Propargylation of CoQ0 through the Redox Chain Reaction

Robert Pawlowski, Maciej Stodulski*, and Jacek Mlynarski*

Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

Supporting Information

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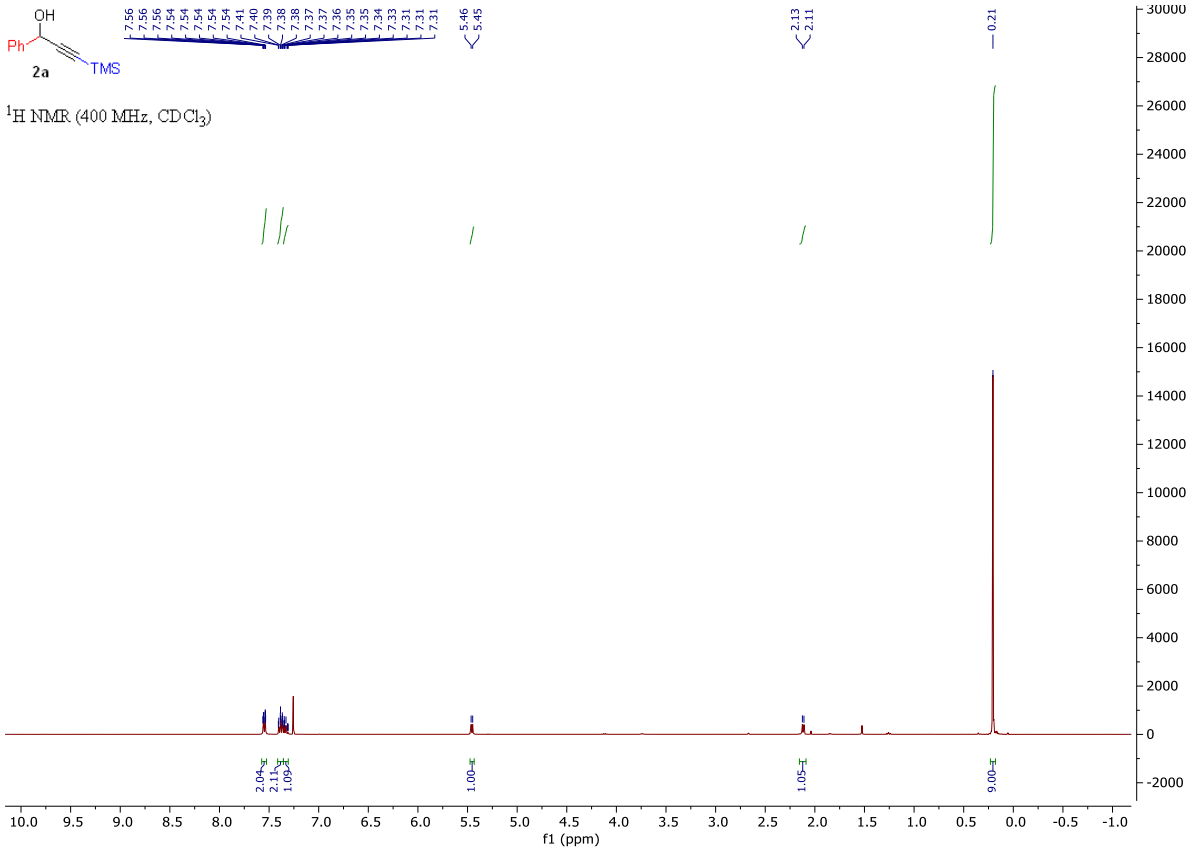
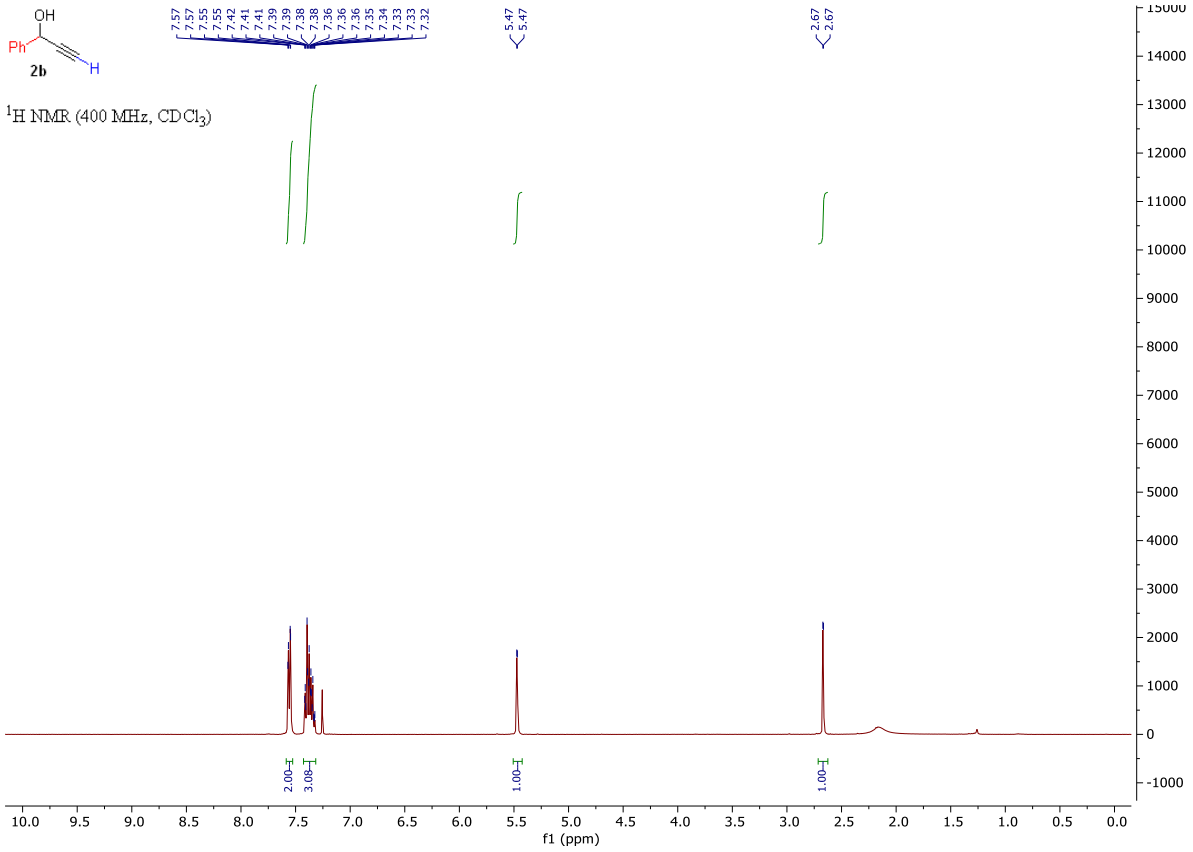
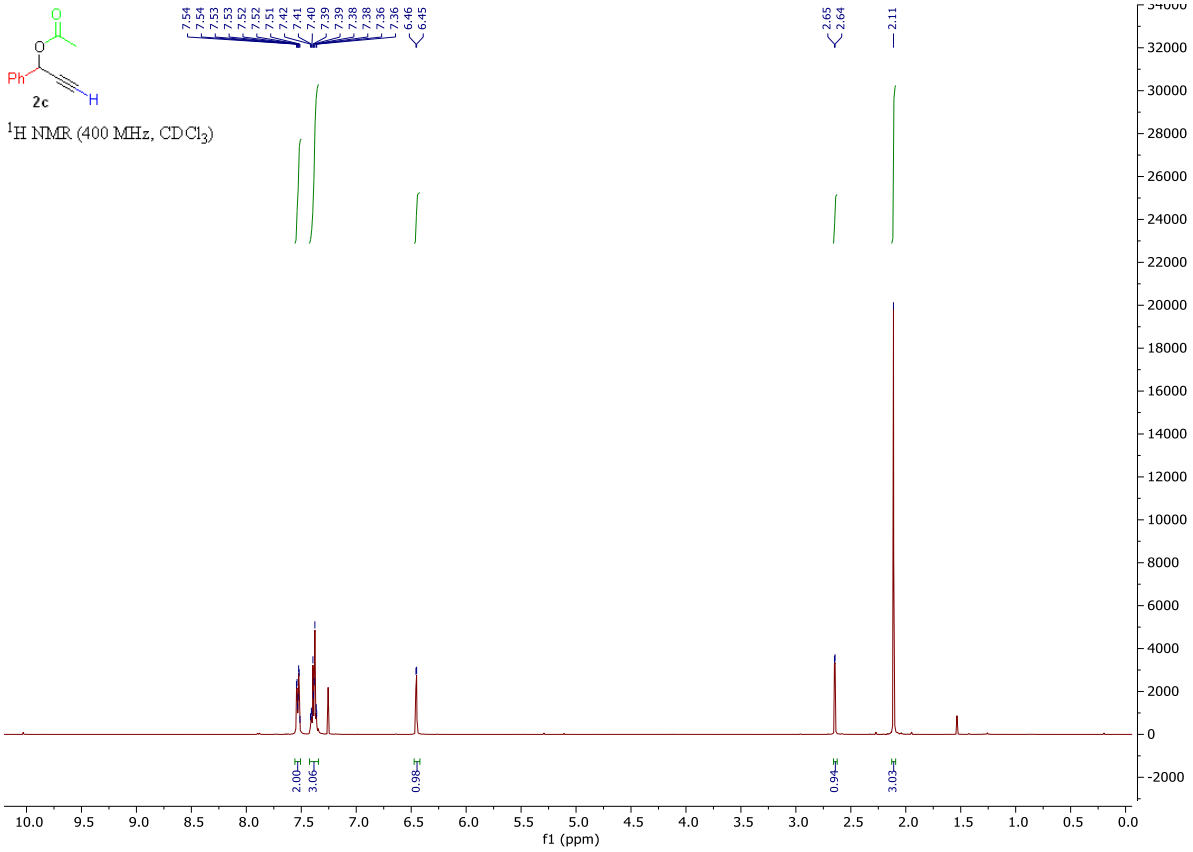
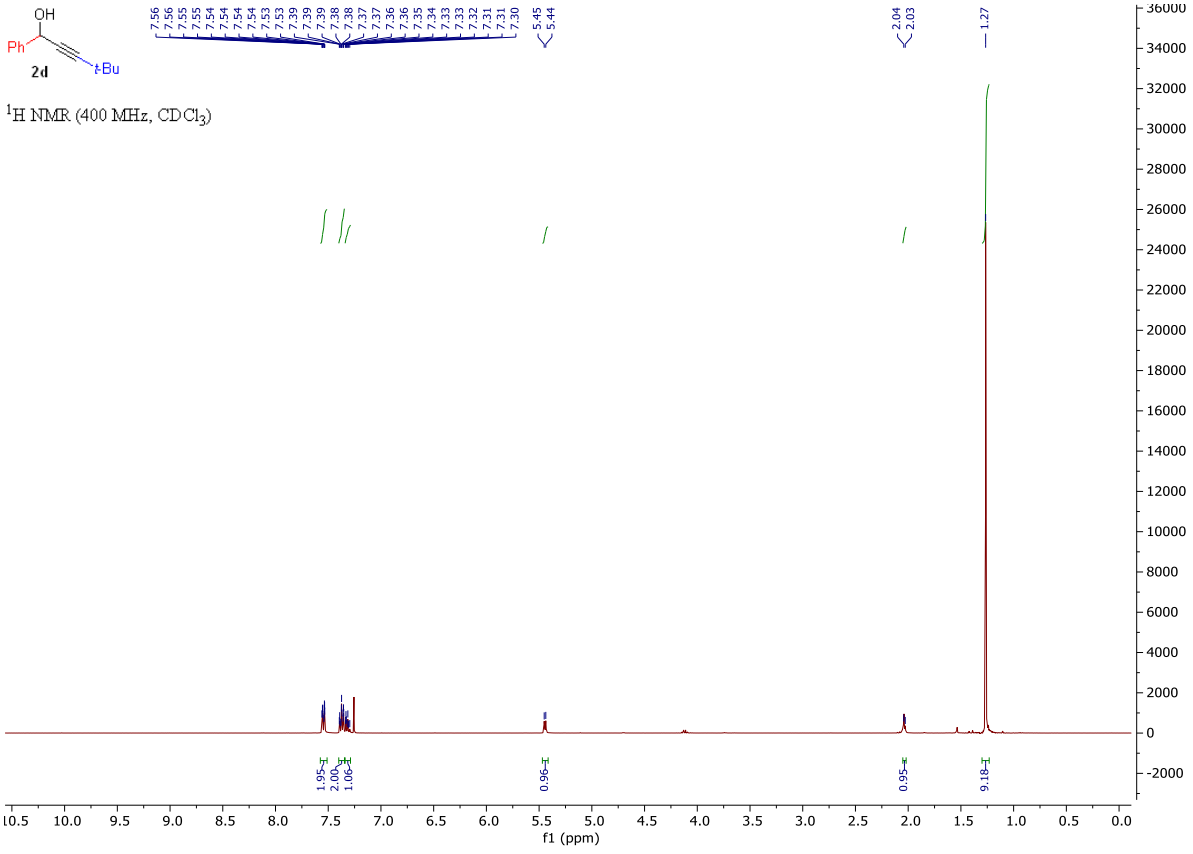
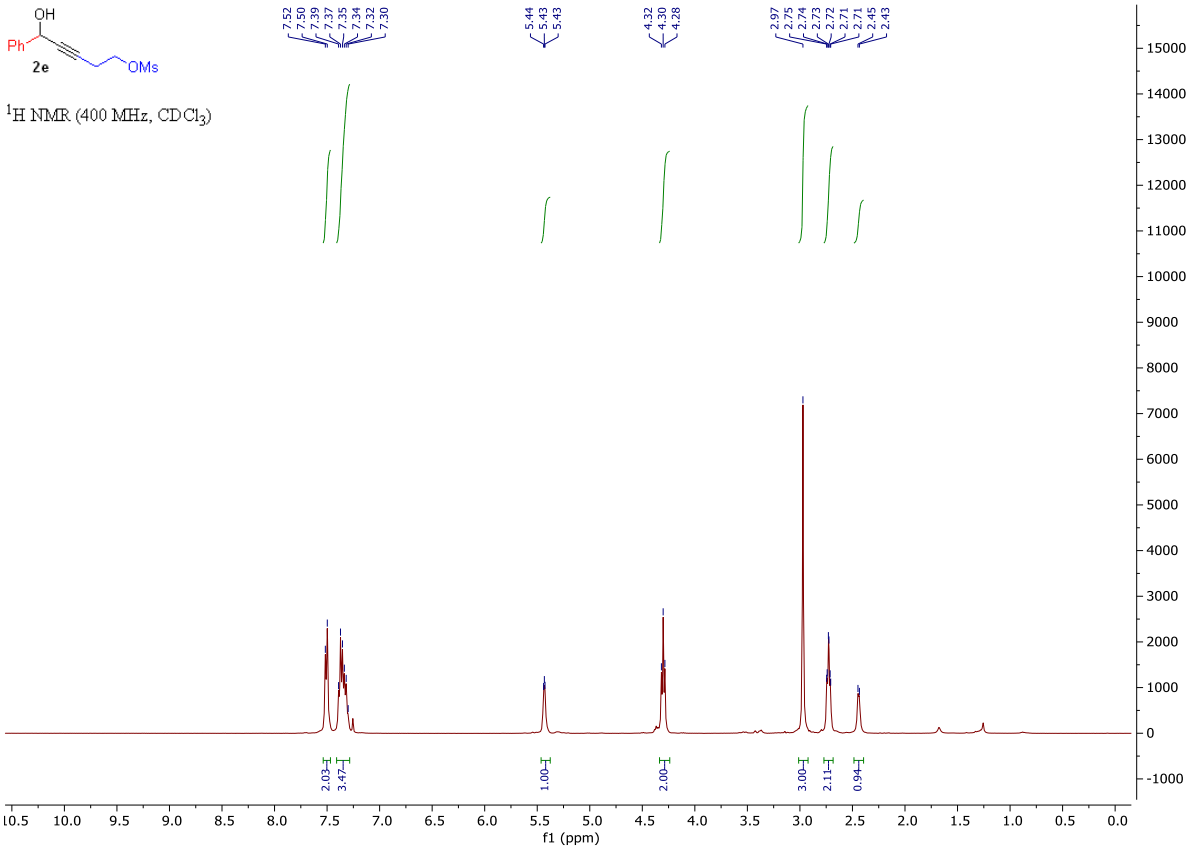
1. Copies of ^{1}H and ^{13}C NMR spectra

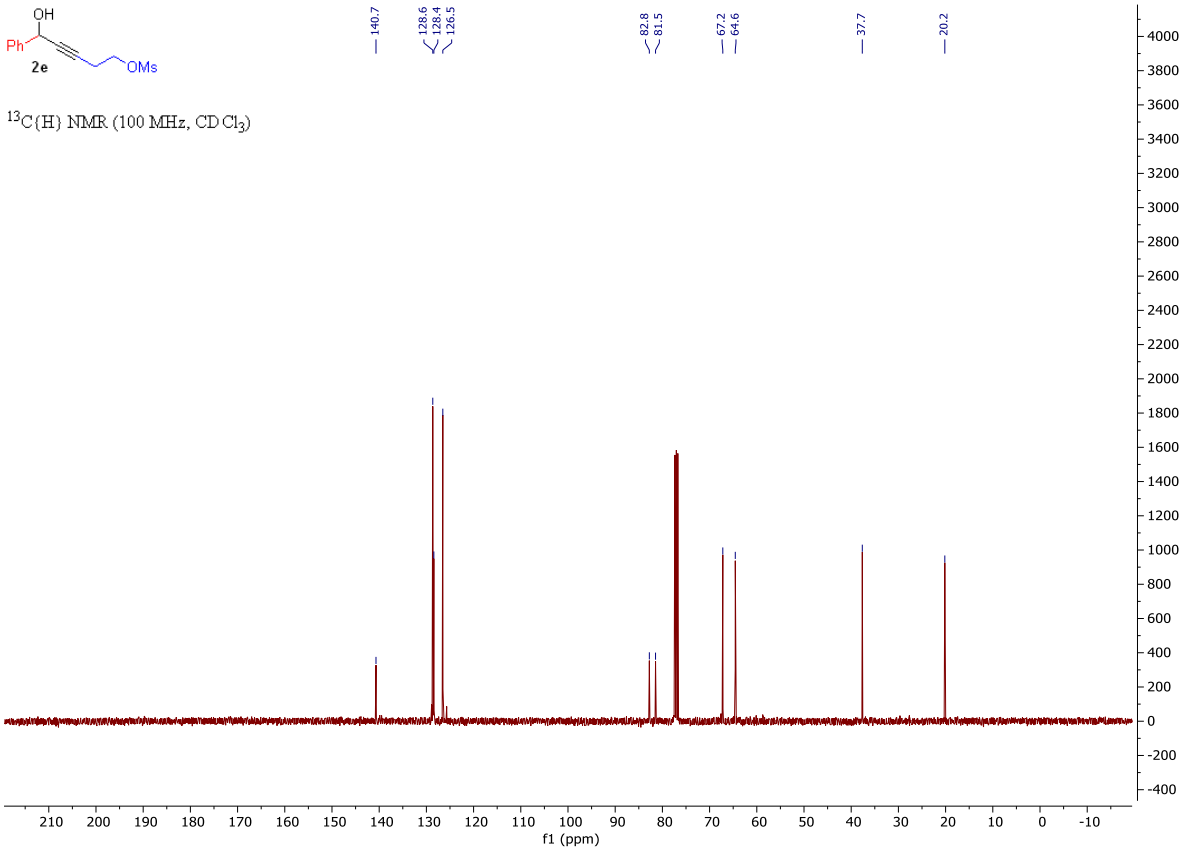


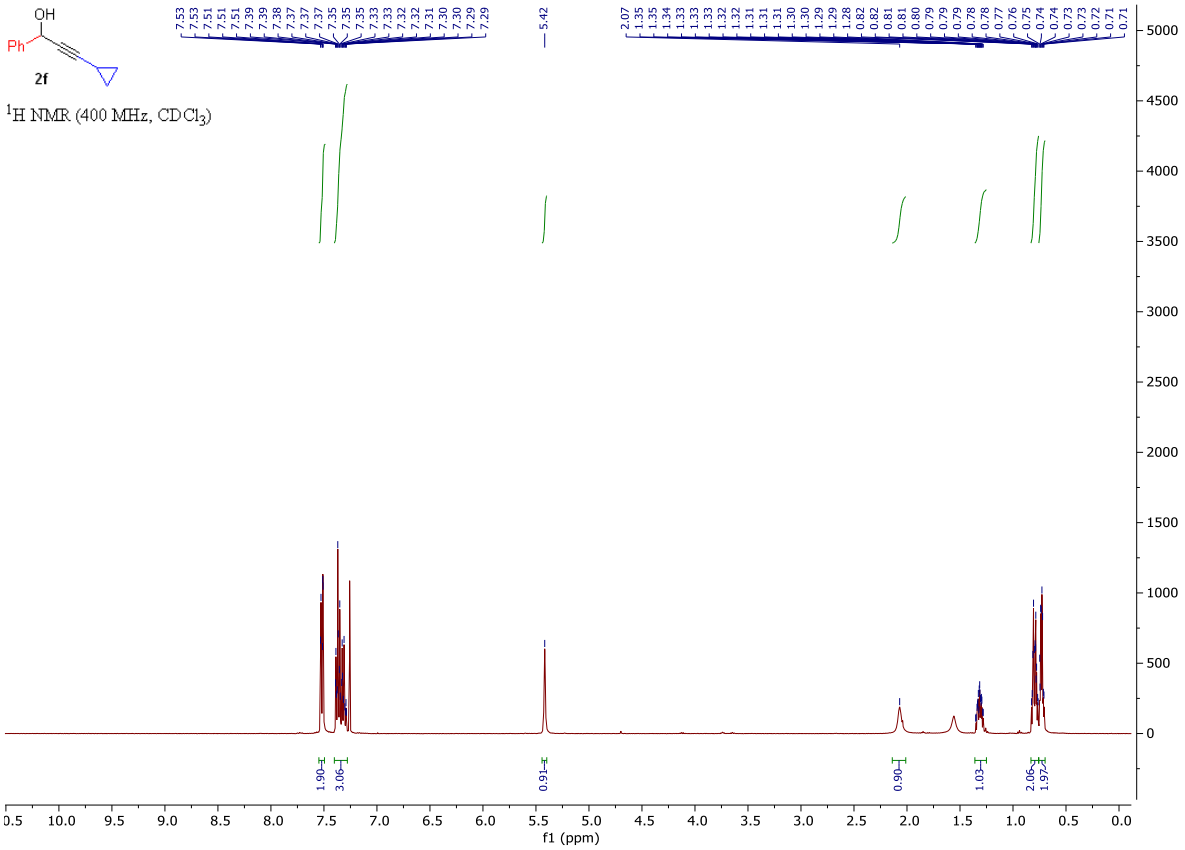


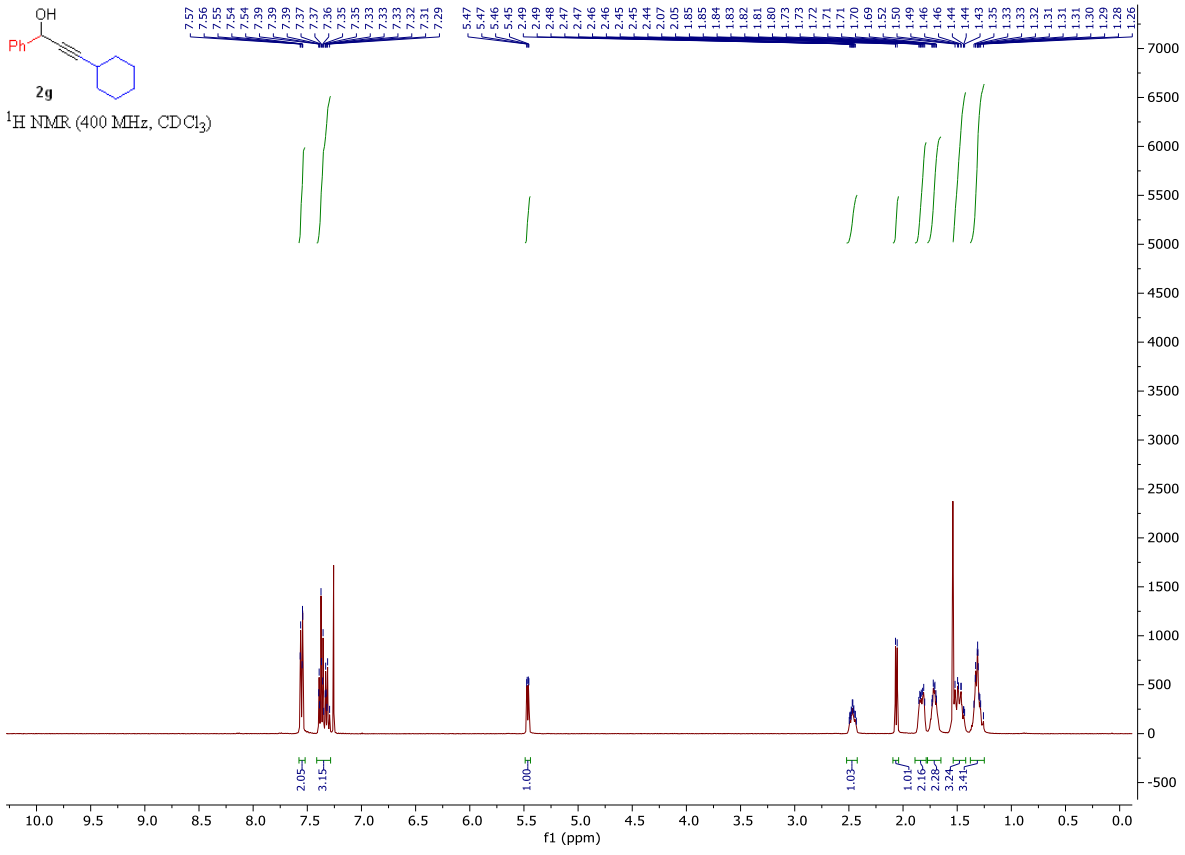

2c
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

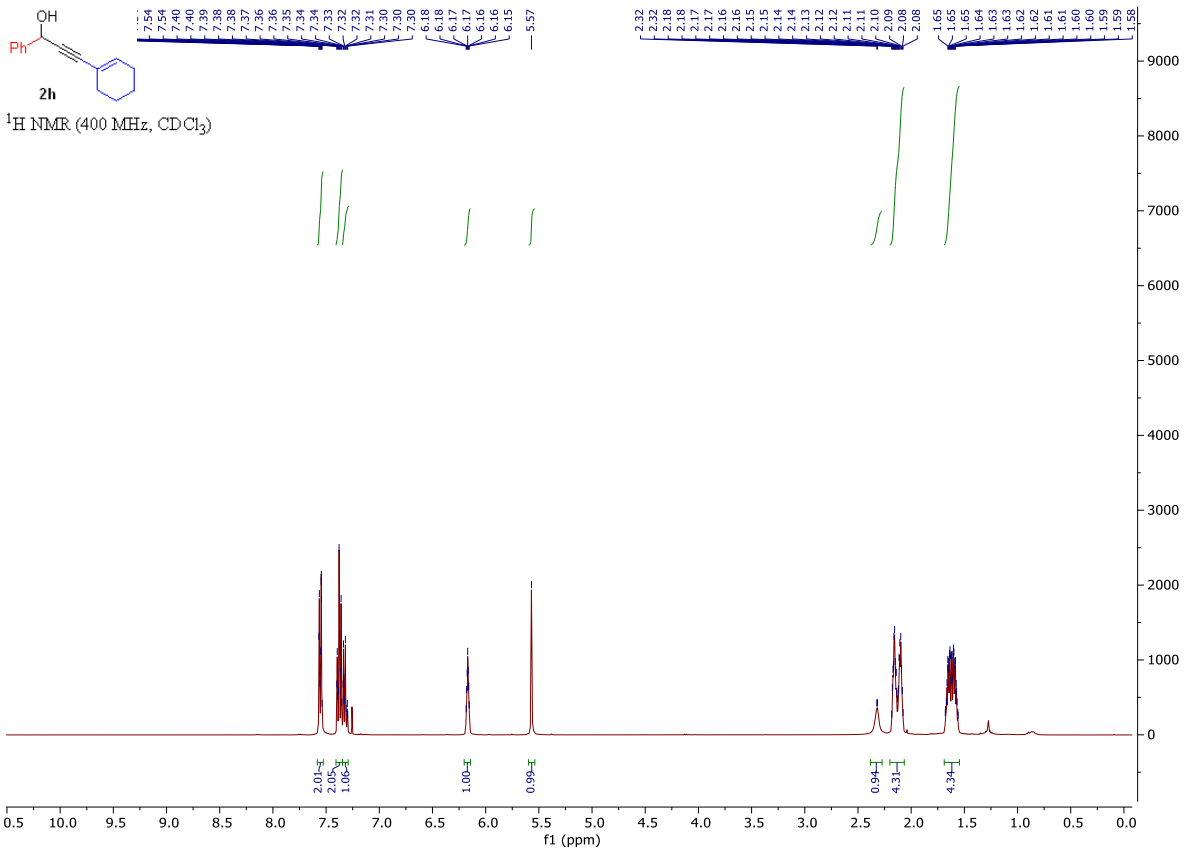

2d
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

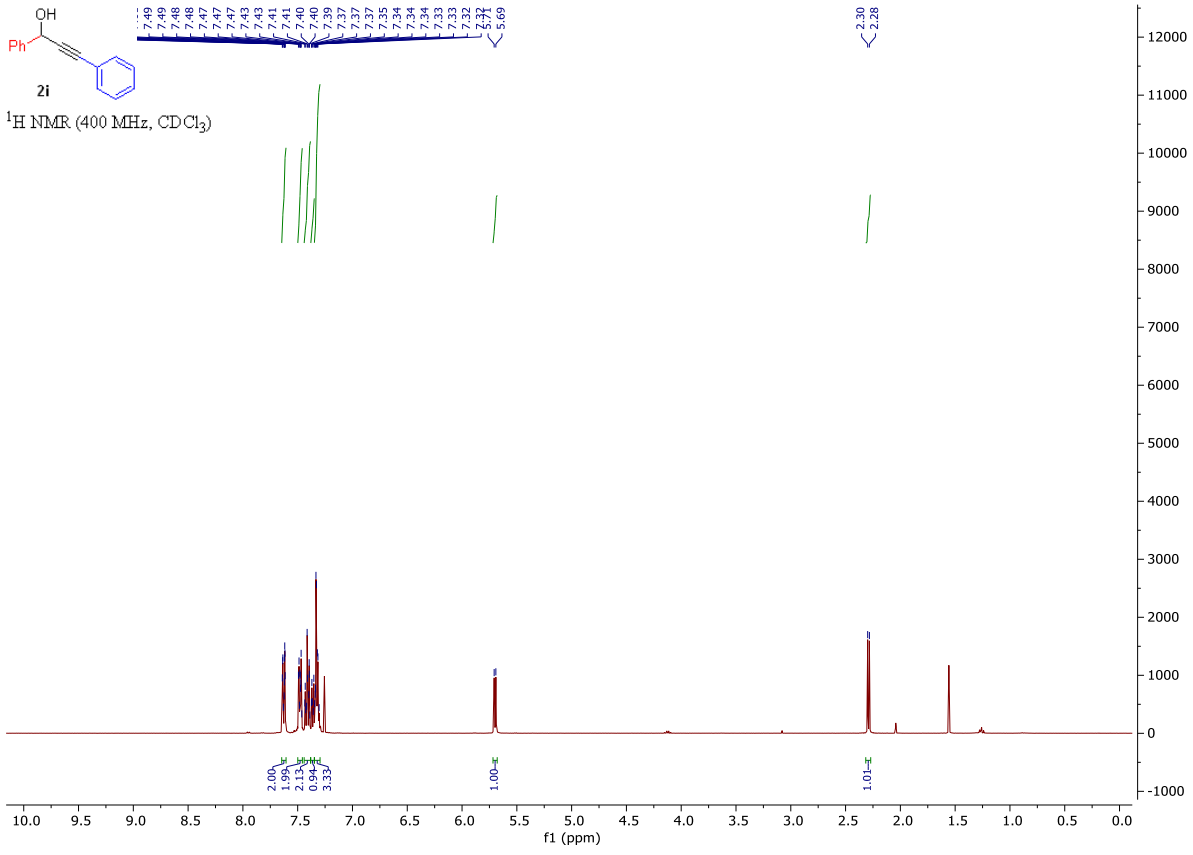

OH
Ph
2e
OMs
^{1}H NMR (400 MHz, CDCl$_3$)
7.52
7.50
7.39
7.37
7.35
7.34
7.32
7.30
5.44
5.43
5.43
4.32
4.30
4.28
2.97
2.75
2.74
2.73
2.72
2.71
2.71
2.45
2.43
2.03
3.47
1.00
2.00
3.00
2.11
0.94
f1 (ppm)

