Supporting Information

Highly Stereoselective Methylene Transfers onto Butanediacetal-Protected Chiral Non-Racemic Sulfinyl Imines Using S-Ylide Technology

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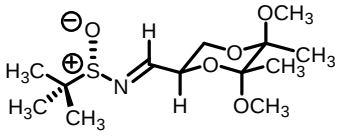
General Experimental Considerations

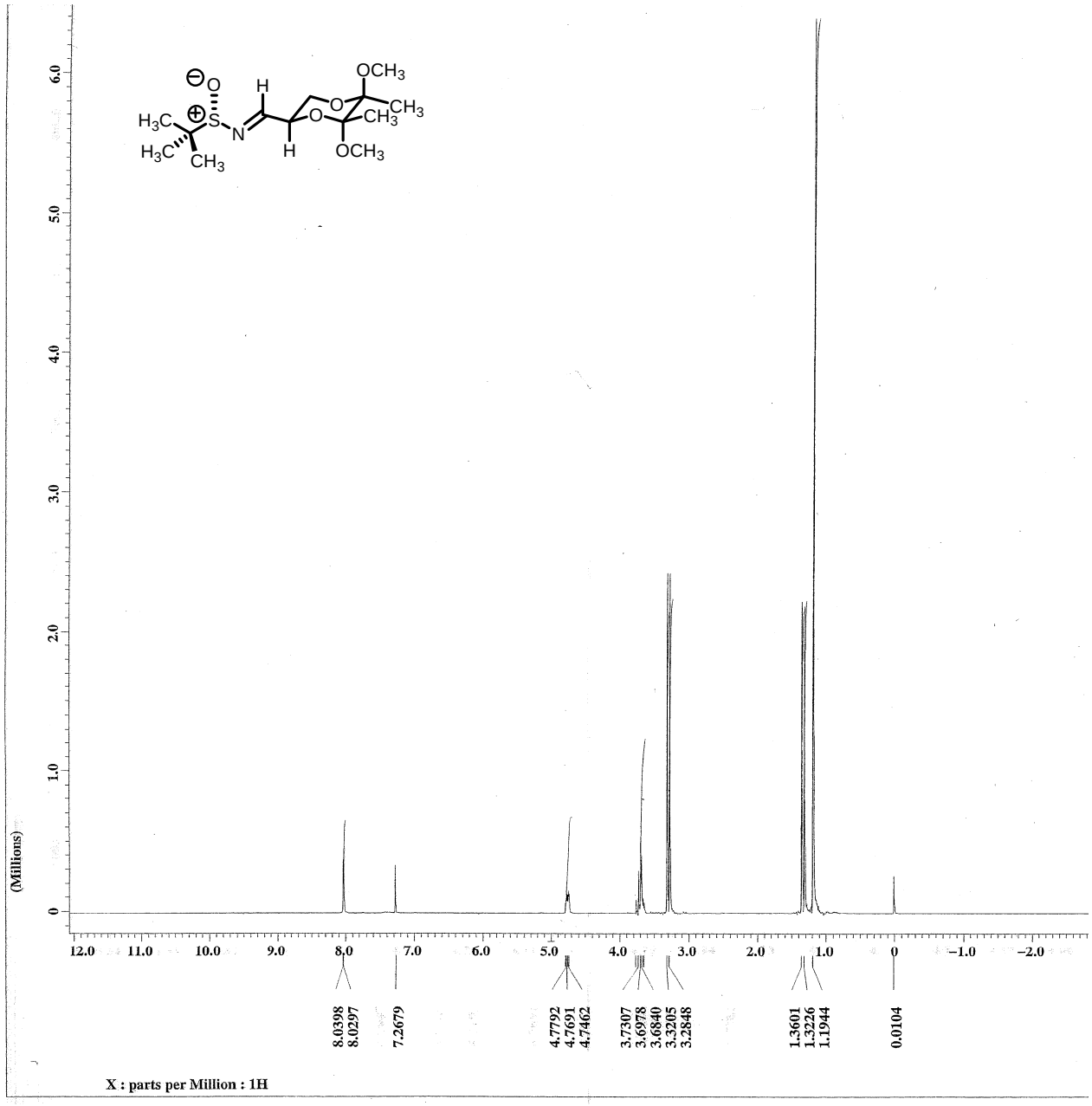
^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained as solutions in $CDCl_3$. Chemical shifts were reported in parts per million (ppm, δ) and referenced to δ 7.27 (^{1}H NMR) and δ 77.00 (^{13}C NMR) when using $CDCl_3$. Infrared spectra were recorded using a JASCO FT/IR-4100 and were reported in wavenumbers (cm^{-1}). Optical rotations were recorded on a JASCO P-1020 digital polarimeter and are reported as follows: $[\alpha]^{T}$ (c = g/100mL, solvent). TLC analyses were performed on Whatman flexible aluminium backed TLC plates with a fluorescent indicator. Detection was conducted by UV absorption (254 nm) and charring with 10% KMnO4 in water. Except for the aziridines and oxiranes, the purification of all materials by column chromatography was performed using silica gel. All chromatographic separations of aziridines and oxiranes were performed using neutral alumina. All chemicals used for synthetic procedures were reagent grade or better. Solutions were concentrated in vacuo with a rotary evaporator and the residue was purified by the specified procedure.

Representative procedure for the preparation of butanediacetal-protected sulfinyl imines[1]

To a 50 ml round-bottomed flask equipped with a stir bar and septum was added aldehyde (1.5 equiv) as a solution in anhydrous dichloromethane (3.0 mL). Next added was anhydrous copper sulfate (2.0 equiv) and 2-methyl-2-propane sulfinamide (1.0 equiv). The reaction mixture was allowed to stir under an argon atmosphere for a period of 24h at which time the reaction was monitored by TLC until complete. When complete as judged by TLC analysis, the reaction mixture was filtered through a Celite plug and rinsed with dichloromethane. After concentration of the filtrate in vacuo, the crude reaction mixture was immediately purified by silica gel chromatography (radial chromatography) using a gradient eluent system of hexanes and EtOAc (9:1) to afford analytically pure *N*-sulfinyl imine.



[S(S), N(E)]-2-methyl-N-[((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)methylene]-2-propanesulfinamide (4) From the combination of 0.242 g (2 mmol) (*S*)-(-)-2-methyl-2-propane sulfinamide, 0.612 g (3 mmol) (2*R*,5*R*,6*R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde and 0.640 g (4 mmol) $CuSO_4$, 0.758 g (82%) of the title compound was isolated as an white solid after silica gel chromatography. Analytical data: $[\alpha]_D^{25}$ +87.5 (*c* 1.0, $CHCl_3$); mp 107-109°C; IR (cm^{-1}) 3090, 2952, 1628, 1455, 1210, 1089; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 3.0, 1H), 4.79-4.73 (m, 1H), 3.76-3.64 (m, 2H), 3.32 (s, 3H), 3.28 (s, 3H), 1.36 (s, 3H), 1.32, (s, 3H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 99.6, 98.2, 69.6, 60.2, 56.8, 48.3, 48.1, 22.4, 17.7, 17.6; TLC R_f 0.38 (EtOAc/hexane, 2/8); HRMS (ESI) calculated mass 308.1532 ($C_{13}H_{25}NO_5S$ (M+H)); found 308.1537.


(Millions)
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4.0
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
8.0398
8.0297
7.2679
4.7792
4.7691
4.7462
3.7307
3.6978
3.6840
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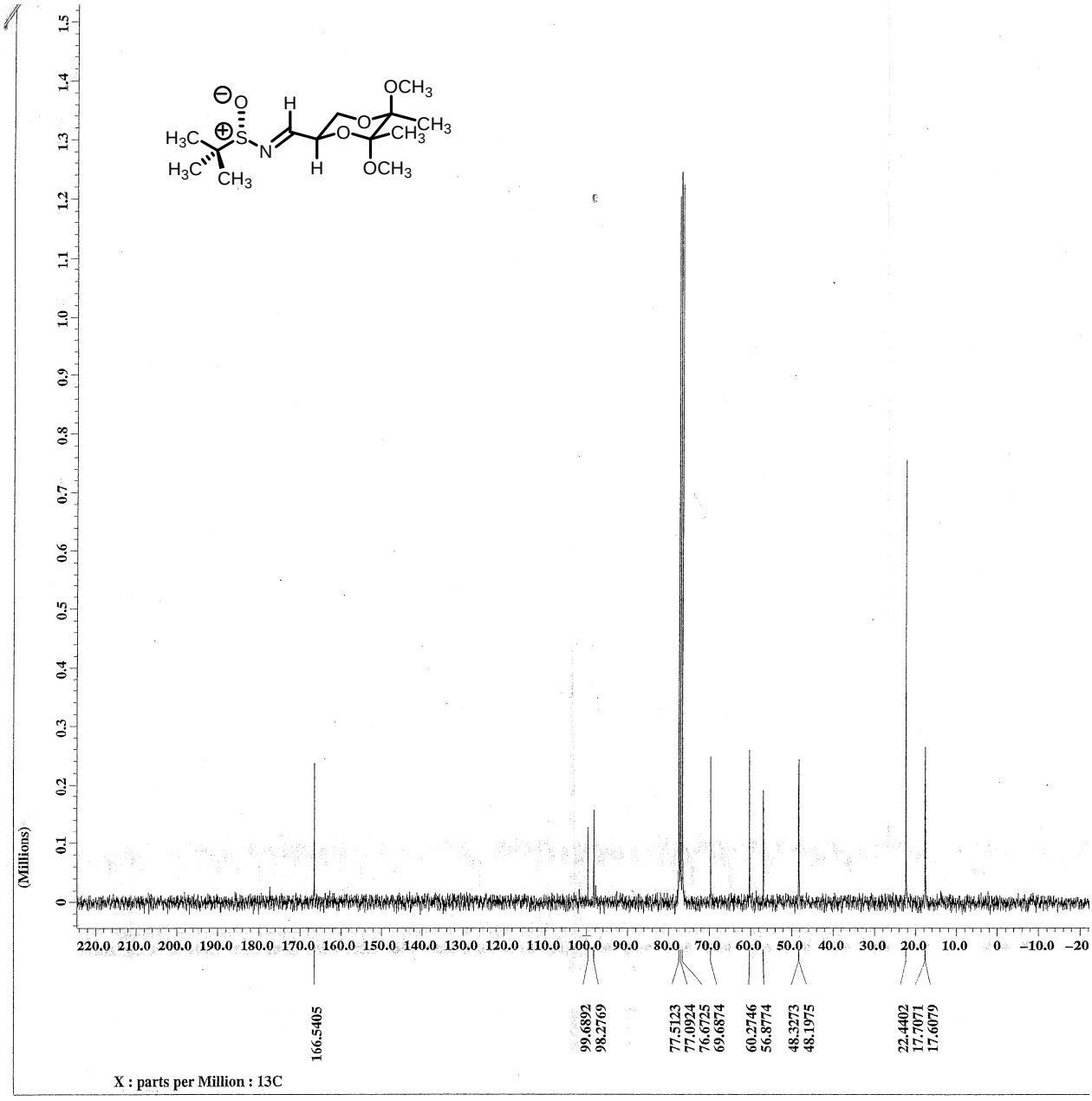
1.1944
0.0104
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C
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98.2769
77.5123
77.0924
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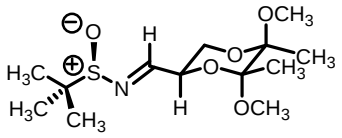
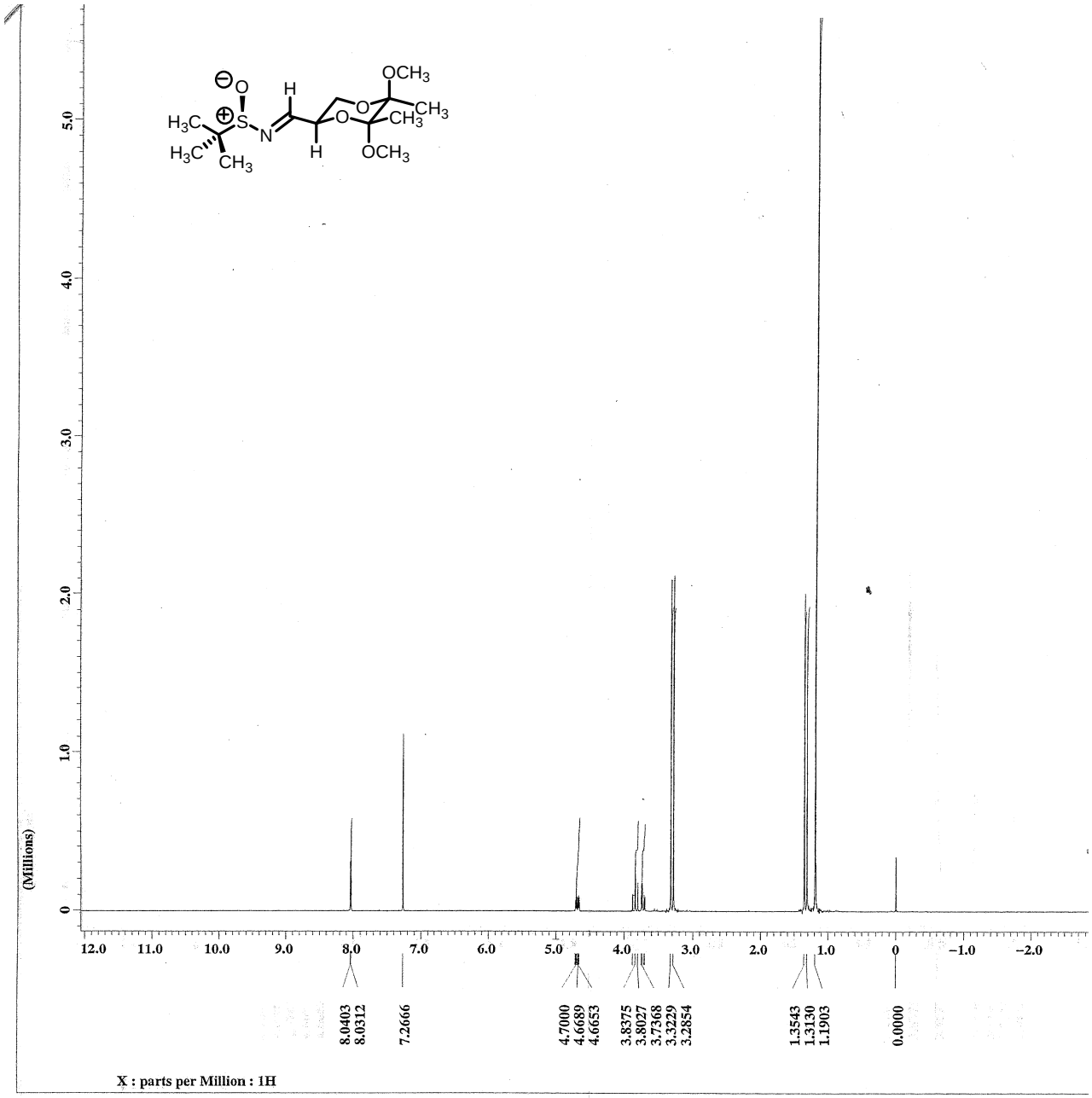
56.8774
48.3273
48.1975
22.4402
17.7071
17.6079



