

Substitution Controlled Functionalization of *ortho*-Bromobenzylic Alcohols via Palladium Catalysis: Synthesis of Chromenes and Indenols

Lodi Mahendar and Gedu Satyanarayana*

Department of Chemistry, Indian Institute of Technology, Hyderabad

Ordnance Factory Estate Campus, Yeddemailaram – 502 205, Medak District, Andhra Pradesh, India

Fax: +91(40) 2301 6032

E-mail: gvsatya@iith.ac.in

Supporting Information

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The requisite precursors have been achieved as described below (Tables):

Table: 1

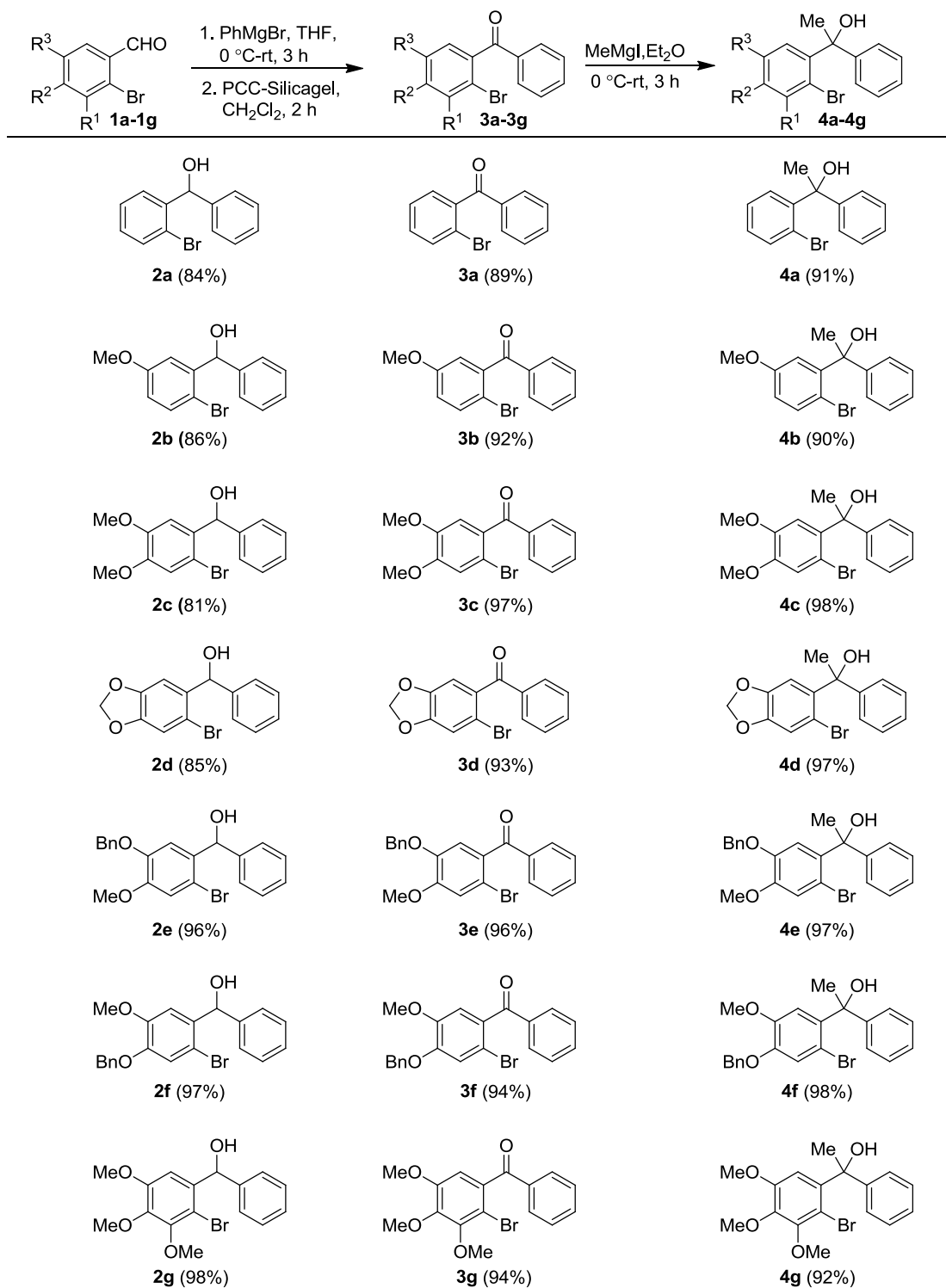


Table: 2

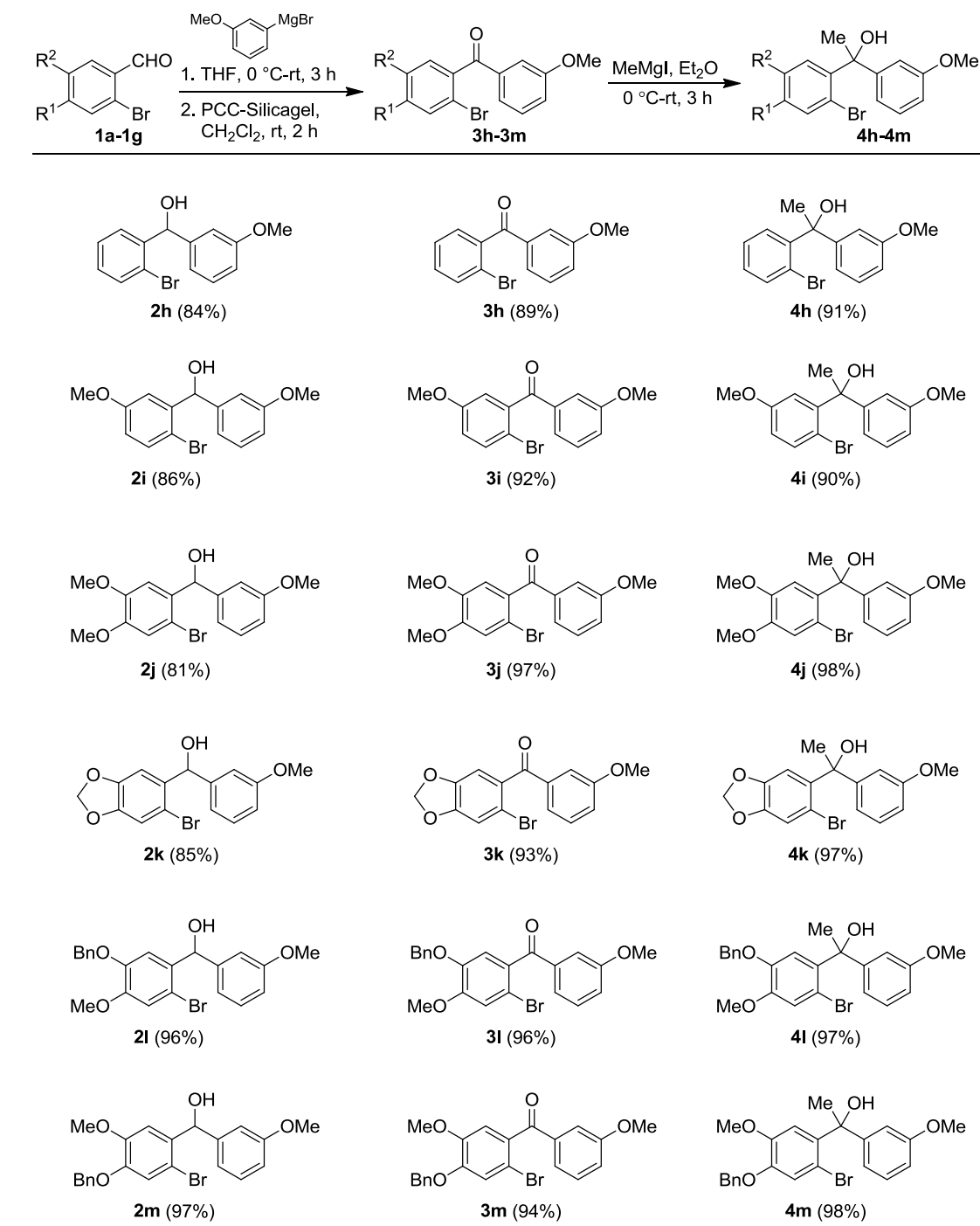


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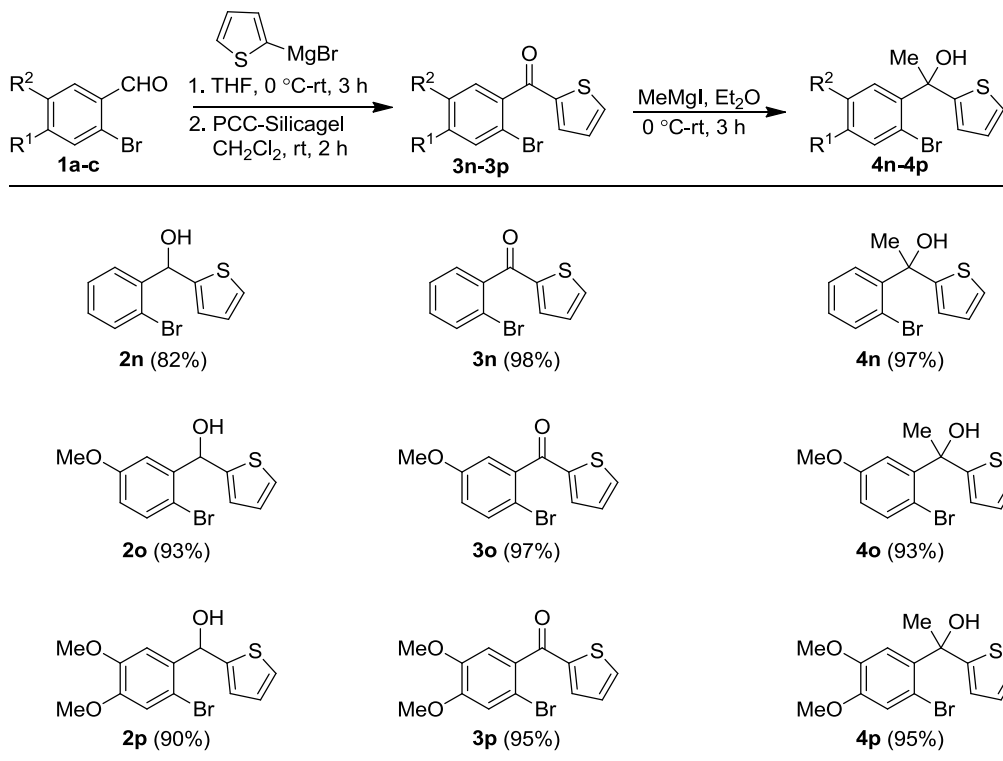


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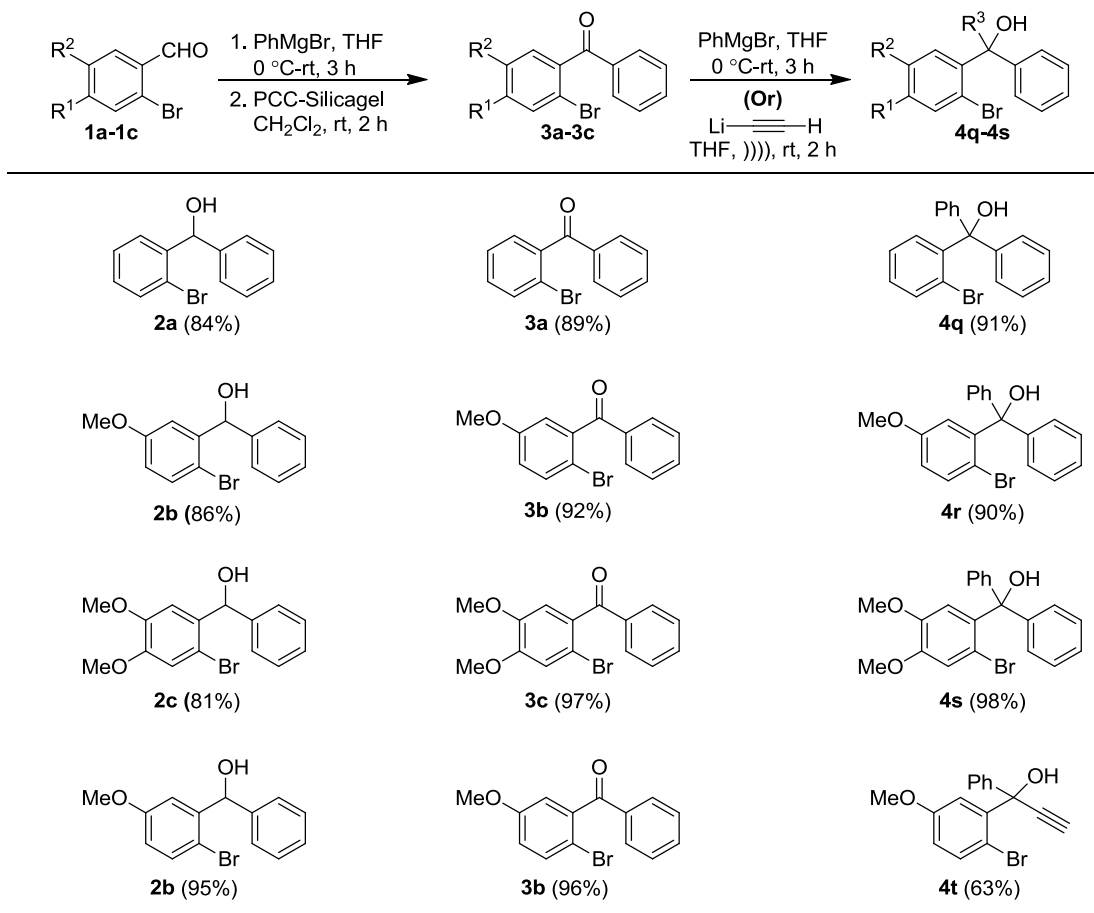


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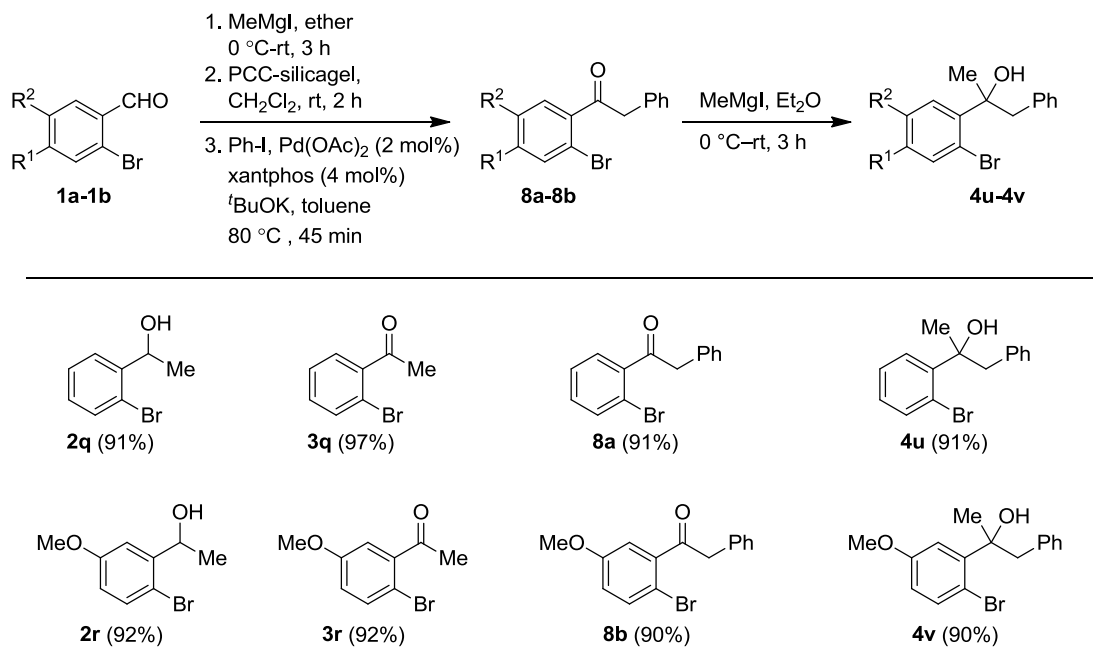


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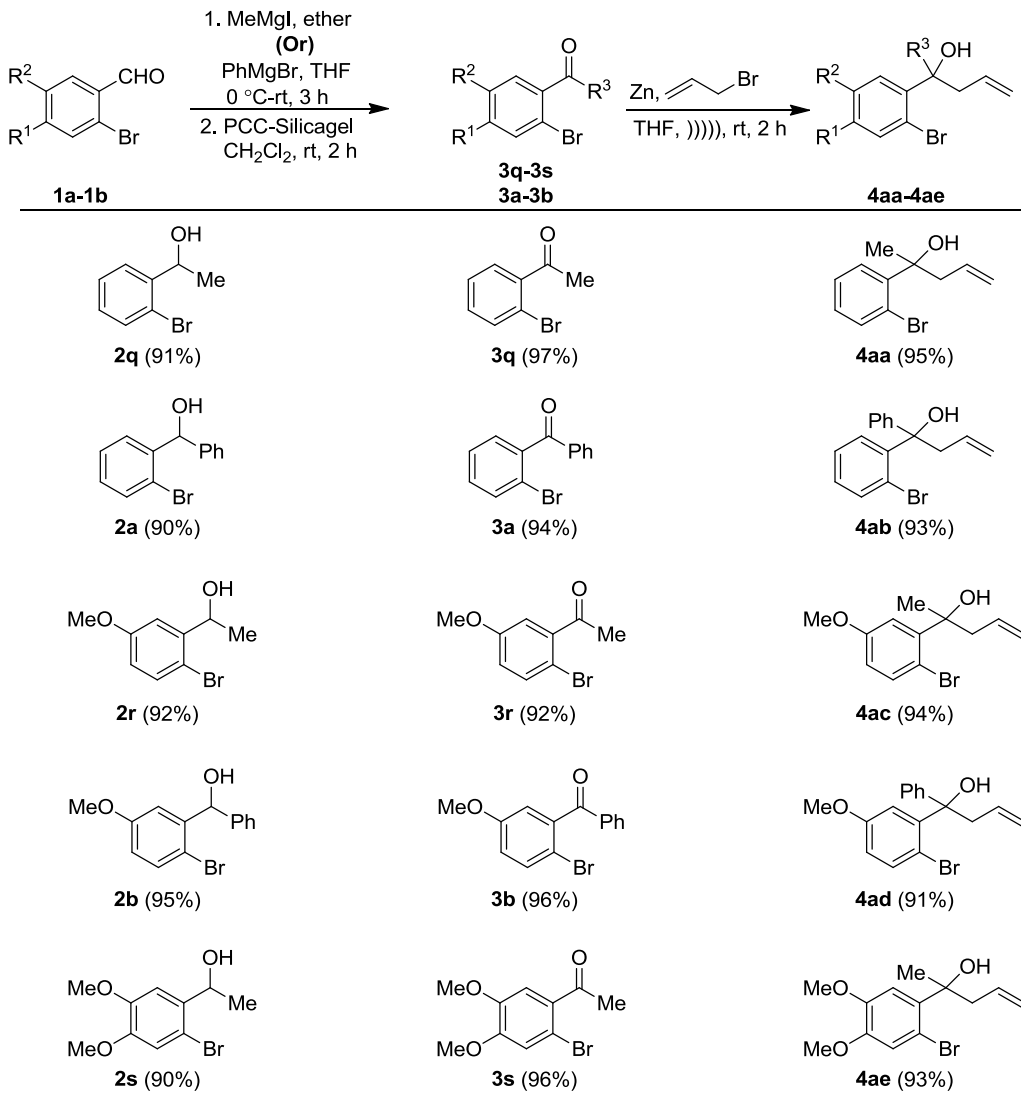
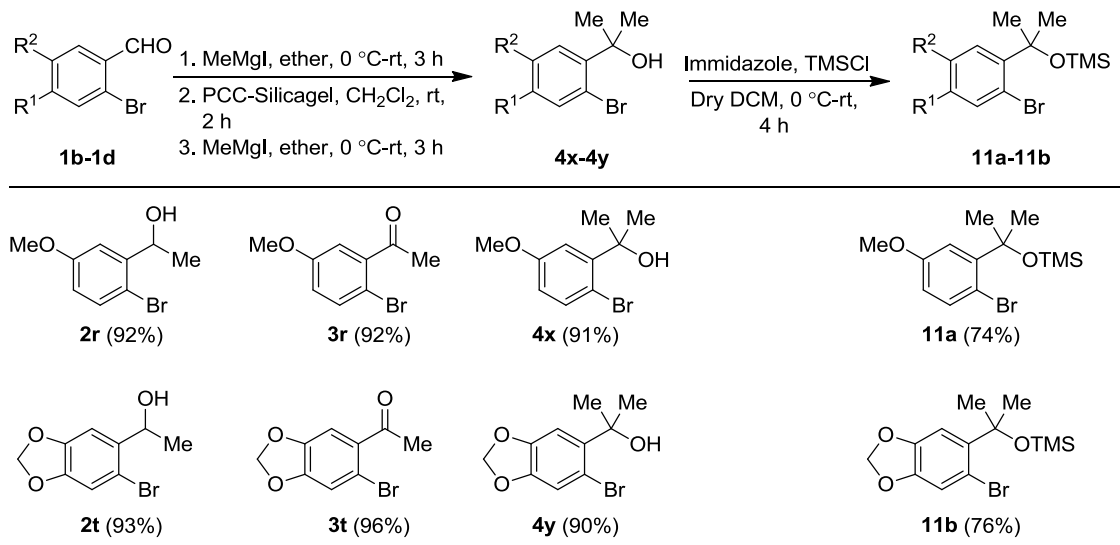
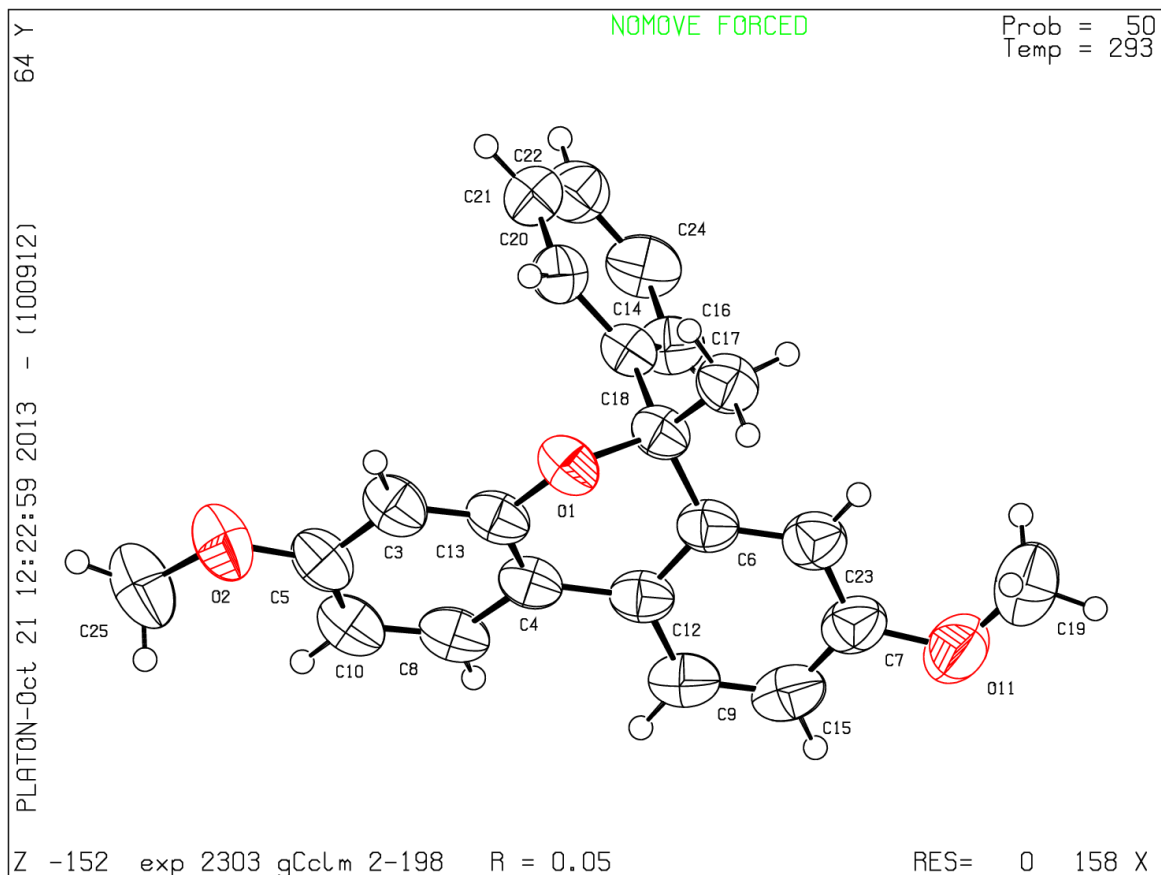


Table: 7



X-ray crystal structure data for the cyclic biaryl ether (5b): CCDC 965704



Operator	K. Ravikumar
Diffractometer	Oxford Super Nova
CCDC	965704
Empirical formula	C ₂₂ H ₂₀ O ₃
Formula weight	332.38
Temperature/K	293
Crystal system	monoclinic
Space group	Cc
a/Å	17.4301(8)
b/Å	16.1897(6)
c/Å	6.7149(3)
α/°	90.00
β/°	112.144(5)
γ/°	90.00
Volume/Å ³	1755.10(12)

Z	4
ρ_{calc} mg/mm ³	1.212
m/mm ⁻¹	0.641
F(000)	680.0
Crystal size/mm ³	0.19 × 0.17 × 0.14
2 Θ range for data collection	7.74 to 142.28°
Index ranges	-19 ≤ h ≤ 20, -17 ≤ k ≤ 15, -7 ≤ l ≤ 8
Reflections collected	4142
Independent reflections	2352[R(int) = 0.0195]
Data/restraints/parameters	2352/2/229
Goodness-of-fit on F ²	0.953
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0470, wR ₂ = 0.1194
Final R indexes [all data]	R ₁ = 0.0521, wR ₂ = 0.1347
Largest diff. peak/hole / e Å ⁻³	0.11/-0.19

1. Check CIF/ Platon report (full structure check) for 5b:

Bond precision: C-C = 0.0045Å Wavelength=1.54184

Cell: a=17.4301(8) b=16.1897(6) c=6.7149(3)
 alpha=90 beta=112.144(5) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1755.10(14)	1755.10(12)
Space group	C c	Cc
Hall group	C-2	yc ?
Moiety formula	C22 H20 O3	C22 H20 O3
Sum formula	C22 H20 O3	C22 H20 O3
Mr	332.38	332.38
Dx, g cm ⁻³	1.258	1.212
Z	4	4
Mu (mm ⁻¹)	0.662	0.641
F000	704.0	680.0
F000'	706.10	
h, k, lmax	21, 19, 8	20, 17, 8
Nref	3413[1711]	2352
Tmin, Tmax		
Tmin'		

Correction method= Not given

Data completeness= 1.37/0.69

Theta(max)= 71.140

R(reflections)= 0.0470(2080)

wR2(reflections)= 0.1347(2352)

S = 0.953

Npar= 229

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Click on the hyperlinks for more details of the test.

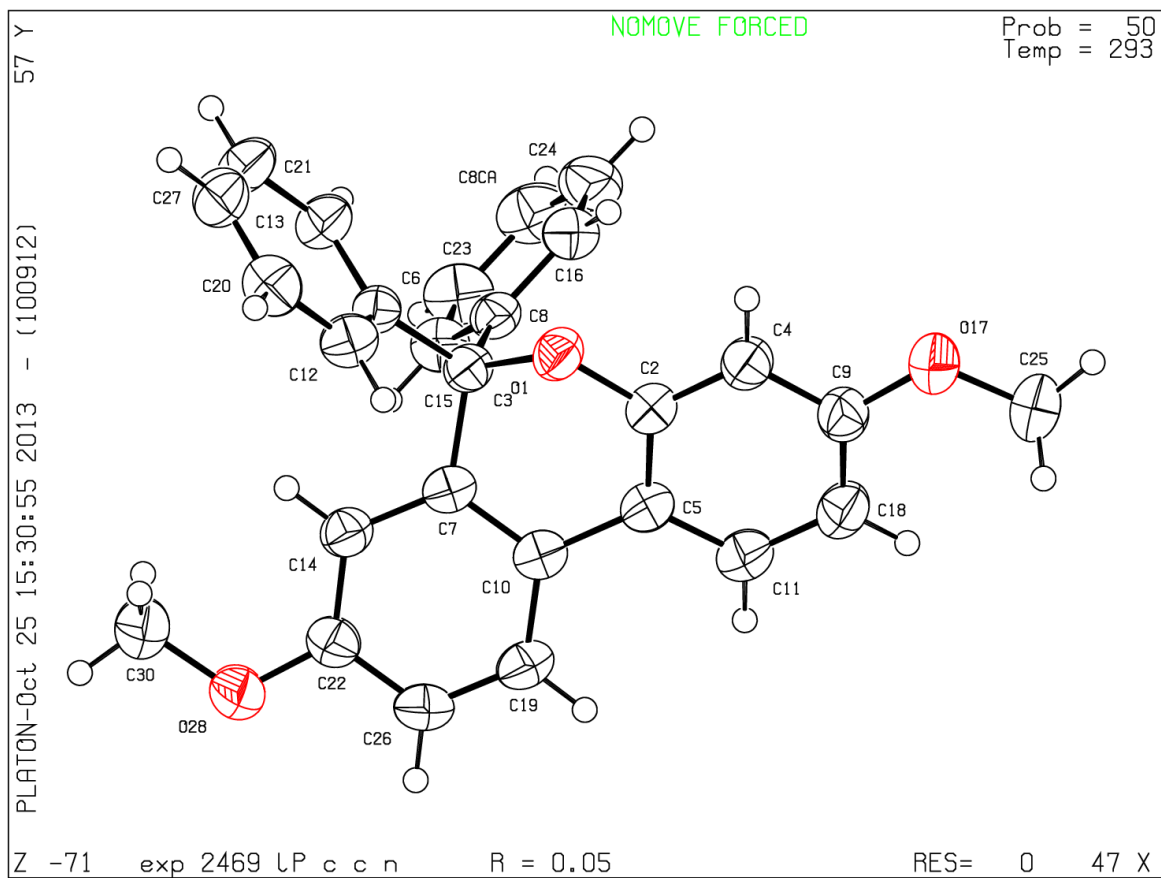
Alert level C

ABSMU01_ALERT_1_C The ratio of given/expected absorption coefficient lies outside the range 0.99 <> 1.01
Calculated value of mu = 0.662
Value of mu given = 0.641
DENS01_ALERT_1_C The ratio of the submitted crystal density and that calculated from the formula is outside the range 0.99 <> 1.01
Crystal density given = 1.212
Calculated crystal density = 1.258
SHFSU01_ALERT_2_C The absolute value of parameter shift to su ratio > 0.05
Absolute value of the parameter shift to su ratio given 0.100
Additional refinement cycles may be required.
STRVA01_ALERT_4_C Flack test results are ambiguous.
From the CIF: _refine_ls_abs_structure_Flack 0.600
From the CIF: _refine_ls_abs_structure_Flack_su 0.300
PLAT046_ALERT_1_C Reported Z, MW and D(calc) are Inconsistent 1.258
PLAT052_ALERT_1_C Info on Absorption Correction Method Not Given . Please Do !
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ... Please Check
PLAT054_ALERT_1_C Medium Crystal Dimension Missing (or Error) ... Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ... Please Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds 0.0045 Ang.

Alert level G

PLAT032_ALERT_4_G Std. Uncertainty on Flack Parameter Value High . 0.300
PLAT128_ALERT_4_G Alternate Setting for Input Space-Group Cc Ia Note
PLAT152_ALERT_1_G The Supplied and Calc. Volume s.u. Differ by ... 2 Units
PLAT199_ALERT_1_G Reported _cell_measurement_temperature (K) 293 Check
PLAT200_ALERT_1_G Reported _diffrn_ambient_temperature (K) 293 Check
PLAT792_ALERT_1_G The Model has Chirality at C18 (Verify) R
PLAT951_ALERT_5_G Reported and Calculated Kmax Values Differ by .. 2
0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
11 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
7 **ALERT level G** = General information/check it is not something unexpected
12 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
1 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

X-ray crystal structure data for the cyclic biaryl ether (5r): CCDC 968817



Operator	K. Ravikumar
Instrument	Oxford Super Nova
CCDC	968817
Empirical formula	C ₂₇ H ₂₂ O ₃
Formula weight	394.45
Crystal system	orthorhombic
Space group	<i>Pccn</i>
a/Å	29.0006(11)
b/Å	17.3475(10)
c/Å	7.9792(4)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å ³	4014.2(3)
Z	8

ρ_{calc} mg/mm ³	1.305
m/mm ⁻¹	0.668
F(000)	1664.0
Crystal size/mm ³	0.18 × 0.16 × 0.13
2 Θ range for data collection	5.94 to 141.4°
Index ranges	-35 ≤ h ≤ 31, -20 ≤ k ≤ 13, -6 ≤ l ≤ 9
Reflections collected	10097
Independent reflections	3799[R(int) = 0.0306]
Data/restraints/parameters	37990/0/273
Goodness-of-fit on F ²	0.974
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0457, wR ₂ = 0.1356
Final R indexes [all data]	R ₁ = 0.0644, wR ₂ = 0.1574
Largest diff. peak/hole / e Å ⁻³	0.12/-0.17

1. Check CIF/ Platon report (full structure check) for 5r:

Bond precision: C-C = 0.0026 Å Wavelength=1.54180

Cell: a=29.0006 (11) b=17.3475 (10) c=7.9792 (4)
 alpha=90 beta=90 gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	4014.2 (3)	4014.2 (3)
Space group	P c c n	P c c n
Hall group	-P 2ab 2ac	-P 2ab 2ac
Moiety formula	C27 H22 O3	C27 H22 O3
Sum formula	C27 H22 O3	C27 H22 O3
Mr	394.45	394.45
Dx, g cm ⁻³	1.305	1.305
Z	8	8
Mu (mm ⁻¹)	0.668	0.668
F000	1664.0	1664.0
F000'	1668.90	
h, k, lmax	35, 21, 9	35, 20, 9
Nref	3861	3799
Tmin, Tmax	0.887, 0.917	0.584, 1.000
Tmin'	0.887	

Correction method= MULTI-SCAN

Data completeness= 0.984

Theta (max)= 70.700

R(reflections)= 0.0457 (2790)

wR2(reflections)= 0.1574 (3799)

S = 0.974

Npar= 273

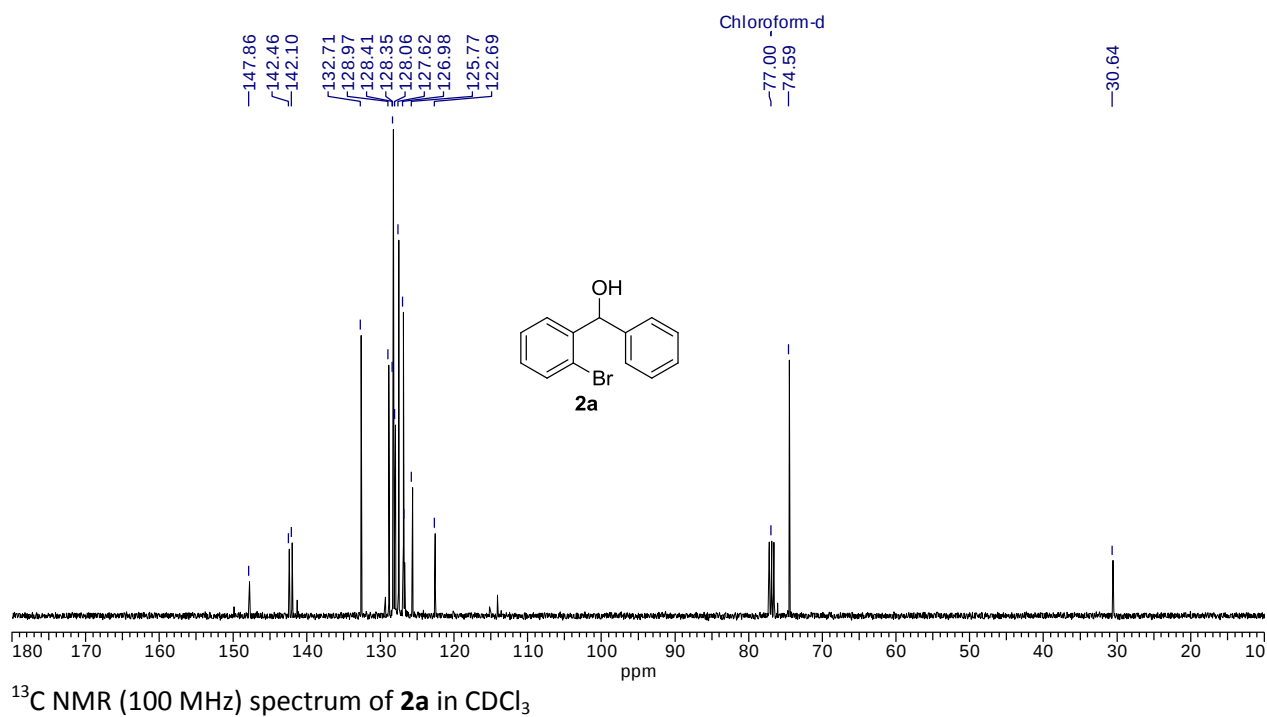
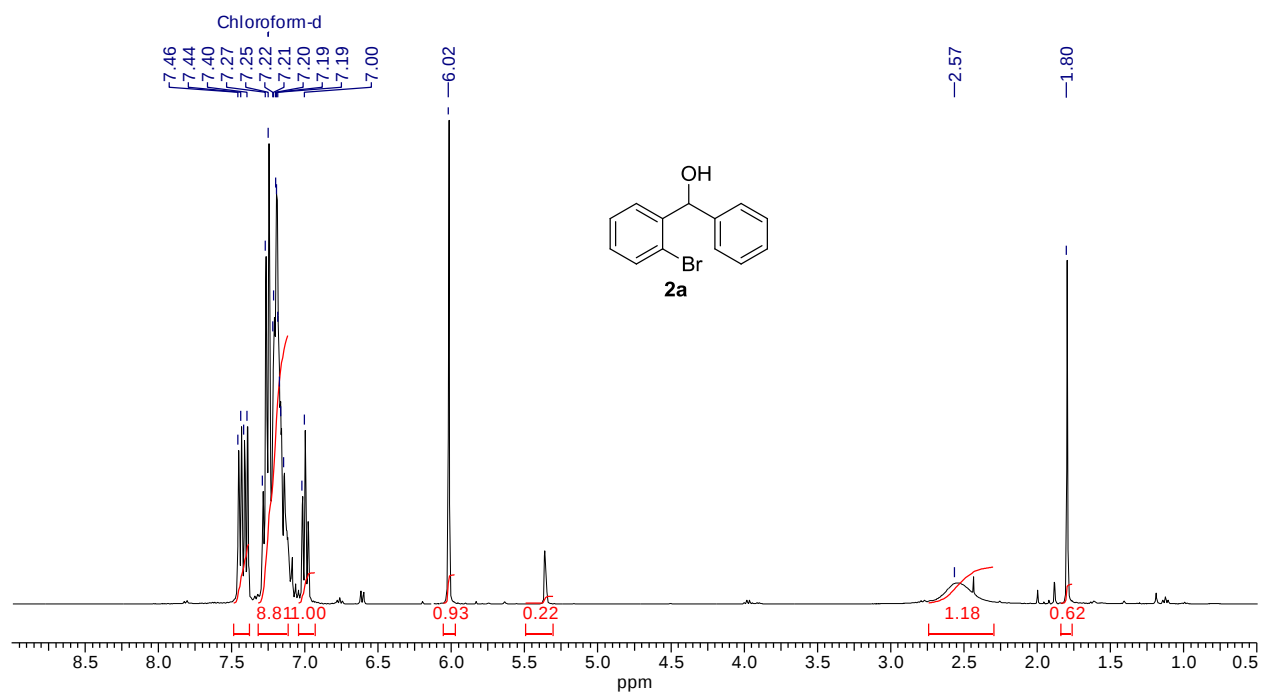
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Click on the hyperlinks for more details of the test.

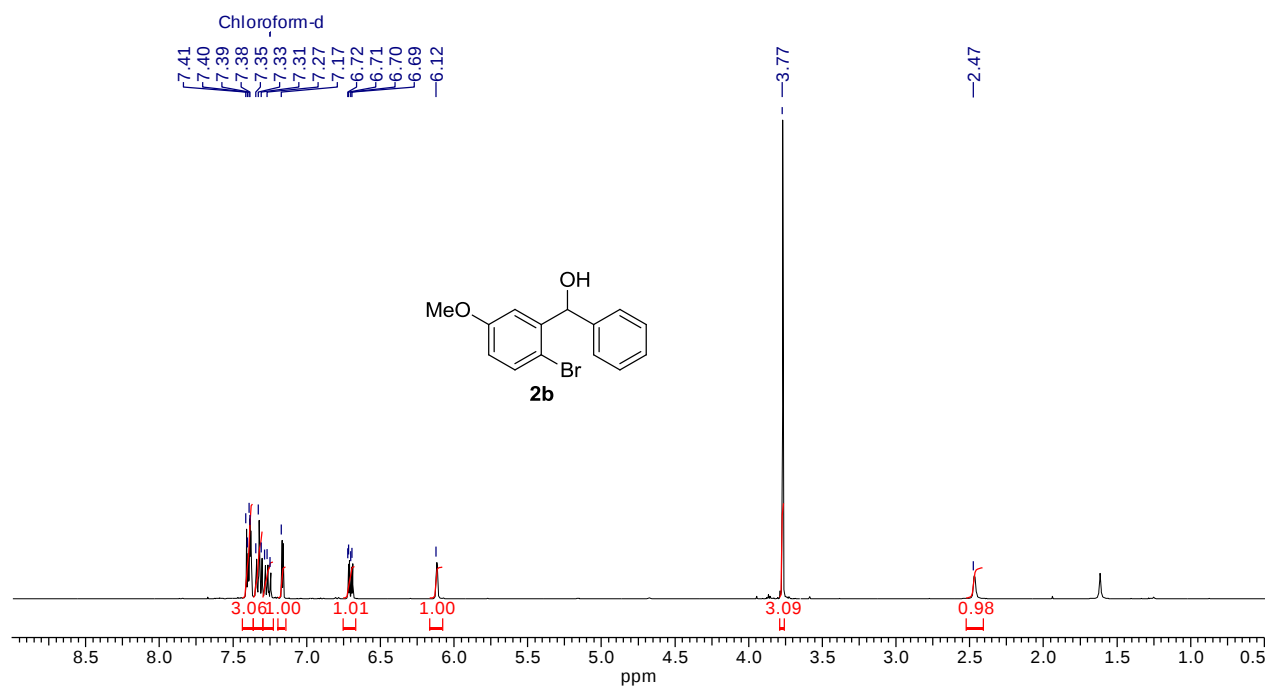
Alert level G

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PLAT093_ALERT_1_G No su's on H-positions, refinement reported as . mixed
PLAT199_ALERT_1_G Reported _cell_measurement_temperature (K) 293 Check
PLAT200_ALERT_1_G Reported _diffn ambient temperature (K) 293 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 2

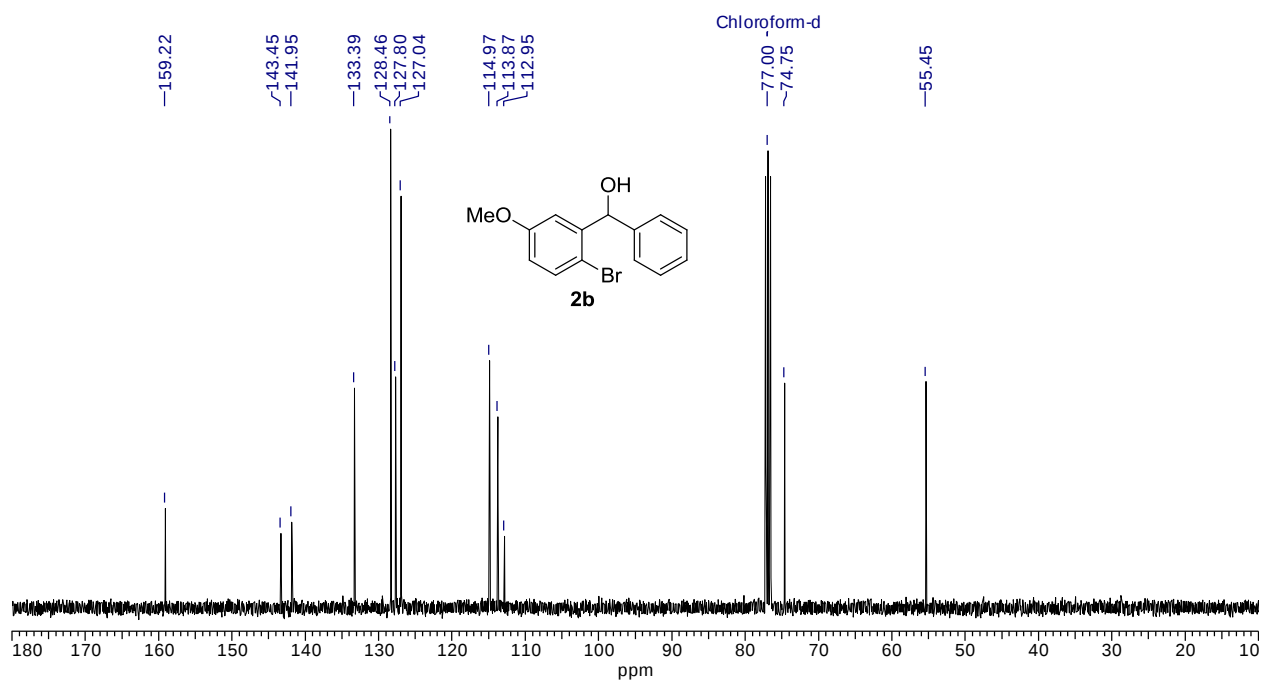
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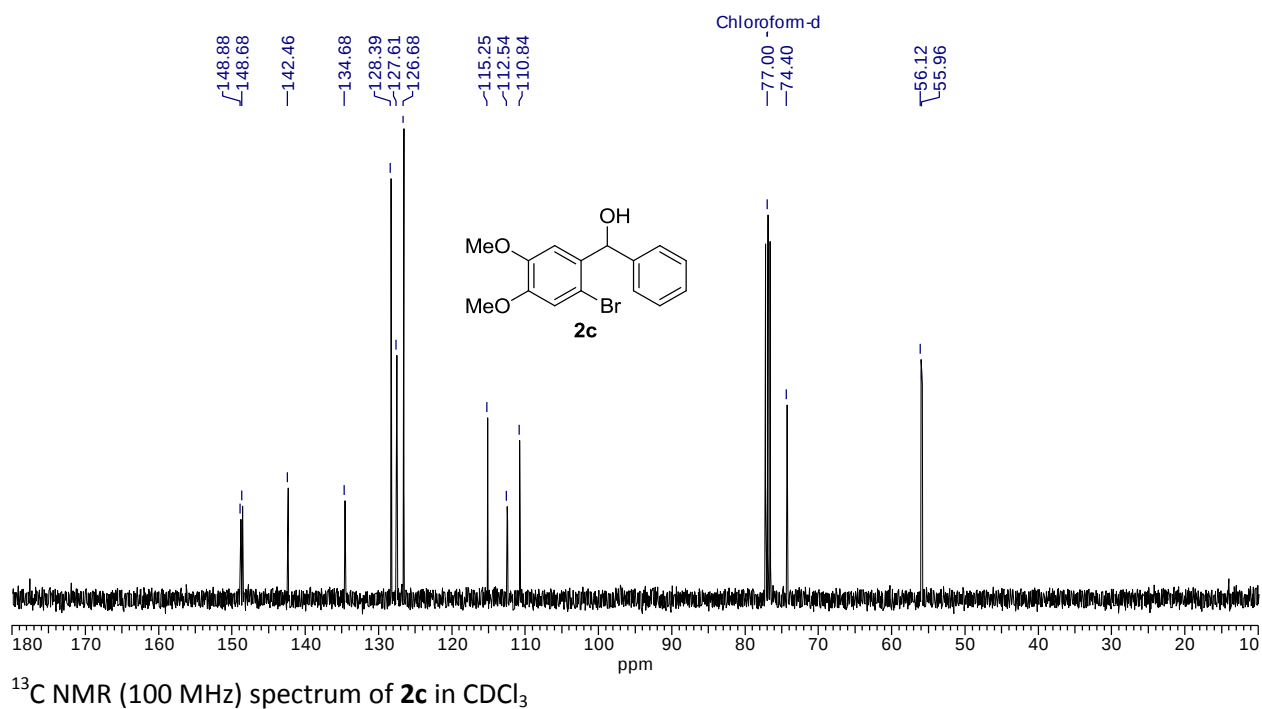
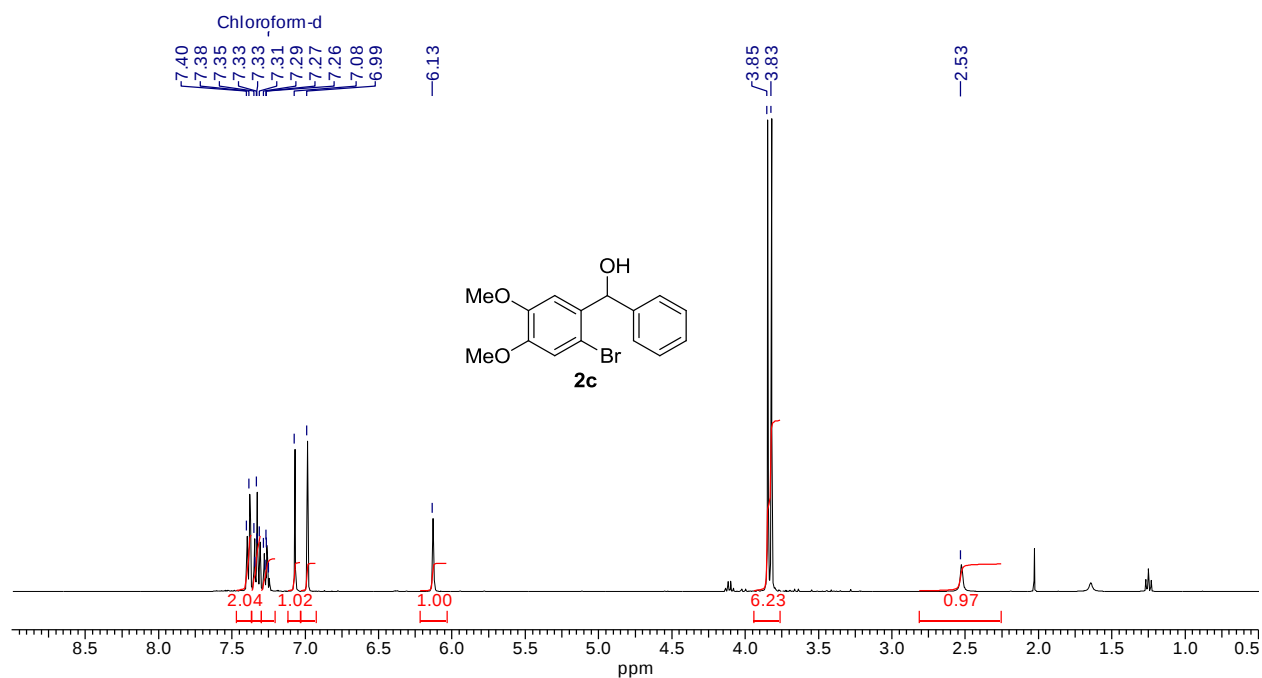


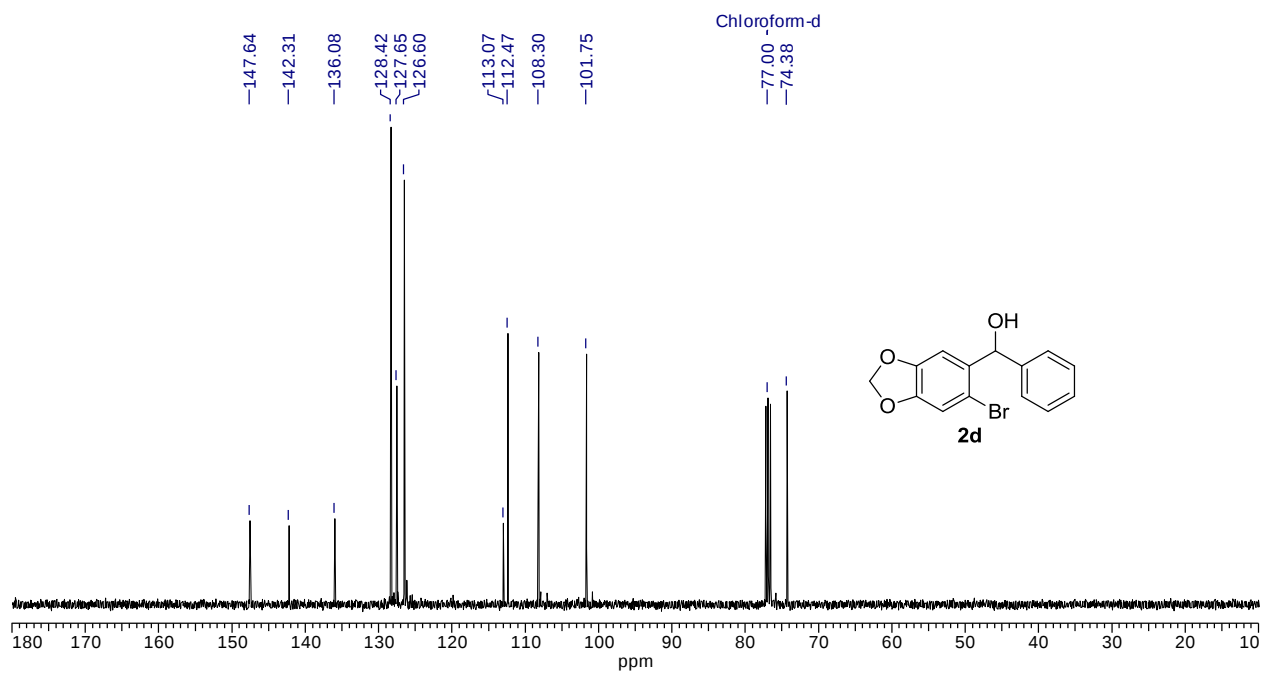
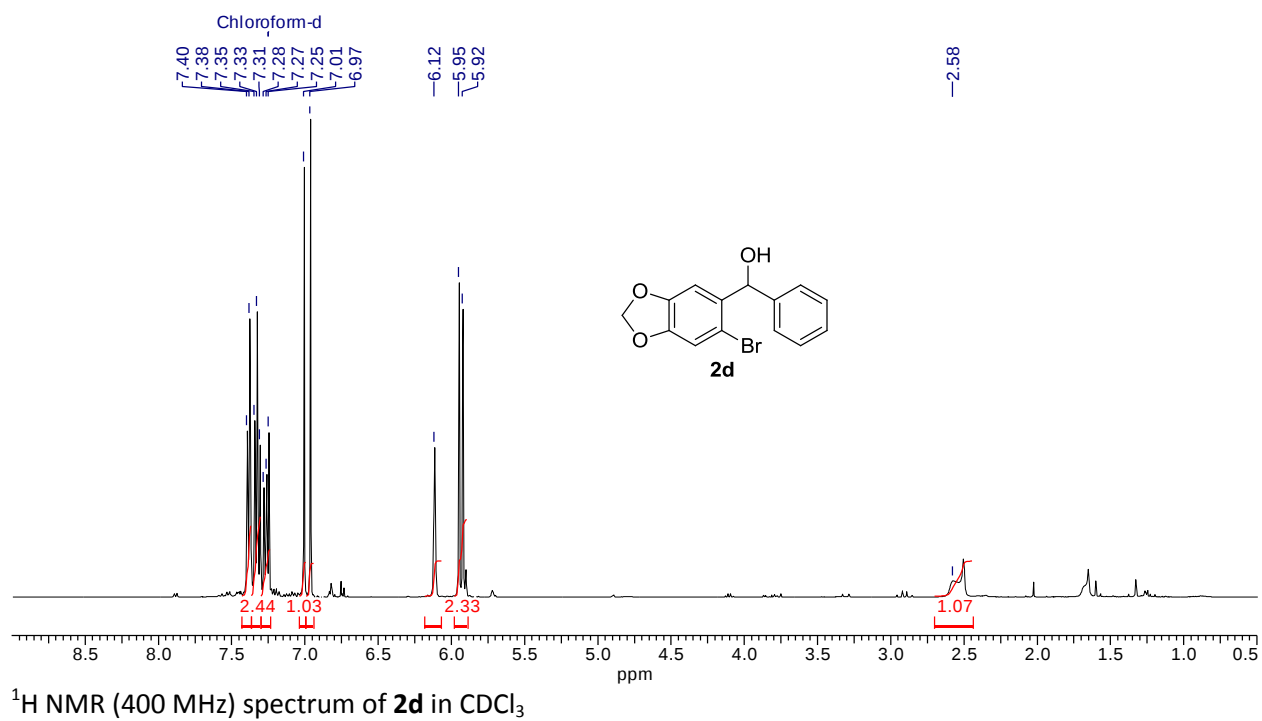


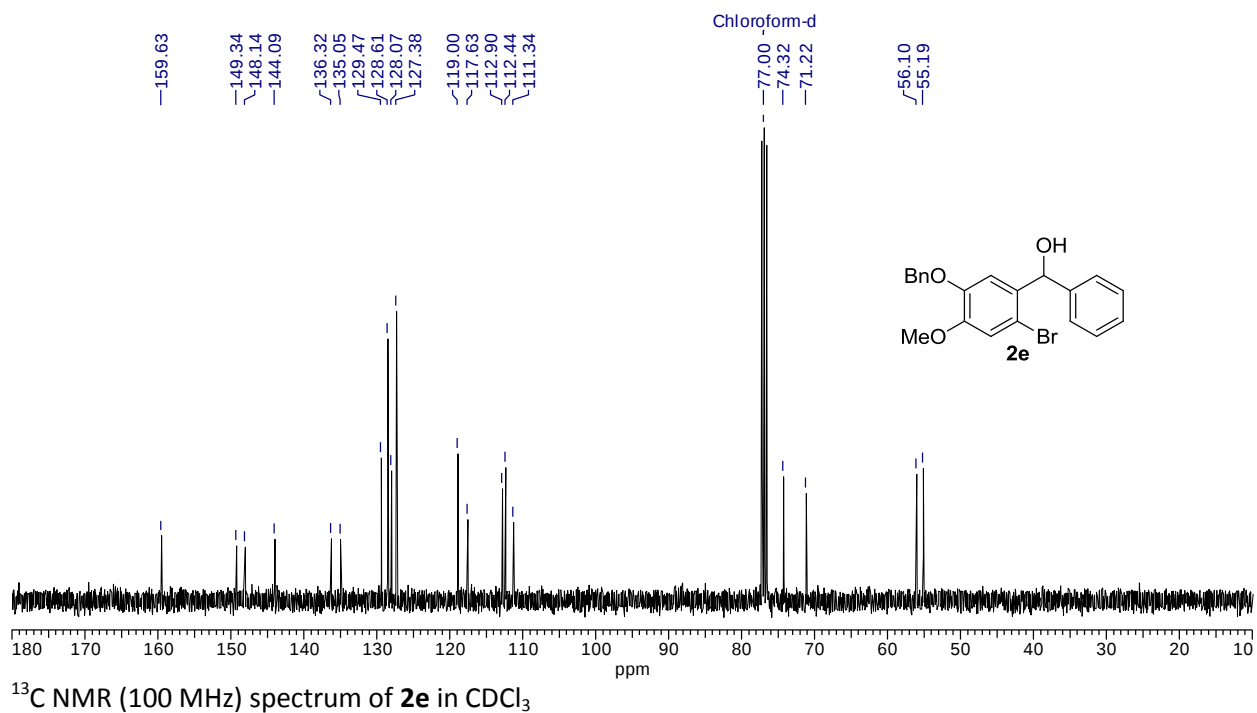
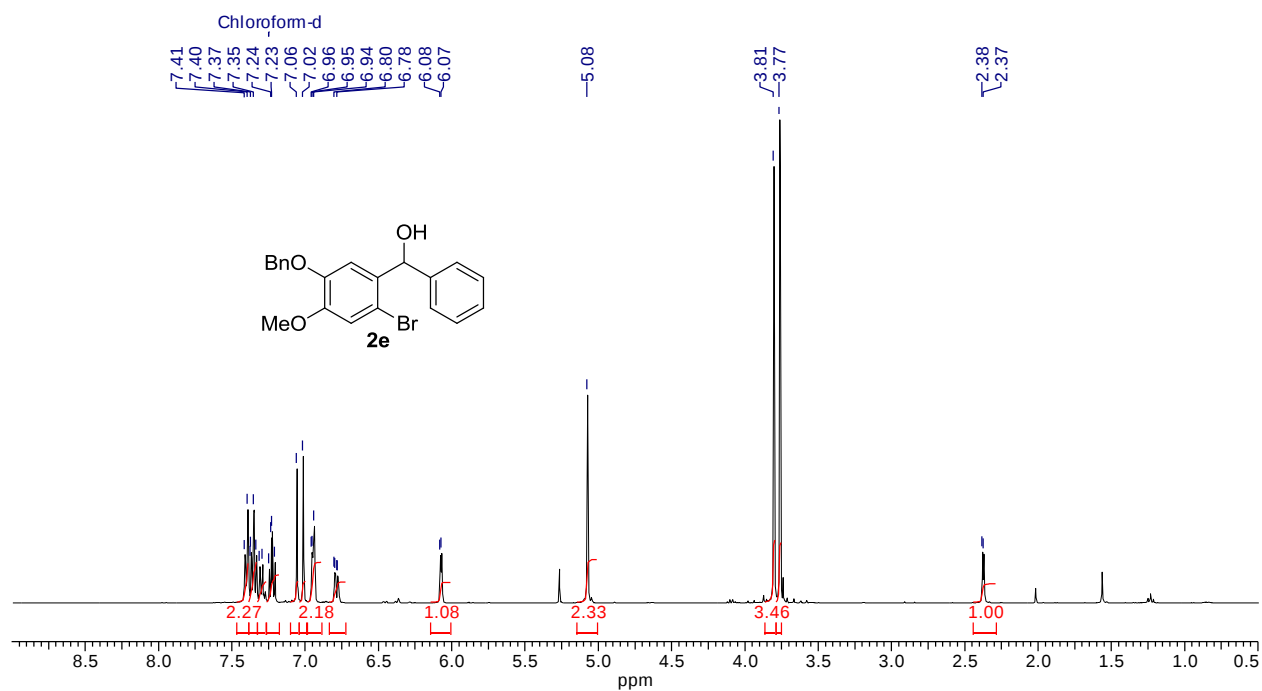
^1H NMR (400 MHz) spectrum of **2b** in CDCl_3

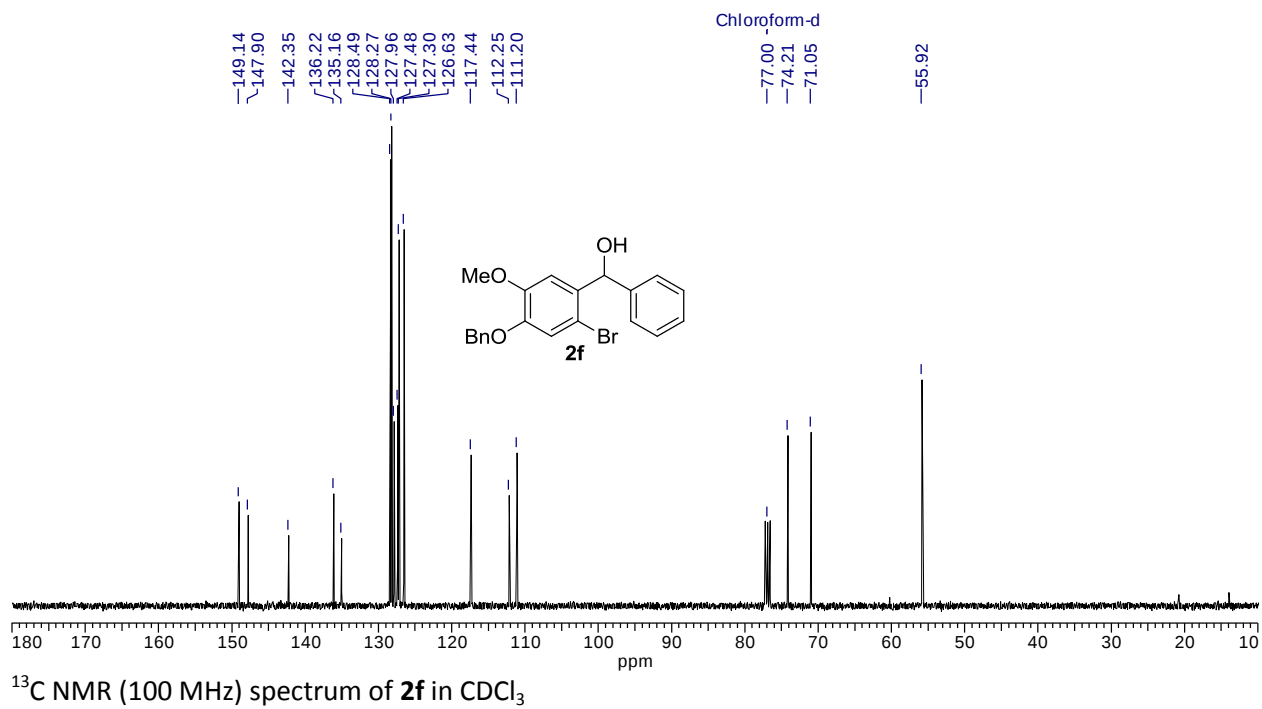
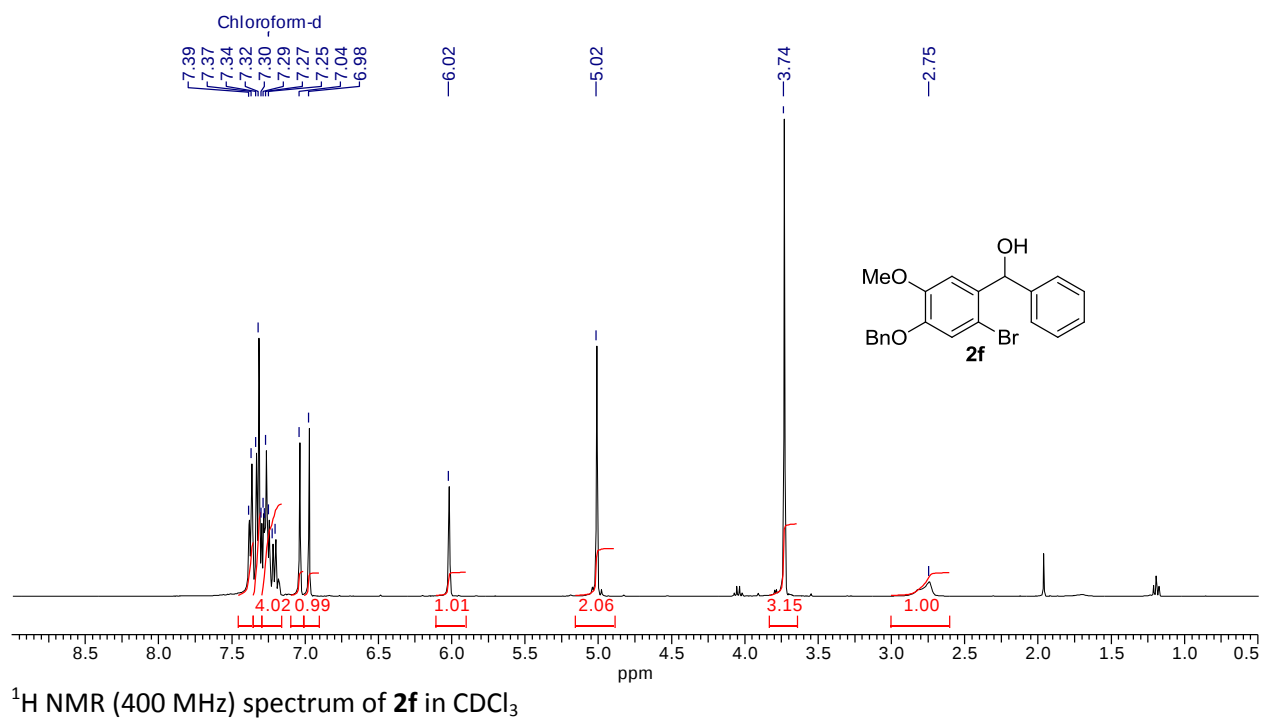


