Supplementary Information

A rhodium-catalyzed C–H activation/cyclization approach toward the total syntheses of cassiarin C and 8-*O*-methylcassiarin A from a common intermediate

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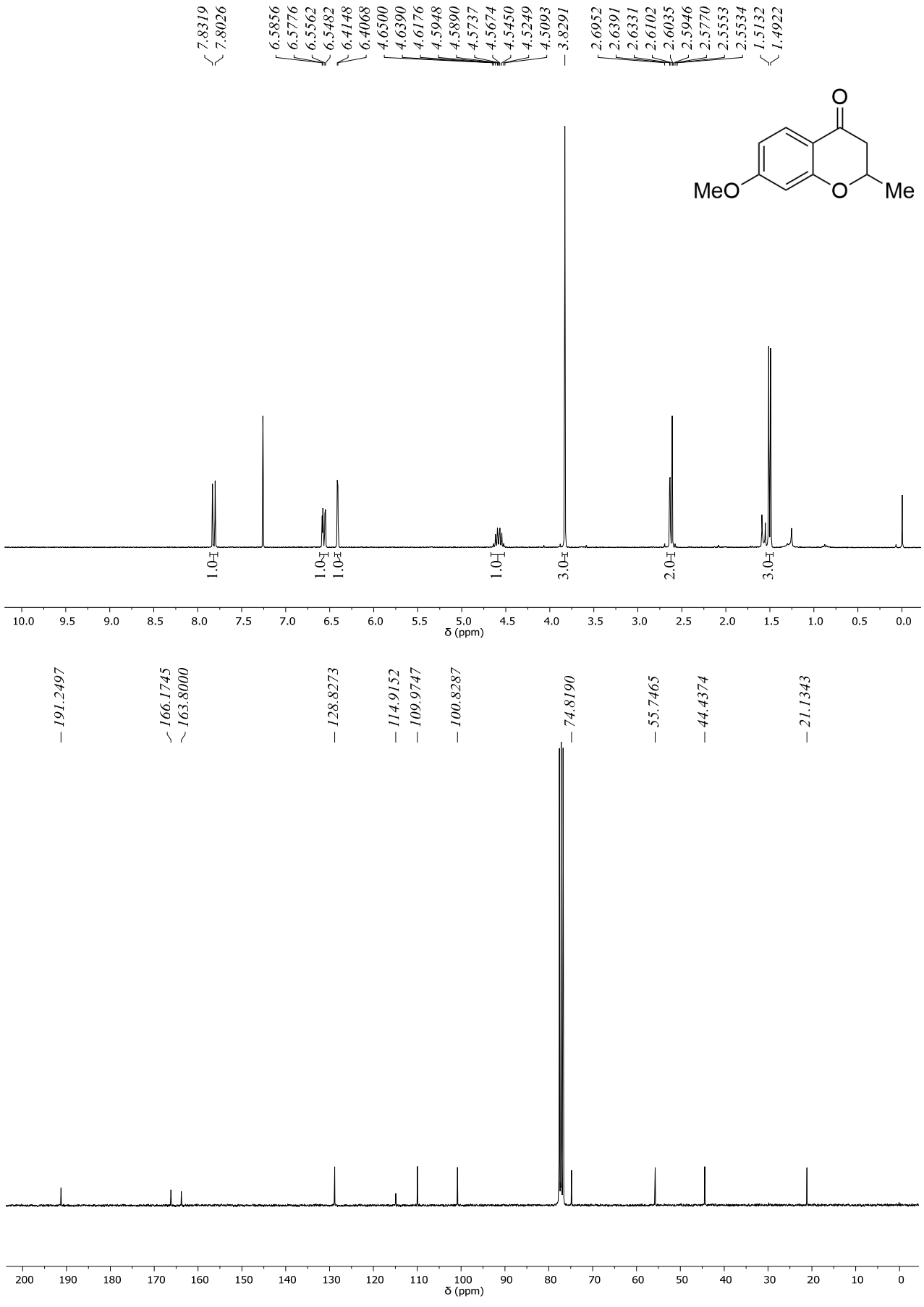


Figure S1: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **10** in $CDCl_3$.

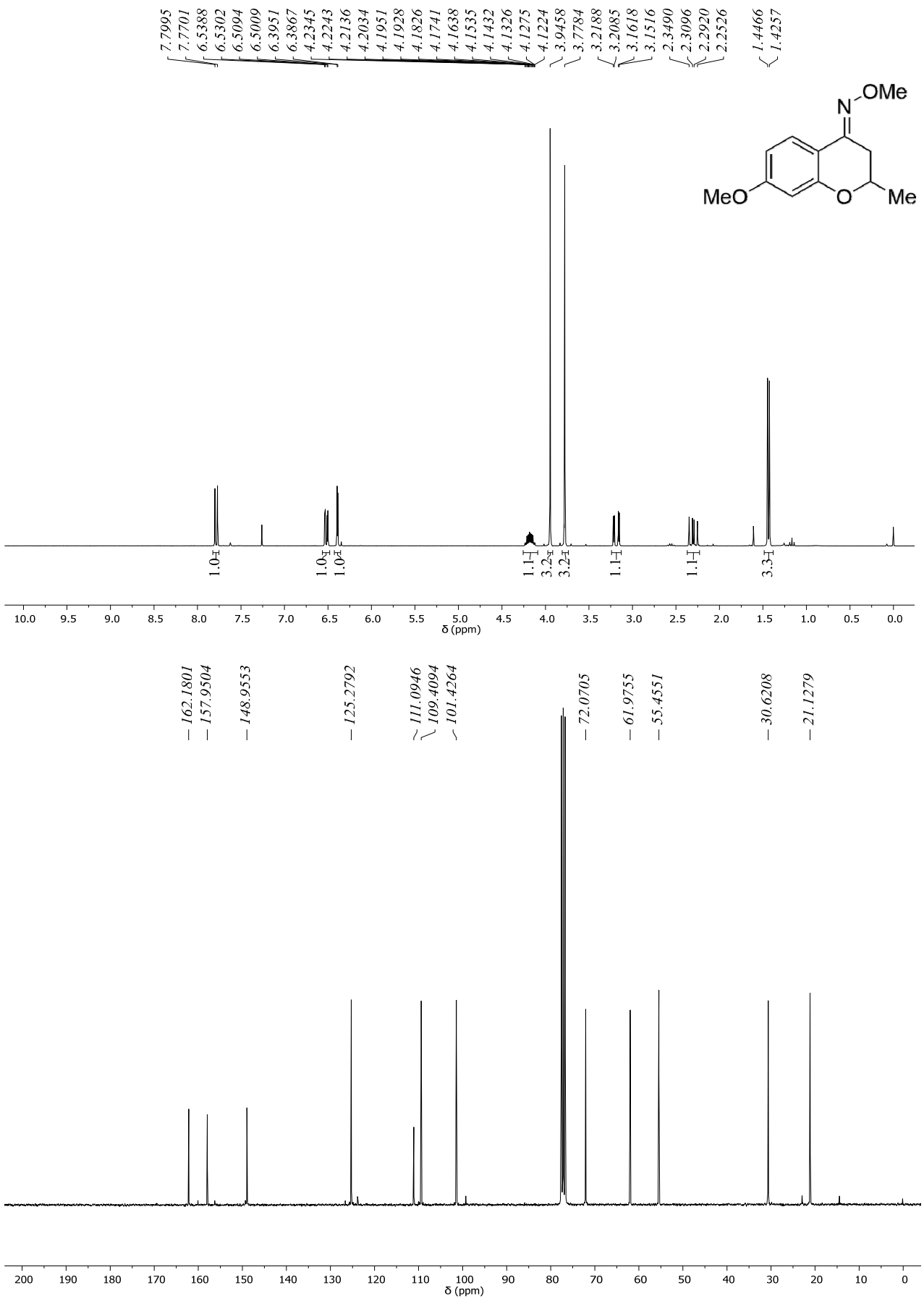


Figure S2: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound (*E*)-**11a** in $CDCl_3$.

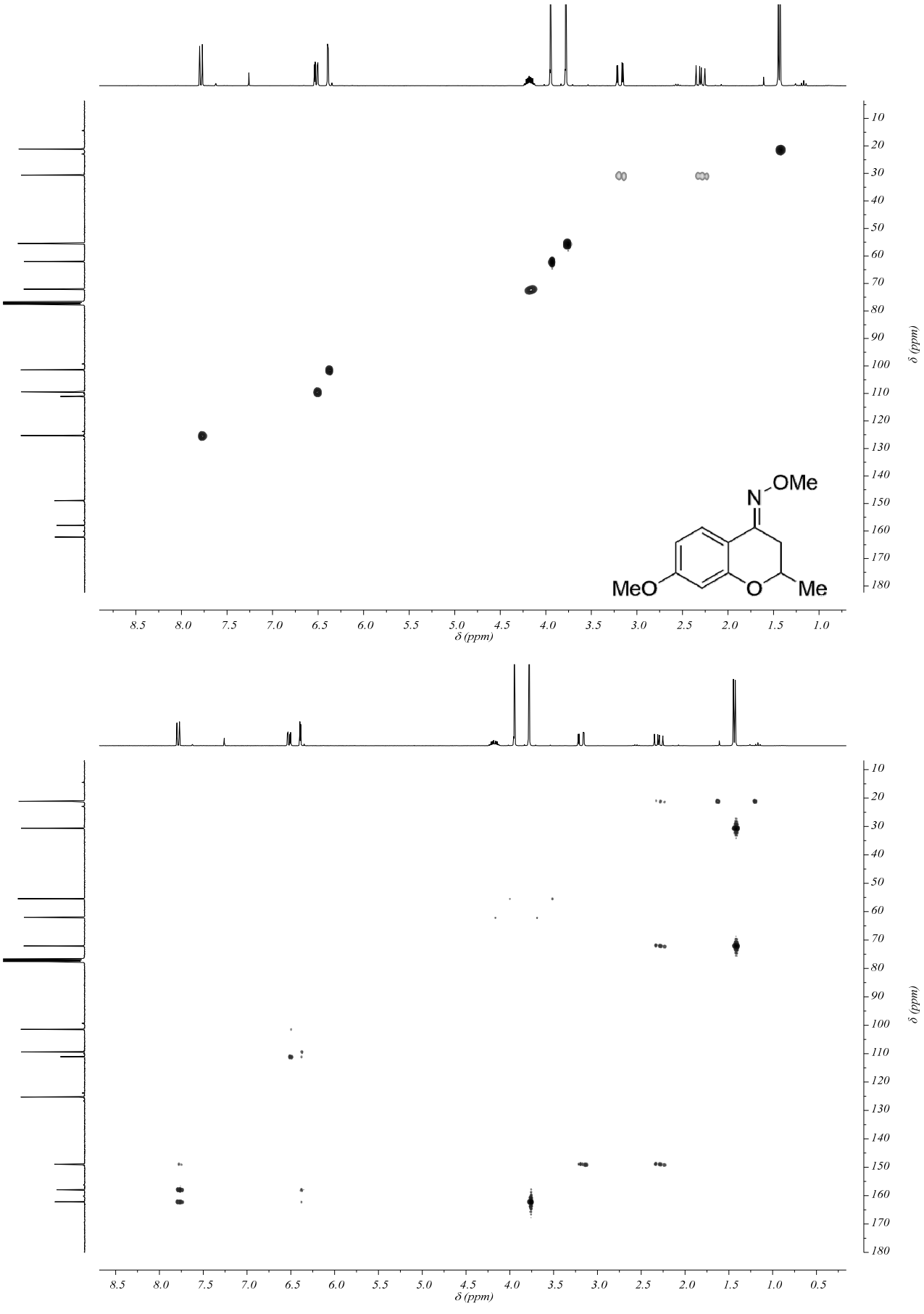


Figure S3: HSQC (top) and HMBC (bottom) spectra of compound (*E*)-**11a** in $CDCl_3$.

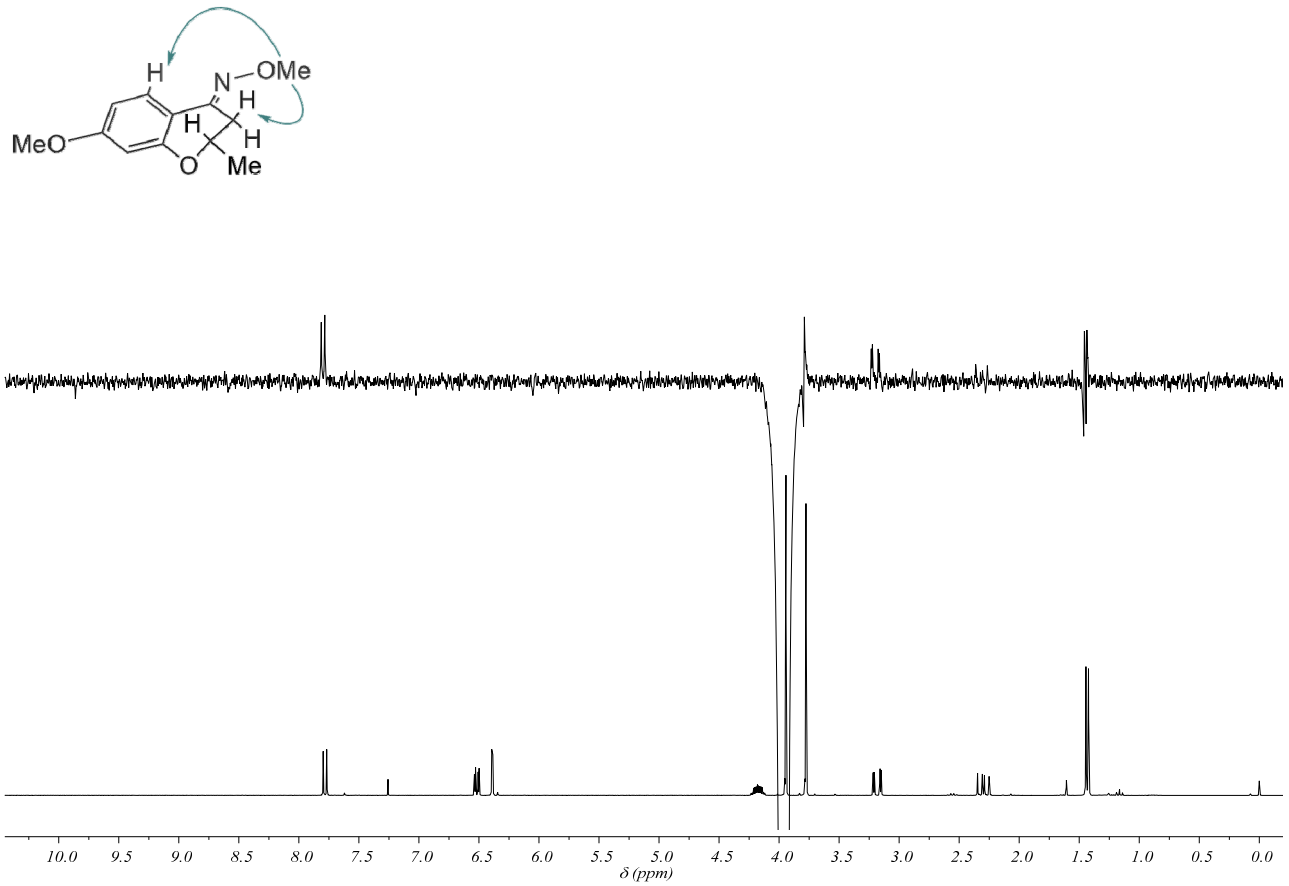


Figure S4: NOE spectra of compound (*E*)-**11a** in $CDCl_3$.

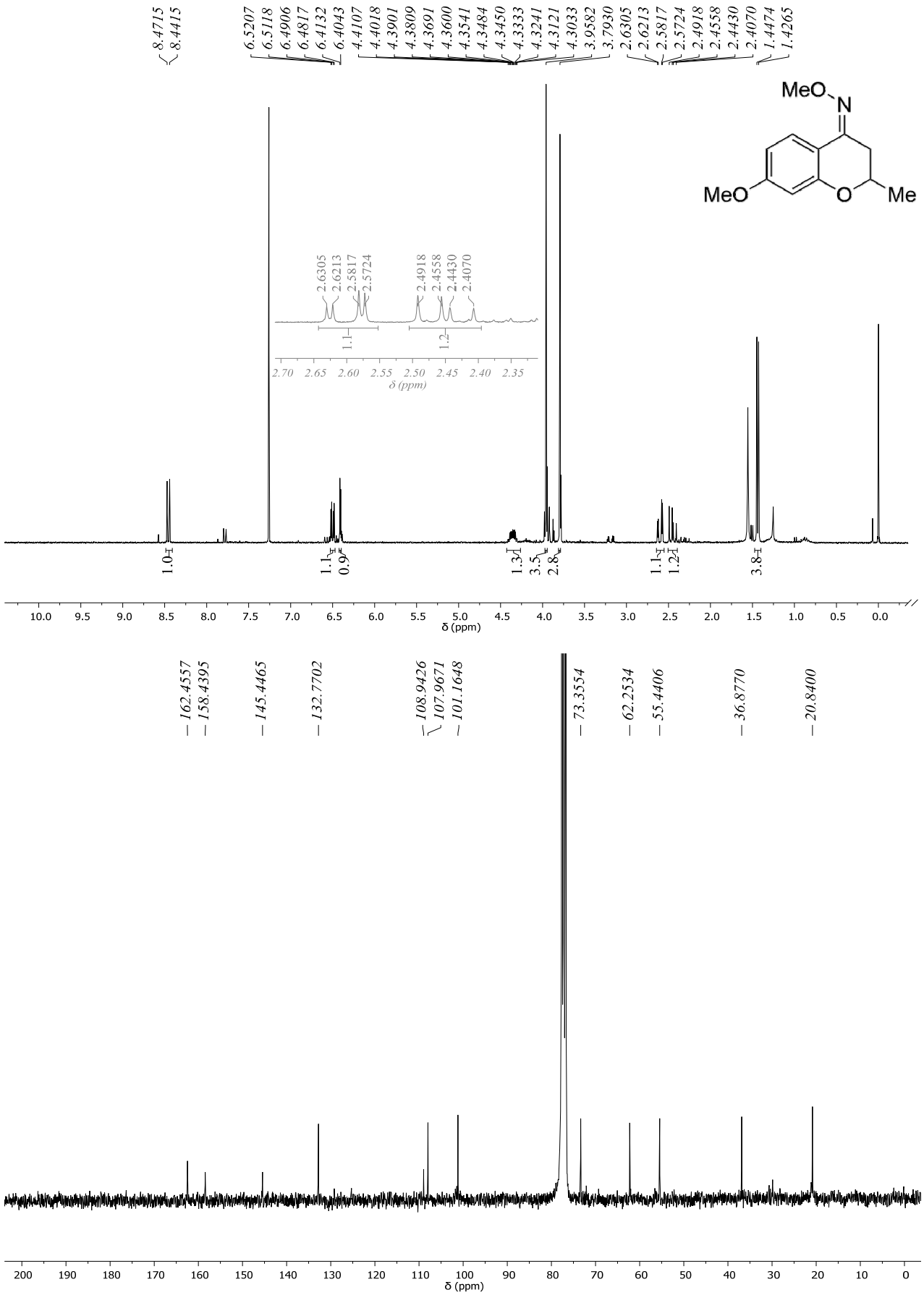


Figure S5: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound (*Z*)-**11a** in $CDCl_3$.

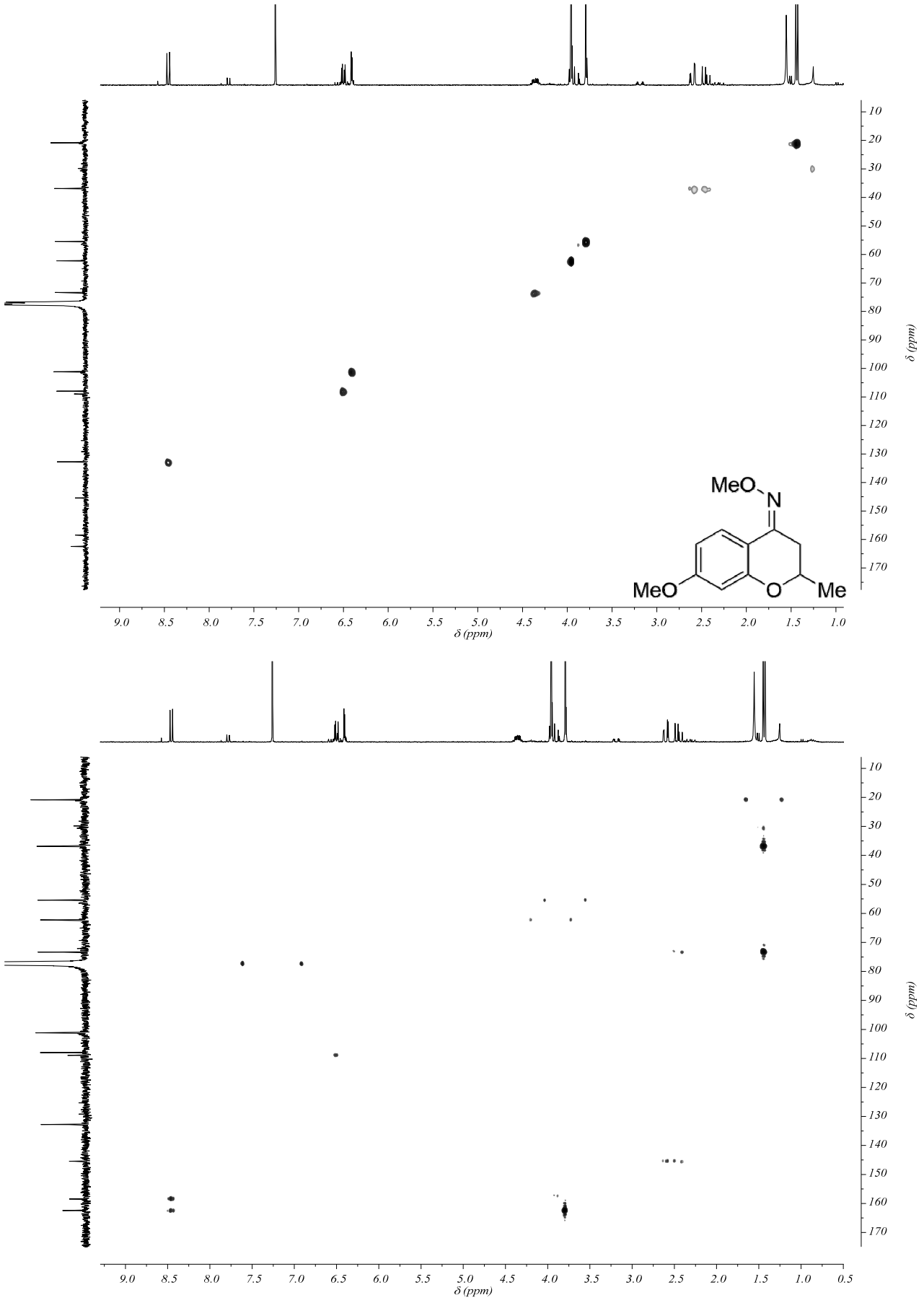


Figure S6: HSQC (top) and HMBC (bottom) spectra of compound (*Z*)-**11a** in $CDCl_3$.

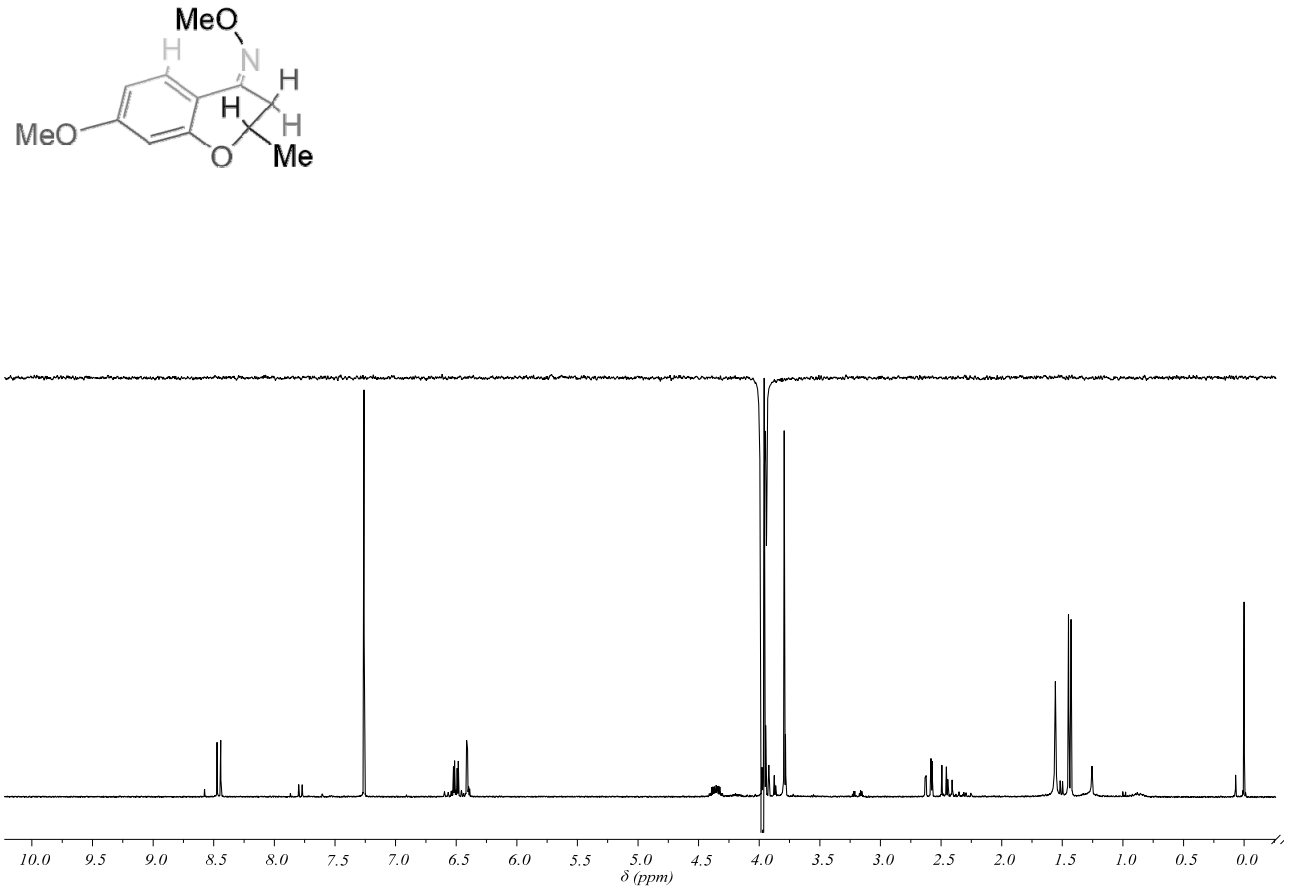


Figure S7: NOE spectra of compound (*Z)*-**11a** in $CDCl_3$.

