Supporting Information

Ni-CATALYZED THREE-COMPONENT COUPLING OF 4-METHYLENE-2-OXAZOLIDINONES, ALKYNES, AND TRIMETHYLALUMINUM

Tatsuya Yamahira, Ryo Ninokata, Gen Onodera, Masanari Kimura *
Graduate School of Engineering, Nagasaki University, 1-14, Bunkyo machi, Nagasaki, 852-8521, Japan

General procedures

Distillation were carried out in a Kugelrohr apparatus (SIBATA glass tube oven GTO-350RG). Boiling points are meant to refer to the oven temperature (± 1 °C). Microanalyses were performed by the Instrumental Analysis Center of Nagasaki University. Analysis agreed with the calculated values within ± 0.4%. High resolution mass spectra (HRMS) were measured with JEOL JMSDX303. Infrared spectra were recorded with a JASCO A-100 or SHIMAZU FTIR-8700 infrared spectrophotometer. 1H and 13C magnetic resonance spectra were measured on JEOL-GX400 instrument with tetramethylsilane as an internal standard. Chemical shift values were given in ppm downfield from the internal standard.

Toluene was dried and distilled from sodium immediately prior to use under nitrogen atmosphere. Tetrahydrofuran, 1,4-dioxane, DMSO, CPME, n-hexane, DMA, NMP, and DMF were purchased as anhydrous grade solvent and used without further purification under nitrogen atmospher. Me_3Al, Me_2Zn, Et_3Al, Et_2Zn, DIBAL-H were purchased and used without further purification. $Me_2Al(OMe)$ was prepared by reacting Me_3Al (1.0 M hexane solution) and methanol (Wako). $Ni(cod)_2$, PPh_3, $P(c\text{-}Hex)_3$, $P(OPh)_3$, dppe, and Xantphos were purchased and used without further purification. 5,5-Dimethyl-4-methylene-2-oxazolidinone was prepared from according to the literature.[1]

Preparation of $Me_2Al(OMe)$: A 25 mL of two-necked round-bottomed flask, equipped with a magnetic stir bar, a rubber septum and an air condenser at the top of which is attached a three-way stopcock fitted a nitrogen balloon. Me_3Al (1.0 M hexane solution, 2.0 mL, 2.0 mmol) are placed in the flask under nitrogen atmosphere. The stirring solution are cooled 0 °C and methanol (64.3 mg, 2.0 mmol) are dropwised over 5 min. This reaction completes for 30 min.

General procedure for multi-component coupling reaction (entry 1, Table 1): A 25 mL of two-necked round-bottomed flask, equipped with a rubber septum and an air condenser at the top of which is attached a three-way stopcock fitted a nitrogen balloon. *N*-*p*-Toluenesulfonyl-5,5-dimethyl-4-methylene-2-oxazolidinone (281.3 mg, 1 mmol) and $Ni(cod)_2$ (13.8 mg, 0.05 mmol) are placed in the flask and purged with nitrogen. Freshly distilled toluene (5 mL), 4-octyne (220.4 mg, 2.0 mmol), and Me_3Al (1.2 mL of 1 M hexane solution; 1.2 mmol) are successively added while stirring the solution with a magnetic stirrer. The stirring is continued for 24 h at 60°C. After the reaction completes, the reaction mixture is diluted with ethyl acetate (20 mL). The organic phase is washed with sat. $NaHCO_3$ (2 x 20 mL) and brine (2 x 20 mL), and then dried over magnesium sulfate, filtered, and concentrated. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to give a pale yellow oil, which was subjected to column chromatography over silica gel (hexane/EtOAc = 11/1 v/v) to give **1a** (232.5 mg, 64%). **(5*E*)-*N*-(2,6-Dimethyl-5-propyl-2,5-nonadienyl)-*p*-toluenesulfonamide** (**1a**): IR (neat) 3277 (br), 2959 (s), 2930 (m), 2870 (m), 2343 (w), 1599 (w), 1456 (m), 1381 (m), 1325 (m), 1165 (s), 1092 (m), 665 (m) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz) δ 0.85 (t, J = 7.3 Hz, 3 H), 0.87 (t, J = 7.3 Hz, 3 H), 1.26-1.41 (m, 4 H), 1.48 (s, 3 H), 1.54 (s, 3 H), 1.67 (s, 3 H), 1.87 (s, 3 H), 1.88 (t, J = 7.3 Hz, 2 H), 1.98 (t, J = 7.3, 2 H), 3.03 (s, 2 H), 5.32 (s, 1 H), 6.75 (d, J = 8.3 Hz, 2 H), 7.81 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 14.4, 18.1, 20.3, 21.0, 21.5, 21.7, 22.4, 32.9, 33.8, 36.6, 125.4, 127.4, 128.8, 129.4, 132.2, 133.4, 138.0, 143.3; High-resolution MS, calcd for $C_{21}H_{33}NO_2S$: 363.2232. Found m/z (relative intensity): 363.2226 (M+, 100), 361 (2), 348 (2).

(*E*)-5-Ethyl-2,6-dimethyl-*N*-*p*-toluenesulfonylocta-2,5-dien-3-amine (**1b**): IR (neat) 3275 (s), 2964 (s), 2934 (s), 2874 (m), 1598 (w), 1454 (w), 1373 (m), 1325 (m), 1165 (s), 1092 (m), 814 (m), 739 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.84 (t, J = 7.3 Hz, 3 H), 0.94 (t, J = 7.3 Hz, 3 H), 1.45 (s, 3 H), 1.58 (s, 3 H), 1.75 (s, 3 H), 1.82 (q, J =7.3 Hz, 2 H), 2.00 (q, J = 7.3 Hz, 2 H), 2.42 (s, 3 H), 2.77 (s, 2 H), 5.19 (s, 1 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.3, 13.8, 17.7, 20.4, 21.0, 21.5, 23.5, 27.3, 33.4, 125.5, 127.4, 129.5, 129.6, 132.3, 134.4, 137.9, 143.4; High-resolution MS, calcd for $C_{19}H_{29}NO_2S$: 335.1919. Found m/z (relative intensity): 335.1911 (M+, 100), 333 (2).

(Z)-2-Methyl-5,6-diphenyl-*N*-*p*-toluenesulfonylhepta-2,5-dien-3-amine (**1c**): IR (neat) 3277 (s), 3045 (m), 2918 (m), 2866 (m), 2363 (w), 1744 (w), 1599 (s), 1491 (s), 1445 (s), 1367 (s), 920 (m), 812 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (s, 3 H), 1.45 (s, 3 H), 2.09 (s, 3 H), 2.44 (s, 3 H), 3.39 (s, 2 H), 5.09 (s, 1 H), 6.76-7.07 (m, 10 H), 7.27 (d, J = 8.3 Hz, 2 H), 7.68 (d, J = 8.3, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.2, 21.2, 21.5, 36.4, 124.4, 125.7, 125.8, 126.5, 127.2, 127.5, 128.8, 129.5, 131.4, 134.05, 134.12, 135.9, 137.9, 142.0, 143.2, 144.1; High-resolution MS, calcd for $C_{27}H_{29}NO_2S$: 431.1919. Found m/z (relative intensity): 431.1934 (M+, 100), 429 (1), 416 (4).

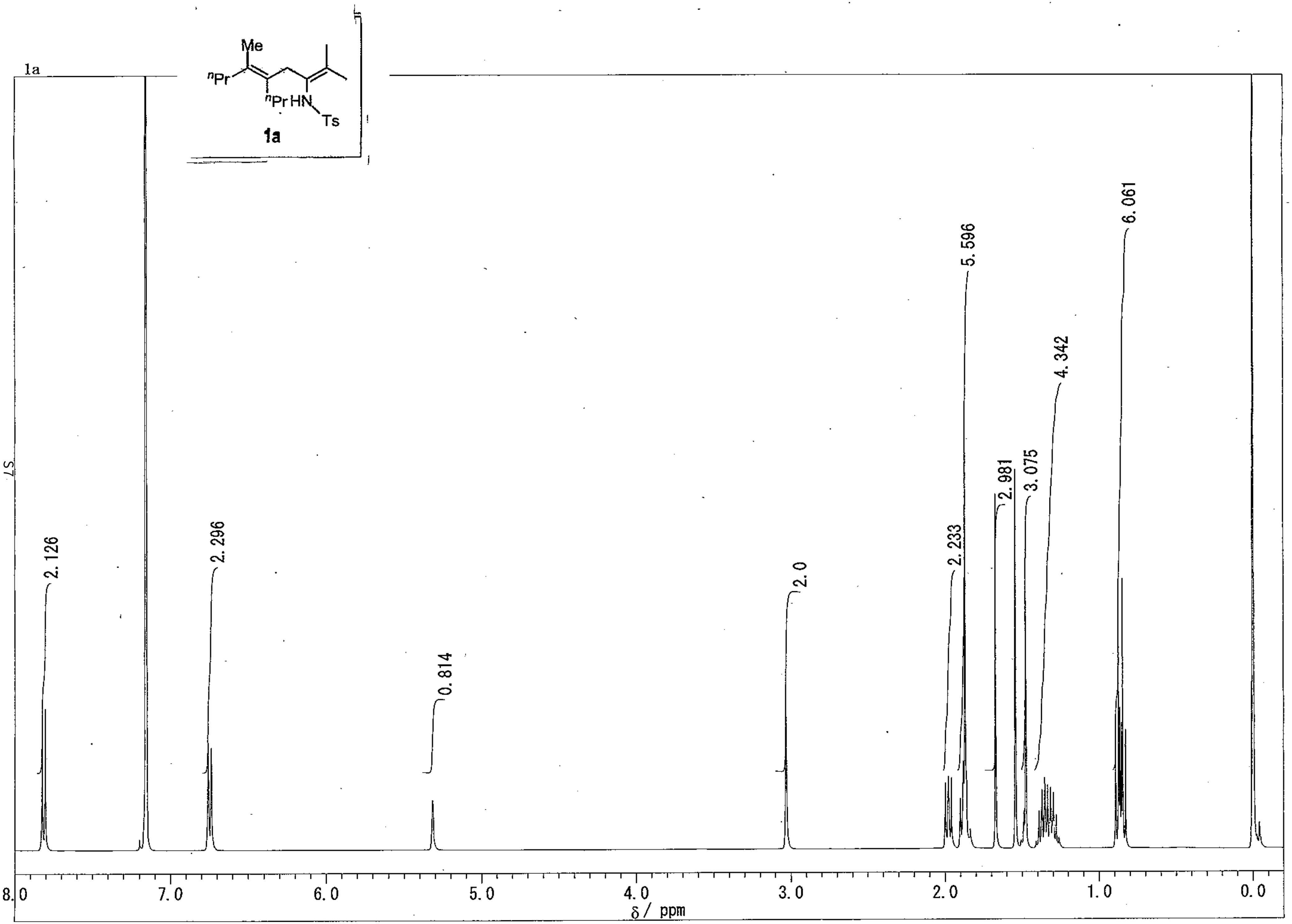
2,5,6-Trimethyl-*N*-*p*-toluenesulfonylhepta-2,5-dien-3-amine (**1d**): IR (neat) 3296 (w), 3055 (w), 2920 (w), 2862 (w), 1599 (w), 1494 (w), 1373 (m), 1323 (m), 1265 (s), 1165 (s), 1092 (m), 739 (s), 706 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (s, 3 H), 1.46 (t, 3 H), 1.58 (s, 3 H), 1.62 (s, 3 H), 1.74 (s, 3 H), 2.42 (s, 3 H), 2.77 (s, 2 H), 5.21 (s, 1 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H); 13C NMR ($CDCl_3$, 100 MHz) δ 17.2, 20.3, 20.4, 20.84, 20.87, 21.5, 35.8, 123.6, 125.3, 127.3, 128.2, 129.4, 132.2, 137.9, 143.3; High-resolution MS, calcd for $C_{17}H_{25}NO_2S$: 307.1606. Found m/z (relative intensity): 307.1608 (M+, 100), 305(1), 292 (13).