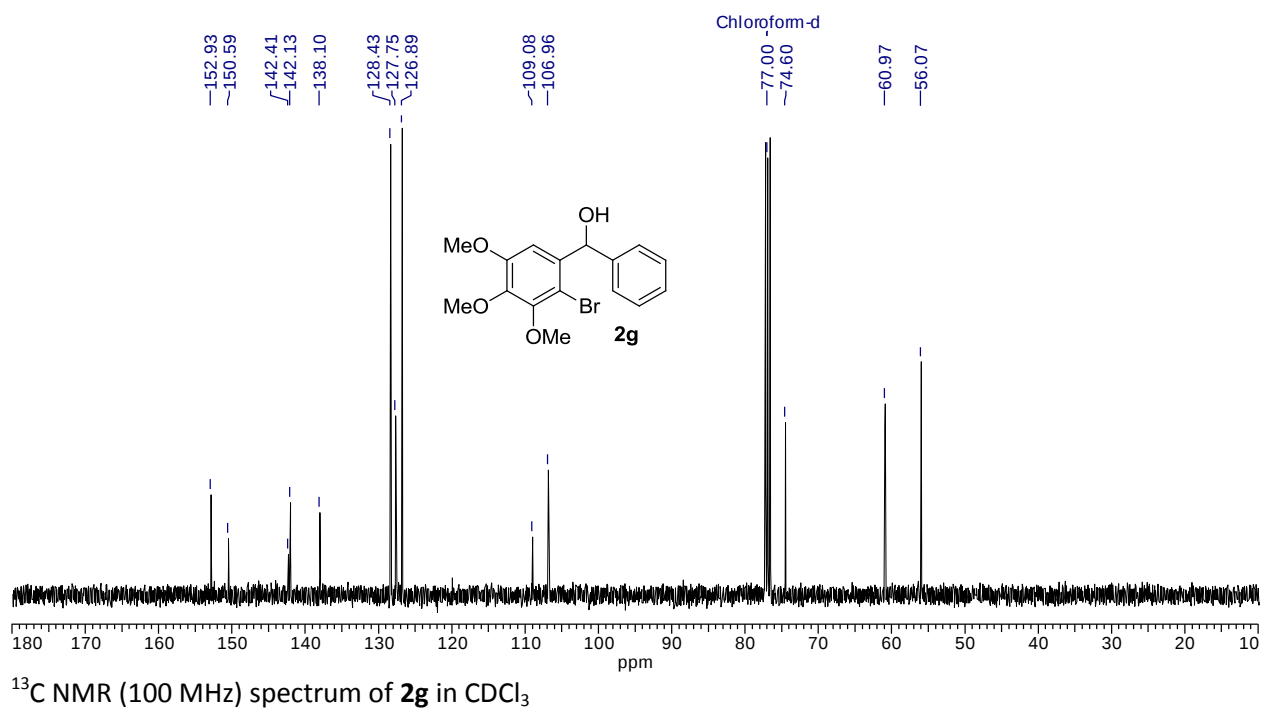
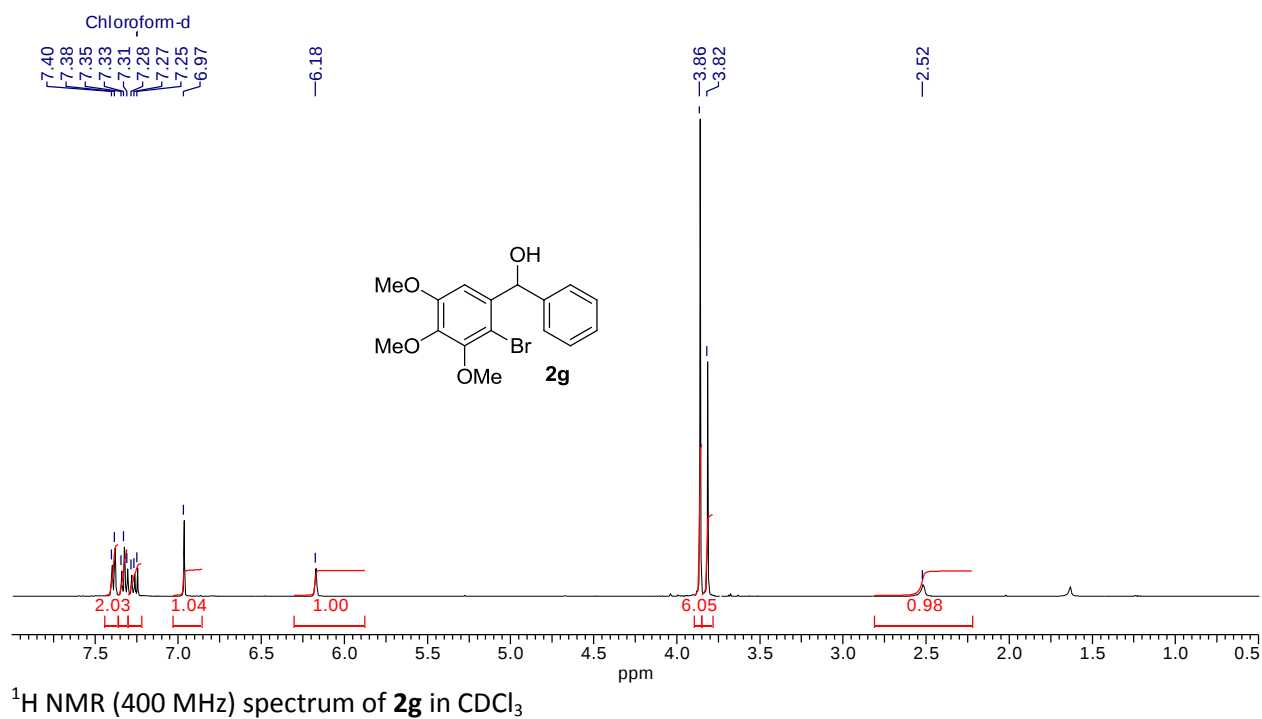
^{13}C NMR (100 MHz) spectrum of **2b** in CDCl_3

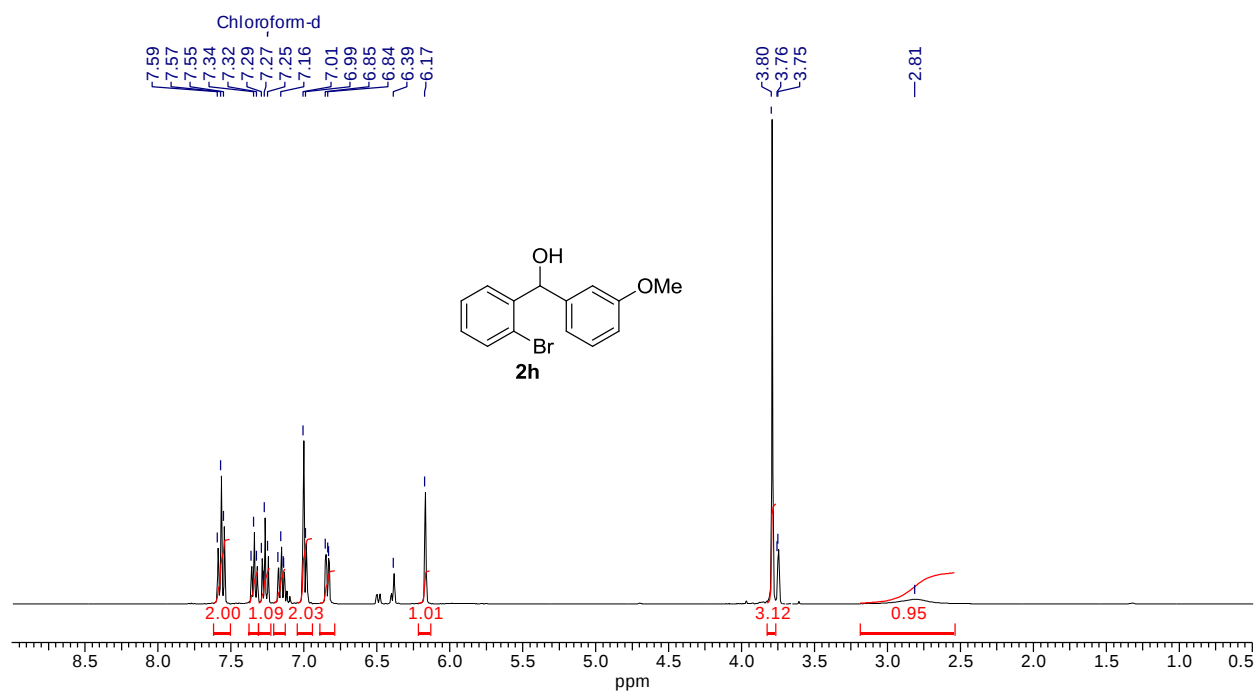




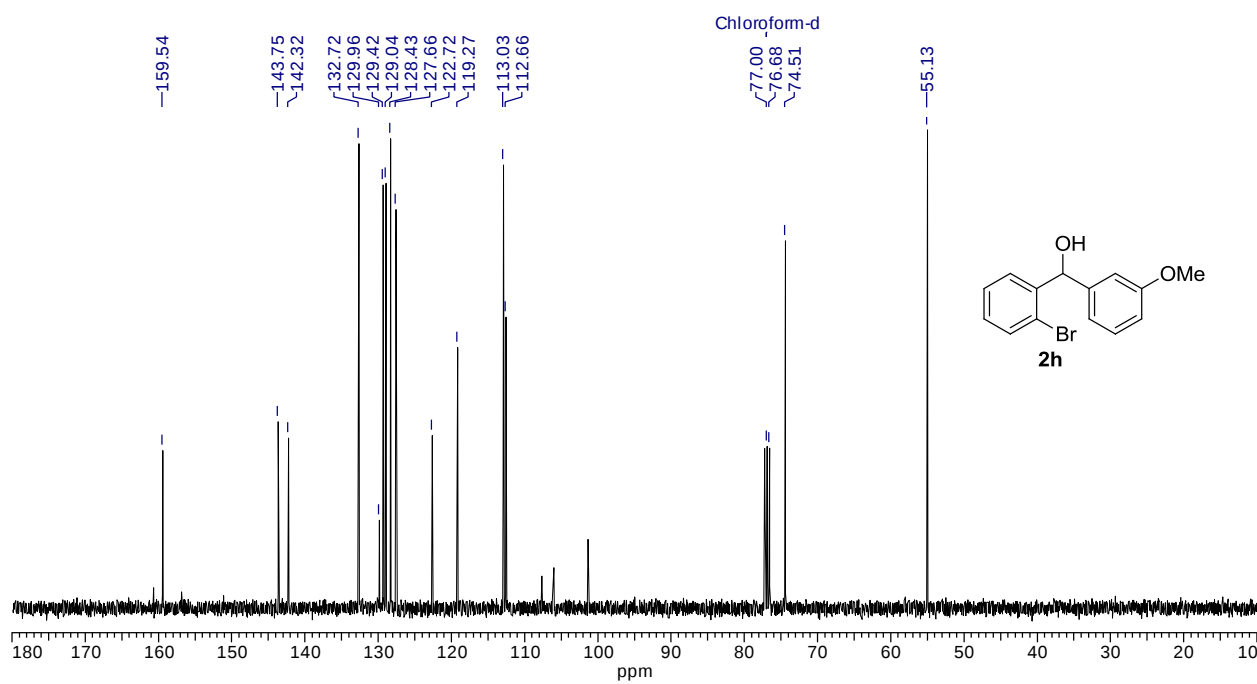




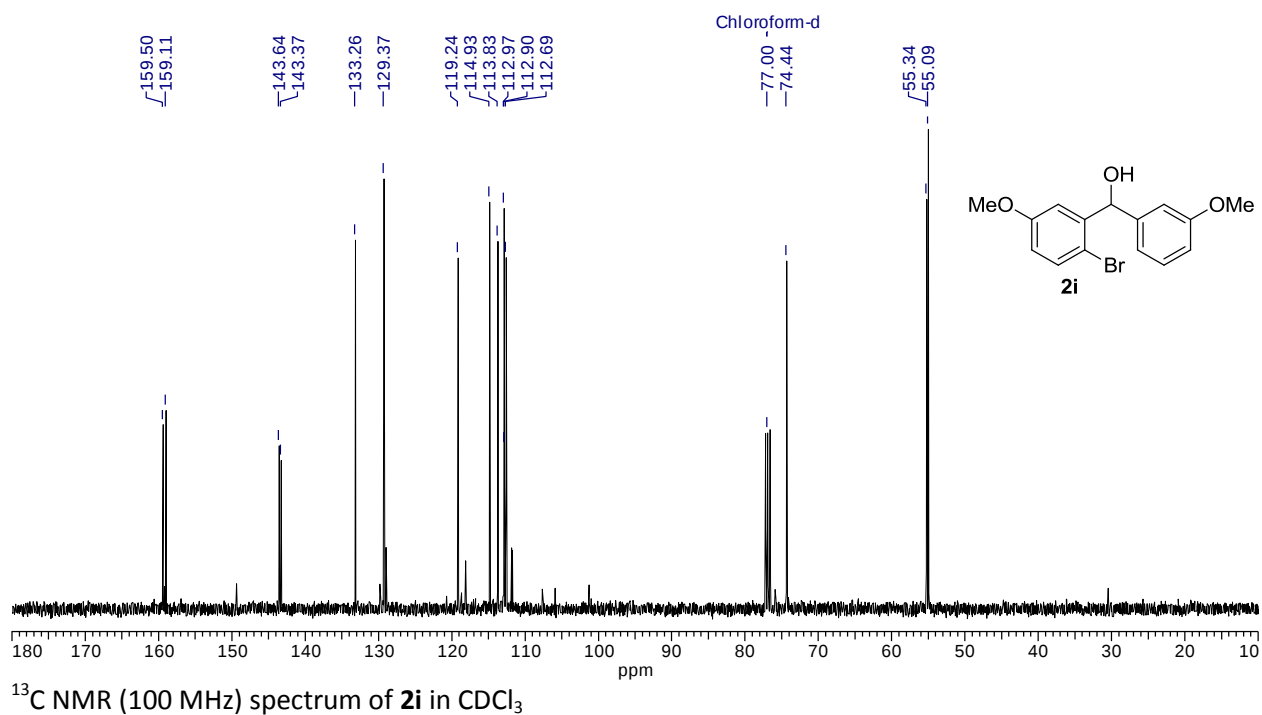
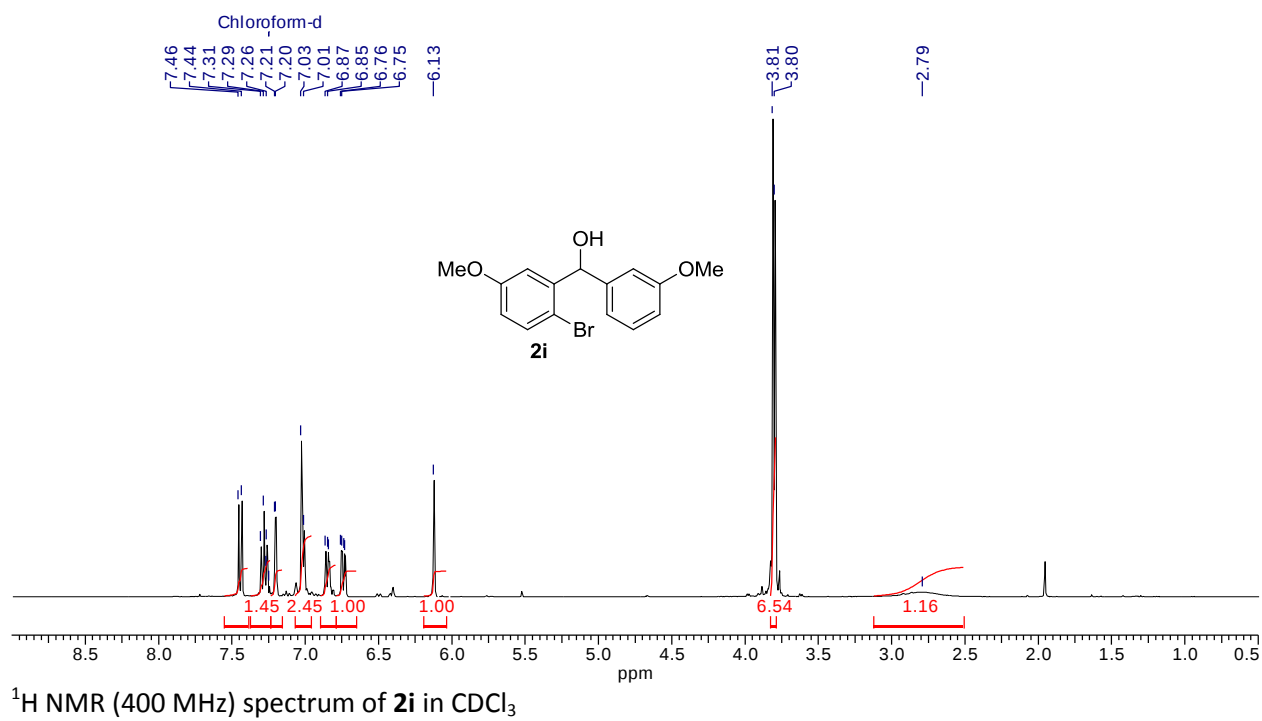


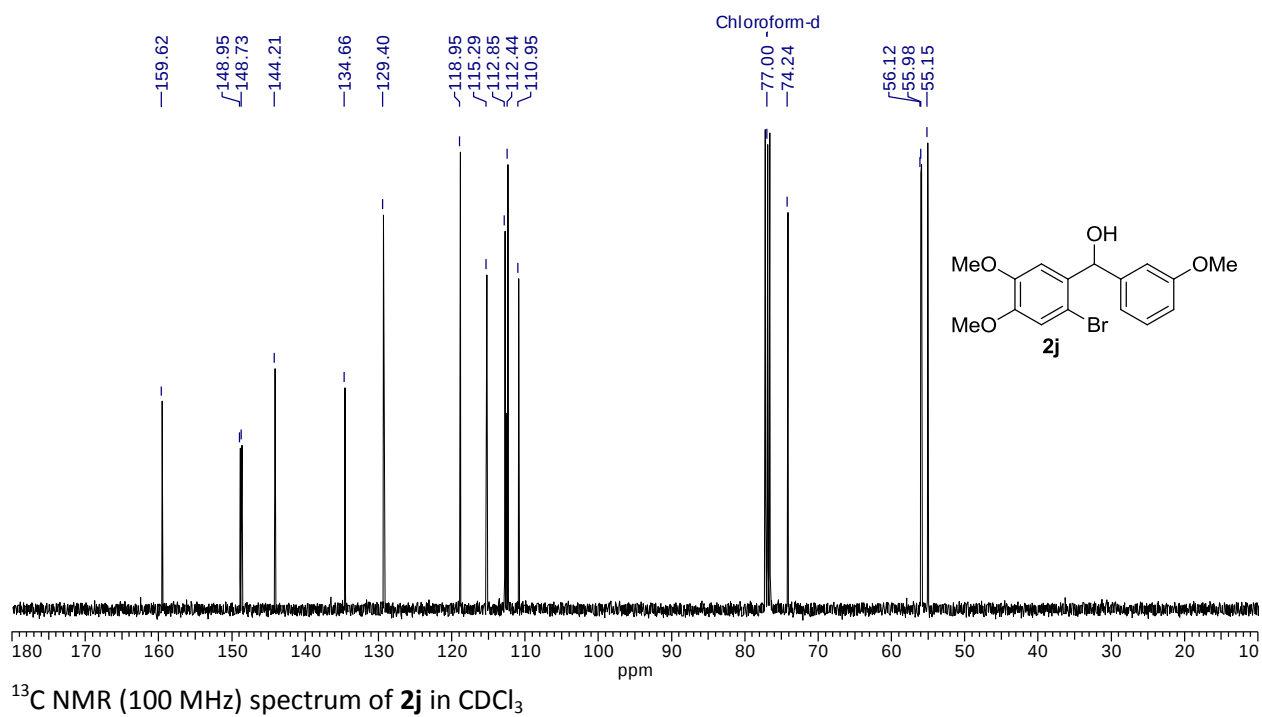
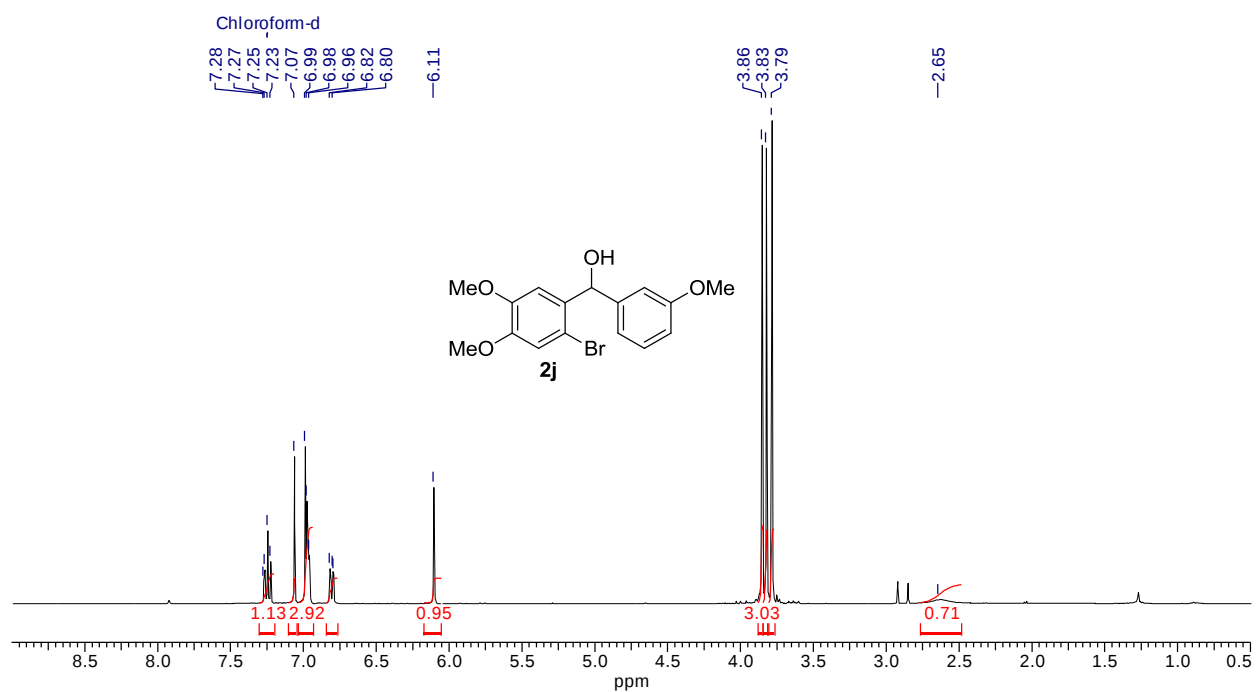


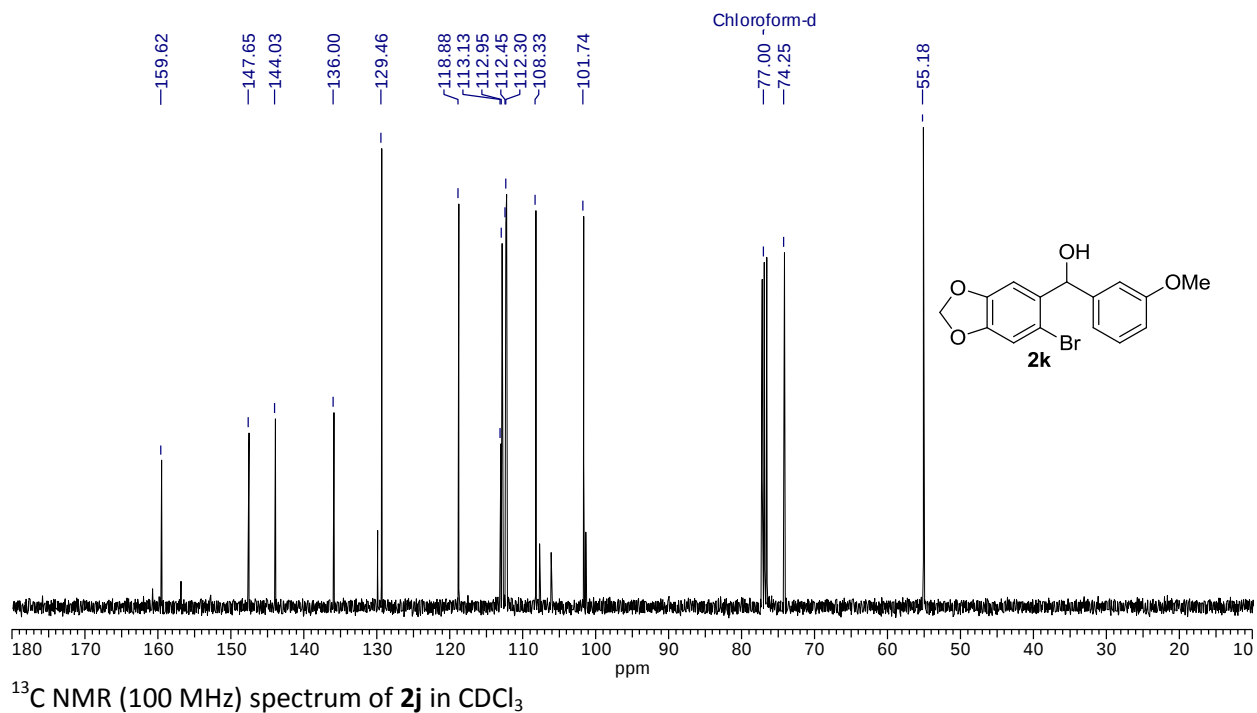
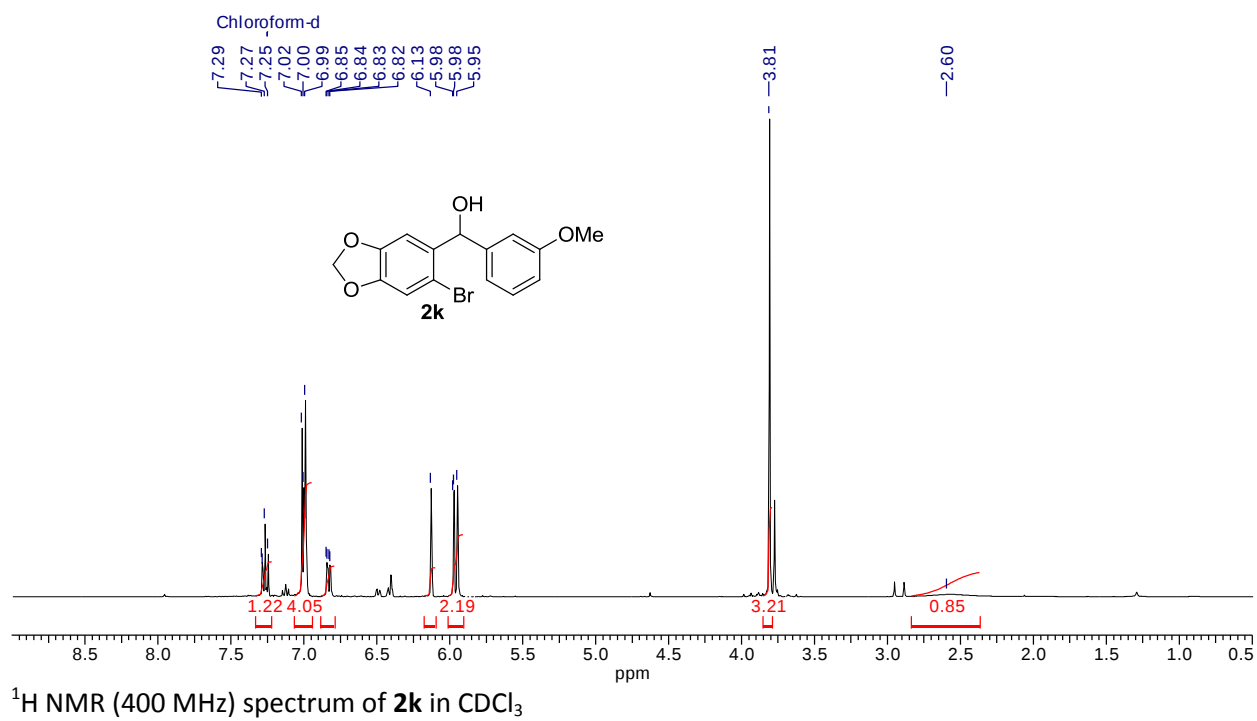
¹H NMR (400 MHz) spectrum of **2h** in CDCl₃

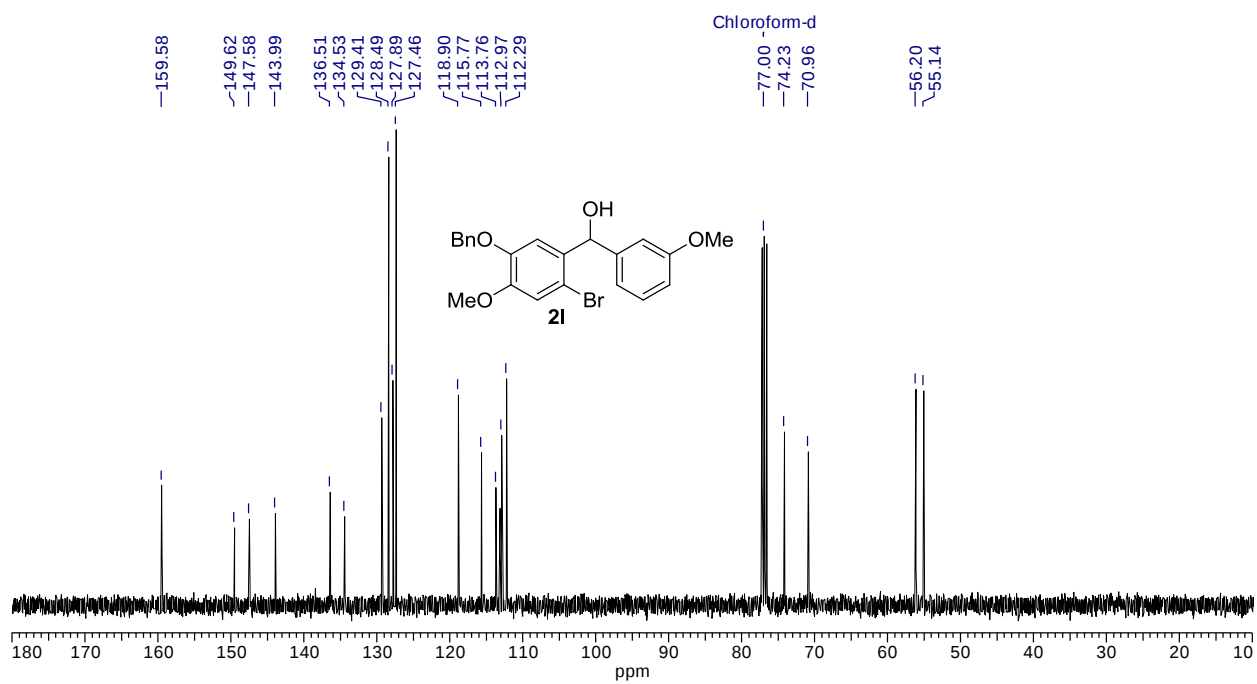
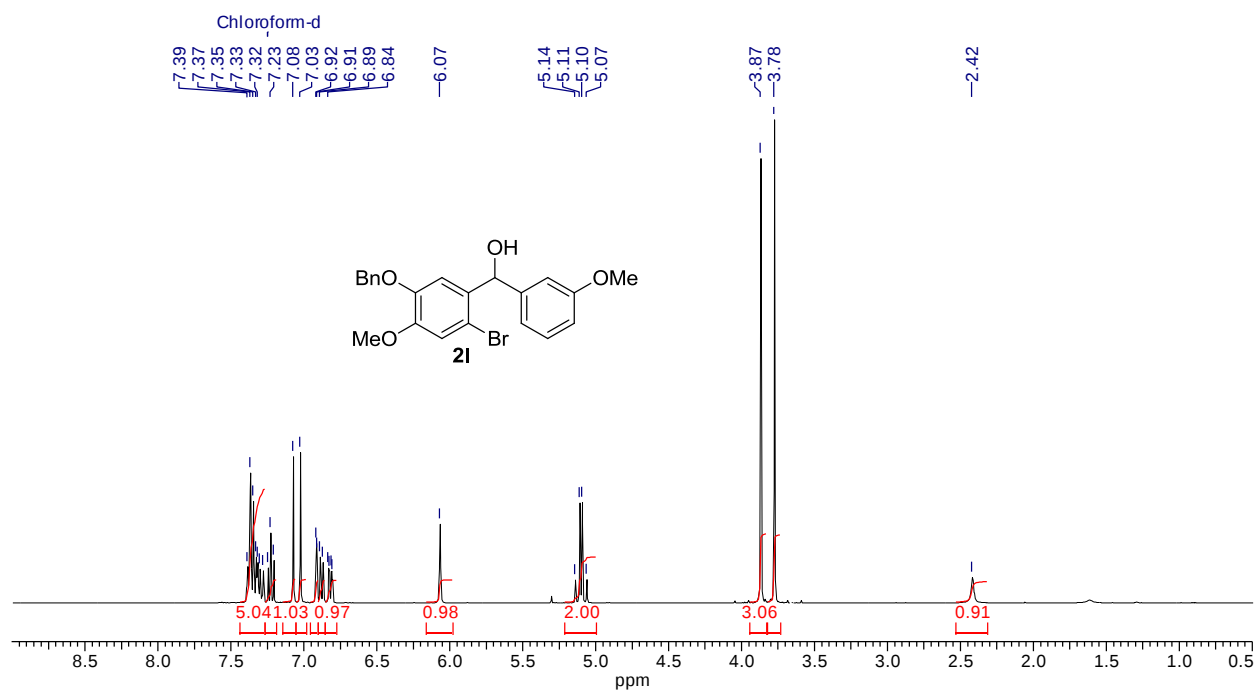


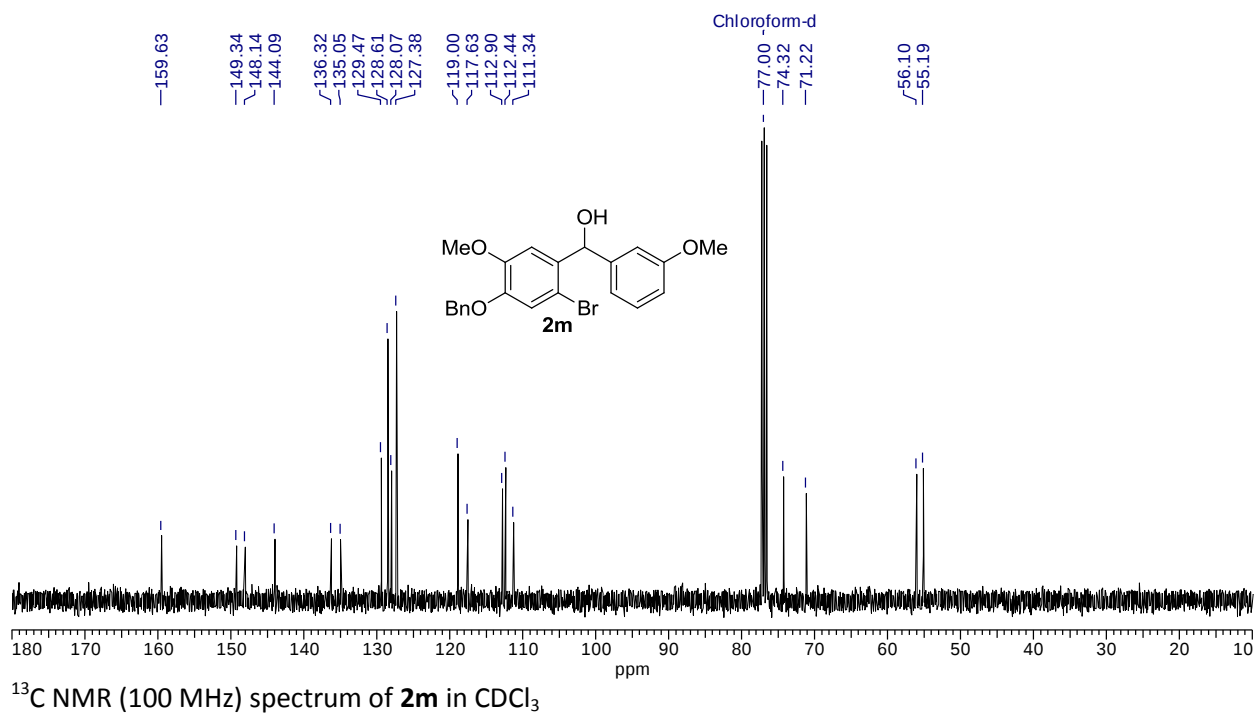
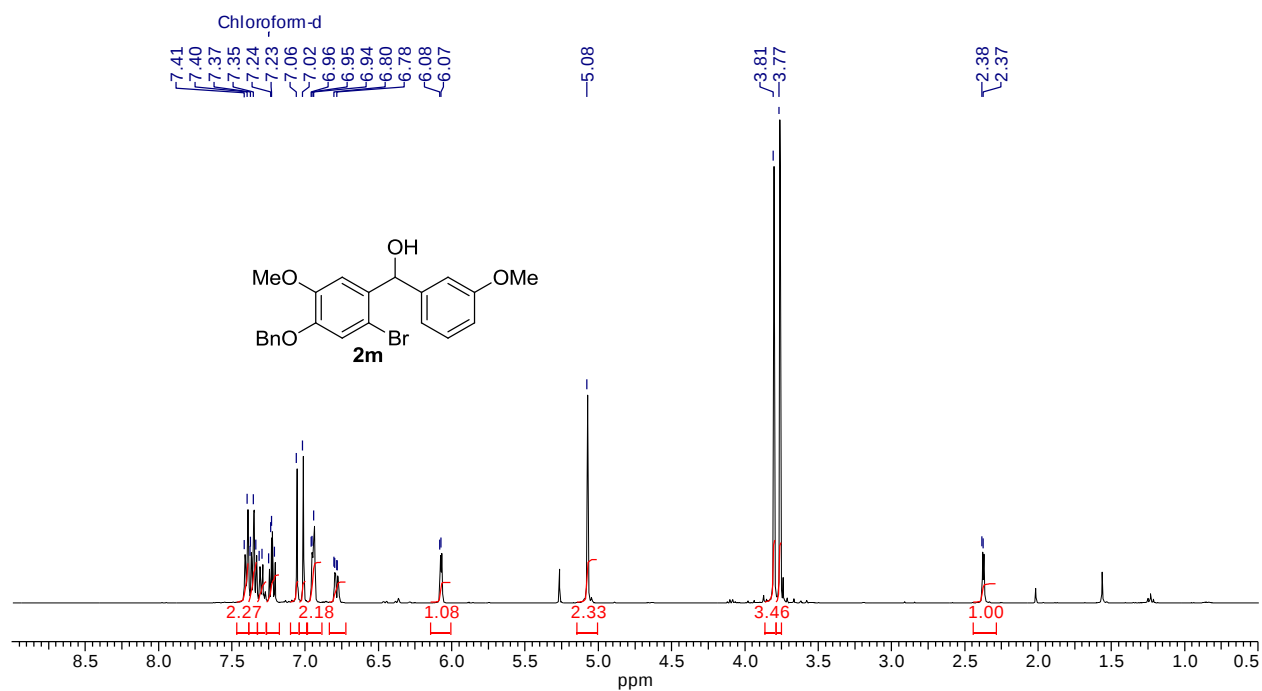
¹³C NMR (100 MHz) spectrum of **2h** in CDCl₃

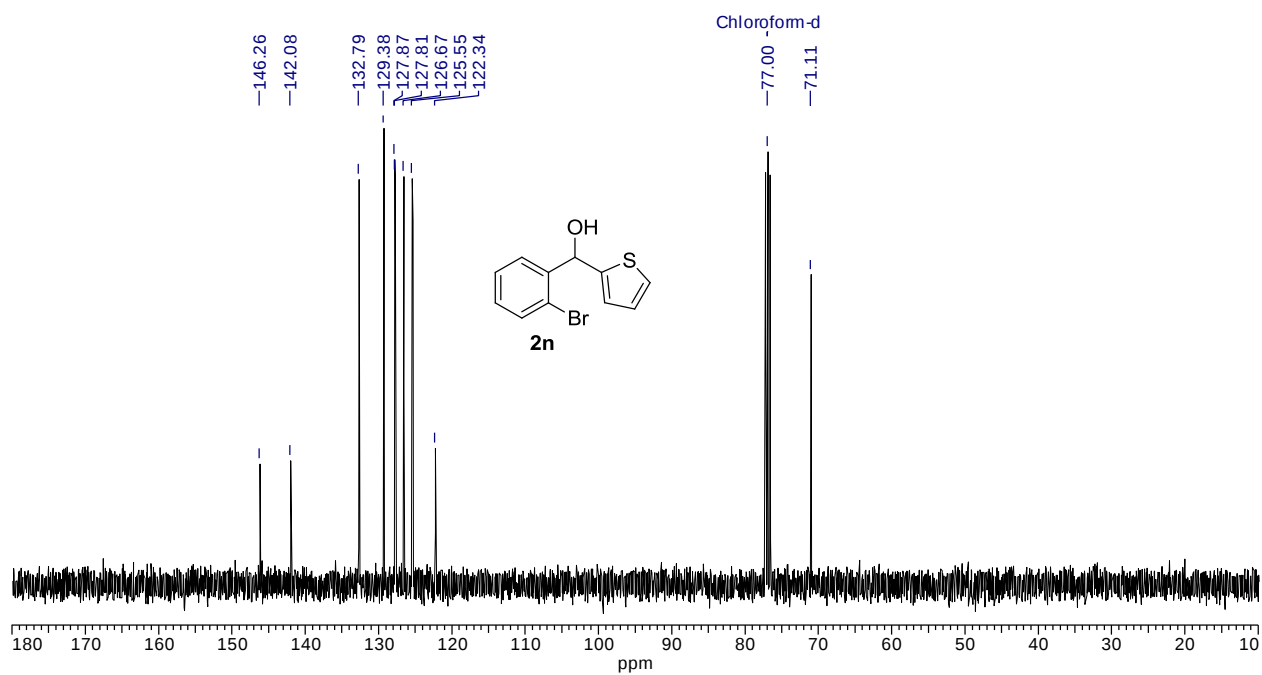
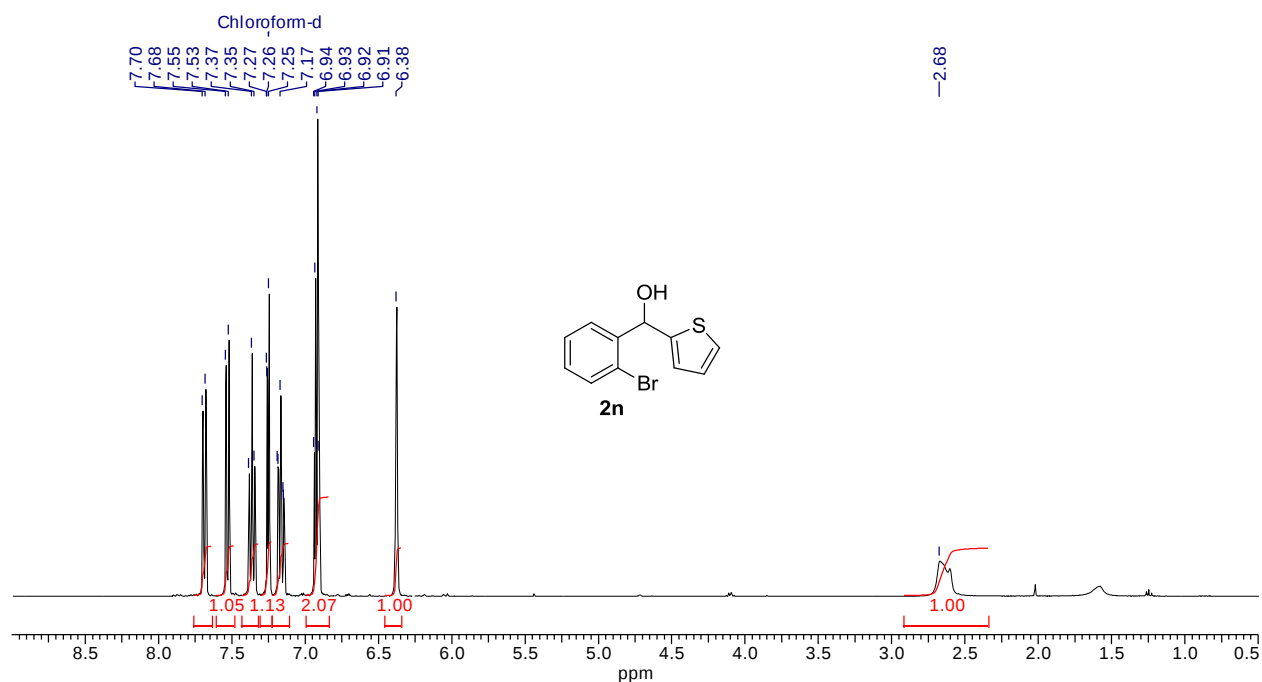


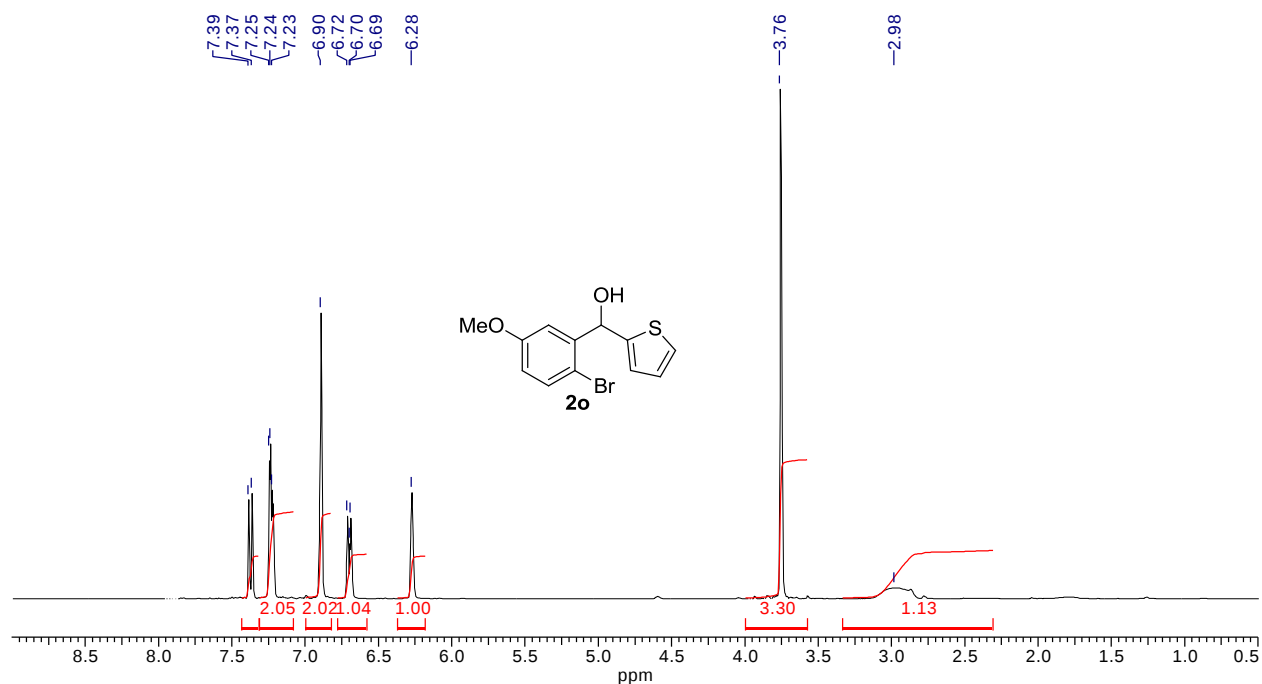




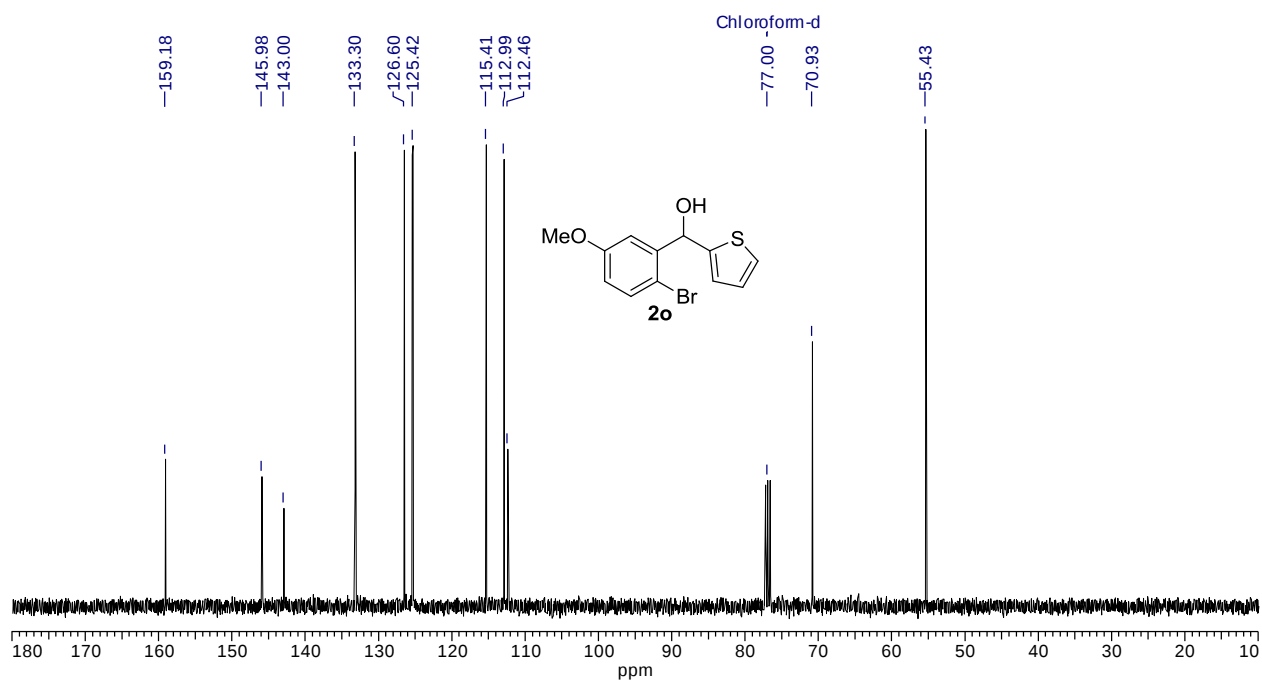




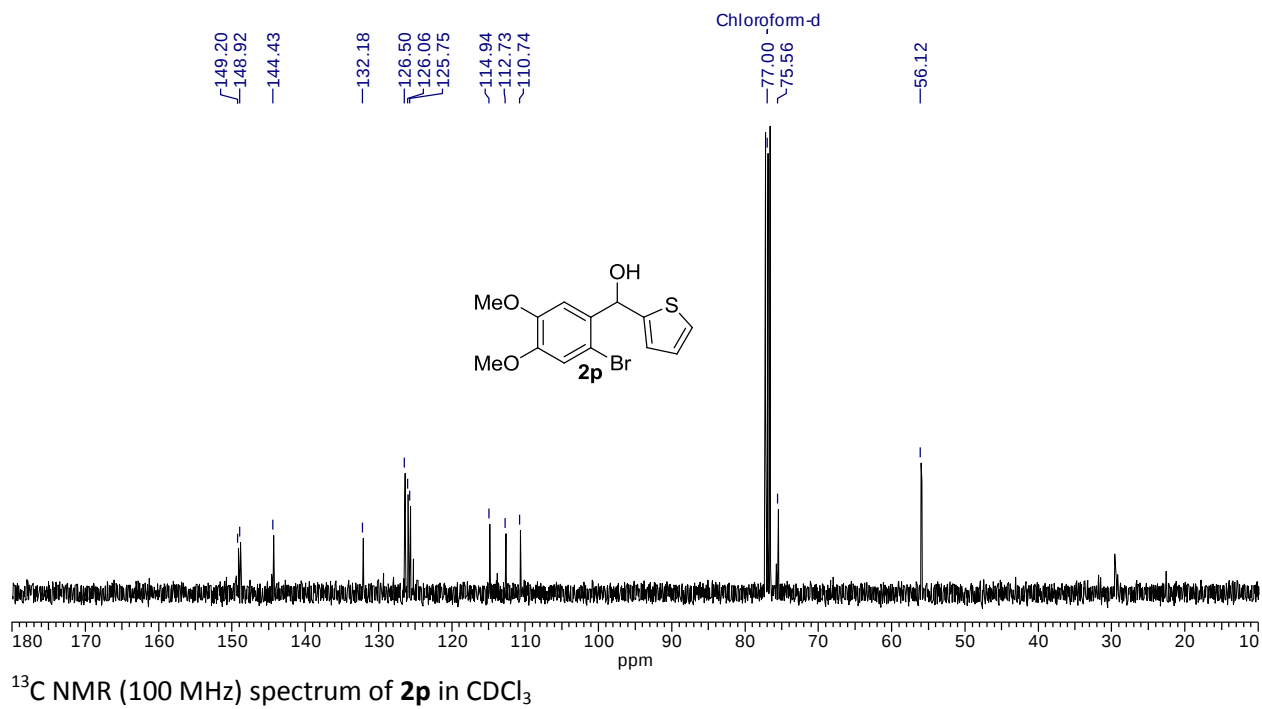
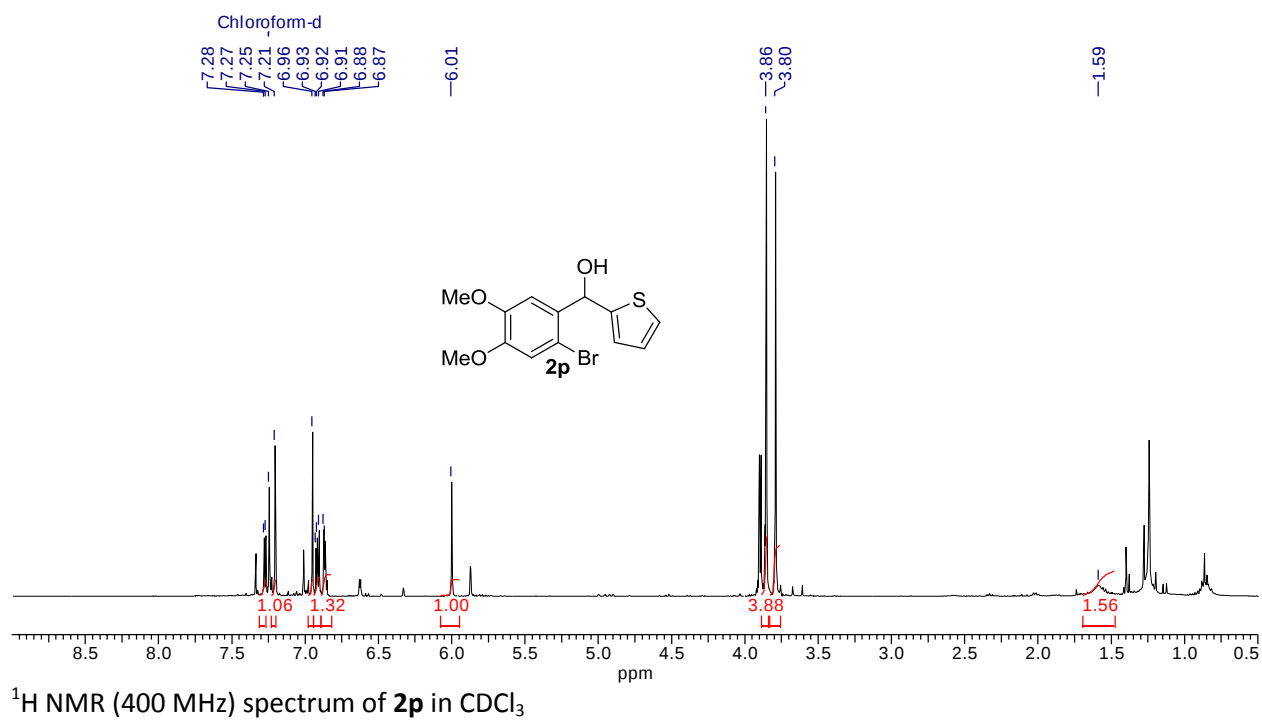


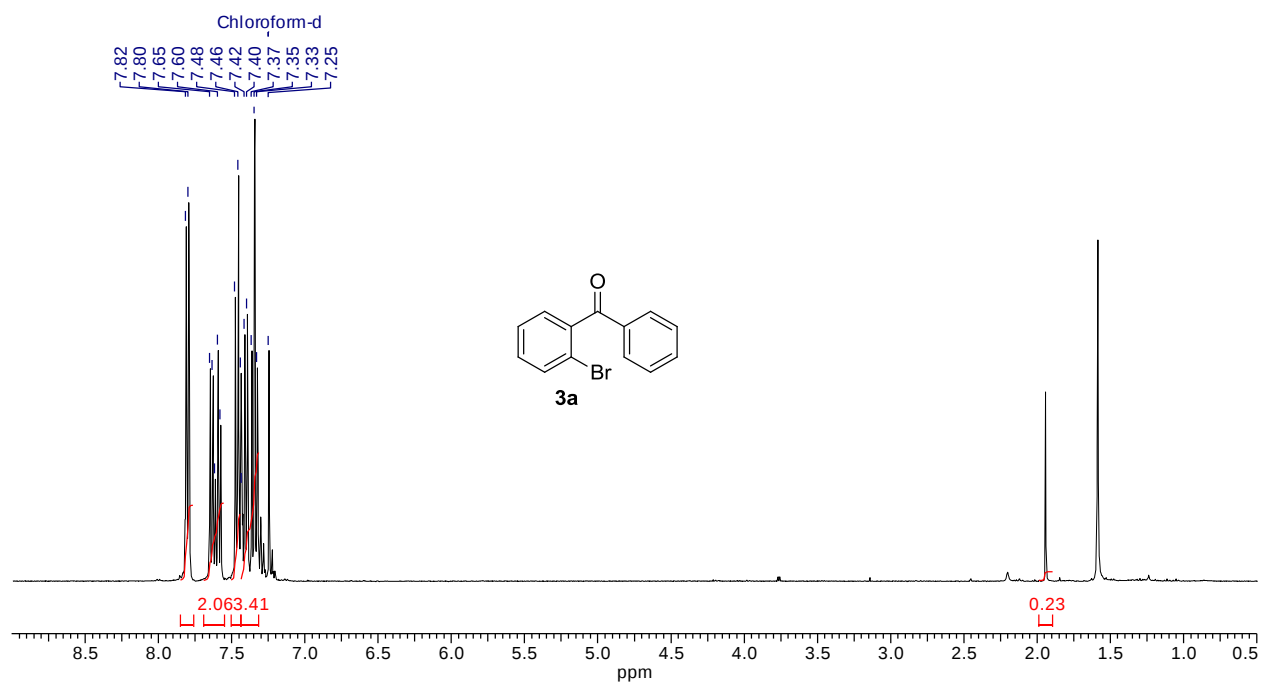


¹H NMR (400 MHz) spectrum of **2o** in CDCl₃

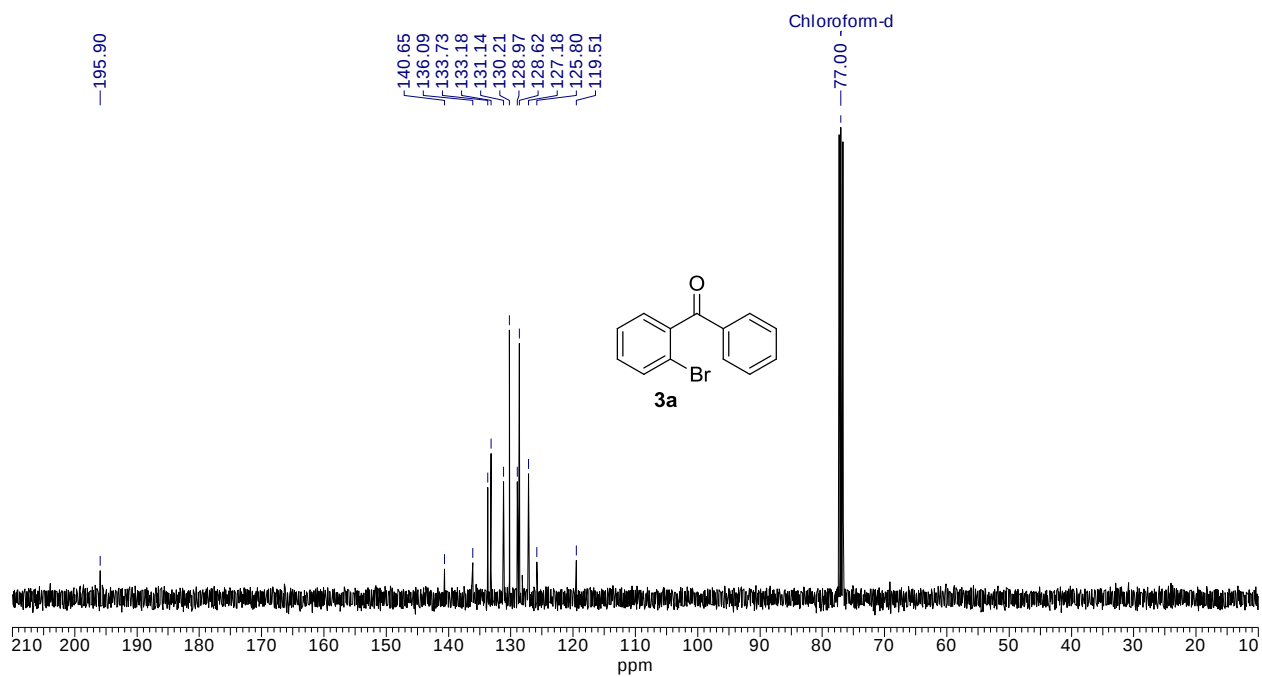


¹³C NMR (100 MHz) spectrum of **2o** in CDCl₃

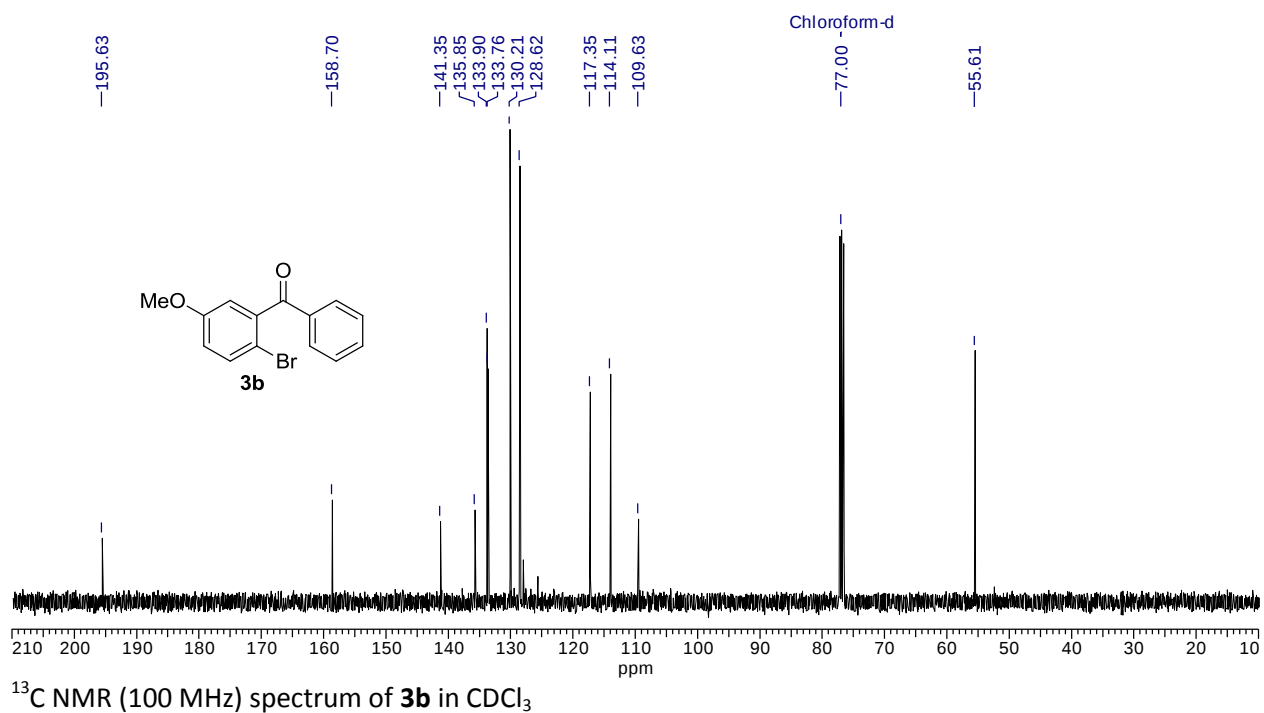
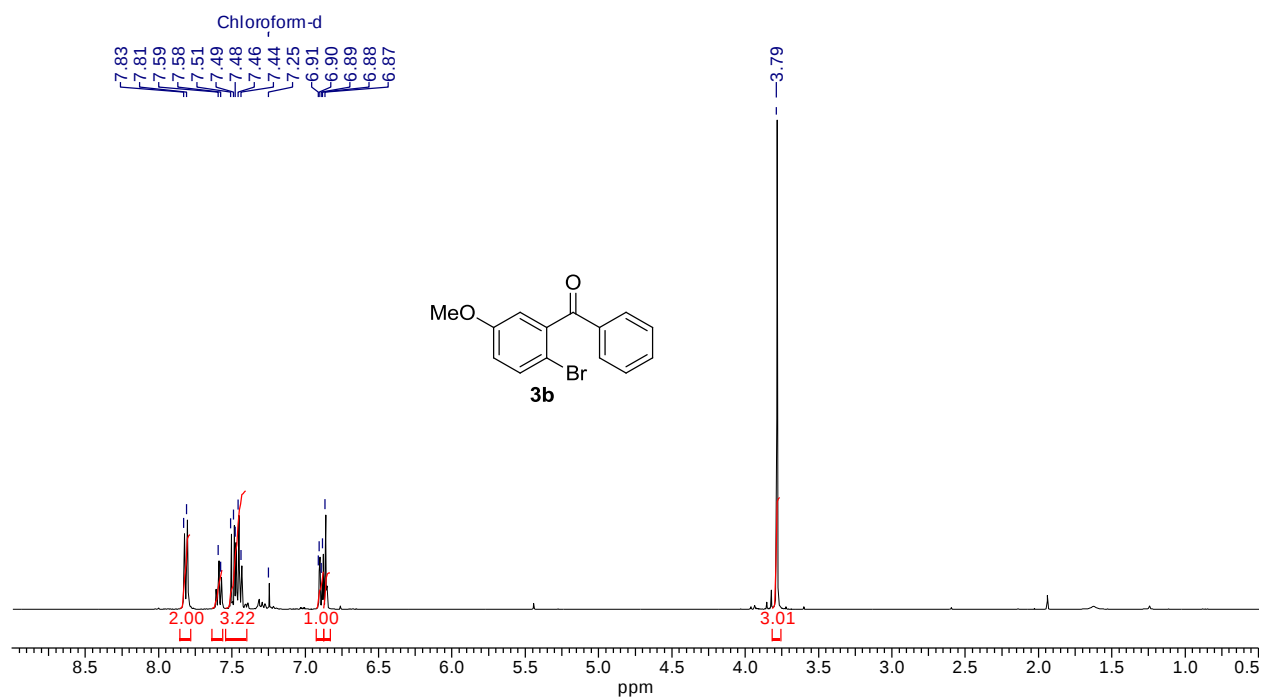