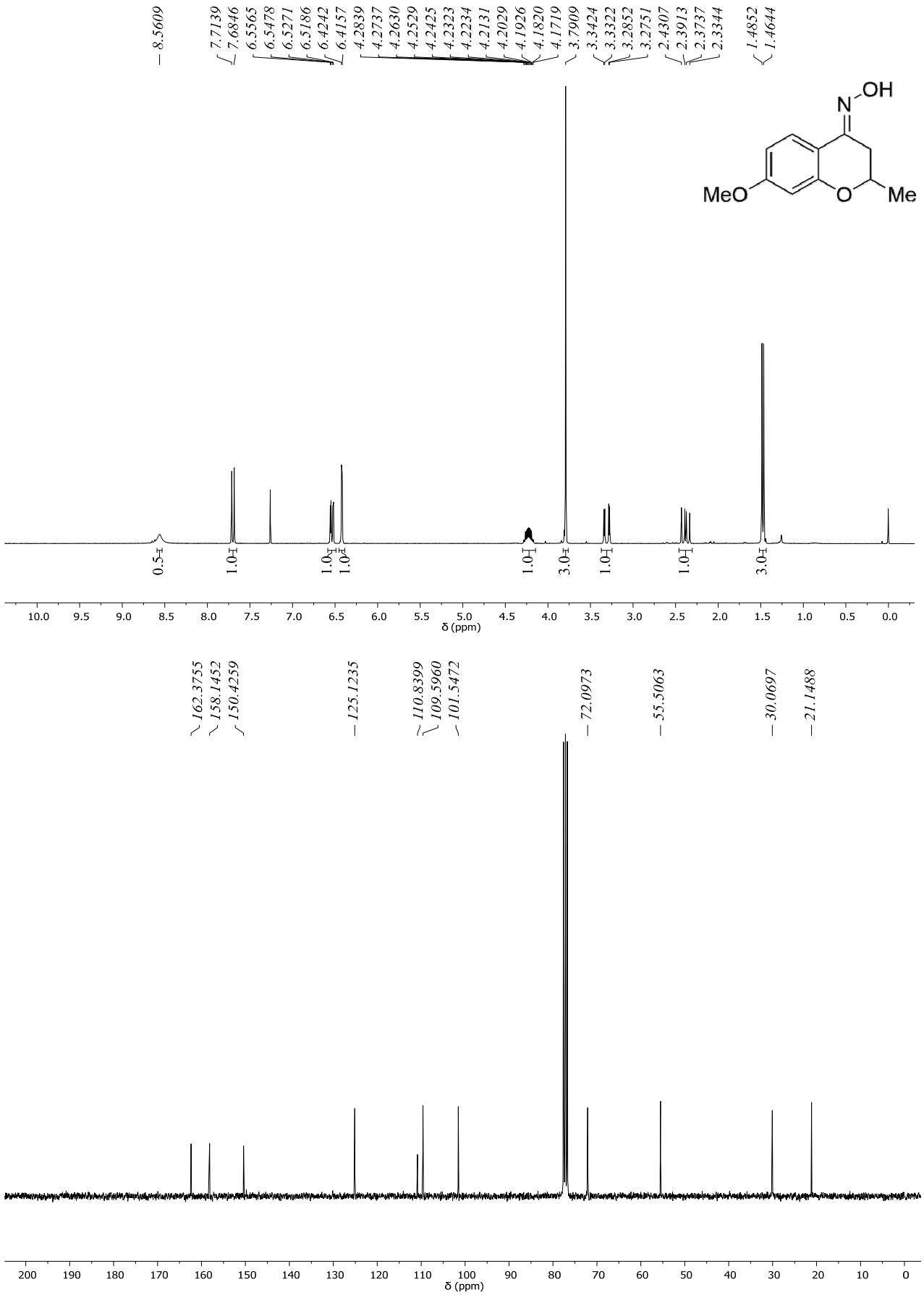


Figure S8: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound (*E*)-**11b** in $CDCl_3$.

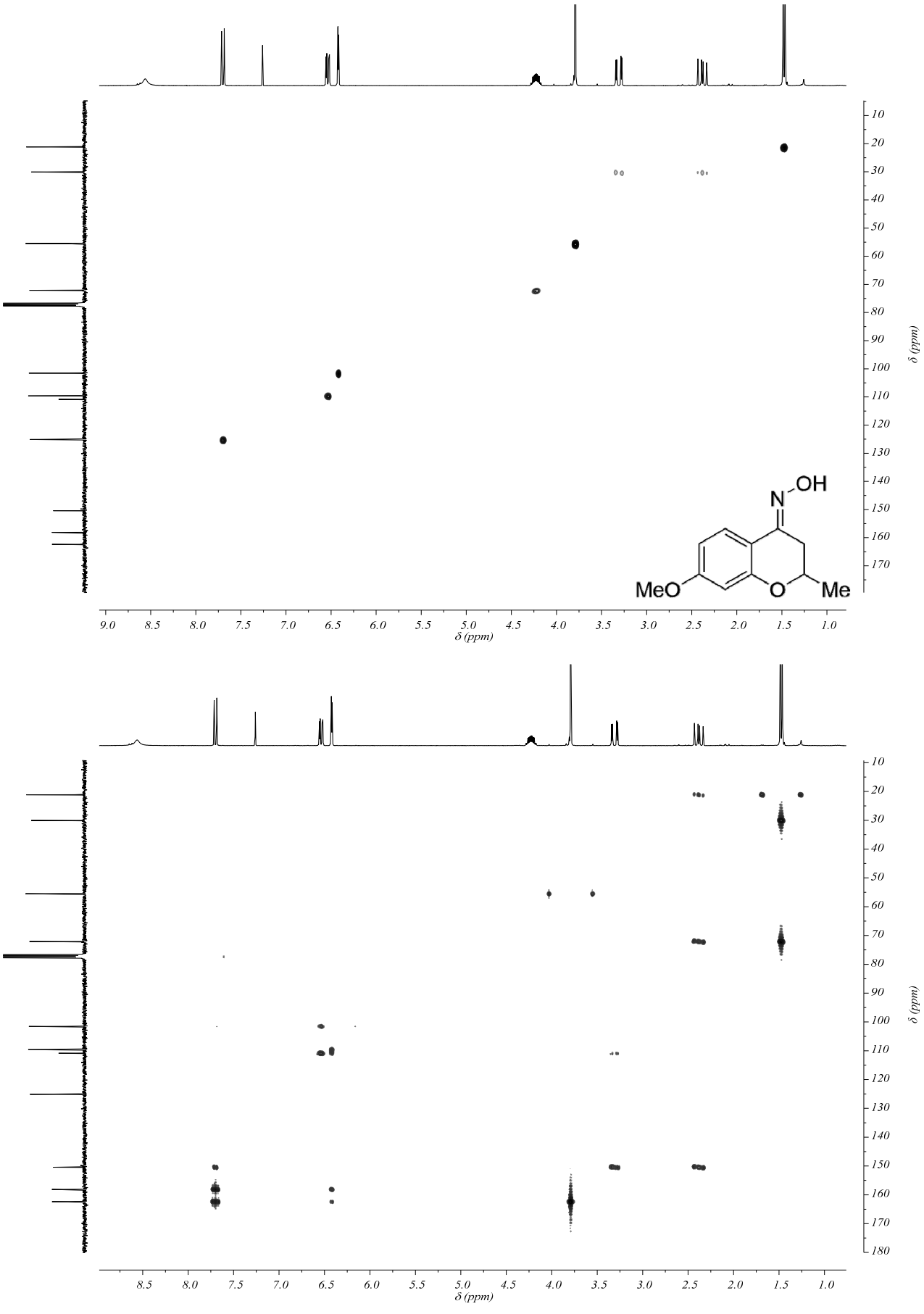


Figure S9: HSQC (top) and HMBC (bottom) spectra of compound (*E*)-**11b** in $CDCl_3$.

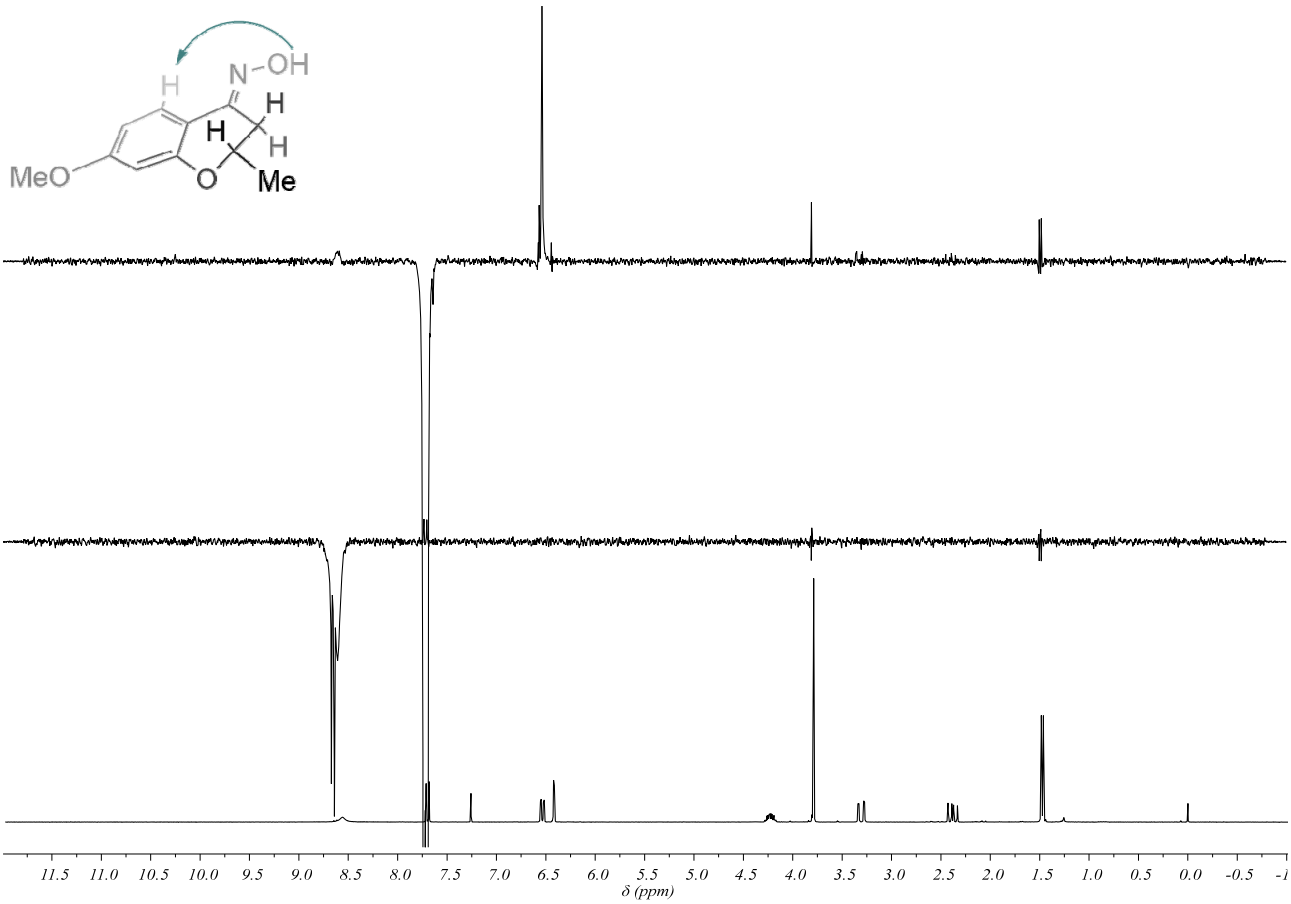


Figure S10: NOE spectra of compound (*E*)-**11b** in $CDCl_3$.

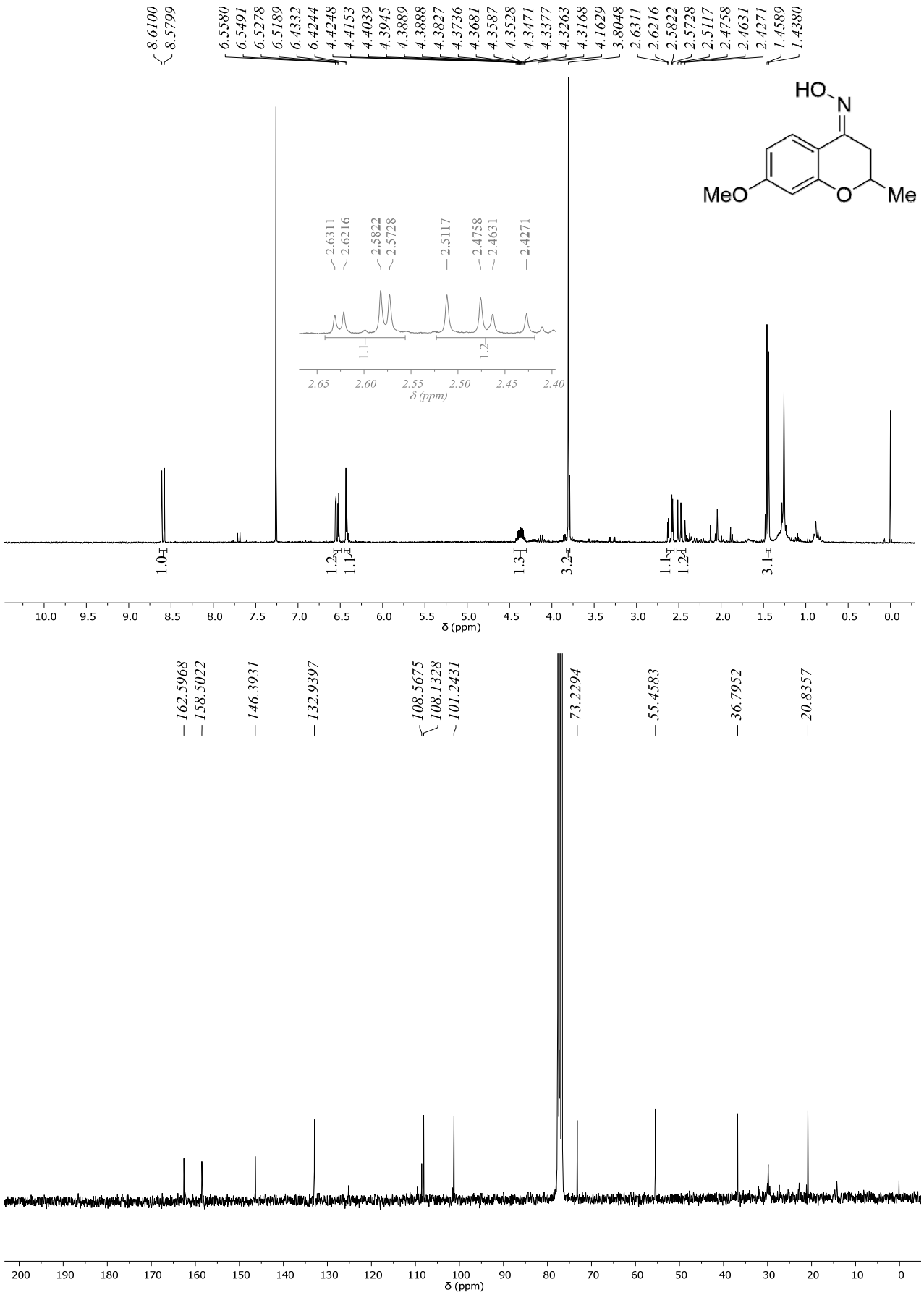


Figure S11: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound (*Z*)-**11b** in $CDCl_3$.

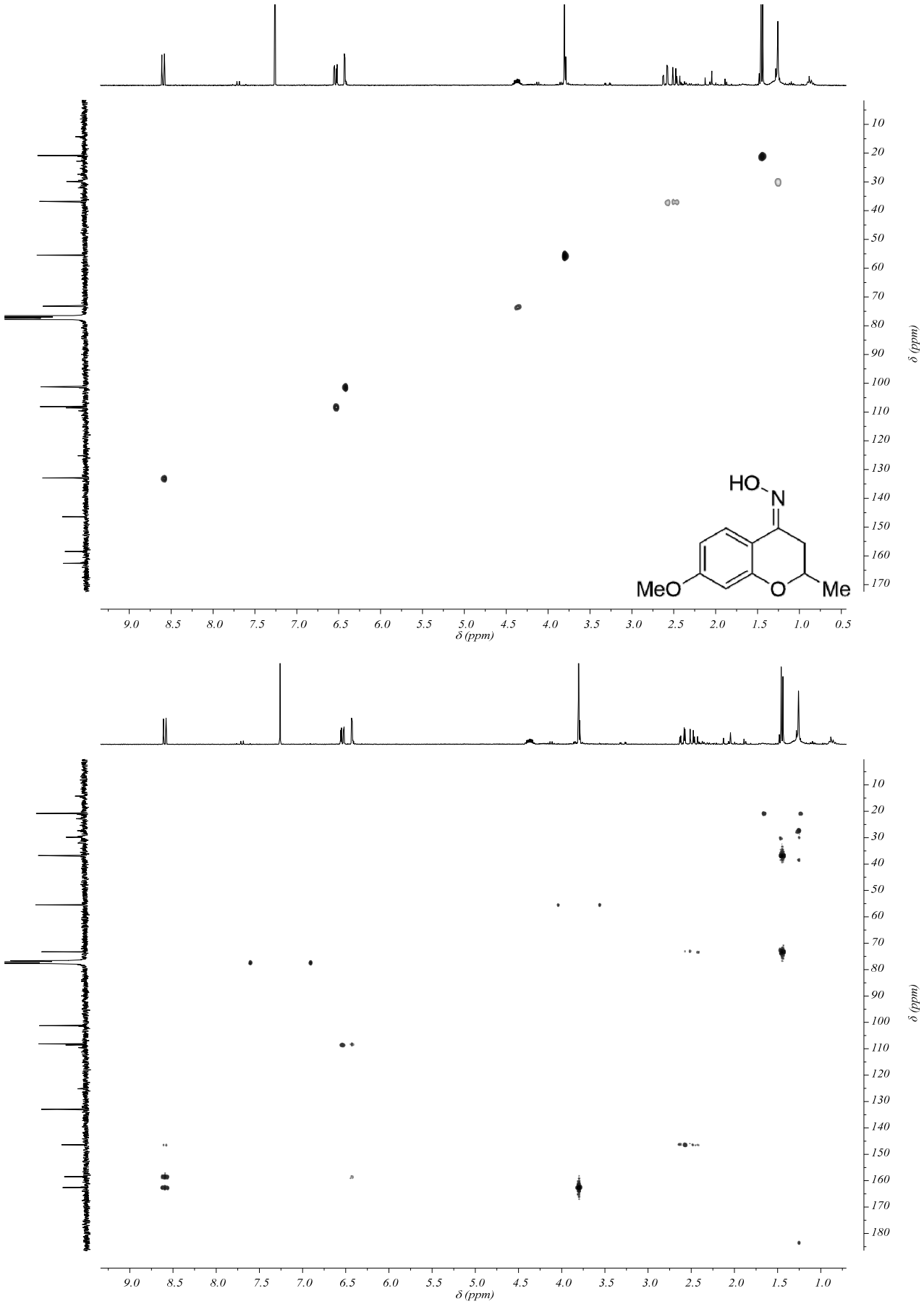


Figure S12: HSQC (top) and HMBC (bottom) spectra of compound (*Z*)-**11b** in $CDCl_3$.

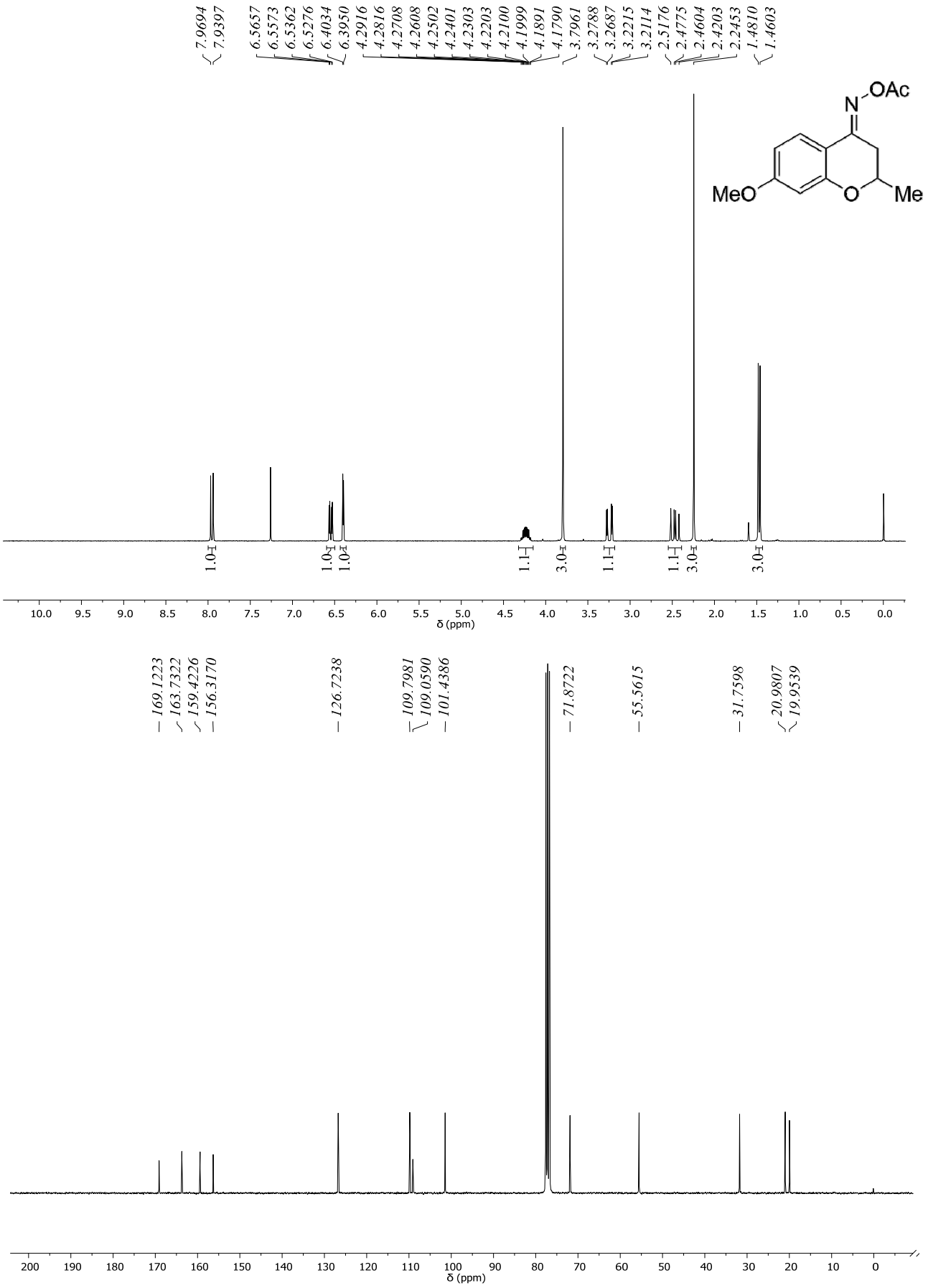


Figure S13: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **11c** in $CDCl_3$.

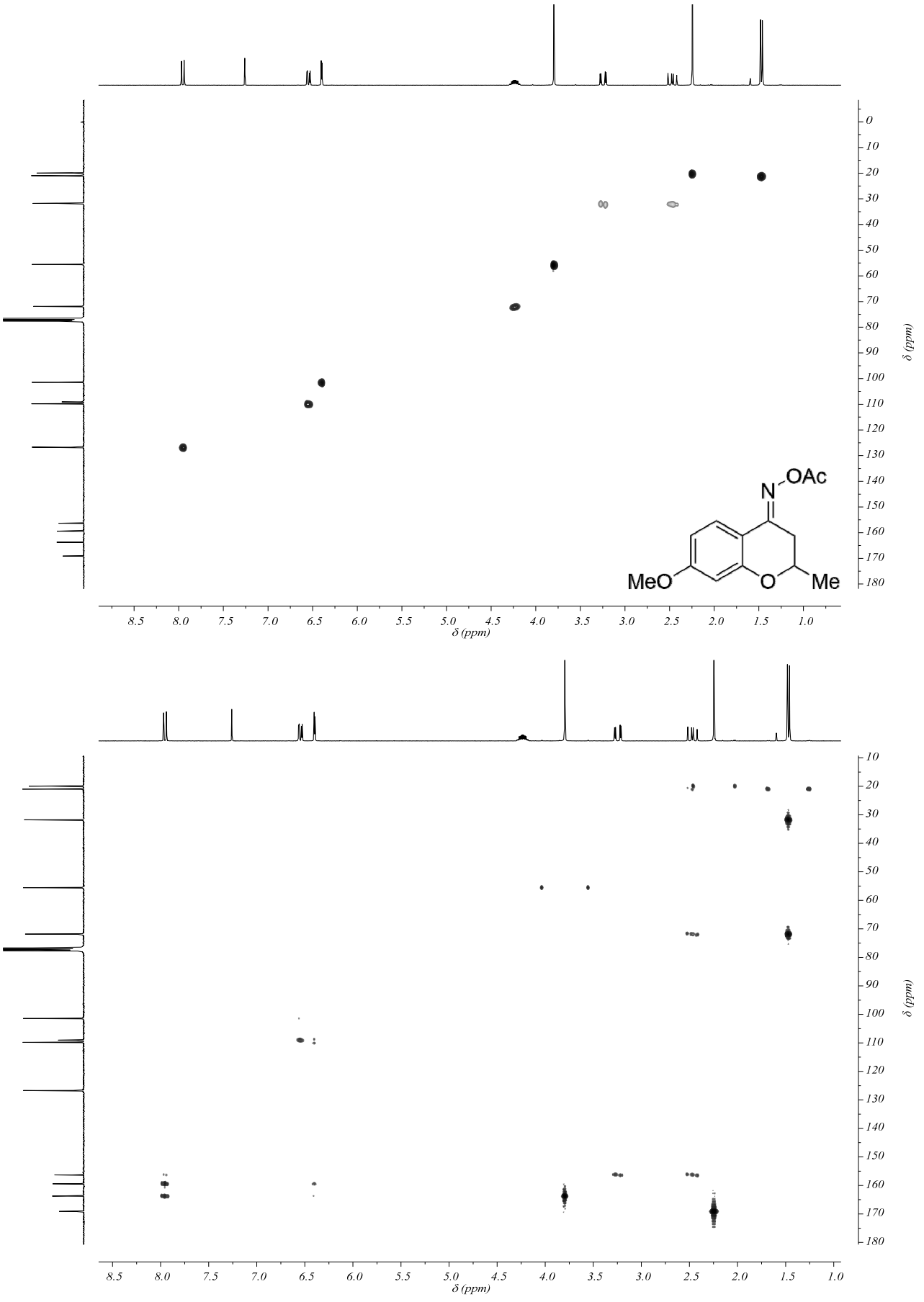


Figure S14: HSQC (top) and HMBC (bottom) spectra of compound **11c** in $CDCl_3$.

