Electronic Supplementary Information

Ring-fused dimethoxybenzimidazole-benzimidazolequinone (DMBBQ): tunable halogenation and quinone formation using NaX/Oxone

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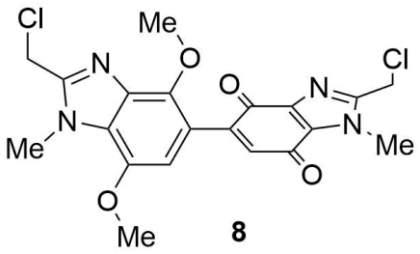
NMR spectra



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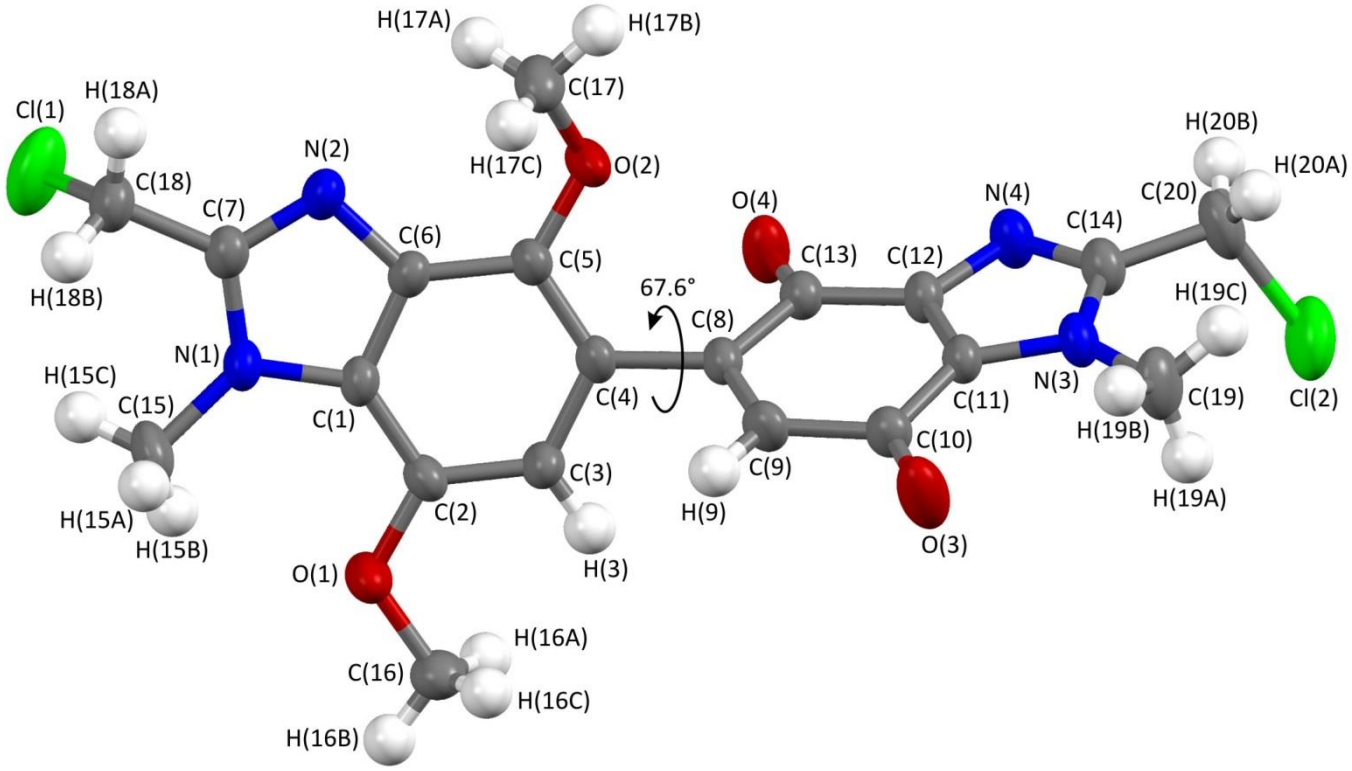
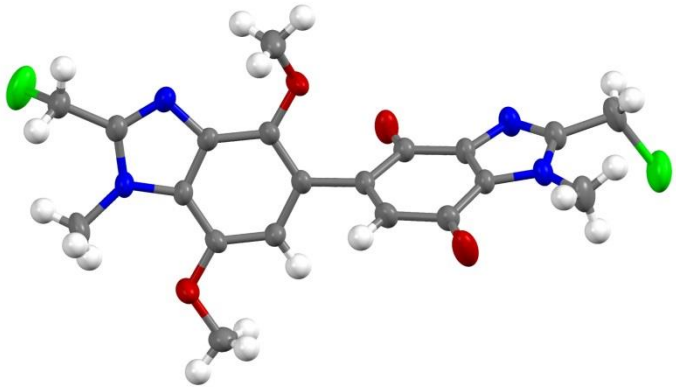


Figure S1. Molecular structure of 2,2'-bis(chloromethyl)-4',7'-dimethoxy-1,1'-dimethyl-1*H*,1'*H*-[5,5'-bibenzimidazole]-4,7-dione (**8**) determined from single-crystal X-ray diffraction at 299 K with anisotropic displacement ellipsoids of 50% probability except for hydrogen atoms, which are shown at a fixed radius of 0.3 Å. The torsion angle highlighted is calculated from the angle between the best planes through the substituted benzimidazole and benzimidazolequinone rings including atoms O(1) to O(4) using the program Mercury from CCDC.

Table S1. Single-crystal X-ray data and structure refinement for 2,2'-bis(chloromethyl)-4',7'-dimethoxy-1,1'-dimethyl-1*H*,1'*H*-[5,5'-bibenzimidazole]-4,7-dione (**8**).



Identification code	pk_1
Empirical formula	$C_{20}H_{18}Cl_2N_4O_4$
Formula weight	449.2
Temperature / K	299
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	10.7210(7)
b / Å	14.6163(11)
c / Å	12.7288(11)
α / °	90
β / °	97.406(7)
γ / °	90
Volume / Å^3	1978.0(3)
Z	4
ρ_{calc} / g cm^{-3}	1.509
μ / mm^{-1}	0.365
F(000)	928
Crystal size / mm^3	0.50 × 0.30 × 0.20
Radiation	Mo Kα (λ = 0.71073 Å)
2θ range for data collection / °	6.766 to 58.484
Completeness to 2θ = 50.484°	99.7%
Max. and min. transmission	1.0 to 0.93128
Index ranges	$-7 \le h \le 14$, $18 \le k \le 18$, $-16 \le l \le 16$
Reflections collected	9557
Absorption correction	Semi-empirical from equivalents
Independent reflections	4593 [R_{int} = 0.0320]
Data/restraints/parameters	4593/0/275
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.027
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0599, wR_2 = 0.1393
Final *R* indexes [all data]	R_1 = 0.1107, wR_2 = 0.1726
Largest diff. peak/hole / e Å^{-3}	0.38/−0.34

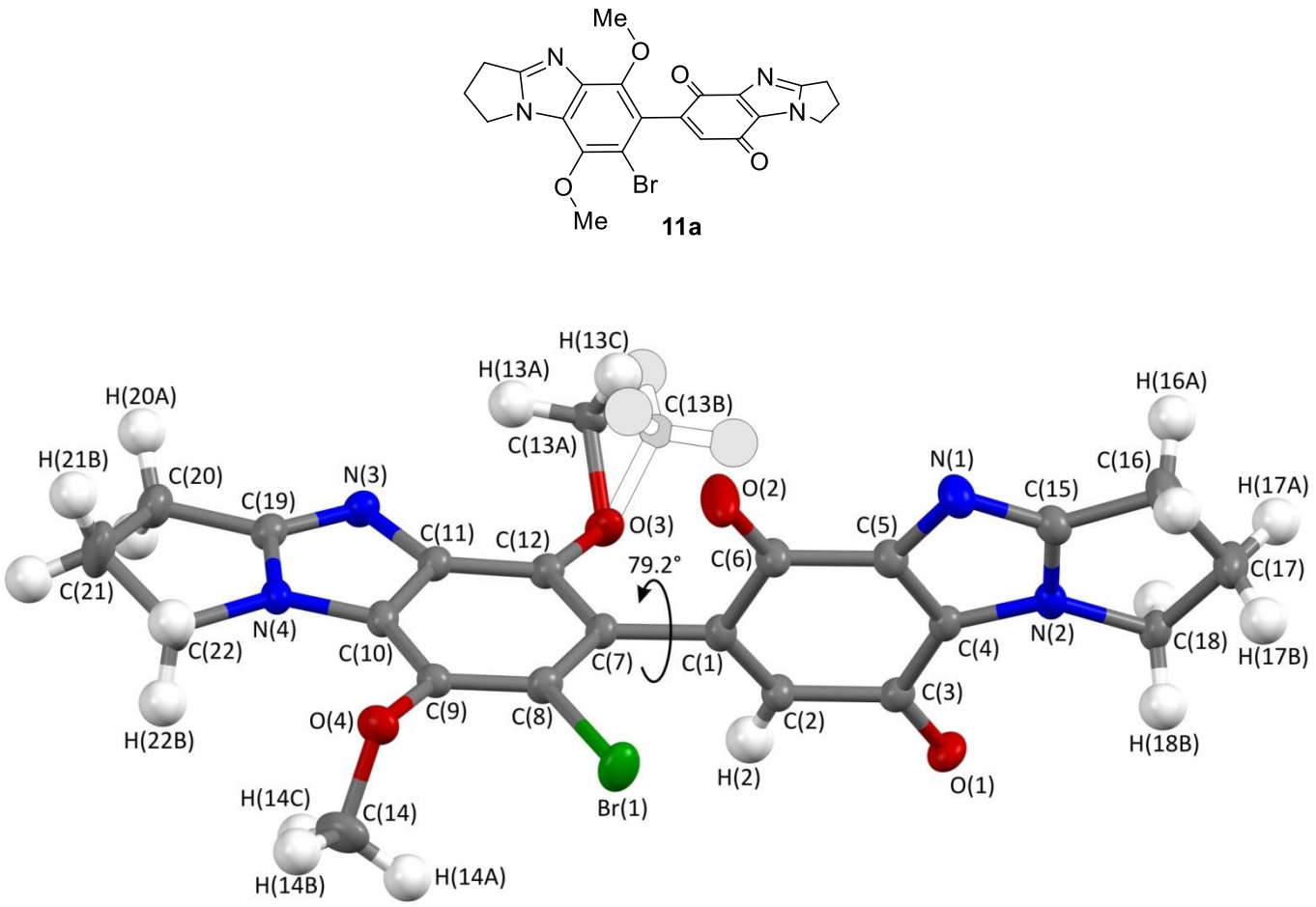
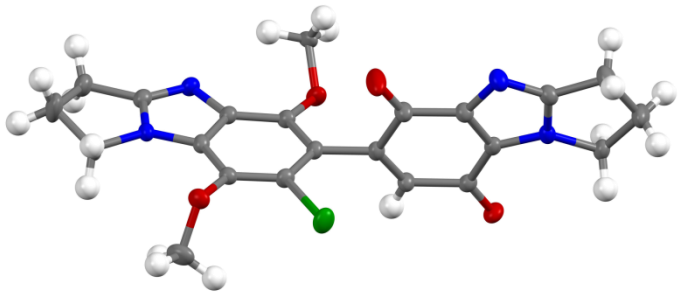


Figure S2. Molecular structure of 7'-bromo-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (**11a**) determined from single-crystal X-ray diffraction at 150 K with anisotropic displacement ellipsoids of 50% probability except for hydrogen atoms, which are shown at a fixed radius of 0.3 Å. The structure was determined at a default temperature of 150 K from full spheres of data collected to a resolution of at least 0.84 Å with each 1° scan frame in ω collected twice. The positions of all non-hydrogen atoms were refined freely with anisotropic displacement parameters except for the disordered methoxy group, where similarity distance constraints were applied in SHELXL. The torsion angle highlighted is calculated from the angle between the best planes through the substituted benzimidazole and benzimidazolequinone rings including atoms Br(1) and O(1) to O(4) using the program Mercury from CCDC. The crystal structure exhibits significant positional disorder of the O(3) methoxy group: this disorder is illustrated using an outline mode for the alternative position B for the methoxy-group carbon atom labelled as C(13B). The latter atom was refined with a single isotropic displacement parameter and is shown as a sphere; hydrogen atoms attached to C(13B) have not been labelled as they contribute little towards the X-ray scattering.

Table S2. Single-crystal X-ray data and structure refinement for 7'-bromo-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (**11a**).



Identification code	exp_2189
Empirical formula	$C_{22}H_{19}BrN_4O_4$
Formula weight	483.32
Temperature / K	150
Crystal system	orthorhombic
Space group	*Pbcn*
a / Å	23.3635(2)
b / Å	9.58790(10)
c / Å	17.6817(2)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	3960.82(7)
Z	8
ρ_{calc} / g cm^{-3}	1.621
μ / mm^{-1}	3.171
F(000)	1968
Crystal size / mm^3	0.415 × 0.271 × 0.183
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.568 to 145.55
Index ranges	$-28 \le h \le 28$, $-11 \le k \le 11$, $-21 \le l \le 21$
Reflections collected	68493
Absorption correction	Semi-empirical from equivalents
Independent reflections	3921 [R_{int} = 0.0494, R_{sigma} = 0.0130]
Data/restraints/parameters	3921/76/351
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.153
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0431, wR_2 = 0.1161
Final *R* indexes [all data]	R_1 = 0.0434, wR_2 = 0.1163
Largest diff. peak/hole / e Å^{-3}	0.80/−0.83

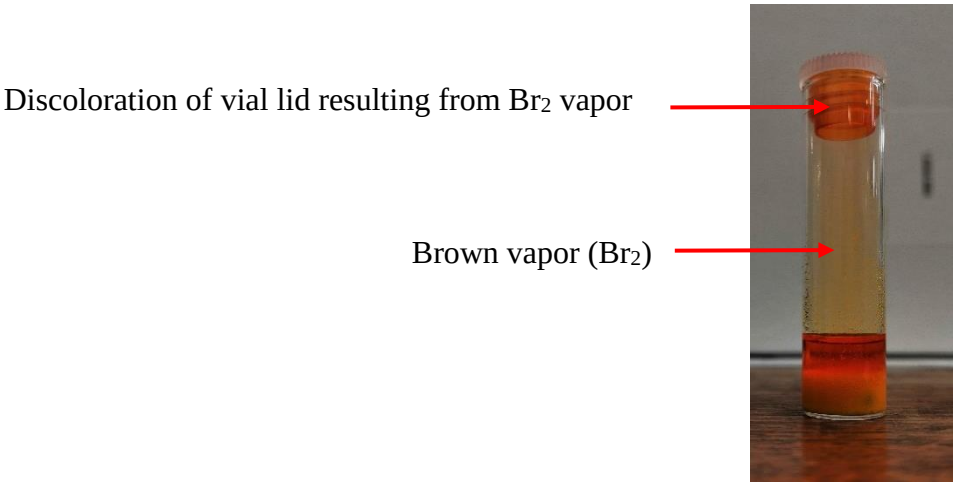
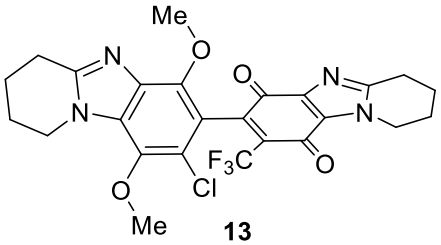


Figure S3. Photographic evidence for *in situ* Br_2 evolution from a reaction sample of DMBBQ **5a** under Method B conditions (Scheme 4) after 2 h.



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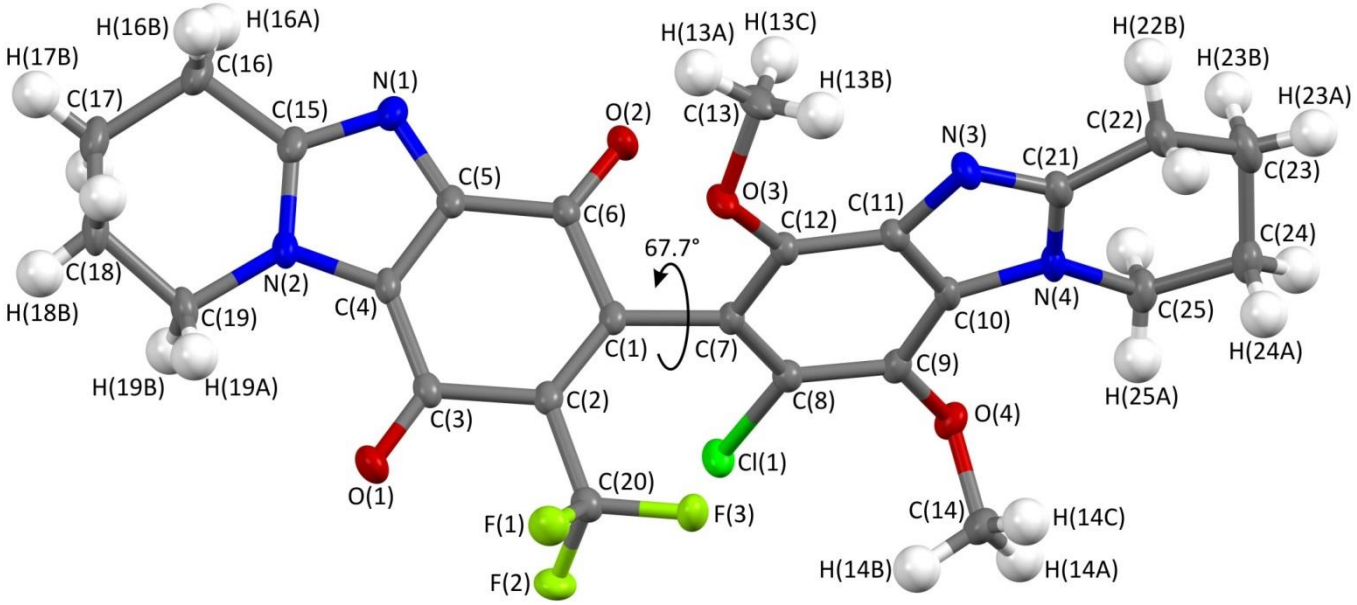
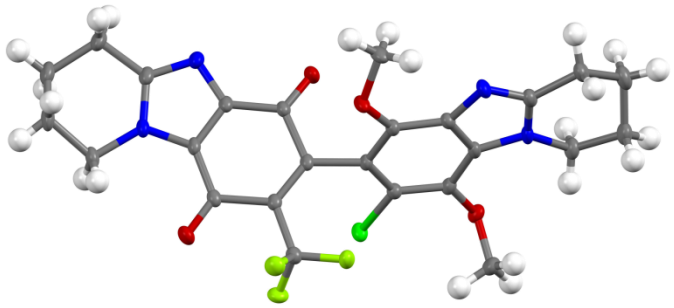


Figure S4. Molecular structure of 8'-chloro-6',9'-dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (**13**) determined from single-crystal X-ray diffraction at 100 K with anisotropic displacement ellipsoids shown at 50% probability except for hydrogen atoms, which are shown at a fixed radius of 0.3 Å. Full spheres of data were collected to a resolution of at least 0.84 Å with each 1° scan frame in ω collected twice. The crystal was measured at 100 K as a degree of thermal disorder of the cyclohexane ring was suspected at 150 K. The positions of all non-hydrogen atoms were refined freely with anisotropic displacement parameters. The torsion angle highlighted is calculated from the angle between the best planes through the substituted benzimidazole and benzimidazolequinone rings including atoms Cl(1) and O(1) to O(4) using the program Mercury from CCDC.

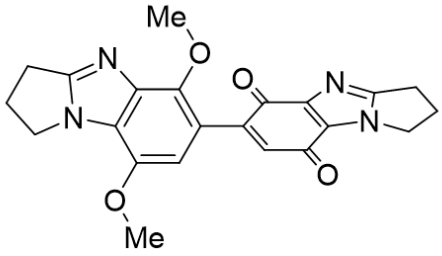
Table S3. Single-crystal X-ray data and structure refinement for 8'-chloro-6',9'-dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (**13**).

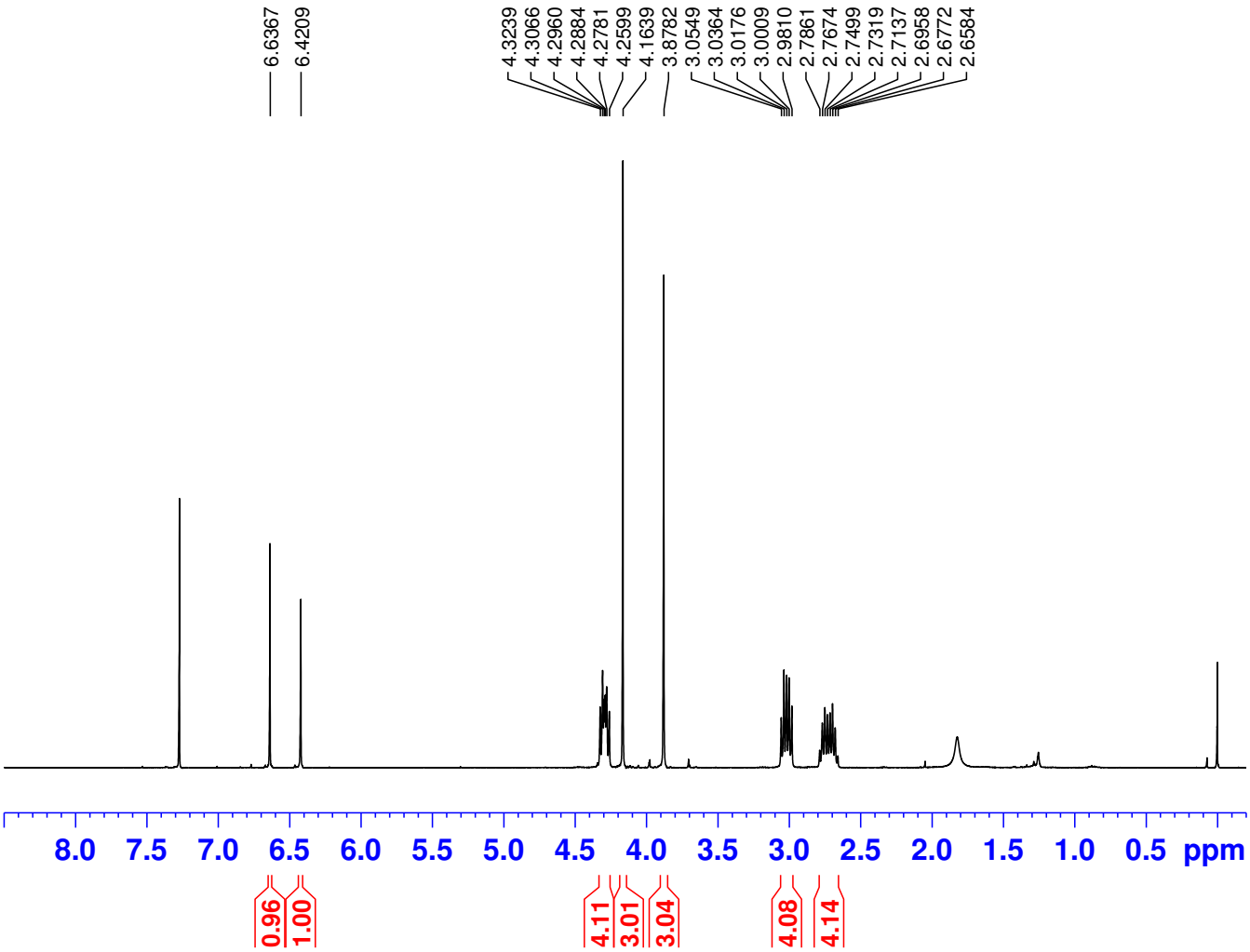


Identification code	exp_2141
Empirical formula	$C_{25}H_{22}ClF_3N_4O_4$
Formula weight	534.91
Temperature / K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	16.9129(3)
b / Å	16.4330(2)
c / Å	8.5648(2)
α / °	90
β / °	104.382(2)
γ / °	90
Volume / Å^3	2305.81(8)
Z	4
ρ_{calc} / g cm^{-3}	1.541
μ / mm^{-1}	2.065
F(000)	1104
Crystal size / mm^3	0.118 × 0.112 × 0.069
Radiation	Cu Kα (λ = 1.54184 Å)
2θ range for data collection / °	7.62 to 145.384
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-10 \le l \le 10$
Reflections collected	38841
Absorption correction	Semi-empirical from equivalents
Independent reflections	4551 [R_{int} = 0.0484, R_{sigma} = 0.0211]
Data/restraints/parameters	4551/0/422
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.055
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.0970
Final *R* indexes [all data]	R_1 = 0.0428, wR_2 = 0.1019
Largest diff. peak/hole / e Å^{-3}	0.71/−0.27