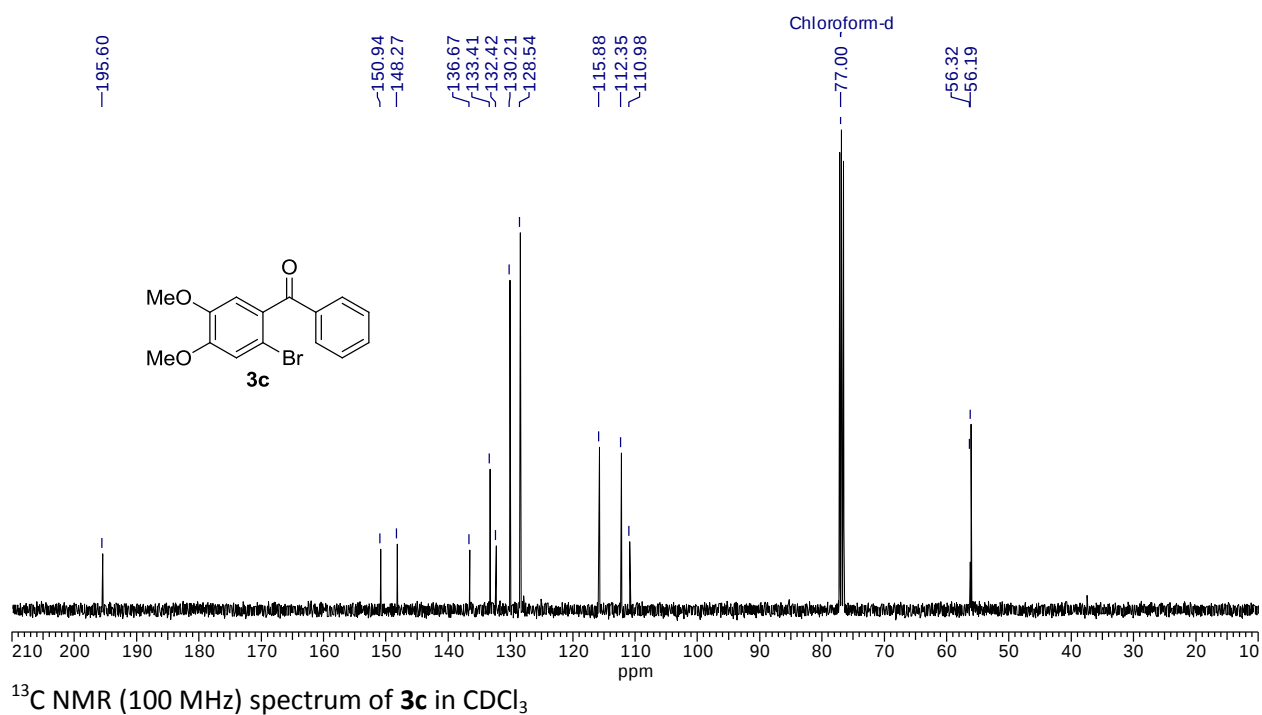
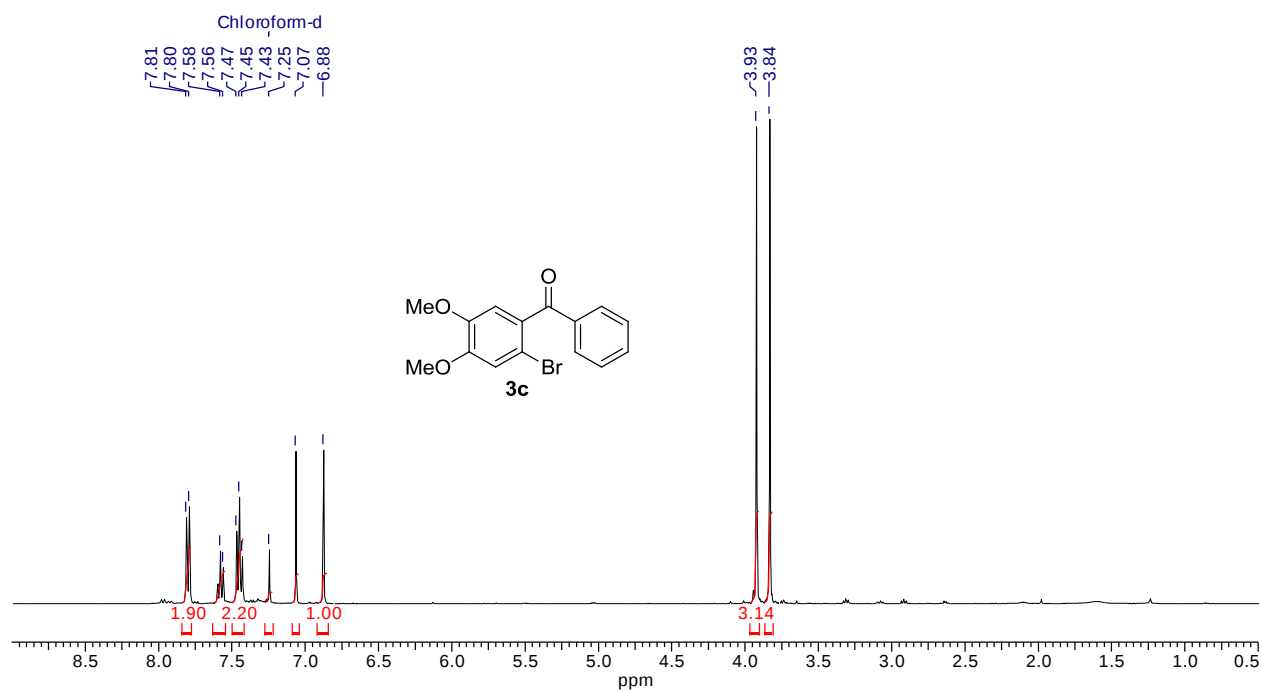


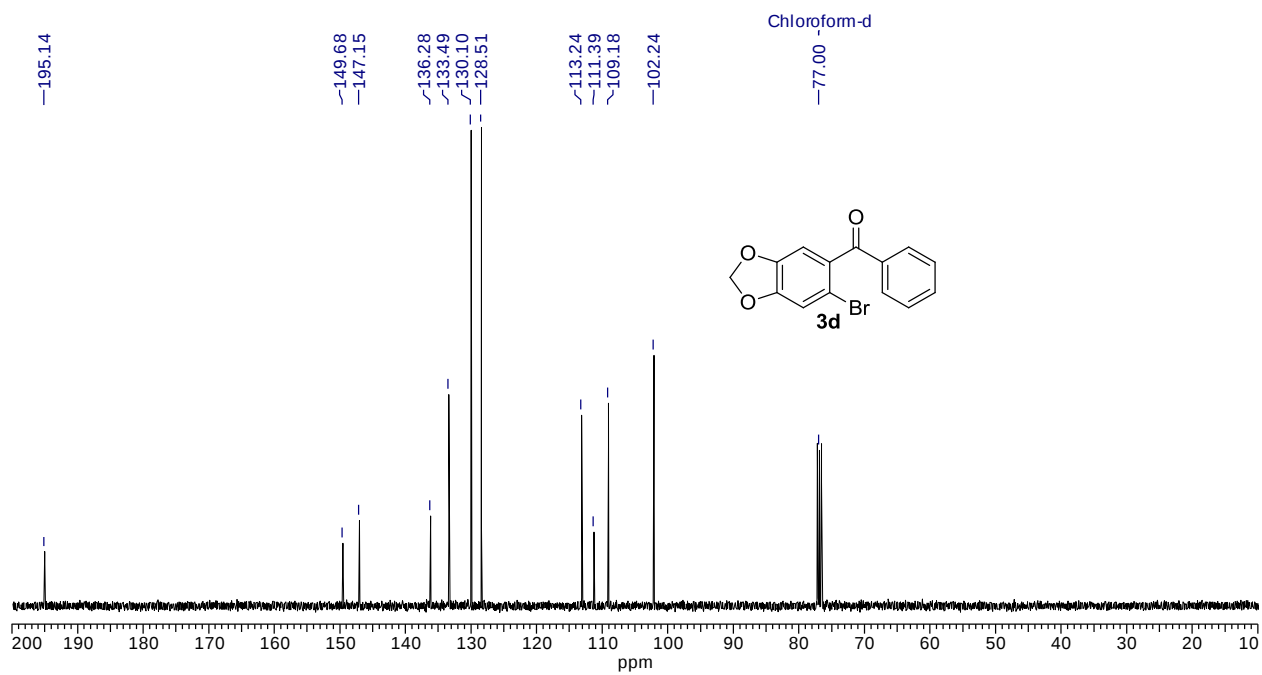
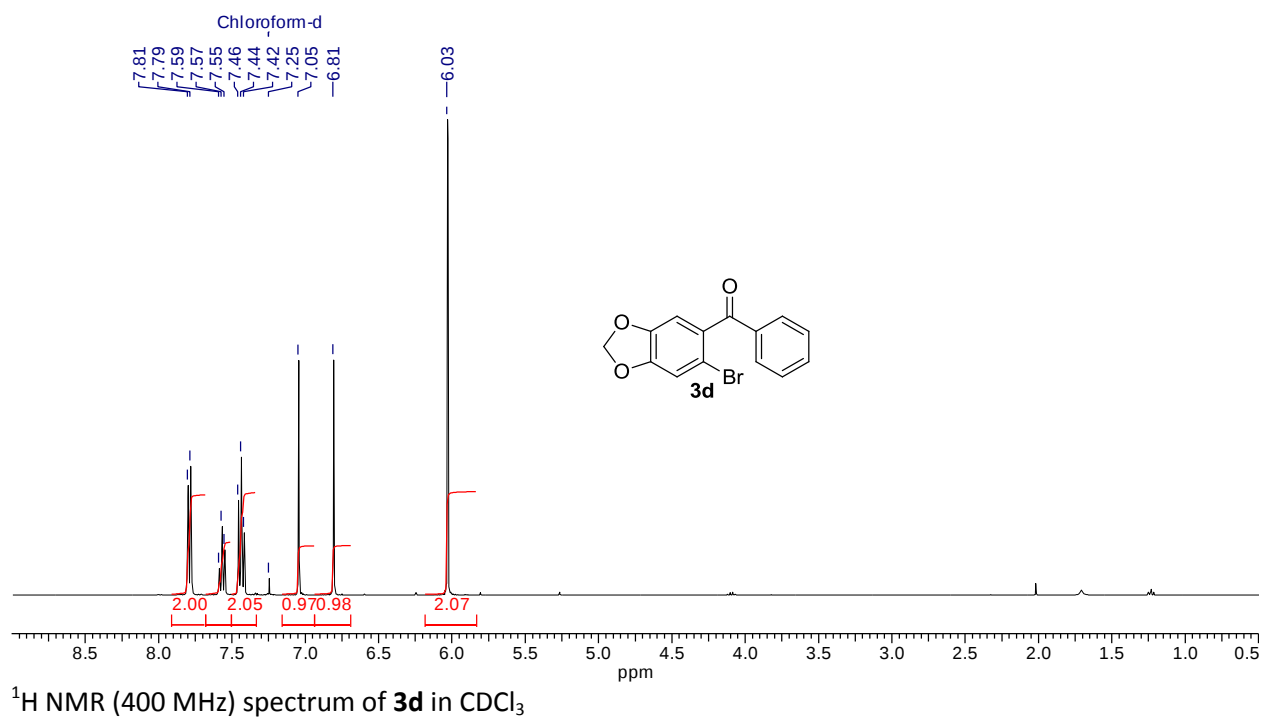
^1H NMR (400 MHz) spectrum of **3a** in CDCl_3

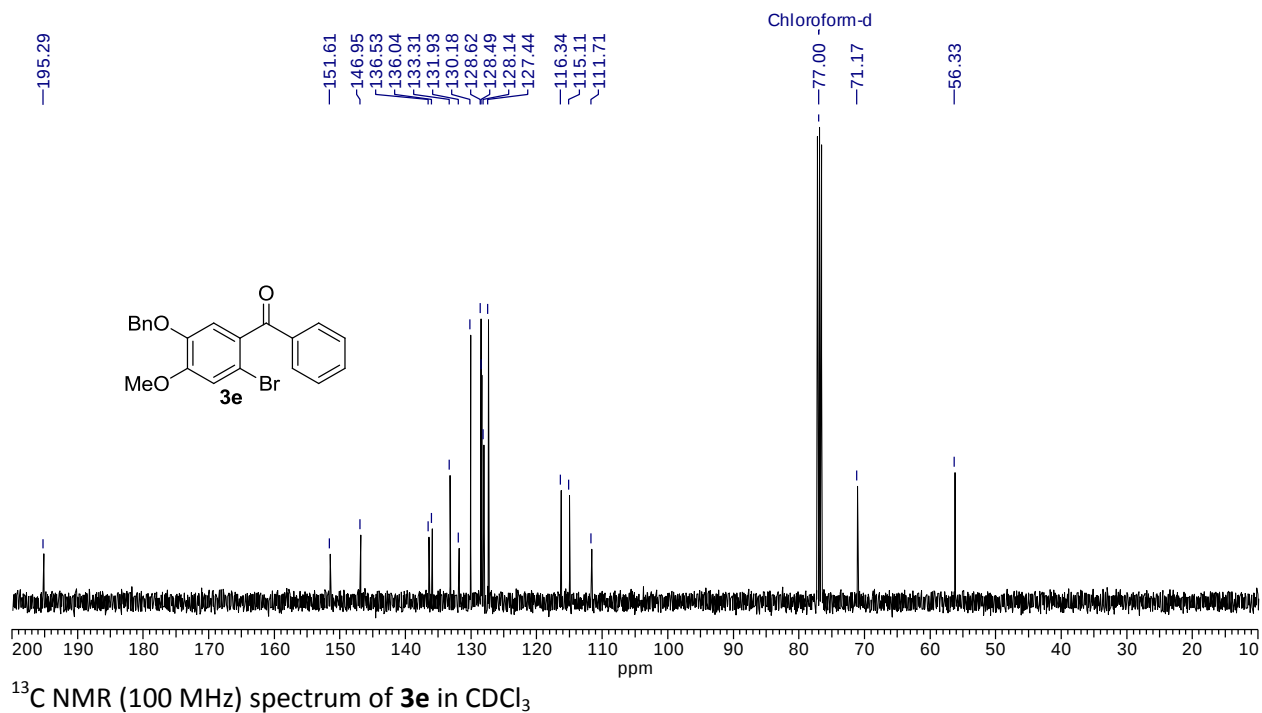
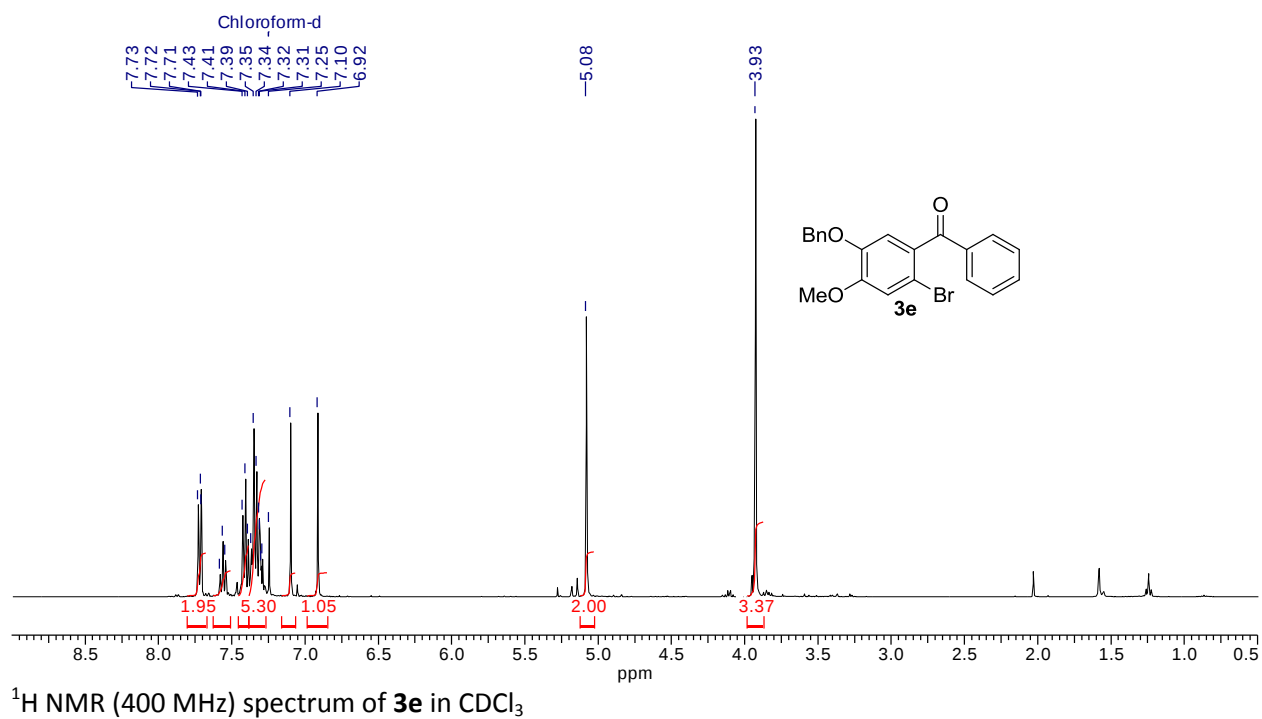


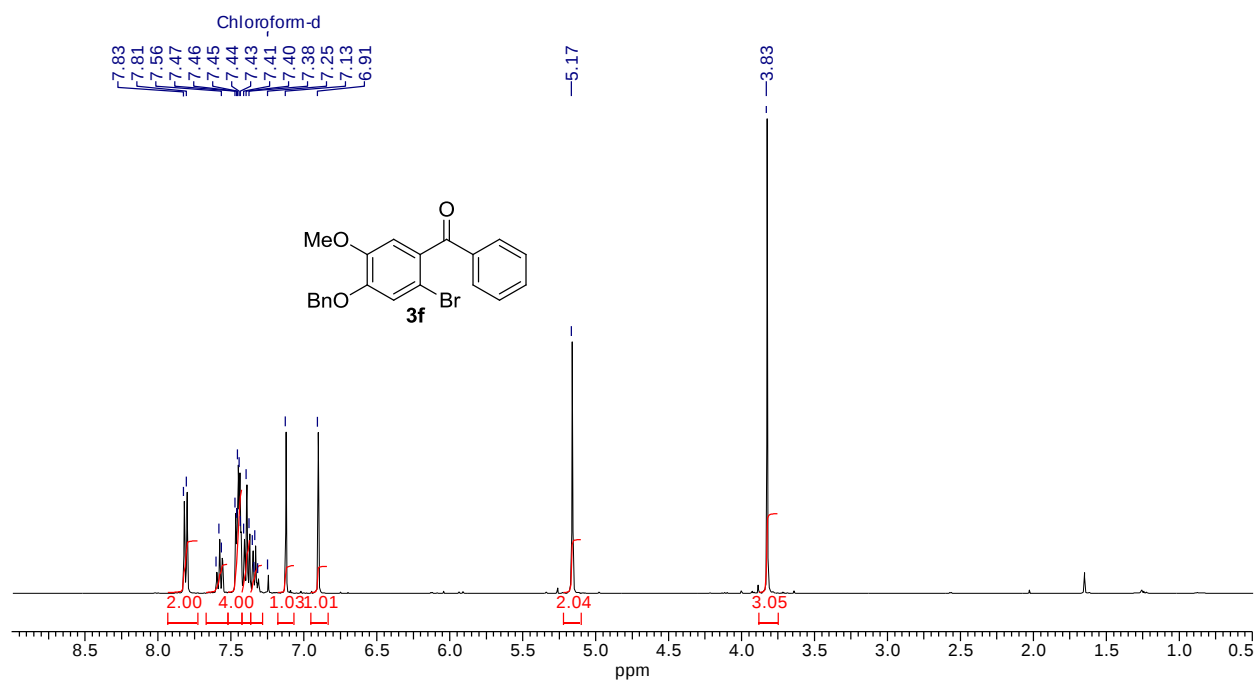
^{13}C NMR (100 MHz) spectrum of **3a** in CDCl_3



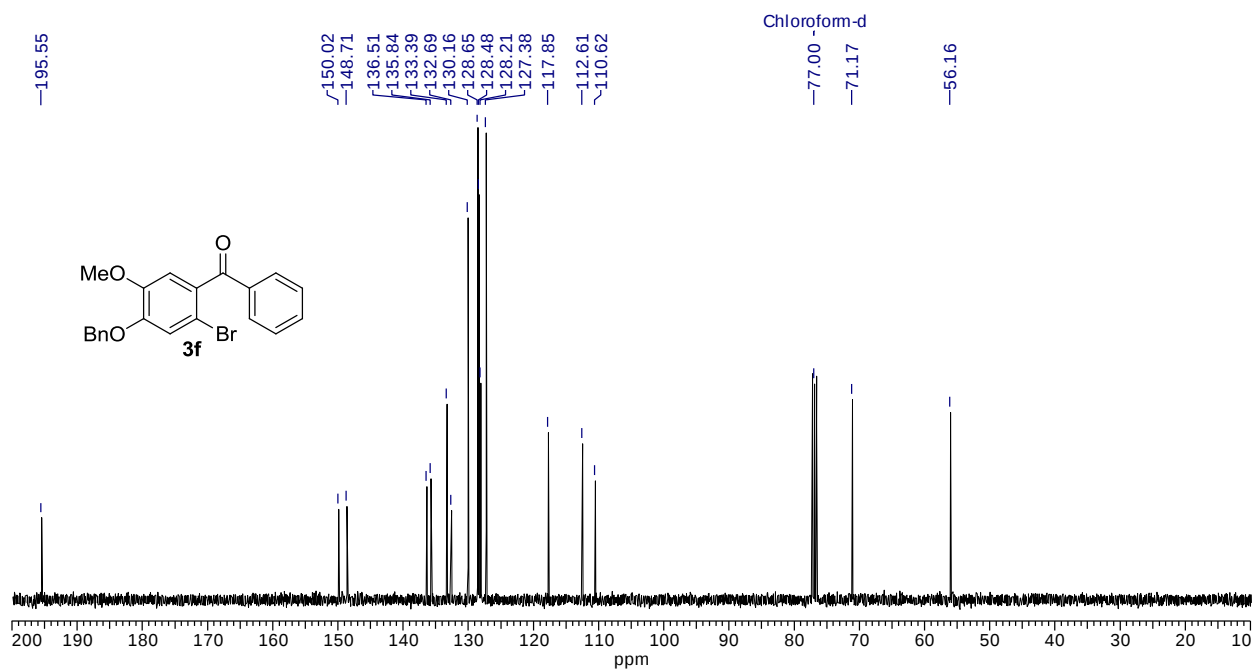




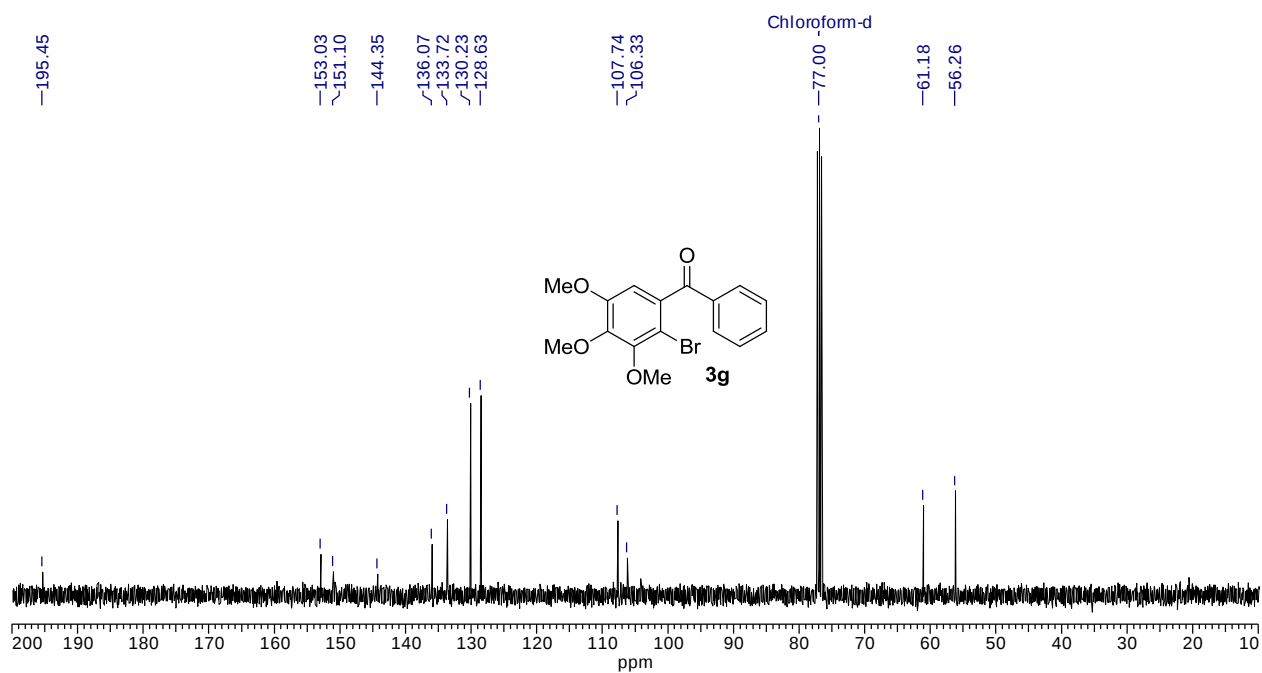
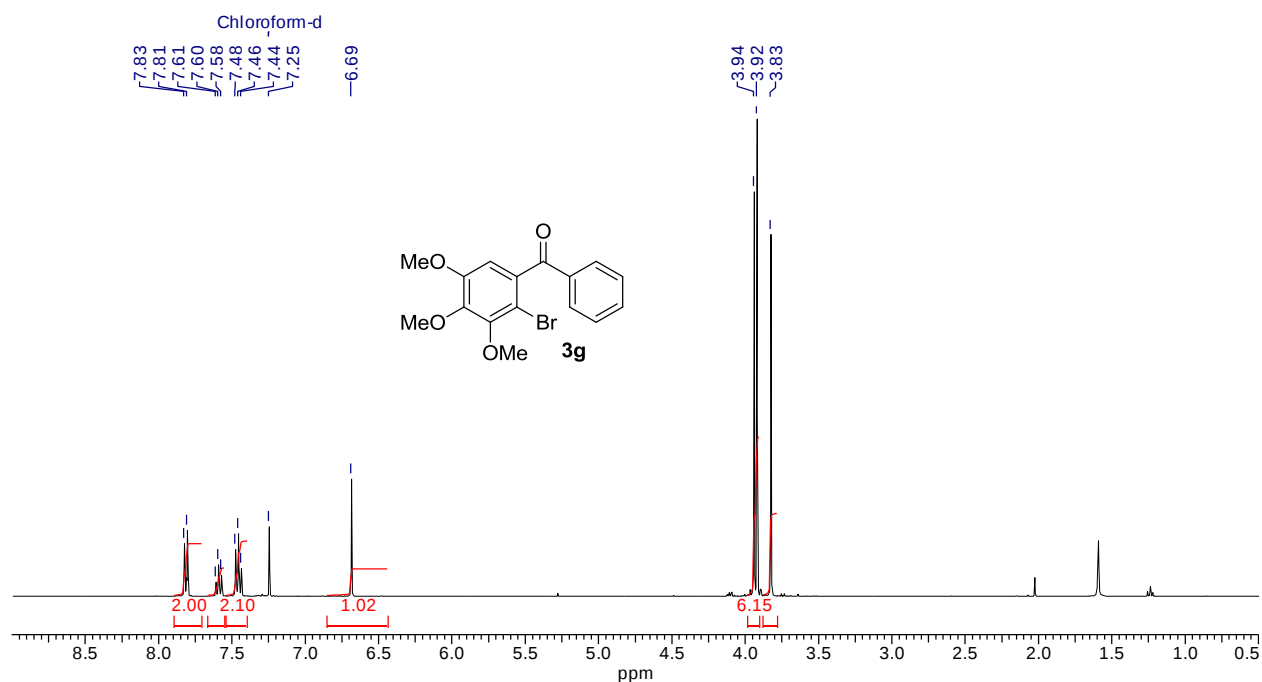


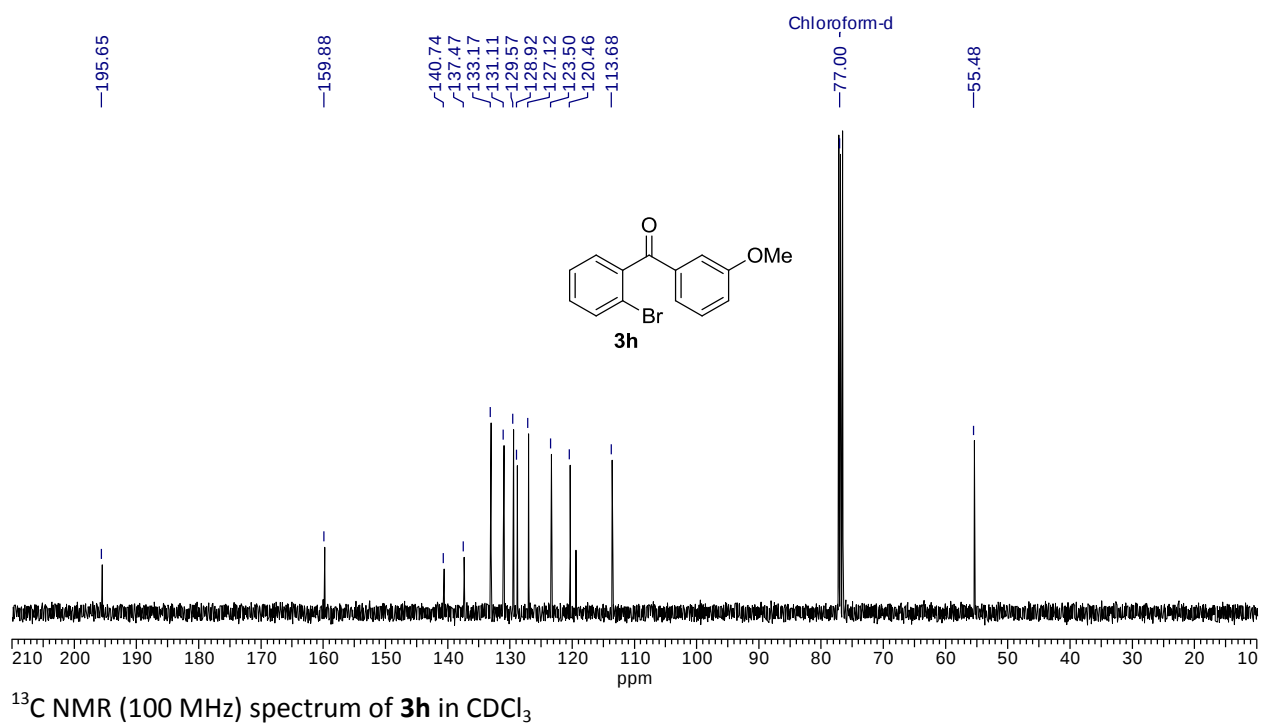
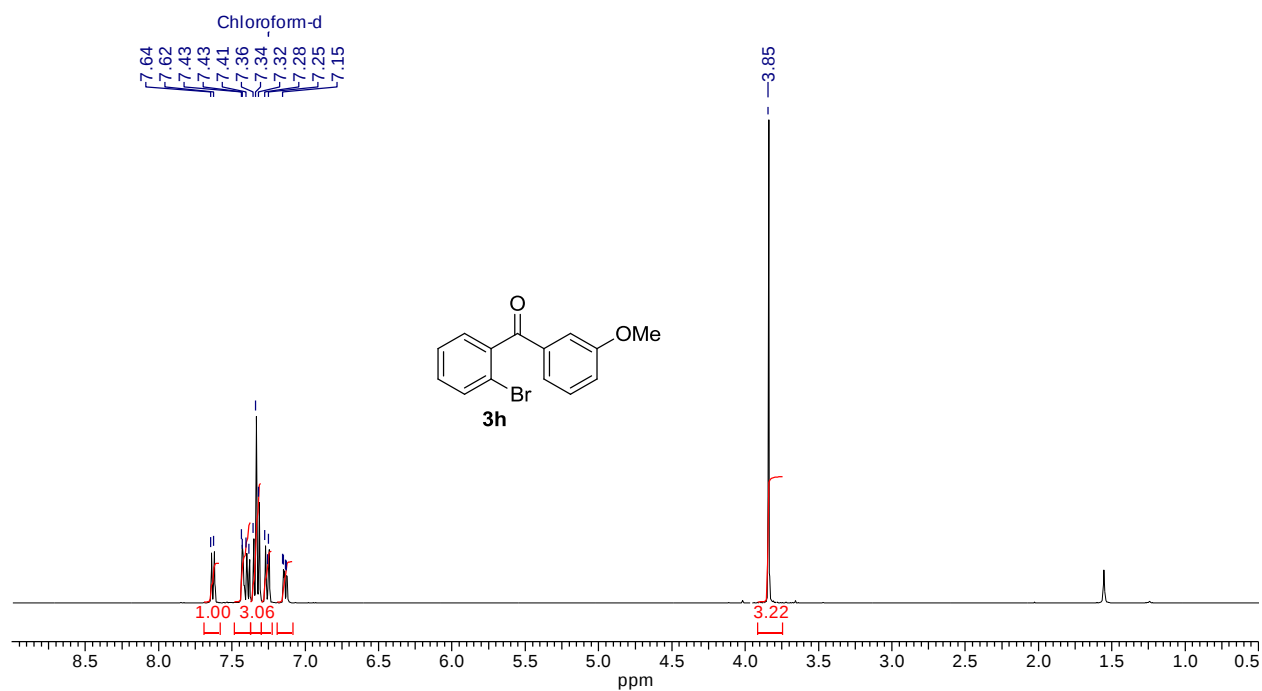


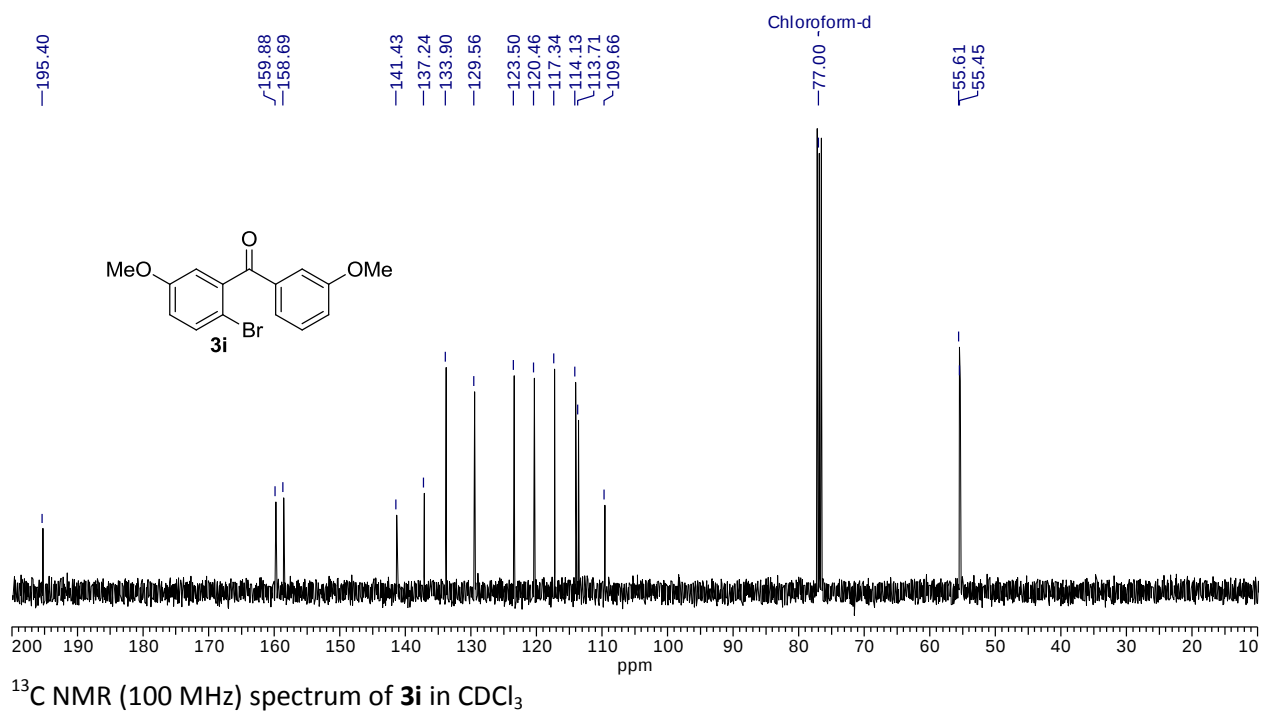
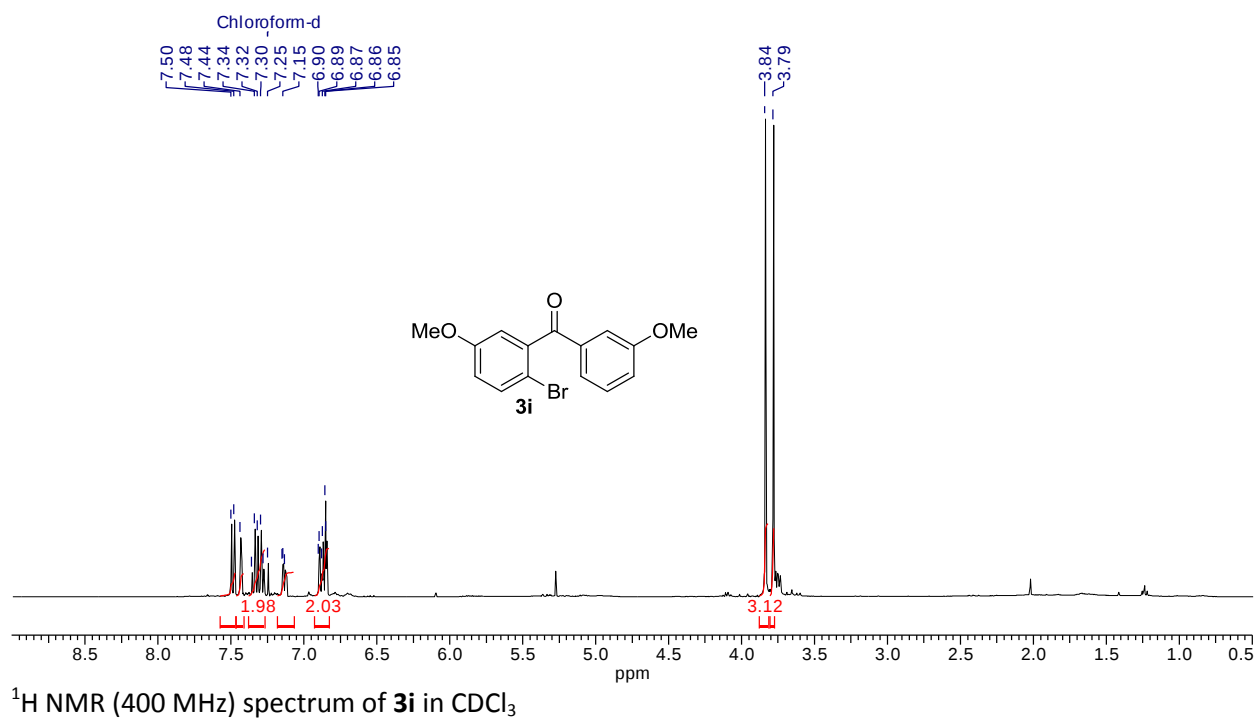
¹H NMR (400 MHz) spectrum of **3f** in CDCl₃

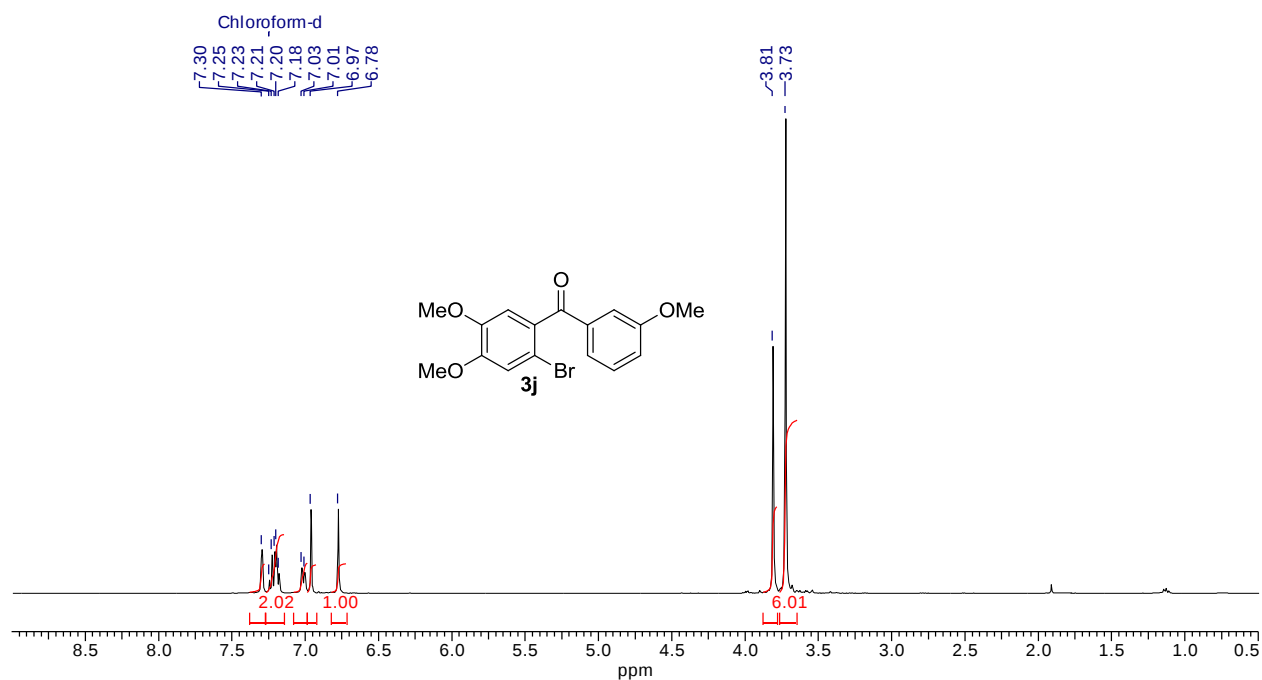


¹³C NMR (100 MHz) spectrum of **3f** in CDCl₃

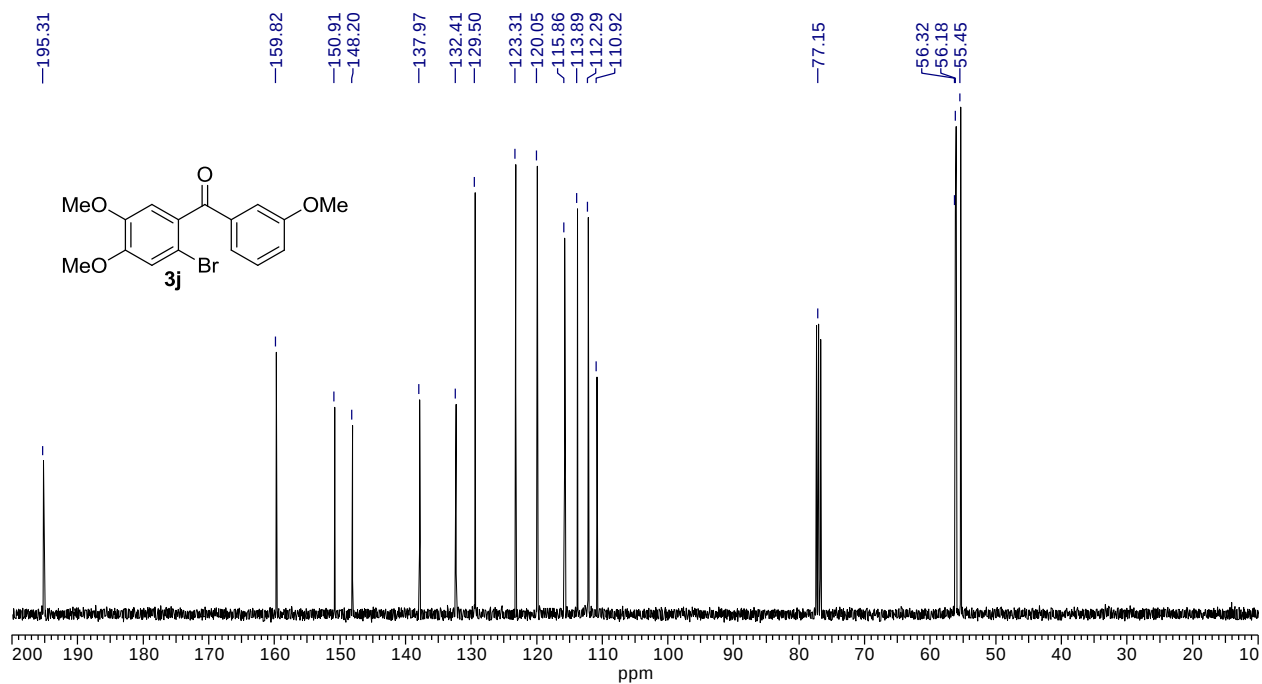




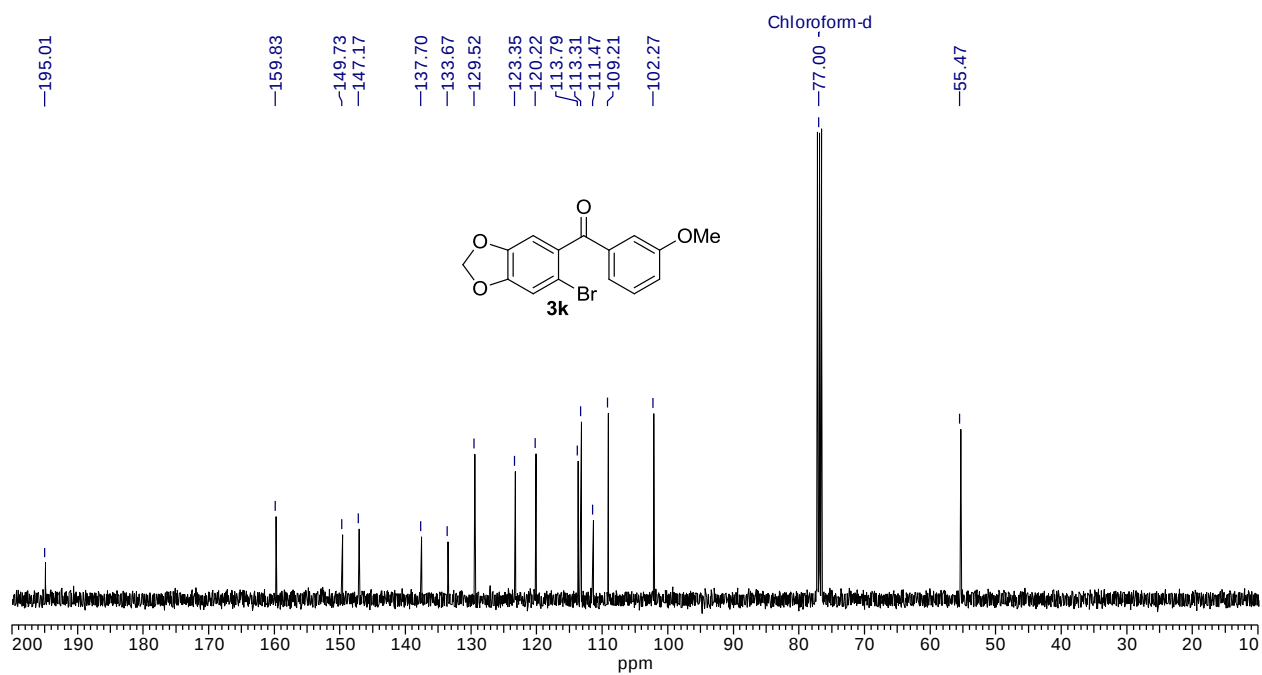
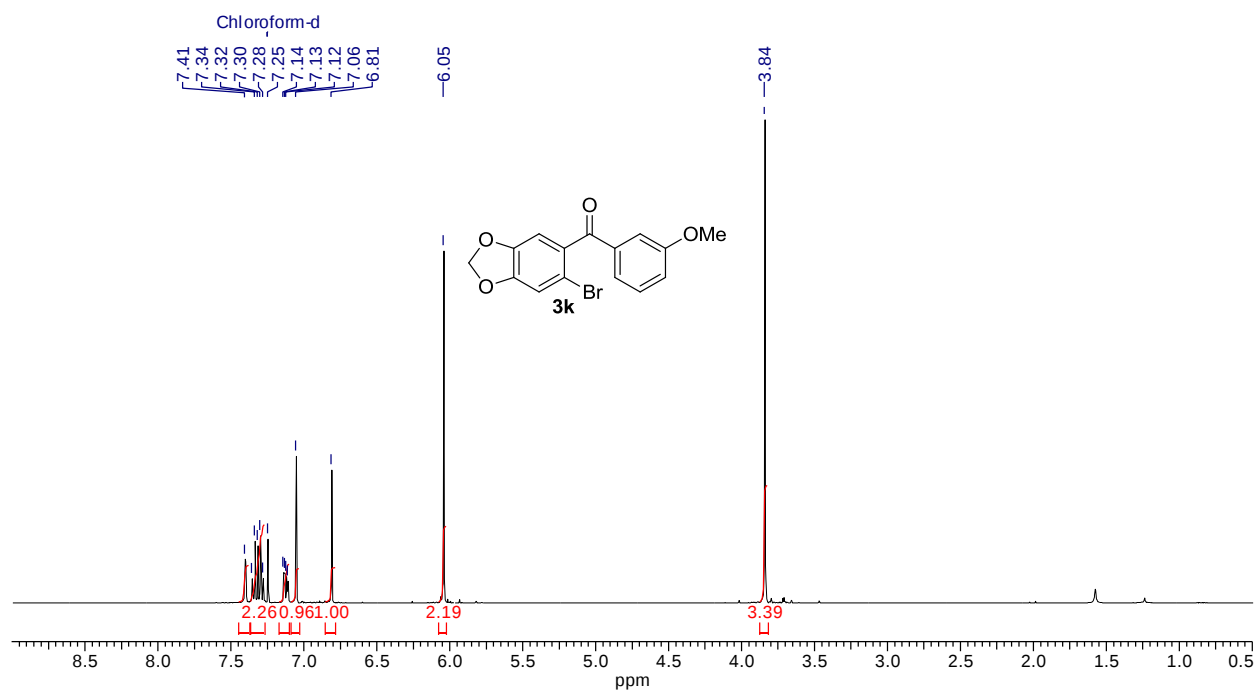


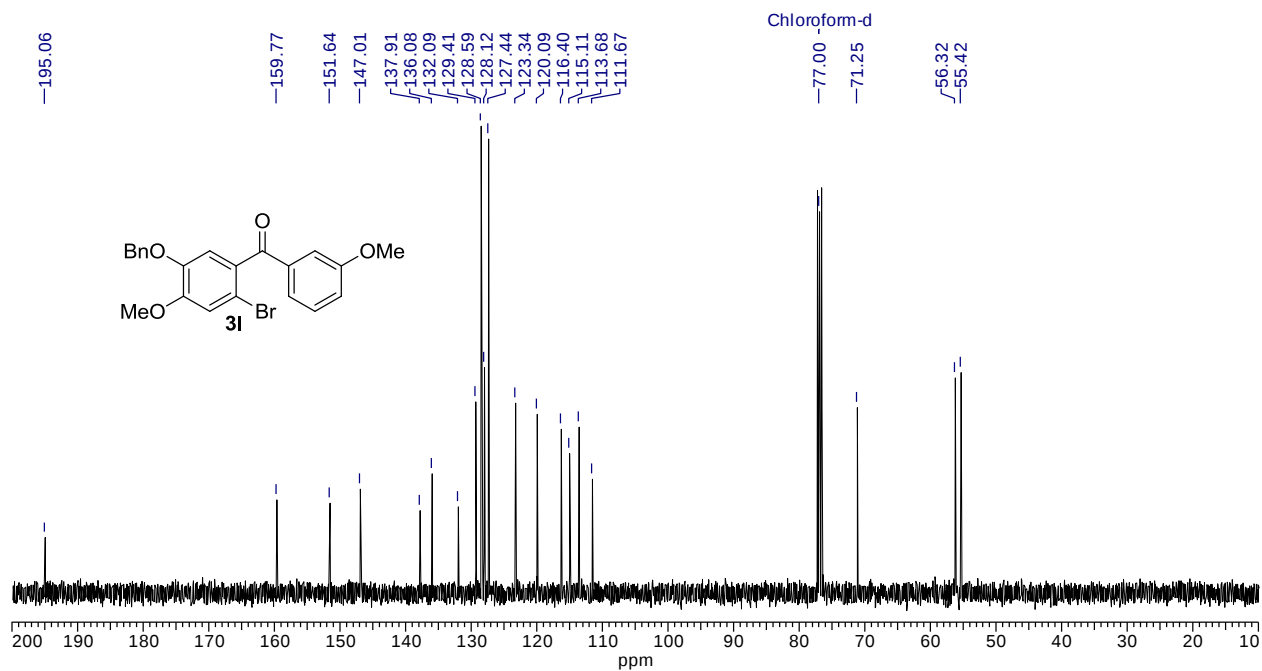
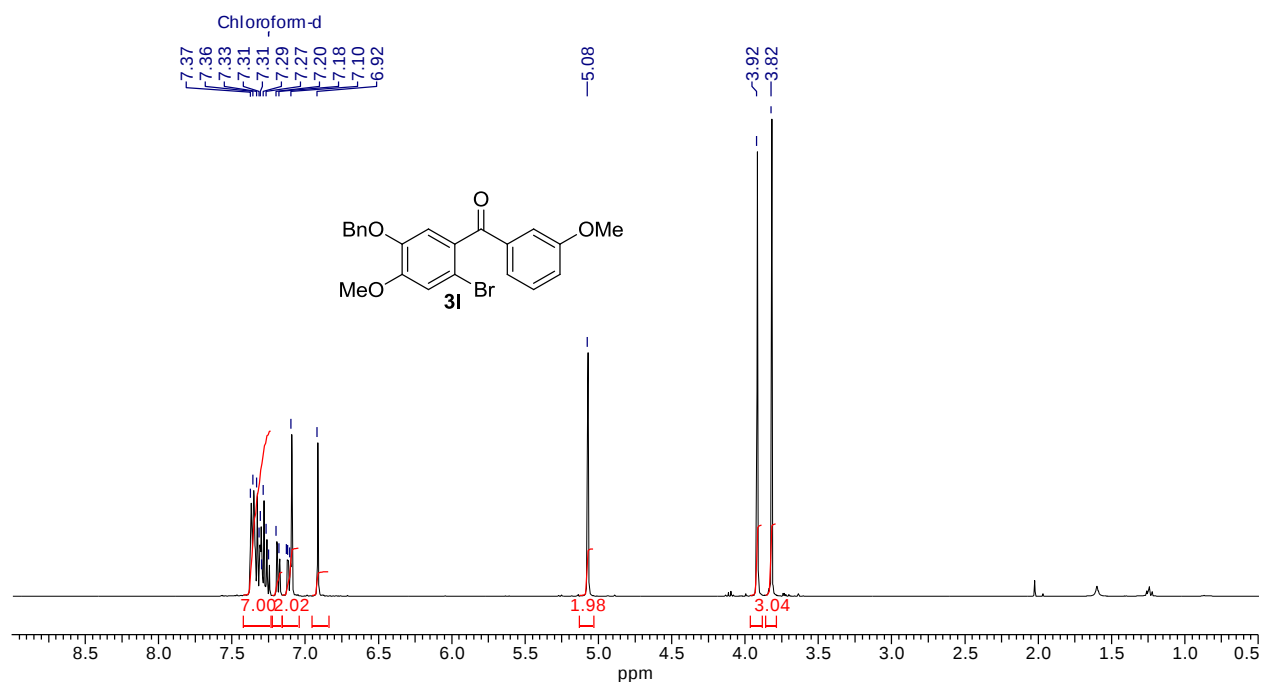


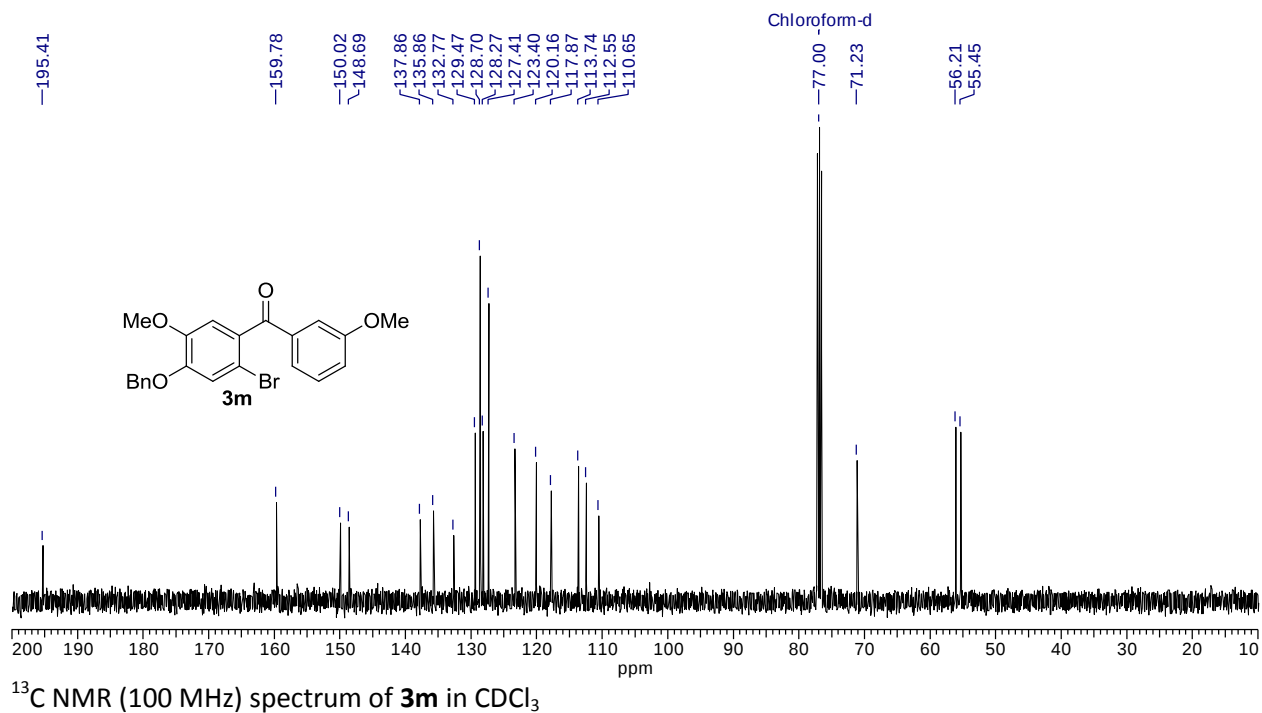
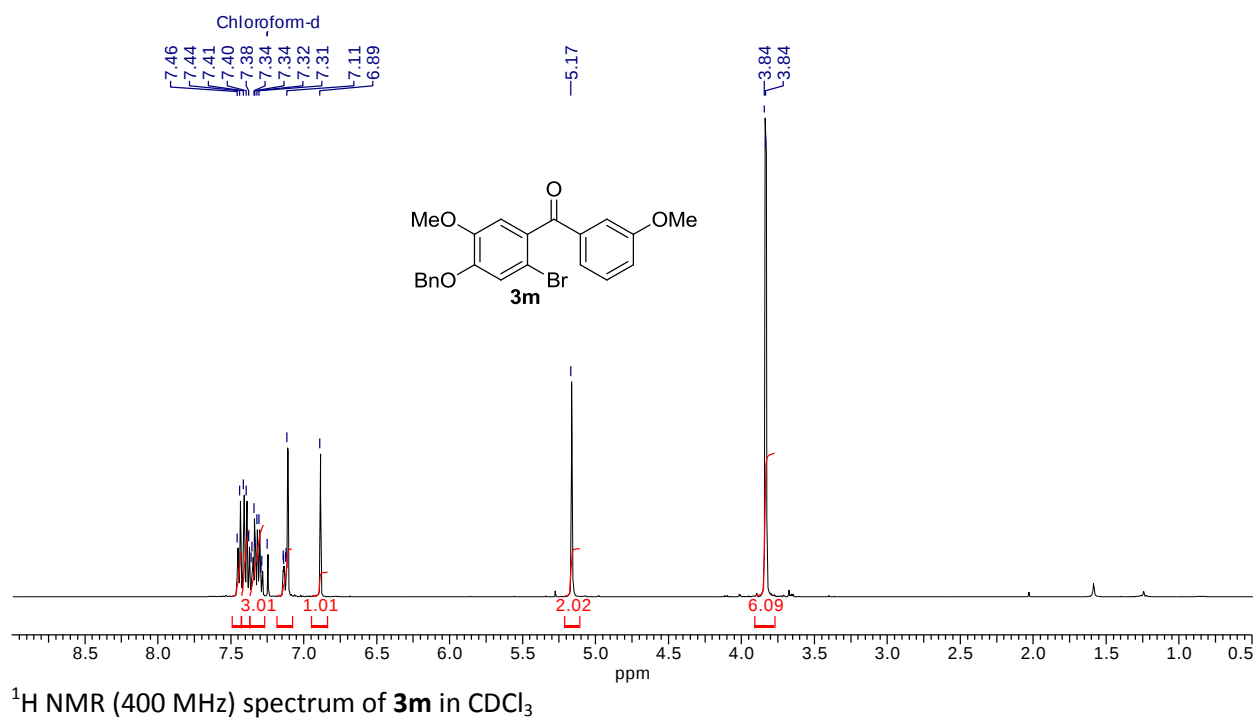
^1H NMR (400 MHz) spectrum of **3j** in CDCl_3

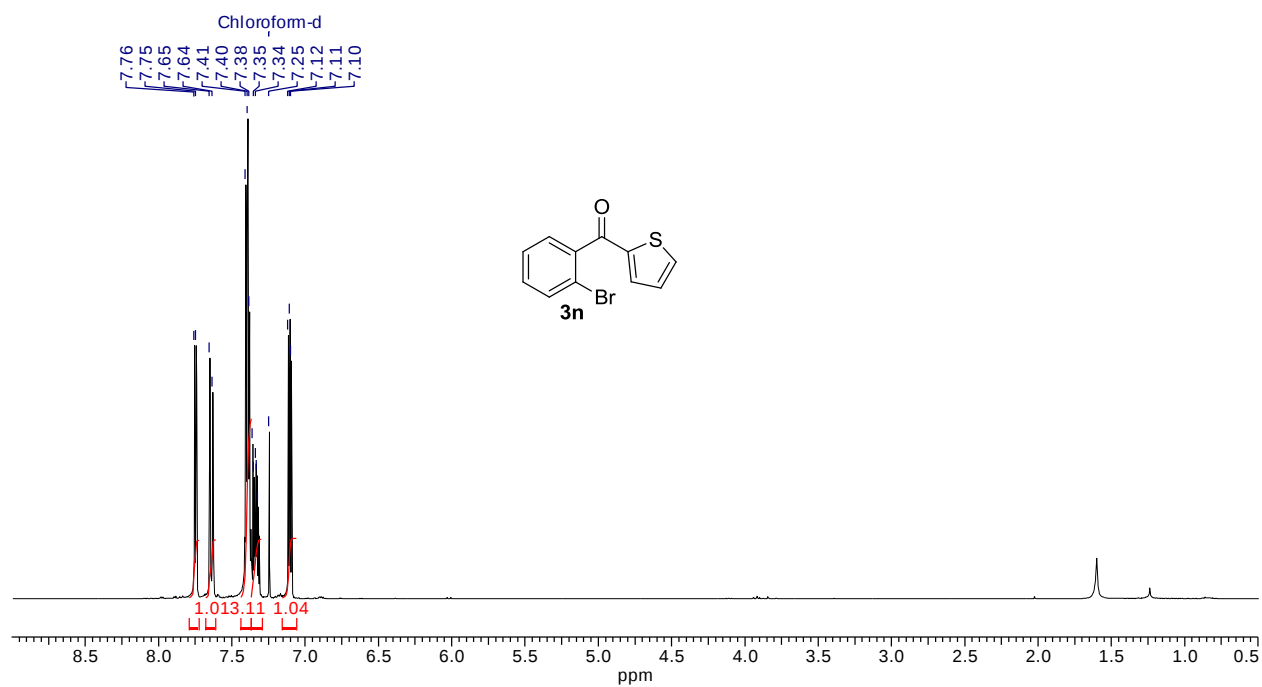


^{13}C NMR (100 MHz) spectrum of **3j** in CDCl_3

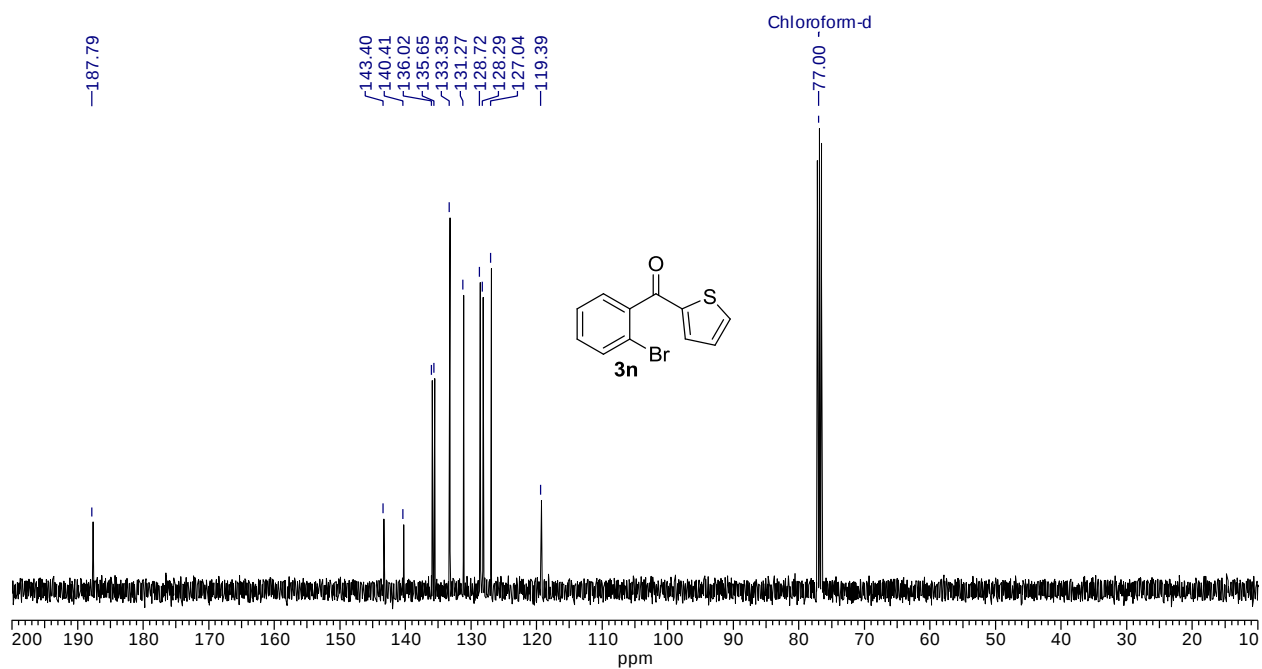




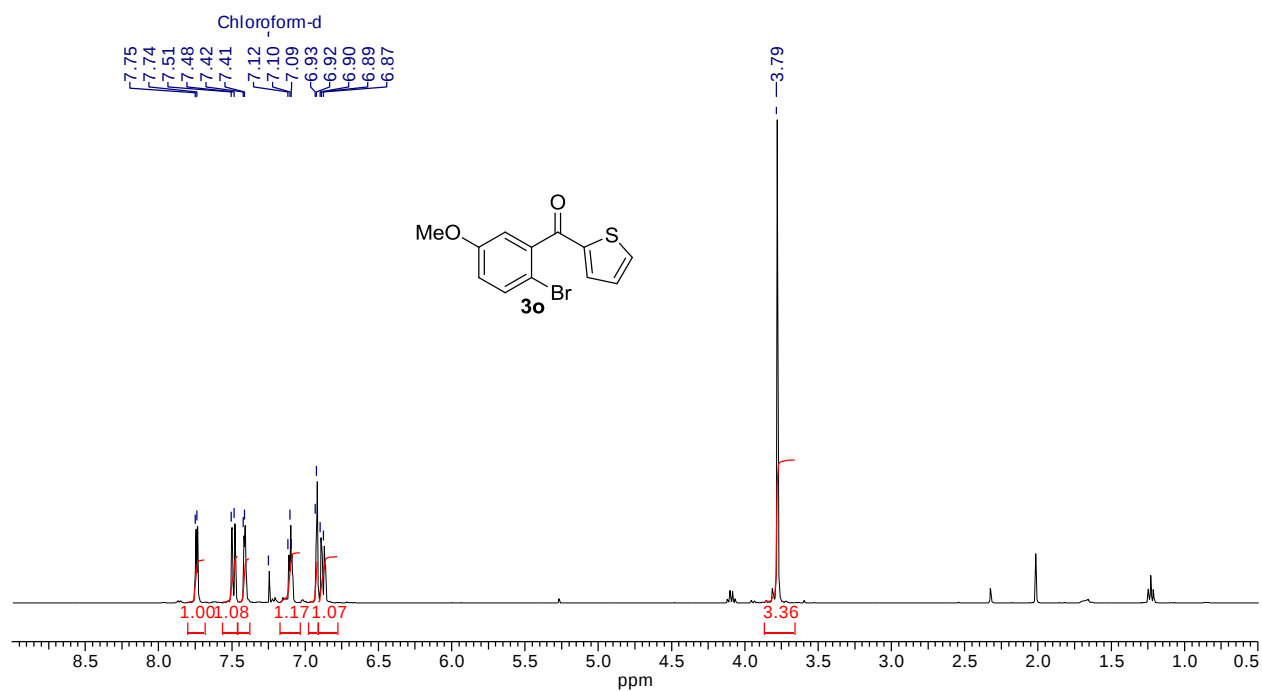




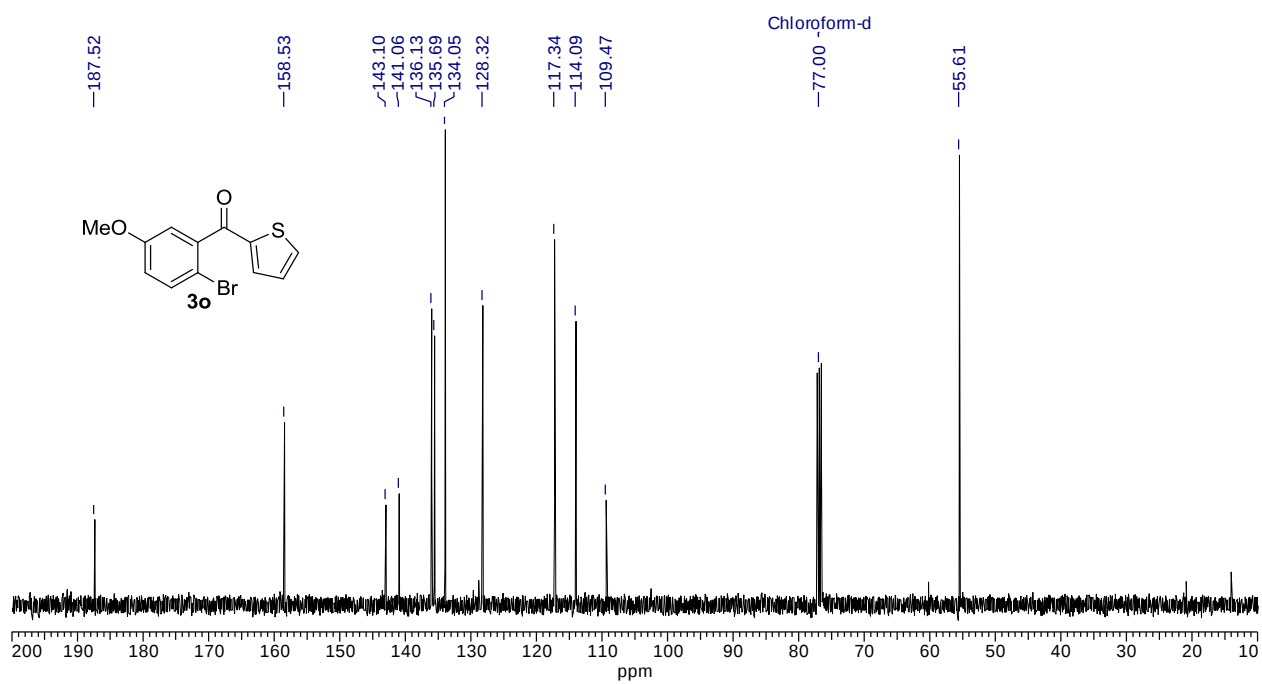
^1H NMR (400 MHz) spectrum of **3n** in CDCl_3