[S(R), N(E)]-2-methyl-N-[((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)methylene]-2-propanesulfinamide (5) From the combination of 0.242 g (2 mmol) (*R*)-(-)-2-methyl-2-propane sulfinamide, 0.612 g (3 mmol) (2*R*,5*R*,6*R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde and 0.640 g (4 mmol) $CuSO_4$, 0.465 g (74%) of the title compound was isolated as an white solid after silica gel chromatography. Analytical data: $[\alpha]_D^{25}$ -274.5 (*c* 1.0, $CHCl_3$); mp 113-115°C; IR (cm^{-1}) 2981, 2951, 1624, 1456, 1213, 1134, 1087; ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.7, 1H), 4.70-4.66 (m, 1H), 3.87-3.80 (m, 1H), 3.72-3.69 (m, 1H), 3.32 (s, 3H), 3.28 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 99.2, 98.2, 68.8, 60.1, 57.0, 48.2, 48.1, 22.3, 17.6, 17.5; TLC R_f 0.38 (EtOAc/hexane, 2/8); HRMS (ESI) calculated mass 308.1532 ($C_{13}H_{25}NO_5S$ (M+H)); found 308.1523.


(Millions)
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2.0
1.0
0
12.0
11.0
10.0
9.0
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
8.0403
8.0312
7.2666
4.7000
4.6689
4.6653
3.8375
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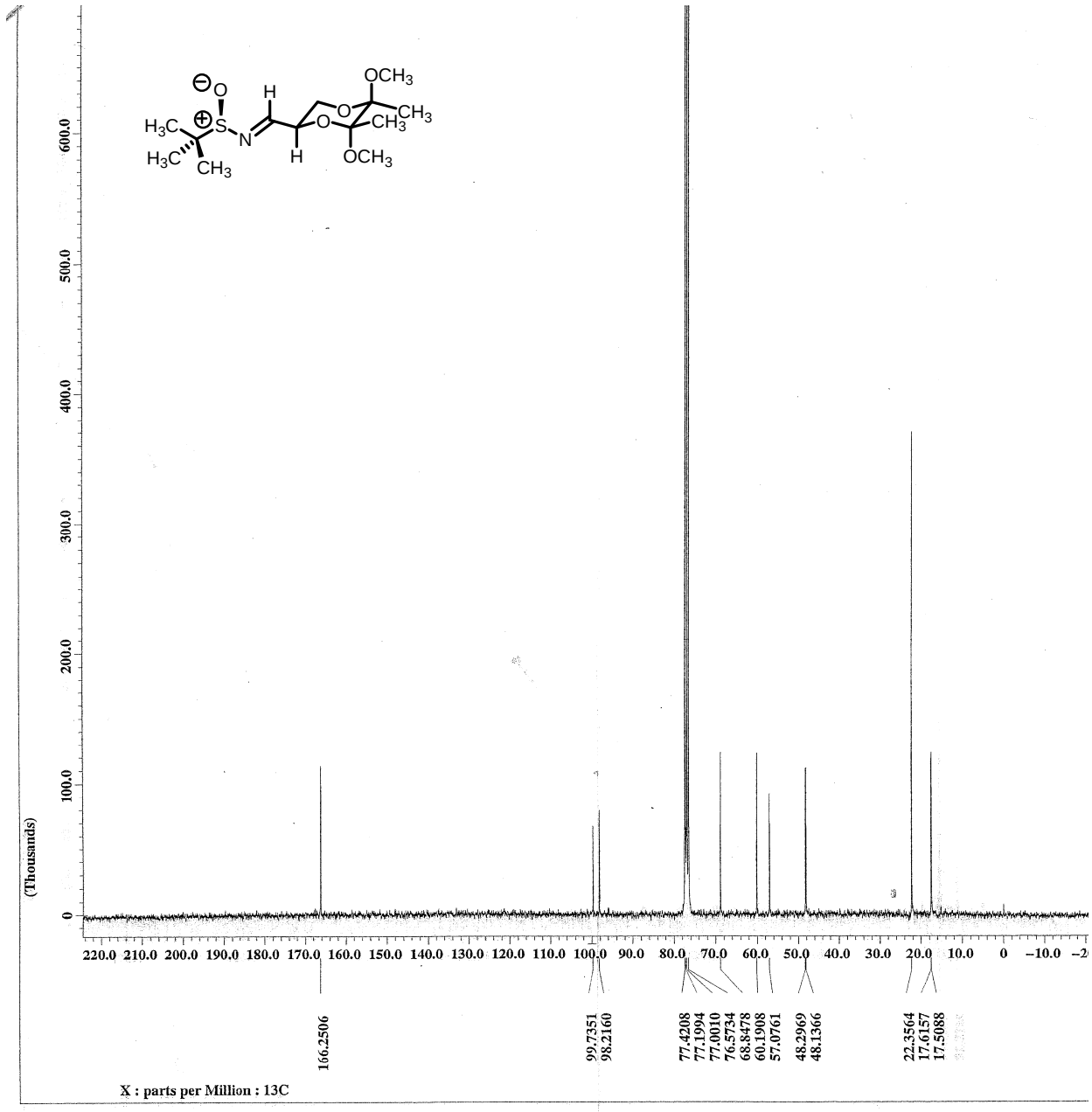
1.1903
0.0000
X : parts per Million : 1H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500.0
400.0
300.0
200.0
100.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0
166.2506
99.7351
98.2160
77.4208
77.1994
77.0010
76.5734
68.8478
60.1908
57.0761
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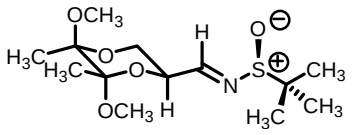
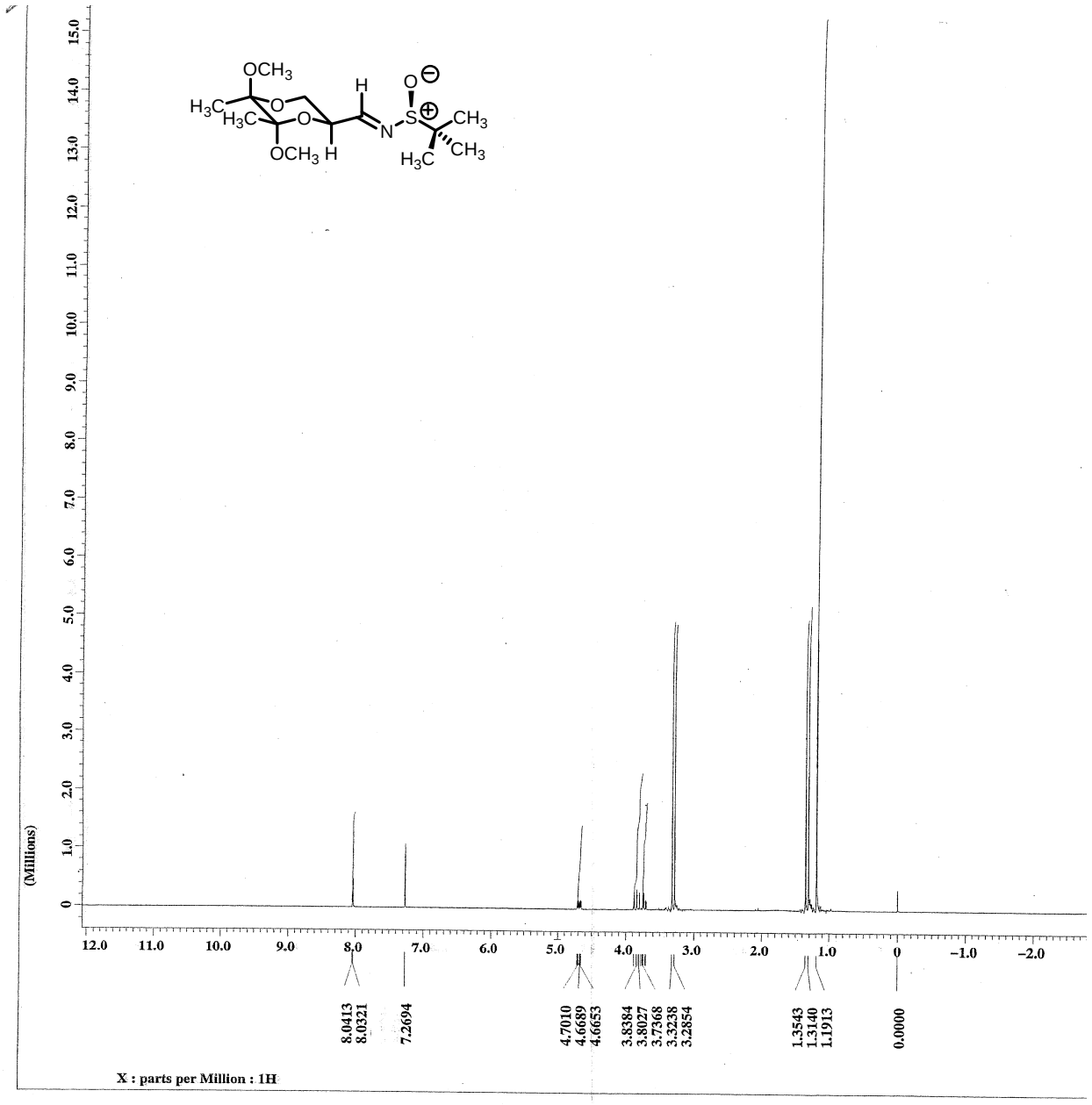
17.5088
X : parts per Million : 13C



[S(S), N(E)]-2-methyl-N-[((2R,5S,6S)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)methylene]-2-propanesulfinamide (ent-5) From the combination of 0.242 g (2 mmol) (*S*)-(-)-2-methyl-2-propane sulfinamide, 0.612 g (3 mmol) (2*S*,5*S*,6*S*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde and 0.640 g (4 mmol) $CuSO_4$, 0.440 g (71%) of the title compound was isolated as an white solid after silica gel chromatography. Analytical data: $[\alpha]_D^{25}$ +275.0 (*c* 1.0, $CHCl_3$); mp 112-113°C, IR (cm^{-1}) 2982, 2944, 1625, 1456, 1267, 1087; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.7, 1H), 4.71-4.65 (m, 1H), 3.87-3.80 (m, 1H), 3.74-3.69 (m, 1H), 3.32 (s, 3H), 3.28 (s, 3H), 1.35 (s, 3H), 1.31 (s, 3H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 99.7, 98.2, 68.8, 60.2, 57.0, 48.3, 48.1, 22.3, 17.6, 17.5; TLC R_f 0.40 (EtOAc/hexane, 2/8). HRMS (ESI) calculated mass 308.1532 ($C_{13}H_{25}NO_5S$ (M+H)); found 308.1537.


