Supporting Information

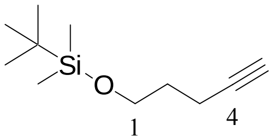
Studies on Transannulation Reactions Across a Nine-Membered Ring: the Synthesis of Natural Product-like Structures.

Mudassar Iqbal, Richard J. G. Black, Joby Winn, Andrew T. Reeder, Alexander J. Blake and Paul A. Clarke

General Experimental Details

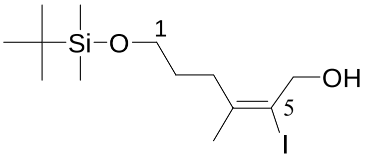
All reactions were carried out under N_2 unless otherwise specified. IR analyses were carried out on ThermoNicolet Avatar 370 FT-IR and ThermoNicolet IR100 spectrometer using NaCl plates or cesium fluoride solution cell. Nuclear magnetic resonance spectra were recorded on a Jeol EX-270 MHz, a Jeol ECX-400 MHz, a Jeol ECS-400 MHz and Bruker AV-500 MHz spectrometer at ambient temperature; chemical shifts are quoted in parts per million (ppm) and were referenced as follows: chloroform-*d*, δ_H 7.26 ppm; chloroform-*d*, δ_C 77.0 ppm, benzene-*d*, δ_H 7.16 ppm; benzene-*d*, δ_C 128.02 ppm, for the processing of 'fid' data the software delta and mestrec were used for Jeol 270 MHz and 400 MHz system and topspin was used for Bruker AV 500 MHz. The following abbreviations have been used to describe the signal multiplicity; s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); app (apparent); br (broad) and *J* (coupling constant in Hz). The mass spectrometry was performed by the University of York mass spectrometry service ESI or EI ionisation techniques, for accurate mass the samples were submitted to Swansea Mass spectrometry centre. Melting points were determined using a Stuart SMP3 apparatus and remain uncorrected. Optical rotaions were carried out at ambient temperature using a JASCO DIP-370 digital polarimeter. The molecular modelling calculations were carried out using AMI method on the Spartan `08, interatomic distances were calculated by using Spartan student version. Thin layer chromatography was performed on glass-backed plates coated with Merck Silica gel 60 F_{254}. Silver nitrate impregnated TLC plates were prepared by absorbing a silver nitrate solution on the plates and activating at 120 °C in oven for one night. The plates were developed using ultraviolet light, acidic aqueous ceric ammonium molybdate, basic aqueous potassium permanganate, ethanolic anisaldehyde or ninhydrin dip. Liquid chromatography was performed using forced flow (flash column) with the solvent systems indicated. The stationary phase was silica gel 60 (220-240 mesh) supplied by Fluorochem or silica gel Merck TLC grade 11695 supplied by Sigma-Aldrich. The silver nitrate impregnated silica was prepared by adsorbing silver nitrate on silica (10% w/w). Dichloromethane was distilled from calcium hydride; THF and diethyl ether were distilled from sodium-benzophenone; toluene was dried over sodium wire prior to use. All other solvents and reagents were used as received from commercial suppliers.

Experimental Procedures and Data for Compounds not Reported in the Main Paper

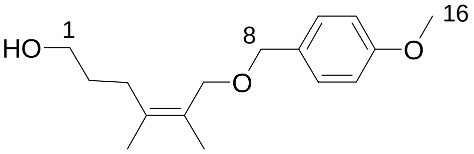


***tert*-Butyldimethyl(pent-4-ynloxy)silane** Imidazole (9.7 g, 143 mmol) was added to a solution of 4-pentyn-1-ol (5 g, 59 mmol) dissolved in DMF (50 mL) under an N_2 atmosphere at 25 °C and stirred until all solids had dissolved. TBSCl (10.7 g, 71 mmol) was then added to the solution with stirring continued for a further 4 h. After this period the mixture was washed with water (50 mL) and extracted with Et_2O (4 x 50 mL). The organics were combined the washed with brine (100 mL) before being dried over $MgSO_4$ and concentrated *in vacuo* to yield a colourless oil which did not require further purification (11.7 g, 100%). IR (film): ν_{max} 2926, 2855, 1471, 1457, 1387, 1255, 1106, 835, 776 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ 3.67 (2H, t, J = 6.3 Hz, H-1), 2.25 (2H, dt, J = 7.0, 2.8 Hz, H-3), 1.91 (1H, t, J = 2.8 Hz, H-5), 1.70 (2H, m, H-2), 0.87 (9H, s, CH_3-TBS), 0.05 (6H, s, CH_3-TBS) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 84.2 (C, C-4), 68.2 (CH, C-5), 61.4 (CH_2, C-1), 31.5 (CH_2, C-2), 25.9 (CH_3, TBS),

18.3 (C, TBS), 14.8 (CH_2, C-3), -5.4 (CH_3, TBS) ppm. HRMS (ESI): found (M + H^+): 199.1513, $C_{11}H_{23}OSi$ requires (M + H^+): 199.1507.

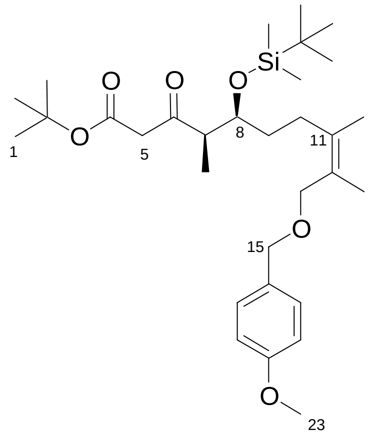


(*E*)-6-(*tert*-butyldimethylsilanyloxy)-2-iodo-3-methylhex-2-en-1-ol DIBAL-H (1 M in CH_2Cl_2, 20 mL, 20 mmol) was added a solution of **49** (4.0 g, 10 mmol) in dichloromethane : hexane, 2:1, (60 mL) at -78°C, under a nitrogen atmosphere and stirred for 3 h. The solution was treated with methanol (15 mL) and then saturated aqueous Rochelle's salt (1 M, 20 mL) and allowed to stir for 1 h upon warming to 25 °C. The solution was extracted with CH_2Cl_2 (2 x 50 mL) and washed with brine (100 mL) before being dried over $MgSO_4$ and concentrated *in vacuo.* Purification *via* flash column chromatography on silica gel with a mobile phase of petroleum ether: EtOAc, 20:1, yielded a pale yellow oil (3.4 g, 92 %). IR (film): ν_{max} 3395, 2927, 2856, 1634, 1471, 1387, 1361, 1255, 1103 cm^{-1}. ^1H NMR ($CDCl_3$, 270 MHz): δ 4.39 (2H, d, *J* = 6.6 Hz, H-6), 3.58 (2H, t, *J* = 5.9 Hz, H-1), 2.77 (1H, t, *J* = 7.0 Hz, OH), 2.43 (2H, t, *J* = 7.0 Hz, H-3), 1.92 (3H, s, Me-4), 1.62 (2H, m, H-2), 0.88 (9H, s, CH_3-TBS), 0.05 (6H, s, CH_3-TBS) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.5 (C, C-4), 104.2 (C, C-5), 68.3 (CH_2, C-6), 61.2 (CH_2, C-1), 30.7 (CH_2, C-2), 29.6 (CH_2, C-3), 29.5 (CH_3, C-4), 25.9 (CH_3, TBS), 18.3 (C, TBS), -5.3 (CH_3, TBS) ppm. HRMS (ESI): found (M + H^+): 271.0898, $C_{13}H_{28}IO_2Si$ requires (M + H^+): 271.0904.



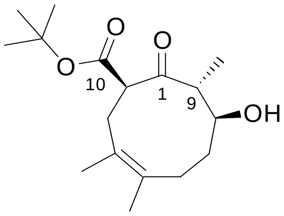
(*Z*)-4,5-dimethyl-6-(*para*-methoxybenzyloxy)-hex-4-en-1-ol TBAF (1M in THF, 17.8 mL, 17.8 mmol, 2 equiv) was added to a solution of **51** (3.8 g, 8.9 mmol, 1 equiv) in THF (20 mL) under a nitrogen atmosphere at 25 °C. The solution was allowed to stir for 1 h before being diluted with Et_2O (50 mL) and washed with saturated $NaHCO_3$ solution (40 mL) followed by brine (50 mL). The ether extracts were then dried over $MgSO_4$, and concentrated *in vacuo.* Purification *via* flash column chromatography on silica gel with a mobile phase of petroleum ether : EtOAc, 10:1, yielded the desired alcohol as a yellow oil (2.3 g, 98%). IR (film): ν_{max} 3403, 2926, 2866, 2359, 2243, 1733, 1634, 1627, 1496, 1454, 1436, 1375, 1350, 1243, 1212, 1072 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.26-6.85 (4H, m, aromatics), 4.41 (2H, s, H-8), 3.92 (2H, s, H-9), 3.78 (3H, s, H-1), 3.49 (2H, dt, *J* = 6.1, 5.8

Hz, H-16), 2.41 (1H, t, *J* = 6.1 Hz, H-17), 2.18 (2H, t, *J* = 7.0 Hz, H-14), 1.71 (3H, s, H-12), 1.65 (3H, s, H-13), 1.62 (2H, dt, *J* = 7.0, 6.1 Hz, H-15) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ 159.2 (C, aromatic), 134.1 (C, C-11), 130.2 (C, C-10), 129.7 (CH, aromatic), 126.2 (C, aromatic), 113.8 (CH, aromatic), 72.1 (CH$_2$, C-8), 70.5 (CH$_2$, C-9), 61.2 (CH$_2$, C-16), 55.2 (CH$_3$, C-1), 30.5 (CH$_2$, C-15), 29.7 (CH$_2$, C-14), 18.3 (CH$_3$, C-13), 17.9 (CH$_3$, C-12) ppm. MS (ESI): m/z 287 (M + Na$^+$), HRMS (ESI): found (M + H$^+$): 265.1798, $C_{16}H_{25}O_3$ requires (M + H$^+$): 265.1800.

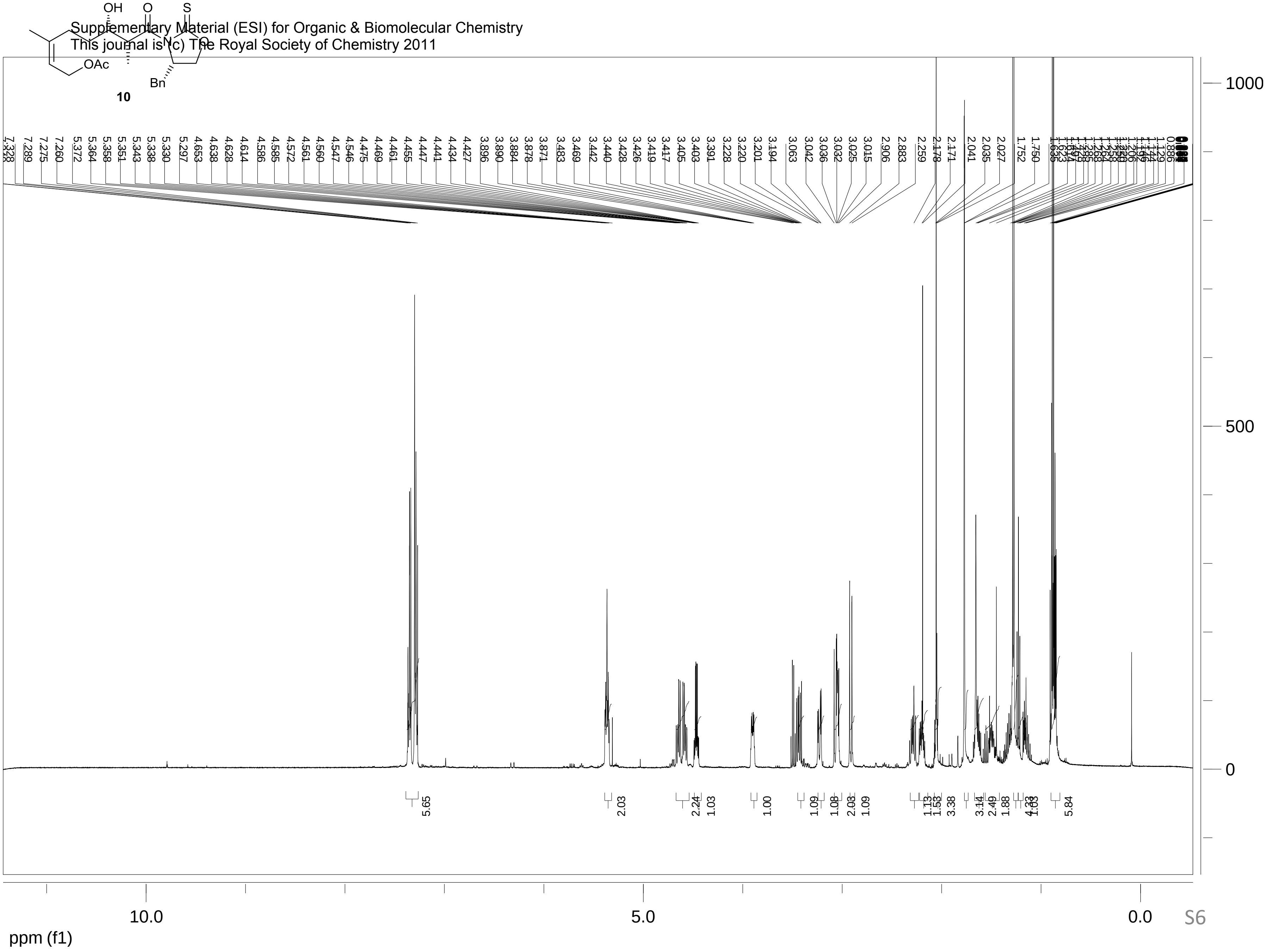


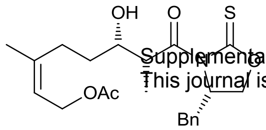
(4*R*,5*S*)-ethyl 10-(benzyloxy)-5-(*tert*-butyldimethylsilyloxy)-4,8,9-trimethyl-3-oxodec-8-enoate To a mixture of SnCl$_2$ (40 mg, 0.46 mmol, 0.1 equiv) and *tert*-butyl diazoacetate (1 g, 7.0 mmol, 1.5 equiv) in dry CH$_2$Cl$_2$ (2 mL), at 25 °C, was added the aldehyde **55** (2 g, 4.6 mmol, 1.0 equiv) dissolved in dry CH$_2$Cl$_2$ (5 mL) *via* cannula, and the reaction was heated to 35 ^{o}C and stirred for 16 h. The mixture was then cooled to room temperature, diluted with Et$_2$O (50 mL), and washed with water (40 mL) then the layers were separated. The aqueous phase was extracted with Et$_2$O (2 x 20 mL), the organic phases were combined, washed with brine (50 mL), dried over MgSO$_4$, and the solvents concentrated *in vacuo*, to give the crude as a yellow oil. Purification *via* flash column chromatography on silica gel eluting with petroleum ether : EtOAc, 20:1, gave the *β*-ketoester as a pale yellow oil (1.49 g , 67 %). $[\alpha]^{24}_{D}$ -19.2 (c = 1.40, CHCl$_3$). ν_{max} (solution; CDCl$_3$): 2952, 2930, 2857, 1739, 1712, 1634, 1613, 1512, 1461, 1367, 1246, 1149, 1065, 1034, 951, 833 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.27-6.86 (4H, m, Ar-H), 4.38 (2H, s, H-15), 3.98-3.86 (1H, m, H-8), 3.91 (2H, s, H-13), 3.80 (3H, s, H-23), 3.52 (1H, d, *J* = 15.7 Hz, H-5), 2.78 (1H, dq, *J* = 7.0, 4.0 Hz, H-7), 2.19-2.10 (1H, m, H-10), 1.90 (1H, dt, *J* = 12.5, 4.4 Hz, H-10), 1.70 (3H, s, C-12 Me), 1.67 (3H, s, C-6 Me), 1.56-1.50 (2H, m, H-9), 1.45 (9H, s, H-1), 1.05 (3H, d, *J* = 6.8 Hz, C-7 Me), 0.90 (9H, s, TBS-Me), 0.07 (6H, s, TBS-Me) ppm. ^{13}C NMR (100 MHz, CDCl$_3$) δ = 205.8 (C-6), 166.8 (C-4), 159.2 (C-Ar), 133.6 (C-11), 130.9 (C-12), 129.5 (CH-Ar), 125.8 (C-Ar), 113.8 (CH-Ar), 81.7 (C-2), 74.1 (C-15), 71.7 (C-13), 70.3 (C-8), 55.3 (C-23), 50.7 (C-7), 33.5, (C-9), 30.8 (C-10), 25.9 (CH$_3$, TBS), 18.9 (CH$_3$, C-11), 18.1 (C, TBS), 17.0

(CH_3, C-12), 11.8 (CH_3, C-7), -4.3 (CH_3, TBS), -4.1 (CH_3, TBS) ppm. HRMS (ESI): found (M + Na$^+$): 571.3425, $C_{31}H_{52}NaO_6Si$ requires (M + Na$^+$): 571.3422.

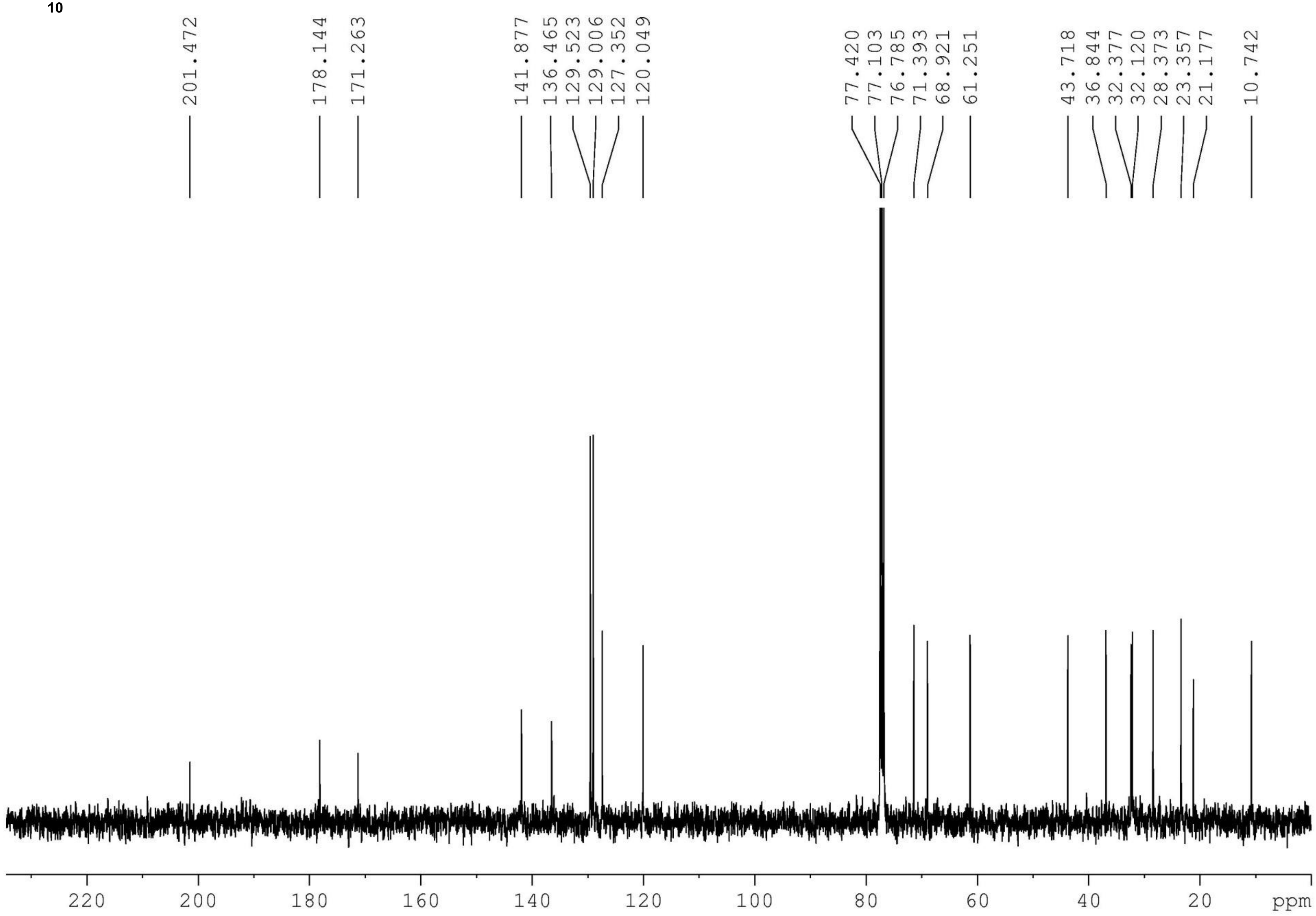


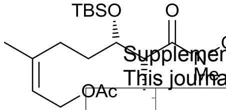
(2*R,8*S*,9*R*)-2-(*tert*-Butoxycarbonyl)-4,5,9-trimethyl-8-hydroxy-cyclonon-4-enone** To a solution of a mixture of diastereomers of **42a/b** (403 mg, 0.98 mmol) in acetonitrile (7 mL) was added a 48 % aqueous HF solution (987 μl, 23.7 mmol, 24 equiv) at room temperature. The reaction mixture was stirred at 25 °C for 16 h, diluted with Et_2O (50 mL) and quenched with saturated aqueous $NaHCO_3$ solution (5 mL). The layers were separated and the organic phase was washed with saturated aqueous $NaHCO_3$ solution (3 x 10 mL). The combined aqueous washings were extracted with Et_2O (4 x 10 mL). The combined organics were washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo* leaving the alcohol as a mixture of inseparable diastereoisomers (286 mg, 100 %). $[\alpha]^{24}_D$ -22.9 (c = 0.60, $CHCl_3$). ν_{max} (solution; $CDCl_3$): 3435, 2981, 2933, 1734, 1699, 1643, 1455, 1369, 1265, 1149, 1030, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (1H, dt, *J* = 8.8, 5.1 Hz, H-8 minor), 3.62 (1H, dd, *J* = 11.4, 1.8 Hz, H-2 major), 3.54 (1H, dt, *J* = 9.5, 2.6 Hz, H-8 major), 3.46 (1H, dd, *J* = 11.0, 1.8 Hz, H-2 major), 2.92 (1H, dd, *J* = 14.3, 11.4 Hz, H-3), 2.81 (2H, m, H-9 minor), 2.71 (2H, m, H-9 major), 2.34 (1H, d, *J* = 14.3 Hz, H-3), 2.24 (1H, m, H-6), 2.10 (1H, m, H-6), 1.92 (1H, m, H-7), 1.82 (1H, m, H-7), 1.73 (3H, s, C-4 Me minor), 1.68 (3H, s, C-4 Me major), 1.64 (3H, s, C-5 Me minor), 1.62 (3H, s, C-4 Me major), 1.42 (9H, s, $^{t-}$Bu), 1.29 (3H, d, *J*= 7.0 Hz, C-9 Me major), 1.07 (3H, d, *J*= 7.0 Hz, C-9 Me minor) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 213.8 (C-1 minor), 211.8 (C-1 major), 168.7 (C-10 major), 162.8 (C-10 minor), 132.7 (C-5 minor), 130.2 (C-5 major), 126.4 (C-4 major), 119.8 (C-4 minor), 82.1 (C, $^{t-}$Bu major), 81.5 (C, $^{t-}$Bu minor), 74.1 (C-8 minor), 70.1 (C-8 major), 57.6 (C-2 minor), 56.0 (C-2 major), 54.3 (C-9 major), 53.2 (C-9 minor), 35.3 (C-7, major), 35.2 (C-6. major), 34.7 (C-7 minor), 33.3 (C-6 minor), 29.5 (C-3 major), 28.9 (C-3 minor), 28.0 (CH_3, $^{t-}$Bu), 20.5 (CH_3, C-5 minor), 19.8 (C-5 major), 18.3 (CH_3, C-4 minor), 17.7 (CH_3, C-4 major), 15.2 (CH_3, C-9 major), 14.0 (CH_3 C-9 minor) ppm. HRMS (ESI): found (M + Na$^+$): 319.1880, $C_{17}H_{28}NaO_4$ requires (M + H$^+$): 319.1869.


OH
O
S
N
O
OAc
Bn
10
7.328
7.289
7.275
7.260
5.372
5.364
5.358
5.351
5.343
5.338
5.330
5.297
4.653
4.638
4.628
4.614
4.586
4.585
4.572
4.561
4.560
4.547
4.546
4.475
4.469
4.461
4.455
4.447
4.441
4.434
4.427
3.896
3.890
3.884
3.878
3.871
3.483
3.469
3.442
3.440
3.428
3.426
3.419
3.417
3.405
3.403
3.391
3.228
3.220
3.201
3.194
3.063
3.042
3.036
3.032
3.025
3.015
2.906
2.883
2.259
2.178
2.171
2.041
2.035
2.027
1.752
1.750
1.635
1.623
1.285
1.268
1.264
1.258
1.206
1.196
1.146
1.144
1.129
0.886
5.65
2.03
2.24
1.03
1.00
1.09
1.08
2.03
1.09
1.13
1.53
3.38
3.14
2.49
1.88
4.33
1.03
5.84
1000
500
0
10.0
5.0
0.0
ppm (f1)

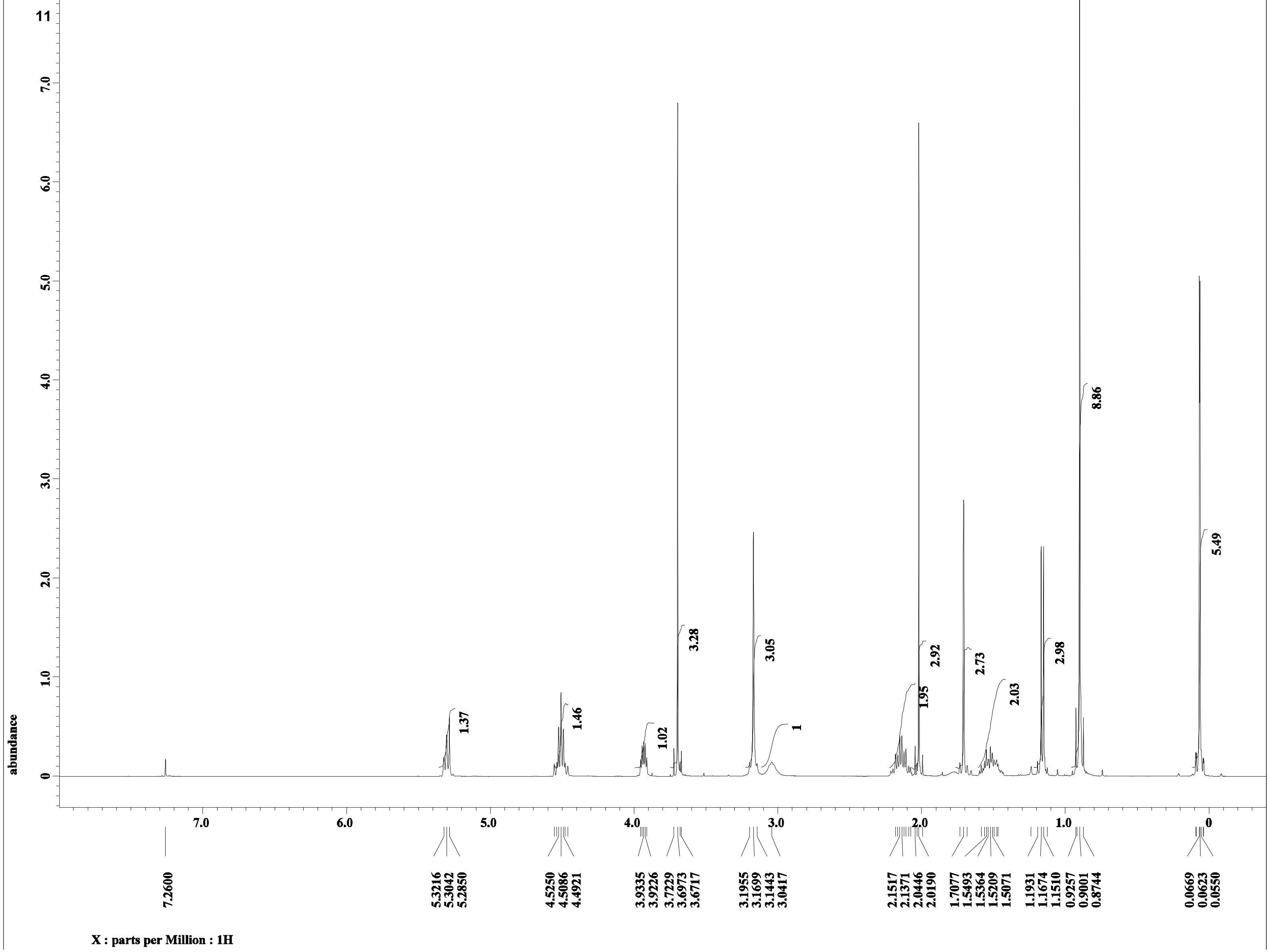

OH
O
S
N
O
OAc
Bn

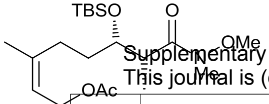
10


201.472
178.144
171.263
141.877
136.465
129.523
129.006
127.352
120.049
77.420
77.103
76.785
71.393
68.921
61.251
43.718
36.844
32.377
32.120
28.373
23.357
21.177
10.742
220
200
180
160
140
120
100
80
60
40
20
ppm

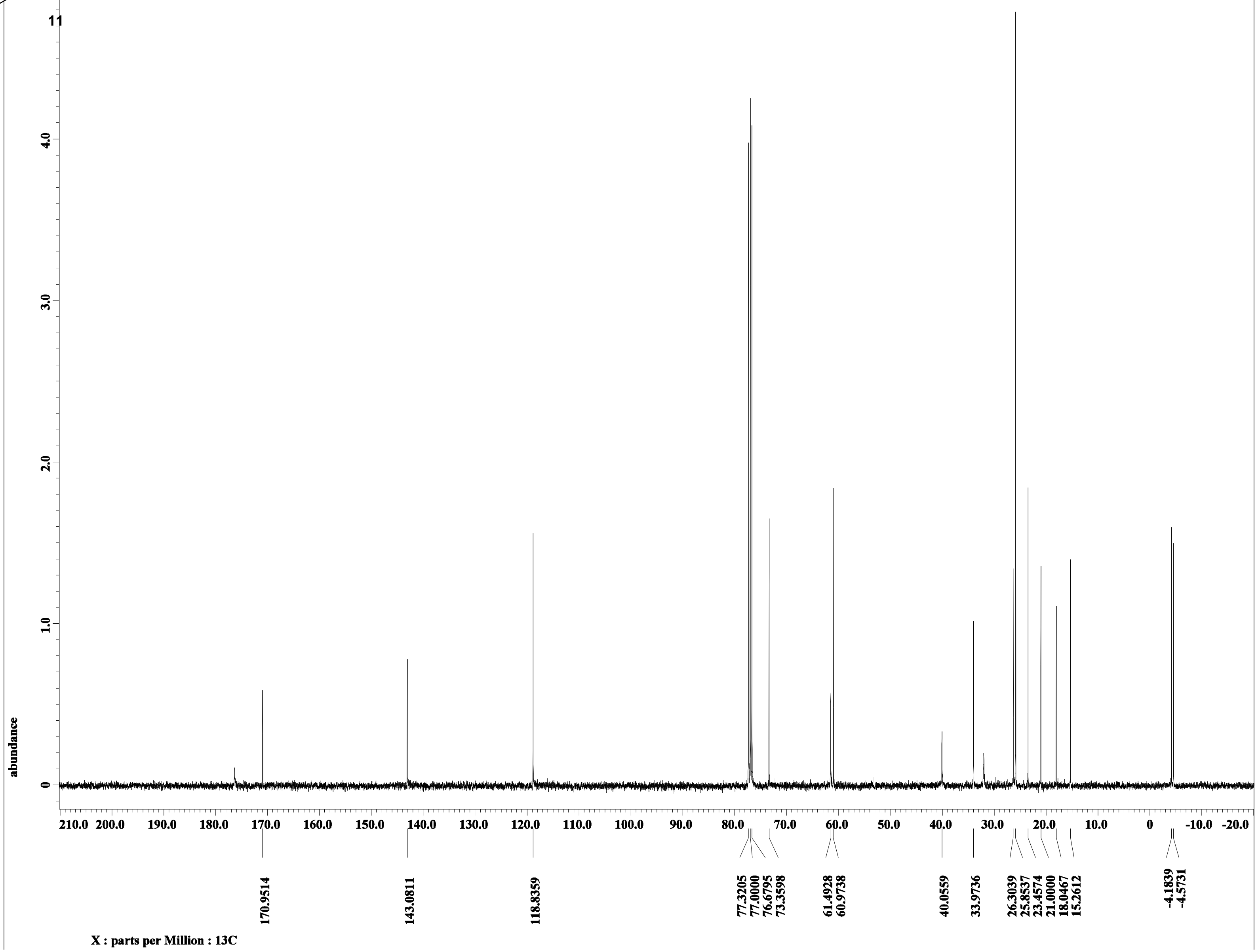

TBSO
O
OMe
N
Me
OAc

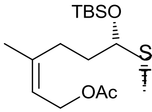
11


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
1.37
1.46
1.02
3.28
3.05
1
1.95
2.92
2.73
2.03
2.98
8.86
5.49
7.2600
5.3216
5.3042
5.2850
4.5250
4.5086
4.4921
3.9335
3.9226
3.7229
3.6973
3.6717
3.1955
3.1699
3.1443
3.0417
2.1517
2.1371
2.0446
2.0190
1.7077
1.5493
1.5364
1.5209
1.5071
1.1931
1.1674
1.1510
0.9257
0.9001
0.8744
0.0669
0.0623
0.0550
X : parts per Million : 1H

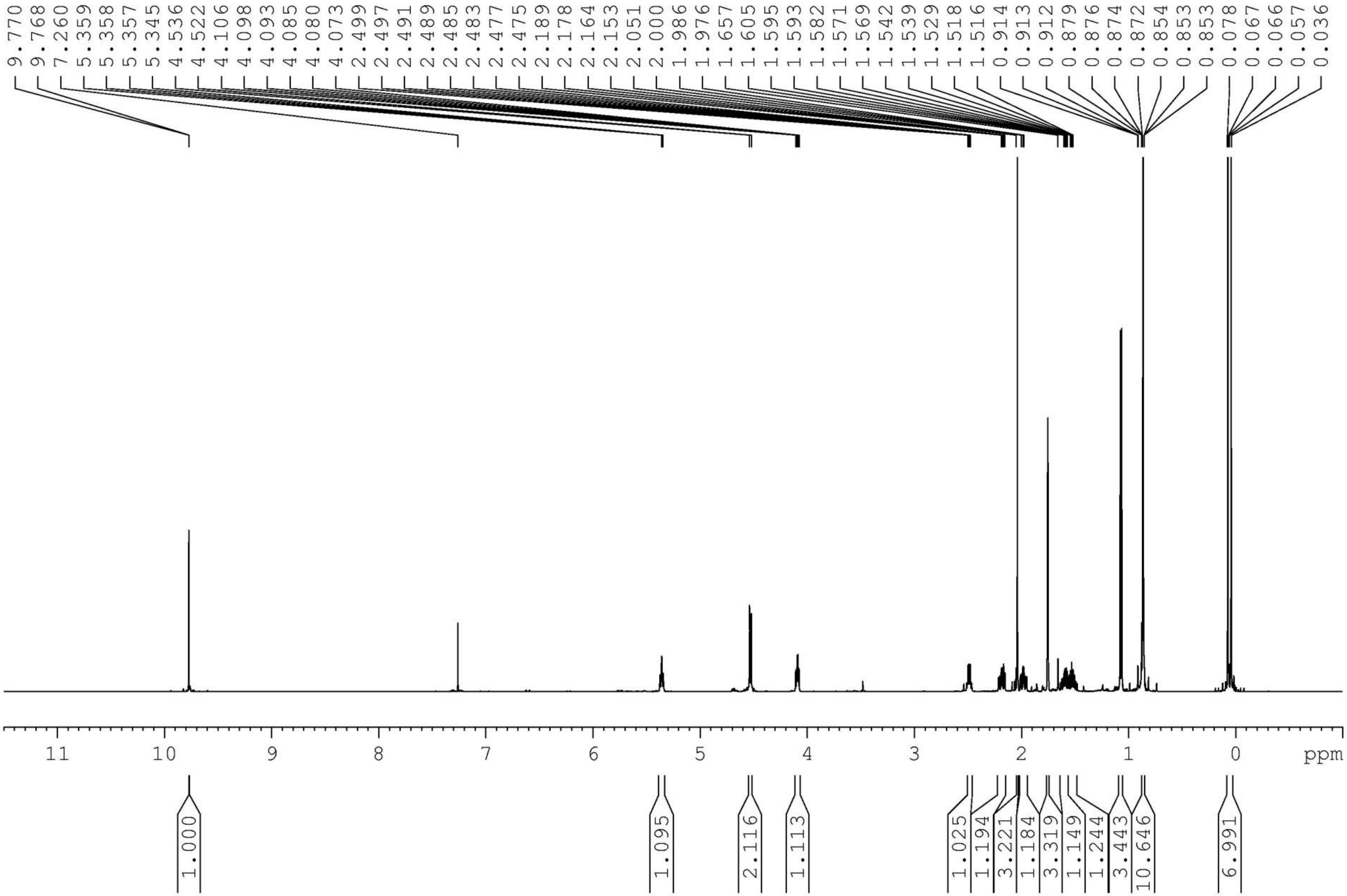

TBSO
O
OMe
N
Me
OAc

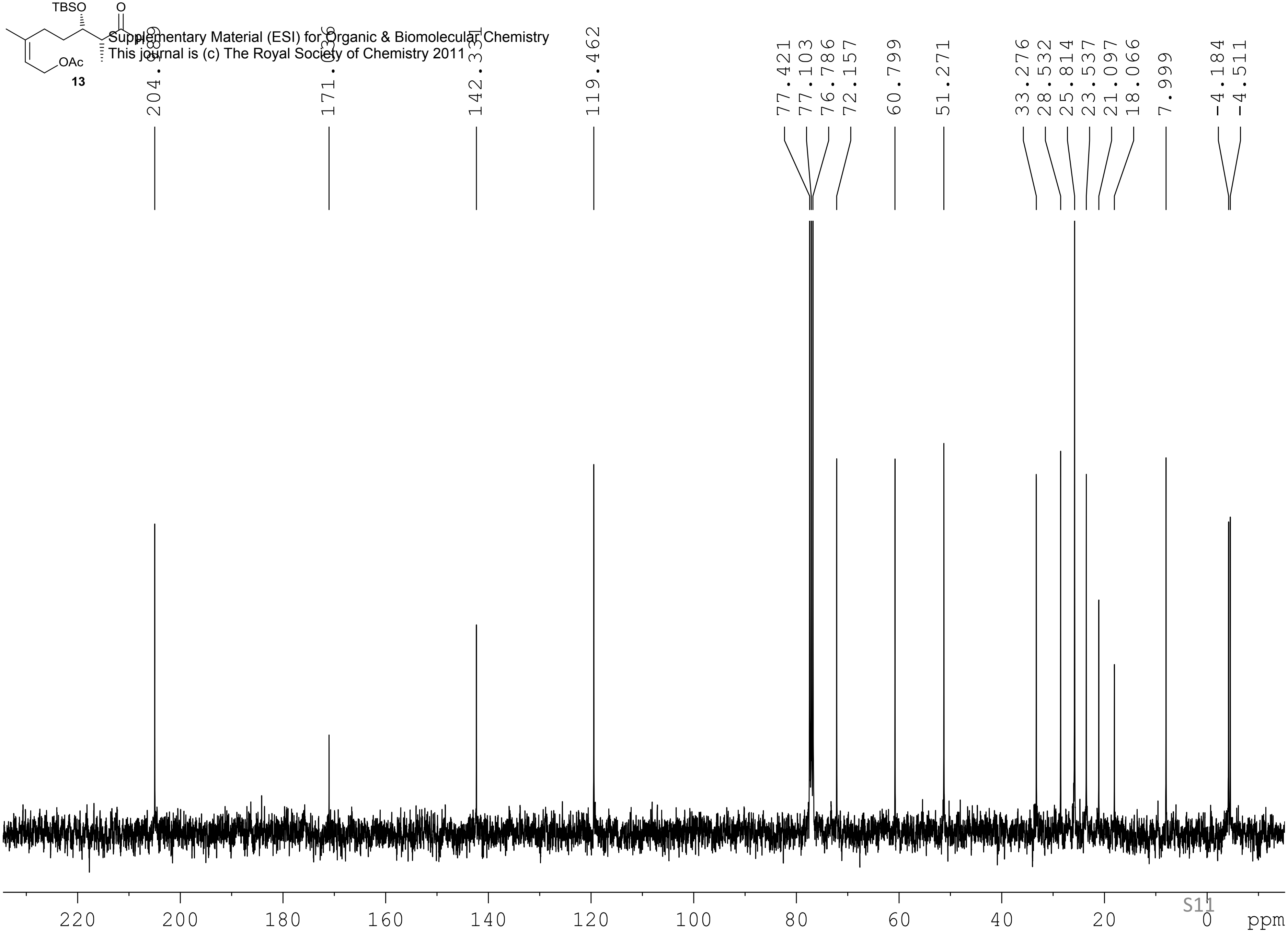
11


abundance
0
1.0
2.0
3.0
4.0
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
170.9514
143.0811
118.8359
77.3205
77.0000
76.6795
73.3598
61.4928
60.9738
40.0559
33.9736
26.3039
25.8537
23.4574
21.0000
18.0467
15.2612
-4.1839
-4.5731
X : parts per Million : 13C