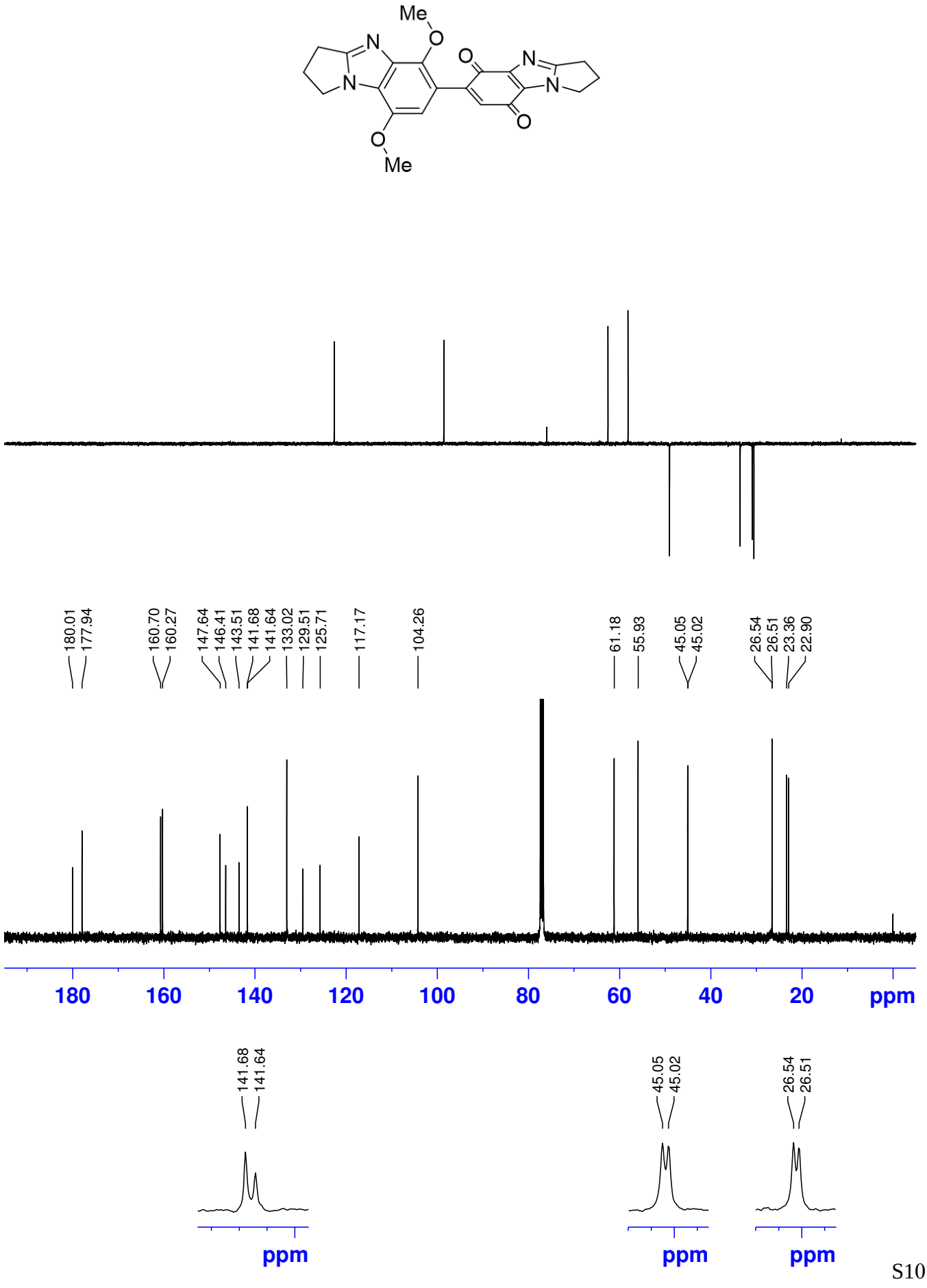
NMR Spectra

^{1}H NMR (400 MHz) of 5',8'-Dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (5a) in $CDCl_3$

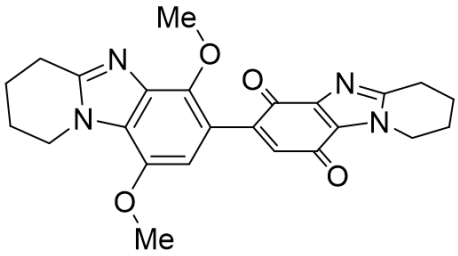


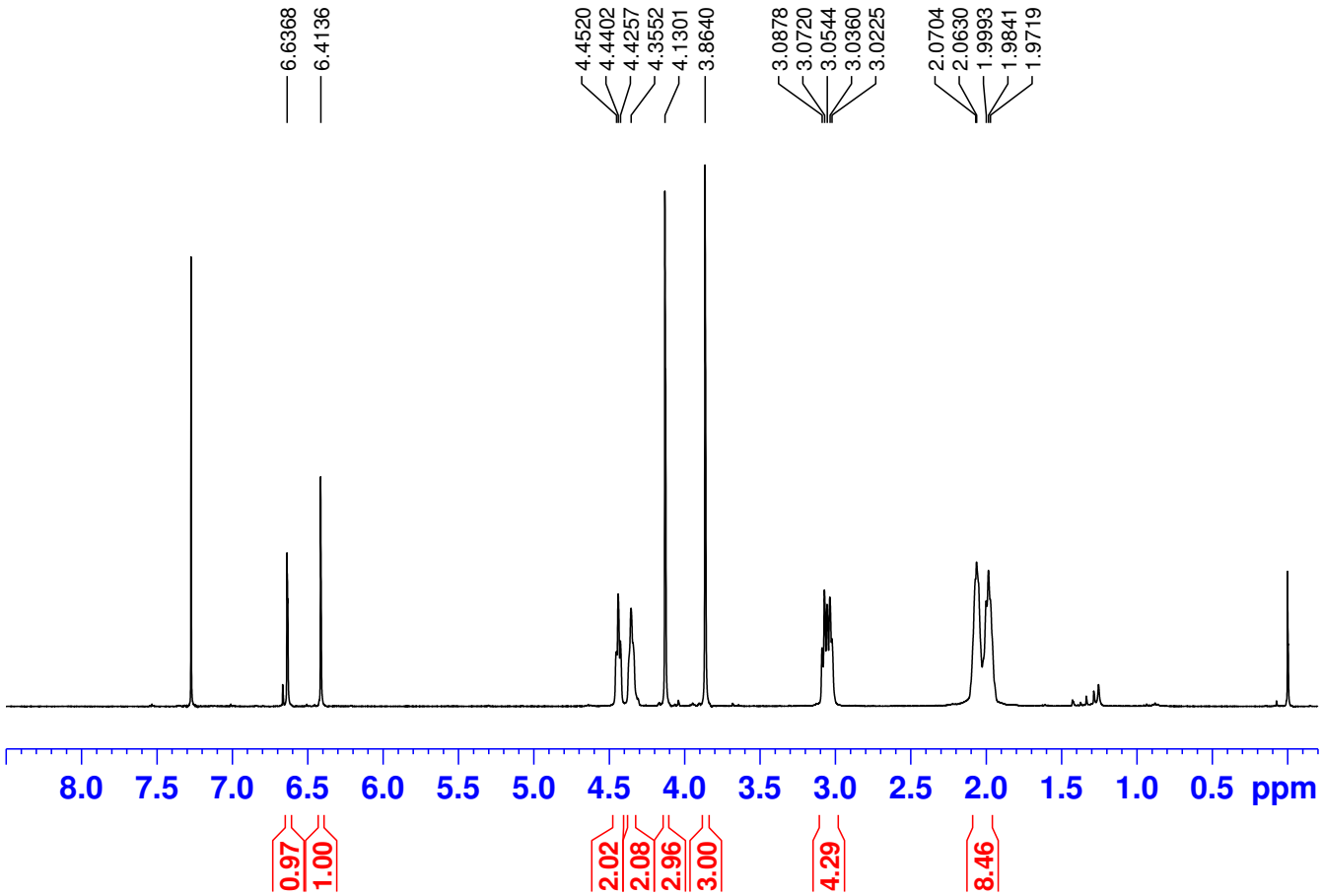


^{13}C NMR (100 MHz) of 5',8'-Dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (5a) in $CDCl_3$

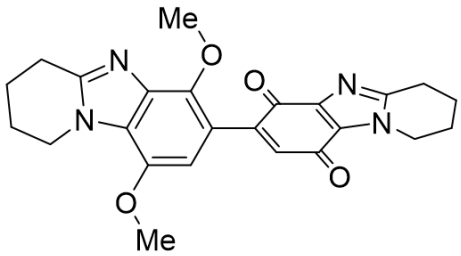


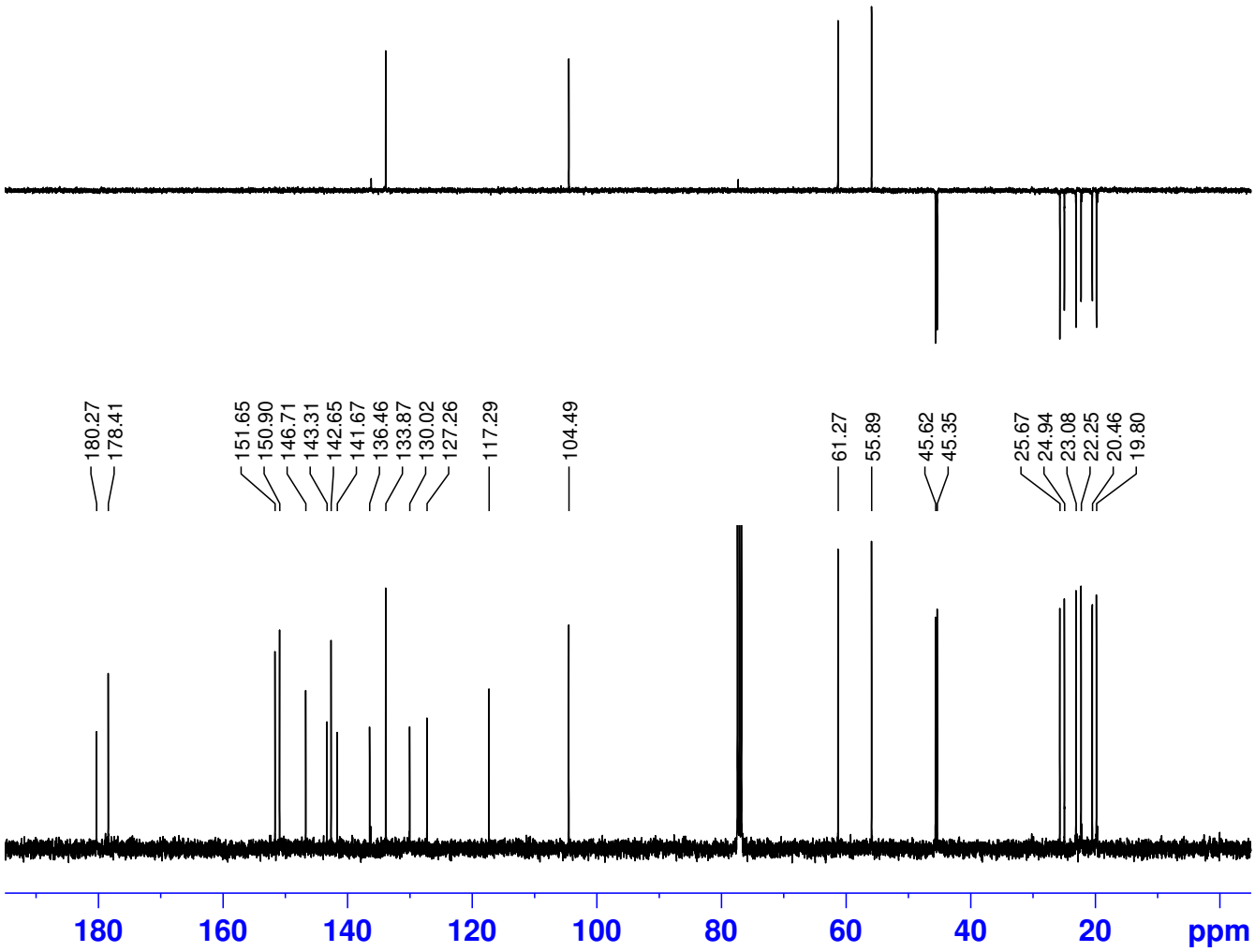
^{1}H NMR (400 MHz) of 6',9'-Dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (5b) in $CDCl_3$



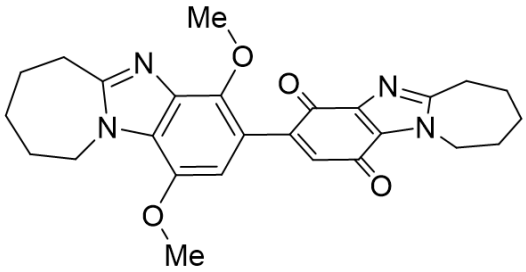


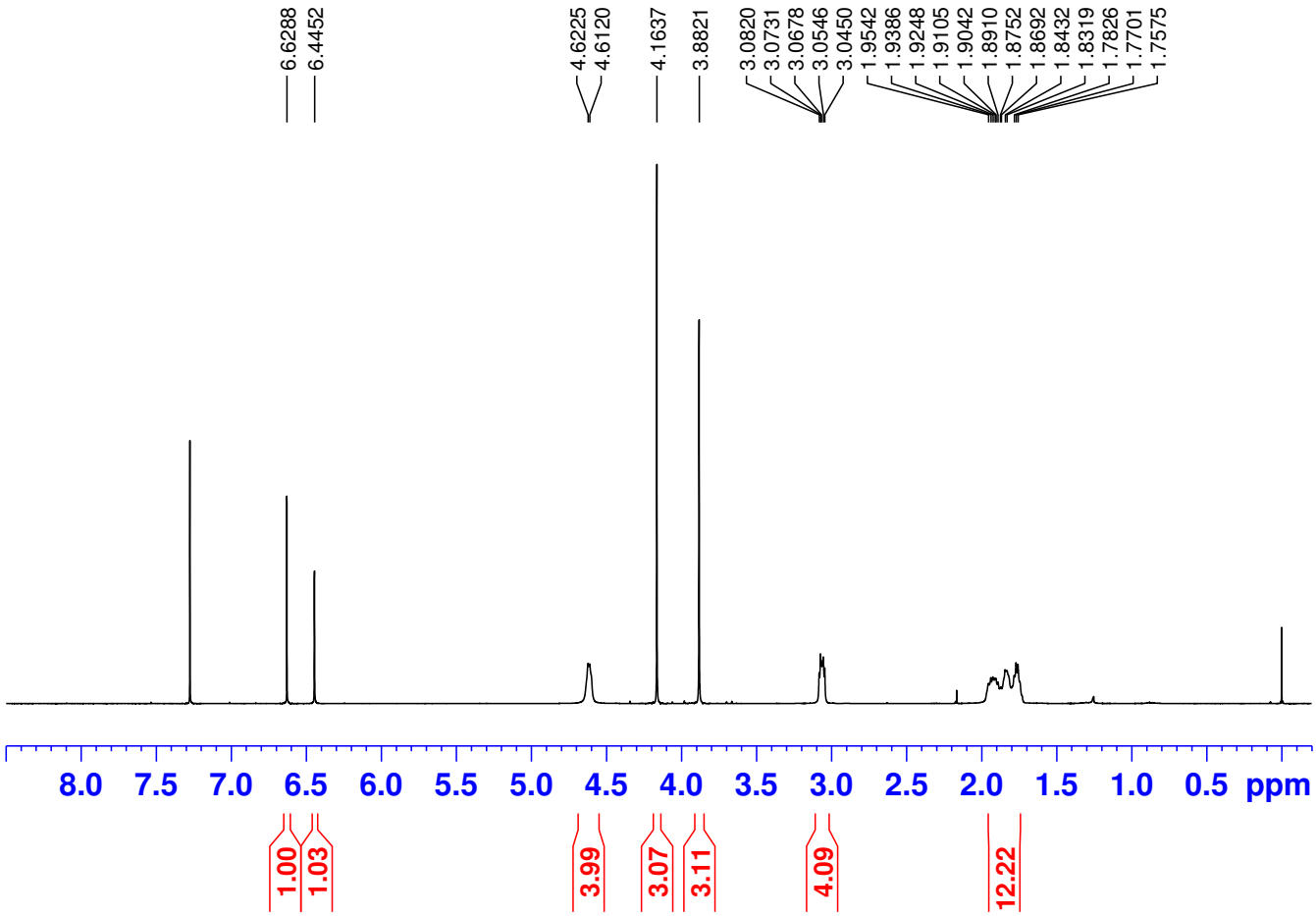
^{13}C NMR (100 MHz) of 6',9'-Dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (5b) in $CDCl_3$



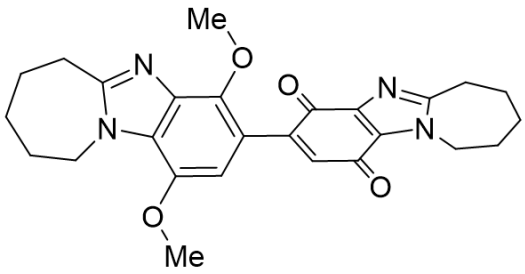


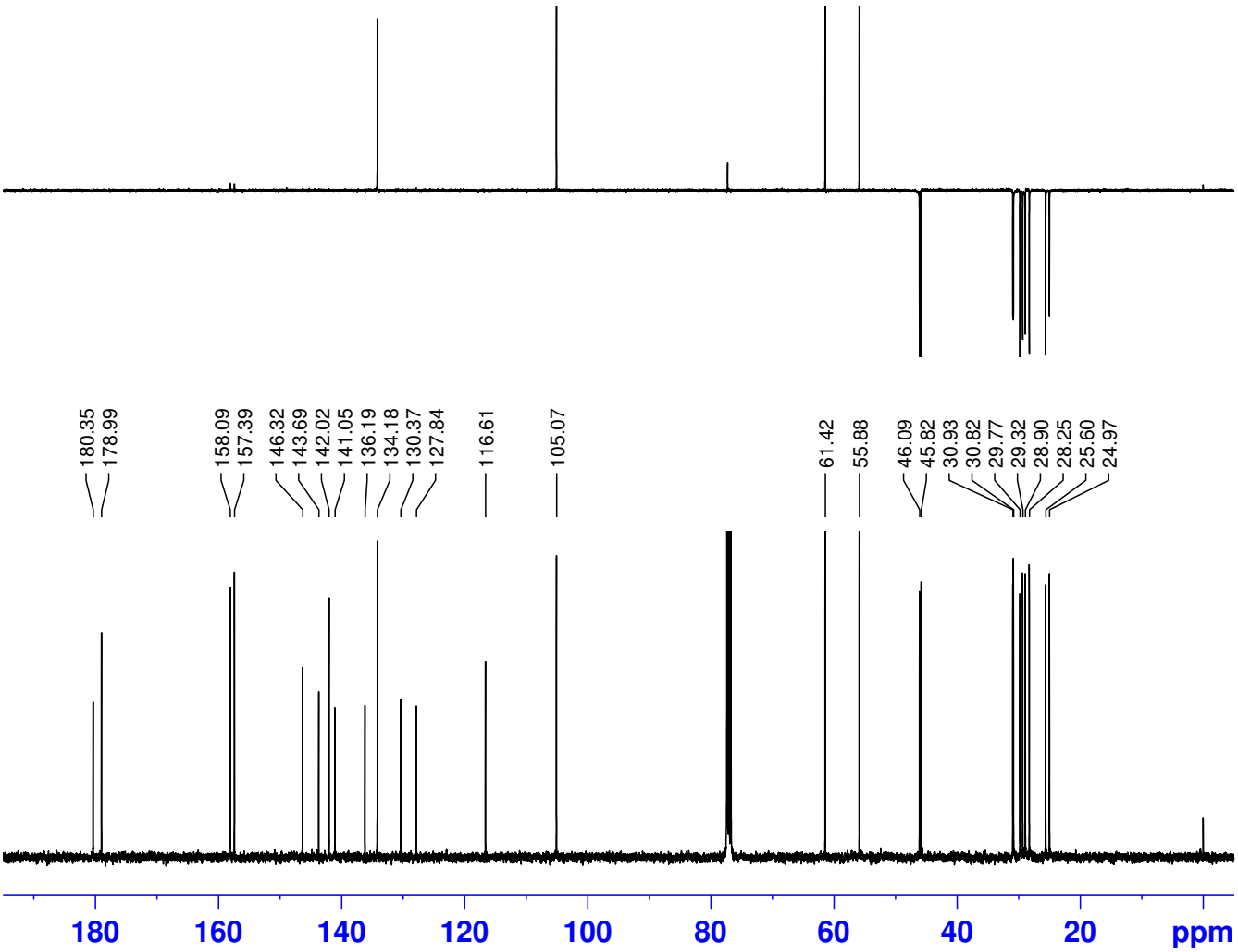
^{1}H NMR (400 MHz) of 1',4'-Dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (5c) in $CDCl_3$

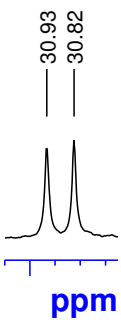




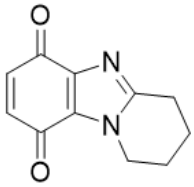
^{13}C NMR (100 MHz) of 1',4'-Dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (5c) in $CDCl_3$

