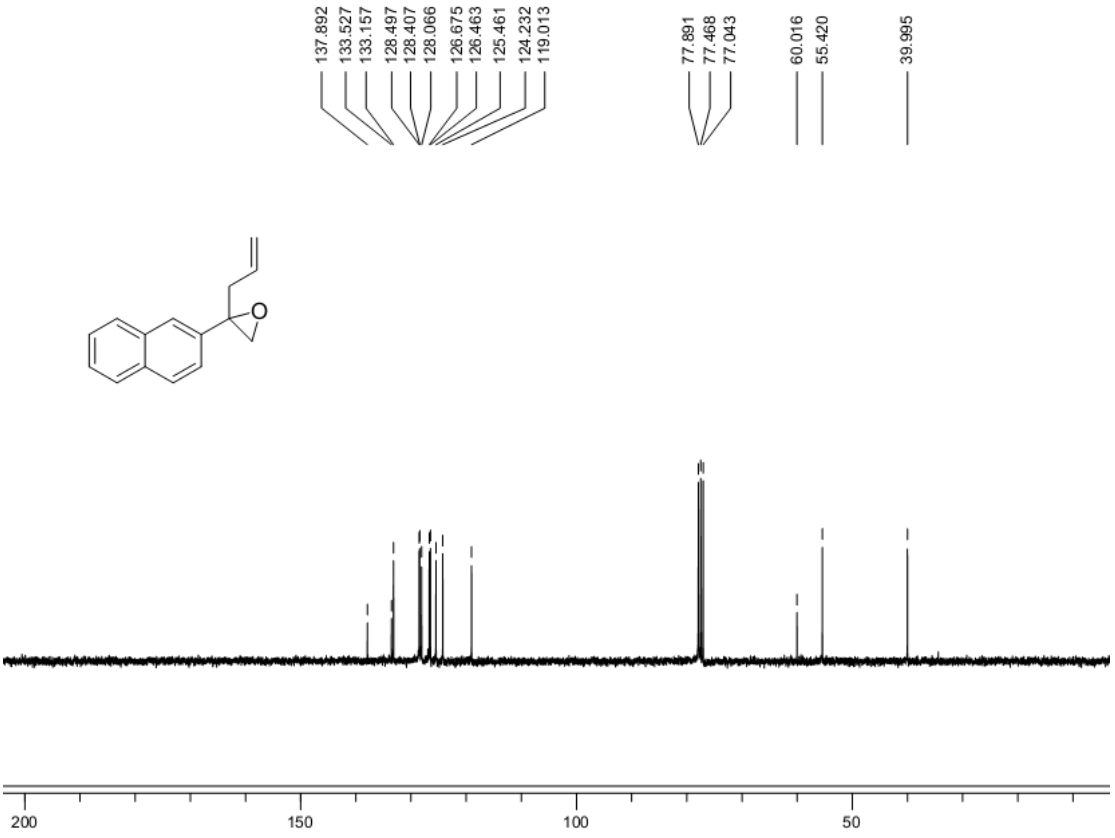


3h

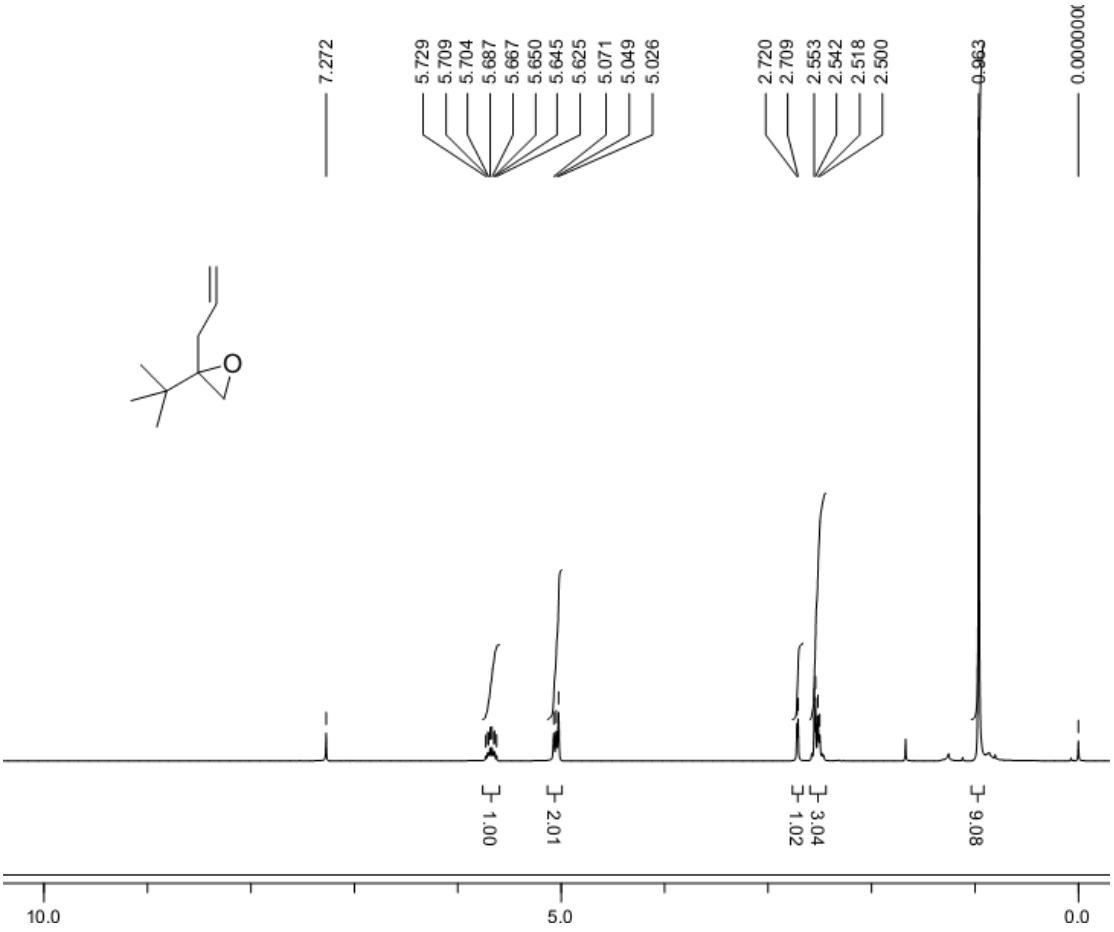


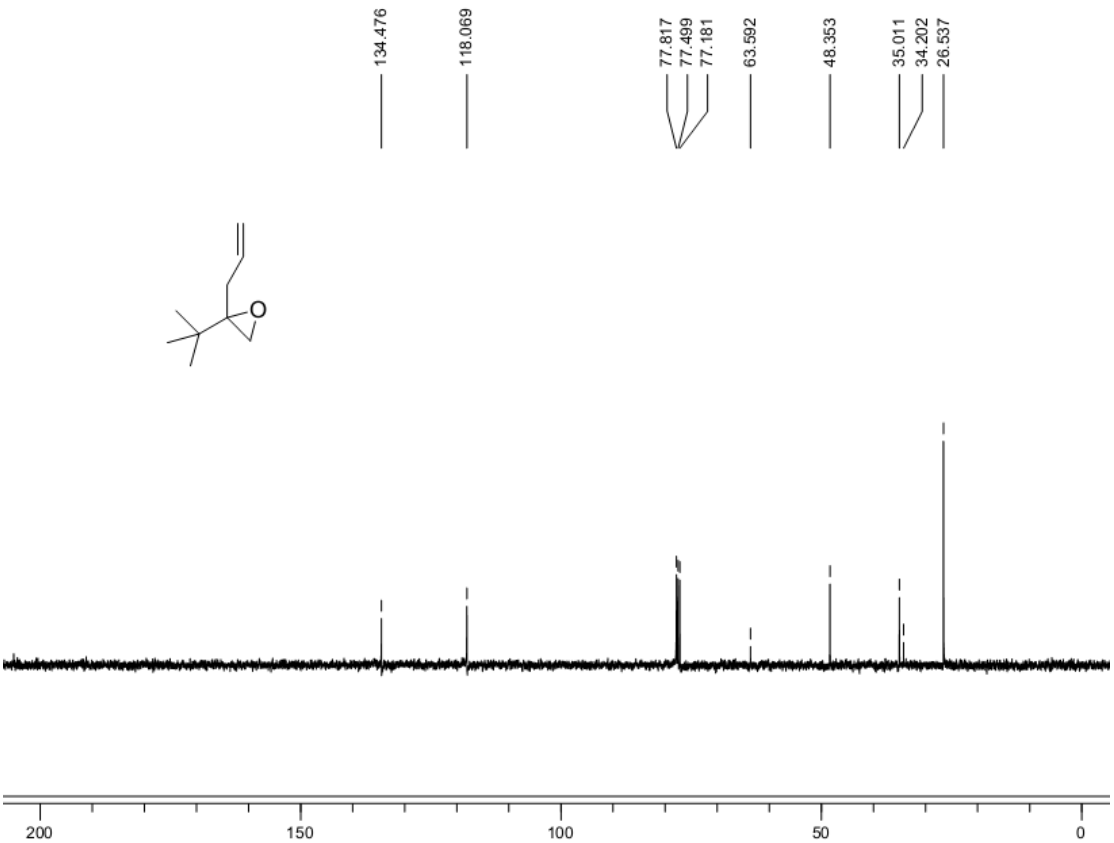
3i