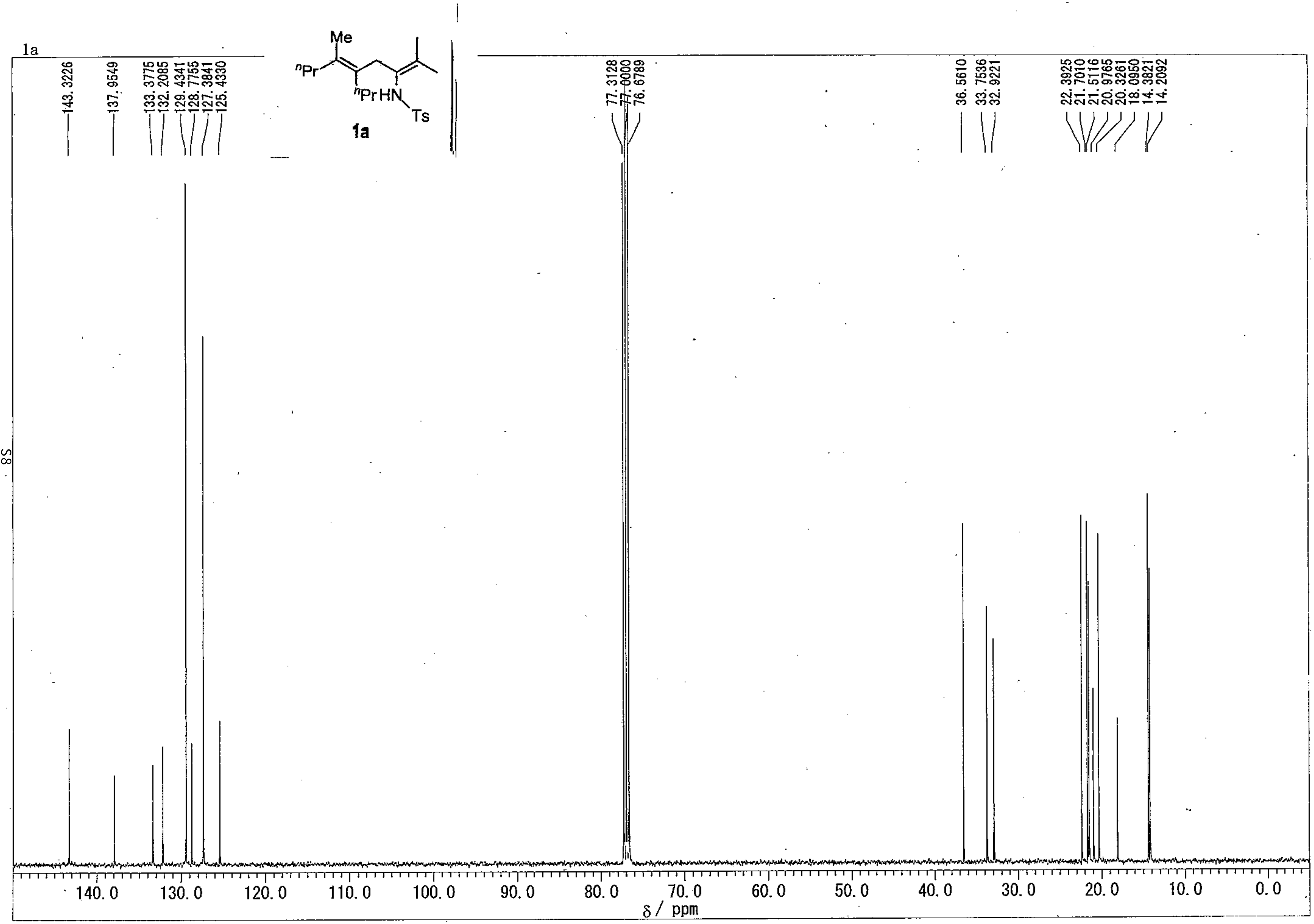
(*E*)-2,5,6,7-Tetramethyl-*N*-*p*-toluenesulfonylocta-2,5-dien-3-amine (**1e**, major isomer) and **5-isopropyl-2,6-dimethyl-*N*-*p*-toluenesulfonylhepta-2,5-dien-3-amine** (**1e'**, minor isomer): (a mixture of regioisomers in a 1.8 : 1 ratio): IR (neat) 3275 (w), 2963 (m), 2932 (m), 2930 (m), 2870 (w), 1599 (w), 1323 (m), 1265 (m), 1165 (s), 1092 (m), 814 (w), 739 (s) cm^{-1}; ^{1}H NMR (C_6D_6, 400 MHz, major isomer) δ 0.92 (d, J = 6.8 Hz, 6 H), 1.47 (s, 3 H), 1.50 (s, 3 H), 1.50 (s, 3 H), 1.55 (s, 3 H), 1.89 (s, 3 H), 2.81 (sept, J = 6.8 Hz, 1 H), 3.00 (s, 2 H), 5.48 (s, 1 H), 6.78 (d, J = 8.3 Hz, 2 H), 7.82 (d, J = 8.3 Hz, 2 H); ^{1}H NMR (C_6D_6, 400 MHz, minor isomer) δ 0.91 (d, J = 6.8 Hz, 6 H), 1.47 (s, 3 H), 1.58 (s, 3 H), 1.58 (s, 3 H), 1.74 (s, 3 H), 1.87 (s, 3 H), 2.70 (sept, J = 6.8 Hz, 1 H), 3.05 (s, 2 H), 5.56 (s, 1 H), 6.75 (d, J = 8.3 Hz, 2 H), 7.28 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz, major isomer) δ 11.9, 16.5, 20.4, 20.6, 20.9, 21.5, 30.3, 36.2, 122.4, 125.3, 127.4, 129.5, 132.3, 137.7, 138.0, 143.3; ^{13}C NMR ($CDCl_3$, 100 MHz, minor isomer) δ 20.6, 20.9, 21.2, 21.4, 21.5, 21.6, 30.5, 31.2, 126.1, 127.5, 129.4, 129.6, 130.0, 132.7, 138.2, 143.3; High-resolution MS (major isomer), calcd for $C_{19}H_{29}NO_2S$: 335.1919. Found m/z (relative intensity): 335.1922 (M+, 100), 333 (1), 320 (3); High-resolution MS (minor isomer), calcd for $C_{19}H_{29}NO_2S$: 335.1919. Found m/z (relative intensity): 335.1930 (M+, 100), 333 (1), 320 (3).

(*E*)-Dimethyl-6-(trimethylsilyl)-*N*-*p*-toluenesulfonylhepta-2,5-dien-3-amine (**1f**, major isomer) and **2,6-dimethyl-5-(trimethylsilyl)-*N*-*p*-toluenesulfonylhepta-2,5-dien-3-amine** (**1f'**, minor isomer): (a mixture of regioisomers in a 4.0 : 1 ratio): IR (KBr, major isomer) 3260 (s), 3252 (s), 2953 (s), 2862 (s), 2719 (m), 1904 (w), 1601 (s), 1402 (s), 1157 (s), 953 (m), 754 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, 400 MHz, major isomer) δ 0.10 (s, 9 H), 1.49 (s, 3 H), 1.55 (s, 3 H), 1.62 (s, 3 H), 1.73 (s, 3 H), 2.42 (s, 3 H), 2.90 (s, 2 H), 5.20 (s, 1 H), 7.28 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H); ^{1}H NMR (CDCl$_3$, 400 MHz, minor isomer) δ 0.08 (s, 9 H), 1.43 (s, 3 H), 1.61 (s, 3 H), 1.71 (s, 3 H), 1.87 (s, 3 H), 2.42 (s, 3 H), 3.00 (s, 2 H), 5.36 (s, 1 H), 7.27 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$, 100 MHz, major isomer) δ 0.4, 17.9, 20.4, 20.7, 21.5, 22.0, 36.4, 125.1, 127.4, 129.5, 131.8, 132.4, 137.8, 141.3, 143.4; 13C NMR (CDCl$_3$, 100 MHz, minor isomer) δ 0.8, 20.7, 21.3, 21.5, 21.8, 26.1, 34.7, 125.8, 127.5, 128.2, 129.4, 129.8, 138.4, 143.2, 149.2; High-resolution MS (major isomer), calcd for $C_{19}H_{31}NO_2SSi$: 365.1845. Found m/z (relative intensity): 365.1856 (M+, 100), 363 (35), 350 (47); High-resolution MS (minor isomer), calcd for $C_{19}H_{31}NO_2SSi$: 365.1845. Found m/z (relative intensity): 365.1856 (M+, 100), 350 (37).