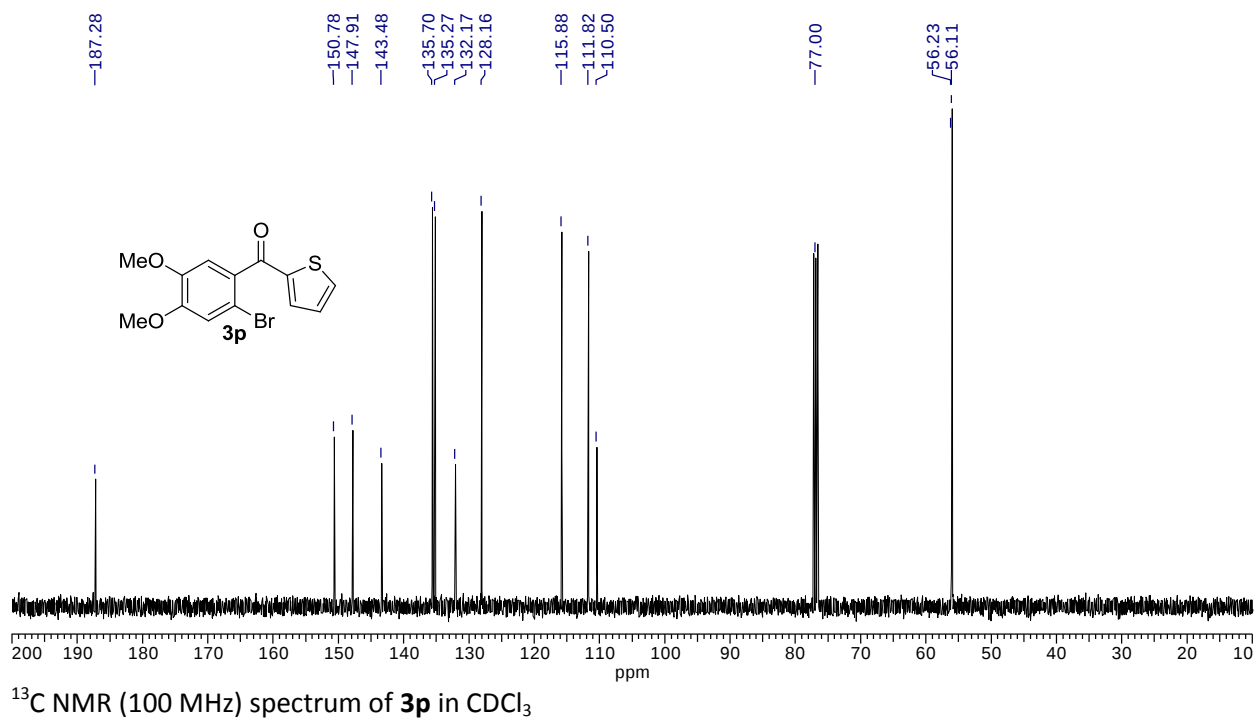
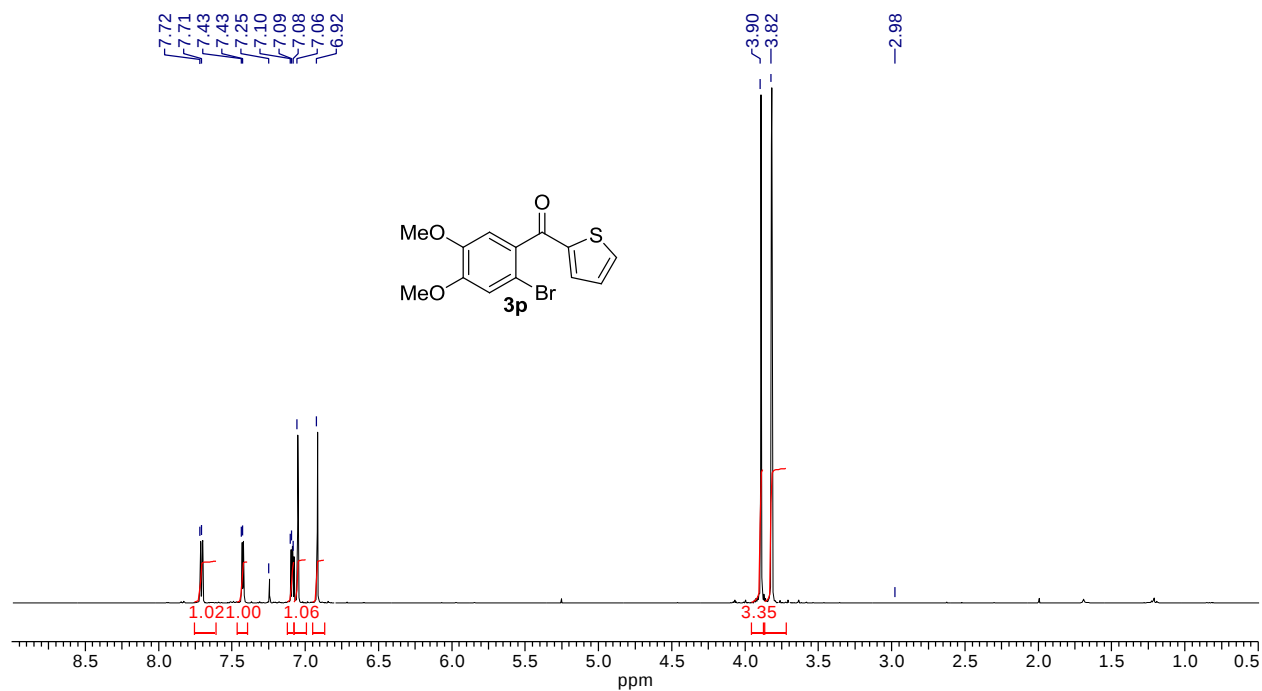
^{13}C NMR (100 MHz) spectrum of **3n** in CDCl_3

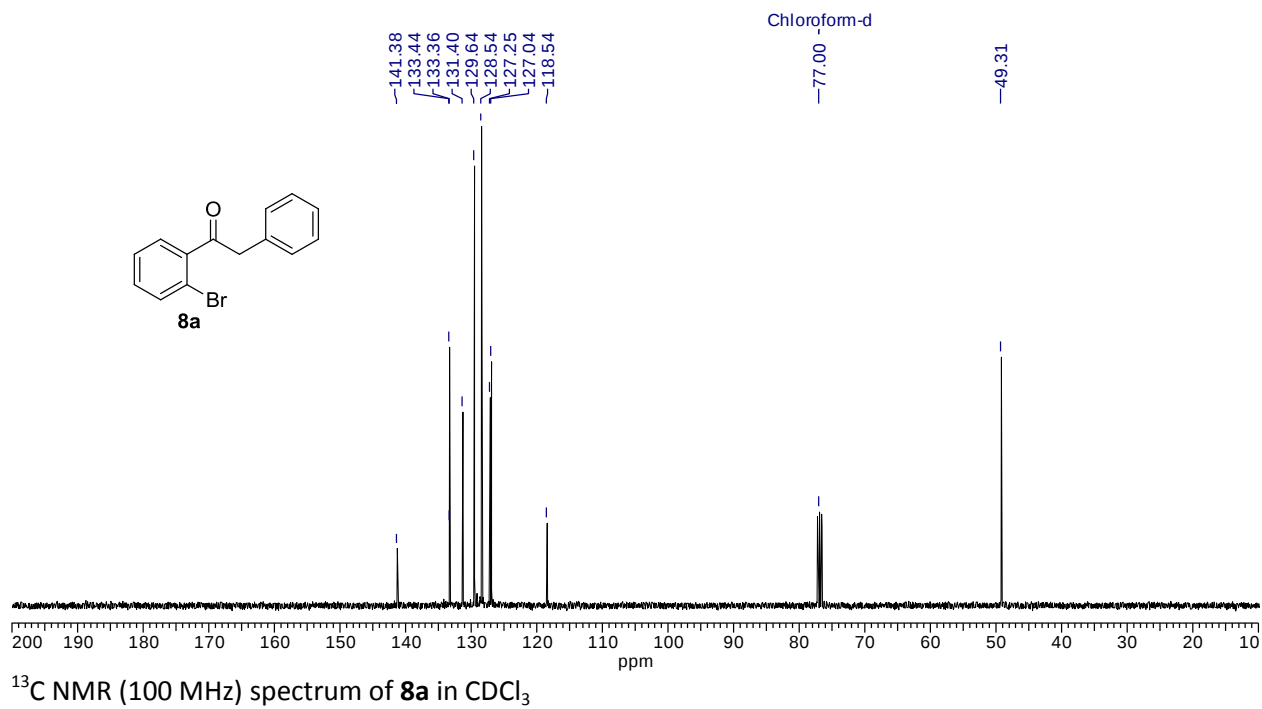
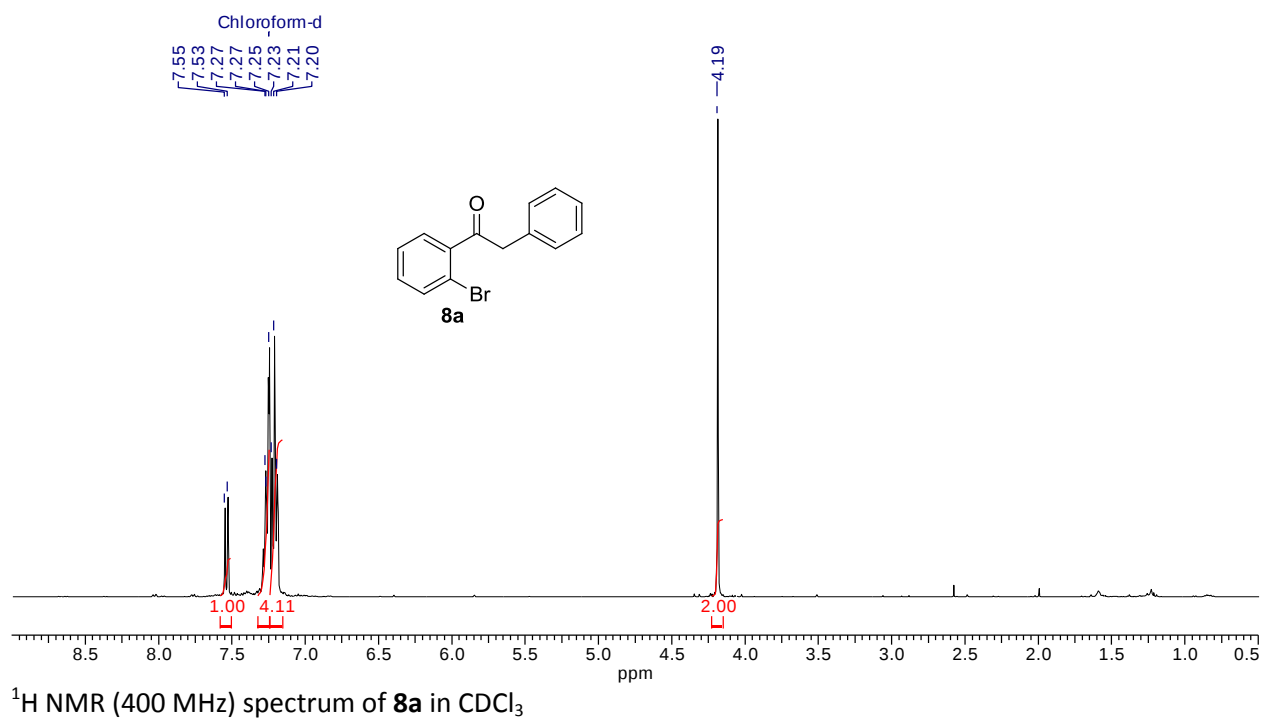


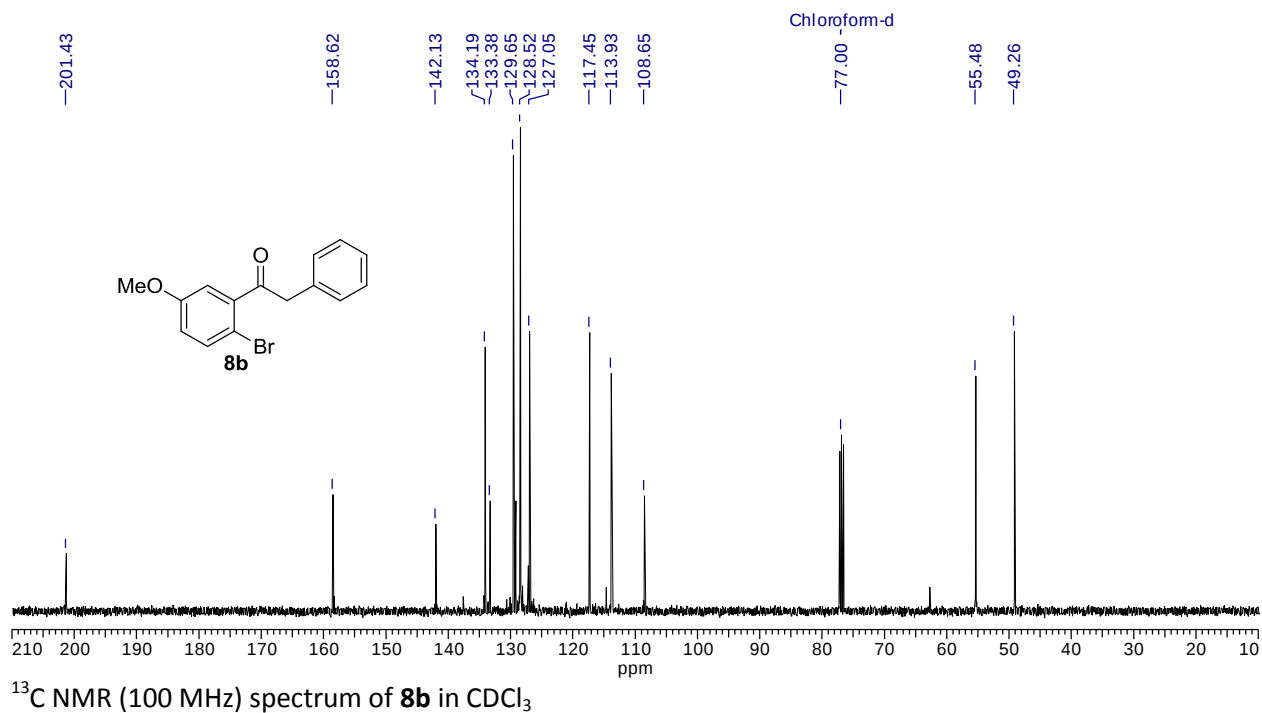
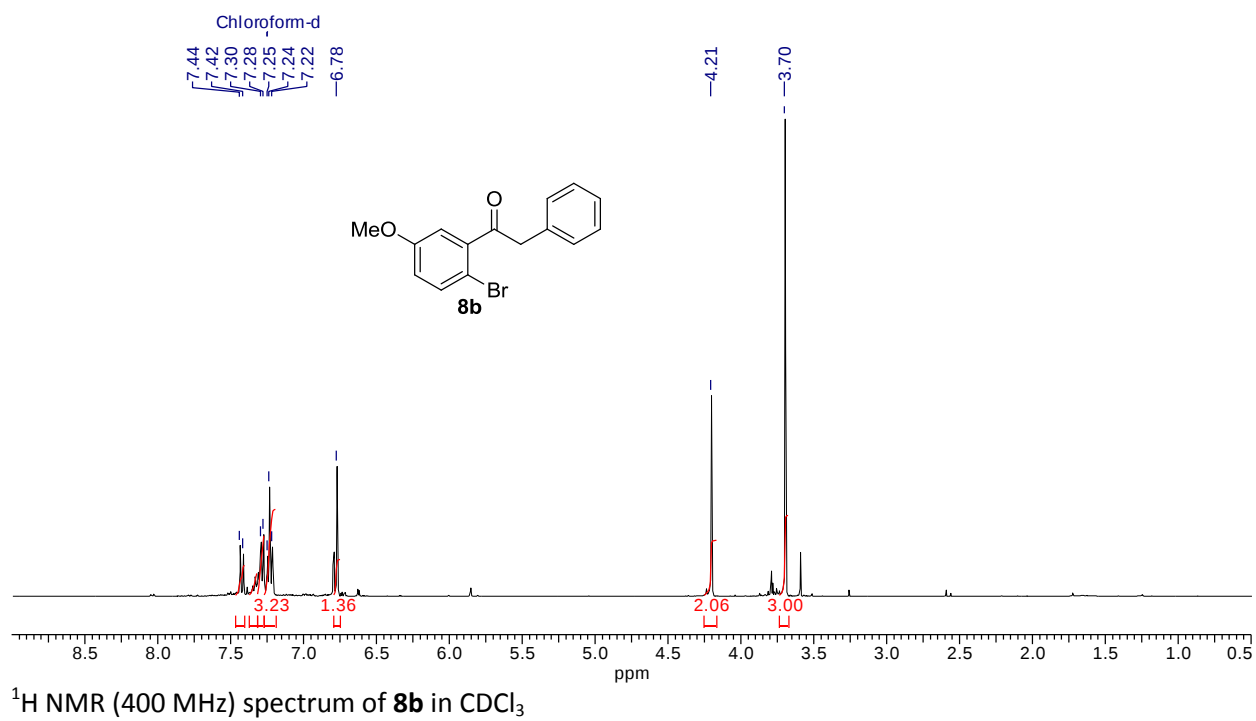
^1H NMR (400 MHz) spectrum of **3o** in CDCl_3

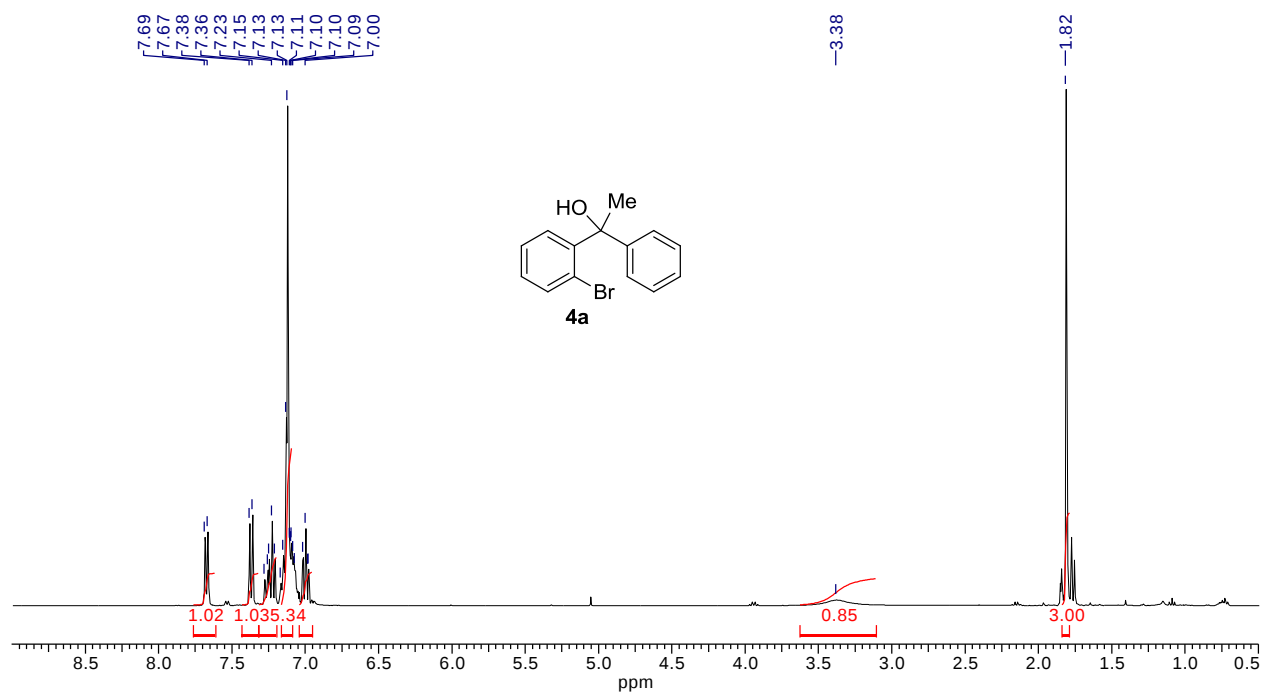


^{13}C NMR (100 MHz) spectrum of **3o** in CDCl_3

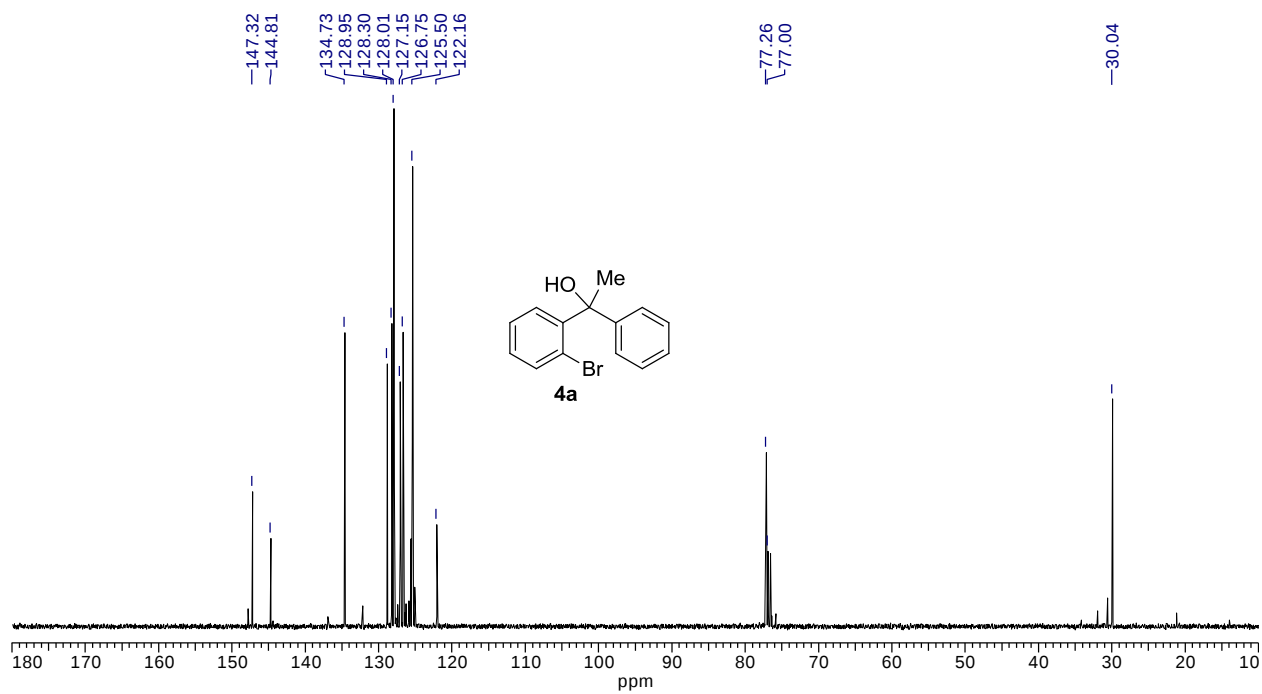




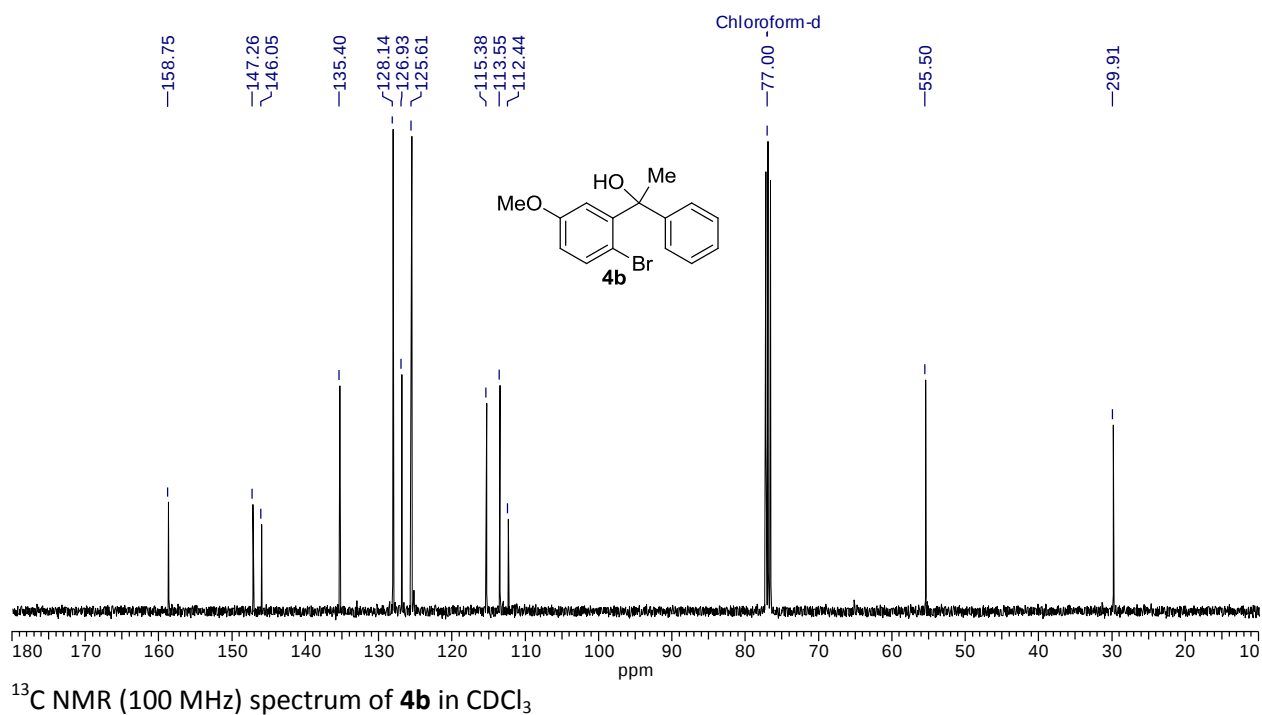
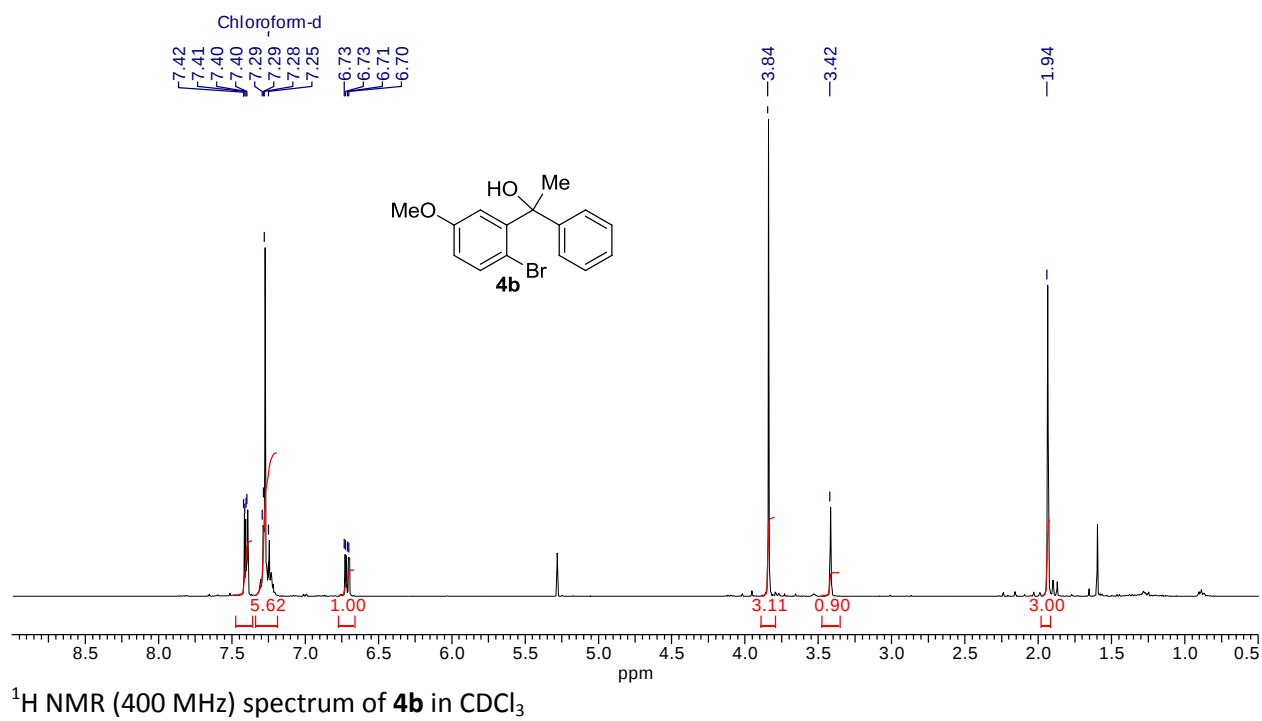


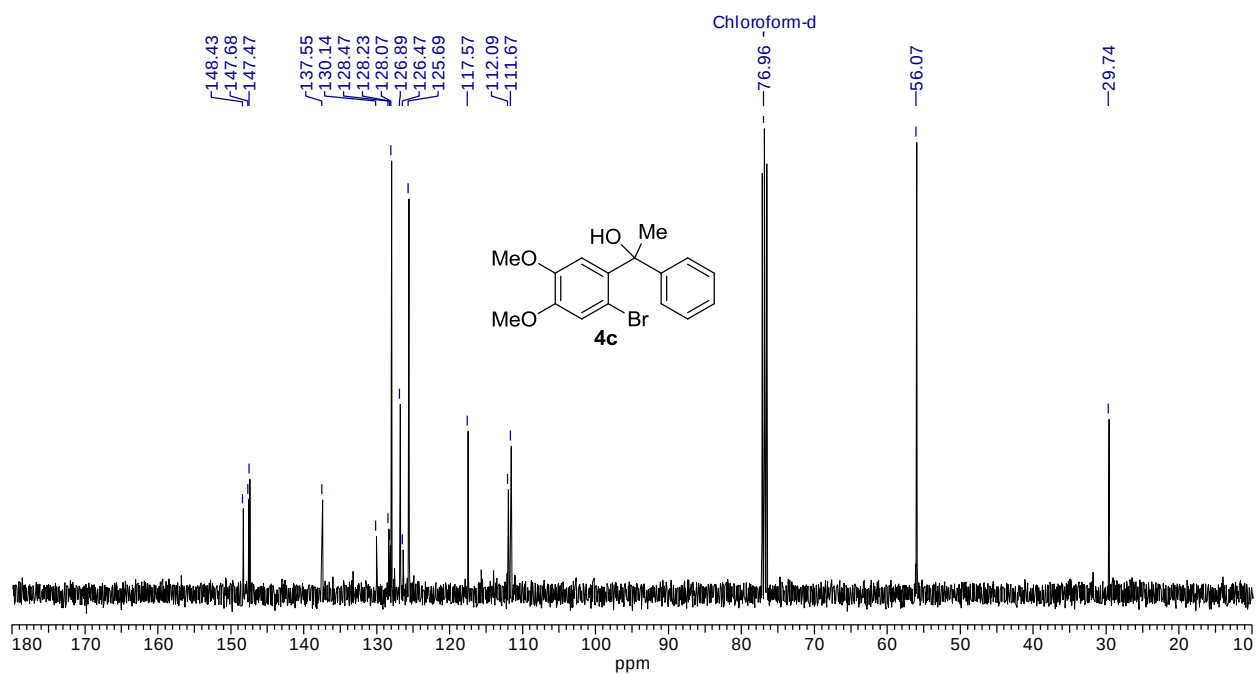
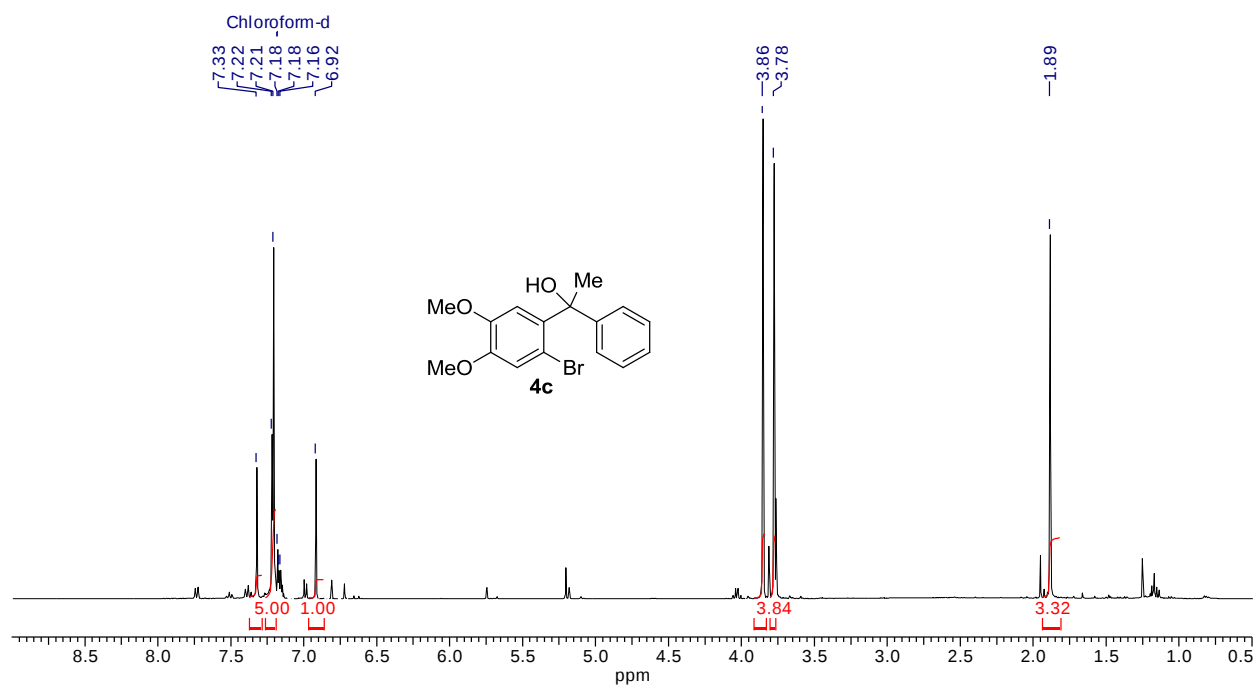


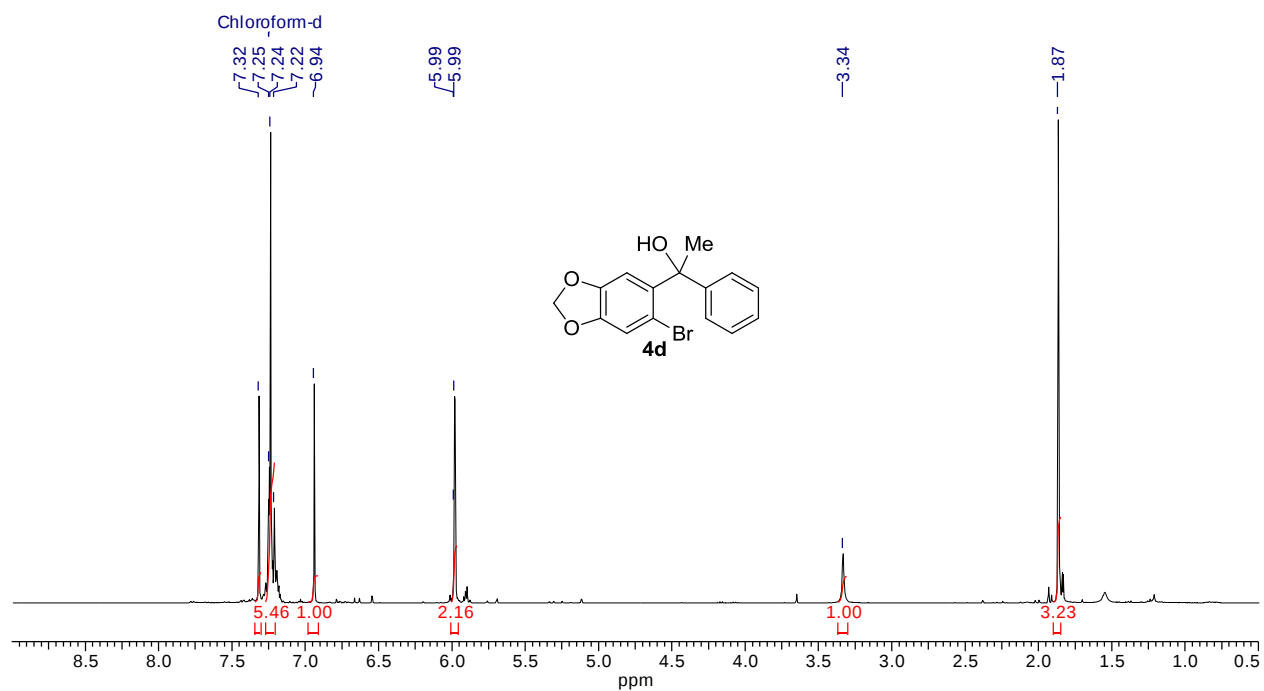
¹H NMR (400 MHz) spectrum of **4a** in CDCl₃



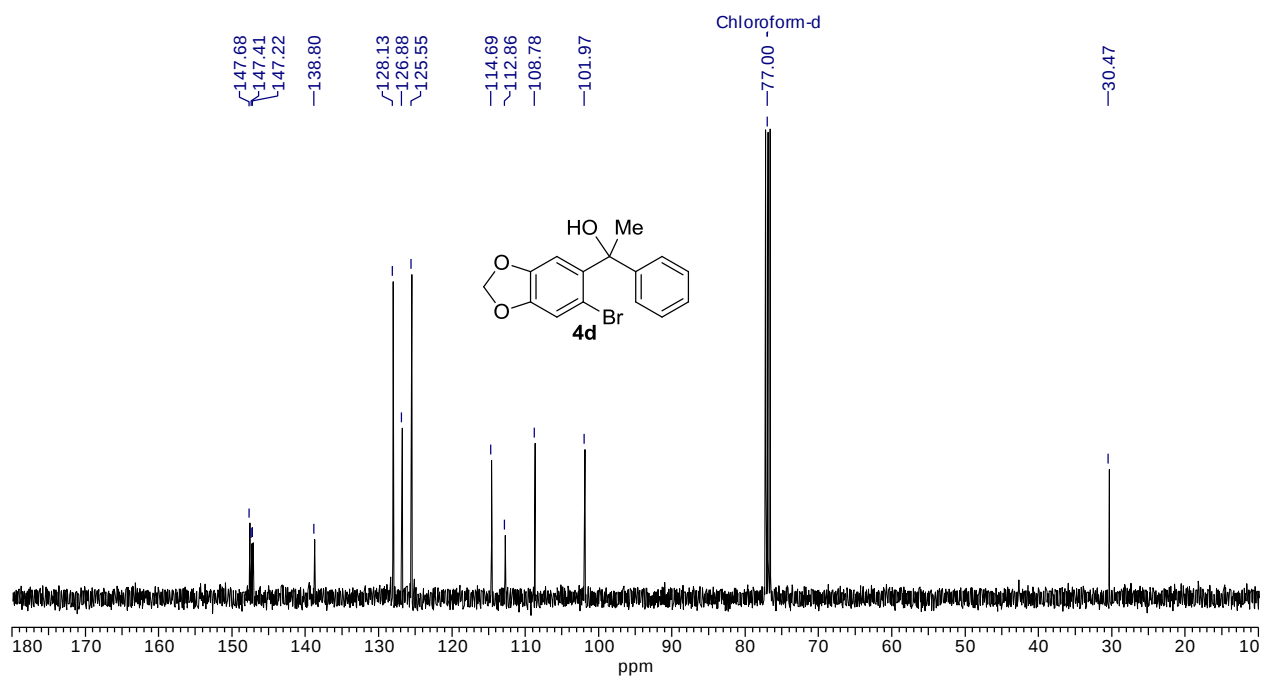
¹³C NMR (100 MHz) spectrum of **4a** in CDCl₃



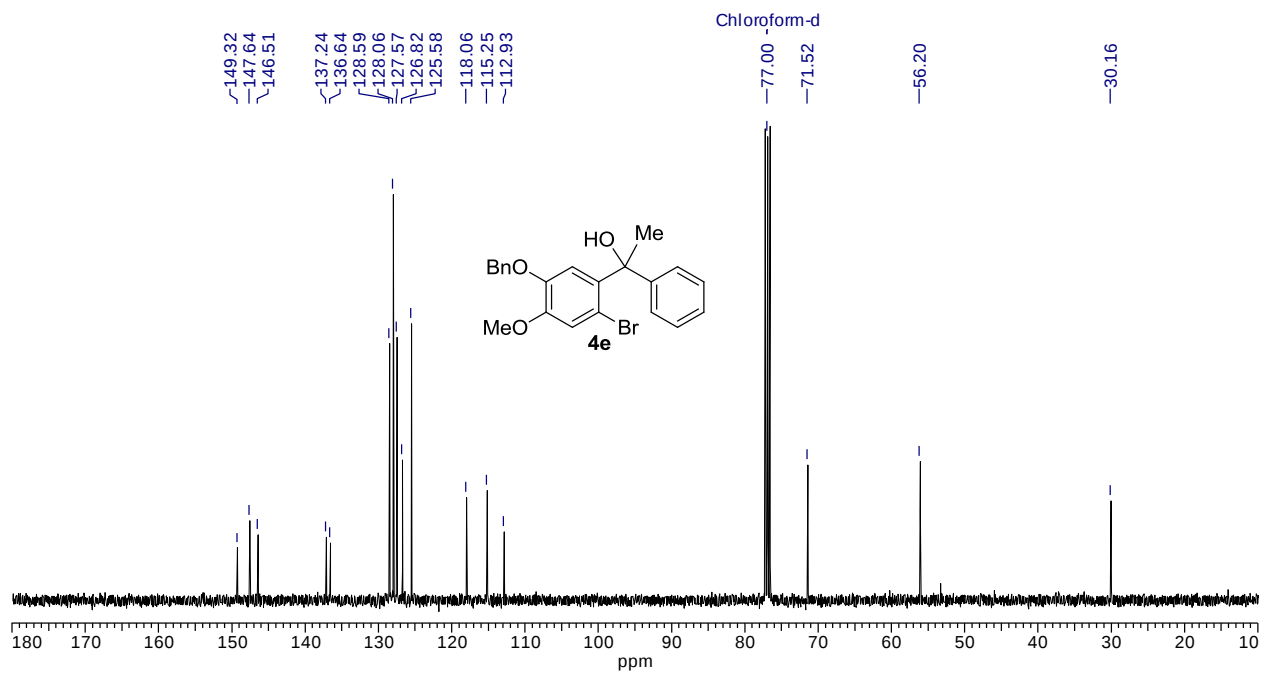
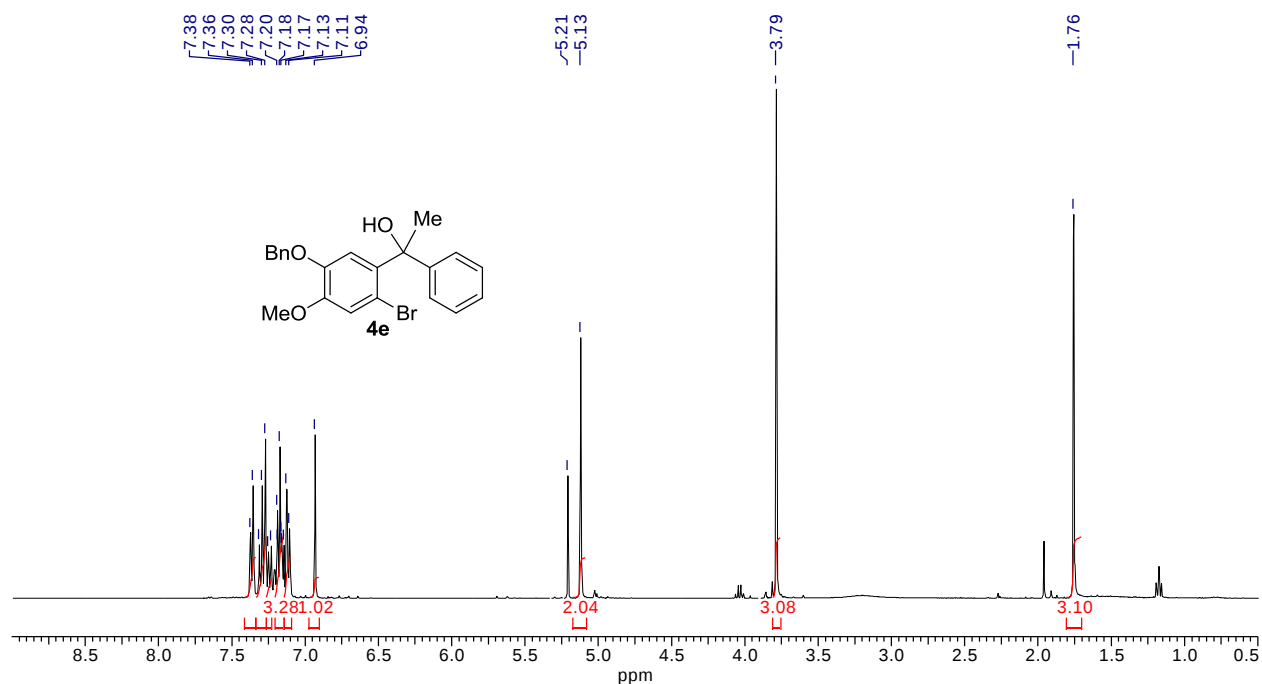


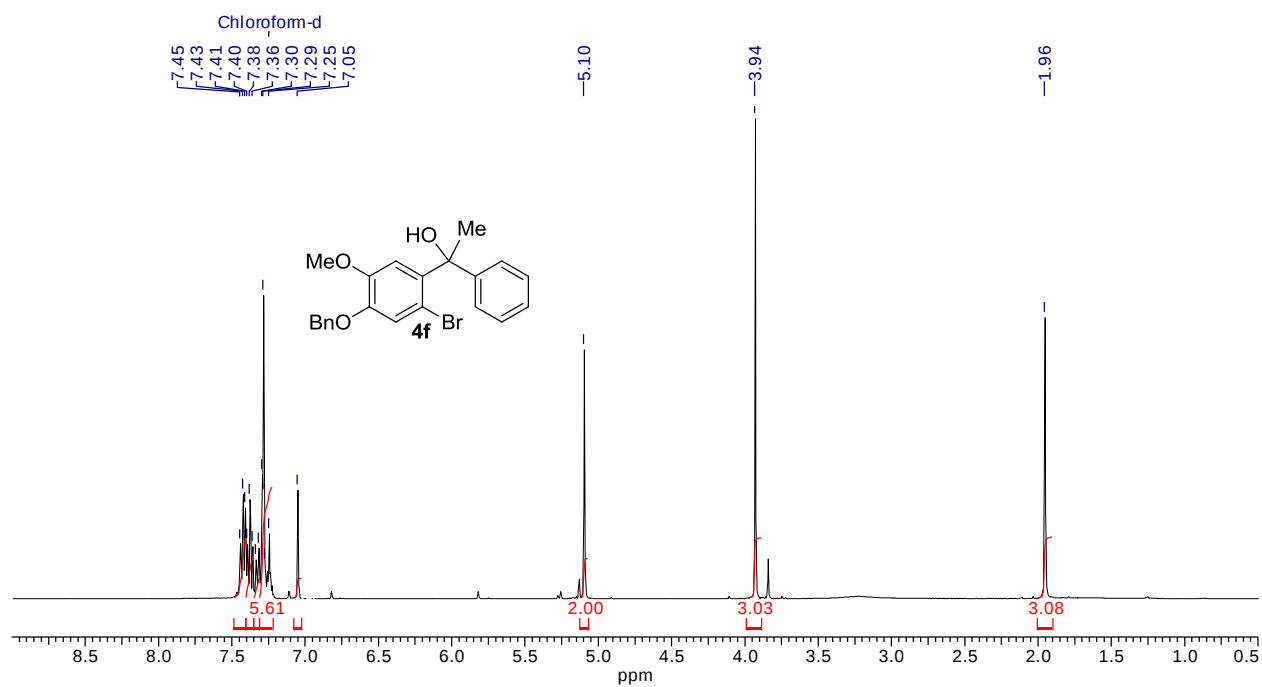


^1H NMR (400 MHz) spectrum of **4d** in CDCl_3

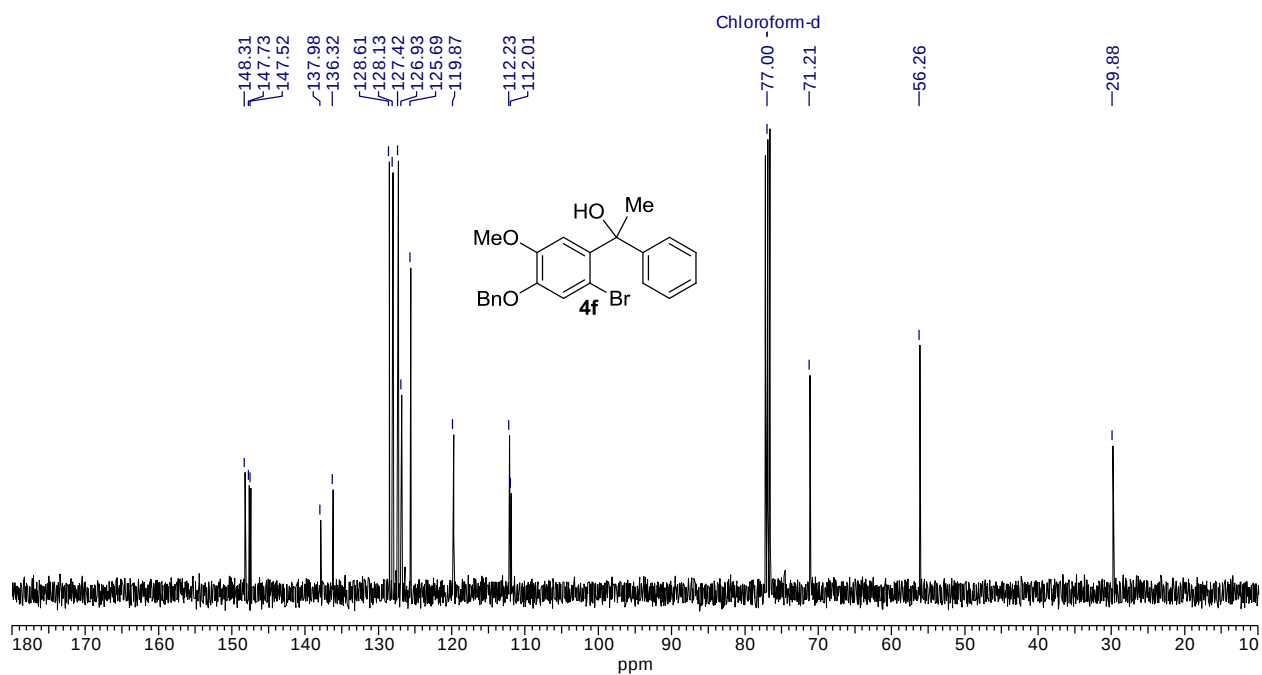


^{13}C NMR (100 MHz) spectrum of **4d** in CDCl_3

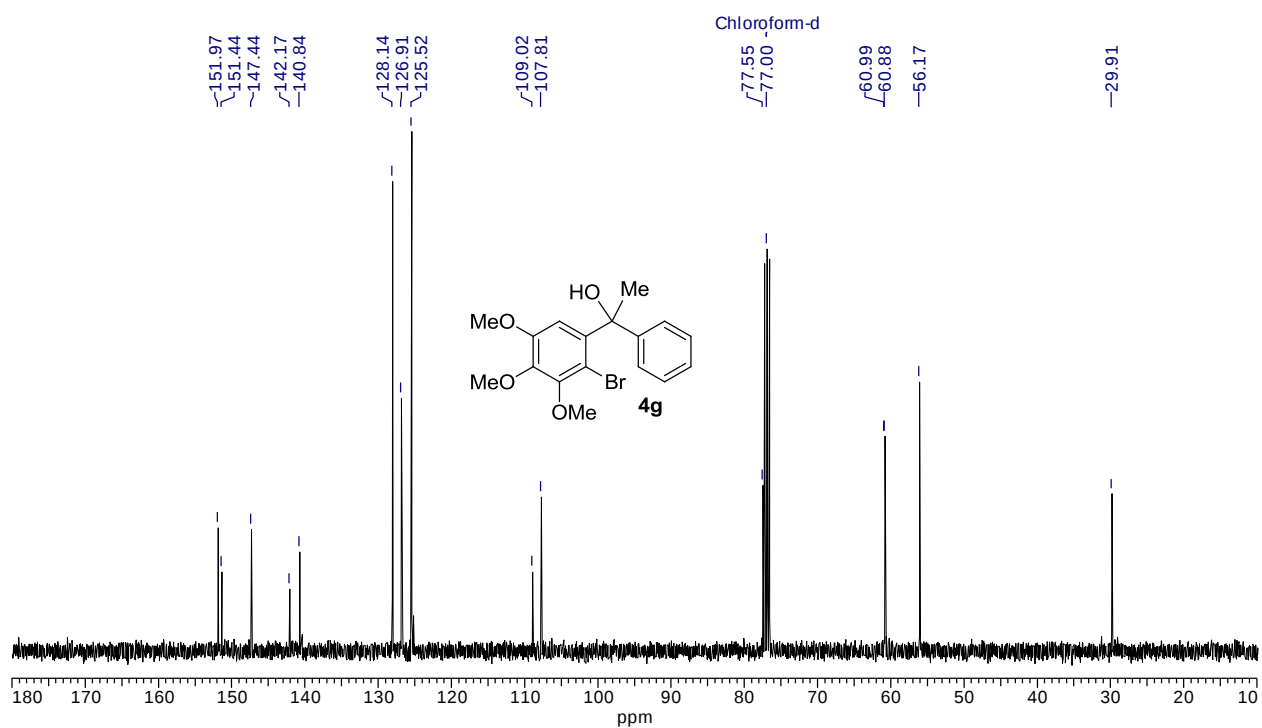
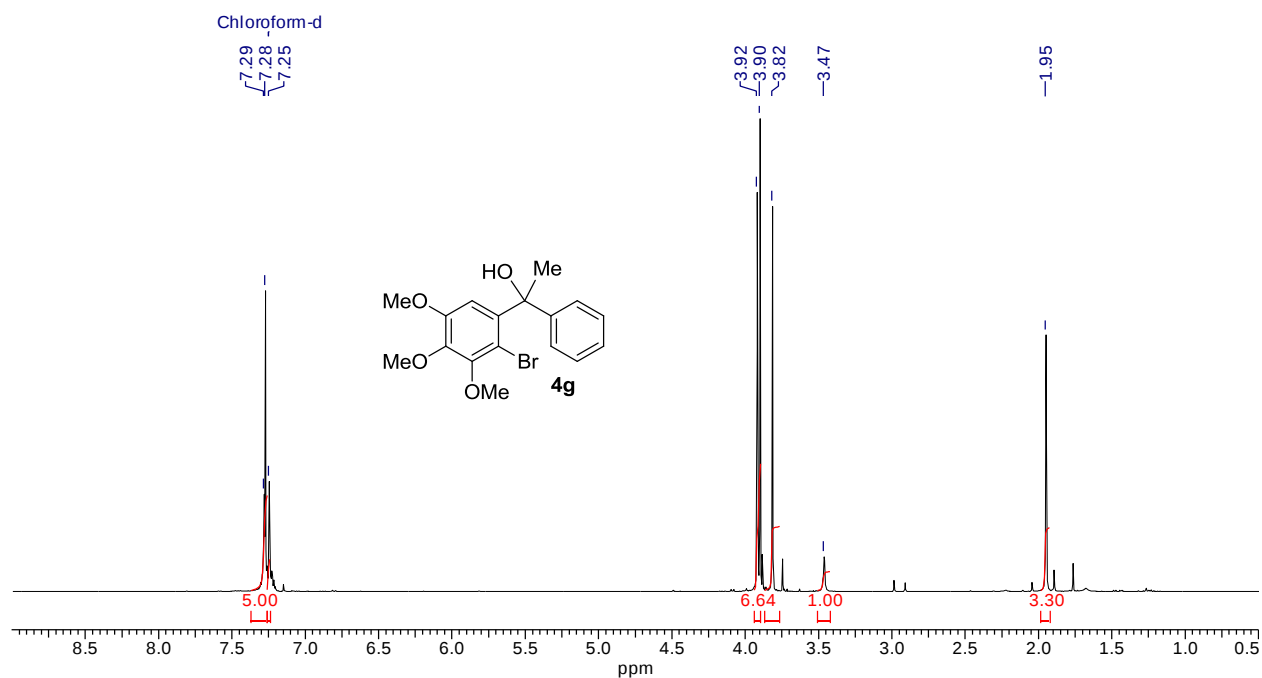


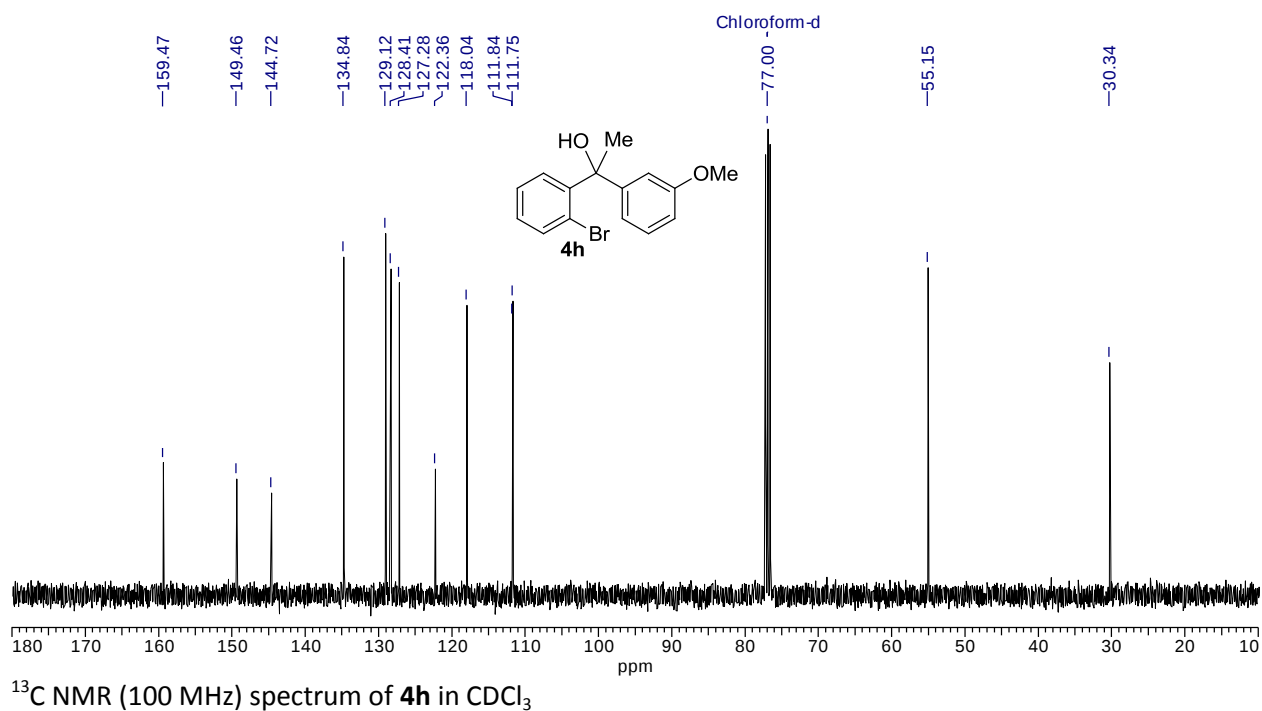
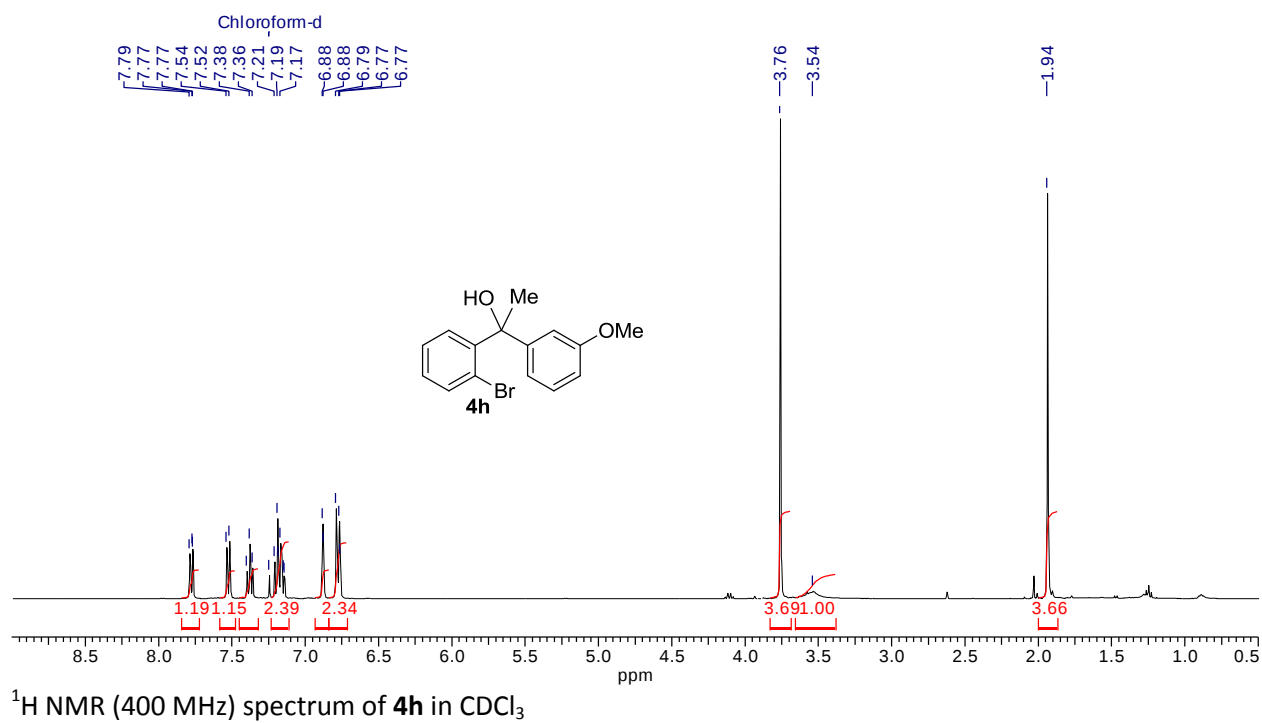


