Supporting Information

S-Methylidene ~~Transfer~~ Agents:
Preparation of Chiral Non-Racemic ~~Carbocycles~~Heterocycles

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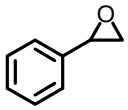
General Experimental Considerations

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained as solutions in $CDCl_3$. Chemical shifts were reported in parts per million (ppm) and referenced to δ 7.27 (^{1}H NMR) and δ 77.00 (^{13}C NMR). Infrared spectra were recorded using a FT IR and reported in wavenumbers (cm^{-1}). Analytical high pressure liquid chromatography (HPLC) was performed with a built-in photometric detector using a (*R*,*R*)-Whelk-O 1 column (4.6 mm × 25cm). Solvents for HPLC analyses were of spectroscopic grade and filtered before use. GC analyses were performed using a ZB-5 with guardian (30 meter + 5 meter guardian end, 0.25 mm ID, and 0.25 μm film thickness). Optical rotations were recorded on a digital polarimeter and are reported as follows: $[\alpha]^{T}$ (*c*, solvent) where *c* = g/100mL. TLC analyses were performed on flexible aluminium backed TLC plates with a fluorescent indicator. Detection was conducted by UV absorption (254 nm) followed by charring with 10% $KMnO_4$ in water. Solutions were concentrated in vacuo using a rotary evaporator. The resulting residue was purified using a neutral alumina column (150 mesh, 58Å) unless specified otherwise. All chemicals used for synthetic procedures were reagent grade or better.

Representative procedure for ~~sulfonium methylidene~~methylene epoxidations

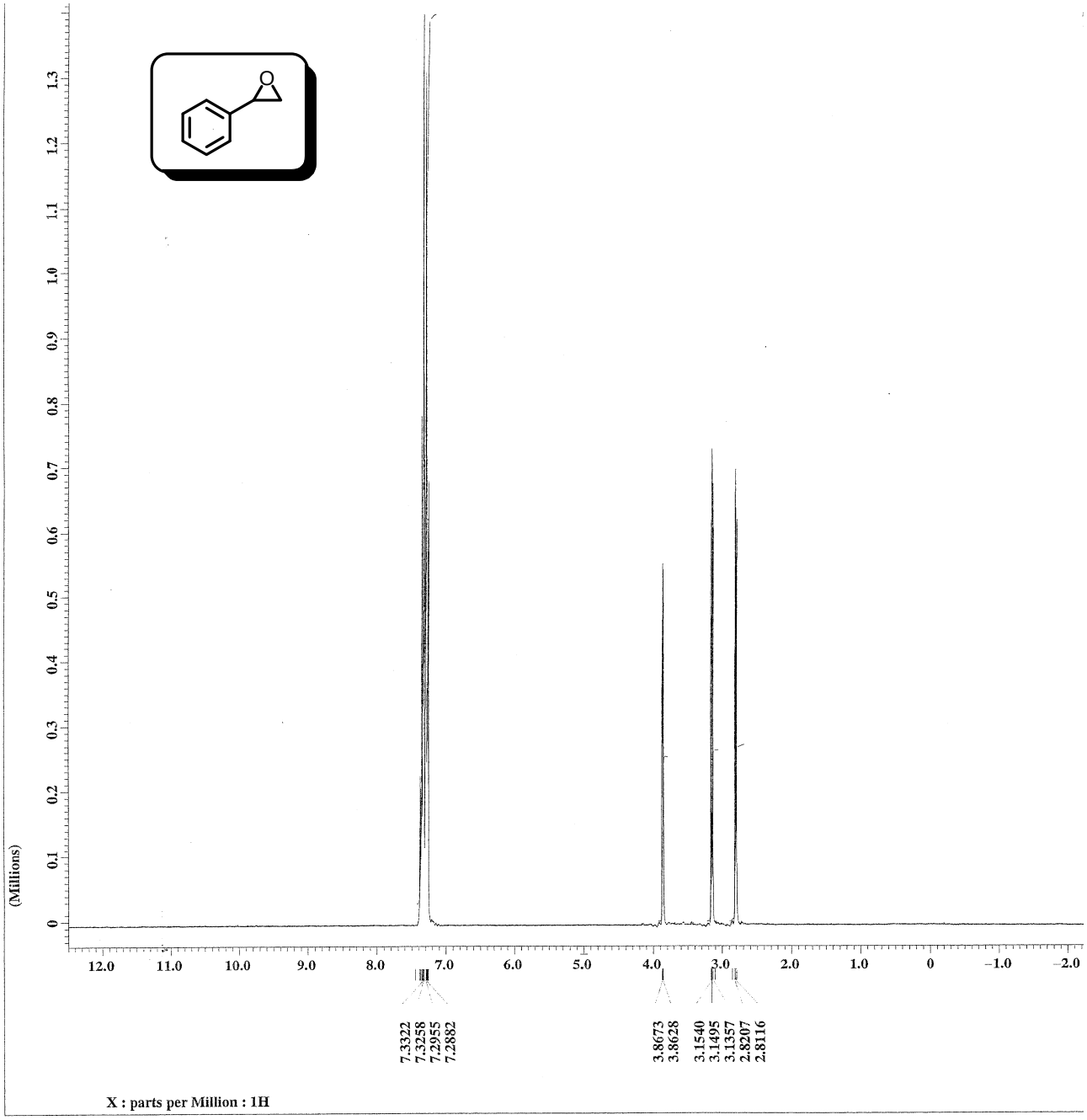
An oven-dried 25 mL round-bottomed flask was equipped with a stir bar, septum, and water-jacketed condenser. The system was next charged with aldehyde (1.0 mmol, 1.0 equiv), cesium carbonate (2.0 equiv) and THF (3.0 mL). To this slurry was added a solution of betaine (2.0 equiv) in THF (2.0 mL) via syringe in two equal portions at 6 h intervals. The system was externally heated to 80 °C (sand bath) and the reaction mixture was allowed to stir for a period of 12 h. After cooling to room temperature, the reaction mixture was filtered over a pad of Celite, concentrated in vacuo and then immediately purified by chromatography (neutral alumina (150 mesh, 58 Å)) using a gradient eluent system of hexanes and ethyl acetate to afford analytically pure oxirane.

2-Phenyloxirane



C_8H_8O
Mol. Wt.: 120.15

From the combination of benzaldehyde (0.106 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.114 g (95% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.28 (m, 5H), 3.86 (dd, J = 2.4, J = 2.4 1H), 3.15 (dd, J = 4.1, J = 4.1, 1H), 2.81 (dd, J = 2.7, J = 2.7, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 128.4, 128.1, 125.4, 52.2, 51.1; TLC R_f 0.31 (EtOAc/hexane, 1/9). The analytical data obtained is consistent with commercial and previously reported material.[1]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0.6
0.5
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0.2
0.1
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
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7.3258
7.2955
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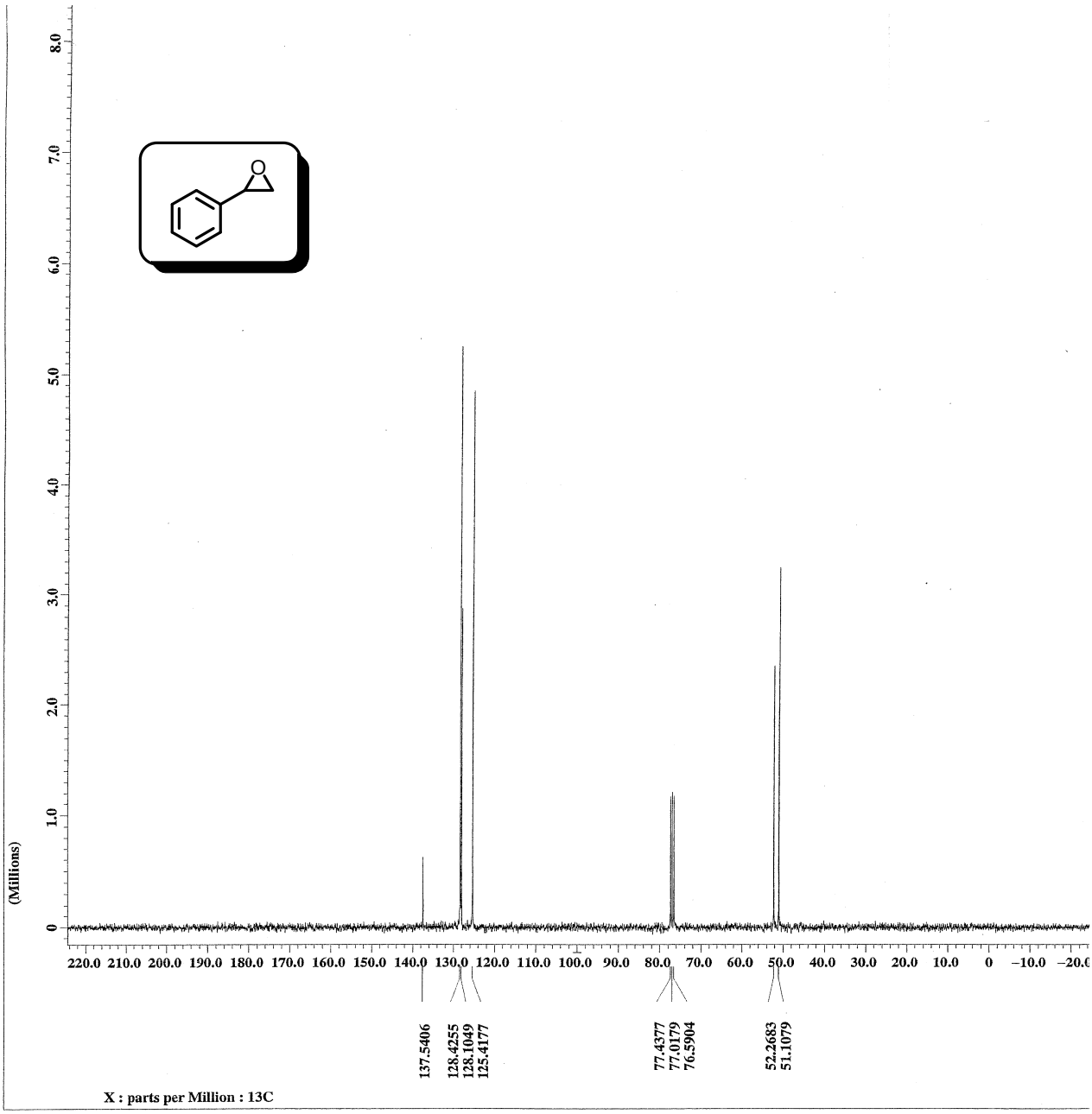
2.8116
X : parts per Million : 1H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6.0
5.0
4.0
3.0
2.0
1.0
0
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137.5406
128.4255
128.1049
125.4177
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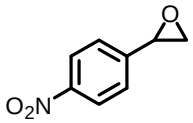
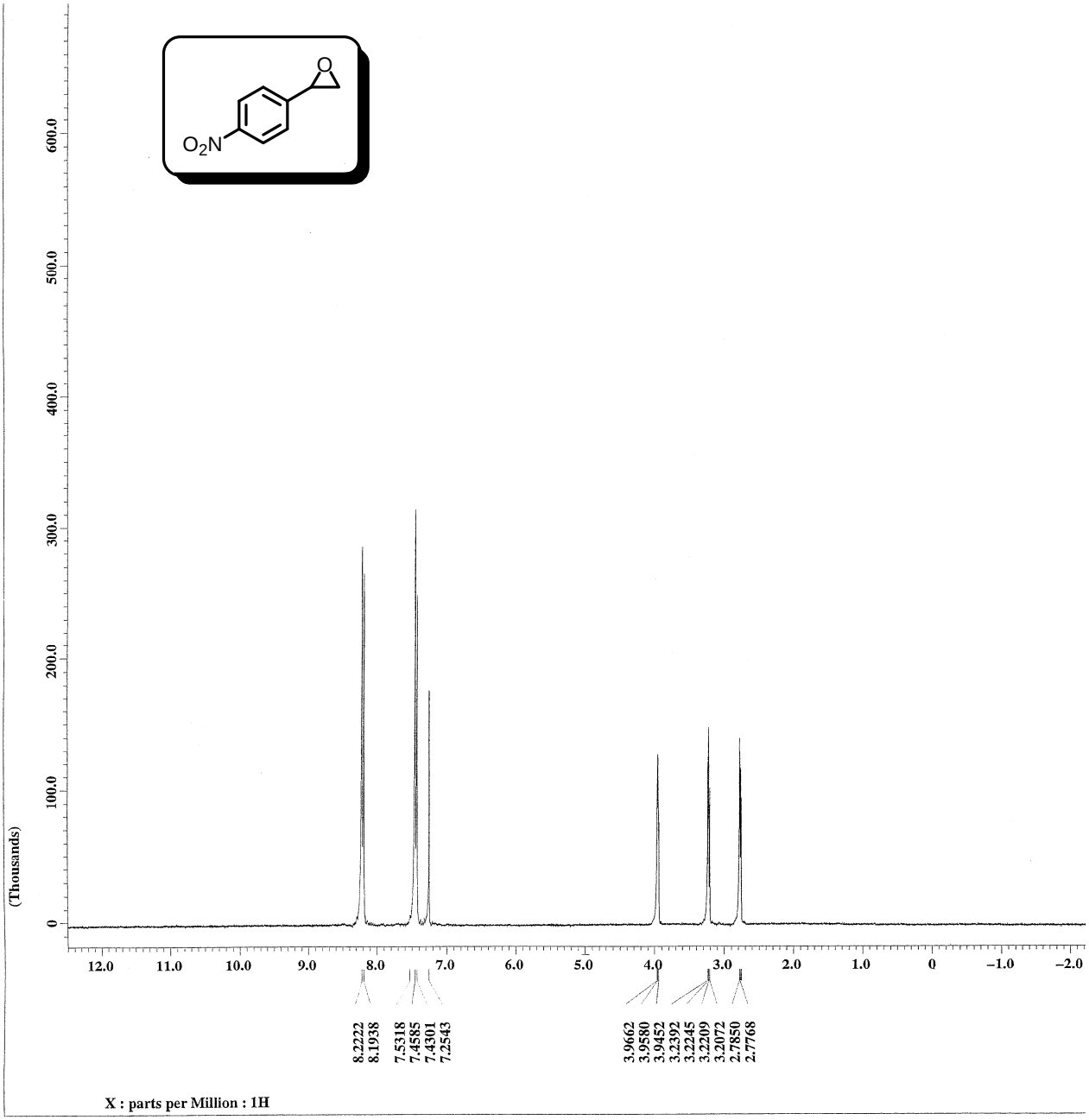
77.0179
76.5904
52.2683
51.1079
X : parts per Million : 13C