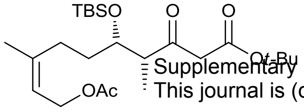

TBSO
O
H
OAc

13

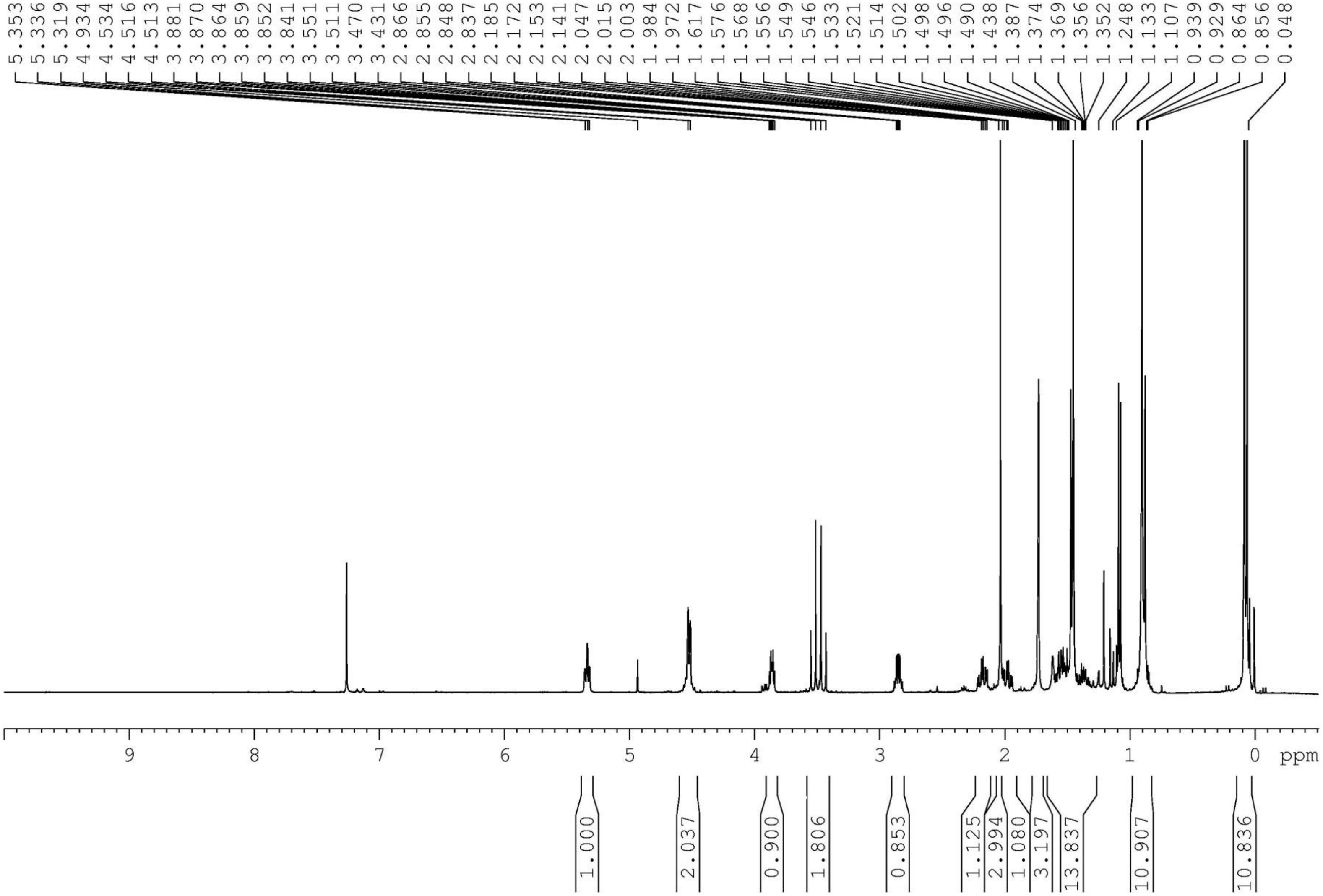

9.770
9.768
7.260
5.359
5.358
5.357
5.345
4.536
4.522
4.106
4.098
4.093
4.085
4.080
4.073
2.499
2.497
2.491
2.489
2.485
2.483
2.477
2.475
2.189
2.178
2.164
2.153
2.051
2.000
1.986
1.976
1.657
1.605
1.595
1.593
1.582
1.571
1.569
1.542
1.539
1.529
1.518
1.516
0.914
0.913
0.912
0.879
0.876
0.874
0.872
0.854
0.853
0.853
0.078
0.067
0.066
0.057
0.036
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.095
2.116
1.113
1.025
1.194
3.221
1.184
3.319
1.149
1.244
3.443
10.646
6.991

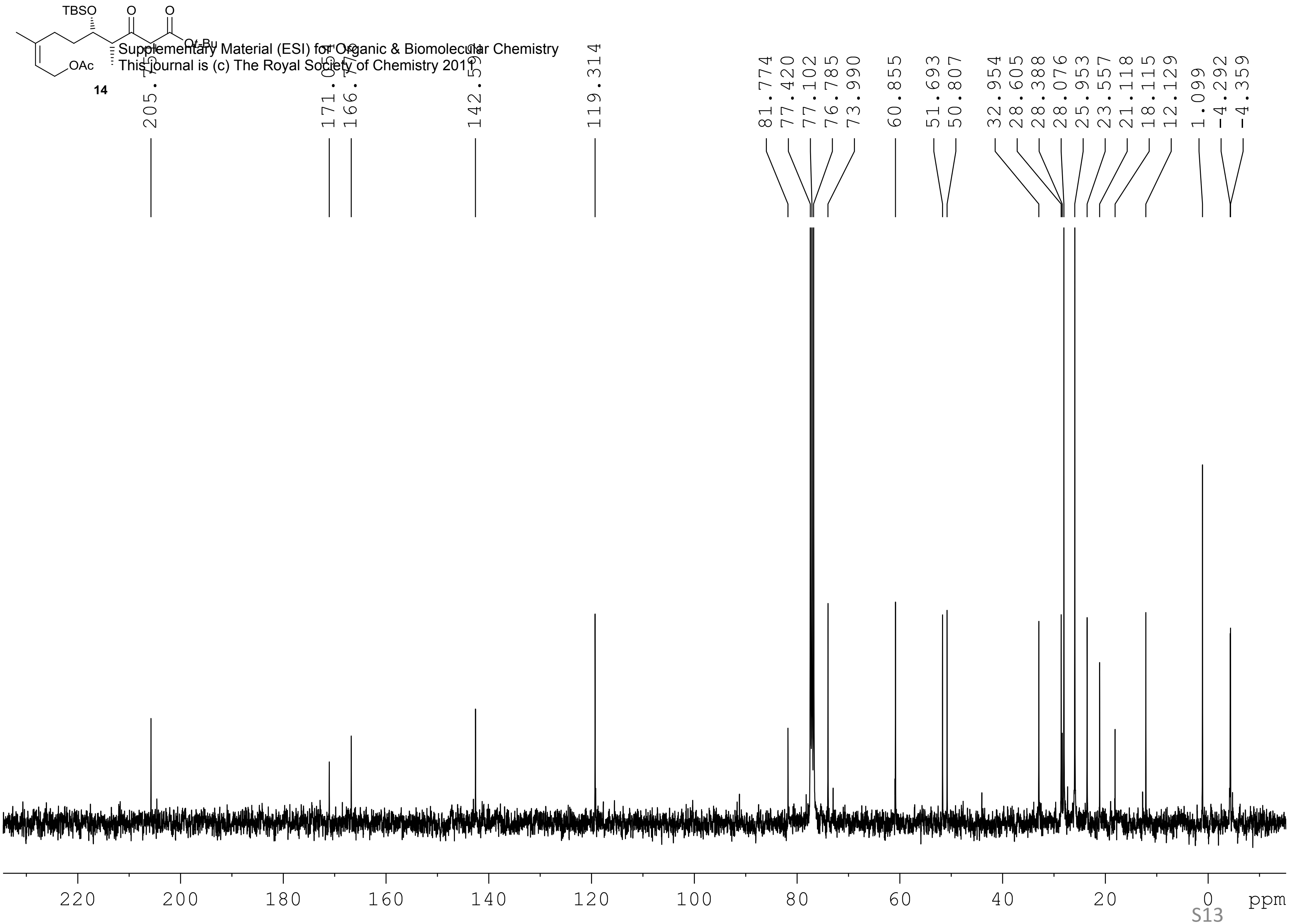

TBSO
O
H
OAc
204.989
171.036
142.331
119.462
77.421
77.103
76.786
72.157
60.799
51.271
33.276
28.532
25.814
23.537
21.097
18.066
7.999
-4.184
-4.511
220
200
180
160
140
120
100
80
60
40
20
0
ppm

13

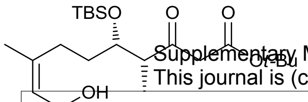

TBSO
O
O
Ot-Bu
OAc

14

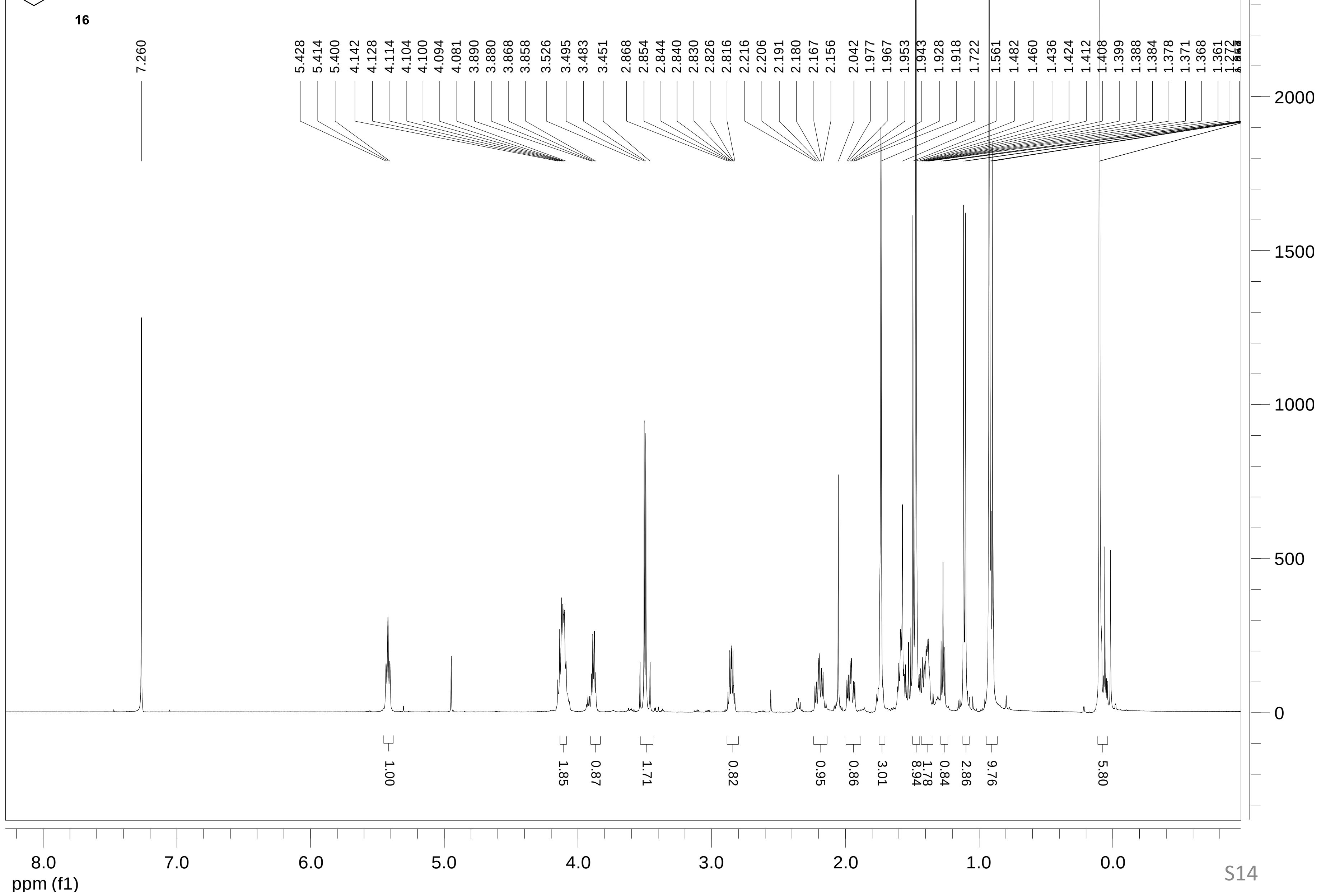

5.353
5.336
5.319
4.934
4.534
4.516
4.513
3.881
3.870
3.864
3.859
3.852
3.841
3.551
3.511
3.470
3.431
2.866
2.855
2.848
2.837
2.185
2.172
2.153
2.141
2.047
2.015
2.003
1.984
1.972
1.617
1.576
1.568
1.556
1.549
1.546
1.533
1.521
1.514
1.502
1.498
1.496
1.490
1.438
1.387
1.374
1.369
1.356
1.352
1.248
1.133
1.107
0.939
0.929
0.864
0.856
0.048
9
8
7
6
5
4
3
2
1
0 ppm
1.000
2.037
0.900
1.806
0.853
1.125
2.994
1.080
3.197
13.837
10.907
10.836

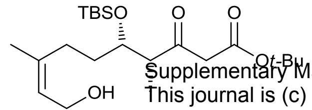

14

TBSO
O
O
Ot-Bu
OAc
205.75
171.05
166.77
142.59
119.314
81.774
77.420
77.102
76.785
73.990
60.855
51.693
50.807
32.954
28.605
28.388
28.076
25.953
23.557
21.118
18.115
12.129
1.099
-4.292
-4.359
220
200
180
160
140
120
100
80
60
40
20
0
ppm

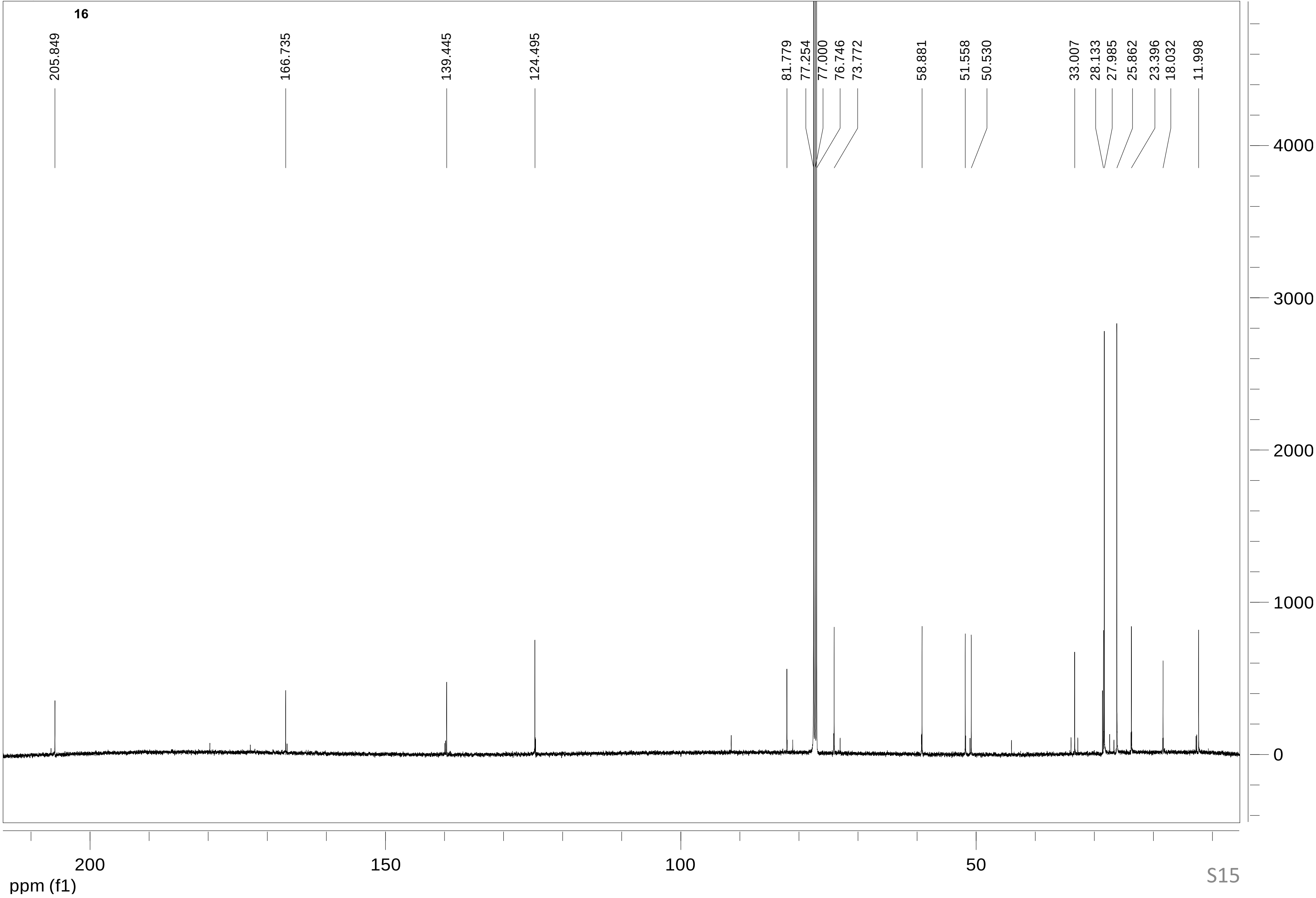

TBSO
O
O
Ot-Bu
OH

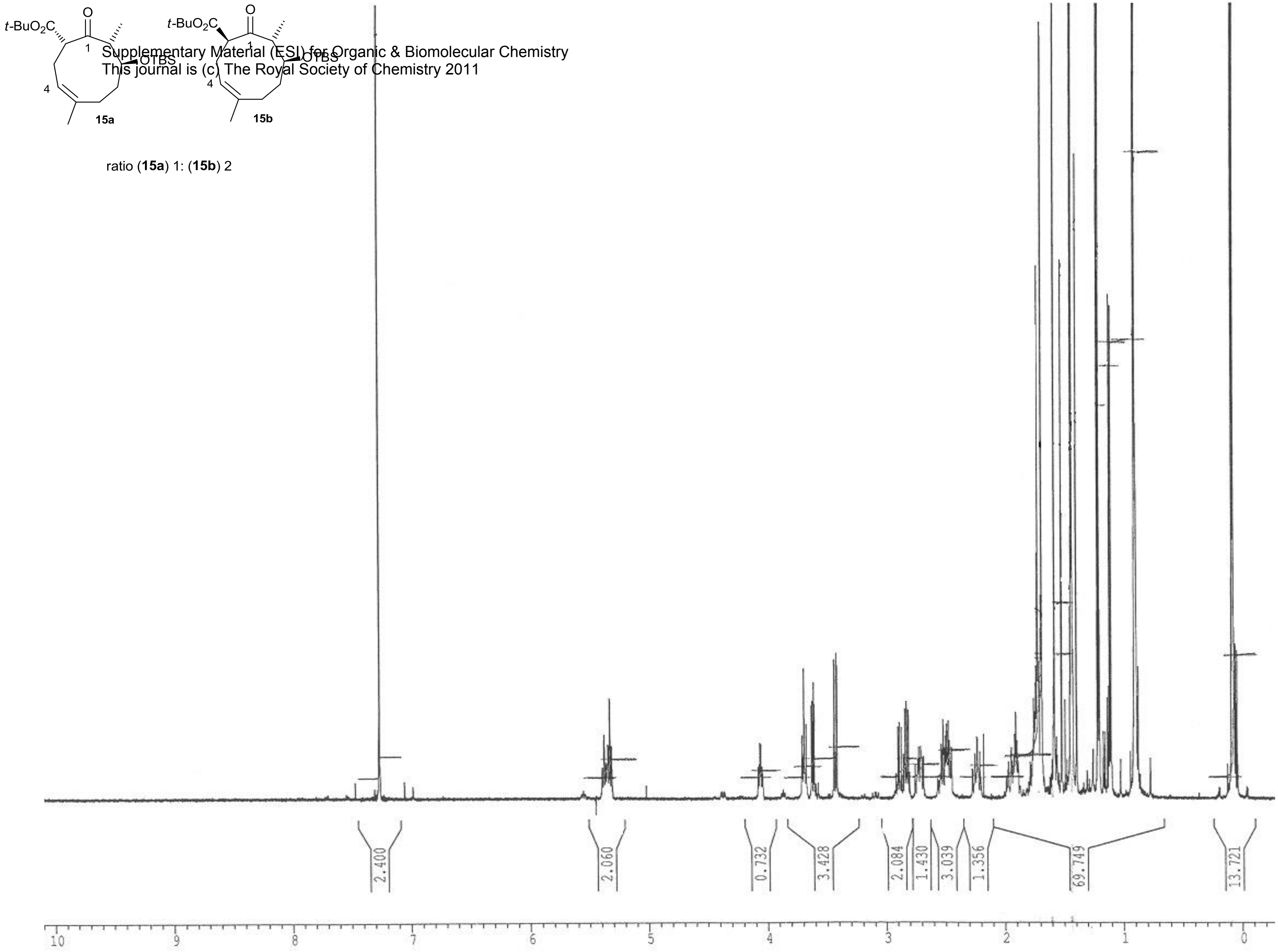
16

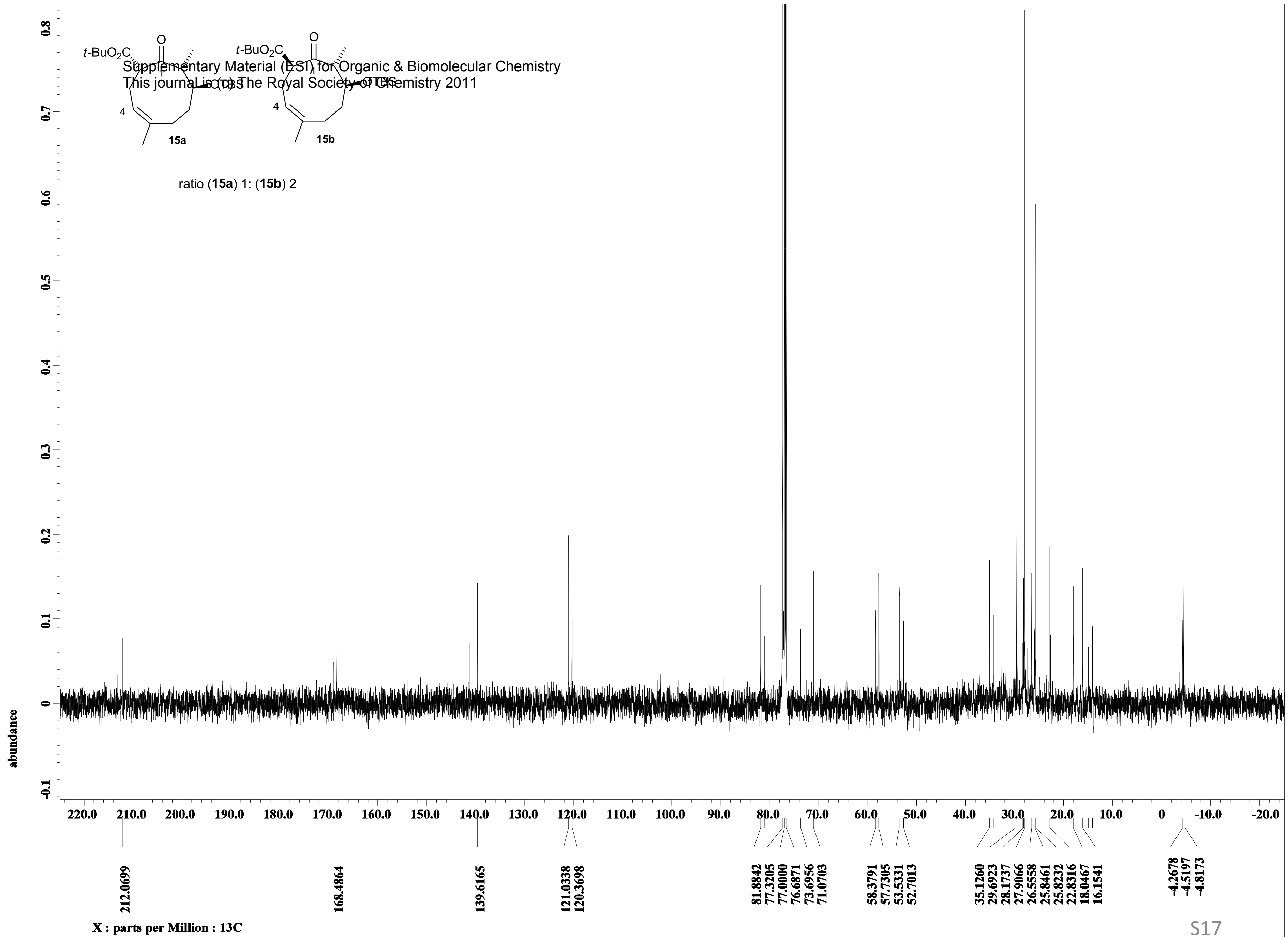

7.260
5.428
5.414
5.400
4.142
4.128
4.114
4.104
4.100
4.094
4.081
3.890
3.880
3.868
3.858
3.526
3.495
3.483
3.451
2.868
2.854
2.844
2.840
2.830
2.826
2.816
2.216
2.206
2.191
2.180
2.167
2.156
2.042
1.977
1.967
1.953
1.943
1.928
1.918
1.722
1.561
1.482
1.460
1.436
1.424
1.412
1.408
1.399
1.388
1.384
1.378
1.371
1.368
1.361
1.272
1.00
1.85
0.87
1.71
0.82
0.95
0.86
3.01
8.94
1.78
0.84
2.86
9.76
5.80
2000
1500
1000
500
0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

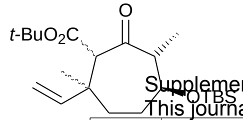

TBSO
O
O
Ot-Bu
OH

16

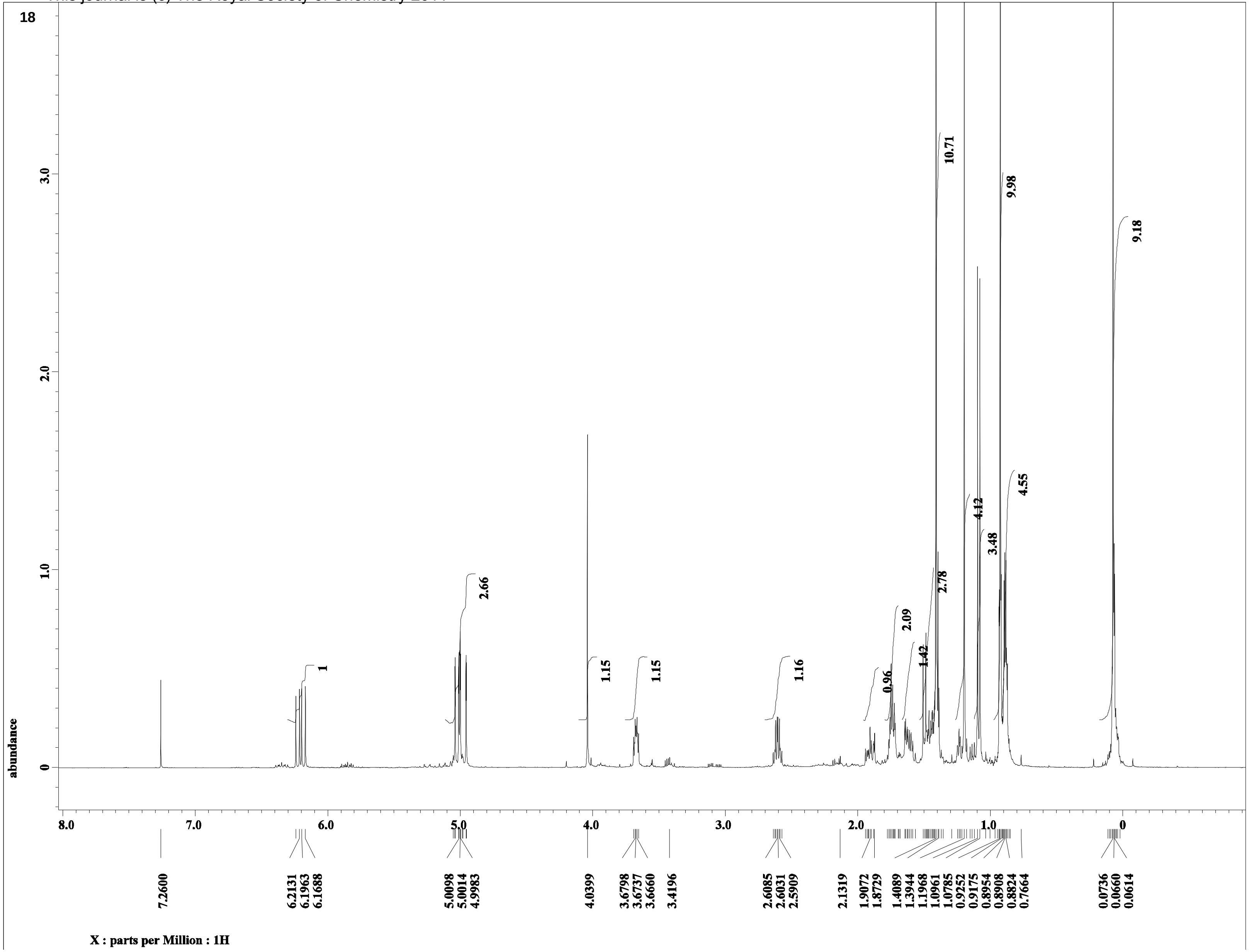

205.849
166.735
139.445
124.495
81.779
77.254
77.000
76.746
73.772
58.881
51.558
50.530
33.007
28.133
27.985
25.862
23.396
18.032
11.998
4000
3000
2000
1000
0
200
150
100
50
ppm (f1)

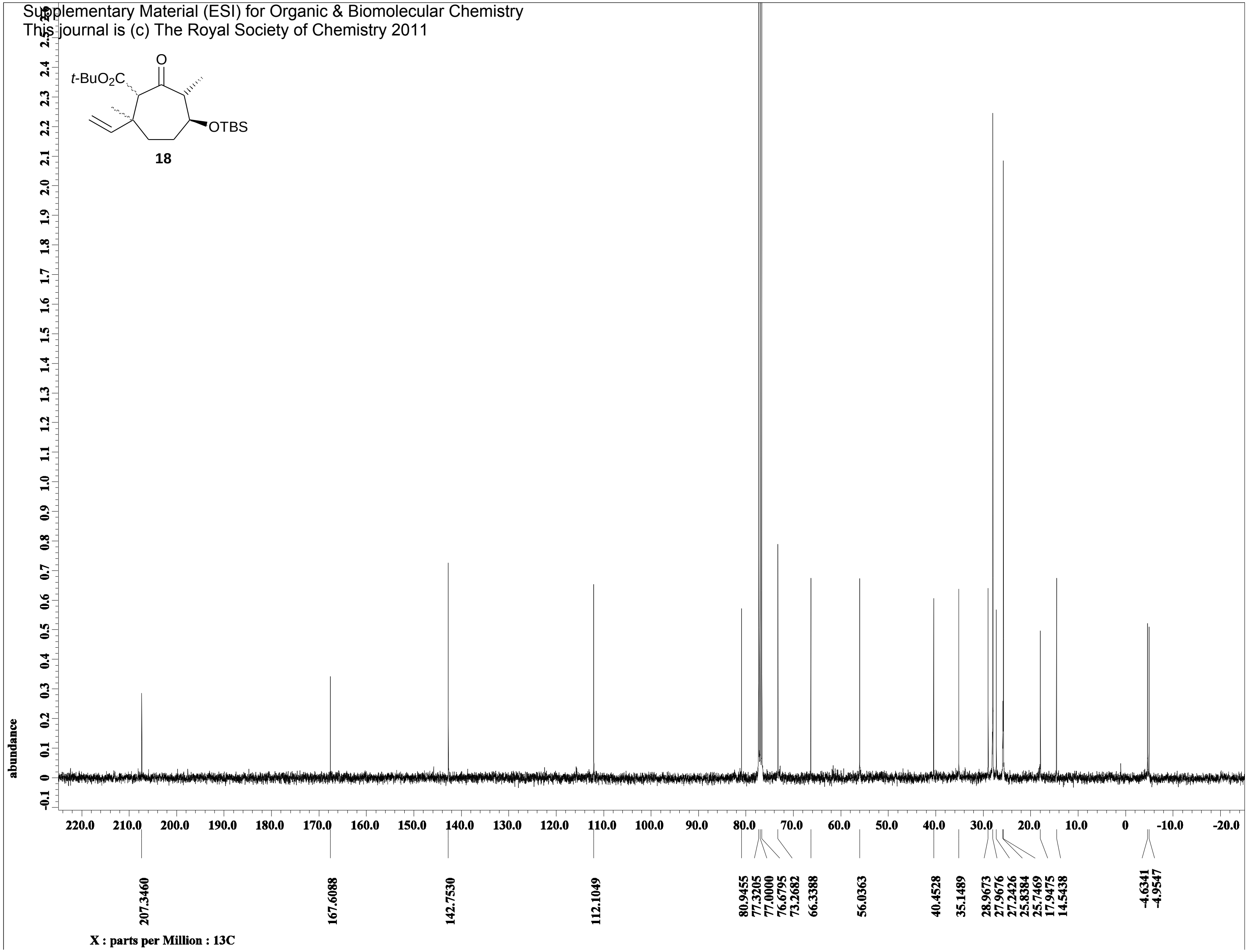

t-BuO2C
O
1
4
OTBS
15a
t-BuO2C
O
1
4
OTBS
15b
ratio (15a) 1: (15b) 2
2.400
2.060
0.732
3.428
2.084
1.430
3.039
1.356
69.749
13.721
10
9
8
7
6
5
4
3
2
1
0

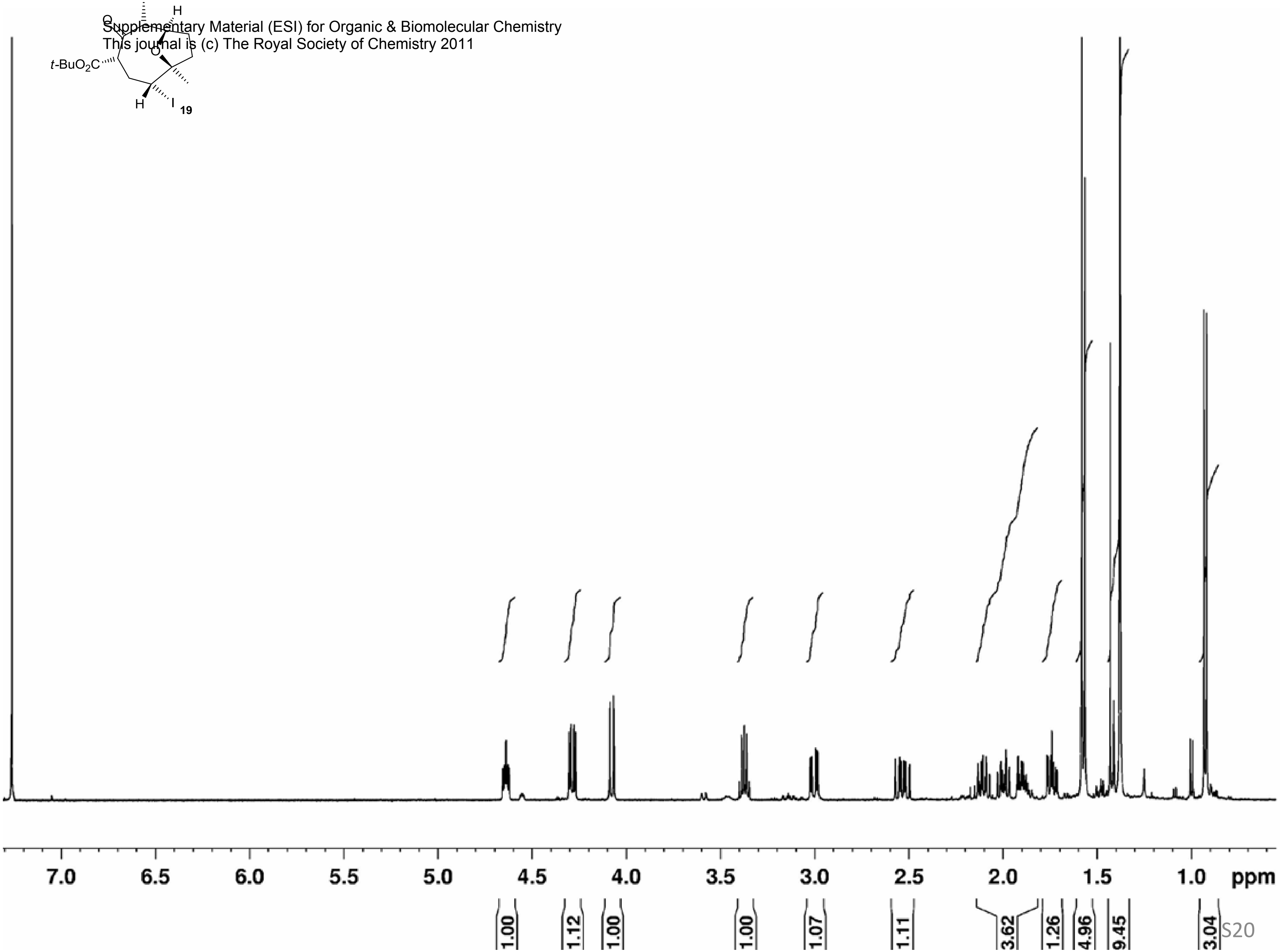

t-BuO$_2$C
O
OTBS
4
15a
t-BuO$_2$C
O
OTBS
4
15b
ratio (**15a**) 1: (**15b**) 2
abundance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
212.0699
168.4864
139.6165
121.0338
120.3698
81.8842
77.3205
77.0000
76.6871
73.6956
71.0703
58.3791
57.7305
53.5331
52.7013
35.1260
29.6923
28.1737
27.9066
26.5558
25.8461
25.8232
22.8316
18.0467
16.1541
-4.2678
-4.5197
-4.8173
X : parts per Million : 13C

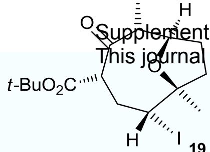

O
t-BuO2C
OTBS

18

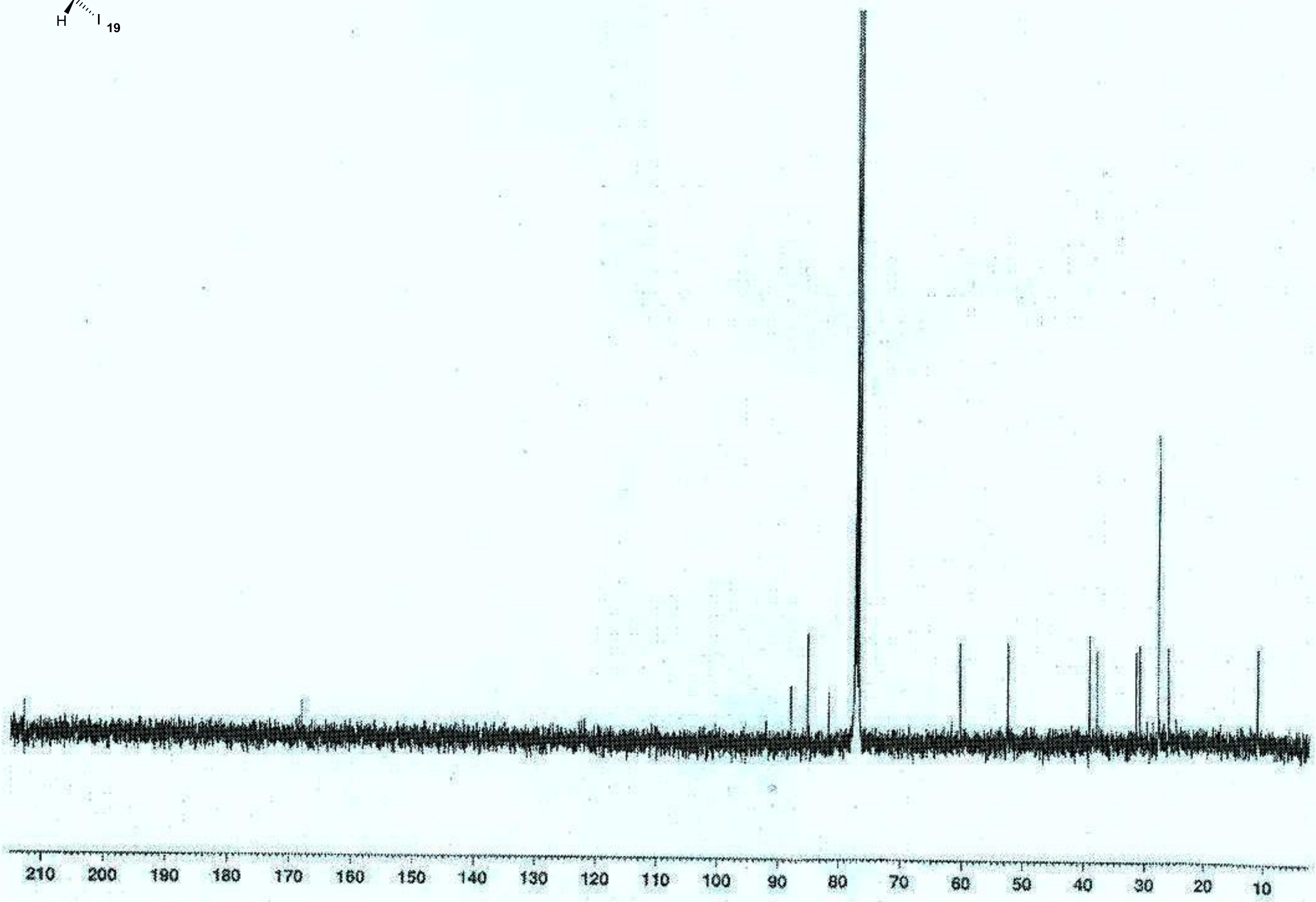

abundance
0
1.0
2.0
3.0
1
2.66
1.15
1.15
1.16
0.96
2.09
1.42
2.78
10.71
4.12
3.48
9.98
4.55
9.18
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2600
6.2131
6.1963
6.1688
5.0098
5.0014
4.9983
4.0399
3.6798
3.6737
3.6660
3.4196
2.6085
2.6031
2.5909
2.1319
1.9072
1.8729
1.4089
1.3944
1.1968
1.0961
1.0785
0.9252
0.9175
0.8954
0.8908
0.8824
0.7664
0.0736
0.0660
0.0614
X : parts per Million : 1H