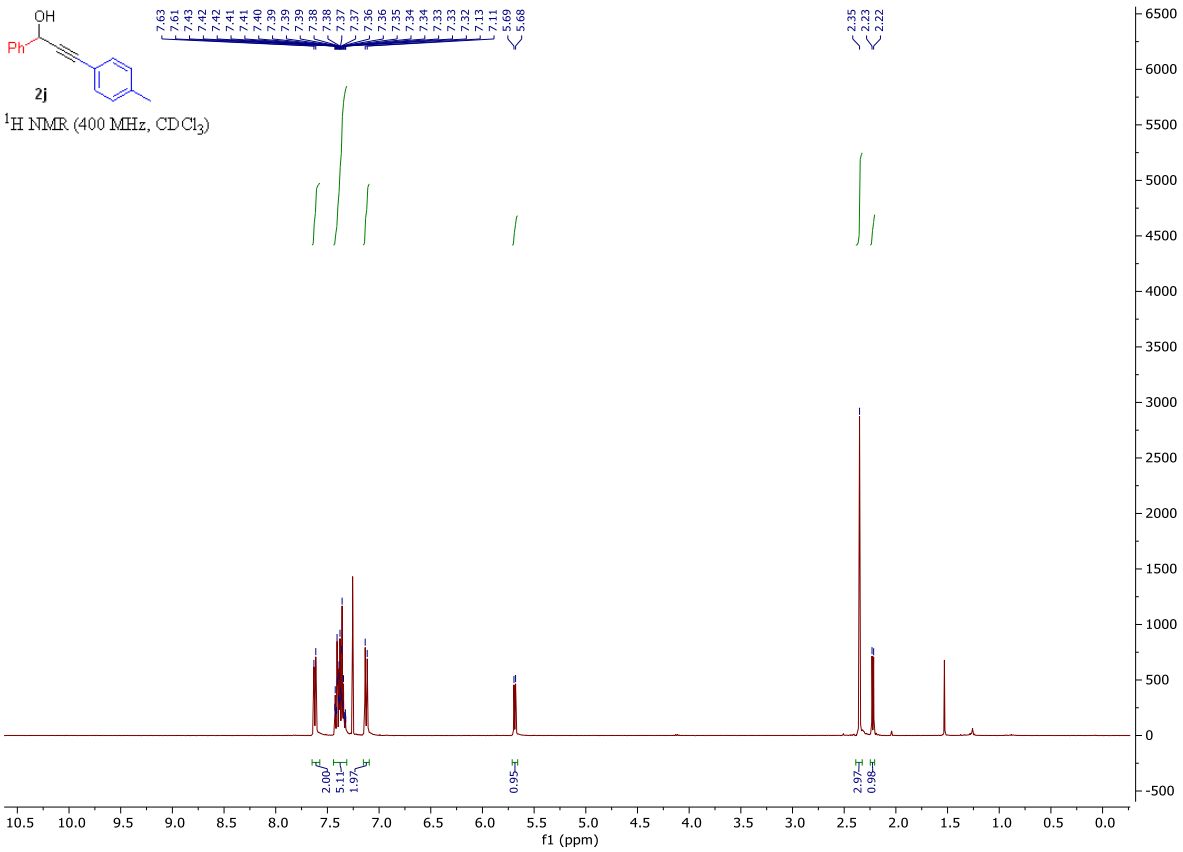

OH
Ph
2e
OMs
^{13}C{H} NMR (100 MHz, CDCl$_3$)
140.7
128.6
128.4
126.5
82.8
81.5
67.2
64.6
37.7
20.2
f1 (ppm)

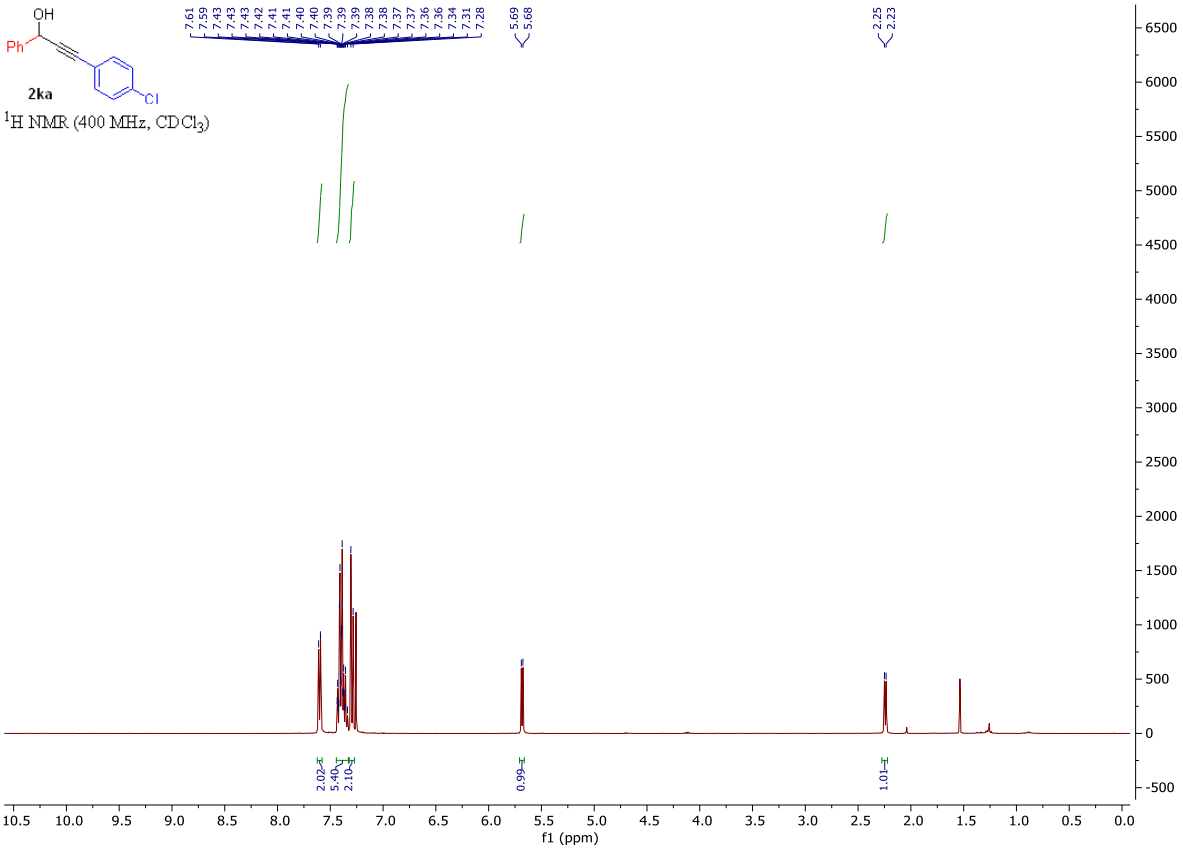

OH
Ph
2f
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

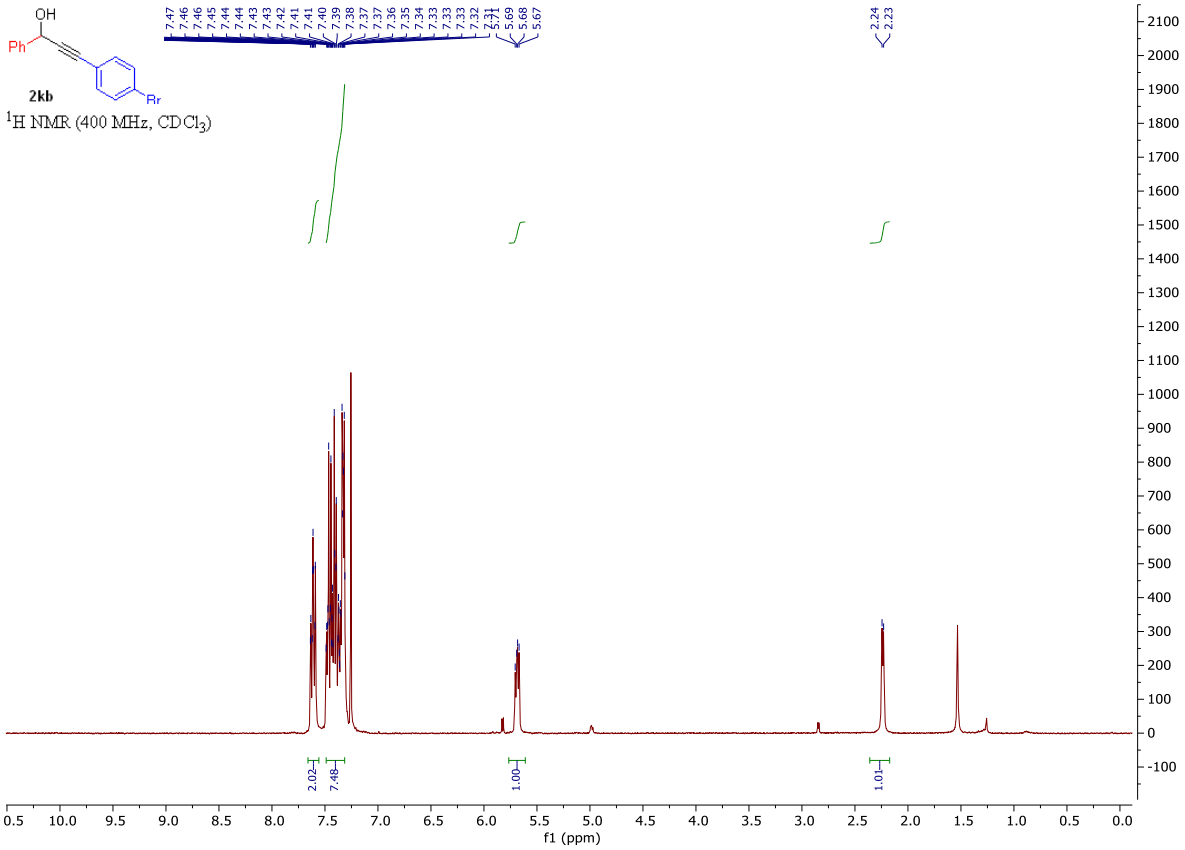

OH
Ph
2g
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

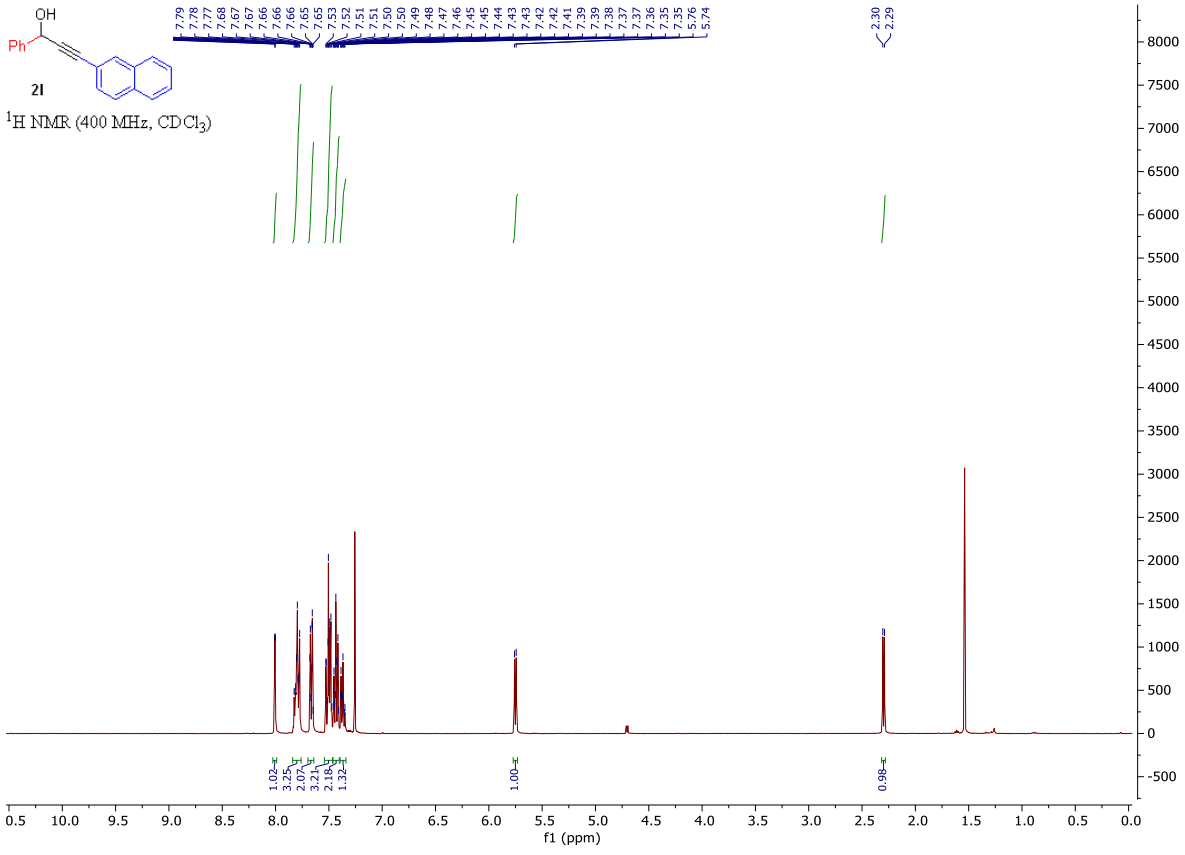

OH
Ph
2h
1H NMR (400 MHz, CDCl3)
f1 (ppm)

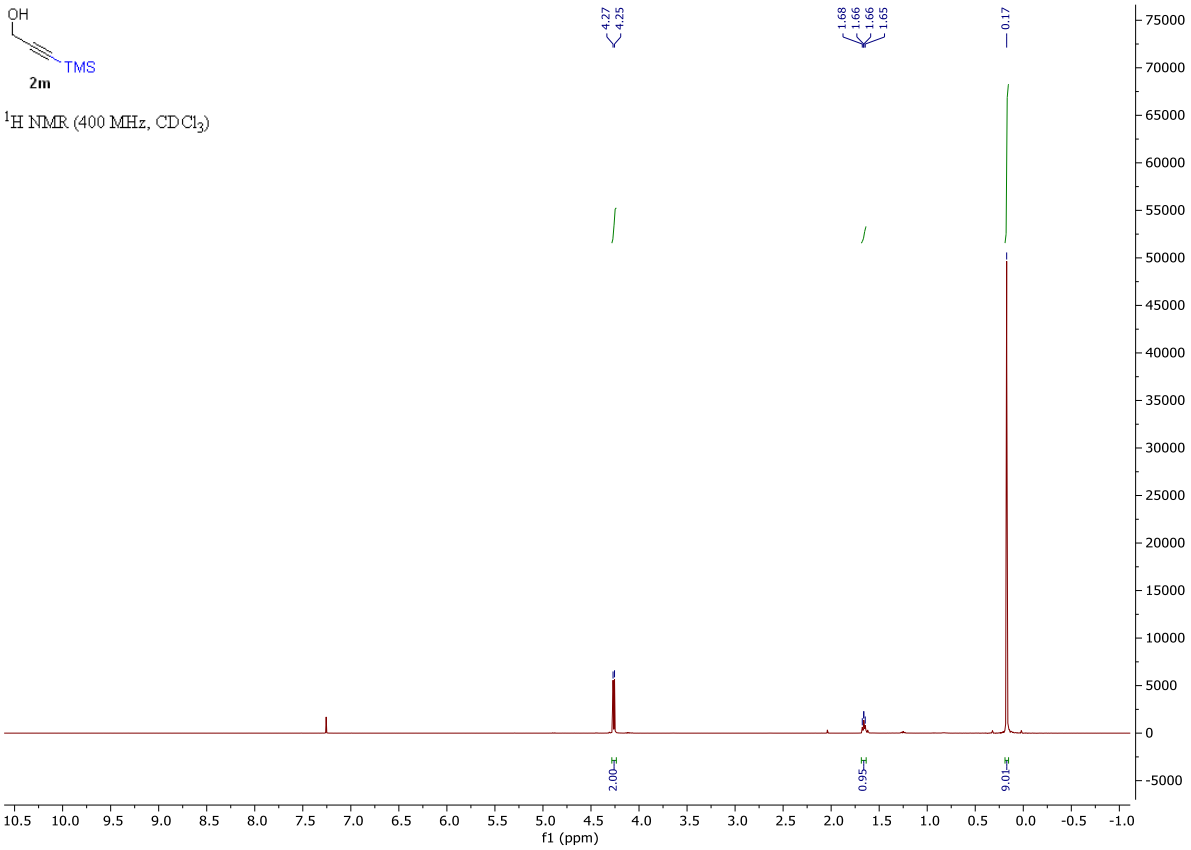

OH
Ph
2i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

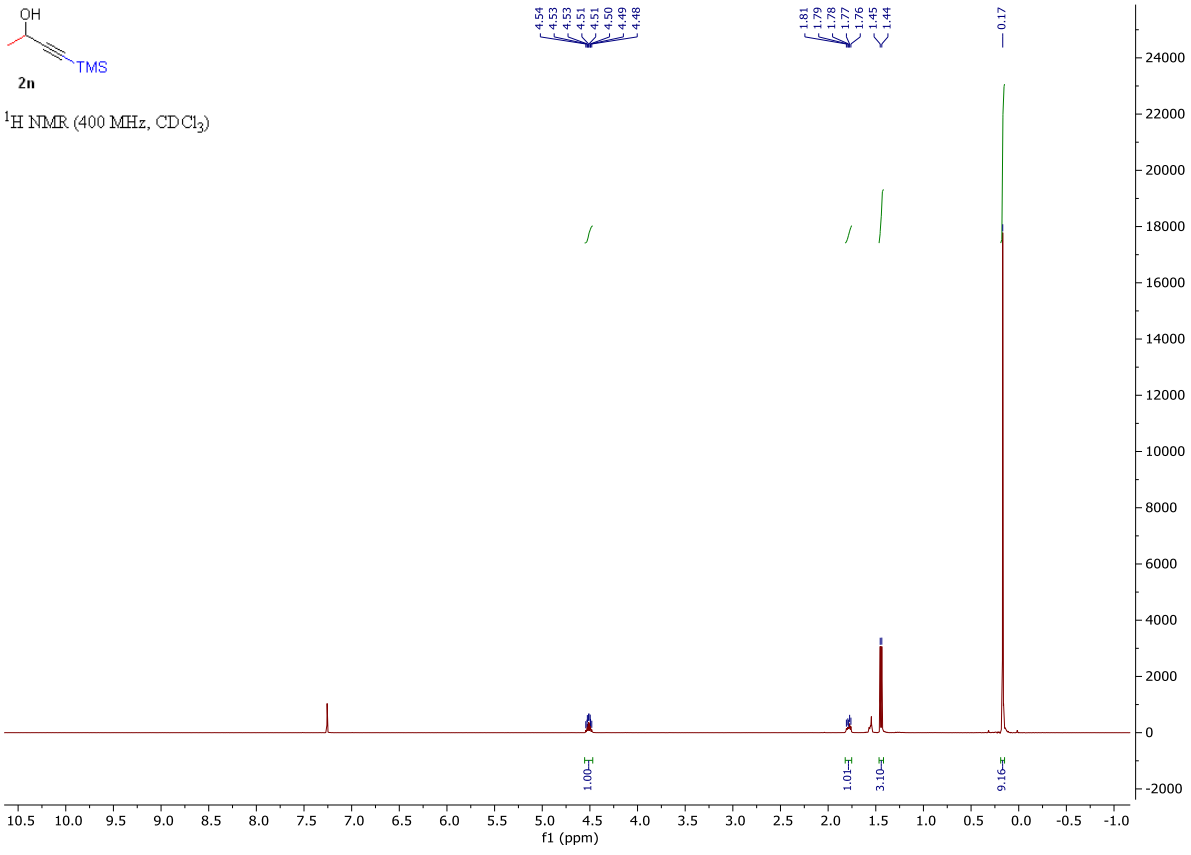

OH
Ph
2j
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

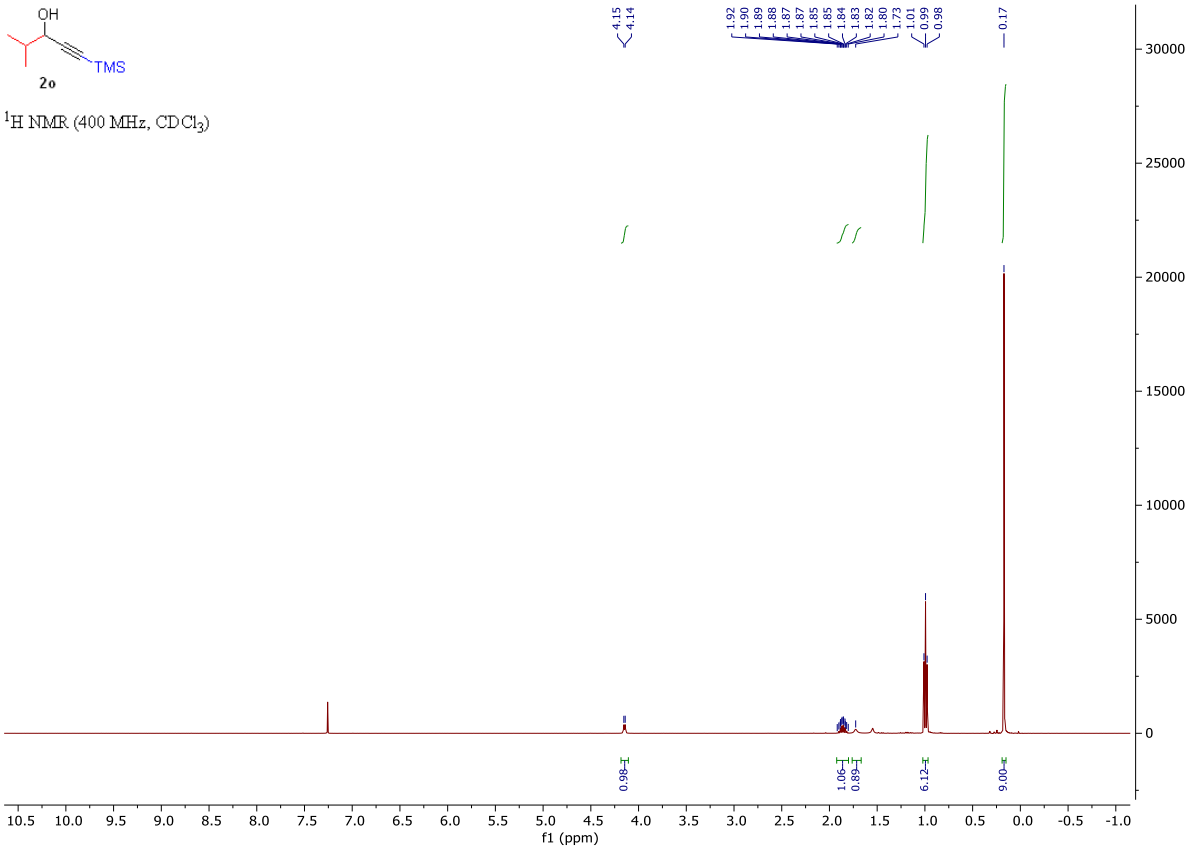

OH
Ph
Cl
2ka
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

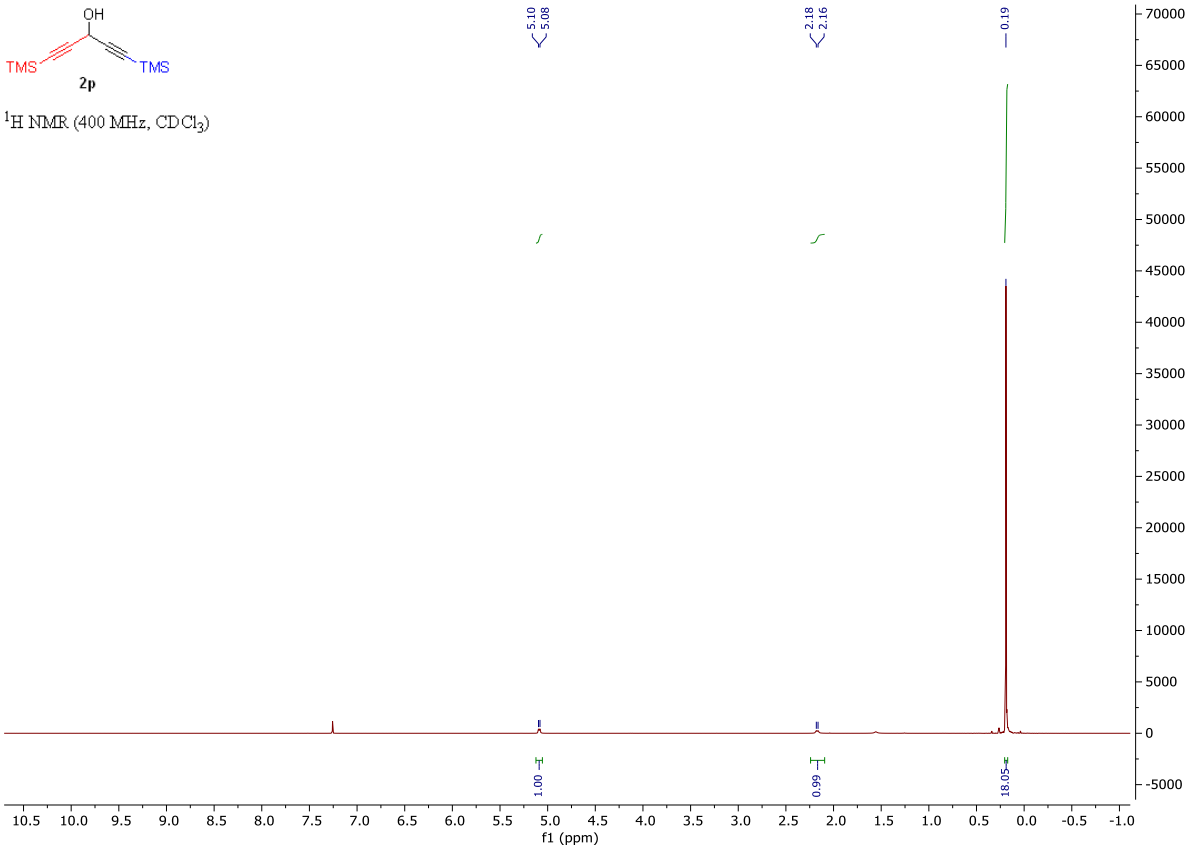

OH
Ph
Pr
2kb
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

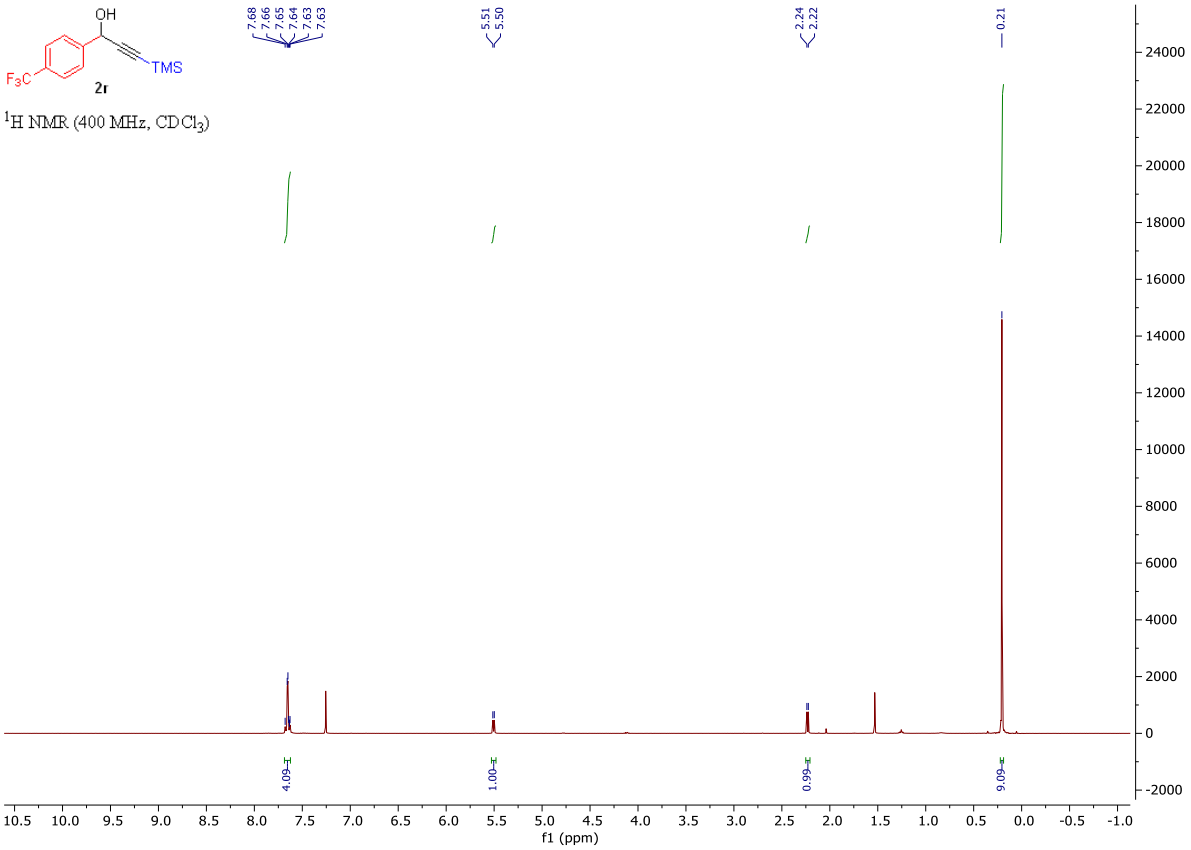

OH
Ph
2l
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

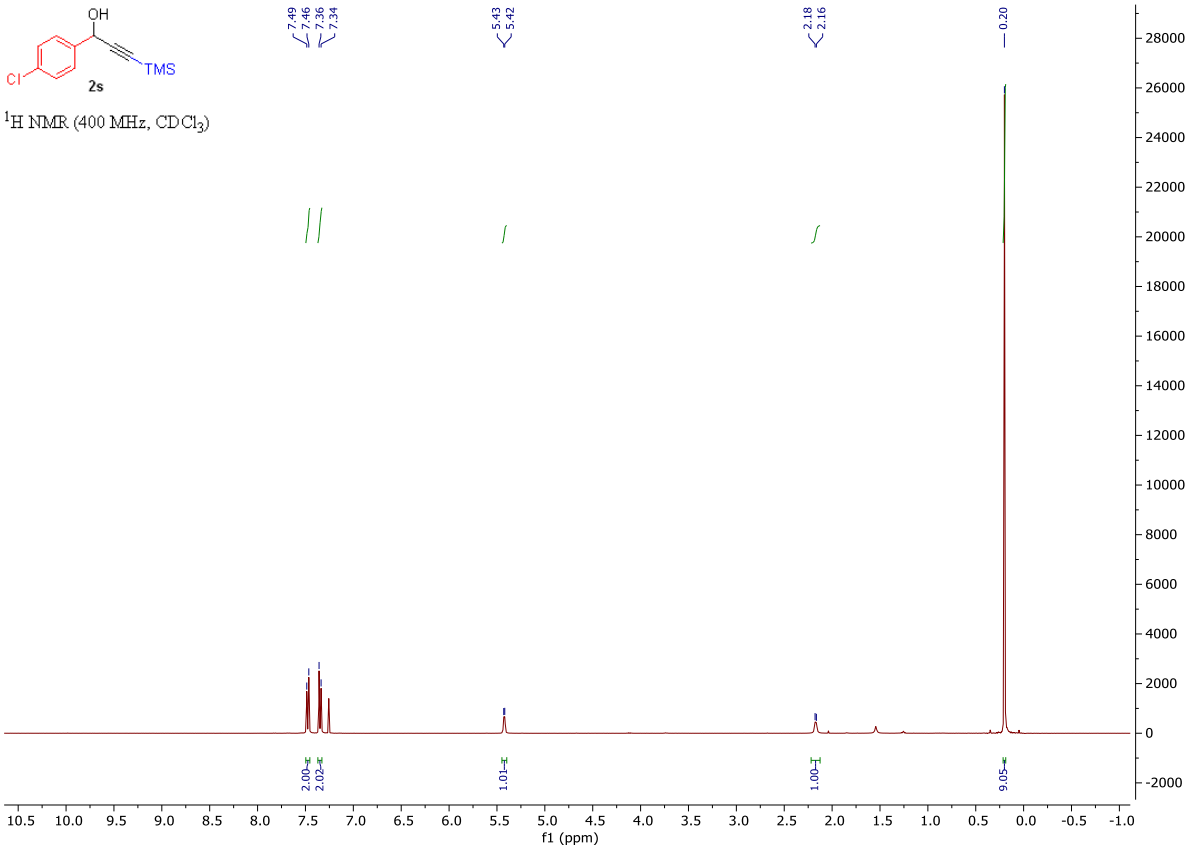

OH
TMS
2m
^{1}H NMR (400 MHz, $CDCl_3$)
4.27
4.25
1.68
1.66
1.66
1.65
0.17
2.00
0.95
9.01
f1 (ppm)