OCH3
H
O
H3C
H3C
O
O
S
CH3
N
OCH3
H
H3C
CH3
(Millions)
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14.0
13.0
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
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
8.0413
8.0321
7.2694
4.7010
4.6689
4.6653
3.8384
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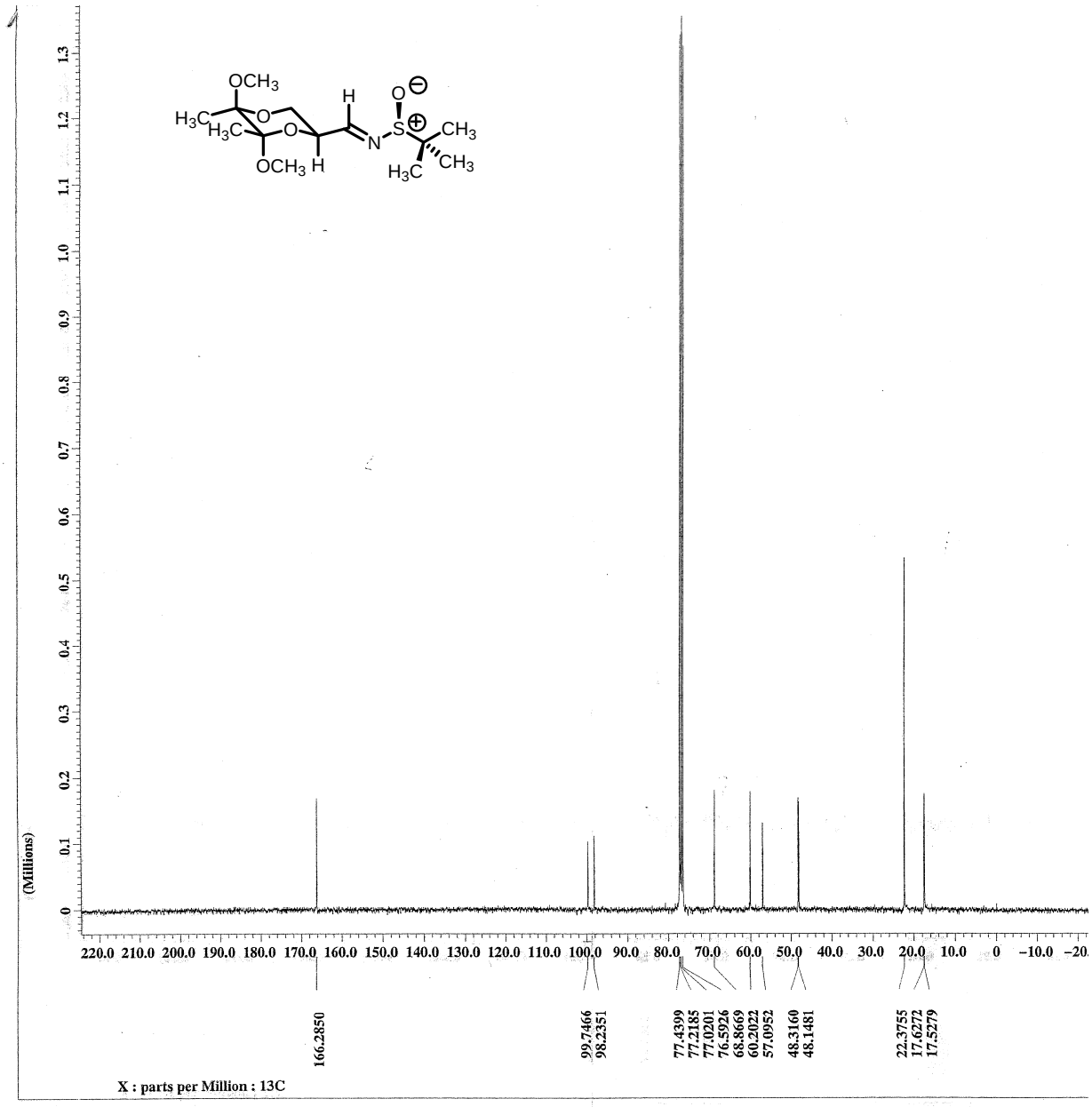
3.2854
1.3543
1.3140
1.1913
0.0000
X : parts per Million : 1H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H
O
H3C
H3C
O
O
N
S
CH3
OCH3
H
H3C
CH3
(Millions)
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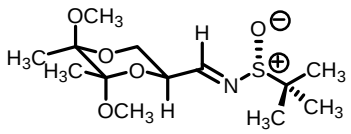
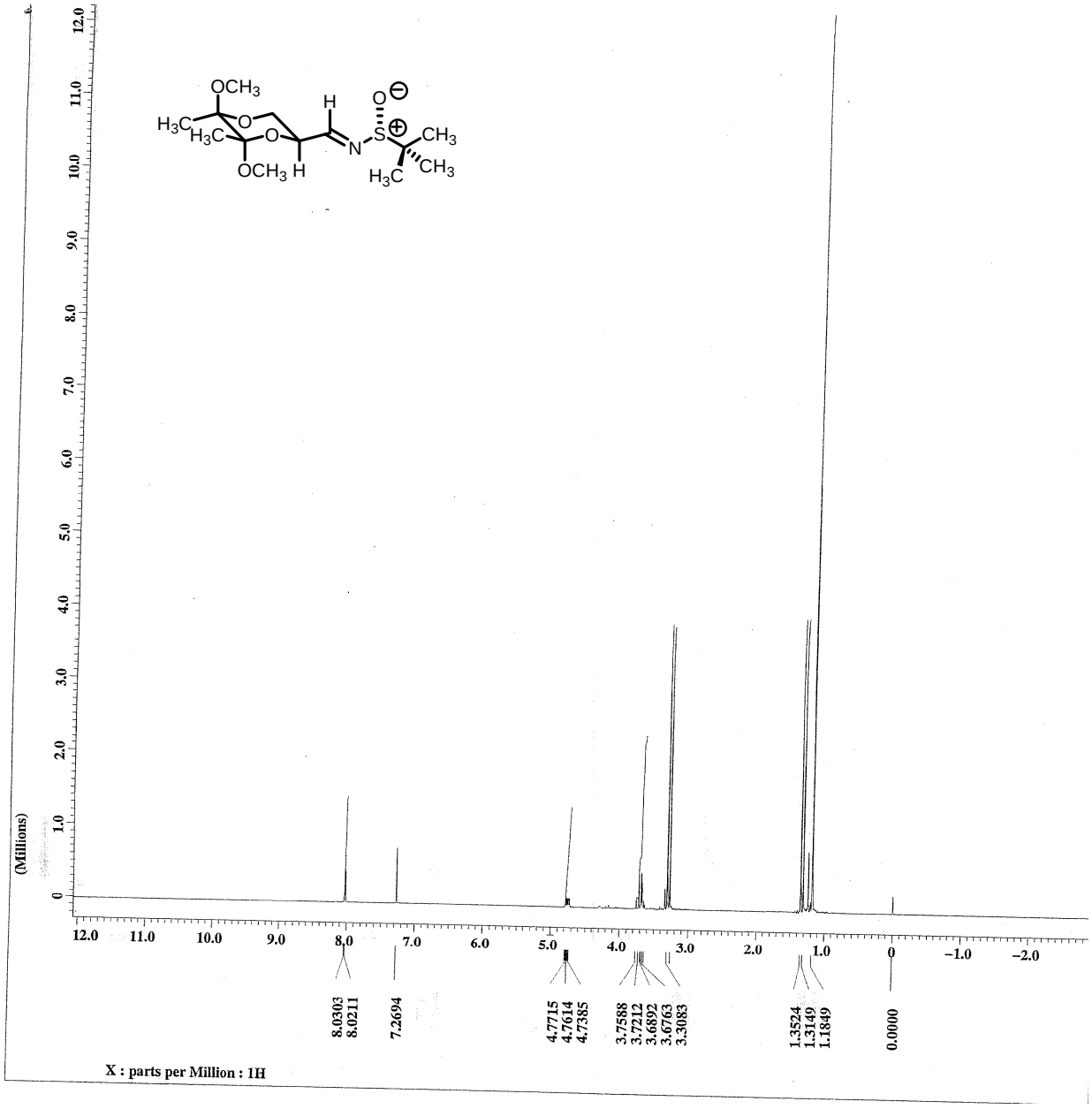
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20.
166.2850
99.7466
98.2351
77.4399
77.2185
77.0201
76.5926
68.8669
60.2022
57.0952
48.3160
48.1481
22.3755
17.6272
17.5279
X : parts per Million : 13C



[S(R), N(E)]-2-methyl-N-[((2R,5S,6S)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)methylene]-2-propanesulfinamide (ent-4) From the mixture of 0.242 g (2 mmol) (*R*)-(-)-2-methyl-2-propane sulfinamide, 0.612 g (3 mmol) (2*S*,5*S*,6*S*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde, and 0.640 g (4 mmol) $CuSO_4$, 0.435 g (70%) of the title compound was isolated as an white solid after silica gel chromatography. Analytical data: $[\alpha]_D^{25}$ -88.0 (*c* 1.0, $CHCl_3$), mp 106-108°C IR (cm^{-1}) 2979, 2925, 1626, 1457, 1211, 1143, 1089; ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.7, 1H), 4.77-4.73 (m, 1H), 3.75-3.66 (m, 2H), 3.30 (s, 3H), 3.25 (s, 3H), 1.35 (s, 3H), 1.31, (s, 3H), 1.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 99.4, 98.0, 69.4, 60.0, 56.6, 48.1, 47.9, 22.2, 17.5, 17.4; TLC R_f 0.39 (EtOAc/hexane, 2/8). HRMS (ESI) calculated mass 308.1532 ($C_{13}H_{25}NO_5S$ (M+H)); found 308.1531.


OCH3
H3C
H3C
O
O
H
O
S
N
CH3
CH3
H3C
OCH3 H
(Millions)
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11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
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8.0211
7.2694
4.7715
4.7614
4.7385
3.7588
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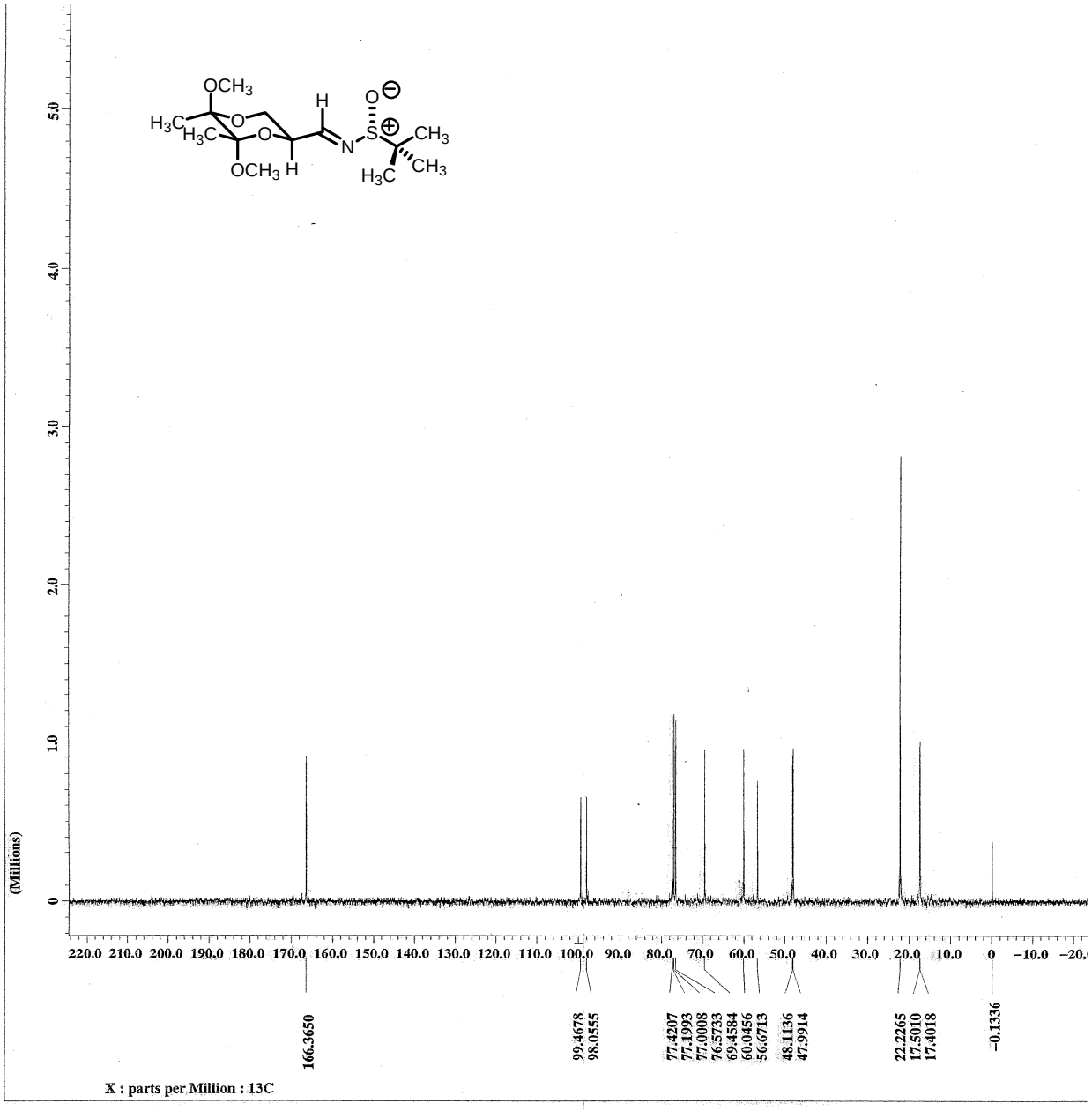
0.0000
X : parts per Million : 1H