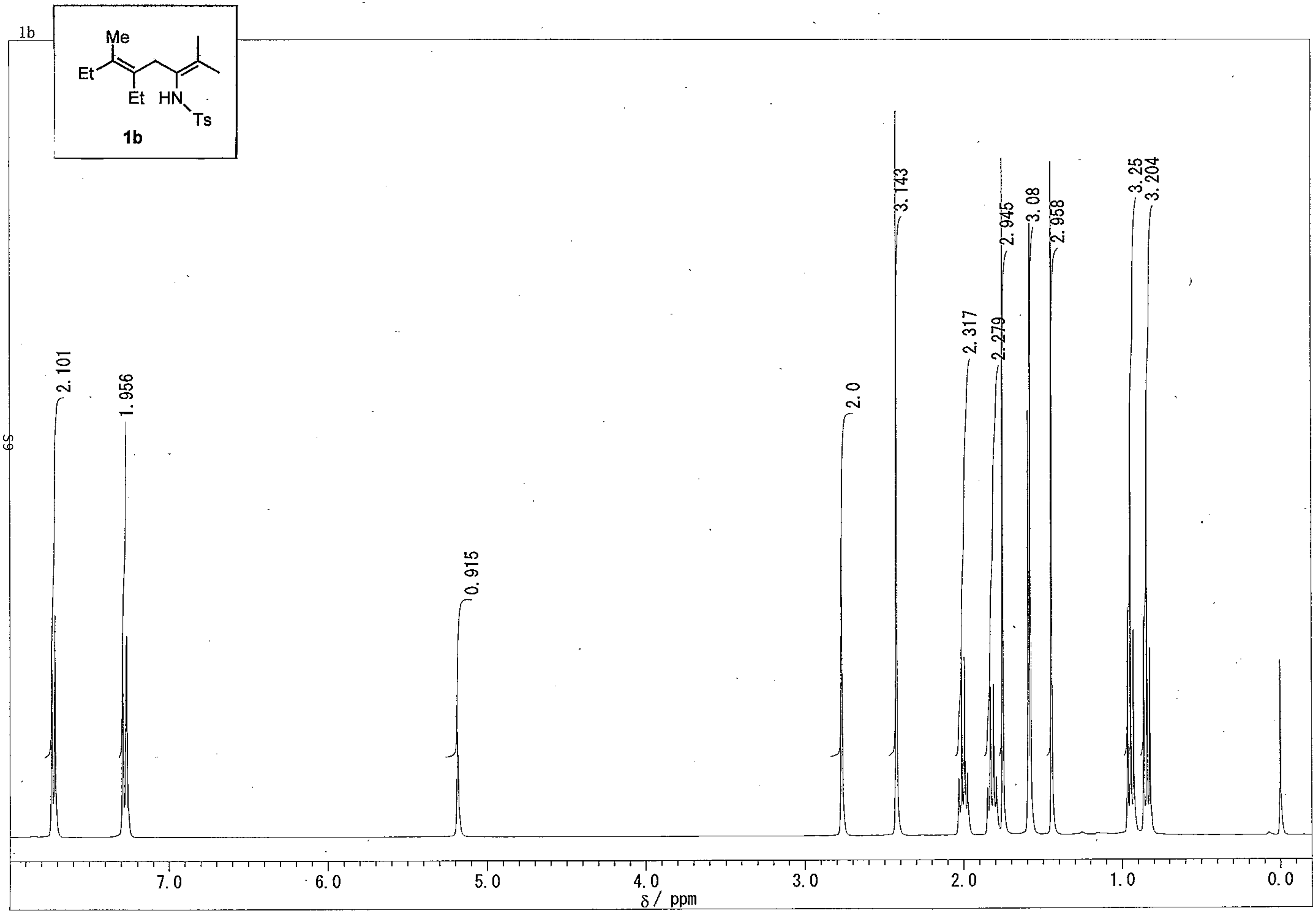
Reference

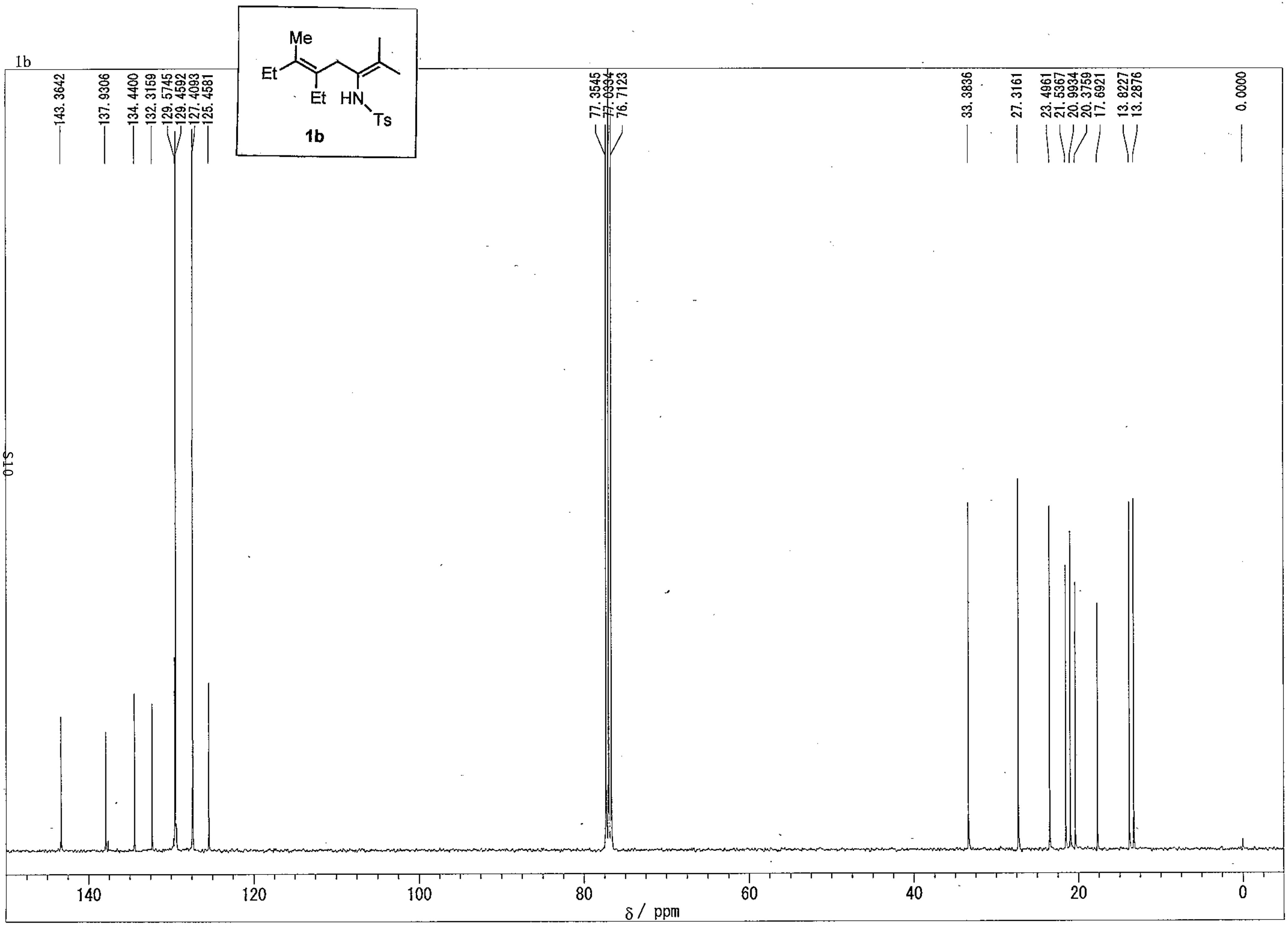
M. Kimura, S. Kure, Z. Yoshida, S. Tanaka, K. Fugamai and Y. Tamaru, *Tetrahedron Lett.*, 1990, 31, 4887; Y. Tamaru, M. kimura, S. Tanaka, S. Kure and Z. Yoshida, *Bull. Chem. Soc.*1990, 67, 2838.