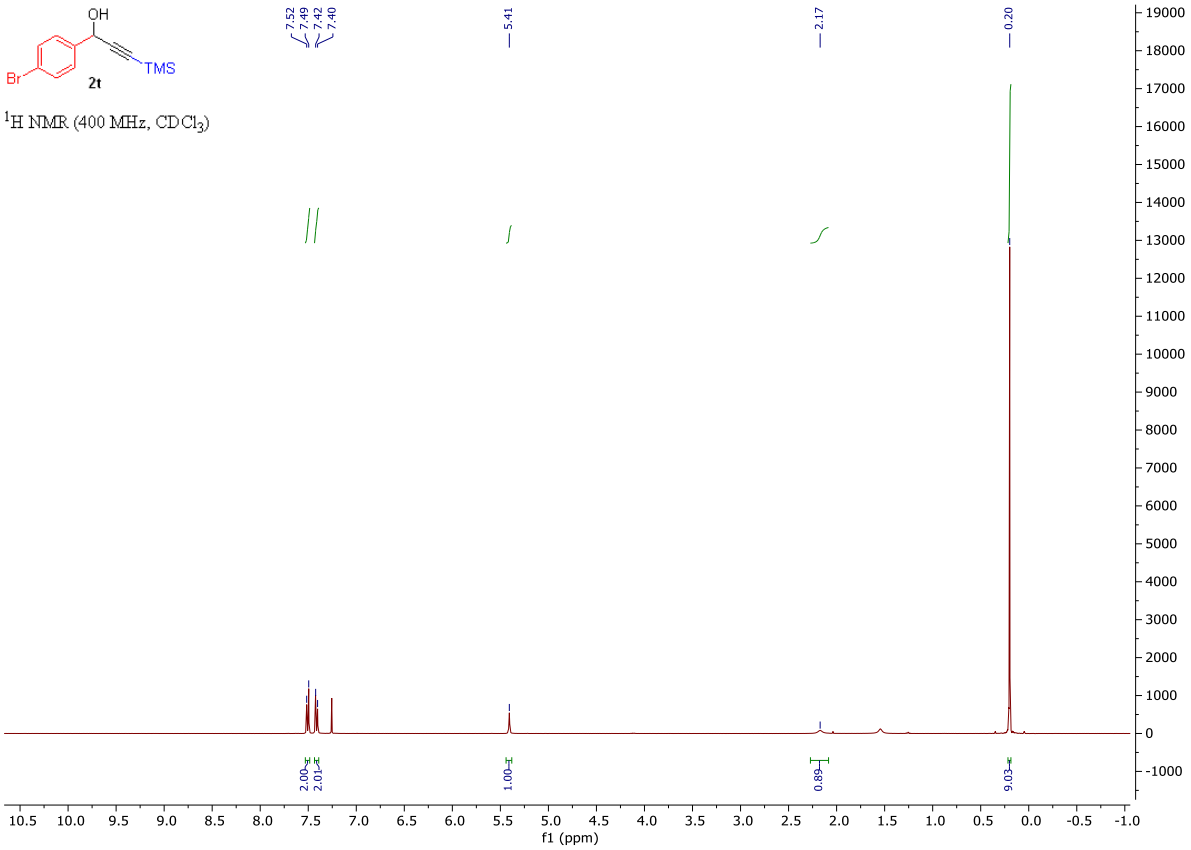

OH
TMS
2n
^{1}H NMR (400 MHz, $CDCl_3$)
4.54
4.53
4.53
4.51
4.51
4.50
4.49
4.48
1.81
1.79
1.78
1.77
1.76
1.45
1.44
0.17
1.00
1.01
3.10
9.16
f1 (ppm)

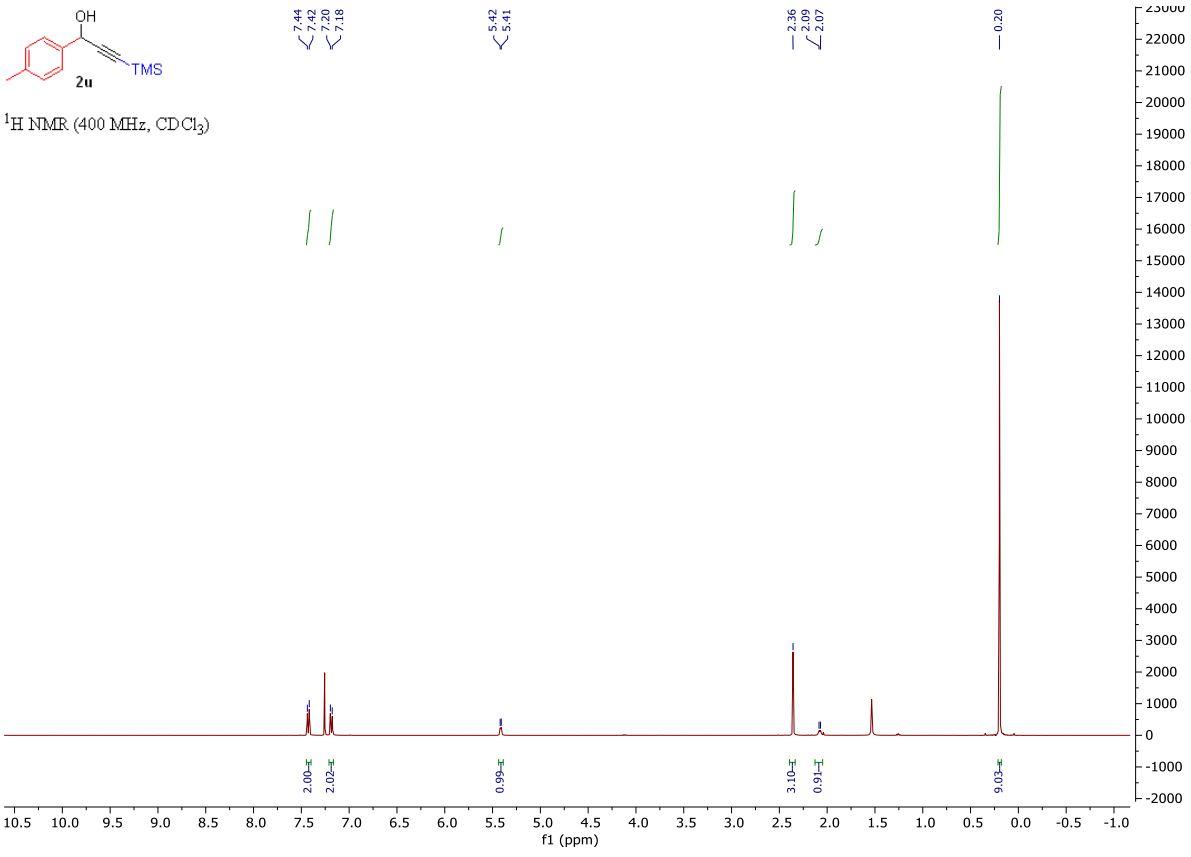

OH
TMS
2o
^{1}H NMR (400 MHz, $CDCl_3$)
4.15
4.14
1.92
1.90
1.89
1.88
1.87
1.87
1.85
1.85
1.84
1.83
1.82
1.80
1.73
1.01
0.99
0.98
0.17
0.98
1.06
0.89
6.12
9.00
f1 (ppm)

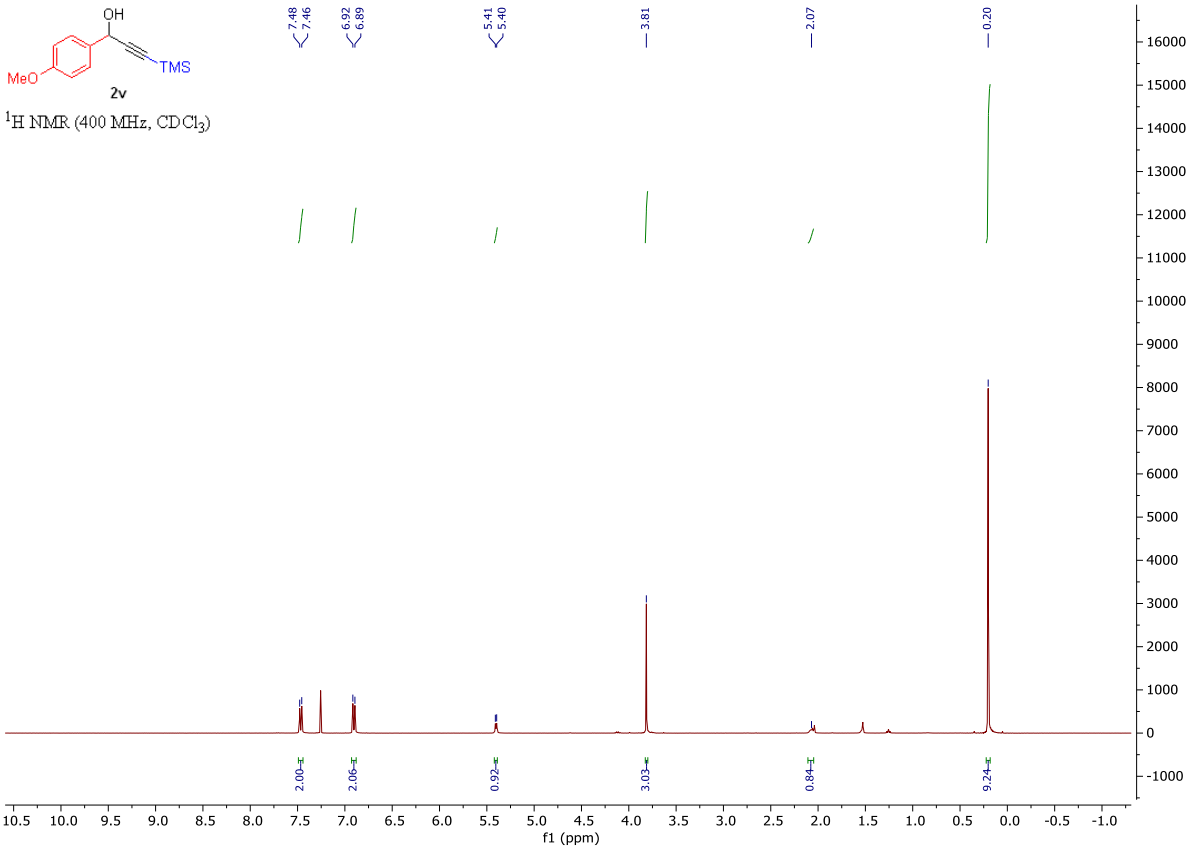

OH
TMS
TMS
2p
^{1}H NMR (400 MHz, $CDCl_3$)
5.10
5.08
2.18
2.16
0.19
1.00
0.99
18.05
f1 (ppm)

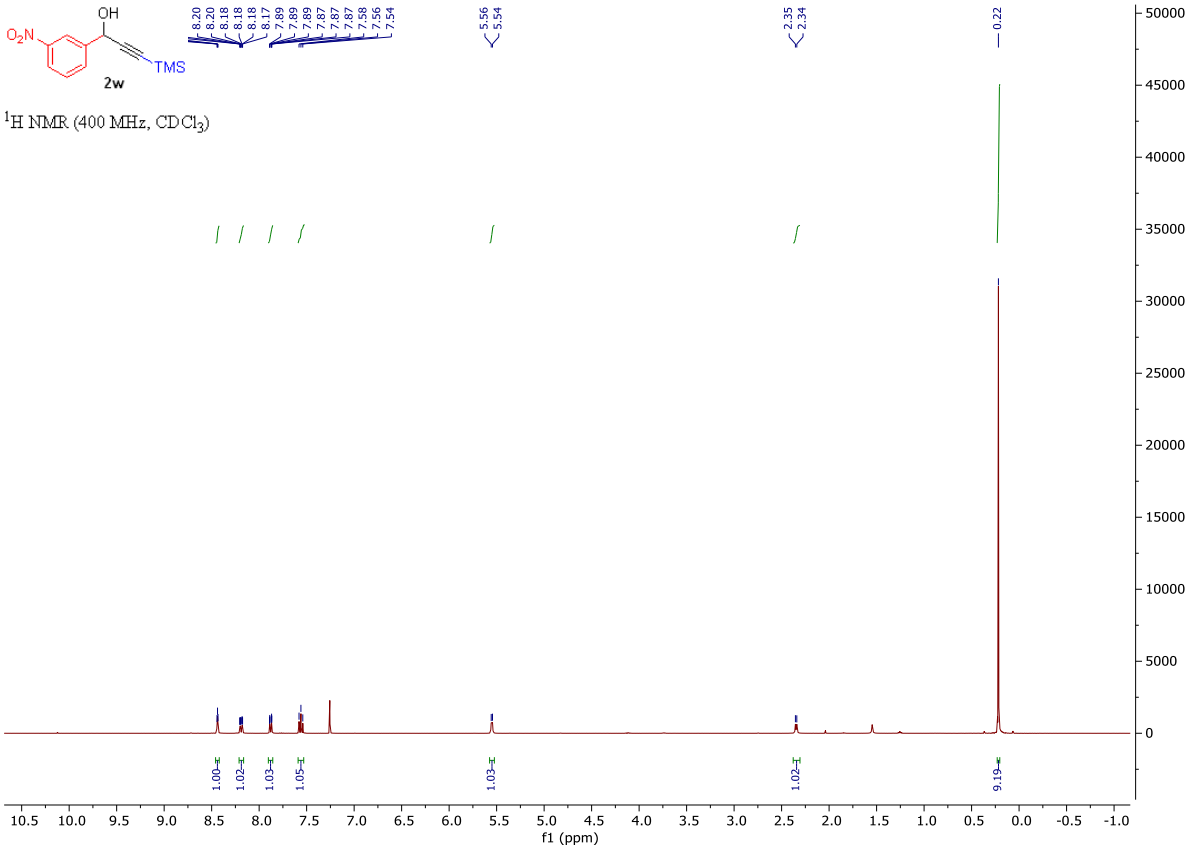

OH
TMS
F3C
2r
1H NMR (400 MHz, CDCl3)
7.68
7.66
7.65
7.64
7.63
7.63
5.51
5.50
2.24
2.22
0.21
4.09
1.00
0.99
9.09
f1 (ppm)

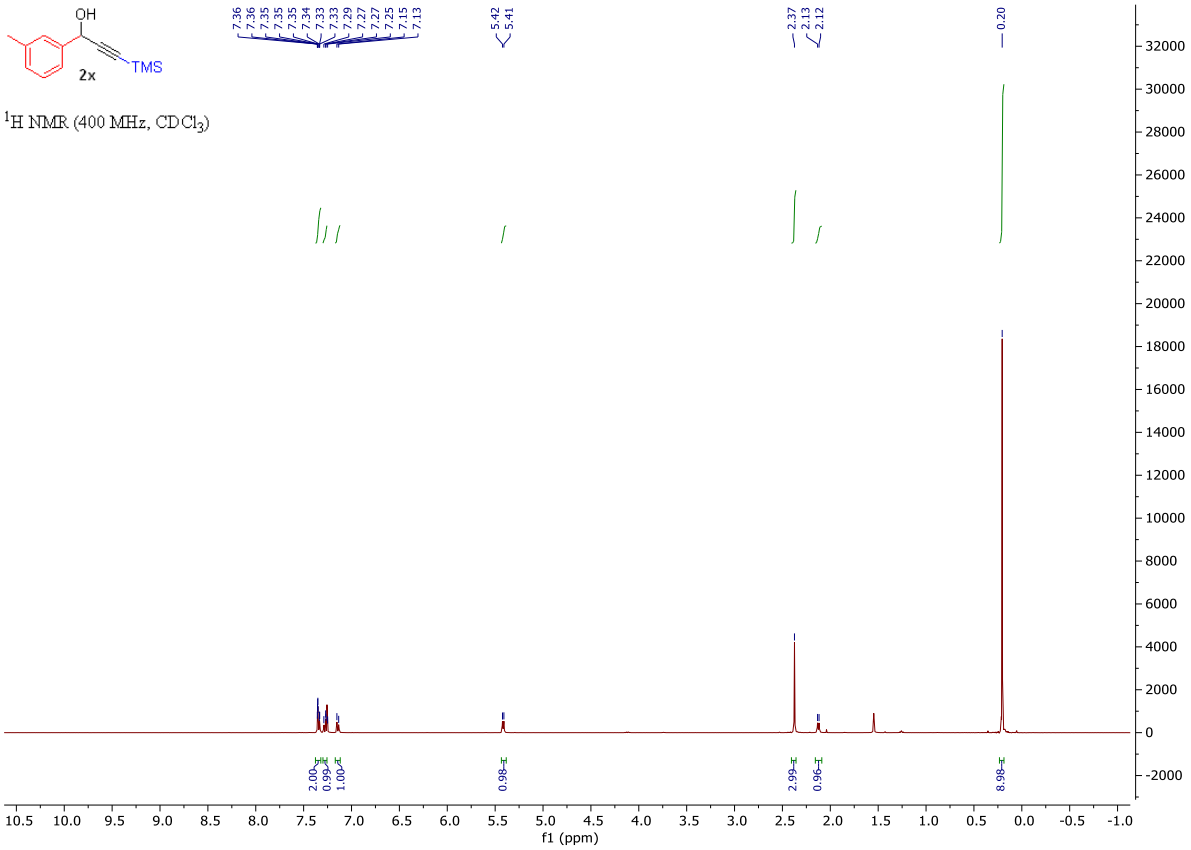

OH
TMS
Cl
2s
1H NMR (400 MHz, CDCl3)
7.49
7.46
7.36
7.34
5.43
5.42
2.18
2.16
0.20
2.00
2.02
1.01
1.00
9.05
f1 (ppm)

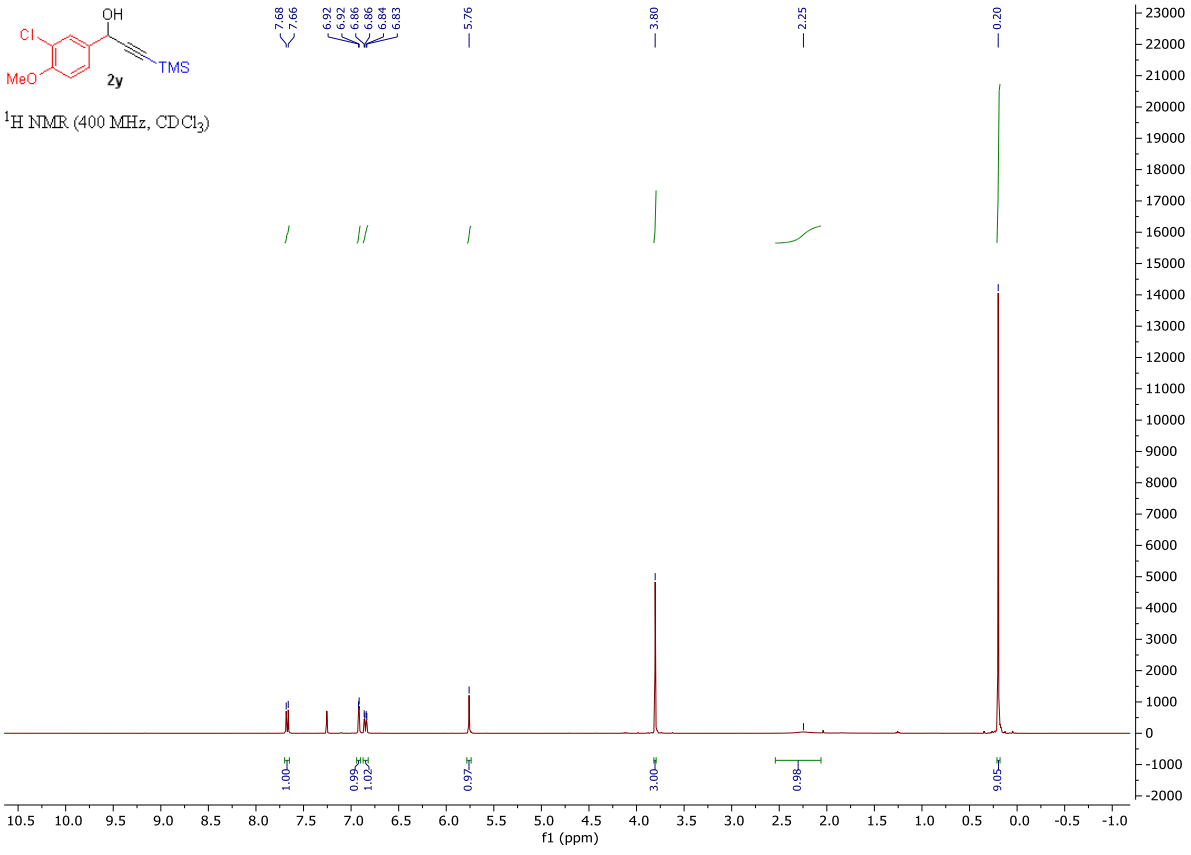

OH
Br
TMS
2t
^{1}H NMR (400 MHz, $CDCl_3$)
7.52
7.49
7.42
7.40
5.41
2.17
0.20
2.00
2.01
1.00
0.89
9.03
f1 (ppm)

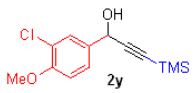

OH
TMS
2u
^{1}H NMR (400 MHz, $CDCl_3$)
7.44
7.42
7.20
7.18
5.42
5.41
2.36
2.09
2.07
0.20
2.00
2.02
0.99
3.10
0.91
9.03
f1 (ppm)


OH
MeO
TMS
2v
^{1}H NMR (400 MHz, $CDCl_3$)
7.48
7.46
6.92
6.89
5.41
5.40
3.81
2.07
0.20
2.00
2.06
0.92
3.03
0.84
9.24
f1 (ppm)

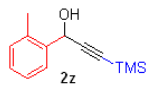

OH
O_2N
TMS
2w
^{1}H NMR (400 MHz, $CDCl_3$)
8.20
8.20
8.18
8.18
8.18
8.17
7.89
7.89
7.89
7.87
7.87
7.87
7.58
7.56
7.54
5.56
5.54
2.35
2.34
0.22
1.00
1.02
1.03
1.05
1.03
1.02
9.19
f1 (ppm)


OH
TMS
2x
^{1}H NMR (400 MHz, $CDCl_3$)
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.29
7.27
7.27
7.25
7.15
7.13
5.42
5.41
2.37
2.13
2.12
0.20
2.00
0.99
1.00
0.98
2.99
0.96
8.98
f1 (ppm)

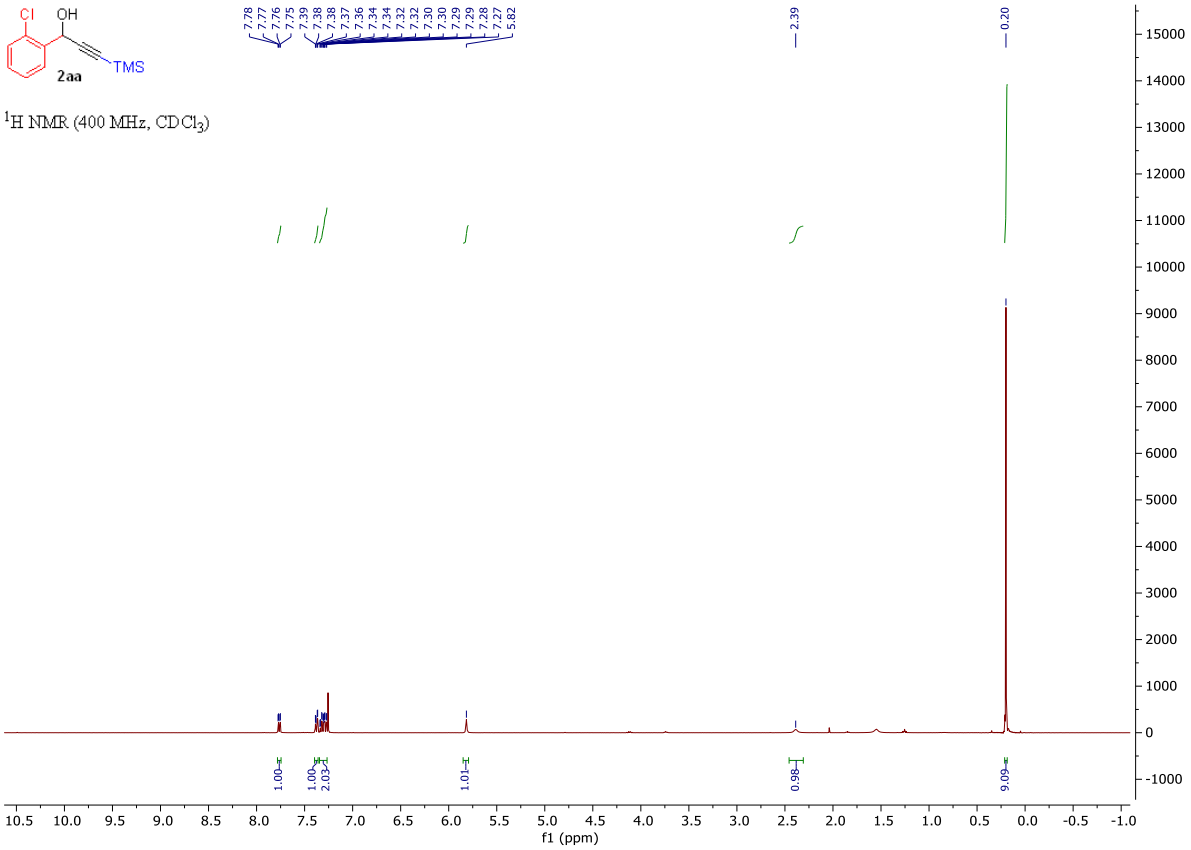

OH
Cl
MeO
TMS
2y
^{1}H NMR (400 MHz, $CDCl_3$)
7.68
7.66
6.92
6.92
6.86
6.86
6.84
6.83
5.76
3.80
2.25
0.20
1.00
0.99
1.02
0.97
3.00
0.98
9.05
f1 (ppm)

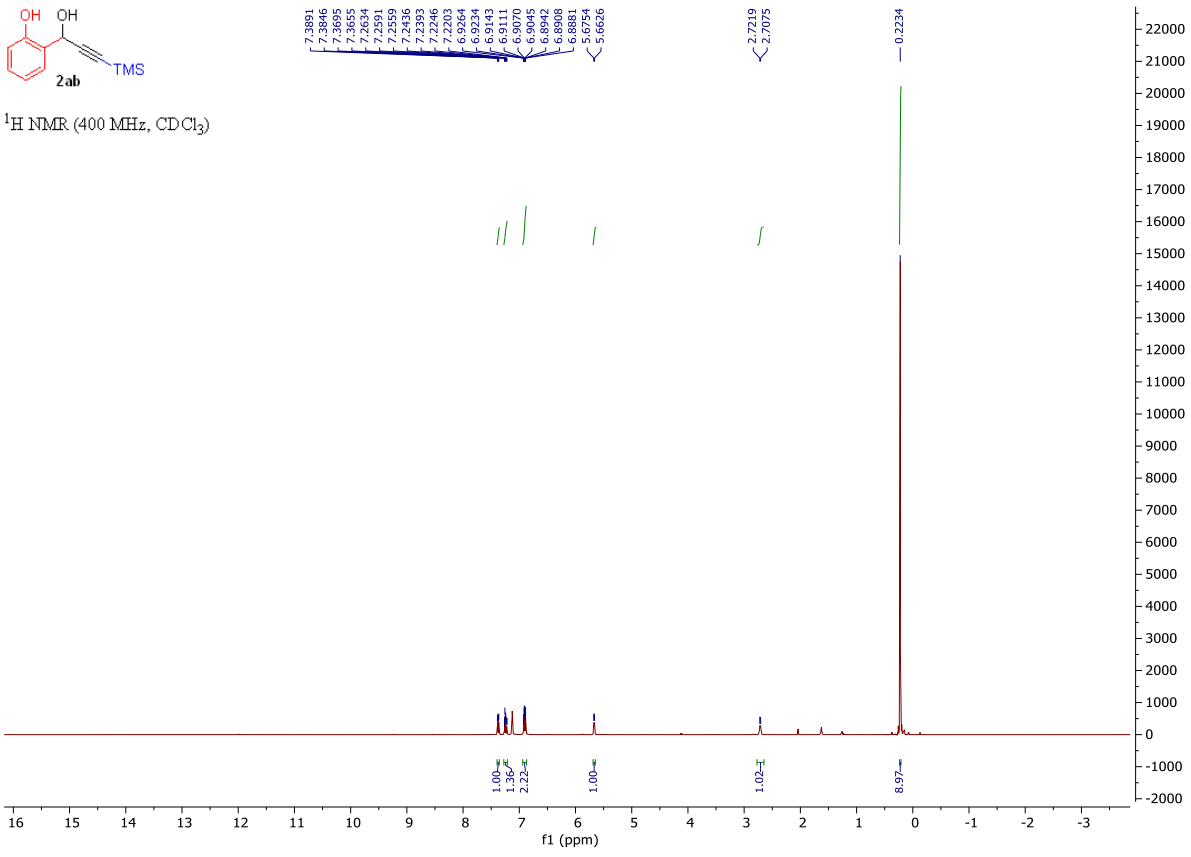


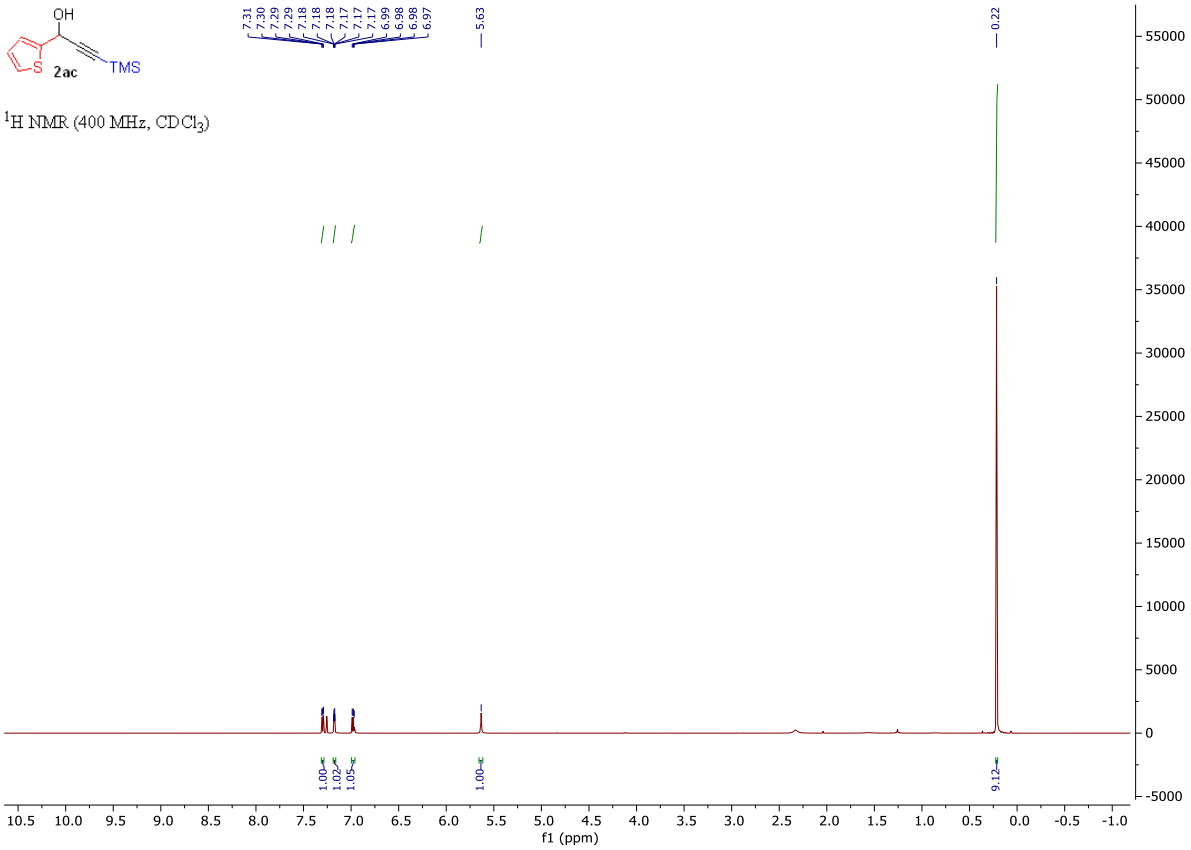
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)