OCH3
H
O
H3C
O
H3C
O
S
CH3
N
OCH3
H
H3C
CH3
(Millions)
5.0
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.
166.3650
99.4678
98.0555
77.4207
77.1993
77.0008
76.5733
69.4584
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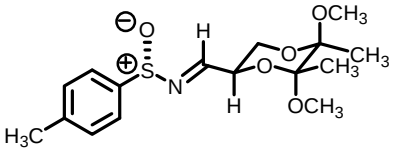
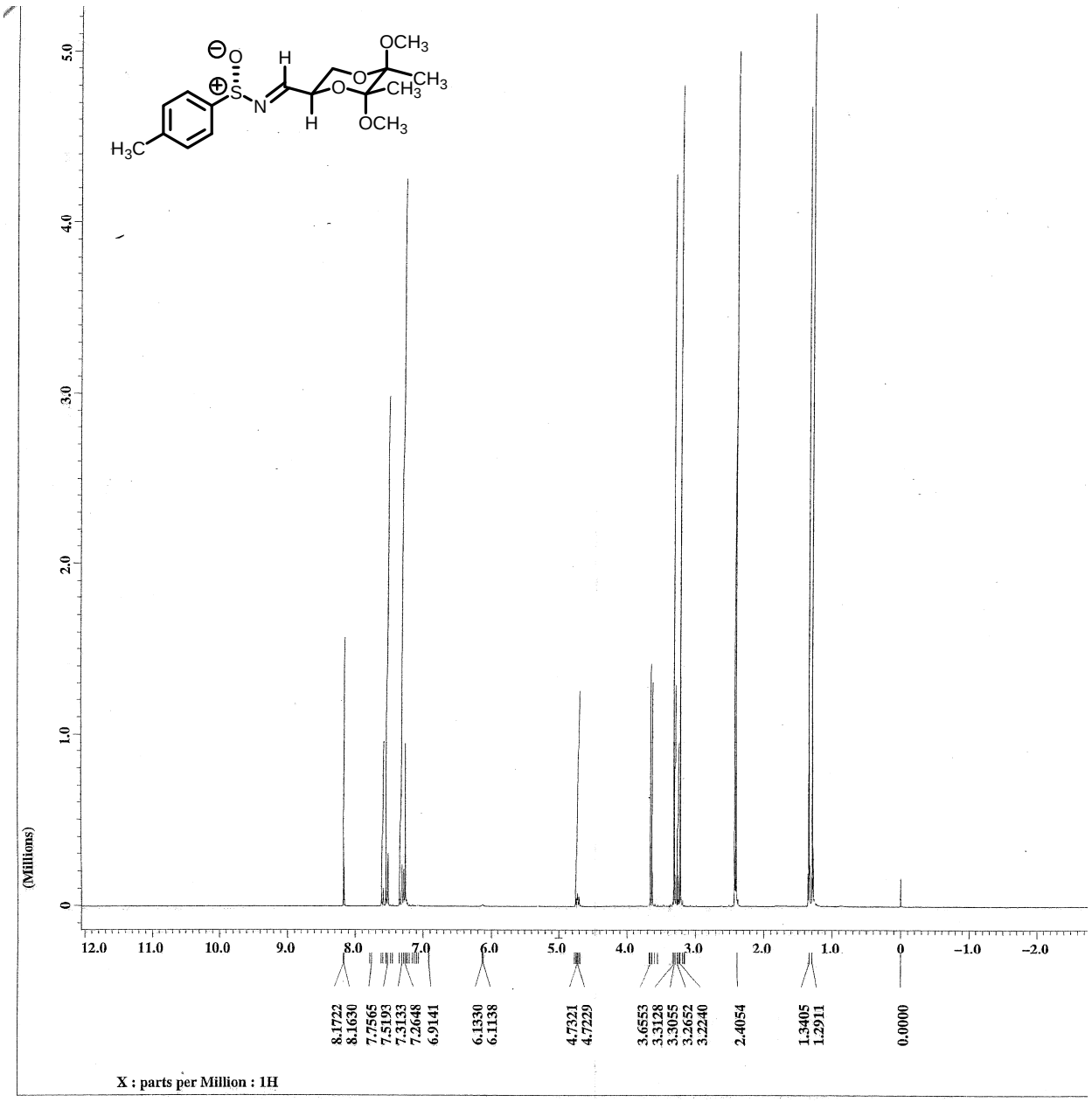
X : parts per Million : 13C



[S(S), N(E)]-4-methyl-N-[((2S,5R,6R)-5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)methylene]phenylsulfinamide (7) From the mixture of 0.310 g (2 mmol) (*S*)-(-)-*p*-toluenesulfinamide, 0.612 g (3 mmol) (2*R*,5*R*,6*R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde and 0.640 g (4 mmol) $CuSO_4$, 0.470 g (68%) of the title compound was isolated as an oil after silica gel chromatography. Analytical data: $[\alpha]_D^{25}$ -75 (*c* 1.0, $CHCl_3$), IR (cm^{-1}) 2947, 2833, 1718, 1627, 1596, 1447, 1255, 1036; ^1H NMR (75 MHz, $CDCl_3$) δ 8.16 (d, *J* = 2.7, 1H), 7.54-7.51(m, 2H), 7.34-7.28 (m, 2H), 4.75-4.68 (m, 1H), 3.67-3.62 (m, 1H), 3.31 (s, 3H), 3.30-3.23 (m, 1H), 3.22 (s, 3H), 2.40 (s, 3H), 1.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 163.8, 129.8, 129.6, 129.5, 127.8, 127.1, 124.6, 99.7, 98.1, 68.9, 60.0, 48.3, 48.1, 21.1, 17.6, 17.5; TLC R_f 0.33 (EtOAc/hexane, 3/7); HRMS (ESI) calculated mass 342.1375 ($C_{16}H_{23}NO_5S$ (M+H)); found 342.1375.


OCH3
H
O
S
N
O
CH3
CH3
H
OCH3
H3C
(Millions)
5.0
4.0
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
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8.1630
7.7565
7.5193
7.3133
7.2648
6.9141
6.1330
6.1138
4.7321
4.7229
3.6553
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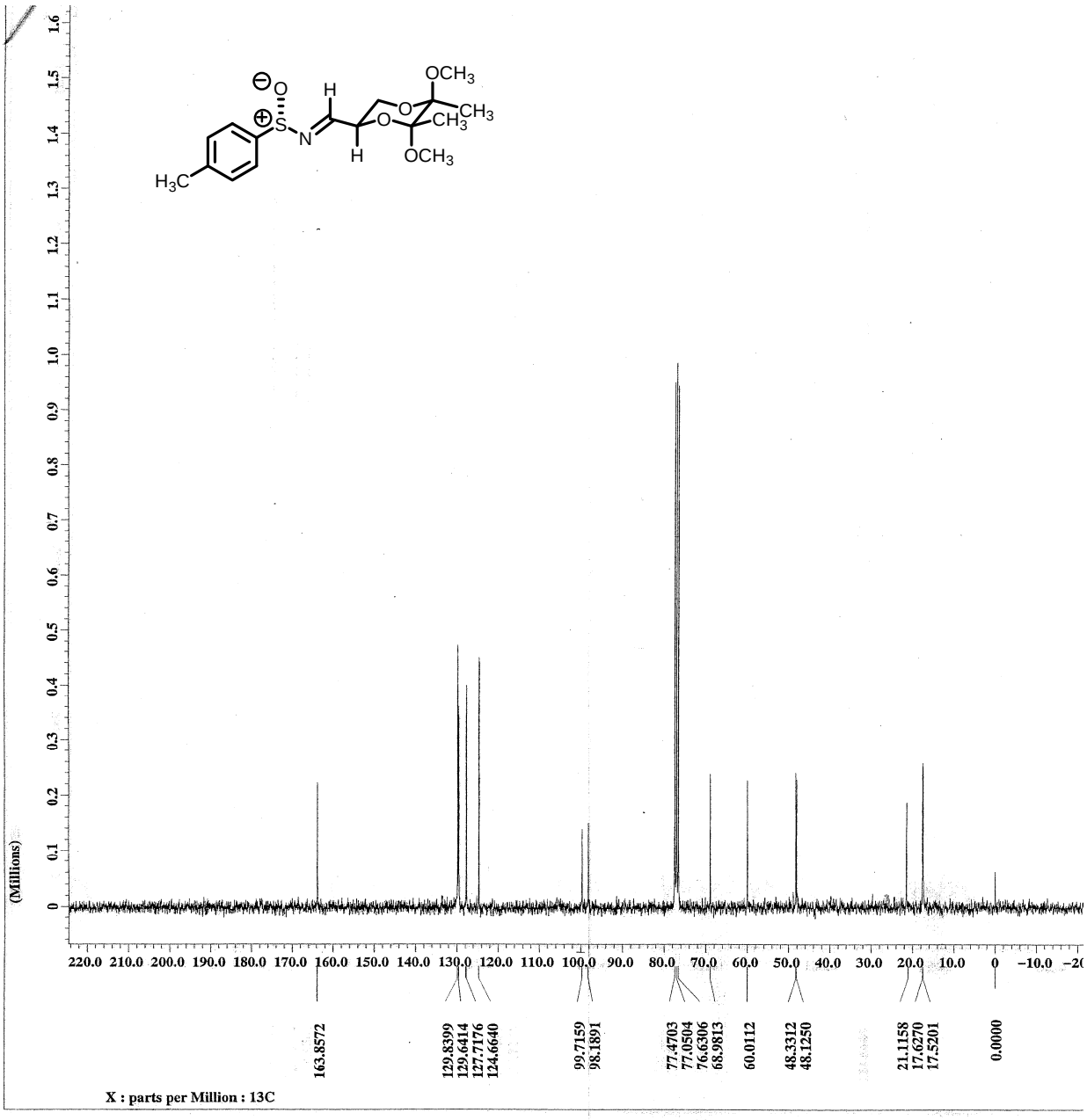
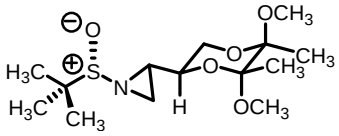
X : parts per Million : 1H

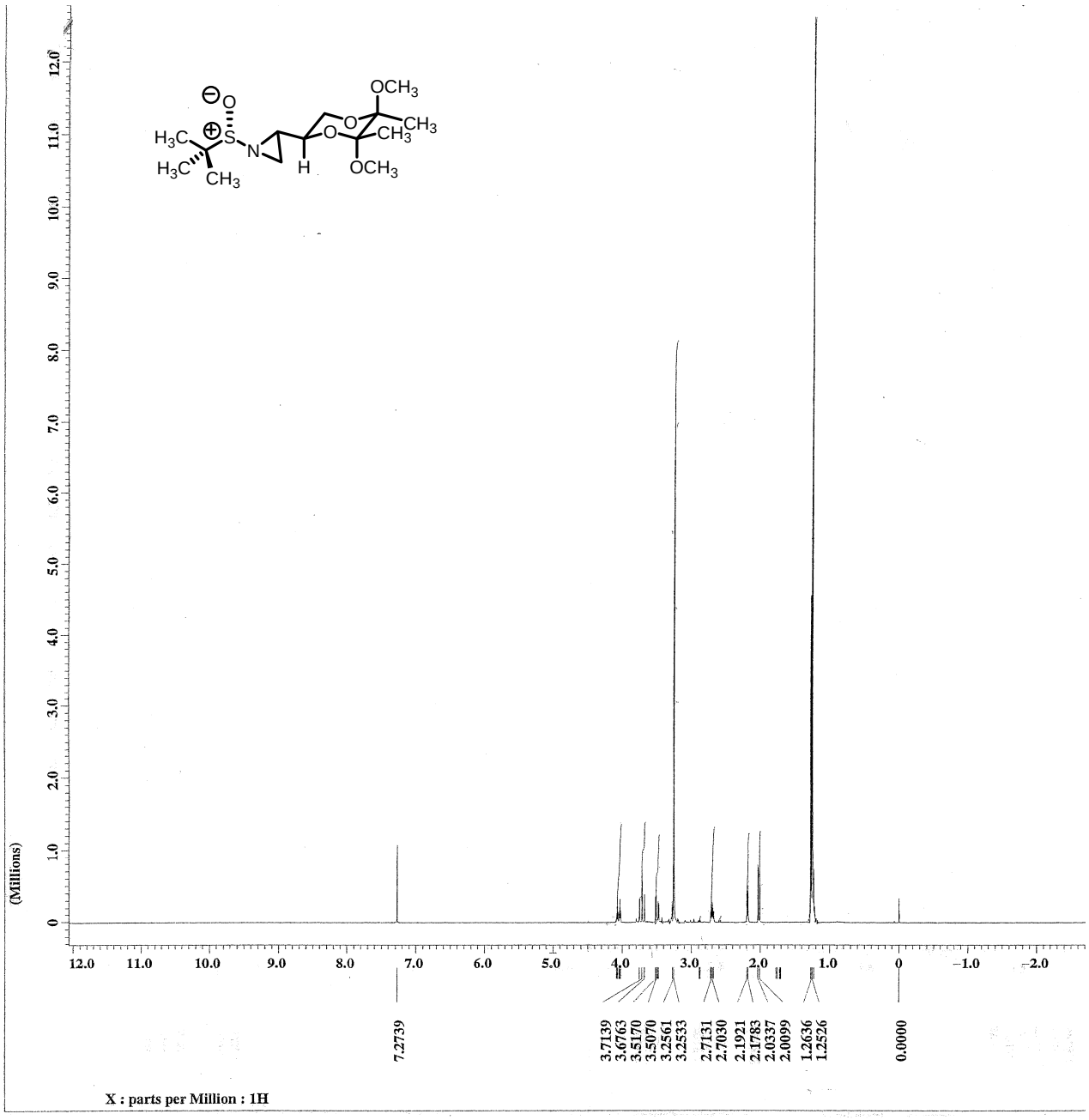

OCH3
H
O
S
N
O
CH3
CH3
H
OCH3
H3C
(Millions)
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −20
163.8572
129.8399
129.6414
127.7176
124.6640
99.7159
98.1891
77.4703
77.0504
76.6306
68.9813
60.0112
48.3312
48.1250
21.1158
17.6270
17.5201
0.0000
X : parts per Million : 13C

Representative procedure for methylene transfers onto butanediacetal-protected sulfinyl imines

An oven-dried 25 mL round-bottomed flask was equipped with a stir bar, septum, and condenser. To this system was added butanediacetal-protected sulfinyl imine (1.0 equiv (1.0 mmol)), cesium carbonate (2.0 equiv), THF (3.0 mL) and as a solution, sulfonium salt (1.5 equiv) in THF (2.0 mL). The solution of sulfonium salt was added dropwise over a period of no more than 10min via syringe. The system was externally heated to 80°C (sand bath). The reaction mixture was allowed to stir for a period of 10h to assure completion of reaction. After cooling to room temperature, the reaction mixture was concentrated in vacuo and immediately purified by chromatography using neutral alumina and a gradient eluent system of hexanes and EtOAc (9:1) to afford analytically pure aziridine.