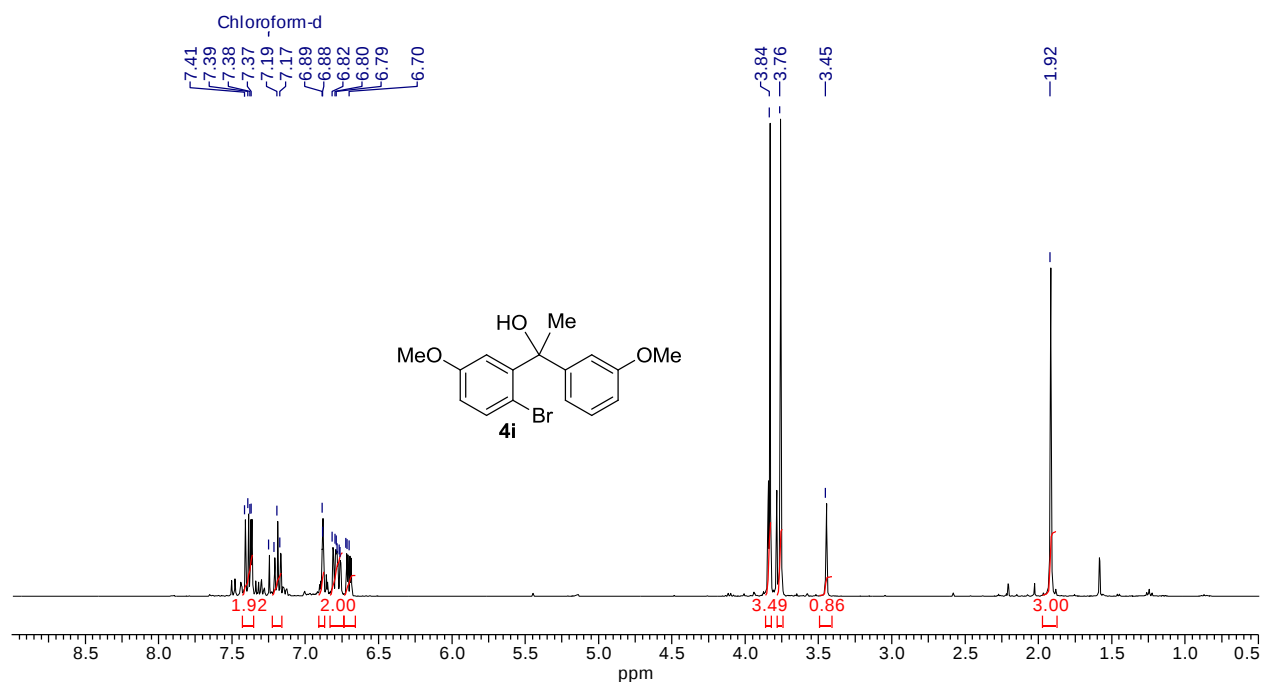
¹H NMR (400 MHz) spectrum of **4f** in CDCl₃



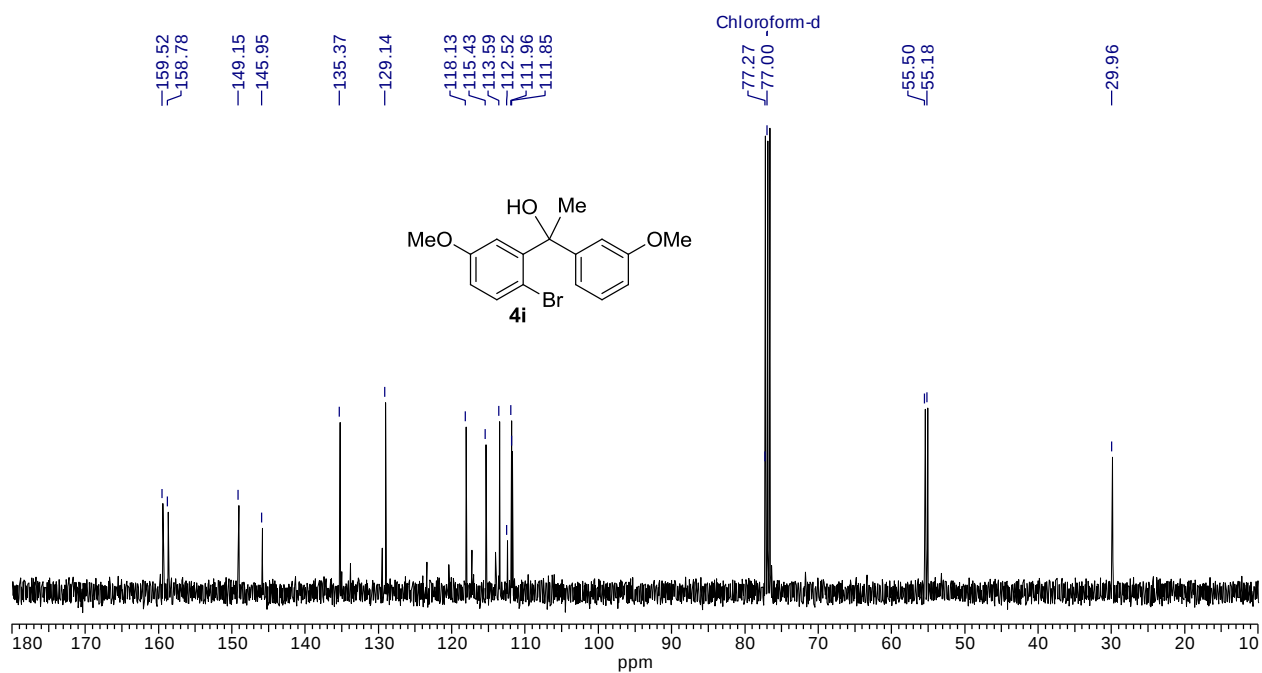
¹³C NMR (100 MHz) spectrum of **4f** in CDCl₃



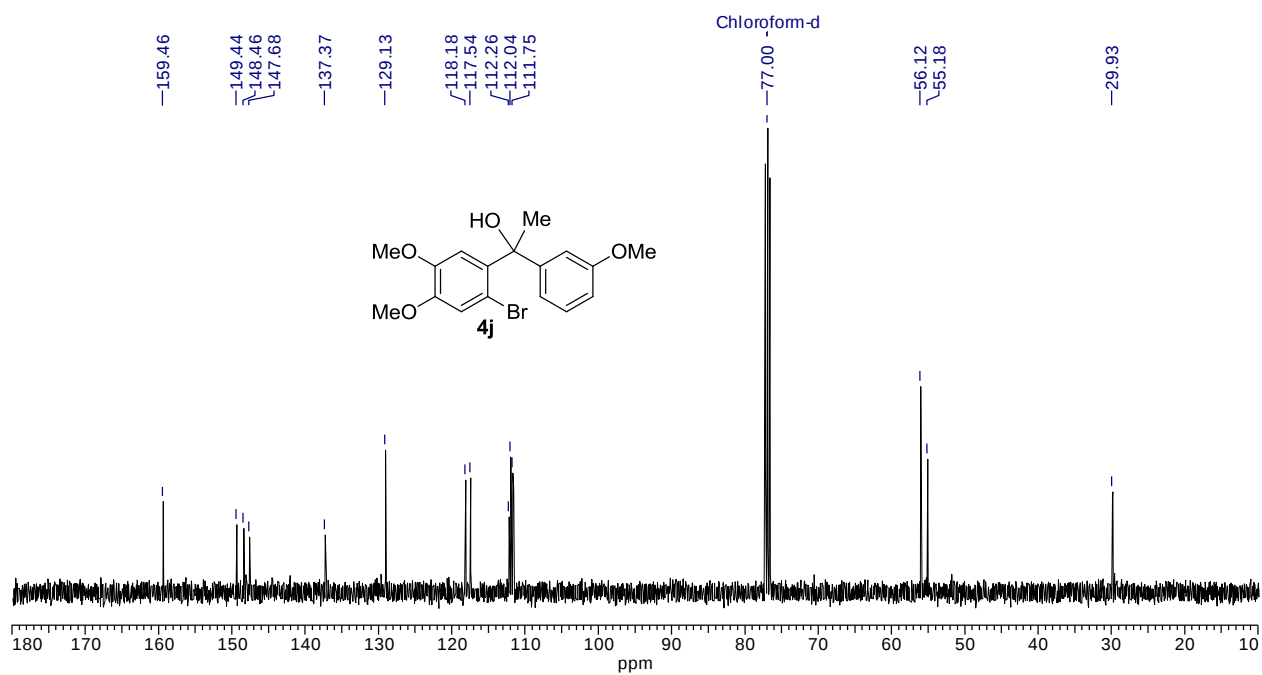
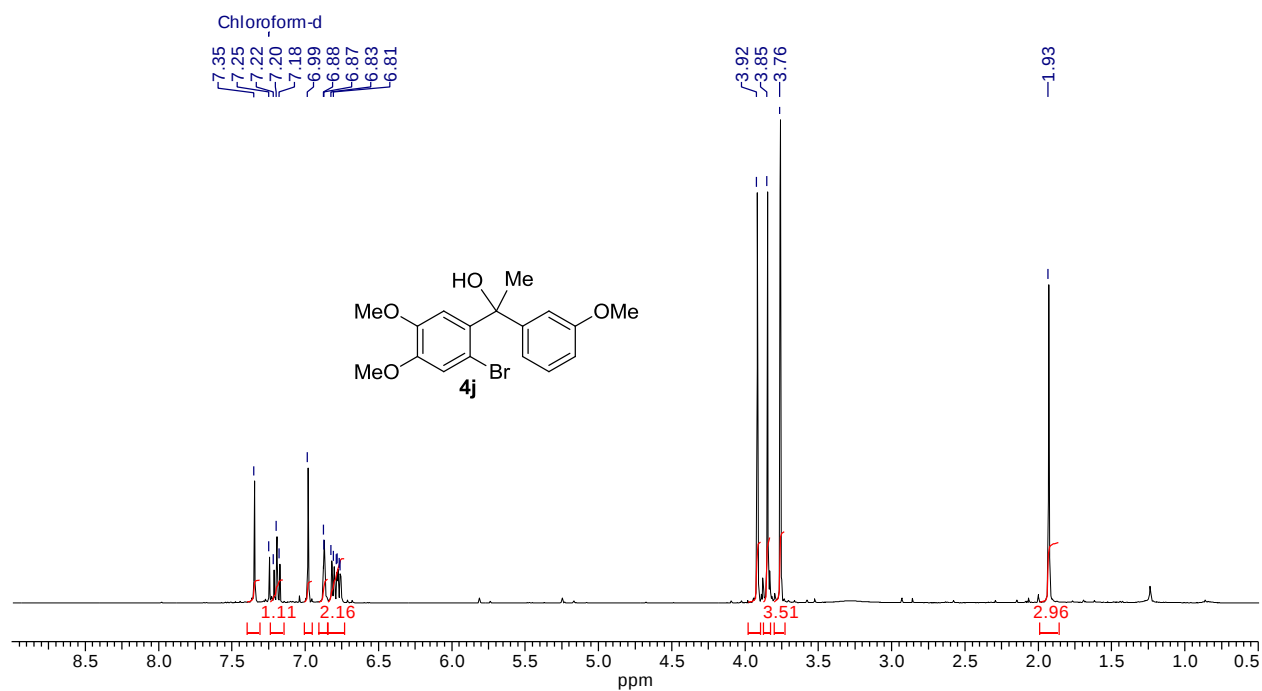


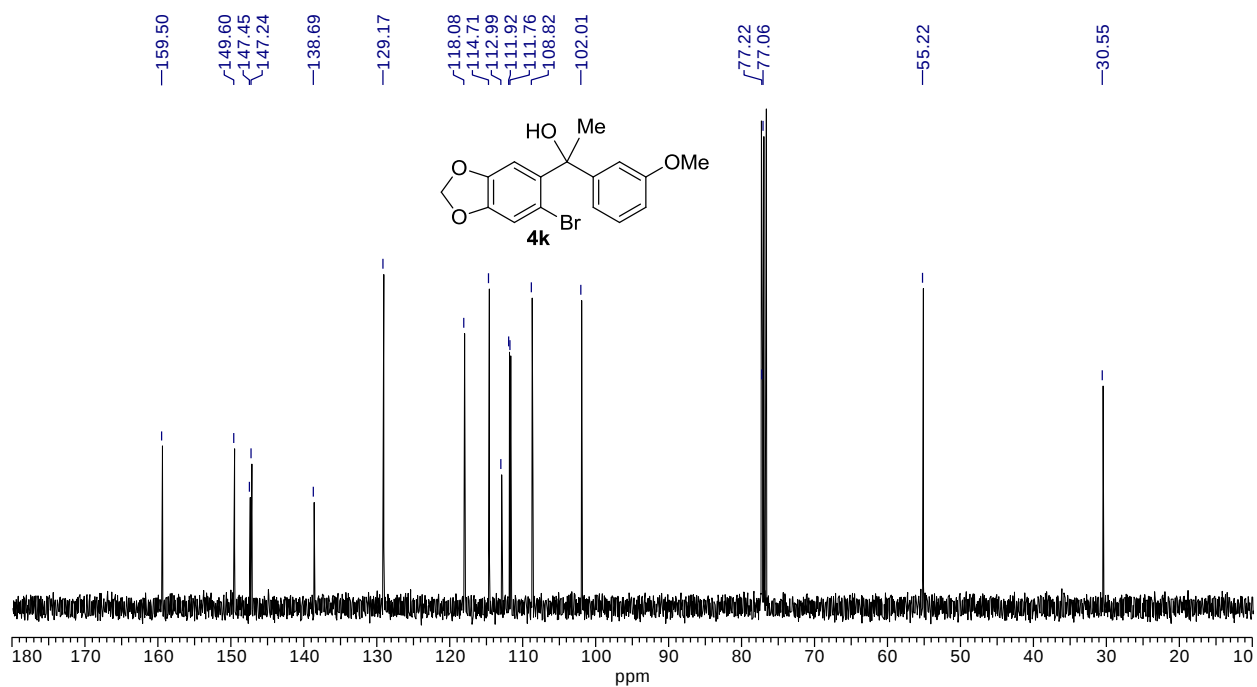
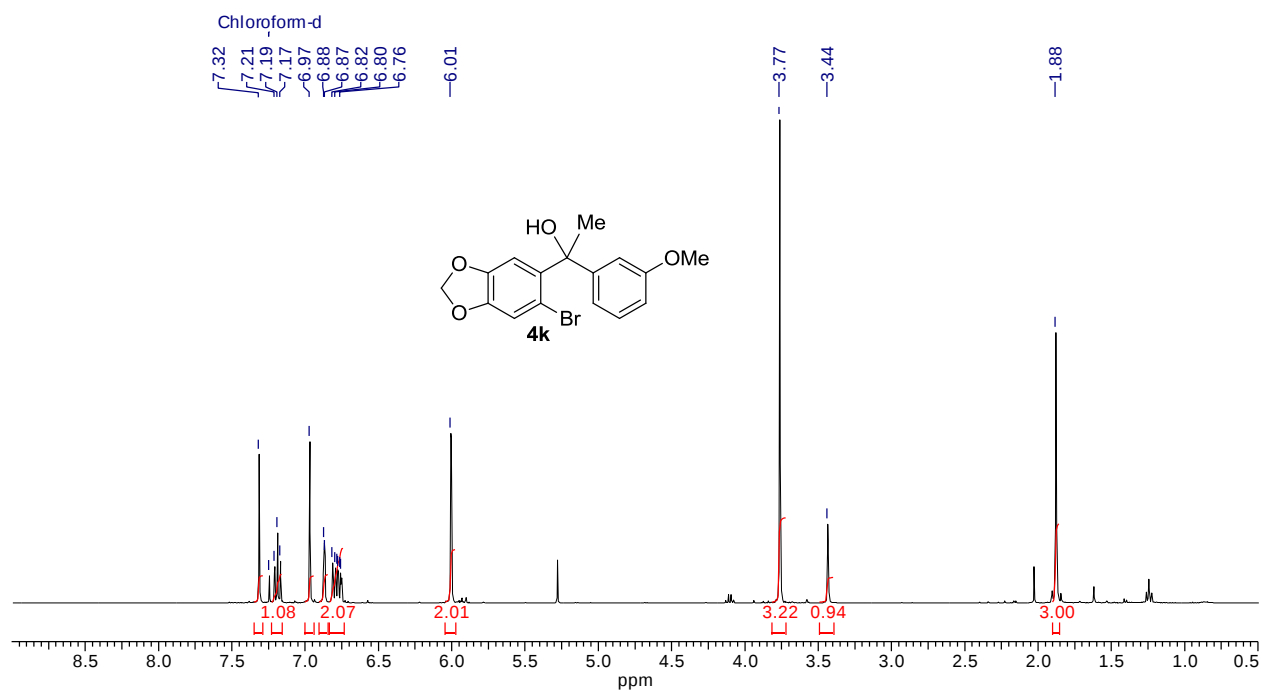


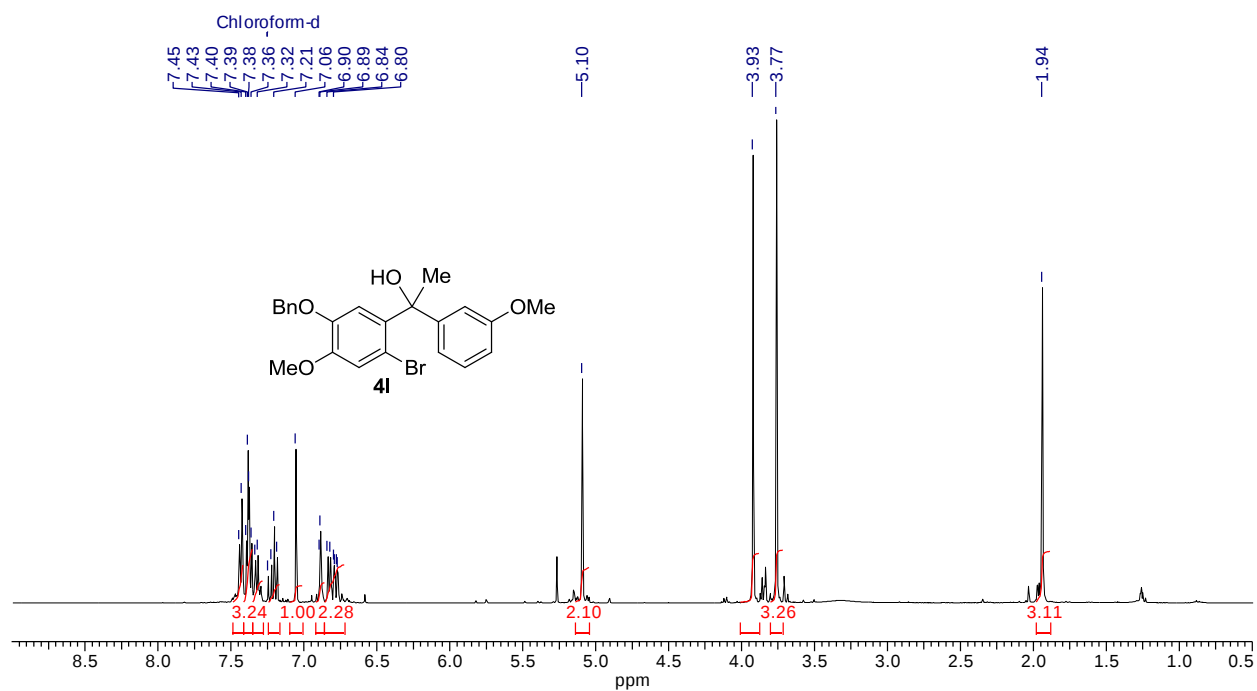
¹H NMR (400 MHz) spectrum of **4i** in CDCl₃



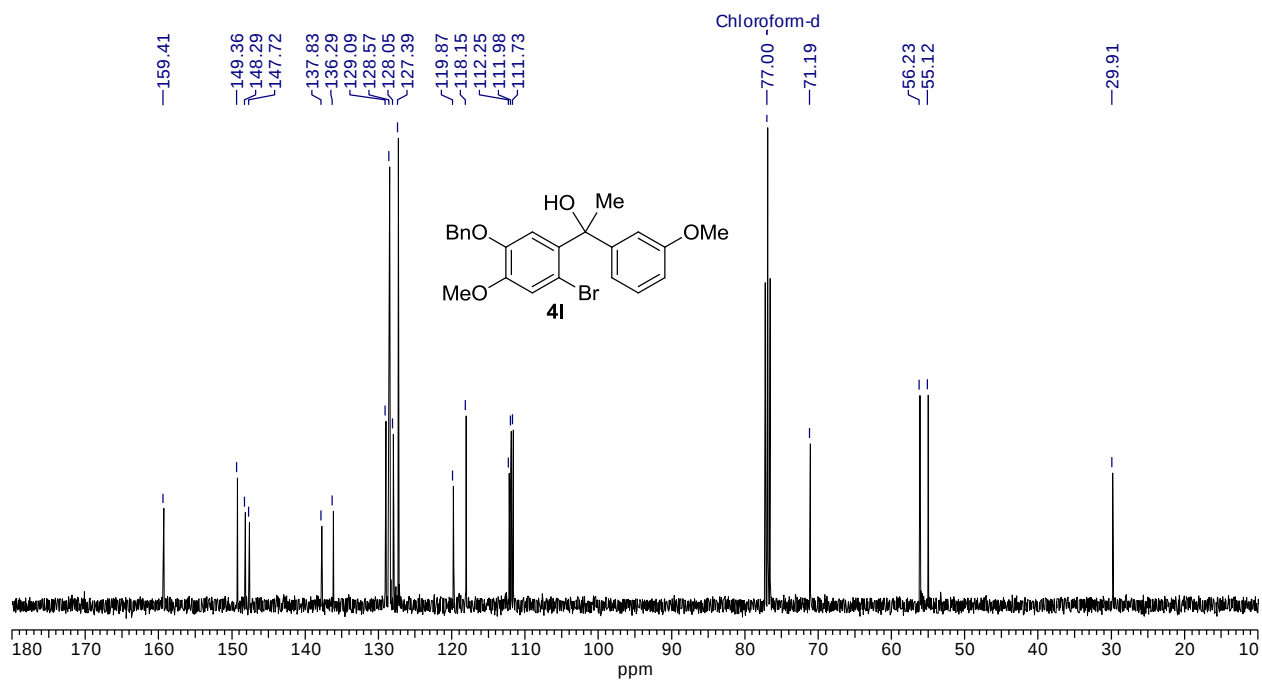
¹³C NMR (100 MHz) spectrum of **4i** in CDCl₃



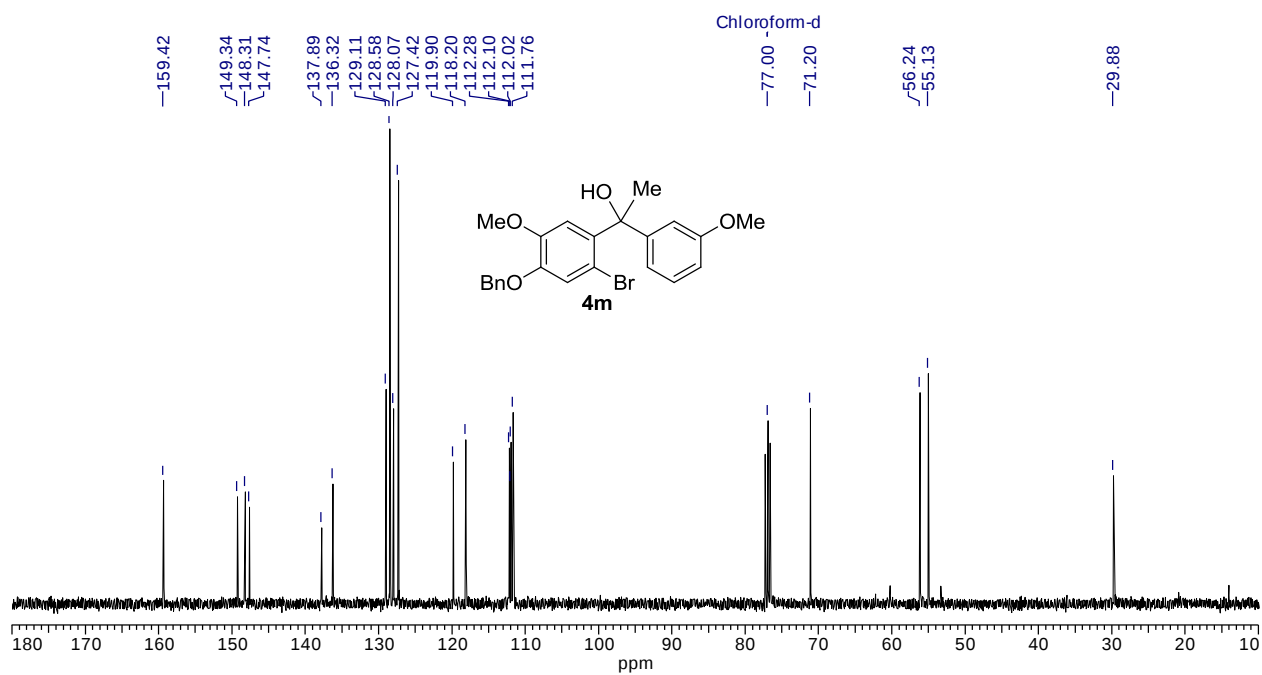
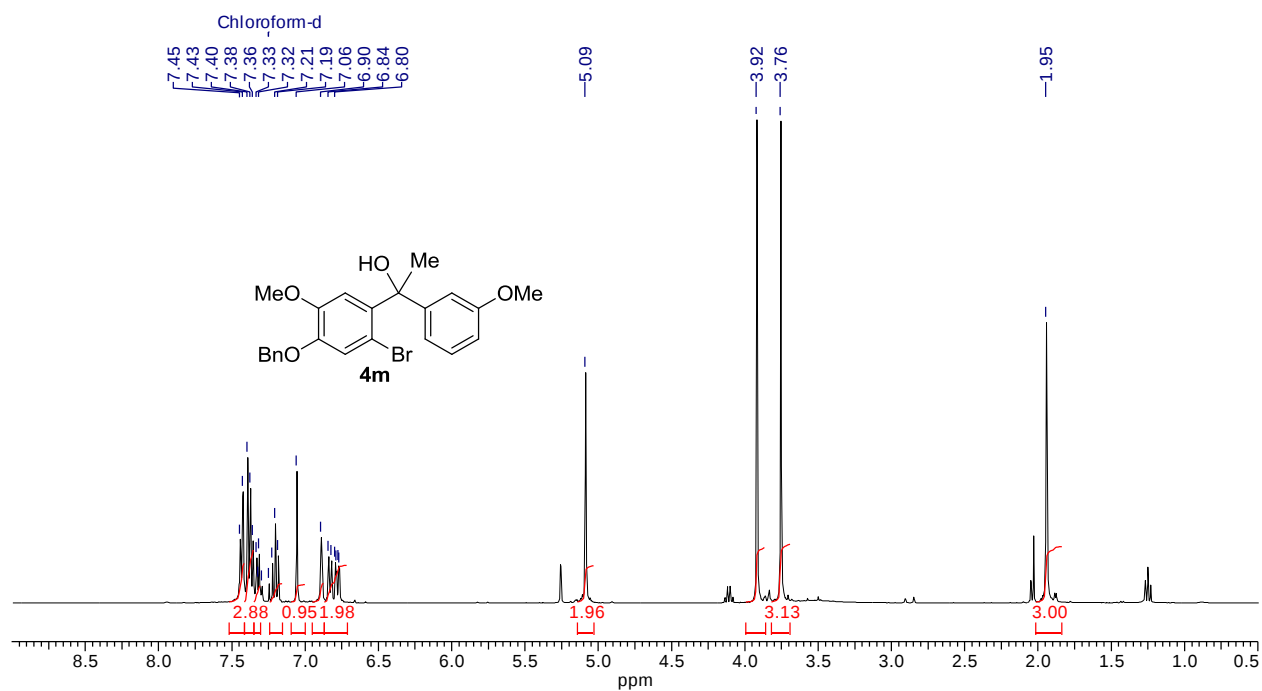


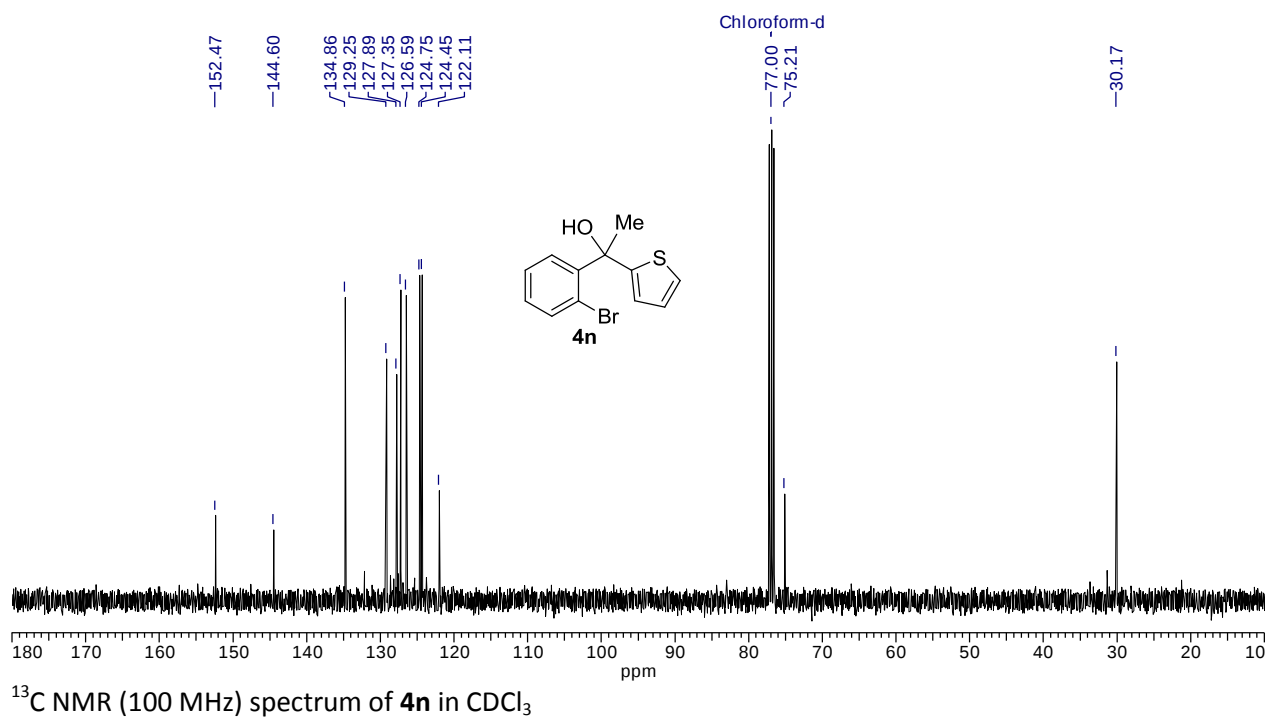
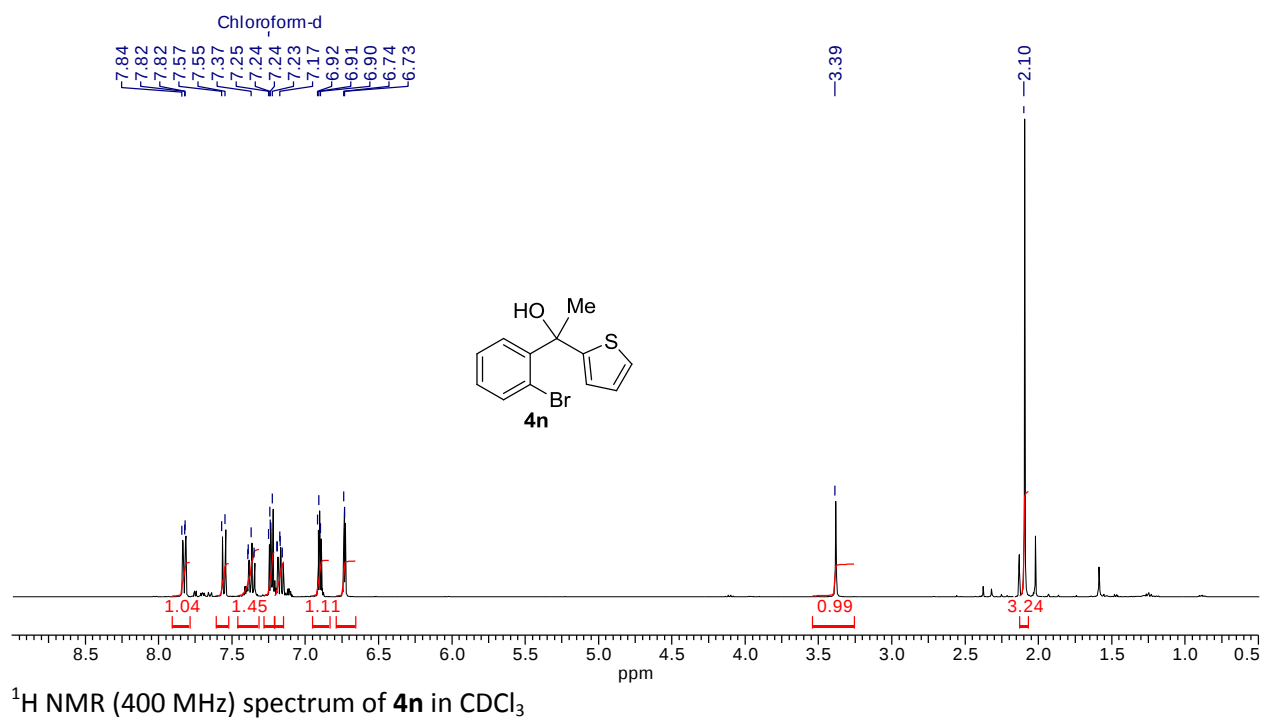


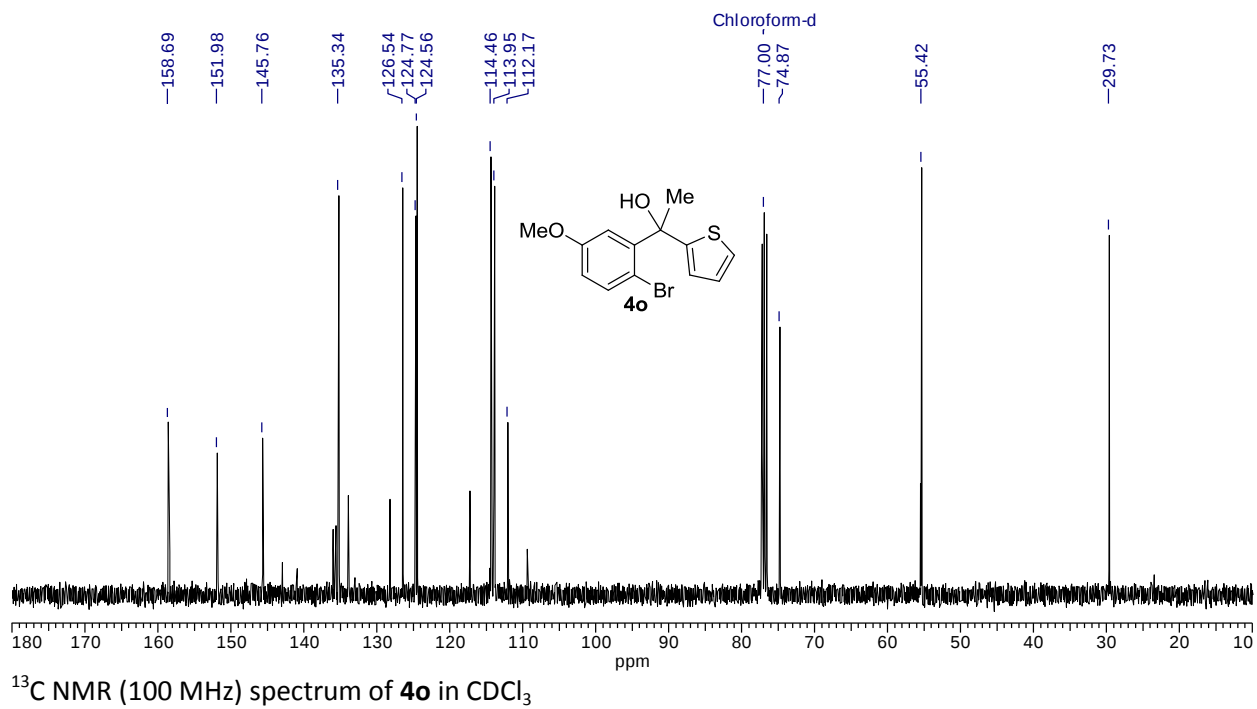
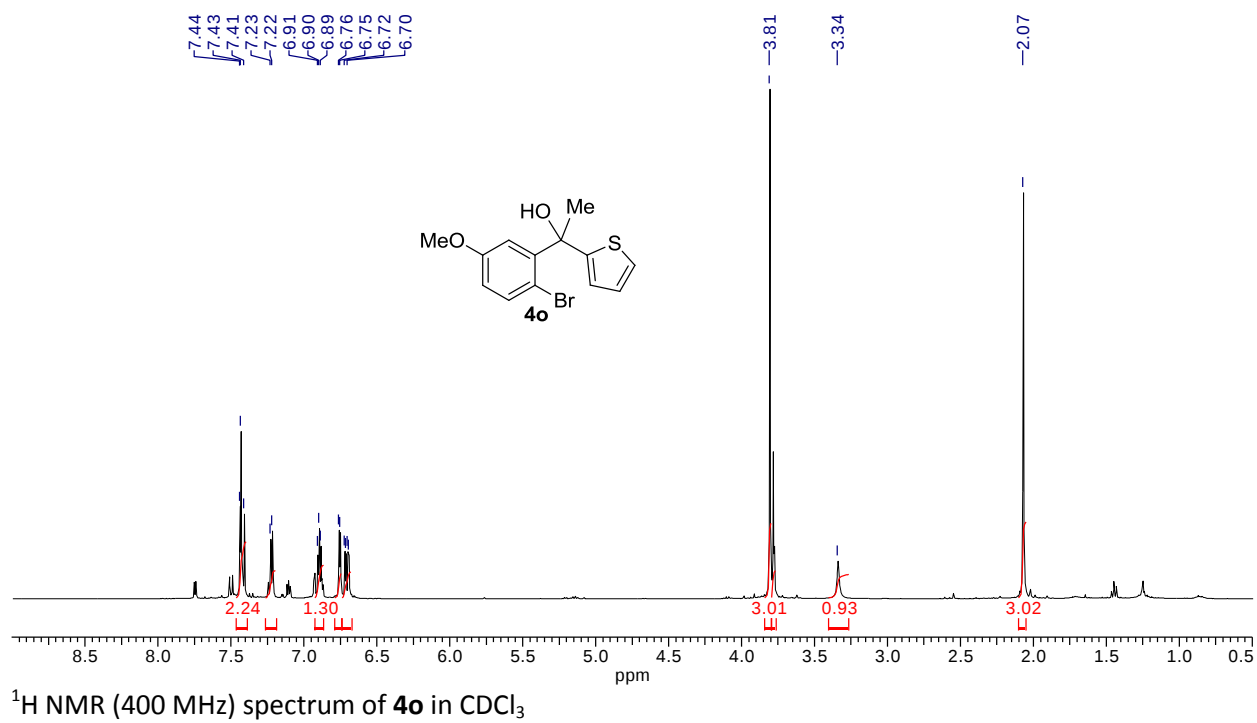
¹H NMR (400 MHz) spectrum of **4I** in CDCl₃

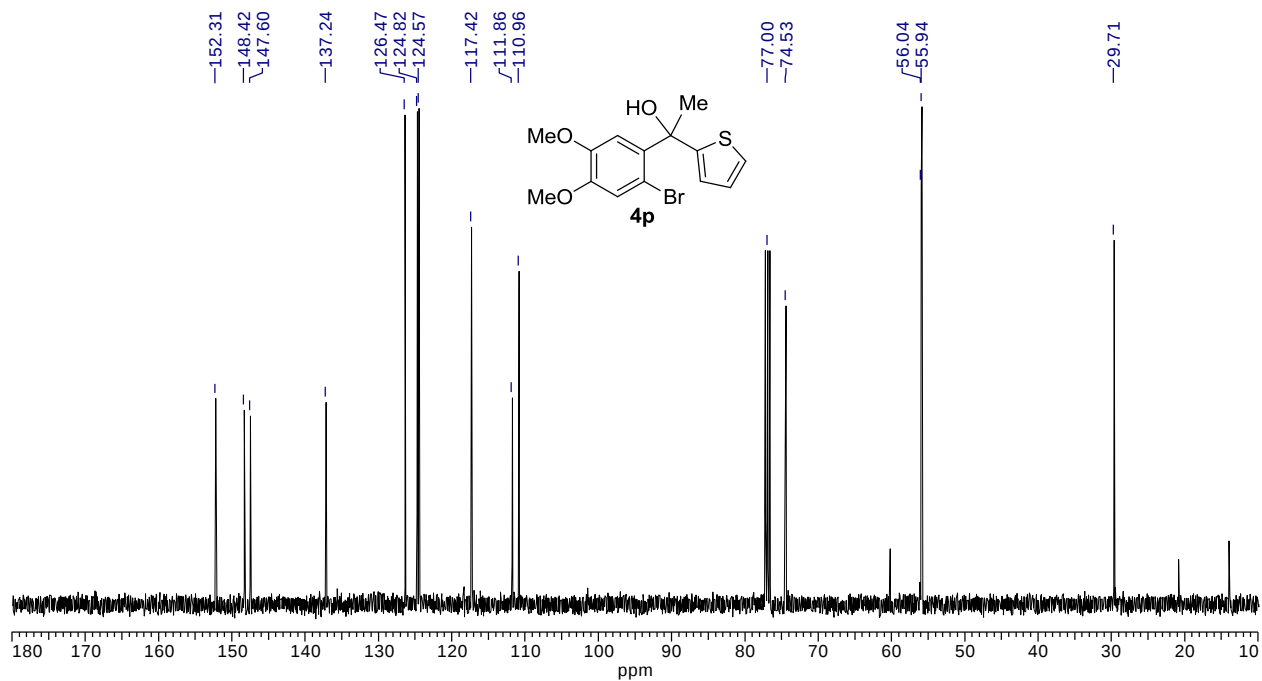
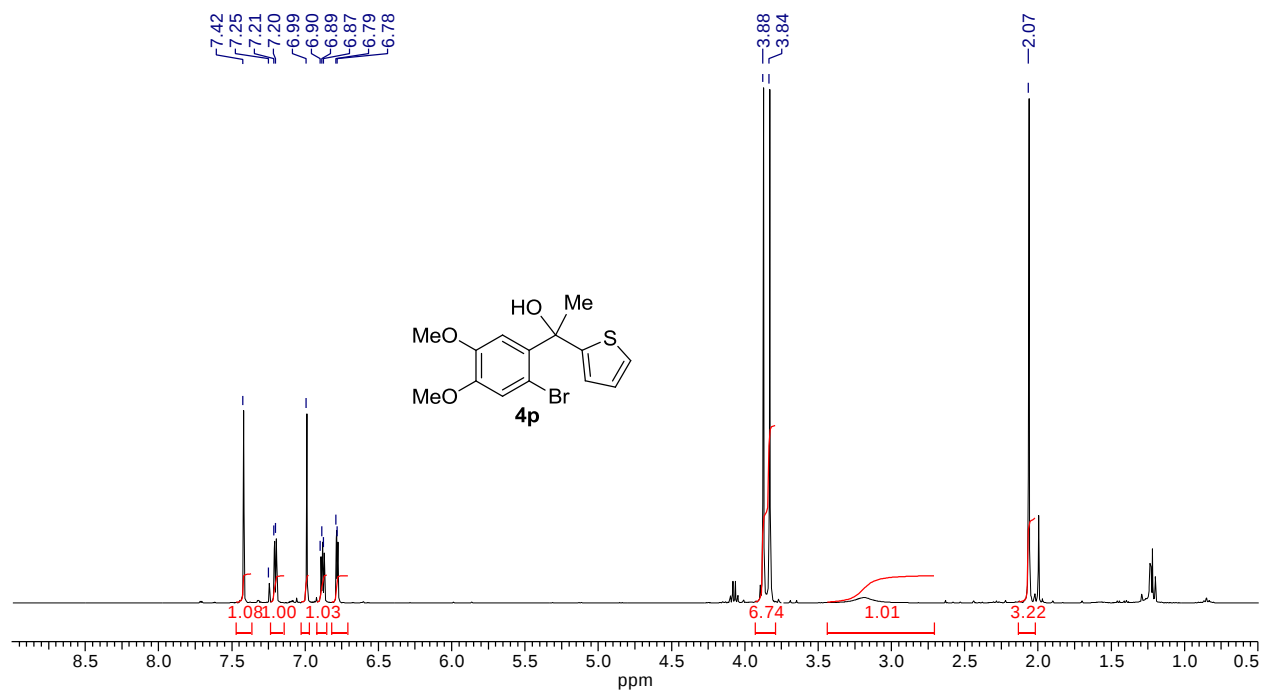


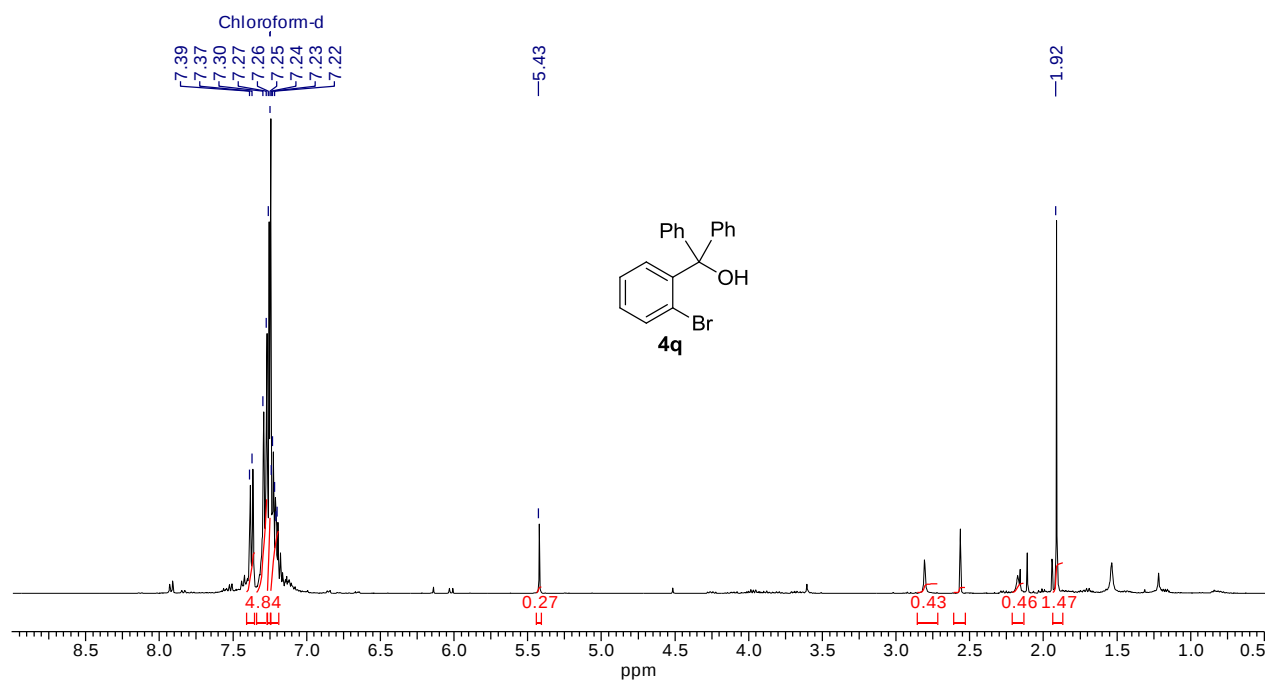
¹³C NMR (100 MHz) spectrum of **4I** in CDCl₃



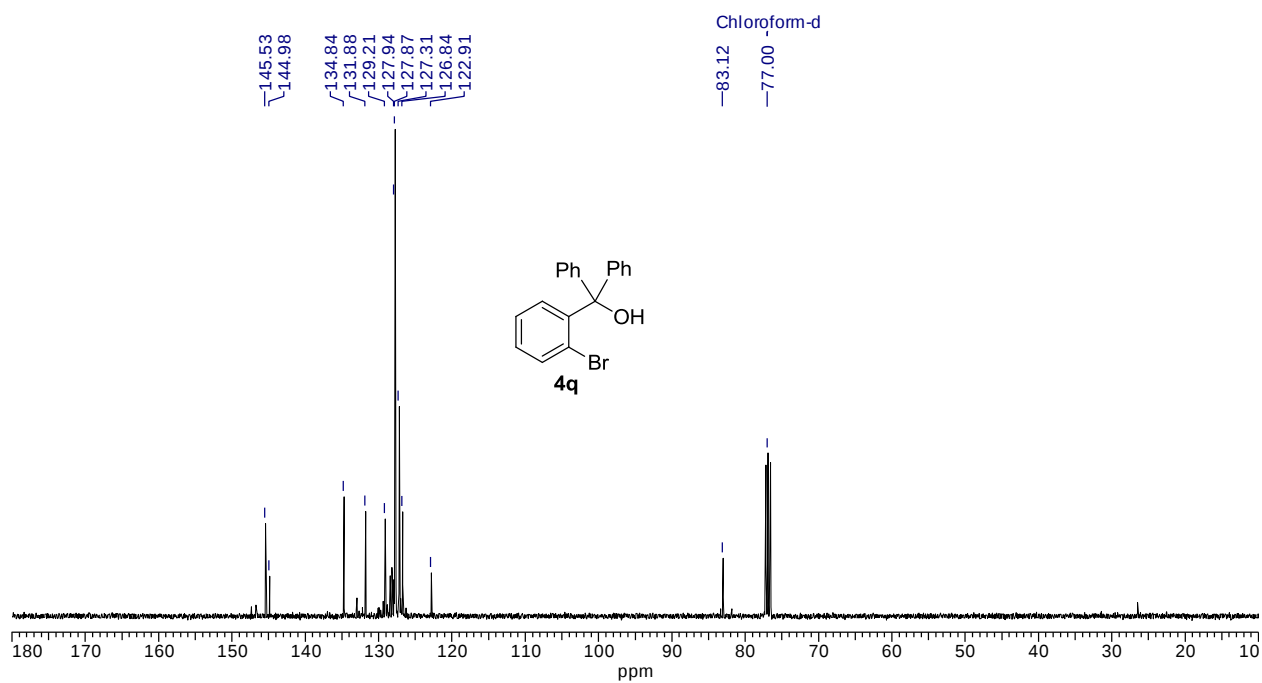




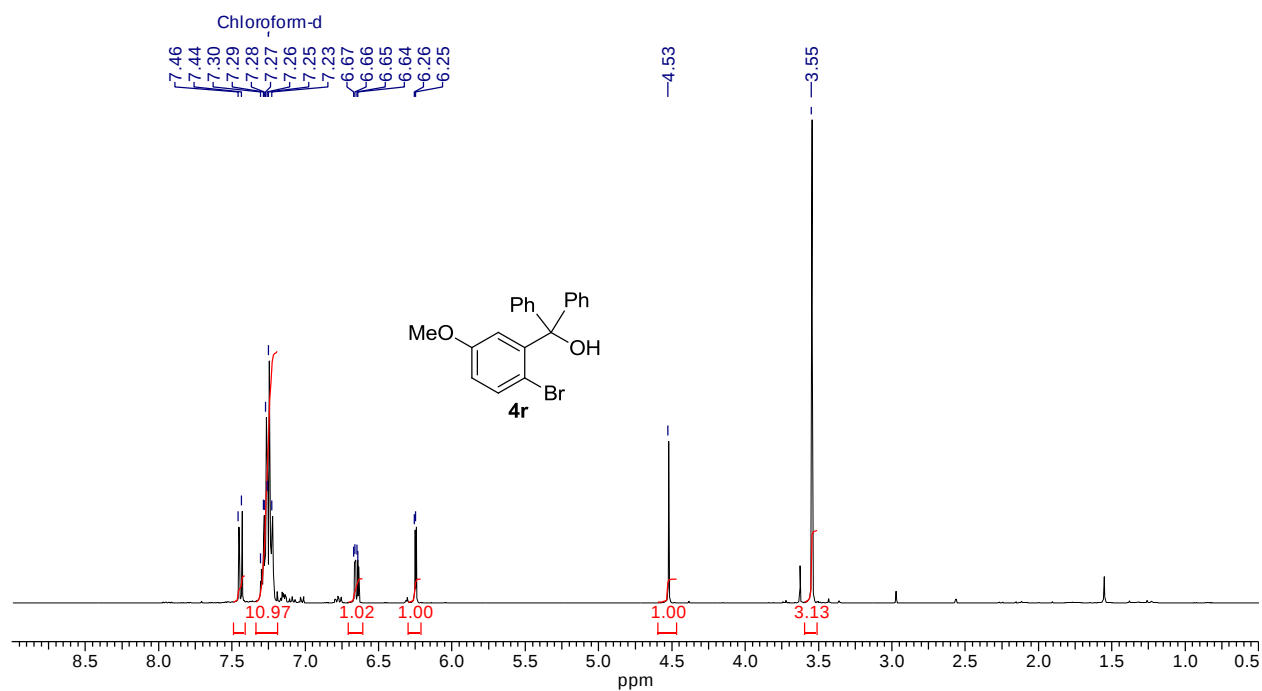




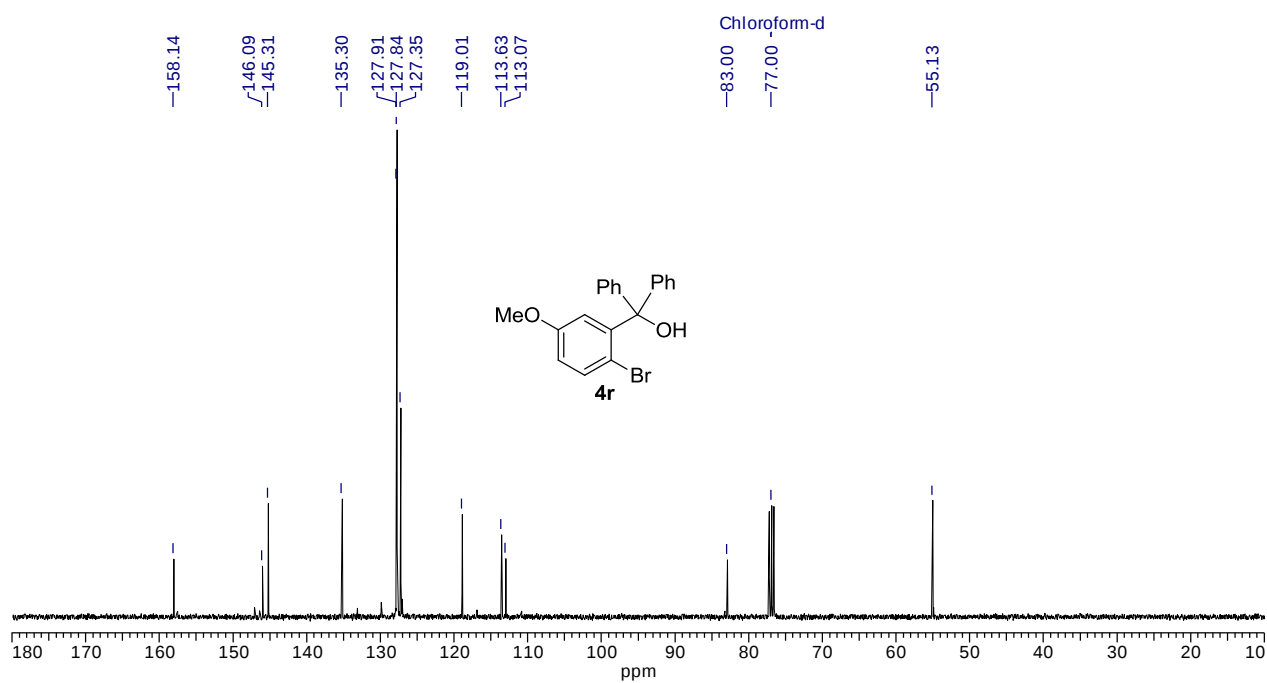
^1H NMR (400 MHz) spectrum of **4q** in CDCl_3



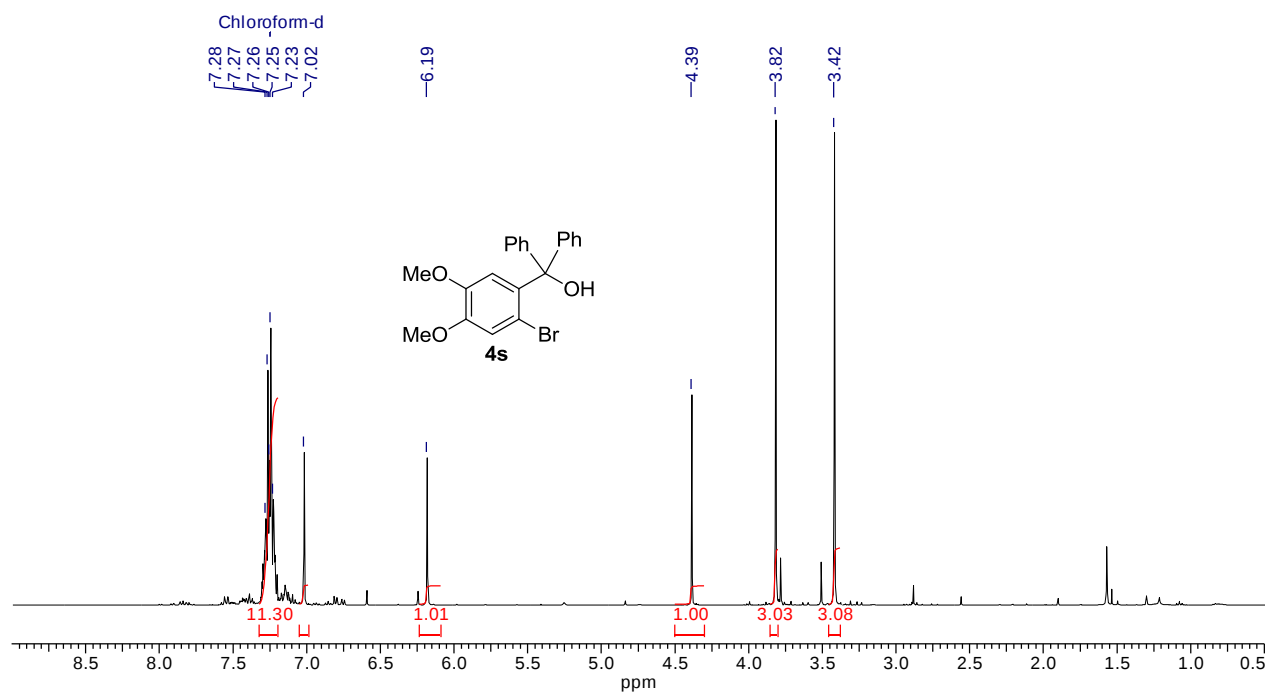
^{13}C NMR (100 MHz) spectrum of **4q** in CDCl_3



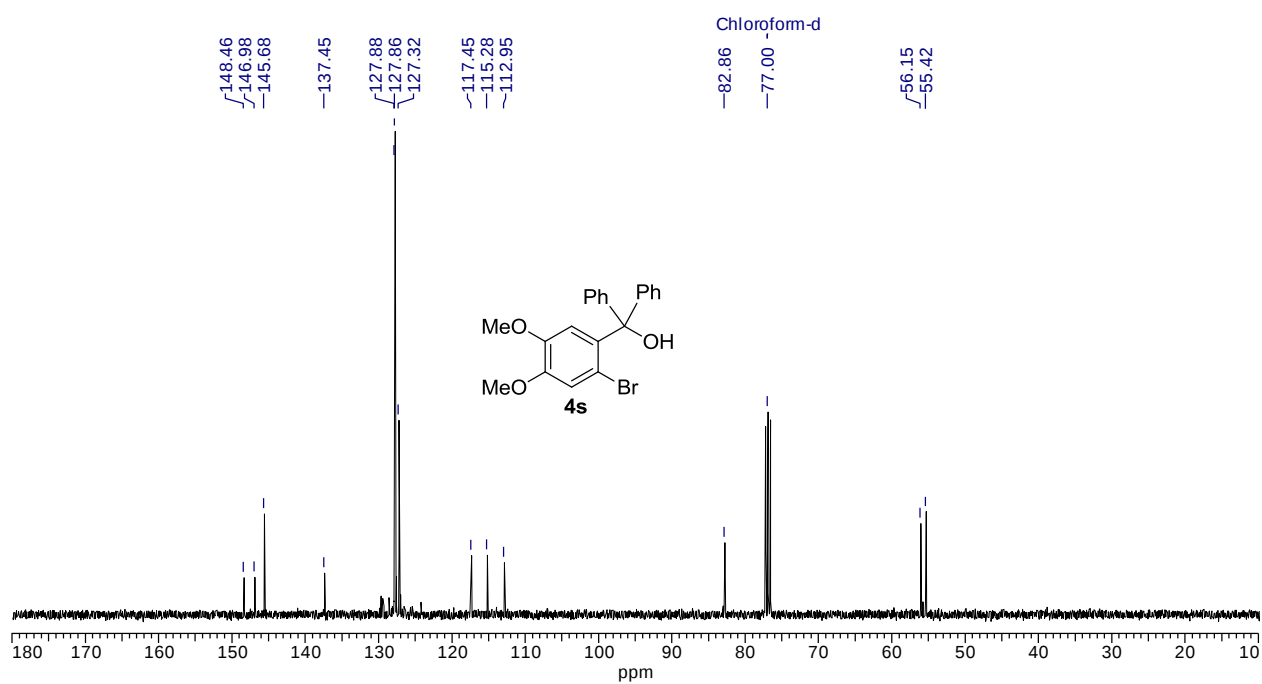
¹H NMR (400 MHz) spectrum of **4r** in CDCl₃



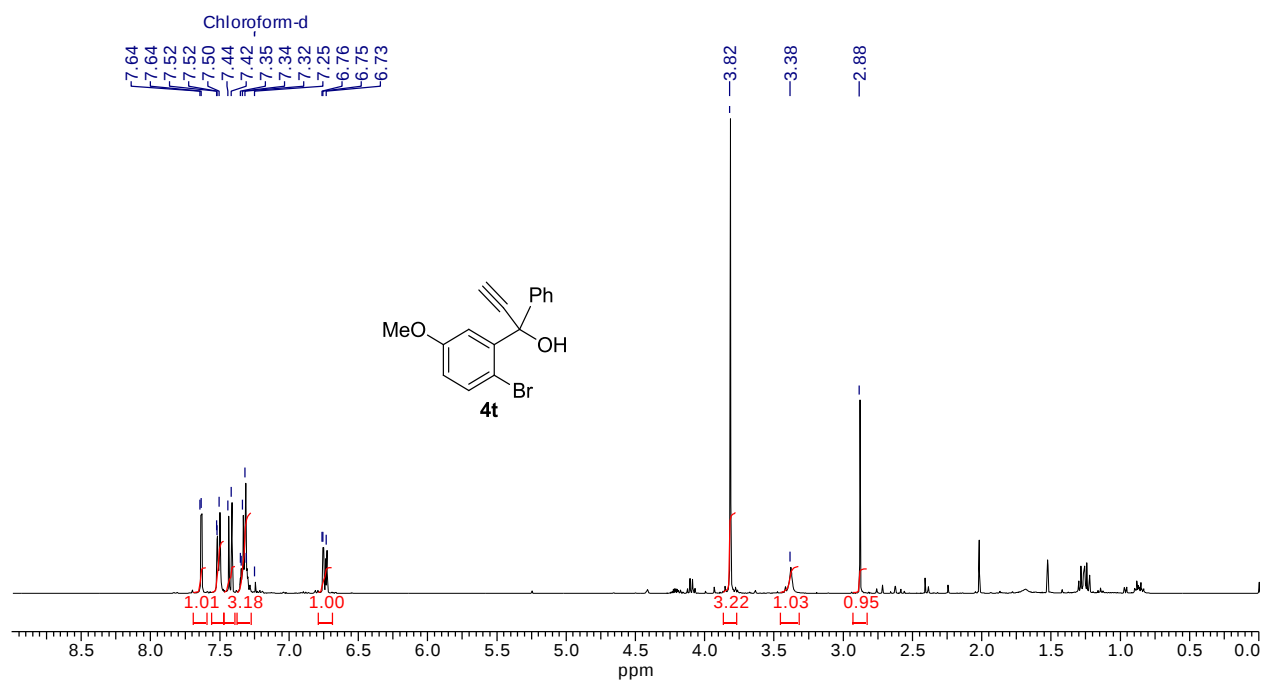
¹³C NMR (100 MHz) spectrum of **4r** in CDCl₃



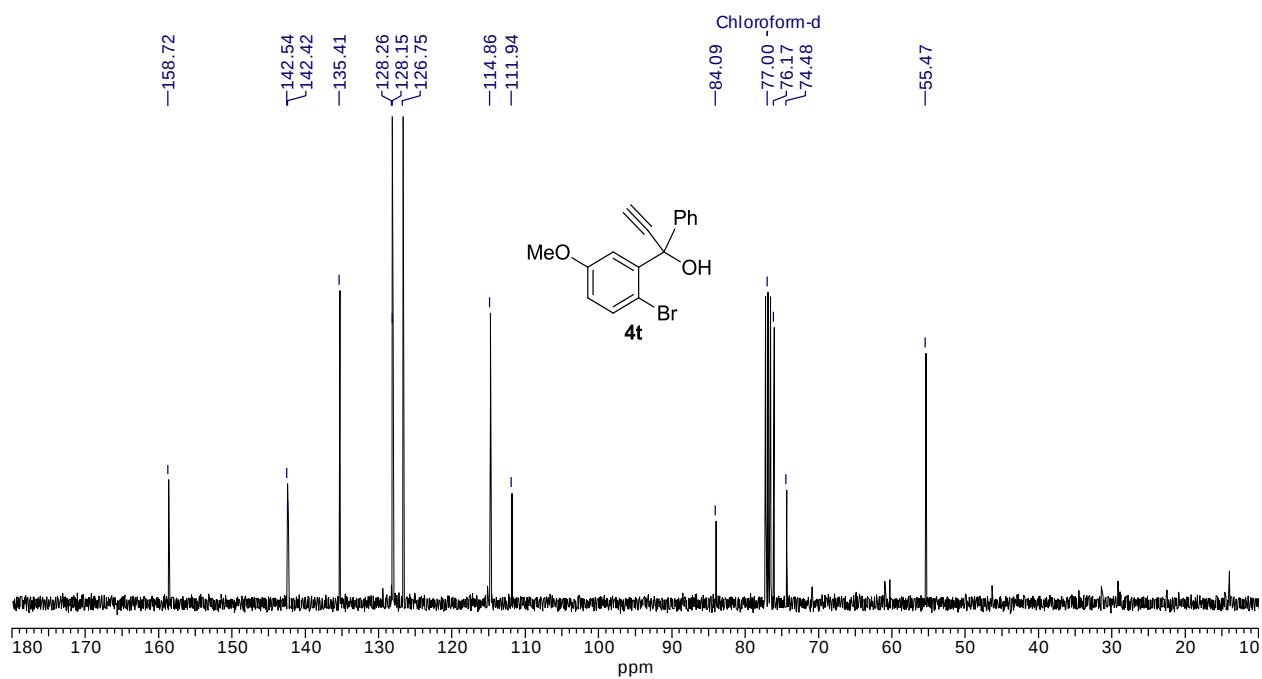
^1H NMR (400 MHz) spectrum of **4s** in CDCl_3