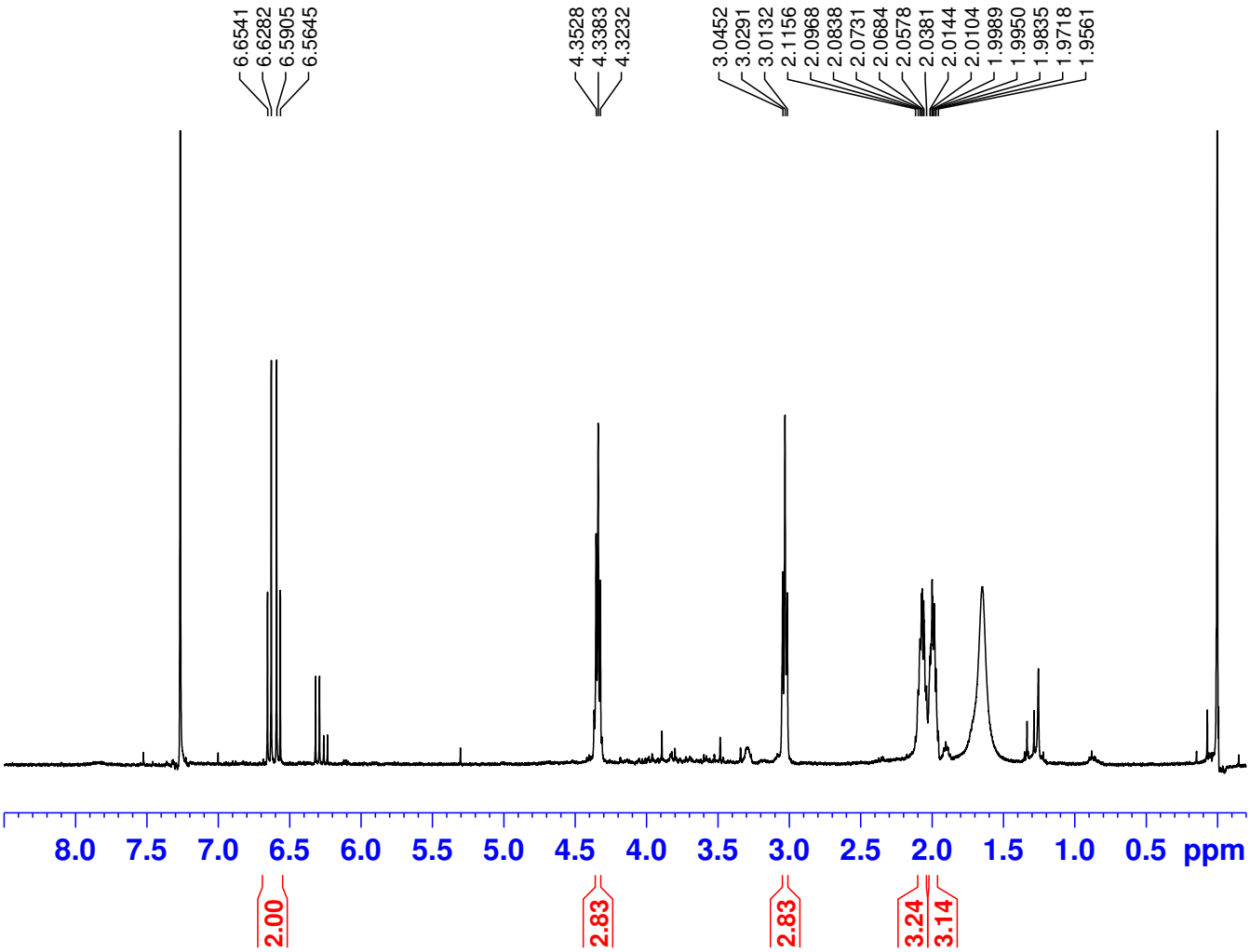




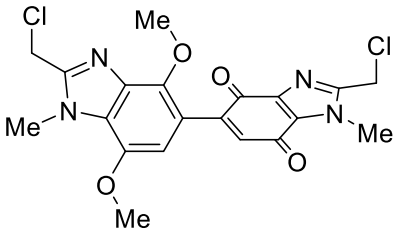


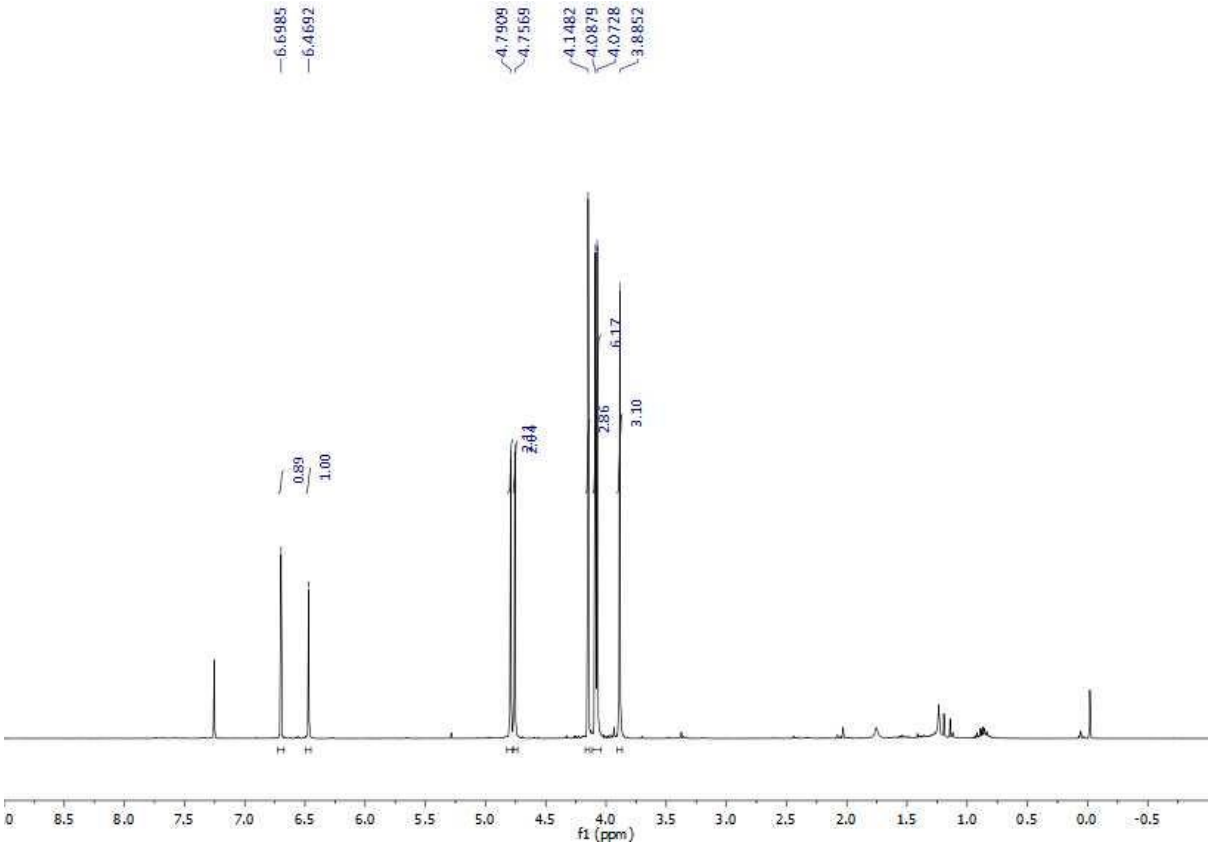
^{1}H NMR (400 MHz) of 1,2,3,4-Tetrahydropyrido[1,2-*a*]benzimidazole-6,9-dione (7) in $CDCl_3$



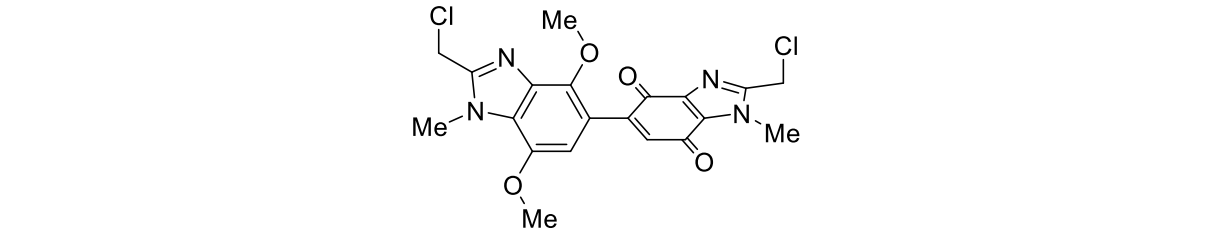


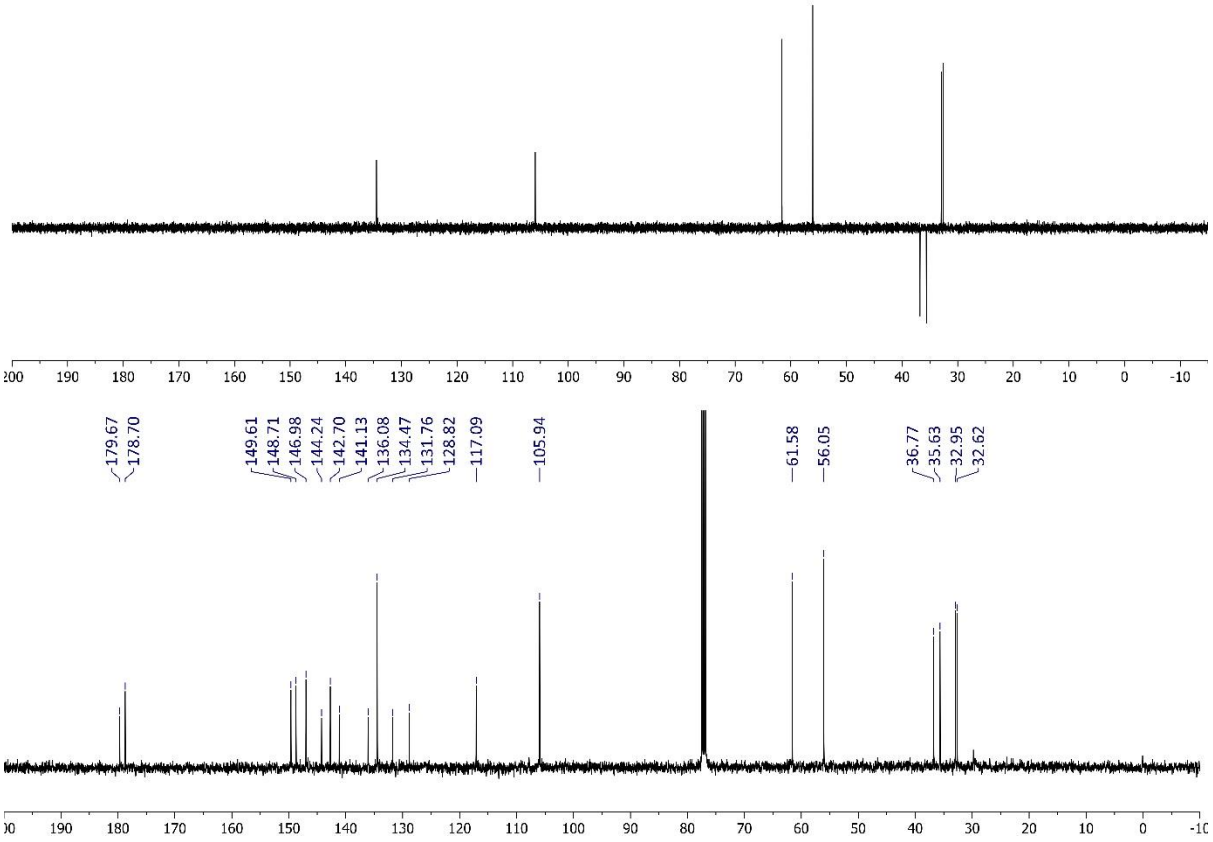
^{1}H NMR (400 MHz) of 2,2'-Bis(chloromethyl)-4',7'-dimethoxy-1,1'-dimethyl-1*H*,1'*H*-[5,5'-bibenzimidazole]-4,7-dione (8) in $CDCl_3$



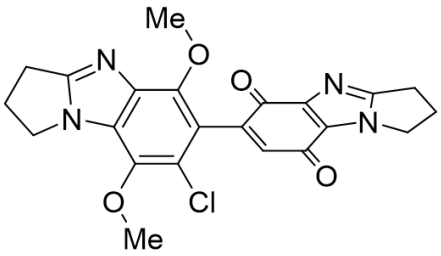


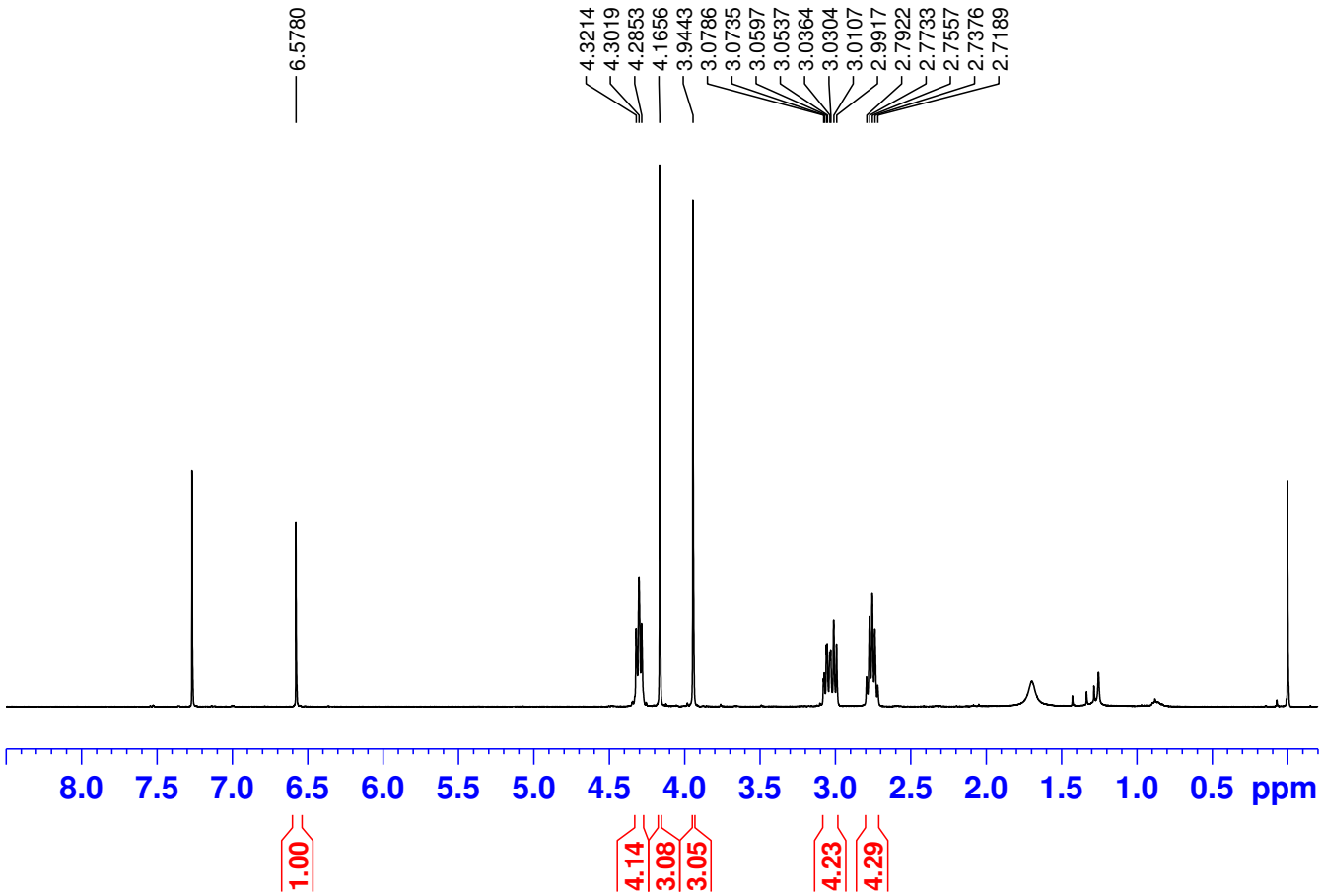
^{13}C NMR (100 MHz) of 2,2'-Bis(chloromethyl)-4',7'-dimethoxy-1,1'-dimethyl-1*H*,1'*H*-[5,5'-bibenzimidazole]-4,7-dione (8) in $CDCl_3$



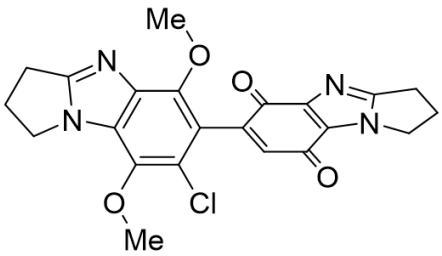


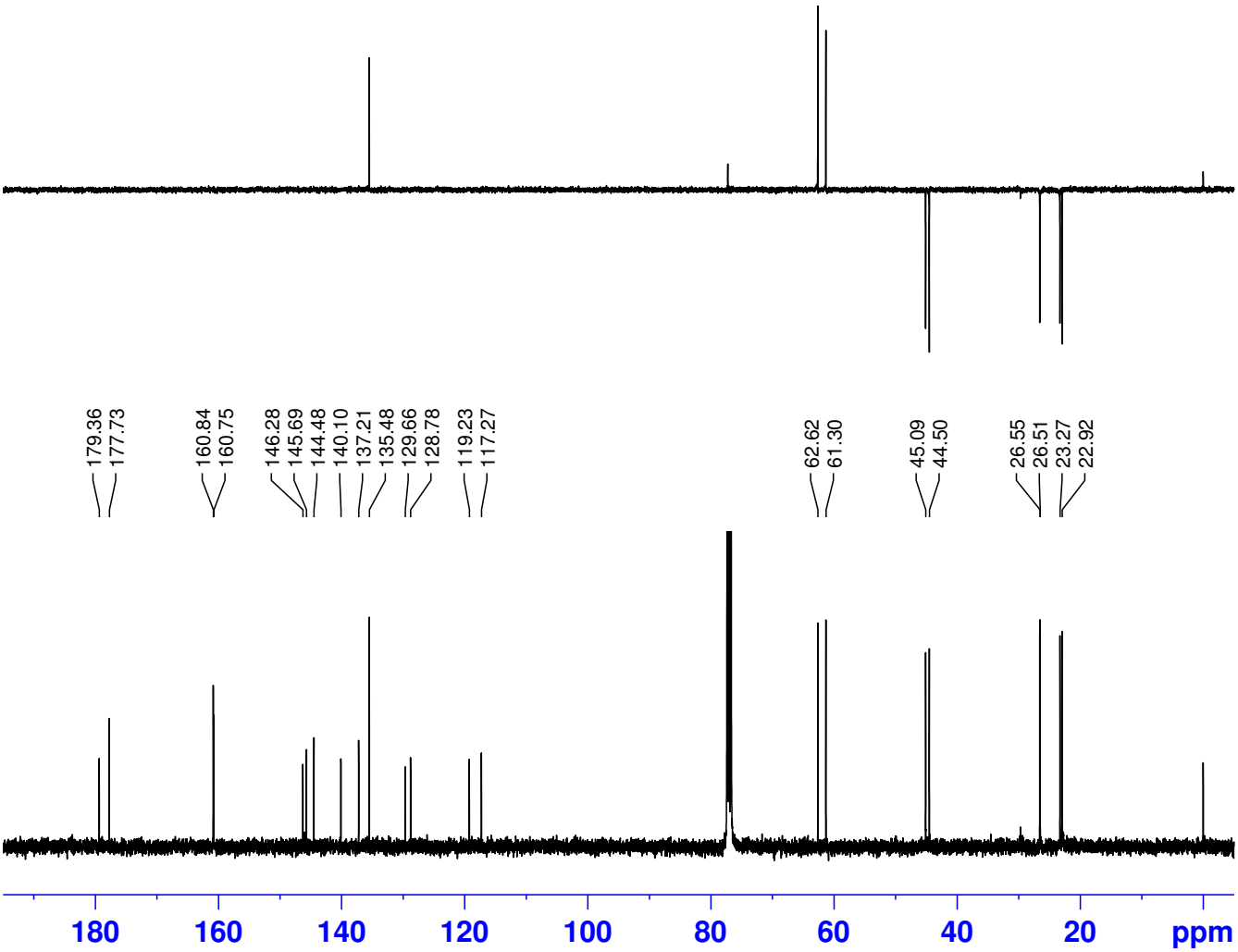
^{1}H NMR (400 MHz) of 7'-Chloro-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (9a) in $CDCl_3$

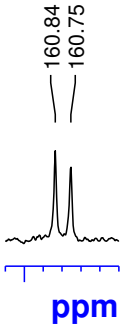




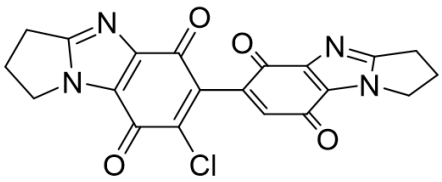
^{13}C NMR (100 MHz) of 7'-Chloro-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (9a) in $CDCl_3$

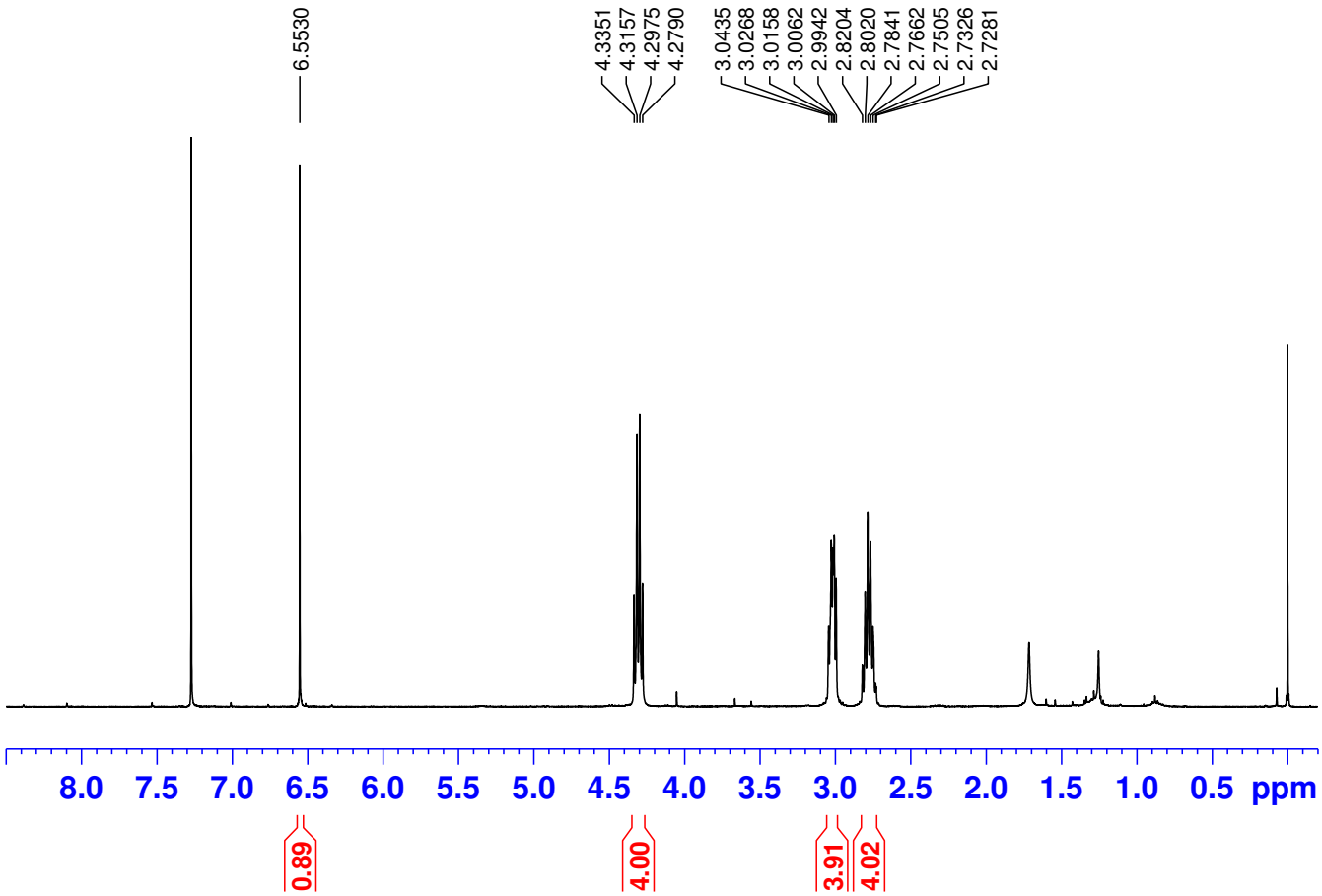




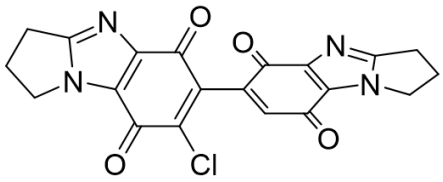


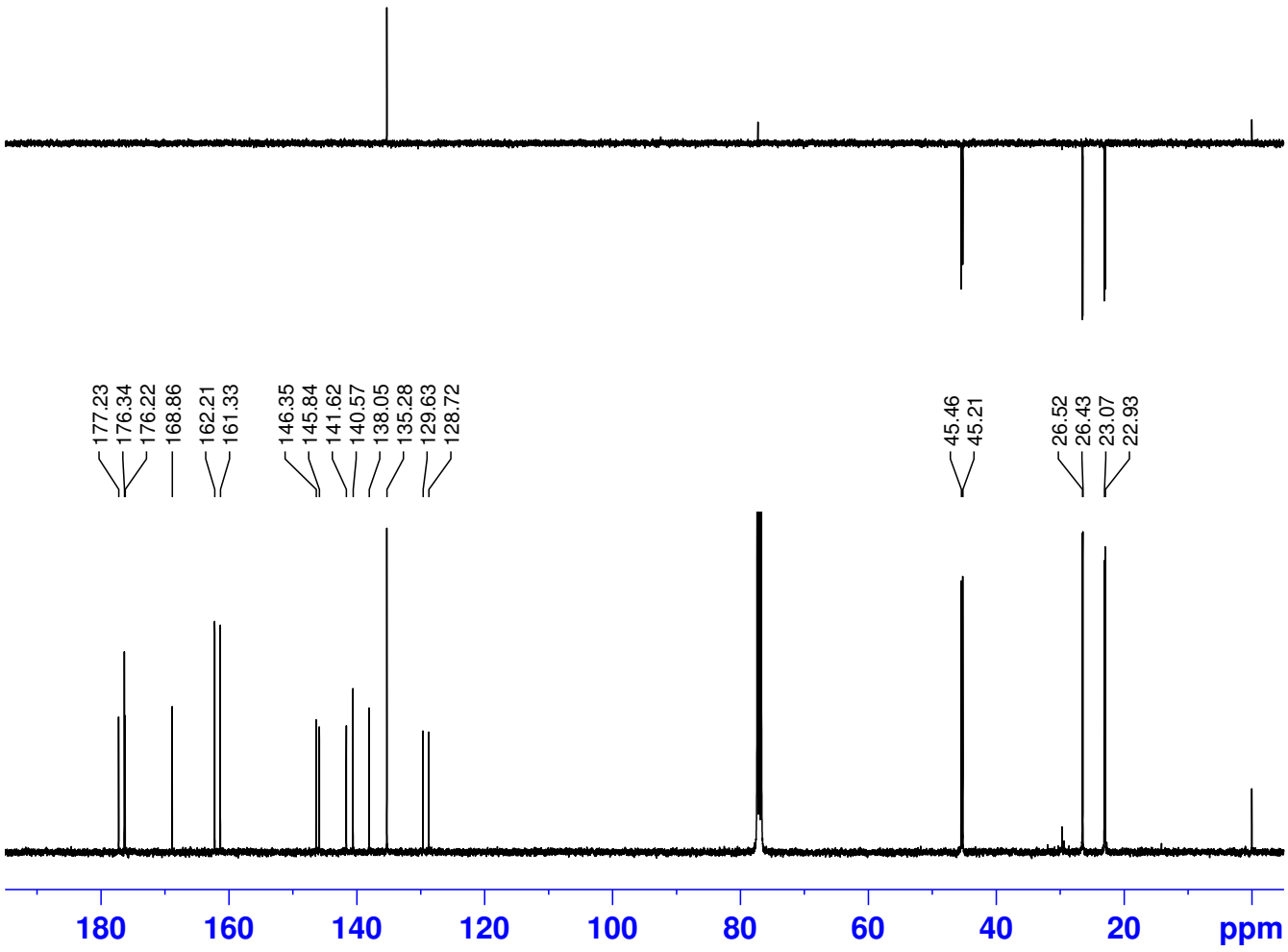
^{1}H NMR (400 MHz) of 7-Chloro-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,5',8,8'-tetrone (10a) in $CDCl_3$