1-[S(S*)-(1,1-dimethylethyl)sulfinyl]-2-[(2S*,5R*,6R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)]aziridine From the combination of imine **4** (0.307 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.284 g (92% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of >95:5. Analytical data: IR (cm^{-1}) 3051, 2950, 1456, 1374, 1267, 1120, 1079; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.08-4.02 (m, 1H), 3.75-3.67 (dd, *J* = 11.2, 1H), 3.51-3.46 (m, 1H), 3.25-3.26 (m, 6H), 2.71-2.68 (m, 1H), 2.18 (d, *J* = 4.1, 1H), 2.01 (d, *J* = 7.1, 1H), 1.27-1.23 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 99.2, 97.9, 65.2, 61.0, 56.7, 47.96, 47.90, 29.9, 24.9, 22.5, 17.6, 17.4; TLC R_f 0.34 (EtOAc/hexane, 1/9); HRMS (ESI) calculated mass 322.1688 ($C_{14}H_{27}NO_5S$ (M+H)); found 322.1687.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CH3
OCH3
H
H3C
H3C
CH3
(Millions)
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3.0
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3.6763
3.5170
3.5070
3.2561
3.2533
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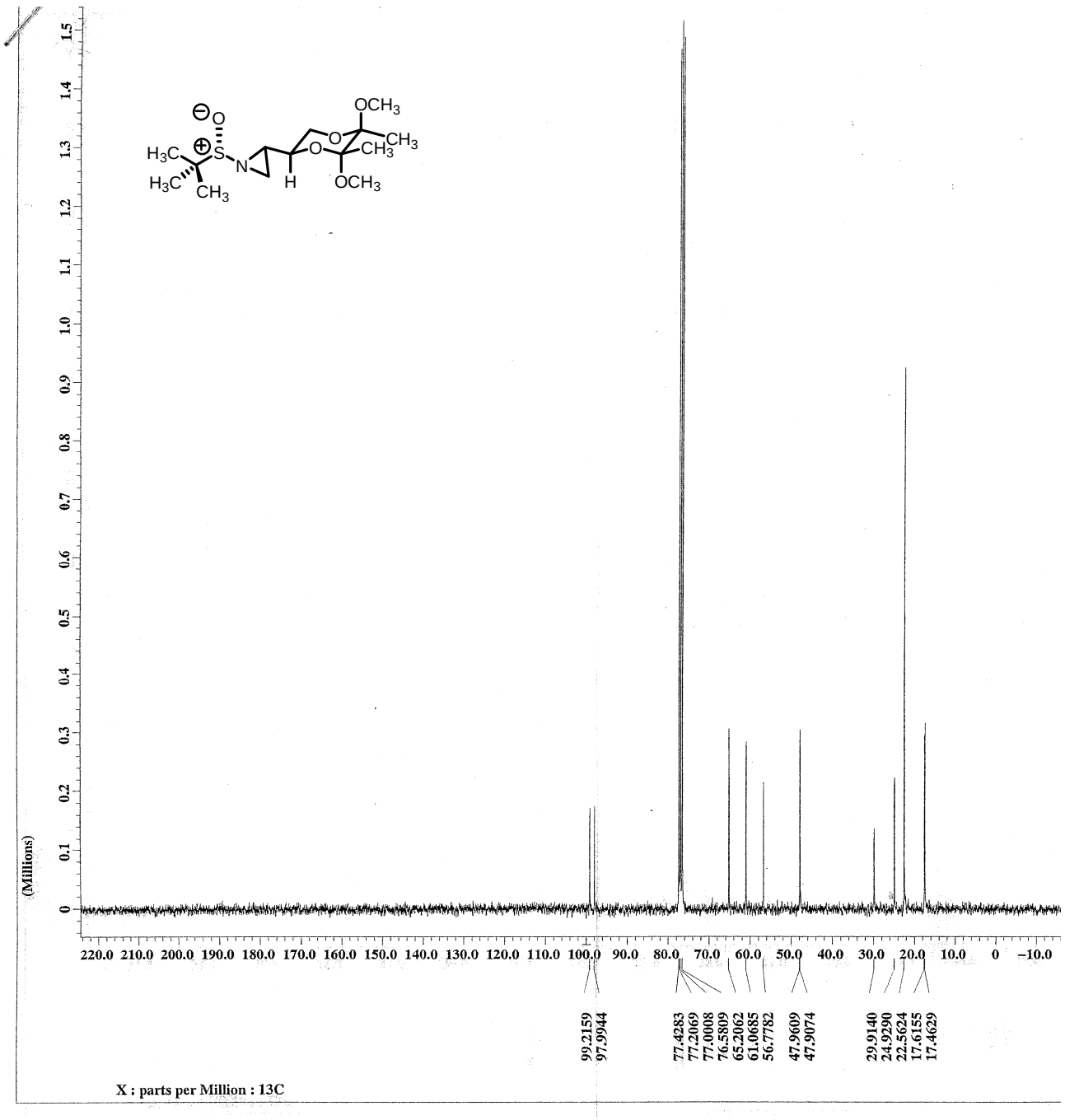
1.2526
0.0000
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C
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77.2069
77.0008
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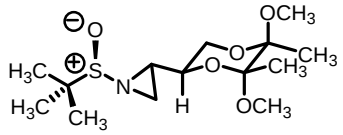
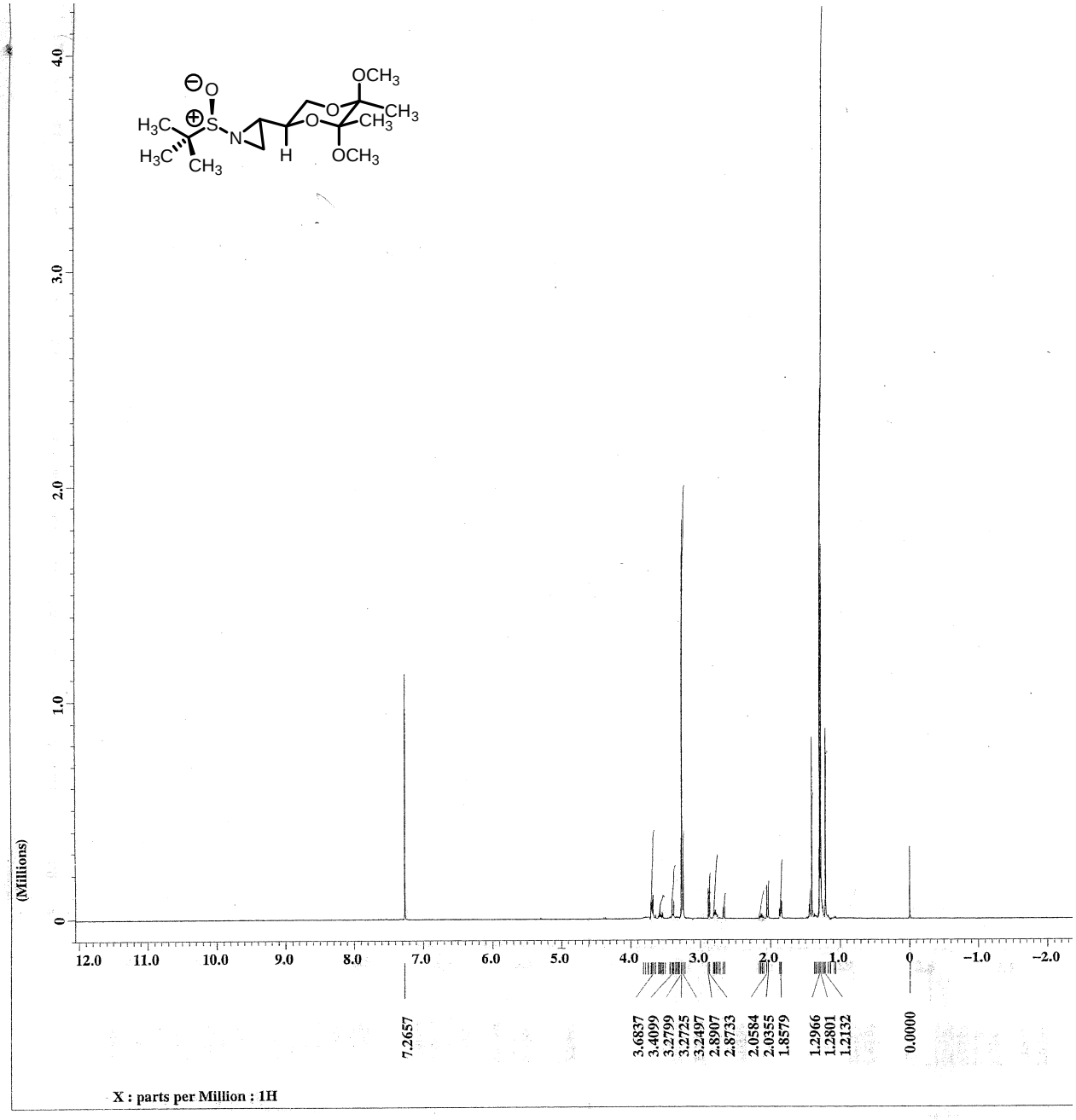
24.9290
22.5624
17.6155
17.4629



1-[S(R*)-(1,1-dimethylethyl)sulfinyl]-2-[(2S*,5R*,6R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)]aziridine From the mixture of imine **5** (0.307 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.272 g (88% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 78:22. Analytical data: IR (cm^{-1}) 2951, 2831, 1456, 1373, 1213, 1120, 1076; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71-3.64 (m, 2H), 3.40-3.38 (m, 1H), 3.30-3.22 (m, 6H), 2.81-2.75 (m, 1H), 2.04 (d, J = 6.7, 1H), 1.87-1.84 (m, 1H), 1.29-1.21 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 99.1, 99.0, 98.0, 68.9, 68.8, 61.1, 60.4, 60.0, 57.2, 56.8, 32.4, 30.9, 29.8, 29.6, 24.4, 24.3, 24.2, 23.2, 22.6, 22.5, 17.6, 17.5, 17.4; TLC R_f 0.30 (EtOAc/hexane, 1/9); HRMS (ESI) calculated mass 322.1688 ($C_{14}H_{27}NO_5S$ (M+H)); found 322.1696.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N
O
CH3
CH3
H3C
CH3
H
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(Millions)
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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
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3.2725
3.2497
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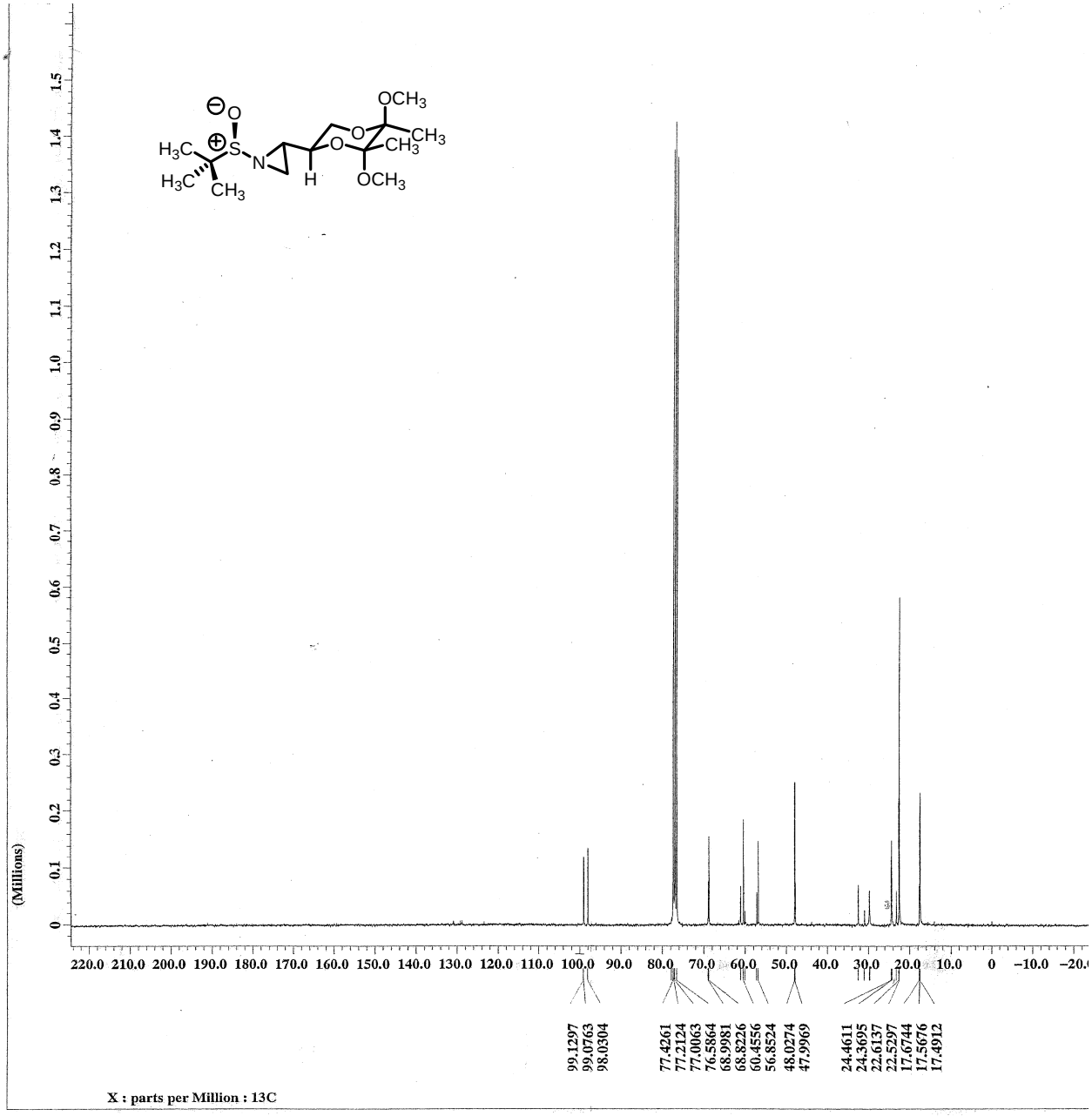
X : parts per Million : 1H