2-(4-Nitrophenyl)oxirane



$C_8H_7NO_3$
Mol. Wt.: 165.15

From the combination of 4-nitrobenzaldehyde (0.151 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.160 g (97% yield) of the title compound was isolated as a yellow solid after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, J = 8.2, 2H), 7.44 (d, J = 8.2, 2H), 3.95 (dd, J = 3.8, J = 3.8, 1H), 3.22 (dd, J = 4.1, J = 4.1, 1H), 2.77 (dd, J = 2.4, J = 2.4, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.8, 145.2, 126.2, 123.8, 51.6, 51.4; TLC R_f 0.35 (EtOAc/hexane, 1/9); melting point 84-85°C (literature melting point 85°C).[2] The analytical data obtained is consistent with commercial and previously reported material.[2]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400.0
300.0
200.0
100.0
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(Thousands)
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
8.2222
8.1938
7.5318
7.4585
7.4301
7.2543
3.9662
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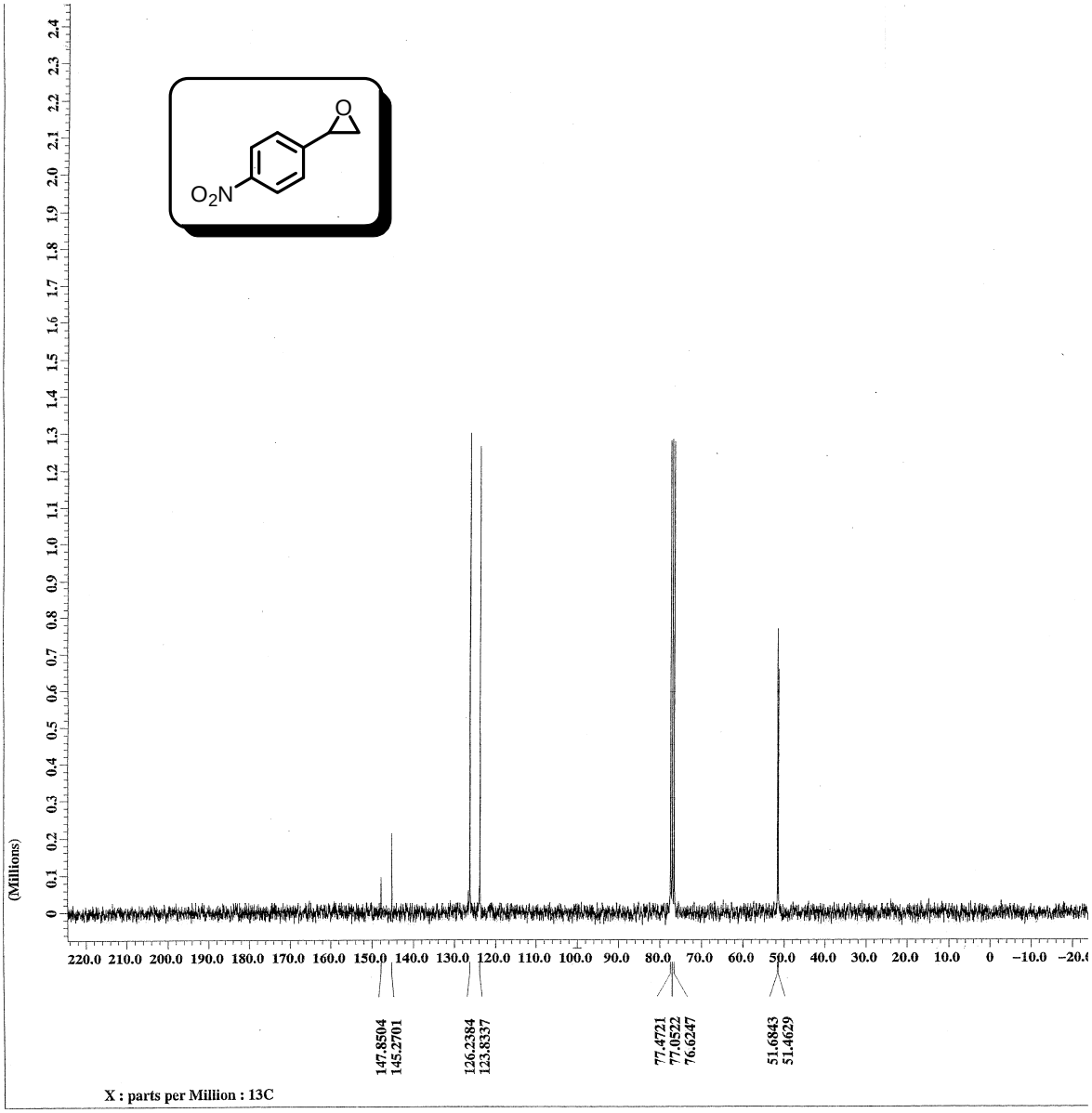
2.7768
X : parts per Million : 1H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O2N
(Millions)
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220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
147.8504
145.2701
126.2384
123.8337
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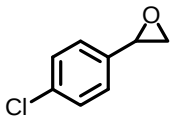
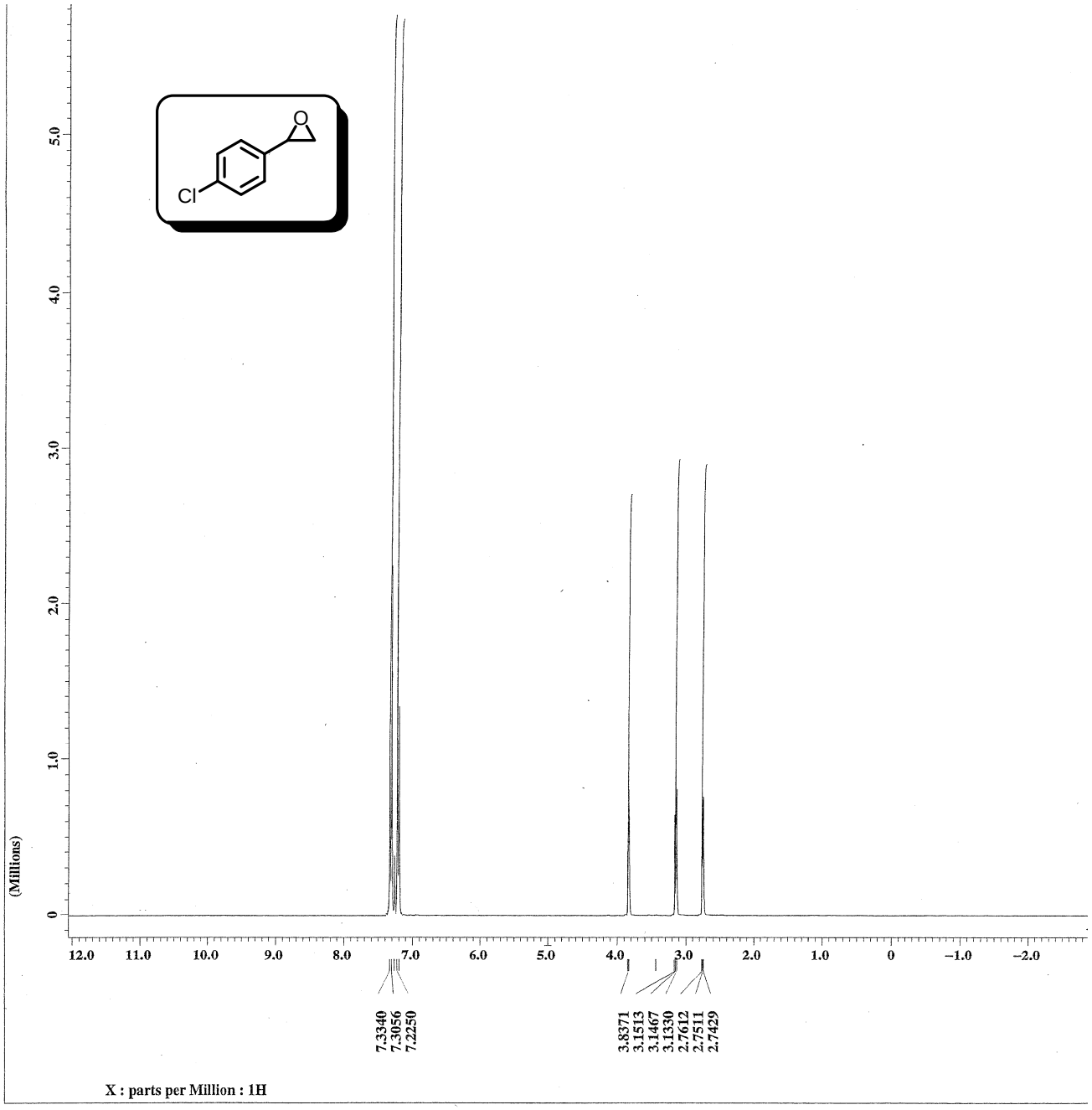
51.4629
X : parts per Million : 13C

2-(4-Chlorophenyl)oxirane



C_8H_7ClO
Mol. Wt.: 154.59

From the combination of 4-chlorobenzaldehyde (0.140 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.149 g (97% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.5, 2H), 7.20 (d, *J* = 8.5, 2H), 3.84 (dd, *J* = 2.7, *J* = 2.7, 1H), 3.15 (dd, *J* = 4.1, *J* = 4.1, 1H), 2.75 (dd, *J* = 2.4, *J* = 2.4, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 133.7, 128.7, 128.6, 126.7, 51.6, 51.1; TLC R_f 0.35 (EtOAc/hexane, 1/9). The analytical data obtained is consistent with commercial and previously reported material.[2,3]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7.0
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4.0
3.0
2.0
1.0
0
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−2.0
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7.3056
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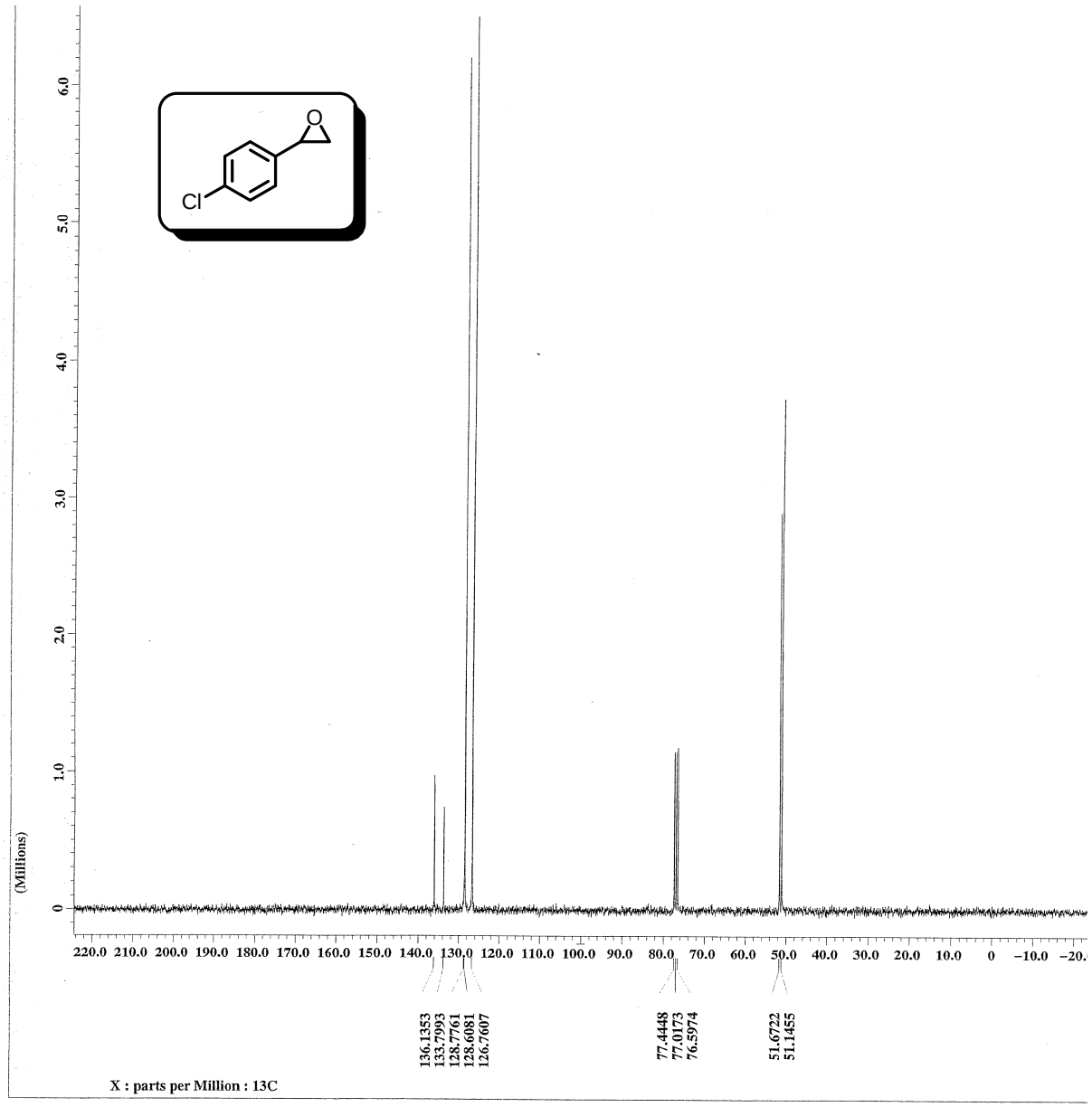
X : parts per Million : 1H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Cl
(Millions)
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2.0
1.0
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136.1353
133.7993
128.7761
128.6081
126.7607
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76.5974
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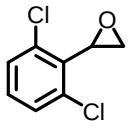
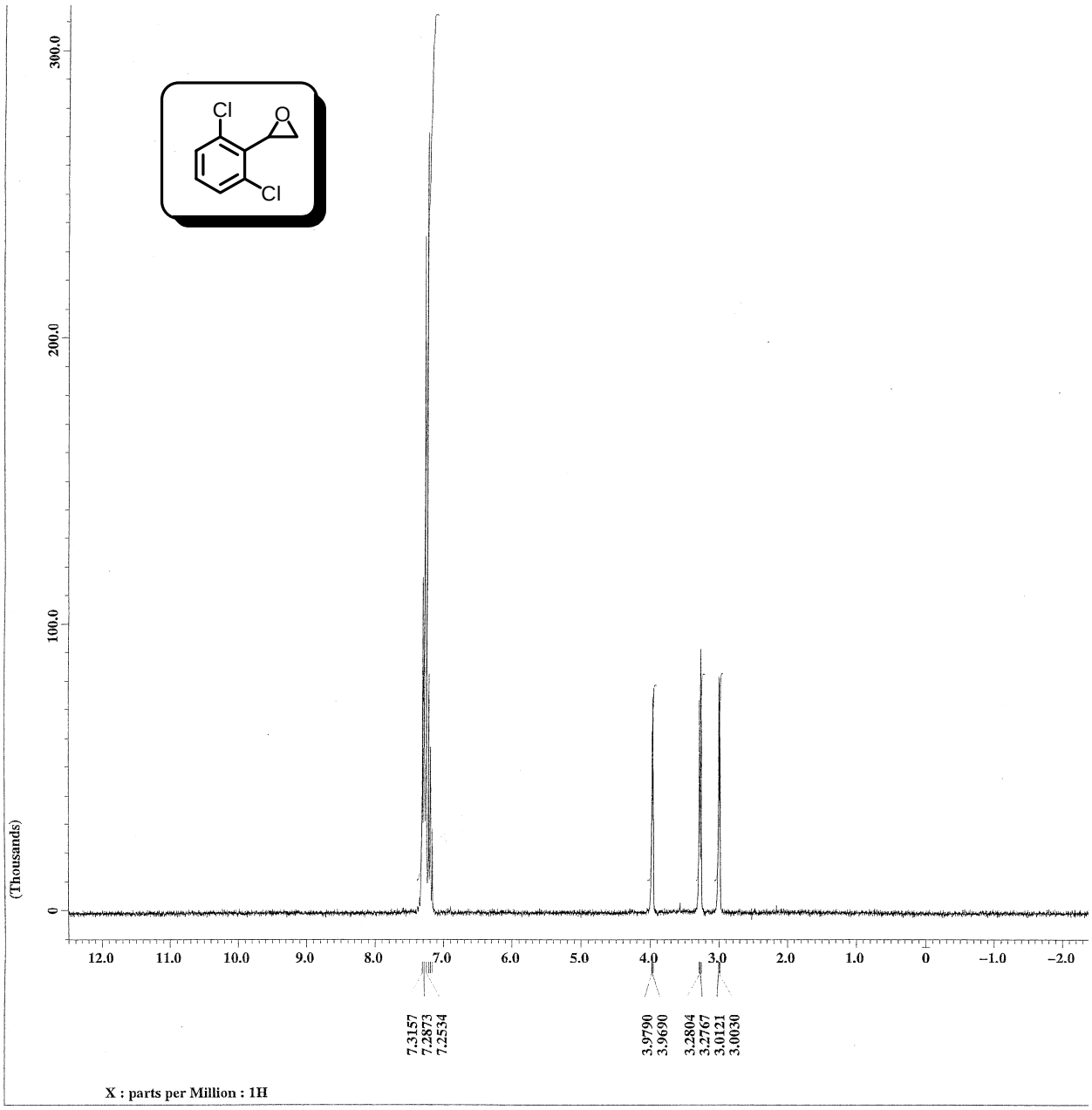
X : parts per Million : 13C