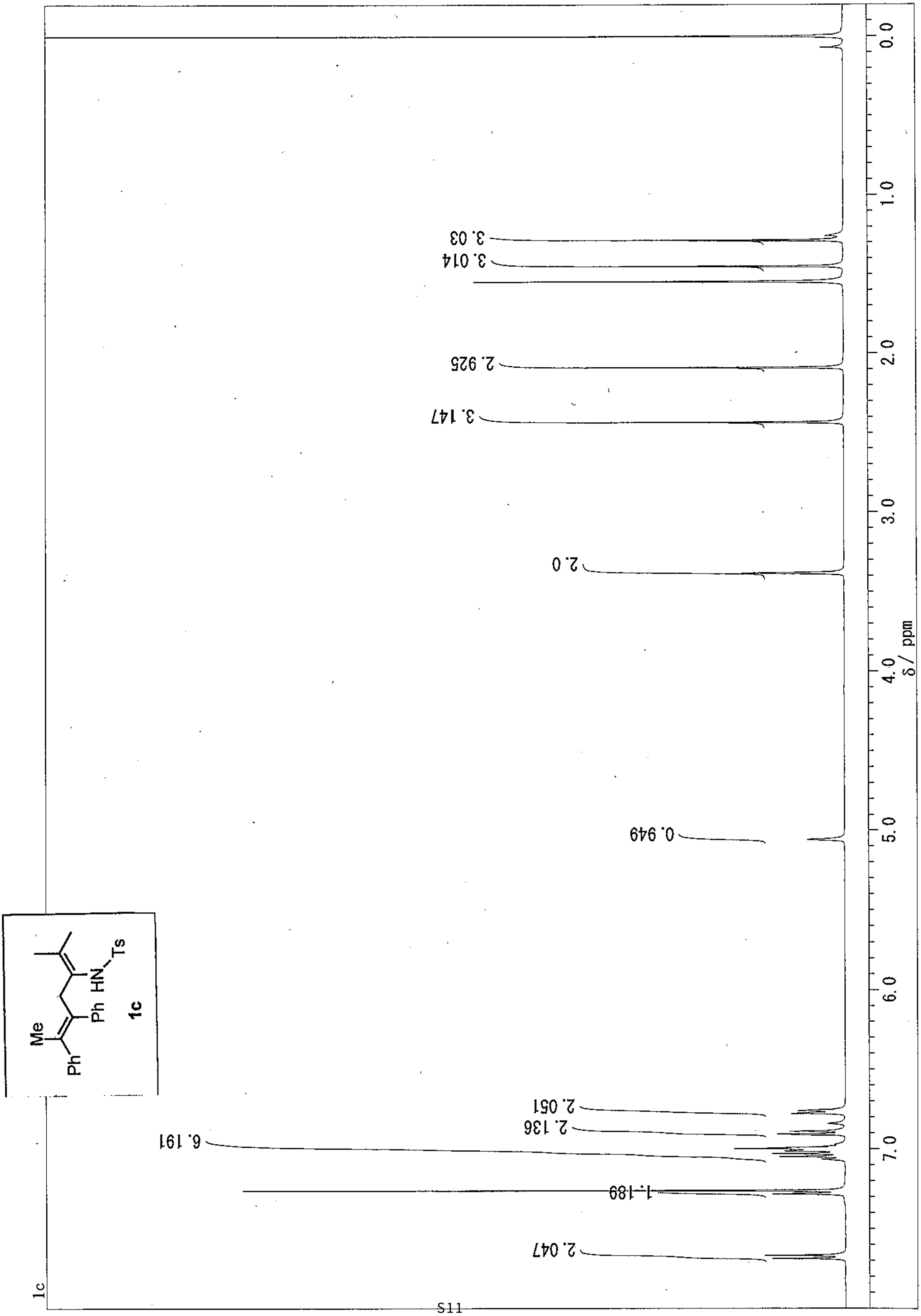

1a
Me
ⁿPr
ⁿPrHN
Ts
1a
2.126
2.296
0.814
2.0
2.233
5.596
2.981
3.075
4.342
6.061
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm

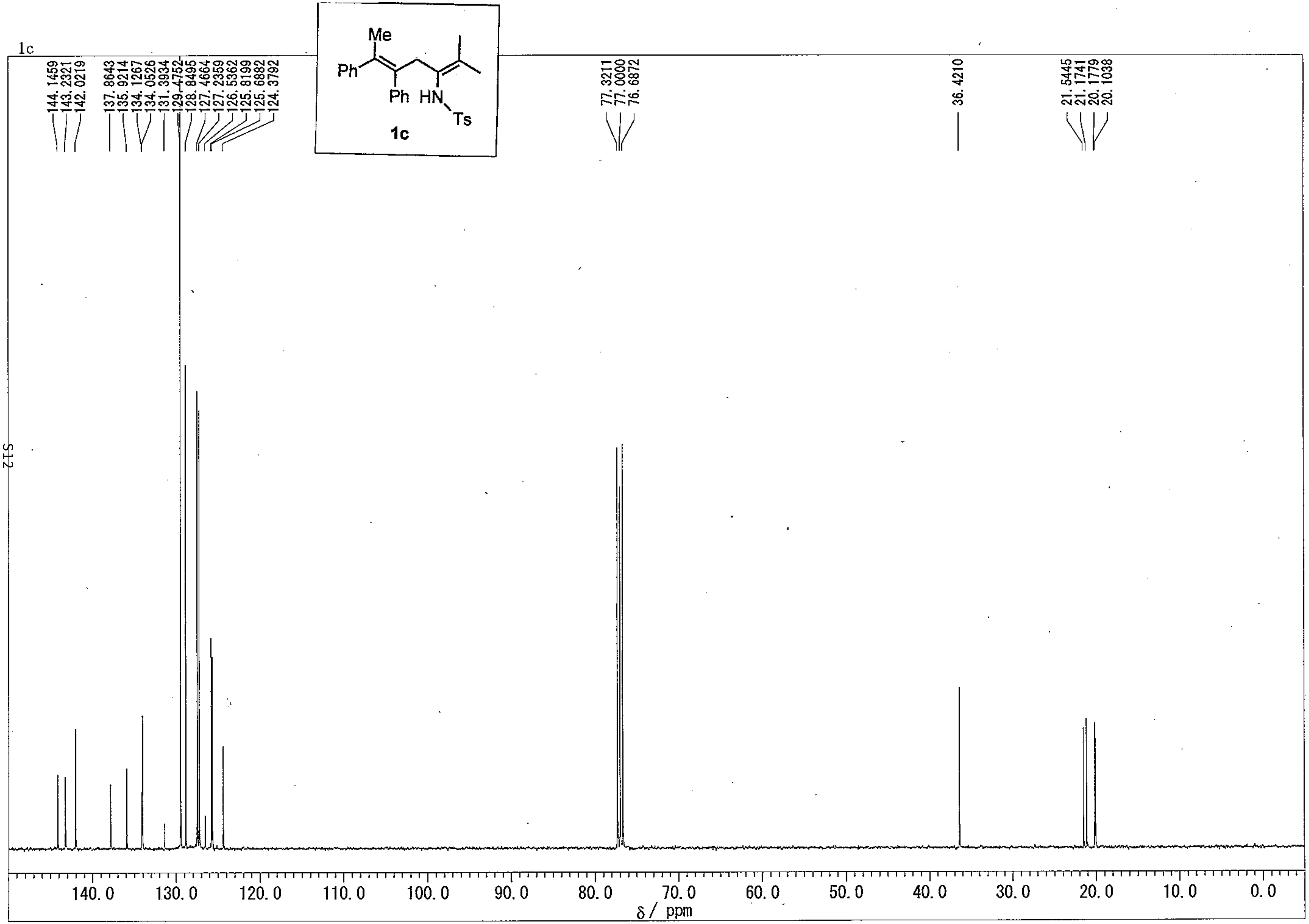

1a
143.3226
137.9549
133.3775
132.2085
129.4341
128.7755
127.3841
125.4330
Me
ⁿPr
ⁿPr HN
Ts
1a
77.3128
77.0000
76.6789
36.5610
33.7536
32.9221
22.3925
21.7010
21.5116
20.9765
20.3261
18.0950
14.3821
14.2092
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm

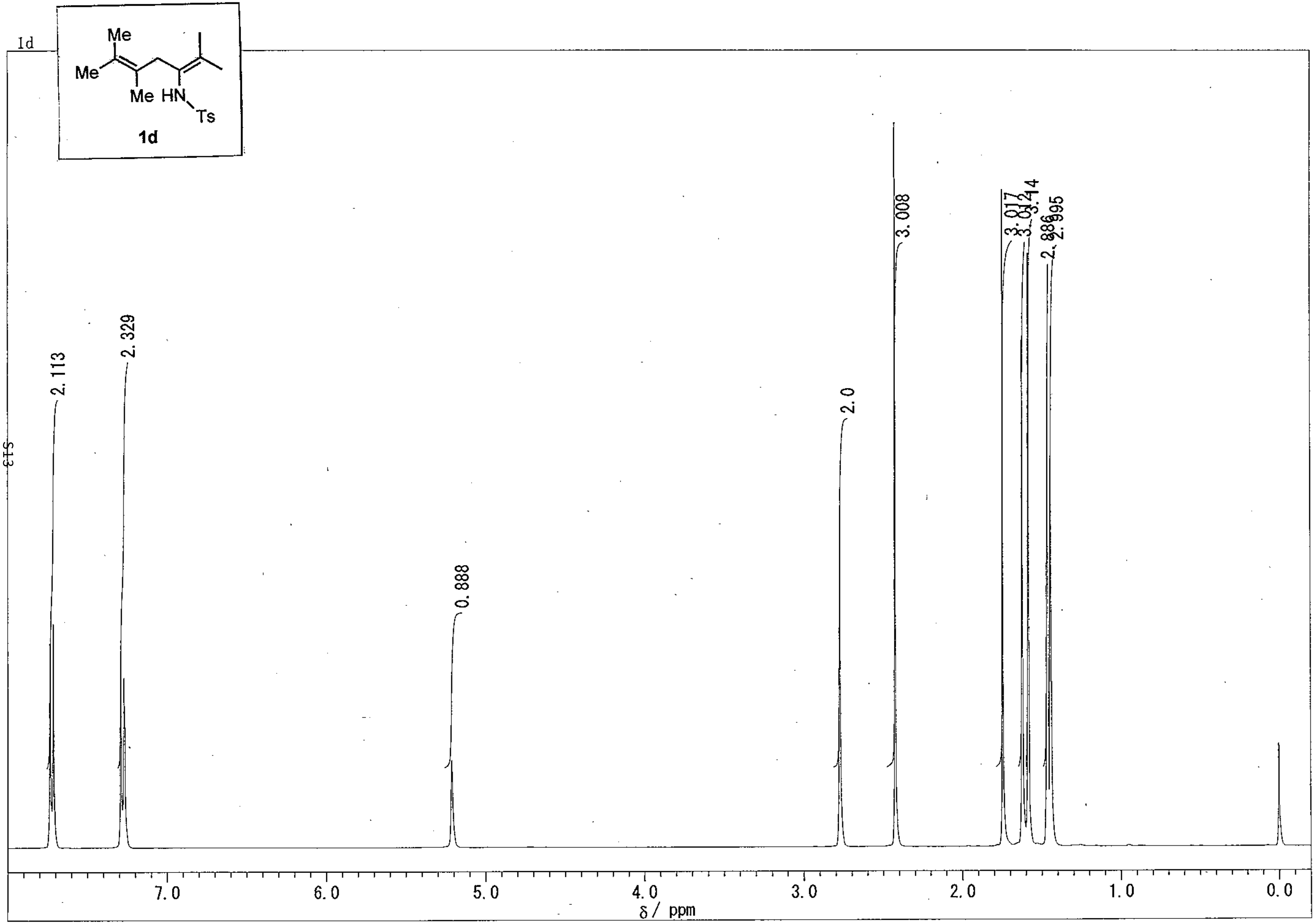
]

