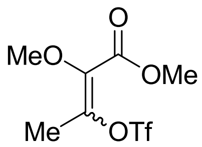
Internal Azomethine Ylide Cycloaddition Methodology for Access to the Substitution Pattern of Aziridinomitosene A

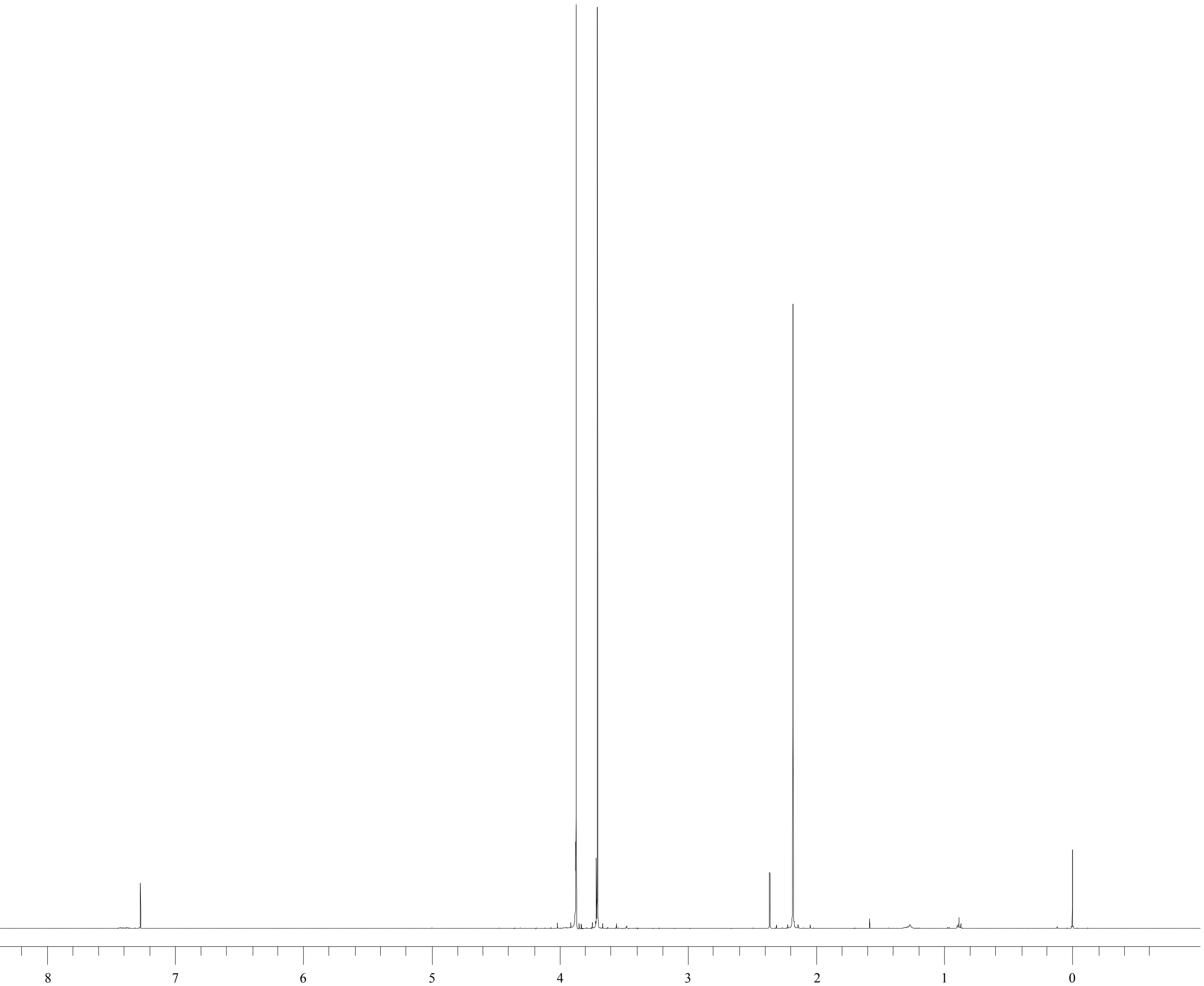
Drew R. Bobeck, Don L. Warner and Edwin Vedejs*

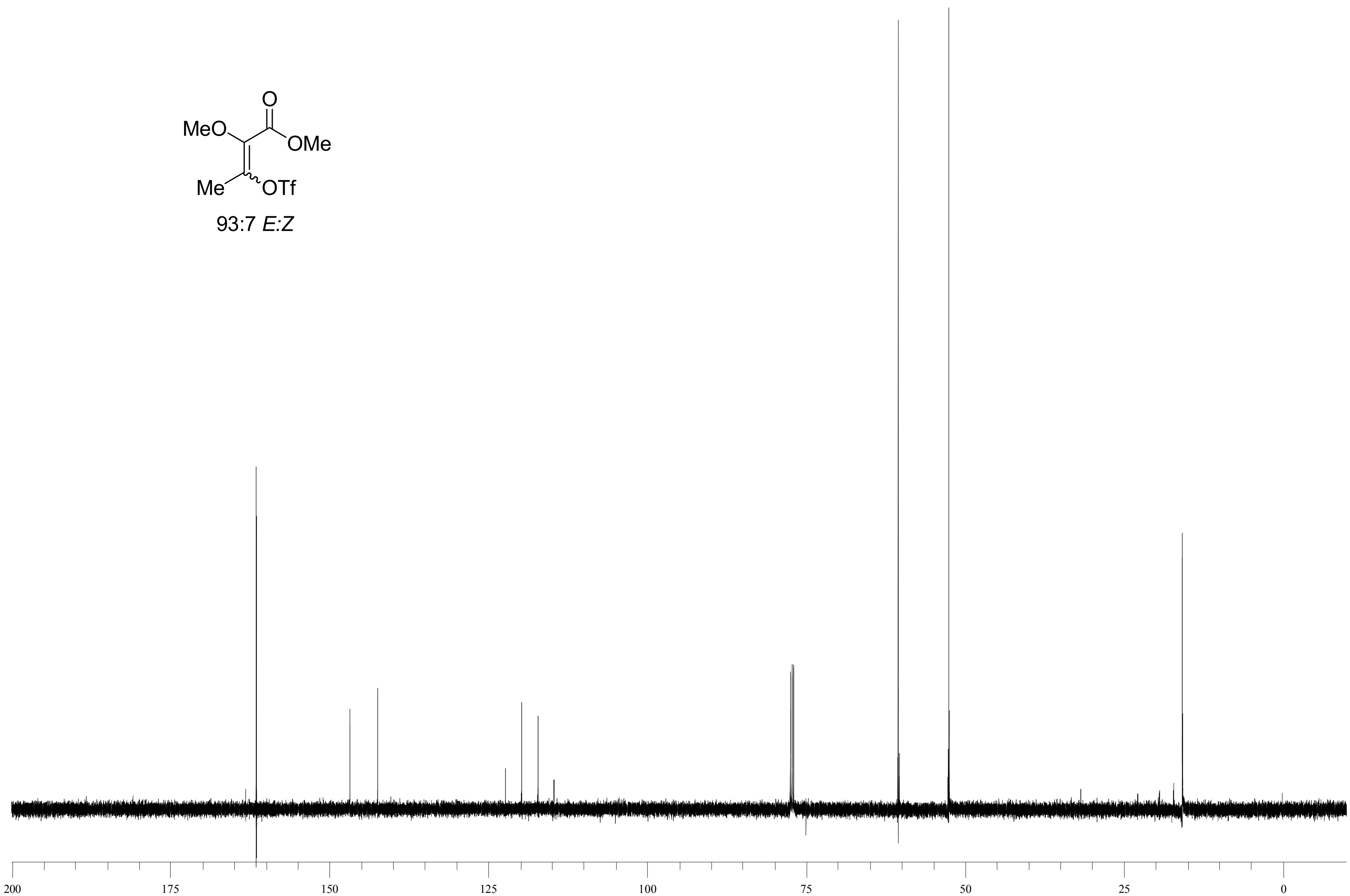
Department of Chemistry, University of Michigan, Ann Arbor Michigan, 48109