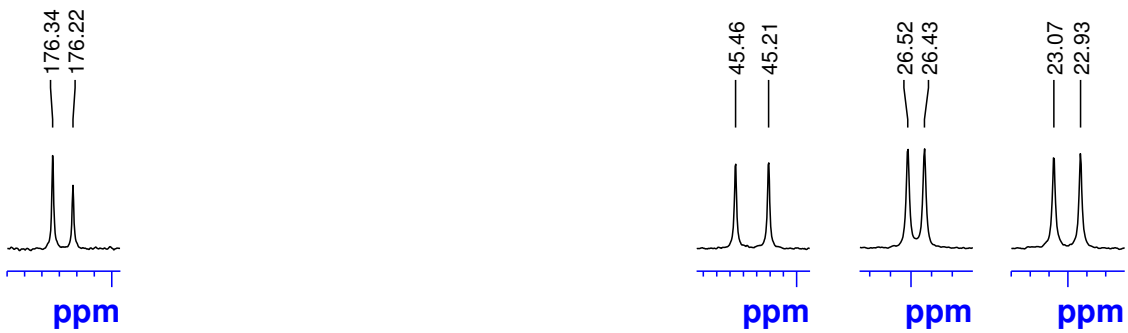




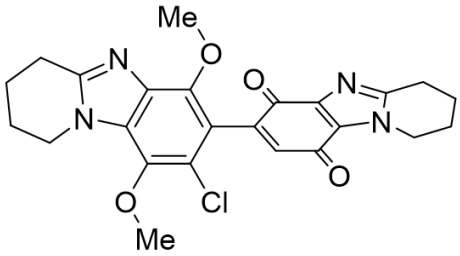
^{13}C NMR (100 MHz) of 7-Chloro-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,5',8,8'-tetrone (10a) in $CDCl_3$

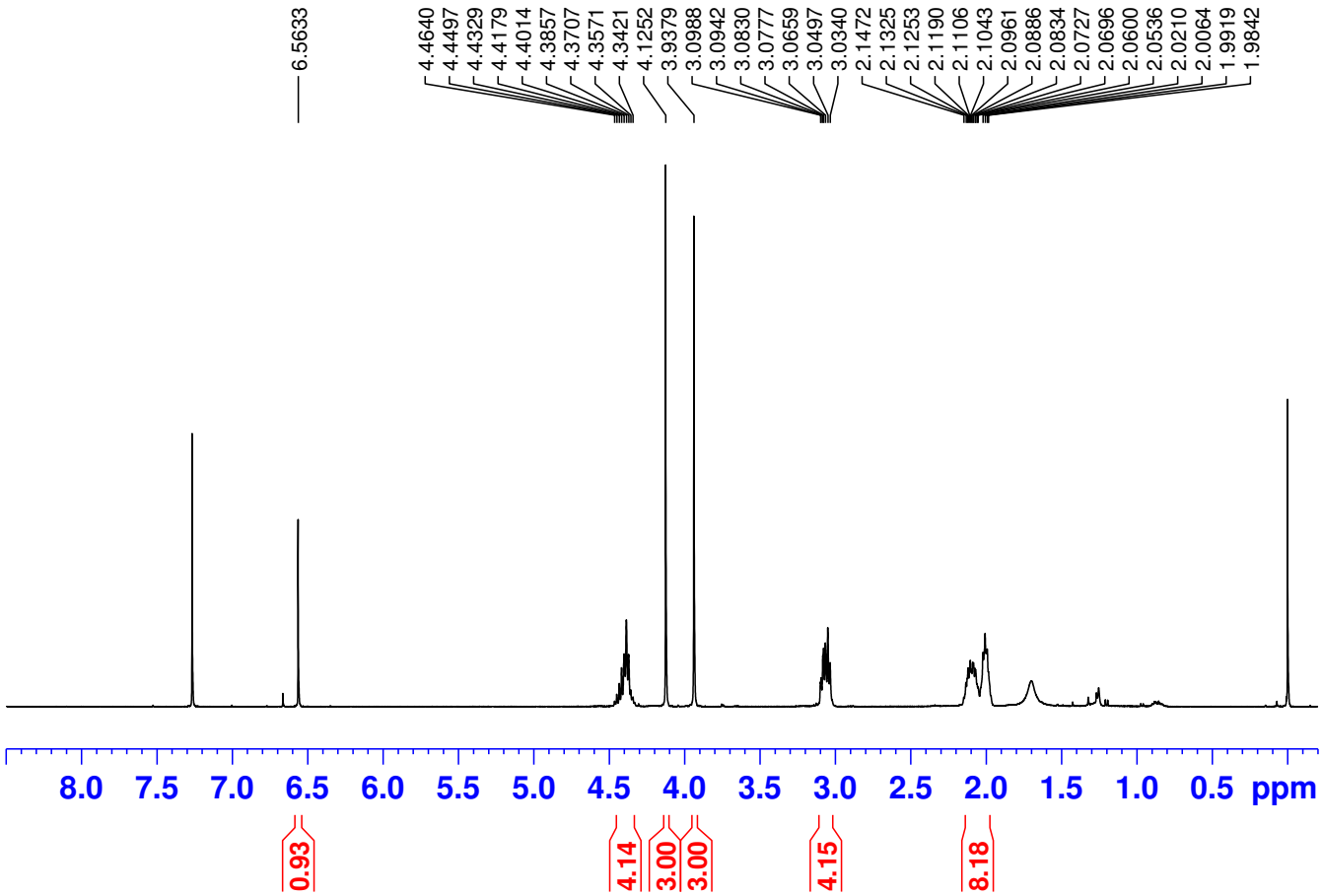




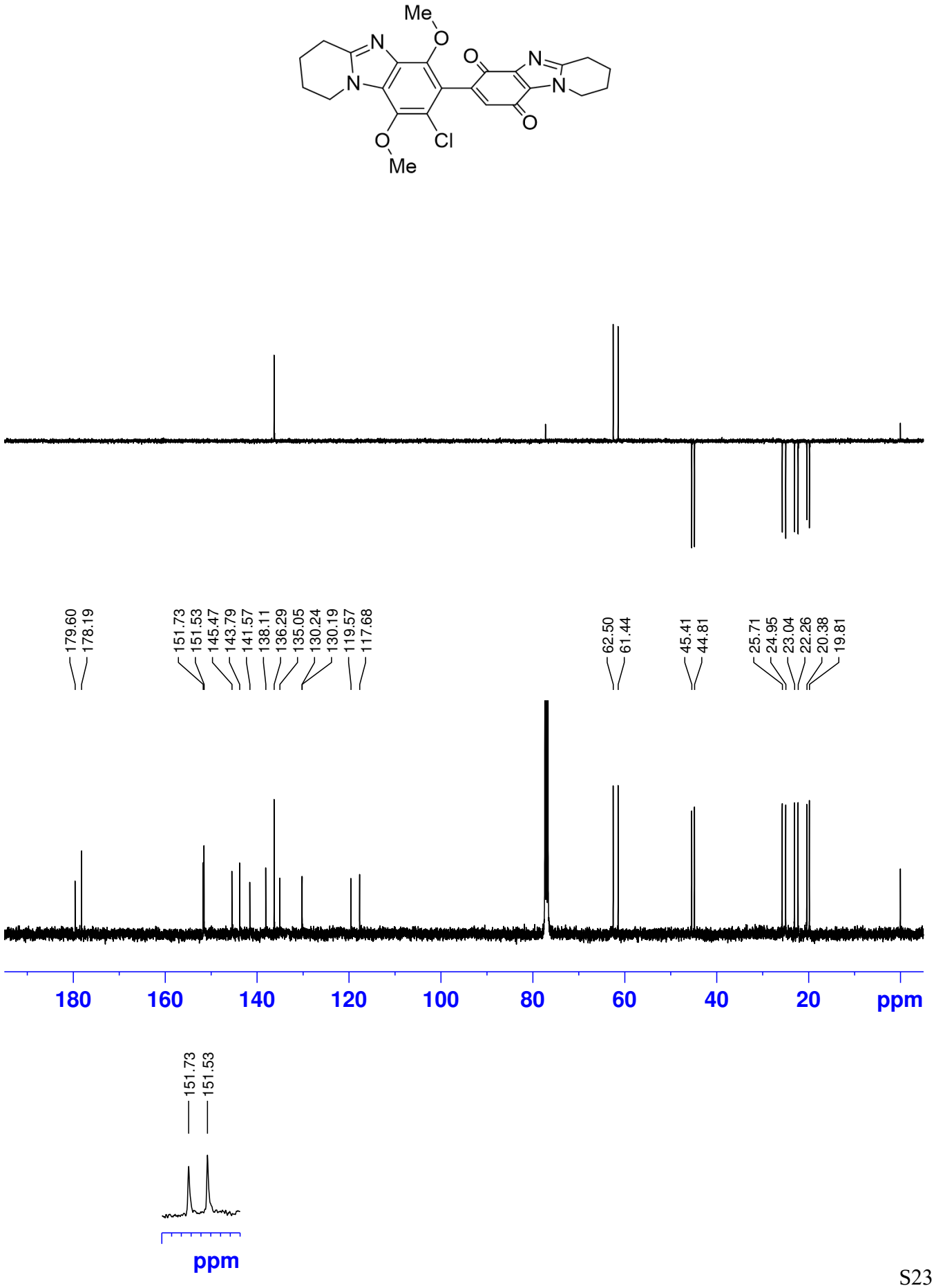


^{1}H NMR (400 MHz) of 8'-Chloro-6',9'-dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (9b) in $CDCl_3$

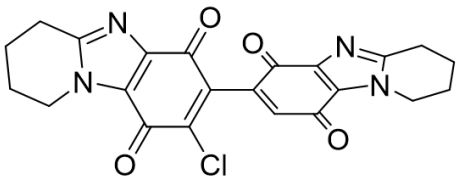


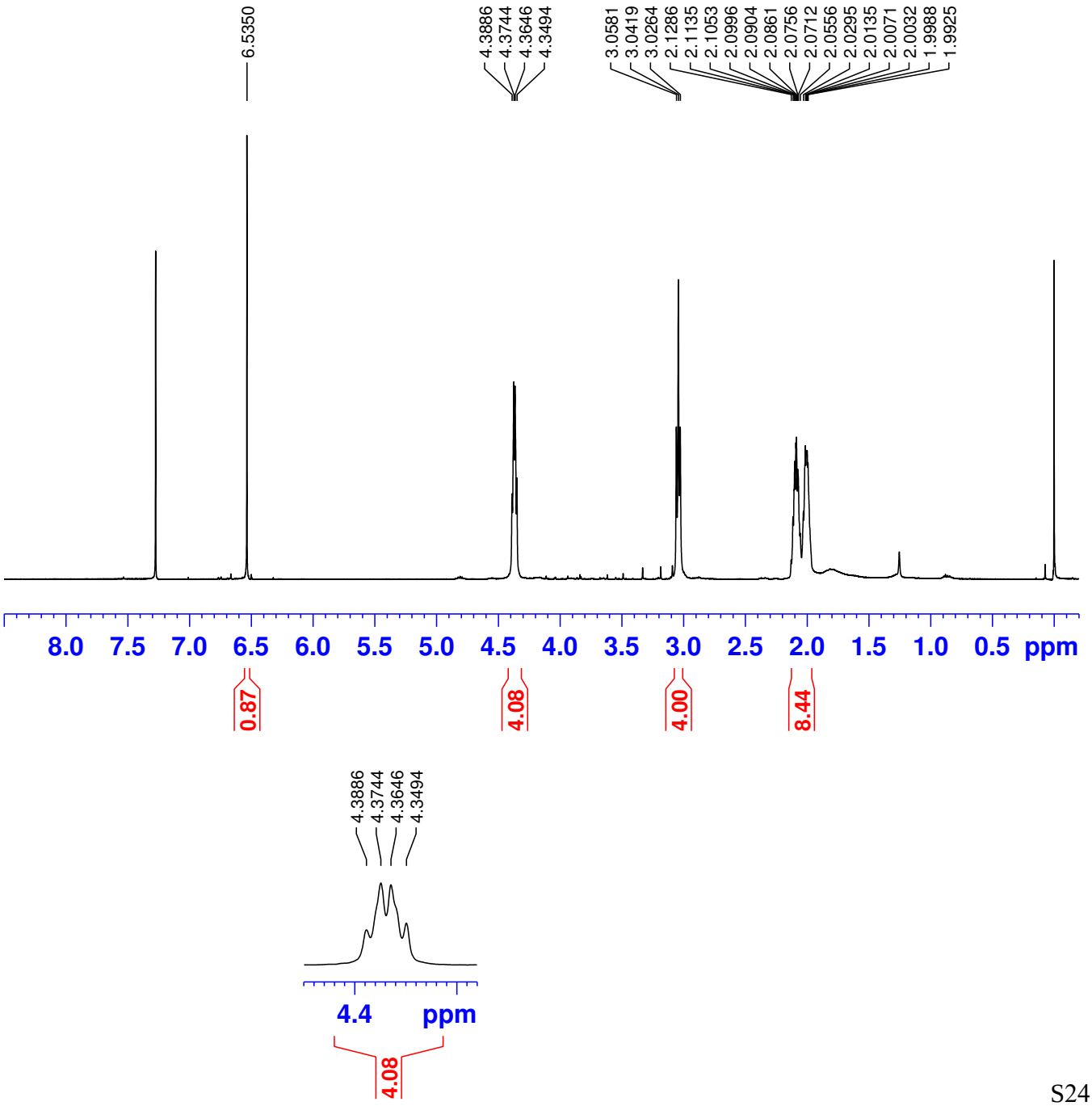


^{13}C NMR (100 MHz) of 8'-Chloro-6',9'-dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (9b) in $CDCl_3$

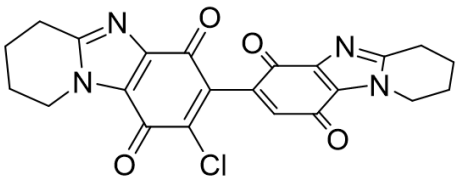


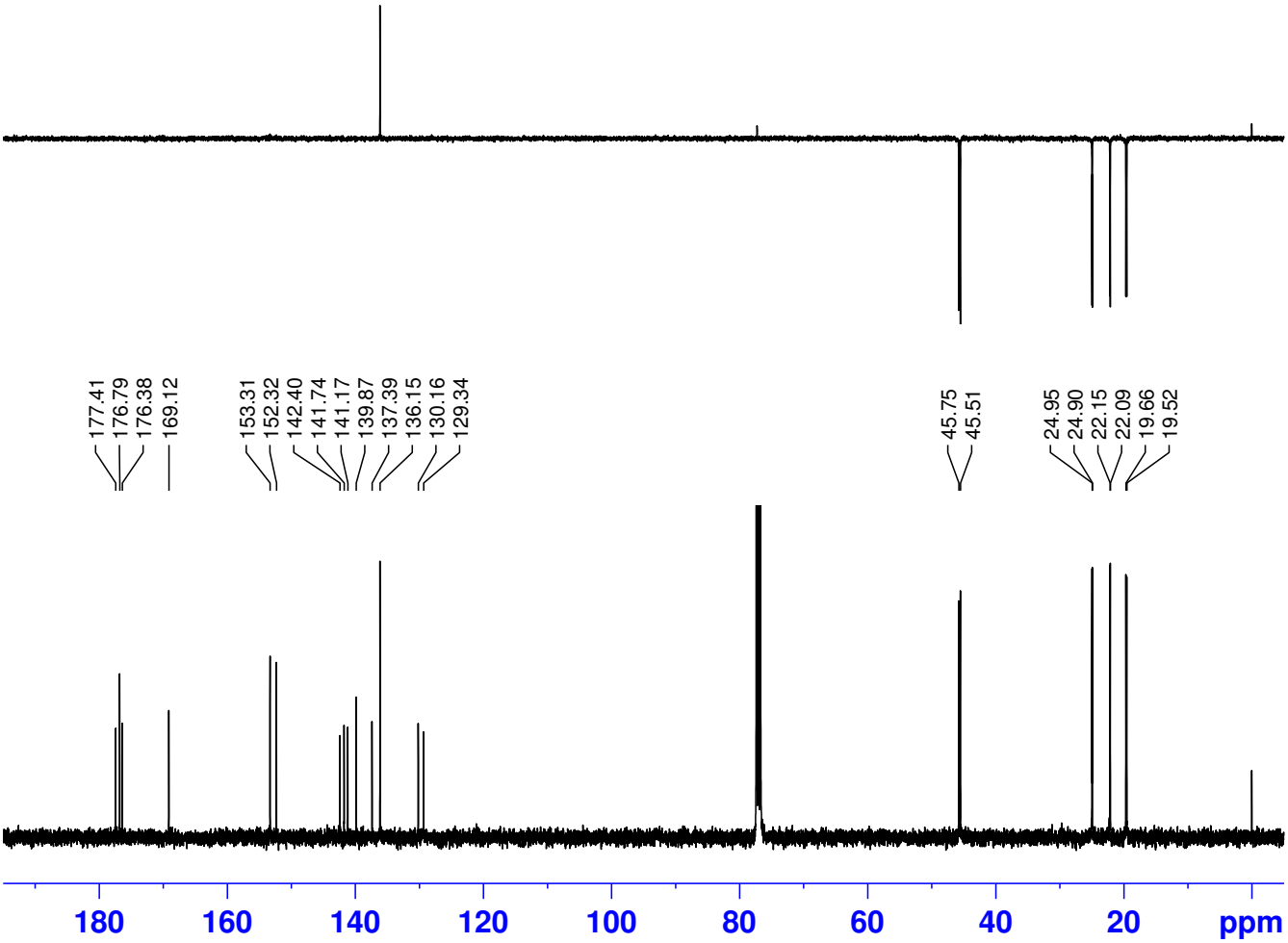
^{1}H NMR (400 MHz) of 8-Chloro-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (10b) in $CDCl_3$

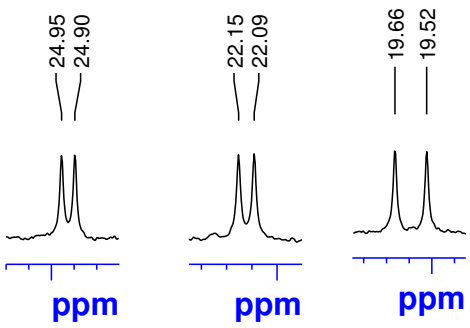




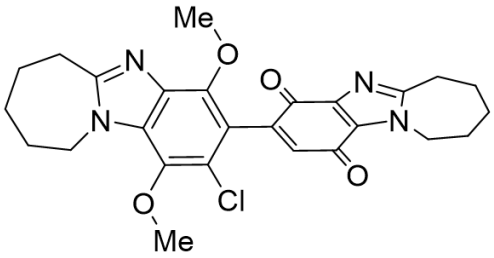
^{13}C NMR (100 MHz) of 8-Chloro-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (10b) in $CDCl_3$

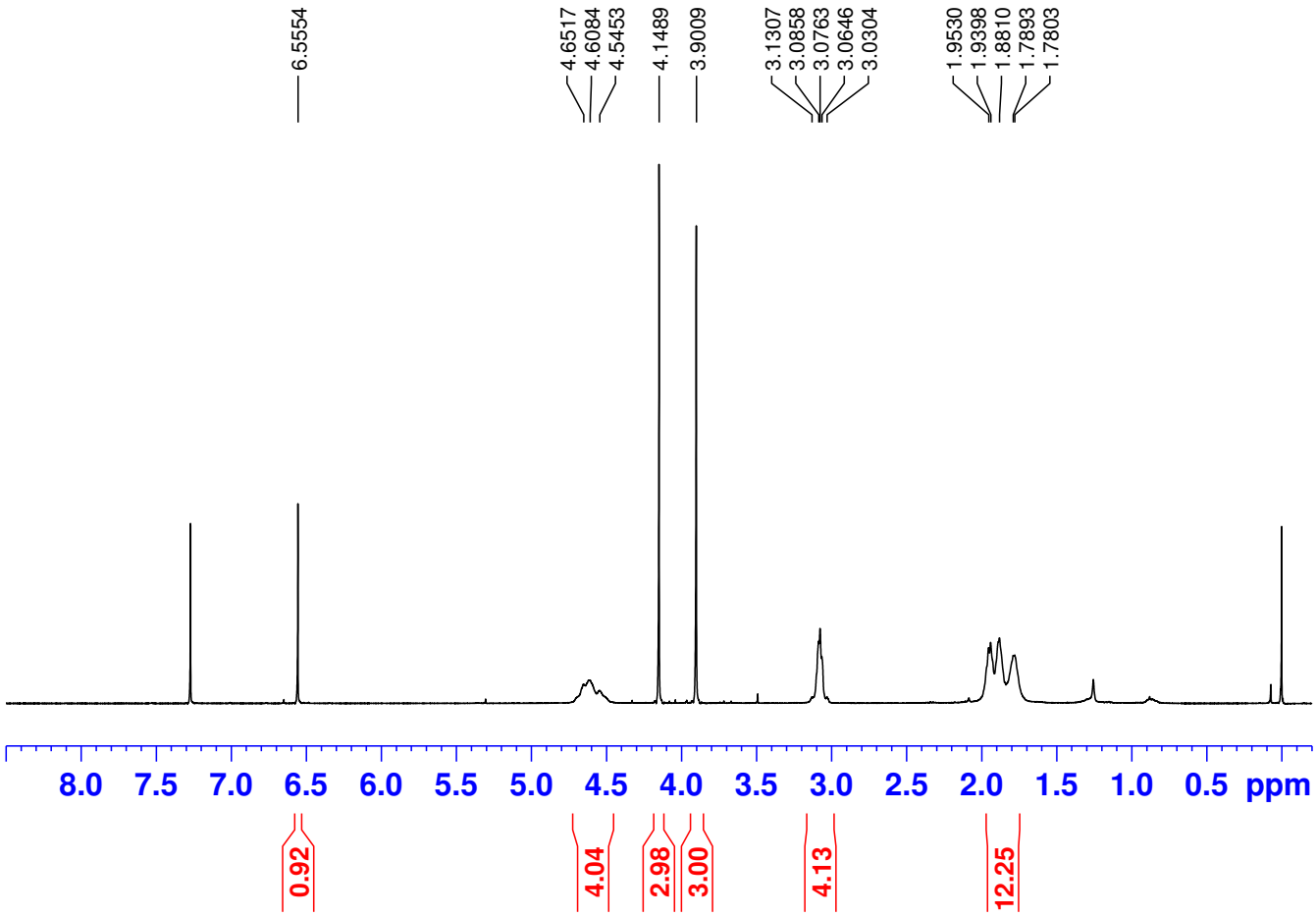




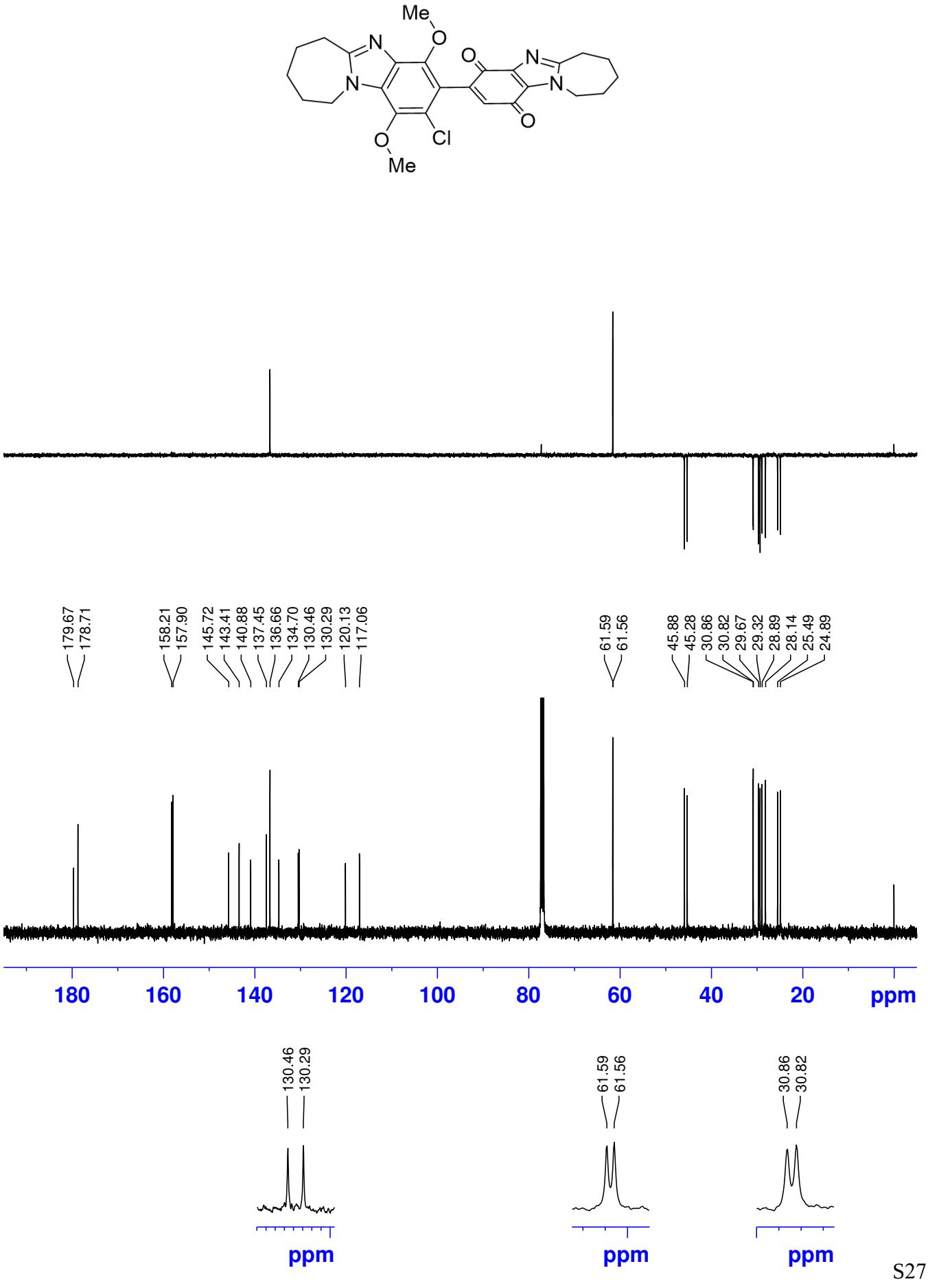


^{1}H NMR (400 MHz) of 2'-Chloro-1',4'-dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (9c) in $CDCl_3$