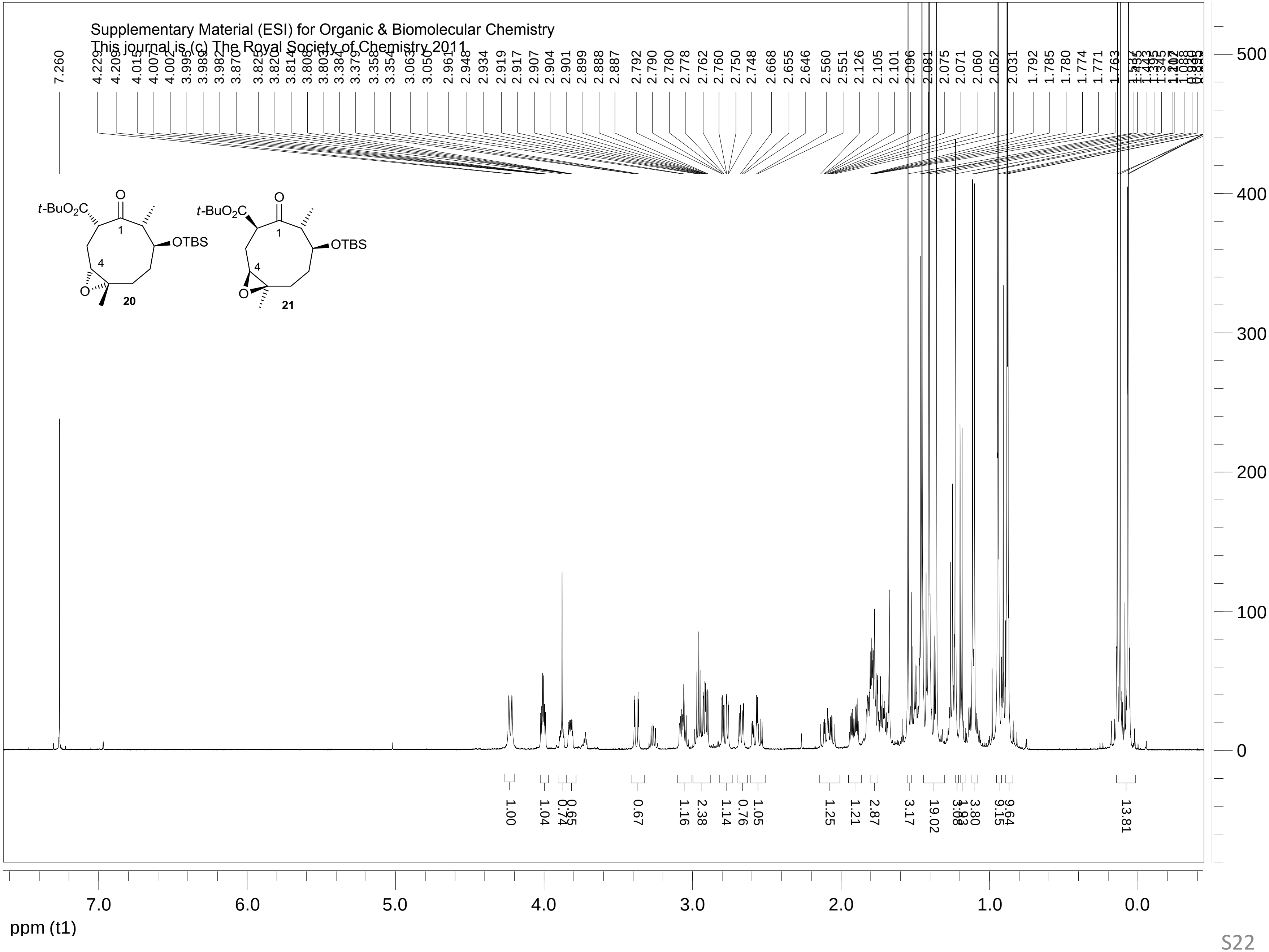

t-BuO$_2$C
O
OTBS
18
abundance
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
207.3460
167.6088
142.7530
112.1049
80.9455
77.3205
77.0000
76.6795
73.2682
66.3388
56.0363
40.4528
35.1489
28.9673
27.9676
27.2426
25.8384
25.7469
17.9475
14.5438
-4.6341
-4.9547
X : parts per Million : 13C

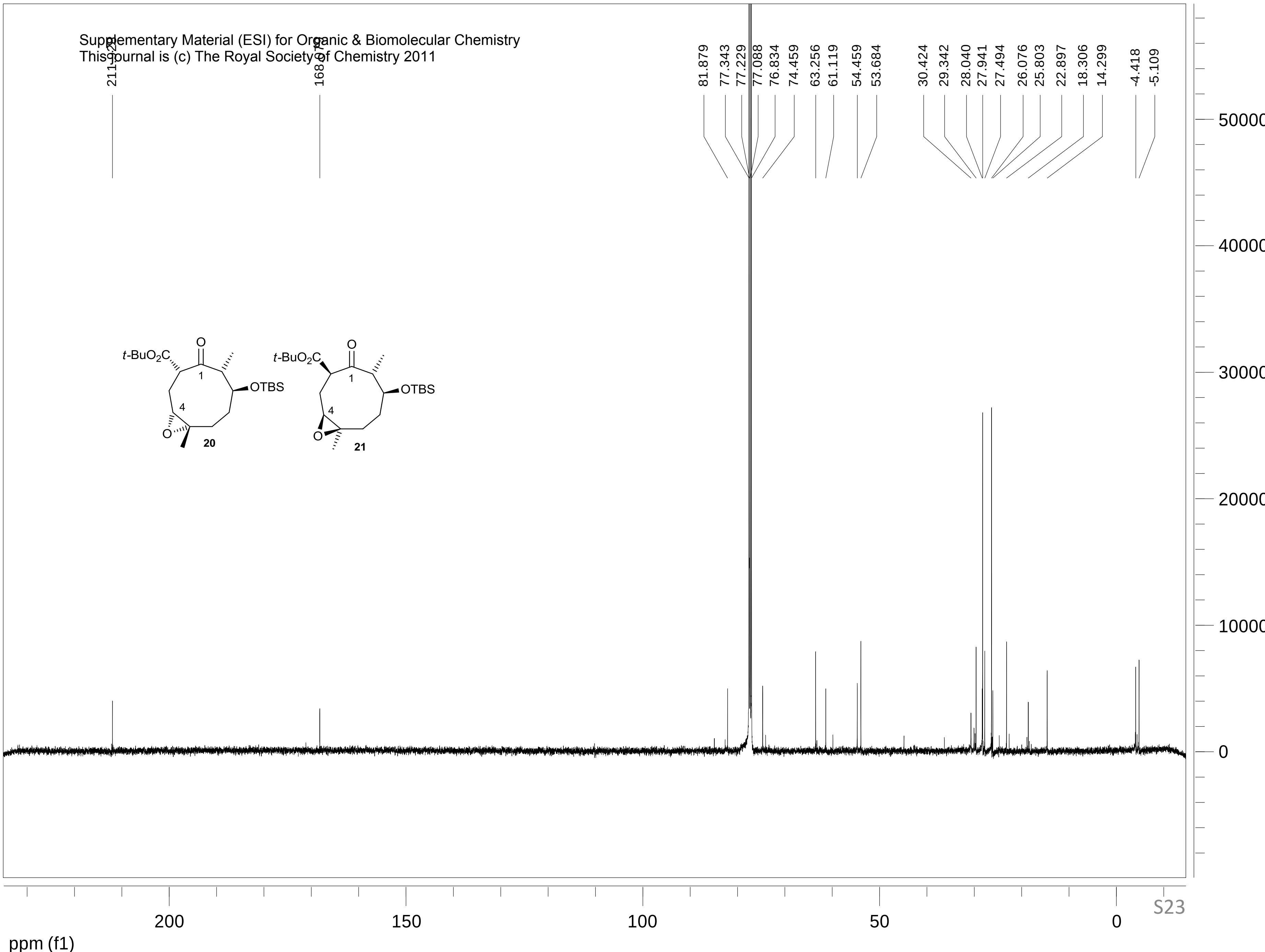

O
H
t-BuO2C
O
H
I
19
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.12
1.00
1.00
1.07
1.11
3.62
1.26
4.96
9.45
3.04

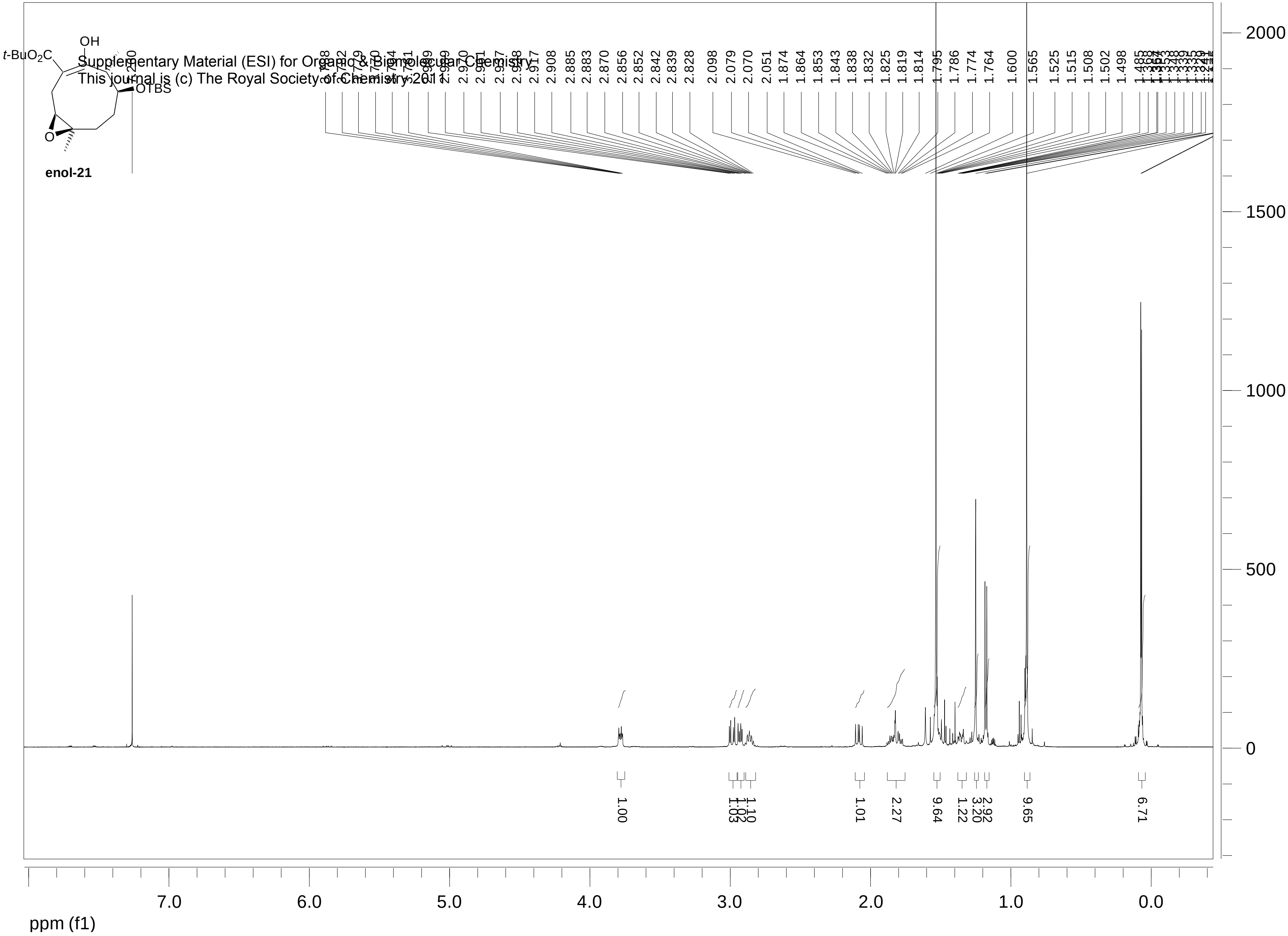

O
H
O
t-BuO2C
H
I

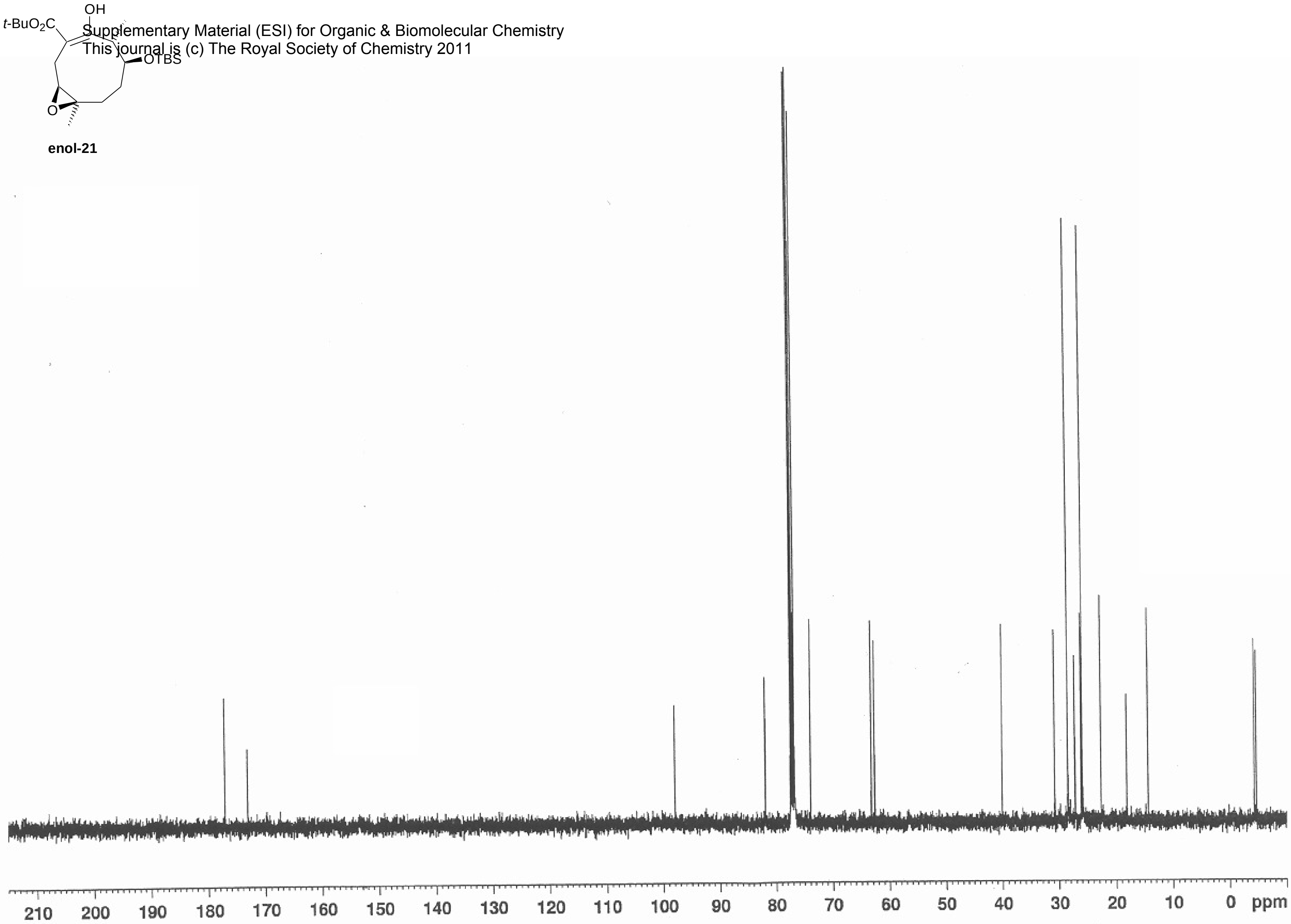
19


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

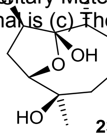

7.260
4.229
4.209
4.015
4.007
4.002
3.995
3.989
3.982
3.870
3.825
3.820
3.814
3.808
3.803
3.384
3.379
3.358
3.354
3.063
3.050
2.961
2.948
2.934
2.919
2.917
2.907
2.904
2.901
2.899
2.888
2.887
2.792
2.790
2.780
2.778
2.762
2.760
2.750
2.748
2.668
2.655
2.646
2.560
2.551
2.126
2.105
2.101
2.096
2.081
2.075
2.071
2.060
2.052
2.031
1.792
1.785
1.780
1.774
1.771
1.763
t-BuO2C
O
1
4
OTBS
20
21
1.00
1.04
0.74
0.65
0.67
1.16
2.38
1.14
0.76
1.05
1.25
1.21
2.87
3.17
19.02
3.80
9.15
9.64
13.81
500
400
300
200
100
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


211.2
168.07
81.879
77.343
77.229
77.088
76.834
74.459
63.256
61.119
54.459
53.684
30.424
29.342
28.040
27.941
27.494
26.076
25.803
22.897
18.306
14.299
-4.418
-5.109
50000
40000
30000
20000
10000
0
200
150
100
50
0
ppm (f1)
t-BuO2C
O
1
4
OTBS
O
20
t-BuO2C
O
1
4
OTBS
O
21

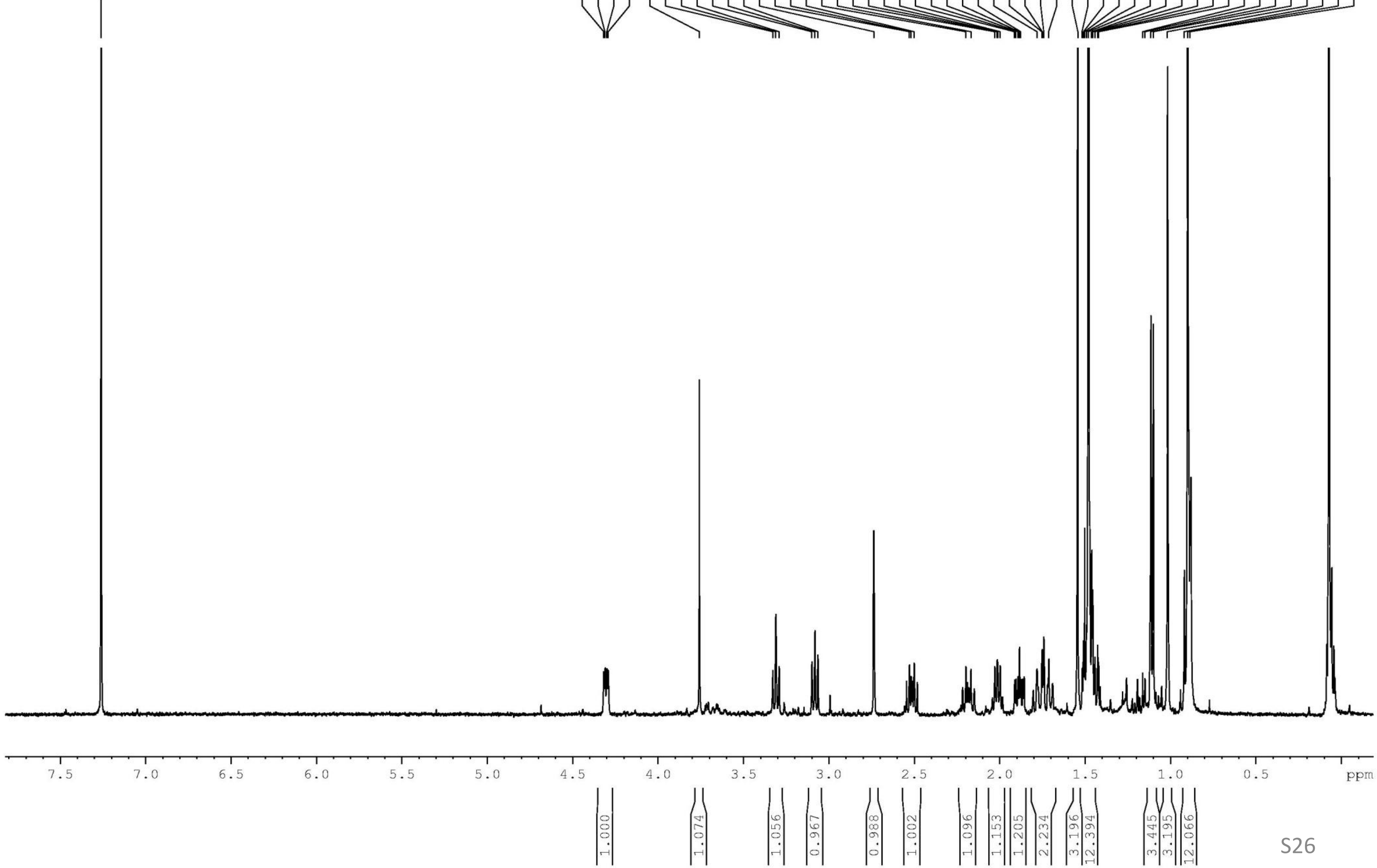

t-BuO2C
OH
OTBS
O
enol-21
7.260
2.970
2.917
2.908
2.885
2.883
2.870
2.856
2.852
2.842
2.839
2.828
2.098
2.079
2.070
2.051
1.874
1.864
1.853
1.843
1.838
1.832
1.825
1.819
1.814
1.795
1.786
1.774
1.764
1.600
1.565
1.525
1.515
1.508
1.502
1.498
1.485
1.00
1.03
1.02
1.10
1.01
2.27
9.64
1.22
3.20
2.92
9.65
6.71
2000
1500
1000
500
0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


OH
t-BuO2C
OTBS
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

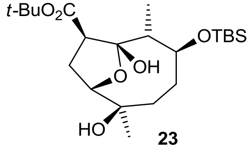
enol-21


OH
O
OTBS
HO

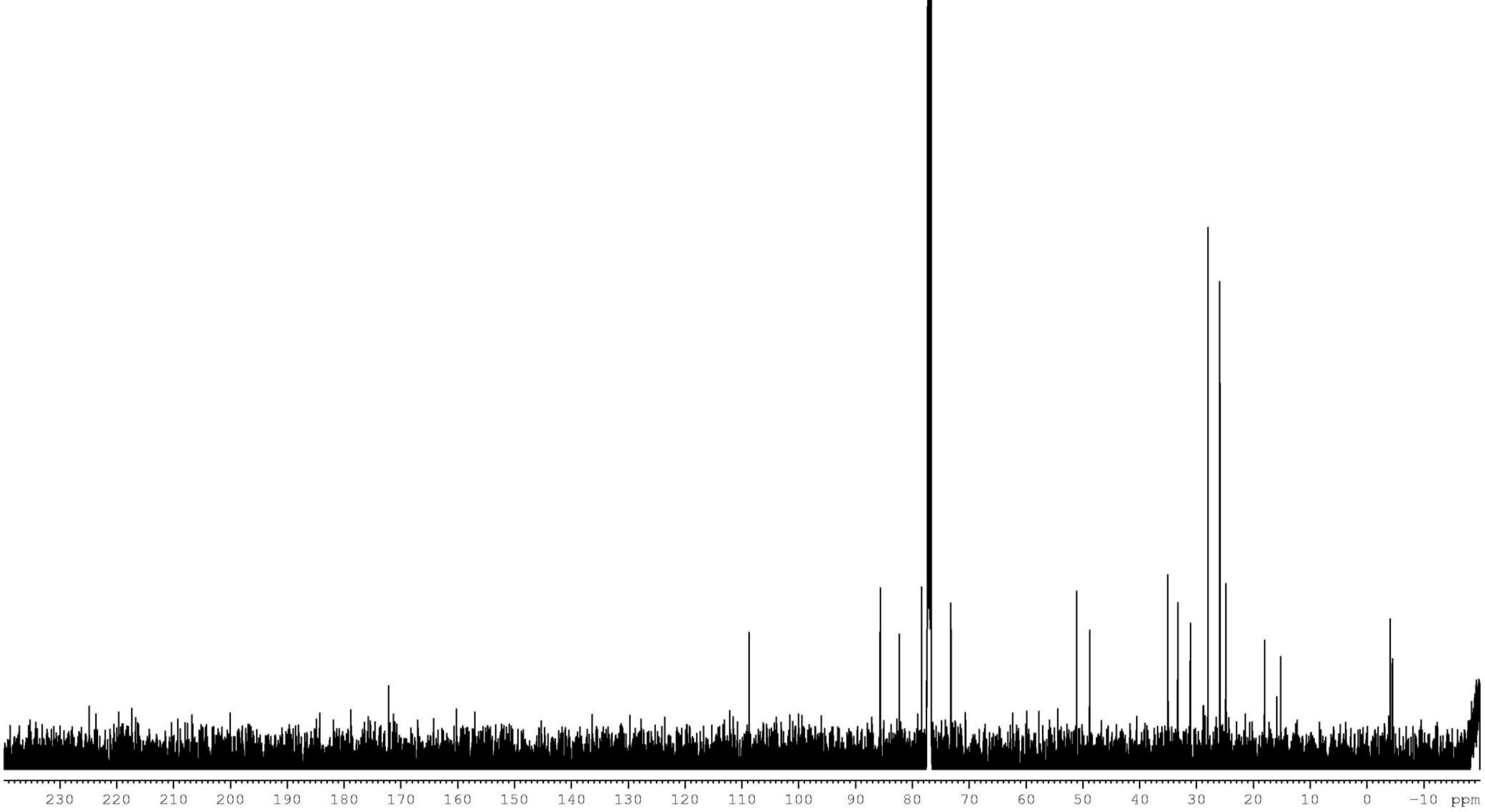
23

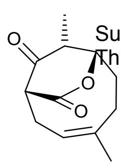

MI-4-9-2
7.260
4.318
4.310
4.300
4.292
3.757
3.329
3.310
3.292
3.099
3.082
3.064
2.735
2.528
2.517
2.500
2.198
2.168
2.029
2.015
2.010
1.996
1.913
1.904
1.893
1.885
1.876
1.782
1.753
1.751
1.742
1.712
1.541
1.517
1.510
1.502
1.492
1.481
1.461
1.455
1.442
1.427
1.421
1.163
1.149
1.115
1.101
1.017
0.919
0.899
0.885
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.074
1.056
0.967
0.988
1.002
1.096
1.153
1.205
2.234
3.196
12.394
3.445
3.195
12.066

MI-4-9-2-C13

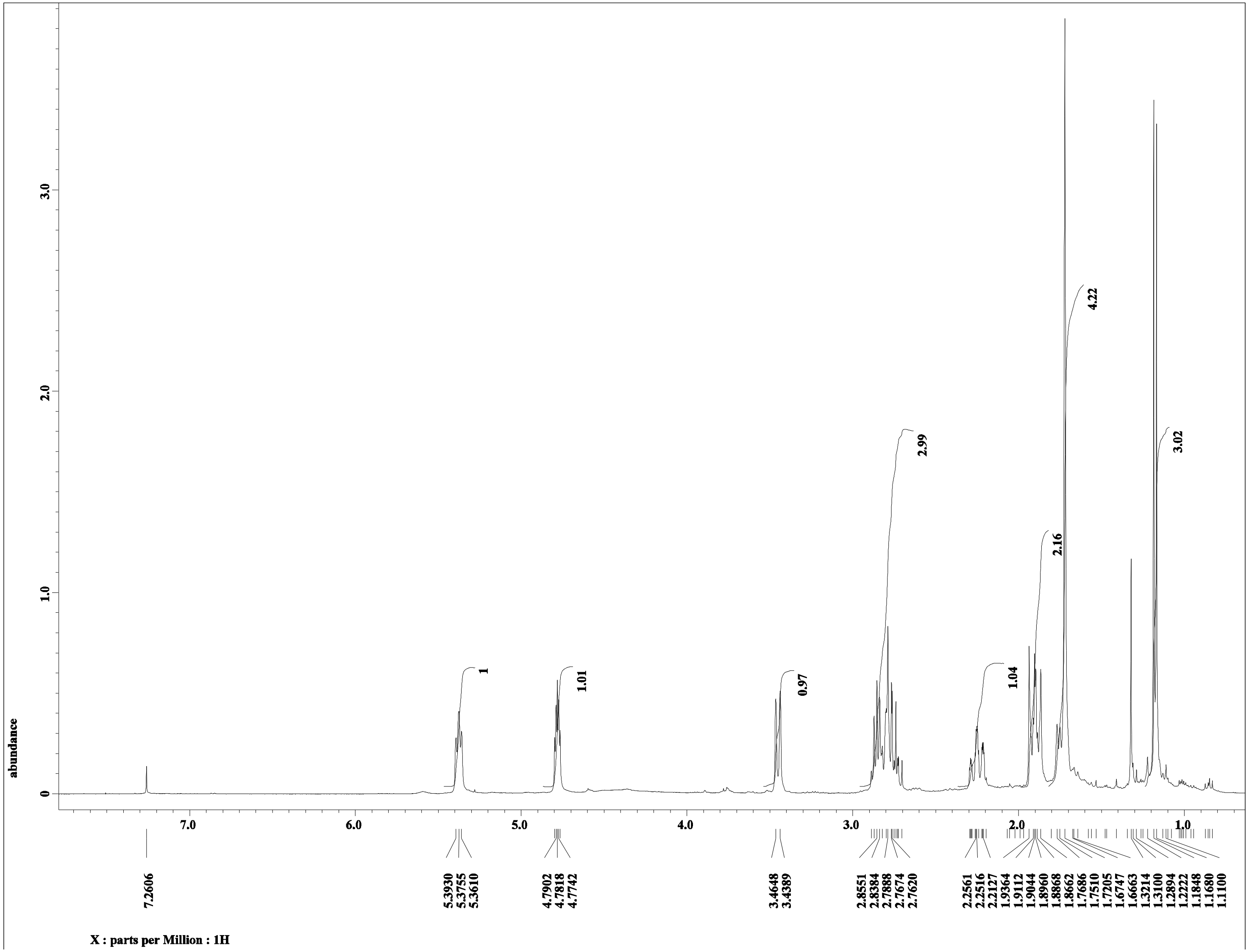

t-BuO2C
OTBS
O
OH
HO

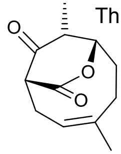
23


108.774
85.678
82.315
78.374
73.214
51.078
48.798
35.037
33.302
31.103
27.966
25.878
24.849
18.030
15.149
-4.108
-4.492
172.536
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

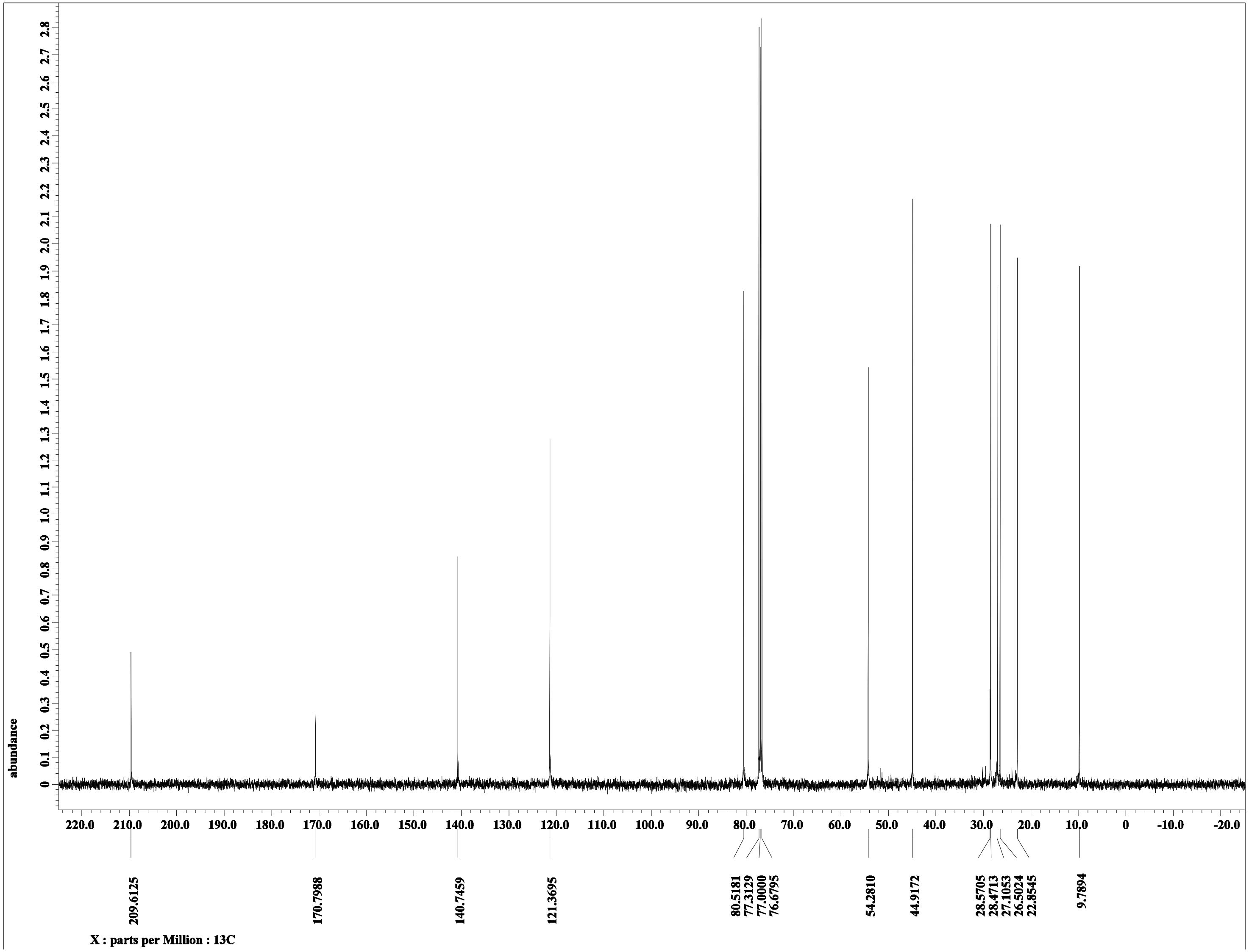


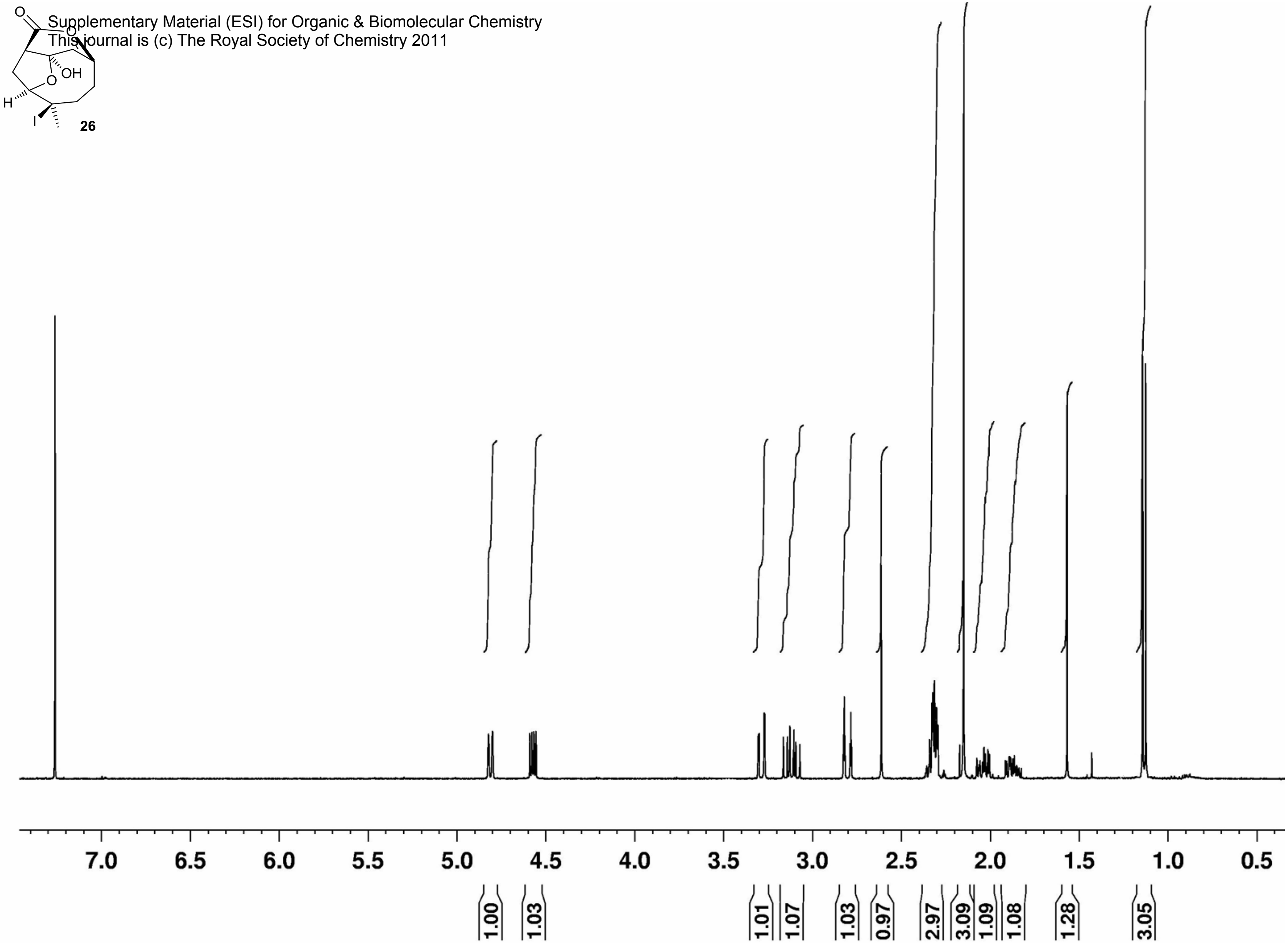
24

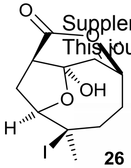

abundance
0
1.0
2.0
3.0
1
1.01
0.97
2.99
1.04
2.16
4.22
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.2606
5.3930
5.3755
5.3610
4.7902
4.7818
4.7742
3.4648
3.4389
2.8551
2.8384
2.7888
2.7674
2.7620
2.2561
2.2516
2.2127
1.9364
1.9112
1.9044
1.8960
1.8868
1.8662
1.7686
1.7510
1.7205
1.6747
1.6663
1.3214
1.3100
1.2894
1.2222
1.1848
1.1680
1.1100
X : parts per Million : 1H



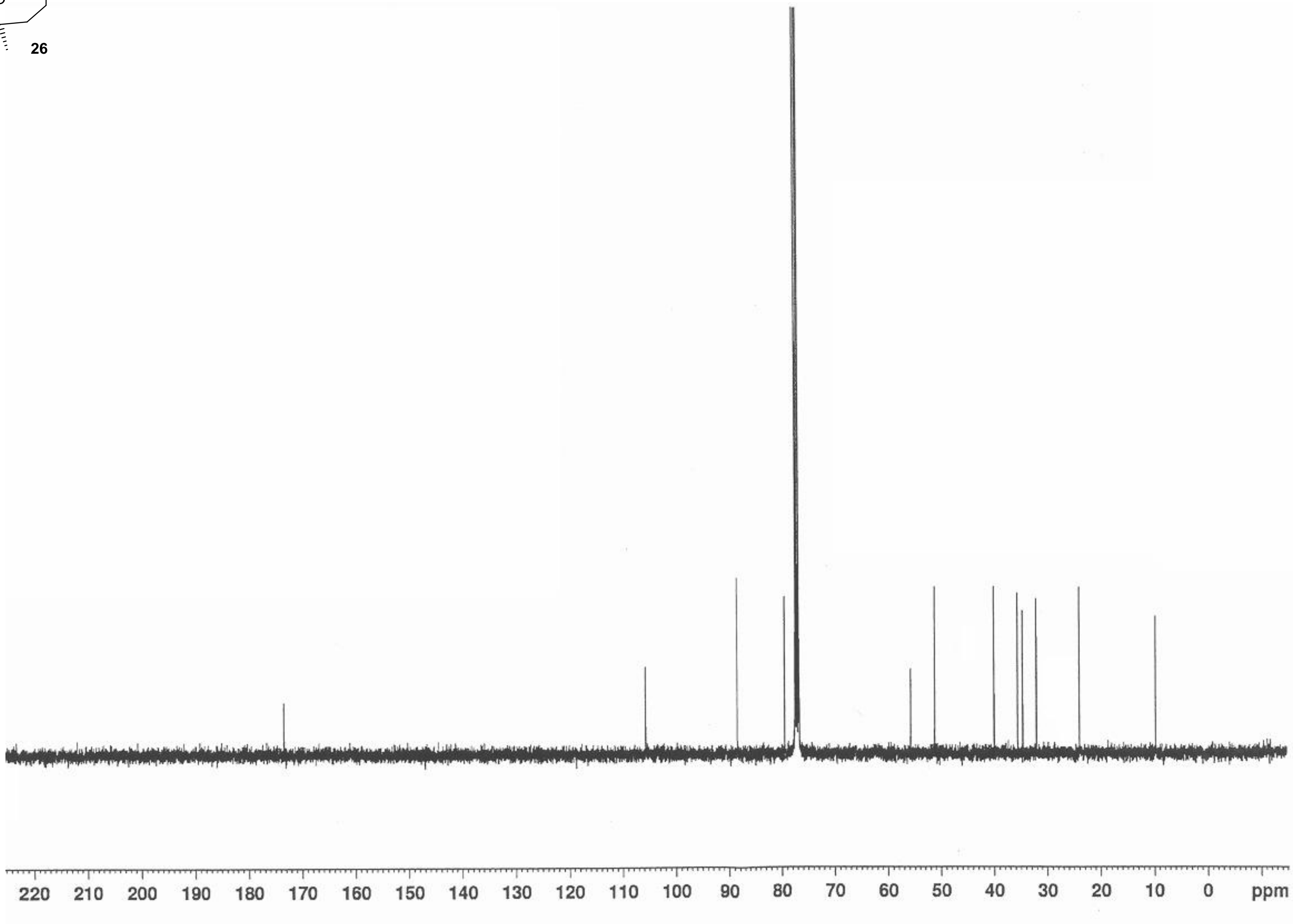
24

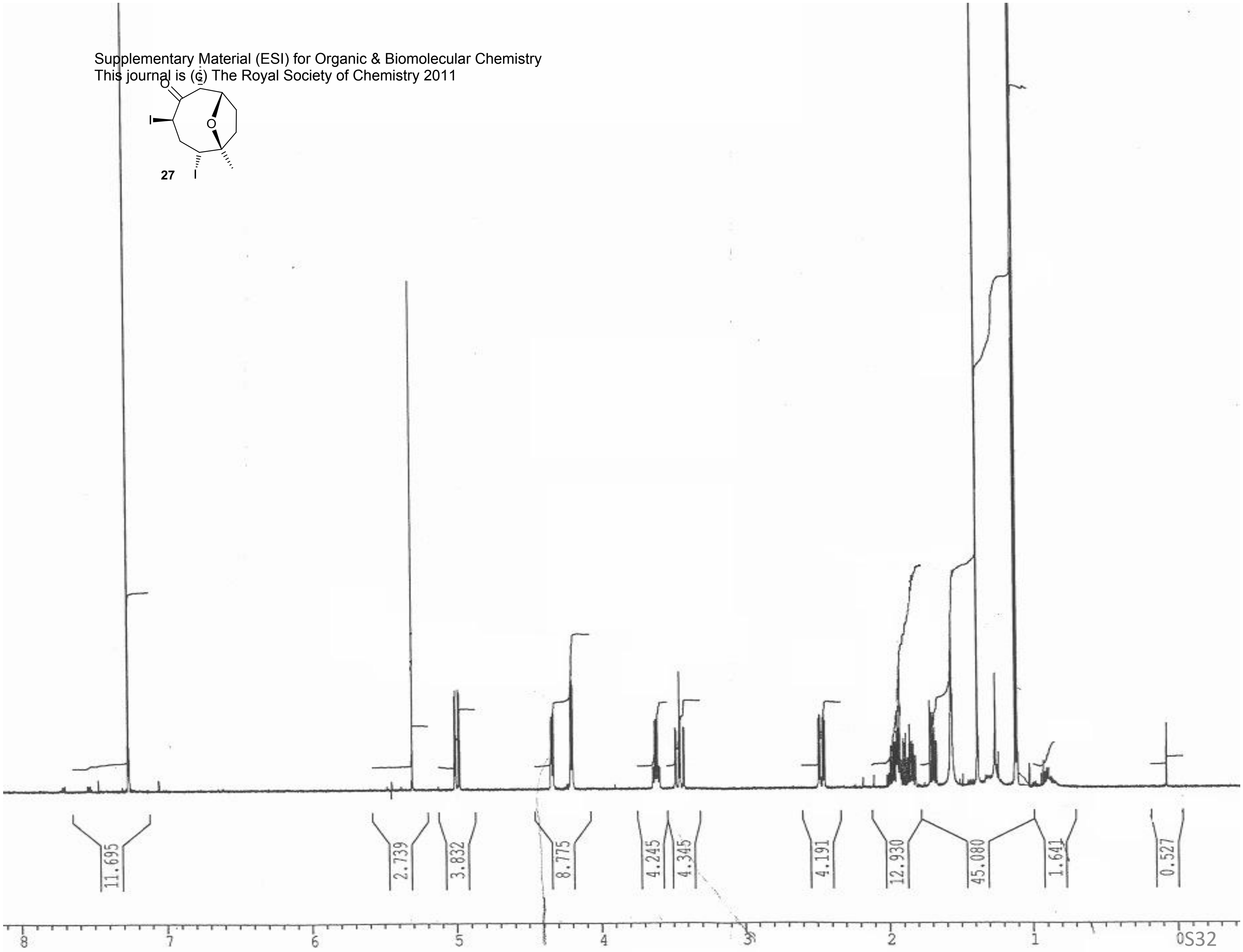

abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
209.6125
170.7988
140.7459
121.3695
80.5181
77.3129
77.0000
76.6795
54.2810
44.9172
28.5705
28.4713
27.1053
26.5024
22.8545
9.7894
X : parts per Million : 13C

