

Supporting Information

Hetero-type Benzannulation Leading to Substituted Benzothiophenes

Taro Kono, Ryosuke Sasaki, Hideki Goto, Masatoshi Kakuno, and Yoo Tanabe*

*Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, 2-1
Gakuen, Sanda, Hyogo, 669-1337, Japan*

tanabe@kwansei.ac.jp

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Corresponding Author:

Professor Yoo Tanabe

Department of Chemistry, School of Science and Technology, Kwansei Gakuin University,
2-1 Gakuen, Sanda, Hyogo, 669-1337, Japan

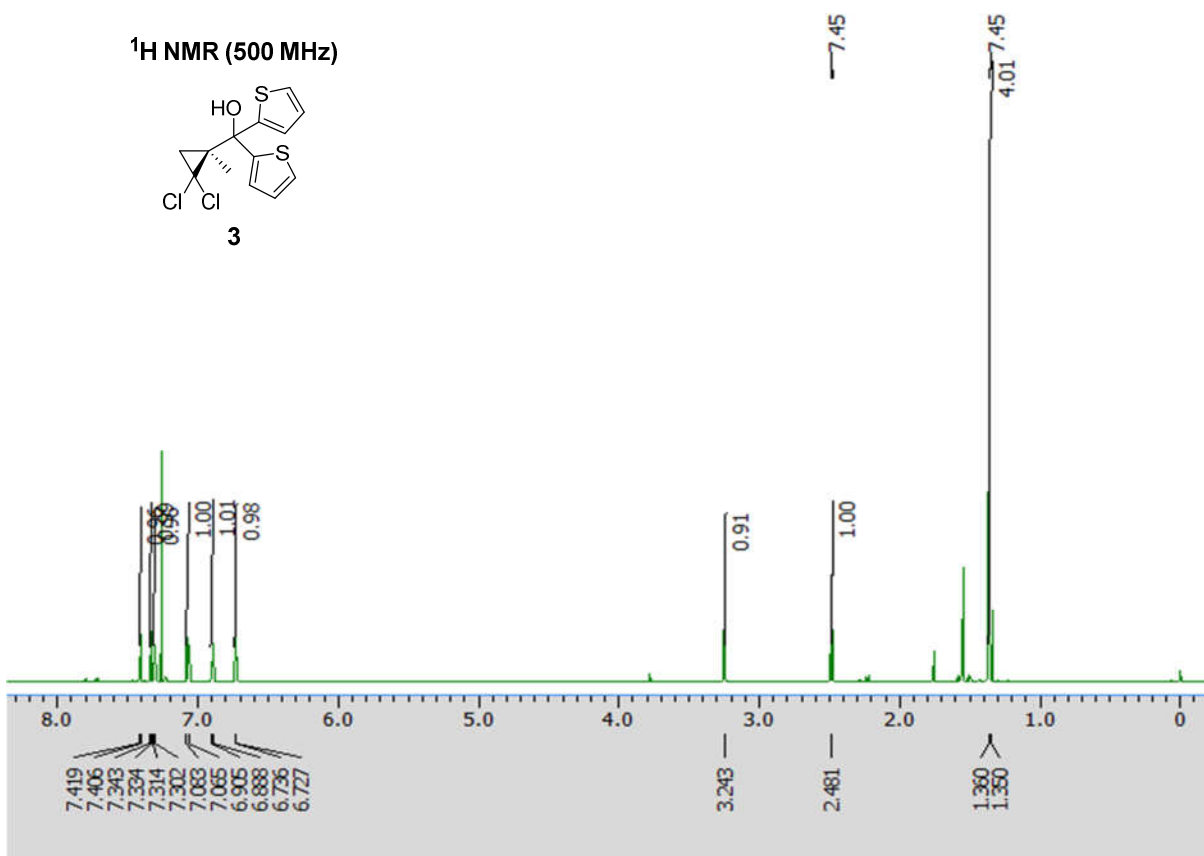


Figure S1: ^1H NMR (500 MHz, CDCl_3) Spectrum of the Compound 3

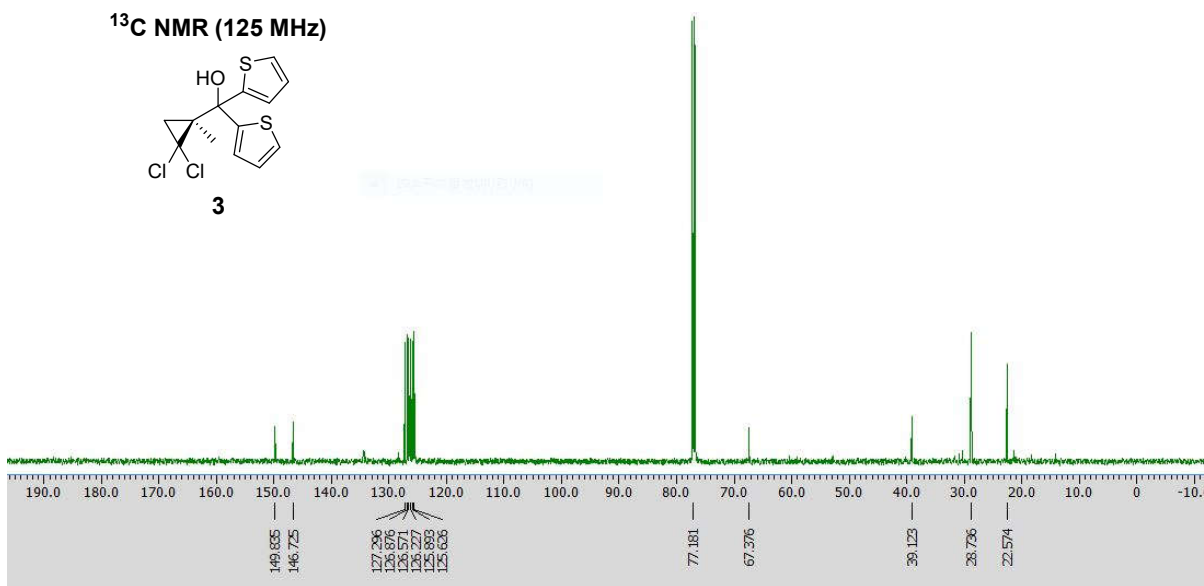


Figure S2: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of the Compound 3

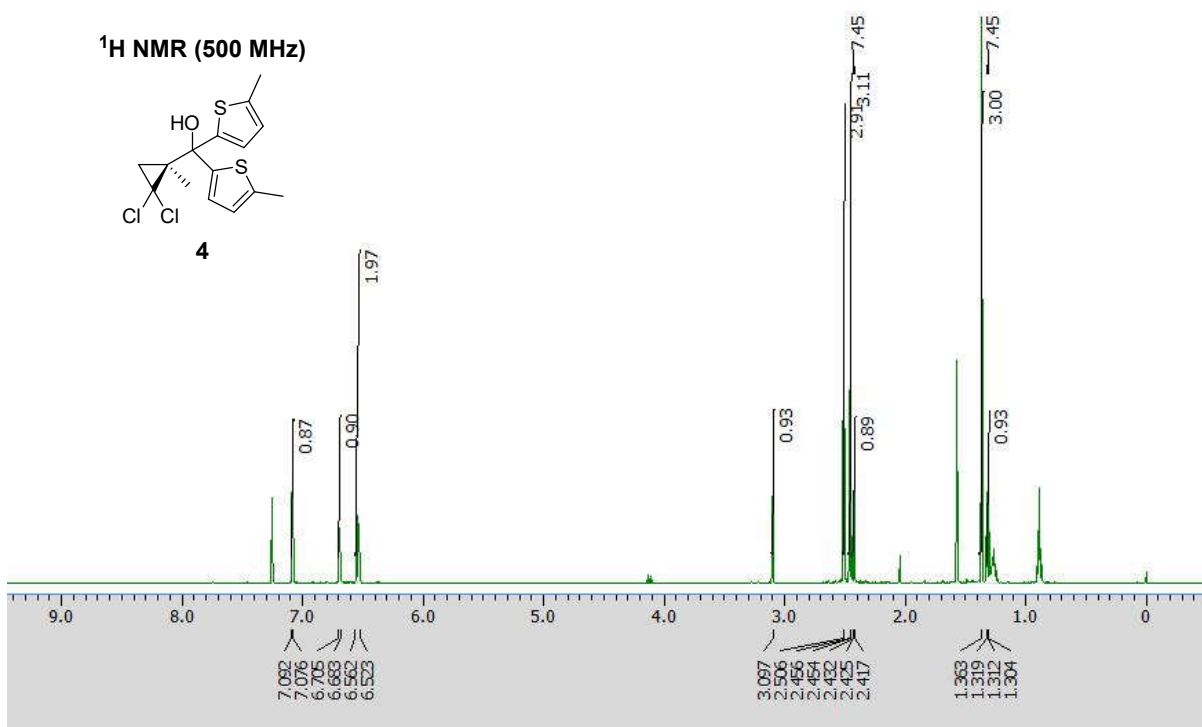


Figure S3: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 4

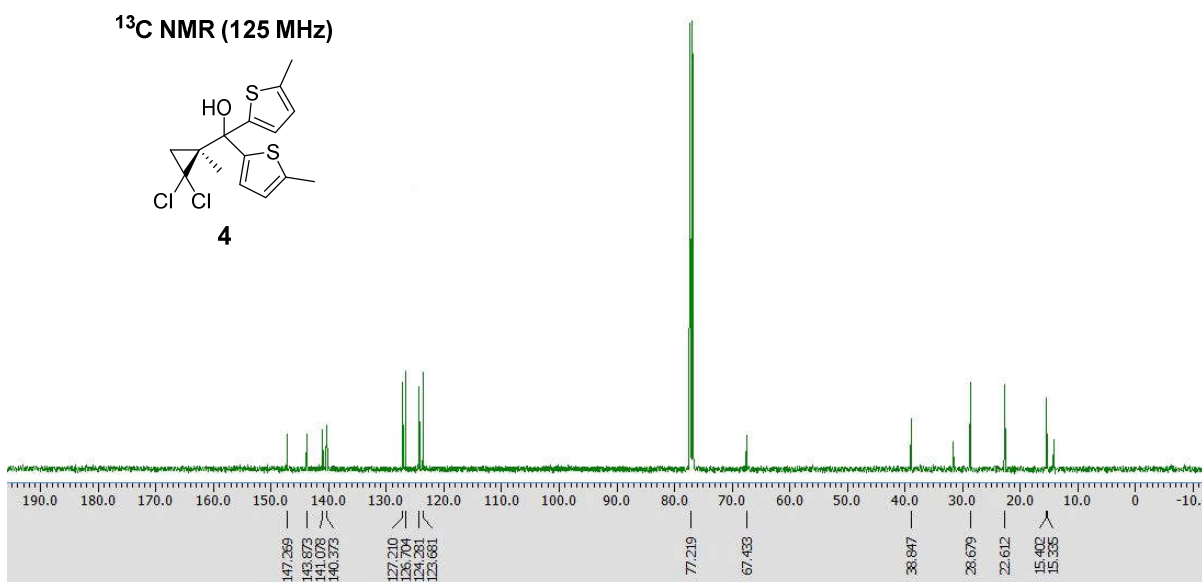