2-(2,6-Dichlorophenyl)oxirane



$C_8H_6Cl_2O$
Mol. Wt.: 189.04

From the combination of 2,6-dichlorobenzaldehyde (0.175 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.185 g (98% yield) of the title compound was isolated as a low melting solid after purification by column chromatography. Analytical data: IR (cm^{-1}) 3000, 2926, 1583, 1430, 1264, 1090, 894, 778, 736; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.20 (m, 3H), 3.96 (dd, *J* = 2.7, *J* = 2.7, 1H), 3.27 (dd, *J* = 3.0, *J* = 3.0, 1H), 3.01 (dd, *J* = 2.7, *J* = 2.7, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.1, 133.0, 129.9, 128.4, 50.2, 49.4; HRMS (EI) calculated mass 187.9796 ($C_8H_6Cl_2O$), found: 187.9793; TLC R_f 0.35 (EtOAc/hexane, 1/9); melting point 39-40 °C; GC (ZB-5) t_R 9.28 min.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5.0
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−1.0
−2.0
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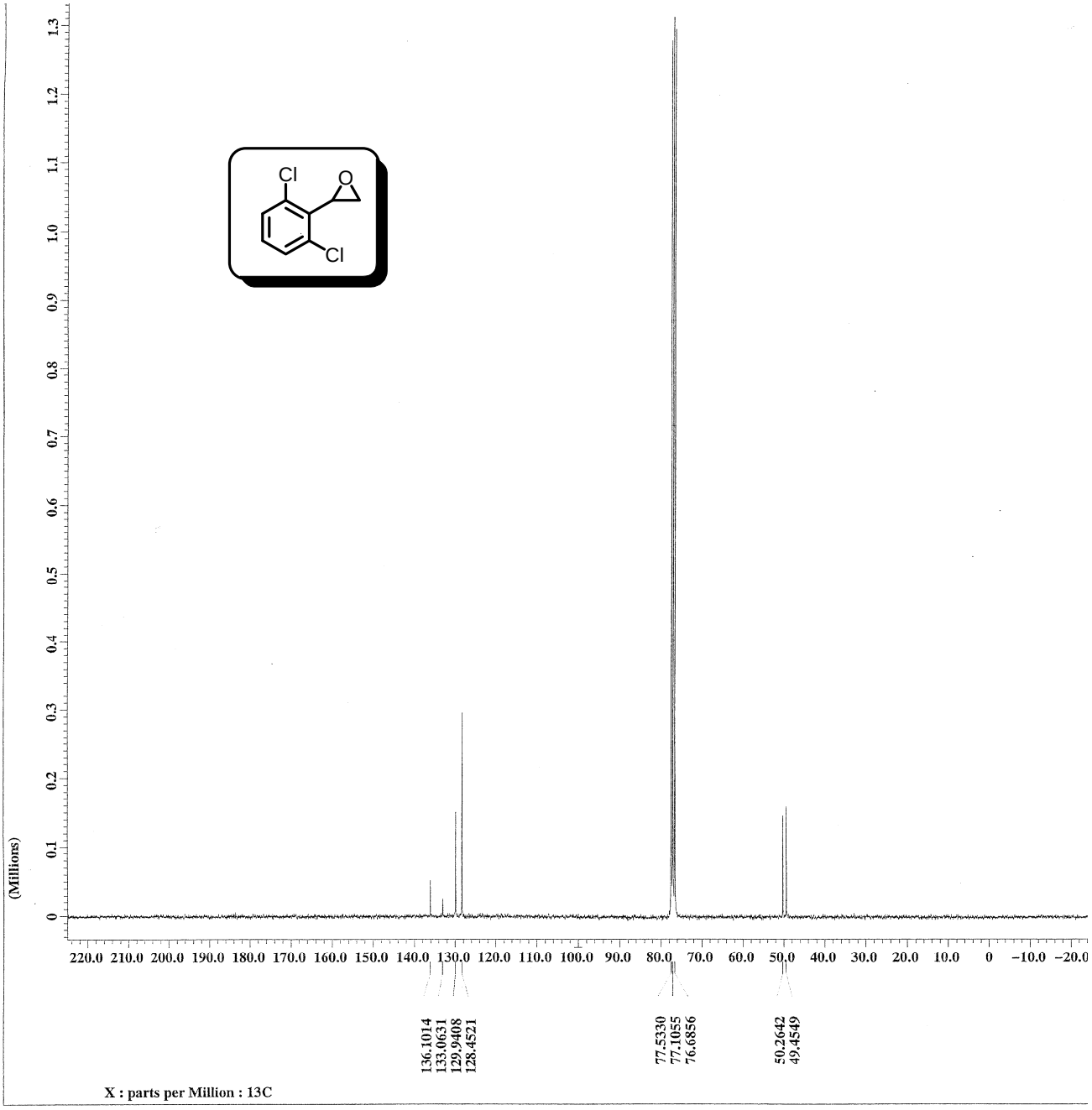
3.0030
X : parts per Million : 1H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Cl
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.0
136.1014
133.0631
129.9408
128.4521
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77.1055
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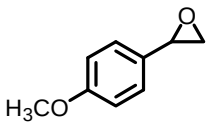
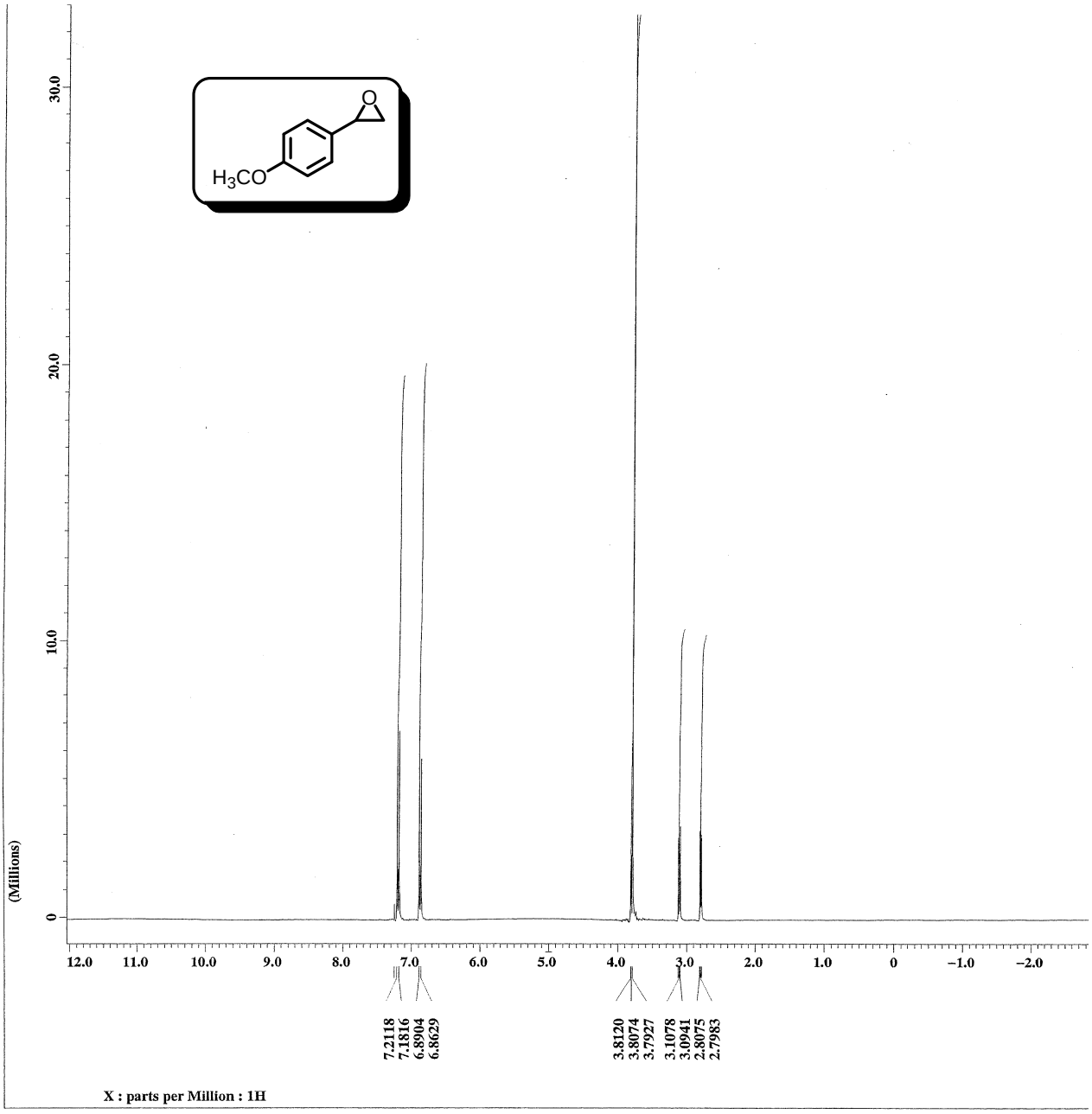
50.2642
49.4549
X : parts per Million : 13C

2-(4-Methoxyphenyl)oxirane



$C_9H_{10}O_2$
Mol. Wt.: 150.17

From the combination of 4-methoxybenzaldehyde (0.150 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.129 g (86% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 8.2, 2H), 6.80 (d, J = 8.2, 2H), 3.82-3.79 (m, 4H), 3.10 (dd, J = 4.1, J = 4.1, 1H), 2.79 (dd, J = 2.7, J = 2.7, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 129.4, 126.8, 113.9, 55.2, 52.2, 50.9; TLC R_f 0.38 (EtOAc/hexane, 1/9). The analytical data obtained is consistent with commercial and previously reported material.[4]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3.0
2.0
1.0
0
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−2.0
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7.1816
6.8904
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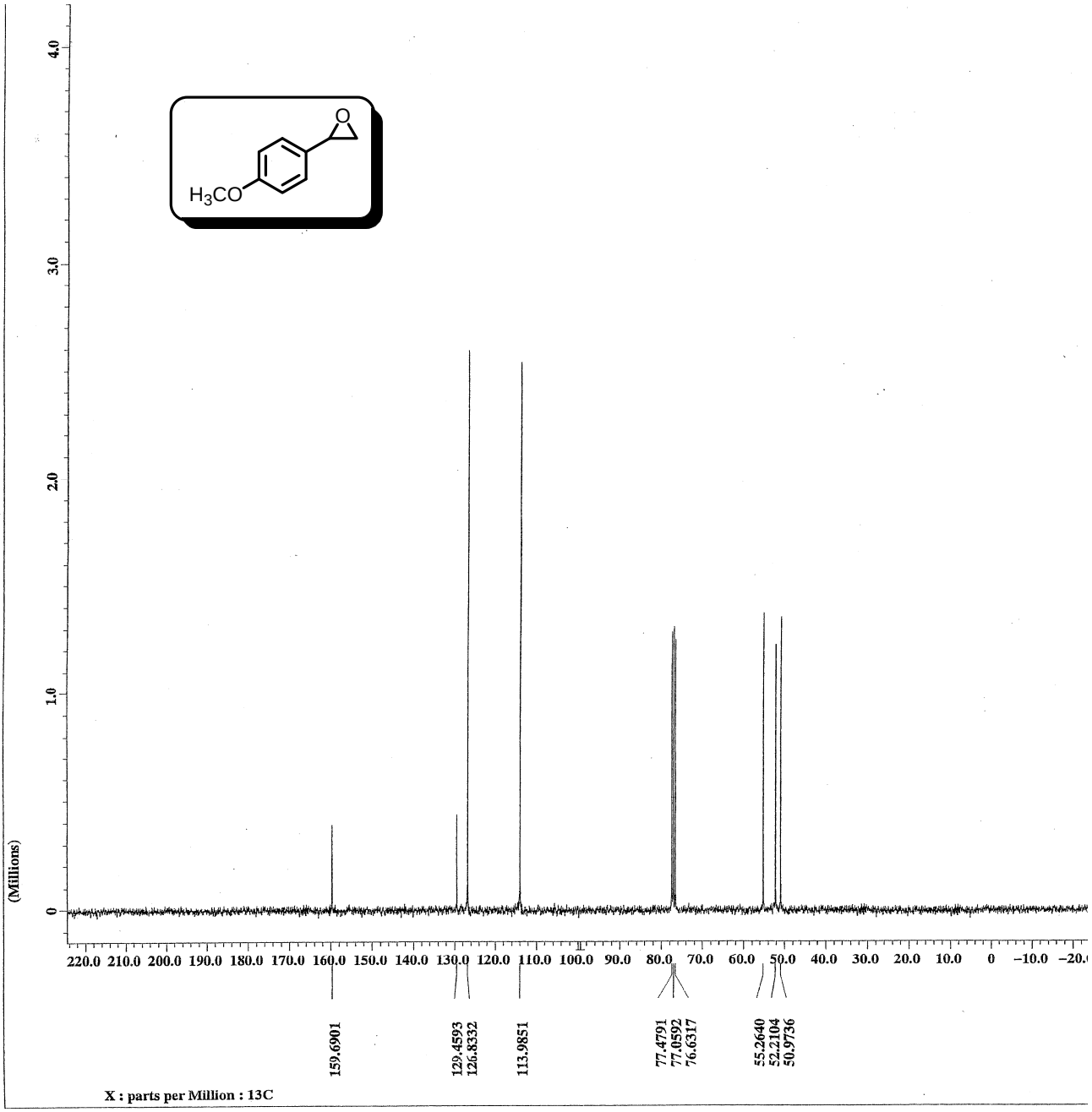
2.7983
X : parts per Million : 1H