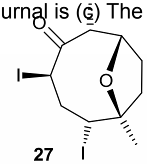

O
O
OH
O
H
I
26
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
1.00
1.03
1.01
1.07
1.03
0.97
2.97
3.09
1.09
1.08
1.28
3.05


O
O
OH
O
H
I

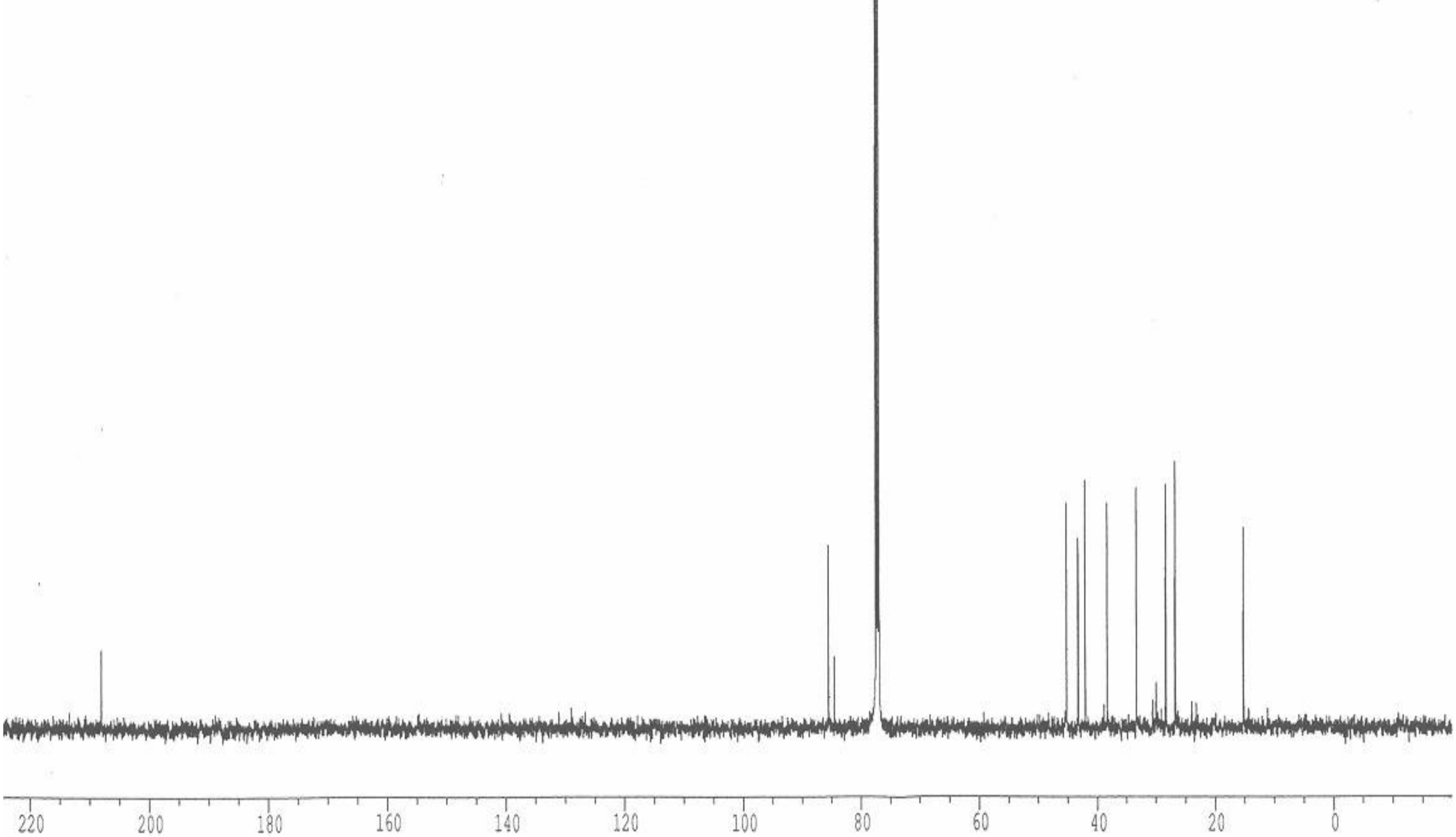
26

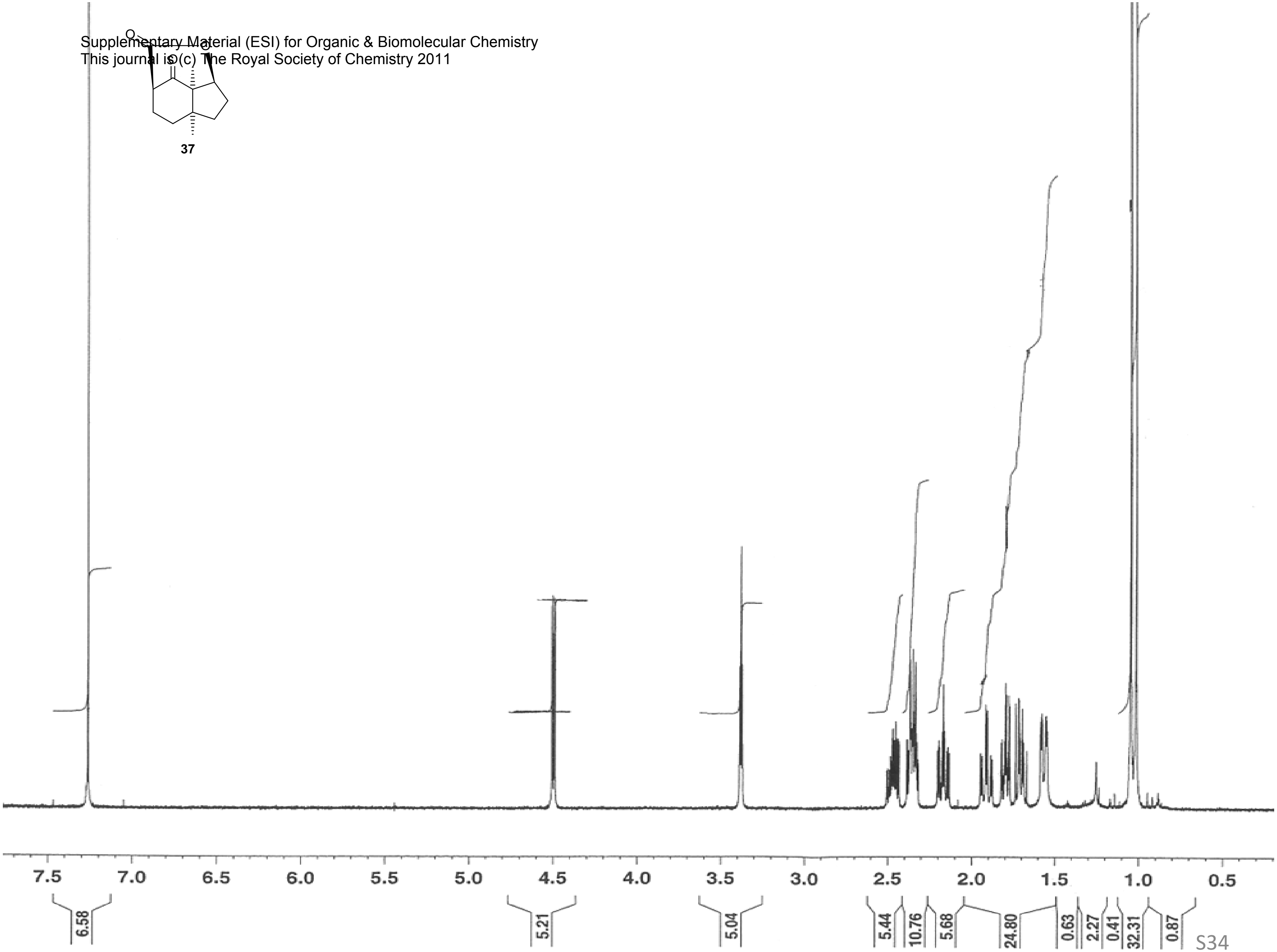

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


27
11.695
2.739
3.832
8.775
4.245
4.345
4.191
12.930
45.080
1.641
0.527
8
7
6
5
4
3
2
1
0

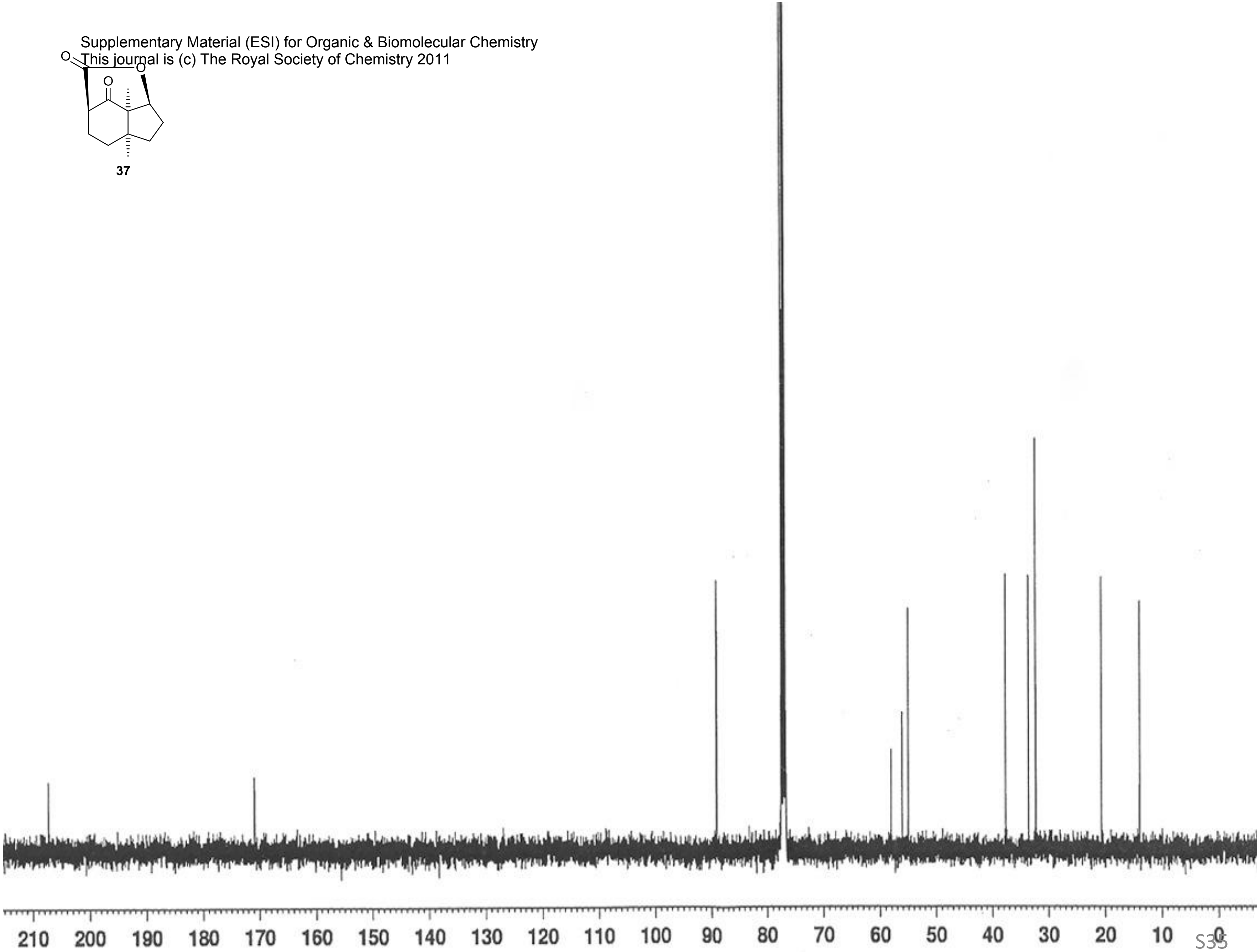


27



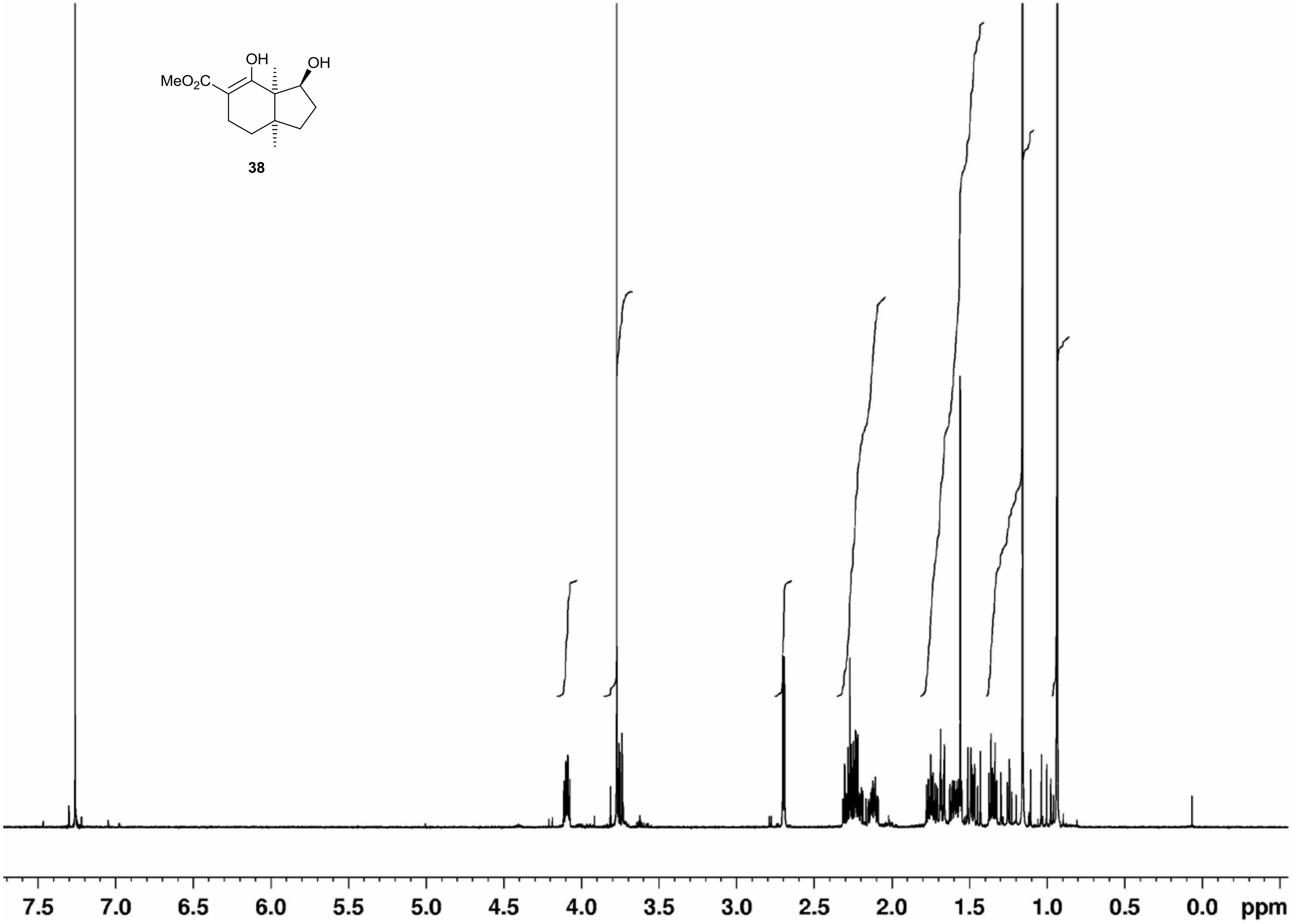

O
O
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
6.58
5.21
5.04
5.44
10.76
5.68
24.80
0.63
2.27
0.41
32.31
0.87

37



37

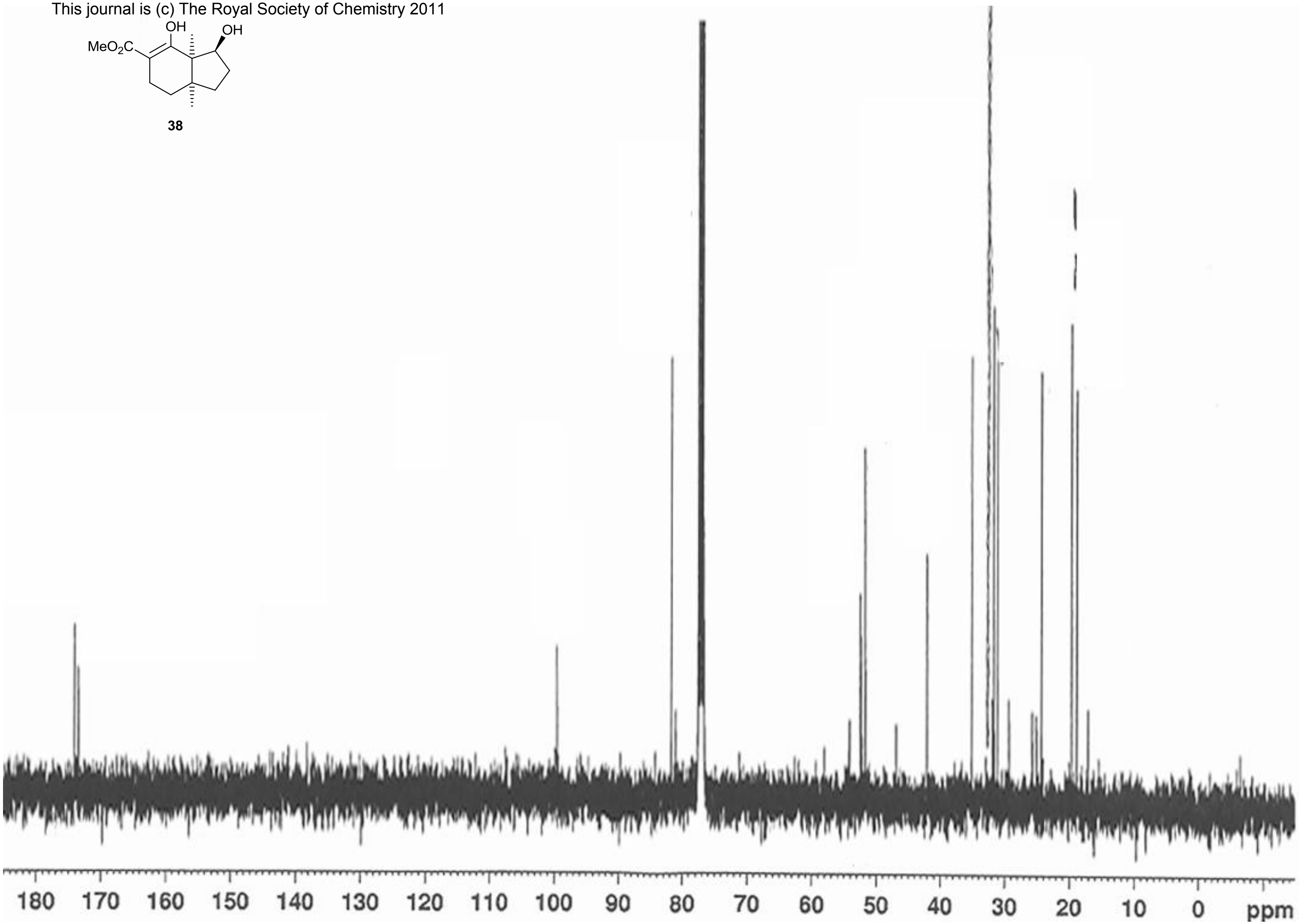
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

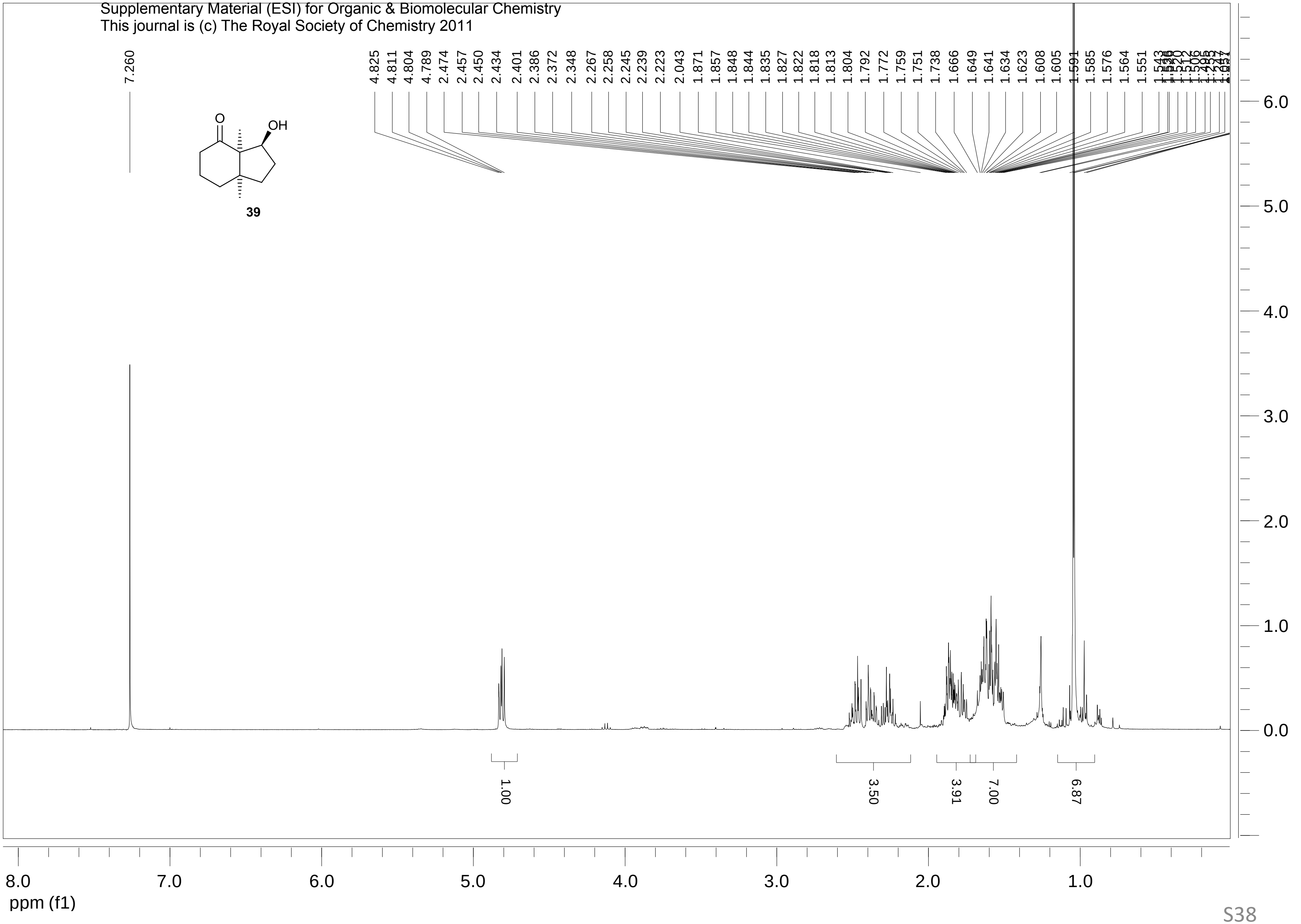


38

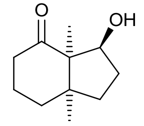
OH
OH
MeO2C

38

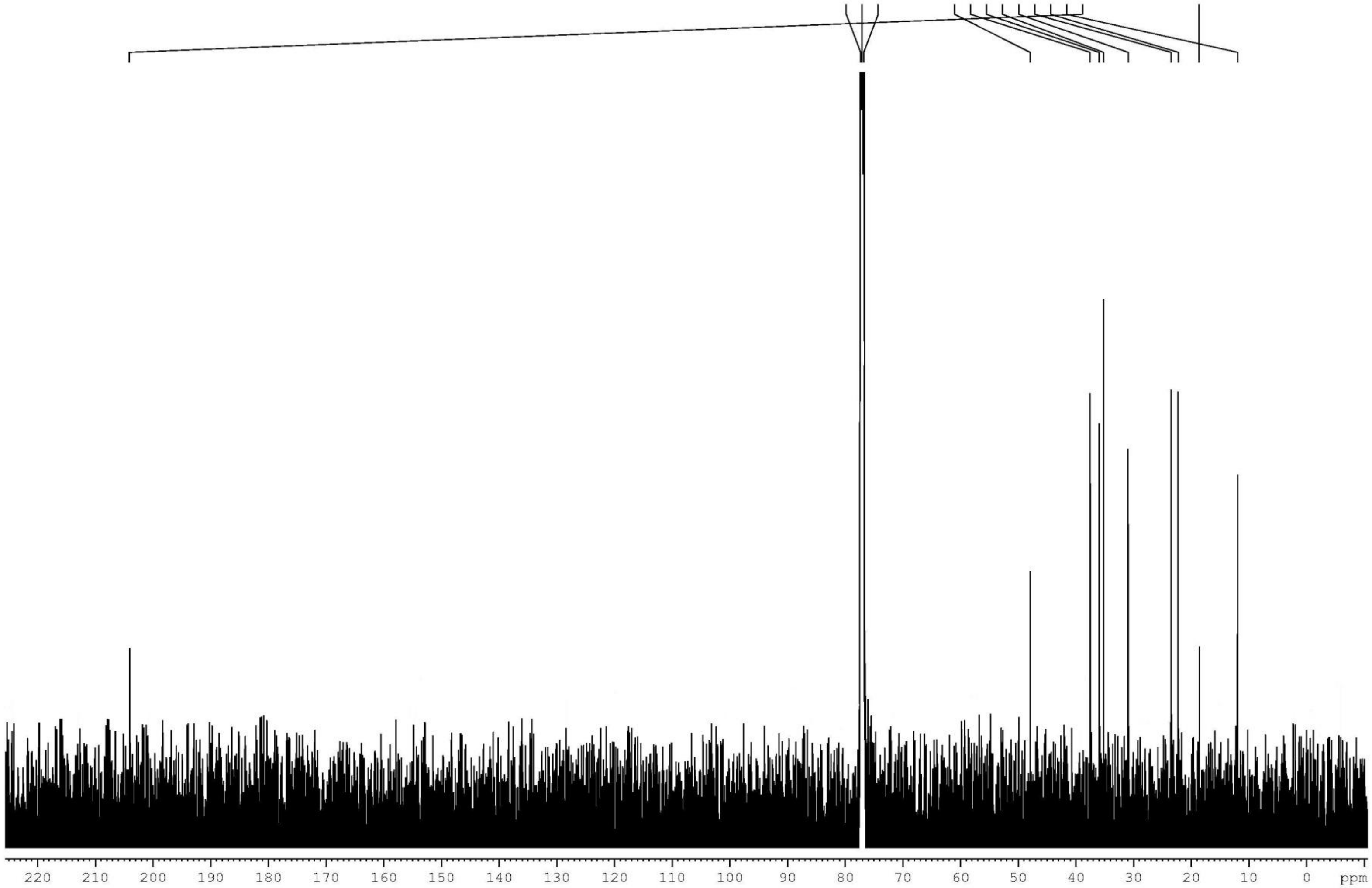

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

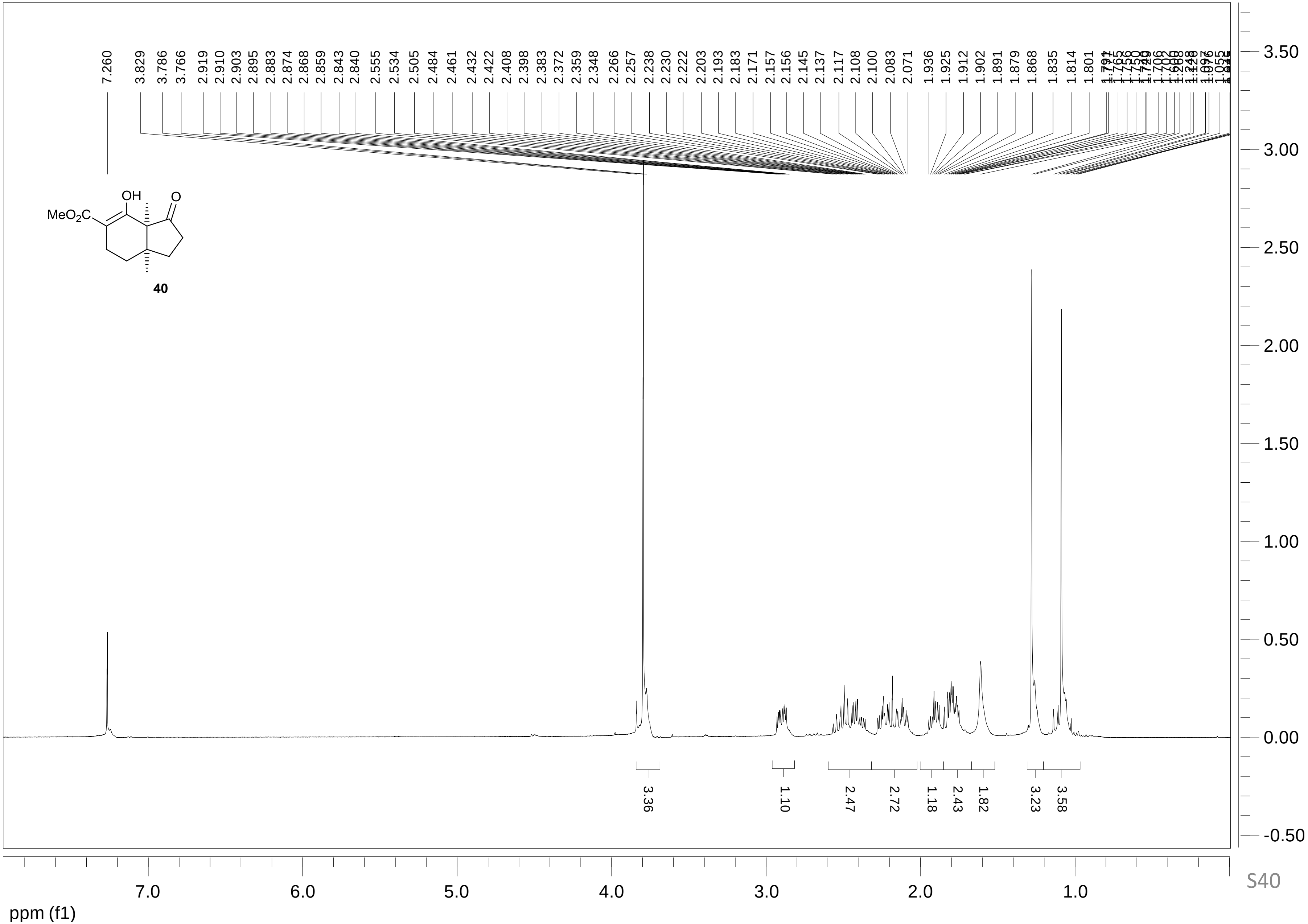

7.260
4.825
4.811
4.804
4.789
2.474
2.457
2.450
2.434
2.401
2.386
2.372
2.348
2.267
2.258
2.245
2.239
2.223
2.043
1.871
1.857
1.848
1.844
1.835
1.827
1.822
1.818
1.813
1.804
1.792
1.772
1.759
1.751
1.738
1.666
1.649
1.641
1.634
1.623
1.608
1.605
1.591
1.585
1.576
1.564
1.551
1.543
1.520
1.512
1.506
O
OH
39
1.00
3.50
3.91
7.00
6.87
6.0
5.0
4.0
3.0
2.0
1.0
0.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

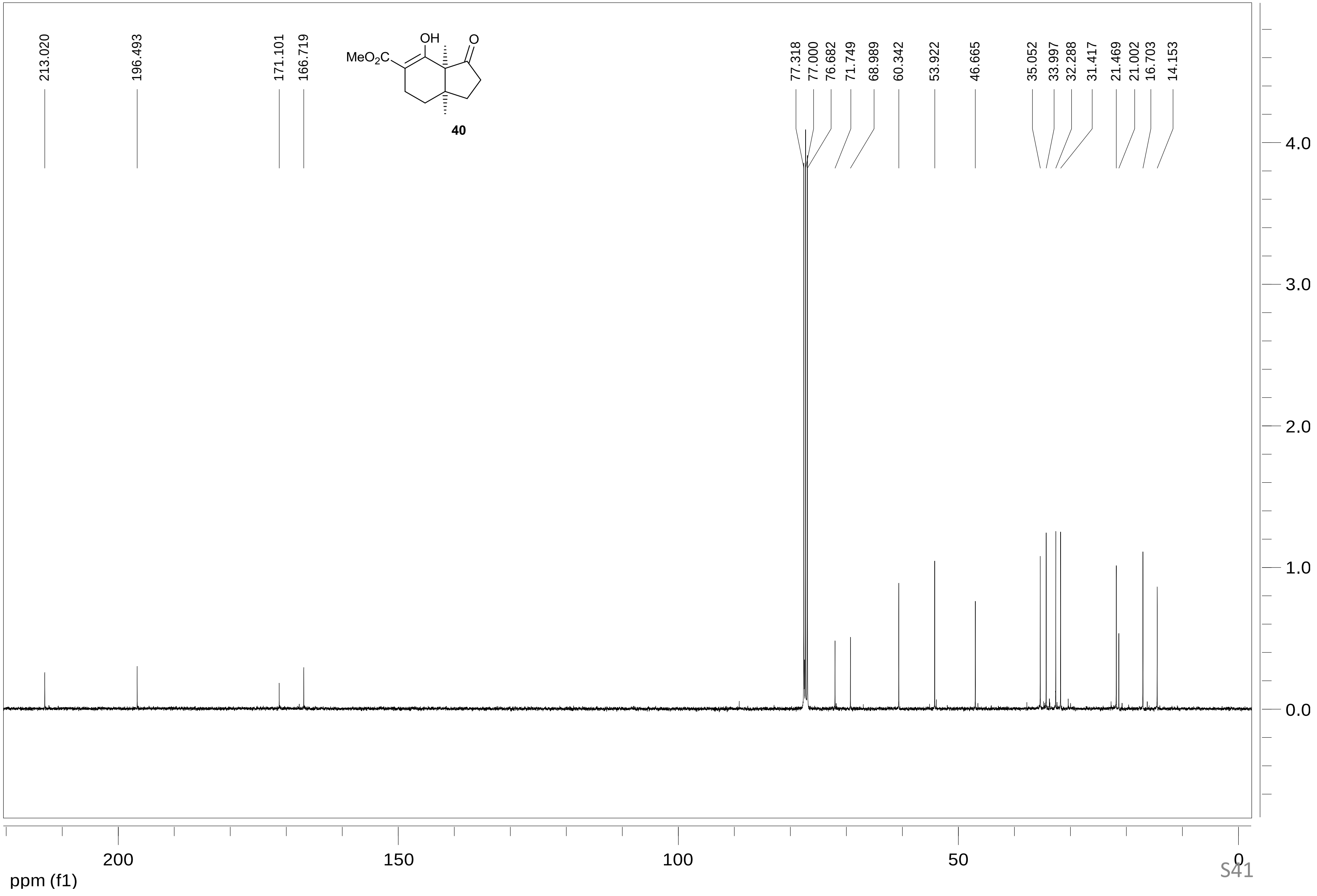
ATR-9-52-2(13C)

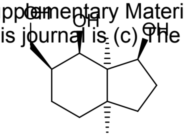


39

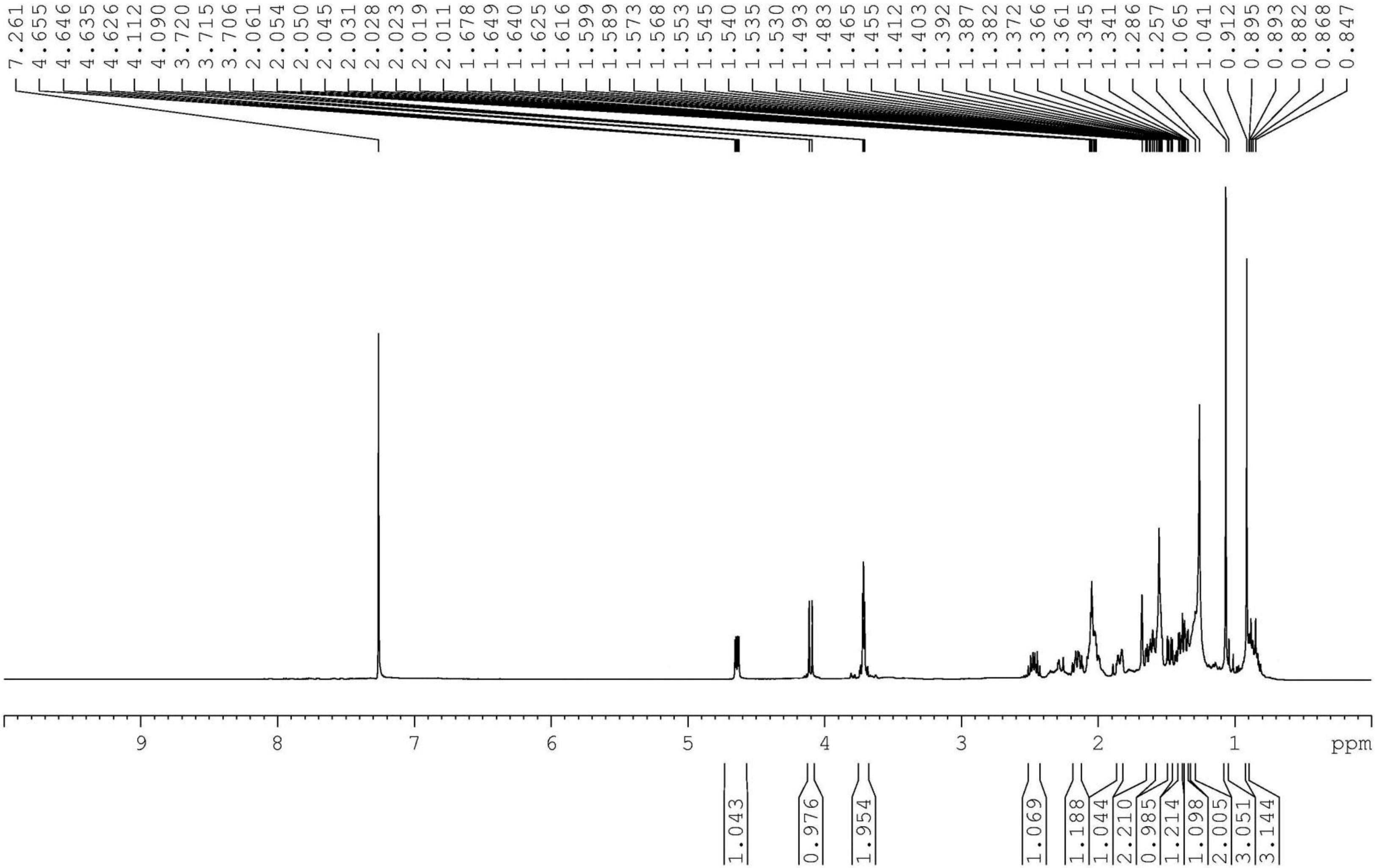


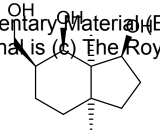

7.260
3.829
3.786
3.766
2.919
2.910
2.903
2.895
2.883
2.874
2.868
2.859
2.843
2.840
2.555
2.534
2.505
2.484
2.461
2.432
2.422
2.408
2.398
2.383
2.372
2.359
2.348
2.266
2.257
2.238
2.230
2.222
2.203
2.193
2.183
2.171
2.157
2.156
2.145
2.137
2.117
2.108
2.100
2.083
2.071
1.936
1.925
1.912
1.902
1.891
1.879
1.868
1.835
1.814
1.801
1.706
1.076
1.055
OH
O
MeO2C
40
3.36
1.10
2.47
2.72
1.18
2.43
1.82
3.23
3.58
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
-0.50
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


213.020
196.493
171.101
166.719
MeO2C
OH
O
40
77.318
77.000
76.682
71.749
68.989
60.342
53.922
46.665
35.052
33.997
32.288
31.417
21.469
21.002
16.703
14.153
4.0
3.0
2.0
1.0
0.0
200
150
100
50
0
ppm (f1)