Supporting Information

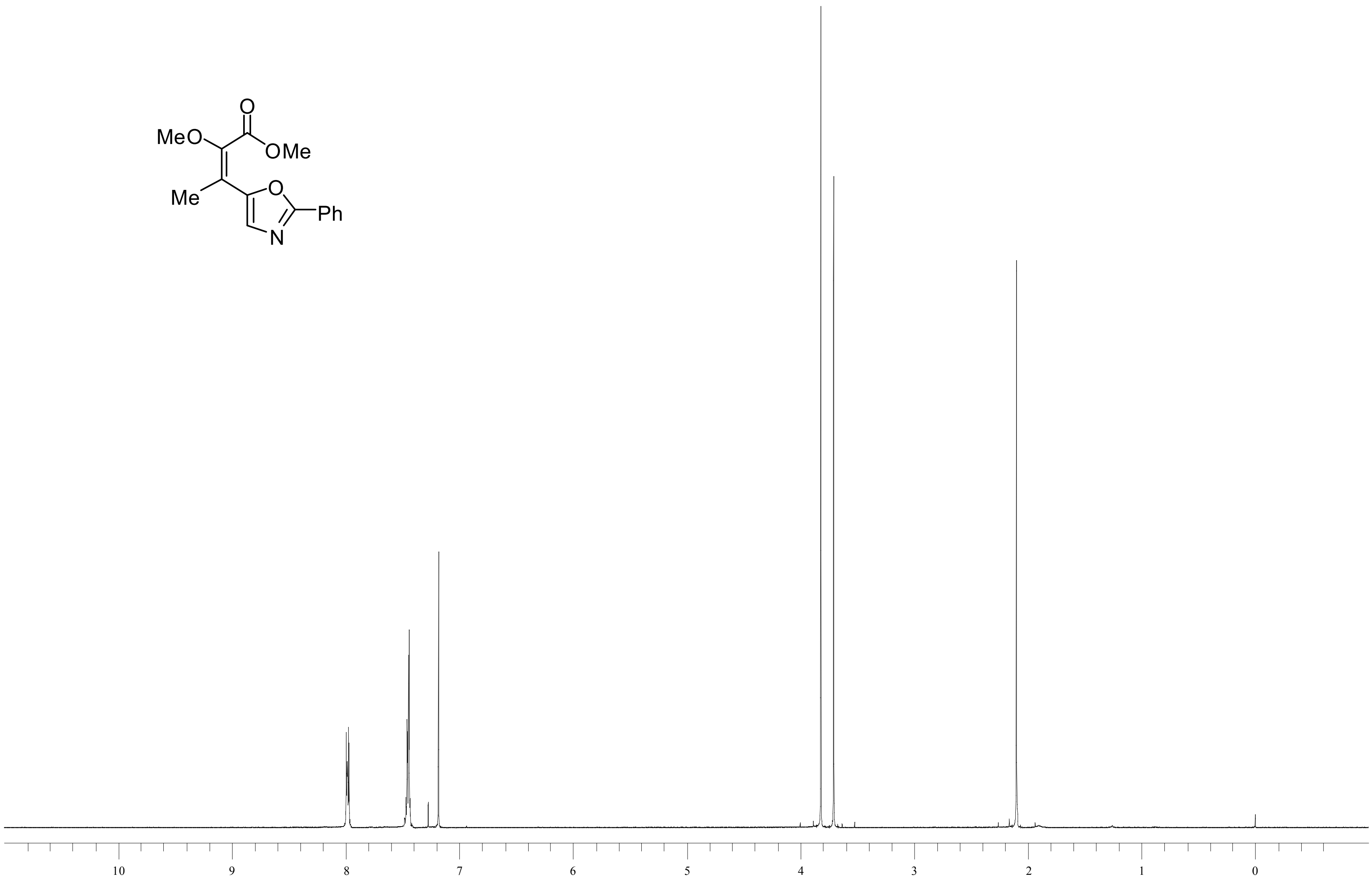


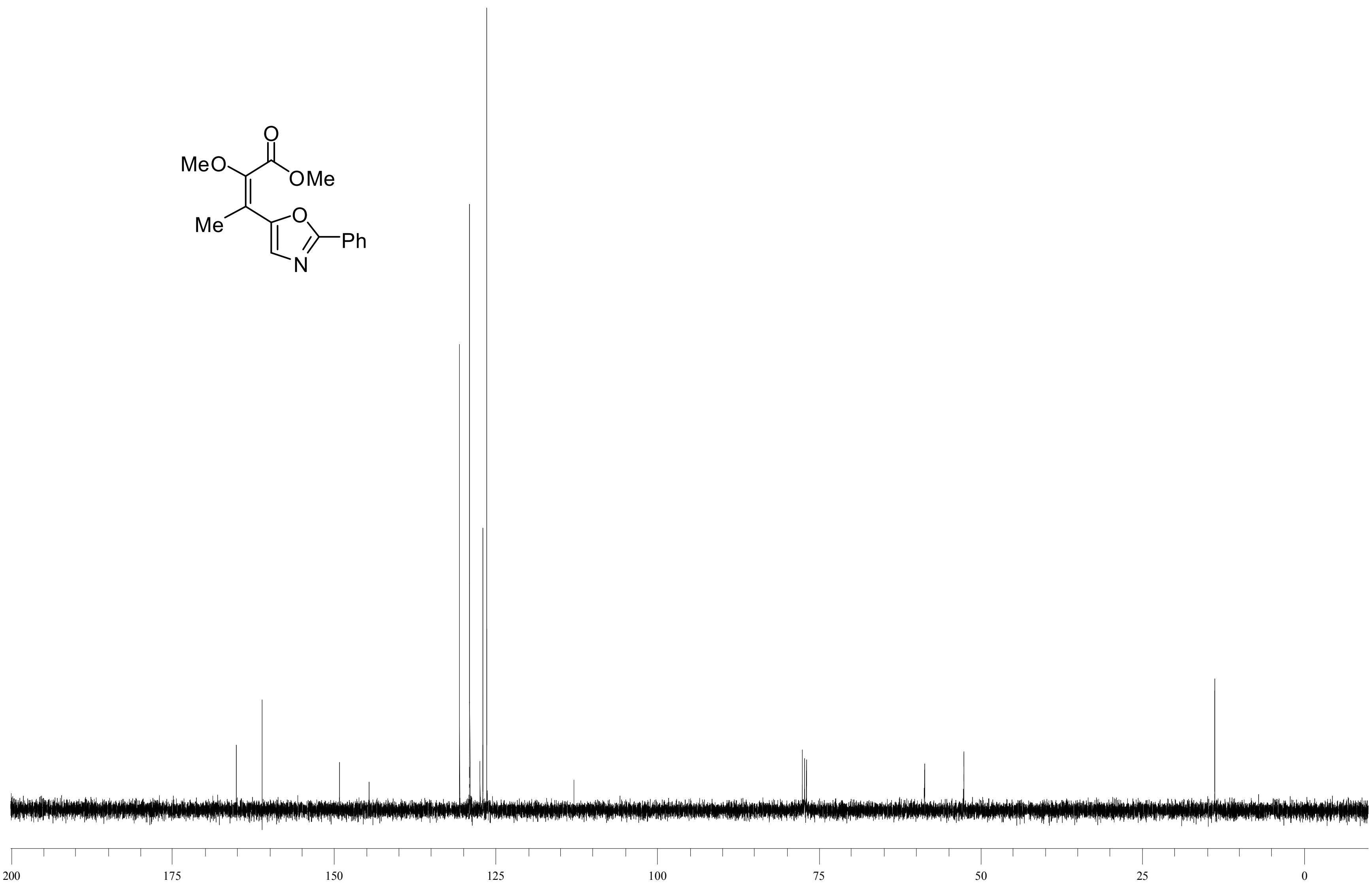
93:7 *E*:*Z*

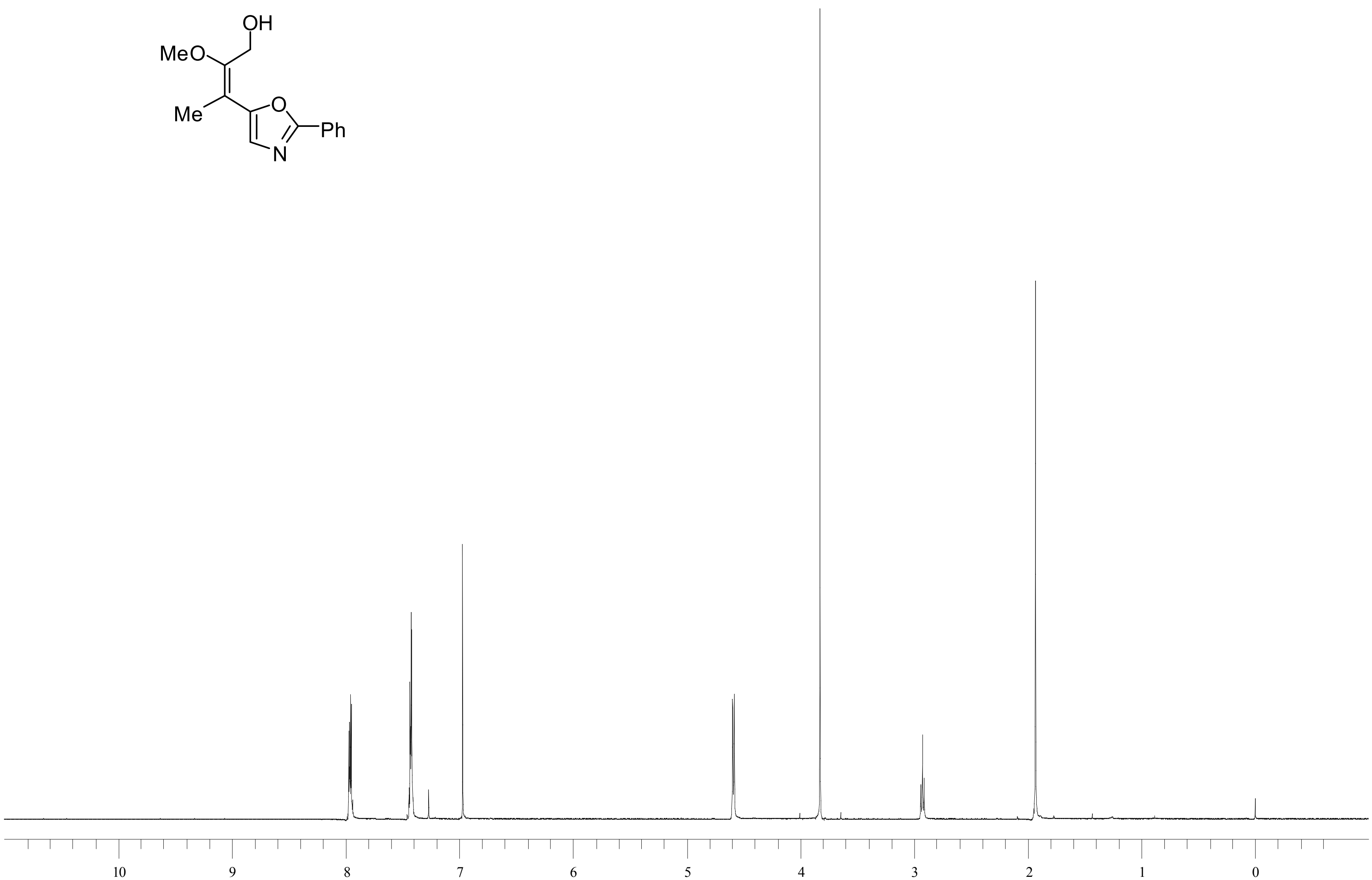


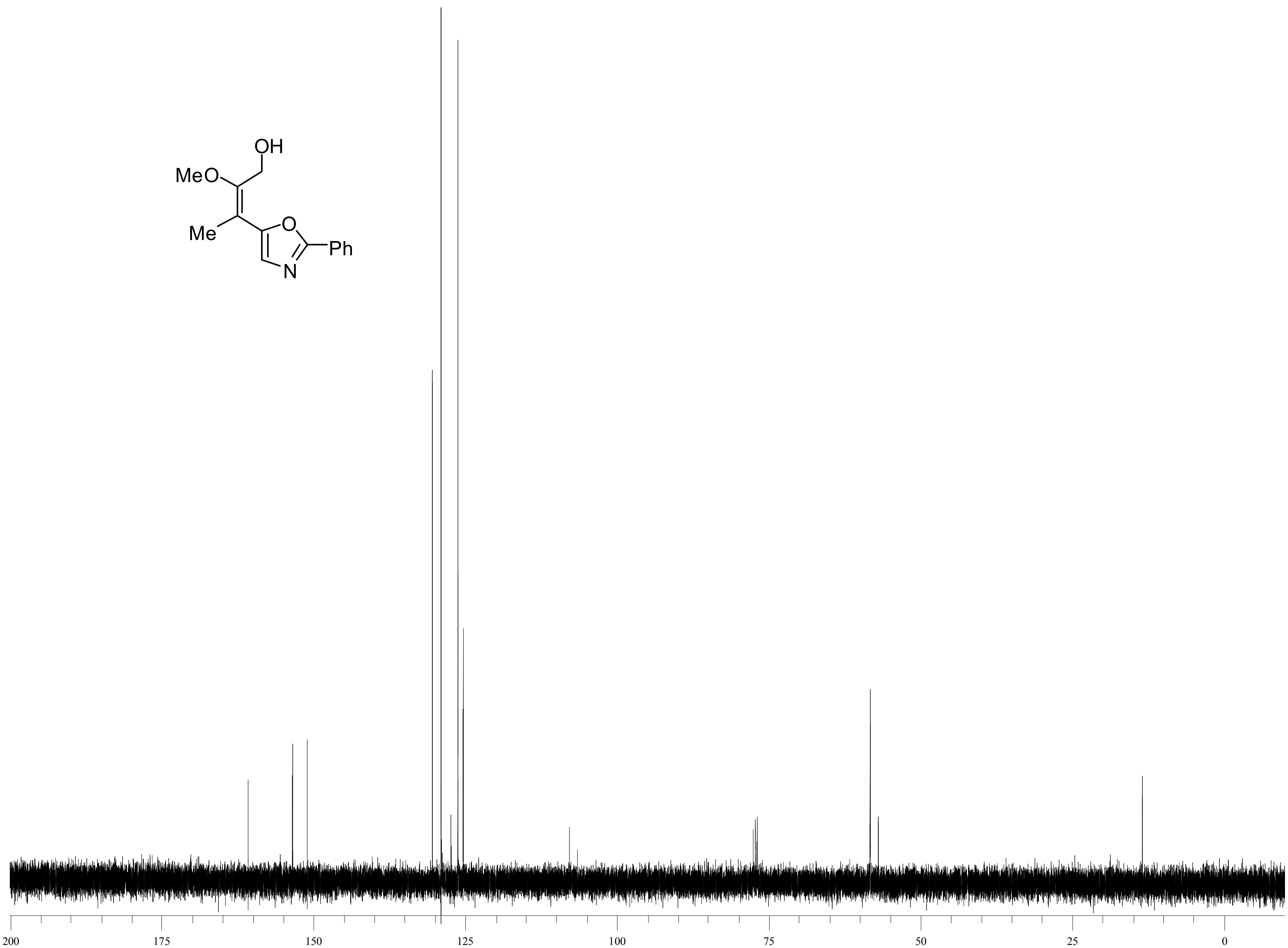


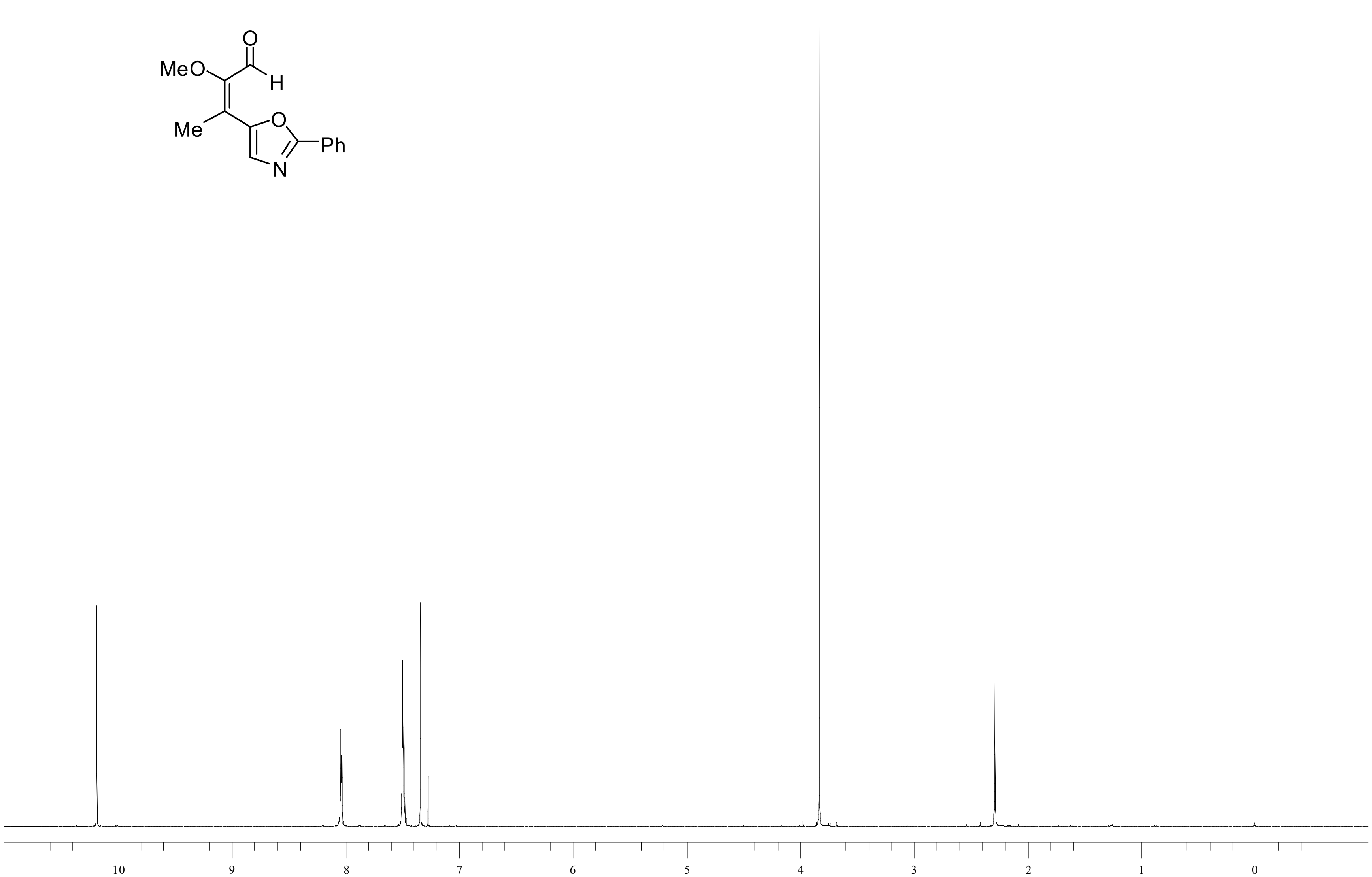
93:7 *E:Z*

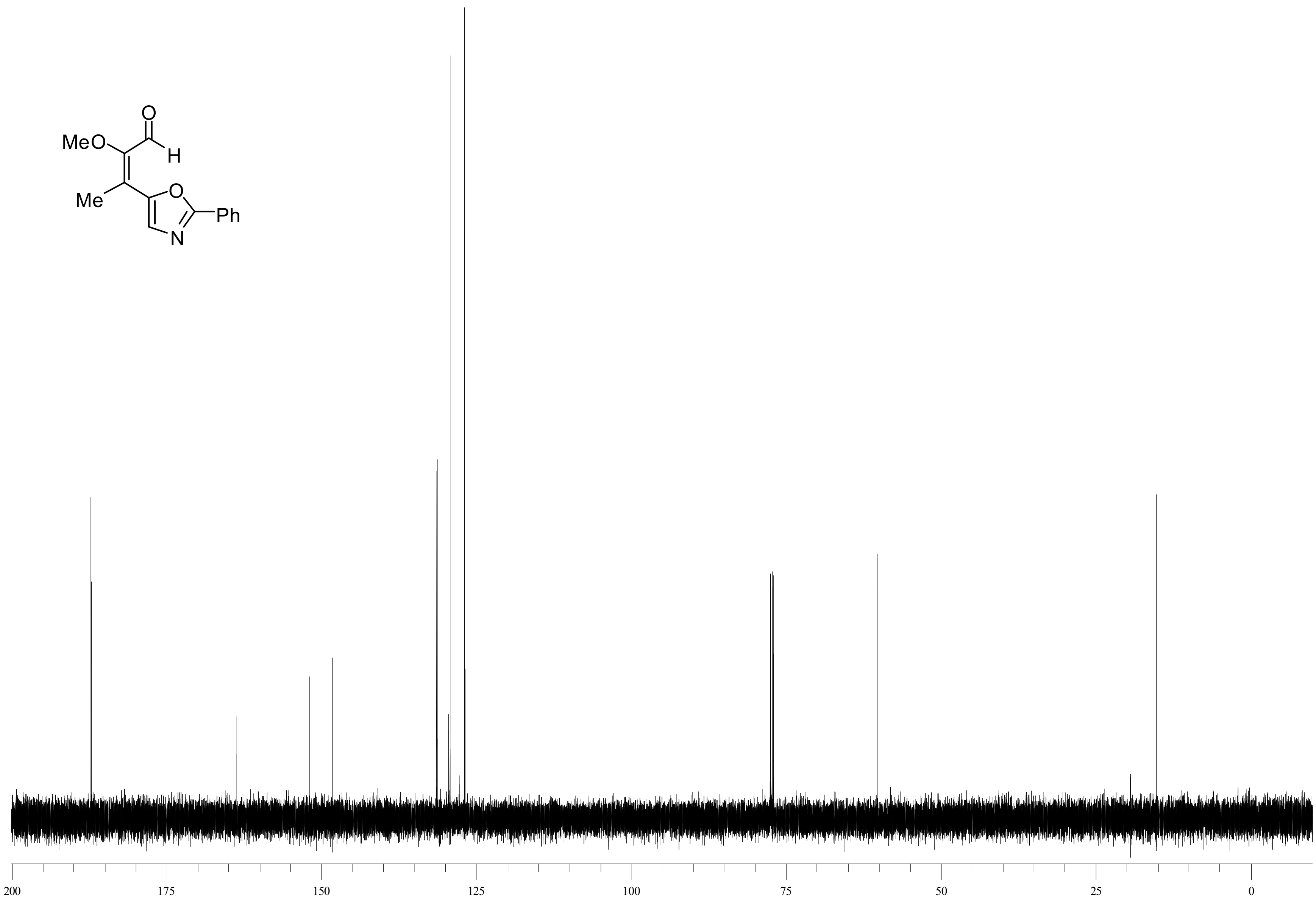

MeO
O
OMe
Me
O
Ph
N
10
9
8
7
6
5
4
3
2
1
0

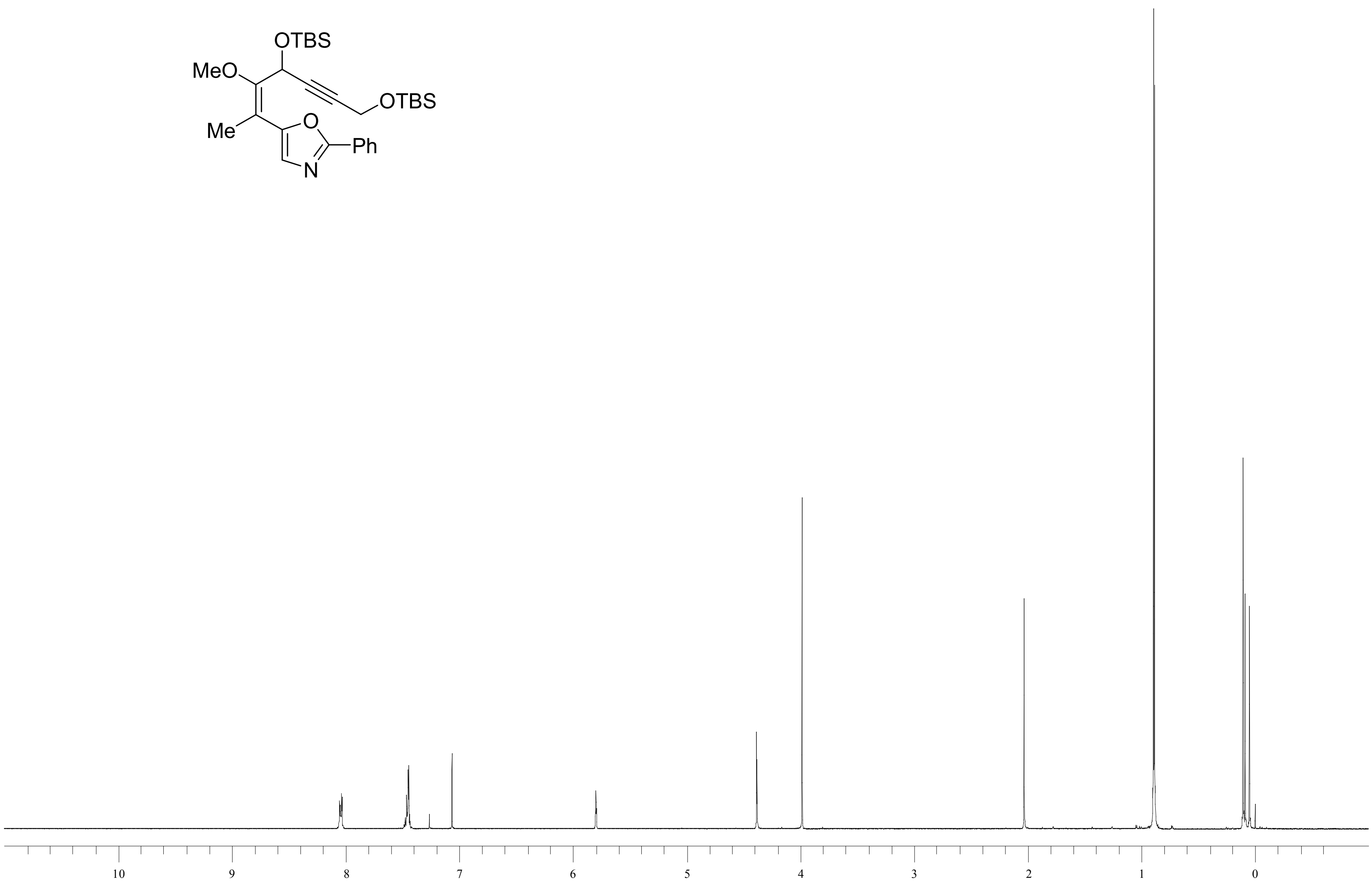

MeO
O
OMe
Me
O
Ph
N
200
175
150
125
100
75
50
25
0

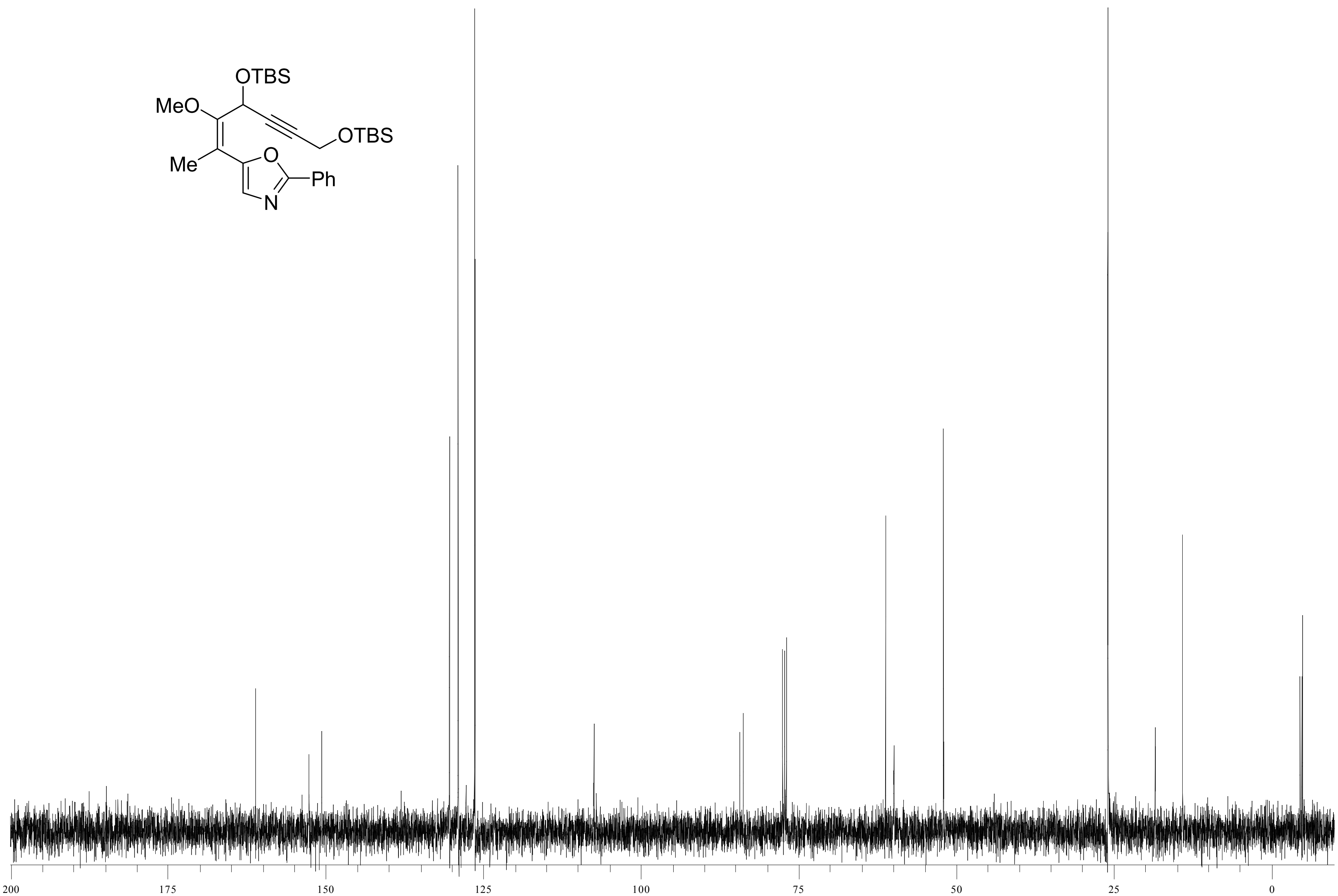

OH
MeO
Me
O
N
Ph
10
9
8
7
6
5
4
3
2
1
0

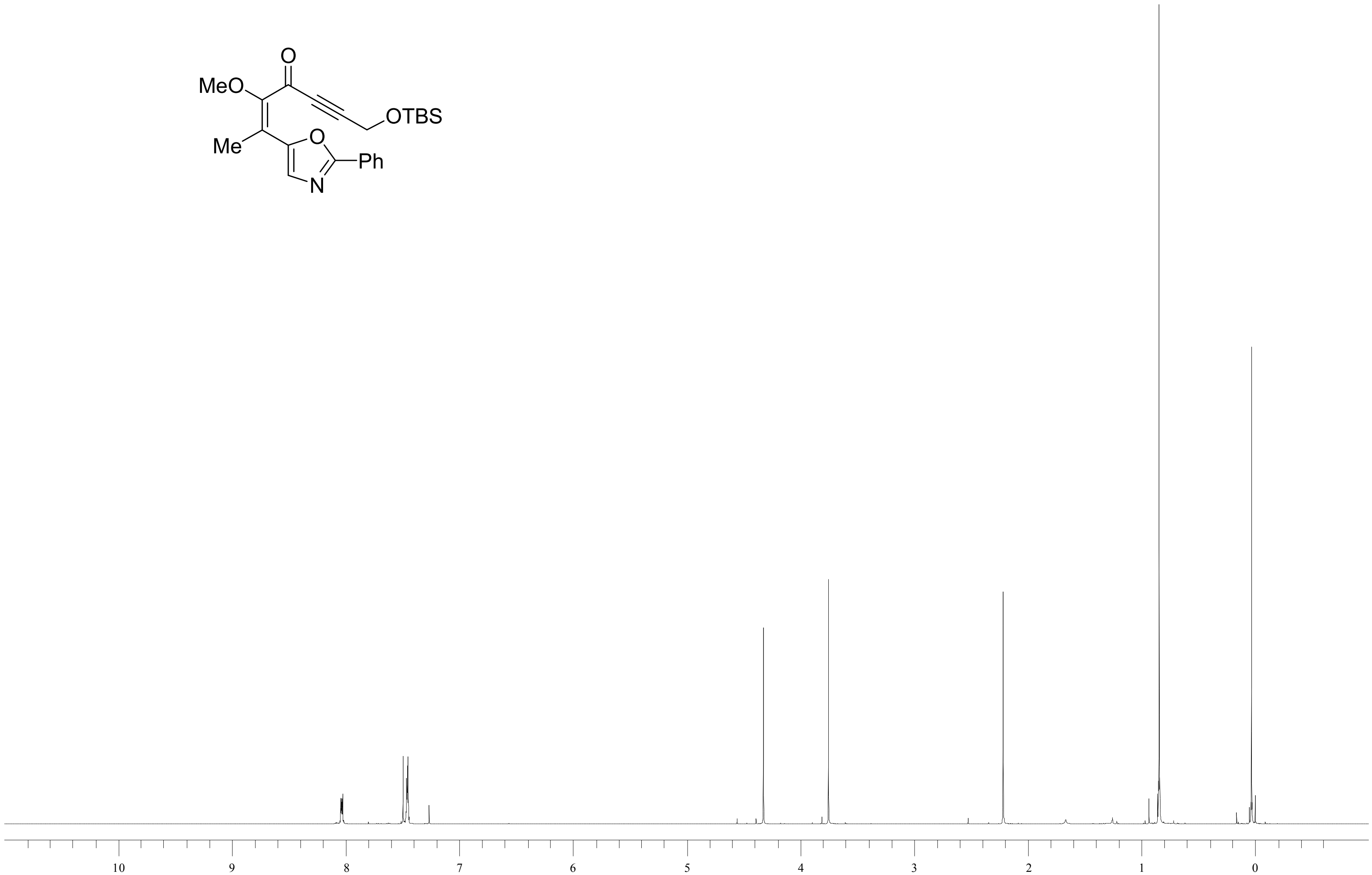

OH
MeO
Me
O
N
Ph
200
175
150
125
100
75
50
25
0

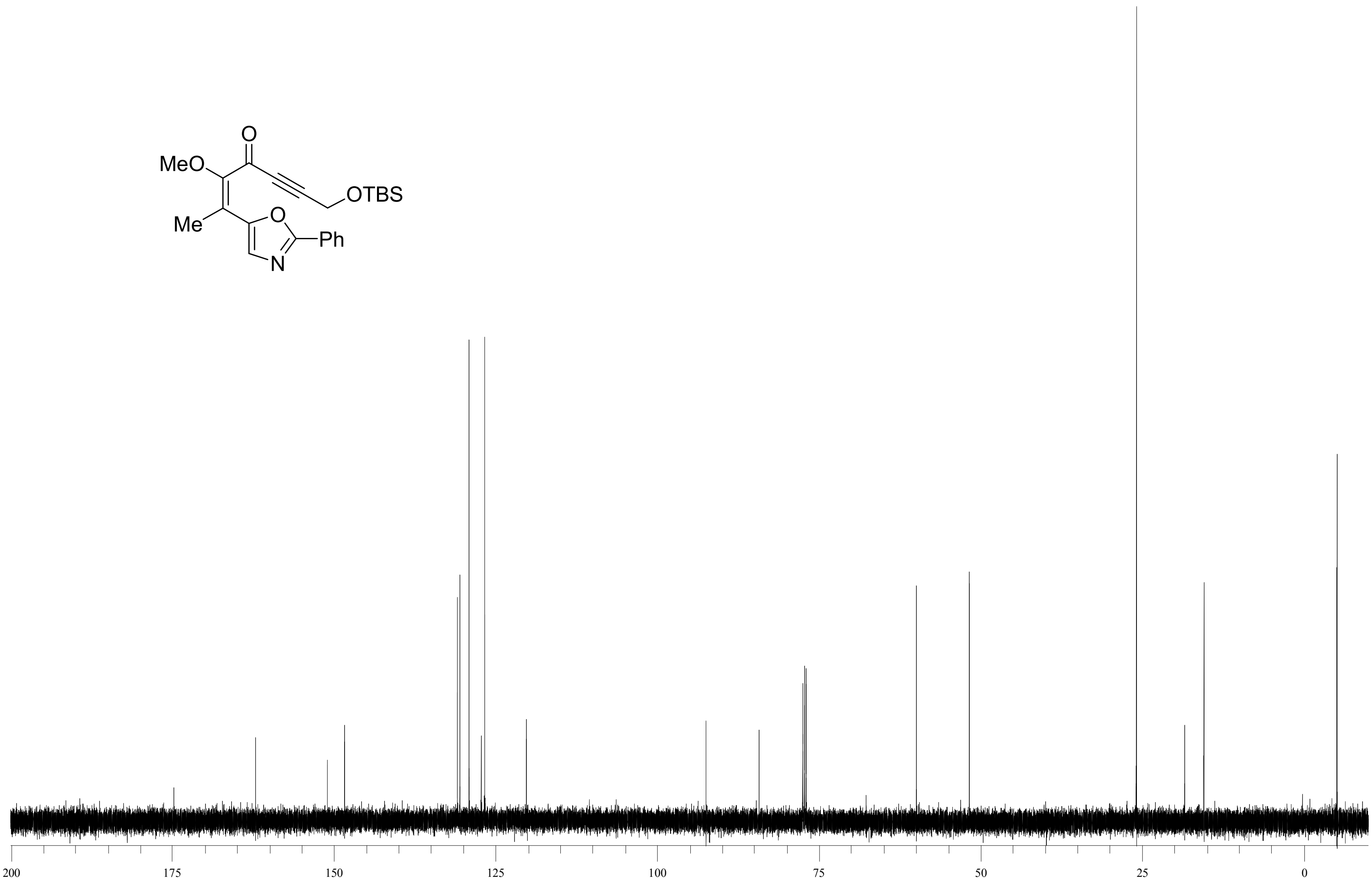

MeO
O
H
Me
O
N
Ph
10
9
8
7
6
5
4
3
2
1
0


MeO
O
H
Me
O
N
Ph
200
175
150