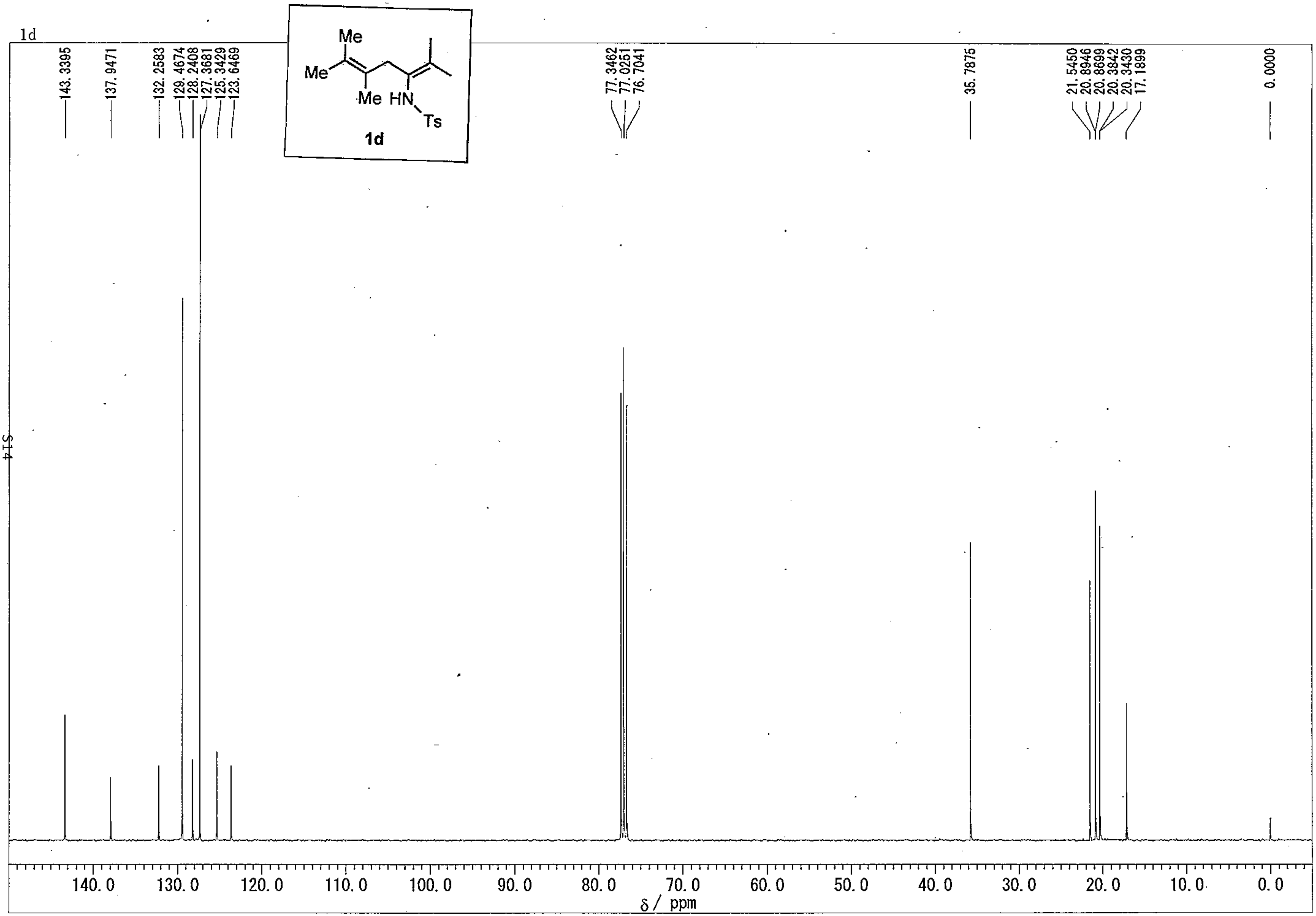

1b
Me
Et
Et
HN
Ts
1b
2.101
1.956
0.915
2.0
3.143
2.317
2.279
2.945
3.08
2.958
3.25
3.204
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm


1b
143.3642
137.9306
134.4400
132.3159
129.5745
129.4592
127.4093
125.4581
77.3545
77.0334
76.7123
33.3836
27.3161
23.4961
21.5367
20.9934
20.3759
17.6921
13.8227
13.2876
0.0000
Me
Et
Et
HN
Ts
1b
140
120
100
80
60
40
20
0
δ / ppm

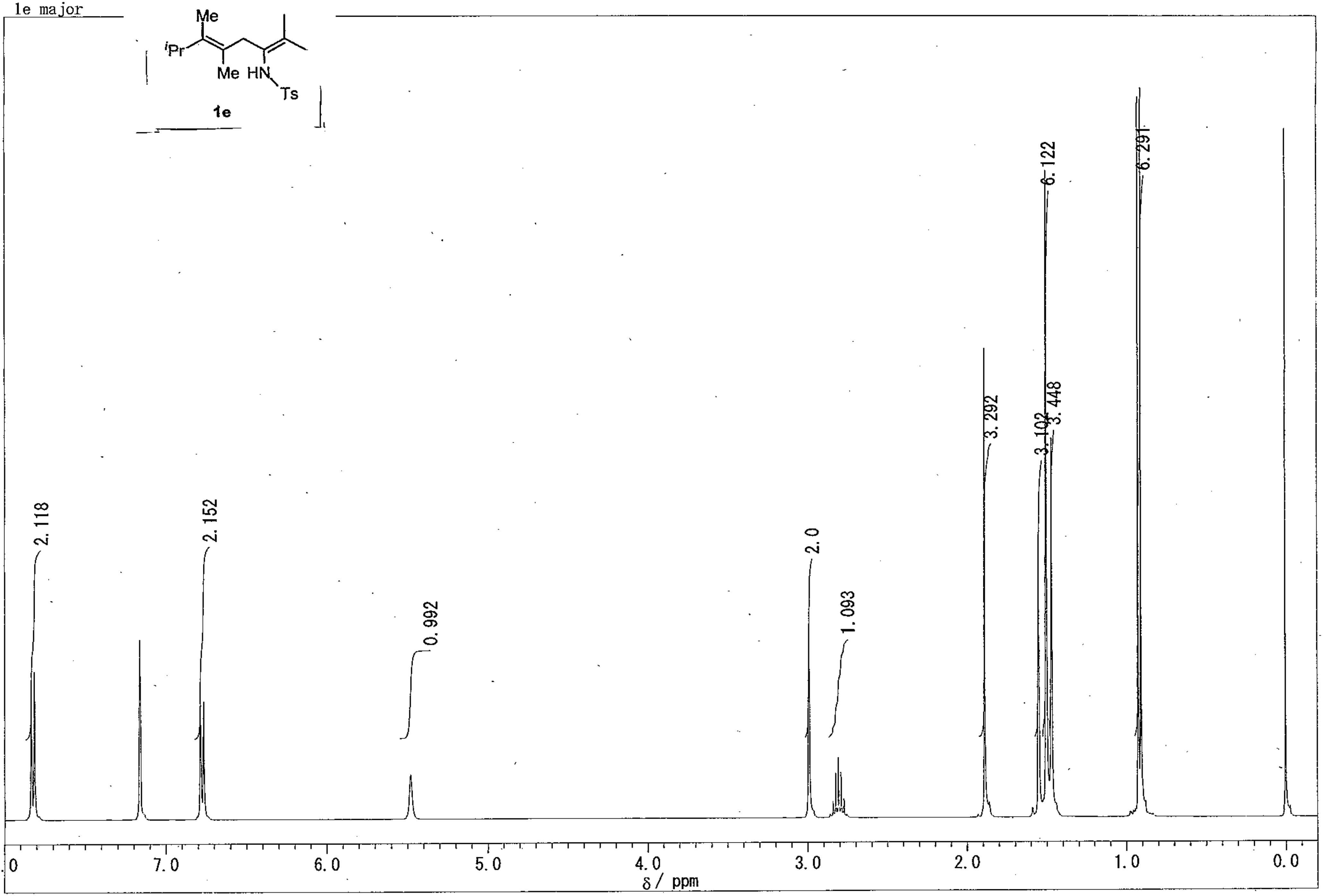

1c
3.03
3.014
2.925
3.147
2.0
0.949
2.051
2.136
6.191
1.189
2.047
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
δ / ppm
Me
Ph
Ph
HN
Ts
1c