Figure S4: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 4

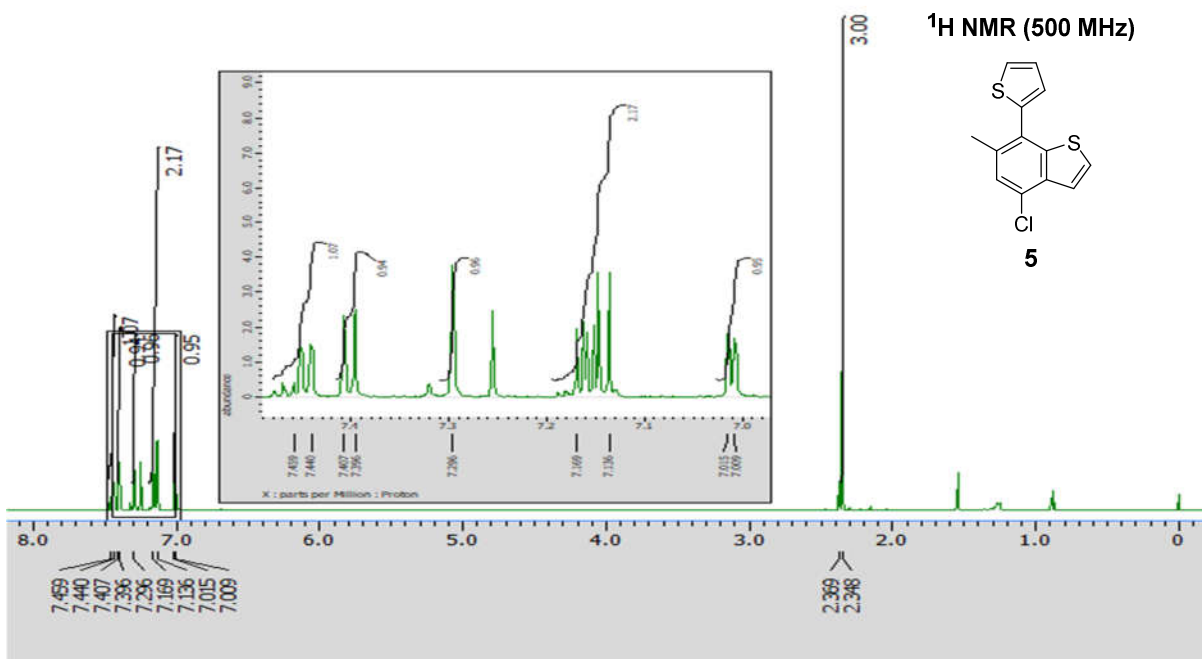


Figure S5: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 5

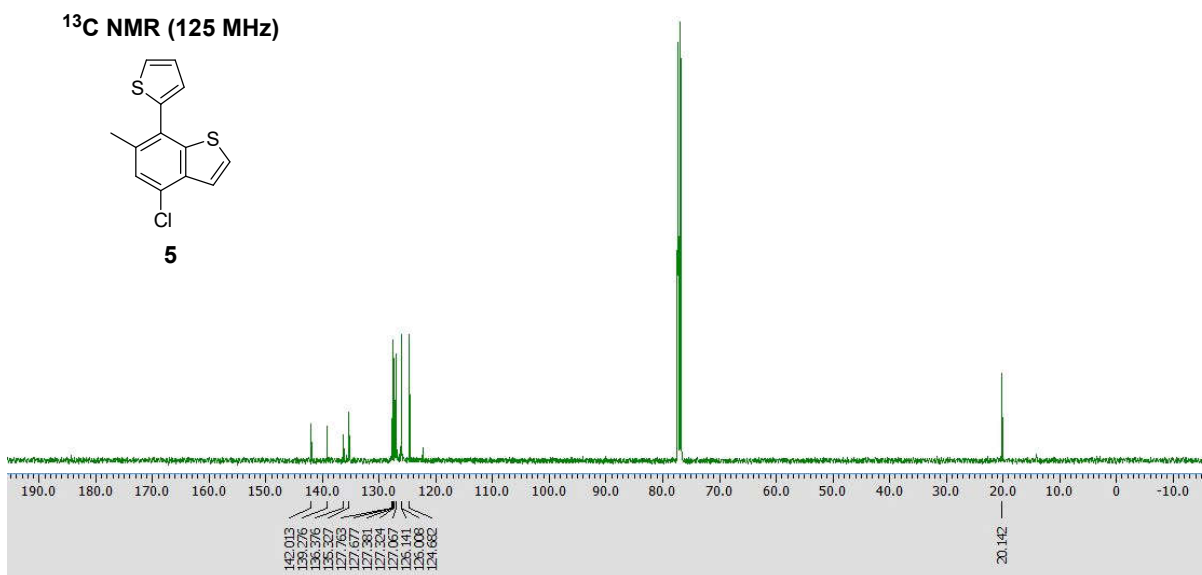


Figure S6: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 5

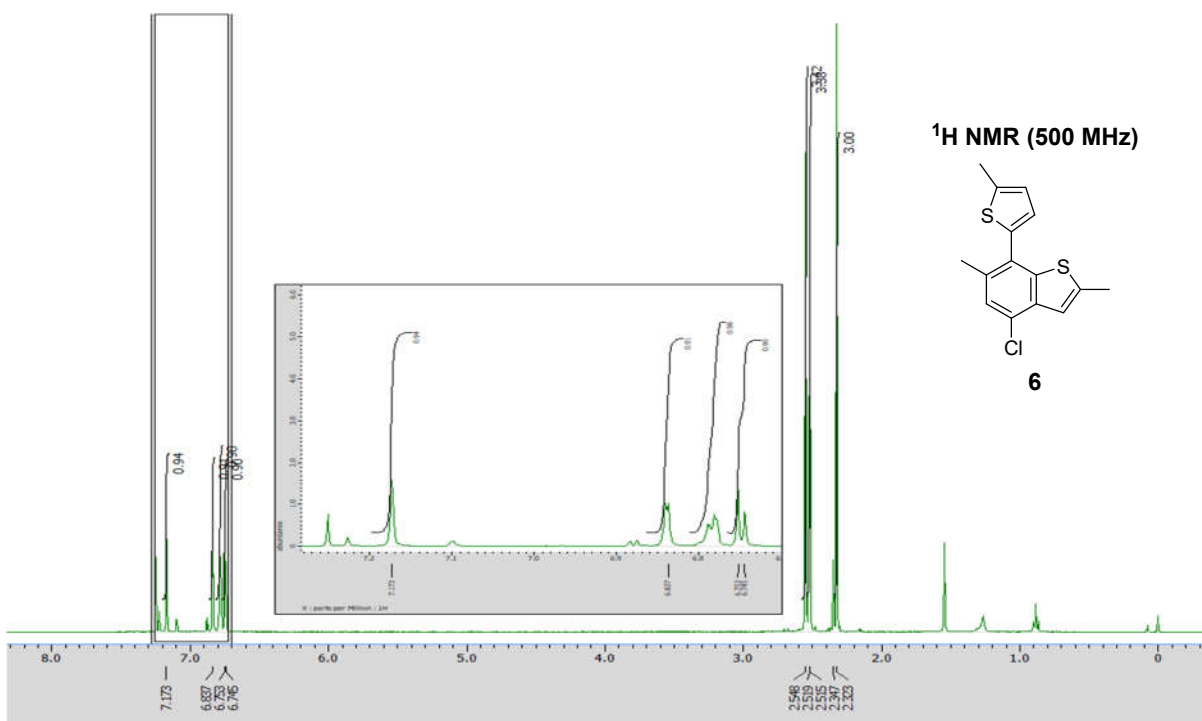


Figure S7: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 6

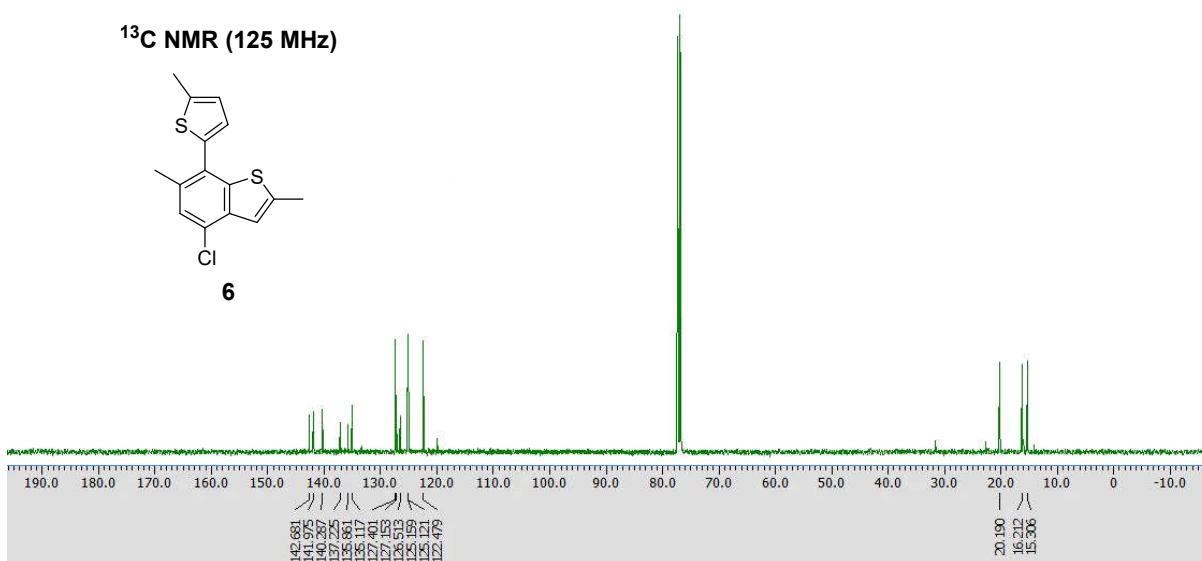


Figure S8: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 6

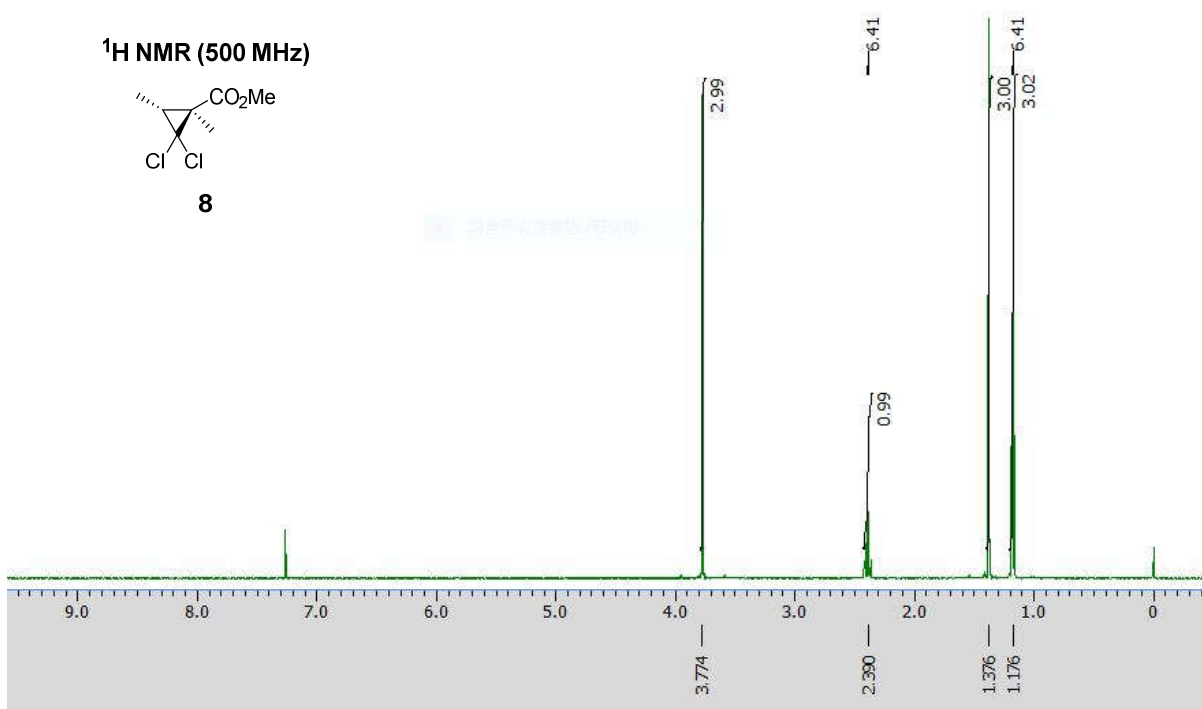


Figure S9: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 8

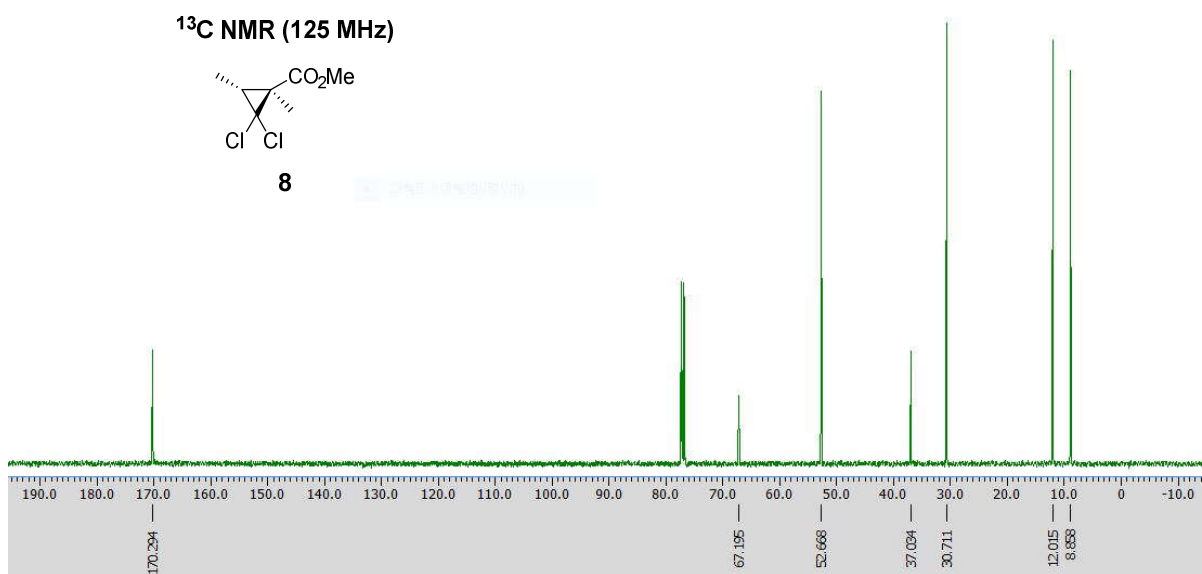


Figure S10: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 8

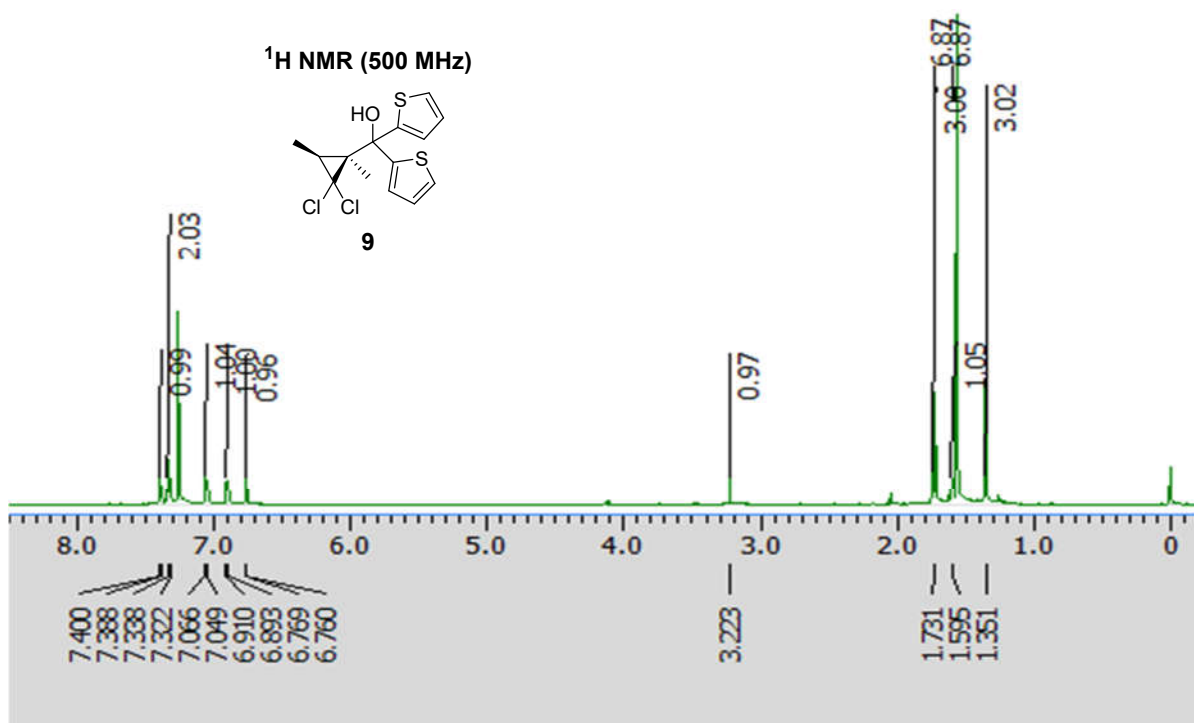


Figure S11: ^1H NMR (500 MHz, CDCl_3) Spectrum of the Compound 9

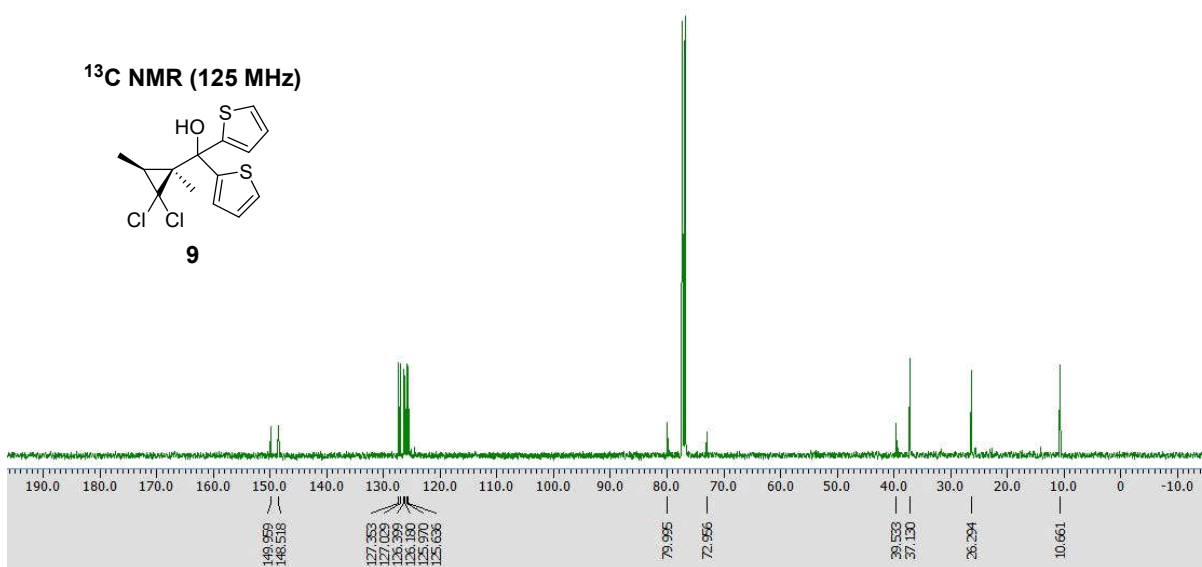


Figure S12: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of the Compound 9