(Millions)
X : parts per Million : 13C
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77.0063
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68.8226
60.4556
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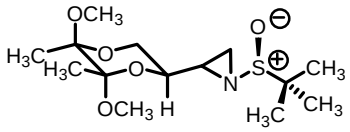
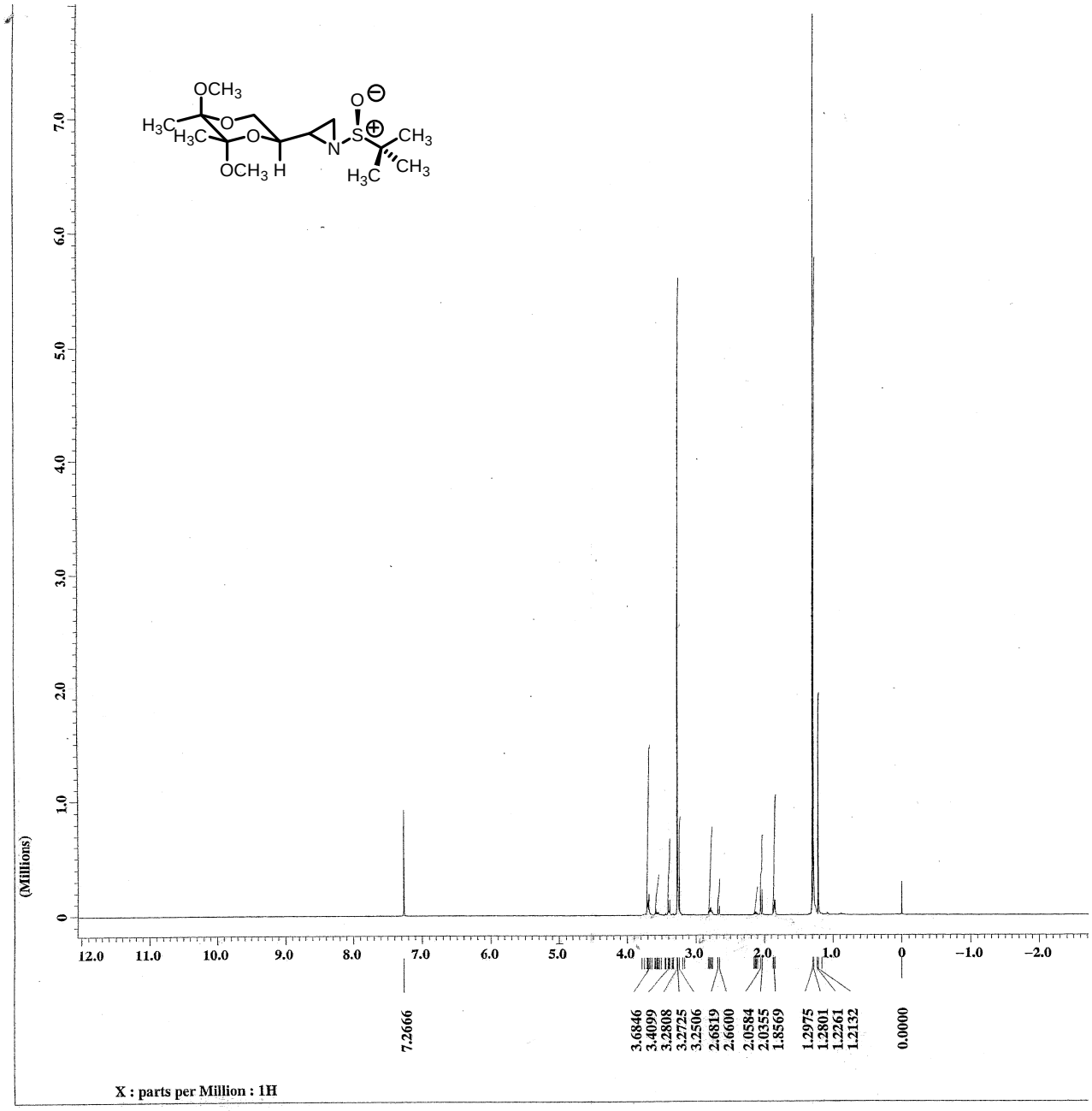
22.6137
22.5297
17.6744
17.5676
17.4912



1-[S(S*)-(1,1-dimethylethyl)sulfinyl]-2-[(2R*,5S*,6S*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)]aziridine From the mixture of imine *ent*-**5** (0.307 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.274 g (89% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 79:21. Analytical data: IR (cm^{-1}) 3051, 2989, 2954, 1454, 1375, 1266, 1120, 1076; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.71-3.66 (m, 2H), 3.40-3.38 (m, 1H), 3.28-3.25 (m, 6H), 2.80-2.76 (m, 1H), 2.04 (d, J = 6.7, 1H), 1.87-1.84 (m, 1H), 1.32-1.21 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 99.1,99.0, 98.0, 69.0, 68.8, 61.2, 60.4, 57.2, 56.8, 32.5, 29.8, 24.4, 23.2, 22.6, 22.5, 17.8, 17.6, 17.5; TLC R_f 0.30 (EtOAc/hexane, 2/8); HRMS (ESI) calculated mass 322.1688 ($C_{14}H_{27}NO_5S$ (M+H)); found 322.1687.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H3C
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O
OCH3
H
N
S
O
CH3
H3C
CH3
(Millions)
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3.2506
2.6819
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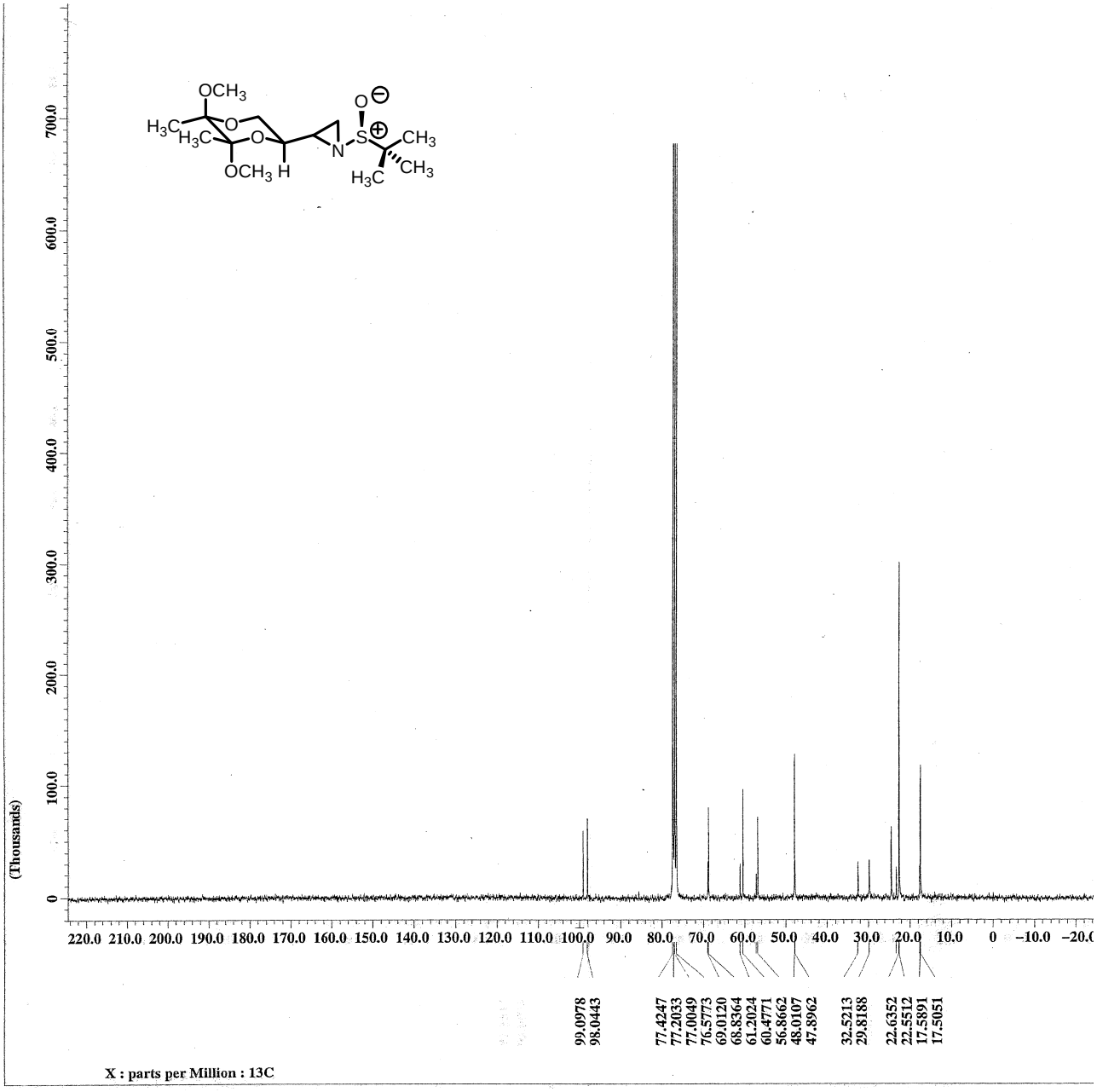
1.2801
1.2261
1.2132
0.0000
X : parts per Million : 1H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H3C
H3C
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O
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N
S
O
CH3
CH3
H3C
(Thousands)
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100.0
200.0
300.0
400.0
500.0
600.0
700.0
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
99.0978
98.0443
77.4247
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77.0049
76.5773
69.0120
68.8364
61.2024
60.4771
56.8662
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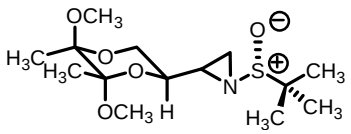
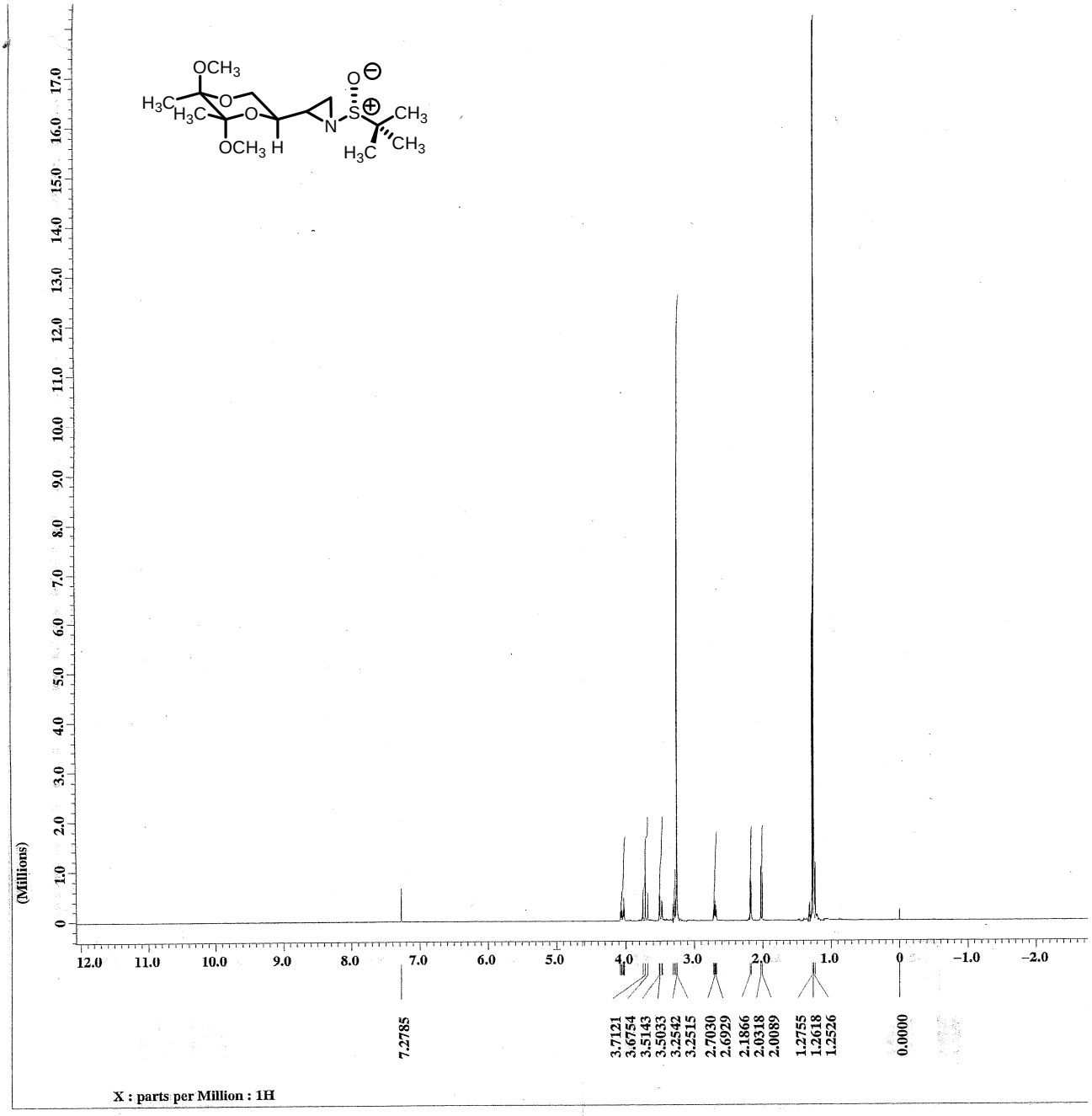
X : parts per Million : 13C