(Millions)
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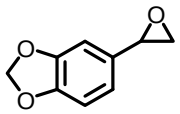
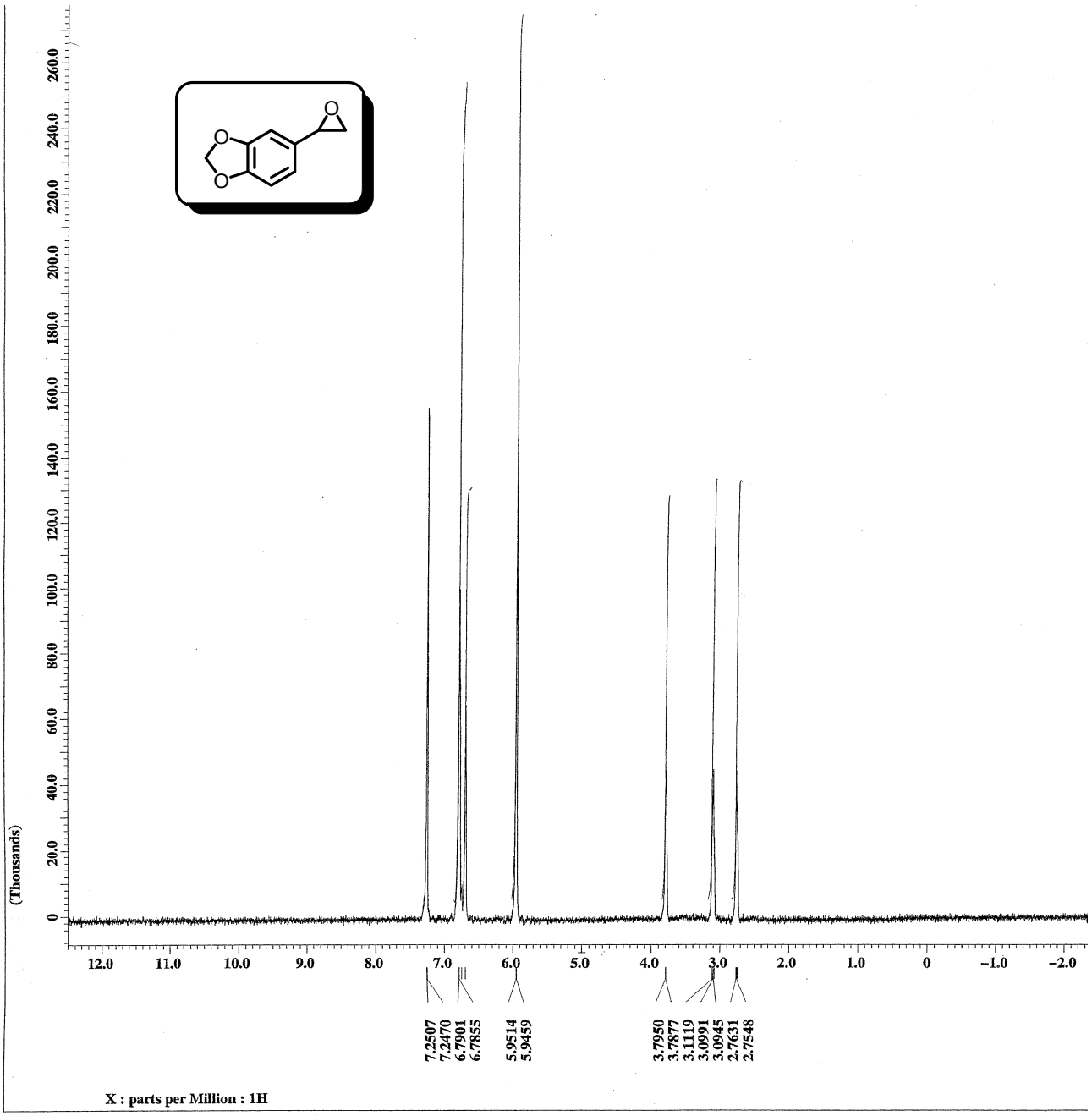
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.
159.6901
129.4593
126.8332
113.9851
77.4791
77.0592
76.6317
55.2640
52.2104
50.9736
X : parts per Million : 13C

2-(3,4-Methylenedioxyphenyl)oxirane



$C_9H_8O_3$
Mol. Wt.: 164.16

From the combination of 3,4-methylenedioxybenzaldehyde (0.150 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5.0 mL of THF, 0.150 g (92% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: IR (cm^{-1}) 2906, 1607, 1502, 1440, 1241, 1096,1034; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.79-6.69 (m, 3H), 5.94 (d, J = 1.6, 2H), 3.78 (dd, J = 2.4, J = 2.4, 1H), 3.09 (dd, J = 3.8, J = 3.8, 1H), 2.74 (dd, J = 2.4, J = 2.4, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.1, 147.7, 131.5, 119.7, 108.3, 105.4, 101.2, 52.4, 51.1; HRMS (EI). Calculated mass 164.0472 ($C_9H_8O_3$), found: 164.0474; TLC R_f 0.36 (EtOAc/hexane, 1/9); GC (ZB-5) t_R 7.26 min. The analytical data obtained is consistent with commercial material.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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
7.2507
7.2470
6.7901
6.7855
5.9514
5.9459
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3.7877
3.1119
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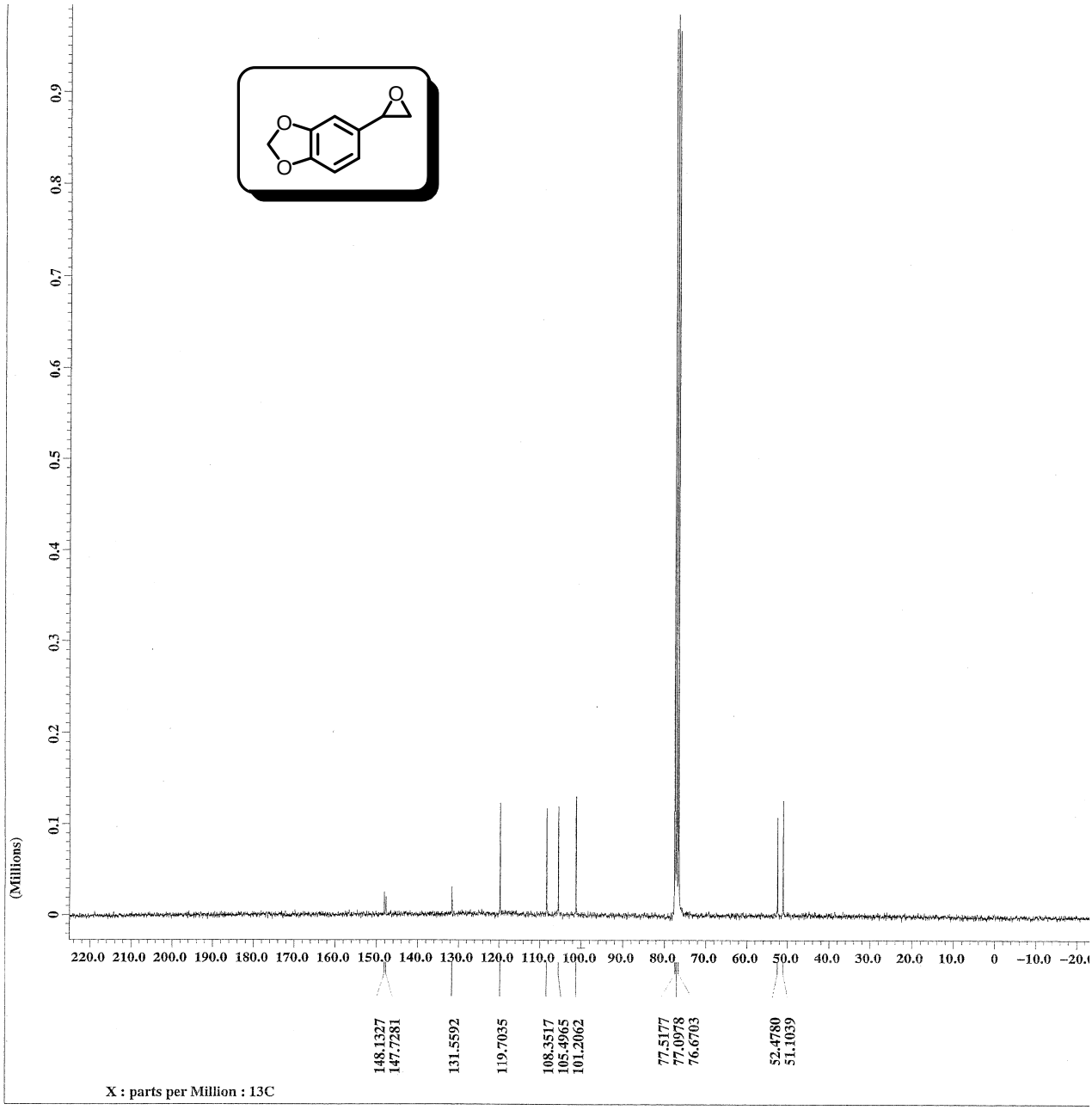
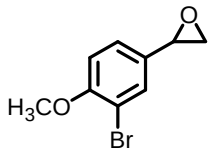
3.0945
2.7631
2.7548
X : parts per Million : 1H

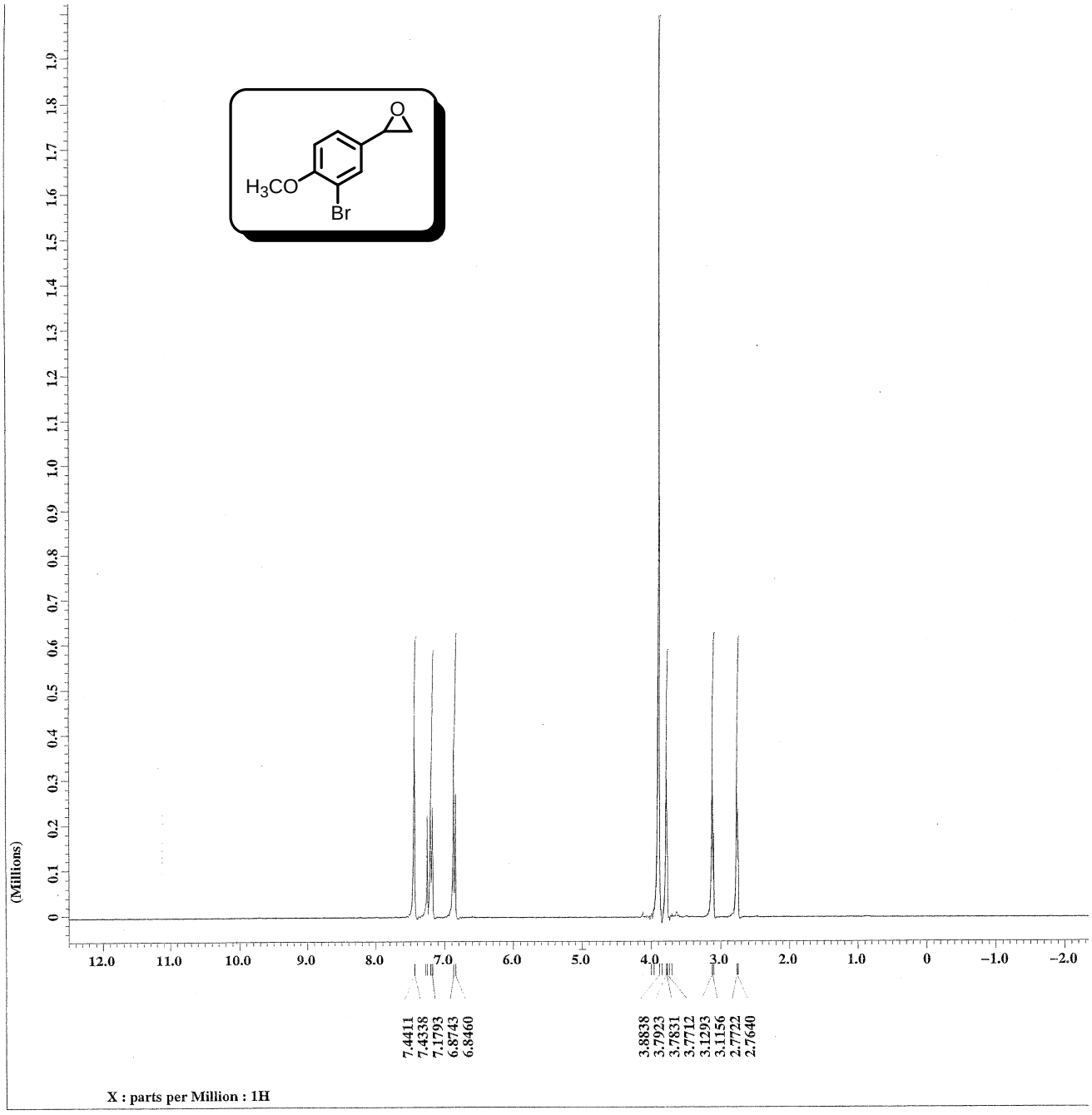

(Millions)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
148.1327
147.7281
131.5592
119.7035
108.3517
105.4965
101.2062
77.5177
77.0978
76.6703
52.4780
51.1039
X : parts per Million : 13C

2-(3-Bromo-4-methoxyphenyl)oxirane



$C_9H_9BrO_2$
Mol. Wt.: 229.07

From the combination of 3-bromo-4-methoxybenzaldehyde (1.374 g, 6.00 mmol), cesium carbonate (3.912 g, 12.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (3.984 g, 12.00 mmol) in 30.0 mL of THF, 1.20 g (93% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: IR (cm^{-1}) 3045, 2989, 1603, 1439, 1261, 1051, 726, 673; ^1H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4, 2H), 7.25-7.17 (m, 1H), 6.86 (d, J = 8.4, 1H), 3.88 (s, 3H), 3.78 (dd, J = 2.7, J = 2.7, 1H), 3.11 (dd, J = 4.1, J = 4.1, 1H), 2.76 (dd, J = 2.7, J = 2.7, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.9, 131.2, 130.5, 125.9, 111.9, 56.4, 51.5, 51.1; HRMS (ESI) calculated mass 228.9858 ($C_9H_9BrO_2$); found, 228.9864; TLC R_f 0.35 (EtOAc/hexane, 1/9); GC (ZB-5) t_R 11.23 min.