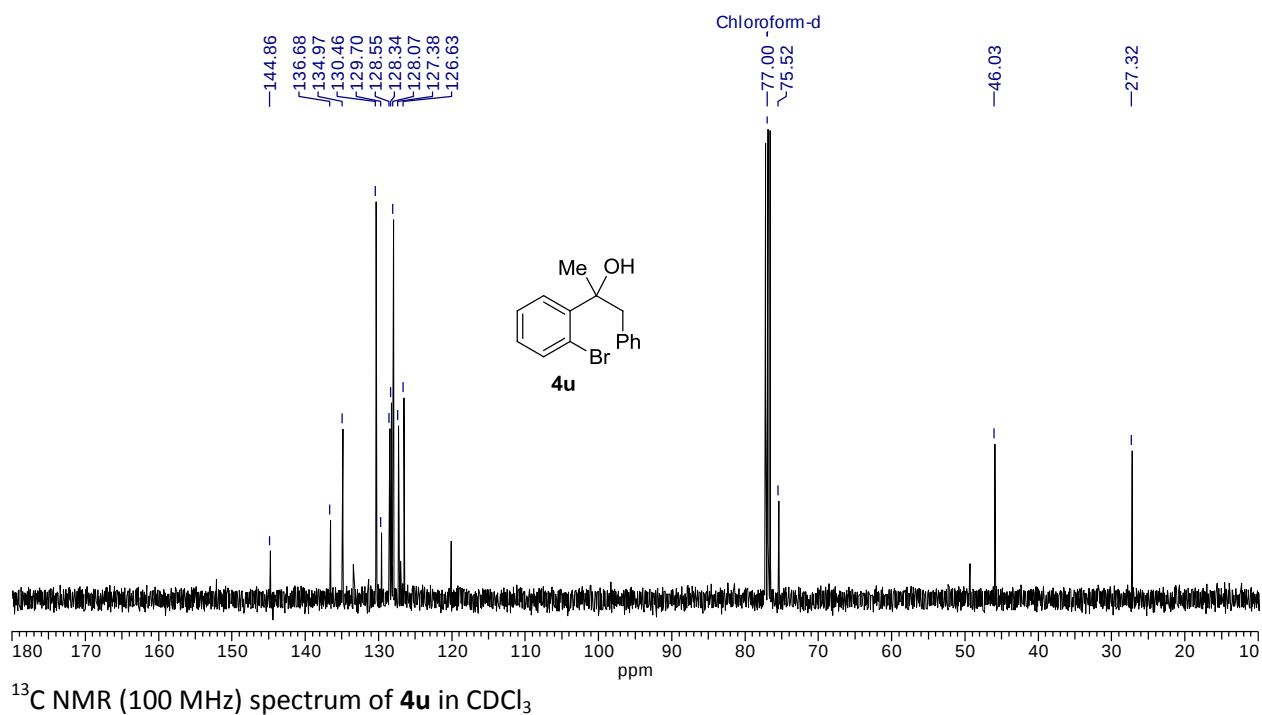
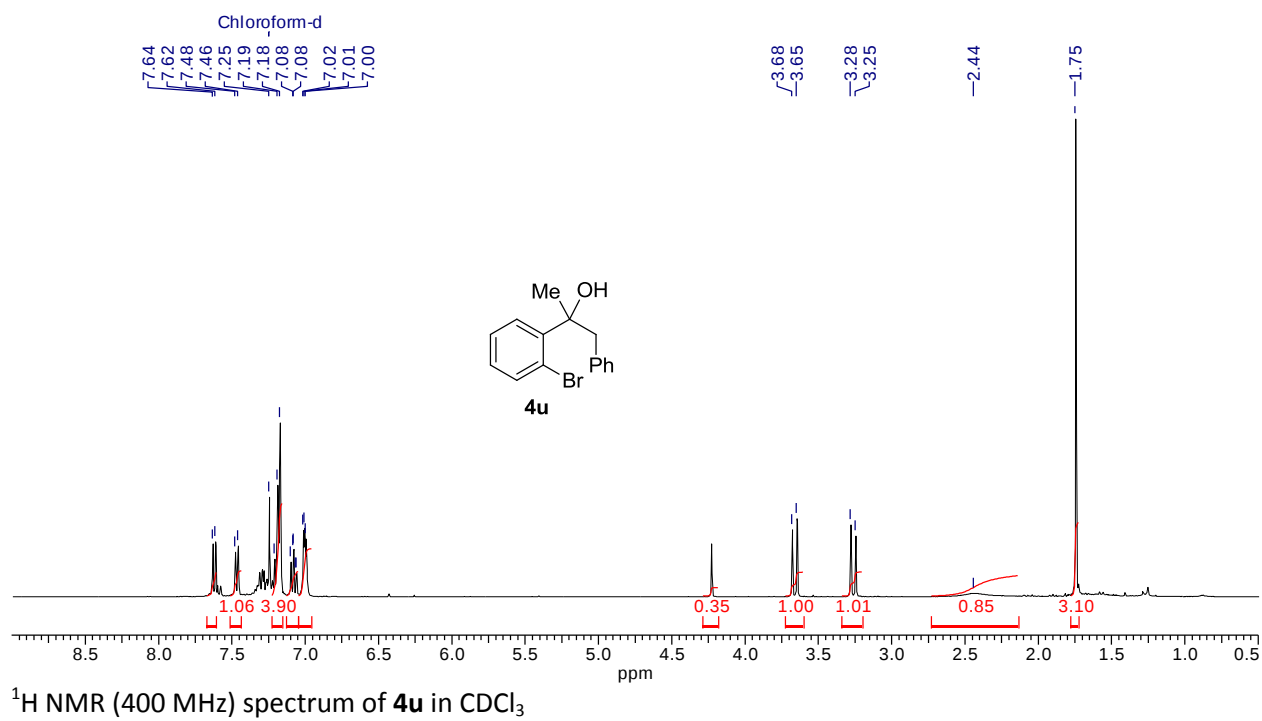
^{13}C NMR (400 MHz) spectrum of **4s** in CDCl_3

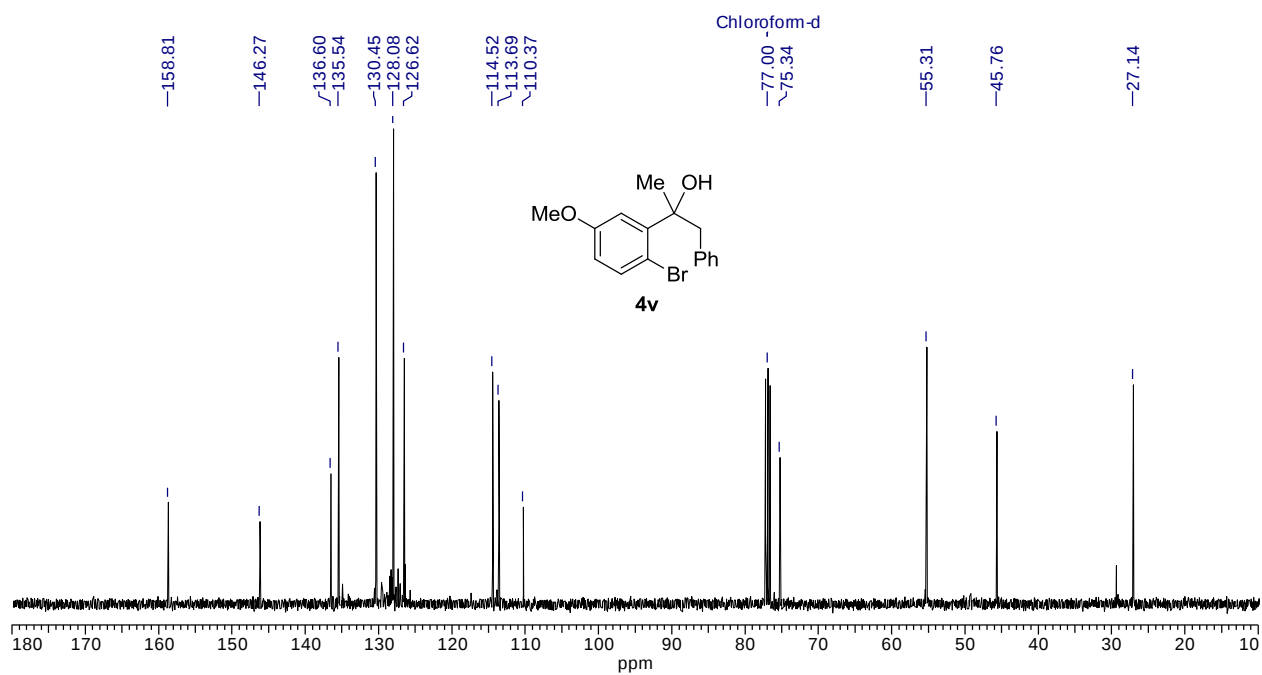
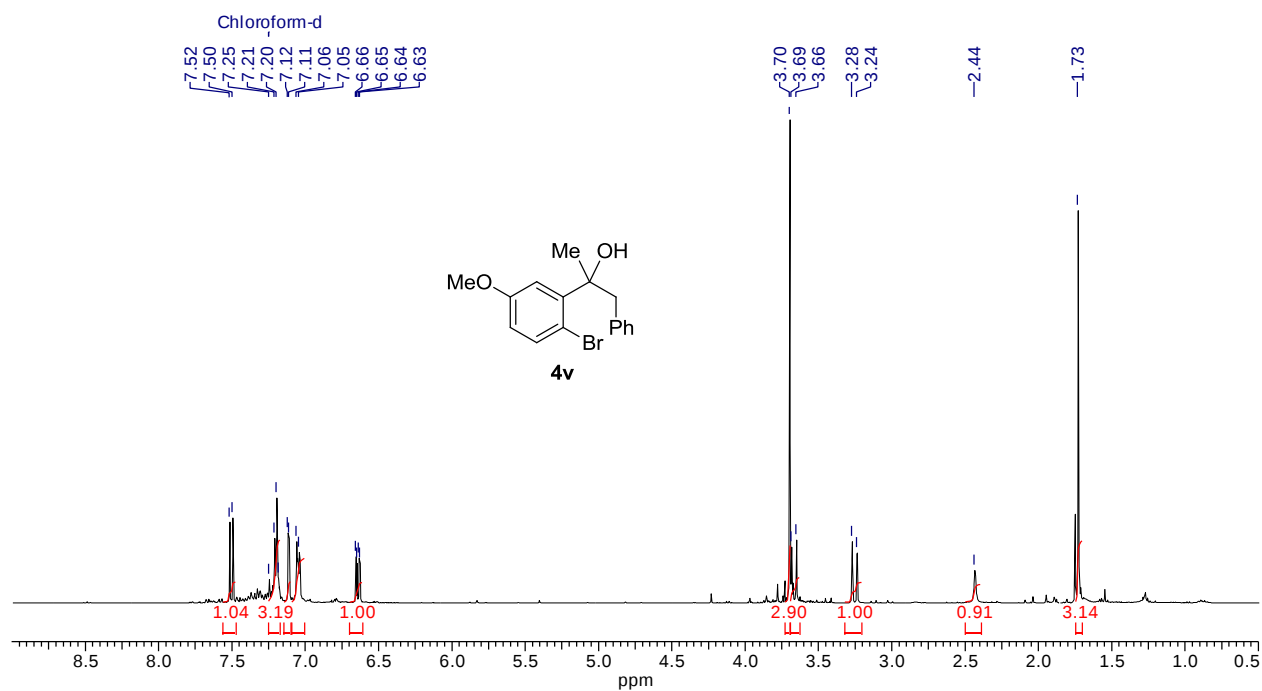


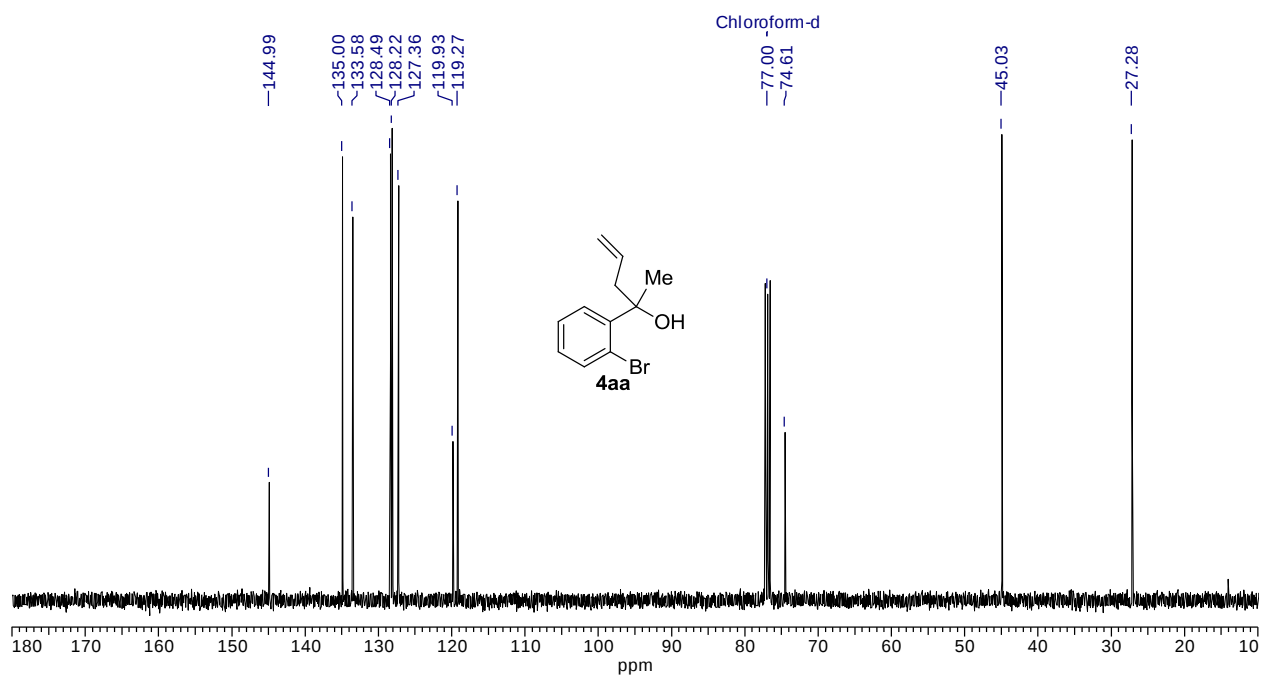
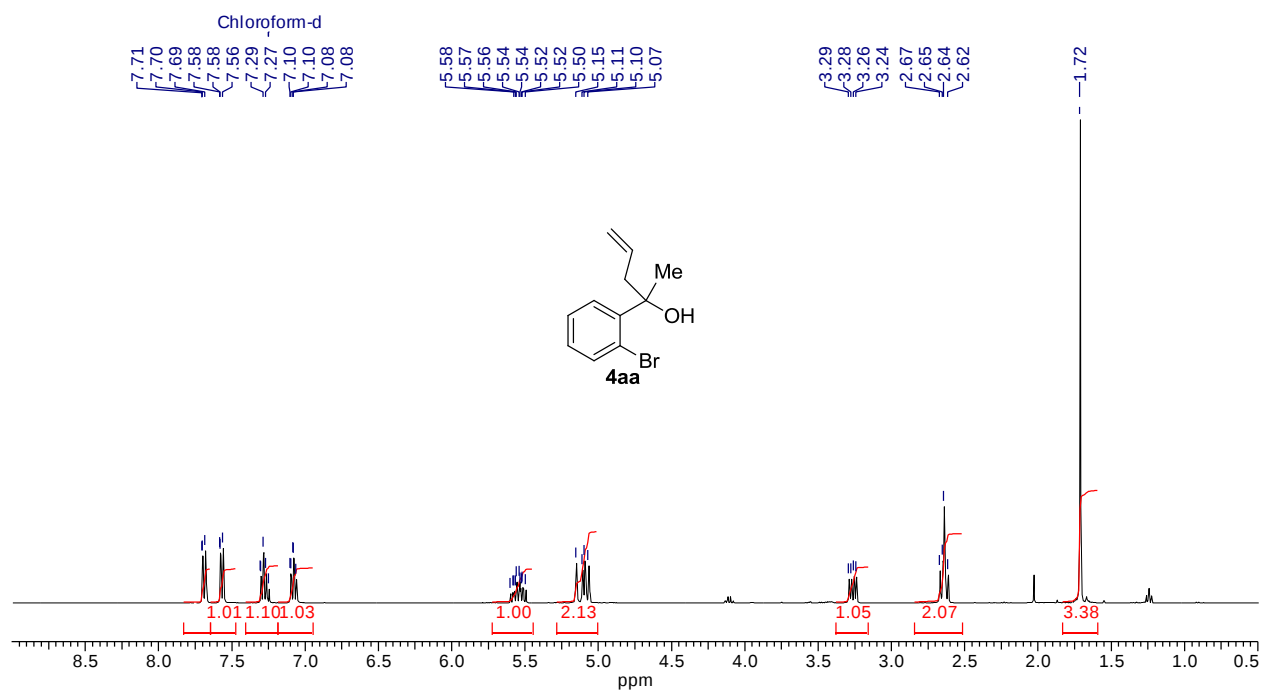
¹H NMR (400 MHz) spectrum of **4t** in CDCl₃

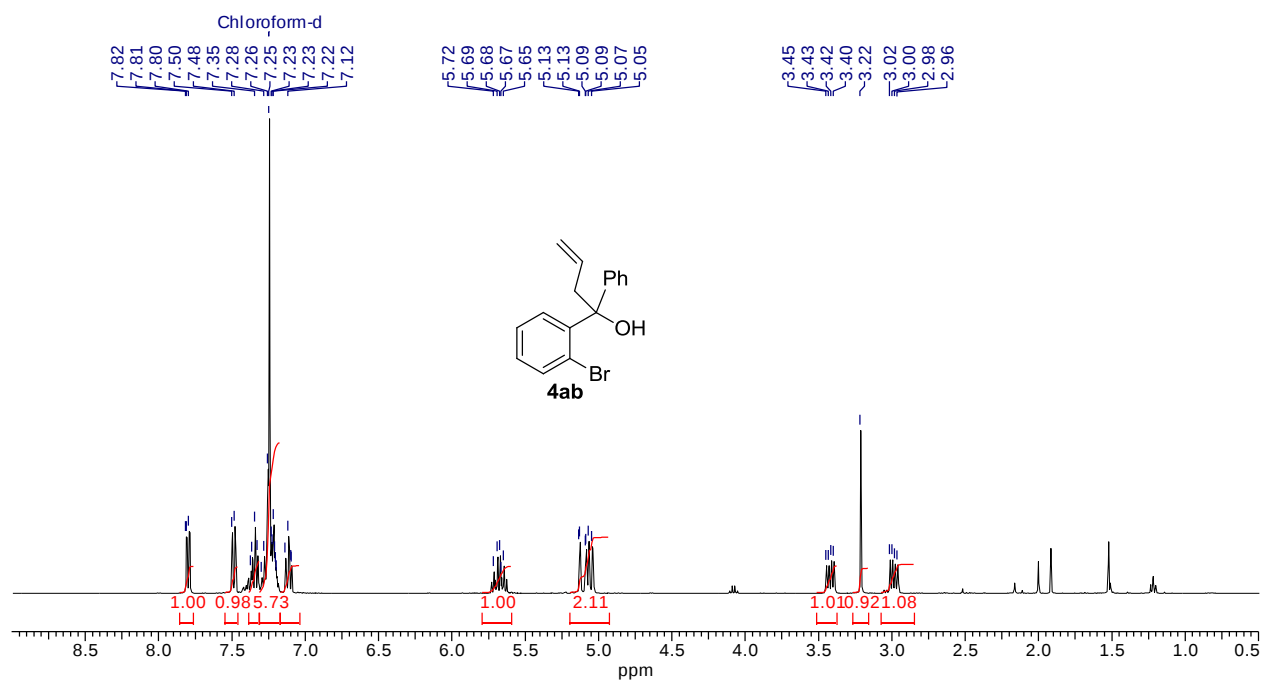


¹³C NMR (100 MHz) spectrum of **4t** in CDCl₃

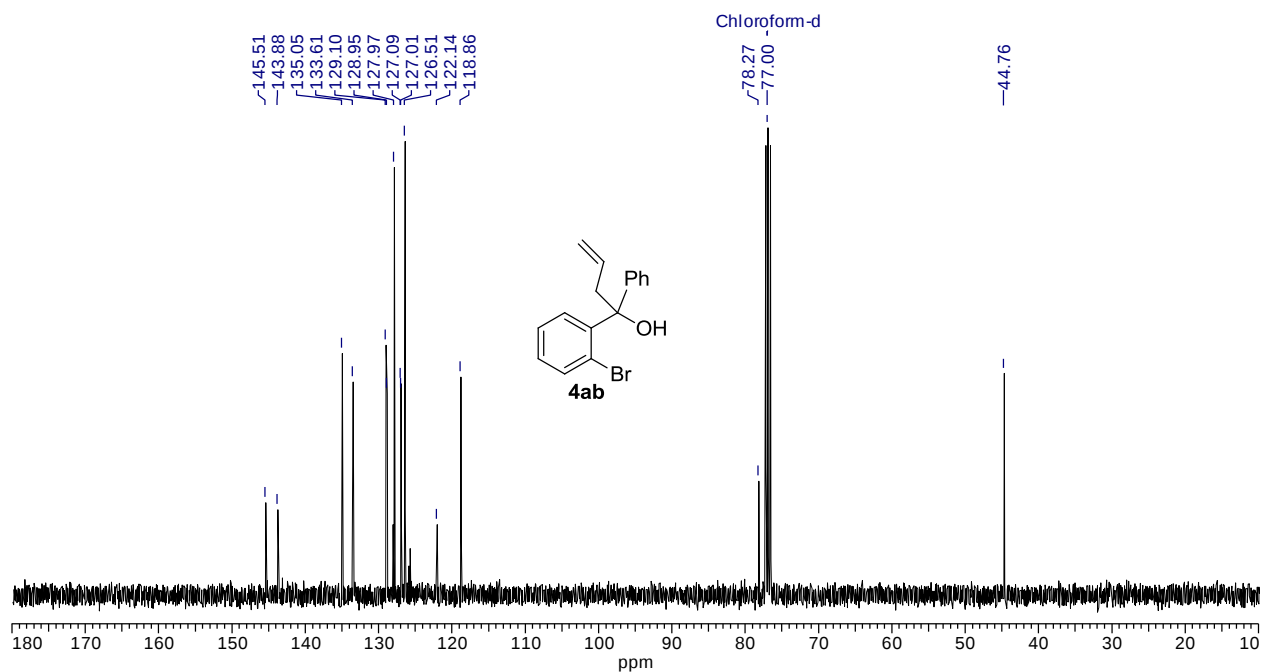




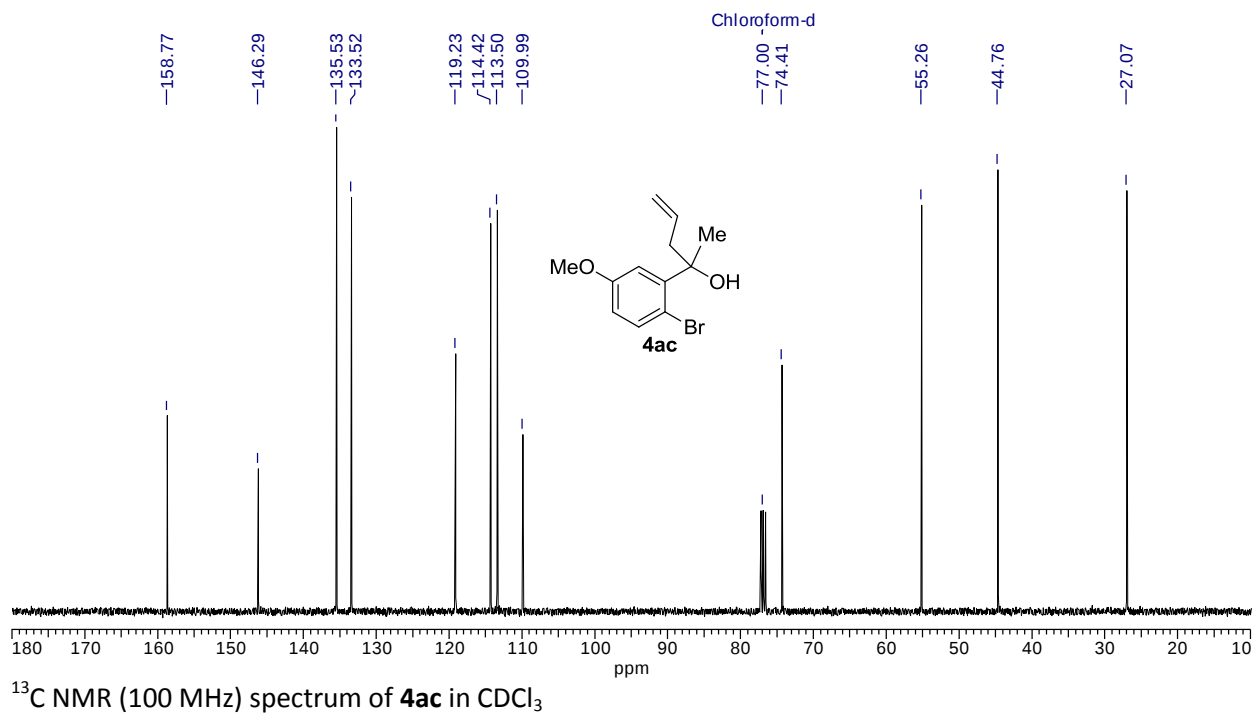
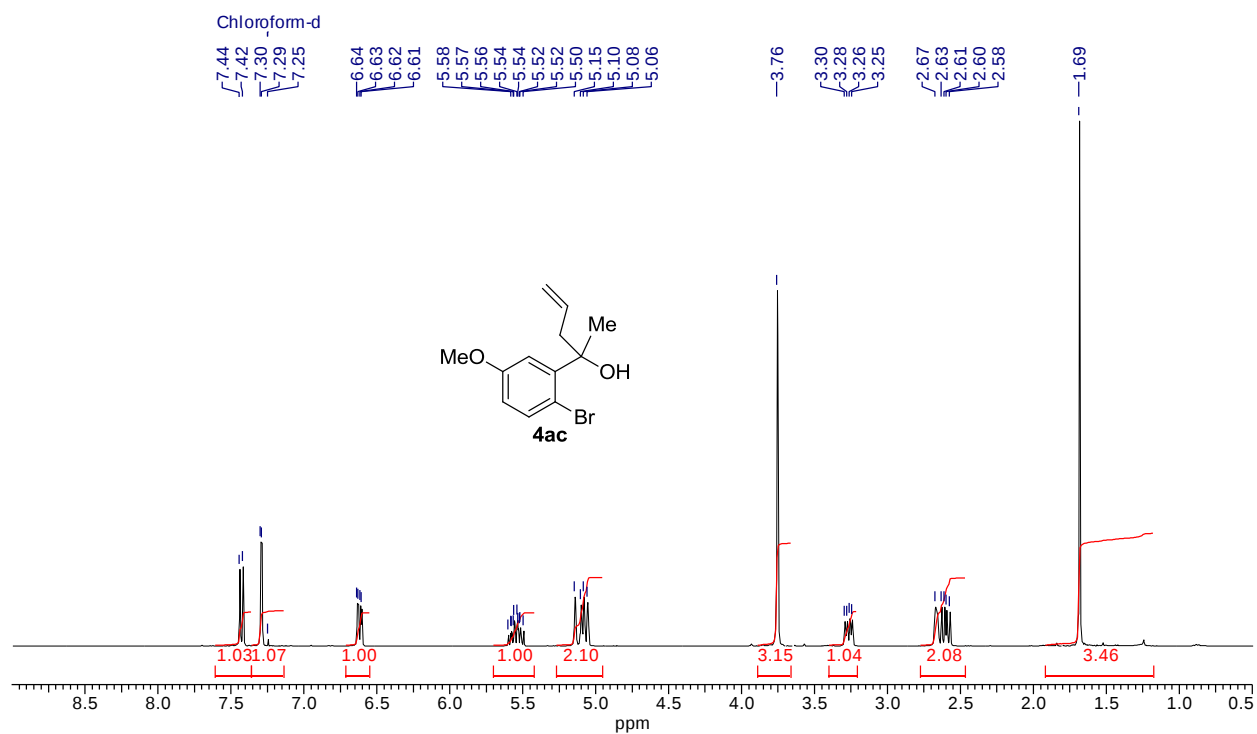


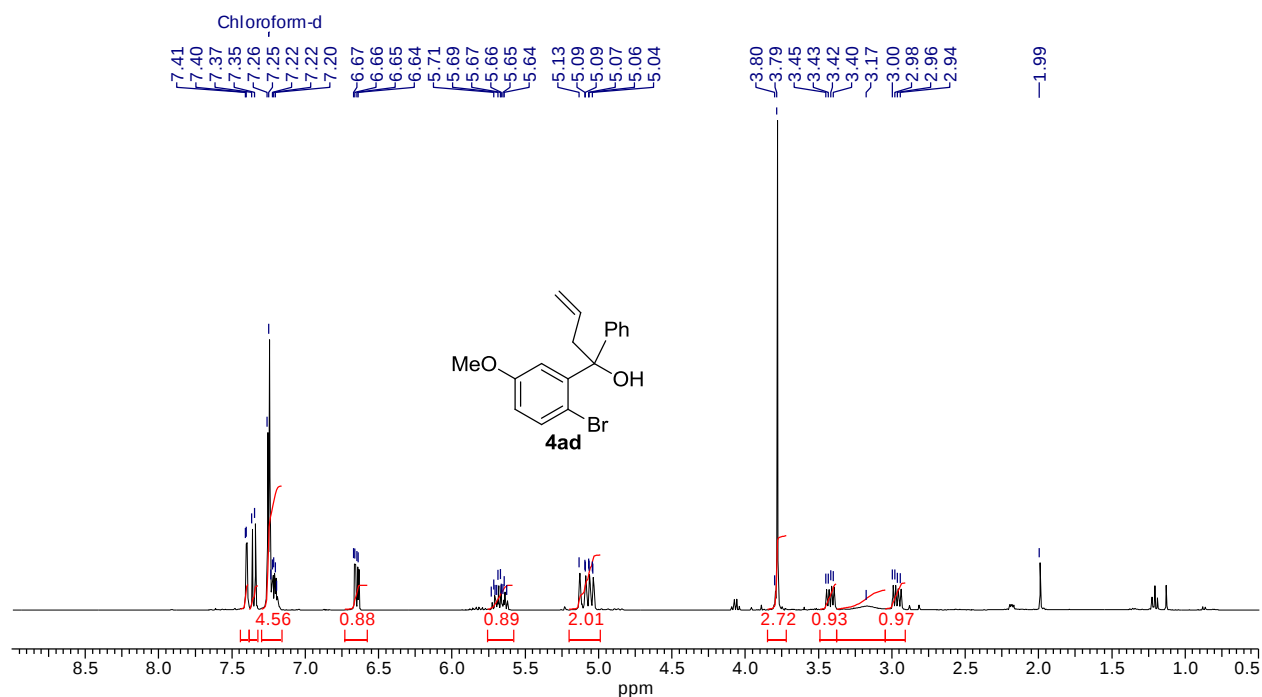


¹H NMR (400 MHz) spectrum of **4ab** in CDCl₃

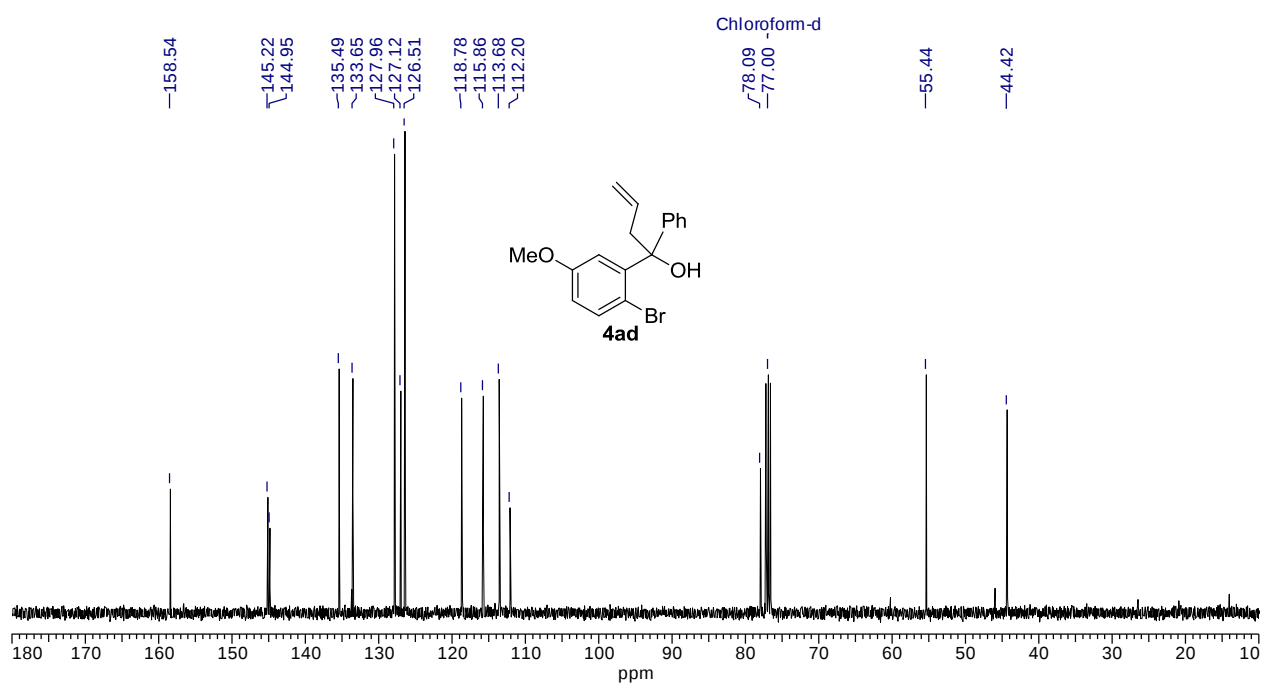


¹³C NMR (100 MHz) spectrum of **4ab** in CDCl₃

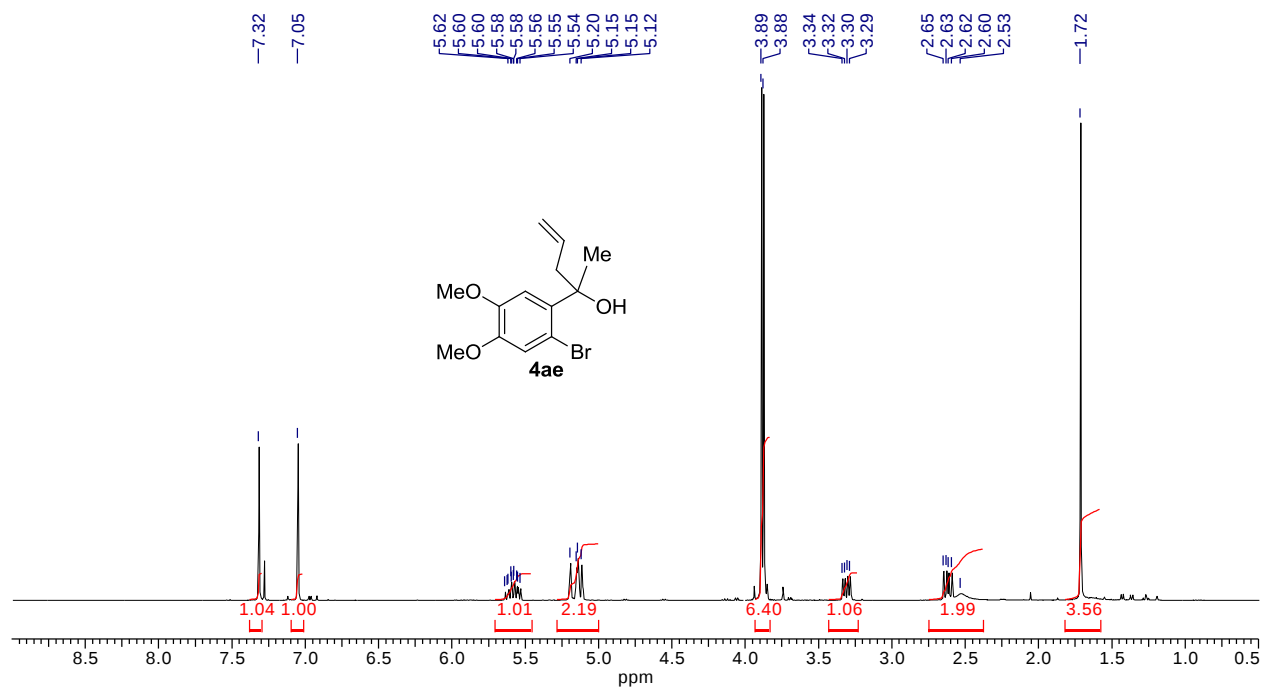




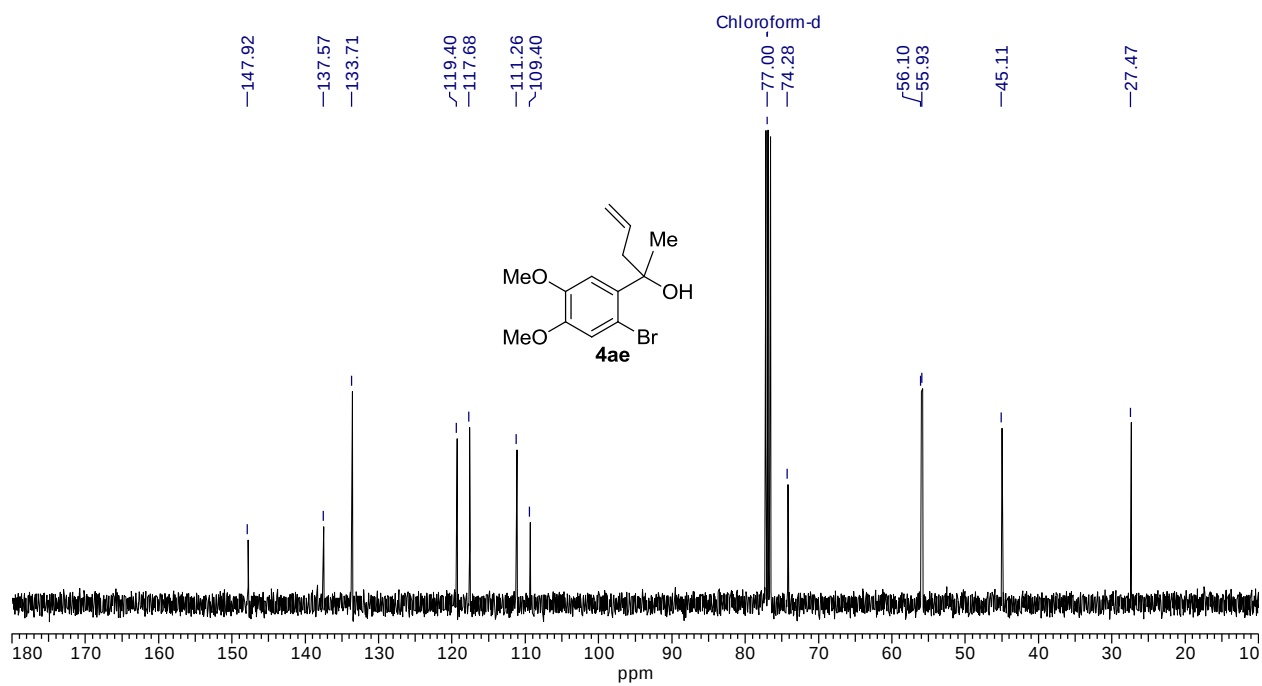
¹H NMR (400 MHz) spectrum of **4ad** in CDCl₃



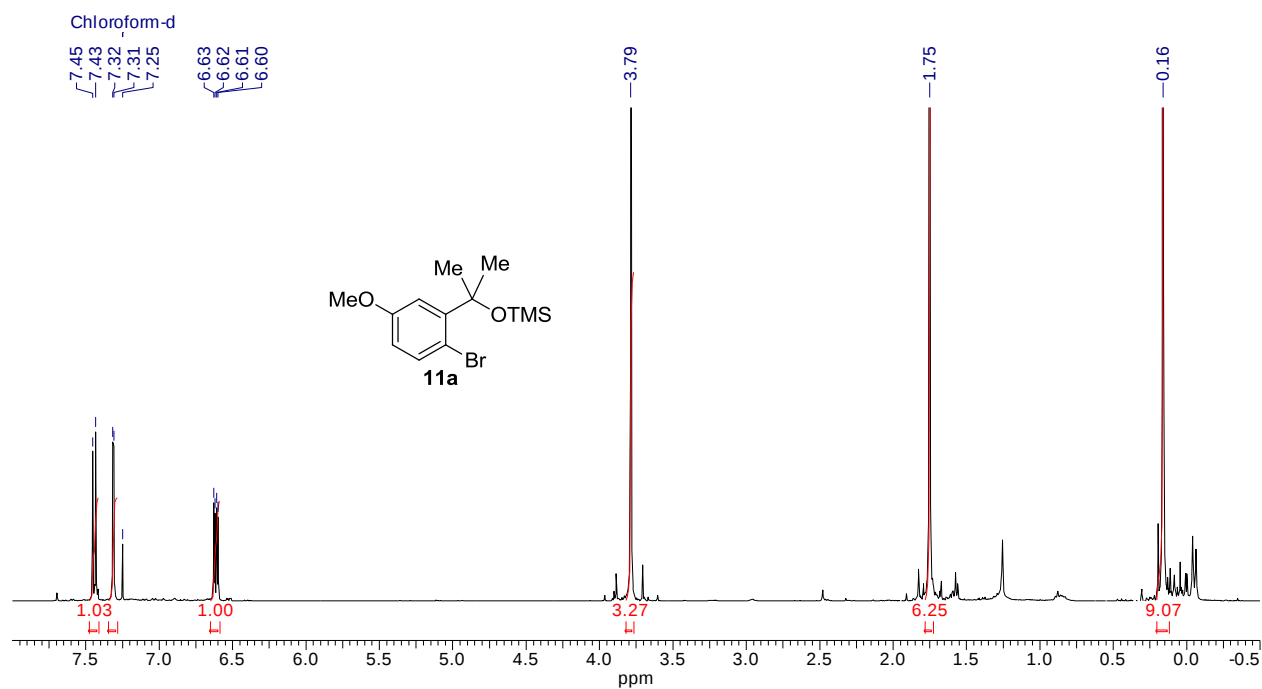
¹³C NMR (100 MHz) spectrum of **4ad** in CDCl₃



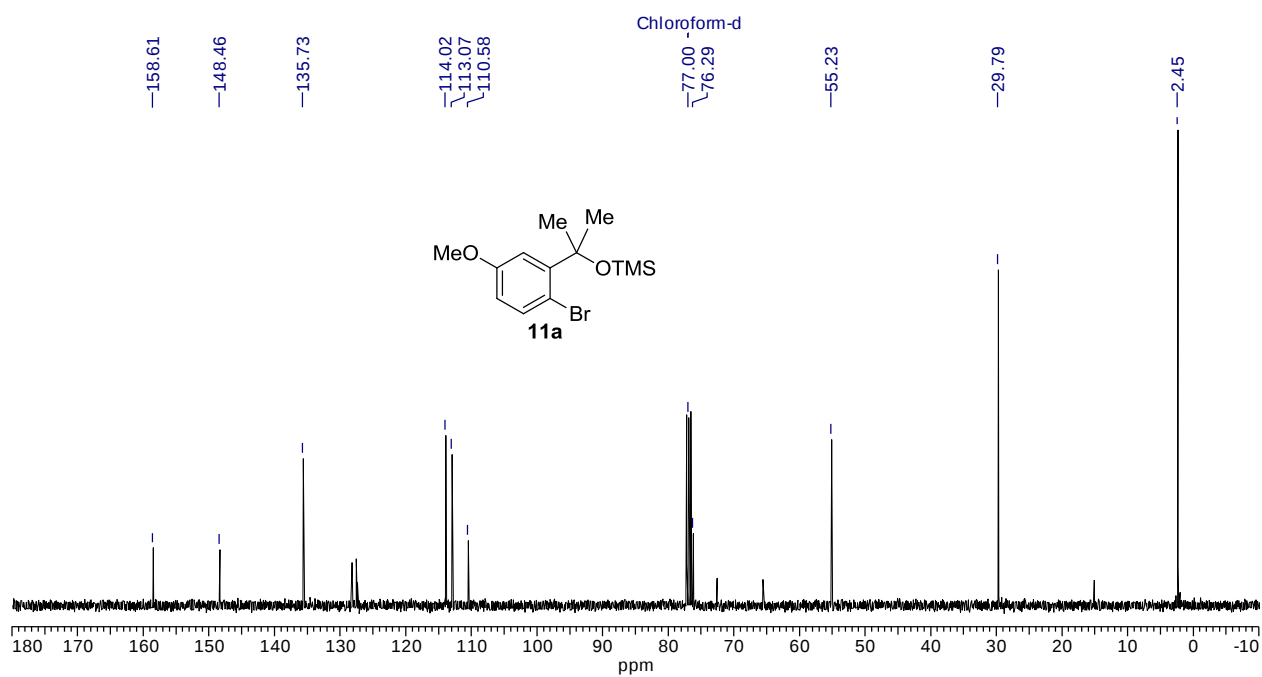
¹H NMR (400 MHz) spectrum of **4ae** in CDCl₃



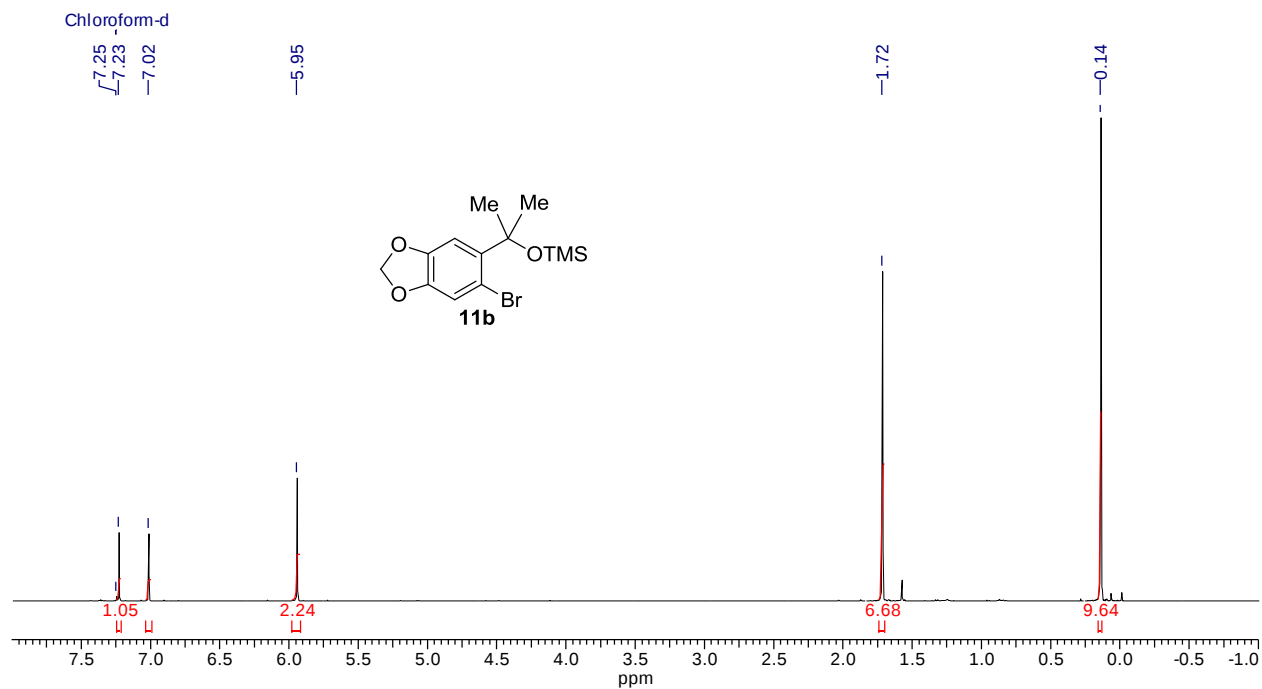
¹³C NMR (100 MHz) spectrum of **4ae** in CDCl₃



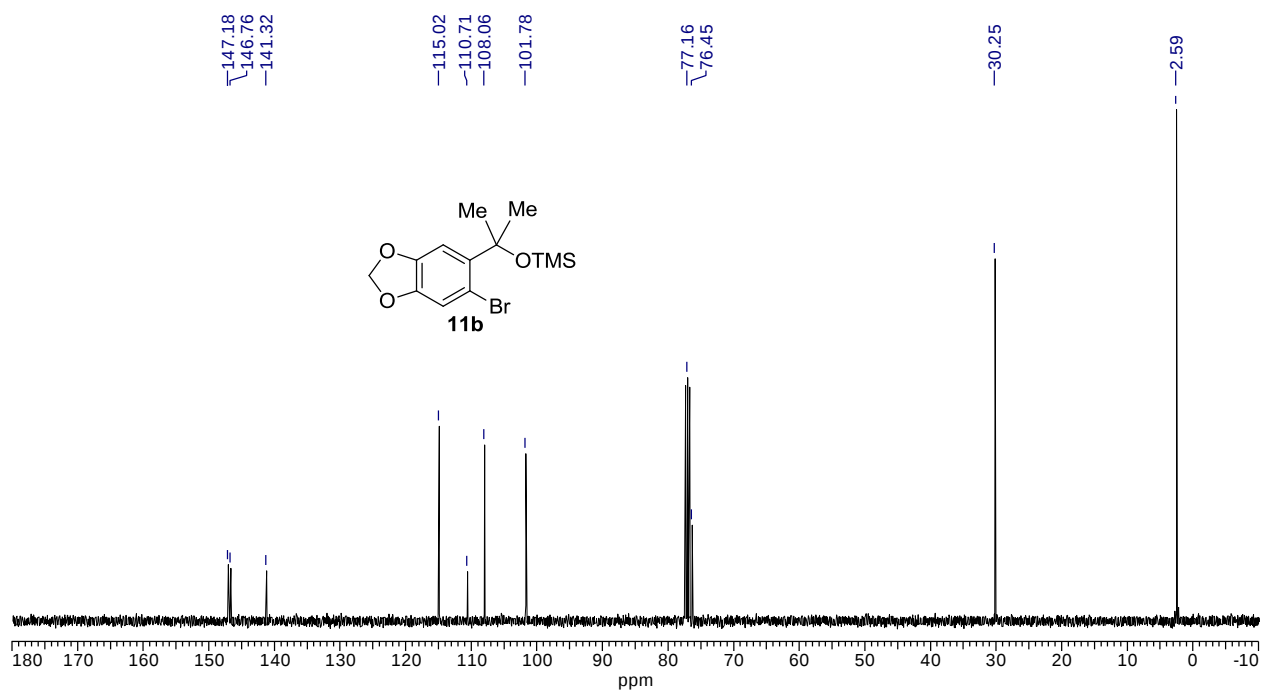
^1H NMR (400 MHz) spectrum of **11a** in CDCl_3



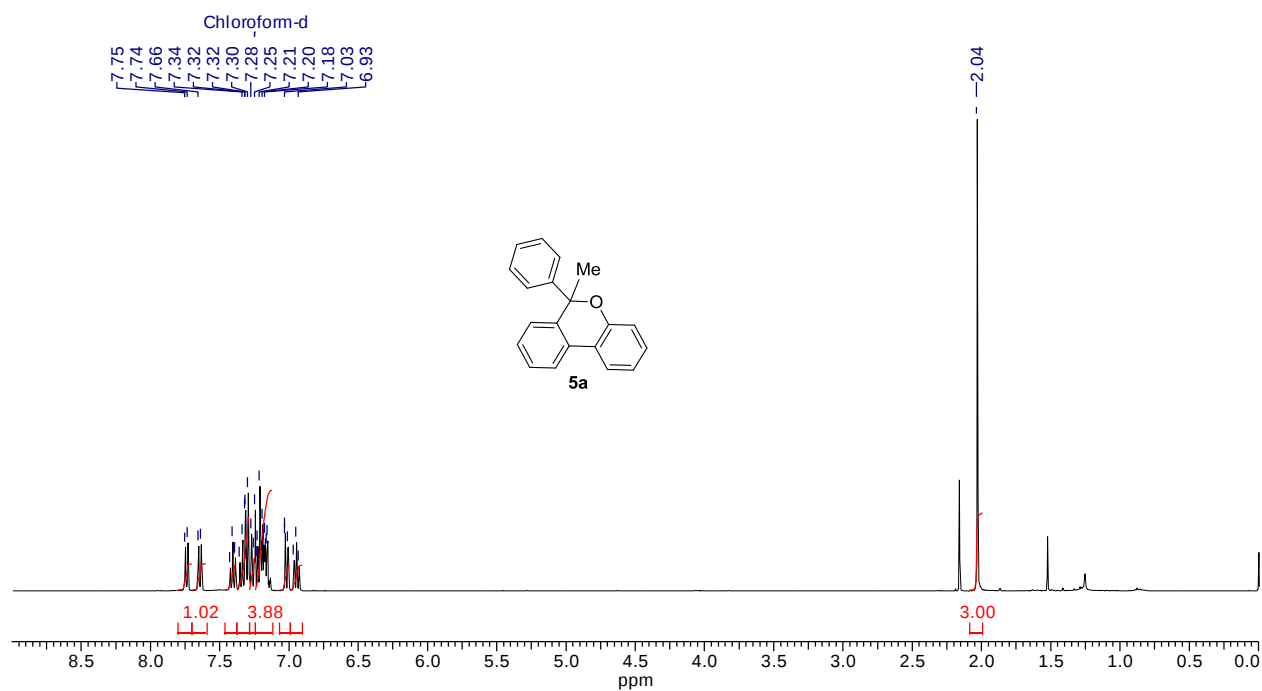
^{13}C NMR (100 MHz) spectrum of **11a** in CDCl_3



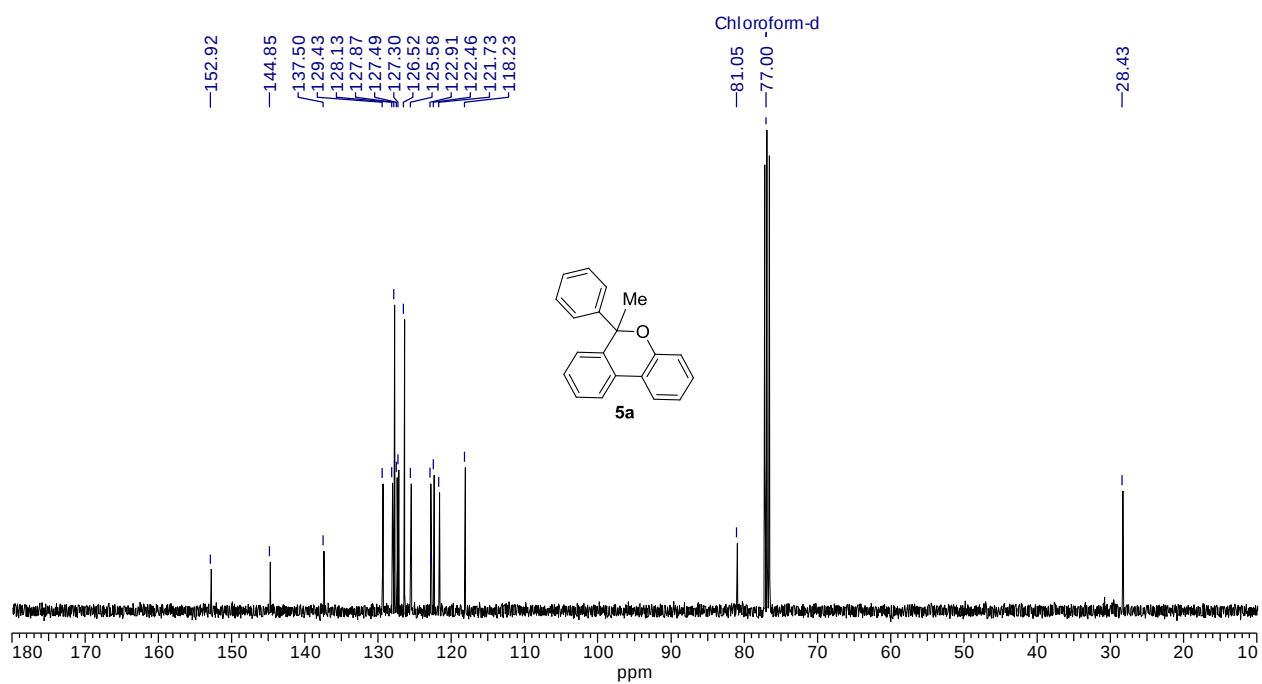
^1H NMR (400 MHz) spectrum of **11b** in CDCl_3



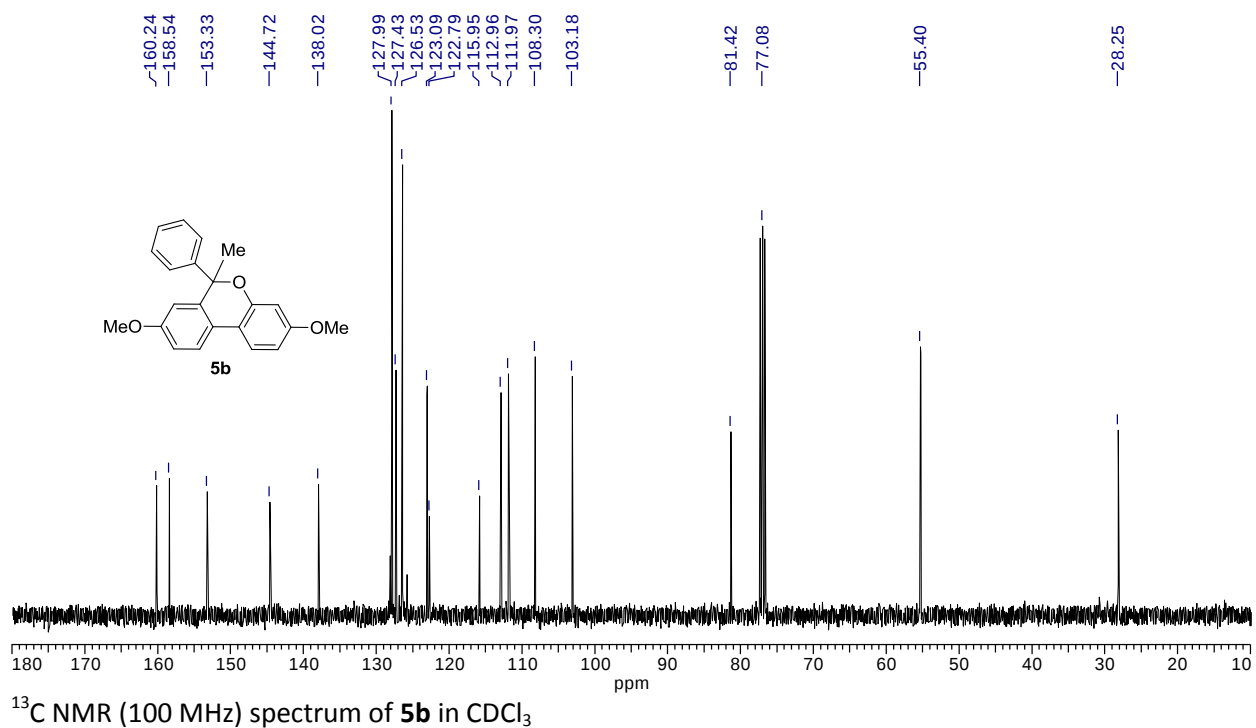
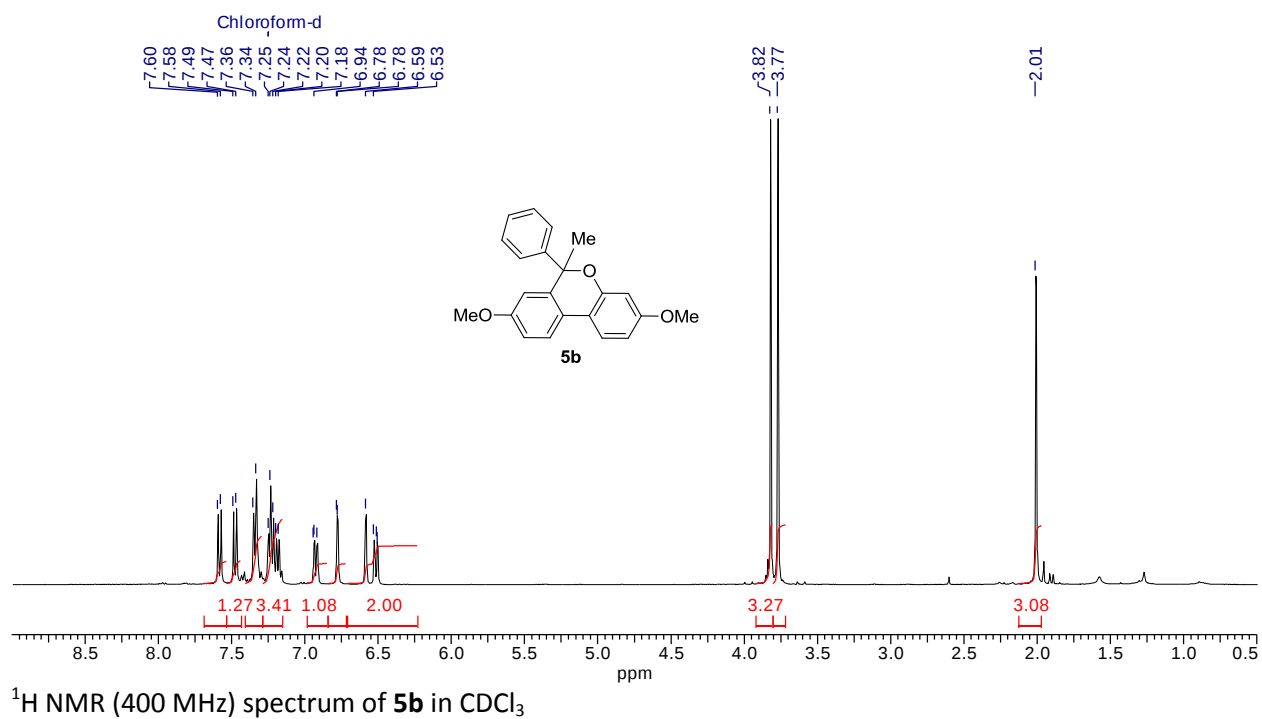
^{13}C NMR (100 MHz) spectrum of **11b** in CDCl_3

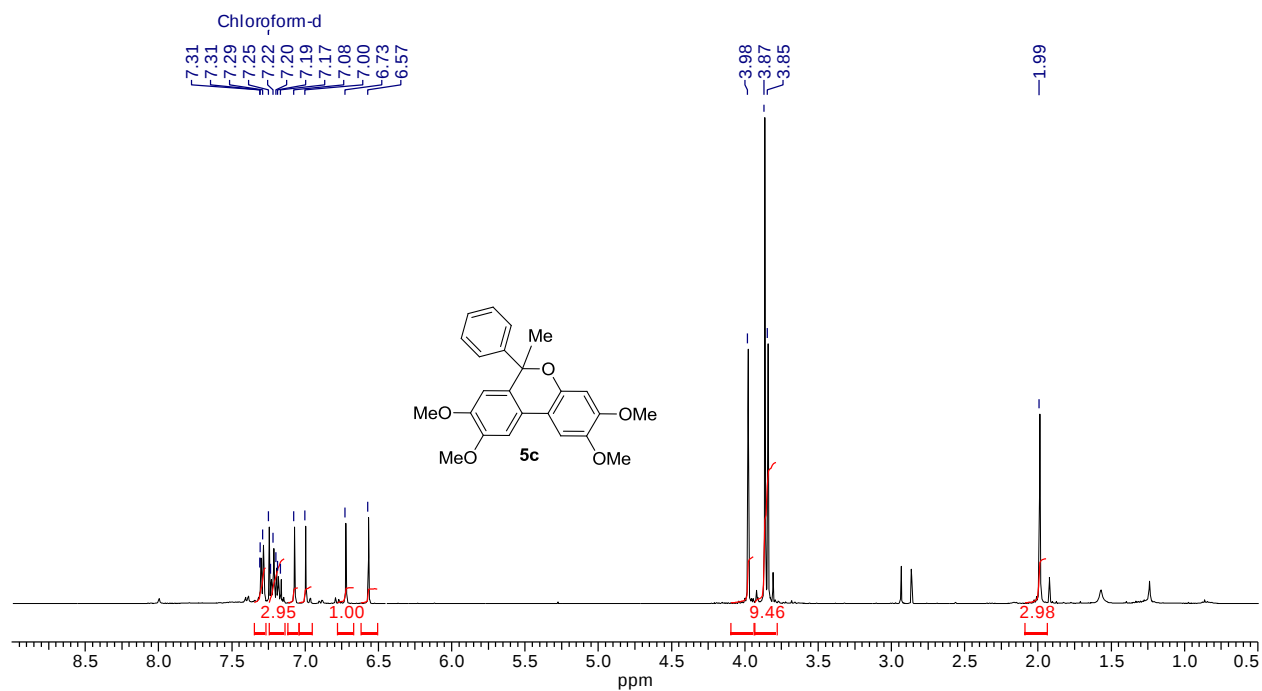


^1H NMR (400 MHz) spectrum of **5a** in CDCl_3

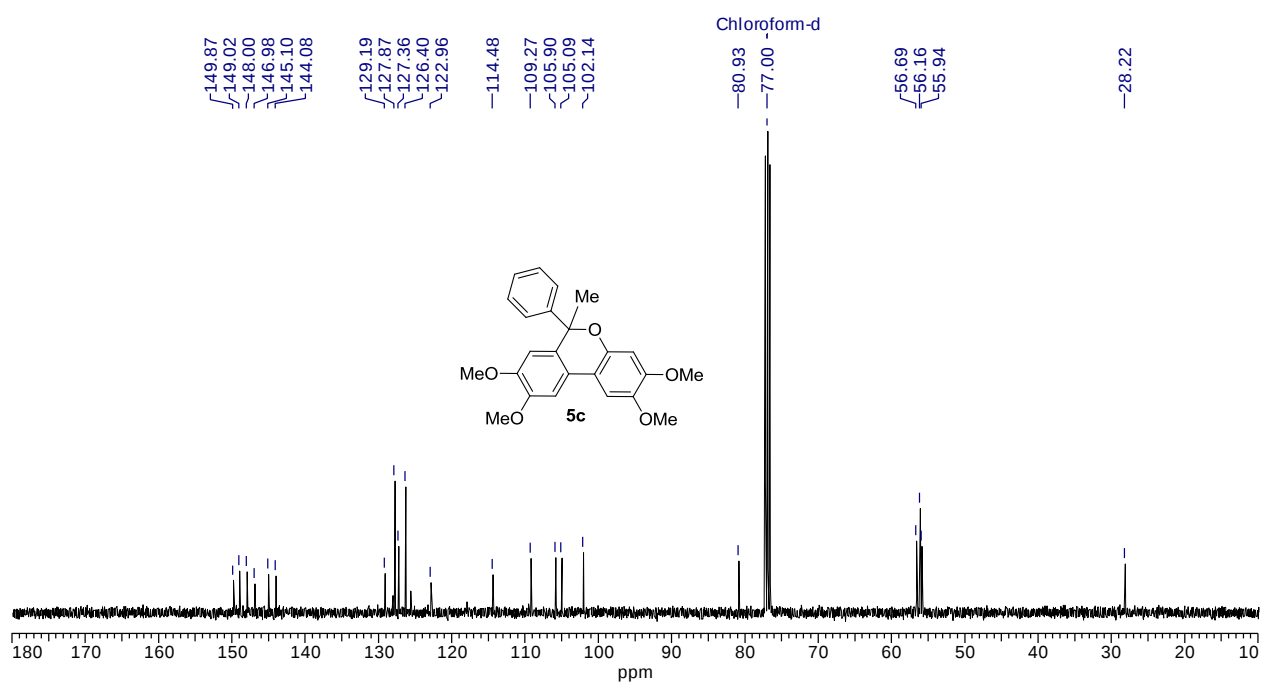


^{13}C NMR (100 MHz) spectrum of **5a** in CDCl_3

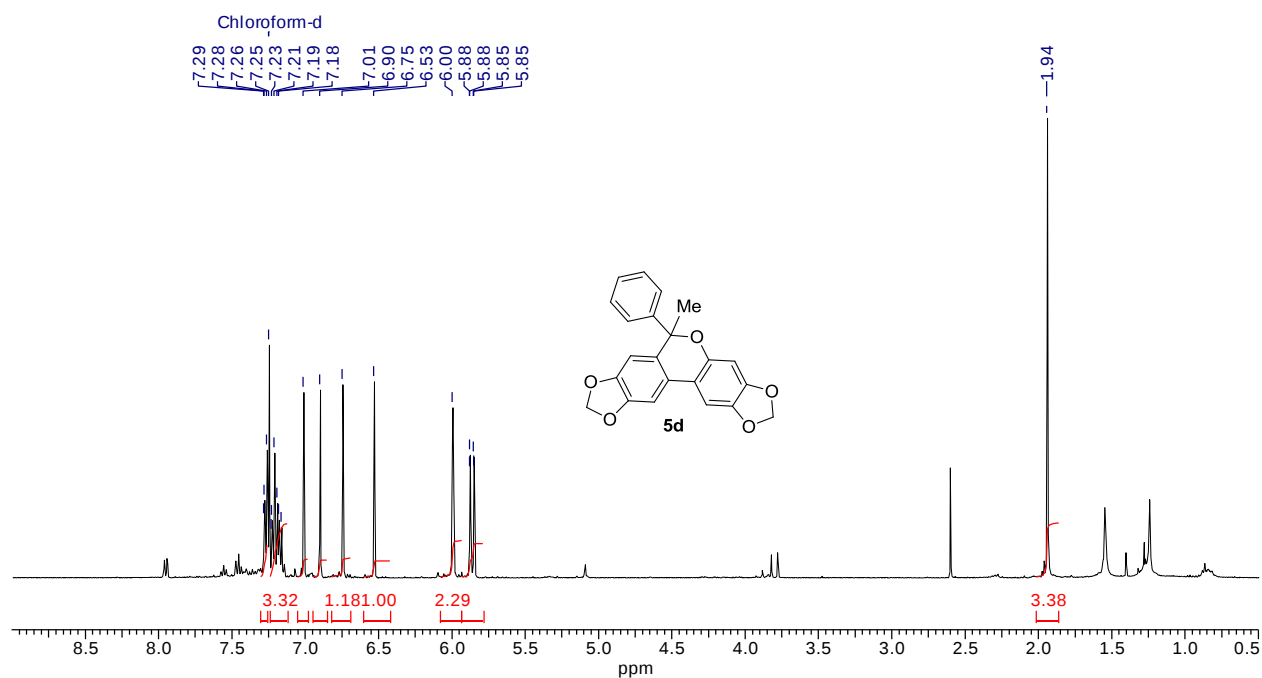




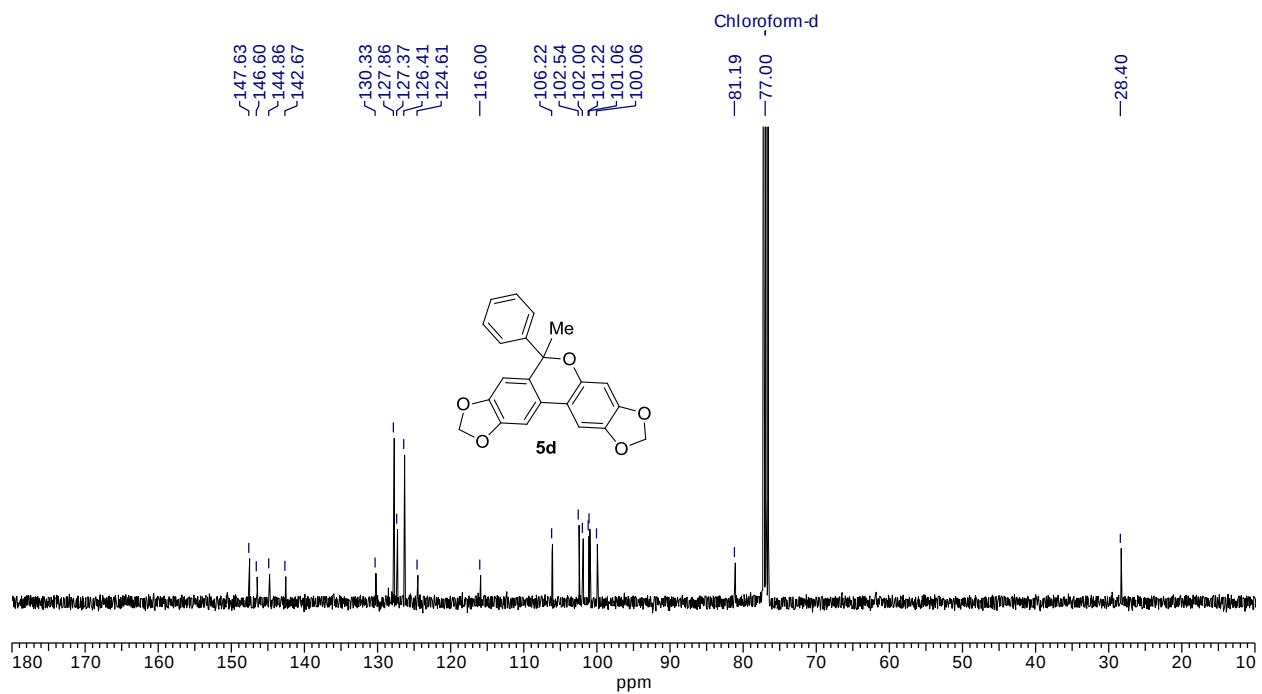
^1H NMR (400 MHz) spectrum of **5c** in CDCl_3