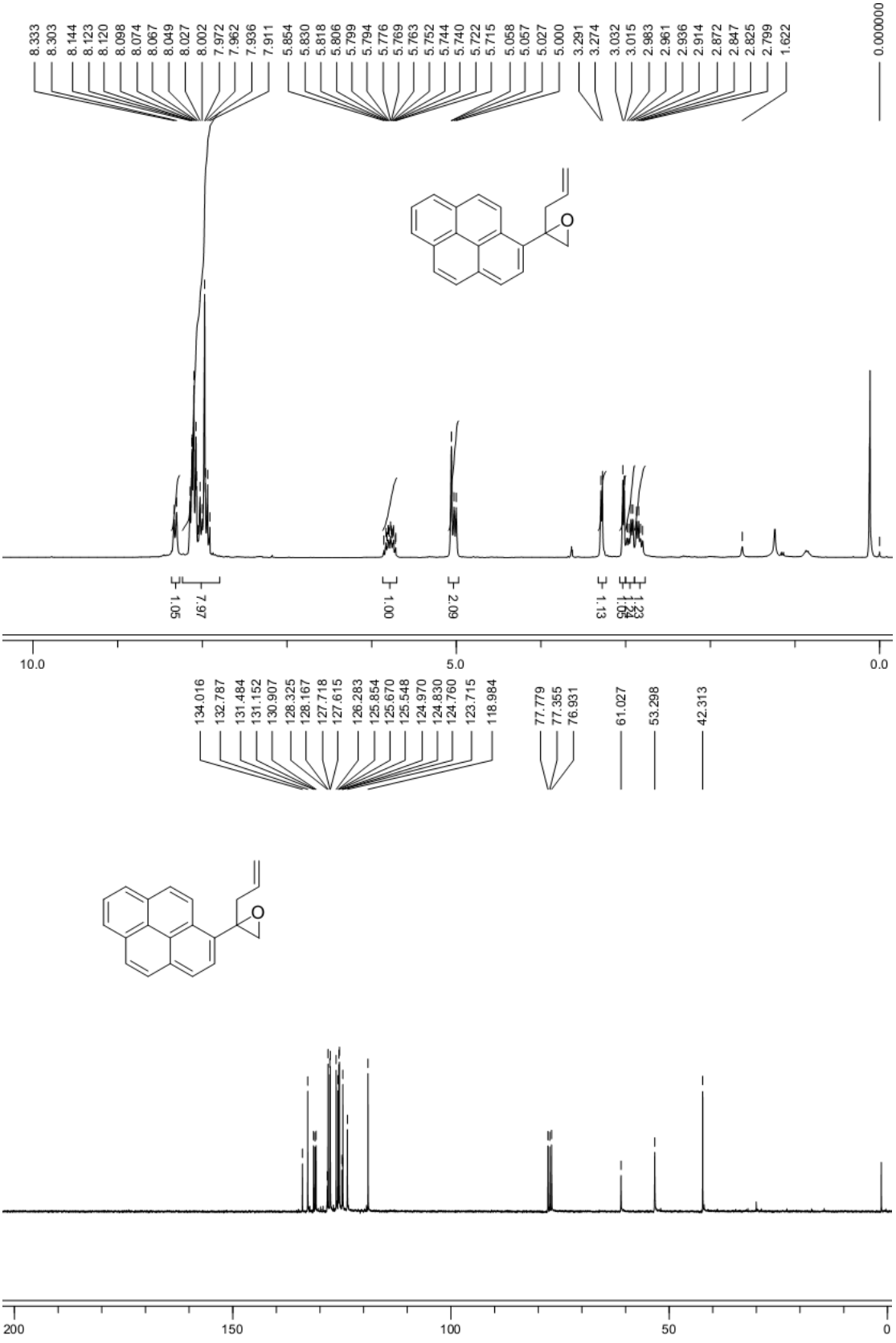


3j

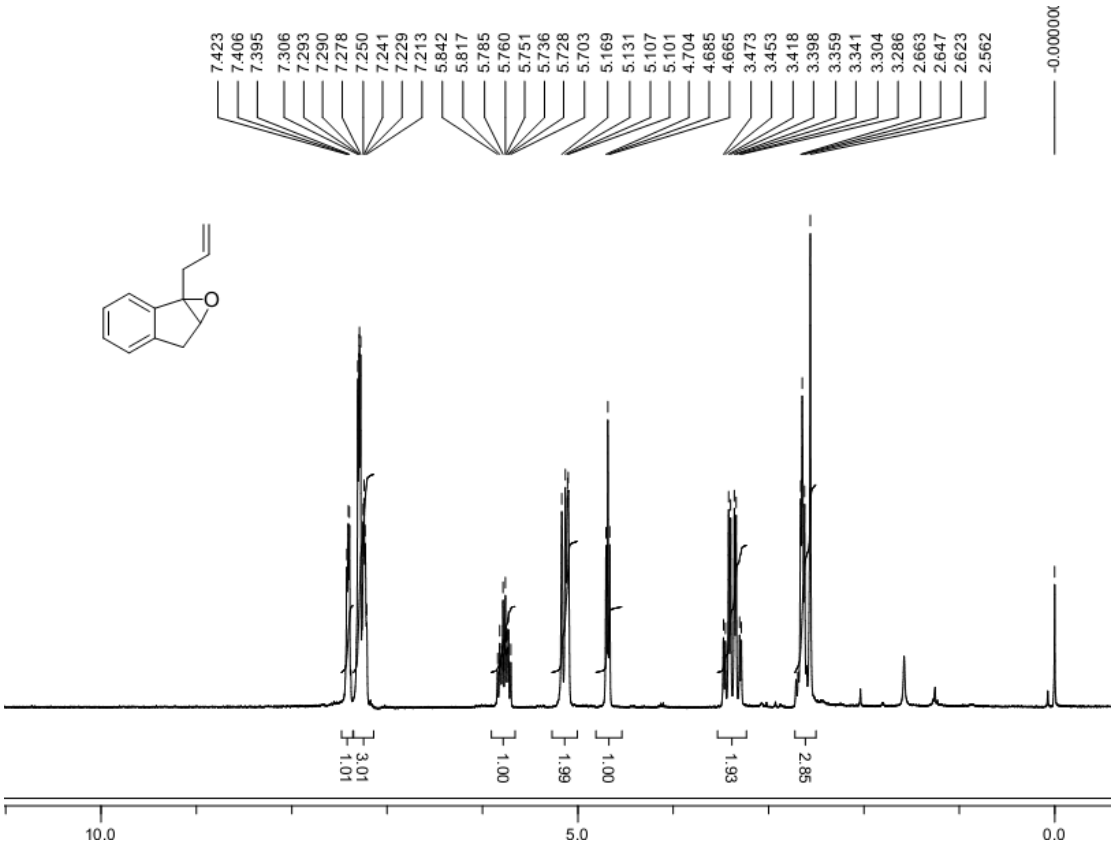


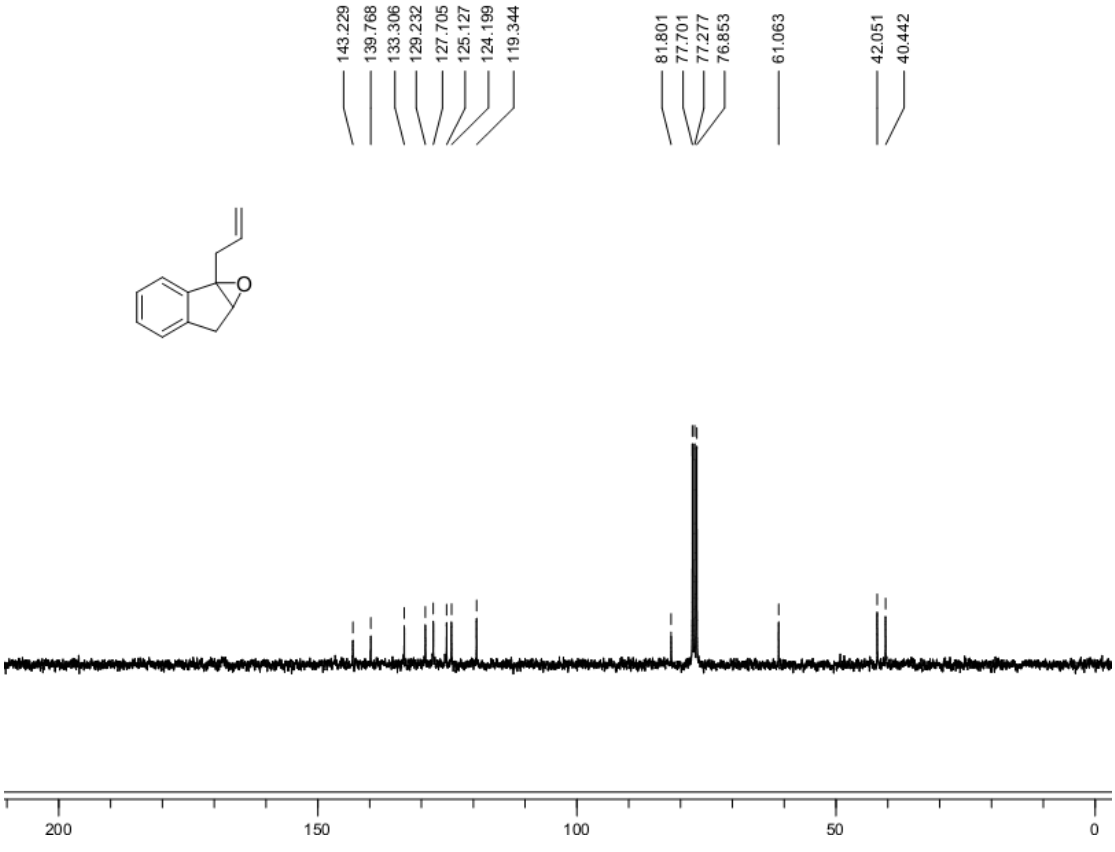


3k