(Millions)
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
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1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
O
H3CO
Br
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
7.4411
7.4338
7.1793
6.8743
6.8460
3.8838
3.7923
3.7831
3.7712
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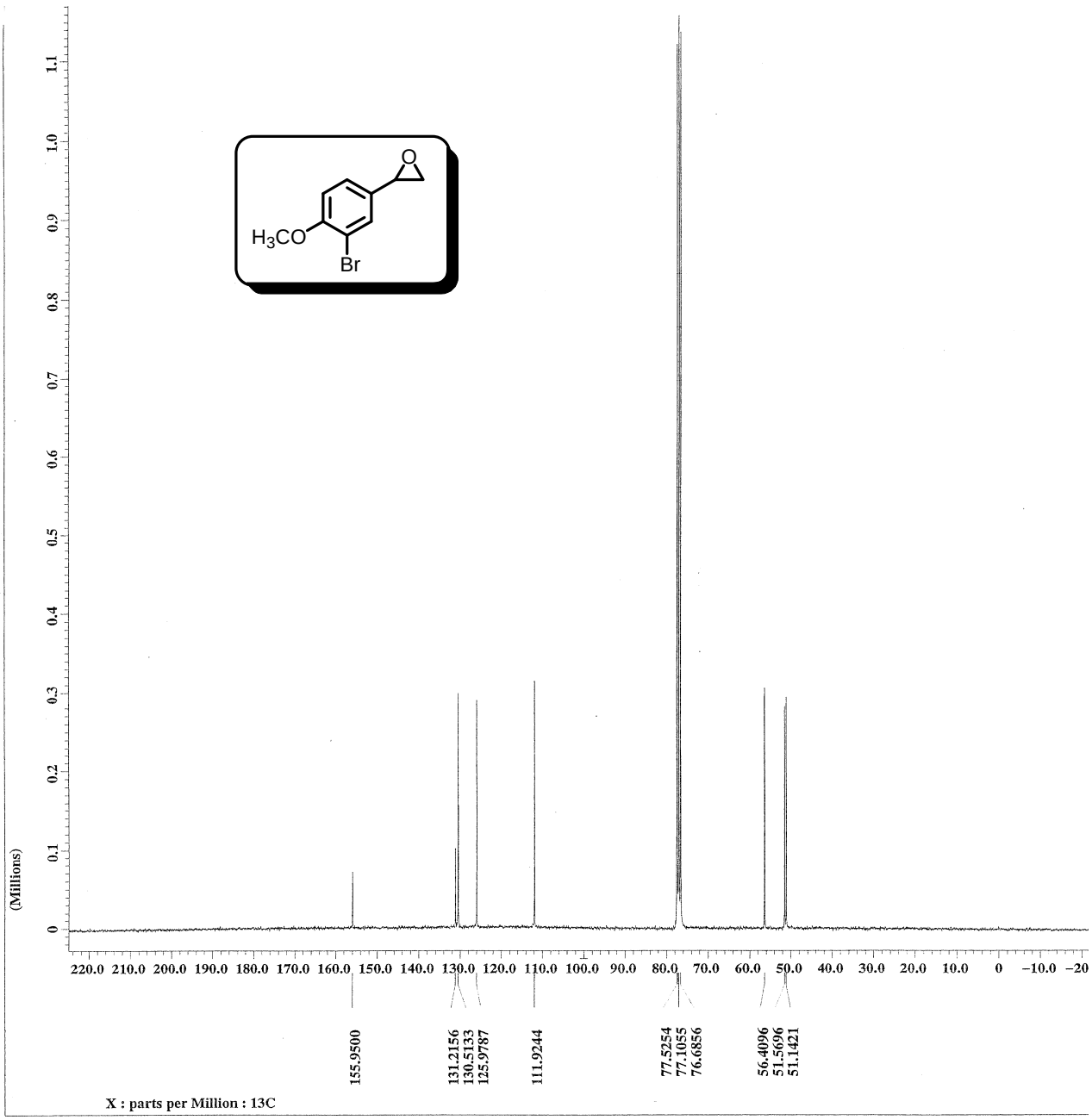
3.1156
2.7722
2.7640
X : parts per Million : 1H


O
H3CO
Br
(Millions)
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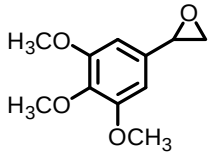
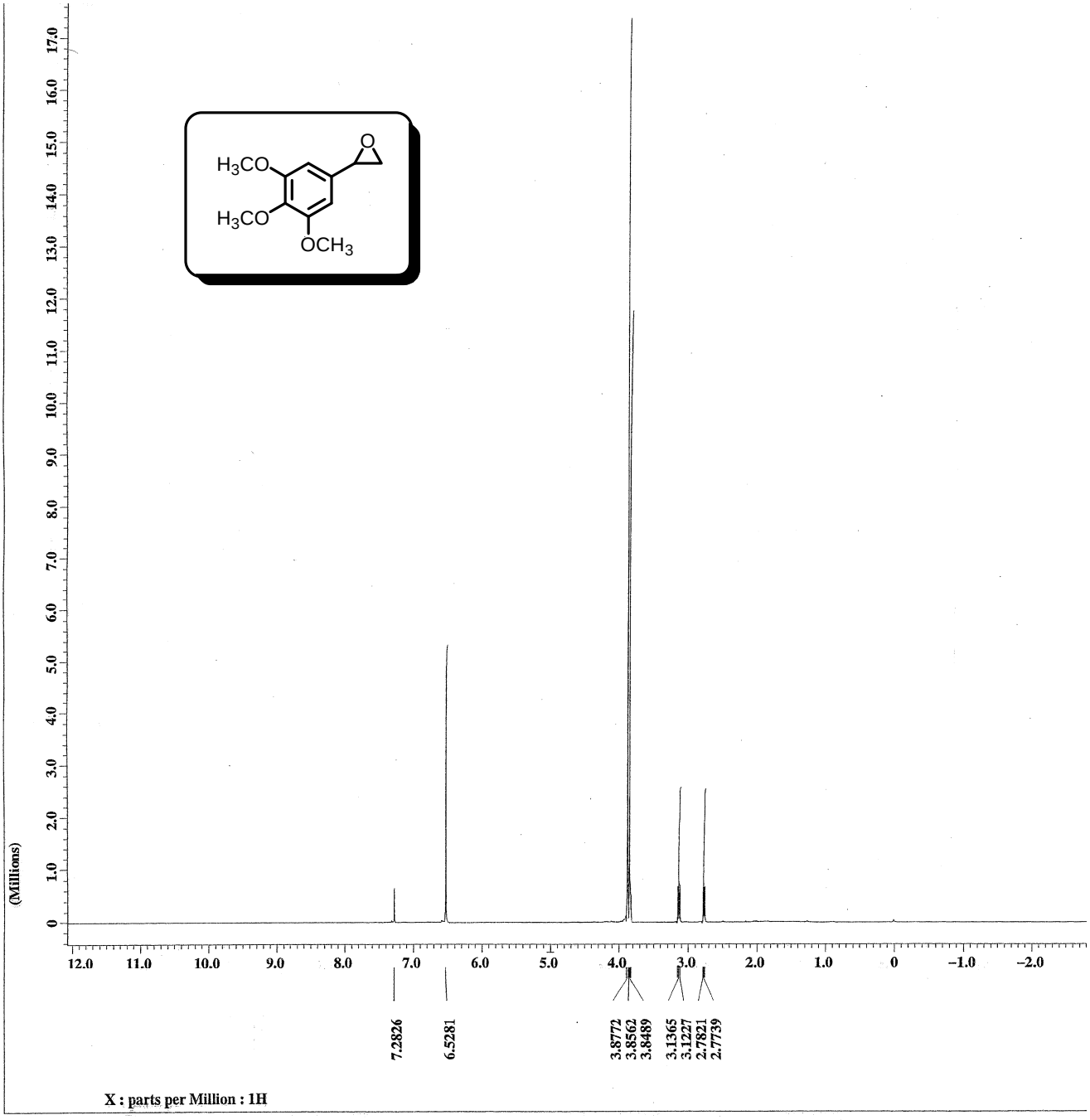
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20
155.9500
131.2156
130.5133
125.9787
111.9244
77.5254
77.1055
76.6856
56.4096
51.5696
51.1421
X : parts per Million : 13C

2-(3,4,5-Trimethoxyphenyl)oxirane



$C_{11}H_{14}O_4$
Mol. Wt.: 210.23

From the combination of 3,4,5-trimethoxybenzaldehyde (1.960 g, 10.00 mmol), cesium carbonate (6.520 g, 20.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (6.640 g, 20.00 mmol) in 50 mL of THF, 1.91 g (91% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (s, 2H), 3.84-3.78 (m, 10H), 3.14 (dd, J = 4.1, J = 4.1, 1H), 2.77 (dd, J = 2.7, J = 2.7, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 139.0, 137.7, 133.2, 106.5, 102.1, 60.8, 56.0, 52.5, 51.1; TLC R_f 0.33 (EtOAc/hexane, 1/9). The analytical data obtained is consistent with previously reported material.[5]


(Millions)
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9.0
8.0
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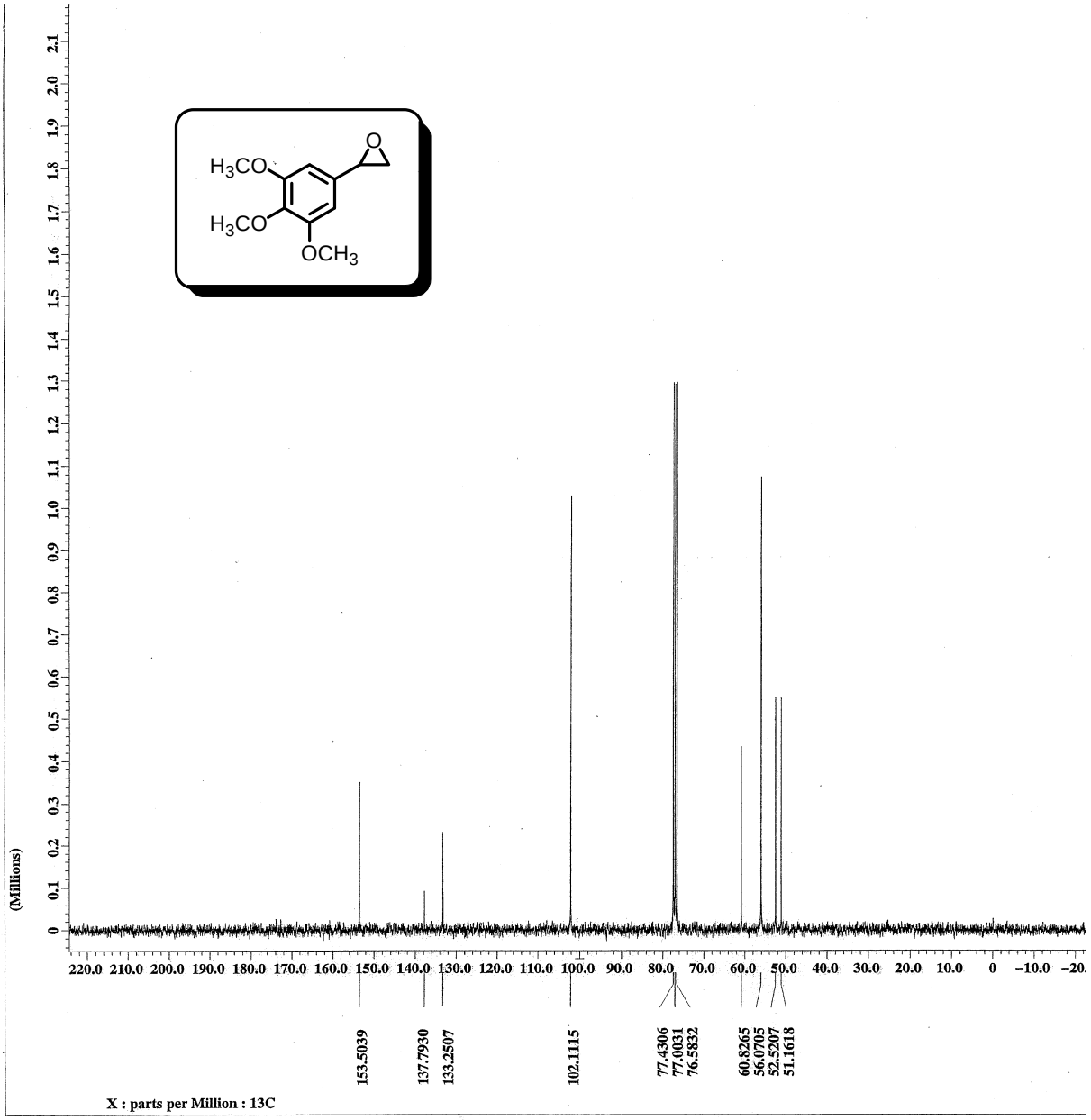
3.0
2.0
1.0
0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
H3CO
H3CO
OCH3
O
7.2826
6.5281
3.8772
3.8562
3.8489
3.1365
3.1227
2.7821
2.7739
X : parts per Million : 1H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H3CO
OCH3
O
(Millions)
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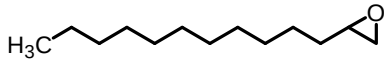
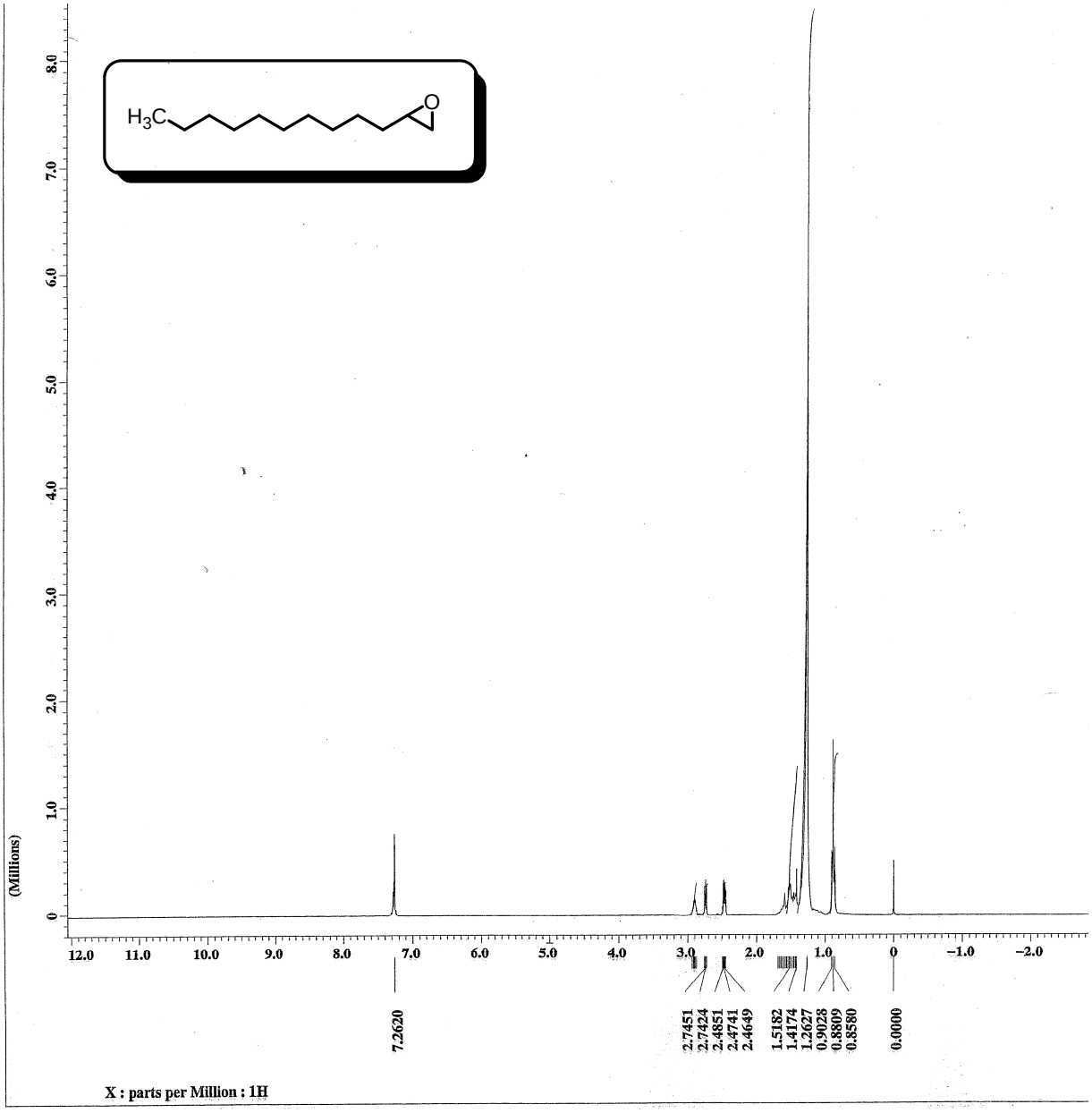
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.
153.5039
137.7930
133.2507
102.1115
77.4306
77.0031
76.5832
60.8265
56.0705
52.5207
51.1618
X : parts per Million : 13C