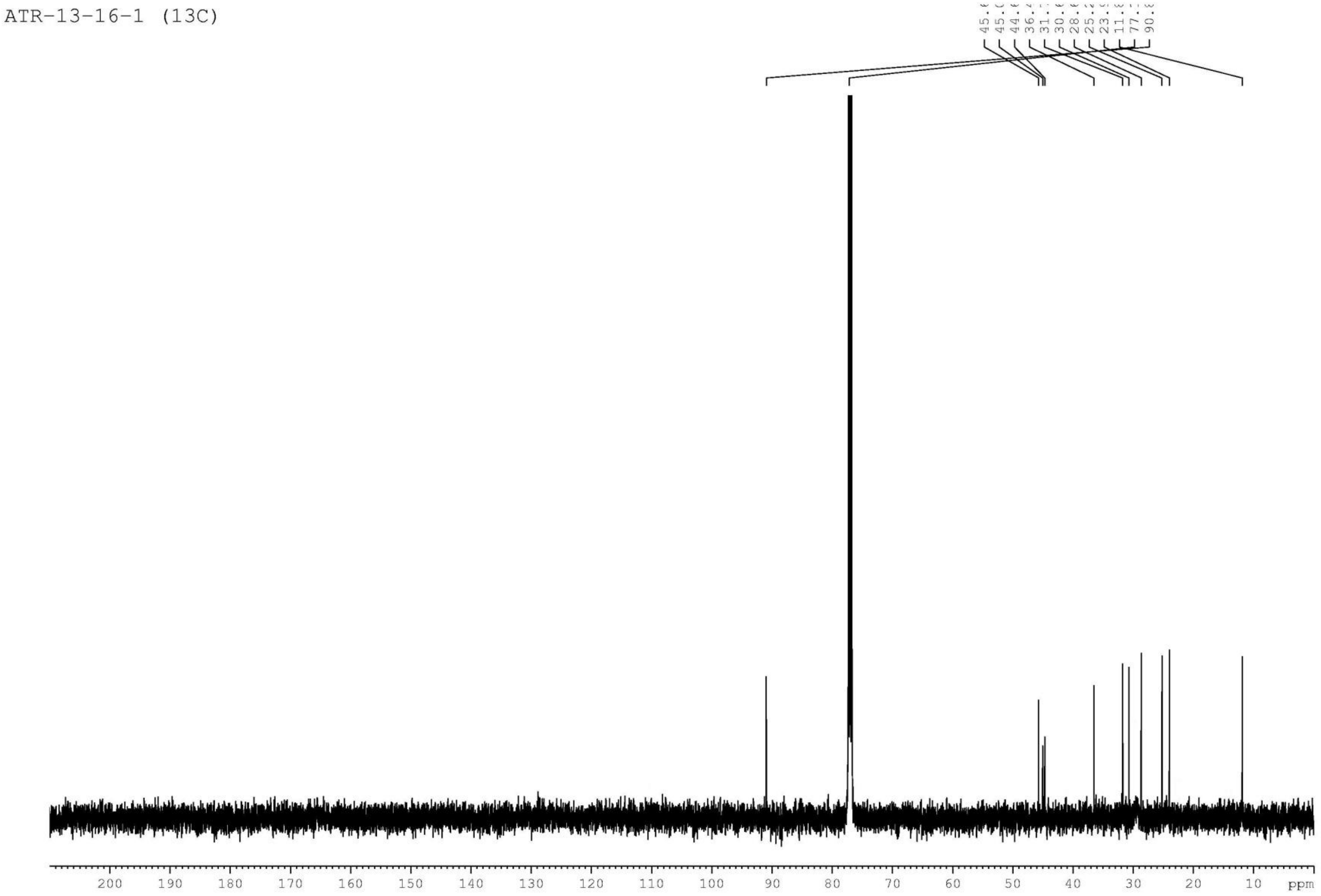

OH
OH
OH

41

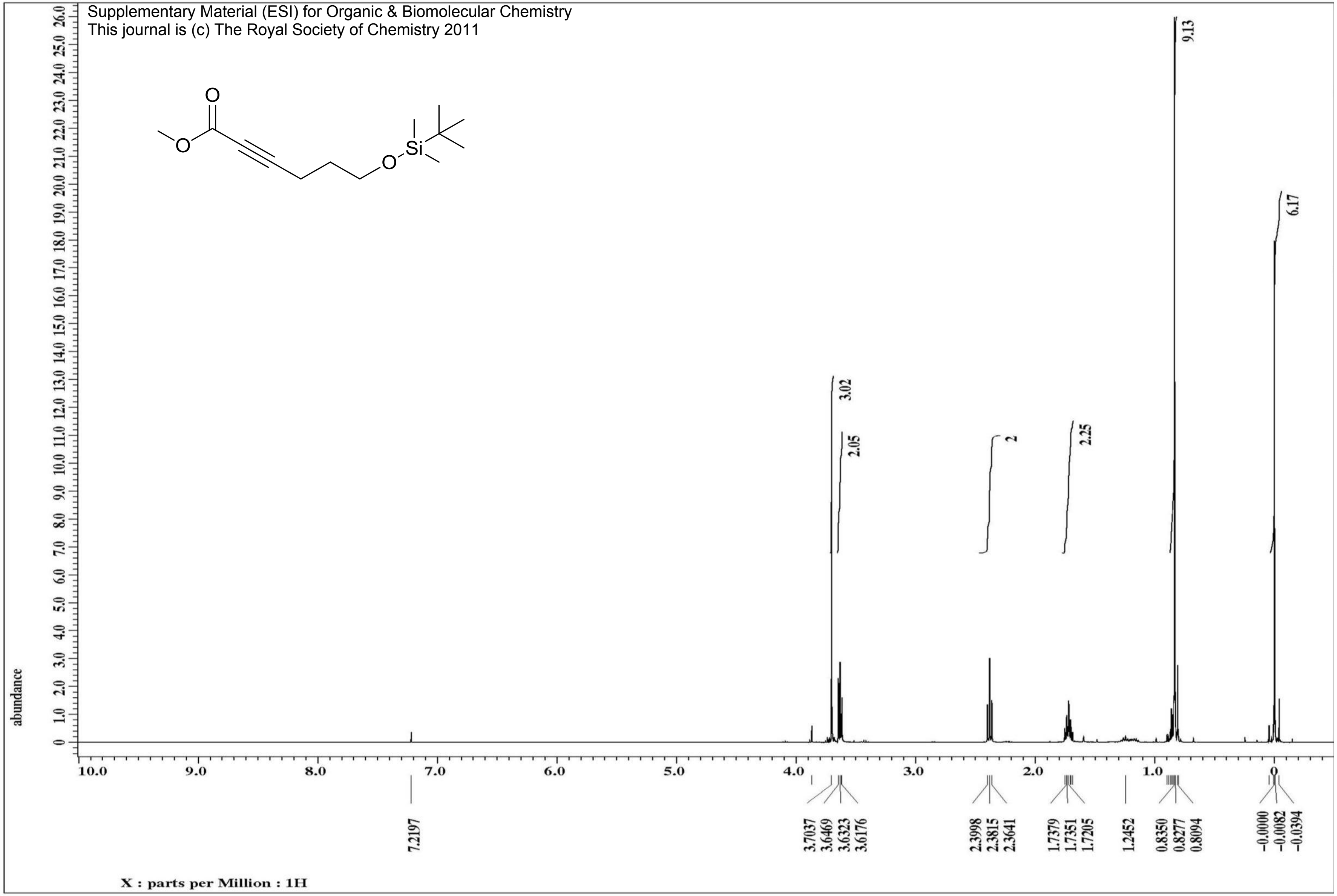

7.261
4.655
4.646
4.635
4.626
4.112
4.090
3.720
3.715
3.706
2.061
2.054
2.050
2.045
2.031
2.028
2.023
2.019
2.011
1.678
1.649
1.640
1.625
1.616
1.599
1.589
1.573
1.568
1.553
1.545
1.540
1.535
1.530
1.493
1.483
1.465
1.455
1.412
1.403
1.392
1.387
1.382
1.372
1.366
1.361
1.345
1.341
1.286
1.257
1.065
1.041
0.912
0.895
0.893
0.882
0.868
0.847
9
8
7
6
5
4
3
2
1
ppm
1.043
0.976
1.954
1.069
1.188
1.044
2.210
0.985
1.214
1.098
2.005
3.051
3.144


OH
OH
OH

41

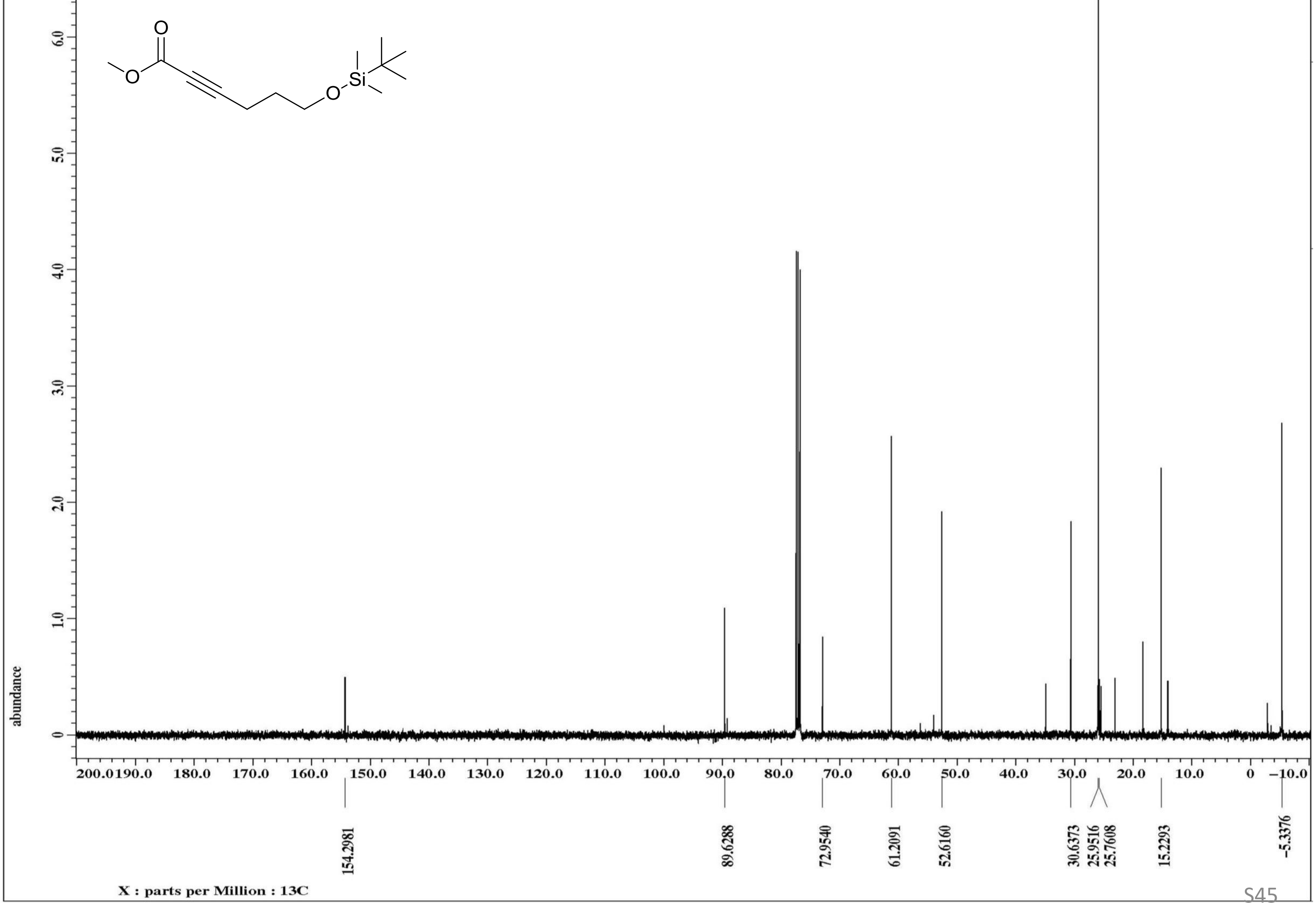

ATR-13-16-1 (13C)
45.
45.
44.
36.
31.
30.
28.
25.
23.
11.
77.
90.
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Compound **48**

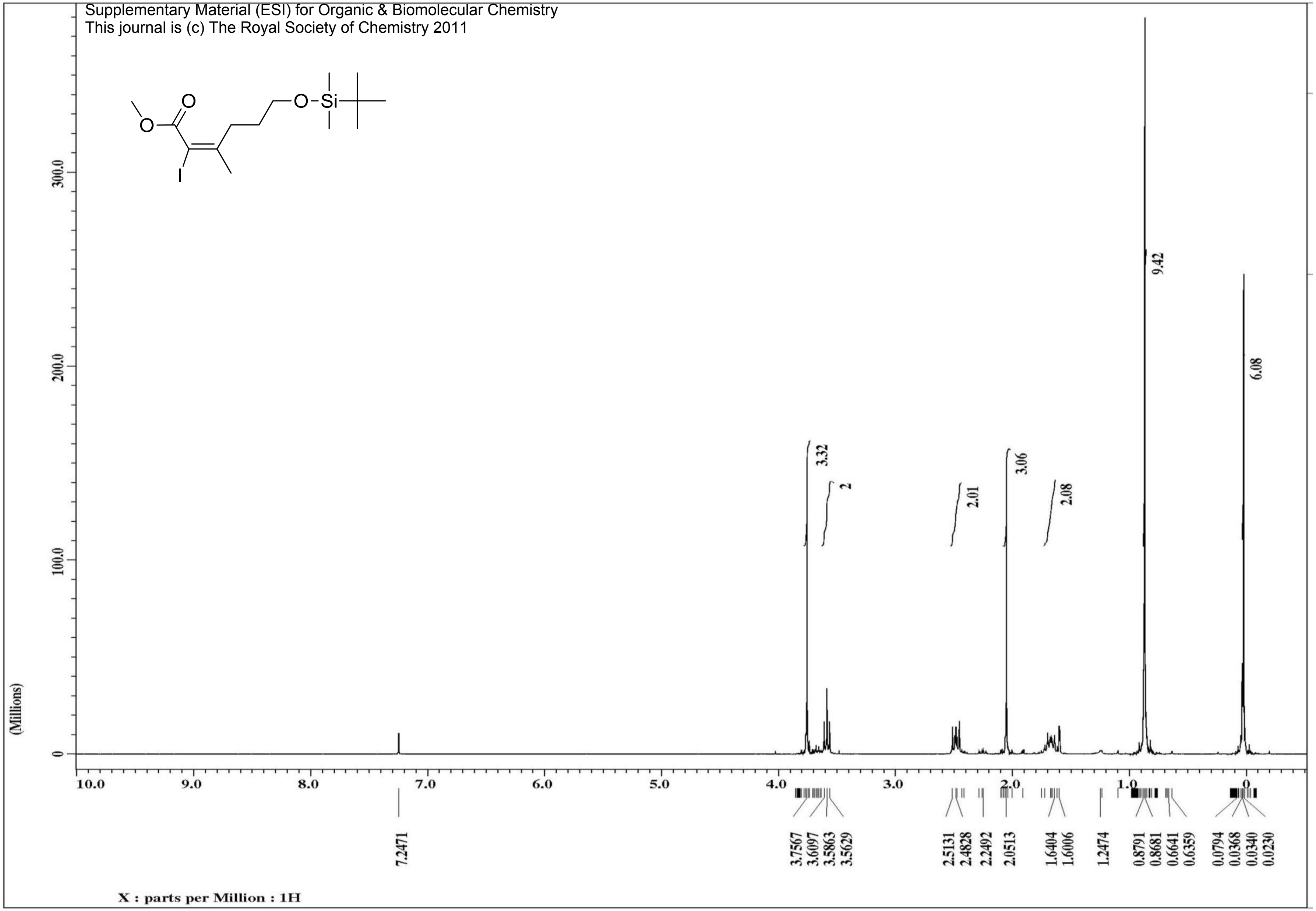


O
O
O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
26.0
3.02
2.05
2
2.25
9.13
6.17
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2197
3.7037
3.6469
3.6323
3.6176
2.3998
2.3815
2.3641
1.7379
1.7351
1.7205
1.2452
0.8350
0.8277
0.8094
-0.0000
-0.0082
-0.0394
X : parts per Million : 1H

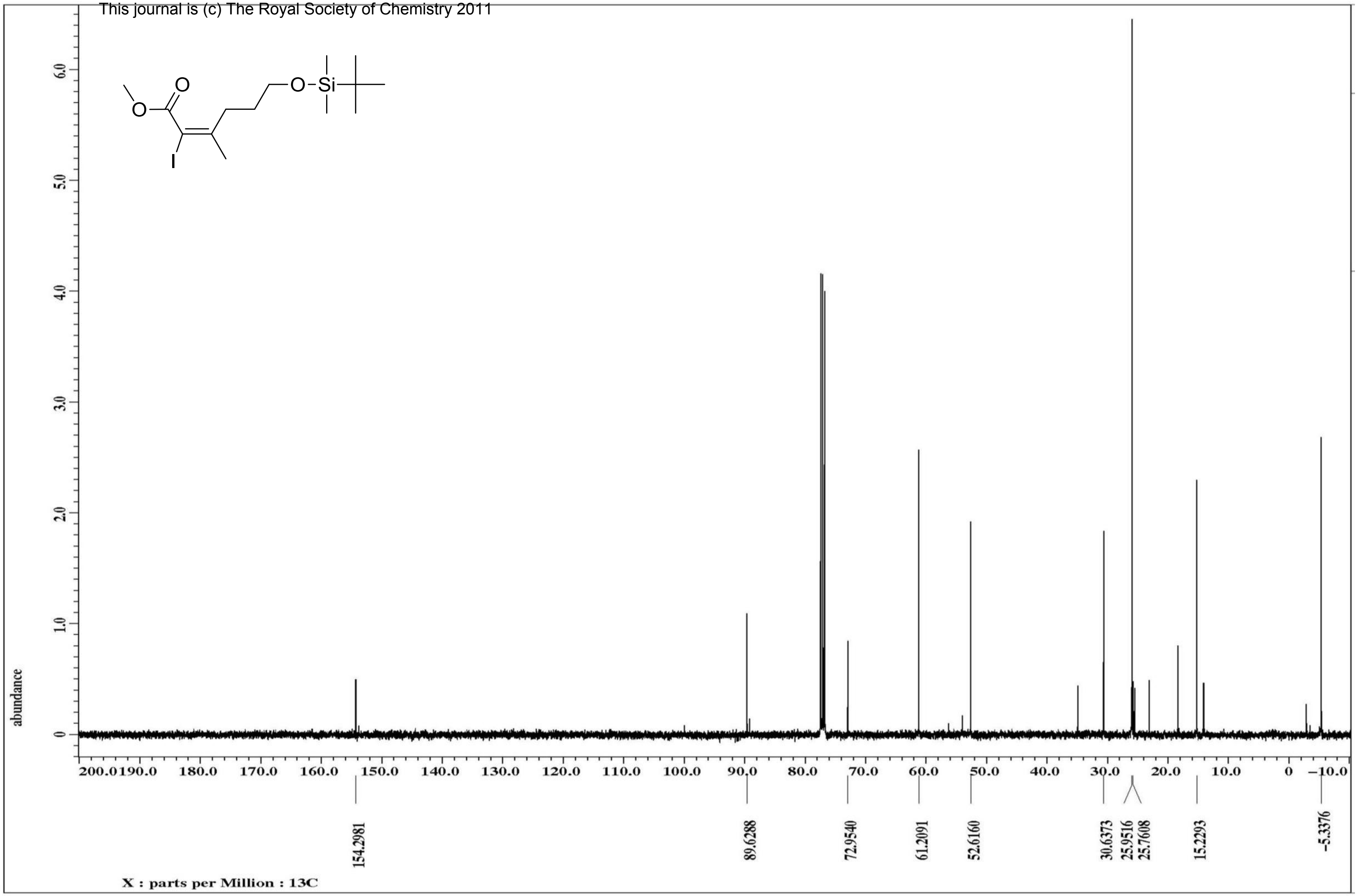
Compound **48**


O
O
O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
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
154.2981
89.6288
72.9540
61.2091
52.6160
30.6373
25.9516
25.7608
15.2293
−5.3376
X : parts per Million : 13C

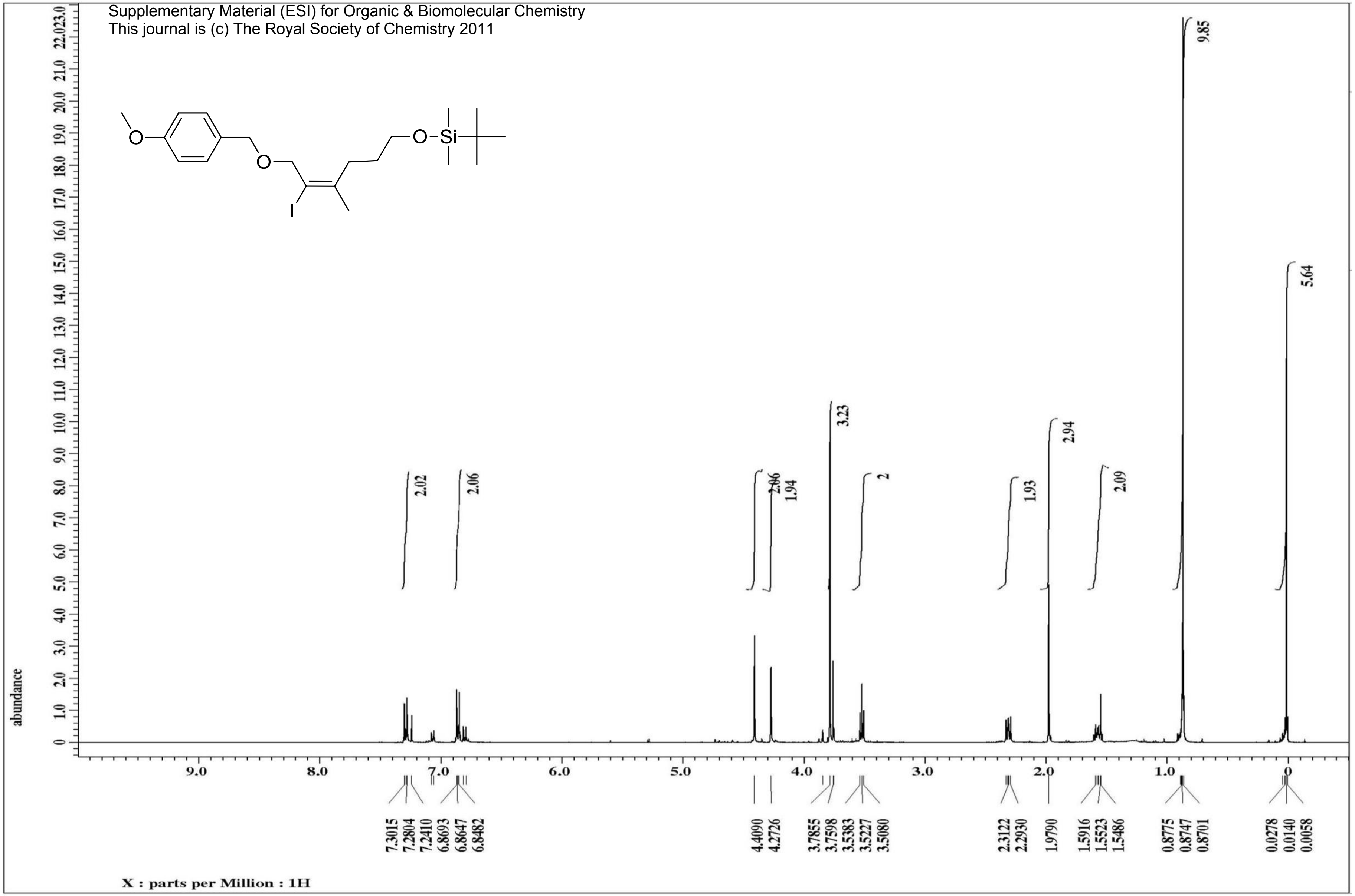
Compound **49**


O
O
I
O
Si
(Millions)
0
100.0
200.0
300.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H
3.32
2
2.01
3.06
2.08
9.42
6.08
7.2471
3.7567
3.6097
3.5863
3.5629
2.5131
2.4828
2.2492
2.0513
1.6404
1.6006
1.2474
0.8791
0.8681
0.6641
0.6359
0.0794
0.0368
0.0340
0.0230

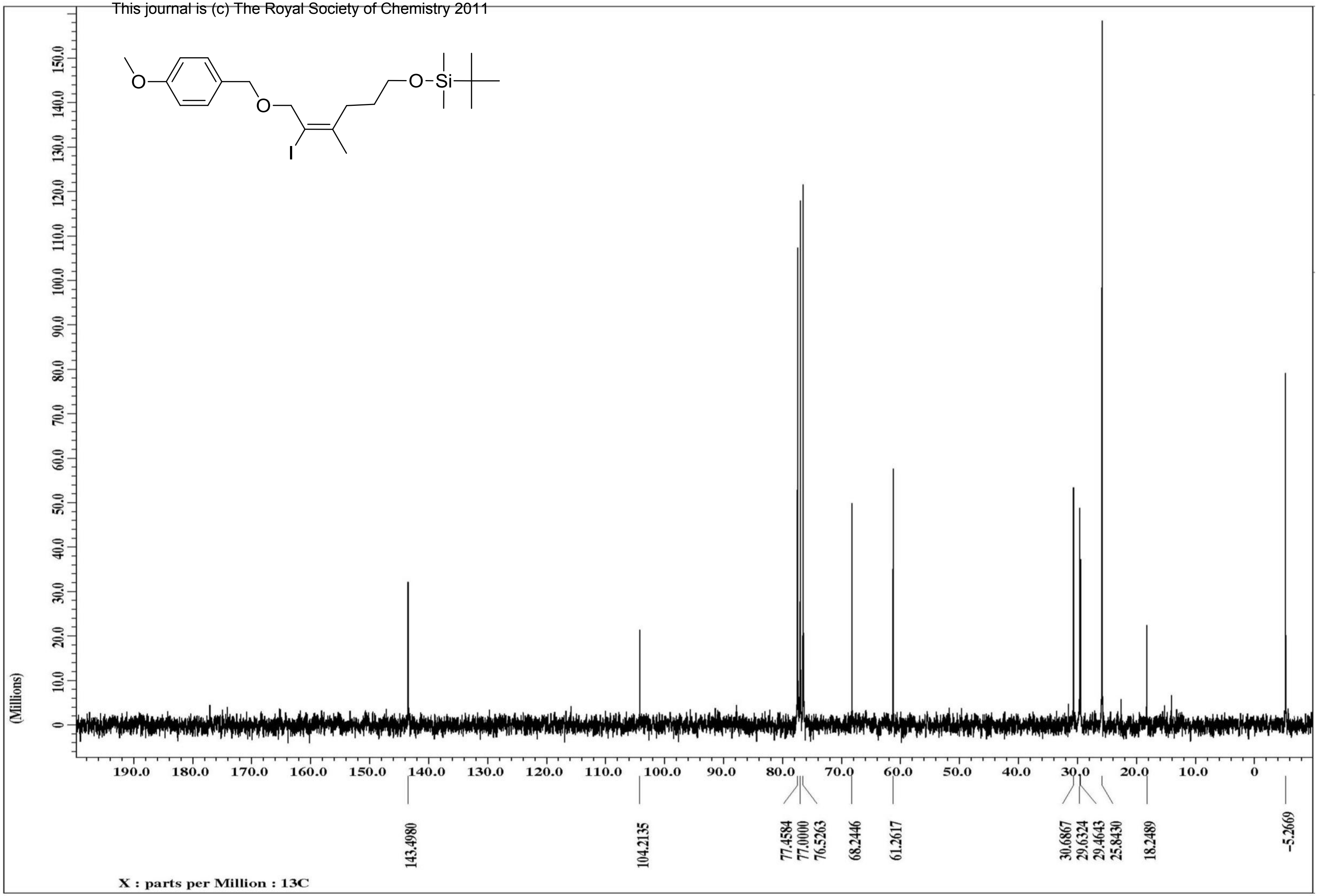
Compound **49**


abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
O
O
O
Si
I
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
154.2981
89.6288
72.9540
61.2091
52.6160
30.6373
25.9516
25.7608
15.2293
−5.3376
X : parts per Million : 13C

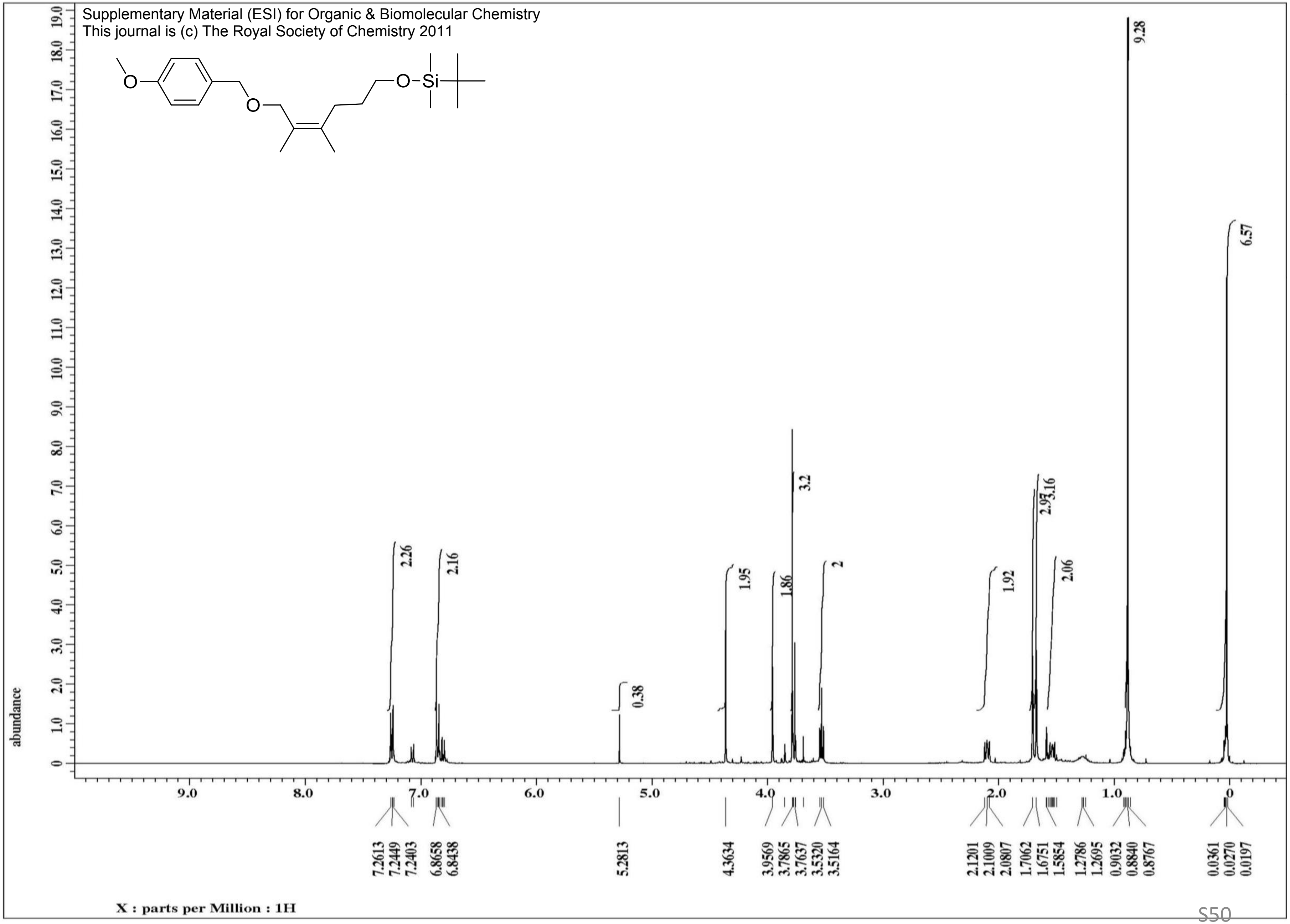
Compound **50**


O
O
I
O
Si
abundance
2.02
2.06
2.06
1.94
3.23
2
1.93
2.94
2.09
9.85
5.64
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3015
7.2804
7.2410
6.8693
6.8647
6.8482
4.4090
4.2726
3.7855
3.7598
3.5383
3.5227
3.5080
2.3122
2.2930
1.9790
1.5916
1.5523
1.5486
0.8775
0.8747
0.8701
0.0278
0.0140
0.0058
X : parts per Million : 1H

Compound **50**

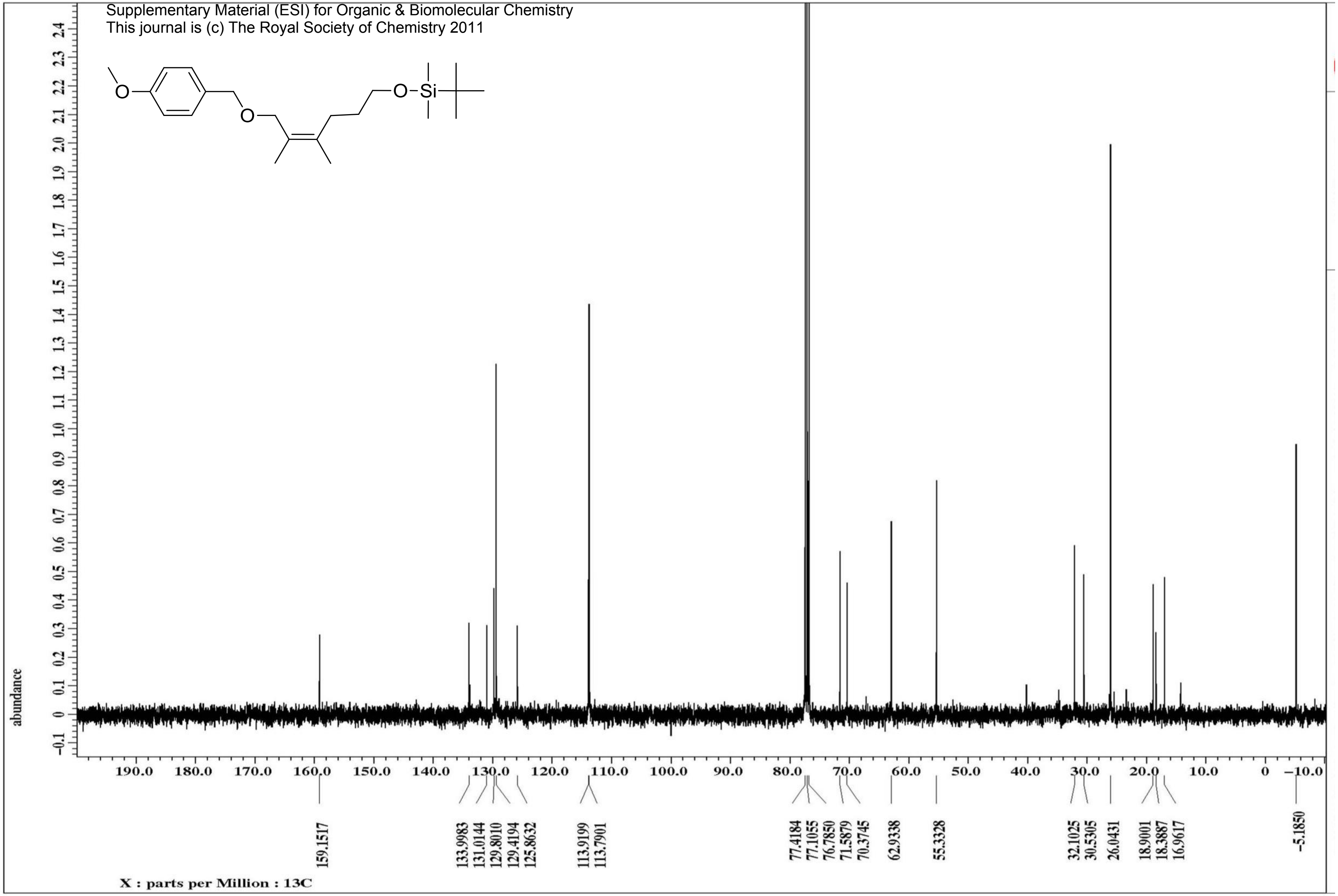

O
O
I
O
Si
(Millions)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
143.4980
104.2135
77.4584
77.0000
76.5263
68.2446
61.2617
30.6867
29.6324
29.4643
25.8430
18.2489
-5.2669
X : parts per Million : 13C

Compound **51**



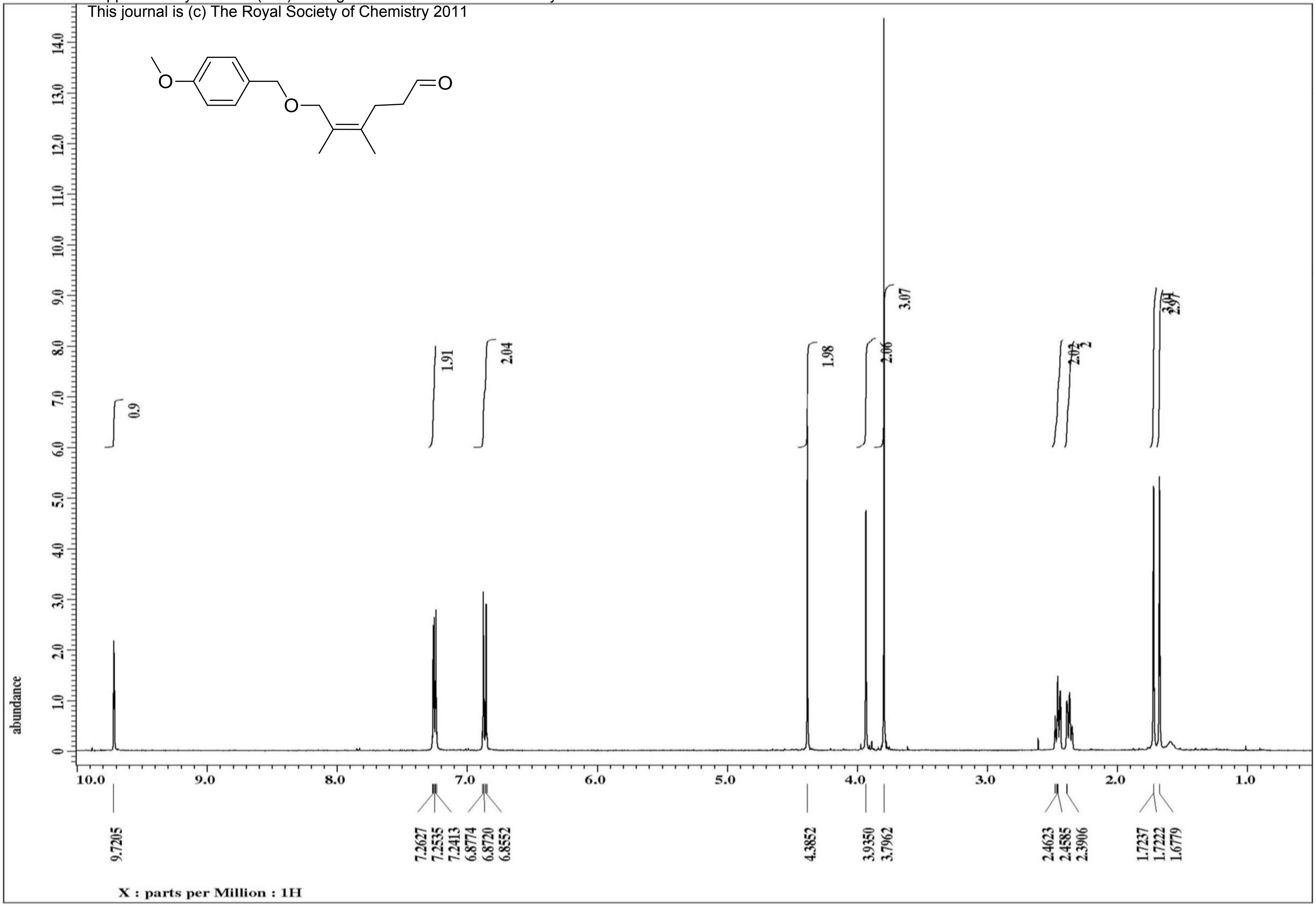
O
O
O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.26
2.16
0.38
1.95
1.86
3.2
2
1.92
2.97
3.16
2.06
9.28
6.57
7.2613
7.2449
7.2403
6.8658
6.8438
5.2813
4.3634
3.9569
3.7865
3.7637
3.5320
3.5164
2.1201
2.1009
2.0807
1.7062
1.6751
1.5854
1.2786
1.2695
0.9032
0.8840
0.8767
0.0361
0.0270
0.0197
X : parts per Million : 1H

Compound **51**

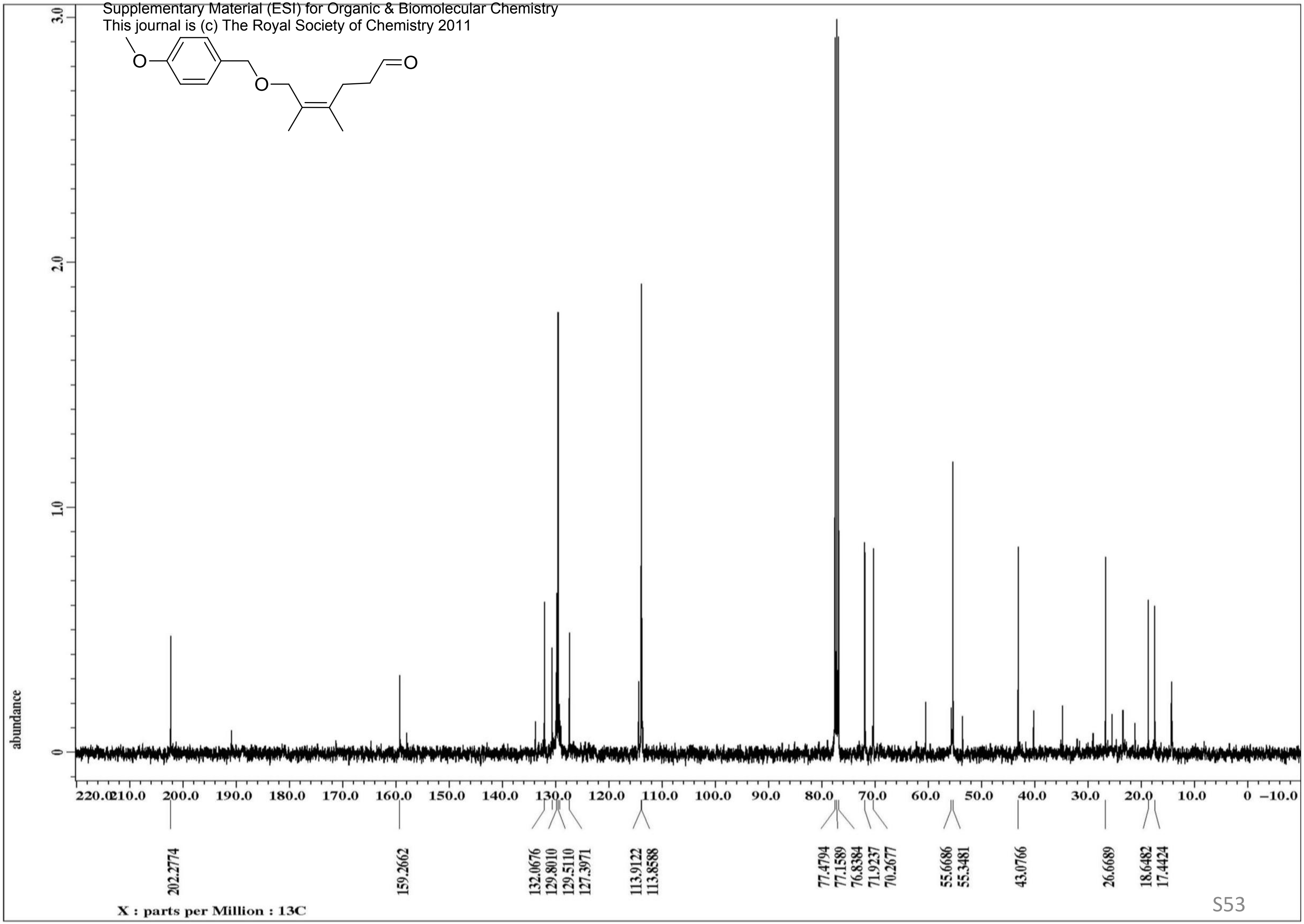


O
O
O
Si
abundance
-0.1
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
159.1517
133.9983
131.0144
129.8010
129.4194
125.8632
113.9199
113.7901
77.4184
77.1055
76.7850
71.5879
70.3745
62.9338
55.3328
32.1025
30.5305
26.0431
18.9001
18.3887
16.9617
-5.1850
X : parts per Million : 13C