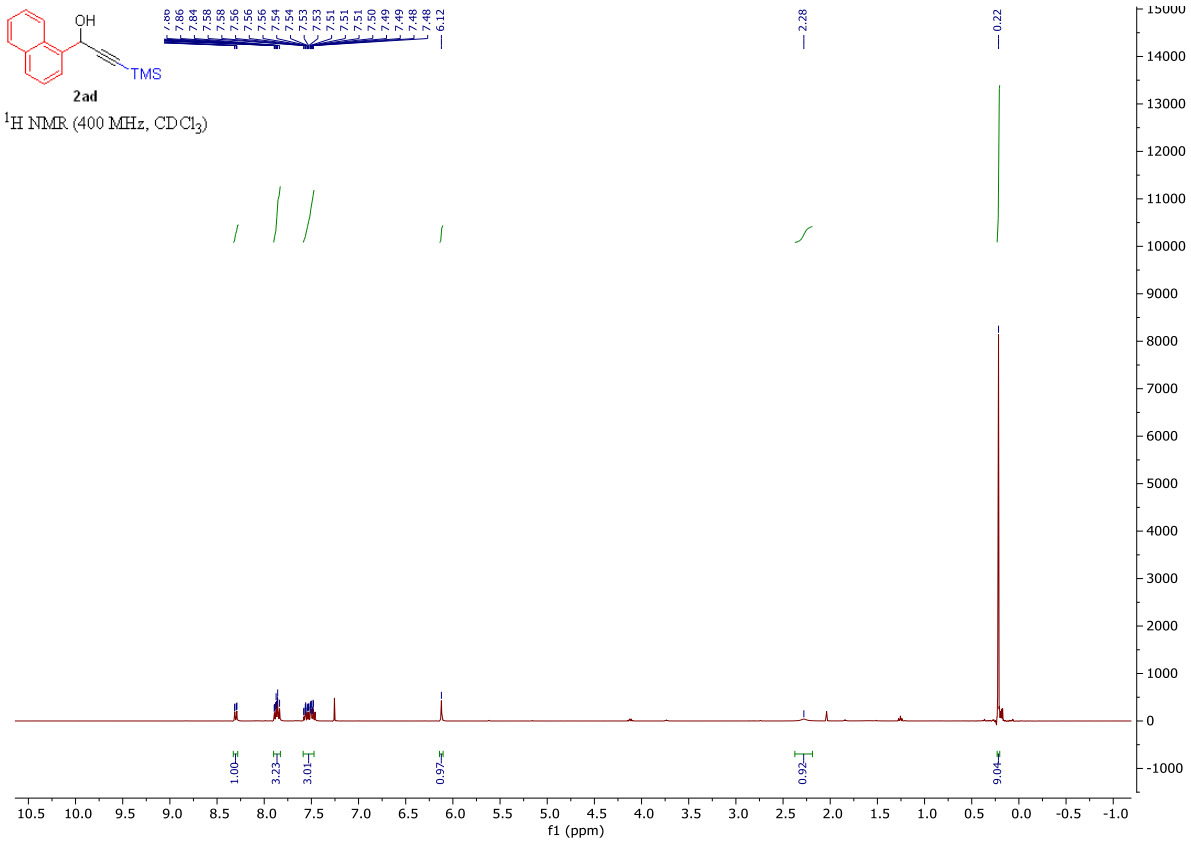


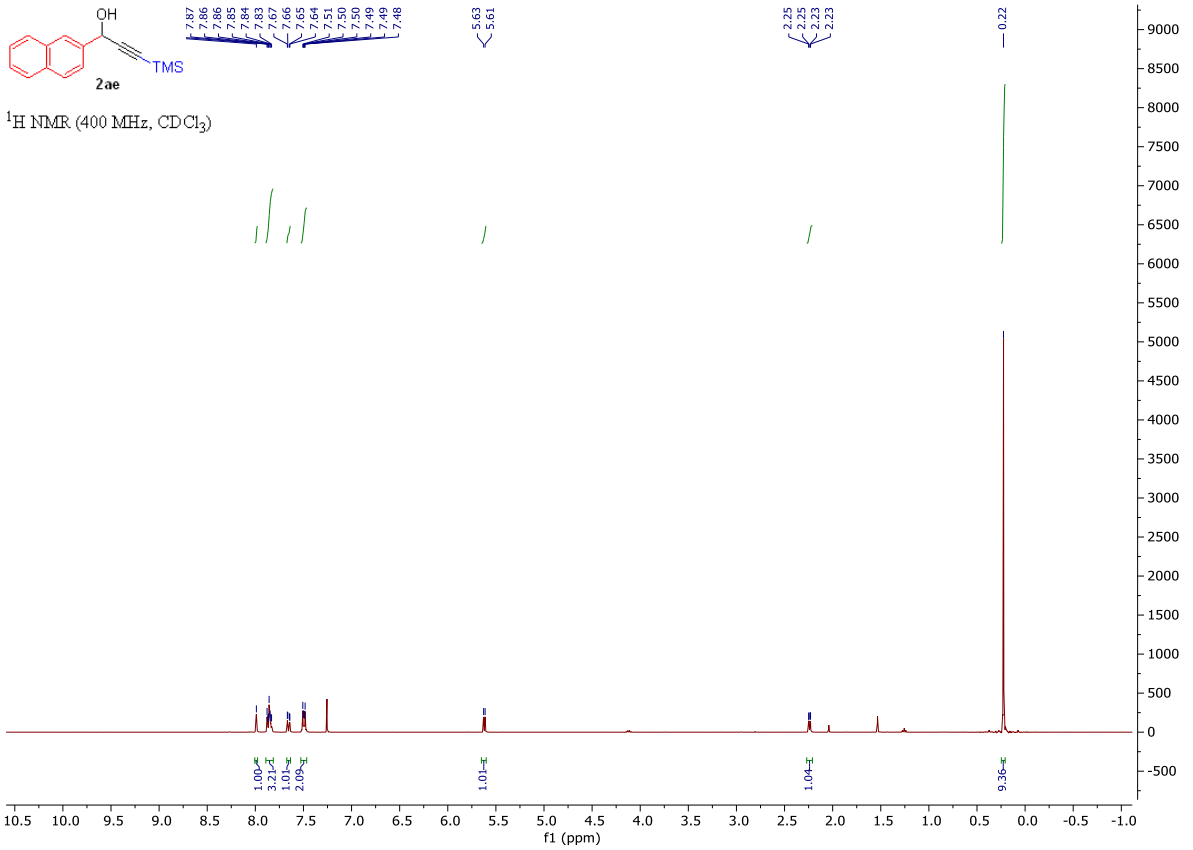
^{1}H NMR (400 MHz, $CDCl_3$)

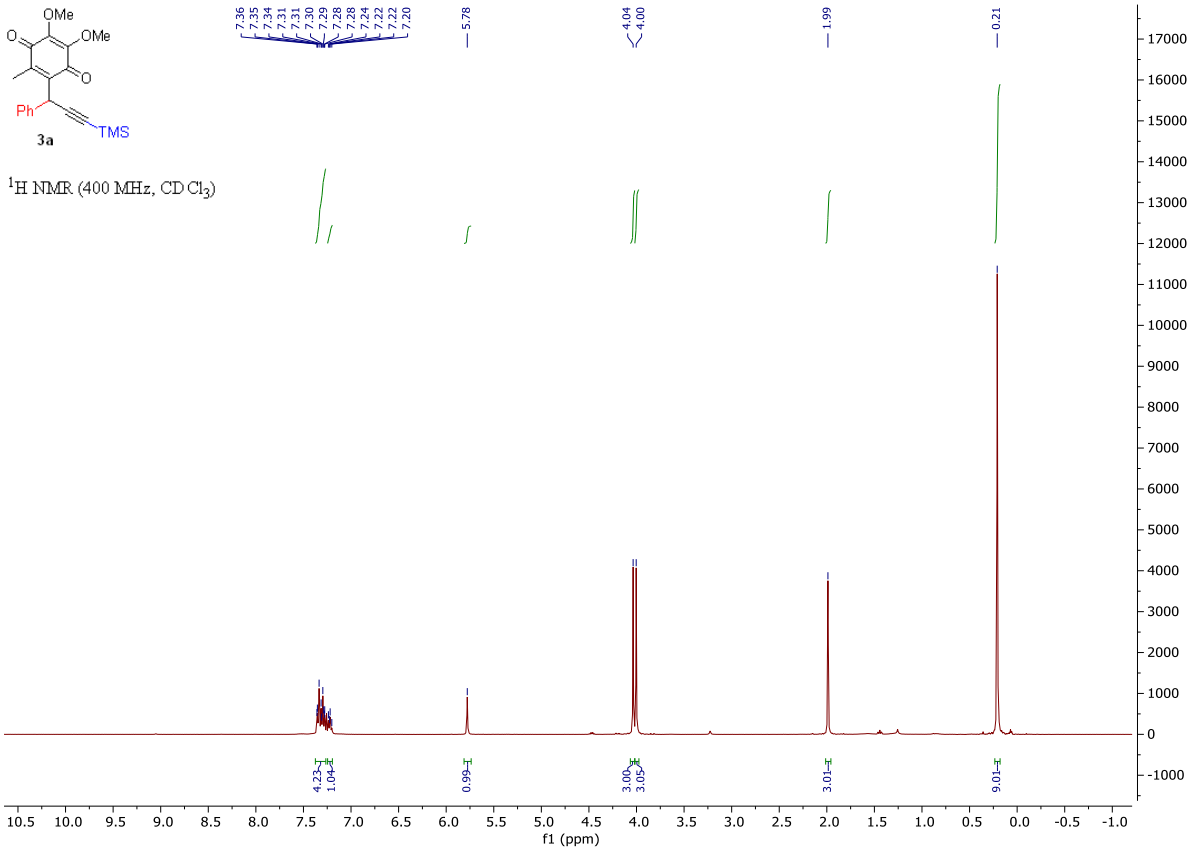

Cl
OH
TMS
2aa
^{1}H NMR (400 MHz, $CDCl_3$)
7.78
7.77
7.76
7.75
7.39
7.38
7.38
7.37
7.36
7.34
7.34
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.27
5.82
2.39
0.20
1.00
1.00
2.03
1.01
0.98
9.09
f1 (ppm)

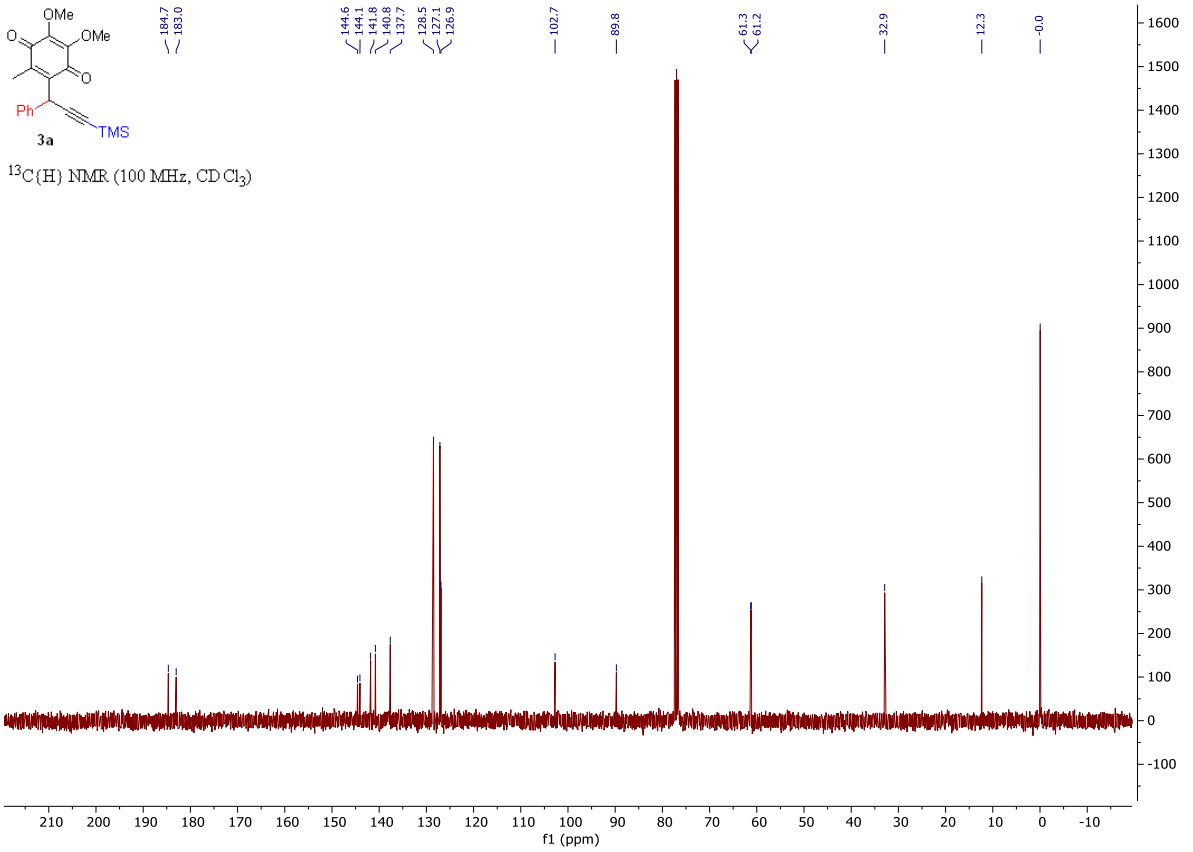

OH
OH
TMS
2ab
^{1}H NMR (400 MHz, $CDCl_3$)
7.3891
7.3846
7.3695
7.3655
7.2634
7.2591
7.2559
7.2436
7.2393
7.2246
7.2203
6.9264
6.9234
6.9143
6.9111
6.9070
6.9045
6.8942
6.8908
6.8881
5.6754
5.6626
2.7219
2.7075
0.2234
1.00
1.36
2.22
1.00
1.02
8.97
f1 (ppm)

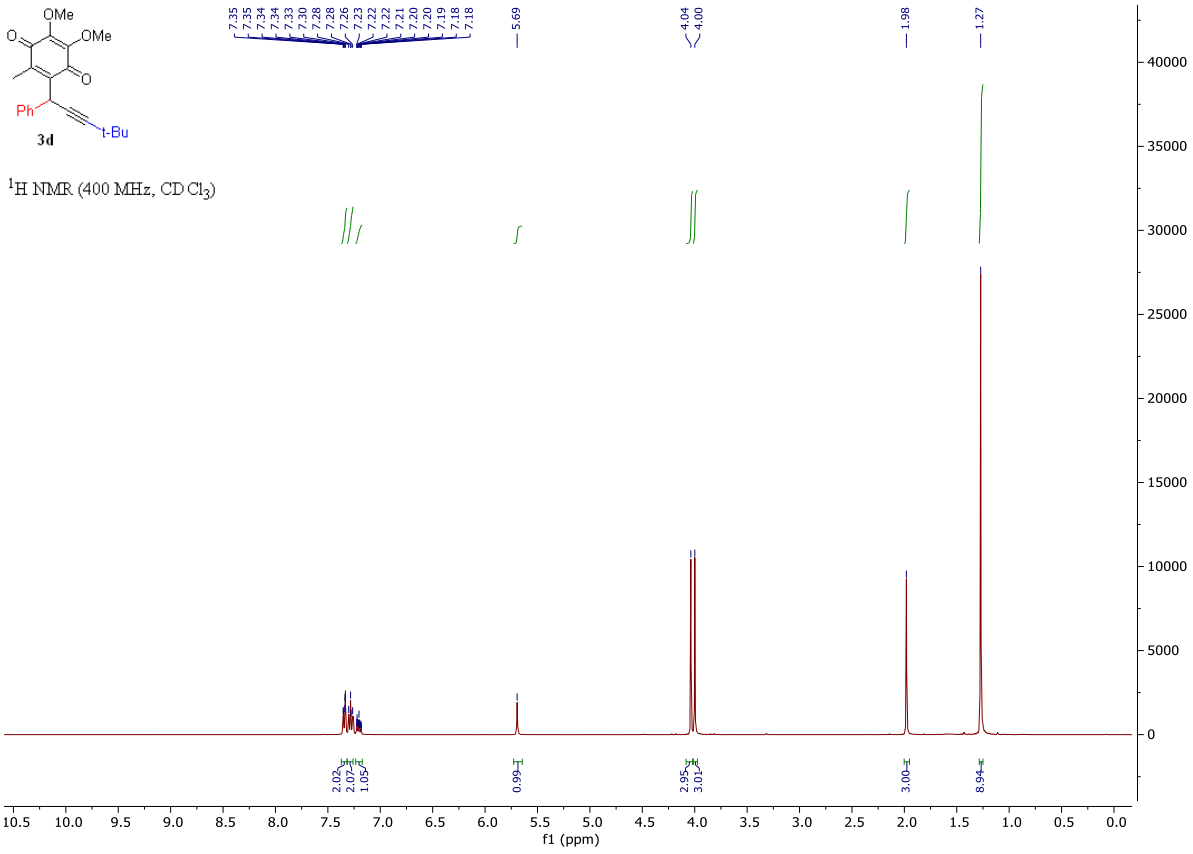

OH
TMS
2ac
^{1}H NMR (400 MHz, $CDCl_3$)
7.31
7.30
7.29
7.29
7.18
7.18
7.17
7.17
7.17
6.99
6.98
6.98
6.97
5.63
0.22
1.00
1.02
1.05
1.00
9.12
f1 (ppm)

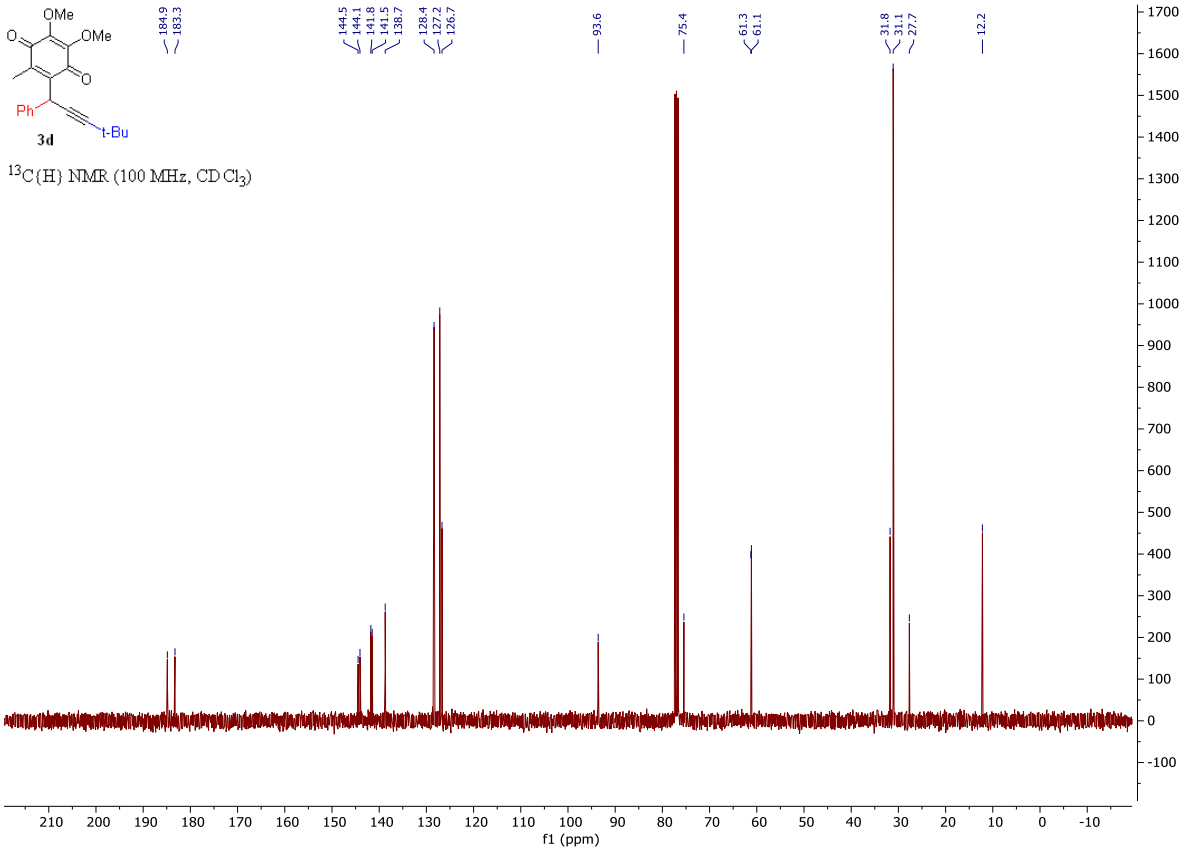

OH
TMS
2ad
^{1}H NMR (400 MHz, $CDCl_3$)
7.86
7.84
7.58
7.58
7.56
7.56
7.56
7.54
7.54
7.53
7.53
7.51
7.51
7.50
7.49
7.49
7.48
7.48
6.12
2.28
0.22
1.00
3.23
3.01
0.97
0.92
9.04
f1 (ppm)

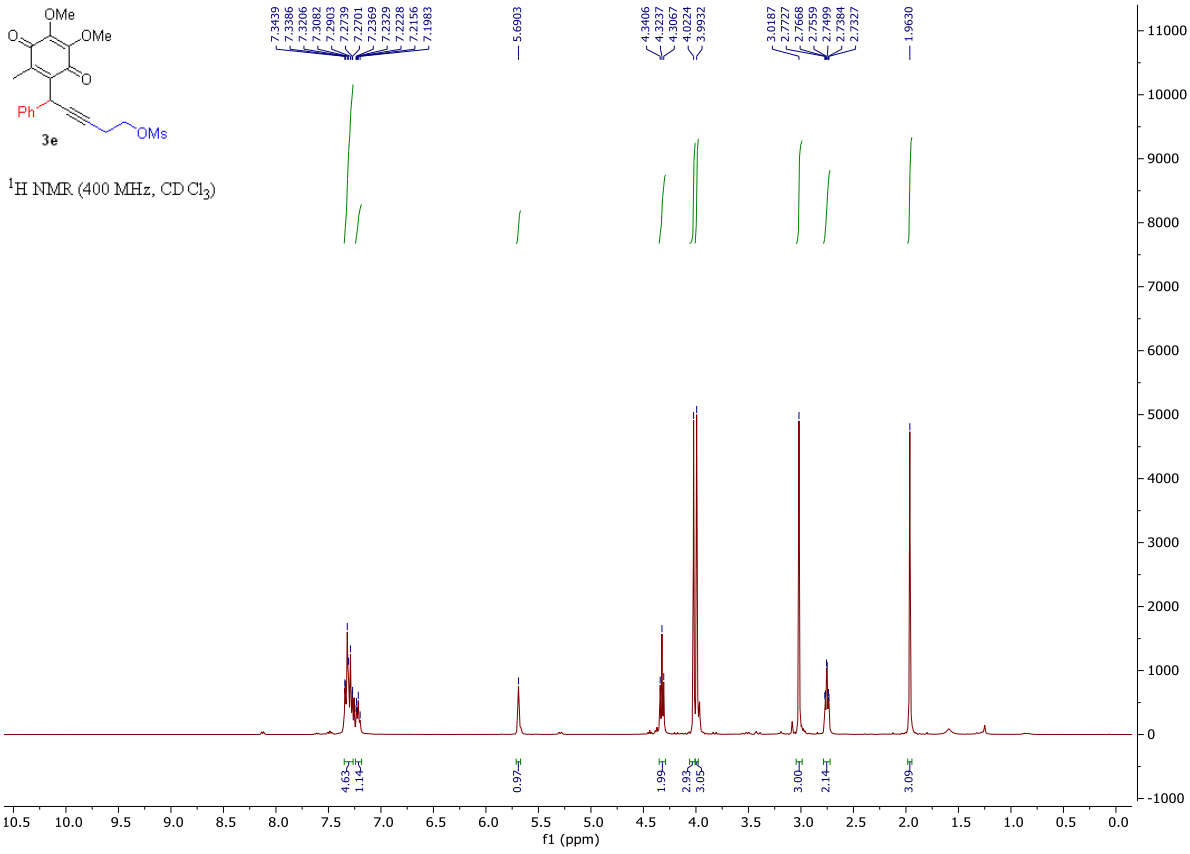

OH
TMS
2ae
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

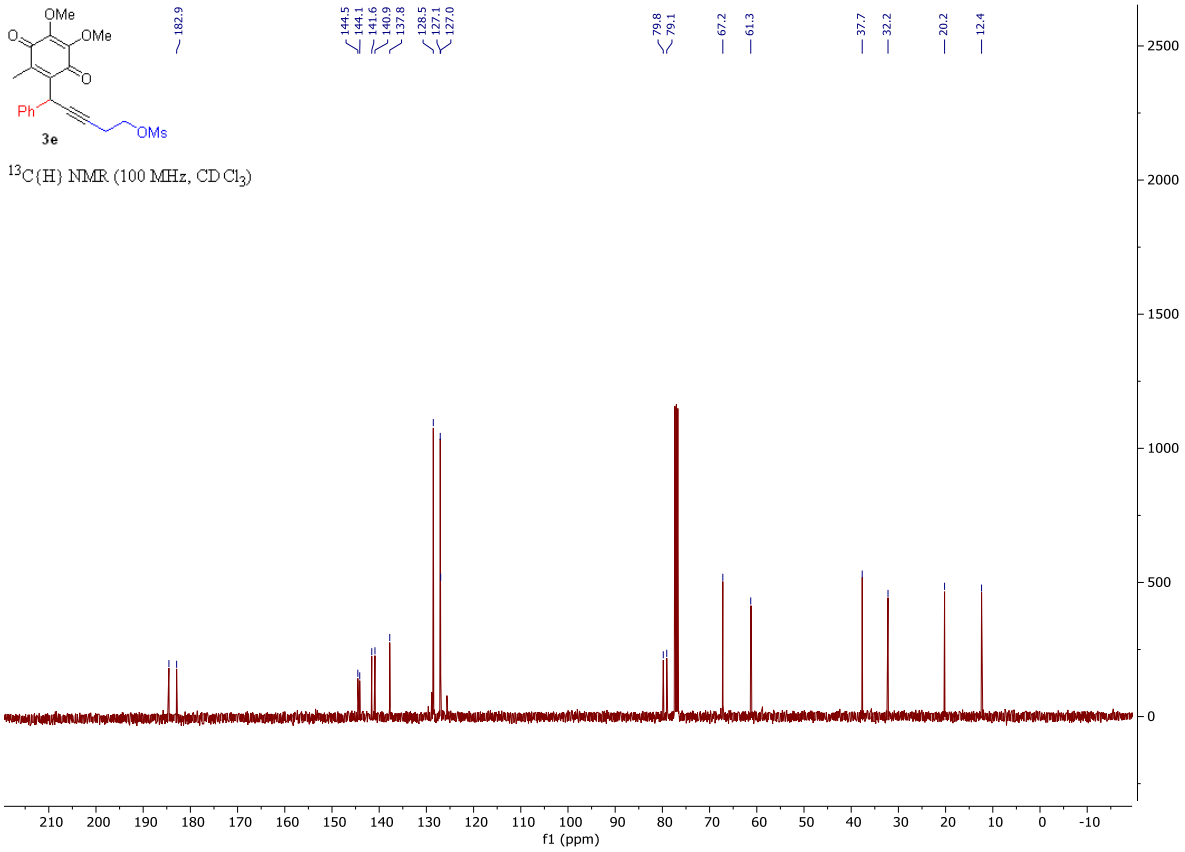

OMe
OMe
O
O
Ph
TMS
3a
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)

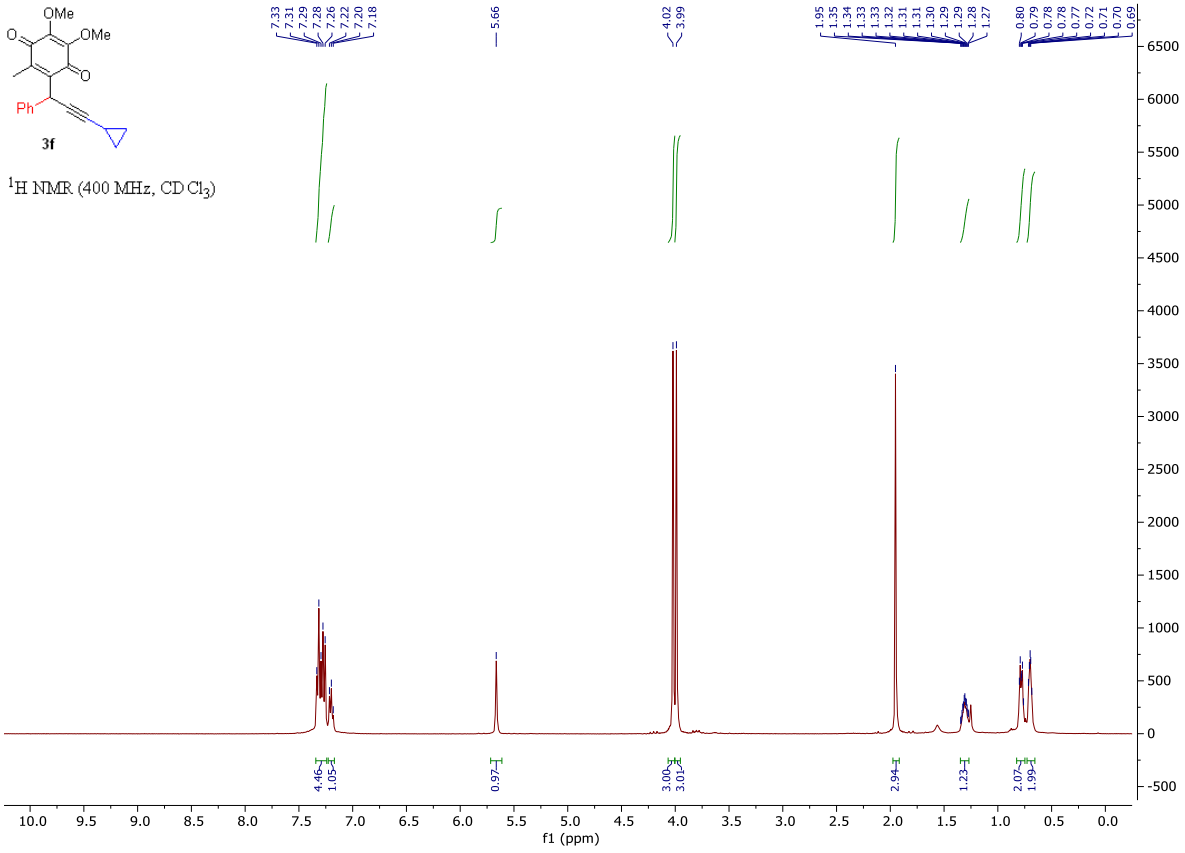

OMe
OMe
O
O
Ph
TMS
3a
184.7
183.0
144.6
144.1
141.8
140.8
137.7
128.5
127.1
126.9
102.7
89.8
61.3
61.2
32.9
12.3
-0.0
^{13}C(H) NMR (100 MHz, CD Cl$_3$)
f1 (ppm)