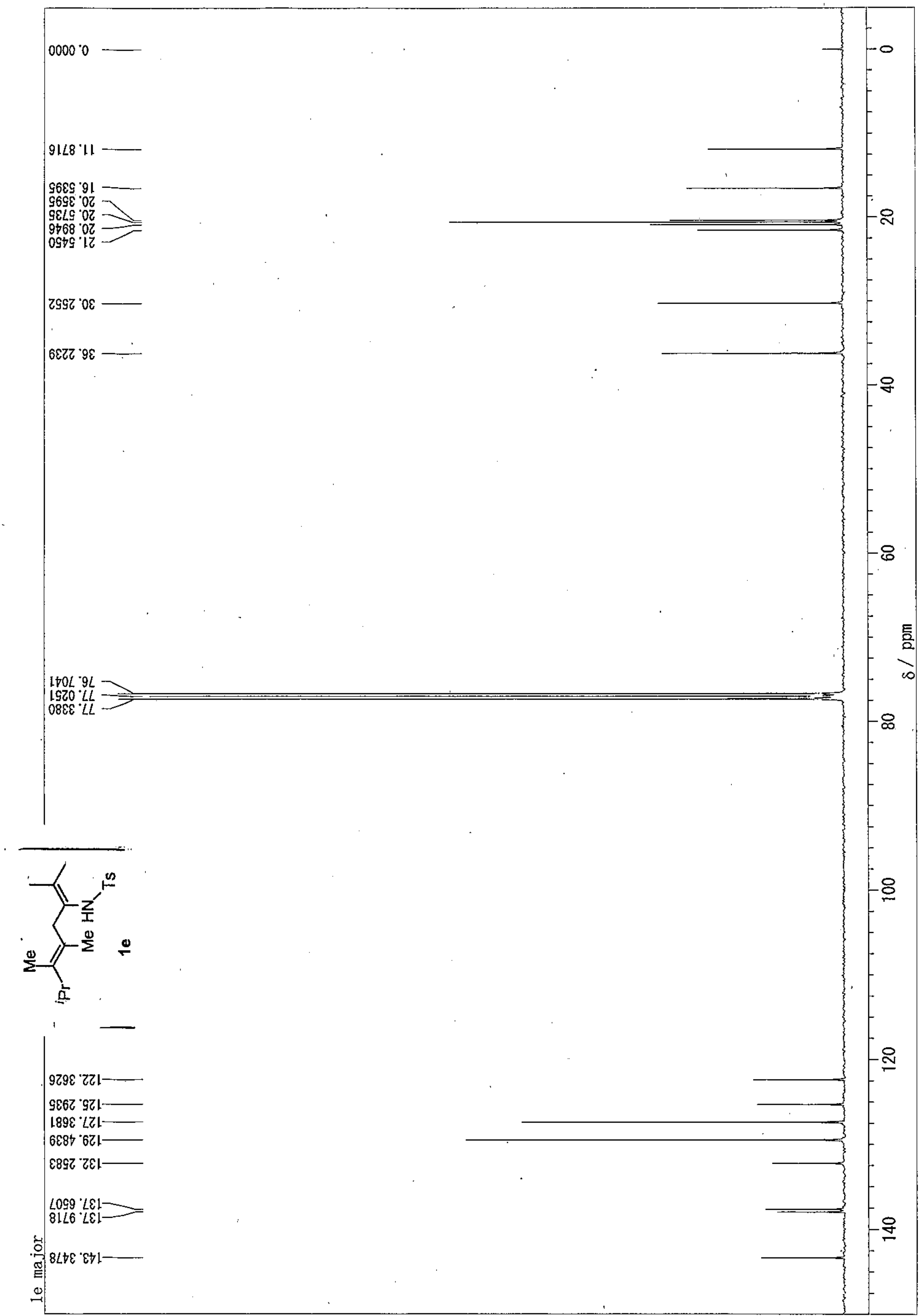

1c
144.1459
143.2321
142.0219
137.8643
135.9214
134.1267
134.0526
131.3934
129.4752
128.8495
127.4664
127.2359
126.5362
125.8199
125.6882
124.3792
Me
Ph
Ph
HN
Ts
1c
77.3211
77.0000
76.6872
36.4210
21.5445
21.1741
20.1779
20.1038
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm

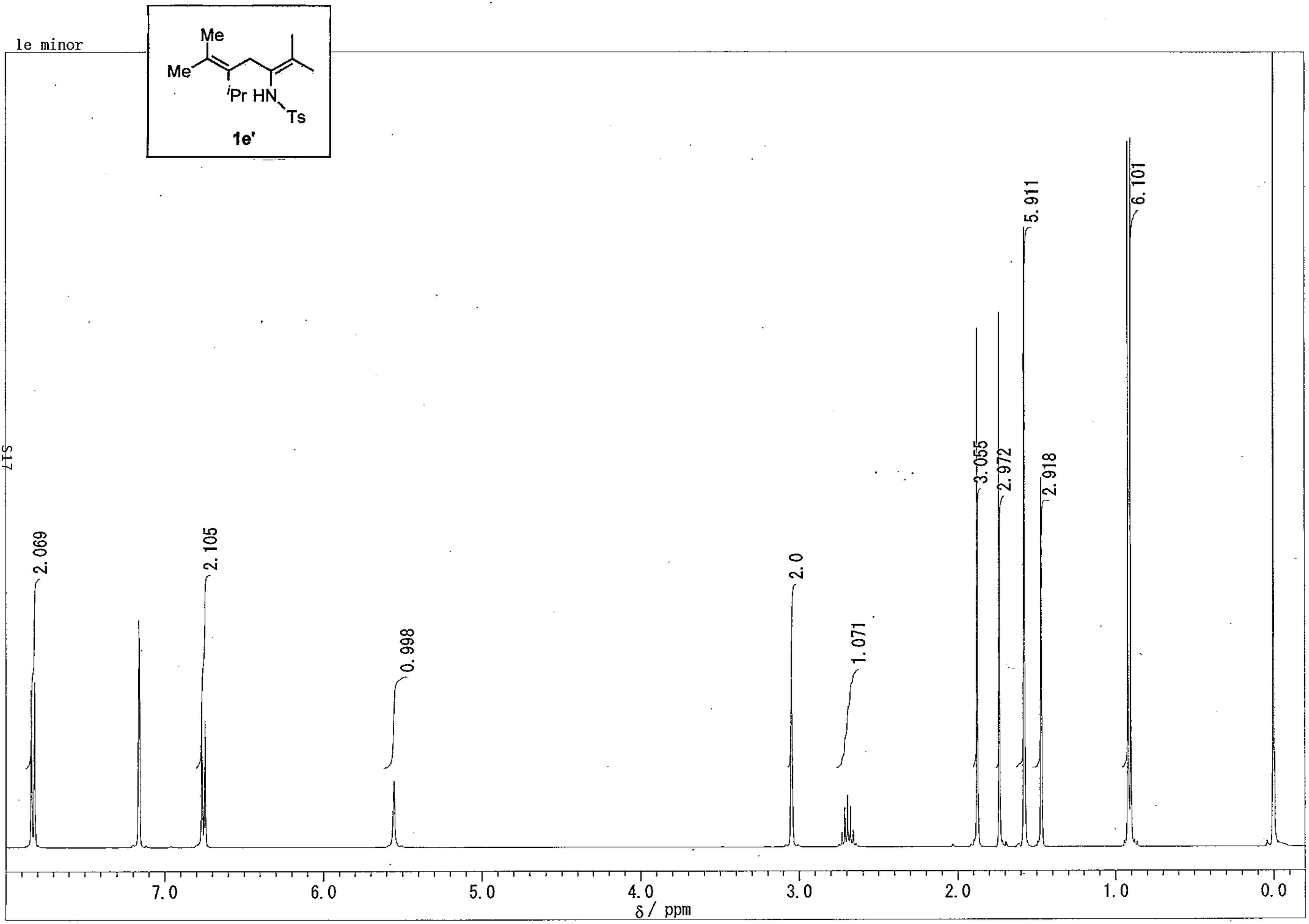

1d
Me
Me
Me
HN
Ts
1d
2.113
2.329
0.888
2.0
3.008
3.017
3.012
3.14
2.886
2.995
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm