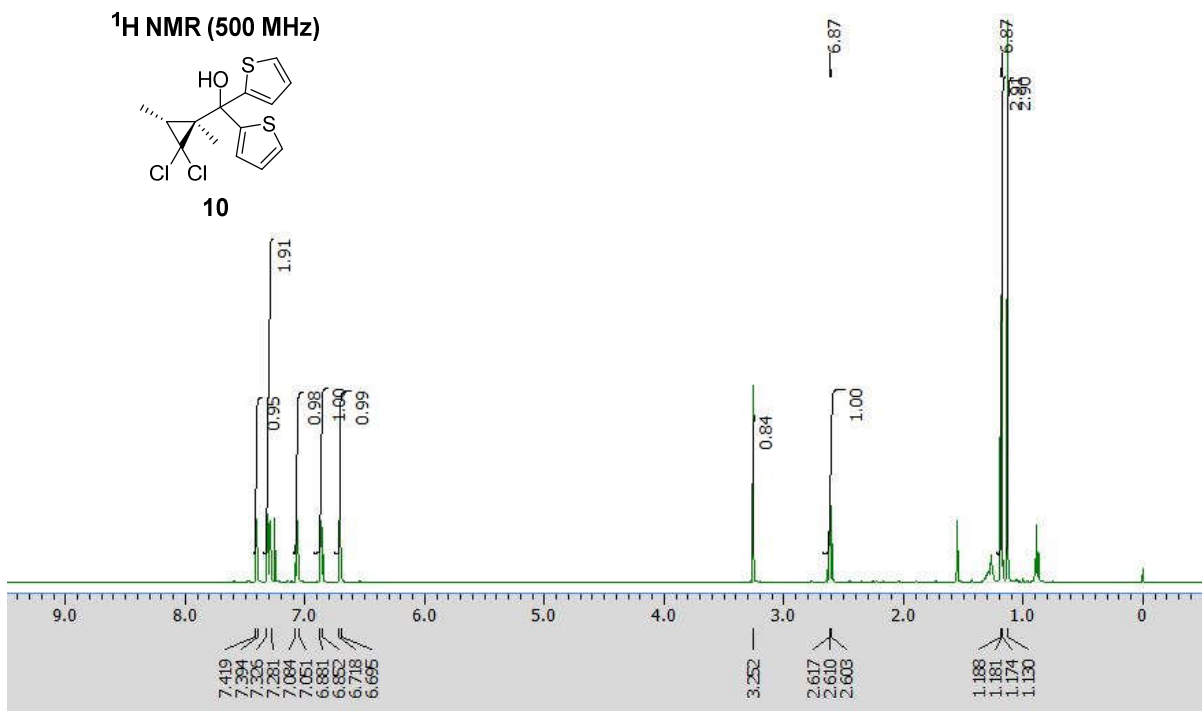


Figure S13: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 10

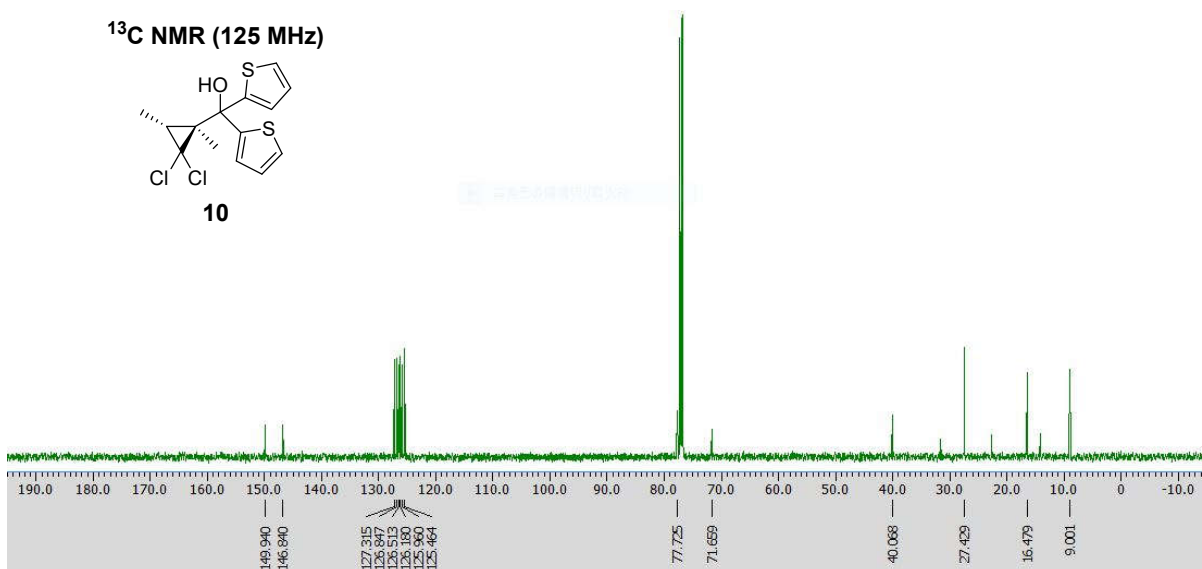


Figure S14: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 10

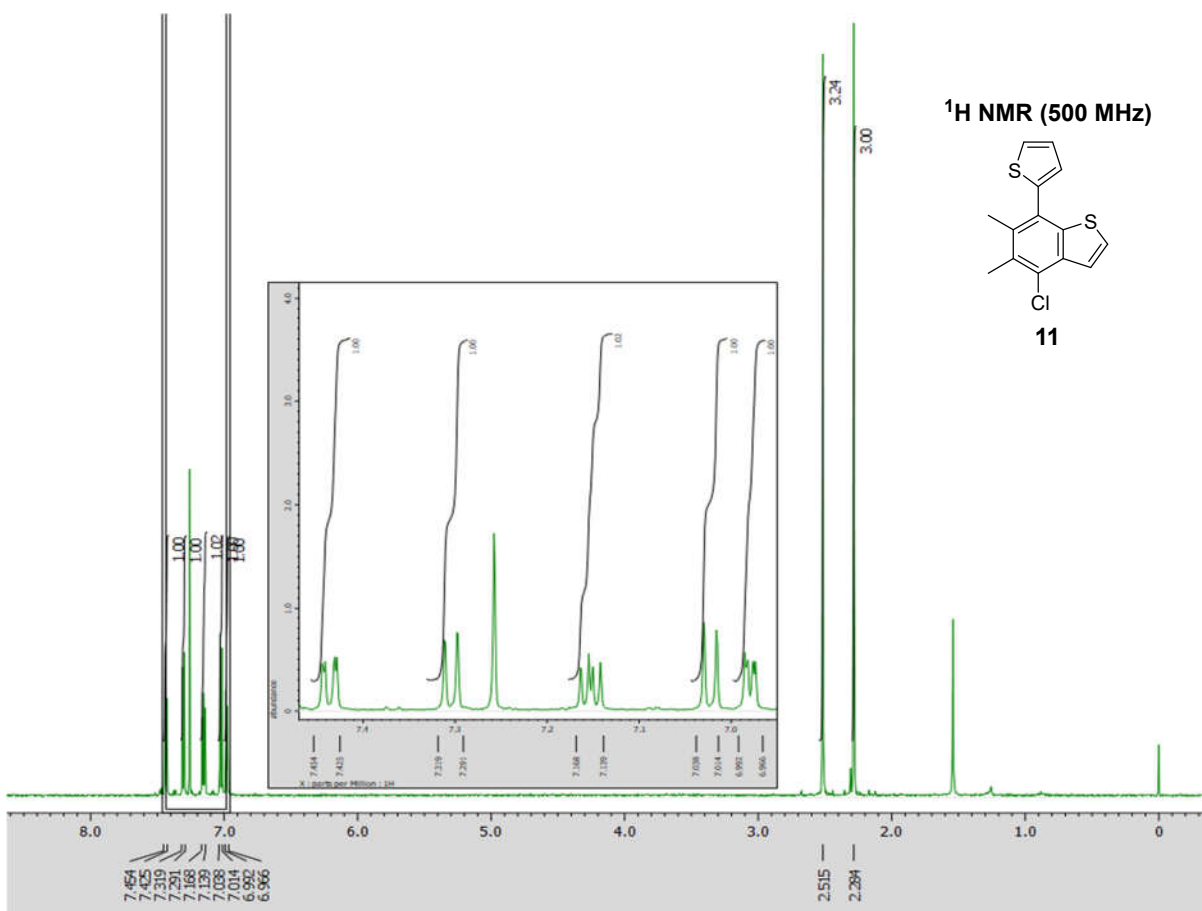


Figure S15: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 11

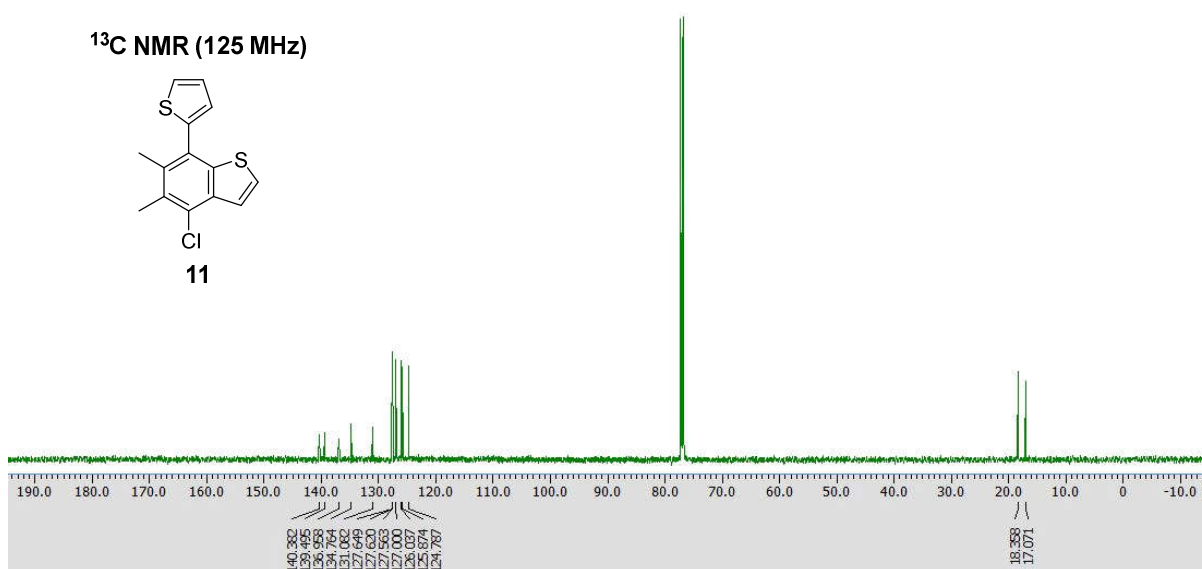


Figure S16: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 11

¹H NMR (500 MHz)