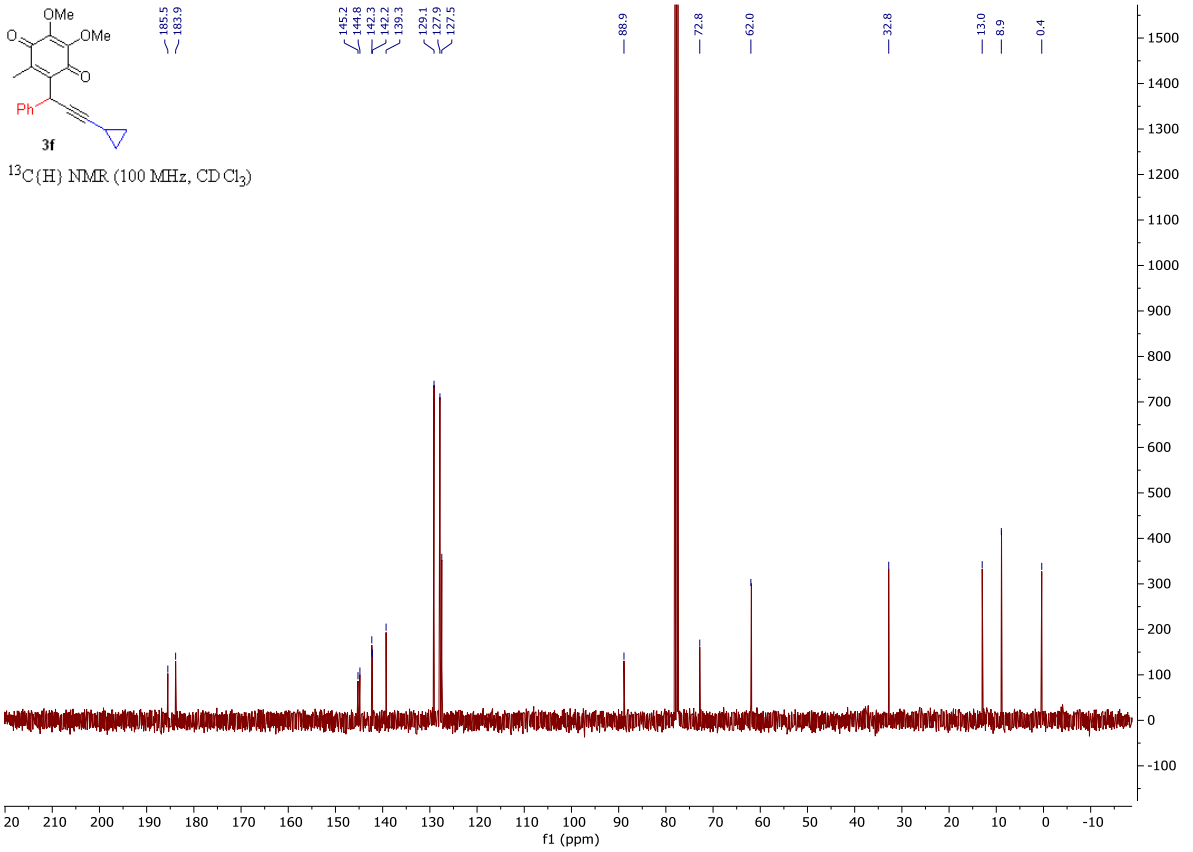

OMe
OMe
O
O
Ph
t-Bu
3d
7.35
7.35
7.34
7.34
7.33
7.30
7.28
7.28
7.26
7.23
7.22
7.21
7.20
7.20
7.19
7.18
7.18
7.18
5.69
4.04
4.00
1.98
1.27
2.02
2.07
1.05
0.99
2.95
3.01
3.00
8.94
^{1}H NMR (400 MHz, CD Cl$_3$)
f1 (ppm)


OMe
OMe
O
O
Ph
t-Bu
3d
184.9
183.3
144.5
144.1
141.8
141.5
138.7
128.4
127.2
126.7
93.6
75.4
61.3
61.1
31.8
31.1
27.7
12.2
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)

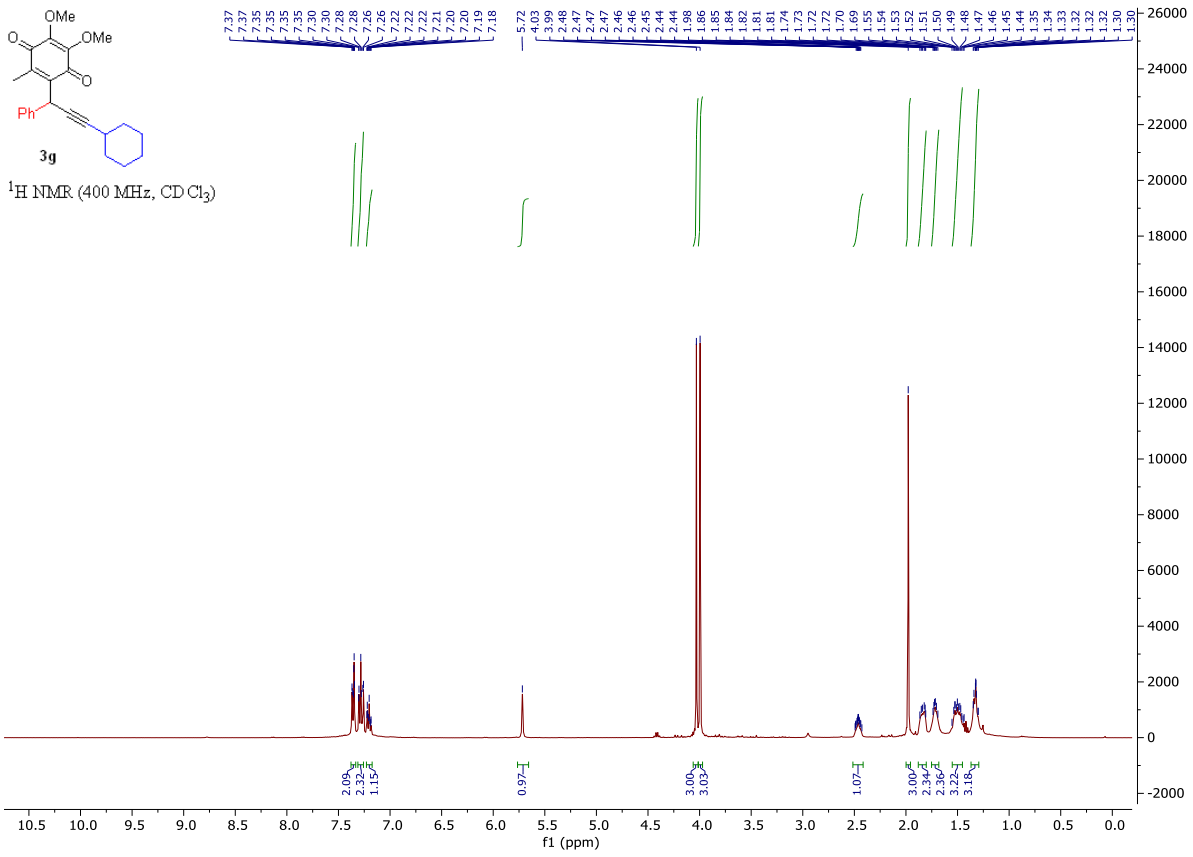

OMe
OMe
O
O
Ph
OMs
3e
7.3439
7.3386
7.3206
7.3082
7.2903
7.2739
7.2701
7.2369
7.2329
7.2228
7.2156
7.1983
5.6903
4.3406
4.3237
4.3067
4.0224
3.9932
3.0187
2.7727
2.7668
2.7559
2.7499
2.7384
2.7327
1.9630
4.63
1.14
0.97
1.99
2.93
3.05
3.00
2.14
3.09
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


OMe
OMe
O
O
Ph
OMs
3e
182.9
144.5
144.1
141.6
140.9
137.8
128.5
127.1
127.0
79.8
79.1
67.2
61.3
37.7
32.2
20.2
12.4
^{13}C(H) NMR (100 MHz, CD Cl$_3$)
f1 (ppm)

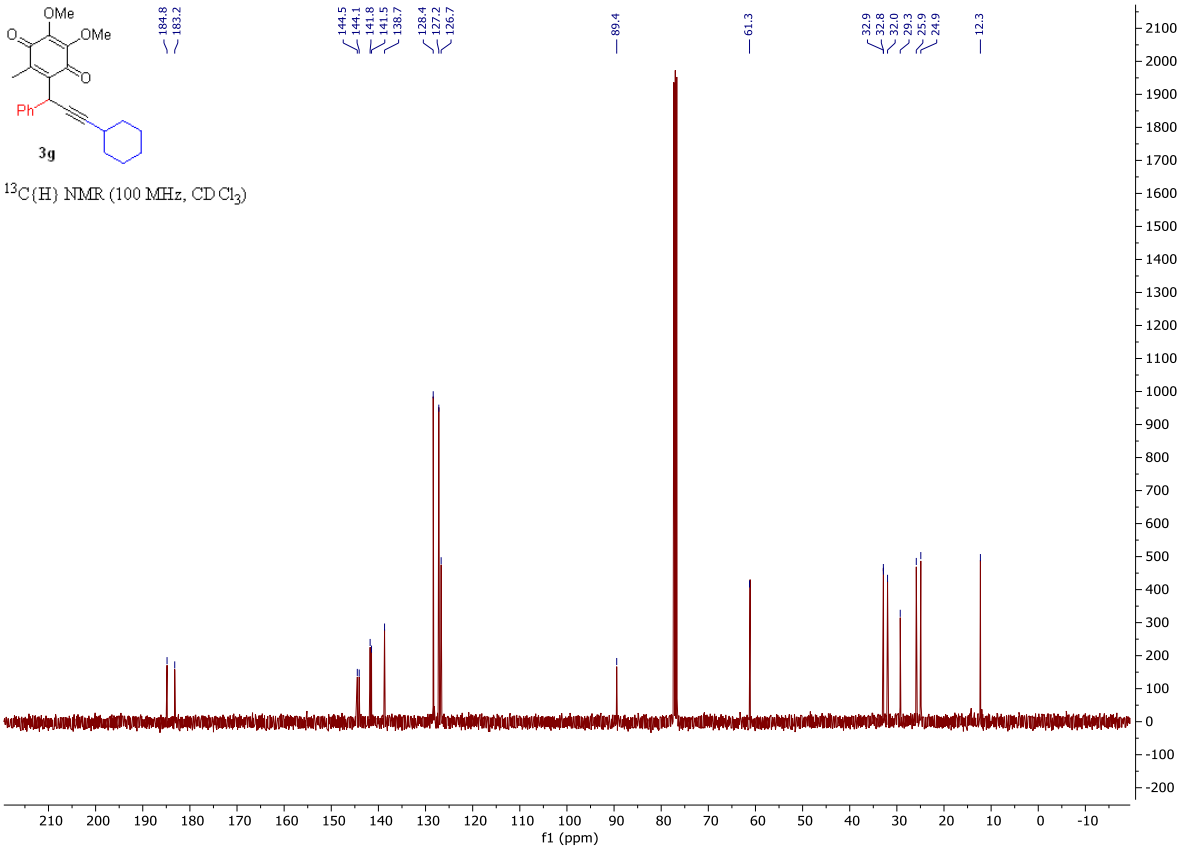

OMe
OMe
O
O
Ph
3f
^{1}H NMR (400 MHz, CD Cl$_3$)
7.33
7.31
7.29
7.28
7.26
7.22
7.20
7.18
5.66
4.02
3.99
1.95
1.35
1.34
1.33
1.33
1.32
1.31
1.31
1.30
1.29
1.29
1.28
1.27
0.80
0.79
0.78
0.78
0.77
0.72
0.71
0.70
0.69
4.46
1.05
0.97
3.00
3.01
2.94
1.23
2.07
1.99
f1 (ppm)



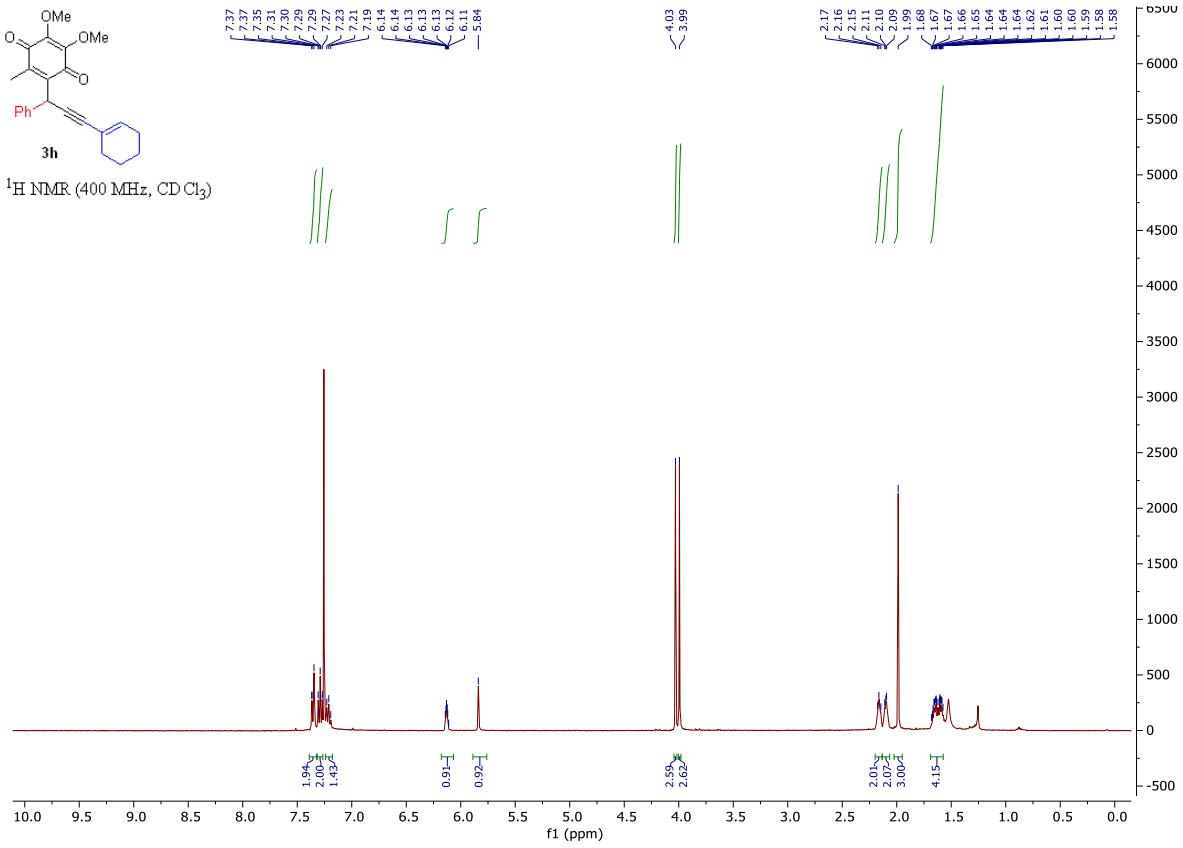
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



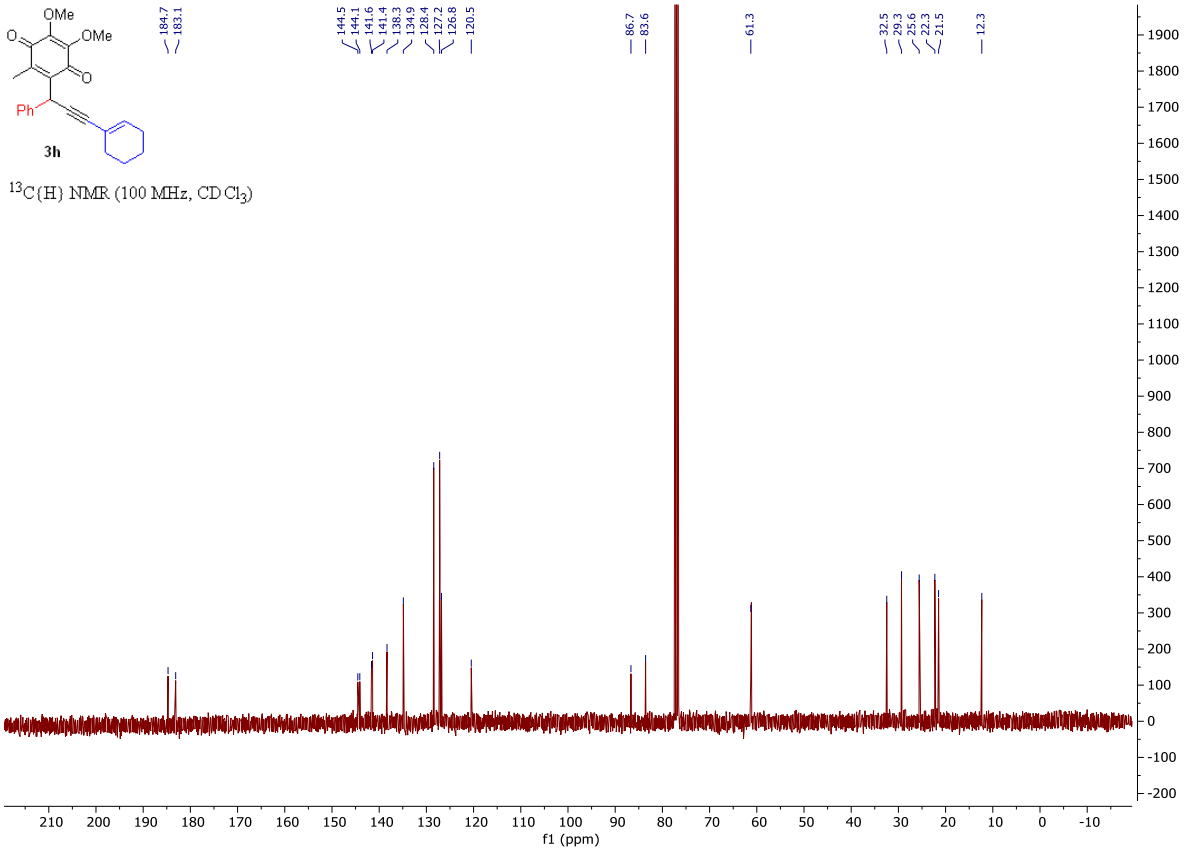
^{1}H NMR (400 MHz, $CDCl_3$)

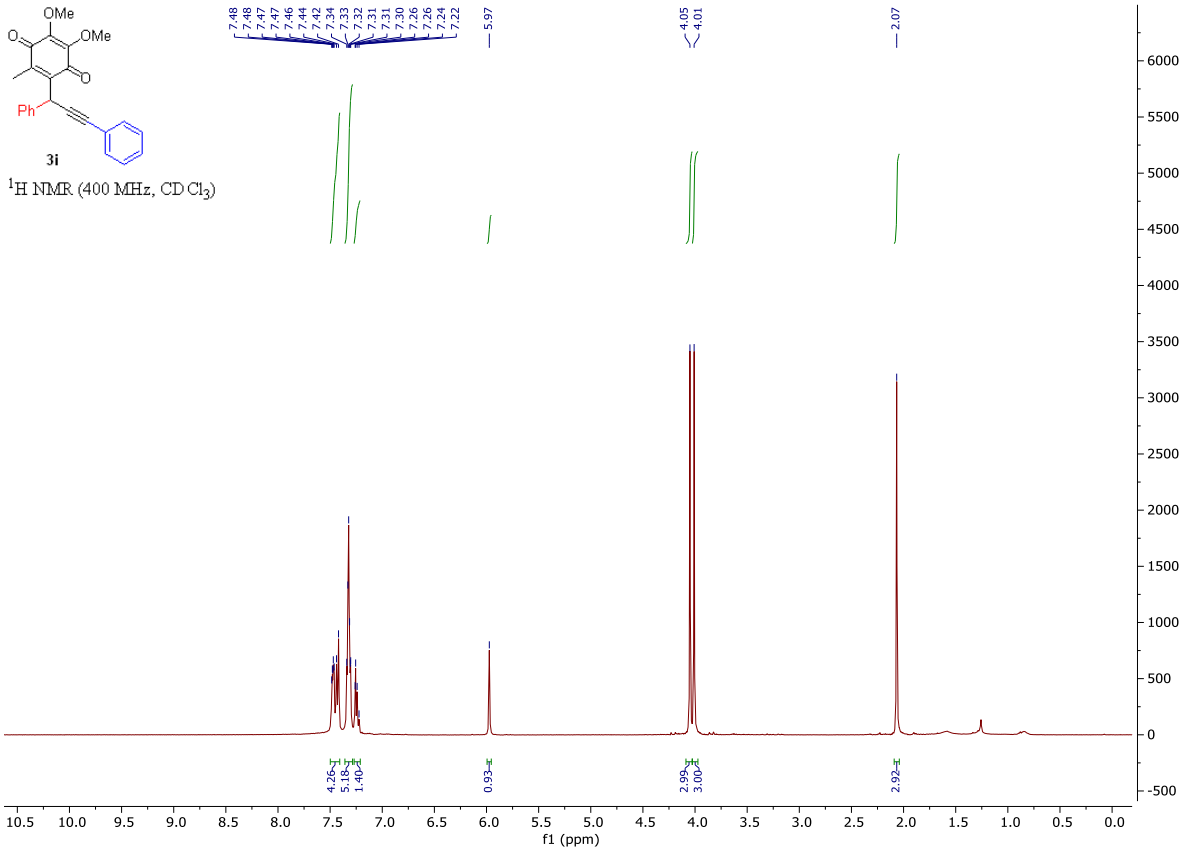


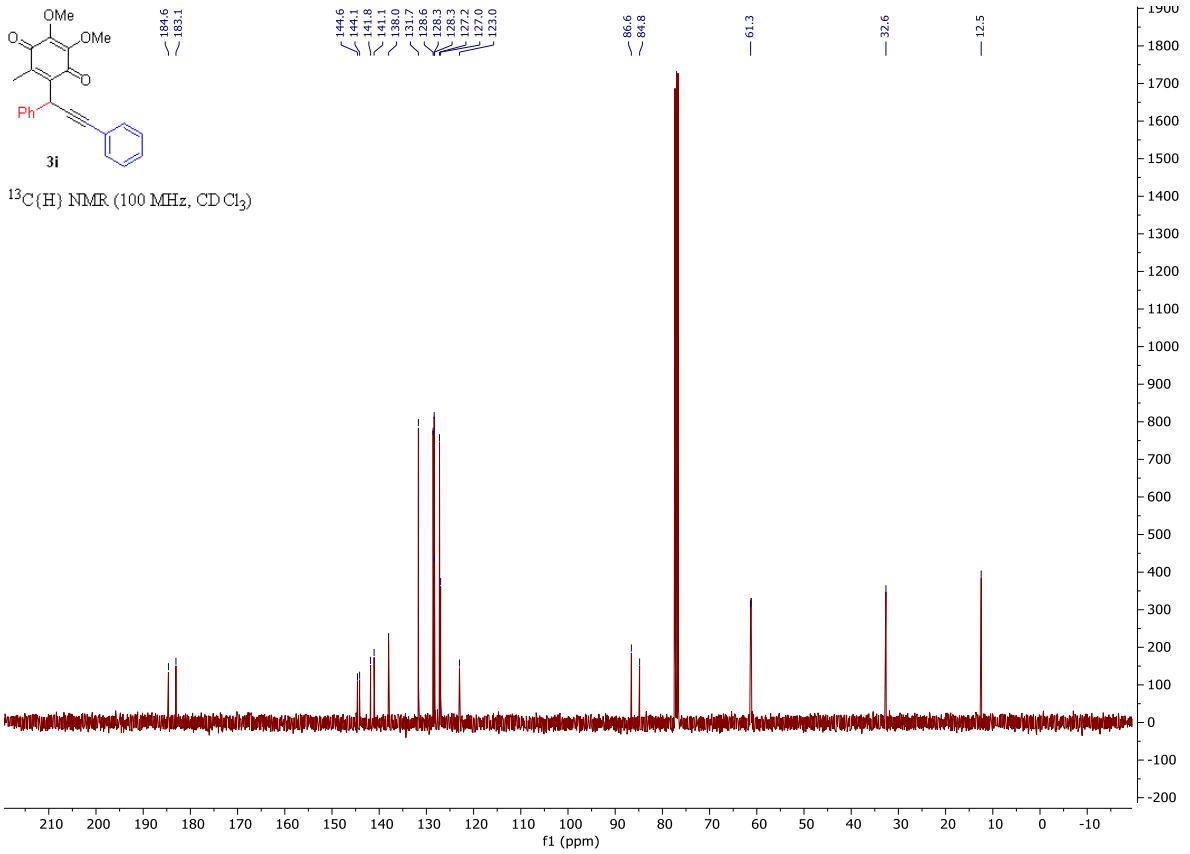
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



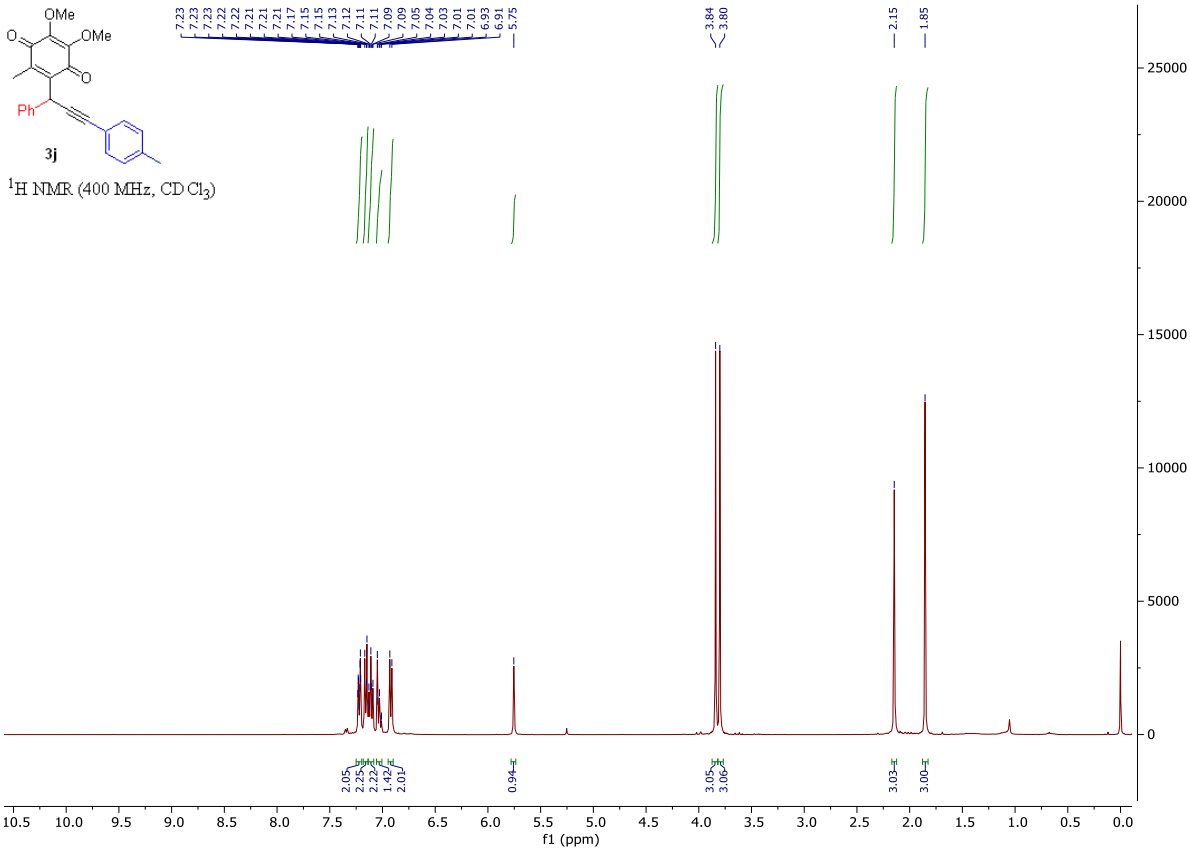
^{1}H NMR (400 MHz, $CDCl_3$)


OMe
OMe
O
O
Ph
3h
^{13}C{H} NMR (100 MHz, CD Cl$_3$)
184.7
183.1
144.5
144.1
141.6
141.4
138.3
134.9
128.4
127.2
126.8
120.5
86.7
83.6
61.3
32.5
29.3
25.6
22.3
21.5
12.3
f1 (ppm)

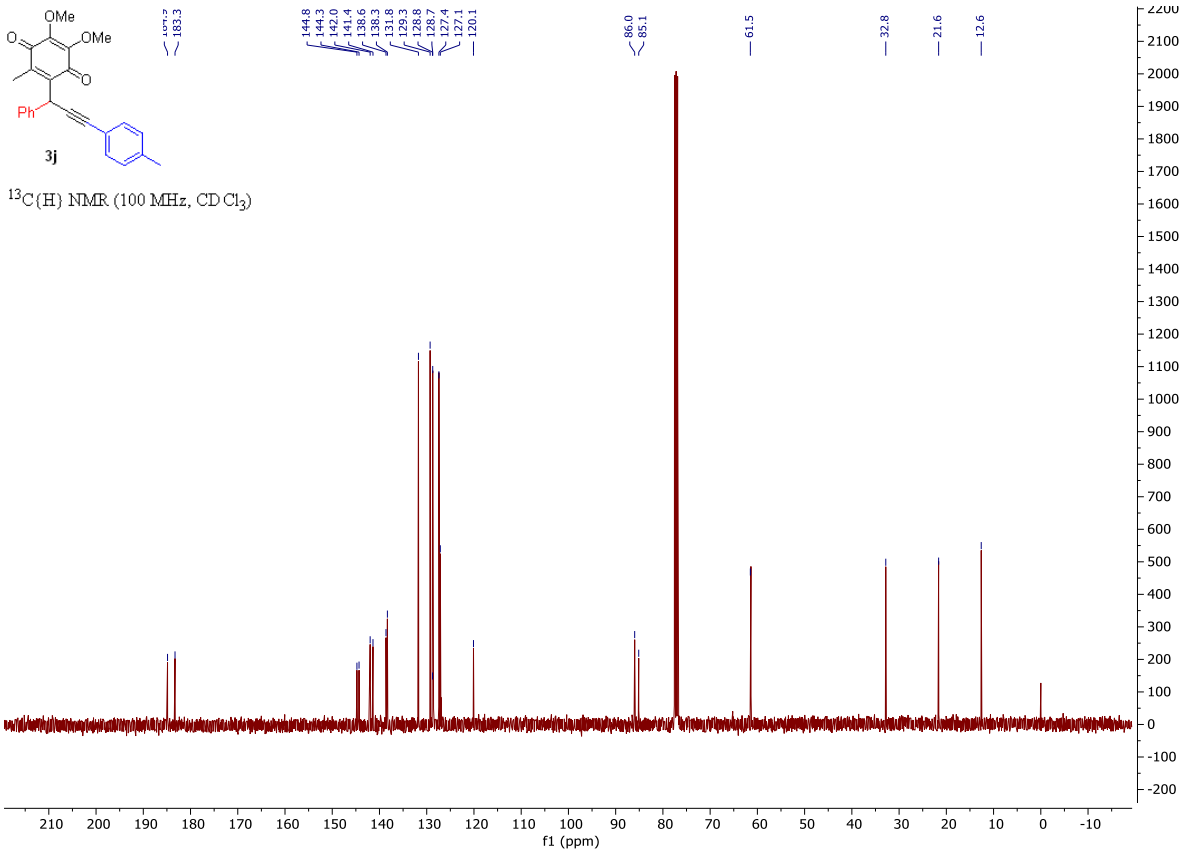

OMe
OMe
O
O
Ph
3i
^{1}H NMR (400 MHz, CD Cl$_3$)
7.48
7.48
7.47
7.47
7.46
7.44
7.42
7.34
7.33
7.32
7.31
7.31
7.30
7.26
7.26
7.24
7.22
5.97
4.05
4.01
2.07
4.26
5.18
1.40
0.93
2.99
3.00
2.92
f1 (ppm)