125
100
75
50
25
0

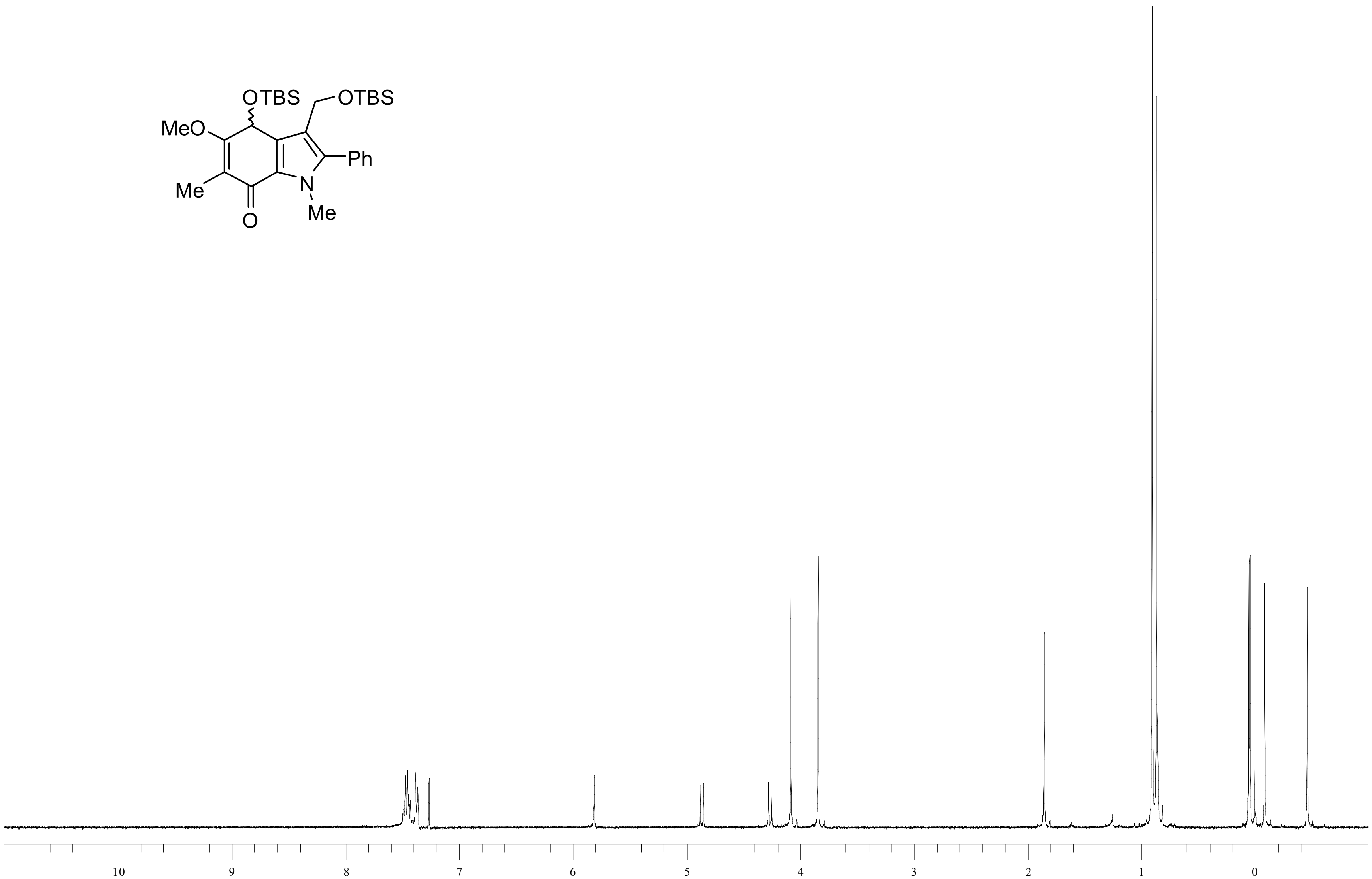

OTBS
MeO
OTBS
Me
O
Ph
N
10
9
8
7
6
5
4
3
2
1
0

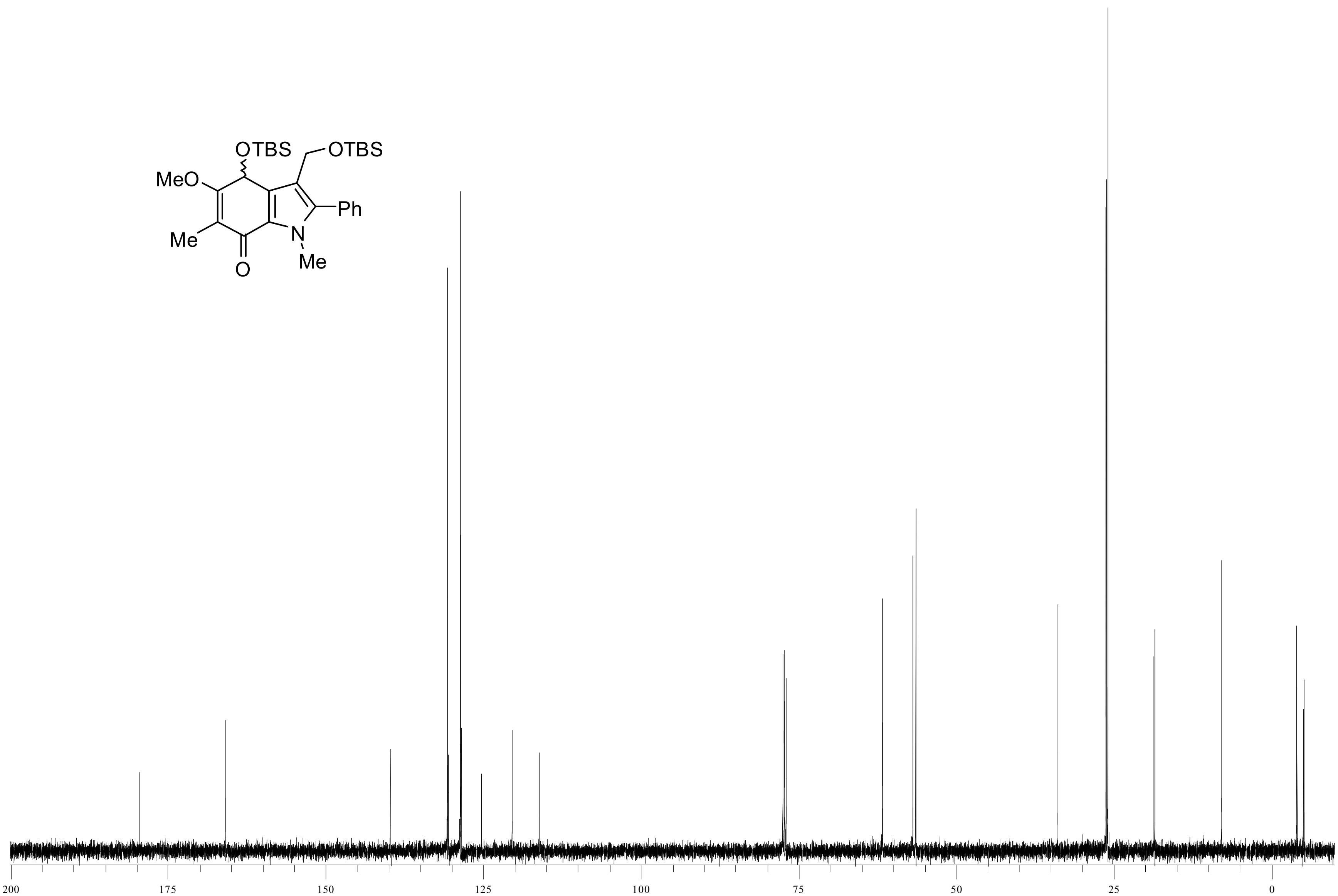

OTBS
MeO
OTBS
Me
O
Ph
N
200
175
150
125
100
75
50
25
0

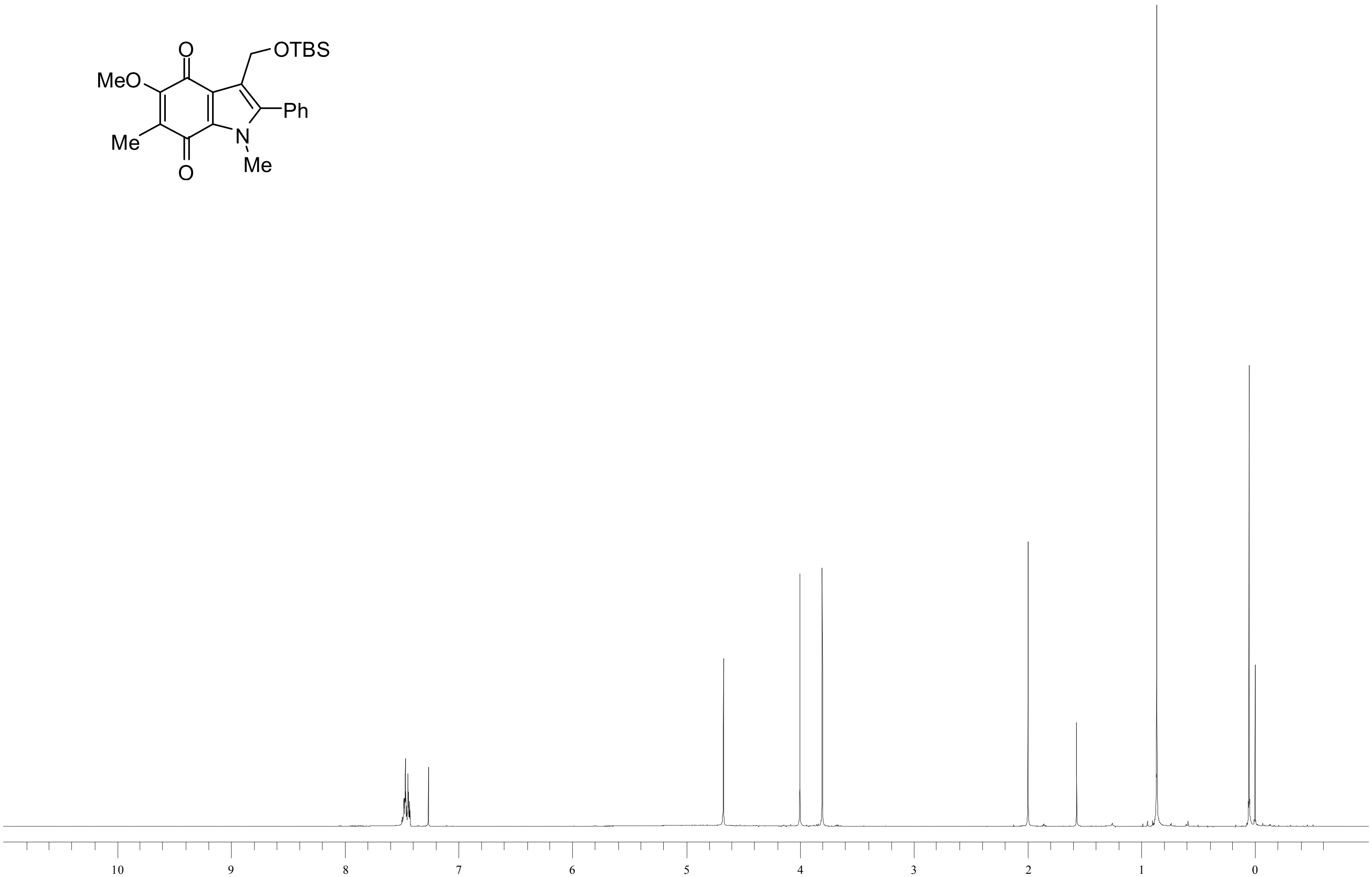

O
MeO
OTBS
Me
O
Ph
N
10
9
8
7
6
5
4
3
2
1
0

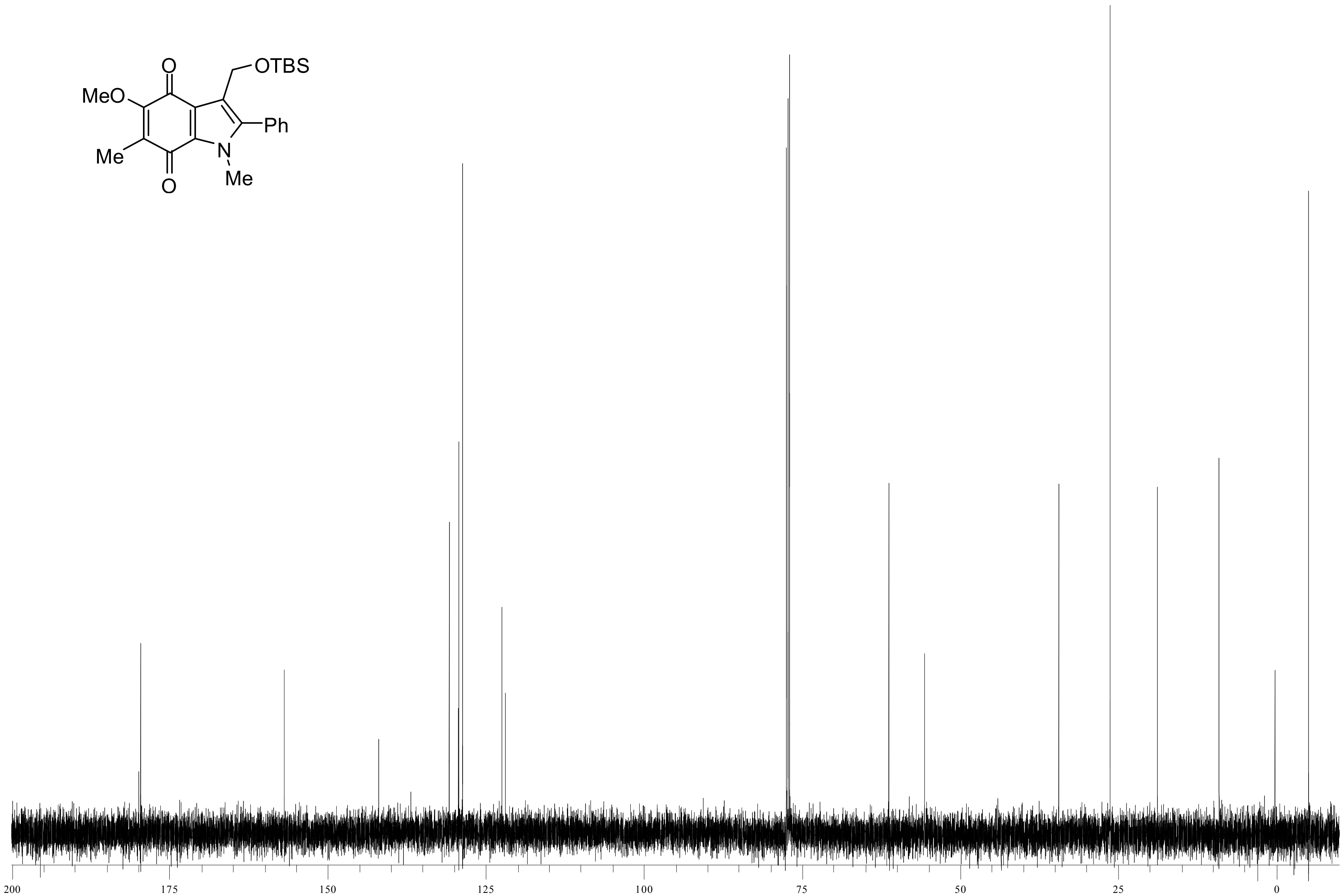


O
MeO
OTBS
Me
O
Ph
N
200
175
150
125
100
75
50
25
0

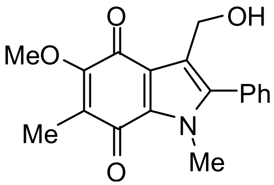

OTBS
OTBS
MeO
Ph
Me
N
Me
O
10
9
8
7
6
5
4
3
2
1
0


OTBS
OTBS
MeO
Ph
Me
N
Me
O
200
175
150
125
100
75
50
25
0

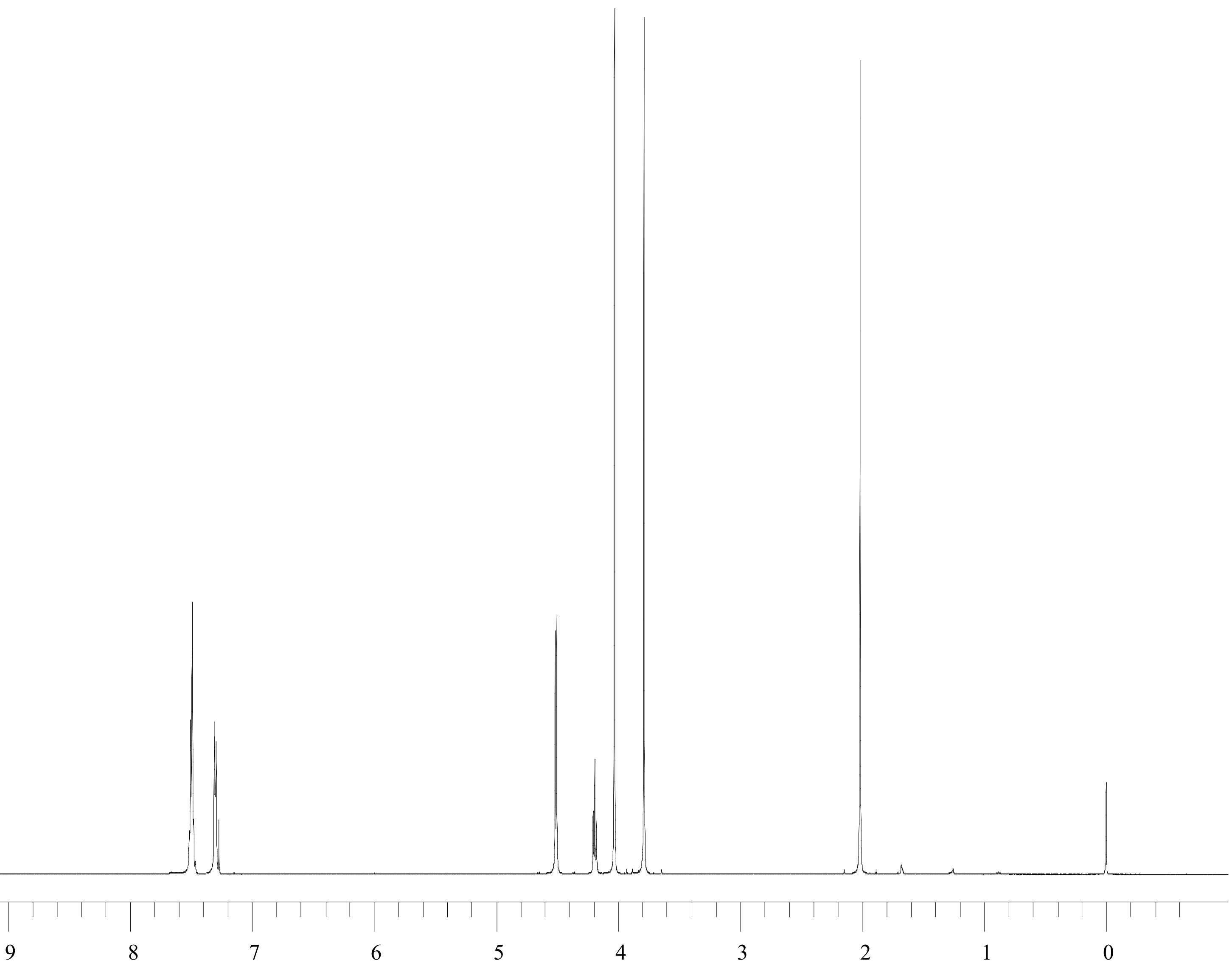

OTBS
MeO
Ph
Me
N
Me
O
O
10
9
8
7
6
5
4
3
2
1
0



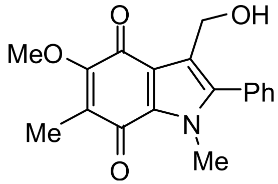
OTBS
MeO
Ph
Me
N
Me
O
O
200
175
150
125
100
75
50
25
0