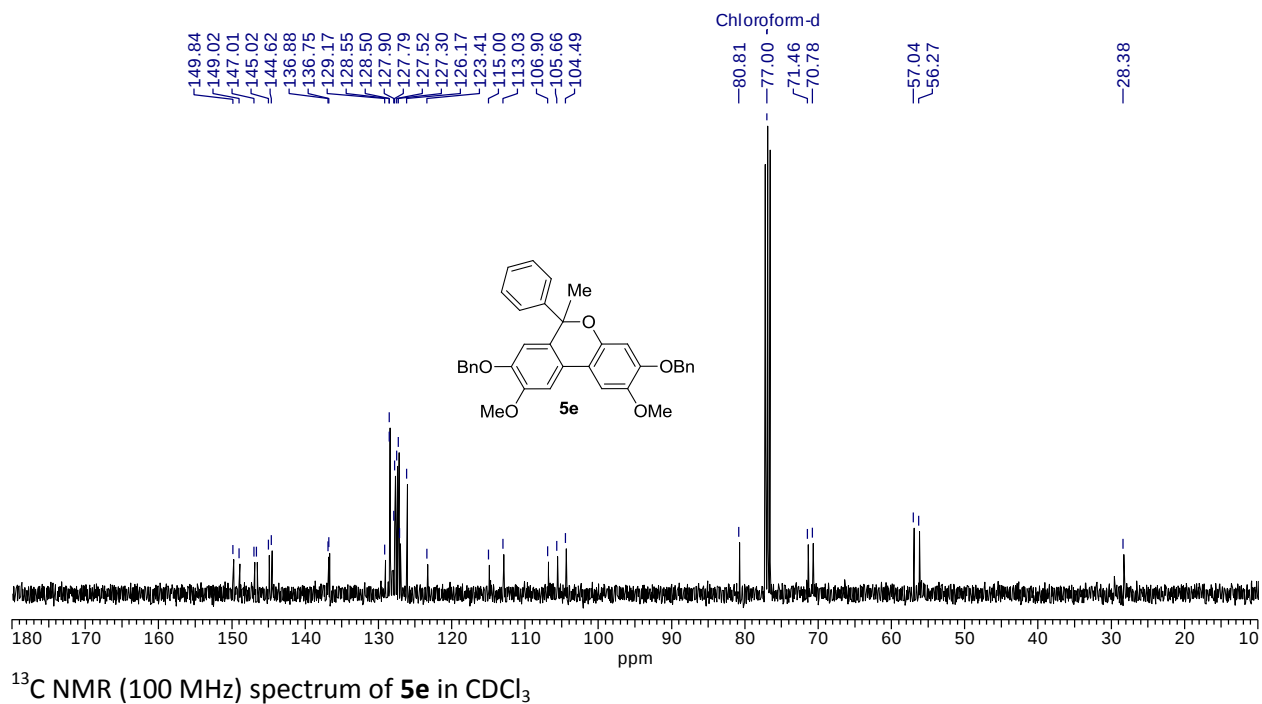
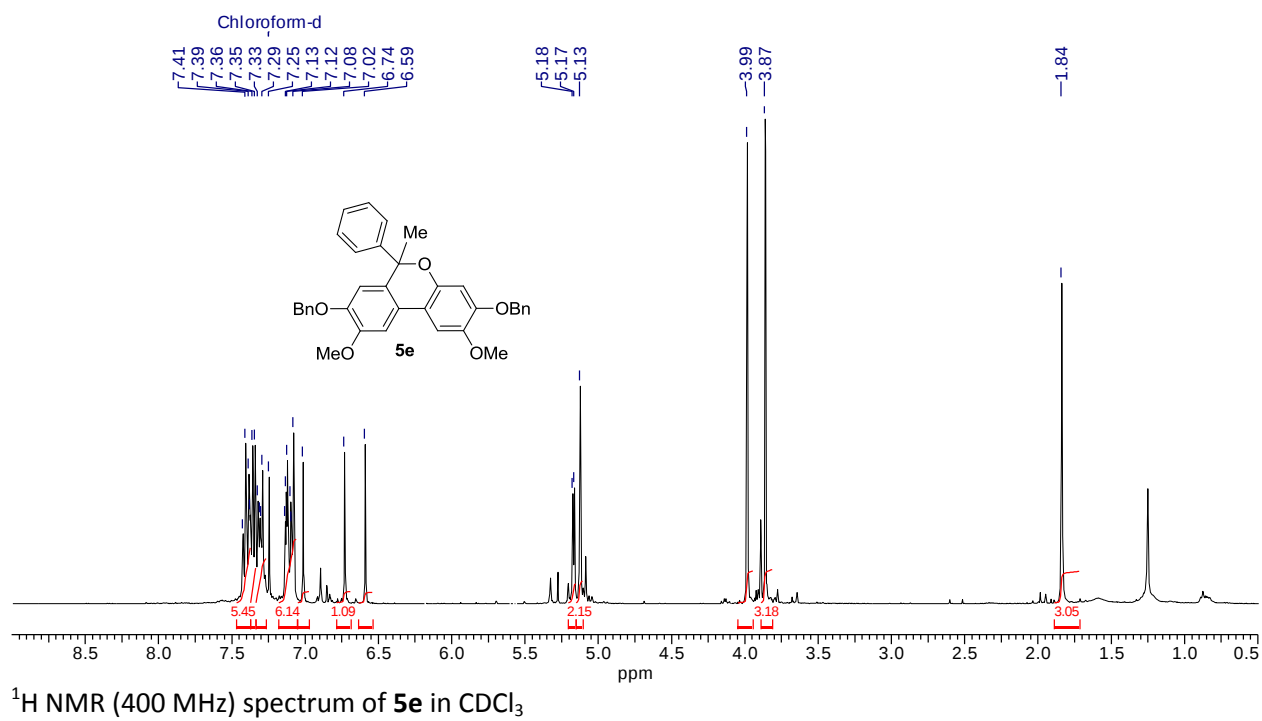
^{13}C NMR (100 MHz) spectrum of **5c** in CDCl_3

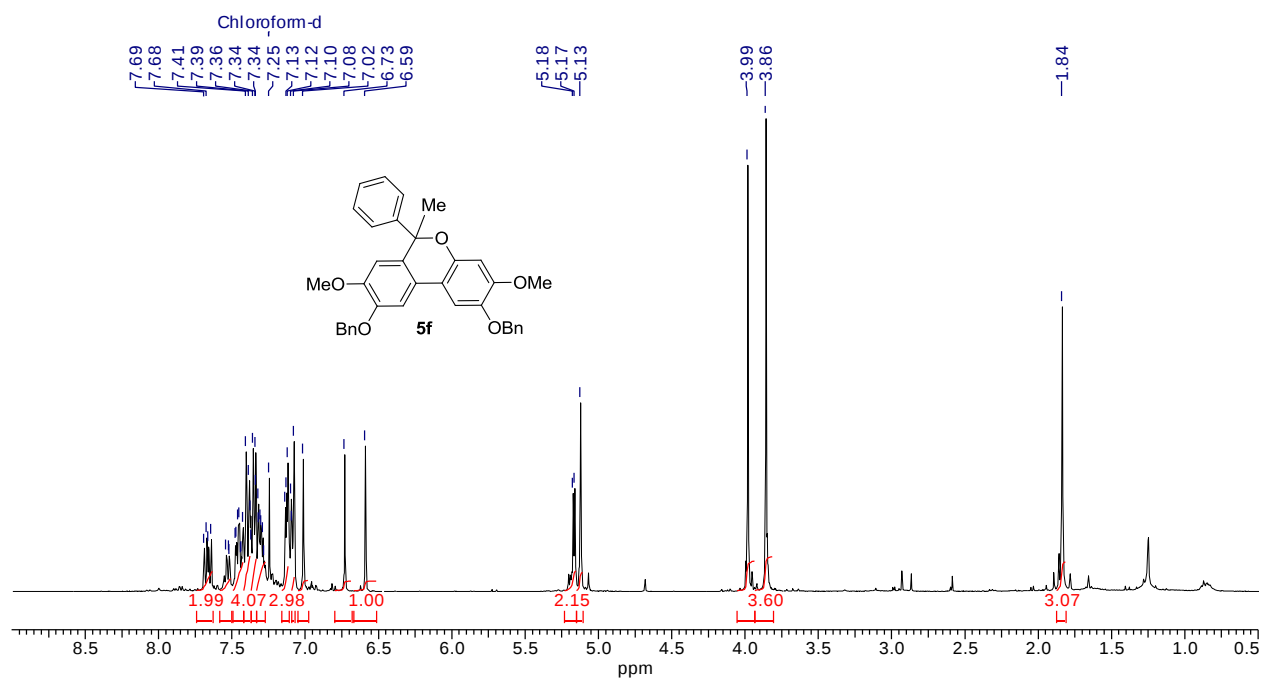


^1H NMR (400 MHz) spectrum of **5d** in CDCl_3

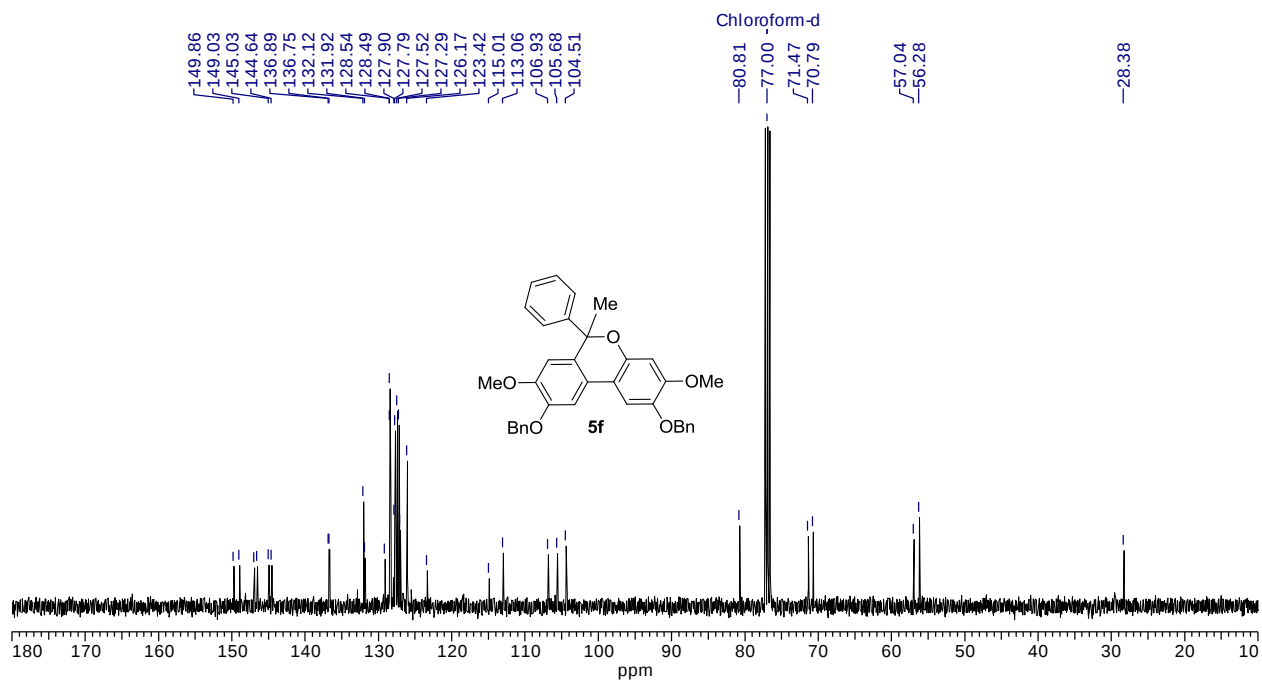


^{13}C NMR (100 MHz) spectrum of **5d** in CDCl_3

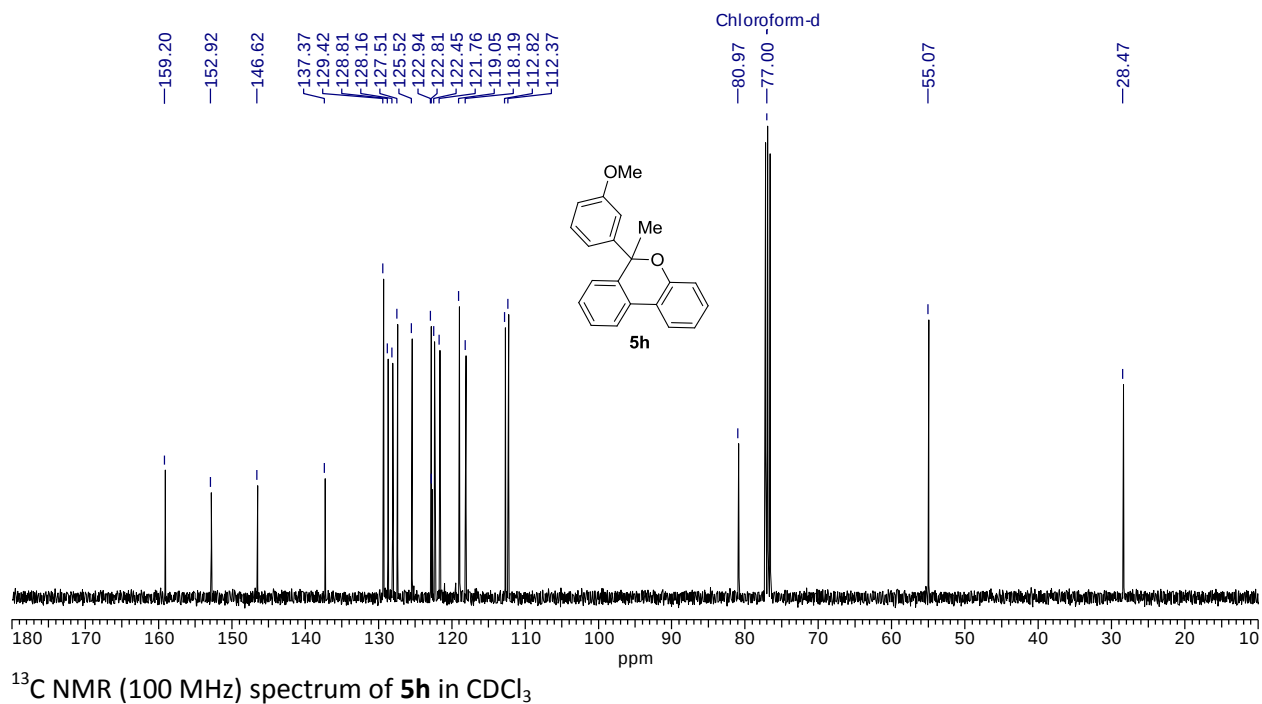
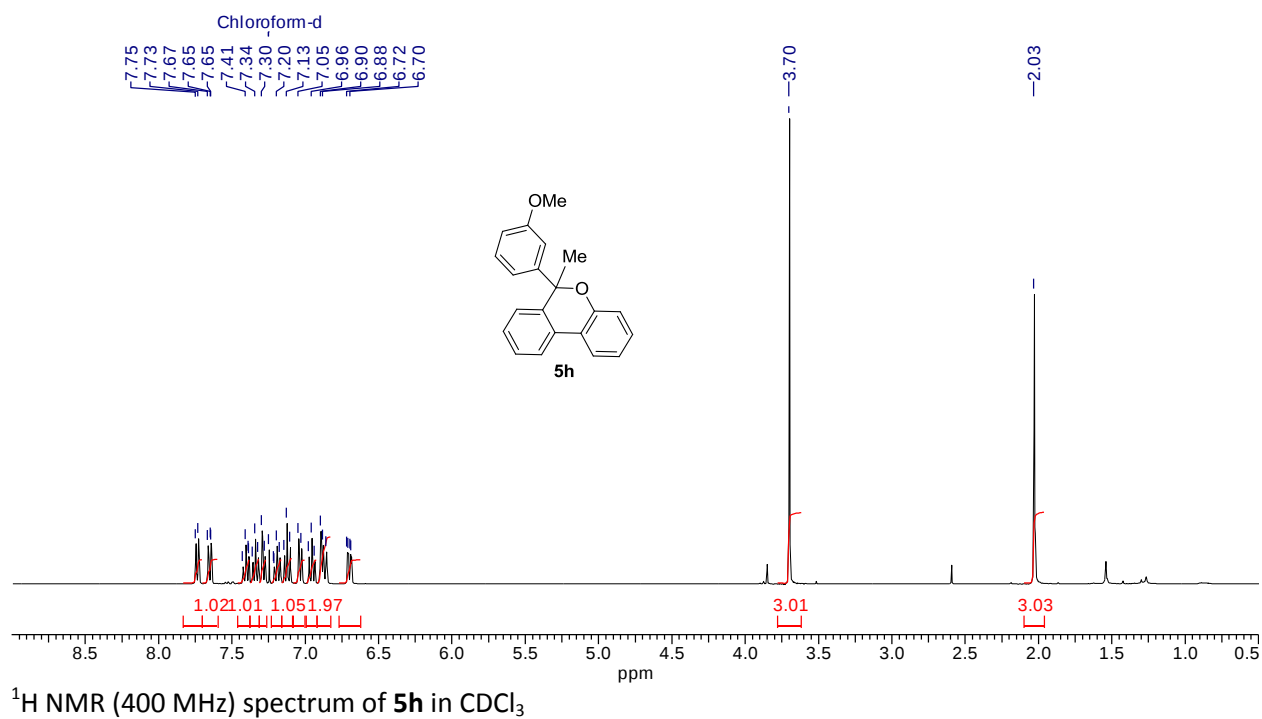


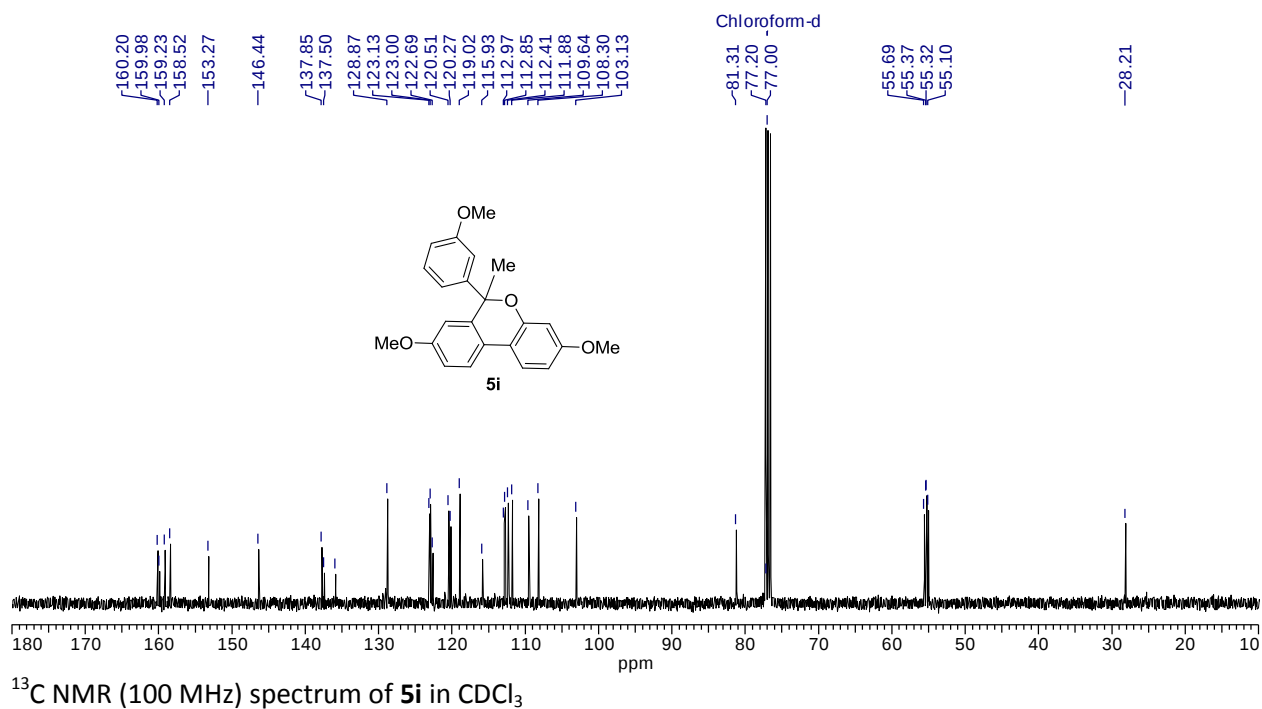
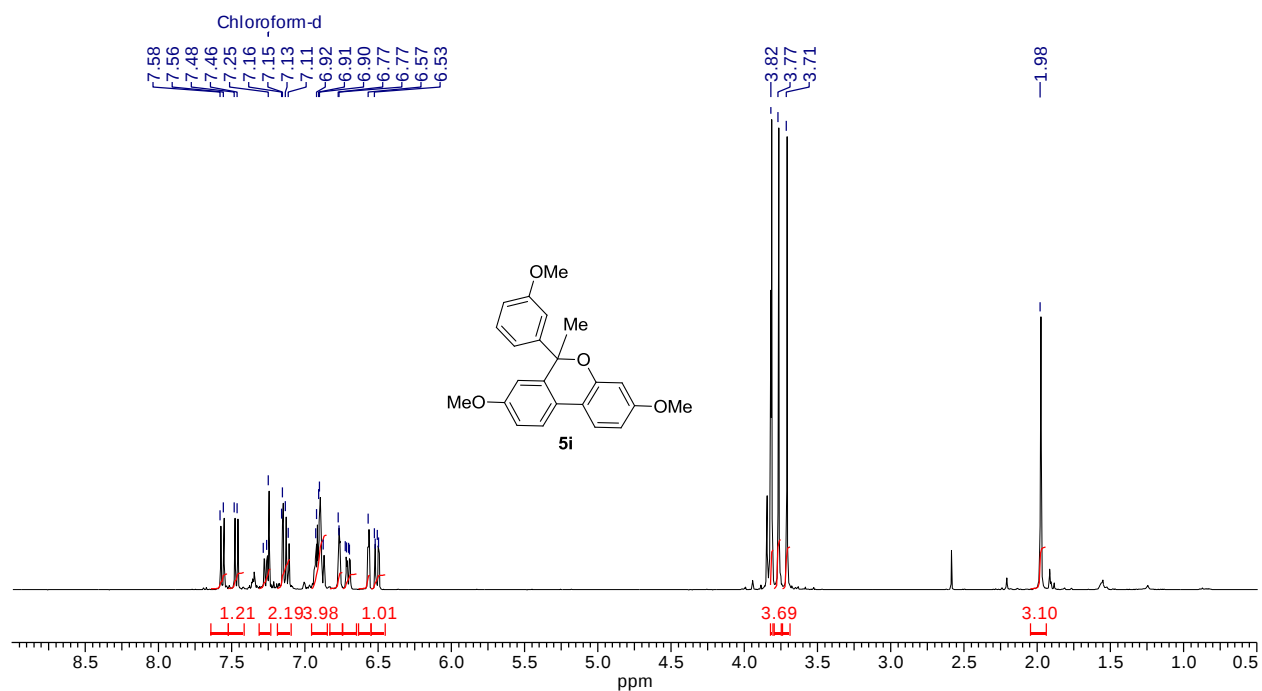


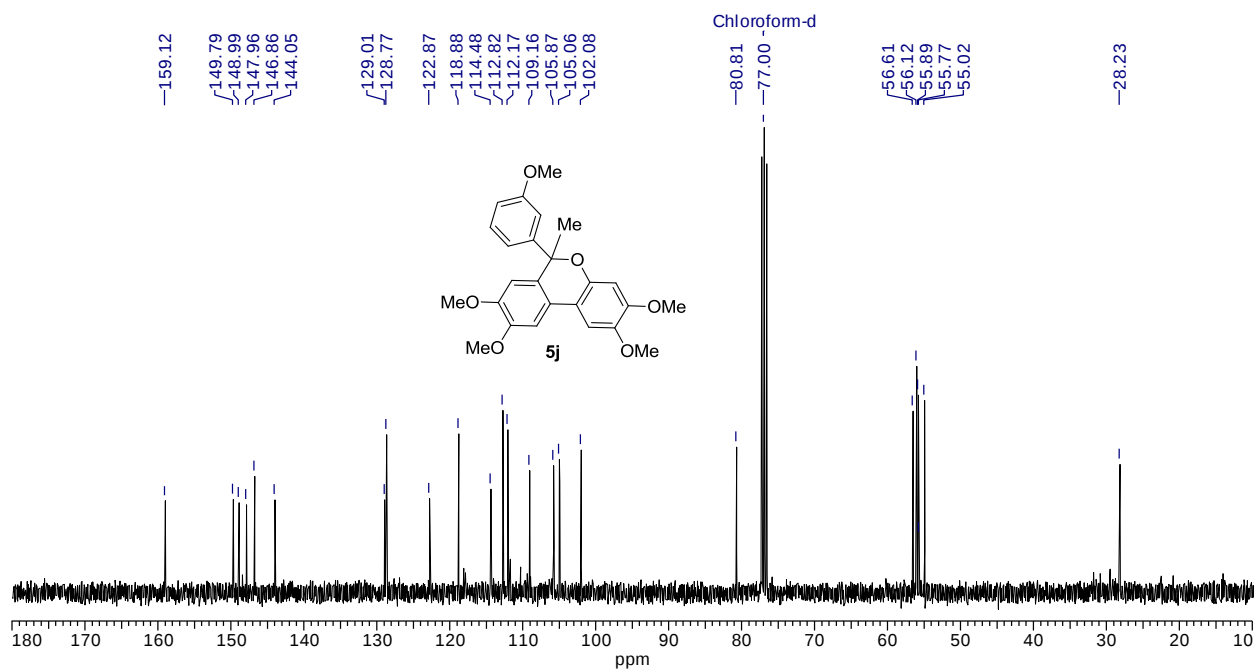
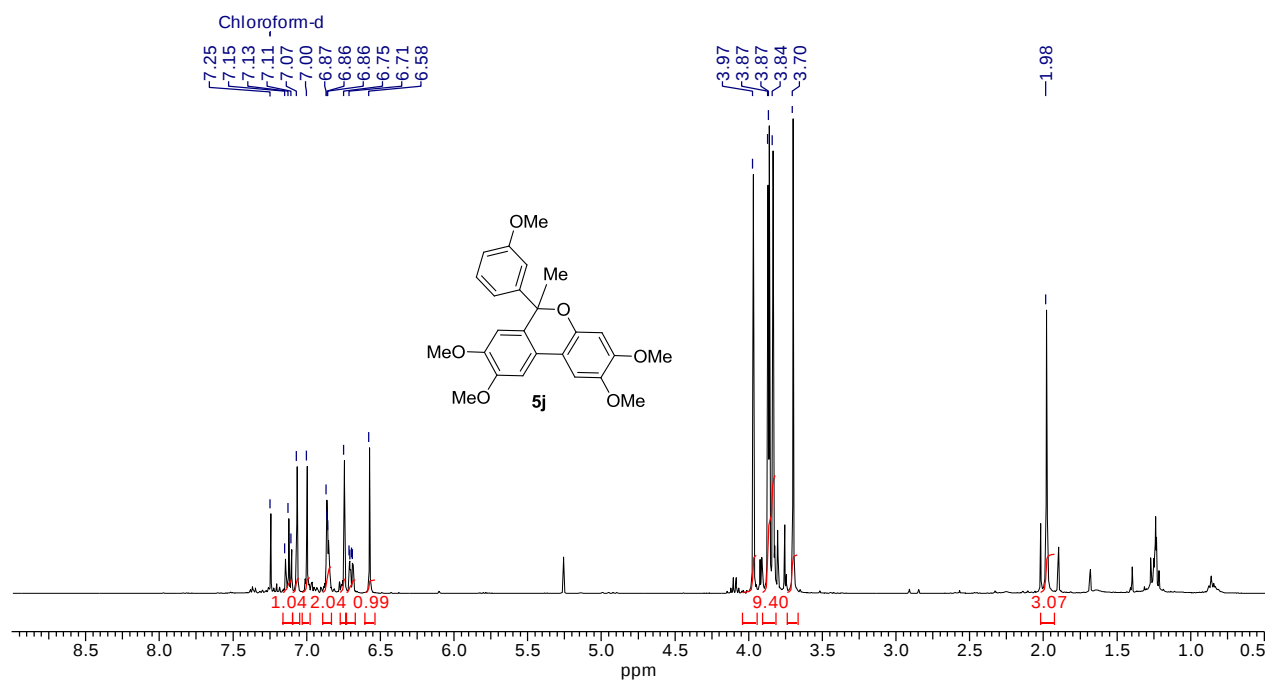
¹H NMR (400 MHz) spectrum of **5f** in CDCl₃

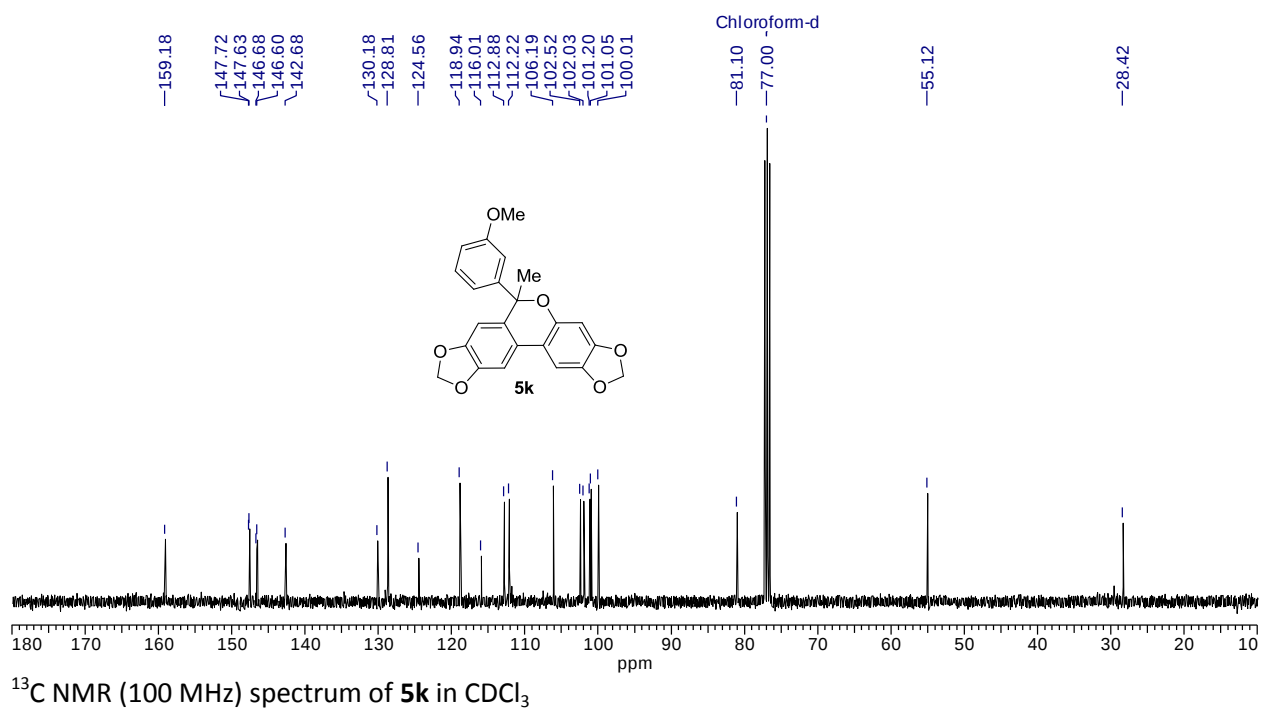
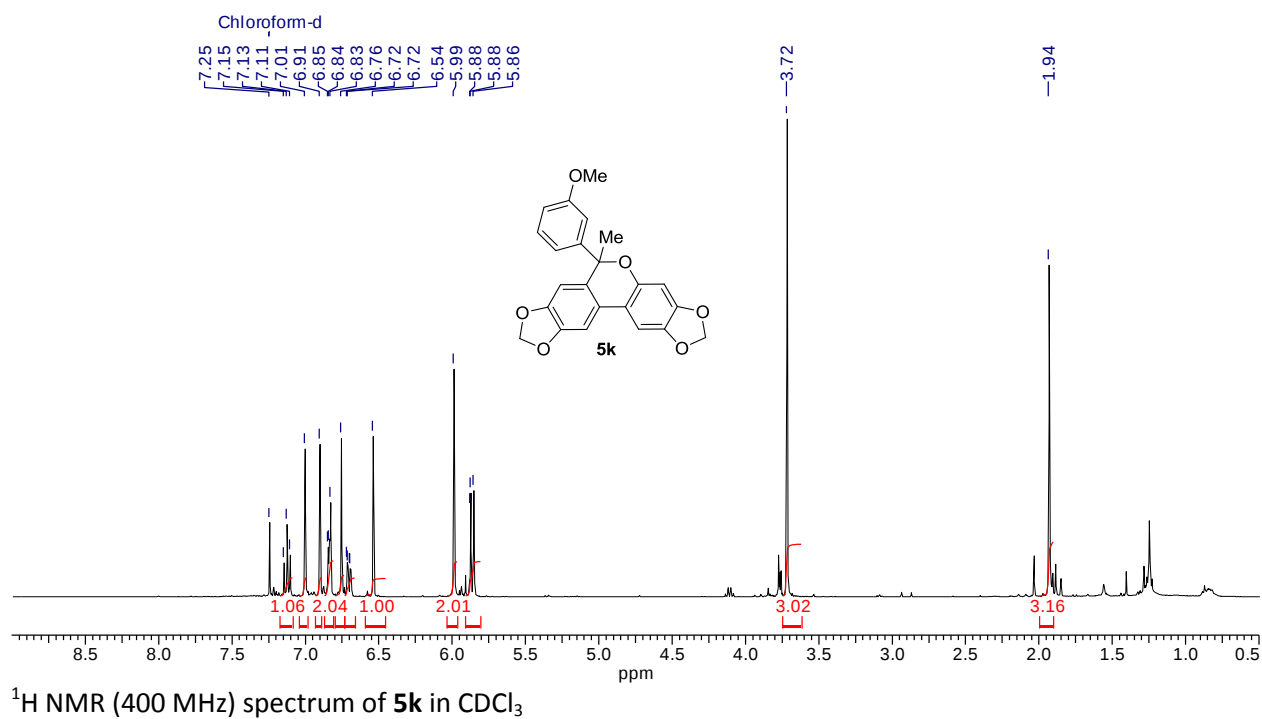


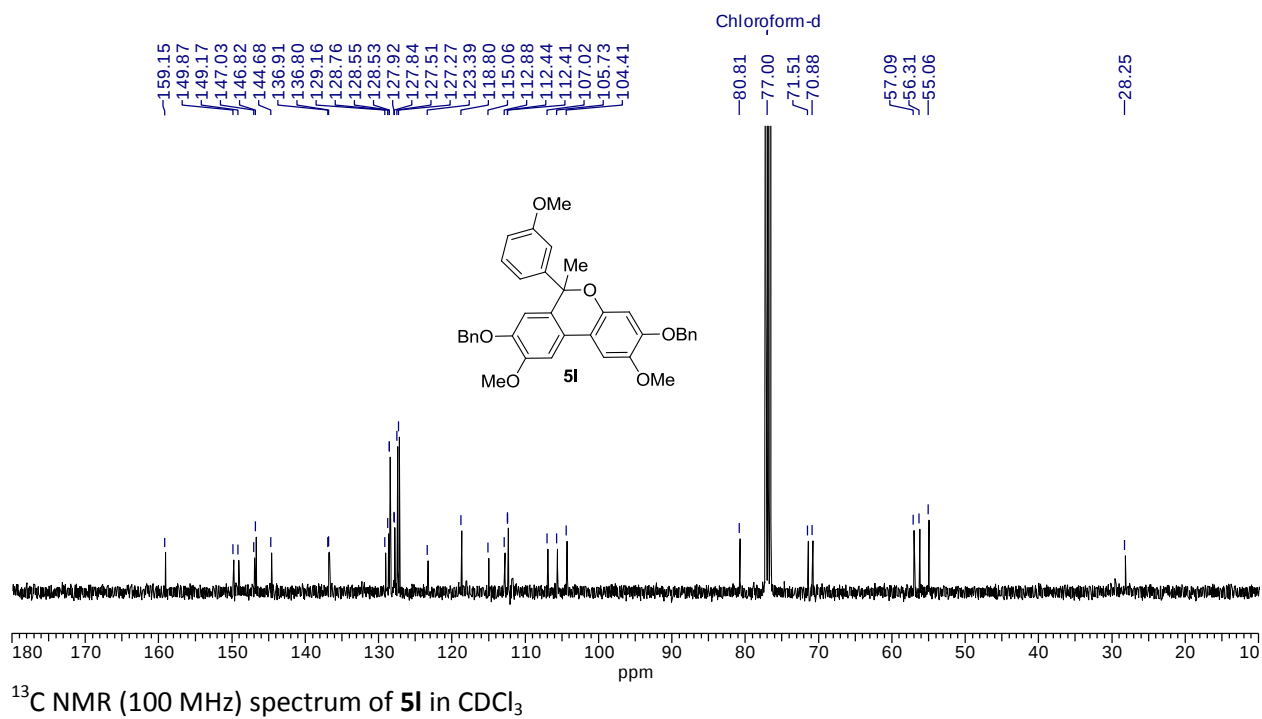
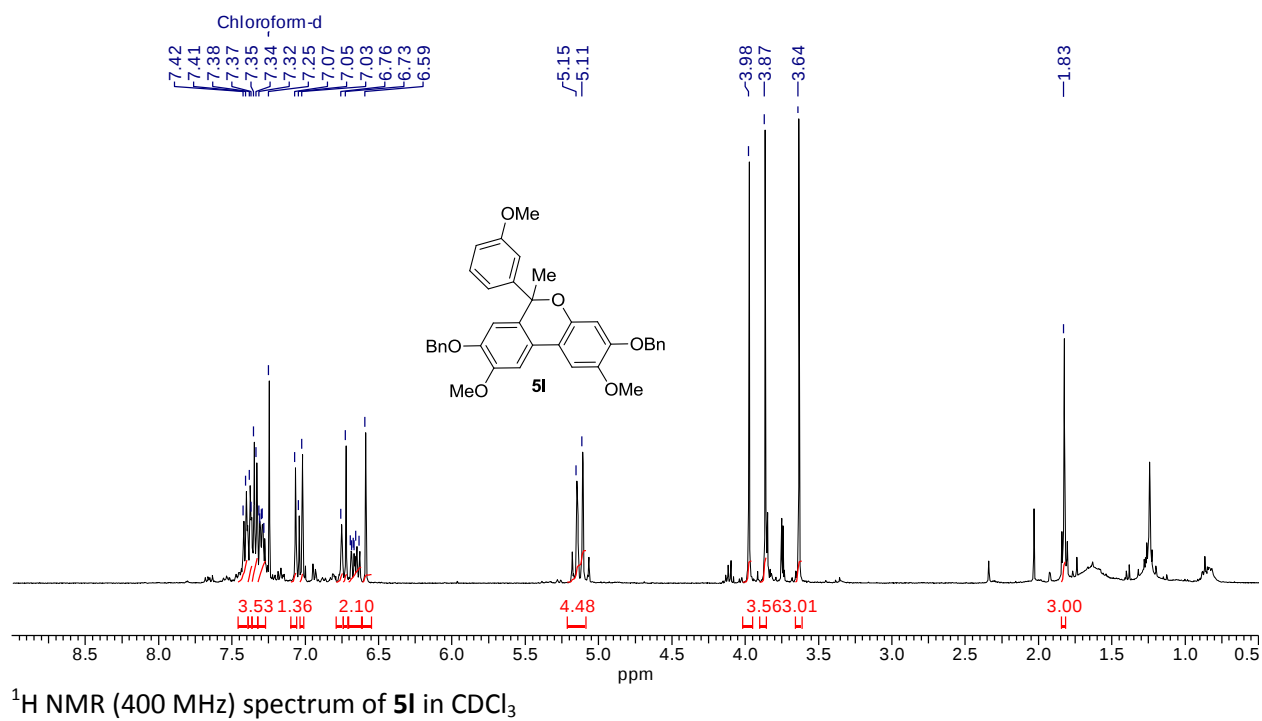
¹³C NMR (100 MHz) spectrum of **5f** in CDCl₃

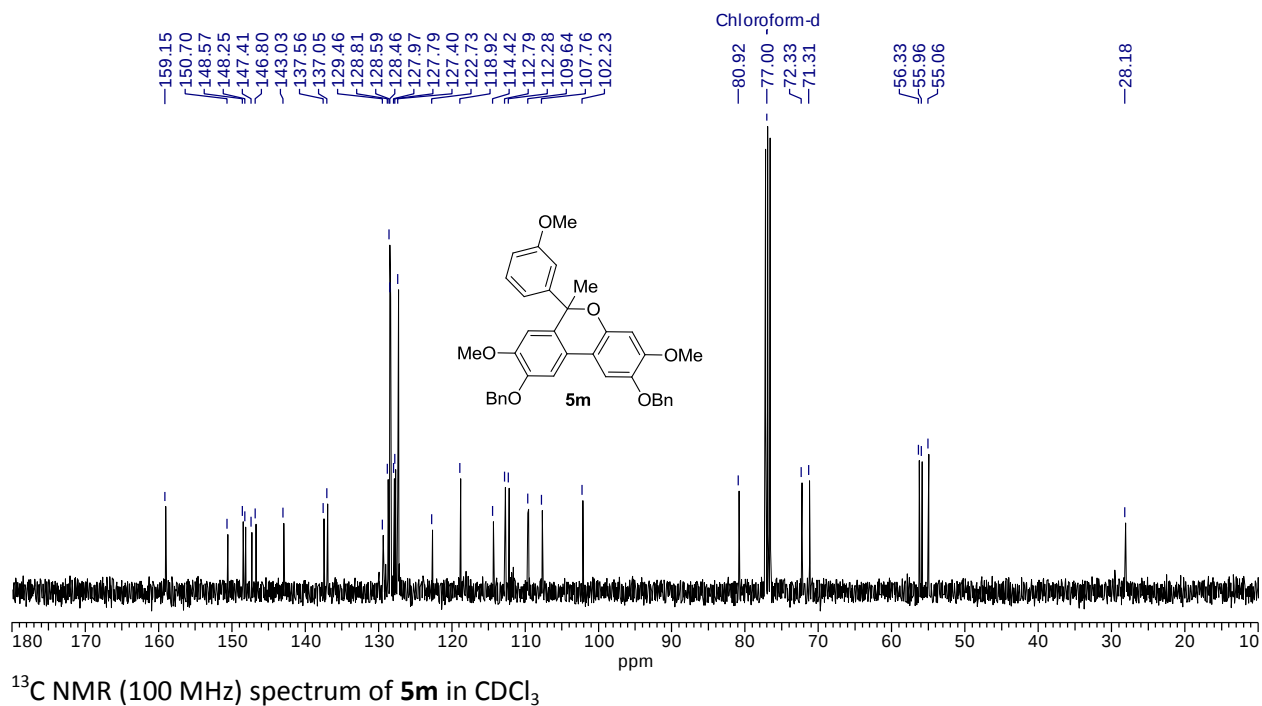
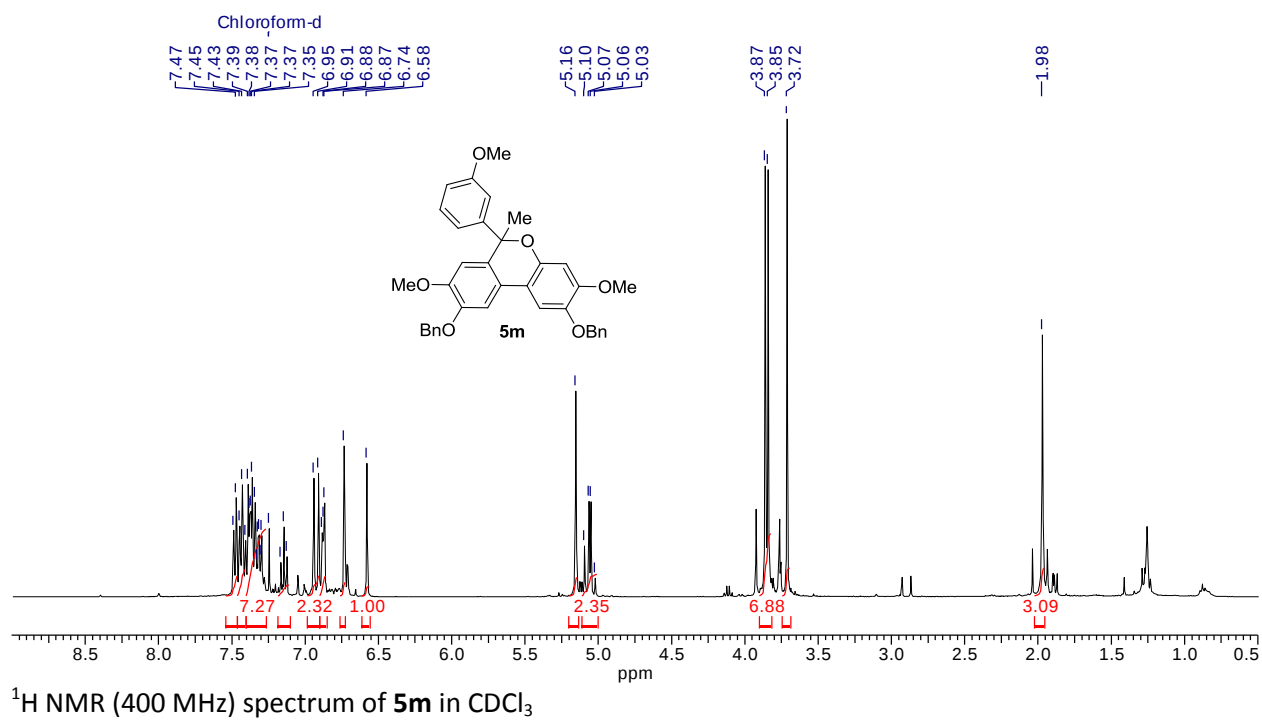


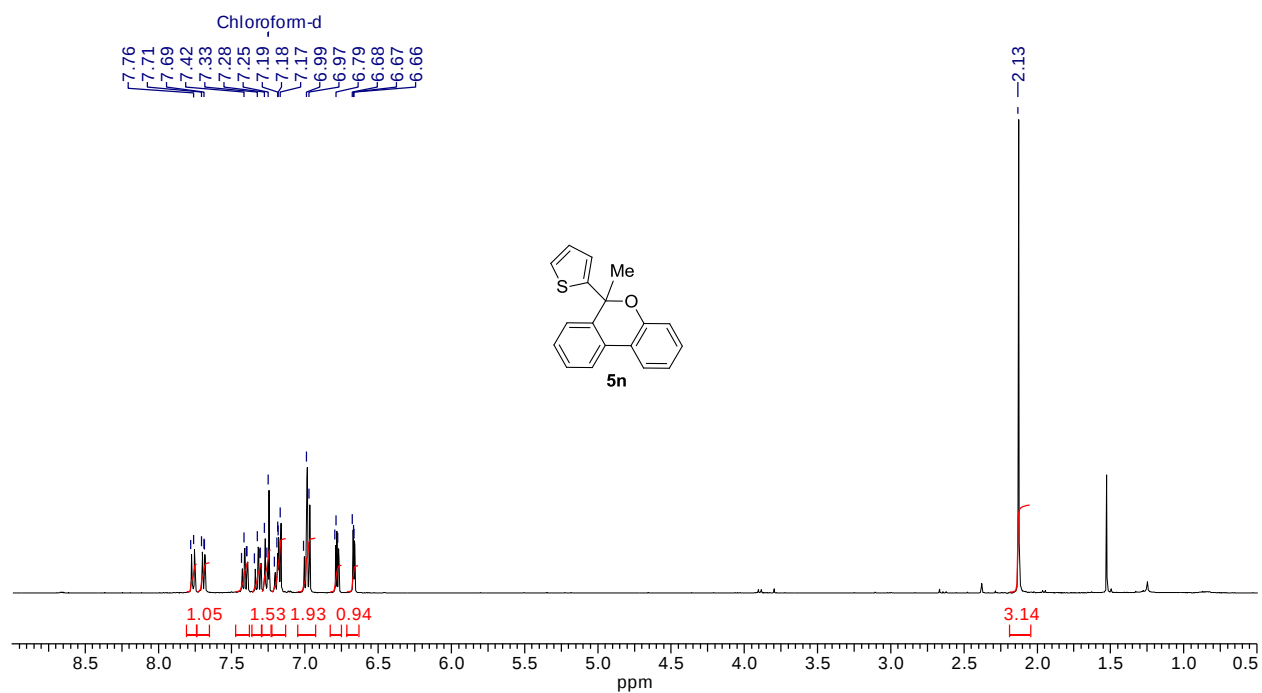




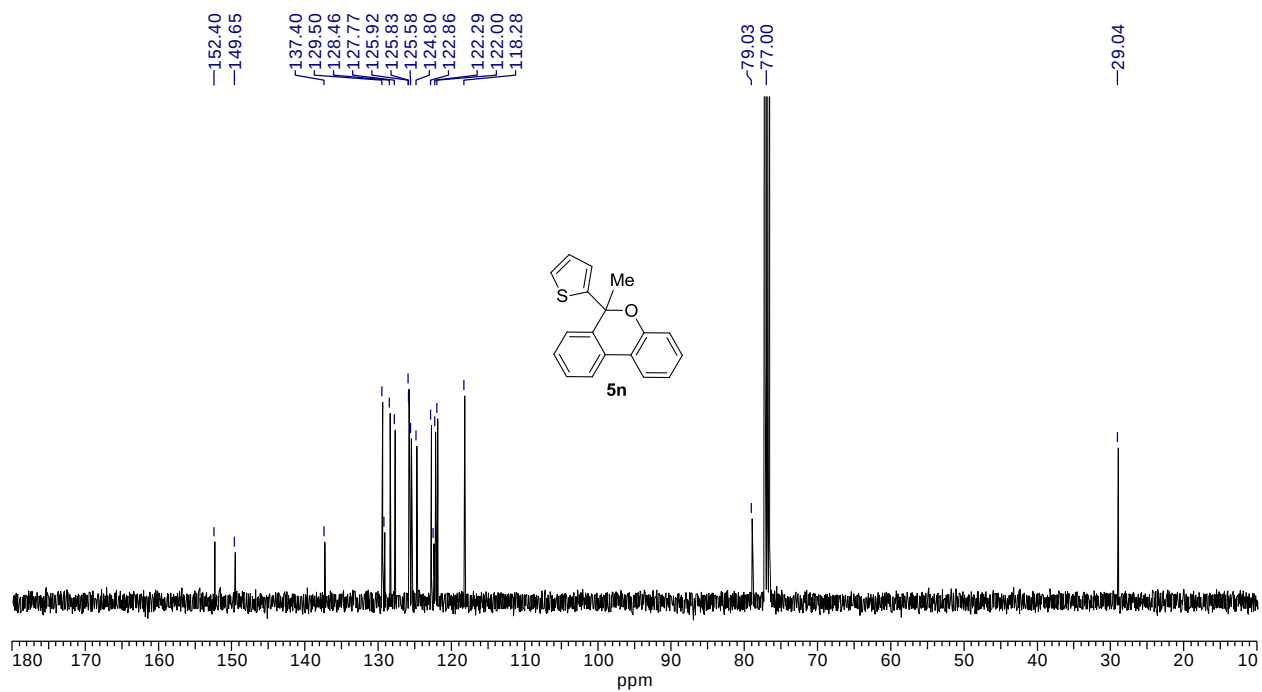




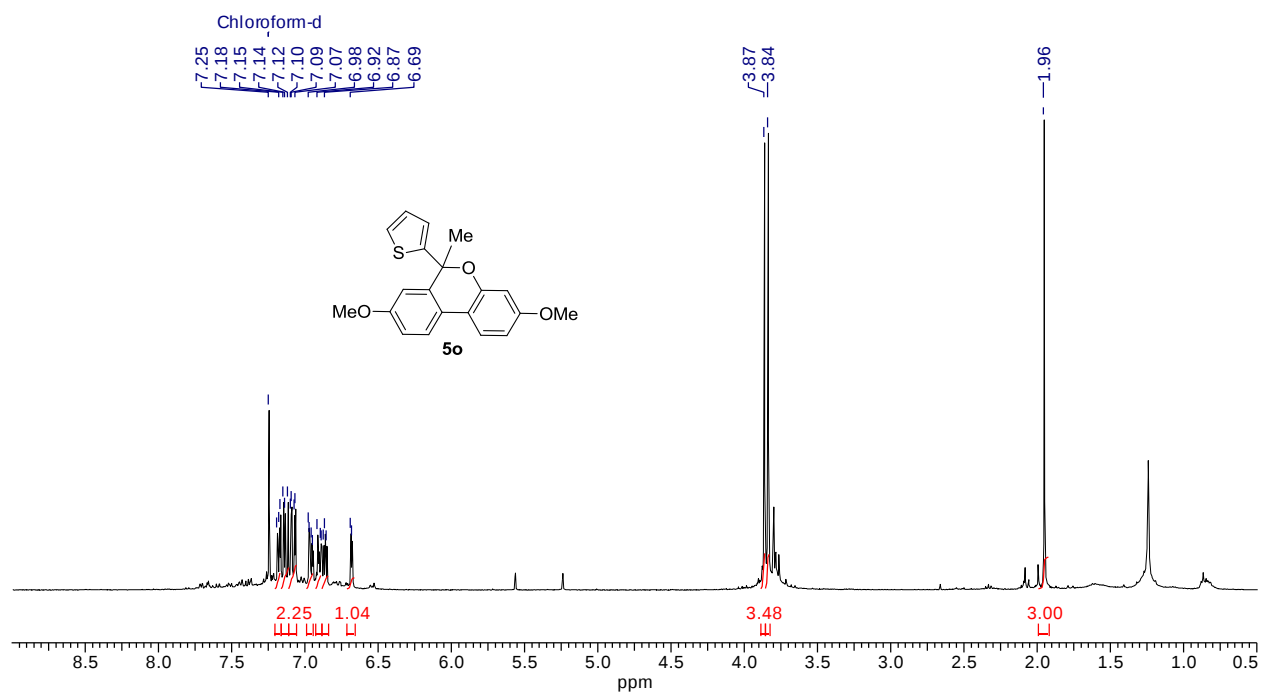




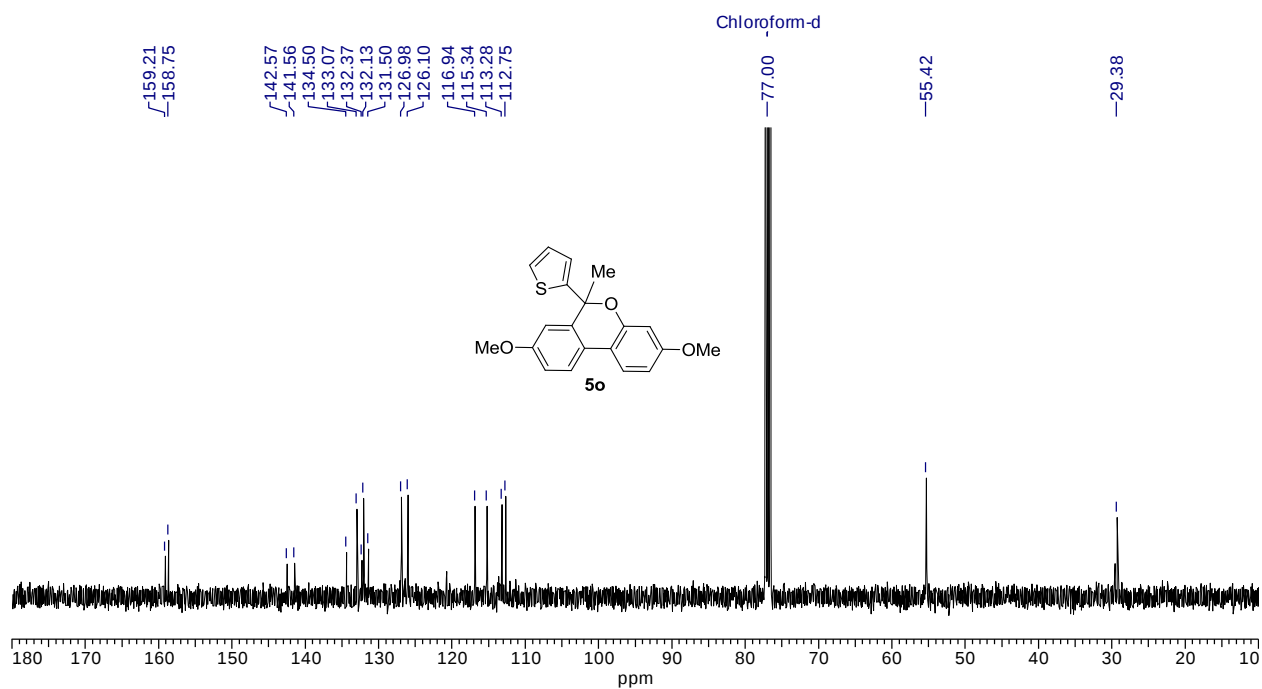
¹H NMR (400 MHz) spectrum of **5n** in CDCl₃



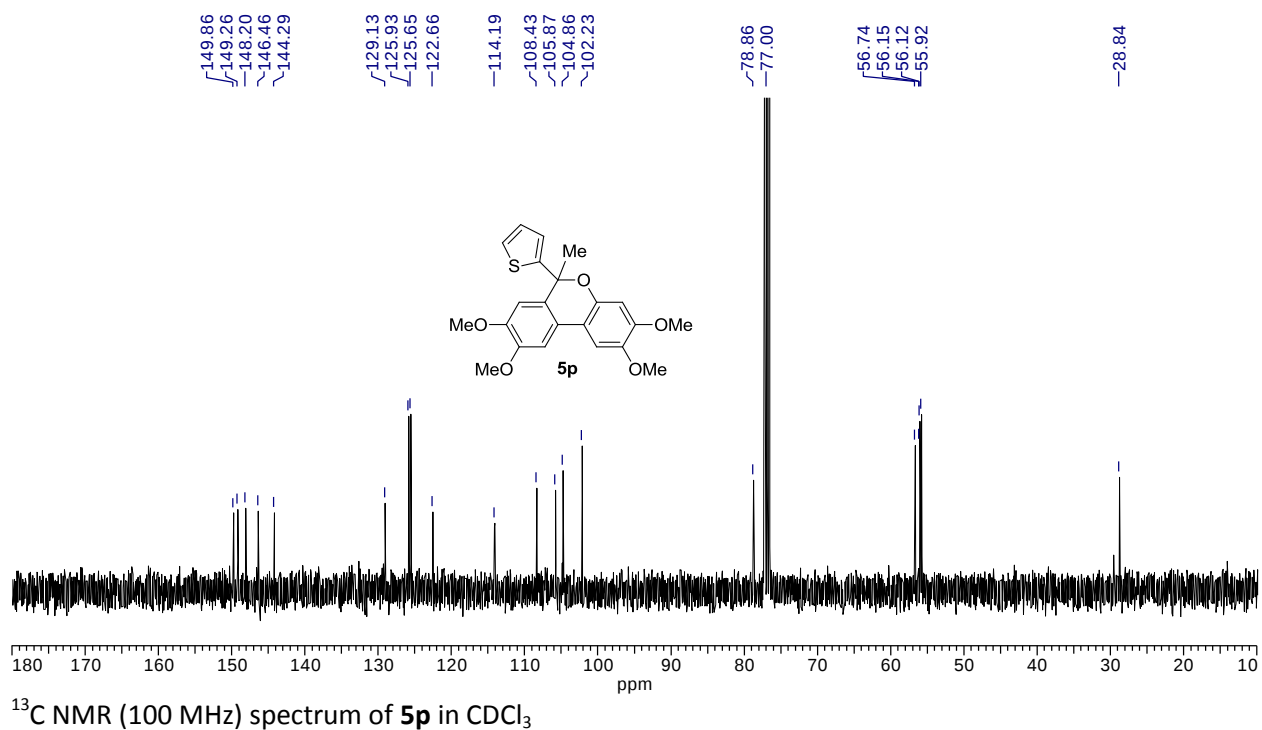
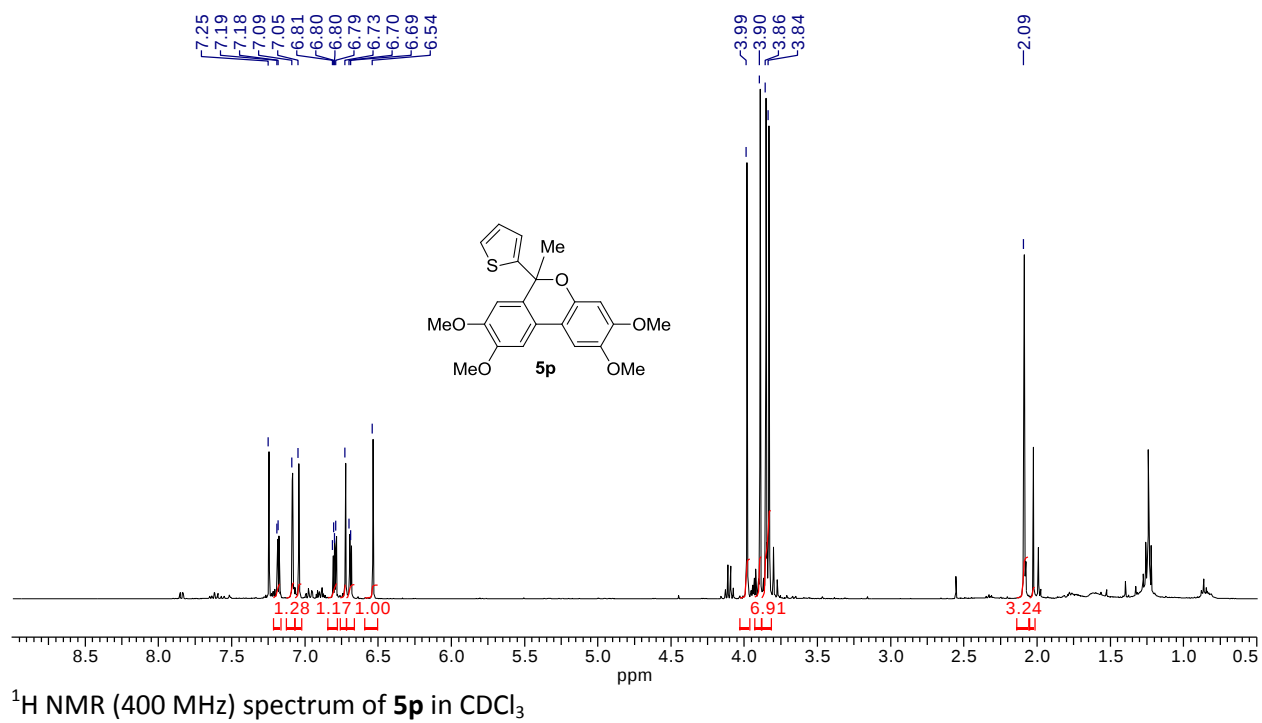
¹³C NMR (100 MHz) spectrum of **5n** in CDCl₃