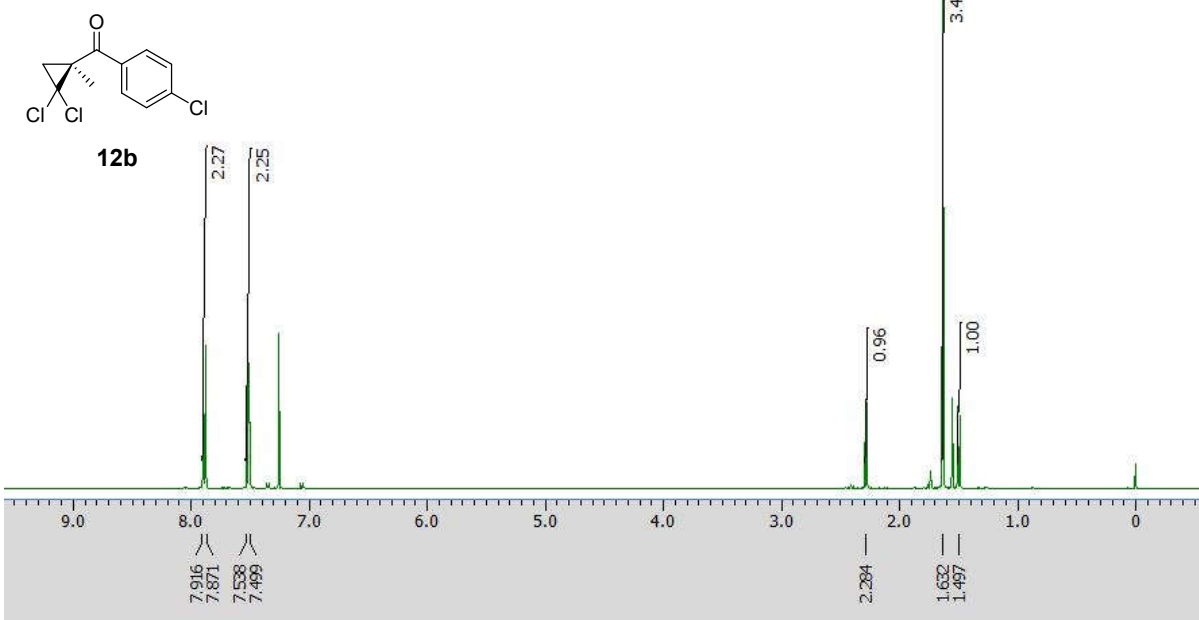


Figure S17: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound **12b**

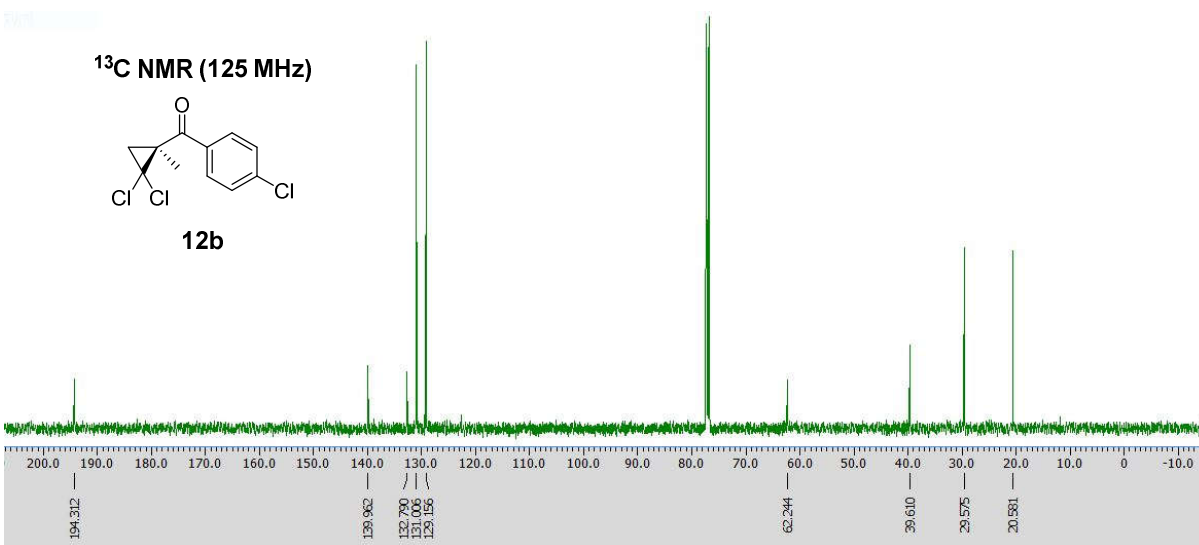


Figure S18: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound **12b**

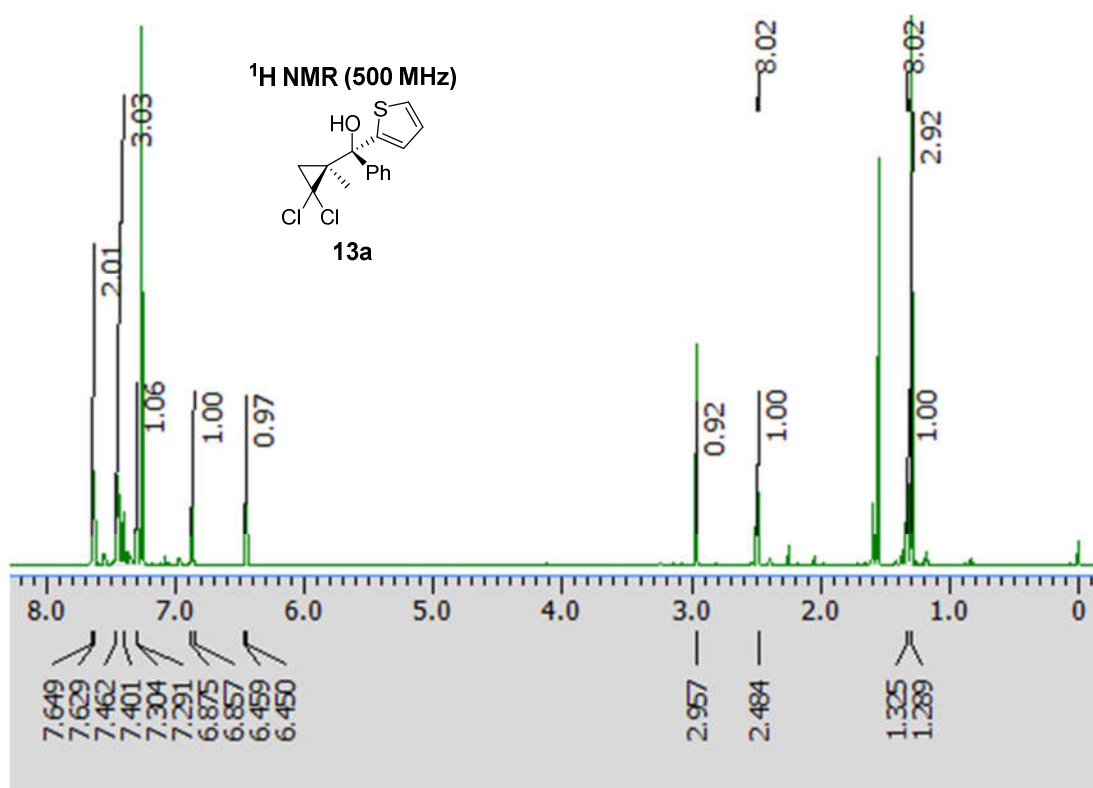


Figure S19: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 13a

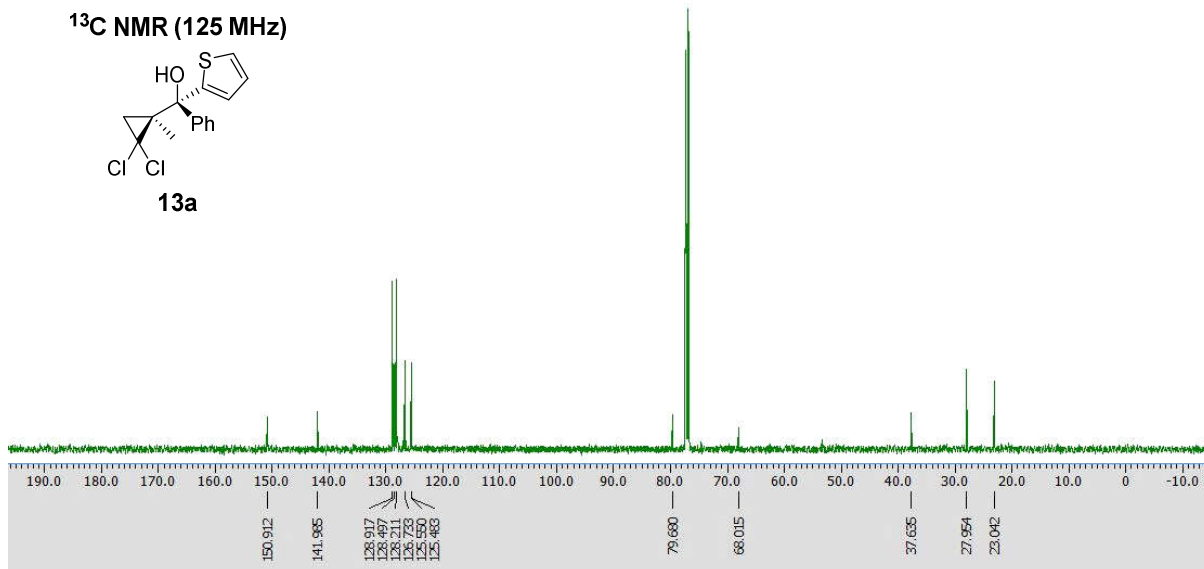


Figure S20: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 13a

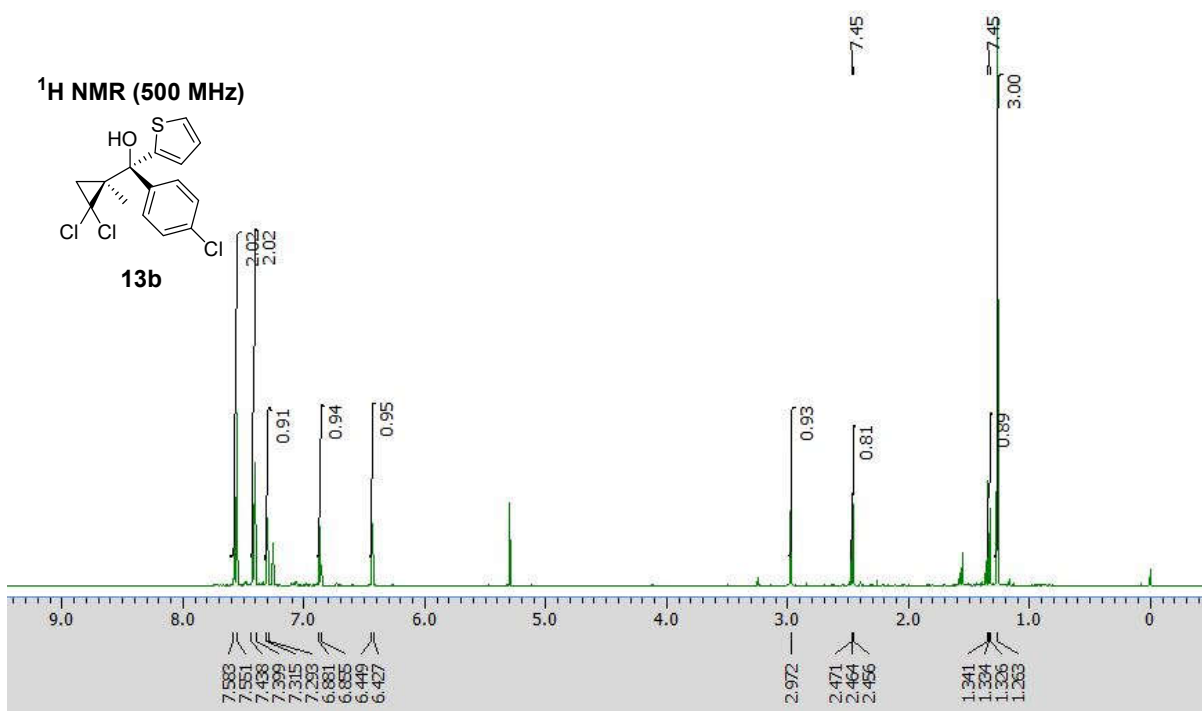


Figure S21: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 13b