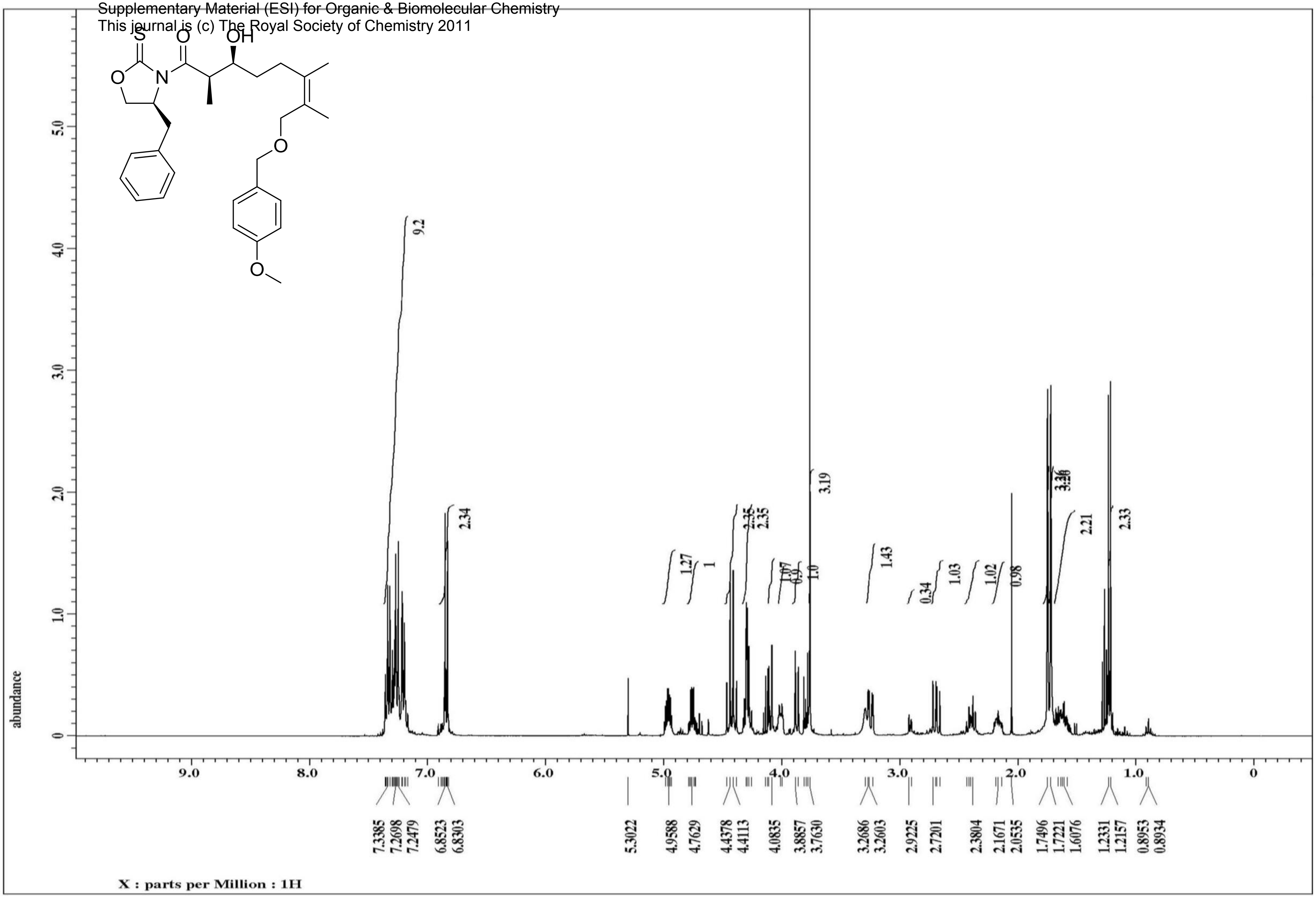
Compound **46**


O
O
O
abundance
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
0.9
1.91
2.04
1.98
2.06
3.07
2.02
2
3.01
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
9.7205
7.2627
7.2535
7.2413
6.8774
6.8720
6.8552
4.3852
3.9350
3.7962
2.4623
2.4585
2.3906
1.7237
1.7222
1.6779
X : parts per Million : 1H

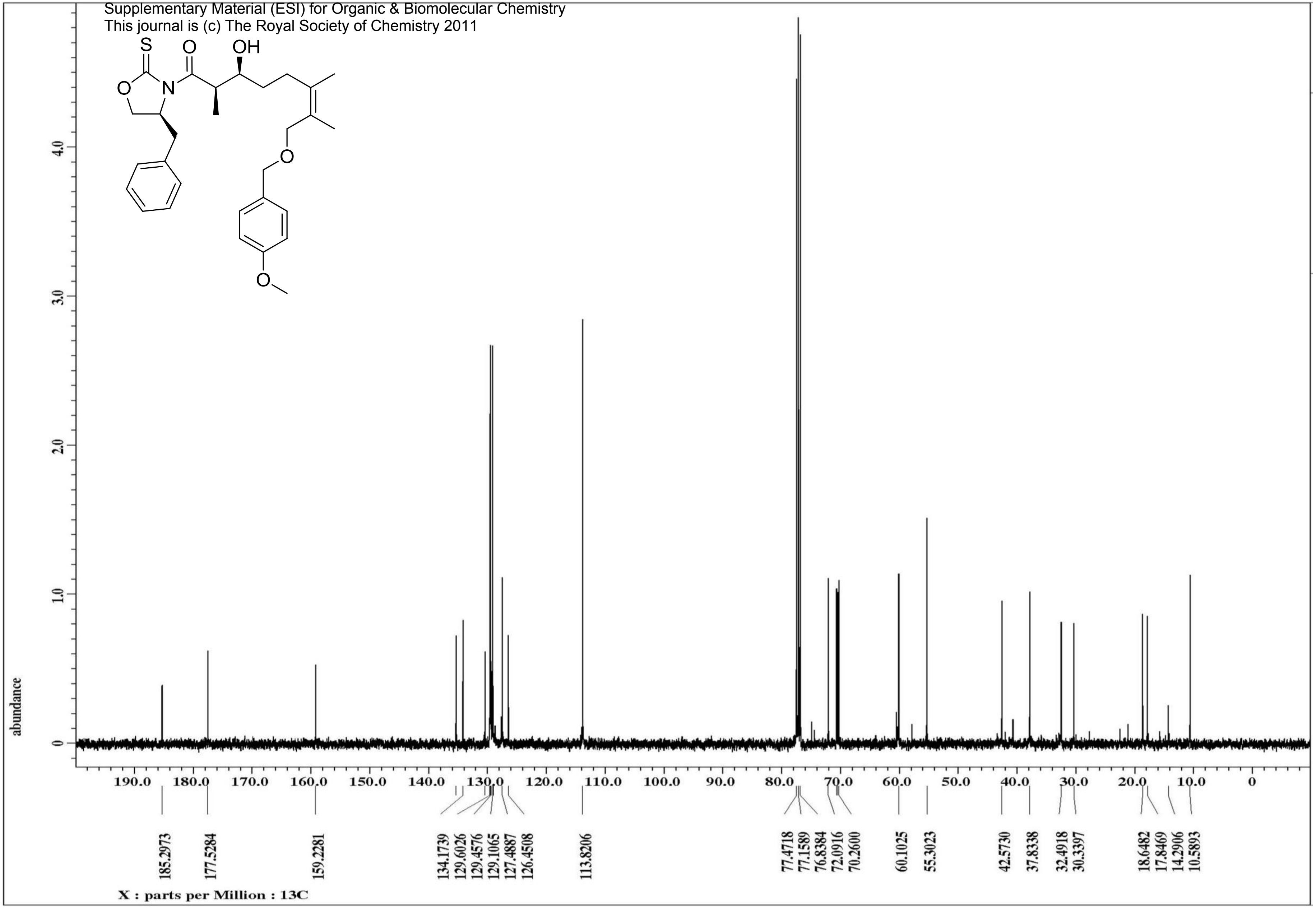
Compound **46**


O
O
O
3.0
2.0
1.0
0
abundance
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
202.2774
159.2662
132.0676
129.8010
129.5110
127.3971
113.9122
113.8588
77.4794
77.1589
76.8384
71.9237
70.2677
55.6686
55.3481
43.0766
26.6689
18.6482
17.4424
X : parts per Million : 13C

Compound **53**

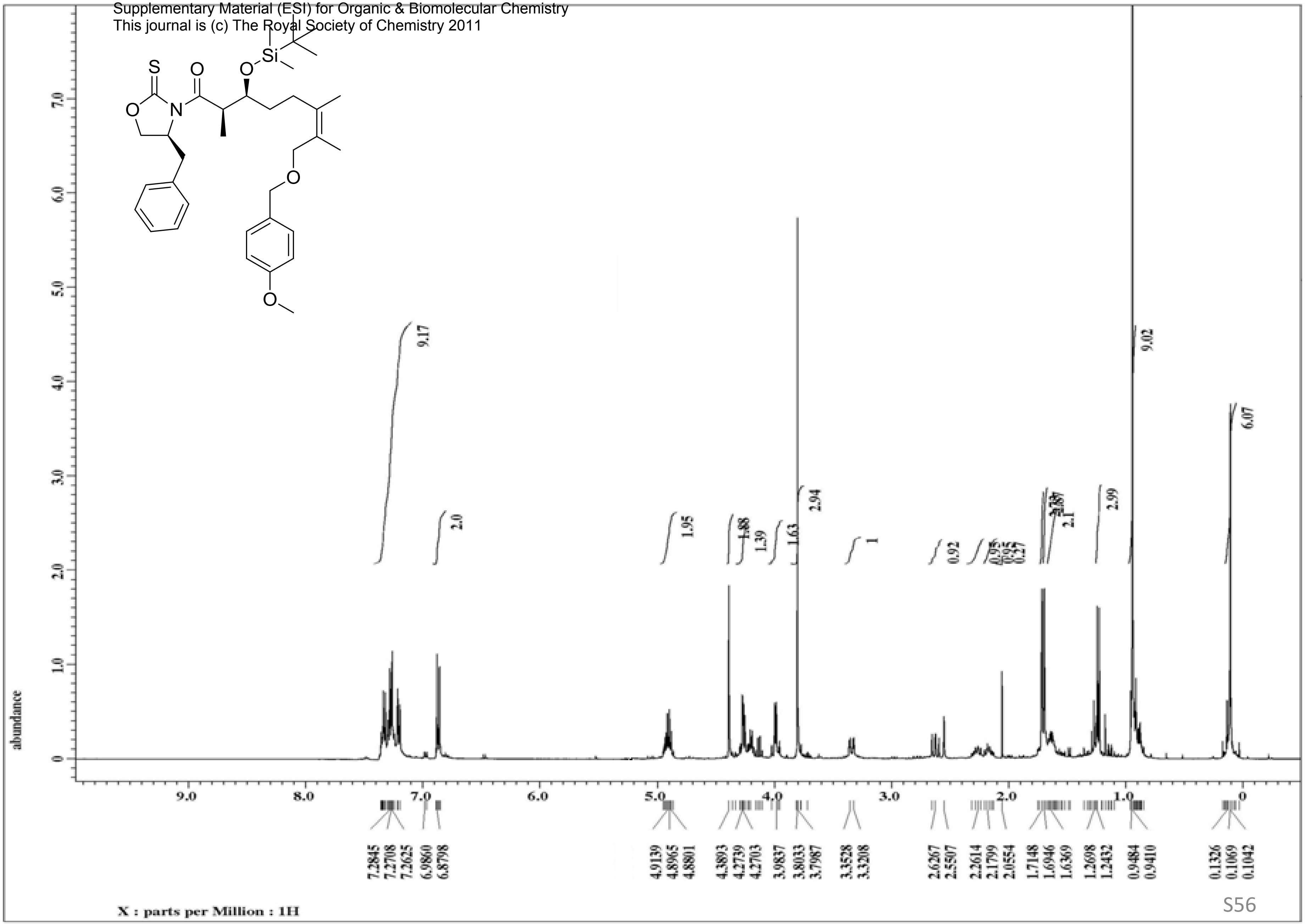

S
O
OH
O
N
O
O
abundance
0
1.0
2.0
3.0
4.0
5.0
9.2
2.34
1.27
1
2.35
2.35
1.07
0.9
1.0
3.19
1.43
0.34
1.03
1.02
0.98
3.36
2.21
2.33
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.3385
7.2698
7.2479
6.8523
6.8303
5.3022
4.9588
4.7629
4.4378
4.4113
4.0835
3.8857
3.7630
3.2686
3.2603
2.9225
2.7201
2.3804
2.1671
2.0535
1.7496
1.7221
1.6076
1.2331
1.2157
0.8953
0.8934
X : parts per Million : 1H

Compound **53**

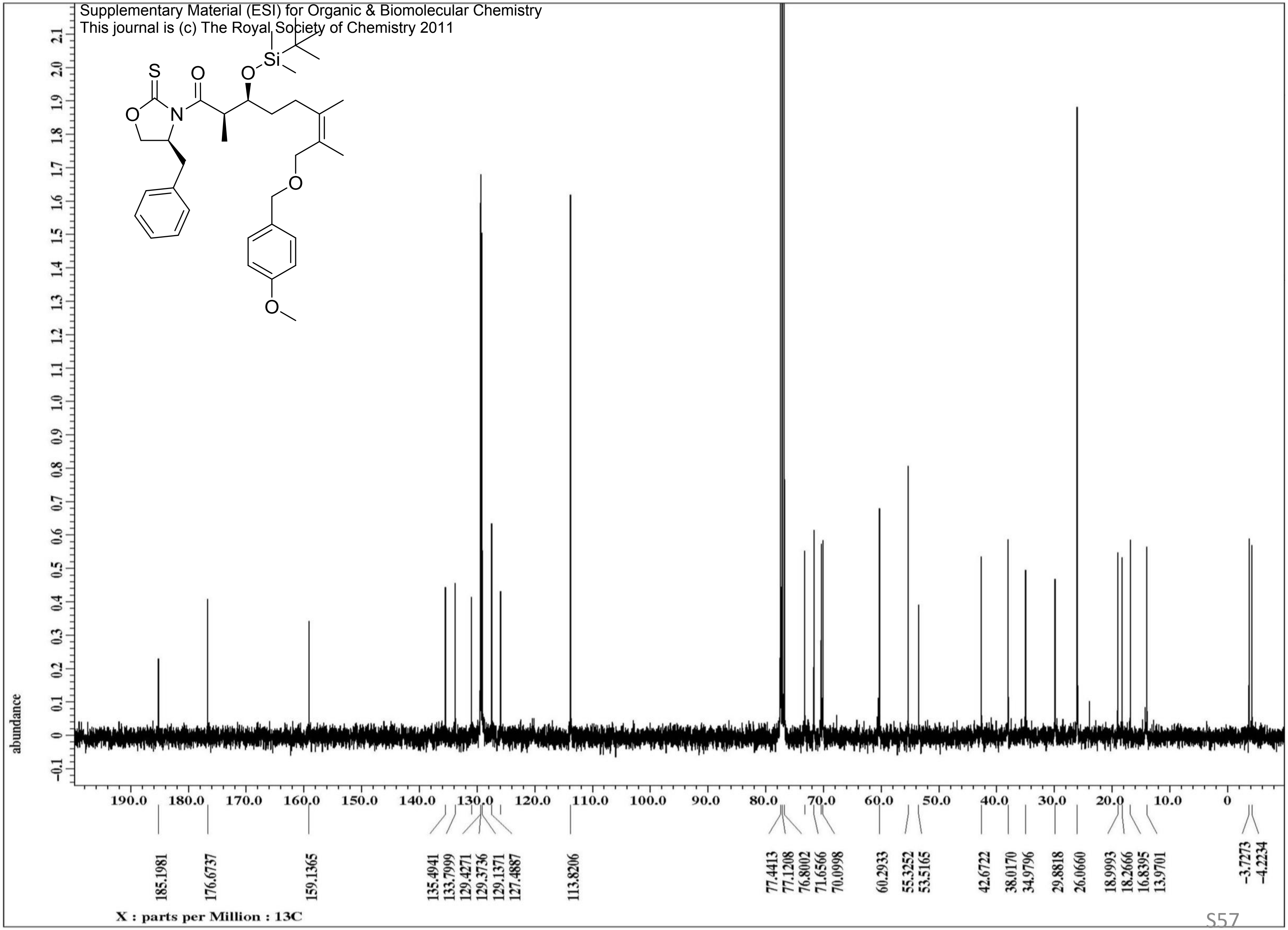


S
O
OH
O
N
O
O
abundance
0
1.0
2.0
3.0
4.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
185.2973
177.5284
159.2281
134.1739
129.6026
129.4576
129.1065
127.4887
126.4508
113.8206
77.4718
77.1589
76.8384
72.0916
70.2600
60.1025
55.3023
42.5730
37.8338
32.4918
30.3397
18.6482
17.8469
14.2906
10.5893
X : parts per Million : 13C

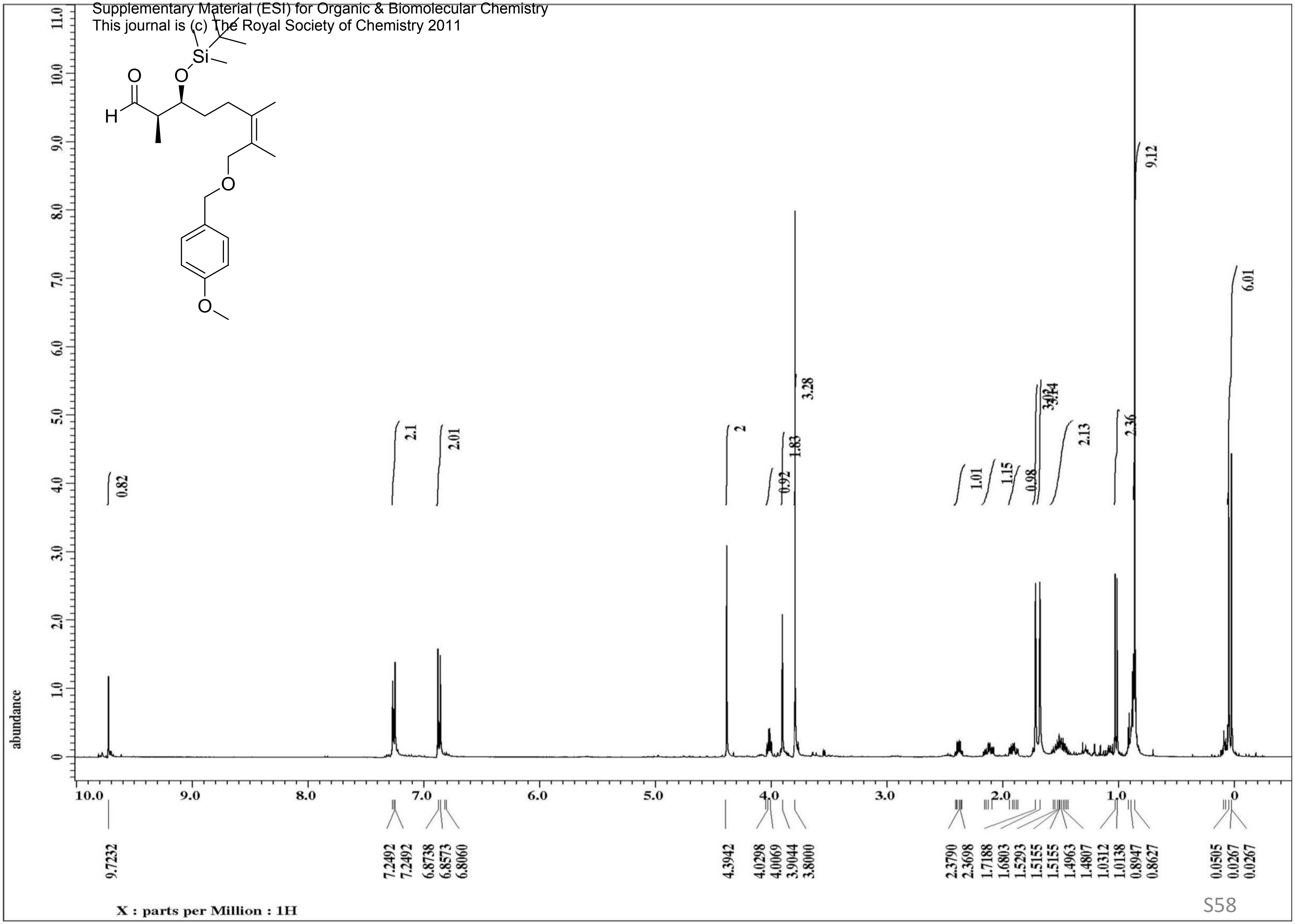
Compound **54**


abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
9.17
2.0
1.95
1.88
1.39
1.63
2.94
1
0.92
2.1
2.99
9.02
6.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2845
7.2708
7.2625
6.9860
6.8798
4.9139
4.8965
4.8801
4.3803
4.2739
4.2703
3.9837
3.8033
3.7987
3.3528
3.3208
2.6267
2.5507
2.2614
2.1799
2.0554
1.7148
1.6946
1.6369
1.2698
1.2432
0.9484
0.9410
0.1326
0.1069
0.1042
X : parts per Million : 1H

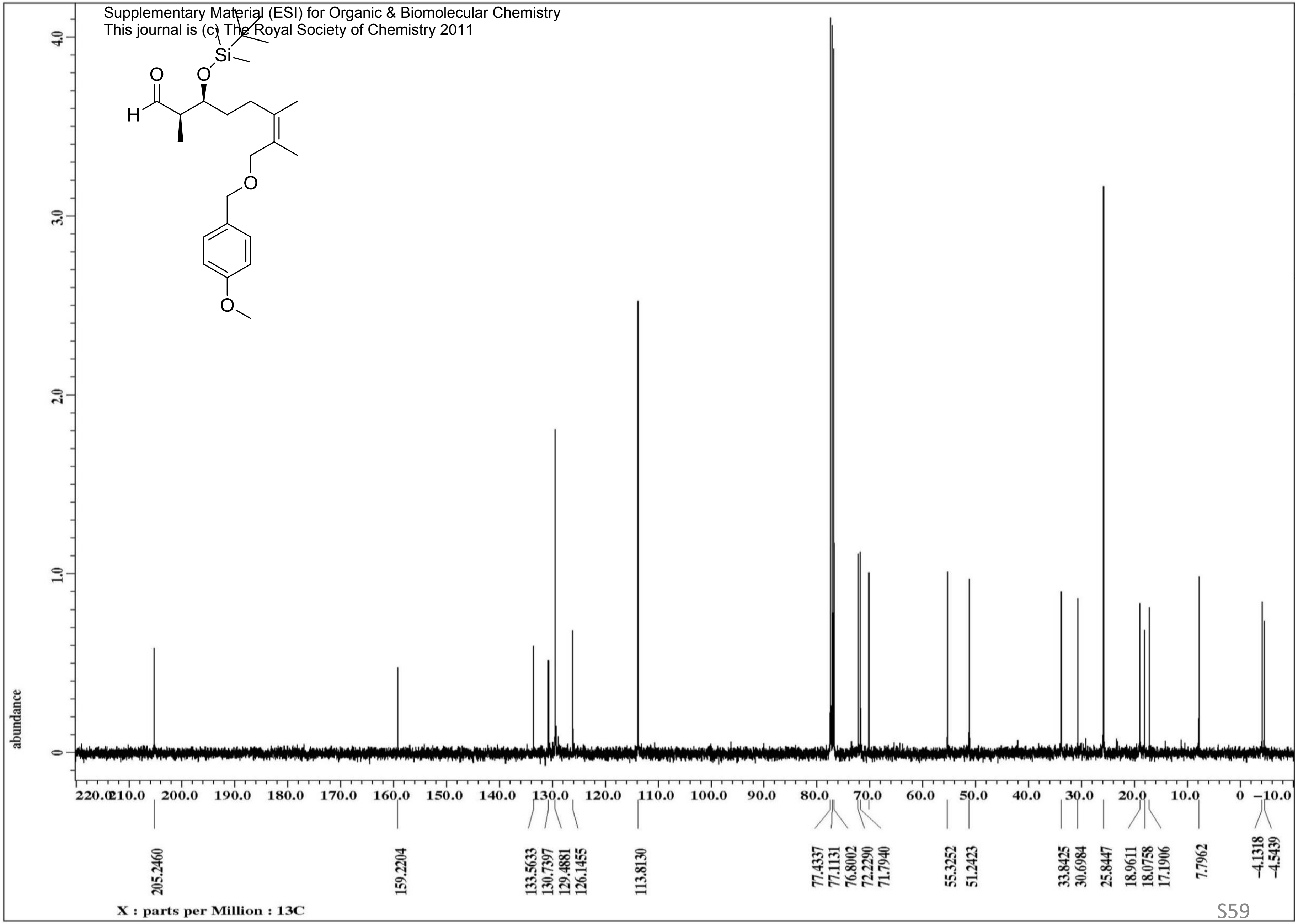
Compound **54**


S
O
N
O
O
Si
O
O
abundance
2.1
2.0
1.9
1.8
1.7
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
−0.1
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
185.1981
176.6737
159.1365
135.4941
133.7999
129.4271
129.3736
129.1371
127.4887
113.8206
77.4413
77.1208
76.8002
71.6566
70.0998
60.2933
55.3252
53.5165
42.6722
38.0170
34.9796
29.8818
26.0660
18.9993
18.2666
16.8395
13.9701
−3.7273
−4.2234
X : parts per Million : 13C

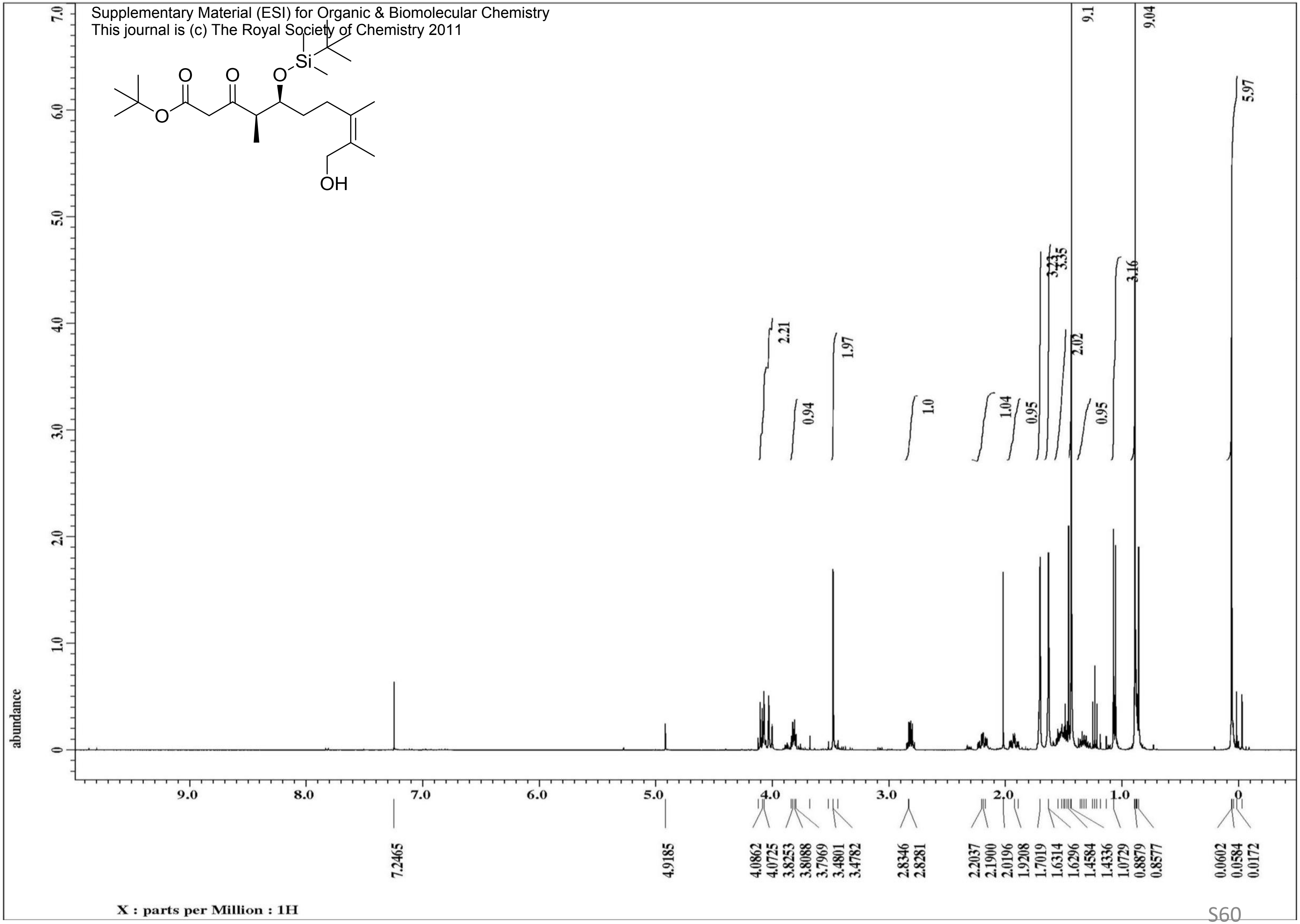
Compound **55**


O
H
O
Si
O
O
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0.82
2.1
2.01
2
0.92
1.83
3.28
1.01
1.15
0.98
3.02
3.14
2.13
2.36
9.12
6.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
9.7232
7.2492
7.2492
6.8738
6.8573
6.8060
4.3942
4.0298
4.0069
3.9044
3.8000
2.3790
2.3698
1.7188
1.6803
1.5293
1.5155
1.5155
1.4963
1.4807
1.0312
1.0138
0.8947
0.8627
0.0505
0.0267
0.0267
X : parts per Million : 1H

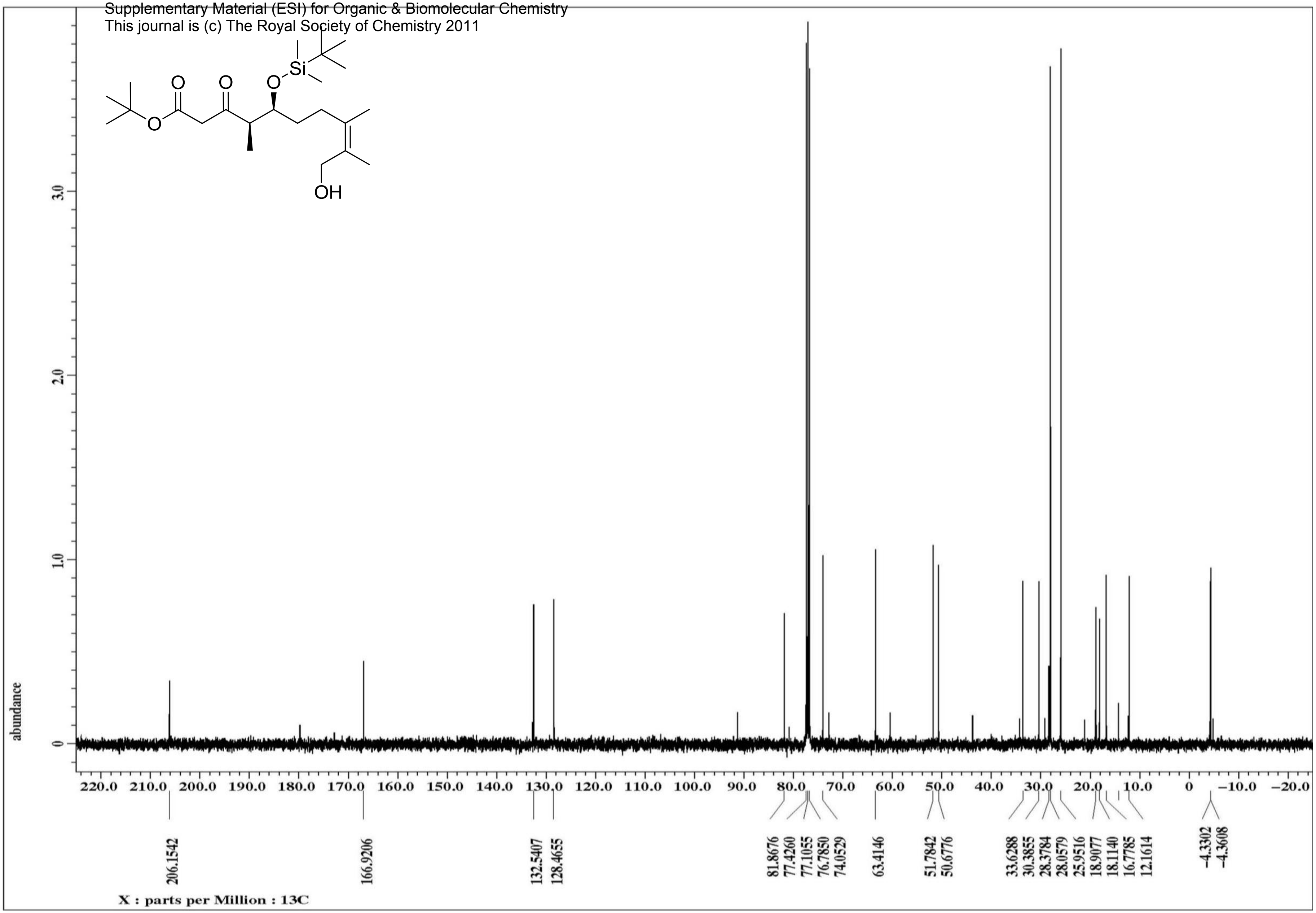
Compound **55**


O
H
O
Si
O
O
abundance
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
205.2460
159.2204
133.5633
130.7397
129.4881
126.1455
113.8130
77.4337
77.1131
76.8002
72.2290
71.7940
55.3252
51.2423
33.8425
30.6984
25.8447
18.9611
18.0758
17.1906
7.7962
−4.1318
−4.5439
X : parts per Million : 13C

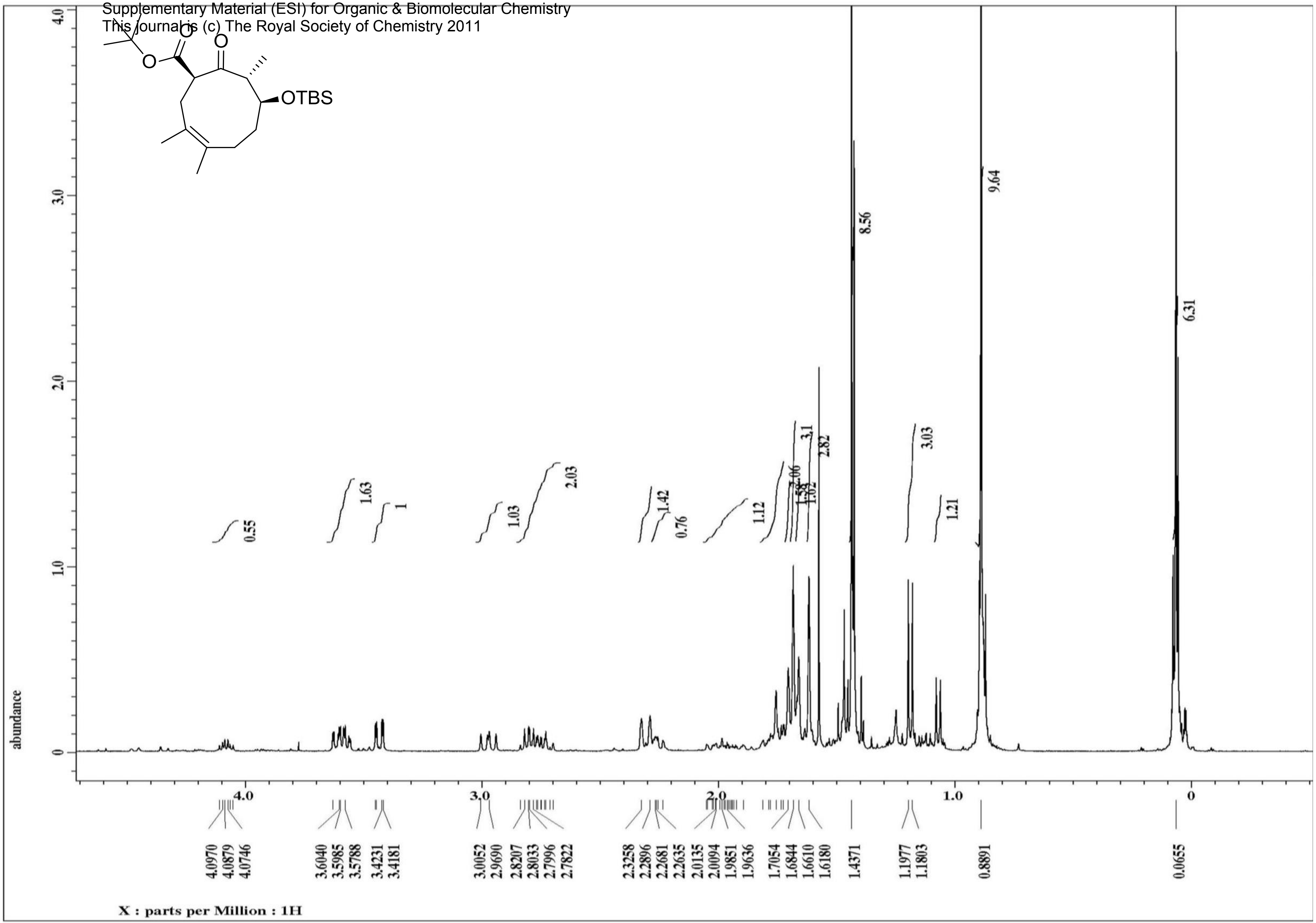
Compound **56**


O
O
O
Si
OH
abundance
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.21
0.94
1.97
1.0
1.04
0.95
3.23
3.35
2.02
9.1
0.95
3.16
9.04
5.97
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2465
4.9185
4.0862
4.0725
3.8253
3.8088
3.7969
3.4801
3.4782
2.8346
2.8281
2.2037
2.1900
2.0196
1.9208
1.7019
1.6314
1.6296
1.4584
1.4336
1.0729
0.8879
0.8577
0.0602
0.0584
0.0172
X : parts per Million : 1H

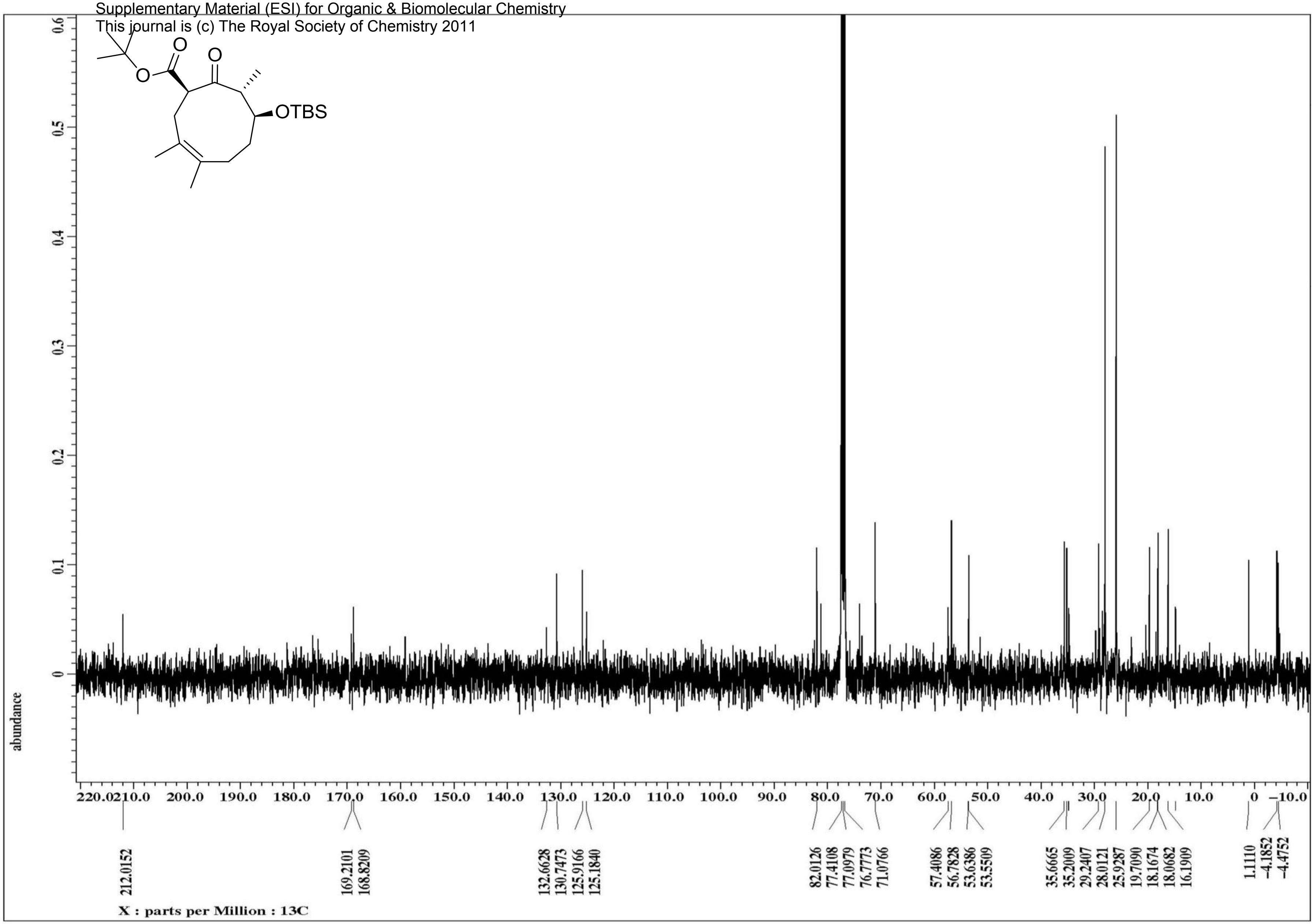
Compound **56**


O
O
O
Si
O
OH
abundance
0
1.0
2.0
3.0
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
206.1542
166.9206
132.5407
128.4655
81.8676
77.4260
77.1055
76.7850
74.0529
63.4146
51.7842
50.6776
33.6288
30.3855
28.3784
28.0579
25.9516
18.9077
18.1140
16.7785
12.1614
−4.3302
−4.3608
X : parts per Million : 13C