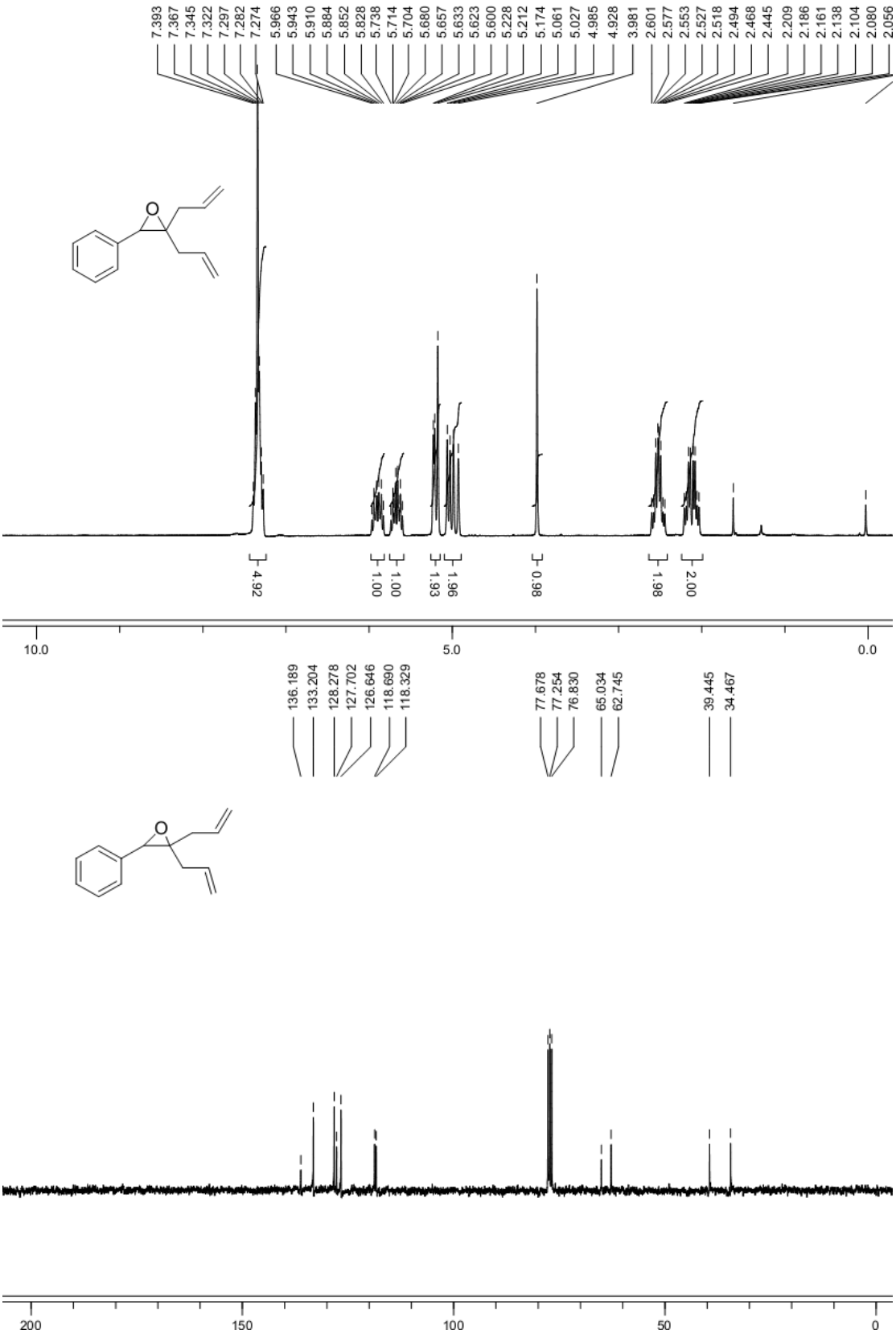


3l

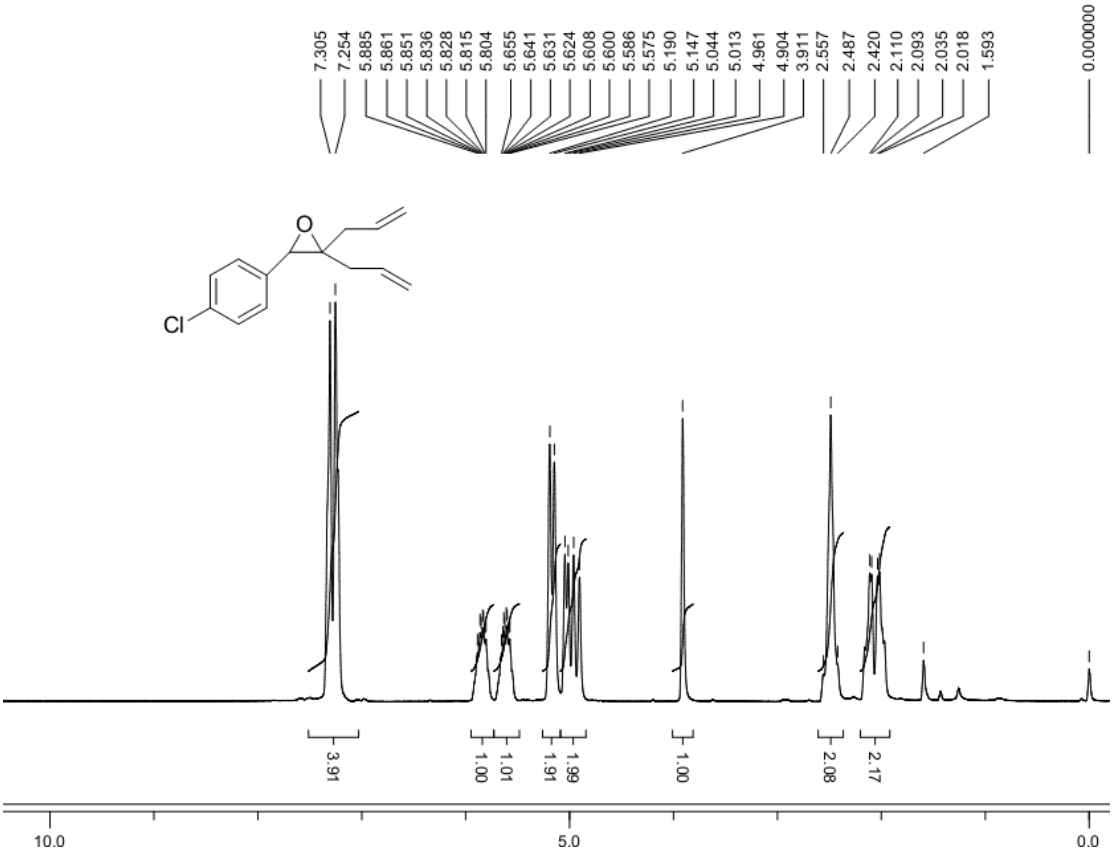


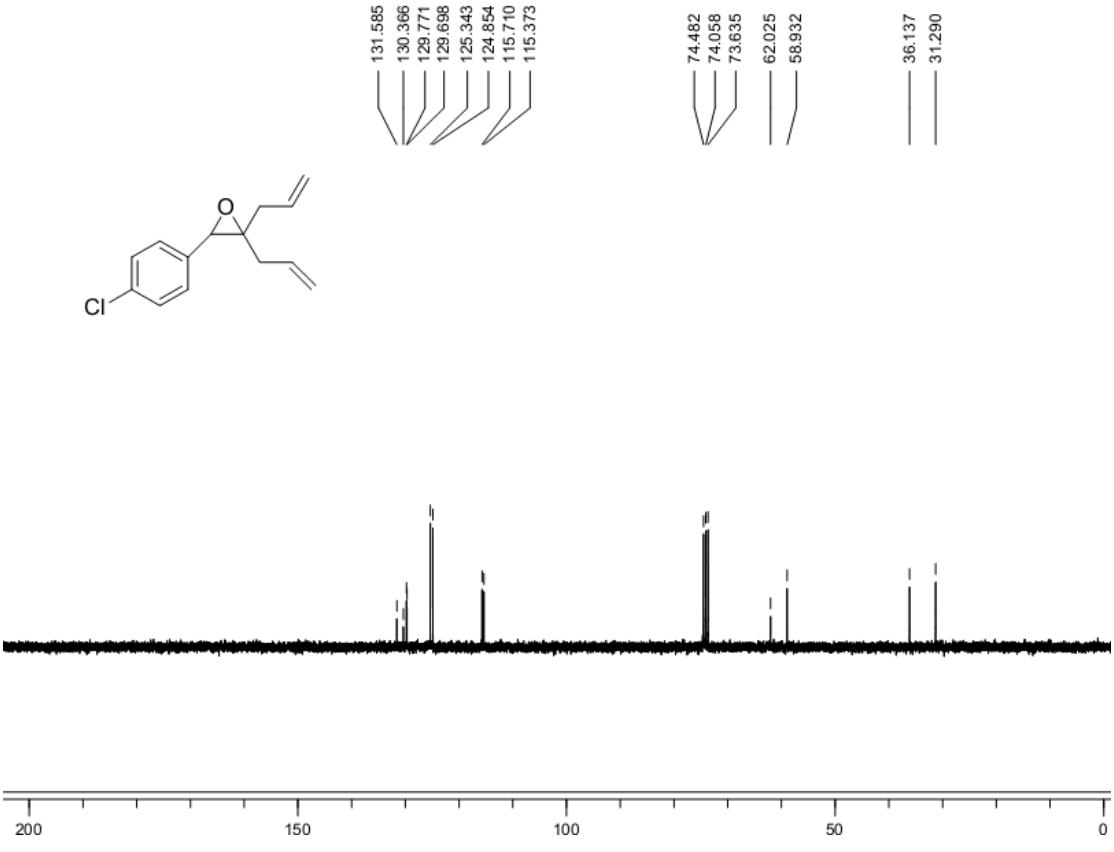


5a