1,2-Epoxytridecane



$C_{13}H_{26}O$
Mol. Wt.: 198.34

From the combination of dodecylaldehyde (0.184 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5 mL of tetrahydrofuran, 0.174 g (95% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.93-2.87 (m, 1H), 2.74 (dd, J = 4.9, J = 4.9, 1H), 2.46 (dd, J = 2.7, J = 2.7, 1H), 1.66-1.41 (m, 20H), 0.88 (t, J = 6.8,1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9, 47.6, 32.4, 30.16, 30.0, 29.9, 29.8, 29.6, 26.5, 23.2, 16.36, 14.6,; TLC R_f 0.43 (EtOAc/hexane, 1/9). The analytical data obtained is consistent with previously reported material.[6]


H3C
O
(Millions)
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6.0
5.0
4.0
3.0
2.0
1.0
0
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10.0
9.0
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7.0
6.0
5.0
4.0
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2.0
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2.7424
2.4851
2.4741
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1.4174
1.2627
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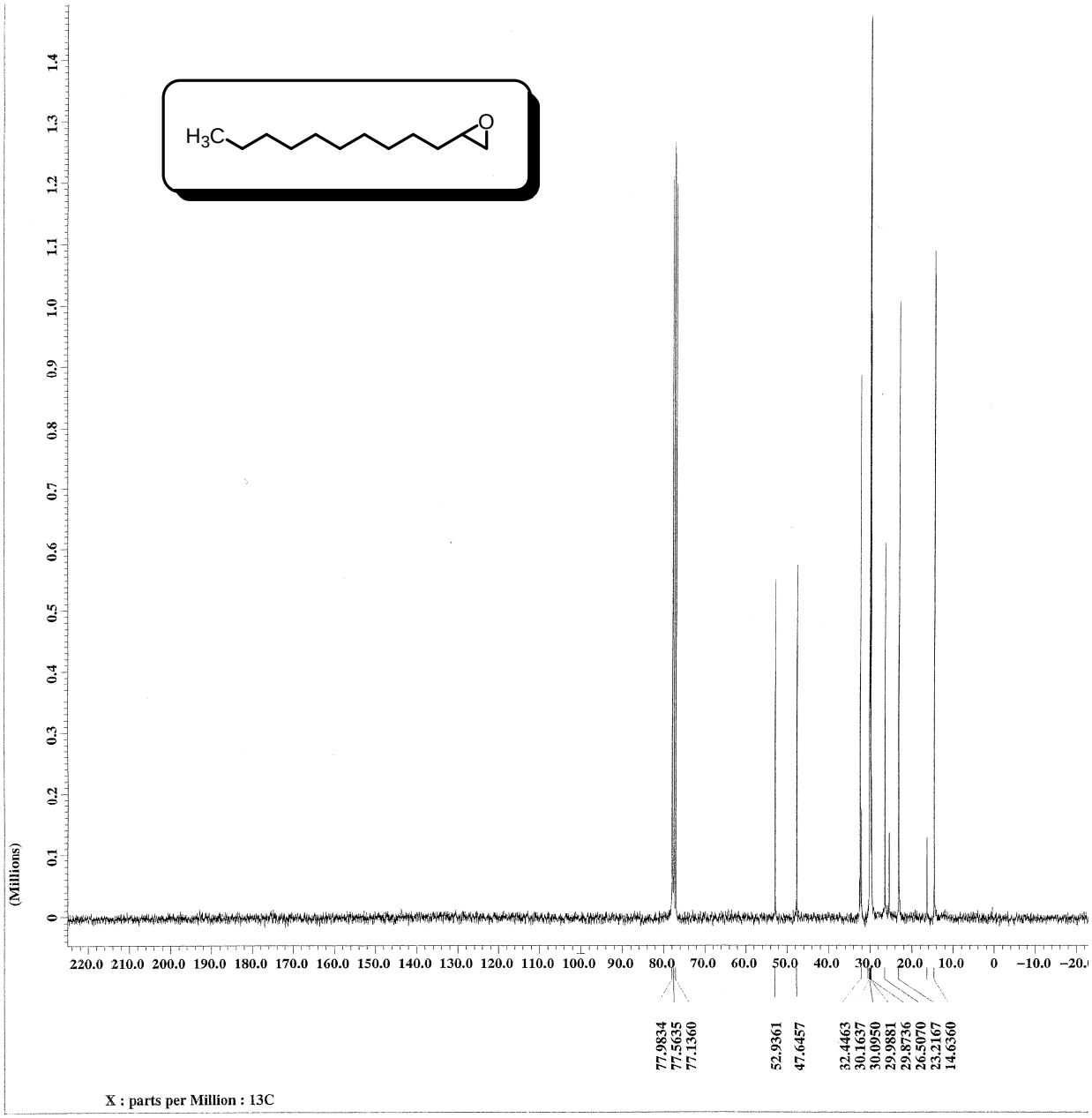
0.8580
0.0000
X : parts per Million : 1H


H3C
O
(Millions)
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.
77.9834
77.5635
77.1360
52.9361
47.6457
32.4463
30.1637
30.0950
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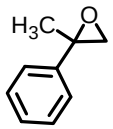
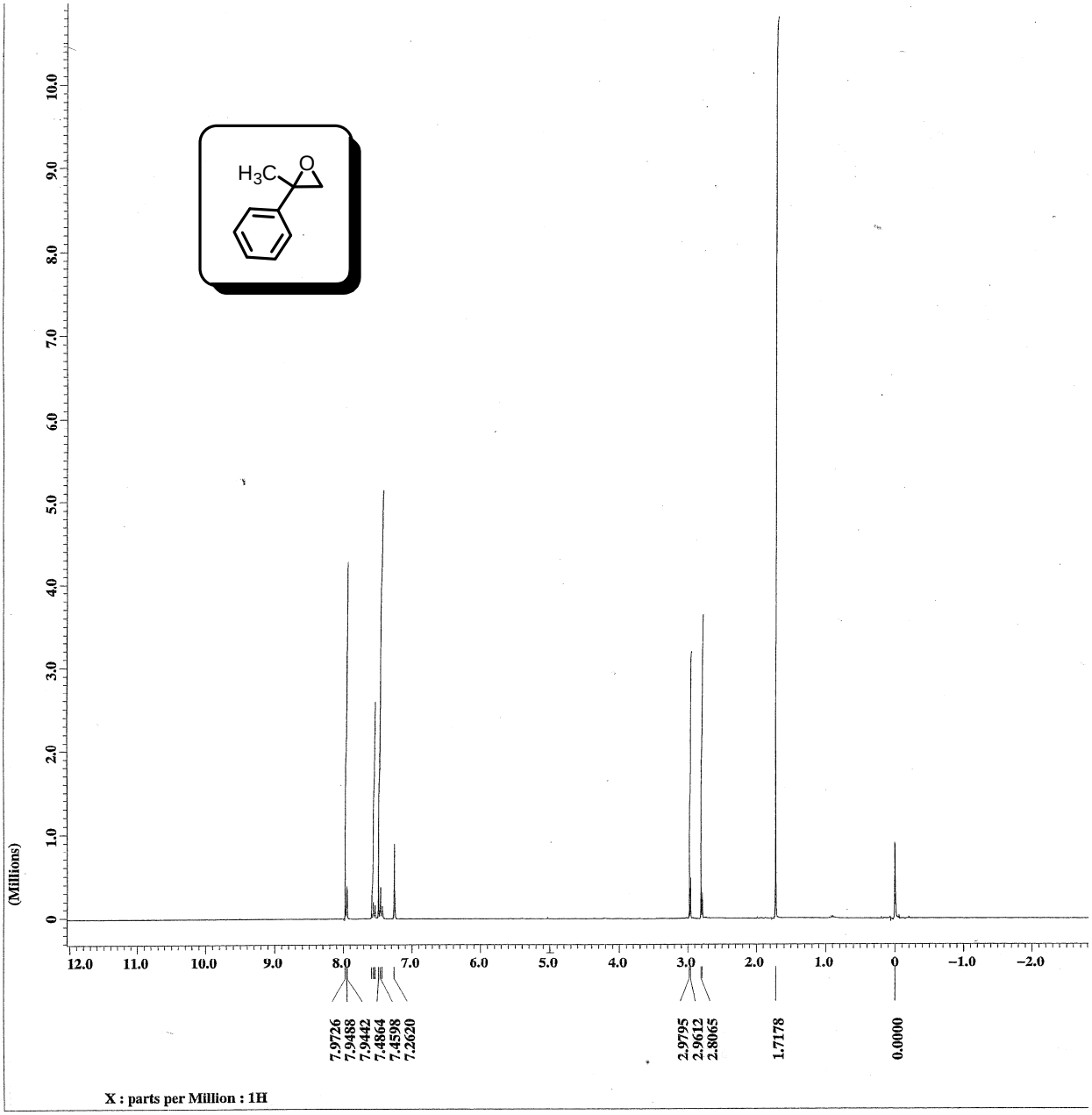
29.8736
26.5070
23.2167
14.6360
X : parts per Million : 13C

2-Methyl-2-phenyloxirane



$C_9H_{10}O$
Mol. Wt.: 134.18

From the combination of acetophenone (0.120 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and carboxymethylmethylphenylsulfonium trifluoromethanesulfonate (0.664 g, 2.00 mmol) in 5 mL of tetrahydrofuran, 0.103 g (86% yield) of the title compound was isolated as an oil after purification by column chromatography. Analytical data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d , *J* = 7.1, 2H), 7.55 (t, *J* = 7.6, 1H), 7.45(t, *J* = 7.6, 2H), 2.96 (d, *J* = 5.4,1H), 2.79 (d, *J* = 5.4,1H), 1.71 (s, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.9, 47.6, 32.4, 30.16, 30.0, 29.9, 29.8, 29.6, 26.5, 23.2, 16.36, 14.6,; TLC R_f 0.43 (EtOAc/hexane, 1/9); The analytical data obtained is consistent with previously reported material.[6]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O
(Millions)
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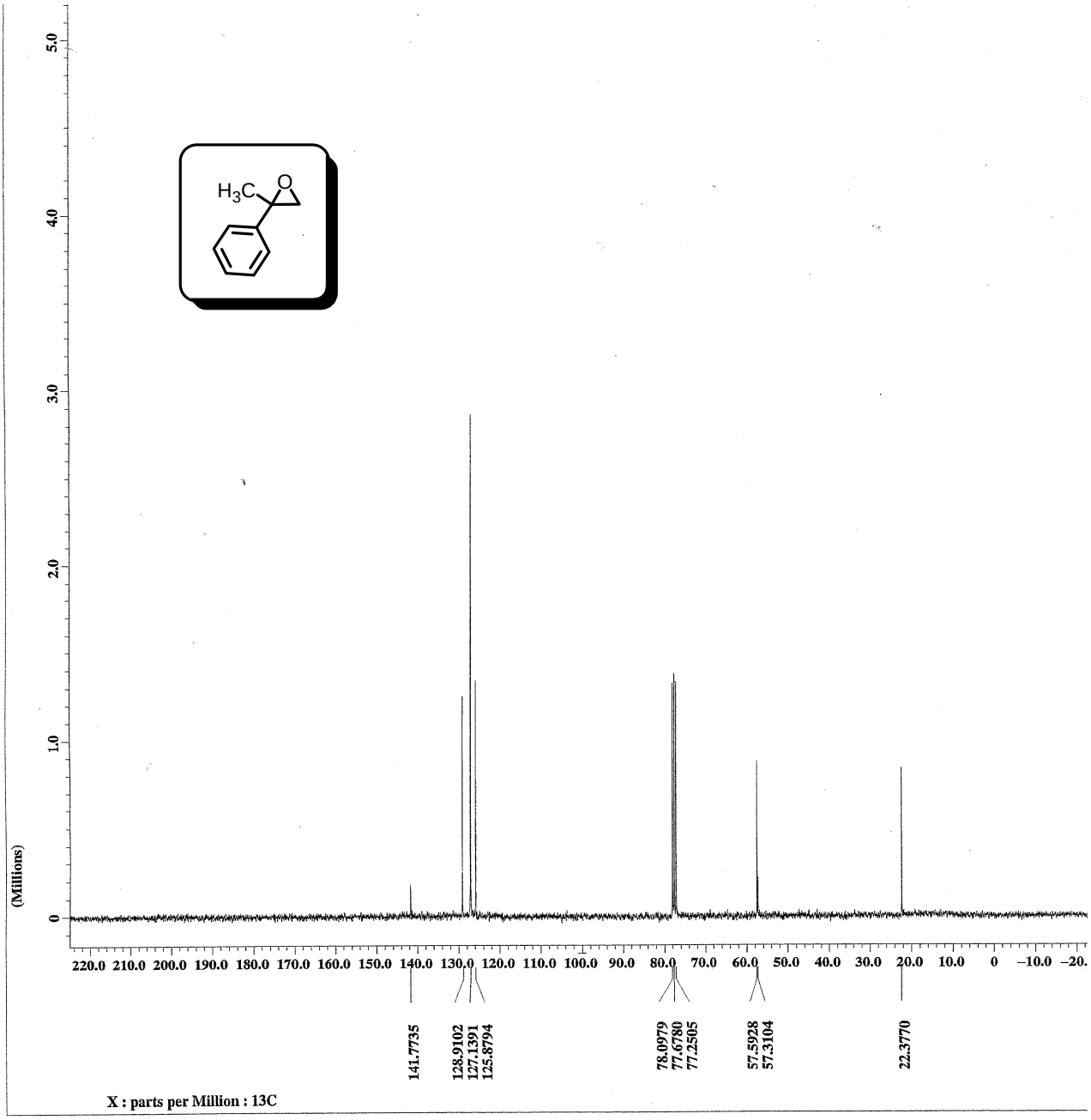
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
7.9726
7.9488
7.9442
7.4864
7.4598
7.2620
2.9795
2.9612
2.8065
1.7178
0.0000
X : parts per Million : 1H