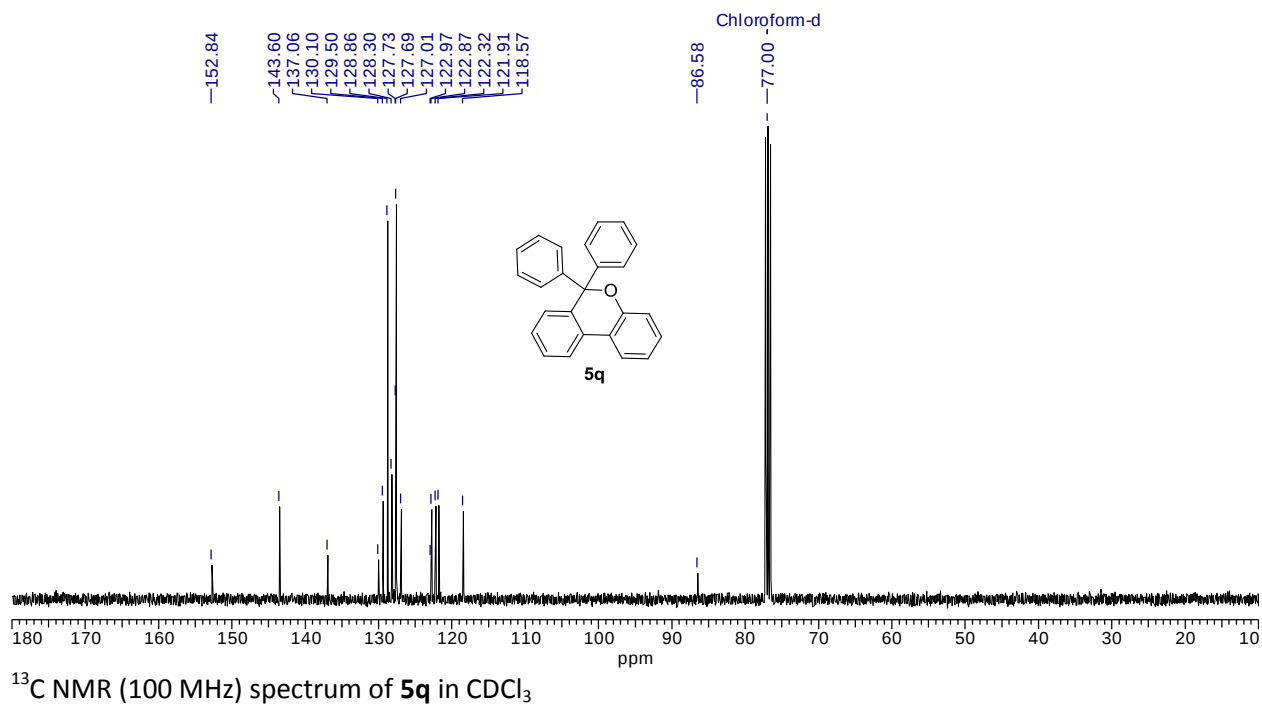
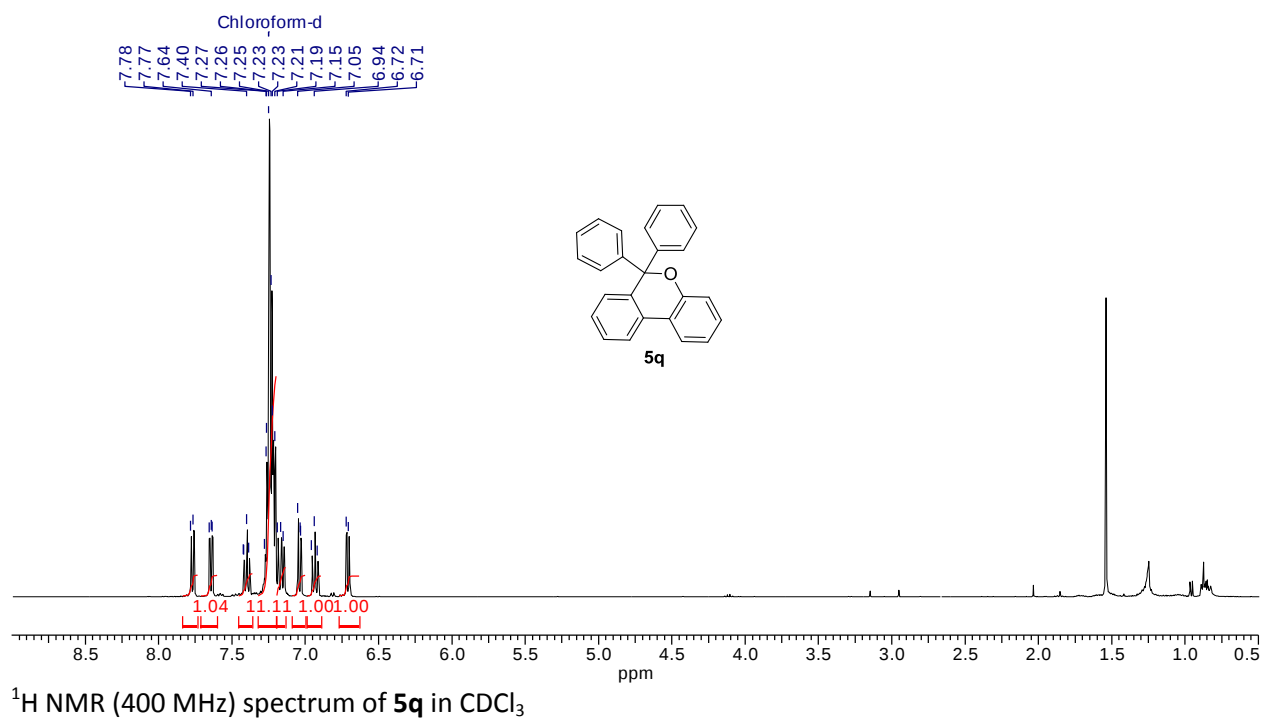


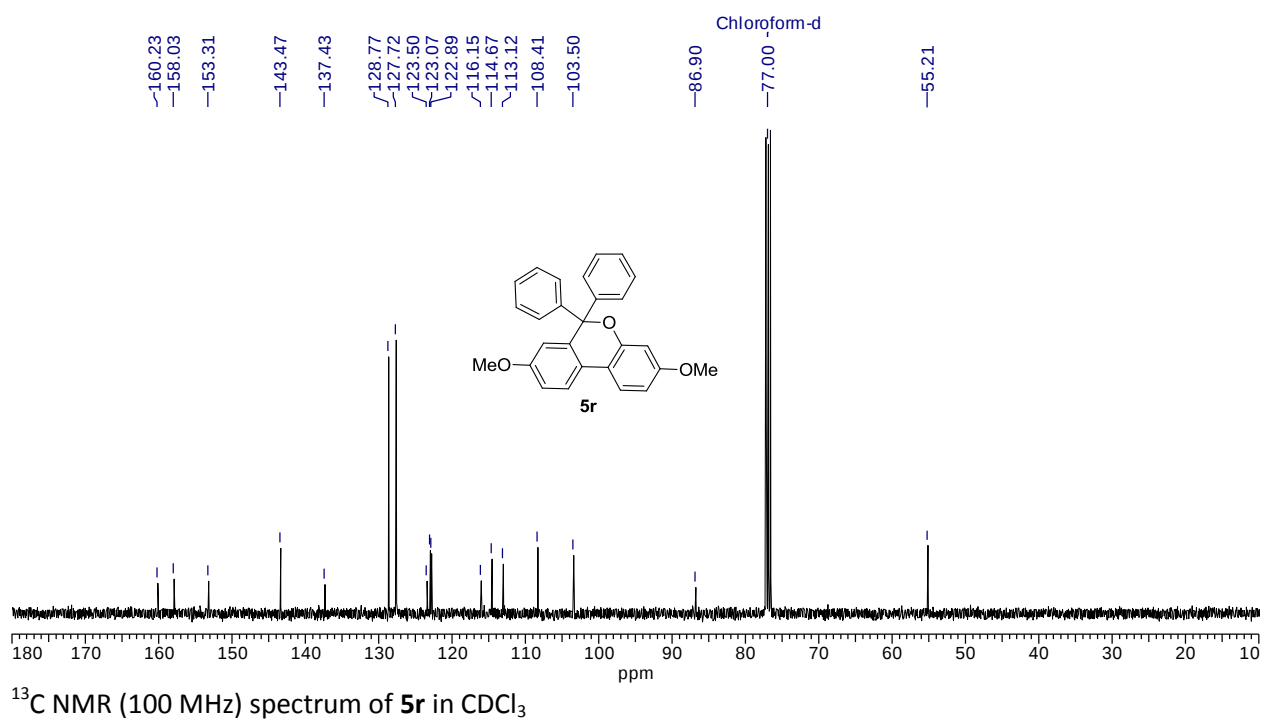
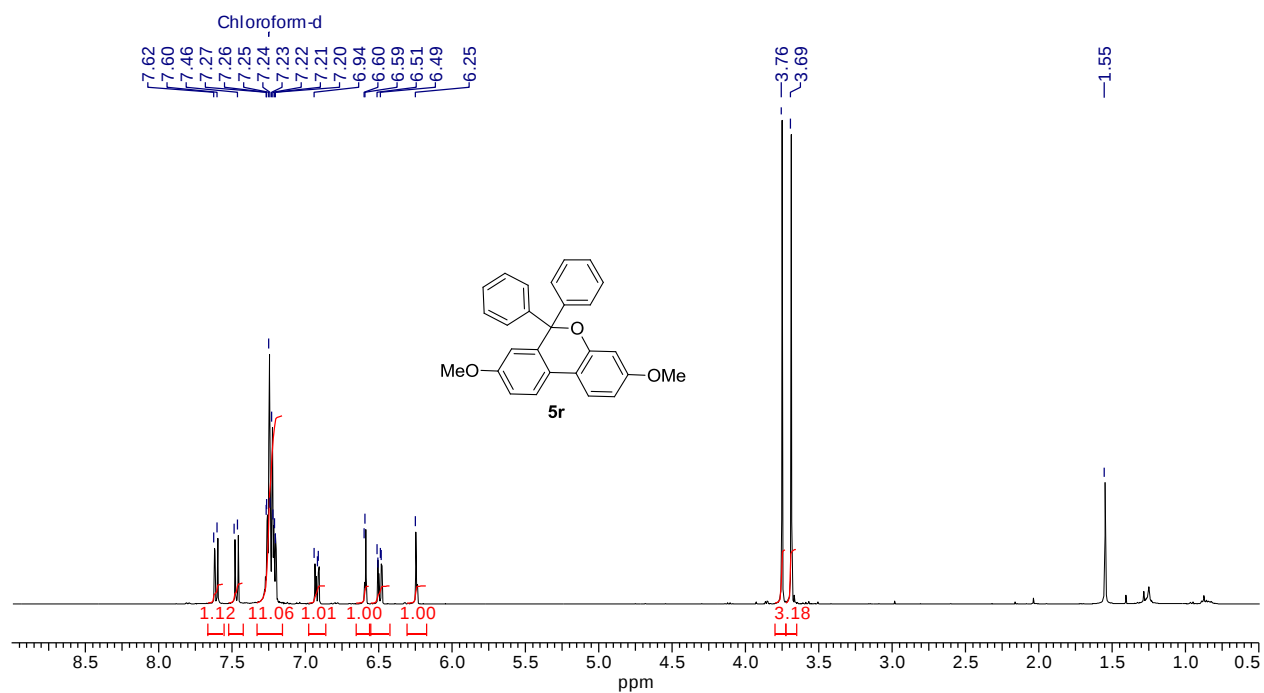
¹H NMR (400 MHz) spectrum of **5o** in CDCl₃

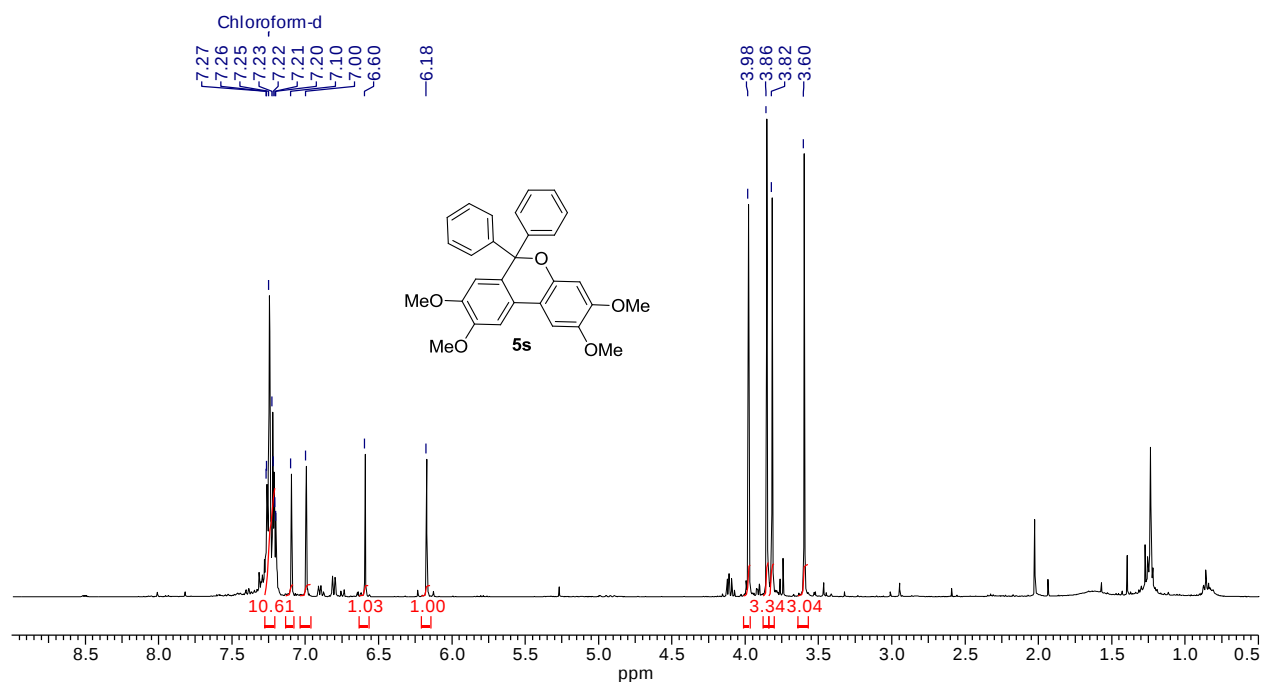


¹³C NMR (100 MHz) spectrum of **5o** in CDCl₃

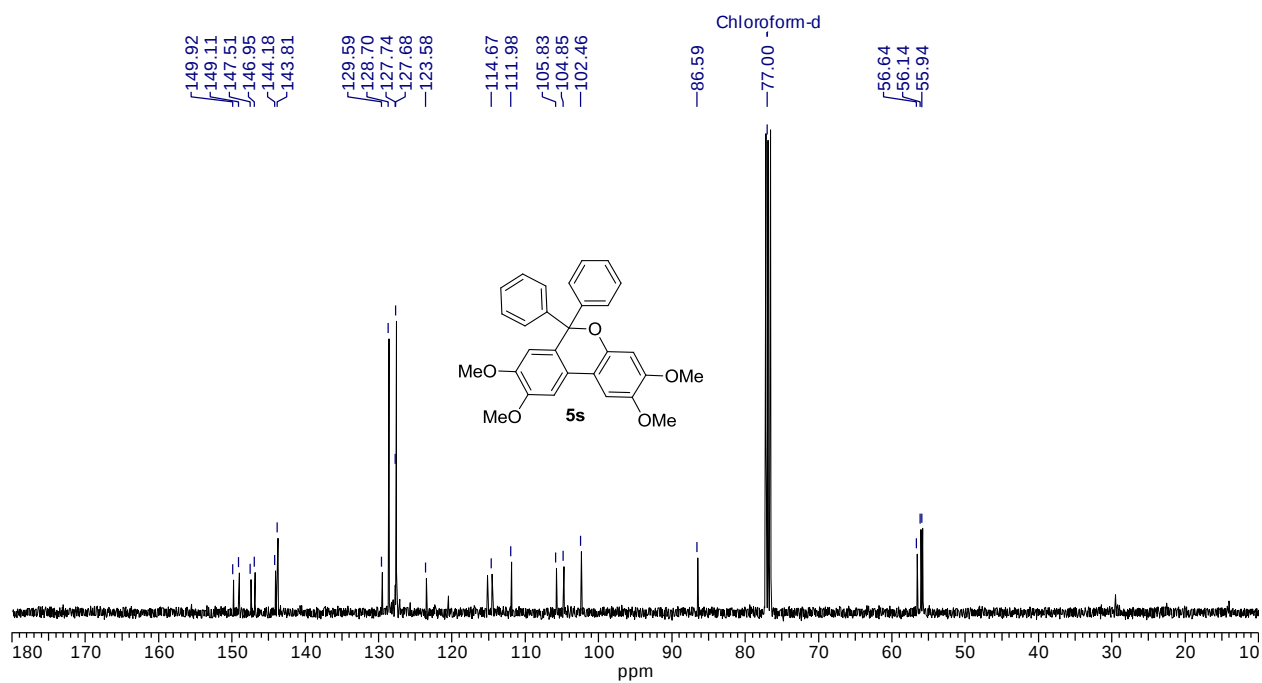




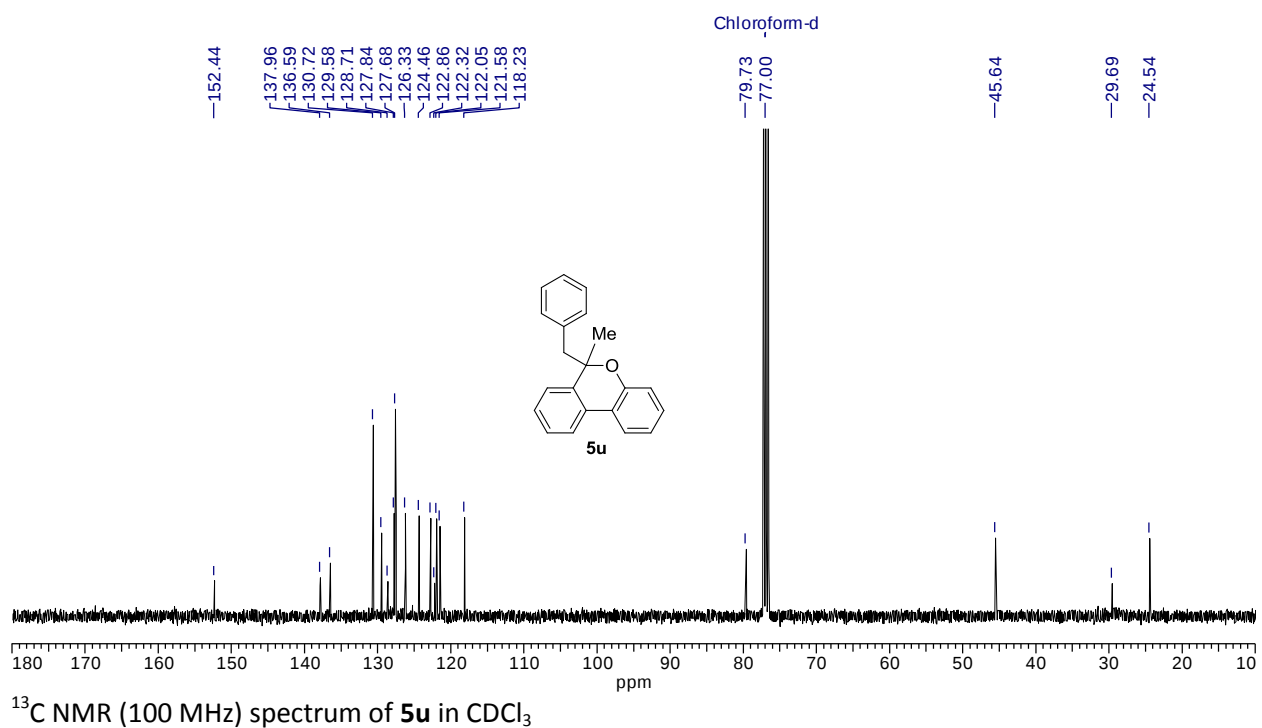
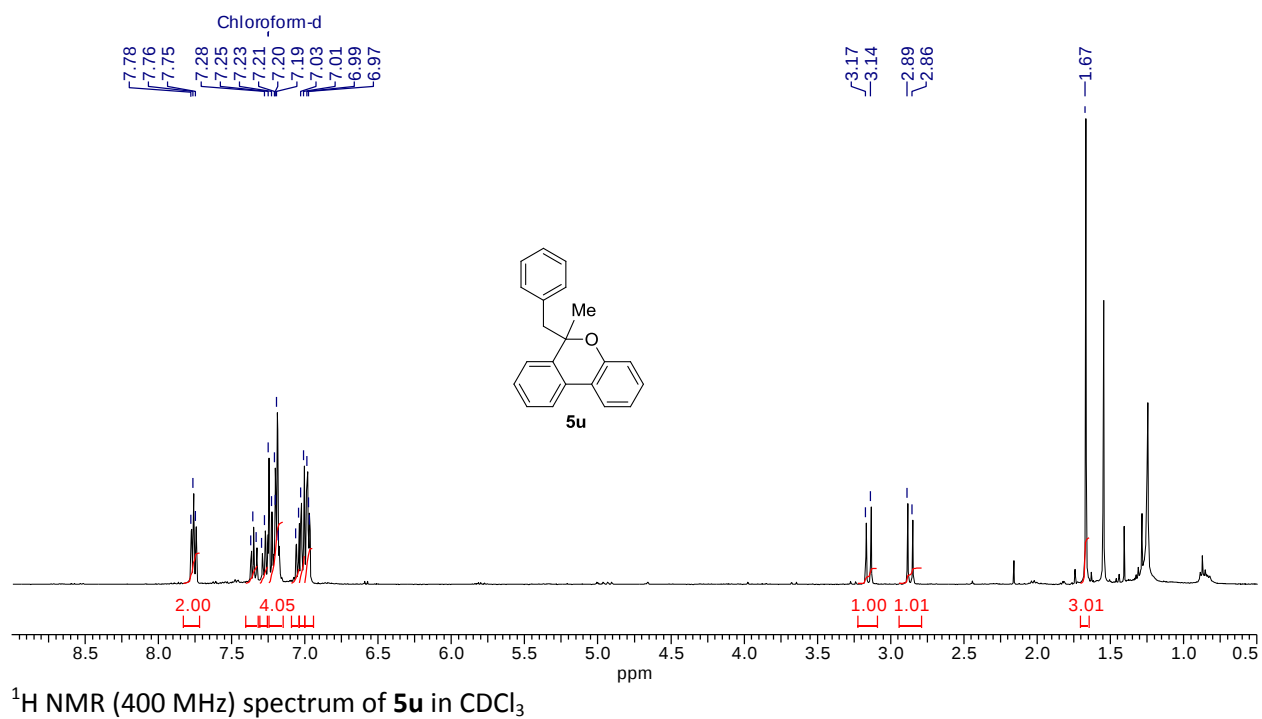


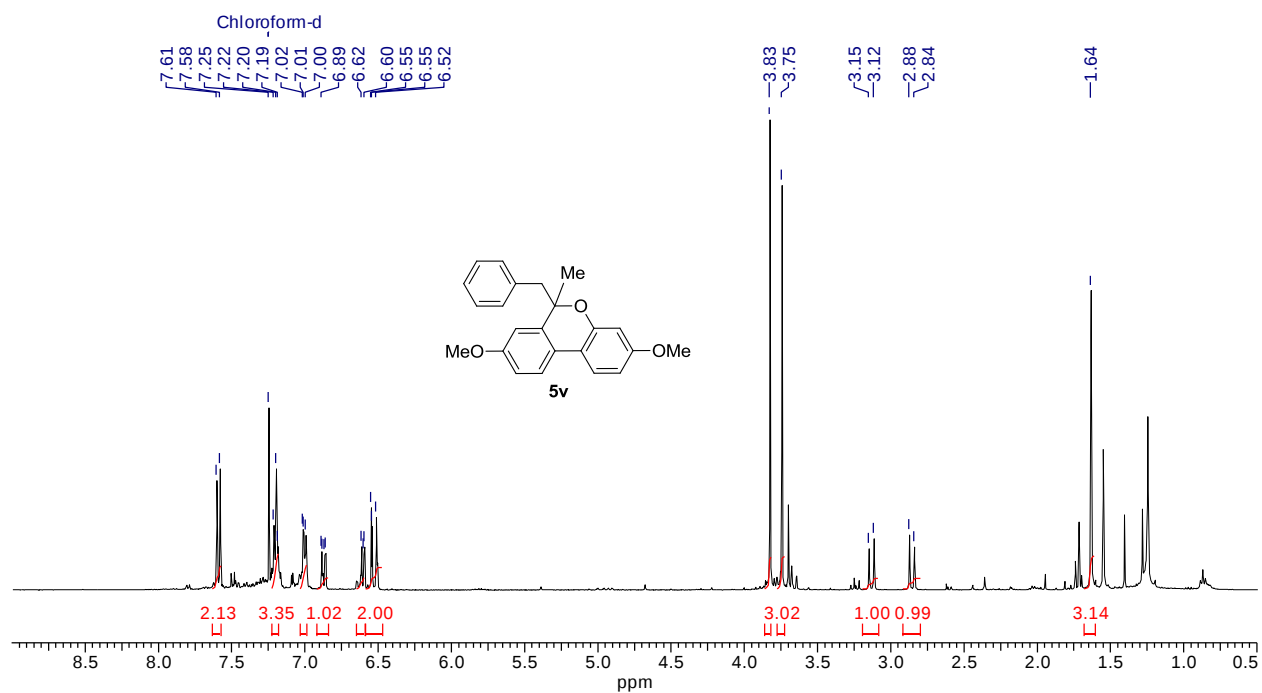


^1H NMR (400 MHz) spectrum of **5s** in CDCl_3

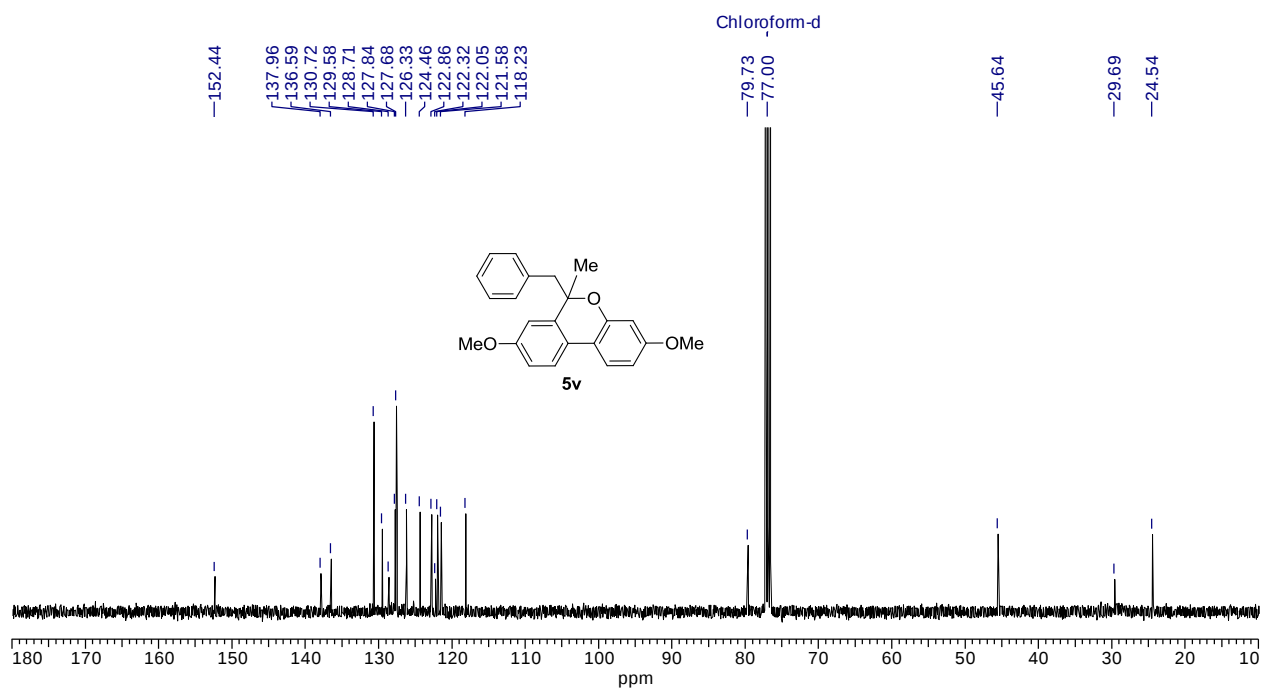


^{13}C NMR (100 MHz) spectrum of **5s** in CDCl_3

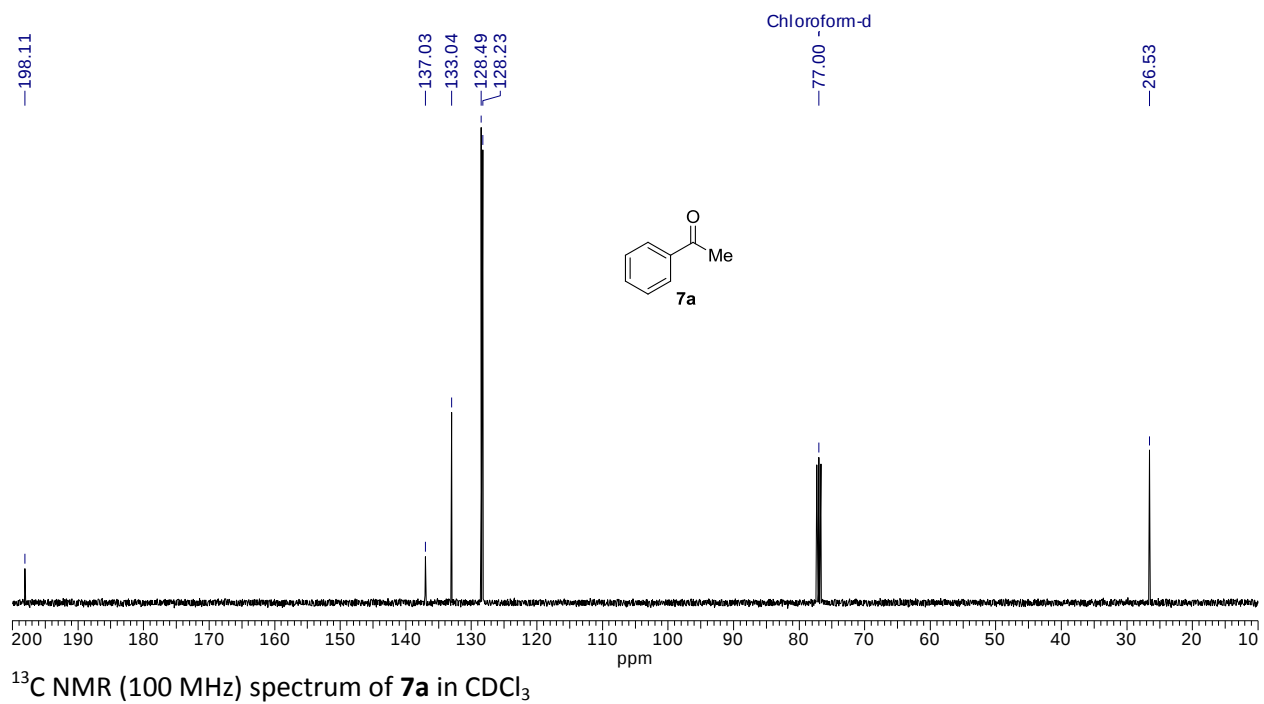
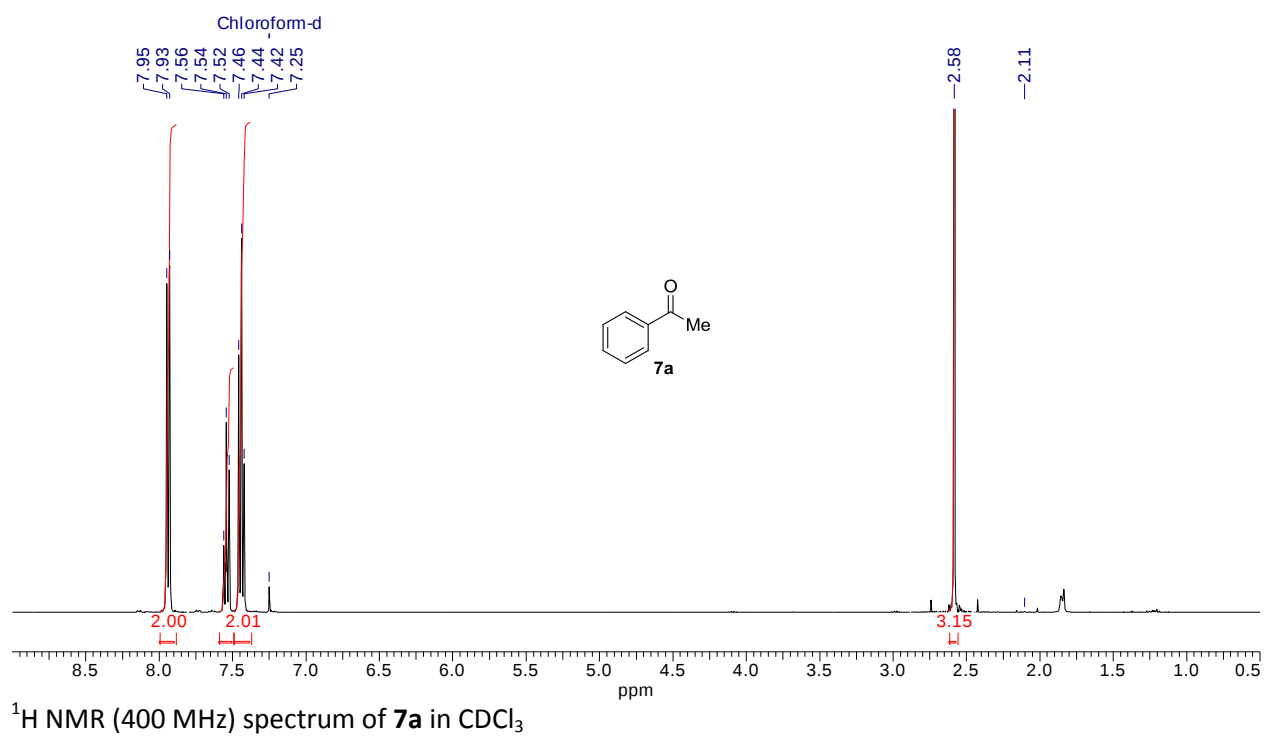


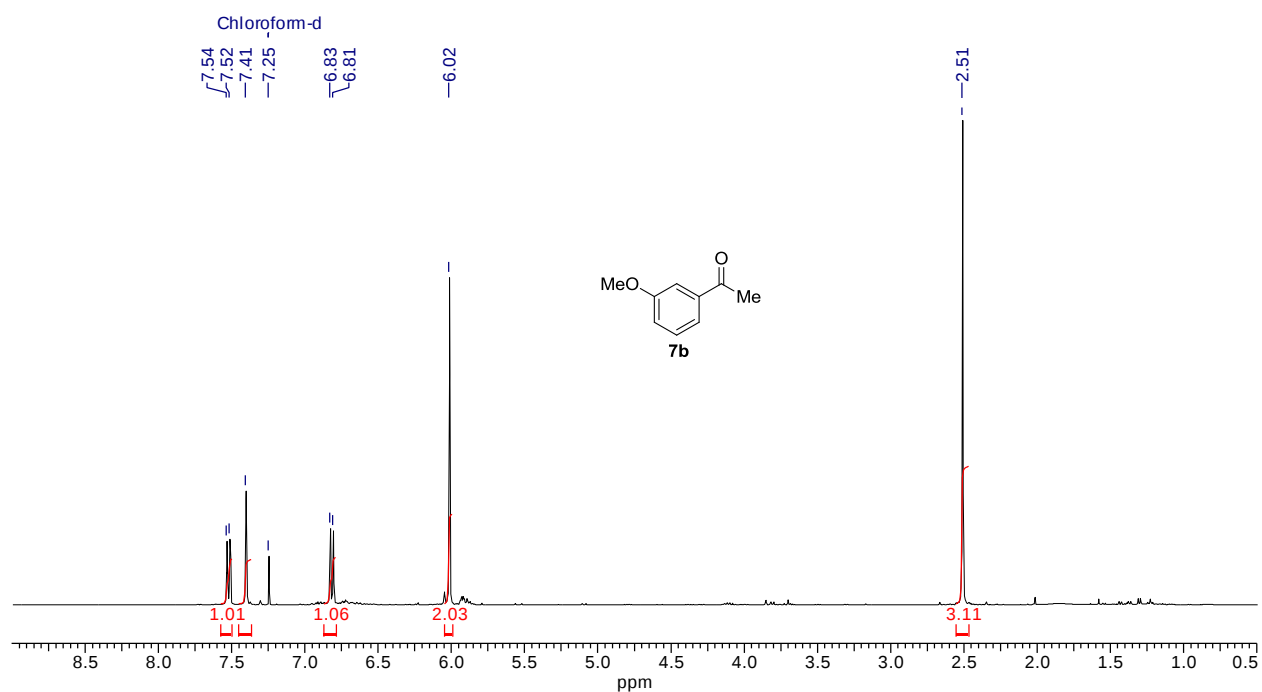


¹H NMR (400 MHz) spectrum of **5v** in CDCl₃

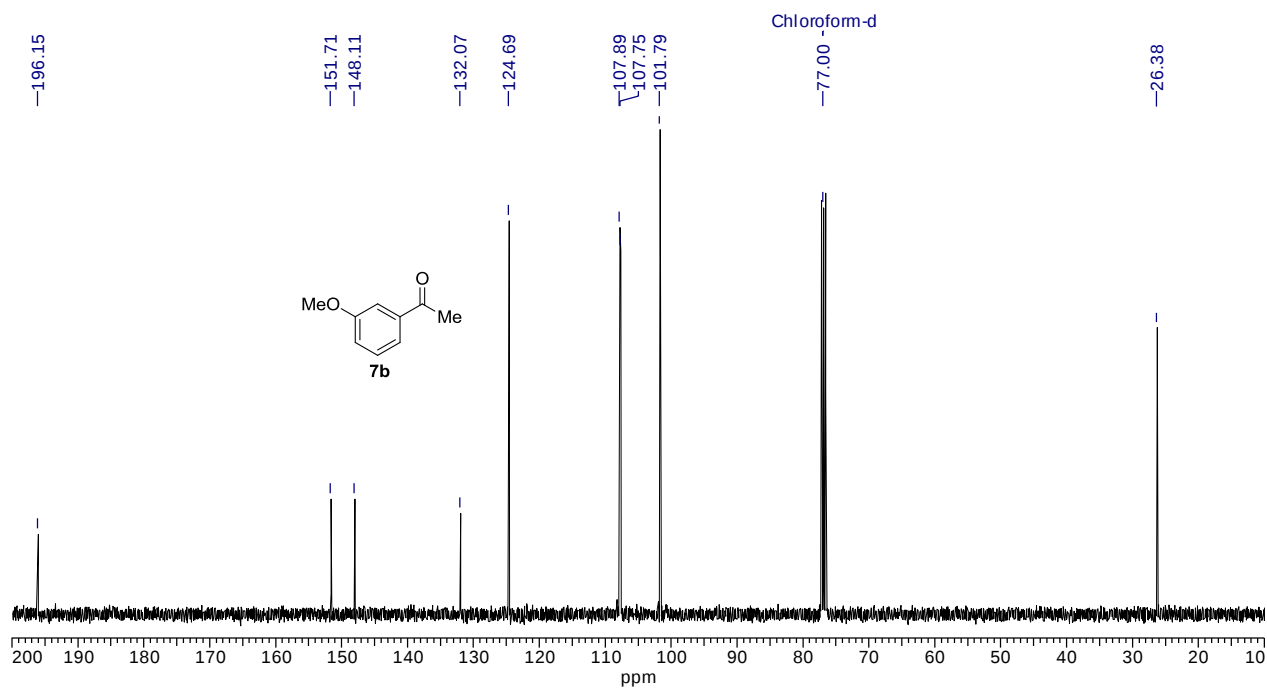


¹³C NMR (100 MHz) spectrum of **5v** in CDCl₃

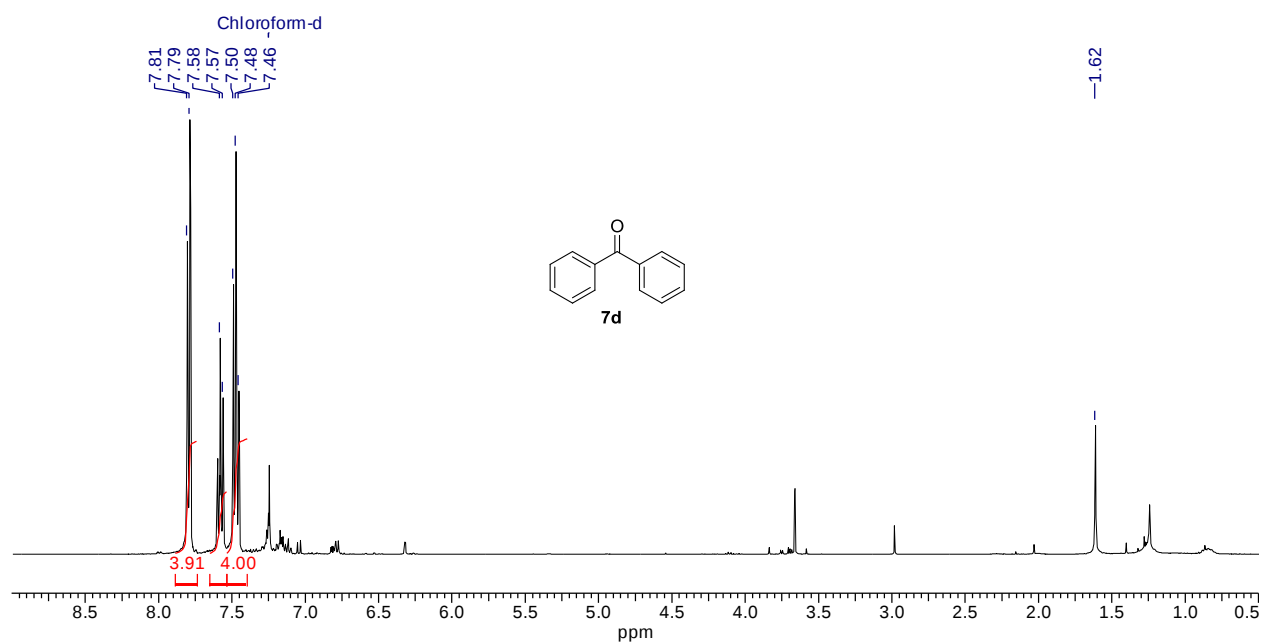




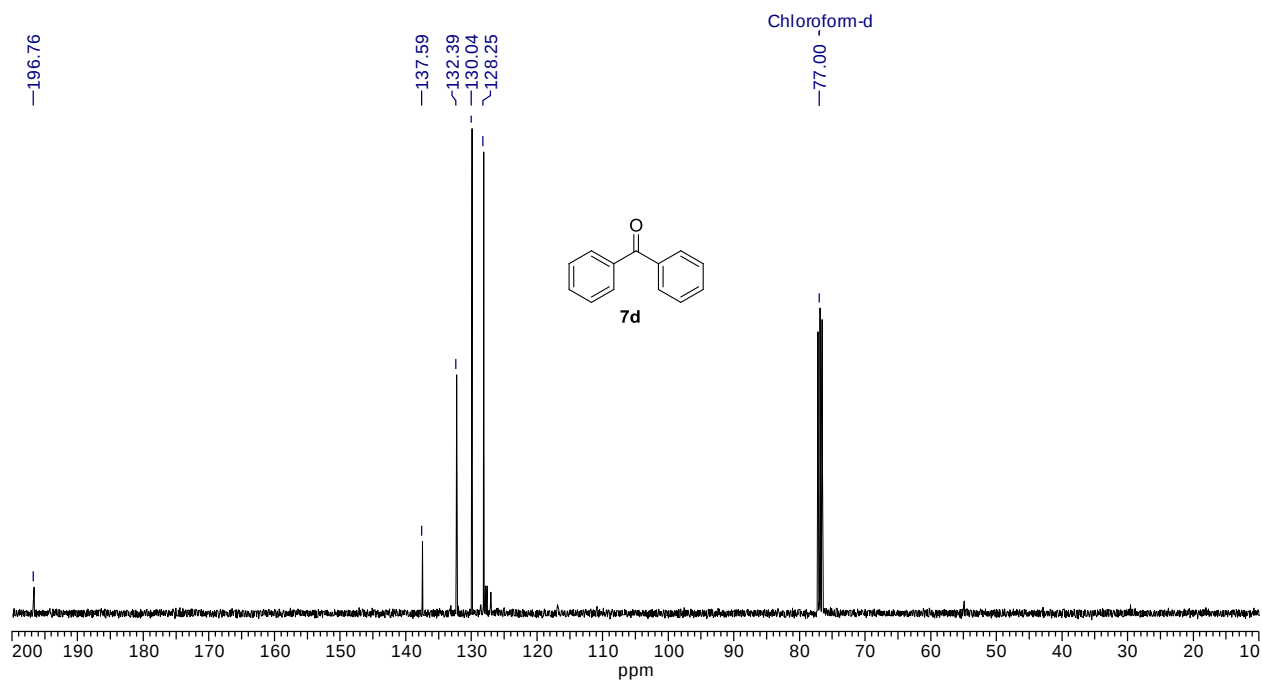
^1H NMR (400 MHz) spectrum of **7b** in CDCl_3



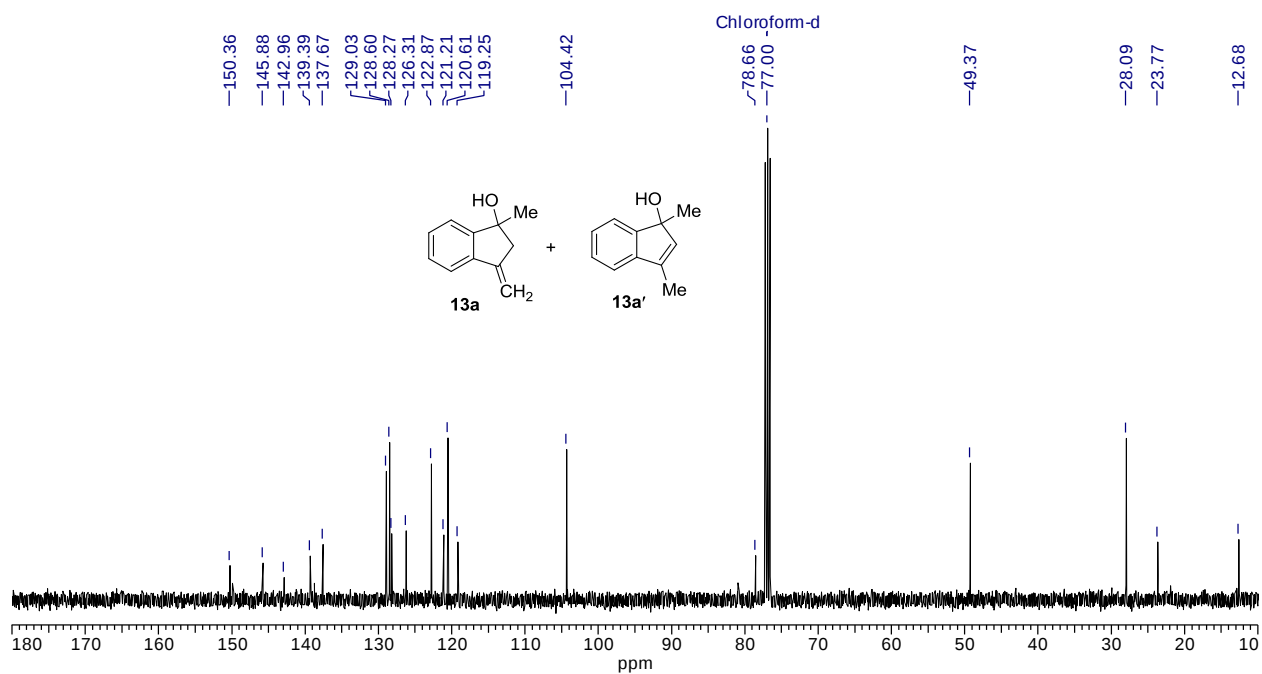
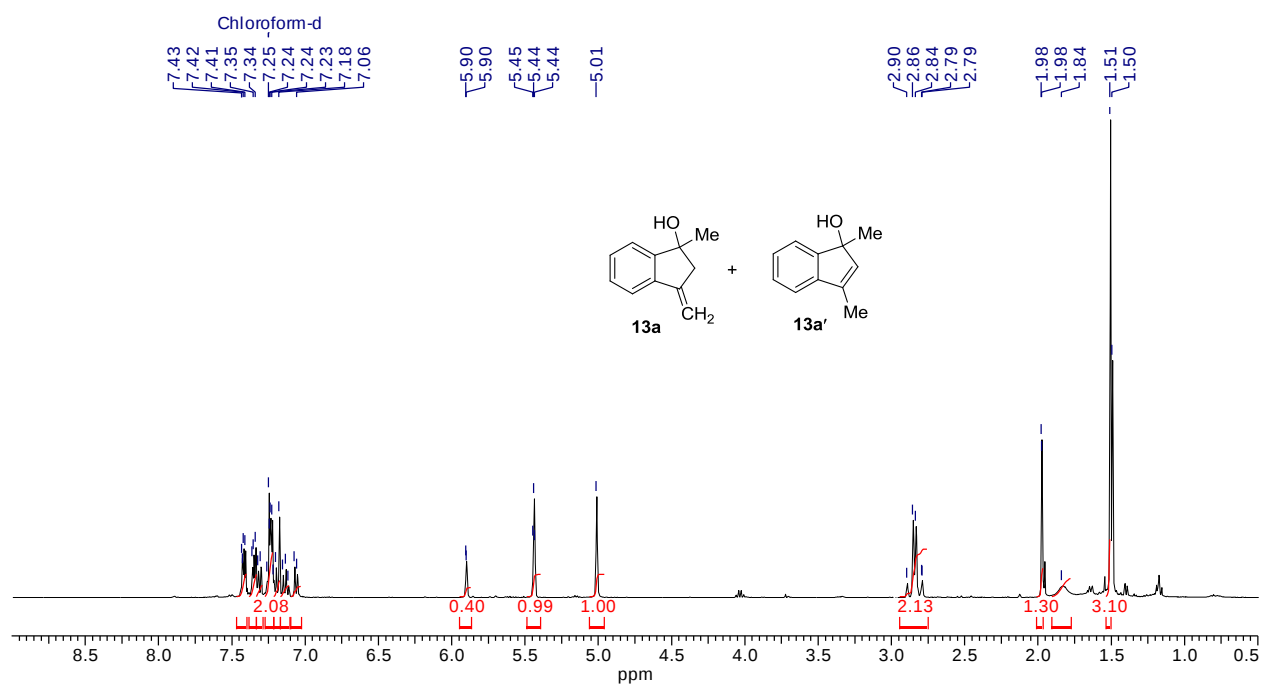
^{13}C NMR (100 MHz) spectrum of **7b** in CDCl_3

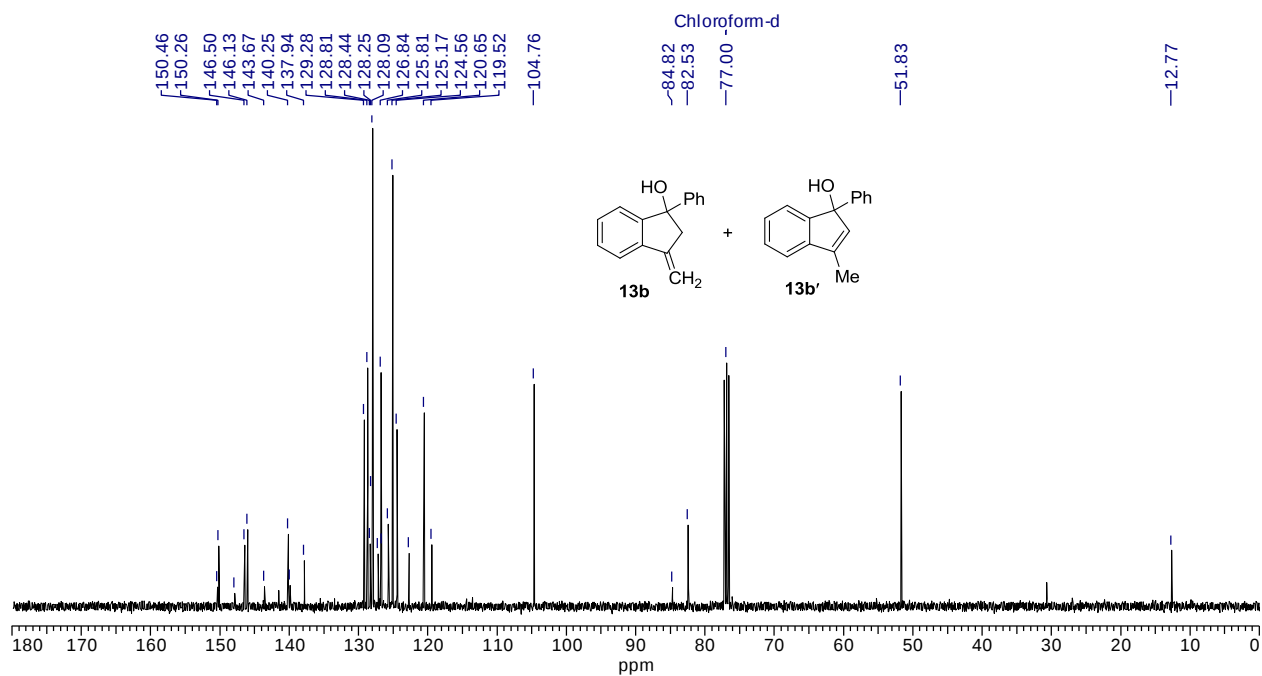
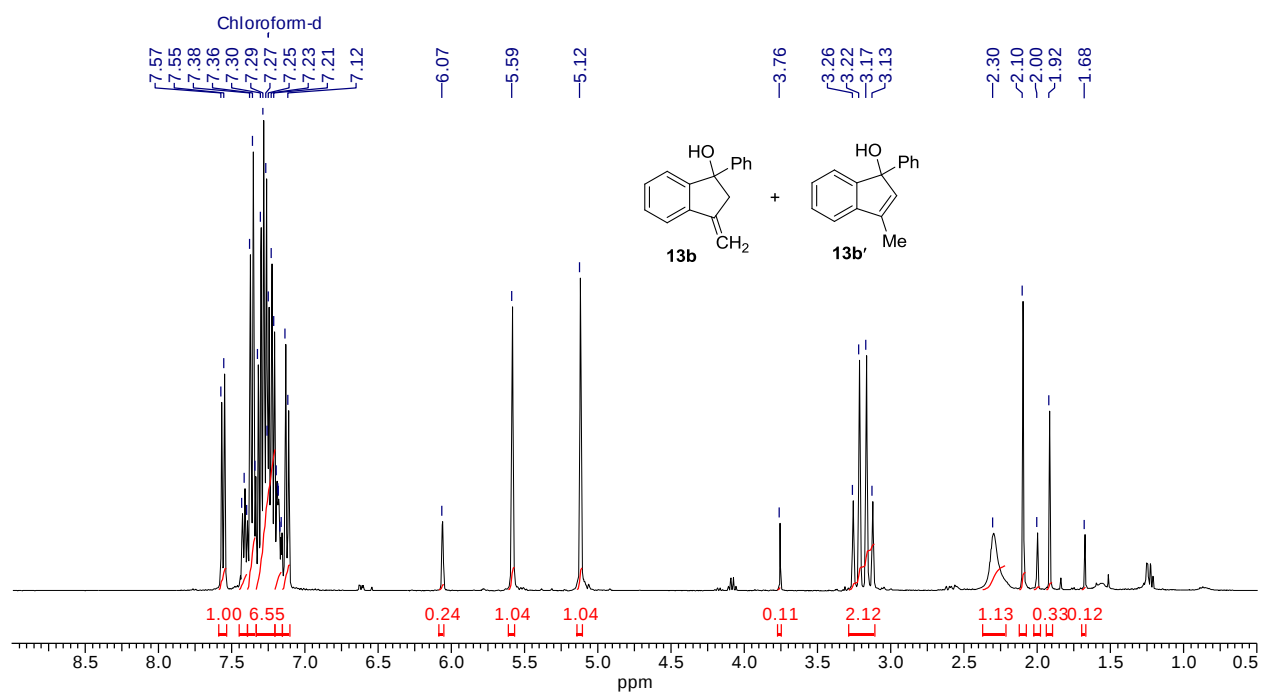


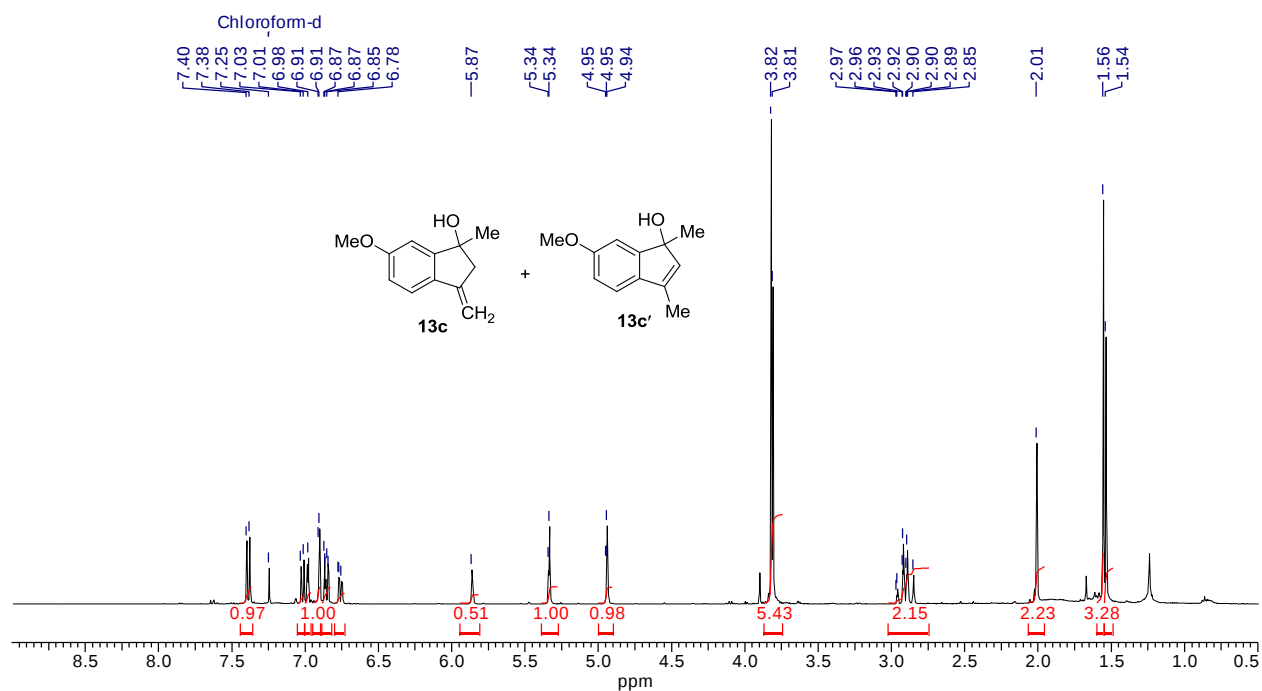
^1H NMR (400 MHz) spectrum of **7d** in CDCl_3



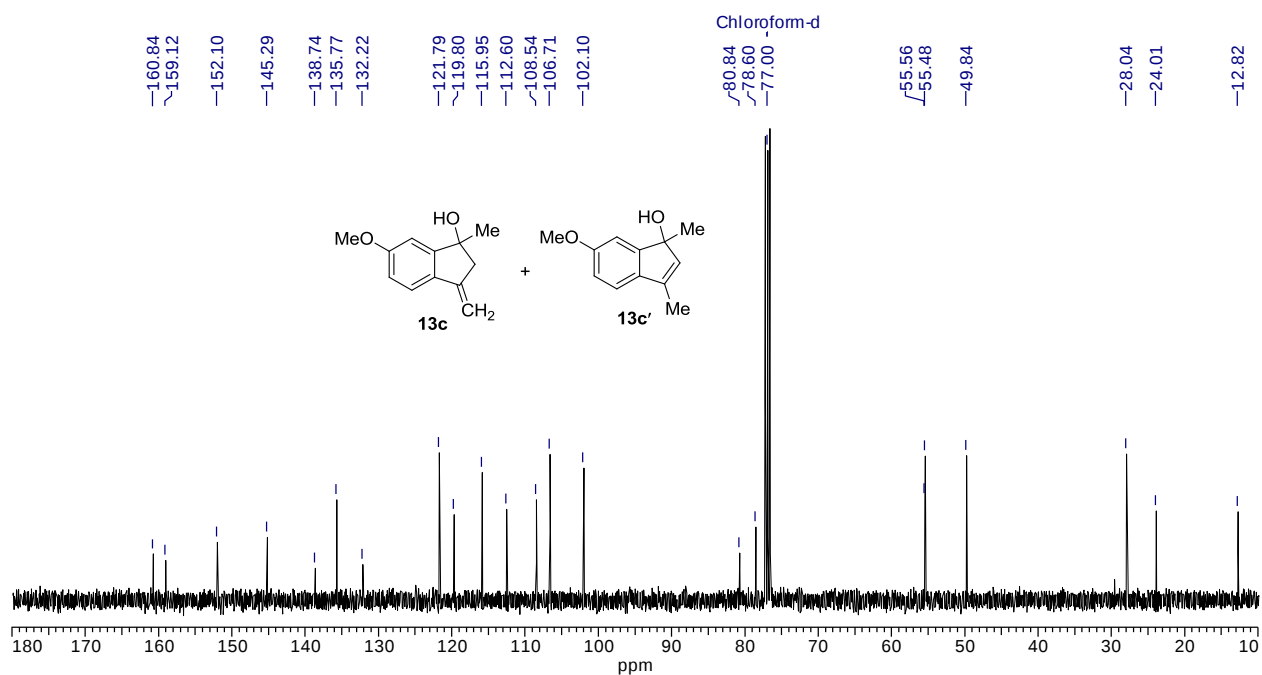
^{13}C NMR (100 MHz) spectrum of **7d** in CDCl_3



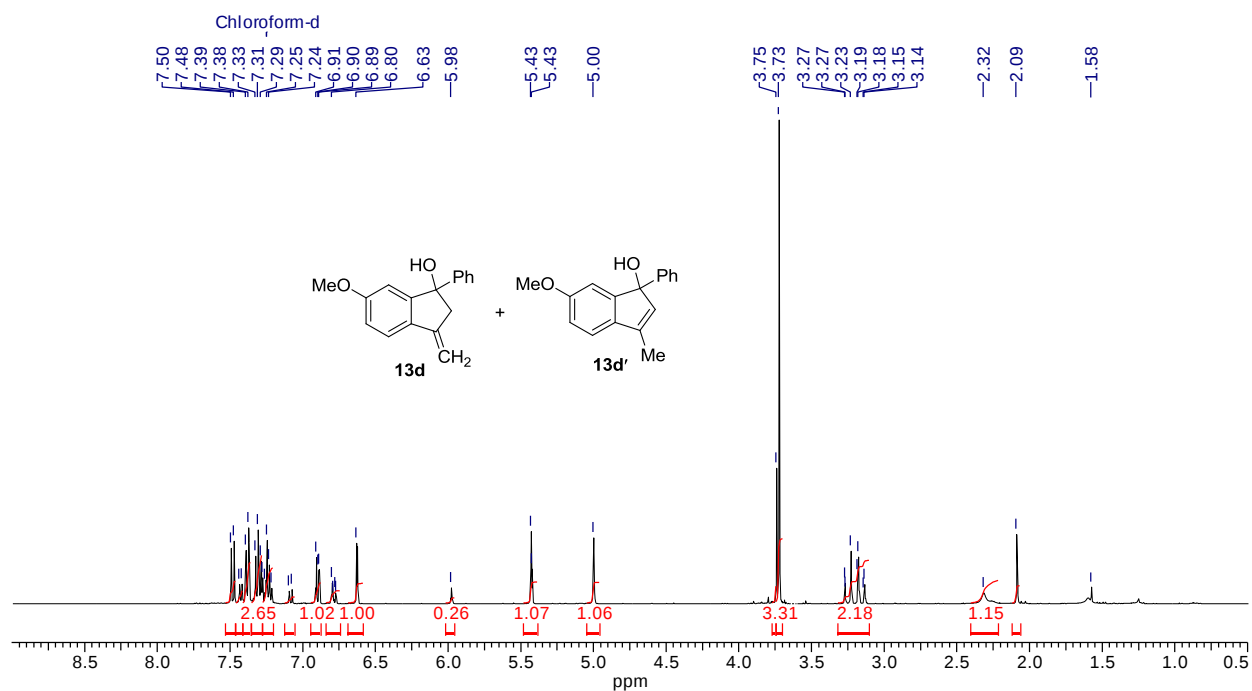




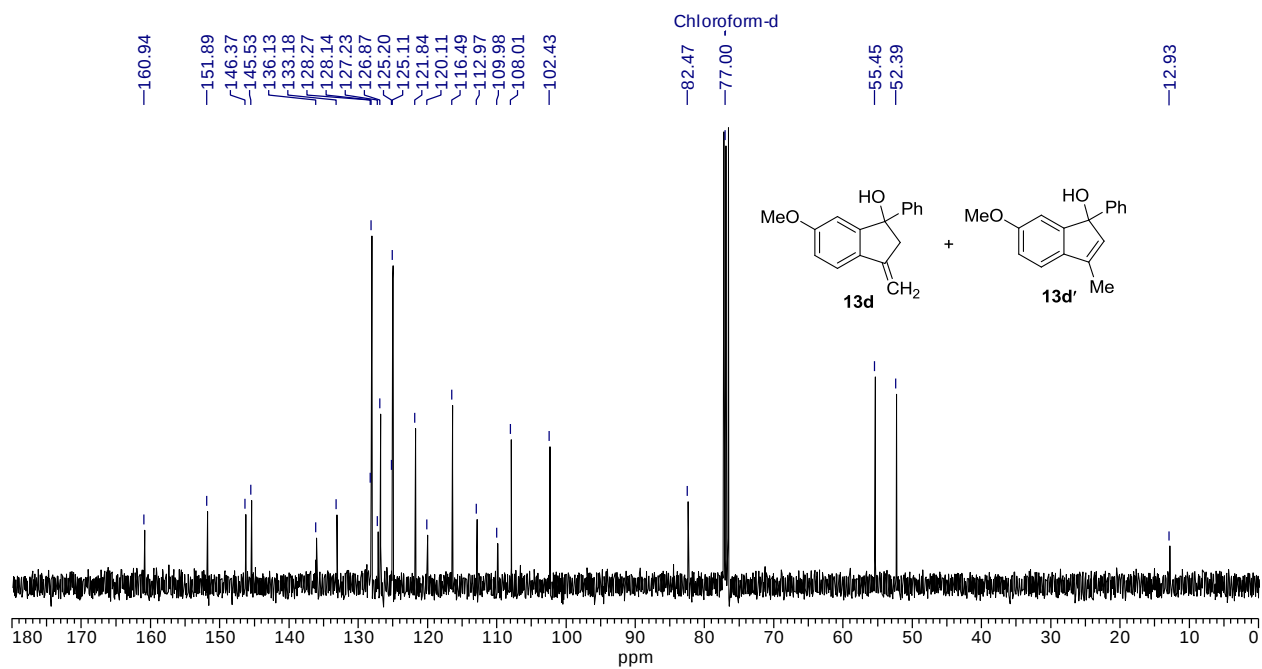
¹H NMR (400 MHz) spectrum of 13cc' in CDCl₃



¹³C NMR (100 MHz) spectrum of 13cc' in CDCl₃



¹H NMR (400 MHz) spectrum of **13dd'** in CDCl₃



¹³C NMR (100 MHz) spectrum of **13dd'** in CDCl₃