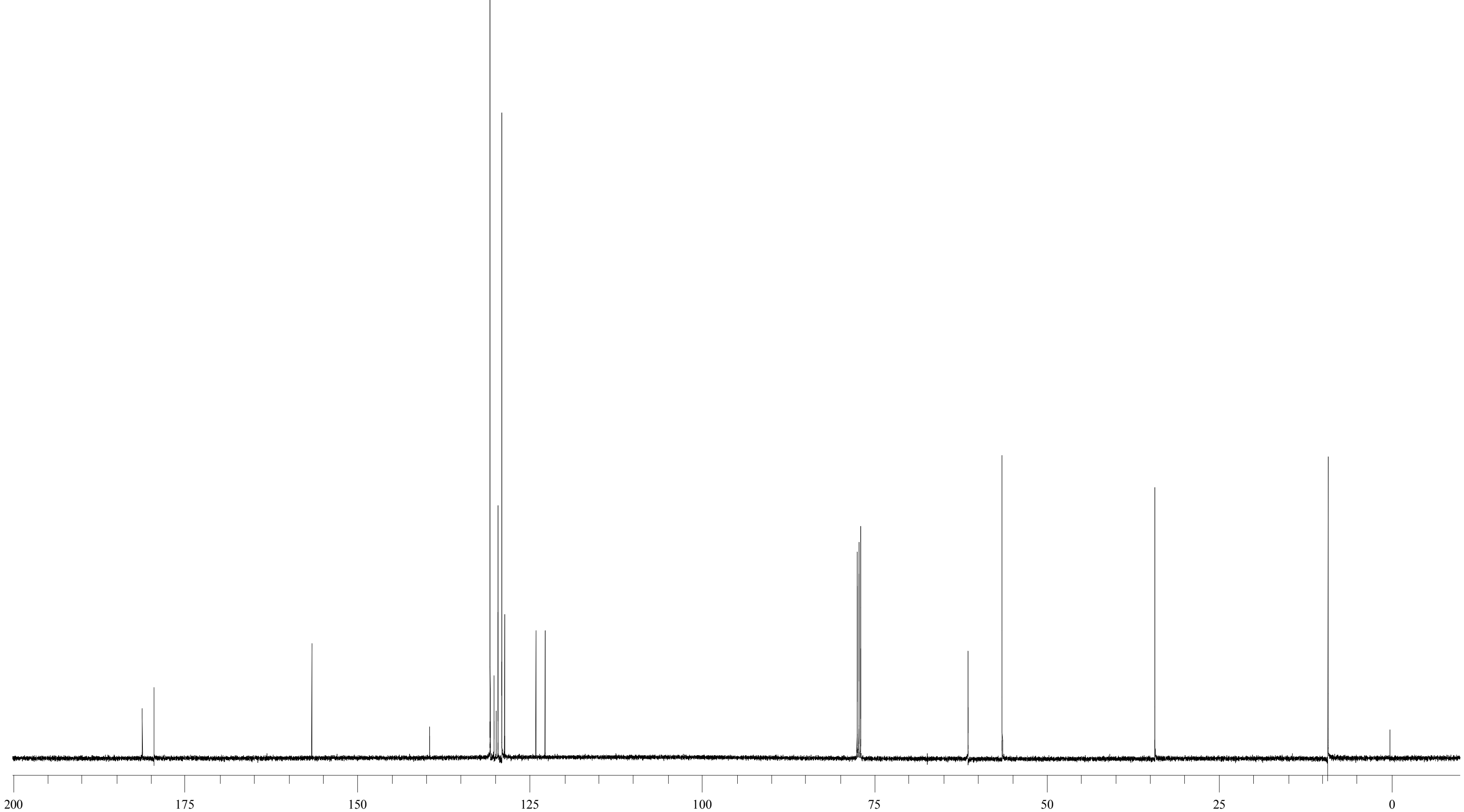


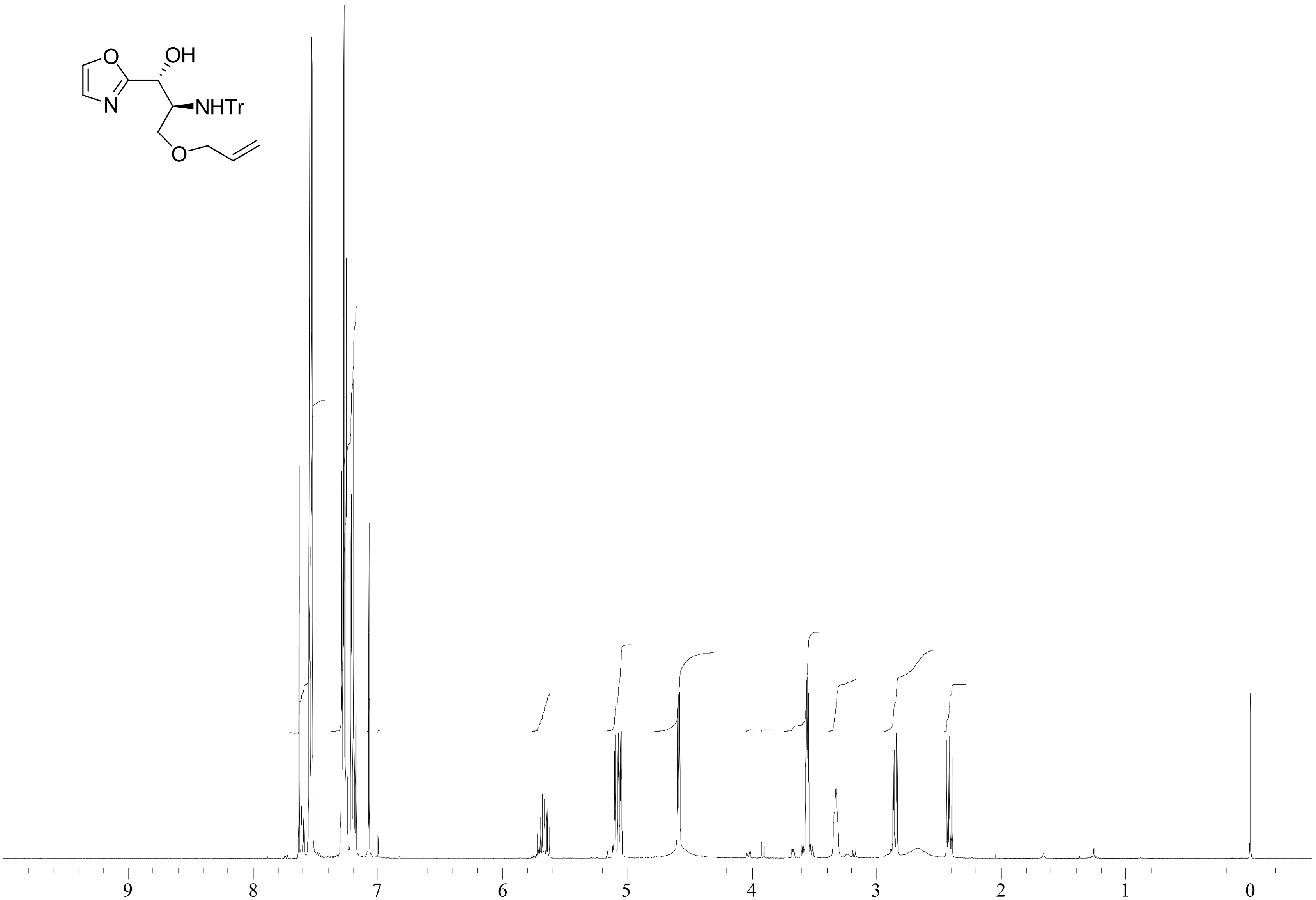
MeO
O
OH
Ph
Me
N
Me
O

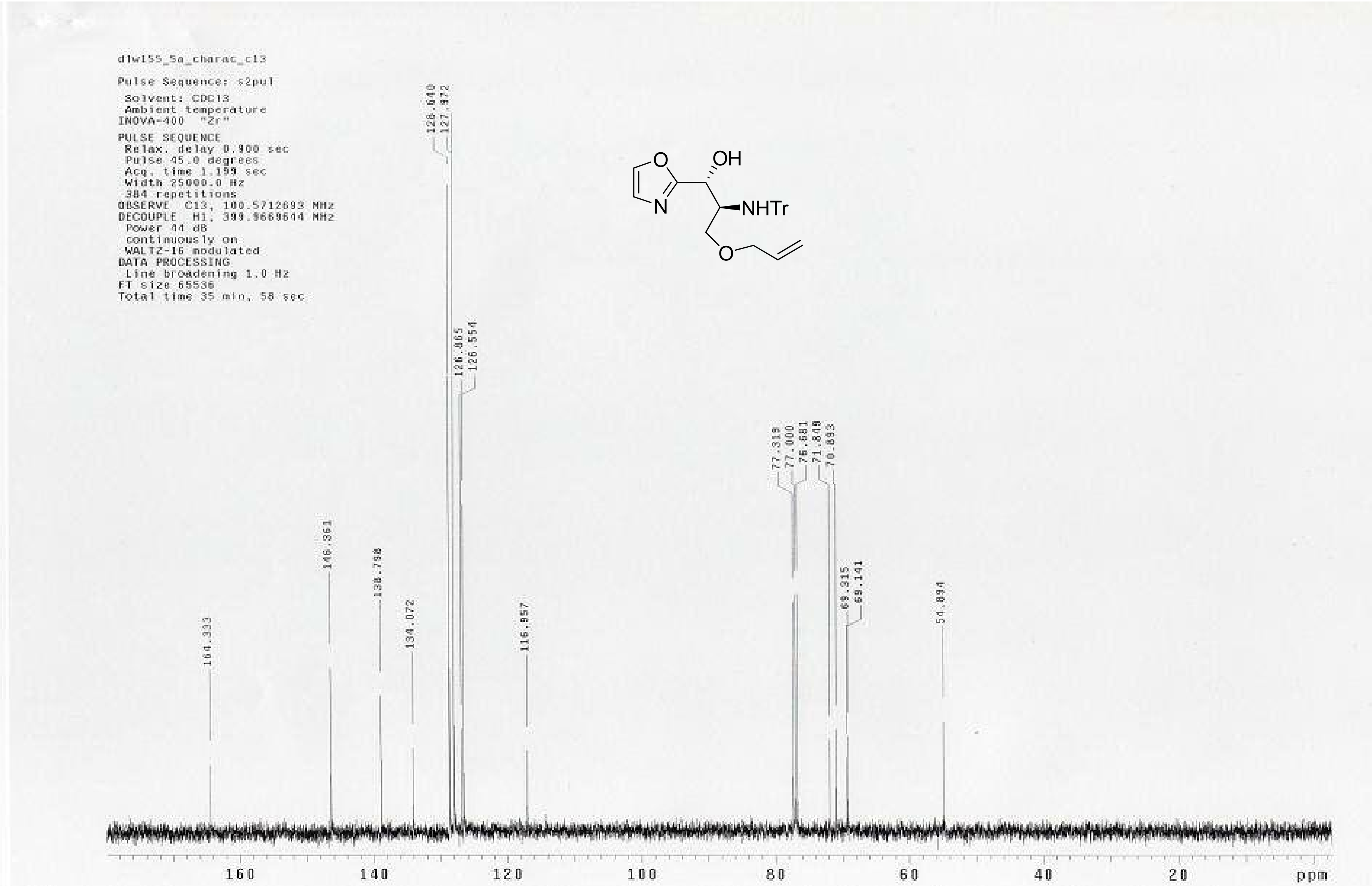


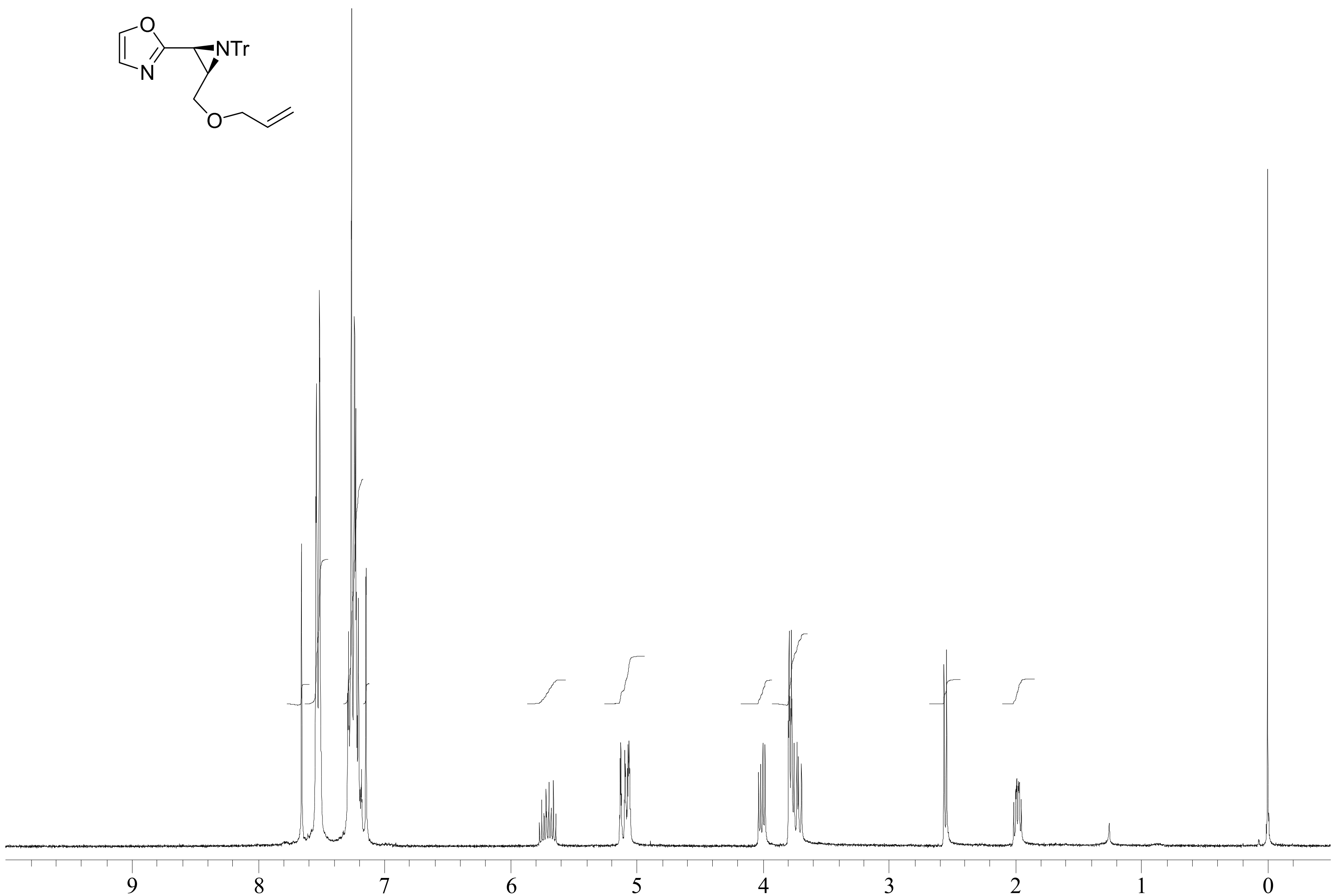
10
9
8
7
6
5
4
3
2
1
0

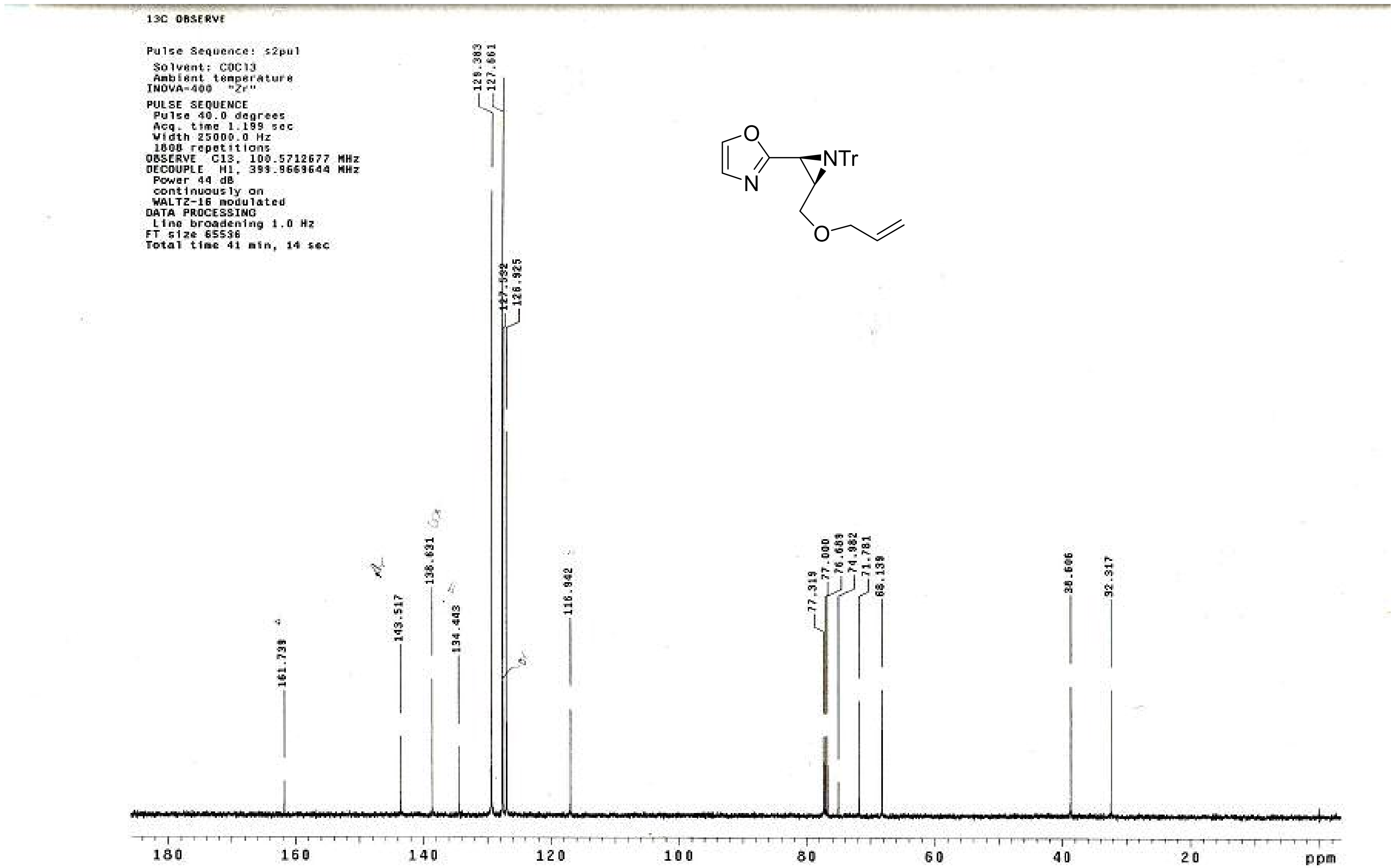

OH
MeO
Ph
Me
N
Me
O
O


200
175
150
125
100
75
50
25
0

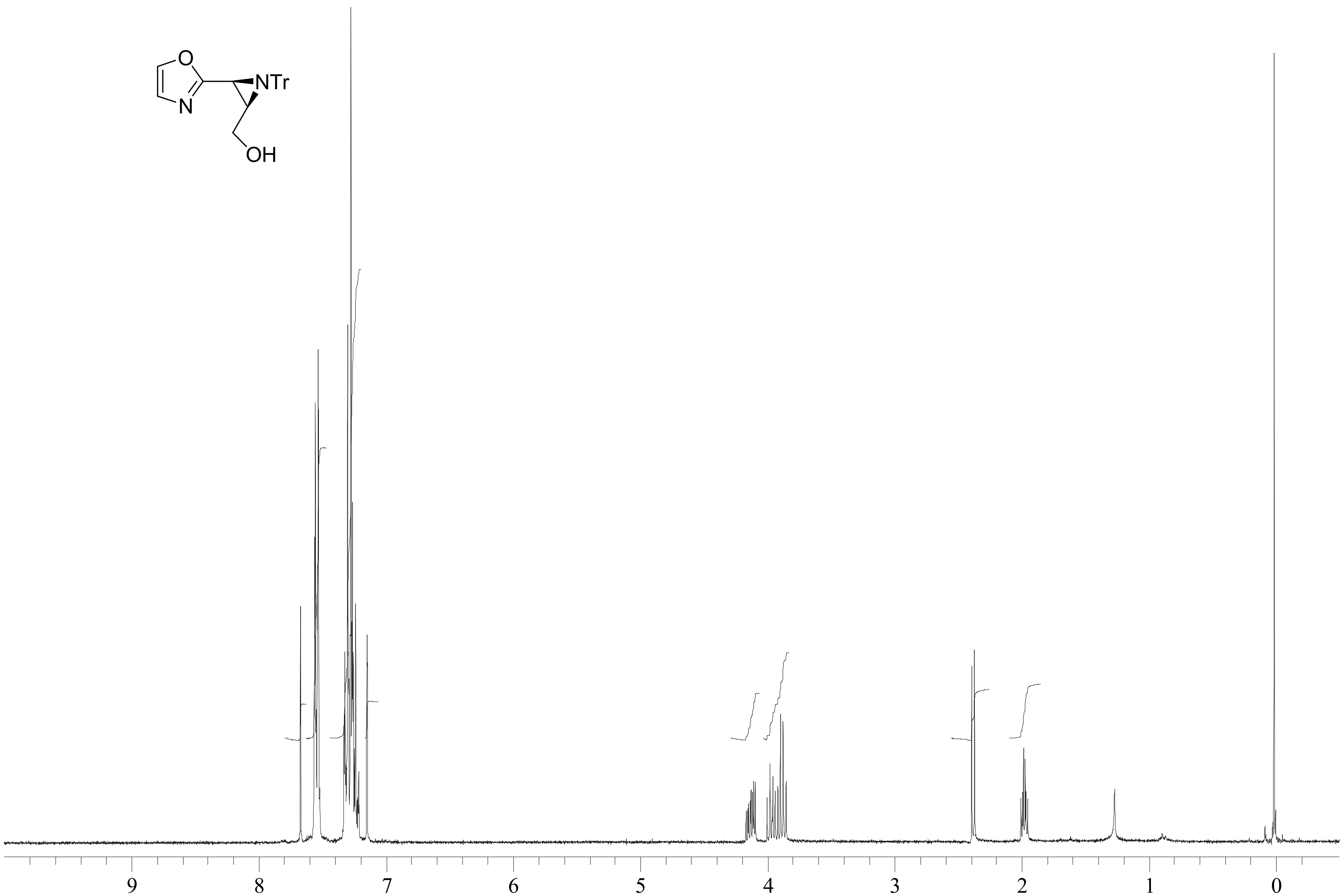

OH
O
N
NHTr
O
9
8
7
6
5
4
3
2
1
0

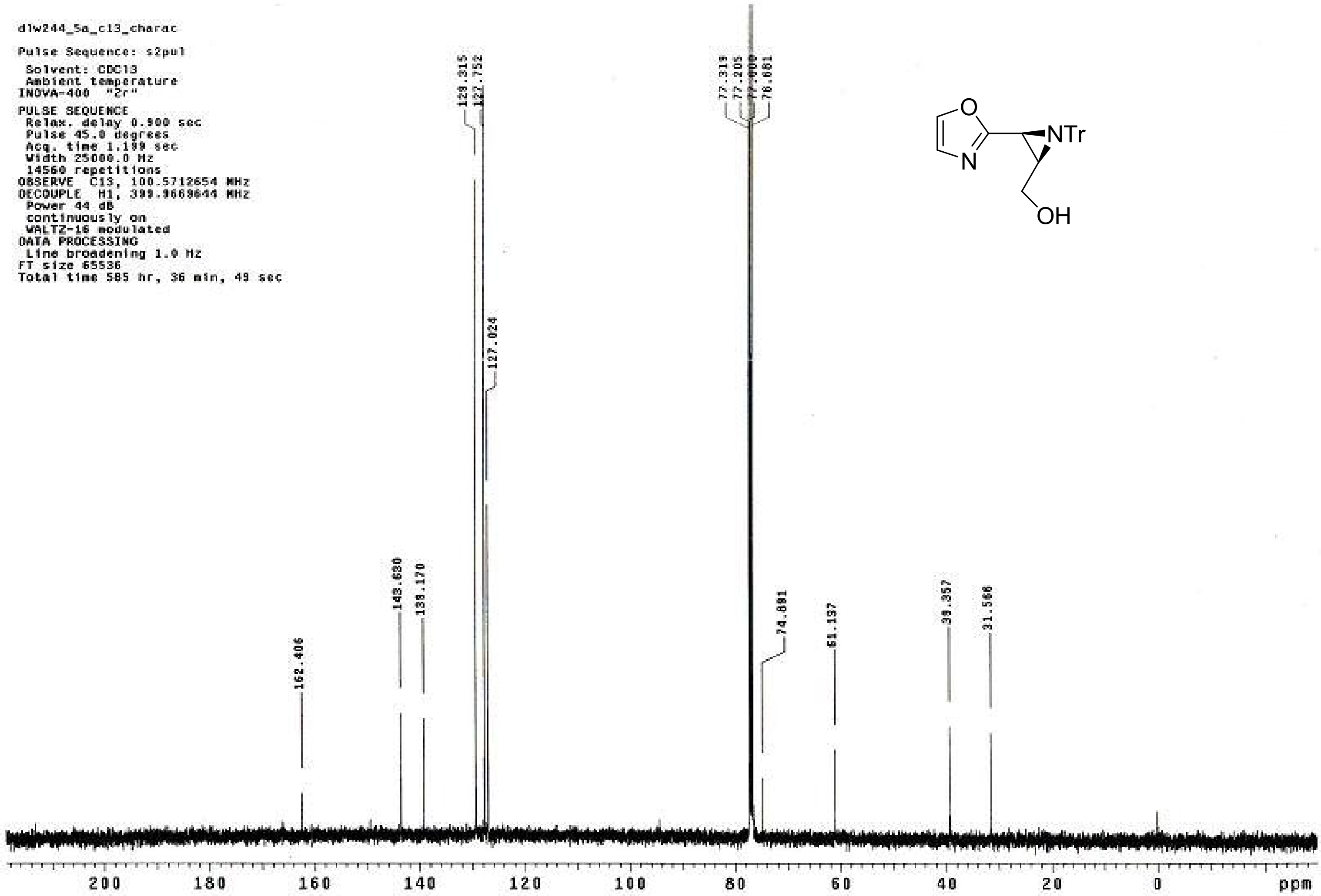

dlw155_5a_charac_c13
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "2r"
PULSE SEQUENCE
Relax. delay 0.900 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
384 repetitions
OBSERVE C13, 100.5712693 MHz
DECOUPLE H1, 399.9669644 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 58 sec
OH
NHTr
O
N
164.333
146.361
138.798
134.072
128.640
127.972
126.865
126.554
116.857
77.318
77.000
76.681
71.849
70.893
69.315
69.141
54.894
160
140
120
100
80
60
40
20
ppm