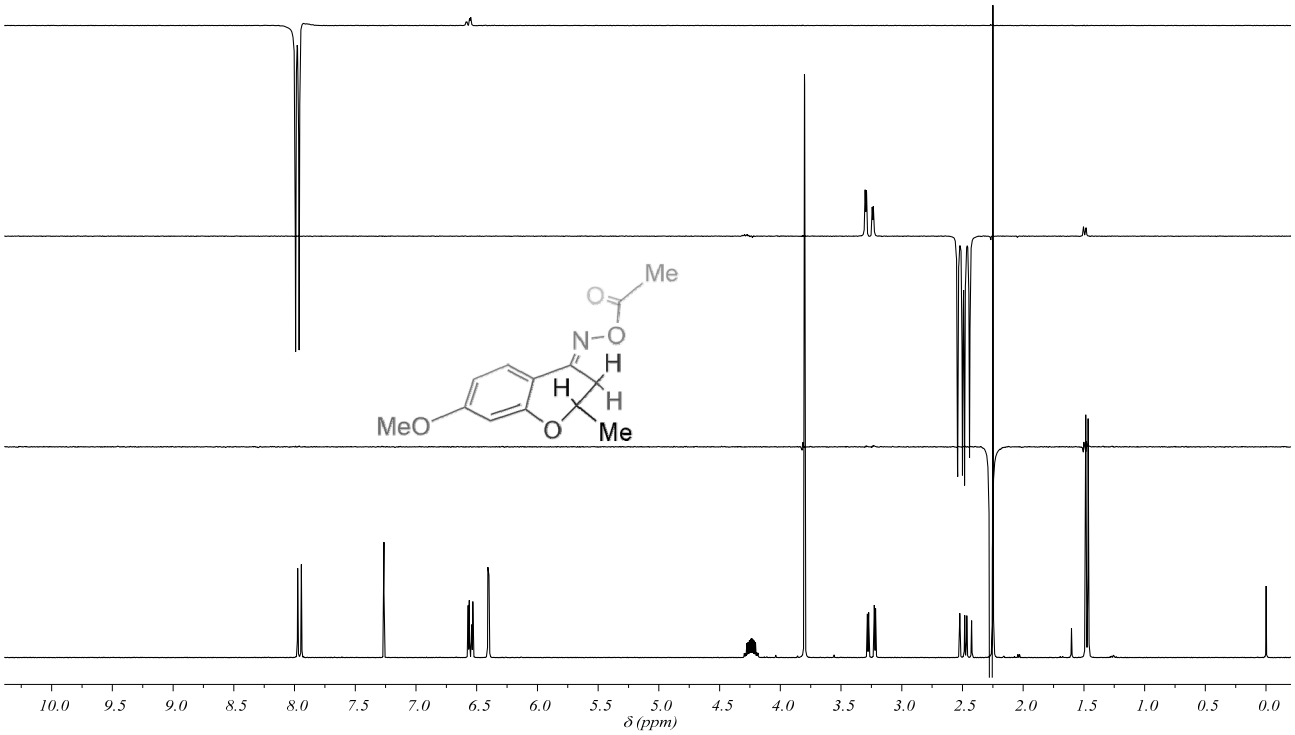


Figure S15: NOE spectra of compound **11c** in $CDCl_3$.

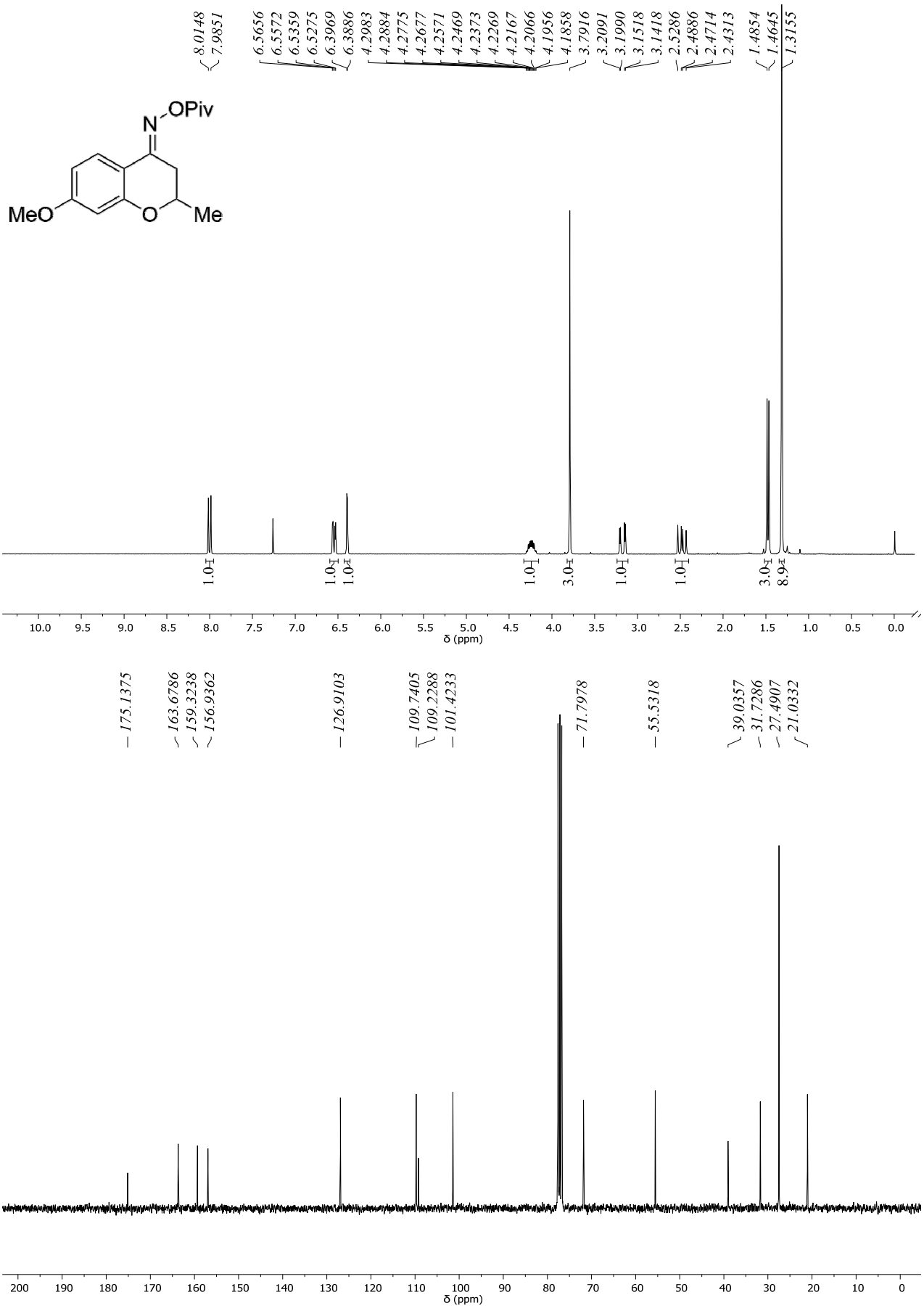


Figure S16: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **11d** in $CDCl_3$.

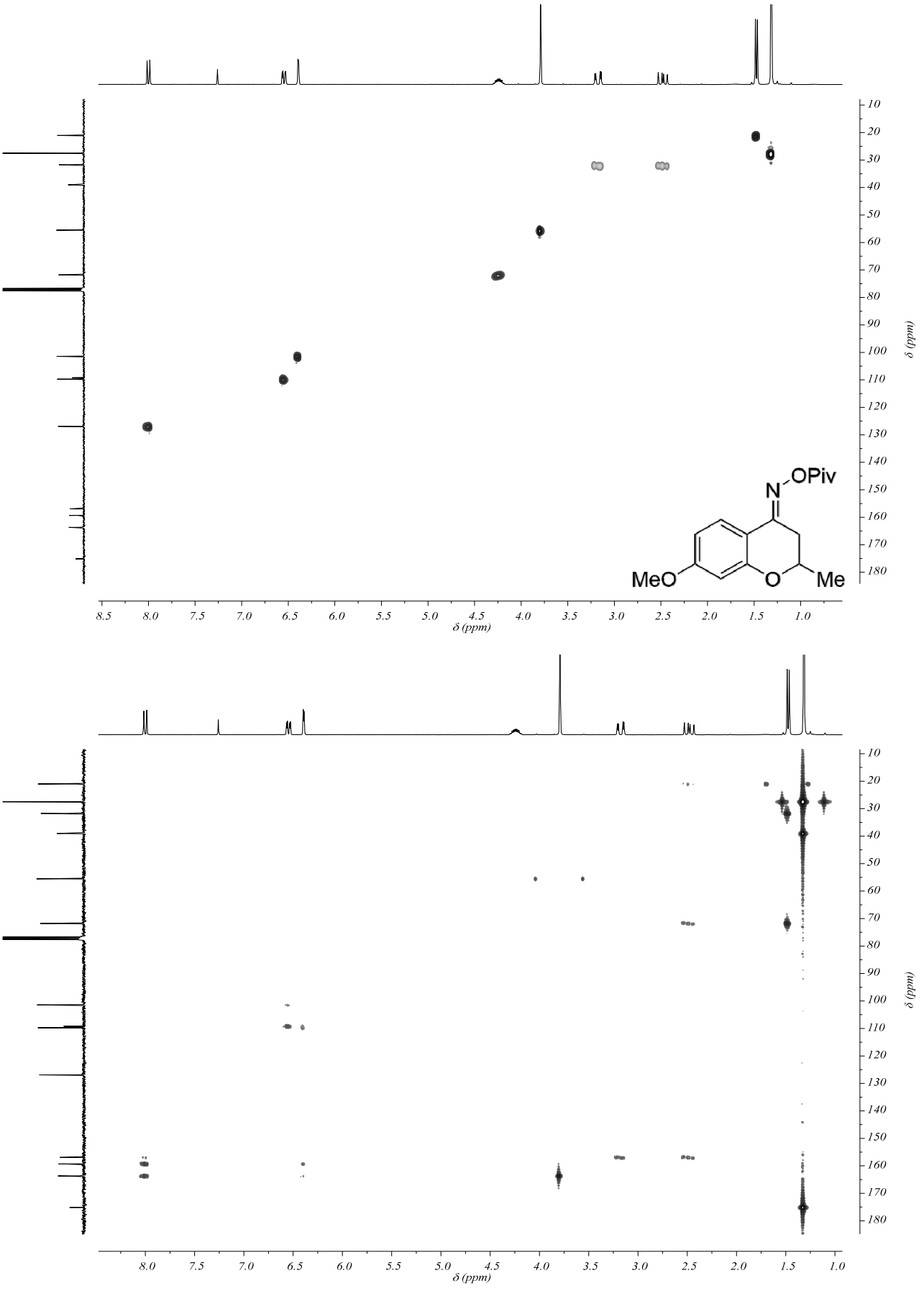


Figure S17: HSQC (top) and HMBC (bottom) spectra of compound **11d** in $CDCl_3$.

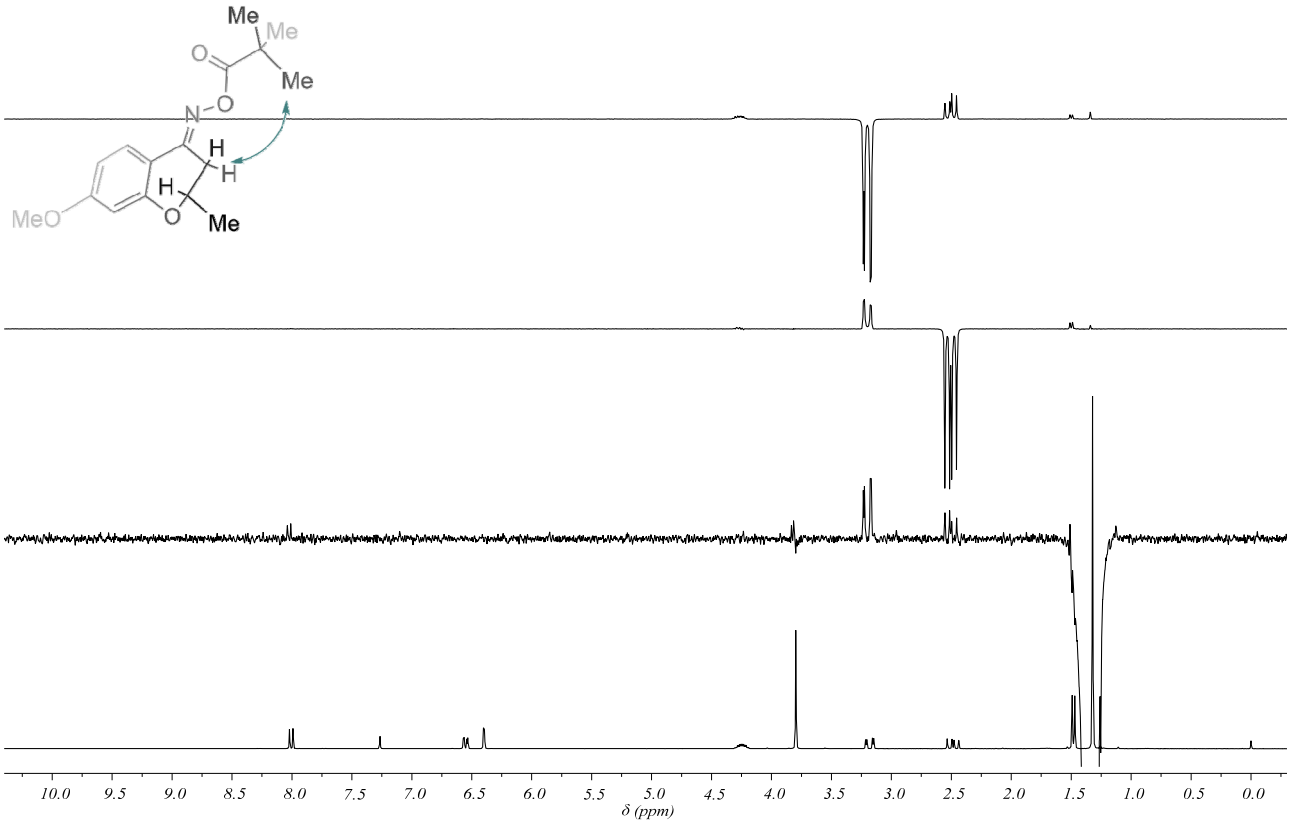


Figure S18: NOE spectra of compound **11d** in $CDCl_3$.

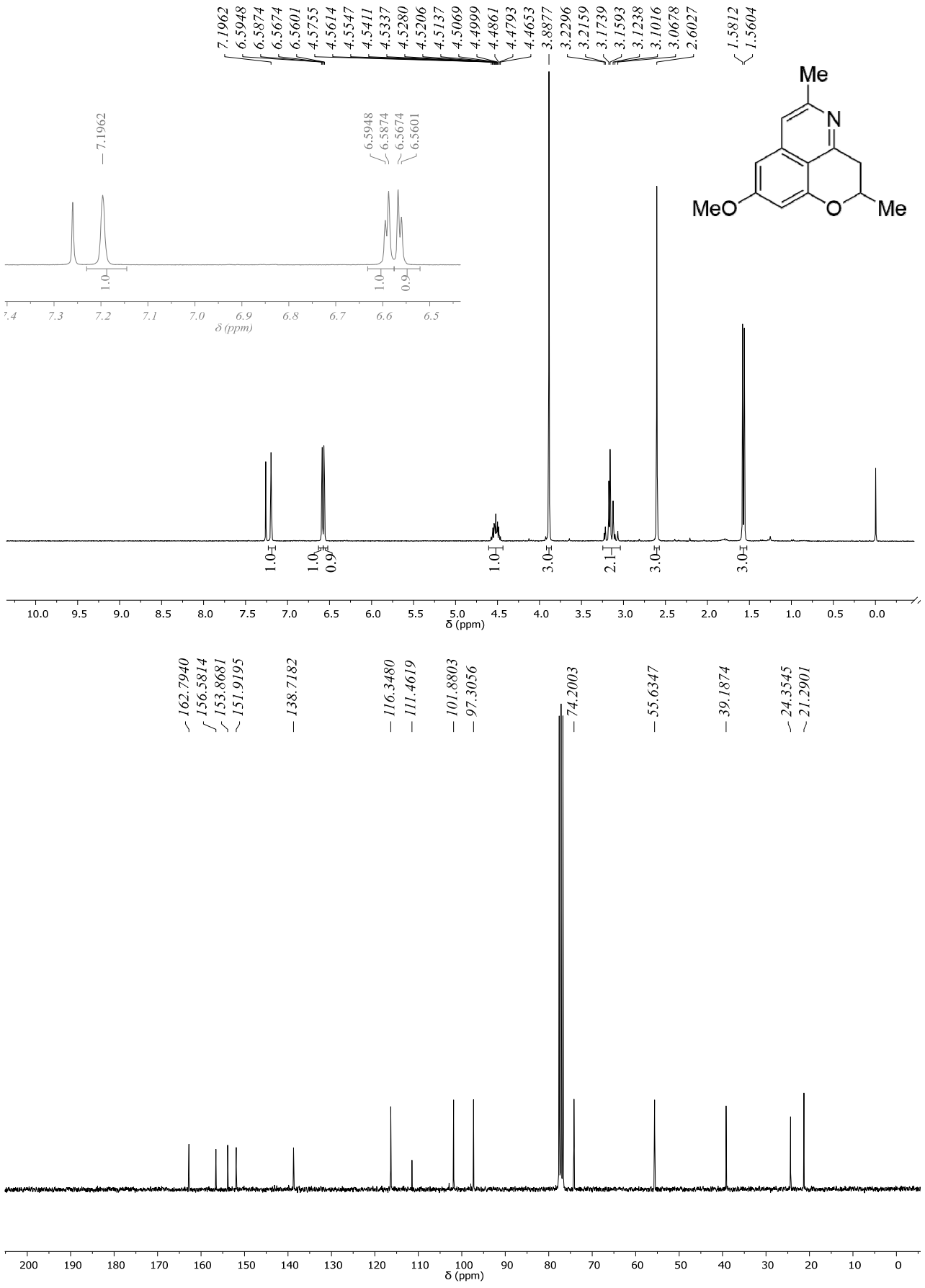


Figure S19: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **17** in $CDCl_3$.

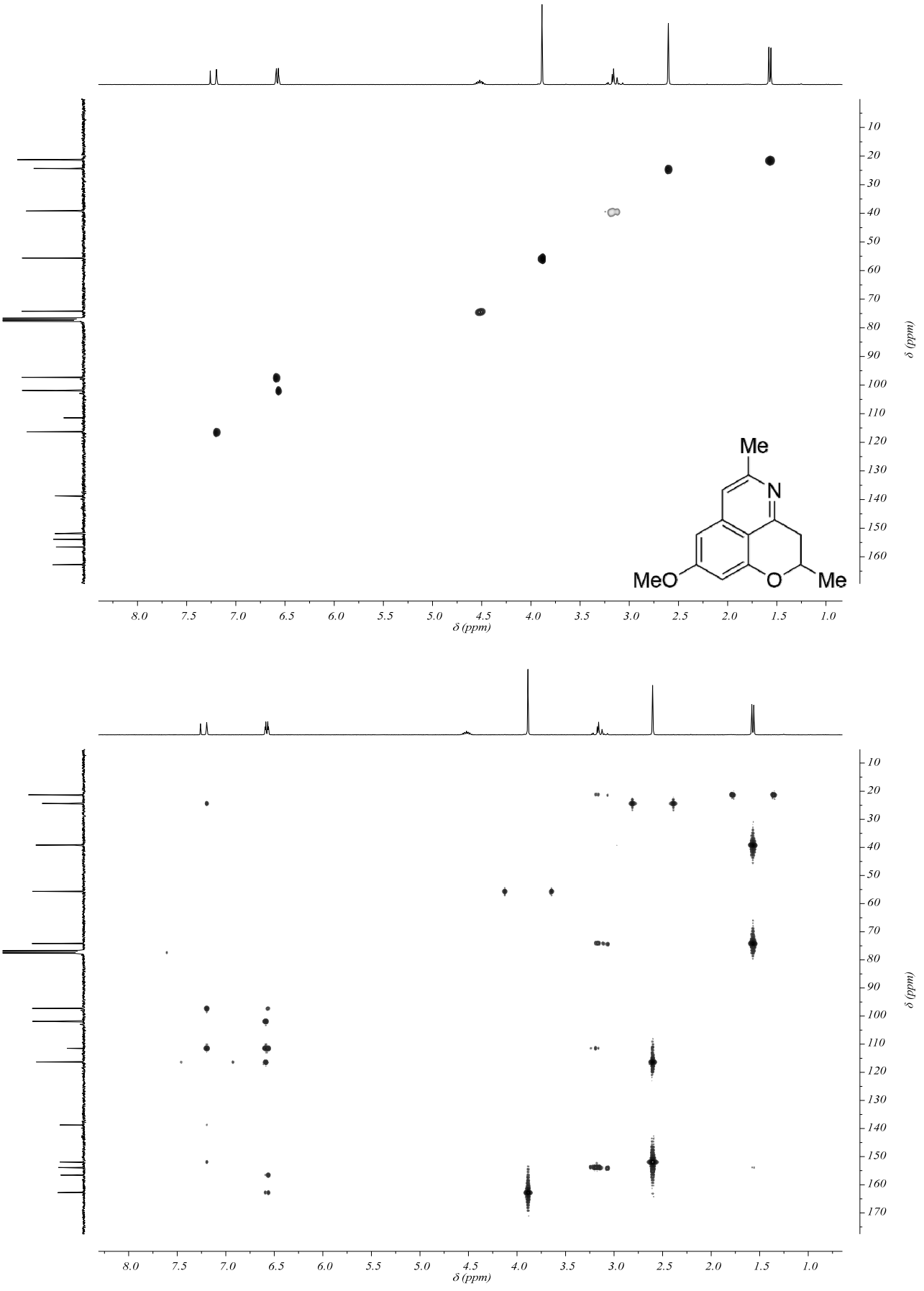


Figure S20: HSQC (top) and HMBC (bottom) spectra of compound **17** in $CDCl_3$.

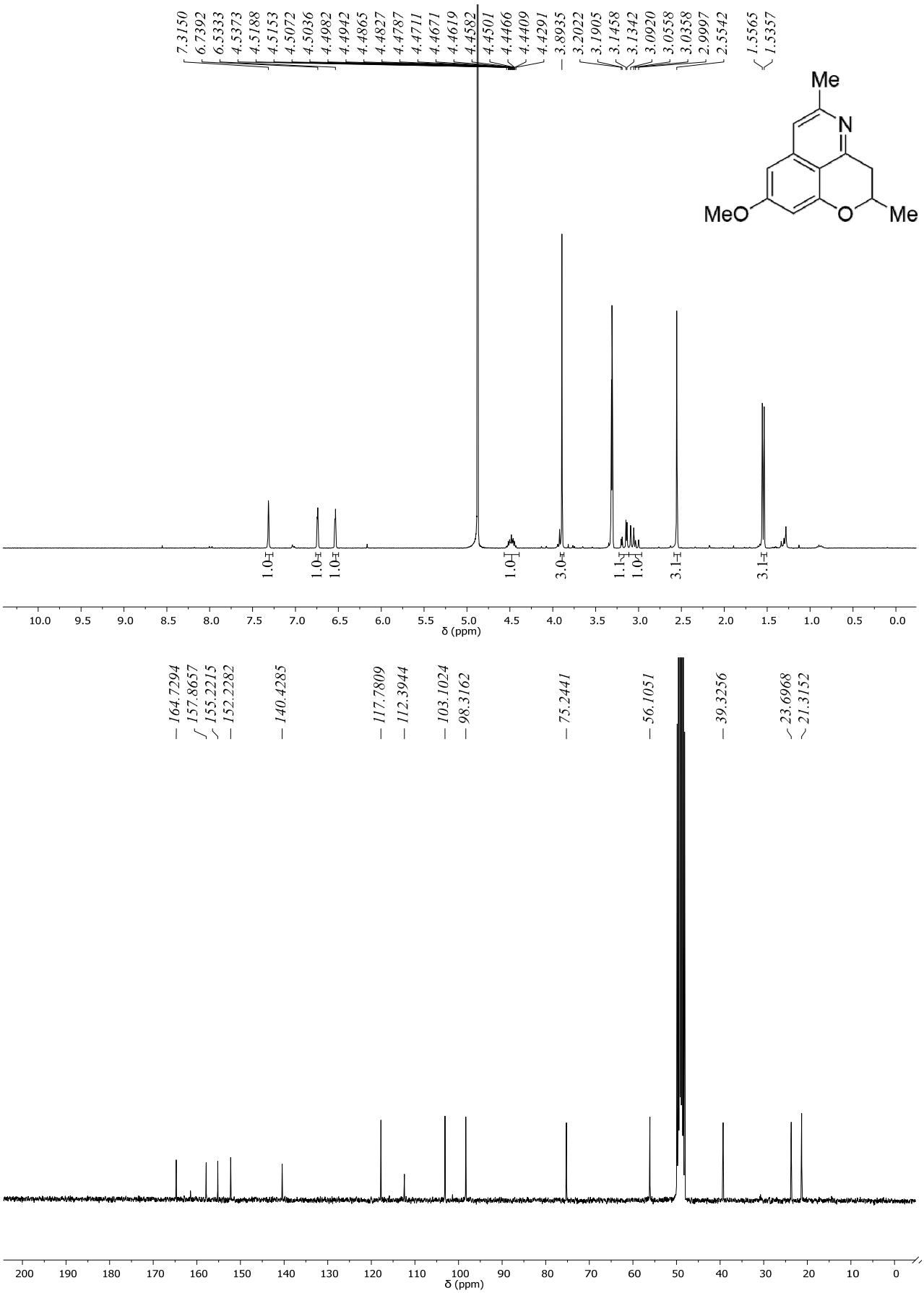


Figure S21: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **17** in CD_3OD.