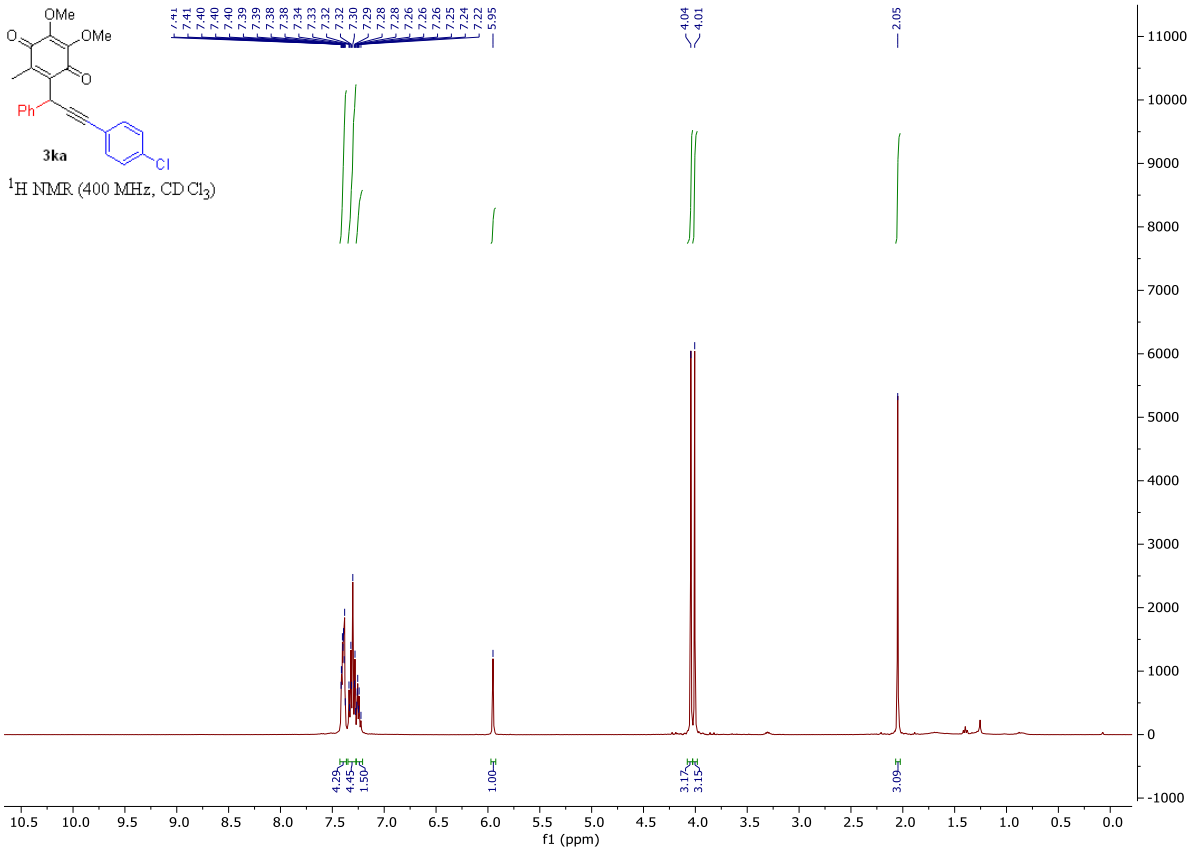


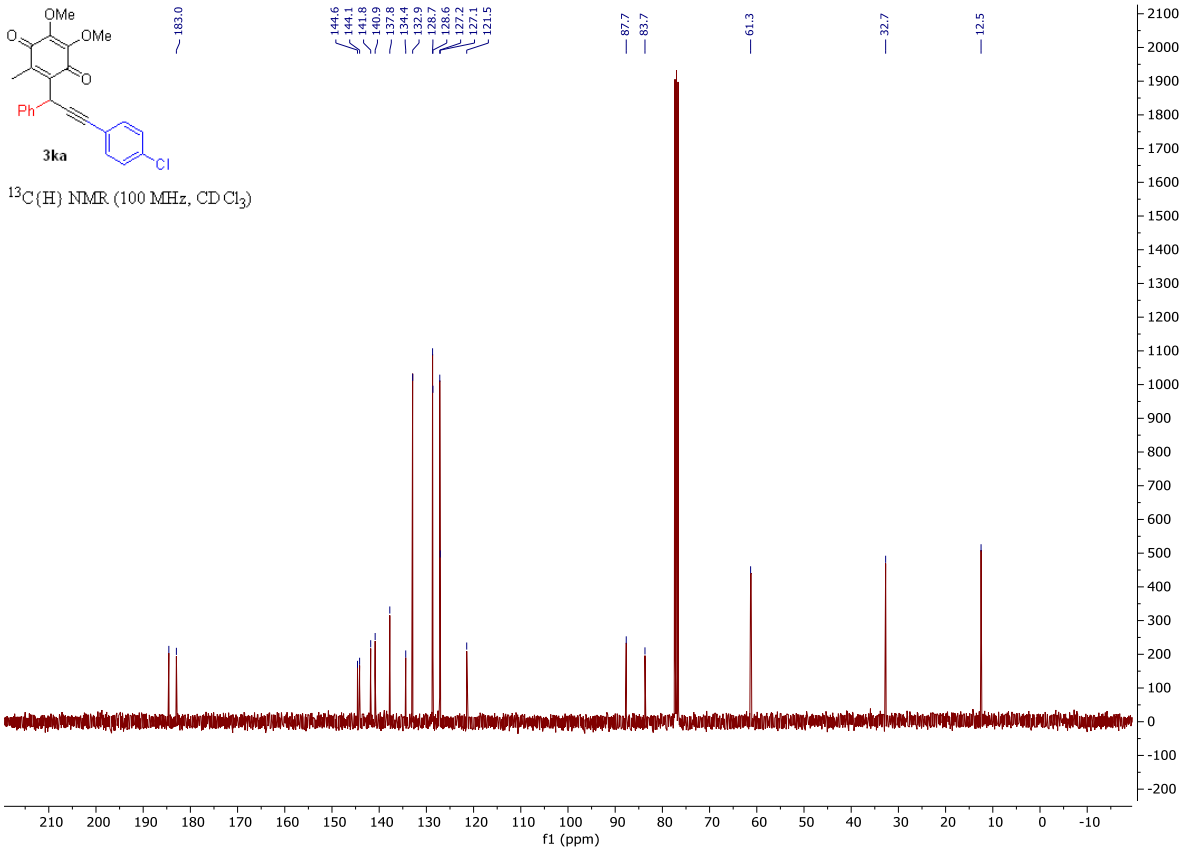
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



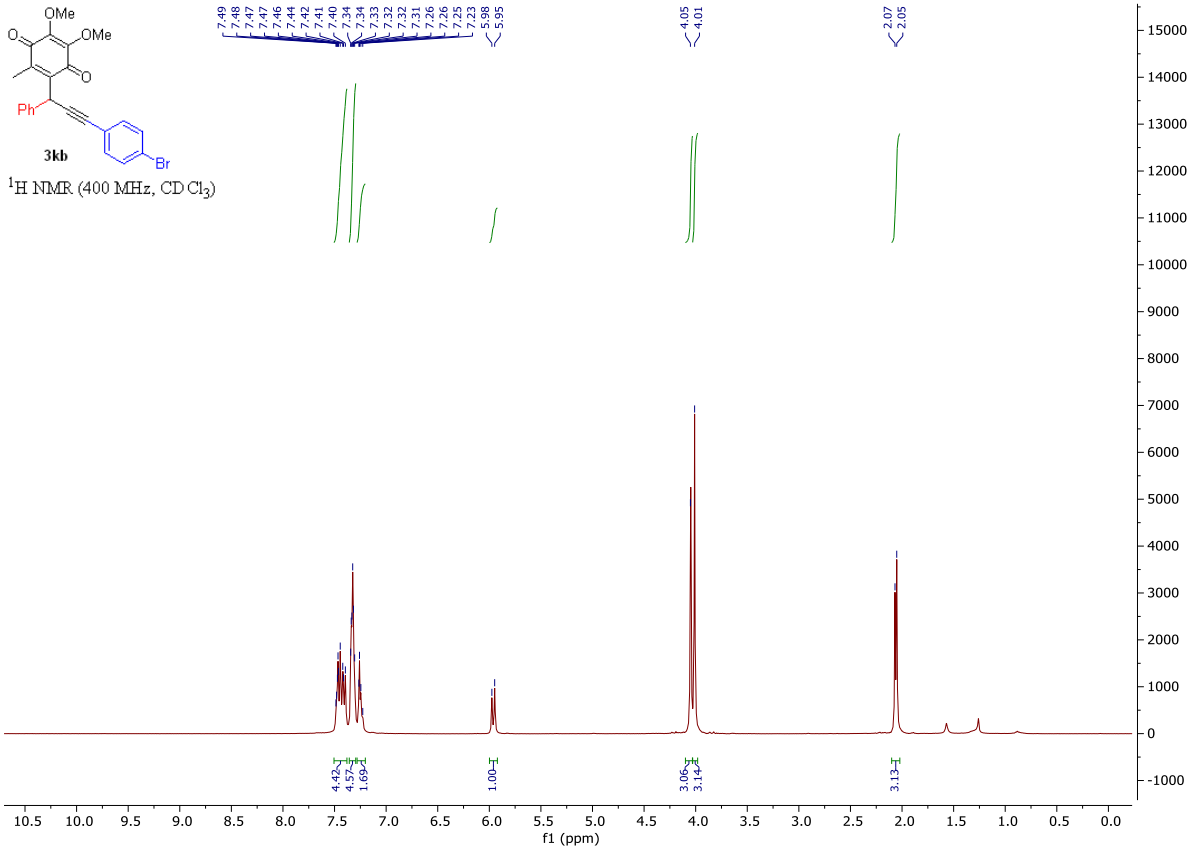
^{1}H NMR (400 MHz, $CDCl_3$)


OMe
OMe
O
O
Ph
3j
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
183.3
144.8
144.3
142.0
141.4
138.6
138.3
131.8
129.3
128.8
128.7
127.4
127.1
120.1
86.0
85.1
61.5
32.8
21.6
12.6
f1 (ppm)

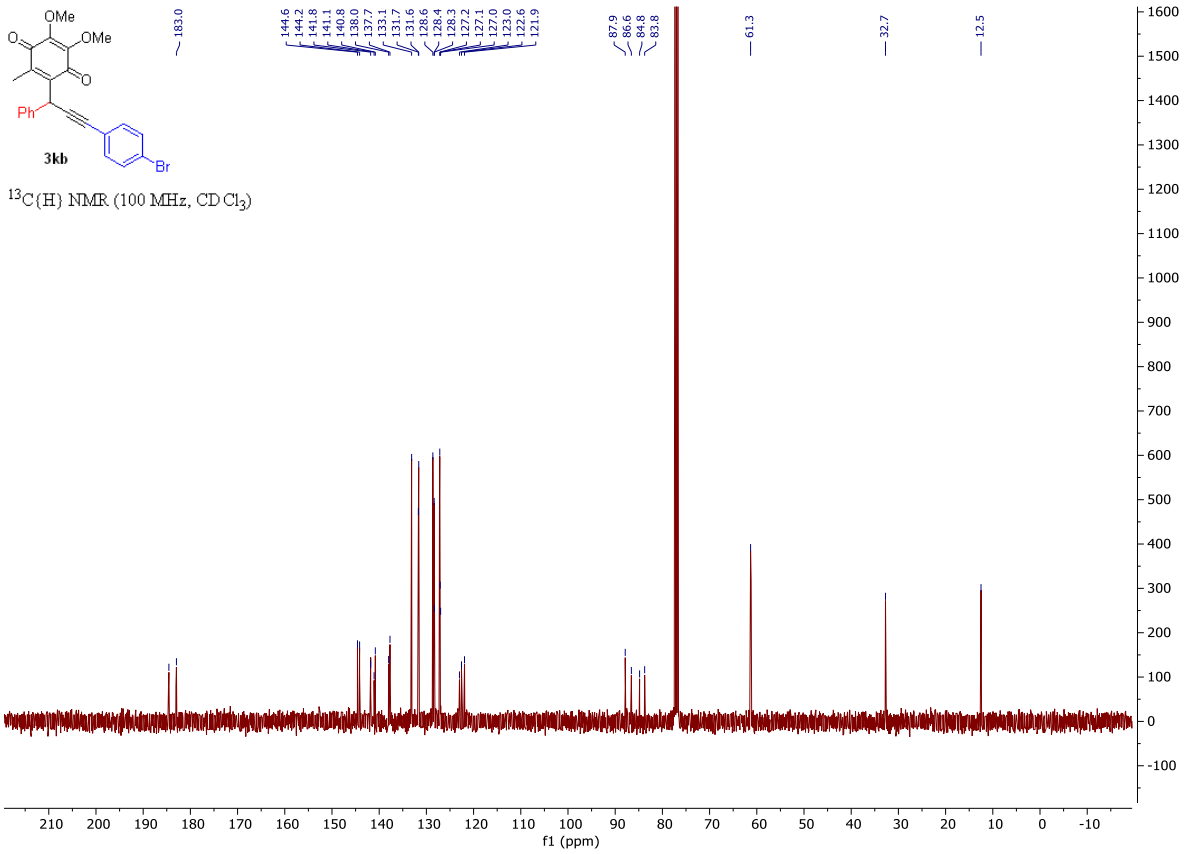

OMe
OMe
O
O
Ph
Cl
3ka
^{1}H NMR (400 MHz, $CDCl_3$)
7.41
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.34
7.33
7.32
7.32
7.30
7.29
7.28
7.28
7.26
7.26
7.26
7.25
7.24
7.22
5.95
4.04
4.01
2.05
4.29
4.45
1.50
1.00
3.17
3.15
3.09
f1 (ppm)



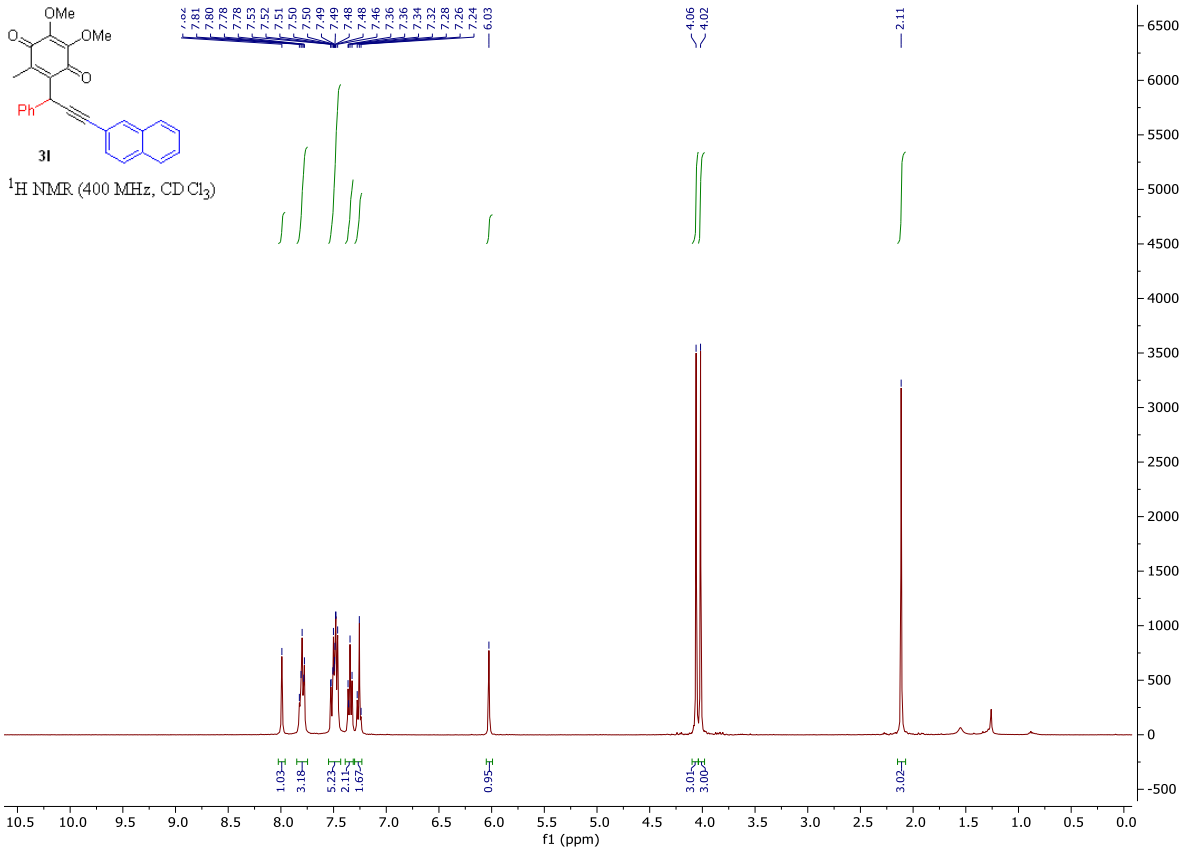
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



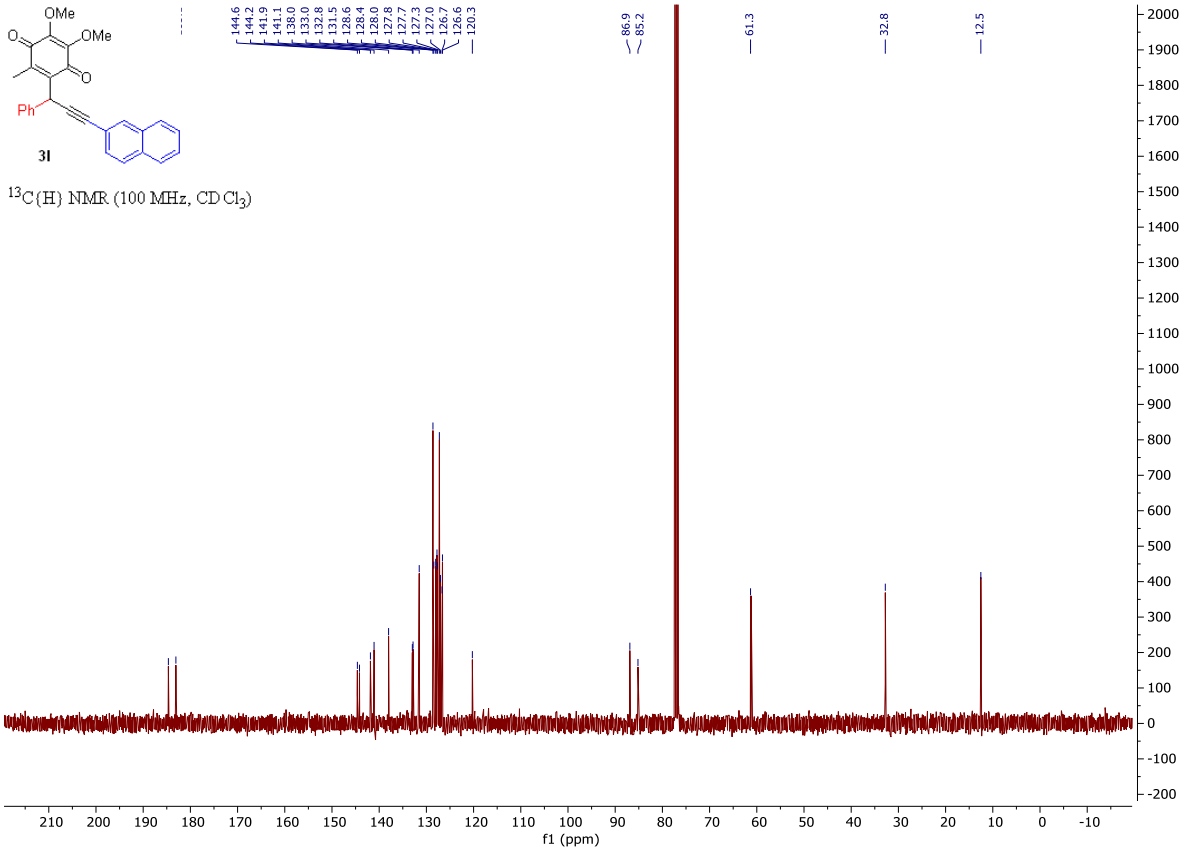
^{1}H NMR (400 MHz, $CDCl_3$)



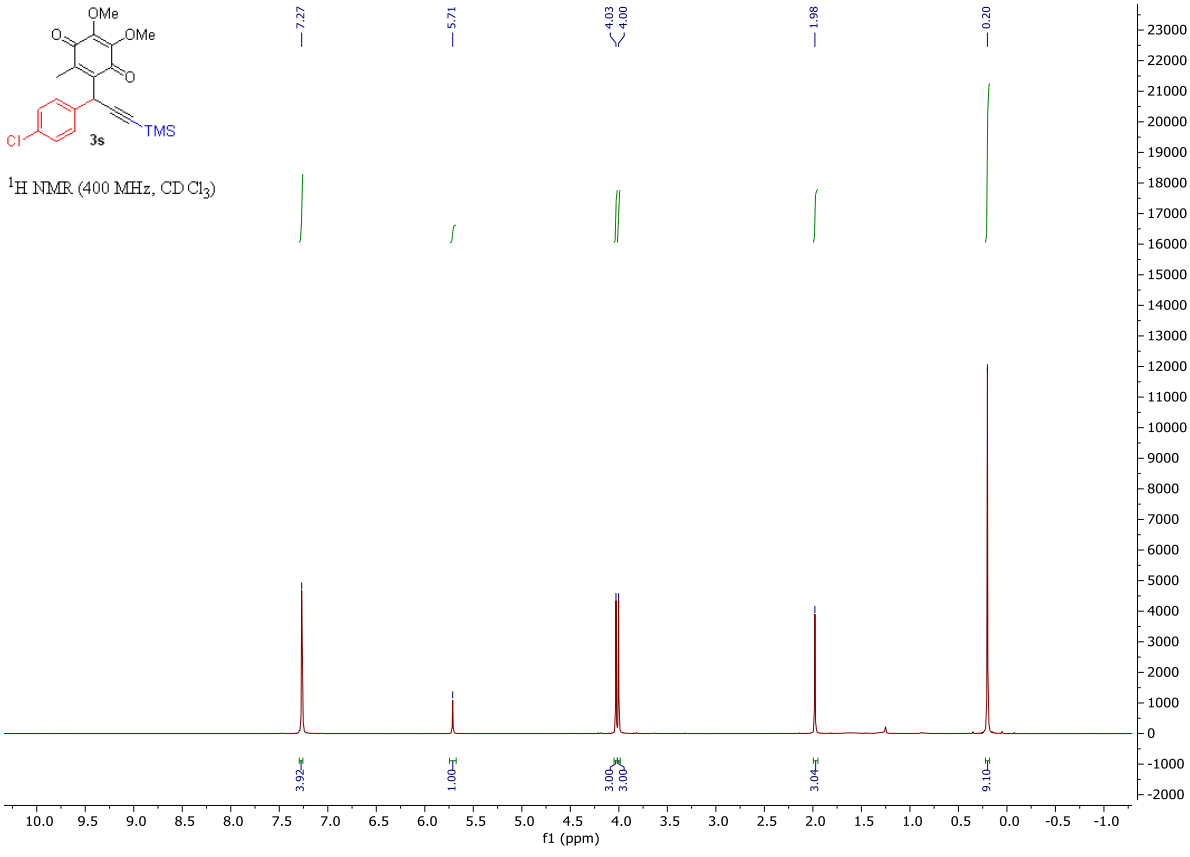
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



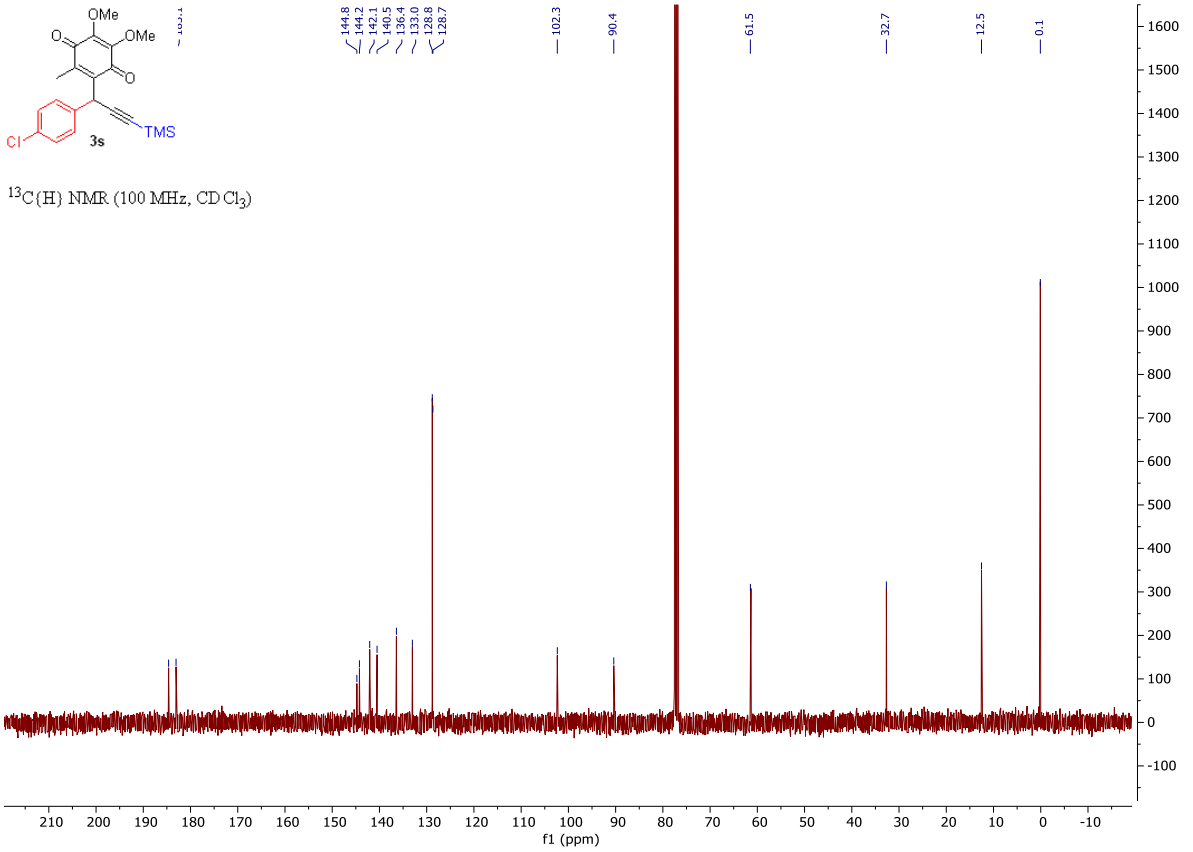
^{1}H NMR (400 MHz, $CDCl_3$)

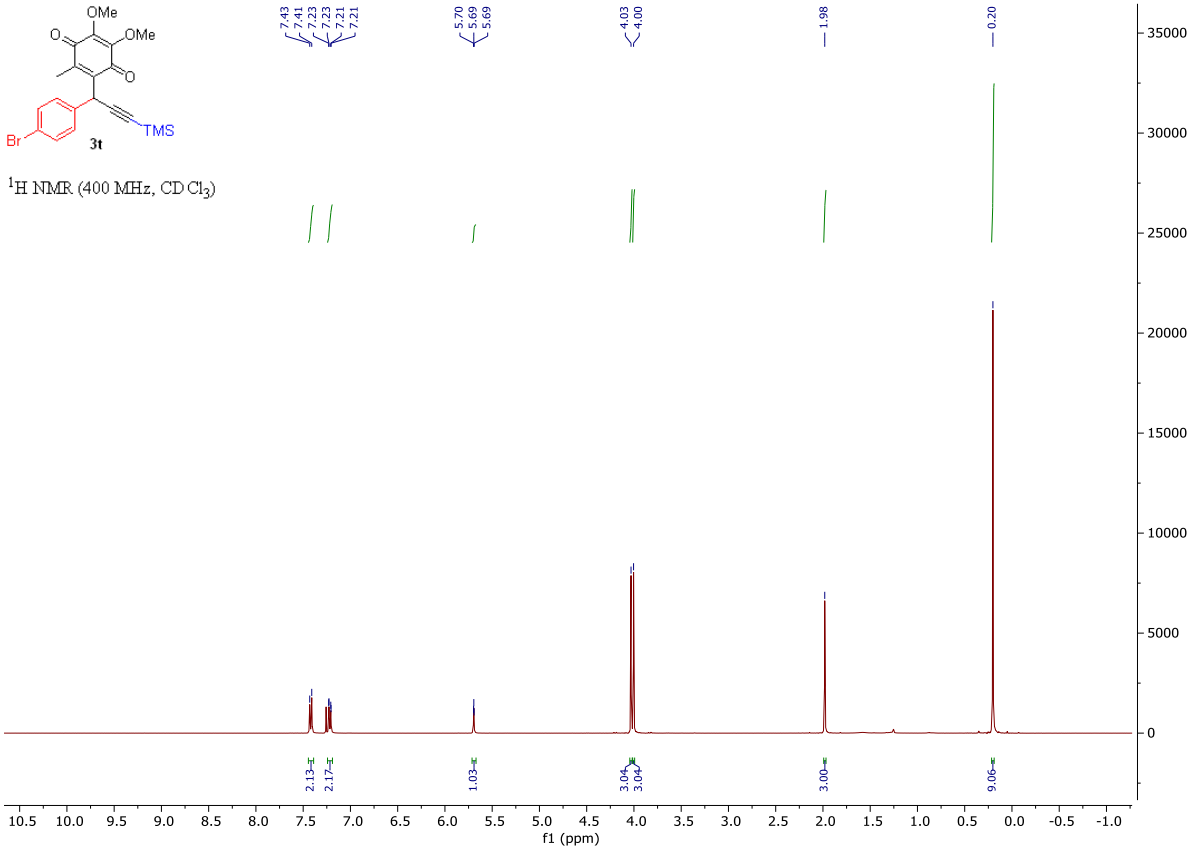


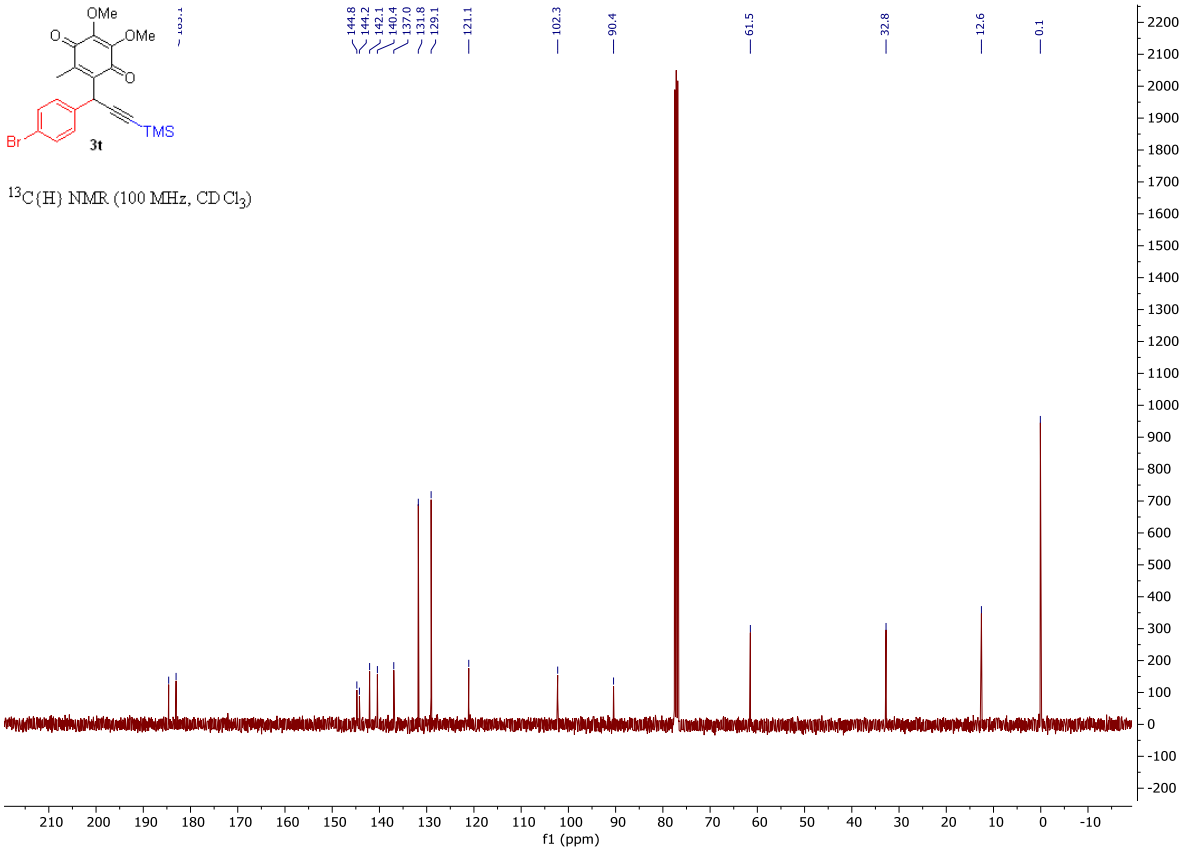
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)