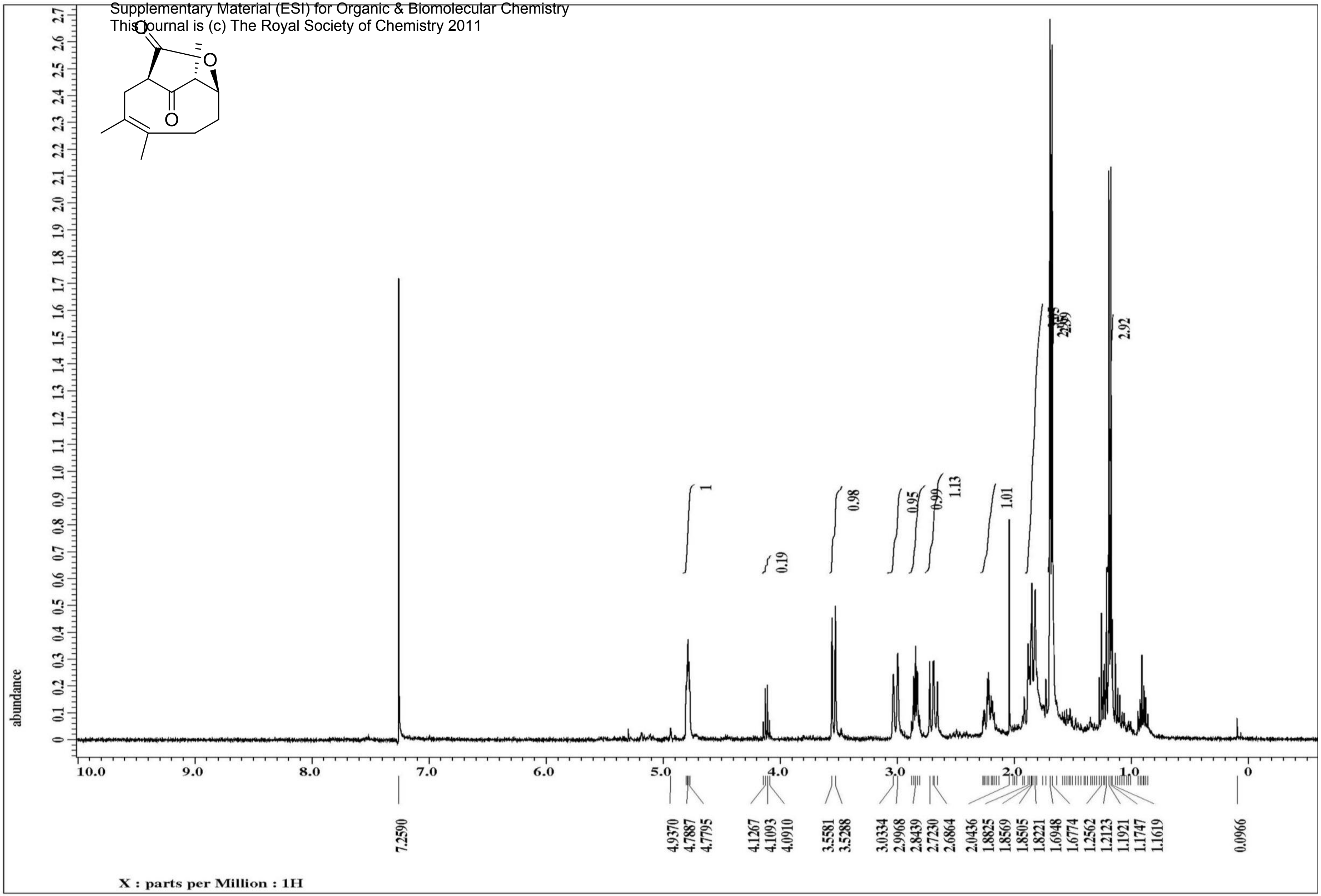
Compound **42**


OTBS
O
O
O
abundance
4.0
3.0
2.0
1.0
0
0.55
1.63
1
1.03
2.03
1.42
0.76
1.12
3.06
1.58
1.02
3.1
2.82
8.56
3.03
1.21
9.64
6.31
4.0
3.0
2.0
1.0
0
4.0970
4.0879
4.0746
3.6040
3.5985
3.5788
3.4231
3.4181
3.0052
2.9690
2.8207
2.8033
2.7996
2.7822
2.3258
2.2896
2.2681
2.2635
2.0135
2.0094
1.9851
1.9636
1.7054
1.6844
1.6610
1.6180
1.4371
1.1977
1.1803
0.8891
0.0655
X : parts per Million : 1H

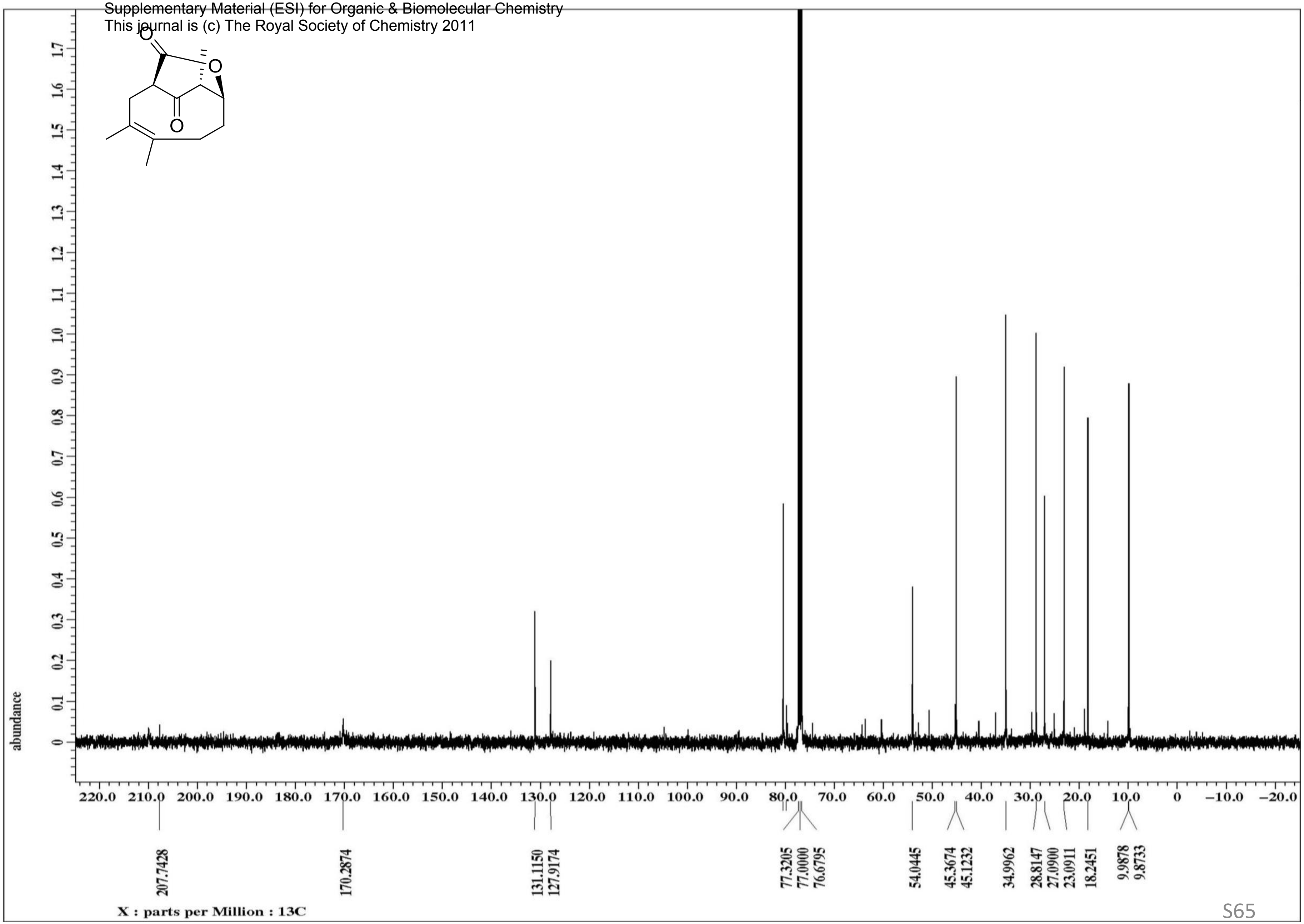
Compound **42**


OTBS
abundance
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
212.0152
169.2101
168.8209
132.6628
130.7473
125.9166
125.1840
82.0126
77.4108
77.0979
76.7773
71.0766
57.4086
56.7828
53.6386
53.5509
35.6665
35.2009
29.2407
28.0121
25.9287
19.7090
18.1674
18.0682
16.1909
1.1110
−4.1852
−4.4752
X : parts per Million : 13C

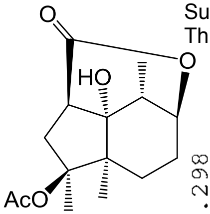
Compound **43**


abundance
0
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
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
O
O
O
O
1
0.19
0.98
0.95
0.99
1.13
1.01
2.92
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2590
4.9370
4.7887
4.7795
4.1267
4.1093
4.0910
3.5581
3.5288
3.0334
2.9968
2.8439
2.7230
2.6864
2.0436
1.8825
1.8569
1.8505
1.8221
1.6948
1.6774
1.2562
1.2123
1.1921
1.1747
1.1619
0.0966
X : parts per Million : 1H

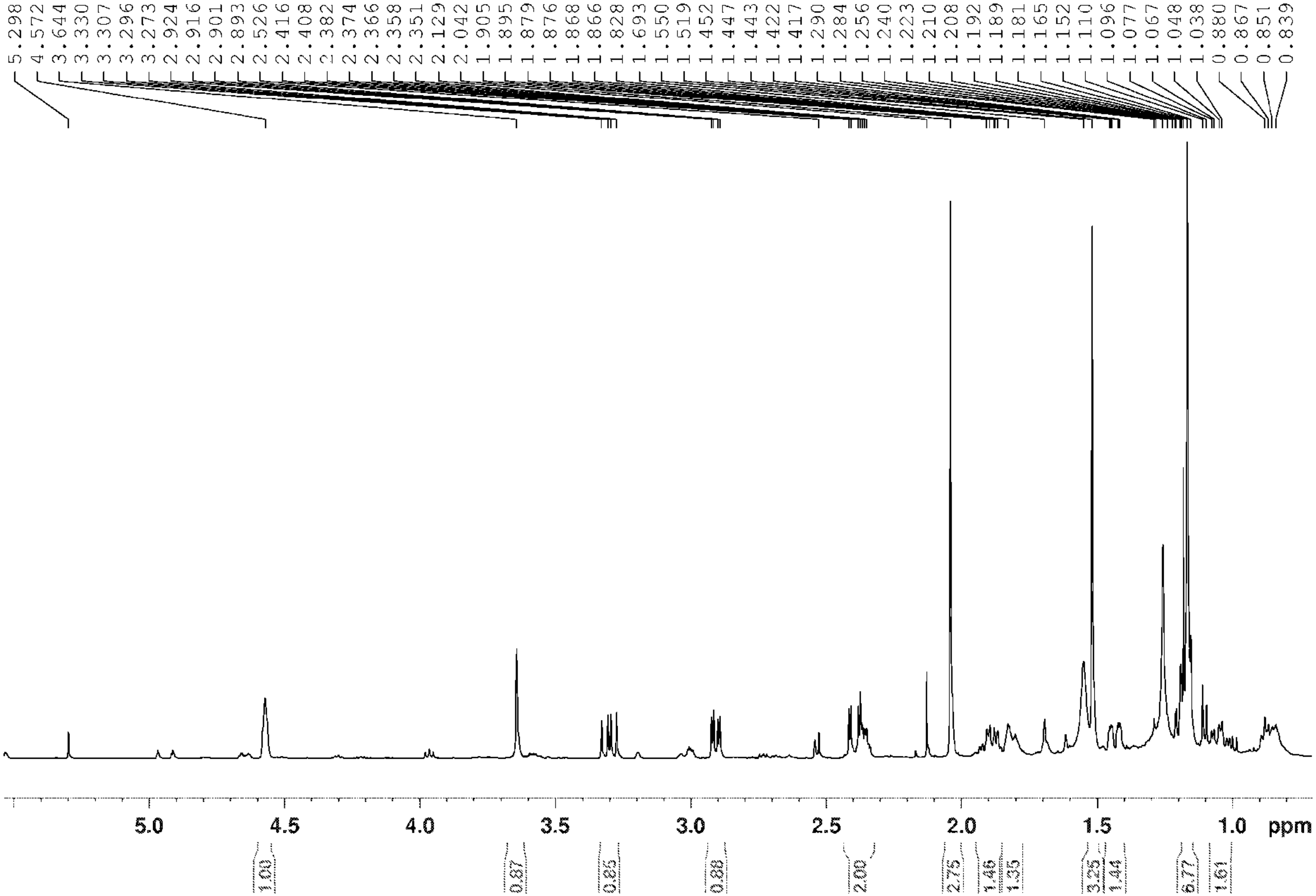
Compound **43**


abundance
0
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
1.7
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
207.7428
170.2874
131.1150
127.9174
77.3205
77.0000
76.6795
54.0445
45.3674
45.1232
34.9962
28.8147
27.0900
23.0911
18.2451
9.9878
9.8733
X : parts per Million : 13C

Compound **57**

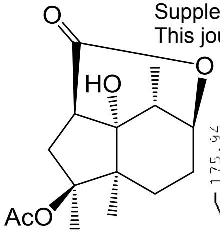


O
O
HO
AcO

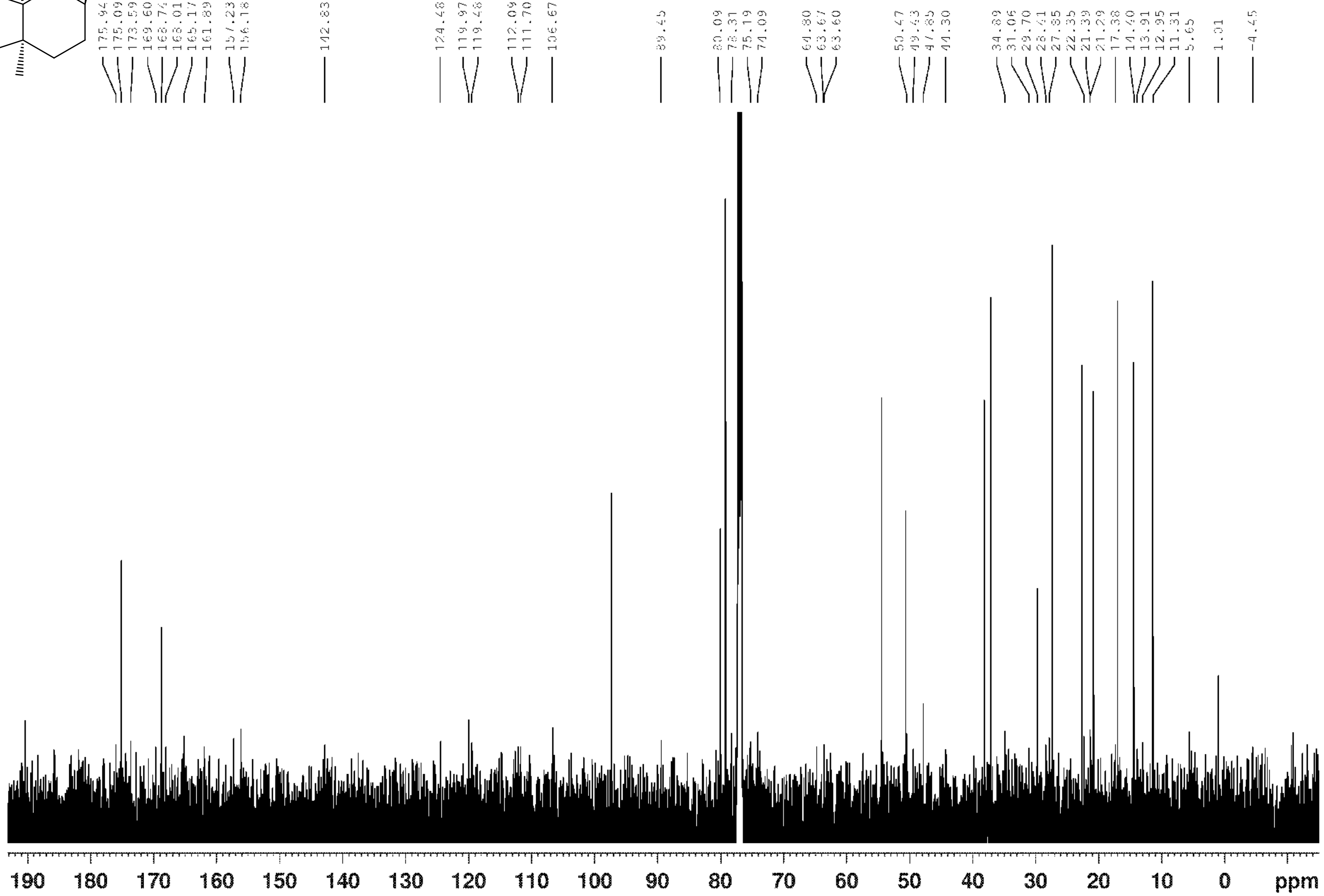


5.298
4.572
3.644
3.330
3.307
3.296
3.273
2.924
2.916
2.901
2.893
2.526
2.416
2.408
2.382
2.374
2.366
2.358
2.351
2.129
2.042
1.905
1.895
1.879
1.876
1.868
1.866
1.828
1.693
1.550
1.519
1.452
1.447
1.443
1.422
1.417
1.290
1.284
1.256
1.240
1.223
1.210
1.208
1.192
1.189
1.181
1.165
1.152
1.110
1.096
1.077
1.067
1.048
1.038
0.880
0.867
0.851
0.839
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
0.87
0.85
0.88
2.00
2.75
1.46
1.35
3.25
1.44
6.77
1.61

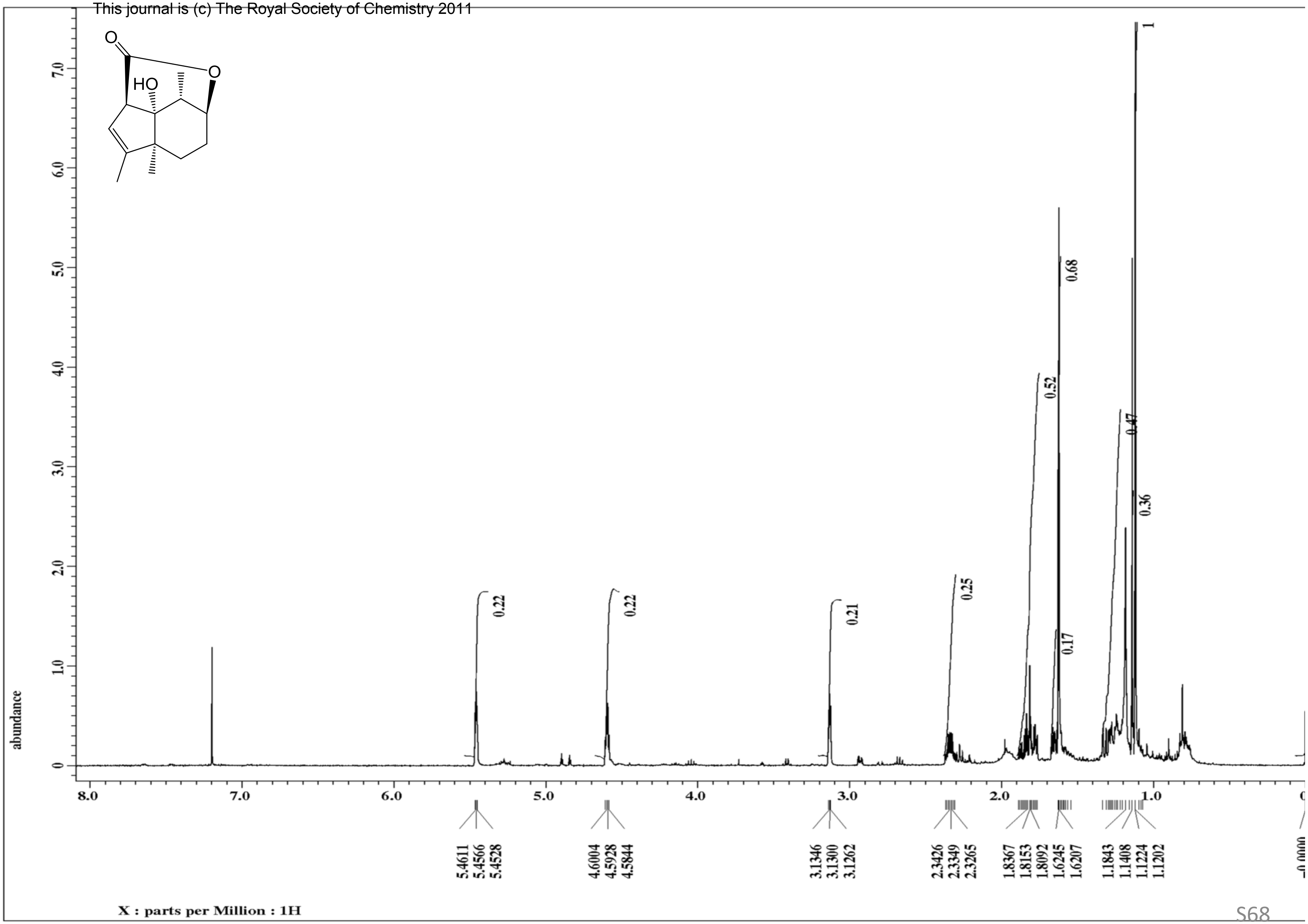
Compound **57**



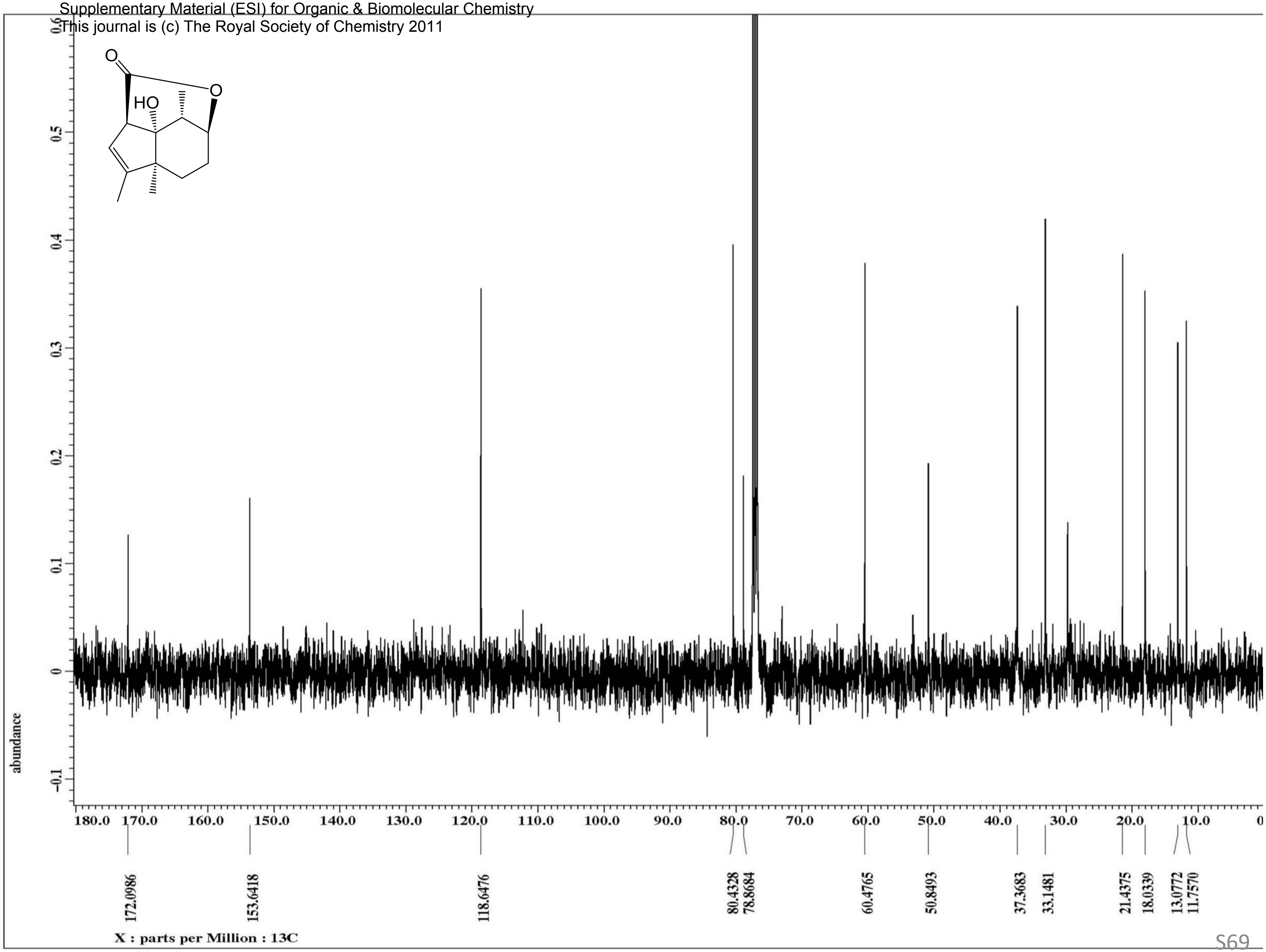
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2011



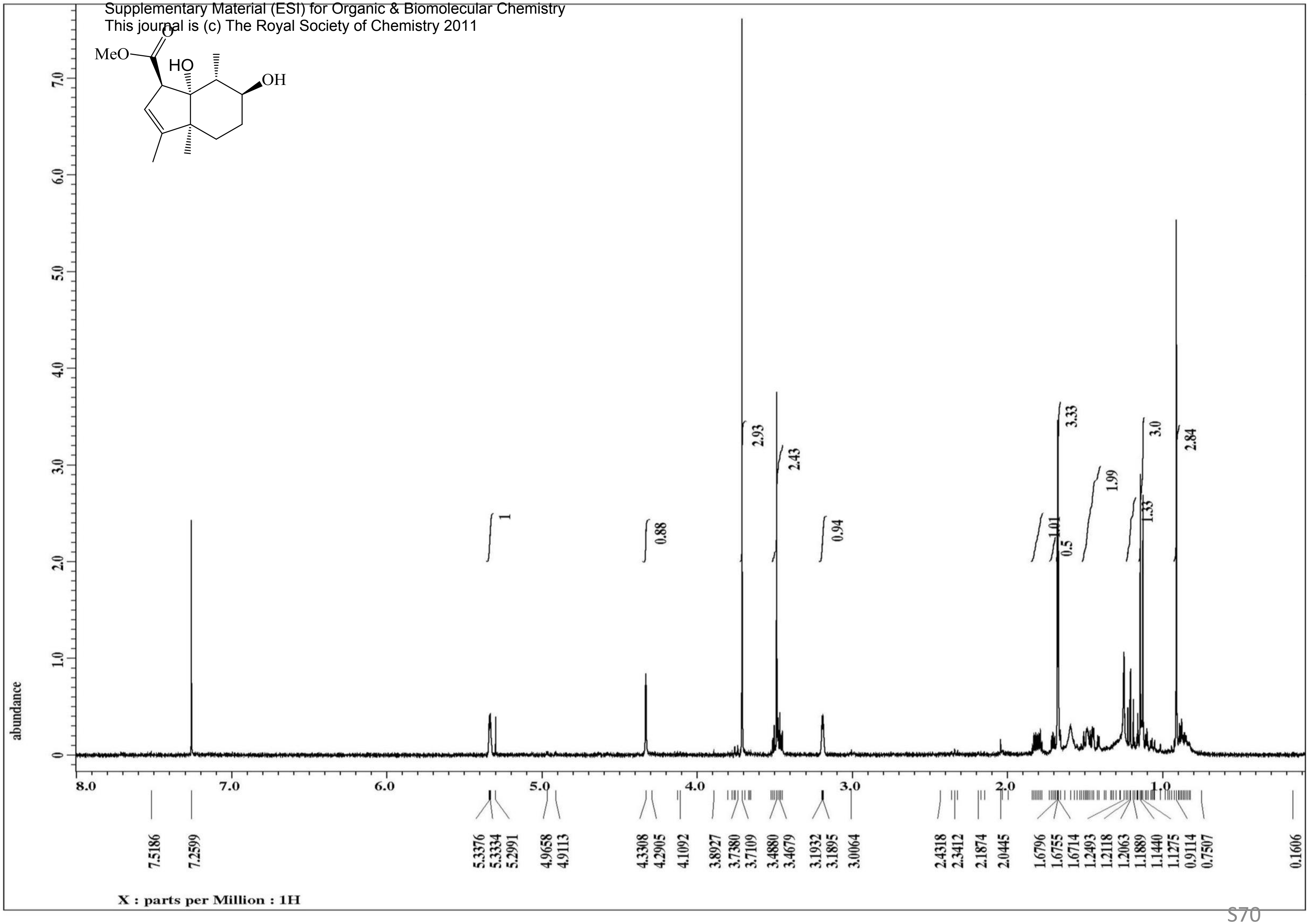
Compound **58**


O
HO
O
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.22
0.22
0.21
0.25
0.52
0.17
0.68
0.47
0.36
1
5.4611
5.4566
5.4528
4.6004
4.5928
4.5844
3.1346
3.1300
3.1262
2.3426
2.3349
2.3265
1.8367
1.8153
1.8092
1.6245
1.6207
1.1843
1.1408
1.1224
1.1202
-0.0000
X : parts per Million : 1H

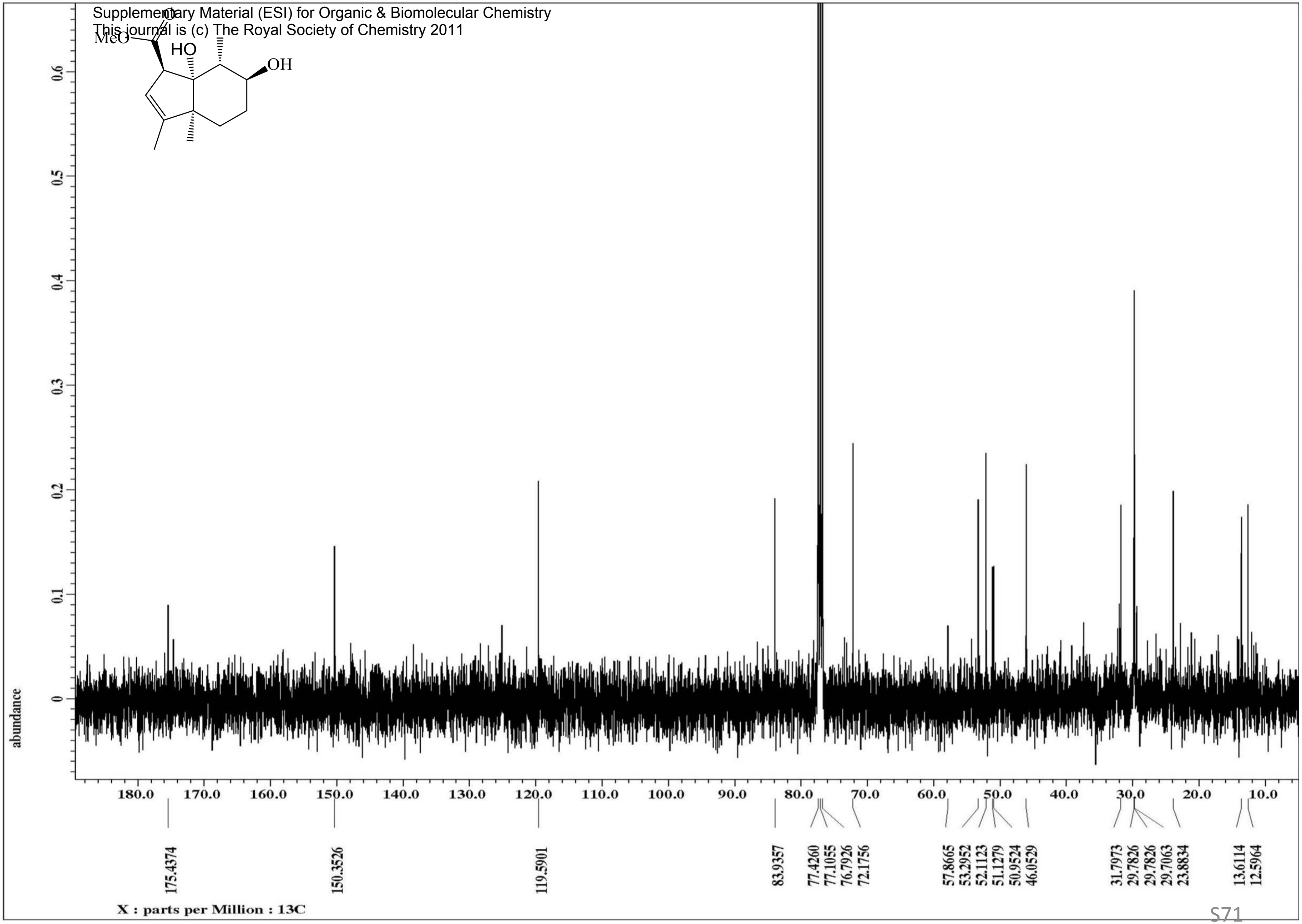
Compound **58**


O
O
HO
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
−0.1
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
172.0986
153.6418
118.6476
80.4328
78.8684
60.4765
50.8493
37.3683
33.1481
21.4375
18.0339
13.0772
11.7570
X : parts per Million : 13C

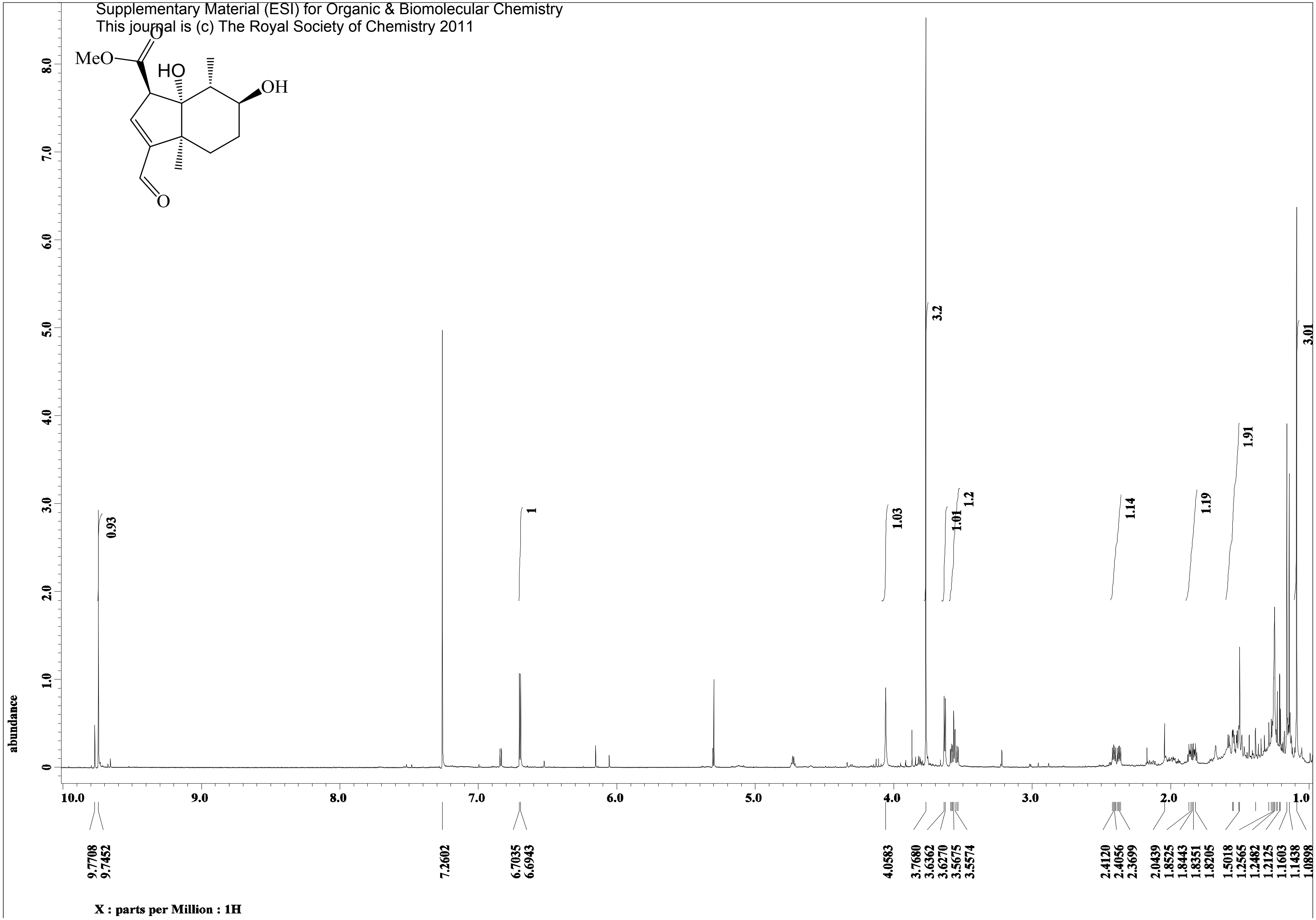
Compound **60**


MeO
O
HO
OH
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
X : parts per Million : 1H
1
0.88
2.93
2.43
0.94
1.01
0.5
3.33
1.99
1.33
3.0
2.84
7.5186
7.2599
5.3376
5.3334
5.2991
4.9658
4.9113
4.3308
4.2905
4.1092
3.8927
3.7380
3.7109
3.4880
3.4679
3.1932
3.1895
3.0064
2.4318
2.3412
2.1874
2.0445
1.6796
1.6755
1.6714
1.2493
1.2118
1.2063
1.1889
1.1440
1.1275
0.9114
0.7507
0.1606

Compound **60**

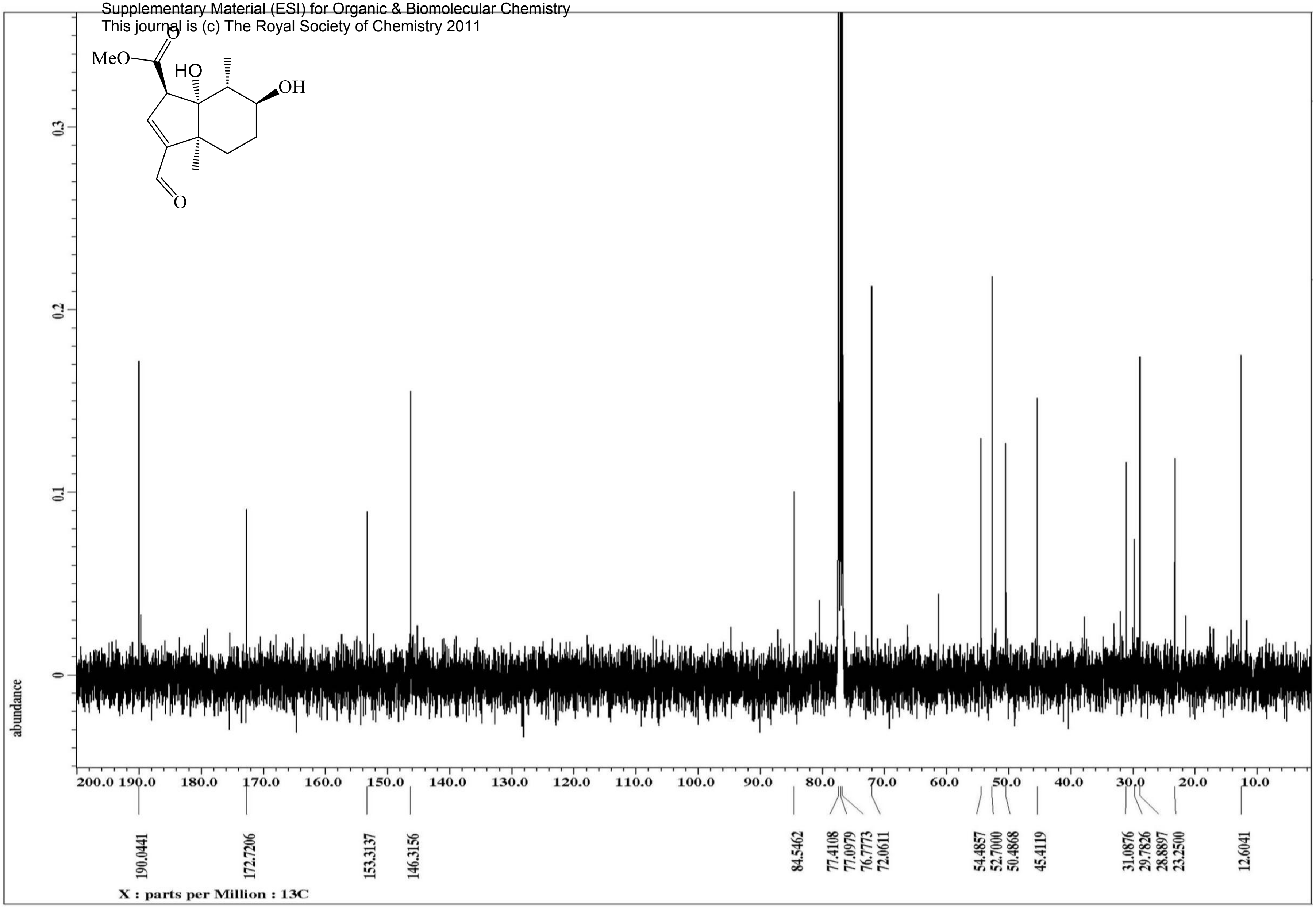

MeO
O
HO
OH
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
175.4374
150.3526
119.5901
83.9357
77.4260
77.1055
76.7926
72.1756
57.8665
53.2952
52.1123
51.1279
50.9524
46.0529
31.7973
29.7826
29.7826
29.7063
23.8834
13.6114
12.5964
X : parts per Million : 13C