(Millions)
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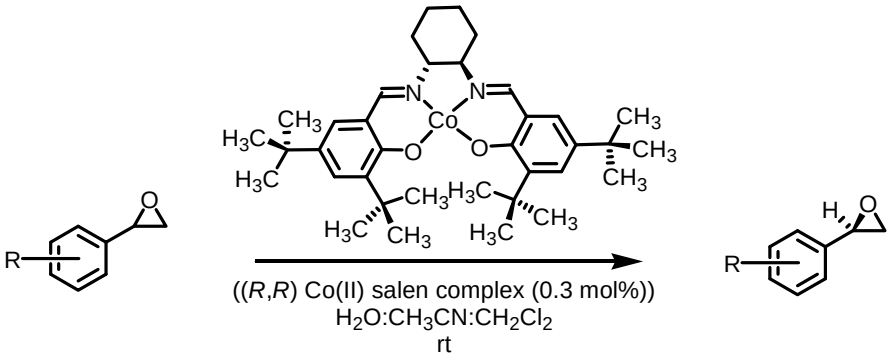
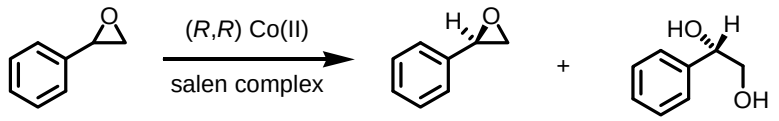
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.
141.7735
128.9102
127.1391
125.8794
78.0979
77.6780
77.2505
57.5928
57.3104
22.3770
X : parts per Million : 13C

Representative procedure for the kinetic resolution of aryl oxiranes



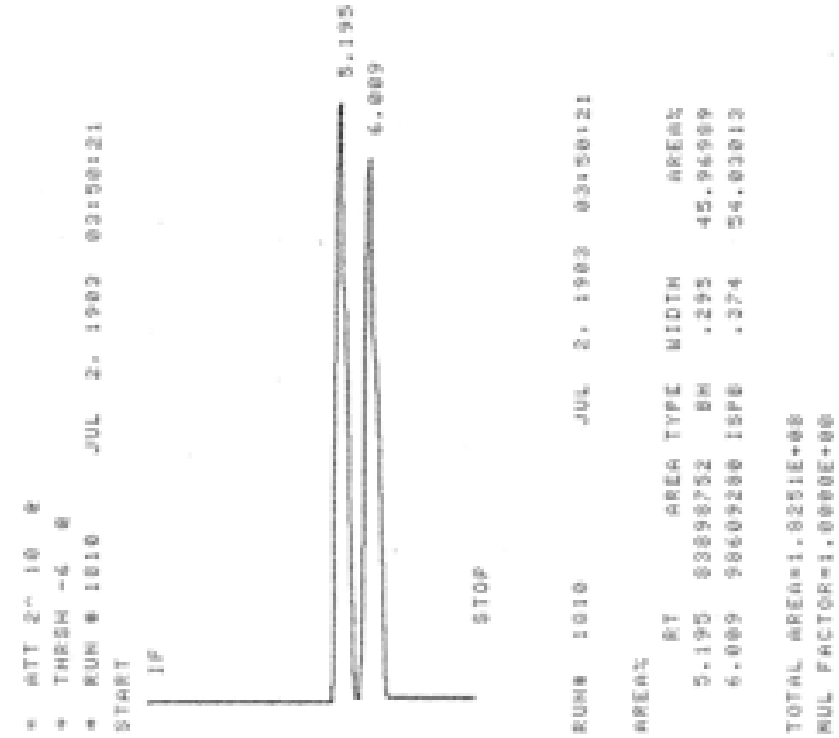
To a 25 mL round bottom flask with stir bar, was added oxirane (12.5 mmol), H_2O (7.5 mmol), a 1:1 mixture of CH_2Cl_2 and CH_3CN (0.25 ml), and the colbalt(II) salen complex (0.3 mol%). The reaction mixture was allowed to stir at room temperature. During that time, the reaction was monitored by ^1H NMR using as markers the diagnostic peaks associated with oxirane and diol. Upon observing 50% conversion, the reaction was judged as complete. Workup involved filtering the reaction mixture through a plug of anhydrous Mg_2SO_4. The resulting organic solution was then concentrated in vacuo. Prior to HPLC analysis the reaction mixture was purified by column chromatography using neutral alumina (hexanes). All HPLC analyses were performed using a (*R*,*R*)-Whelk-O 1 column (25 cm x 4.6 mm, 5μm). The mobile phase was hexanes:IPA at a flow rate ranging between 0.9 mL/min to 1.0 mL/min with a detector wavelength of 220nm. Prior to and post each HPLC analysis, runs using chiral racemic aryl oxiranes were performed. In addition to HPLC analyses, optical rotations of chiral non-racemic material were obtained and compared to published values when possible.

(2R)-2-Phenyloxirane

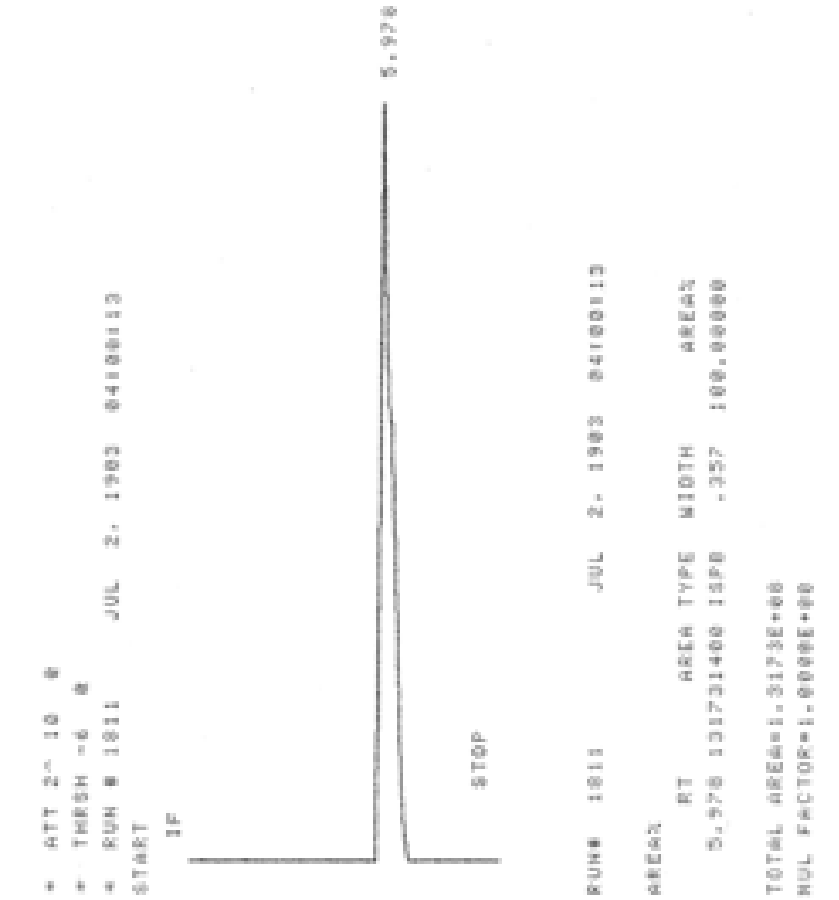


To a mixture consisting of chiral racemic 2-phenyloxirane (1.5 g, 12.5 mmol), H_2O (0.14 ml, 7.5 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.25ml) was added the colbalt(II) salen complex (0.020 g (*R*,*R*)). While monitoring by ^1H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.69 g of enantiopure (>99%) (2*R*)-2-phenyloxirane was obtained (46% recovery). Supplemental data: HPLC (Regis (*R*,*R*)-Whelko-O1 column (hexanes:IPA (99:1), 1.0 mL/min, and λ = 220nm) t_R (minor) 5.19 min *(S)*, t_R (major) 6.00 min *(R)*. Specific rotation of oxirane $[\alpha]_D^{21}$ -24 (*c* 1.00, $CHCl_3$), [literature $[\alpha]_D^{31}$ -23.7 (*c* 1.01, $CHCl_3$) for 99% ee][1] and specific rotation of diol $[\alpha]_D^{21}$ +67 (*c* 1.00, $CHCl_3$), [literature $[\alpha]_D^{31}$ +67 (*c* 1.00, $CHCl_3$) for 99% ee (commercial)].

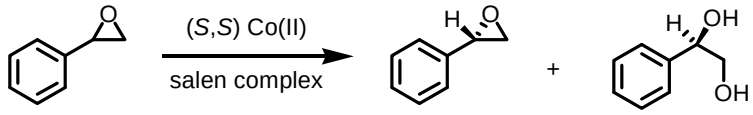
Racemic



Resolved

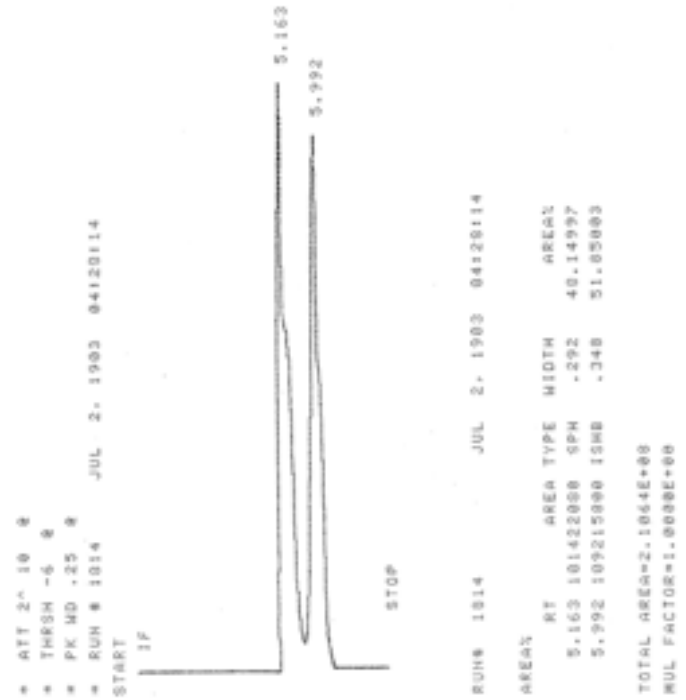


(2S)-2-Phenyloxirane

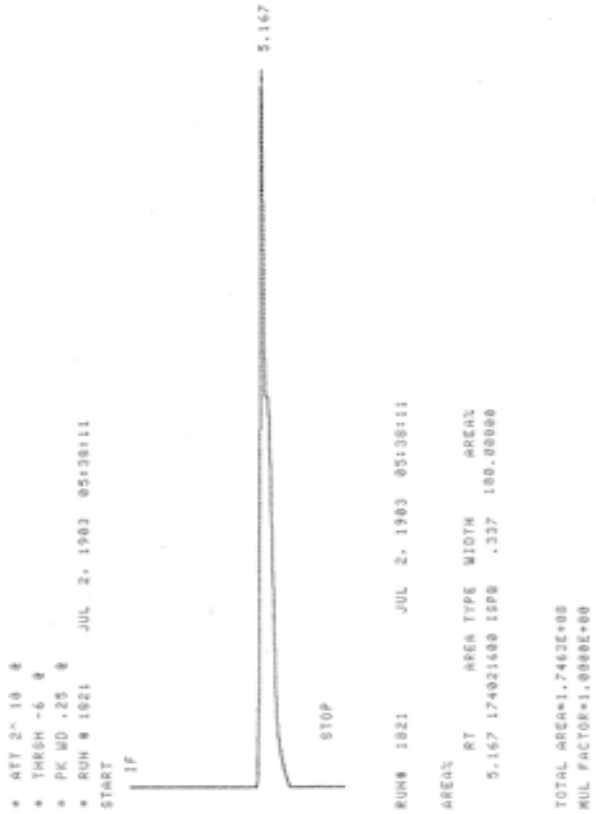


To a mixture consisting of chiral racemic 2-phenyloxirane (1.5 g, 12.5 mmol), H_2O (0.14 ml, 7.5 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.25ml) was added the colbalt(II) salen complex (0.020 g (*S*,*S*)). While monitoring by ^1H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.688 g of enantiopure (>99%) (2*S*)-2-phenyloxirane was obtained (47% recovery). Supplemental data: HPLC (Regis (*R*,*R*)-Whelko-O1 column (hexanes:IPA (99:1), 1.0 mL/min, and λ = 220nm) t_R (major) 5.19 min *(S)*, t_R (minor) 6.00 min *(R)*. Specific rotation $[\alpha]_D^{21}$ +24 (*c* 1.00, $CHCl_3$), [literature $[\alpha]_D^{22}$ +24.1 (*c* 1.67, $CHCl_3$) for 99% ee].[7]