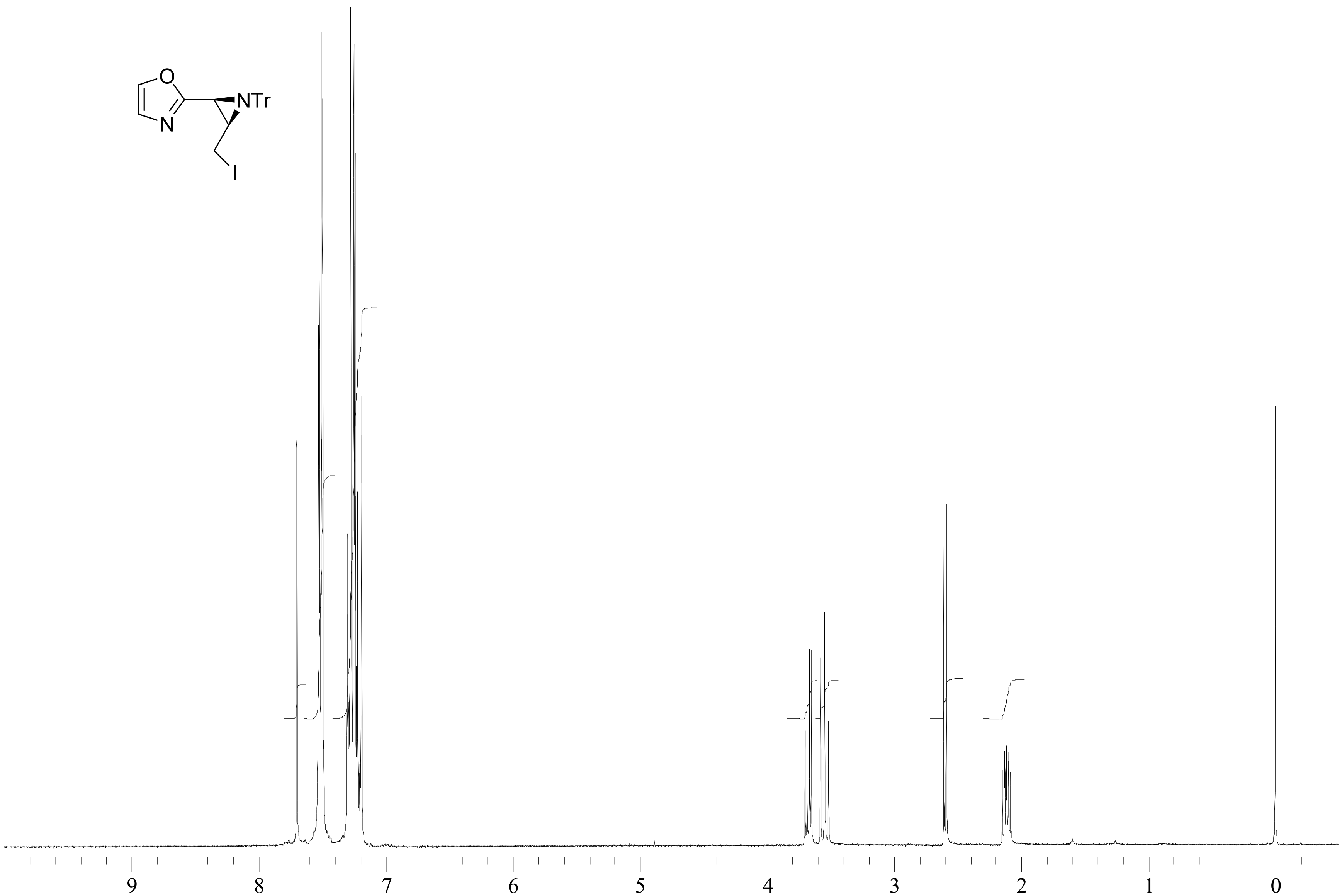

O
N
NTr
O
9
8
7
6
5
4
3
2
1
0

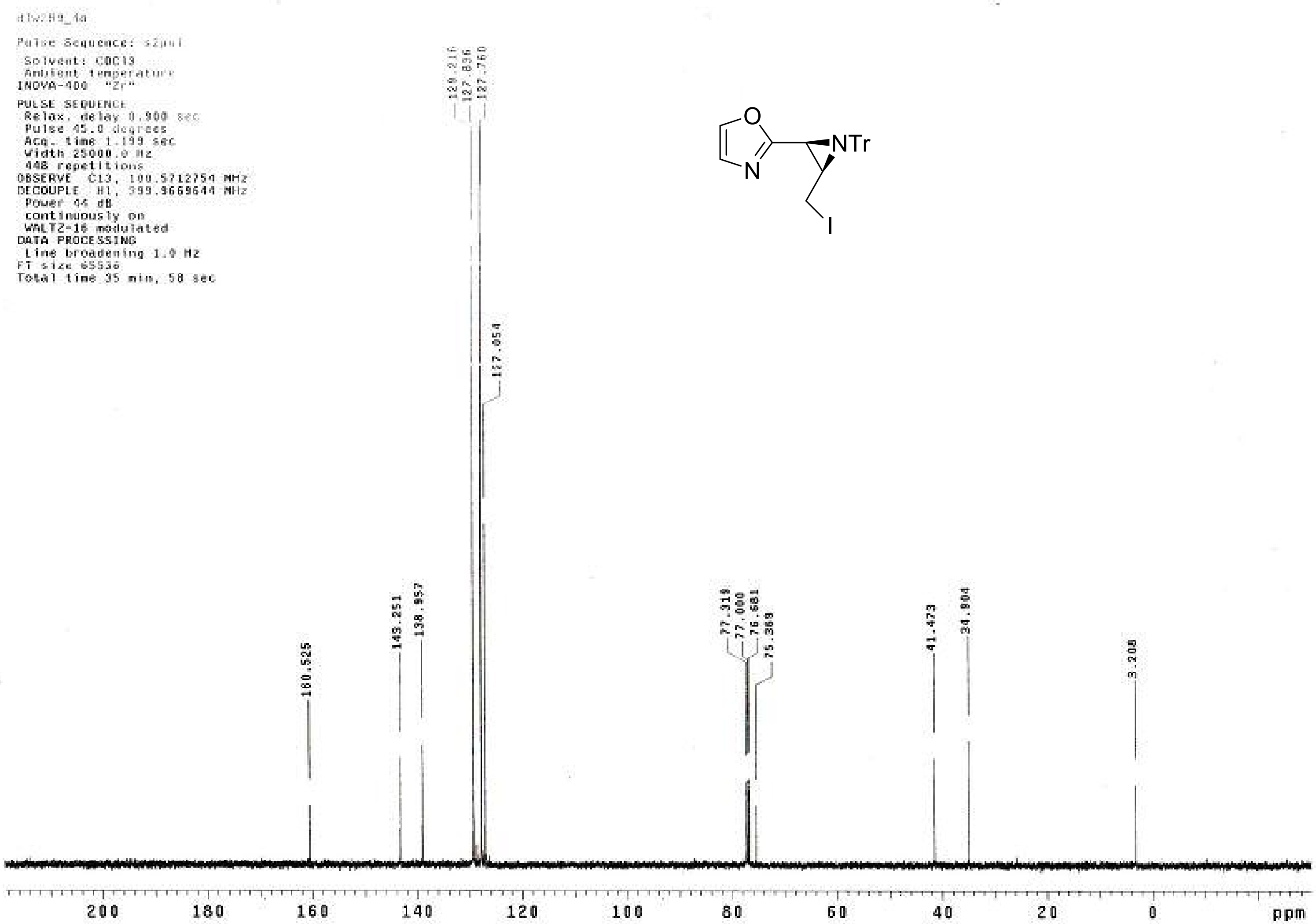


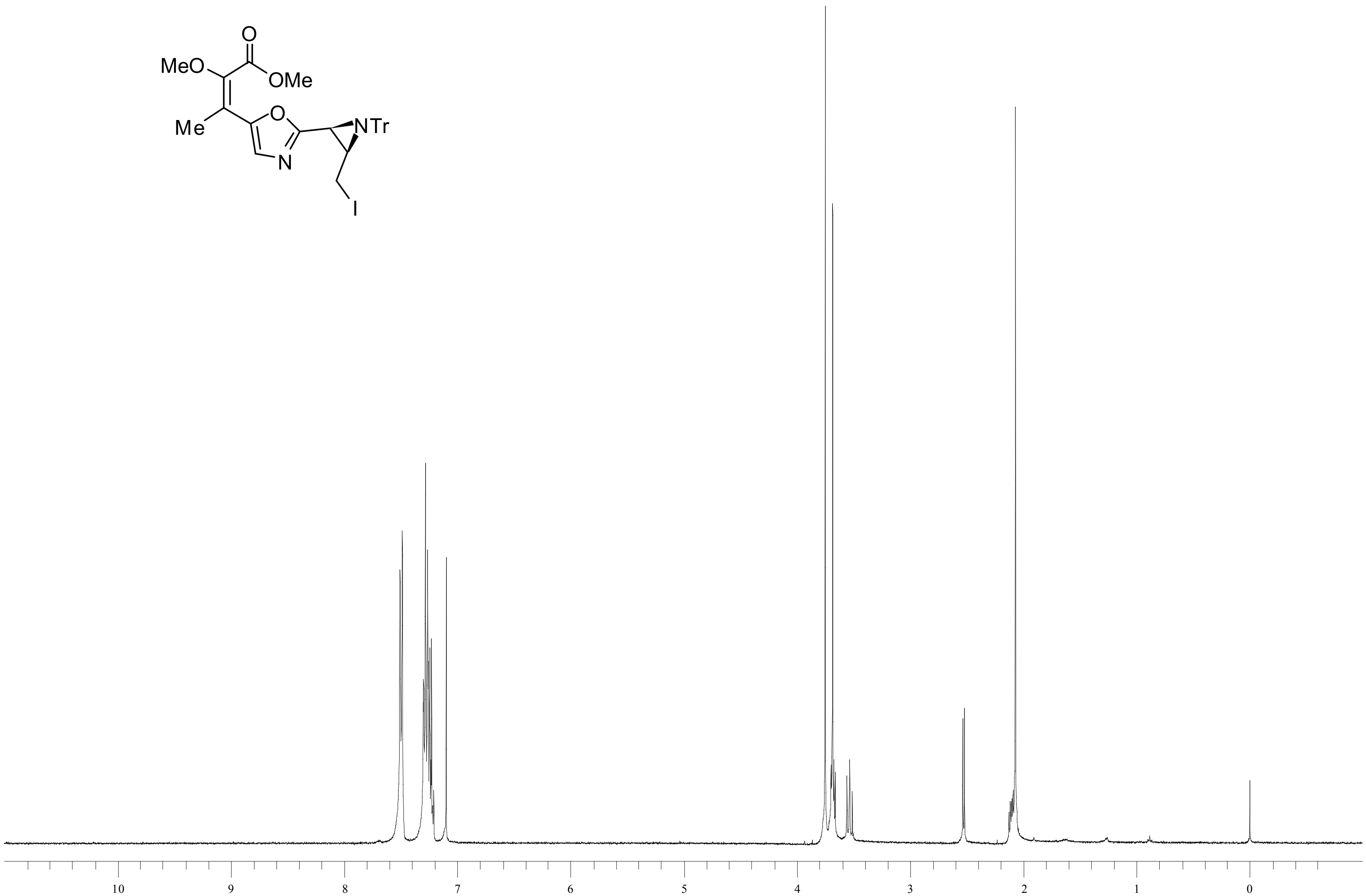
13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "2r"
PULSE SEQUENCE
Pulse 40.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
1808 repetitions
OBSERVE C13, 100.5712677 MHz
DECOUPLE H1, 399.9669644 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 41 min, 14 sec
129.383
127.661
127.582
126.925
161.739
143.517
138.631
134.443
116.942
77.319
77.000
76.683
74.982
71.781
68.139
38.606
32.317
NTr
O
N
180 160 140 120 100 80 60 40 20 ppm

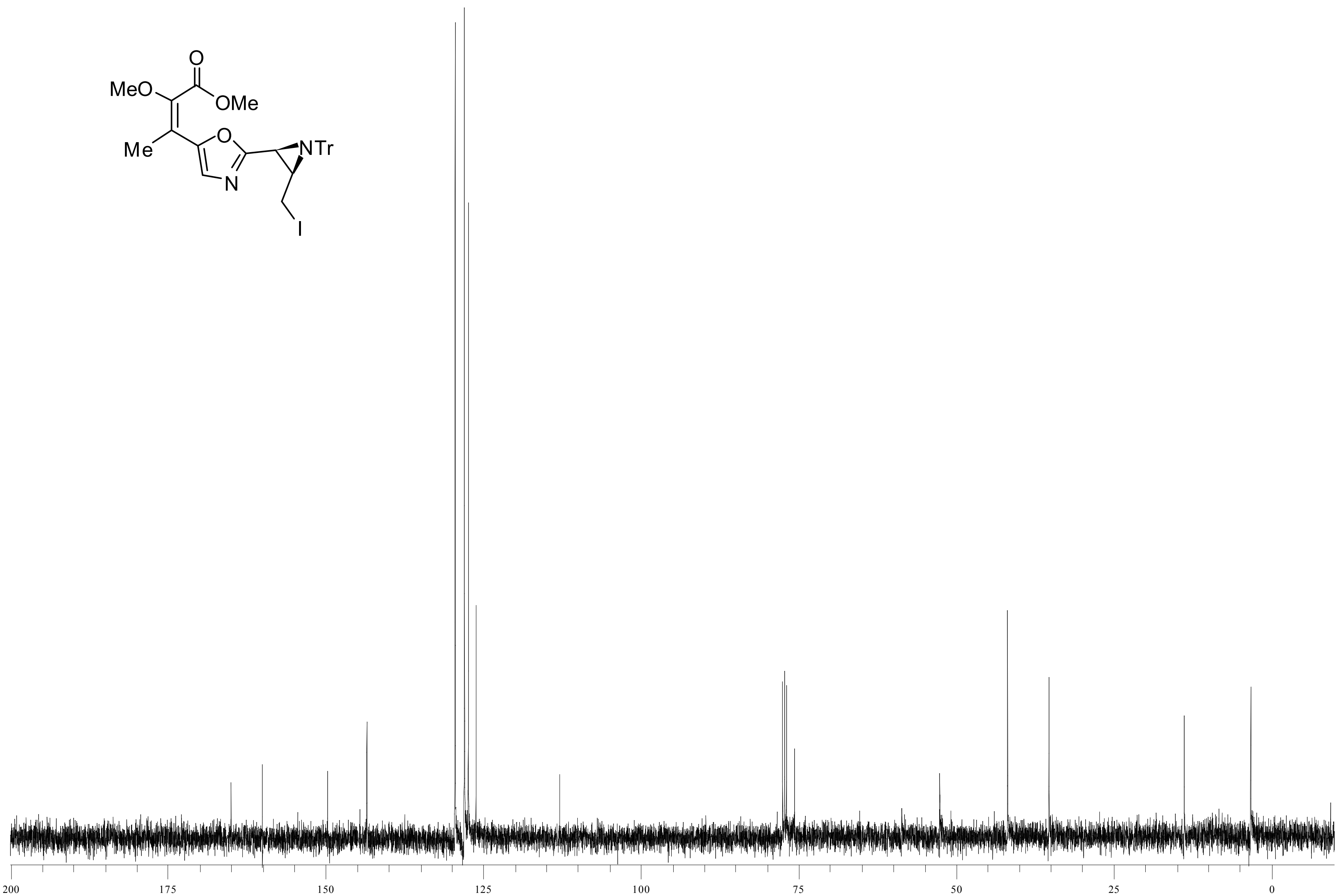

NTr
O
N
OH
9
8
7
6
5
4
3
2
1
0

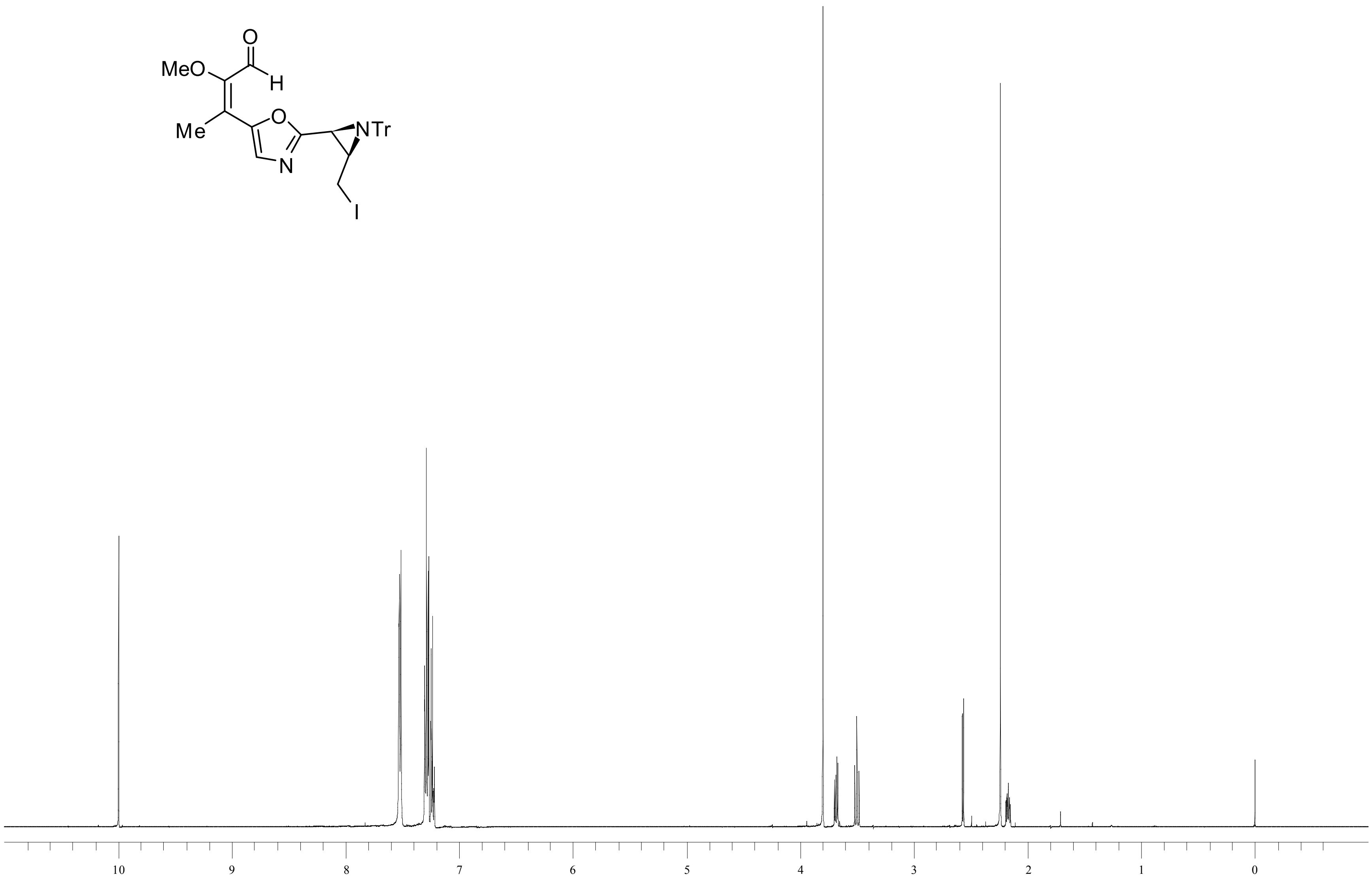

dlw244_5a_c13_charac
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "Zr"
PULSE SEQUENCE
Relax. delay 0.900 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
14560 repetitions
OBSERVE C13, 100.5712654 MHz
DECOUPLE H1, 399.9669644 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 585 hr, 36 min, 49 sec
162.406
143.630
139.170
129.315
127.752
127.024
77.318
77.205
77.000
76.681
74.881
61.137
39.357
31.568
NTr
OH
O
N
200
180
160
140
120
100
80
60
40
20
0
ppm

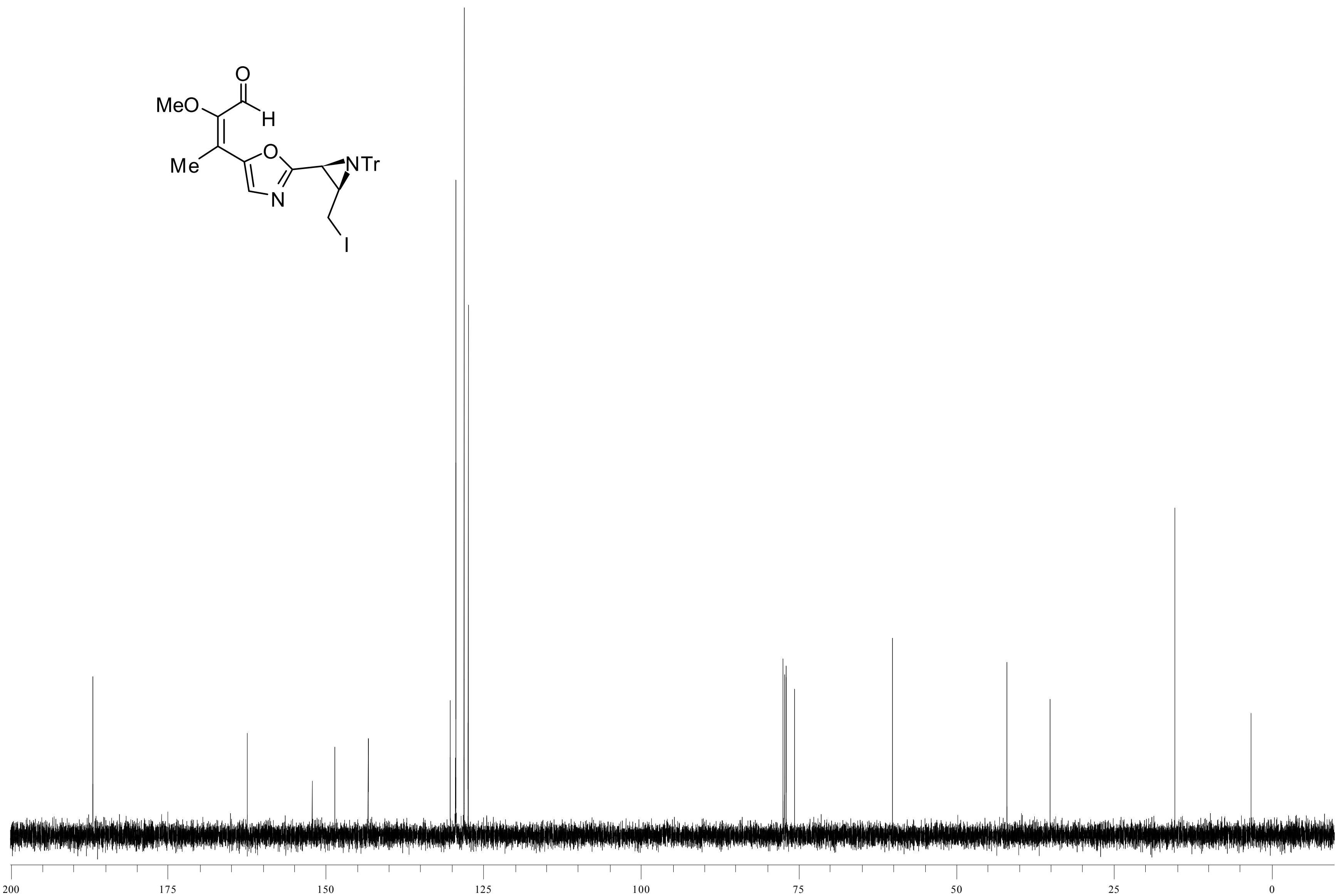

O
N
NTr
I
9
8
7
6
5
4
3
2
1
0


dlw289_4a
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "Zr"
PULSE SEQUENCE
Relax. delay 0.900 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
448 repetitions
OBSERVE C13, 100.5712754 MHz
DECOUPLE H1, 399.9669644 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 35 min, 58 sec
NTr
O
N
I
129.216
127.836
127.760
127.054
160.525
143.251
138.957
77.318
77.000
76.681
75.369
41.473
34.904
3.208
200
180
160
140
120
100
80
60
40
20
0
ppm