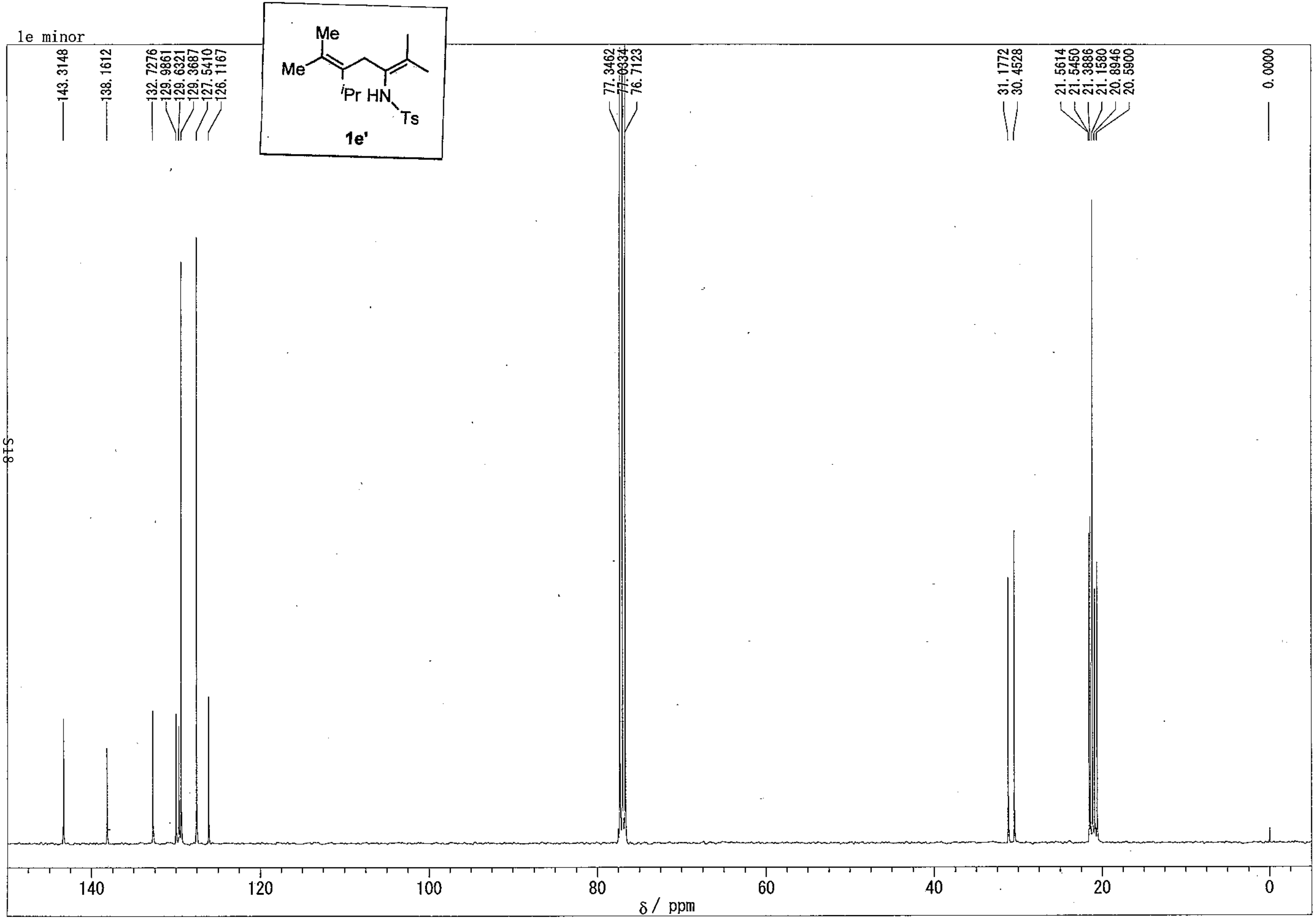

1d
143.3395
137.9471
132.2583
129.4674
128.2408
127.3681
125.3429
123.6469
Me
Me
Me
HN
Ts
1d
77.3462
77.0251
76.7041
35.7875
21.5450
20.8946
20.8699
20.3842
20.3430
17.1899
0.0000
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
δ / ppm

1e major


Me
iPr
Me
HN
Ts
1e
2.118
2.152
0.992
2.0
1.093
3.292
3.102
3.448
6.122
6.291
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm


1e major
0.0000
11.8716
16.5395
20.3595
20.5735
20.8946
21.5450
30.2552
36.2239
76.7041
77.0251
77.3380
122.3626
125.2935
127.3681
129.4839
132.2583
137.6507
137.9718
143.3478
0
20
40
60
80
100
120
140
δ / ppm
Me
iPr
Me
HN
Ts
1e


1e minor
Me
Me
iPr HN
Ts
1e'
2.069
2.105
0.998
2.0
1.071
3.055
2.972
5.911
2.918
6.101
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm

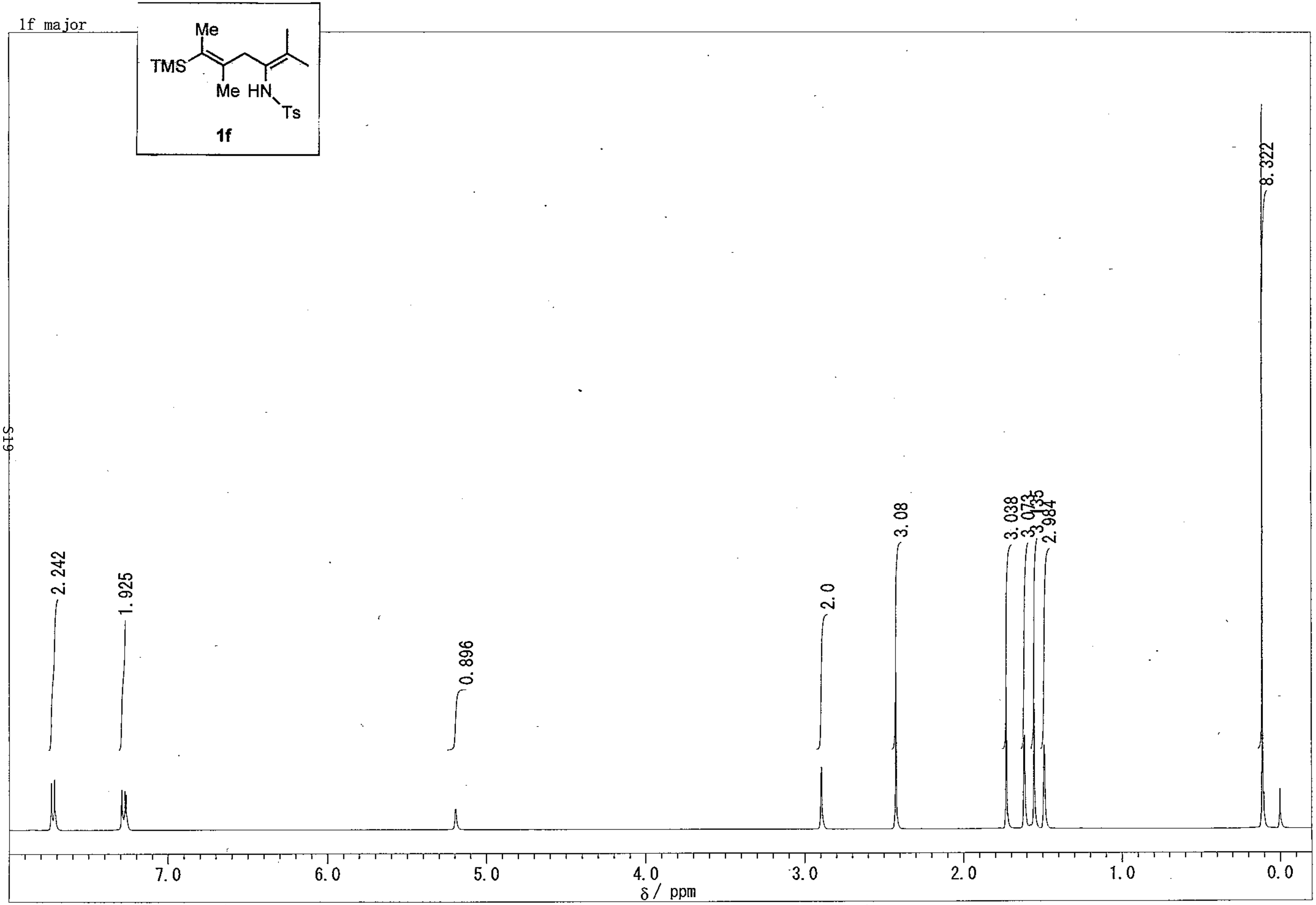


1e minor

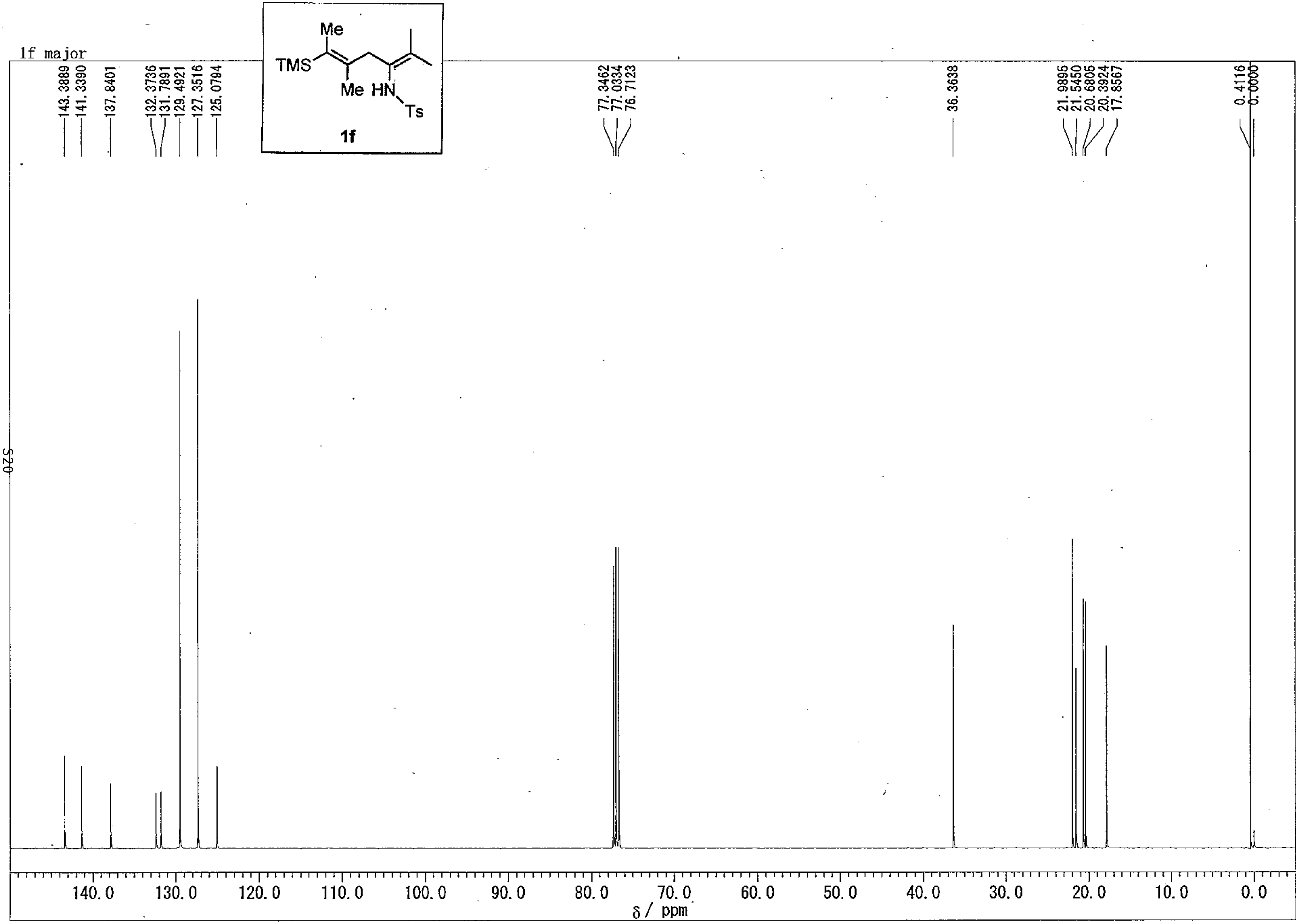
1e'