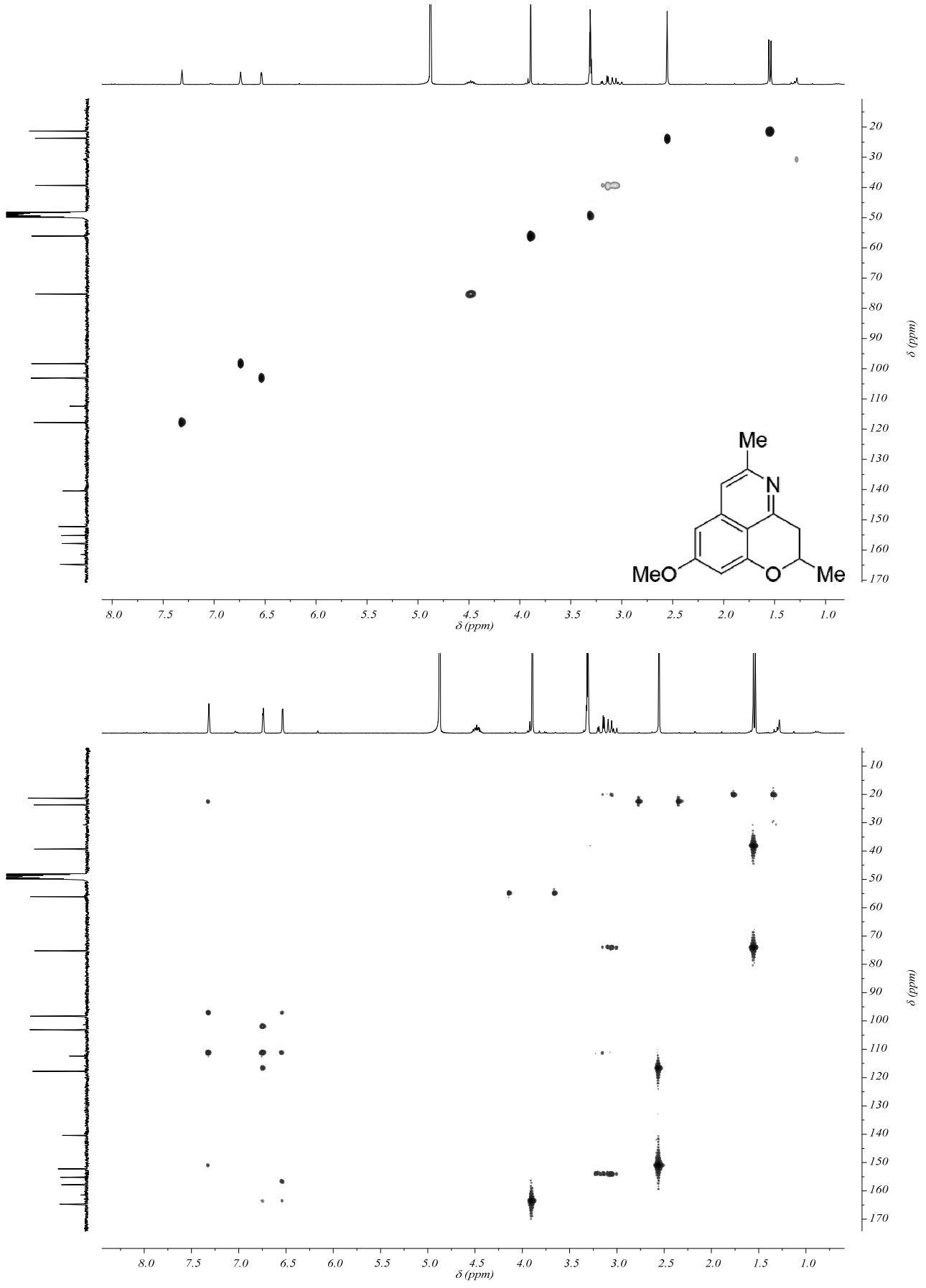


Figure S22: HSQC (top) and HMBC (bottom) spectra of compound **17** in CD_3OD.

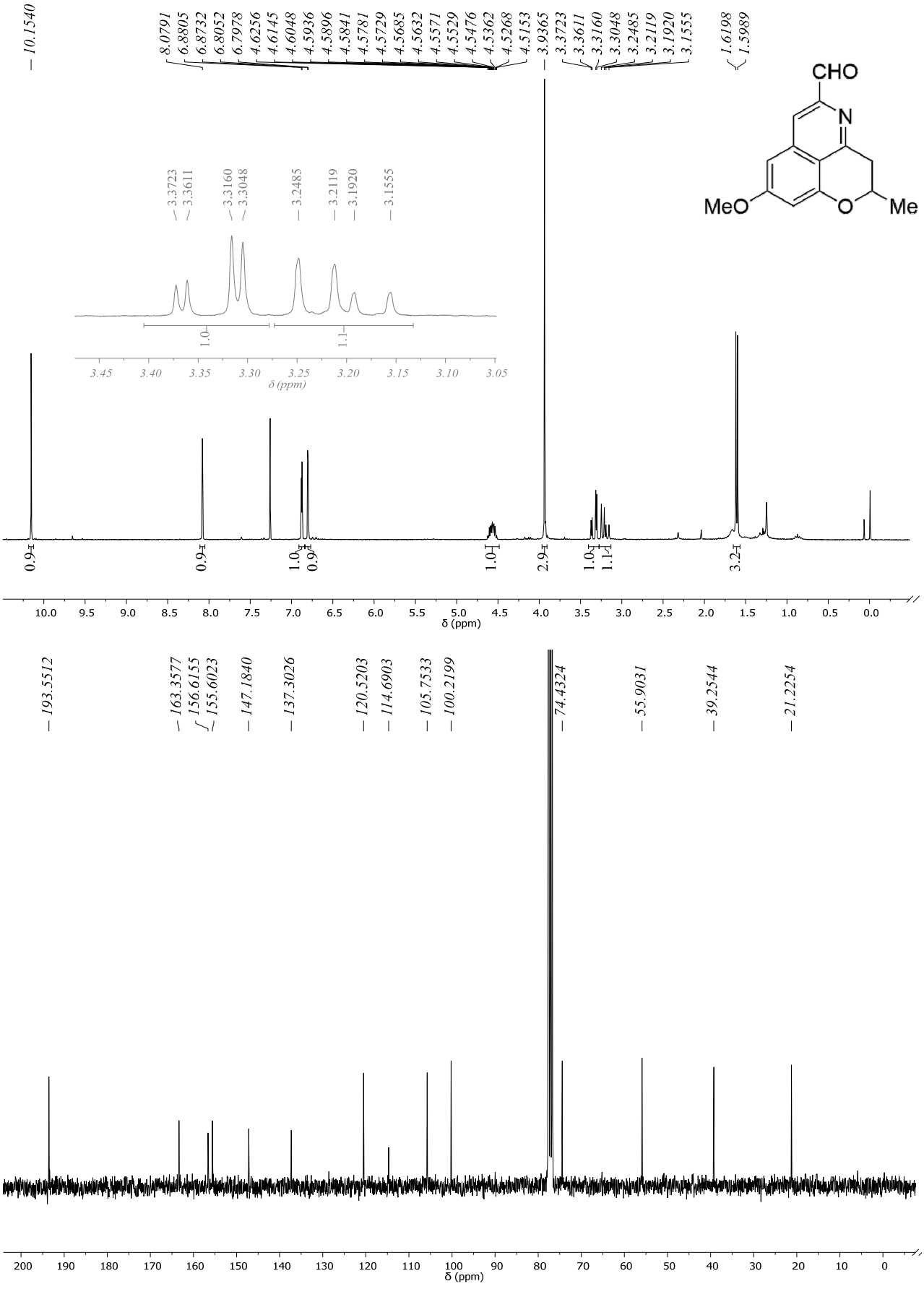


Figure S23: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **18** in $CDCl_3$.

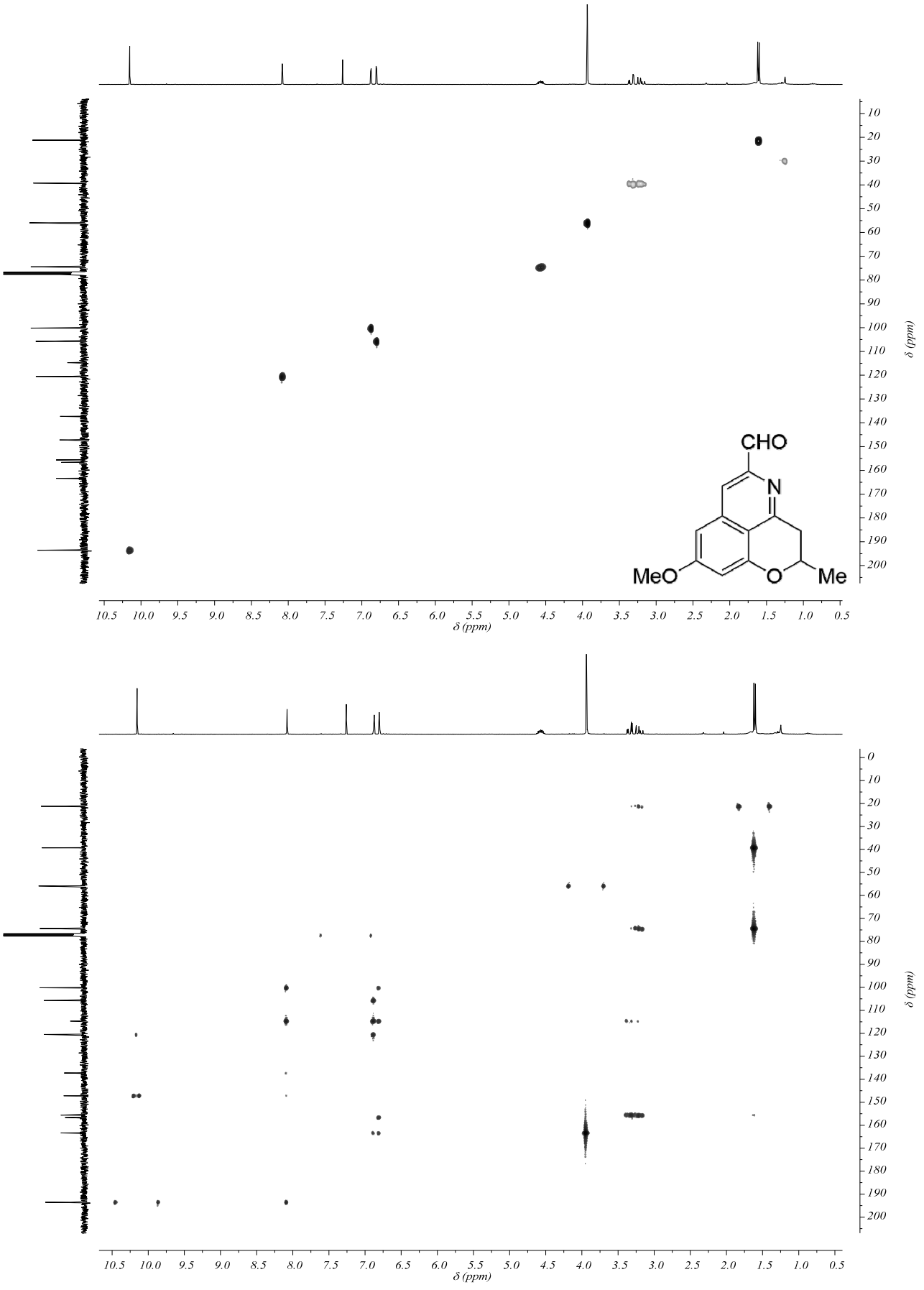


Figure S24: HSQC (top) and HMBC (bottom) spectra of compound **18** in $CDCl_3$.

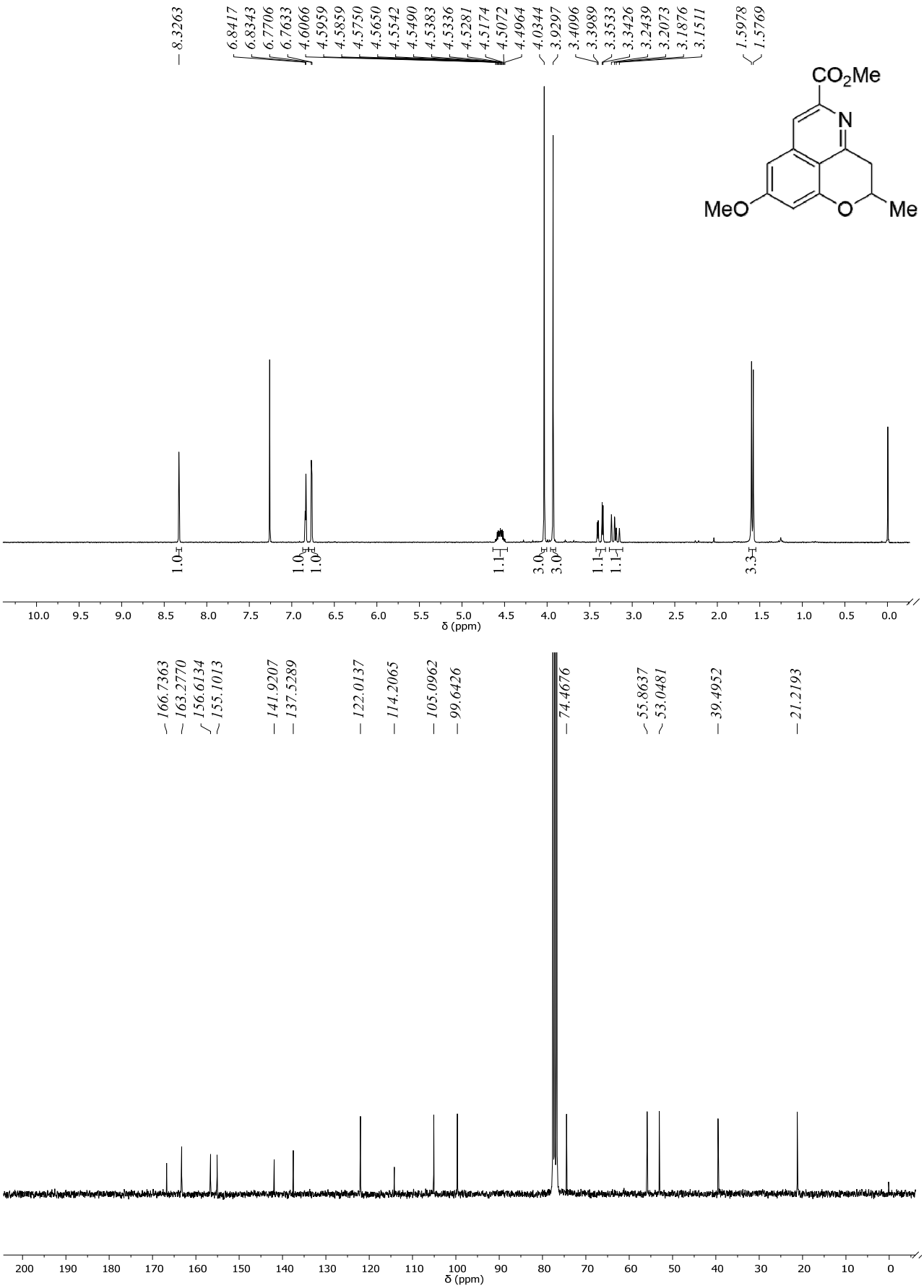


Figure S25: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **19** in $CDCl_3$.

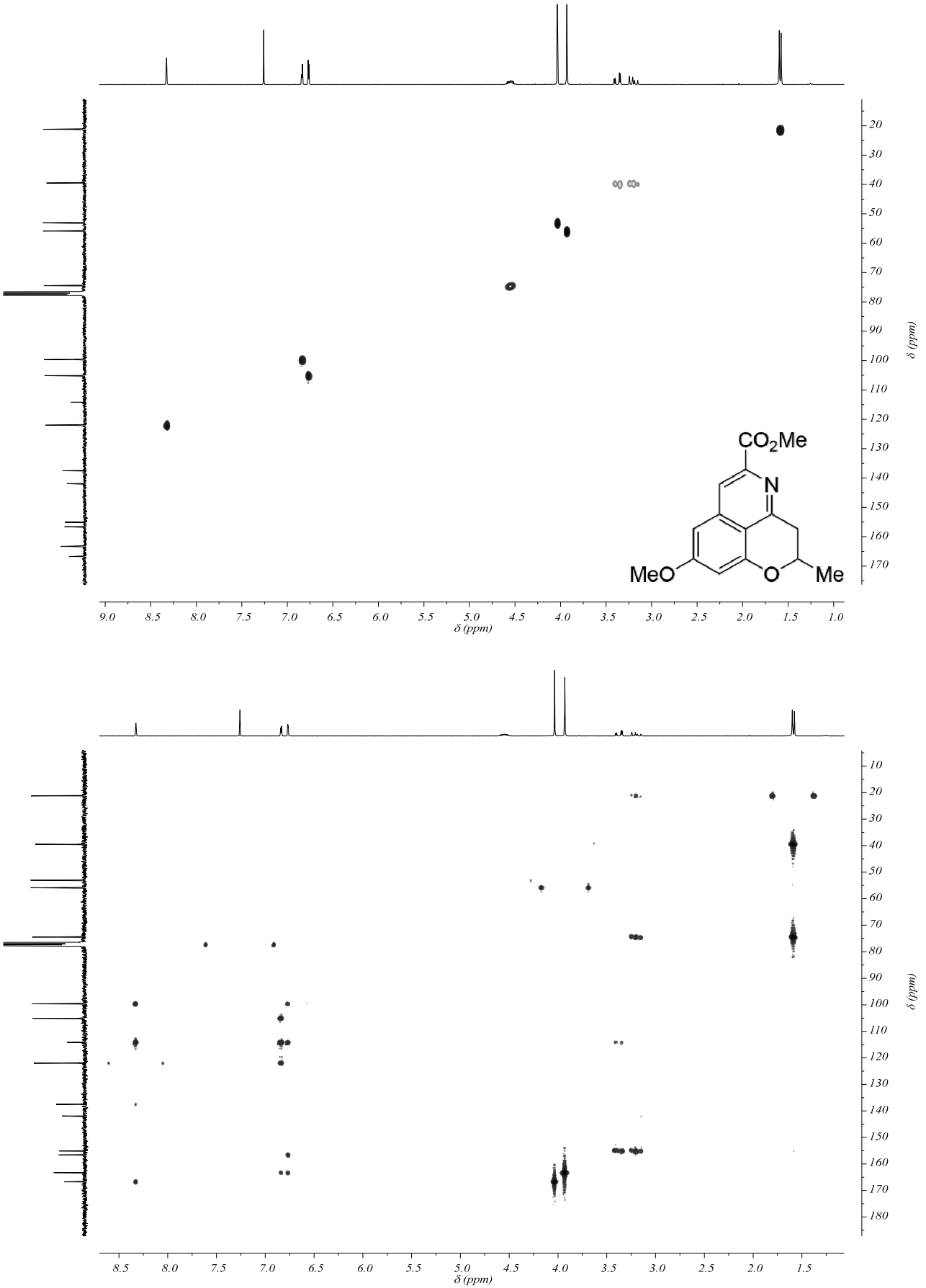


Figure S26: HSQC (top) and HMBC (bottom) spectra of compound **19** in $CDCl_3$.

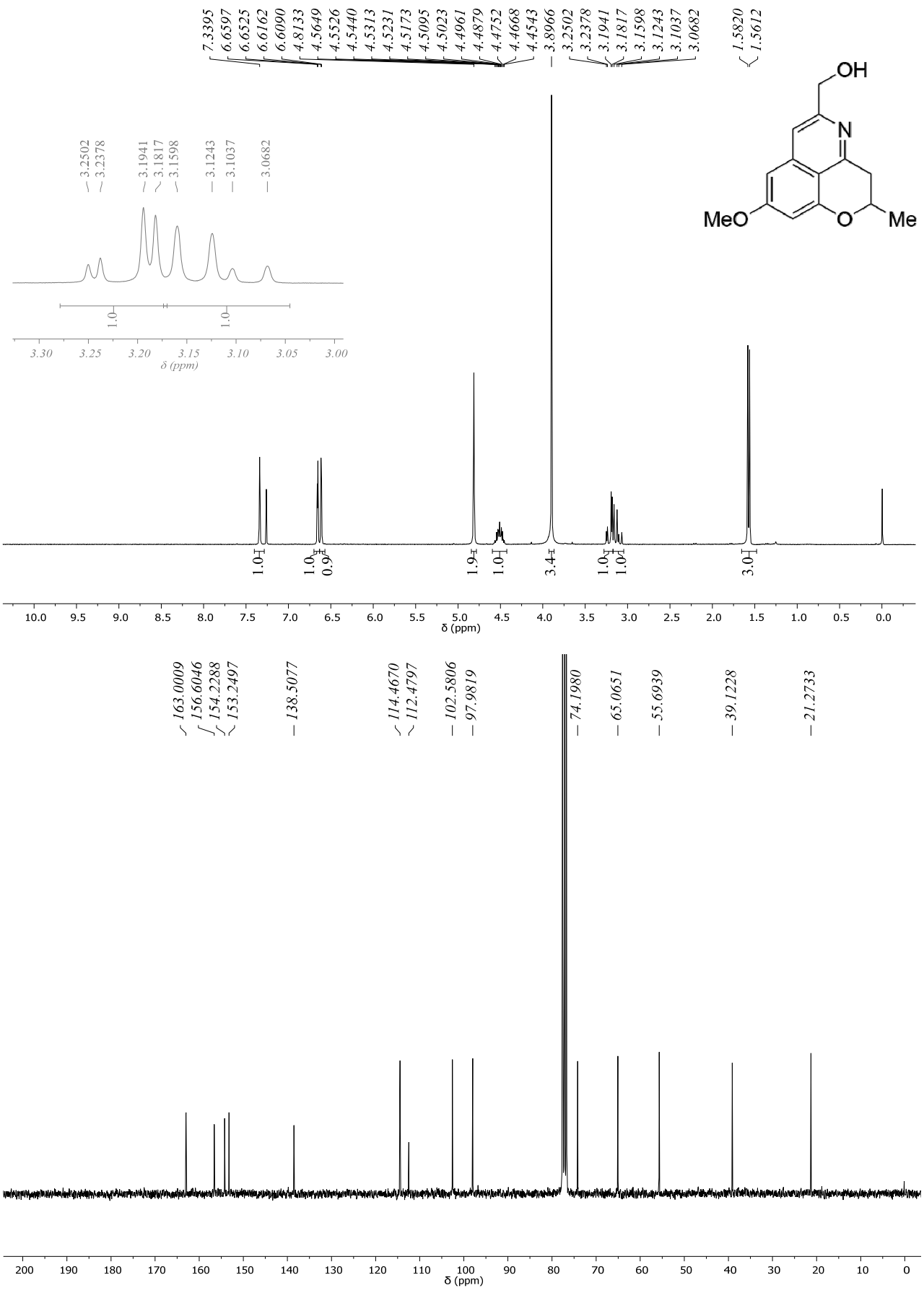


Figure S27: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **20** in $CDCl_3$.

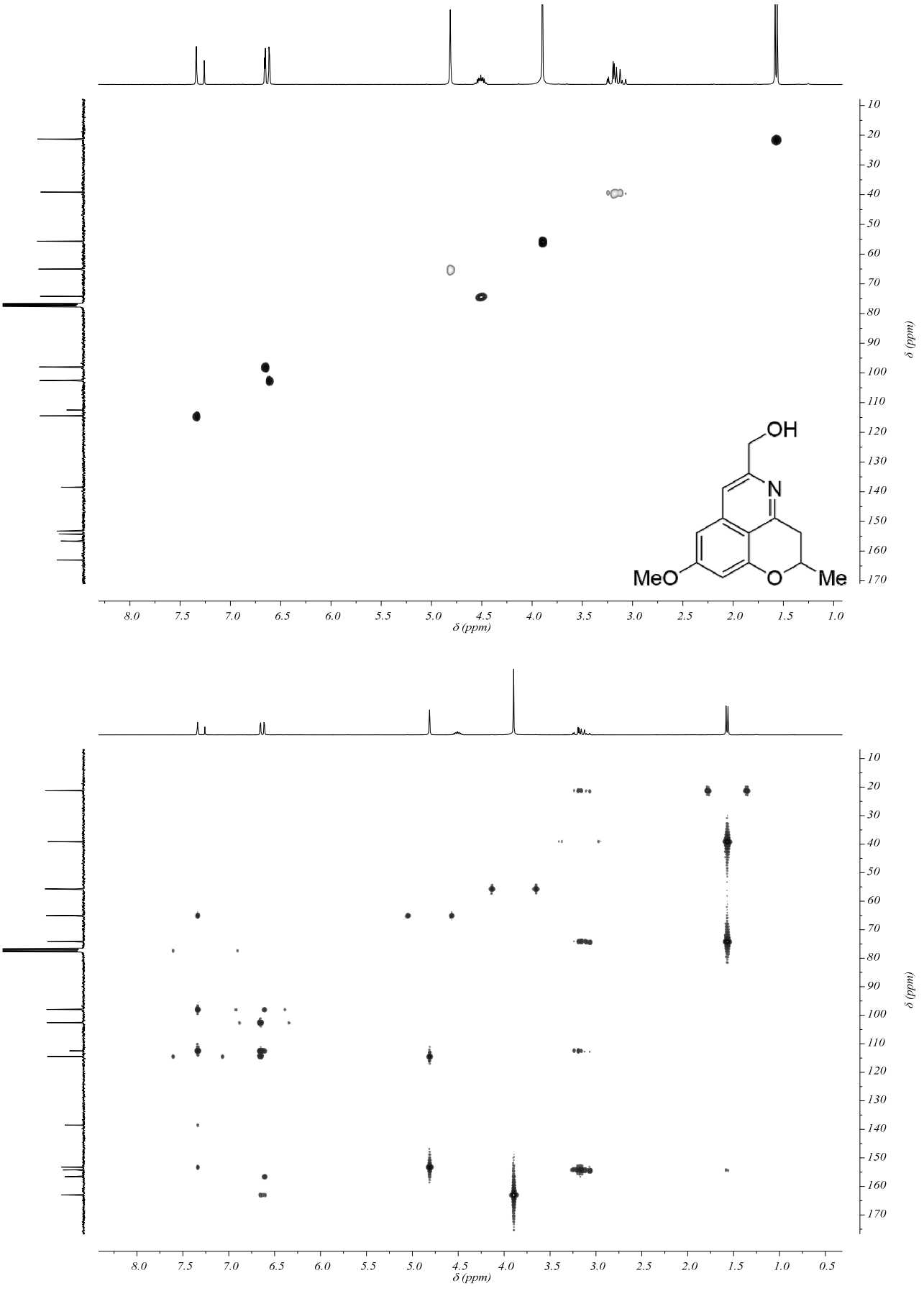


Figure S28: HSQC (top) and HMBC (bottom) spectra of compound **20** in $CDCl_3$.