1-[S(R*)-(1,1-dimethylethyl)sulfinyl]-2-[(2R*,5S*,6S*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)]aziridine From the mixture of imine *ent*-**4** (0.307 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.289 g (94% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 95:5. Analytical data: IR (cm^{-1}) 2951, 2831, 1456, 1373, 1210, 1120, 1079; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07-4.01 (m, 1H), 3.74-3.67 (dd, J = 11.0, J = 11.0, 1H), 3.51-3.46 (m, 1H), 3.25-3.26 (m, 6H), 2.72-2.67 (m, 1H), 2.18 (d, J = 4.1, 1H), 2.02 (d, J = 6.8, 1H), 1.27-1.25 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 99.2, 98.0, 65.2, 61.0, , 56.7, 47.9, 47.8, 29.9, 24.9, 22.5, 17.6, 17.4; TLC R_f 0.30 (EtOAc/hexane, 2/8); HRMS (ESI) calculated mass 322.1688 ($C_{14}H_{27}NO_5S$ (M+H)); found 322.1678.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H3C
H3C
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O
OCH3
H
N
S
O
CH3
H3C
CH3
(Millions)
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16.0
15.0
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12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
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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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3.6754
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3.2542
3.2515
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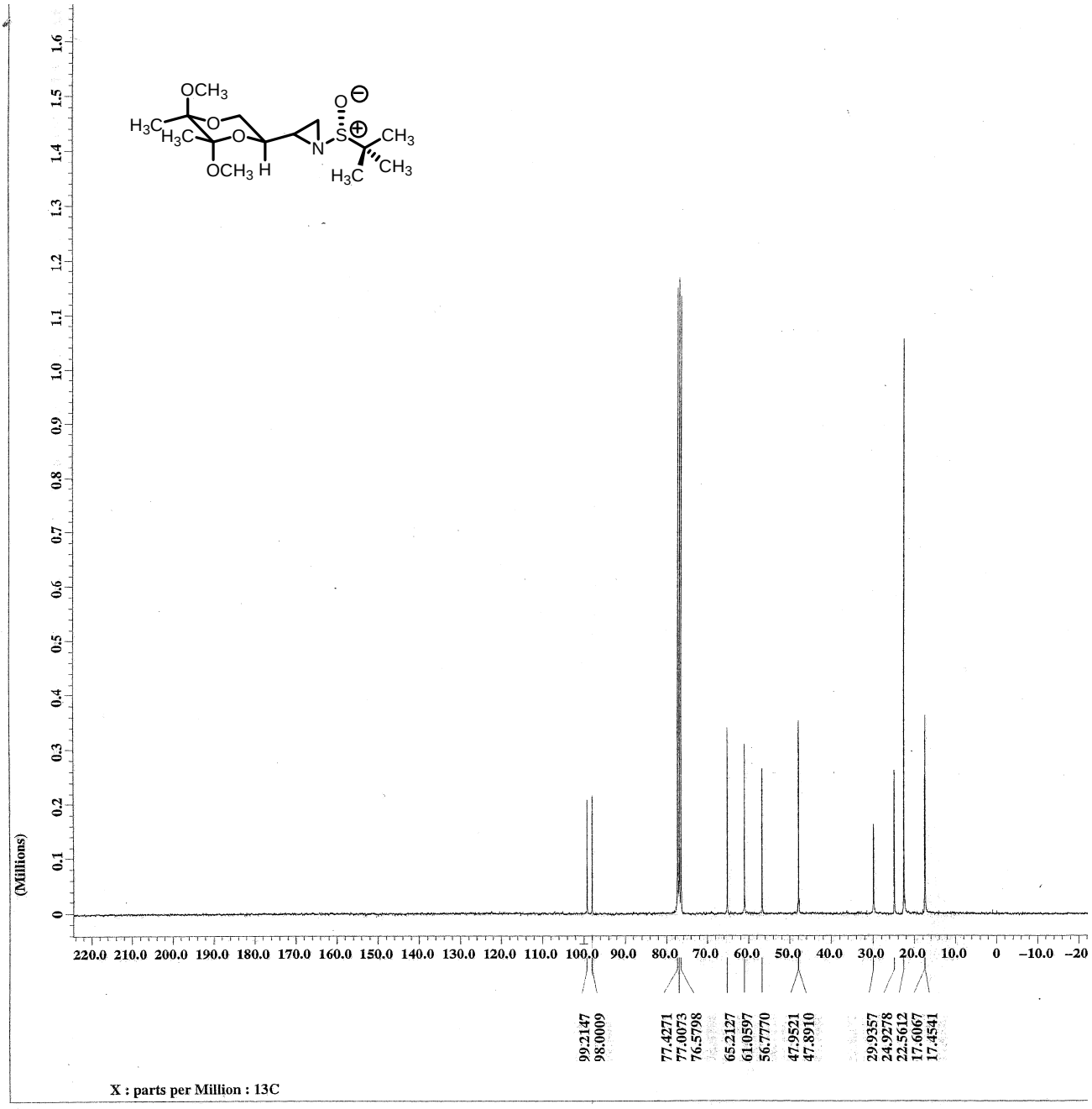
1.2526
0.0000
X : parts per Million : 1H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H3C
H3C
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O
N
S
O
CH3
OCH3
H
H3C
CH3
(Millions)
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0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
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
99.2147
98.0009
77.4271
77.0073
76.5798
65.2127
61.0597
56.7770
47.9521
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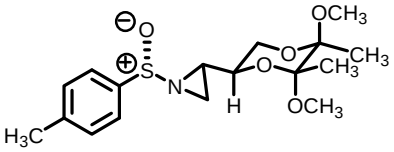
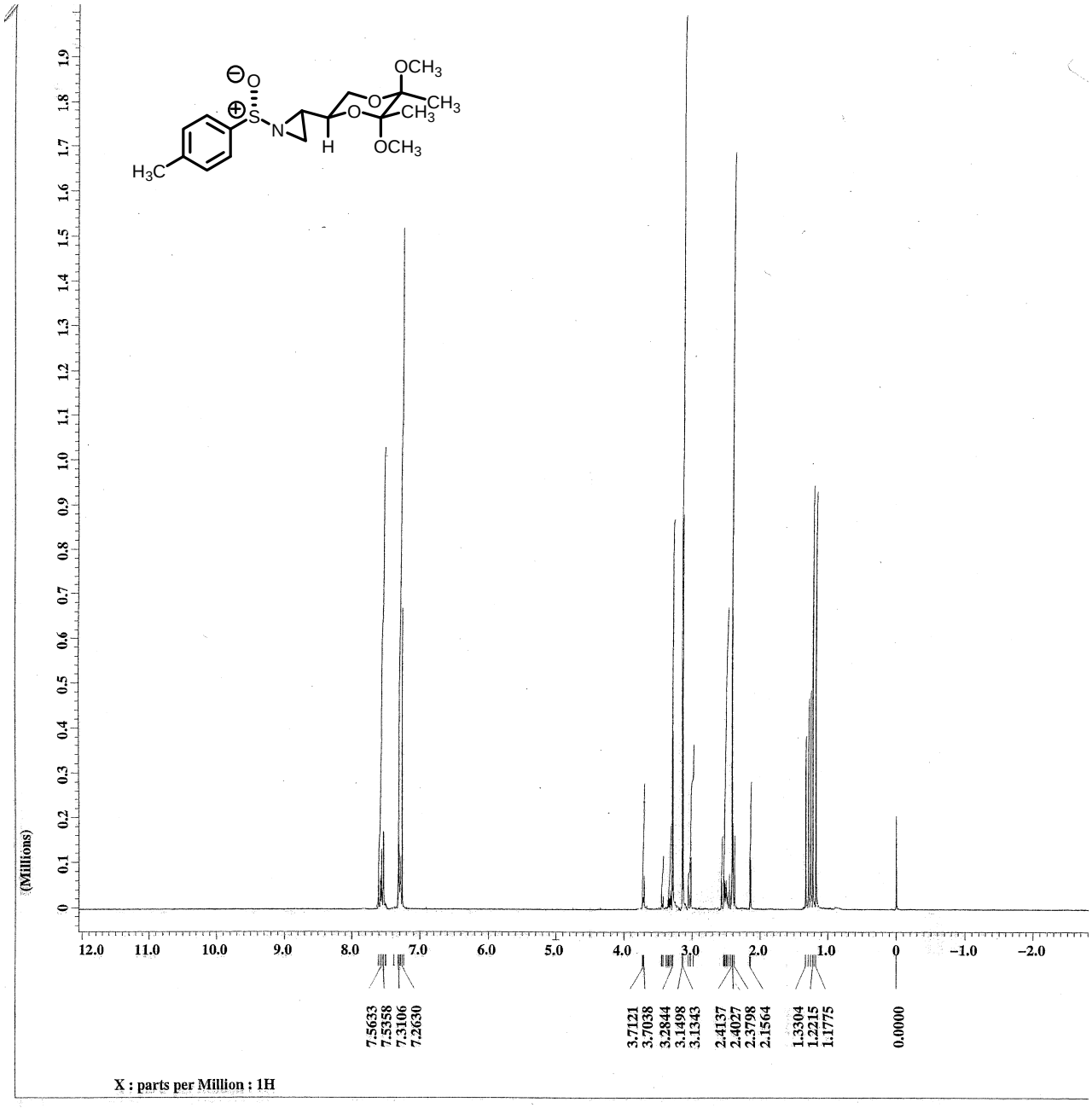
X : parts per Million : 13C