Me
Me
iPr HN
Ts
143.3148
138.1612
132.7276
129.9861
129.6321
129.3687
127.5410
126.1167
77.3462
77.0334
76.7123
31.1772
30.4528
21.5614
21.5450
21.3886
21.1580
20.8946
20.5900
0.0000
140
120
100
80
60
40
20
0
δ / ppm

1f major


Me
TMS
Me
HN
Ts
2.242
1.925
0.896
2.0
3.08
3.038
3.073
3.135
2.984
8.322
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm

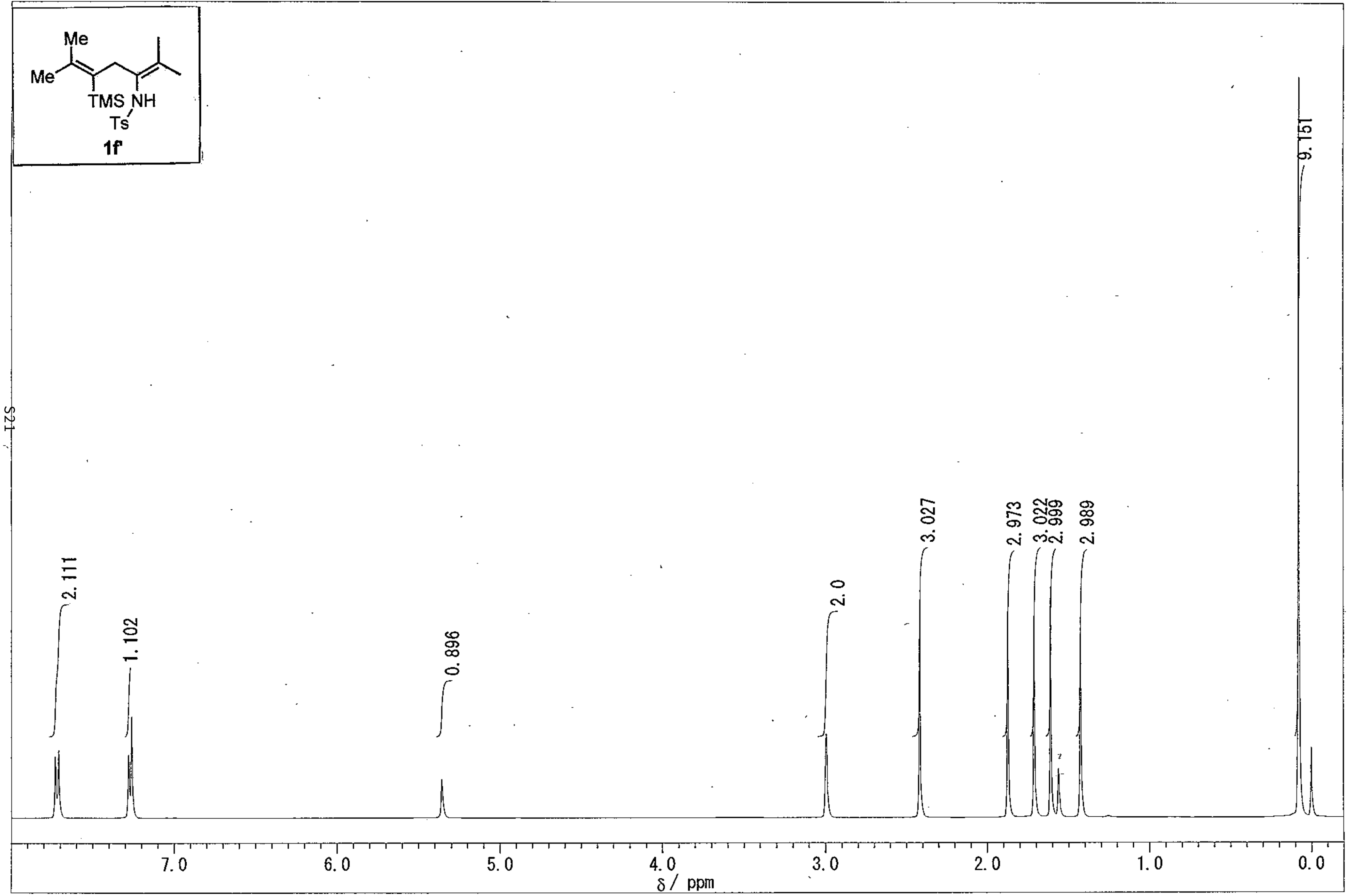
1f



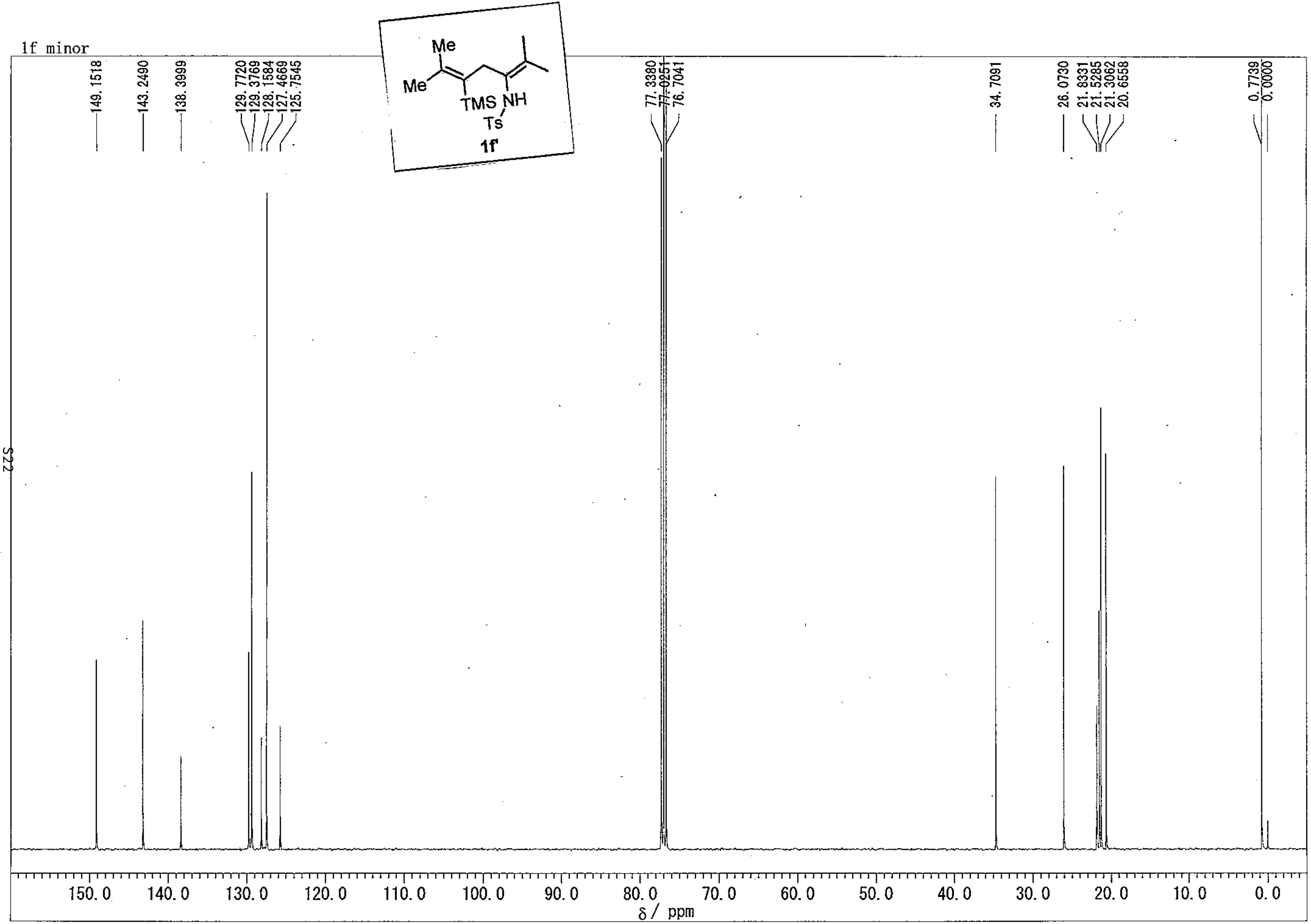
1f

1f major
TMS
Me
Me
HN
Ts
143.3889
141.3390
137.8401
132.3736
131.7891
129.4921
127.3516
125.0794
77.3462
77.0334
76.7123
36.3638
21.9895
21.5450
20.6805
20.3924
17.8567
0.4116
0.0000
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
0.0
δ / ppm

1f minor


1f'

Me
Me
TMS
NH
Ts
2.111
1.102
0.896
2.0
3.027
2.973
3.022
2.999
2.989
9.151
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ / ppm


1f minor

149.1518
143.2490
138.3999
129.7720
129.3769
128.1584
127.4669
125.7545
77.3380
77.0251
76.7041
34.7091
26.0730
21.8331
21.5285
21.3062
20.6558
0.7739
0.0000
Me
Me
TMS
NH
Ts
1f'
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
0.0
δ / ppm