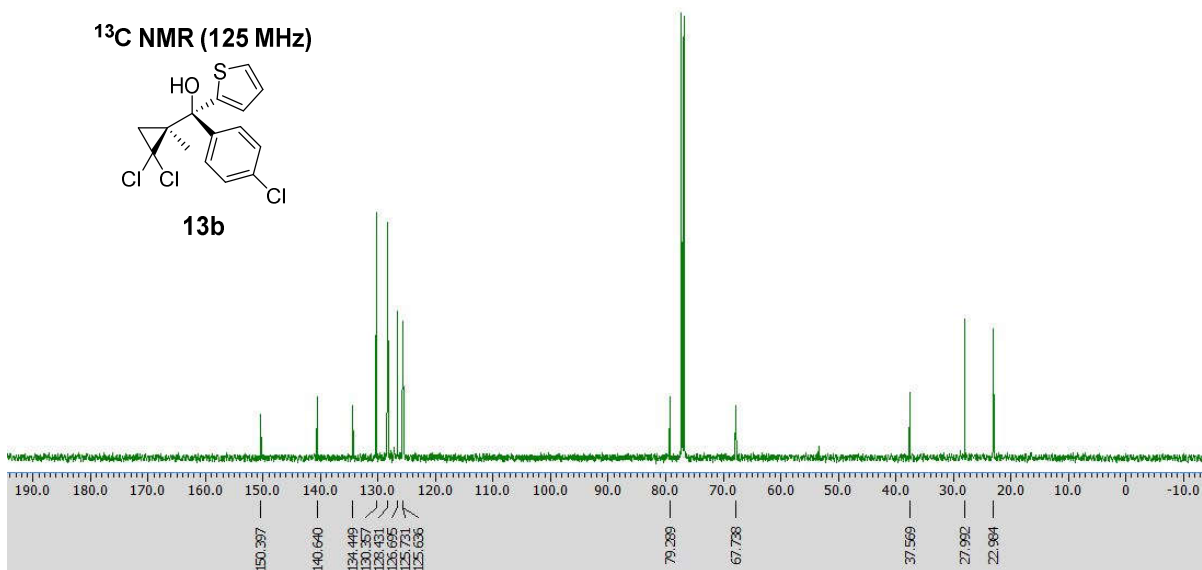


Figure S22: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 13b

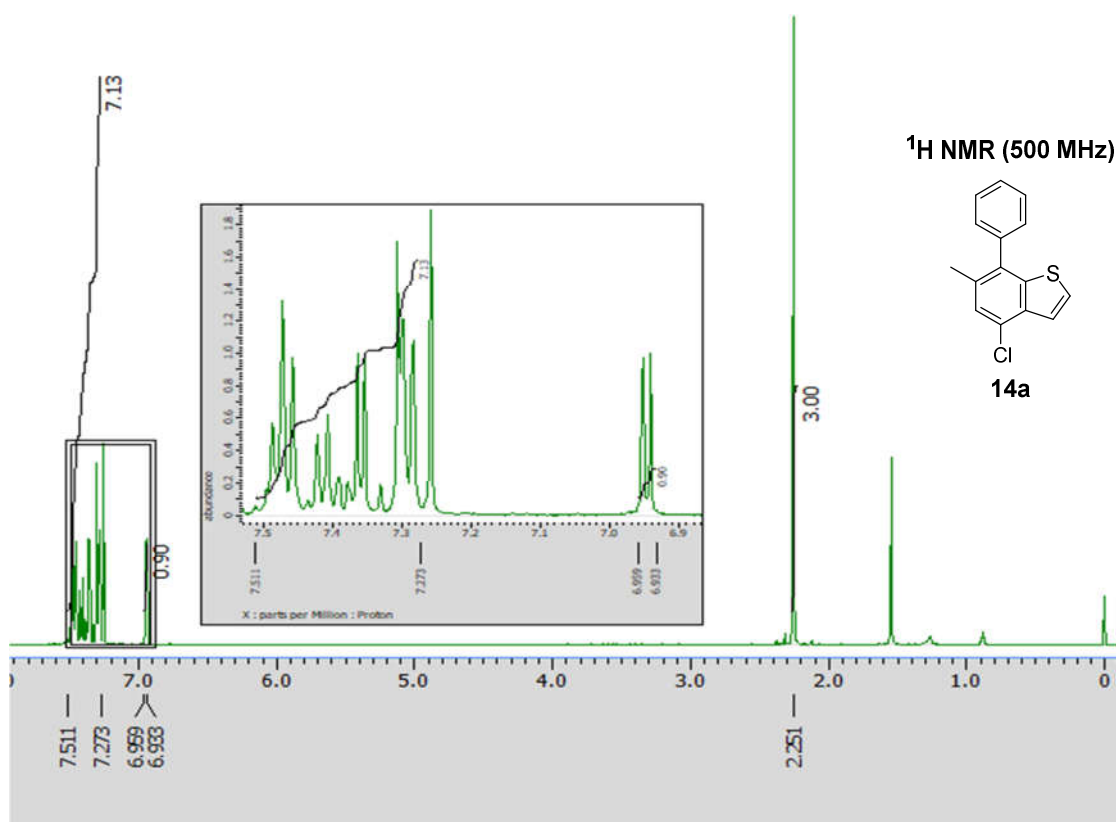


Figure S23: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 14a

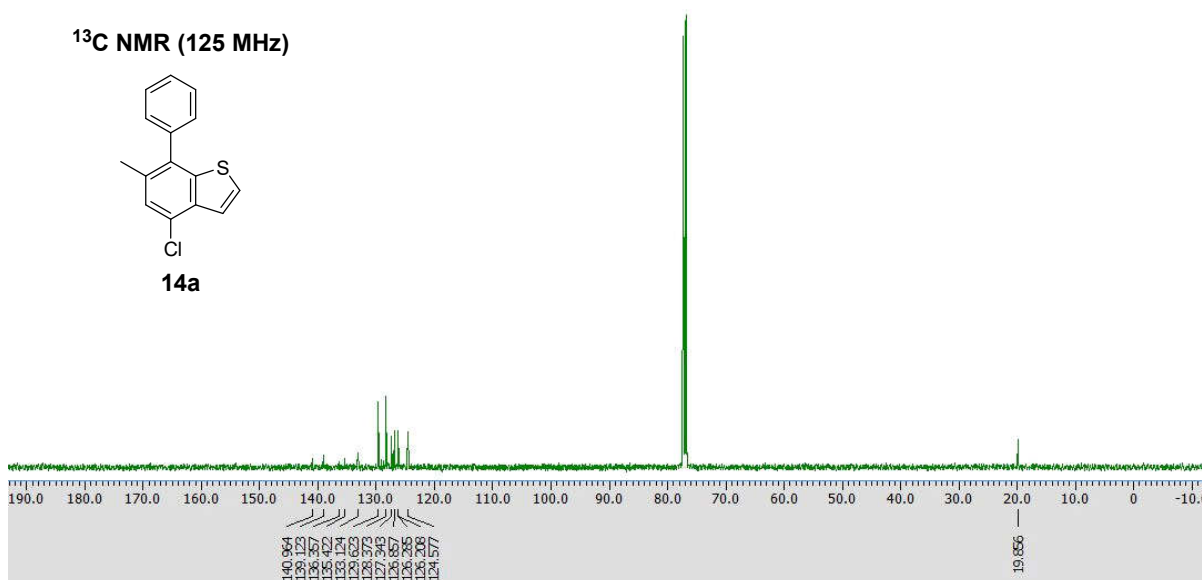


Figure S24: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 14a

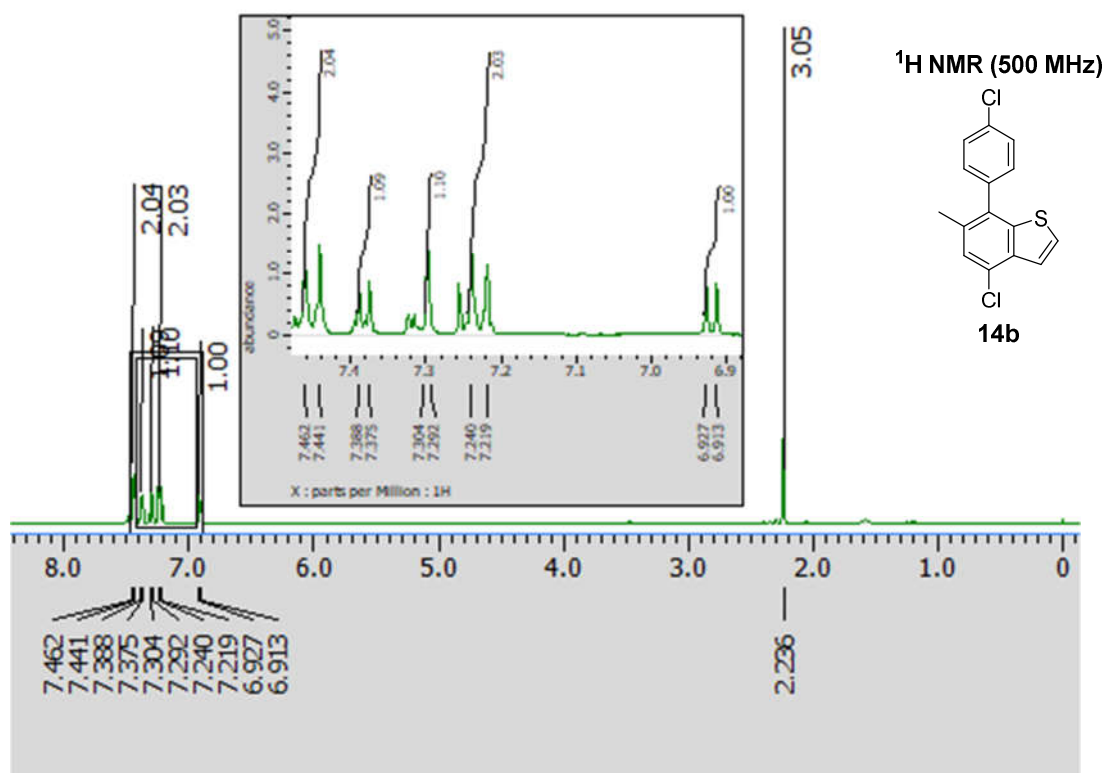


Figure S25: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound **14b**

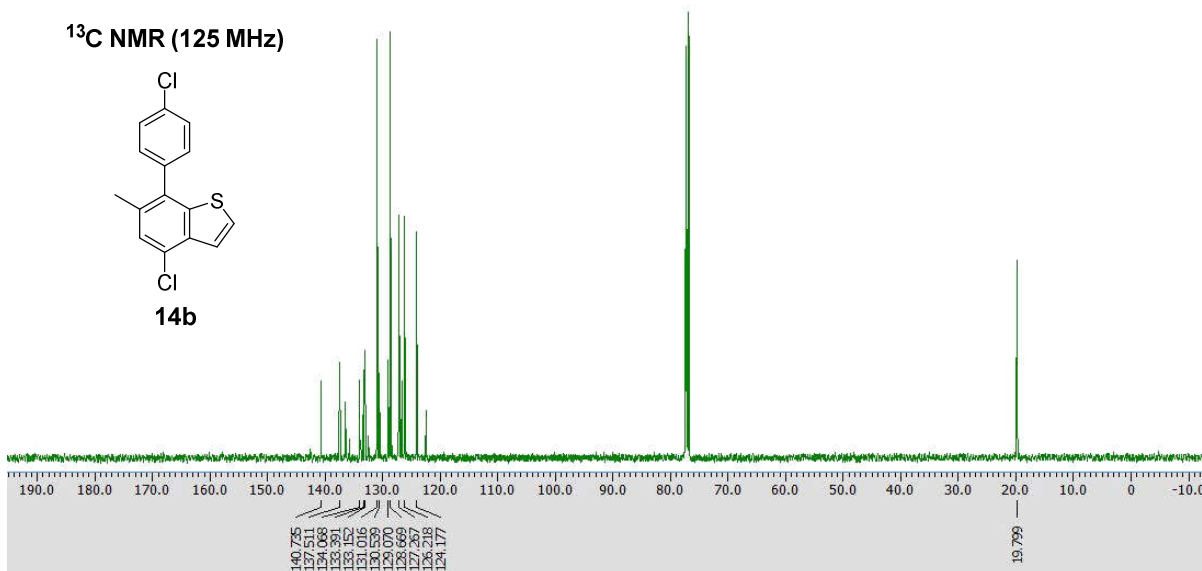


Figure S26: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound **14b**