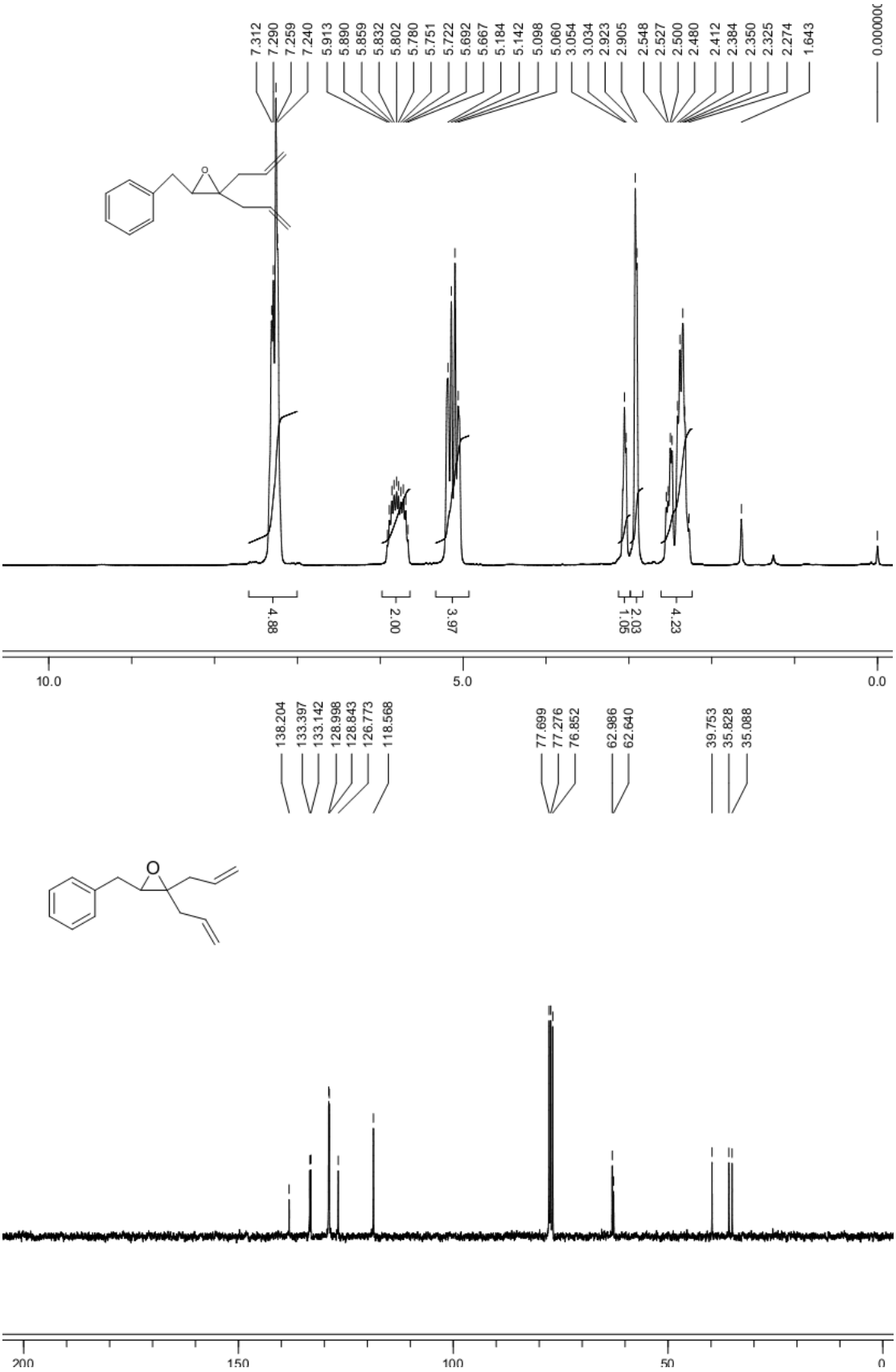


5b





5c



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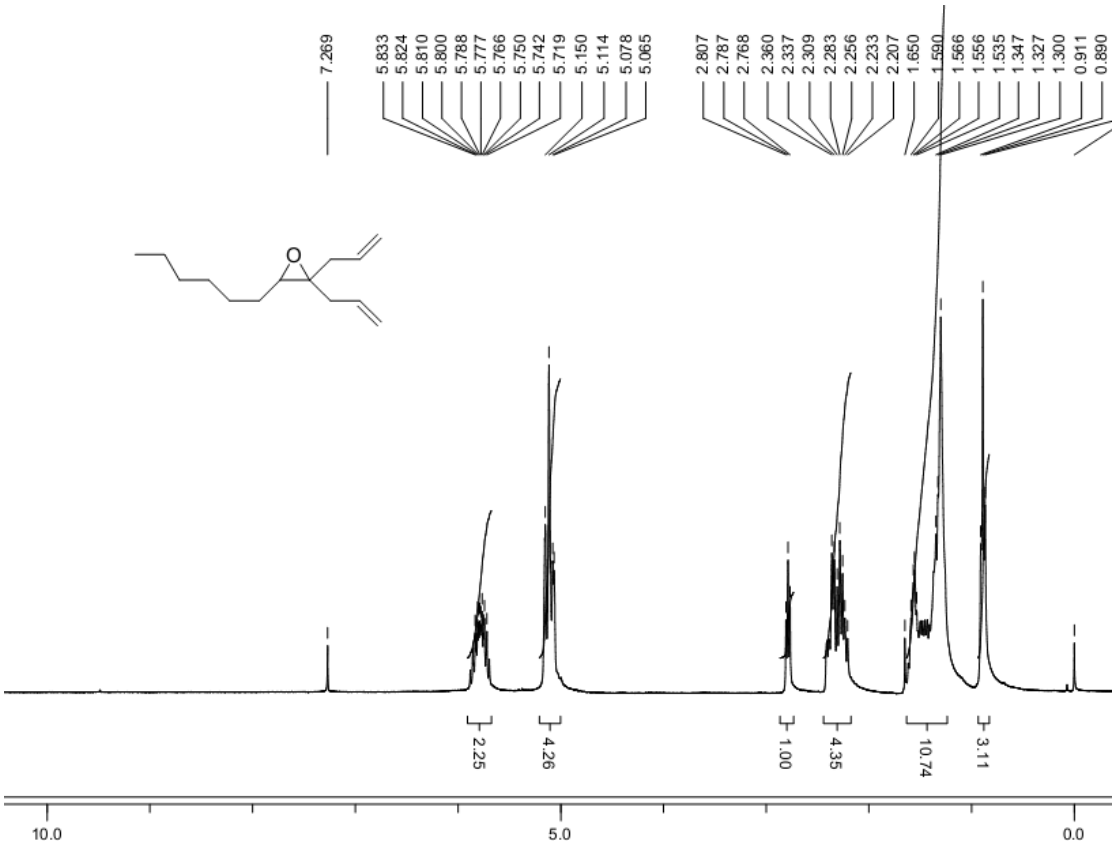