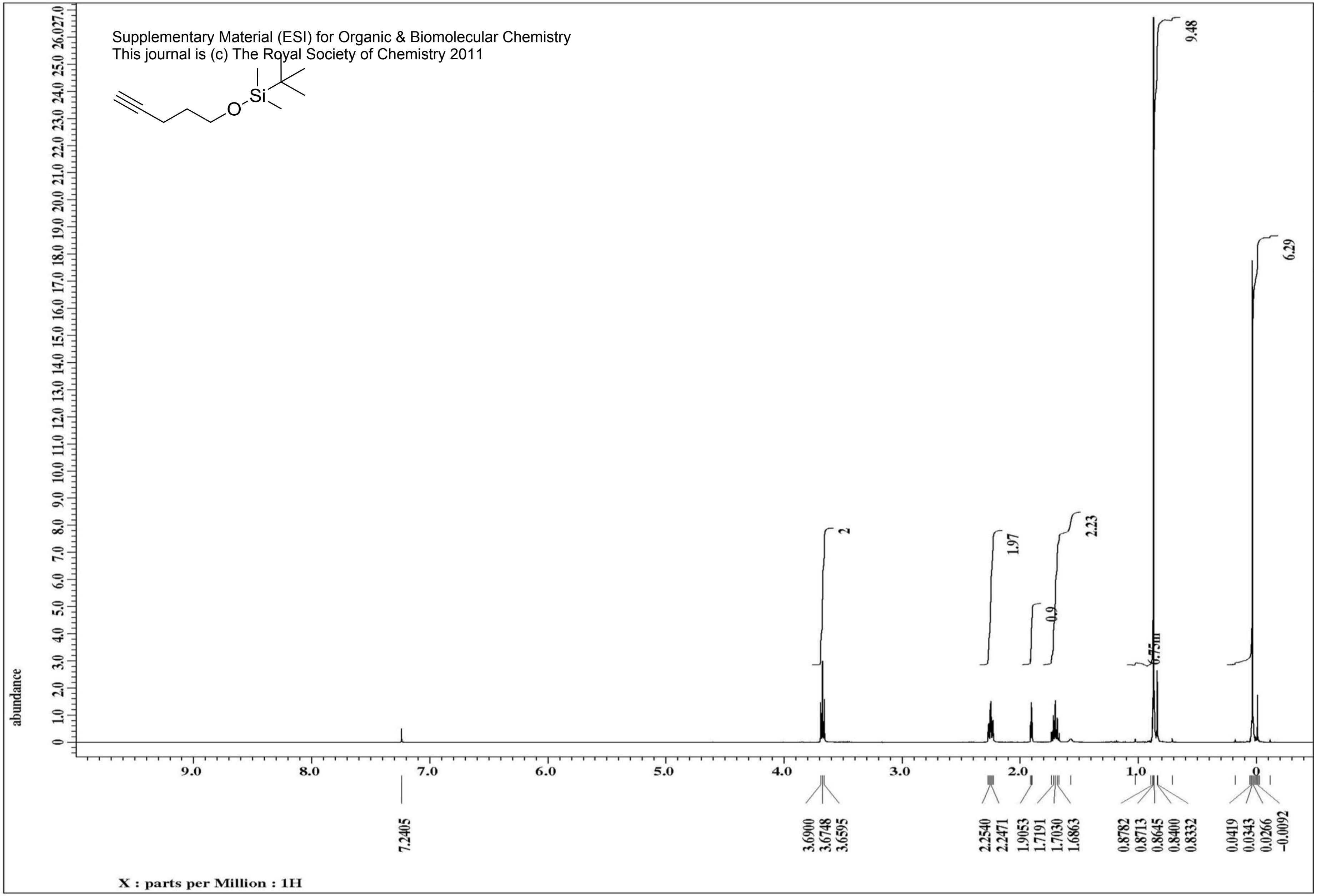
Compound **61**

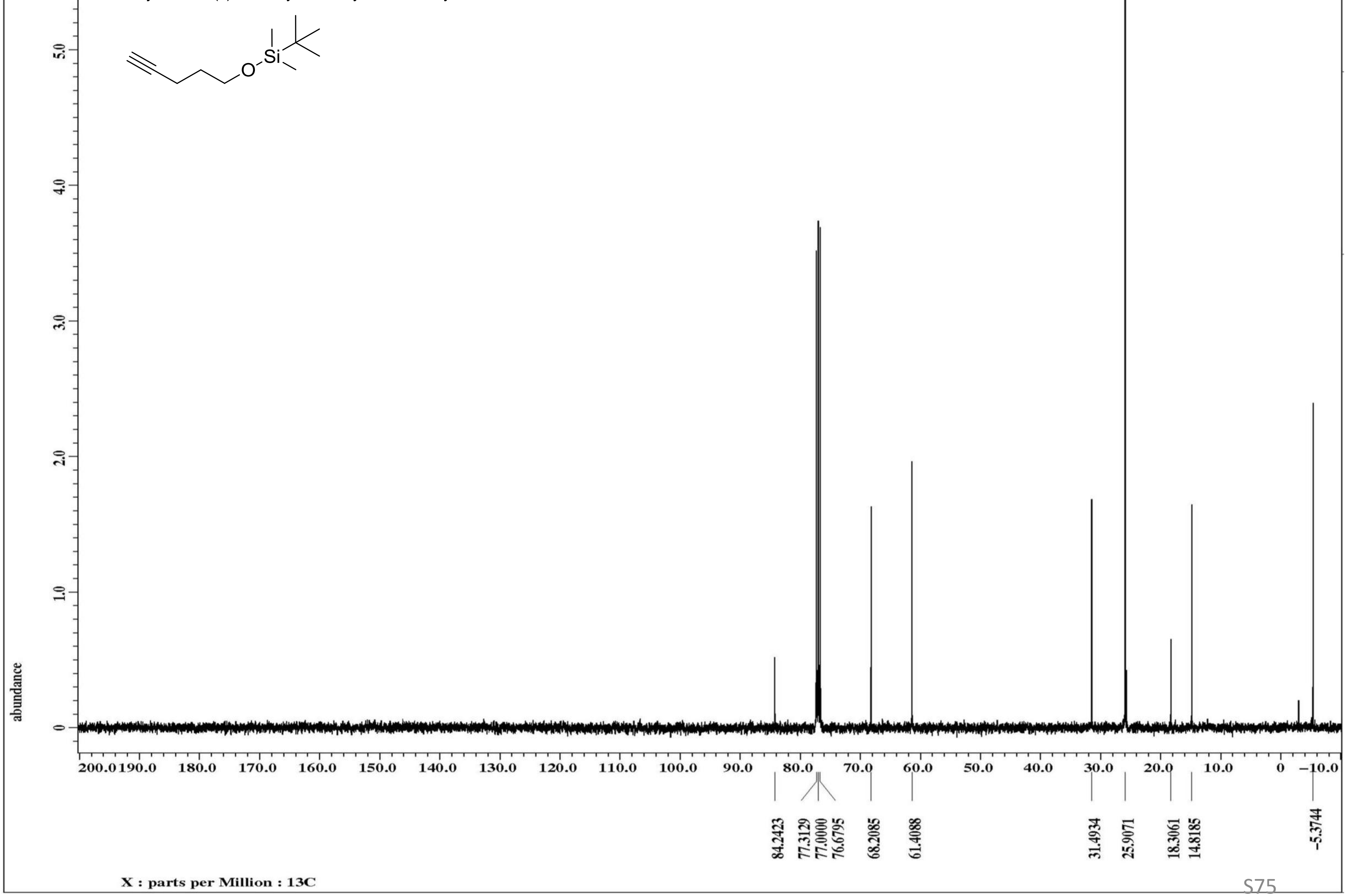


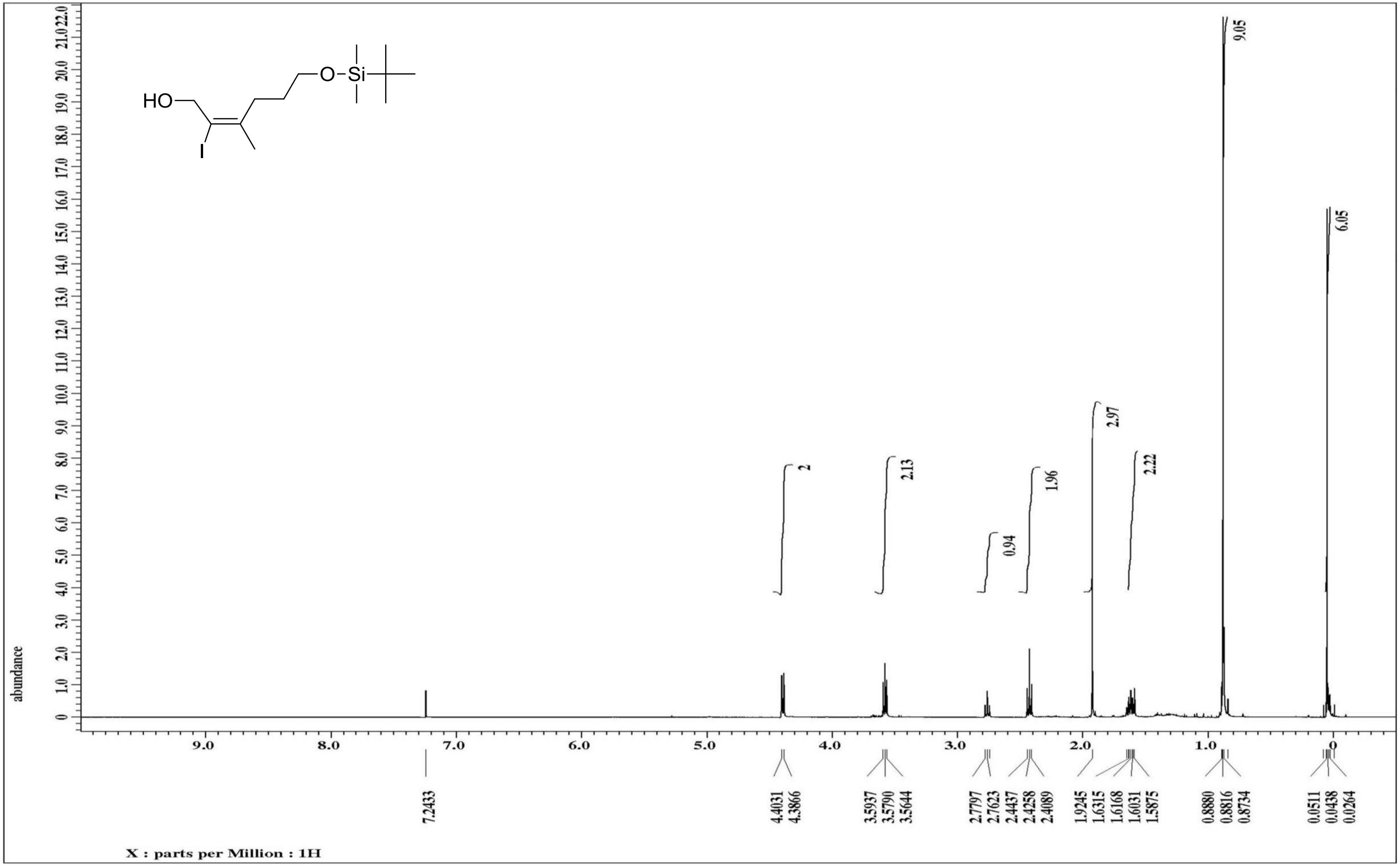
MeO
O
HO
OH
O
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.93
1
1.03
3.2
1.01
1.2
1.14
1.19
1.91
3.01
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
9.7708
9.7452
7.2602
6.7035
6.6943
4.0583
3.7680
3.6362
3.6270
3.5675
3.5574
2.4120
2.4056
2.3699
2.0439
1.8525
1.8443
1.8351
1.8205
1.5018
1.2565
1.2482
1.2125
1.1603
1.1438
1.0898
X : parts per Million : 1H

Compound **61**

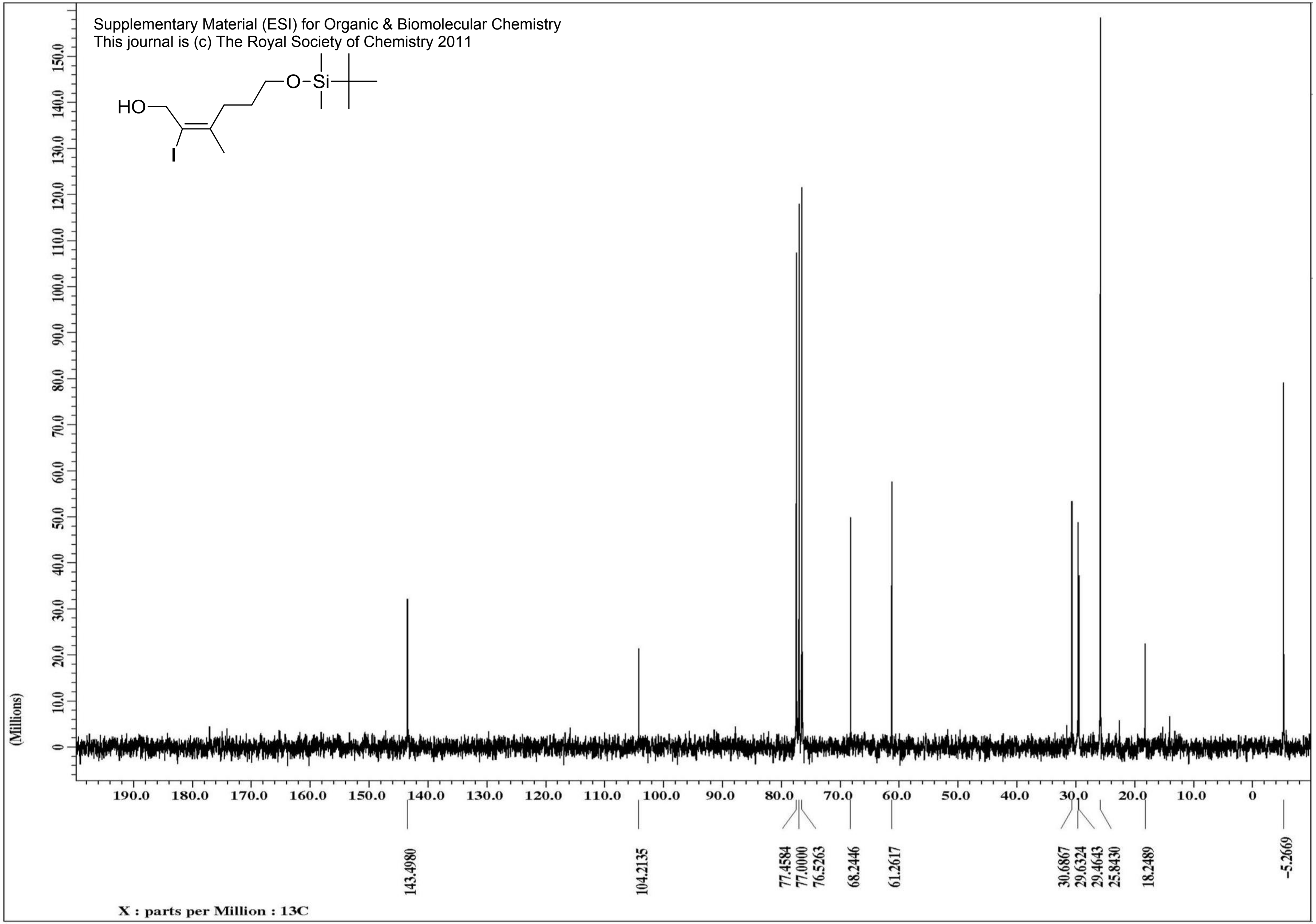

MeO
O
HO
OH
O
abundance
0
0.1
0.2
0.3
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
190.0441
172.7206
153.3137
146.3156
84.5462
77.4108
77.0979
76.7773
72.0611
54.4857
52.7000
50.4868
45.4119
31.0876
29.7826
28.8897
23.2500
12.6041
X : parts per Million : 13C

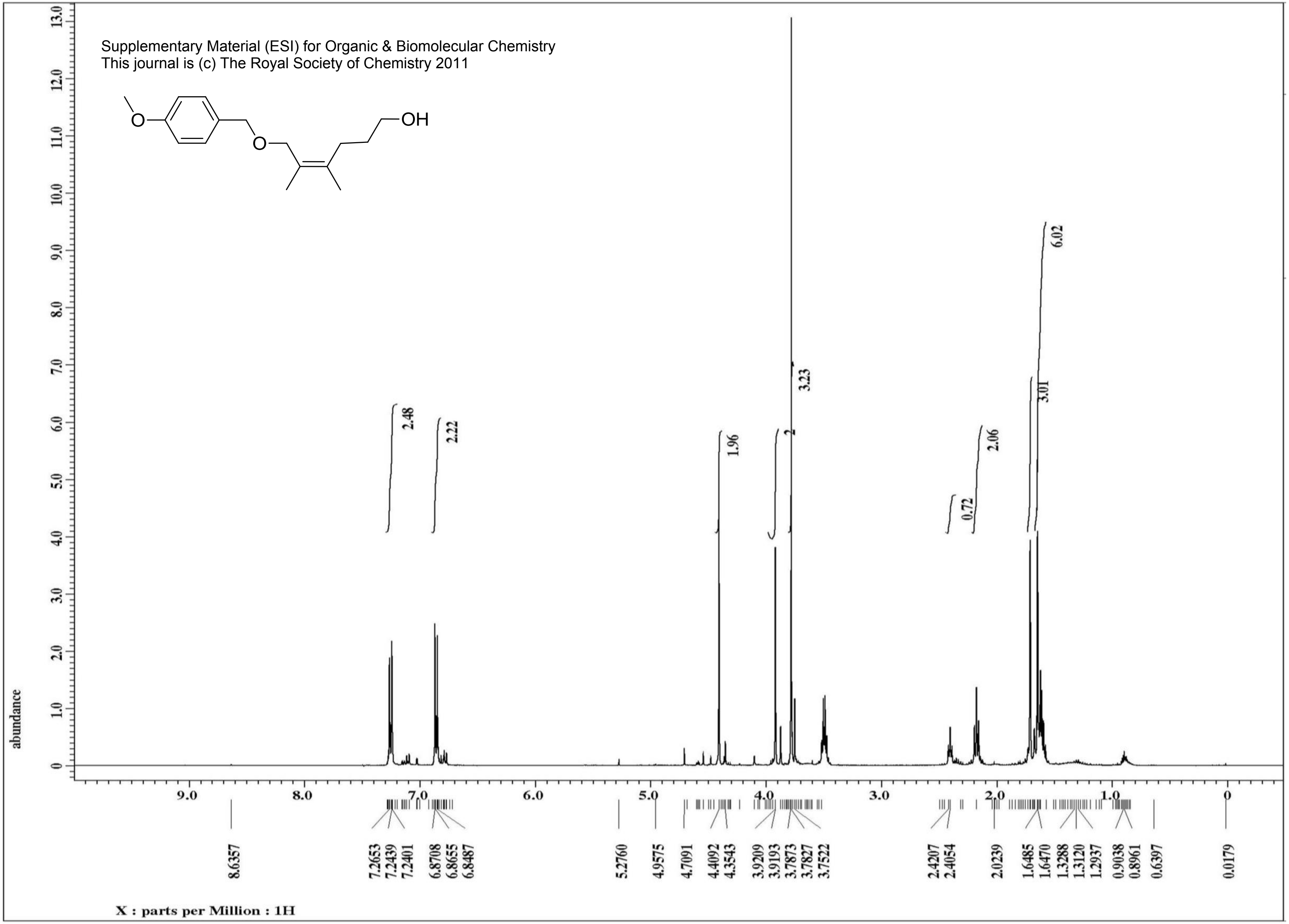

O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
23.0
24.0
25.0
26.0
27.0
9.48
6.29
2
1.97
0.9
2.23
6.75m
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2405
3.6900
3.6748
3.6595
2.2540
2.2471
1.9053
1.7191
1.7030
1.6863
0.8782
0.8713
0.8645
0.8400
0.8332
0.0419
0.0343
0.0266
−0.0092
X : parts per Million : 1H


O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
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
84.2423
77.3129
77.0000
76.6795
68.2085
61.4088
31.4934
25.9071
18.3061
14.8185
−5.3744
X : parts per Million : 13C

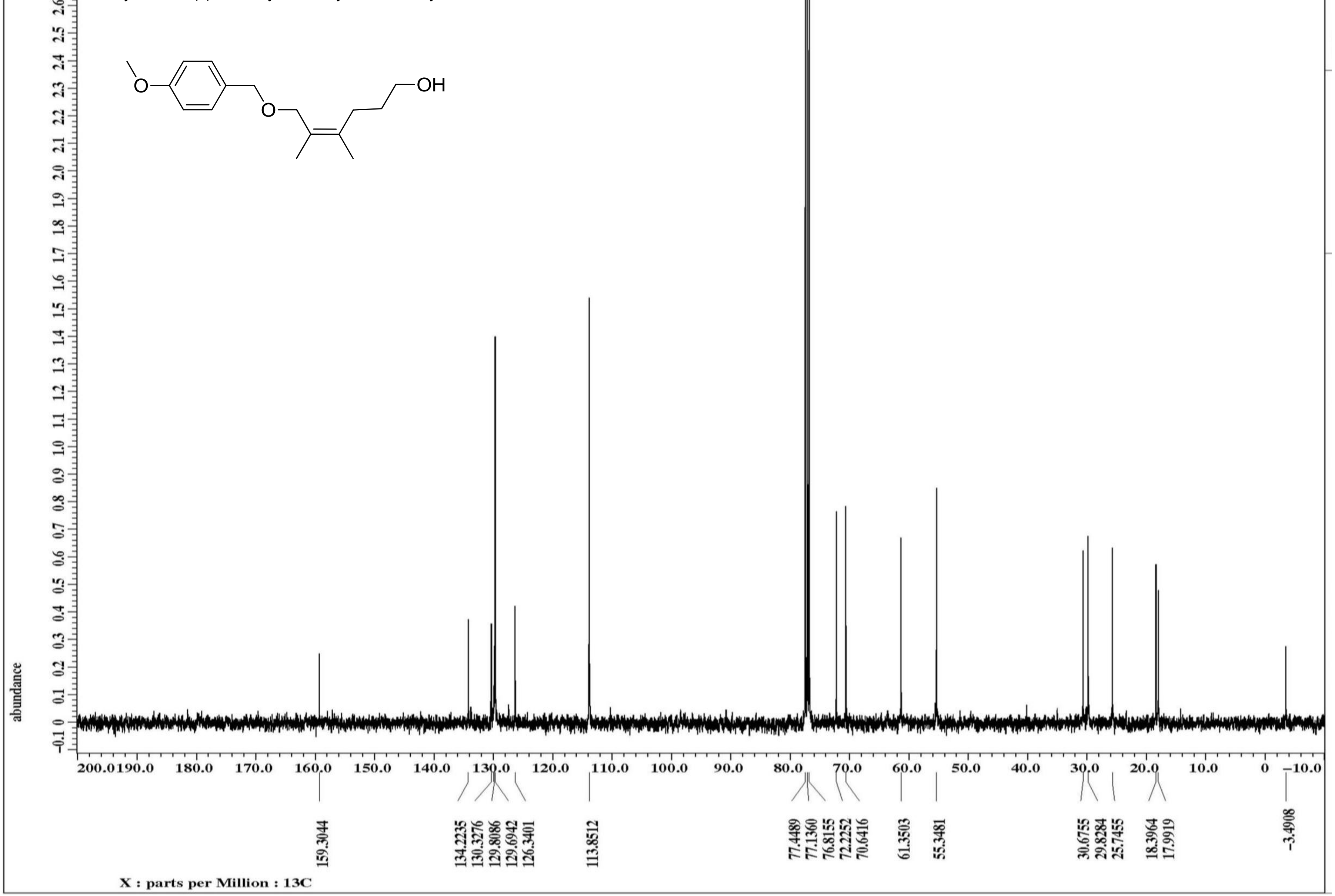

HO
I
O
Si
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
20.0
21.0
22.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2
2.13
0.94
1.96
2.97
2.22
9.05
6.05
7.2433
4.4031
4.3866
3.5937
3.5790
3.5644
2.7797
2.7623
2.4437
2.4258
2.4089
1.9245
1.6315
1.6168
1.6031
1.5875
0.8880
0.8816
0.8734
0.0511
0.0438
0.0264
X : parts per Million : 1H

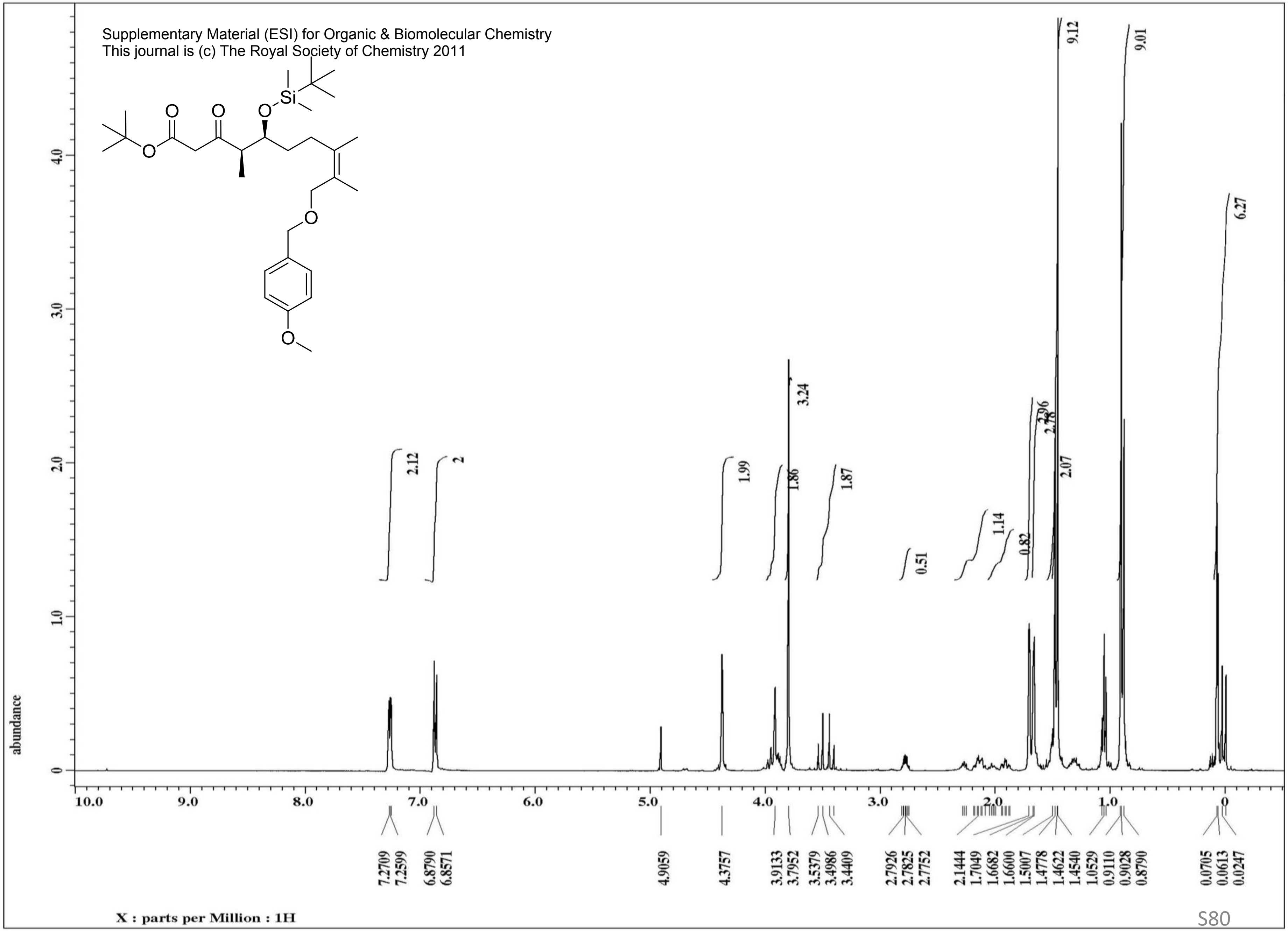
Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is (c) The Royal Society of Chemistry 2011

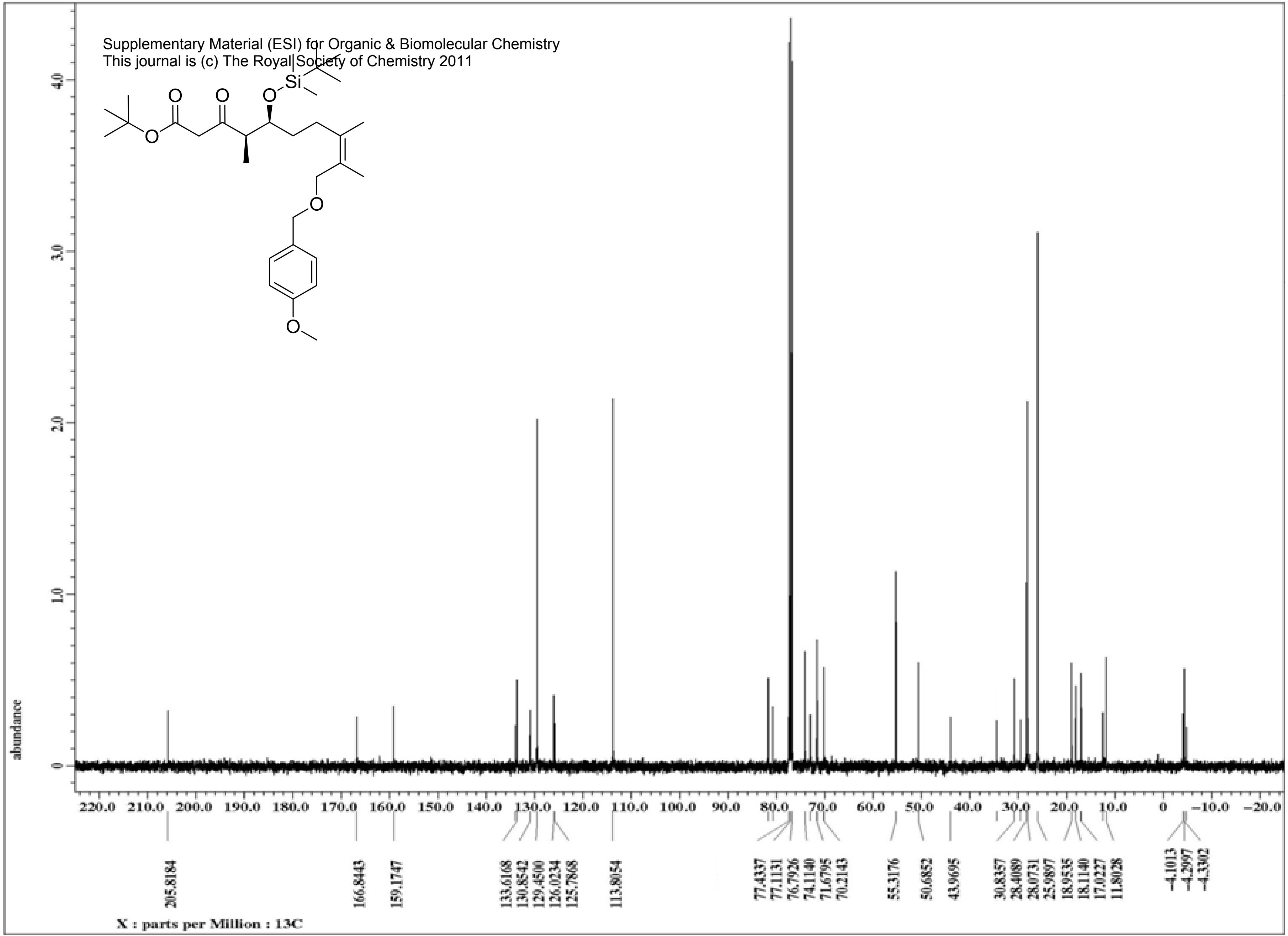


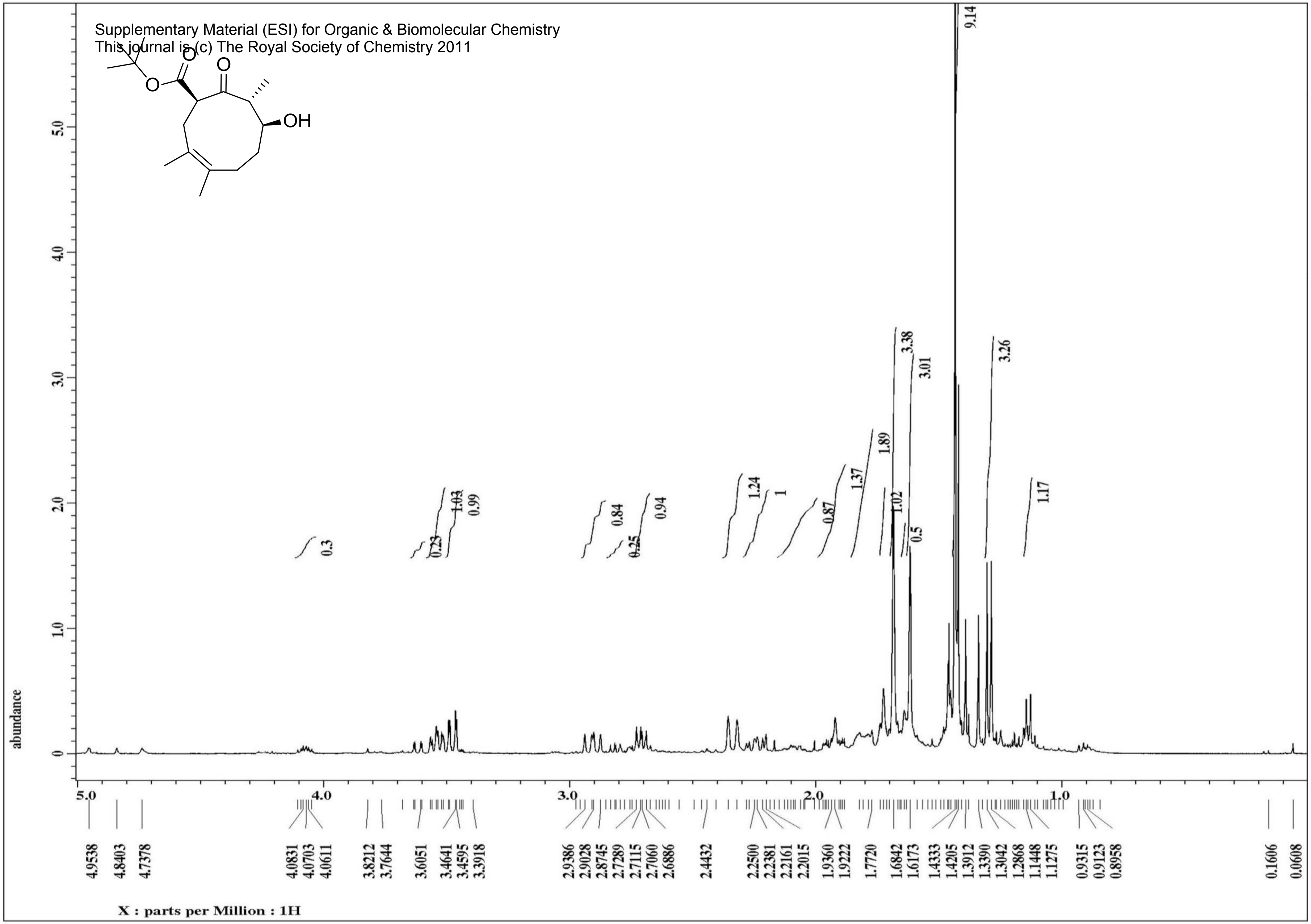


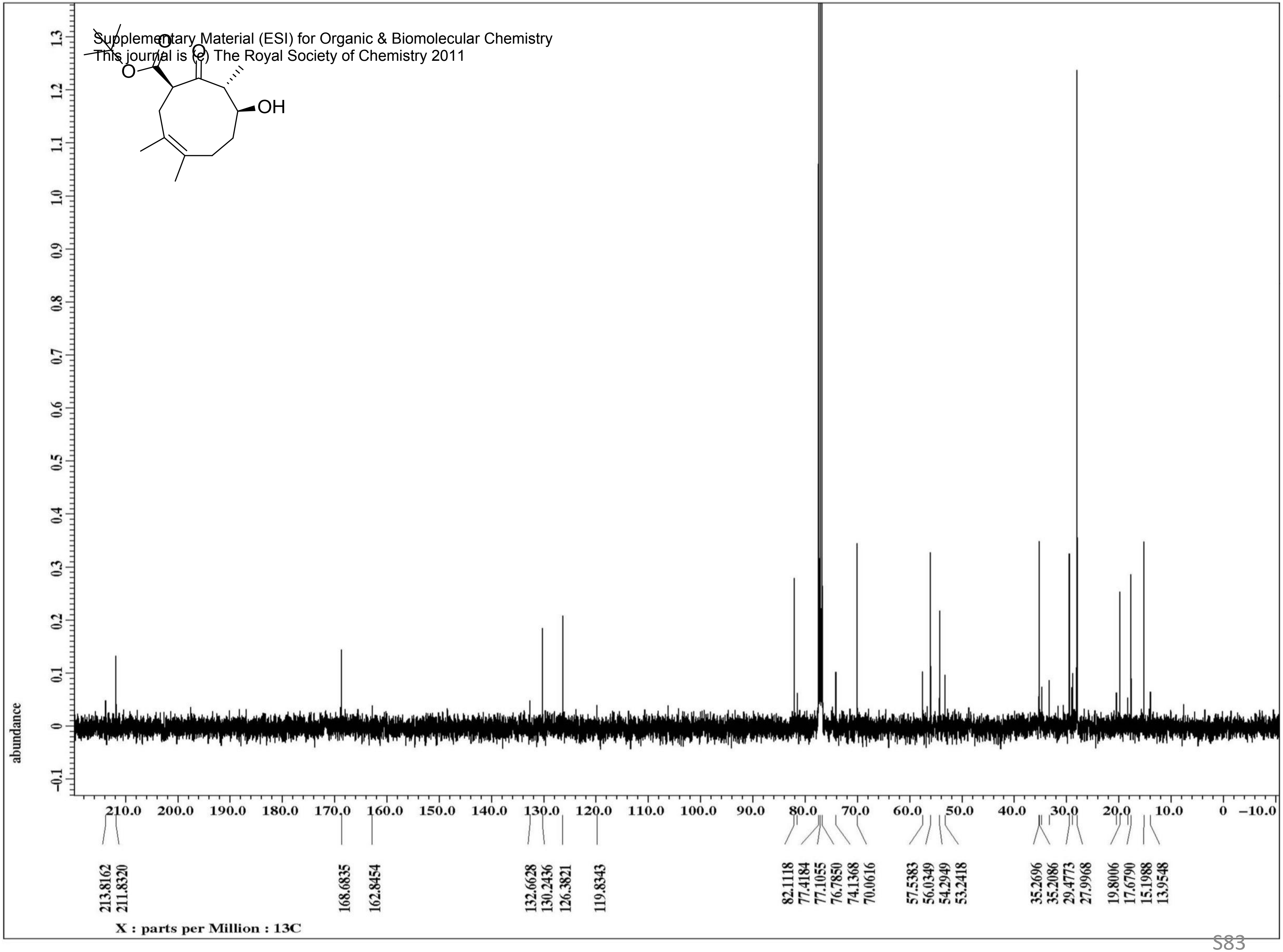
OH
O
O
abundance
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.48
2.22
1.96
2
3.23
0.72
2.06
3.01
6.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.6357
7.2653
7.2439
7.2401
6.8708
6.8655
6.8487
5.2760
4.9575
4.7091
4.4092
4.3543
3.9209
3.9193
3.7873
3.7827
3.7522
2.4207
2.4054
2.0239
1.6485
1.6470
1.3288
1.3120
1.2937
0.9038
0.8961
0.6397
0.0179
X : parts per Million : 1H


O
O
OH
abundance
-0.1 0 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 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6
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
159.3044
134.2235
130.3276
129.8086
129.6942
126.3401
113.8512
77.4489
77.1360
76.8155
72.2252
70.6416
61.3503
55.3481
30.6755
29.8284
25.7455
18.3964
17.9919
-3.4908
X : parts per Million : 13C


abundance
0
1.0
2.0
3.0
4.0
X : parts per Million : 1H
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.12
2
1.99
1.86
3.24
1.87
0.51
1.14
0.82
2.96
2.78
2.07
9.12
9.01
6.27
7.2709
7.2599
6.8790
6.8571
4.9059
4.3757
3.9133
3.7952
3.5379
3.4986
3.4409
2.7926
2.7825
2.7752
2.1444
1.7049
1.6682
1.6600
1.5007
1.4778
1.4622
1.4540
1.0529
0.9110
0.9028
0.8790
0.0705
0.0613
0.0247
O
O
O
Si
O
O
O


O
O
O
Si
O
O
O
abundance
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
−20.0
205.8184
166.8443
159.1747
133.6168
130.8542
129.4500
126.0234
125.7868
113.8054
77.4337
77.1131
76.7926
74.1140
71.6795
70.2143
55.3176
50.6852
43.9695
30.8357
28.4089
28.0731
25.9897
18.9535
18.1140
17.0227
11.8028
−4.1013
−4.2997
−4.3302
X : parts per Million : 13C


O
O
O
OH
abundance
0
1.0
2.0
3.0
4.0
5.0
9.14
3.38
3.01
3.26
1.89
1.37
1.24
1
1.02
1.03
0.99
0.84
0.94
0.87
1.17
0.5
0.3
0.23
0.25
5.0
4.0
3.0
2.0
1.0
4.9538
4.8403
4.7378
4.0831
4.0703
4.0611
3.8212
3.7644
3.6051
3.4641
3.4595
3.3918
2.9386
2.9028
2.8745
2.7289
2.7115
2.7060
2.6886
2.4432
2.2500
2.2381
2.2161
2.2015
1.9360
1.9222
1.7720
1.6842
1.6173
1.4333
1.4205
1.3912
1.3390
1.3042
1.2868
1.1448
1.1275
0.9315
0.9123
0.8958
0.1606
0.0608
X : parts per Million : 1H


OH
O
O
O
abundance
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
−0.1
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
213.8162
211.8320
168.6835
162.8454
132.6628
130.2436
126.3821
119.8343
82.1118
77.4184
77.1055
76.7850
74.1368
70.0616
57.5383
56.0349
54.2949
53.2418
35.2696
35.2086
29.4773
27.9968
19.8006
17.6790
15.1988
13.9548
X : parts per Million : 13C