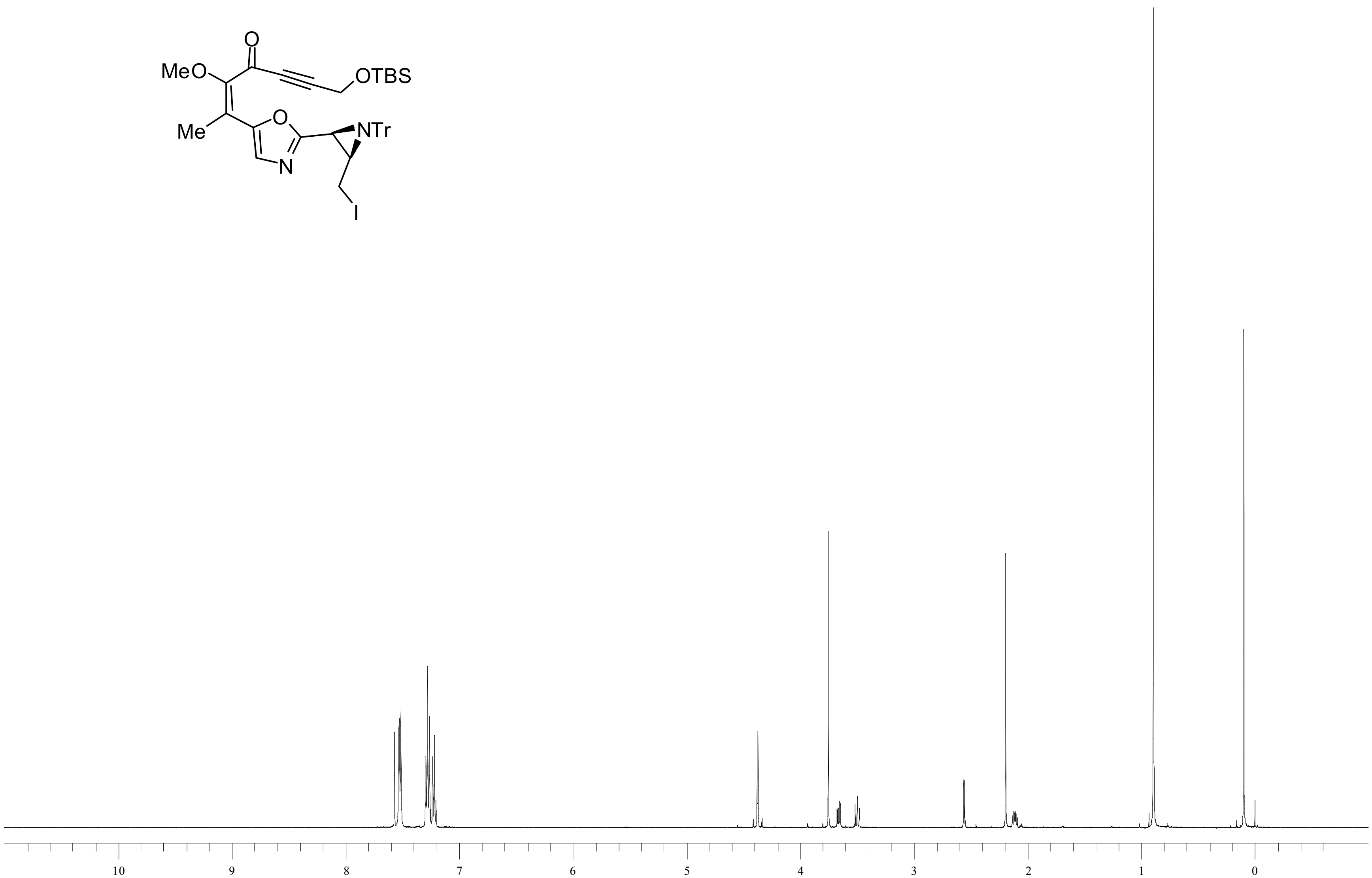

MeO
O
OMe
Me
O
N
NTr
I
10
9
8
7
6
5
4
3
2
1
0

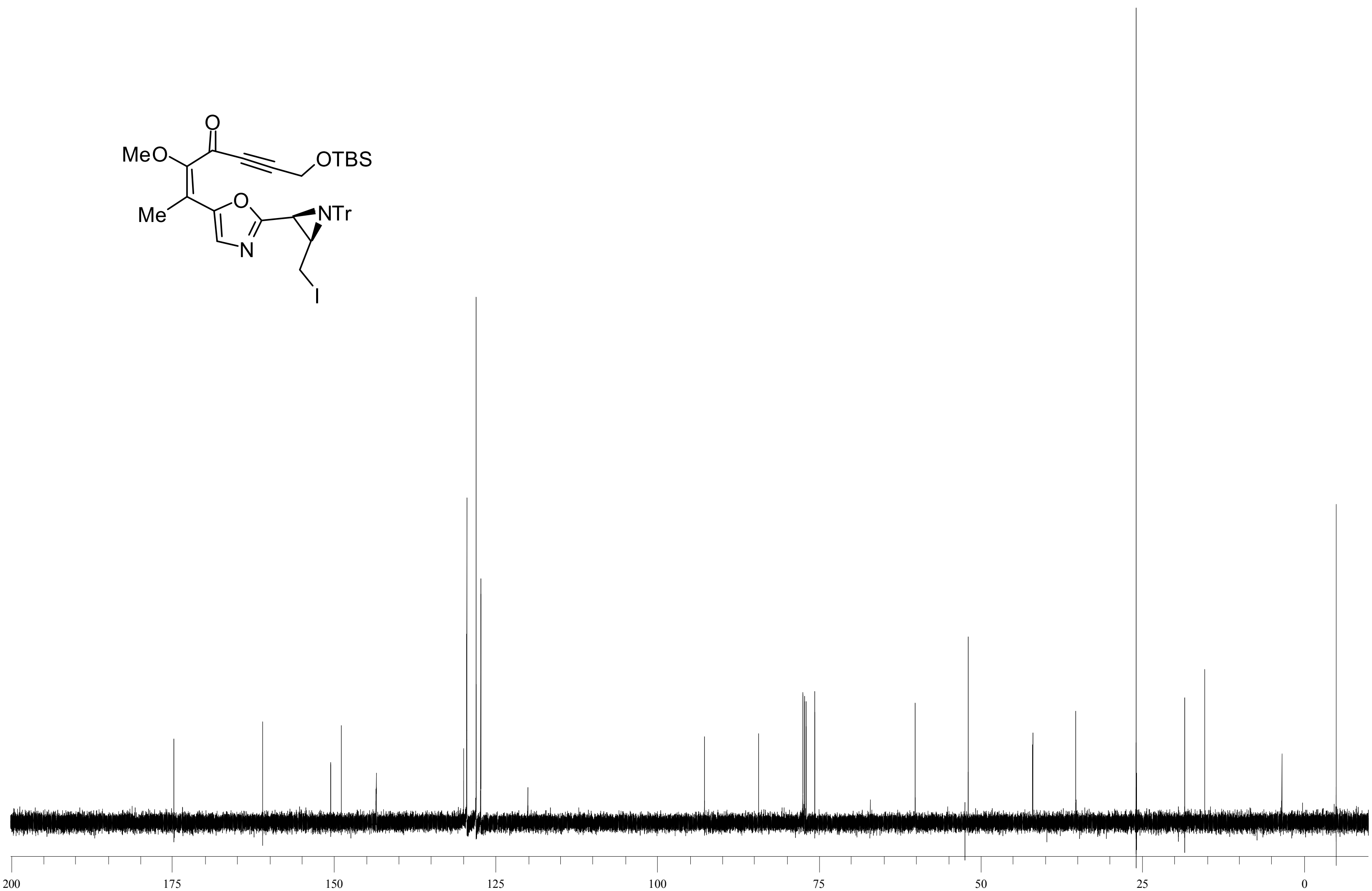

O
MeO
OMe
Me
O
NTr
N
I
200
175
150
125
100
75
50
25
0

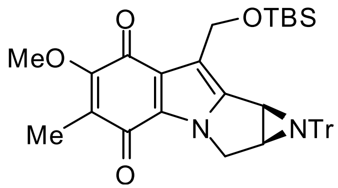

MeO
O
H
Me
O
NTr
N
I
10
9
8
7
6
5
4
3
2
1
0

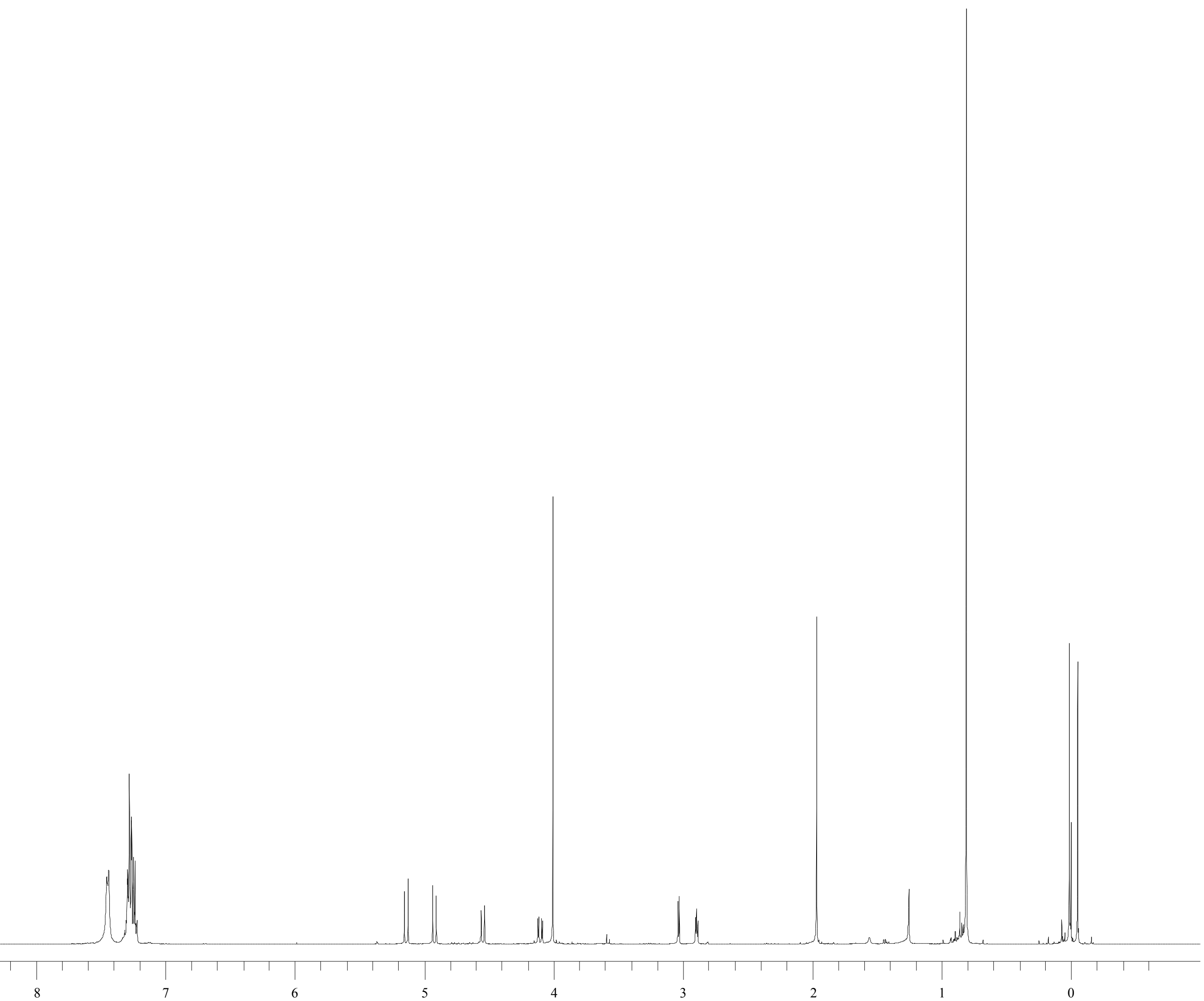


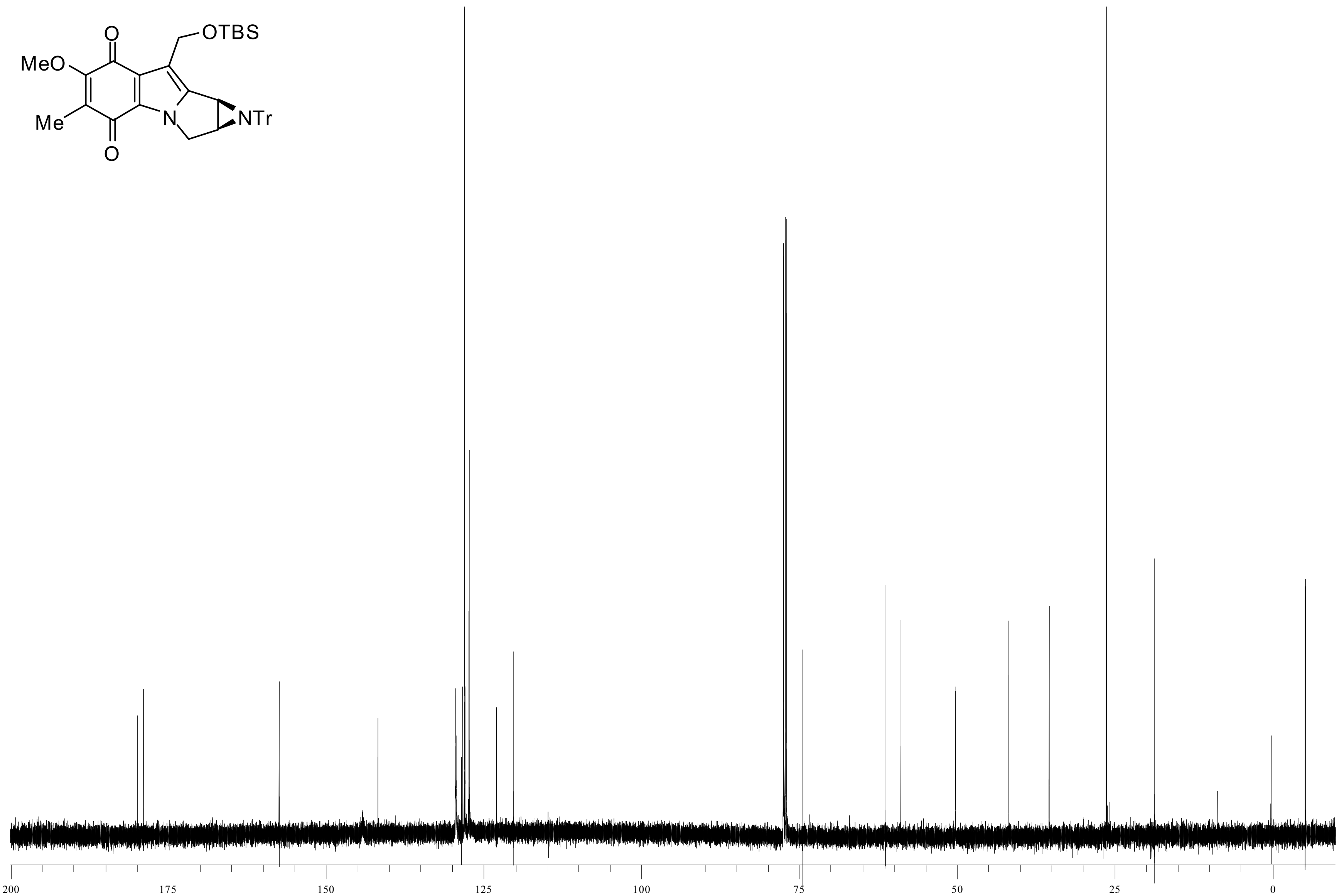
MeO
O
H
Me
O
N
NTr
I
200
175
150
125
100
75
50
25
0