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5.766
5.750
5.742
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5.150
5.114
5.078
5.065
2.807
2.787
2.768
2.360
2.337
2.309
2.283
2.256
2.233
2.207
1.650
1.590
1.566
1.556
1.535
1.347
1.327
1.300
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O
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5.0
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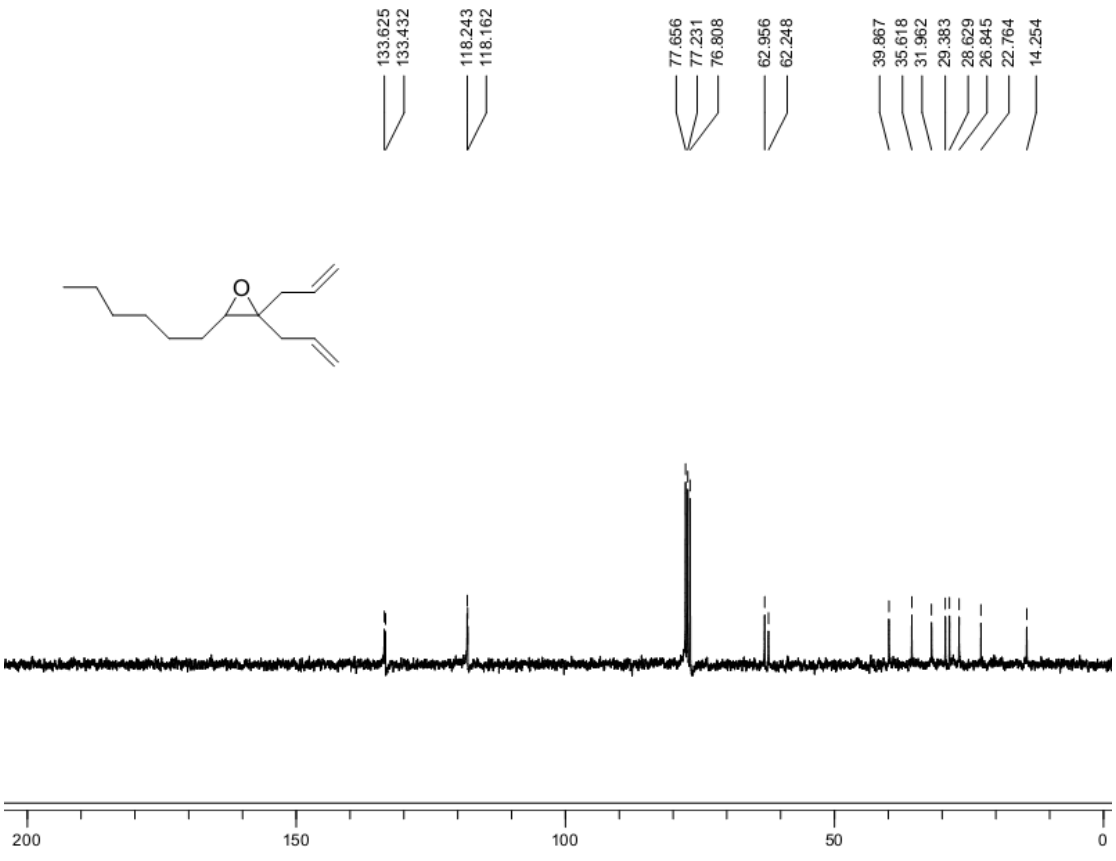
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26.845
22.764
14.254
O
200
150
100
50
0

5e