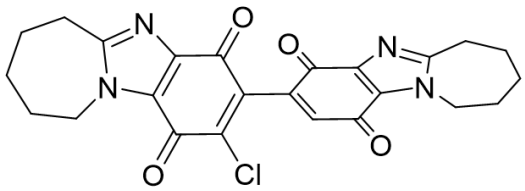


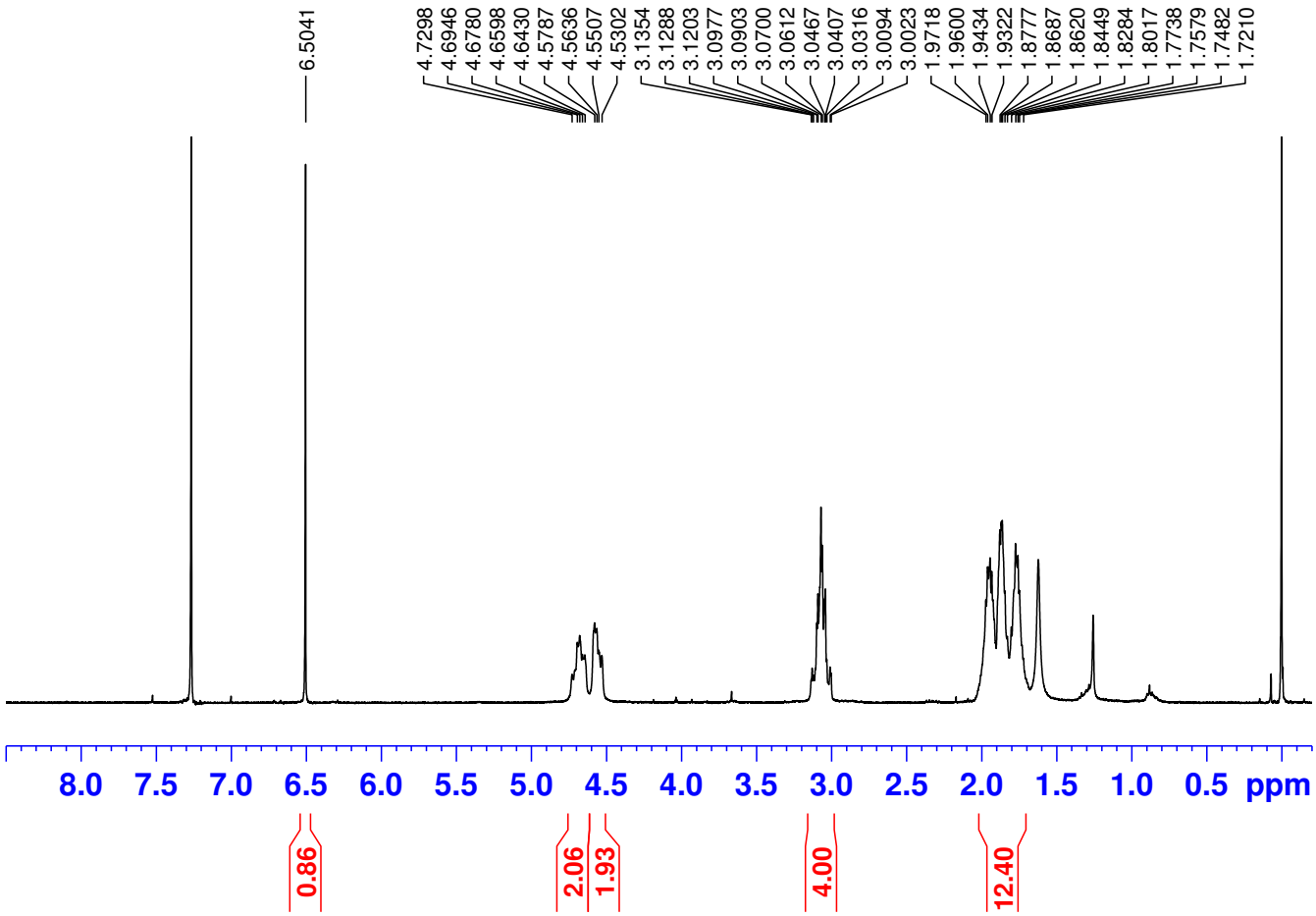


^{13}C NMR (100 MHz) of 2'-Chloro-1',4'-dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (9c) in $CDCl_3$

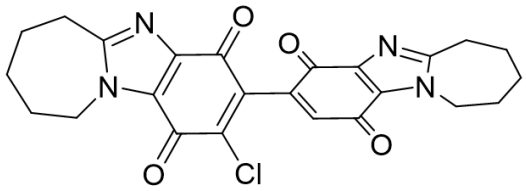


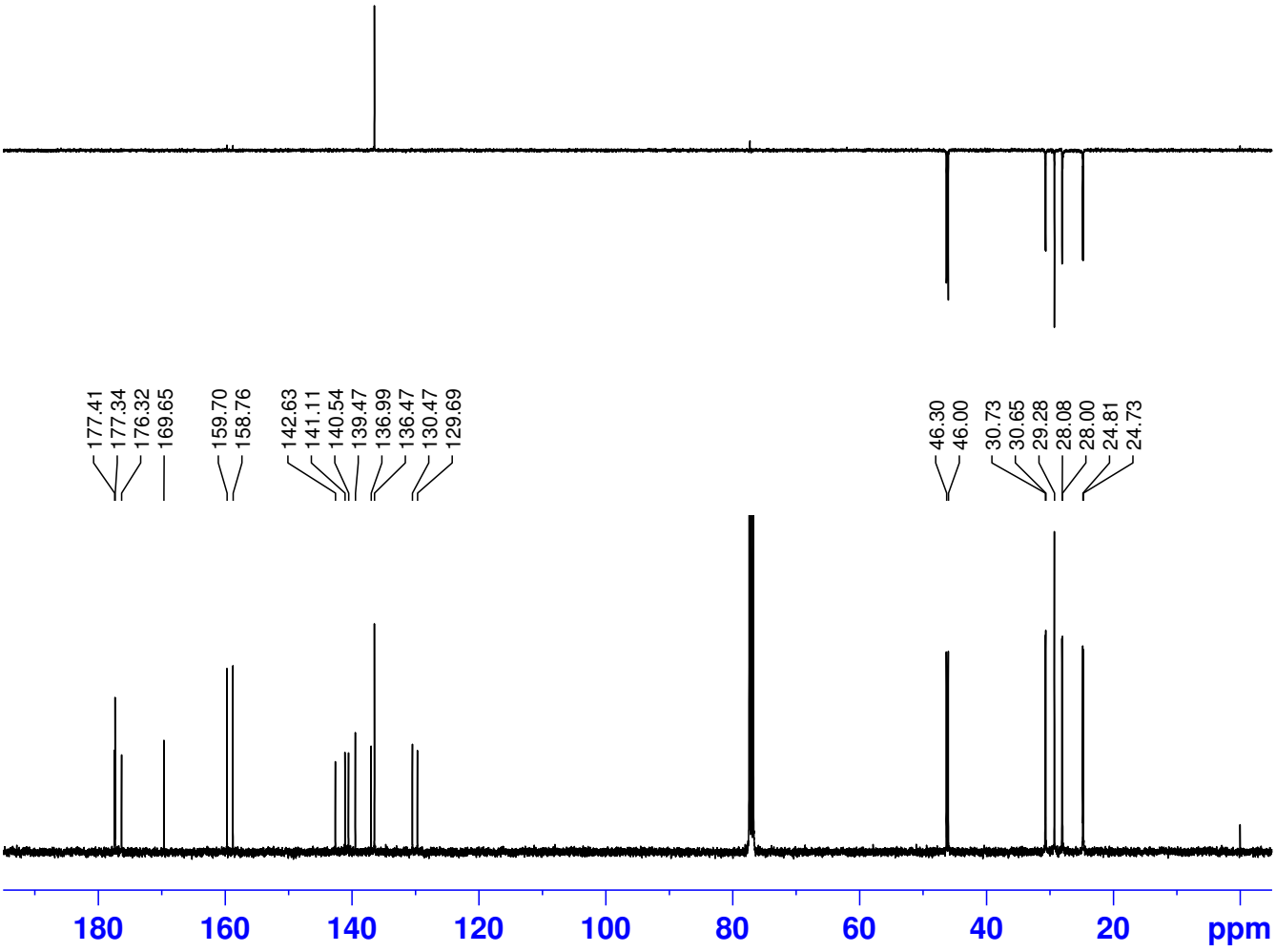
^{1}H NMR (400 MHz) of 2-Chloro-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,1',4,4'-tetrone (10c) in $CDCl_3$

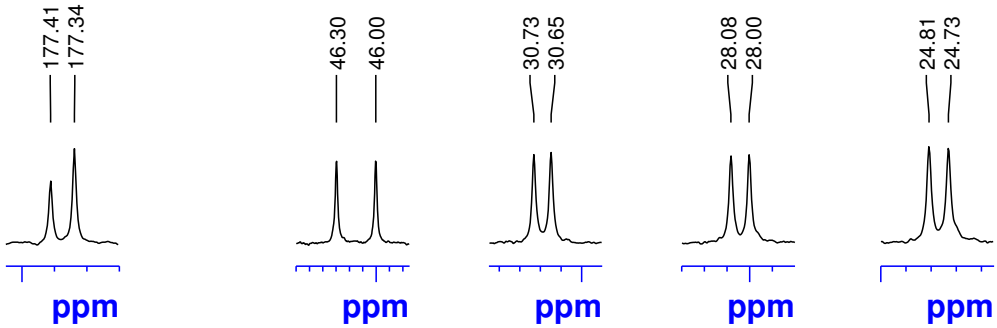




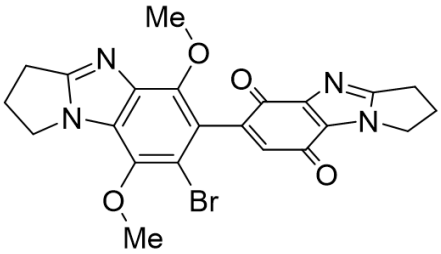
^{13}C NMR (100 MHz) of 2-Chloro-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,1',4,4'-tetrone (10c) in $CDCl_3$

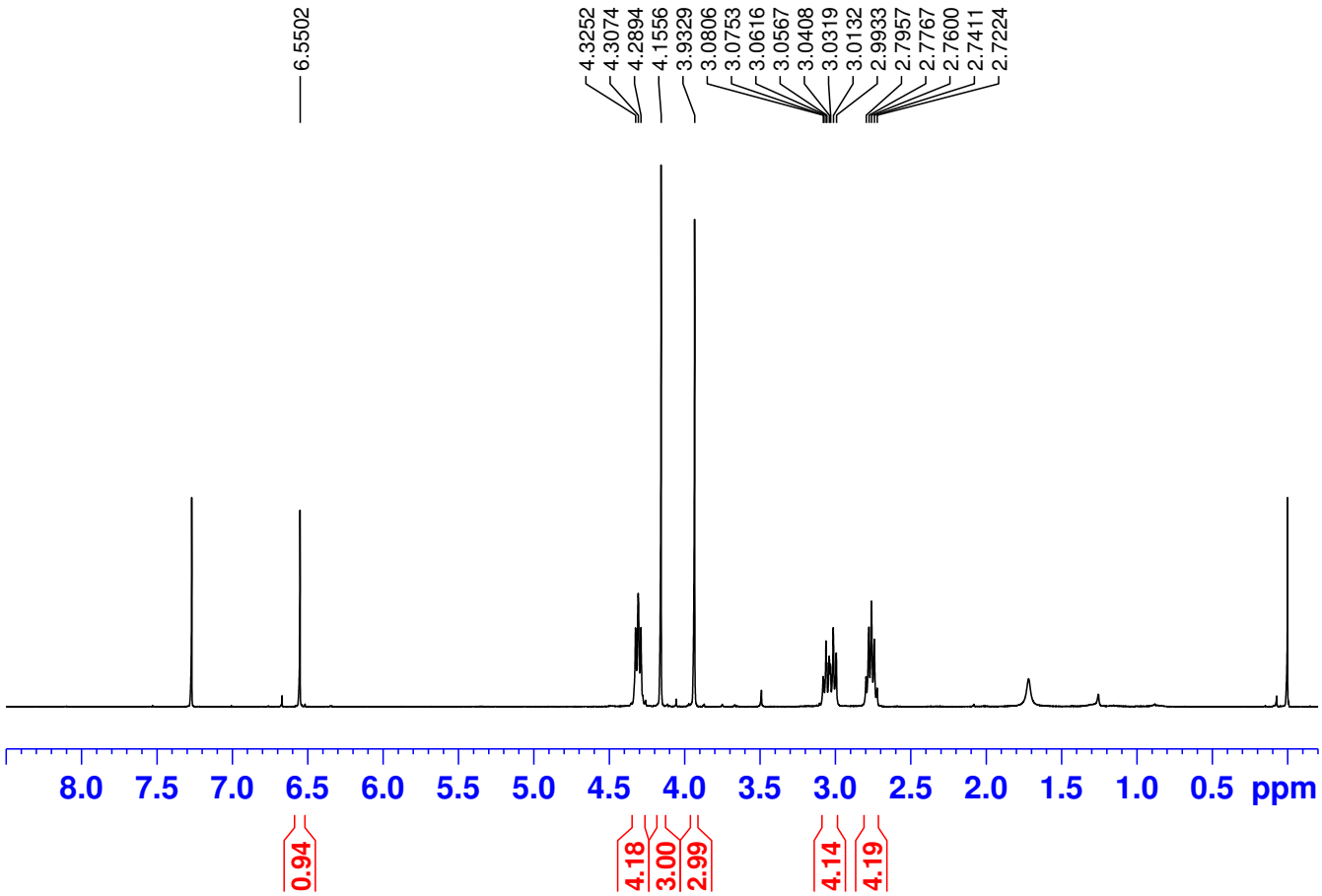




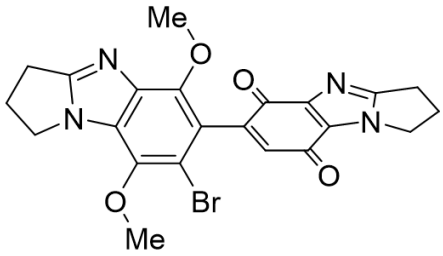


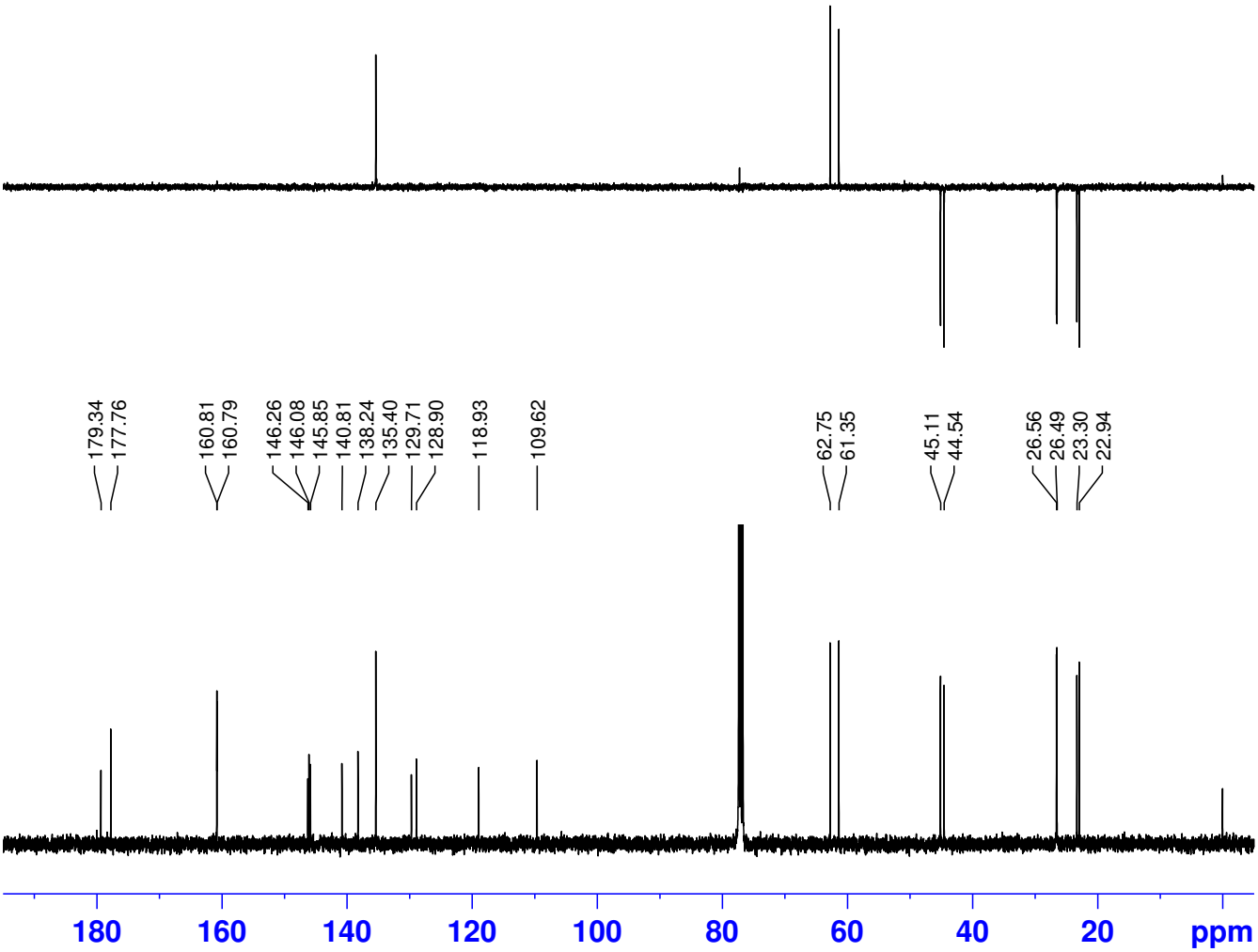
^{1}H NMR (400 MHz) of 7'-Bromo-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (11a) in $CDCl_3$

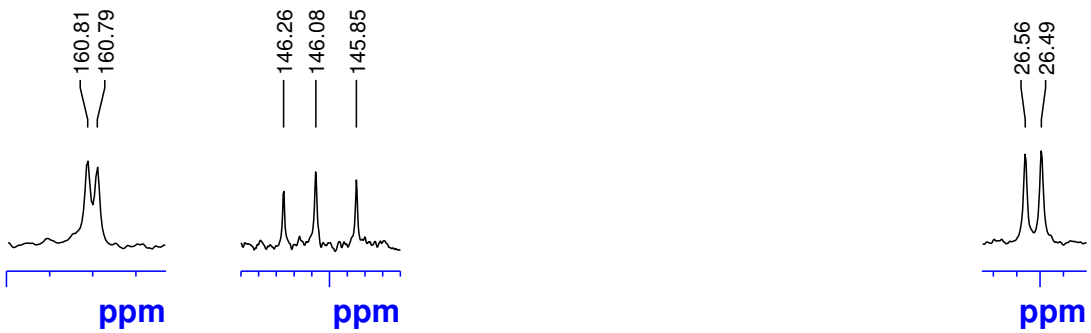




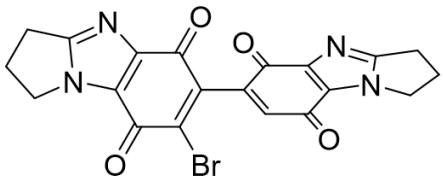
^{13}C NMR (100 MHz) of 7'-Bromo-5',8'-dimethoxy-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,8-dione (11a) in $CDCl_3$