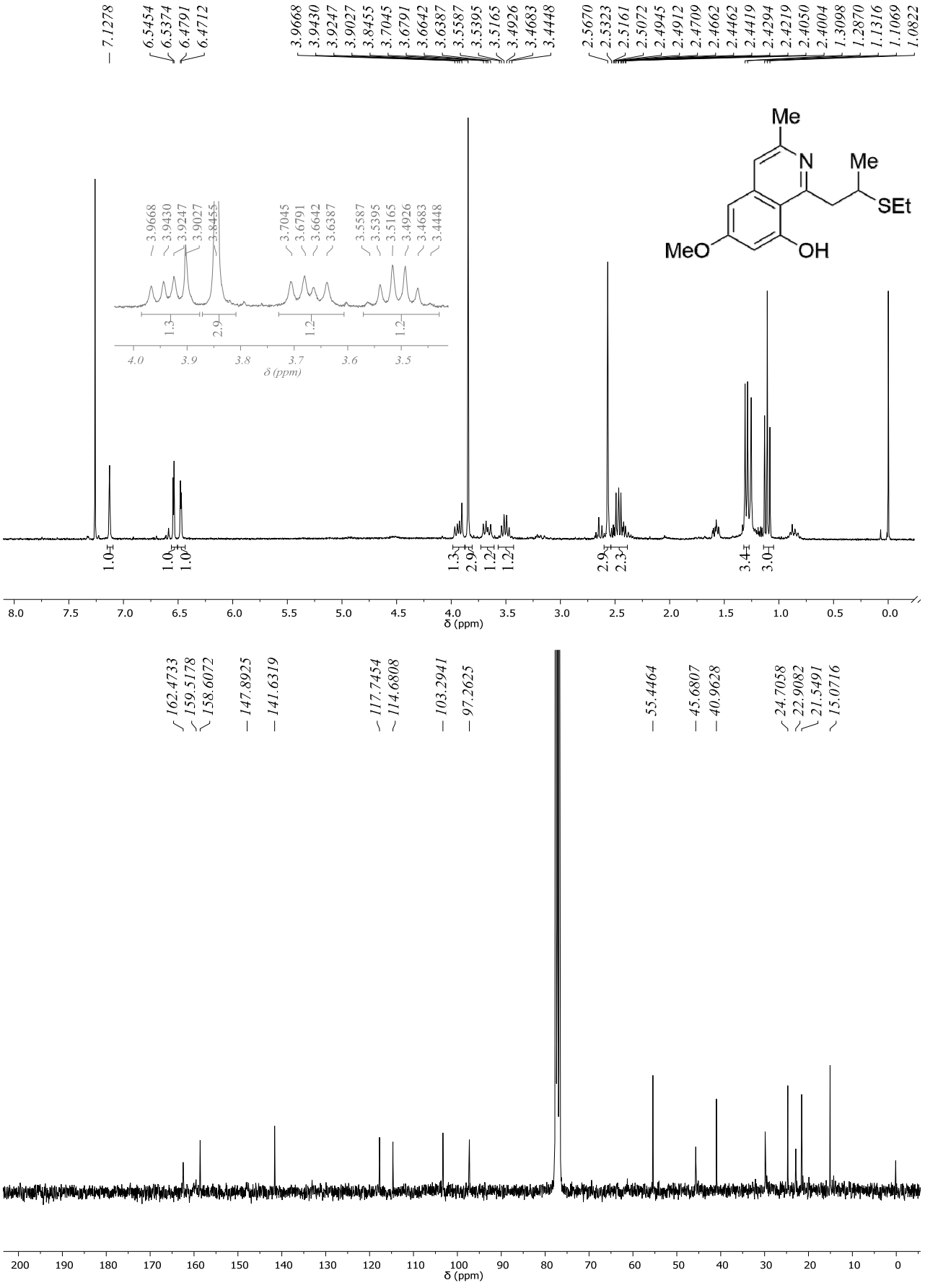


Figure S29: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **22** in $CDCl_3$.

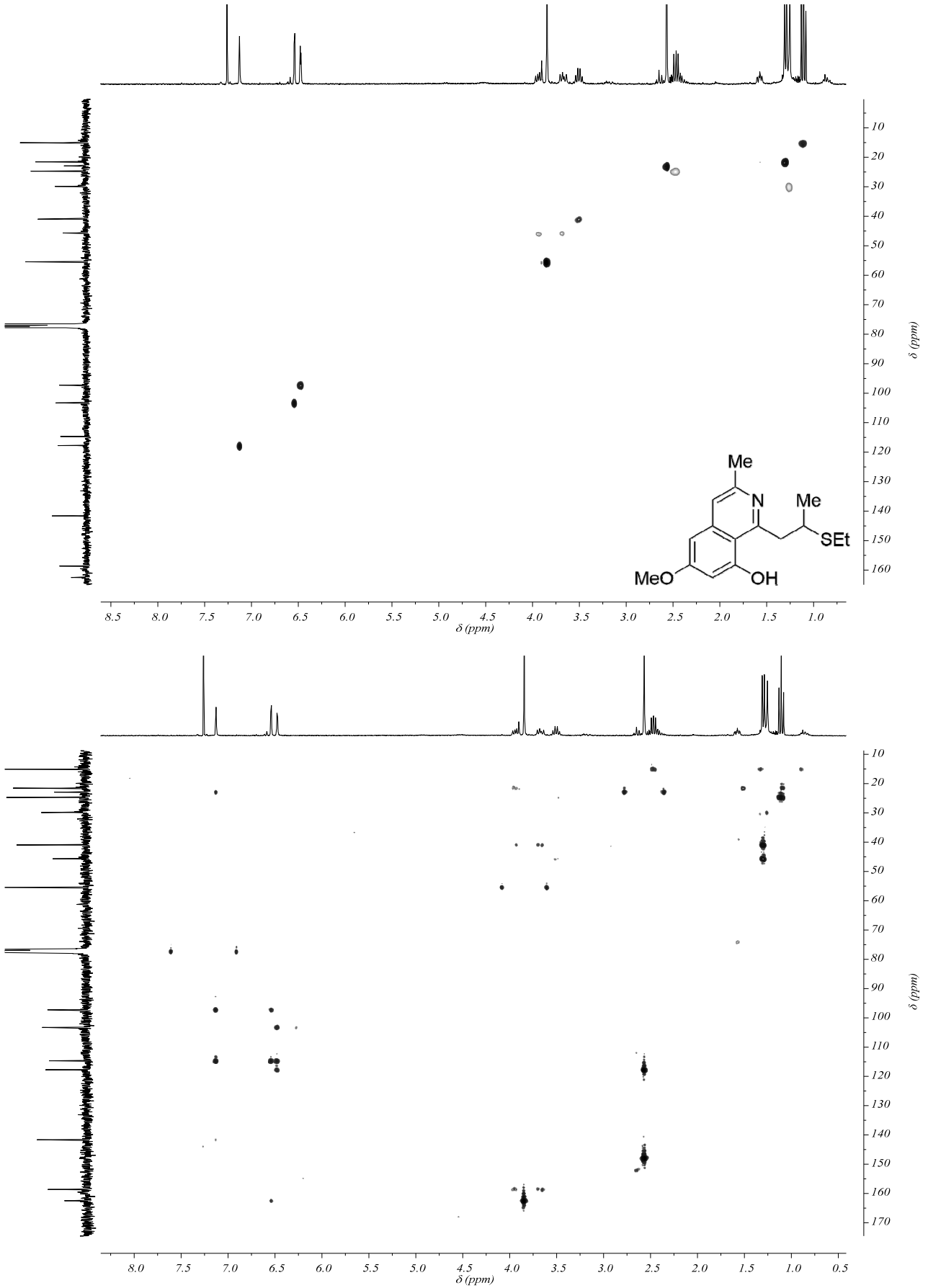


Figure S30: HSQC (top) and HMBC (bottom) spectra of compound **22** in $CDCl_3$.

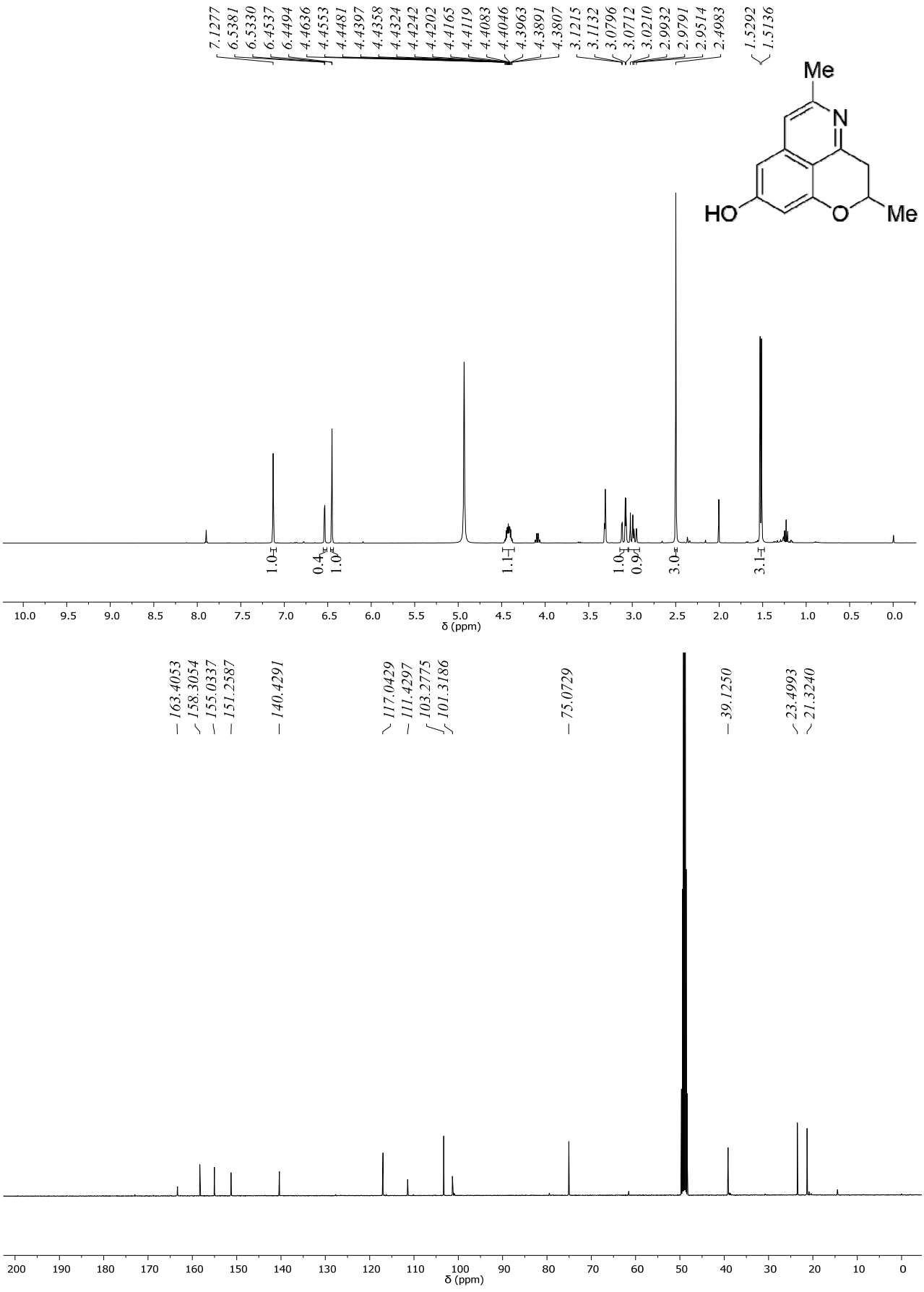


Figure S31: 400 MHz ^{1}H (top) and 100 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **1d** in CD_3OD.

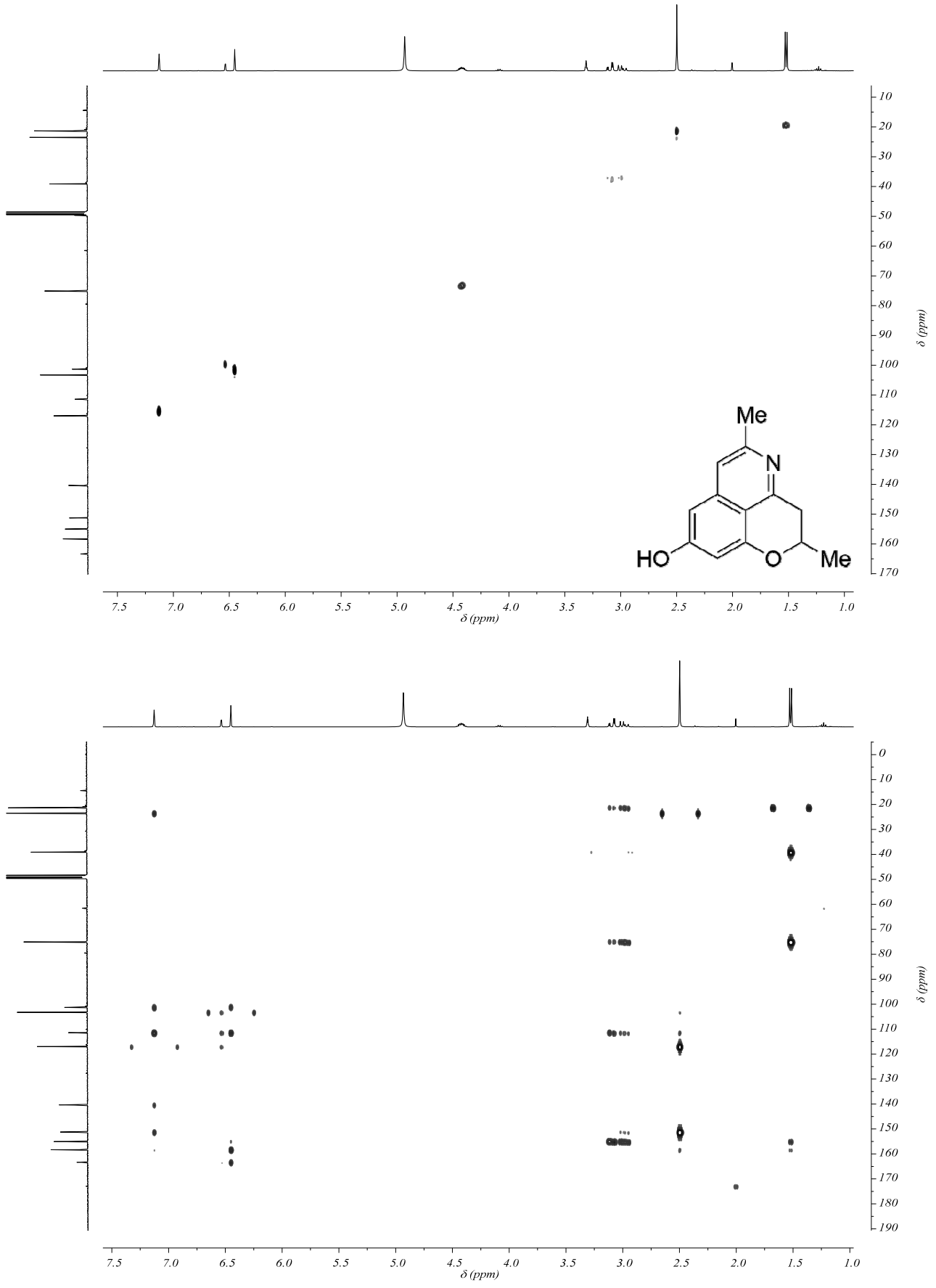


Figure S32: HSQC (top) and HMBC (bottom) spectra of compound **1d** in CD_3OD.

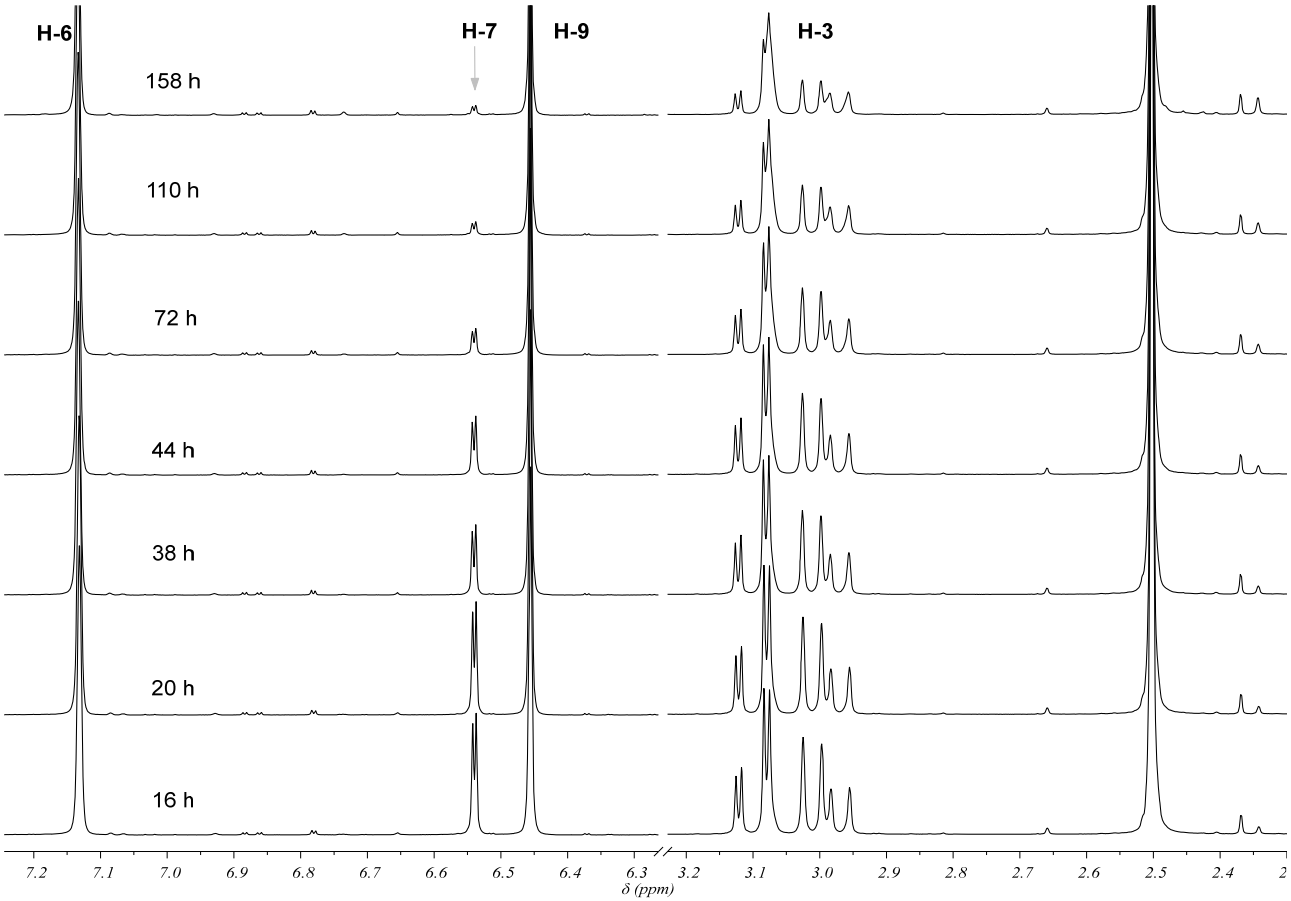


Figure S33: 400 MHz ^{1}H NMR spectra of H/D-exchange of compound **1d** in CD_3OD.

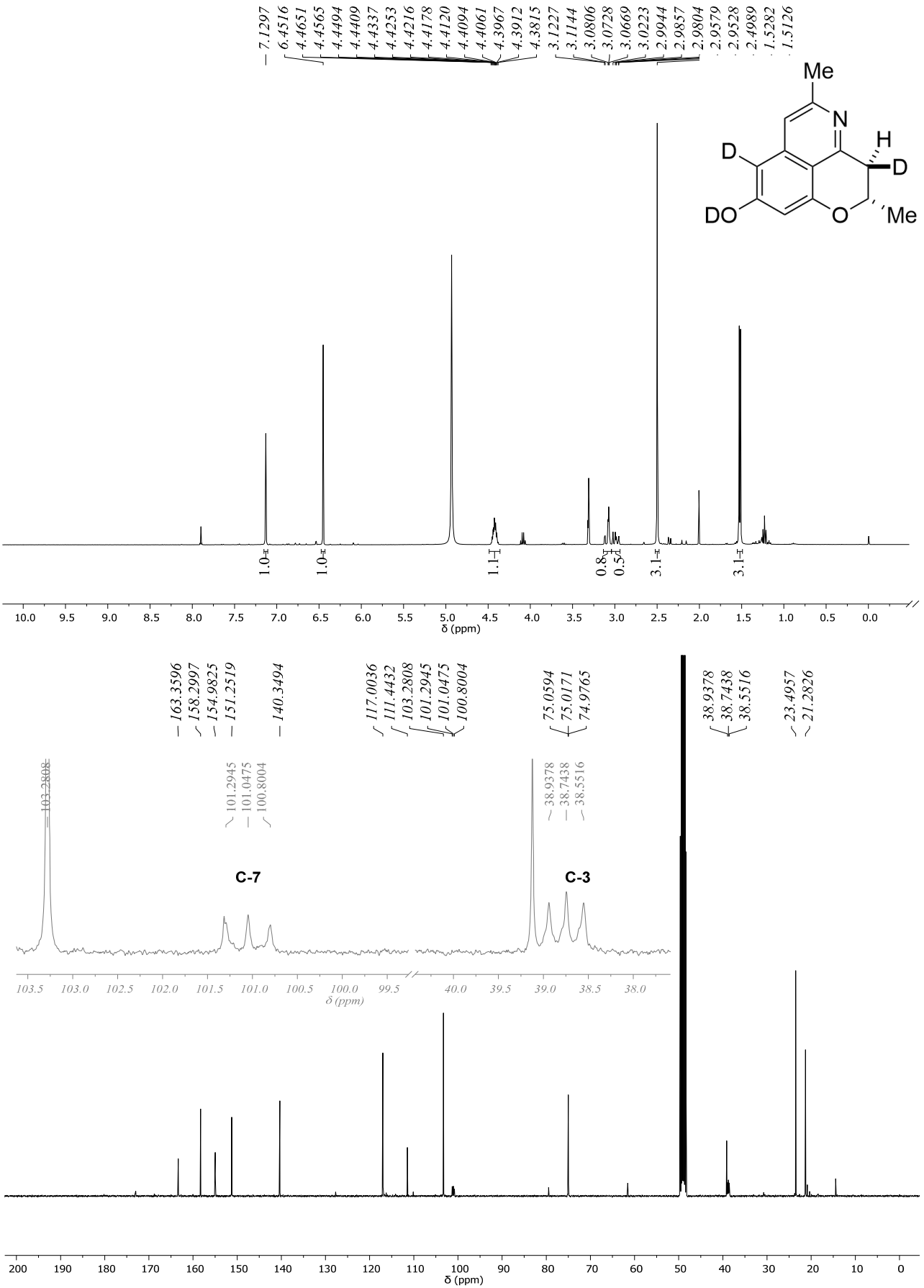


Figure S34: 400 MHz ^{1}H (top) and 100 MHz ^{13}C{^{1}H} (bottom) NMR spectra of compound **[3β,7-*d*$_2$]-1d** in CD_3OD.

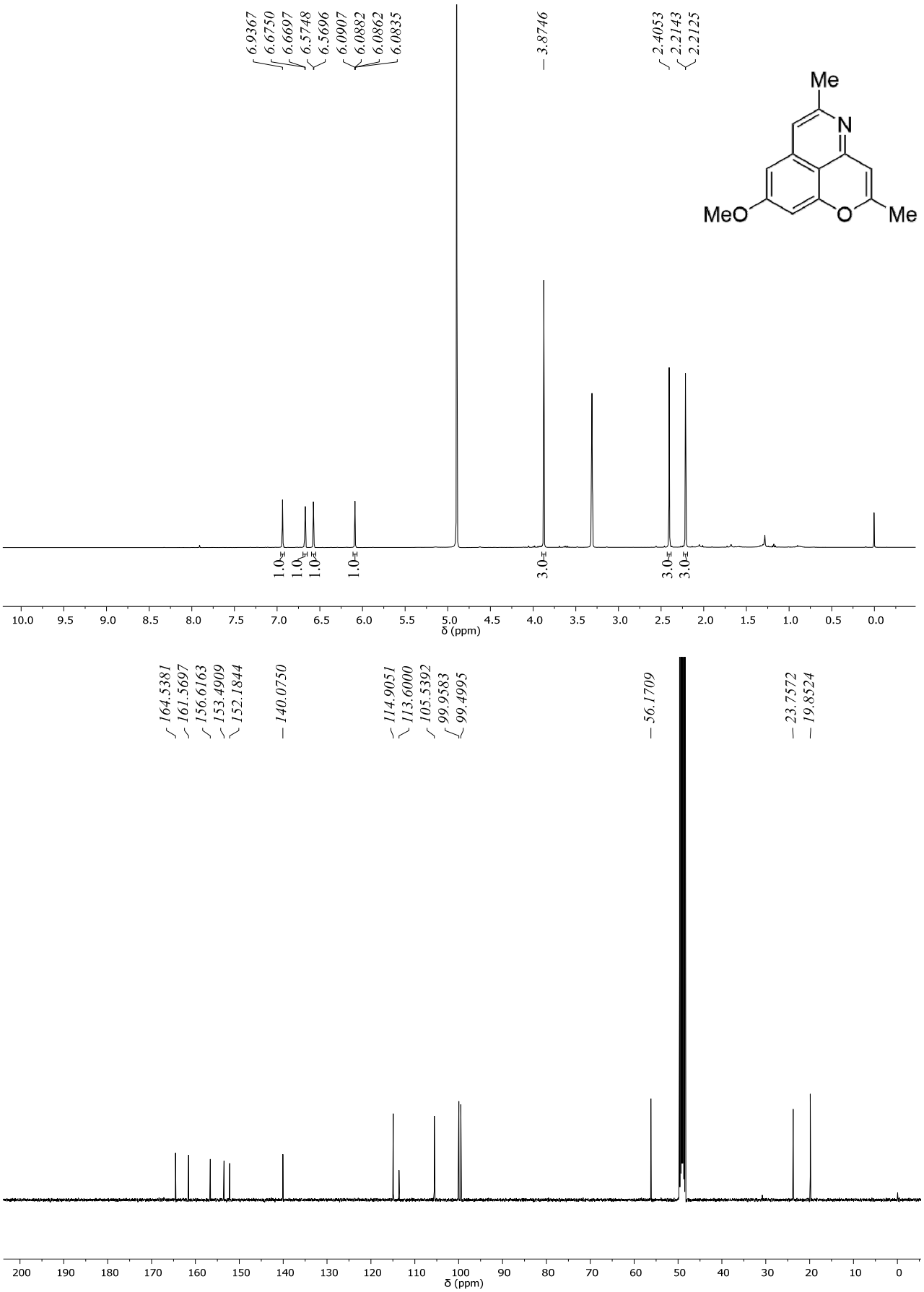


Figure S35: 400 MHz ^{1}H (top) and 100 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **1m** in CD_3OD.