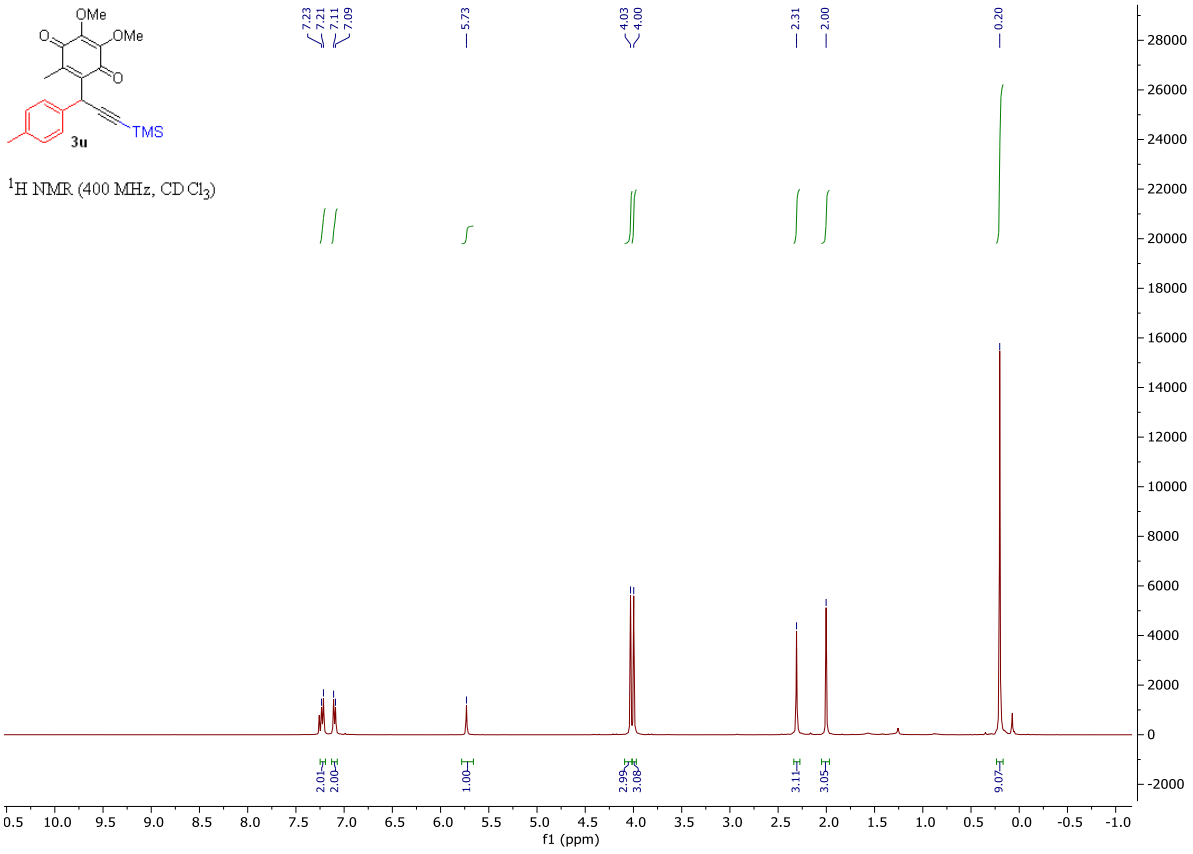


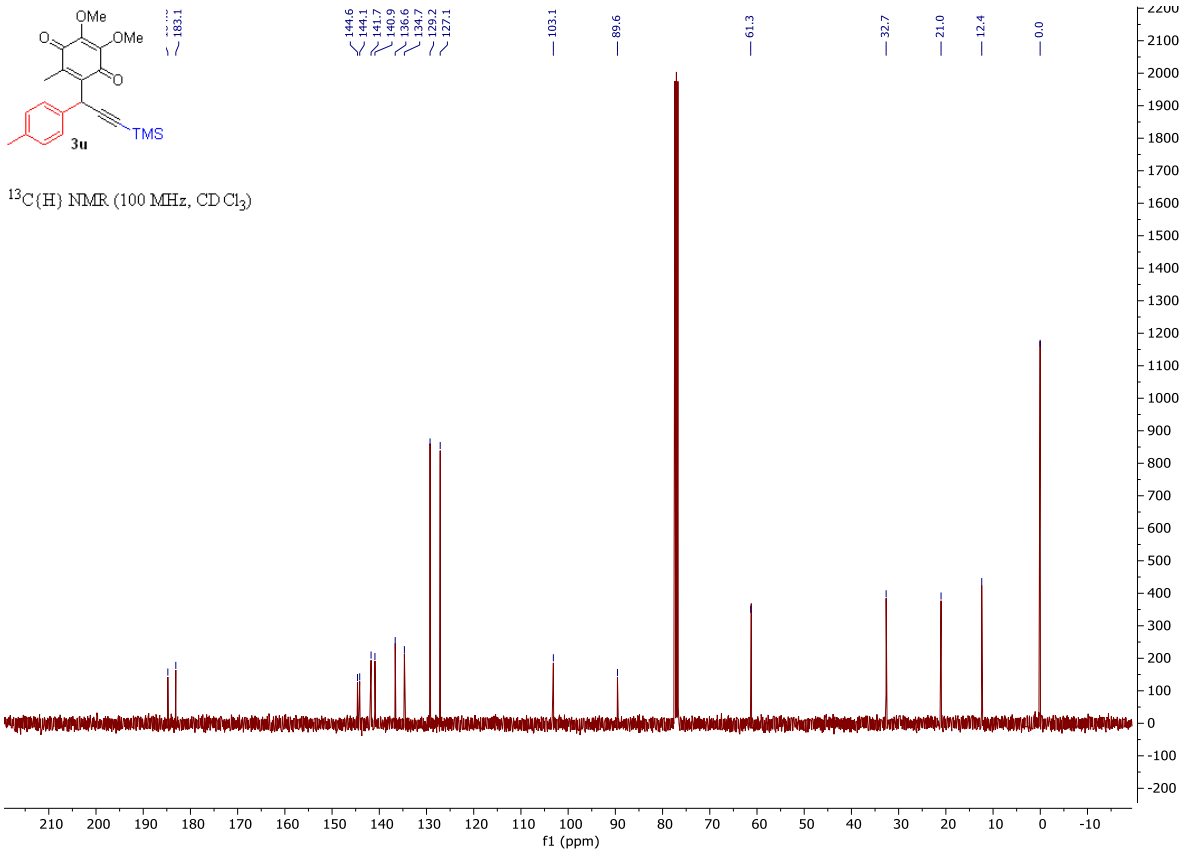
^{1}H NMR (400 MHz, $CDCl_3$)


OMe
OMe
O
O
Cl
TMS
3s
144.8
144.2
142.1
140.5
136.4
133.0
128.8
128.7
102.3
90.4
61.5
32.7
12.5
0.1
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)

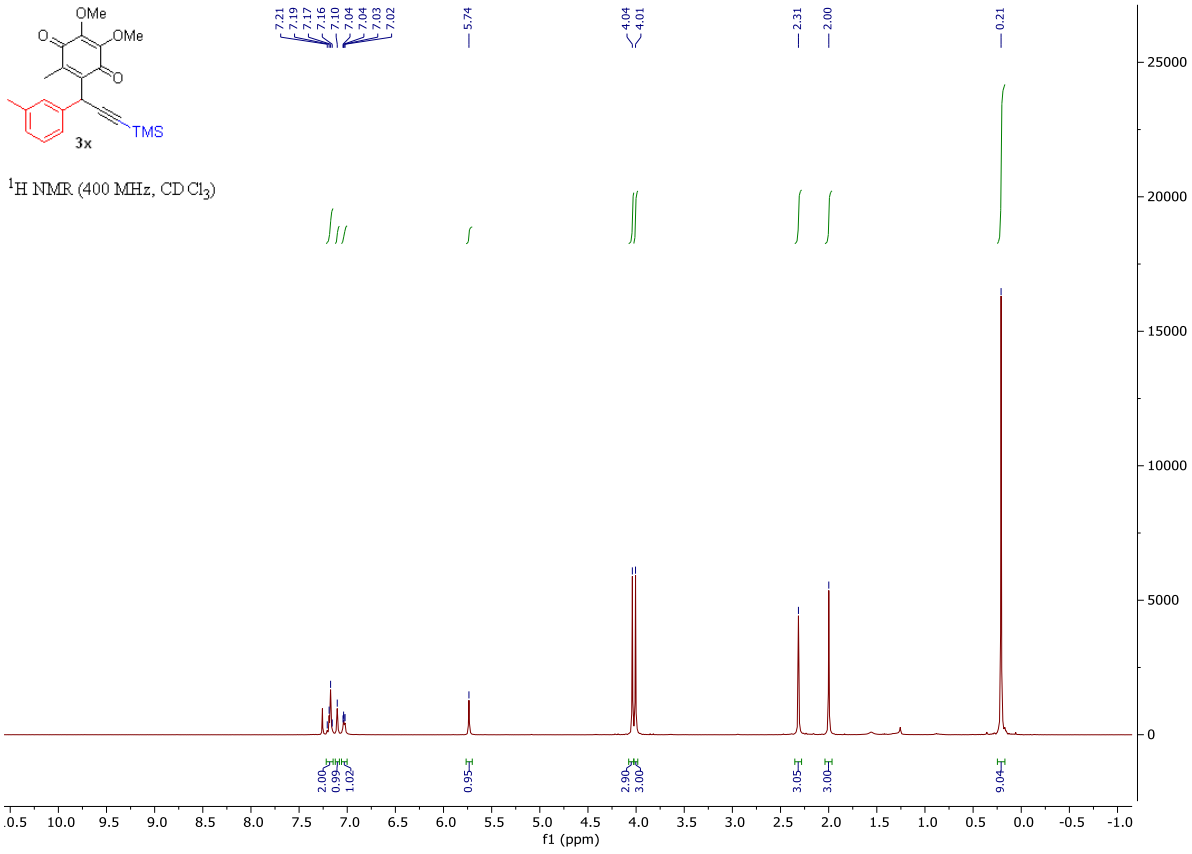

OMe
OMe
O
O
Br
TMS
3t
7.43
7.41
7.23
7.23
7.21
7.21
5.70
5.69
5.69
4.03
4.00
1.98
0.20
^{1}H NMR (400 MHz, $CDCl_3$)
2.13
2.17
1.03
3.04
3.04
3.00
9.06
f1 (ppm)


OMe
OMe
O
O
Br
TMS
3t
144.8
144.2
142.1
140.4
137.0
131.8
129.1
121.1
102.3
90.4
61.5
32.8
12.6
0.1
^{13}C{H} NMR (100 MHz, CD Cl$_3$)
f1 (ppm)

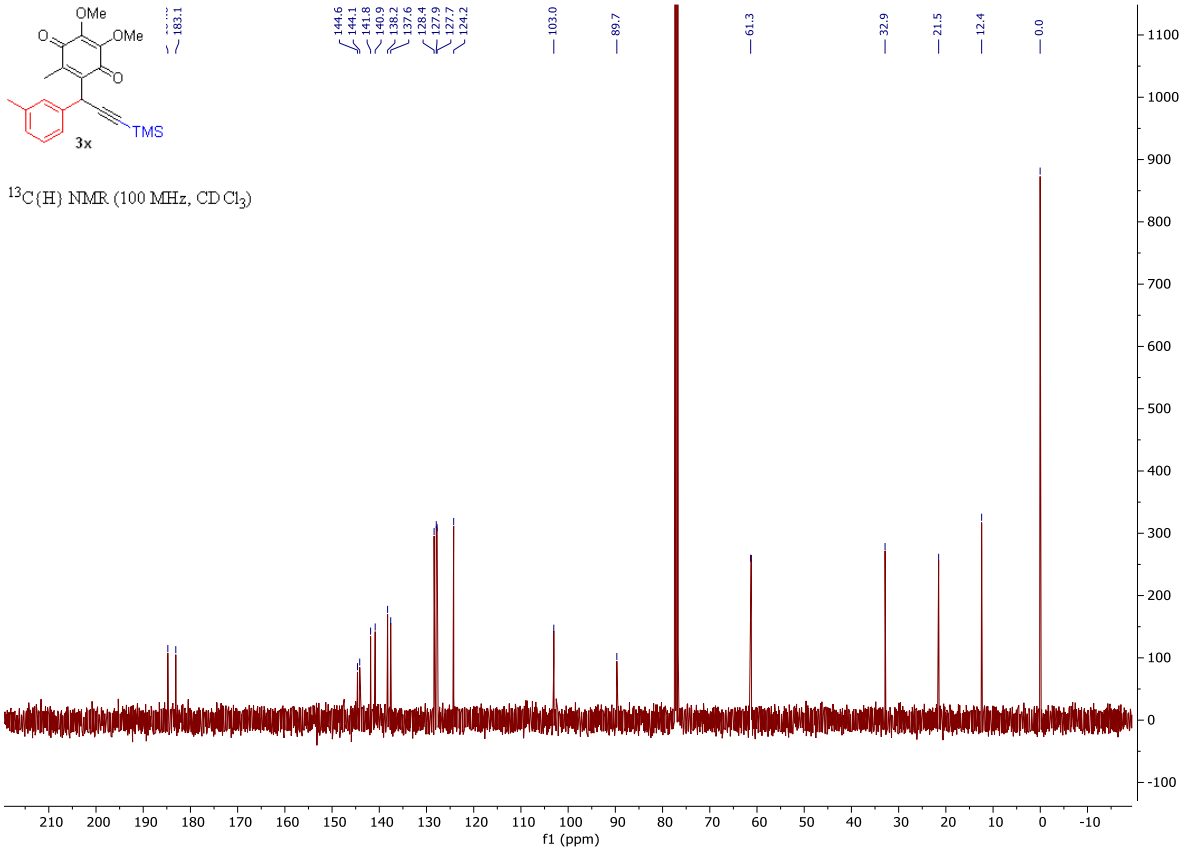

OMe
OMe
O
O
TMS
3u
7.23
7.21
7.11
7.09
5.73
4.03
4.00
2.31
2.00
0.20
^{1}H NMR (400 MHz, CD Cl$_3$)
2.01
2.00
1.00
2.99
3.08
3.11
3.05
9.07
f1 (ppm)

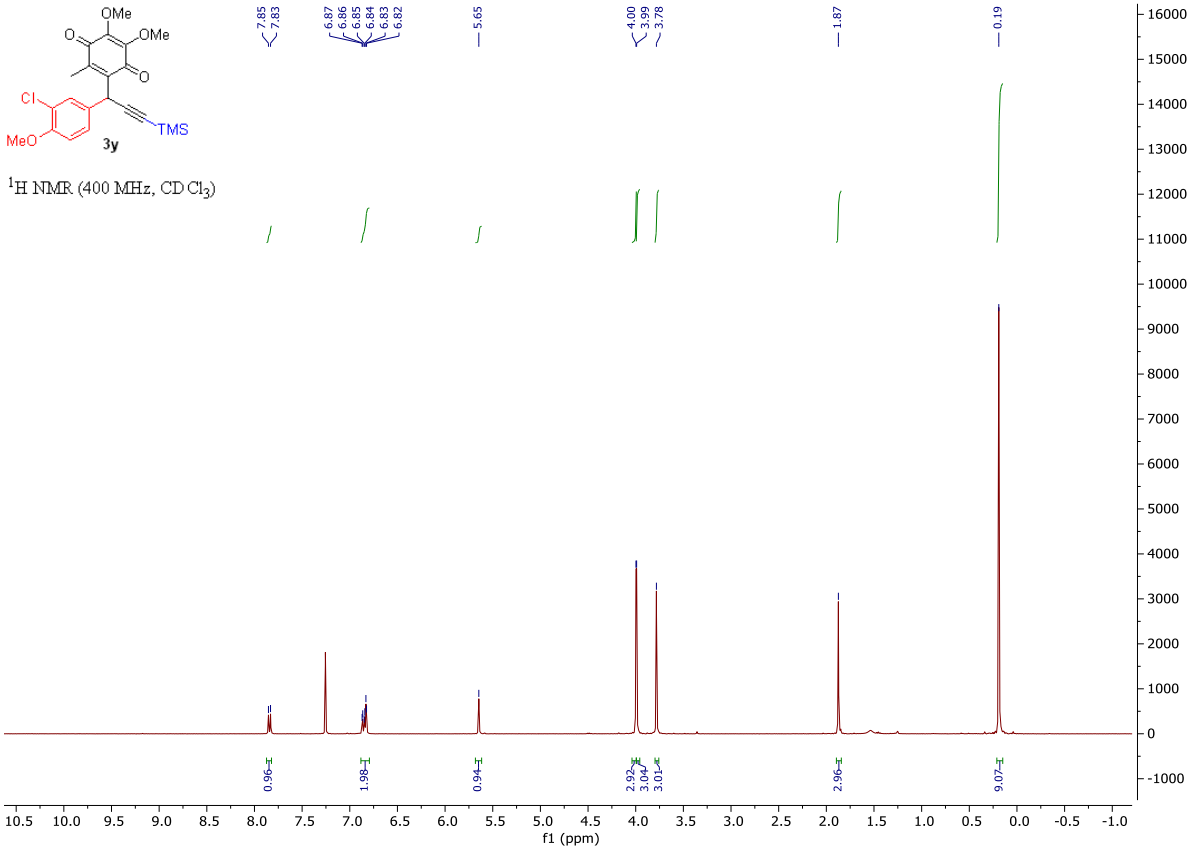


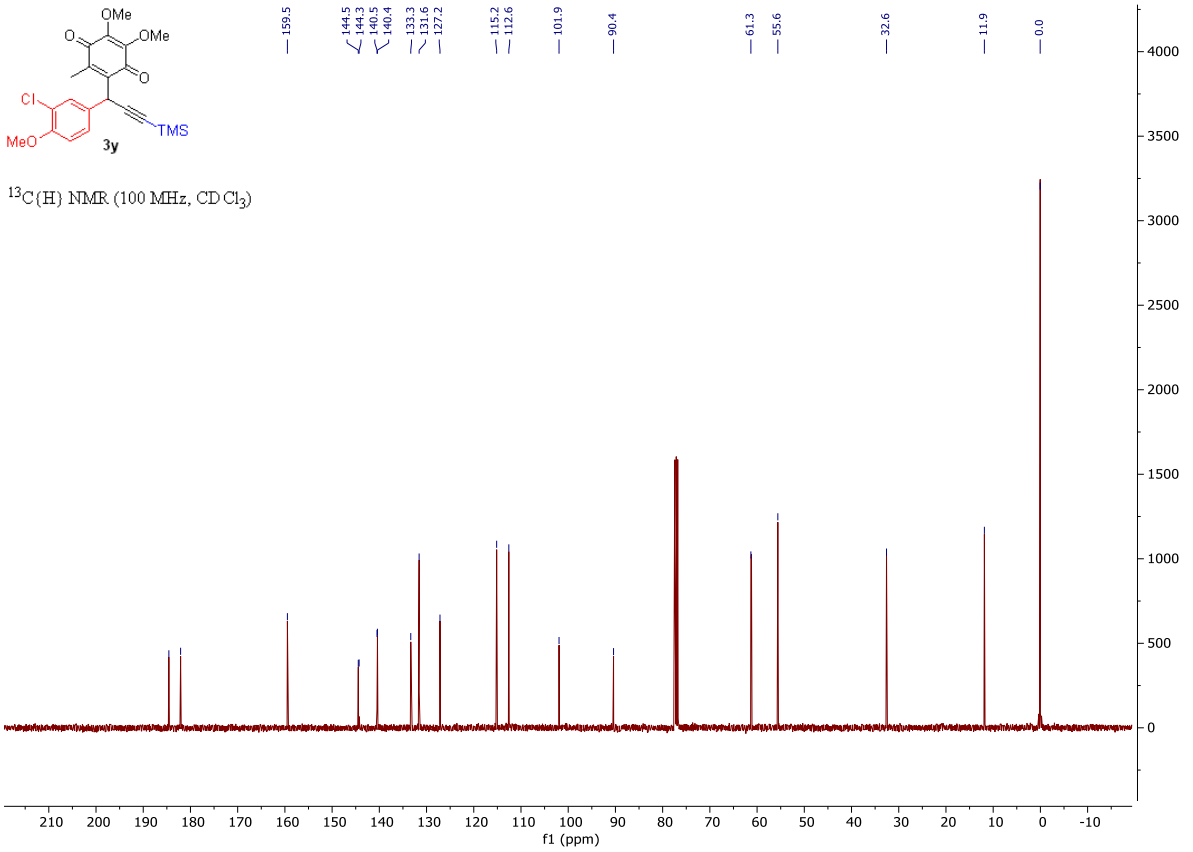
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



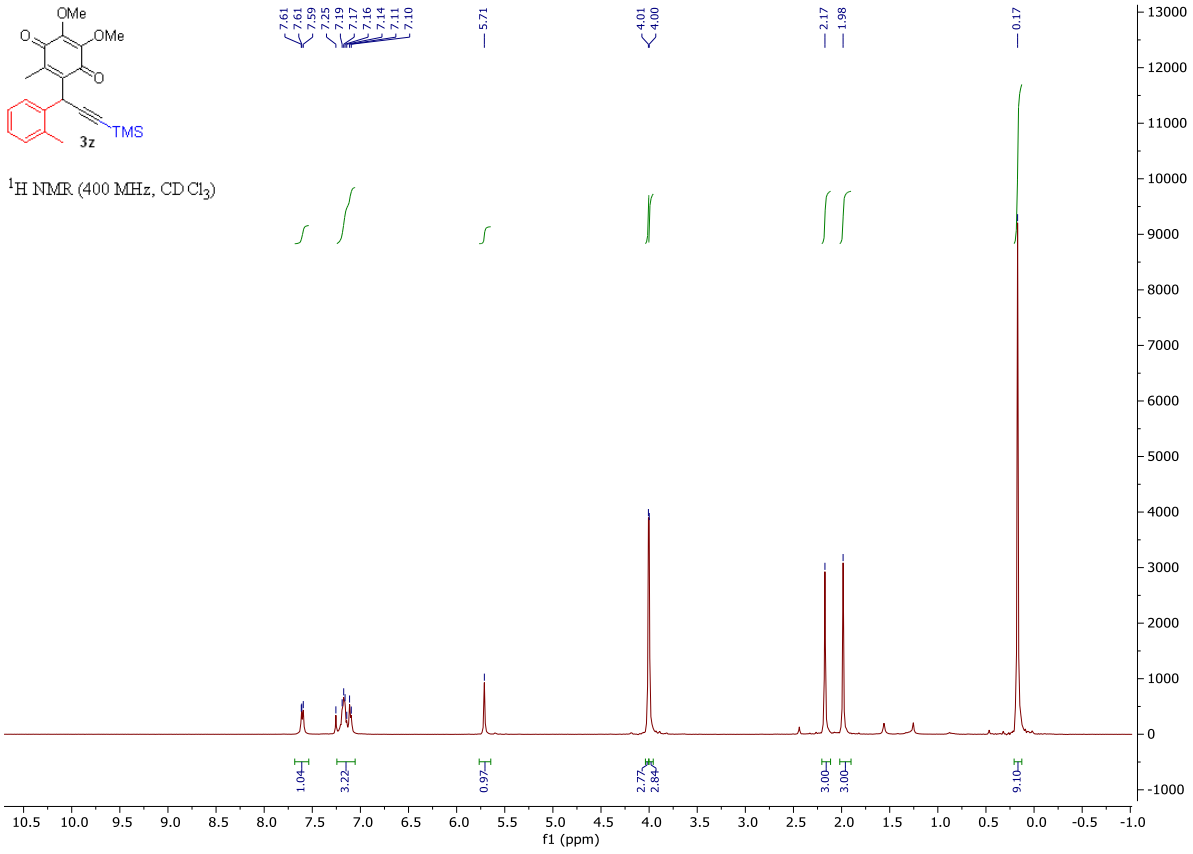
^{1}H NMR (400 MHz, $CDCl_3$)


OMe
OMe
O
O
TMS
3x
183.1
144.6
144.1
141.8
140.9
138.2
137.6
128.4
127.9
127.7
124.2
103.0
89.7
61.3
32.9
21.5
12.4
0.0
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)

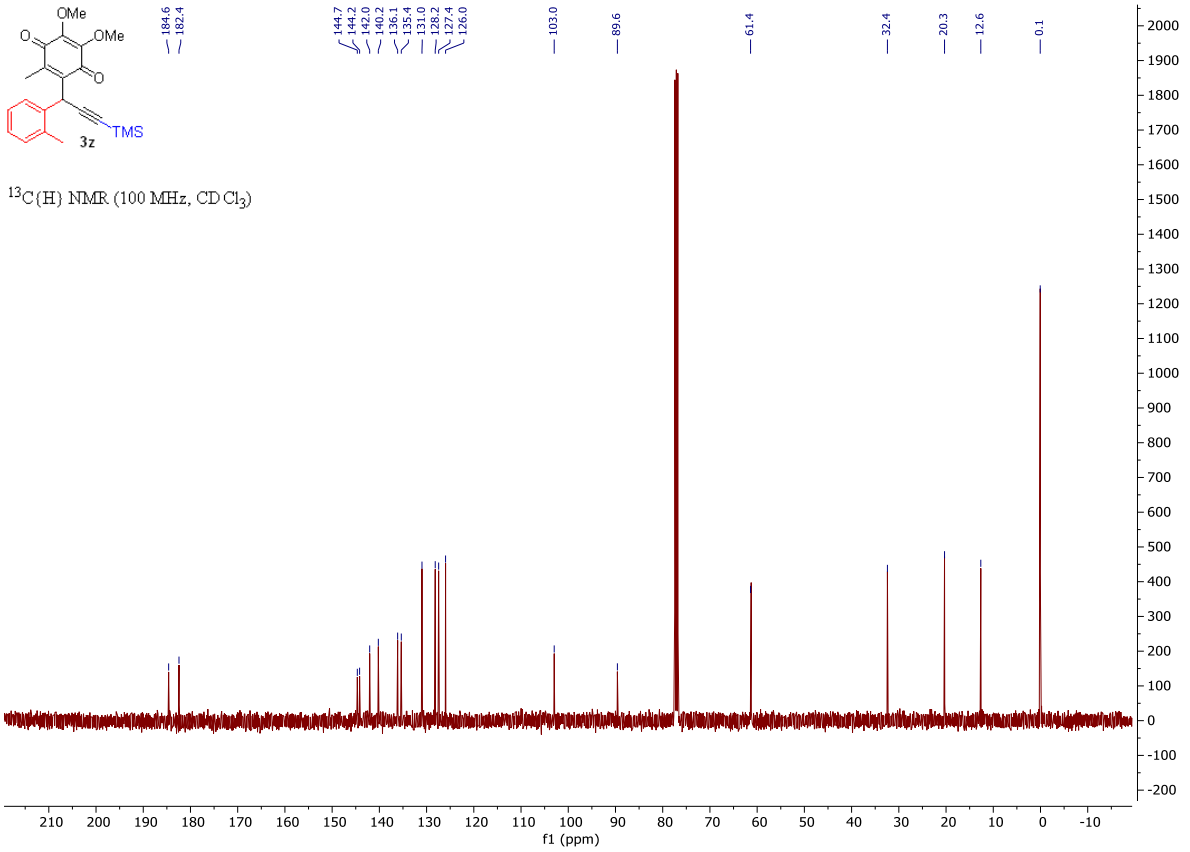

OMe
OMe
O
O
Cl
MeO
TMS
3y
7.85
7.83
6.87
6.86
6.85
6.84
6.83
6.82
5.65
4.00
3.99
3.78
1.87
0.19
^{1}H NMR (400 MHz, $CDCl_3$)
0.96
1.98
0.94
2.92
3.04
3.01
2.96
9.07
f1 (ppm)

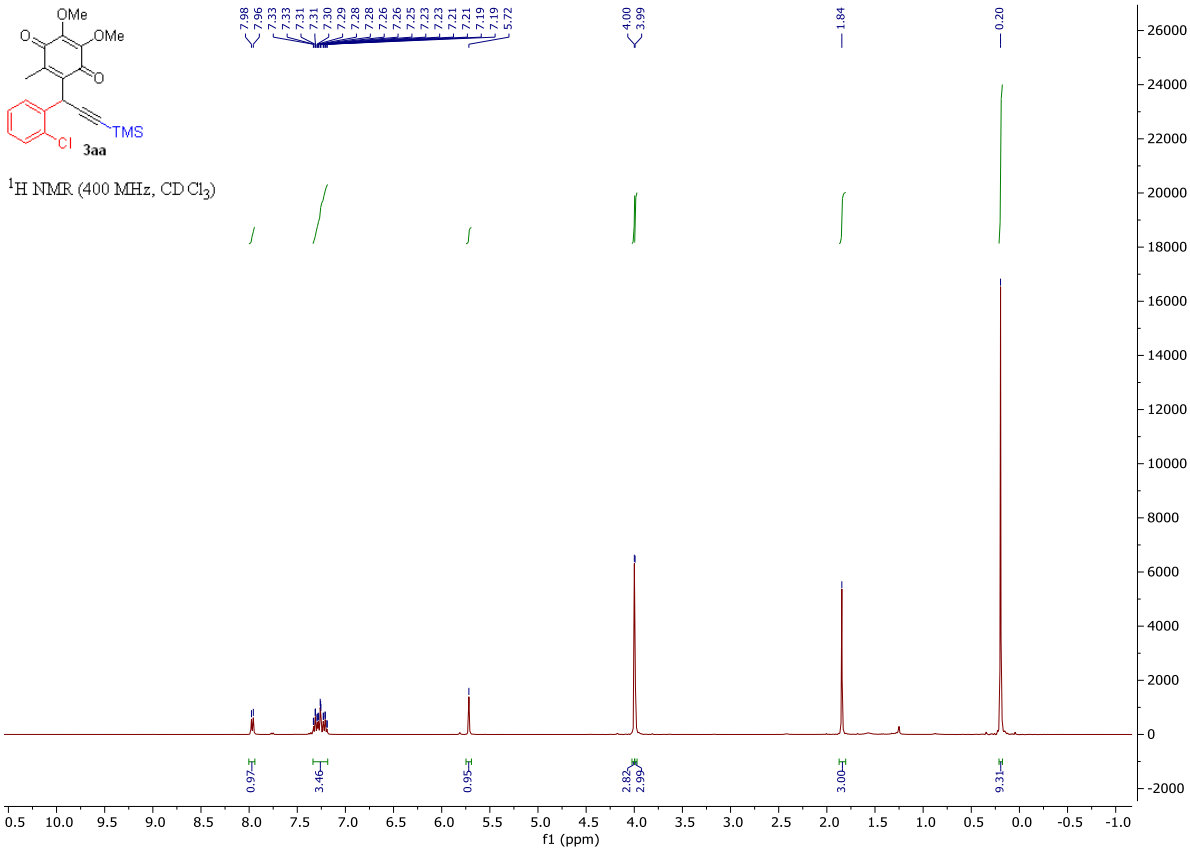


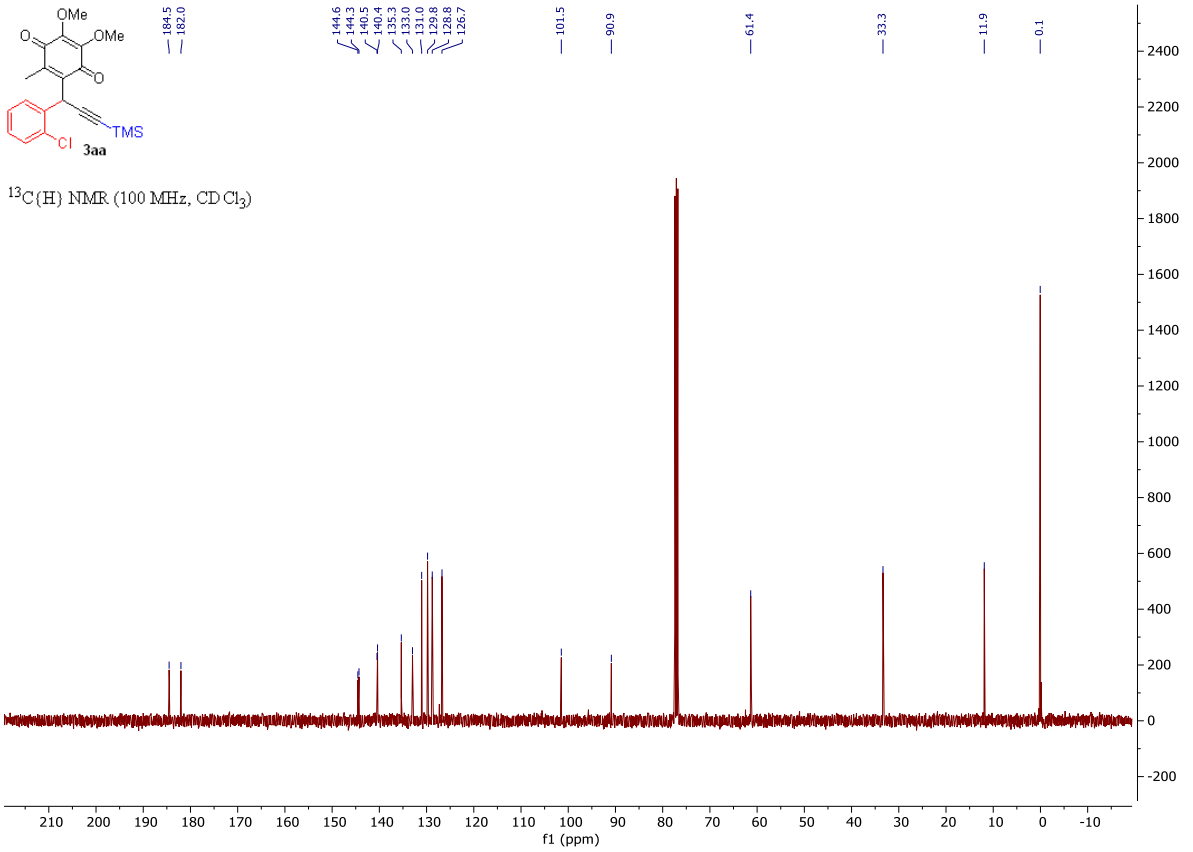
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)