Control Reaction: Aziridination reaction of 7



1-[S(S*)-(4-methylphenyl)sulfinyl]-2-[(2S*,5R*,6R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexyl)]aziridine From the combination of imine **7** (0.341 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.284 g (80% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 67:33. Analytical data: IR (cm^{-1}) 2947, 2919, 1446, 1375, 1212, 1119, 1035; ^{1}H NMR (300 MHz, $CDCl_3$) δ7.60-7.49 (m, 4H), 7.32-7.28 (m, 4H), 3.72-3.70 (m, 2H), 3.45-3.42 (m, 1H), 3.36-3.33 (m, 1H), 3.29 (s, 3H), 3.28 (s, 3H), 3.14 (s, 3H), 3.13 (s, 3H), 3.05-2.98 (m, 2H), 2.56 (d, J = 3.0, 1H), 2.53-2.44 (m, 4H), 2.41-2.43 (m, 6H), 2.14 (d, J = 4.0, 1 H), 1.28 (s, 3H), 1.25 (s, 3H), 1.22 (s, 3H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 141.8, 141.7, 129.5, 129.4, 124.8, 124.5, 99.1, 98.9, 98.0, 97.7, 68.2, 67.9, 60.8, 60.5, 48.1, 48.0, 47.9, 47.8, 34.7, 32.0, 29.6, 28.0, 27.5, 19.7, 17.7, 17.6, 17.5, 17.3; TLC R_f 0.30 (EtOAc/hexane, 2/8); HRMS (ESI) calculated mass 356.1532 ($C_{17}H_{25}NO_5S$ (M+H)); found 356.1537.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CH3
OCH3
H
H3C
(Millions)
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9.0
8.0
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3.2844
3.1498
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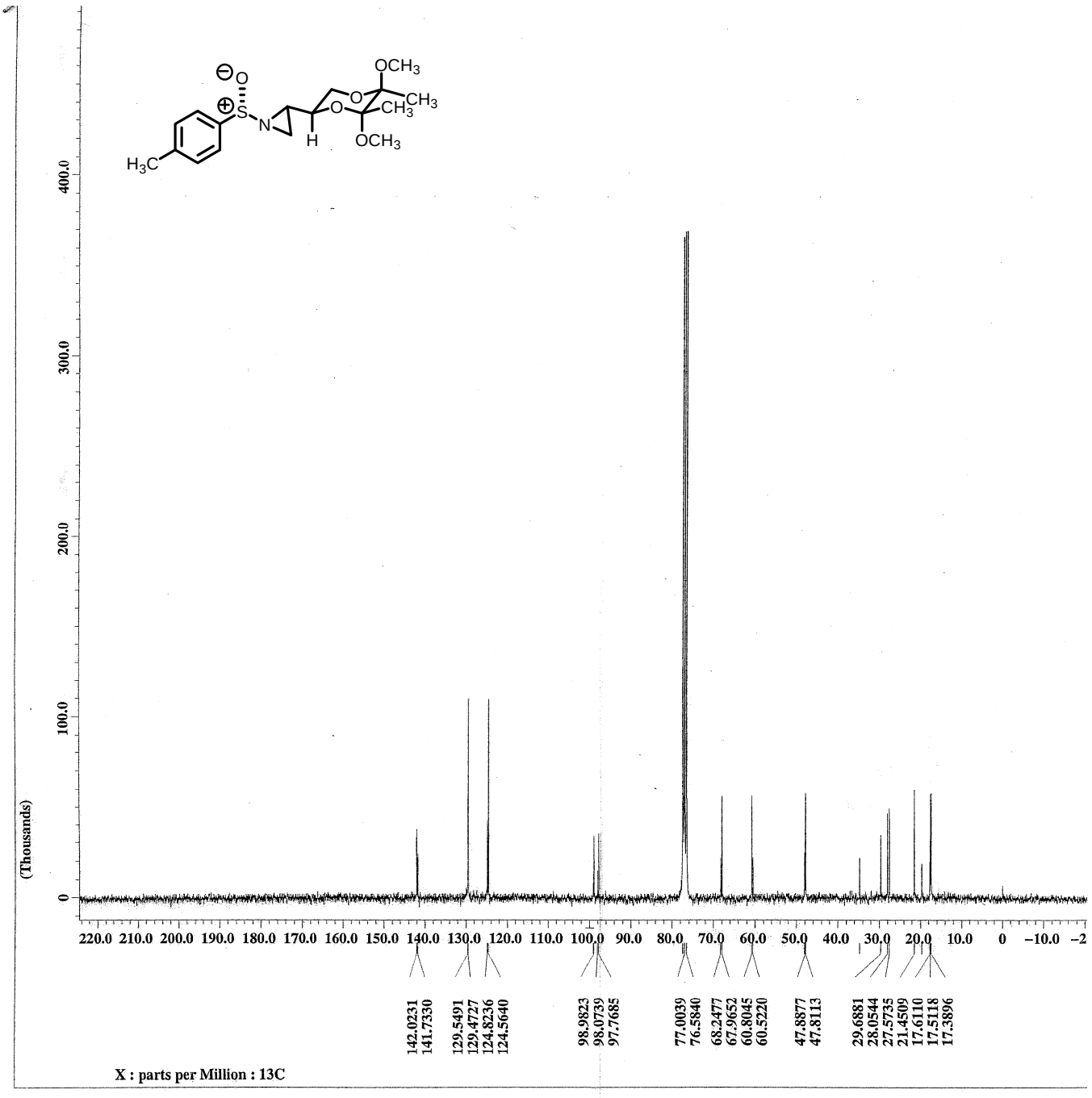
X : parts per Million : 1H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CH3
OCH3
H
H3C
(Thousands)
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0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.0 −2
142.0231
141.7330
129.5491
129.4727
124.8236
124.5640
98.9823
98.0739
97.7685
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60.5220
47.8877
47.8113
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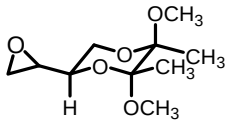
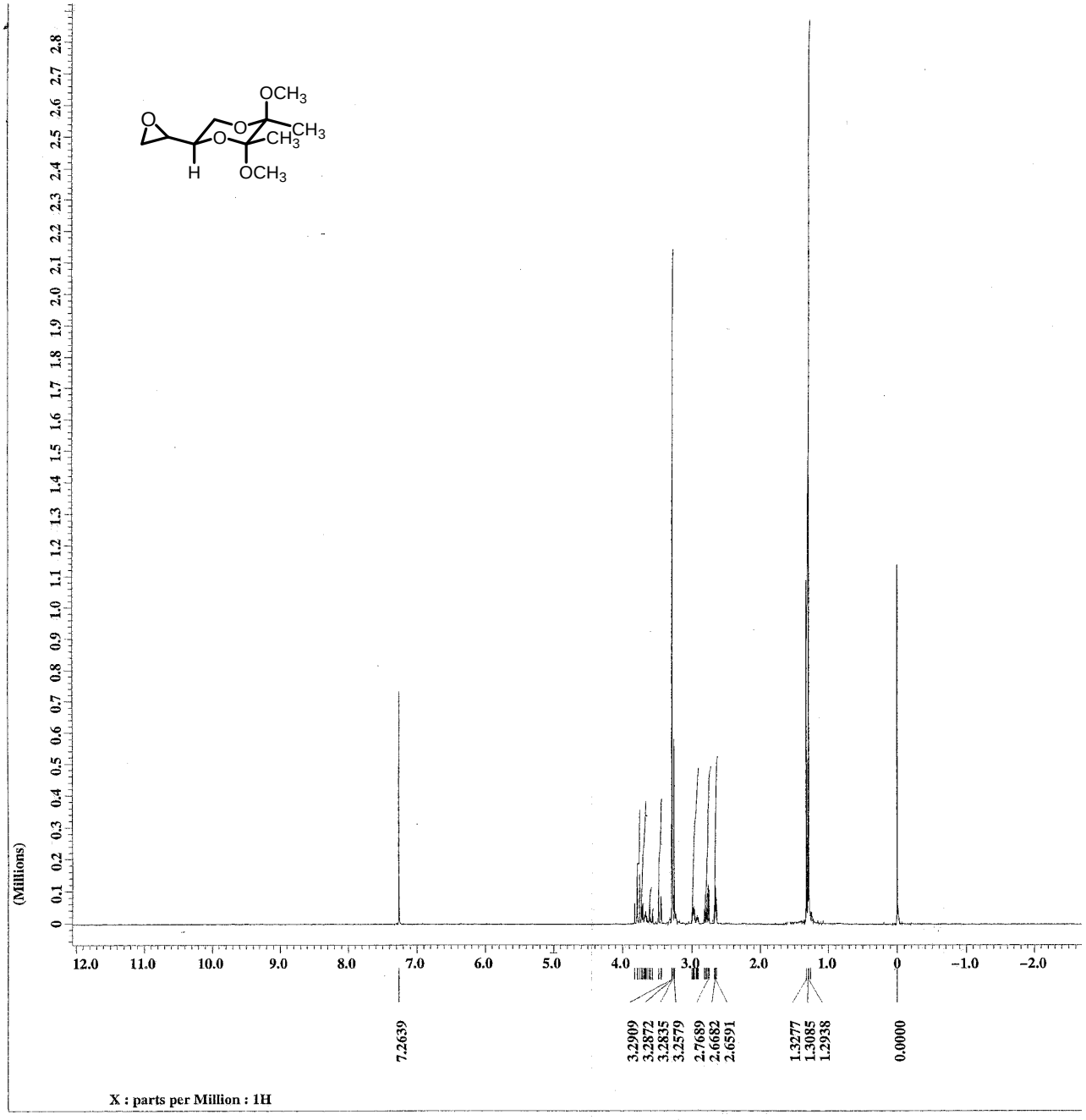
X : parts per Million : 13C

Control Reaction: Epoxidation reaction of 3



2-(5,6-Dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)oxirane From the combination of (2*R*,5*R*,6*R*)-2-(5,6-dimethoxy-5,6-dimethyl-1,4-dioxacyclohexane)carboxyaldehyde (**3**) (0.204 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.176 g (80% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 60:40. Analytical data: IR (cm^{-1}) 2992, 2948, 1373, 1258, 11210, 1035; ^{1}H NMR (300 MHz, $CDCl_3$) δ3.82-3.75 (m, 1H), 3.73-3.67 (m, 1H), 3.48-3.44 (m, 1H), 3.29-3.24 (m, 6H), 3.00-2.90 (m, 1H), 2.82-2.75 (m, 1H), 2.68-2.64 (m, 1H), 1.32-1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 99.0, 98.0, 68.8, 68.2, 60.8, 59.9, 50.6, 48.0, 47.9, 45.1, 43.1, 17.7, 17.5; TLC R_f 0.30 (EtOAc/hexane, 1/9); HRMS (ESI) calculated mass 241.1052 ($C_{10}H_{18}O_5$ (M+Na)); found 241.1052.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O
O
O
CH3
CH3
H
OCH3
(Millions)
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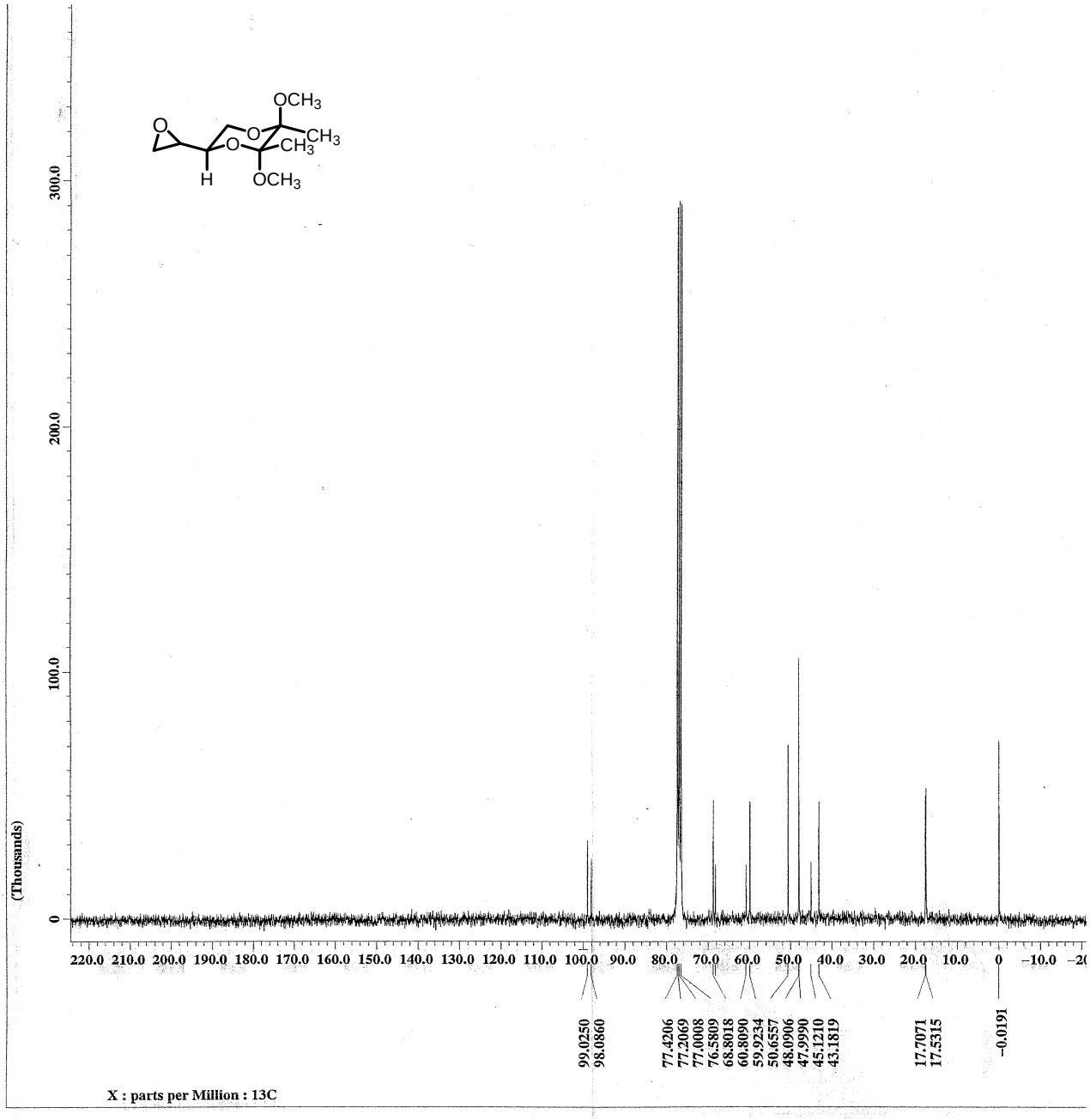
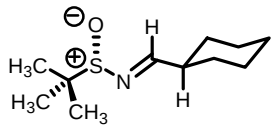
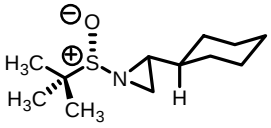
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0
7.2639
3.2909
3.2872
3.2835
3.2579
2.7689
2.6682
2.6591
1.3277
1.3085
1.2938
0.0000
X : parts per Million : 1H


OCH3
O
O
CH3
O
CH3
H
OCH3
300.0
200.0
100.0
0
(Thousands)
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
99.0250
98.0860
77.4206
77.2069
77.0008
76.5809
68.8018
60.8090
59.9234
50.6557
48.0906
47.9990
45.1210
43.1819
17.7071
17.5315
−0.0191
X : parts per Million : 13C

Control Reaction: Aziridination of 6



[S(S), N(E)]-2-methyl-N-[(cyclohexyl)methylene]-2-propanesulfinamide (6) Using the representative procedure for the preparation of *N*-sulfinyl imines, from the combination of 0.242 g (2 mmol) (*S*)-(-)-2-methyl-2-propane sulfinamide, 0.336 g (3 mmol) cyclohexanecarboxaldehyde, and 0.640 g (4 mmol) $CuSO_4$, 0.399 g (92 %) of the title compound was obtained as an oil after purification on silica gel chromatography. The analytical data obtained was consistent with that previously reported.[1]



1-[S(S*)-(1,1-dimethylethyl)sulfinyl]-2-[cyclohexyl]aziridine From the combination of imine **6** (0.215 g, 1.00 mmol), cesium carbonate (0.652 g, 2.00 mmol), and sulfonium salt **1** (0.498 g, 1.5 mmol) in 2.0 mL of THF, 0.187 g (81% yield) of the title compound was obtained after purification by column chromatography using neutral alumina. Prior to purification, a small aliquot was removed and analyzed by ^{1}H NMR. Measured by NMR was a diastereomeric ratio of 61:39. The analytical data obtained was consistent with that previously reported.[1]

References

1 (*a*) D. D. Staas, K. L. Savage, C. F. Homnick, N. N. Tsou, R.G. Ball, *J. Org. Chem*., 2002, **61**, 8276; (*b*) D. Morton, D. Pearson, R. A. Field, R. A. Stockman, *Synlett*, 2003, 1985.