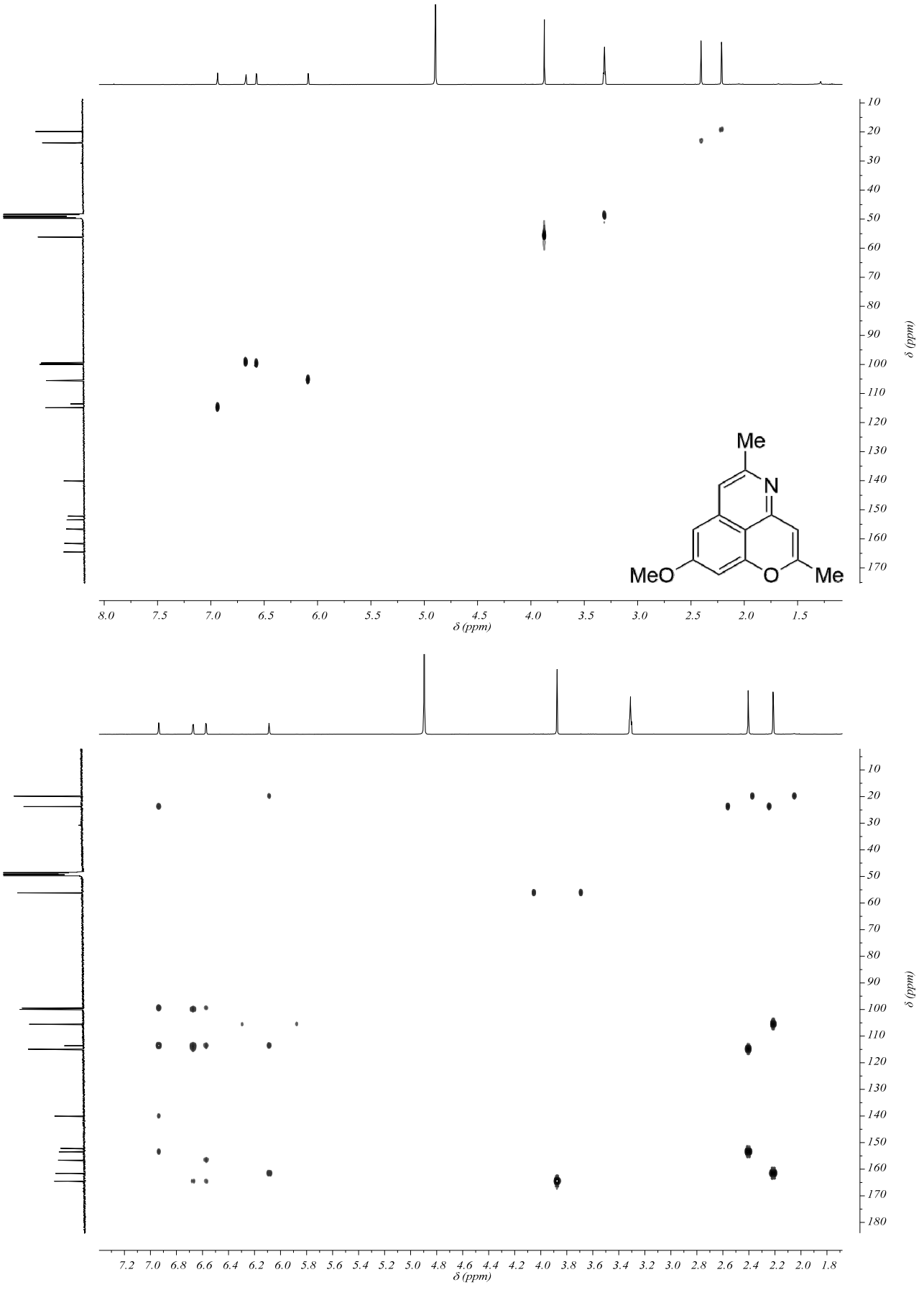


Figure S36: HSQC (top) and HMBC (bottom) spectra of compound **1m** in CD_3OD.

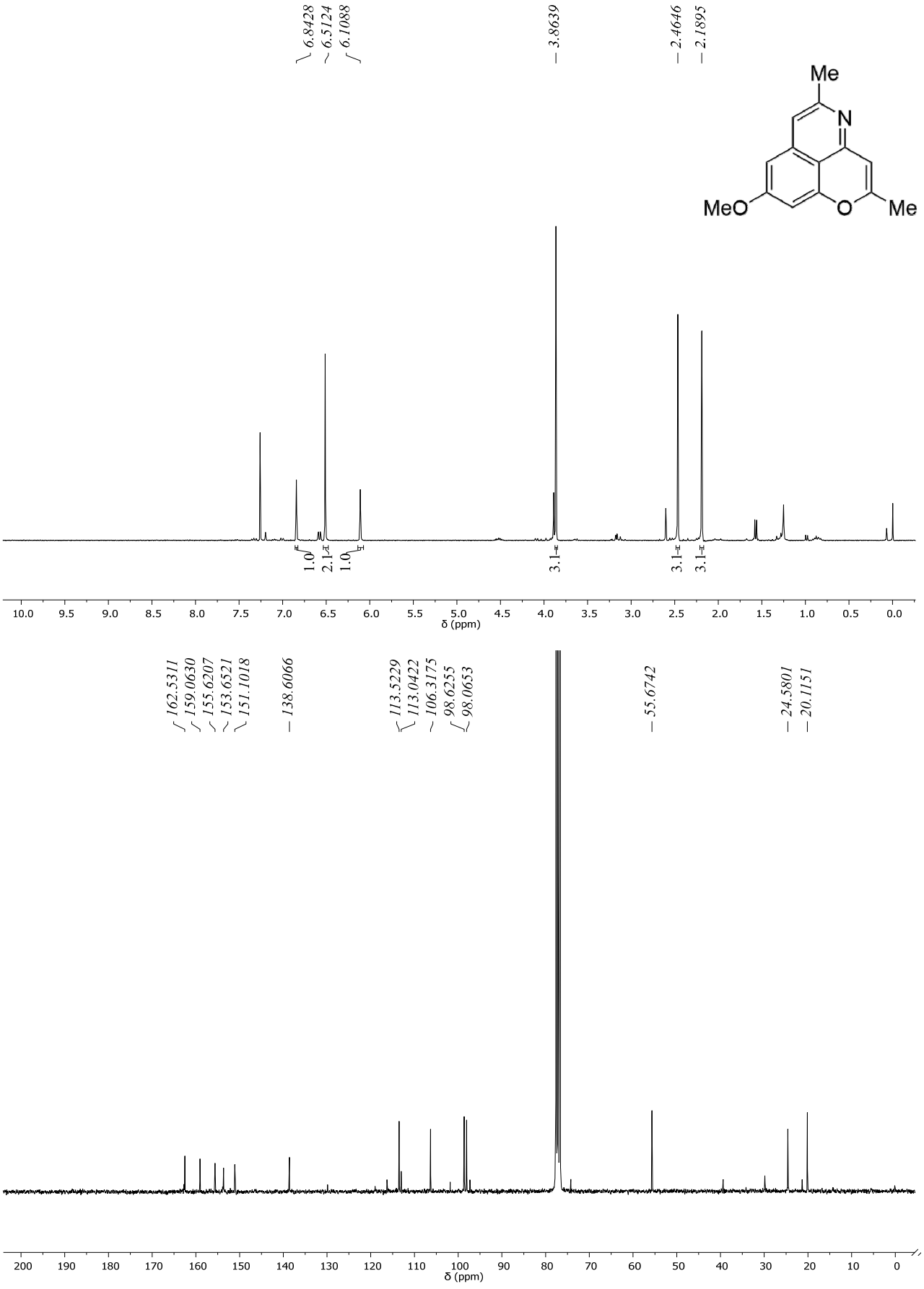


Figure S37: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **1m** in $CDCl_3$.

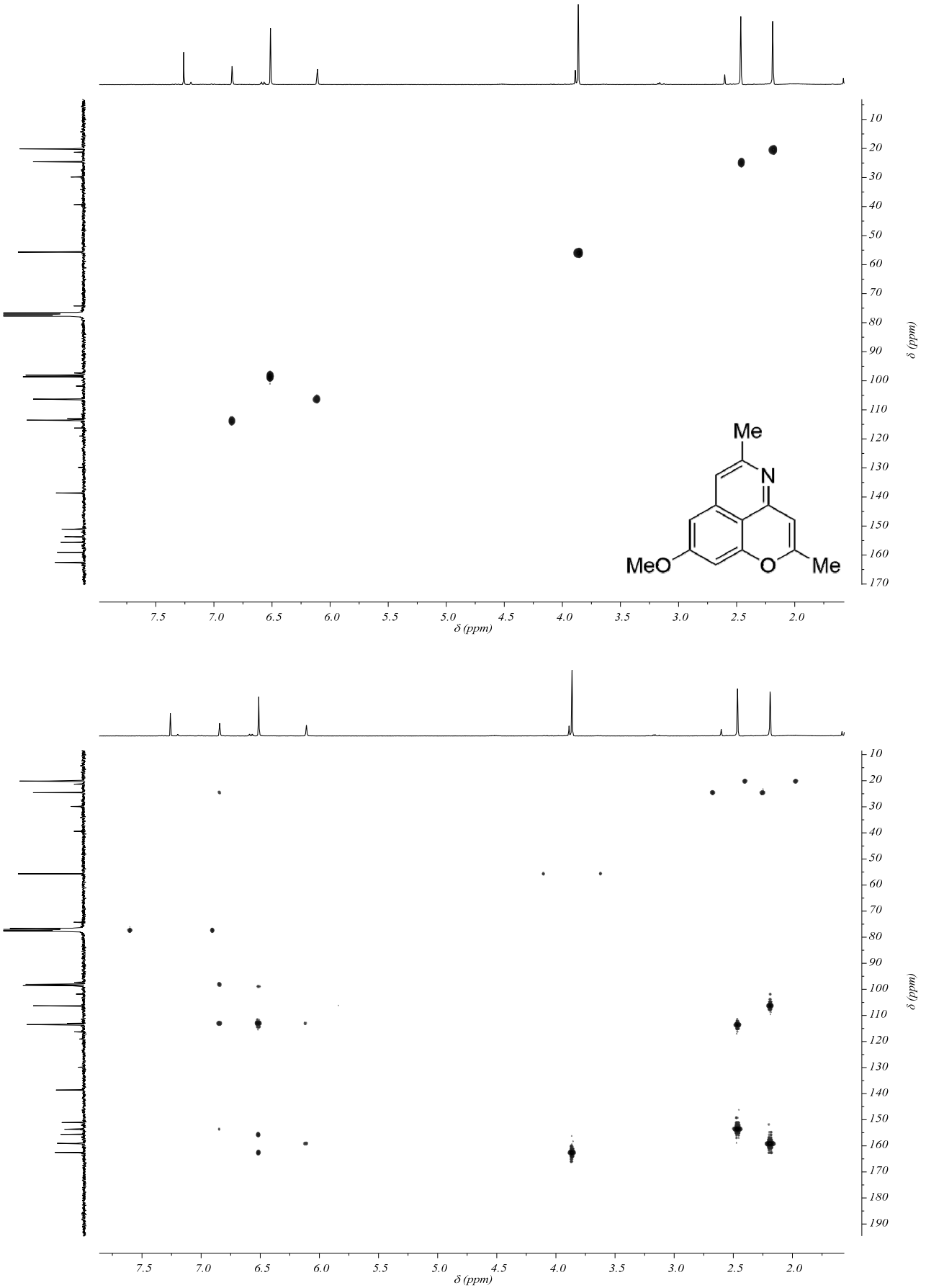
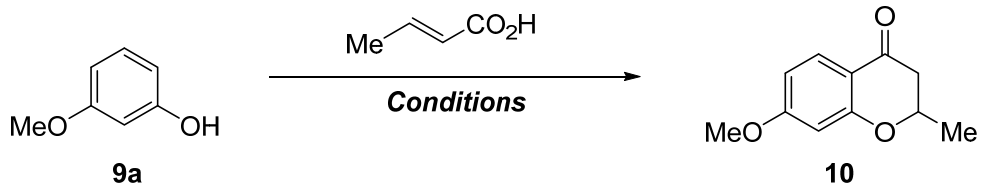


Figure S38: HSQC (top) and HMBC (bottom) spectra of compound **1m** in $CDCl_3$.

Table S1. Reaction conditions for formation of 7-methoxy-2-methylchroman-4-one (**10**).[a]



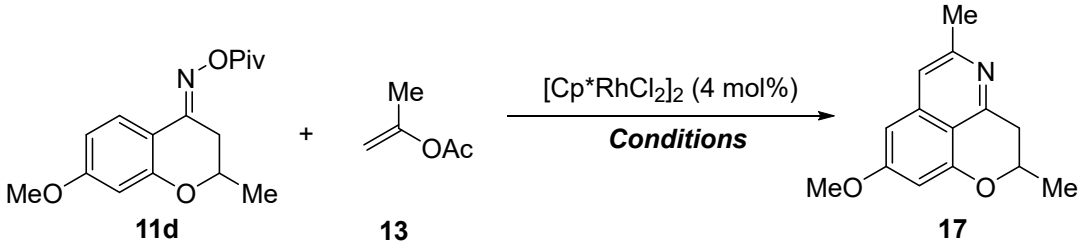
9a **10**

Entry N°	Conditions				Yield (%)[b]
	Promoter (equiv.)	Solvent	Temp. (°C)	Time (h)	
1	$ZnCl_2$ (2.0)		180	0.67	17
2	$Bi(OTf)_3$ (20 mol%)	PhMe	110	24	14
3	$BF_3{\cdot}OEt$		80	18	0
4	MsOH		90	20	13
5	MsOH		100	20	18
6	$MsOH/P_2O_5$		70	24	0
7	TfOH (5.0)	CH_2Cl_2	40	36	5
8	TfOH (5.0)	DCE	90	6	73
9	TfOH (2.5)	DCE	90	6	17
10	MsOH (5.0)	DCE	90	6	0

[a]The reactions were run using **1** (0.8 mmol) and crotonic acid (0.88 mmol).

[b]Yield isolated by column chromatography.

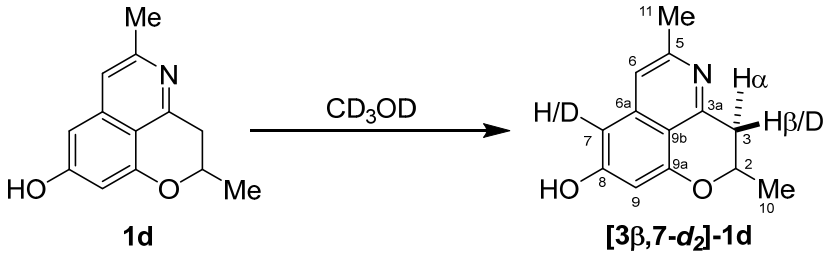
Table S2. Optimization of reaction conditions with isopropenyl acetate (**13**).[a]



Entry N°	[Ag] salt	Oxidant (equiv.)	Additive (equiv.)	Solvent	Temp. (°C)	Yield (%)			
						12	**6**	**4**	**2**
1[b]	$AgSbF_6$	-	-	MeOH	100	8	0	0	52
2	$AgSbF_6$	-	-	MeOH	100	30	0	27	39
3	$AgBF_4$	-	-	MeOH	100	19	0	17	36
4	$AgSbF_6$	-	-	TFE	100	16	40	0	30
5	$AgSbF_6$	-	-	*t*-BuOH	100	30	7	0	44
6	$AgSbF_6$	-	-	HFIP	100	18	0	0	58
7	$AgSbF_6$	-	-	DCE	100	4	19	0	36
8[c]	$AgSbF_6$	-	-	-	100	22	0	0	32
9[b,d]	$AgSbF_6$	-	-	MeOH	120	25	0	0	36
10[d]	$AgSbF_6$	-	-	MeOH	120	31	4	0	47
11[d]	$AgSbF_6$	-	-	*t*-BuOH	120	18	19	0	33
12	$AgSbF_6$	-	-	HFIP:MeCN	90	4	20	0	50
14[e]	-	-	CsOAc (0.3)	MeOH	70	12	42	42	0
15[e]	-	-	CsOAc (0.3)	MeOH	100	12	0	23	34
16[e]	-	-	$Zn(OAc)_2$ (0.5), PivOH (0.5)	DCE	100	9	21	0	0
17	$AgSbF_6$	AgOAc (1.0)	-	MeOH	60	11	30	23	0
18	$AgSbF_6$	AgOAc (1.0)	MS	HFIP	100	12	54	0	11
19	$AgSbF_6$	AgOAc (2.0)	PivOH (3.0)	DCE	90	11	27	0	0

[a]General reaction conditions unless otherwise specified: **6** (0.15 mmol), **8** (0.45 mmol), $[RhCp^*Cl_2]_2$ (4 mol%), $AgSbF_6$ (20 mol%), oxidant, additive, solvent (1 mL) under Ar atmosphere for 56 h in pressure tubes. [b]*O*-acetyl oxime **5** was used as a starting material. [c]Isopropenyl acetate (**8**) was used as the solvent. [d] 24 h. [e] The reaction was carried out using **8** (1.5 mmol) for 72 h.

Table S3. H/D-exchange reaction of **1d**.[a]



1d **[3β,7-d_2]-1d**

Entry N°	Time (h)	Integral H-6	Integral H-7	Integral H-3β
1	16	1	0.4199	0.8991
2	20	1	0.3717	0.8782
3	38	1	0.2355	0.8072
4	44	1	0.2002	0.7843
5	72	1	0.0964	0.6736
6	110	1	0.0515	0.5526
7	158	1	0.0387	0.4319

[a]H/D-exchange reaction was monitoring by ^{1}H NMR of a ~0.02 M solution of **1d** in CD_3OD. The measuring temperature was 25 °C inside the device and the NMR tube was kept at room temperature (25 °C) between measurements.

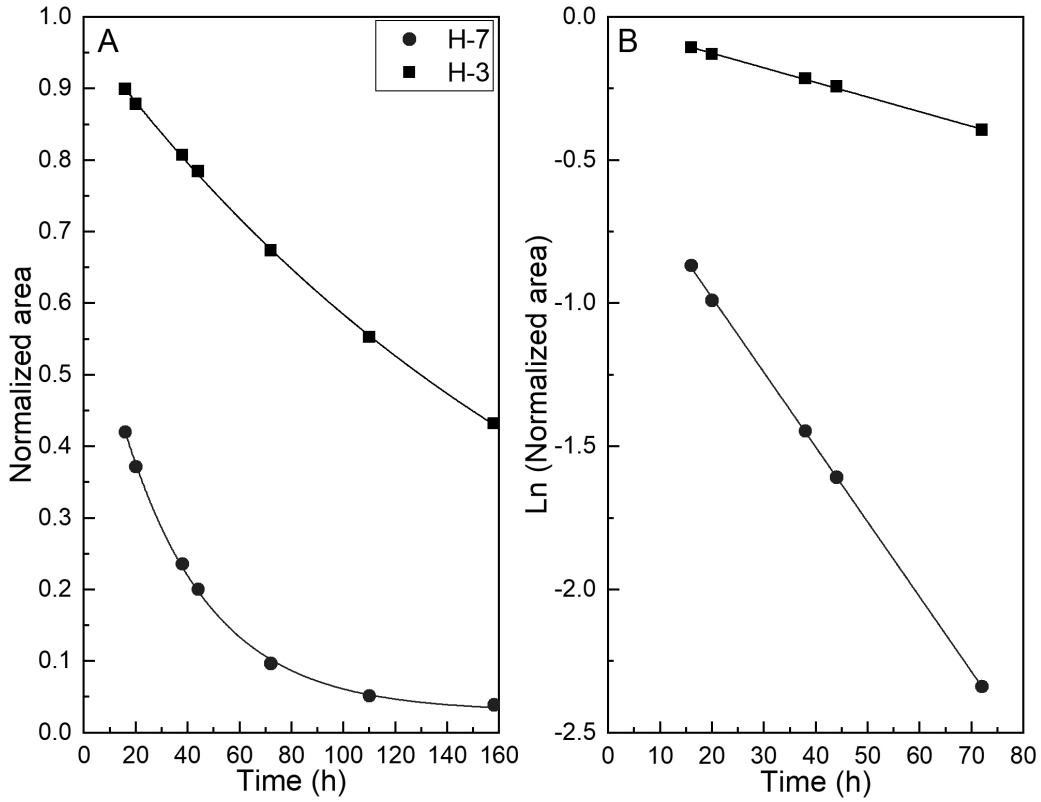


Figure S39. A) H/D exchange of compound **1d** at the H-3β (■) and H-7 (●) sites. B) Semilogarithmic representation of the data in the time interval 20-72 h.

For the equation: Area of H-3 = A*exp(-t/t_1) + y_0

y_0= -0.05055 ± 0.06092

A= 1.02571 ± 0.05759

t_1= 208.70786 ± 18.29862

n= 7

r^2= 0.99974

Adj. r^2= 0.99961

For the equation: ln (Area of H-3) = y_0 + b*t

y_0= -0.02364 ± 0.00475

b= -0.00511 ± 1.10666E-4

n= 5

Pearson's r= -0.9993

k_{obs} (s^{-1})= -b/3600= 1.42E-6

$t_{1/2}$ (h)= -ln(2)/b= 136

For the equation: Area of H-7 = A*exp(-t/t_1) + y_0

y_0= 0.02976 ± 0.00433

A= 0.62867 ± 0.01132

t_1= 33.37459 ± 1.16967

n= 8

r^2= 0.99937

Adj. r^2= 0.99905

For the equation: ln (Area of H-7) = y_0 + b*t

y_0= -0.45689 ± 0.0073

b= -0.02614 ± 1.70075E-4

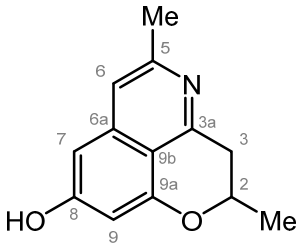
n= 5

Pearson's r= -0.99994

k_{obs} (s^{-1})= -b/3600= 7.26E-6

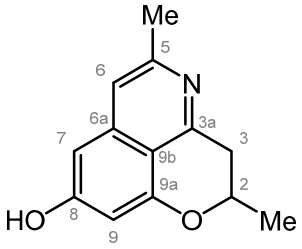
$t_{1/2}$ (h)= -ln(2)/b= 26.5

Table S4. Spectroscopic comparison of ^{1}H NMR data of cassiarin C (**1d**).



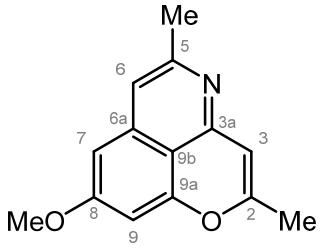
Proton N°	Morita & Co-Workers:[1] (CD_3OD, 400 MHz)	Hibino & Co-Workers:[2] (CD_3OD, 300 MHz)	This Report: (CD_3OD, 400 MHz)	Δδ (ppm)
2-Me	1.56 (d, J = 6.0)	1.54 (d, J = 6.2)	1.52 (d, J = 6.3)	-0.04
2	4.53–4.45 (m)	4.53–4.41 (m)	4.55–4.42 (m)	-0.07
3	3.13 (dd, J = 16.8 and 3.2) 3.06 (dd, J = 16.8 and 10.9)	3.18–2.27 (m)	3.10 (dd, J = 16.8 and 3.3) 2.99 (dd, J = 16.8 and 11.0)	-0.03 -0.07
5-Me	2.53 (s)	2.52 (s)	2.50 (s)	-0.03
6	7.20 (s)	7.19 (s)	7.13 (s)	-0.07
7	6.57 (d, J = 2.0)	6.57 (d, J = 2.0)	6.54 (d, J = 2.1)	-0.03
9	6.48 (d, J = 2.0)	6.47 (d, J = 2.0)	6.45 (d, J = 2.1)	-0.03

Table S5. Spectroscopic comparison of $^{13}C\{^{1}H\}$ NMR data of cassiarin C (**1d**).



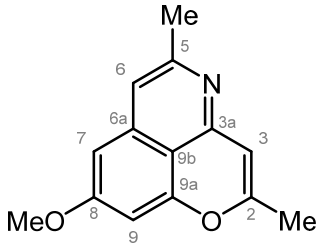
Carbon N°	Morita & Co-Workers:[1] (CD_3OD, 100 MHz)	Hibino & Co-Workers:[2] (CD_3OD, 75 MHz)	This Report: (CD_3OD, 100 MHz)	Δδ (ppm)
2	73.7	75.1	75.0	+1.7
2-Me	19.9	21.3	21.3	+1.4
3	37.8	39.1	39.1	+1.3
3a	153.6	155.1	155.0	+1.4
5	149.9	151.1	151.3	+1.4
5-Me	22.1	23.4	23.5	+1.4
6	115.6	117.1	117.0	+1.4
6a	139.1	140.5	140.4	+1.3
7	100.0	101.4	101.3	+1.3
8	159.1	163.6	163.4	+4.3
9	103.1	103.3	103.3	+0.2
9a	156.9	158.4	158.3	+1.4
9b	110.6	111.5	111.4	+0.8

Table S6. Spectroscopic comparison of ^{1}H NMR data of 8-*O*-Methyl cassiarin A (**1m**).