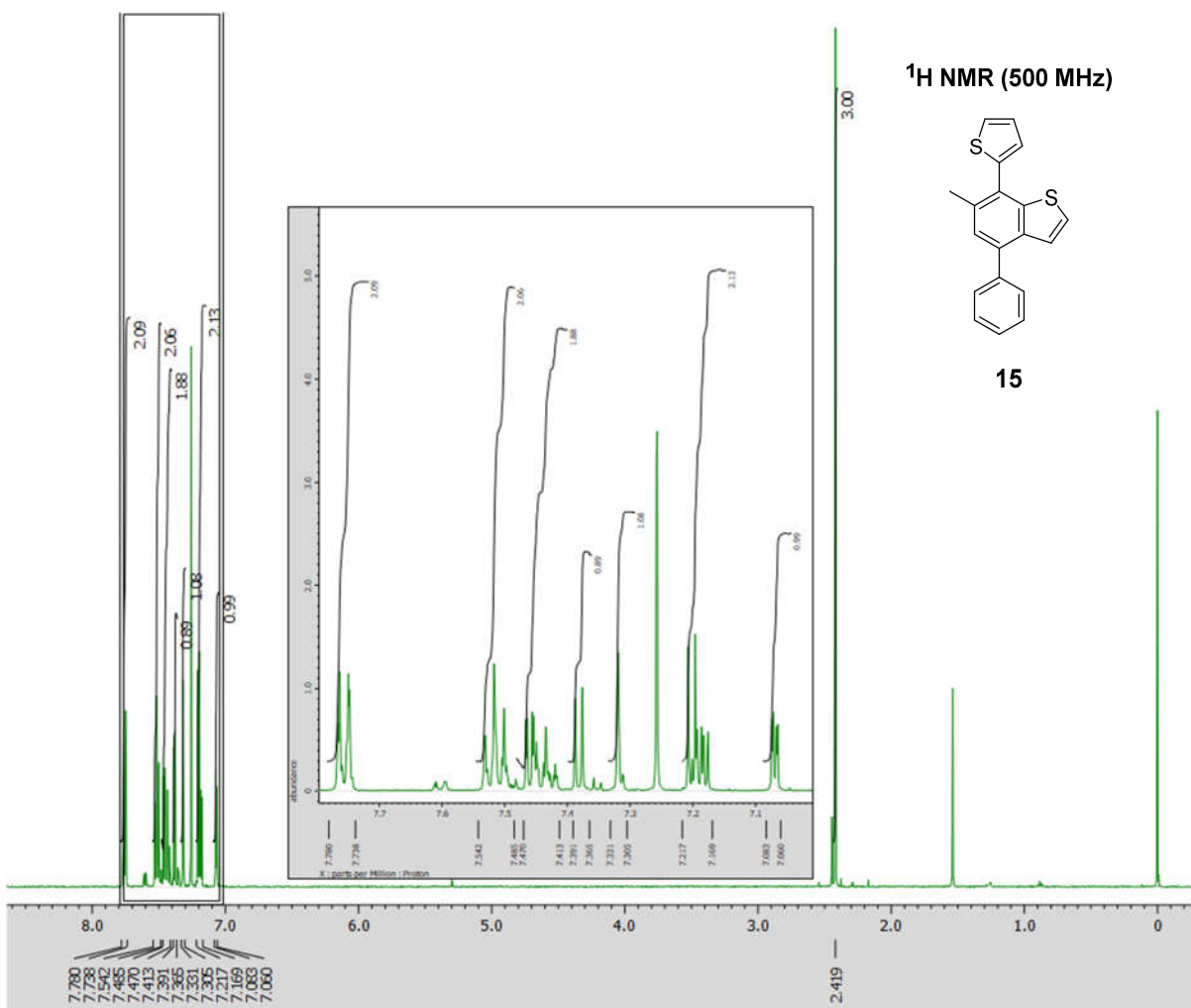


Figure S27: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 15

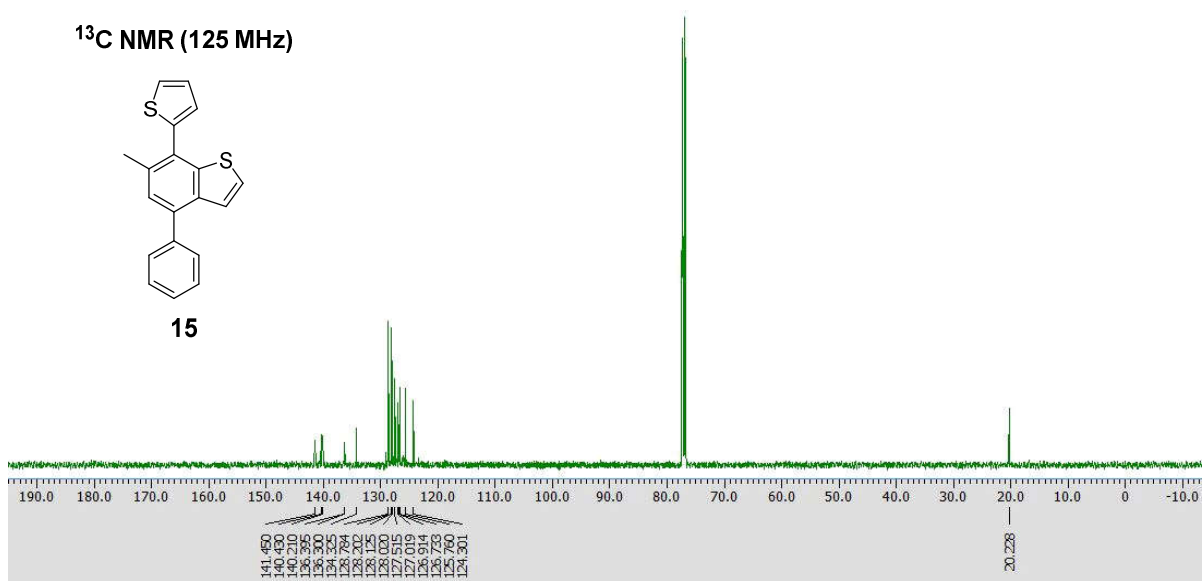


Figure S28: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 15

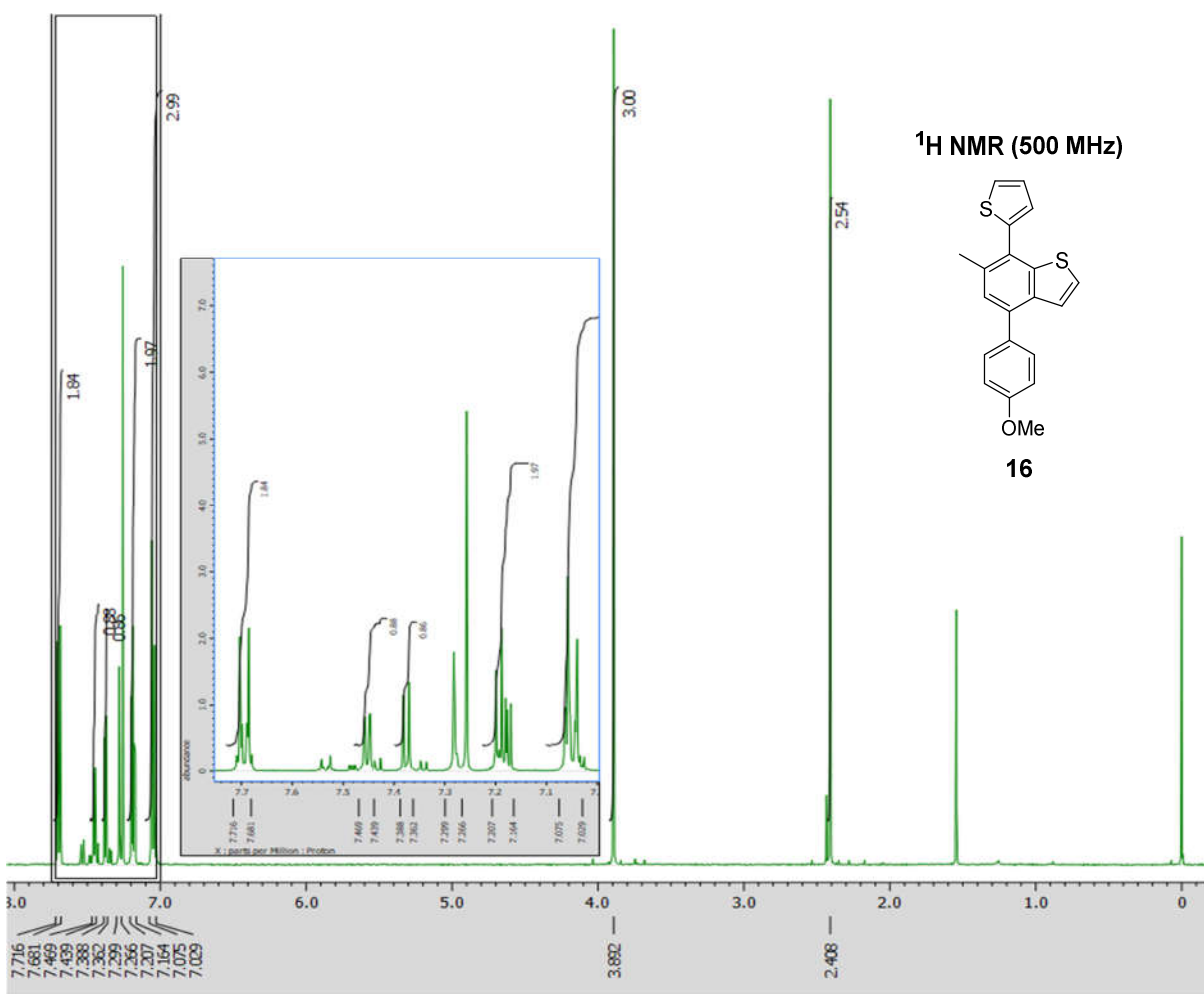


Figure S29: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 16

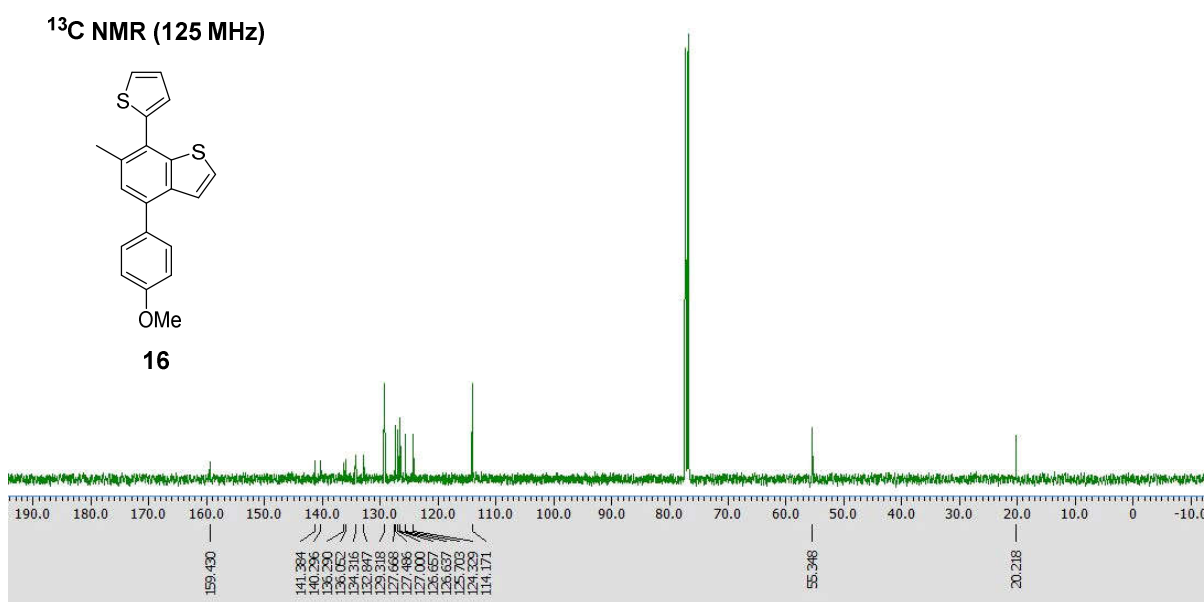


Figure S30: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 16

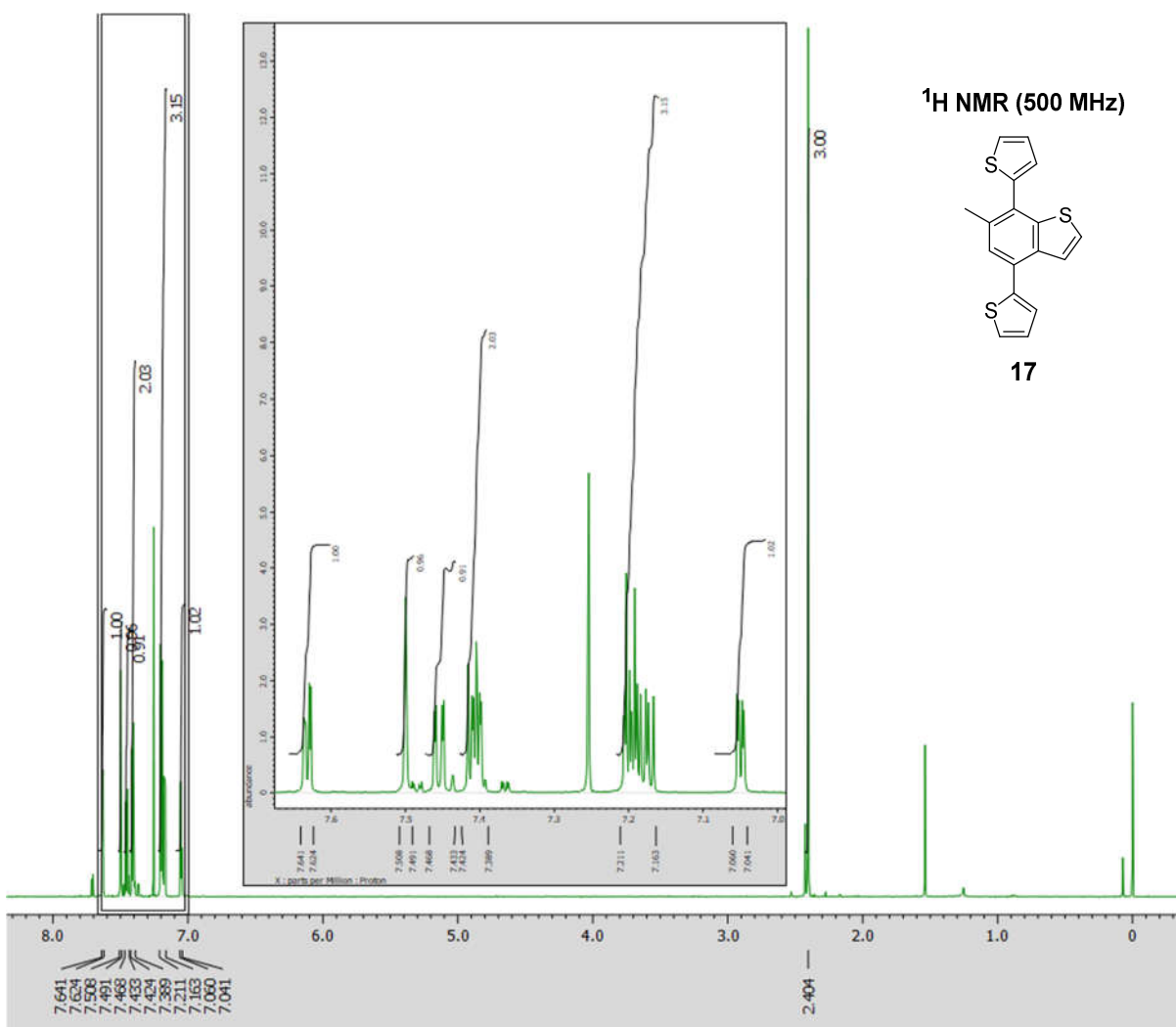


Figure S31: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 17