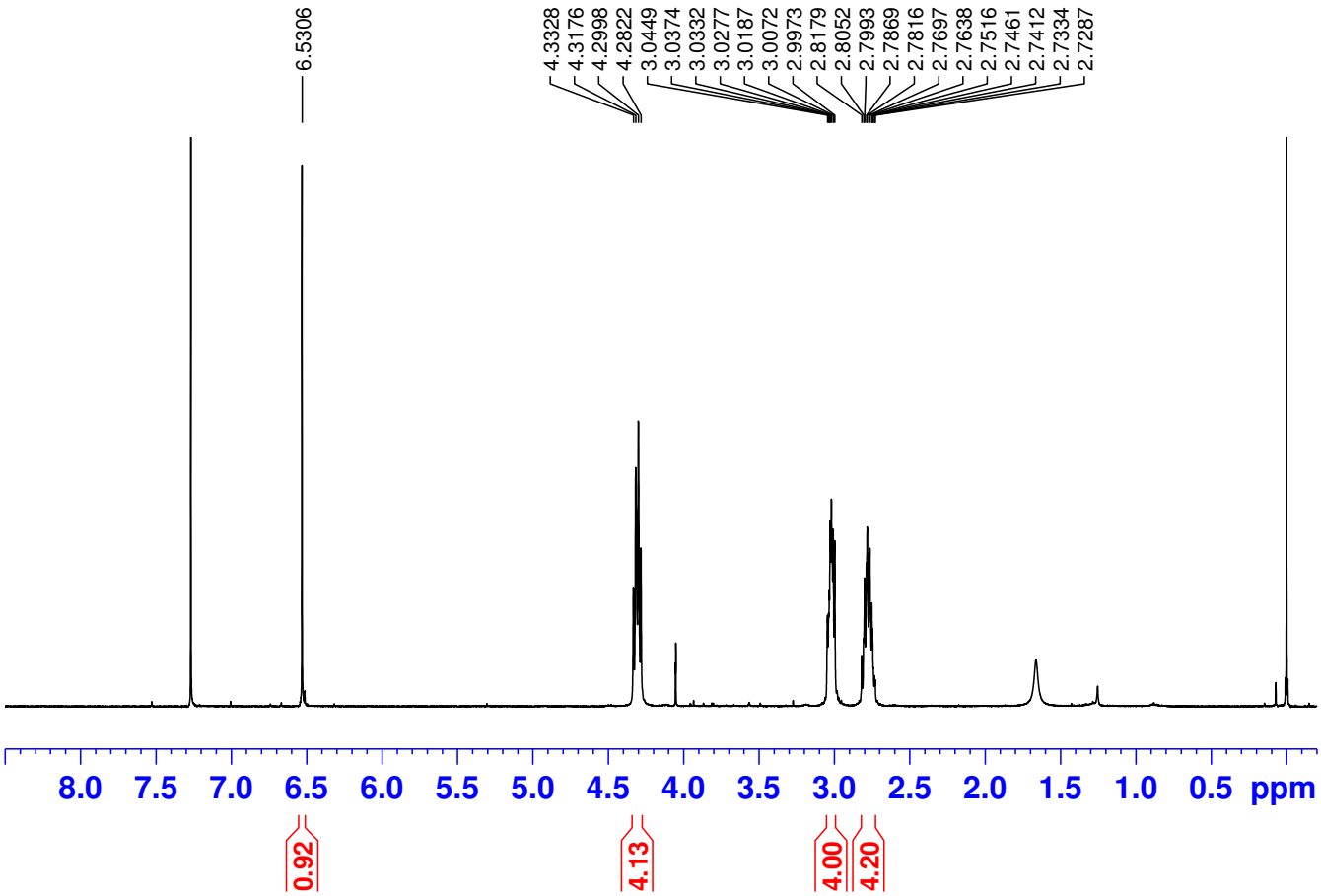




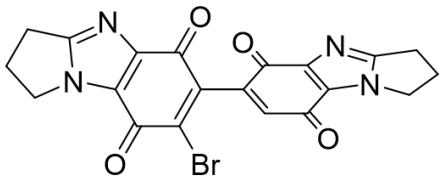


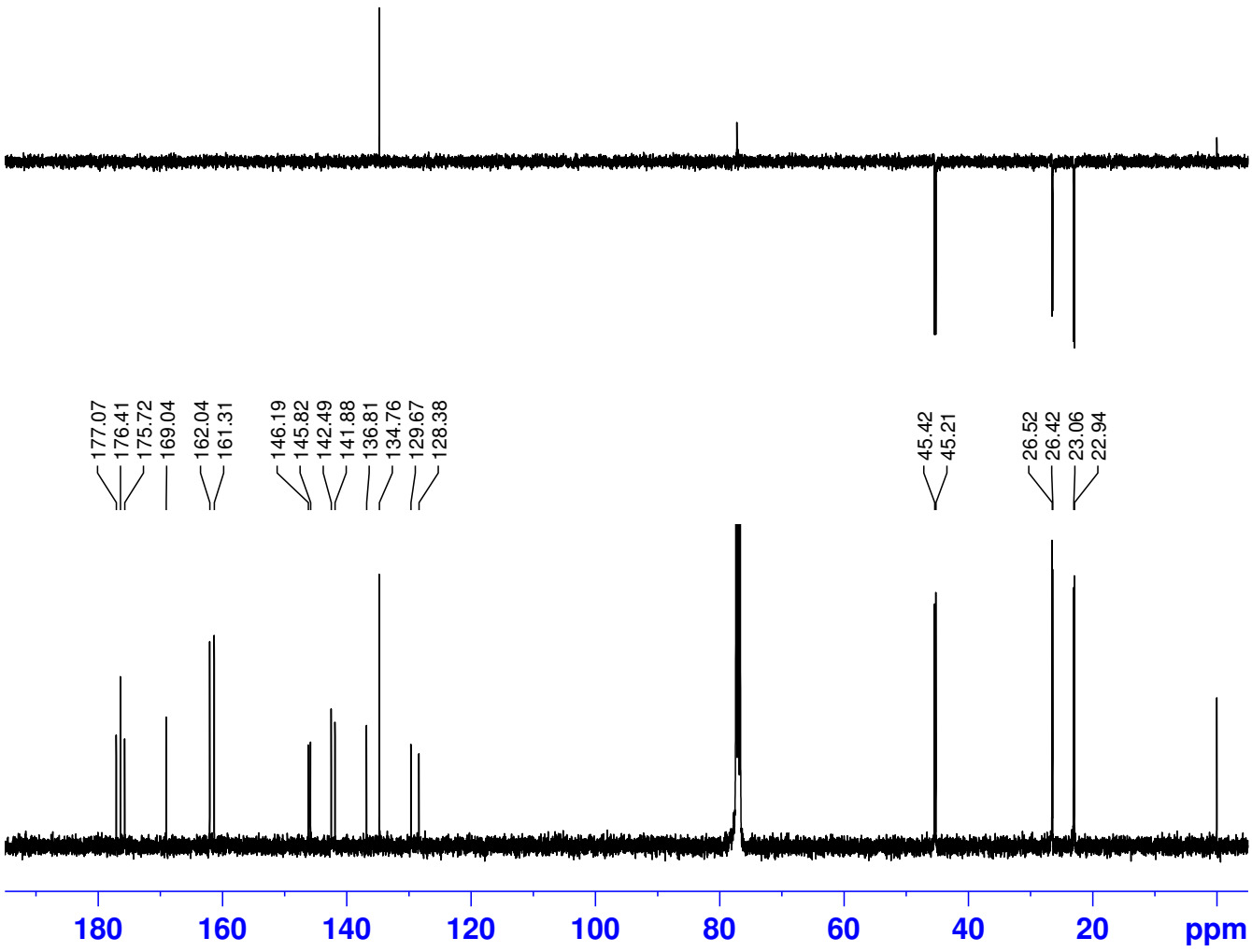
^{1}H NMR (400 MHz) of 7-Bromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,5',8,8'-tetrone (12a) in $CDCl_3$

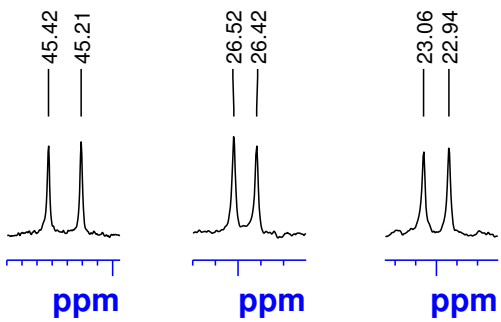




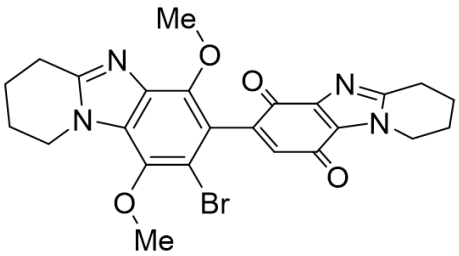
^{13}C NMR (100 MHz) of 7-Bromo-2,2',3,3'-tetrahydro-1*H*,1'*H*-[6,6'-bipyrrolo[1,2-*a*]benzimidazole]-5,5',8,8'-tetrone (12a) in $CDCl_3$

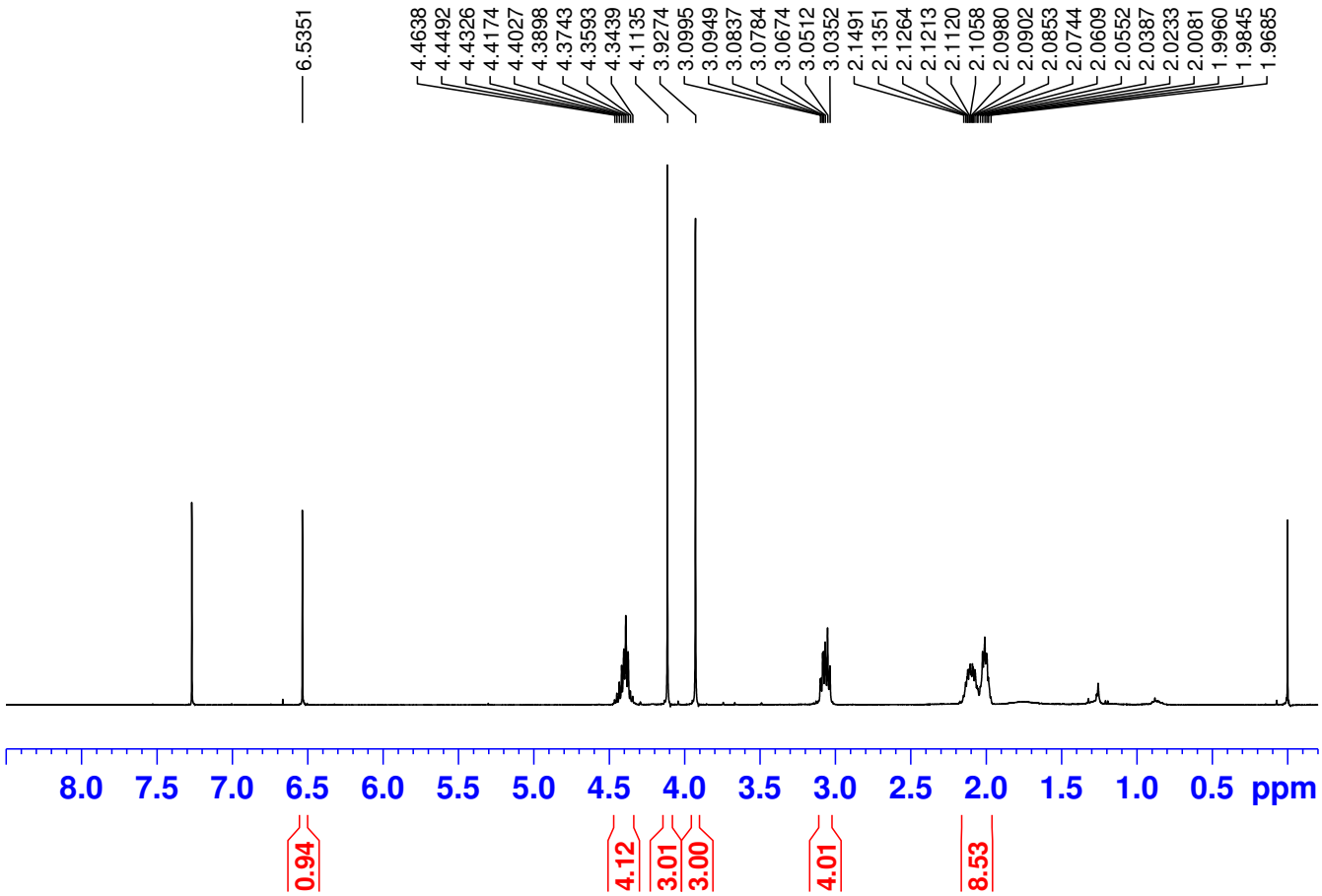




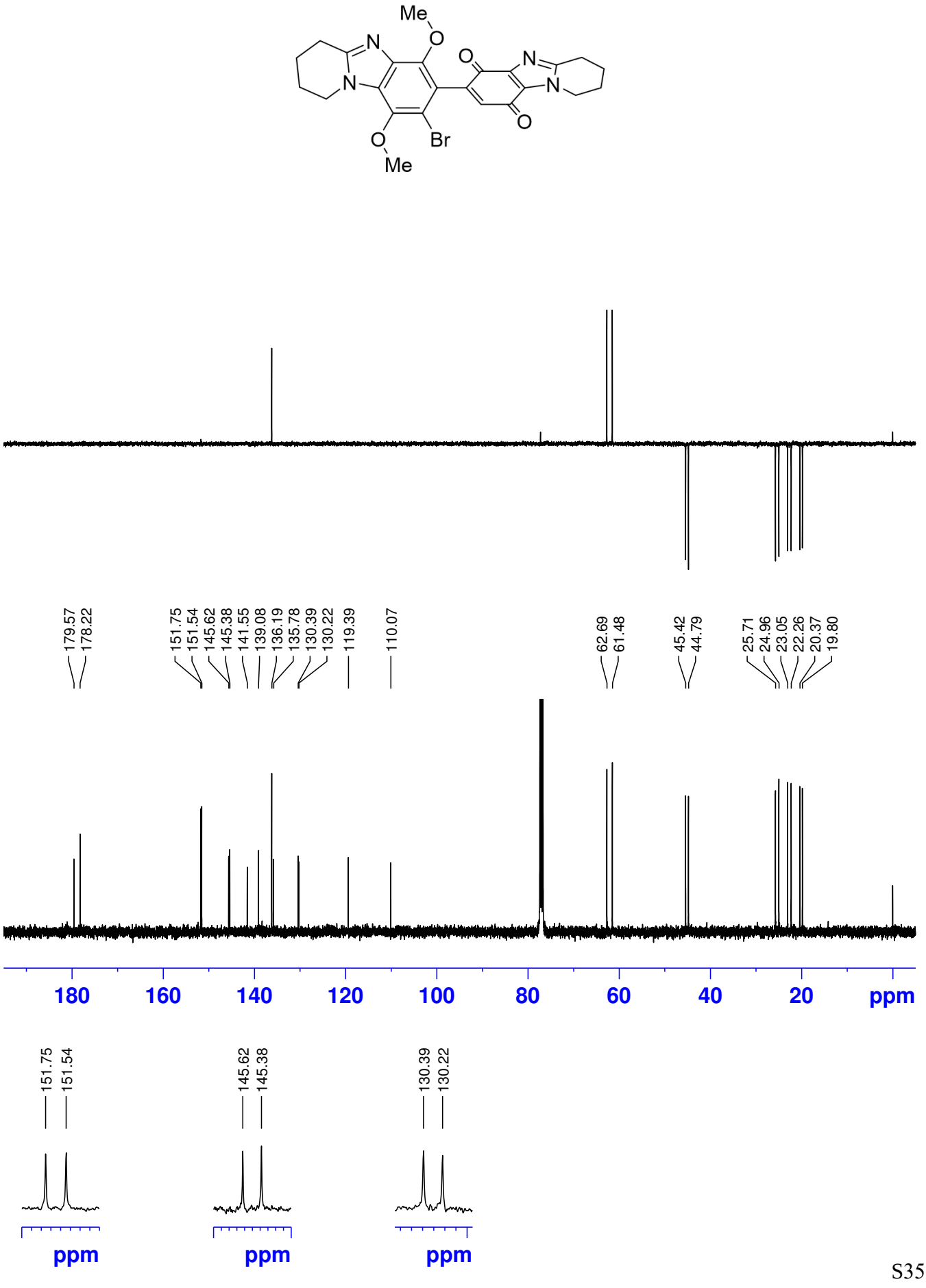


^{1}H NMR (400 MHz) of 8'-Bromo-6',9'-dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (11b) in $CDCl_3$

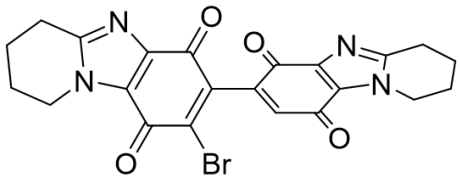


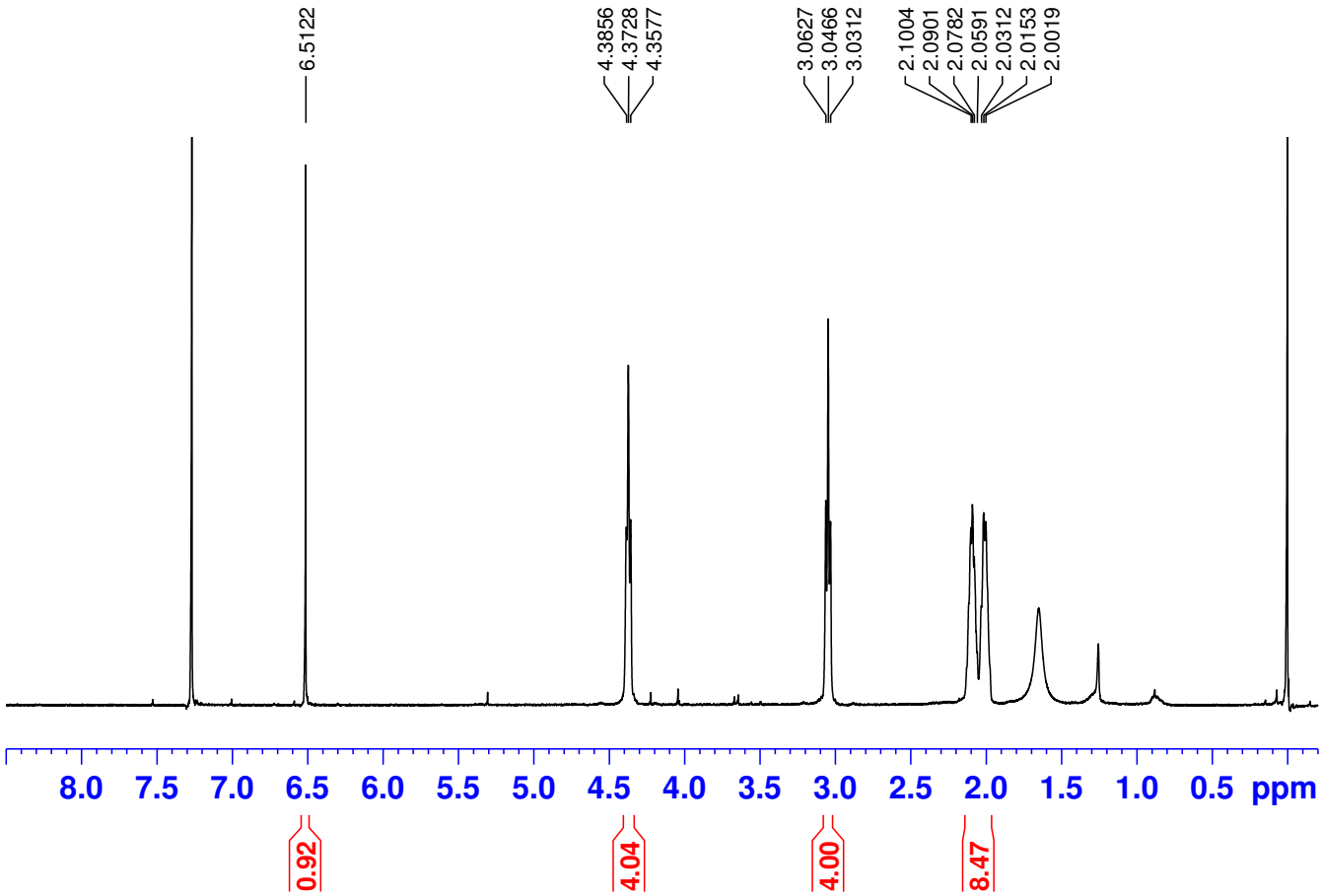


^{13}C NMR (100 MHz) of 8'-Bromo-6',9'-dimethoxy-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (11b) in $CDCl_3$

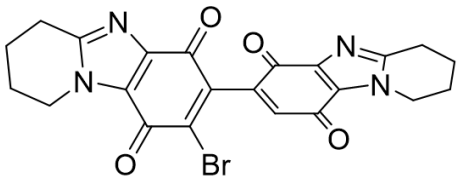


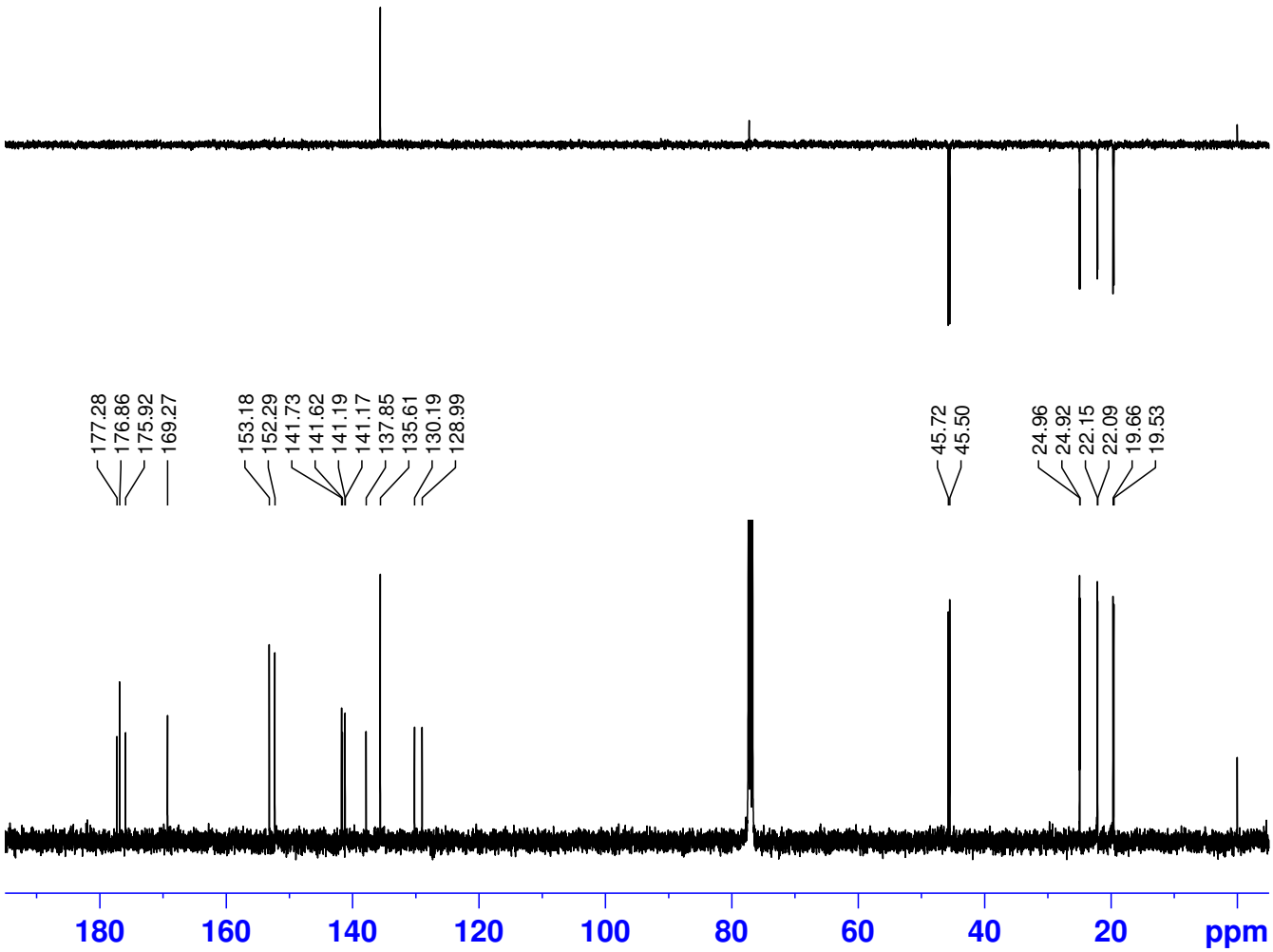
^{1}H NMR (400 MHz) of 8-Bromo-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (12b) in $CDCl_3$

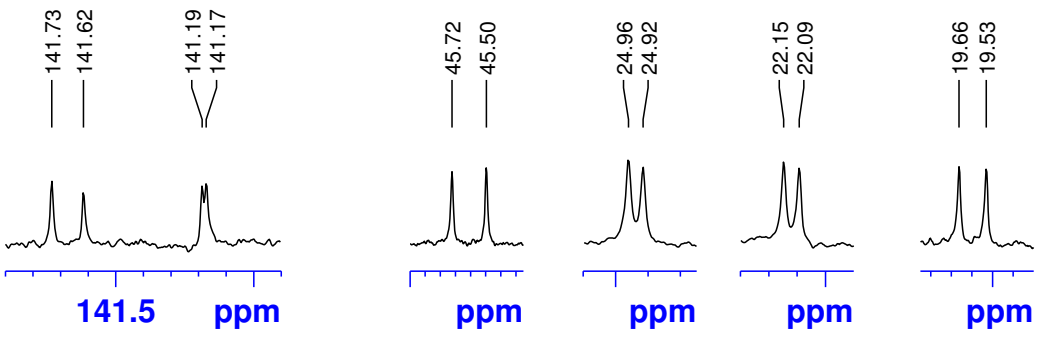




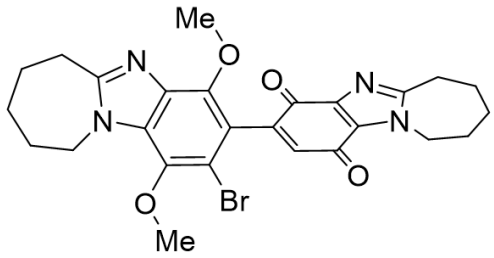
^{13}C NMR (100 MHz) of 8-Bromo-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (12b) in $CDCl_3$