Proton N°	Morita & Co-Workers:[3] (CD_3OD, 400 MHz)	This Report: (CD_3OD, 400 MHz)	Δδ (CD_3OD, ppm)	Ye & Co-Workers:[4] ($CDCl_3$, 500 MHz)	This Report: ($CDCl_3$, 300 MHz)	Δδ ($CDCl_3$, ppm)
2-Me	2.21 (d, *J* = 0.8)	2.21 (d, *J* = 0.8)	0.00	2.23 (s)	2.19 (s)	+0.04
3	6.09 (d, *J* = 0.8)	6.09 (q, *J* = 0.8)	0.00	6.14 (s)	6.11 (br s)	+0.03
5-Me	2.41 (s)	2.40 (s)	+0.01	2.38 (s)	2.46 (s)	-0.08
6	6.94 (s)	6.94 (s)	0.00	6.74 (s)	6.84 (s)	-0.10
7	6.57 (d, *J* = 2.1)	6.57 (d, *J* = 2.1)	0.00	6.52 (s)	6.51 (s)*	+0.01
8-OMe	3.88 (s)	3.87 (s)	+0.01	3.80 (s)	3.86 (s)	-0.06
9	6.67 (d, *J* = 2.1)	6.67 (d, *J* = 2.1)	0.00	6.58 (s)	6.51 (s)*	+0.07

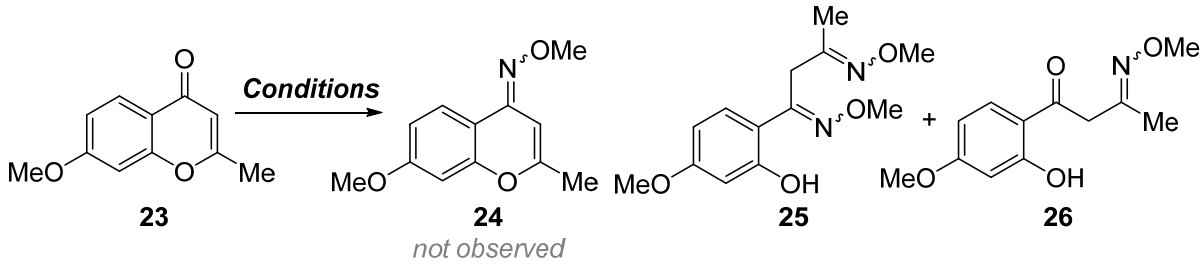
Table S7. Spectroscopic comparison of $^{13}C\{^{1}H\}$ NMR data of 8-*O*-Methyl cassiarin A (**1m**).



Carbon N°	Ye & Co-Workers:[3] ($CDCl_3$, 125 MHz)	Morita & Co-Workers:[4] (CD_3OD, 100 MHz)	This Report: ($CDCl_3$, 75 MHz)	This Report: CD_3OD, 100 MHz)	Δδ ($CDCl_3$, ppm)	Δδ (CD_3OD, ppm)
2	162.4 (s)	160.3	159.1	161.6	-3.3	+1.3
2-Me	21.2 (q)	18.5	20.1	19.8	-1.1	-1.1
3	104.2 (d)	103.8	106.3	105.5	+2.2	+1.7
3a	151.6 (s)	150.5	151.1	152.2	-0.5	+1.7
5	148.6 (s)	-	153.6	153.5	+5.0	-
5-Me	23.5 (q)	22.1	24.6	23.8	+1.1	+1.7
6	114.5 (d)	113.5	113.5	114.9	-1.0	+1.4
6a	136.9 (s)	138.4	138.6	140.1	+1.7	+1.7
7	103.4 (d)	98.2	98.1	99.5	-5.3	+1.3
8	166.8 (s)	163.1	162.5	164.5	-4.3	+1.4
8-OMe	56.6 (s)	54.8	55.7	56.2	-0.9	+1.4
9	98.4 (d)	98.2	98.6	100.0	+0.2	+1.8
9a	155.5 (s)	155.0	155.6	156.6	+0.05	+1.6
9b	112.8 (s)	112.0	113.0	113.6	+0.2	+1.6

Experiments aimed to perform the direct methoximation of chromenone 23.

Table S8. Transformation of chromenone **23** with methoxylamine hydrochloride.[a]



23 **24** *not observed* **25** **26**

Entry N°	Conditions					Yield (%)		
	$MeONH_2 \cdot HCl$ (equiv.)	Promoter (equiv.)	Base (equiv.)	Solvent	Time (h)	**23**	**25**	**26**
1	2	$CeCl_3$ (4%mol)	NaOAc (2.0)	MeOH	20	62	0	0
2	3	-	Py	Py	8	7	36	44
3	2	$CeCl_3$ (4%mol)	Py	Py	4	24	26	45

[a]The reactions were run under Ar atmosphere, using **23** (0.3 mmol) and at 60°C.

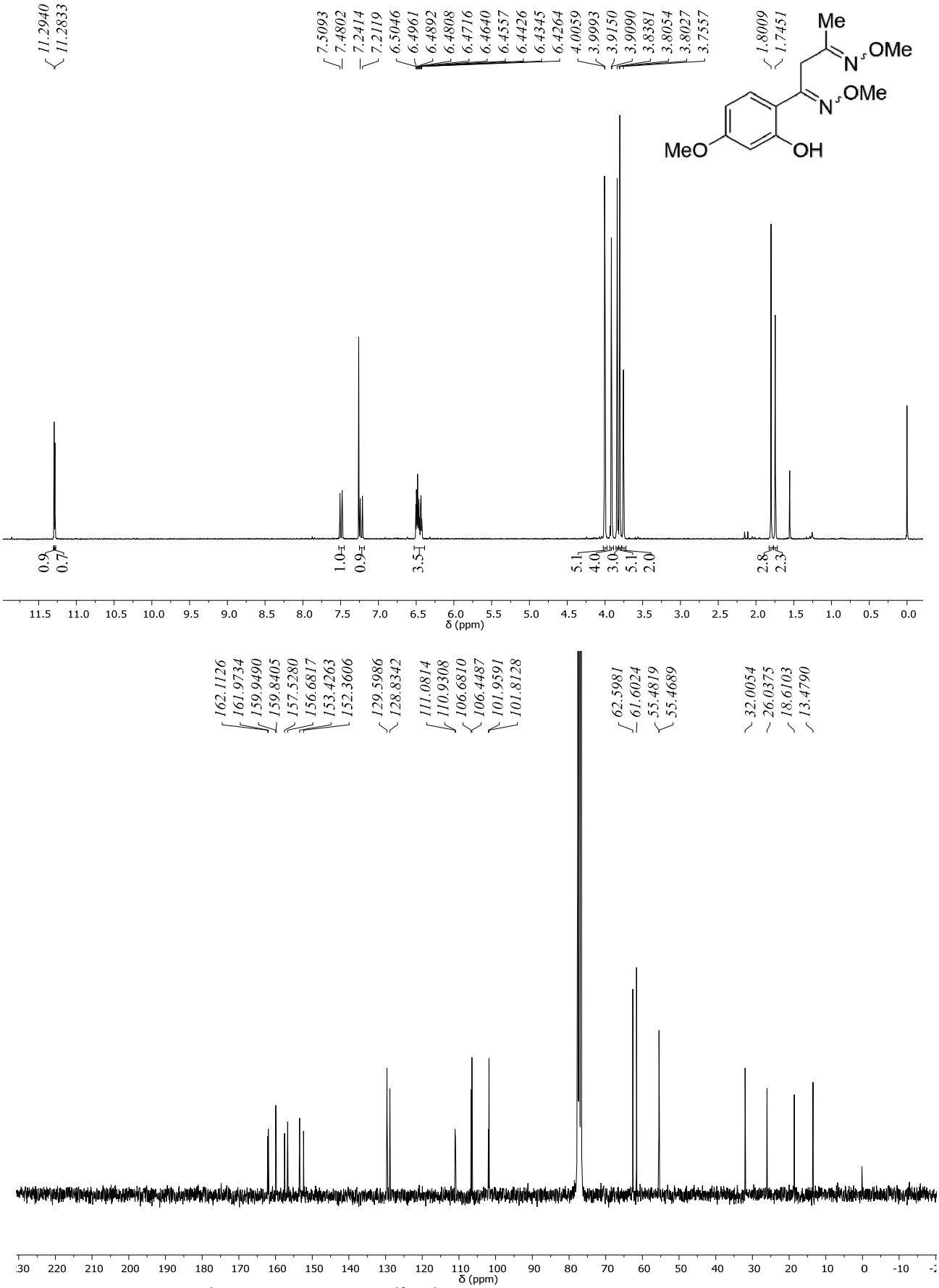


Figure S40: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **25** in $CDCl_3$.

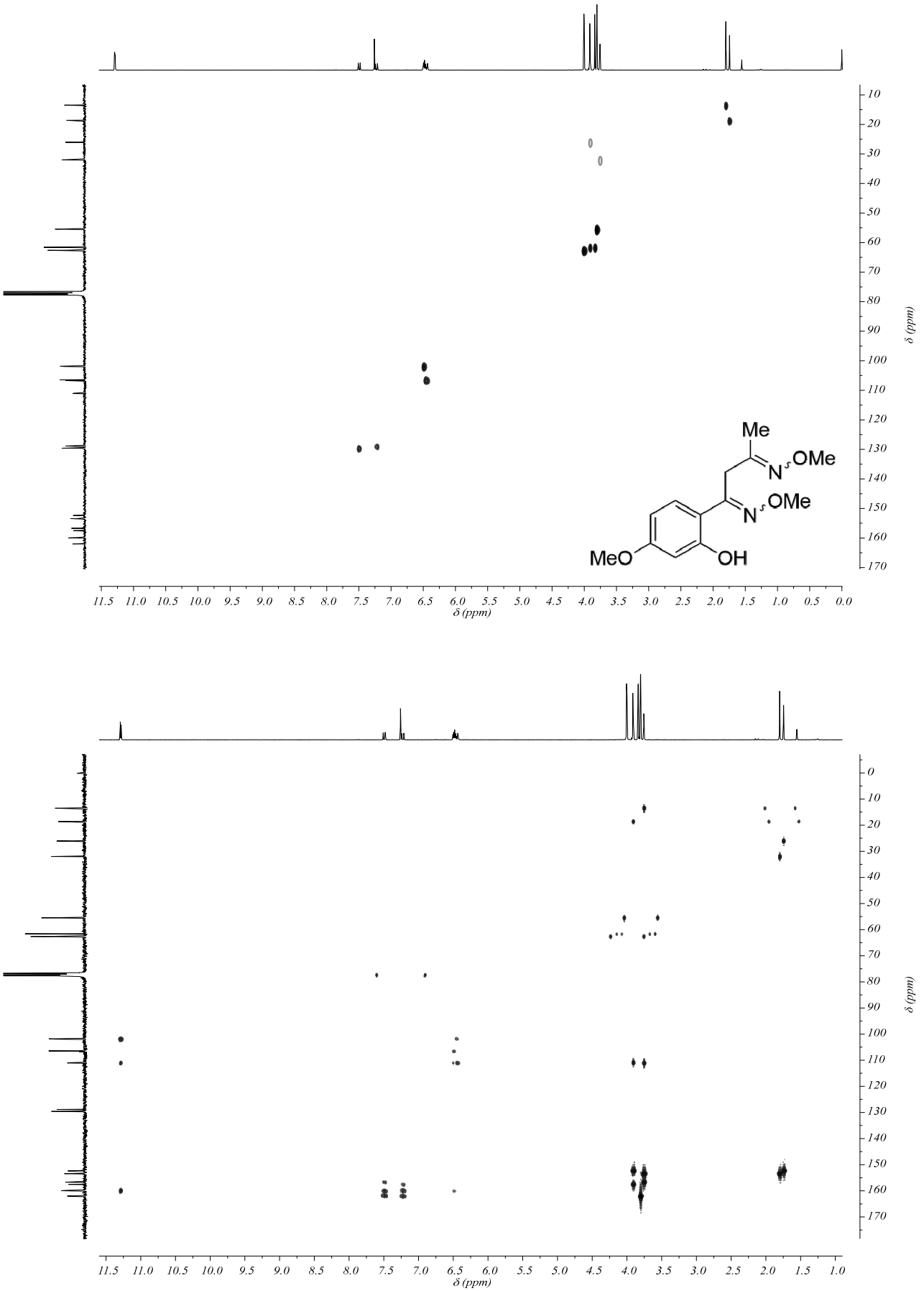


Figure S41: HSQC (top) and HMBC (bottom) spectra of compound **25** in $CDCl_3$.

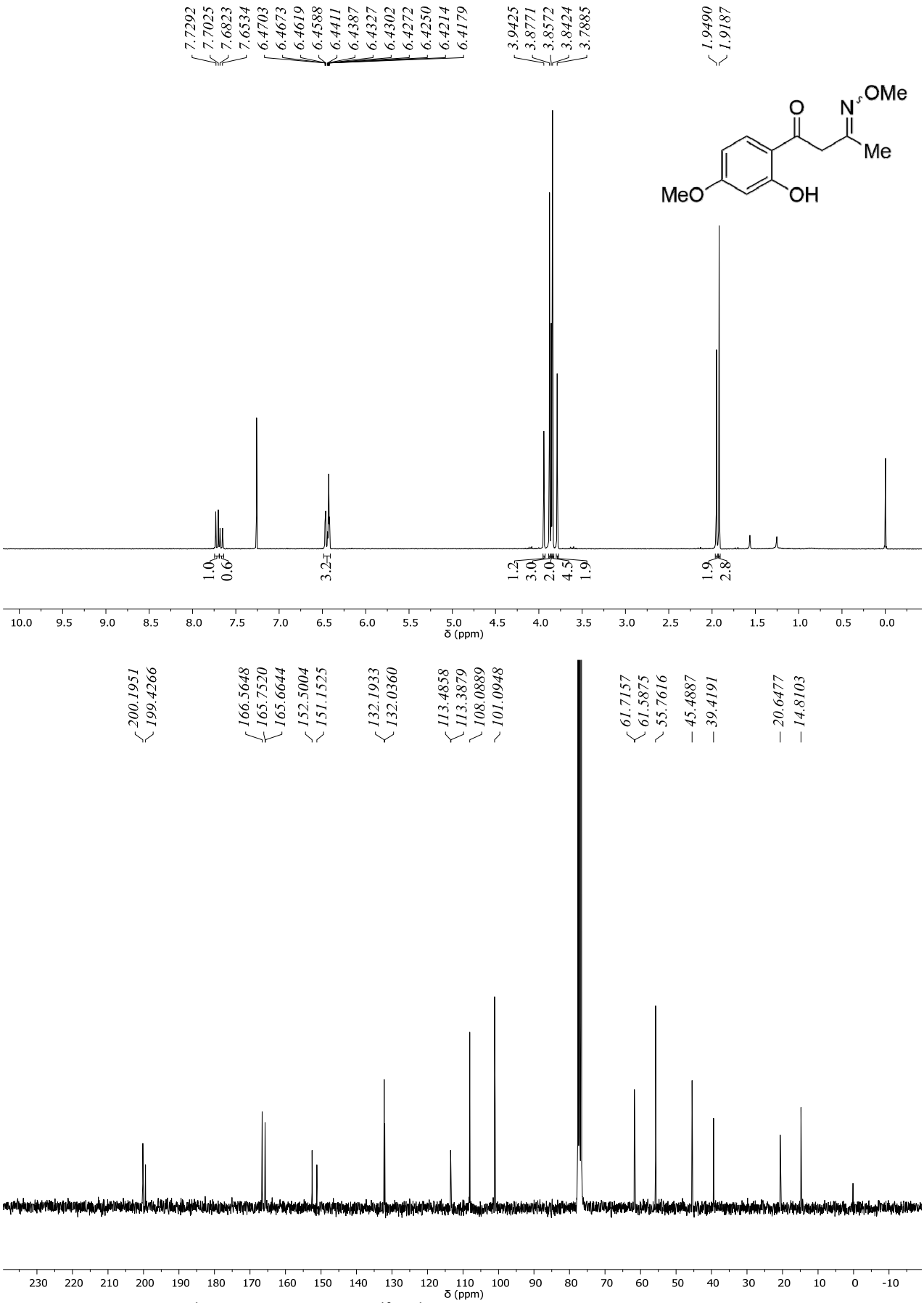


Figure S42: 300 MHz ^{1}H (top) and 75 MHz $^{13}C\{^{1}H\}$ (bottom) NMR spectra of compound **26** in $CDCl_3$.

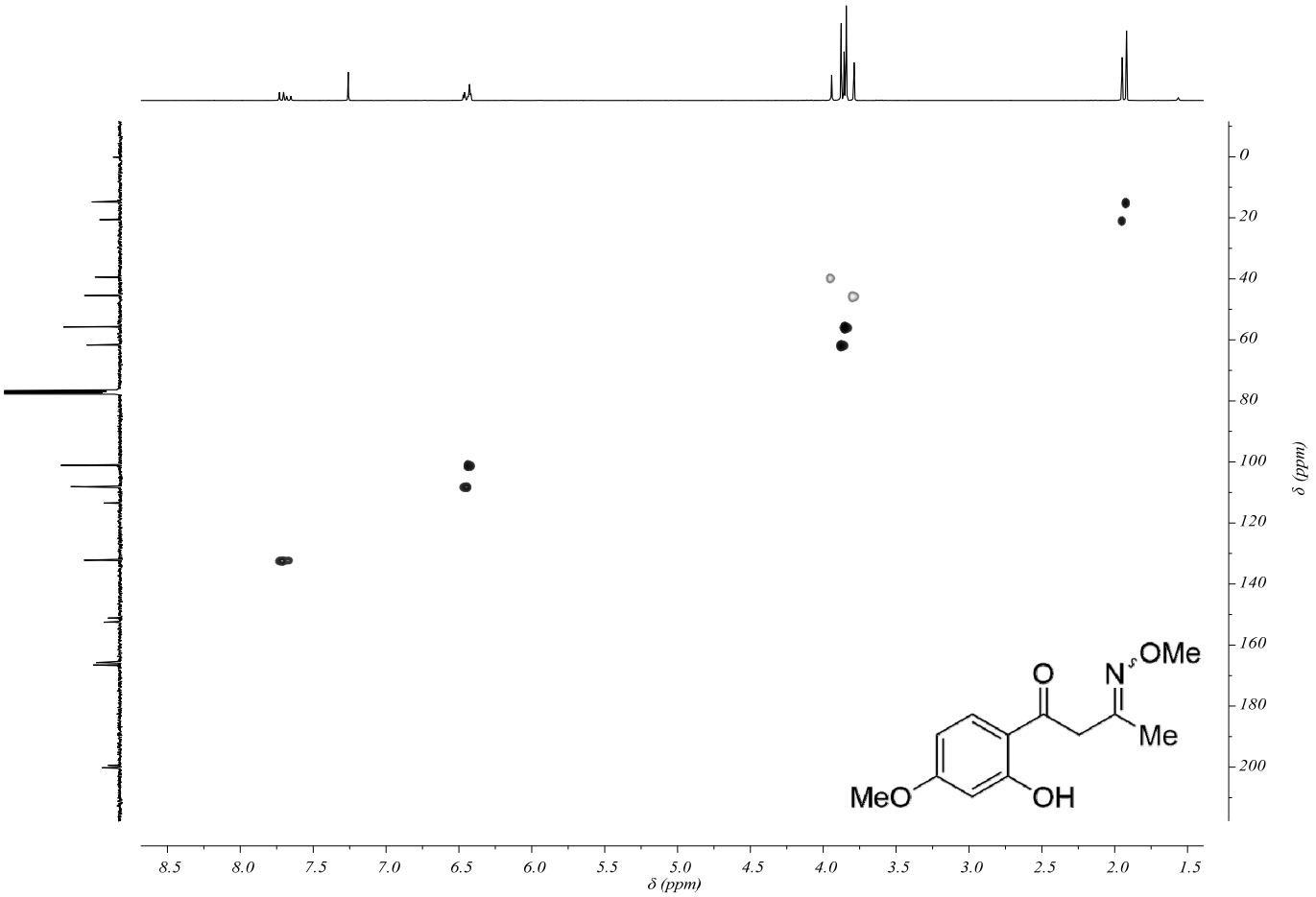
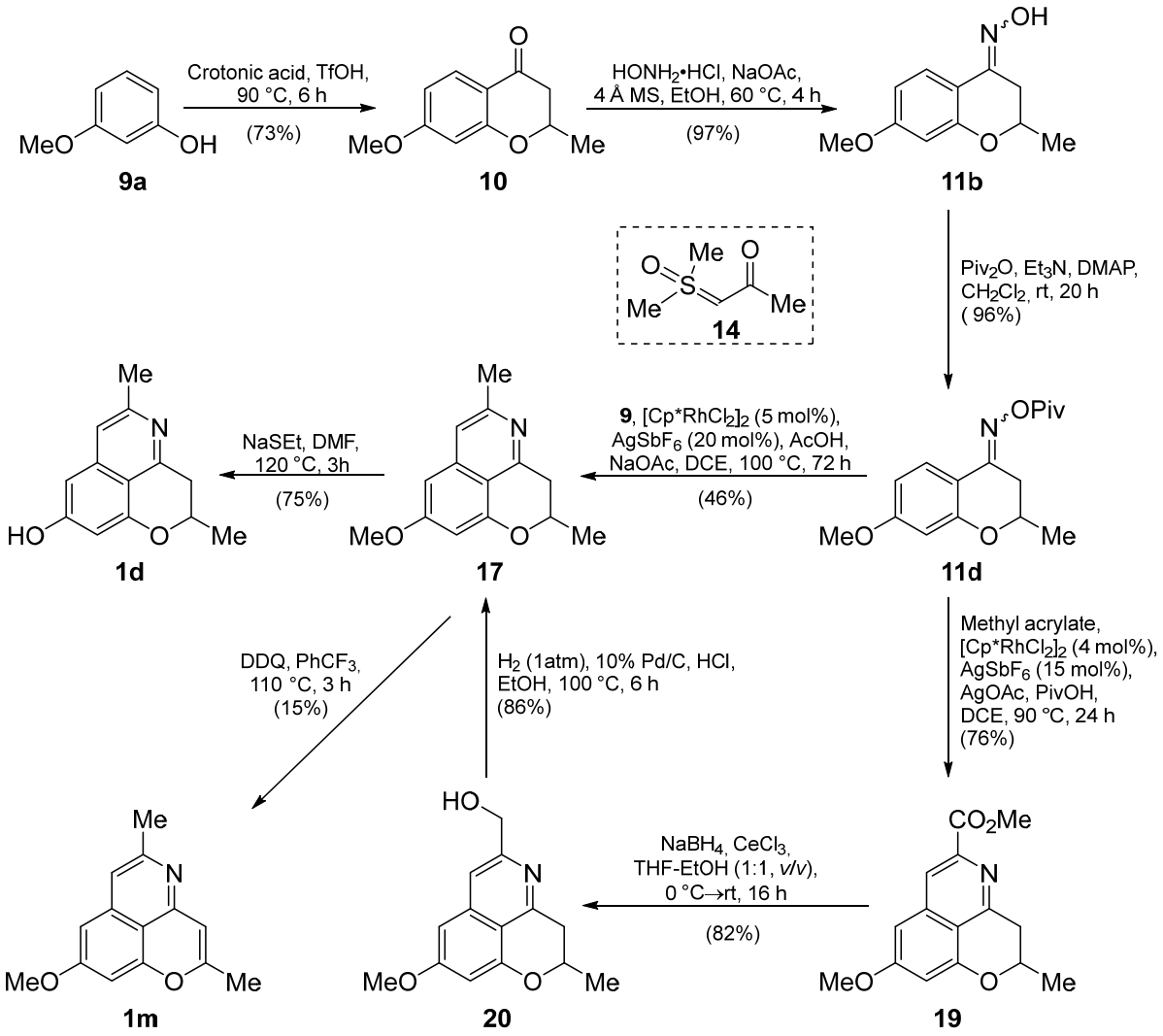


Figure S43: HSQC spectrum of compound **26** in $CDCl_3$.



Scheme S1. Total synthesis of cassiarin C (**1d**) and 8-*O*-methylcassiarin A (**1m**).

Computational Methods

Conformational searches for the reactants, transition states, and the products were run using the conformational search module of Hyperchem with the MM+ method.[5] Suitable structures were then successively optimized at the M062X/6-311+G** level with Gaussian09,[6] including the solvent (MeOH, ε= 32.70) via the Solvation Model based on Density (SMD).

Frequency calculations were made to confirm the nature of the stationary points and to evaluate their thermochemical properties. To confirm the presence of a transition state, imaginary frequency were computed and the obtained structure linked by intrinsic coordinate reaction calculations (IRCs). The molecular orbitals of the reactants were calculated to analyze the frontier orbital interactions at the M062X/6-311+G** level of theory.

For energy optimization and frequency calculation of the deuterium-labeled compounds, the input was performed in Gaussview 5.0 and the isotopes were added with its module edit atom list. The thermodynamic parameters showed to be different to those calculated for H compounds.