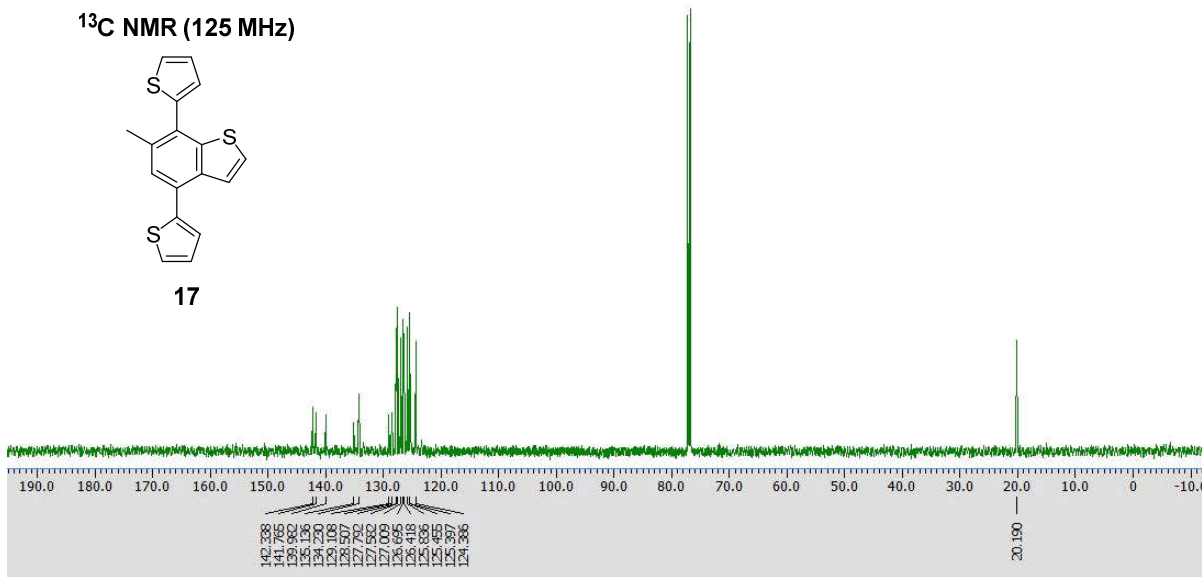


Figure S32: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 17

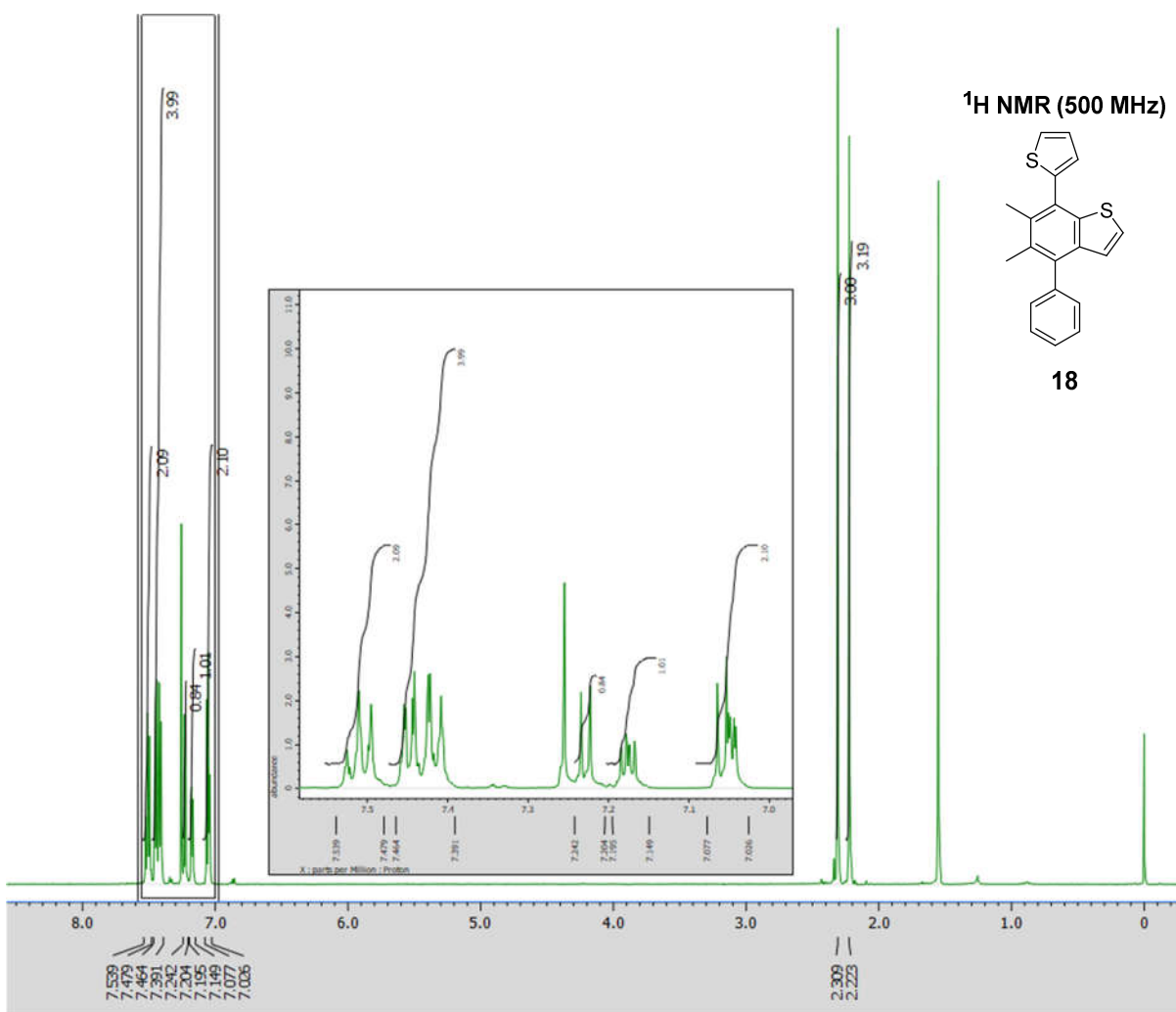


Figure S33: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 18

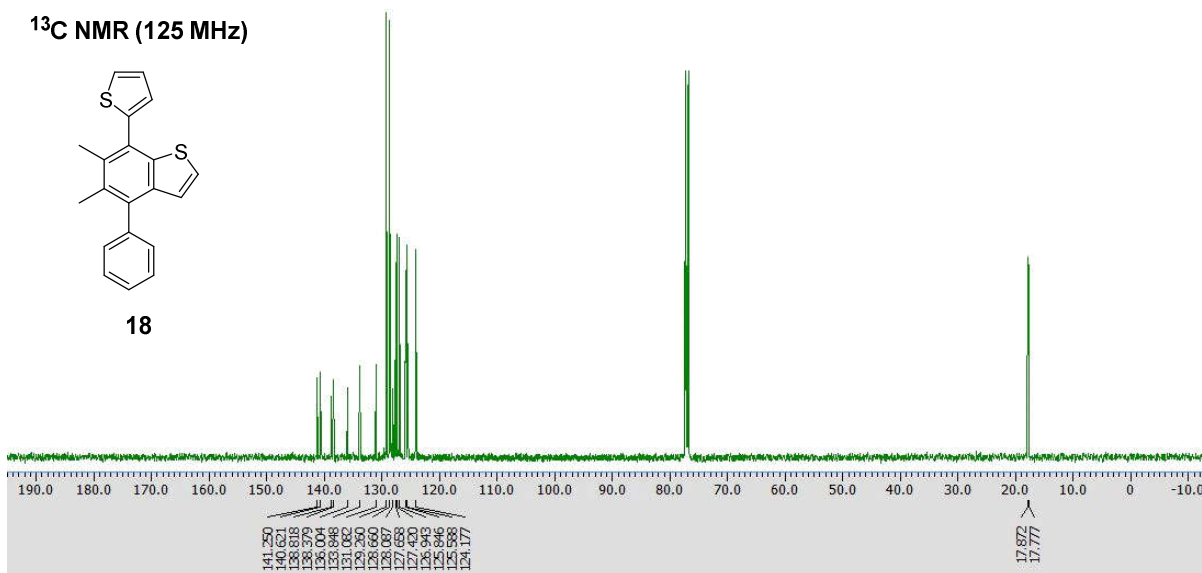


Figure S34: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 18

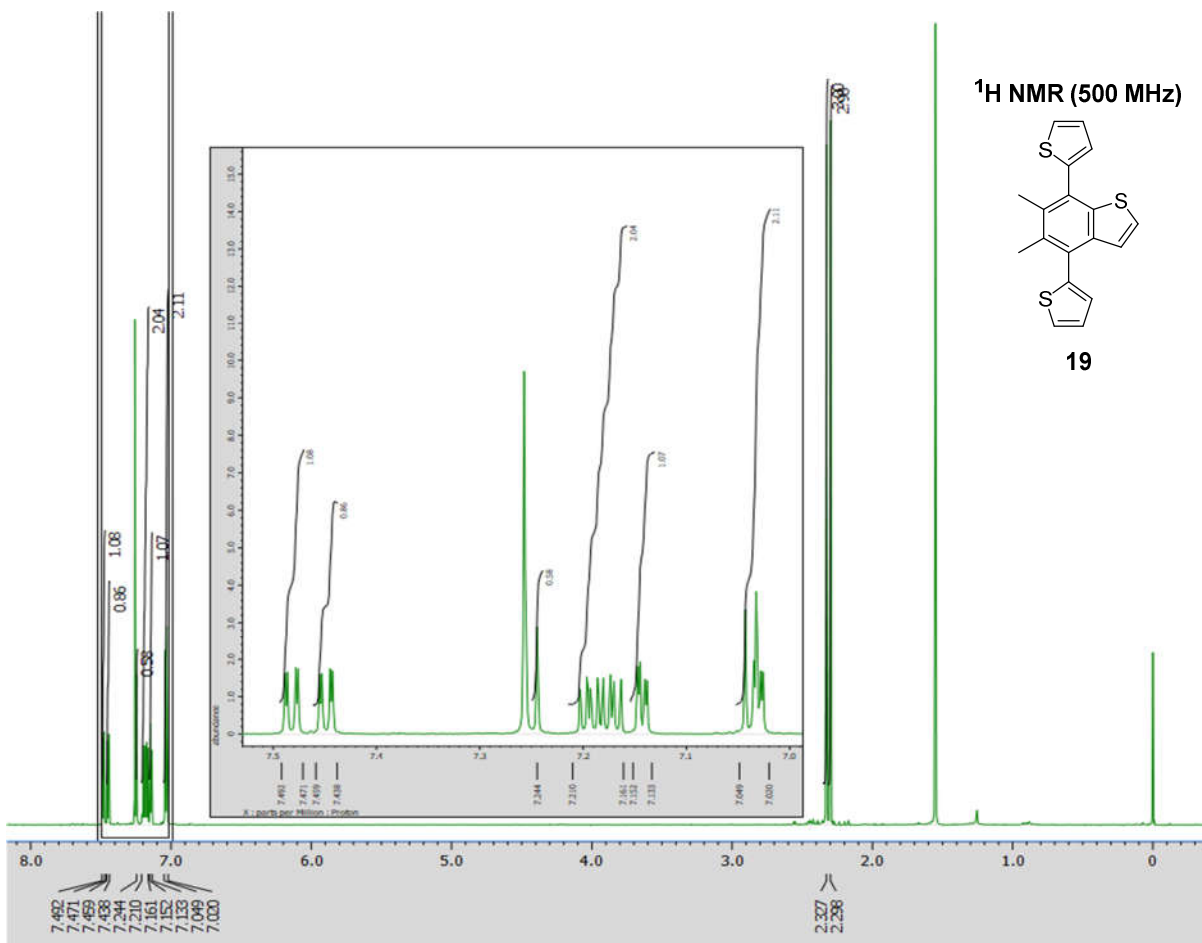


Figure S35: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 19

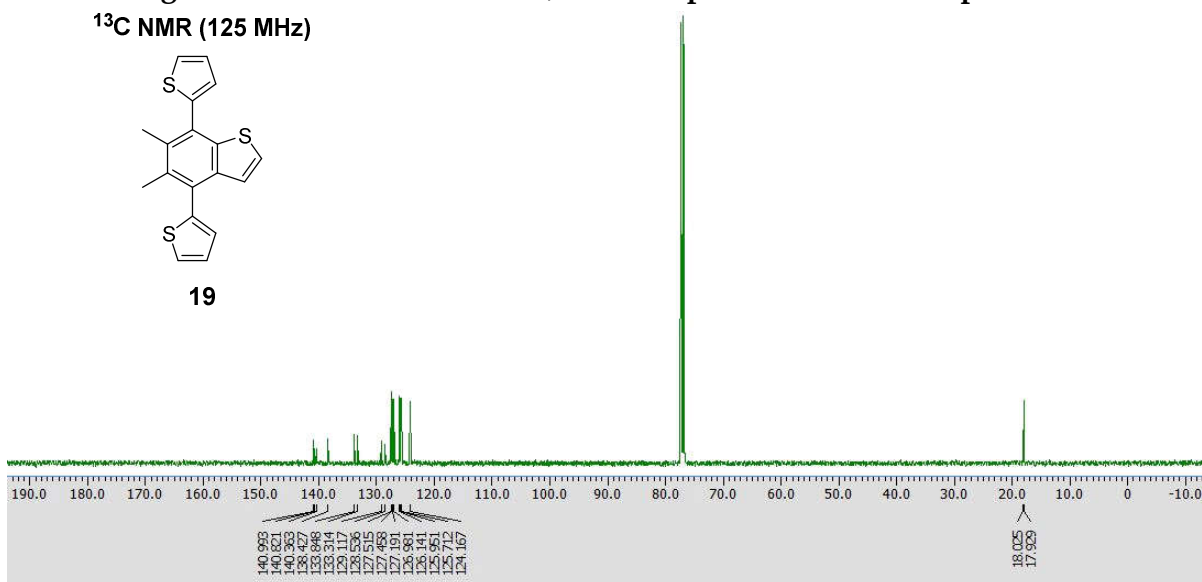
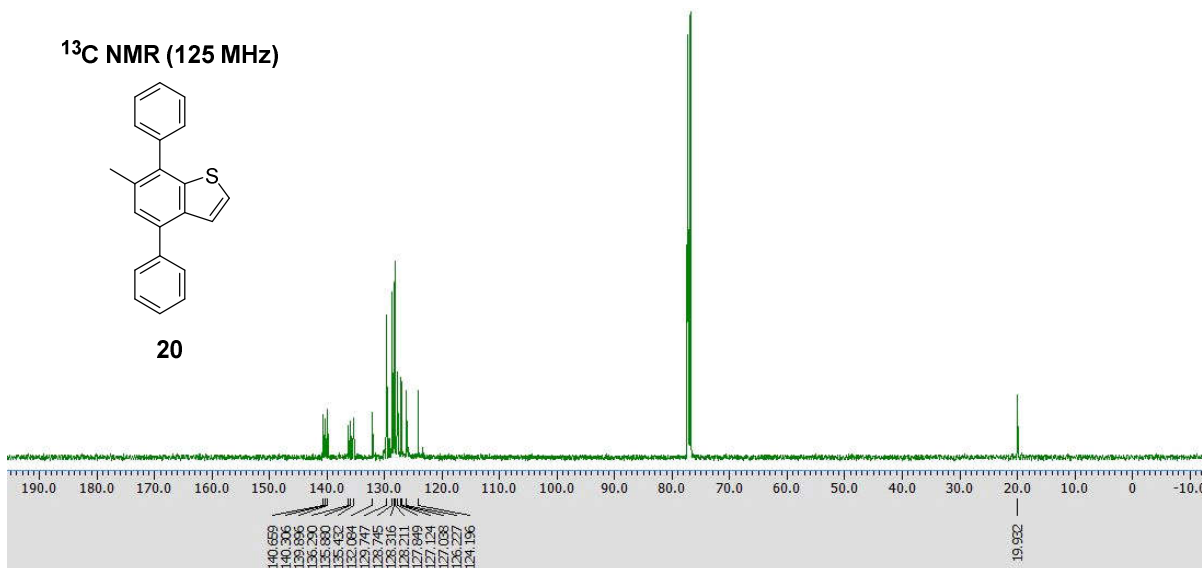
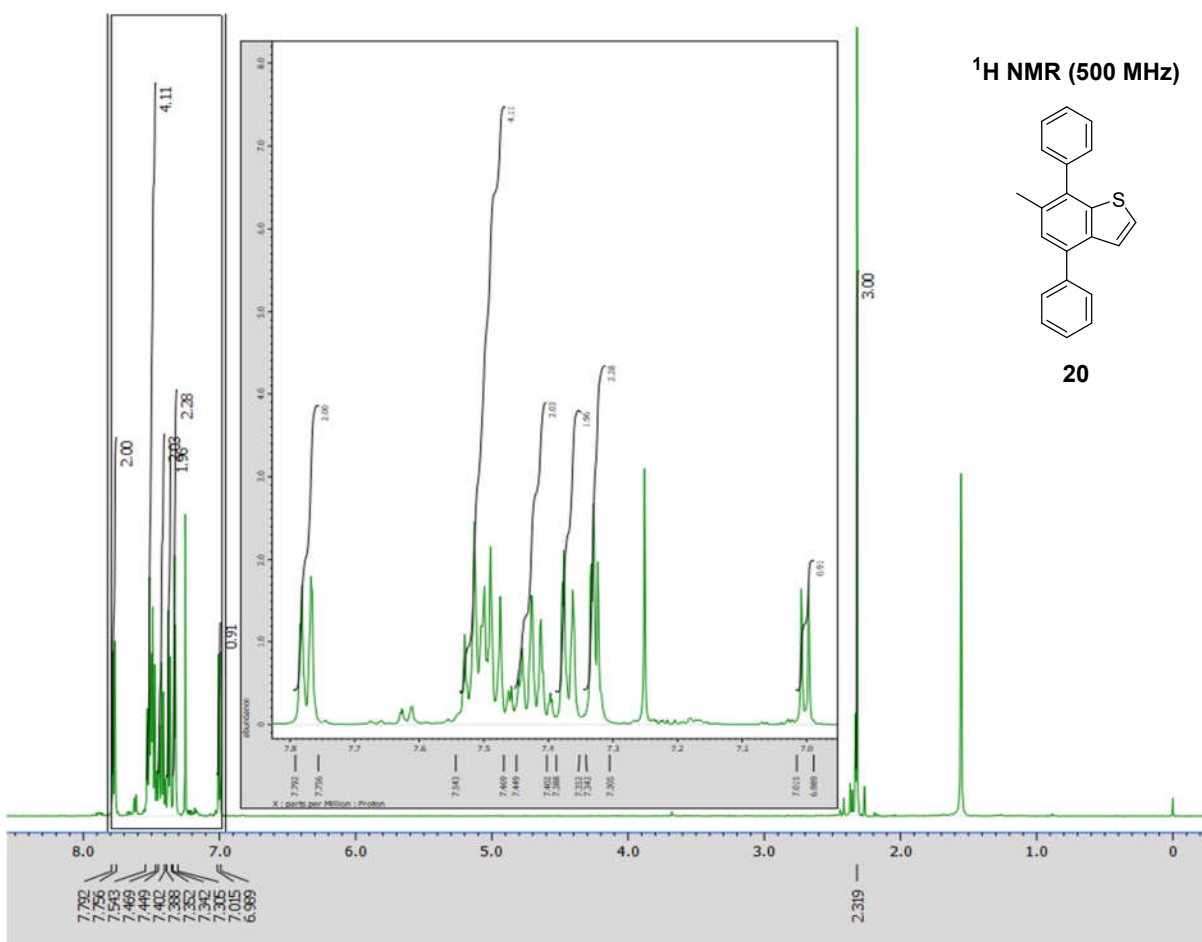