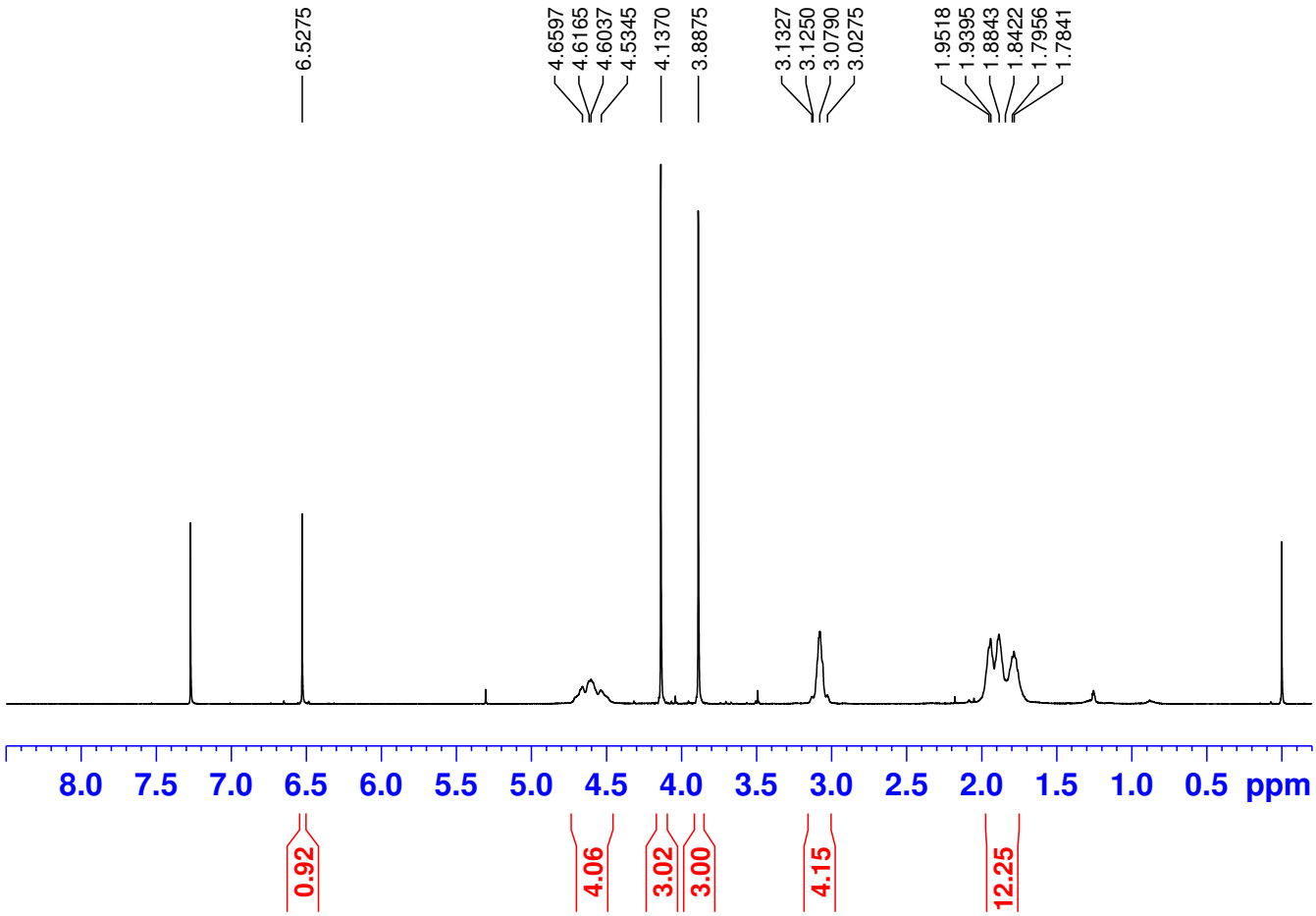




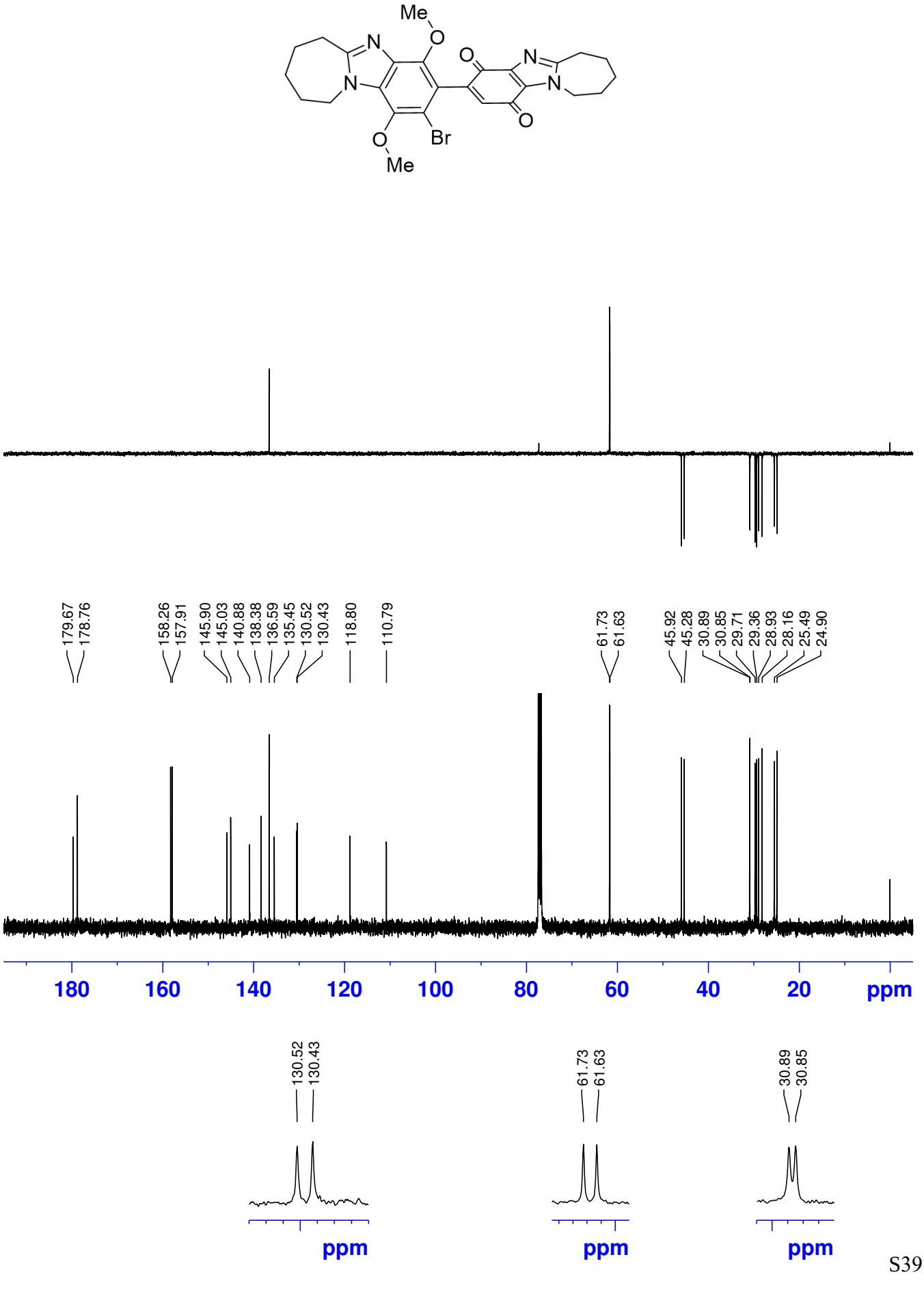


^{1}H NMR (400 MHz) of 2'-Bromo-1',4'-dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (11c) in $CDCl_3$

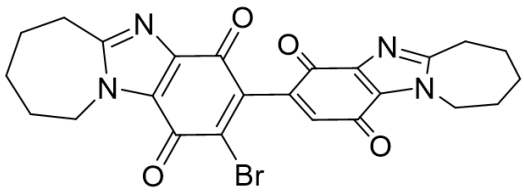


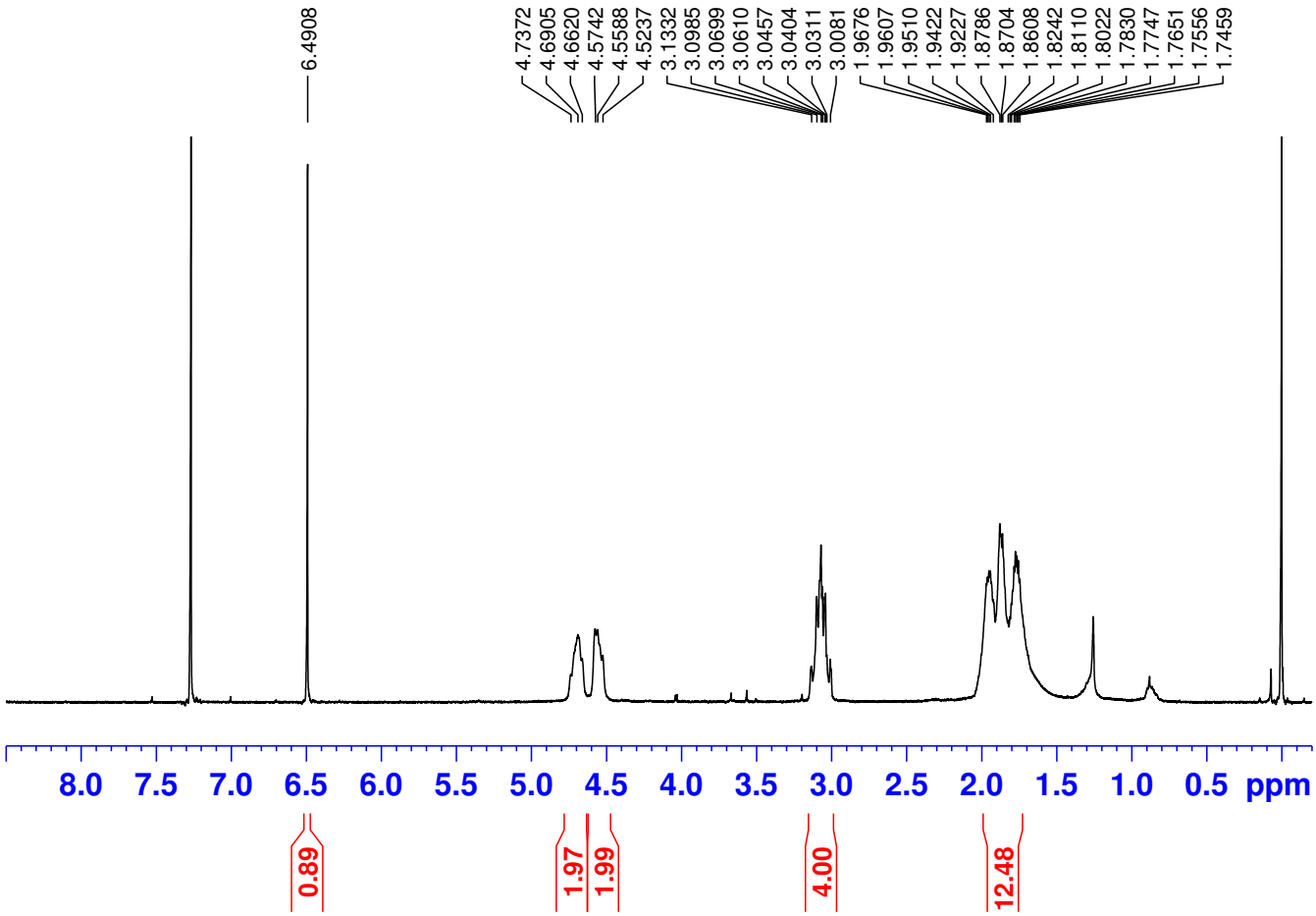


^{13}C NMR (100 MHz) of 2'-Bromo-1',4'-dimethoxy-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,4-dione (11c) in $CDCl_3$

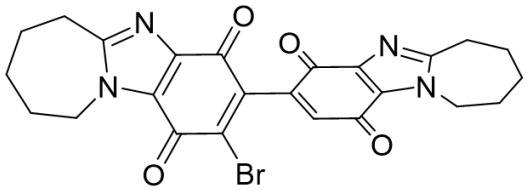


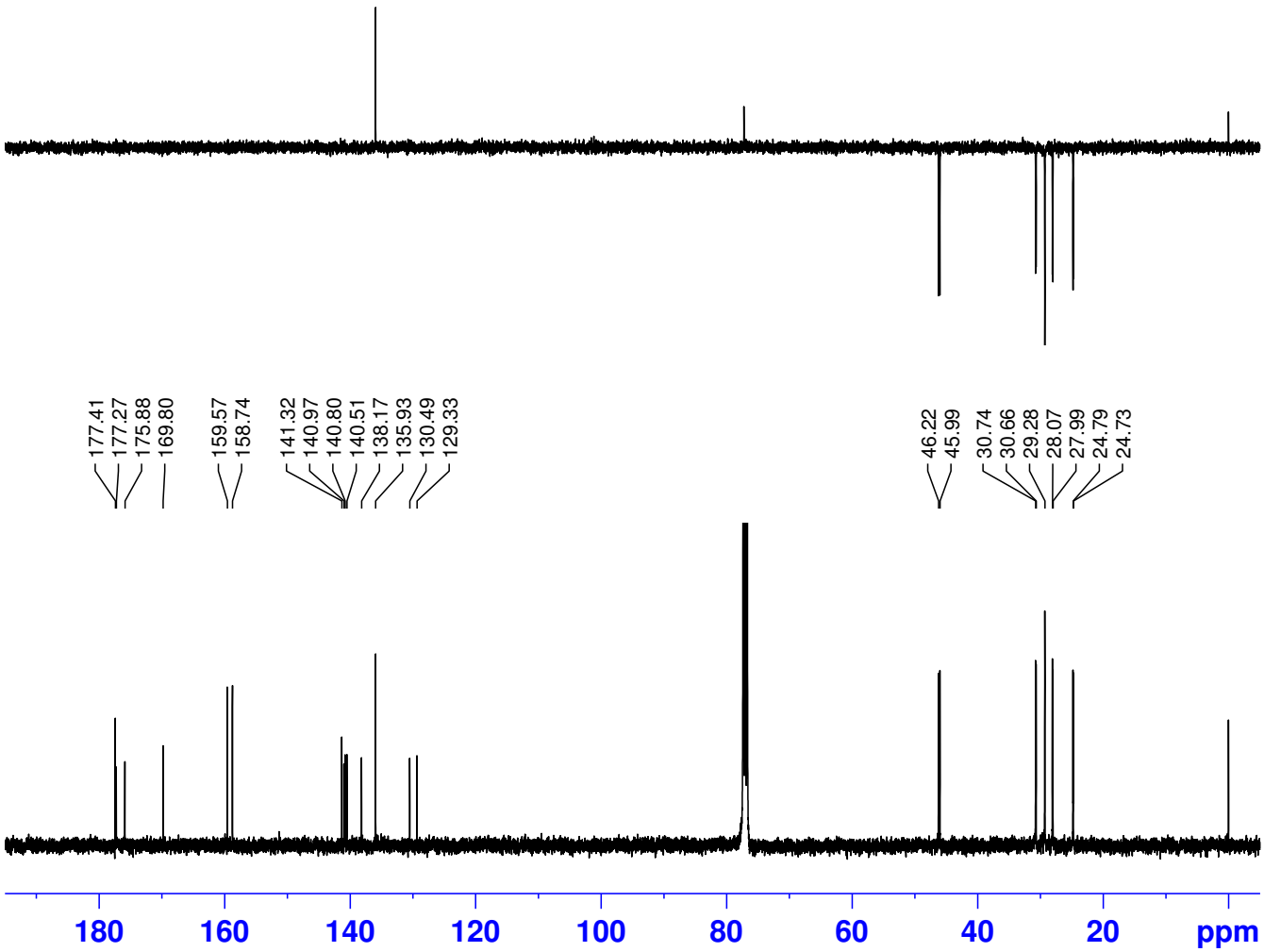
^{1}H NMR (400 MHz) of 2-Bromo-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,1',4,4'-tetrone (12c) in $CDCl_3$

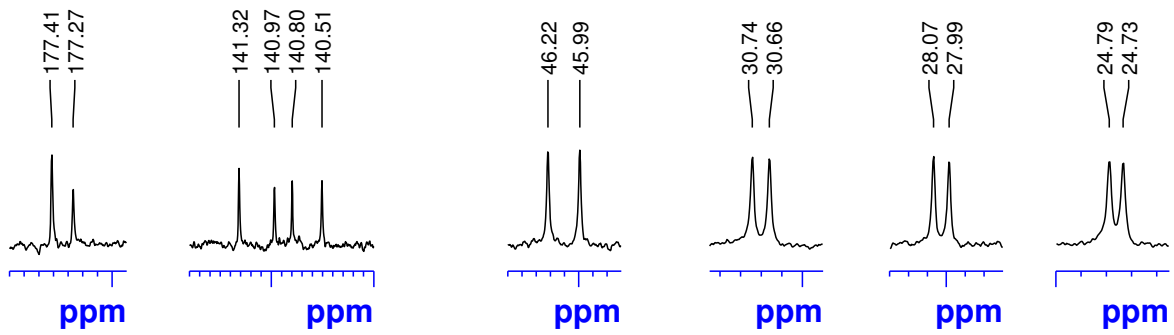




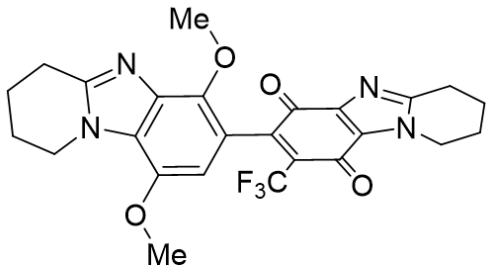
^{13}C NMR (100 MHz) of 2-Bromo-7,7',8,8',9,9',10,10'-octahydro-6*H*,6'*H*-[3,3'-biazepino[1,2-*a*]benzimidazole]-1,1',4,4'-tetrone (12c) in $CDCl_3$

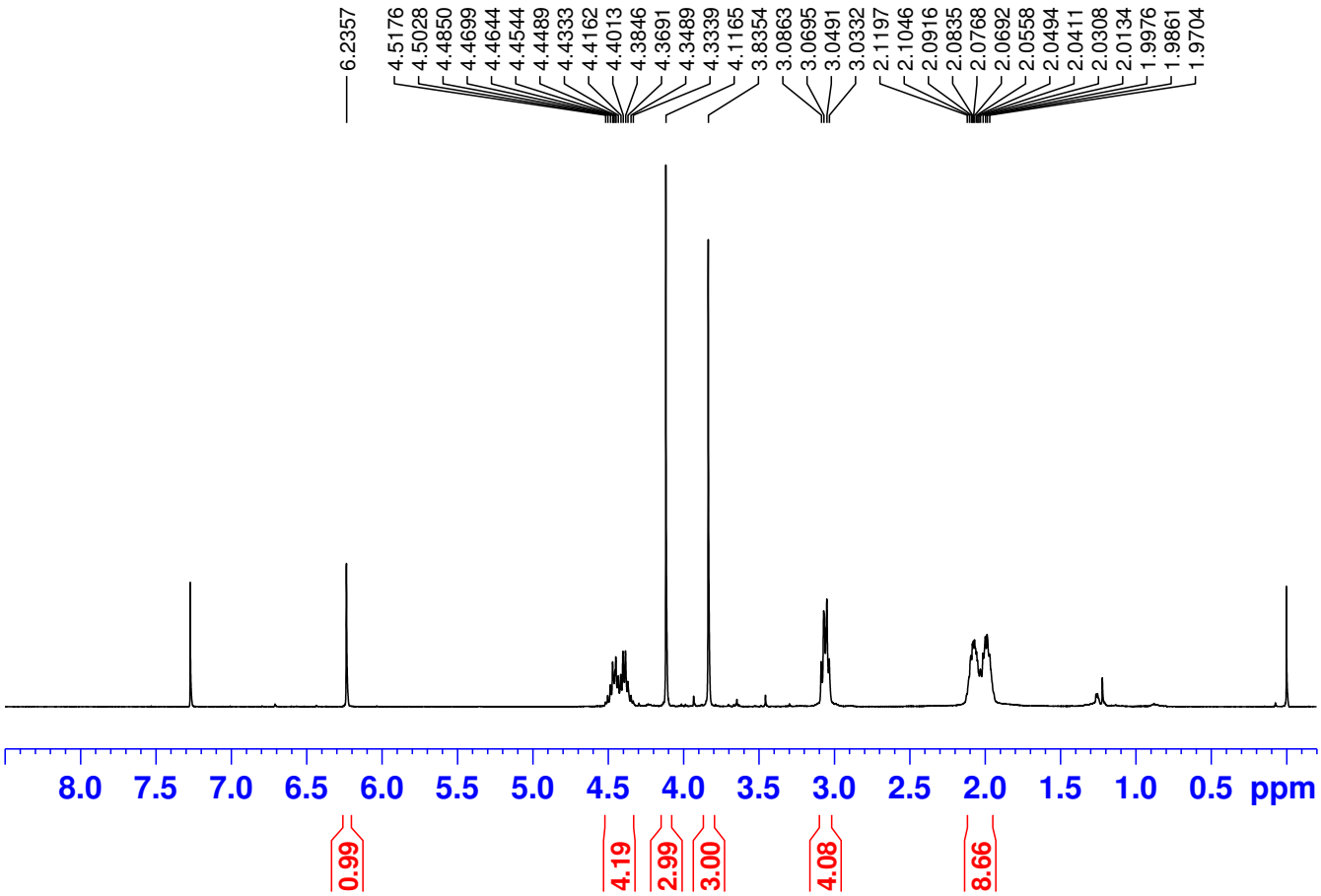




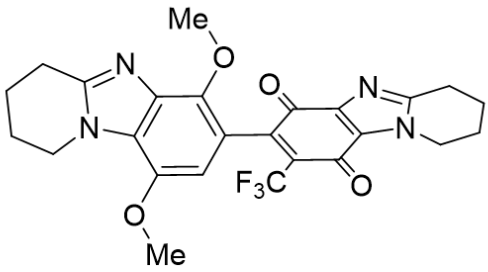


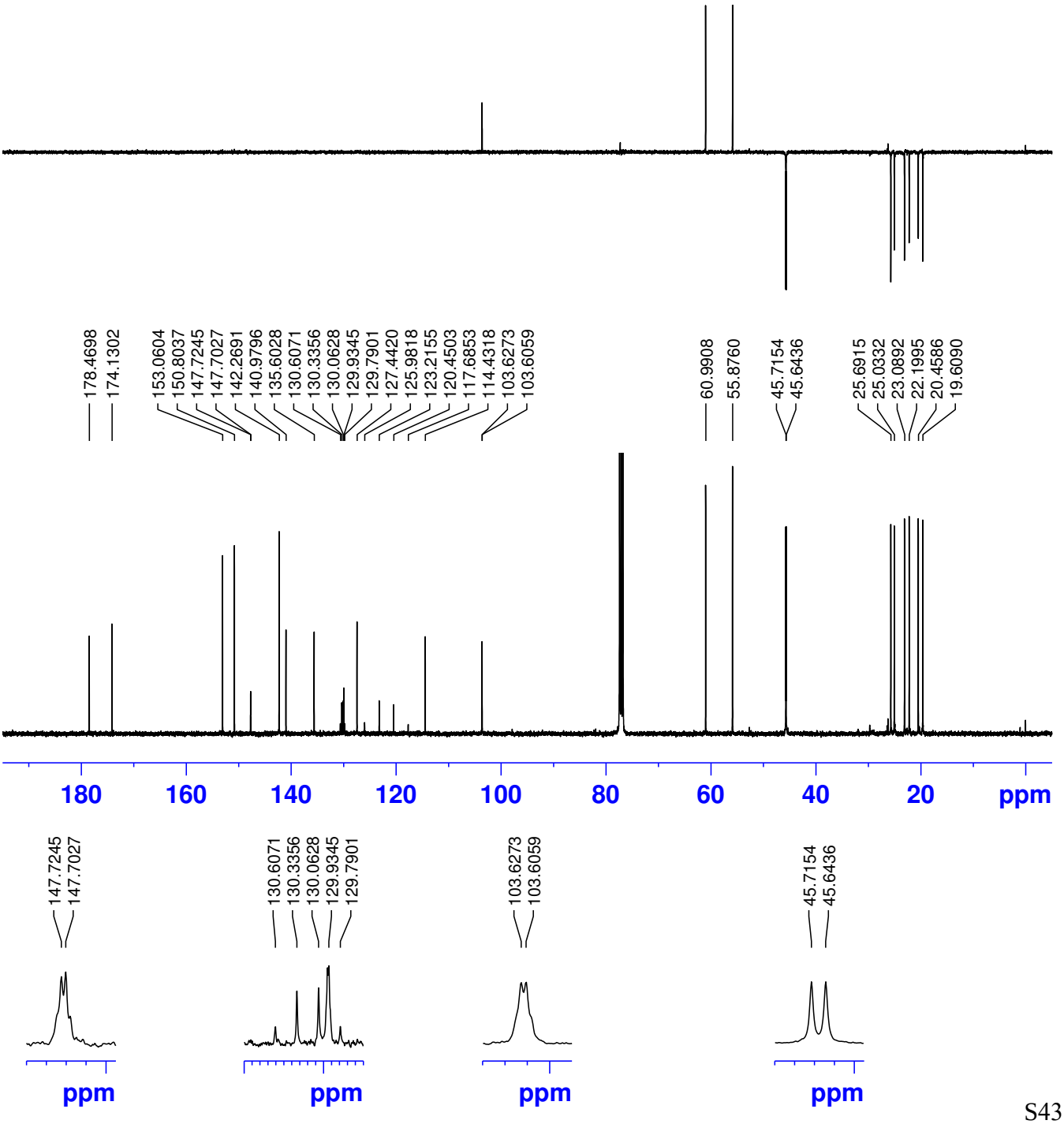
^{1}H NMR (400 MHz) of 6',9'-Dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (5d) in $CDCl_3$