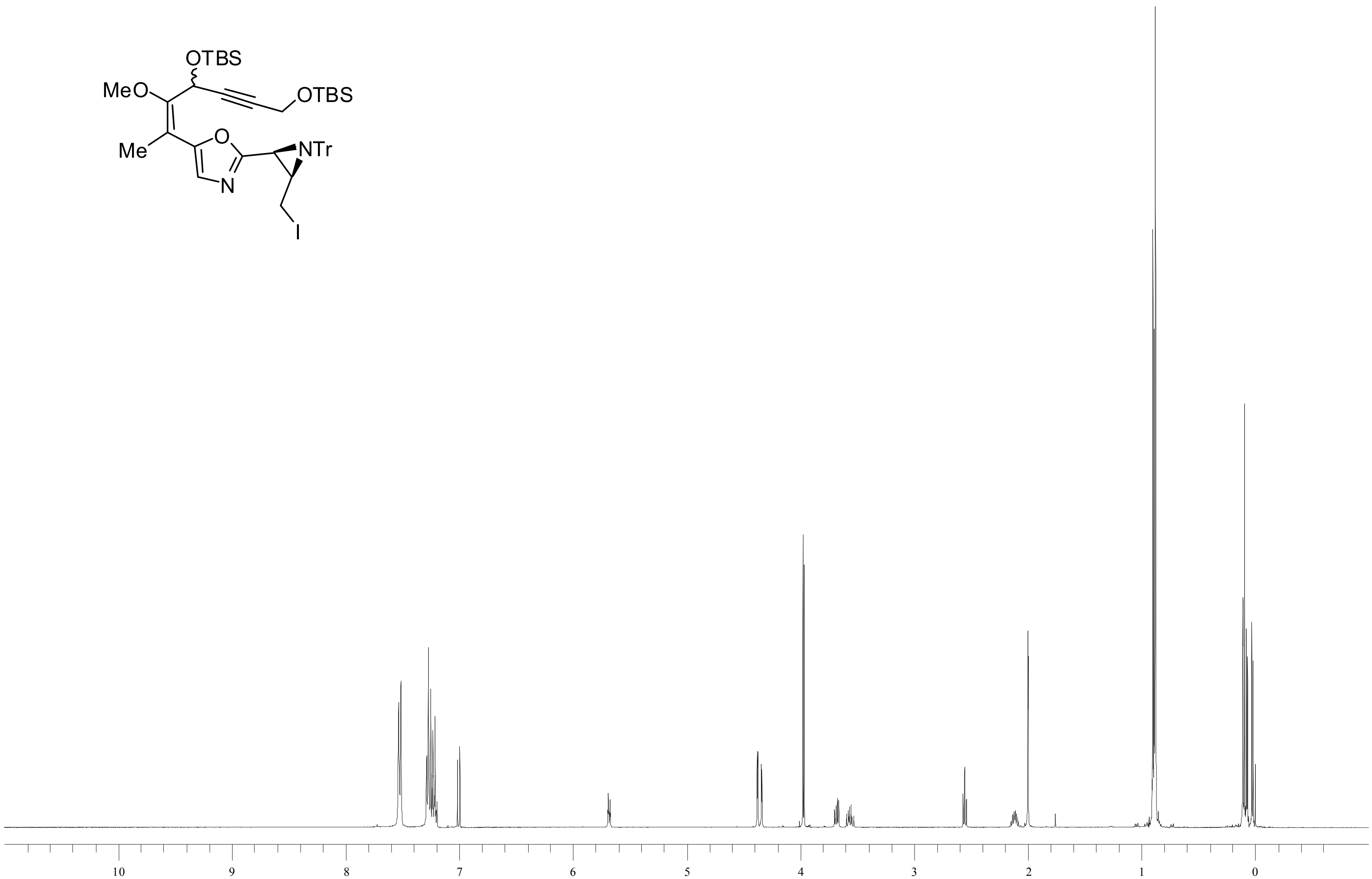

MeO
O
OTBS
Me
O
N
NTr
I
10
9
8
7
6
5
4
3
2
1
0

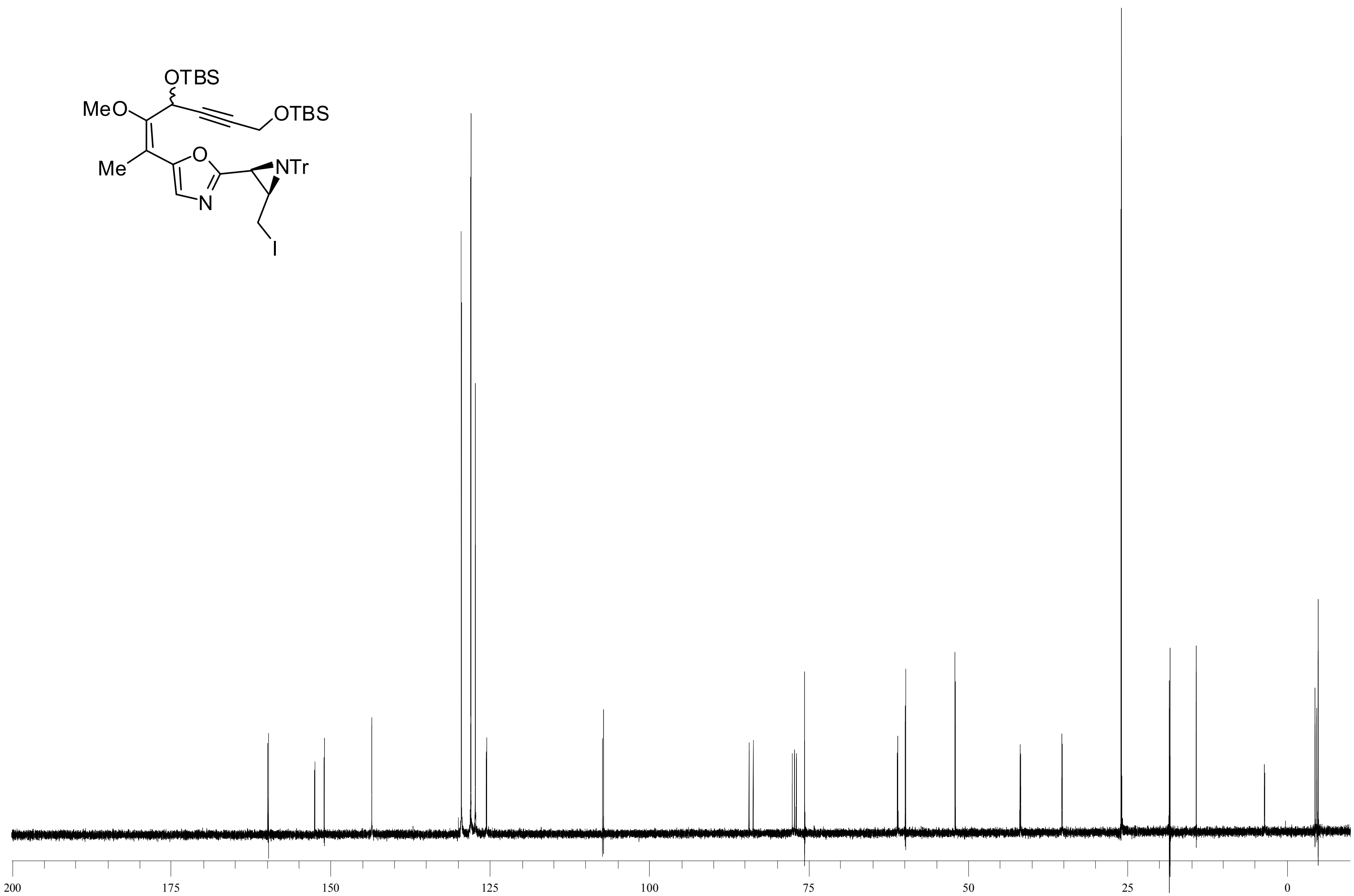

MeO
O
OTBS
Me
O
NTr
N
I
200
175
150
125
100
75
50
25
0

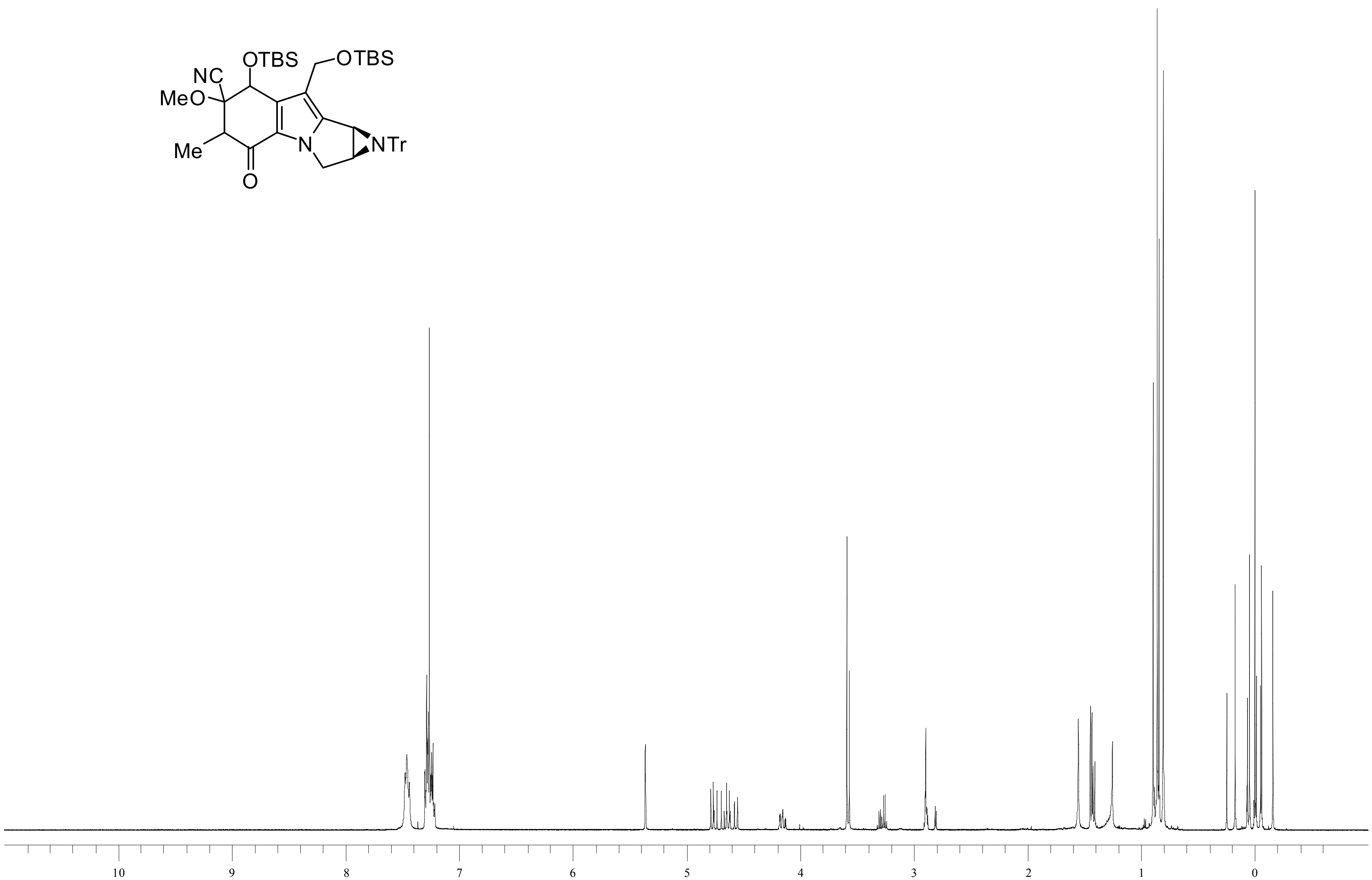

OTBS
MeO
Me
N
NTr
O
O


10
9
8
7
6
5
4
3
2
1
0

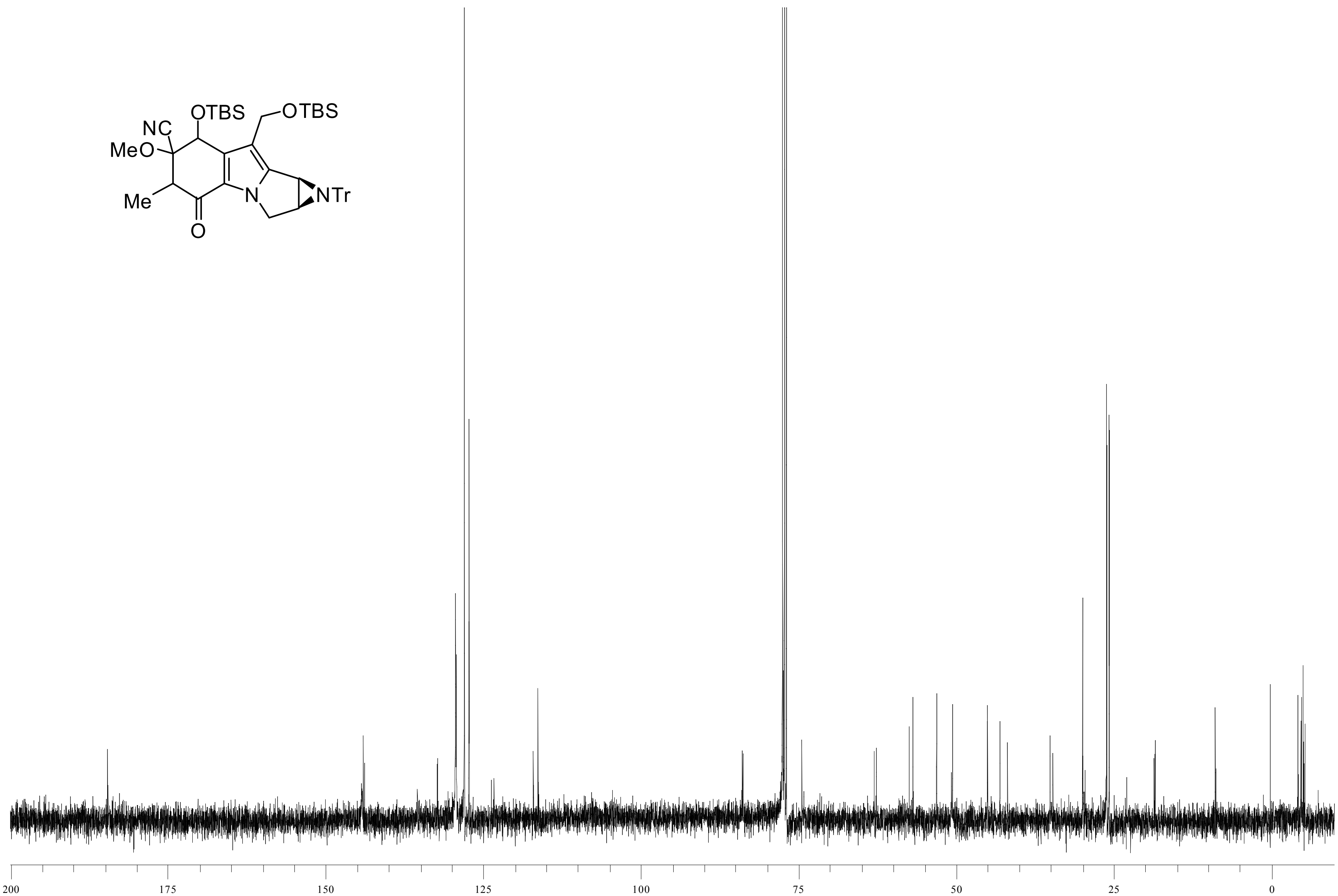

OTBS
MeO
Me
O
O
N
NTr
200
175
150
125
100
75
50
25
0

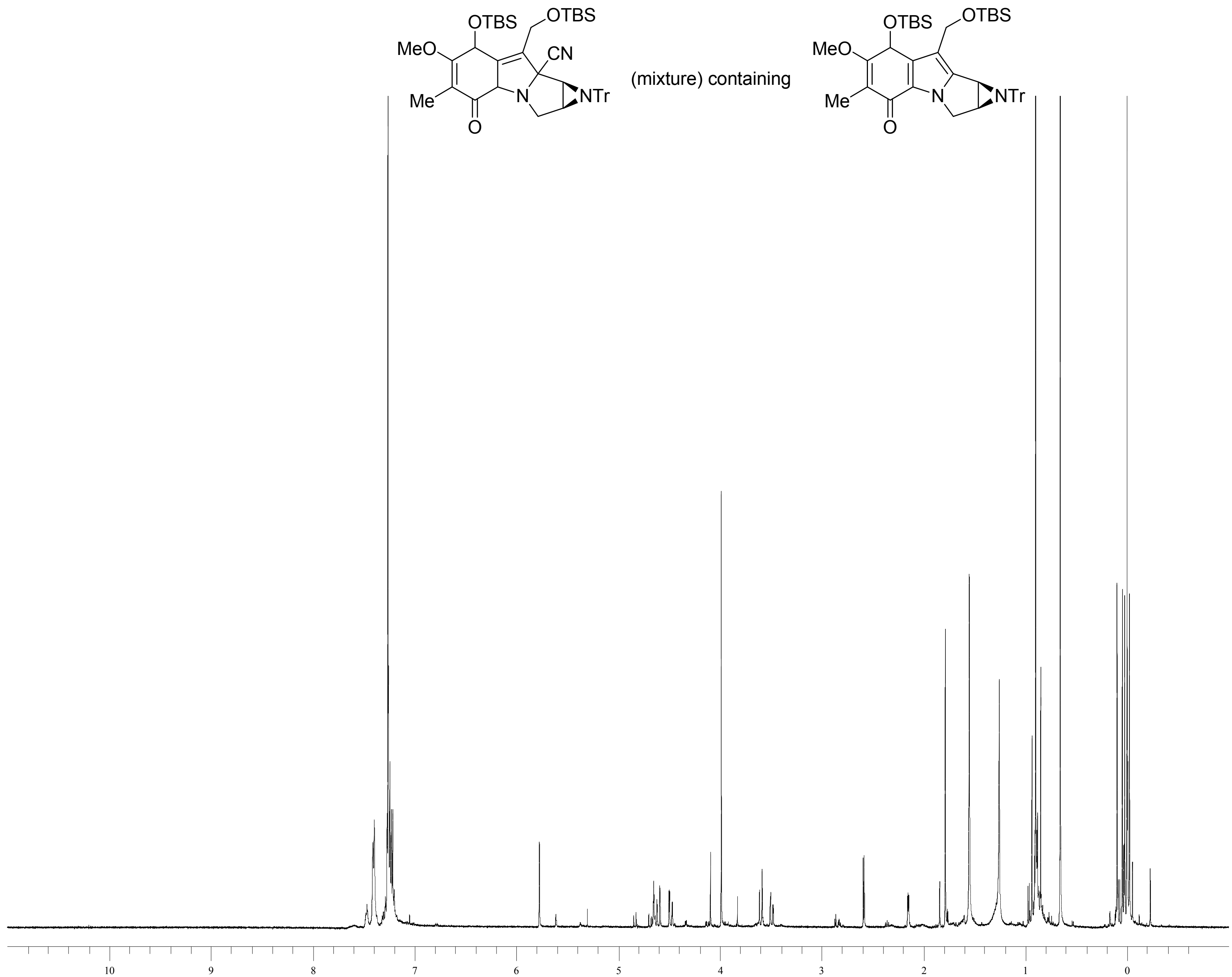

OTBS
MeO
OTBS
Me
O
N
NTr
I
10
9
8
7
6
5
4
3
2
1
0

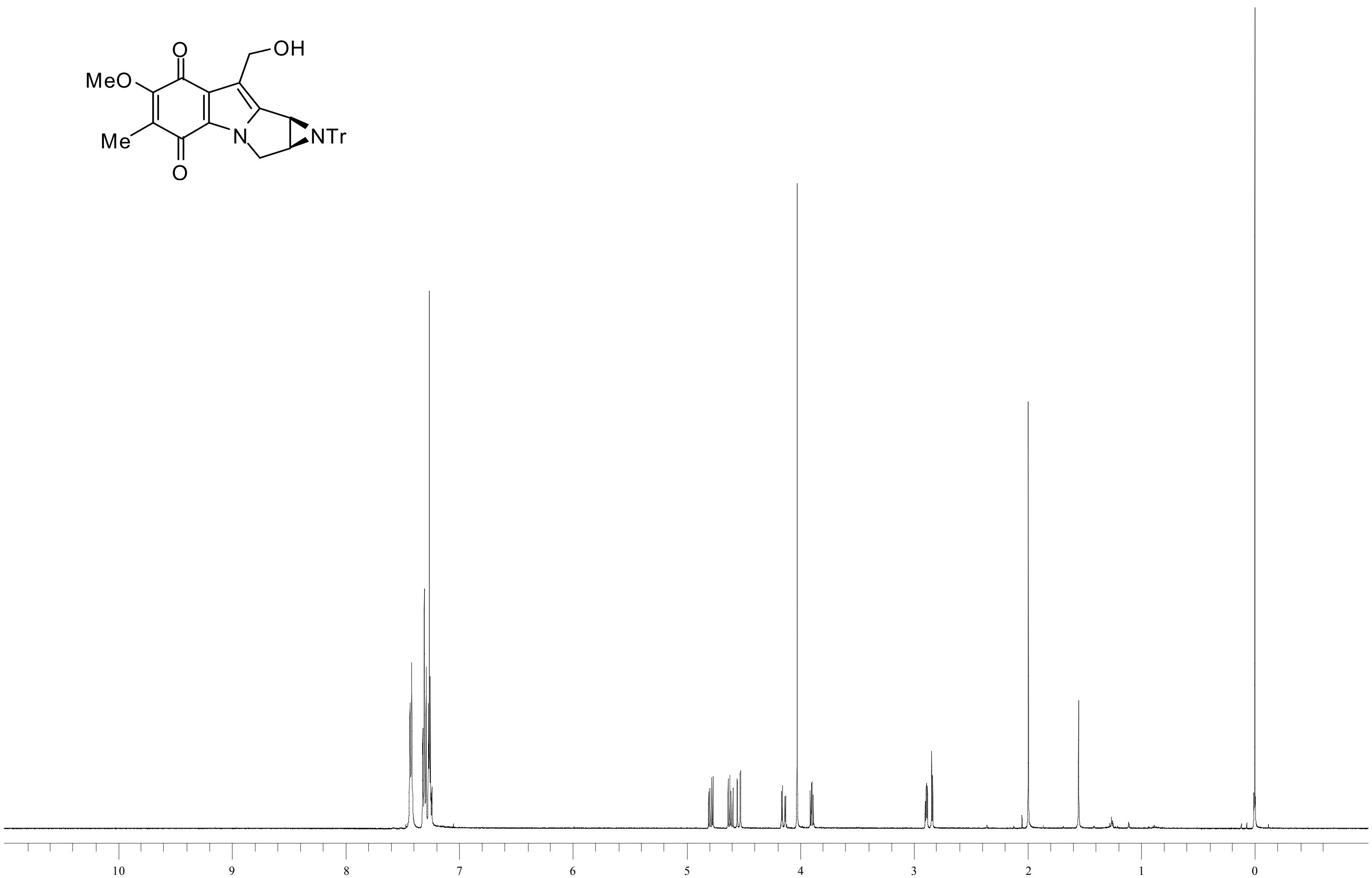

OTBS
MeO
OTBS
Me
O
NTr
N
I
200
175
150
125
100
75
50
25
0

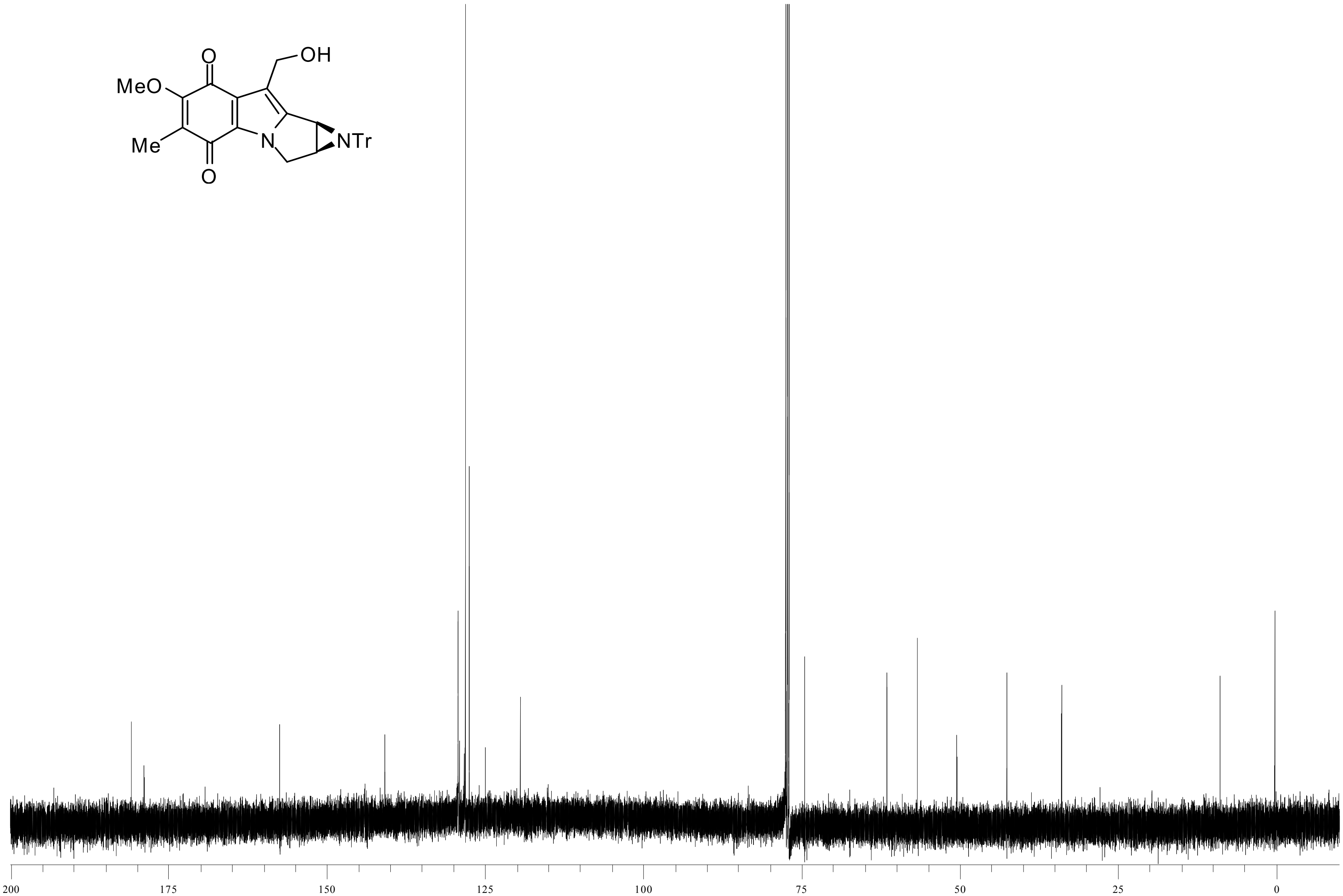


OTBS
OTBS
NC
MeO
Me
O
N
NTr
10
9
8
7
6
5
4
3
2
1
0

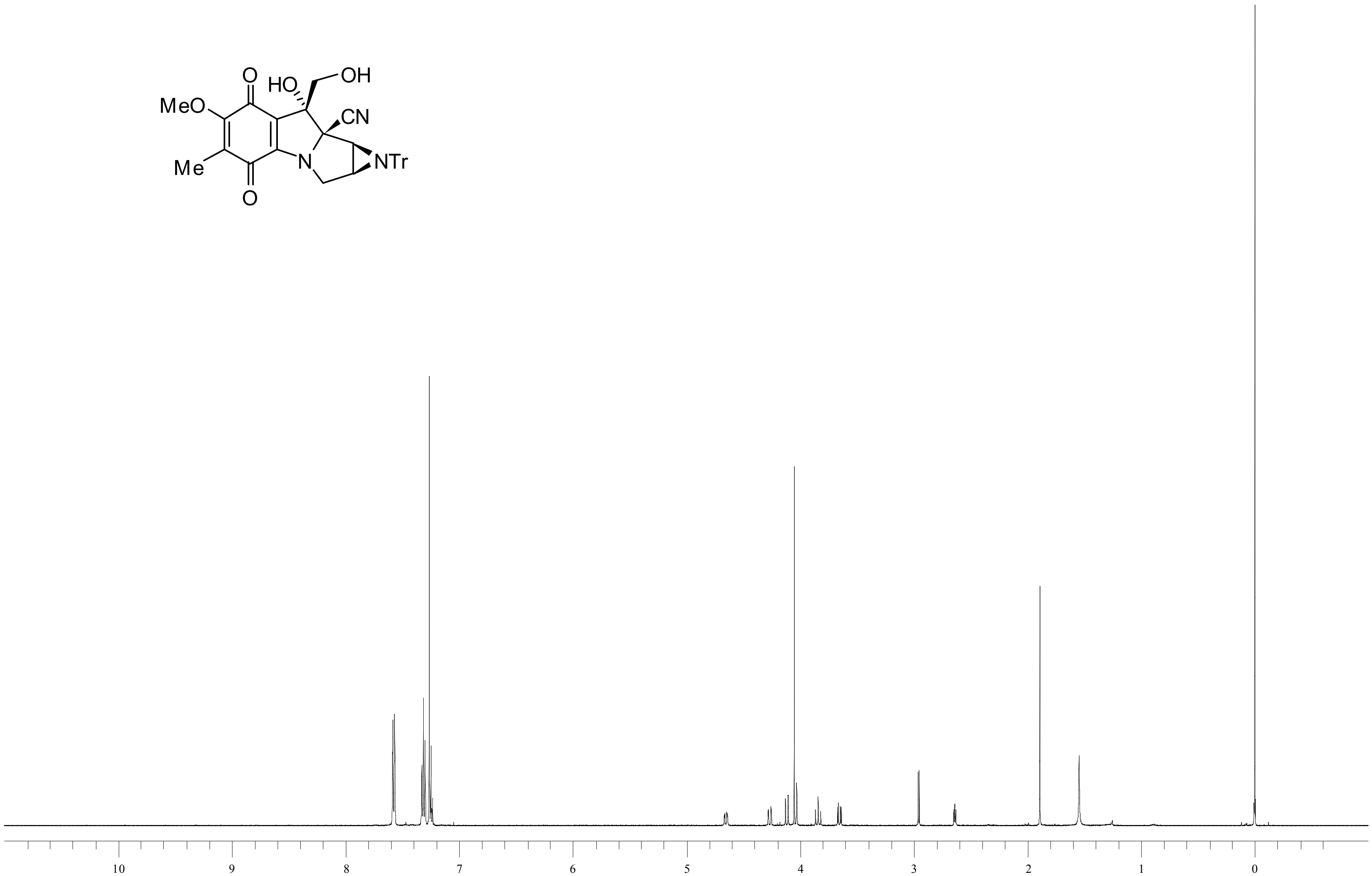

OTBS
OTBS
NC
MeO
Me
O
N
NTr
200
175
150
125
100
75
50
25
0

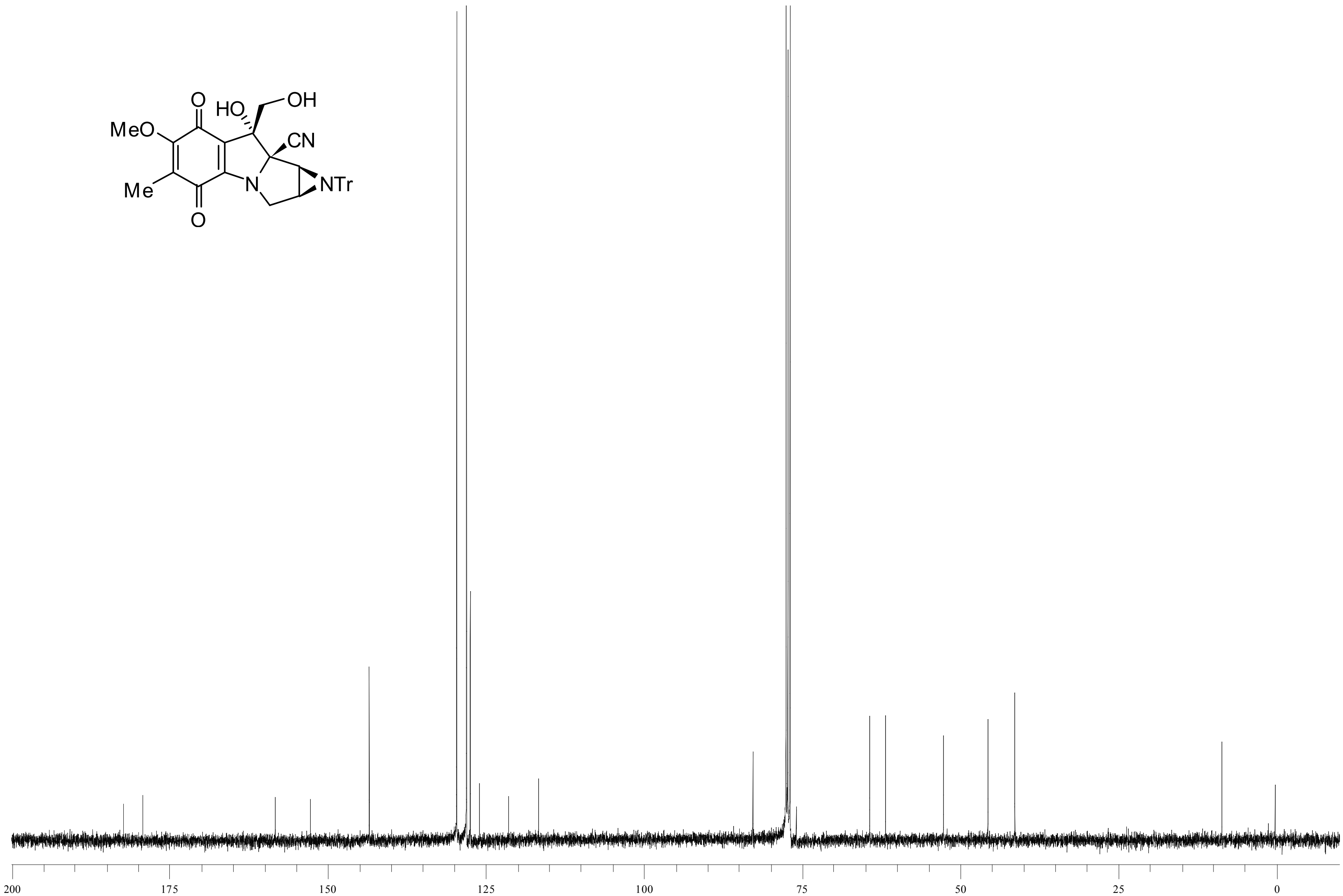

OTBS
OTBS
MeO
CN
Me
N
NTr
O
(mixture) containing
OTBS
OTBS
MeO
Me
N
NTr
O
10
9
8
7
6
5
4
3
2
1
0