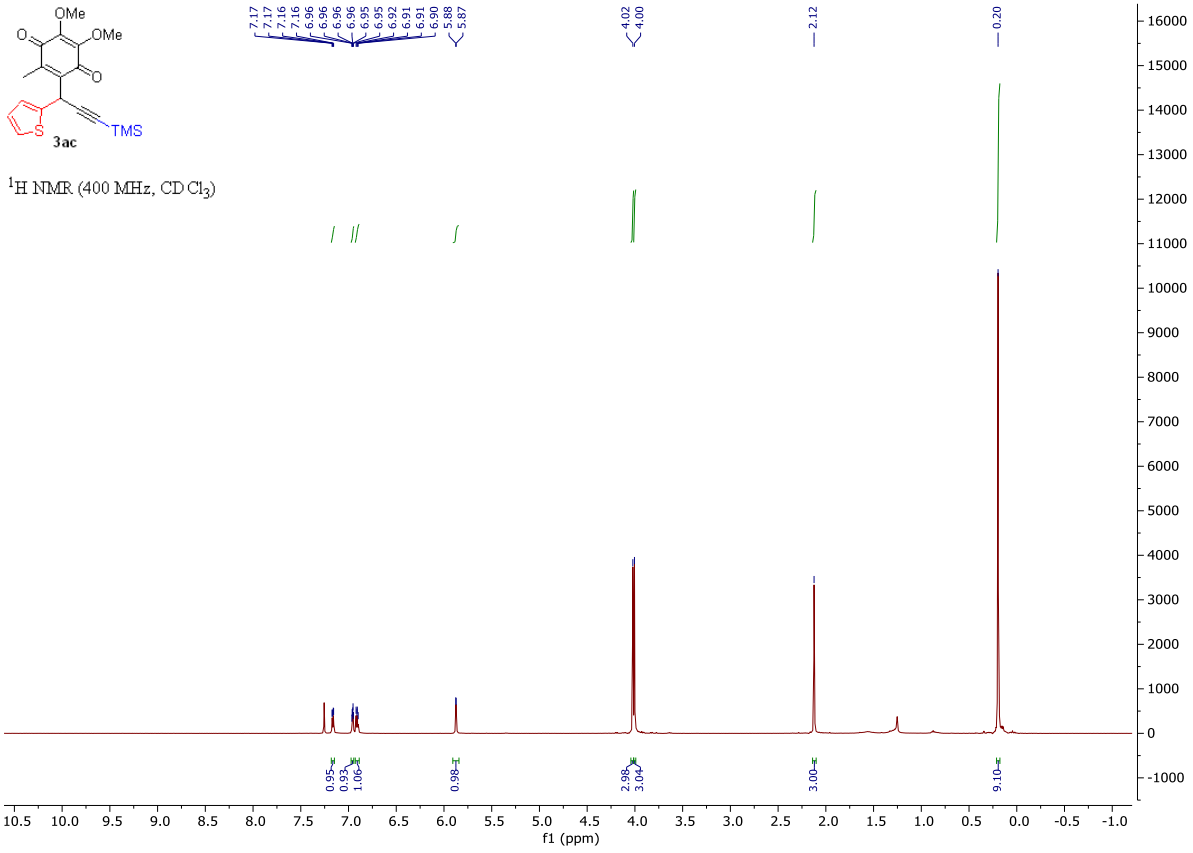


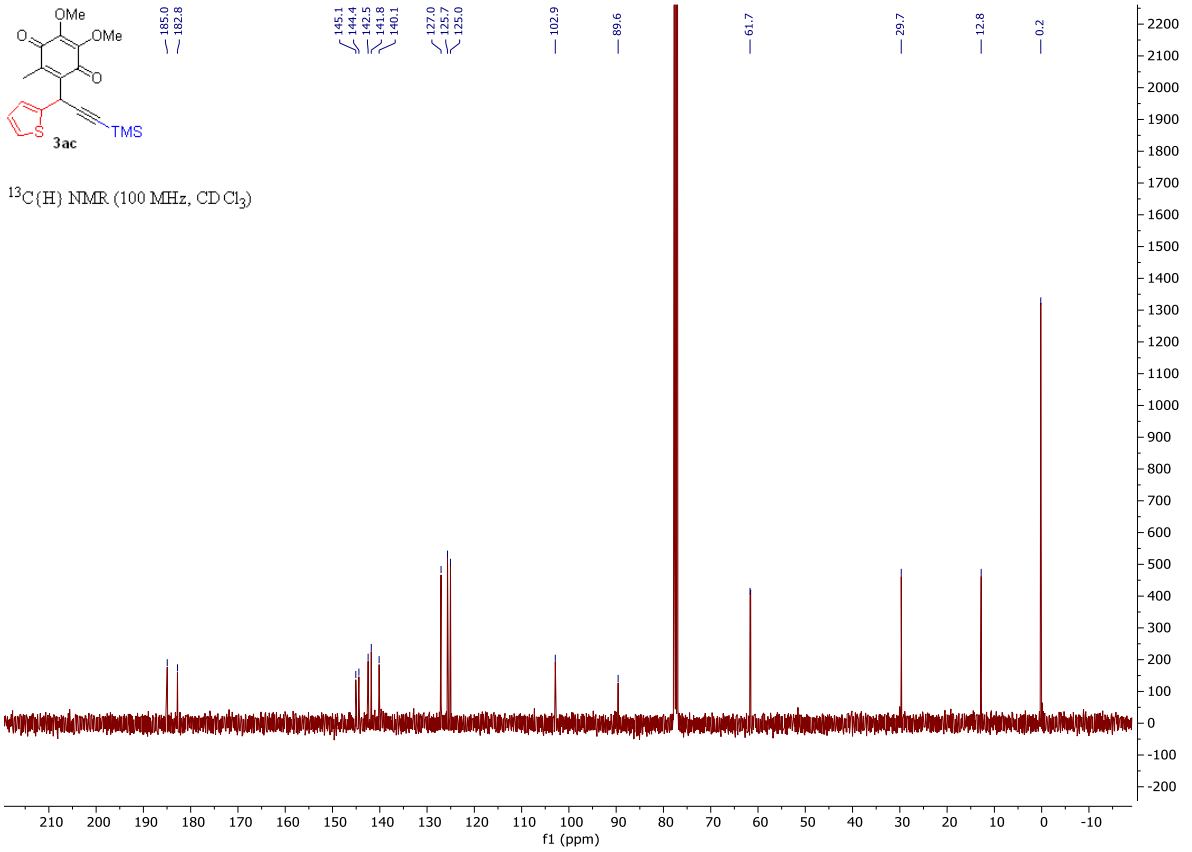
^{1}H NMR (400 MHz, $CDCl_3$)

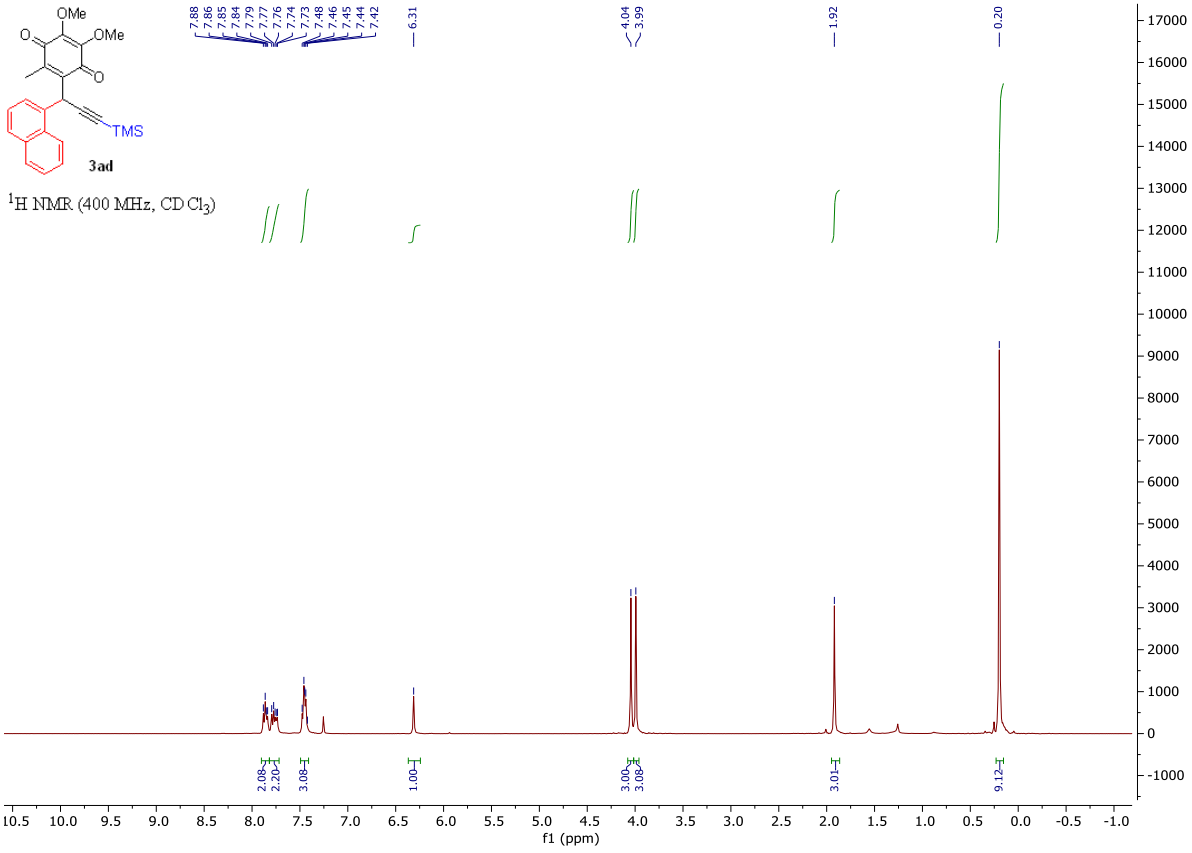

OMe
OMe
O
O
TMS
3z
184.6
182.4
144.7
144.2
142.0
140.2
136.1
135.4
131.0
128.2
127.4
126.0
103.0
89.6
61.4
32.4
20.3
12.6
0.1
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)

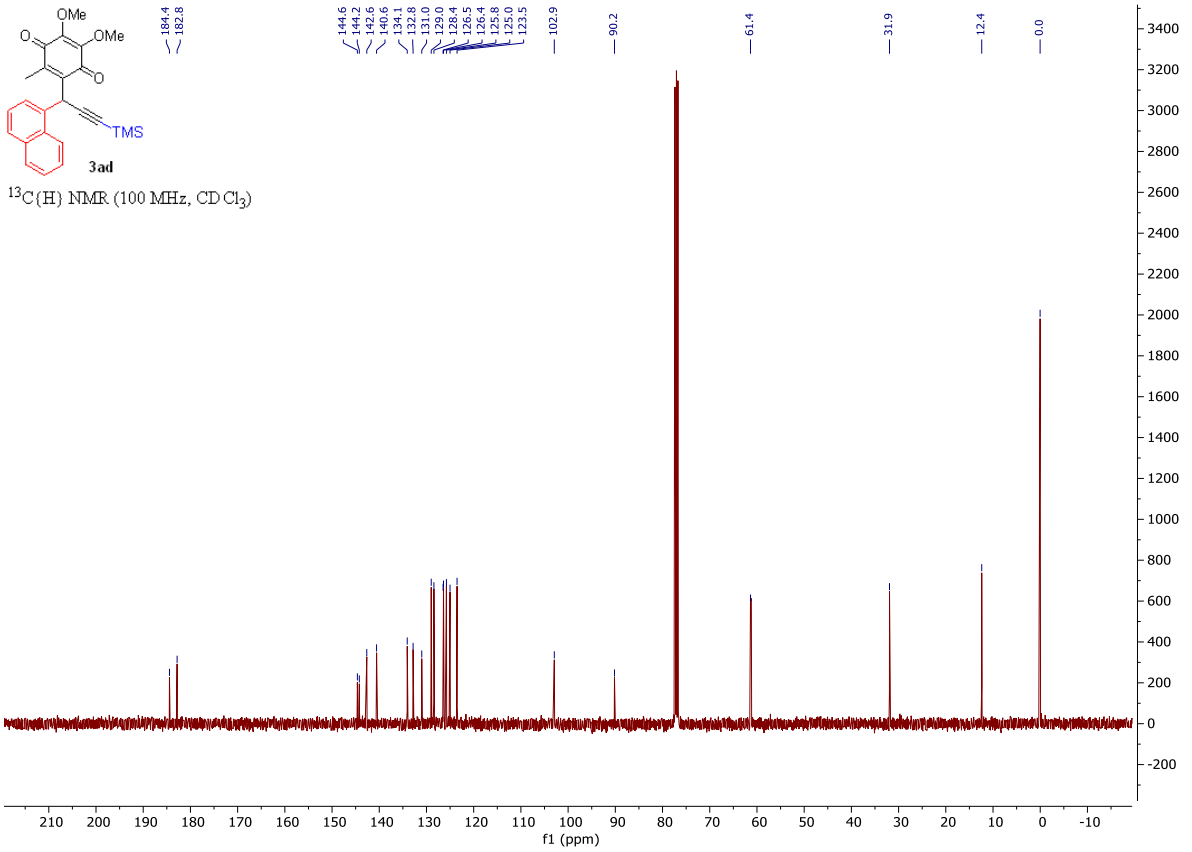

OMe
OMe
O
O
TMS
Cl
3aa
7.98
7.96
7.33
7.33
7.31
7.31
7.30
7.29
7.28
7.28
7.26
7.26
7.25
7.23
7.23
7.21
7.21
7.19
7.19
5.72
4.00
3.99
1.84
0.20
0.97
3.46
0.95
2.82
2.99
3.00
9.31
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


OMe
OMe
O
O
TMS
Cl
3aa
184.5
182.0
144.6
144.3
140.5
140.4
135.3
133.0
131.0
129.8
128.8
126.7
101.5
90.9
61.4
33.3
11.9
0.1
^{13}C{H} NMR (100 MHz, CD Cl$_3$)
f1 (ppm)

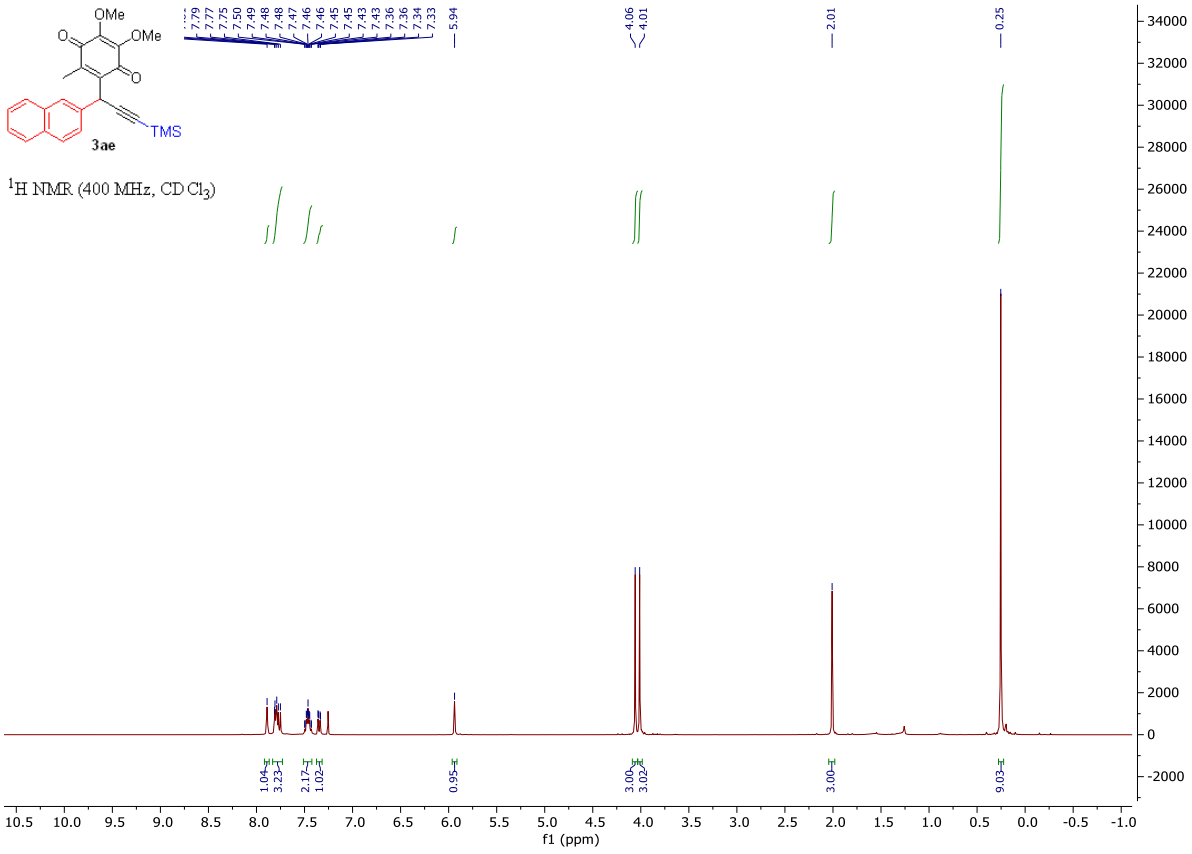

OMe
OMe
O
O
TMS
S
3ac
7.17
7.17
7.16
7.16
6.96
6.96
6.96
6.96
6.95
6.95
6.92
6.91
6.91
6.90
5.88
5.87
4.02
4.00
2.12
0.20
^{1}H NMR (400 MHz, CD Cl$_3$)
0.95
0.93
1.06
0.98
2.98
3.04
3.00
9.10
f1 (ppm)


OMe
OMe
O
O
TMS
S
3ac
185.0
182.8
145.1
144.4
142.5
141.8
140.1
127.0
125.7
125.0
102.9
89.6
61.7
29.7
12.8
0.2
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)

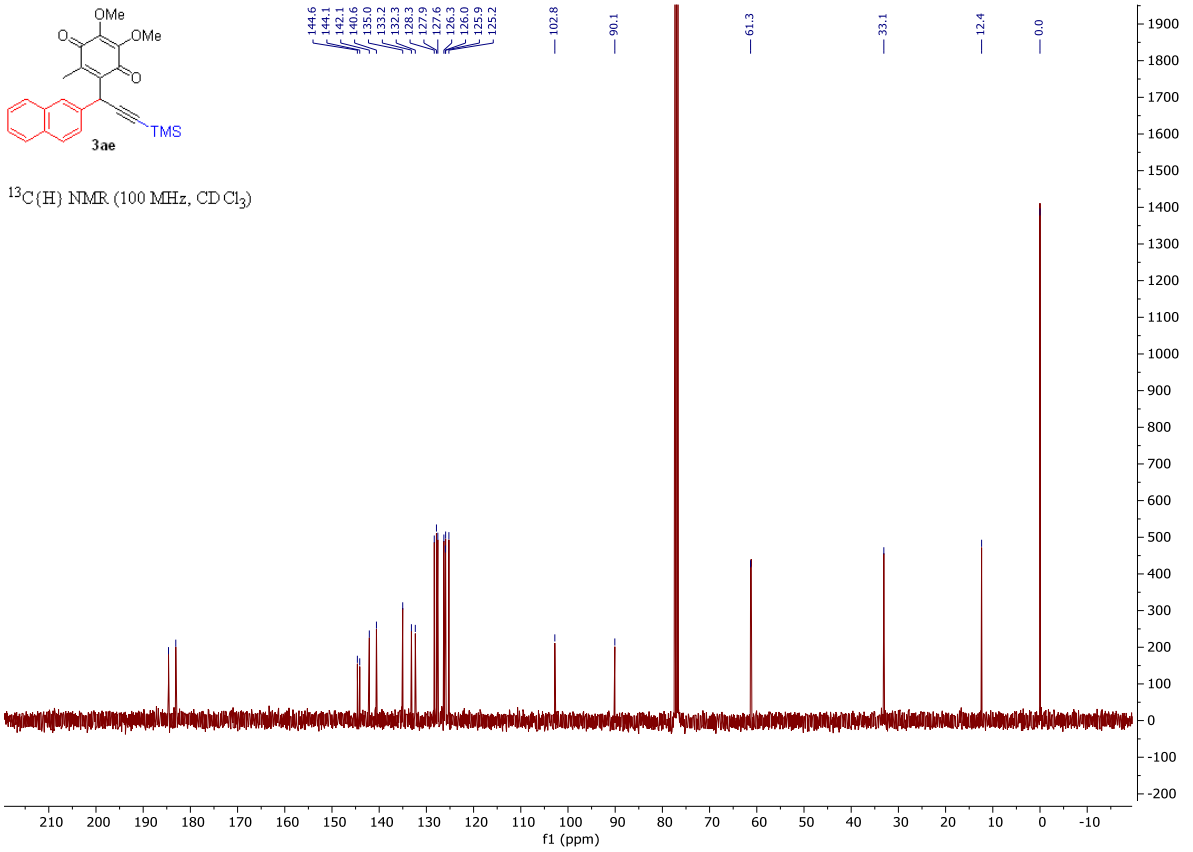

OMe
OMe
O
O
TMS
3ad
7.88
7.86
7.85
7.84
7.79
7.77
7.76
7.74
7.73
7.48
7.46
7.45
7.44
7.42
6.31
4.04
3.99
1.92
0.20
2.08
2.20
3.08
1.00
3.00
3.08
3.01
9.12
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

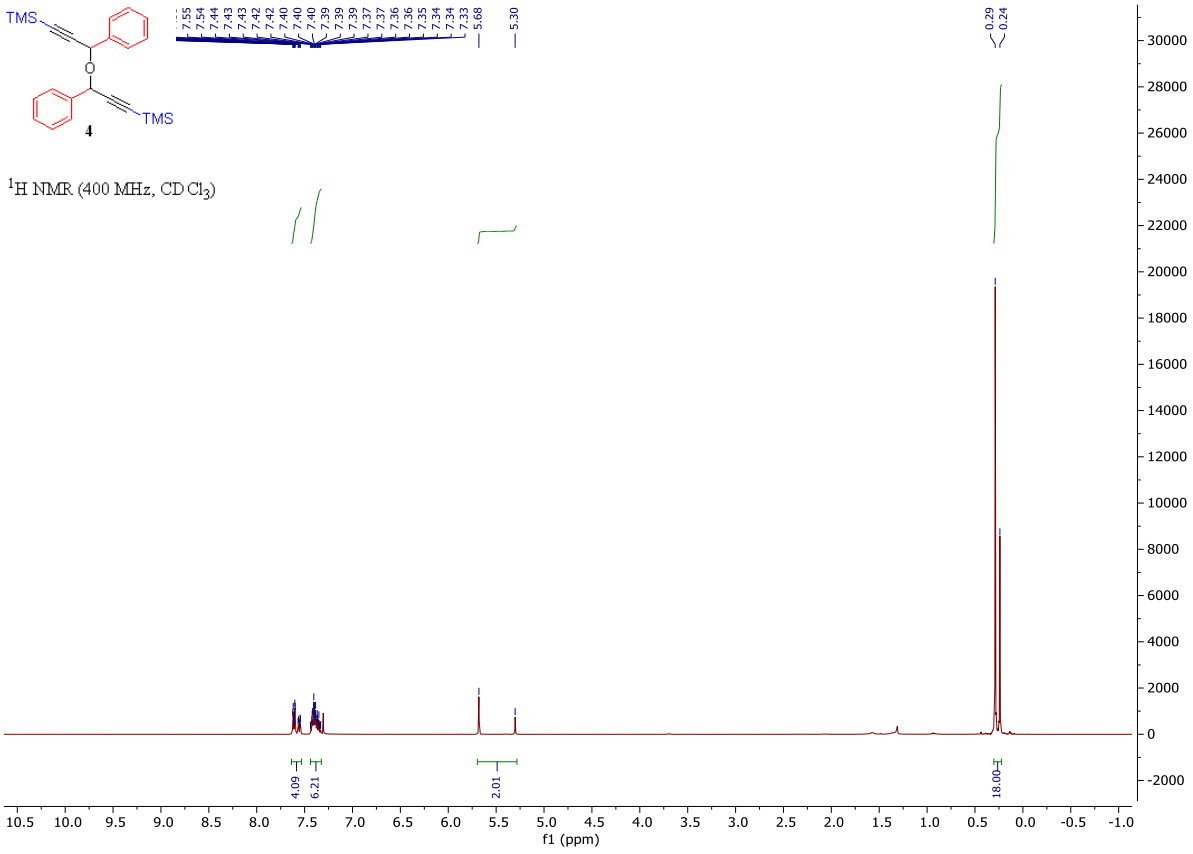


$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)


OMe
OMe
O
O
TMS
3ae
144.6
144.1
142.1
140.6
135.0
133.2
132.3
128.3
127.9
127.6
126.3
126.0
125.9
125.2
102.8
90.1
61.3
33.1
12.4
0.0
$^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$)
f1 (ppm)


TMS
O
TMS
4
7.55
7.54
7.44
7.43
7.43
7.42
7.42
7.40
7.40
7.40
7.39
7.39
7.39
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.33
5.68
5.30
0.29
0.24
^{1}H NMR (400 MHz, $CDCl_3$)
4.09
6.21
2.01
18.00
f1 (ppm)

2. Mechanistic studies – LCMS analysis of raw reaction mixture

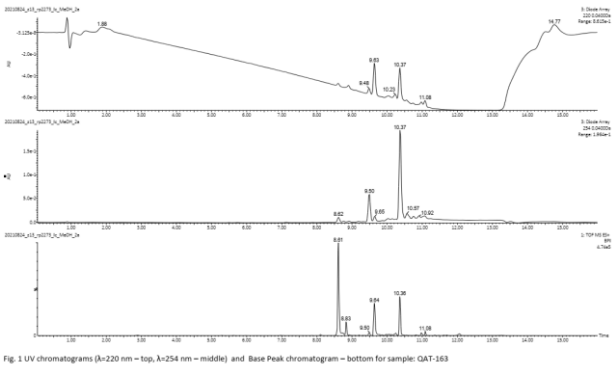


Fig. 1 UV chromatograms (λ=220 nm – top, λ=254 nm – middle) and Base Peak chromatogram – bottom for sample: QAT-163

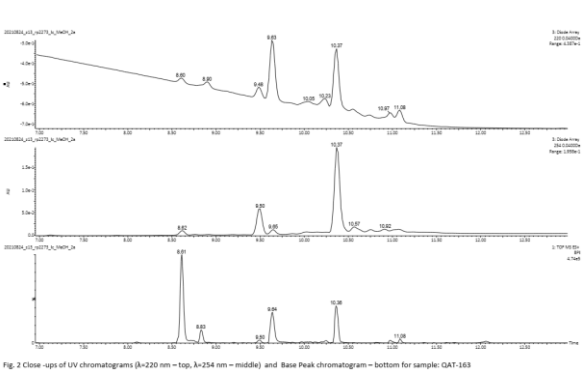


Fig. 2 Close -ups of UV chromatograms (λ=220 nm – top, λ=254 nm – middle) and Base Peak chromatogram – bottom for sample: QAT-163

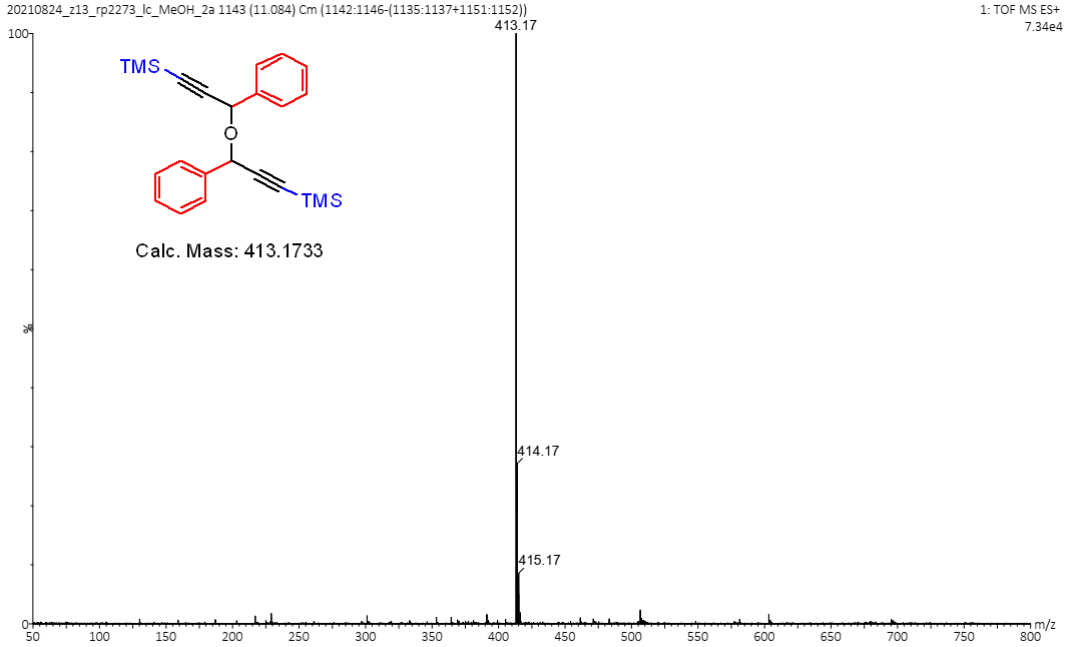


Fig.11 MS spectrum of the rt=11.08 peak

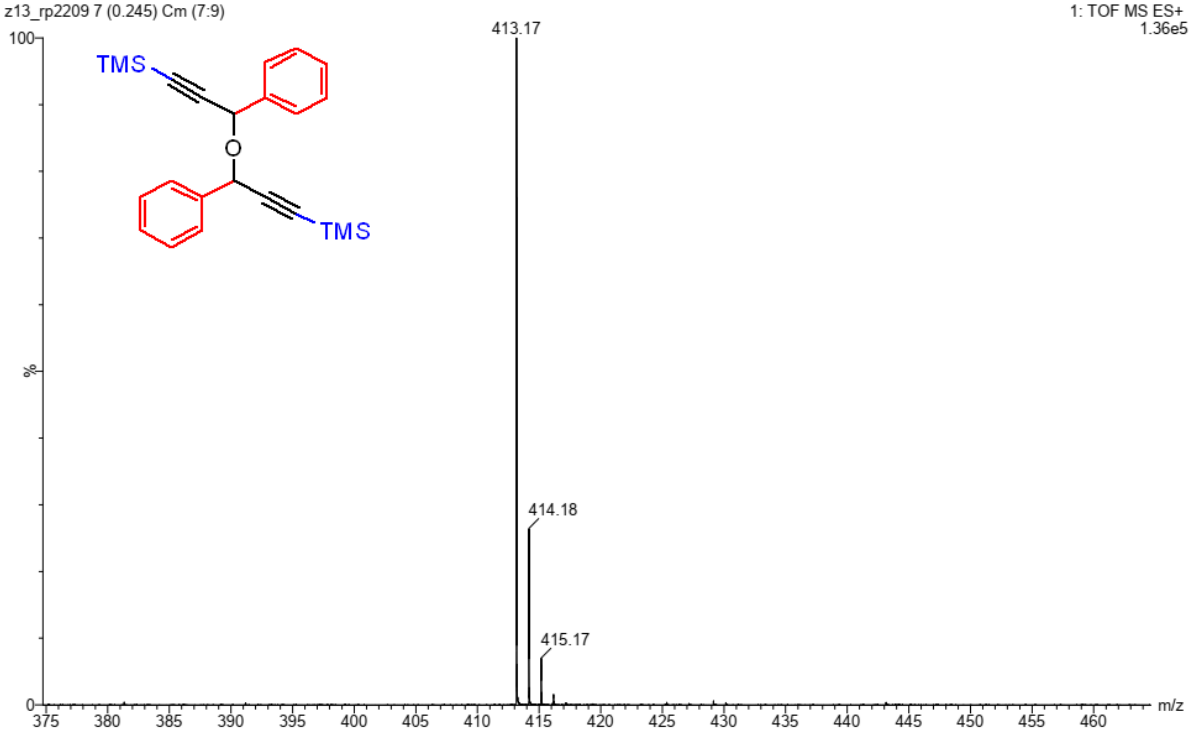
Experimental Instrument Parameters - MS	QAT-163
Polarity	ESI +
Capillary Voltage (kV)	3.00
Source temp. [C]	120.0
Sampling Cone	60.0
Source Offset	50.0
Source Gas Flow (mL/min)	0.00
Desolvation temp. [C]	250.0
Cone Gas [L/h]	100.0
Desolvation Gas Flow [L/h]	700.0
Nebuliser Gas Flow[bar]	4.5

Experimental Instrument Parameters - LC	QAT-163			
Solvent A	0.1% formic acid in water			
Solvent B	Methanol			
Run time	16.00 min			
Flow rate	0.30 ml/min			
Gradient table	time [min]	%A	%B	Curve
	0.00	95	5	-
	0.50	95	5	6
	10.00	0	100	6
	12.00	0	100	6
	13.00	95	5	6
	16.00	95	5	6

QAT-134

z13_rp2209 7 (0.245) Cm (7:9)

1: TOF MS ES+
1.36e5



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

20 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-200 O: 0-1 Na: 0-1 Si: 2-2

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na	Si
413.1740	413.1733	0.7	1.7	11.5	C24 H30 O Na Si2	755.1	0.044	95.65	24	30	1	1	2
	413.1757	-1.7	-4.1	14.5	C26 H29 O Si2	758.2	3.136	4.35	26	29	1		2