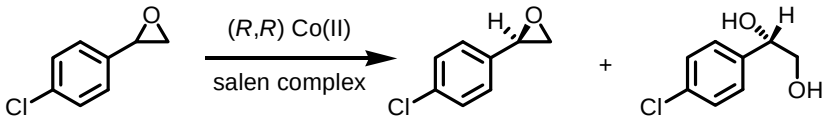
Racemic



Resolved

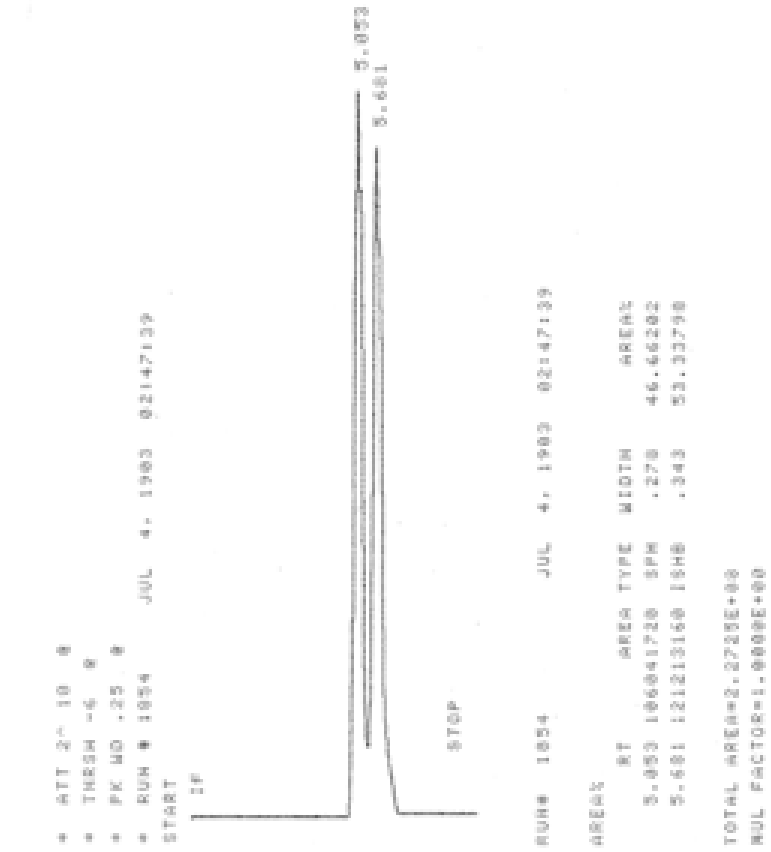


(2R)-2-(4-chlorophenyl)oxirane

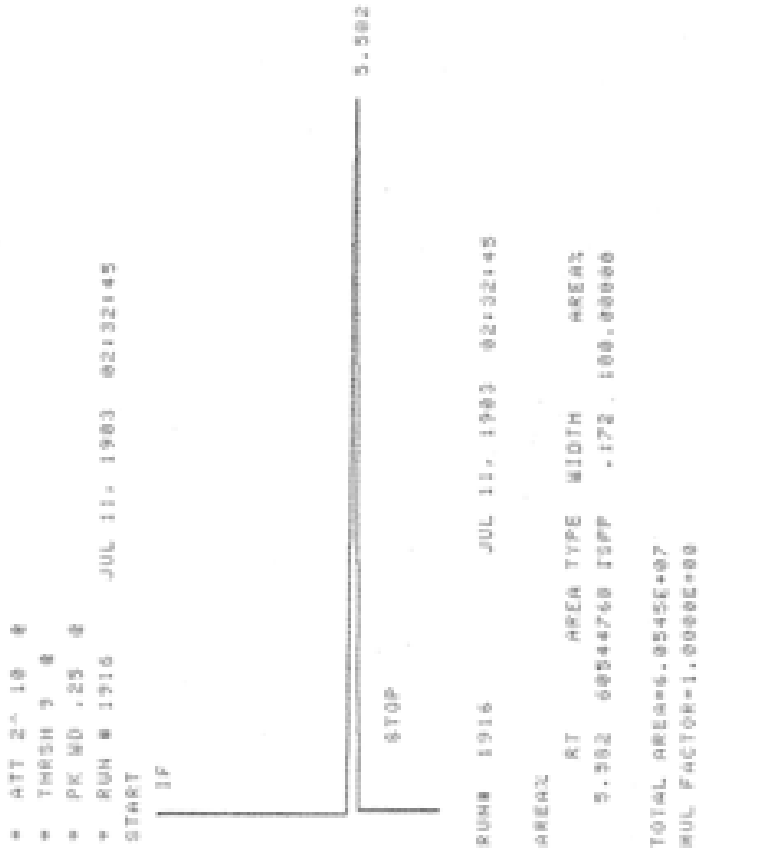


To a mixture consisting of chiral racemic 2-(4-chlorophenyl)oxirane (1.5 g, 12.5 mmol), H_2O (0.14 ml, 7.5 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.25ml) was added the colbalt(II) salen complex (0.020 g (*R*,*R*)). While monitoring by ^{1}H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.850 g of enantiopure (>99%) (2*R*)-2-(4-chlorophenyl)oxirane was obtained (45% recovery). Supplemental data: HPLC (Regis (*R*,*R*)-Whelko-O1 column (hexanes:IPA (99:1), 0.8 mL/min, and λ = 220nm) t_R (minor) 5.05 min *(S)*, t_R (major) 5.60 min *(R)*. Specific rotation $[\alpha]_D^{21}$ -17.2 (*c* 1.0, $CHCl_3$), [literature value for enantiomer $[\alpha]_D$ +19.3 (*c* 1.16, $CHCl_3$) for 99% ee].[2]

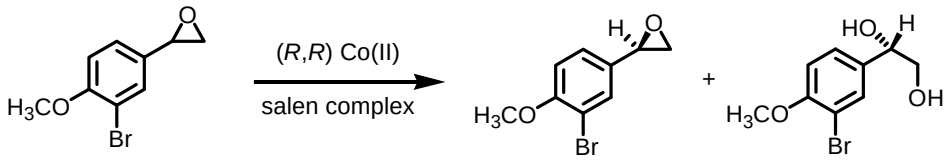
Racemic



Resolve

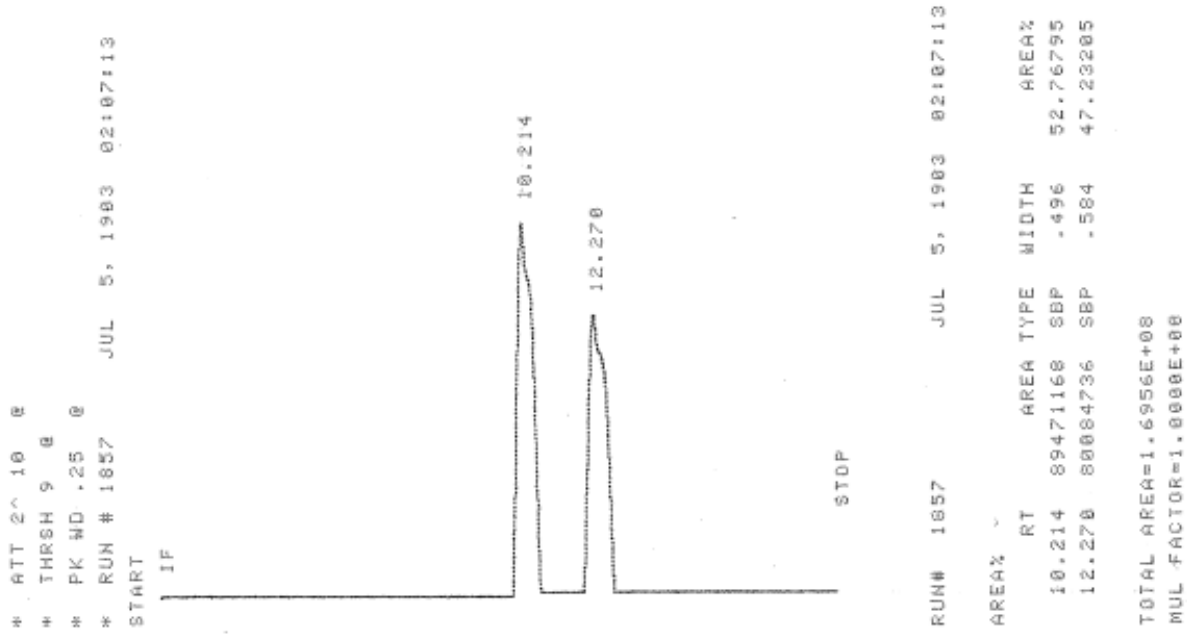


2-(3-bromo-4-methoxyphenyl)oxirane

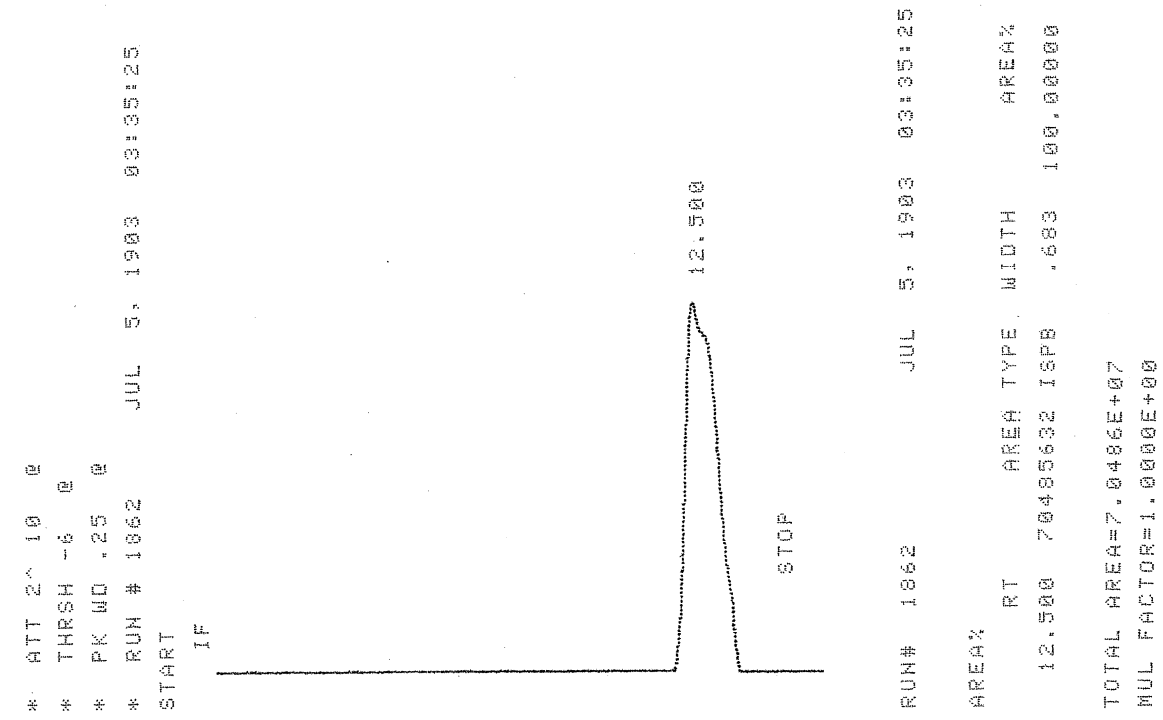


To a mixture consisting of chiral racemic 2-(3-bromo-4-methoxyphenyl)oxirane (1.4 g, 6.0 mmol), H_2O (0.06 ml, 3.6 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.12ml) was added the colbalt(II) salen complex (0.010 g (*R*,*R*)). While monitoring by ^1H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.576 g of enantiopure (>99%) 2-(3-bromo-4-methoxyphenyl)oxirane was obtained (42% recovery). Supplemental data: HPLC (Regis (*R*,*R*)-Whelko-O1 column (hexanes:IPA (99:1), 1.0 mL/min, and λ = 220nm) t_R (minor) 10.21 min, t_R (major) 12.27 min. Specific rotation $[\alpha]_D^{21}$ –9.8 (*c* 0.1, $CHCl_3$).

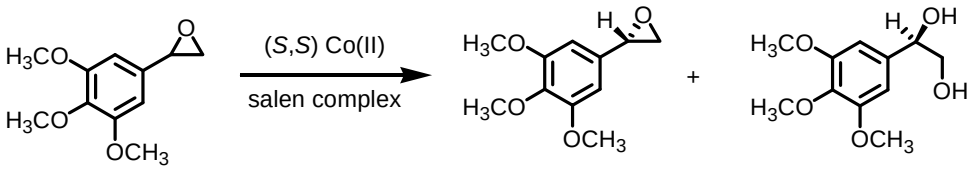
Racemic



Resolved

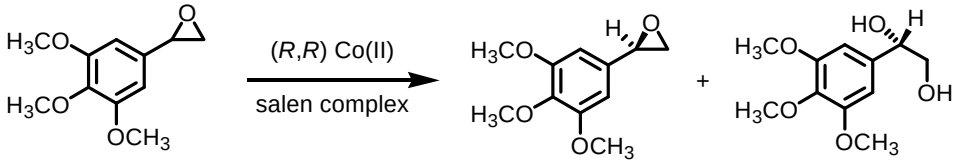


(2S)-2-(3,4,5-trimethoxyphenyl)oxirane



To a mixture consisting of chiral racemic 2-(3,4,5-trimethoxyphenyl)oxirane (1.3 g, 6.25 mmol), H_2O (0.07 ml, 3.75 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.12ml) was added the colbalt(II) salen complex (0.010 g (*S*,*S*)). While monitoring by ^{1}H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.383 g of enantiopure (>99%) (2*S*)-2-(3,4,5-trimethoxyphenyl)oxirane was obtained (43% recovery). Supplemental data: Efforts to resolve the enantiomers using chiral HPLC were unsuccessful. Specific rotation $[\alpha]_D^{24}$ +13.8 (*c* 1.80, $CHCl_3$), [literature $[\alpha]_D$ +15.5 (*c* 1.80, $CHCl_3$)].[5]

(2R)-2-(3,4,5-trimethoxyphenyl)oxirane



To a mixture consisting of chiral racemic 2-(3,4,5-trimethoxyphenyl)oxirane (0.65 g, 3.1 mmol), H_2O (0.04 ml, 1.32 mmol) and 1:1 CH_2Cl_2:CH_3CN (0.06 ml) was added the colbalt(II) salen complex (0.005 g (*R*,*R*)). While monitoring by ^1H NMR, the reaction mixture was allowed to stir at room temperature. After 6 days, the reaction was judged as complete. After purification of the resolved oxirane by column chromatography using neutral alumina, 0.273 g of highly enriched (2*R*)-2-(3,4,5-trimethoxyphenyl)oxirane was obtained (42% recovery). Supplemental data: Efforts to resolve the enantiomers using chiral HPLC were unsuccessful. Specific rotation $[\alpha]_D^{24}$ -9.8 (*c* 0.1, $CHCl_3$).

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