Figure S36: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 19



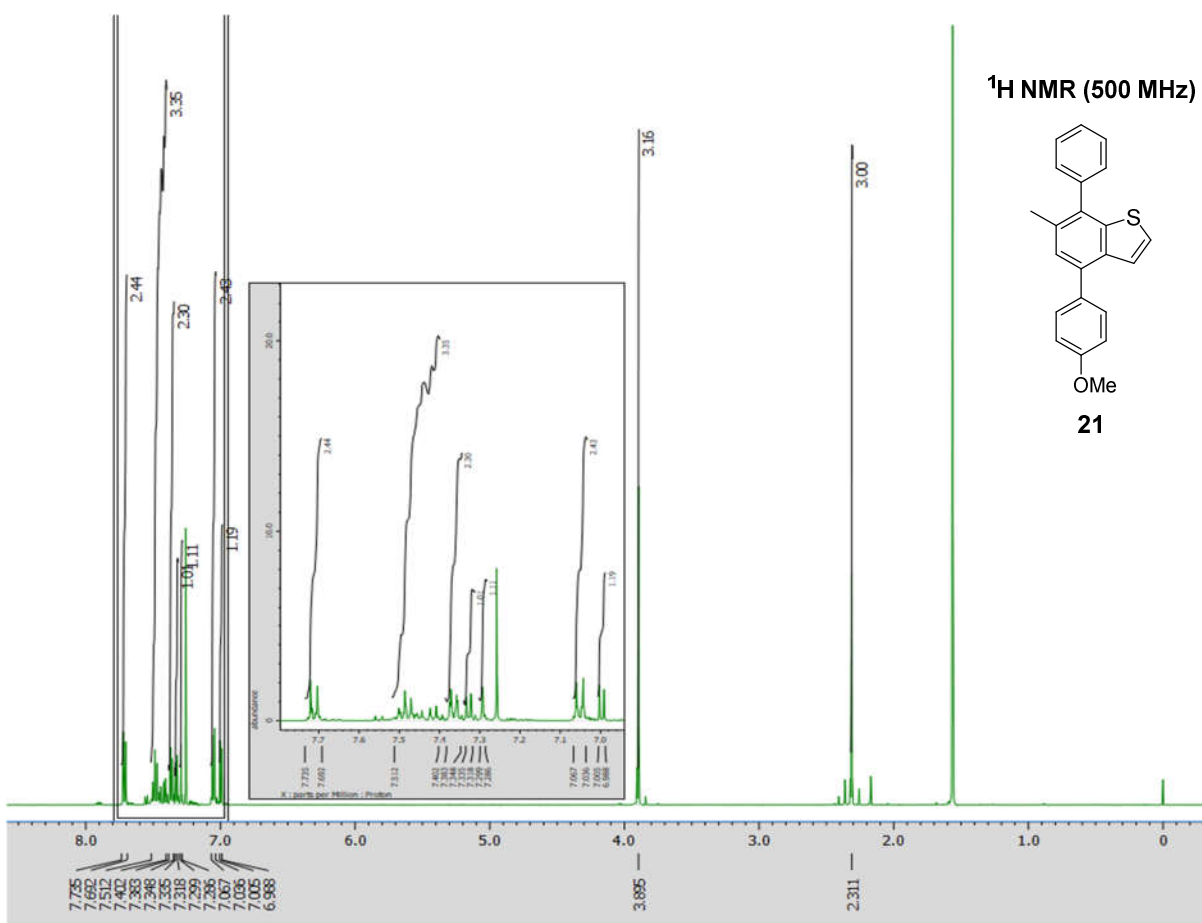


Figure S39: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound **21**

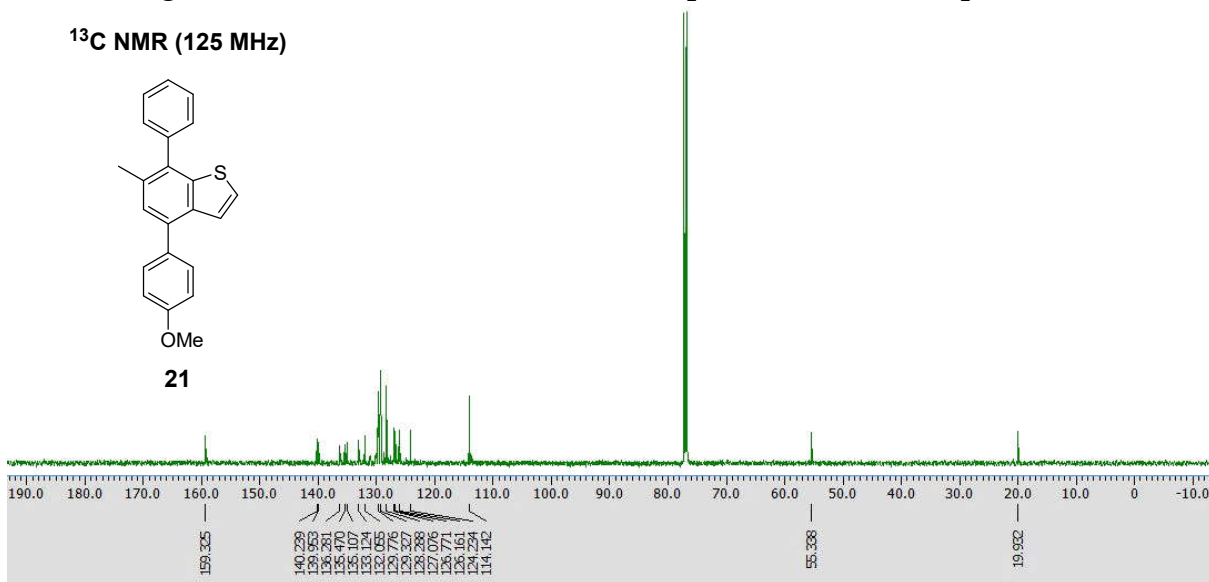


Figure S40: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound **21**

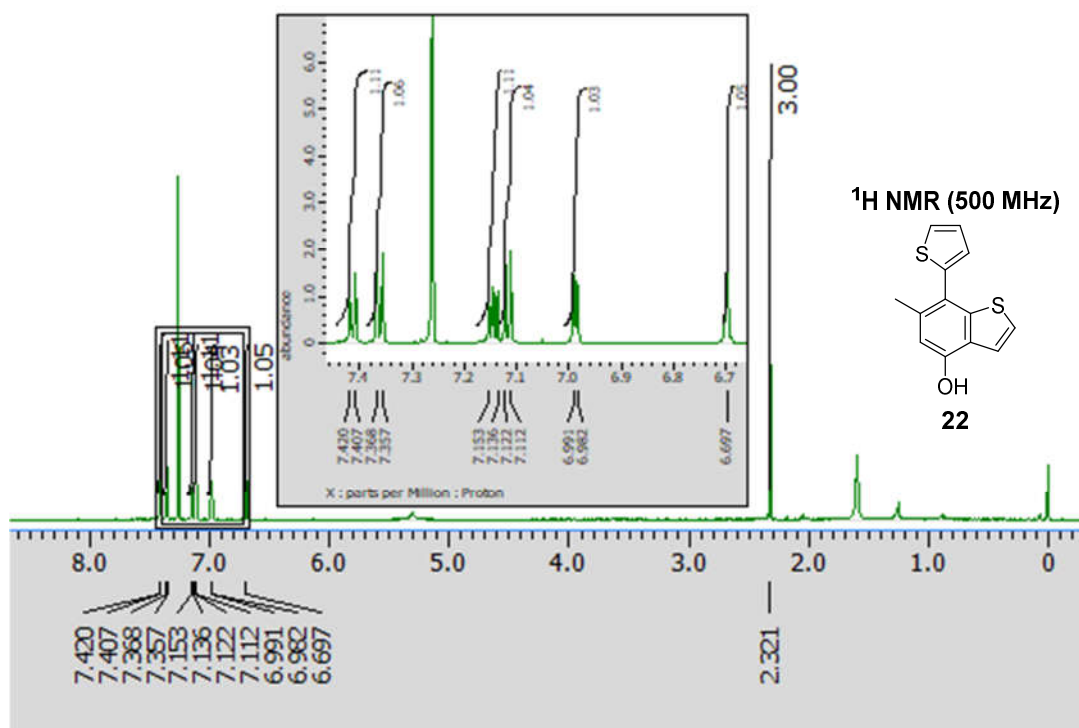


Figure S41: ¹H NMR (500 MHz, CDCl₃) Spectrum of the Compound 22

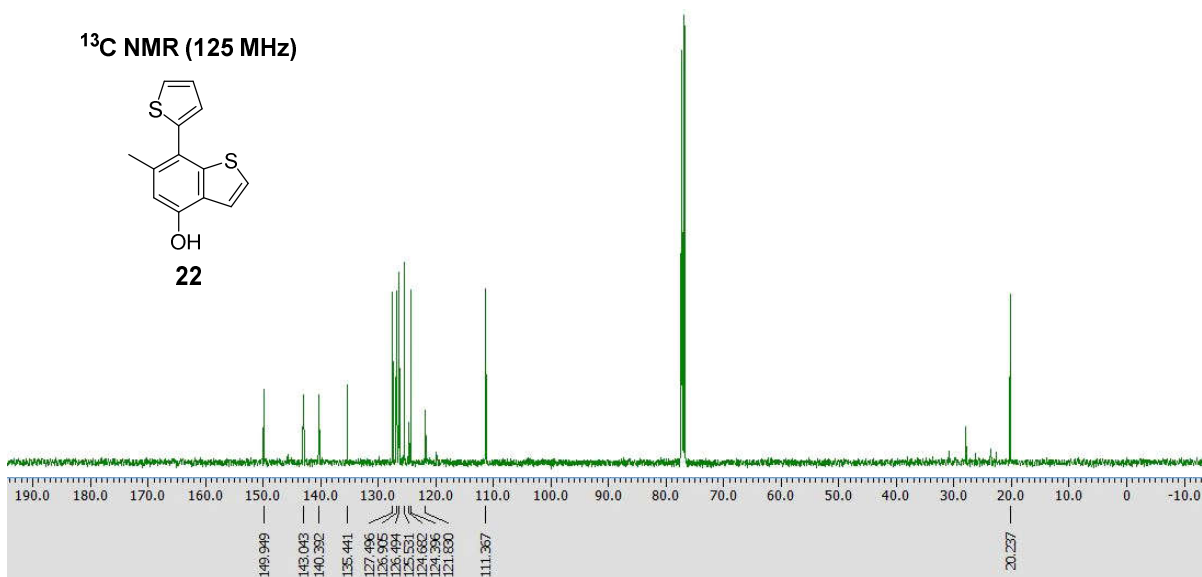
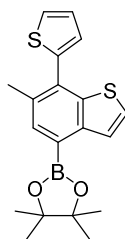


Figure S42: ¹³C NMR (125 MHz, CDCl₃) Spectrum of the Compound 22

^1H NMR (500 MHz)



23

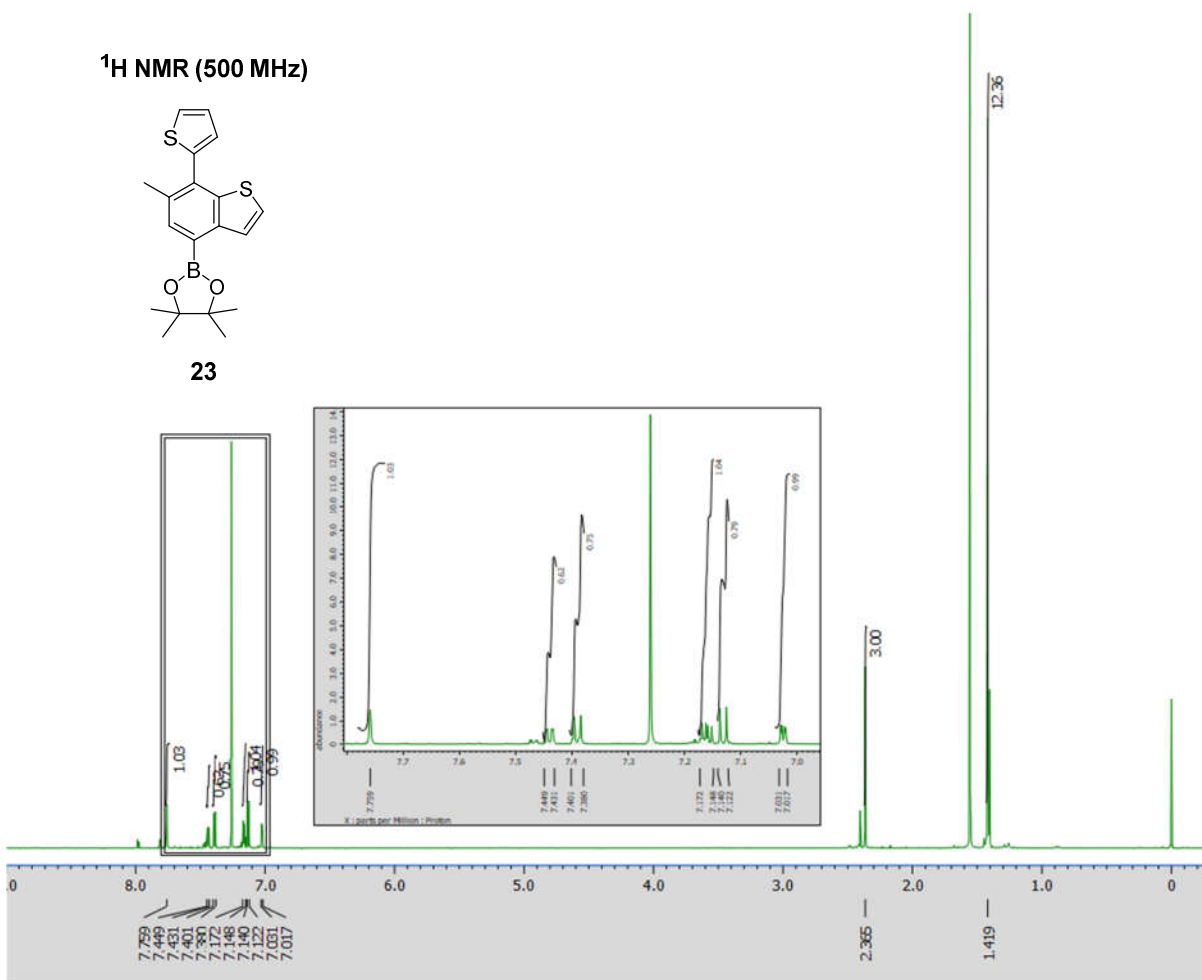
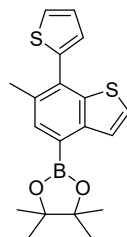


Figure S43: ^1H NMR (500 MHz, CDCl_3) Spectrum of the Compound 23

^{13}C NMR (125 MHz)



23

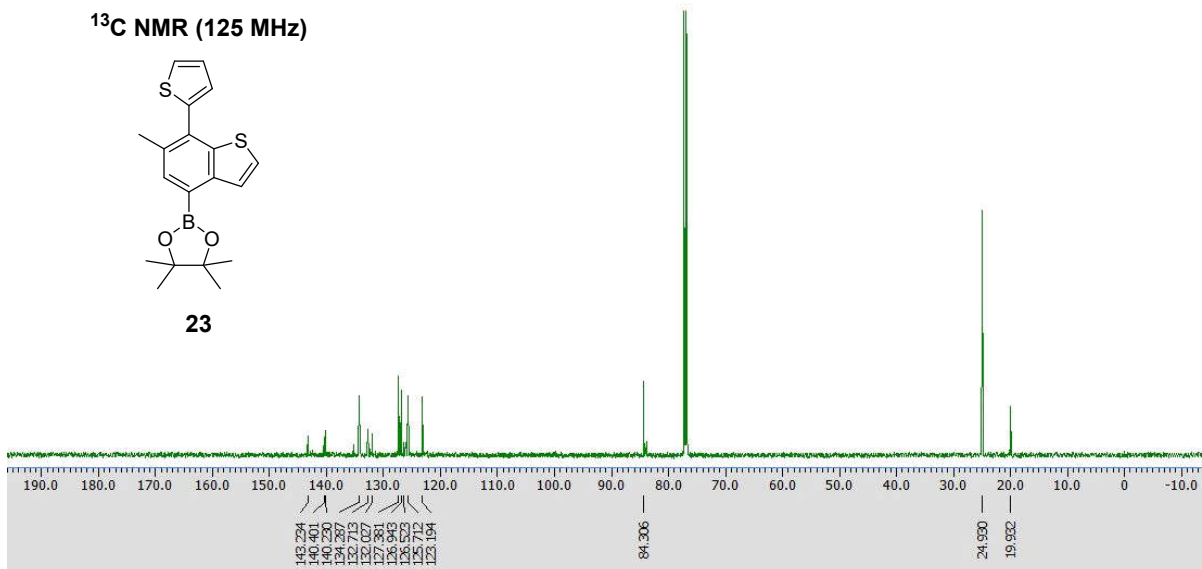
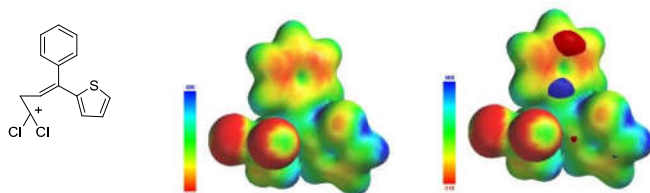


Figure S44: ^{13}C NMR (125 MHz, CDCl_3) Spectrum of the Compound 23

Electronic Supporting Information of Free Energy Calculation

Free energy calculation with structure prediction was carried out by Spartan'18 vl.1.0. Both electronstatic map and HOMO map of the key cation intermediate indicated higher potential of the benzene core than that of the thiophene one. Despite the calculation results, the orientation of cyclization was clearly reversed to afford benzothiophenes, probably because benzannulations through the chelation pathway predominated over that through inherent non-chelation pathway.



Electronstatic map

HOMO map

SPARTAN '18 MECHANICS PROGRAM: (Win/64b)

Release 1.1.0

Frequency Calculation

Adjusted 3 (out of 84) low frequency modes

Reason for exit: Successful completion

Mechanics CPU Time : .05

Mechanics Wall Time: .05

SPARTAN '18 Quantum Mechanics Driver: (Win/64b)

Release 1.1.0

Job type: Geometry optimization.

Method: RB3LYP

Basis set: 6-31G(D)

Number of basis functions: 289

Charge : +1

Number of electrons: 144

Parallel Job: 4 threads

SCF model:

A restricted hybrid HF-DFT SCF calculation will be performed using Pulay DIIS + Geometric Direct Minimization

Optimization:

	Step	Energy	Max
Grad.	Max Dist.		
1	-1858.343993	0.031568	
	0.145783		
2	-1858.354386	0.015594	
	0.164037	3	-1858.359075
	0.013586	0.157298	
4	-1858.363126	0.009610	
	0.144933		
5	-1858.366715	0.008565	
	0.120323		
6	-1858.370170	0.008484	
	0.105662	7	-1858.373775
	0.008219	0.102849	
8	-1858.377397	0.011830	
	0.106177		
9	-1858.380156	0.021907	
	0.092763		
10	-1858.382868	0.025624	
	0.109034		
11	-1858.382728	0.025570	
	0.101842		
12	-1858.388255	0.007980	
	0.079968	13	-1858.389199
	0.008362	0.113925	
14	-1858.388929	0.017324	
	0.077904		
15	-1858.390038	0.003001	
	0.084951		
16	-1858.389595	0.008815	
	0.053453		
17	-1858.390338	0.002467	
	0.038322		

18	-1858.390437	0.001734	
	0.053614		
19	-1858.390525	0.002765	
	0.017620		
20	-1858.390568	0.000495	
	0.009459	21	-1858.390573
	0.000721	0.005781	22
	-1858.390576	0.000207	
	0.001555		

<step 2>

Job type: Frequency calculation.

Method: RB3LYP

Basis set: 6-31G(D)

Reason for exit: Successful completion

Quantum Calculation CPU Time :

1:15:47.25

Quantum Calculation Wall Time:

20:02.05

Cartesian coordinates

Atom	X	Y	Z
C	0.388218	0.794267	-3.873766
C	-0.024720	0.300190	-1.137853
C	0.528621	1.835649	-2.946288
C	0.023157	-0.486973	-3.447431
C	-0.176797	-0.738321	-2.097570
C	0.305875	1.602656	-1.598521
C	-0.256352	0.052169	0.269731
C	-0.783667	1.181612	1.070959
C	0.011203	-1.198646	0.865227
S	1.253751	-2.299712	0.231958
C	0.940267	-3.426428	1.469625
C	-0.082040	-3.034486	2.327046

C	-0.588003	-1.774337	
2.004904	C	-0.776214	
1.330088	2.590399		
H	0.547840	0.987182	-4.930506
H	0.811872	2.828220	-3.281613
H	-0.123594	-1.281796	-4.171685
H	-0.528111	-1.715003	-1.785334
H	0.432272	2.414100	
-0.891543	H	-1.570280	
1.732320	0.562329		
H	1.527603	-4.335201	1.532235
H	-0.429512	-3.641881	3.154298
H	-1.409703	-1.307873	2.533478
H	-0.335605	0.555937	3.207302
H	-1.637338	1.827873	3.026738
C	0.178403	2.155500	1.812000
Cl	1.900394	1.761618	1.905224
Cl	-0.127541	3.881278	1.598655

Temperature Corrections for 298.15 K

Zero-Point Energy=	0.199341 (Hartree/Particle)
Thermal correction to Energy=	0.213513
Thermal correction to Enthalpies=	0.204719
Thermal correction to Gibbs Free Energies=	0.152477
Sum of electronic and thermal Energies=	-1858.390576
Sum of electronic and thermal Enthalpies=	-1858.177062
Sum of electronic and thermal Free Energies=	-1858.238100
LUMO=	-7.45(eV)
HOMO=	-10.74(eV)