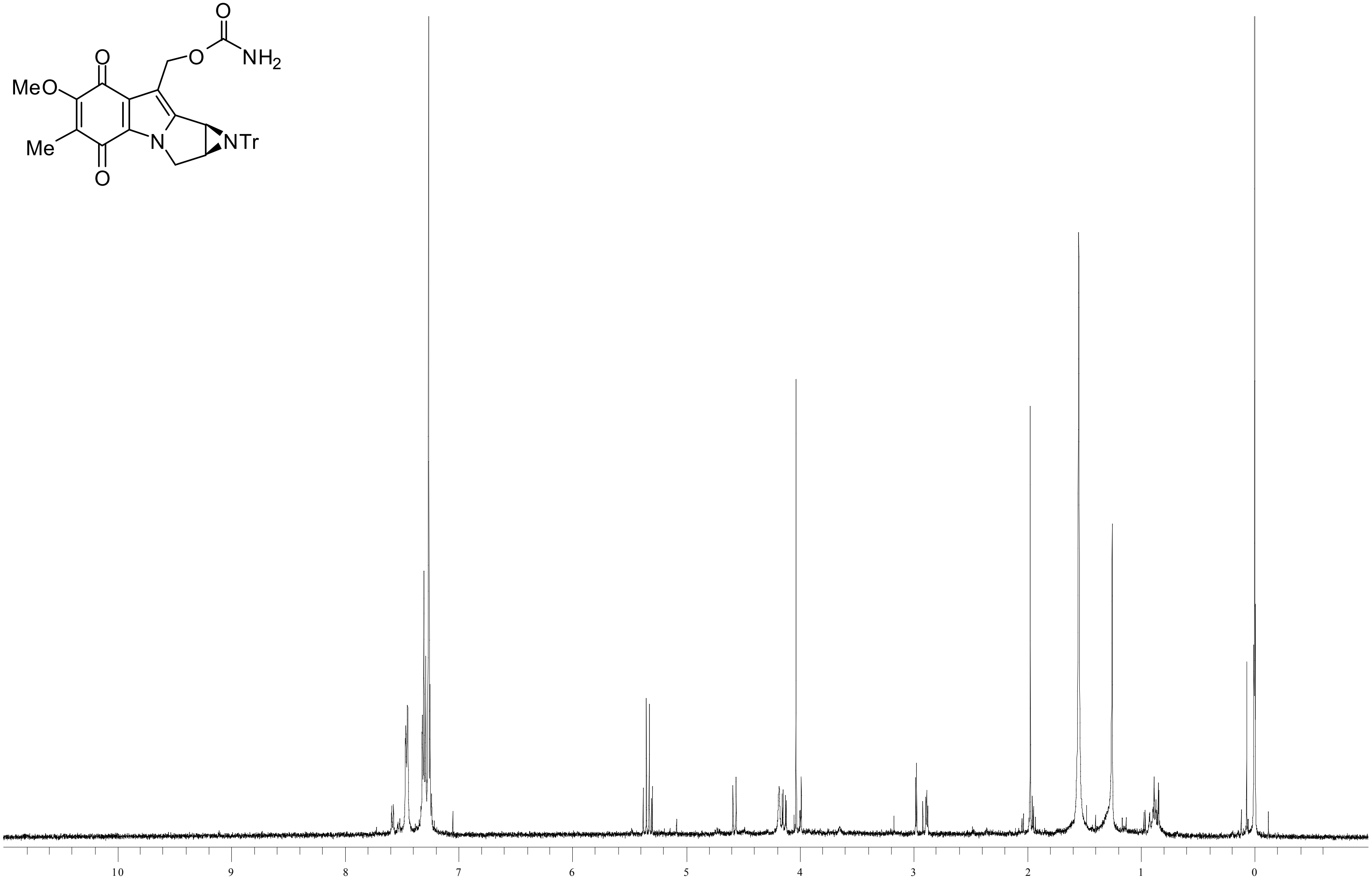

OH
MeO
O
O
Me
N
NTr
10
9
8
7
6
5
4
3
2
1
0



O
OH
MeO
NTr
Me
N
O
200
175
150
125
100
75
50
25
0


O
HO
OH
MeO
CN
NTr
N
Me
O
10
9
8
7
6
5
4
3
2
1
0


MeO
Me
O
O
HO
OH
CN
N
NTr
200
175
150
125
100
75
50
25
0



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O
NTr
Me
N
O
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9
8
7
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1
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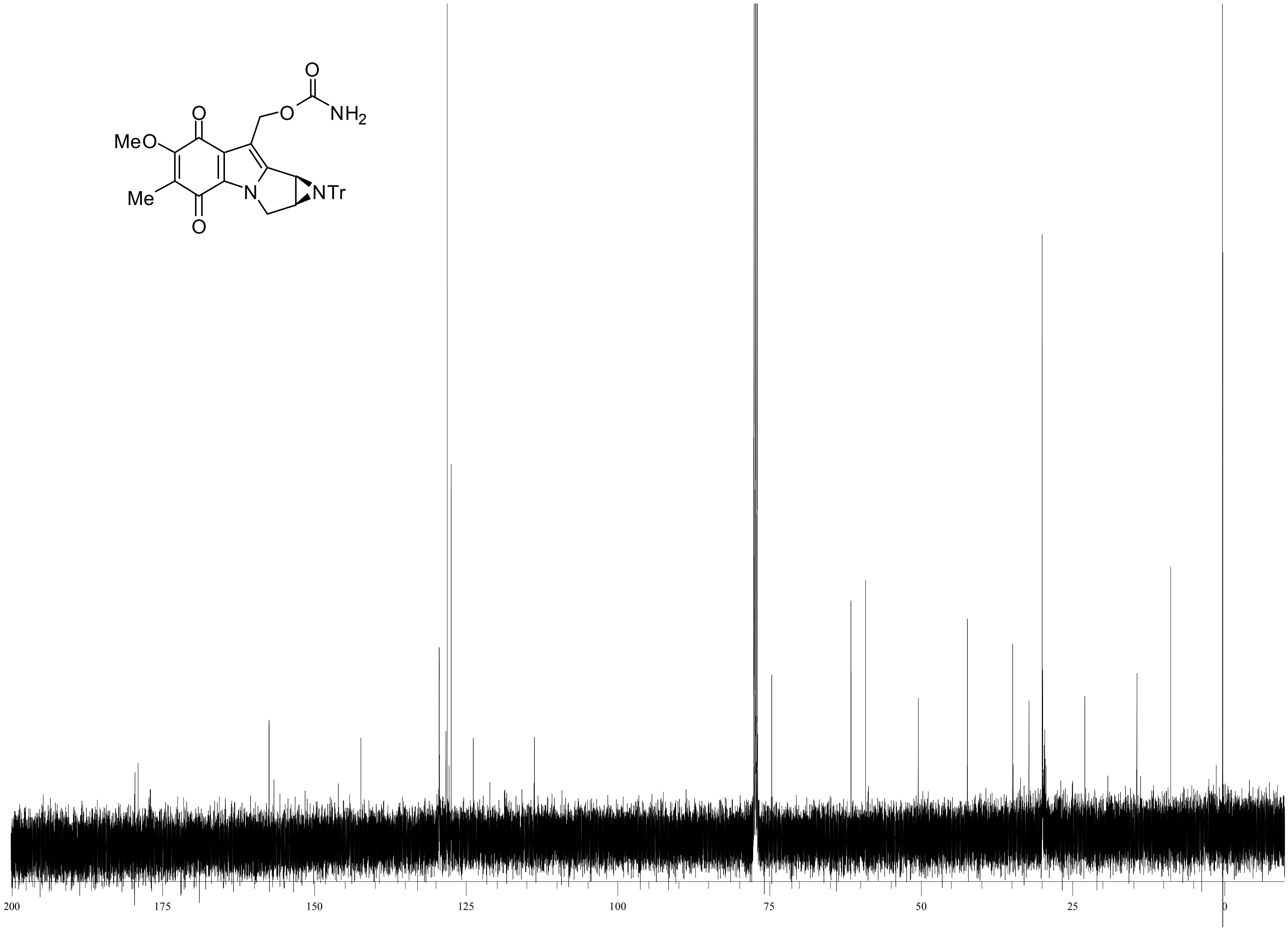
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NTr
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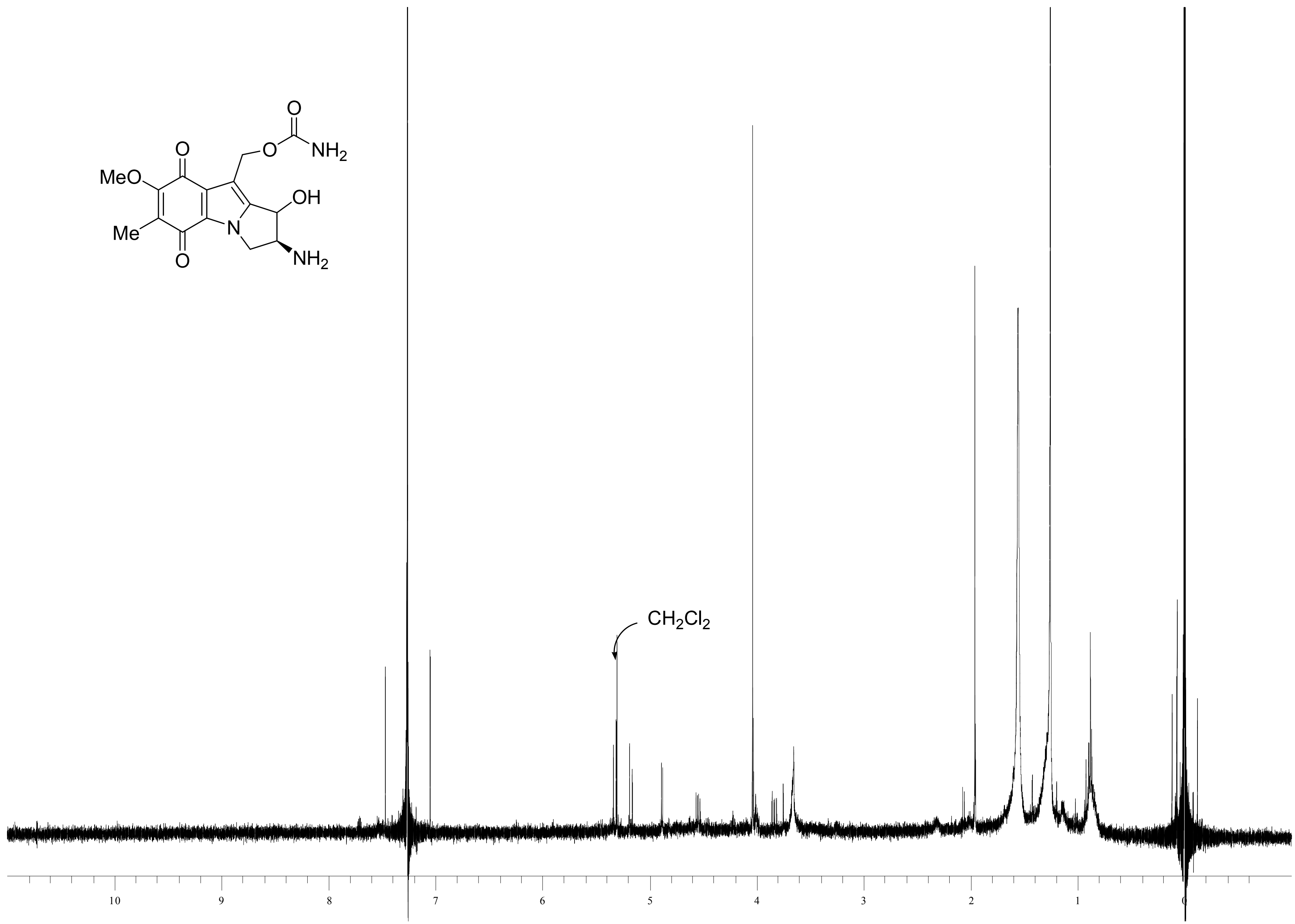
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Me
OH
NH2
O
NH2
N
CH2Cl2
10
9
8
7
6
5
4
3
2
1
0

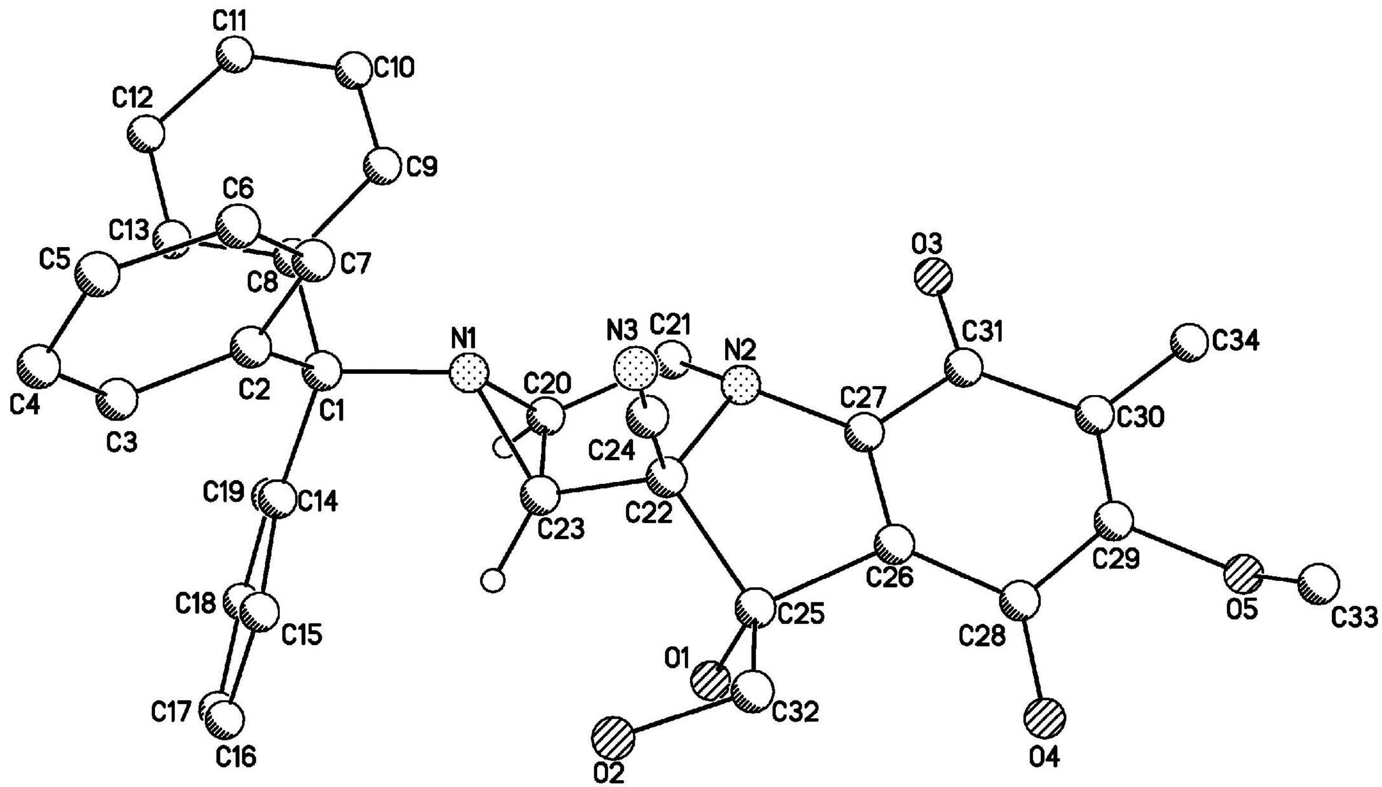
Structure Determination.

Orange needles of quinone **55** were grown from a hexane/ethyl acetate solution at 25 ºC. A crystal of dimensions 0.36 x 0.08 x 0.06 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.969 cm from the crystal. A total of 2513 frames were collected with a scan width of 0.5º in ω and phi with an exposure time of 90 s/frame. The integration of the data yielded a total of 20438 reflections to a maximum 2θ value of 33.10º of which 1081 were independent and 912 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 2315 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)2(1)2 with Z = 4 for the formula $C_{34}H_{29}N_3O_5{\bullet}(C_6H_{14})_{0.5}$. Due to the limited data, only nitrogen and oxygen atoms were refined anisotropically, all carbon atoms refined isotropically and the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0928 and wR2 = 0.2662 [based on I > 2sigma(I)], R1 = 0.1054 and wR2 = 0.2744 for all data.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.01, Bruker Analytical X-ray, Madison, WI, 2003.


C11
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C12
C9
C6
C13
C5
C7
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O3
N3
C21
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C2
C1
C4
C20
C27
C30
C3
C24
C19
C14
C22
C23
C29
C26
C18
C25
O5
C33
C15
C28
O1
C17
C32
C16
O4
O2

Table 1. Crystal data and structure refinement for quinone **55**.

Identification code	quinone **55**
Empirical formula	$C_{37} H_{36} N_3 O_5$
Formula weight	602.69
Temperature	108(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2
Unit cell dimensions	a = 32.158(9) A alpha = 90º. b = 8.977(3) Å beta = 90º. c = 11.478(3) Å gamma = 90º.
Volume	3313.7(16) A^3
Z, Calculated density	4, 1.208 Mg/m^3
Absorption coefficient	0.081 mm^{-1}
F(000)	1276
Crystal size	0.34 x 0.04 x 0.02 mm
θ range for data collection	1.88 to 16.55º.
Limiting indices	-25<=h<=25, -7<=k<=7, -9<=l<=9

Reflections collected / unique	20438 / 1081 [R(int) = 0.1692]
Completeness to θ = 16.55	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9984 and 0.9731
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1081 / 0 / 212
Goodness-of-fit on F^2	1.339
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.2662
R indices (all data)	R1 = 0.1054, wR2 = 0.2744
Absolute structure parameter	-4(10)
Extinction coefficient	0.020(5)
Largest diff. peak and hole	0.509 and -0.319 e.A^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for quinone **55**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(1)	2927(4)	11679(14)	9422(10)	35(4)

O(2)	2470(4)	9309(15)	10343(10)	41(4)
O(3)	3521(4)	11426(15)	5336(12)	48(4)
O(4)	2104(4)	12451(17)	7486(12)	55(5)
O(5)	2177(4)	13386(16)	5253(12)	52(5)
N(1)	3824(5)	8550(20)	9190(14)	41(5)
N(2)	3359(4)	9975(17)	7441(12)	25(5)
N(3)	2857(5)	6770(20)	8193(14)	40(5)
C(1)	4089(6)	7870(20)	10170(17)	30(6)
C(2)	3918(6)	6360(20)	10462(18)	31(6)
C(3)	3947(6)	5750(20)	11572(19)	36(6)
C(4)	3809(5)	4330(20)	11806(19)	34(6)
C(5)	3650(6)	3480(20)	10886(18)	40(6)
C(6)	3609(6)	4100(30)	9810(20)	44(7)
C(7)	3750(6)	5520(20)	9560(20)	47(7)
C(8)	4523(6)	7620(20)	9688(18)	32(6)
C(9)	4623(7)	7780(20)	8510(20)	52(7)
C(10)	5010(8)	7510(30)	8085(19)	59(7)
C(11)	5317(7)	6970(20)	8821(19)	48(7)
C(12)	5224(6)	6750(20)	9958(18)	42(7)
C(13)	4833(6)	7120(20)	10416(19)	39(6)
C(14)	4102(6)	8980(20)	11262(17)	33(6)
C(15)	3764(7)	9000(30)	12017(19)	45(7)
C(16)	3765(7)	9930(20)	12955(18)	44(6)
C(17)	4087(6)	10890(20)	13098(19)	45(7)
C(18)	4410(7)	10890(30)	12290(19)	51(7)
C(19)	4428(6)	9940(20)	11378(16)	30(6)
C(20)	3861(6)	10060(30)	8919(17)	35(6)
C(21)	3786(6)	10480(20)	7696(17)	38(6)
C(22)	3133(6)	9390(20)	8530(18)	29(6)
C(23)	3473(6)	9540(20)	9434(19)	41(7)
C(24)	2991(7)	7920(30)	8335(18)	30(7)
C(25)	2763(6)	10530(20)	8709(16)	25(6)
C(26)	2719(6)	11150(20)	7416(15)	21(6)
C(27)	3074(6)	10860(20)	6908(18)	33(6)
C(28)	2419(7)	12050(20)	6919(19)	29(6)

C(29)	2499(8)	12540(30)	5770(20)	51(7)
C(30)	2836(7)	12390(20)	5169(18)	36(6)
C(31)	3175(8)	11560(20)	5770(20)	41(7)
C(32)	2381(5)	9870(20)	9222(16)	26(6)
C(33)	2930(6)	13030(20)	3967(18)	51(7)

Table 3. Bond lengths [Å] and angles [deg] for **55**.

O(1)-C(25)	1.42(2)
O(2)-C(32)	1.41(2)
O(3)-C(31)	1.23(2)
O(4)-C(28)	1.26(2)
O(5)-C(33)	1.38(2)
O(5)-C(29)	1.42(3)
N(1)-C(20)	1.40(3)
N(1)-C(23)	1.47(2)
N(1)-C(1)	1.54(2)
N(2)-C(27)	1.35(2)
N(2)-C(21)	1.48(2)
N(2)-C(22)	1.54(2)
N(3)-C(24)	1.13(2)
C(1)-C(2)	1.50(3)
C(1)-C(8)	1.52(3)
C(1)-C(14)	1.60(3)
C(2)-C(7)	1.39(3)
C(2)-C(3)	1.39(3)
C(3)-C(4)	1.38(2)
C(4)-C(5)	1.40(3)
C(5)-C(6)	1.36(3)
C(6)-C(7)	1.39(3)
C(8)-C(9)	1.40(3)

C(8)-C(13)	1.38(2)
C(9)-C(10)	1.36(3)
C(10)-C(11)	1.39(3)
C(11)-C(12)	1.35(3)
C(12)-C(13)	1.40(2)
C(14)-C(19)	1.37(2)
C(14)-C(15)	1.39(3)
C(15)-C(16)	1.36(3)
C(16)-C(17)	1.36(3)
C(17)-C(18)	1.39(3)
C(18)-C(19)	1.35(2)
C(20)-C(23)	1.45(3)
C(20)-C(21)	1.47(3)
C(22)-C(24)	1.41(3)
C(22)-C(23)	1.51(3)
C(22)-C(25)	1.59(3)
C(25)-C(32)	1.49(2)
C(25)-C(26)	1.59(3)
C(26)-C(27)	1.31(2)
C(26)-C(28)	1.38(2)
C(27)-C(31)	1.48(3)
C(28)-C(29)	1.41(3)
C(29)-C(30)	1.29(3)
C(30)-C(31)	1.49(3)
C(30)-C(34)	1.53(3)
C(33)-O(5)-C(29)	114.7(17)
C(20)-N(1)-C(23)	61.0(12)
C(20)-N(1)-C(1)	120.2(17)
C(23)-N(1)-C(1)	121.9(15)
C(27)-N(2)-C(21)	122.7(15)
C(27)-N(2)-C(22)	104.4(15)
C(21)-N(2)-C(22)	112.4(14)
C(2)-C(1)-C(8)	106.9(15)
C(2)-C(1)-N(1)	108.6(15)
C(8)-C(1)-N(1)	107.5(15)

C(2)-C(1)-C(14)	113.3(16)
C(8)-C(1)-C(14)	110.6(15)
N(1)-C(1)-C(14)	109.8(14)
C(7)-C(2)-C(3)	119.9(19)
C(7)-C(2)-C(1)	117.7(18)
C(3)-C(2)-C(1)	122.2(19)
C(4)-C(3)-C(2)	121(2)
C(3)-C(4)-C(5)	118(2)
C(6)-C(5)-C(4)	120(2)
C(5)-C(6)-C(7)	122(2)
C(2)-C(7)-C(6)	118(2)
C(9)-C(8)-C(13)	117.1(19)
C(9)-C(8)-C(1)	123.2(18)
C(13)-C(8)-C(1)	119.5(17)
C(10)-C(9)-C(8)	122(2)
C(9)-C(10)-C(11)	120(2)
C(12)-C(11)-C(10)	119(2)
C(11)-C(12)-C(13)	122(2)
C(8)-C(13)-C(12)	120(2)
C(19)-C(14)-C(15)	122(2)
C(19)-C(14)-C(1)	119.3(16)
C(15)-C(14)-C(1)	118.7(17)
C(16)-C(15)-C(14)	120(2)
C(17)-C(16)-C(15)	119(2)
C(16)-C(17)-C(18)	119(2)
C(19)-C(18)-C(17)	123(2)
C(18)-C(19)-C(14)	116.4(19)
N(1)-C(20)-C(23)	61.9(14)
N(1)-C(20)-C(21)	116.6(19)
C(23)-C(20)-C(21)	109.2(17)
N(2)-C(21)-C(20)	105.2(16)
C(24)-C(22)-C(23)	115.3(17)
C(24)-C(22)-N(2)	110.0(17)
C(23)-C(22)-N(2)	100.7(15)
C(24)-C(22)-C(25)	112.5(17)

C(23)-C(22)-C(25)	113.2(17)
N(2)-C(22)-C(25)	103.8(15)
C(20)-C(23)-N(1)	57.1(13)
C(20)-C(23)-C(22)	111.7(18)
N(1)-C(23)-C(22)	111.6(17)
N(3)-C(24)-C(22)	176(2)
O(1)-C(25)-C(32)	111.8(15)
O(1)-C(25)-C(22)	105.3(14)
C(32)-C(25)-C(22)	114.3(16)
O(1)-C(25)-C(26)	108.8(14)
C(32)-C(25)-C(26)	115.8(15)
C(22)-C(25)-C(26)	99.8(14)
C(27)-C(26)-C(28)	123(2)
C(27)-C(26)-C(25)	105.7(17)
C(28)-C(26)-C(25)	130.6(17)
C(26)-C(27)-N(2)	120.2(19)
C(26)-C(27)-C(31)	120(2)
N(2)-C(27)-C(31)	119.9(19)
O(4)-C(28)-C(26)	121.0(19)
O(4)-C(28)-C(29)	123(2)
C(26)-C(28)-C(29)	116(2)
C(30)-C(29)-C(28)	128(2)
C(30)-C(29)-O(5)	117(2)
C(28)-C(29)-O(5)	115(2)
C(29)-C(30)-C(31)	115(2)
C(29)-C(30)-C(34)	127(2)
C(31)-C(30)-C(34)	117.8(19)
O(3)-C(31)-C(30)	121(2)
O(3)-C(31)-C(27)	121(2)
C(30)-C(31)-C(27)	118(2)
O(2)-C(32)-C(25)	109.8(15)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($A^2 \times 10^3$) for quinone **55**. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
O(1)	41(8)	34(9)	30(9)	-16(8)	-4(7)	9(8)
O(2)	32(8)	56(11)	35(10)	6(9)	-1(7)	8(8)
O(3)	44(10)	51(10)	47(9)	-4(8)	15(9)	12(8)
O(4)	36(10)	82(12)	46(10)	1(10)	-4(9)	6(10)
O(5)	46(10)	57(11)	52(10)	-3(9)	9(9)	-8(9)
N(1)	23(11)	67(15)	34(12)	17(12)	-2(9)	3(10)
N(2)	18(10)	29(10)	27(11)	7(10)	7(8)	-1(9)
N(3)	36(12)	37(14)	46(13)	3(11)	-5(10)	-15(11)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($A^2 \times 10^3$) for quinone **64**.

	x	y	z	U(eq)
H(1A)	2767	12419	9407	52
H(2A)	2655	8652	10295	61
H(3A)	4063	6333	12183	43
H(4A)	3822	3933	12573	41
H(5A)	3570	2477	11013	48
H(6A)	3480	3537	9206	53
H(7A)	3733	5917	8794	56
H(9A)	4412	8093	7980	62

H(10A)	5070	7684	7287	71
H(11A)	5588	6763	8533	58
H(12A)	5428	6328	10457	50
H(13A)	4783	7034	11229	47
H(15A)	3532	8370	11879	54
H(16A)	3543	9905	13502	53
H(17A)	4091	11555	13742	54
H(18A)	4629	11595	12385	61
H(19A)	4654	9947	10846	36
H(20A)	4051	10689	9399	42
H(21A)	3811	11570	7595	46
H(21B)	3989	9981	7175	46
H(23A)	3402	9812	10256	49
H(32A)	2160	10635	9274	31
H(32B)	2279	9054	8716	31
H(33A)	1887	11802	4439	91
H(33B)	1612	13260	4667	91
H(33C)	1712	12142	5716	91
H(34A)	2704	13699	3734	77
H(34B)	2954	12216	3401	77
H(34C)	3192	13584	3995	77

Table 6. Hydrogen bonds for quinone **55** [Å and º].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1A)...O(2)#1	0.84	1.88	2.697(18)	163.2
O(2)-H(2A)...O(4)#2	0.84	2.87	3.297(18)	113.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y+1/2,-z+2 #2 -x+1/2,y-1/2,-z+2

Selected experimental procedures;

Oxidation of 32 with KHMDS and NCS

A solution of silyl ether **32** (11.6 mg, 0.0214 mmol) in THF (0.7 mL) was cooled to -78 ºC and KHMDS (0.32 mL of a 0.133 M solution in THF, 0.0428 mmol) was added. The yellow-green solution was stirred at -78 ºC for 10 min then NCS (0.37 mL of a 0.115 M solution in THF, 0.0428 mmol) added. The now orange solution was stirred at -78 ºC for an additional 10 min then the cooling bath was removed and the orange solution was poured into saturated aqueous sodium bicarbonate and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$), filtered, and solvents were removed (aspirator). The orange oil was purified by preparative TLC on silica gel (20 cm X 20 cm X 1000 μm, 20% EtOAc/hexanes eluent) to give 6.5 mg (72%) of indoloquinone **31**.

Oxidation of 32 with DBU and NCS

To a solution of NCS (0.37 mL of a 0.115 M solution in THF, 0.0420 mmol) in THF (0.4 mL) cooled to -78 ºC was added DBU (6 μL, 0.0420 mmol) and a solution of silyl ether **32** (11.4 mg, 0.0210 mmol) in THF (0.7 mL including flask and cannula washings) via cannula dropwise over 1 min. The light orange solution was warmed to 0 ºC over 10 min and stirred an additional 10 min. The usual workup and purification by preparative TLC gave 7.6 mg (84%) of indoloquinone **31** and 1.9 mg of the starting silyl ether **32** (16%).

Oxidation of 32 with KHMDS and PhSeCl

A solution of silyl ether **32** (12.0 mg, 0.0221 mmol) in THF (0.7 mL) was cooled to -78 ºC and KHMDS (0.33 mL of a 0.133 M solution in THF, 0.0443 mmol) was added. The yellow solution was stirred at -78 ºC for 10 min then PhSeCl (8.5 mg in 0.2 mL THF, 0.044 mmol) added. The now orange solution was stirred at -78 ºC for an additional 10 min then the cooling bath was removed. The usual workup and purification by preparative TLC gave 6.7 mg (74%) of indoloquinone **31**.

Oxidation of 32 with Phosphazene and NCS

To a solution of NCS (0.35 mL of a 0.115 M solution in THF, 0.0406 mmol) in THF (0.4 mL) cooled to -78 ºC was added phosphazene base P_1-*t*-butyl (10 µL, 0.0406 mmol). A solution of silyl ether **32** (11.0 mg, 0.0203 mmol) in THF (0.6 mL including flask and cannula washings) was added via cannula dropwise over 1 min. The light orange solution was warmed to 0 ºC over 10 min and stirred an additional 30 min and then warmed to rt over 30 min and stirred an additional 12 h. The usual workup and purification by preparative TLC gave 4.8 mg (56%) of indoloquinone **31** and 4.1 mg (37%) of the starting silyl ether **32**.

Oxidation of 32 with KHMDS and $PhI(OAc)_2$

A solution of silyl ether **32** (9.2 mg, 0.017 mmol) in THF (0.7 mL) was cooled to -78 ºC and KHMDS (0.26 mL of a 0.133 M solution in THF, 0.034 mmol) was added. The yellow solution was stirred at -78 ºC for 10 min then $PhI(OAc)_2$ (0.30 mL of a 0.113 M solution in THF, 0.034 mmol) was added. The light-orange solution was stirred at -78 ºC for an additional 30 min then warmed to rt and stirred an additional 30 min. The usual workup and purification by preparative TLC gave 4.8 mg (69%) of indoloquinone **31**.