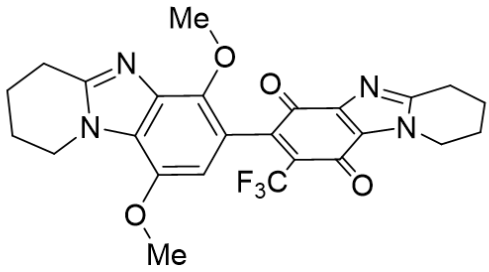


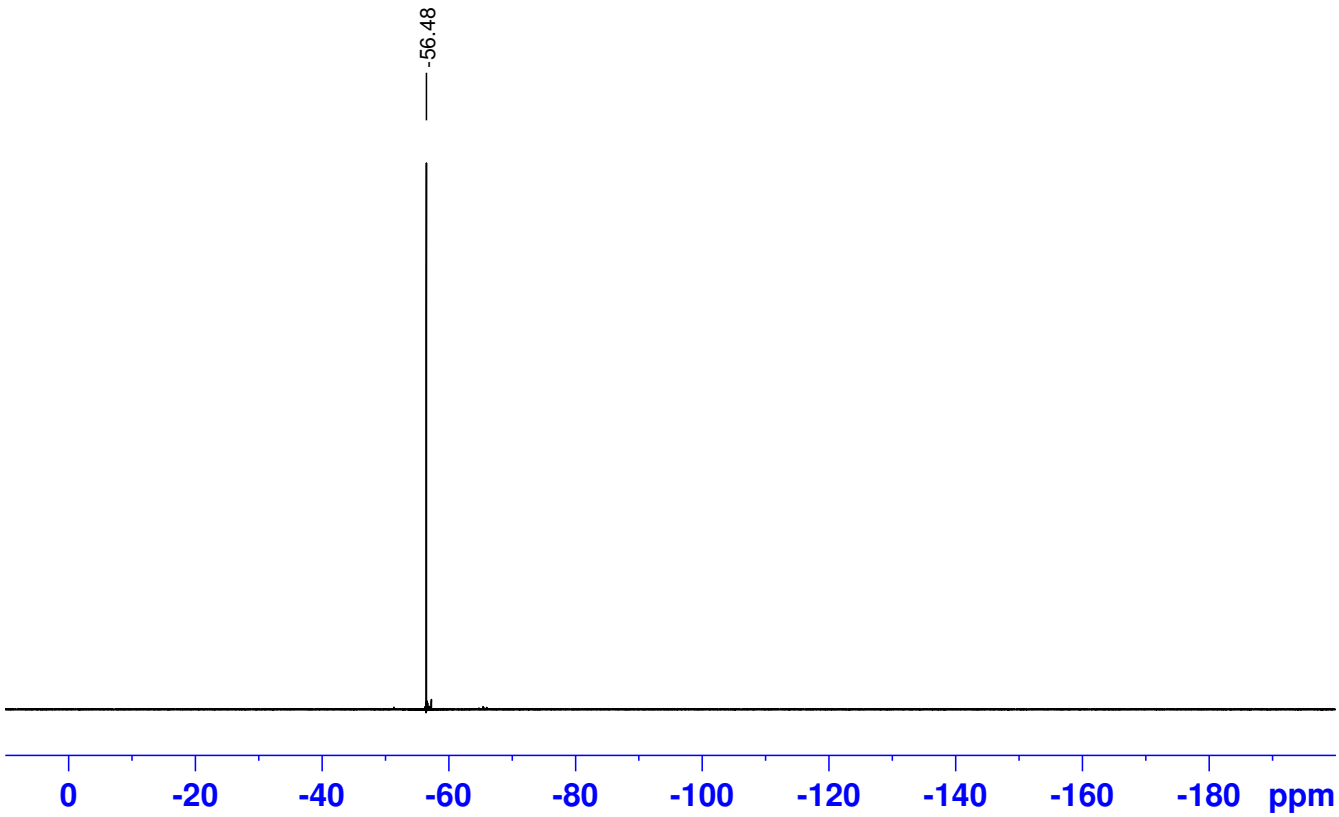
^{13}C NMR (100 MHz) of 6',9'-Dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (5d) in $CDCl_3$



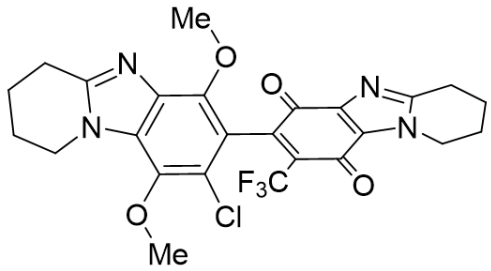


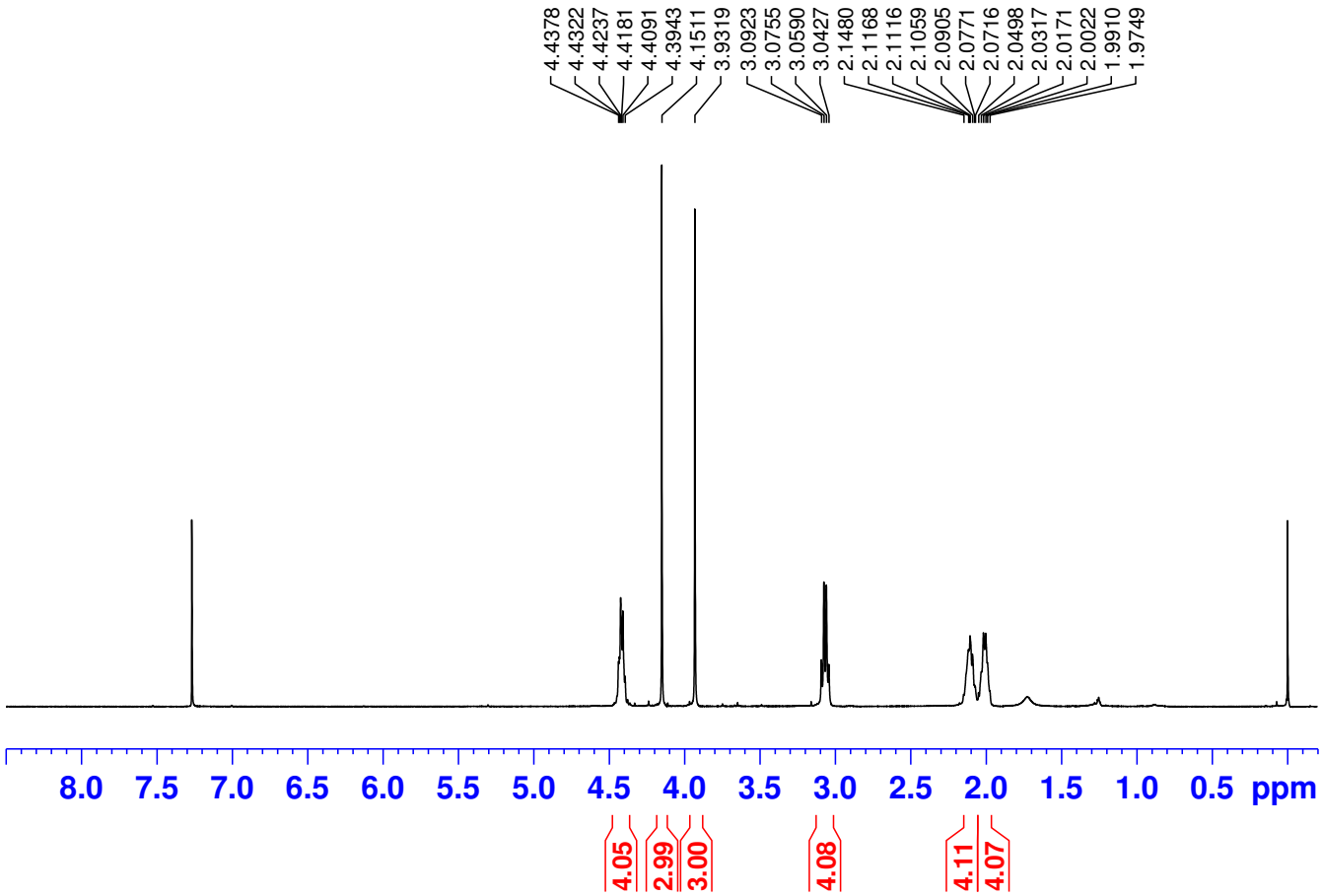
^{19}F NMR (376 MHz) of 6',9'-Dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (5d) in $CDCl_3$



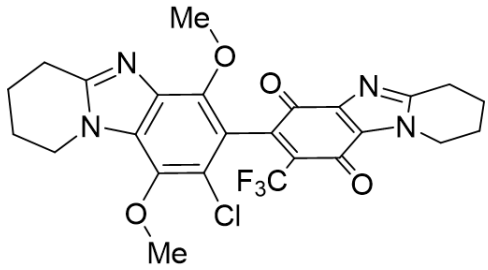


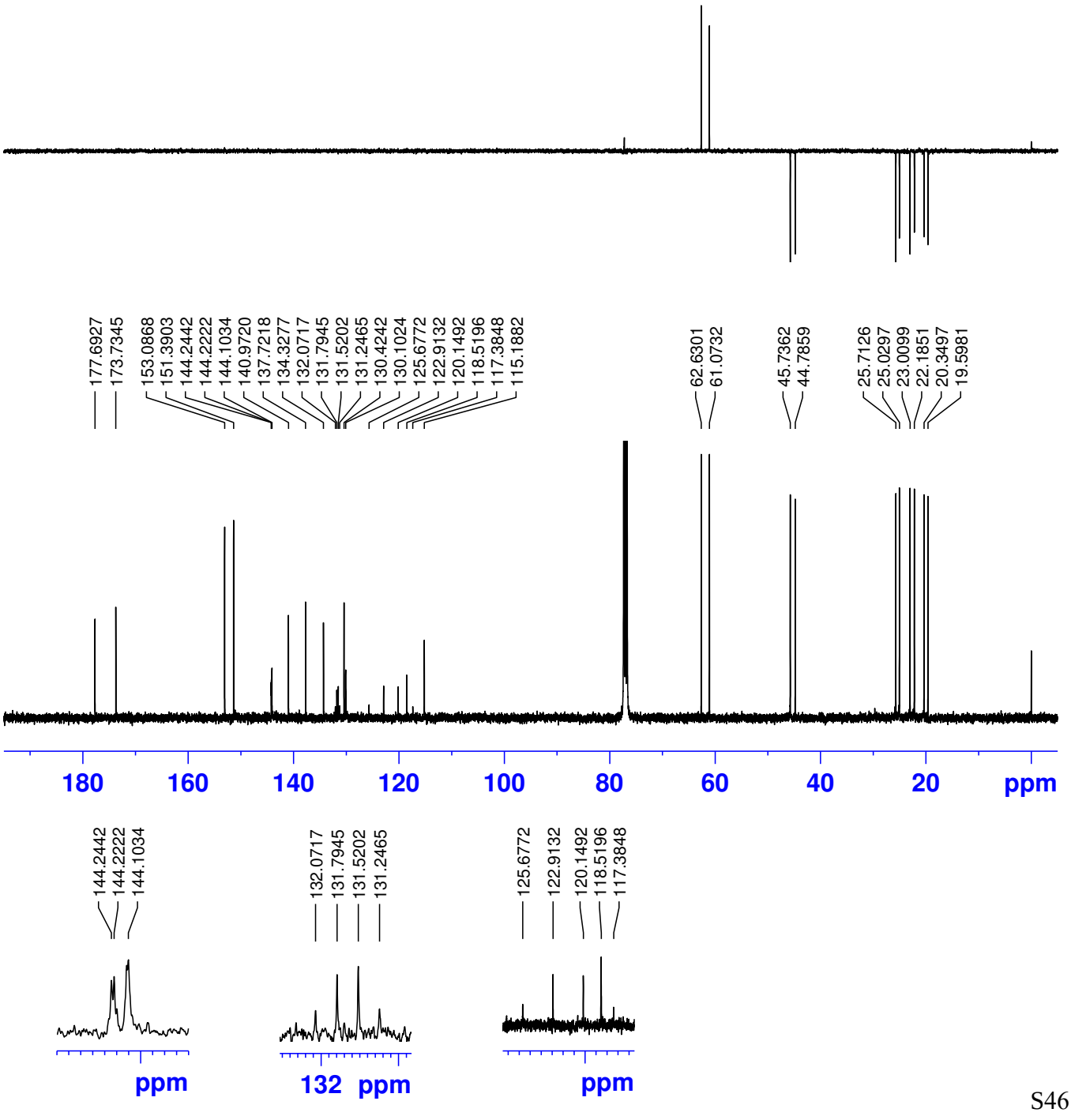
^{1}H NMR (400 MHz) of 8'-Chloro-6',9'-dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (13) in $CDCl_3$



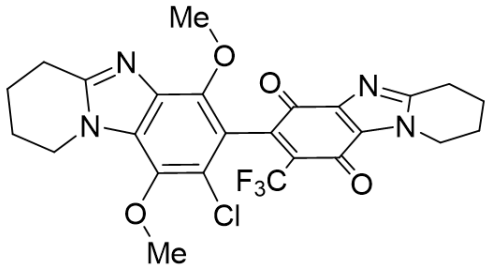


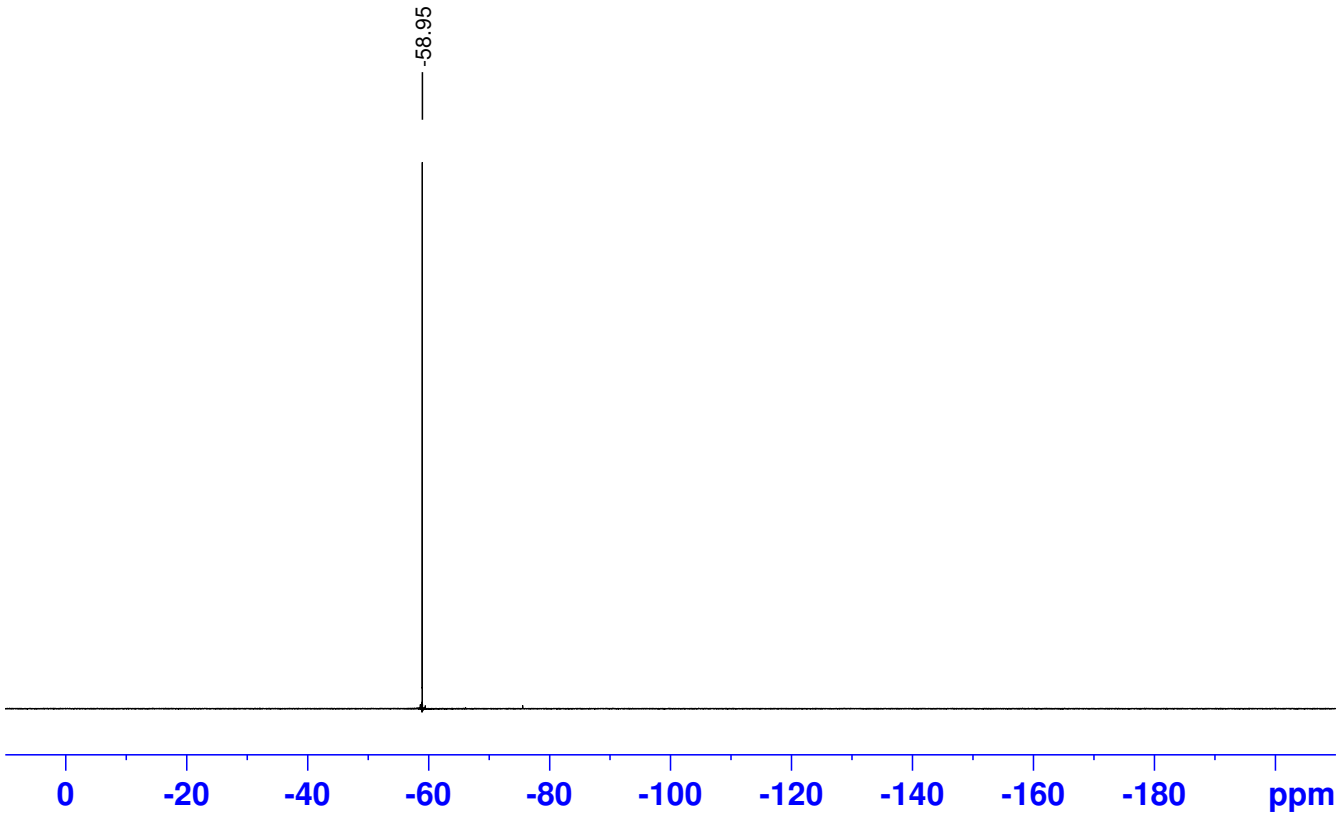
^{13}C NMR (100 MHz) of 8'-Chloro-6',9'-dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (13) in $CDCl_3$



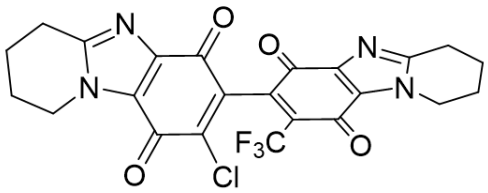


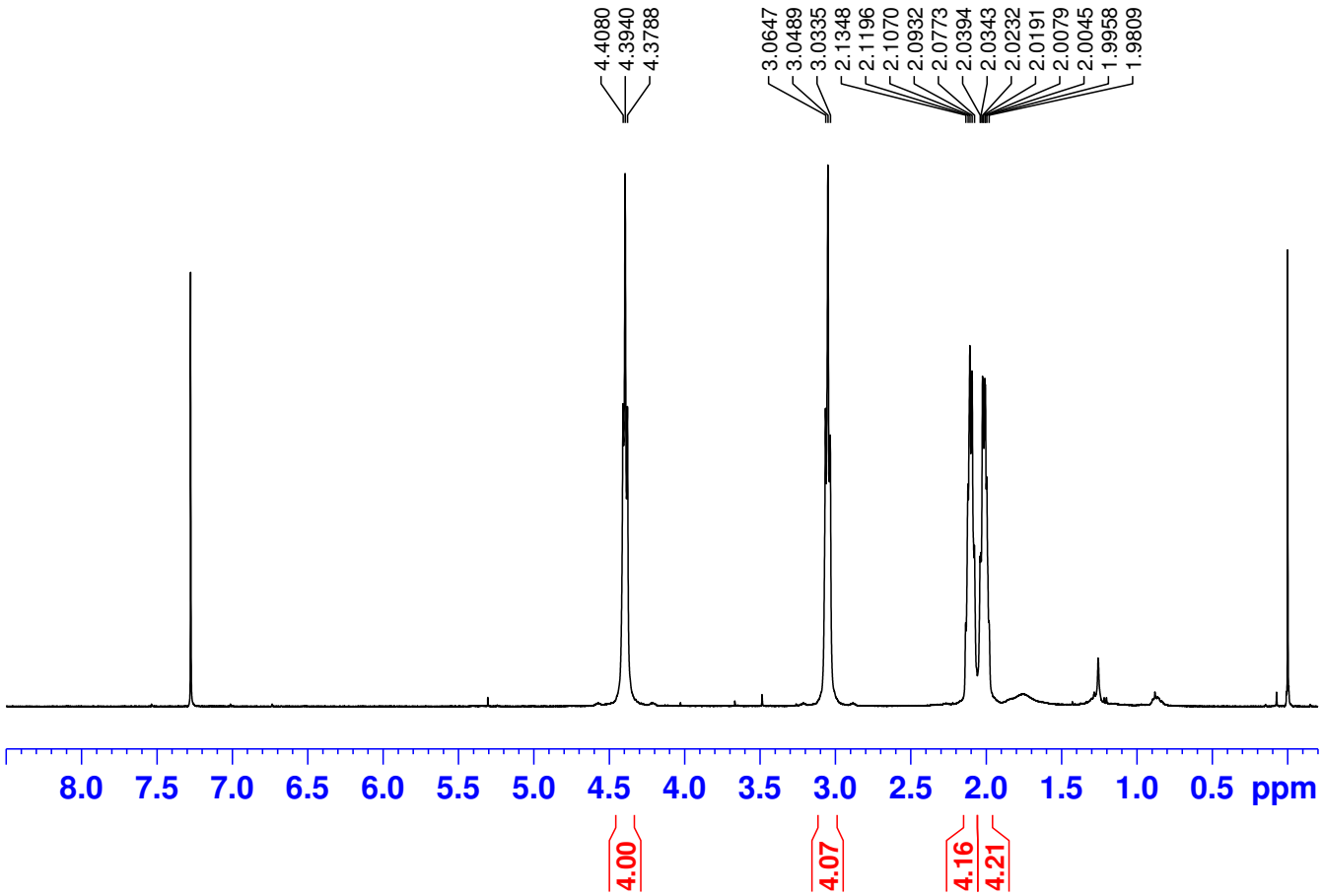
^{19}F NMR (376 MHz) of 8'-Chloro-6',9'-dimethoxy-8-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,9-dione (13) in $CDCl_3$



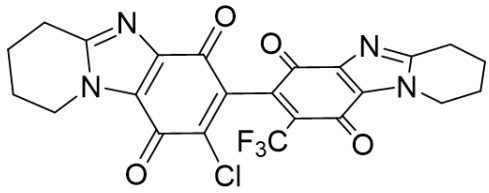


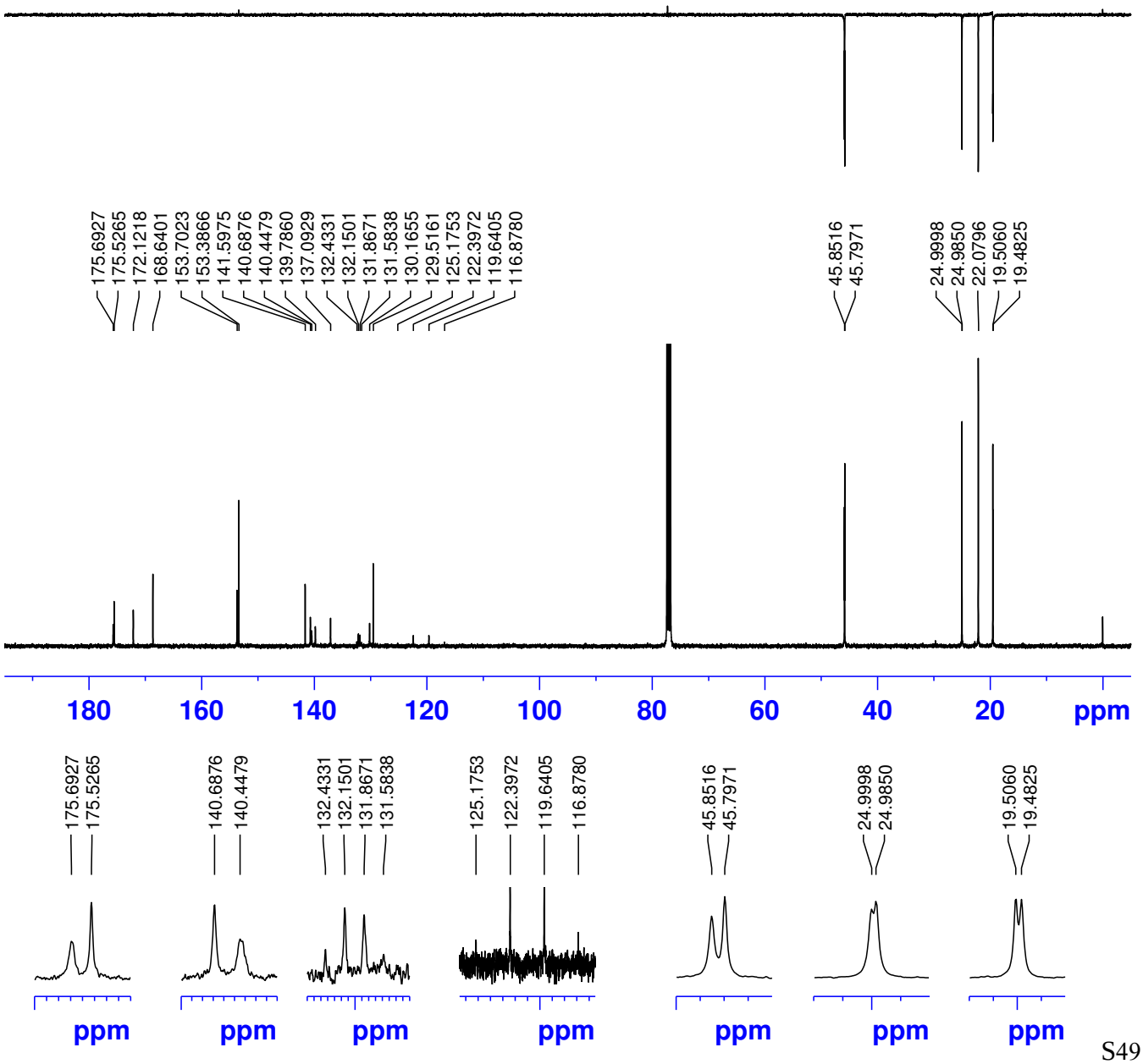
^{1}H NMR (400 MHz) of 8-Chloro-8'-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (14) in $CDCl_3$





^{13}C NMR (100 MHz) of 8-Chloro-8'-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (14) in $CDCl_3$





^{19}F NMR (376 MHz) of 8-Chloro-8'-(trifluoromethyl)-1,1',2,2',3,3',4,4'-octahydro[7,7'-bipyrido[1,2-*a*]benzimidazole]-6,6',9,9'-tetrone (14) in $CDCl_3$