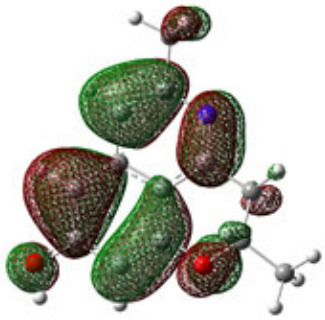
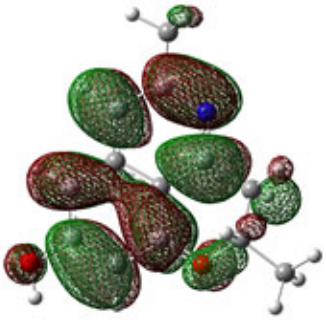
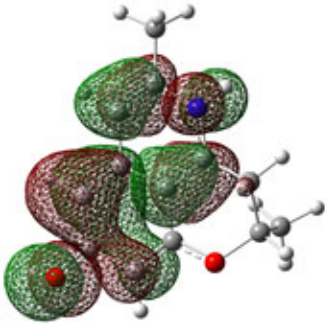
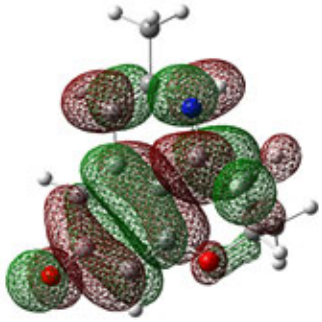
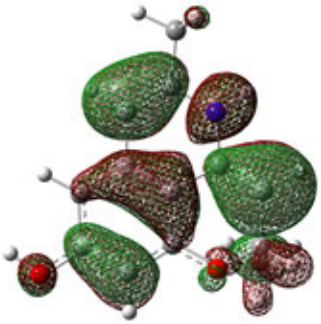
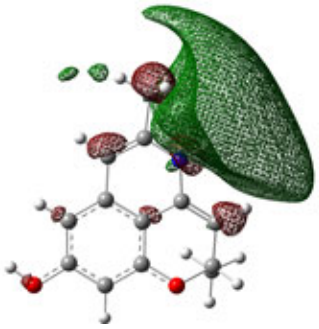
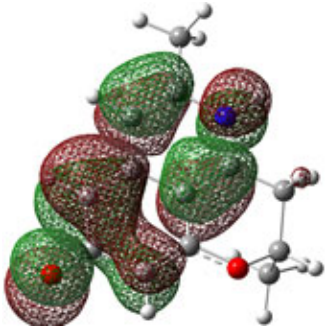
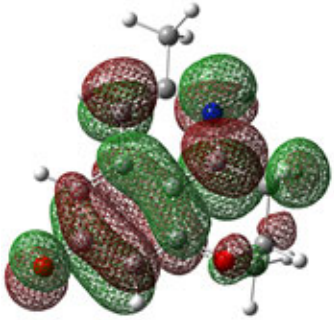
The keywords used for the TS were:

opt=(calcfc,ts,noeigentest) freq 6-311+g(d,p) scrf=(solvent=methanol,pcm,smd,dovacuum) m062x temperature=298

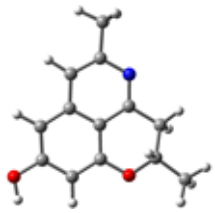
The keywords used for the intermediates were:

opt=(calcfc,noeigentest) freq 6-31g(d) scrf=(solvent=methanol,pcm,smd,dovacuum) m062x temperature=298

Molecular orbitals of the starting materials and intermediates

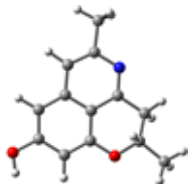
 1d_HOMO	 1d_LUMO	 *i*_HOMO
 *i*_LUMO	 *ii*_HOMO	 *ii*_LUMO
 *iii*_HOMO	 *iii*_LUMO	

Cartesian Coordinates

 **1d**	M062x/6-311+G** SCF: -708.3590008 Correction ZPE: 0.235918 Correction Free energy: 0.197064 Sum of free energies: -708.161937

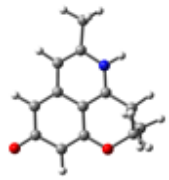
0 1

C	0.51978800	2.45727800	0.06161400
C	-0.83759100	2.68620300	-0.00606400
C	-1.77482700	1.62974300	-0.07018300
C	-1.32289600	0.33361300	-0.07573700
C	0.07002500	0.05747200	-0.03062300
C	0.99074700	1.12909100	0.04463600
C	0.55734200	-1.27107800	-0.11011700
N	1.83496000	-1.56628800	-0.08505700
C	2.73998000	-0.54139100	0.01678800
C	2.36634100	0.77634500	0.07879900
O	-2.22391900	-0.67708900	-0.15145500
C	-1.78366700	-1.95448000	0.37423900
C	-0.46528300	-2.36084100	-0.26626200
O	-1.26161700	3.97712900	0.00338100
C	4.17975100	-0.95858900	0.04887200
C	-2.90092400	-2.93489600	0.11057700
H	1.20986000	3.29099000	0.11669100
H	-2.83825900	1.84060600	-0.10483000
H	3.11831100	1.55479200	0.14669700
H	-1.63732600	-1.81711100	1.45212400
H	-0.10193900	-3.28453000	0.18838900
H	-0.62518400	-2.55012900	-1.33497500
H	-2.22492800	4.02265500	-0.05166200
H	4.36275700	-1.61886300	0.90109200
H	4.43142600	-1.51778000	-0.85640900
H	4.84191900	-0.09568600	0.12432000
H	-3.82563800	-2.60064900	0.58474800
H	-3.06944900	-3.03939000	-0.96422400
H	-2.63469900	-3.91202300	0.51879800

 **[3β-*d*]-1d**	M062x/6-311+G** SCF: -708.3590008 Correction ZPE: 0.229191 Correction Free energy: 0.190039 Sum of free energies: -708.1689618

0 1

C	0.51978800	2.45727800	0.06161400
C	-0.83759000	2.68620300	-0.00606400
C	-1.77482700	1.62974300	-0.07018300
C	-1.32289600	0.33361300	-0.07573700
C	0.07002500	0.05747200	-0.03062300
C	0.99074700	1.12909100	0.04463600
C	0.55734100	-1.27107800	-0.11011700
N	1.83496000	-1.56628800	-0.08505700
C	2.73998000	-0.54139200	0.01678800
C	2.36634100	0.77634500	0.07879900
O	-2.22391900	-0.67708900	-0.15145500
C	-1.78366700	-1.95448000	0.37423900
C	-0.46528400	-2.36084100	-0.26626200
C	4.17975100	-0.95858900	0.04887100
C	-2.90092400	-2.93489600	0.11057700
O	-1.26161700	3.97712900	0.00338100
H	1.20986100	3.29099000	0.11669100
H	-2.83825900	1.84060600	-0.10483000
H	3.11831200	1.55479200	0.14669700
H	-1.63732700	-1.81711100	1.45212400
H(iso=2)	-0.10194000	-3.28453000	0.18838900
H	-0.62518400	-2.55012900	-1.33497500
H	4.36275700	-1.61886400	0.90109200
H	4.43142600	-1.51778000	-0.85640900
H	4.84191900	-0.09568700	0.12432000
H	-3.82563800	-2.60064900	0.58474800
H	-3.06945000	-3.03938900	-0.96422400
H	-2.63470000	-3.91202300	0.51879800
H	-2.22492800	4.02265600	-0.05166200

 ***i***	M062x/6-311+G** SCF: -708.35461 Correction ZPE: 0.233136 Correction Free energy: 0.194154 Sum of free energies: -708.160456

0 1

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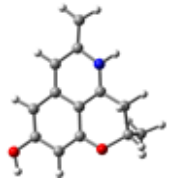
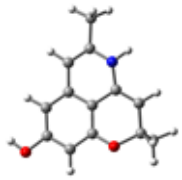
C	-2.45129800	-0.37811900	-0.21414300
C	-1.39570400	0.47241700	-0.31010900
C	-0.05442700	-0.01794500	-0.18400900
C	0.15711800	-1.41740900	0.05962400
C	1.01191700	0.84616400	-0.31775000
N	2.26087300	0.37791800	-0.20020500
C	2.54915700	-0.95075000	0.04561200
C	1.52646200	-1.83397500	0.17459700
O	-1.61117000	1.79014900	-0.56868800
C	-0.59703000	2.71425800	-0.10534600
C	0.77529300	2.28989600	-0.62280700
O	-3.26428100	-2.56738900	0.10608900
C	3.99867000	-1.29353900	0.15036400
C	-0.66211800	2.84528300	1.40585600
H	-0.76553100	-3.33207500	0.34221600
H	-3.46319400	0.00103100	-0.30781400
H(iso=2)	3.03464700	1.03104200	-0.29266000
H	1.75488500	-2.87583600	0.36490400
H	-0.87609000	3.65856300	-0.57076600
H	1.55301000	2.91100200	-0.17258400
H	0.82525800	2.42221200	-1.70868100
H	4.46610300	-0.73144200	0.96348600
H	4.11901100	-2.35842200	0.34297100
H	4.51985500	-1.03921900	-0.77655800
H	-1.67759300	3.10389900	1.71208200
H	-0.36771700	1.91993200	1.90818000
H	0.01084000	3.64149300	1.73124700

 ***iv***	M062x/6-311+G** SCF: -708.3118056 Correction ZPE: 0.228452 Correction Free energy: 0.189417 Sum of free energies: -708.1223886

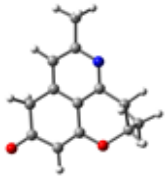
0 1

C	-1.27246500	-2.07854300	0.15986200
C	-2.41185700	-1.34330800	0.01295600
C	-2.41115600	0.07201500	-0.22025200
C	-1.21437700	0.71480100	-0.30775200
C	0.01454000	-0.00795500	-0.17573000
C	0.00824800	-1.43666500	0.06667100
C	1.21846100	0.64480700	-0.30929700
N	2.36704100	-0.03127800	-0.19328100
C	2.47407700	-1.41759900	0.05382000
C	1.21013400	-2.09568100	0.17651000
O	-1.19174900	2.04814200	-0.56376300
C	-0.02494500	2.77670100	-0.10779500
C	1.24664600	2.10784400	-0.62185400
C	3.70552200	-1.98373300	0.15229800
C	-0.06421600	2.92668300	1.40239500
O	-3.60676800	-1.98893600	0.10445300
H	-1.33696600	-3.14530100	0.34017000
H	-3.34464500	0.61394400	-0.31781700
H(iso=2)	3.23487100	0.48659600	-0.29145700
H	1.23169300	-3.16427600	0.35573000
H	-0.13210300	3.75325300	-0.57819300
H	2.12202200	2.58306100	-0.17278000
H	1.32126500	2.22578600	-1.70800300
H	3.79642500	-3.04414700	0.34413600
H	4.60566200	-1.39120700	0.04342400
H	-1.01198400	3.37346900	1.70888200
H	0.05108700	1.96452000	1.90830900
H	0.74727300	3.58337000	1.72341900
H(iso=2)	-4.33740700	-1.36996900	-0.01937400

 *ii*	M062x/6-311+G** SCF: -708.3357214 Correction ZPE: 0.228183 Correction Free energy: 0.188426 Sum of free energies: -708.1472954

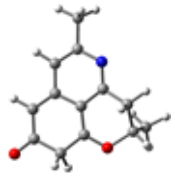
0 1

C	-0.81314300	-2.23890000	0.20493400
C	-2.11186500	-1.78428500	0.00824600
C	-2.38443000	-0.44259300	-0.27134800
C	-1.32491500	0.44879600	-0.33395300
C	-0.00876800	0.02262400	-0.11914100
C	0.25456100	-1.33526600	0.12726200
C	1.06647800	1.00000500	-0.24435800
N	2.35104300	0.46614500	-0.24738400
C	2.63270900	-0.85063500	0.03599300
C	1.63885200	-1.74820900	0.24336300
O	-1.58343600	1.73727400	-0.68801800
C	-0.65702200	2.74478800	-0.20010400
C	0.77381900	2.30900900	-0.36427100
C	4.08785200	-1.19182900	0.08604900
C	-1.01228500	3.07492600	1.24426000
O	-3.18695300	-2.61996000	0.07362800
H	-0.62989800	-3.29067400	0.40047300
H	-3.40139300	-0.10741000	-0.43600400
H(iso=2)	3.12754200	1.10897500	-0.34052900
H	1.88109500	-2.78191600	0.45316200
H	-0.86628100	3.60890300	-0.83195400
H	1.54149300	3.06598800	-0.47445800
H	4.22354000	-2.25146500	0.29810900
H	4.56757700	-0.95723300	-0.86841600
H	4.59029200	-0.60840200	0.86293600
H	-0.84913700	2.20393100	1.88606000
H	-2.05576200	3.39121200	1.32331700
H	-0.37342300	3.88678700	1.59997800
H(iso=2)	-2.90089500	-3.52081900	0.27254800

 ***v***	M062x/6-311+G** SCF: -708.3470206 Correction ZPE: 0.23238 Correction Free energy: 0.192286 Sum of free energies: -708.1547346

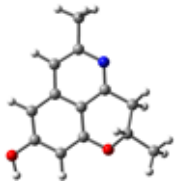
0 1

C	-1.08108800	-2.23030200	0.28758300
C	-2.41579800	-1.58619600	-0.01371900
C	-2.47355100	-0.16222000	-0.22905500
C	-1.34124800	0.58738900	-0.27338000
C	-0.00876400	-0.00209600	-0.15034400
C	0.12825300	-1.36563100	0.11048500
C	1.13731600	0.77713400	-0.34102700
N	2.36495100	0.27626800	-0.25797700
C	2.50779700	-1.03358000	0.01079800
C	1.41609700	-1.87961300	0.19336800
O	-1.45233300	1.90323300	-0.49377600
C	-0.34090000	2.76259600	-0.10544500
C	0.95698800	2.22564200	-0.68976600
C	3.91377800	-1.54549300	0.10103400
C	-0.32349700	2.91051300	1.40445600
O	-3.42826400	-2.28829900	-0.02185300
H	-1.13172400	-2.56537600	1.33161400
H(iso=2)	-0.99234600	-3.14001700	-0.31311900
H	-3.44242200	0.30603600	-0.35861700
H	1.57452600	-2.93329200	0.39416000
H	-0.59004000	3.71537000	-0.56992600
H	0.93725700	2.32387700	-1.78057700
H	1.80017500	2.81002500	-0.31734800
H	4.44583600	-1.34839900	-0.83326200
H	4.44956800	-1.02631600	0.90013400
H	3.93471400	-2.61654700	0.30117300
H	-0.08203000	1.96712800	1.90178500
H	-1.29602300	3.25597900	1.76010000
H	0.43033100	3.64931700	1.68483700

 ***vi***	M062x/6-311+G** SCF: -708.3231497 Correction ZPE: 0.231702 Correction Free energy: 0.191999 Sum of free energies: -708.1311507

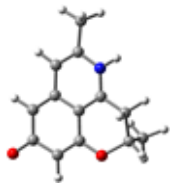
0 1

C	2.39770700	-1.24109700	0.03757200
N	2.37471300	0.12150400	-0.24853800
C	1.27843700	-2.00665800	0.17674000
C	-0.02810500	-1.42982300	0.06188800
C	-0.02674900	-0.00413300	-0.16692500
C	1.21277400	0.69206600	-0.34407600
C	-1.19531900	-2.16228200	0.17186400
C	-2.46664600	-1.54042700	0.03872100
C	-2.51756200	-0.04566000	-0.23238500
C	-1.22172300	0.67472200	-0.25627300
O	-1.31905200	1.97797500	-0.36675200
C	-0.11854600	2.78847700	-0.12511000
C	1.09748600	2.12995600	-0.75649900
C	3.77123300	-1.81707800	0.16401200
C	0.00397500	3.01179200	1.36911400
O	-3.54897600	-2.14509500	0.12172400
H	1.37128500	-3.06838300	0.37401800
H	-1.15743300	-3.22810800	0.36624700
H	-3.17856700	0.43104700	0.49929100
H(iso=2)	-3.00026600	0.09973900	-1.20858600
H	-0.34340700	3.72417300	-0.63304500
H	1.99646900	2.68309000	-0.48128500
H	1.00525500	2.15555100	-1.84814300
H	4.32963400	-1.64885200	-0.76136100
H	3.74170100	-2.88561500	0.37568300
H	4.31364000	-1.30735300	0.96573800
H	-0.91290500	3.45464800	1.76137800
H	0.20310600	2.07771800	1.90097300
H	0.83095100	3.69964500	1.55721700

 **[7-*d*]-1d**	M062x/6-311+G** SCF: -708.3590009 Correction ZPE: 0.229274 Correction Free energy: 0.190127 Sum of free energies: -708.1688739

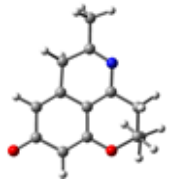
0 1

C	0.51980700	2.45727300	0.06161400
C	-0.83757000	2.68620800	-0.00606400
C	-1.77481500	1.62975600	-0.07018100
C	-1.32289400	0.33362300	-0.07573400
C	0.07002500	0.05747100	-0.03061700
C	0.99075600	1.12908400	0.04463800
C	0.55733200	-1.27108200	-0.11011200
N	1.83494700	-1.56630100	-0.08505500
C	2.73997600	-0.54141200	0.01678700
C	2.36634700	0.77632700	0.07879900
O	-2.22392300	-0.67707100	-0.15145400
C	-1.78368400	-1.95446800	0.37423900
C	-0.46530100	-2.36083800	-0.26625800
C	4.17974300	-0.95862100	0.04886600
C	-2.90094800	-2.93487400	0.11057000
O	-1.26158300	3.97713900	0.00337900
H(iso=2)	1.20988400	3.29098100	0.11668800
H	-2.83824500	1.84062800	-0.10483000
H	3.11832400	1.55476700	0.14669500
H	-1.63734700	-1.81710100	1.45212400
H	-0.10196600	-3.28452900	0.18839500
H	-0.62519900	-2.55012400	-1.33497100
H	4.36274400	-1.61890100	0.90108300
H	4.43141100	-1.51780900	-0.85641800
H	4.84191700	-0.09572400	0.12432000
H	-3.82565900	-2.60062400	0.58474200
H	-3.06947200	-3.03935800	-0.96423200
H	-2.63473000	-3.91200600	0.51878400
H(iso=2)	-2.22489100	4.02268300	-0.05167700

 ***iii***	M062x/6-311+G** SCF: -708.35461 Correction ZPE: 0.229833 Correction Free energy: 0.190744 Sum of free energies: -708.163866

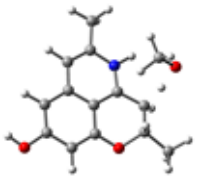
0 1

C	2.54915700	-0.95074900	0.04561200
N	2.26087300	0.37791900	-0.20020500
C	1.52646200	-1.83397500	0.17459700
C	0.15711900	-1.41740900	0.05962300
C	-0.05442700	-0.01794500	-0.18400900
C	1.01191700	0.84616400	-0.31775000
C	-0.92174800	-2.27442000	0.15896800
C	-2.26228900	-1.79847800	0.02017600
C	-2.45129700	-0.37811900	-0.21414300
C	-1.39570400	0.47241600	-0.31010900
O	-1.61117000	1.79014900	-0.56868900
C	-0.59703100	2.71425800	-0.10534600
C	0.77529300	2.28989700	-0.62280600
C	3.99867000	-1.29353800	0.15036500
C	-0.66211900	2.84528300	1.40585600
O	-3.26428100	-2.56738900	0.10609000
H(iso=2)	3.03464700	1.03104300	-0.29266000
H	1.75488600	-2.87583600	0.36490300
H	-0.76553100	-3.33207600	0.34221500
H	-3.46319400	0.00103100	-0.30781400
H	-0.87609100	3.65856300	-0.57076600
H	1.55301000	2.91100200	-0.17258300
H(iso=2)	0.82525800	2.42221200	-1.70868000
H	4.51985600	-1.03921600	-0.77655700
H	4.11901200	-2.35842200	0.34297000
H	4.46610200	-0.73144300	0.96348800
H	-1.67759500	3.10389700	1.71208200
H	-0.36771700	1.91993200	1.90818000
H	0.01083800	3.64149400	1.73124800

 ***vii***	M062x/6-311+G** SCF: -708.3178727 Correction ZPE: 0.231234 Correction Free energy: 0.191189 Sum of free energies: -708.1266837

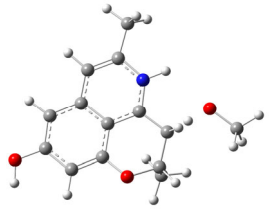
0 1

C	2.66276000	-0.56424500	0.00062100
N	2.29291100	0.63382300	-0.30354800
C	1.72493800	-1.65379900	0.42362200
C	0.27838300	-1.37741900	0.15687400
C	-0.05298600	0.00221200	-0.11193500
C	0.93213000	0.92611500	-0.29460600
C	-0.68721500	-2.32148500	0.19345500
C	-2.08777700	-1.97471800	-0.02556300
C	-2.41496400	-0.58318800	-0.26168800
C	-1.44298200	0.36360100	-0.29556600
O	-1.76953400	1.64344800	-0.57218400
C	-0.84450100	2.66903500	-0.12390300
C	0.56789900	2.34173400	-0.58899700
C	4.11024800	-0.91110400	-0.03141100
C	-0.96332300	2.84411600	1.37978700
O	-2.97368700	-2.85208000	-0.00246400
H	1.87526600	-1.76278500	1.50906100
H(iso=2)	2.04699100	-2.60504900	-0.00833800
H	-0.45465500	-3.36390200	0.38541000
H	-3.45326600	-0.31308000	-0.41579700
H	-1.19697300	3.56748200	-0.62840300
H	1.28352300	3.01116500	-0.10477300
H	0.66901700	2.49538600	-1.67084200
H	4.72170800	-0.02381900	-0.18612400
H	4.28755600	-1.62334700	-0.84422300
H	4.39788100	-1.41155200	0.89757000
H	-2.00387800	3.03022100	1.65268800
H	-0.60801900	1.96299000	1.92058900
H	-0.36542200	3.70347000	1.69105300

 ***ii*TS**	M062x/6-311+G** SCF: -824.027078055 Correction ZPE: 0.266235 Correction Free energy: 0.221815 Sum of free energies: -823.805263 Imaginary frequency: 1 (-971.8274)

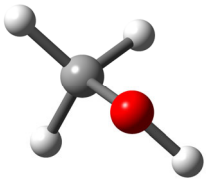
0 1

C	2.65305700	-1.16861700	0.33270400
C	3.26782200	0.07390100	0.32917000
C	2.55808300	1.26410400	0.07718300
C	1.20514800	1.20037500	-0.15621300
C	0.54277800	-0.05750100	-0.15328500
C	1.28119700	-1.24784000	0.06194200
C	-0.81729200	-0.11201700	-0.52557100
N	-1.36689300	-1.32149300	-0.70265600
C	-0.71438200	-2.51492400	-0.46906600
C	0.58280300	-2.49043200	-0.06815800
O	0.52857100	2.32848300	-0.45021800
C	-0.89575200	2.29819100	-0.11252200
C	-1.60839000	1.08998700	-0.67401400
C	-1.52626700	-3.74914700	-0.67965100
C	-1.47582500	3.60687700	-0.59099800
O	4.59123100	0.21978500	0.56083200
H	3.23260700	-2.06784000	0.51068000
H	3.07818100	2.21410500	0.06924000
H(iso=2)	-2.35173500	-1.35552700	-0.96097100
H	1.10126500	-3.42345900	0.11338600
H	-0.92122400	2.25068100	0.98325000
H	-1.99048900	1.21315700	-1.69210800
H	-0.93344300	-4.63304800	-0.45025400
H	-2.41089300	-3.73715700	-0.03706900
H	-1.86675300	-3.80726700	-1.71696700
H	-1.39105600	3.68450000	-1.67794500
H	-0.96112700	4.45189800	-0.13015800
H	-2.53318200	3.65361900	-0.32099600
H(iso=2)	5.00586800	-0.63913500	0.71978400
O	-3.66496100	0.42467600	0.80190800
C	-3.03951200	-0.19883400	1.88737800
H(iso=2)	-3.39290000	0.19277400	2.85332500
H(iso=2)	-1.94328500	-0.04835400	1.87479300
H(iso=2)	-3.20573400	-1.28865700	1.89814600
H(iso=2)	-2.66738000	0.84186800	0.02887100

 ***ii*TS (α-attack)**	M062x/6-311+G** SCF: -824.023843936 Correction ZPE: 0.266052 Correction Free energy: 0.220795 Sum of free energies: -823.803049 Imaginary frequency: 1 (-967.23)

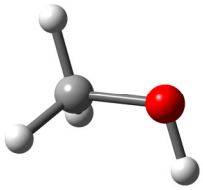
0 1

O	-3.70925100	0.06961100	0.69723800
C	-4.67888700	-0.91087000	0.45375900
H (iso=2)	-5.63200000	-0.47991800	0.11092600
H(iso=2)	-4.90418400	-1.51356700	1.34775900
H(iso=2)	4.35548500	-1.61845200	-0.33281700
H(iso=2)	-2.67209100	-0.30000400	-0.04630800
C	2.92185300	0.70396500	0.40772000
C	3.30822100	-0.61402900	0.21988900
C	2.40335500	-1.61115200	-0.19499200
C	1.08372900	-1.27756500	-0.39667700
C	0.65237200	0.06008600	-0.19190400
C	1.58798200	1.05926500	0.18120300
C	-0.68222000	0.39652100	-0.49172900
N	-1.02158300	1.69173400	-0.44053500
C	-0.16538400	2.71099800	-0.07447400
C	1.11589500	2.40761200	0.25656500
O	0.22926900	-2.21301700	-0.85038800
C	-1.18325500	-2.01442200	-0.50667900
C	-1.67428900	-0.61165800	-0.81005000
C	-0.75052300	4.08419300	-0.07709300
C	-1.36385400	-2.40529000	0.95217200
O	4.60579700	-0.91439400	0.44823800
H	3.65368100	1.44539800	0.70488300
H	2.74014500	-2.63006900	-0.35001300
H(iso=2)	-1.98969600	1.93127700	-0.64861500
H	1.79198800	3.20142200	0.54793200
H	-1.69394500	-2.73270000	-1.14646000
H	-2.06027900	-0.47737500	-1.82432500
H	-1.63934600	4.12127700	0.55824400
H	-0.02054600	4.80384300	0.28998100
H	-1.04963500	4.36622600	-1.09039200
H	-0.90133100	-1.67392700	1.62210200
H	-0.92348100	-3.38724900	1.14017400
H	-2.42960600	-2.45031800	1.18601100
H(iso=2)	4.78040500	-1.85152900	0.28770800

	M062x/6-311+G** SCF: -115.713966 Correction ZPE: 0.038732 Correction Free energy: 0.015114 Sum of free energies: -115.698852

0 1

C	0.66856500	-0.01984400	0.00000400
O	-0.74871300	0.12386300	-0.00000800
H(iso=2)	1.09378200	0.98362000	-0.00008100
H(iso=2)	1.01396700	-0.55072100	-0.89156300
H(iso=2)	1.01396700	-0.55057500	0.89165800
H(iso=2)	-1.14340100	-0.75416400	0.00002800

	M062x/6-311+G** SCF: -115.7140789 Correction ZPE: 0.042099 Correction Free energy: 0.01876 Sum of free energies: -115.6953189

0 1

C	0.66856400	-0.01984400	0.00000400
O	-0.74871300	0.12386300	0.00000600
H(Iso=2)	1.09378200	0.98362000	-0.00035200
H(Iso=2)	1.01393400	-0.55092300	-0.89145500
H(Iso=2)	1.01400100	-0.55037200	0.89176600
H	-1.14340000	-0.75416400	-0.00002700

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